#### PERIODICO di MINERALOGIA

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DIPARTIMENTO DI SCIENZE DELLA TERRA



An International Journal of
Mineralogy, Crystallography, Geochemistry,
Ore Deposits, Petrology, Volcanology
and applied topics on Environment, Archaeometry and Cultural Heritage

# Evaluating the role of geological formations in the heavy metals concentration in the Qarasu River and Gorgan Bay, North of Iran

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# **ARTICLE INFO**

#### **ABSTRACT**

Submitted: July 2025 Accepted: September 2025 Available on line: October 2025

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Doi: 10.13133/2239-1002/19013

How to cite this article: Razavi S.S. et al. (2025) Period. Mineral. 94, 265-279 The catchment area of the Qarasu River is among the most important water suppliers to Gorgan Bay. It is located in the north of Iran, in the southern part of the Caspian Sea. This study investigates the role of geological units in the accumulation of heavy metals in the sediments of the Qarasu River and Gorgan Bay. To this end, 21 samples (rock, sediment, and water) were analyzed using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method. The value of heavy metals in the studied samples are approximately for cobalt 1-27 (average 13 ppm), chromium 134-7 (average 88 ppm), copper 6-59 (average 32 ppm), nickel 1-76 (average 42 ppm), lead 1-49 (average 23 ppm), vanadium 8-185 (average 100 ppm), zinc 9-157 (average 99 ppm). The concentration of heavy metals progressively increases as one moves away from the river's source toward the coast of Gorgan Bay. In general, the main sources of heavy metals are the Gorgan schist and the minor Shemshak formation. Human involvement in the concentration of heavy metals in the Qarasu River and the shores of Gorgan Bay is very low to rare.

Keywords: Qarasu River; Gorgan Bay; heavy metals; geological units.

## INTRODUCTION

Sediment and soil geochemistry are essential for identifying the primary source of potential mineralization, sediment provenance, environmental conditions, and environmental pollution (Kouankap et al., 2024; Ndema Mbongué et al., 2025; Yiika et al., 2025). Heavy metals are naturally present in the environment and typically occur in low concentrations under normal conditions (Yiika et al., 2022). However, a significant amount of these metals may enter the environment due to their high concentration in the source, as well as through human activities. As a result, environmental pollution by heavy metals has become a persistent global problem (Gayathri et al., 2021; Laha et al., 2022; Kachoueiyan et al., 2023a; Tiabou et al.,

2024a). These conditions are especially important in river and coastal environments, because these environments receive heavy metals carried by surface waters (Nguyen et al., 2016; Yiika et al., 2024; Ndema et al., 2024; Tiabou et al., 2025a). Heavy metals may be dissolved or accumulated in sediments within water ecosystems, and their bioavailability is influenced by factors such as conductivity, pH, salinity, and the amount of organic matter present (Kachoueiyan et al., 2023b; Tiabou et al., 2025b; Taghavi et al., 2025).

In recent years, extensive studies have been conducted on the effects of soils, river sediments, and human activities on the concentration of heavy metals in aquatic environments (Barandovski et al., 2020; Gaberšek and



Gosar, 2021; Žibret and Čeplak, 2021; Kos et al., 2022).

Heavy metals enter surface waters in both dissolved and particulate forms, associated with suspended particles. These metals accumulate in bottom sediments, thereby providing a protective barrier for living organisms against excessive exposure to these pollutants (Tiabou et al., 2024a; Afahnwie et al., 2025). The concentrations of heavy metals in surface waters do not fully reflect the actual degree of pollution in the aquatic environment, as these metals can exist in various forms, including undissolved forms (Ismukhanova et al., 2022; Yiika et al., 2023; He et al., 2024).

Additionally, sediments serve as the final destination for the accumulation of heavy metals in the aquatic environment. However, they can act as a source of pollution under certain conditions (Simou et al., 2024a; Kachoueiyan et al., 2024a). Therefore, the geochemical characteristics of sediments and soils can significantly help in identifying and interpreting the source of pollution (Humbatov et al., 2015; Tiabou et al., 2024b; Suh et al., 2025). The concentration of heavy metals in sediments is dependent on the function of aquatic ecosystems, and the change in metal concentration in sediments is smaller than in water. Therefore, most research in this area has focused on evaluating heavy metals in the sedimentary phase (Simou et al., 2024b; Tiabou et al., 2025b). After entering the aquatic environment, metals are deposited in sediments through physical, chemical, or biological processes (Ghanbarpour et al., 2013; Kachoueiyan et al., 2024b).

Considering the importance of studying heavy metals in sediments, it is essential to determine their concentrations and identify their sources. Therefore, numerous studies have been conducted to determine the concentration of heavy metals in water environments worldwide (Nguyen et al., 2016; Duodu et al., 2017; Rasul et al., 2022; Tiabou et al., 2025b). Besides, since the Caspian Sea is a closed environment with no tides, all pollutants discharged into it accumulate in the basin of the sea and its bays, such as Gorgan Bay and the surrounding wetlands. Indeed, the Qarasu River is considered one of the most important sources of water and heavy metals to this bay (Bagheri et al., 2013). Accordingly, the present study investigates the role of geological formations in the concentration of heavy metals in the Qarasu River and Gorgan Bay.

