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Assessment of Ecological Hazard of Heavy Metals (Cr, Zn, Cu, Pb) in Surface Sediments of The Bashar River, Yasouj, Iran

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Background & Aims of the Study: Heavy metals pollution in aquatic ecosystems threats living organisms' health and environment. Hence, the present study aims to assess concentration of lead, chromium, copper, zinc and their ecological risk in the surface sediments of the Bashar River during the summer and winter seasons.

Materials & Methods: This is a field study; sampling of surface sediment was done in 8 stations in 2016. The samples were digested by the composition of ratio of 1:4 Percholoric acid and Nitric acid and then were analyzed by atomic absorption spectrophotometry. Statistical analysis of all data was also done using SPSS 21 and various criteria were used to fine the amount of contamination of heavy metals.

Results: The results showed that the average total concentration of Zn, Cu, Pb and Cr in the summer were (48.16, 39.2, 14.45 and 10.35) and as for winter was (39.88, 26.93, 12.23 and 10.301) mg/kg respectively. In addition, evaluating geo-accumulation indexes, pollution load and pollution factor indicated the low pollution status of the area in both seasons.

Conclusions: According to the results, pollution status and the RI level of heavy metals in the Bashar River is low and similar in summer and winter. Also, the sources and changes in elements concentration in different stations and seasons may be as a result of the institution of various urban and industrial contamination sources along the river, and its physical and geo-biochemical changes in water flow volume entering the river, especially in winter.

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Background

Heavy metals are the most toxic and hazardous pollutants in the environment (1) whose occurrence in various ecosystems, especially aquatic ecosystems, due to properties for instance high stability, high toxicity, mutagenicity, carcinogen, etc. serves as a threat. Heavy metals come into the environment from different sources for example natural processes, human activities and atmospheric deposition. Though, given rapid population growth, the economic life improvement, and as a consequence of widespread human activities, the function of human resources in the creation and entry of these pollutants into aquatic ecosystems, especially sediments, is far more than other sources (1). After entering the aquatic ecosystems, these elements can be dangerous to living organisms, and they accumulate through various chemical derivatives, such as absorption or sedimentation and adsorption of suspended particles. Therefore, sediments can be measured as the final reservoir of heavy metals (2). But when changes in environmental circumstances such as pH, electrical conductivity, oxidation and reduction reactions, organic matter, salinity, chemical and biological oxygenation of water or sediments, these elements can be released from sediments in the aqueous environment and a permanent source contributes to ecological hazards to aquatic organisms (1). In the meantime, aquatic ecosystems and surface water resources such as rivers and lakes, receive the maximum levels of pollution from human actions which, along with many uses, including drinking, agricultural, industrial, etc., exploits Food and commercial resources from these sources cause many harm to organisms, especially humans (2).

However, the existence of some metals (such as iron, manganese, cobalt, copper and zinc) as nutrient elements is important for the biological activity of living organisms (3), But the findings show that sediments of aquatic ecosystems contain large amounts of environmental pollutants such as mercury, lead, chromium and cadmium, which are potentially toxic and hazardous to aquatic environments and organisms (4). Meanwhile, sediments in estuaries and rivers are heavily influenced by severe pollution from human activities (3). Consequently, surface sediments of these areas are used to accurately assess the contamination of heavy metals (4), since sediments constantly absorb pollutants and thus more pollute than the water columns (5). Besides the continuous absorption of pollutants, the suspended particles in the water column before settling on sediments absorb pollutants in the water column, which results in this accumulation of pollutants in sediments. Also, heavy metals exist in diverse forms (organic, mineral, and stable) of various fractions in sediments, which have special forms of mobility, bioavailability and different potential toxicity for them (5,6). Therefore, studying the qualitative characteristics of surface sediments and measuring the pollution of heavy metals in rivers and sediments is an significant management tool for assessing the health of aquatic ecosystems (4). Because high accumulation of heavy metals in these areas can lead to ecological changes simultaneously by changing the physical and chemical factors of the aquatic environment or sediments (6). Contamination of aquatic ecosystems with heavy metals can be confirmed by studying water, sediment and living organisms plus a wide range of environmental indicators such as ecological risk assessment, geomagnetic storm index, pollution factor, pollution index, etc. In this regard, the ecological risk assessment index of toxic metals in aqueous environment (5) which, based on the concentration and toxicity of each metal, indicates the probable ecological hazard of all metal, as well as the environmental hazard of the total metals (4,7).

Incidentally, one of the most important water drainage estates in the country, which has been affected by various environmental damages, such as the introduction of various organic and inorganic pollutants for instance heavy metals, has been affected by Bashar River in Yasouj city in recent decades. According to the available evidence, excessive influx of pollutants from human activities such as the raise of the Yasuj city, agricultural and recreational actions, and the increasing in human population density along the river's boundary, the lack of a sewage treatment system and urban wastewater discharges with abundant pollutions to the Basher river, threatened the ecosystem and its creatures life which can create problems for the health and life of the local community.

