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RESEARCH ARTICLE

The Concentration of Some Heavy Metals in Phragmites Australis and Ceratophyllum. Demersum Plants in the Euphrates River, Iraq

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ABSTRACT

The current study was conducted monthly in four stations in the waters of the Euphrates River in the area extending from AL-Hindiyah District Project to AL-Kifl district in central Iraq for the period from November to August of the year 2023. The study aimed to measure some of the chemical and physical characteristics of the water of the Euphrates River and to examine the study population of Phragmites australis and C. demersum plants, as well as to evaluate the concentrations of four heavy metals: cadmium, lead, mercury and zinc in the plants studied.the physical and chemical included temperatures of air and water , pH, electrical conductivity, Total dissolved solids, total hardness ,calcium hardness ,the magnesium hardness , Chloride). The current study determined the effect of monthly variations of the months and stations of the study on four heavy metals (Cd, Pb, Hg, and Zn) in P. australis and C. demersum. The highest concentration of cadmium was recorded in the P. australis, and the lowest concentration in the C. demersum, while the plant type displayed significant differences, as the highest concentration of cadmium was recorded in the C. demersum, with a statistically significant difference during the study months and stations from what was recorded in P. australis. As for lead, the highest concentration was recorded in the C. demersum), while no concentration both plants. As for Hg, there was a significant effect of locations and months, as the highest concentration was recorded in the P. australis, while the concentration was not recorded in several stations and in different months. In context of zinc, the results indicated that its highest concentration was in the C. demersum, and the lowest concentration in the P. australis plant. There was an effect of plant type, with a statistically significant difference, as the highest value was recorded in the C. demersum, while the concentration of zinc was lower in the reed plant.

INTRODUCTION

Phytoremediation has a vital role in the ecology field, as plants can play an important role in eliminating or reducing pollutants, and there are many aquatic plants that can withdraw and accumulate heavy metals from polluted areas (Maktoof et al., 2020). Phragmites australis (P. australis) and Ceratophyllum demersum (C. demersum) plants have a high ability to the vegetative reproduction and biomass production even in low nutrient conditions. Recently, the interest in using the plant to treat and remove the accumulation of heavy metals has increased (Coppa et al., 2020).

Heavy metals are toxic in nature and therefore cause serious health diseases in humans and plants, even at very low concentrations, as these metals enter the water system through agricultural activity and industrial discharges. It is necessary to get rid of excess amounts of heavy metals in soil and water to avoid negative consequences, and most floating and submerged aquatic plants have the ability to tolerate high levels of heavy metals through the formation of phytochelatins. P. australis plant showed a wide ability to tolerate cadmium, chromium, copper, and lead (CanoRuiz et, 2020) and it also has a great ability to absorb a wide range of metals such as Pb, Ni, Zn, Cd, M0, Fe,, Mn, Hg, and Cr (Delplace et, 2020).

Water and air are polluted with heavy metals, and high concentrations of heavy metals pose an environmental concern (Luo et al., 2020).

Fresh water is the water that occurs naturally on the surface of the Earth, such as in swamps, ponds, rivers, lakes, and streams, or underground, as in groundwater and underground streams. This water is generally characterized by the presence of low concentrations of dissolved salts and other dissolved solids. An exception to this term is sea water and salt water even though they contain water rich in mineral salts, as in springs (Asma, 2022,).

Physical and chemical properties greatly affect aquatic life, its diversity and density (Prabhu et al., 2022). Interactions between the physical and chemical properties of water play an important role in the formation, distribution, and abundance of aquatic organisms. The physical and chemical properties have been studied by many foreign researchers, including a study by Jayalakshmi et al in India to evaluate the physicochemical factors of water and wastewater of the Krishna River in the city of Vijayawada, the study included seven study sites: the first three sites were slightly polluted while all four sites were highly polluted as a result of water contamination with industrial, agricultural and domestic waste. These factors were also studied by (2008) for river water, especially in western Maharashtra in India, and it was found that river water falls within the Krishna standard specifications of the World Health Organization.

Temperature, as an important physical factor, affects the solubility of gases present in water, as it greatly affects the solubility of gases, especially oxygen gas and carbon dioxide, as their solubility decreases with increasing temperature. Hauer & Lamberti explained that a temperature increase of 10 °C significantly increases the speed of chemical reactions by 2-3 times.

Water depth also plays an important role in determining a large number of properties, especially physical ones, such as the amount of light transmittance, thermal distribution, flow speed, sedimentation rates, etc., which affects the nature of the chemical properties, such as the dissolution of substances, the level of basicity and acidity, salts, and nutrients, as these factors and their predecessors directly affect the biomass of various organisms, especially plant ones, and all of these factors are affected by the level of pollution present in the Aquatic environment.

Electrical conductivity expresses the total concentration of dissolved substances in water, and it represents a measure of the ability of an aqueous solution to conduct electrical current, and this ability depends on the presence of ions, their concentration, and temperature.

In Japan, it is possible to use electrical conductivity as a measure of FCD, as the permissible FCD level in water is 1000/100 ml or less, and the relationship between electrical conductivity and FCD depends on the environment surrounding the river, whether it is in an urban area or surrounded by special places such as agricultural lands, farms, or mines.

Mahmood pointed out some sources of environmental pollution in the water of the Euphrates River between the cities of Hit and Ramadi. He indicated that the physical characteristics were within permissible limits, except for the electrical conductivity and suspended solids, which exceeded these limits, and that the chemical characteristics such as chlorides, calcium, sodium, potassium, magnesium, fluoride, and chlorides were within Permissible limits except for sulphates, bicarbonates and phosphates.

In a study conducted on the Diwaniyah River, it was found that the release of wastewater from treatment plants led to an increase in hardness values. Many researchers stated that the water of the Euphrates River was hard in most of the years in which the biology of the river's waters was studied.

Chlorides are important negative ions. Because most chlorine salts tend to dissolve in water and are not biodegradable, removing chloride from water and wastewater is a difficult process. The main techniques for removing chloride are classified into four categories: chemical precipitation, adsorption, oxidation, and membrane separation. It can be converted into metal chloride, precipitates, and metal oxychloride by adding double-layer metal precipitates, also the adsorption is an effective method.

