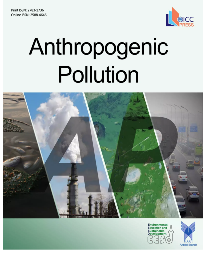

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Ecological risk assessment of potentially toxic metals in water and sediments of urban river ecosystems (case study: Zarjub River and Gohar Rood in Rasht, Iran)

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Original Research

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Abstract:

The Zarjub River and Gohar Rood represent serious pollution concerns among urban rivers in northern Iran, as they discharge into the international Anzali Lagoon. This study aimed to evaluate the concentration of potentially heavy metals (PTMs) in the water and sediments of these two rivers. To this end, water and sediment samples were taken from 10 sampling stations along the two rivers, and then physicochemical factors and concentration of PTMs were measured; moreover, environmental indices were calculated. Results showed that the water pH, DO, and TDS were 6.7, 4.9, and 316.5, respectively. In addition, the concentration of Fe, Pb, Al, Hg, and Cd in water samples were 0.166, 0.1, 0.1, 1, and 0, and their concentration in sediment samples was equal to 41686.1, 70.031, 12721.9, 0.1, and 0.1, respectively. The geo-accumulation index (I_{geo}), enrichment factor (EF), contamination factor (CF), ecological risk index (ERI), and potential ecological risk (PER) were also calculated for the water and sediment samples. The measurement of PTMs and the above-mentioned indices demonstrated that the water of the studied rivers does not contain high levels of heavy metals, whereas their sediments contain high levels of PTMs. The study findings suggested that these two urban rivers are not in a hazardous state in terms of PTMs; however, it is necessary to further manage and control the entry of urban wastewater into these two rivers.

Keywords: Heavy metals; Running waters; Sediments; Ecological indicators; Southern Caspian Sea

1. Introduction

Population growth, elevated wastewater production, industrial development, and the application of chemical fertilizers and pesticides in agriculture have resulted in various forms of pollution, with water resources being the primary recipients of these contaminants (Lazaro et al., 2006). Aquatic ecosystems, particularly urban rivers, experience heightened exposure to pollution compared to other environments (Yaya et al., 2019). In addition to various pollutants, elevated concentrations of PTMs in river water and sediments constitute a serious global environmental issue (Edet and Offiong, 2002; Tiwari et al., 2015). Their high concentration, persistence, biomagnification, and toxicity have raised considerable concerns among governments and the public (Ali and Khan, 2018). PTMs originate from both natural and anthropogenic sources (Wei and Yang, 2010; Muhammad et al., 2011). The primary natural source of heavy metals is the weathering of bedrock (Allan, 1975), while the main anthropogenic sources encompass industrial products, fertilizers, and agricultural wastewater (Krishna et al., 2009; Bhuiyan et al., 2011). The extraction of mineral resources and their applications in industry and agriculture have increased the concentration of PTMs in biogeochemical cycles (Ali et al., 2019). PTMs are toxic even at low concentrations and threaten the life of living organisms. They may also enter the human body, accumulate in tissues, and affect the nervous system and blood circulation. Since these elements are not metabolized in the body and may accumulate in muscles, bones, and joints, they can cause various diseases in the human body (Wu et al., 2018). As a result, PTMs are extensively utilized as indicators for environmental monitoring, and their toxicity to humans, animals, and plants has attracted great attention (Grossman and Krueger, 1995). Due to population growth and industrial and urban development, the discharge of heavy metals into aquatic ecosystems and the resulting contamination have turned into a global issue (Lazaro et al., 2006).

The PTMs contamination in surface sediments has garnered increased attention due to their toxicity and persistence (Lin et al., 2008; Jiang et al., 2014); therefore, they are considered a valuable source of information regarding environmental and geochemical pollution (Uluturhan et al., 2011). Over 90% of the overall burden of PTMs in aquatic ecosystems is associated with suspended particles and sediments (Varol and Şen, 2012; Raknuzzaman et al., 2016). Consequently, sediments may accumulate diverse pollutants and toxic agents, particularly PTMs, which can be quantified in surface sediments via multiple ways, including liquid effluent discharges, vehicular emissions, brick kilns, and chemicals from various urban, industrial, and agricultural practices (Shikazono et al., 2012; Varol and Şen, 2012; Islam et al., 2017). There are various indices for assessing the environmental risk of heavy metals in surface sediments based on total content (Yang et al., 2016). For example, the geo-accumulation index (I_{geo}), enrichment factor (EF), and contamination factor (CF) of heavy metals in sediment are calculated using the total content of heavy metals and their respective values.

Many studies have measured the concentration of PTMs in water and sediments of urban rivers in different parts of the world, such as in Bangladesh (Mohiuddin et al., 2011; Islam et al., 2015; Islam et al., 2017; Ali et al., 2022b; Hoque et al., 2023), Malaysia (Haris et al., 2017; Ismail et al., 2013), China (Xiao et al., 2013, Deng et al., 2022), India (Jamwal et al., 2016), and Nigeria (Olatunji and Osibanjo, 2013). Therefore, it is essential to assess the severity of metal pollution by cataloging concentrations and distribution within the river ecosystem. Heavy metals are found in sediments in multiple chemical forms and experience structural changes due to processes such as dissolution and precipitation. The behavior of heavy metals in surface sediments is significantly affected by their association with various geochemical phases (Morillo et al., 2004). Nevertheless, there is not enough information about the total concentration of heavy metals to assess the environmental impacts of contaminated sediments (Chandra-Sekhar et al., 2003). Consequently, geochemical processes are of special importance and interest in the evaluation of the potential environmental impacts and ecotoxicity of heavy metals (Wang et al., 2010; Islam et al., 2015).

