



Estimation of Heavy Metal Concentrations in Euphrates River Water and Sediments in Thi Qar City

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ABSTRACT

The Euphrates River is one of Iraq's most important water sources. Ecological research was undertaken on this river along the stretch of Thi Qar City, beginning in the northwest at Al-Batha City and ending in the south at Al-Chibayish City, with the aim to determine the effect of several heavy metal contaminants on the river water and sediments. The study began in the spring of 2022 and ended in the winter of 2023. The heavy metals (Pb, Cu, Cd, and Zn) were extracted using the Atomic Absorption Spectrophotometer, and their amounts were later estimated. It was found that the heavy metals have higher concentrations in the river water at Chibayish City compared to that of Al-Batha City (as a control group). The quantity of the heavy metals in the river water decreased in such order: Zn> Cu> Pb> Cd. In the case of the sediment, the concentrations decreased in descending order: Cu> Pb>Zn>Cd. This study found that heavy metal concentrations in water and sediments are normal in Iraq, with sediments having a higher concentration than water due to the untreated pollutants thrown into the river by the estuaries.

INTRODUCTION

Heavy metals are one of the most harmful pollutants that enter the freshwater ecosystem, thus disrupting its natural balance and affecting humans whether directly or indirectly (Ateshan *et al.*, 2019; Ateshan *et al.*, 2020). River water worldwide contains a wide range of pollutants, including a number of heavy metal elements such as zinc, copper, cadmium, and lead due to the dumping of industrial waste and various types of chemical fertilizers (Khan *et al.*, 2018; Al Sailawi *et al.*, 2020). Although the presence of certain heavy metals is important, they are highly toxic as they cannot be decomposed either by microorganisms or other natural means; hence, they remain in the environment for long stretches of time and can be transferred over long distances by wind, rain, and storm (Jamal *et al.*, 2013; Ateshan & Saxena, 2015). They can also bio-accumulate in the body of living organisms via air, water, and soil, with increasing concentrations as the

food chain ascends, thus resulting in perpetual toxicity (**Jamal *et al.*, 2013**). For humans, this is highly hazardous since we are at the top of the food chain, being the ultimate repository for such bioaccumulation (**Khan *et al.*, 2018**; **Ha *et al.*, 2019**). According to research, heavy metal pollution in rivers is contributed by household wastes as well as mining and agricultural activities, i.e., via the usage of pesticides and fertilizers, which cause an imbalance in the river ecosystem (**Ateshan *et al.*, 2019**; **Weldeslassie *et al.*, 2019**).

Weldeslassie (2019) illustrated that the main cause of water pollution is the direct discharge of untreated wastewater into rivers and water aquifers, which carries pollutants in the form of heavy elements, pesticides, and others. Heavy metal elements are present in rivers, whether in the water, the suspended load, or the sediments at the bottom. Short-term estimations of their concentrations cannot accurately capture the intensity of the pollution owing to variations in water discharges, suspended load, imbalance, and stability of the pollution source, as well as irregularity. While some of these pollutants are released locally, the focus is on the bottom sediments as they are a more stable indicator of these elements, considering that they are traps for various elements (**Khan *et al.*, 2018**).

Natural sediment consists of a mixture of sand, clay, and organic matter. The proportions of these components vary according to the types of sediment. There is an overlap with heavy metal elements depending on the nature of the sediment and the prevailing chemical and physical conditions. **Wittmann and Forstener (2022)** postulated that heavy metal concentrations are higher in the sediment than in the water by 103–105 times because sediments act as traps for pollutants and they originate from polluted water (**Ha *et al.*, 2019**; **Ateshan *et al.*, 2020**).

Heavy metal pollution in rivers and water systems in densely populated industrial areas can be reflected by its high concentrations in the sediments (**Mokarram *et al.*, 2020**; **Jasim *et al.*, 2021**). **Sany (2014)** elucidated that the sediment reflects the degree of pollution in the aquatic environment. Research has also indicated that heavy metal elements that are not associated with silicate structures in the sediment originate from polluted water (**Saha *et al.*, 2017**; **Kttafah *et al.*, 2020**). For these reasons, this study was set out to examine heavy metal concentrations in the sediments taken from the selected sites.

