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Metal Concentrations in *Padina* Species and Associated Sediment from Nayband Bay and Bostaneh Port, Northern Coast of the Persian Gulf, Iran

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Abstract

The status of metal concentrations including Pb, Cd, Cu, Ni, Zn and Fe in six species of Padina were determined in polluted (Nayband Bay) and unpolluted (Bostaneh port) areas on the Coast of the Persian Gulf. The mean concentrations of metals in the sediment of two locations were: Pb (12.64), Cd (3.59), Cu (21.74), Ni (17.00), Zn (32.00) and Fe (677.53) µg g^{-1} dry weight, respectively. In the present research, mean metal content in sediments and algae decreased in the following order:
Fe > Zn > Pb > Ni > Cu > Cd. The highest Metal Pollution Index (MPI) value was recorded in *Padina borgessenii was* 25.02 at Nayband Bay. The positive correlations between metal contents in the sediment and almost in all species indicated that these algal species could absorb metals from sediments and play role as biomonitoring σ gents.

Keywords: *Metals, Persian Gulf, Seaweeds, Padina species*

1. Introduction

The Persian Gulf has been the most important area in the Middle East during the last two decades. This importance is not only because of wars and political conflicts which have devastated many of the countries surrounding the Persian Gulf, but also because of its huge reserves of oil, gas and consequently there are also diverse inputs of pesticides, and other agrochemical contaminants into the marine environment (Al-Saleh et al., 1999 and Hamza et al. 2009).

The 1991 oil spill necessitated major marine environmental studies to assess the extent of pollution in biota, water and sediments (Basham et al., 1993). It has been reported that the same species growing in different areas subjected to different environmental parameters might respond differently to metal concentrations (Hall et al., 1979 and Buo-Olayan et al., 1996).

The Nayband Bay and Bostaneh port are situated on the Northern coast of the Persian Gulf. The Nayband Bay (1st station) is near several gas refineries and chemical plants, which caused this marine area to be heavily polluted, whereas the Bostaneh port was (2[nd] station) is considered as an unpolluted area.

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Metals such as Cu, Fe and Zn are essential micronutrients but could become toxic at concentrations higher than the amount required for normal growth (Nies , 1999). Since previous studies showed that these elements higher concentration therefore they were chosen as representative trace elements and indices for environmental pollution (Kazemi et al., 2012; Dadolahi et al., 2011 and Momboya., 2007). High levels of metal (e.g., cadmium, copper, lead and zinc) in aquatic ecosystems are regarded as serious pollutants because they could be toxic and incorporated into the food chain (EPC., 1996 and Al-Shwafi et al., 2008). Macroalgae from marine environment used for pollution studies showed toxicity of metal in macroalgae in marine environments largely depends on the biological availability of the metal (Sunda and Huntsman., 1998). Macroalgae are major primary producers in the marine environments and play an important role in food chains. Additionally, they have the ability to accumulate high levels of various metals in their cell walls (Salgado et al., 2005; Burdin and Bird., 1994). Accumulation of metals in seaweeds and sediments have been reported by many researchers (Alahverdie et al., 2012; Dadoalahi et al., 2011; Maboya , 2007 and Abdallah et al.,2006). Metal content and accumulation in seaweed and sediment are recognized as a suitable bioindicators for evaluating the range of contamination in marine ecosystems. For instance, *Padina gymnospora* can be used as a pollution bioindicator (Ferletta et al.,1996 and Moboya, 2007). In this study, six species of *Padina* was selected as bioindicators to investigate the metal accumulation in polluted and unpolluted areas. The metals content in sediments was determined since sediments also showed the pollution in the marine environment (Karbassi and Bayati, 2005).The objectives of this study were to determine the concentrations of metal in some *Padina* species and associated sediment samples located in the Nayband Bay and Bostaneh port and to find out which algal species were better biodicators of metals.

2. Material and methods

The brown algae *Padina* species (Phaeophyceae, Dictyotaceae) and the surface sediments were collected from the intertidal regions of Nayband Bay (27°28'N; 52°35'E) and Bostaneh port (26°30'N; 56°41'E) Persian Gulf during May and June 2011 (Figure 1).

