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Evaluation of Heavy Metal Contamination and Ecological Risk Assessment in Sediments of Karun using Aquatic Pollution Indices

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Background & Aims of the Study: The current study was designed to determine the quality of sediments in Karun in Ahvaz, Iran, according to aquatic pollution indices.
Materials and Methods: The sediment samples were obtained from six river stations in summer and winter. The sediment samples were air-dried, sifted, homogenized, and stored in plastic bags, and the concentrations of metals were determined in the laboratory.
Results: The obtained findings revealed that the mean concentrations of lead, zinc, chrome, and cadmium were 26.27, 72.36, 53.47, and 3.85 mg/kg dw in summer and 13.41, 59.54, 30.28, and 0.42 mg/kg dw in winter, respectively. According to the mean scores of the potential ecological risk index (PERI), in two seasons, the sediment enrichment with metals was observed in the order of Cd > Pb > Cr > Zn; however, according to biological toxicity test (the effects range-median quotient), the sequences of the metals during summer and winter were Cd > Cr > Zn > Pb and Zn > Cr > Pb > Cd, respectively. The comparison of indices between stations showed that in summer, stations 3 and 4 were medium-low priority side according to the mean effects range-median quotient (mERM-Q) and were reported with moderate ecological risk based on the PERI. In winter, stations 2 and 4 had a medium-low priority side and moderate ecological risk according to mERM-Q and PERI, respectively. The results of hazard quotient (HQ) and modified hazard quotient also showed that the HQ values of Pb and Zn (0.1<HQ<1), as well as Cr and Cd (1<HQ<10), were indicative of potential and moderate hazards in these ecosystems, respectively.
Conclusion: Based on all the indices, station 4 was the most contaminated site, and Cd was reported with the highest risk. Therefore, entering the wastewater canal and input contaminants, especially cadmium into Karun can be regarded as a major concern.

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Background

Recently, the rapid advancement of urban and industrial growth has turned into a matter of concern for the aquatic environment and changed the aquatic system with the progressively high release of contaminants into these ecosystems (1). Among these toxic contaminations, the contamination with heavy metals in aquatic environments due to its potential hazards and related threats to human health and aquatic organisms has been identified as a serious menace to these ecosystems and has attracted great attention (2).

Metal contaminations are discharged from different sources, including the natural sources of heavy metals and anthropogenic activities related to industrialization and urbanization (e.g., vehicular exhaust, industrial wastage, mining operations, residential sewage, and agricultural activities). The aforementioned sources are significant reasons for the contamination with heavy metals in aquatic environments (3, 4). Among the various types of pollutants, being contaminated with heavy metals is of significant concern due to their environmental perseverance, potential toxicity, profusion, bioaccumulation, and incorporation into the food webs in aquatic habitats. The aforementioned incorporation poses potential risks to the environment and leads to adverse effects on humans due to the use of polluted seafood (5).

In an aquatic habitat, sediments are significant and dynamic portions of the aquatic ecosystems that work as the final receptors of contaminations and known storeroom of heavy metals due to their major trend of adsorbing onto solid phases (6). Consequently, bed sediments are indicative of contamination with heavy metal due to their hydrophobicity and trend to accumulate in the sediment (7). As a matter of fact, sediments commonly provide useful information regarding the condition of environmental contamination (8). Therefore, bed sediments, which show the state of the pollution, assess the quality of aquatic environments as optimal tools (9).

With altering physical and chemical conditions and in responding to certain disorders, the heavy metals accumulated in the sediments of many aquatic regions may be released into the surrounding water, posing a possible menace to ecosystems (10). Accordingly, because metal-contaminated sediments are potentially hazardous to the overlying water section, it is required to procure data on the quality of sediment and condition of its related environmental threat.

In the surface sediment, different indicators have been created for the evaluation of the ecological risk of heavy metals. The indicators include modified pollution index (MPI) (11), toxic risk index (TRI) (12), multiple probable effect concentrations quality (mPECQs) (13), and bioavailable metal index (BMI) (14). For instance, to evaluate the combined risk of numerous and potential ecological hazards of heavy metals in sediment, the models, such as the potential ecological risk index (PERI), were also utilized (15). Moreover, hazard quotient (HQ) and modified hazard quotient (mHQ) can be used for the assessment of the relative toxicity and level of contamination with heavy metals in sediments (16).

Different studies have examined metal concentration, spatial distribution of heavy metals, and metal concentration risk estimate in the sediments from the aquatic areas of rivers in the world, including the Pearl River in China (17), Buriganga River in Bangladesh (18), Ganga in India (19), Mic in Romania (20), and river in the Ponce Enriquez Area, Ecuador (21). According to numerous studies, there has currently been metal contamination in multiple river systems originated from anthropogenic activities, and Karun is no exception to this situation.

As the largest and the longest river in Iran, Karun flows down the Zagros Mountains into the Khuzestan Plain (22). Karun is vital for agricultural and domestic water supply in this area. In addition, Karun has a potential biological diversity, because this river is an appropriate ecosystem that created habitats and food sources for different aquatic organisms, such as kinds of fish, algae, birds, and other living things (23).

Nevertheless, the discharge of various toxic pollutants to the environment of Ahvaz, Iran, such as air and aquatic ecosystems, is expanding due to different activities in the city around this region that are the most critical factors threatening the air (24, 25). Furthermore, the discharge of various toxic pollutants leads to the drastic water quality degradation of the aquatic systems, such as rivers, and threat to aquatic organisms (3). Consequently, it is required to check the concentration, distribution, influence, and source of heavy metals in Karun sediments to protect human health and environment.

