Anal. Method Environ. Chem. J. 3 (4) (2020) 60-71

AMECJ

Research Article, Issue 4
Analytical Methods in Environmental Chemistry Journal
Journal home page: www.amecj.com/ir

Determination and investigation of heavy metal concentrations in sediments of the Persian Gulf coasts and evaluation of their potential environmental risk

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ARTICLE INFO:

Received 22 Aug 2020
Revised form 20 Oct 2020
Accepted 15 Nov 2020
Available online 30 Dec 2020

Keywords:
Heavy metals,
Analysis,
Sediments of the Persian Gulf coasts,
Flame/electrothermal atomic absorption spectrometry,
Environmental risk

ABSTRACT

The contamination of coastal sediments with toxic heavy metals caused to a serious concern due to their environmental consequences. The aim of this study was to determine the concentration of heavy metals such as lead (Pb), copper (Cu), nickel(Ni) and manganese (Mn) in the sediments of the Persian Gulf coast in Kangan and Siraf ports in Bushehr province. In this regard, the sampling was performed in 10 stations with different uses in two depths of 0-5 and 5-20 cm along the coast of the Persian Gulf. The concentration of heavy metals was measured after drying, acid digestion and microwave by using flame atomic absorption spectrometry (F-AAS). Ecological risk index was used to assess the potential of environmental risk due to heavy metal pollution in the coastal sediments of the study area and the sensitivity of the biological community to toxic substances. Then statistical analysis in SPSS environment was used for analyzing the data. The results showed that the average concentrations of Mn(II), Ni(II), Cu(II) and Pb(II) was measured 121.47, 11.51, 11.59 and 5.30 in surface sediments, and 131.59, 10.81, 12.56 and 4.88 μg g^{-1} in deep sediments. The results of the ecological risk index with the value of less than 150, showed a low environmental risk of heavy metals detected in the region. Also, the results of multivariate statistical analyzes indicated the existence of a correlation and common origin of Cu, Ni and Mn. In general, this study led to a better understanding of the contamination of heavy metals in the region and considered it necessary to try to prevent, control and reduce the amount of pollution in the sediments of the Persian Gulf coast. All analysis validated by electrothermal atomic absorption spectrometry(ET-AAS) after dilution samples with DW.

1. Introduction

Heavy metals as the inorganic pollutants are considered as one of the serious threats in natural ecosystems due to their non-degradability, the environmental stability, the toxicity to various aquatic species and biological magnification [1]. Heavy metal pollution results from rapid urbanization and human activities including electricity generation, transportation, fossil fuel combustion, use of various chemicals, and other related activities [2, 3]. Heavy metals are metals with a specific density of less than 5 g cm^{-2} [4]. In the

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https://doi.org/10.24200/amecj.v3.i04.122

aquatic ecosystem, a number of metals such as Zn, Fe, Mn and Ni are required for the activity of biological systems. For example, diseases such as skin diseases are the result of removing essential elements such as zinc from the diet of living beings. However, the high concentrations of heavy metals can be toxic to human organisms. While some heavy metals such as; Cd, Ni, Hg, and Pb are not essential for the activity of biological systems, their presence in aquatic ecosystems causes toxicity to living organisms [5]. Also, some metals such as Pb have caused the most concern due to their toxic and carcinogenic properties. In addition, due to the fact that the amount of Pb that enters the environment through human activities is higher than the Pb that enters the environment from natural sources, the high concentration of this metal in the environment can be considered as an indicator of the level of pollution caused by human activities in the region [6]. Coastal areas are the point of connection between land and ocean, which are more important than other marine habitats due to their ecological sensitivity to pollutants, transmission of contaminants in the food chain and poisoning of living organisms [7]. Since the beginning of the industrial revolution and the subsequent increase in industry growth, the large amounts of toxic pollutants have been discharged into the coastal environment, causing metal pollution of the sediments. Heavy metals in the coastal environment originate from two natural and human sources [1, 3]. Metal contaminants in coastal sediments are precipitated by adsorption, hydrolysis, and co-sedimentation, while a small fraction of free metal ions remain in the water column. However, when environmental conditions such as pH change, the metals in the sediment enter the water, as a result, the sediments can also act as a secondary source of metals [8]. Since more than 90% of heavy metal pollution entering the marine ecosystem originates from terrestrial sources [9], the coastal sediments are often referred to as heavy metal reservoirs or inlets [9]. Some researchers have been performed to investigate and identify the concentration of heavy metals and evaluation of their potential environmental risk on the coastal area i.e on the coastal sediments of Kerala, India [6], on the surface sediments along the southeast coast of the Caspian Sea [10], on surface sediments of the Sobi Shoal, China [11] and on the coastal sediments of northern part along the Persian Gulf [3]. The results of environmental risk index in the study of Arfaeinia et al. (2019) on coastal sediments of the Persian Gulf showed that the industrial, agricultural, urban and natural areas are in the category of very high, considerable, moderately and low environmental risk levels, respectively. Due to the lack of data on the abundance and distribution of heavy metals in sediments of the coastal areas of the world, especially the Persian Gulf coast, and the possible consequences of these pollutions, especially their negative impact on marine ecosystem and the life of living things, further studies on the extent of heavy metal pollution are necessary. The different techniques such as; flame atomic absorption spectrometry (F-AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma spectrometry (ICP), inductively coupled plasma mass spectrometry (ICP-MS), electrothermal atomic absorption spectrometry (ETAAS) and others were used for determination heavy metals in water, industrial wastewater and sediment samples. As difficulty matrixes in biological, industrial wastewater and sediment samples sample preparation based on solid phase extraction(SPE) or liquid-liquid extraction (LLE) and microwave digestion/acid digestion was used before determination of heavy metals by instruments.

