Environmental pollution assessment of trace elements in the exchangeable and residual fractions of core samples in Khor Al-Zubair sediments

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Abstract

Heavy metals residue phase in sediments from five sites (including ten depths for each site) located in Khor Al-Zubair, southern Iraq were evaluated using this investigation. Investigations for ICPOES and FA for determination of their respective concentrations like Cd, Cr's, Cu, Fe (Iron), Mn, Na (sodium), Pb (latenum), Si (Silicon) s and for Zn(zinc). Contamination was assessed, and anthropogenic sources were identified using geochemical indices. The results indicated that cadmium (Cd), and zinc (Zn) are the most important pollutants in residual phase with extremely higher CF-value and EF-values as well as positive Igeo indices, mainly at Site 4 by substantial industrial inputs besides petroleum contaminants. Lead (Pb) and vanadium(V) showed moderate enrichment, while manganese (Mn), chromium (Cr), copper(Cu), iron(Fe), sodium(Na) and silicon(Si) predominantly gave Igeo < 0, remaining under the basal crust. At the spatial scale Sites 2, 4 and 5 were hot spots of contamination whereas the low values at Site 3 were attributed to hydrodynamic strength and distance from industrial inputs. This residual-bank phase, in contrast with the more labile one, hinges its focus on long-term accumulation processes and enables a better understanding of contamination dynamics. This could lead to remobilization into the aquatic environment, as well as bioaccumulation along the food chain which would imply that high concentrations of Cd, Zn and Pb may be released. Such findings highlight a very important need for continuous monitoring and regulation of discharges from industrial and marine environments, as well as treatment options, to ensure ecosystem and public health in southern Iraq.

Keywords: Heavy metals contamination, Sediment geochemistry, Khor Al-Zubair, Heavy Metals, Environmental pollution assessment

Introduction

Pollution is often defined as the introduction of harmful materials or contaminants into the environment that cause adverse alterations to its physical, chemical, or biological characteristics affecting ecosystems and living organisms [1]. Heavy metals are considered a significant group of environmental pollutants with regard to their toxicity, long-term stability and accumulation in sediments and soils **[2]**. While some of these compounds, including iron, zinc and copper are required for biological purposes at trace levels, they turn into toxic pollutants when they reach higher levels interfering with physicochemical or the biological status in ecosystems **[3].**

Environmental deterioration in Iraq, especially Basra Governorate, has increased due to population increase, industrial expansion and activities related to the oil production **[4]**. Municipal wastes, industrial discharges and petroleum byproducts are the most significant sources of heavy metal pollution in aquatic ecosystems **[5].**

Khor Al-Zubair, in southern Iraq, is one of the country's primary waterways and a key gauge for navigation as well as industry and oil transit. But doing so has put increasing environmental pressures, placing it at high risk of accumulating heavy metals in sediment **[6].**

Despite having ecological and economic implications, little is currently known about the distribution and concentration of heavy metals in Khor Al-Zubair sediments. Plasma (ICP) have been applied to assay trace element levels of cadmium, chromium, copper, iron, manganese and sodium lead silicon vanadium zinc. Geochemical measures including the contamination factor (CF), enrichment factor (EF), and geo-accumulation index (Igeo) are used to assess the contamination condition and confine natural vs anthropogenic signals.

Generally, the objective of this study is to evaluate heavy metal concentrations in five studied stations of Khor Al-Zubair, southern Iraq and identify their sources and potential origins thus providing a scientific basis for assessing impacts on environment and planning pollution abatement plans in region.

Material and Methods

Description of the study area:

The northwest Arabian Gulf's Khor Al-Zubair port is an important marine gateway for Iraq. It is used for navigation, industry, fishing and oil transportation in Iraq, but also tend to various sedimentation processes that need continuous dredging to ensure proper functioning and safety of the navigational channels **[7].** Khor Al-Zubair is a natural outlet body of water located in the southern Iraq with an area of such that it extends to some 42 km. The channel varies in width from approximately 1 to 3 km and in water depth from about 10 to 20 m depending on location.

