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ORIGINAL ARTICLE

Assessment of Pollution by Heavy Metals in the Water and Sediment of Al-Khosur River Bed

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ABSTRACT
The study was conducted on Al-Khosur River basin passing through the city of Mosul from the waterfalls region to its confluence with Tigris River at the Old Bridge. Six sites were selected along the river. Water and sediment samples were collected from there. The study was carried out at the laboratories of Mosul University, through the period from September 2021 A.D. to May 2022 A.D. The concentrations of heavy metals (lead, cadmium and zinc), in water and sediment were measured quarterly. The results indicated that the heavy metals in the water had the highest concentrations in the fourth site in three elements Pb, Cd and Zn, which amounted to (0.64, 0.62 and 0.49) mg/L, respectively. This can be attributed to the bad quality of the civilian subtractions and estuaries discharged in the river which contain high concentration of heavy metals. The results also indicated high rates of heavy metals in the sediments at the fourth site as it reached the concentration of (3.18, 0.92 and 2.85) mg/kg, for Pb, Cd and Zn, respectively. The concentrations of heavy metals in the sediments increased four times for lead and zinc and two times for cadmium due to the increment in water and the contact period between water and sediment due to undecomposition for heavy metals.
Keywords: Heavy metals, Al-Kosur River, Mosul environment, Water, Sediment.

INTRODUCTION
Al-Khosur River is considered as one of the peculiarities of Mosul city the center of Nineveh Governorate North of Iraq and its water identity. It is a seasonal river due to the lack of discharge water in it [(1)] . Al-Khosur River originates from the outskirts of Nineveh Governorate at Jabal Maqlub, the heights of the Komel River, Wadi Al-Maleh, Bashiqa and Al-Shekhan, then flows into the middle of the city of Mosul in the Tigris River on the left bank [(2)] . Al-Khosur River depends on run off from rain water and numbers of small springs, so it is seasonal rivers, which is characterized by abundant water in the winter and dryness in the summer, despite the fact that the area of the Al-Khosur River basin is about (1000) km^2 [(3)] . Topography of region attected on the river is characterized by its steep slope in the upper part, which gradually decreases as the river heads south until it reaches the lowest steepness at its mouth .

Al-Khosur River is one of the most important ancient tributaries of the Tigris River, and traces of its valley are still visible in the archaeological city of Nineveh to the present time [(4)] . Al-Khosur River was previously limited in drainage, and then its drainage increased after the implementation of irrigation projects constructed by the Assyrian kings, especially King Sennacherib (700 BC). The river became permanently flowing. Through the time, the river became seasonal due to the discharge of water that reaches it, as well as the valley of many springs such as Al-Nawaran springs.

The great expansion in the city of Mosul, especially on the left side, which led to the burial of some valleys in the region, transforming them into channels for the waste water, in addition to the dumping of many areas adjacent to the Al-Khosur River and their domestic waste disposal directly to the river, which made the running water in the river as waste water (except for the rainy season) they are subtractions for different activities (sewage, agricultural, service, solid and semi-solid waste...etc.) [(5)] .

The impurities in the Al-Khosur River appears clearly during summer due to the interruption of rain in which it cause the lack of discharge, on the other hand the continuity of wastes within and outside the city led to the transformation the river into a channel for wastewater, including sewage water. Also, the rise in temperatures during the summer it accompanied by the emission of fouls odors and appearance of many insects. At the end portable contaminants with Al-Khosur River discharged in the Tigris River, transferring to it the concentrations of pollutants and large amounts of sediment [(3)] . In the winter and during heavy rain periods, the solid waste scattered in the streets densely reaches Al-Khosur River and ends up in the Tigris River [(5)] .

Heavy metals are those that have a density greater than 6 g/cm^3 and that become toxic even at very low concentrations, as these pollutants are considered one of the most dangerous environmental pollutants [(6)] . Heavy metals are found in nature in very low concentrations and enter the aquatic environment through two main sources. The first of them is a natural source resulting from the natural concentration of these elements in the earth's crust, which by means of weathering and erosion processes, as well as other natural activities such as volcanoes, leads to the transfer of these elements to water [(7)] . Despite the low concentration of heavy metats, they are considered very dangerous, and they are characterized by their ability to survive in living environments and accumulated in living bodies, as well as its accumulated in the bodies and not analyzed, as its concentration increases through the food chain through its intrusion into the food chain [(8)] therefore, it is very dangerous.

