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Study of Monthly Changes in the Concentration of Some Heavy Elements in the Muscles of the Bunni Fish *Mesopotamichthys sharpeyi* in Two Selected Areas of Al-Hawizeh Marsh - Southern Iraq

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ABSTRACT

The concentrations of heavy metals (Cd, Co, Cu, Fe, Ni, and Mn) were studied in the muscles of the Bunni fish *Mesopotamichthys sharpeyi*, which belongs to the Cyprinidae family. Elements' concentrations were measured using a flame atomic absorption spectrometer at two selected stations of Al-Hawizeh marsh, southern Iraq. The fish were weighed; their average weight was 905g, and their average length was 400mm. The results showed that the high concentrations of heavy metal values (Cd, Co, Cu, Fe, Ni, Mn) were in fish muscles and reached 10.31, 35.77, 21.56, 62.03, 13.0, 14.17µg/ g dry weight at Um Al-Nia'aj station and 7.11, 16.62, 12.11, 55.37, 8.45, 4.24µg/ g dry weight at Al-Adaim station, respectively. Additionally, the lowest concentrations of these heavy metals reached 1,3, 4.04, 55.37, 1.62, 1.91µg/ g dry weight at Um Al-Nia'aj station and 0, 0, 2.04, 18.03, 0, 1.97µg/ g dry weight at Al-Adaim station. The results of the current study showed that the concentrations of the heavy metals studied were at their lowest limits in the muscles, except Cu, and were within the global and local permissible limits.

INTRODUCTION

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Iraq has a vast water area of 4.4 million acres, which includes different environments represented by the Tigris and Euphrates rivers and their tributaries, the Shatt al-Arab, reservoirs, lakes, and marshes (World Organization for Agricultural Development, 1986). The waters of the marshes and rivers constitute 70% of the total area of water bodies in the country and are an essential source of fish wealth (Al-Shamaa, 2005).

The marshes of southern Iraq are a unique water system since the Mesopotamian marshes are among the largest water bodies in the Middle East and occupy large areas of south Iraq (**Akbar** *et al.*, **2005**). The survival of the Iraqi marshes depends on the water system of the Tigris and Euphrates rivers, as the marshes are located in the southern part of Iraq between the governorates of Basrah, Maysan, and Dhi Qar (**Habib**, **2008**). The

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southern marshes consist of three main areas: the eastern marshes, known as the Um Al-Nia'aj marsh; the central marshes, known as the Zajri or Abu Alam marshes; and the southern marshes, known as Al-Adaim. The area of the marshes ranges between 15,000 & 20,000km² (Ajeel *et al.*, 2006). The largest of these marshes is the Um Al-Nia'aj marsh, which extends from the northeast of the city of Amara to the northeast of Basrah and from Iranian lands to the Tigris River in the West (Nomas, 2005). The marshes comprise 17% of the area of Iraq, as water covers about 3.8 million acres of Iraqi land, 2.3 million acres of which are covered by marsh water (Al-Shamaa, 2005; Fayyad & Ali, 2005).

Mesopotamichthys sharpeyi is a species of fish belonging to the family Cyprinidae, part of the order Cypriniformes. Originally classified under the *Barbus* genus, it was later reclassified to *Mesopotamichthys* (Abdullah, 2020). This fish species is primarily found in the waters of the Tigris-Euphrates river system, specifically in Iraq and parts of Syria and Turkey (Al-Zireg, 2018; Al-Juboury *et al.*, 2019; Al-Saad *et al.*, 2020; Alwan *et al.*, 2021).

M. sharpeyi has been identified as an endangered species within the Iraqi marshlands and is listed on the red list of threatened species. Overfishing and marsh destruction have led to a significant decline in its population, estimated at more than 80% since 1977. Additionally, large dam projects upstream on the Tigris River pose a threat by reducing water flow, which is crucial for the biodiversity of marshes downstream where this species resides. Due to its limited distribution, *M. sharpeyi* is a focal point for studies on native species and environmental changes' impacts on freshwater ecosystems. However, comprehensive information about this species remains sparse (**Freyhof, 2014; Huckstorf, 2017**).

