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Assessing some heavy metals pollutions in sediments of the northern Persian Gulf (Bushehr province)

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Abstract

Background: Land and water pollution by heavy metals is a universal issue. Although the pollution affects all countries, but its range and severity vary hugely. The pollution of the marine environment by heavy metals is a worldwide problem. Marine sediments can be sensitive indicators for monitoring contaminants in aquatic environments.

Methods: The concentration of 10 elements (As, Cd, Cr, Cu, Al, Fe, Ni, Pb, Sb, and Zn) was determined in the sediments of four shoreline stations including Imam Hassan port, Ameri port, Bushehr port, and Nayband Bay at the west Persian Gulf from March to December 2017. The elements were measured by inductively coupled plasma mass spectrometry (ICP-MS). Data were analyzed using SPSS version 16.

Results: The contamination of the sediments was assessed based on the geoaccumulation index (Igeo) and enrichment factor (EF). Spearman correlation matrix was calculated between all the trace metals and major elements as well as corresponding sampling regions. Statistically significant inter-elemental correlations (e.g., Cr-Fe, Cr-Al, Cr-Ni, Cr-Zn, and Cr-Cu) were found between some metals. High EF levels for Fe, Al, and Pb suggest that metals in the sediments of the northern Persian Gulf could have originated from anthropogenic sources.

Conclusion: The contamination pattern of sediments is affected by factors such as sedimentation patterns, physical and chemical properties of the sediments. For example, sediments with fine-grained and high surface area-to-volume ratio can act as good absorbents for many pollutants.

Keywords: Heavy metals, Geologic sediment, Persian Gulf, Bushehr

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Introduction

The pollution of marine environment by heavy metals is a worldwide problem. Although the pollution affects all countries, but its range and severity vary hugely. In this regard, marine sediments can be sensitive indicators for monitoring contaminants in aquatic environments (1,2). The sediments are used as a stock for heavy metals and thus, need special investigation in projecting aquatic pollution research. Accumulation of heavy metals happen in upsaid sediments in aquatic environments by biological mechanisms. Sediment is a habitat and major nutrient source for aquatic organisms. These processes become toxic to sediment-dwelling organisms, resulting in death, reduced growth, reproductive impairment, and prevent species diversity (3,4). Heavy metals pollute marine sediments and other aquatic ecosystems, which happen due to industrialization (5,6).

Great quantities of pollutants, directly or indirectly, are discharged into the marine environment every day. In this regard, heavy metals are considered as serious pollutants of the aquatic environments due to their accumulative behavior (7,8). Heavy metals are one of the constituents that affect the marine ecosystems. Potential toxicity of heavy metals in an aquatic ecosystem is determined by their chemical form. Some elements are necessary for human health in trace amounts (Co, Cu, Cr, and Ni), while others are carcinogenic or toxic, mainly affecting the central nervous system (Hg, Pb, and As), the kidneys or liver (Hg, Pb, Cd, and Cu), or skin, bones and teeth (Ni, Cd, Cu, and Cr) (9). Heavy metals that have been recognized in the polluted environment include As, Cu, Cd, Pb, Cr, Ni, Hg, and Zn. The toxicity of trace metals

arises from their interference with an organism's uptake of essential metal ions such as sodium and calcium. For example, cadmium and zinc block the uptake of calcium ions, which are important for bone and teeth growth.

The interaction of some heavy metals with enzymes and their tendency to bind to the protein and other biological tissues also cause trace metal poisoning in organisms (10,11).

The Persian Gulf is a relatively shallow semi-enclosed sea with poor flushing characteristics. Thus, pollution discharges into the sea are diluted more slowly than into open marine ecosystems (12). The Persian Gulf has been facing many environmental challenges like biodiversity loss, industrial pollution, and harmful effluents (13). Additionally, environmental incidents, ship traffic, transportation, oil pollutants, and oil spills can cause different pollutants including heavy metals (14,15). Iran has the longest water joint border in the Persian Gulf and it has a way through the Strait of Hormuz and Makran Sea (Oman) to the Indian Ocean from the east. It leads to Arvand River in Khuzestan province from the west, which is composed of two Tigris and Euphrates rivers in Iraq as well as Karun River attachment in Iran (16).

The aim of this study was to determine the concentration of 10 metals (As, Cu, Cd, Pb, Cr, Ni, Zn, Fe, Al, and Sb) in sediments of the Persian Gulf.

Materials and Methods

Bushehr is located at 28° 55′ 19.84″ N and 50° 50′ 4.76″ E in southwestern Iran and around the northern of the Persian Gulf. In this study, 12 sampling sites in four regions of Imam Hassan port, Bushehr port, Ameri port, and Nayband Bay (Figure 1) were selected during March to December 2017.

