The concentrations of cobalt and nickel elements in aquatic plants exposed to urban wastes in Al-Diwaniyah River / Iraq

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Abstract:

The purpose of this study was to determine whether or not the addition of sewage and industrial water affected the concentration of cobalt and nickel in aquatic plants across all four seasons in the Al-Diwaniyah Governorate of Iraq. Three sites were used to collect samples of aquatic plants (reeds and Ceratophyllum) over the duration of a year, beginning in the summer of 2021in July and continuing through the autumn of 2021 in October, winter of 2022 in January, and spring of 2022 in April. The first site is located near the city's entrance in Diwaniyah. Highest values of concentrations were in summer, in the third location, where the Cobalt concentration in the reed plant was 6.08 µg kg^{-1}, and the amount of it that was found in the ceratophyllum was 14.40 µg kg-1, Cobalt concentrations were 0. 204 µg kg-1 in the reed plant and 4.02 µg kg-1 in the ceratophyllum at the first location, respectively, during the winter, during the summer month, the third site had the greatest concentration of Nickel at 24.67 µg kg-1, which was found in the reed plant. In contrast, 114.4 µg kg-1 was recorded in ceratophyllum, Cobalt concentrations were 7.09 µg kg1 in the reed plant at the first site and 42.01 µg kg-1 in the ceratophyllum at the second site, respectively; both plants were at their lowest in the winter.

Keywords: Cobalt, Nickel, Urban Wastes, aquatic plants, Iraq

Introduction

Aquatic plant is varied, common, and climatically adaptable because it may thrive in a wide range of water conditions, different types of plant families have been used as life guides to study water pollution with heavy metals and because of their high ability to absorb and safely store elements within their tissues without risking toxicity or death. Bioremediation [1] Floating, fully submerged, or partially submersible plant forms that are able to complete their whole life cycles in water are considered aquatic plants. Or, they can be plants whose seeds germinate in water or somewhere on a body of water and must spend part of their life cycle in water. Some aquatic plants are rich in proteins and carbohydrates and can be eaten by humans. They are also important for fish and other aquatic life [2]. Worldwide, reeds are among the most common perennials, which are distinguished by their ability to withstand harsh environments and severe, hazardous pollution. Cane is both a vital part of a balanced ecosystem and a valuable resource for humans, as it is used in industries and as animal feed. However, in some regions, it is also viewed with caution due to its potential to cause harm.

The ceratophyllum or (Shelant) is a group of submerged aquatic bushes, and the plants are dark green in color, and their individual heights can reach 20 to 100 centimeters. Each leaf is bi-forked once or twice, and its length varies from 1 to 2.5 centimeters. The tips of the plant's branches seem like the tail (cat tail) because of the dense clustering of leaves at the ends of the branches. Newly developed side branches characterize these perennial plants. There is a limited ability to see the flowers [3]. Several varieties of aquatic plants in the Al-Diwaniyah River were tested for their ability to absorb and store heavy metals, and the results showed that these plants were able to gather and store Nickel and Cobalt at concentrations far higher than those found in the water itself as shown by the study [4]. Alternatively, it was hypothesized that increased temperatures would accelerate evaporation processes, which would raise the concentration of heavy metals in the sediments. According to [5], industrial waste from textile and rubber companies can have an impact on river water quality; this waste has been shown to increase BOD values by a large amount, as described in the study. The purpose of this investigation was to examine the seasonal variation in the content of Cobalt and Nickel in reed and ceratophyllum at several places along the Diwaniyah River.

The selection of *Phragmites australis* (reed) and *Ceratophyllum demersum* was based on their ecological abundance in the Diwaniyah River and their well-documented capacity for heavy metal accumulation. These species differ in morphology and ecological niche, where reeds are emergent plants while *Ceratophyllum* is fully submerged, allowing for a comparative assessment of metal uptake efficiency under varying exposure conditions. Previous studies have demonstrated their effectiveness as bioindicators and phytoremediators in polluted aquatic systems [8][12][15]

Human waste and partially treated industrial waste from nearby textile and rubber factories are two major contributors to pollution in the Diwaniyah River, moreover, agricultural effluent is discharged into the river, reducing the river's appropriateness for human, agricultural, and industrial uses [6] [7]. Emergent Aquatic Plants, such as *Phragmites australis* and sedge *Typha domingensis*, exist on both

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sides of the river, in addition to the presence of *Ceratophyllum demersum*, a subemergent Aquatic plant.