Aims of the study

The present study aimed to study the concentration levels of heavy metals (i.e., lead, zinc, chrome, and cadmium) in the sediments of Karun in which there are water supply points for treatments in Ahvaz and Mollasani, Iran, in two different seasons. Moreover, the current study surveyed the impact of contamination with heavy metals using several approaches, namely PERI, biological risk index, HQ, and mHQ.

Materials & Methods

Study area and sediment sampling

Karun was the study site in the current study located in Ahvaz in Khuzestan Province, Iran. Karun (30º20′-34º5′ N, 48º10′-52º30′ E), with the spatial extent of 67,257 km^2 and length of 950 km^2 is the biggest and the longest river in Iran. This river originates from the Zagros Mountains and flows down into the Khuzestan Plain. The river is the major water source for different applications, including domestic, various industries, and agriculture uses, in this city (26). Due to the extensive area of this complex and importance of this river, a section of the river which is the location of water supply points for treatments in Ahvaz and Mollasani was considered the study area (Figure 1).

Six stations along Karun in this study were selected from the water supply points in Ahvaz and Mollasani. A total of 36 sediment samples with a depth of 0-10 cm were collected from this station in summer and winter in 2015 and 2016. The sediment samples were put into polyethylene bags, saved in a cool box at 4°C, and transported to the laboratory quickly for analysis. Then, all the samples were air-dried at room temperature, sifted, homogenized, and stored in plastic bags for chemical analysis.

Chemical analysis of metals

The concentration of heavy metals in sediment samples was determined according to Yap et al. (2002). About 1 g of the dried sediment samples was weighed and placed into

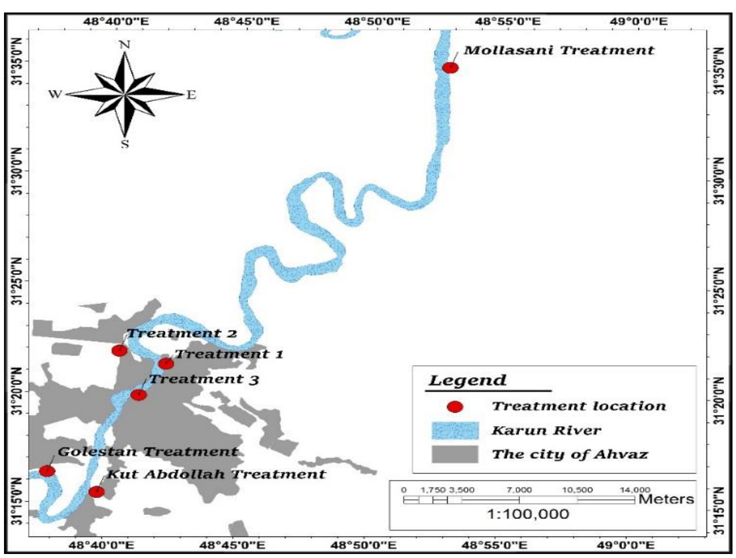

Figure 1) Map of investigated area and location of sampling sites in Karun, Iran

a polytetrafluoroethylene (PTFE) tube. Each PTFE tube was placed in a heating block. Then, the sediment samples were digested by adding a combination of nitric acid (65%) and concentrated perchloric acid (60%) with a ratio of 4:1 through exposure to 40°C for 1 h and 140°C for 4 h (27). After the digestion process, the solution was filtered and saved in 50 mL polypropylene tubes. Finally, the concentrations of Pb, Zn, Cr, and Cd in the sediment samples from Karun were determined using an atomic absorption spectrophotometer (Perkin Elmer Analyst 300, PerkinElmer, Inc., USA).

Quality assurance/Quality control

For each metal, a recovery study was carried out for the more precise assessment of the accuracy and reliability of the concentrations of the heavy metals obtained in the analysis. Linear calibration graphs were obtained using six consecutive blank concentration measurements for all of the studied metals. The limit of detection (LOD) and limit of quantification (LOQ) for metals were analyzed in this study. According to the findings, it was shown that the LOD and LOQ for Pb, Zn, Cr, and Cd were 0.613, 0.273, 0.957, and 0.095 mg/kg, as well as 1.86, 0.83, 2.92, and 0.29 mg/kg, respectively. In addition, the linear correlation coefficient (r) values of the aforementioned metals were reported as 0.986, 0.993, 0.957, and 0.995, respectively.

Data analysis

Assessment of sediment contamination and associated environmental risk

Different techniques were used for the assessment of contamination with heavy metals and associated environmental risk. Four indices were utilized in the present study, including the PERI, biological risk index (the mean effects range-median quotient [mERM-Q]), based sediment quality guidelines (SQGs) to specify the environmental risk of heavy metals, HQ, and mHQ, for the assessment of contamination with heavy metals in sediments.

- Potential ecological risk index

The PERI was utilized for the identification of the potential ecological risk (PER) degrees of heavy metals (i.e., Pb, Zn, Cr, and Cd) in sediments based on the toxicity of heavy metals and response of the environment (28). Equation 1 and 2 were used for the calculation of the environmental risks of heavy metals in the sediment.

$$E_r^i = T_r^i C_f^i \qquad \text{Equation (1)}$$

$$C_f^i = C_0^i / C_n^i \qquad \text{Equation (2)}$$

Moreover, equation 3 was utilized in order to calculate the comprehensive environmental risks of heavy metals in the sediment (RI).

$$PER = \Sigma E_r^i = \Sigma T_r^i C_f^i \qquad \text{Equation (3)}$$

Where *PER* is measured as the sum of the PER for heavy metals in sediments, which was established by Hakanson (1980). The E_r^i is the potential environmental risk factor of the metal i (i.e., Pb, Zn, Cr, and Cd), and T_r^i is the biological toxic response factor for individual metal. The toxic response factors for Pb, Zn, Cr, and Cd were reported as 5, 1, 2, and 30, respectively. The C_f^i is the contamination factor of metal i in sediment, C_0^i is the content of concentration of metal i in samples, and C_n^i is a reference value related to metals. The E_r^i and *PERI* values of heavy metals in the sediment are classified into five and four levels depending on the apart values presented in Table 1, respectively (28, 29).

