

Evaluating the Levels of Heavy Metals Pollution in the Water and Sediments of Khor Al-Zubair, Southern Iraq, Using Heavy Metal Pollution Index (HPI)

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ARTICLE INFO

Article History:

Received: May 29, 2025

Accepted: Aug. 1, 2025

Online: Aug. 19, 2025

Keywords:

Heavy metals,
Heavy metal
pollution index,
Khor AL- Zubair

ABSTRACT

The present study aimed to assess the levels of heavy metal contamination in the water and sediments of Khor Al-Zubair using the Heavy Metal Pollution Index (HPI). Three stations were selected: the first at the Mangrove, the second at the Army Canal, and the third at the Free Zone. Samples were collected quarterly from January to December 2024, at low tide, with one sample taken from each station per sampling period. The pH values of the water were in the alkaline range, and the soil texture at all stations was silty and clayey. The results indicated that the region was particularly rich in nickel, followed by lead in both water and sediments, cobalt in the water, cadmium in the sediments, and then cadmium in the water and cobalt in the sediments. Copper was the least abundant metal in both water and sediments. When compared with global environmental guidelines (WHO) and the local River Conservation System (2011), the concentrations of all measured metals in both water and sediments exceeded the permissible limits and were higher than previously recorded concentrations in the region. Sediment samples consistently showed higher metal concentrations than water samples. This is attributed to the silty clayey soil, which has a high capacity to retain heavy metals, as well as to the elevated sedimentation rates of these metals in the study area.

INTRODUCTION

Heavy metals pose a serious threat to human health, living organisms, and marine ecosystems due to their toxicity, persistence, and potential for bioaccumulation (Naser, 2013; Alhamadany *et al.*, 2021). High concentrations of heavy metals in marine ecosystems are a major pollutant because they can be toxic and may enter the food chain. Once bioaccumulated in marine organisms, these metals can exceed threshold levels, posing risks to both the environment and human health (Huang *et al.*, 2022).

Heavy metals are defined as transition metals located between the second and sixth groups of the periodic table, with a density exceeding 5g/ cm³ (Aldoghachi, 2022). They

are sometimes found naturally in the Earth's crust in trace amounts—hence the term *trace metals*. In living organisms, certain heavy metals occur at very low concentrations because they are essential for biological functions (**Balasubramanian, 2012; Abed *et al.*, 2025**). However, they are unique since they are highly stable, persist in the environment for long periods without decomposition, cannot be eliminated through metabolic processes, and are resistant to weathering (**Al-Tamimi & Al-Farjawi, 2008**). Furthermore, they can biomagnify and bioaccumulate as they move through different trophic levels in the food chain, ultimately reaching humans (**Yaseen *et al.*, 2018**).

In sediments, heavy metals occur in several chemical forms: as exchangeable metals loosely bound to particles; bound to carbonates and therefore sensitive to pH changes; associated with iron oxides and partially amorphous manganese; bound to amorphous and weakly crystalline iron oxides; linked to organic matter and sulfides; and as residual metals strongly incorporated within minerals, which are related to the origin or formation of sediments (**Al-Atbee *et al.*, 2019**).

The sources of heavy metal pollution in Khor Al-Zubair are diverse. Industrial facilities in the area, particularly petrochemical, fertilizer, and iron and steel plants, are the primary contributors to the accumulation of these metals in water and sediments (**Al-Imarah *et al.*, 2018**). Sediments may also release heavy metals back into the water when their surfaces become saturated, especially under conditions of increased temperature and water flow (**Al-Haidarey *et al.*, 2010**).

Khor Al-Zubair is a tidal marine inlet located in the northern Arabian Gulf, characterized by a mixed tidal system with both daily and semi-daily tides, although the latter predominates (**Al-Ramadan, 1986**). The waterway experiences two types of tidal cycles—rising and falling—showing slight variations in height and timing. This navigation channel is approximately 40km long and 40km deep, ranging from 10–20m in depth and 1–2km in width at high tide (**Hassan *et al.*, 2023**). Economically, it is an important site for fisheries and shipping. However, the discharge of industrial wastewater from petrochemical, fertilizer, and iron and steel industries, along with untreated sewage, has significantly altered water quality and contributed to pollution (**Al-Shaheen & Abdullah, 2021**).

