Risk assessment, geochemical speciation, and source apportionment of heavy metals in sediments of an urban river draining into a coastal wetland

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Abstract

Thirty sediment samples were collected from the Gohar Rood River (Iran) to assess the elemental concentrations, origins, and probable environmental risks in the riverine system. In this study, fifteen elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Cr at all sites were exceeded the SEL (Severe Effect Level) value. Zn, Mn, Co, and Cr showed a moderate level of contamination, based on pollution index (PI), modified pollution index (MPI), and enrichment factor (EF). The modified hazard quotient (mHQ) represented low to extreme severity of pollution for some elements. The multi-linear regression of the absolute principal component score model indicated that largest contributors of Zn, Cu, Pb, Sb, and Mo to the riverine sediment were from agricultural runoff, domestic, and municipal sewage. Based on the modified BCR (the European Community Bureau of Reference) fractionation scheme, Mn, Co, and Zn indicated a medium to high risk to the local environment.

Keywords: Heavy metals, Risk assessment, MLR-APCS model, Geochemical fraction, River sediments.

Highlights

- Apart from Cr and As all investigated elements concentration were lower than their SEL values.
- Zn in sediment showed the highest enrichment factor, classed as significant enrichment.
- TRIi values for As, Cd, Cu, Pb, Ni, and Zn exhibited no toxicity risk (TRI ≤ 5).
- PCA-MLR and MLR-APCS models indicated sediment metal concentrations influenced by several anthropogenic sources of pollution.
- Metal fractionation results demonstrated high mobility for Mn, Co, Zn and V.

1. Introduction

Urban rivers are a necessary component of the global geochemical cycle, particularly those elements that are influenced by urban development and activities. They provide essential resources for human life such as aquatic products, drinking water, and support urban agriculture. Therefore, in most settlements, agricultural centres and industrial plants have been settled close to rivers (Castro et al., 2021). The heavy metals pollution in urban riverine sediments has become more intense with the fast development of urbanization and industrialization and has attracted a high deal of attention because of the related threats to aquatic organisms and human health (Sun et al., 2019; Zhang et al., 2017). Heavy metals in both dissolved and suspended phases are known as the most harmful types in the aquatic environment among various types of pollutants (Deng et al., 2021). Exposure to heavy metals has been related to different adverse health impacts such as kidney damage, impaired intelligence, developmental and behavioural problems, cancer, and even death in some cases of exposure to very high concentrations (Alomary and Belhadj, 2007). The reactivity and mobility of elements in sediment and water can affect their toxicity, bioavailability, and distribution in the riverine ecosystem (Devi and Bhattacharyya, 2018). Evaluation of the total elements concentration alone thus cannot determine the bioavailability or toxicity of elements (Shrivastava and Banerjee, 2004). It has been widely known that elemental speciation into various phases is the most dependable criterion to assess the toxicity of elements, as well as their biogeochemical transformation and ultimate fate (Liu et al., 2008; Sundaray et al., 2011). Although heavy metals are naturally ubiquitous in the environment, large amounts of metals entered aquatic ecosystems with the rapid increase in anthropogenic activities (Xiao et al., 2022). Heavy metals enter river sediments mostly from anthropogenic activities including residential areas, industrial plants, smelting, corroded underground pipes, road runoff, sewage effluents, combustion, agriculture, and transport emissions (Algül and Beyhan, 2020). Approximately 85% of the heavy metals will eventually deposit and accumulate in surface sediments of the aquatic environment (Xiao et al., 2019). Heavy metals inputs can be in dissolved or particulate forms, and most of the elements have a strong affinity to accumulate in sediment (Todorović et al., 2001). Sediments serve as both carriers and sink for different contaminants, including heavy metals and also play a considerable role in the re-suspension of the deposited pollutants back into the water column under certain conditions (Taghinia Hejabi et al., 2011). There is no doubt regarding the considerable role that sediments play in maintaining the trophic status of waterbodies, as well as their role in the biogeochemical cycle (Xiao et al., 2021). The release of elements from sediments into the water body is

controlled by the river basin characteristics (organic matter, pH, redox potential, etc.), which can influence the solubility of the element and, as a result, the elemental bioavailability, and also their speciation (Almeida et al., 2020). Elements in riverine sediments occur are in different forms, including those present in the lattice of silicate minerals or secondary minerals like oxides, sulfates, carbonates, or phosphates; complexed with organic matter; adsorbed on surfaces of manganese, iron oxyhydroxides, and clay (Todorović et al., 2001).

The environmental behaviour and ecological risk of elements in sediment have received wide consideration, thus sediment metal concentration assessment can help assess the quality of the aquatic ecosystem (Cui et al., 2021). Moreover, the concentration of the total elements cannot be applied to estimate short-term ecological risks, because it does not reflect the reactivity, bioavailability, or mobility of specific elements (Sauvé et al., 2000), but risk assessment based on total concentration is an important tool to identifying contamination sources (Liao et al., 2021). Mobility and bioavailability change with the chemical speciation of heavy metals in sediment, leading to different ecological risk outcomes (Sun et al., 2019). Therefore, elements chemical speciation e.g., using a sequential extraction method is necessary to understand their mobility and bioavailability (Wang et al., 2010). The European Community Bureau of Reference (BCR) standard method is a widely used sequential extraction procedure for evaluating the chemical speciation of elements and also their ecological risks and environmental hazards (Gao et al., 2018; Zhang et al., 2017). Based on the BCR method, the bioavailability of the toxic elements are related to the specific chemical fractions (Devi and Bhattacharyya, 2018).

In recent years, the investigation of heavy metals contamination in the northern regions of Iran has mostly focused on the coastal sediments of the Caspian Sea and Anzali wetland (Bastami et al., 2018; Charkhabi et al., 2008; Gharibreza and Masoumi, 2021; Nematollahi et al., 2021; Reza et al., 2012; Vosoogh et al., 2016), however, no comprehensive environmental research in the northern rivers of the country, especially the Gohar Rood River (Gilan province) has been carried out (Ghavidel and Moatar, 2009). Given its importance, a detailed evaluation of the heavy metals in the river sediment is required. River Gohar Rood is one of the important rivers in Gilan province, because it crosses the Rasht city passes through major urban areas, and receives hospital, domestic and industrial wastewater before its confluence into the Anzali coastal wetland which is located on the southern shores of the Caspian Sea (Mahmoudi et al., 2015). Urban areas have increased significantly, affecting the river that is used for recreation, irrigation, industrial, and domestic uses. Therefore, river quality monitoring program has become crucial to safeguard water resources and protect

public health. The effect of anthropogenic activities on this urban river could be reduced through early identification of its quality and diagnosis of potential pollution sources. To provide a scientific basis for evaluating the effect of anthropogenic activities on the river environment, the main aims of this study were to: (1) determine the spatial distribution and total concentration of the selected elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, V, Zn, and Sc) in sediment samples in the Gohar Rood River; (2) evaluate the potential environmental risk of selected elements via pollution indices; (3) identify and apportion potential sources of elements through a combination of multivariate statistics; (4) estimate the potential bioavailability of the selected elements in the sediments.

2. Material and Methods

2.1. Study area

The Gohar Rood River is located in the Rasht city (Gilan province) between 49˚32' 06" E to 49˚35'53" E and 37˚05' 44"N to 37˚ 10' 28" N (Fig. 1). The Gohar Rood River is one of the tributaries of the Sefidrood River (Iran's second-longest river). The river is approximately 50 km long, rises at 700m above mean sea level in Saravan mountains in the Alborz Mountain range of north-western Iran. The river merges into River Pirbazar downstream of the Rasht city before finally draining into Anzali International wetland (Saberinia et al., 2021). Gohar Rood River flows in lowland areas with high groundwater levels, and in its route, in addition to the effect on groundwater resources. Residential areas located on the banks of the river discharge 90% of their effluent into the river via pipes, domestic sewage along with hospital, industrial, agricultural, and even waste disposal, and the resulting leachate plays an significant role in the contamination of this river (Mohammadi Golrang et al., 2021). Municipal wastewater including domestic and hospital wastewaters are mainly discharged into Gohar Rood from western part of Rasht. Furthermore, some industrial units in the near catchment, with little or no wastewater treatment, discharge their untreated wastewater. Moreover, runoff from agriculture (upstream of the city) enters Gohar Rood river through leaching and runoff of water-soluble fertilizers and pesticides or agricultural effluents (Ghavidel and Moatar, 2009). Discharging of sewage effluents, domestic and industrial wastewater is likely contribute a range of pollutants, including heavy metals in the river, which may have influenced/altered the riverbed sediment quality (Mohammadi Golrang et al., 2021).

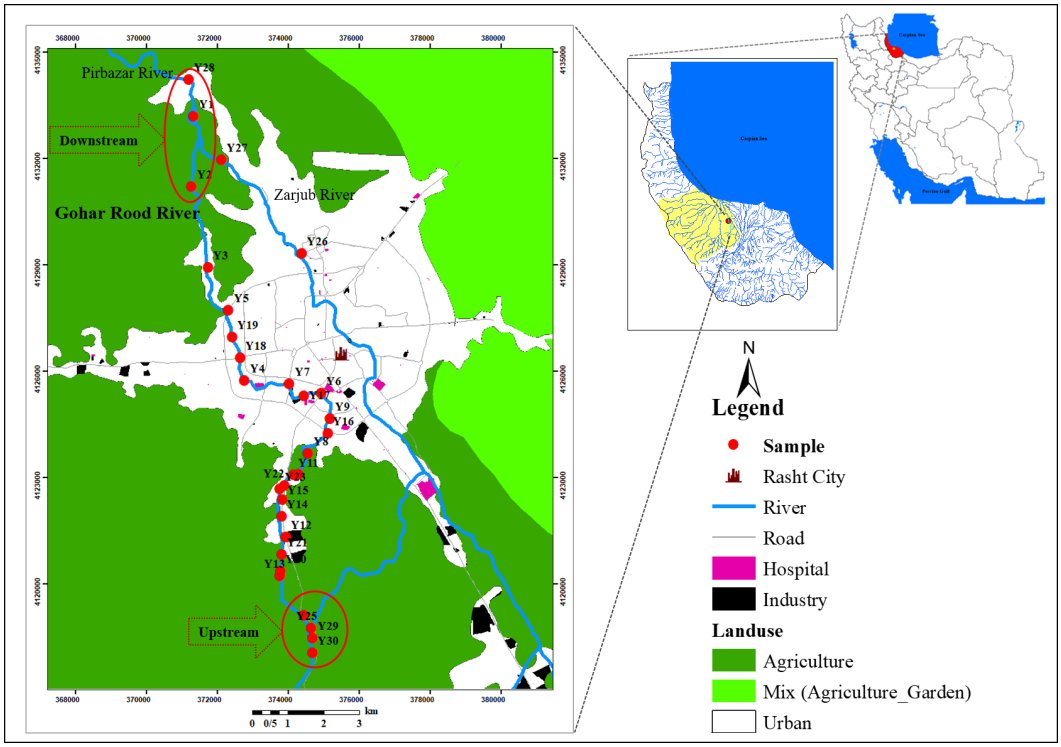

Fig. 1. Sediment sampling stations across the Gohar Rood River reach.