The current study aims to measure the concentrations of some heavy metals in the water and its reflection on the presence of these elements in the sediments of Al-Khosur River Basin.

MATERIALS AND METHODS
Six sites were identified along the river basin (the waterfalls region, Al-Sukkar bridge, Al-Qadisiyah bridge, The Old bridge of Al-Muthanna, Al-Sueis bridge and the last location was at stone bridge, which is near from Mosul old bridge). Water samples were collected with 3 replicates for each site. As for the sediment samples, they were collected by removing the surface layer of sediments for 10 cm depth and collecting a composite sample from the sediment [(9)] .

Figure 1: Aerial map of the city of Mosul and the sampling sites on the Khosur River

The collecting the samples were carried out during the four seasons, from October 2021 until May 2022. After the collecting the samples, they were placed in nylon bags and in the laboratories of environment of researches center drying airly and to ensure complete drying, they were placed in the oven to measure the concentrations of heavy elements (lead, cadmium and zinc) on them.

Determination of heavy metals concentrations in water: Water can carried heavy metals within it. Heavy metals was measured after taking a certain weight from the sample and adding an appropriate amount of hydrochloric acid (HCl) to make water content acidic and decrease the pH value to about 2, which is the value at which heavy elements turn into soluble materials. Then it tested using the Atomic Absorption Spectrophotometer in the laboratories of the University of Mosul in the College of Agriculture. To obtain the concentration of elements in mg/l standard solution on standard cures must be used [10-15] .

Determination of heavy metals concentrations in sediment: Sediment of rivers is affecting by its water and impact on it. Heavy metals in sediment was measured by taking a certain dried weight passing through a sieve No. 2 whose openings are 2 mm in diameter, 2 ml of distilled water was added, to the sediment sample. Then 6 ml of hydrochloric acid and 2 ml of nitric acid were slowly added. The condenser is placed on the glass beaker and left for 16 hours at room temperature. To complete the dissolving, samples were put. On a Hot Plate at a temperature of 60°C for two hours. Preventing the toxicity and dangerous of emissions of gases, samples must be put on a hood to avoid the emission [9] . After the samples were cooled and filtered, the volume is completed to 50 ml and placed in plastic containers. Atomic absorption device were the utilized for readings, then projected onto the standard curve for each element and finding the concentrations of the elements in the unit mg/kg dry soil.

The statistical analysis: Data were analyzed according to the working experiment system and Complete Randomized Design. The means were compared using Duncan multiple-Domain Test. The various treatments which are significantly different were distinguished various letters at the likelihood level of 5% [16] .

RESULTS AND DISCUSSION

Heavy metals in Water: Lead (Pb): The results showed that the values of lead in water ranged from (0.07 to 0.64) mg/l, as it was noted in Table (1). The lowest concentration was founding in the summer in the first site, as the region is far from pollution sources, when the highest concentration occurred in autumn season in the fourth site as a result of the huge amount of pollutants that are thrown into the river in addition to the proximity of the site to the public street, where many lead compounds are produced from car exhaust [17] . These values are higher than the Iraqi standards of conservation of rivers and water from pollution No. 25 of 1967, which specified that the values of lead in rivers should not exceed 0.1 mg/L [18] . Comparison between the sites, the average readings of the first site were the lowest (0.17) mg/L, while the highest values of the average readings of the different seasons were in the fourth site, at (0.47) mg/L. Statistical analysis at the probability level of 5% showed that there are significant differences between sites and seasons because they are affecting by human activities which reflecting on the concentrations of lead released or reaching the river. These results were diverged than what was recorded by(Al-Shamaa and Al-Nuaimi, 2019), as the concentrations of lead in the waters of the Al-Khosur River during the autumn season ranged between (0.75-0.95) mg/l. While [19] stated that the concentration of lead element in the Al-Khosur River was 0.134 mg/l. The different concentrations of lead in different locations and times means that its presence is affected by the sources of pollution and their differences in terms of concentrations and quantities.

