Detection of Cadmium and lead metals contamination in the water and Carp fish of AL- Delmj marsh

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Abstract

The current study showed Samples of fish were taken during two separate seasons, the first of which lasted from October 21 to December 15, 2021, and the second of which lasted from April 25 to June 30, 2022. From the center of the AL-Dalamj Marsh, samples were taken (5) times each day from (10) different locations and methods, Testing was done on three components from the sample, which are (liver, gills and muscles). In conjunction with the fisherman, it was decided upon by the marsh's officials to take samples at several locations throughout the marsh. 50 Samples from Cyprinus Carpio for every season Heavy metals are well-known environmental pollutants due to their toxicity and ability to bioaccumulate in the bodies of living organisms at various stages of the food chain Heavy metal contamination in the environment can occur from different natural and anthropogenic sources. The natural sources of heavy metals are mainly volcanic eruption and weathering of metal-bearing rocks, while the anthropogenic sources of heavy metals include agricultural and industrial activities, combustion of fossil fuel and gasoline, waste incinerators, mining, etc. The mobilization of these heavy metals to the aquatic ecosystem alters the physicochemical property of water which is hazardous for aquatic organisms. Heavy metals mainly enter the fish body through gills, body surface and digestive tract during ingestion of metal accumulated food materials.

The current study showed that the concentration of cadmium (Cd) in the organs of carp fish fish was significantly increased from its means in the while the means, as it reached (0.176) µg/gm (0.5266) f irst season decreased in the second season for carp fish,

As for the lead element (Pb) the study showed that its means concentrations in the organs of carp fish was significantly increased from its means in the first season, as it reached (8.796µg/gm) while the means decreased in the second season(4.213) for carp fish , , The results of water samples analysis showed that the means were the highest concentrations of Pb during the second season of the study and they were (0.061µg/gm) and the highest concentrations of Cd during the first season of the study and they were (0.016±µg/gm).

The study concluded that the fish in the Dalmaj Marsh were affected by pollution with heavy metals of all kinds and exceeded the limits set by public health organizations, We found that the percentage of the cadmium element in the water according to the world Health Organization 2003 (WHO) in the water is (0.003 µg/gm) and in the fish (0.5 µg/gm)while the percentage of the lead element in the water is (0.001 µg/gm)and in the fish is (2.0 µg/gm) which requires great attention to the aquatic environment and support for that important productive sector.

Keyword: *fish, heavy metal, contamination, carp, lead cadmium, Dalmaj Marsh.*

INTRODUCTION

Fish wealth is an important source of food security in most countries of the world, and in Iraq in particular, due to its relatively mild climate, rich water environment, and great diversity of fish. Therefore, the current study sheds light on the extent to which fish are affected by environmental pollutants arising from industries, such as heavy metals, because of their negative impact on fish and Human health and thus knowledge of the extent of pollution of the water environment in AL-dalmaj marshes (Khalef et al., 2021). Minerals including iodine and phosphorus, as well as vitamin D, are found in fish ,Omega-3 polyunsaturated fatty acids are abundant in fatty fish, and can lower "bad" (LDL) cholesterol by lowering levels of triglycerides and other compounds considered to be good for fish,. Docosahexaenoic and eicosapentaenoic acids, both of which are omega-3 (n-3) fatty acids,are the most important preventive factors for cardiovascular disease and are essential components of human nutrition (Baranda et al 2018).

Due to the ability of heavy metals to accumulate inside the bodies of aquatic organisms such as fish, it is a worldwide major concern, As a result, the increasing concentration of heavy metals along the food chain poses a threat to both human health and the environment, as the levels of heavy metals in the environment, especially in aquatic ecosystems, have risen steadily at a rate alarming in recent decades as a result of the industry Development, It is now an important regional and global issue so many environmental conditions and bioaccumulation in fish tissues are affected by a variety of environmental factors including temperature, pH, salinity, etc. (Malik et al. 2009). Received attention in many parts of the world is the tendency of these elements to accumulate especially in soft and hard tissues such as muscles and liver, due to their high toxicity and cumulative nature, heavy metals play an important role in life interactions, they accumulate in the organs of living organisms and have an effect on their function because they are not decomposed or susceptible to the environment in the natural cycle (Mitra, et al., 2022) Natural activities such as erosive processes, severe rainfall, storms, and fires are examples of natural sources of heavy elements or the human source that includes everything human intervention in its composition such as waste Rubber,textile and household waste as well as the use of fertilizers and pesticides that contain heavy metals that reach the water through the sewers(Aydin Bilogchane et al, 2004).