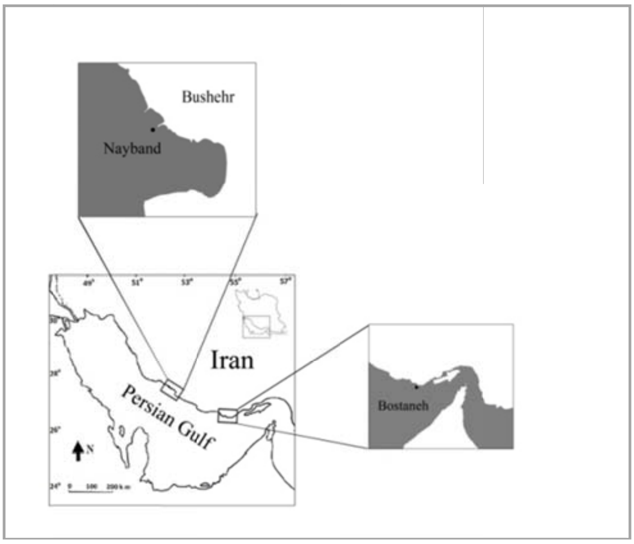

Fig. 1: Locations of sampling for seaweeds and sediments on the intertidal Coast of Persian Gulf of Iran

Six species of *Padina* were collected from each site. The samples were picked by hand and divided. They were washed three times in sea water. Later, they were left to dry at room temperature on absorbent paper. For measuring the element contents in sediments and algal samples, the samples were made into a fine powder, and then a 100 mg fraction of each sample was taken and digested by 10 ml Nitric Acid. Algal samples of *Padina* species and sediments were analyzed for Cd , Ni, Cu, Pb , Fe and Zn content using AAS. A fully computer-controlled flame atomic absorption spectrometer (Savant AA Sigma; GBC Scientific Equipment Ltd., Dandenong, Australia) with a deuterium background corrector was used for metal ion determination. All statistical analyses were performed by SPSS version 12. Analytical precision gave a mean error of 5 percent. Mean values of three replicates were calculated. All data were tested for normality and homogeneity of variance before the parametric statistical analysis.

Variability between seaweeds and sampling sites was analyzed for each metal by one-way ANOVA.

The instrument was calibrated based on a linear six-point calibration curve for Ni and Pb (0.5, 1, 10, 50 and 100 mg L-1); and for Cu, and Cd (0.1, 0.5, 1, 10 and 50 mg L-1). Standard calibration curves for Ni and Cd with (r^2 = 0.99), and Cu (r^2 = 0.99), and Pb (r^2 = 0.97) and Zn (r^2 = 0.97) were generated. To detect differences between individual means, the Tukey's Multiple Comparison test was used. The relationships between metal concentrations in the sediments and macroalgal species were evaluated by simple correlation coefficients. The overall metal contents of algae at the sites were compared on a regional basis using the metal pollution index (MPI) calculated using the formula for mussel:

MPI = (M_1 ×M_2 × M_n) 1/n, where M_n is the concentration of metal. (Abdallah et al., 2006; Dadolahi et al., 2011). The ratio between the metal concentration in the organism and that in the associated sediment was determined by calculating their respective BSAF (Szefer et al. 1999).

3. Results

The concentrations ± SD of the metal (on dry weight basis) are presented in Tables 1and 2. Algae collected from the Nayband Bay had higher concentration of metals than those from the Bostaneh. Figure 2 shows Cd, Pb, Ni, Cu, Zn and Fe levels in the seaweeds.

