ORIGINAL ARTICLE



Levels and sources of heavy metals pollution in the water and sediments of Al-Diwaniyah River, Iraq

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Abstract

This study aims to examine the levels of heavy metals in Al-Diwaniyah River to investigate pollution levels and identify their possible sources. Eight heavy metals (i.e., Mn, Ni, Pb, Zn, Cr, Cu, As, and Cd) were measured on the surface water and river bed sediments of three stations in 2020–2021. Results showed low concentrations and uniform distribution of the majority of heavy metals (except Pb) in the river water. Despite the high levels of heavy metals in the sediments, they were within permissible levels, except for Ni, Pb, and As. On the surface water and bed sediments, Pb mainly came from a textile factory, traffic pollution, and agricultural drainage water. Mn, Ni, and As in sediments may have been derived from a combination of sources, such as atmospheric deposition, resulting from fossil fuel combustion, and waste water influx from agricultural, industrial, and residential activities. However, the sources of Zn, Cu, Cr, and Cd were unclear owing to the drastic decrease in their concentrations, whether in the water or sediments. Physicochemical parameters played important roles in the concentration and accumulation of heavy metals in the river's water and sediments.

Keywords Al-Diwaniyah river · Physicochemical parameter · Heavy metals · Wastewater · Surface water · Bed sediments

Introduction

Concerns about heavy metal contamination are prevalent worldwide owing to their adverse risks to humans, animals, plants, and the entire ecosystem (Khan and Ghouri 2011; Das et al. 2014; Wu et al. 2014). Heavy metals are among the most common environmental pollutants because of their toxicity, persistence, and non-degradability in the environment (Raulinaitis et al. 2012; Majhi and Biswal 2016). Given such concerns, numerous studies have focused on water scarcity and the deterioration of congenial water quality (Al-Asadi 2016; Odukoya et al. 2017; Al-Asadi et al. 2019; Al-Asadi et al. 2020; Shafiuddin Ahmed et al. 2021). The majority of heavy metals in the aquatic environment of rivers are solid and remain insoluble for a long time (Kabata-Pendias and Pendias 2001; Guo and He 2013; Algul and Beyhan 2020). Therefore, these metals tend to deposit on the

river bed, where sediments have the ability to absorb metals into their particles (Edokpayi et al. 2016; Al-Asadi et al. 2019). Sediment quality has been identified as an important indicator or geo-marker of water pollution (Meng Chuan and Yunus 2019). In particular, concentrations of heavy metals in water are occasionally below the detected limits (Jain et al. 2004; Salati and Moore 2010). However, these metals are not permanently bound to the particles of benthic sediments because they are redistributed into the sediments and water column owing to changes in environmental conditions (Li et al. 2000; Aradpour et al. 2020). The release of heavy metals from contaminated bed sediments can act as secondary non-point sources of these metals to the water column, and can cause significant damage to the aquatic system (Thevenon et al. 2011; Varol et al. 2012; Niu et al. 2015).

Heavy metals mainly enter the aquatic environment of rivers as a result of several sources, including natural and anthropogenic. The main natural sources of metals in rivers are chemical weathering of rocks, soil leaching, and atmospheric depositions. However, metals with the highest concentrations were from anthropogenic sources, such as untreated industrial effluents, agricultural chemical wastes, and domestic sewage (He et al. 2005; Singh et al. 2011; Tylmann et al. 2011; Tchounwou et al. 2012). Accordingly,

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understanding the distribution of metals and sources of pollutants in the aquatic environment of rivers is important for pollution control.

Given the dominant dry desert climate, Al-Diwaniyah River is the most important source of freshwater of Al-Qadisiyah province and has been used for various purposes, including domestic water supply, irrigation, and industrial uses. Apart from the river water, there is an influx of untreated wastewater as a result of various human activities. Hence, pollution levels in the river water and its sediments should be monitored and assessed to manage the contaminant input into the river course. Doing so will contribute in minimizing harmful concentrations and preventing them from reaching toxic levels. Only a few studies have investigated heavy metals in Al- Diwaniyah River, such as Alkam et al. (2014) and Kadhum et al. (2020), which provided appropriate understanding of the spatial variation of metal levels in the surface sediment of the river. However, some important metals have not been examined. Therefore, the available data on heavy metals in the river are extremely limited, and the examination of water quality can constitute a challenge. To fill in this research gap, concentrations of heavy metals in the River environment must be measured to reveal their different sources. Therefore, the elements Manganese (Mn), Nickel (Ni), Lead (Pb), Zinc (Zn), Chromium (Cr), Copper (Cu), Arsenic (As), and Cadmium (Cd) were measured; heavy metals spatial variation levels in the River was analayzed; and the factors affecting their variation were evaluated.

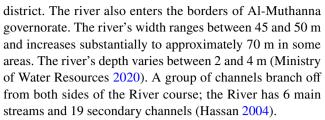
Limits in water and sediment quality based on international guidelines were used to evaluate the possible toxicity of the River. Pearson correlation analysis was also performed to uncover pollution sources in the bed sediments of the River.

The main goals of this study are as follows: (1) determine the spatial and temporal variations of eight heavy metals in Al-Diwaniyah River, (2) investigate the possible sources of heavy metals, and (3) assess the River water and bed sediment pollution with heavy metals and its suitability for different purposes.

Materials and methods

Site description

Al-Diwaniyah River is located in central Iraq within the borders of the Al- Qadisiyah governorate, between 31° 30′–32° 14′ N and 44° 42′–45° 16′ E (Fig. 1). The River is approximately 121 km long within the Al- Qadisiyah governorate, and passes through four main administrative units: Al-Saniyah sub-district, central Al- Qadisiyah governorate (Al-Diwaniyah), Al-Sader sub-district, and Al-Hamza



Al-Diwaniyah River's water feeding depends primarily on rain fall and snow melting in the headwaters of the Euphrates River in Turkey and Syria, representing 98% of running water in the Euphrates River. Iraq's contribution decreases to approximately 2% of the total water flow in the River (Al-Asadi 2017). River water discharge rate is approximately 50 m³/s in 2010–2020 (Ministry of Water Resources 2020). The river course area is located within a desert climate region, which is characterized by high temperature and drought during summer and moderate heat and rainfall during winter.