Aims of the study:

Therefore, the consideration of the environmental hazard of heavy metals concentration in these ecosystems is very essential due to the limited studies carried out in this area and the lack of basic information about its status. In this study, the ecological risk of some heavy metals evaluated in the surface sediments of the Bashar River in different seasons of the year.

Materials & Methods

Study area

The study area includes the Bashar River in the Yasuj city, center of Kohgiluyeh and Boyerahmad. The river is about 190 km long and is situated at 51° 20' to 51°, 48' E and 30° 18' to 30° 52' N in Kohgiluyeh and Boyer Ahmad provinces. According to the available evidence, this river is the most important source of water in the city, which originates from the southeast of Boyer Ahmad and the mountains of the Sepidan and Mamasani in Fars province, and passes through to the northwest (lower Boyer Ahmad) the major sources of this river are Ganjgon Rivers, Tizab and Tang Sorkh. This river, which flows most in the east and northeast of the province, passes through from Yasouj (8). According to the land use around the river, sampling points were selected; Figure (1) shows the position of the studied area and the sampling points.

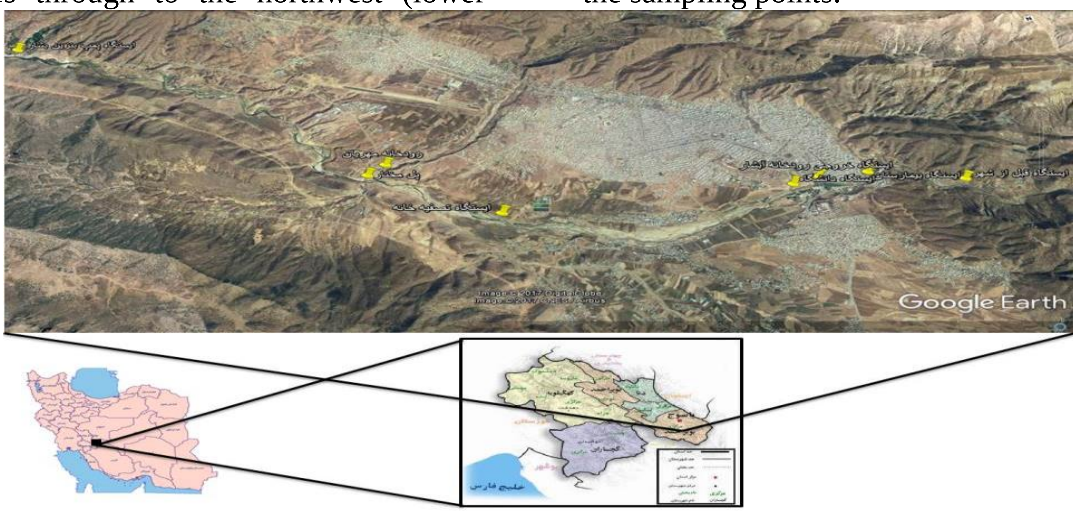

Figure 1) Location of study area and sampling stations

Table 1) Name and geographical characteristics of sampled stations

Station Number	Discription	Longitude	Latitude
1	10 Km Before city	51 37 36.58	30 39 32.12
2	Beshar river	51 36 22.9	30 38 60.51
3	Near Sajad hospital	51 36 26.42	30 38 42.83
4	Yasouj university	51 36 54.49	30 38 45.51
5	Front of waste water treatment	51 32 4.40	30 39 91.39
6	Mokhtar bridge	51 3 42. 36	30 40 18.48
7	Mehraban river	51 31 12.52	30 40 63.53
8	Out of city	51 28 84.41	30 44 2.38

Sample preparation and analysis

In order to measure the concentration of heavy metals in Bashar river sediments in summer and winter 2016 and 2017 respectively, 8 stations were selected and at each station 3 samples were taken at different points simultaneously from surface sediments (depth 0 to 5 cm) sampling site in a 20×20 cm plot (Table 1). The station and specimens were selected to illustrate the state of entry of heavy metal contaminants and their sources to the river as much as possible (Fig. 1). Finally, heavy metals (lead, chromium, copper and zinc) were measured in samples collected from river bed sediments. These specimens were collected in special plastic bags, and after coding in ice flask, they were transferred to the laboratory and stored at 4 °C until the experiments were carried out.

To prepare the collected samples, they were placed in an oven at 70 °C for 24 hours to dry completely. One gram of each dried sample was poured into PTFE digestive tubes (Polytetra fluoride ethylene) and added 10 ml of 65% nitric acid (Merck, Germany) and 70% perchloric acid (Merck, Germany) with a 1: 4 ratio. PTFE tubes were placed on a heater at 40

°C for one hour and then the temperature increased to 140 °C for 3 hours. The contents of each tube were flushed from Whatman No. 1 paper, and were discharged with 25 ml of deionized water. To the quality control, three blank samples were placed along with other samples. Finally, samples were measured by atomic absorption spectroscopy (AAS) device 797 VA Computrace, manufactured by Metrohm, Switzerland (9). Limit of detection (LOD) in AAS for chrome, lead, zinc and copper concentrations were 0.31, 0.45, 0.21 and 0.5 µg/g, correspondingly, and the recovery was achieved in the range of 90 to 97%.