Materials and Methods

The study was conducted at three locations along the Diwaniyah River (Al-Sunniyah, Rifaat district, and Al-Sudair) representing upstream, midstream, and downstream pollution gradients. These sites were selected based on their varying exposure to urban, industrial, and agricultural discharges. Dominant aquatic plants (*Phragmites australis* and *Ceratophyllum demersum*) were selected for analysis due to their abundance and ecological relevance.

Samples of water, aquatic plants, agricultural soils, and cultivated plants were collected seasonally (summer 2021, autumn 2021, winter 2022, and spring 2022). Soil samples were taken at two distances (100 m and 5000 m from the river) and three depths (0–30, 30–60, and 60–90 cm). All samples were properly labeled, preserved, and transported to the laboratory for analysis.

Soil samples were air-dried, sieved (2 mm), and subjected to physical and chemical analyses, including particle size distribution, bulk density, pH, electrical conductivity (EC), cation exchange capacity (CEC), carbonate content, organic matter, and soluble ions, following standard procedures [10].

Water samples were filtered and analyzed for cobalt and nickel concentrations. Plant samples were washed, oven-dried at 65°C for 48 hours, ground, and digested using a mixture of concentrated acids (H_2SO_4, HNO_3, and $HClO_4$). Heavy metals (Co and Ni) in soil, water, and plant samples were determined using Atomic Absorption Spectrophotometry (AAS, Shimadzu AA-7000), following standard methods [11].

Statistical analysis was performed using SAS (2012) under a randomized complete block design (RCBD). Differences between means were evaluated using the Least Significant Difference (LSD) test at a significance level of $p \leq 0.05$. Each treatment was conducted in triplicate to ensure statistical reliability. The Atomic Absorption Spectrophotometer (AAS) model was used for metal analysis following standard calibration procedures. Quality control was ensured using standard reference materials. Data were analyzed using SAS (2012), and means were compared using LSD at a significance level of $p \leq 0.05$. [12]

Results and Discussion

The concentrations of cobalt found in aquatic plants during each of the four seasons

Table (1) shows a clear seasonal and locational variation in cobalt concentrations in the studied aquatic plants. The highest values were

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recorded in the summer, particularly at location 3, reaching 6.08 mg kg^{-1} in reeds and 20.16 mg kg^{-1} in water hyacinth Figure (1),. The lowest values were recorded during the winter for reeds (0.204 mg kg^{-1}) and in the autumn for water hyacinth (0.228 mg kg^{-1}).

The superior cobalt accumulation of water hyacinth (Ceratophyllum demersum) compared to reeds can be explained by its being a fully submerged plant, which increases its surface area of direct contact with the aquatic environment and enhances the absorption and accumulation of heavy metals in its tissues. This finding is consistent with the results of [6], who indicated that submerged plants have a higher efficiency in accumulating heavy metals compared to emerging plants. These results are consistent with the study by [11], which showed that heavy metal concentrations in aquatic plants increase during the summer due to higher temperatures and increased plant physiological activity, leading to increased uptake and accumulation of these elements. Also [12] indicated that environmental factors such as temperature and reduced water volume due to evaporation contribute to increased heavy metal concentrations in aquatic systems during the summer.

The significant increase in cobalt concentrations at the third site is attributed to increased pollution sources from urban and industrial activities. This aligns with [13], who stated that downstream areas often exhibit higher heavy metal concentrations due to pollutant accumulation.Conversely, the decrease in concentrations during the winter may be due to a dilution effect resulting from increased water flow and reduced plant activity. This is consistent with the findings of [14] , who demonstrated that lower temperatures reduce the efficiency of biosynthesis of heavy metals. This increase in metal concentration during summer may be attributed to higher evaporation rates and reduced water volume, which leads to increased metal concentration in aquatic systems [9].

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Table(1): The concentration of cobalt found in representative samples of aquatic plants throughout each of the four seasons (micrograms kg^{-1}).