Continuous dredging is required to maintain safe navigation channels due to sedimentation processes. The Khor Al Zubair port is geographically located in southern Iraq at approximately 28°11′30″N, 48°57′12″E, about 60 km southwest of Basra city, within the Mesopotamian plain and Arabian Gulf coastal zone **[8].** According to the regional tectonic framework, the research area is located on the Arabian Plate's unstable shelf zone in the Mesopotamian plain **[9].**

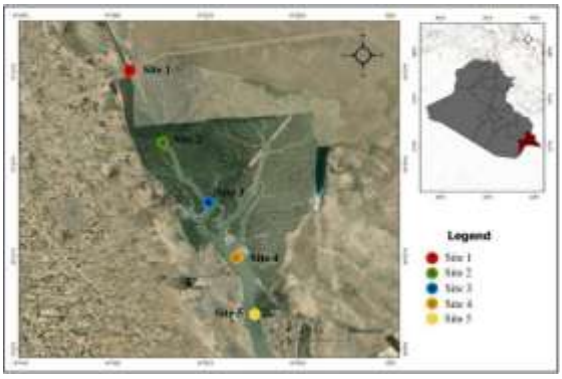

Fig. 1. Map showing the location of the sampling area in southern Iraq.

Table .1 locations, the research area's latitude and longitude.

Latitude	Longitude	Site
30° 20'04.5"	47° 48'44.1"	1
30° 16'57.4"	47° 50'09.6"	2
30° 14'22.3"	47° 52'08.6"	3
30° 11'57.8"	47° 53'20.1"	4
30° 09'31.2"	47° 54'08.6"	5

Methodology

Fieldwork:

Sediment samples were collected from the Khor Al-Zubair area at five sites, with a distance of approximately 3 km between each site. A tube was used to collect the samples at a depth of one meter. From each location, three samples were gathered, put in plastic bags, and brought to the lab.

Laboratory work:

After the samples were collected from the study sites and subsequently transferred to the laboratory, they were air-dried. Thereafter, the samples were ground using an electric mill and sieved through a metal sieve with 63 mesh openings, in order to prepare them for subsequent analysis.

Extraction of Residual Fraction:

For the extraction of the residual fraction of heavy metals, 0.5 g of soil was taken and 40 ml of distilled water was added. Then, 5 ml of HF was added and the residue dissolved with the aid of H2O and transferred into a Teflon container after cleaned. Then the solution was evaporated to near dryness, and treated with a 1:1 hydrochloric acid/perchloric acid mixture. After adding distilled water to get the amount up to 50 ml, the produced solution was put into plastic bottles so that Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) could measure it.

Conversion of concentration units:

Concentrations of analyzed elements determined by ICP-OES were expressed in µg g⁻ ¹ on a dry weight basis. Given 1 µg g⁻ ¹ is similar to 1 part per million (ppm), all elemental concentrations were considered as ppm values before the geochemical indices calculations. We converted the mg/kg concentrations to µg/m2/yr values for consistency with background crustal data used in CF, EF and Igeo equations. To ensure methodological consistency and comparability with environmental geochemical studies published previously, all calculations were conducted on concentrations reported in ppb.

Determination of Contamination Factor (CF):

The research region's soil contamination level was assessed using the Contamination Factor (CF) (Table 1). The CF is expressed using the equation **[10].**

$$\mathrm{CF} = \mathrm{Mc}/\mathrm{Bc} \qquad (1)$$

Where: Mc: Measured concentration of the metal. Bc: Background concentration of the same metal.

Table 2. The classification of contamination factor [10].

Indication of Contamination	CF Value

Low contamination	CF<1
Moderate contamination	1 ≤ CF ≤ 3
Considerable contamination	3 ≤ CF<6
Very high contamination	CF>6

Determination of Enrichment Factor (EF):

Enrichment Factor (EF) Index (Table 2) was calculated to assess contribution from anthropogenic sources in relation to normal crustal extract of samples **[11].** EF is determined by the formula:

$$\mathrm{EF} = \left(\frac{\mathrm{CM}}{\mathrm{CFe}}\right)\mathrm{Sample}\ \left(\frac{\mathrm{CM}}{\mathrm{CFe}}\right)\mathrm{Crust} \qquad (2)$$

Where: CM/CFe: Ratio of trace metal concentration to Fe in the sample. (CM/CFe)crust: Reference ratio in the Earth's crust. Because of its immobility and dominance in the crust, Fe (5.2%) was chosen as the reference element.

