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Metal Pollution in Seaweed and Related Sediment of the Persian Gulf, Iran

M. Alahverdi · M. Savabieasfahani

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Abstract Nickel, cadmium, copper and lead in the sediment and seven species of algae from six locations in the Bushehr Province on the Coast of the Persian Gulf were determined. Sampling sites represent areas of importance in seaweed harvest and areas near sources of anthropogenic pollution. The mean concentrations of metals in the sediment (across all six collection sites, and collection periods) were: Pb (42.4 ± 2.7), Cd (7.4 ± 1), Ni (38.1 ± 3.7), and Cu (8.3 ± 1.2) μg g^{-1} dry weight. High significant positive correlations existed between metals in *cervicornis, corticata,* and *pavonica* algae and the sediment, suggesting these species of algae are suitable for biomonitoring of the area.

Keywords Seaweed · Bioaccumulation · Metal · Persian Gulf · Biosediment accumulation factor (BSAF)

Persian Gulf is chronically exposed to oil pollution associated with exploration, exploitation, refining, and routine handling of oil. War related pollution has recently been added to this list. Frequent mass mortality of corals in this area is attributed to a combination of extreme water temperatures and high sedimentation/turbidity. The brown algae have been reported to have been most harshly affected by pollution. Reduction in algae population due to pollution is suggested to threaten food chain integrity in the area (Buo-Olayan and Subrahmanyam 1996). Worldwide, the use of algae (including *Ulva, Sargassum*, *Padina*, and *Cystoseira*) in biomonitoring, has been well established. Metal content and accumulation in seaweed and sediment are recognized as a suitable bioindicator for assessing the degree of contamination in marine ecosystems. However, since sediment composition varies according to particle size, rate of deposition, rate of particle sedimentation, and presence and amount of organic matter direct measurement of metal in the sediment is often misleading when it comes to assessing the risks that metals pose to the local ecosystems. Bioavailability of metal contaminants to local ecosystems can be better evaluated by calculating the Biosediment accumulation factor (BSAF = Cx/Cs, where Cx and Cs are the mean concentrations of metals in a biological organism and in associated sediment). We selected *Acanthophora, Gracilaria,* and *Sargassum* because they are common in the area and although in Iran algae is not used as food, but algae is cultivated and used in production of food ingredients, and manufacturing of drugs and health products.

We selected Ni, Cd, Cu, and Pb because they are petroleum related. Gondal et al. (2006) reported on elemental analysis of Arabian crude oil residue samples which included Cu, and Ni. Lead is also found in petroleum and it originates from tetraethylic lead. Lead and cadmium are found in petroleum and have been reported on by Al-Swaidan (1994). These metals are also listed in the Dangerous Substances Directive (76/464/EEC) and its annex (a list of substances originally published by the European Economic Community in 1976), as substances that pose particular concern in aquatic environments, due to their high production volume, environmental persistence, and bioaccumulation properties. Our objective was to

M. Alahverdi
Khorramshahr University of Marine Science and Technology, Marine Biology, P.O. Box 669, Khorramshahr, Khuzestan, Iran

M. Savabieasfahani (✉)
University of Michigan School of Public Health, 1415 Washington Heights, EHS Room Number: M6016, Ann Arbor, MI 48109-2029, USA
e-mail: mozhgan@umich.edu

measure Ni, Cd, Cu, and Pb in seven common seaweed species (green: *Ulva interstinalis*, brown: *Padina pavonica, Cystoseira myrica*, *Sargassum angustifolium*, and red: *Acanthophora spicifera, Gracilaria corticata, Hypnea cervicornis*), and associated sediment from six sites in Bushehr Province (Fig. 1). Seaweed from these areas is used in local food industry, drug manufacturing, and health products in Iran. We wanted to: (1) measure metal levels in seaweed and associated sediment form sites that are important in seaweed harvest (Olee, Taheri, and Haleh); and areas close to sources of pollution (Ganaveh, University of Bushehr, and Nuclear power facilities), (2) find which species of algae is a better bioindicator of metals by evaluating correlations between sediment and algae metal.

