HEAVY METALS INDICIES IN SHATT AL-ARAB RIVER, BASRAH PROVINCE, IRAQ. I: SEDIMENTS ادلة التلوث بالعناصر الثقيلة في نهر شط العرب


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HEAVY METALS INDICIES IN SHATT AL-ARAB RIVER, BASRAH PROVINCE, IRAQ. I: SEDIMENTS

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ABSTRACT

In this study, total concentration of nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were investigated along different sites of Shatt Al-Arab river in Basra South Iraq by using Atomic absorption. Geo accumulation index (I_{geo}) and Contamination Factor (CF) and Pollution Load Index (PLI) and Enrichment factor(EF) were computed and compared in different sites of the sediment. Total concentration of metals in sediment samples found to be in this order: Fe > Mn> Ni> Zn> Cu> Pb> Cr> Co> Cd. I_{geo} results indicated that the sediment strongly to extremely polluted for Cd and the other indexes results showed that the sediment is unpolluted for Pb in all station expect Al-Ashar and Cd were applied to metals also to investigate on I_{geo} results. The results of the present study showed that the sediment of Shatt Al-Arab is threatened by pollutants related to rivers entering it. So to preserve the environment of the sediment deterioration, the main act is to prevent the discharge of wastewater to rivers entering it.

KEY WORDS: Shatt AL-Arab, Heavy metals, Sediment Quality, geo-accumulation index, Pollution Load Index

INTRODUCTION

Assessment of heavy metals as toxic pollutants in environment has a significant importance in environmental pollution studies. Surficial sediments of water resources have a high potential in releasing heavy metals to the upper water environment, hence sediment analysis presents guidelines to the authorities for monitoring the environmental systems.

Assessing contamination of pollutants is to understand source, concentration, distribution and effects in environment especially in the estuarine and coastal water because the aquatic life is influenced by these type of pollutants (Nobi *et al.*, 2010). There are lithogenic and anthropogenic sources for heavy metals extensively enter into environment. The concentration and distribution of the heavy metals are affected by sedimentary structure, mineralogical compound, hydrodynamic transports, industrial discharges, effluents and shipping activities (Vallejuelo *et al.*, 2010; Vallejuelo *et al.*, 2010; Hart, 1982).

Heavy metals pollution mostly from anthropogenic activities represents a serious problem for human health (Harrison, 1981). Nevertheless, the terrestrial and aquatic ecosystem received elevated inputs of heavy metals as a result of an increase in atmospheric deposition and anthropogenic activities. Furthermore, they reported that heavy metals contamination in aquatic ecosystem is of critical concern, as the effect of heavy metals toxicity and their accumulation in aquatic habitats (Gibson and Farmer, 1986).

Trace metals are among the most common environmental pollutants and their occurrence in waters, sediments and biota indicate the presence of natural or anthropogenic sources. The remains of trace metals in aquatic environments has led to serious concerns about their influence on plants and animals life (Sheikh *et al.*, 2007; Zvinowanda *et al.*, 2009).

The assessment of sediment enrichment with elements can be carried out in many ways. The most

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common ones are the index of geo-accumulation index (I_{geo}), pollution load index (PLI) Enrichment factor (EF) and Contamination factor(CF). The I_{geo} has been widely used as a measure of pollution in freshwater sediment (Singh, 1997), while the pollution load index (PLI) represents the number of times by which the heavy metal concentrations in the sediment exceeds the background concentration, and gives a combined indication of the overall level of heavy metal toxicity in a particular sample (Priju and Narayana, 2006). Pollution Load Index (PLI) was used to evaluate the extent of pollution by heavy metals in the environment. The range and class are same as I_{geo}. PLI for a particular site has been calculated following the method planned by Tomlinson (1980).

The aim of this study is measure the concentration of some heavy metals and their association with various geochemical substrates in sediments of Shatt AL-Arab river and to assess the influence of anthropogenic activities in sediment pollution.