- Biological risk index (mERM-Q) based sediment quality guidelines

The SQGs assess potential environmental toxicity associated with metals in freshwater systems in accordance with the value of the effect range medium (ERM). The effects range-

Table 1) Utilized scale to describe potential ecological risk for monomial factors, potential ecological risk for multinomial factors, effects range-median quotient, and mean effects range-median quotient (Long and Ingersoll, 2005)

Evaluation of potential ecological risk				Evaluation of biological risk	
E_r^i	Potential ecological risk for monomial factor	R_i or PER	Potential ecological risk for multinomial factors	ERM-Qi and mERM-Q	Biological toxicity risk for monomial and multinomial factors
<40	Low ecological risk	<95	Low ecological risk	<0.1	Low priority side
40-80	Moderate ecological risk	95-190	Moderate ecological risk	0.1– 0.5	Medium-low priority side
80-160	Considerable ecological risk	190-380	Considerable ecological risk	0.5 – 1.5	High-medium priority side
160-320	High ecological risk	>380	Very high ecological risk	>1.5	High priority side
>320	Very high ecological risk				

E_r^i: Potential ecological risk for monomial factor
R_i: Potential ecological risk for multinomial factors
ERM-Q: Effects range-median quotient
mERM-Q: Mean effects range-median quotient

median quotient (ERM-Q) was presented in the current study to specify the feasible biological effect of single metals (30). Moreover, the mERM-Q was introduced to survey the potential effects of multiple heavy metal contamination in sediments and can be measured using equations 4 and 5 (29).

$$\text{mERM-Q}=\sum_{i=1}^{n}(\text{ERM}-\text{Qi})/n \qquad \text{Equation (4)}$$

$$\text{ERM-Qi}=\text{Ci}/\text{ERMi} \qquad \text{Equation (5)}$$

where *mERM-Q* is the mean effects range-median quotient of metal i (i.e., Pb, Zn, Cr, and Cd), *Ci* is the total content of chosen metal, *ERMi* is the effect range-median of metal i, and *n* is the number of selected metals. The ERM-Qi and mERM-Qi values are categorized into four classes (Table 1).

- *Hazard quotient*

In aquatic environments, the specific potential for toxicity caused by the contamination of heavy metals in the study area sediments to the environment and living things can be estimated through the calculation of the HQ of the selected metals (31) utilizing equation 6.

$$HQ = \frac{C_{metal}}{SQG} \qquad \text{Equation (6)}$$

where, C_{metal} is the observed concentration of metal sediment in mg kg^{-1}, and *SQG* is the sediment quality guideline in mg kg^{-1} (31). The SQG values in the present study were set at the threshold effect level (TEL) for the computation of the HQ (Pb=35, Zn=123, Cr=37.3, and Cd=0.6) (32). For the toxicity description, the HQ values were utilized for the exhibition of the potential risk to the environmental receiver. According to Feng et al. (2011), no adverse effect is indicated at HQ < 0.1, and potential hazards are expected to be low at 0.1< HQ < 1; however, within the range of 1 < HQ < 10, moderate hazards are probable, and finally, HQ > 10 shows the potential of high hazards.

- *Modified hazard quotient*

A new indicator for the investigation of the sediment pollution of heavy metals according to the level of their contamination was formularized and introduced in this study. This new method made it possible to evaluate pollution by comparing the concentration of heavy metal sediment with the distributions of synoptic adverse environmental effects for different threshold levels (i.e., TEL, PEL, and SEL) indicated by MacDonald et al. (2000). The definition of mHQ of metals is an important and useful evaluation approach that explains the risk degree of each heavy metal to aquatic systems and living things. This index is calculated by the application of the following mathematical equation:

$$\mathrm{mHQ} = \left[C_i\left(\frac{1}{TEL_i}+\frac{1}{PEL_i}+\frac{1}{SEL_i}\right)\right]^{\frac{1}{2}} \quad \text{Equation (7)}$$

where C_i is the calculated sediment concentration of the metal, and TEL_i, PEL_i, and SEL_i are the threshold effect level, probable effect level, and severe effect level for i metal, respectively. In the formula of this index, the square root is stated as a drawdown function for mathematical and classified considerations.

According to the suggested categorization of mHQ, mHQ < 0.5, 0.5 < mHQ < 1.0, 1.0 < mHQ < 1.5, 1.5 < mHQ < 2.0, 2.0 < mHQ < 2.5, 2.5 < mHQ < 3.0, 3.0 < mHQ < 3.5, and mHQ > 3.5 indicate nil to very low severity of contamination, very low severity of contami-nation, low severity of contamination, moderate severity of contamination, considerable severity of contamination, high severity of contami-nation, very high severity of contamination, and extreme severity of contamination, respectively.

Statistical analysis

Statistical analysis of the data was carried out using SPSS software (version 19.0), and Excel software (2013) was applied to draw diagrams. The Shapiro-Wilk test was conducted for the assessment of the normality of the data related to the concentration of heavy metals. One-way analysis of variance was performed to identify significant differences in the concentration of metal sediment in different sites. In addition, the t-test statistical analysis was used to compare the concentration of metals between two seasons. In the present study, ArcGIS software (10.3) was also employed for mapping the spatial distribution of mHQ.

