Assessment of Heavy and Trace Metal Pollution in the Karun River, Iran

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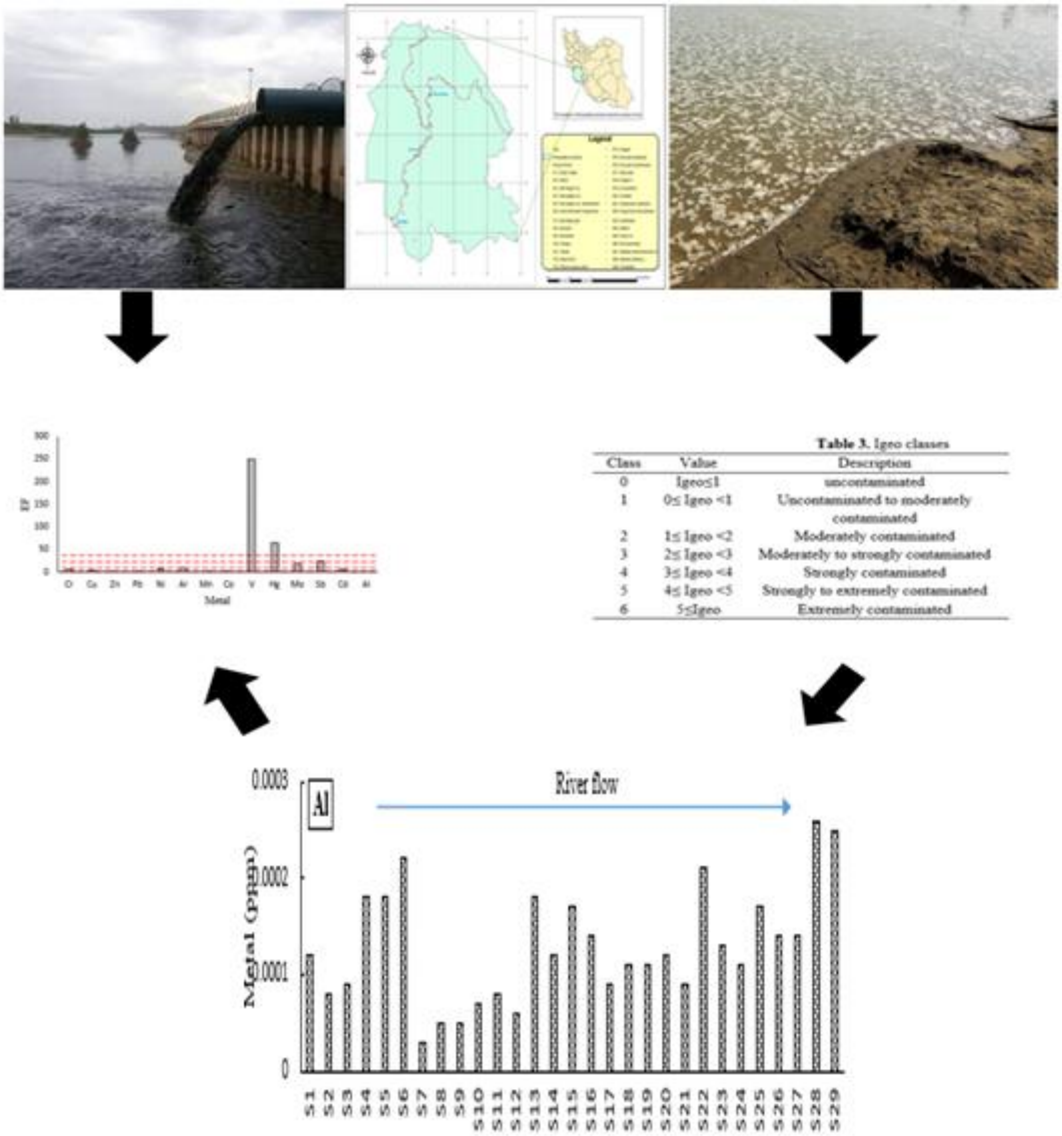


Table 3. Igeo classes

Class	Value	Description
0	Igeo≤1	uncontaminated
1	0≤ Igeo <1	Uncontaminated to moderately contaminated
2	1≤ Igeo <2	Moderately contaminated
3	2≤ Igeo <3	Moderately to strongly contaminated
4	3≤ Igeo <4	Strongly contaminated
5	4≤ Igeo <5	Strongly to extremely contaminated
6	5≤Igeo	Extremely contaminated

ABSTRACT

The Karun River, the longest and highest water flow river in Iran, has experienced heavy and trace metal pollution in recent years. While previous studies have evaluated the water quality of the river, not all sections from north to south have been examined for all metals. To address this gap, a study was conducted between March and June 2022 to evaluate the concentration of 15 heavy and rare metals in the river. Geoaccumulation index (Igeo), Potential Ecological Risk (RI), Enrichment Factor (EF), and the Contamination Factor (CF) were used to assess water quality. The results showed that despite some metals exceeding the Iranian standard, all metals had negative Igeo values, indicating an uncontaminated condition. The contamination levels of all metals were low, with a CF value less than one, and RI values were generally below 0.01, except for vanadium and mercury. The Karun River was categorized as moderate and significant enrichment for all metals except for aluminum, lead, and cobalt, with chromium and copper having particularly high EF values at some stations. Zinc, manganese, nickel, arsenic, molybdenum, and cadmium were also in the moderate enrichment category, while antimony, vanadium, and mercury were in the very high and extremely high enrichment categories, respectively. The study concludes that the concentrations of metals in the Karun River are within permissible limits, indicating low risk of metal pollution. However, continuous monitoring is necessary to maintain the permissible limits and identify potential sources of metal pollution in the future to prevent contamination of these essential water resources.

Keywords: Heavy Metal Pollution, Geoaccumulation Index, Potential Ecological Risk, Enrichment Factor, Contamination Factor,

1. Introduction

Heavy and trace metals are a significant environmental concern, as they can have adverse effects on human health and the environment. Heavy metals, such as lead, cadmium, and mercury, are toxic even at low concentrations, and can cause damage to the nervous system, kidneys, and reproductive organs (Wrzecińska *et al.*, 2021). Trace metals, such as copper, zinc, and nickel, are essential micronutrients for living organisms, but can also be toxic at high concentrations (Andresen *et al*., 2018). The sources of heavy and trace metals in the environment are diverse, including natural sources such as weathering of rocks and soils, as well as anthropogenic sources such as industrial and agricultural activities (Yin et al., 2021). Exposure to heavy and trace metals can occur through various pathways, including ingestion of contaminated food and water, inhalation of airborne particles, and skin contact (Soodan *et al.*, 2014).