Table 1: Concentration of lead (mg/l) in water samples of Al-Khosur River.

Sites Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Autumn	0.11 n	0.52 d	0.56c	0.64 a	0.58 b	0.54 c	0.49 a
Winter	0.30 k	0.39 h	0.44f	0.48 e	0.44 f	0.41 g	0.41 b
Spring	0.18m	0.30 k	0.36i	0.39gh	0.38h	0.32 j	0.32 c
Summer	0.07o	0.25 l	0.31 jk	0.36 i	0.30 k	0.26 l	0.26 d
Mean	0.17 e	0.36 d	0.42 b	0.47 a	0.43 b	0.38 c	

Transactions that have taken the character themselves are not significantly different at the level of 5%.

Cadmium (Cd): The results of the study indicated that the concentrations of cadmium were ranged between (0.12-0.62) mg/l, where it was noted that the lowest value of cadmium appeared during the summer in the first site, while the highest value was recorded during the autumn in the fourth site Table (2) explain the values of cadmium through different sites and seasons. The reason may be attributed to the presence of effluent estuaries and to the high traffic density which has become clearly visible in recent times, where the increased friction of tires with the ground leads to an increase in cadmium [17] . These values are higher than the Iraqi standards for the conservation of rivers and water from pollution No. 25 of 1967, which specified that the concentration of cadmium in rivers should not be more than 0.1 mg/L [18] . It is noted through the statistical analysis at the probability level of 5% that there are significant differences between locations and seasons. The variations in cadmium concentrations were recorded by [20] that the concentration of cadmium in the estuary waters of the Al-Khosur River was (44) µg/L. While [21] indicated that the concentration of cadmium in Garraf River water was (0.0091) µg/l.

Table 2: Concentration of cadmium (mg/l) in water samples of Al-Khosur River.

Sites Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Autumn	0.20 n	0.50 de	0.58b	0.62 a	0.58 b	0.51 d	0.50 a
Winter	0.24 m	0.44 g	0.50de	0.59 b	0.53c	0.46 f	0.46 b
Spring	0.20 n	0.34 k	0.41 h	0.49e	0.45 f	0.40 hi	0.38 c
Summer	0.12 o	0.30 i	0.38 ij	0.42 g	0.40 hi	0.38 j	0.33 d
Mean	0.19 f	0.39 e	0.47 c	0.53 a	0.49 b	0.44 d	

Transactions that have taken the character themselves are not significantly different at the level of 5%.

Zinc (Zn): The results of the study showed that the concentrations of zinc element ranged between (0.08-0.49) mg/l as shown in table (3), where the lowest value was recorded in the summer in the first site, due to the absence of estuaries that increase the concentrations of heavy metals in water. While the highest value was recorded during winter in the fourth site, this is due to the presence of estuaries and the waste water of agricultural, industrial and domestic areas were washed away by rain water during estuaries that flow into Al-Khosur catchment area then reached river bed [20] . Al-Khosur River is unpolluted with zinc and within the Limited value of the determinants of river conservation. The highest concentration of zinc was 0.5 mg/L [18] . The statistical

analysis at the 5% probability level shows the significant differences in the concentration of zinc between locations and seasons [22] mentioned that the concentration of zinc in the waters of the Benue River was 3.628 mg/l, which is within (WHO) Limitation. It [20] founded that the highest concentration of zinc in the waters of Tigris River was 2.528 mg/L.

Table 3: Concentration of zinc in (mg/l) in water samples of Al-Khosur River.

Sites Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Autumn	0.20 n	0.50 de	0.58b	0.62 a	0.58 b	0.51 d	0.50 a
Winter	0.24 m	0.44 g	0.50de	0.59 b	0.53c	0.46 f	0.46 b
Spring	0.20 n	0.34 k	0.41 h	0.49e	0.45 f	0.40 hi	0.38 c
Summer	0.12 o	0.30 i	0.38 ij	0.42 g	0.40 hi	0.38 j	0.33 d
Mean	0.19 f	0.39 e	0.47 c	0.53 a	0.49 b	0.44 d	

Transactions that have taken the character themselves are not significantly different at the level of 5%.