River sediment serves as a reliable indicator of pollution levels within a river. Several studies have demonstrated the different concentrations of heavy metals in sediments (Lim et al., 2013) and soils (Thomasi et al., 2015; Praveena et al., 2015). Sediment also functions as a reservoir for heavy metals and, thereby, a scientific indicator of their concentration. Most recent studies on the contamination of water resources with heavy metals have assessed the total concentration of these metals in sediments of rivers and lakes (Lin et al., 2022). The health of surface waters is generally influenced by sediment quality, which impacts microbial activity and their food sources, as well as the overall water health (Sunderland). Additionally, the contamination of freshwater resources with heavy metals poses a serious challenge to the management of water resources in contemporary times (Wang et al., 2010). Rivers and flowing waters have received less attention as sources of drinking water, compared to lakes and still waters, and are not considered valuable in terms of environmental protection. Rivers generally receive a remarkable amount of heavy metals from local sources, farms, industries, and construction projects and store them in their sediments (Li et al., 2019). Considering the effects of human activities on water resources, alongside river pollution and its environmental consequences, it is necessary to monitor water quality in rivers and regulate pollution levels as a fundamental criterion for evaluating surface waters. Metal mining and smelting accounted for the primary source of heavy metal pollution in surface water (Li et al., 2007; Liu et al., 2010). As another example, heavy metal pollution in Lake Manzala, Egypt, primarily originates from agricultural drainage water, sewage effluent, and industrial waste (Bahnasawy et al., 2011).

In 2004, the concentration of heavy metals in the water of the Niger River in Nigeria was as follows: 50 mg/L for cadmium, 30 mg/L for lead, 2,080 mg/L for chromium, and 780 mg/L for nickel (Olatunji and Osibanjo, 2013). These figures for the Korotoa River in Bangladesh were reported to be 11 mg/L for cadmium, 35 mg/L for lead, 83 mg/L for chromium, and 46 mg/L for arsenic (Islam et al., 2015). The high concentration, toxicity, biomagnification, and hyperaccumulation of heavy metals in surface waters have caused serious concerns among governments and the general public (Ali and Khan, 2018; Ali et al., 2019).

Most previous studies on heavy metal pollution have predominantly focused on small spatial scales, exemplified by river systems (An et al., 2009), and a few studies have addressed heavy metal pollution at larger spatial scales. This study analyzed PTM pollution in some rivers and lakes around the world from 1972 to 2017 in order to identify sources of heavy metal pollution in five continents over the past five decades and then propose strategies for controlling metal pollution in surface water bodies. Nearly all of the heavily populated cities in the southern Caspian Sea have long been situated along rivers for easier access to water. Rasht, the most populated city in the area, is traversed by the Zarjub River and Gohar Rood, both of which regrettably receive industrial, agricultural, and urban wastewater.

The development of human activities within the Zarjub River watershed, particularly in Rasht Industrial Town, has resulted in a significant influx of pollutants into the river in recent decades. This river irrigates the Pirbazar region, an area dedicated to rice cultivation (Khaledian et al., 2014). These two rivers serve as the primary water source for Anzali Lagoon, as they enter this aquatic ecosystem at their terminus. Consequently, the contamination of these rivers with toxic substances and hazardous nosocomial waste threatens the ecological integrity of the international Anzali Lagoon. Many studies have measured the concentration of organic chlorine in the sediments of this river (Yousefzadeh et al., 2021), the effects of industrial pollution on this river (Ghodrati et al., 2007), and the pollution load entering it (Bizhani-Manzar and Mahjouri, 2014). However, a few studies have investigated the concentration of PTMs in this river. The presence of sources of pollutants such as landfills, two industrial towns, and the discharge of untreated wastewater of Rasht into this river explain why this study focuses on these elements. This study aims to assess the physicochemical properties of water and sediments, measure the concentration of PTMs in water and sediments, and evaluate the pollution level in these two rivers using various indicators. This study also estimates the possible risk of these elements using geological and ecological indicators.

2. Materials and methods

The Zarjub River is a tributary of the Pirbazar River, originating from the Hezar Marz Mountains, situated south of Rasht. Upon traversing the eastern region of Rasht, known as Zarjub, it integrates with surface runoff and urban and industrial wastewater from the city's eastern and southern sectors, subsequently converging with Gohar Rood to create the Pirbazar River (figure 1), which eventually flows into Anzali Lagoon. The headwaters of the Zarjub River in Saravan, Sangar, Guilan Province, serve as a landfill for urban waste, resulting in the transfer of pollution to these rivers (Eskandari, 2011). In this study, the water and sediment samples were taken from 10 sampling stations selected along the Zarjub River and Gohar Rood (figure 1 and Table 1).

Water samples were collected from the 10 designated stations following the standard method (APHA 2012). The samples were poured into polyethylene bottles, which had been treated with nitric acid and rinsed with deionized water, and subsequently transported to a laboratory for analysis. Water temperature, pH (a WAGTEG PH meter, standard number BH-4500), electrical conductivity (EC) (a WAGTEG EC meter, UK, standard number B 2510), and dissolved oxygen (DO) (a DO meter, standard number BO

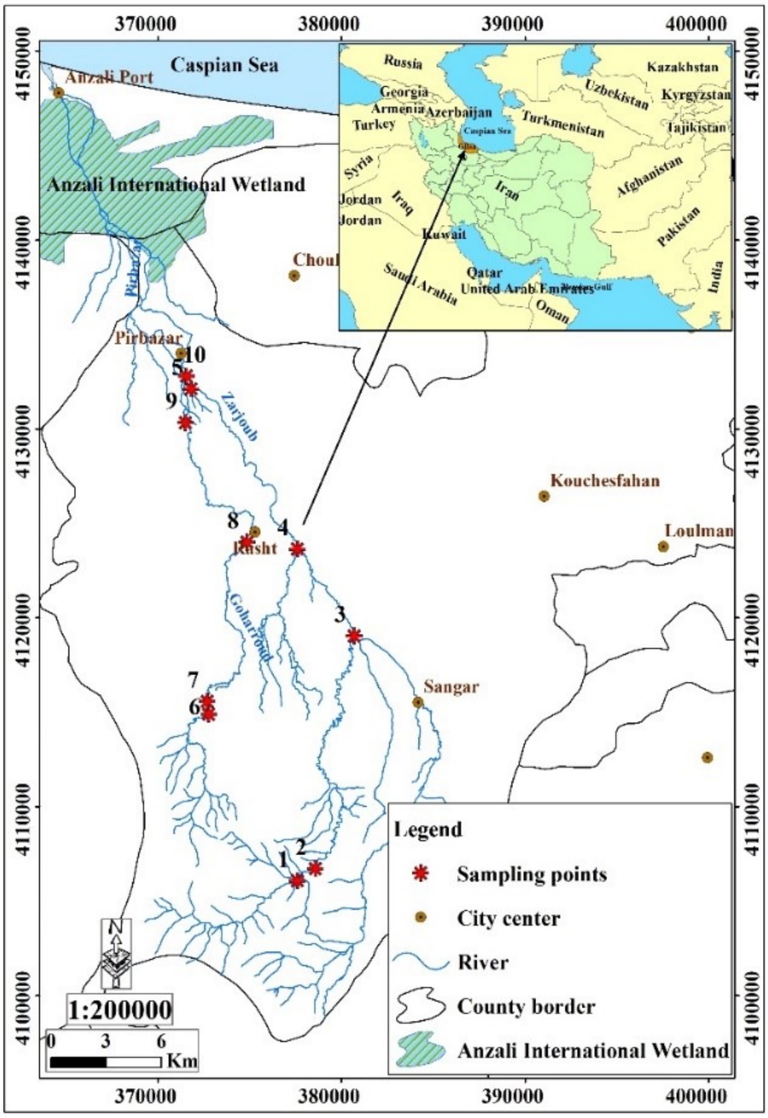

Figure 1. Geographic location of sampling stations in the Zarjub River and Gohar Rood.