Trace metals are often referred to as heavy metals because they share similar physical and chemical properties with the heavy metals. Heavy metals are a group of elements with high atomic weights and densities, such as lead, cadmium, and mercury, that have a tendency to accumulate in the environment and living organisms (Jannetto and Cowl, 2023). Similarly, trace metals, such as copper, zinc, and nickel, also have high atomic weights and densities, and can accumulate in the environment and living organisms at low concentrations (Somerville *et al.*, 2020). In addition, both heavy and trace metals can be toxic at high concentrations, and can have adverse effects on human health and the environment (Mahar *et al*., 2016).

Rivers are important freshwater resources that are essential for human and ecosystem health. However, many rivers around the world are contaminated with heavy and trace metals, which are toxic to human and aquatic life. The presence of heavy and trace metals in river water can have harmful effects on aquatic life. For example, a study conducted in the River Ganga in India found elevated levels of lead, cadmium, and mercury, which were associated with significant reductions in the abundance and diversity of aquatic macroinvertebrates (Uddin *et al.*, 2021). Similarly, a study conducted in the River Thames in the UK found that elevated levels of copper and zinc were associated with reduced growth and survival of freshwater mussels (Ollard and Aldridge., 2023). These findings demonstrate the negative impact of heavy and trace metal contamination on aquatic ecosystems. In addition to harming aquatic life, heavy and trace metals in river water can also pose a threat to human health. For example, a study conducted in the River Nile in Egypt found that the concentration of lead in the river water exceeded the World Health Organization's (WHO) recommended levels, which may increase the risk of lead poisoning in humans (Wang et al., 2022). Lead exposure can cause a range of health effects, including cognitive impairment, developmental delays, and cardiovascular disease (Shvachiy *et al*., 2018). Similarly, a study conducted in the River Yamuna in India found that the concentration of arsenic in the river water exceeded the WHO's recommended levels, which may increase the risk of arsenic toxicity in humans (Asim and Nageswara Rao., 2021). Arsenic exposure has been linked to a range of health effects, including skin lesions, cancer, and cardiovascular disease (Fleming *et al*., 2021).

Furthermore, heavy and trace metals in river water can be transported through the food chain, leading to potential exposure in humans who consume contaminated fish or other aquatic organisms. For example, a study conducted in the River Danube in Europe found that the concentration of mercury in fish exceeded the European Union's (EU) maximum allowable levels (Zolfaghari, 2018). Mercury exposure can cause a range of health effects, including neurological and developmental effects (Mortazavi *et al*., 2018).

Indexes are important tools for monitoring heavy metals in rivers as they provide a standardized approach to assess the level of contamination and help identify potential sources of pollution. Several indexes have been developed to evaluate water quality and assess the degree of heavy metal pollution in rivers, including the Geoaccumulation index (Igeo), Potential Ecological Risk (RI), Enrichment Factor (EF), and the Contamination Factor (CF) (Dogra *et al*., 2020). Studies have used these indexes to assess heavy metal pollution in rivers worldwide, including the Yellow River in China, the Danube River in Europe, and the Cauvery River in India (Sheikholeslami and Hall, 2023). These indexes can help identify the sources of heavy metal pollution, evaluate the effectiveness of pollution control measures, and inform management strategies to reduce the risks associated with heavy metal contamination in rivers.

Iran is a country located in the Middle East that is characterized by a diverse range of ecosystems, including rivers that are important freshwater resources for human and ecosystem health. The Karun River is the largest river in Iran and is of great importance for the country's economy, environment, and culture. It is a major source of water for agriculture, industry, and domestic use, and provides habitat for a variety of flora and fauna (Zare-Shahraki *et al*., 2022). Despite its importance, the Karun River is facing various environmental challenges, such as pollution. The river has been impacted by industrial, agricultural, and urban development, resulting in contamination from heavy metals, pesticides, and other pollutants (Silva *et al*., 2024). These environmental issues have the potential to negatively impact the river's ecosystem, human health, and the economy. Efforts are being made to address these challenges and protect the Karun River. The Iranian government has implemented various policies and programs to conserve the river's water resources, promote sustainable development, and reduce pollution (ISIRI, 2018). In addition, researchers are conducting studies to monitor and assess the river's water quality and identify sources of pollution (Dehvari *et al*., 2023). Studies have shown that the river is contaminated with various heavy metals, including lead, cadmium, mercury, chromium, and copper (Moravej *et al*., 2017). The contamination is mainly attributed to human activities such as industrial, agricultural, and urban development, as well as untreated wastewater discharges. The levels of heavy metal contamination in the Karun River have been found to exceed the permissible limits set by national and international standards. For example, a study conducted in 2019 reported that the concentrations of lead, cadmium, and chromium in the river sediments exceeded the permissible limits set by the Iranian Standard (Rastmanesh *et al*., 2019). Another study conducted in 2023 found that the concentrations of pollution in the river water were in the moderate levels (Dehvari *et al*., 2023).

Despite the significance of the problem, there is a lack of comprehensive studies on monitoring the contamination levels of the river with all heavy metals, through the analysis of the sediments collected from it. Therefore, this study was carried out to evaluate the pollution levels of the river using the pollution indicators.

2. Materials and methods

2.1. Study area

The objective of this study was to investigate the concentration of heavy metals in the sediments of the Karun River, from March to June 2022. To accomplish this, 29 surface sediment samples were collected using a Van Veen Grab sampler with a cross-sectional area of 0.1 square meters, and a winch tool was employed to obtain samples from a depth of 1 to 1.4 m. Table 1 outlines the characteristics of the sampling points, and Figure 1 depicts the range of sediment sampling. This study investigated a total of 15 heavy and trace metals, including Cr, Cu, Zn, Pb, Ni, As, Mn, Fe, Co, V, Hg, Mo, Sb, Cd and Al.

