Heavy metals concentrations in Sediments of Al-Delmaj Marsh, Al-Qadisiya /Wasit Governorates/ Southern Iraq

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Article History

Received on: 02/03/2020
Revised on: 13/03/2020
Accepted on: 12/04/2020

Keywords:

Heavy metals, Sediments,
Al-Delmaj Marsh.

DOI: <https://doi.org/10.29350/jops.2020.25.2.176>

ABSTRACT

The seasonal study of heavy metals were taken during February 2018 to November 2018. The concentration of heavy metals were determined (Cd, Cr, Cu, Zn, Ni, Pb, Fe), by using Flame Atomic Absorption Spectrophotometer (FAAS) for sediment sample at Ten stations along Al-Delmaj Marsh they are (St.1, St.2 before water recharge, St.2 after water recharge, St.3, St.4, St.5 before water discharge, St.5 after water discharge, St.6, St.7, St.8), the stations were selected to cover all the marsh area. The Total Organic Carbon (TOC%) were analyzed. The results obtained for the sediment samples were low except for Fe and Pb which were relatively high. Which were followed the order : (Fe > Pb > Zn > Ni > Cr > Cu > Cd). Whereas the highest mean also the lowest mean concentration in some stations because of the fewness sources of pollution in this region whereas the highest mean concentration in other stations because of there are a lot of pollution sources such as: (sewage pollutants, municipal waste, and fertilizer waste). there is a variation in the concentrations of studied elements they were ranged as follows: Cd: (0.222 - 0.283 µg/g), Cr: (1.472 - 1.685 µg/g), Cu: (0.305 - 0.362 µg/g), Zn: (1.947 - 2.826 µg/g), Ni: (1.738 - 2.206 µg/g), Pb: (3.696 - 4.921 µg/g), and Fe: (10.95 - 13.247 µg/g). The concentrations of heavy metals are very importance to know the locations of pollution, its percentage and causes, sources and methods of treating pollution to preserve public health. The rate of Total Organic Carbon in the studied area were ranged (0.55- 0.97), and this indicates the influence of sediments in the presence of a source of organic materials, due to the degradation process that occurs in the area sediments.

1. Introduction

Heavy metals include (Ni, pb, Cd, Cu, Fe, Cr,..etc). Their presence and properties in the soils generally depends on the parent rock derived from them. Measuring the concentrations of these elements can lead to identification the source of pollution in water systems and soils [6,3].

These elements are one of the most dangerous of inorganic pollutants, which had spreaded in the environment since the beginning of the industrial revolution, and their significantly accumulation lead to the transformation of more toxic complex compounds to remain for a long time in the environment were causing imbalance in the natural balance of the ecosystem, as well as, increasing their rates were damaged the soil characteristics and the destruction the biological diversity in the environment. Heavy metals pollution became a major environmental problem, due to their toxicity, non-degradable and

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constant nature. This leads to their aggregation in plants, microorganisms and other aquatic organisms, that are transmitted to humans through the food chain, this leads to multiple health problems [15]. In naturally aquatic environments, the elements are ordinarily at the concentrations differing from nanogram to microgram in a liter. These elements are essential and necessary to sustain the life of living organisms such as copper, zinc, and iron which play main roles in the functioning of enzyme systems. On the other hand, at higher concentrations become toxic. The other group of elements are non-essentially, it contains elements that pollute the environment and harm its revival even when it exists at high levels.

2. Materials and Methods

Sediment samples were collected seasonally, for the period from February 2018 to November 2018, from ten sampling stations for analysis and estimation the concentration of some heavy metals (Cd, Cr, Cu, Zn, Ni, Pb and Fe) as shown in Fig. (1). (sta.1, sta.2 before water recharge, sta.2 after water recharge, sta.3, sta.4, sta. 5 before water discharge, sta.5 after water discharge, sta. 6, sta.7, sta.8) in the Al-Delmaj marsh, the samples sites were selected based on field surveys. Sediment samples were taken seasonally from each stations by using (a Van veen grab sampler), the water was allowed to drain off, using polyethylene bags then the samples were placed in an ice box until reaching the laboratory. The heavy metals were extracted according to the method of [11]. Sediment samples heavy elements were measured by using Flame Atomic Absorption Spectrophotometer (FAAS). The Total Organic Carbon content in the sediment samples was determined according to the burning method [14].

