ISSN: 1648-6897 / eISSN: 1822-4199

VILNIUS TECH
Vilnius Gediminas Technical University

JOURNAL of ENVIRONMENTAL ENGINEERING & LANDSCAPE MANAGEMENT

2025
Volume 33
Issue 1
Pages 1–12
https://doi.org/10.3846/jeelm.2025.21832

EVALUATION OF HEAVY METAL POLLUTION IN GROUNDWATER RESOURCES OF KONARO AREA, IRANSHAHR, SE IRAN: IMPLICATION FOR OPHIOLITIC ROCKS IMPACT

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Highlights:
- all of the indices are vital and reliable for examining the risk of heavy metal contamination in Konaro's ophiolitic region;
- validation via pollution evaluation indices and statistical analyses confirms that the low to moderate concentration of heavy metals in Konaro's groundwater samples results from the lack of acidity;
- the dearth of agricultural activities and urbanization in the vicinity of the river, leading to minimal aquifer pollution, also contribute to this condition.

Article History:
- received 01 July 2023
- accepted 30 April 2024

Abstract. This study, it has been attempted to investigate the heavy metals pollution in groundwater resources of Konaro area. Accordingly, eight representative groundwater samples from wells and qanat were collected in December 2017 from rural settlements commonly used for irrigation and drinking. Analysis of lead, zinc, iron, chromium, copper and nickel as heavy metals was conducted by the ICP-MS approach. The results of analyzes indicate that the concentration of heavy metals in the groundwater of the study area is lower than the permissible limit. Results of HEI, HPI, and Cd contamination indices show that 62.5% of samples in the Konaro area fall into the medium pollution group, and the rest of the samples fall into the low pollution group due to their heavy metals content. Studies show that all samples of groundwater in the Konaro area have low to moderate contamination and that the overall contamination rate is not dangerous. Correlations between heavy metals indicators demonstrate that HPI is strongly correlated with HEI and C_d also HEI with C_d. Therefore, it is evident that all of the indices are important and reliable to study the risk of heavy metals pollution in the Konaro ophiolitic area. Pollution evaluation indices and statistical analysis confirm that the low to medium level of heavy metals in Konaro groundwater samples is owing to the lack of acidity, poor agriculture and poor urbanization around the river and thus the lack of contamination of the aquifer.

Keywords: heavy metals, pollution indices, geogenic sources, ophiolitic area, Konaro, Iranshahr.

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1. Introduction

Groundwater resources can be potentially a target for various sources of contaminations. One major step towards characterization of contamination sources and the associated parameters, is to conduct groundwater quality assessment through different methods. When dealing with heavy metals, calculation of pollution indices is among well-known techniques of contamination characterization. The objectives of this study include primary assessment of physicochemical parameters of the groundwater and heavy metal concentrations and finding distributions using multivariate statistical methods in the study area indings of our study can be used in devising preventive measures to control pollution in the study area and similar regions where the groundwater resource would be relied upon for drinking purposes in the future. Heavy metals pollution is accounted for a major pollution in the natural environment are that can pose a serious threat to ecosystems because of their biodegradation potential, toxicity and sustainability (Moslempour & Shahdadi, 2013). Globally, over five billion inhabitants are dependent on groundwater and surface water systems since people use these resources in numerous ways such as potable water, housing crop production, and manufacturing applications (Akhtar et al., 2019).

Khan, Hydrodynamic evaluation of groundwater flow systems is usually based on comprehensive information on groundwater chemistry. In general, contaminants in groundwater are filtered by soil components, making them more suitable for drinking than surface water and also having better temperature, natural quality, and better vulnerability (Saidi et al., 2010). Some inorganic substances, such as zinc, iron, copper, nickel, etc., are necessary for the development of animals and plants, but these substances are harmful for animals or plants when the concentrations go above the acceptable limitations (Vardhan et al., 2019).

