Environmental Monitoring of Heavy Metals in Seaweed and Associated Sediment from the Strait of Hormuz, I.R. Iran

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Abstract: The status of Pb, Cd, Cu, Ni, Zn and Fe in sediment and 11 dominant seaweed species from the Strait of Hormuz during 4 seasons (autumn 2007 until summer 2008) at 13 different sites were determined. etals were extracted from sample homogenates by hot concentrated nitric acid (65%) and extracts were analyzed by an atomic absorption spectrophotometer. The annually mean metals in the sediment were: Pb (23.10), Cd (4.15), Cu (9.40), Ni (18.19), Zn (41.93) and Fe (20871) μ g gG¹ dry weight. In the present research, mean metal levels in sediment and algae decreased in the following order: Fe > Zn > Pb > Ni > Cu > Cd. Among all species, *Padina pavonica* and *Ulva compressa* showed maximum time and space distribution and high significant positive correlations existed between metals in *Padina pavonica* and *Ulva compressa* and the sediment, suggesting these algal species as suitable tools for biomonitoring of the area.

Key words: Seaweed % Bioaccumulation % Sediment % Heavy Metals % Strait of Hormuz

INTRODUCTION

The Persian Gulf is a shallow semi-enclosed sea and major threats to the marine environments of this area come from repeated oil spills and algal blooms that have frequently killed fish and other marine biota. At the narrowest point of the Persian Gulf (the Strait of Hormuz), it narrows to only 34 miles wide, with Iran to the north and Oman to the south. Despite a steady decrease in petroleum discharges from shipping operations of the Persian Gulf littoral countries during the past 30 years [1]. The Persian Gulf represents a stressed ecosystem due to its location within the richest oil province in the world hosting more than 67 % of the world oil reserve. The oil-related activities besides other development and anthropogenic activities result in a number of marine pollution problems. Another serious concern in the Persian Gulf is the algal blooms that seem to have become more frequent and longer in durations. Intensive industrialization of the area is thought to have lead to serious damage to the Persian Gulf marine environment [2].

The anthropogenic contamination of marine ecosystems is a very important stress factor and defines the necessity for systematic monitoring and control of contaminants (e.g. heavy metals) that affect marine biota. Habitat destruction, as a consequence of reckless industrial development and release of toxic anthropogenic pollutants, is the most serious contemporary challenge to survival of biological systems on earth. Severe pollution threatens marine ecosystems, which continue to receive large volumes of industrial waste, without adequate treatment facilities to protect flora and fauna. Metals, wellknown for their persistence in the environment and their ability to bioaccumulation and biomagnifications in the food chain [3], are often responsible for irreparable damage to the marine environments. Despite the urgent need to assess the environmental impact of the various sources of pollution and contamination, a few researches have been done and virtually no studies have focused on remediation; highlighting the need for monitoring programs to determine contaminant levels and bioavailability as first steps to protecting these ecosystems.

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Organisms which accumulate contaminants in their tissues (biomonitors) can be used to assess the health of coastal environments, including presence, levels and changes of contaminants. Among the various organisms, seaweed has been used as biomonitors of metal contamination [4, 5] and sediment metal levels have also been extensively reviewed. As cited in Besada *et al.* [6] some of seaweeds have high capacity of metal accumulation, thus they can be used as metal pollution indicators in estuarine and coastal waters.

Large amounts of seaweeds are growing along the northern areas of the Persian Gulf. Their wide distribution and abundance in this area could very well be used in assessing their bioaccumulating potential contamination by heavy metals. Since sediment composition varies according to particle size, rate of deposition, rate of particle sedimentation and presence and amount of organic matter [7] direct measurement of metal in the sediment is often misleading when it comes to assessing the risks that metals pose to the local ecosystems. At the present time, metal content and accumulation in seaweed and sediment are recognized as a suitable bioindicator for assessing the degree of contamination in marine ecosystems.

The immediate objective of this study was to measure Pb, Cd Cu, Ni, Zn and Fe in 11 dominant seaweed species and associated sediment samples from 13 sampling sites in Hormuzgan Province on the shorelines of north part of the Strait of Hormuz. In addition we aimed to find which species of algae could be better bioindicator for metal contamination in the study area by evaluating correlations between sediment and algae metal levels.

MATERIALS AND METHODS

All sampling sites have been selected based on topographical and biological (species diversity, dispersal) properties. Sampling of seaweed and sediment were conducted seasonally from November 2007; and in January, May and July 2008 and they were collected from intertidal regions at 13 sampling sites along the coastline of the Hormuzgan Province (north side of the Strait of Hormuz). All sampling sites were to cover almost sensitive regions of the north side of the Strait of Hormuz including 9 sites along the mainland and 4 sites around the Hormuz Island (Figure 1).

During present study, eleven seaweeds (3 Chlorophya, 4 Phaeophyta and 4 Rhodophyta) species were collected. It is important to note that the species collected were not found at all sites throughout the year.

Seaweed samples were collected during low tide as far as possible of the same ages, size and healthy in appearance and sorted out according to species. Where this is not possible the samples were obtained by diving. Algal samples were rinsed thoroughly with seawater on-site and placed in plastic bags, transferred to the laboratory as soon as possible and stored in a fridge (less than 4°C) before further processing. Samples were initially washed under a jet of tap water and rinsed in distilled water to remove any mineral particles and organisms adhering to plant tissue as far as possible. Samples were washed three times with double distilled water and dried at 75°C for 24 h [8, 9]. The dried seaweed materials were ground by using a glass mortar to a fine powder and then redried for 3 hours and stored in plastic vials.

Sediment samples were collected from the same sampling sites and samples were collected from the upper layer (0-5 cm) and placed in washed plastic bags. Any visible materials or organisms i.e. large stones and shells were removed from the samples. Samples were stored in ice-chest and immediately transferred to laboratory. The coarser sediment fractions (> 63 µm) were separated by wet sieving with ASTM sieves. The sediments were dried at room temperature and subsequently homogenized in a glass mortar with pestle [8]. Triplicate subsamples of powdered seaweeds and sediments were digested according to Abdallah and Abdallah [10]. A Varian Model Spectra AA 220 FS (Mulgrave, Victoria, Australia) flame absorption spectrometer with deuterium background corrector was used to measure Pb, Cd Cu, Ni, Zn and Fe in seaweed and sediment samples.

