Evaluation of Some Physiochemical Parameters and Heavy Metal Contamination in Hara Biosphere Reserve, Iran, Using a New Pollution Index Approach

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ABSTRACT

Background: The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, due to their potential toxic effects and ability to bio-accumulate in aquatic ecosystems. Heavy metals are sensitive indicators for monitoring changes in the aquatic environment.
Methods: In this study, total concentrations of Cr, Pb, Cu, Zn, and Fe were measured in water and sediments from nine sites, based on ecological conditions and human activities and the effects of sediment pH and sediment organic matter on bioavailability of selected metals were determined. Modified degree of contamination (mCd) was computed in order to determine anthropogenically derived sediment contamination.
Results: Mean concentration of metals in water found to be in the following order: Pb > Fe > Zn > Cu > Cr, while in sediment samples it was Fe > Cr > Zn > Pb > Cu. The average content of examined metals in water was higher than the chronic values in marine surface water guideline values. Mean content of Cr, Pb and Fe in sediments were higher than average of the less contaminated sample but Cu and Zn were lower than this guideline value. In the study area, mCd values were less than 1.5 with values ranging from 0.71 to 1.02.
Conclusion: The results of this study indicated with a decrease in organic matter and pH in sediments, the concentration of copper and iron increased. Base on modified contamination degree, the sediments of Hara Biosphere Reserve are considered to be in the zero to very low contamination status.
Keywords: Bio-Accumulate, Copper, Heavy Metals, Lead, Mcd, Water Pollution.

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INTRODUCTION

Heavy metals, including both essential and non-essential elements, have a particular significance in eco-toxicology. They are highly persistent and all have the potential to be toxic to living organisms. Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentration in water and sediments [1]. Human activities have led to accumulation of toxic metals in the natural environment [2] and the extensive exploitation of natural resources has led to increased pressure on land and water systems. The result has been an increased load and dispersion of metals (copper, cadmium, mercury, lead, etc.) into the bio-geosphere. Elevated concentrations of pollutants in these systems have resulted in bioaccumulation of toxic metals and a serious environmental problem, which threatens aquatic ecosystems and human health [3]. Heavy metals pollution in aquatic ecosystems caused by industrialization has been reported by many researchers around the world [2-4].

Many large industrial factories, including metal processing, cement factories, paint manufacturing plants, petroleum and petrochemical industries, and shipbuilding plants are located along the coast of the Persian Gulf. Effluents from these factories have caused severe contamination of water and sediments in the Persian Gulf and Hara Biosphere Reserve.

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Heavy metals released into aquatic systems are generally bound to particulate, which eventually settle down and become incorporated into sediments. Surface sediment is the most important reservoir of metals and other pollutants in aquatic environments. Sediment-bound pollutants can be taken up by rooted aquatic macrophytes and other aquatic organisms [5-7].The purpose of this study was to determine the concentrations of lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), and iron (Fe) in water and sediments, to investigate the effects of sediment pH and sediment organic matter on the bioavailability of selected metals in Hara Biosphere Reserve. Furthermore, in this study, the pollution level attributed to heavy metals was evaluated using the modified degree of contamination (mC_d) in order to determine anthropogenically derived sediment contamination.

MATERIALS AND METHODS

Study Area

The study area is located in southern Hormozgan province with 85686 hectares areas, located between Bandar Khamir and Qeshm Island. This region is known as Ramsar International Wetland Site and is on the list of Iranian protected areas and the UNESCO Man and the Biosphere Program (MAB) Convention list [8]. Hara Biosphere Reserve has a vast biological diversity and lies at a latitude of 26º45’ to 26º58’N and longitude of 55º30’ to 55º50’E situated in the middle of Mehran and Gourzin River delta in Qeshm Island. Because of its vicinity to Bandar Abbas and being situated on the sidelines of the northern coast of Qeshm Island, this region has seen a dramatic increase in urban and industrial pollution.