Data analysis

Statistical analysis of all data was also done using SPSS 21 and 2010 Office Excel software. In this study, various criteria, including (contamination factor, geocoding index and degree of contamination, degree of contamination and ecological risk index) were used to assess the amount of contamination of heavy metals.

Geo-accumulation index accumulation coefficient:

The geo-accumulation index introduced by Müller (1969) is a common method for estimating the severity of contamination of heavy metals. Which is obtained by obtaining the concentration of heavy metals in the sediment sample to the background concentration of that metal. This index is based on equation 1 (10).

$$I_{geo} = \mathrm{Log}_2 \frac{C_n}{1.5B_n} \qquad (1)$$

In this equation: Igeo Geochemical accumulation index or severity index of sediment, C_n: Heavy metal concentration in sediment (mg/kg) and B_n: background concentration (element concentration in shale, Table 2), coefficient of 1.5 in order to minimize The effect of a probable vary in the concentrations of the ground, which is generally recognized to the lithological changes of sediments and the effect of ground factors. Mueller pointed out 7 different categories for this index, in which the highest significance of the elements is at least 100 times the reference values (11) (Table 3).

Table 2) The concentration of elements in the average shale (mg/kg)

Hg	Cd	Pb	Zn	Ni	Co	V	Cu	Cr	Fe
0.4	0.38	20	95	50	19	130	45	90	4700

Table 3) Gradation of sediment contamination level based on the geochemical index of molar (1969) (11)

Index of geoaccumulation Value	Index of geoaccumulation Class	Contamination Level
0	0	Uncontaminated
0-1	1	Uncontaminated to moderately
1-2	2	Moderately contaminated
2-3	3	Moderately to strongly contaminated
3-4	4	high contaminated
4-5	5	high to extremely contaminated
5	6	Extremely contaminated

Contamination factor (CF):

The contamination coefficient and degree of contamination can be descriptive the contamination related to the heavy metals and the contamination of the sediment environment. In this study the average shale has been used as a background (Table 4). The Hackanson (1980) contamination coefficient is resulting from equation (12):

$$\mathrm{CF} = \frac{C_i}{C_n} \qquad (2)$$

In this regard, C_i: the concentration of the element in the sample and C_n: the concentration of the same metal in the reference material (mean shale).

Degree of contamination:

Generally, the total contamination coefficients of the pollutants indicate the total degree of sediment contamination, which is referred to as Hakanson contamination (12) (Table 4)

$$\mathrm{Cd} = \sum_{i=1}^{8} CF^i \qquad (3)$$

Table 4) Hackson's classification based on the coefficient of contamination (CF) and degree of contamination (Cd) of sediment

Degree of contamination	Description	Contamination factor	Description
Cd < 6	Low degree of	Cf ≤1	Low degree of
6≤ Cd <12	Moderate degree of	1≤Cf≤ 3	Moderate degree of
12≤ Cd<24	Considerable degree of	3≤Cf≤ 6	Considerable degree of
Cd ≥ 24	Very high degree of	Cf ≥ 6	Very high degree of

Modified degree of contamination (mCd):

Because of the constraints presented by Hakanson (1980) on the degree of contamination, (12) Abrahim (2005) presented corrected correlation 5 based on the degree of infection (13):

$$mCd = \frac{\sum_{I=1}^{8} C_f^i}{n} \qquad (4)$$

That C_F is the contamination factor and n is the number of parameters studied. Relationship 5 allows for a wide variety of heavy metals to be studied and studied without limitation. According to the general relation of this index, caused by the averaging process, the individual effects of accumulation of pollutants in the last result of the general example of contamination in the region will be amortized and disappeared. Abrahim (2005) categorizes the level of sediment pollution the basis of the quantitative index of the modified index of degree of contamination is presented in Table 5 (13).

Pollution Load Index (PLI):

This index is presented to determine the level of pollution and can supply an approximate of the level of contamination of metals. This index can be planned by multiplying the metal pollution indexes in the formulas below.

$$\mathrm{PLI} = \sqrt[4]{\mathrm{CF_{Pb}} \times CF_{Cr} \times \mathrm{CF_{Zn}} \times \mathrm{CF_{Cu}}} \qquad (5)$$

In this formula, CF is a contamination factor which is obtained from formula (2). Here Ci is concentration of heavy metals in the sediment sample and Cn is the frequency of the metal in the local area. The values of the pollution index vary from zero (non-contaminated) to 10 highly contaminated ones, typically less than 1 values indicate non-contamination and values larger than one indicating contamination with heavy metals (4).