Table 1. Location specifications and geographical coordinates of the collected samples

Code	Station Name	Latitude	Longitude	River Name	River location	Geographical location
S1	Cham Golak	3593941	264372	Dez	Dez	North
S2	Dezful	3503353	298716	Dez		
S3	Haft Tapeh Co.	3555770	257090	Dez		
S4	Pars paper Co.	3553982	263109	Dez		
S5	Pars paper Co. downstream	3554008	263199	Dez		
S6	Imam Khomeini Sugarcane	3503796	294001	Dez		
S7	Dez-Band ghir	3503353	298716	Dez		
S8	Gotvand	3583203	264372	Karun	Karun (before confluence of the Dez)	North
S9	Shooshtar	3571395	295966	Karun		
S10	Gargar	3548808	298189	Gargar		
S11	Shatit	3548164	298027	Shatit		
S12	Band Ghir	3548240	297790	Karun		
S13	Ramin power plant	3503353	298716	Karun	Karun (after confluence of the Dez)	Central
S14	Zargan	3486812	297974	Karun		
S15	Koroush upstream	3473031	286891	Karun		
S16	Koroush downstream	3472866	285134	Karun		

S17	New side	3473663	279914	Karun		
S18	Bridge 5	3470712	281225	Karun		
S19	Choneibieh	3465933	278092	Karun		
S20	Omoteir	3461882	277031	Karun		
S21	Sugarcane upstream	3460393	268380	Karun		
S22	Sugarcane downstream	3452699	259094	Karun	Karun	South
S23	Darkhoein	3438753	250854	Karun		
S24	Mared	3404165	252867	Karun		
S25	Soap Co.	3377462	246758	Karun		
S26	Khorramshahr	3370953	232039	Arvand		
S27	Abadan petrochemical Co.	3369752	227878	Arvand	Arvand	
S28	Abadan Refinery	3359797	236530	Arvand		
S29	Choeibieh	3358919	238201	Bahmanshir	Bahmanshir	

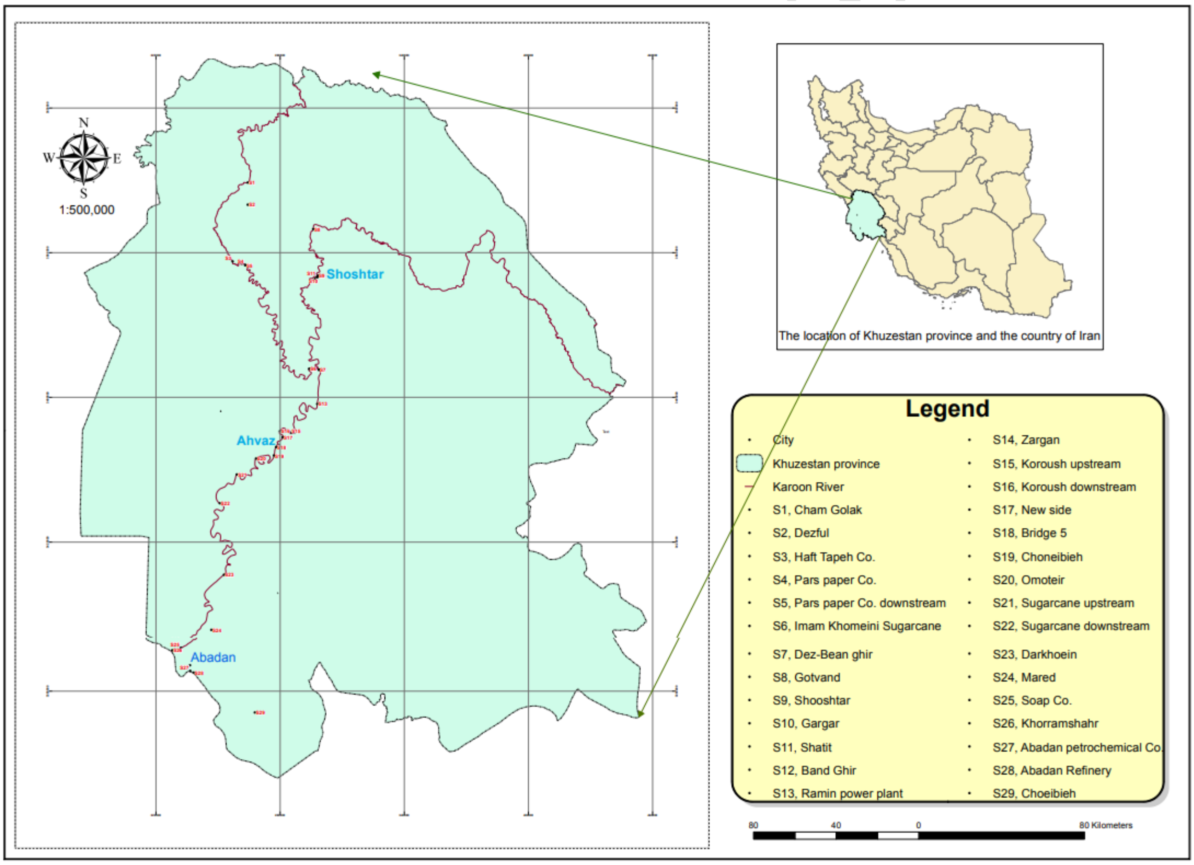


Figure 1. Location of sampling points in the Karun River

2.2. Sampling and determining the concentration of heavy metals

The sediment samples collected from the locations indicated in Figure 1 were transferred to plastic containers and stored in a cold room at -20 degrees Celsius before being transported to the laboratory.

The samples were then dried at 50 degrees Celsius and sieved through a 230 mesh. To prevent excessive heating, about five grams of each sample were slowly ground into a powder before undergoing decomposition through an HCI HNO3 and HF digestion method. For heavy metal measurement, one gram of each sample was mixed with 7 ml of concentrated nitric acid (HNO3) and hydrochloric acid (HCL) in a 3:1 ratio. The mixture was poured into test tubes and placed on a hot plate set at 95 degrees Celsius for 1 hour to extract heavy metals. After cooling, 5 ml of HF was added to each sample, and the solutions were transferred to a 50 ml volumetric flask and diluted with IN HCI. The prepared samples were filtered through Whatman 42 filter paper, and the atomic absorption device model was used to measure the samples in accordance with Iran's standard number one.

2.3. Monitoring of heavy metals

The permissible concentrations of studied metals in the Karun River sediments were calculated based on the Iranian Standard (ISIRI1053) recommended levels (Table 2).