Figure (1) : Map of Al-Dalmaj Marsh showing sampling locations

3.Results and Discussion:

Results of the present study are shown in (Table 1), The concentration of Cd in the sediment samples during summer was (0.311 $\mu\text{g/g}$) in station (1), the lowest concentration reached (0.153 $\mu\text{g/g}$) in station (2) before water recharge and at average (0.222 $\mu\text{g/g}$) for all stations. In autumn season the concentration reached the highest concentration (0.429 $\mu\text{g/g}$) in station (2) after water recharge, and its lowest concentration (0.202 $\mu\text{g/g}$) in station (8) and at mean (0.283 $\mu\text{g/g}$) for all stations, while in winter season concentration report the highest concentration to (0.346 $\mu\text{g/g}$) in station (1) and its lowest concentration (0.175 $\mu\text{g/g}$) in station (2) before recharge and at average (0.241 $\mu\text{g/g}$) for all stations. In the spring season, reached its highest concentration to (0.321 $\mu\text{g/g}$) in station (1), and its lowest concentration (0.167 $\mu\text{g/g}$) in station (2) before water recharge and at mean (0.223 $\mu\text{g/g}$) for all station. When comparing the results, the highest concentrations of this element were in the autumn season reached (0.429 $\mu\text{g/g}$) in station (2) after water recharge and lowest concentrations in the winter season reached (0.175 $\mu\text{g/g}$) in station (2) before water recharge. The increasing of Cd in the autumn season may due to increased human activities and continuous release of pollutants by soil washing process without treatment [13]. The concentration of Cr in the summer season (Table 1) equal to (2.453 $\mu\text{g/g}$) in station (1), and the lowest concentration (0.685 $\mu\text{g/g}$) in station (7) and at mean (1.472 $\mu\text{g/g}$) for all stations. In the autumn season the concentration reached the highest concentration (2.544 $\mu\text{g/g}$) in station (1), and the lowest concentration equal to (0.971 $\mu\text{g/g}$) in station (8) and at mean (1.677 $\mu\text{g/g}$) for all stations. In winter season, the highest concentration in the sediment sample was (2.829 $\mu\text{g/g}$) in station (1), and the lowest concentration (0.944 $\mu\text{g/g}$) in station (7), at mean (1.685 $\mu\text{g/g}$) for all stations. In the spring season sediment sample reached the highest concentration was (2.653 $\mu\text{g/g}$) in station (1), and the lowest concentration (0.855 $\mu\text{g/g}$) in station (7), at mean (1.587 $\mu\text{g/g}$) for all stations. the concentrations of the element in the sediment sample among the seasons are very small, the highest concentrations for the element were found in station (1) because of sewage pollution and using of fertilizers in the surrounding area, the lowest concentrations at station (7) reached (0.685 $\mu\text{g/g}$) in the summer season sediment sample.

Table (1): Seasonal variations concentrations of (Cd and Cr) $\mu\text{g/g}$ from the study stations

Stations	Cd ($\mu\text{g/g}$)				Cr ($\mu\text{g/g}$)			
	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
1	0.311	0.336	0.436	0.321	2.453	2.544	2.829	2.653
2 before	0.153	0.317	0.175	0.167	2.002	2.233	2.032	2.003
2 after	0.179	0.429	0.194	0.186	2.091	2.322	1.495	2.102
3	0.201	0.256	0.187	0.175	1.232	1.527	1.426	1.311
4	0.213	0.219	0.216	0.204	1.544	1.611	1.828	1.766
5 before	0.239	0.237	0.248	0.222	1.424	1.721	1.625	1.586
5 after	0.255	0.332	0.286	0.246	1.038	1.811	1.744	1.099
6	0.214	0.296	0.228	0.23	1.127	1.022	1.202	1.201
7	0.248	0.211	0.285	0.266	0.685	1.013	0.944	0.855
8	0.210	0.202	0.247	0.214	1.124	0.971	1.327	1.296
Mean	0.222	0.283	0.241	0.223	1.472	1.677	1.685	1.587