Samples were obtained from the upper layer (5 cm depth) of sediments. Ten square meters of each area was sampled. The sediments were collected from the intertidal areas once low tides. Sediments were transferred to polyethylene containers and transported to the laboratory at 4°C. The

samples were dried at 105°C for at least 24 hours (17). The samples were sieved through a 63 micron stainless steel sieve and agitated vigorously to produce homogeneity (18). One gram of each sample was digested in a mixture of concentrated HNO3 (65%) and HClO4 (60%) in the ratio of 4:1, first, at a low temperature (40°C) for 1 hour and then, at a high temperature (140°C) for 4 hours (19). The digested samples were then diluted to a certain capacity (25 mL) with double distilled water (DDW). The sample was then filtered through Whatman No. 40 filter paper. The heavy metals concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) (scheme code was MMS-01: Detection limited were in ppm) in Zarazma Co.

The geoaccumulation index (Igeo) is used to determine the level of contamination in sediments (20). For this purpose, the current concentrations is compared to pre-industrial levels using the following equation:

$$I_{geo} = \log_2 C_n / 1.5B_n$$

where *Cn* is the measured concentration of the element n in the pelitic sediment fraction (< 2 Am) and *Bn* is the geochemical background value in fossil argillaceous sediment (average shale). The quality of the sediments is divided into six classes by Igeo: unpolluted (Igeo < 0), unpolluted to moderately polluted (0 < Igeo < 1), moderately polluted (1 < Igeo < 2), moderately to strongly polluted (2 < Igeo < 3), strongly polluted (3 < Igeo < 4), strongly to extremely polluted (4 < Igeo < 5), and extremely polluted (5 < Igeo). Concentrations of the geochemical background are increased each time by the constant 1.5 in order to allow value fluctuations of a given substance in the environment as well as very small anthropogenic influences (21).

The enrichment factor (EF) is based on the standardization of a tested element against a reference one. According to contamination standards based on the EF, the following classes are obtained: EF < 2 (deficiency to minimal enrichment), $2 \leq EF < 5$ (moderate enrichment), $5 \leq EF < 20$ (significant enrichment), $20 \leq EF < 40$ (very high enrichment), and $EF \geq 40$ (extremely high enrichment) (22). A reference element is the one characterized by low-frequency current variability. The most common reference elements are Sc, Mn, Ti, Al, and Fe (23). The EF is calculated using the following expression:

$$EF = [(Me)_s / (Fe)_s] / [(Me)_b / (Fe)_b]$$

where $(Me)_s$ and $(Me)_b$ are the concentrations of metal and normalizer, respectively. Also, $(Fe)_s$ and $(Fe)_b$ denote the sample and background sediments, respectively. Data were analyzed using SPSS version 16.

Results

Table 1 shows the concentrations of heavy metals in sediment samples collected from intertidal zone from four regions in the Bushehr province.
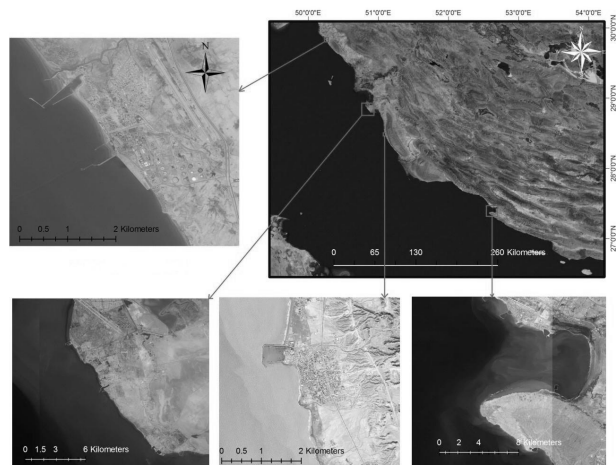
The obtained Igeo values for these four regions are shown

Figure 1. Sampling areas.

Table 1. Mean concentrations of each metal analyzed (mg/kg)

Metals	Region			
	Ameri Port	**Bushehr Port**	**Imam Hassan Port**	**Nayband Bay**
As	16.24±8.76	5.03±0.15	3.31±2.65	1.55±0.49
Cr	16.82±3.05	14.29±7.79	10.96±3.30	10.19±5.97
Cu	5.5±0.88	5.5±2.83	3.75±0.49	3.45±0.77
Pb	12.27±4.59	2.77±0.38	3.03±0.02	6.35±4.30
Zn	14.20±1.41	11.45±8.13	8.45±1.06	4.75±0.78
Al	3980±462.4	4189±5 3143.09	3828.5±688.01	695±173.2
Fe	8420±1824.3	5360±3309.26	4141±642.05	773.5±193.04
Ni	18.07±2	13.4±6.36	11.8±3.25	8.19±2.25
Sb	0.45±0.07	0.35±0.21	0.35±0.07	0.55±0.07
Cd	0.07±0.04	0.18±0.01	0.10±0.04	BDL*

*BDL: Below detection limit.

in Table 2.