Table 2. Allowable water limit for metals (ppm) based on Iranian Standard (ISIRI, 2018)

	Cr	Cu	Zn	Pb	Ni	As	Mn	Fe	Co	V	Hg	Mo	Sb	Cd	Al
Allowable limit for metals	0.05	1.0	3.0	0.01	0.07	0.01	0.1	0.3	0.002	0.1	0.006	0.07	0.02	0.003	0.1

2.4. Pollution assessment indicators

The concentration of heavy metals at each sampling point was evaluated using four indicators, including Geoaccumulation index (Igeo), Potential Ecological Risk (RI), Enrichment Factor (EF), and the Contamination Factor (CF). The indicators are described below. It is essential to note that these indicators require consideration of the reference element. A reference element is an important factor that needs to be considered while evaluating the concentration of heavy metals in sediments. The reference element should be stable in soil, have no vertical mobility, and not be affected by anthropogenic activities. Commonly used reference elements include Al, Fe, Mn, Rb, total organic carbon, and grain size (Keshavarzi *et al*., 2013; Leermakers *et al*., 2007; Pourret *et al*., 2006). Aluminum is a conservative element and a major component of clay minerals, making it a popular choice for several researchers (Müller, 1979; Sutherland, 2000). Iron has also been used by many authors in studies on marine and estuarine sediments (Daskalakis *et al*., 2015; Leermakers *et al*., 2007). However, it is important to note that Iron is not a matrix element, and its geochemistry is similar to that of many trace elements in oxic and anoxic environments (Leermakers *et al*., 2007). For many years, background values were based on Earth crust and soil values (Alloway, 2013).

2.5. Geoaccumulation index (Igeo)

The geo-accumulation index (Igeo), developed by Muller (1969), is a measure used to determine the level of heavy metal contamination in sediment. The Igeo is expressed as:

$$Igeo = Log2\left(\frac{Cn}{1.5Bn}\right) \quad (1)$$

The geo-accumulation index (Igeo), which quantifies the concentration of heavy metal pollutants in sediment, is calculated by dividing the concentration of the metal pollutant Cn by the geochemical background concentration of the pollutant in sediment Bn. The Igeo is then classified into seven categories, ranging from unpolluted to severely contaminated, as established by Chakravarty and Patgiri (2009), Fagbote and Olanipekun (2010), and Sabo *et al*. (2013). Muller's categorization of the Igeo is presented in Table 3.

Table 3. Igeo classes

Class	Value	Description
0	Igeo≤1	uncontaminated
1	0≤ Igeo <1	Uncontaminated to moderately contaminated
2	1≤ Igeo <2	Moderately contaminated
3	2≤ Igeo <3	Moderately to strongly contaminated
4	3≤ Igeo <4	Strongly contaminated
5	4≤ Igeo <5	Strongly to extremely contaminated
6	5≤Igeo	Extremely contaminated

2.6. Enrichment factor (EF)

The calculation of the enrichment factor used the formula originally introduced by Buat-Menard and Chesselet (1979), as shown below in equation (2).

$$EF = \frac{\left(\frac{Cx}{Cref}\right)Sample}{\left(\frac{Bn}{Bref}\right)Background} \qquad (2)$$

In order to determine the level of contamination of a chemical element in the examined environment, the concentration of the element in the sample (Cx) is compared to the concentration of the element in a reference environment (Cref). Additionally, the concentration of a reference chemical element in the examined environment (Bn) is compared to the concentration of the same reference element in a reference environment (Bref). The authors of this study followed the environmental work of Salomons and Förstner (1984) while performing these comparisons. Categorization of the EF is presented in Table 4.

Table 4. EF categories

Class	Value	Description
0	EF≤2	Deficiency to minimal enrichment
1	2≤ EF <5	Moderate enrichment
2	5≤ EF <20	Significant enrichment
3	20≤ EF <40	Very high enrichment
4	40≤ EF	Extremely high enrichment

2.7. Contamination factor (CF)

The CF is a useful indicator to express the level of metal contamination in sediment. The CF is defined as the ratio between the metal content in the sediment and the background value of the metal. This factor is an effective tool for monitoring pollution over time and can be calculated as follows:

$$\mathrm{CF} = \frac{C\ heavy\ metal}{\mathrm{C\ background}} \qquad (3)$$

Hakanson (1980) has classified the CF into four categories, as presented in Table 5.

Table 5. CF classes

Class	Value	Description
0	CF<1	Low contamination
1	1≤CF<3	Moderate contamination
2	3≤CF<6	Considerable contamination
3	6≤CF	High contamination

2.8. Potential ecological risk (RI)

Hakanson (1980) proposed a method to assess the environmental behavior of heavy metal contaminants in sediments using the potential ecological risk index (RI). The primary purpose of this index is to highlight the contaminant agents and prioritize areas for further contamination studies. The RI is calculated as the sum of all risk factors for heavy metals in sediments, where E_r^i is the monomial potential ecological risk factor, CF is the contamination factor, and T_r^i is the toxic response factor. The toxic response factor reflects the potential hazard of heavy metal contamination by indicating the toxicity of particular heavy metals and the environmental sensitivity to contamination. The formula for calculating the potential ecological risk index is given below:

$$E_r^i = T_r^i \times CF$$

$$RI=\sum_{i=1}^{n} E_r^i \qquad (4)$$

Hakanson (1980) proposed the terminology used to describe the risk factors and potential ecological risk index (RI), as shown in Table 6.