Table 1. Geographic coordinates of sampling stations along the Zarjub River and Gohar Rood.

Number	N	E
1	4106078.496	377613.203
2	4106723.816	378587.143
3	4119055.181	380706.46
4	4123657.17	377603.693
5	4132137.502	371824.79
6	4114909.217	372778.839
7	4115579.1	372695.692
8	4124011.696	374874.087
9	4130346.352	371524.692
10	4132801.458	371564.445

4500) were recorded at each sampling station. The concentration of iron, lead, aluminum, and mercury in water samples was also measured in a laboratory.

Sediment samples were collected from the surface sediments of the river bed under the established methods in physical and chemical sedimentology (Tuker, 1989). Samples were collected using a plastic shovel from a depth of 10 to 20 cm and transported to the laboratory in labeled special bags. Since the moisture content of the sediments was very high, the samples were first kept in the open air for 24 hours and then dried in an oven at 75 °C for 24 hours (Tuker, 1989). Finally, the samples were weighed and then granulated using a shaker sieve. Particles smaller than 63 microns from the samples were sent to a laboratory for ICP-MS analysis (ICP-Varian model 710-ES, Australia) in order to measure the concentration of PTMs (iron, lead, aluminum, mercury, and cadmium). Iron and aluminum were selected as the reference elements, whereas lead, mercury, and cadmium served as the three contaminant elements according to their sources (**Zhang2025**; Ali et al., 2022a; Gao et al., 2025). The pollution indices were calculated in Excel and statistical analyses were performed in SPSS-25.

Geo-accumulation index (I_{geo})

The geo-accumulation index (Muller, 1969) was employed to estimate soil contamination with PTMs. To this end, the following equation was used to calculate the ratio of heavy metal concentration in soil to the metal background concentration (BC):

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

In this equation, I_{geo}, C_i, and C_{ri} denote the geo-accumulation index or pollution severity index, the heavy metal concentration in soil, and the metal BC, respectively. The coefficient 1.5 serves as a correction factor to mitigate the impact of potential alterations in the metal BC, which are typically attributed to variations in soil lithology and human factors. This coefficient isolates natural fluctuations in the concentration of a specific substance in the environment, thereby highlighting even minor changes induced by anthropogenic effects (Haris et al., 2017). Mueller proposed seven categories for this index; the values in the highest category are at least 100 times the reference values (Zhang et al., 2007) (Table 2).

Table 2. Soil quality classification based on the geo-accumulation index (Muller, 1969).

Soil quality	Value	Class
Uncontaminated	$I_{geo} < 0$	1
Uncontaminated to moderately contaminated	0-1	2
Moderately contaminated	1-2	3
Moderately to heavily contaminated	2-3	4
Heavily contaminated	3-4	5
Heavily to extremely contaminated	4-5	6
Extremely contaminated	$5 < I_{geo}$	7

Enrichment factor (EF)

The enrichment factor (EF) effectively differentiates between natural and anthropogenic sources of pollution (Izah et al., 2017). To calculate this index, a reference element is selected that remains immobile and is unaffected by human activities, such as Al, Li, Sc, Fe, Ti, and Zr. The enrichment factor (EF) is calculated using the following equation:

$$EF = \frac{(\frac{C_x}{C_{ref}})\text{Sample}}{(\frac{C_x}{C_{ref}})\text{Background}}$$

In this equation, $(\frac{C_x}{C_{ref}})$Sample denotes the ratio of the concentration of the target metal (measured in the soil) to the reference metal in the sample and $(\frac{C_x}{C_{ref}})$Background represents the ratio of the concentration of the target metal to the reference metal in the BC. An EF of less than 1 indicates the natural origin of the element; an EF between 1 and 10 suggests a combination of natural and anthropogenic sources; and an EF greater than 10 signifies that human activities are the primary source of the given element. Higher values of EF demonstrate the greater effect of human factors on soil contamination with a given element. Table 3 presents the soil classification based on EF.

Table 3. EF classification (Kowalska et al., 2018).

Class	Contamination level	EF
1	Low	$EF < 2$
2	Moderate	$5 > EF \geq 2$
3	High	$20 > EF \geq 5$
4	Very high	$40 > EF \geq 20$
5	Extremely high	$EF \geq 40$

Contamination factor (CF)

This factor allows us to compare the concentration of a given element with its natural values and, thereby, determine the level of contamination with that element.

$$CF = \frac{C_n}{B_n}$$

In this equation, CF, C_n, and B_n represent the contamination factor, the element concentration in the contaminated sample, and the concentration of the same element in a standard soil sample or its natural concentration in the sampling area, respectively. Table 4 presents the classification proposed by Hakanson (1980) for assessing heavy metal pollution.

Table 4. CF classification for sediment contamination (Hakanson, 1980).

Class	Contamination level	CF value
1	Low contamination	$CF < 1$
2	Moderate contamination	$3 > CF \geq 1$
3	Considerable contamination	$6 > CF \geq 3$
4	Very high contamination	$CF \geq 6$

Degree of contamination ($C_{\mathbf{deg}}$)

Hakanson (1980) proposed an equation for assessing contamination levels. In this equation, CF represents the contamination factor, while n denotes the number of heavy metals being investigated. Table 5 presents a classification of C_{dge} values.

$$C_{deg} = \sum_{i=1}^{n} CF$$

Table 5. Classification of degree of contamination (Kowalska et al., 2018).

