



Application of geo-accumulation index (I-geo) for assessment the sediments contamination with heavy metals at Shatt Al-Arab River-Iraq

Makia M. Al-Hejuje¹, Hamid T. Al-Saad^{2*}, Najah A. Hussain¹

¹Department of Ecology, College of Sciences, University of Basrah, Iraq

^{2*} College of Marine Science, University of Basrah, Iraq

Abstract Surface Sediments were collected from five stations along the Shatt Al-Arab river from December, 2012 to November, 2013 to determine the monthly variation of seven heavy metals (Cd , Cu , Fe , Mn , Ni , Pb and Zn) concentrations and distribution between the exchangeable and residual phases .Results showed that the concentrations of the previous metals in the exchangeable phase of sediments were (7.96, 20.27, 4104.61, 663.18, 75.70, 74.97, 46.33) $\mu\text{g/g}$ -dry weight, respectively, while in the residual phase were (5.12, 23.84, 16381.18, 328.91, 158.94, 30.00, 59.88) $\mu\text{g/g}$ -dry weight, respectively .Enrichment Factors (EF) of the heavy metals in sediment was calculated which ranged from 0.74 to14.05. The low values of EF show that the enrichment of sediment by heavy metals was by natural process, while EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. Index of geoaccumulation (Igeo) were applied to assess the sediments contamination with heavy metal. According to Igeo values the surface sediments of Shatt Al-Arab river can be classified as unpolluted with Fe and Zn, while unpolluted-moderately polluted with Cu, Mn and Pb, and moderate-strongly polluted with Cd and Ni .

Keywords Shatt Al-Arab River, Heavy Metals, Sediments pollution, (EF), I-geo

Introduction

Heavy metal is a term taken to include the metallic elements with an atomic weight greater than 40, which have specific gravity greater than 5 g / cm^3 . Some of heavy metals (e.g. copper, zinc, nickel, manganese and iron) are essential trace elements to living organisms and play irreplaceable roles in the functioning of critical enzyme systems, but become toxic at higher concentrations. Others, such as lead and cadmium, have no known biological function, and may be toxic even at trace levels to exposure [1].

Although water analysis is useful in the assessment of rivers pollution with heavy metals, sediments can also serve as pollution indicator. The strong binding affinity of heavy metals result in low concentrations in water and high concentrations in sediments [2].

In sediments, there are six different geochemical forms of metals associated with sediments. In the first one these metals are associated with the sediment in the most labile obtained manner; these are called exchangeable metals. The second fraction extracts are united mainly with carbonates and is highly sensitive to pH changes. In the third, the metals bonded to Mn oxide and partly amorphous Fe oxide and in the fourth one, to amorphous and poorly crystalline Fe oxide. In the fifth, the metals associated with the organic material and sulfides are released. Finally, the residual fraction, a portion of metals are strongly bonded to the lithogenic minerals of the sediments [3,4].

The accumulation of heavy metals in sediments, even when present in low concentrations in the overlying water column, is dependent on various factors such as the sediment particles, the properties of the adsorbed compounds and the prevailing physicochemical conditions [5]. High metal concentration were measured in



sediments, indicating historical contamination of these areas [6]. Sediments are considered as a good reservoirs sink for heavy metals in the aquatic ecosystems, and under changing environmental condition they may be release to water column by various processes of remobilization [7].

Several numerical sediment quality indexes were recently developed to provide interpretative tools for assessing chemical pollution [8]. Heavy metal pollution indices are a useful and a relatively easy way to assess the composite of overall heavy metal pollution. Several method have been previously proposed the index of geo-accumulation (I_{geo}) of heavy metals in the sediments [9]. Enrichment Factors (EF) of metal concentration above the baseline concentrations was used as a second criterion in the pollution assessment in sediments, and HEI: heavy metal evaluation index [10] to calculate the overall water and sediments pollution with heavy metals.

Because of the proximity to population centers, agricultural and industrial regions, Shatt Al-Arab have often received inputs of heavy metals, and the sediments may show significant metal contamination. Therefore, the main goal of the present study is to determine the temporal and spatial variations of heavy metals at the sediments of Shatt Al-Arab river, to highlight relationships among metals pollution, to calculate the enrichment factors (EF), and to apply geo-accumulation (I_{geo}) as an effective tool to assess the sediments pollution with heavy metals.

Materials and Methods

Five stations were selected along the middle part of Shatt Al-Arab River, Southern of Iraq. Sampling points were geo-located using geographical positioning system (GPS) at the following coordinates: 30.36 623 N and 47.45 662 E (station 1); 30.34 915 N and 47.46 368 E (station 2); 30.33 755 N and 47.47 563 E (station 3); 30.30 376 N and 47.51 328 E (station 4); and 30.27 251 N and 48.02 810 E (station 5). Surface sediments samples (approximately 5-10 cm) were collected monthly from each station during Dec., 2012 to Nov., 2013 period using an Ekman Grab sampler. After retrieval of the sampler, the water was allowed to drain off. To avoid disturbing, the surface layer of the samples was preserved using polyethylene bags, then the samples were placed in an ice box until reaching the laboratory [1].