The accuracy of the analysis for algal and sediment samples was assured by the inclusion of DORM-3 (Fish protein) (National Research Council of Canada) reference material and GBW07313 (Marine sediment, China) reference material to all laboratory assays. Each reference sample was subjected to the same digestion/extraction procedure as the unknowns; the recovery of elements compared favorably with the certified and reference values (Table 1). Instrument performance and calibration was ascertained through the use of known aqueous standards.

All statistical analyses were performed by SPSS version 12 for window. Analytical precision gave a mean error of 5 per cent. Mean values of three replicates were calculated. All data were tested for normality of distribution and homogeneity of variance before the non-parametric statistical analysis. Variability between seasons and sampling sites was analyzed for each metal by Kruskal-Wallis one-way ANOVA. Two-way ANOVA

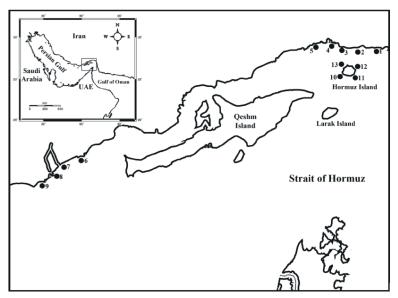


Fig. 1: Map showing the locations of the study area

Table 1: Results of quality assurance

	Certified values		Values in this stu	ıdy	Recovery (per cent)		
Metal	DORM-3	BGW07313	DORM-3	GBW07313	DORM-3	GBW07313	
Pb	0.39	29.3	0.32	25.7	91	88	
Cd	0.29	0.25	0.23	0.27	96	108	
Cu	15.5	424	14.1	398	91	94	
Ni	1.28	150	1.13	161	88	107	
Zn	51.3	180	54.7	197	106	109	
Fe	347	423	334	504	96	119	

was used to assess the variability between location and species during different periods for each metal. The relationships between heavy metals concentrations in the sediments and macroalgal species were evaluated by Spearman correlation coefficients (p was set at # 0.05).

RESULTS AND DISCUSSION

During present research, highest value of Pb (29.7), Cu (15.2), Zn (43.5) and Fe (44840) μg gG¹ dry weight were recorded in site 11 and Cd and Ni concentrations of 5.8 and 28.0 μg gG¹ dry weight showed higher in sites 4 and 9, respectively (Table 2). The results showed that the pattern of metal levels in sediment samples was decreased as follow: Fe > Zn > Pb > Ni > Cu > Cd. Statistical studies using Kruskal-Wallis one-way analysis of variance (ANOVA) showed significant (p<0.05) variations to Cd, Cu and Pb during different periods. Meanwhile, variations during different sites showed significant to Ni, Zn and Fe. One-way analysis of variance

with Tukey's HSD test showed remarkable differences (p<0.01) to Cu, Cd and Pb between sites around the Hormuz Island (10-13) with sites along mainland coastal areas (1-9). During this study, mean metals concentrations (across all sites and periods) were: Pb (23.1), Cd (4.2), Cu (9.4), Ni (18.9), Zn (41.9) and Fe (20871) μ g gG¹ dry weight. Results of this research were compared with other areas and in some cases showed higher and lower than the others (Table 3).

The results of six heavy metals (Pb, Cd, Cu, Ni, Zn and Fe) in eleven seaweed species from thirteen locations are presented in Table 4. The pattern of metal levels in seaweeds was decreased as following order: Fe > Zn > Ni > Pb > Cu > Cd. Among the metal concentrations, Fe showed the highest (688-27790 μg gG¹ dry weight) in all the species and in the majority of species Cd was found to be lowest level (0.2-8.7 μg gG¹ dry weight). The data for the toxic Pb, Cu, Ni and Zn are in the range 1.4-47.1, 3.0-42.0, 5.0-100.0 and 27.4-105.0 μg gG¹ dry weight, respectively (Table 4).

Table 2: Metals concentrations (mean \pm S.D) in sediment ($\mu g \ g G^1$ dry weight) during all periods

Site	Pb	Cd	Cu	Ni	Zn	Fe
1	24.6±2.1	4.1±0.6	12.2±1.1	12.1±2.2	-	-
2	21.7±2.0	4.8±0.9	9.8±1.4	14.5±4.1	-	-
3	22.0±1.8	4.2±0.9	7.6 ± 1.2	15.9 ± 3.2	-	-
4	20.1±2.2	5.8±0.7	11.0±1.5	17.8±1.7	-	-
5	26.0±3.5	5.5±0.8	7.2±1.6	13.2±2.0	-	-
6	19.9±2.8	4.1±0.9	4.2±0.9	22.1±3.2	-	-
7	25.1±2.4	5.7±0.8	3.8 ± 0.5	19.2±2.1	-	-
8	19.2±2.1	5.4 ± 0.7	6.1±1.2	21.0 ± 2.4	-	-
9	20.5 ± 2.7	3.8±0.9	6.3±1.4	28.0 ± 3.4	-	-
10	24.5±2.3	2.8±1.0	14.9 ± 2.1	-	42.1±2.8	14143±448
11	29.7±3.4	2.4 ± 0.5	15.2±1.9	-	43.5±3.9	44840±514
12	22.1±2.1	2.8±0.4	13.6±1.7	-	40.8±4.7	15382±350
13	24.5±3.1	2.5±0.3	9.8±1.1	-	41.2±5.9	9121±231

 $Table \ 3: \ Heavy \ metals \ concentrations \ (\mu g \ gG^1 \ dry \ weight) \ in \ surface \ sediments \ from \ different \ areas \ in \ the \ Persian \ Gulf$

Area	Pb	Cd	Cu	Ni	Zn	Fe	Reference
UAE	2.01	0.6	4.5	-	-	3238	[22]
Qatar / Bahrain	7.9	0.2	5.8	14.5	3.8	-	[23]
Oman	1.2	0.16	3.25	-	5.74	5400	[22]
Kish Island	4.22	0.28	3.42	5.48	6.38	-	[14]
Present study	23.1	4.15	9.4	18.19	41.93	20871	Present study

Table 4: Metal concentrations (mean \pm S.D) in μg gG^1 dry weight for all species during four seasons sampling