Materials and Methods

The studied sites are areas of importance in seaweed harvest (Olee, Taheri, and Haleh) and areas close to sources of anthropogenic pollution (Ganaveh, University of Bushehr, and Nuclear power facilities). Samples were collected in October 2008 and January, May, and July 2009. Locations of sampling sites were recorded using a global positioning system (GPS): (#1) Ganaveh Port (29°39′N, 50°24′E), (#2) University of Bushehr (28°54′N, 50°49′E), (#3) Bushehr Nuclear Power Facilities (28°50′N, 50°52′E), (#4) Village of Olee (27°49′N, 51°55′E), (#5) Taheri Port (27°40′N, 52°20′E), and (#6) Haleh village (27°24′N, 52°38′E) (Fig. 1).

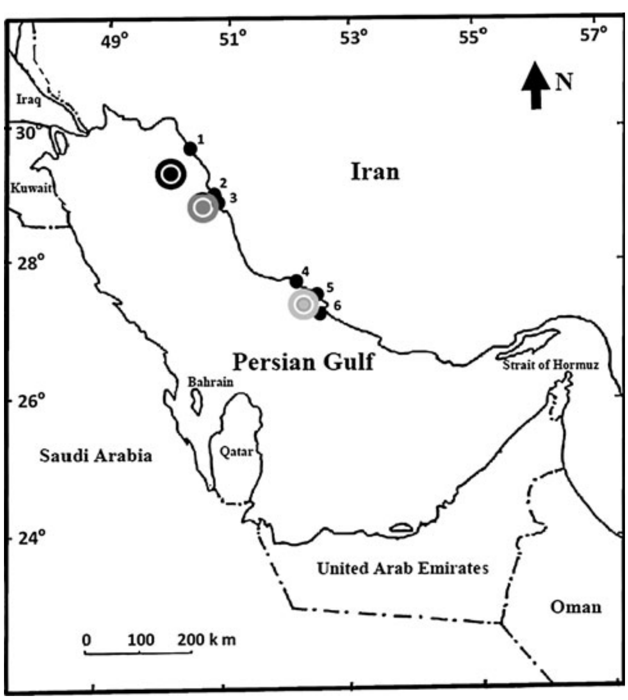

Fig. 1 Numbers (*1–6*) indicate sampling sites; *circles* indicate location of industrial facilities: Ganaveh Port (*1*), University of Bushehr (*2*), Nuclear power facilities (*3*), Village of Olee (*4*), Taheri port (*5*), and Village of Haleh (*6*)

Seven species of seaweeds were sampled (0.5–1 kg) at low tide, in the intertidal zone at the depth of $\leq$1 m. Five–8 cm from the tip of the algae was removed. At the same spots, surface sediment (top 5 cm) was collected ($n = 3$). Seaweed was rinsed with DDW, oven dried (at 105°C for 48 h) to constant weigh then crushed, homogenized, and stored in sterile bottles. Samples (1–2 g) were digested and refrigerated until analysis. For digestion (12 h on a hot plate at 140°C), samples were placed in sealed flasks with 10 mL HNO_3/HCl (1:3 v/v) to prevent sample loss. Digests were filtered through acid-cleaned 0.45 mm filters, diluted to 25 mL with DDW and stored at 4°C for analysis. Sediment samples were made into a fine powder, sieved using a 63 µm nylon mesh, and the <63 µm size fraction was used for digestion. Metal determination was done by a flame atomic absorption spectrophotometer. 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 ($r^2 = 0.97$) were generated. Blanks were run with each batch of samples (ten samples in each batch) and run similarly. The flame composition was acetylene 2.0 and air 13.5 (L/min). The nebulizer aspiration flow rate was kept between 5.5 and 6.0 mL/min. Detection limits in the sample tests were: Ni (0.05 µg g^{-1}), Cd (0.02 µg g^{-1}), Cu (1 µg g^{-1}) for and Pb (2 µg g^{-1}). All statistical analyses were performed by SPSS version 12. Analytical precision gave a mean error of 5 %. Mean values of three replicates were calculated. All data were tested for normality and homogeneity of variance before the parametric statistical analysis. Variability between seasons and sampling sites was analyzed for each metal by one-way ANOVA. To detect differences between individual means, we used Tukey's Multiple Comparison test. The relationships between heavy metal's concentrations in the sediments and macroalgal species were evaluated by simple correlation coefficients (p was set at $\leq$0.05).