In laboratory the sediment samples were dried in an oven at 50 °C, grind finely in an electrical mortar and sieved through a 63 μ m mesh sieve, stored in polyethylene bags until analysis.

Total Organic Carbon (TOC)

Total organic carbon was determined according to burning method [11]. Two grams of dried and sieved sediments were put in pre-weighted crucible and burned at 550 °C for 48 hrs. The difference in mass of crucible and sediments sample before and after burning was calculated as TOC.

Grain Size Analysis (%)

Mean grain size analysis was carried out (in the sedimentary lab/ sediments department / Marines sciences center/ Basrah University) using the standard sieving (63 μ m pore size) and pipet techniques according to [12]. The grain size (sand, silt, and clay) was determined as percentage of sediments.

Exchangeable Metals in Sediments

One gram of the fraction of the grinded and sieved sediments (< 63 μ m) was put in 50 mL polyethylene tube. The exchangeable heavy metals were extracted by using 30 mL HCl 0.5N for over night in an orbital shaker with 300 rpm, the solution was centrifuged at 5000 rpm for 20 minute, the supernatant was filtered using pre-cleaned filter paper (Watman No. 1) to remove some of the suspended matters. The filtrate was decanted and stored in tightly stopper polyethylene vials to be ready for analysis [13].

Residual Metals in Sediments

The residual metals in sediments were extracted according to [14]. The residue from the above mentioned steps was washed by 40 mL deionized water centrifuge for 20 minutes to remove the residual of the exchangeable phase. Then samples were digested with 5 ml concentrated HNO₃ acid in poly tetra fluoro ethylene (PTFE) vessels at 70° C on hot plate near dryness state. The digestion was further proceeded with 1:1 mixture of



concentrated HClO_4 and HF acids, digested near dryness state. The residue was dissolved in 30 mL of 0.5N HCl, allowed on hot plate at 70° C and then made up to 30 mL with deionized water, filtered using pre-cleaned filter paper (Watman No. 1). The samples were stored in tightly stopper polyethylene vials to be ready for analysis.

To check for contamination of the digestion procedure and sample manipulation, a blank solution was prepared and carried through each set of the analyses. Blank solutions were prepared for sediment samples by being treated in the same way of filtration and digestion, but without samples [1]. Then, all the samples were analyzed using Flame Atomic Absorption Spectrophotometer (FAAS).

Geoaccumulation Index (I_{geo}):

Accumulation of metal concentration above the baseline concentrations was used as a criterion in the pollution assessment in sediments. The I_{geo} was introduced by [9].

Where:

$$I_{\text{geo}} = \log_2 [C_n / 1.5 B_n]$$

C_n : is the measured concentration of the examined metal "n" in the sediments.

B_n : is the geochemical background concentration of the metal "n".

1.5: is the factor used because of possible variations in background values due to lithological variability.

The classification of sediments pollution as in (Table 1) below:

Table (1): Categories of I_{geo} classes:

I_{geo} value Sediment status

 $I_{\text{geo}} \leq 0$ unpolluted

$0 \leq I_{\text{geo}} \leq 1$ unpolluted- moderately

$1 \leq I_{\text{geo}} \leq 2$ moderately polluted

$2 \leq I_{\text{geo}} \leq 3$ moderate – strongly polluted

$3 \leq I_{\text{geo}} \leq 4$ strongly polluted

$4 \leq I_{\text{geo}} \leq 5$ strongly-extremely polluted

$5 \leq I_{\text{geo}}$ extremely polluted

Enrichment Factors (EF)

A common approach to estimate how much the sediment impacted with heavy metal (naturally and anthropogenically) is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels. The EF is defined as follows [15]:

$$EF = (M/Fe)_{\text{Sample}} / (M/Fe)_{\text{Background}}$$

The (M/Fe) Sample is the ratio of metal and Fe concentrations in the sample, and (M/Fe) is the ratio of metal and Fe concentrations of the background.

Five contamination categories are recognized on the basis of the enrichment factor as follows: [16].

EF < 2 is deficiency to minimal enrichment

EF 2 – 5 is moderate enrichment

EF 5 – 20 is significant enrichment

EF 20 – 40 is very high enrichment

EF > 40 is extremely high enrichment

As the EF values increase, the contributions of the anthropogenic origins also increase. According to [17], EF values between 0.5 and 1.5 indicate the metal is entirely from crustal materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic.

Statistical Analysis

Analysis Of Variance (One- way ANOVA) was applied by Minitab ver.16 software and Relative Least Significant Differences (RLSD) values were calculated to identify the existence of temporal and spatial



significant differences. The relationship between the indices and parameters was tested using the Pearson's Correlation Coefficients.