The coast of the Persian Gulf in the south of Iran, due to its high biodiversity, rich natural resources, warm climate and natural attractions, attracts millions of tourists annually. Consequently, the discharge of municipal and industrial wastewater has caused the presence of various pollutants, including heavy metals in the sediments of this area the objective of this study is to measure the concentration of heavy metals in the coasts of the Persian Gulf i.e Kangan and Siraf ports to estimate the extent of heavy metal pollution and evaluation of their potential environmental risk in the region. All heavy metals were determined by microwave digestion/acid digestion coupled to F-AAS.

2. Experimental

2.1. Instrumental

Determination of lead (Pb), copper (Cu), nickel(Ni) and manganese (Mn) was performed with a flame atomic absorption spectrometer (F-AAS), with an air-acetylene flame, was used for determination in surface and deep sediments samples (GBC, model plus 932, Aus). Copper based on wavelength 324.7 nm, slit 0.5 nm, lamp current 3.0 mA (1-5 mg L^{-1}), lead based on wavelength 217.0 nm, slit 1.0 nm, lamp current 5.0 mA (2.5-20 mg L^{-1}), nickel with wavelength 232.0 nm, slit 0.2 nm, lamp current 4.0 mA (1.8-8 mg L^{-1}) and manganese by wavelength 279.8 nm, slit 0.2 nm, lamp current 5.0 mA (1-36 mg L^{-1}) were selected. The spectra GBC electrothermal atomic absorption spectrometer (ET-AAS, Plus 932, Australia) using a graphite furnace module (GF3000, GBC) was used for validation of results. The operating parameters for the metal of interest were set as recommended by the manufacturer book. The light of hollow cathode lamp (GBC) adjusted on the furnace tube or burner. All samples were performed using sample volumes of 20 µL and 1000-2000 µL by auto-sampler for ET-AAS and F-AAS. respectively. The instrumental conditions and temperature programming for the graphite atomizer are listed in **Table 1a and 1 b.**

2.2. Reagents

All reagents were of analytical grade from Merck Germany. The lead (Pb), copper (Cu), nickel(Ni) and manganese (Mn) stock solution was prepared from an appropriate amount of the nitrate salt of this analyte as 1,000 mg L^{-1} solution in 0.01 mol L^{-1} HNO_3 (Merck). Standard solutions were prepared daily by dilution of the stock solution. Ultrapure water (18 MΩ.cm) was obtained from Millipore Continental Water System (Bedford, USA).

2.3. Area of study

Persian Gulf is a border and semi-enclosed sea with an area of about 226,000 square kilometers, which is located at latitude 24° to 30° 30′ north latitude and 48° to 56° 25′ east longitude surrounded by the land. This sea has a dry and subtropical climate with a minimum water exchange and an average depth of 35-40 meters. Various factors such as limited circulation, shal-

Table 1a. Instrumental conditions for heavy metal determination by F-AAS

Parameters	Cu	Pb	Mn	Ni
Wavelength (nm)	324.7 nm	217.0 nm	279.8 nm	232.0 nm
Slit (nm)	0.5 nm	1.0 nm	0.2 nm	0.2 nm
Lamp current (mA)	3.0 mA	5.0 mA	5.0 mA	4.0 mA
Injection mode	Automatic	Automatic	Automatic	Automatic
Working range (mg L^{-1})	1-5	2.5-20	1-36	1.8-8
Mode	Peak integration	Peak integration	Peak integration	Peak integration

