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Metal Contamination in the Sediments of Tidal Flat for Iraq Costal

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Abstract: ***In this study, the concentrations of heavy metals were measured ,using Atomic Absorption Spectrophotometer (AAS) for 16 sediment samples collected at different stations in Kour Al-zuber during 2015. To assess the levels of sediment contaminations, the background values of the different elements were defined, depending on the international standards in add the metal contamination in the sediments was also evaluated by applying enrichment factor (EF), Contamination factor (CF), geo-accumulation index (I-geo) , pollution load index (PLI) , Degree of Contamination (dC) and Modified Degree of Contamination (mdC) .The mean concentrations measured in mg/kg were 70.31±12.39 for Co, 657.02±152.39 for Mn,12.20±2.51 for Ni, 95.38±35.92 for Zn, In case of Co. Zn at most of sites, their concentrations in the sediments were more than the background values. However, the average values for Mn and Ni their concentrations in the sediments were less than the background values. In general, the order contamination factors of heavy metals in the present study could be arranged is Co>Zn>Ni> Mn. Considering All assessing criteria, Co is Responsible for significant amount of heavy metal contamination, while Zn was responsible for moderate to high contamination. Station 3 contains highest amount of heavy metals contamination and station 3 Contains lowest amount of heavy metal contamination. The relatively high levels of Co and Zn in Kour Al-zuber tidal flat sediments are due to the discharges of untreated wastewater of desalination plant, electrical power station, refinery plant, textile industry, oil spills from the oil pipes, as well as domestic wastewater.***

Keywords: Kour Al-Zuber tidal flat sediments ,Heavy metals, contamination factor, Enrichment factor ,I-geo. and polluted indexes

1. Introduction

Marine pollution is a global environmental problem. Human activities in the coastal area and marine water contribute to the discharge of various kinds of pollutants such as heavy metals (Fe, Zn, Cu, Co, Pb, And Ni) into the marine ecosystems (1, 2). Heavy metals in the marine environment are resulting by both natural processes (e.g., rock weathering and volcanic eruptions) and anthropogenic activities (e.g., urbanization, industrialization, agriculture, and aquaculture), it has become a serious concern worldwide, The contamination is especially significant in the estuarine and coastal sediments which usually act as a sink acceptance the heavy metals through had sorption on to suspended matter and subsequent sedimentation (1, 3). Sediment pollution by heavy metals has been observed as a critical problem in marine environment due to their toxicity ,persistence , bioaccumulation, and non degradability In the Environment, Therefore, heavy metal distribution and speciation offers a more realistic evaluation of their actual environmental impact (4, 5).Heavy metals in sediments could significantly impact the health of marine ecosystem they can act as sources of heavy metals, imparting them into the water and degrading water quality (6-8).

To date, many researchers have conducted extensive surveys of heavy metal contamination in sediments they used several types of the parameter to assessment the pollution In the area of Northern Arabian Gulf, (2, 3, 9-11).

There are many different kinds of parameters can be used to describe the assessment the sediment pollution of heavy metals like enrichment factor (EF), Contamination factor (CF), geo-accumulation index (I-geo) And pollution load index (PLI) Degree of Contamination (dC)and Modified Degree of Contamination (mCd) etc…To assess the environmental impact of contaminated sediments, information on total concentrations is not enough and particular interest is the total trace metal content that may take part in further biological processes (12).

The aim of the present study is to investigate the distribution of heavy metals (Co, Mn , Ni, and Zn) and to evaluate the contamination levels of the Kour Al-Zuber tidal flat sediments. By used different kinds of parameters.

2. Materials and Methods

2.1 Sediment sampling

Sixteen of sediments samples were collected along the Kour Al-Zuber tidal flat (Fig.1,). The surface samples were collected in summer 2015. The sediments were placed in polyethylene bags and transported to the laboratory, to air dried in the laboratory than ground to a fine powder and sieved through 106 μm stainless steel mesh. The samples were then stored in a polyethylene container ready for digestion and analysis. The dried sediments were digested by mixture of HF $HClO_4$-HNO3 (13) after that brought into solution in 0.5M HCl (50 ml). Total concentration of four heavy metals(Co, Mn , Ni and Zn) in samples were analyzed by AAS. The data were statistically analyzed using the software SPSS v-19.0.