Table 5) Gradation of sediment contamination level based on modified contamination index (mCd)

(mCd)	Description
mCd < 1.5	Zero to very low degree of contamination
1.5≤ mCd<2	Low degree of contamination
2≤ mCd <4	Moderate degree of contamination
4≤ mCd<8	High degree of contamination
8≤ mCd <16	16 Very high degree of contamination
16≤ mCd <32	Extremely high degree of contamination
mCd ≥ 32	Ultra high degree of contamination

Ecological Risk Assessment:

The ecological risk assessment Index was first used by Hackson (1980) to fine the risk of pollution by heavy metals. Derived from the toxicity of metals, corrective methods have been used by various researchers such as Wang et al. (2013) (14). According to Hakanson (1980), the toxicity response factor for mercury, cadmium, copper, lead, nickel, chromium and zinc metals is 40, 30, 5, 5, 2 and 1, respectively. In this study, the ecological risk potential was calculated founded on the following equation (3).

$$E_r^i = \frac{C^i}{C_0^i} \times T_r^i \qquad (6)$$

$$RI = \sum_{i=1}^{7} E_r^i \qquad (7)$$

In the equations E_r^i is ecological hazard potential index, C^i, and C_0^i the measured value, and the rate of the natural values (background value), alike to the factor of the toxicity of the metal, Table 6, shows the ecological and environmental risk of heavy metals in the study

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Table 6) Ecological risk assessment levels of trace metals

E_r^i	Ecological risk for heavy	RI	Ecological risk of environment
$E_r^i \leq 40$	Low Risk	$RI \leq 150$	**Low Risk**
$40 \leq E_r^i \leq 80$	Moderate Risk	$150 \leq RI \leq 300$	**Moderate risk**
$80 \leq E_r^i \leq 160$	Considerable Risk	$300 \leq RI \leq 600$	**considerable risk**
$160 \leq E_r^i \leq 320$	High Risk	$RI \geq 600$	**significantly high risk**
$E_r^i \geq 320$	Very High Risk	-	-

Results

The concentration range (minimum and maximum concentration) of the four heavy metals calculated in the basin sediments of the Bashar River in the part of Yasuj city in terms of mg/ kg in both dry and wet seasons (summer and winter), are accessible in Table (7). The results showed that the highest and the lowest mean concentration of metals in both seasons was related to chromium and zinc (10.35±3.04 and 48.16±11.5, respectively) in Summer and winter (10.301±2.6 and 39.88±6.63) mg/kg dry weight, the total concentration of heavy metals in Bashar river sediments were as (Zn>Cu>Pb>Cr) (Table 7)

The relationship of the concentration of metals in both dry and wet season by using independent T-test showed a significant difference in Cu between two seasons at 95% level (Fig. 2). The results of the estimate of the quantity of geo-accumulation index are existing in Table (8). These findings signify that the values of heavy metals for all specimens are less than zero, representative that the region is not polluted or very low contaminated (Table 8).

The results of the revise showed that most of the samples are in the low pollution class or medium pollution. Meanwhile, for copper metal only, in some stations such as stations 4 and 5, in the different seasons, the pollution factor was moderate according to table (4), but for other metals, the coefficient of pollution was low (Table 9). Also, the findings of the study on the degree of contamination of the metals studied in different stations showed that the degree of pollution in the region was low. Also, the results of the study of the corrected pollution index showed that the contamination of the sediments of the area in terms of the concentration of measured metals in both seasons is in two classes of very low degree of contamination (Table 5) (Table 10).

Table 7) the mean concentrations of metals in different stations (mg/kg dry weight)

Heavy Metal Concentrations (mg/kg)								
Station	Winter				Summer			
	Zn	Cu	Cr	Pb	Zn	Cu	Cr	Pb
1	31.01±1.99	16.91±1.99	6.075±0.86	8.46±0.085	32.3±5.71	16.425±3.86	5.06±1.28	9.85±0.208
2	42.83±4.69	33.23±9.96	9.83±2.35	11.01±0.67	48.6±0.98	42.63±0.98	10.78±0.60	13.65±0.75
3	44.96±7.26	27.03±6.17	8.01±0.28	11.73±2.07	34.37±3.35	46.67±2.77	14.53±7. 6	11.59±2.12
4	51.82±8.68	47.78±1.41	12.23±3.39	17.54±1.92	49.045±2.26	46.67±3.65	8.67±3.17	13.93±6.18
5	31.175±0.62	17.71±1.87	11.43±3.15	17.41±6.25	60.56±1.29	63.3±1.25	13.63±1.25	20.18±3.12
6	39.28±6.10	24.44±3.71	11.21±0.62	9.93±0.32	66.15±6.71	42.05±4.4	12.91±2.61	19.98±2.51
7	38.66±1.21	24.66±1.07	11.42±0.48	11.19±0.16	41.037±1.29	23.1±2.09	7.46±1.25	11.24±1.31
8	40.28±0.1	23.7±0.05	12.23±0.059	10.99±0.05	53.21±7.43	32.75±4.78	9.76±1.08	15.49±1.7
Average	39.88±6.63	26.93±9.23	10.301±2.06	12.23±3.19	48.16±11.5	39.2±13.18	10.35±3.04	14.45±3.67