Heavy metals

Heavy metals are those elements that have an atomic number greater than (20) and a density greater than 2 g/cm3. They are materials of natural origin and spread in nature very widely and move between parts of the environment and its components continuously from one place to another and from one form to another (Aumar, 2000) (24). Trace elements can enter the geochemical environment as a result of the decomposition of aquatic plant and animal organisms after their death (Doan et al., 2016) (25). Where heavy metals are concentrated in plant biomass (Manara et al., 2021). The process of accumulating heavy metals in plants usually occurs through the roots of plants. P. australis and Ceratophyllum can absorb and accumulate these heavy metals from the soil. Previous studies have focused on the efficiency of constructed wetlands in removing heavy metals and the ability of aquatic plants to process heavy metals. (AL-Abbawy et al., 2021) conducted a study that included the effect of six aquatic plants (Azolla filiculoides, Potamnogeto pectinatus, Demersum ceratophyllum, Najas marina, Phragmites australis, and Typha domingensis) on the bioaccumulation of cadmium, iron, chromium, zinc, copper, and lead in the Hawizeh marsh in southern Iraq. Their results showed that the concentrations of cadmium, chromium, and iron in aquatic plant tissues were higher than the limits recommended by the World Health Organization (WHO), while zinc, copper, and lead were within recommended limits, and the percentage of accumulation of trace metals in Demersum ceratophyllum and Najas marina was higher than the rest of aquatic plants.

Sources of heavy metals include both natural and anthropogenic sources; Natural geological processes, such as weathering and erosion of rocks in the Earth's crust, are considered the primary sources of heavy elements on the surface of the Earth, which lead to an increase in the concentrations of heavy elements in the surface soil or atmospheric dust, which then move to other places as a result of wind erosion or as a result of the flow of water on the surface of the water or its dissolution and transfer to water (Flem et al., 2018). As for anthropogenic sources, industrial activity is considered a major source of heavy metal pollution in the environment. Many industries, including petroleum industries, oil refineries, iron, steel, copper, glass, aluminum, tanning factories, fertilizers, pesticides, gasoline, and other various industries; Heavy metals can also reach water through contamination with industrial or consumer waste. Irrigation with wastewater also causes the deposition of large amounts of toxic heavy metals in the soil, air, and water, which are inevitably absorbed by plants, and these toxic heavy metals are absorbed by humans (Enyoh et al., 2020). Aims of current study included the identifying the concentrations of heavy metals in water bodies, such as plants, if any, and study some of the relevant physical and chemical characteristics of river water.

METHODOLOGY

The study area

The study area included the selection of four stations from the waters of the Euphrates River to collect the study models, starting from Al-Hindiyah District, through Al-Hindiyah District, until Al-Kifl District Figure (1).

As shown Figure .1 is the AL- Sada AL-Hindiyah; the station is AL-Hindiyah District; the station is Al-Hindiya District; the station is Al-Kifl District

Determination the physical and chemical properties of water

Temperature

The temperature of air and water was measured directly in the field using an ordinary graduated thermometer from 0-100°C.

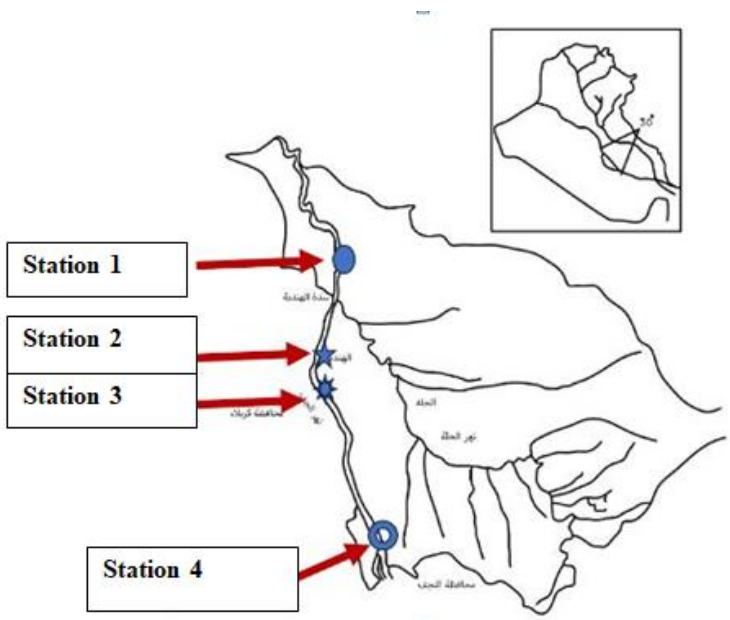

Figure 1. Study location: The station.

pH

The pH level was measured directly in the field using a pH measuring device after HANNA 011-9811 assay, manufactured by Ble Company, with standard buffer solutions (4, 7, and 9).

Electrical conductivity

The electrical conductivity of water was measured in the field using a Conductivity Meter, type Portable HI 9811-0.HI 9811-5, manufactured by HANNA, and the result was expressed in microsiemens/cm. Salinity values were also calculated in terms of electrical conductivity and expressed in parts per thousand, after multiplying it by a factor of 0.064.

Total dissolved solids (T.D.S.)

Total dissolved substances were measured directly in the field using a T.D.S. Meter device type of HI9811-0.HI 9811-5 Portable manufactured by HANNA and the output was expressed in mg/L.

Total Hardness

Total hardness was estimated by titration with 0.01 EDTA-2N solution, using Eriochrome Black T (EBT) as a guide, and the result was expressed in mg/L.

Calcium hardness

The method described by (Lind, 1979) was followed by titration with EDTA-2Na solution, adding (1 N) of NaOH (1) solution, using Murexid dye as a guide, and expressing the result in units of mg/L.

Magnesium hardness

Magnesium values were extracted using the mathematical method referenced by (Lind, 1979) (36) and with the following equation:

mg Mg+2 /L= [mEq hardness /L - mEqCa+2/L] x 12.16

mEq hardness /L= mg hardness] x 0.0499

mEqCa +2 = mgCa+2] x 0.0499

The product was expressed in mg/L.

Chlorides

About 25-50 ml of river water was taken and we put it in a conical flask. We added a few drops of potassium chromate to it, and when a yellow color formed, we flushed it with silver nitrate until the color changed to red (Turbd) and the amount coming from the burette was counted.

Measurement of heavy metal concentrations in aquatic plant samples:

The plant samples were washed with tap water and then with warm distilled water at a temperature of 38°C to remove small invertebrates stuck to them (37). After that, the plant parts were washed with deionized distilled water and dried at a temperature of (70°C), then they have been grind and passed through a sieve of capacity (40mesh). After that, the dried and ground plant samples were digested with a tetric-perchloric acid mixture (HClO HNO3) by adding 2.5 ml of nitric acid to 0.5 g of the plant sample for 24 hours, after which it was placed at a temperature of 80°C for an hour on a heat plate, after which it was cooled air-wise for a period of time; then 2.5 ml of perchloric acid (HCIO) was added at a temperature of 180°C for 2 to 3 hours on a hot plate until the color changed from dark brown to clear, colorless. After that, the samples were filtered with Whatman No. 42 filter paper, then the volume was completed to 10 ml (2001, Jones).