MATERIALS AND METHODS

Sampling and Experimental analysis

Water samples and surface sediment samples were collected from six stations along the Shatt Al-Arab river The first station is Al-Qurna in North of Basra, the second is AL-Diar, and third station is Al-Qurma, Al-Ashar Abo AL-Khaseeb and Al-Fao for the purpose of analysis and estimation the concentration of Cd, Co, Cr, Cu, Fe, Mn , Ni, Pb and Zn during one year and for four seasons of the year.

Analysis of sediments Preparation One gram of dried air sediment sample was transferred to 100 mL Teflon tube and wet digested with concentrated HNO3 and HCL (1:3 v/v) on a hot plate. The tubes were cooled and volumes prepared with double distilled water in volumetric flask. The digested samples were analyzed for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn according to Parks *et al.* (1996) using Atomic Absorption Spectrophotometers Technique. Statistical analysis of ANOVA were applied to better understand of metals variation and significant differences between stations. In this research four indexes are used to assess the pollution of 'sediment, Geo-accumulation Index (I_{geo}), Enrichment Factor (EF), Contamination factor (CF) and Pollution Load Index (PLI). The Geo-accumulation Index (I_{geo}) introduced by Muller (1969) to assess contamination level or degree. It is expressed as in equation and Table 1 shows the geochemical index which includes various degrees of contamination (Vallejuelo *et al.,* 2010; Sinex and Helz, 1981; Singh *et al.,* 2003).

Determination of geo accumulation index

The geo accumulation index I geo values were calculated for different metals as introduced by Muller (1969) is as follows :

$$I_{geo} = \log^2 C_n / 1.5 B_n \quad .. (1)$$

Where, C_n is the measured concentration of element n in the sediment and B_n is the geo accumulation background for the element n which is either directly measured in precivilization sediments of the area or taken from the literature (average shale value described by Kabata-Pendias (2011). The factor 1.5 is introduced to include possible variation of the background values that are due to lithologic variations (Al-Lami and Al-Jaberi, 2002).

Contamination factor (CF)

Contamination factor (CF) was determined following equation according to Tomlinson *et al.* (1980),

$$CF = C_m \text{ Sample} / C_m \text{ Background} \quad .. (2)$$

Equation 3 show the Pollution Load Index (PLI) (Kabata-Pendias, 2011). PLI is obtained as Concentration Factors (CF) (Equation 2). CF is ratio between the concentration of heavy metals in study area and background level. This index is quickly understood by unskilled personal in order to compare the pollution status of different places and it varies from 0 (unpolluted) to 10 (highly polluted).

$$PLI = (CF_1 * CF_2 * \ldots CF_n)^{\wedge}1/n \quad .. (3)$$

Enrichment factor(EF)

Enrichment Factors (EF) were considered to estimate the abundance of metals in sediment samples. EF was calculated by a comparison of each tested metal concentration with that of a reference metal (Muller, 1981). The normally used reference metals are Mn, Al and Fe (Liu *et al.,* 2005). In this study iron was used as a conservative tracer to differentiate natural from anthropogenic components, following the hypothesis that its content in the earth crust has not been troubled by anthropogenic activity and it has been chosen as the element of normalization because natural sources (98%) greatly dominate its contribution (Tippie, 1984). According to Rubio and Vilas (2000), the EF is defined as follows:

EF =(M/Fe sample)/(M/Fe background)

Where EF is the enrichment factor, (M/Fe) sample is the ratio of metal and Fe concentration of the sample and (M/Fe) background is the ratio of metals and Fe concentration of a background. Five contamination categories are reported on the basis of the enrichment factor (Sutherland, 2000). EF <2 deficiency to minimal enrichment.