The concentration of Cu (Table 2) during summer season equal to (0.381 $\mu\text{g/g}$) in station (2) after water recharge which represented the highest concentration, the lowest concentration was reached (0.241 $\mu\text{g/g}$) in station (8) and at mean (0.305 $\mu\text{g/g}$) for all stations. In the autumn season (Cu), the highest concentration was reached (0.527 $\mu\text{g/g}$) in station (5) before water discharge, the lowest concentration (0.264 $\mu\text{g/g}$) in station (1) and at mean (0.362 $\mu\text{g/g}$) for all stations. While in the sediment samples of the winter season, the highest concentration reached (0.427 $\mu\text{g/g}$) in station (2) before water recharge, the lowest concentration was (0.306 $\mu\text{g/g}$) in station (6) and at mean (0.361 $\mu\text{g/g}$) for all stations. In the spring season, the highest concentration was reached (0.411 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration (0.298 $\mu\text{g/g}$) in station (6) and at mean (0.345 $\mu\text{g/g}$) for all station. The convergence in large concentrations of sediment samples which appeared in the autumn season reached (0.527 $\mu\text{g/g}$) in station (5) before water discharge, the lowest concentration appeared among the seasons in the summer season (0.241 $\mu\text{g/g}$) in station (8). The fluctuation in Cu concentrations is mainly due to the different source of pollution such as the discharge of industrial wastes, sewage pollution. The concentration of Ni (Table 2), the highest concentration appeared in the sediment samples of the summer season reached (2.744 $\mu\text{g/g}$) in station (2) before water recharge, and the lowest concentration was (1.296 $\mu\text{g/g}$) in station (8) and at mean (1.738 $\mu\text{g/g}$) for all stations, while in the autumn season the highest concentration reached (3.023 $\mu\text{g/g}$) in station (4), and the lowest concentration (1.544 $\mu\text{g/g}$) in station (5) before water discharge and at mean (2.206 $\mu\text{g/g}$) for all stations, whereas in the winter season the highest concentration reached (3.208 $\mu\text{g/g}$) in station (2) before water recharge, the lowest concentration (1.434 $\mu\text{g/g}$) in station (8) and at mean (2.122 $\mu\text{g/g}$) for all stations.

Table (2) Seasonal variations concentrations of (Cu and Ni) $\mu\text{g/g}$ from the study stations

Stations	Cu ($\mu\text{g/g}$)				Ni ($\mu\text{g/g}$)			
	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
1	0.312	0.264	0.36	0.354	1.753	1.73	1.937	1.854
2 before	0.356	0.366	0.427	0.398	2.744	2.627	3.208	2.938
2 after	0.381	0.454	0.405	0.411	2.002	2.122	2.135	2.022
3	0.313	0.369	0.422	0.386	1.347	2.032	1.626	1.428
4	0.318	0.395	0.364	0.339	1.950	3.023	3.032	2.022
5 before	0.294	0.527	0.361	0.343	1.326	1.544	1.624	1.427
5 after	0.267	0.342	0.327	0.312	1.544	1.594	1.746	1.629
6	0.299	0.313	0.306	0.298	2.121	2.744	3.032	2.316
7	0.274	0.295	0.317	0.302	1.296	2.543	1.455	1.329
8	0.241	0.303	0.329	0.314	2.299	2.103	1.434	1.359
Mean	0.305	0.362	0.361	0.345	1.738	2.206	2.122	1.832

In the spring season appeared the highest concentration (2.938 $\mu\text{g/g}$) in station (2) before water recharge, the lowest concentration reached (1.329 $\mu\text{g/g}$) in station (7) and at mean (1.832 $\mu\text{g/g}$) for all stations. There are variations in nickel concentrations among the seasons and stations. The highest concentration appeared in the winter season sediment samples in station (2) before water recharge reached (3.208 $\mu\text{g/g}$), while the lowest concentration appeared in the