Results and Discussion

Table 1 indicates the range of values for trace metal concentrations (µg/g) which previous investigators have deemed "unpolluted" sediment in this area. Cd in our sediment samples is higher than these areas, while sediment Cu is in the lower ranges of values reported for unpolluted areas. Nickel is in the medium range, and Pb appears similar to other unpolluted areas. The high levels of metals in seaweeds reflect the high bioavailability of metals in these waters and the capacity of the seaweed to accumulate heavy metals.

Figures 2 and 3 show Ni, Cd, Cu and Pb levels we found in sediment and seaweed. We evaluated the efficiency of metal bioaccumulation in the seven species of seaweed by calculating their respective BSAF (Table 2), which is defined as the ratio between the metal concentration in the organism and that in the associated sediment (Szefer et al. 1999). The highest BSAF was obtained for Cu in *A. spicifera*. The lowest BSAF value was for Pb and Ni, which may be explained by higher levels of these metals in the sediment. Average BSAFs for Pb and Ni was significantly <1; a comparison between BSAFs of Cd and Cu with that of Pb and Ni indicates that, with the exception of *Enteromorpha intestinalis* and *C. myrica*, capacity of seaweed for bioaccumulation of ingestible Pb and Ni is low considering the high levels we have observed in the sediment. A strong correlation between metal levels in the sediment and the seaweed indicates that metal in the sediment may easily become available to the seaweed. Table 3 indicates correlations and suggests that both Ni, Cd, can best be monitored in *H. cervicornis*, while Cu and Pb bio monitoring is beset done in *G. corticata* and *P. pavonica*.

Ganaveh is closest to the most heavily industrialized areas of the Gulf. Nickel in *U. interstinalis* is higher than those found in Kuwaiti Coast but lower than Saudi Coast, in the same algae (Table 4). Elevated Ni maybe attributed to oil pollution (Al-Homaidan 2008) and Ni in rock formations. we compared metals between algae species to detect interspecific differences. Maximum concentrations of Ni,

Table 1 Range of values for trace metal concentrations (μg/g) in unpolluted marine sediments of different areas in the Persian Gulf

Reference area	Ni	Cd	Cu	Pb
Unpolluted sediment of Kuwait[a]	86–120	0.5–2	15–30	20–30
Unpolluted sediment of Kuwait[b]	115.9	0.21	27.5	7
Unpolluted sediment of Kuwait[c]	150–209	ND	34–50	ND
Unpolluted sediment of Saudi Arabia[d]	24–50	3.2–4.5	6.8–13.8	0.7–1.7
Unpolluted sediment of Saudi Arabia[c]	4–116	ND	2.27	ND
Unpolluted sediment of Saudi Arabia[e]	8–28	0.1–.0.25	3–6	1.7–4.4
Unpolluted sediment of the northeastern Qatar[c]	4.9–6.7	ND	2.7–3.6	ND
Unpolluted sediment of Qatar and Bahrain[c]	0.2–12.8	ND	3.8–4	ND
Unpolluted sediment of Bahrain[c]	9–20	0.01–0.8	1.5–17.6	0.5–24
Unpolluted sediment of Oman[e]	12.8–25	0.02–1.9	1.3–7	0.5–5.2
Unpolluted sediment of United Arab Emirates[e]	9.9–46	0.06–0.7	1.7–14	1.2–7.2
Northeastern Iranian coast[f]	103	1.25	22.5	25
Persian Gulf, present study (Iran)	**17.76–73.33**	**4.67–10.5**	**5–14**	**18.33–69.5**

Highlighted bold values are from the current study (Iran)

ND not determined

[a] Anderlini et al. (1986)

[b] Literathy et al. (1989)

[c] Basaham and Al-lihaibi (1993)

[d] Sadiq and Zaidi (1985)

[e] Fowler et al. (1993)

[f] Anderlini et al. (1986)