After that, the concentrations of heavy metals (cadmium, lead, zinc, and mercury) were measured with an atomic absorption spectrophotometer, which was calibrated with the following standard solutions:

$6H_2O$ Zn (NO3)(2), Cd(NO3)2 4H2O and Pb(NO3)(2); and the yield was expressed in mg/kg.

RESULTS

1. Physical and chemical water tests

1.1 Temperature of air

Figure (2) shows that the air temperature during the study period from November to August for the year (2023) ranged between (17-51°C), where the lowest average air temperature was recorded in Station (1 and 2) and during the months: January, March and December, respectively; and the highest air temperatures were recorded in August at stations (4 and 3) (49.1, 50.6°C), respectively. The results of the analysis showed significant statistical differences in time and location in the air's temperature between the stations and months of the study, at a significance level of 0.05.

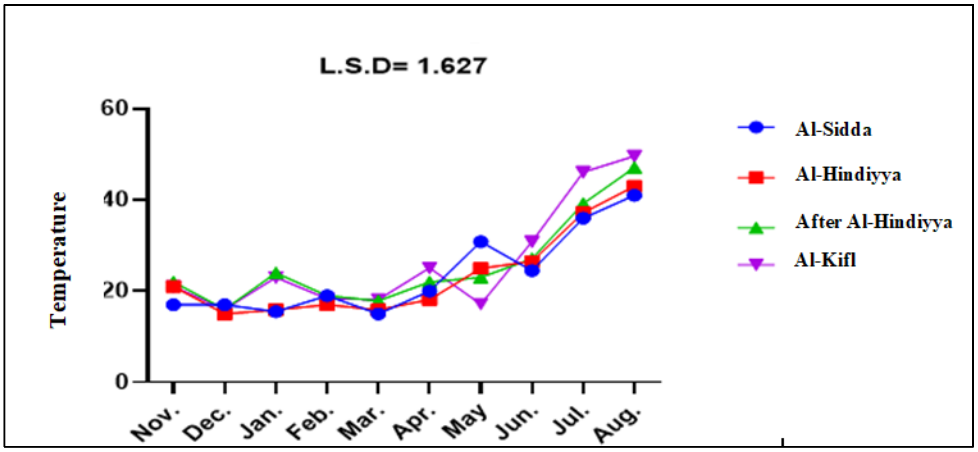

Figure 2. Monthly variations of air temperature at the study stations

1.2 Temperature of water

Figure (3) shows that the water's temperature for the study stations, where the temperature ranged between (16-42°C) at (1, 2, 3, and 4 stations, with the lowest water temperature of (12 °C) recorded in December at station1, while the highest water's temperature of 39°C was recorded at station 3 and in August. Water's temperatures at station 1 and 2 also ranged between 17-37°C during the months of the study; the significant statistics between station locations and months of study at a significance level of 0.05.

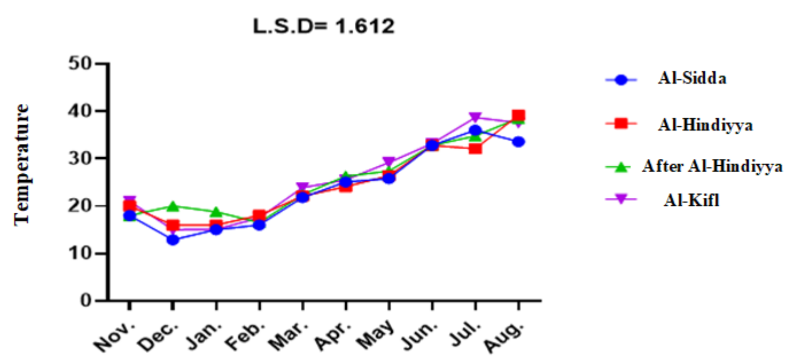

Figure 3. Monthly variations of water temperature at the study stations

1.3 pH

The data shown in Figure (4) indicated that the pH values had changed at the stations and during the months of the study (from November to August in of 2023, where locational changes (stations) and temporal changes (months) were recorded, but these changes were not significant at probability 0.05 level, neither between locations nor during the months of the study. The highest pH value of 8.9 was recorded at station 4 in November, while the lowest pH value was 6.8 at station 1 in February.

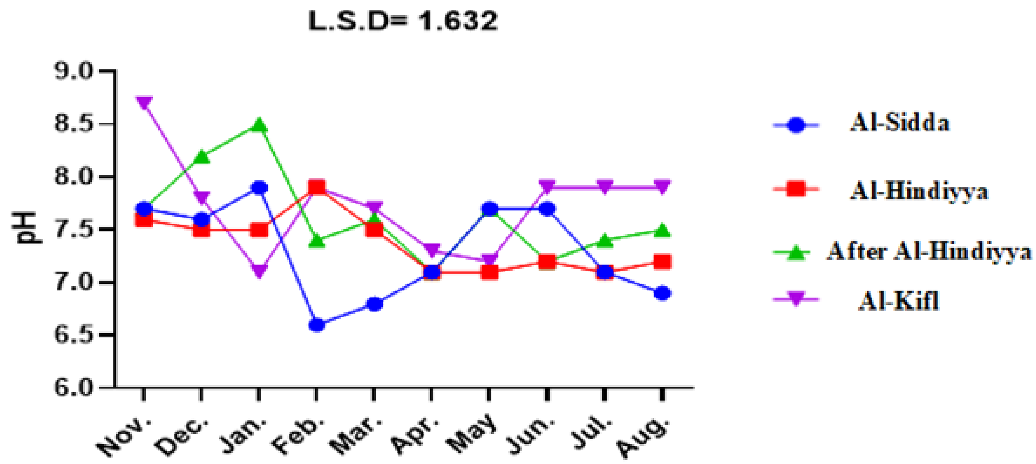

Figure 4. Monthly variations of pH at the study stations

1.4 Electrical conductivity

The statistical results in Figure (5) showed that the highest value of electrical conductivity (EC) was recorded at station (4) during the month of January (1890 micro-Siemens/cm); while the lowest value was recorded (1279 micro-Siemens/cm) in November at station 4