Groundwater chemistry is affected by various factors, including the geology and type of local lithological units, weathering of rocks, water quality introduced into the aquifers, and hydro chemical reactions (Coetsiers & Walraevens, 2006; Subramani et al., 2005; Dabiri et al., 2017). Heavy metals behavior in aquatic systems is largely unpredictable and dependent on parameters, including local lithology, water source, and biogeochemical processes (World Health Organization [WHO], 1993). Heavy metal contamination in groundwater resources has been proven in various ways, including natural and anthropogenic origin in various studies (Belkhiri et al., 2017; Bhuiyan et al., 2010; Jahanshahi & Zare, 2015; Kale et al., 2010). Generally, factors such as pH, cation exchange capacity, metals concentration, oxidation status of mineral components, organic carbon, and redox potential can control the amount of metals solubility in groundwater and soil (Musa et al., 2013).

Regular monitoring of the concentration of heavy metals in groundwater to maintain the health of the ecosystem is inevitable. Heavy metals contamination indicators, including HEI, C_d, and HPI are indices that can assess the level of contamination and quality of groundwater using the influence of the concentration of several metal elements (Brindha et al., 2016; Omran, 2016; Singh et al., 2017; Barahouei et al., 2021). Pollution indices are measured using analyzed heavy metals values in each sample of the study area and values presented in WHO standards. Many researchers around the world have used the indices presented in this study to investigate the metal contamination in waters in their studied area (Ahamed et al., 2018; Belkhiri et al., 2018; Gyamfi et al., 2019; Jahanshahi & Zare, 2015; Kumar et al., 2012; Pawar & Pawar, 2016; Saadat et al., 2024). Besides calculating pollution indices, statistical analysis was also used to interpret the results better and provide more accurate conclusions. The Konaro seasonal river lacks surface water flow due to continued droughts. Therefore, water is provided for agricultural and drinking purposes of the local people use by drilling wells in riverbeds and qanats. The impact of ophiolitic units and heavy metals contamination in groundwater and surface in the Konaro ophiolitic zone has not been addressed so far. Therefore, this study attempts to investigate the following: analyzing the measured physicochemical factors as well as the content of heavy metals in groundwater of the region, the impact of different lithological units of the ophiolitic complex on heavy metal concentration, calculation of pollution indices to evaluate the health risk of groundwater drinking for organisms and finally to perform statistical processing for Identification of variables affecting heavy metals.

2. Materials and methods

2.1. Study area

The location of the Konaro river basin has been in southeast Iran, Sistan and Baluchistan Province and Iranshahr City. The study area location is between the eastern longitudes of 60° 50′ to 61° 15′ and northern latitudes of 27° 05′ to 27°20′. The hydrological system of the study area included rivers, floodwaters, and streams originating from the heights of the basin. This basin system has been expanded from east to west and includes several large and small floodwaters often without a specific name. These floodwaters flow to the Konaro River. This river supplies the Iranshahr Plain after flowing. In the case of rainfall and occurrence of seasonal flood, the river flows into the plain, and during years with low rainfall, the main river flow is cut off. As shown in Figure 1, the geological lithologies in the Konaro area include ophiolitic and non-ophiolitic units. Most outcrops of ophiolitic units are found in the southwestern part of the region. Ophiolitic unites in the study area include coloured mélange, sheet flow and pillow lava, diabasic sheeted dikes, isotropic gabbros and serpentinized peridotites. Non-ophiolitic unites in the Konaro area are mainly flycshes (shale with sandstone) and limestones. Quartz, feldspar, calcite, muscovite, talc, chlorite, hornblende, serpentine, and augite are the dominant minerals of the Konaro River sediments derived from erosion of the rocks in the region. Therefore, it is assumed that ophiolitic units of the area can play a significant role in imposing heavy metals on the water and soil of the area.