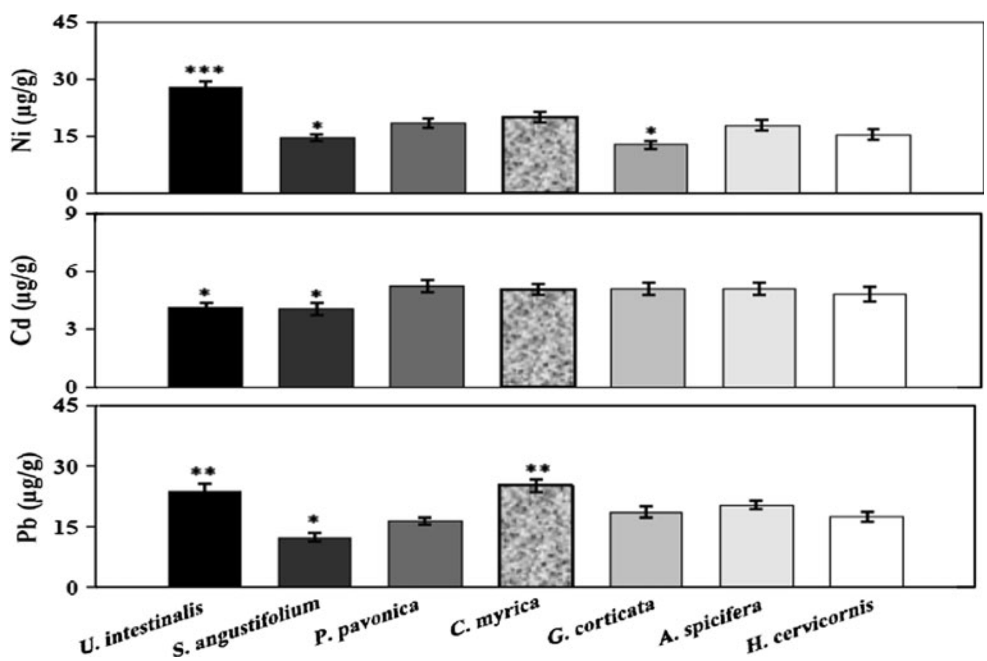

Fig. 2 Seaweed concentrations of Ni, Cd, Cu and Pb collected from the coastal area of the Bushehr Province in Iran. *Error bars* indicate the mean of three replicate samples (n = 3) ± SEM (μg g^{-1} dry weight). *Significant at $p \leq 0.05$; **significant at $p \leq 0.01$; and ***significant at $p \leq 0.001$