2.2. Field survey, sampling and sample preparation

Thirty surface sediment (0–5 cm) samples, covering the entire stretch of the Gohar Rood River were taken using a grab sampler. Samples were collected in July 2021, at the end of the dry season. Three samples were taken randomly from the downstream area of the Gohar Rood River, which were significantly affected by urbanized activity; 21 sampling stations were in midstream located along the river urban runoff through the city of Rasht, and four were in the upstream area, surrounded by farmlands (Fig. 1 and Table S1). In the laboratory, the samples were air-dried at room temperature, before crushing them using an agate mortar and pestle. Part of the samples was passed through a 2 mm sieve for the measurement of physicochemical parameters. The remaining sample portions were sieved through a 220 mesh (63 µm) for total metal concentrations and the geochemical fractionation of heavy metals.

2.3. Laboratory methods

The calcium carbonate and organic matter (OM) contents of sediment samples were determined via the loss on ignition (%LOI) method (Yavar Ashayeri et al., 2018; Zaharescu et al., 2009). The sediment electrical conductivity (EC) and pH were determined in aqueous suspensions (1:5, w/v sediment/water) by a pH/EC meter (Eutech instrument, Waterproof CyberScan PCD 650, Singapore) (Ryan et al., 2007). The sediment cation exchange capacity was determined following the method described in Kahr and Madsen (1995). The particle

size distribution and texture of sediments were measured by the hydrometer method (Gee and Bauder, 1986).

For total elemental analysis, 0.5 g of each sediment sample (<63 μm) was digested in Aqua Regia, before being analysed for by inductively coupled plasma mass spectrometry (ICP-MS) at Zarazma Mineral Studies Laboratory, Iran. For quality assurance and control (QA/QC), analysis of certified reference materials (Geostats 308-12, 903-13, 907-13 and OREAS 902, 903, 905), analytical duplicates, and reagent blanks were employed. All blank extractions were below the detection limit. The recovery rate of the selected elements from the certified reference materials ranged from 80% to 110%.

2.4. Sequential extraction procedure

Heavy metals in sediments are bound to several geochemical phases with various strengths and represent different behaviour with regard to remobilization (Guo et al., 2015). In this study, five samples were selected to assess geochemical fractions, mobility, and availability of heavy metals in sediment by using a modified BCR-sequential extraction procedure, which includes a three-step sequential extraction method. The analysis of residual fractions was considered step four. The procedure is summarized in Table 1 and full details are presented elsewhere (Gao et al., 2018; Li et al., 2013; Yavar Ashayeri et al., 2020).

Table 1 Successive stages of the modified BCR sequential extraction procedure used for sediments.

Step	Fraction	Extractant	Procedure
F1	Acid soluble/exchangeable fraction (exchangeable metal and carbonate-associated fractions)	20 ml of 0.11 M Acetic acid	16 h shaking at 25 ºC
F2	Reducible fraction (fraction associated with Fe and Mn oxides)	20 ml of 0.1 M Hydroxyl ammonium chloride, pH 2 with HNO_3	16 h shaking at 25 ºC
F3	Oxidizable fraction (fraction bound to organic matter)	10 ml of 8.8 M H_2O_2, 25 mL of 1 M ammonium acetate at pH 2	2 h shaking at 85 ºC 16 h shaking at 25 ºC
F4	Residual fraction	10 ml of a mixture of 12 M HCl and 15.8 M HNO3 in a 3:1 ratio	evaporated to near dryness

After each step, the extracts were decanted into polyethylene containers and stored at 4 °C for analysis. Finally, elements concentration in each fraction was analyzed using ICP-optical emission spectrometry (OES) at Zarazma Mineral Studies Company (Iran). The detection limits were 0.10 mg l^{-1} for Mn, Fe, and Al and 0.05 mg l^{-1} for Cr, Co, Cd, As, Cu, Ni, Mo, Sb, Sc, Zn, V, and Pb. Also, reagent blank and certified reference material (GBW 7312) were

used in the modified BCR sequential extraction procedure. An internal examination was done for fractionation analysis by comparing the results of the pseudo-total content with the total elements concentration extracted in the four steps. The recovery percentage of all elements ranged from 70 to 120%, which is within the acceptable range.

2.5. Pollution assessment indices

A coupling of specific and combined methods has been used to determine the pollution level and sediment environmental quality. The direct evaluation of enrichment and ecological risks of elements in sediments is commonly quantified through the relationship between geochemical background concentrations and their total elemental concentrations (Kim et al., 2021). In this study, the shale average content is used as the background value (Turekian, K; Wedepohl, 1961).

2.5.1. Enrichment factor (EF)

EF, a linear relation between a reference element with the element of interest under natural sedimentation situations is a useful index to determine the element contamination enrichment level in the sediments/soils. To minimize the effects of mineralogical and textural variation between samples, the concentrations were normalized to element data to geochemical reference material (Lim et al., 2021). In this study, Sc element was applied as a geochemical normalizer. The variation coefficient of Sc was only 0.08, suggesting that the element was not affected by environmental disturbances.

2.5.2. Pollution index (PI), modified degree of contamination (mDc), and modified pollution index (MPI)

The pollution index (PI) is generally used for environmental contamination assessment by a certain element (Hakanson, 1980), while the modified degree of contamination (mDc) can create an integrated assessment of heavy metal pollution in a sampling site as a whole (Abrahim and Parker, 2008). To evaluate the overall contamination of the sediments with multiple elements the modified pollution index (MPI) was used (Brady et al., 2015).

2.5.3. Modified ecological risk index (MRI)

The modified ecological risk index (MRI) has been widely applied to more accurately assess different levels of the potential ecological risk of elements in sediments (Brady et al., 2015; Yavar Ashayeri and Keshavarzi, 2019). This approach considers not only background content

and measured amount of elements but also environmental sensitivity, toxicity, and multi-element synergetic effects to element contamination (Wang et al., 2020). In the MRI concept, the standardized response coefficient (Tr^i) for toxicity of each element in the sediment used were: Cd = 30, As = 10, Co = Pb = Cu= Ni= 5, Cr = 2, and Zn = 1 (Hakanson, 1980; Li et al., 2018). The brief description, mathematical equations, and detailed classification of these indices are given in Supplementary Information (Table S2 and Table S3).

2.5.4. Toxic Risk Index (TRI) and Modified hazard quotient (mHQ)

The toxic risk index (TRI) is developed as a new model for the integrated toxicity risk evaluation in the environment depending on the TEL (threshold effect level) and PEL (probable effect level) effects (Zhang et al., 2016). The TRI values in sediment samples were computed as:

$$TRI_i = \sqrt{\frac{(C_i/TEL_i)^2+(C_i/PEL_i)^2}{2}} \quad (1)$$

The integrated TRI for multiple elements can be assessed by Eq (2).

$$TRI = \sum_{i=1}^{n} TRI_i \quad (2)$$

To interpret the TRI values, the level of toxicity risk is categorized into five classes: TRI ≤ 5 (no toxicity risk), 5 < TRI ≤ 10 (low toxicity risk), 10 < TRI ≤ 15 (moderate toxicity risk), 15 < TRI ≤ 20 (considerable toxicity risk), and TRI > 20 (very high toxicity risk) (Abbasi et al., 2021; Ustaoğlu and Islam, 2020).

The modified hazard quotient (mHQ) is utilized to determine sediment pollution by comparing element concentrations in the sediment with the synoptic negative ecological impact distributions for the threshold levels (PEL, SEL (severe effect level), and TEL) (Benson et al., 2018), which are given in Table S4. This method can be used as an important technique as it elucidates the extent of hazard each element poses to the sediment-dwelling organisms and aquatic habitat (Liao et al., 2021). The mHQ is calculated as:

$$mHQ = \sqrt[n]{\frac{C_i}{TEL_i} + \frac{C_i}{PEL_i} + \frac{C_i}{SEL_i}} \quad (3)$$

where the measured concentration of element is denoted as C_i, n is the number of investigated elements, TEL_i, PEL_i, and SEL are the TEL, PEL, and SEL values of the corresponding element, respectively. The mHQ values are classified as: mHQ > 3.5 (extreme severity of pollution); 3.0 ≤ mHQ < 3.5 (very high severity of pollution); 2.5 ≤ mHQ < 3.0 (high severity of pollution); 2.0 ≤ mHQ < 2.5 (considerable severity of pollution); 1.5 ≤ mHQ < 2.0 (moderate severity of pollution); 1.0 ≤ mHQ < 1.5 low severity of pollution; 0.5 ≤ mHQ < 1.0

(very low severity of pollution); mHQ < 0.5 (nil to very low severity of pollution) (Rahman et al., 2022).

2.5.5. Risk assessment code (RAC)

The risk assessment code (RAC) was employed to evaluate the environmental risk and mobility of the non-stable chemical phase of elements (Ke et al., 2017). The categorization of the RAC for evaluating element contamination was expressed as the exchangeable fraction (% F1, BCR) in sediment. According to RAC, sediment samples can be categorized as very high risk (51- 75%), high risk (31- 50%), medium risk (11-30%), low risk (1-10%), and no risk (<1%).