RESULT AND DISCUSSION

Heavy Metals concentration

Analysis values of heavy metals are given in Table 1. The mean value and the range, SD and standard Error are given. The order of the mean concentrations of examined heavy metals: Fe>Mn>Ni >Zn>Cu> Pb>Cr>Co>Cd. The results indicated that the entire tested heavy metal exhibit higher values than the Interim sediment quality guideline (ISQG) for fresh water sediments, while Cd and Cr displayed higher values than the Probable effect level (PEL).

The range of the measured heavy metals concentrations (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the sediment at depths 0-10 cm of the studied area shown in table (1). The results reflect that the average concentrations of the studied heavy metals were relatively lower in Al-Qurna Al-Dair and Al-Karma than the other studied sites (Table 1). The maximum average concentrations area is the Al-Ashar site which shows high concentrations of the measured heavy metals (Cd, Co, Cr, Cu, Fe, Mn,

Table 1. Concentration of heavy metals (mg/Kg) for sediments of Shatt Al-Arab river

Element	Maxi	Mini.	Mean	SD	Std. Er	Element	Maxi.	Mini.	Mean	SD	Std. Er
		Al-Qurna						AL-Diar			
Cd	6	5	6	0.37	0.21	Cd	6.52	6.21	6.38	0.16	0.09
Co	9	8	9	0.55	0.32	Co	10	9.73	9.79	0.09	0.05
Cr	21	20	21	0.47	0.27	Cr	24	22	23	1.01	0.58
Cu	28	26	27	1.07	0.62	Cu	32	30	31.39	1.16	0.67
Fe	1265	1255	1260	5.06	2.92	Fe	1350	1310	1328	20.13	11.62
Mn	165	160	163	2.56	1.48	Mn	183	180	181	1.67	0.97
Ni	36	35	36	0.29	0.17	Ni	41	40	41	0.53	0.31
Pb	24	22	23	1.07	0.61	Pb	28	24	26	2.20	1.27
Zn	32	30	31	0.72	0.42	Zn	34	32.	33	0.92	0.53
		Al-Qurma						Al-Ashar			
Cd	9	08	09	0.60	.35	Cd	13	12	12	0.21	0.12
Co	12	11	11	0.30	0.17	Co	18	18	18	0.14	0.08
Cr	31	30	30	0.13	0.08	Cr	51	51	51	0.05	0.03
Cu	34	31	32	1.13	0.65	Cu	43	38	41	2.40	1.39
Fe	1435	1420	1428	7.55	4.36	Fe	2674	266	1870	1388	801
Mn	191	185	189	2.64	1.53	Mn	263	260	261	1.41	0.82
Ni	45	44	45	0.22	0.13	Ni	54	52	53	0.96	0.55
Pb	28	26	27	1.31	0.75	Pb	50	46	48	1.94	1.12
Zn	35	33	34	0.48	0.28	Zn	60	57	58	1.48	0.86
		AL-Khaseeb						Al-Fao Abo			
Cd	11	11	11	41	0.24	Cd	11	11	11	0.15	.09
Co	13	13	13	20	0.11	Co	14	14	14	0.13	.08
Cr	39	38	38	85	0.49	Cr	42	40	41	1.02	.59
Cu	37	33	35	1.62	0.93	Cu	38	36	37	1.18	.68
Fe	2543	25	1691	1443	832	Fe	2628	2536	2567	52	31
Mn	204	200	201	2.49	1.44	Mn	218	210	213	4	2.48
Ni	50	48	49	93	0.54	Ni	52	50	51	1	.59
Pb	34	32	32	1.08	0.62	Pb	38	37	38	0.40	.23
Zn	43	40	41	1.14	0.66	Zn	46	45	45	0.64	.37

Ni, Pb and Zn) with average concentration of 12.44,18.14 , 50.66, 40.65, 1870.33, 261.72, 53.34, 48.19 and 58.80 ppm respectively. While the lowest concentration are present in Al-Qurna station, where the heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) have the average concentration of 5.64 , 8.57, 20.65, 27.31, 1260.30, 162.99, 35.90, 23.18 and 31.45 ppm respectively (Table 1).