The study aimed to compare the concentration of some heavy elements in the muscles of the *M. sharpeyi* fish in the Um Al-Nia'aj, and the Al-Adaim marshes, observing the monthly changes in the accumulation of heavy elements in the muscles of the studied fish, considering that monitoring the monthly variations is essential for assessing environmental health and formulating effective management strategies for this ecologically sensitive area.

MATERIALS AND METHODS

Description of the study area

Al-Hawizeh marsh is a water body concerted between Iraq and Iran in terms of location and food resources. It is approximately 70km from Al-Ammara. It extends between (Latitude/ Longitude: 31°00'-31°45'N, 47° 25'-47° 50'E). The area is distributed by 79% for the Iraqi part and 21% for the Iranian part (Al-Ali, 1994; Domad, 2008). The Iraqi part of the marsh is distributed by 67 and 33% to both Maysan and Basra provinces,

respectively. The marsh contains many bodies like Al-Sannaf, Um Al-Nia'aj, Abu-Athbah, Al-Adaim, Al-Doob, Al-Jakah, Al-Saffia and Al-Khabta Marshes.

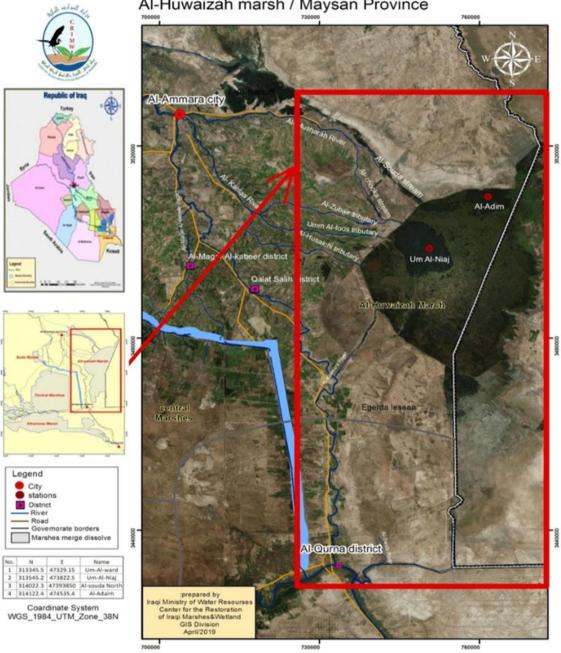
The current study chose two locations within Al-Hawizeh marsh: Al-Adaim and Um Al-Nia'aj (Fig. 1).

Al-Adaim (31° 41¢ 22.36²N; 47°45' 35.40" E) is located in the northeast section of the Al-Hawizeh marsh. It occupies an area between 40-80km² and receives water from Iraq and Iranian rivers. When the snow melts in the Iranian and Turkish mountains, the water level increases in the Tigris and the Al-Karkhah rivers. This excess water raises the water level of Al-Sanna'f marsh, which in turn enters north Al-Huwaizah (Al-Adaim marsh). Al-Karkeh River originates in the mountains of Iran and discharges into Al-Hawizeh marshlands (**Partow, 2001**). The Al-Adaim marsh is about 63.55km from the center of Al-Amarah City.

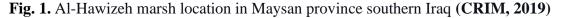
Um Al-Nia'aj ($31^{\circ} 35 \notin 45.15^{2}$ N; $47^{\circ}38' 22.50''$ E) is one of the largest open water bodies partially dried during the drying of the marshes in 1990. It occupies an area between 140-200km². The primary water sources of Um Al-Nia'aj are the Al-Zubair and Umm Al-Toos Rivers or the so-called Abu-Kassaf River. Um Al-Nia'aj marsh is far away, about 46.5km from the center of Al-Amarah City. This area is characterized by visible areas, static and clear water in the autumn and summer, and low turbidity in winter and spring. Large villages are established near this marsh, such as Abu Khassaf village.