2.6. Statistical analysis

All statistical tests were carried out using SPSS Statistics 26 (SPSS Inc., USA). The identification of heavy metals sources via distinguishing the anthropogenic portion to element accumulation in sediments is essential to evaluate environmental processes and river environmental protection (Deng et al., 2021). Multivariate statistical techniques (e.g., principal component analysis, PCA, multiple linear regression, MLR, and absolute principal component scores, APCS) were used on source identification and apportionment of selected elements in the sediments. Data suitability for principal components was estimated via the Kaiser-Meyer-Olkin (KMO) and Bartlett's tests. PCA was performed to cluster elements that behaved similarly or dissimilarly to interpret their possible origins. To carry out the MLR model, the total element concentrations and PCA factor scores were selected as dependent and independent variables, respectively. Then, the obtained standardized regression coefficients were used to quantify the proportional contribution of each source. The detailed steps of the PCA-MLR receptor model have been described by Yavar Ashayeri et al. (2018). The MLR-APCS method not only qualitatively specifies the load species of each contaminant's origin, but also quantitatively specifies the mean origin share to its elements and the contribution rate at each station. These models have been explained in detail by Yavar Ashayeri and Keshavarzi (2019). Prior to geostatistical analyses, the data normality was assessed using the Shapiro-Wilk test ($p < 0.05$). To apply the statistical tests, the concentrations of elements below the detection limit were replaced with 75% of the corresponding detection limits. Spatial distribution maps of elements in sediments were plotted with ArcGIS 10.8 software.

3. Results and Discussion

3.1. Geochemistry of sediment samples

Results of the physicochemical properties and elements concentration in sediments are summarized in Table 2. The clay values varied between 24.88 and 80.88%, with a mean of 35.85%. The percent silt varied between 4.56 to 44%, with a mean of 13.1%. The sand percentage in the sediment samples varied from 9.12 to 70.56%, with an average of 51.05%. Figure 2 illustrates the particle size distribution in the sediments. Comparison of the mean clay, silt, and sand particles indicated the sediments are mostly composed of clay and sand particles in the sampling area. Based on the texture, sediments can be classified as sandy clay loam (Fig. S1).

Table 2 Descriptive statistics for investigated elements concentration and physicochemical characteristics of sediments in the study areas.

Element (mg kg^{-1})	DL	Mean	Median	Std. Deviation	Minimum	Maximum	CV%	Average Shale *
Al	100	73230.43	72197	7105.31	56547	88976	9.70	80000
As	0.1	18.42	17.1	6.03	9.6	33.8	32.75	13
Cd	0.1	0.1	0.08	0.06	ND	0.3	53.88	0.3
Co	1	33.97	31.5	9.93	20	57.5	29.23	19
Cr	1	175.2	166.5	32.92	144	291	18.79	90
Cu	1	59.53	58	23.18	35	121	38.94	45
Fe	100	60660.8	59860	7123.04	49896	76388	11.74	47200
Mn	5	1802.33	1364	1242.99	728	5905	68.97	850
Mo	0.1	1.45	1	1.06	ND	5	73.01	2.6
Ni	1	58.2	58	5.07	50	71	8.72	68
Pb	1	30	27.5	8.02	18	49	26.74	20
Sb	0.5	1.17	1.15	0.48	ND	2.5	41.21	1.5
V	1	165	167	14.43	140	189	8.75	130
Zn	1	213.4	169	163.6	91	700	76.66	95
Sc	0.5	13.13	13.35	1.07	10.9	15.9	8.12	13
pH		7.01	7.01	0.27	6.42	7.8		
EC (mS/cm)		2.39	2.50	1.14	0.05	4.4		
CEC (meq/100g)		23.74	21.64	11.27	14.79	75.03		
OM (%)		6.14	5.84	2.41	1.96	10.29		
$CaCO_3$ (%)		0.94	0.81	0.54	0.32	2.92		
Sand (%)		51.05	57.02	16.08	9.12	70.56		
Silt (%)		13.1	10.46	7.92	4.56	44		
Clay (%)		35.85	33.24	11.63	24.88	80.88		

*Average Shale values adapted from Turekian, K; Wedepohl (1961). DL: Detection Limit (mg kg^{-1}), ND: Not Detect.

The percentages of $CaCO_3$ were found to vary between 0.32 and 2.92%, with a mean of 0.94%. The maximum $CaCO_3$ was measured at the Y25 site, which can be due to the occurrence of cretaceous rocks like massive sandy limestone in the upstream area (Hazermoshar et al., 2016). The organic matter (OM) (based on loss-on-ignition method) content in the sediments ranged between 1.96 and 10.29%, with a mean of 6.14 %. The maximum OM amount was observed at the sampling Y11 station, which could be because of

the high vegetation cover. The CEC ranged between 14.79 and 75.03 meq/100g, with an average amount of 23.74 meq/100g. Also, the mean CEC level indicates the sediments have a medium capacity to retain elements via adsorption mechanisms (Abbasi et al., 2021; Yavar Ashayeri and Keshavarzi, 2019). However, the pH can affect the mobility of elements, and when the pH is between 6.5 to 7, element solubility becomes relatively low (Sun et al., 2013; Ustaoğlu and Islam, 2020). The pH of sediments varied between 6.42 to 7.80, with a mean value of 7.01, which means the investigated sediment samples are slightly acidic to neutral to alkaline. The EC ranged from 0.05 to 4.40 mS/cm, with an average of 2.39 mS/cm, which indicated a very low salinity of riverine sediments in the study area.

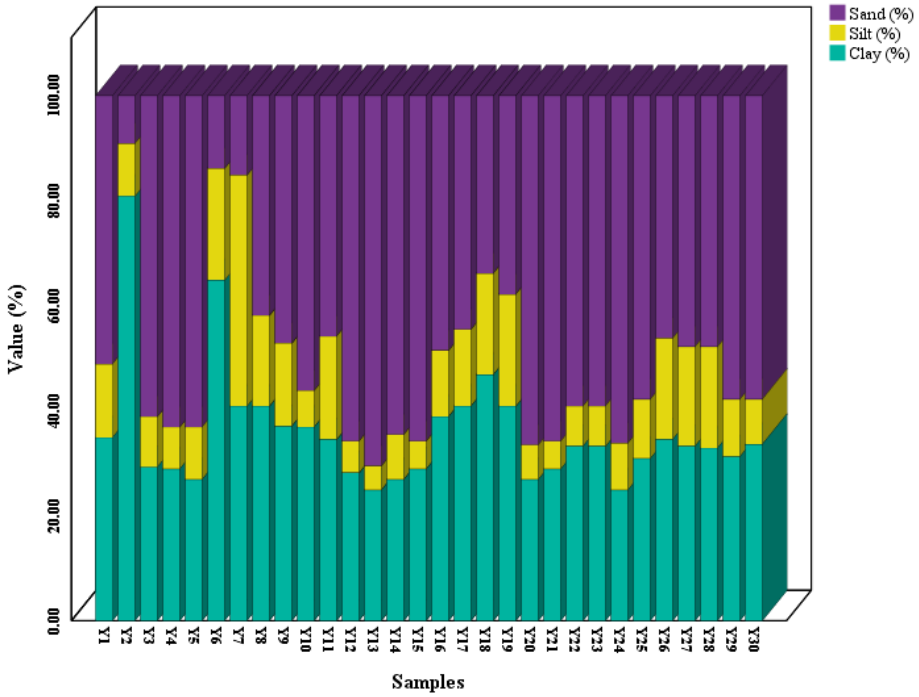

Fig. 2. Diagram of the particle size distribution in the sediment samples.

Fe and Al are the predominant elements, occurred in most sediments in high amounts compared to other elements (Table 2), because nearly all the lower and upper earth's crust contain high Fe and Al contents. Mn is the third element with relatively high concentrations (Diami et al., 2016; Turekian, K; Wedepohl, 1961). The coefficient of variation (CV = standard deviation*100/mean) can be utilized to qualitatively examine elemental spatial variability. A modified version of the classification for CV suggested by Hu et al. (2008) is regarded as strong variability (CV ≥ 100%), moderate variability (10% < CV < 100%), and low variability (CV ≤ 10%). In this study, Al represented low variability whereas the Fe and Mn exhibited moderate variability. The elements concentration in the sediments was also

compared with the Severe Effect Level (SEL), Probable Effect Level (PEL), and Threshold Effect Level (TEL) values (Table S4). The Fe and Mn amounts in 100% of the sediments were observed to be higher than the SEL values of 40000 mg kg^{-1} and 1100 mg kg^{-1}, respectively (MacDonald et al., 2000). The findings revealed that the levels of Fe and Mn in the Gohar Rood River were more than those observed in Pazarsuyu Stream (Turkey), Hooghly River Estuary (India), Mahanadi River (India), Dhaleshwari River (Bangladesh), Amur River (Russia), and Elbe River (Germany) (Table 3).

The highest Zn concentration was found at the Y13 station (midstream), while the lowest was at the Y29 site, located upstream of the Gohar Rood River. The CV for the concentration of Zn in sediment samples exhibited moderate variability. The Zn concentrations determined in the sediment samples were lower than 23.33%, 66.67%, and 10% of their TEL, PEL, and SEL values, respectively. The mean Zn concentration in the Gohar Rood River sediments was more than those from Pazarsuyu Stream (Turkey), Halda River (Bangladesh), Haihe River (China), Hooghly River Estuary (India), Mahanadi River (India), Hooghly River Estuary (India), Kangryong River estuary (Korea), Dohezar River (Iran), Karoon River (Iran), and Zayanderood River (Iran). The Cr concentration in 100% of the sediments was higher than the PEL and SEL values. High Cr value can be due to the existence of tannery industry surrounding the study area, which discharges effluents enriched with Cr into the Gohar Rood River. The mean value of Cr in the sediments of Gohar Rood River are higher than those of Pazarsuyu Stream (Turkey), Halda River (Bangladesh), Amur River (Russia), Mahanadi River (India), Hooghly River Estuary (India), Kangryong River estuary (Korea), Dohezar River (Iran), Karoon River (Iran), Zayanderood River (Iran), exception of Dhaleshwari River (Bangladesh) and Elbe River (Germany) (Table 3).

The highest concentration of V was detected in Y1 station, located in downstream of the study area (Pirbazar River). Also, the higher levels of Cu, Ni, Co, Pb, and As in the sediments were detected at Y5, Y7, Y15, Y4, and Y14 sampling points, respectively. These sampling stations are in the central part of the Gohar Rood River in Rasht city, where the river receives effluents from residential, hospitals, industrial units, and agricultural area located on the riverbanks. The Cu values found in 96.67% of stations were lower than the PEL. This rise in Cu amount in sediments can be because of urban wastes disposal, intensive utilization of fertilizers and pesticides, and the weathering of the bedrock (Ustaoğlu and Islam, 2020). The mean value of Cu was lower than those of Pazarsuyu Stream (Turkey) and Elbe River (Germany) but higher than Dhaleshwari River (Bangladesh), Halda River (Bangladesh), Haihe River (China), Amur River (Russia), Mahanadi River (India), Hooghly River Estuary

(India), Kangryong River estuary (Korea), Dohezar River (Iran), Karoon River (Iran), Zayanderood River (Iran) (Table 3).

