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Original Article

Heavy metal pollution in water, sediment, and Asian clam, *Corbicul fluminea*, in three different regions of the Euphrates River

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Abstract: The Euphrates River, a vital waterway in the Middle East, faces numerous environmental threats. The Asian clam, *Corbicula flaminea*, is an invasive bivalve species native to Southeast Asia, known for its rapid growth and limited lifespan. This study aimed to estimate the heavy metal pollution of Manganese, Nickel, Strontium, Vanadium, Cadmium, Lead, Iron, and Copper using *C. flaminea*, sediments, and water samples collected from three different regions along the Euphrates River in the two seasons of winter and summer seasons. The results showed that the sediment (493.82±12.08) had the greatest mean Mn content, followed by Mollusca (104.915±33.215) and water (147.6±78.4). Similarly, sediment had the greatest mean Ni content (104.565±24.335), followed by mollusks (32.29±5.91) and water (19.8±3.6). With the highest amount found in water samples (1338.5±121.5), Sr revealed the greatest variances across the three sample types, followed by Mollusca (296.785±148.215) and sediments (227.795±27.105). The sediment also contained a significant amount of V (32.655±7.245). The samples from Al-Fadhli showed higher concentrations of Cd, Cu, Ni, Pb, and Sr in the winter and higher concentrations of other heavy metals, Mn, V, and Fe, in the summer.

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Introduction

The Euphrates River is a significant waterway in the Middle East, as it crosses Turkey, Syria, and Iraq to the Persian Gulf. The river provides water for millions of people in the area, and its environment is home to many flora and fauna. However, several environmental threats undermine the Euphrates River's water quality and ecological health (Akullian et al., 2015). Industrial activities, especially in the river's downstream parts in Syria and Iraq, are major contributors to Euphrates' pollution. Untreated industrial wastewater is a major contributor to river pollution because it carries a wide variety of contaminants, such as heavy metals and organic pollutants, into the water system. Accidental spills and leaks from industries like oil and gas extraction and mining may also pollute rivers (Alengebawy et al., 2021). Pollution of the Euphrates River also originates from agricultural activities. Agricultural pesticides and fertilizers pollute the river's water and sediment via runoff and leaching. In addition, nutrient loading and bacterial pollution may be exacerbated by raising animals and disposing of untreated animal waste in rivers. Insufficient treatment and toxins entering sediment and groundwater threaten human and environmental health. Reducing pollution involves sustainable agriculture practices, improved wastewater treatment facilities, community education, and awareness-raising (Agul and Beyhan, 2020).

The Asian clam, *Corbicul fluminea*, is endemic to the waters of Southeast Asia. One of the most invasive bivalves has spread over the Americas, Europe, and the Atlantic Ocean (Al-Rawi, 2020). Probably brought there as a food source by Chinese immigrants. It was first documented in North America on the Pacific Coast in 1924 (Gomes et al., 2018; Awad Turki and Abid Maktoof, 2019). As early as 1971 (Hammood, 2011) reports of the species were made in the James River, and by 1975, it was discovered in the tidal freshwater Potomac River near the Atlantic coast (Issa

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Table 1. Longitude and Latitude of the studied stations.

Region	Longitude	Latitude
Suq al-Shiyookh	640312	3419119
Nasiriyah	618637	3435136
Al-Fadhli	626735	3426057

and Qanbar, 2016). *Corbicul fluminea* has been present in Chesapeake Bay tributaries since the 1970s, but little evidence exists in York River and Mattaponi and Pamunkey Rivers (Krzymowski, 2021). It matures quickly to a maximum length of 50 mm and lives for two to four years (Losso and Ghirardini, 2010; Mitra et al., 2022). Corbicula is an invasive species that threatens most U.S. River systems because its establishment is facilitated by human-caused disturbances (Moor et al., 2001). There have been reports of as many as 2,000 clams per square meter where Corbicula is predominated by benthos (Parra et al., 2021). Over 10,000 Corbicula were counted on a single square meter in Lake Tahoe in 2010 (Singh et al., 2022). Asian clams are ubiquitous and may be found in any substrate. However, they favor those with finer grains like sand (Sojka and Jaskuła, 2022).