As a result of accidents or improper handling, as well as inhalation and absorption in some situations, heavy metals can accumulate in soil, human and animal tissues. Through normal biogeochemical cycles, heavy metals have been present on the earth from its creation (Masindi and Muedi, 2018). Aquatic creatures' varying living habitats, feeding habits, and nutritional status are likely factors in their varying amounts of heavy metal deposition. (Liu et al., 2022, Rajeshkumar et al., 2018). Many industries including pharmaceutical and paper manufacturing, preservatives, the agriculture sector, Moreover, the caustic soda and chlorine industries discharge mercury (Hg) into the environment (Ibrahim et al., 2019). Cadmium, which is frequently used in electroplating for a number of purposes, including batteries, dyes, textiles, and metallic coatings, is found in soil and rocks, including coal and mineral fertilizers (Saini and Dhania, 2020). These behaviors collectively are to blame for the rise in heavy metal contamination in the environment.

The Methods

The Study Area (AL-Dalmaj Marsh)

Al-Dalamj Marsh is a remote wetland that is less than 20 meters above sea level and has an estimated extent of 120 Dunums According to Figure, it is situated northeast of Al-Diwaniyah Governorate and southwest of Wasit Governorate (3-2). The feeding channel within the boundaries of Al-Diwaniyah city feeds the marsh with water from the broader estuary. The marsh has a depth that ranges from roughly 1 meter at its shallowest point to 4.5 meters at its deepest point. Despite being located in a semi-desert region, it is a significant place for biodiversity because birds and fish are the most common vertebrate species in marshes (Mohamed et al., 2014).

Figure (1): location of AL-Dalmaj marsh

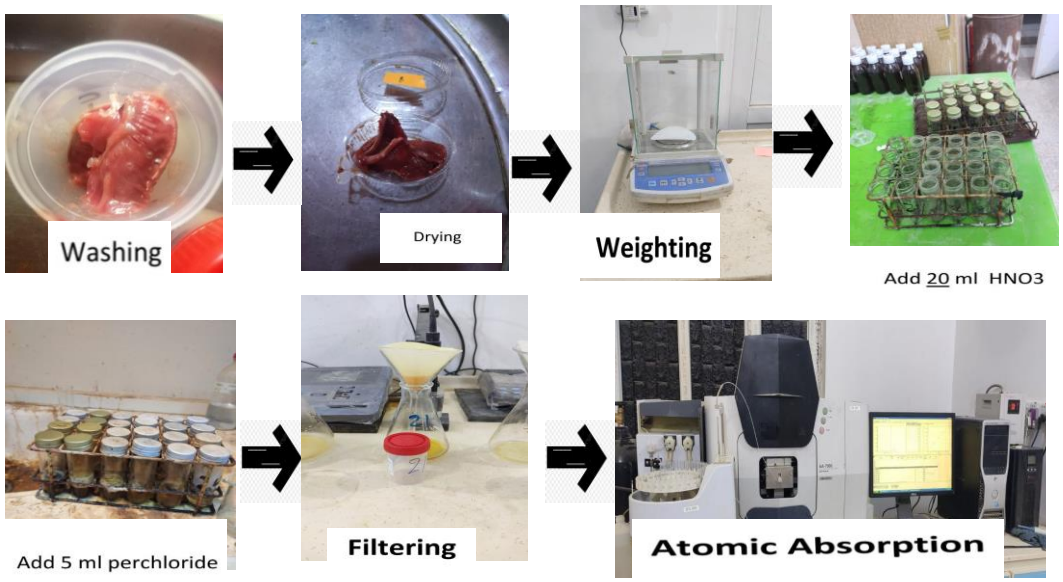
Gathering sample data

A. Fish samples: (50) Samples of Cyprinus Carpio fish were taken during two separate seasons, the first of which lasted from October 21 to December 15, 2021, and the second of which lasted from April 25 to June 30, 2022. From the center of the AL-Dalamj Marsh, samples were taken (5) times each day from (10) different locations and methods. Testing was done on three components from each sample, which are (liver, gills and muscles). In conjunction with the fisherman, it was decided upon by the marsh's officials to take samples at several locations throughout the marsh.