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MATERIALS AND METHODS

Heavy metal concentrations in the Euphrates River, specifically along the city of Thi Qar, were estimated using river water samples taken from three sites namely the Al-Batha area as the control area because there are no infected people who excrete liquid waste in it, the city center (near the iron bridge), and the city of Al-Chibayish. The river water samples were taken quarterly, i.e., during the four seasons (summer, autumn, spring, and winter) throughout the year.

Estimation of heavy metal concentrations in the water

Estimations were carried out to determine the concentration levels of zinc, copper, cadmium and lead in the river water samples, using the method suggested by APHA, Standard Methods for the Examination of Water and Wastewater, 16th edition, Washington, DC, 1985.

Sample preparation

A total of 50ml of water was collected from the three sites throughout the four seasons in 2022-2023. The water sample was put into a clean 100ml glass beaker, which was subsequently added with 5ml of concentrated nitric acid for digestion purposes. The beaker was then heated on a hot plate and was left there for continued heating until pre-drying. Subsequently, 5ml of concentrated nitric acid was added to the sample while it continued to heat to form a precipitate. Post-cooling, 25ml of deionized distilled water was added. The mixture was then filtered utilizing a 0.20 μ m filtration membrane in preparation to estimate the heavy metal concentrations. Next, the absorbance of these digested samples were measured using an Atomic Absorption Spectrophotometer, a type of PYE Unicam model sp9, to determine the wavelength and current used for each heavy element (Table 1).

Table 1. Wavelength and current used for the heavy elements under study

Element	Wavelength (μ m)	Current (mA)
Copper	324.8	5
Zinc	213.9	10
Cadmium	228.8	6
Lead	217.0	6

The conversion of the atomic absorption measurement into concentration units was done using the regression equations recorded in the linear regression analysis of the

various standard concentrations of the heavy metals. The results were expressed in units (mg of metal per liter of sample water).

Estimation of heavy metal concentrations in sediments

Heavy metal concentrations in the bottom sediments of the Euphrates River were estimated using the sediment samples taken from the selected sites.

Sample preparation

After the samples of sediments were collected from the river at a depth of 20–40cm from the bottom, they were placed in plastic bags and taken to the laboratory to undergo drying. The heavy metal concentrations were estimated using the method proposed by **Cheng (2019)**. A total of 0.5 grams of dry soil was placed in a glass beaker, which was then added with 5ml of the digestion solution comprising concentrated sulfuric acid (H_2SO_4), concentrated nitric acid (HNO_3), and perchloric acid (HClO_4) at a ratio of 3:1:1. Moreover, a cover was put on the beaker for an hour to prevent evaporation of the concentrated acids. The sample was then heated at 90°C inside the hood for two hours, and subsequently diluted with the addition of 25ml of deionized distilled water. The sample's absorbance was estimated utilizing an atomic absorption spectrometer. The conversion of the absorbance rate into concentration units was carried out by referring to the regression equations for the standard curves of the heavy elements under study and across the results in a unit (micrograms of metal per gram of weight soil dry).

Statistical analysis

The statistical analysis was carried out using the complete randomized design (CRD) averages via Duncan's multiple range test, as recommended by **Al-Rawi and KhalafAllah (1980)**. By employing the ready-made statistical program SAS 2001, the analysis was carried out at a $P \leq 0.05$ significant level

RESULTS AND DISCUSSION

Heavy metal concentrations in water

Zinc

Based on the results presented in Table (2), there is an increase in zinc concentration in the Euphrates River during the winter season, i.e., when the rain and torrents wash the heavy metals into the river. Its increasing concentration as the water moves toward the city center and south of the city is due to the untreated pollutants thrown into the river by the estuaries. Table (3) presents the annual zinc concentration rate in the Euphrates River, with the lowest being 0.469mg/ L in Batha City during spring. This is due to the abundance of rain and torrential rains which caused the river water to be diluted and spread out. The highest concentration rate was recorded in the city of Al-Chibayish, i.e., 1.961mg/ L during winter. This is because the wastewater from the residential,

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agricultural, and industrial areas was washed away by the rain and torrential rains via the outfalls. Higher zinc concentration was recorded in the city of Chibayish during summer, i.e., at 2.528mg/ L. This is due to the phenomenon of water evaporation in the summer owing to the high temperatures in addition to the river's low level (**Dugdale *et al.*, 2017; Abdullah *et al.*, 2022**). The concentration rate for zinc throughout the year was concluded to be within the approved limits set by the World Health Organisation (**WHO, 2020**).