Corbicula fluminea has a unique reproductive process, androgenesis, and asexual offspring (Sousa et al., 2008). Its embryos are brooded in the adult demibranchs, much as mussel embryos; however, Corbicula does not need a fish host to mature. Seasonal shifts in temperature are closely related to the peak times for reproduction, which are autumn and spring (Zhou et al., 2008). They achieve sexual maturity in as little as six months, and their high reproductive rates and ability to colonize new territories help their spread and expansion (Zhou et al., 2016). Corbicula is a filter-feeder, impacting nutrition availability and turbidity, with potential benefits or negative impacts depending on context. In Washington DC, submerged vegetation flourished, while nuisance algae declined (Margiana et al., 2022). On the other hand, the invasion of Corbicula in Lake Tahoe, California resulted in the formation of nutrient hotspots due to the concentration of clam bio deposits. Bacteria and filamentous algae flourished in these zones (Arif et al., 2023). Corbicula impacts human activity and stream populations, causing shells to block intake screens in water pipelines and hydroelectric and nuclear power facilities (Parra et al., 2021). Stakeholders in the United States estimate that control and mitigation expenses amount to billions of dollars annually (Gomes et al., 2018). Based on the above-mentioned background, this study was conducted to estimate water pollution using *C. flaminea*, sediments, and water samples collected from three different regions of the Euphrates River.

Materials and Methods

ampling: To explore different aspects of pollution, this work considered three locations for sampling (Table 1) and three types of samples, viz. water, Corbicula calm, and sediment from each site during two seasons of winter and summer. The first station (St. 1) was in the middle of Thi-Qar Province, in the southern Iraqi city of Nasiriyah, in regions adjacent to thermal energy pollution and sewage pumps entering from the riverbanks. A river diver was used to collect samples from the river bank and bottom. The second station, which runs through farms and orchards in Al-Fadhli (St. 2), is an agricultural village south of Nasiriyah. The third station meets marshes and swamps in the Suq al-Shiyookh district (St. 3), known as the city of Marshes south of Thi-Qar Province, characterized by the presence of plants such as *Phragmites australis* and *Ceratophyllum demersum*.

Water samples were collected in 2.5L bottles from the sampling stations about 30 cm below the surface. To prevent metal adsorption on the inner surface of the container, the water samples were kept by adding 5 ml of HNO_3 (55%) per liter and storing them at 4°C before analysis. Sediment samples were collected at each station from a depth of 10 cm using a sediment collector with an acid-washed plastic scoop and then transported to the laboratory in polyethylene bags.

They were dried and pulverized using a ceramic mortar and sieved by a 2 mm sieve to remove stones and contaminants before being stored in labeled plastic bottles until the heavy metals were extracted. Mollusca were collected seasonally at the three stations based on the Quadrat method. The collection of Molluscs was done by hand and rinsed multiple times in distilled water before being stored in a refrigerated container. When the samples were brought to the lab, the soft tissues were isolated on the filter papers with plastic forceps, dried at the laboratory temperature, and then placed in the freeze-dryer until dried. Then, they put it in a dryer until it reached room temperature. The materials were thoroughly pulverized in a ceramic mortar and stored in clean, labeled plastic crates until the heavy metals were measured.

Extraction of heavy metals: Three different methods were used to extract the heavy metals from water, sediment, and clams.

Extraction of heavy metals from water: The water sample was treated following APHA. A 50 ml of the water sample was added to a 100 ml beaker, after which 5 ml of concentrated nitric acid was added. The beaker was positioned on the hot plate, slightly removed before reaching a boiling point, and then returned to the plate to continue heating until completely dried and white salt formation occurred. An addition of 2 ml of nitric acid was made until a black color was achieved, after which the beaker was returned to the hot plate by adding 5 ml of ion-free water to ensure complete digestion. The white salt was dissolved with a few drops of 0.5 N hydrochloric acid and then transferred to a 50 ml bottle. The beaker was rinsed several times with ion-free water, with the washings added to the sample until the desired volume was reached. The sample was then filtered through a filter paper of 0.45 μ and stored in sealed bottles until the measurement process was done.

