



## Use of Sequential Extraction Methods to Evaluate the Environmental Impact of Trace Metal in the Iraqi Coastlines

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**Abstract:** The geochemical distribution of several trace metals (lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni), chrome (Cr), cobalt (Co) and iron (Fe)) was investigated using five sequential extraction procedures to provide information on their distribution and environmental impacts on the Iraqi coastal sediments. Sediment samples were collected from 16 sites along the coast to determine the concentrations of the above metals. The concentration and ratios of these metals were estimated in the sediment extract (concentration on the exchange surfaces, carbonates, manganese oxides and iron oxides, organic matter and those associated with the remainder) using extraction methods (magnesium chloride, 1 molar of sodium acetate, 0.5 molar of hydroxylamine hydrochloride, 0.2 molar of ammonium oxalate, concentrated nitric acid and 25% of hydrofluoric acid) to extract and separate the above fractions in order. The results indicated that the total sediment content of Pb and Cd were higher than their rate of occurrence in the crust, while copper, zinc, nickel, chrome, cobalt and iron were within those limits. According to the I-geo the metals Cr, Cu and Zn are considered at unpolluted class while Ni and Pb were ranged from moderately to strongly level. On the other had Cd was found at extremely level as its I-geo exceeded the highest-class value. These metals are bonded to different power bonds. Pb, Cr and Co have dominant in exchangeable and carbonates fraction. Iraqi tidal flats is characterized by very high risk considering Cr, Pb, Co and Cu which represented by RAC values, so they can move to the solution to become available for living.

**Keywords:** Costal sediments, Geochemical distribution, Iraq, Sequential extraction, Trace metals.

## Introduction

Many trace metals in the Iraqi surface water and sediments are resulted from human activity including the waste of sewage discharged directly into rivers whether by individuals or by factories located on river banks such as fertilizers, power stations, oil refinery, pesticides, organic fertilizers, plant residues and heavy sewage, especially in

inland rivers (Hassan *et al.*, 2008; Abdulnabi, 2016). Dust is also considered as a main source of elements. Many studies suggested that dust in the southern regions of Iraq is contaminated with trace metals and control their presence in the components of the earth's crust (Hassan, 2011; Hassan *et al.*, 2017). These metals are associated rapidly with the sediment

throughout their absorption by surface particles being part in precipitation processes and their incorporation into biogenic material (Gargouri *et al.*, 2011). Trace metals are moved toward estuaries and coastal environments through rivers, runoff, and land-based point sources. They are thought to be significant pollutants when the levels exceeding the acceptable limit. (Abdulnabi *et al.*, 2019). Sediments have a high ability to absorb trace metals, so the latter are not available in the environment as raw materials. However, changes in chemical and physical properties (such as pH, salinity, dissolved oxygen, oxidation reduction potential, etc.) give a chance to those metals to return into the water environment. That's why sediments is considered as important sources of metals in the environment (Hassan *et al.*, 2011 Abdulnabi, 2016).

Total concentration of trace metals cannot give a clear explanation of the ecological and environmental impact of the element's behavior on sediments (Hassan *et al.*, 2008). The process of elements' movement and their transition depends on the nature of their association. Sediment separators depend on the migration and transformation process, biological toxicity and bioavailability of trace metals in the sediment which mainly depend on the fractionation of trace metals (Hassan *et al.*, 2008; Alimohammad Kalhori *et al.*, 2012). Single and sequential extraction methods have been widely applied to characterize the impact of element behavior in sediments (Galán *et al.*, 2003).

The extraction methods have been developed for the optional displacement of elements from different facets by gradually increasing the strength of the extraction solutions while increasing the bond strength of the elements with the sediments (Tessier *et al.*,

1979). In the first fraction, trace metals associated with the exchange sites, the absorption of trace elements on the surfaces of clay minerals, carbonates, organic, changes in chemical water composition may affect sorption-desorption processes, which is a non-specific adsorption on surfaces. For the second fraction the significant concentrations of trace metals can be associated with sediment carbonates, this portion is subject to changes in pH (Tessier *et al.*, 1979). The third fraction binding complex Iron, manganese oxides and their hydroxides act as ion stores. It is a well-established condition. These oxides are excellent recovery material for unstable trace elements and thermodynamics reduction conditions (Tessier *et al.*, 1979). The fourth fraction is organic matter. Galán *et al.* (2003) shown in his study that most trace elements are associated with organic matter in the form of organic compounds and different strengths based on the type of the bond. The bonds reduce the toxicity of the elements as a result of obstructing their movement and controlling their bio-chemical in the aquatic environment. The organic matter has a high exchange capacity. It contains effective groups such as carboxyl and phenol groups, which act to bind elements and finally the non-bioavailable the Residual phase (Sarkar *et al.*, 2014).

The residual solid should mainly contain primary and secondary minerals that may contain traces of metals within their crystal structure (Tessier *et al.*, 1979; Okoro *et al.*, 2012; Matabane *et al.*, 2021).

