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Research Article

Investigation of Selenium and Manganese Levels in Al-Dalmaj Marsh, Iraq by Using ICP-AES

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Abstract

In this study, the levels of selenium and manganese were evaluated in water, sediments, and fish from al-Dalmaj marshal , which is located in central Iraq. It is important for supplying fish to the provinces and is considered the main basin where agricultural runoff, rainwater, and other waters accumulate. These levels were found during measurements using an ICP-AES device (Inductively Coupled Plasma Atomic Emission Spectroscopy).Samples were collected between March and July 2024. Average values were: water — Mn 4,880.48 µg L^{-1}, Se 274.09 µg L^{-1}; fish — Mn 1,408.06 µg L^{-1}, Se 142.12 µg L^{-1}; sediment — Mn 25,587.99 µg L^{-1}, Se 232.42 µg L^{-1}. The measurements exceeded the limit allowed by the World Health Organization (WHO), which indicates environmental risks to human health. Continuous monitoring and taking necessary measures to reduce risks and limit pollution are recommended.

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Introduction :

Heavy metals are naturally occurring elements that can play important roles in biological processes when present at trace levels. Elements such as iron, zinc, copper, and manganese are required for normal metabolic functions; however, elevated concentrations can become toxic to living organisms[1]. In contrast, metals including arsenic, cadmium, lead, and mercury have no known biological function and may cause adverse health effects even at relatively low concentrations[2]. These elements can enter aquatic environments through various pathways, including agricultural runoff, industrial effluents, sewage discharge, and atmospheric deposition.[3]. confirming elemental toxicity can be challenging because its clinical symptoms often resemble those of other disorders. Elements such as manganese (Mn) and selenium (Se) play important roles in ecosystems and biological systems; however, they can become toxic when present at elevated concentrations[4]. Selenium is a naturally occurring metalloid that is essential for human and animal health in trace amounts but may lead to adverse effects when intake exceeds safe levels[5]. It is involved in several physiological processes, as selenium is a key component of selenoproteins that support antioxidant defense mechanisms, regulate thyroid hormone metabolism, influence reproductive functions, and contribute to neuroprotective activities[6]. Selenium plays important role in normal physiological functions by supporting antioxidant defense systems. It is an essential component of selenoproteins, which are involved in thyroid hormone metabolism, regulation of reproductive functions, and neuroprotective processes. Among trace elements, selenium is known for a very narrow margin between dietary deficiency and toxicity[7]. Its toxic effects are strongly influenced by its chemical form, as inorganic and organic selenium species exhibit different biological behaviors and levels of bioavailability [3]. Over recent decades, optimizing selenium intake has been recognized as major public health concern due to its narrow range between deficiency and toxicity. Low selenium status has been linked to increased risks of mortality[8], impaired immune response, cognitive decline, and thyroid dysfunction. In addition to dietary exposure, selenium and other trace metals can be introduced into the environment through both natural and anthropogenic sources, including mining activities, industrial processes, sewage discharge, and atmospheric deposition, which may ultimately influence their availability in aquatic ecosystems[5]. The Dalmaj marsh is one of the important water bodies in Iraq, as it provides a vital environment for many aquatic organisms. This research was motivated by the global environmental significance of these marshes, for their unique biodiversity, their role as a world heritage site, and, finally, as a home for the Marsh Arabs[9]. Including fish and birds. However, increased human activities may lead to the accumulation of heavy elements in the water, posing a threat to the ecological balance and health of living organisms Figure no. 1 show the effect of selenium on fish [4]. This study aims to assess Mn and Se levels to inform local environmental management.