The concentration of Pb observed in Y3-Y5, Y13 (midstream), Y24 (upstream) sites was lower than its PEL value of 91.3 mg kg^{-1}. The relatively high Pb concentration in some sediment samples could have been influenced by urban runoff and the roadside dust near the river (Shikazono et al., 2011). The mean Pb sediment concentration was higher than all other rivers considered here, except for Pazarsuyu Stream (Turkey), Elbe River (Germany), Mahanadi River (India), and Zayanderood River (Iran). The sediment Ni concentrations revealed 100% of the sediment samples were between its PEL and SEL levels. The mean Ni concentration in the study area was higher than those concentrations observed from Halda River (Bangladesh), Haihe River (China), Hooghly River Estuary (India), Kangryong River estuary (Korea), Karoon River (Iran), but lower than Haihe River (China) and Karoon River (Iran). Arsenic (As) concentrations at sites Y14 and Y15 (midstream) exceeded its SEL value; at sites Y1-Y9, Y11, Y17-Y19, Y29, and Y30 it was between its TEL and PEL levels and was between the PEL and SEL levels in the remaining stations. The findings revealed that the level of elemental concentration for As and Co in the Gohar Rood River was more than that observed in other rivers considered here (Table 3).

Table 3 Comparison of mean elements concentration (mg kg^{-1}) in sediments of the Gohar Rood River with other rivers in the world**.**

Locations	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Reference
This study	73230.4	18.4	0.1	34	175.2	59.5	60660.8	1802.3	58.2	30	213.4	This study
Pazarsuyu Stream, Turkey	45060	15.8	0.7	20.6	60.4	114	42024	1137	23.3	72.1	138	(Ustaoğlu and Islam, 2020)
Dhaleshwari River, Bangladesh	-	-	-	-	186	1.8	42.7	3.1	-	8.8	-	(Rahman et al., 2022)
Halda River, Bangladesh	-	2.7	0.1	-	31.9	31.9	-	-	26.7	20.5	71.9	(Hossain et al., 2021)
Haihe River, China	-	-	0.2	-	-	45	-	-	64	15	133	(Zhang et al., 2021)
Amur River, Russia	-	-	-	-	36.3	7.4	25400	768	-	19.2	-	(Sorokina and Zarubina, 2011)
Elbe River, Germany	-	-	-	-	386	206	33400	1230	-	122	-	(Garzanti et al., 2010)
Mahanadi River, India	60000	-	4.2	-	72	36	-	1133	55	131	137	(Sundaray et al., 2011)
Hooghly River Estuary, India	-	4	0.2	-	31.8	16.7	23322	482	19.8	10.7	46.9	(Mondal et al., 2020)
Kangryong River estuary, Korea	-	-	-	12.7	15.2	17	-	-	15.5	3.1	68.3	(Lim et al., 2021)
Dohezar River, Iran	-	15	-	-	64	18	-	-	-	25.1	68	(Sartipi Yarahmadi and Ansari, 2018)
Karoon River, Iran	11700	4.3	0.2	-	48.8	20.5	-	-	73.7	8.1	48.9	(Keshavarzi et al., 2015)
Zayanderood River, Iran	78500	-	0.2	-	61.7	29.7	-	-	25.3	35.1	126	(Rastegari Mehr et al., 2012)

3.2. Pollution and Ecological risk assessment

3.2.1. Enrichment Factor (EF) and Pollution index (PI)

The EF values varied between 0.03 to 8.79 for the elements considered in the study (Fig. S2). The highest EF value among all sampling stations was found for Zn at Y3 (EF = 8.8) and Y5 (FE = 8.6) sites, suggesting significant enrichment. The calculated EF values for Al, Cd, Fe, Sb, Ni, Mo (except for site Y3), and V in all sampling points showed little to no enrichment, indicating natural variation in their levels, while the EF value for Mo at site Y3 indicates a moderate enrichment. In general, the EF values for As, Co, Cr, Cu, Pb, Mn (except for Y14 and Y15 sites), and Zn (except for Y3-Y5 sites) indicate minimal to moderate enrichment due to low EF levels. However, Mn at Y14 and Y15 sites and Zn at Y3-Y5 sites showed significant enrichment, probably influenced by anthropogenic activities near these sampling stations (Fig. 3). The mean EF values of heavy metals in the sediments were ranked as: Zn (2.32) > Mn (2.16) > Cr (1.94) > Co (1.74) > Pb (1.51) > As (1.42) > Cu (1.34) > Fe (1.28) > V (1.26) > Al (0.91) > Ni (0.850 > Sb (0.78) > Mo (0.57) > Cd (0.35). The mean EF value of Zn and Mn indicated a moderate enrichment, while the rest of the heavy metals no to minimal enrichment.

The Pollution Index (PI) values of elements in the sediments are reported in Table 4. The PI values indicated a moderate degree of contamination for Co (exception of Y15 site), Cr (exception of Y12), Fe, and V in all the sampling stations ($1 \leq PI < 3$), while those for Co at the Y15 site and for Cr at Y12 site were 3.03 and 3.23, respectively, indicating considerable pollution with these elements. The PI values for Ni, As, Al, Cu, Mo, and Sb ranged from low to moderate level of contamination, whereas the PI for Cd was generally low, suggests little to no anthropogenic influence. However, PI values for Pb (except for site Y2 (PI <1)) and Zn (except for sites Y3-Y5 ($PI \geq 6$) and Y29 (PI <1)), showed a moderate degree of contamination. The PI values for Mn showed low contamination at Y4 and Y19 sites, considerable contamination at Y11, Y13, and Y22 sites, and very high contamination at Y14 and Y15 sites, while the PI values in other sites indicate moderate contamination levels.

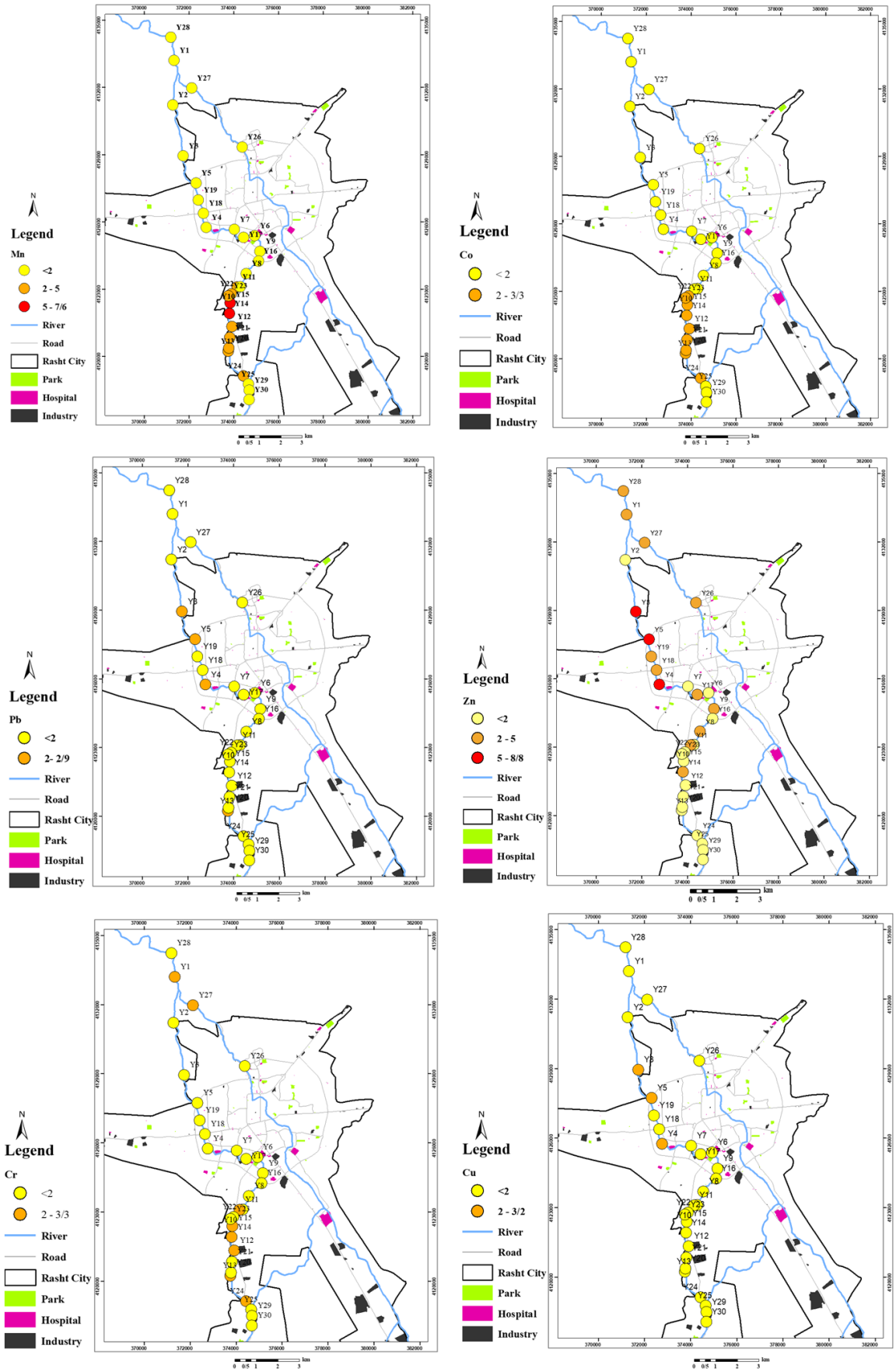

Fig. 3. Spatial distribution map of Enrichment Factor (EF) values for selected elements in the sediments of Gohar Rood River.

The highest PI values of 7.37 and 7.32 for Zn were found at Y3 and Y5 sites, respectively, among all investigated elements. Generally, the mean PI values decreased in the following order: Zn (2.25: moderate) > Mn (2.12: moderate) > Cr (1.95: moderate) > Co (1.79: moderate) > Pb (1.50: moderate) > As (1.42: moderate) > Cu (1.32: moderate) > Fe (1.29: moderate) > V (1.27: moderate) > Al (0.92: low) > Sb (0.78: low) > Mo (0.56: low) > Cd (0.35: low) which demonstrated that sediments in the Gohar Rood River were likely polluted due to the input of domestic, municipal, and industrial wastewaters. Also, this study indicated that the mean concentrations of all metals (exception of Al, Cd, Mo, and Ni) in the sediments were higher than their corresponding average shale values.