The Iraqi coastal sediments are potentially exposed to the impacts sourced by river pollutants, and marine pollutants. The aim of this study was to assess the accumulation and spatial distribution of eight trace metals (cadmium, chromium, copper, cobalt, lead, nickel, iron and zinc) and to evaluate the level

geochemically through specific and sequential extraction according to the element bond strength, either on the surfaces exchange and/or organic bonds. Metals availability was used to assess the possible origin and the environmental impact in the sediment samples from Iraqi coast.

## Materials & Methods

### Sampling

The sediment samples were collected from 14 to 17/4/2015 from 16 sites of surface layer (0-

15 cm) along the Iraqi tidal flat of Khor Abdullah and Khor Al-Zubair covering a coastline of about 40 km (Fig. 1). The samples were kept and transported by polyethylene bags the laboratory at the Marine Science Centre, where they were air dried to remove the gravel and impurities. The sediments were sieved by 2 mm sieve. In order to determine the distribution of minerals in sediments fractions. Serial extraction was carried out as described below based on 0.5 g of air-dried sieved sediment sample for each location. Two replicates were taken for each site.

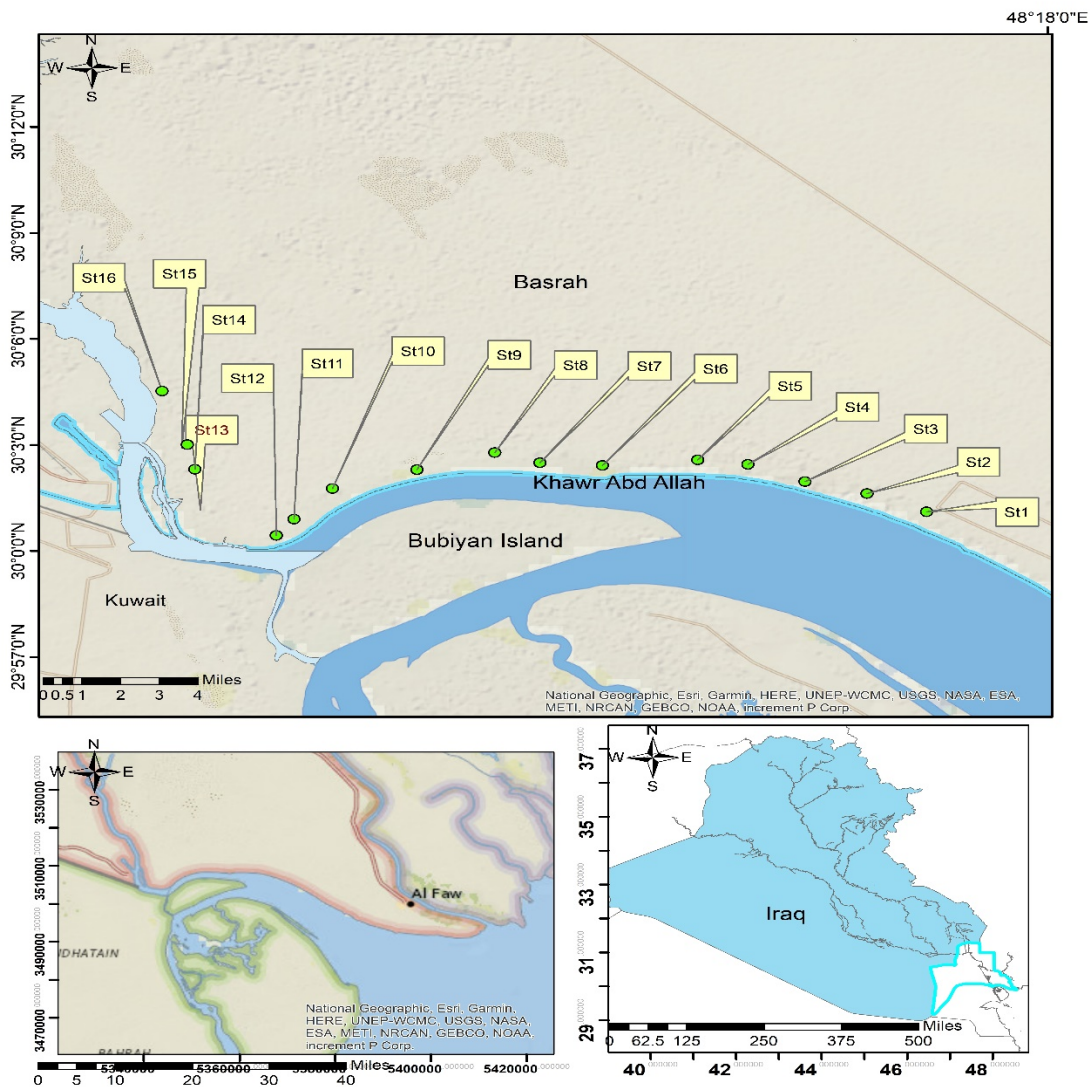


Fig. (1): Sampling stations along the Iraqi coastlines.