A total of 75-145 monthly samples of bunni *M. sharpeyi* fish purchased from fishermen working at Al-Hawizeh Marsh in Al-Adaim and Um, Al-Nia'aj stations, respectively, from January to December 2022, were analyzed. The lengths and weights of the fish were taken, and the studied bunni fish ranged between 380 and 420mm, with an average length of 400mm and weights ranging from 730 to 1080g with an average weight of 905g. The method mentioned in **ROPME (1982)** was adopted to digest fish muscle samples and estimate their trace element content. After collecting and preparing the samples, 0.5g of the dried and ground samples were weighed in glass tubes, and 3ml of a mixture of concentrated perchloric acid HClO₄ and nitric acid HNO₃ were added at a ratio of 1:1.

The tubes were placed in a water bath at 70°C for 30 minutes, then transferred to a heating plate to complete the digestion process (until the mixture becomes clear). After filtration or separation by centrifugation to remove the remaining undigested parts (fibers), the filtrate was taken, and the volume was completed with deionized distilled water to 25ml. The samples were kept in tightly sealed plastic bottles until the examination was carried out by flame atomic absorption spectrometry. The result was expressed in micrograms/g dry weight. The statistical program (SPSS) was used to analyze the results statistically, and the significance of the differences between the averages was tested using the Revised Least Significant Difference (RLSD) test at a significance level of 0.05, as explained by **Al-Rawi and Khalaf Allah (2000)**.



Al-Huwaizah marsh / Maysan Province



RESULTS

Environmental factors

Table (1) shows the measurements of environmental factors during the study period. The pH was high in the Al-Adaim station at 8.60 during the winter compared to its lowest value in the spring, 7.10, while the Um Al-Nia'aj marsh had the highest and lowest values of 8.25 and 7.05 during the winter and spring, respectively. As for salinity, it reached 4.79 ‰ in Al-Adaim station during the summer season, while it decreased to its lowest value during the winter season at 2.22, while in Um Al-Nia'aj marsh, the highest value was 0.90 and the lowest value was 0.75 ‰ in fall and spring, respectively. For dissolved oxygen, its highest and lowest concentration was recorded at 10.83, 8.33mg/ L during winter and summer in Al-Adaim, and its highest and lowest values in Um Al-Nia'aj marsh were 11.01, 8.99mg/ L during the winter and summer. For the water temperature, it recorded its highest value in Al-Adaim during summer, reaching 28.6°C, while the lowest value was 12.5°C in winter. In comparison, the highest value was 28.2°C during summer, and the lowest was 11.9°C in winter.

Station	Season	РН	Salinity ‰	Dissolved oxygen mg/L	Water temperature C°
Al-Adaim	Autumn	8.10	2.31	10.05	14.4
	Winter	8.60	2.22	10.83	12.5
	Spring	7.10	3.16	10.54	20.8
	Summer	7.40	4.79	8.33	28.6
Um,Al-Nia'aj	Autumn	8.10	0.90	10.41	14.2
	Winter	8.25	0.60	11.01	11.9
	Spring	7.05	0.75	10.57	20.5
	Summer	7.50	0.92	8.99	28.2

Table 1. Environmental factors during the study period

Cadmium (Cd)

The results shown in Fig. (2) shows the monthly and site concentrations of cadmium ($\mu g/g$ dry weight) in the muscles of the studied fish. The results show a significant difference between the rates at a probability of *P*<0.05. The highest concentration of the bunni fish during August at Um Al-Nia'aj station was 10.31 μ g/g dry weight, and 7.11 μ g/g(dry weight in October at Al-Adaim station, the lowest concentration was 2.2 μ g/g dry weight in April at Um Al-Nia'aj station. No concentration was recorded in the winter months (January, February, and March) in Al-Adaim marsh, as it was below the sensitivity level of the atomic absorption spectrometer. A significant difference was found between the two stations at a probability level of *P*<0.05 and between the study months.