Table 6. Igeo classes

Class	Er Value	RI value	Description
0	Er<40	RI<95	Low potential ecological risk
1	40≤ Er <80	95≤RI<190	Moderate ecological risk
2	80≤ Er <160	190≤RI<380	considerable ecological risk
3	160≤Er <320	-	High ecological risk
4	320≤Er	380≤RI	Very high contamination

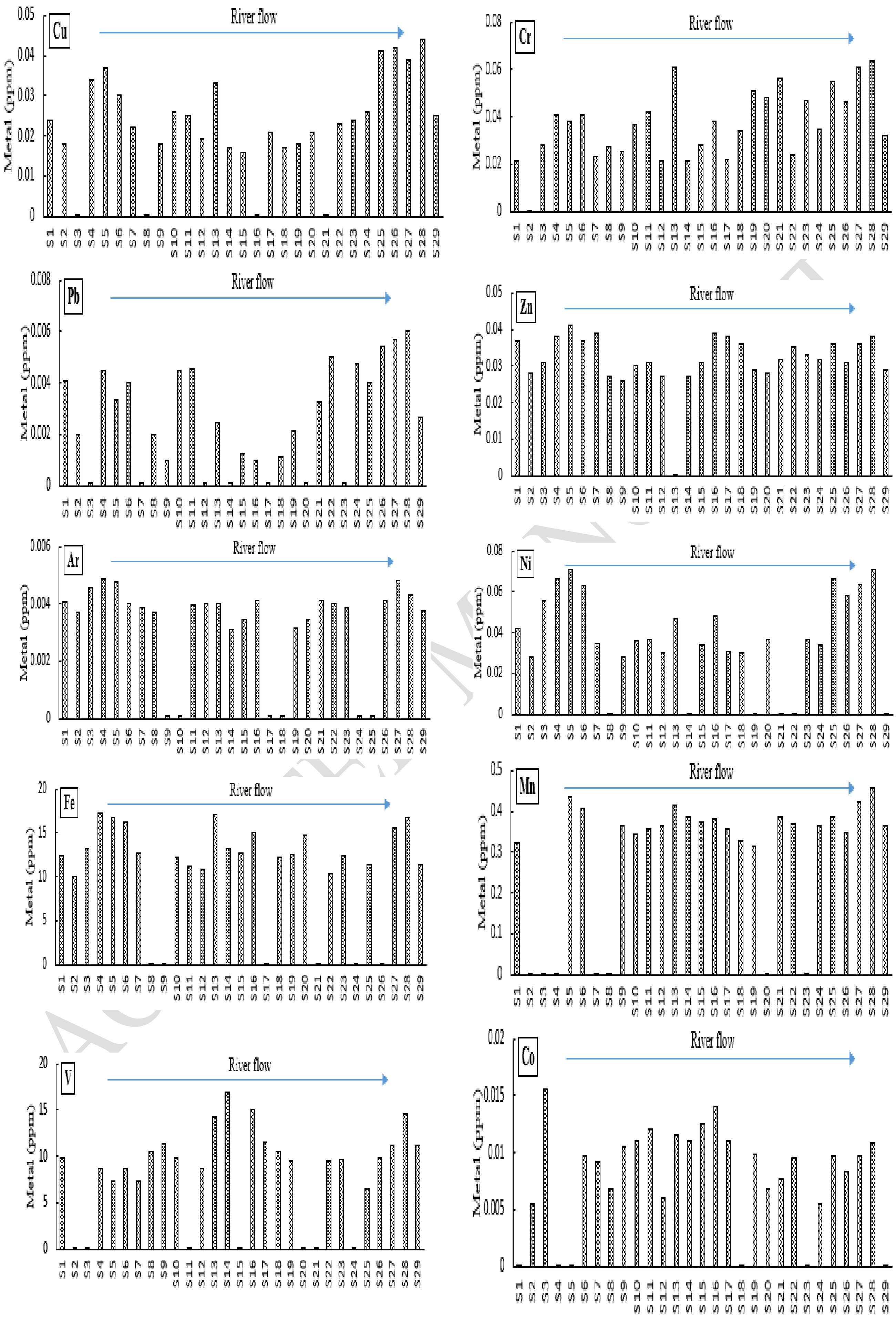
3. Results and Discussion

3.1. Amounts of metals in different parts of Karun river

The concentrations of 15 heavy metals in the Karun River are presented in Figure 2. The concentrations of these metals were reported for each region, as shown in Table 1. The regions included the northern part of the study area, Dez and Karun rivers, central region, and southern region of Karun and Arvand rivers. The overall status of the Karun River was also evaluated. The permissible limit of chrome in the Iranian standard is 0.05. Results of our study indicate that the concentration of chromium in the Dez River and the beginning of the Karun River was below the permissible limit. However, in the middle and end of the river, the concentration of chromium increased and exceeded the permissible limit. This finding highlights the potential sources of heavy metal pollution in the middle and end of the Karun River, which may include significant risks to the local ecosystem and human health. Few similar studies have been published since less than one decade ago, which corroborate our findings on heavy metal pollution in the Karun River.

The concentrations of copper, zinc, arsenic, mercury, molybdenum, cadmium, and aluminum in the sediment samples from the Karun and Dez rivers were found to be lower than the permissible limit of Iranian standards. Therefore, there is no concern about these metals in terms of potential health risks to humans and the environment. Regarding the water quality of Karun river, various studies have been done, but not all of them were about the investigation of sediments. Most of the researches have been focused on heavy metals in the body of aquatic animals. These studies have shown that the amount of heavy metals in the body of aquatic animals is significant in some places. The results showed that the copper concentration varied between 0.033-0.037 and the zinc concentration between 0.26-0.45 ppm. In addition, these researchers reported that the concentration of these two metals was almost similar in all parts of the Karun River. The reason is probably that the accumulation of zinc in the aquatic body has occurred and its amount is higher than the concentration of zinc metal in the sediments. The elevated levels of manganese, iron, cobalt, and vanadium in the Karun and Dez rivers are of concern due to the potential risks they pose to human health and the environment.

Our results showed that the skewness of the studied metals, except for aluminum and lead, was negative, indicating that the concentration of pollution at the end of this river is higher than at the beginning. The changes of the studied metals along the Karun River confirms the increased concentration of heavy metals.


