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Geochemical Evaluation of Heavy Metals (Cd, Cr, Fe, and Mn) in Sediment of Shatt Al-Basrah, Iraq

Abstract- In this study, the sediment of Shatt Al-Basrah canal, was evaluated to illustrate the distribution of 4 heavy metals Cd, Cr, Fe and Mn in sediments collected from 5 sites. The assessment of heavy metals was conducted using three indices; the geo-accumulation index (I-geo), the enrichment factor (E.F.) and Pollution Index (PI). According to I-geo, the sediments collected from all sampling locations were unpolluted by Cd, Cr and Fe, where their values are less than 0 (<0), except Mn ranged between 0.98 to 1.37, the Igeo values for Mn show that sediments of Shatt Al-Basrah are unpolluted to moderately polluted for all sampling locations. Based on The enrichment factor, the sediment of Shatt Al-Basrah canal are classified as followed; significant enrichment for Cd, moderate enrichment to significant enrichment for Cr and deficiency to minimal enrichment for Mn. PI, which is based on individual metal Concentrations, shows that all sampling sites have no pollution effect for Cd, Cr and Mn, except Fe, which cause Slightly pollution affect in all site.

Keywords- Heavy Metal, accumulation, indices, sediment.

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1. Introduction

In the last few years, the attention in the problems that are associated with pollution of the environment as a result of the extensive assortment of chemical pollutants (such as heavy metals) has increased [1]. High concentrations of heavy metals from anthropogenic and geological sources are being released into the aquatic ecosystem [2]. Heavy metals are considered one of the most critical contaminants in the environment due to their persistence, toxicity and bioaccumulation problems [3]. The continuous discharge of huge volumes of domestic and industrial waste into the aquatic system has led to increase the levels of heavy metals in the river, which finally accumulate in sediment. High concentrations of metals can be very toxic, since

the metals can resist degradation, and could possibly settle for a long period in the ecosystem. On the other hand, Heavy metals in the rivers also can be participated by a natural event such as weathering of the rock with the dissolution of metals in water [4]. The associations of heavy metals with sediments are not stable endless or under dynamic situations of the environment. If the equilibrium is disturbed, heavy metals may be released and return to the water column by a variety of remobilization methods. In the aquatic system, therefore, sediments can show a two role, both as a possible source and as a carrier of pollution [5]. Sediment, as a part of the aquatic environment, can deliver a record of depositional history and is taking into account a sink for metals released into an aquatic ecosystem due to

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the longer lifetime of heavy metals in sediment. They can also be considered as point sources of pollution throughout anthropogenic activities [6]. The present study aimed to assess the sediment quality for Shatt Al-Basrah canal by using ecological indices depending on the concentration of heavy metals and investigating the distribution pattern of the pollutant in this canal.

2. Material and Methods

Shatt Al-Basrah canal is a non-natural canal extent from Al-Hammar marshes into Khor Al-Zubair in Al-Basrah and finally to the Arabian Gulf and its length is about 38 Km. this canal was built to carry irrigation drainage from the middle and southern area of Iraq [6-8]. The canal is able to drain water at about 325 m³/sec during the flood

and 1050 m³/sec through ebb tides to Khor Al-Zubair [9].

Five locations were chosen for collecting the sedimentary samples during 2014 -2015 at Shatt al Basrah (figure1); Van Veen grabs sampler was used for collecting the samples. In the laboratory, the sediment was dried (105 C°) by using the oven until it loses its moist content. The dried samples were sieved by 200 μm mesh sieve. To measure the heavy metals (HMs) concentration (Cd, Cr, Fe, Mn) the Atomic Absorption Spectrophotometry device (model AAS 6300, Shimadzu) was used according to the Standard Methods [10]. The measured concentrations for the studied metals were compared against sediment quality guidelines ISQG for sediment [11].



Figure 1: Sampling sites

Table 1: The Mean values of HMs in selected sites (mg/kg)

Sites	Cd	Cr	Fe	Mn
1	0.0166	0.9207	98.806	2.8829
2	0.0114	0.9004	109.72	2.8521
3	0.0162	0.8292	82.387	2.2424
4	0.0163	0.8851	76.452	2.2661
5	0.0183	1.0734	100.20	2.9302

3. Results and Discussion

Table 1 illustrates the mean concentration of heavy metals (HMs) that are found in Shatt Al-Basrah canal during the current study.

I. Calculation of Pollution Indices

a. The geo-accumulation index (I-geo)

Is a common measure to assess the pollution of heavy metal in sediments, which was initially

defined by [12] to find out heavy metals contamination in sediments, by comparing current concentrations with pre-industrial levels, this index was calculated as follows:

$$I - geo = \log_2 (C_n / 1.5 B_n)$$

Where C_n is the measured value of the observed metal in the sediment samples and B_n represent the geochemical background content of the same metal. The constant value of 1.5 is used to reduce the effect of potential deviations in the background values, which might be familiar to anthropogenic influences. In this study, the average of world surface rock given by [13] was used as the geochemical background value. The following classification is given for I-geo as reported by [14] Table 2.