3.2.2. Modified degree of contamination (mDc) and Modified pollution index (MPI)

The modified degree of contamination (mDc) and modified pollution index (MPI) results in the sediments are presented in Table 4. The mDc values varied from 0.98 to 1.78 with an average value of 1.31, which demonstrates unpolluted to moderate levels of contamination. The mDc values indicated moderate level of pollution for Y3-Y5, Y14, and Y15, while other sites (exception Y2 and Y29) were only slightly polluted, with Y2 and Y29 sites showing no anthropogenic influence. The MPI values varied from1.16 to 6.36 with an average value of 2.51. The mean MPI value indicated moderate contamination. The MPI values at Y3-Y5, Y14, and Y15 stations indicate they are heavily polluted where Zn, Mn, Cu, and Pb were the dominant contaminants. Site Y11 is moderately to heavily polluted; sites Y1, Y12, Y13, and Y21-Y24 are moderately polluted, and the other sites have been only slightly polluted. In general, the mDc and MPI values illustrated almost the same distributions among the investigated points, however, it seems that MPI has overestimated the contamination level in the sediments compared to mDc, which is calculated using the EF (Fig. 4).

3.3.3. Modified ecological risk index (MRI), Toxic Risk Index (TRI) and Modified hazard quotient (mHQ)

The values of the potential risk of each element (Er^i) and MRI are given in Table 4. The lowest and highest values of Er^i in the sediments were observed for Zn and Cd, respectively. Furthermore, all the investigated elements show low risk at all points. Moreover, the MRI values varied from 41.2 to 88.6 with a mean value of 58.4. The MRI results for all sampling points showed low ecological risk (MRI < 150). The spatial distribution of MRI values is illustrated in Fig. 4. According to the TRI_i values, As, Cd, Cu, Pb, Ni, Zn, and Cr (except for site Y12) exhibited no toxicity risk (TRI ≤ 5) in all sampling locations, while the TRI_i value

for Cr at sampling point Y12 indicated low toxicity risk (5 < TRI ≤ 10) (Table 4). Moreover, the values of TRI among all sampling points varied from 9.3 to 15.3, with the maximum value at site Y3 and the minimum value at site Y29. According to the classification of TRI, the TRI values at sampling points Y2, Y19, Y29, and Y30 indicated low toxicity risk. Only at the sampling point Y3 a considerable toxicity risk (15 < TRI ≤ 20) was demonstrated. Also, moderate toxicity risk was measured at the rest of the sampling points with TRI values between 10 to 15 (Fig. 4), as the values of TRI with a mean 11.8 indicated moderate toxic risk.

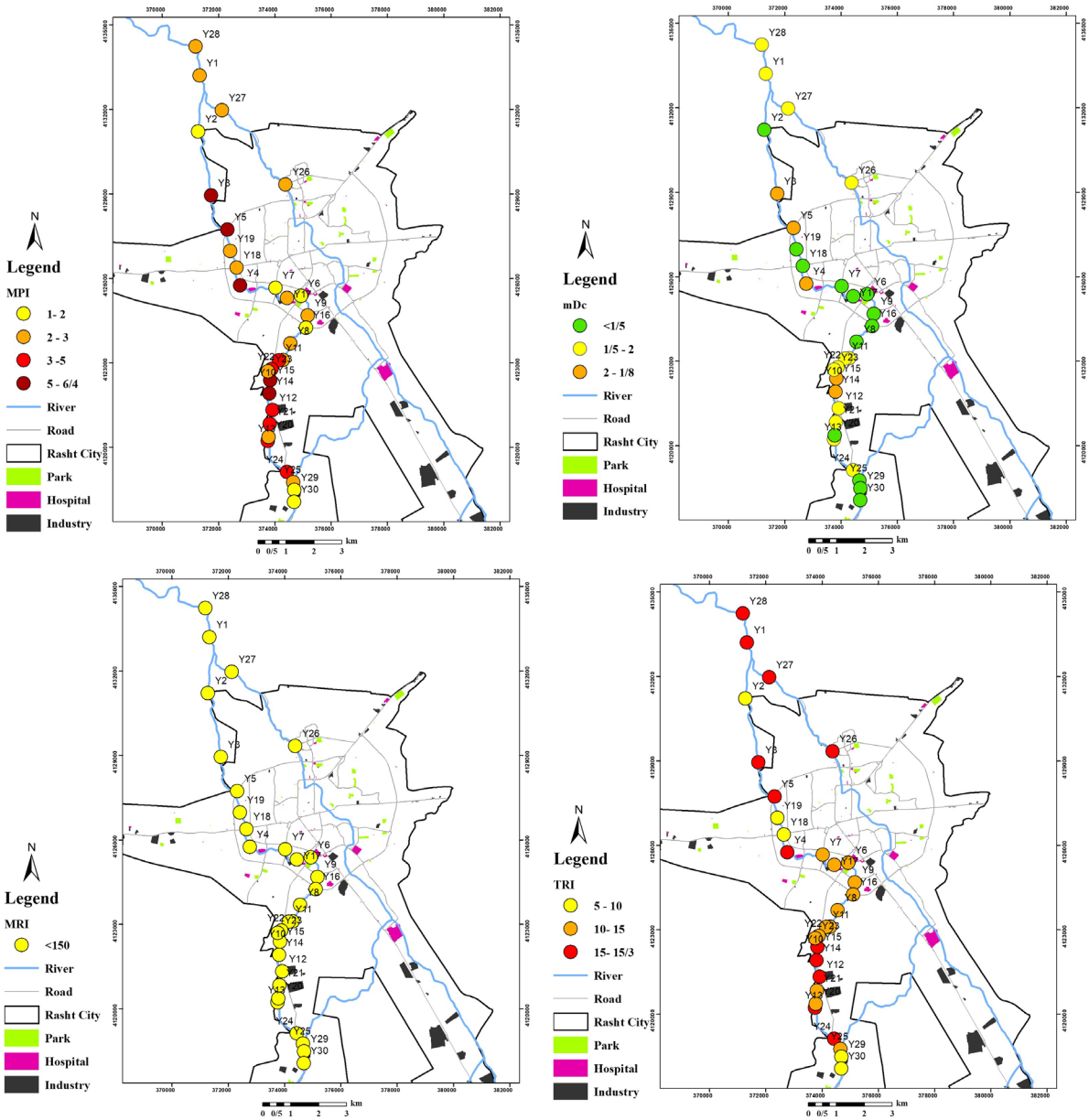

Fig. 4. Spatial distribution map of modified degree of contamination (mDc), modified pollution index (MPI), modified ecological risk index (MRI), and toxic risk index (TRI) values in the sampling sites from the Gohar Rood River.

The TRI results are in good agreement with the other contamination assessment indices. According to the results, the TRI equation demonstrated higher toxicity risk compared to the MRI index because the TRI method uses values of the TEL and PEL, providing better information for the elements toxicity risk evaluation. It is critical to notice that MRI and TRI are mostly applied for comprehensive ecological risk estimation of location-specific status and aggregative pollution impacts by toxic elements in the environment. Although the assessment levels of these two methods are not totally consistent, their impacts are primarily similar, suggesting that each one of them could be used as a reliable and effective for contamination toxicity risk assessment of potentially toxic elements (Benson et al., 2018; Liao et al., 2021).

Table 4 Result of toxic risk index (TRI), modified hazard quotient (mHQ), pollution index (PI), modified degree of contamination (mDc), modified pollution index (MPI), potential risk of element (Er^i), and modified ecological risk index (MRI) for selected elements in the sediments.

Element	**PI**													
	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	V	Zn
Min	0.71	0.74	0.25	1.05	1.6	0.78	1.06	0.86	0.03	0.74	0.9	0.25	1.08	0.96
Max	1.11	2.6	1	3.03	3.23	2.69	1.62	6.95	1.92	1.04	2.45	1.67	1.45	7.37
Mean	0.92	1.42	0.35	1.79	1.95	1.32	1.29	2.12	0.55	0.86	1.50	0.78	1.27	2.25

Element	**Er^i**									**MRI**	**mDc**	**MPI**
	As	Cd	Cr	Cu	Pb	Ni	Zn	Co				
Min	6.9	6.1	2.7	3.7	4.3	3.6	0.9	5.6		41.2	0.98	1.16
Max	28.6	32	6.6	15.9	14.3	4.9	8.8	16.5		88.6	1.78	6.39
Mean	14.2	10.5	3.9	6.7	7.6	4.2	2.3	8.9		58.4	1.31	2.51

Element	**TRI_i**							**TRI**	**mHQ**					
	As	Cd	Cr	Cu	Pb	Ni	Zn		As	Cd	Cr	Cu	Pb	Ni	Zn
Min	1.2	0.1	3	0.7	0.4	2.2	0.6	9.3	1.58	0.39	2.6	1.22	0.89	2.2	1
Max	4.3	0.4	6	2.4	1.1	3.1	4.4	15.3	2.96	0.79	3.7	2.26	1.46	2.62	3
Mean	2.3	0.1	3.6	1.2	0.6	2.6	1.3	11.8	2.16	0.45	2.86	1.56	1.13	2.37	2

The mHQ was computed using Eq. (3), and its data for each element is presented in Table 4. In this study, mHQ values for As at sites Y4-Y6, Y11, Y18, Y19, Y29, and Y30 indicate moderate severity of pollution, while at sampling sites Y1-Y3, Y7-Y10, Y16, Y17, Y20-Y23, and Y25-Y28 and Y12-Y15 and Y24 showed considerable and high severity of pollution, respectively. mHQ values for Cd revealed that 83.3% of the samples showed no to very low severity of pollution, with Y11, Y14, Y19, Y23, and Y28 sampling points showing a very low degree of pollution. mHQ values for Cr exhibited that sites Y2-Y11, Y14, Y16-Y23, Y25, and Y28-Y30 had high severity of pollution, while sites Y1, Y13, Y15, Y24, Y26, and Y27 showed very high severity of pollution, and Y12 site exhibited extreme severity of pollution. It was also revealed that sites Y2, Y7, Y12-Y16, Y20-Y23, Y25, Y29, and Y30 had

low severity of Cu pollution, while sites Y1, Y6, Y8-Y11, Y17-Y19, Y24, and Y26-Y28, and sites Y3-Y5 showed moderate severity of pollution and considerable severity of Cu pollution, respectively. For Zn, the results showed that sites Y2, Y6, Y7, Y12, Y13, y15, Y16, Y20-Y25, Y29, and Y30 had low severity of pollution, while sites Y1, Y8-Y11, Y14, Y17-Y19, and Y26-Y28 were in the moderate severity of pollution range, and site Y4 and sites Y3 and Y5 were in high and very high severity of pollution, respectively. On the other hand, for Pb all the sediment sampling sites (except sites Y2 and Y6) indicated very low degree of pollution and sites Y2 and Y6 were in low severity of pollution. mHQ values for Ni showed that almost all the sediment sampling sites (except sites Y6, Y7, and Y28) were in considerable severity of pollution, while mHQ values in sites Y6, Y7, and Y28 were in high severity of pollution. The mean mHQ values indicated that the level of sediments contamination by the selected elements increased in the following order: Cd < Pb < Cu < Zn < As < Ni < Cr. Results suggest that in the study area Cr recorded a high severity of pollution followed by Ni and As , with considerable risk to the faunal and floral communities.