### **Sequential extraction methods (SE)**

The procedure adopted was following to Akcay *et al.* (2003). The exchangeable fraction (F1) was extracted at room temperature using 10ml, of 1M MgCl<sub>2</sub>. The pH of 6H<sub>2</sub>O was adjusted to five using nitric acid for one-hour horizontal jab and centrifugal for 10 minutes with 120 rpm for separating the extract from sediment. It was then completed to 25 ml (this process is repeated with each fractions was used) to be ready for measuring the investigated metals: lead, cadmium, copper, zinc, nickel chrome cobalt and iron. Atomic Absorption Spectrometry (AAS) type (Phoenix 986AA) used to determine these metals.

### **Metals associated with carbonates (F2)**

The remaining sediments from the first step were shook (using Shaker of Sartorius-Certomat II- Germany) for 5 h with 10 ml of 1M NaOHAC and pH adjusted to 5 using the HOAC at room temperature (Akcay *et al.*, 2003).

### **Metals associated with the Fe-Mn-oxides (F3)**

The remaining sediment from the second step were extracted at a temperature of 96±1°C with 20 ml of 0.04M NH<sub>2</sub>OH.HCl in 25% (v/v). The samples were centrifuged for 30 min then their sizes was completed to 25ml (Akcay *et al.*, 2003).

### **Metals Associated with the organic material (F4)**

Four ml of 0.02 M HNO<sub>3</sub> and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> (with pH adjusted to 2.0 with HNO<sub>3</sub>) were added to the residual from step 3 then heated for 2 hours at 83 ±1°C. The samples were heated again to 85±2° after adding another 3 ml of 30% H<sub>2</sub>O<sub>2</sub> (with pH adjusted to 2 with HNO<sub>3</sub>), 5ml of 3.2 M NH<sub>4</sub>OAC in 20% (v/v) HNO<sub>3</sub> were added after cooling the

samples. The samples were then diluted to 20 ml and centrifuged for 30 min then their size were completed to 25ml (Akcay *et al.*, 2003).

### **Residual (F5)**

Metals associated with the remaining part (in the crystalline structure of clay minerals) were extracted by taking the deposit from the previous step and a digested acid 12.5 ml of 8M HNO<sub>3</sub> in a water bath for 3 hours at 85°C were diluted and the size was completed to 25ml. (Pagnanelli *et al.*, 2004).

### **Geo-accumulation Index (Igeo)**

The concentration of elements in the earth's crust was adopted as a reference concentration of the elements. The classification proposed by Müller (1979) for the calculation of the Geo accumulation index (I-geo) is as following:

#### **I-geo=log<sub>2</sub>(C.sed/1.5C.earth)**

C. sed: Concentration of the element in sediments.

C. earth: Concentration of the element in the reference sample (earth's crust)

### **Risk Assessment Code (RAC)**

The trace metals are bonded to different power bonds where they can move to the solution to become available for living organisms. RAC evaluates the metals availability in sediments based the metals ratio in exchangeable and carbonates fractions. The ranges of classification presented in table (1) is following Perin *et al.* (1985).

### **Statistical analysis**

One sample t-test was applied to compare between the stations, including standard deviation standard error and mean, using statistical analysis software (*SPSS version 20*). Move to method.

**Table (1): Risk assessment code (RAC) classification Perin *et al.*, 1985).**

Class.	Risk	Metal in exchangeable and carbonate fractions (%)
1	No risk	<1
2	Low risk	1–10
3	Medium risk	11–30
4	High risk	31–50
5	Very high risk	>50

## Results & Discussion

**Total concentration** The means, standard deviations and the means background of trace elements in continental crust are in table (2). The surface sediments indicated that the total of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn were

43.87, 34.01, 98.47, 42.24, 1329.38, 122.05, 159.37 and 74.87 mg/kg respectively. Total concentration of trace metals, which includes all geochemical forms (such as metals in the crystalline structure of Fe-Mn-oxides or clay minerals which are not available in the environment) gave a confusing idea of the expected effect of elements concentration in sediments. However, such measurement is important to estimate the changes generated by different effects for instance (change in natural phenomena like erosion, washing to groundwater, changes in non-natural additives (anthropogenic factors)) that may potentially affect the comparison with the concentration in the earth's crust or the reference samples (Hassan *et al.*, 2008).