C_{dge}	Degree of contamination
$8<C_{dge}$	Low
8-16	Moderate
16-32	High
$C_{dge}>32$	Very high

Ecological risk index (ERI)

This index is calculated using the following equation:

$$E_r^i = T_r^i \times PI_i$$

In this equation, T_r^i and PI_i denote the contamination intensity and contamination index. Table 6 presents the 5 classes of ERI.

Table 6. Contamination risk level based on ERI (Kowalska et al., 2018).

Class	Contamination degree	E_r^i
1	Low	$E_r^i < 40$
2	Moderate	$40 \leq E_r^i < 80$
3	High	$80 \leq E_r^i < 160$
4	Very high	$160 \leq E_r^i < 320$
5	Extreme	$320 \leq E_r^i$

Potential ecological risk (PER)

PER is an index for assessing the ecological risk caused by heavy metals in water, air, and soil. Proposed by Hakanson (1980), this index is calculated using the following formula:

$$RI = \sum_{i=1}^{n} E_r^i$$

In this equation, n represents the number of heavy metals and E_r^i denotes ecological risk. Soil quality is categorized into five classes according to potential ecological risk (Table 7).

Table 7. Soil quality classification based on PER (Kowalska et al., 2018).

RI	PER
$RI < 90$	Low
$90 \leq RI < 180$	Moderate
$180 \leq RI < 360$	High
$360 \leq RI < 720$	Very high
$720 \leq RI$	Extremely high

3. Results

Physicochemical parameters of water and concentration of heavy metals in water and sediments were measured at the 10 studied stations in the Zarjub River and Gohar Rood. Table 8 presents the mean and standard deviation of pH, EC, TDS, DO, TEMP, total hardness, density, soil texture, organic matter (%), clay, and silt in the studied stations.
Table 9 presents the mean concentration of heavy metals in the water of the Zarjub River and Gohar Rood across various stations. The results showed that the concentrations of lead, aluminum, and mercury in the water of the two rivers remained constant, measured at 0.1, 0.1, and 1 mg/L, respectively. The concentration of iron also showed a relatively stable pattern in the water of these two rivers, with a mean of 0.166, a maximum of 0.2, and a minimum of 0.1 mg/L.
The correlation analysis examined the relationships between different variables (Table 10). The results showed a positive and significant correlation between total hardness and iron concentration in sediments ($r = 0.669$, $p < 0.05$). The soil texture also showed a strong and positive correlation with iron concentration in sediments ($r = 0.864$, $p < 0.01$). In contrast, silt and organic matter percentage exhibited a negative and significant correlation ($r = -1.000$, $p < 0.01$, and $r = -0.493$, $p < 0.05$). In addition, there was a positive and significant correlation between aluminum and mercury concentrations in water samples ($r = 0.647$, $p < 0.05$, and $r = 0.685$, $p < 0.05$).
The mean concentration of PTMs in sediment samples taken from the 10 studied stations is shown in Table 11. The results revealed a significant difference between the stations in the concentration of heavy metals. The highest concentration of iron (Fe) was observed in stations 1 (65,952 mg/kg) and 2 (64,820 mg/kg), while its lowest concentration was measured at station 6 (25,792 mg/kg). The highest (110.4 mg/kg) and the lowest (49.14 mg/kg) concentrations of lead (Pb) were measured at stations 6 and 7, respectively. In addition, the highest concentration of aluminum (Al) was observed at stations 1 (14,532 mg/kg) and 2 (14,755 mg/kg),

Table 8. The mean value of water physicochemical parameters and soil characteristics in the water and sediment samples collected from different stations along the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
pH	7	7	6	8	7	6	6	7	7	6	6.7±0.67
EC	275c	725b	680b	931a	804b	220c	348c	747b	825b	798b	635.3±255.10
TDS	136b	362a	353a	419a	395a	110b	175b	373a	441a	401a	316.5±125.23
DO	8	4	6	5	5	6	4	3	4	4	4.9±1.44
TEMP	23b	23b	26a	23.1b	21b	23b	23b	23b	22b	21b	22.81±1.40
Total hardness	350b	540a	530a	275b	290b	205b	210b	340b	350b	342b	343.2±114.52
Density	998.14b	998.1b	998.07b	998.12b	998.2a	998.14b	998.1b	998.14b	998.18a	998.2a	998.139±0.04
Soil texture	45 a	25 b	0	0	0	0	0	0	0	0	7±15.49
Organic matter (%)	23.938b	26.98b	40.666b	38.511b	35.55b	17.033c	41.98b	47.93b	43.099b	62.991a	37.8678±13.06
Clay	60b	55b	35b	80a	55b	10c	15c	60b	85a	90a	54.5±27.53
Silt	40c	45c	65b	20d	45c	90a	85a	40c	15d	10d	45.5±27.53

Different letters indicate significant differences ($p < 0.05$)

whereas its lowest concentration was measured at Station 10 (10,975 mg/kg). Conversely, the concentrations of mercury (Hg) and cadmium (Cd) remained constant across all stations, recorded at 0.1 mg/kg (Fig. 2).

The one-way ANOVA test results indicated significant differences in heavy metal concentrations in sediment samples among the studied stations ($p < 0.05$). The LSD test for the detailed analysis of means also revealed significant differences among the groups ($p < 0.05$).

The hierarchical clustering analysis (Fig. 3) using the average linkage method showed the highest similarity and the lowest distance (0.000 to 0.810) between the concentration of PTMs (Hg, Cd, Pb, and Al) in water and sediment samples; moreover, they were in the same cluster in the early stages of accumulation (stages 1 to 5). In contrast, the Fe concentration in sediment samples was distinguished from other variables by a very large distance (1.709 × 109 to 1.737 × 109), as it merged in the last stage of accumulation (stage 14). This suggests the different behavior or origin of this metal compared to other elements. Clustering of soil physicochemical variables (such as soil texture, organic matter percentage, and clay and silt compositions) in the intermediate stages (stages 6 to 10) also showed a similar distribution pattern.