3.3. Source apportionment of potentially toxic elements

Principal component analysis was applied to classify the selected elements in the sediment samples using Varimax rotation. The Kaiser-Meyer-Olkin (KMO) value was 0.57, with *p* values close to zero ($p < 0.05$). The data indicated that the PCA results were accurate and can be applied to examine the contribution of pollution origins. It has been proven that multiple linear regression (MLR) following PCA (PCA-MLR) is a quantitative source contribution model for heavy metals (Deng et al., 2021). The percentage contribution of each principal factor (PC) was evaluated using multiple linear regression ($p < 0.05$, $R^2 = 0.6$).

Three of the principal factors (PCs) had eigenvalues values > 1, meaning they account for 75.8% of the total variance (Table 5). The elements with high loads on PC1 were Zn, Sb, Pb, Cu, and Mo, accounting for 29.7% of the variance. The PCA results further explain that Zn, Cu, Pb, Sb, and Mo originated from the same sources. Considering the EF values, Cu, Zn, Pb, Sb, and Mo revealed minimal to moderate level of enrichment at similar sampling stations, which were close to roads and downstream of the sewage effluent outfalls. Pb is an indicator element for vehicle fuel exhausts in urban areas (Deng et al., 2021). Pb and Zn as alloy components have different uses in motor vehicles. In addition, Mo is found in the fertilizers and pesticides (Abbasi et al., 2021; Ustaoğlu and Islam, 2020). Jin et al. (2019) reported that Zn and Cu as the necessary trace elements for plants are absorbed by surface sediments when used in chemical fertilizers. Also, around the Gohar Rood River there are horticulture farms.

This could be of importance because Cu is a widely used element in fungicides and insecticides (Wojciechowska et al., 2019). Therefore, PC1 was considered as an anthropogenic source including domestic, agricultural, and municipal sewage, with the contributions of 26.9%.

PC2 explained 29.2% of the total variance and was associated with Fe, As, Co, Mn, and Cr. Amorphous Mn and Fe oxides have higher sorption capacities for As and hence tend to be associated with the mobility of As (Smedley, 1993; Zheng et al., 2020). This suggests that Fe and Mn oxides play a significant role in the distribution of As, Co, and Cr in the sediments (Fandeur et al., 2009; Ma et al., 2007). Among these elements, Fe and Mn were identified to be the most abundant elements in the sediments, which indicates these elements basically are of natural origins (Diami et al., 2016). Also, Mn, Fe, As, Co, and Cr in sampling points of Y12-Y15, located downstream of industrial plants (such as Iranbarak Wool Weaving plant), and in Y24 station demonstrated moderate enrichment factor values. As was reported by Siddiqui and Pandey, the high Mn concentration results from the discharge of untreated industrial wastewater into the river water (Siddiqui and Pandey, 2019). Arsenic in the sediments is possibly associated with industrial wastewater discharges (Proshad et al., 2022). Thus, it is assumed that PC2 could be the mixed sources containing anthropogenic origin such as industrial wastewater and natural origin, together accounting for 40.5% variability in the dataset.

The PC3 was related to V, Cd, Ni, Sc, and Al, accounting for 17.0% of the variance in the dataset. These elements at all sites indicated depletion or minor enrichment, indicating the concentrations of these elements were most probably controlled by geogenic sources in the study area. Also, Cd concentrations were largely uniformly distributed within a very low range, indicating this element originated from lithogenic sources. Therefore, elements in PC3 can be considered of natural origin, with the contributions of 32.6% (Table 5).

After determining the sources of contamination via the principal component analysis, the MLR–APCS receptor model was applied to quantify the toxic element contributions from each source in the sediment samples. The contribution rates of toxic elements based on MLR–APCS are shown in Table 5. To determine the accuracy of the MLR-APCS model, the ratio between measured to estimated values (M/E) was utilized. The M/E ratio for the investigated elements was observed 1 for all the elements. Coefficient of regression values for elements were mostly higher ($R^2 > 0.5$) with all having significance of $P < 0.05$, suggesting acceptable model results for the analysis of contamination sources in the Gohar Rood River. The PC1 was the largest contributor to Zn, Cu, Pb, Sb, and Mo due to

agricultural runoff, domestic, and municipal sewage influences. The contribution rates from identified sources for these elements were 63.5%, 66.8%, 83.2%, 95.2%, 67.5%, respectively. The PC2 was related to Fe, As, Co, Mn, and Cr which were mostly affected by the mixed sources (industrial wastewater and natural origin). Their contribution rates were 95.5%, 85.7%, 76.4%, 49.9%, and 78.0%, respectively. The PC3 was V, Cd, Ni, Sc, and Al for natural sources, contributing to 50.1%, 79.0%, 54.9, 39.9%, and 43.1% respectively.

Table 5 Rotating component matrix and source contributions of each element by the MLR-APCS model in surface sediments of the Gohar Rood River.

Component	Rotated component matrix			MLR– APCS model data (%)			R^2	M/E
	PC1	PC2	PC3	PC1	PC2	PC3		
Zn	**0.90**	-0.25	-0.26	**63.5**	17.9	18.6	0.9	1
Cu	**0.89**	-0.30	-0.14	**66.8**	22.6	10.6	0.9	1
Pb	**0.87**	0.11	-0.06	**83.2**	10.7	6.1	0.8	1
Sb	**0.80**	0.03	-0.01	**95.2**	3.0	1.7	0.6	1
Mo	**0.72**	-0.33	-0.02	**67.5**	30.9	1.6	0.6	1
Fe	-0.03	**0.94**	0.01	3.5	**95.5**	1.0	0.9	1
As	-0.11	**0.92**	-0.05	9.9	**85.7**	4.4	0.9	1
Co	-0.25	**0.91**	-0.03	20.8	**76.4**	2.8	0.9	1
Mn	-0.25	**0.74**	-0.49	16.8	**49.9**	33.2	0.9	1
Cr	0.03	**0.68**	0.16	3.0	**78.0**	19.0	0.5	1
V	-0.30	0.44	**0.74**	20.1	29.8	**50.1**	0.8	1
Cd	-0.17	0.01	**-0.66**	20.3	0.7	**79.0**	0.5	1
Ni	-0.46	0.07	**0.65**	38.9	6.2	**54.9**	0.6	1
Sc	-0.57	-0.38	**0.63**	36.2	23.9	**39.9**	0.9	1
Al	-0.38	-0.42	**0.61**	26.8	30.1	**43.1**	0.7	1
Variance (%)	29.7	29.2	17.0					
MLR (%)	**26.9**	**40.5**	**32.6**					

3.5. Speciation of heavy metals

Geochemical partitioning of elements can help better understand their environmental behaviour and bioavailability. The distribution of the elements (Zn, Mn, Cr, V, Cu, Co, Pb, Ni, Fe, Al, and As) among the various forms in the riverine sediment samples was examined based on their concentrations in the four fractions extracted by the modified BCR sequential extraction scheme (Table 6). The observed similarities in the distributions of studied elements in the four fractions indicate that the elements are controlled by the same sources or geochemical forms. Results indicated that distribution of Al (93.39-96.65%), Cr (83-88.33%), Fe (72.77-91.02%), As (71.43-86.67%), and Cu (60.82-80.68%) in the residual fraction of sediments was dominated, suggesting that these elements were bound in lattices of primary mineral and secondary silicate mineral of the sediments. Therefore, they are usually considered stable and are not likely have any impact on the ecosystem (Li et al., 2014). The

Pb and Ni contents in the F4 fraction (residual) were 56.29% and 68.45%, respectively, indicating that Ni is likely immobilized in aluminosilicate minerals and has little bioavailability significance (Zhang et al., 2017). After the F4 fraction, the mean highest values of Fe, As, and Pb were found in the F2 fraction, which in the BCR scheme is specified as the reducible fraction, while Cu, Al, and Cr were found in the oxidizable fraction (F3). The concentration of elements in the F2 fraction can be associated with the Mn and Fe oxides content of the sediments. In fact, the Mn–Fe oxy-hydroxides are the major scavenger for all metals (Filgueiras et al., 2002). The existence of Cu in the oxidizable fraction of the sediments is hardly surprising as Cu has a strong affinity for humic substances as in OM (Sundaray et al., 2011). Moreover, the low value of Cu in the oxidizable fraction in the study area might be related to the low OM content and/or the neutral pH values of the sediments, which limits the formation of stable complexes. The mean values of the different Co fractions followed the decreasing order of F4 > F2 > F1 > F3, while Mn was unique, the mean highest concentrations were found in F1, F2, and F4, respectively. The data demonstrate that a greater Mn value in the F1 fraction can have negative effects on aquatic biota because this fraction is very unstable and could easily become bioavailable (Devi and Bhattacharyya, 2018). The highest Zn content was mostly in the F4 fraction. V was largely associated with the F4 fraction; however, it exhibited relatively high contents in the F2 and F3 fractions, 27.51% and 23.49% of its total concentration, respectively. Except Mn, Co, Pb, and Zn, the mean distribution of other elements in the exchangeable fraction was Ni > Cu > As > V > Cr. The potentially mobile fraction was calculated as the sum of the first three fractions of the BCR fractionation scheme (F1+F2+F3) determined in the sediments, which is regarded to be the important factor for the evaluation of bioavailability and potential ecological risk (Pérez-López et al., 2008). Fig. 5 shows the potentially mobile fraction for the elements in sediments.

Table 6 The distribution of investigated elements in the four geochemical factions in the selected sediments samples from the Gohar Rood River.

