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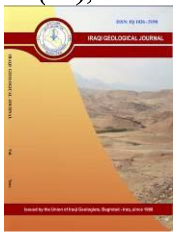

Evaluate Sediment Contamination with some Heavy Metals. A Case Study of the Al-Gharraf River in Wasit, Iraq

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Abstract

This study aimed to determine the amount of heavy metal pollution in the Al Garraf River sediment in Wasit, Iraq. Seven samples were gathered from the Al-Gharraf River in July 2021. GPS was used to determine the geographic location of these samples. The pollution level in the Al Gharraf River sediments caused by manganese, chromium, cadmium, cobalt, zinc, nickel, copper, and lead pollution indices such as enrichment factor, geo-accumulation, contamination factor, and pollution load were used to analyze the situation. Although geo-accumulation has mostly been used to evaluate contamination in freshwater sediment, one of the most frequently utilized factors is an enrichment to quantify to determine degrees of anthropogenic contamination and ratios of enrichment. On the other hand, the pollution load index is calculated as the number of times the concentration of heavy metals in sediments exceeds the concentration and level and is used for estimating the total amount of toxicity of heavy metals in samples. At the same time, our study discovered that cadmium is heavily polluted (contamination value is 5.70) in Al Gharraf River sediments, while nickel (1.51) and lead (1.75) are moderately polluted, but that the metals manganese, cobalt, chromium, zinc, and copper are not.

Keywords: Iraq; Al Gharraf River; Pollution level; Contamination; Sediment

1. Introduction

Al-Gharraf River is the main branch of the Tigris River, and its properties are thus derived from the Tigris River. It passes through these cities in the west of the Al-Kut city to the south: Al-Muafakiah, Al-Haay in the province of Wasit and Al-Fajer, Qalaat Sekar, Al-Refaee, Al-Naser, and finally Al-Bada'a district in Dhi-Qar, where it branched to Al-Bada'a river and Al-Shatrah river (Al-Gizzy, 2005) (Fig.1). Historically, the Al-Gharraf River is an artificial canal constructed by the King of Lagash (2395-2425 BC) during Urnamekina. Its Arabic name means that it has a lot of water taken from Tigris; during spring floods, it had other names such as the Red River for the lot of silt (Al-Haidary, 2006). Al-Gharraf River is the country's primary source of water for public and agricultural needs, and it has had a significant impact on the country's socioeconomic aspects. Commercial, agricultural, and home wastewater, which make up most wastewater in many cities, is collected from the river. The growth of contaminants in the river has been a recent cause of concern associated with the development of the region (AL-Zamili, 2007).

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Mesopotamia is a large lowland region with flat terrain. The Tigris and Euphrates Rivers run across central and southern Iraq, and the Mesopotamian Zone is covered in Quaternary sediments that cover a whole Mesozoic and Cenozoic section (Jassim and Goff, 2006). The Gharraf River runs across the flood plains of Mesopotamia. The Mesopotamian plan includes a lake and marsh complex in southern Iraq, which includes the ancient Tigris-Euphrates-Karun Delta and current tidal flats and the Shatt Al- Arab, Karun estuary delta. The majority of the lower Mesopotamian Plain is currently a flat, expansive terrain with shallow fresh-brackish water lakes (usually less than 3 m deep). The Mesopotamian Plain's Quaternary deposits are more than 250 meters thick. The main river is approximately 230 km long, 50-90 m wide, and 7-13 m deep, and the river sector in this study is approximately 45 km wide, extending from Al-Kut to Al-Haay city. The basin was inhabited by more than a million individuals using approximately 432,000 m3 / year of processed water and moving within the sediment plain across an agricultural area of approximately 215019 ha in the southwest of Iraq (MOA and I, 1991; Jawad et al., 2009).

This study employed pollution indicators to assess the severity and anthropogenic pollution found in river sediments. The following are the indices: “EF (Enrichment Factor), I-geo (Geo accumulation Index), CF (Contamination Factor) and Pollution Load Index (PLI)”. This research aimed to find out how much heavy metals (HM) contamination there was in the Al-Gharraf River sediment from Kut City to Al-Haay District in Iraq's Wasit.