Indices

Several indices were used to assess the metal contamination levels in the sediment samples, Geo-accumulation index (I-geo), Contamination Factor (CF),Pollution Load Index (PLI) and Enrichment Factors (EF). World surface rock average data of heavy metals which was used as background values were taken from Kabata-Pendias (2011).

Geo-accumulation index

The calculated results of I-geo (Table 2), indicate that Cd can be considered to be a strongly to extremely polluted, while the I_{geo} values of fe show practically unpolluted in Al-Qurna Al-Diar and Al-Karma to moderately polluted degree the other stations . With few exceptions Co, Cr, Cu, Mn, Ni and Zn exhibit unpolluted degree. Furthermore, Pb and Ni displayed practically unpolluted degree in all stations expect in Al-Ashar was moderately polluted with Pb. On the basis of the mean values of I-geo, sediments in the Shatt Al-Arab river are enriched for metals in the following order: Cd> Fe> Pb> Ni> Cr> Cu > Zn >Mn and the pollution levels for the sites in the following order: 5>2>1.

Enrichment factor

Enrichment Factors (EF) were considered to estimate the abundance of metals in sediment samples. EF was calculated by a comparison of each tested metal concentration with that of a reference metal (Muller,1981). The normally used reference metals are Mn, Al and Fe (Liu *et al.*, 2005). In this study iron was used as a conservative tracer to differentiate natural from anthropogenic components, following the hypothesis that its content in the earth crust has not been troubled by anthropogenic activity and it has been chosen as the element of normalization because natural sources (98%) greatly dominate its contribution (Tippie, 1984). According to Rubio and Vilas (2000).

As shown in Table 3, average EF values for heavy metals have an order Cd>Ni>Pb>Cu>Zn> Cr>Mn, suggesting that sediment samples was significant

Table 2. Classified grades of I- geo, CF and PLI indices and Enrichment Factor (After Tomlinson *et al.*, 1980; Boszke *et al.*, 2004; Rabee *et al.*, 2011).

E.F	PLI	CF contamination factor	I-geo
<2 deficiency to minimal enrichment	<1 Perfection (class 0)		≤ 0 (class 0), Practically unpolluted
2-5 moderate enrichment	=1 Baseline level (class 1).	<1 Low contamination (class 1).	0 < to ≤ 1(class 1), slightly polluted
5-20 significant enrichment,	>1 Deterioration on site quality (class 2)	1≤ CF < 3 Moderate contamination (class 2).	1< to ≤ 2 (class 2), Moderately polluted
20 - 40 very high enrichment		3 ≤ CF ≤ 6 Considerable contamination (class 3).	2 < to ≤ 3 (class 3), moderately severely polluted
>40 extremely high enrichment.		>6 Very high contamination (class 4).	3< to ≤ 4 (class 4), Severely polluted
			4< to ≤ 5 (class 5), Severely extremely polluted
			> 5 (class 6), Extremely polluted

Table 3. Enrichment factor for the sediments samples of the Shatt Al-Arab River

Station	Zn	Pb	Ni	MN	Cu	Cr	Co	Cd
Al-Qurna	0.189	0.634	0.712	0.061	0.417	0.082	0.324	14.917
AL-Diar	0.190	0.674	0.768	0.065	0.454	0.086	0.351	16.007
Al-Qurma	0.181	0.650	0.784	0.062	0.437	0.107	0.373	20.029
Al-Ashar	0.238	0.888	0.713	0.066	0.418	0.135	0.462	22.177
Abo AL-Khaseeb	0.185	0.661	0.721	0.056	0.400	0.113	0.357	21.243
Al-Fao	0.134	0.511	0.500	0.039	0.280	0.081	0.261	14.393

enrichment in all station expect Al-Ashar and Abo Al-Kasseb were very high enrichment with Cd, while the other metals study full with deficiency to minimal enrichment. In contrast, the rest of the metals show moderate or minimal enrichment in the study area. With respect to specific sites, high EF values (e.g., 22.177 for Cd, 0.888 for Pb, 0.135 for Cr, 0.784 for Ni, 0.454 for Cu and 0.238 for Zn) are found at Al-Ashar station, which was located at the city center downstream and continuously receives a vast amount of wastewater and other wastes of the city.