Season	Site	Pb	Cd	Cu	Ni	Zn	Fe
U. compressa Autumn 2007	3	18.5±3.1	5.1±0.6	9.9±2.1	18.3±2.5	-	-
	4	18.3±4.3	5.3±1.2	10.0±3.1	44.9±10.5	-	-
	5	19.9±2.5	5.5±1.7	7.8 ± 2.2	25.1±5.7	-	-
	6	20.0±3.1	5.6±1.1	8.0 ± 2.6	17.5±3.1	-	-
	7	20.1±2.6	5.5±1.3	8.1±3.0	18.1±2.6	-	-
	8	19.9±2.2	4.9 ± 0.9	9.9±2.7	18.7±3.1	-	-
	9	20.2±3.4	5.0±1.1	10.2±3.4	25.1±3.5	-	-
	10	47.1±5.0	6.1±0.8	15.7±1.5	-	59.1±4.3	2498±110
	12	42.7±3.3	5.2±2.6	14.8±0.6	-	52.4±5.5	9994±360
Winter 2008	1	24.9 ± 4.2	3.5±1.0	12.4±4.2	45.3±10.5	-	-
	2	27.6±4.6	3.8±1.1	11.5±3.5	75.0 ± 10.7	-	-
	3	25.1±5.3	5.0±1.4	12.8±3.8	55.1±9.4	-	-
	4	25.0±4.4	5.1±2.1	7.5 ± 2.4	33.5±8.4	-	-
	5	24.9 ± 6.2	3.1±0.9	7.5 ± 2.2	30.4±7.3	-	-
	6	20.2±3.7	3.3±1.2	7.6 ± 2.9	52.5±9.3	-	-
	7	19.3±3.8	3.1±1.5	8.8±3.5	75.0 ± 10.6	-	-
	8	21.2±4.3	4.2±1.4	9.3±2.7	45.2±8.9	-	-
	9	20.3±3.7	3.8±1.1	9.0±3.1	$74.8 \pm 9,6$	-	-
	10	10.1±0.9	7.6 ± 0.1	18.4±1.0	-	53.3±11	9832±470
Spring 2008	1	35.1±7.2	5.8 ± 2.1	12.2±3.2	57.5±7.4	-	-
	4	25.0±5.3	6.0 ± 2.3	13.1±4.1	68.5±9.8	-	-
	5	32.5±4.9	7.5 ± 3.1	8.4±3.1	40.0±6.2	-	-
	6	14.3±3.4	3.4±0.8	10.0±2.9	68.0 ± 8.9	-	-
	7	13.6±2.8	3.7±0.5	9.4±2.5	57.4±6.5	-	-
	8	15.4 ± 4.1	4.1±0.3	9.7±3.1	68.4 ± 9.2	-	-

Table 4: Continued

Table 4: Continued		27.5.62	50.06	0.0.22	47.5.60		
Summer 2008	4	37.5±6.2	5.8±0.6	8.8±2.3	47.5±6.9	-	-
	5	25.0±4.7	4.0±0.5	13.8±4.1	32.5±5.4	-	-
	6	27.5±5.3	3.3±0.7	12.5±2.8	35.0±5.1	-	-
	7	25.0±4.4	4.5±1.1	7.5±3.2	40.0±9.3	-	-
	8	26.3±6.4	5.4±1.4	8.9±2.8	25.0±6.8	-	-
	9	27.6±5.1	5.9±1.5	6.8±2.5	32.4±8.5	-	-
C. membranacea Summer		32.6±6.7	5.8±2.3	4.8±2.0	24.3±4.5	-	-
	2	35.0±6.2	6.0±2.2	12.5±3.2	32.6±4.7	-	-
	3	25.0±5.3	4.6±1.8	4.9±1.9	20.2±3.2	- 27.5.1.1	-
	10	22.6±1.1	0.9±0.1	3.0±0.6	-	37.5±1.1	17470±500
	11	30.4±5.1	0.8±0.4	25.4±2.6	-	30.1±2.7	19000±465
	12	14.2±5.9	2.0±0.9	13.5±1.0	-	37.7±5.8	11659±189
****	13	11.9±0.4	0.6±0.1	8.7±3.7	-	29.6±0.7	12903±388
Winter 2008	13	4.6±0.6	2.2±0.3	22.6±1.3	-	82.9±10	688±190
C. taxifolia Autumn 2007	10	23.4±0.7	3.8±0.2	25.5±2.9	-	39.3±1.8	4729±914
Spring 2008	2	21.1±4.3	3.2±1.1	8.1±3.1	72.6±9.5	-	-
	3	20.1±4.7	3.3±0.9	9.9±2.9	70.6±10.4	-	-
Summer 2008	10	24.5±0.5	0.6 ± 0.1	8.5±0.7	-	44.3±3.7	16013±178
	11	44.4±2.6	0.8 ± 0.1	23.4±1.1	=	24.5±1.7	27790±145
	12	20.2±0.8	0.9±0.1	6.2±1.8	-	50.5±0.4	10934±446
P. pavonica		Pb	Cd	Cu	Ni	Zn	Fe
Autumn 2007	1	20.1±4.3	5.0±1.7	5.0±1.5	12.6±3.1	-	-
	2	10.0 ± 2.5	$7.5\pm 2,1$	10.0±3.1	10.0 ± 2.2	-	-
	3	12.5±3.4	5.0±1.9	30.0±6.7	9.9±1.6	-	-
	4	13.2±3.1	6.3±2.1	28.5±5.3	12.5±2.7	-	-
	10	12.2±0.3	8.1±1.2	42.1±26.7	-	55.3±4.5	7020±173
	11	61.0±3.8	$8.4{\pm}1.0$	56.8 ± 4.6	-	70.4±13	3249±128
	12	2.7 ± 0.6	6.4 ± 0.2	22.2±0.9	-	72.1±1.9	9673±106
	13	30.8 ± 0.8	7.4 ± 0.4	27.0±3.3	-	67.8±1.5	10377±327
Winter 2008	1	23.1±7.0	5.5±1.7	12.5±2.9	80.0 ± 8.9	-	-
	2	17.5±5.1	4.0±1.1	8.0 ± 2.6	75.0 ± 6.4	-	-
	3	9.2 ± 2.1	4.0±1.6	18.5±5.1	80.0±9.5	-	-
	4	12.6±3.4	5.2±1.9	21.6±4.8	74.3±6.9	-	-
	10	14.3±1.6	7.3±1.0	12.4 ± 0.7	-	45.9±3.8	6232±272
	11	47.9±6.3	4.0 ± 0.8	42.0±6.1	-	54.5±5.9	2743±825
	12	22.9±2.3	8.0±0.2	12.7±0.5	-	40.8±1.2	3991±828
	13	13.5±2.2	5.5±1.2	44.4±4.8	-	41.1±8.1	1386±224
Spring 2008	1	11.1±2.3	3.0±1.1	8.2 ± 2.4	52.5±4.6	-	-
	2	14.0±5.3	4.5±1.2	7.8 ± 2.2	70.0±8.9	-	-
	3	22.7±5.1	5.0±1.8	10.0±3.1	77.5±6.7	-	-
	4	23.4±3.1	6.3±2.2	9.5±2.1	70.4±9.2	-	-
	10	10.4±0.9	2.7 ± 0.8	5.6 ± 2.8	-	29.6±2.7	8360±103
	11	6.2±0.3	1.7±0.6	7.7±2.1	-	48.4±9.0	14554±375
	12	1.4±0.3	4.6±1.3	9.3±4.0	-	27.4±3.4	9360±217
	13	14.0±1.1	1.9±0.1	5.6±2.1	-	34.0±3.0	11010±281
Summer 2008	1	20.0±3.2	5.3±2.1	11.0±3.2	22.6±6.1	-	-
	2	24.6±5.1	6.0±2.3	7.5±2.4	31.0±8.3	-	-
	3	20.3±3.9	5.5±1.8	12.1±4.1	35.0±5.2	-	-
	4	23.5±4.9	6.8±2.6	11.9±3.9	30.9±6.9	-	_
				9.2±0.4	2 3.7 = 0.7	42.8±0.7	17984±186
	10	1/./+09	1./+01				
	10 12	17.7±0.9 22.5±0.9	1.7±0.1 0.2±0.1	3.1±0.1	-	37.3±1.4	9028±152