The Al-Gharraf River’s geographical position lies between (45˚48'22"E 32˚30'07"N) to (46°02'05"E 32°09'45"N), as shown in Table 1 and Fig.1. As a result of agriculture's reliance on irrigated land, pesticides, fertilizers, and industries, as well as poor sanitation and rubbish techniques of collection, the amount of contaminants entering the Al-Gharraf River has increased as the main source of drinking for humans and everyday use (Collins, 1975). This location gives the climate characteristics of the region, such as the high rate of sun radiation, high temperature, few occasions of rain, low humidity, and high rate of evaporation.

2. Materials and Methods

2.1. Collection of Samples and Analysis

The pollution analysis requires the collection of sediment samples, which were collected in July 2021 at seven locations from the Al Gharraf River sediment (Table1) and (Fig.1). The samples collected for HM (manganese, chromium, cadmium, cobalt, zinc, nickel, copper, lead, and zirconium) were analyzed using four key indices to detect sediment contamination in the Al-Gharraf River.

- EF (Enrichment factor)
- CF (Contamination factor)
- PLI (Pollution load index)
- Geo-accumulation Index (I-geo)

Table 1. All sample stations are located in the Al Gharraf River

Stations	Coordinate
S.1	45˚48'22"E 32˚30'07"N
S.2	45˚50'59"E 32˚25'25"N
S.3	45˚56'00"E 32˚22'50"N
S.4	45˚55'02"E 32˚19'43"N
S.5	45˚55'51"E 32˚15'47"N
S.6	45°59'56"E 32°12'05"N
S.7	46°02'05"E 32°09'45"N

All samples were brought to the Department of Geology at the University of Baghdad's College of Science, where soil samples were oven dried at 60°C, and 10 grams of powder samples were used to detect elements using the x-ray fluorescence method (the result of analysis shown in Table 2).

Table 2. Heavy metals concentrations of Al-Gharraf River sediments in ppm, as well as background values for the earth's crust, as of July 2021 (Taylor and Mclennan,1985)

Sample No.	Mn	Cr	Cd	Co	Zn	Ni	Cu	Pb	Zr
S.1	545.5	98.8	0.89	3.3	59.9	113.8	39.9	11.8	88.7
S.2	625.8	99.2	1.4	7.9	60.4	132.9	41.5	29.5	86.8
S.3	540.3	90.5	0.98	11.3	50.1	98.7	33.4	16.3	78.2
S.4	541.1	84.2	0.91	9.2	49.4	86.7	31.2	15.5	77.1
S.5	686.4	85.3	1.1	10.4	60.1	103.8	42.6	23.7	78.5
S.6	692.4	97.8	1.3	7.8	70.5	122.4	45.7	28.8	89.6
S.7	699.3	98.9	1.4	12.5	73.5	135.4	48.5	30.3	88.6
Taylor and Mclennan,1985	950	100	0.2	25	70	75	55	12.5	165

2.2. Sediment Analysis Precision

Precision is a term that describes how well a group of results agrees with one another. The departure of a collection of outcomes from the arithmetic mean (Table 3) is how precision is commonly expressed.

The standard deviation is used to calculate the precision. The relative standard deviation (R.S.D.) from the confidence level, 63 %, is shown in the following equation; in this example, the precision will be acceptable to 5-15 percent (Stanton, 1966).

R.S.D % = (σ /X) 100 R.S.D

At a confidence level of 95%, the relative standard deviation (R.S.D.) might be calculated.

R.S.D % = (2 σ /X) 100

In this case, an accuracy of 25% will be accepted (Maxwell, 1968). The sample number S.1 was picked for analysis three times to check that our analyses were acceptable; precision appears acceptable (Table 3).

