Al-Kufa University Journal For Biology: 2023. Vol. 15 No. 3 P: 147 -154
ISSN (Print)2073-8854 ISSN (Online): 2311-6544

Original Research Paper: *Journal homepage : https://journal.uokufa.edu.iq/index.php/ajb/index*

Estimation Of Some Heavy Metals In The Dalmaj Marsh Water, Al-Diwaniya City, Iraq

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Article history
Received: 10 / 8 /2023
Revised: 12 / 10 /2023
Accepted: 17 / 10 /2023
DOI:
10.36320/ajb/v15.i3.12691

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Abstract: *Climate change has been an alarming global issue over the past twenty years. Iraq is internationally considered the fifth country in the world under the consequences of climate change due to human activities. Thus, the present study has focused on investigating Pollution by heavy metals in the water of marshlands as they are unique habitats and are recorded as natural heritage by UNESCO. The current study aimed to investigate concentration of heavy metals of Cd, Pb and Ni in water of the Dalmaj Marsh, located in AL-Diwaniyah City, in Iraq. This area is characterized as heavily polluted due to wastewater discharge and agricultural activities using fertilizers. Clean plastic containers that had previously been cleaned with distilled water and then with deionized water were used to collect samples. Water samples were gathered in situ from surface water. Digestion by HCL and HNO3, HF and HCIO4 acids have been used and finally, samples were centrifuged to extract heavy metals from collected samples. The results show that there has been a variation in heavy metals in the three studied sites. The mean values of concentrations in water were 1.96, 4.27, and 2.11µg/l for Cd, Pb and Ni, respectively. Pollutants such as pesticides, sewage discharge, irrigation and electronic waste are the main pollutants in the Pollution of freshwater bodies, including marshes. These findings provide crucial background data for further research to obtain better management and protection for Iraqi freshwaters.*

***Keywords*:** *Heavy metals, Pollution. Human activities, the Dalmaj Marsh, Climate change*

1. Introduction

There has been a significant change in the climate for the last decades, and this event has been confirmed during scientific conferences worldwide. Such as the 2021 United Nations Climate Change Conference that has been held in the UK and Italy. This climate change has negatively impacted the ecosystem, especially in lentic and lotic water bodies, which are important in providing better human services. As a result, efforts are needed to mitigate and tackle the consequences of destroying lotic (running water), such as rivers and lentic

(standing water), such as lakes [1; 2; 3; 4; 5; 6]. There is no doubt that environmental contamination is becoming worse all around the world. All of this may directly be linked to human activity, such as the contamination of heavy metals in Iraq.

The Sources of heavy metals can be either mining processes, human activities, industrial operations, pesticides, iron and fertilizers [7]. In certain situations, freshwater and estuarine ecosystems that have not yet been contaminated by Pollution are at risk because of metal deposits left behind from previous human activity [8].

Several studies have been conducted worldwide and in Iraq to investigate the level of contamination of heavy metals in water bodies. [9] studied heavy metals in the AL-Hilla River, and the author pointed out that the concentration of metals is high in the suspended phase and low in the dissolved phase. [10] have studied the concentration of heavy metals in the water and sediment of southern marshes, and the authors find a high concentration of Cu, Fe, Ni in the water in East Hammar Marshes. The concentration of heavy metals of Cd, Cu, Pb, Zn in mollusca, sediment and in water of East Hammar Marshes has been studied [11]. The author has noticed temporal changes in concentration of heavy metals in Cd, Cu, Pb, Zn as a result of seasonal changes of water level and changes in suspended particles in water. The heavy metals of Pb, Cd, Co, Cu, As and Cr in Al-Hawizeh Marsh are studied and show noticeable Pollution by heavy metals of Cd and Pb [12]. The seasonal changes in concentration of heavy metals in water and sediment of East Hammar Marshes are studied, and find that the channel area of the marsh is highly polluted with Zn, Pb, while in the pond marsh is polluted with Cd, Co, Mn, Cu. [13]. The concentration of heavy metals in Shat Al-Arab shows a continuous increase in the concentration of heavy metals of Ni, Cu, Cd, Co, Fe, and Pb in water, sediment and snails [14]. Heavy metals concentration in snail, sediment and water of AL-Garaf River – in Thi Qar /South of Iraq has been studied, and the study indicates that Ni has a high value in water compared with others [15]. The effects of heavy metals on trophic levels in sediments, zooplankton and water of Al-Diwaniya River has been investigated, and the study reveals that there is an increase of heavy metals in the river based on trophic levels in zooplankton, fish, phytoplankton and plant [16].