#### **GEOLOGICAL SETTING**

Gorgan Bay is located between latitudes 45°, 37°, and 36° and longitudes 54°, 5°, and 53°. The bay is 54 km long, about 12 km wide (maximum), 360 km in area, and 2.5 km deep at its deepest point (Khoshravan and Nasehi, 2015). The catchment of the Qarasu River is located in the eastern part of the Alborz Mountain and has an area

of about 13,061 km<sup>2</sup>. The coastal plain of Golestan is one of the largest plains and most important basins in Iran (Khoshravan and Ghafari 2014). The plain has an eastwest trend and is extended over an area of approximately 4727 km<sup>2</sup> on the eastern slope of the Alborz heights (Rabat Qarabeel, Daniyal Nabi, and Nardin). The total area of the plain reaches 5035 km<sup>2</sup> (Khoshravan and Khoshravan, 2014). The rivers making up the Qarasu catchment (i.e., Kordkoi, Shasat Kalate, Ziarat, and Garambadasht rivers) flow into Gorgan Bay after joining each other in the vicinity of Qarasu village.

Gorgan Bay is located in the southeast of the Caspian Sea. This bay is 54 km long, about 12 km wide (maximum), 360 km in area, and 2.5 km deep in its deepest part (Khoshravan et al., 2019). The bay stretches from east to west. Its head is located in the west, and the narrow and long margin of Miankale separates it from the sea. The bed of the bay is marshy in the eastern, southern, and western parts, and many small rivers originating from the southern mountains flow into it. The most important rivers that flow into Gorgan Bay are Qarasu, Nokandeh, Bagu, Khurshid Kalah, and Pasandeh Sar. Qarasu is the most important one, with the others often being temporary or seasonal.

The major rock units of the study area, which are most widespread in the Oarasu catchment, are the Gorgan schists, Khoshyilagh, Shemshak, and Lar formations (Figure 1). Fine-grained and coarse-grained Quaternary sediments are also observed in the area, which are investigated in this study as stream sediments. Ghanbarpour et al. (2013) also considered these units as the most important and extensive formations in the area. However, other rock units in the area are not widespread (see Haeri Ardakani et al., 2000). Figures 1, 2, and 3 show the geological map of formations, outcrops, and thin sections, respectively. Gorgan schists (Figures 2a and 3a) have a fine to medium grain size, with the parent rock being mainly preserved in most of them. These rocks are mostly composed of sedimentary rocks, such as sandstones with immature texture, quartz arenite, quartz wacke, and, to some extent, volcanic rocks, including basaltic lavas and tuffs. The main minerals of these schists include chlorite, epidote, albite, and quartz, although calcite and biotite are also present, albeit in some cases. The igneous rocks, often observed in the form of dykes and sills, are diverse. At the sampling locations and where the river meets the formations, they mostly exhibit a composition similar to that of basalt (Figures 2b and 3b).

Rameh and Mousavi (2012), studying the Khoshyilagh formation, showed that the carbonate environment was the primary sedimentary environment of this formation, with debris flow deposits also formed due to the influx of cut rivers. Besides, studying the thin sections and



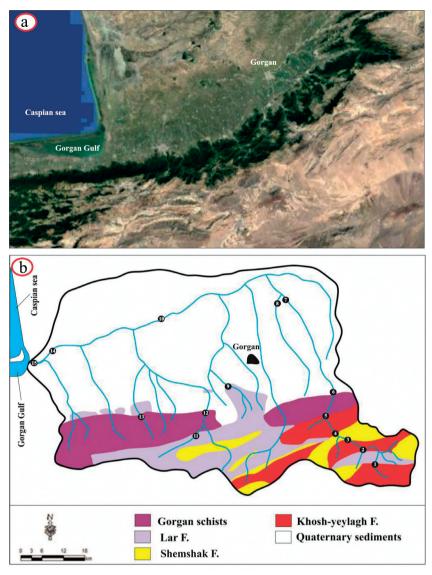


Figure 1. A: A- Satellite image of the study area. B: Location of the study area, exposed geological formations, the watershed of the Qarasu River and the location of sediment sampling from the Qarasu River (modified from Haeri Ardakani et al. 2000).

field observations confirmed that most of the samples are composed of carbonate and detrital grains, such as quartz and feldspar (Figures 2c and 3c). The Lar Formation is primarily composed of pure carbonate, including calcite and dolomite, where dolomite is formed by the replacement of calcite (Abdolmaleki et al., 2016). Consequently, fossil parts are well-preserved (Figures 2d and 3d). Similar results were obtained by Asghari et al. (2013).

The Shemshak Formation in the study area can be distinguished by its dark appearance, which contrasts with that of other sedimentary rocks. Upon studying the thin sections, it appears that this formation is primarily composed of alternating sandstone with good textural

maturity and shale (Figures 2e, 3e, and 3f). Quaternary and stream sediments, which exhibit a great diversity in grain size, type, and abundance of components (Figures 2f, 3g, and 3h), change according to the proximity of the river to the outcrop of each formation.