The principal component analysis (PCA) showed (Fig. 4) that the first two components (i.e., PC1 and PC2) together explain more than 94.46% of the total variance of the data (PC1: 78.947%, PC2: 15.521%). The first component (PC1) is strongly influenced by total hardness (loading: 0.596) and Fe concentration in sediment samples (loading: 0.797), indicating the key role of these parameters in the data variability. The second component (PC2) mainly demonstrated a positive correlation with density (loading: 0.905) and Pb concentration in sediment samples (loading: 0.874) and a negative correlation with soil texture (loading: −0.121). This pattern suggests that changes in soil composition (such as clay and silt percentage) and concentrations of PTMs (especially lead and iron) have the greatest effects on the dispersion of samples. The variables related to the concentration of PTMs in water samples (e.g., Hg water and Cd sediment) showed negligible effects on principal elements, which is probably due to the low and uniform concentration of these elements in this aquatic environment. These results explain why this study focused on soil parameters and sedimentary metals as key factors for distinguishing samples.

Geo-accumulation index (I_{geo})

Table 12 presents the mean of I_{geo} for heavy metals in the sediments of the Zarjub River and Gohar Rood. The results indicated that this index was near zero for mercury and cobalt, while it exhibited significant values for iron, lead,

Table 9. The mean concentration of heavy metals in water samples collected from different stations along the Zarjub River and Gohar Rood.

HM \ St.	1	2	3	4	5	6	7	8	9	10	Mean±SD
Fe	0.2	0.2	0.2	0.2	0.18	0.17	0.1	0.14	0.17	0.1	0.166±0.3
Pb	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1±0
Al	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1±0
Hg	1	1	1	1	1	1	1	1	1	1	1±0

Table 10. Correlation coefficient between physicochemical factors and PTMs.

	Correlations														
	Total hardness	Density	Soil texture	Organic matter (%)	Clay	Silt	Fe S.	Pb S.	Al S.	Hg S.	Cd S.	Fe Water	Pb Water	Al Water	Hg Water
Total hardness	1														
Density	-.382	1													
Soil texture	.327	-.152	1												
Organic matter (%)	.050	.318	-.493	1											
Clay	.221	.534	.068	.540	1										
Silt	-.221	-.534	-.068	-.540	-1.000**	1									
Fe Sediment	.669*	-.492	.864**	-.310	.062	-.062	1								
Pb Sediment	-.031	-.367	.084	.239	-.249	.249	.245								
Al Sediment	.473	-.653*	.725*	-.675*	-.407	.407	.819**	.070	1						
Hg Sediment	.076	-.348	.401	-.018	-.056	.056	.508	.462	.419	1					
Cd Sediment	.338	-.412	.101	.251	-.214	.214	.310	.201	.273	.095	1				
Fe Water	.455	-.302	.429	-.644*	.049	-.049	.463	-.508	.604	-.210	-.119	1			
Pb Water	-.116	.439	.320	.211	.274	-.274	.068	-.226	-.138	.100	.292	-.327	1		
Al Water	.136	-.103	.823**	-.336	.028	-.028	.647*	.079	.521	.039	.377	.341	.403	1	
Hg Water	-.096	.646*	.356	.156	.347	-.347	.074	-.295	-.028	-.028	.163	-.104	.685*	.448	1

* Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed).

and aluminum.

Enrichment factor (EF)

Table 13 presents the mean of EF for heavy metals in the sediments of the Zarjub River and Gohar Rood. The results showed that this index was near zero for mercury and

Table 11. The mean concentration of heavy metals in sediment samples collected from different stations along the Zarjub River and Gohar Rood.

Sediment	1	2	3	4	5	6	7	8	9	10	Mean±SD
Fe	65952^{d}	64820^{d}	48765^{c}	37675^{b}	29732^{ab}	25792^{a}	38405^{b}	37470^{b}	34395^{b}	33855^{b}	41686.1±13859.46
Pb	72.98^{b}	73.74^{b}	65.23^{b}	53.88^{a}	51.44^{a}	49.14 a	110.4^{d}	93.22^{c}	69.28^{b}	61^{b}	70.031±19.26
Al	14532^{d}	14755^{d}	13777^{c}	12460^{b}	12500^{b}	12600^{b}	12820^{b}	11700^{a}	11100^{a}	10975^{a}	12721.9±1307.75
Hg	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1±0
Cd	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1±0

Different letters indicate significant differences ($p < 0.05$).

Table 12. The geo-accumulation index (I_{geo}) for heavy metals in the sediments of the Zarjub River and Gohar Rood.

	1	2	3	4	5	6	7	8	9	10
Fe	0.910795957	0.881634	0.71035	0.606811	0.477345	0.410802	0.601199	0.642712	0.621857	0.619066
Pb	0.001007853	0.001003	0.00095	0.000868	0.000826	0.000783	0.001728	0.001599	0.001253	0.001115
Al	0.200686664	0.200687	0.200687	0.200687	0.200687	0.200687	0.200687	0.200687	0.200687	0.200687
Hg	1.381E-06	1.36E-06	1.46E-06	1.61E-06	1.61E-06	1.59E-06	1.57E-06	1.72E-06	1.81E-06	1.83E-06
Cd	1.381E-06	1.36E-06	1.46E-06	1.61E-06	1.61E-06	1.59E-06	1.57E-06	1.72E-06	1.81E-06	1.83E-06

Table 13. The enrichment factor (EF) for heavy metals in the sediments of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
(Fe)	9.5	9.4	7.1	5.5	4.3	3.8	5.6	5.4	5	4.9	6.05±1.99
(Pb)	106.4	107.3	95	78.9	74.7	71.5	160	135	100	88.5	101.73±27.77
(Al)	1	1	1	1	1	1	1	1	1	1	1
(Hg)	0	0	0	0	0	0	0	0	0	0	0
(Cd)	0	0	0	0	0	0	0	0	0	0	0

