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DISTRIBUTION OF HEAVY METALS IN CORE SEDIMENTS OF SOUTHERN IRAQ WATERWAYS

The object of the study is heavy metals in the Shatt Al-Arab River. Shatt Al-Arab River is considered one of the most important internal rivers in Iraq due to its multiple economic and social importance. In addition, this river has an important strategic location. Despite its importance mentioned above, the Shatt Al-Arab River suffers from various wastes from many and varied sources, which have directly affected the quality of its water and consequently the quality of the community of living organisms that live in it. Levels and distribution of certain heavy metals, Cd, Cu, Fe, Mn, Ni, and Pb, were determined in core sediments from Southern Iraq Waterways. Six sites were investigated, two in the lower reaches of Al-Hammar Marsh, 1) El-Barka, 2) El-Garmah, and four sites along Shatt Al-Arab River, 3) Al-Ashar, 4) Abu Al-Khaseeb, 5) Abu Floos Port, and 6) Al-Faw. The results indicate that Al-Faw station was distinguished by the fact that the highest values of heavy elements were obtained at this station and all depths, except Cd at Al-Ashar station at a depth of 25 cm (26.1375 μ/gm), Cu at a core depth of 50 cm (4.9635 μ/gm), Ni at a core depth of 25 cm (5.2483 μ/gm), and surface water (2.9021 μ/gm) and Pb in surface water at Abu Floos Port station (3.5001 μ/gm). The lowest concentrations of heavy elements for Cu, Mn, and Ni are in all depths of core sediments. Other elements, Cd, Pb, and Fe, were higher; on the other hand, higher levels of concentrations for all studied heavy metals were recorded at a depth of 100 cm. Iron was the highest in all depths of core sediments.

Keywords: *sediments, heavy metals, atomic absorption, Southern Iraq Waterways, Shatt Al-Arab River.*

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1. Introduction

The waters and sediments of Southern Iraq Waterways, represented by Marshlands and Shatt Al-Arab River, are contaminated with heavy metals from different sources, mainly atmospheric deposits of gaseous emissions from oil production fields and electric generators, surface runoff from agriculture areas after rainfall, and tides from the Arabian Gulf [1].

The Tigris, Euphrates, Shatt Al-Arab rivers, and North West Arabian Gulf areas showed certain levels of heavy metals in surface sediments [2]. Although they were lower in concentrations, heavy metals were recorded at certain levels in the surface sediments from Southern Iraq Marshlands [3]. Surface sediment records explain contamination levels at present, whereas sediment cores provide a historical record of variations in natural and anthropogenic input. The geochemistry of sediments, particularly cores, provides information about environmental pollution [4].

Sediments serve as reservoirs for pollutants such as chemical elements extracted from the water column. The concentrations of heavy elements Cd, Cu, Fe, Mn, Ni, Pb, and Zn were recorded in sediments from the Tigris, Euphrates, and Shatt Al-Arab rivers [5]. They concluded that the concentrations of studied heavy metals were high except for Cd and Ni.

The whole area of the Arabian Gulf is contaminated with heavy metals from different sources [6], in which heavy metals Cd, Cr, Cu, Fe, Ni, Pb, and Zn were recorded in the surface sediments of the Eastern Arabian Gulf.

Southern marsh Al-Hammar and Shatt Al-Arab River are subject to variable pollutants such as petroleum hydrocarbons, fertilizers and pesticides, and heavy metals, which could arise from different sources such as population growth, waste discharge, historic waste of the Iraq-Iran war 1980–1988, and agriculture activities.

The aim of this paper is to investigate the presence and distribution of heavy elements in core sediments from Southern Iraqi Waterways, Al-Hammar Marsh, and Shatt Al-Arab River.