Table 3. Precision results of sample in S.1of Al-Gharraf River

Elements	Number of Analyses			X ± σ	R.S.D %	
	1	2	3		(σ /X) 100	(2 σ /X) 100
Mn	545.5	550.2	553.6	549. 7±33. 09	6.02	12.04
Cr	98.9	100.2	97.1	98.7 ±2.2	2.2	4.4
Cd	0.95	0.89	0.85	0.89 ±0.07	7.8	15.7
CO	3.3	3.5	3.1	3.3 ±0.28	8.4	16.9
Zn	59.9	61.5	62.9	61.4 ±2.12	3.45	6.9
Ni	113.8	116.1	110.7	113.5 ±3.82	3.36	6.73
Cu	39.3	42.5	43.2	41.6 ±2.94	7.06	14.13
Pb	11.8	11.6	12.5	11.9 ±0.67	5.6	11.2

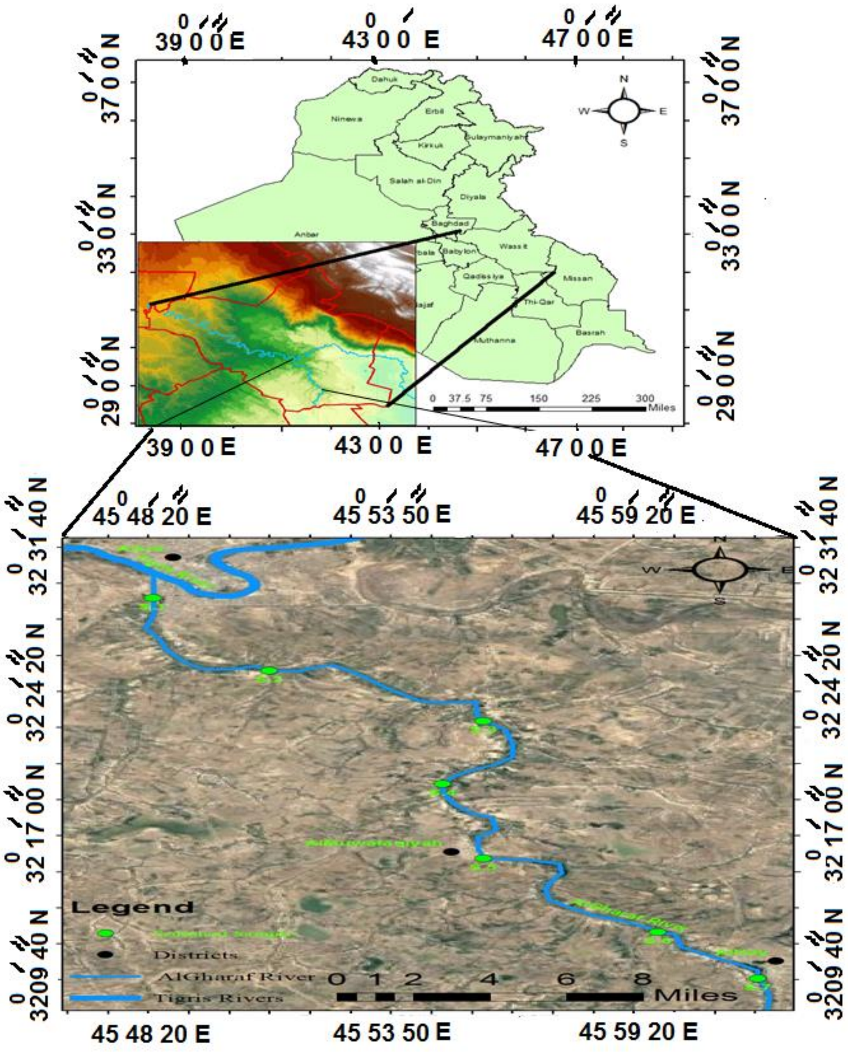

Fig.1. Sediment sampling map of Al-Gharraf River

3. Heavy Metal Pollution Assessment

Determination of the natural levels of HM in sediments is very important in order to determine the mineral content in the sediments of the Al-Gharraf River. HMs' anthropogenic sources, such as solid waste and liquid, may be introduced into the system from industries in the Al-Gharraf River sediments, in addition to natural sources. There are a variety of sediment pollution indicators that may be used to determine the extent of HM contamination. Four indices were chosen to evaluate the contamination level of manganese, chromium, cadmium, cobalt, zinc, nickel, copper, and lead in the Al Gharraf River sediments for this purpose and to achieve the study's objectives. (The EF (Enrichment factor) and PLI (Pollution Load Index), CF (Contamination factor), and I-geo (Geo-accumulation Index), were employed to assess metal pollution in sediment is a problem that needs to be addressed of Al Gharraf river sediments shown in Table 2.

