

Original Article

Heavy Metals Contamination in the Surface Sediments of Talar River, North of IranYaser Vakilzadeh¹ **Kazem Shabani Gorji**^{2*} Jalil Ghalamghash³ Mohammad Reza Noura²

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Abstract

Background and Purpose: The contamination by potentially toxic element (PTE) is a common environmental issue in worldwide rivers. The present study examined PTEs concentration in sediments of Talar River which is one of the main rivers in the Southern Caspian Basin.

Materials and Methods: The sediment samples (n= 44) were collected from top 0–5 cm of surface sediment in the main channel and floodplain of Talar River using a Van-Veen grab sampler. The concentrations of trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Principal component analysis (PCA) was used to evaluate possible relationships between the observed variables and source identification. Enrichment factor (EF) was also applied to determine the integrated effects of different elements and evaluate the sediment quality.

Results: The average concentration of all elements except Mo were found to be higher than the concentration of elements in upper continental crust (UCC). The result of enrichment factor (EF) indicated that most elements were unpolluted and showed minimal to moderate contamination level. Multivariate statistical analysis indicated Pb, Cu, V, Zn, Cd, Co and Ni typically have anthropogenic sources. Whereas Mn, Sb, Sc, Mo and As showed geogenic source.

Conclusion: It was concluded that sediments in Talar River was then experiencing slightly polluted status originated from local anthropogenic sources in the basin which might potentially pose detrimental effects on both ecological and health conditions in the basin.

Keywords: Heavy metals, Sediment, River, Talar

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1. Introduction

Due to the persistence of trace elements in aquatic environments, they can enter food chains and consequently accumulate in animals' tissues (1-3). The contamination by potentially toxic element (PTE) is a common environmental issue worldwide (4, 5). Sediment is an important proxy of the environmental condition in riverine environments and is regarded as the final precipitating medium for PTEs (6-8). River sediments are considered as one of the major sources/sinks of trace metals and a good indicator of background pollution of the river (9-11). The chemical composition of river sediments is influenced by natural and anthropogenic pollutants (12). The main sources of trace metals in river environments include local lithologies, surface runoff, atmospheric precipitation and anthropogenic activities (13). However, economic development, urban expansion and consequently the uncontrolled inputs of pollutants from anthropogenic sources and over the last decades degraded the quality of aquatic environments (14). Among all pollutants in aquatic environments, trace metals are considered as the important contaminants due to their biological accumulation, ecological toxicity, and persistence (15-17). It is estimated that nearly 85% of the trace metals loads entering aquatic systems are deposited in sediments in various forms (14).

The flocculation and precipitation are the main deposition mechanisms of trace metals into river sediments (11, 13). The changes in chemical conditions of aquatic environments can lead to the release of trace metals from sediments into overlying waters causing secondary pollution (9, 18).

PH, temperature and oxygen levels in river water can influence chemical behaviors of trace metals in river sediments (19).

Trace metals in riverine systems can be accumulated and biomagnified to a high degree in sediment and the aquatic food chain, leading to detrimental effects on aquatic organisms (20).

Investigating the distribution and sources of potentially toxic elements (PTEs) in rivers is very important to understand the contamination and associated ecological risks of trace metals, and it improves watershed ecosystem safety. It also manages environmental and ecological risk factors in riverine environments (21).

Talar River, as one of the important rivers entering the southern basin of the Caspian Sea, passes through several cities and is exposed to input of various anthropogenic contaminants.

There is a lack of data on the concentration of trace metals in the sediments of the Talar River. Mohammadi et al. (2019) undertook research on the As, Cu, Cr and Ni concentration in Talar river sediments. They showed a positive correlation between heavy metals and land uses in Talar River which varied with the level of agricultural and urbanization development at sub-watershed. However, this study did not cover most of the important toxic metals and their sources. The main objectives of this study were to characterize the concentration of several trace elements in sediments of Talar River, assess the degree of contamination using environmental and geochemical indices, and determine the main sources of trace metals in river sediments and identify the influence of possible pollution sources.