Al-Diwaniyah River is the main source of fresh water for the 696,701 population of the Al-Qadisiyah governorate, representing 51.24% of the governorate's total population of 1,359,642 (Ministry of Planning 2020). However, central Al-Diwaniyah is the largest beneficiary of water, and the people depend on the river completely for all their daily uses because there is no other water source in the study area. The river water is also used for agricultural purposes because it spreads along the River. Extensive agricultural land is estimated at 33,859 ha (Ministry of Agriculture 2020).

The study area includes some factories, such as textile, rubber and dairy, as well as an electric power plant. All domestic, agricultural, and industrial wastes are disposed directly into the River without treatment.

Sample collection and analysis

Water samples were collected from three important stations with different conditions (Table 1; Fig. 1). Station No. 1 was considered the control because of its relative clean water. Station No. 2 is located in the center of Al-Diwaniyah governorate, which represents population density, where domestic sewage influx is a possible source of pollution. The impact of agricultural activities is considerably prevalent in Station No. 3.

Water samplings were carried out during the summer (August) and fall (November) in 2020 and winter (February) and spring (May) in 2021. Water samples were collected from the three selected sites from the middle course of the River at about 10–15 cm below the water surface by the hand. Similarly, Sediment samples from the same sites were also collected using a Van Veen Grab. Three wastewater samples were collected from an electric station, domestic sewers, and agricultural drainage, which discharged into the River. Physicochemical properties, such as total dissolved solids (TDS), pH, and water temperature, were measured



Fig. 1 Map of Al-Diwaniyah River and the sampling stations

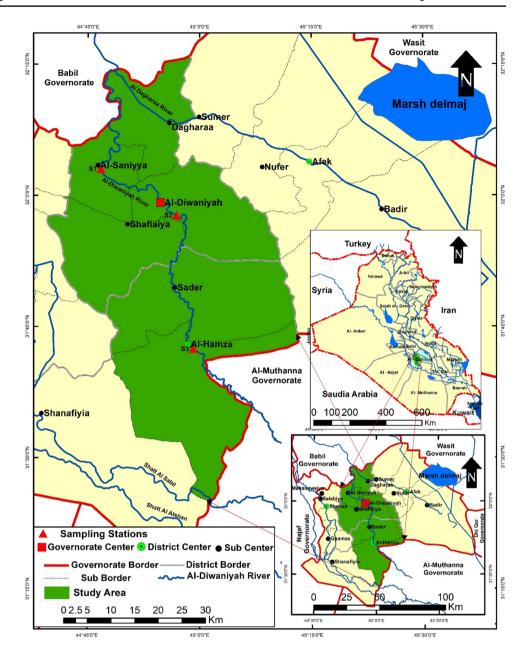


Table 1 Geographic locations of sampling stations in the Al-Diwaniyah River

| Sampling stations | Stations name | Longitude | Latitude |
|-------------------|---------------|-------------|-------------|
| No. 1 (S 1) | Al-Saniyya | 44° 46′ 31″ | 32° 03′ 16′ |
| No. 2 (S 2) | Al-Diwaniyah | 44° 56′ 53″ | 31° 57′ 39″ |
| No. 3 (S 3) | Al-Hamza | 44° 59′ 10″ | 31° 42′ 33′ |

in the field using a Horiba U-10 device (APHA 2017). In particular, 1-L surface water samples were collected (using clean bottles) for each season at the measuring stations and acidifed with nitric acid (0.5%). Moreover, 1 kg of bed-sediment samples were placed in plastic bags. All samples were

stored at 10–15 °C and sent thereafter to the US Science Lab for analysis using an atomic absorption spectrophotometer (Model AA-7000, SHIMADZU, Japan) to determine heavy metals levels.

Results and discussion

Factors affecting heavy metals concentrations

Physical and chemical properties of water and sediments

The physicochemical properties of river waters should be studied to detect heavy metal levels and their spatial and



temporal variations. Because of the effect of these parameters in leading the behavior of the aquatic environment on activating the processes of dissolving and transporting heavy metals in the running water or activating the processes of deposition of that metal at the river bed (Ferati et al. 2015). Thus, the physicochemical properties of the water and sediments of Al-Diwaniyah River can determine the extent of pollution in the River.

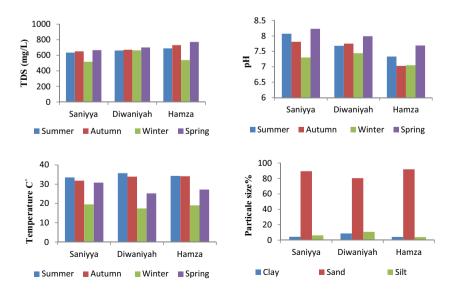
Table 2 and Fig. 2 show the physical and chemical parameters of the Al-Diwaniyah River water samples. The river's water temperatures showed minor variations in the selected stations, with a low coefficient of variation (CV) value of 1.528. The average water temperature recorded at the Al-Diwaniyah station was 28.5 °C during the study period, the lowest was 17.4 °C in the winter, and the highest was 35.7 °C in the summer.