3.1. EF (Enrichment Factor)

The EF is a method for evaluating the anthropogenic effect on sediments by comparing metals extracted from human activities to those derived from natural or mixed metal sources (Davis and Dewiest, 1966). The EF equation aims to decrease the metal variability associated with the sediment ratio variable. The EF method normalizes the HM content measured with respect to the reference metal of the sample, such as Zn or Al (Drever, 1997). In this analysis, as a moderate portion compared to relative enrichment, zircon was commonly used in geochemical studies (Blaser et al., 2000) and zircon is a product of rock weathering and not of human resources. The (EF, enrichment factors) was determined according to the following equation:

$$EF = (M / Zircon)_{\text{for sediment}} / (M / Zircon)_{\text{for the earth's crust}} \quad (1)$$

Where: M, the concentration of HMs in ppm and Zircon concentrations in ppm are measured in a sample of sediments/crust of the earth. According to (Hernandez et al., 2003; Fong et al., 2008), (EF) has been graded into five groups (Table.4). In the order Cd > Pb > Ni > Cr > Zn > Cu > Mn > Co, the mean EF values for elements in the Al Gharraf River sediments were given (Table 5) and (Fig.2).

Table 4. Enrichment factor categories according to (Hernandez et al., 2003; Fong et al., 2008).

Value	Soil dust quality
EF < 2	Minimal
2 < EF < 5	Moderate
5 < EF < 20	Significant
20 < EF < 40	Very high
EF > 40	Extremely high

Table 5. Results pollution assessment of enrichment factor for the studied samples.

Station/Elements	Mn	Cr	Co	Zn	Ni	Cu	Pb	Cd
S.1	1.07	1.84	0.24	1.59	2.82	1.35	1.75	8.27
S.2	1.25	1.88	0.60	1.64	3.36	1.34	4.48	13.3
S.3	1.20	1.72	0.95	1.51	2.77	1.28	2.75	9.31
S.4	1.22	1.80	0.78	1.51	2.47	1.21	2.65	9.72
S.5	1.52	1.79	0.87	1.80	2.91	1.62	3.98	11.56
S.6	1.34	1.80	0.57	1.85	3.01	1.53	4.24	11.96
S.7	1.37	1.84	0.93	1.95	3.36	1.64	4.51	13.03
Mean	1.28	1.81	0.70	1.69	2.95	1.42	3.48	11.02

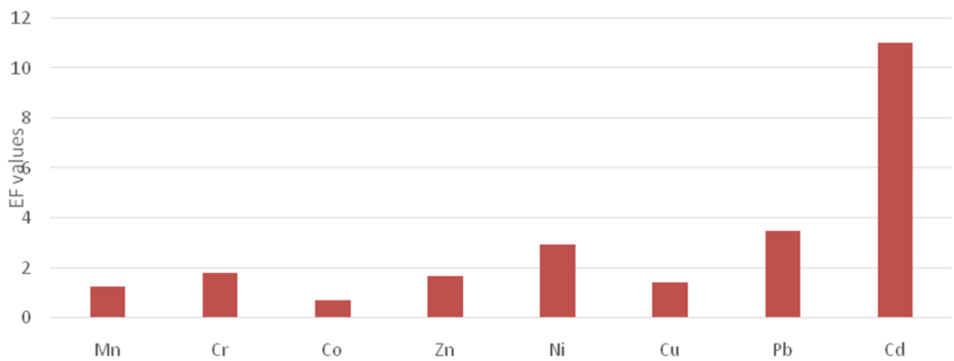

Fig. 2. Mean values of the Enrichment Factor

3.2. Contamination Factor (CF) and Pollution Load Index (PLI)

The Contamination Factor was calculated using the eq.2 (Tomlinson et al., 1980) (Table 6). The level of metal contamination has been determined by using the (CF) where Cm is concentration, which may be computed as follows:

$$CF = Cm_{\text{Sample}} / Cm_{\text{Background}} \quad (2)$$

Table 6. Categories of the studied sediment pollution according to the grading of the CF and PLI indices after (Tomlinson et al.,1980)