Table 1b. Temperature programing for heavy metal determination by ET-AAS

Step	**Temperature Cu (°C)**	**Temperature Pb (°C)**	**Temperature Mn (°C)**	**Temperature Ni (°C)**	**Ramp time (s)**	**Hold time (s)**	**Ar flow rate (mL min^{-1})**
Drying	120	120	130	130	20	10	300
Ashing	800	400	700	900	40	10	300
Atomization	2300	2000	2400	2400	1	2	0.0
Cleaning	2500	2200	2600	2600	1	3	300

low depth, high water temperature and salinity have caused the Contaminants remain stable in this area for a long time. Kangan port with a population of 60187 people is located in the south of Bushehr province and on the coast of the Persian Gulf. Kangan city is the place implementation of a large part of South Pars refinery projects. The economic background of its people has been agriculture, fishing and marine trade. Also, Siraf port with a population of 6992 people is in the central part of Kangan city in Bushehr province. This port is located between Kangan and Assaluyeh ports and has a special characteristic due to its location between the two regions of South Pars energy and Kangan energy region. Also, the its historical area and the beautiful sea of Siraf has attracted many tourists. The name of each station and the geographical coordinates of the sampling points are presented in **Table 2** and shown in **Figure 1.**

Table 2. Geographical coordinates of sampling stations

Station name	Station location	Geographical coordinates	
		X	Y
S_1	Siraf port	635084	3059458
S_2		634398	3059481
S_3		632126	3060955
K_1	Kangan port	607211	3075796
K_2		603885	3079199
K_3		603295	3079640
K_4		602444	3080053
K_5		601383	3080147
K_6		600489	3080150
K_7		599667	3080196

Fig. 1. Location of the study area and sampling stations

2.4. Sampling method

In order to determine the concentration of heavy metals, sampling was performed in January 2018. For sampling, 10 stations were selected in the lower tidal line of the Persian Gulf coast where sediment has the most contact with water. Accurate sampling points were determined using the Global Positioning System (GPS). Coastal sediments were collected in the lower tidal line in a transect with a length of 1000 m using 30 x 30 cm quadrats in three replications and two depths of 0-5 and 5-20 cm. During sampling, natural waste pieces such as wood and stone were removed from the sampling area. Then 2 + 0.5 kg of sediment sample was collected from each station using a stainless steel shovel and metal ruler from the surface and subsurface layer. Samples collected from both depths were placed separately in sealed bags and transferred to the laboratory after numbering. The samples taken to the laboratory were dried at room temperature and stored until further analysis.

2.5. Procedure for determination of heavy metals

A composite sample of three replicates in the surface and deep sediments of each station was separated and completely powdered and homogenized by mortar. Then the homogenized sample was passed through a 63-micron sieve. This method was performed because heavy metals are often associated with small grains [12], One gram of dry sediment was weighed and digested in PTFE tubes using a mixture of 7 ml HNO_3, 5 ml $HClO_4$ and 2 ml HF at 200 ° C for 8 hours. After cooling, the samples were filtered through Whatman 42 µm filter paper and finally diluted and then adjusted to 25 cc volume using distilled water. The diluted samples were centrifuged at 400 rpm for 6 minutes and stored in special plastic containers. For validation, Some of samples digested by microwave digestion method (MWM) and compared to proposed procedure. 5 replicate samples and 2 blank samples were used with the aim of accuracy of analytical results and eliminating the error caused by the test process. Also, all plastic and glass containers for digestion and measurement of heavy metals were immersed in 10% nitric acid for 24 hours and then washed three times with distilled water before use. Finally, the concentrations of heavy metals such as, Ni, Pb, Mn and Cu were measured by the flame atomic absorption spectrometer (AAS) GBC model. The results were validated by electrothermal atomic absorption spectrometry (GBC, Pal 3000, ET-AAS).

2.6. Potential environmental risk index

The potential environmental risk index is widely used to evaluate the potential environmental risk of heavy metal pollution in the coastal sediments and the sensitivity of the biological community to toxic substances. Equation 1 was proposed by Hakanson in 1980 [13] for calculating the potential environmental risk was proposed as follows:

$$RI = \sum_{i=1}^{n} Er = Tr \times Cf = Cs / Cb$$

where Cf is the contamination index of heavy metal, C_s is heavy metal concentration in the sample, Cb is the background value of the each heavy metal (element concentration in shale), RI is the total potential environmental risk of heavy metals in sediment, Er is the potential environmental risk index of each metal and Tr is as a toxicity response factor, by showing the toxicity potential of heavy metals and environmental sensitivity to contamination, indicate the potential risk of heavy metal contamination. toxic response factor values for Pb, Cu, Ni and Mn are 5, 5, 5 and 1, respectively [14]. **Table 3** shows the environmental risk status classification of the studied heavy metals. Also in this study, the average shale presented by Turekian and Wedepohl in 1961[15] was used as the background concentration to determine the amount of sediment contamination to heavy elements (**Table 4**).