Cu
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V
Co
River flow
Metal (ppm)
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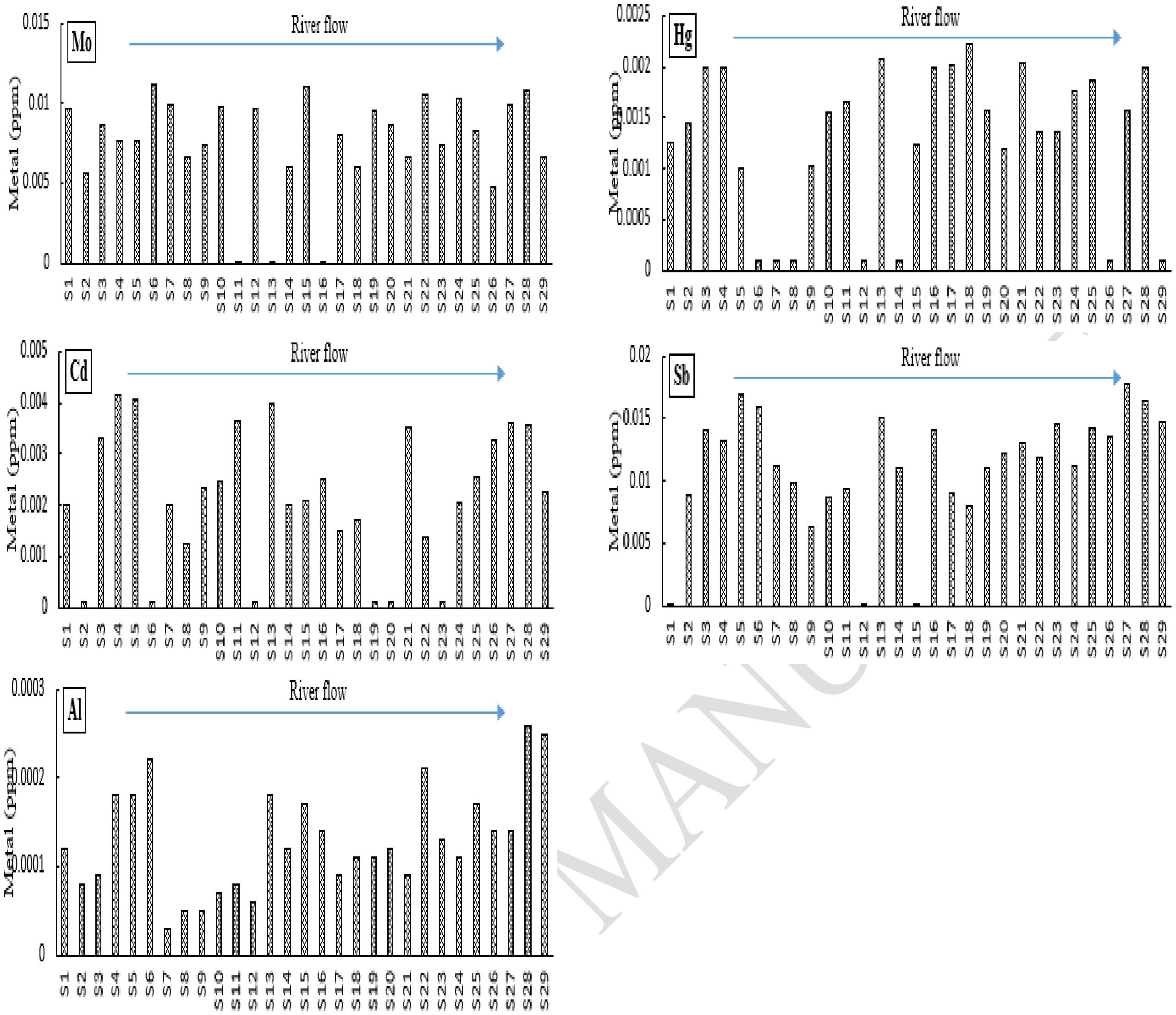

Fig 2. Changes of studied metals along the Karun River (During the 4-month study)

3.2. Igeo results

Figure 3 illustrates the average concentration of these metals along the length of the Karun River. Although in Table 2, the concentration of manganese, vanadium and cobalt elements was higher than the Iranian standard, all metals had negative Igeo values, indicating uncontaminated condition. As it states in Material and Methods, Igeo is a commonly used index for quantifying the degree of metal pollution in sediments and soils. A low Igeo value indicates that the metal concentrations in sediments or soils are within background levels and are not considered to be polluted. One possible reason for the low Igeo value in the river could be the presence of natural background levels of metals in the sediment (Saha *et al*., 2020). A study by Zhang *et al*. (2018) found that the Igeo values for metals in sediment samples from the Han River in China were low due to the presence of natural background levels of metals. Another possible reason for the low Igeo value in the river could be the effectiveness of existing management strategies to prevent metal pollution. According to Keshavarzi *et al*. (2018), the Igeo values for metals in sediment samples from the Zanjanrood River in Iran were low as a result of the successful implementation of environmental regulations and management practices aimed at preventing metal pollution. On the other hand, no increasing or decreasing trend in the Igeo values was observed along the Karun River for any of the studied metals. It could be influenced by the seasonality of the river flow. A study by Chang *et al*. (2018) found that the concentrations of metals in a river in Taiwan varied according to the season, with higher concentrations observed during the rainy season due to increased runoff and erosion. As the sampling was conducted during the spring season, when the Karun catchment area experiences no rain or floods, all the metals had an Igeo value that fell within the uncontaminated category.