Preparation of fish samples

- The samples are washed and dried
- Weigh one gram of the dry sample
- Add HNO 3 (20 ml) then leave it overnight
- Heat the sample then 5 ml of perchloride acid then digest the samples near dryness
- Add an amount of distilled water
- Filter the samples then complete the volume to (25 ml) of Distilled water
- We put the samples in the atomic spectrometer, and the heavy elements are measured

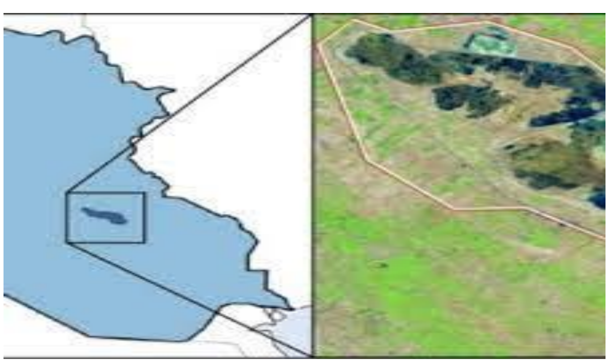
Figure (2) displays the three components (liver, gills, and muscles) of the aforementioned fish samples



Water samples:

Fifty samples were taken each season. To determine the amount of heavy metals in the water, samples were taken 30 cm below the surface. Five-liter polyethylene bottles were utilized, and the bottles were rinsed with diluted hydrochloric acid (10%) and then washed with distilled water using clear and opaque 250-liter bottles (Winkler bottles).

Figure (3): samples of water



Extraction of heavy metals from fish tissue:

Dry tissue samples of the liver, muscles, and gills were weighed to yield a weight of 1 gm. Overnight, 20ml of concentrated nitric acid was added. The samples were heated to (80 ^{o}C), and then (4 ml) of concentrated Perochloric acid and hydrofluoric acid were added in a ratio of 1:1. (1:1). Before adding distilled water the digestion was completed to the point of dehydration. After being treated with distilled water, the sample was weighed to (25 ml) (ROPME, 1983).

Extraction of heavy metals from water

After the sample had dried out in 1 liter of water at 80 degrees Celsius, it was digested by adding 6 ml of strong hydrochloric acid and 1:1 nitric acid. It was heated to (80 °C) and nearly dried off before receiving (4 ml) of a concentrated pro chloric and hydrofluoric acid combination in a 1:1 ratio. A near-dry phase of the solution was achieved through evaporation, and the precipitate was then dissolved in 20 ml of diluted (0.5) hydrochloric acid and allowed to sit for ten minutes. Centrifugation was used to separate the sample for 20/3000 rpm. The solution was drawn out and put into a volumetric vial (25 ml) In order to measure the samples with a Flame Atomic Absorption Spectrophotometer and express the results in g/g dry weight, the samples were maintained in polyethylene vials.

Dimensions of Large Items

Using a Flame Atomic Absorption model, heavy metals in the extracted samples were assessed (ASc, 7000-AA S). Once the standard solutions (solutions Standard) for the items under examination had been created using the techniques described in

(APHA, 2003).

Calculation of heavy metals concentrations in fish tissues

E con = the sample's elemental content, expressed as a dry weight concentration of (µg/g).

A= element's concentration (in mg/L) as determined by the calibration curve.

df = Dilution factor

D= Dry Weight of sampl

Calculation of heavy metals concentrations in Water

E con = the sample's elemental content, expressed as a dry weight concentration of (µg/g).

A= element's concentration (in mg/L) as determined by the calibration curve.

B= The filter sample's final volume (ml).

C=Filter sample initial volume (ml).

Statistical analysis

Statistical Analysis System version (SAS) was used to do the data analysis. For identifying the significant differences between the two groups, one- and two-way ANOVA, least significant differences (LSD), and unpaired T-test were utilized. $p< 0.05$. (steel ,et al, 1997)

Result

Comparisons between concentrations of heavy metals according to seasonal variations

Result of Cd contamination:

The findings of the current work revealed that the concentration of Cd was found that the highest value of cadmium was for carp in the first season (0.29 µg/gm) and the lowest percentage was(0.12 µg/gm). In the second season the highest percentage was (0.21 µg/gm), and the lowest percentage (0.11 µg/gm)

Result of Pb contamination:

The findings of the current work revealed that the concentration of Pb was found that the highest value of lead was for carp in the first season (12.91 µg/gm) and the lowest percentage was(6.02 µg/gm). In the second season the highest percentage was (7.91 µg/gm), and the lowest percentage (2.04 µg/gm)