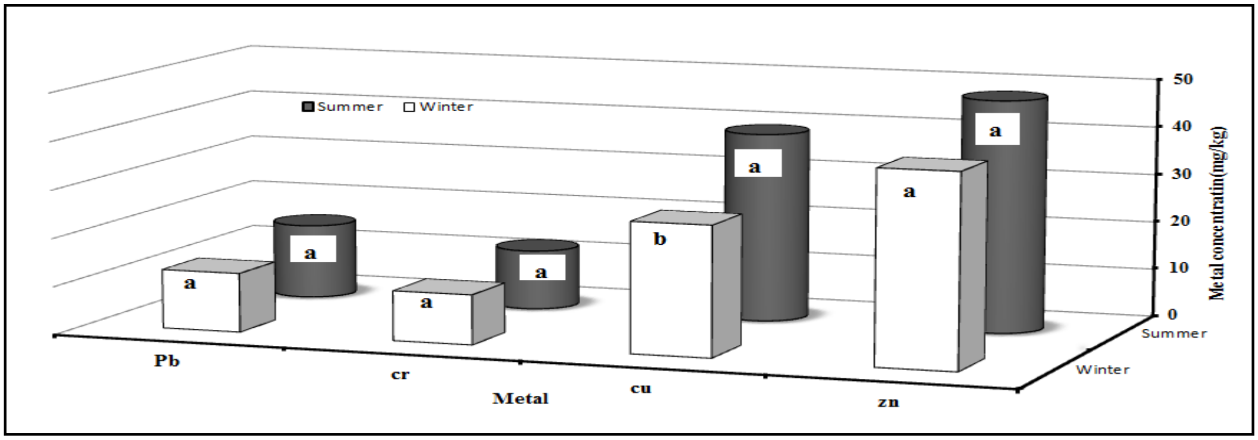

Figure 2) The comparison of the concentration of metals in the two seasons

Table 8) Geochemical accumulation index values in the study area

Average values of Igeo for each metal								
	Winter				**Summer**			
Station	Zn	Cu	Cr	Pb	Zn	Cu	Cr	Pb
1	-2.199	-1.997	-4.473	-1.889	-2.141	-2.039	-4.735	-1.653
2	-1.734	-1.022	-3.780	-1.447	-1.552	-0.663	-3.646	-1.136
3	-1.664	-1.320	-4.075	-1.354	-2.052	-0.532	-3.216	-1.372
4	-1.459	-0.498	-3.464	-0.774	-1.539	-0.532	-3.959	-1.106
5	-2.240	-1.930	-3.561	-0.785	-1.234	-0.093	-3.309	-0.572
6	-1.859	-1.465	-3.589	-1.595	-1.107	-0.683	-3.386	-0.586
7	-1.882	-1.453	-3.563	-1.423	-1.796	-1.547	-4.176	-1.415
8	-1.823	-1.510	-3.464	-1.448	-1.421	-1.043	-3.790	-0.953

The values of the degree of contamination index correlated with the measured elements in the sediments of the Bashar River was showed in Table 10.

Table 9) Results of the values of the contaminant factor and the degree of contamination related to the metals measured in the studied sediment

Contamination factor (Cf)												
Station				**Winter**						**Summer**		
-	Zn	Cu	Cr	Pb	Degree of contamination	Class*	Zn	Cu	Cr	Pb	Degree of contamination	**Class***
1	0.326	0.375	0.067	0.404	1.174	Low	0.34	0.365	0.056	0.476	1.23	**Low**
2	0.45	0.738	0.109	0.55	1.848	Low	0.511	0.947	0.12	0.682	2.261	**Low**
3	0.473	0.6	0.089	0.58	1.749	Low	0.361	1.037	0.16	0.579	2.14	**Low**
4	0.545	1.061	0.135	0.87	2.63	Low	0.516	1.037	0.096	0.696	2.258	**Low**
5	0.317	0.393	0.127	0.87	1.709	Low	0.63	1.406	0.151	1.01	3.2	**Low**
6	0.413	0.543	0.124	0.496	1.577	Low	0.696	0.94	0.143	0.99	2.773	**Low**
7	0.407	0.548	0.126	0.559	1.641	Low	0.431	0.51	0.082	0.562	1.59	**Low**
8	0.424	0.527	0.135	0.549	1.636	Low	0.56	0.72	0.108	0.774	2.171	**Low**
Sum	3.358	4.788	0.916	4.728	13.79	Low	4.055	6.96	0.92	5.78	17.72	**Low**

*Category, as stated in the Degree of contamination.

Table 10) Modified degree of contamination of the modified mCd index

Modified degree of contamination (mCd)							
	Winter				**Summer**		
Zn	Cu	Cr	Pb	Zn	Cu	Cr	Pb
0.419	0.598	0.114	0.61	0.506	0.871	0.115	0.721

In general, the study of the index of metals pollution in the summer and winter seasons showed that the PLI values for all stations are less than 1. This indicates that the region is not contaminated with heavy metals. Also, according to the table, it can be stated that the pollution rate of the river in summer is far more than in winter. Also the highest rate of contamination in station 5 (in front of wastewater treatment plant) in the summer and station 4 (adverse Yasouj University) in winter were evaluated (Table 11).