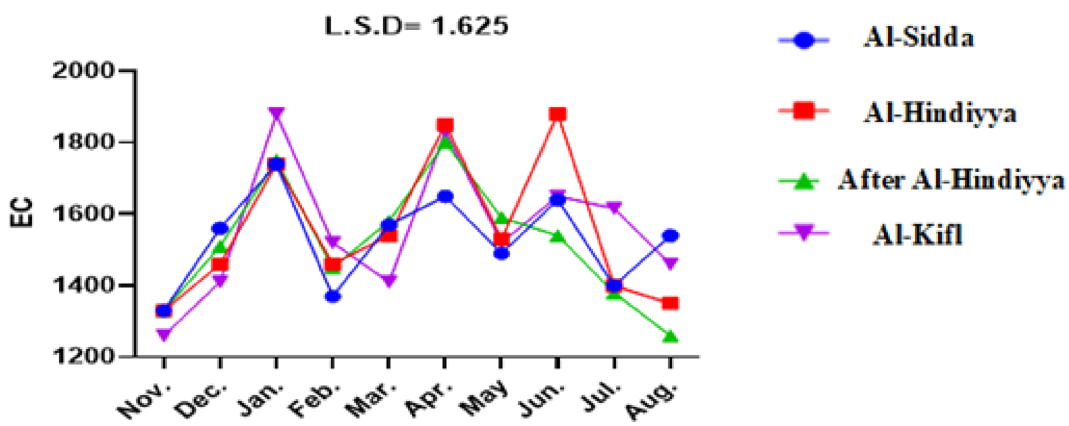

Figure 5. Monthly variations of electrical conductivity at the study stations

1.5 Total dissolved solids

The data in Figure (6) show that the value of TDS ranged between (670-912 milligrams/liter during the months of the study, but without statistical differences. The lowest value was (667 milligrams/liter) that recorded in station (1 and 2) in November, while the highest value was (4 and 2) that recorded in the months January, April, and June. Nevertheless, no significant differences were recorded in the values of TDS among all stations and months of the study at the probability level of 0.05.

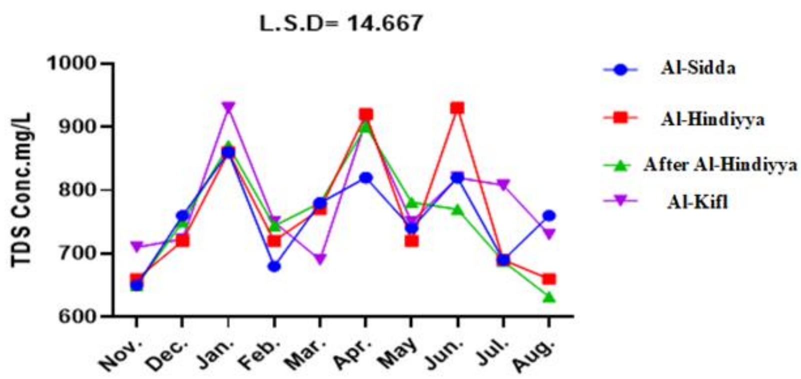

Figure 6. Monthly variations in total dissolved solids at the study stations

1.6 Total hardness

Figure (7) shows that the total hardness value was significantly higher (910 mg/L) at station (4) compared to the rest of the stations, while the lowest value (361 mg/L) was recorded at station (2) in February, with significant differences. On the other hand, the total hardness values ranged between (515-841 mg/L in station 1) and ranged between (766-361) mg/L in station 2). It ranged between (738-374) at station (3) and between (901-441) at station (4) during the months of the study, where significant differences at the level of significance (0.05) were recorded at the level of stations, in addition to the presence of significant differences at the level of months.

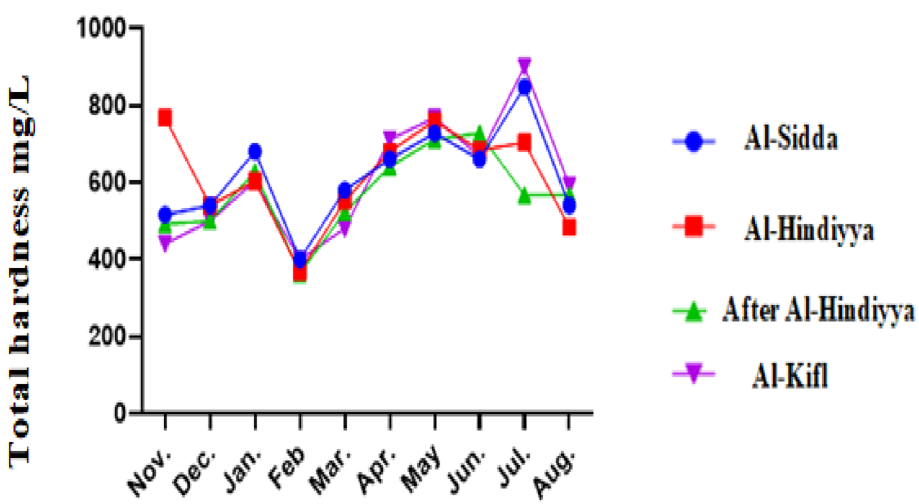

Figure 7. Monthly variations in total hardness values at the study stations.

1.7 Calcium hardness

The lowest calcium hardness values (362 mg/L) were recorded at stations (1 and 3) during the month of February, while the highest calcium hardness was (901 mg/L) that recorded during July, with a significant difference at the 0.05 level, as shown in Figure (8).

1.8 Magnesium hardness

Magnesium hardness values ranged (167-765), (131-84), (146-68), and (173-77) at stations (1, 3, and 4), respectively, with statistically significant differences between the months of the study from November to August and at a significance level (0.05). The stations also differed significantly in the values of magnesium hardness, as it was 118.0 in station (2); while the lowest value was 111.0 in station (3). On the other hand, the months of the study had a significant effect on magnesium hardness levels, as the highest value recorded was 179 mg/L in July at station (4) and the lowest value recorded was 69 mg/L in station (3) During February, as shown in Figure (9).