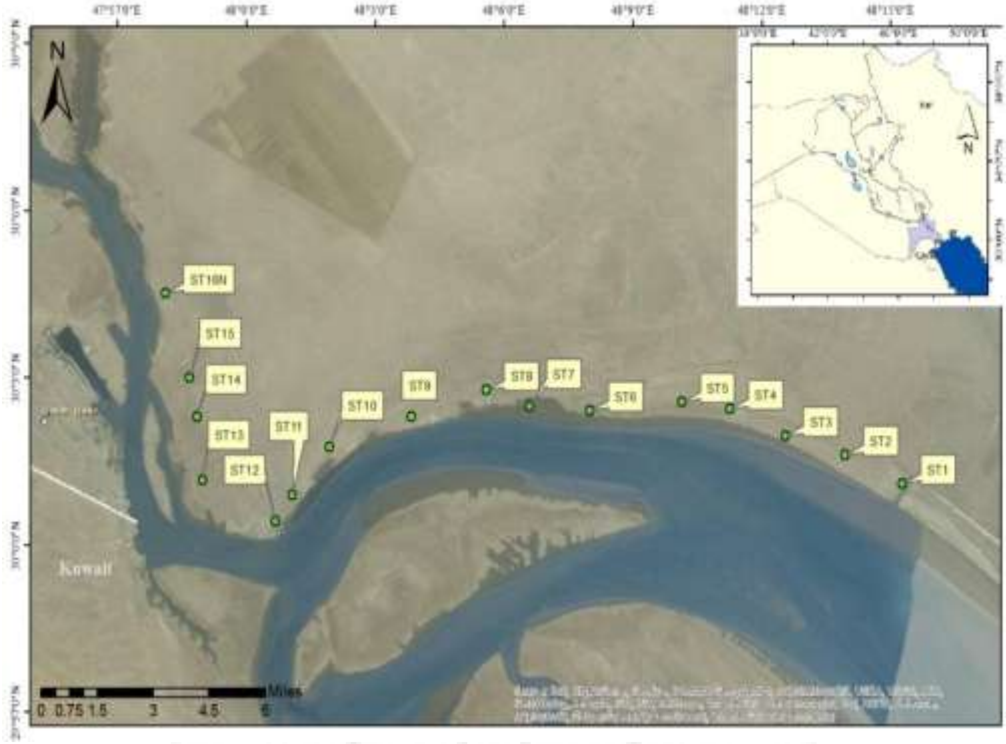


Fig. 1: Location of sampling sites in the Iraqi tidal flat

2.2. Assessment of Metal Contamination

To evaluate the degree of contamination in the sediments, we used six parameters: based on the following approaches: (a) Contamination Factor (CF) ,(b) Contamination Degree (Cd) (c) Modified Contamination Degree (MdC) , (d) Enrichment Factor (EF) ,(e) Geo accumulation Index(Igeo) and (f) Pollution Load Index (PLI) .

The background concentrations considered for the calculation of EF, I-geo , were the element concentrations in(14).

Table 1: Classified grades of CF, dC, mdC ,EF, I- geo and PLI indices.

CF contamination factor(19)	dC (19)	mdC (18)	EF (17)	I-geo (16)	PLI (15)
<1 Low contamination(class 1).	<8 low degree of contamination	mCd <1.5Nile to very low degree of contamination	<1 indicates no enrichment	≤ 0 (class 0), Practically unpolluted	<1 Perfection (class 0)
1≤CF< 3 Moderate contamination(class 2).	8<Cd<16 moderate dgree of contamination	1.5≤mCd<2 low dgree of contamination	<3 is minor enrichment	0 < to ≤ 1(class 1), slightly polluted	1 Baseline level (class 1).
3≤ CF≤6 Considerable contamination (class 3).	16<Cd≤32 considerable dgree of contamination	2≤mCd<4 moderate dgree of contamination	3-5 moderate enrichment	1< to ≤ 2 (class 2), Moderately polluted	>1 Deterioration on site Quality (class 2)
>6 Very high contamination (class 4).	≥32 very high degree of contamination	4≤mCd<8 high degree of contamination	5-10 is moderate to severe enrichment	2< to ≤ 3 (class 3), moderately severely polluted	
		8≤mCd<16 very high degree of contamination	10-25is severe enrichment	3< to ≤ 4 (class 4), Severely polluted	
		16≤mCd<32 extremely high degree of contamination	25-50 is very severe enrichment	4< to ≤ 5 (class 5) , Severely extremely polluted	
		mCd>32 ultra high dgree of contamination	>50 extremely severe enrichment	> 5 (class 6), Extremely polluted	