Water Sampling

Samples (sediments and water) were collected in September 2011 from nine sites in three replicates based on ecological conditions and human activities in Hara Biosphere Reserve, Persian Gulf, Iran. All reagents used were of supra-pure quality. Prior to any analysis, all equipments, glassware, and plastic containers were soaked in 10% HNO_3 and then rinsed with deionized water before use. Water samples were collected into acid washed, 250-ml plastic bottles from approximately 30 cm below the water surface and acidified to $pH < 2$ with nitric acid. The water samples were filtered using a 0.45 lm nitrocellulose membrane filter. Determination of Cr, Cu, and Zn were carried out by graphite furnace atomic absorption spectrometer (Perkin Elmer, AA3030) [1].

Sediment Sampling

Sediment samples were collected using a grab sampler. Samples were dried at 110℃ for 24 hours to achieve a constant weight. After cooling, the sample was passed through a 63-µm mesh and stored in polyethylene bottles until chemical treatment with acid digestion. Due to the strong association between metals and fine-grained sediments, the fraction with particle size of less than 63 µm was used for analyses. To determine total concentration in the extract, 1g of the sediment sample was digested with 16 ml mixture of concentrated HCl and HNO_3 at a ratio of (3:1 v/v) for 6 hours at 90℃ and then 4 ml of concentrated $HClO_4$ was added. The samples were, then, filtered through a Whatman No. 42 filter and diluted to 50.0 ml with deionized water. Eventually, the solution was stored in a refrigerator at 4°C for analysis [9-11].

Modified Degree of Contamination (Mc_d)

Degree of contamination (C_d) which was first introduced by Hakanson (1980) [12] was originally a method to calculate an overall pollution factor, based on integrating data from a series of seven specific heavy metals and an organic pollutant named Polychlorinated biphenyl (PCB). Individual contamination factors are calculated based on the following formula:

$$C_f = M_x / M_b$$

Where, M_x = concentration of the element in samples and M_b = background concentration of the element. The overall degree of contamination is calculated by the following formula:

$$C_d = \sum_{i=1}^{8} C_f^i$$

In general, all eight substances must be analyzed in order to calculate the correct C_d for the range of classes defined by Hakanson (1980) [12]. Since it is not always possible to analyze all of the components used for this index, a variation of this method was proposed by Abrahim (2005) [13]. Abrahim presented a modified and generalized form of Hakanson's equation for the calculation of the overall degree of contamination at a given sampling site, which is as follows:

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n}$$

Where, n = number of analyzed elements, i= ith element (or pollutant) and C_f= Contamination factor. This method produces the final degree of contamination based on the available contaminant determinations. The classification of the sediments according to the modified degree of contamination includes the following gradations **(**Table 1):

Table 1. Classification of the sediments according to the modified degree

Nil to very low degree of contamination	$mC_d < 1.5$
Low degree of contamination	$1.5 < mC_d < 2$
Moderate degree of contamination	$2 < mC_d < 4$
High degree of contamination	$4 < mC_d < 8$
Very high degree of contamination	$8 < mC_d < 16$
Extremely high degree of contamination	$16 < mC_d < 32$
Ultra high degree of contamination	$mC_d \geq 32$

RESULTS

The mean concentrations of heavy metals in water and sediments for each sampling site are shown in Tables 2 and 3, respectively. Mean concentrations of the examined metals in water for Pb, Cr, Cu, Zn, and Fe were 4.01, 0.09, 0.13, 0.34, and 2.10 mg L^{-1}, respectively. Heavy metal concentrations in the water samples decreased in the sequence of Pb > Fe > Zn > Cu > Cr. Mean concentrations of the examined metals in sediments for Pb, Cr, Cu, Zn, and Fe were 37.80, 73.09, 16.09, 39.54 µg g^{-1}, and 3.74% of dry weights, respectively, allowing arranging the metals from higher to lower mean content in this area as: Fe > Cr > Zn > Pb > Cu. The values of pH and organic matter content in sediments are presented in Table 4. Modified degree of contamination (mC_d) and contamination factor (C_f) values for describing the contamination levels in sediments are shown in Table 5. Pearson's correlation coefficient matrix in the selected heavy metals and physicochemical parameters of sediments is presented in Table 6.