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Table 4: Continued

Table 4: Continued							
C. sinuosa Winter 2008	3	32.5±7.2	3.5±1.4	7.4 ± 2.5	60.1±12.2	-	-
	10	46.8 ± 2.1	9.5±0.3	13.7±1.1	-	43.9 ± 0.3	4277±160
	11	26.9 ± 3.4	6.1±1.0	28.9 ± 0.8	-	49.4±5.5	7382±326
	12	8.3±1.3	2.7 ± 0.2	13.5±1.4	-	39.3 ± 2.2	1655±284
S. angustifolium Autumn 2007	1	17.5 ± 4.2	6.0 ± 2.1	5.0±1.5	6.0 ± 2.1	-	-
	2	8.3±3.1	6.8±3.3	7.6 ± 2.2	7.5±1.8	-	-
	3	12.6±4.1	5.0±2.1	5.5±3.1	5.0±1.4	-	-
	4	14.2±3.6	6.3±1.9	5.9±1.8	6.3±2.3	-	-
Spring 2008	1	9.3±4.0	2.5±0.9	7.0±2.3	57.5±8.4	-	-
	2	11.0±2.7	2.8±0.6	5.1±2.1	60.0±10.5	-	-
Summer 2008	1	15.0±3.1	4.5±0.7	5.3±1.6	18.5±3.8	-	-
	2	21.0±5.2	4.5±1.1	7.3±2.9	16.0±5.1	-	-
	3	14.0±4.1	4.0±1.2	5.0±2.4	17.8±3.6	-	-
	4	15.1±4.1	5.0±2.1	9.8±3.1	20.0±4.1	-	-
C. myrica		Pb	Cd	Cu	Ni	Zn	Fe
Autumn 2007	1	20.5±3.2	5.0±1.2	5.0±2.1	10.8±1.8	-	-
	2	12.7±4.1	7.5±3.1	7.5±2.4	10.0±2.5	-	-
	3	20.2±3.8	5.0±2.2	4.9±1.6	12.5±3.2	-	_
	4	22.3±4.5	6.9±3.4	5.2±2.4	11.3±4.1	_	-
Winter 2008	2	27.5±5.1	5.0±2.2	12.8±4.2	79.9±10.4	_	-
Spring 2008	3	16.5±4.5	3.3±1.0	7.3±3.2	67.5±9.1	_	_
Spring 2000	4	11.0±3.1	4.3±1.2	5.0±1.9	75.0±9.4	_	
Summer 2008	2	27.4±5.7	3.8±0.8	7.5±2.1	20.0±3.1		
Summer 2000	3	21.8±4.2	4.5±0.6	8.3±3.1	28.5±2.6		
	4	32.5±7.2	4.5±0.0 6.0±1.1	12.5±2.7	32.6±4.2	_	_
C. parvula Spring 2008	1	15.5±4.3	4.3±1.8	8.5±2.7	60.0±5.9	_	_
C. parvida Spring 2008	10	15.2±1.0	4.3±1.8 0.8±0.2	13.2±2.2	00.0±3.9	32.9±2.1	9485±169
	11	7.3±1.1	0.8±0.2 0.2±0.1	13.2±2.2 11.3±4.5	-	32.9±2.1 105±7.9	
					-		13570±20
	12	3.8±0.6	1.7±0.4	9.3±1.8	-	34.4±1.7	10471±253
a	13	14.5±1.1	1.0±0.1	6.6±2.9	-	31.8±0.6	10812±175
Summer 2008	2	22.5±4.3	5.8±1.4	10.8±3.1	30.0±6.1	-	-
G. corticata Winter 2008	5	22.5±4.8	5.7±1.4	15.0±3.7	88.510.1	-	-
	6	18.5±3.9	4.8±2.1	10.0±1.8	86.0±7.2	-	-
	7	27.5±5.7	4.3±1.5	9.3±2.7	96.3±6.1	-	-
	8	25.1±5.3	5.1±1.8	13.8±2.4	100.0±9.3	-	-
	9	26.2±6.4	6.2±3.3	12.8±3.1	85.4±6.9	-	-
Spring 2007	4	25.0±4.3	5.4±2.1	25.1±4.3	88.3±6.9	-	-
A. specifera Spring 2008	1	21.3±4.2	4.0 ± 2.1	10.0 ± 2.6	74.3±4.8	-	-
	2	25.0±2.3	6.3±1.8	5.5±1.3	75.1±4.2	-	-
	3	20.2±3.6	5.1±1.3	10.0 ± 3.3	73.5±5.7	-	-
	4	24.2 ± 3.7	5.3±1.5	5.8±2.1	82.5±6.9	-	-
Summer 2008	1	27.6±6.8	5.6 ± 2.1	25.1±6.4	27.5±4.3	-	-
	2	22.8±4.3	6.0±3.6	11.3±3.6	25.0±2.8	-	-
	3	23.6±5.5	7.1±3.5	12.5±2.6	23.9±3.1	-	-
J. rubens Autumn 2007	1	20.8±4.5	7.5±1.8	7.4±2.1	15.0±2.7	-	-
	2	35.0±7.3	7.3±2.1	7.5±2.4	14.9±2.2	-	-
	3	36.2±4.1	8.7±3.1	6.8±3.1	13.8±1.6	-	-
Winter 2007	4	30.0±6.9	4.5±1.8	10.1±2.8	42.8±4.3	-	_