Results and Discussion

Sediments are considered as a good reservoirs sink for heavy metals in the aquatic environments. The clay and heavy minerals (minerals were weathered from the older clastic successions from northern Iraq) may form an important source for the natural pollution by the heavy metals in the recent sediments. Most of the pollution came from the wastewater contributed to the rivers [18].

The concentrations of heavy elements in both the exchangeable and residual phases of sediments were illustrated in table (2).

Table 2: The concentrations of heavy elements in Sediments (mean \pm Standard deviation (SD)) and Enrichment Factor(EF) at the studied stations

Stations	Heavy elements	Concentration in Sediments ($\mu\text{g/g}$ dry weight)			Enrichment Factor (EF)
		Exchangeable Mean \pm SD	Residual Mean \pm SD	Total Mean \pm SD	
Station 1	Cd	7.667 \pm 4.408	5.416 \pm 3.587	13.083 \pm 7.754	12.20
	Cu	22.204 \pm 4.484	22.519 \pm 3.202	44.723 \pm 6.770	1.29
	Fe	5728 \pm 2311	15936 \pm 3652	21664 \pm 4242	1.00
	Mn	774.7 \pm 328.6	416.3 \pm 265.9	1191.1 \pm 532.0	2.39
	Ni	86.00 \pm 28.86	161.78 \pm 39.94	247.78 \pm 61.46	9.95
	Pb	77.15 \pm 29.34	28.73 \pm 18.07	105.88 \pm 37.96	2.72
	Zn	39.895 \pm 8.352	56.284 \pm 5.864	96.18 \pm 11.43	0.74
Station 2	Cd	7.882 \pm 4.451	5.134 \pm 3.641	13.016 \pm 8.035	12.55
	Cu	21.680 \pm 4.540	24.207 \pm 5.070	45.887 \pm 9.170	1.37
	Fe	3964 \pm 1888	16995 \pm 2278	20958 \pm 3421	1.00
	Mn	664.8 \pm 287.0	322.3 \pm 95.2	987.2 \pm 373.0	2.05
	Ni	81.33 \pm 29.25	162.29 \pm 40.53	243.62 \pm 62.16	10.11
	Pb	74.09 \pm 27.07	29.09 \pm 16.46	103.18 \pm 38.27	2.74
	Zn	47.059 \pm 6.705	62.268 \pm 11.930	109.33 \pm 15.53	0.87
Station 3	Cd	8.075 \pm 4.695	5.023 \pm 3.559	13.098 \pm 8.185	13.24
	Cu	21.784 \pm 4.197	24.537 \pm 4.461	46.321 \pm 7.686	1.45
	Fe	4334 \pm 1857	15650 \pm 3849	19984 \pm 4373	1.00
	Mn	655.9 \pm 312.0	319.6 \pm 78.0	975.5 \pm 368.7	2.12
	Ni	80.42 \pm 28.49	163.37 \pm 43.98	243.79 \pm 63.60	10.61
	Pb	76.84 \pm 30.36	30.31 \pm 14.54	107.15 \pm 40.34	2.98
	Zn	51.864 \pm 5.979	58.547 \pm 11.174	110.41 \pm 14.87	0.92
Station 4	Cd	7.842 \pm 4.865	5.032 \pm 3.607	12.799 \pm 8.601	12.57
	Cu	22.907 \pm 4.266	25.497 \pm 4.030	48.389 \pm 7.863	1.47
	Fe	3670 \pm 1774	16929 \pm 2430	20572 \pm 3154	1.00
	Mn	637.9 \pm 326.0	308.8 \pm 76.1	948.6 \pm 383.4	2.00
	Ni	77.18 \pm 28.85	161.40 \pm 40.26	241.04 \pm 61.73	10.19
	Pb	78.68 \pm 28.47	31.04 \pm 15.88	110.82 \pm 38.86	2.99
	Zn	59.322 \pm 11.797	61.922 \pm 10.606	121.57 \pm 19.41	0.98
Station 5	Cd	8.325 \pm 4.780	5.019 \pm 3.569	13.344 \pm 8.301	14.05
	Cu	12.986 \pm 2.354	22.450 \pm 4.875	35.436 \pm 5.564	1.15
	Fe	2791 \pm 1082	16397 \pm 2266	19188 \pm 1917	1.00
	Mn	580.4 \pm 313.9	277.5 \pm 72.7	857.9 \pm 354.3	1.94
	Ni	53.68 \pm 19.14	145.88 \pm 39.15	199.56 \pm 51.52	9.04
	Pb	68.40 \pm 24.83	30.85 \pm 12.66	99.25 \pm 34.10	2.87
	Zn	34.614 \pm 6.455	60.379 \pm 9.115	94.99 \pm 13.29	0.83



The concentrations of cadmium in the exchangeable phase was ranged from (7.667 $\mu\text{g/g}$ dry weight) at station 1 to (8.325 $\mu\text{g/g}$ dry weight) at station 5. Non-significant differences ($P>0.05$) were found among stations. In the residual phase of sediments it's ranged from (5.019 $\mu\text{g/g}$ dry weight) at station 5 to (5.416 $\mu\text{g/g}$ dry weight) at station 1. Non-significant differences ($P>0.05$) were found among stations (Table 2).