Table 2. Means and SD of metal concentrations in water (mg L^{-1}) from nine sites in Hara Biosphere Reserve, Iran.

Fe	Pb	Cu	Zn	Cr	Station
1.95 ± 0.09	4.24 ± 0.24	0.18 ± 0.05	0.58 ± 0.10	0.08 ± 0.02	1
2.06 ± 0.14	3.57 ± 0.42	0.13 ± 0.05	0.29 ± 0.09	0.07 ± 0.01	2
2.34 ± 0.17	4.19 ± 0.14	0.10 ± 0.00	0.19 ± 0.08	0.04 ± 0.01	3
1.98 ± 0.13	3.41 ± 0.58	0.15 ± 0.03	0.22 ± 0.06	0.05 ± 0.01	4
2.20± 0.12	4.69 ± 0.64	0.16 ± 0.07	0.16 ± 0.03	0.04 ± 0.01	5
2.23 ± 0.15	3.68 ± 0.53	0.14 ± 0.04	0.69 ± 0.10	0.34 ± 0.04	6
2.23 ± 0.12	4.10 ± 0.55	0.16 ± 0.05	0.39 ± 0.09	0.13 ± 0.01	7
2.22 ± 0.17	3.61 ± 1.35	0.13 ± 0.06	0.43 ± 0.06	0.07 ± 0.02	8
1.60 ± 0.09	4.59 ± 0.36	0.06 ± 0.02	0.14 ± 0.05	0.04 ± 0.00	9
2.10 ± 0.25	4.01 ± 0.66	0.13 ± 0.05	0.34 ± 0.19	0.09 ± 0.08	Average
-	0.008	0.003	0.081	-	CCC [a]

[a] CCC ''chronic'' in marine surface water; used by NOAA [14]

Table 3. Means and SD of metal concentrations in sediments ($\mu g\ g^{-1}$) from nine sites in Hara Biosphere Reserve, Iran.

	Percentage		$\mu g\ g^{-1}$	Station	
Fe	Pb	Cu	Zn	Cr	
4.05 ± 0.73	37.47 ± 1.43	16.90 ± 2.74	46.31 ± 3.08	79.39 ± 4.20	1
3.64 ± 0.21	31.53 ± 4.10	15.50 ± 1.01	42.46 ± 2.49	75.00 ± 9.05	2
3.53 ± 0.22	39.33 ± 6.02	13.85 ± 0.88	36.25 ± 4.48	60.12 ± 1.95	3
3.36 ± 0.20	31.44 ± 7.80	18.21 ± 5.03	42.01 ± 2.62	80.09 ± 8.09	4
4.13± 0.82	38.89 ± 0.81	20.19 ± 7.05	46.78 ± 9.66	70.61 ± 2.97	5
3.77 ± 0.44	48.48 ± 8.66	18.70 ± 2.90	42.13 ± 1.06	95.16 ± 8.76	6
4.25 ± 0.87	42.75 ± 0.75	16.74 ± 4.23	38.19 ± 3.67	73.89 ± 4.50	7
3.52 ± 0.69	37.70 ± 1.25	13.06 ± 4.58	31.36 ± 9.32	67.29 ± 3.44	8
3.42 ± 0.34	32.58 ± 0.92	11.70 ± 0.87	30.43 ± 4.68	56.32 ± 0.73	9
3.74 ± 0.52	37.80 ± 6.61	16.09 ± 4.18	39.54 ± 7.27	73.09 ± 1.20	Average
2.9	10	19	74	7	Average of the less contaminated sample[a]

[[a]15]

Table 4. Mean levels of pH and percentage of organic matter (%) in sediments from nine sites in Hara Biosphere Reserve, Iran.