2. Materials and Methods

Sediment cores were collected from six sampling stations, as shown in Fig. 1, two sites in the lower reaches of Al-Hammar Marsh:

1) El-Barghah;

- 2) El-Garmah, and four sites along Shatt Al-Arab River;
- 3) Al-Ashar;
- 4) Abu Al-Khaseeb;
- 5) Abu Floos Port;
- 6) Al-Faw City.

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46°30'0"E 46°40'0"E 46°50'0"E 47°0'0"E 47°10'0"E 47°20'0"E 47°30'0"E 47°40'0"E 47°50'0"E 48°00"E 48°10'0"E 48°30'0"E 48°30'0"E 48°40'0"E

Fig. 1. Location map of Southern Iraq Waterways, Southern Marsh, stations 1 and 2, and Shatt Al-Arab River, stations 3, 4, 5 and 6

Core sediments were collected utilizing a core samples from the middle of the waterways. Core sediments were kept in Aluminum foil, transferred to the Marine Science Center lab, Basra University (Iraq), cut into pieces each of 25 cm, and kept in the fridge before analysis. Following the same procedure set by [3], samples of core sediments, freeze-dried crushed, and a certain amount were weighed and wet digested by a 3:1 acid mixture of HNO3:HCl. After complete digestion, samples were poured into a 50 ml volumetric flask, and volume completed to 50 ml by distilled water, then heavy metals, Cd, Cu,

Fe, Mn, Ni, and Pb, were determined by adopting the atomic absorption spectrophotometry, using the atomic absorption instrument model Angstrom AA320N air acetylene flame Atomic Absorption Spectrophotometer fitted with special Hallow Cathode Lamps for each element.

3. Results and Discussion

3.1. Results. Cd showed an increase for all core samples, with a little increase from El-Barka, (station 1) at Al-Hammar Marsh, dawn to Al-Faw, (station 6) at Shatt Al-Arab estuary. Cu showed the same behavior as Cd. Fe showed higher levels in all cores, a great increase with depth, and a higher level at Al-Faw, although it shows an alternative level at core 50 cm for most stations. Mn showed little increase with stations from 1 to 6, while it showed great changes at deep cores. Ni and Pb showed slight changes for all stations from El-Barka to Al-Faw and a slight increase from surface sediments toward bottom cores.

3.1.1. Surface sediments. The highest values obtained in the surface sediments were for Fe and Cd at the Al-Faw station, reaching 77.287 μ /gm and 15.305 μ /gm, respectively, and the lowest was 0.8055 μ /gm for Cd at the El-Barka station. At the same time, no presence of Mn was recorded at the El-Barka and El-Garmah stations (Fig. 2, 3, Table 1).

Fig. 3. Variation of Fe concentration for different cores cm in the studied station

Table 1

Recorded concentrations of heavy elements in core sediments from Iraq Southern Waterways