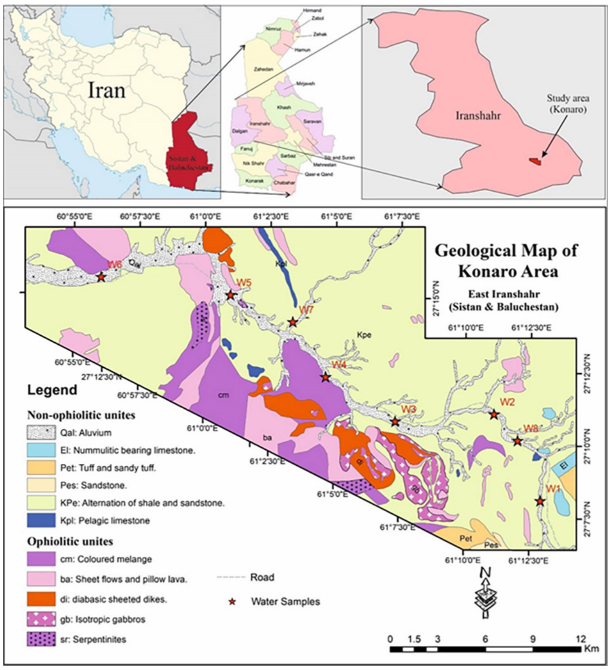

Figure 1. Geology map of the study area and groundwater sampling points (modified from geology map)

2.2. Analytical procedure and sample collection

Since the groundwater resources were limited, only 8 groundwater samples were taken in December 2017 to study the chemical properties of groundwater in the Ophiolitic region of Kenaro (Figure 1). The reason that the number of samples is not more than eight is due to the fact that after successive droughts, most of the wells in the region have dried up and the other reason is the low population density and low number of settlements along this river. For the investigation of the chemical characteristics of each source, the groundwater samples were taken from the wells and qanat in this survey. The samples were kept in polyethylene bottles, and after filtering the samples, 0.15 cc nitric acid (pH ≤ 2) was added to each bottle to stabilize the heavy metals and was quickly transferred to the university laboratory. A portable device was utilized to measure temperature, electrical conductivity (E_C), and pH. To remove suspended sediment of the water samples, they should be filtered in the laboratory. To analyze some of the important chemical properties, standard methods (American Public Health Association, 1998) were employed sulfate (SO_4^{2-}) by spectrophotometric turbidimetry; bicarbonate (HCO_3^-) by titration with HCl, chloride (Cl^-) by standard $AgNO_3$ titration; calcium (Ca^{2+}) and magnesium (Mg^{2+}) by titration using standard EDTA; potassium (K^+) and sodium (Na^+) by flame photometry in the chemistry laboratory of the Islamic Azad University of Zahedan Branch. The second part of groundwater sent to ZarAzma Company in Kerman for heavy metals analyzed by the ICP-MS method.

2.3. Pollution assessment indices

Three important and valid pollution indices are used for the determination of the heavy metal contamination level in the Konaro groundwater for various uses. Three indices of HPI, HEI, and C_d were applied in this survey, which are degree of contamination, heavy metal pollution index, and heavy metal evaluation index, respectively. These indicators show the total water quality over heavy metals. The mentioned approaches are carried out via monitored values to the highest acceptable concentration as well as the optimum number of factors. Water quality in the degree of contamination (C_d) index is achieved by the sum of the contamination parameters of the component having a higher value than the upper admissible limit. HPI and HEI indicators, which are heavy metal pollution and heavy metal assessment indices, respectively, are estimated using the ratio of metal monitoring concentrations to WHO (2011) at the maximum acceptable concentration in potable water (Prasanna et al., 2012).

2.3.1. Degree of contamination (C_d)

The combined influence of several water quality factors on household water is summarized by the C_d factor (Backman et al., 1998; Prasanna et al., 2012). Based on the studies conducted by Backman et al. and Edet and Offiong, the contamination index (C_d) has three levels: low (C_d < 1), medium (C_d = 1 – 3), and high (C_d > 3). The degree of contamination factor (C_d) is calculated by Eqs (1) and (2) in the following:

$$C_d = \sum_{i=1}^{n} C_{fi}; \quad (1)$$

$$C_{fi} = \frac{M_i}{S_i} - 1. \quad (2)$$

In this equation, C_{fi}, S_i, and M_i indicate the contamination parameter, the upper admissible concentration, and the amount monitored of the *i*th component, respectively. Ionic species, as well as elements having monitored values lower than the upper admissible concentration, were not considered in the calculation.