The average pH value of the water was 7.62, indicating that the river water tends to be slightly alkaline. A minor discrepancy was observed between the stations' measurements and study seasons regarding the pH values because the highest value recorded in the spring at Al-Saniyya station was 8.23, whereas the lowest value was recorded at 7.03 in the

Table 2 Physicochemical parameters of the Al-Diwaniyah River water

| Stations | Season | pН | $\text{Temp.}(C^{\circ})$ | TDS | Water | Particle | size (%) | |
|---------------|--------|-------|---------------------------|--------|-------------------|----------|----------|-------|
| | | | | | velocity (m/s) | Clay | Sand | Silt |
| | Summer | 8.07 | 33.5 | 634.24 | | | | |
| | Autumn | 7.81 | 31.8 | 650.88 | | | | |
| | Winter | 7.30 | 19.5 | 517.12 | 0.714 | 4.33 | 89.41 | 6.26 |
| | Spring | 8.23 | 30.8 | 665.6 | | | | |
| Al-Saniyya | Mean | 7.85 | 28.9 | 616.96 | | | | |
| | Summer | 7.68 | 35.7 | 661.76 | | | | |
| | Autumn | 7.75 | 33.9 | 671.36 | | | | |
| | Winter | 7.44 | 17.4 | 662.72 | 0.666 | 8.73 | 80.44 | 10.83 |
| | Spring | 7.99 | 25.2 | 700.16 | | | | |
| Al-Diwaniyah | Mean | 7.71 | 28.05 | 674 | | | | |
| | Summer | 7.33 | 34.3 | 688.64 | | | | |
| | Autumn | 7.03 | 34.1 | 730.24 | | | | |
| | Winter | 7.05 | 19 | 538.24 | 0.625 | 4.16 | 91.87 | 3.97 |
| | Spring | 7.69 | 27.2 | 771.2 | | | | |
| Al- Hamza | Mean | 7.3 | 28.65 | 682.08 | | | | |
| Total average | | 7.62 | 28.533 | 657.68 | 0.668 | 5.74 | 87.24 | 7.02 |
| S.D | | 0.285 | 0.436 | 35.495 | 0.044 | 2.590 | 6.016 | 3.492 |
| C.V | | 3.740 | 1.528 | 5.397 | 6.586 | 45.12 | 6.895 | 49.74 |

Fig. 2 Values of TDS, pH, temperature, and particle size at three Al-Diwaniyah River stations





autumn at Al-Hamza station. Apparently, there is a gradual decrease in pH values by descending toward the south of the River, where the mean pH values at Al-Saniyya station was the highest at 7.85 and decreased to 7.71 at Al-Diwaniyah station. Al-Hamza station recorded the lowest average value in the study season at 7.3. The CV value for the pH values was recorded at 3.740 at the selected stations.

The average concentration of TDS in the river water was approximately 657.68 mg/L, with minor spatial variation between 616.96 and 682.08 mg/L at Al-Saniyya and Al-Hamza stations, respectively. For temporal variation, note that the value of TDS decreased in the winter to 517.12 mg/L, and concentrations increased to 771.2 mg/L in the spring. The pattern of TDS values increased from north to south along the River, in which CV value was recorded at 5.397 between the selected stations.

Table 3 Heavy metals levels in wastewater (mg/L) draining into the Al-Diwaniyah River course

| Heavy metals | Household sewer | Agricultural drains | Power station sewers |
|--------------|-----------------|---------------------|----------------------------|
| Mn | 0.2296 | 0.2319 | 0.0628 |
| Ni | 0.088 | 0.0396 | 0.0884 |
| Pb | ND | 0.1922 | 0.0549 |
| Zn | 0.04 | 0.0012 | 0.0089 |
| Cr | 0.0594 | 0.0483 | ND |
| Cu | 0.0304 | 0.0107 | 0.0071 |
| Cd | 0.0054 | ND | 0.0040 |
| As | 0.0041 | 0.0095 | 0.0007 |

ND not detected

Table 4 Concentrations of heavy metals (mg/L) in the Al-Diwaniyah River water for the three stations

| Stations | Season | Metals | | | | | | | |
|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | | Pb | Mn | Ni | Cr | Zn | Cu | As | Cd |
| | Summer | 0.0011 | 0.0360 | ND | ND | ND | 0.0350 | 0.0010 | ND |
| | Autumn | 0.0960 | 0.0170 | 0.0820 | 0.0610 | ND | ND | 0.0076 | ND |
| | Winter | 0.0230 | 0.0230 | ND | ND | 0.0007 | ND | 0.0021 | ND |
| | Spring | ND | 0.0071 | 0.0491 | ND | ND | 0.0101 | 0.0024 | ND |
| Al- Saniyya | Mean | 0.0300 | 0.0207 | 0.0327 | 0.0152 | 0.0001 | 0.0112 | 0.0032 | ND |
| | Summer | 0.0130 | ND | 0.0080 | ND | ND | 0.0012 | 0.0010 | 0.0030 |
| | Autumn | ND | ND | ND | 0.0920 | 0.0650 | ND | 0.0085 | 0.0020 |
| | Winter | 0.0140 | 0.0460 | ND | 0.0306 | 0.0001 | ND | 0.0035 | 0.0013 |
| | Spring | 0.1050 | 0.0560 | ND | ND | 0.0188 | 0.0128 | 0.0026 | ND |
| Al- Diwaniyah | Mean | 0.0330 | 0.0255 | 0.0020 | 0.0306 | 0.0209 | 0.0035 | 0.0039 | 0.0015 |
| | Summer | 0.3670 | 0.0140 | 0.0105 | ND | ND | 0.0044 | 0.0017 | ND |
| | Autumn | 0.1280 | ND | ND | ND | 0.0160 | 0.0010 | 0.0076 | 0.0010 |
| | Winter | 0.0470 | 0.0517 | ND | ND | 0.0009 | 0.0083 | 0.0047 | 0.0004 |
| | Spring | ND | 0.0216 | 0.0398 | ND | ND | ND | 0.0029 | ND |
| Al- Hamza | Mean | 0.1355 | 0.0218 | 0.0125 | ND | 0.0042 | 0.0034 | 0.0042 | 0.0003 |
| Total average | | 0.0661 | 0.0226 | 0.0157 | 0.0152 | 0.0084 | 0.0060 | 0.0037 | 0.0006 |

For the river bed texture, discrepancy was substantial between the sand content and the clay and silt contents. Sand constituted the largest proportion, which is approximately 87.24% of the total particles of the river bed sediments. Clay and silt have 5.74 and 7.02%, respectively, of the total sediments. A minor discrepancy was noted in the distribution of particle size between the stations. In particular, Al-Hamza station recorded the highest percentage of sand content at 91.87% of the total particles (Table 2).