The concentrations of copper in the exchangeable phase was ranged from (12.986 $\mu\text{g/g}$ dry weight) at station 5 to (22.907 $\mu\text{g/g}$ dry weight) at station 4. Significant differences ($P<0.01$) were found among stations. In the residual phase of sediments it's ranged from (22.450 $\mu\text{g/g}$ dry weight) at station 5 to (25.497 $\mu\text{g/g}$ dry weight) at station 4. Non-significant differences ($P>0.05$) were found among stations (Table 2).

The concentrations of iron in the exchangeable phase ranged from (2791 $\mu\text{g/g}$ dry weight) at station 5 to (5728 $\mu\text{g/g}$ dry weight) at station 1. Significant differences ($P<0.01$) were found among stations. The concentrations of iron in the residual phase of sediments ranged from (15650 $\mu\text{g/g}$ dry weight) at station 3 to (16995 $\mu\text{g/g}$ dry weight) at station 2. Non-significant differences ($P>0.05$) were found among stations.

In sediments, the concentrations of manganese in the exchangeable phase ranged from (580.4 $\mu\text{g/g}$ dry weight) at station 5 to (774.4 $\mu\text{g/g}$ dry weight) at station 1. Non-significant differences ($P>0.05$) were found among stations. The concentrations of manganese in the residual phase of sediments ranged from (277.5 $\mu\text{g/g}$ dry weight) at station 5 to (416.3 $\mu\text{g/g}$ dry weight) at station 1. Non-significant differences ($P>0.05$) were found among stations.

In sediments, the concentrations of nickel in the exchangeable phase ranged from (53.68 $\mu\text{g/g}$ dry weight) at station 5 to (86.00 $\mu\text{g/g}$ dry weight) at station 1. Significant differences ($P<0.05$) were found among stations. The concentrations of nickel in the residual phase of sediments was ranged from (145.88 $\mu\text{g/g}$ dry weight) at station 5 to (163.37 $\mu\text{g/g}$ dry weight) at station 3. Non-significant differences ($P>0.05$) were found among stations or among seasons.

The concentrations of lead in the exchangeable phase of sediments ranged from (68.40 $\mu\text{g/g}$ dry weight) at station 5 to (78.68 $\mu\text{g/g}$ dry weight) at station 4. Non-significant differences ($P>0.05$) were found among stations. The concentrations of lead in the residual phase of sediments ranged from (28.73 $\mu\text{g/g}$ dry weight) at station 1 to (31.04 $\mu\text{g/g}$ dry weight) at station 4. Non-significant differences ($P>0.05$) were found among stations.

In sediments, the concentrations of zinc in the exchangeable phase ranged from (34.614 $\mu\text{g/g}$ dry weight) at station 5 to (59.322 $\mu\text{g/g}$ dry weight) at station 4. Significant differences ($P<0.01$) were found among stations. The concentrations of zinc in the residual phase of sediments ranged from (56.284 $\mu\text{g/g}$ dry weight) at station 1 to (62.268 $\mu\text{g/g}$ dry weight) at station 2. Non-significant differences ($P>0.05$) were found among stations (Table 2).

High concentrations of Cd, Mn, and Pb in the exchangeable phase as compared with the residual phase of sediments could be attributed to those incorporated into the sediment from aqueous solution by processes such as adsorption and organic complication. The exchangeable metals included those originated from anthropogenic sources, this finding was in agreement with [7]. Significant correlations between heavy metals in the surface sediments (Table 6) suggested that they had the same geochemical behaviors or sources, this suggestion was in agreement with [19,20].

The high concentrations of Fe in the sediments was attributed to naturally oxy(hydro)oxides of shipwrecks [21]. The present study found natural concentration - nearest to contamination of Fe in the sediments in spite of the presence of many shipwrecks in the studied area, this may be due to remobilized Iron found in the sediments to the water column as dissolved or particulates forms, or may be due to self-purification which occurred by benthic organisms and the aquatic plants that accumulates iron in their bodies, therefore, the sediments represent a potential risk for the aquatic environment. Lead was found in Winter higher than in Summer, it may be due to the less soluble of pb containing minerals in natural water, this was in agreement with [1,3,22].

According to the ranges of Enrichment Factor for Cd (12.20-14.05), Cu (1.15-1.47), Mn (1.94-2.39), Ni (9.04-10.61), Pb (2.72-2.99) and Zn (0.74-0.98) the sediments of Shatt Al-Arab River can be classified as minimal enrichment with Cu and Zn, moderate enrichment with Mn and Pb, and significant enrichment with Ni and Cd.