Concentration	Site	Type of plant	Season / year
4.44	First	Reed	Summer season (July)
4.98	Second		
6.08	Third		
14.40	First	Ceratophyllum	
18.51	Second		
20.16	Third		
2.99	First	Reed	Autumn season (October)
3.09	Second		
3.52	Third		
0.228	First	Ceratophyllum	
0.778	Second		
7.78	Third		
0.204	First	Reed	Winter season (January)
0.214	Second		
1.066	Third		
4.02	First	Ceratophyllum	
5.40	Second		
8.62	Third		
0.23	First	Reed	Spring season (April)
1.86	Second		
2.34	Third		
9.32	First	Ceratophyllum	
7.71	Second		
6.33	Third		
*0.387	---	----	LSD value

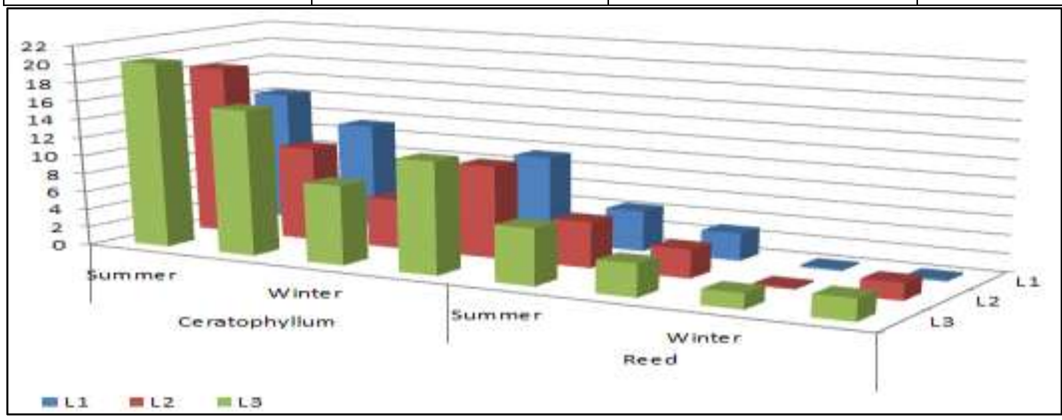

Figure1: Concentrations of cobalt in aquatic plants during the four seasons.

The concentration of nickel that is present in aquatic plants during each of the four seasons.

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Table (2) shows a clear variation in nickel concentrations in aquatic plants depending on location and season. The highest values were recorded in summer at location 3, reaching 114.4 mg kg^{-1} in water hyacinth and 24.67 mg kg^{-1} in reeds, while the lowest concentrations were recorded during winter, particularly at location 1. Figure (2)

This high concentration at location 3 reflects the direct impact of industrial activities, especially textile factory waste, which is a major source of heavy metals in surface waters. This finding is consistent with the study by [15], which demonstrated high concentrations of elements (Ni, Co, Pb, etc.) in the Diwaniyah River due to industrial waste discharge. It consistent with those of the study by [17], which dealt with the assessment of water pollution of the Euphrates River within the city of Ramadi using heavy metal pollution indicators. The study showed high concentrations of elements such as nickel in the surface waters of urban areas as a result of human activities and untreated discharges.

The results showed that water hyacinth was significantly more effective than reed in absorbing nickel. This is attributed to its completely submerged nature and its high capacity for absorbing and accumulating elements without exhibiting obvious toxicity symptoms. This finding aligns with the findings of [6] and [11] ,who suggested that aquatic plants are effective bioremediation agents due to their ability to accumulate heavy metals in their tissues.

Furthermore, the seasonal variation in nickel concentrations, which rise in summer and fall in winter, is consistent with [12] assertion that higher temperatures and increased evaporation rates lead to higher pollutant concentrations, while rainfall and increased runoff in winter reduce them.

The results also showed significant differences between seasons and locations for the water hyacinth plant, while the differences were less clear in the sugarcane plant, indicating a difference in absorption efficiency between plant species, which was confirmed by the study of [13], which indicated that the morphological and physiological characteristics of plants greatly affect their ability to accumulate heavy metals.

Seasonal variations in metal concentrations can be attributed to environmental factors such as temperature, water flow rate, and evaporation. Higher temperatures during summer increase metabolic activity and metal uptake by plants, in addition to concentrating pollutants due to water evaporation. Conversely, lower concentrations in winter may result from dilution effects and reduced biological activity. In the study by [16] this is directly reflected in the increased accumulation of heavy metals in aquatic plants as a result of

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absorption and bioaccumulation processes, which reinforces the link between water pollution and its transfer to biotic levels within the riverine ecosystem.

The findings of the current study are consistent with those of[14], conducted on the Euphrates River branch in the city of Diwaniyah. That study revealed significant concentrations of heavy metals, including nickel and cobalt, in the river water due to the discharge of sewage and industrial waste. The study also indicated that nickel concentrations exceeded the limits permitted by Iraqi and World Health Organization standards, with a clear increase in pollution levels downstream towards urban areas.