MATERIALS AND METHODS

Study area

Three stations were selected in Khor Al-Zubair, southern Iraq, with their coordinates presented in Table (1) and Fig. (1). The study area is notable for containing the Khor Al-Zubair oil port, which accommodates giant oil tankers and includes approximately 15 berths, a gas export terminal, and a free zone for receiving container ships and goods. It is also a major industrial zone, hosting numerous large industrial units, most notably

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petrochemical, fertilizer, and iron and steel plants, in addition to smaller factories producing industrial gases.

Commercial fishing is active in the area, targeting fish and other aquatic life such as shrimp, with small and medium-sized boats used for fishing operations. A marina is located near the first station, where boats are regularly washed and cleaned. The region is characterized by tidal activity, experiencing daily ebb and flow. The creek has an average depth of approximately 15 meters, extends for about 40km, and is roughly 700 meters wide.

Table 1. Coordinates of study stations

Station	Name of station	N	E
St1	Mangrove	30°19'33.00"	47°48'56.90"
St2	Army Chanel	30°14'23.30"	47°52'21.90"
St3	Free zone	30°9'53.80"	47°54'1.80"

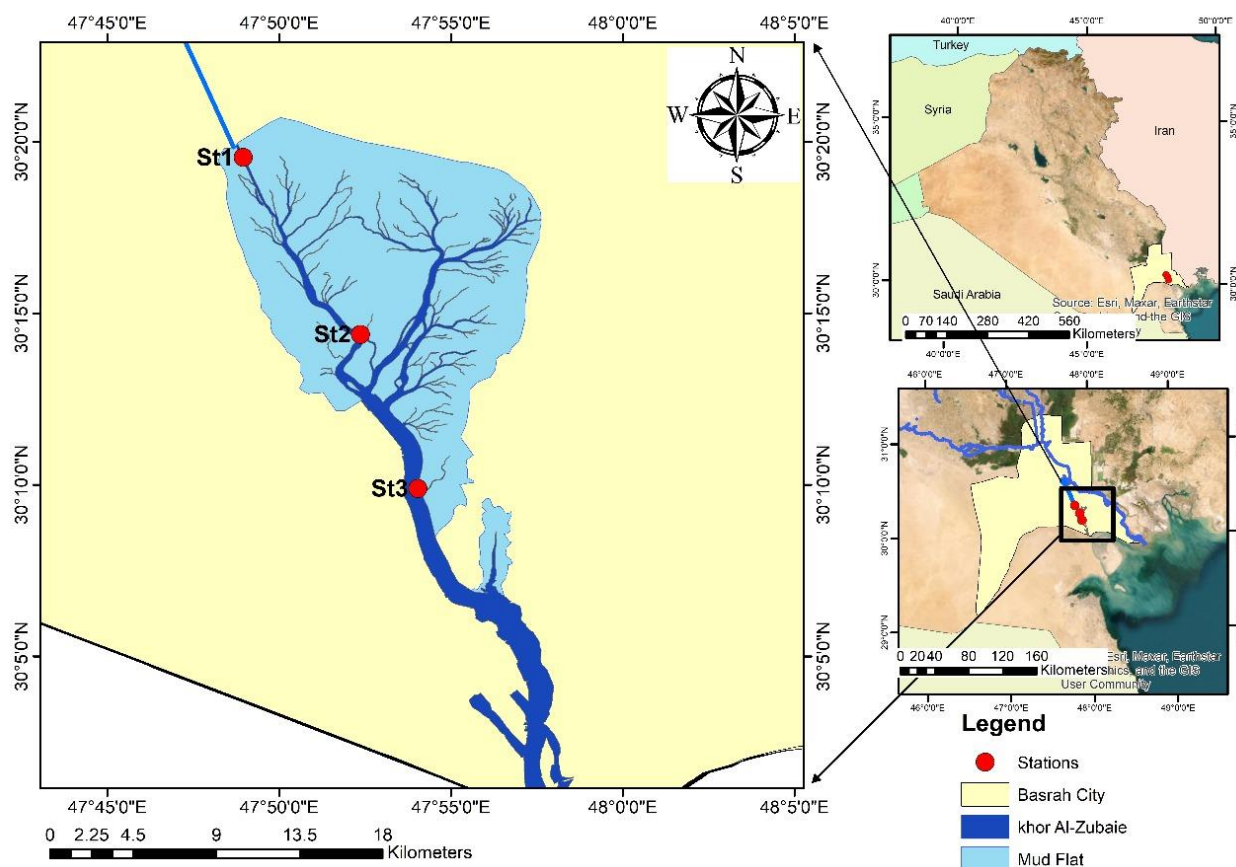


Fig. 1. Map showing study and sample collection stations

Sampling

Samples were collected seasonally at the rate of one sample per season during low tide from the study sites in Khor Al-Zubair between January and December 2024. Water samples were taken at a depth of 20– 30cm using 500mL polyethylene bottles filled completely and preserved with a few drops of concentrated nitric acid (HNO₃) to prevent precipitation of heavy metals. Sediment samples were collected in nylon bags after removing the surface layer, using a hand shovel to obtain sediments from partially submerged areas. In the field, the pH of the water was measured using a German-made pH 3110 WTW meter.

Laboratory work

Sediment samples were air-dried, ground, and sieved through a 63µm sieve, then stored in nylon bags until digestion. Water samples were digested following the method described by **Baird *et al.* (2017)**. In this procedure, 100mL of water was treated with 5mL of concentrated HNO₃ and 1mL of concentrated hydrochloric acid (HCl), then placed on a hot plate until completely dry. The residue was diluted with deionized water to 25mL and stored in plastic containers until analysis. Concentrations of cadmium, lead, nickel, copper, and cobalt were measured using an atomic absorption spectrometer.