2.3.2. Heavy metal pollution index (HPI)

HPI indicator was created through specifying weight (W_i) or rank for each selected factor. The rank is a specified value varying between 0 and 1, indicating its relative significance to individual quality observations. There has been an inverse relationship between the rank and the standard admissible value (S_i) for each factor (Mohan et al., 1996; Horton, 1965; Prasanna et al., 2012; Reddy, 1995). The concentration limits, including the highest desirable (ideal) value (I_i) and the standard permissible value (S_i) for each factor, in this study, were obtained from WHO (2011) standard (Table 1). The highest permissive value of drinking water (S_i) represents the highest admissible concentration of potable water in the absence of an alternative water source. The standard limit for the same factors in potable water is represented by the favorable highest value (I_i) (Bhuiyan et al., 2010; Prasanna et al., 2012). The HPI index is measured by the following Eq. (3) suggested by Mohan et al. (1996) and applied by Prasanna et al. (2012):

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \text{ (Mohan et al., 1996).} \quad (3)$$

In this equation, W_i, Q_i, and n are the unit weight of the *i*th factor, the sub-index of the *i*th factor, and the number of the adopted factors, respectively. The calculations for the Q_i parameter are presented in the following Eq. (4).

$$Q_i = \sum_{i=1}^{n} \frac{|M_i - I_i|}{S_i - I_i} \times 100 \text{ (Mohan et al., 1996).} \quad (4)$$

In this formulation, M_i, S_i, and I_i are heavy metal, standard, and ideal *i*th factor values, respectively. Nevertheless, the relationship has validity in conditions where M_i is higher than I_i. For other cases, I_i should be removed from the numerator. Low values of the HPI index, and in particular below 100, indicate that the samples under study are not contaminated with heavy metals and have no adverse health effects. When HPI values are equal to 100, it shows the risk of threshold and probability of adverse effects on health, and when HPI values are above 100 indicates that the groundwater studied is unusable for drinking.

Table 1. Concentration limits, i.e., the standard permissible value (S) and highest desirable value (I) for each parameter, were taken from WHO standard (μg/l)

	Cr	Cu	Fe	Ni	Pb	Zn
Standard permissible value (S)	10	1000	300	20	50	5000
Highest desirable value (I)	–	50	100	–	–	3000

2.3.3. Heavy metal evaluation index (HEI)

HEI index demonstrates the total water quality by considering heavy metals (Edet & Offiong, 2002; Prasanna et al., 2012), measured based on Eq. (5).

$$\mathrm{HEI} = \sum_{i=1}^{n} \frac{M_i}{S_i}. \quad (5)$$

In this equation, S_i and M_i are the maximum allowed concentration (MAC) and monitored value and of the ith factor, respectively.

3. Results and discussion

3.1. Physicochemical features

Table 2 presented the analytical results of the physicochemical properties of Konaro groundwater samples. The pH values varying from 7.43 to 8.40 measured in Konaro groundwater samples indicate (Table 2) that samples are mostly slightly alkaline. Electrical conductivity (E_C) plays a key role in specifying salinity risk and water suitability for irrigation purposes. According to Table 2, the E_C parameter had values in Konaro groundwater samples between 948 to 1842 μS/cm, with an average value of 1185.8 μS/cm. Furthermore, the values of total dissolved solids (TDS) in the groundwater samples of the studied area were between 582 mg/l to 1212 mg/l, indicating that the level of dissolved solids in Konaro groundwater is good. The concentration of sulfate anion in the samples of the Konaro region is 1.24 to 12 mg/l, indicating the level of sulfate in Konaro groundwater is excellent. According to WHO, for potable water, sulfate anion limit is 250 mg/l. In agricultural waters, the chloride ion is the most important source of toxicity. Soil cannot absorb and retain chloride ions, so it moves with water and is absorbed by plants, moving during transpiration and eventually accumulating in the leaves (Ayers & Westcot, 1994). The chloride ion content in groundwater samples of Konaro area was between 0.6 and 3 mg/l (Table 2). The highest value suggested by the WHO for chloride ions in potable water is about 200 mg/l.

3.2. Heavy metal concentration

Groundwater quality in the Konaro area is assessed by the concentration of heavy metals (chromium, iron, copper, lead, zinc, and nickel). The concentrations of selected heavy metals from various sites in the groundwater samples in the Konaro ophiolitic area are presented in Table 3. The heavy metals concentration measured in the groundwater samples in the study area decreases as follows: Fe > Cr > Ni > Zn > Cu > Pb (Figure 2).