2. Materials and Methods

Talar River with a length of 150 km is located in Mazandaran Province in north of Iran. Its basin covers a total area of 2800 km² and the main stream flows from northern part of Alborz mountain ranges to southern part of Caspian Sea (22) (Fig. 1). On its way toward Caspian Sea, the river flows through several urbanized areas including Pol-e-Sefid, Zirab, Shirgah, Ghaemshahr and Kiakola and enters the Caspian Sea in the Mir-rud area.

Extensive outcrops from the Paleozoic to the present can be seen in the catchment area of the river. Geologically, the studied area is dominated by Jurassic and Lower Cretaceous carbonate rocks, shale, sandstone, siltstone with thin coal seams (23). Moreover, Miocene marl and calcareous sandstone and Pliocene conglomerate form the major lithological units in Cenozoic (24).

The sampling network has been extended in the Talar river watershed along the main river channel from upstream of the basin to the sea according to the United States EPA's (USEPA) criteria for sampling (25). The number and location of samples were determined on the basis of our primary field observation, evaluation of potential point/non-point pollution sources, and the situation of population centers, location of industrial zones, agricultural practices, and

river geomorphology. The sediment samples (n= 44) were selected from main channel and floodplain of Talar River (Fig.1). At each station, three composite samples with approximate mass of 200 g were collected. The samples were collected from top 0–5 cm of surface sediment using a Van-Veen grab sampler. The sampling sites were distributed uniformly in the upstream (n= 20) and the plain (n= 24) with the average distance of about 3.5 km across the river.

All sediment samples were air-dried at room temperature, pulverized in a mortar, filtered through a polyethylene sieve having pores of 63 µm aperture (20). The <63-µm bulk sediments have been digested using nitric acid (HNO₃), perchloric acid (HClO₄), and hydrofluoric acid (HF). For this purpose, approximately 0.5 g of subsample was digested in Teflon tubes using a mixture of nitric acid, hydrofluoric acid and perchloric acid. The mixture was then heated to temperature of approximately 110 °C until all residues were completely decomposed. Next, to remove residual HF, 20 mL nitrate solution (2%) was added to the dissolution (11, 26, 27). Total concentrations of trace elements were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) in chemical lab of Geological Survey of Iran.