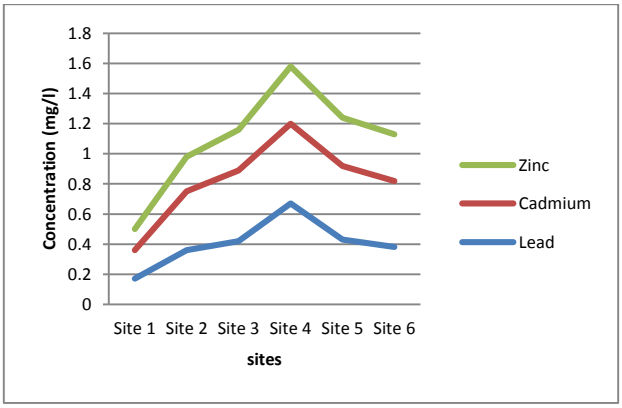

Figure 2: Annual average concentrations of heavy metals in water

Figure (2) shows that the concentrations of heavy metals in the waters of Al-Khosur River were directly affected by human activity and the sources of pollutants thrown into the river, making the fourth site near the old Al-Muthanna Bridge one of the most polluted sites. While it decreases slightly in the fifth and sixth sites due to the presence of aquatic plants near their, which slightly the effect by absorption of pollutants in the fifth and sixth sites.

Heavy metals in Sediments: Lead (Pb): The results analytical showed that the concentration of lead in the sediments varied between (1.04-3.18) mg/kg. Where the lowest value was recorded in the summer in the first site, while the highest value was observed in the autumn in the fourth site, and this may be attributed to the large amount of pollutants that were thrown into the River by civil and industrial outfalls. This conducted to an increase in this element and accumulation in the soil. The presence of high concentrations of heavy metals in the sediments is due to their presence in the river water in high concentrations, which causes these elements to be deposited in the sediments, as the heavy metals are less soluble in water. The statistical analysis showed that there were significant differences in the results of the statistical analysis of the concentration of lead element in the sediments during the study seasons and locations. These results are agreement with the results of [20] , which was mentioned that the concentrations of heavy metals in sediments are higher than their concentrations in water. The results were similar to those of [22] , where it was reported that the highest concentration of lead in the sediments of the Garraf River was 3.2 mg/kg, while [23] reported that the average concentration of lead in the sediments of Lake Burullus was 13 mg/kg.

Table 4: Concentration of lead in (mg/kg) in sediment samples of Al-Khosur River.

Sites Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Autumn	1.21j	2.26 ef	2.80b	3.18 a	2.82b	2.76bc	2.51 a
Winter	1.16j	2.15 g	2.74 bc	2.81 b	2.80b	2.70 c	2.40 b
Spring	1.09 k	2.12g	2.46 d	2.48d	2.42d	2.32 e	2.15 c
Summer	1.04 k	1.74i	2.04h	2.24 f	2.14g	2.01h	1.87 d
Mean	1.12 e	2.07 d	2.51 b	2.68 a	2.55 b	2.45 c	

Transactions that have taken the character themselves are not significantly different at the level of 5%.

Cadmium: The studied results indicated that the concentration of cadmium ranged between (0.37-0.92) mg/kg as shown in Table (5), where the lowest value was found during the summer season in the first location, while the highest value was observed during the autumn season in the fourth location. This is due to the increase in the amount of this element in the water, as increasing its concentration in the water leads to an increase in the sediment [24] . The statistical analysis showed significant differences in the concentration of cadmium between locations and seasons. (Al-Sarraj et al., 2019) documented that the concentrations of cadmium in the sediments of the Tigris River ranged between (0.100-0.242) µg/g of dry weight. As for (Ali et al., 2020), he indicated that the concentration of cadmium in the sediments of the Garraf River in the summer was 0.022 mg/kg of soil. (Eid et al., 2020) also mentioned that the average concentration of cadmium in the sediments of Lake Burullus in Egypt was 0.19 mg/kg. These results means that the concentrations of heavy metals in water and sediment are differ from on site to another.