Extraction of heavy metals from *C. fluminea*: The samples were treated following the method described by ROPME as follows: one gram of sample powder was taken (in three replicates) and placed into Pyrex digestion tubes. For each sample, 4.5 mL of concentrated nitric acid and 1.5 mL of concentrated perchloric acid were added. The sample was then shaken well and left for 24 hours to complete the initial digestion process. Then, the tubes were positioned in the block digester at an approximate temperature of 70ºC for three hours, with the time extended if digestion was not complete. The beaker was heated to a temperature of 70ºC until the volume of the sample was reduced to approximately 2 ml, taking care to prevent the sample from drying out. The sample was dissolved in ion-free water and transferred to a 50 ml beaker (preservation bottles), while the previous beaker was washed several times with ion-free water, and the washings were added to the sample to reach a volume of 50 ml. The sample was then centrifuged at a speed of 3500 rpm using plastic tubes for 30 min. The resulting filtrate was collected and transferred to the original preservation bottles. The sample was then stored in the refrigerator until it was required for the measurement process.

Extraction of heavy metals from sediments: Sediment sample collection was done following the instructions described by Moor et al. (2001), which include the following; the samples were dried at 105°C for 3 h. About 0.2 g of sample was accurately weighed into a container and placed in a microwave pressure vessel. After adding 4 ml of concentrated nitric acid and 0.5 ml of concentrated hydrofluoric acid, the samples were digested using microwave power, progressively increasing up to 400 W for 40 min. After cooling, the solutions were accurately diluted to 100 ml with water. In addition, open digestion in a glass beaker was performed with 0.5 g of sample, accurately weighed, by heating with 12 ml of water for 45 min, followed by evaporation almost to dryness. To the hot residue, 2.5 ml of concentrated hydrochloric acid and 2.5 ml of hydrogenperoxide were added, followed by accurate dilution to 50 ml with water. One replicate per digestion method was done for each sample. They were analysed directly by ICP-MASS.

Determination of heavy metal contents: The heavy metal contents, including the Manganese, Nickel, Strontium, Vanadium, Cadmium, Lead, Iron, and

Table 2. The heavy metal concentrations in different sample types in the Nasiriyah station.

Heavy metals	Water	Mollusca	Sediment	sig
Cadmium	0.185±0.085	1.515±0.385	6.61±6.39	0.513
Copper	4.65±0.05	52.09±32.69	41.43±13.17	0.354
Manganese	147.6±78.4	104.915±33.215	493.82±12.08	0.021
Nickel	19.8±3.6	32.29±5.91	104.565±24.335	0.048
Lead	0.185±0.085	11.545±0.555	33.755±23.745	0.345
Strontium	1338.5±121.5	296.785±148.215	227.795±27.105	0.01
Vanadium	7.35±2.25	2.255±0.355	32.655±7.245	0.031
Iron	89.35±22.65	356.59±258.21	1625.225±829.675	0.215

Table 3. The heavy metal concentration levels in different sample types in the Al-Fadhli region.

Heavy metals	Water	Mollusca	Sediment	sig
Cadmium	9.15±9.05	1.655±1.245	4.93±4.77	0.702
Copper	178.25±173.75	67.925±16.325	33.17±8.03	0.62
Manganese	698.5±521.5	76.275±37.475	526.74±100.56	0.44
Nickel	29.9±14.9	16.72±6.58	119.75±28.95	0.058
Lead	78.05±77.95	19.45±19.05	21.01±14.59	0.648
Strontium	1382±148	182.875±80.625	243.435±35.465	0.006
Vanadium	6.45±1.25	1.5±0	40.94±15.16	0.09
Iron	79.75±10.45	389.24±315.86	1578.03±702.87	0.183

Copper of all samples, were determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using Thermo Scientific iCAP Qc system. All quantitative measurements in triplicates, in standard mode (STD), were performed using the instrument's software Qtegra; relative standard deviation (RSD) values were calculated, being less than 10%. Several well-known isobaric interferences were automatically corrected. The results were presented as mean ± standard error and the significance level of the probability test.