CF	PLI
	< 1 Perfection (class 0)
< 1 Low contamination (class 1)	= 1 Baseline Level (class 1)
1≤CF< 3 (class 2), Moderate contamination	> 1 Deterioration on site quality (class 2)
3≤ CF ≤6 (class 3), Considerable contamination	
> 6 Very high contamination (class 4)	

In the Al-Gharraf river, the contamination factor (CF) was determined for manganese, chromium, cadmium, cobalt, zinc, nickel, copper, and lead, and the results are provided in Table 7. The PLI is a quick and easy way to evaluate the quality of a site quality. The pollutant load index was derived using the equation below (Tomlinson et al., 1980), where (PLI) is expressed as:

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times \ldots \times CFn} \quad (3)$$

Where: CF1 is the first contamination factor, n is the total number of study metals at each location (Table 7) and (Fig. 3). In the area bordered by the AlGharaf River, the PLI (Pollution Load Index) for Manganese, Chromium, Cadmium, Cobalt, Zinc, Nickel, Copper, and Lead was calculated, and the results are currently in the (Table 7). PLI scores in the Al Gharaf river sites range from 0.85 to 1.34, indicating local pollution and being classed as well as class 0 to class 2 “Perfection to Deterioration on site quality.

Table 7. CF and PLI values of HMs in sediments of the Al-Gharraf river

Site	Mn	Cr	Cd	Co	Zn	Ni	Cu	Pb	PLI
S1	0.57	0.98	4.45	0.13	0.85	1.52	0.72	0.94	0.85
S2	0.65	0.99	7.00	0.32	0.86	1.77	0.75	2.36	1.18
S3	0.56	0.91	4.90	0.45	0.72	1.32	0.61	1.30	0.98
S4	0.75	0.84	4.55	0.37	0.71	1.16	0.57	1.24	0.94
S5	0.72	0.85	5.50	0.42	0.86	1.38	0.77	1.89	1.12
S6	0.73	0.97	6.50	0.31	1.01	1.63	0.83	2.30	1.21
S7	0.73	0.99	7.00	0.50	1.05	1.81	0.88	2.42	1.34
Mean	0.67	0.93	5.70	0.35	0.86	1.51	0.73	1.75	1.09

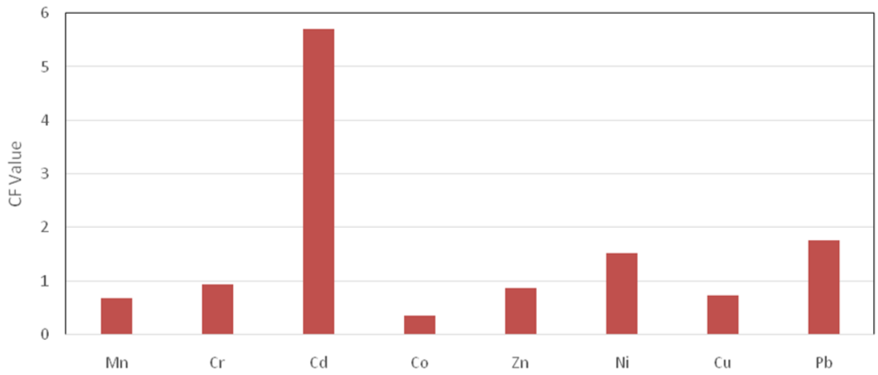

Fig. 3. Values of CF and PLI in sediments of Al Gharraf River

3.3. Geo Accumulation Index (Igeo)

When it comes to the concentrations of elements in the two-part micron range, the I-geo was principally described by (Muller, 1979). This guide is written in the following format:

$$I\text{-}geo = \log_2 (Cn / 1.5 * Bn) \quad (4)$$

1.5 it the constant for anthropogenic effects and variations in environmental material Bn: geochemical background value, Cn: element concentration measured in the soil. Geo-accumulation Index has seven levels, Ranging from "Class 6, I-geo > 5, extremely contaminated" to Class 0, I-geo =0 completely clean (Table 8).