3. Results and Discussion

3.1 Contents of heavy metals

A total of 16 tidal flat sediment samples were investigates for four heavy metals. Descriptive statistics such as mean, minimum, maximum, median and standard deviation used in this study are shown in Table 2. Fig. 2. Most of the elements have a wider geo variations of several magnitudes.

Cobalt is an important and essential element for living plant and animal nutrition although it is present at lesser trace level (20). In this study the minimum Co concentration was 53.89 mg/kg in station 12 while the maximum was 92.96

mg/kg in station 3. This value more than the rang of Co concentration in crust (9-12 mg/kg) (14). The range of Mn concentrations in sediment was 716-1400 mg/kg with mean value 1058 mg/kg (14). In this study Mn concentration ranges from , 357.67-843.07 mg/kg with a mean value of 657.02 mg/kg. The minimum Mn concentration was found in station 3 while the maximum was found in station 5. This shows that Mn was under the probable effect level (PEL) reported in all standers use in this study . the minimum Ni concentration was about 8.14mg/kg in station 12 and the maximum was 16.28 mg/kg in station 3 with mean value 12.20. This shows that Ni was under the probable effect level (PEL) reported by all The permission used in the study. A moderately high positive correlation with Zn was established. In this study the range for Zn was 64.53-189.06 mg/kg with mean value 95.38 mg/kg which was exceed the PEL limit of 66 reported by (14) in all station except station 12 which was the concentration of Zn was 64.53 mg/kg .while it was under the probable effect level (PEL) reported by The other permission used in the study .

Table 2: Concentration of heavy metals(mg/kg)in the sediments samples of Iraqi tidal flat during the study period compares with other stander concentration

Elemant Conc mg/kg	Mean	Std. Deviation	Minimum	Maximum	Median	Kabta	USEPA SQG	Mean shale conc.	World surface rock average
Co	70.31	12.40	53.89	92.96	67.36	10.5	-	29	13
Mn	657.02	125.40	357.67	843.07	644.82	1058	30	850	750
Ni	12.20	2.52	8.14	16.29	12.65	20	16	68	49
Zn	95.38	35.92	64.53	189.06	84.30	66	110	95	127