Results

- Concentrations of metal sediment

Table 2 tabulates the descriptive statistics and mean concentrations of heavy metals (i.e., Pb, Zn, Cr, and Cd) in the surface sediment gathered from Karun. The concentrations of Pb, Zn, Cr, and Cd were within the ranges of 23.9-29.1, 59.9-89.2, 53.4-59.9, and 3.3-4.7 mg/kg dw, with the mean values of 26.27, 72.36, 53.47, and 3.85 mg/kg dw in summer, respectively. Furthermore, the concentrations of

Table 2) Mean±standard deviation concentration of heavy metals (mg/kg dw) in sediments at different sampling stations in Karun in Iran during two seasons

Station (S)	Metal (mean±standard deviation)			
	Lead	**Zinc**	**Chrome**	**Cadmium**
Summer				
S_1	26.9±0.5	66.7±4.5	47.7±1.3	3.5±0.5
S_2	24.8±7.4	87.4±6.8	56.8±3.2	3.3±0.4
S_3	28.4±8.2	68.8±10.7	53.9±10.2	4.3±0.5
S_4	29.1±1.05	89.2±4.9	59.9±0.2	4.7±0.4
S_5	23.9±3.9	59.9±3.7	48.6±3.06	3.6±0.3
S_6	24.5±4.2	61.8±11.2	53.7±6.6	3.4±0.3
Mean	26.2±4.2	72.3±7.01	53.4±4.1	3.8±0.4
Winter				
S_1	8.54±4.7	67.0±14.7	31.9±0.7	0.45±0.05
S_2	16.43±5.4	58.3±5.02	30.7±1.2	0.47±0.08
S_3	11.11±1.9	49.7±8.5	27.8±0.8	0.32±0.08
S_4	25.5±2.2	72.4±10.7	31.9±0.3	0.65±0.05
S_5	8.6±3.3	53.08±4.1	31±0.5	0.31±0.1
S_6	10.2±1.6	56.7±1.4	28.2±1.7	0.36±0.28
Mean	13.4±3.2	59.5±7.4	30.2±0.9	0.42±0.1

Table 3) Ecological risks of heavy metals and potential ecological risk indices in sediments of different sites of Karun in Iran during two seasons

Station (S)	Er				PERI
	Lead	Zinc	Chrome	Cadmium	
Summer					
S_1	5.85	0.91	1.59	115.76	124.11
S_2	5.40	1.19	1.89	108.59	117.07
S_3	6.14	0.93	1.80	143.15	152.02
S_4	6.33	1.21	2.00	154.24	163.79
S_5	5.21	0.81	1.62	119.67	127.32
S_6	5.34	0.84	1.79	112.50	120.47
Winter					
S_1	1.87	0.91	1.06	14.67	18.51
S_2	3.57	0.79	1.02	15.42	20.81
S_3	2.42	0.68	0.93	10.53	14.55
S_4	5.55	0.98	1.07	21.20	28.80
S_5	1.87	0.72	1.03	10.21	13.83
S_6	2.22	0.77	0.94	11.93	18.73

Note: Er is the monomial and PERI is the multinomial potential ecological risk indices of heavy metals.

Pb, Zn, Cr, and Cd were within the ranges of 8.5-25.5, 49.7-72.4, 27.8-31.9, and 0.31-0.65 mg/kg dw, with the mean values 13.41, 59.54, 30.28, and 0.42 mg/kg dw in winter. In addition, the total concentration of metals in sediment was reported as Zn > Cr > Pb > Cd.

- Ecological and biological risks and contamination assessment

In the present study, the indices, such as ecological risks (E_r^i), PER, monomial biological risk indices (i.e., ERM-Qi), multinomial biological risk indices (i.e., mERM-Q), HQ, and mHQ, in different stations and seasons (i.e., winter and summer) were applied in order to evaluate the pollution levels of heavy metals in Karun sediments.

- Ecological risks and potential ecological risks

According to the results shown in Table 3, the monomial potential ecological risks indices (E_r^i) in two seasons indicated that the potential ecological factors (E_r^i) related to heavy metals in summer were all less than 40 except for Cd.

As presented in Table 3, the outcomes of the calculation of multinomial potential ecological risk indices of the four heavy metals (i.e., Pb, Zn, Cr, and Cd) at all sampling sites indicated that the PERI in two seasons was different. Accordingly, the PERI values in the sampling stations were within the ranges of 117 to 163 and 13.83 to 28.80 in summer and winter, respectively. Moreover, the PERI of these metals at all sampling stations was higher in summer than that reported in winter.

- Monomial (effects range-median quotient) and multinomial (mean effects range-median quotient) biological risk indices

Table 4 tabulates the results of monomial biological risk indices (i.e., ERM-Qi) in summer and winter. In accordance with the classification of mERM-Q, the values of multinomial biological risk indices in the sampling sites were 0.12 to 0.38, which illustrates medium-low priority side at all sampling stations in two seasons (Table 4).

- Hazard quotient

Table 5 tabulates the outcome outputs of HQ calculation for the selected metals (i.e., Pb, Zn, Cr, and Cd) in this studied aquatic ecosystem. Based on the obtained results, during summer, the HQ values of Pb and Zn were within the range of 0.1 < HQ < 1 indicating that the metals

Table 4) Monomial (effects range-median quotient) and multinomial (mean effects range-median quotient) biological risk indices of heavy metals in sediments of different sites of Karun in Iran during two seasons

Station (S)	ERM-Qi				mERM-Qi
	Lead	Zinc	Chrome	Cadmium	
Summer					
S_1	0.24	0.25	0.33	0.39	0.30
S_2	0.23	0.32	0.39	0.37	0.32
S_3	0.26	0.25	0.37	0.49	0.34
S_4	0.26	0.33	0.41	0.53	0.38
S_5	0.22	0.22	0.34	0.41	0.29
S_6	0.22	0.23	0.37	0.38	0.30
Winter					
S_1	0.08	0.25	0.22	0.05	0.149
S_2	0.15	0.22	0.21	0.05	0.157
S_3	0.10	0.18	0.19	0.04	0.128
S_4	0.23	0.27	0.22	0.07	0.198
S_5	0.08	0.20	0.21	0.03	0.130
S_6	0.09	0.21	0.19	0.04	0.134

ERM-Qi: Effects range-median quotient
mERM-Qi: Mean effects range-median quotient
Note: ERM-Qi is the monomial and mERM-Q is the multinomial biological risk indices.