pH	Organic matter	Station
8.30 ± 0.21	0.98 ± 0.12	1
8.44 ± 0.03	0.40 ± 0.14	2
8.39 ± 0.01	0.99 ± 0.16	3
7.99 ± 0.05	1.67 ± 0.46	4
7.68 ± 0.23	0.59 ± 0.14	5
8.12 ± 0.11	0.98 ± 0.31	6
8.10 ± 0.07	0.68 ± 0.04	7
7.90 ± 0.11	1.60 ± 0.67	8
7.84 ± 0.04	0.81 ± 0.32	9
8.08 ± 0.09	0.96 ± 0.26	Average

Table 5. Modified degree of contamination (mC_d) and contamination factor (C_f) of sediments at nine sites Hara Biosphere Reserve, Iran.

		mCd	C_f	Station		
	Cu	Zn	Cr	Fe	Pb	
0.89	0.37	0.48	0.88	0.86	1.87	1
0.79	0.34	0.44	0.83	0.77	1.57	2
0.81	0.3	0.38	0.66	0.75	1.96	3
0.80	0.4	0.44	0.88	0.71	1.57	4
0.90	0.44	0.49	0.78	0.87	1.94	5
1.02	0.41	0.44	1.05	0.8	2.42	6
0.92	0.37	0.4	0.82	0.9	2.13	7
0.80	0.29	0.33	0.74	0.74	1.88	8
0.71	0.26	0.32	0.62	0.72	1.62	9

Table 6. Pearson's correlation coefficients between heavy metals, pH, and organic matter in sediments of Hara Biosphere Reserve, Iran.

Organic matter	pH	Cu	Zn	Cr	Fe	Pb	
						1	Pb
					1	0.51	Fe
				1	0.28	0.47	Cr
			1	0.63	0.54	0.13	Zn
		1	0.87**	0.72*	0.55	0.36	Cu
	1	-0.14	0.17	0.18	-0.04	0.007	pH
1	-0.21	-0.11	-0.29	0.09	-0.52	-0.09	Organic matter

* High positive correlation between Cr and Cu (r = 0.720, $P<0.05$)

* High positive correlation between Cu and Zn (r = 0.875, $P<0.01$)

DISCUSSION

Metals discharged into near shore areas of marine environments are mostly partitioned between the sediment and water column phases. In an aquatic environment, sediments have a high contamination capacity, especially for heavy metals [16]. According to the data presented in Tables 2 and 3, the concentrations of metals were far pollutants are higher in the sediments compared to those calculated for the same metals in water, which is due to accumulated contamination in the reserve sediments over the years [17]. Baldantoni *et al*. (2005) [18] reported that the element accumulation in sediment is the result of long-term exposure, whereas element concentration in water is mainly the result of recent contamination. Mean concentrations of examined metals (Cr, Pb, Cu, Zn, and Fe) in water were above the chronic values in marine surface water guidelines proposed by National Oceanic and Atmospheric Administration (NOAA) indicating the potential for these metals to produce chronic effects in marine biota. In general, the mean concentrations of metals in water found in this study exceeded those reported for Bahia Blanca Estuary and Alvarado Lagoon [19]. Nevertheless, in this study, the concentrations of the examined metals in water of the study area were lower than what was described for the Gulf of Cambay [20].

Average content of Pb, Cr, and Fe in the sediments of the study area were higher than the average of the less contaminated sample [15] which may reflect anthropogenic effects, but mean concentrations of Cu and Zn in sediments were lower than that of the less contaminated sample. These may be related to human activities, including shipping and transport, urban and domestic wastewater, agriculture, industrial wastewater at ship-building plants, desalination facilities, coastal activities (for example, marinas, jetties, ports and harbors), and fishing boats [21].

The comparison of the total concentrations of the selected heavy metals in the sediments with those from other countries showed that the concentrations of of Cr, Pb, Cu, Zn, and Fe in the study area sediments are relatively lower than that for the North Newington estuarine wetlands, Homebush Bay, [22] and Kumho River, Korea [23]. The difference in the metal levels in the sediments of the Hara Biosphere Reserve with other regions may be due to differences in industrial and urban contamination sources or the number of parameters such as clay content, pH, organic matter, and environmental factors, which control the solubility and, therefore, the availability of metals [1].