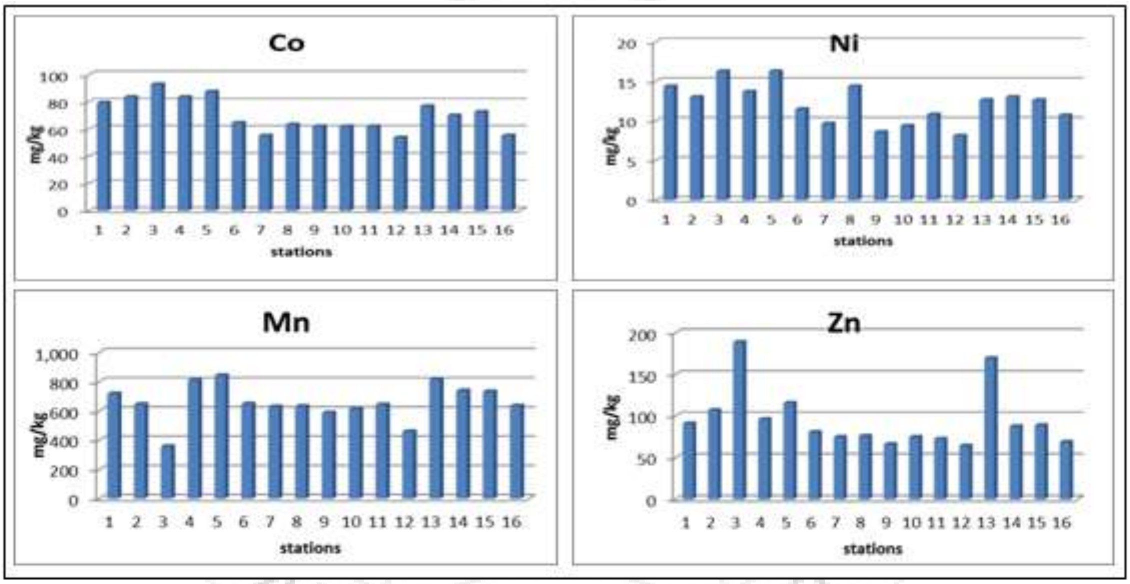


Figure 2: Concentration of heavy metals(mg/kg)in the sediments samples of tidal flat during the study period

3.2 Methods for estimating pollutant impact:

Number of calculation methods have been put forward for quantifying the degree of metal enrichment in sediments (table1). Various authors have proposed pollution impact scales (or ranges) to convert the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity. Six methods are discussed in the following sections along with proposed modifications.

3.2.2.Contamination factor (CF):

sediment samples collected from Khor Al-Zubair According to Hakanson(19) fall under the category of Considerable contamination degree (class3) to very high contamination (class4) for Co it was ranged between 5.13-8.85 with mean value 6.69. The heights value recorded in station 3 (table3. Fig 3.) In the second order of pollution it was Zn with ranged 0.97-2.86 its mean value 1.44 it was fall into low contamination (class 1) to moderate contamination (class 2). while all stations were unpolluted to low polluted with Mn and Ni with CF less than 1. The elements can be ordered according to the values of the EF as follows: CFCo>CFZn>CFMn>CFNi.

Table 3: of heavy metals in stations of Iraqi tidal flat

	Mean	Std. Deviation	Minimum	Maximum	Median
CFCo	6.70	1.18	5.13	8.85	6.42
CFNi	0.61	0.13	0.41	0.81	0.63
Cf Mn	0.62	0.12	0.34	0.80	0.61
CFZn	1.45	0.54	0.98	2.86	1.28
EFCo	11.27	4.12	8.76	26.19	10.12
EFNi	1.02	0.39	0.78	2.41	0.92
EFZn	2.49	1.64	1.74	8.47	1.95
I-geoCo	2.14	0.25	1.77	2.56	2.10
I-geoMn	-1.30	0.31	-2.15	-0.91	-1.30
I-geoNi	-1.33	0.31	-1.88	-0.88	-1.25
I-geoZn	-0.13	0.45	-0.62	0.93	-0.23
PLI	1.37	0.24	0.97	1.76	1.37
dC	14.79	6.08	11.39	37.07	13.21
MdC	84.57	14.69	60.07	108.65	84.54

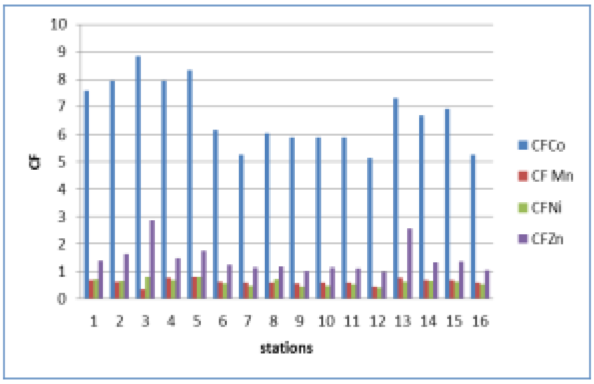
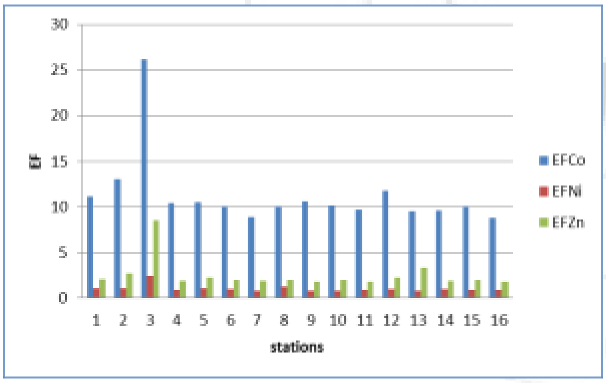