Table 3. Classification of heavy metal environmental risk assessment index [16]

risk levels Description	Category	risk levels Description	Category
Low risk	RI ≤ 150	Low risk	Er ≤ 40
Moderate risk	150 ≤ RI ≤ 300	Moderate risk	40 ≤ Er ≤ 80
Considerable risk	300 ≤ RI ≤ 600	Considerable risk	80 ≤ Er ≤ 160
High risk	RI ≥ 600	High risk	160 ≤ Er ≤ 320
-	-	Very high risk	ER ≥ 320

Table 4. Concentration of metals in average shale (ppm)

Metals	Pb	Cu	Ni	Mn
Average	20	45	68	850

2.7. Statistical analysis

Data analysis was performed using SPSS statistical software version 22. First, the normality of the data was evaluated by Kolmogorov-Smirnov test. Then, in order to understand the changes in the concentration of heavy metals at two depths of 0–5 and 5–20 cm, the mean equality tests of two independent societies were used. Also, the importance of the relationship between heavy metals was analyzed using Pearson correlation analysis. In addition, cluster analysis was used to explain the correlation pattern between heavy metals, identify potential sources and group them based on their similarities and differences. The significance level of statistical tests was considered 5% (95% confidence level).

3. Results and Discussion

3.1. Heavy metal determination in surface and deep sediments

The results of measuring the concentration of heavy metals in surface and deep sediments of 10 sampling stations in Kangan and Siraf ports are presented in **Table 5**. The highest and lowest mean concentrations of the studied metals in surface and deep sediments were related to Mn and Pb with the amount of 121.47 44.20 ± and 5.30 7.09 ± µg g^{-1} dry weight of surface sediment and 131.59 70.64 ± and 4.88 8.08 ± µg g^{-1} dry weight of deep sediment, respectively. Among the studied heavy metals in the surface sediments of the study area, Pb and Cu with the variation coefficients of 1.33 and 23 had the highest and lowest values, respectively. Also, in deep sediments, Pb and Cu with the variation coefficients of 1.65 and 0.28 had the highest and lowest values, respectively. A variation coefficient of less than 1 and indicates low variability, while a variation coefficient of greater than 1 indicates high variability and non-uniform distribution of the studied heavy metals in sediment [17]. In this study, only lead metal in surface and deep sediments had a variation coefficient of greater than 1. Moreover, the different techniques for heavy metal determination (µg g^{-1}) in surface and deep sediments of Kangan and Siraf ports coasts was used and shown in **Table 6**. Also, the results of comparing the concentrations of heavy metals such as, Cu, Mn, Ni and Pb in surface and deep sediments of the coasts of Kangan and Siraf ports showed that there is no significant difference between their average concentrations at two depths (P> 0.05) (**Table 7**).

Table 5. Descriptive statistics of heavy metal concentration (μg g^{-1}) in surface and deep sediments of Kangan and Siraf ports coasts

Depth of sampling	Descriptive statistics	Heavy metals			
		Pb	Cu	Ni	Mn
Surface sample	minimum	0	7.55	3.27	70.72
	maximum	17.82	16.57	28.37	203.3
	Average	5.30	11.59	11.51	121.47
	Standard deviation	7.09	2.76	7.07	44.20
	Coefficient of variation	1.33	0.23	0.61	0.36
	skewness	1.19	0.32	1.53	0.95
	kurtosis	-0.05	-0.38	3.37	-0.13
Deep sample	minimum	0	8.77	2.37	53.62
	maximum	22.25	20.97	28.87	294.6
	Average	4.88	12.56	10.81	131.59
	Standard deviation	8.08	3.64	7.65	70.64
	Coefficient of variation	1.65	0.28	0.70	0.53
	skewness	1.71	1.57	1.48	1.44
	kurtosis	1.67	2.46	3.06	2.44

Table 6. Different techniques for heavy metal determination (μg g^{-1}) in surface and deep sediments of Kangan and Siraf ports coasts (n=5, mean SD < 5%)

	Techniques	Heavy metals			
		Pb	Cu	Ni	Mn
Surface sample	F-AAS	5.30	11.59	11.51	121.5
	ICP	5.41	11.06	12.02	119.9
	ET-AAS	5.23	10.93	11.42	125.7
Deep sample	F-AAS	4.88	12.56	10.81	131.59
	ICP	5.12	12.14	11.24	126.82
	ET-AAS	4.73	12.35	11.03	124.27