Depth, cm	Elements	Stations					
		1-El-Barka	2-El-Garmah	3-Al-Ashar	4-Abu Al-Khaseeb	5-Abu Floos	6-Al-Faw
Surface	Cd	0.8055	5.6385	9.666	11.277	12.898	15.3045
	Сu	1.6545	2.122	2.565	2.988	3.145	3.551
	Fe	46.372	26.11984	46.3722	57.4132	68.451	77.287
	Мn	0.00	0.00	0.9361	1.8722	1.8722	2.8083
	Ni	0.1145	0.8542	1.6554	2.6501	2.9021	1.0033
	Pb	0.1045	0.1205	1.9015	2.0065	3.5001	3.0201
25	Cd	16.915	19.332	26.1375	21.7485	23.459	23.9991
	Сu	1.6545	1.7822	1.9988	2.1552	3.309	3.5589
	Fe	90.511	92.5333	93.5362	94.9526	97.160	99.369
	Мn	2.8983	3.1183	3.7444	3.9433	4.6805	4.9915
	Ni	1.244	2.62415	2.62415	2.62415	5.2483	4.1055
	Pb	3.0045	4.0205	5.9015	7.065	9.5001	10.0201
50	Cd	24.171	24.3735	24.7655	24.9795	25.57	25.976
	Сu	3.309	3.309	3.309	3.309	4.9635	4.9035
	Fe	154.57	105.9936	132.492	119.2428	156.78	187.697
	Мn	5.3305	5.6166	7.4888	9.361	10.297	10.8922
	Ni	5.2201	5.5483	5.8413	5.9991	6.2483	6.7481
	Pb	5.1045	7.1025	7.0515	9.1265	10.450	13.9221
75	Cd	26.581	28.1918	28.3998	29.1095	29.803	33.0255
	Сu	5.1135	6.618	6.618	6.618	8.2725	9.927
	Fe	196.52	190.1977	275.1299	267.7534	353.13	517.5143
	Mn	14.041	16.8498	20.5942	27.1469	28.083	43.9967
	Ni	6.9444	7.2113	7.8024	7.7455	7.872	13.1205
	PЪ	9.1605	9.1605	10.6055	12.4865	12.416	16.4221
100	Cd	33.831	34.635	36.3344	36.6547	37.659	38.1298
	Сu	9.927	11.5815	13.236	13.8847	14.221	15.1101
	Fe	333.43	264.984	432.8072	439.4318	514.51	845.7406
	Mn	46.805	65.527	72.6654	78.9987	90.555	96.8298
	Ni	14.744	15.7009	20.9932	23.61735	23.617	31.4898
	PЪ	20.642	24.9633	33.2844	41.6055	45.660	45.7605

3.1.2. Core depth 25 cm. The depth of 25 cm was characterized by the fact that the highest values obtained were for iron and cadmium elements also at Al-Faw and Al-Ashar stations, where they reached 99.369 μ/gm and 26.1375 μ /gm respectively, and the lowest was 1.244 μ /gm for Ni at El-Barka station (Fig. 3, 4).

3.1.3. Core depth 50 cm. Fig. 3, 5 show that the highest values obtained at a depth of 50 cm were for Fe and Cd at the Al-Faw station, where they reached 187.697 μ /gm and 25.976 μ /gm, respectively, and the lowest for Cu at El-Barka, El-Garmah, Al-Ashar and Abu Al-Khaseeb stations, where they reached 3.309 μ/gm.

3.1.4. Core depth 75 cm. The highest values obtained at this depth were for Fe and Mn at Al-Faw station, reaching 517.51 and 43.997, and the lowest for Cu at El-Barka station, reaching 5.11 (Fig. 3, 6).

3.1.5. Core depth 100 cm. Fig. 3, 7 show that the highest values were obtained at the Al-Faw station for Fe and Mn, reaching 845.74 and 96.83 respectively, and the lowest was 927.9 for copper at the El-Barka station.

5-Abuztloos

6-Al-Faw

3-Al-Ashar

1-El-Barka

2- Elamah

Concentration. μ/gm

Concentration. $\mu\ell g m$

Fig. 5. Variation of heavy metals concentration for core 50 cm in the studied station

■Cd \Box Cu Mn Ni Pb

Fig. 7. Variation of heavy metals concentration for core 100 cm in the studied station

3.2. Discussion. High concentrations of pollutants such as heavy metals and petroleum hydrocarbons in the water column of any water body lead to the accumulation of these pollutants in the bottom surface sediments and then in different layers of core sediments, which change with time and circumstances.

Bottom and core sediments from Southern Iraq Waterways, represented by Al-Hammar Southern Marsh and Shatt Al-Arab River, are contaminated to certain levels with heavy metals. They showed an increase downstream from station 1 to station 6, which indicates two phenomena: 1 – the river is unable to clean itself, i. e., selfpurification is rare, and 2 – water discharge in Southern Iraqi waterways was law or not detected [7]. Most heavy metal concentrations in core sediments increase from the bottom to the upper layers [8], while in this study, the reverse is recorded. The concentrations of all studied heavy metals were increased from surface to deep core, this was explained based on sedimentation rate during the past few decades when sinking vessels were huge especially during the Iraq-Iran war 1980–1988.