Table 5) Comparison of hazard quotient of heavy metals in sediments of different sites of Karun in Iran during two seasons

Station (S)	Hazard quotient			
	Lead	Zinc	Chrome	Cadmium
Summer				
S_1	0.77	0.54	1.28	6.02
S_2	0.71	0.71	1.52	5.64
S_3	0.81	0.56	1.45	7.44
S_4	0.83	0.73	1.61	8.02
S_5	0.68	0.49	1.30	6.22
S_6	0.70	0.50	1.44	5.85
Winter				
S_1	0.25	0.54	0.86	0.76
S_2	0.47	0.47	0.82	0.80
S_3	0.32	0.40	0.75	0.55
S_4	0.73	0.59	0.86	1.10
S_5	0.25	0.43	0.83	0.53
S_6	0.29	0.46	0.76	0.62

could create potential threats to the aquatic creatures and biological systems under investigation. Nevertheless, the HQ values of Cr and Cd were reported between 1 and 10 ($1<HQ<10$) at all studied sites during summer. However, the HQ values of all metals were between 0.1 and 1 ($0.1<HQ<1$) in winter.

- Modified hazard quotient

Table 6 tabulates the evaluated values of mHQ for the sediments of all the surveyed sites during summer and winter; however, figures 2 and 3 depict the spatial distributions of the obtained values of mHQ.

Discussion

The difference in the concentration of metals at different stations probably reflected the

Table 6) Modified hazard quotient (mHQ) for heavy metals in sediment of different sites of Karun in Iran during two seasons

Metal	Sampling stations					
	S_1	S_2	S_3	S_4	S_5	S_6
Lead	VL (N)	VL (N)	VL (N)	VL (N)	VL (N)	VL (N)
Zinc	N (N)	VL (N)	N (N)	VL (N)	N (N)	N (N)
Chrome	L (VL)	L (VL)	L (VL)	L (VL)	L (VL)	L (VL)
Cadmium	ES (VL)	VH (VL)	ES (N)	ES (VL)	ES (N)	VH (N)

ES: Extreme severity of contamination
VH: Very high severity of contamination
H: High severity of contamination
L: Low severity of contamination
VL: Very low severity of contamination
N: Nil to very low severity of contamination
Note in parenthesis: Summer
Note not in parenthesis: Winter

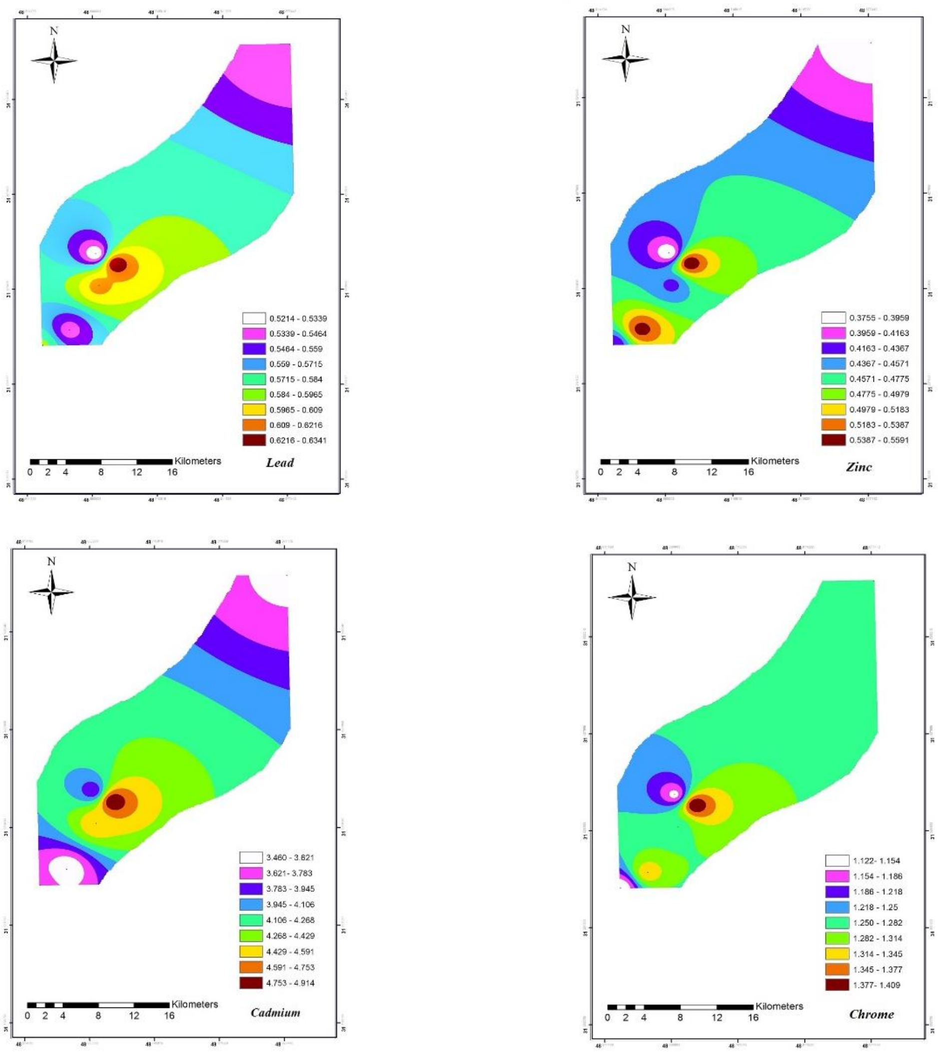

Figure 2) Spatial representation of modified hazard quotient of chosen metals in sediments of different stations during summer in Karun in Iran