Table 7. Results of comparing the concentration of heavy metals in surface and deep sediments

Metal	Test statistics	significance level
Pb	0.122	0.904
Cu	-0.671	0.511
Ni	0.210	0.836
Mn	-0.384	0.705

3.2. Correlation analysis and determination of heavy metals origin

The results of Pearson correlation among the studied metals are presented in **Table 8**. Accordingly, in sediment samples, there is a positive and moderate correlation between Cu and Ni as well as Ni and Mn at the level of 1% and 5%, respectively ($P < 0.05$). As the concentration of Ni increases, the concentrations of Cu and Mn increase. This correlation can be the result of geological property, common resources, or similar behaviors of these elements. Also, all metals in cluster analysis were classified into two statistically significant clusters based on the similarity and dissimilarity among different groups. The first cluster was divided into 2 subgroups. The first subgroup consisted of Cu and Ni with similar geological property which had positive and significant correlation, and the second group included Mn, which may be derived from both human and natural resources. The second cluster contained Pb metal, with less similarity and greater distance compared to the first cluster. Pearson correlation was used for hierarchical cluster analysis and the results were presented as a dendrogram chart (**Fig. 2**). The results of cluster analysis almost confirmed the results of correlation analysis.

Table 8. Pearson correlation coefficient of heavy metals studied

Metal	Pb	Cu	Ni	Mn
Pb	1			
Cu	0.104	1		
Ni	-0.332	0.583**	1	
Mn	-0.263	0.175	0.444*	1

* Significance at the level of 0.05   ** Significance at the level of 0.01

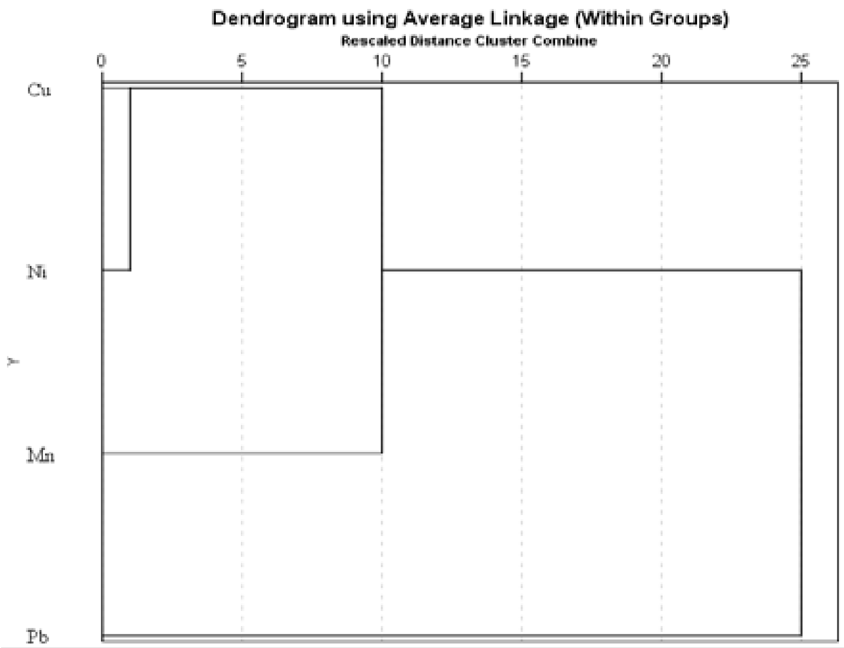

Fig. 2. Results of heavy metal cluster analysis in coastal sediments

3.3. Environmental risk evaluation

The results of environmental risk evaluation of heavy metals in the surface and deep sediments of the studied stations were less than 150, which indicated the low environmental risk of heavy metals in Kangan and Siraf coastal areas. Also, the individual environmental hazard index of the studied metals was less than 40 and showed the descending order of Pb> Cu> Ni> Mn for surface and deep sediments.

3.4. Discussion

Nowadays one of the most important global environmental problems is pollution caused by heavy metals. High concentrations of metals along with high durability, inherent toxicity and consequently accumulation in the food chain play an important role in ecosystems and human health. Therefore, this study has identified the concentration of heavy metals in the collected samples of surface and deep sediments of the Persian Gulf coastal area in Kangan and Siraf ports.