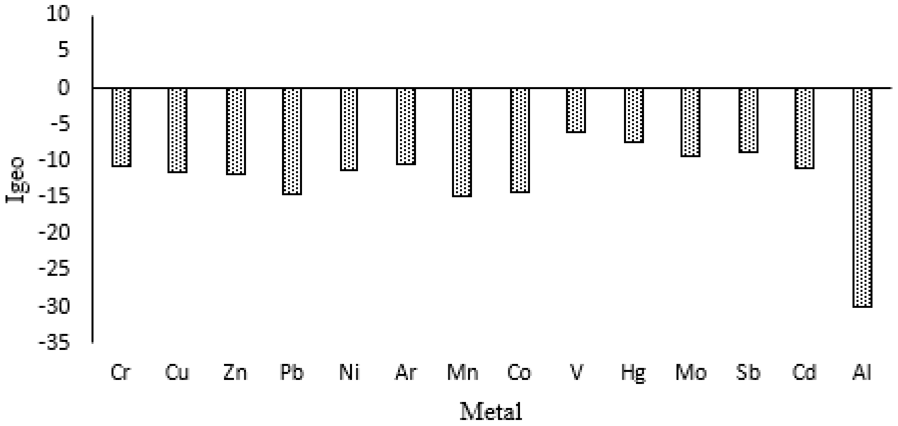

Fig 3. Average Igeo results along with Karun River

3.3. CF results

Figure 4 illustrates the average CF for each of the studied metals along the Karun River. The findings indicate that the CF values for all metals were less than one, indicating low contamination levels. A low CF value indicates that the metal concentrations in sediments or soils are within background levels and are not considered to be contaminated. a study by Zhang *et al*. (2018) found that the CF values for metals in sediment samples from the Han River in China were low due to the presence of natural background levels of metals. Furthermore, the low CF values in the river could be attributed to the dilution effect of the river flow. A study by Wang *et al*. (2018) found that the CF values for metals in sediment samples from a river in China decreased downstream due to the dilution effect of the river flow. However, it's important to note that the specific reasons for the low CF values in the Karun River would depend on the specific study and the metals that were analyzed. It's also possible that other factors, such as the seasonality of the river flow or the mixing of metals from different sources, could have contributed to the low CF values. In addition, the high concentration of iron in the Karun River may contribute to the reduction of the CF values, as iron is used as a reference metal to calculate this factor. However, the average concentration of iron in the river is 35.2 times higher than the permissible limit for this metal (Table 2), indicating potential environmental concerns. The high concentration of iron in the Karun River could be attributed to both natural and anthropogenic sources. One possible natural source of iron in the Karun River is the weathering and erosion of rocks and soils in the river catchment area. A study by Hemmati and Bakhtiari (2012) found that the high concentration of iron in the Karun River sediments was mainly due to the natural weathering of iron-rich rocks in the river catchment area. Another possible source of iron in the Karun River could be anthropogenic activities such as industrial and agricultural practices. A study by Esmaili-Sari *et al.* (2016) found that the high concentration of iron in the Karun River water was mainly due to the discharge of industrial effluents and agricultural runoff into the river. In addition, the high concentration of iron in the Karun River could also be influenced by the seasonality of the river flow. A study by Khodadoust *et al.* (2014) found that the concentration of iron in the Karun River water was higher during the dry season compared to the wet season due to reduced dilution by the river flow.

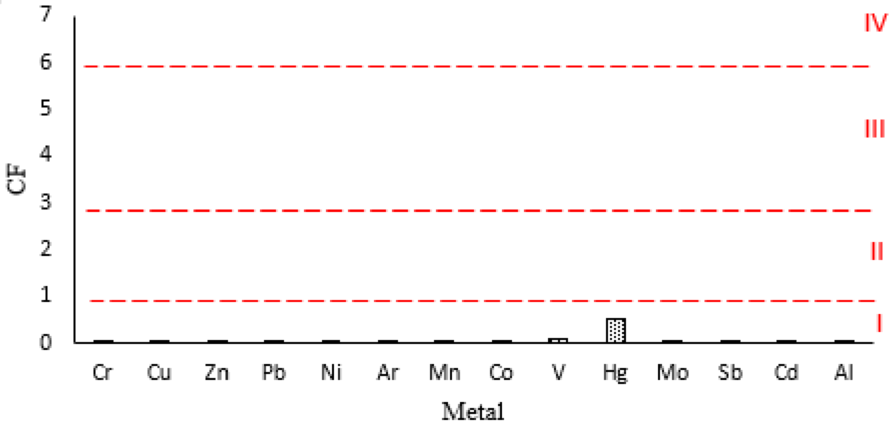

Fig 4. Average CF results along with Karun River

3.4. RI results

Figure 5 illustrates the average index for each metal in the Karun River. With the exception of vanadium and mercury, the RI values in the Karun River was below 0.01. The average of RI value for vanadium and mercury was 0.05 and 0.012, respectively. While the RI for vanadium was zero at few sampling points, it ranged from 0.19 to 0.09 at other points. This is higher compared to other metals. The RI value for mercury was 0.04 in Karun River (in some stations between S6-S14) and in the Choeibieh station (S29), which is the southernmost part of the Karun River. These points are located far from industrial activities along the Karun River, which could explain the low value of this factor for mercury in these stations. However, the RI value for all metals was within the uncontaminated category. These results were consistent with the observations of Esmaili-Sari *et al.* (2016). They revealed that the levels of heavy metals in the water and sediment samples of Karun River were generally low and did not exceed the permissible limits set by the Iranian Standard, however, they only used lead, cadmium, chromium, copper, nickel, and zinc concentration to evaluate RI values. A low potential ecological risk in a river could be due to several factors, including the absence or reduced levels of pollutants, effective management strategies to prevent pollution, and the ability of the river ecosystem to recover from environmental stressors. Furthermore, the low RI value in a river could also be attributed to the presence of natural attenuation processes, such as sedimentation and biodegradation, that can reduce the concentration and toxicity of pollutants in the river. Esmaili-Sari *et al.* (2016) noted that the low levels of heavy metals in Karun River could be attributed to the absence of large-scale industrial activities and the limited use of agrochemicals in the river catchment area. To pun in a nutshell, the factors mentioned could contribute to the low value of RI in the Karun River.