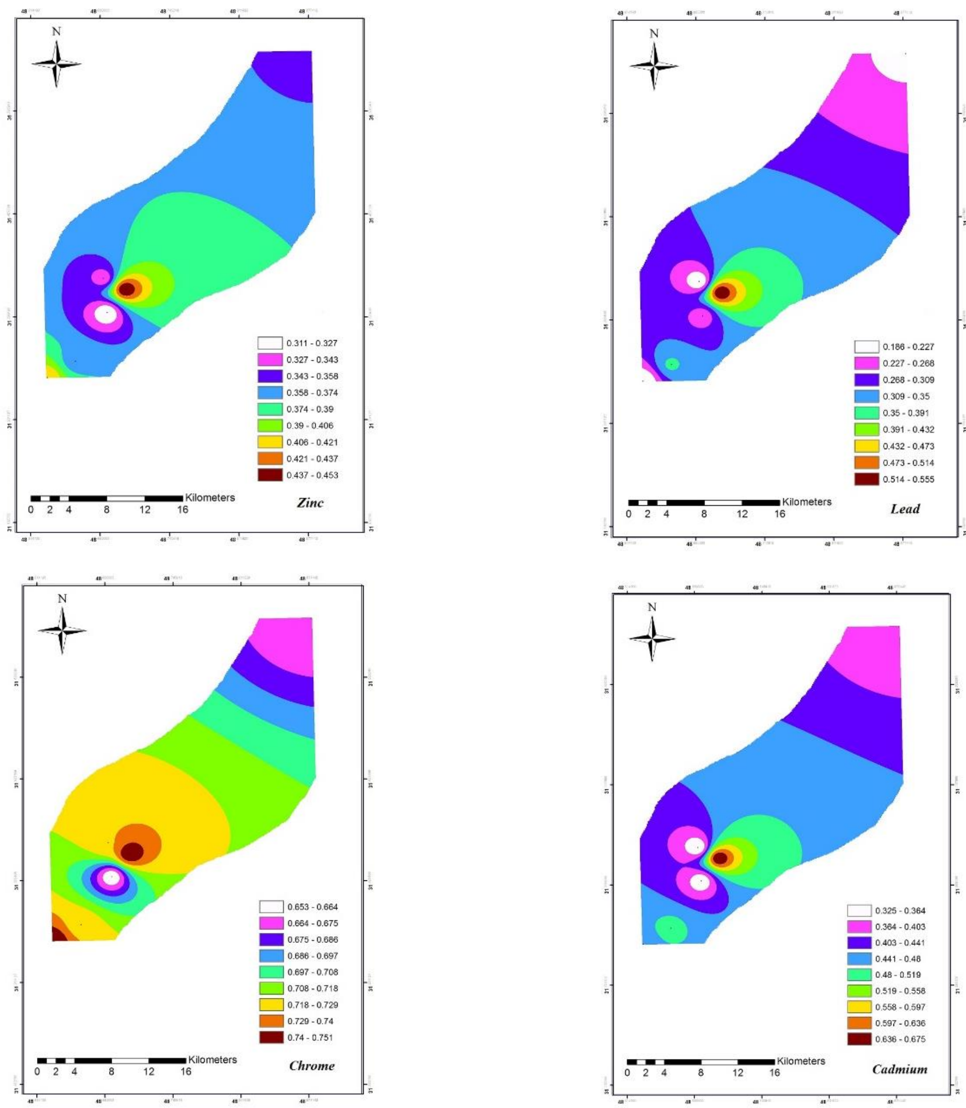

Figure 3) Spatial representation of modified hazard quotient of metals in sediments of different sites during winter in Karun in Iran

different anthropogenic inputs into each station of the river. For instance, the high amounts of metals, such as zinc, lead, and chromium, in aquatic systems are generally identified due to the discharge of the wastewater caused by the agricultural (pesticides and fertilizers) and industrial activities and residential sewage in the literature (33). Therefore, in the present study, the higher concentrations of Zn than other metals in the sediments of the Karun were connected to the large surface runoff releases into the river from different activities in the region. Consequently, these activities in the vicinity of this river are likely in the principal contamination sources of various metals (3).

In spite of the fact that Zn is a required metal for the growth of plants and animals, it can be toxic to some aquatic organisms at high amounts (34). The distribution of heavy metals displays difference among the different surveyed sampling sites of this river in two seasons, which could be due to the differences in the source of heavy metals, dominant physiochemical status, and multiple responses, such as adsorption, flocculation, and redox condition in the sediments (35).

The highest concentration of heavy metals (Pb=27.3, Zn=80.8, Cr=43.9, and Cd=2.67 mg/kg) were observed in the station 4 (S_4) in which there were water supply points for treatment 1 in Ahvaz. This part is located in the midstream of the study extent in Karun where the urban wastewater channel of Ahvaz arrives at the river. The wastewater release has no strict rule; therefore, it can be an acceptable reason for rising the concentration of metals in this site. The lowest mean concentrations of Pb, Zn, Cr, and Cd (i.e., 16.25, 56.49, 39.8, and 1.95 mg/kg) were also observed in the treatment 2 of Karun. The concentrations of metal in the samples were reported in the descending site order of $S_4 > S_2 > S_3 > S_1 > S_6 > S_5$. The descending order of heavy metals among the sampling sites did not indicate a downstream pattern.

For example, in S_4 and S_3 sites situated at the midstream of the study range of the river, the concentrations of metals were higher than some places in the downstream of the river, such as S_1. This could be the result of the metal input in sediments based on station-specific characteristics, including the flow of the stream, contamination sources, and waste discharge from the urban areas (36). These results are similar to the findings of a study conducted by Barhounmi et al. (2019).