The Geo-accumulation Index (I_{geo})

To understand the current environmental status and the metal contamination with respect to natural environmental, I_{geo} should be applied as common criterion to evaluate the heavy metal pollution in sediments and to determine metals contamination in sediments, by comparing current concentrations with natural values. The chemical contaminations in the sediments were evaluated by comparison with the Consensus-Based Sediment Quality Guidelines of Wisconsin [23]. These criteria are shown in Table (3). Present study shows that all the sites are considered as unpolluted with iron and zinc, but unpolluted – moderately polluted with Cu, Mn and Pb, and moderate-strongly polluted with Cd and Ni. This could be attributed to the high concentrations of these metals in surface sediments that exceeded the world surface rock average.

Table 3: Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG)

Metals in $\mu\text{g/g}$ Dry Weight	Consensus Based Sediment Value ($\mu\text{g/g}$ dry wt)
Cadmium	0.99
Copper	32
Lead	36
Nickel	23
Zinc	120
Iron	20000
Manganese	460

Wisconsin Department of Natural Resources. (2003)

The I_{geo} values for cadmium in sediments ranged from (2.18, moderate-strongly polluted) at station 4 in Summer to (3.22, strongly polluted) at station 5 in Autumn (Table 4). Non-significant differences ($P > 0.05$) were found among stations or among seasons.

The I_{geo} values for copper in sediments ranged from (-0.52, unpolluted) at station 5 in Winter to (0.05, unpolluted-moderately polluted) at station 3, 4 in Autumn (Table 4). Significant differences ($P < 0.01$) were found among stations, the lowest mean value (-0.45 unpolluted) was found at station 5, but the highest mean value (-0.01) was found at station 4. Non-significant differences ($P > 0.05$) were found among season.

The I_{geo} values for iron in sediments referred unpolluted state, which ranged from (-0.97, unpolluted) at station 3 in Spring to (-0.30, unpolluted) at station 1 in Winter (Table 4). Non-significant differences ($P > 0.05$) were found among stations or among seasons.

The I_{geo} values for manganese in sediments ranged from (-0.06, unpolluted) at station 4 in Spring to (1.21, moderately polluted) at station 1 in Autumn (Table 4). Non-significant differences ($P > 0.05$) were found among stations. Whereas significant differences ($P < 0.05$) were found among seasons, the lowest mean value (0.13, unpolluted-moderately polluted) was found in Summer and the highest mean value (0.84) was found in Autumn. The I_{geo} values for nickel in sediments ranged from (2.35, moderate-strongly polluted) at station 5 in Winter to (2.96, moderate - strongly polluted) at station 4 in Spring (Table 4). Non-significant differences ($P > 0.05$) were found among stations or among seasons.

The I_{geo} values for lead in sediments ranged from (0.58, unpolluted-moderately polluted) at station 5 in Spring to (1.35, moderately polluted) at station 3 in Winter (Table 4). Non-significant differences ($P > 0.05$) were found among stations. Whereas significant differences ($P < 0.01$) were found among seasons, the highest mean value (1.27, moderately polluted) was recorded in Winter and the lowest mean value (0.67, unpolluted-moderately polluted) was recorded in Spring.

The I_{geo} values for zinc in sediments referred that the sediments were unpolluted with zinc at all the studied stations along the studied period. The I_{geo} values ranged from (-1.03, unpolluted) at station 1 in Winter to (-0.51, unpolluted) at station 4 in Summer and Autumn (Table 4). Significant differences ($P < 0.01$) were found among stations, the highest mean value (-0.58, unpolluted) at station 4 and the lowest mean value (-0.94, unpolluted) at station 5. Whereas non-significant differences ($P > 0.05$) were found among seasons.



Table 4: The I-geo values and the sediments pollution status descriptions at the studied stations during the studied periods

Stations	Season	I-geo Cd value	I-geo Cu value	I-geo Fe value	I-geo Mn value	I-geo Ni value	I-geo Pb value	I-geo Zn value
Station 1	Winter	2.88	-0.15	-0.30	0.70	2.64	1.26	-1.03
	Spring	2.85	-0.07	-0.62	0.44	2.92	0.78	-0.92
	Summer	2.42	-0.18	-0.31	0.03	2.85	0.86	-0.83
	Autumn	3.09	-0.06	-0.76	1.21	2.81	0.64	-0.87
Station 2	Winter	2.94	-0.14	-0.61	0.38	2.60	1.20	-0.76
	Spring	2.88	-0.01	-0.59	0.27	2.92	0.61	-0.84
	Summer	2.22	-0.16	-0.41	0.10	2.83	0.85	-0.70
	Autumn	3.12	-0.06	-0.55	0.82	2.77	0.77	-0.63
Station 3	Winter	2.97	-0.18	-0.55	0.41	2.58	1.35	-0.83
	Spring	2.87	-0.02	-0.97	0.16	2.92	0.66	-0.77
	Summer	2.20	-0.13	-0.50	0.24	2.83	0.86	-0.73
	Autumn	3.16	0.05	-0.50	0.76	2.78	0.77	-0.53
Station 4	Winter	2.98	-0.08	-0.39	0.37	2.59	1.29	-0.66
	Spring	2.62	0.00	-0.87	-0.06	2.96	0.75	-0.69
	Summer	2.18	0.01	-0.60	0.19	2.87	0.94	-0.51
	Autumn	3.14	0.05	-0.47	0.73	2.69	0.80	-0.51
Station 5	Winter	2.87	-0.52	-0.63	-0.07	2.35	1.25	-1.00
	Spring	2.94	-0.29	-0.58	0.06	2.69	0.58	-1.01
	Summer	2.24	-0.51	-0.65	0.08	2.55	0.76	-0.86
	Autumn	3.22	-0.49	-0.76	0.70	2.36	0.63	-0.88

Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG)

The special trends of TOC and heavy metals sampled during the study confirmed the significant role of domestic sewage as a source of anthropogenic pollution to river. Most of heavy metals forms were bonded with crystal and amorphous iron oxides and manganese oxides and less bonded with organic matter and exchangeable forms [24].

The variations in metal partitioning in sediments depended on the variation in the mineralogical composition as well as grain size composition within the mud fraction of the sediments [25]. Organic carbon can be bonded with some fractions of metals in tight form and, therefore its content in sediment may influence the metal enrichment rates of river [26]. The < 63 μm fraction was used because this fraction consisted primarily on clay and silt particulates [7]. Grain size fractions represent the most mobile sediments within river systems and will therefore be of primary importance for the downstream disposal of contaminants [27]. Table (5) gave the percentage of the grain size and the TOC content for the sediments of the present studied stations.

Table 5: Grain size (%) & Total Organic Carbon (TOC %) in the sediments of the studied area during the studied period. (Mean \pm Standard Deviation (SD)).

Stations	Season	Sand (%) (Mean \pm SD)	Silt (%) (Mean \pm SD)	Clay (%) (Mean \pm SD)	TOC% (Mean \pm SD)
Station 1	Winter	7.22 \pm 5.54	73.19 \pm 2.86	19.59 \pm 4.00	10.07 \pm 3.70
	Spring	8.00 \pm 5.57	71.00 \pm 5.20	21.00 \pm 3.61	9.63 \pm 2.60
	Summer	8.00 \pm 5.00	71.33 \pm 11.02	20.67 \pm 12.50	7.63 \pm 0.69
	Autumn	10.33 \pm 6.03	64.33 \pm 13.61	25.33 \pm 13.05	6.35 \pm 1.52
Station 2	Winter	2.53 \pm 2.17	75.03 \pm 7.73	21.11 \pm 9.62	10.30 \pm 3.81
	Spring	3.00 \pm 2.65	72.67 \pm 1.53	24.33 \pm 1.15	9.08 \pm 1.90
	Summer	3.67 \pm 3.05	58.33 \pm 18.48	38.00 \pm 19.29	6.93 \pm 1.78
	Autumn	4.67 \pm 0.58	78.00 \pm 7.00	17.33 \pm 6.81	8.28 \pm 1.96



Station 3	Winter	6.69 ± 7.25	75.79 ± 18.41	17.53 ± 15.13	12.69 ± 5.08
	Spring	2.33 ± 0.58	74.00 ± 11.00	23.67 ± 10.50	9.78 ± 0.23
	Summer	2.33 ± 1.53	51.00 ± 13.00	46.67 ± 13.58	8.28 ± 1.54
	Autumn	1.33 ± 0.58	59.67 ± 7.09	39.00 ± 7.55	6.63 ± 1.27
Station 4	Winter	4.42 ± 3.21	73.98 ± 12.54	21.60 ± 9.81	10.83 ± 5.58
	Spring	6.00 ± 6.25	71.00 ± 7.21	23.00 ± 1.00	9.69 ± 0.46
	Summer	2.33 ± 2.31	73.33 ± 2.89	24.33 ± 4.51	10.16 ± 3.76
	Autumn	1.33 ± 0.58	56.67 ± 25.79	42.00 ± 26.21	9.98 ± 1.68
Station 5	Winter	6.57 ± 6.76	74.05 ± 13.01	19.39 ± 11.20	9.83 ± 2.43
	Spring	2.67 ± 1.53	70.33 ± 0.58	27.00 ± 2.00	8.41 ± 1.37
	Summer	5.33 ± 4.04	76.33 ± 11.15	18.33 ± 14.84	5.48 ± 0.47
	Autumn	1.00 ± 0.00	43.67 ± 12.74	55.33 ± 12.74	6.87 ± 1.40

Farkas *et al.* [27] found that Cd, Cu and Zn significantly correlated with the TOC content of sediments, while in the present study there was non-significant correlation found between the TOC % and most of the studied metals in the sediments (Table 6). This difference in results may be due to the effects of the other geochemical parameter in the sediments metals, or due to the different studied environment, whereas the present study was in agreement with [28, 29] who found non-significant correlation were found between the TOC % and the studied metals in sediments. The industrial activities around water bodies were the most important agents for releasing heavy metals in the area under study, this finding was in agreement with [7,30].