Both organic matters and pH are the most important factors that control the availability of heavy metals in soil and sediments [24]. Organic matter has a high specific storage capacity for heavy metals. A decrease in pH will increase the competition between metals and hydrogen ions for binding sites and may dissolve metal complexes, releasing free metal ions into the water column. An increase in pH is generally accompanied by a decrease in the solubility of many toxic heavy metals in water [1].

Table 6 shows that there was a negative correlation between pH and organic matter and Fe and Cu in sediments. The results indicated that the concentration of Cu and Fe increased with decreasing pH levels and percentage of organic matter present in the sediments. Additionally, Pb and Zn concentrations in sediments were negatively correlated with organic matters. Pearson correlation coefficients showed that there were positive correlations between Cu and Zn ($r = 0.875$, $P<0.01$) and Cr and Cu ($r = 0.720$, $P<0.05$) in sediments. It is hypothesized that metals with similar high positive correlations are possibly from the same pollutant sources [25].

A number of calculation methods have been put forward for quantifying the degree of metal enrichment in sediments. Various authors [12,26] have proposed pollution impact scales for converting the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity. In this study, the modified degree of contamination (mC_d) introduced by Abrahim (2005) [13] was used to assess the pollution load of metals in sediments. According to the results shown in Table 5, mC_d values in the study area were less than 1.5 with values ranging from 0.71 to 1.02 indicating zero to very low contamination in the sediments of Hara Biosphere Reserve.

CONCLUSION

The results of this study showed that heavy metal concentrations in water were described in the descending order of Pb > Fe > Zn > Cu > Cr, while in sediment samples, these values were Fe > Cr > Zn > Pb > Cu. The average concentrations of Cr, Pb, Cu, Zn, and Fe in water were higher than the chronic values proposed by marine surface water guidelines, indicating the potential of these metals for producing chronic effects in marine biota. Comparison of the results of measuring the concentration of mentioned metals with the mean of the less contaminated sample showed high contamination levels for Cr, Pb, and Fe while mean concentrations of Cu and Zn in sediments were lower than the mean of the less contaminated sample. The findings of this study also showed that with a decrease in organic matter and pH in sediments, copper and iron concentrations increased. Based on the modified contamination degree, the sediments of Hara Biosphere Reserve are considered to be in the zero to very low contamination status.

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REFERENCES

1. Ebrahimpour M, Mushrifah I. Heavy metal concentrations in water and sediments in Tasik Chini, a freshwater lake, Malaysia. Environmental monitoring and assessment. 2008;141(1):297-307.
2. Karbassi A, Bayati GRN-BI. Environmental geochemistry of heavy metals in a sediment core off Bushehr, Persian Gulf. Iranian Journal of Environmental Health Science & Engineering. 2005;2(4):255-60.
3. Sasmaz A, Obek E, Hasar H. The accumulation of heavy metals in Typha latifolia L. grown in a stream carrying secondary effluent. ecological engineering. 2008;33(3):278-84.
4. Al-Masri M, Aba A, Khalil H, Al-Hares Z. Sedimentation rates and pollution history of a dried lake: Al-Oteibeh Lake. Science of the Total Environment. 2002;293(1):177-89.
5. Cardwell A, Hawker DW, Greenway M. Metal accumulation in aquatic macrophytes from southeast Queensland, Australia. Chemosphere. 2002;48(7):653-63.
6. Demırezen D, Aksoy A. Accumulation of heavy metals in Typha angustifolia(L.) and Potamogeton pectinatus(L.) living in Sultan Marsh (Kayseri, Turkey). Chemosphere. 2004;56(7):685-96.
7. Kumar IN, Sajish PR, Kumar RN, BASIL G, Shalendra V. An Assessment of the Accumulation Potential of Pb, Zn and Cd by Avicennia marina (Forssk.) Vierh. in Vamleshwar Mangroves, Gujarat, India. Notulae Scientia Biologicae. 2011;3(1):36-40.
8. Neinavaz E, Karami M, Danehkar A. Investigation of Great Egret (Casmerodius albus) breeding success in Hara Biosphere Reserve of Iran. Environmental monitoring and assessment. 2011;179(1):301-7.
9. Tüzen M. Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry. Microchemical Journal. 2003;74(3):289-97.
10. El-Rjoob A-WO, Massadeh AM, Omari MN. Evaluation of Pb, Cu, Zn, Cd, Ni and Fe levels in Rosmarinus officinalis labaiatae (Rosemary) medicinal plant and soils in selected zones in Jordan. Environmental monitoring and assessment. 2008;140(1):61-8.
11. Nowrouzi M, Pourkhabbaz A, Rezaei M. Bioaccumulation and Distribution of Metals in Sediments and Avicenna marina Tissues in the Hara Biosphere Reserve, Iran. Bulletin of environmental contamination and toxicology. 2012:1-6.
12. Hakanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research. 1980;14(8):975-1001.
13. Abrahim G. Holocene sediments of Tamaki Estuary: characterisation and impact of recent human activity on an urban estuary in Auckland, New Zealand: ResearchSpace@ Auckland; 2005.
14. Long ER, MacDonald DD, Smith SL, Calder FD. Incidence of adverse biological effects