Table (1): Concentration of Pb and Cd

Carp	Organs	First season	Mean	Second season	Mean
Concentration of Pb (µg/gm)ppm	Liver	7.46±2.27a	8.796	2.69±1.2b	4.213
	Gills	6.02±0.73a		7.91±2.27a	
	Muscles	12.91±1.08a		2.04±0.73b	
Concentration of Cd (µg/gm)ppm	Liver	1.17±0.98a	0.5266	0.11±0.5b	0.176
	Gills	0.12±0.03a		0.21±0.09a	
	Muscles	0.29±0.07a		0.21±0.10a	

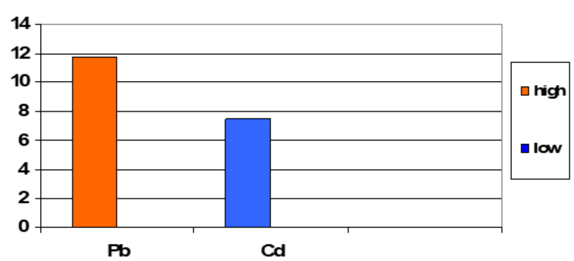
Comparisons between concentrations of heavy metal according to body organs

1-Liver

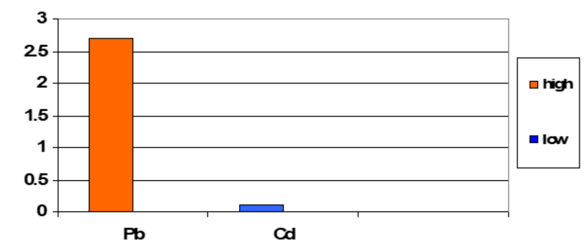
For the Cd , the 1st season based on the liver samples from the carp fish revealed potentially ($p<0.05$) higher levels (1.17±0.98µg/gm) ,the 2nd season according to the liver samples from the carp fish demonstrated potentially ($p<0.05$) lower concentrations (0.11±0.5)

For Pb, the 1st season for the liver samples from the Carp fish uncovered potentially ($p<0.05$) higher concentrations (17.33±7.56µg/gm). Moreover, the 2nd season for the liver samples from the fish detected significantly ($p<0.05$) higher levels of carp (2.69±1.2µg/gm).

Figure (4): Liver of carp



first season



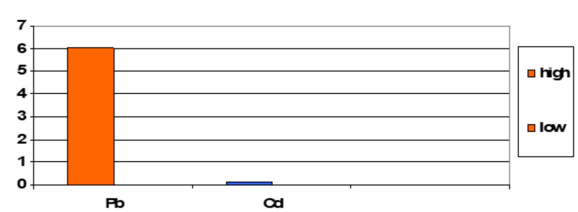
Second season

2- Gills

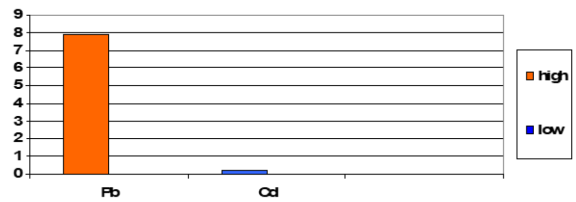
In the case of Cd, the 1st season based on the gill samples from the carp fish revealed that the levels are almost similar with the second season as the concentrations were(0.12±0.03 µg/gm and 0.21±0.09 µg/gm respectively)

For Pb, the 1st season for the gill samples from the Carp fish uncovered It was found that the levels were slightly lower than in the second season, as they were in the first season (6.02±0.73 µg/gm) and in the second (7.91±2.27 µg/gm) season

Figure (5): Gills of carp



first season



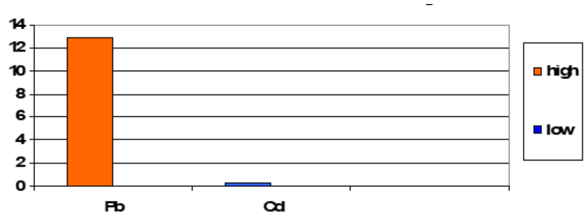
Second season

3- Muscles

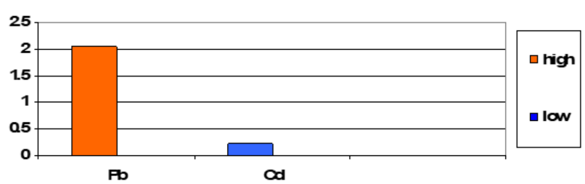
In the case of Cd, the 1st season based on the Muscles samples from the carp fish revealed that the levels were slightly lower than in the second season, as they were in the first season (0.29±0.07 µg/gm) and in the second season (0.21±0.10 µg/gm)

For Pb, the 1st season for the Muscles samples from the Carp fish uncovered It was found It was found that the levels were significantly higher than in the second season, as they were in the first season (12.91±1.08 µg/gm) and in the second season (2.04±0.73 µg/gm).