Waste water

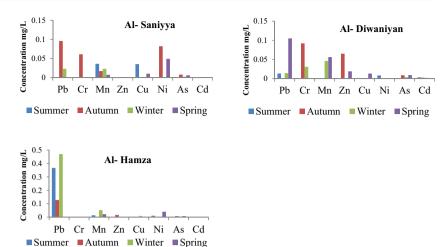
Table 3 shows the levels of heavy metals in the most important sources of waste water. Such heavy metals as As and Mn in the wastewater of various human activities in the Al-Qadisiyah governate have low concentrations, ranging between 0.007 and 0.2319 mg/L, respectively. Meanwhile, some heavy metals, such as Cr, Cd, and Pb, were not present. Low levels of heavy metals in the waste water indicate scarcity of factories and that fertilizers, pesticides, and chemicals are not used in the study area.

Determination of metals concentrations in the river water

The results of laboratory analysis of heavy metal levels in the Al-Diwaniyah River are summarized in Table 4 and Fig. 3. Table 3 shows that the average total concentrations of heavy metals in the water course vary between 0.0006 and 0.0661 mg/L for Cd and Pb, respectively. Several of the studied heavy metals may be absent in some seasons, particularly Ni, Cd, Zn, and Cu. With the exception of Pb, all



Fig. 3 Distribution of heavy metal levels (mg/L) in the Al-Diwaniyah River water for the three stations

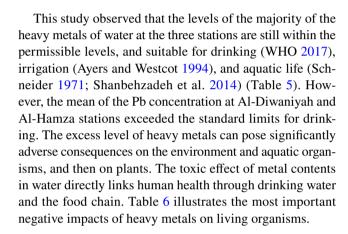


heavy metals dissolved in water are of low concentrations. The reason for the low concentrations of heavy metals can be attributed to the limited human and industrial activities (except for textile and rubber factories) in the study area. The low solubility of heavy metals in water and the tendency to adsorb with the suspended particles lead to an increase in the deposition process at the river bed. Moreover, river water alkalinity contributes to a decrease in the solubility of heavy metals and increase in the adsorption process (Al-Asadi 2016; Al-Asadi et al. 2019; Al-Asadi et al. 2020).

The relative high concentration of Pb (i.e., 0.0011–0.3670 mg/L) in the river water, particularly at Al-Hamza station, may be caused by the increase use of gasoline and agricultural drainage water. Textile factories dump untreated pollutants in the River, which are considered a possible source of heavy metals (Shafiuddin Ahmed et al. 2021). Despite the strong adsorption of Pb on sediment particles (Hejabi et al. 2011), its high levels in Al-Diwaniyah River may indicate that Pb was more mobile than the majority of other heavy metals. This result reflects the intensity of lead pollution sources in the River.

The velocity of water current and water discharge play an important role in the variations of heavy metal concentrations. An increase in discharges contributes to a dilution of metal levels, while an increase in the current velocity leads to turbulence of the water column. It contributes to an increase in the heavy metal concentrations of water owing to the mixing process with the metal content of the bottom sediments (Al-Asadi et al. 2019).

Despite the non-uniform random variation of metal levels of the river water in the four seasons, the spatial variation of their levels generally tends to increase at Al-Diwaniyah station. The reason can be attributed to the relative increase in anthropogenic activities and presence of textile and rubber factories in the city of Al-Diwaniyah. Variations in the heavy metal levels have taken the following pattern: Pb > M n > Ni > Cr > Zn > Cu > As > Cd.



Concentration of heavy metals in sediments

Table 7 and Fig. 4 show the heavy metal levels in the bottom sediments of the Al-Diwaniyah River and CV values. Given the results of the laboratory analyses of the three stations within the study area, note that there is a clear and significant discrepancy among the concentrations of heavy metals in the river sediments. As the heavy metal levels ranged from 0.011 to 976.76 mg/L for CD and Mn, respectively, the

Table 5 Comparison of heavy metals level (mg/L) in the Al-Diwaniyah River water with international standard values

| Heavy metals | Present study | Drinking | Irrigation | Aquatic |
|--------------|---------------|----------|------------|---------|
| Pb | 0.0661 | 0.01 | 0.5 | 0.10 |
| Mn | 0.0226 | 0.4 | 2 | 0.1 |
| Ni | 0.0157 | 0.07 | 0.20 | 0.15 |
| Cr | 0.0152 | 0.05 | 0.10 | 0.05 |
| Zn | 0.0084 | 0.02 | 0.20 | 0.15 |
| Cu | 0.0060 | 2 | 0.2 | _ |
| As | 0.0037 | 0.01 | 0.10 | 1 |
| Cd | 0.0006 | 0.003 | 0.01 | 0.05 |



Table 6 The effect of heavy metal contamination on humans, plants, and aquatic organisms

| Heavy metals | Heavy metals The effects on humans | The effects on agriculture | The effects on aquatic |
|--------------|--|--|---|
| Pb | Low IQ, short term memory loss, low birth weight, peripheral nerve inflammation | Slow growth, change in branching pattern, dwarfing of leaves, obstruction of vital processes | Soft tissue damage in fish. Decreased ability to grow and reproduce in fish |
| Mn | Low IQ in children, depression, mood change, tremors | Dwarf, wrinkled leaves, necrotic pests | Inhibition of bacteria and algae growth. Manganese is a major catalyst for the aquatic environment |
| ïŻ | Respiratory diseases and skin allergies | Decreased bacterial activity, accumulation of toxic metals in bacteria | Enlargement of the cell membrane due to the nickel-carrying protein |
| Cr | Diabetes, cardiovascular blockage, nosebleeds | Inhibits the growth of buds, reduces the number and area of leaves, burns on the margins of the leaves | Inhibits the growth of buds, reduces the number and area It is toxic to the aquatic environment due to being a strong of leaves, burns on the margins of the leaves corrosive oxidizing agent |
| Zn | Weakening the growth process, anemia, bone failure, vomiting, diarrhea, bloody urine, liver and kidney failure | Reduce leg length, chlorosis, necrotic spots | Problems with fertilization in fish. Low high-density lipoprotein |
| Cu | Abdominal pain, diarrhea, vomiting, kidney failure, anemia | Necrosis at the tip of the leaves, reduced development of Damage to the internal organs of aquatic animals lateral roots, stunted growth | Damage to the internal organs of aquatic animals |
| As | Stroke, spleen enlargement, weight loss | Poor seed germination, inhibition of deep growth | Redness of cod and shellfish |
| Cd | Bronchitis, hepatotoxicity in the blood, nausea, abdominal cramps, shortness of breath | Growth problems | Kidney damage in aquatic organisms (seals). Death of fish |