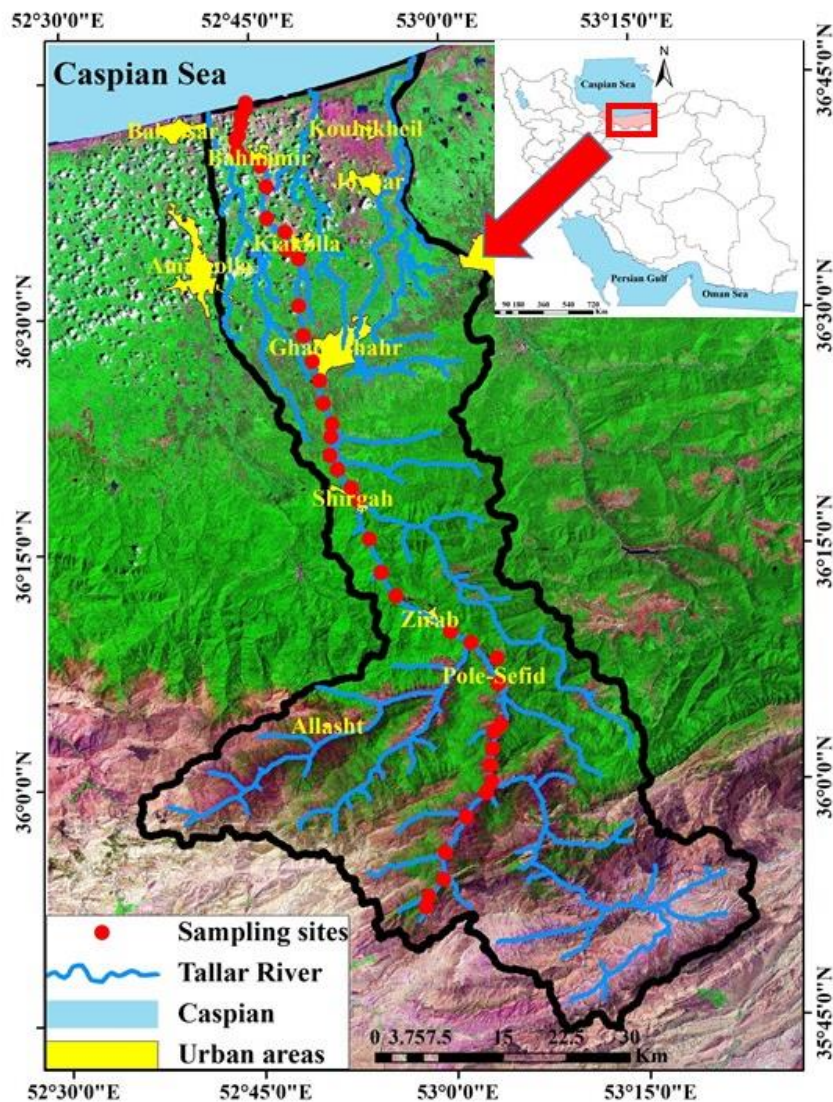


Fig 1. The sampling sites in Talar River basin. The sample locations are shown with red circles

One common method for evaluating anthropogenic effects on sediments and soils was to calculate the enrichment coefficient (EF). EF for different elements can be calculated based on equation 1 (28):

$$(1) \quad EF = \frac{[C_n]/[C_x]_{\text{Sediment}}}{[B_n]/[B_x]_{\text{Background}}}$$

where C_n and C_x are the concentration of element of interest and reference element in the sediment sample, B_n and B_x are the

concentration of the element of interest and reference element in the geochemical background. In this study, Sc is selected as reference element and world average shale (29) is considered as geochemical background environment (29-31). Enrichment factor has empirically divided the enrichment coefficient into 5 categories (32) (Table 1).

Table 1. Classification of enrichment factor (EF) (32)

Enrichment factor	Categories of contamination
EF<2	Depletion to minimal enrichment (no or minimal pollution)
2–5	Moderate enrichment (moderate pollution)
5–20	Significant enrichment (significant pollution)
20–40	Very high enrichment (very strong pollution)
EF> 40	Extreme enrichment (extreme pollution)

Contamination factor (CF), is commonly used to show the contamination level of potential toxic elements in sediments suggested using the following equation (33):

$$(2) \quad Cf = \frac{C_{sample}}{C_{background}}$$

Where C_{sample} is the concentration of metal in a specific sediment sample and $C_{background}$ is the concentration of same element at a background site, reference value or a national criterion. In this study, the concentration of elements in world average shale was considered as reference values (29). There are four qualitative classification to describe the contamination factor (34): $Cf < 1$, low

contamination; $1 \leq Cf < 3$, moderate contamination; $3 \leq Cf < 6$, considerable contamination and $Cf \geq 6$, very high contamination.

Muller (35) introduced a quantitative measure of the level of contamination in aquatic sediments. This index can be calculated using the following formula:

$$(3) \quad I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n}$$

Where C_n is the concentration of the element in the sample and B_n is the concentration of the element in the geochemical background concentration. This index was classified in 6 classes as indicated in Table 2.

Table 2. Classification of the geo-accumulation index (I_{geo}) (35)

I_{geo} value	Class	Designation of sediment quality
$I_{geo} \leq 0$	0	Unpolluted
$0 < I_{geo} \leq 1$	1	Unpolluted to moderately polluted
$1 < I_{geo} \leq 2$	2	Moderately polluted
$2 < I_{geo} \leq 3$	3	Moderately to strongly polluted
$3 < I_{geo} \leq 4$	4	Strongly polluted
$4 < I_{geo} \leq 5$	5	Strongly to extremely polluted
$I_{geo} > 5$	6	Extremely polluted

Shapiro-Wilk test ($p > 0.05$) was conducted in order to evaluate the normality of the data distribution. Then, Spearman correlation and principal component analysis (PCA) were used to evaluate the possible relationships between the

observed variables and their source identification after normalization of all non-normal elemental data.