Table 1. Metal concentrations (mean±S.D) µg g^{-1} dry weight in each species

Padina sp. Nayband Bay	**Cd**	**Pb**	**Ni**	**Cu**	**Fe**	**Zn**	**MPI**
P.gymnospora	2.42±0.02	17.55±0.05	30.14±04.60	6.97±0.036	164.04±0.14	53.57±0.04	21.96
P.pavonica	1.80±0.03	22.22±0.02	12.20±0.02	9.08±0.038	552.89±0.05	34.62±0.056	22.21
P.tetrastromatica	1.65±0.03	19.86±0.28	10.30±0.43	8.18±0.04	160.61±0.05	22.49±0.03	15.49
P.borgesenii	1.72±0.02	18. 70±0.05	26.76±0.04	10.18±0.07	587.25±0.04	33.15±007	25.02
P.boryana	2.2±0.002	11.03±0.03	27.92±0.03	6.27±0.03	863.23±0.03	24.61±0.05	22.51
P.australis	2.14±0.03	12.94±0.05	17.42±0.03	13.98±4.03	736.98±0.03	21.56±0.05	23.18
Padina sp. Bostaneh	**Cd**	**Pb**	**Ni**	**Cu**	**Fe**	**Zn**	**MPI**
P.gymnospora	0.76±0.01	4.82±0.03	13.72±0.03	2.16±0.05	34.19±0.061	19.83±0.025	6.72
P.pavonica	0.47±0.02	18.46±0.02	3.74±0.03	4.76±0.04	154.05±0.03	20.81±0.057	9.29
P.tetrastromatica	1.03±0.02	6.16±0.04	4.60±0.05	5.84±0.04	97.75±006	9.63±0.02	7.67
P.borgesenii	1.70±0.03	11.33±0.004	17.43±0.04	5.5±0.031	514.47±0.07	24.99±0.04	17.87
P.boryana	0.64±0.006	4.31±0.021	14.34±0. 3	2.15±0.04	638.33±0.02	14.65±0.04	10.07
P.australis	0.61±0.037	3.50±0.05	15.66±0.04	2.34±0.03	101.61±0.04	11.01±0.05	6.92
Total	1.42±0.67	12.57±6.54	16.17±8.35	6.45±3.58	383.78±284.002	24.24±11.6	185.91

Table 2. Concentration of metal (mean±S.D) µg g^{-1} dry weight in sediments collected from Bostaneh and Nayband

	Cd	**Pb**	**Ni**	**Cu**	**Fe**	**Zn**	**MPI**
Nayband Bay	5.45±0.05	20.05±0.02	18.90±000	27.10±0.03	905.02±0.03	42.03±0.03	38.51
Bostaneh	1.73±0.03	5.23±0.02	15.11±0.02	16.43±0.03	450.04±0.05	22.03±0.03	17.73

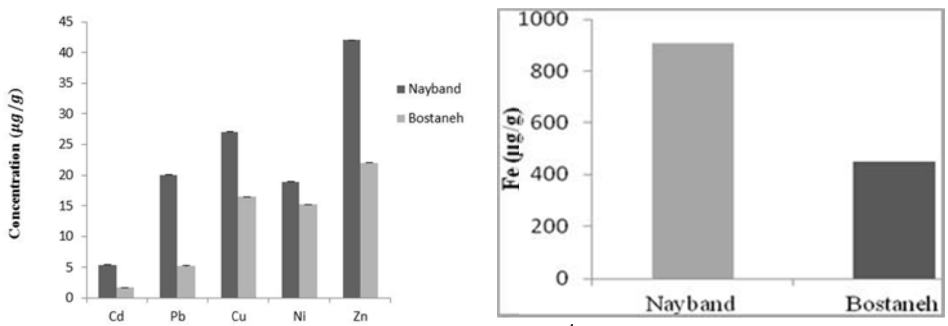

Fig. 2: Metal concentrations (mean±S.D) of Ni, Cd, Cu and Pb, Zn, Fe in µg g^{-1} dry weight for all species collected from the Nayband Bay and Bostaneh in Iran

The concentration of Cd was between 0.47 to 2.42 µg g^{-1} dry weights. The highest concentration was determined in the *Padina gymnospora* in Nayband Bay and the minimum concentration in the *Padina pavonica* species in Bostaneh port. The minimum concentration of Cu was observed in the *Padina boryana* and *Padina gymnospora* species (2.15) µg g^{-1} dry weight in Bostaneh and the maximum concentration was in the *Padina australis* species (14) µg g^{-1} dry weight was observed in Nayband.The highest level of Pb was found in *Padina pavonica* (22.2) µg g^{-1} dry weight in Nayband and the lowest level was found in *Padina australis* (3.5) µg g^{-1} dry weight in Bostaneh. The maximum value of Zn (53.6) µg g^{-1} dry weight was found in *Padina gymnospora*, in Nayband Bay near the oil gas refinery and the minimum value of (9.63)µg g-1 dry weights was found in Padina tetrostromatica in Bostaneh. The mean metals in the sediment of two locations were: Pb (12.6), Cd (3.), Cu (21.7), Ni (17), Zn (32.0) and Fe (677.5) µg g^{-1} dry weight that was given with the results of other sites which are presented in Tables 2-4.