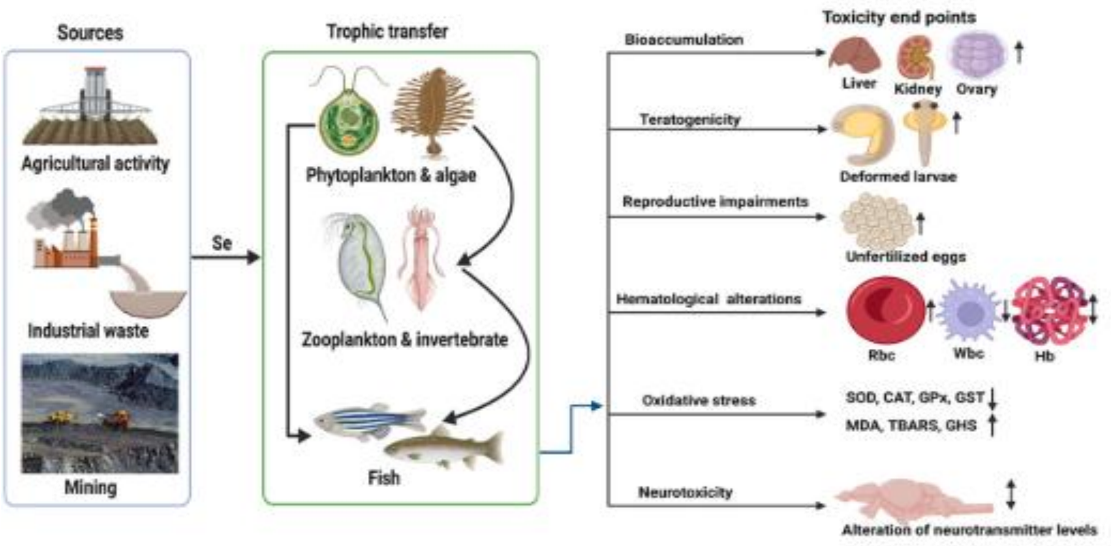

Figure no. 1: The effect of Selenium on fish [4].

This research aims to measuring the levels of manganese and selenium in water, sediment and fish in the Al- Dalmaj marsh and Comparison of concentrations with international environmental standards ,Also, Study the impact of these minerals on the ecosystem in the region.

1- Materials and methods :

2-1 Study Location :

The samples were collected in different areas the sampling campaign was conducted between March and July2024,covering seasonal changes in water levels and environmental conditions, in the Dalmaj marsh, Iraq. The site includes permanent and variable water sources, allowing monitoring of the impact of environmental changes on mineral levels. The marshes are important areas as they are one of the most important ecological systems in the world due to their unique biodiversity, as they are considered an economic resource that supports the Iraqi and global economy [10].Iraqi marshes are unique in a balanced ecosystem and occupy large areas of the sedimentary plain in southern and central Iraq, forming the natural basin of the Tigris and Euphrates rivers, dependent on the nutrition of these two rivers since the beginning of their formation, and therefore, receiving sediments dredged during the long course of the two rivers, as well as dusty sediments carried by wind. Marshs are distinguished by presence large number of aquatic plants and the Iraqi marshes have great biological and plant diversity[11] .

The term "seasonal variation in water and sediment quality" refers to changes in elements of water and sediment that are present at the ideal level for optimal plant and animal growth . These elements are crucial for the development of both plants and animals in the aquatic body. Marsh lands are exposed to many pollutants found in water, such as hydrocarbons and heavy metals[12] . Their presence and properties depend on the type of pollution that enters the medium from natural and industrial sources . It turns into toxic complex compounds when gathered for long periods, causing an imbalance in the aquatic medium and changing the properties of the soil and the biological diversity in the medium. Figure No. 2 shows a map of the area from which the samples were collected.

Figure No. 2: a map of the Dalmaj marsh

2-2 Sample collection :

Samples from the Dalmaj marsh were collected from different places in a way that covered all the area at different distances and includes ; 15 samples of water ,15 samples of fish and 15 samples of sediment.

2-3 Preparing the samples:

Water: The samples were filtered by a micro filter of 0.45 µl to get rid of all impurities and add nitric acid HNO_3 to maintain the stability of minerals and the non-growth of algae in the water during the storage period.

Fish: The fish were collected from the site fishing nets and from the same places to collect water and then take from each (barble, spondy and poetice of fins) fish part of the muscles and part of the gills and was digested by strong acids($HCl+HNO_3$) and converted into a liquid and filtered micro filter 0.45 µl and becomes ready for measurement.

Sediments: The sediment was collected from the same place to collect water and placed in laboratory bags and was transported to the laboratory and dried by Oven at a temperature of 80 ˚C for three days after that it was grinded, sieved and prepared for measurement.

2-4 Analytical By ICP-AES :

Determining metal ions in tap water and mineral waters with low and high levels of concentration for some elements remains one of the essential tasks of controlling its quality and safety. To solve this task, several methods are used: Atomic Absorption with Flame Atomization (AAS), Atomic Absorption with Electro thermal Atomization (AAS ET), Atomic Emission Spectrometry (ICP EOS), Mass Spectrometry with Inductively Coupled Plasma (ICP MS). Each of these methods has its advantages and disadvantages: different sensitivity, accuracy, and selectivity [13] Samples were analyzed using inductively coupled plasma atomic emission spectrometry ICPE-9000 MULYITYPE ICP, SHIMADZU), with selenium and manganese measured according to international laboratory standards[14].

2- Results And Discussion :

3-1 Manganese and selenium levels in different environments:

Manganese and selenium concentrations in water, fish and sediments were analyzed, and the results showed the following in Table 1 :

Table 1: Mean concentrations (±SD) of Mn and Se in water, fish, and sediment.