Table 3. The classification of enrichment factor (EF) [11].

Indication of Enrichment	EF Value
No enrichment	EF<1
Minor enrichment	1–3
Moderate enrichment	3–5
Moderate to severe enrichmer	5–10
Severe enrichment	10–25
Very severe enrichment	25–50
Extremely severe enrichment	EF>50

Determination of Geo-Accumulation Index (Igeo):

The Geo-Accumulation Index (Igeo) (Table 3) was used to assess the extent of metal contamination in the soils **[12].** The following formula may be used to get it:

$$\mathrm{Igeo} = \log 2\left(\frac{\mathrm{Cn}}{1.5\mathrm{Bn}}\right) \qquad (3)$$

Where: Cn: Measured concentration of element n in the soil. Bn: Background concentration of element n. The constant 1.5 accounts for possible variations in background values due to lithogenic effects.

Table 4. The classification of (Igeo) [12].

Soil Pollution Case	Igeo Value
Practically unpolluted-(background)	<1
Unpolluted to moderately polluted	1–2
Moderately polluted to polluted	2–3
Strongly polluted	3–4
Strongly to extremely polluted	4–5
Extremely polluted	>5

Results and discussion

The concentrations of trace elements in the residual fraction are presented in Table 5 and expressed in $\mu g\ g^{-1}$ (equivalent to ppm).

Table 5. Average concentrations of Residual ions ($\mu g\ g^{-1}$, Dry Weight) in soil samples from Khor Al-Zubair.

Site 5	Site 4	Site 3	Site 2	Site 1	Element
1.43	3.495	1.176	1.642	1.489	Cd (Cadmium)
81.198	121.125	69.872	86.272	92.157	Cr (Chromium)
43.929	49.101	42.915	46.162	34.708	Cu (Copper)
7959.709	9790.525	8167.078	9502.987	34.708	Fe (Iron)
345.073	414.99	297.258	369.085	301.025	Mn (Manganese)
1998.261	2084.156	2271.482	1847.808	1848.68	Na (Sodium)
12.332	30.296	6.496	27.701	10.865	Pb (Lead)
15173.551	22177.82	21513.755	2708.024	14961.247	Si (Silicon)
18.523	20.121	14.516	8.652	4.624	V (Vanadium)
76.185	1661.388	57.312	69.191	58.6	Zn (Zinc)

1. Cadmium (Cd): Cadmium, geochemically active pico-elements (hcn), are removable at a concentrations of 1.17–3.50 **µg g**$^{-1}$ (i.e., much higher than the values indicated). The lowest Site 4 (3.495) result could signal legacy industrial input or legacy environmental accumulation.

2. Chromium (Cr): With higher concentrations (69.87–121.13 **µg g**^{1}) suggesting that the residual phase has a high natural prevalence. The outliers at Site 4 show the highest concentrations, potentially indicating rich deposits of chromium or past pollution.

3. Copper (Cu): By these postulations, the medium concentrations (34.71–49.10 **µg g**$^{-1}$) indicate that copper is a relative stable form in sediments. The variation among sites suggests differences in sources of copper or sediment composition.

4. Iron (Fe): For Fe, the residual phase has very high concentrations (7959–9790 **µg g**$^{-1}$) due to silicate and oxide correlations. –highlight anomalous value, site 1 is low (34.71), and replace to sampling anomaly or unique lithology.

5. Manganese (Mn): Moderate to high concentrations (297–415 **µg g**$^{-1}$) 22929574 indicative of manganese bound in stable oxide forms. The peak (Site 4) represents oxide-rich depositional environment.