Table 3. Metal concentrations (µg g^{-1} dry weight) in *Padina species* from different areas in the Persian Gulf and in the world

References		**Cd**	**Pb**	**Cu**	**Ni**	**Zn**	**Fe**
Buo-Olayan the Kuwait Coast1996	*P.gymnospora*	-	20.8	465	7.25	510	2500
NayBand persent Study		**2.42**	**17.55**	**6.97**	**30.14**	**53.57**	**164**
Bostaneh persent Study		**0.76**	**4.82**	**2.16**	**13.72**	**19.83**	**34**
Strait of Hormuz Dadolahi et al .,2011	*P.pavonica*	5.0	18.4	16.9	46.5	48.7	8304
Hormuzgan province Dadolahi et al., 2011		5.1	18.9	10.95	44.4	-	-
Bushehr Alahverdi et al.,2012		3.22-7.02	9.33-22.1	4.33-10.03	10.58-27.92	27.4-72.1	2743-17984
Suez Abdallah et al.,2005		6.6	38.9	10.7	13	74.8	-
MarsAlam Abdallah et al.,2005		1.1	7.4	2.9	4.9	5.7	-
Black Sea,Tuzen et al.,2009		2.27 (µg/kg)	2859 (µg/kg)	3.35	5.20	15.7	591
NayBand persent Study		**1.8**	**22.22**	**9.08**	**12.2**	**34.62**	**552.89**
Bostaneh persent Study		**0.47**	**18.46**	**4.76**	**3.74**	**20.81**	**154.05**
Bushehr Alahverdi et al.,2012	*P.tetrastromatica*	0.6	5.15	3.88	3.54	-	-
The Kuwait Coast Buo-Olayanet al.,1996		-	2.2	175	9.1	406	3000
NayBand persent Study		**1.65**	**19.86**	**8.18**	**10.3**	**22.49**	**160.61**
Bostaneh persent Study		**1.03**	**6.16**	**5.84**	**4.6**	**9.63**	**97.75**
The Kuwait Coast Buo-Olayanet al.,1996	*P.boryana*	-	10.8	405	13.3	515	3500
The Gulf of Aden Al-Shwafi et al., 2008		0.65	0.9	5.14	3.3	3.5	50.3
NayBand *persent Study		**2.2**	**11**	**6.27**	**27.92**	**24.61**	**863.23**
Bostaneh *persent Study		**0.64**	**4.31**	**2.15**	**14.34**	**14.65**	**638.33**

Table 4. Metal concentrations (µg g^{-1} dry weight) in surface sediments from different areas in the Persian Gulf and Gulf of Aden

Reference	**Area**	**Cd**	**Pb**	**Cu**	**Ni**	**Zn**	**Fe**
Dadolahi 2011	Hormoz	4.15	23.1	9.4	18.19	41.93	20871
Alahverdi2012	Bushehr	4.61-10.5	18.33-69.5	5-14	17.79-23.23	-	-
Kazemi2012	Intertidal Zone of Persian Gulf of Iran	0.98-1.52	1.47-180.78	3.86-5.13	-	5.99-44.42	-
Al-Saleh1999	NW Gulf	-	-	7	91	3.4	1826
Szefer1999	Gulf of Aden,Yemen	0.9–3.3	50–800	10–120	18–30	50–350	40–100
*present study	Nayband Bay*	5.54	20.05	27.0567	18.9	42	905
	Bostaneh port*	1.733	5.22	16.433	15.108	22	450