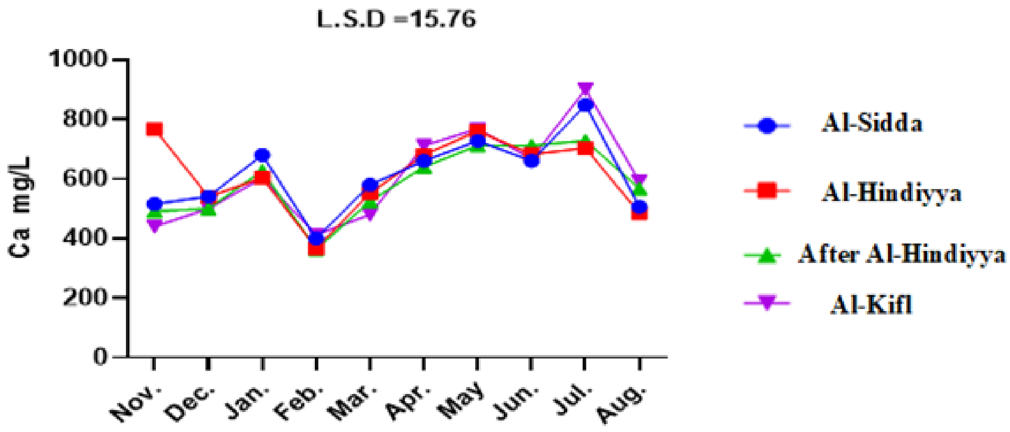

Figure 8. Monthly variations in calcium hardness values at the study stations.

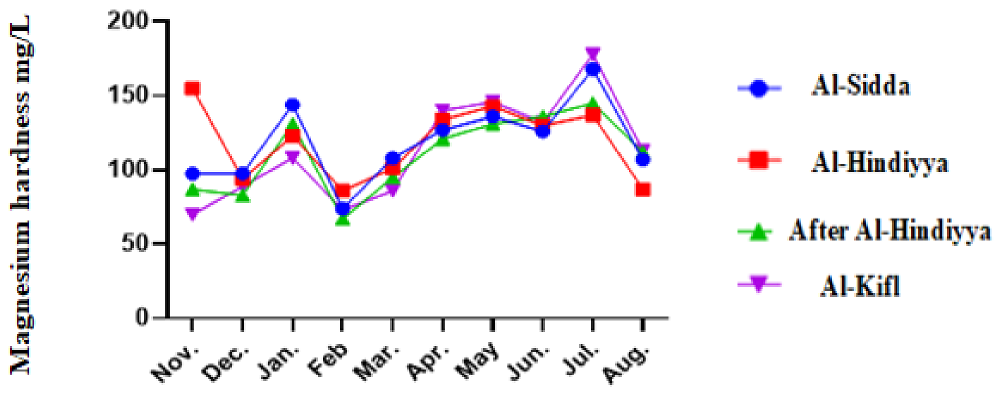

Figure 9. Monthly variations in magnesium hardness values at the study stations.

1.9 Chlorides

Figure (10) shows that there is a significant effect of the study stations and months (from January to August) on the concentration of chlorides, as station (4) recorded the highest concentration of chlorides at 344.0 mg/L during January, while the lowest concentration of chlorides was 181.0 mg/L at station (2) during November.

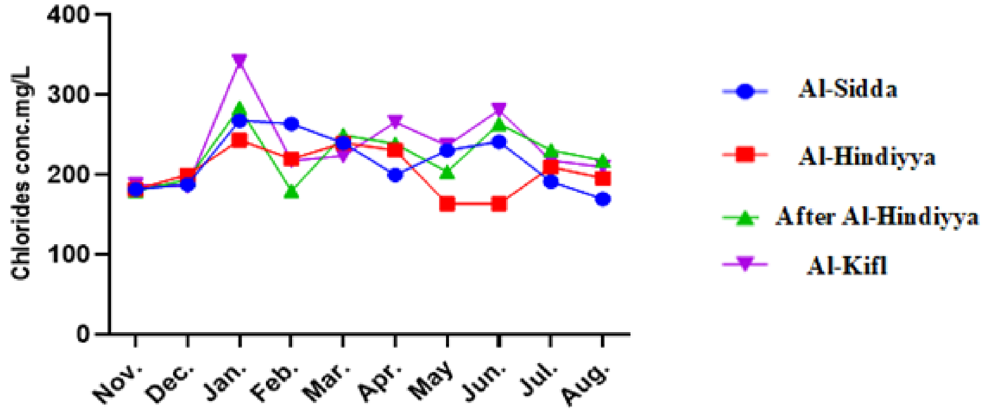

Figure 10. Monthly variations in chloride values at the study stations.

Heavy metals

Cadmium concentration

Table (1) shows that there are significant differences in the concentration of cadmium between the study sites. The highest concentration was (3.05 mg/kg) in station (1), followed by station (4), where it was (2.03 mg/kg), while the lowest concentration of cadmium was (1.49 mg/kg) recorded at station (3), which was not statistically different from its concentration at station (2).

In addition, the results of the statistical analysis showed that there were significant differences in the concentration of cadmium according to the months of the study, and the highest concentration was (4.19 mg/kg) that recorded in of July, while the lowest concentration was recorded in November (0.64 mg/kg); however, no significant differences were recorded between January and February.

Table (1) indicates that there is a significant effect of the type of plant on the concentration of cadmium, as the highest concentration was recorded in the C. demersum plant (2.06 mg/kg) compared to what was recorded in the P. australis plant.

Regarding the concentration of cadmium in P. australis plants, the statistical results showed that the highest concentration was in station (1) in the month of July, where it was 13.06 mg/kg compared to the rest of the months and stations.

As for the concentration of cadmium in the C. demersum plant, statistical results showed that the highest concentration of cadmium in the C. demersum plant was in December at station (1), where it was recorded at 12.34 mg/L; as explained in Table (1).

Table 1: The effect of stations, months and plants on the concentration of cadmium in mg/kg

Months	Plant	Stations			
		1	2	3	4
November	P. australis	0.42	0.34	0.85	0.58
	C. demersum	1.35	0.34	0.85	0.38
December	P. australis	0.61	0.37	1.47	0.34
	C. demersum	12.34	0.65	0.45	0.77

January	P. australis	1.59	1.00	0.36	0.34
	C. demersum	0.90	1.00	0.45	3.24
February	P. australis	0.41	1.21	0.34	4.01
	C. demersum	0.33	1.59	0.34	0.34
March	P. australis	3.13	2.14	1.57	2.43
	C. demersum	2.81	1.46	1.45	2.10
April	P. australis	0.34	1.78	1.21	2.96
	C. demersum	1.29	2.15	2.72	1.91
May	P. australis	0.79	0.92	2.99	4.97
	C. demersum	1.34	0.34	0.39	0.91
June	P. australis	1.86	2.19	3.04	2.66
	C. demersum	2.19	2.95	1.35	1.81
July	P. australis	13.06	2.51	0.45	3.78
	C. demersum	4.39	2.35	2.82	4.18
August	P. australis	1.04	2.40	6.07	0.47
	C. demersum	10.79	2.62	0.56	2.33
LSD at 0.05		1.46			
Effect of plant species		P. australis		C. demersum	
		1.98		2.06	
LSD at 0.05		0.23			

Hg concentration

Table (2) shows a significant effect of the study sites on the concentration of Hg metal, as the lowest concentration was recorded in station (4), which reached (0.17 mg/kg) when compared to stations (1, 2, and 3).