**Table (2): The geochemical forms, total concentration of trace metals, mean, Std. deviation and background of trace elements. (F1) Metals associated the exchangeable fraction, (F2) Metals associated with carbonates, (F3) Metals associated with the Fe-Mn-oxides, (F4) Metals Associated with the organic material and (F5) Residual.**

Metals Fraction	Statistic	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
F1	Mean	3.32	8.41	54.26	5.90	18.75	0.04	96.09	1.96
	Std. Deviation	0.33	3.97	17.64	1.68	4.97	0.00	6.94	1.00
F2	Mean	2.60	9.03	27.33	10.91	37.36	21.16	31.65	4.68
	Std. Deviation	0.50	2.30	7.13	5.81	24.75	5.01	5.94	6.60
F3	Mean	11.12	7.30	11.33	10.73	663.72	29.15	10.15	21.36
	Std. Deviation	2.53	2.76	11.16	6.73	29.02	7.05	4.80	12.31
F4	Mean	19.76	0.02	0.00	2.02	0.52	0.15	11.08	12.48
	Std. Deviation	5.16	0.00	0.00	0.90	0.17	0.02	2.72	3.62
F5	Mean	7.07	9.24	5.54	12.66	629.02	71.54	10.39	34.40
	Std. Deviation	9.16	2.72	4.13	4.15	16.55	22.90	6.08	11.36
LSD <sub>p&lt;0.05</sub>		3.74	1.10	5.54	1.75	18.60	7.99	21.26	7.79
Total		43.87	34.01	98.47	42.24	1349.38	122.05	159.37	74.87

Background of trace metal in continental crust (mg.kg<sup>-1</sup>) (Kabata-Pendias, 2010)

Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
0.10	10.00	100.00	55.00	5000.00	20.00	15.00	70.00

The concentrations of all the elements were higher than the rate of their occurrence in the crust except iron which was within the limits. Nevertheless the geo accumulation index (I-

geo according to Müller's classification (as illustrated in tables (3 and 4) and presented in fig. (2) indicating that the concentration of the metals Cr, Cu and Zn (in class 0) are

considered at unpolluted class while the concentration of Ni in class (2) and Pb in class (3) were classified as moderately and strongly polluted, respectively, where ranged from moderately to strongly level.

On the other had Cd was found at extremely level (class 6) as its I-geo exceeded the highest-class value. Therefore, these sediments at the surveyed sites can be considered as potential environmental / human hazards. Several studies have also reported similar type of pollution classification in adjacent areas (Hassan *et al.*, 2008; Alkinani *et al.*, 2019). The Iraqi coasts are characterized by high to

very high level of Cd contamination unpolluted to moderately level of Pb while unpolluted for the other investigated metals. The sources of this metal could be from dust fallout as Hassan *et al.* (2021) found that dust contamination of Cd, Pb and Cr because of the high occurrence in whole locations south Basrah city or from increasing petroleum extraction activities and marine navigation in this area as reported by Saleh *et al.* (2021). The trace metal pollution distributed along Shatt Al-Arab River and the Iraqi marine environment found to be with no significant differences spatial basis (Abdulnabi *et al.*, 2019).

**Table (3): Classification for I-geo accumulation index (Müller, 1979)**

I-geo	Class	Quality of sediment
≤0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
>5	6	Extremely polluted

**Table (4): I-geo index: mean, Std. deviation minimum and maximum value for the surface sediments along the Iraqi coast.**

	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
Mean	8.09	1.12	-0.65	-1.05	-2.51	1.98	2.82	-0.62
Std. Deviation	0.46	0.32	0.35	0.41	0.18	0.41	0.1	0.53
Minimum	7.22	0.41	-1.39	-1.91	-3.41	0.53	2.7	-2.42
Maximum	9.23	1.73	-0.05	0.27	-2.35	2.54	3.17	0.61
Class	6	2	0	0	0	2	3	0

**Distribution of elements metals fractions in sediments**

Exchangeable metals (F1). In this fraction trace metals settle on the surface of the sediments or on their essential components namely clays, Fe and Mn hydrated oxides, and

organic matter. The presence of a high trace metals percentage on exchange surfaces may provide a chance to be part of the food chain

during the release into the water through dissociation (Yuan *et al.*, 2004).

Figs. (3 & 4) show low concentrations and percentages of Fe, Ni, and Zn in this fraction.

Tessier *et al.* (1979) suggested that iron oxides should not dissolve at pH 7.0, so the iron concentrations in F1 were actually very low.