Sediment samples were digested according to **Sturgeon *et al.* (1982)** after sieving through 63µm mesh. A mixture of concentrated HCl and HNO₃ in a 1:1 ratio was added, and the sample was evaporated to near dryness on a hot plate at 80°C. A second 1:1 mixture of concentrated HCl and hydrofluoric acid (HF) was then added, followed by another evaporation to near dryness. Finally, 20mL of 0.5% HCl was added, and the sample was diluted with demineralized water to 25mL before being stored in plastic bottles for analysis with an atomic absorption spectrometer.

Soil texture was determined once during the study period at the three stations following the method described by **Folk (1974)**.

Heavy metal pollution index (HPI)

The HPI was calculated according to the method described by **Reza and Singh (2010)**, which assesses the combined effect of all measured heavy metals on the overall quality of water. In this index, a weight (WiW_iWi) is assigned to each element, ranging from zero to one, reflecting the relative importance of each element in the calculation:

$$W_i = K / S_i$$

Where: Wi = unit weight of the ith metal; K = 1 (constant of proportionality); Si = recommended standard value of the ith metal.

The sub-index for each metal (Qi) was calculated as:

$$Q_i = 100 v_i / S_i$$

Where: Qi = sub-index of the ith metal; vi = observed concentration of the ith metal (µg L⁻¹).

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The overall HPI was then calculated according to **Mohan *et al.* (1996)** as:

$$\text{HPI} = \Sigma(Q_i \times W_i) / \Sigma W_i$$

Where: n = number of metals analyzed.

An HPI value of 100 is considered the critical pollution threshold. Values above this level indicate increasingly critical contamination and greater potential risk to public health.

Statistical analysis

The statistical program Minitab 16.3 was used for analysis of variance (ANOVA), and significant differences were determined using the RLSD test to identify temporal and spatial variations. In addition, Canoco version 4.54 was applied for principal component analysis (PCA) to explore possible relationships between variables.

RESULTS

A decrease in pH toward acidity leads to the sedimentation of heavy elements, and when its value increases, minerals precipitate, so it is a basic factor in the dissolution and release of elements in water (**Mitra *et al.*, 2018**). Table (2) summarizes the pH results at the three study stations:

The highest average pH value of the water was recorded at the first station (8.52 ± 0.33), followed by the third station (8.45 ± 0.23) and the second station (8.29 ± 0.18). All values remained in the alkaline range throughout the study period. Statistical analysis showed no significant differences ($P > 0.05$) between stations or seasons.