It is of note that, for the sake of brevity and the impossibility of using the word "formation" for stream sediments and the Gorgan schist, the prefix "Unit" or "geological unit" is used in this study.

## **MATERIALS AND METHODS**

This research examines the levels of heavy metals in the Qarasu River and Gorgan Bay, as well as the influence of geological units. To this end, 21 samples (4 rock samples,



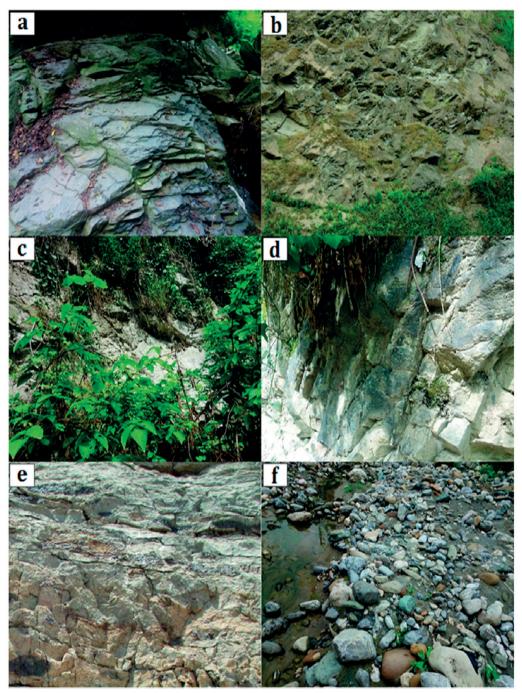


Figure 2. Geological units of the study area. A: Gorgan Schist, B: Mafic rocks within Gorgan Schist, C: Shemshak Formation: Interbedded sandstone and shale, D: Khoshyilagh Formation, E: Lar Carbonate Formation, F: Alluvial sediments.

11 sediment samples, and 6 water samples) were collected, of which 15 were in different parts of the river and 6 from the coastal parts of Gorgan Bay (Figure 1). Sampling was conducted randomly, considering the lithological changes along the river's path after completing the geological map of the Qarasu catchment. Afterward, research objectives, i.e., the role of geological units in the concentration of

heavy metals in the Qarasu River and Gorgan Bay, were investigated based on the obtained data. To identify the rock units, despite studying the geological map, field observations are often taken into consideration. Additionally, thin sections were prepared for microscopic studies of rock units where further study was needed.

To analyze the heavy metals cobalt (Co), including



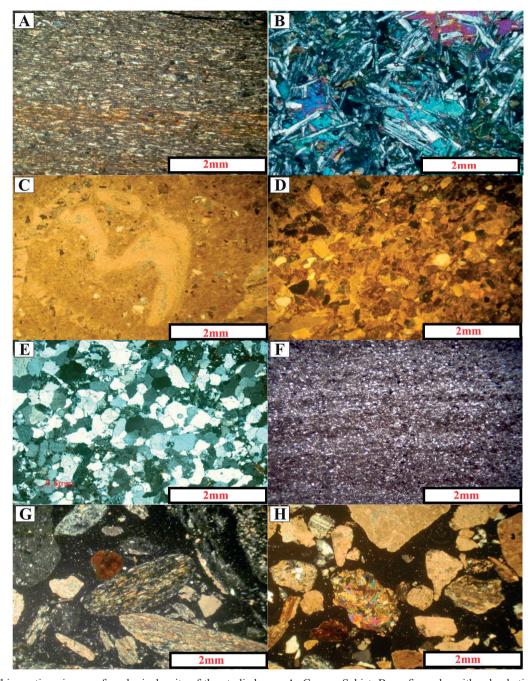


Figure 3. Thin sections image of geological units of the studied area. A: Gorgan Schist, B: mafic rocks with subaphetic texture due to partial placement of plagioclase in pyroxene, within Gorgan Schist, C: Lar carbonate formation with distinct fossil fragments, D: Khoshyilagh detrital-carbonate formation, E: Sandstone Shemshak formation, F: shale of Shemshak formation, G: alluvial sediments consisting of fragments of Gorgan schist. H: Alluvial sediments consisting of igneous and carbonate parts.

chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn), the samples were dried and sieved to a #200 mesh size. The Zarazma Laboratory reported the concentrations of heavy metals (Tehran, Iran) using the inductively coupled plasma mass spectrometry (ICP-MS) method. The ICP-MS device measures the

mass of element ions produced by a high-temperature argon plasma. The ions produced in the plasma are separated based on their mass-to-charge ratio, enabling the detection and quantification of unknown substances. The methodology is based on the location of sampling and the units through which the river has passed. The values



of changes in heavy metals are evaluated, and the role of geological units in the concentration of these elements is investigated. Moreover, the clustering method and correlation coefficient are used to identify the relationships between the geological units of the area and heavy metals. as well as between heavy metals themselves. Notably, the numerical values obtained from the ICP analysis were rounded to make the changes more objective and facilitate better calculations. The detection limit is 0.01 ppm for Tb, 0.02 ppm for Dy and Sm, 0.05 ppm for Er, Gd, Ho, Pr and Yb, 0.1 ppm for As, Cd, Ga, Ta, Th, U, Eu, Lu and Tm, 0.5 ppm for Ce, Hf, Sc, Y and Nd, 1.0 ppm for Ba, Co, Cr, Cu, La, Nb, Ni, Pb, Rb, Sr, V, W and Zn, and 5.0 ppm for Zr. The uncertainty of the measurements using internal laboratory standard materials falls within the 95% confidence interval with a coverage factor of k=2.