Figure 3: The contamination factors (CF) of heavy metals in stations of Iraqi tidal flat

3.2.2 Enrichment Factors (EF)

The EF is an importune measure of geochemical trends, and it is used form a king comparisons between areas according to pollution degrees (21). It is method normalizes the measured heavy metal content with deference to a sample reference metal such as Fe or Al or Mn (3, 9, 22). Hassan(3) planned Fe as an acceptable normalization element to be used in the calculation of the enrichment factor since they considered the Fe distribution was not related to other heavy metals in river sediment . Fe usually has a relatively high natural concentration, and is therefore not expected to be substantially enriched from anthropogenic sources in estuarine sediments (23). AlKhuziea(11) applied a similar approach and used Mn for EF calculations in a study of marine sediment . In this study we used Mn for EF calculations in tidal flat sediment.



Fig(4). The enrichment factors (EF's) of heavy metals in stations of Iraqi tidal flat

The enrichment factors (EF's) of heavy metals in the tidal flat sediments at the sixteen stations (Table 3,Fig 4) revealed that they were (moderate enrichment to sever enrichment EF 3-5) to (very sever enrichment EF 25-50) in Co especially at station 3. The range of EF's varied 8.75-26.18 with mean value 11.27 for Co, 0.77-2.41 with mean value 1.02 for Ni its fall into no enrichment to minor. If the enrichment values is high that is indicate an anthropogenic source of heavy metals, mainly from activities such as industrialization, urbanization, deposition of industrial waste.

The enrichment value for Zn was 1.74-8.47 with mean value 2.49 it is fall into (minor enrichment - moderate enrichment) to (moderate - severe enrichment). In general, the lowest enrichment factor for heavy metals Co, Ni, Zn in the sediment samples were recorded at station12 8.75,0.77,1.74 respectively. while the EF for station 3 was highly with Co, Ni and Zn with respect in this study . The elements can be arranged according to the values of the EF as follows: EFCo>EFZn>EFNi. These high levels of the enrichment factors might be related to the anthropogenic effect from several sources. Zhang and Liu (24) suggests that increasing in the concentration of metal may be associated to crustal materials or natural weathering processes.

3.2.3.Geo accumulation Index

The index of geo accumulation (I-geo)was assessed based on the values proposed by Müller 1969 who classified the geochemical index for 6 degrees(Table1), Lu et al (2009) defined the constant 1.5 as a constant introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments. This application was considered by many researchers (9-11)

According to the Muller scale (Müller, 1981), the calculated results of I-geo values (Table 3 and Fig5) indicate that Co can be considered as (moderately polluted class 2) to (moderately severely polluted class 3) at most of the study stations I-geo >1).

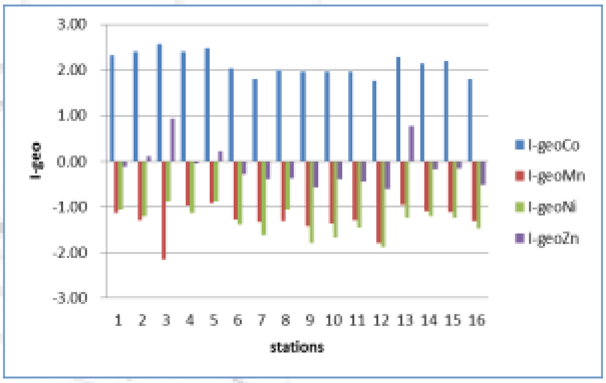


Figure 5: The Geo accumulation Index (I-geo) of heavy metals in the tidal flat sediments at the sixteen stations.

The minimum value 1.77 in station 12 and the maximum 2.56 in station 3 .This result not agreement with Al-Jabriea (10) who indicates that the concentrations Of Co In the sediments of his sites are unpolluted and lower than the background.The other metals (Mn, Ni and Zn) had the same behavior of pollution it was fall into (practically un polluted class 0) to (slightly polluted class 1) less pollution .The minimum value -2.15 station 3 and the maximum 0.91 in station 5 with mean value -1.30 for Mn , The minimum value -1.88 station 12 and the maximum -0.88 in station 3 with mean value -1.32 for Ni , The minimum value -0.61 station 12 and the maximum 0.93 in station 3 with mean value -0.12 for Zn .