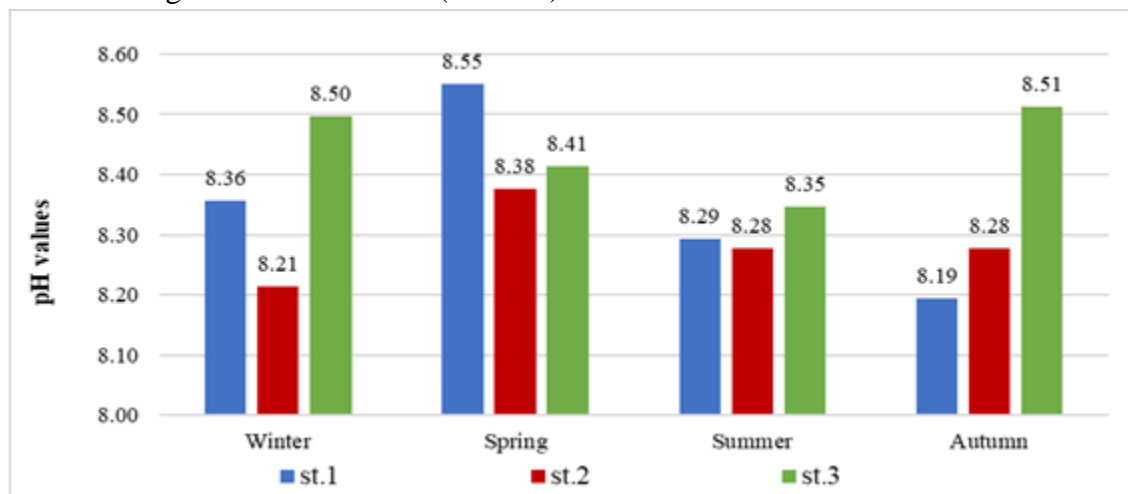


Fig. 2. pH values at the study stations.

Heavy elements are a major environmental concern in urban areas that suffer from heavy element pollution, which has various sources, including human sources such as industrial emissions and traffic, and natural sources, where the soil acts as a natural store

and sink for heavy elements and other various pollutants (Al-Hejuje *et al.*, 2017). The results of soil texture (Fig. 3) showed that the soil type in the study area is silty to silty clayey at all study stations.

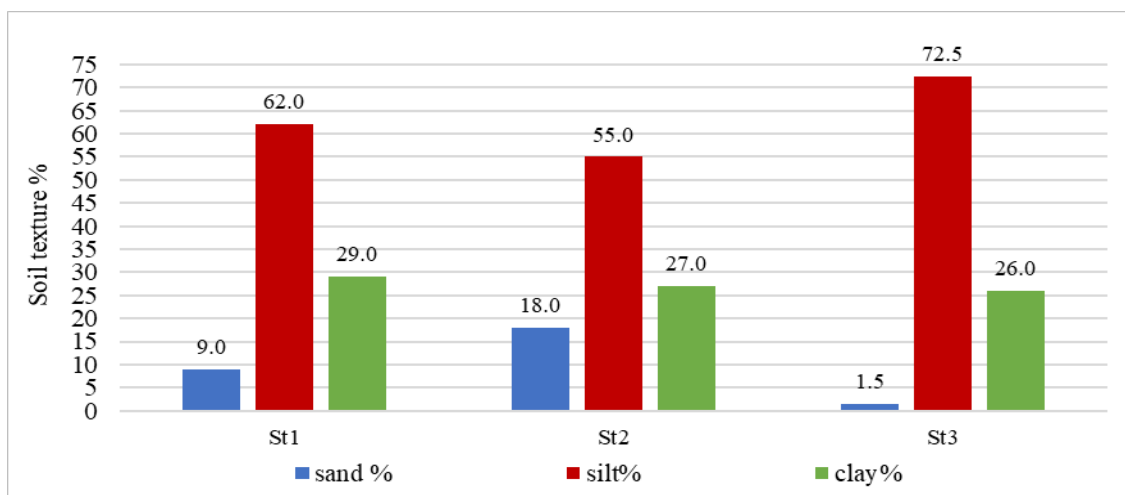


Fig. 3. Soil texture at the study stations

Tables (3, 4) represent the concentrations of heavy elements in the water and sediments of Khor Al-Zubair. Five elements were selected. The study recorded high concentrations of heavy elements (Cd, Pb, Ni, Cu, Co) in the water, as most of the elements exceeded the limits permitted by the Iraqi systems for rivers maintenance affiliated with the **Ministry of Environment (2010)** and the **US-EPA (2022)**, except for the copper element, which recorded concentrations below the mentioned environmental limits for all stations and seasons. As for the other sediments, they recorded concentrations higher than the water in all stations and seasons, which exceeded the limits of **CCME (1999)** and the limits of **CBSQG (2003)** for all elements except for the copper element, whose results were close to those of **CBSQG (2003)**.