Element	F1 (%)			F2 (%)			F3 (%)			F4 (%)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Al	0.19	0.79	0.38	0.44	2.35	1.47	2.57	4.57	3.39	93.39	96.65	94.76
As	5.00	9.74	8.05	5.00	9.74	8.05	3.33	9.09	6.32	71.43	86.67	77.58
Co	4.07	26.97	20.30	22.47	63.96	37.03	4.03	4.42	4.88	27.10	44.94	37.79
Cr	2.37	3.04	2.64	2.37	3.04	2.64	9.68	9.97	9.00	83.00	88.33	85.73
Cu	4.40	12.45	9.18	2.12	9.38	4.38	6.62	5.94	10.39	60.82	80.68	76.05
Fe	0.10	0.24	0.17	8.43	26.17	16.87	0.57	0.81	0.85	72.77	91.02	82.11
Mn	18.06	56.93	43.69	22.90	76.36	38.09	1.60	1.68	2.09	3.76	26.25	16.14
Ni	9.09	21.90	13.10	8.57	15.30	11.98	7.93	7.85	6.47	61.90	72.66	68.45
Pb	3.34	8.50	5.12	8.95	47.59	23.70	18.58	16.81	14.88	39.66	67.09	56.29

V	2.68	3.33	2.90	23.67	32.89	27.51	20.04	21.47	23.49	39.91	51.28	46.10
Zn	2.15	38.59	12.51	18.24	38.42	29.44	2.29	4.39	4.29	31.59	74.50	53.75

F1: Exchangeable Fraction, F2: Reducible Fraction, F3: Oxidizable Fraction, F4: Residual Fraction

The potentially mobile elemental fraction in the sediment samples was in the following order: Mn (81.77%) > Co (57.33%) > Zn (41.95%) > V (30.41%) > Pb (28.83%) > Ni (25.08%) > Fe (17.04%) > As (16.10%) > Cu (13.56%) > Cr (5.27) > Al (1.85%). This indicates that Mn, Co, Zn, and V are more mobile than the other elements.

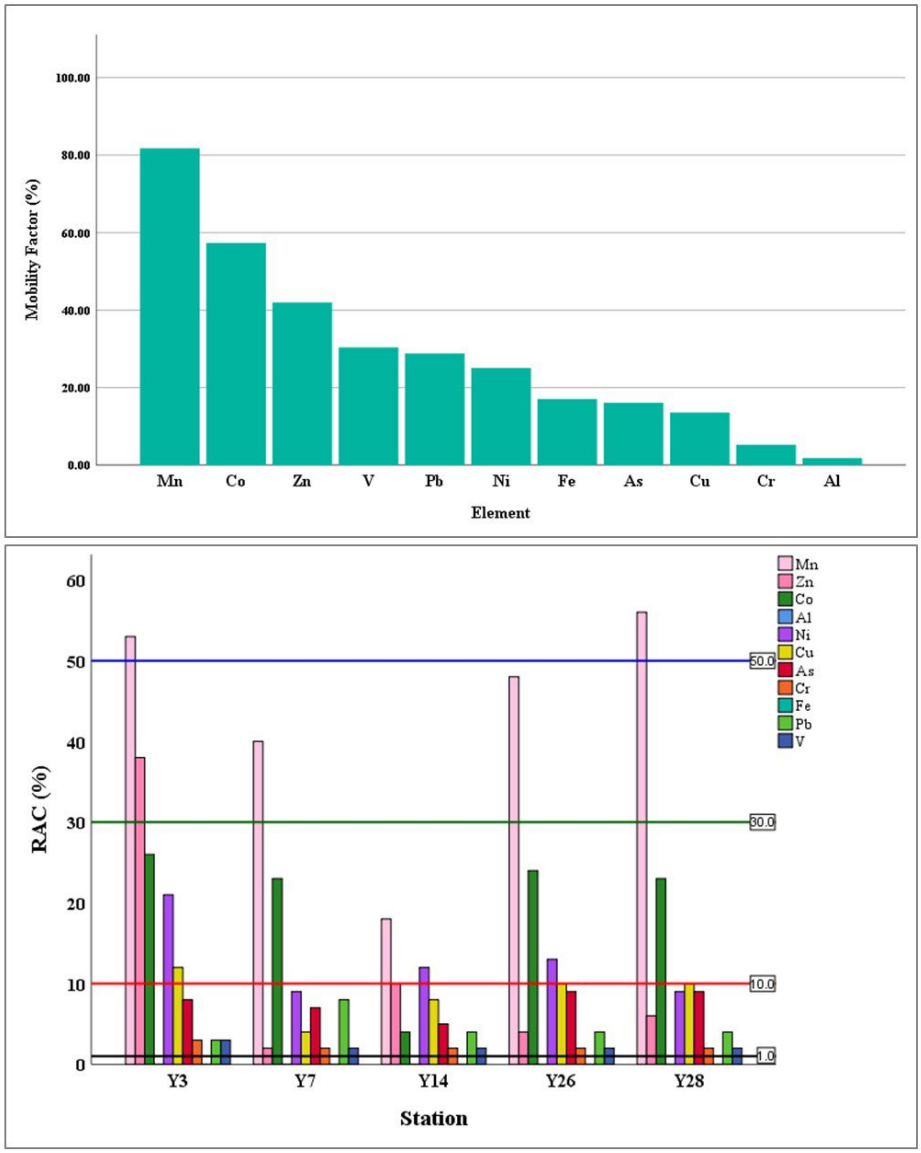

Fig. 5. The mobility factor and risk assessment code (RAC) for Mn, Zn, Co, Al, Ni, Cu, As, Cr, Fe, Pb, and V in the five sediment sampling points from the Gohar Rood River.

The risk assessment codes (RAC) for the elements were evaluated based on the percentage of elements associated with the exchangeable fraction (BCR fractionation scheme), since the

exchangeable fraction is considered the most bioavailable fraction to biota (Guillén et al., 2012). The RAC of the investigated elements is given in Fig. 5. According to the RAC classification (Ke et al., 2017), low risk (1-10%) was observed in all sites for As, Pb, and V, while Zn at sites Y7, Y26 (midstream), and Y28 (downstream), Ni at Y28 , Cu at Y7 and Y14 (midstream), and Co at Y14 showed a low risk. The RAC exhibited a medium risk in the rest of the sites for Co, Ni, and Cu. Zn presented high risk (31- 50%) at Y3 (midstream), with a medium risk being observed at the Y14 site. Mn indicated the highest potential bioavailable hazard, particularly at Y3, Y7, Y26, and Y28 sampling points, suggesting more than 30% of the exchangeable fraction, with a medium risk being observed at the Y14 site. Al and Fe showed no risk in any of the sampling points. In general, the potential environmental risk by the investigated elements increased in the following order Fe (0.17%) < Al (0.38%) < Cr (2.64%) < V (2.90%) < Pb (5.12%) < As (8.05%) < Cu (9.18%) < Zn (12.51%) < Ni (13.10%) < Co (20.30%) < Mn (43.69%), representing that Mn was the main element for ecological risk in the Gohar Rood River.

4. Conclusions

This study is the first that comprehensively evaluated concentrations, spatial distributions, contamination and risk levels, sources apportionment, and mobility of heavy metals in sediments of the Gohar Rood River. The contamination evaluation based on the EF and PI exhibited that Zn, Mn, Co, and Cr were the most elevated elements in the sediments, and the mean MPI value revealed sediments were moderately polluted. Therefore, much more regard should be paid to Zn, Mn, Co, and Cr contamination in the whole study area. Nevertheless, the TRI index exhibited only a low toxicity risk of Cr. The mHQ indicated that 76.7% of the sediment samples have high severity level of Cr contamination. In general, the evaluation of pollution and potential risk levels for the investigated elements using the proposed indices identified probable contamination hotspot sites. The PCA-MLR model identified three sources of sediment contamination: anthropogenic sources (26.9%), mixed sources i.e., anthropogenic and natural occurrence (40.5%), and natural occurrence (32.6%) in the study area. Considering that the river passes through major urban areas, it is inferred that agricultural runoff, domestic, and municipal sewage were responsible for the higher accumulation of Zn, Cu, Pb, Sb, and Mo in this area. In contrast, the main source for V, Cd, Ni, Sc, and Al was of a natural origin in the APCS-MLR model. Based on the BCR fractionation scheme, all the elements except Mn and Co demonstrated predominance in the residual phase, indicating that the elements have a strong association with the minerals'

crystalline structures, and hence, under the current situation of the river present lower mobility and bioavailability. The mean RAC of Zn, Co, Ni, and Mn posed medium to high environmental hazards due to high mobility. In general, this study evaluated the level of contamination caused by elements in sediments of the Gohar Rood River systematically, which could aid to formulate policies and take suitable measures to manage and prevent toxic elements' contamination in this river ecosystem.

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Supplementary material

Risk assessment, geochemical speciation, and source apportionment of heavy metals in sediments of an urban river draining into a coastal wetland

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1. Material and Methods

Table S1 Details of sediment sampling points from the Gohar Rood River.

Number	X	Y	Name Of Station	Number	X	Y	Name Of Station
Y1	372011.6	493251.0	Downstream	Y16	371523.0	493530.0	Midstream (Urban)
Y2	371907.0	493250.0	Downstream	Y17	371556.9	493502.1	Midstream (Urban)
Y3	371753.6	493310.3	Midstream (Urban)	Y18	371631.0	493348.8	Midstream (Urban)
Y4	371610.3	493354.1	Midstream (Urban)	Y19	371650.1	493339.1	Midstream (Urban)
Y5	371714.6	493334.5	Midstream (Urban)	Y20	371316.5	493438.8	Midstream (Urban)
Y6	371559.6	493522.1	Midstream (Urban)	Y21	371331.6	493439.7	Midstream (Urban)
Y7	371608.3	493445.2	Midstream (Urban)	Y22	371434.8	493441.4	Midstream (Urban)
Y8	371504.6	493507.9	Midstream (Urban)	Y23	371432.0	493436.2	Midstream (Urban)
Y9	371537.0	493532.2	Midstream (Urban)	Y24	371236.5	493505.7	Upstream
Y10	371445.5	493457.5	Midstream (Urban)	Y25	371224.8	493514.9	Upstream
Y11	371445.0	493452.0	Midstream (Urban)	Y26	371807.6	493457.3	Midstream (Urban)
Y12	371347.6	493443.6	Midstream (Urban)	Y27	371932.0	493324.0	Midstream (Urban)
Y13	371311.9	493437.4	Midstream (Urban)	Y28	372045.0	493244.5	Downstream
Y14	371406.5	493438.6	Midstream (Urban)	Y29	371215.9	493516.4	Upstream
Y15	371421.9	493439.6	Midstream (Urban)	Y30	371202.3	493516.6	Upstream

1.1. Enrichment factor (EF)

EF, a linear relation between a reference element with the element of interest under natural sedimentation situations is a useful index to determine the element contamination enrichment level in the sediments. To minimize the effects of mineralogical and textural variation between samples, the concentrations were normalized to element data to geochemical reference material (Lim et al., 2021). In this study, Sc was applied as a geochemical normalizer. The variation coefficient of Sc was only 0.08, suggesting that the element was affected by negligible environmental disturbances. The EF can be calculated as follows:

$$EF = \frac{(A_i/B_i)_{samlpe}}{(A_i/B_i)_{average\ shale}} \quad (1)$$

where $(A_i/B_i)_{samlpe}$ represents the ratio of the measured concentrations of each element and Sc, and $(A_i/B_i)_{average\ shale}$ is the ratio of the average shale content of each element and Sc.