Correlation coefficients were calculated for each metal in different species and sediment (Table 5). The uptake of heavy metals was high (with the exception of Cd) by all of the species. The MPI (Metal Pollution Index) was calculated in two studied areas for both sediments and algae. For sediment samples, the highest MPI values in Nayband Bay and the lowest in Bostaneh were 38.5 and 17.7, respectively. The highest Metal Pollution Index (MPI) value was recorded in *Padina borgessenii* (25.1) at Nayband Bay. Among algal species at Bostaneh the highest value of MPI was recorded in *Padina borgesenii* (17). The efficiency of metal bioaccumulation in the six species of seaweed was determined by calculating their respective BSAF (Tables 6 and 7). The highest BSAF (Biosediment Accumulatiom Factor) was obtained for Ni in *Padina gymnospora* (1.6), (except to P.boryana and P.borgesenii) and the lowest BSAF value was for Fe in *Padina gymnospora* (0.05), which may be explained by higher levels of these metals in the sediment.

Table 5. Significant correlations between metal concentrations in sediment and six species of seaweed from Nayband Bay and Bostaneh Port at the coast of the Persian Gulf

Species	Cd	Pb	Ni	Cu	Fe	Zn
Padina gymnospora	-1**	1**	0.95**	1**	1**	1**
Padina pavonica	-1**	1**	1**	1**	1**	1**
Padina tetrostomatica	-0.99**	1**	0.99**	1**	1**	1**
Padina borgessenii	-0.82*	-0.33 *ns*	1**	1**	0.39 *ns*	1**
Padina boryana	-1**	1**	1**	1**	1**	1**
Padina australis	-1**	1**	1**	0.93**	1**	1**

ns Not significant at the level of 0.05
* Significant at the level of 0.01
** Significant at the level of 0.001

Table 6. Mean BSAF from Nayband Bay on the coast of the Persian Gulf, Iran

BSAF	Cd	Pb	Ni	Cu	Fe	Zn
P.gymnospora	0.44	0.88	1.60	0.26	0.18	1.28
P.pavonica	0.5	1.76	0.71	0.42	0.61	0.82
P.tetrastromatica	0.46	1.57	0.61	0.38	0.18	0.54
P.borgesenii	0.48	1.5	1.60	0.47	0.65	0.80
P.boryana	0.61	0.87	1.64	0.29	1.27	0.59
P.australis	0.58	1.02	1.025	0.64	1.088	0.51

BSAF Biosediment Accumulatiom Factor (BSAF = Cx/Cs, where Cx and Cs are the mean concentrations of metals in the organism and in associated sediment, respectively)

Table 7. Mean BSAF from Bostaneh port on the coast of the Persian Gulf, Iran

BSAF	Cd	Pb	Ni	Cu	Fe	Zn
P.gymnospora	0.22	0.38	0.8	0.1	0.05	0.62
P.pavonica	0.13	1.46	0.22	0.22	0.23	0.65
P.tetrastromatica	0.3	0.49	0.27	0.27	0.14	0.3
P.borgesenii	0.46	0.9	1.03	0.26	0.76	0.78
P.boryana	0.18	0.34	0.84	0.098	0.94	0.46
P.australis	0.17	0.3	0.92	0.11	0.15	0.35

BSAF Biosediment Accumulatiom Factor (BSAF = Cx/Cs, where Cx and Cs are the mean concentrations of metals in the organism and in associated sediment, respectively)

Table 8 shows the global baseline values and sediment quality guidelines. The US National Oceanic and Atmospheric Administration (NOAA) guidelines were used to evaluate the quality of metal contamination in Nayband Bay and Bostaneh coastal sediments. ERL and ERM are “effects range low” and “effects range medium”, respectively (De Mora and Sheikholeslami., 2002; Kazemi et al., 2012 and Dadolahi et al., 2011).