3. Result

Table 3 lists the statistical summary of the heavy metal concentrations in the surficial sediment samples. The concentrations of trace elements in Talar River sediments exhibited a wide range of variations throughout the studied sites. The average concentration of all elements except Mo were higher than the concentration of elements in upper continental crust (UCC)

(36). Most elements showed average concentration lower than world average shale (Table 3). Only Cr showed values higher than global shale (29). The average concentration of elements followed the order of: Mn (666.4) > Cr (105.2) > V (82.7) > Zn (67.9), Ni (43.6) > Cu (28.5) > Pb (18.3) > Co (13.7) > As (9.8) > Sc (9.3) > Mo (1.1) > Sb (0.6) > Cd (0.1).

Table 3. The statistical summary of trace elements concentration (mg/kg) in sediments of Talar river

Elements	Minimum	Maximum	Median	Mean	Std. Deviation	Average shale ¹	UCC ²
Cd	0.10	0.26	0.15	0.16	0.04	0.3	0.1
Co	4.87	20.19	14.41	13.75	3.39	19	11.6
Mn	215.33	953.35	673.91	666.49	154.05	850	527
Mo	0.63	2.56	1.01	1.11	0.36	2.6	1.4
Ni	21.77	72.71	41.04	43.62	12.47	68	18.6
Pb	9.94	25.49	18.98	18.32	3.45	20	17
Sc	3.07	16.47	9.38	9.35	2.40	13	7
As	4.76	21.05	10.02	9.84	2.67	13	2
Cr	65.40	179.21	104.68	105.27	19.33	90	35
Cu	12.58	45.03	27.42	28.52	7.61	45	14.3
V	28.85	130.09	81.11	82.70	19.95	130	53
Zn	14.00	108.60	67.77	67.90	20.55	95	52
Sb	0.29	2.82	0.56	0.60	0.36	1.5	0.31

1. Data from (29)

2. Upper continental crust (36)

Figure 2 indicated the box plot diagram of the EF in the sediments in the study area. Most of the elements showed minimal to moderate contamination. The highest EF were attributed to Cr, Zn, Pb, As and Mn, respectively. Among the investigated

metals, Sn, Sb, Mo and Cd showed the minimum EF values. Values for those metals were relatively close to the natural background, suggesting they were not significantly affected by anthropogenic activities (37).