Figure (6): Muscles of carp



first season



Second season

Concentrations of heavy metals in water

The levels of Cd, and Pb in the marsh water where the several fish species were retrieved for sample were measured, we looked at samples of the water. We found that the highest value of water was in the element lead (0.039) and the lowest percentage was in the element cadmium (0.015), We discovered also that the concentrations of these heavy metals in the water were (0.0160.002 and 0.0140.004g/gm), (0.0350.01 and 0.0740.04g/gm), and (0.0160.01 and 0.0610.04g/gm), for the Cd, There were no significant (p0.05) variations in the Cd concentration (0.0140.004g/gm) during the second season and that (0.0160.002g/gm) during the first season. When compared to the concentrations in the water from the first season, the second season showed potentially (p0.05) greater values for Pb. The levels of heavy metals in the marsh water where the collected samples of the fish species under study were taken are shown in Tables (2) Concentration of heavy metals in marsh water.

Tables (2) Concentration of heavy metals in marsh water

Water	Concentration (µg/gm)		Mean	LSD
	First season	Second season		
Cd	0.016±0.002a	0.014±0.004a	0.015	0.031
Pb	0.016±0.01a	0.061±0.04b	0.039	

Discussion

One of the most poisonous substances to living things, including fish, is Cd, a non-essential component that has the potential to have a persistent harmful effect even at low quantities (Rajeshkumar & Li, 2018).The current investigation showed that Cd levels varied between the first and second seasons. This supports earlier literature that expressed the same idea. The spring and summer seasons, which were preceded by a time of extremely high temperatures (mean of 35°C), were when high cadmium levels were found. Following that, the cadmium levels fell below the analysis method's detection limit. Disruptions in muscle homeostasis and an increase in cadmium intensity in the metallothionein-like proteins are two temperature-related mechanisms that cause cadmium to bioaccumulate (Guinot et al., 2012) Given that cadmium buildup mostly occurs in the liver and kidney, it is plausible that cadmium concentrations did not exceed the World Health Organization's (WHO, 2000) highest permissible limits of 1-50 g/kg. Nevertheless, some of the amounts found during the spring and summer exceeded the WHO's highest cadmium accumulation standards. During the dry season, levels were greater, however during the rainy season, cadmium bioavailability was reduced due to increased oxygenation and the presence of organic and inorganic particles (Nevárez et al., 2015).

Also,The results of the current investigation suggested that Pb may accumulate in fish organs differently depending on the season. According to Rajeshkumar et al. (Rajeshkumar et al., 2018), Our findings show that Cd and Pb concentrations vary significantly throughout seasons, Therefore, it is becoming evident that human activities, including industrialization, are to blame for the collapse of these natural ecosystems (Hu et al., 2010) In a study to determine the amounts of cadmi um, nickel, and lead detected in the bodies of fish captured in a Malaysian river, Hashim et al. (Hashim et al., 2014) made this discovery. Gill nets were used to catch fish during the dry and wet seasons. There were 13 different kinds and 78 different fish. Analysis of the muscles using an atomic absorption spectrometer and a graphite furnace. The average Cd level in Chitala chitala (0.076 mg/kg) was significantly higher than the critical threshold limits established by the EC, WHO, and FAO. Barbonymus gonionatus and Tachysurus maculatus had mean Cd levels that were only somewhat alarming when compared to the other species. There were no fish samples with Ni levels more than the 0.5-0.6 mg/kg WHO recommended range. Pb levels in Osteochilus hasseltii (0.169 mg/kg) and T. maculatus (0.156 mg/kg) are exceedingly high. The amounts of heavy metals were found to be substantially higher during the wet season, Fish that devour everything had the highest quantities of Cd and Ni, while carnivorous fish had the highest concentrations of Pb. There was a strong positive connection between fish weight and Cd and Pb tissue values.