^aSingh and Kalamdhad (2011)

^bBaby et al. (2010)

^cMoore and Ramamoorthy (1984)

^dHenson and Chedrese (2004)

eErdogan (2009)

^fFurini (2012)

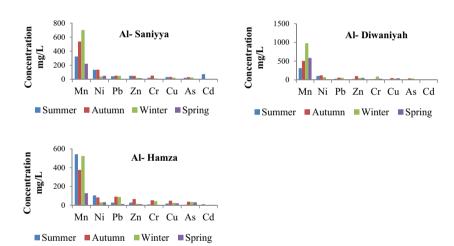
^gNaidu and Mooison (1994)



Table 7 Concentrations of heavy metals (mg/L) in the sediments of Al- Diwaniyah River

| Stations | Season | Heavy m | etals | | | | | | |
|---------------|--------|---------|--------|-------|--------|-------|-------|-------|-------|
| | | Mn | Ni | Pb | Zn | Cr | Cu | As | Cd |
| | Summer | 324.00 | 134.00 | 42.80 | 50.50 | 21.50 | 31.80 | 21.70 | 0.73 |
| | Autumn | 536.88 | 137.80 | 52.20 | 48.70 | 52.90 | 33.15 | 30.33 | 0.01 |
| | Winter | 700.56 | 40.10 | 50.10 | 20.49 | 12.38 | 24.38 | 25.91 | 0.40 |
| | Spring | 221.00 | 50.38 | 2.82 | 15.32 | 0.0 | 2.28 | 4.10 | 0.33 |
| Al-Saniyya | Mean | 445.61 | 90.57 | 36.98 | 33.75 | 21.69 | 22.90 | 20.51 | 0.36 |
| | Summer | 313.00 | 104.00 | 31.11 | 22.50 | 19.80 | 13.60 | 3.90 | 0.50 |
| | Autumn | 506.64 | 121.90 | 60.28 | 100.90 | 20.80 | 49.15 | 40.41 | 0.01 |
| | Winter | 976.76 | 73.00 | 58.25 | 49.86 | 91.43 | 35.59 | 37.81 | 0.32 |
| | Spring | 585.00 | 20.25 | 9.87 | 53.66 | 33.42 | 43.87 | 8.18 | 0.52 |
| Al-Diwaniyah | Mean | 595.35 | 79.78 | 39.87 | 56.73 | 41.36 | 35.55 | 22.57 | 0.33 |
| | Summer | 543.00 | 104.00 | 27.50 | 27.70 | 8.20 | 17.10 | 5.40 | 0.10 |
| | Autumn | 376.18 | 82.60 | 91.30 | 65.70 | 52.90 | 48.05 | 37.45 | ND |
| | Winter | 524.14 | 29.30 | 86.80 | 15.35 | 43.33 | 25.66 | 33.62 | 0.22 |
| | Spring | 128.00 | 31.04 | 12.68 | 10.70 | 2.47 | 20.14 | 31.00 | 0.38 |
| Al-Hamza | Mean | 392.83 | 61.73 | 54.57 | 29.86 | 26.72 | 27.73 | 26.86 | 0.17 |
| Total average | | 477.93 | 77.36 | 43.80 | 40.11 | 29.92 | 28.72 | 23.31 | 0.28 |
| S.D | | 105.05 | 14.56 | 9.43 | 14.52 | 10.21 | 6.38 | 3.24 | 0.10 |
| C.V | | 21.981 | 18.83 | 21.52 | 36.19 | 34.13 | 22.21 | 13.89 | 35.71 |

Fig. 4 Levels of heavy metals (mg/L) in the Al-Diwaniyah River sediments at the three stations



distribution pattern of heavy metals in the river sediments at the different measurement stations was in the following order: Mn > Ni > Pb > Zn > Cr > Cu > As > Cd.

Note that the heavy metal concentrations in the bed sediments are significantly higher than the levels in the River water. These high levels can indicate an increased accumulation of heavy metals in the river bed compared with solubility and mobility. This result is due to several factors, including the physicochemical properties of water, current velocity, and sediment grain size.

Geographical distribution shows that heavy metal levels in the sediment samples were significantly varied among the three stations as CV of the metal levels increased between 13.89 and 36.196 for As and Zn, respectively. This increase

could be caused by variations in physicochemical properties in water and sediments of different stations, and/or as a result of receiving different discharges of pollutants. In general, the majority of the metal levels tend to increase at Al-Diwaniyah station owing to an increase in the number of households and industrial pollutants. However, Al-Saniyya station represents the lowest concentrations of the studied metals, except for Ni. The reason is that the station represents the upstream of the river cores. Thus, levels of heavy pollutants are reduced.

The availability of heavy metals in the benthic sediments of the Al-Diwaniyah River course vary along the four seasons. However, there is a general tendency for the concentrations of the majority of metals to increase and



decrease in autumn and spring, respectively. The reason for this seasonal variation may be the physicochemical properties of water, which influence levels of reaction, adsorption, solubilization, mobilization, and deposition; and ejections amount vary of human waste, especially the residues of agricultural production.