Table 2. Average concentrations of heavy metals in the Euphrates River for the year under study

Metals	Location	Elemental concentration rate				
		Spring	Summer	Autumn	Winter	Mean
Zinc	Al-Batha	0.365	0.600	0.391	0.521	0.469
	Downtown	0.986	1.272	1.30	1.800	1.339
	Al-Chibayish	1.037	2.528	1.800	2.479	1.961
Copper	Al-Batha	0.040	0.094	0.070	0.040	0.061
	Downtown	0.176	0.387	0.197	0.122	0.220
	Al-Chibayish	0.264	0.468	0.244	0.170	0.288
Cadmium	Al-Batha	0.001	0.003	0.002	0.001	0.001
	Downtown	0.002	0.007	0.004	0.003	0.004
	Al-Chibayish	0.004	0.008	0.006	0.005	0.005
Lead	Al-Batha	ND	0.012	0.006	ND	0.004
	Downtown	0.205	0.276	0.347	0.248	0.269
	Al-Chibayish	0.304	0.403	0.347	0.248	0.325

* ND = Not Detected

Copper

Table (2) shows the rates of copper concentration in the Euphrates River throughout the year under study, namely 0.288, 0.220, and 0.061mg/ L for the three selected sites, respectively. The concentration of copper increases as the water courses through the river. This is due to the liquid and polluted waste it receives. The lowest concentration of copper is identified in the city of Batha during the winter and spring seasons, i.e., at 0.040mg/ L. This is due to the dilution and diffusion phenomenon that occurs in the Euphrates River caused by rain. As for the two locations in the city center and south of the city, an increase in copper concentration was observed for all the seasons. This is ascribed to the pollutants that were expelled with the untreated effluents which were dumped directly into the river from the outfalls. The highest value of copper concentration in the summer was recorded in the city of Chibayish at 0.468mg/ L. However, despite the high concentration of copper in the Euphrates River, it is still within the natural limits internationally permitted by the WHO, i.e., 12mg/ L in freshwater and

3mg/ L in drinking water. Copper is more toxic in water hardness with low alkalinity (Fetter, 1980).

Cadmium

Table (2) presents the rates of cadmium concentrations at the studied sites along the Euphrates River during the four seasons. The concentrations range between 0.001–0.006mg/ L. The lowest value was recorded in Al-Batha city during the winter and spring seasons at 0.001mg/ L. The highest value was recorded in the Chibayish region during the summer, i.e., at 0.006mg/ L. This is traced back to a large number of untreated wastes and pollutants dumped into the river from the estuaries located on both sides of the river, in addition to the accumulated concentrations in agricultural soil which comes from various fertilizers that were washed away by the rain during winter. These findings are in line with that of **Al-Shawi *et al.* (2022)**, which indicated cadmium concentrations of 0.03-ND and 0.009- ND mg/L, respectively, in the Euphrates River within the city of Thi Qar. In this current study, the concentrations of cadmium are within the normal limits.