The concentration of heavy metals of Fe, Pb and Co in water samples has been found to be high in Shatt Al-Arab river. [17]. [18] has studied the concentration of heavy metals in the Dalmaj marsh and find that the concentration of Hg, Pb, Zn, Mn, Ni, Co, Cd, and Cu are high compared with limited values of the World Health Organisation. In the same context, the Pollution of the Shatt Al-Arab River by Zn, Mn, Cd, Fe, Pb, Cu and Ni has been examined and it has been found that the heavy metals exceeded the limited values [19]. Water quality and heavy metal pollution are studied in Al-Gharraf River [20]. The authors find that Cd concentration ranges between 0.002 and 0.089 ppm while in Pb it ranges between 0.31 and 0.21 ppm. These values exceeded recommended limits of both Iraqi and WHO organisations. [21] has studied the effects of heavy metals on tissues of fish, water and sediment samples from Derbendikhan Lake. The researcher finds that Pollution is higher in sediments than in fish or water much of which is due to human activities. It can be argued that increased human activities and changes in the quality of water bodies in Iraq have a strong impact on the aquatic ecosystems such as what has been studied in the Shatt Al-Arab river [22] and in Bahr Al-Najaf [23]. Similarly, [24] have investigated Pollution in the Euphrates River by heavy metals and found a high concentration of Mn, Zn, Cu, Cd, Fe, and Pb in water, sediment and mollusc. This refers to the pollution risk of the aquatic ecosystem, and it needs an urgent solution to prevent potential toxic effects on human needs. In addition, [25] has examined heavy metal concentration in water and sediment of Shatt Al-Arab River,

and finds that there has been a high concentration of heavy metals there and this is because of industrial activities, sewage discharge, and soil weathering that led to increased concentration of heavy metals higher than limited values.

This study aims to study Pollution by heavy metals in the Dalmaj Marsh in Al-Diwaniyah City.

Methodology

Description of study sites

The Dalmaj Marsh is situated in the southern portion of the middle alluvial plain and is surrounded by the Wasit, Thi Qar, and Al-Qadisiyah governments. From the east, the Al-Garaph River surrounds the lake, and from the west, the Euphrates River is represented by the northern and 324900"-3800 east AL-Diwaniyah River. The lake is formally situated between the administrations of Wasit and Al-Qadisiyah. The great water basin is a sizable open lake of water with a depth of more than 2.5 meters. However, the lake is distinguished by the existence of landfall ecosystems and is represented by dry sections in the true desert with sand dunes. Ponds and shallow water that are not deeper than one meter is also included in this. Due to the Ministry of Water Resources' control over the main estuary's flow and the lake's dependence on rainfall, the water level in Dalmaj Marsh is unpredictable. Reeds and papyrus, as well as submerged plants and dry soil dotted with shrubs and terrestrial species, are features of the marsh's southern region. The dam surrounds the deep, open region that makes up the eastern portion of the marsh, making it a crucial habitat for gulls, or more specifically seagulls and fish, particularly *Cyprinion* sp.

Table (1) shows Study sites

Site number	Coordinate	
	Longitude (E)	Latitude (N)
1	452729.161	320505952
2	452204130	321041126
3	452129192	321109916

Figure.(1). study area of selected sites on the Dalmaj Marsh. (from: https://earthexplorer.usgs.gov/)

Sample collection

Samples were collected by clean polyethylene containers previously washed with distilled water. Water samples were collected from surface layer within depth approximately (20-30) cm, and samples were prepared for sex months.

Heavy metals in water

A 100-1000 ml of water sample was dried at temperature 80C, in Teflon beaker, 6 ml of mixed concentred HCL and HNO3 (1:1) proportion, that dried at 80C°. then, 4 ml of mixed concentred acids of HF and HCIO4 (1:1) proportion added. Subsequently, the sediment was dissolved in 20 ml of diluted 0.5 N HCL and left for 10 minutes, and then separated by centrifugation (3000 rounds/minute) for 20 minutes. The solution, was thereafter, transferred to a volumetric bottle of 25 ml, and the sediment was washed with deionized distilled water. The volume was completed to 25 ml with deionized distilled water. The samples were preserved until the time of measuring heavy metals by flame atomic spectrophotometer. The results were expressed as µg/l [26].