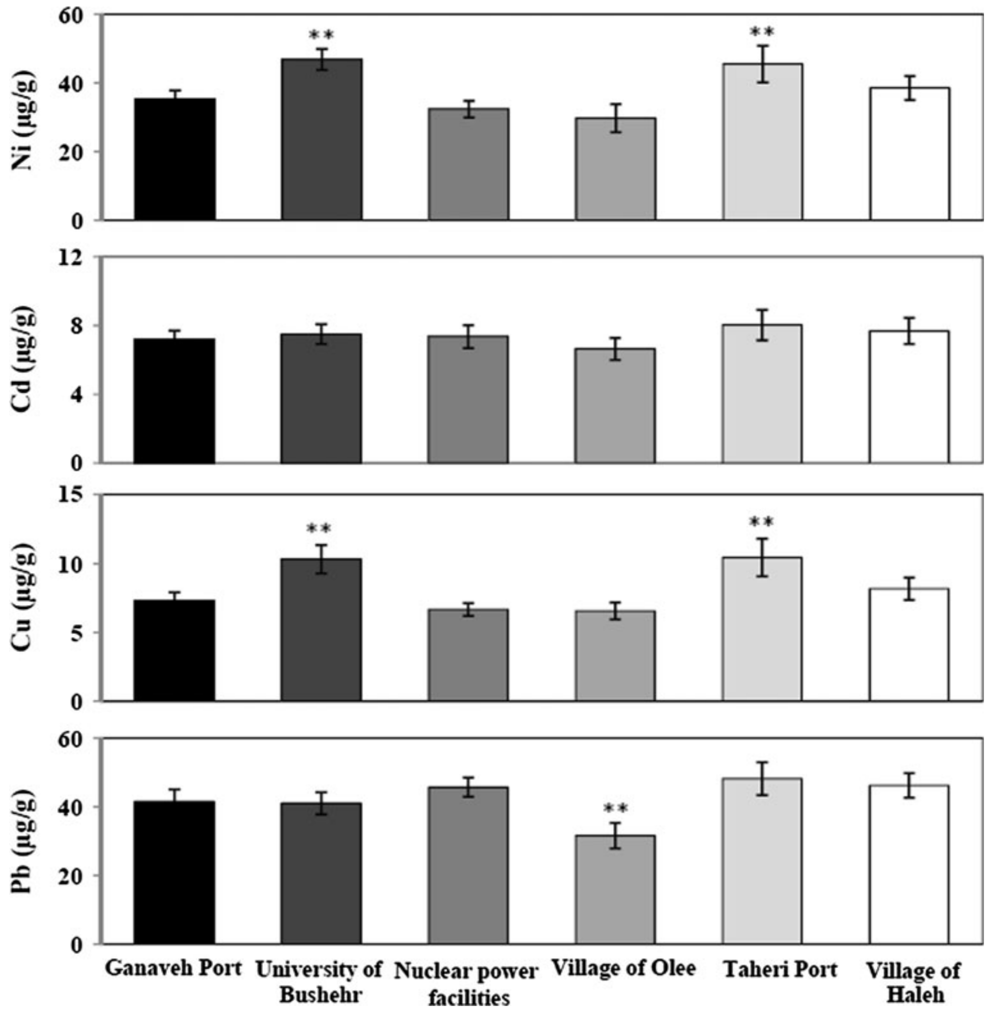

Fig. 3 Sediment concentrations of Ni, Cd, Cu and Pb from the Iranian coast of Bushehr Province. *Error bars* indicate the mean of three replicate samples (n = 3) ± SEM ($\mu g\ g^{-1}$ dry weight). *Significant at $p \leq 0.05$; **significant at $p \leq 0.01$; and ***significant at $p \leq 0.001$

Table 2 Mean BSAF from Bushehr Province on the coast of the Persian Gulf, Iran

BSAF	Ni	Cu	Cu	Cd	Pb
E. intestinalis	0.73	0.88	0.88	0.56	0.56
S. angustifolium	0.38	0.64	0.64	0.54	0.29
C. myrica	0.52	0.79	0.79	0.68	0.59
P. pavonica	0.48	0.85	0.85	0.70	0.39
A. spicifera	0.47	1.39	1.39	0.69	0.48
G. corticata	0.34	0.87	0.87	0.68	0.44
H. cervicornis	0.40	0.64	0.64	0.65	0.41

BSAF biosediment accumulatiom 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, respectiveyl)

Table 3 Significant correlations between metal concentrations in sediment and seven local species of seaweed from Bushehr Province on the coast of the Persian Gulf, Iran

	Ni	Cu	Cd	Pb
E. intestinalis	0.04^{ns}	0.25^{ns}	0.40*	0.40*
C. myrica	0.40*	0.39*	0.53**	0.28^{ns}
S. angustifolium	0.39*	0.05^{ns}	0.16^{ns}	0.26^{ns}
P. pavonica	0.43*	0.36*	0.66**	0.66**
A. spicifera	0.14^{ns}	0.005^{ns}	0.45**	0.62**
G. corticata	0.33^{ns}	0.48**	0.29^{ns}	0.01^{ns}
H. cervicornis	0.85**	0.09^{ns}	0.82**	0.18^{ns}

ns Not significant at the level of 0.05

* Significant at level 0.01

** Significant at level 0.001

Cd, Cu and Pb were found in *U. intestinalis*, *P. pavonica*, *A. spicifera*, and *C. myrica* respectively. *G. corticata* had least Ni, *S. angustifolium* contained lowest Cd, Pb, and Cu. Nickel was significantly lower in *S. angustifolium* and *G. corticata* when compared to *C. myrica* ($p < 0.05$; Fig. 2). Cadmium in algae >2 $\mu g\ g^{-1}$ have been coined for polluted environments (Lozano et al. 2003). Domestic sewage and Cd in rock formations have been suggested as the source of Cd pollution. Further, galvanized steel use in the Assaloyeh oil and gas facilities contain cadmium coating which can end up in these waters. Copper contamination