Heavy metals are affected by oil pollution and related industries, ship activity and sewage inflow as the common pollution in the study area. In this study, the highest concentrations of heavy metals in surface and deep sediments include Mn, Cu, Ni and Pb, respectively. Also in other studies conducted in the Persian Gulf coast of Bushehr province, including the study by Hosseini and Habibi et al [18,19], the concentration of Mn, Ni and Cu in the region is higher than Pb. The study by Arfaeinia et al on the concentration of heavy metals in the coasts of Asaloyeh in Persian Gulf showed that due to the high concentration of industries in this region, the concentration of pollutants is much higher than other coasts of the Persian Gulf [3]. The high concentration of heavy metals in industrial and commercial areas compared to non-industrial areas showed that human activities strongly affect the concentration and distribution of heavy metals in the environment. Industrial and agricultural wastewater, solid and liquid wastes and atmospheric emissions increase the concentration of metals in sediments of the area. Atmospheric sediments can affect large areas according to population distribution and industrial activities [3]. Also, erosion and washing of urban soils by floods and sewage can be other possible sources of sediment pollution and accumulation of heavy metals on the coast [20]. The results of comparing the concentrations of heavy metals in the two coastal areas of Kangan and Siraf showed the existence of concentration differences between them, which can be due to various reasons such as the number and type of pollutants in the environment, the distance from the source of contamination to the sampling site, sediment texture and mineralogical compositions, physical and chemical properties of sediment such as pH and temperature, amount of sediment organic matter and also the effect of environmental factors on metal deposition in sediment. The presence of heavy metals in the stations located in Kangan and Siraf ports can be attributed to various agricultural activities such as vegetables planting in greenhouses, using fertilizers and soil conditioners, drip irrigation pipes, repair of agricultural equipments and the use of pesticides. In addition, the existence of petrochemical and refining industries and their discharge of effluents to the coast, as well as high human activities such as the movement of ships and fishing boats and their discharge of sewage and waste can be considered as the effective factors in the increase of heavy metal concentrations on the coastal areas. Furthermore, the heavy metal pollution in the region could be due to the use of small rivers water to irrigate agricultural lands. Rivers water may be contaminated by discharge of municipal and industrial wastewater from the upstream wastewater treatment plants. Irrigation with contaminated water significantly increases the levels of various pollutants including heavy metals, PAHs and PCBs in coastal sediments [3]. In this study, stations K_7 and K_2 showed the highest concentrations of heavy metals in surface and deep sediments, respectively. Station K_7 is located near an area with high agricultural activities and Station K_2 is adjacent to the commercial wharf of Kangan port. The study by Wang et al also showed that the samples collected from agricultural soil contained large amounts of heavy metals. The high concentrations of Cu, Ni and Mn in the station K_7 sediments indicated their common sources and similar behavior [21]. In addition, the results of multivariate statistical analyzes showed the common origin of Cu, Ni and Mn and their correlation. The presence of Ni in the sediments of the Persian Gulf coast is probably due to the geological origin and human activities related to oil products in the region [22]. The ground sources of nickel include minerals such as clay, sandstone and basalt [20]. The study by Arfaeinia et al was showed that the origin of Ni in the region is probably due to dyes used in machinery and ships industry [3]. In addition, the concentration of Mn in sediment may increase due to human activities such as discharge of municipal and industrial wastewater, use of agricultural fertilizers and consumption of diesel fuel in motor boats. Also, Mn is easily removed from igneous and metamorphic rocks due to weathering of rocks and in interaction with surface and groundwater, and is released into aquatic environments [23]. Cu is also widely used due to its special physical properties and usually accumulates in soils and sediments following human activities [20]. In this study, the highest concentrations of Cu were identified near residential areas with agricultural activities. As a result, the presence of Cu in the region can be due to the discharge of municipal sewage and agricultural pesticides on the coastal area and also the release of paint used in conveyors, ships and vessels in the water environment which is in line with the study by Haghshenas et al [24]. The concentration of Pb in nature is low, so human activities increase the concentration of Pb in the environment [6]. Pb in the environment comes from the oil industry, lead-containing paints and leaded gasoline. The concentration of Pb metal from dyes is related to the proximity of the structures to the coastal areas and their age. While the amount of Pb due to the displacement of ships and the emission of polluted gases by vehicles depends on the volume of traffic [20]. Among the studied stations, stations S_2 and K_5 showed the highest Pb concentrations in surface and deep sediments, respectively. These two stations are located near the fishing port, residential and industrial areas. As a result, high concentrations of Pb can result from high-traffic shipping activities, release of paint from the ships' body, proximity to roads and road transport, fishing boat activity, and pollution from industrial wastewater discharge [25]. In general, factors such as high temperature and humidity on the shores of the Persian Gulf accelerate the corrosion process of metal smithereens, which mostly include Cu and Ni alloys. Also, the oil-richness of the region, the existence of activities related to the oil industry and the transport of metal-containing sediment particles by rivers and surface runoff, cause the discharge of metals in the environment and their accumulation in the sediments of the region [3].