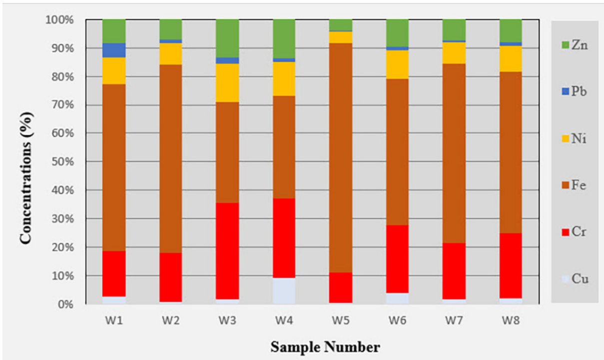

Figure 2. Heavy metal concentrations in the Konaro area

It is suggested that most of the heavy metals must be within this range for the proper functioning of metabolic activities in the human body. Fe, Cr and Ni are the most

Table 2. Field measurements and analytical data (concentrations are expressed in mg/l and E_C in μmhos/cm)

Samples	EC	pH	TDS	TH	$SO4^{2-}$	HCO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
W1	1128	7.47	738	10.48	4.6	4.9	1.4	1.4	1.7	7.6	0.1
W2	1842	7.43	1212	12.35	12	4.7	0.6	0.5	2.7	14	0.2
W3	1014	7.47	668	11.11	3	4.7	2	0.5	2.4	6.6	0.1
W4	997	7.43	651	9.56	2.2	5.1	2.3	0.7	1.9	6.8	0.1
W5	948	8.23	600	11.27	1.6	4.2	3	0.4	2.5	5.7	0.1
W6	970	7.75	582	13.61	1.24	4.5	1.8	1.5	2.4	7.1	0.1
W7	951	8.10	627	9.88	1.9	4.6	2.6	0.5	2.1	6.2	0.1
W8	1651	8.40	1010	11.45	1.7	4.7	0.9	0.8	2.3	9	0.1
Min	948	7.43	582	9.56	1.24	4.2	0.6	0.4	1.7	5.7	0.1
Max	1842	8.40	1212	13.61	12	5.1	3	1.5	2.7	14	0.2
Mean	1188	7.79	761	11.21	3.53	4.7	1.8	0.8	2.25	7.88	0.11
WHO					450	*	250	100	50	200	*

Table 3. Heavy metals concentration in the groundwater samples (mg/kg) of studied area

Samples	Cr	Ni	Pb	Zn	Fe	Cu
W1	16.36	9.54	5.31	8.46	60	2.8
W2	18.13	7.95	1.28	7.49	70	0.9
W3	19	7.7	1.15	7.51	20	0.9
W4	23.25	9.75	1.2	11.25	30	7.65
W5	22.17	8.69	0.69	8.37	170	0.9
W6	23.25	9.75	1.13	9.25	50	3.65
W7	22.17	8.41	0.53	8.37	70	1.8
W8	24.15	9.71	1.18	8.51	60	2.1
Min	16.4	7.70	0.53	7.49	20	0.9
Max	24.2	9.75	5.31	11.25	170	7.65
Mean	21.1	8.94	1.56	8.65	66	2.59
Median	22.17	9.12	1.17	8.42	60	1.95
Standard deviation	2.84	0.86	1.54	1.19	46	2.27
WHO (2011)	50	70	10	3000	–	2000
Average of the area soils (mg/l)	450	163	14	73	35 687	42
Average of the world soils[a]	54	20	21.5	64	0.1–10(%)	20

Note: [a](Kabata-Pendias & Mukherjee, 2007).

important heavy metals in groundwater samples in the Konaro area. Cu, Zn, and Pb are at lower concentrations. Cu, Cr, Zn, Fe, and Ni concentrations could be the result of erosion of surrounding rocks such as ultramafic and mafic. A comparison of the measured heavy metal concentrations in different sampling points with the standards indicates that all the heavy metals studied are in the permissible range and have no hazards.

The distribution of heavy metal concentrations in the groundwater samples of the Konaro area does not indicate a regular and continuous trend from the beginning to the end of the sampling route. Therefore, the increase or decrease of each heavy metal in different samples is influenced by the dominant lithological units around each sample (Figure 3).