Table 2. Mean and standard deviation of heavy metals in water $\mu\text{g. l}^{-1}$ of the three study stations during seasonal variation

Element	St1	St2	St3	US -EPA (2022)	Iraqi systems for rivers maintainance (2010)
Cd	66.83±19.62	67.98±15.23	63.76±11.84	5	5
Pb	116.19±17.62	125.97±13.21	142.99±6.34		50
Cu	36.78±5.22	39.01±9.94	36.75±9.41	1000	50
Ni	123.67±24.84	130.73±28.69	138.90±22.49		50
Co	75.52±14.86	87.05±17.70	90.63±12.64	50	50

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Cadmium concentrations in water were highest at the second station, with an average of $67.98 \pm 15.23 \mu\text{g L}^{-1}$, followed by the first station ($66.83 \pm 19.62 \mu\text{g L}^{-1}$) and the lowest average at the third station ($63.76 \pm 11.84 \mu\text{g L}^{-1}$) (Table 2). Statistical analysis showed no significant differences ($P > 0.05$) between stations. Seasonally, the highest concentration ($77.6 \mu\text{g L}^{-1}$) was recorded at the second station in summer, while the lowest ($51.2 \mu\text{g L}^{-1}$) was observed at the first station in autumn. No significant seasonal differences ($P > 0.05$) were detected.

In sediments, the highest average cadmium concentration was recorded at the third station ($144.64 \pm 51.50 \mu\text{g g}^{-1}$ dry weight), followed by the second station ($132.33 \pm 79.58 \mu\text{g g}^{-1}$ dry weight), and the lowest at the first station ($113.68 \pm 69.57 \mu\text{g g}^{-1}$ dry weight) (Table 3). Seasonally, the highest concentration ($218.5 \mu\text{g g}^{-1}$ dry weight) occurred at the third station in summer, while the lowest ($92.4 \mu\text{g g}^{-1}$ dry weight) was recorded at the first station in autumn. Statistical analysis revealed no significant differences ($P > 0.05$) between stations or seasons.

Overall, cadmium concentrations in sediments were higher than in water. Statistical analysis indicated an inverse correlation between cadmium concentrations in water and sediments. The highest concentrations in both matrices were recorded during summer at all stations, and no clear spatial distribution pattern of cadmium was observed across the study sites.

Table 3. Mean and standard deviation of heavy metals in sediments $\mu\text{g g}^{-1}$ dry weight of the three study stations during seasonal variation

Element	St1	St2	St3	CCME (1999)	CBSQG (2003)
Cd	113.68±69.57	132.33±79.58	144.64±51.50	3.5	0.99
Pb	179.38±55.56	167.38±53.24	161.70±45.04	91.3	36
Cu	36.78±5.22	39.01±9.94	36.75±9.41	197	32
Ni	123.67±24.84	130.73±28.69	138.90±22.49	-	23
Co	75.52±14.86	87.05±17.70	90.63±12.64	-	-

The spatial distribution of lead in water showed a decreasing pattern from the third station toward the first station. The highest average concentration was recorded at the third station ($142.99 \pm 6.43 \mu\text{g L}^{-1}$), followed by the second station ($125.97 \pm 13.21 \mu\text{g L}^{-1}$), and the lowest at the first station ($116.19 \pm 17.62 \mu\text{g L}^{-1}$) (Table 2). Statistical analysis revealed a significant difference ($P \leq 0.05$) between the first and third stations. Seasonally, the highest concentration ($150.4 \mu\text{g L}^{-1}$) was recorded at the third station in winter, while the lowest ($144.0 \mu\text{g L}^{-1}$) was observed in autumn at the same station.