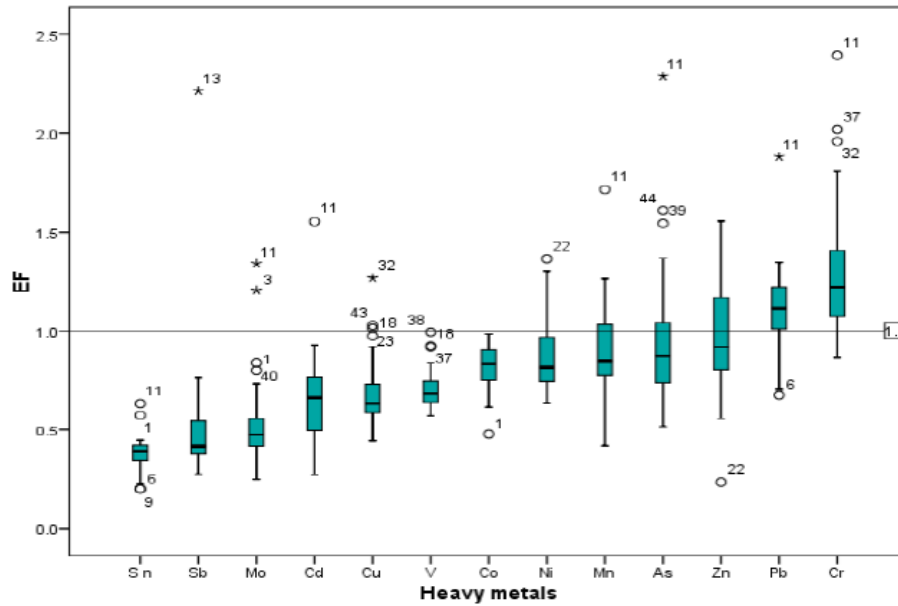


Fig 2. Boxplot diagram of EF in the sediment samples of Talar River

The result of I_{geo} also indicated that all samples were classified as unpolluted (Fig. 3). Cr, Pb, Zn, as and Mn showed the highest I_{geo} in the study area. Moreover, all

samples showed CF values < 1 indicating low contamination in the samples (Fig. 4). In some samples, Cr and Pb displayed moderate contamination.