Table8. The values of the geo accumulation factor (Igeo) depend on (Muller, 1981)

Value	Class	Soil contamination
I-geo ≤ 0	0	Uncontaminated
0 < I-geo < 1	1	Uncontaminated to moderately
1 < I-geo < 2	2	Moderately
2 < I-geo < 3	3	Moderately to heavily
3 < I-geo < 4	4	Heavily
4 < I-geo < 5	5	Heavily to extremely
I-geo ≥ 5	6	Extremely

The sequence of HM I-geo Accumulation index values in Al-Gharraf river sediments was Ni<Cr<Zn<Cu<Mn<Co<Pb<Cd (Table 9 and Fig. 4).

Table 9. The values of pollution assessment of geoaccumulation factor in the Al-Gharraf river sediments.

Metals Site	Mn	Cr	Co	Zn	Ni	Cu	Pb	Cd
S.1	- 1.38	- 0.64	- 3.50	- 0.81	0.02	- 1.04	- 0.66	1.56
S.2	- 1.18	- 0.59	- 2.24	- 0.79	0.24	- 0.99	0.65	2.22
S.3	- 1.39	- 0.72	- 1.73	- 1.06	- 0.18	- 1.30	- 0.20	1.71
S.4	- 1.39	- 0.83	- 2.02	- 1.08	- 0.37	- 1.40	- 0.27	1.60
S.5	- 1.05	- 0.81	- 1.85	- 0.80	- 0.12	- 0.95	0.33	1.87
S.6	- 1.04	- 0.61	- 2.26	- 0.57	0.12	- 0.85	0.62	2.11
S.7	- 1.02	- 0.60	- 1.58	- 0.51	0.26	- 0.76	0.69	2.22
Mean	- 1.21	- 0.68	- 2.16	- 0.80	- 0.03	- 1.04	0.16	1.89

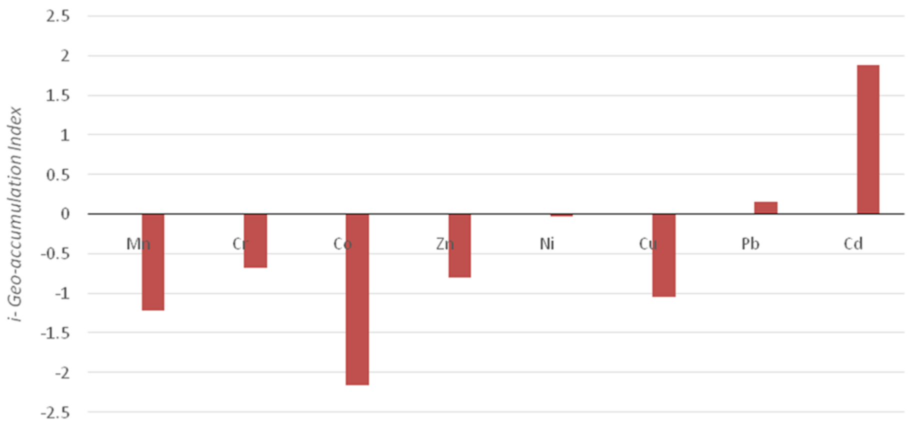

Fig.4. Mean values of I-geo

4. Results and Discussion

It's critical to understand the typical grade of HMs before evaluating the quantity of HMs in sediments of AL Gharraf River in Wasit Province. Anthropogenic sources like as sewage and solid waste firms can introduce HMs into the water supply. However, utilizing the EF as a working instrument to estimate the amount of metal pollution in the soil (Franco-Uria et al., 2009) (Table 10). Cd enrichment factors EF= 11.02 in the AL Gharraf River sediments have a significant human impact (Table 10), respectively. Pb and Ni have Moderate Enrichment (EF values of 3.48 and 2.95, respectively), but Mn, Cr, Co, and Zn have "Deficiency to Minimal" Enrichment (EF values of 1.28, 1.81, 0.70, and 1.96, respectively), showing effects of irrigation, phosphate fertilizers, and sewage sludge (Kabata-Pendias and Mukherjee, 2007). Also, Ali et al. (2021) illustrated that there was an increase in the concentration of HM (Co, Ni, Cd) in the sediments as a result of the proximity of the study area to oil industries activities, causing the emission of high concentrations of heavy elements.