Table 2: I-geo categories

I-geo Value	Rank
<0	practically unpolluted
0-1	unpolluted - moderately polluted
1-2	moderately polluted
2-3	moderately - strongly polluted
3-4	strongly polluted
4-5	strongly - extremely polluted
> 5	extremely polluted

The results of Table 3 showed that I-geo values of Cd ranged from -4.64 to -4.06, from -7.16 to -6.64 for Cr, from -9.96 to -8.96 for Fe and from 0.98 to 1.37 for Mn. All sites have Igeo for Cd, Cr and Fe less than 0 (<0), According to the classification of Muller's, which indicate that's all sediments sites were unpolluted. The Igeo for Mn ranged between 0.98 to 1.37, the Igeo values for Mn point out that Shatt Al-Basrah sediments are unpolluted to moderately polluting with Mn for all sampling sites.

Table 3: Geo-accumulation Index (I-geo) of HMs in Shatt Al-Basrah sediments

Sites	Metals			
	Mn	Fe	Cr	Cd
Site 1	1.3 5	-9.96	-6.79	-4.06
Site 2	1.1 7	-8.96	-6.97	-4.64
Site 3	0.9 8	-9.96	-7.16	-4.32
Site 4	1	-9.96	-6.96	-4.32
Site 5	1.3 7	-8.96	-6.64	-4.06
All samples	1.2 2	-9.20	-6.79	-4.32

b. The enrichment factor (E.F.)

Is a useful tool to reveal the condition and grade of ecological pollution [15]. The calculations of E.F. compare each value of parameter with the background level, either from a global or regional average composition, or from a local site, using older deposits formed under similar conditions, but without the impact of anthropogenic [16-17]. The mathematical calculation of EF was done by using the method suggested by [18] as follows:

$$EF = \frac{(M/Fe)_{sample}}{(M/Fe)_{background}}$$

Where EF is the enrichment factor, (M/Fe) sample is the metal ratio, and Fe concentration of the sample and (M/Fe) background is the metals ratio and Fe concentration of a background [18]. Based on the enrichment factor (EF), five categories of contamination are reported, as shown in table 4 [19].

Table 4: EF categories

EF Value	Rank
<2	deficiency - minimal enrichment
2-5	moderate enrichment
5-20	significant enrichment
20-40	very high enrichment
>40	Extremely high enrichment

The results of the present study showed that EF of Cd ranged from 16.67 at site 2 to 33.3 at site 4 (Table 5). However, the results also indicated that the sediments of Shatt Al-Basrah are categorised as very high enrichment for Cd, except site 2 that has EF value more than 5 and less than 20 and Shatt Al-Basrah sediments are categorized as significant enrichment for Cd. The EF values for Cr in Shatt Al-Basrah sediments ranged from 4.21 at site 2 to 6.32 at site 4. Most sampling sites have EF more than 5 and less than 20 suggesting that Shatt Al-Basrah sediments are categorized as significant enrichment for Cr, except Site 2 the EF value was more than 2 and less than 5 and Shatt Al-Basrah sediments are classified as moderate enrichment for Cr (Table 5). All sampling sites (S1, S2, S3, S4, and S5) have EF values for Mn less than 2 suggesting that Shatt Al-Basrah sediments are categorized as a deficiency - minimal enrichment for Mn (Table 5).

c. Pollution Index (PI)

Is a useful tool to evaluate water pollution of any aquatic ecosystem, where it gathers many parameters to attain at a certain value which can be compared with the standard value to assess the level of pollution [20]. Pollution index (PI) is based on the calculation of individual heavy metal and can be characterized into five classes (Table 6) [21].

Table 5: Enrichment Ratio (ER) of HMs in the sediments of Shatt Al-Basrah

Sites	EF		
	Cd	Cr	Mn
1	28.3	4.74	1.5
2	16.6 7	4.21	1
3	31.6 7	5.26	1.5
4	33.3	6.32	1
5	30	5.23	1
All samples	28.3	10.5	1.5 3

Table 6: PI categories

PI Value	Rank
<1	No effect
1-2	slightly affected
2-3	moderately affected
3-5	strongly affected
>5	seriously affected

PI can be calculated according to the following

$$\text{Equation, } PI = \frac{\sqrt{\left(\frac{C_i}{S_i}\right)_{max}^2 + \left(\frac{C_i}{S_i}\right)_{min}^2}}{2}$$

Where C_i : the concentration of each metal and S_i : the metal level consistent with criteria of sediment quality [21]. The results of PI (table 7) were ranked from No effect to slightly affect for all metal Cd (0.097-0.122) Cr (0.127-0.145) Fe (1.128-1.352) Mn (0.194-0.221). Most of the variables have PI value less than 1, except for Fe where values larger than 1 in all sites, which will fall in the rank of "slightly affected." So, the sampling sites have slightly affected contamination for Fe and no effect for others parameter Cd, Cr and Mn. The slightly high value of Fe concentration that raises the PI value can be returned in the first place to anthropogenic metals loaded from industrial activity, where the studied area is characterized by the presence of industrial complex plant [22].

Table 7: Pollution Index (PI) for Sediment of Shatt Al-Basrah

sites	PI			
	Cd	Cr	Fe	Mn
1	0.10	0.12	1.30	0.22
	2	8	3	1
2	0.09	0.13	1.35	0.21
	7	4	2	8
3	0.11	0.12	1.19	0.20
	4	7	2	0
4	0.11	0.13	1.12	0.19
	6	3	8	4
5	0.12	0.14	1.27	0.21
	2	5	5	9

4. Conclusion

In the end, the Results of the current work showed that there was contamination with iron in the sediment of Shatt Al-Basrah as indicated by the Pollution Index, and the high values for the enrichment factor were for the cadmium in all sites. More attention and considerations need to pay for these concentrations of heavy metals to keep them at a low level or keep them even lower.

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