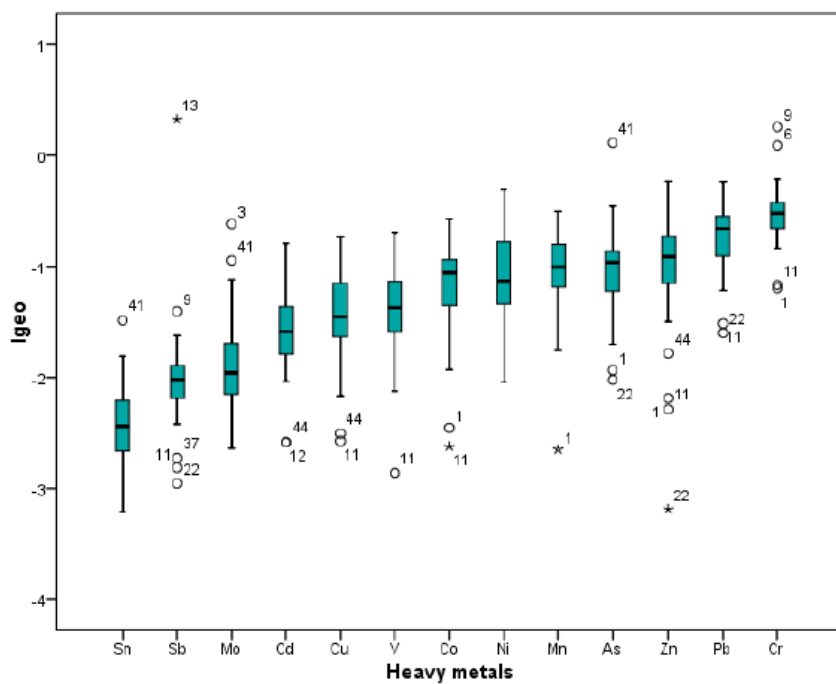


Fig 3. Boxplot diagram of I_{geo} in the sediment samples of Talar River

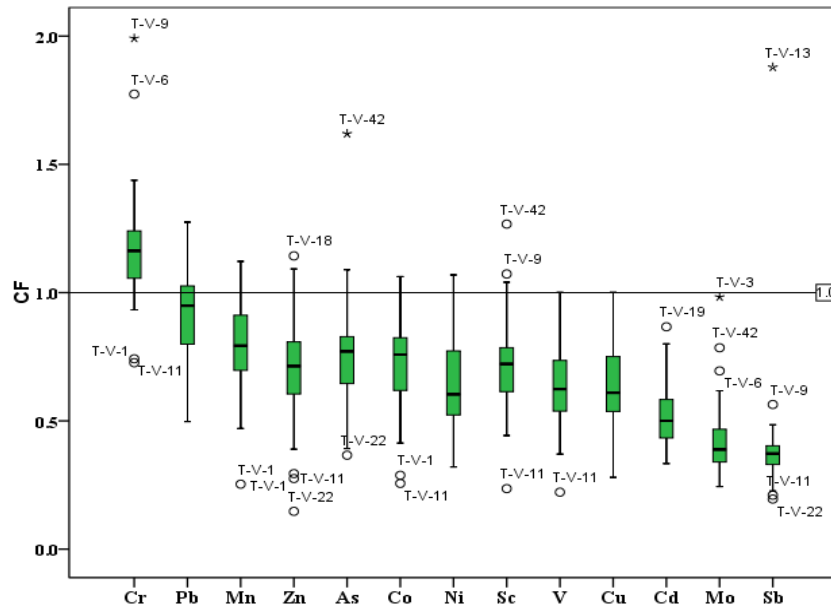


Fig. 4. Boxplot diagram of contamination factor (CF) in the sediment samples of Talar River

Table 4 represents the results of the Spearman correlation matrix among the studied elements of Talar River sediments. Most elements showed medium to strong correlation with each other. This may imply that these elements had the same sources or similar geochemical behavior and were incorporated in sediments in a similar way.

The results displayed the strong positive correlation between Co and Cr (0.67), Ni (0.73), Pb (0.76), Sc (0.84) and V (0.81). Also, the elemental pairs Ni/Sc (0.72), Ni/V (0.71), Cu/V (0.72), Cu/Zn (0.62), Zn/V (0.66) showed strong correlations; whereas, As, Mo, Cd and Sb showed the lowest associations with other examined elements.

Table 4. Spearman correlation coefficients for the metal concentrations

	Cd	Sb	Mo	As	Cr	Co	Ni	Pb	Sc	Cu	V	Zn	Mn
Cd	1.00												
Sb	-0.05	1.00											
Mo	0.17	0.22	1.00										
As	0.04	.323*	0.12	1.00									
Cr	0.18	0.26	0.28	0.24	1.00								
Co	.403**	.422**	.334*	.357*	.676**	1.00							
Ni	.593**	0.05	.324*	0.15	.499**	.733**	1.00						
Pb	.347*	.444**	.302*	.350*	.399**	.765**	.575**	1.00					
Sc	0.24	.349*	.423**	.387**	.611**	.842**	.724**	.793**	1.00				
Cu	0.21	0.19	0.11	.343*	.534**	.595**	.530**	.628**	.651**	1.00			
V	.332*	.298*	0.28	.427**	.619**	.819**	.712**	.712**	.873**	.725**	1.00		
Zn	.462**	0.17	0.12	0.26	.394**	.576**	.536**	.653**	.482**	.623**	.664**	1.00	
Mn	-0.01	.370*	0.18	.299*	.528**	.594**	.375*	.540**	.602**	.393**	.451**	.364*	1.00

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

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

Factor analysis of sampling data generated three major factors which cumulatively explain 70.70 % of the total data variance as shown in Table 5. The first component (PC1) explained 59.63% of the total variance as it showed strong association with most variables including Pb, Cu, V, Zn, Cd, Co and Ni. This group included the main heavy metals that were typically considered to be anthropogenic pollutants, originating mainly from industrial and untreated sewage (38, 39). It has been stated that trace elements from anthropogenic sources can originate from

different segments, such as urban sewer, agricultural and industrial activities (19, 40). PC2 accounted for 13.67% of the total variance, and displayed the strongest weight for Mn, Sb, Sc and As. Meanwhile, PC3 displayed about 9.37% of the total variance and showed the loading of Mo. Thus, it seemed that both PC2 and PC3 dominantly controlled natural or geogenic sources. However, the relatively medium to large loadings of Co, Cr, Cu and Pb in PC2 can be described by mixed natural-anthropogenic sources for these elements.