Table 8. ERL and ERM guideline values for metals µg g^{-1} (dry weight) and sediments collected from Nay Band and Bostaneh on the Coast of the Persian Gulf, Iran

Element	ERL Guideline	ERM Guideline	NayBand	Bostaneh
Cu	34	270	27	16.43
Pb	47	220	20	5.2
Cd	1.2	9.6	5.45	1.73
Ni	21	52	18.9	15.11
Zn	150	410	42	22

ERL effect range-low, ERM effect range-medium

4. Discussion

Seaweeds could be excellent indicators of natural and/or artificial changes in biodiversity (in terms of both abundance and composition) due to changes in biotic and anthropogenic factors. The effect of trace metal pollution on marine algae was observed at Nayband Bay and Bostaneh locations, 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 (Kazemi et al., 2012 and Alahverdi et al., 2012). Nayband Bay can be considered as a polluted area with excess of Cadmium, Copper and Lead (2.20 and 10 µg g-1 dry weight respectively) in the algal samples (Kazemi et al., 2012 and Lozano et al., 2003).

High levels of Pb in algae of Nayband Bay can be attributed to combustion of fossil fuels and oil pollution (Alahverdi etal., 2012). Domestic sewage and rock formations have been suggested as the source of Cd pollution. Furthermore, galvanized steel use in the Assaloyeh oil and gas facilities contain Cadmium coating which can end up in these waters (Alahverdi et al., 2012). Iron was the most predominant metal in the algal species compared to other metal from two locations, followed by Zn> Ni >Pb> Cu> Cd. This result coincided with the results given from Gulf of Aden and Hormoz (Al-Shwafi et al., 2008 and Dadolahi et al., 2011).

The presence of high concentrations of Fe and Cu in marine plants could be attributed to the fact that they are important micronutrients for various metabolic functions of the plants (Al-Shwafi et al. 2008). Zinc is one of elements that frequently are used for monitoring polluted areas. It has been suggested that Zn is taken up by both absorption and active transportation, since it is an important nutrient in algal metabolism (Lobban and Harrison, 1994). The comparison reviews for metal concentrations (µg g^{-1} dry weight) in algae from various locations around the world and the present study is shown in Table 3. The result of this comparison revealed that, Zn level was very high in *Padina gymnospora*. The brown alga *Padina gymnospora* could be used as a pollution bio indicator, particularly zinc (Karez et al., 1994 and Moboya, 2007). The cell walls play the main role in zinc accumulation in *Padina gymnospora* (Amado Filho G. M. et al., 1996) and if these species lived in a heavy metal contaminated area they would modify their polysaccharide content as defense mechanism. (Andrade et al., 2010). The present results were similar to those reported from the other sites of the Persian Gulf (Dadolahi et al., 2011). The findings of MPI in this study showed a variation in the concentration of all six trace metals analyzed in different *Padina species*. These variations in MPI values of seaweeds obtained from the two areas, might reflect the bioaccumulation effects on marine algae. Higher MPI indicated more metals uptake by seaweeds in such an area (Forsberg, 1988). A strong correlation between metal levels in the sediment and the seaweed indicated that metal in the sediment might easily become available to the seaweed (with the exception of Cd). The significant correlations among these metals in studied algae might be due to their common origin or anthropogenic effects. The results of this study are in agreement with the previous studies on the sediments of Bostaneh (Kazemi et al., 2012). Regarding to the concentration factors, Zn and consequently Fe are the most bioaccumulated elements in all studied species algae in Nayband Bay, while in Bostaneh, the highest values of bioaccumulation was belonged to Pb. The latter result agreed with results given from studies of Egyptian coasts (Abdallah et al., 2006). Average BSAFs for Zn, Fe, Cu and Cd was significantly <1; The highest mean BSAF value belong to Ni (except of Pb) that 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 might indicate direct input of oil pollutants in this area. (Dadolahi et al., 2011). Based on the results of Table 8, the measured concentrations of Cd approximately exceeded the ERL guideline, it means that Cadmium remains in the sediments and threatens the biological communities. Based on these results, sediment results showed that the concentrations of Pb, Cu, Zn and Ni at all sampled sites in the Persian Gulf did not exceed the ERL and ERM of NOAA Guidelines but the amount of Nickel was near to ERL. This almost indicated that the existing concentrations of metals in these sediments were not sufficiently high to cause adverse biological effects. Previous studies in the Persian Gulf based on variations of contaminant source input agreed with the results of the present study (Kazemi et al., 2012 and Dadolahi et al., 2011).

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