4. Conclusions

The coast of the Persian Gulf is an important and strategic region that contributes to the economic growth of the country due to its beautiful scenery and rich resources of oil and gas. However, there is a possibility of contamination of these beaches with heavy metals due to various land and sea activities, mismanagement of solid wastes and discharge of various industrial and municipal wastewaters. The results of this study showed that heavy metals are pervasive in surface and deep sediments of all studied stations and the distance from the source of pollution, environmental conditions and sediment characteristics have caused differences in the frequency and concentration of these pollutants in different stations. The concentrations of heavy metals such as Pb, Cu, Mn and Ni in surface and deep sediments were studied and determined by F-AAS, which almost all stations had the highest concentration of Mn and the lowest concentration of Pb. Observations showed that there is a positive correlation between Cu and Ni as well as Ni and Mn ($P < 0.05$). As the concentration of Ni increases, so does the concentration of Cu and Mn. Also, the results of multivariate statistical analyzes have well confirmed the existence of this relationship. All samples were validated by microwave digestion method coupled to ET-AAS. In addition, the ecological risk assessment index to determine the environmental risk of heavy metals showed that the sediment contamination status of these metals was not in a dangerous and critical state. However, regular management and preventive measures are necessary to prevent the increase of heavy metal pollutants in the environment.

5. Acknowledgments

The authors wish to thank from the anonymous reviewers for their valuable comments.

6. References

[1] I. Ahmed, B. Mostefa, A. Bernard, R. Olivier, Levels and ecological risk assessment of heavy metals in surface sediments of fishing grounds along Algerian coast, Mar. Pollut. Bull., 136 (2018) 322-333.

[2] S. Dobaradaran, T.C. Schmidt, I. Nabipour, N. Khajeahmadi, S. Tajbakhsh, R. Saeedi, M.J. Mohammadi, M. Keshtkar, M. Khorsand, F. Faraji Ghasemi, Characterization of plastic debris and association of metals with microplastics in coastline sediment along the Persian Gulf, Waste Manag., 78 (2018), 649–658.

[3] H. Arfaeinia, S. Dobaradaran, M. Moradi, H. Pasalari, E. Abouee Mehrizi, F. Taghizadeh, A. Esmaili, M. Ansarizadeh, The effect of land use configurations on concentration, spatial distribution, and ecological risk of heavy metals in coastal sediments of northern part along the Persian Gulf, Sci. Total Environ., 653 (2019) 783-791.

[4] H. Aslam, T. Ali, M.M. Mortula, A.G. Attaelmanan, Evaluation of microplastics in beach sediments along the coast of Dubai, UAE, Mar. Pollut. Bull., 150 (2020) 110739.

[5] Atlanta centers for disease control (ACDC) US department of health and human services, national institute for occupational safety and health (NIOSH). Adult blood lead epidemiology and surveillance (ABLES), 2017. https://www.cdc.gov/niosh/topics/ables/description.html

[6] G. Suresh, V. Ramasamy, M. Sundarrajan, K. Paramasivam, Spatial and vertical distributions of heavy metals and their potential toxicity levels in various beach sediments from high-backgroundradiation area, Kerala, India, Mar. Pollut. Bull., 91 (2014) 389-400.

[7] M. Mohammedi Galangash, E. Solgi, Z. Bozorgpanah, The study of heavy metals concentration in pontogammarus maeoticus and surficial sediment in Coastal areas of the Caspian sea; Guilan Province, (Iran. J. Biol.) J.. Animal Res., 30 (2017).

[8] E. Vetrimurugan, V.C. Shruti, M.P. Jonathan, P.D. Roy, B.K. Rawlins, D.M. Rivera-Rivera, Metals and their ecological impact on beach sediments near the marine protected sites of Sodwana Bay and St. Lucia, South Africa, Mar. Pollut. Bull., 127 (2018) 568-575.

[9] K. Bigus, A. Astel, P. Niedzielski, Seasonal distribution of metals in vertical and horizontal profiles of sheltered and exposed beaches on Polish coast, Mar. Pollut. Bull., 106 (2016) 347-359.

[10] K.D. Bastami, H. Bagheri, V. Kheirabadi, G. Ghorbanzadeh Zaferani, M.B. Teymori, A. Hamzehpoor, F. Soltani, S. Haghparast, S.R. Moussavi Harami, N. Farzaneh Ghorghani, S. Ganji, Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian sea, Mar. Pollut. Bull., 81 (2014) 262-267.