## **RESULTS**

Table 1 shows the values of seven heavy metals and the distance of the sampling locations from the source of the river. Cobalt values increase variably with distance from the source of the river. The lowest and highest amounts are 1 and 27 ppm in Samples Gh1 and No. Gh6, respectively (Figure 4a), and 12.9 ppm on average. Samples near the estuary, i.e., Gh14 and Gh15, and also in the sediment samples from Gorgan Bay, i.e., Gh17-Gh21, have experienced no significant changes in the values of this element. Chromium, with the same behavior as cobalt, has an increasing trend until near the Gorgan River in each of the main branches of the Qarasu River. After that, its values do not show much change until the samples from the Gorgan Bay (Figure 4b). The lowest and highest amounts are 7 ppm in sample Gh9 and 134 ppm in sample Gh15, respectively, with an average of 87.6 ppm.

Copper ranges from 6 to 59 ppm in Samples Gh9 and Gh6, respectively, and an average of 32.23 ppm (Figure 4c). The concentrations of heavy metals from the Qarasu River to the coast of the Gorgan Sea exhibit a clear ascending trend. Coastal samples and Gorgan Bay

Table 1. Amounts of heavy metals and the distance traveled by the river in the rock units of the studied area in kilometers.

| Samples | The amount of river flow from the geological formations of the area from the source to the sampling location |             |          |                   |              |                | amount of elements(ppm) |     |    |    |     |     |     |
|---------|--|-------------|----------|-------------------|--------------|----------------|-------------------------|-----|----|----|-----|-----|-----|
| Samples | Lar  | Khoshyilagh | Shemshak | Gorgan-<br>sch1st | Alluvial fan | Gorgan<br>Gulf | Co                      | Cr  | Cu | Ni | Pb  | V   | Zn  |
| Gh1     | 0  | 6           | 0        | 0                 | 0            | 0              | 1                       | 31  | 9  | 1  | 1   | 13  | 10  |
| Gh2     | 14   | 13          | 0        | 0                 | 0            | 0              | 4                       | 34  | 13 | 4  | 2   | 25  | 21  |
| Gh3     | 14   | 17          | 0        | 0                 | 0            | 0              | 4                       | 35  | 14 | 4  | 1.9 | 27  | 23  |
| Gh4     | 14   | 20          | 5        | 0                 | 0            | 0              | 9                       | 42  | 19 | 8  | 5   | 42  | 38  |
| Gh5     | 14   | 35          | 5        | 0                 | 0            | 0              | 9                       | 59  | 29 | 10 | 9   | 52  | 43  |
| Gh6     | 14   | 35          | 5        | 6                 | 0            | 0              | 27                      | 73  | 59 | 35 | 12  | 105 | 94  |
| Gh7     | 14   | 35          | 5        | 6                 | 25           | 0              | 13                      | 91  | 35 | 39 | 21  | 102 | 95  |
| Gh8     | 0  | 0           | 0        | 0                 | 24           | 0              | 12                      | 105 | 37 | 43 | 31  | 108 | 93  |
| Gh9     | 15   | 0           | 0        | 0                 | 0            | 0              | 4                       | 7   | 6  | 14 | 1   | 12  | 9   |
| Gh10    | 50   | 38          | 11       | 9                 | 200          | 0              | 12                      | 112 | 38 | 53 | 35  | 117 | 103 |
| Gh11    | 9  | 0           | 0        | 0                 | 0            | 0              | 3                       | 8   | 7  | 13 | 2   | 8   | 11  |
| Gh12    | 15   | 0           | 3        | 6                 | 0            | 0              | 21                      | 121 | 42 | 76 | 27  | 167 | 157 |
| Gh13    | 0  | 0           | 0        | 6                 | 0            | 0              | 24                      | 88  | 52 | 71 | 47  | 185 | 130 |
| Gh14    | 70   | 38          | 14       | 41                | 310          | 0              | 16                      | 131 | 43 | 69 | 47  | 139 | 138 |
| Gh15    | 73   | 38          | 14       | 50                | 328          | 0              | 15                      | 134 | 44 | 71 | 49  | 142 | 140 |
| Gh16    | 73   | 38          | 14       | 50                | 328          | 1              | 18                      | 131 | 43 | 68 | 39  | 146 | 143 |
| Gh17    | 73   | 38          | 14       | 50                | 328          | 1              | 19                      | 133 | 44 | 65 | 26  | 142 | 142 |
| Gh18    | 73   | 38          | 14       | 50                | 328          | 2              | 17                      | 127 | 42 | 61 | 33  | 146 | 140 |
| Gh19    | 73   | 38          | 14       | 50                | 328          | 2              | 14                      | 129 | 40 | 63 | 34  | 144 | 137 |
| Gh20    | 73   | 38          | 14       | 50                | 328          | 3              | 15                      | 124 | 41 | 62 | 35  | 140 | 138 |
| Gh21    | 73   | 38          | 14       | 50                | 328          | 3              | 14                      | 125 | 41 | 60 | 31  | 141 | 134 |