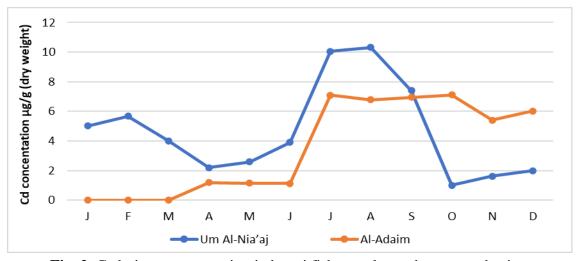


Fig. 2. Cadmium concentration in bunni fish muscles at the two study sites

Cobalt (Co)

Fig. (3) indicates the concentration of the cobalt (Co), as the highest and lowest concentrations were recorded at Um Al-Nia'aj station, with a concentration of 35.77 and $3\mu g/g$ dry weight in June, and September, respectively, while the highest concentration of the element was recorded at Al-Adaim station, 16.62 $\mu g/g$ dry weight in August. The lowest concentration was below the device's sensitivity level from January to June. A significant difference was found between the two stations at a probability level of *P*<0.05 and between the study months.

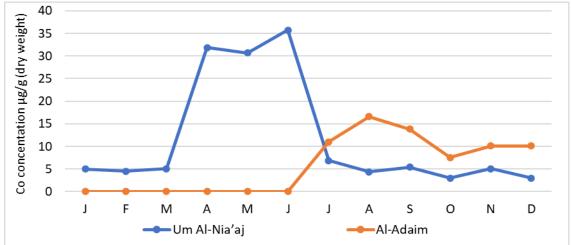
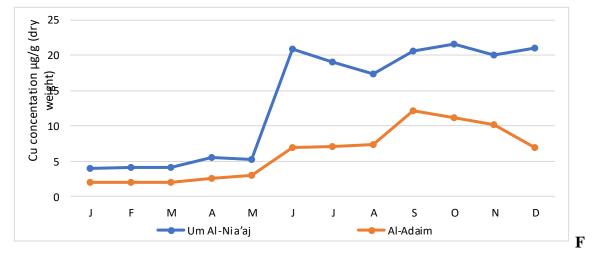


Fig. 3. Cobalt concentration in bunni fish muscles at the two studied stations Copper (Cu)

Copper (Cu)

The highest concentration of copper Cu (21.56, 12.11 μ g/g dry weight) was during October and September, and the lowest concentration (4.04, 2.04 μ g/g dry weight) was during January and February at Um Al-Nia'aj and Al-Adaim stations, respectively (Fig. 4). The results of the statistical analysis showed the presence of significant differences at the level of *P*<0.05 between the two sites, as well as at the same probability level, and

there are significant differences between the winter and the summer months for both stations.



ig. 4. Copper concentration in bunni fish muscles at the two stations

Iron (Fe)

The results of the iron concentrations in the muscles of the studied the bunni fish showed that the highest concentration $62.03\mu g/g dry$ weight, was obtained during April at Um Al-Nia'aj station and $55.37\mu g/g dry$ weight, during April and May at Al-Adaim station. The lowest value was obtained at Um Al-Nia'aj station, $26.04\mu g/g dry$ weight in July, and $18.03\mu g/g dry$ weight in March at Al-Adaim station (Fig. 5). The results of the statistical analysis showed the presence of significant differences at the level of *P*<0.05 between the two stations, as well as at the same probability level; there are substantial differences between months.

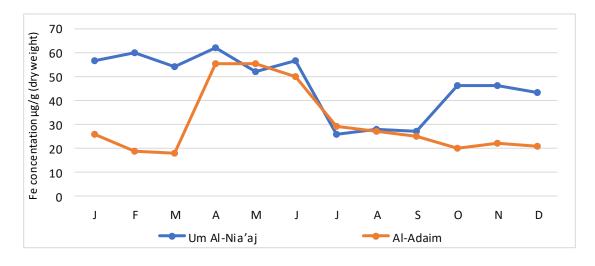


Fig. 5. Iron concentration in bunni fish muscles at the two stations

Nickel (Ni)

Fig. (6) shows the concentration of nickel $\mu g/g$ (dry weight) in the muscles of the studied bunni fish, as the highest concentration reached 13.0 $\mu g/g$ dry weight at Um Al-Nia'aj station during February and October and 8.45 $\mu g/g$ dry weight at Al-Adaim station during July. The lowest concentration was 1.62 $\mu g/g$ dry weight in July at Um Al-Nia'aj station, and it was below the device's sensitivity level at Al-Adaim station during November and December. The results of the statistical analysis showed significant differences at the level of *P*<0.05 between the two sites, as well as at the same probability level, and there are significant differences between months.