Matrix	Mn Mean (Mg.L-1	(Se Mean (Mg.L-1	Mn Std Dev	Se Std Dev
Water	4880.48	274.09	17059.76	94.62
Fish	1408.06	142.12	1076.05	46.67
sediment	25587.99	232.42	6754.47	13.04

The raw data obtained by inductively coupled plasma optical emission was entered into and processed using Microsoft Excel and SPSS(Statistical Package for the Social Sciences). The concentration determined from the calibration curve were corrected where necessary for instrumental drift followed by any dilution factors applied, such as the initial sample mass and final digest mass. The final results for the sample location or population were then subjected to calculation of descriptive statistics such as arithmetic mean, standard deviation, relative standard deviation, median, geometric mean, 95% confidence interval and range as appropriate. Suitable significance testing, namely Grubb's outliers, F-test, t-test, one-way analysis of variance (ANOVA) and interaction effect test were then undertaken as showed in Table 2.Regression analysis was also utilized to determine the linearity of the calibration curve for arsenic by the ICP-OES investigated in this research.

ANOVA and T-test Results

Table 2: Results of ANOVA and T-tests for Mn and Se among water, fish, and sediment samples.

Test	F/T value	p-value	Conclusion
ANOVA Mn	20.76	3.200e-07	Highly significant ($p < 0.001$)
ANOVA Se	18.32	1.100e-06	Highly significant ($p < 0.001$)
T-test Mn (Water vs Fish)	0.91	3.750e-01	Not significant
T-test Mn (Water vs Sediment)	-4.94	3.900e-05	Highly significant ($p < 0.001$)
T-test Mn (Fish vs Sediment)	-13.70	9.300e-10	Highly significant ($p < 0.001$)
T-test Se (Water vs Fish)	5.66	2.800e-06	Highly significant ($p < 0.001$)
T-test Se (Water vs Sediment)	2.04	5.400e-02	Not significant
T-test Se (Fish vs Sediment)	-7.44	8.200e-07	Highly significant ($p < 0.001$)

The heavy metal levels of these media and the correlation for these elements between these media at $P<0.05$. The highest mean values for most elements were found in sediment when compared with water and fish samples. A possible explanation is that sediment is long-term growth materials; therefore, several trace elements accumulate in sediment

.

Table 3: Comparison of measured Mn and Se concentrations with WHO permissible limits.

Element	WHO permissible (Mg.L-1)	Water (Mg.L-1)	Sediment (Mg.L-1)	Fish (Mg.L-1)	Status compared to WHO
Mn	400	4880.48	1408.06	25587.99	Exceeds WHO in water and fish; extremely high in sediments
Se	50	274.09	142.12	232.42	Exceeds WHO in all compartments

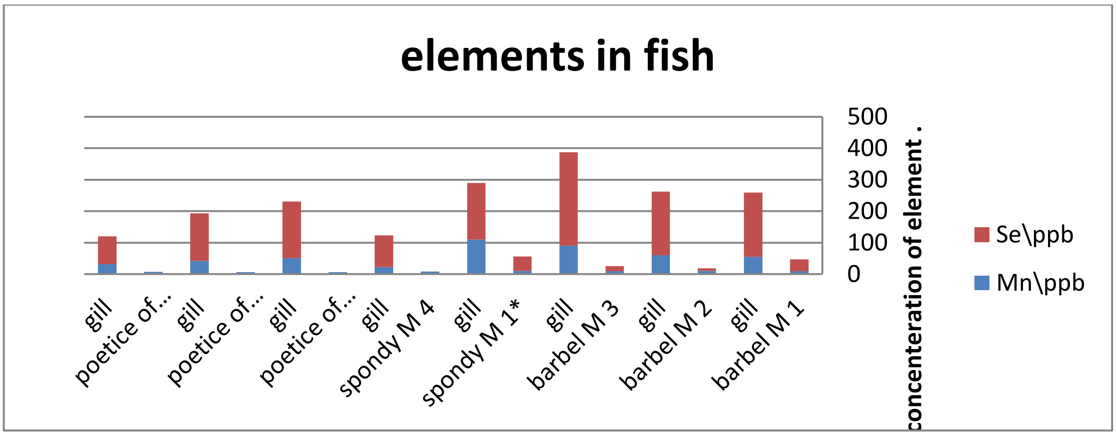

Figure . 3: Concentrations of elements in the gills and muscles of various types of fish