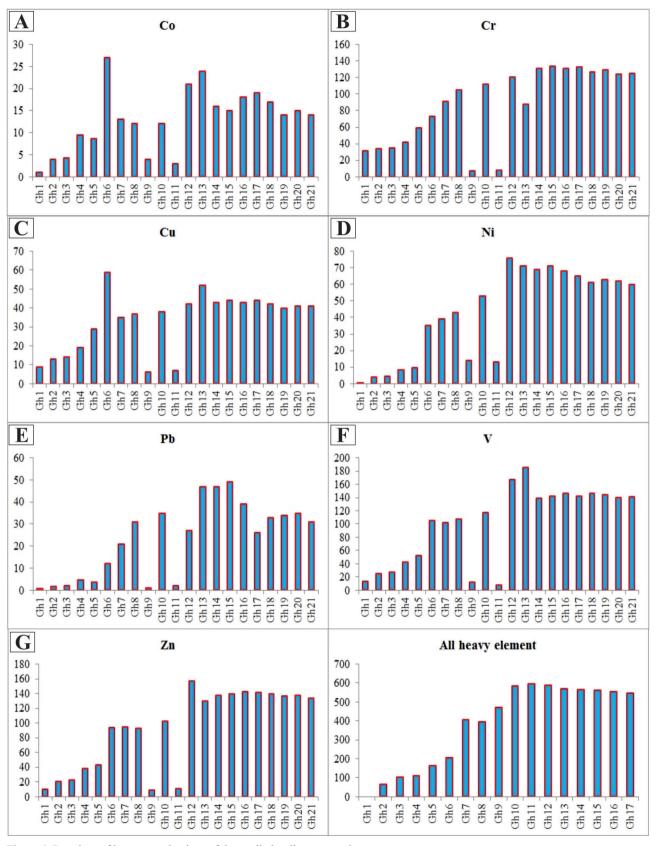


Figure 4. Bar chart of heavy metal values of the studied sediment samples.



samples have almost identical amounts of copper (Figure 4c). Ni variably increases with distance from the source of the river (Figure 4d). In this respect, 1 and 76 ppm are the minimum and maximum values of Ni in Sample Gh1 and in Sample Gh12, respectively, with 42.38 ppm on average. As shown in Figure 4d, there are no significant changes in the values in the samples close to the estuary (i.e., Gh14 and Gh15) and sediment samples from Gorgan Bay (i.e., Gh17-Gh21). Like most other heavy metals, lead has an increasing trend until near the Gorgan River in each of the main branches of the Qarasu River. After that, the values do not show large changes until the Gorgan Bay samples (Figure 4e). The lowest and highest amounts of this heavy metal are 1 in sample Gh1 and 49 in sample Gh15, respectively, with an average of 23.28.

Vanadium is present in the range of 8 to 185 ppm, with the lowest and highest amounts in samples Gh11 and Gh13, respectively, and an average of 100 ppm. The content of heavy metals in the samples from the Qarasu River to the coast of Gorgan Bay shows a definite increasing trend. Coastal samples and Gorgan Bay samples have approximately equal concentrations of this metal (Figure 4f). Zinc increases variably with distance from the source of the river. The minimum content is 9 ppm in Sample Gh9, and the highest concentration is 157 ppm in Sample Gh12, with an average of 99.33 ppm (Figure 4g). There are no significant changes in the values of this element in the samples near the estuary (i.e., Gh14 and Gh15) and in the sediment samples from Gorgan Bay (i.e., Gh17-Gh21).

In general, the concentration of heavy metals increases as they move away from the river source and approach the coast of Gorgan Bay (Figure 4h). In other words, the entry of heavy metals from the source has increased, and other elements have been washed and transported in various forms from the sediments (Abdolmaleki and Tavakoli, 2016), which are probably concentrated in Gorgan Bay as

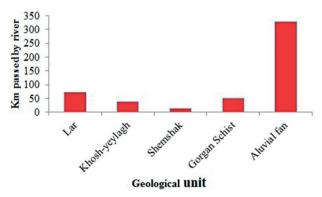


Figure 5. Distance of river crossing from the geological units of the study area.

the final destination.

According to Figure 4, in the samples from Gh16 and so on, which are related to the coasts of Gorgan Bay, the amount of heavy metals decreases as they move away from the coast. Considering the amounts of heavy metals and the sampling locations, it appears that the sediments before and after the river passes through the Gorgan and Shemshak schist geological units do not exhibit significant changes.

#### DISCUSSION

The distance that the Qarasu River has passed through the hard geological units is in decreasing order, from the geological unit of Lar (73 km), Schist Gorgan (50 km), Khoshyilagh (38 km), and Shemshak (14 km), representing a total distance of 328 km (Figure 5).