6. Sodium (Na): Concentrations were elevated (1847–2271 **µg g**$^{-1}$) and are possibly associated with clay minerals or feldspars. Site 3 displays the maximum value, possibly affected by marine contribution or mineralogical diversities.

7. Lead (Pb): Lead was present in stable minerals forms at lower to moderate concentrations (6.50–30.30 **mg kg**$^{-1}$). Once again, Site 4 has the highest value and this may

be a reflection of historical industrial activity or accumulation over time.

8. Silicon (Si): The concentration (2708–22178 **mg kg^{-1}**) type of silicate-rich sediment is very High. Also, a very low in site 2 can be an evidence of clay enrichment or loss of quartz fraction.
9. Vanadium (V): The uniform enhancements at all sites (4.62–20.12 **mg kg^{-1}**) suggest incorporation of vanadium into stable matrix of minerals. The highest Site value, pertaining to vanadium-bearing clays or oxides, is shown above.
10. Zinc (Zn): Variable (57.31–1661.39 **mg kg^{-1}**) with an outlier at Site 4 peak potentially due to anthropogenic input or localized increase in resistant zinc frames.

Concentration analysis revealed that Khor Al-Zubair has high concentration of heavy metals (Cr, Pb and Zn) at some sites positive in light of current SQGs indicating the legacy effect industrialization activity is a critical importance to coastal environments and even geochemically inert play an imminent role in long-term ecological threats to coastal environment **[13].**

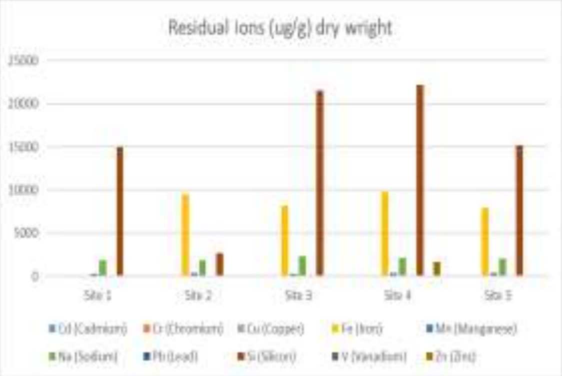

Fig. 2. Histogram of average exchangeable ion concentrations (μg/g, Dry Weight) in soil samples from Khor Al-Zubair.

Evaluation of soil contamination by heavy metals based on the Contamination factor (CF):

The contents of heavy metals in soil, such as cadmium, chromium, copper, iron, manganese, sodium, lead and vanadium were assessed based on the Contamination Factor (CF) (Table). The ratio of the observed element concentration in the samples to its natural background value in soil was used to standardize this indicator according to the method proposed by **[14].**

Table 6. Classification [14]

CF Value	Pollution Degree
CF<1	Low contamination
1<CF<3	Moderate contamination
3<CF<6	High contamination
CF>6	Very high contamination

Highly Polluted Elements (High CF)

- **Cadmium (Cd):** Elevated values at **Site 4**, due to its proximity to industrial and residential areas, leading to accumulation from industrial discharges and shipping activities.

- **Lead (Pb):** High values at **Site 4**, linked to nearby human and industrial pollution sources, where lead can be easily mobilized into the aquatic environment.
- **Zinc (Zn):** Elevated values at **Sites 4 and 5**, associated with the accumulation of industrial and urban discharges at the end of the channel, which enhances zinc deposition in sediments.

Limited Pollution Elements (Low CF):

- **Chromium (Cr):** Generally low values, with a relative increase at **Site 4** due to industrial discharges and metallurgical waste.
- **Copper (Cu):** Limited values, with a relative increase at **Site 3** influenced by shipping activities and corrosion of marine structures.
- **Iron (Fe):** No significant contamination observed, reflecting the natural background of sediments away from direct human influence.
- **Manganese (Mn):** Limited values, with some increases at **Site 5** due to accumulation of discharges at the channel's end.
- **Sodium (Na):** Limited contamination, with variations linked to natural processes such as evaporation and salt accumulation at the beginning of the channel.
- **Silicon (Si):** Generally low values, reflecting the mineralogical nature of silicate-rich sediments rather than anthropogenic inputs.
- **Vanadium (V):** Limited values, with some increases at **Site 5** due to continuous deposition of mineral inputs.