Table 10. Metals in Al Gharraf River Sediments: Mean and Range of EF Values and Category

HM	**Al Gharraf River Sediments, EF value**		**Category**
	Mean	**Range**	
Mn	1.28	1.07 - 1.52	Deficiency to minimal enrichment
Cr	1.81	1.72 - 1.88	Deficiency to minimal enrichment
Cd	11.02	8.27 - 13.3	Significant enrichment
Co	0.70	0.24 - 0.95	Deficiency to minimal enrichment
Zn	1.69	1.51 - 1.95	Deficiency to minimal enrichment
Ni	2.95	2.47 - 3.36	Moderate enrichment
Cu	1.42	1.21 - 1.64	Deficiency to minimal enrichment
Pb	3.48	1.75 - 4.51	Moderate enrichment

Heavy metals of cadmium have contamination values of 5.70, indicating that these metals are above their background "Considerable Contamination Class3" and represent anthropogenic inputs as well as discrete external sources such as industrial activity and runoff from agriculture. While Ni and Pb heavy have Values of contamination factor of 1.51and 1.75, respectively, suggesting that these metals are significantly more valuable than the average "Moderate Contamination Class2" and take into account both man-made and natural sources Mn, Co, Cr, and Zn HM have contamination factor values of 0.67, 0.93, 0.35, and 0.86, indicating that these metals are "Low Contamination Class1" and take into account both man-made and natural sources (Table 11). The mean of PLI1.09 reflects Deterioration on site quality (Class 2). The action of sediments could explain the increased values of the PLI component in the Al-Gharaf river of automobile oil spillage. In addition to the consequences of untreated toxic waste discharged into the study area's main rivers by businesses, some anthropogenic activities damaged the soil with Pb, Ni, and Cd.

Table 11. Enrichment Factor Values and Category of the Heavy Metals in Sediments of Al Gharraf River.

HM	**CF value of Al Gharraf River Sediments**		**CF Category**
	Mean	**Range**	
Mn	0.67	0.56- 0.75	Low contamination class1
Cr	0.93	0.84- 0.99	Low contamination class1
Cd	5.70	4.45- 7.00	Considerable contamination class3
Co	0.35	0.13- 0.50	Low contamination class1
Zn	0.86	0.71- 1.05	Low contamination class1
Ni	1.51	1.16- 1.81	Moderate contamination class2
Cu	0.73	0.57- 0.88	Low contamination class1
Pb	1.75	0.94- 2.42	Moderate contamination class2

Sediments of the Al Gharraf River were found to be free of Mn, Cr, Co, and Ni contamination. Cu and Zn contamination ranges from moderately contaminated to uncontaminated and moderately polluted by Pb and Cd contamination (Table 12).

Table 12. Mean and Range of I-geo values as well as metal grades in Al-Graaff River

HM	I-geo value of Al Gharraf River Sediments		I-geo grade of contamination
	Mean	**Range**	
Mn	-1.21	-1.39- -1.02	Uncontaminated
Cr	-0.68	-0.83- -0.59	Uncontaminated
Cd	1.89	1.56- 2.22	Moderately
Co	-2.16	-3.50- -1.58	Uncontaminated
Zn	-0.80	-1.08- -0.51	Uncontaminated
Ni	-0.03	-0.37- 0.26	Uncontaminated
Cu	-1.04	-1.40- -0.76	Uncontaminated
Pb	0.16	-0.66- 0.69	Uncontaminated to moderate

5. Conclusions

Concentrations of heavy metals including Mn, Cr, Co, Cd, Zn, Ni, Cu, and Pb in the Al-Garraf River have been connected to significant clay contamination in the studied sediments, as well as spills of oil, gasoline, and volatile odors from neighboring oil wells (Al-Ahdab Oil Field). Obviously, the contamination had a greater impact on sites with a relatively high clay component of sediments than on sites with relatively high sand content. Percentage of total sediment These locations are in the direction of the winds, which transfer pollutants to them and the effect of volatile vapors from the field. According to the findings, sediment contamination with these HMs is thought to come from a variety of sources, including urban, petroleum, and industrial waste, effluent, and erosion.

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