In sediments, lead concentrations were at their highest values at the first station ($179.38 \pm 55.56 \mu\text{g g}^{-1}$ dry weight), followed by the second ($167.38 \pm 53.24 \mu\text{g g}^{-1}$ dry weight) and the third ($161.70 \pm 45.04 \mu\text{g g}^{-1}$ dry weight) stations (Table 3). The maximum

seasonal concentration ($234.3\mu\text{g g}^{-1}$ dry weight) was recorded at the first station in summer, while the lowest ($103.2\mu\text{g g}^{-1}$ dry weight) occurred at the second station in autumn. No significant differences ($P > 0.05$) were observed between stations, but seasonal differences were significant ($P \leq 0.05$). Overall, lead concentrations were significantly higher in sediments than in water ($P \leq 0.05$), with an inverse correlation between the two matrices.

For copper in water, the highest average concentration was recorded at the second station ($39.01 \pm 9.94\mu\text{g L}^{-1}$), followed by the first ($36.78 \pm 5.22\mu\text{g L}^{-1}$) and third ($36.75 \pm 9.41\mu\text{g L}^{-1}$) stations (Table 2). The maximum concentration ($53.3\mu\text{g L}^{-1}$) occurred in summer at the second station, while the lowest ($24.6\mu\text{g L}^{-1}$) was in winter at the third station. Statistical analysis showed no significant differences ($P > 0.05$) between stations or seasons.

Copper concentrations in sediments were the highest at the third station ($84.51 \pm 20.08\mu\text{g g}^{-1}$ dry weight), followed by the second ($72.04 \pm 8.42\mu\text{g g}^{-1}$ dry weight) and the first ($64.92 \pm 6.48\mu\text{g g}^{-1}$ dry weight) stations (Table 3). The highest seasonal concentration ($105.1\mu\text{g g}^{-1}$ dry weight) occurred in summer at the second station, and the lowest ($56.9\mu\text{g g}^{-1}$ dry weight) was in autumn at the first station. No significant spatial or seasonal differences ($P > 0.05$) were detected.

Nickel in water followed a descending pattern from the third to the first station, with average concentrations of 138.90 ± 22.49 , 130.73 ± 28.69 , and $123.67 \pm 24.84\mu\text{g L}^{-1}$, respectively (Table 2). The highest value ($169.4\mu\text{g L}^{-1}$) occurred in summer at the third station, while the lowest ($100.3\mu\text{g L}^{-1}$) was in winter at the first station. No significant differences ($P > 0.05$) were observed between stations or seasons.

In sediments, nickel concentrations were highest at the third station ($215.10 \pm 36.98\mu\text{g g}^{-1}$ dry weight), followed by the second ($213.45 \pm 37.60\mu\text{g g}^{-1}$ dry weight) and the first ($194.88 \pm 37.37\mu\text{g g}^{-1}$ dry weight) stations (Table 3). Seasonal peaks occurred in summer at all stations, with the lowest concentrations in autumn at the first station. Values ranged from 256.1 to $151.4\mu\text{g g}^{-1}$ dry weight. No significant spatial or seasonal differences ($P > 0.05$) were found.

Cobalt concentrations in water were the highest at the third station ($90.63 \pm 12.64\mu\text{g L}^{-1}$), followed by the second ($87.05 \pm 17.70\mu\text{g L}^{-1}$) and the first ($75.52 \pm 14.86\mu\text{g L}^{-1}$) stations (Table 2). The maximum seasonal concentration ($106.7\mu\text{g L}^{-1}$) was recorded in spring at the second station, and the minimum ($58.2\mu\text{g L}^{-1}$) was observed in spring at the first station. No significant differences ($P > 0.05$) were detected between stations, but seasonal differences were significant ($P \leq 0.05$).

In sediments, cobalt was highest at the second station ($163.49 \pm 60.32\mu\text{g g}^{-1}$ dry weight), followed by the first ($162.10 \pm 47.70\mu\text{g g}^{-1}$ dry weight) and the third ($154.70 \pm 53.56\mu\text{g g}^{-1}$ dry weight) stations (Table 3). The highest seasonal value ($213.8\mu\text{g g}^{-1}$ dry weight) was in summer at the second station, while the lowest ($84.4\mu\text{g g}^{-1}$ dry weight)

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was in winter at the same station. No significant spatial differences ($P > 0.05$) were found, but seasonal differences were significant ($P \leq 0.05$).