Table 11) The values of the pollution load index of the Bashar River (Yasuj) surface sediments by the station

	Station	1	2	3	4	5	6	7	8
PLI Index	Summer	0.242	0.446	0.432	0.435	0.608	0.552	0.318	0.430
	Winter	0.24	0.376	0.349	0.51	0.342	0.343	0.354	0.359

The results of ecological and environmental risk assessment of heavy metals are presented in Table 12. In general, these findings indicate that most of the studied stations are in the lower risk category in terms of the ecological risk of heavy metals. Besides, the trend of total risk changes for each metal in the region is evaluated in the summer and winter, respectively (Cr> Zn> Lead> Copper) and (Cr> Zn> Copper> Lead) (Table 12).

Table 12) Results of Ecological and Environmental Risk Indicators (RI) for Metals Measured in Surface Sediments

	Heavy metal									
Station	Winter					Summer				
-	Zn	Cu	Cr	Pb	RI*	Zn	Cu	Cr	Pb	**RI**
1	0.326	1.879	0.135	2.024	**4.364**	0.340	1.825	0.113	2.384	**4.662**
2	0.450	3.69	0.218	2.750	**7.11**	0.511	4.738	0.239	3.412	**8.9**
3	0.473	3.004	0.178	2.933	**6.589**	0.361	5.186	0.323	2.898	**8.768**
4	0.545	5.309	0.271	4.38	**10.51**	0.516	5.186	0.193	3.484	**9.379**
5	0.317	1.968	0.254	4.353	**6.893**	0.637	7.033	0.302	5.047	**13.020**
6	0.413	2.715	0.249	2.483	**5.862**	0.696	4.672	0.286	4.99	**10.65**
7	0.407	2.740	0.254	2.798	**6.198**	0.432	2.567	0.165	2.811	**5.976**
8	0.424	2.633	0.272	2.74	**6.078**	0.560	3.638	0.216	3.872	**8.288**
Sum	3.358	23.94	1.832	24.47	**53.611**	4.055	34.845	1.84	28.90	**69.650**

Discussion

So as to study the amount of contamination in sediments, there are several methods that can be compared with reference values, normal limits of the area, global standards and also whit other parts of the world. Given that, the aim of this study was to determine the concentration of heavy metals in the studied area, results showed that highest and lowest mean concentrations were found for zinc and chromium in summer and winter. Finally, changes in concentration of metals from the highest to the lowest were found on zinc, copper, lead and chromium in both seasons. On the other hand, the results show that the concentration of metals within the city in both seasons is far higher than those outside the city (before and after the city), which indicates the impact of city activities, including runoff, sewage urban concentrations of pollutants, that are consistent with Guan et al. (2016) (17).

Assessment of the concentration of metals at the stations showed that the highest concentration of zinc and chromium in summer was 66.15±6.71 and 13.66±1.525 mg/kg in the bridge of the Mukhtar station, and the lead and copper metals Respectively, was 20.18±2.12 and 63.3±1.25 mg/kg, respectively, at the treatment station. In general, besides the pre-city station (station 1), located around the other sampling stations, residential and urban areas are located and the sewage of these areas is untreated into the river. This factor can increase the concentration of a variety of pollutants in the stations. Also, the high concentrations of metals in the two Mukhtar bridge and refinery stations could be due to their location in the downstream of the Belko industrial estates, bituminous factories, with the entrance of the wastewater treatment stand to the river, along with the existence of agricultural actions in the surrounding areas, it is the result of the burden of pollution from current activities such as industrial and urban wastewater in the upstream areas. Zinc is one of the most plentiful elements in the earth's crust (on the 25th most abundant element), which is between 0.0005% and 0.20% of the crust of the earth. But can be deposited in the form of $ZnCO_3$ in aqueous environments, whose high levels can be indicative of human activities and a high rate of sedimentation (16). The most significant human resource is the non-ferrous metal industry and agricultural activities. In 2004, Kilemade et al measured the concentration of heavy metals Cd, Pb, Cu, and Zn in Cork port sediments and found that these sediments had a high concentration of these heavy metals. The cause for the occurrence of these contaminations was the factors such as urban and industrial sewage in the area. Chromium metal is bounded by its low tendency to dissolve in water and often with iron oxides, and is mostly deposited by granular particles in the form of a floating phase and deposited in sediments. Chrome and its compounds have diverse industrial applications, mainly in the leather industry and according to available evidence, the concentrations enhance with the arrival of the wastewater from the industrial and urban centers (17). On the other hand, lead and copper are generally used in urban and industrial environments, which through runoff and wastewater urban and industrial enter the aquatic environment and thus sediments. Therefore, the main source of these can be the entry of untreated urban and domestic wastewater in addition to the wastewater treatment plant in the city (18).