3.2 Discussion

The results showed the highest concentrations of manganese in sediments, suggesting strong adsorption or deposition processes.in conterast, Selenium was most concentrated in water, likely due to its mobility and solubility[4]. Fish tissues samples contained the lowest levels, indicating limited bioaccumulation in these species[12].When Compared to WHO standards (Mn: 400 Mg.L-1) , Se: 50 Mg.L-1) many values in water exceeded safe limits, indicating potential ecological concern.The measured concentrations of Mn and Se in water, fish, and sediment samples were compared with the World Health Organization (WHO) permissible limits (Table 3)[15].To evaluate the differences in Mn and Se concentrations among water, fish, and sediment, one-way ANOVA followed by pairwise T-tests was performed (Table 3).The results of this study demonstrate clear variations in manganese (Mn) and selenium (Se) concentrations among water, fish, and sediment samples collected from Al-Dalmaj Marsh.

Manganese (Mn) The highest Mn concentrations were observed in sediments (25,587.99 Mg.L-1), indicating that

Mn tends to deposit and accumulate in bottom layers. Water samples also contained elevated Mn levels (4,880.48 Mg.L-1), which exceeded the WHO permissible limit of 400 Mg.L-1 by more than 12-fold (Table 3). Fish tissues showed lower levels (1,408.06 Mg.L-1), but still higher than WHO standards for water, suggesting potential bioaccumulation. Statistical analysis confirmed these differences: ANOVA showed highly significant variation ($p < 0.001$), while pairwise T-tests showed that the major differences were between sediment and both water and fish (Table 2).

Selenium (Se)

Se concentrations were highest in water (274.09 Mg.L-1), more than five times the WHO permissible limit of 50 Mg.L-1 . Sediments (232.42 Mg.L-1) also contained elevated levels, while fish tissues (142.12 Mg.L-1) had the lowest Se values but still exceeded WHO guidelines (Table 3). ANOVA results showed highly significant differences among media ($p < 0.001$). T-tests indicated significant variation between water and fish, and between fish and sediment, while differences between water and sediment were not significant ($p \approx 0.05$), suggesting similar contamination sources for these two media.

Ecological and Health mplications

Increased concentrations of manganese and selenium in water and sediments raise concerns about environmental safety and human health [16]. These levels may affect aquatic organisms through oxidative stress and neurological effects[17], These levels may affect aquatic organisms through oxidative stress and neurological effects[18]. The presence of both elements at levels exceeding permissible limits indicates the presence of pollution such as agricultural water pollution, industrial wastewater, and natural geochemical pollution[19] .

Comparison with Other Studies

Similar findings of elevated manganese and selenium levels in water systems were found in regional research across Iraq and neighboring countries, where areas exposed to agricultural and urban drainage and rivers showed pollution exceeding international standards[20]. This supports the conclusion that Al-Dalmaj Marsh is under significant environmental stress[21].

Summary of Findings

Sediments are the main place where manganese is stored, while water is the main medium for selenium. The limits allowed by the WHO have been exceeded in almost all media, and statistical analyses have confirmed that the varying concentrations of manganese and selenium were very significant. This study underscores the need for further research on seasonal variations and for enhanced pollution control strategies.

Discussion of Differences

Manganese (Mn): The average concentration in water (4880.48 Mg.L-1) is almost 12 times higher than the WHO limit. Fish tissues (1408.06 Mg.L-1) also exceeded the permissible limit, reflecting possible bioaccumulation. Sediment concentrations (25587.99 Mg.L-1) were extremely high, showing sediments as a contamination reservoir.

Selenium (Se): Water samples contained 274.09 Mg.L-1 , more than 5 times higher than the guideline value. Fish tissues (142.12 Mg.L-1) exceeded safe levels, raising concerns about transfer through the food chain. Sediments (232.42 Mg.L-1) showed persistent accumulation.

The selenium and manganese concentrations in the Al-Dalmaj marshes significantly exceed established standards, indicating environmental and public health risks that require mitigation measures. The variability in manganese levels in the water (high standard deviation) reflects fluctuating environmental conditions. This elevation can be attributed to agricultural runoff, untreated wastewater, industrial waste, and the natural geochemical movement of sediments.

ANOVA results indicated highly significant differences in Mn and Se levels among the studied media ($p < 0.001$). Pairwise T-tests showed that Mn levels were significantly higher in sediments compared to water and fish, while Se levels differed significantly between water and fish as well as fish and sediments

4. Conclusions

This study shows that there are high levels of manganese and selenium, especially in water and sediments, and we emphasize the need for continuous environmental monitoring and pollution control because they may pose risks to aquatic life and human health. Future studies should investigate the sources and pathways of these minerals and assess their biological impact in more detail. It is recommended to implement pollution control programs, regulate agricultural discharges, and raise awareness among local fishermen regarding metal bioaccumulation risks.

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