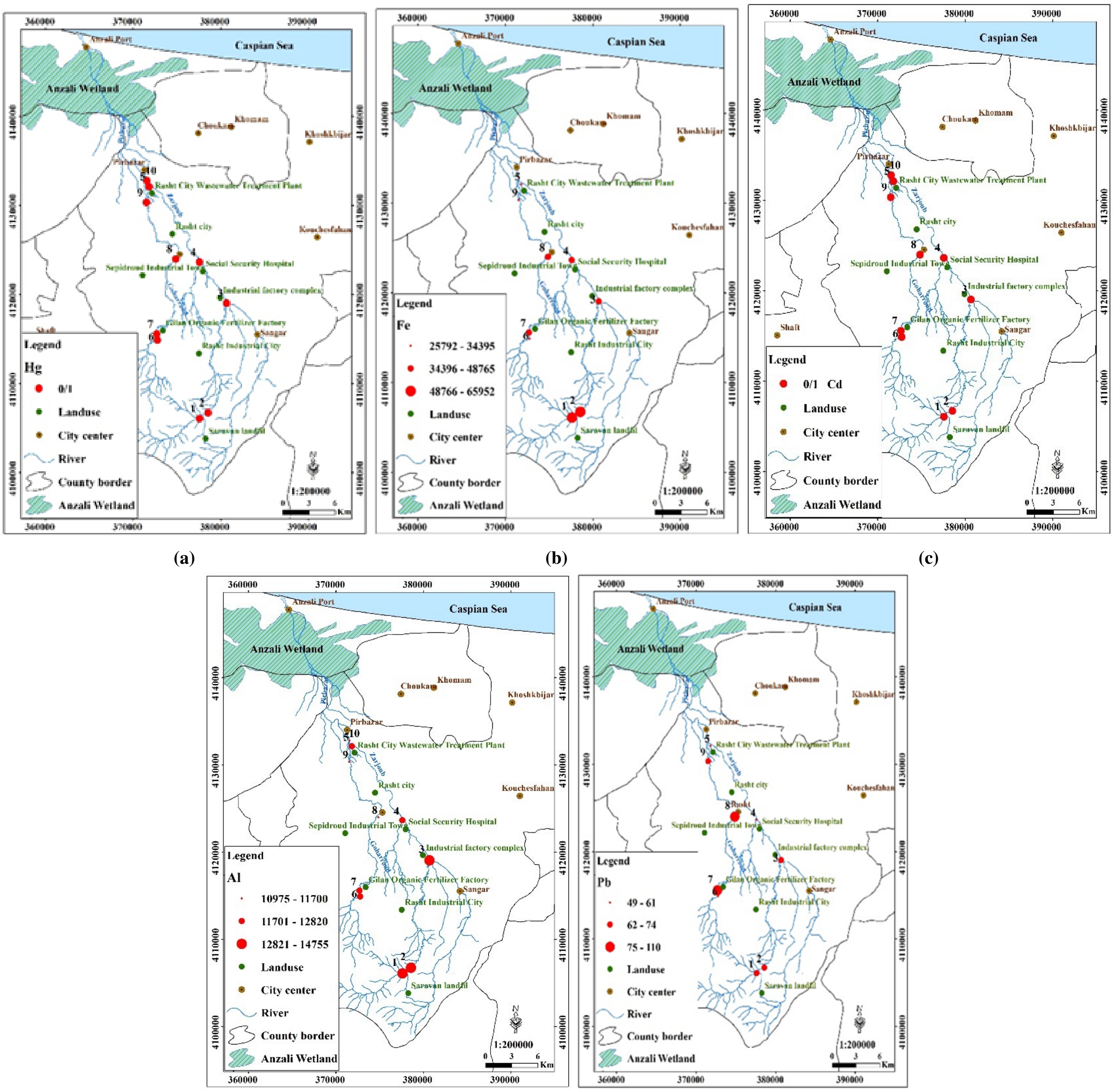

Figure 2. The mean concentration of heavy metals in sediment samples collected from the 10 stations along the Zarjub River and Gohar Rood (a = Hg, b = Fe, c = Cd, d = Al, e = Pb).

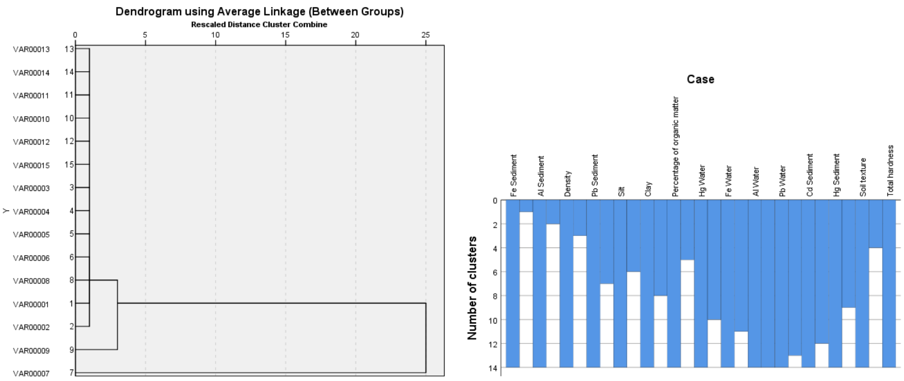

Figure 3. Hierarchical cluster analysis using the average linkage method.

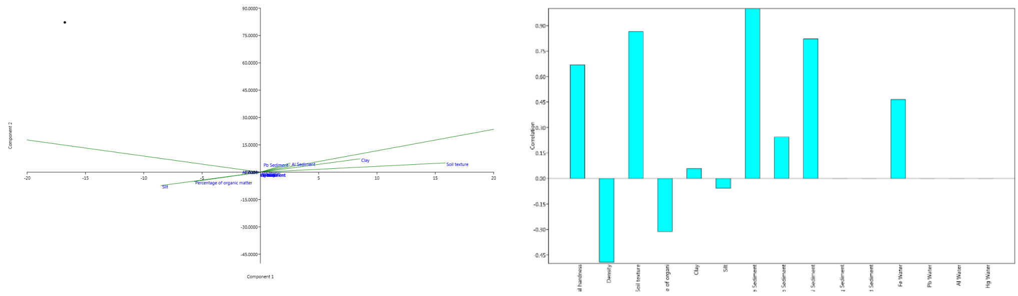

Figure 4. Principal Component Analysis (PCA).

cobalt, while it exhibited significant values for iron, lead, and aluminum.

Contamination factor (CF)

Table 14 presents the mean of CF of heavy metals in the sediments of the Zarjub River and Gohar Rood. The results demonstrated that this index was near zero for mercury and cobalt, while it exhibited significant values for iron, lead, and aluminum.

Ecological risk index (ERI)

Table 15 presents the mean of ERI of heavy metals in the sediments of the Zarjub River and Gohar Rood. The results demonstrated that this index was near zero for mercury and cobalt, while it exhibited significant values for iron, lead, and aluminum.

Potential ecological risk (PER)

Table 16 presents the mean of PER for heavy metals in the sediments of the Zarjub River and Gohar Rood. The results showed a significant difference between the stations in this regard.
Tables 17, 18, 19, and 20 present the mean of the above-mentioned indices for water samples collected from 10 stations along the Zarjub River and Gohar Rood. The result demonstrated the low contamination of these rivers with mercury and cobalt and their moderate contamination with iron, lead, and aluminum.