In winter, the highest concentrations of zinc, chromium, copper, 51.82±8.68, 12.23±38.38, 47.78±1.41 mg/kg in Bashar bridge and for lead metal, 17.54±1 mg/kg was obtained at the refinery station of the city. Also, the consequences showed that the lowest concentration of these metals in both seasons was obtained at pre-city sampling site. One of the most important reasons for this is the introduction of a large amount of urban runoff and wastewater, especially in winter, from urban wastewater effluents (urban and industrial effluent discharges) into the river around the station and sampling sites. Because of the fact that the station is strongly affected by the arrivals caused by the location of the main outburst runoffs in Yasuj, and as a result of the entrance of a large part of the city's wastewater and runoff in winter.

So as to find out the amount of sediment contamination, it is compulsory to evaluate the concentration of elements in the region with a well-known standard in the same area. In the present study, due to the lack of a definite standard for pollution in the studied area, international standards were used in other countries. However, in comparisons, one should be careful since there are various differences in the properties or physical parameters of the environment between their concentration at the site and at different times (19). Indeed, their average concentration was less or more depending on the type of metal and the place of measurement. Overall, the concentration of metals in sediments in the region was within the range of measured values in similar studies in other parts of the world (Table 13). One of these studies is the study by Ma et al. (2016), which investigated the levels of heavy metals in zinc, lead, and copper in the Yellow River sediments in China (2). Also, Ghashlaghi and Rostami (2016), which limited the concentrations of chromium, copper, lead and zinc in the Sangrood River of Mazandaran province, were 86.6, 63.6, 35 and 25 mg/kg, respectively (20),this is more than chromium, copper and lead than the present study. On the other hand, the study of Ekeanyanwu et al. (2011), which calculated the metals in the sediments of the Okumesh River, Nigeria, is much higher (21). Also, among the measured elements, the concentration of lead metal in summer was higher than the average in the Earth's crust (Table 13) which could be caused by different human activities or the property of environmental and geological factors such as dynamic changes in water in different locations. Bilos et al. (1998) reported that changes in the concentration of heavy metals in sediment or suspended particles were due to dynamic water changes (22). Conversely, the effective factors on the settlement of elements in river, especially in the Bashar River with high slope and rocky bedding prevent the sedimentation of suspended particles on the river bed. Another issue that seems to play a function in the process of changes in the concentration of metals in the river sediments, extensive construction activities such as the construction of multiple bridges on the river, the harvesting of sand from the floor, causing severe disturbance in the river environment. In this regard, the expansion of urban activities, construction, industrial, fishing, and tourism are among the factors affecting the river's environment. This requires a periodic monitoring of pollutants and appropriate scientific research.

Alternatively, since aquatic ecosystems are abundant in contact with or live in floor of river, sediments can act as a main route to pollute aquatic organisms.

Table 13) Comparison of mean total concentration of metals (mg/kg) studied with some rivers of other areas

Location		Cr	Zn	Cu	Pb	Reference
Yellow River, China		-	22.42	17.342	17.18	(19)
Yangtze Rive, China		33.64	66.91	17.46	30.47	(23)
Karnaphuli,Bangladesh		20.3	-	-	43.69	(24)
Okumeshi River, Nigeria		0.81	-	-	0.45	(24)
Siahrood River-Mazandaran, Iran		86.6	25	63.6	35	(20)
Mean world sediment		72	95	33	19	(17)
Mean crust		100	75	40	14	(17)
Present study	**Summer**	10.35±3.04	48.16±11.5	39.2±13.18	14.45±3.67	-
	Winter	10.301±2.06	39.88±6.63	26.93±9.23	12.23±3.19	

That's why, sediment standards have been developed and to forecast the possibility of adverse effects in aquatic animals that are in contact with them. The Sediment Quality Guidelines (SQGs) and the National Oceanic and Atmospheric Administration (NOAA) have been selected to compare the concentration of metals in sediments. SQGs and NOAA standards are used to evaluate the level of contamination and the effect of pollutants on existing organisms (25). In the NOAA standard, there is a dual risk of contamination of metals in sediments that are presented as ERL (Effect Rang Low) to the extent that less than 10% of the biological communities are at risk and ERM (Effect Range Medium), which is present in less than 50% of the biological communities at risk. . Sediment Quality Standard (SQGs) with TEC (Threshold effect concentration) and PEC (Probable Effect Concentration) indicate the threshold of effect of concentration and concentration of effect. In the Canadian Sediment Quality Standard, two levels of LEL (Lowest Effect Level) indicate a level of contamination that is tolerable for most bulky animals and has no specific effect on biological communities, and SEL (Sever Effect Level) indicates severe contamination the health of benthic organisms is compromised and if the infection is higher than this. Precise sediment toxicity tests should be performed (26). In the present study, the average annual concentrations of metals (lead, chromium, copper and zinc) in the sediments of the region compared to the standards stated except for copper, which are higher than the standard LEL, are much lower than the other standard concentrations of metals Which indicated a significant non-contamination of the area with these metals (Table 14). However, it should be noted that due to the location of the city and the view of the development of the region and various projects in progress in this area and the burden of pollution caused by current agricultural and industrial activities in the area and around the river, to adopt appropriate measures that can It is compulsory to help reduce pollutants. On the other hand, increasing the copper concentration in evaluation with the LEL standard will have a potential negative effect on the bentic species.