The same table also shows the effect of the months of study on the concentration of Hg metal, it significantly increase in May, while significantly decreased in August.

On the other hand, the results of the statistical analysis recorded non-significant differences in the concentration of Hg between P. australis (0.28 mg/kg) and C. demersum (0.30 mg/kg).

Regarding the concentration of Hg metal in P. australis plants, the statistical results showed that the highest concentration of Hg in this plant was in station (1) in the month of May, where it reached 0.52 mg/kg, while the lowest concentration in stations (3 and 4) in the month of February amounted to 0.00 mg/kg. Also, station (4) was recorded 0.00 mg/kg in the months of (March, April, July, and August).

As for the concentration of Hg in the C. demersum plant, the highest concentration of Hg was in station (1) during March, where it was recorded at 0.45 mg/kg, while the lowest concentration was in station (4) in the months of (November, February and July), respectively, and in station (1 and 2), in the month of August.

Table 2. The effect of stations, months and plants on the concentration of Hg in mg/kg

Months	Plant	Stations			
		1	2	3	4
November	P. australis	0.33	0.33	0.34	0.34
	C. demersum	0.34	0.34	0.34	0.00
December	P. australis	0.01	0.33	0.34	0.33
	C. demersum	0.33	0.38	0.34	0.33
January	P. australis	0.34	0.34	0.34	0.01
	C. demersum	0.34	0.34	0.34	0.34
February	P. australis	0.33	0.34	0.00	0.00
	C. demersum	0.34	0.34	0.34	0.00
March	P. australis	0.34	0.33	0.34	0.00
	C. demersum	0.45	0.33	0.34	0.33
April	P. australis	0.33	0.33	0.34	0.00
	C. demersum	0.45	0.35	0.34	0.33
May	P. australis	0.52	0.33	0.33	0.34
	C. demersum	0.39	0.36	0.34	0.34
June	P. australis	0.43	0.36	0.34	0.34
	C. demersum	0.33	0.34	0.34	0.34
July	P. australis	0.33	0.33	0.33	0.00
	C. demersum	0.33	0.33	0.33	0.00
August	P. australis	0.33	0.33	0.33	0.00
	C. demersum	0.00	0.34	0.34	0.00
LSD at 0.05		0.87			
Effect of plant species		P. australis		C. demersum	
		?		?	
LSD at 0.05		?			

Lead metal concentration

The results of Table (3) show lead metal significantly increase (7.56 mg/kg) at station (2), followed by station (1) (5.05 mg/kg), while significantly decrease at station (4); however, non-significant difference was recorded between lead concentrations between stations (1 and 3).

In context of season effect, the same table shows that the high rate of lead concentration was in August and March (12.14 and 10.67 mg/kg), respectively; while the lowest concentration (0.85 and 1.02 mg/kg) during the months of November and December, respectively.

As for the effect of the plants under study on lead concentration, there is a significant increase in the concentration of lead in the C. demersum plant (5.91 mg/L kg) over its concentration in the P. australis plant (4.11 mg/kg).

As for the concentration of lead in the P. australis plant, the statistical results showed that the highest concentration was in P. australis in station (1) in August, where it was recorded at 21.84 mg/kg; while its lowest concentration in this plant was at station (4) during August, it recorded (0.00) mg/kg).

As for the concentration of Pb in the C. demersum plant, the statistical results showed that the highest concentration was in station (2) during March (28.70 mg/kg), while the lowest value was in station (4) in June and April, respectively.

Table (3): The effect of stations, months and plants on the concentration of Pb in mg/kg

Months	Plant	Stations			
		1	2	3	4
November	P. australis	0.49	0.39	1.31	0.37
	C. demersum	1.18	1.97	0.41	0.69
December	P. australis	1.97	0.42	0.34	0.55
	C. demersum	0.02	0.36	2.36	2.17
January	P. australis	3.29	3.59	0.34	0.77
	C. demersum	0.53	3.76	4.47	0.37
February	P. australis	1.80	0.88	2.54	0.65
	C. demersum	4.79	7.90	4.92	6.58
March	P. australis	8.20	10.66	1.26	15.04
	C. demersum	19.39	28.70	0.79	1.37
April	P. australis	7.37	8.19	6.83	0.00
	C. demersum	1.79	1.33	2.81	0.00
May	P. australis	5.86	5.46	17.80	0.61
	C. demersum	0.69	12.30	0.60	0.97
June	P. australis	0.66	2.50	1.37	0.84
	C. demersum	12.19	19.12	13.67	0.00
July	P. australis	0.33	2.73	1.37	1.33
	C. demersum	0.36	4.10	13.67	9.57
August	P. australis	21.84	19.13	5.47	0.00
	C. demersum	8.32	17.77	17.77	6.86

LSD at 0.05	1.33	
Effect of plant species	P. australis	C. demersum
	4.11	5.92
LSD at 0.05	0.21	

Zinc concentration

According to the results of the statistical analysis displayed in Table (4), zinc showed a significant increase (22.82 mg/kg) at station (1) compared to the rest of the stations included in the study.

As for the effect of months, the results of the statistical analysis showed that there were significant differences in the concentration of zinc during the months of the study; the highest concentration was (33.25 mg/kg) in the month of March, while the lowest concentration was (9.71 mg/kg) in November.

The type of plant also had a significant effect on the concentration of zinc. The highest concentration was (29.79 mg/kg) in the C. demersum plant, while the lowest concentration was (9.65 mg/kg) in P. australis plant.

With regard to the concentration of zinc in P. australis plant, the statistical results showed that the highest concentration in the reed plant was at station (2) during March, where it reached (45.82 mg/kg), and the lowest concentration was in station (1) during February, where it reached (1.18 mg/kg).

As for the concentration of zinc in C. demersum plant, the statistical results showed that the highest concentration in C. demersum plant at station (3) was in July, reaching (58.52 mg/kg); while the lowest was also at station (3) in June, reaching (7.31 mg/kg).