Results

The levels of metal elements in three different samples collected from the Nasiriyah region, water, mollusca, and sediment, are shown in Table 2. Differences were found in the levels of metal elements between the three samples, e.g., the mean concentration of Mn was highest in sediment (493.82±12.08) followed by mollusca (104.915±33.215) and water (147.6±78.4). Similarly, the mean concentration of Ni was highest in sediment (104.565±24.335), followed by Mollusca (32.29±5.91) and water (19.8±3.6). Sr showed the most differences between the three sample types, with the highest level recorded in water (1338.5±121.5) followed by Mollusca (296.785±148.215) and sediments (227.795±27.105). However, V was recorded as a strong high level in sediments (32.655±7.245).

Tables 3 and 4 summarize the results of the studied metals in the samples collected from the second and third stations, i.e., the Al-Fadhli Suq Al-Shiyookh district, respectively. In station 3, the sediment showed a significantly higher level of V (36.275±9.225), and in the water samples, a significantly higher level of Cu (219.26±17.74). The heavy metals in studied samples according to season are shown in Table 5. Except for Sr, which indicated the contrary, the samples from Nasiriyah revealed higher amounts of heavy metals in the winter. The samples from Al-Fadhli revealed higher concentrations of Cd, Cu, Ni, Pb, and Sr in the winter and higher concentrations of other heavy metals, Mn, V, and Fe, in the summer. The samples from the Suq al-Shiyookh revealed levels of Cd, Cu, Ni, Pb, and Sr that were higher in the winter.

Discussions

Heavy metal pollution in rivers is an environmental issue of global significance, posing severe risks to

Table 4. The heavy metal concentration levels in different sample types in the Suq al-Shiyookh district.

Heavy metals	Water	Mollusca	Sediment	sig
Cadmium	7.35±7.25	36.765±35.535	2.83±2.17	0.537
Copper	219.26±17.74	91.575±31.875	52.84±12.34	0.006
Manganese	4650.9±4649.1	174.595±64.695	505.17±64.33	0.506
Nickel	40.05±27.85	24.47±0.17	111.675±9.025	0.067
Lead	374.05±373.95	27.91±9.49	26.555±3.245	0.507
Strontium	1458±642	254.35±118.35	220.78±31.02	0.165
Vanadium	6.3±1.4	2.33±0.33	36.275±9.225	0.038
Iron	277.25±234.75	452.46±152.14	1363.025±542.375	0.211

Table 5. The heavy metals concentrations in the two seasons in the studied regions.

Metals	Nasiriyah		Al-Fadhli		Suq al-Shiyookh		P-Value
Season	Winter	Summer	Winter	Summer	Winter	Summer	
Cadmium	0.75±0.57	4.78±4.11	7.06±5.62	3.42±3.13	29±22.05	2.29±1.3	0.407
Copper	122.3±51.85	375.25±118.76	478.6±372.84	389.07±149.40	3137.23±3081.54	416.54±96.09	0.426
Manganese	25.93±6.47	78.50±29.60	27.7±8.87	83.21±40.17	34.8±16.91	82.66±29.47	0.973
Nickel	4.15±3.97	26.16±15.66	64.86±46.89	14.14±10.86	261.83±243.32	23.84±3.29	0.428
Lead	9.56±4.91	55.88±16.32	136.03±108.83	50.19±17.64	166.07±136.50	76.37±24.59	0.447
Strontium	1040.66±305.98	201.38±30.69	1009.16±382.49	196.37±51.32	1096.23±517.94	192.52±33.45	0.994
Vanadium	5.53±2.23	22.64±10.85	4.8±1.80	27.73±15.79	4.86±1.64	25.07±12.40	0.978
Iron	264.5±175.63	1116.27±698.91	288.2±208.53	1076.48±645.15	386.36±173.99	1008.79±472.79	0.999

aquatic ecosystems and human health (Sousa et al., 2008). Understanding the pathways of heavy metal pollution and employing comprehensive monitoring strategies encompassing sediments, water, and bioindicators, such as *C. fluminea*, are pivotal steps toward effective management and remediation (Margiana et al., 2022). Heavy metals can enter rivers through various anthropogenic activities, such as industrial discharge, agricultural runoff, and urban waste disposal (Lei et al., 2022). Once introduced into the river systems, these metals do not degrade and can bioaccumulate in living organisms, causing harmful effects ranging from growth impairment to acute toxicity (Issa and Qanbar, 2016).