Mn concentrations in the sediments were significantly high because its average concentration varied between 392.83 and 595.35 mg/L at Al-Hamza and Al-Diwaniyah stations, respectively. The reason for this diverse Mn level may be the presence of blacksmithing workshops along the River and municipal wastewater discharges. Moreover, fossil fuel waste in the atmosphere increases the adsorption of Mn with the surfaces of solid particles, thereby contributing to an increase in its deposition (Chan et al. 2002.) Runoff generated by rainfall can drive these pollutants toward both sides of the River.

The average levels of Ni varied between 61.735 and 90.57 mg/L at Al-Hamza and Al-Saniyya stations, respectively. Apparently, the presence of Ni in anthropogenic wastes of 0.088 and 0.0396 mg/L contributed to the high levels of its presence in the river, as well as atmospheric deposition, because fossil fuel combustion is a major source of Ni (90%). Ni is one of the most traceable metals resulting from oil pollution, second only to vanadium (Kabata-Pendias and Pacyna 2001).

The average concentration of Pb varies from 36.98 to 54.57 mg/L in the bottom sediments of the River. The highest and lowest concentrations of metal were recorded at Al-Hamza and Al-Saniyya stations, respectively.

Average Zn concentration varied between 29.862 and 56.73 mg/L at Al-Hamza and Al-Diwaniyah stations, respectively. Waste influx from the nearby rubber factory was likely responsible for the presence of high Zn content at Al-Diwaniyah station. Non-solid waste from the rubber factory is one of the most important sources of zinc and copper in the aquatic environment (Kurian 2012). The average levels of Cr in the river sediments varied between 21.695 and 41.362 mg/L at Al-Saniyya and Al-Diwaniyah stations, respectively. The reason for the high concentration at Al- Diwaniyah station may be the increase in burning of wastes in areas near the River, particularly in the Sayed Muhail area, as well as blacksmiths and corrosion of steel bridge columns in the River.

Table 8 Comparison of heavy metal concentrations (mg/L) in the Al-Diwaniyah River sediments with previous studies and international standards

| Heavy metals | Mn | Ni | Pb | Zn | Cr | Cu | As | Cd |
|------------------------|--------|-------|-------|--------|-------|-------|-------|------|
| Present study | 477.93 | 77.36 | 43.80 | 40.11 | 29.92 | 28.72 | 23.31 | 0.28 |
| Alkam et al. (2014) | _ | _ | 9.74 | 23.18 | _ | 15.71 | _ | 1.67 |
| Kadhum et al. (2020) | _ | _ | 63.23 | 156.15 | _ | 67.52 | _ | 1.29 |
| Guidelines for aquatic | 500 | 50 | 35 | 123 | 37.3 | 35.7 | 5.9 | 0.6 |

Average Cu concentration ranged from 22.902 to 35.552 mg/L in the sediment samples. The highest mean concentration of Cu was observed at Al-Diwaniyah station, possibly owing to the discharge from the rubber factory. The mean levels of As ranged from 20.512 to 26.869 mg/L in the River sediments. The maximum concentration of As was observed at Al-Hamza station. The possible reason for the high concentration at Al-Hamza station was the influx of pollutants from agricultural drains of fertilization and agricultural pesticides, thereby promoting As availability in the study area (Aide et al. 2016). Cd levels in the river bed sediments decreased by 0.17 and 0.36 mg/L at Al-Hamza and Al-Saniyya stations, respectively. These values are the lowest concentrations of heavy metals studied in the river sediments. The reason for the low level can be attributed to the scarcity of Cd from human sources in the study area, which lacks mining and battery factories.

The study of heavy metals in the benthic sediments of Al-Diwaniyah River indicated that the levels of Pb, Zn, Cu, and Cd were significantly lower than the levels reported by Kadhum et al. (2020). However, these findings (except for Cd) were higher than the findings of Alkam et al. (2014) (Table 8). The levels of Ni, Pb, and As exceeded the permissible limits of sediment quality guidelines by CCME (2001) (Table 8). High concentrations of these metals caused damage to the water environment and various activities, while the remainder of the metals were within the permissible levels.

Sources of contamination

Pearson correlation coefficient was used to explore the linear relationship among the distributions of heavy metals in the surface sediments of Al-Diwaniyah River to identify the factors controlling the transport and accumulation of these metals (Table 9). The results showed that pH plays a major role in the accumulation of heavy metals in the river bed in all seasons except spring (i.e., correlation coefficients were positively correlated between 0.785 and 0.994). Meanwhile, water temperature was negatively correlated with the majority of the heavy metals (r = -0.197 to -0.992).

The relationship between TDS and levels of heavy metals is seasonally varied (positive and negative) and the power of r varied between -0.071 and 0.998. In general, the relationship between the majority of heavy metals and the



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Table 9 Matrix of Pearson's correlation coefficient of heavy metals in the Al-Diwaniyah river sediments