The concentrations recorded in this study are consistent with previous findings reported by *Al-Saad et al. (2006)*, *Al-Hashim et al. (2022)* and *Azadeh et al. (2022a)*.

Heavy metal pollution index (HPI)

The highest HPI value (162.89) was recorded at the third station during summer, and the lowest (108.94) at the first station in autumn (Table 4). Overall, the index values indicate critical levels of heavy metal pollution, as cadmium, lead, nickel, and cobalt concentrations exceeded permissible limits set by the Iraqi River Conservation System (2010) and US-EPA (2022). Copper was the least abundant metal, and its concentrations generally did not exceed permissible limits, except for the highest value recorded in summer at the second station.

Table 4. Seasonal variations in heavy metal pollution index (HPI) values for the water at the study stations

Station	Season	HPI (Cd)	HPI (Pb)	HPI (Cu)	HPI (Ni)	HPI (Co)	HPI	Water status
St1	Winter	114.68	207.40	61.60	100.32	159.58	120.41	Polluted
	Spring	139.74	259.18	74.40	130.71	186.85	146.90	Polluted
	Summer	153.86	265.98	86.92	155.72	141.42	156.35	Polluted
	Autumn	103.20	196.96	71.32	108.13	116.34	108.94	Polluted
St2	Winter	118.19	248.88	64.40	102.13	140.94	124.98	Polluted
	Spring	147.01	280.09	76.20	150.56	213.30	156.67	Polluted
	Summer	155.15	261.53	106.68	159.82	194.59	162.54	Polluted
	Autumn	123.46	217.29	65.56	110.44	147.57	127.42	Polluted
St3	Winter	120.89	300.76	49.20	127.57	155.47	131.72	Polluted
	Spring	125.36	269.89	72.80	141.10	190.47	137.58	Polluted
	Summer	152.21	285.16	94.84	169.38	212.23	162.89	Polluted
	Autumn	136.14	288.08	77.56	117.57	166.88	144.65	Polluted

DISCUSSION

The accumulation of heavy elements in water and marine sediments is a serious environmental problem associated with industrial waste and sewage discharge near industrial facilities (*Amin & Almahasheer, 2022*). In this study, the concentrations of elements in water followed the order: $Ni > Pb > Co > Cd > Cu$, with nickel showing the highest concentration and copper the lowest among the elements measured. All recorded concentrations in water exceeded the environmental limits set by the **Iraqi River Conservation System (2010)** and **US-EPA (2022)**. The elevated levels may be attributed to intensive human activity, including oil export from nearby ports, as well as emissions

from petrochemical, fertilizer, iron, and steel plants (Azadeh *et al.*, 2022b). Additional contributing factors include urban expansion, washing of fishing boats, direct wastewater discharge into the waterway, and exhaust emissions from vehicles, boats, and ships (Al-Hejuje *et al.*, 2017).

Variations in heavy metal concentrations can also result from interactions within the aquatic environment, such as absorption or adsorption by aquatic plants and plankton, unequal wastewater inputs, storm events, and fuel combustion, particularly during summer due to increased electricity generation (Reza & Singh, 2010a). Furthermore, untreated sewage discharge from the Hamdan Industrial Station and the Shatt al-Basra Canal, via the Shatt al-Basra Regulator, has been linked to elevated pollutant levels, including heavy metals and petroleum hydrocarbons (Galo & Resen, 2024; Hazza & Jassim, 2024).

Seasonally, cadmium, copper, and nickel concentrations in water were at their highest values during summer; lead peaked in winter, and cobalt peaked in spring. The summer increases may be linked to higher temperatures and evaporation rates, which concentrate dissolved substances (Aldoghachi, 2022; Karim *et al.*, 2022). Spatially, the second station recorded the highest cadmium, copper, and cobalt levels, while the third station had the highest lead and nickel concentrations, likely due to the large number of industrial units and petroleum-loading ports in these areas (El-Sorogy *et al.*, 2020).