Spearman correlation matrix was calculated between all the trace metals (and also major elements) and corresponding sampling regions (Table 3).

EF was used as an index to evaluate anthropogenic influences of heavy metals in sediments. When $0.5 \leq EF \leq 1.5$, the trace metals might have originated entirely from crustal materials or natural weathering processes, while when $EF > 1.5$ suggested that a significant portion of trace metals is provided by other sources (24).

Discussion

In this study, sediment pollution was assessed using geoaccumulation index (Igeo) and EF. As can be seen in Table 1, metal levels in all areas of the sample sites in terms of frequency were Fe> Al> Cr> Ni> Zn> As> Pb> Cu> Sb> Cd. The relatively high concentrations of heavy metals during winter coincide principally with decreasing rate of organic matter decomposition, due to a low water temperature (25). The highest concentrations of Fe and Al were found in Ameri port while the lowest values of Cd were reported in Nayband Bay. Fe, Al, and Pb levels were found to be higher than the other metals in the four regions (Table 2). Approximately, 42% of the samples were included in Class 0. A small percentage of the samples was included in Class 2, 3, and 4 for Al, Fe, Cd, and Pb. There were significant inter-elemental correlations (e.g., Cr-Fe, Cr-Al, Cr-Ni, Cr-Zn, and Cr-Cu). Inverse correlations

Table 2. Index of geoaccumulation for sampling regions

Region	Class								
	Fe	**Al**	**Cd**	**Pb**	**Ni**	**As**	**Zn**	**Cu**	**Sb**
Imam Hassan	0	2	0	0	0	1	0	0	1
Bushehr	3	3	2	2	0	1	0	0	1
Ameri	4	3	0	3	0	1	0	0	1
Nayband	3	2	0	2	0	0	0	0	1

Table 3. The Spearman correlation matrix between element levels in the sediment of the Persian Gulf

	Cr	Al	Fe	Ni	As	Cu	Pb	Zn	Sb	Cd
Cr	1									
Al	.934	1								
Fe	1.000**	.927	1							
Ni	.997**	.901	.998**	1						
As	.857	.639	.865	.891	1					
Cu	.947	.999**	.940	.917	.667	1				
Pb	.131	-.233	.150	.213	.557	-.195	1			
Zn	.996**	.961*	.995**	.986**	.816	.971	.046	1		
Sb	-.724	-.923	-.711	-.664	-.310	-.907	.589	-.780	1	
Cd	.317	.570	.303	.253	.072	.546	-.715	.381	-.756	1

*Correlation is significant at the 0.05 (2-tailed); ** Correlation is significant at the 0.01 (2-tailed).

Table 4. Enrichment factor in sampling regions

Metals Region	As	Cr	Cu	Pb	Zn	Al	Fe	Ni	Sb	Cd
Imam Hassan	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2
Bushehr port	EF<2	EF<2	EF<2	EF<2	EF<2	2<EF<5	2<EF<5	EF<2	EF<2	EF<2
Ameri port	EF<2	EF<2	EF<2	2<EF<5	EF<2	2<EF<5	2<EF<5	EF<2	EF<2	EF<2
Nayband Bay	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2	EF<2

were observed between Sb and Cd with almost all other elements, suggesting a positive strong significant correlation among Cr, Al, Fe, Ni, and Cu, which were clustered in the first class. Sb had a negative correlation with other elements in the first class. High EF level for Fe, Al, and Pb demonstrated that the levels of metals in sediments of the Persian Gulf could have originated from anthropogenic sources (Table 4). According to these results, the presence of these metals in the same groups might reflect a similar behavior or suggest common bio-originated sources.

The highest mean concentrations of Pb (12.27 mg/kg), Ni (18.07 mg/kg) and As (16.24 mg/kg) were reported in the Ameri port. This concentration was similar to the results of Ganugapenta et al (26) and Zhuang & Gao (27) but lower than that of El Tokhi et al (21). The pollution in the Ameri port was higher than other ports, due to the increase in the amount of agricultural wastewater, industrial wastewater, oil pollution and shipping in this port compared to the other ports.

Conclusion

Oil extraction and recent regional wars in the Persian Gulf have released millions of oil barrels, including detectable trace metals, to the sea. Seawater desalination plants in the Persian Gulf with a capacity of millions cubic meters freshwater per day are another sources of heavy metal pollution in the area. In addition to pollutants, the contamination pattern of sediments is affected by factors such as sedimentation patterns, physical and chemical properties of the sediments. For example, sediments with fine-grained and high surface area-to-volume ratio can act as good absorbents for many pollutants.

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Ethical issues

The authors have thoroughly observed ethical issues and no data from the study has been or will be published separately elsewhere.

Competing interests

The authors declared no competing interests.

Authors' contributions

All authors contributed in all aspects of this research like performing surveys and experiments, preparing the figures and tables, designing the experiments, analyzing the data graphical elaborations, writing the manuscript, and providing critical revision of the paper.

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