Lower concentration of heavy metals in the groundwater samples of the studied area compared to the average values of the area soils, the world soils, and WHO (Table 1), indicates their geogenic origin. Also, the lack of industrial and urban centers in the study area has reduced the possibility of anthropogenic contamination. Investigation of the spatial distribution of heavy metals in groundwater samples of the studied area shows that the highest concentrations of Cr and Ni are in samples W4, W6 and W8, the highest concentrations of Cu and Zn in sample W4 and the highest concentrations of Fe and Pb are in samples W5 and W1, respectively (Figure 4). As seen in the geological map of the Konaro area in Figure 1, most of the outcrops of the ophiolitic units in the studied area,

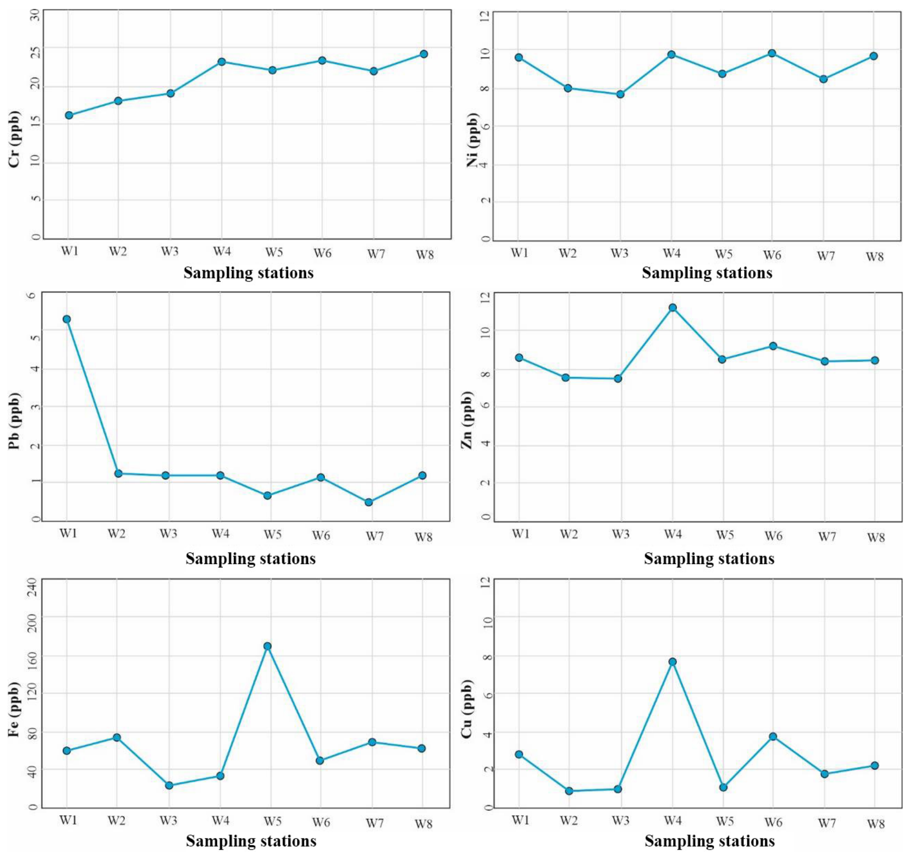

Figure 3. Variation of heavy metals (Cr, Ni, Pb, Zn, Fe, and Cu) at groundwater samples of the study area

including coloured mélanges rocks, are exposed around of samples W4, W6 and W8. Ultramafic and gabbroic rocks in coloured mélanges are the source of Ni and Cr. Basaltic lavas and diabasic dikes can be the source of imposing Cu and Zn metals. The erosion and weathering of these units and the release of trace elements are the major reasons for the increase of the concentration of these elements in the area.

Cr is an element in Cr-spinel an chromitite minerals in coloured mélanges rocks that the major reason for the increase in Cr concentration in samples W4, W6 and W6 (Figure 4a).