within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management. 1995;19(1):81-97.

15. Christophoridis C, Dedepsidis D, Fytianos K. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. Journal of hazardous materials. 2009;168(2):1082-91.
16. Korfali SI, Davies BE. Speciation of metals in sediment and water in a river underlain by limestone: role of carbonate species for purification capacity of rivers. Advances in Environmental Research. 2004;8(3):599-612.
17. Namminga HE, Wilhm J, editors. Effect of high discharge and an oil refinery cleanup operation on heavy metals in water and sediments in skeleton creek. Proc Oklahoma Acad Sci; 1976; **56:**133-8.
18. Baldantoni D, Maisto G, Bartoli G, Alfani A. Analyses of three native aquatic plant species to assess spatial gradients of lake trace element contamination. Aquatic botany. 2005;83(1):48-60.
19. Vazquez G, Diaz R, Salvador L, Sharma VK. Dissolved metals in Alvarado lagoon, Mexico. Environment international. 1998;24(7):721-7.
20. Srinivasa Reddy M, Basha S, Joshi H, Ramachandraiah G. Seasonal distribution and contamination levels of total PHCs, PAHs and heavy metals in coastal waters of the Alang–Sosiya ship scrapping yard, Gulf of Cambay, India. Chemosphere. 2005;61(11):1587-93.
21. Kazemi A, Bakhtiari AR, Kheirabadi N, Barani H, Haidari B. Distribution Patterns of Metals Contamination in Sediments Based on Type Regional Development on the Intertidal Coastal Zones of the Persian Gulf, Iran. Bulletin of environmental contamination and toxicology. 2012:1-4.
22. MacFarlane G, Pulkownik A, Burchett M. Accumulation and distribution of heavy metals in the grey mangrove, Avicennia marina(Forsk.) Vierh: biological indication potential. Environmental Pollution. 2003;123(1):139-51.
23. Kim Y, Kim B-K, Kim K. Distribution and speciation of heavy metals and their sources in Kumho River sediment, Korea. Environmental Earth Sciences. 2010;60(5):943-52.
24. Karaca A. Effect of organic wastes on the extractability of cadmium, copper, nickel, and zinc in soil. Geoderma. 2004;122(2):297-303.
25. Mansouri B, Ebrahimpour M. Heavy Metals Characteristics of Wastewater Stabilization Ponds. American-Eurasian Journal of Agricultural and Environmental Sciences. 2011;10(5):763-8.
26. Muller G. Index of geoaccumulation in sediments of the Rhine River. Geojournal. 1969;2(3):108-18.