Blank solutions

Blank solutions were prepared for all samples of water,. Samples were processed and analysed as same as the original samples but without the samples. This is in order to

measure Pollution as a result of using various chemicals or even due to laboratory conditions, where these concentrations were subtracted from the original ones.

Heavy metal ions measurement

The measurement of ions of heavy metals by on Flame Atomic Absorption Spectrophotometer when standard solutions were previously prepared[26].

Statistical Analysis

The SPSS software was used to obtain statistical analysis to calculate a less significant (LSD) P value at (<0.05).

Results and discussion

The statistical analysis of findings shows that the Cd concentration in water significantly differed at ($p<0.05$) among studied sites and season. Seasonally, Cd concentration in water ranges from 0.8µg/l in winter season at S1, while the highest value in phase is 3.576 µg/l in summer season at S2.

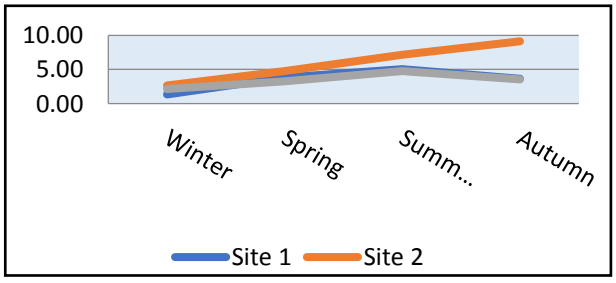

Figure (2): Cd concentration in water µg/l

The Cadmium (Cd): Natural sediments can be frequently contaminated with toxic heavy metals such as lead and cadmium and deposit to the water body and be toxic to other life forms, they may be integrated into both animals and plants, including food crops. At the time, heavy metals have been dissolved in water; they are used for domestic and agricultural purposes [26; 27].

Lead (Pb): The statistical analysis of findings shows that the Pb concentration in water were significantly different at ($p<0.05$) among studied sites and season. Seasonally, Pb concentration in water is ranged from lowest value 1.350 µg/l in winter season at S1, while the highest value is 9.132 µg/l in autumn season at S2.

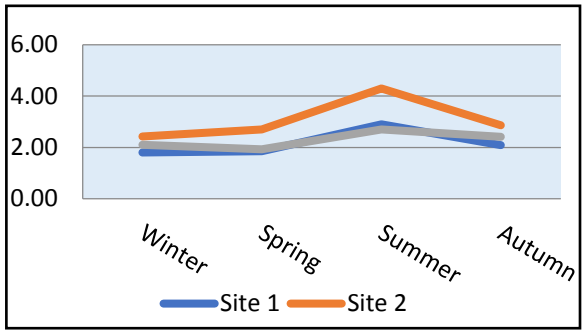

Figure (3): Pb concentration in dissolved in water µg/l

Nickel (Ni): The statistical analysis of findings shows that the Ni concentration in water was significantly different at ($p<0.05$) among studied sites and season. Seasonally, Ni concentration in water is ranged from lowest value 0.877 µg/l in winter season at S1, while the highest value is 3.770 µg/l in summer season at S2.

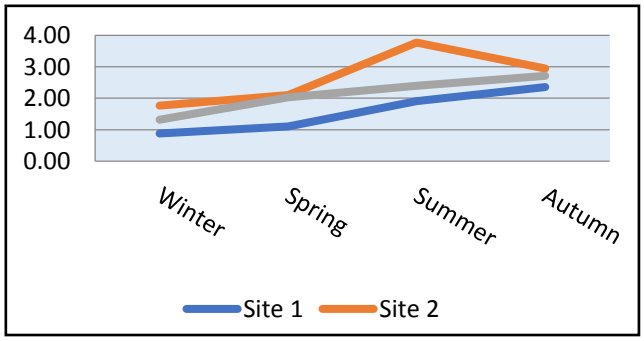

Figure (4): Ni concentration in water µg/l

Table (2): Mean and SD of heavy metals among sites of the Dalmaj Marsh

Sites	Cd	Pb	Ni
S1	1.505±0.554	3.476±1.402	1.560±0.635
S2	2.640±0.593	5.920±2.554	2.645±0.820
S3	1.743±0.549	3.420±0.978	2.115±0.552
LSD, sites ($p<0.05$)	0.092	0.084	0.113