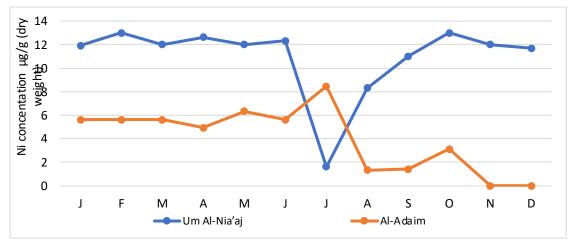


Fig. 6. Nickel concentration in bunni fish muscles at the two stations

Manganese (Mn)

The results in Fig. (7) showed that the highest and lowest concentrations of manganese in the muscles of the studied bunni fish were 14.17 and $1.91\mu g/g$ dry weight at Um Al-Nia'aj station during June, October, and November, respectively, as for Al-Adaim station, the highest and lowest concentrations were recorded at 4.24, $1.97\mu g/g$ dry weight during February and August, respectively.

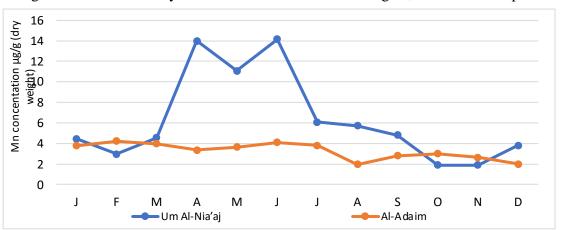


Fig. 7. Manganese concentration in bunni fish muscles at the two stations

The results of the statistical analysis showed that there were significant differences at the level of P<0.05 between the two sites. Also, at the same probability level, there were significant differences between months at Um Al-Nia'aj station, and no significant differences at Al-Adaim station during the months of the year.

DISCUSSION

Bunni fish *M. sharpeyi* are common in marshlands and inland rivers, they are economically important, have a high commercial value, and are desired by consumers in Iraq. However, the stock of this fish has been declining due to overfishing and other factors, the most important of which is the introduction of alien species, in addition to environmental changes, most significant is the decline in water levels and pollution (IUCN, 2022). Al-Hawizeh Marsh has high levels of organic metals (Al-Haidarey, 2009). Turbid water discharged from the Al-Karkah River on the Iranian side may also affect the heavy metal concentrations in the marsh.

The variation in the concentrations could be attributed to the interactions between multiple factors affecting the concentrations of dissolved metals, such as the phytoplankton and aquatic plants densities which absorbed or adsorbed the ionic metals, and the fuel burn emissions within the marsh during the summer season (Al-Hejuje, 2014). The presence of heavy metals in aquatic environments has led to serious concerns about their influence on plant and animal life (Bilgin & Konanc, 2016). HMs in Mesopotamian marshes are easily influenced by environmental factors such as surface runoff, groundwater, sediment dissolution, atmosphere deposition, and anthropogenic pollutants (Al-Saad *et al.*, 2008).

Most aquatic organisms including fish can accumulate heavy metals inside their bodies at concentrations that exceed what is found in the aquatic environment (Park & Presley, 1997). Hogstrand et al. (1996) confirmed that heavy elements such as zinc, cobalt, and copper are divalent compounds and can cross the chloride cell membrane in the gills, where these elements are transported through the blood linked to many proteins such as albumin and metallothionein to reach the various tissues of the body (Handy, 1993). The values of cadmium extracted from fish muscles decreased during the different months, as the values were fluctuating and low, as they showed an increase in the concentration of this element during August and October at Um Al-Nia'aj, and Al-Adaim stations which reached 10.31 and 7.11 μ g/g dry weight, respectively. The results agreed with the study of Joyeux et al. (2004) on Mugil spp. and Centropomus spp. Catch from Vitria Bay in Brazil showed that the concentration of cadmium during the spring and autumn months is higher than in the winter and summer months. This may be because during the winter, fish growth stops, and during the spring, the metabolic activities of the organism increase, and thus, growth increases until it reaches its peak during the summer. It was also noted that the free cadmium ion Cd+ constitutes 84% of the total cadmium

concentration in fresh water, while it constitutes only 3% in salt water. The high resistance shown by fish exposed to cadmium in salt water compared to freshwater fish may be attributed to physiological differences between species.