summer season sediment sample in station (7) reached (1.296 $\mu\text{g/g}$). Also the fluctuation in Ni concentrations among the stations and seasons due to the different source of pollution such as sewage wastes, and using of fertilizers. The concentration of Pb. (Table 3), the summer season sediment samples, was the highest concentration reached (4.436 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (3.112 $\mu\text{g/g}$) in station (8) and at mean (3.696 $\mu\text{g/g}$) for all stations, while in the autumn season sediment samples were the highest concentration reached (6.233 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (2.853 $\mu\text{g/g}$) in station (5) after water discharge and at mean (3.997 $\mu\text{g/g}$) for all stations, whereas in the winter season, the highest concentration reached (6.252 $\mu\text{g/g}$) in station (2) before water recharge, the lowest concentration was (4.034 $\mu\text{g/g}$) in station (8) and at mean (4.921 $\mu\text{g/g}$) for all stations, In the spring season, the highest concentration reached (5.643 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (3.618 $\mu\text{g/g}$) in station (7) and at mean (4.361 $\mu\text{g/g}$) for all stations. The concentrations of the element in the sediment samples in winter and spring seasons are more than in summer and autumn seasons, the highest concentration appeared in the winter season reached (6.252 $\mu\text{g/g}$) in station (2) before water recharge, while the lowest concentration appeared in the autumn season reached (2.853 $\mu\text{g/g}$) in station (5) after water discharge. Due to high rainfall then increasing the washing process, also increasing sewage pollutants.

The concentration of Zn. (Table 3), in the summer season sediment samples, the highest concentration was reached (2.534 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (1.035 $\mu\text{g/g}$) in station (1) and at mean (1.947 $\mu\text{g/g}$) for all station, while in the autumn season sediment sample, the highest concentration reached (3.643 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (1.126 $\mu\text{g/g}$) in station (1) and at mean (2.165 $\mu\text{g/g}$) for all station. Whereas in the winter season, the highest concentration reached was (4.315 $\mu\text{g/g}$) in station (8), the lowest concentration was (1.244 $\mu\text{g/g}$) in station (1) and at mean (2.826 $\mu\text{g/g}$) for all stations. In the spring season, the highest concentration reached (3.616 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (1.112 $\mu\text{g/g}$) in station (1) and at mean (2.409 $\mu\text{g/g}$) for all stations.

Table (3) Seasonal variations concentrations of (Pb and Zn) $\mu\text{g/g}$ from the study stations

Stations	Pb ($\mu\text{g/g}$)				Zn ($\mu\text{g/g}$)			
	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
1	3.465	3.63	4.633	3.659	1.035	1.126	1.244	1.112
2 before	4.254	5.643	6.252	5.428	2.416	2.433	4.308	3.528
2 after	4.436	6.233	5.344	5.643	2.534	3.643	3.126	3.616
3	4.416	4.231	5.683	5.42	2.330	1.253	3.753	3.416
4	3.628	3.102	4.035	4.011	1.426	2.643	1.746	1.544
5 before	3.726	2.972	4.527	4.123	1.547	1.767	1.889	1.684
5 after	3.264	2.853	5.034	4.024	1.852	1.655	2.033	1.942
6	3.543	3.641	4.75	3.868	2.002	2.544	3.167	2.011
7	3.125	4.262	4.924	3.618	2.021	2.232	2.686	2.122
8	3.112	3.412	4.034	3.816	2.316	2.361	4.315	3.118
Mean	3.696	3.997	4.921	4.361	1.947	2.165	2.826	2.409

The variations in the concentrations of the element in the sediment sample between the seasons and studied stations, the highest concentration in the winter season in station (1) for all stations. The lowest concentration in effects of interior rivers discharge and sewage pollutants. The lowest concentration in the summer season was (1.035 $\mu\text{g/g}$) in station (1).