Founded on the estimation of the geochemical accumulation index of molars, the value of sediments for all of the studied metals is due to the negative values of the zero (non-polluted) values (Table 3). These results are in agreement with the findings of Salah et al. (2012) (29) and Mahdinia and colleagues (2016) on the survey of geoscience data in coastal regions of Bushehr province (30). In addition, based on this index, the highest accumulation of lead and copper was found in sediment samples. The results of the study of the contamination factor and the degree of contamination of metals at different stations along the river showed that all samples were in the low pollution class. Also, the study of level of contamination in different stations showed that in the area studied, the station facing the treatment plant in summer and the station of Bashar bridge in winter season had the highest degree of contamination of 3.053 and 2.45 respectively.

Table 14) Comparison of mean concentrations of lead, chromium, copper and zinc metals (mg/kg dry weight) with NOAA and SQGs

Sediment quality		Cr	Zn	Cu	Pb	Reference
Metal background		-	100	15.00	5	(27)
ERL		81	150	34	47	(25)
ERM		370	410	270	218	(25)
TEC		43.4	121	31.6	38.8	(25)
PEC		111	459	149	128	(26)
LEL		26	120	16	31	(26,28)
SEL		110	820	110	250	(28)
Present study	**Summer**	10.35±3.04	48.16±11.5	39.2±13.18	14.45±3.67	-
	Winter	10.301±2.06	39.88±6.63	26.93±9.23	12.23±3.19	

ERL, Effect Rang Low; ERM, Effect Range Medium; TE , Threshold effect concentration; PEC, Probable Effect Concentration; LEL, Lowest Effect Level; SEL, Sever Effect Level

To be according to the results of categorization of the modified pollution index, river sediments are in very low class of pollution, and between the two copper and lead metal elements have the highest degree of contamination in both seasons (Table 10). This is an expression of the effect anthropogenic resources are due to the fact that these elements result from the release of industrial waste and urban runoff (1,31).
Moreover, the amount of contamination load for all sediment samples was less than 1 in both seasons. This indicates that the region is not polluted by heavy metals and their low toxicity. Also, according to the present estimates, the amount of pollution in the river in summer is far more than in winter, and between stations in the summer of station 5 (facing wastewater treatment plant) and in winter season, the station of 4 areas of Yasuj University has the highest order contamination is 0.606 and 0.486 (Table 11). This is caused by the impact of a

huge amount of urban runoff and sewage treatment around the two stations.
The results of the ecological risk assessment and the environmental risk of heavy metals, river sediments at all stations were classified for all the metals surveyed at low ecological risk level. Also, derived from the calculations, the highest and lowest ecological risk is related to chromium and copper in both seasons. Also, the findings of the study on the environmental hazard index of these metals in river sediments is low, less than 150, based on the obtained (Table 12). In general, comparing the concentration of metals and assessing their related environmental indicators such as geochemical accumulation indexes, pollution factor, degree of contamination, degree of contamination, pollution burden and ecological risk assessment of heavy metals of Bashar river in summer and winter Shows that these factors are much higher than in winter at most stations in summer and the results are in agreement with the findings of Khan et al. (2017) to study the pollution status of the Ganges River in the country (7). One of the most important reasons for this can be to raise the amount of water entering the river in the winter, which carries the sediment deposited in the substrate. Because in winter the quantity of river water has increased greatly and, because of its slope, does not allow precipitation of suspended particles and specks contained in the river containing heavy elements.

Conclusion

The present study was conducted to measure the concentration of heavy metals of lead, chromium, copper and zinc and assess their ecological risk in different seasons (summer and winter) in Bashar River surface sediments. Finally, the highest average concentration of metals was observed in summer and stations in the city limits. In addition, the evaluation of metal concentrations and their ecological risk suggests that in summer the ecological risk is far higher than in winter. Principally, seasonal variations in their concentration and their ecological risk are affected by different factors such as physical processes, bio-geochemistry, such as the roughness of the river bed, changes in the volume of water entering the river, especially in winter. Also, the environmental indicators such as geo-accumulation index, pollution index and pollution factor, indicated low pollution status in both seasons in the region were studied. Generally based on the results, calculating the ecological parameters of metals and comparing the concentration of the elements measured with the SQGs sediment quality criterion can be concluded that river sediments in terms of measured metals have contamination and low ecological risk. The concentration of pollutants in the city boundary indicates the impact of various human activities, such as untreated urban and industrial sewage, urban runoff, and the concentration of industrial centers on the periphery of the river.

Footnotes

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