The results showed an apparent fluctuation in the values of cobalt element, as it showed a difference in concentration between months from imperceptible values to significant increases in the muscle tissues of the studied fish, as the highest concentrations were recorded at the two study stations, respectively, in June $35.77\mu g/g$ dry weight and August $16.62\mu g/g$ dry weight, which are lower when compared to the results of **Al-Edreesi** *et al.* (2002) upon studying fish in the Al-Hodeidah region in Yemen. The concentration of cobalt element recorded in the studied species in the two study areas may be due to the petroleum content in the two areas or to the petroleum and gas waste of fishing boats containing this element.

The concentration of copper in the muscles of the studied bunni fish recorded low levels during the winter months (January 4.04 μ g/ g dry weight at Um Al-Nia'aj station and February 2.04 μ g/ g dry weight at Al-Adaim station), in addition the concentration of copper in the studied fish increased during October (21.56 μ g/ g dry weight) at Um Al-Nia'aj station, and September (12.11 μ g/ g dry weight) at Al-Adaim station. The reason may be due to the nature of the feeding of this species, as it is known that brown fish are herbivorous, while the results of the current study recorded values close to what was recorded by **Abdullah and Abdul-Hassan (1993)** in a *Johnius belengeri* fish. The low copper in the fish muscles may be due to the amounts of calcium carbonate in the water, as Iraqi soils contain this substance, which dissolves in water. Thus, the water is rich in it (**Hassan, 2007**).

Iron concentrations extracted from the tissues of the studied fish were recorded at both sites; iron is one of the essential elements that are always in high concentrations in the muscles, and it recorded its highest values during April at both stations, $62.03\mu g/g$ dry weight at Um Al-Nia'aj station and $55.37\mu g/g$ dry weight at Al-Adaim. This is consistent with **Al-Saad** *et al.* (1997), who found in their study of ten species of fish caught from the Arabian Gulf and Shatt al-Arab that they contained different concentrations of heavy metals, and iron recorded the highest percentage among them in the muscles of the studied species. Additionally, the concentrations of the elements in the current study are less than what **Ahdy** *et al.* (2007) found. The increase during this period may be due to the rainfall, which consequently washes the nearby soils, carrying some heavy metals to the aquatic environment. Moreover, the increase of this element in the environment may be due to the remnants of wars and the quantities of metals used in building boat hulls in the region.

The concentration of nickel in the muscles of *Mugil* spp. fish during winter (**Joanna & Michael, 2005**) is higher than the concentrations of the results of the current study. As for

the muscles of brown fish, low levels of element concentration were recorded, in agreement with the findings of **Sauk** *et al.* (1999), who showed in their study on codfish *Boreogadus saido* that low levels of nickel concentration in the muscles were recorded, while nickel recorded a noticeable increase in the Um Al-Nia'aj marsh area during February $(13\mu g/g dry weight and 8.45\mu g/g dry weight)$ in Al-Adaim. This may be due to the high petroleum content in the area, human activities, falling dust, factory fumes, and oil and gasoline combustion products, in addition to the presence of nickel with oil in the area.