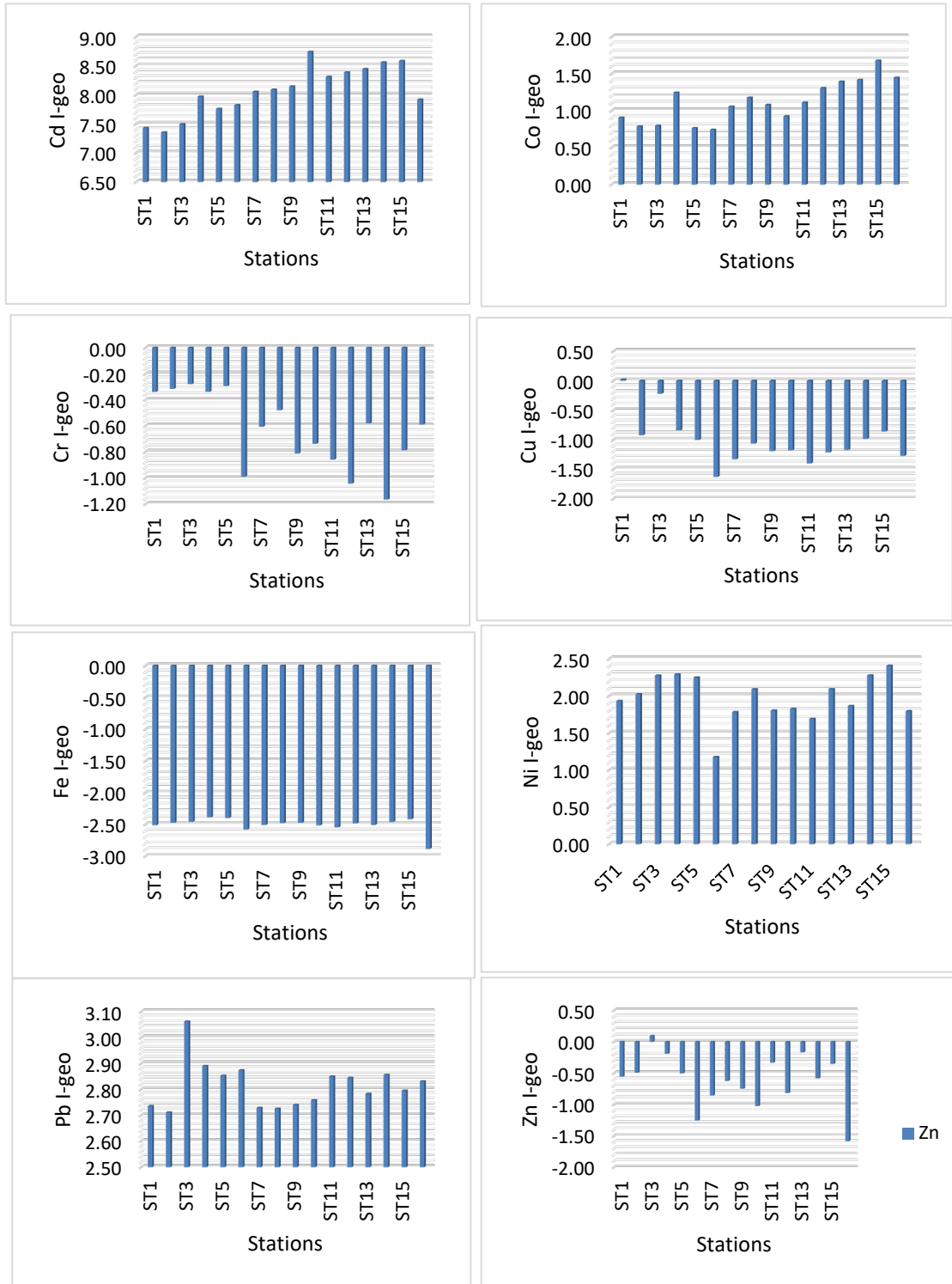
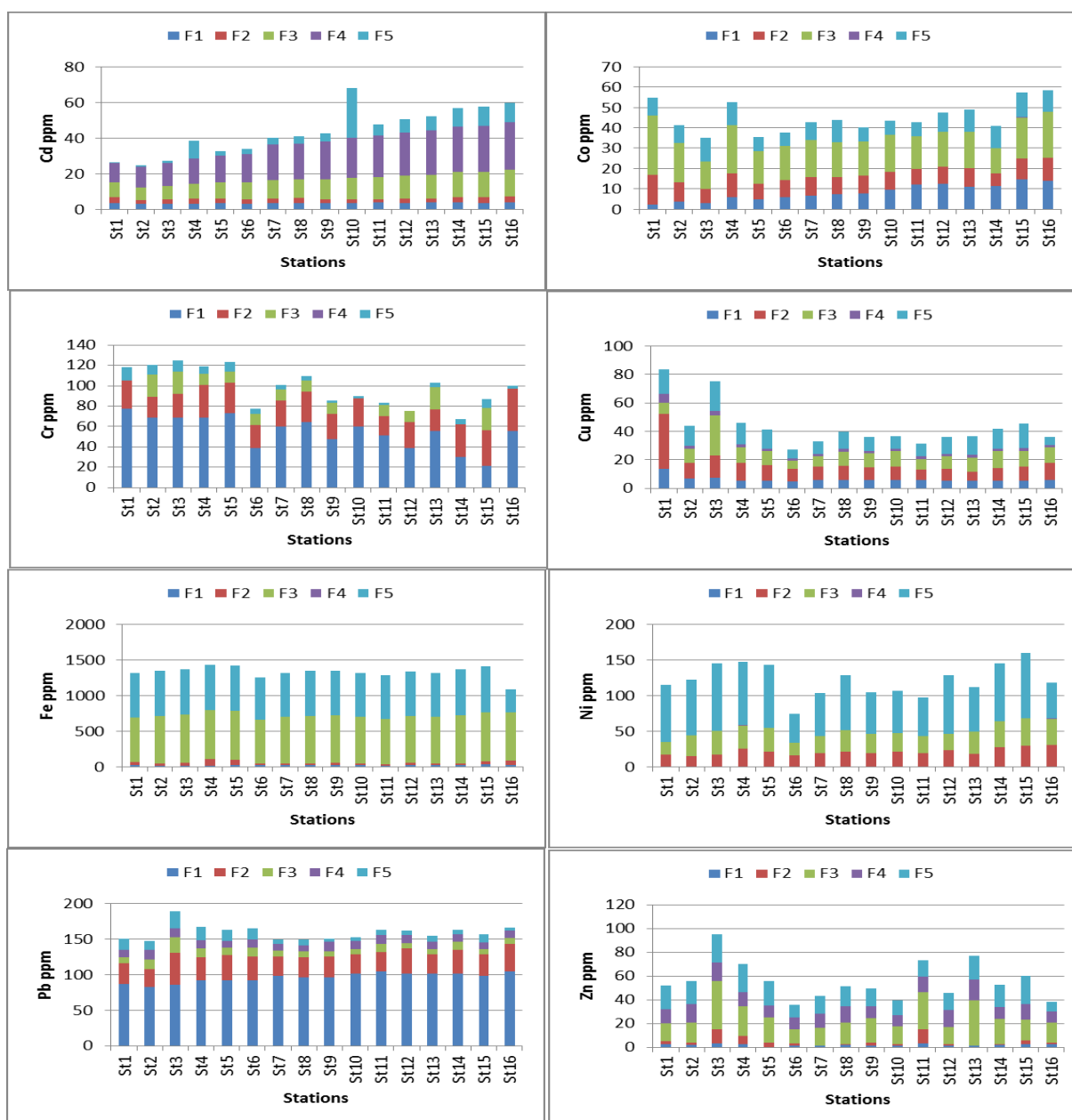