Table 4. The effect of stations, months and plants on the concentration of zinc in mg/kg

Months	Plant	Stations			
		1	2	3	4
November	P. australis	2.84	4.02	3.09	4.84
	C. demersum	16.36	16.35	17.37	12.81
December	P. australis	6.26	1.98	1.52	4.27
	C. demersum	16.75	16.38	20.02	20.47
January	P. australis	6.43	5.10	5.15	5.31
	C. demersum	19.43	30.04	19.33	23.87
February	P. australis	1.18	4.61	5.54	2.66
	C. demersum	18.57	9.43	15.65	27.98
March	P. australis	28.77	45.82	22.71	15.64
	C. demersum	40.51	45.06	38.75	28.75
April	P. australis	19.44	6.80	18.59	12.23
	C. demersum	41.75	46.65	26.13	32.85

May	P. australis	7.33	7.09	4.07	3.54
	C. demersum	58.48	51.03	21.67	41.78
June	P. australis	7.75	4.78	5.73	16.41
	C. demersum	56.51	23.16	7.31	20.38
July	P. australis	18.42	21.79	10.82	8.18
	C. demersum	37.47	42.96	58.52	40.01
August	P. australis	9.09	12.15	7.52	6.63
	C. demersum	43.08	27.54	39.04	21.35
LSD at 0.05		1.63			
Effect of plant species		P. australis		C. demersum	
		9.65		29.79	
LSD at 0.05		0.26			

DISCUSSION

Lead accumulation in P. australis and C. demersum

Lead is a toxic metal even at low concentrations in plants, as it is considered toxic at a concentration of 30-300ppm. P. australis, which is widespread in freshwater environments such as the Euphrates River, is considered a means of treating toxins, as it had used in treating wastewater and removing unpleasant odors and purifying it in many European countries such as British and Denmark (Uka et al, 2012; Wikipedia, 2014,) due to its ability to absorb Heavy metals such as lead. In the current study, lead concentration increased in August and March, while it decreased to the lowest concentration during November and December, respectively. Also, the stations differed in the concentrations of lead; the highest concentration reached (7.56 mg/kg) at station (2), which was statistically different as compared with other study stations, followed by station 1 (5.05 mg/kg), while the lowest concentration was at station (4). The results in the same table showed that the highest percentage of lead concentration was in the C. demersum plant compared to the P. australis plant.

Heavy metals are more concentrated in the roots of P. australis than in the branches and leaves. A similar study was conducted on two sites in the Kharazi Valley in Iraq on the P. australis plant (Al-Sinjari, 2019).

In Iran, a study was conducted in Hamidan Province, which showed lead accumulation in reed plants of the same species (Cheraghi et al, 2011).

Phytoremediation technology is used to absorb and reduce heavy metals from the environment by storing them in plant tissues (Lajayer et al., 2019), and for aquatic plants such as P. australis and C. demersum has a superior ability to absorb pollutants and heavy elements such as lead and others at high levels, regardless of their concentrations in the aquatic environment (Anand et al., 2019).

The ability of aquatic plants to accumulate heavy elements depends on several environmental factors, including temperature, season, and pH, as well as the age, type, and adaptation of the plant to the aquatic environment. The differences in lead concentrations in aquatic plants are attributed to P. australis and C. demersum in the summer to the effect of household waste, industrial waste from power and oil stations, and agricultural waste from phosphate fertilizers that flow into the river and accumulate in varying proportions in P. australis and C. demersum (Mahmoud et al., 2018). In addition, differences in the genetic characteristics of plant species and environmental conditions contribute to the ability of the plant to accumulate heavy elements.

As for heavy metal concentrations during the study months, irrigation operations in the winter and continuous irrigation of river sides to remove P. australis and C. demersum during the study period, in addition to the lack of rain in the winter during the study, because the heavy rainfall and the flow of river water caused many dissolved salts, including heavy elements such as lead into the Euphrates River, thus accumulate on aquatic plants (Netshiongolwe et al., 2020).

Because P. australis is an emerging aquatic plant that contains parts of it in water and part of it in the air, unlike C. demersum, which is completely submerged in water, it also absorbs heavy metals through atmospheric sediments that contain pollutants and in turn they move to the part immersed in river water (Brezinova and Vymazal., 2015) . It has been proven that C. demersum is characterized by its ability to absorb higher levels of lead compared to P. australis in most months of the year. The results of the current study are consistent with a previous study that reached similar results (Al-Rubaie & Al-Kubaisi, 2015; Ahmed et al., 2018; Chandra et al., 2018).

The ability of C. demersum to tolerate high levels of lead compared to other aquatic plants, such as P. australis. It is explained on the basis that the walls of the C. demersum plant contain negatively charged ions that uptake positive lead metal ions from river water.

In general, the plant cell wall carries negative charges (anions) due to the carboxyl groups of pectic acid. As a result, these negative charges attract positive charges to them and prevent them from escaping again into the external environment; the negative charge on the cell wall is due to the hypothesis of the difference in electrical potential, as the concentration of hydrogen H^+ ions in the solution is less than their concentration on the cell wall, and in this case a difference in electrical potential occurs, making the cell wall negative and leading to the attraction of positive cations represented by heavy metals, as river water contains different concentrations of heavy metals, including lead (Polechońska & Klink, 2021); and the current outcomes is consistent with the study of Cameselle & Gouveia (2019).

Cadmium accumulation in P. australis and C. demersum

Cadmium is a toxic heavy metal that can enter the air, water, and soil and accumulate in plants through phosphate fertilizers and industrial wastes thrown into river water. Moreover, it does not decompose and remains for long periods in water, plants, and aquatic organisms (Yang et al., 2018). It is concentrated in the roots of aquatic plants at a high rate compared to rest of the plant through the root cortex, where it forms large stable molecular complexes or large insoluble organic molecules by binding with proteins, sugars and nucleic acids in the roots of aquatic plants such as reeds, especially wastewater, which is considered a pollutant. With the element cadmium and thus its accumulation in aquatic plants, this leads to high concentrations in plants.

The highest significant concentrations recorded in station (1) which is Al-Saddah town, and Station (4), which is Al-Kifl town could be attributed to waste from human activities, such as usage of fertilizers, sewage, in addition to industrial waste; also, the electricity generation are located near the Al-Saddah area. Moreover, in Al-Kifl area, which is characterized by density, the population is rural in nature, with waste from agricultural activities, fertilizers, and other various human activities, such as factory waste.

Cadmium metal is often found in natural waters in the active state as low-molecular inorganic complexes, where cadmium ions constitute more than 90% of the total cadmium concentrations in low-salinity freshwater, such as the Euphrates River, and therefore aquatic plants accumulate the highest percentage of cadmium metal (Moiseenko et al., 2020).