Table 6: The Pearson's correlation coefficients between total heavy metals in sediments and the related variables measured in Shatt A-Arab river.

Variables	Cd	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1						
Cu	0.70 **	1					
Fe	-0.20 ^{NS}	-0.03 ^{NS}	1				
Mn	0.39 **	0.38 **	0.10 ^{NS}	1			
Ni	0.38 **	0.60 **	-0.03 ^{NS}	-0.10 ^{NS}	1		
Pb	0.34 **	0.15 ^{NS}	-0.16 ^{NS}	0.24 ^{NS}	-0.46 **	1	
Zn	0.27 *	0.53 **	-0.01 ^{NS}	0.43 **	-0.05 ^{NS}	0.33 *	1
Sand %	-0.09 ^{NS}	-0.12 ^{NS}	0.02 ^{NS}	0.25 ^{NS}	0.03 ^{NS}	-0.03 ^{NS}	-0.22 ^{NS}
Silt %	0.21 ^{NS}	0.18 ^{NS}	-0.10 ^{NS}	-0.16 ^{NS}	0.14 ^{NS}	0.24 ^{NS}	-0.01 ^{NS}
Clay %	-0.18 ^{NS}	-0.15 ^{NS}	0.10 ^{NS}	0.08 ^{NS}	-0.14 ^{NS}	-0.22 ^{NS}	0.07 ^{NS}
TOC%	0.07 ^{NS}	0.14 ^{NS}	0.17 ^{NS}	0.29 *	-0.14 ^{NS}	0.23 ^{NS}	0.16 ^{NS}

** : Significant correlation at P<0.01 ; * : Significant correlation at P<0.05 NS: Non- Significant correlation(P>0.05) .

Conclusion

Sediment pollution in the present study was assessed using geoaccumulation index (Igeo) and enrichment factor (EF). Based on values of Igeo, the surface sediments can be classified as unpolluted with Fe and Zn, while unpolluted to moderately polluted with Cu, Mn and Pb, and moderate to strongly polluted with Cd and Ni.

The elevated values identified for Cd, Ni and Pb are probably a result of anthropogenic activities in Shatt Al-Arab river. These sources mainly include the effluent of wastewater plants which released large amounts of Pb and Cd compounds into the river. The mean concentrations of some of the heavy metals were high in the sediment samples considered but not beyond the values recommended in Consensus-Based Sediment Quality Guidelines of Wisconsin. According to EF results, the source of Cd, Ni, Pb and Mn in Shatt Al-Arab sediments was anthropogenic, while for Cu and Zn was natural. Further research has to be carried out to determine the concentration of heavy metals in the various organs of the aquatic animals in the environment and the speciation of heavy metals in sediment of this environment to determine their mobility.