The main minerals of mafic rocks, including pyroxenes in gabbros, have Ni. Gabbroic rocks in this area are exposed both as separate units and together with coloured melange. Separate gabbroic units have less weathering, and samples with coloured melanges are highly tectonized and are more likely to release heavy metals. Therefore, Ni concentrations increased in samples W4, W6, and W8 (Figure 4b). The lithologies belong of the extrusive sequence of the ophiolite, including pillow lava and diabasic dikes, can usually contain amounts of Cu and Zn. Most outcrops of pillow lava and diabasic dikes are in southeastern sample W4 and may be the source of the imposition of Cu and Zn in sample W4 (Figures 4c and 4d). The only important stream from within the pillow lava and diabasic dike unites is upstream of W4. The concentration of iron in sample W5, which is a sample of qanat water and is taken from an approximate depth close to the ground, shows the highest amount (Figure 4e). This is probably due to the higher oxidant conditions in this sample. The highest concentration of Pb is in sample W1 (Figure 4f), which can be caused by human pollution with the pump motor available to extract water from the well. Because in other groundwater samples, the concentration of Pb is much lower, and also, ophiolitic rocks do not have high levels of Pb. The outer surface of the metal pipes of the sump pump motor is insulated with lead to prevent corrosion and rust, with continuous use, lead enters the water composition.

3.3. Classification of water

For the classification of groundwater samples in the Konaro river basin, a two-variable diagram, pH against total heavy metals, such as chromium, iron, copper, nickel, zinc, and lead in μg/l) was used (Ficklin et al., 1992; Caboi et al., 1999; Hizir et al., 2023; Islam et al., 2024). Figure 5 presented the relationship between total calculated heavy metals (μg/l) and pH in groundwater samples of the Konaro ophiolitic area. As can be seen, the total groundwater samples are classified as near neutral and low metallic in the study area. The low metallic content of these samples cannot pose a serious threat to consumers of drinking water. No sample was placed into the high metal field.

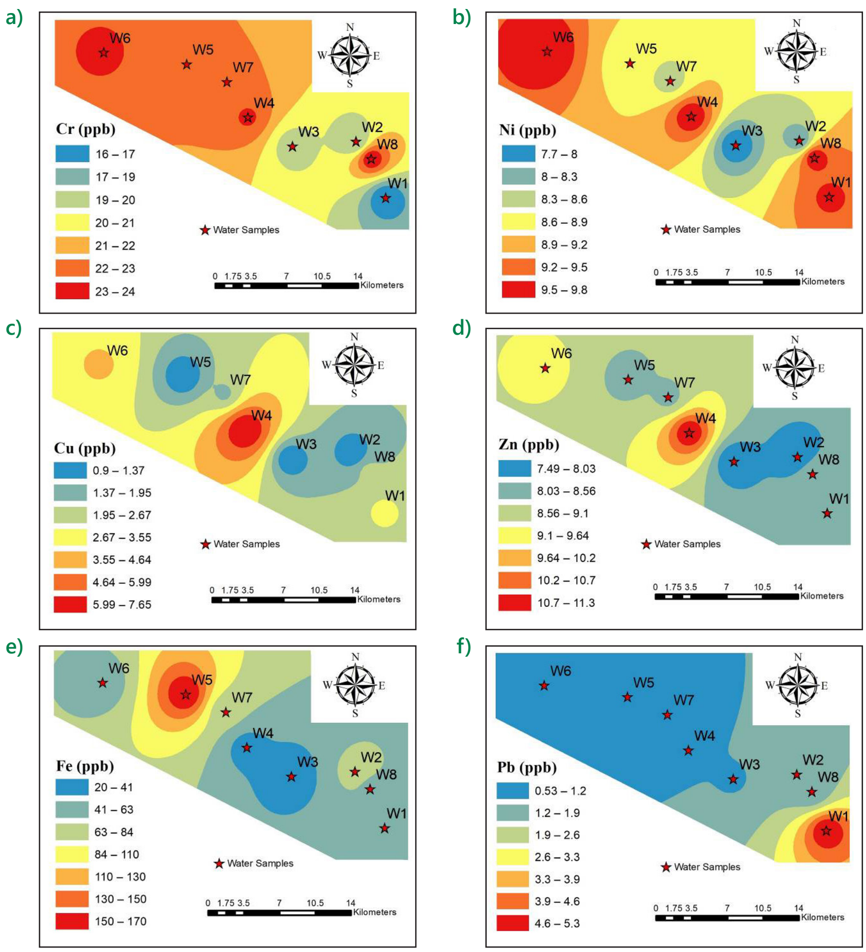

Figure 4. Spatial distribution of metal elements (μg/l) in groundwater samples of Konaro