Sediments must be fine and clean for chemical analysis. Therefore, they should be ground by hand mortar and then

screened with a 63 μ metal sieve to remove large particles and debris.

Within study of the Shatt Al-Arab River [9] reported that it was critically and seriously polluted by heavy metals. Water draining from heavily urbanized, industrialized, and agriculturized areas around the Shatt Al-Arab River introduces significant amounts of pollutants such as petroleum hydrocarbons, pesticides, and heavy metals to the river. Then, metals are deposited on the river's bottom surface, accumulating in different layers with time. Within study of heavy metals in surface sediments from the Shatt Al-Arab River [10] reported contamination by Cr, Cu, Ni, Pb, and Zn as well as slight contamination

with Fe and Mn, while considered as not contaminated with Co and V.

Sites 1 and 2 of this study are located within the southern part of Al-Hammar Marsh, Basrah Province, and they receive pollutants by suspended materials from the Tigris and Euphrates rivers flow waters [3].

Trace elements were reported as contaminants in 20–58 cm core sediments at sites in Iraq rivers, extending from Hilla city in the middle sector down to the Euphrates and Shatt Al-Arab rivers in Southern Iraq [11].

In the whole cores, Iron showed the highest levels, followed by cadmium, manganese, Nickel, lead, then Cupper, so the increase of heavy elements with core depth followed the trend, Cu < Pb < < Ni < Mn < Cd < Fe.

One of the most polluting sources in Basra Province is the Abadan crude oil refinery estate, which is located inside Iranian territory on the Eastern Bank of Shatt Al-Arab River (Fig. 8) between stations 4 (Abu Al-Khaseeb) and station 5 (Abu Floos).

The results of the current study showed an increase in the concentration of heavy elements with increasing core depth. One of the reasons that led to this increase in the concentration of heavy elements is the increase in salts, which work to increase the deposition of minerals in the soil at different depths, in addition to river dredging operations, tides, and water movement, which help transport heavy elements from one area to another.

The presence and quantifying chemical elements in core sediments is of importance to understand natural environmental processes and monitor the degree of anthropogenic distribution. Moreover, a baseline could be established for the chemical elements profile or concentration in core sediments in the study area and compared with other areas of the same texture and environmental pollution history. Differences in concentrations of chemical elements in core sediments of Southern Iraq water ways depend on grain size and amount of organic matter.

Fig. 8. Abadan crude oil refineries inside the Iranian territories on the eastern bank of Shatt Al-Arab river

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4. Conclusions

Water and sediments of Southern Iraq Waterways are suffering impacts from many sources such as industrial activities, traffic, urban areas, agriculture, dust fallout, as well as sinking vessels and oil spills. They can move downstream from one site to another within the same area, causing the spread of contaminants in the water and sediments underneath. The most affected sectors are human beings, which use water for drinking, domestic, liaise, and other important uses, and fish, which use food in the bottom surface sediments.

The results indicate that Al-Faw station was distinguished by the fact that the highest values of heavy elements were obtained at this station and all depths, except Cd at Al-Ashar station at a depth of 25 cm (26.1375 μ /gm), Cu at a core depth of 50 cm (4.9635 μ /gm), Ni at a core depth of 25 cm (5.2483 μ /gm), and surface water (2.9021 μ /gm) and Pb in surface water at Abu-Floos Port station $(3.5001 \mu/\text{gm})$. The lowest concentrations of heavy elements for Cu, Mn, and Ni are in all depths of core sediments. Other elements, Cd, Pb, and Fe, were higher; on the other hand, higher levels of concentrations for all studied heavy metals were recorded at a depth of 100 cm. Iron was the highest in all depths of core sediments.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

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Data availability

Data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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