Table 5. Principal components, loadings and percentage variance explained after Varimax rotation

Elements	Component		
	PC1	PC2	PC3
Mn	0.33	0.66	0.15
Pb	0.68	0.48	0.17
Cu	0.71	0.41	-0.18
V	0.79	0.43	0.10
Zn	0.80	0.19	-0.11
Cd	0.71	-0.39	0.21
Co	0.74	0.47	0.31
Sb	-0.01	0.73	0.29
Cr	0.51	0.44	0.26
As	0.19	0.63	-0.13
Ni	0.86	0.06	0.27
Mo	0.13	0.13	0.88
Sc	0.10	0.91	0.23
% of variance	37.16	21.33	10.50
Cumulative %	37.16	58.50	69.01

Extraction Method: Principal Component Analysis.
 Rotation Method: Varimax with Kaiser Normalization.
 a. Rotation converged in 4 iterations.

4. Discussion

In this study the concentration, distribution and sources of potentially toxic elements were determined in the surface sediments of Talar River in north of Iran. Conducting

the analysis of PTEs in the sediment samples revealed that the average concentration values of all elements except Cr were lower than global shale (29). The pattern of metals distribution was not

uniform through river path, but higher pollution loads were observed near urban and agricultural areas and close to industrial zones.

Table 3 indicated the comparison of toxic metal concentration in sediments of Talar Rive with some selected rivers in Iran and other countries. The concentration of all elements in Talar River is higher than those in Tajan River which is located in the neighbor watershed as well as Karoon River which is the longest river in Iran. This is the case compared with Itacaiúnas River (Brazil) and Old Brahmaputra River (India). However, Talar River showed higher concentration of As, Cr, Cu, Pb, Ni and Zn with respect to Kor River in south of Iran, but lower concentration of Cd and Mo. The concentration of elements in Talar River sediments was lower than those Luan in China and Tisza River in

Serbia. The reason can be attributed to difference in geological characteristics, industrial activities, level of urbanization, and agricultural practices in watersheds of these rivers.

The positive correlation between Mn and the elements including Cr, Pb, V, Co, Cu, Ni, Sc and Zn indicated the presence of Mn-hydroxyoxides and its important role in adsorbing of these elements in sediments of the Talar River (41, 42). The positive correlation of some elements can also be attributed to their similar geochemical behaviors. For example, Cu, Zn, As and Pb were geochemically chalcophile elements which mostly showed association with sulfur (S) in geological environments (43). Ni, Co, Mo and Mn are siderophile (44) elements and V, Cr, Sc are lithophile elements (45).

Table 3. Comparison of mean potentially toxic metal concentrations (mg/kg) in the sediments of Talar River with selected rivers in different parts of the world

River	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn	Reference
Talar, Iran	9.84	0.16	105.2	28.52	1.11	43.62	18.32	67.9	This study
Tajan, Iran	4.11	0.33	54.29	18.00	-	33.42	17.88	50.4	(46)
Kor, Iran	6.15	0.238	83.4	20.29	1.51	104.41	7.47	46.56	(47)
Karoon, Iran	3.01	-	37.69	20.92	-	42.08	9.69	44.62	(48)
Gomti, India	-	2.42	8.15	5	-	15.17	40.33	41.67	(49)
Luan, China	5.14	0.14	71.47	45.68	-	-	22.1	75.51	(26)
Old Brahmaputra, India		0.48	6.6	6.2			7.60	52.70	(50)
Itacaiúnas, Brazil	1.60	0.02	46.16	30.05	0.44	11.55	10.26	25.04	(51)

The results of statistical analysis indicated that toxic metals in the Talar River sediments had two main geogenic and anthropogenic sources. The association of Mn with elements in PC2 may imply that absorption by Mn-hydroxyoxides controls the behavior of As and Sb in Talar River sediments. Among the studied elements,

Mo and Sb showed the lowest enrichment with respect to background values. However, the relatively medium to large loadings of Co, Cr, Cu and Pb in PC2 can be described by mixed natural-anthropogenic sources for these elements. Overall, contamination indices revealed an unpolluted to slightly polluted status in the

studied stations. Generally, all indices showed that Talar River sediments did not show a major risk of pollution. It is necessary to develop longtime monitoring and contamination control management of toxic metals in Talar River and its corresponding sites.

Conflicts of Interest

None declared.

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