During present research, mean heavy metals values demonstrate similar accumulation patterns Fe > Zn > Ni > Pb > Cu > Cd in three Chlorophyta species. Meanwhile, in Phaeophyta and Rhodophyta species (except to *Jania rubens*) the pattern of heavy metals bioaccumulation was decreased as follow: Fe > Pb > Cu > Cd. However, no clear pattern observed to Ni and Zn metals. In *Jania rubens* species, metals accumulation was ordered as follow: Pb > Ni > Cu > Cd (Table 5).

In the present study for all cases, two-way ANOVA revealed statistically significant differences (p<0.05) in Ni, Pb and Cu content in different species. Whereas, significant (p<0.01) variation to Cu and Pb between sampling sites were observable. On the other hand, interaction between species and sites showed significant differences (p<0.05) in Ni and Cu concentrations.

During present research, Pb concentration in different algal species decreased as following order: *Jania rubens* > *Colpomenia sinuosa* > *Caulerpa taxifolia* > *Ulva compressa*, *Gracilaria corticata* > *Acanthophora specifera* > *Cladophoropsis membranacea* > *Cystoseira myrica* > *Padina pavonica* > *Sargassum angustifolium* > *Champia parvula*. Among all species, Pb concentrations varied from 13.1 to 30.5 µg gG¹ dry wt. The concentrations of Pb found in *Jania rubens* in this study showed higher compared to other areas (Table 6). High levels of Pb in alga of study area could be attributed to combustion of fossil fuels and oil pollution. However, no significant differences observed in Pb values between different classes of seaweeds (Table 7).

All algal species showed approximately similar pattern of Cd levels: Jania rubens > Acanthophora specifera > Colpomenia sinuosa > Gracilaria corticata > Cystoseira myrica > Padina pavonica > Ulva compressa > Sargassum angustifolium > Cladophoropsis membranacea > Champia parvula > Caulerpa taxifolia. The highest and lowest cadmium concentrations in different species observed from 2.1 to 7.0 µg gG¹ dry wt, respectively (Table 5). Cadmium in algae > 2 µg gG¹ dry wt. has been coined for polluted environments [11]. Influx of domestic sewage has been suggested as one of the main causes of Cd contamination in these waters. High levels of Cd may also be due to content of local rock formation. According to Al-Abdali et al. [12] CaCO3 in rock formation contain much Cd impurely. In addition, much of the steel use in the Bandar Abbas Port and industrial facilities to contain coating which can be end up in the nearby waters of the area. In the present study, Cd was more concentrated in red and brown seaweeds,

compared to the green seaweed. Jania rubens and Colpomenia sinousa showed higher Cd accumulation which was in agreement with Rao [13] and Dadolahi et al. [14]. Cadmium levels in algal species showed higher than those reported from other areas (Table 6) and among different classes of seaweeds it was more accumulated by Phaeophyta and Rhodophyta than Chlorophyta (Table 7). Mean levels of Cu ranged from highest value of 16.9 in Padina pavonica to minimum value of 6.4 µg gG¹ dry wt. in Sargassum angustifolium (Table 5) Copper concentration in this area showed higher in some species (e.g. Ulva intestinalis; Padina sp.; Champia parvula) and in some cases lower (e.g. Sargassum angustifolium; Acanthophora specifera) than those reported from other areas of the world (Table 6). During this study and among three classes of seaweeds, copper showed more concentrated in Chlorophyta species compare to others (Table 7). The presence of Cu in high concentrations causes great danger to all marine organisms, including fish crustacean, phyto- and zeo- plankton, algae and filter feeders. Industrials effluents from the extensive oil production, high traffic shipping, loading and transport facilities off coasts of the Province of Hormuzgan could act as source of Cu pollution. On the other hand, effluents from industrial and agricultural centres may be entering the seawater and may become a source of Cu contamination. Also, fish boats painted with Cu antifouling coatings could be another source of Cu pollution in areas of study. According to Giusti [15] and Caliceti et al. [16] copper contamination is associated with algal levels of $> 20.00 \,\mu g \, g^{-1} \, dry \, wt$.

Nickel levels in seaweed species followed this pattern: Gracilaria corticata > Caulerpa taxifolia > Colpomenia sinuosa > Acanthophora specifera > Padina pavonica > Champia parvula > Ulva compressa > Cystoseira myrica > Cladophoropsis membranacea > Sargassum angustifolium and Jania rubens. Mean Ni concentration varied between 21.5 and 90.8 µg gG¹ dry wt. It showed the lowest and highest values at Sargassum angustifolium and Gracilaria corticata, respectively (Table 5). In this study, nickel values showed lower in Acanthophora specifera than those reported by Al-Homaidan [17] but it was higher than those reported by Denton et al. [18] (Table 6). Meanwhile, in other species nickel contained showed higher levels than those reported from other areas. During present study, nickel values decreased in different classes of seaweeds as following order: Rhodophyta > Chlorophyta > Phaeophyta (Table 7).