[11] M. Zhang, P. He, G. Qiao, J. Huang, X. Yuan, Q. Li, Heavy metal contamination assessment of surface sediments of the Subei Shoal, China: Spatial distribution, source apportionment and ecological risk, Chemosphere, 223 (2019) 211-222.

[12] N. Harikrishnan, R. Ravisankar, A. Chandrasekaran, M. SureshGandhi, K.V. Kanagasabapathy, M.V.R. Prasad, K.K. Satapathy, Assessment of heavy metal contamination in marine sediments of East coast of Tamil Nadu affected by different pollution sources, Mar. Pollut. Bull., 121 (2017) 418-427.

[13] L. Hakanson, An ecological risk index for

aquatic pollution control, a sedimentological approach, Water Res., 14 (1980) 975–1001.

[14] H. Delshab, P. Farshchi, B. Keshavarzi, Geochemical distribution, fractionation and contamination assessment of heavy metals in marine sediments of the Asaluyeh port, Persian Gulf, Mar. Pollut. Bull., 115 (2016) 401-411.

[15] K.K. Turekian, K.H. Wedepohl, Distribution of the elements in some major units of the Earth's Crust, Bull. Geol. Soc. Am., 72 (1961) 175-192.

[16] M. Mohammadizadeh, K.D. Bastami, M. Ehsanpour, M. Afkhami, F. Mohammadizadeh, M. Esmaeilzadeh, Heavy metal accumulation in tissues of two sea cucumbers, Holothuria leucospilota and Holothuria scabra in the northern part of Qeshm island, Persian gulf, Mar. Pollut. Bull., 103 (2015) 354–359.

[17] S. Liu, Y. Zhang, S. Bi, X. Zhang, X. Li, M. Lin, G. Hu, Heavy metals distribution and environmental quality assessment for sediments off the southern coast of the Shandong Peninsula, China, Mar. Pollut. Bull., 100 (2015) 483-488.

[18] M. Hosseini, S.B. Nabavi, R. Golshani, S.N. Nabavi, A. Raeesi sarasiab, The heavy metals pollution (Cd, Co, Pb, Cu and Ni) in sediment, liver and muscles tissues of flounder Psettodes erumei from Busheher Province, Persian Gulf, (Iran. J. Biol.) J. Animal Res., 28 (2014) 441-449.

[19] S. Habibi, A. Safahieh, H. Pashazanoosi, Determining the level of impurity of coastal sediments in Bushehr province in relation to heavy metals (Cu, Pb, Ni, Cd), J. Marine Sci. Technol., 11 (2013) 84-95.

[20] A. Ranjbar Jafarabadi, A. Riyahi Bakhtiyari, A. Shadmehri Toosi, C. Jadot, Spatial distribution, ecological and health risk assessment of heavy metals in marine superficial sediments and coastal seawaters of fringing coral reefs of the Persian Gulf, Iran, Chemosphere, 185 (2017) 1090-1111.

[21] Y. Wang, X. Zou, C. Peng, S. Qiao, T. Wang, W. Yu, S. Khokiattiwong, N. Kornkanitnan, Occurrence and distribution of microplastics in surface sediments from the Gulf of Thailand, Mar. Pollut. Bull., 152 (2020) 110916.

[22] M. Saadati, M. Soleimani, M. Sadeghsaba, M.R. Hemami, Bioaccumulation of heavy metals (Hg, Cd and Ni) by sentinel crab (Macrophthalmus depressus) from sediments of Mousa Bay, Persian Gulf, Ecotoxicol. Environ. Saf., 191 (2020) 109986.

[23] S.M. El Baz, M.M. Khalil, Assessment of trace metals contamination in the coastal sediments of the Egyptian Mediterranean coast, J. Afr. Earth Sci., 143 (2018) 195-200.

[24] A. Haghshenas, M. Hatami-manesh, M. Sadeghi, M. Mirzaei, B. Mohammadi Bardkashki, Determination and ecological risk assessment of heavy metals (Cd, Pb, Cu, Zn) in surface sediments of coastal regions of Bushehr Province, J. Environ. Health Eng., 5 (2018) 359-374.

[25] M. Sharifinia, M. Taherizadeh, J. Imanpour Namin, E. Kamrani, Ecological risk assessment of trace metals in the surface sediments of the Persian Gulf and Gulf of Oman: evidence from subtropical estuaries of the Iranian coastal waters, Chemosphere, 191 (2018) 485-493.