Table 4 *Ulva* (green seaweed), *Padina*, *Sargassum*, and *Cystoseira* (brown seaweed), and *Gracilaria*, *Hypnea* and *Acanthophora* (red seaweed) metal concentrations (μg g^{-1} dry weight) from various geographical locations

Region	Metal levels (μg g^{-1} dry weight)			
	Ni	Cd	Cu	Pb
U. intestinalis, Coast of the Persian Gulf (Kuwait)[a]	6.5–8.5	ND	60–120	2.2–9.1
Ulva sp., Moreton Bay (Australia)[b]	ND	0.4	15	5.75
U. intestinalis, Delmarva Peninsula (USA)[c]	0.69–1.6	ND	0.69–16.9	3.2–4.55
Ulva sp., San Jorge Gulf (Patagonia Argentina)[d]	0.99–4.11	2.83–3.54	1.74–3.81	0.82–1.72
U. lactuca, Saudi coast of the Persian Gulf[e]	26.31–32.37	0.81–0.95	8.41–18.5	13.9–17.67
U. intestinalis present study	**16–50.33**	**2.89–5.33**	**4.89–9.56**	**11–51**
P. pavonica, North of Sri Lanka[f]	21.5	3.9	40.8	18.4
P. pavonica, West coast of Aegean Sea (Greece)[g]	18.3–32.3	1.2–1.6	3–3.7	0.02–2.1
P. pavonica, Tenerife Island (Spain)[h]	ND	0.57–1.66	ND	3.99–22.1
Padina sp., Tanapag Lagoon (Saipan)[i]	0.88–1.65	< 0.11–1.72	1.3–25.3	<0.27–5.47
P. pavonica, present study	**10.58–27.92**	**3.22–7.02**	**4.33–10.03**	**9.33–22.11**
S. subrepandum, Red Sea coast (Saudi Arabia)[j]	0.52	0.07	ND	0.45
S. angustifolium, Coast of the Persian Gulf (Kuwait)[a]	3.5	ND	85	7.1
Sargassum sp., West coast of Aegean Sea (Greece)[g]	13.7	0.07	2.1	0.02
S. angustifolium, Saudi coast of the Persian Gulf[e]	ND	1.2–1.35	4.9–6.6	12.05–16.76
S. binderi, Gulf of Aden (Yemen)[k]	2.8	0.76	10.2	2.4
S. angustifolium, present study	**5.33–28.58+**	**2.27–8.47**	**3.18–7.22**	**6.67–28.22**
C. myrica, Red Sea coast (Saudi Arabia)[b]	0.49	0.07	ND	1.66
C. myrica, Saudi coast of the Persian Gulf[e]	ND	0.62–1.33	6.65–10.8	8.84–14
C. myrica, Saudi coast of the Persian Gulf[l]	7.3	ND	ND	ND
C. myrica, Gulf of Aden (Yemen)[k]	4.73	0.53	14.1	5.3
C. myrica, present study	**10–43.06**	**3.33–7.53**	**3.67–9.84**	**12.67–42.45**
H. musciformis, Red Sea coast (Saudi Arabia)[j]	1.04	0.09	ND	0.55
H. cornuta, Saudi coast of the Persian Gulf[l]	40.7	ND	ND	ND
H. cornuta, Gulf of Aden (Yemen)[k]	2.35	0.93	2.31	2.8
H. musciformis, Arabian Sea (Pakistan)[m]	0.03–0.05	0.01–0.02	0.03–0.14	0.05–0.09
H. cervicornis, present study	**4.33–22.44**	**2.78–7.33**	**3.67–10.45**	**6.11–23.22**
G. verrucosa, West coast of Aegean Sea (Greece)[g]	4.6–15.8	0.06–0.9	2.1–14.9	0.02–14.7
G. foliifera, Gulf of Aden (Yemen)[k]	7.3	0.55	9.83	0.93
G. corticata, Arabian Sea (Pakistan)[m]	0.03	0.01–0.02	0.01–0.04	0.05–0.08
G. corticata, present study	**7.44–20.33**	**3.67–7.92**	**3.67–12.67**	**10.67–29.22**
A. najadiformis, Red Sea coast (Saudi Arabia)[j]	1.7	0.07	ND	1.19
A. spicifera, Saudi coast of the Persian Gulf[l]	57.4	ND	ND	ND
A. spicifera, Tanapag Lagoon (Saipan)[i]	1.78–2.07	0.13–0.7	2.88–30.5	0.49–8.14
A. spicifera, present study	**6.89–37**	**3.22–8.12**	**3.09–28.89**	**14.56–29.45**