Table 5: Metal concentrations (mean±S.D) in µg gG¹ dry weight for all species during sampling

Species	Pb	Cd	Cu	Ni	Zn	Fe
Chlorophyta						
Ulva compressa	24.2±8.1	4.8±1.2	10.3 ± 2.8	43.8±18.9	54.9±3.6	7441
Cladophoropsis membranacea	22.0±10.9	2.9 ± 2.3	11.9±8.4	25.7±6.3	43.4±21.9	12344
Caulerpa taxifolia	25.6±9.4	2.1±1.5	13.6±8.5	71.6±1.4	39.7±11.1	14867
Phaeophyta						
Padina pavonica	18.4±11.8	5.0±2.1	16.9±13.6	46.5±28.2	48.7±14.6	8304
Colpomenia sinuosa	28.6±15.9	5.5±3.1	15.9±9.2	60.1±4.5	44.2±5.1	4438
Sargassum angustifolium	13.8±3.8	4.7±1.4	6.4±1.6	21.5±6.9	-	-
Cystoseira myrica	21.2±6.7	5.1±1.3	7.6 ± 2.9	34.8 ± 28.3	-	-
Rhodophyta						
Champia parvula	13.1±6.6	2.3 ± 2.2	9.9 ± 2.3	45.0±21.2	51.0±36.0	11085
Gracilaria corticata	24.1±3.2	5.3±0.7	14.3±5.7	90.8±10.2	-	-
Acanthophora specifera	23.5±2.4	5.6±1.0	11.5±6.6	54.5±27.4	-	-
Jania rubens	30.5±7.0	7.0±1.8	7.9±1.5	21.6±14.1	-	_

Table 6: Heavy metals concentrations (µg gG1 dry wt.) in different seaweed species from different areas

Species	Location	Pb	Cd	Cu	Ni	Zn	Fe	References
Ulva lactuca	Persian Gulf	15.0	0.85	10.21	-	40.0	850	[4]
Ulva intestinalis	Persian Gulf	2.32	0.44	3.42	1.37	8.94	-	[14]
Ulva intestinalis	Strait of Hormuz	24.2	4.84	10.33	43.81	54.93	7441	Present study
Caulerpa sp.	Red Sea	2.5	0.93	20.5	-	7.9	90	[24]
Caulerpa taxifolia	Strait of Hormuz	25.62	2.1	13.6	71.6	39.65	14867	Present study
Padina sp.	Persian Gulf	0.96	1.31	2.71	1.05	7.23	-	[14]
Padina boryana	Red Sea	0.9	0.65	5.14	-	3.50	50	[24]
Padina pavonica	Strait of Hormuz	18.44	5.02	16.87	46.51	48.65	8304	Present study
Sargassum binderi	Oman Sea	1.4	0.64	3.8	1.11	4.2	-	[8]
Sargassum angustifolium	Persian Gulf	7.1	N.D	85.0	3.5	18.6	-	[25]
Sargassum angustifolium	Strait of Hormuz	13.8	4.74	6.35	21.46	-	-	Present study
Champia parvula	Persian Gulf	4.47	1.07	2.05	1.35	8.72	-	[14]
Champia parvula	Strait of Hormuz	13.13	2.3	9.95	45.0	51.03	11085	Present study
Acanthophora specifera	Persian Gulf	N.D	-	-	57.4	-	-	[17]
Acanthophora specifera	Siapan	4.32	0.42	16.7	1.93	-	-	[18]
Acanthophora specifera	Strait of Hormuz	23.53	5.93	11.46	54.54	-	-	Present study
Jania rubens	Persian Gulf	1.76	1.43	0.97	0.88	4.59	-	[14]
Jania sp.	Mediterranean Sea	-	1.2	20.1	-	-	-	[10]
Jania rubens	Strait of Hormuz	30.5	7.0	7.95	21.63	-	_	Present study

Table 7: Metal concentrations (mean \pm S.D) in $\mu g \ g G^1$ dry weight in different classes of seaweed

	Pb	Cd	Cu	Ni	Zn	Fe
Chlorophyta	23.95±1.80	3.27±1.41	11.95±1.64	47.04±23.12	45.99±7.97	11550±3775
Phaeophyta	20.53±6.21	5.09±0.29	11.68±5.47	40.72±16.48	46.53±3.15	6371±2733
Rhodophyta	22.82±7.19	5.05±1.97	10.92 ± 2.68	52.98±28.73	51.03±4.68	11085±341

Mean values of Zn concentrations were measured at six species and among them the maximum values of 54.93 µg gG¹ dry wt. observed in *Ulva compressa* (Table 5). However, no significance variations were observed between Zn vales in different species. Among all the species, *Ulva compressa* showed higher uptake probably because green seaweeds have more capacity, more tolerant or higher need for Zn. In this study, *Ulva compressa* near desalination plants showed more Zn accumulation compared to Cd and Cu. This was in agreement with Foster [19], who reported

that elevated Zn concentrations inhibited Cd uptake by seaweeds due to competition for binding sites. The competition between metals for algal sites could decrease the accumulation of those elements which exhibited lower concentration levels in environment (water or sediment) or which are present in less available forms (e.g. Cd). Zinc values from this area showed higher than those reported from other areas (Table 6). In this research, Zn levels in different classes of seaweeds decreased as follow: Chlorophyta > Rhodophyta > Phaeophyta (Table 7).

Fe metal values were analysed at six species and among all metals concentrated by algal, Fe levels found too high. Among different species, *Caulerpa taxifolia* and *Colpomenia sinuosa* showed the highest and lowest values of 14867 and 4438 µg gG¹ dry wt. respectively (Table 5). The main sources of Fe in our study area (sites around the Hormuz Island) were due to a huge iron mine in operation at this area and because of that Fe values always showed high. However, the mean Fe level showed higher than those reported from other areas (Table 6). Among different classes of seaweeds, Chlorophyta species showed more Fe accumulated compare to others (Table 7).

Accumulation of metals depend on the type of polysaccharides in the algae and since various elements have different electronegativity (tends to accept electrons) probably this can affects on the metals uptake in algae at different levels [20]. However, variations in the metals contents of seaweeds could be also due to different metals electronegativity values as in this study metals in higher electronegativity values (e.g. Fe, Ni and Cu) were concentrated more than other metals with lower values (e.g. Cd).

In this study, presence of positive or negative relationships between some metals in Chlorophyta, Phaeophyta and Rhodophyta species reflected the synergistic or antagonistic interactions of ions in binding with the anionic sites offered by the plants (Tables 8-10). The synergistic interactions of Pb with Zn in Ulva compressa, Pb with Cd, Ni, Fe and Cd with Ni, Zn and Cu with Ni in Cladophoropsis membranacea and Pb with Ni and Fe in Caulerpa taxifolia were observed (Table 8). The synergistic interactions of Pb with Cu, Zn and Cd with Cu, Zn and Cu with Zn in Padina pavonica and Pb with Cu in Cystoseira myrica were also observed (Table 9). Whereas, there was no significant synergistic correlations between metals in red algal species observed. However, antagonistic interactions of Pb with Fe, Cd with Ni and Zn with Fe in *Ulva compressa* and Pb with Zn, Cd and Zn with Fe in Cladophoropsis membranacea and Pb with Zn and Cd with Ni, Fe and Cu with Ni, Zn and Zn with Fe in Caulerpa taxifolia were observed (Table 8). The antagonistic interactions of Pb with Fe, Cd with Ni, Fe and Cu with Fe in Padina pavonica and Cd with Ni in Sargassum angustifolium and Cystoseira myrica were observed. However, there was significant antagonistic correlation coefficient between Cu and Cd with Ni in Acanthophora specifera and Gracilaria corticata, respectively (Table 10).