Cadmium in the body's tissues and organs have been The increased tissue concentration level was influenced by dietary cadmium. According to earlier research, the liver, followed by the gills and the muscles, reported the highest levels of cadmium. Concentrations have been observed to increase in direct proportion to the amount of cadmium in the animal's meal or water supply, as well as the duration of the animal's exposure to the pollutant. Additionally, research have shown that the amount of cadmium buildup varies depending on the organ. According to Ng and Wood, when rainbow trout, Oncorhynchus mykiss, were fed the oligochaete, Lumbriculus variegatus, and exposed to different amounts of Cd in the water, the stomach accumulated the most Cd, followed by the kidney, liver, gills, and muscles (2008) (Y-T Ng & Wood 2008).

The residual content of a substance in all tissues is determined by the mass balance between its ingestion through food or water, feces or pseudo-feces removal, and preservation through physiological processes, including some that are thought to be protective detoxifying processes involving thiol molecules like metallothionein and glutathione (Turner, 2015).

These organs absorb the majority of heavy metals. The lamella, which is involved in the ion transfer process during osmoregulation, may get damaged as a result of heavy metal ingestion through the gills. According to Fonseca et al., metals have been linked to harmful effects such as the growth of filament epithelium, lamellar fusion, and epithelial necrosis. (Fonseca et al,.2017), Bioaccumulation of heavy metals is used for environmental evaluation since aquatic life is in close contact with polluted water. Concentrations of metal in fish tissues serve as good indicators of metal pollution in aquatic systems. Fish that are omnivorous and herbivorous both eat algae, a food source that concentrates heavy metals (Al-Kahtani, 2009). The type of fish, the chemical composition, and the physical characteristics of the water, in addition to the heavy metal, all affect how much of the metal is taken up by the animal.

During prolonged exposure to heavy metals, liver heavy metal buildup rises over time. At the 0.001 level of significance, every finding was significant. Heavy metal buildup in the gills and liver followed these orders, respectively: Cd > Pb > Ni. Lead and cadmium bioaccumulated at considerably higher rates in Cyprinus carpio tissues than the other heavy metals tested (Common carp).

Cd concentrations in the Korotoa River were reported to be 11 g/L in the winter and 8 g/L in the summer (Islam et al., 2015). The Cd content in the water of the Buriganaga River was estimated to be 9.34 g/L by Ahmad et al. (Ahmad et al., 2010).

The levels of cadmium in water has been shown to reduce after a rainy season by a number of authors. The dilution caused by rain and runoff was just one of the factors linked to this phenomenon. During the rainy season, water reservoirs are able to store significantly more water than usual. Under the government initiative "Monitoring of surface waters," the level of pollution in lakes caused by priority compounds is evaluated. No reservoir in the study surpassed the permitted values for lead, cadmium, or nickel. Based on the literature study, it appears that Gwodziski (Gwoździński et al., 2014), analyzed water quality of unscreened lakes in Bory Tucholskie, close to the park's southern perimeter, discovered identical Pb and Cd values in their samples as were reported in the studied waterways. The values found in the current study were substantially lower when compared to heavy metal concentrations in the water of lakes Miedwie and Dbie in North-West Poland. (Gwoździński et al., 2014).

The recent study discovered that heavy metal contamination that made their way into surface waters are primarily concentrated in bottom sediments, which is consistent with previous research. The sedimentary architecture is relatively fixed in comparison to the fluid water column, slowing the biological hydrolysis of metallic bonds and impeding their rapid resuspension (Kara et al., 2017; Xu et al., 2014).

Conclusions

1- We conclude from the findings that the summer season had a higher concentration of heavy metals than the winter season in all types of fish studied, almost all in water samples.

2- The fish livers had the highest concentrations of heavy metals compared to the other of the organs.

3-Cd and Pb were the two most concentrated elements in fish organs within the permissible limits

4-The waters of Marsh al-Dalmaj and the fish that are caught are polluted with lead and cadmium, more than the permissible limits.

Recommendations

1- Intensify studies in all water in Iraq to search for heavy metal concentrations and measure their compatibility with permissible concentrations because of their importance in human health.

2- Fixing the genetic map of fish that live in the waters of Iraq because of its role in preserving them from overfishing and extinction- Encouraging veterinarians to invest in the field of fish farming, which has an important impact on national income.

3- Treating polluted water in marshes, rivers and lakes through modern technologies such as nanotechnology

4- Establishing quality control over the fish caught in polluted areas and condemned the polluted fish to a large extent because of its effect on public health.

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