References

- [1]. Al-Hejuje, M.M. (2014). Application of Water Quality and Pollution Indices to Evaluate the Water and Sediments Status in the Middle Part of Shatt Al-Arab River. Ph.D. Thesis. University of Basrah, college of Science, Biology department, 240 pp.
- [2]. Bakan, Gülfem; Hülya Böke Özkoc; Sevtap Tülek; Hüseyin Cüce (2010). Integrated Environmental Quality Assessment of Kizilirmak River and its Coastal Environment. *Turk. J. Fish. Aquat. Sci.*, 10(4): 453-462.
- [3]. Hassan, W.F. (2007). Geochemical and hydrochemical Study at Shatt Al-Arab Chanal Sediments and Overlying Water. Ph.D. Thesis, College of Agriculture, University of Basrah. 205 pp
- [4]. Al-Haidarey M. J. S. (2009). Assessment and sources of Some Heavy Metals in Mesopotamian Marshes. Ph. D. Thesis, College of Science for Women, University of Baghdad, Iraq. 158 pp.
- [5]. Christophoridis, C.; Dedepsidis, D.; Fytianos, K. (2009). Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. *J. Hazardous Materials*, 168: 1082-1091.
- [6]. De Jonge, M.; De Vijver, B.V.; Blust, R.; and Bervoets, L. (2008). Responses of aquatic organisms to metal pollution in a lowland river in Flanders: A comparison of diatoms and macroinvertebrates. *Sci. Total Environ.*, 407: 615-629.
- [7]. AL-Hejuje, M.M. (1999). Distribution of Cobalt, Nickel, Manganese and Iron in the sediments from Al-Ashar and Al-Khandak canals connected with Shatt Al-Arab River, Basrah. *Marina Mesopotamica*, 14(2): 365-379.
- [8]. Balasim, H. M. (2013). Assessment of some heavy metals pollution in water, sediments and *Barbus xanthopterus* (Heckel, 1843) in Tigris River at Baghdad city. M.Sc Thesis. College of Science, University of Baghdad. 159 pp.
- [9]. Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geol. J.*, 2(3):108-118. Cited by: Farkas, A.; Erratico, C.; and Viganò, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere*, 68: 761-768.
- [10]. Bhuiyan, M.A.H.; Islam, M.A.; Dampare, S.B.; Parvez, L.; and Suzuki, S. (2010). Evaluation of hazardous metal pollution in irrigation and drinking water systems in the vicinity of a coal mine area of northwestern Bangladesh. *J. Hazardous Materials*, 179: 1065-1077.
- [11]. Ball, F.D. (1964). Loss on ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *J. Soil Sci.*, 15: 84-92.
- [12]. Folk, R.L. (1974). *Petrology of Sedimentary Rocks*. Hemphill Publishing Co. Austin, Texas. USA, 182 pp.
- [13]. Chester, R. & Voutsinou, F.G. (1981). The initial Assessment of Trace Metal Pollution in Coastal Sediments. *Mar. Poll. Bull.*, 12(3): 84-91.
- [14]. Sturgeon, R. E., Desaulniers, J. A. H., Berman, S. S., and Russell, D. S. (1982) Determination of trace metals in estuarine sediments by graphite-furnace atomic absorption spectrometry, *Analatical Chem. Acta.*, 134: 288-291.
- [15]. Ergin, M. Saydam, C. Basturk, O. Erdem, E. and Yoruk, R. (1991). Metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the northeastern Sea of Marmara. *Chemical Geology*, 19(3,5): 269-285.
- [16]. Sutherland, R.A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39(6): 611-627.
- [17]. Zhang, J. and Liu, C.L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China – weathering features, anthropogenic impact and chemical fluxes. *Estuar. Coast. Shelf Sci.*, 54, 1051–1070.
- [18]. Al-Juboury, A.I. (2009). Natural Pollution by Some Heavy Metals in the Tigris River, Northren Iraq. *Inte. J. Environ. Res.*, 3(2):189-198.



- [19]. Song, Y.; Ji, J.; Mao, C. Yang, Z.; and Yuan, X. (2010). Heavy metal contamination in suspended solids of Changjiang River –environmental implication. *Geoderma*, 159:286-295.
- [20]. Manoj, K; Padhy, P.K.; and Chaudhury, S. (2012). Study of Heavy Metal Contamination of the River Water through Index Analysis Approach and Environmetrics. *Bull. Environ. Pharmacol. & Life Sci.*, 1(10):7-15.
- [21]. Al-Sharifi, F; Al-Kandari, A.; Al-Khalaf, B.; Al-Rifay , I.; and Al-Mudhf, H.F. (2009). Trace metals and total organic carbon concentrations at intertidal area in Sulaibikhat Bay. *Kuwait J. Sci. Eng.*, 36(2A): 125-145.
- [22]. Reza, R.; and Singh, G. (2010). Heavy metals contamination and its indexing approach for river water. *Intern. J. Envi.Sci.Technol.*, 7(4):785-792.
- [23]. Wisconsin Department of Natural Resources. (2003). Consensus based sediment quality guidelines (CBSQG, 2003). Recommendations for use and application. Department of interior, Washington D.C. 20240 pp 17.
- [24]. Al-Sabah, B.J.J. (2007). Study of Physiochemical Behavior of Polluted Mineral Elements for Water and Sediments of Shatt AL-Arab. Ph.D. Thesis, College of Agriculture, University of Basrah, 223 pp.
- [25]. Basaham, A.S. (2010). Distribution and Partitioning of Heavy Metals in Subtidal Sediments of the Arabian Gulf Coast of Saudi Arabia. *JKAU: Earth Sci.*, 21(1): 201-222.
- [26]. Suthar, S.; Nema, A.K.; Chabukdhara, M.; and Gupta, S.K. (2009). Assessment of metals in water and sediments of Hindon River, India: Impact of industrial and urban discharges. *J. Hazardous Materials*, 171:1088-1095.
- [27]. Farkas, A.; Erratico, C.; and Viganò, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere*, 68: 761-768.
- [28]. Mahmood, Amal A. (2008). Concentrations of pollutants in water, sediments and aquatic plants in some wetlands in South of Iraq. Ph.D. Thesis. University of Basrah, college of science, biology department, 244 PP.
- [29]. Hassan, F.M.; Saleh, M.M.; and Salman, J.M. (2010). A study of physicochemical parameters and nine heavy metals in the Euphrates River, Iraq. *E-Journal of Chemistry*, 7(3):685-692.
- [30]. Nowrouzi, Mohsen and Pourkhabbaz, Alireza (2014). Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Hara Biosphere Reserve, Iran. *Chemical Speciation and Bioavailability*, 26(2) :99-105