The order of contribution of various heavy metals on the basis of I-geo follows:

I-geo Co> I-geo Zn> I-geo Mn> I-geo Ni .

Although the nature of the I-geo calculation ,which involves the logarithmic function and a background multiplication factor of 1.5,is somewhat different from other pollution calculation methods discussed in this study.

3.2.4.Degree of Contamination, modified degree of contamination and Pollution Loud index:

As show in table6 and Fig 6 the degree of contamination (dC), calculated for each station together with the interpretations is presented in Table 3. 75% of the samples give moderate degree of contamination (MDC). while 25% give low degree of contamination (LDC). Although, the degree of contamination in the sediment samples is not very high, there should be thorough monitoring of the level of these heavy metals in the sediment of the tidal flat so as to prevent relative health hazards to man and the livestock in the area.

The assessment of the overall contamination of the sediment was based on dC. The sediment was classified as moderate degree of contamination . The minimum values of the contamination degree was presented in station 12 (6.95) while the maximum value in station 3 (12.86). The dC as proposed in the present study is based on integrating and be around all the available analytical data for a set of sediment samples. This modified method can therefore provide an integrated assessment of the overall enrichment and contamination impact of groups of pollutants in the sediment. While if we depended on Modified degree of contamination(mCd) the result of this study was between(1.74-3.22)with mean value (2.34) it was fall into between Low degree to moderate degree.

The Pollution Load Index (PLI) was calculated for each of the study stations according to the methods of (15). It is based on the contamination factor(CF)of each metal in the sediment where values of PLI=1 indicates heavy metal loads close to the background level, and values above 1 indicate pollution. All sediment samples of the present locations had a pollution loud index greater than 1(Table3. Fig6). So, the sediments in Khor Al-Zubair were heavily or moderately polluted. The pollution loud index(PLI) is a simple method to assess the extent of pollution by metals (15).

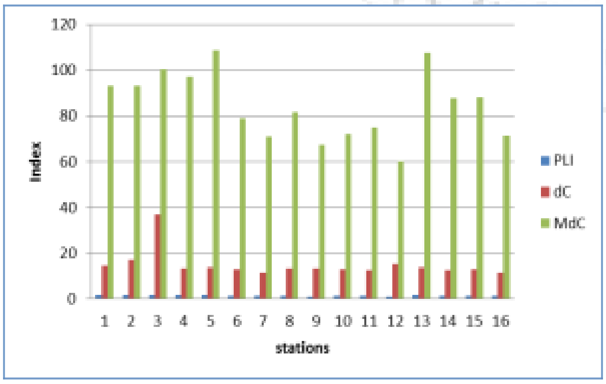


Figure 6: Degree of Contamination, modified degree of contamination and Pollution Loud index in stations of Iraqi tidal flat

4. Conclusions

To investigate the status of metal contamination in the tidal flat of Iraqi coastal sediments Co, Mn ,Ni and Zn concentrations Were estimated in sixteen sampling sites. The order of the mean concentrations of tested heavy metals: Mn>Zn >Co>Ni. International sediment quality guidelines (WHO, USEPA and CCME), Contamination factor (CF), Contamination degree(C d), Modified degree of contamination(mCd), Enrichment factor (EF), Geo-accumulation index (I Geo) and Pollution load index (PLI) Were applied for assessment of contamination. According to sediment quality guidelines, the tidal flat of Iraqi coastal Sediments were polluted by Co, Zn while unpolluted with Mn and Ni.

In general, I geo indices for most heavy metals were negative; this imply that mean concentration of heavy metals tidal flat Sediments are lower than world surface rock average. Considering All assessing criteria, Co is Responsible for significant amount of heavy metal contamination, while Zn was responsible for moderate to high contamination. Station 3 contains highest amount of heavy metals contamination and station 3 Contains lowest amount of heavy metal contamination.

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