Contamination factor

Generally sediments have been used as environmental indicators, and this ability to identify heavy metal contamination sources and monitor contaminants is also well documented. Thus, the accumulation of metals in the sediments is strongly controlled by the nature of the substrate as well as the physicochemical conditions controlling dissolution and precipitation (Kabata-Pendias, 2011). The level of metal contamination was expressed by the contamination factor (Al-Lami and Al-Jaberi, 2002). Contamination Factor (CF) was used to determine the contamination status of sediment in the current study.

The average CF values for different heavy metals in the sediments of Shatt Al-Arab river (Table 4) are Cd>Fe>Pb>Ni> Cu>Zn>Cr>Mn (Table 4). For all sites along the Shatt Al-Arab river, the CF value for Cd is >6, indicating that this environment are very highly contaminated with Cd, while CF value for Co is full into class 1 and 2 displayed Low to moderate contamination. on the other hand the sediments are moderate contamination with Cu, Ni and Pb. The pollution levels for the sites in the following order: 3>1>2, suggesting that the site located in the downstream is more seriously polluted by heavy metals than other sites, attributed to the feeding river input.

Pollution Load Index

Pollution Load Index (PLI) was used to evaluate the extent of pollution by heavy metals in the environment.

The value of PLI ranges from 2.11 in the Al-Ashar station in city center to 1.15 in Al-Qurna station in upstream site (Table 4), indicated moderately to strongly polluted. However, Al-Ashar station displayed the highest PLI value and reflects the highest presence of all the examined heavy metals; indicating that this site is considerably affected by different anthropogenic activities, while Al-Qurna station exhibit the lowest contamination factors of all the studied heavy metals, Therefore, this site has the lowest PLI.

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Table 2. I-geo values for sediments samples of the Tigris River

Station	Zn	Pb	Ni	Mn	Fe	Cu	Cr	Co	Cd
Al-Qurna	-1.654	0.092	0.259	-3.283	0.749	-0.514	0.138	-0.877	4.648
AL-Diar	-1.570	0.256	0.444	-3.126	0.825	-0.313	0.152	-0.685	4.826
Al-Qurma	-1.536	0.308	0.578	-3.073	0.929	-0.265	0.203	-0.493	5.253
Al-Ashar	-0.752	1.148	0.830	-2.600	1.318	0.060	0.338	0.204	5.789
Abo AL-Khaseeb	-1.259	0.576	0.700	-2.980	1.173	-0.150	0.256	-0.312	5.582
Al-Fao	-1.120	0.806	0.777	-2.893	1.775	-0.061	0.276	-0.163	5.623

Table 4. Pollution Load Index (PLI) and Contamination factor (CF) for the sediments samples of the Shatt Al-Arab

Station	PLI	CF							
		Zn	Pb	Ni	Mn	Fe	Cu	Cr	Co	Cd
Al-Qurna	1.151	0.477	1.599	1.795	0.154	2.521	1.050	0.207	0.817	37.600
AL-Diar	1.280	0.505	1.792	2.040	0.172	2.657	1.207	0.228	0.933	42.533
Al-Qurma	1.432	0.517	1.857	2.239	0.178	2.856	1.248	0.305	1.066	57.200
Al-Ashar	2.110	0.891	3.323	2.667	0.247	3.741	1.564	0.507	1.728	82.956
Abo AL-Khaseeb	1.666	0.627	2.236	2.437	0.190	3.382	1.352	0.383	1.208	71.844
Al-Fao	1.874	0.690	2.622	2.570	0.202	5.135	1.438	0.414	1.340	73.911

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