Fig. (2): The distribution of the I-geo value in the surface sediments along the Iraqi coast.

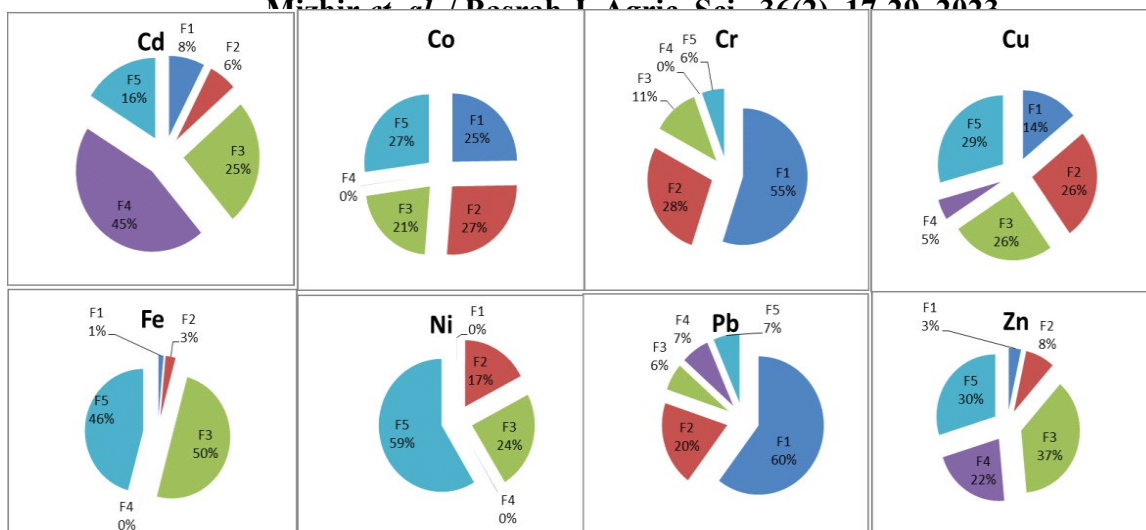


**Fig. (3): An extraction concentration percentage of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn along the Iraqi coastal sediments (F1) Metals associated the exchangeable fraction, (F2) Metals associated with carbonates, (F3) Metals associated with the Fe-Mn-oxides, (F4) Metals Associated with the organic material and (F5) Residual.**

Both Pb and Cr have dominant in exchangeable fraction constituting approximately 60% and 55% of their total concentration (Fig. 4). Organisms do not use lead in acting processes, so it will accumulate and remains in non-decomposing parts such as cellulose. The percentages of the trace metals associated with F1 follow the order: Pb > Cr >

Co > Cu > Cd > Zn > Fe > Ni. The main pollution source of Pb maybe air pollution and fertilizers, whereas Cd and Fe were attributed to natural sources. Fe is a low-moving metal, its accumulation on the surface could be attributed to the accumulation of non-decomposing organic matter (Kabata-Pendias, 2010).