4. Discussion

Both the number of PTMs and the extent of contamination they cause have been increasing since the 1970s. Bedrock weathering, mining and waste disposal, and mining were the main sources of PTM contamination in the 1970s, 1980s, and 1990s, respectively. However, waste disposal and rock weathering were the major sources during the 2000s and 2010s.
Studies conducted around the world about the concentration of PTMs in aquatic ecosystems indicate that their levels were comparatively low during the 1970s and 1980s, but started an increasing trend in the 1990s. The contamination of these ecosystems with heavy metals has transitioned from single-metal to multiple-metal contamination over time. The primary sources of heavy metal contamination during the 1970s, 1980s, and 1990s were bedrock weathering, mining and waste disposal, and mining operations, respectively. In the 2000s and 2010s, waste disposal and rock weathering emerged as the predominant sources of

Table 14. The contamination factor (CF) for heavy metals in the sediments of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
(Fe)	1.32	1.30	0.975	0.753	0.594	0.516	0.768	0.749	0.688	0.677	0.83±0.277
(Pb)	3.65	3.69	3.261	2.694	2.572	2.457	5.52	4.661	3.464	3.05	3.50±0.962
(Al)	1.82	1.84	1.722	1.558	1.562	1.575	1.603	1.462	1.387	1.372	1.59±0.163
(Hg)	2	2	2	2	2	2	2	2	2	2	2.00±0
(Cd)	1	1	1	1	1	1	1	1	1	1	1.00±0

Table 15. The ecological risk index (ERI) of heavy metals in the sediments of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
(Fe)	67.97	69.74	37.14	22.14	13.82	10.39	23.04	21.93	18.48	17.91	30.25±21.53
(Pb)	0.971	0.989	0.775	0.53	0.48	0.439	2.208	1.571	0.866	0.675	0.95±0.55
(Al)	1	1	1	1	1	1	1	1	1	1	1
(Hg)	0	0	0	0	0	0	0	0	0	0	0
(Cd)	0	0	0	0	0	0	0	0	0	0	0

Table 16. The potential ecological risk (PER) of heavy metals in the sediments of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
RI	69.91	71.71	39.69	23.2	14.78	11.32	28.46	25.07	20.18	19.26	32.35±21.69

Table 17. The enrichment factor (EF) for heavy metals in the water of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
EF(Fe)	0.2	0.2	0.2	0.2	0.18	0.17	0.1	0.14	0.17	0.1	0.166±0.039
EF(Pb)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1±0
EF(Al)	1	1	1	1	1	1	1	1	1	1	1±0
EF(Hg)	0	0	0	0	0	0	0	0	0	0	0
EF(Cd)	0	0	0	0	0	0	0	0	0	0	0

Table 18. The contamination factor (CF) for heavy metals in the water of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
CF(Fe)	-5.397	-5.397	-5.397	-5.397	-5.443	-5.468	-5.698	-5.552	-5.468	-5.698	-5.481± -6.99
CF(Pb)	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
CF(Al)	0.0000125	0.0000125	0.0000125	0.0000125	0.0000125	0.0000125	0.0000125	0.0000125	0.0000125	0.0000125	0
CF(Hg)	20	20	20	20	20	20	20	20	20	20	0
CF(Cd)	1	1	1	1	1	1	1	1	1	1	0

Table 19. The ecological risk index (ERI) of heavy metals in the water of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
ERI(Fe)	67.97	69.74	37.14	22.14	13.82	10.39	23.04	21.93	18.48	17.91	30.25±21.53
ERI(Pb)	0.971	0.989	0.775	0.53	0.48	0.439	2.208	1.571	0.866	0.675	0.950±0.55
ERI(Al)	1	1	1	1	1	1	1	1	1	1	1±0
ERI(Hg)	0	0	0	0	0	0	0	0	0	0	0
ERI(Cd)	0	0	0	0	0	0	0	0	0	0	0

Table 20. The potential ecological risk (PER) of heavy metals in the water of the Zarjub River and Gohar Rood.

Station	1	2	3	4	5	6	7	8	9	10	Mean±SD
RI	69.91	71.71	39.69	23.2	14.78	11.32	28.46	25.07	20.18	19.2	32.352±21.69

contamination.

Mining and iron smelting were the primary sources of PTM contamination in the Xiangjiang River in China from the 1970s to the 1980s (**Zhang1989**). In addition, mining activities accounted for the main cause of PTM contamination in the Pilcomayo River in South America during the 1990s (Smolders et al., 2003). It has been reported that waste disposal was the primary source of PTMs in the Buriganga River in Bangladesh during the 2000s (Ahmad et al., 2010). Another study showed that rock weathering emerged as the main cause of PTM contamination in aquatic ecosystems as a result of global warming and increased acid rain during the 2010s (Singh et al., 2005a; Singh et al., 2005b; Singh et al., 2005c). These findings suggest a shift in the main source of PTM pollution from mining operations in the 1970s to waste disposal and rock weathering in the 2010s.

Many other studies around the world have investigated PTMs. For example, Shanbehzadeh et al. (2014) measured PTMs in the water and sediments of the Tembi River in Iran; Simonovski et al. (2003) assessed PTMs in the sediments of the Hawkesbury-Nepean River in Australia; Ciszewski and Turner (2009) examined PTMs in the sediments of the Odra River in Poland; Liu et al. (2015) studied PTMs in the Old Yellow River in China; and Paul (2017) analyzed heavy metal pollution in the Ganga River in India.

The data on the physicochemical characteristics of the Zarjub River and Gohar Rood indicated a mean water temperature of 22.8 °C, a mean pH of 6.7, with fluctuations ranging from 6 to 8. These figures demonstrated no consistent trend across the studied stations. The mean dissolved oxygen in the water of the two rivers was 4.9

mg/liter, with a range of 3 to 8 mg/liter. The electrical conductivity (EC) was equal to 635.3 and the mean total dissolved solids (TDS) was 316.5. In addition, the mean total hardness and water density were 343.2 and 998.139. All these parameters fall within appropriate ranges in these two rivers and exhibit no significant differences compared to other rivers in this basin, including the Sefidrud River (Sharifi et al., 2024).