Figure 6 gives bar charts of the average concentrations of heavy metals in carbonate rocks, sandstones, shales, Gorgan schist, and volcanic rocks. The average values of Gorgan schist and volcanic rocks within Gorgan schist were extracted from the studies of Gravand et al., (2016) and Salehian (2016). Due to the lack of geochemical studies in other geological units of the area, global average values for carbonate, sandstone, and shale rocks (Turekian and Wedepohl, 1961; Faure, 1992; Rudnick and Gao, 2003) are used. To investigate the role of geological units on the content of heavy metals in the studied samples, the Pearson correlation coefficient is first considered. Figure 7 gives the results of this coefficient as bar charts based on the data from Table 1 (Figure 7).

As shown in Figure 7, the correlation coefficient is positive and, in most cases, above 0.5 between the concentration of heavy metals and the distance of the river from the geological units in the study area. As can be inferred, the content of heavy metals is under the control of geological units of the area (Kouankap et al., 2024; Tiabou et al., 2024c). However, the influence of geological units is different based on the values observed in the bar chart (Figure 7) for different elements. Since distinguishing the Gorgan schist and the igneous rocks within it is difficult, and the ratio of igneous rocks to schist is insignificant, we refer to the total of these two Gorgan schist rocks in this study.

Moreover, as there are elements and/or heavy metals in all studied geological units, the correlation coefficient between these units and metals is positive. The important point is the higher value of this coefficient in the most influential geological units. Also, when the values of this coefficient are checked to verify and increase the accuracy of the study, they are compared with the frequency of the values of each element in the shell or region. For instance, if the correlation coefficient between the geological unit of the area and the content of heavy metals is high, the



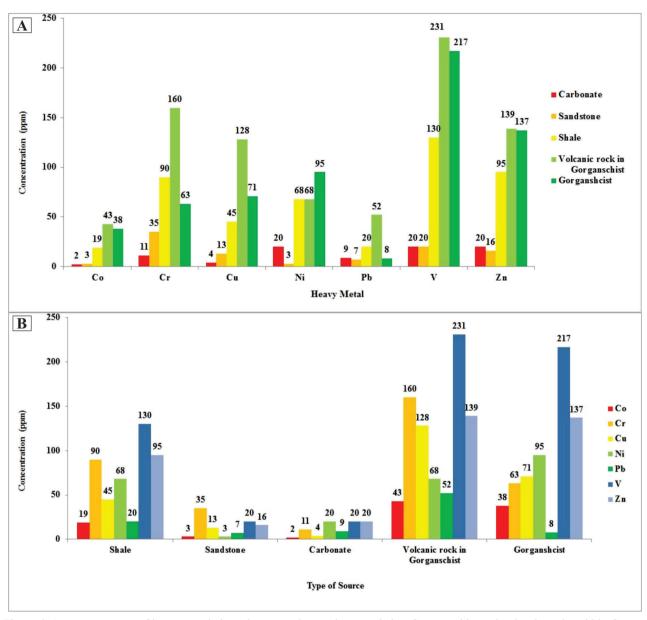


Figure 6. Average amounts of heavy metals in carbonate rocks, sandstones, shales, Gorgan schist and volcanic rocks within Gorgan schist (refer to the text).

abundance of that heavy metal in the geological unit of the region (where the global average is used) should also be high.

Cobalt shows the highest correlation with the Shemshak and Gorgan schist units and the lowest correlation with the Lar unit. The results for this element show a decreasing correlation with the Shemshak, Gorgan schist, Khoshyilagh, alluvial sediments, and Lar (Figure 7a). According to Figure 8a, this heavy metal is more concentrated in shale, Gorgan schist, and volcanic units. Chrome exhibits the highest correlation with Shemshak,

Lar, schist, and alluvium, and the lowest correlation with Khoshyilagh (Figure 7a). Among all the studied heavy metals, cobalt shows the highest correlation coefficient (i.e., 0.74) with the geological units of the Qarasu River catchment and the coasts of Gorgan Bay. According to the reference average values (Figure 8a), it seems that the Lar unit in the area has higher chrome values than the global average. The copper shows the highest correlation with the Shemshak and Gorgan schist geological units and the lowest correlation with the Lar unit, exhibiting a decreasing correlation with the Shemshak, Gorgan schist,



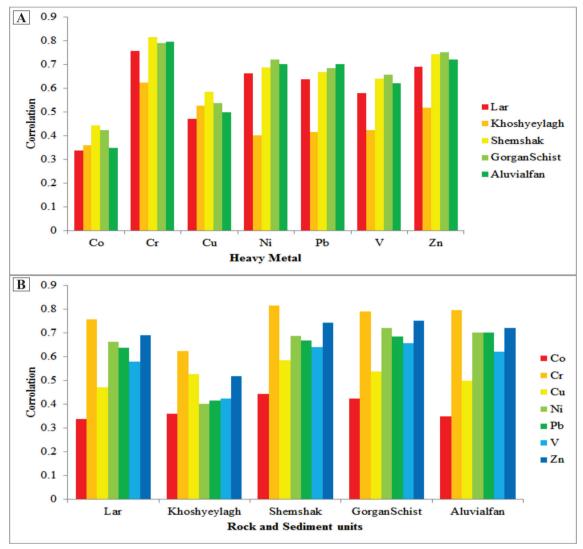


Figure 7. Bar chart of the correlation coefficient of heavy metals with rock-sedimentary units of the study area (watershed of Qarasu River and Gorgan Bay).