Sediments in river ecosystems often act as sinks for these pollutants, storing them for long periods. Heavy metals can bind to particles and settle in sediment layers, impacting the benthic communities and posing a risk of secondary pollution if disturbed (Mitra et al., 2022). Sediment quality is a key determinant of the overall health of aquatic ecosystems and provides a historical record of pollution events. Analyses of sediment samples can reveal the presence, concentration, and distribution of heavy metals, enabling us to understand the extent of contamination and predict potential threats (Sousa et al., 2008; Zhou et al., 206, 2018; Parra et al., 2021; Singh et al., 2022; Sojka and Jaskuła, 2022). Water, the immediate medium of transport for these metals, is a crucial component to monitor. The concentrations of heavy metals in water can show real-time pollution levels and indicate the sources of contamination when combined with flow data. Techniques like atomic absorption spectrometry and inductively coupled plasma mass spectrometry are often employed to detect and quantify these metals in water samples (Lei et al., 2022; Abbas et al., 2022; Hussein et al., 2022; Al-Jassani et al., 2022; Lafta et al., 2023; Sane et al., 2023; Al Anazi et al., 2023; Hjazi et al., 2023). *Corbicul fluminea*, has recently gained attention as a bioindicator of heavy metal pollution. Due to their filter-feeding habit, these clams accumulate heavy metals in their tissues, reflecting the metal load in the environment (Algül and Beyhan, 2020; Krzymowski, 2021). Studying the metal concentration in these organisms gives a biologically relevant measure of the pollution levels that other organisms are exposed to. Furthermore, their widespread distribution and ease of sampling make them a practical choice for monitoring (Althomali et al., 2023; Hjazi et al., 2023; Gupta et al., 2023; Al-Dolaimy et al., 2023; Al-Hawary et al., 2023; Zaman et al., 2023).

The results of this study showed a high level of metal pollution in the site of collection Nasiriyah, which has been studied before for pollution, and showed that the Euphrates River was classified under category 4 (Poor) (Arif et al., 2023). And in the published report of the International Organization for Migration reported that Nasiriyah presented the highest TDS levels, which makes the water unfit for irrigated agriculture according to the model. With respect to BOD_5, the highest levels are found in Thi-Qar (Nasiriyah). Salinity levels are particularly high in Thi-Qar. The results agreed with a previous study that showed the same trace elements that focused on assessing heavy metal contamination in Euphrates River sediments from the Al-Hindiya barrage to Al-Nasiria City, South Iraq (Moor et al., 2001).

The comparison of trace metal levels in the water from three distinct environments – Nasiriyah near an electricity production facility, al-Fadhli agricultural region, and Suq al-Shiyookh with many aquatic plants – indicates different factors impacting the water quality in each location, which showed that the higher levels of heavy metals in the region of Suq al-Shiyookh followed by al-Fadhli and the lower levels of heavy metals are shown in Nasiriyah. the possible reasons for those results can be the electricity production facility in Nasiriyah might have effective emission controls. This might limit the release of heavy metals like Cd, Mn, Ni, Pb, Cu, Sr, V, and Fe into the local water supply (Zhu et al., 2016). In contrast, the farming region of Al-Fadhli may experience agricultural runoff, which can contain high levels of certain heavy metals. This can be due to several reasons, such as using pesticides and fertilizers, or irrigation with contaminated water. Some of these substances can accumulate in the soil and gradually seep into groundwater or runoff into surface water, thereby increasing the heavy metal levels (Awad Turki and Abid Maktoof, 2019). Aquatic plants in Suq al-Shiyookh could play a role in bioremediation, a process that uses living organisms to clean up polluted water. Certain aquatic plants are known to absorb heavy metals from their environment, a process known as phytoremediation. The relatively higher levels of heavy metals in this region might suggest that these plants absorb metals from the water, concentrating them in their tissues. However, it is important to note that this process could be overwhelmed if the input of metals is too high or too continuous (Althomali et al., 2023; Al-Dolaimy et al. 2023; Al-Hawary et al., 2023; Zaman et al., 2023; Khursheed et al., 2023).

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