| | Zn | Cu | Ni | Cr | Pb | Cd | Mn | As | Hd | Temp | TDS | Velo | Q | Clay | Silt | Sand |
|------------------|---------|---------|----------|---------|----------|---------|---------|---------|----------|--------|-----------|--------|-----------|---------|---------|------|
| Summer | | | | | | | | | | | | | | | | |
| Zn | | | | | | | | | | | | | | | | |
| Cn | **666.0 | 1 | | | | | | | | | | | | | | |
| ïZ | 0.985 | 0.983 | | | | | | | | | | | | | | |
| Cr | 0.449 | 0.443 | 0.598 | 1 | | | | | | | | | | | | |
| Pb | 0.920 | 0.917 | 0.974 | 0.764 | 1 | | | | | | | | | | | |
| Cd | 0.657 | 0.652 | 0.779 | 0.969 | 0.900 | 1 | | | | | | | | | | |
| Mn | -0.301 | -0.295 | -0.463 | - 0.987 | - 0.651 | -0.917 | | | | | | | | | | |
| As | 0.995 | 0.994 | *266.0 | 0.536 | 0.954 | 0.729 | -0.394 | _ | | | | | | | | |
| Hd | 0.785 | 0.781 | 0.881 | 906.0 | 0.965 | 0.983 | -0.827 | 0.843 | _ | | | | | | | |
| Temp | - 0.876 | -0.879 | -0.778 | 0.038 | - 0.616 | -0.211 | -0.197 | -0.823 | - 0.388 | _ | | | | | | |
| TDS | -0.770 | - 0.765 | - 0.869 | - 0.916 | - 0.958 | - 0.987 | 0.840 | -0.829 | - 0.999* | 0.366 | 1 | | | | | |
| Velo | 0.960 | 0.962 | 968.0 | 0.181 | 0.773 | 0.420 | -0.022 | 0.927 | 0.580 | -0.976 | -0.560 | | | | | |
| Õ | 0.773 | 0.768 | 0.872 | 0.914 | 096.0 | 986.0 | -0.838 | 0.832 | *666.0 | -0.370 | - 0.997** | 0.564 | 1 | | | |
| Clay | - 0.618 | -0.623 | -0.471 | 0.425 | -0.260 | 0.186 | - 0.564 | -0.537 | 0.002 | 0.921 | - 0.026 | -0.814 | 0.021 | | | |
| Silt | -0.357 | -0.363 | -0.188 | 0.674 | 0.038 | 0.469 | -0.783 | -0.263 | 0.298 | 0.764 | -0.321 | -0.604 | 0.317 | 0.955 | 1 | |
| Sand | 0.473 | 0.479 | 0.312 | -0.574 | 0.090 | -0.353 | 869.0 | 0.384 | -0.174 | -0.840 | 0.198 | 0.701 | - 0.19 | - 0.985 | - 0.992 | _ |
| Autumn | | | | | | | | | | | | | | | | |
| Zn | 1 | | | | | | | | | | | | | | | |
| Cu | 0.790 | _ | | | | | | | | | | | | | | |
| ï | - 0.085 | 8290 – | 1 | | | | | | | | | | | | | |
| Cr | - 0.948 | -0.552 | -0.238 | 1 | | | | | | | | | | | | |
| Pb | -0.002 | 0.612 | - 0.996 | 0.321 | 1 | | | | | | | | | | | |
| Cd | - 0.999 | 0.834 | 0.648 | -0.871 | 0.621 | 1 | | | | | | | | | | |
| Mn | 0.021 | -0.597 | 0.994 | -0.339 | +866.0 - | 0.123 | 1 | | | | | | | | | |
| As | 806.0 | 0.974 | -0.495 | -0.727 | 0.418 | -0.974 | -0.400 | 1 | | | | | | | | |
| $^{\mathrm{hd}}$ | 0.129 | -0.507 | 0.977 | -0.439 | -0.992 | 0.438 | 0.994 | -0.298 | 1 | | | | | | | |
| Temp | 969.0 | 0.990 | -0.774 | | 0.717 | -0.864 | -0.703 | 0.933 | -0.622 | 1 | | | | | | |
| TDS | 0.053 | 0.654 | +666.0 - | | *866'0 | -0.890 | - 0.997 | 0.466 | - 0.983 | 0.753 | 1 | | | | | |
| Velo | 996:0 – | -0.922 | 0.341 | | -0.258 | 9000 | 0.240 | - 0.986 | 0.133 | -0.859 | -0.310 | 1 | | | | |
| \circ | -0.938 | -0.528 | -0.266 | *666.0 | 0.348 | 0.973 | - 0.366 | -0.706 | -0.465 | -0.404 | 0.297 | 0.816 | 1 | | | |
| Clay | 0.937 | 0.525 | 0.269 | - 0.997 | -0.352 | 0.712 | 0.369 | 0.704 | 0.468 | 0.401 | -0.301 | -0.814 | - 0.998** | 1 | | |
| Silt | 0.791 | 0.249 | 0.540 | -0.945 | -0.614 | 998.0 | 0.629 | 0.461 | 0.70 | 0.1111 | -0.570 | -0.604 | -0.954 | 0.955 | 1 | |
| Sand | - 0.862 | -0.370 | -0.431 | 0.979 | 0.508 | 0.097 | -0.524 | -0.571 | -0.613 | -0.237 | 0.460 | -0.701 | -0.984 | - 0.985 | -0.992 | 1 |
| Winter | | | | | | | | | | | | | | | | |
| Zn | 1 | | | | | | | | | | | | | | | |
| Cu | 0.971 | 1 | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |



Table 9 (continued)