Khoshyilagh, and alluvial sediments, as well as the Lar (Figure 7a). The concentration of this heavy metal also shows a good agreement with the abundance of the related reference values (Figure 8a). Nickel, with a slight difference, exhibits a high correlation coefficient (0.65) with Sheshmak, Gorgan schist, alluvial sediments, and Lar. Meanwhile, the values of this coefficient for the Khoshyilagh unit are lower than those of the others, ranging around 0.4. Lead also has almost the same behavior as nickel. Such ratios are also well observed in the average values of the reference (Figure 8a). Vanadium and zinc show a high correlation coefficient with Sheshmak, Gorgan schist, alluvial sediments, and lar. In contrast, the values of this coefficient are lower for the Khoshvilagh unit than for the others (Figure 7a). Generally, the correlation coefficients between the geological units of the area with zinc values are higher than those with vanadium. For these two elements, the reference values have similar proportions (Figure 8a).

Vanadium and zinc show a high correlation coefficient with Sheshmak, Gorgan schist, alluvial sediments, and Lar. Meanwhile, the values of these elements for the Khoshyilagh unit are lower than those of the others (Figure 7a). Overall, the correlation coefficients between geological units and elemental values are higher for zinc compared to vanadium. For these two elements, the reference values have similar proportions (Figure 8a). Figure 7b shows the correlation coefficients of the river crossing distance from the geological units with different elements. According to this figure, the passing distance from the Lar unit has the greatest effect on the abundance of chromium, zinc, lead, and nickel, and the least effect



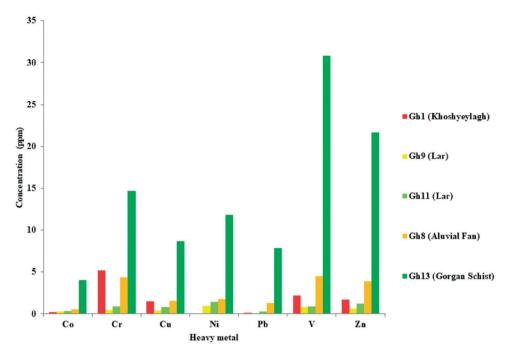


Figure 8. 5 samples that belong to the river sediments in which the river from the source to the sampling location has only one type of the geological units.

on the abundance of vanadium, copper, and cobalt. Such ratios are also seen to a large extent in the frequency of the average values of crustal carbonate rocks (Figure 8b).

The distance from the Khoshyilagh unit with chromium, copper, and zinc shows a significant correlation compared to other metals (Figure 7a). According to Figure 8b, the order of abundance of heavy metals in the present study is similar to the results of the average values of crustal heavy metals according to previous studies. On a global scale, these values for cobalt, nickel, and lead in sandstones are lower than those of other heavy metals. Besides, the distance from the Shemshak unit shows a high correlation with chromium. Then, it shows a decreasing correlation with zinc, nickel, lead, vanadium, copper, and finally with cobalt (Figure 7a). Considering that the lithology of the Shemshak unit is in the sandstone and shale region, it is challenging to compare the results with the reference average values; nevertheless, the ratios are traceable to a large extent.

Additionally, the distance from the Gorgan schist has a significant impact on the amounts of heavy metals, including chromium, zinc, nickel, and lead, with a slight difference (Figure 7b). Furthermore, this geological unit is correlated with vanadium, copper, and cobalt in descending order. These results are largely traceable to the abundance of reference values, except for lead. It appears that the river sediments passing through the Gorgan schist contain significant amounts of lead, rather

than other heavy elements, which may indicate the presence of lead mineralization veins. However, further exploratory studies should be conducted to support this issue.

River sediments are also very similar to the Gorgan schist. Essentially, the river sediments, Shemshak unit, and Gorgan schist exhibit a high degree of correlation with heavy metals (Figure 7b). This similarity is likely due to their shared origin. As mentioned in the geological setting section, the main origin of the Gorgan schist was probably shale and sediment from Chile. The Shemshak unit is also predominantly shale in the study area. According to Figure 6, elements of heavy metals in carbonate and sandstone rocks are less abundant than in other cases, so the main controllers of heavy metals in river sediments are the Shemshak unit and Gorgan Schist. So far, we have explored the correlation between geological units and their comparative roles in the concentration of heavy metals. In the following, an attempt is made to examine the impact of each geological unit more precisely. For this purpose, several samples were selected and collected in a manner that allows the river to pass through a geological unit from its source to the sampling location. The bar chart of Figure 8 shows 5 samples that only show the composition of the river affected by a geological unit. On the vertical axis, the concentration of heavy metals is given per kilometer. The role of Gorgan schist is clearly evident in the concentration of various metals, with the



total amount of heavy metals in the sediments of the river crossing from Gorgan schist being 2.5 times higher than in all other units. To take this number into account, two points should be considered.