The results showed a significant decrease in the concentration of manganese extracted from the tissues of the bunni fish during the study period, as the values were low and fluctuated in shape. The results are consistent with what Abaychi and Al-Saad (1988) reached in their study on fish caught from the Shatt al-Arab and the Arabian Gulf, where they found a decrease in the concentration of manganese in the muscles of fish compared to the concentration of the rest of the measured trace elements. The results of the current study are less than those of Sdrkdny-Kiss and Ponta (2008) in their research on a group of freshwater fish, as the concentration of manganese extracted from fish muscles was high. However, according to the European standards, this increase did not have a toxic effect on fish or the environment. The results generally showed slight locational and seasonal changes during the study period. However, the marshes are not polluted with this element because the low concentrations may be due to the quantities of toxins and pesticides used in the fishing area and quantities of agricultural fertilizers leaking from nearby agricultural areas containing this element. Lakes near agricultural lands cause an increase in the concentrations of elements in river fish, as Agbozu et al. (2007) indicated in a study on catfish Synodontis clarias caught from lakes near agricultural lands and household waste dumping areas in the Niger Delta region, a noticeable increase in this element compared to the rest of the elements. The results obtained in this study are less than those obtained in the study of Al-Obeidi and Al-Hamadawi (2023) in the determination of some heavy metals in tissues of Binni M. sharpeyi and water in Al-Dalmaj Marsh/Iraq.

The concentration of cobalt increased during June, iron during April, and nickel during February because these elements are more available during these periods. Cadmium and manganese were more available during August and June, respectively, and the availability of copper increased in September and October (Hassan, 2007).

The study's results showed that the muscles of the studied fish contained low and fluctuating concentrations of cadmium, cobalt, copper, nickel, and manganese. At the same time, iron recorded a noticeable increase among those elements. The results of the current study also proved that the concentration of heavy elements in the fish of the Um Al-Nia'aj, and Al-Adaim shores is within the levels recorded in the region.

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The results of the current study showed that the concentrations of the heavy metals studied (Co, Cd, Cu, Fe, Ni, and Mn) were at their lowest limits in the muscles, which is the edible part of the fish, and were within the permissible limits set by the Food and Agriculture Organization and the World Health Organization (FAO/WHO, 1984), and also according to Malaysian Food Regulations (MFD, 1985) except for Cu, where the highest values obtained at the two study stations were higher than the permissible values of $5\mu g/g dry$ weight (Table 2).

References	Ni	Mn	Fe	Cd	Cu
FAO/WHO 84(Swami <i>et al.</i> , 2001)	—	5.4		2	—
(MFR, 1985) (Swami et al., 2001)		4.5	55	1	—
FDA (2001) (Swami et al., 2001)	80		40	4	5
Turkish Environmental Guidelines (1988) (Demirak, 2006)	—	—	—	-	20
The Saudi Arabian Standards Organization, SASO (1977) (Ali <i>et al.</i> , 2011)					20
FAO (1983) (Sankar et al., 2006)		—	-	—	30

Table 2. Permissible limits for heavy metals in fish ($\mu g/g dry weight$)

CONCLUSION

The results of the study concluded that the concentrations of heavy metals (cadmium, cobalt, copper, iron, nickel, and manganese) in the muscles of the bunni fish (*M. sharpeyi*) were highest at the Um Al-Nia'aj station, while the values were significantly lower at the Al-Adaim station. Moreover, cadmium, cobalt, Iron, and copper were observed to be among the highest concentrations of metals in fish muscles, while nickel and manganese were lower than the rest of the metals. Finally, according to international standards, the concentrations of heavy metals in fish muscles were mostly within permissible limits, except for copper, which in some samples was slightly above acceptable limits.

Recommendations

1- Bunni fish *M. sharpeyi* can be used as living evidence, and heavy metal accumulation within allowed muscle limits could be used as human food.

2- It is recommended that continuous studies and monitoring of heavy metal concentrations in water and aquatic ecosystems be conducted to ensure environmental and health safety, especially in areas where there is a clear accumulation of heavy metals, such as the Um Al-Nia'aj station.

3- Measures should be taken to reduce pollution from industrial and agricultural sources that may contribute to the accumulation of heavy metals in the aquatic environment.

4- It is necessary to raise awareness in the local community about the public health effects of consuming fish contaminated with heavy metals, especially about the accumulation of copper and other heavy metals in fish tissues.

5- Further studies should be conducted to determine the impact of these heavy metals on other marine organisms and aquatic ecosystems in general and to develop new strategies to reduce environmental pollution in sensitive areas such as the Iraqi marshes.

6- Recommend reviewing and updating national and international environmental standards to include the latest research on heavy metal pollution, and ensure that health risks to consumers are reduced.

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