The present study specifically focused on cobalt and nickel due to their prevalence in industrial and urban wastes in the study area. Other heavy metals such as lead, mercury, cadmium, and copper were not included within the scope of this study but are recommended for future investigations. This is consistent with what [15] indicated regarding the high concentrations of heavy elements in river water in areas located within the city center and areas where pollutants are discharged, which confirms the existence of a direct relationship between increased pollution in the water and its transfer and accumulation in aquatic plants within the river ecosystem.

Table(2) : The amount of nickel found in representative samples of aquatic plants throughout each of the four seasons (micrograms.kg^{-1}).

Concentration	Site	Type of plant	Season / year
18.99	First	Reed	Summer season (July)
22.41	Second		
24.67	Third		
88.61	First	Ceratophyllum	
90.11	Second		
114.45	Third		
15.33	First	Reed	Autumn season (October)
16.21	Second		
16.88	Third		
67.88	First	Ceratophyllum	
60.43	Second		
76.90	Third		
7.09	First	Reed	Winter season (January)
8.55	Second		
9.99	Third		
44.12	First	Ceratophyllum	
42.01	Second		
58.08	Third		
9.76	First	Reed	Spring season

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10.43	Second		(April)
13.11	Third		
50.23	First	Ceratophyllum	
56.43	Second		
61.43	Third		
11.25	---	----	LSD value

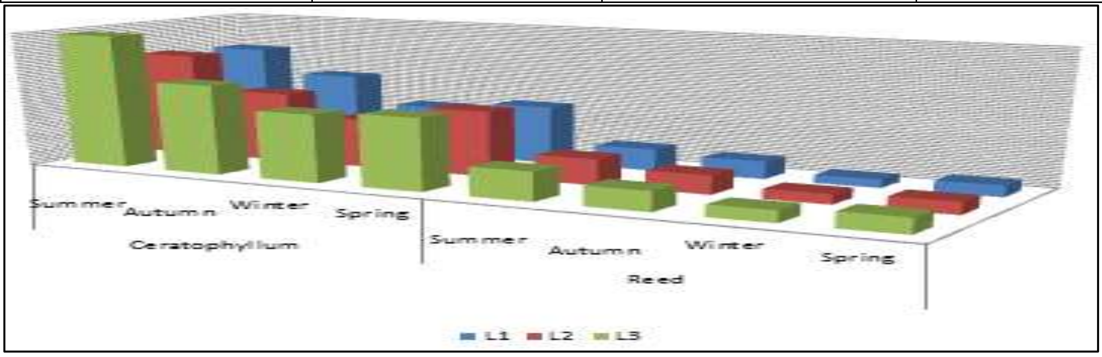

Figure 2: the seasonal variation of nickel concentration in aquatic plants.

Although the present study focused primarily on the accumulation of cobalt and nickel in aquatic plants, it did not include morphological or physiological parameters such as plant height, biomass, or leaf area. Future studies are recommended to integrate these indicators in order to better understand the biological impact of heavy metal accumulation on plant growth and health.

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Conclusion :

The present study demonstrated significant spatial and seasonal variations in cobalt and nickel concentrations in aquatic plants of the Diwaniyah River. The highest concentrations were recorded during the summer season, particularly at the third site, indicating the strong influence of urban and industrial discharges. *Ceratophyllum demersum* showed a higher capacity for metal accumulation compared to reeds, highlighting its potential as an effective bioindicator and phytoremediation agent.These findings emphasize the impact of untreated wastewater on river ecosystems and the need for improved environmental management strategies. Future research should include additional heavy metals and plant physiological parameters to provide a more comprehensive understanding of pollution effects.

The study results indicate a clear increase in the concentrations of cobalt and nickel in aquatic plants downstream, due to the increasing sources of pollution. The highest concentrations were recorded during the summer and the lowest during the winter (and for water hyacinth in the autumn), reflecting the influence of environmental and seasonal factors. Water hyacinth showed a higher efficiency in accumulating these two elements compared to reeds, confirming its importance as a bioindicator and an effective tool in the bioremediation of polluted water.

It is recommended that sewage and industrial wastewater be treated before being discharged into the Diwaniyah River to reduce environmental pollution. Aquatic plants, particularly Ceratophyllum demersum, can be utilized in phytoremediation programs due to their high capacity for absorbing and accumulating heavy metals.

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