Lead

As shown in Table (2), the lowest concentration of lead was found in the city of Batha during winter and spring. The highest concentration was found in the city of Chibayish during summer, i.e., at 0.403mg/ L. This is due to the water evaporation in summer, in addition to the river's low level. **Hussein *et al.* (2023)** found a clear increase in heavy metal concentrations, especially lead and nickel, during rainy days in the Euphrates River within the city of Thi Qar. **Jawed and Shihab (2024)** observed lead concentrations of 0.017- ND and 0.061- ND mg/L, respectively, and attributed the phenomenon to increased temperatures and water evaporation. **Tian *et al.* (2015)** explained that the increase in heavy metal concentrations, including lead, is attributed to the large quantities of liquid waste dumped into the river toward the south of the city. Concentrations are higher in the summer than in the winter related to evaporation and sedimentation, in addition to the disposal of industrial wastewater, car workshop activities, and others. Table (3) shows the average annual concentrations of heavy metal elements (Pb, Cd, Cu, Zn) in the Euphrates River based on water samples taken from the selected sites (Bathaa city, the city center, and Al-Chibayish City) throughout the year. All four elements showed a significant increase in probability level of $P \leq 0.05$ in the city center (Nasiriyah) and the city of Chibayish compared to the city of Batha (control group). The concentrations of the heavy metal elements (Pb, Cd, Cu, Zn) in Chibayish City are 1.961 ± 0.349 , 0.062 ± 0.288 , 0.001 ± 0.005 , and 0.032 ± 0.325 mg/ L of dry weight, respectively, compared to 0.469 ± 0.055 , 0.0130 ± 0.061 , 0.001 ± 0.004 and 0.002 ± 0.009 mg/ L, respectively, in Batha City. The lowest concentration rate was recorded in

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the city of Batha during winter and spring, whilst the highest concentration was recorded in the city of Chibayish during summer.

Table 3. Annual mean concentrations of heavy metals (mg/L) in the Euphrates River within Thi-Qar City and the selected sites

Site \ Parameter	* Zinc con. Mean \pm SD	Copper con. Mean \pm SD	Cadmium con. Mean \pm SD	**Lead con. Mean \pm SD
Batha City	0.055 \pm 0.469 ^b	0.0130 \pm 0.061 ^b	0.001 \pm 0.004 ^b	0.002 \pm 0.009 ^c
Nasiriyah city	0.169 \pm 1.339 ^a	0.057 \pm 0.220 ^a	0.004 \pm 0.008 ^{ab}	0.019 \pm 0.230 ^b
Chibayish city	0.349 \pm 1.961 ^a	0.062 \pm 0.288 ^a	0.001 \pm 0.005 ^a	0.032 \pm 0.325 ^a

* Average \pm standard error is for three replicates.

**Numbers followed by different letters vertically indicate a significant difference at the probability level ($P \leq 0.05$) and vice versa according to Duncan's test.

The heavy metal concentrations in the Euphrates River and the selected sites are as follows in descending order: Chibayish City > Downtown (Nasiriyah) > Batha City. The concentrations according to the element type are as follows in descending order: Zinc > Copper > Lead > Cadmium. The high heavy metal concentrations recorded in Al-Chibayish City (at the end of the river course within the city of Thi Qar) are attributed to various household, industrial, and agricultural wastes.

Concentrations of heavy metals in bottom sediments

Tables (4 and 5) show the variations of heavy metal concentrations (Pb, Cd, Cu, Zn) in the bottom sediments of the Euphrates River taken from the selected sites namely Al-Batha city, downtown (Nasiriyah), and Al-Chibayish City throughout the four seasons of the year. The results in Table (5) show a significant rise in the probability level ($P \leq 0.05$) of heavy metal concentrations for the city center (Nasiriyah) and Chibayish City compared to Batha City (the control group). The concentrations of heavy metal elements (Pb, Cd, Cu, Zn) in the city of Chibayish were 14.97 ± 0.757 , 36.201 ± 0.652 , 0.255 ± 0.027 , and $30.708 \pm 2.341 \mu\text{g/g}$ dry weight, respectively, compared to that of the city of Al-Batha, namely 6.721 ± 0.674 , 12.165 ± 0.962 , 0.100 ± 0.014 , and $14.89 \pm 1.700 \mu\text{g/g}$ dry weight, respectively. The lowest heavy metal concentration was recorded in the city of Batha during winter and spring, whilst the highest concentration was recorded in the city of Chibayish during summer (Table 4).

The heavy metal concentrations in the sediments of the Euphrates River are as follows in descending order: Chibayish City > Downtown (Nasiriyah) > Batha City.

Meanwhile, the heavy metal concentrations according to the type of element are as follows in descending order: Copper > Lead > Zinc > Cadmium. These high heavy metal concentrations are due to the residuals of aquatic organisms and various household industrial and agricultural wastes that have been deposited and accumulated at the bottom of the river (Abdullah *et al.*, 2020; Azemi *et al.*, 2021).