Highlighted bold values are from the current study (Iran)

ND not determined

[a] Buo-Olayan and Subrahmanyam (1996)

[b] Gosavi et al. (2004)

[c] Anish et al. (2007)

[d] Perez et al. (2007)

[e] Al-Homaidan (2007)

[f] Mageswaran and Sivasubramaniam (1984)

[g] Sawidis et al. (2001)

[h] Lozano et al. (2003)

[i] Denton et al. (2009)

[j] El-Naggar and Al-Amoudi (1989)

[k] Al-Shwafi and Rushdi (2008)

[l] Al-Homaidan (2008)

[m] Qari and Siddiqui (2010)

Table 5 Physical and environmental characteristics of sampling sites (values are in mean ± SEM) with associated pollution sources and highest and lowest metal levels in sediment and algae from the Bushehr Province of Iran in the Persian Gulf

Site	Temp (°C)	PH	Salinity (ppt)	Type and pollution sources	Sediment metal levels	Algae metal levels	Tidal area (m)	Bottom substrate	Slope
Ganaveh Port (medium wave action)	29 ± 0.5	8 ± 0.1	38.5 ± 0.6	Khark Island oil facilities, oil transportation discharge water ballast, oil exploitation		Highest Ni, Cu, Pb	400	Gravel and sandy	Relatively low
University of Bushehr (high wave action)	30 ± 0.3	8.1 ± 0.1	38.2 ± 0.4	Urban sewage, industrial activities, power plants	Highest Ni	Lowest Ni	800	Gravel and rocky	Low
Nuclear power facilities (high wave action)	30.6 ± 0.1	8.2 ± 0.2	38 ± 0.3	Urban sewage, industrial activity, ongoing construction			300	Rocky and some Sandy	Relatively steep
Village of Olee (high wave action)	30.9 ± 0.4	8.1 ± 0.1	38 ± 0.3	Chemical factories, fiberglass industrial and oil related activities, aquaculture activities	Lowest Ni, Cd, Cu, Pb	Lowest Cd, Cu	200	Rocky with less Sandy	Relatively steep
Taheri Port (medium wave action)	30.8 ± 0.3	8.3 ± 0.2	40 ± 0.2	Urban sewage, Oil exploration, chemical factories, desalination plant, aquaculture	Highest Cd, Cu, Pb	Lowest Pb	100	Almost sandy	Steep
Village of Haleh (low wave action)	30.7 ± 0.5	8.2 ± 0.2	37.5 ± 0.4	Oil refining, oil exploitation, discharge water ballast, chemical factories, desalination plants		Highest Cd	900	Gravel and some sandy	Low

is associated with algal levels of >20.00 μg g^{-1}. Lozano et al. (2003), coins Pb values >10 μg g^{-1} to algal species from contaminated areas. High levels of Pb in alga of the area can be attributed to combustion of fossil fuels and oil pollution. Collectively, our data and others suggest that the seaweed of the Persian Gulf has been severely affected by metal contamination. The scope of research in the Gulf is currently limited to biomonitoring of sediment, fish, and economically valued invertebrates but, we plan to expand research to conservation, remediation and clean-up work in order to restore these fragile ecosystems to a stable condition. To reverse the current destructive trends, immediate rehabilitation measures must be undertaken to protect the area for the future generation (Table 5).

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