The first station generally recorded the lowest cadmium, nickel, and cobalt concentrations. Temporally, cadmium and lead were lowest in autumn, copper and nickel in winter, and cobalt in spring. These lower levels may be due to dilution from increased water release, reduced evaporation during cooler seasons, and higher water levels (Al-Maarofi *et al.*, 2013). Overall, the third station had the highest heavy metal concentrations, followed by the second station, with the highest seasonal concentrations generally occurring in summer. Some elements exceeded permissible limits by more than tenfold, highlighting severe contamination, likely due to oil spills, heavy ship traffic, fishing boat activity, and proximity to industrial plants (Al-Imarah *et al.*, 2018).

Sediments, recognized as effective bioindicators of aquatic pollution due to their role as final repositories for contaminants (Al-Atbee *et al.*, 2019), showed metal concentrations in the order: Ni > Pb > Cd > Co > Cu. Nickel and lead were the most abundant in sediments, and levels were higher in sediments than in water at all stations. This reflects the tendency of heavy metals to settle into sediments, creating a long-term record of pollution (Al-Hejuje *et al.*, 2018). This pattern may be explained by the low solubility of heavy metals and their strong association with fine-grained particles such as clay and silt, which are of terrestrial origin (Amin & Almahasheer, 2022), the basic pH of the study sites promoting precipitation, and the strong binding affinity of heavy metals

to sediment particles. These findings are consistent with previous studies (Adam *et al.*, 2007; Al-Imarah *et al.*, 2017; Appiah-Opong *et al.*, 2021; Hazza & Jassim, 2024).

Heavy metal pollution index (HPI)

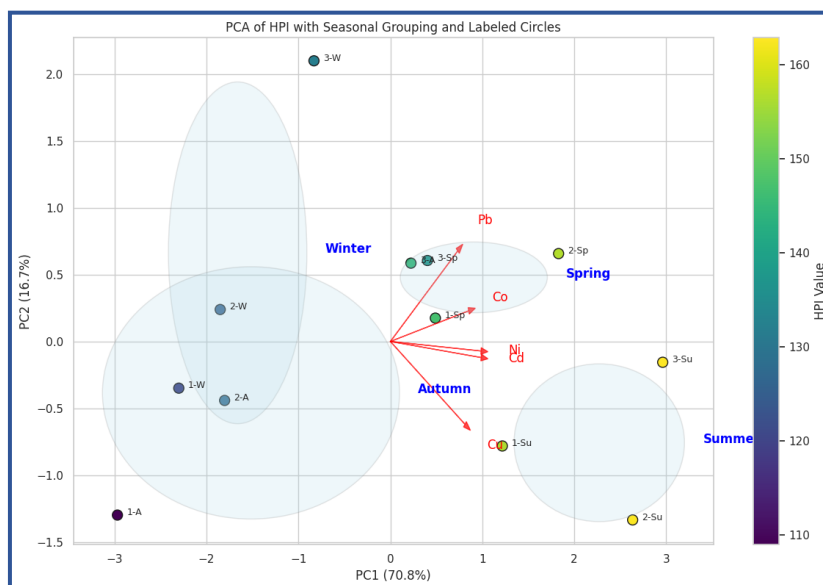


Fig. 4. PCA analysis of the environmental factors affecting the heavy element pollution index

Fig. (4) illustrates the effect of environmental factors on the heavy metal pollution index (HPI). The HPI is an effective tool for assessing the condition of surface water and its contamination with heavy metals, as it compiles multiple datasets into a single value, providing an overall measure of pollution levels (Reza & Singh, 2010b). In the present study, the highest HPI value (162.89) was recorded at the third station during summer, while the lowest (108.94) was recorded at the first station in autumn (Table 4). Overall, the water quality, according to the index, was classified above the critical pollution threshold, indicating elevated concentrations of heavy metals at all stations and in all seasons.

Principal component analysis of the index values revealed a direct correlation between HPI and the metals lead, cobalt, nickel, and cadmium, with copper having the least influence. The strongest correlation was observed with lead, followed by cobalt, confirming that these metals were present in high concentrations. All values exceeded the permissible limits set by the Iraqi River Pollution Conservation System affiliated with the Ministry of Environment (2011) and the US-EPA (2022).

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