Variability in metal accumulation by algae may depend on antagonism interaction between metals for binding with the anionic sites of the plants. In many Rhodophyta, the sulphahydryl groups of carrageenan and sulphated galactans of agar offer many anionic sites for the binding of polyvalent cations. Though, red algae are known for their sulphated galactones, their S content observed to be lower than in green and brown algae and it seems that inorganic S is less in Rhodophyceae. Rao [13] reported that most of SO₄ is in inorganic (ionic) form in green and brown algae whereas organic fraction is more in red algae associated with polysaccharides. However, in metals uptake studies by each species, various conditions must be carefully considered such as geochemical principles including residence time and bond energy (chemical bonding) properties of elements (i.e. ionization energy, charge to radius and mass electronegativity) etc. Although, in this study no measurement on any positive single charge element was carried out, but there is some studies which confirm the antagonism interaction between metals with different charges (e.g. double or triple charged) anionic sites. In this study, Fe, Zn more accumulated by all species probably due to Fe and Zn are as an essential element in seaweeds, higher concentration in sediment and the geochemical principles such as those mentioned earlier. On the other hand, in this study synergistic interactions were observable between metals with the same charges.

During present study, the efficiency of metal bioaccumulation in the eleven species of seaweed by calculating their respective Bio-Sediment Accumulation Factor (BSAF, Table 11) which is defined as the ratio between the metal concentration in the organism and that in the associated sediment [10]. The highest BSAF was obtained for Ni, which could be explained by higher levels of these metals in the sediment. Average BSAF for Ni was significantly > 1; a comparison between BSAF of all elements, maximum values of BSAF (4.99) was observed to Ni in Gracilaria corticata and Colpomenia sinousa showed minimum value of BSAF (0.21) to Fe. Among all metals the BSAF values of Fe to all species showed less than 1. During present research, to compare the total content of metals at the different sampling sites the Metal Pollution Index (MPI) was calculated according to Dadolahi et al. [14], Giusti [15].

$$MPI = (Cf_1 \times Cf_2 \dots Cf_n)^{1/n}$$

Where Cf_i = concentration for the metal i in the sample.

Table 8: Correlations between concentrations of paired metals in Chlorophyta species

Element	Pb	Cd	Cu	Ni	Zn	Fe
Ulva compressa (N= 30, p < 0.05)						
Pb	1.00	0.26	0.23	-0.04	0.48*	-0.57*
Cd		1.00	0.26	-0.36*	-0.02	0.12
Cu			1.00	0.29	-0.16	0.26
Ni				1.00	-	-
Zn					1.00	-0.98*
Fe						1.00
Cladophoropsis membranacea (N= 8, p < 0.05)						
Pb	1.00	0.58*	-0.23	0.88*	-0.68*	0.91*
Cd		1.00	-0.32	0.83*	0.71*	-0.78*
Cu			1.00	0.94*	0.45	-0.31
Ni				1.00	-	-
Zn					1.00	-0.90*
Fe						1.00
Caulerpa taxifolia (N= 6, p $<$ 0.05)						
Pb	1.00	-0.46	0.62	0.99*	-0.95*	0.88*
Cd		1.00	0.22	-0.98*	-0.02	-0.70*
Cu			1.00	-0.99*	-0.77*	0.10
Ni				1.00	-	-
Zn					1.00	-0.71*
Fe						1.00

Table 9: Correlations between concentrations of paired metals in Phaeophyta species

Element	Pb	Cd	Cu	Ni	Zn	Fe
Padina pavonica (N= 31, p < 0.05)						
Pb	1.00	0.26	0.48	0.07	0.44	-0.45
Cd		1.00	0.48	-0.46	0.49	-0.56*
Cu			1.00	-0.21	0.56*	-0.64*
Ni				1.00	-	-
Zn					1.00	0.11
Fe						1.00
Sargassum angustifolium (N= 10, p < 0.05)						
Pb	1.00	0.15	-0.01	-0.41		
Cd		1.00	0.14	-0.88*		
Cu			1.00	-0.01		
Ni				1.00		
Cystoseira myrica (N= 10, p < 0.05)						
Pb	1.00	-0.01	0.66*	-0.10		
Cd		1.00	0.06	-0.51*		
Cu			1.00	0.38		
Ni				1.00		

Table 10: Correlations between concentrations of paired metals in Rhodophyta species

Element	Pb	Cd	Cu	Ni
Acanthophora specifera (N= 7, p < 0.05)				
Pb	1.00	0.41	0.53	-0.37
Cd		1.00	0.05	-0.57
Cu			1.00	-0.67*
Ni				1.00
Gracilaria corticata (N= 7, p < 0.05)				
Pb	1.00	0.05	0.13	0.47
Cd		1.00	0.38	-0.55*
Cu			1.00	-0.19
Ni				1.00

Table 11: Mean BSAF* from Hormuzgan Province on the coast of the Persian Gulf (Strait of Hormuz), Iran. *BSAF, biosediment accumulation factor (BSAF= C_x/C_s , where C_x and C_s are the mean concentrations of metals in the organism and in associated sediment, respectively)