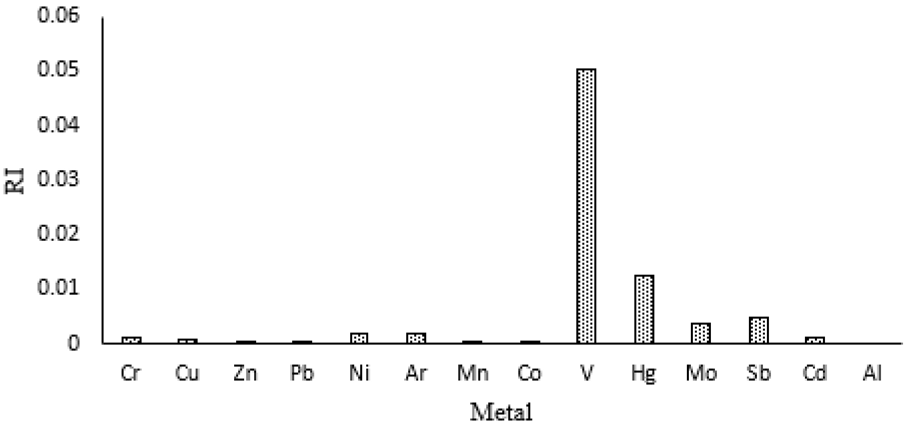

Fig 5. Average RI results along with Karun River

3.5. EF results

While the EF value for chromium in station S22 was 0.2, it ranged from 2.86 to 10.08 in other stations. As a result, with the exception of station S22, the Karun River was categorized as moderate and significant enrichment. On the other hand, as all the values recorded for the EF exceeded 1.5, it can be inferred that a substantial proportion of the chromium did not originate from crustal materials. The EF value for copper in stations S3, S8, S11, and S16 was found to be in the range of 0.02-0.03, while in other stations, it exceeded 3.15, which is consistent with the results obtained for chromium. In reality, the EF value was almost zero in a few stations, but it exceeded two in the majority of stations. The EF value for aluminum was almost identical across all stations, whereas for lead and cobalt, it ranged from 0.02 to 1.7 and 0.01 to 1.48, respectively. Based on the EF values, there was no risk associated with these three metals in the Karun River. For zinc and manganese, the EF values ranged from 0.01 to 3.37 and 0.0 to 2.57, respectively. Consequently, some stations had an EF value of less than two for these two metals, indicating low enrichment. However, the level of enrichment for both metals increased from the start to the end of the Karun River. For the remaining metals, a few stations had an EF value close to zero, but in the majority of stations, the EF value exceeded two, indicating the onset of enrichment in the river. The average EF for the metals studied is depicted in Figure 6, revealing that nickel, arsenic, molybdenum, and cadmium fell under the moderate enrichment category. The enrichment factor can be high due to several factors. One of the primary reasons is the discharge of industrial and municipal effluents into the river, which can contain high concentrations of metals. Another factor that can contribute to high EF values in a river is agricultural practices, such as the use of fertilizers and pesticides (Mohammed *et al*., 2020). In conclusion, the enrichment factor can be high in a river due to the discharge of industrial and municipal effluents, as well as agricultural practices, which introduce metals into the river from anthropogenic sources. Therefore, the EF values for most metals in the Karun River exceed two, indicating that their origin is anthropogenic in nature. Antimony was in the very high enrichment category, and vanadium and mercury were in the extremely high enrichment category. As noted by Worthington *et al.* (2017), mercury is a hazardous metal that is commonly used in industrial processes, and its release into the environment is predominantly attributed to human activities such as coal combustion, mining, and waste incineration. While mining is not a significant factor in the Karun River, the increase in mercury levels is likely linked to sewage and garbage disposal. As highlighted by Fatola *et al.* (2019), vanadium is a metal that is becoming a growing environmental concern due to its potential toxicity and its use in various industrial processes such as steel production and petroleum refining. It is highly likely that these factors have contributed to the increase in vanadium levels in the Karun River. As indicated by Nishad and Bhaskarapillai (2021), antimony is a metal that finds application in several industrial processes, including the manufacturing of flame retardants, batteries, and ceramics. Its release into the environment is primarily attributed to human activities such as metallurgical operations. It is therefore highly likely that the increase in antimony levels in the Karun River is due to these anthropogenic activities.

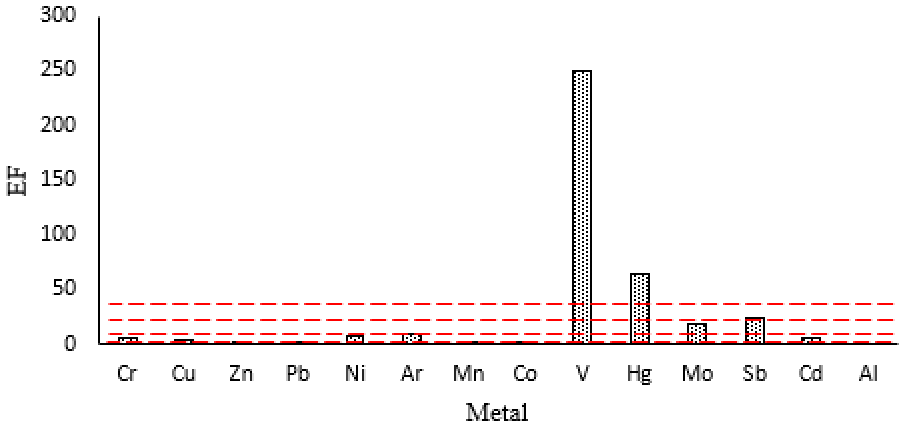

Fig 6. Average EF results along with Karun River

3.6. Conclusion

Although the concentration of some metals exceeded the Iranian standard, all metals had negative Igeo values, indicating an uncontaminated condition. The low Igeo value could be due to natural background levels of metals present in the sediment or successful implementation of environmental regulations and management practices to prevent metal pollution. Additionally, no trend in the Igeo values was observed along the Karun River, which could be attributed to the seasonality of the river flow. As the sampling was conducted during the dry season, when the river experiences no rain or floods, all metals had an Igeo value that fell within the uncontaminated category. The findings suggest that all metals had low contamination levels, with a CF value less than one. The low CF values could be due to the presence of natural background levels of metals, the dilution effect of the river flow, or the high concentration of iron in the river, which is used as a reference metal to calculate CF. However, the high concentration of iron in the Karun River, which exceeds the permissible limit, may indicate potential environmental concerns. The high concentration of iron could be attributed to natural sources such as weathering and erosion of rocks and soils, anthropogenic sources such as industrial and agricultural practices, or the seasonality of the river flow. The RI values for all metals were below 0.01, except for vanadium and mercury, with an average RI value of 0.05 and 0.012, respectively. The low RI values were consistent with the absence or reduced levels of pollutants, effective management strategies, and natural attenuation processes in the river ecosystem. The high RI value for vanadium at some sampling points could be attributed to the proximity to industrial activities. The low RI value for mercury at some stations located far from industrial activities could be due to natural attenuation processes or effective management strategies. These results were consistent with previous studies and could be attributed to the absence of large-scale industrial activities and limited use of agrochemicals in the river catchment area. The Karun River was categorized as moderate and significant enrichment for all metals except for aluminum, lead, and cobalt based on EF values. The EF values for chromium and copper were particularly high in some stations, indicating non-crustal sources such as point and non-point pollution. The EF values for zinc, manganese, nickel, arsenic, molybdenum, and cadmium were also in the moderate enrichment category. Antimony, vanadium, and mercury were in the very high and extremely high enrichment categories, respectively, and their increase in levels is likely due to human activities such as industrial processes, waste disposal, and metallurgical operations. Anthropogenic activities such as discharge of industrial and municipal effluents and agricultural practices are common causes of high EF values in rivers. Based on all the results, the concentrations of metals in the Karun and Dez rivers in Iran are within permissible limits, suggesting that these rivers are not currently at risk of aforementioned metal pollution. However, it is important to continue monitoring the concentrations of metals in these rivers to ensure that they remain within permissible limits. In addition, it is important to identify and address potential sources of metal pollution in the future to prevent contamination of these important water resources.

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