| lable 2 | (commuca) | | | | | | | | | | | | | | | |
|-------------|-----------|---------|---------|---------|---------|---------|---------|---------|--------|---------|---------|--------|---------|---------|--------|---|
| N. | 0.995 | 0.941 | 1 | | | | | | | | | | | | | |
| Cr | 0.859 | 0.957 | 0.803 | - | | | | | | | | | | | | |
| Pb | -0.434 | -0.205 | -0.523 | 0.088 | 1 | | | | | | | | | | | |
| Cd | 0.201 | -0.040 | 0.299 | -0.329 | -0.970 | 1 | | | | | | | | | | |
| Mn | 0.967 | 0.877 | 0.988 | 0.700 | -0.650 | 0.445 | _ | | | | | | | | | |
| As | 0.674 | 0.832 | 0.596 | 0.957 | 0.373 | - 0.588 | 0.463 | 1 | | | | | | | | |
| Hd | 0.854 | 0.704 | 0.902 | 0.468 | -0.839 | 0.681 | 0.959 | 0.192 | _ | | | | | | | |
| Temp | -0.933 | -0.992 | -0.892 | - 0.986 | 0.081 | 0.165 | -0.810 | -0.895 | 0.610 | 1 | | | | | | |
| ADS | 0.963 | .866.0 | 0.931 | 0.965 | -0.175 | -0.071 | 0.862 | 0.848 | 0.682 | - 0.995 | 1 | | | | | |
| Velo | -0.748 | - 0.886 | - 0.677 | -0.982 | -0.274 | 0.500 | -0.553 | -0.994 | -0.294 | 0.937 | - 0.899 | | | | | |
| 0 | -0.057 | -0.295 | 0.044 | -0.560 | -0.875 | 196.0 | 0.200 | - 0.776 | 0.470 | 0.413 | -0.324 | 0.705 | 1 | | | |
| Clay | 0.994 | 0.991 | 0.979 | 0.908 | -0.337 | 0.097 | 0.934 | 0.748 | 0.795 | - 0.966 | 986.0 | -0.814 | -0.162 | | | |
| Silt | 0.981 | 0.905 | 966.0 | 0.743 | -0.601 | 0.388 | .866.0 | 0.517 | 0.939 | -0.845 | 0.892 | -0.604 | 0.138 | 0.955 | 1 | |
| Sand | - 0.998* | -0.952 | - 0.998 | -0.823 | 0.494 | 0.267 | -0.982 | -0.622 | -0.887 | 0.907 | -0.943 | 0.701 | -0.010 | - 0.985 | 0.082 | 1 |
| Spring | | | | | | | | | | | | | | | | |
| Zn | 1 | | | | | | | | | | | | | | | |
| Cu | 0.858 | _ | | | | | | | | | | | | | | |
| ï. | - 0.708 | -0.970 | | | | | | | | | | | | | | |
| Cr | 0.987 | 0.930 | -0.814 | _ | | | | | | | | | | | | |
| Pb | 0.145 | 0.633 | -0.801 | 0.305 | _ | | | | | | | | | | | |
| Cd | 0.938 | 0.983 | - 0.909 | 0.982 | 0.479 | 1 | | | | | | | | | | |
| Mn | 0.995 | 0.804 | -0.637 | 996.0 | 0.050 | 0.900 | 1 | | | | | | | | | |
| As | -0.462 | 090.0 | -0.299 | -0.311 | 0.810 | -0.126 | -0.545 | 1 | | | | | | | | |
| Ηd | 0.161 | -0.369 | 0.583 | -0.002 | -0.953 | -0.191 | 0.250 | -0.950 | 1 | | | | | | | |
| Temp | -0.707 | -0.970 | 0.998** | -0.813 | -0.802 | - 0.909 | -0.637 | -0.300 | 0.583 | _ | | | | | | |
| TDS | -0.291 | 0.243 | -0.470 | -0.130 | 0.905 | 090.0 | -0.381 | 0.983 | -0.991 | -0.471 | 1 | | | | | |
| Velo | -0.774 | - 0.989 | 0.995 | -0.867 | -0.739 | - 0.946 | -0.710 | -0.204 | 0.500 | 0.995 | -0.381 | | | | | |
| 0 | 0.370 | -0.161 | 0.394 | 0.213 | - 0.866 | 0.024 | 0.457 | - 0.995 | 0.977 | 0.395 | 966.0 – | 0.302 | 1 | | | |
| Clay | 0.998 | 0.889 | -0.753 | 0.995 | 0.209 | 0.958 | 0.987 | -0.404 | 0.097 | -0.752 | -0.228 | -0.814 | 0.309 | | | |
| Silt | 0.927 | 0.714 | -0.523 | 0.921 | -0.091 | 0.831 | 0.660 | -0.657 | 0.388 | -0.522 | -0.506 | -0.604 | 0.577 | 0.955 | 1 | |
| Sand | - 0.994 | -0.797 | 0.628 | - 0.963 | -0.037 | - 0.895 | 966.0 – | 0.555 | 0.267 | 0.627 | 0.392 | 0.701 | - 0.468 | - 0.985 | -0.992 | 1 |
| the Halland | 9:: 3- 4 | | | | | | | | | | | | | | | |

2-tailed test of significance is used

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level



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current velocity tends to be varied negatively (r = -0.022)to -0.950), while the relationship between water discharge (Q) and heavy metal concentrations is generally positive (r=0.024-0.999). In addition, there is a significant linear correlation between clay and silt particles with the majority of the heavy metals in three seasons, except summer. By contrast, the relationship between sand and the majority of the heavy metals was negative in all seasons, except summer (r = from - 0.037 to - 0.998).

Correlation analysis between the majority of the physical and chemical parameters with heavy metal levels in the sediments of Al-Diwaniyah River indicated that the correlation was positive or negative varied strong or weak. This result indicated that human activities may be the main contributor for the accumulation of heavy metals in river sediments.

Conclusions

The current study revealed that the concentrations of Mn, Ni, Cr, Zn, Cu, As, and Cd in the waters of Al-Diwaniyah River were low (with the exception of Pb). Heavy metal contents in the bed sediments were higher than that of the river water. This discrepancy in levels indicates an increased accumulation of heavy metals in the river bed compared with dissolution and transport. Mn, Ni, Pb, and As concentrations in the sediments were high, while Zn, Cu, Cr, and Cd had no environmental concern. Despite the existence of residential neighborhoods, spread of irrigated lands, and presence of some industrial activities, all of which dispose their wastes directly into the River without treatment, the low concentrations of the majority of the studied heavy metals in the river water reflect the limited role of these activities in polluting the quality of river water.

However, uncontrolled urban development in the region is likely to increase water pollution level in the future. Water quality in the River reflects the combined effects of natural and human factors. In the surface water and bed sediments, Pb mainly came from the textile factory, traffic pollution, and agricultural drainage water. In addition, Mn, Ni, and As in sediments may have been derived from a combination of sources, such as atmospheric deposition resulting from fossil fuel combustion and waste water influx from agricultural, industrial, and residential activities. Moreover, the sources of Zn, Cu, Cr, and Cd were unclear owing to the drastic decrease in their concentrations, whether in water or sediments. Note also that the physical and chemical properties of water play important roles in the absorption and accumulation of heavy metals in the River. The results of the current study provide beneficial information on water quality along the studied river, whether in the Al-Qadisiyah governorate or adjacent areas. However, the diversity and interaction of natural and human factors affecting the levels of heavy metals in the River requires extensive monitoring to determine a wide range of pollution sources.

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