EF values for describing the enrichment degrees of elements are defined as: deficiency to minimal enrichment (EF < 2), moderate enrichment (2 ≤ EF > 5), significant enrichment (5 ≤ EF > 20), very high enrichment (20 ≤ EF > 40), and extremely severe enrichment (EF ≥ 40) (Sutherland, 2000).

1.2. Pollution index (PI), modified degree of contamination (mDc), and modified pollution index (MPI)

The pollution index (PI) is generally used for environmental contamination assessment by a certain element (Hakanson, 1980), while the modified degree of contamination (mDc) can create an integrated assessment of the heavy metal pollution in a sampling site as a whole (Abrahim and Parker, 2008). Considering to several toxic elements could have an influence on one station, a modified and generalized index, the modified pollution index (MPI) has been established to assess the overall contamination of the sediments with multiple elements by replacing contamination factor with enrichment factor (Brady et al., 2015). They are calculated by the following equations:

$$PI = \frac{C_s}{C_b} \quad (2)$$

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (3)$$

$$MPI = \sqrt{\frac{(Ef_{average})^2 + (Ef_{max})^2}{2}} \quad (4)$$

where, C_s, C_b, n, $Ef_{average}$, and Ef_{max} refer to the target metal concentration at a site, the concentration of the same metal in the selected reference background, number of analyzed elements, an average of enrichment factors, and maximum enrichment factor, respectively. Four qualitative categories are defined to describe the contamination factor and degree of contamination: PI < 1 (low contamination), 1 ≤ PI < 3 (moderate contamination), 3 ≤ PI < 6 (considerable contamination), and PI ≥ 6 (very high contamination) (Hakanson, 1980).

Table S2 Threshold values for sediment quality classification base on the modified degree of contamination (mDc) and modified pollution index (MPI).

Class	mDc [a]	MPI [b]	Sediment qualification
0	mDc < 1.5	MPI < 1	Unpolluted
1	1.5 < mDc < 2	1 < MPI < 2	Slightly polluted
2	2 ≤ mDc < 4	2 < MPI <3	Moderately polluted
3	4 ≤ mDc < 8	3 < MPI < 5	Moderately-heavily polluted
4	8 ≤ mDc < 16	5 < MPI < 10	Heavily polluted
5	16 ≤ mDc < 32	MPI >10	Severely polluted
6	mDc ≥ 32	-	Extremely polluted

[a] adapted from Abrahim and Parker (2008)
[b] adapted from Brady et al. (2015)

1.3. Modified ecological risk index (MRI)

The modified ecological risk index (MRI) has been widely applied to more accurately assess different levels of the potential ecological risk of heavy metals in sediments at a location (Brady et al., 2015; Yavar Ashayeri and Keshavarzi, 2019). This approach considers not only background content and measured amount of elements but also environmental sensitivity,

toxicity, and multi-element synergetic effects to element contamination (Wang et al., 2020). The MRI value was calculated as follows:

$$MRI = \sum_{i=1}^{n} Er^i = \sum_{i=1}^{n} Tr^i \times EF^i \quad (5)$$

where Er^i and EF^i are the potential ecological risk index and enrichment factor of an individual element, respectively. Tr^i is the response coefficient for the toxicity of each element, which can reflect the level of element toxicity and ecological sensitivity to toxic elements contamination (Gao et al., 2013). In the MRI concept, the standardized response coefficient (Tr^i) for the toxicity of each element in the sediment were: Zn = 1, Cr = 2, Co=Ni= Cu= Pb = 5, As = 10, and Cd = 30. Er^i and MRI classifications are used here according to Hakanson (1980) and Zhang et al. (2017), respectively.

Table S3. Threshold values for sediment quality classification base on modified ecological risk index (MRI) and the potential ecological risk index (Er^i).

Class	MRI [a]	Er^i [b]	Ecological risk
1	MRI <150	$Er^i < 40$	Low ecological risk
2	150 ≤ MRI < 300	$40 \leq Er^i < 80$	Moderately ecological risk
3	300 ≤ MRI < 600	$80 \leq Er^i < 160$	Considerable ecological risk
4	-	$160 \leq Er^i < 320$	High ecological risk
5	MRI ≥ 600	$Er^i \geq 320$	Very high ecological risk

[b] adapted from Zhang et al. (2017)

Table S4. Sediment quality guidelines for heavy metals in freshwater ecosystems

Chemical	As	Cd	Cr	Cu	Pb	Ni	Zn
ERL	33	5	80	70	35	30	120
ERM	85	9	145	390	110	50	315
TEL	5.9	0.596	37.3	35.7	35	18	123
PEL	17	3.53	90	197	91.3	36	270
SEL	33	10	110	110	250	75	820

TEL: Threshold effect level, dry weight; ERL: Effect range low, dry weight; PEL: Probable effect level, dry weight; ERM: Effect range median, dry weight; SEL: Severe effect level, dry weight (MacDonald et al., 2000).

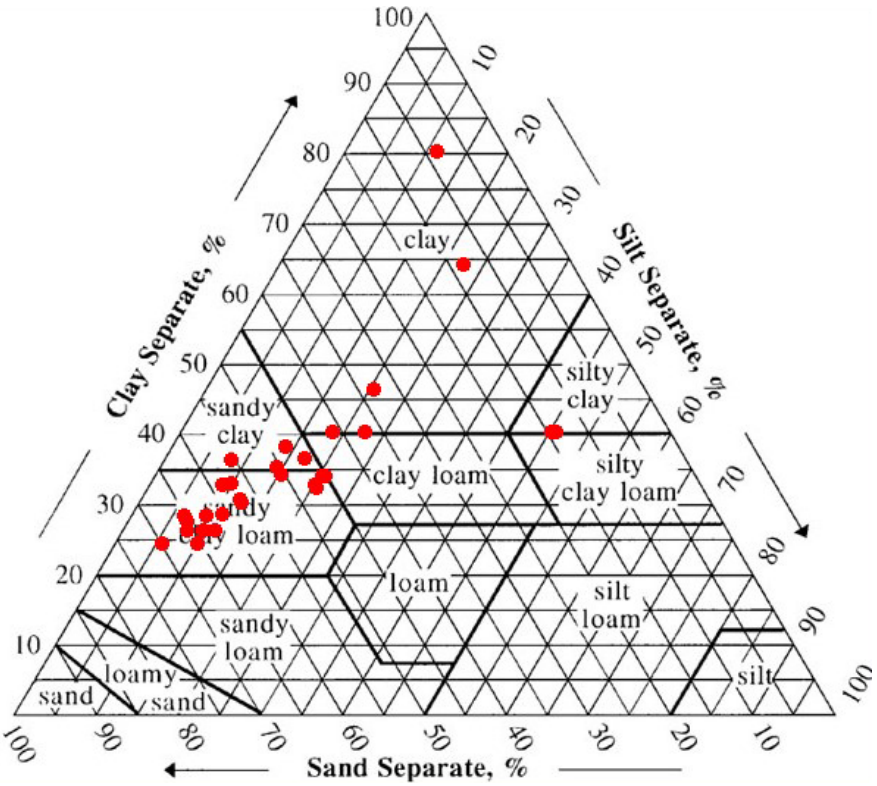

Fig. S1. Ternary plot demonstrating the percentages of clay, silt and sand particles in the surface sediments of the Gohar Rood River.

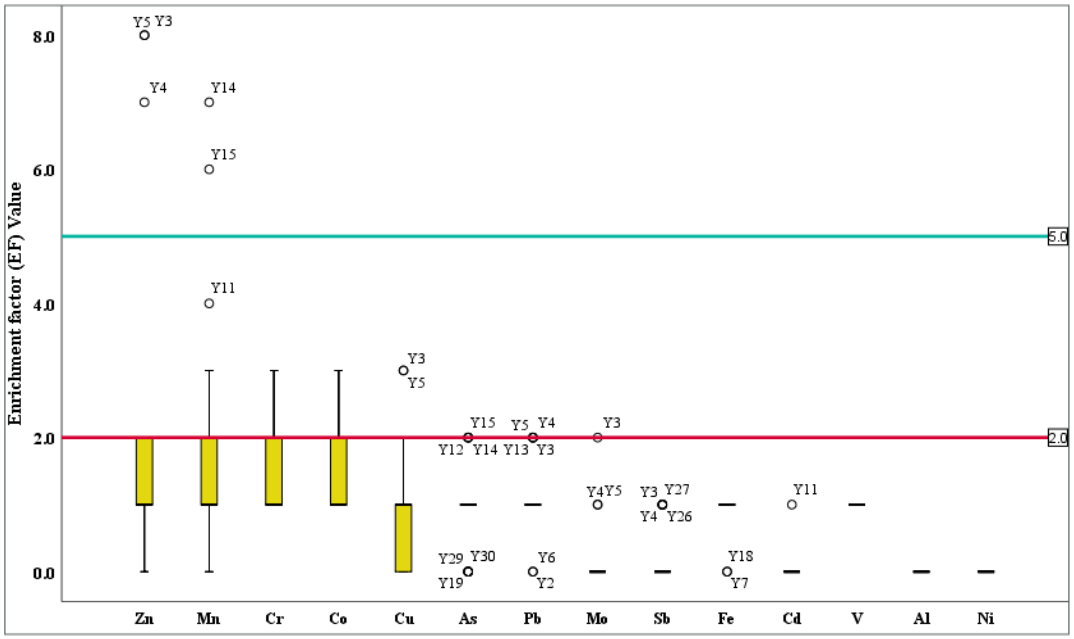

Fig. S2. Enrichment factors (EF) values for investigated heavy elements in the surface sediments of the Gohar Rood River.

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