	Pb	Cd	Cu	Ni	Zn	Fe
Sediment	23.10	4.15	9.40	18.19	41.93	20871
Ulva compressa	24.20	4.84	10.33	43.81	54.93	7441
Cladophoropsis membranacea	22.04	2.86	11.93	25.70	43.38	12344
Caulerpa taxifolia	25.62	2.10	13.60	71.60	39.65	14867
Padina pavonica	18.44	5.02	16.87	46.51	48.65	8304
Colpomenia sinuosa	28.63	5.45	15.88	60.10	44.20	4438
Sargassum angustifolium	13.80	4.74	6.35	21.46	-	-
Cystoseira myrica	21.24	5.13	7.60	34.81	-	-
Champia parvula	13.13	2.30	9.95	45.00	51.03	11085
Gracilaria corticata	24.13	5.25	14.13	90.75	-	-
Acantophora specifera	23.53	5.93	11.46	54.54	-	-
Jania rubens	30.50	7.00	7.95	21.63	-	-
BSAF-1	1.05	1.17	1.10	2.41	1.31	0.36
BSAF-2	0.95	0.69	1.27	1.41	1.03	0.59
BSAF-3	1.11	0.51	1.45	3.94	0.95	0.71
BSAF-4	0.80	1.21	1.79	2.56	1.16	0.40
BSAF-5	1.24	1.31	1.69	3.30	1.05	0.21
BSAF-6	0.60	1.14	0.68	1.18	-	-
BSAF-7	0.92	1.24	0.81	1.91	-	-
BSAF-8	0.57	0.55	1.06	2.47	1.22	0.53
BSAF-9	1.04	1.27	1.50	4.99	-	-
BSAF-10	1.02	1.43	1.22	3.00	-	-
BSAF-11	1.32	1.69	0.85	1.19	-	-
BSAF-mean	0.86	1.11	1.22	2.58	1.12	0.47

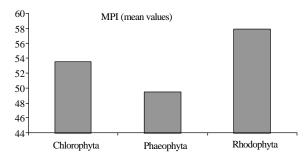


Fig. 2: MPI values in different classes of seaweed

The overall metal burden of *Ulva compressa*, *Cladophoropsis membranacea*, *Caulerpa taxifolia*, *Padina pavonica*, *Colpomenia sinuosa* and *Champia parvula* was compared with metal content in sediments (dominant at almost sites), using the MPI calculated. Among different classes of seaweeds, the MPI values of different classes of seaweed showed the highest and lowest in Rhodophyta in Phaeophyta, respectively (Figure 2). Meanwhile, species MPI values were decreased as following order: *C. taxifolia* > *P. pavonica*, *C. sinousa* > *U. compressa* > *C. membranacea* and *C. parvula* (Figure 3).

Studies on the ecological implication of heavy metal uptake by some researchers such as Abdallah and Abdallah, [10] showed that the metal variation in species from different sampling sites may be related not only to different metal levels, but also to factors such as tidal range, temperature, salinity regimes, dissolved nutrients, type of tissue, age of plant, its nutritional history and the geological structure of the study area. In this study, metals (Cd, Pb and Cu) uptake showed higher by seaweeds at those sites (no. 10-13) where are more exposed to the higher dynamic factors (e.g. water movements and winds). This was consistent with the observation by Forsberg et al. [21] who showed the dynamic factors could affected the metals uptake in seaweed. The effect of wind as mentioned earlier not only increase the transfer of soil particles into the sea, but it also caused water agitation and mixing of sediment particles, both of which may increase the heavy metal loads in the water. On the other hand, the seabed slope at sites 10 to 13 were steeper (compared to other sites) resulting suitable conditions to more water current and mixing. Higher metal levels in sites 10-13 (around the Hormuz Island) were confirmed by higher MPI values of

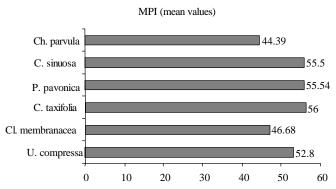


Fig. 3: MPI values in different seaweed species at all sampling periods and sites

Table 12: Comparison of mean MPI values in dominant species between two sampling areas

	1 5		
Species	MPI values (Hormuz Island)	MPI values (mainland)	
U. compressa	15.07	10.87	
Cl. Membranacea	7.38	10.74	
C. taxifolia	11.06	8.52	
P. pavonica	12.89	10.15	
C. sinuosa	14.63	9.24	
Mean values	12.21	9.90	

12.21 in these sites compare to sites 1-9 (Table 12). Higher MPI indicated more metals uptake by seaweeds in such areas [21]. The results demonstrated that the importance physical conditions at chosen sites such as wind and wave action, type of substrate and the slope of the shore will also influence the metal status.

Inputs of materials via atmosphere in marine environment of the Strait of Hormuz are probably significant due to different oil industry activities, high shipping traffic and the presence one of the driest deserts of the world around the Persian Gulf. The mean seasonal wind speed in this area were 49.2 and 60.0, 52.8, 49.2, km/h respectively during autumn, winter, spring and summer (as reported by Bandar Abbass Meteorological Station), respectively. During this period, some elements can be dominant probably associated with the input from the airborne dust, masking and counteracting biological removal associated with phytoplanktonic blooms.

CONCLUSION

Results showed heavy metals concentrations in both sediment and algal species around the Hormuz Island were higher than those sites along the mainland coats. Among all species, *Ulva compressa* and *Padina pavonica* showed maximum time and space distribution. The higher mean BSAF values of Ni and Cu to these species, indicating that both metals probably get into the coastal

area of Hormuzgan Province from the same sources and following a similar distribution pattern. The results revealed concentrations of heavy metals in marine algae of this study were on the approximately higher side as compared to other reports from the different regions. The reasons for higher concentrations in this area may be due to various parameters such as differences in pH, temperature, salinity and other metal-binding nutrients in seawater and high shipping traffic in this area.

Results of the current study can interface with other biomonitoring projects that are ongoing in this area. Studies of metals in oyster clam and shrimp of the area are currently underway. Seaweed ecology in intertidal areas of Hormuz Island, Hormuzgan and Bushehr Provinces will also benefit from the results of our study. Many studies (including ours) validate use of seaweed for biomonitoring of polluted marine environments. While the scope of research in the Gulf area is, at the present, limited to biomonitoring of sediment, fish and invertebrate species (e.g. clam and shrimp) that have economic values; we aspire to expand research in the Persian Gulf to conservation, remediation and clean-up work in order to restore the fragile ecosystems of this area to a stable condition. Ecosystems of the Persian Gulf are seriously threatened by metal contamination. To reserve this toxic trend, immediate rehabilitation measures should be taken to protect the area for the future generation. During present research, lowest of mean BSAF value was for Fe,

which may be explained by higher levels of this metal in the sediment. Meanwhile, Cu showed the highest (except to Ni) mean BSAF value among the all metals which this can be explained by using of this element as micronutrient during photosynthesis. However, the highest mean BSAF value of Ni may be explained by high bioaccumulation of this element in algal species as Ni is one of the largest trace metal constituent of crude oil, hence their presence in high concentration in marine organisms may indicate direct input of oil pollutants in this area.

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