Table 7. The Contamination Factor (CF) of trace metals.

Site 5	Site 4	Site 3	Site 2	Site 1	Elements
9.53	23.3	7.84	10.95	9.93	Cd
0.81	1.21	0.7	0.86	0.92	Cr
0.88	0.98	0.86	0.92	0.78	Cu
39.8	48.95	40.84	47.51	0.17	Fe
0.43	0.52	0.37	0.46	0.38	Mn
1	1.04	1.13	0.92	0.92	Na
1.41	3.47	0.75	3.18	1.25	Pb
0.05	0.07	0.07	0.01	0.05	Si
0.52	0.57	0.41	0.24	0.13	V
1.27	27.69	0.95	1.15	0.97	Zn

Heavy Metals Contamination of Soil Using Enrichment Factor (EF):

The calculation of heavy metal enrichment factors (EF) in soil including Cd, Cr, Cu, Fe, Mn, Na, Pb Si and V is presented in Table 6. The EF is applied here to ascertain the degree to which anthropogenic contributions are responsible for the accumulation of these elements, by comparing metal concentrations within aerosols-paste relative to a single reference element (Fe) versus those from natural sources. These results were classified according to the method proposed by **[15].**

Table 8. Classification [15].

EF Value	Enrichment Level
EF<1	No enrichment
EF = 1–3	Minor enrichment
EF = 3–5	Moderate enrichment
EF = 5–10	Moderate to severe
EF = 10–25	Severe enrichment
EF = 25–50	Very severe enrichment
EF>50	Extremely severe

Highly Polluted Elements:

- **Cadmium (Cd):** Elevated values were recorded at **Site 4**, due to its proximity to industrial and residential areas, which contributes to the accumulation of industrial discharges and shipping activities.
- **Manganese (Mn):** High values appeared at **Sites 3 and 4**, reflecting the influence of human activities and industrial discharges, as well as pollutant accumulation in the mid-channel areas.
- **Lead (Pb):** Elevated values were observed at **Site 4**, linked to nearby human and industrial pollution sources, where lead can be easily released into the aquatic environment.
- **Zinc (Zn):** High values were found at **Sites 4 and 5**, associated with the accumulation of industrial and urban discharges at the end of the channel, which enhances zinc deposition in sediments.
- **Vanadium (V):** Elevated values were recorded at **Site 5**, likely due to industrial influences and continuous deposition of mineral inputs at the channel’s end.

Limited Pollution Elements:

- **Iron (Fe):** No significant enrichment was observed, reflecting the natural background of sediments away from direct human influence.
- **Sodium (Na):** Values remained limited, with variations mainly linked to natural processes such as evaporation and salt accumulation at the beginning of the channel.
- **Silicon (Si):** Generally low values, reflecting the mineralogical nature of silicate-rich sediments rather than anthropogenic inputs.
- **Copper (Cu):** Limited enrichment, with a relative increase at **Site 2** due to shipping activities and corrosion of marine structures.
- **Chromium (Cr):** Mostly low values, with a relative increase at

Site 4 attributed to industrial discharges and metallurgical waste.

Table 9. Enrichment Factor (EF) of trace metals.

Site 5	Site 4	Site 3	Site 2	Site 1	Elements
4766	11651	3919	5473	4964	Cd
3.41	5.08	2.93	3.62	3.89	Cr
3.12	3.49	3.05	3.28	2.47	Cu
39.8	48.95	40.84	47.51	0.17	Fe
2.64	3.18	2.28	2.82	2.3	Mn
1	1.04	1.13	0.92	0.92	Na
2.07	5.09	1.1	4.79	1.89	Pb
1.36	1.99	1.93	0.24	1.33	Si
262	287	207	124	66.44	V
8.3	180	6.2	7.5	6.3	Zn

Evaluation of Heavy Metal Contamination in Soils Using Geo-Accumulation Index (I-geo):

Geo-accumulation index (I-geo) was used in analyzing soil heavy metals pollution including Cd, Cr, Cu, Fe, Mn, Na,Pb2, Si,V and Zn (Table 10). This index rates the air concentration in terms of natural background and classifies it from not polluted to extremely polluted **[16].**

Table 10. Classification [16].