The significant increase of cadmium levels in summer season (July) compared with winter season (November) could be explained due to the large number of human activities and the ability of aquatic plants to absorb the element from the water. However, the decrease in its concentration in the winter is due to continuous irrigation operations, which reduce aquatic plants, especially P. australis. The results of the current study are consistent with a study conducted by(Hassan et al., 2007) on the Al-Gharraf River, which revealed that the decrease in the levels of heavy elements Zn, Cu, and Cd in the winter and their increase in the other seasons of the year, with the exception of the Ni, is due to throwing household sewage waste into the river directly without processing.

Table (1) also indicated that there was a significant effect of the type of plant on the concentration of cadmium, and the highest rate of cadmium concentration was recorded in the C. demersum plant, with a statistical difference from what was recorded in the P. australis plant. The C. demersum plant can be adopted as a vital indicator of water pollution with heavy metals such as cadmium and others, and this is consistent with what was found in the study conducted with Polechohska & Klink (2021).

The C. demersum plant is considered to have a high efficiency in accumulating heavy metals such as cadmium. This ability may be attributed to the conditions surrounding the plant, such as temperature of the river's water, pH, and nutrients, in addition to its high availability compared to P. australis in the water, the duration of accumulation of heavy metals, and the age of the plant, as it is present throughout the seasons of the year in abundance, in addition to variation in the physiological along with genetics characteristics of plant (Farooqi et al., 2021). The current study also coincided with a study conducted by Bello and his colleagues that examined the ability of the P. australis plant to absorb heavy metals, including cadmium, lead, and nickel, as the study revealed accumulation in varying proportions, which indicates its ability for phytoremediation (Bello et al., 2018).

Hg accumulation in *P. australis* and *C. demersum*

He is considered one of the most toxic metals, with extremely harmful impacts on biological activity and plant metabolism, even at low concentrations. Once deposited in the environment, it is retained primarily by organic matter and iron and manganese oxides. Mining regions are the most polluted with Hg, as well as region near river sides, as a result of natural pollutants and human activities, and their accumulation in aquatic plants leads to serious environmental risks (Alengebawy et al., 2021).

The increased concentration of Hg in 1, 2, and 3 stations is due to the large number of human activities and dumping of waste in the Al-Saddah area, as well as in station (3). As this site is exposed to sewage, wastewater, and waste being thrown directly into the river, which in turn accumulates in aquatic plants (Chalkidis et al., 2020) (60). These plants are considered a means of phytoremediation to reduce the toxicity of heavy metals, including mercury, which is considered a highly toxic environmental pollutant, especially organic mercury (Aljerf et al., 2018). The body of the aquatic plant is almost entirely exposed to polluted water through the absorption of mineral ions of heavy metals directly by the leaves and the deposition of particles on the surfaces of the leaves in the floating part of the P. australis plant, as well as through the roots. In general, C. demersum is characterized by a high ability to absorb mercury, which was proven by the current study and previous international and Arab studies (Kumar., 2017).

Hg in the aquatic environment is affected by biological factors, including the activity of microorganisms, especially bacteria, during the methylation process, and abiotic physicochemical factors such as time, temperature, dissolved oxygen in the water, and pH (Price et al., 2012, Mansour et al., 2012).

The increase in Hg levels in summer is mainly due to the increase in biological processes and activities, which leads to an increase in the organic content in the water. Researchers have confirmed that there is a strong correlation between mercury concentrations and the content of organic suspensions, and thus the accumulation of mercury in the bodies of aquatic organisms, including aquatic plants such as P. australis and C. demersum (Veado et al.,2000; Liq et al.,2020). Likewise, the current study showed that as the temperature increased, a decrease in the concentration of Hg was showed in relation to the effect of the months. This proves the existence of a negative relationship between high temperatures and the concentration of Hg in aquatic plants, as it affects the metabolic actions of aquatic plants, because it interferes between Bio-membranes and heavy elements, including Hg (Addy et al., 2004), while it decreased in the winter due to the increase in the pH value for all study stations in the winter season, as there is a close relationship between the pH value and the concentration of Hg in river water and thus its accumulation in aquatic plants.

Accumulation of zinc in *P. australis* and *C. demersum* plants

Zinc is the most common heavy metal in the environment and can be found in dissolved form and sediment in rivers, and excessive accumulation affects the structure of aquatic plants. The results of the current study were supported by what was stated in the study of (Al-Kubaisi, 2017), which indicated the accumulation of high concentrations of zinc in the C. demersum plant.

The high concentration of zinc in the summer is due to its high concentrations in river water and aquatic organisms, including plants, due to the increase in agricultural activities, industrial waste, wastewater, population density on the sides of the river (Behroozi et al., 2021), and the ability of P. australis and C. demersum plants to absorb nutrients and heavy metals such as zinc. As for the decrease in concentrations in the winter, it is due to the high pH values in the winter, as the higher the pH value, the lower the concentration of zinc in the plant, as well as the age of the plant. As the age of the plant increases, the concentration of zinc in the plant decreases, and also the newly grown parts contain a greater concentration of zinc, (the part taken from the study sample), as well as the interaction between minerals and Nutrient interactions. Also, the concentration of zinc is usually decreases with an increase in phosphorus, iron, and manganese in aquatic plant tissues along with the residues of nitrogen fertilizers that are thrown into rivers (Desaulty et al., 2020).

CONCLUSIONS

1. In the current study, the aquatic plants of reeds and shamrock showed accumulation of dissolved heavy elements, namely zinc, mercury, cadmium, and lead, and showed variations in the level of their accumulation in the aquatic plants. This shows their high effectiveness in the phytotreatment of the Euphrates River water and purification of pollutants.

2. Water pollution results from throwing pollutants directly into the river. Consequently, some study stations witnessed variation in the concentrations of heavy metals in reed and shamrock plants due to the ability of these aquatic plants to absorb heavy elements.

3. Iraqi water is an important source of aquatic plants that have the ability to absorb, accumulate heavy metals and purify river water from pollutants.

Recommendations

1. Study the relationship between exposure of river water to various pollutants such as organic materials, trace elements, and algae diversity in different media.

2. The necessity of providing continuous monitoring of the water of the Euphrates River through the establishment of stations to monitor the river's water to determine the quality of the water and the extent to which it is affected by environmental factors.

3. Measuring heavy metals in aquatic organisms and aquatic plants in the water of the Euphrates River and measuring their toxicity.

4. Conduct continuous checks on the level of concentrations of heavy metals in the water of the Euphrates River and the wastes thrown into it from human and industrial activities without

treatment, as well as the wastes of organic fertilizers that release organic and phosphate materials into the river water.

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