Table 5: Concentration of cadmium in(mg/kg) in sediment samples of Al-Khosur River

Sites Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Autumn	0.50 jk	0.68 e	0.78 bc	0.92 a	0.80b	0.77 c	0.74 a
Winter	0.44 m	0.54 i	0.62 g	0.81 b	0.68e	0.65 fg	0.62 b
Spring	0.40 n	0.47 lm	0.58h	0.73 d	0.67ef	0.64g	0.58 c
Summer	0.37 o	0.47 lm	0.49 1kl	0.63 g	0.56 hi	0.52 j	0.50 d
Mean	0.43 f	0.54 e	0.62 d	0.77 a	0.68 b	0.64 c	

Transactions that have taken the character themselves are not significantly different at the level of 5%.

Zinc (Zn): The results of the study showed that the concentrations of zinc in the sediments of Al-Khosur River varied between (0.55-2.85) mg/kg, where the lowest value was recorded during the autumn season in the first site and the highest value recorded during the same season but in the fourth site as shown in Table (6). The high concentrations of heavy metals are attributed to the various wastes (domestic, industrial, and agricultural) that are dumped into the river through estuaries [24] . The results of the

statistical analysis showed that there were significant differences in the concentration of zinc in the sites and seasons during the study period [25]. indicated an increase in zinc in the sediments of Al-Diwaniyah River during the autumn season, and this was attributed to several reasons, including dust storms and polluted rainwater, which carries with it high concentrations of these pollutants. The result of the study agrees with the findings by [20] , which she concluded that the remnants of aquatic organisms as well as the wastewater lead to an increase in the concentrations of heavy metals through their sedimentation and collection at the bottom of the river.

Table 6: Concentration of zinc element (mg/kg) in sediment samples of Al-Khosur River.

Sites Season	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Autumn	0.55 q	2.18g	2.47d	2.85 a	2.57 b	2.53 c	2.19 a
Winter	1.15 n	1.98 j	2.21g	2.44 d	2.38 e	2.31 f	2.08 b
Spring	1.05o	1.88 l	2.03 i	2.07 hi	2.10 h	2.08hi	1.87 c
Summer	1.01p	1.75 m	1.92 k	2.07 hi	2.07 hi	2.04 i	1.81 d
Mean	0.94 f	1.95 e	2.16 d	2.36 a	2.28 b	2.24 c	

Transactions that have taken the character themselves are not significantly different at the level of 5%.

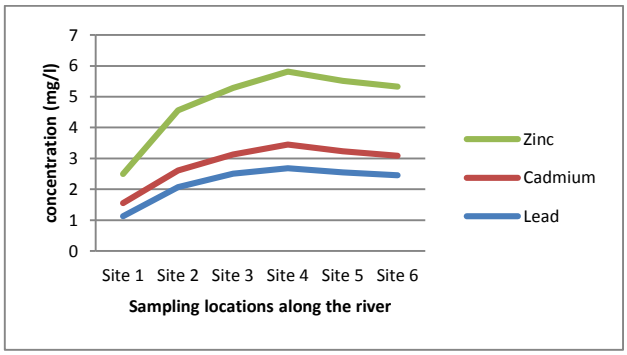

Figure 3: Variation of the average annual values of the elements Pb, Cd, and Zn in the sediment models taken from different sites.

Figures 2 and 3 show that the concentrations of heavy metals in the sediments of Al-Khosur River double their concentrations in the water samples because they accumulate in the sediments continuously.

CONCLUSION

1. The concentrations of heavy metals, lead and cadmium, were higher than the Iraqi determinants of river water, while zinc was among the determinants.
2. The rate of heavy metal concentrations in the sediments increased at the fourth site, as the concentrations of Pb, Cd and Zn reached (3.18, 0.92, 2.85) mg/kg, respectively, as the concentrations of heavy metals in the sediments increase as the concentration in the water increases.
3. The concentrations of heavy metals in the sediments were higher than their counterparts in the water for the same sites due to the accumulative deposition of the elements in the sediment samples comparing with un soluable in the water.

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