I-geo Value	Pollution Category
<1	Unpolluted
1–2	Unpolluted to moderately polluted
2–3	Moderately polluted
3–4	Strongly polluted
4–5	Strong to very strong pollution
>5	Extremely polluted

Highly Polluted Elements (High I-geo):

- **Cadmium (Cd):** High values at Site 4, indicating strong impact of industrial and shipping action causing cadmium build-up.
- **Lead (Pb):** In Site 4, higher values are linked to nearby industrial and human contacts that promote lead deposition.
- **Zinc (Zn):** High values at Sites 4 and 5 from industrial and urban inputs at the channel's end.

Limited or Background Pollution Elements (Low I-geo):

- **Chromium (Cr):** Overall low values mesoforigaleb, but slight increases at Site 4 due to local metallurgical and industrial cpuins.
- **Copper (Cu):** Site 2 and Site 3 exhibit relative increment due to shipping activities and corrosion of marine structures.
- **Iron (Fe):** No pronounced geoaccumulation was detected,

indicating the sediment levels were within natural background values.

- **Manganese (Mn):** Lower values, with only moderate increases at Site 5 from discharges accumulated to the end of the channel.
- **Sodium (Na):** Generally low values, with variations characteristic of natural processes like evaporation and salt deposition at the channel upstream.
- **Silicon (Si):** Preindustrial and low, indicated the mineralogical composition of silicate-rich sediments rather than anthropogenic overloading.
- **Vanadium (V):** Values are limited due to further mineral inputs were continuously added at Site 5.

Table 11. The geochemical accumulation coefficient (I-geo) of trace metals concentration.

Site 5	Site 4	Site 3	Site 2	Site 1	Elements
2.63	3.88	2.23	2.86	2.69	Cd
-0.77	-0.41	-1.12	-0.86	-0.81	Cr
-0.79	-0.69	-0.86	-0.74	-0.98	Cu
5.32	5.61	5.36	5.57	-3.3	Fe
-2.08	-1.82	-2.33	-2.04	-2.3	Mn
-4.17	-4.11	-3.97	-4.34	-4.34	Na
-0.49	0.37	-1	0.63	-0.58	Pb
-5.58	-5	-5.02	-7.44	-5.61	Si
-3	-2.91	-3.27	-3.78	-4.54	V
0.34	3.62	-0.07	0.2	-0.04	Zn

Conclusions

The heavy metal distribution in Khor Al-Zubair sediments indicates that, according to the bioavailability assessment, cadmium (Cd) and zinc (Zn) are considered most important pollutants with very high contamination factor and extreme enrichment values and positive geo-accumulation index at Site 4 which confirms industrial and petroleum pollution hotspot. Moderate to strong enrichment of lead (Pb) and vanadium (V) is also observed at some specific sites suggest anthropogenic contribution from industrial emissions and navigation activities, while chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), sodium (Na) and silicon Si remains unaffected rising largely by their natural geochemical background having negative Igeo values. Geographically, Sites 2, 4 and 5 are areas with concern based on hydrodynamic limitations and anthropic influences, while Site 3 was characterized by a more diluted record of contamination as a function of lower flow velocity and distance neighboring to industrial companies. By contrast, the residual phase emphasizes long-term accumulation processes, which complements information on more recent pollution inputs gained from analysis of the exchangeable phase and provides a fuller overview of fate processes. This study is significant environmentally as the high levels of Cd, Zn and Pb found here may lead to remobilization into the water column and bioaccumulation into the food chain, indicating a great ecological risk with unpredictable health hazards in southern Iraq that need periodic monitoring, more stringent regulation of industrial/maritime discharges and tailored remediation action for protecting aquatic systems and human health.

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