The granulometric characteristics of sediments are of special importance in the study of contaminants in the water and sediments of aquatic ecosystems. The study findings in this regard indicated that the riverbed soil texture of the Zarjub River and Gohar Rood predominantly consists of clay and silt, with minimal presence of sand and gravel. The sediments in these two rivers contain a high percentage of organic matter, with a mean of 37.86%. However, the organic matter content in the sediments increased at the final stations, with a mean of 62.99%. This indicates a significant influx of organic matter due to the discharge of domestic wastewater into these rivers. The analysis of heavy metal concentrations in the water of the two rivers demonstrated that lead, aluminum, and mercury are present in low quantities, exhibiting minimal variation across the sampling stations. Only iron exhibited concentrations ranging from 0.1 to 0.2 mg/liter, primarily attributed to geological and bedrock sources.

The EF and CF indices indicated the low and very low contamination of the Zarjub River and Gohar Rood with heavy metals, respectively. However, the ERI demonstrated the very low contamination of these rivers with lead, aluminum, and mercury but their moderate contamination with iron. The highest concentration of heavy metals in surface sediments of these two rivers was related to iron and then aluminum and lead; mercury and cobalt were also found in very small quantities in surface sediments of these rivers. The geo-accumulation index showed that these two rivers were not contaminated with cobalt and mercury but they were moderately contaminated with iron and aluminum and highly contaminated with lead. The EF and CF indices also showed the same trend, indicating low values for aluminum, mercury, and cobalt, high values for iron, and very high values for lead. The concentration of heavy metals in the sediments of the Zarjub River and Gohar Rood is classified as low according to ERI.

Studies conducted in other parts of the world have reported contradictory values; for instance, the mean cadmium concentration in the Niger River, Africa, was recorded at 0.01 mg/L in the 1980s, 0.05 mg/L in the 2000s, and 19.14 mg/L in the 2010s (Nriagu, 1986; Olatunji and Osibanjo, 2013; Wangboje and Ikhuabe, 2015). In Lake Dongting, China, the mean lead concentrations were recorded at 1.4 mg/L in the 1980s, 3.3 mg/L in 2000, and 3.0 mg/L in 2010 (Liu et al., 2010).

The standards established by the WHO and USEPA were implemented in the 1970s, 1980s, 1990s, 2000s, and 2010s, respectively. The concentrations of heavy metals in rivers and lakes were lower in Europe and North America compared to higher levels observed in Africa, Asia, and South America. In the 2010s, the mean lead concentration in various water bodies was as follows: 0.4 mg/L in Hough Park Lake, North America (Ikem and Adisa, 2011); 0.8 mg/L in the Danube River, Europe (Ilie et al., 2014); 22.2 mg/L in the Pearl River, Asia (Zhao et al., 2011); 27.2 mg/L in the Nile River, Africa (Osman and Klovas, 2010); and 163 mg/L in the Matanza-Riacho River, South America (Magdaleno et al., 2014). However, studies have shown that the extensive application of pesticides and fertilizers is the primary cause of heavy metal contamination in Africa (Mavura and Wangila, 2003). Heavy metals in the Yangtze River in Asia primarily originate from mining activities and the weathering of rocks (Lu et al., 2005). Consequently, regional pollution control strategies must target particular sources of contamination in each region.

Governments and organizations around the world have adopted policies and measures to mitigate heavy metal contamination and regulate the influx of heavy metals. For instance, the US government has mandated regulations concerning the production, processing, commercial use, labeling, and disposal of harmful substances since the 1970s (Babich and Stotzky, 1985). Regarding agricultural metal pollution, the Dutch government introduced regulations in the mid-1980s that restricted the maximum concentration of cadmium (Cd) in phosphorus fertilizers to 35 mg/kg (Anon, 1989). In developed countries, non-toxic natural agents, including polypeptide oligomers, and biological controls have increasingly supplanted traditional pesticides (Wyckhuys et al., 2013; Monteiro et al., 2015). Increased copper concentrations suggest elevated discharge into these locations, potentially resulting from anthropogenic activities, including emissions from vehicles and coal combustion (Li et al., 2012), as well as vehicle lubricants and natural sources like metal content (Fu et al., 2014). The elevated cadmium concentrations in the sediments of the Buriganga River can be attributed to industrial activities, atmospheric emissions, leachates from neutralized nickel-cadmium batteries, and cadmium-coated products (Islam et al., 2015). Additionally, domestic and industrial wastewater, urban runoff, atmospheric deposition, and chemical production, along with steel manufacturing in Dhaka city, are primary causes of the high lead levels observed at certain sites along the Buriganga River (Shikazono et al., 2012). Elevated levels of heavy metals were detected in the surface sediments of the Buriganga River, suggesting that urbanization has increased the contamination of these sediments with heavy metals (Li et al., 2012). Numerous studies in Iran have also addressed this issue, including an investigation into sediment contamination in the Sefidrud River (Eghbali Shamsabad et al., 2010), an analysis of sediment contamination in the Zayanderud (Mirzaei and Solgi, 2016), a study of soil contamination with heavy metals in the Karun River, Khuzestan Province (Shahidi Kaviani and Paykanpoufard, 2020), and an assessment of sediment contamination with heavy metals in the Gandoman Wetland (Ansari Nia et al., 2022).

This study measured the physicochemical parameters and the concentration of PTMs in the water and sediments of these two rivers then employed different indicators to assess the degree of pollution in these two rivers. The measurement of PTMs in the water and surface sediments of the Zarjub River and Gohar Rood in this study indicated that the levels of these metals in the water of these two rivers were below the regulatory standards; however, the concentration of iron and lead in the surface sediments of the rivers may be slightly alarming. These findings suggest that the catchment areas of these two rivers do not contain major sources of heavy metals (partially because the wastewater of industrial units in region is normally treated), and the bedrock weathering and other geological features of the area are the primary causes of heavy metal contamination in the studied rivers. Nevertheless, the very high levels of organic matter indicate a significant inflow of organic matter due to the discharge of human wastewater into these two rivers. This is of great importance because these two rivers flow into Anzali Lagoon, which is not only the habitat of migratory birds and many fish species but also serves as a source of water for farms in this region. This necessitates the construction and completion of water treatment facilities and develop new standards for urban and industrial wastewater. Future studies are recommended to measure the concentration of arsenic, zinc, chromium, and copper in these two rivers at more stations in a 5-year period in order to achieve more realistic understanding of pollution status in these rivers.

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Authors contributions
Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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