Table (3): Mean and SD of heavy metals among seasons of the Dalmaj Marsh

Season	Cd	Pb	Ni
Winter	1.322±0.394	2.040±0.573	1.294±0.632
Spring	1.743±0.511	3.961±0.656	1.710±0.502
Summer	2.694±0.844	5.650±1.131	2.652±0.705
Autumn	2.667±0.265	5.437±2.772	2.193±0.281
LSD, season ($p<0.05$)	0.107	0.097	0.131

The current study shows an increase in concentration of heavy metals in the Dalmaj marsh. The concentration of Cd, Pb, and Ni has fluctuated in the marsh and this is due to time and space in all studied sites in all forms of heavy metals. The entrance of HMs to the water body changes over time, besides the amount of agricultural and industrial wastewater received by different sites in the marsh.

The highest values of HMs have been noticed during the summer season and the lowest ones are ranged between winter, spring and autumn seasons. The S2 recorded high concentration of HMs which may be due to high discharge of wastewater come from other tributaries drainage in the Dalmaj marsh. Furthermore, high temperature plays a major role in dissolving of elements in water. The current study has recorded high value of HMs in summer compared with study of [28] of the same marsh and with [29] in China. High increase of HMs in summer has been noticed in water bodies in southern Iraq [30] and East Hammar marsh [11], and [24] in Euphrates river. The reason for that increases high temperature and high activity of decomposition of microorganisms as well as other physicochemical properties of water, hydrodynamics and biological impacts [31]. However, autumn has noticed an increase Pb concentration in sediment in S1, which could be due to agricultural activity during farming season. This issue has been noticed in lakes of Central Yangtze in china [32]. This trend has been rational due to farming activity [33]. [28] has stated that heavy elements enter the Iraqi marshes from either natural sources such as the fall of dust, erosion or weathering, and the decomposition of dead organisms in the water, or the industrial sources, they are the result of human pollutants from industrial waste such as the waste of some leather, paint and paper factories that seep into the water without treatment and agricultural waste represented by fertilizers, pesticides, domestic sewage waste and other waste that enters the water bodies without treatment. Cadmium has widely been used in different sectors, especially in industrial processes and its discharge to an aquatic ecosystem possess a hazard to aquatic life [34]. The concentration of Cd, Pb, and Ni in the Dalmaj marsh has generally risen and the probable reason is dust storms that occurred many times over the period of study sites.

It has been stated that the heavy metal concentrations in dust storms elevate above baseline levels of standard values [35], especially in areas characterized as they are arid and semiarid regions [36; 37]. It has been stated that the southern Iraqi wetlands acquire trace elements through both man-made and natural sources [38].

Dust deposition, crusty weathering, and dead bi ota in water are examples of natural sources, while sewage wastes, pesticides, and fertilizers as a result of irrigation and industrial effluent are some examples of anthropogenic sources. Therefore, the Dalmaj marsh is not excluded from this phenomenon. Moreover, this study's concentration of Cd dissolved in water is less that of other HMs (i.e. Pb, Ni and Zn). This

status agrees with [11; 39]. Highly recorded heavy metal concentration could be due to using fuels to operate boats' engines in the Dalmaj marsh. However, a minor fluctuation was seen among sampling dates and studied sites. Since the changes in the data were so few, it's possible that they have nothing to do with precipitation at all and are caused by the local geological formation [40,41].

Conclusion

To sum up, the results of the current study show that there is an impact of Pollution on the Dalmaj marsh. heavy metals and other factors no doubt have a significant problem on the marsh's water quality and cause the wetland to be as puddles of muddy water as it is located in the desiccated area or arid or semi-arid area. Better programs for monitoring and management are needed to maintain the existence of the spectacular landscapes as they are being described as “the Garden of Eden”.

Ethical

This work has been carried out at the University of Al-Qadisiyah, College of Science, Department of Biology.

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