In point 1, since a large amount of river sediments originates from the Gorgan schist, heavy metals of schist origin will consequently be about 5 times more prevalent. In Point 2, there are no samples that belong solely to the Shemshak unit among other samples. Therefore, based on the abundance of the Shemshak unit and its comparison with Gorgan schist (Figure 6), this geological unit might be the second in the production of heavy metals in the study area.

Furthermore, the heavy metal concentrations in the Gorgan Bay samples are similar, and these values are comparable to those in the Qarasu River samples near the mouth. Hence, at least in the coastal part of Gorgan Bay, the amount of heavy metals is largely affected by the sediments of the Qarasu River and subsequently the geological units of the region. Table 2 presents the Pearson

Table 2. Pearson correlation coefficient values between heavy metals.

|    | Co    | Cr    | Cu    | N1    | Pb    | V     | Zn |
|----|-------|-------|-------|-------|-------|-------|----|
| Co | 1     |       |       |       |       |       |    |
| Cr | 0.704 | 1     |       |       |       |       |    |
| Cu | 0.950 | 0.833 | 1     |       |       |       |    |
| Ni | 0.785 | 0.919 | 0.831 | 1     |       |       |    |
| Pb | 0.672 | 0.885 | 0.783 | 0.933 | 1     |       |    |
| V  | 0.862 | 0.921 | 0.911 | 0.967 | 0.910 | 1     |    |
| Zn | 0.825 | 0.964 | 0.886 | 0.975 | 0.897 | 0.980 | 1  |

correlation coefficients for the heavy metals in the studied samples. A high correlation coefficient between different metals can mean their common sources, interdependence, and similar behavior during transportation (Gayathri et al., 2021; Xie et al., 2022; Simou et al., 2024c; Yiika et al., 2023, 2024). Considering the high positive values of this coefficient, it is inferred that the heavy metals in the sediment samples of the Qarasu River and the shores of Gorgan Bay originated from a common source.

To complete the correlation results, a clustering diagram can also be applied. As shown in Figure 9, all variables in this study were categorized into three groups. The first category, covering most of the variables, includes the branch of river crossing distances from Shemshak, Khoshvilagh, Gorgan schist, Lar, and heavy metals such as cobalt, copper, lead, and nickel. The second category of heavy metals is vanadium, zinc, and chromium. The third category is the distance of river sediments across the river. The placement of the variables in the first category clearly demonstrates that the most effective sources for heavy metals, including cobalt, copper, lead, and nickel, are Shemshak, Khoshyilagh, Gorgan schist, and Lar units (Islam et al., 2018). The placement of other heavy metals such as vanadium, zinc and chromium in the second category and the connection of this category with the first one, shows that although the main factor in the distribution of these metals are geological units, it is likely that other polluting sources also play a role in their concentration (Yiika et al., 2022; Suh et al., 2025). Considering that the river sediments (where the rivers traveled among alluvial sediments and within the city) are placed in another category and have no tangible connection with the second one, it cannot be concluded that the general urban sewage systems play a role in increasing the metals (Tiabou et al., 2025 a,b; Ndema

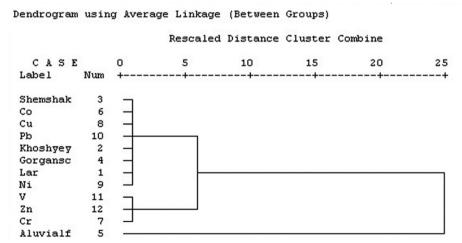


Figure 9. clustering diagram for heavy metals and geological units in Qarasu watersheld and Gorgan bay.



Mbongué et al., 2023, 2024). Otherwise, the second and third categories should be related to each other. It appears that there may be one- or two-point sources along the way that supply or increase the concentration of these heavy metals, which necessitates further studies and more accurate sampling in the city.

#### CONCLUSION

The most important geological units in the study area, which are most widely distributed in the Oarasu watershed, include the Gorgan schists, Khos Yilagh, Shemshak, and Lar formations. These units form different distances from the bedrock of the river due to their different expansion. The Qarasu River and its various branches pass through these units and are often affected by these beds. Therefore, both the sediment components of the river bed and its geochemistry are affected. There is a positive correlation coefficient between the concentrations of heavy metals and the distance of the river from the geological units, in most cases above 0.5. This result suggests that a large amount of heavy metals is under the control of the geological units in the area. Based on the data and evidence of this study, it can be stated that the main sources of cobalt and copper are from the Shemashk and Gorgan schist units. Meanwhile, the main sources of lead, chromium, nickel, vanadium, and zinc are from the Shemashk, Lar, and Gorgan schist units, as well as alluvial sediments. Although the main cause of the accumulation of heavy metals in all samples is attributed to geological units, the source of some heavy metals (e.g., chromium, vanadium, and zinc) may be of human origin.

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