**Fig. (4): Percentages metals Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn associated with the five fractions in the Iraqi coastal sediments (F1) Metals associated the exchangeable fraction, (F2) Metals associated with carbonates, (F3) Metals associated with the Fe-Mn-oxides, (F4) Metals Associated with the organic material and (F5) Residual.**

Metals bound to carbonates (F2). Close percentages and concentration metals (Cr, Co, Cu, Pb) associated with carbonates fractions in the Iraqi coastal sediments appear in figs. (3 & 4). The percentages of the metals follow the order: Cr > Co > Cu > Pb > Ni > Zn > Cd > Fe. Metals in this fraction are at a potential risk to the environment, where they are easy return to the environment.

Trace elements, specially Pb, and Cr, are associated with carbonates as their special preference especially at high pH values, so the reaction admission of lead was in the form of hydroxides, phosphates and carbonates (Kabata-Pendias, 2010; Alimohammad Kalhori *et al.*, 2012).

Associated with the Fe-Mn- oxides (F3): Both iron and zinc predominate this fraction by 50% and 37%, respectively. The other elements have close percentages representing one third of the total concentration exempt. Cr and Pb exhibit low percent in this fraction. The metals, based on their percentages follow the order: Fe > Zn > Cu > Cd > Co > Ni > Cr > Pb. These results are consistent with finding reported by Tessier *et al.* (1979) illustrating

that Fe-Mn-oxide showed a strong scavenging activity of trace metals .

Associated with the organic material (F4): Cadmium and Zinc in F4 represented a significant ratio of the total metal concentration (by 45% and 22%, respectively). The remaining metals in F4 were lower than their respective detection limits.

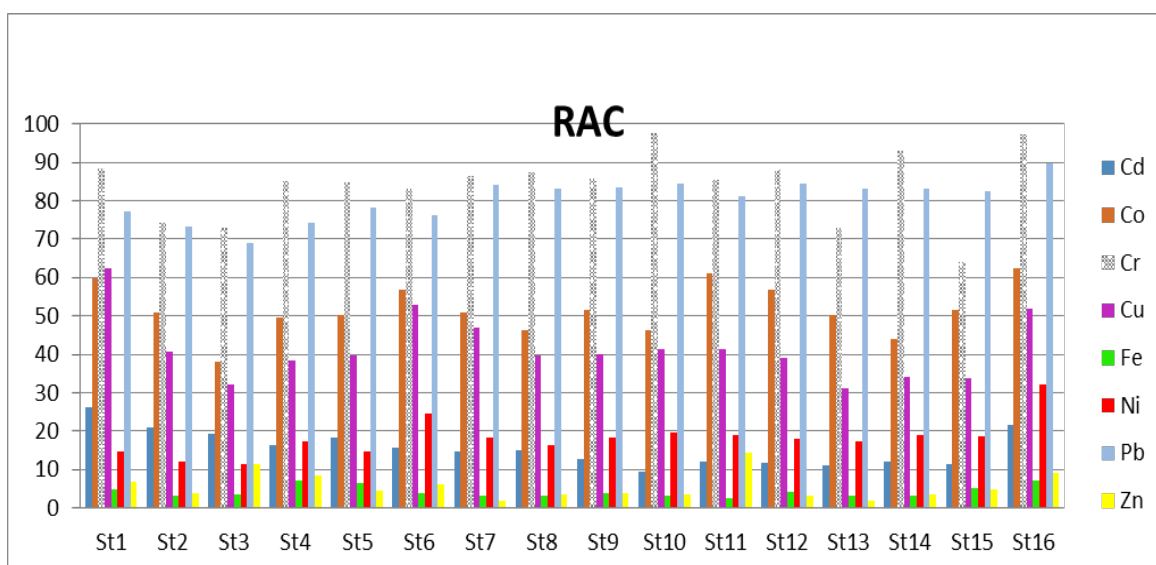
Residual (F5): The results in this fraction were unexpected especially for nickel values, which found to be higher levels compared with other fractions phases. More than 50% of the total Ni concentration appeared in this fraction. The metal can be arranged as follows: Ni > Fe > Zn > Cu > Co > Cd > Pb > Cr based on their percentages. Generally, the samples showed a low Ni concentration in exchangeable fractions, compared with residual fraction which reflected a low potential environmental toxicity. This result confirmed of Alkinani *et al.* (2019) where Ni is generally fixed within the clay structure and iron minerals.

#### **Risk Assessment Code (RAC)**

According to the result in fig. (5) and table (5) the surface sediments of Iraqi tidal flats is

characterized by very high risk considering Cr, Pb, Co and Cu which represented by RAC values of 83.99%, 80.55, 51.36 and 40.87 % respectively an overall of in all of the sampling

sites. However, other metals such as Ni and Cd exhibit medium RCA of 18.31% and 15.17%, respectively. While both of Fe and Zn had low risk with 4.20% and 5.61% respectively.