As previously mentioned, among the different sampling stations, the concentrations of all metals in S_4 were the highest; accordingly, this station can be considered the hotspot of these contaminations. The concentrations of all metals in the two seasons (i.e., summer and winter) indicated a significant difference, along with the seasonal pattern in various stations based on which the highest concentration of metals was observed during summer, and the lowest concentration was reported in winter. These differences can be the result of the lower flow of the river during summer and extreme precipitation in winter.

On the other hand, rainfalls in the wet season are responsible for increasing the flow in the stream water, and in this way, as a result of turbulence and shock to the water in this season, some of the sediments of the river bed and heavy metals inside them are washed by the water flow. However, in summer, with a rise in the evaporation and termination of the precipitation time, higher values of heavy metals accumulate in sediments (37).

According to the PERI ($\mathrm{E_r^i}$) of individual metals (i.e., Pb, Zn, Cr, and Cd) and their classifications, every single metal was indicated with a low PER except Cd that demonstrated considerable ecological risk in summer. These findings are similar to the results of a study conducted by Keshavarzi et al. showing that $\mathrm{E_r^i}$ amounts of As, Cr, Cu, Ni, Pb, and Zn in all sampling stations of Karun are less than 40, and the metals have low PER in the study area.

The potential ecological risk indices for a single heavy metal ($\mathrm{E_r^i}$) displayed that the intensity of these metals in two seasons was in the order of Cd > Pb > Cr > Zn. Therefore, according to these results, Cd was reported with the highest ecological risk, in spite of the fact that the concentrations of this element were lower, compared to other studied elements. In addition, the results of a study performed by Siddiqui and Pandey (19) on the ecological risk of heavy metals showed that based on E_r^i, the severity of contamination was in the order of Cd > Ni > Pb > Cu > Cr > Zn. In the present study, the high ecological risk related to Cd could be the result of the extremely toxic response factor of this element.

Generally, the main source of cadmium in the sediments of Karun can be a consequence of the usage of chemical fertilizer for the agriculture (3) and result from the release of this metal from various industrial wastewater, for instance, electroplating, batteries, mining, and refining processes (38). Furthermore, the highest of the monomial potential ecological risk indices ($\mathrm{E_r^i}$) in two seasons was indicated in station 4 (S_4).

According to the classification of PER, in summer, the four heavy metals in the sediments of all sampling sites were related to moderate ecological risks; however, these stations exhibited low ecological risk in winter. The aforementioned results are consistent with the findings of a study by Sun et al. (2019) that indicated according to the classification of the PERI, there were low ecological risks for total heavy metals in the freezing, normal, and wet periods in all sampling sites. This status can be the result of increasing the dilution of the river during winter (39).

The PER for multinomial regulators showed that the ecological risks of Karun in terms of four heavy metals were sorted as $S_4 > S_3 > S_5 > S_1 > S_6 > S_2$ and $S_4 > S_2 > S_1 > S_6 > S_3 > S_5$ in summer and winter, respectively (Figure 2). The station 4 is located inside the city extent and consequently contributes to the high monomial potential ecological risk indices (E_r^i) and multinomial potential ecological risk indices in this site. Generally, within the extent of the city, urban and industrial wastewaters are entered into Karun; for this reason, some stations, such as the water supply source of treatments 1 and 3 (S_4 and S_3) situated in this region, receive urban and industrial wastewaters.

On the other hand, the stations located downstream of the river can receive a composition of urban industrial and agricultural wastewaters. In the present study, for instance, the water supply points for Kut Abdullah treatment located downstream of the studied region after the discharge area of hospital wastewaters and area of agricultural and animal husbandry activities had also the highest contamination load. Therefore, the difference in ecological risk in various stations in terms of the contamination of heavy metals can be the result of the various inputs of wastewater to any site of the river. This reason is related to the higher concentrations of these metals at those sites that received very large amounts of various wastewaters, such as S_4 and S_2.

Based on the results of monomial biological risk indices (i.e., ERM-Qi), all heavy metals indicated medium-low priority side in summer at all considered stations; nevertheless, in winter, zinc and chromium presented medium-low priority side at all sites. Moreover, lead and cadmium showed a low-priority side at all sites (except at S_4 in which Cd and Pb presented medium-low priority side). The biological risks of pollution in the sediments of Karun were sorted as Cd > Cr > Zn > Pb and Zn > Cr > Pb > Cd in summer and winter, respectively (Figure 3). These results are in line with findings of studies by Wang et al. (2019) and Yang et al. (2014) that showed based on the E_r^i and RI methods, the metal with the highest risk was determined Cd in the sediments.

The PERs and biological risk of heavy metals in aquatic ecosystems are closely linked to the metal chemical speciation in terms of its impact on accessibility and mobility to aquatic organisms (40). In addition, based on the findings of some studies, it was suggested that the metals, such as zinc and cadmium, in the river sediments were largely linked and co-precipitated with exchangeable-carbonate and Fe-Mn oxides-related phases (41).

Consequently, due to the fact that the metals, such as cadmium and zinc, can create biological toxicity and cause a serious hazard to aquatic organisms and human health, it contributes to high risk for these metals based on the E_r^i and PERI method. Nonetheless, for metals, such as chromium and lead, the strong bond of the metals in the sediment can be responsible for their low potential ecological risks. In addition, these metals in the sediment had potentially low mobility and bioavailability to aquatic organisms (42).

The biological risk indices for multinomial regulators (i.e., mERM-Q) showed that the biological risk of pollution to Karun sediments in terms of four heavy metals followed the orders of $S_4 > S_3 > S_2 > S_1 > S_6 > S_5$ and $S_4 > S_2 > S_3 > S_6 > S_5 > S_1$ in summer and winter, respectively.