The concentration of Iron (Table 4), the highest concentration of the summer season sediment samples reached was (19.831 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration was (4.723 $\mu\text{g/g}$) in station (6) and at mean (10.95 $\mu\text{g/g}$) for all stations, In the autumn season, the highest concentrations was reached to (19.842 $\mu\text{g/g}$) in station (2) after water recharge, the lower concentration reached was (4.252 $\mu\text{g/g}$) in station (8) and at mean (11.175 $\mu\text{g/g}$) for all stations, while in the winter season, its concentration rate of sediments are high as it was the highest concentration reached (21.546 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration reached (6.421 $\mu\text{g/g}$) in station (6) and at mean (13.247 $\mu\text{g/g}$) for all stations. Also in the spring season, the highest concentration (20.013 $\mu\text{g/g}$) in station (2) after water recharge, the lowest concentration reached (5.852 $\mu\text{g/g}$) in station (6) and at mean (11.970 $\mu\text{g/g}$) for all stations. The highest concentration appeared in the winter season at station (2) after water recharge reached (21.546 $\mu\text{g/g}$), whereas the lowest concentration appeared in the autumn season in station (8) reached (4.252 $\mu\text{g/g}$). This fluctuation in concentration of Fe due to the seasonal changes and weather conditions of heat, light, wind speed, erosion and sedimentation processes which affect the sedimentation of Iron as a result of oxidation and reduction processes.

Table (4) Seasonal variations concentrations of (Fe $\mu\text{g/g}$) from the study stations

Stations	Summer	Autumn	Winter	Spring
1	14.544	13.622	16.33	15.645
2 before	17.341	17.721	20.426	18.832
2 after	19.831	19.842	21.546	20.013
3	12.543	14.683	15.427	13.686
4	13.686	13.721	16.469	14.714
5 before	7.645	7.891	9.423	8.654
5 after	8.429	7.831	9.949	8.943
6	4.723	6.731	6.421	5.852
7	5.430	5.462	8.541	6.874
8	5.328	4.252	7.943	6.493
Mean	10.95	11.175	13.247	11.970

TOC concentration (Table 5), the highest concentration of TOC% was (0.976 $\mu\text{g/g}$) at station (8) in the winter season, the lowest concentration at the station (5 before water discharge) reached was (0.729 $\mu\text{g/g}$). In the Summer season, the high concentration reached (0.723 $\mu\text{g/g}$) at station (7), the lowest concentration reached (0.557 $\mu\text{g/g}$) at station (5 before water discharge). The highest mean concentration (0.9019 $\mu\text{g/g}$), in the winter season, and the lowest mean concentration (0.6613 $\mu\text{g/g}$) in the summer season. The increase in TOC concentrations in winter season is due to increased water level, and decreased temperature. the absence of a gradient in

the TOC% values for all study stations and different stations, due to the amount of organic matter included in the sediment, the lack of TOC% concentrations in sediments, due to the sediments are Homogeneous in the ratios an grains size, so, have a difference a few of concentrations, while, the high concentrations of the TOC%, because the sediments are heterogeneous in their proportions and the size of the granules. Many previous research papers and studies [2,10,7,8,4,1,5,9,12].

Table (5)Mean concentrations of (TOC %) in stations of different seasons

Stations	Winter	Autumn	Spring	Summer
1	0.925	0.847	0.764	0.675
2 before	0.904	0.858	0.764	0.694
2 after	0.937	0.842	0.776	0.687
3	0.947	0.885	0.795	0.626
4	0.854	0.792	0.702	0.614
5 before	0.729	0.685	0.617	0.557
5 after	0.915	0.812	0.722	0.674
6	0.877	0.823	0.742	0.663
7	0.955	0.9	0.816	0.723
8	0.976	0.883	0.798	0.7
Mean	0.9019	0.8327	0.7496	0.6613

4. Conclusions

1. Heavy elements, when entering the aquatic environment, tend to be dispersed and distributed in living components, so the methods used to monitor the elements in the aquatic environment, by determining their concentrations in water and sediments.
2. Seven elements, are concentrated in sediments, and the elements are : (Cd, Cr, Cu, Ni, Zn, Pb, Fe).
3. In the sediments, the proportions of the metals appeared as follows :

21.546 >	6.252 >	4.315 >	3.208 >	2.829 >	0.527 >	0.429
Fe	Pb	Zn	Ni	Cr	Cu	Cd
Winter	Winter	Winter	Winter	Winter	Autumn	Autumn
2 after	2 before	8 St.	2 before	1 St.	5 before	2 after

4. Analysis (TOC%), showed that the values were (0.55- 0.9), during the different seasons, Winter values > Autumn values > Spring values > Summer values. The absence of a gradient with values (TOC%), due to the difference in the amount of organic matter included in the sediments.

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