**Fig. (5): The trace elements RAC at surface sediments of the Iraqi coast.**

The RCA values are categorized into four levels (very high, high, medium and low) the ratios indicated by RCA. Provide clear results in comparison with the I-geo which adopted the total concentrations. These results illustrated that Cr and Pb could easily release from sediment into water and may affect marine organisms while the sequestration of Ni

and Zn remain for more long time in the sediments. According to Marín *et al.* (2022) the pollution indicators such as RAC and I-geo are affected by the sources of pollution and the homogeneity of samples, in addition to the accurate data on the background condition in the study area and oil transportation.

**Table (5): Risk Assessment Code (RAC) mean, Standard deviation minimum and maximum value of the surface sediments along the Iraqi coast as percentage ratio of the total metal concentration.**

	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
<b>Mean</b>	15.17	51.36	83.99	40.87	4.20	18.31	80.55	5.61
<b>Standard Deviation</b>	5.16	8.80	12.69	8.53	1.69	6.59	5.73	4.95
<b>Minimum</b>	6.24	31.00	61.31	26.9	2.36	9.81	68.31	0.42
<b>Maximum</b>	31.68	70.82	100	63.07	8.60	46.35	96.33	25.19
<b>Risk level</b>	Medium	Very high	High	High	Low	Medium	Very high	Low

## Conclusion

The Iraqi coastal sediments samples were collected along tidal flat of Khor Abdullah and Khor Al-Zubair covering a coastline of about 40 km. In order to evaluate the distribution of trace metals in five fractions. These metals are bonded to different power bonds. Pb, Cr and Co have dominant in exchangeable and carbonates fraction, so they can move to the solution to become available for living organisms. Iraqi tidal flats is characterized by very high risk considering Cr, Pb, Co and Cu which represented by RAC values. Fe and Ni were found in residual. Cd and Zn in organic material fraction for that they are low and moderate polluted according to RAC. The trace metals pollution distributed along the Iraqi marine environment. The sources of this metals could be from increasing petroleum extraction activities and marine navigation in this area or from polluted dust.

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## Contributions of authors

**A.A.M:** Laboratory techniques, wrote and revised the manuscript.

**W.H.F:** Suggestion the proposal of the article, wrote and revised the manuscript.

**D.K.K.A:** Suggestion the proposal of the article, revised the manuscript.

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## Conflicts of interest

The authors declare that they have no conflict of interests.

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## إستخدام طرق الإستخراج المتتابع لتقييم الأثر البيئي للمعادن النزرة في رسوبيات الساحل العراقي

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**المستخلص:** أستخدمت خمسة طرق للإستخلاص المتتابع لدراسة التوزيع الجيوكيميائي لعدد من المعادن الثقيلة (الرصاص والكاديميوم والنحاس والزنك والنيكل والكروم والكوبالت والحديد) لتوفير معلومات عن توزيعها وحركتها وتأثيراتها البيئية على الرواسب الساحلية العراقية. جمعت عينات الرواسب السطحية من ستة عشر موقع تكون موزعة على طول الساحل لقياس تراكيز العناصر المذكورة أعلاه. تم تقدير التركيز الكلي وتركيزها في مستخلص الرواسب (المرتبط مع سطح التبادل والكربونات وأكاسيد المنغنيز وأكاسيد الحديد والمادة العضوية اضافة الى الجزء المتبقي في البناء البلوري) بإستخدام طرق الإستخلاص (كلوريد المغنيسيوم بتركيز 1 مول من أسيتات الصوديوم، 0.5 مول من هيدروكسيل أمين هيدروكلوريد و 0.2 مول من أوكزالات الأمونيوم وحمض النيتريك المركز و 25% من حمض الهيدروفلوريك) لفصل الصور الجيو كيميائية المذكورة أعلاه حسب الترتيب. أشارت النتائج إلى أن المحتوى الكلي للرواسب من الرصاص والكاديميوم أعلى من معدل تواجهها في القشرة الارضية، بينما كانت تراكيز الكروم والنحاس والزنك والحديد ضمن هذه الحدود. تبين نتائج دليل التجمع الجيوكيميائي (I-geo) ان تراكيز كل من Cr و Cu و Zn غير ملوثة في الرواسب. في حين تركيز Ni و Pb ضمن مستوى متوسط الى عالي التلوث. وسجل الـ Cd اقصى مستوى من التلوث. ارتبطت هذه العناصر مع المفصولات المختلفة حسب قوة ربط الاواصر. فقد وجد ان Pb و Cr و Co انتشرت في الجزء المتبادل وأرتبطت مع كاربونات الكالسيوم. حسب دليل مخاطر التلوث (RAC) تصنف الرواسب العراقية الساحلية ضمن مخاطر عالية التلوث بالنسبة لعناصر Cr و Pb و CO و Cu. لذلك هذه العناصر من السهولة ان تصبح جاهزة للأحياء الساحلية والبحرية.

**الكلمات المفتاحية:** الساحل الرسوبي، التوزيع الجيو كيميائي، العراق، الاستخلاص المتتابع، العناصر الثقيلة.