Table 4. Average heavy metal concentrations in the sediments of the Euphrates River throughout the year

Metal	Location	Elemental concentration rates				
		Seasons				Mean
		Spring	Summer	Autumn	Winter	
Zinc	Batha City	5.089	8.221	6.264	7.308	6.720
	Nasiriyah city	10.270	14.095	12.006	12.267	12.159
	Chibayish city	13.703	17.093	14.094	15.008	14.974
Copper	Batha City	11.224	14.649	12.584	10.202	12.164
	Nasiriyah city	20.407	43.533	33.674	26.870	31.121
	Chibayish city	23.468	51.480	39.79	30.611	36.337
Cadmium	Batha City	0.090	0.132	0.114	0.066	0.100
	Nasiriyah city	0.156	0.289	0.199	0.144	0.197
	Chibayish city	0.223	0.322	0.277	0.149	0.242
Lead	Batha City	10.282	18.084	16.657	14.537	14.89
	Nasiriyah city	20.921	30.850	24.467	20.921	24.289
	Chibayish city	23.897	37.233	39.978	28.723	32.45

Table 5. Annual mean heavy metal concentrations (micrograms / g dry weight) in the sediments of the Euphrates River in the city of Thi Qar and the selected sites

Parameters Site	* Zinc con. Mean \pm SD	Copper con. Mean \pm SD	Cadmium con. Mean \pm SD	**Lead con. Mean \pm SD
Batha City	0.674 \pm 6.721 ^c	0.962 \pm 12.165 ^b	0.014 \pm 0.100 ^b	1.700 \pm 14.89 ^b
Nasiriyah City	0.782 \pm 12.160 ^b	4.944 \pm 31.121 ^a	0.032 \pm 0.197 ^a	2.858 \pm 24.29 ^a
Chibayish City	0.757 \pm 14.975 ^a	6.052 \pm 36.201 ^a	0.027 \pm 0.255 ^a	2.341 \pm 30.708 ^a

* Average \pm standard error is for three replicates.

**Numbers followed by different letters vertically indicate a significant difference at the probability level ($P \leq 0.05$) and vice versa according to Duncan's test.

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As expected and prevalent in most bodies of water, it was found that the sediments of the Euphrates River had higher heavy metal concentrations than in the waters of the river. The results obtained for the bottom sediments of the Euphrates River can be compared with the standards of heavy metal elements for sediments, as shown in Table (6) (Engler, 1980) and the WHO permissible limits of soil.

Table 6. Comparison of heavy metal concentrations in the studied sediments with heavy metal standards for sediments and the Earth's crust

Metal	Amount of the element in the studied sediments (µg/mg) of dry weight	Unpolluted	Lightly polluted	Heavily polluted	Natural amount of an element in the earth's crust (mg\ kg)
Zinc	14.975	90>	90-200	<200	80
Copper	36.201	25>	25-25	<50	70
Cadmium	0.255	–	–	<6	0.20
Lead	30.708	40>	40-60	<60	16

CONCLUSION

The heavy metal concentrations in the water of the Euphrates River are as follows in descending order: Zinc > Copper > Lead > Cadmium. The heavy metal concentrations in the sediments are as follows in descending order: copper > lead > zinc > cadmium. Additionally, zinc, copper, and lead have higher concentrations in the river water and sediments compared to cadmium.

Heavy metal concentrations in the sediments are higher than in the waters of the Euphrates River, signifying their environmental importance. The sediments are the final destination for pollutants in the aquatic environment, following their entrance into the food chain. These pollutants pose a threat to the environment and humans. However, the heavy metal concentrations in the sediments are well below local and global thresholds.

RECOMMENDATION

1. Continuing quality control of the Euphrates River water and maintaining its quality and cleanliness is everyone's responsibility. All precautions must be taken to prevent pollution in the river and to protect it from all sources of pollution.
2. Efficient treatment at the source or the central treatment of wastewater is crucial before it is disposed of to the river, with strict adherence to the Iraqi environmental conditions.
3. It should be made mandatory for large industries and commercial activities to treat their wastes at the production site before disposing them into the river.

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