In general, the findings revealed that the concentrations of elements increased with the release of urban sewage and industrial wastewater. In addition, given that most discharges are placed at midstream and downstream of the river, the concentrations also show a rising trend toward downstream (3).

Based on the results of two indices (i.e., PERI and mERM-Q) in two seasons, station 4 was the most contaminated site and identified as the hotspot that received the major part of urban and industrial wastewater in the river, regarding the location of this station, which was placed inside the internal extent of the city. Therefore, it can be concluded that entering the wastewater canal into Karun can be regarded as an important and effective factor for the increase of metal pollution of Karun sediments and should be considered the main concern.

Based on the results, during summer, the HQ values of Pb and Zn were within the range of $0.1 < HQ < 1$, indicating that these metals could pose potential threats to the aquatic creatures and biological systems under study. Nevertheless, the HQ values of Cr and Cd were between 1 and 10 ($1<HQ<10$) at all studied sites during summer. However, in winter, the HQ values of all metals were between 0.1 and 1 ($0.1<HQ<1$). These values illustrated the probability of Cr and Cd to cause moderate hazards in all stations of this biological system in summer. The Cd and Pb are considered toxic to the environment, and the significant amounts of their HQ represented that they might be related to harmful biological and environmental risks.

In the results of this section of the present study, the highest HQ values among other metals were obtained for Cd. This observation is suggestive a potential for adverse biological effects caused by Cd in Karun ecosystems. Furthermore, these findings refer to the fact that the consumption of seafood from these aquatic systems may lead to potential health risks, especially the risk of Cd intoxication. These results are in line with the findings of a study conducted by Benson et al. (2018), showing that the HQ values of Cd, Cu, and Pb were between 1 and 10 ($1<HQ<10$) at all investigated sites. HQ index of this aquatic system in terms of selected heavy metals generally followed the sequences of $S_4 > S_3 > S_2 > S_1 > S_6 > S_5$ and $S_4 > S_2 > S_1 > S_3 > S_6 > S_5$ in summer and winter, respectively.

The mHQs determined by the proposed equation showed that the intensity of sediment-connected pollution caused by the five heavy metals in summer was in the descending orders of Cd > Cr > Pb > Zn and Cr > Cd > Zn > Pb in summer and winter, respectively. This trend is in accordance with other pollution patterns observed for contamination assessment indicators previously published for this area and other reports (43-45). The findings showed that in summer, Cd caused excessive severity of pollution at most stations and very high degree of pollution in S_2 and S_6 stations. Nevertheless, according to the contamination severity classification in this season, Cr was reported with low contamination severity. However, Pb and Zn generally demonstrated a very low to nil degree of contamination. All the studied metals showed nil to very low severity of contamination during winter at all investigated sites.

The outcomes of the present study indicated that the pollution of heavy metals in sediments, especially Cd, became a main ecological problem in the sediments at different sites of Karun, which is in accordance with the findings of other investigations in this field (46). In addition, the contamination of heavy metals in sediments can become incorporated into food chains and increase in comparatively large values in aquatic organisms without any obvious impacts, leading to hazards to human health (47). Consequently, it is essential to carefully check and monitor the contamination of heavy metals, particularly Cd, in the study region.

The obtained data in this study could be beneficial for the development of successful management strategies for the control of the contamination caused by heavy metals in Karun. In addition, all the studied indices (i.e., PERI, mERM-Q, HQ, and mHQ) in this study showed that station 4 was the most contaminated site and identified as the hotspot that receives the major part of urban and industrial wastewater in the river. Therefore, it can be concluded that entering the wastewater canal into Karun can be regarded as an important and effective factor for the increase of the metal pollution of Karun sediments and should be considered a major concern.

Conclusion

The findings of this study revealed valuable information about the concentration of heavy metals in the sediments of different sites with the water supply points for treatments in Ahvaz and Mollasani part of Karun. This study demonstrated that the distribution of concentration of metals was in the order of Zn > Cr > Pb > Cd in all of the sampling sites and showed a significant seasonal variation with the highest amounts in summer and the lowest amounts in winter.

Based on the obtained results, the concentration of heavy metals in the sediments of different sites of Karun showed significant spatial variations. The assessment of the PERs and biological risk indices indicated that Cd had a higher PER than other metals for most of the sites and was the most severe metal pollutant in this area. In addition, the comparison of indices between stations showed that in summer, the pool of treatment 3 and treatment 1 (S_3 and S_4 stations) where the urban wastewater channel enters the river was medium-low priority side according to mERM-Q and has a moderate ecological risk based on PERI.

In winter, the pool of Kut Abdollah treatment and treatment 1 (S_2 and S_4 stations) in which the urban sections of the study area were reported with medium-low priority side and moderate ecological risk, respectively, according to mERM-Q and PERI. In addition to the above-mentioned findings, HQ and mHQ were also employed to assess the sediment-heavy metal relative toxicity and contamination. The HQ values of Pb and Zn ($0.1<HQ<1$), as well as Cr and Cd ($1<HQ<10$), indicated potential hazards and moderate hazards in these ecosystems, respectively.

Based on mHQ, Cd illustrated extreme severity and very high degree of contamination in all stations; however, other metals indicated low and very low degrees of contamination. Generally, based on the results of these indices (i.e., PERI, mERM-Q, HQ, and mHQ) in two seasons, station 4 was the most contaminated site and identified as the hotspot that receives the major part of urban and industrial wastewater in the river. Therefore, it can be concluded that entering the wastewater canal into Karun can be regarded as an important and effective factor for the increase of metal pollution of Karun sediments and should be considered a major concern.

Footnotes

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Conflict of Interest

The authors declare that there is no conflict of interest.

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