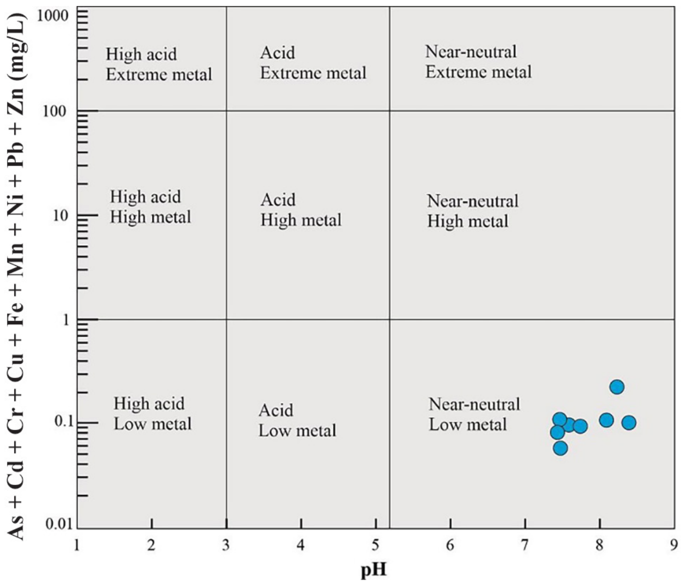

Figure 5. Classification of groundwater samples based on the plot of metal load and pH

3.4. Determination of pollution indices

Table 4 presented the most important pollution indices introduced in the previous sections calculated using the values presented in the WHO standard. According to Table 4, the calculated values of the HPI pollution indicator in the groundwater samples of the studied area varied between 111.49 and 155.42, with a mean value of 136.58. However, the mean HPI index calculated for the groundwater samples in the study area is higher than the admissible index value of 100 suggested by Mohan et al. (1996) for potable water.

In general, the HPI values for all samples (100%) are above the critical limit of 100 (Figure 6).

The calculated values of the HEI pollution index in the groundwater samples of the studied area varied between 2.38 and 3.23, with a mean value of 2.81 (Table 4). As shown in Figure 6, all groundwater samples exceed the warning threshold value of HEI = 1. This indicates that, according to the calculated HEI values, all the groundwater samples (100%) in the studied area are, polluted similar to the calculated results of the HPI.

The calculated values of the C_d pollution indicator in the groundwater samples of the studied area varied between 0.64 and 1.42, with a mean value of 1.11 (Table 4). The results of the C_d pollution index show that 62.5% of groundwater samples in the studied area have values

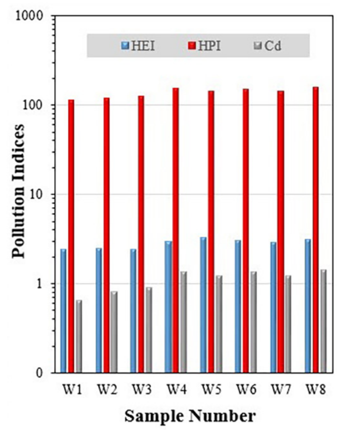

Figure 6. Comparative study of pollution evaluation indices

Table 4. The results of pollution evaluation indices

Samples	HEI	Deviation	Deviation %	HPI	Deviation	Deviation %	Cd	Deviation	Deviation %
W1	2.42	–0.39	–13.72	111.49	–25.09	–18.37	0.64	–0.47	–42.50
W2	2.47	–0.34	–12.01	118.24	–18.34	–13.43	0.81	–0.29	–26.49
W3	2.38	–0.43	–15.38	123.79	–12.78	–9.36	0.90	–0.21	–18.63
W4	2.95	0.14	4.88	150.90	14.32	10.48	1.33	0.22	19.80
W5	3.23	0.43	15.14	140.40	3.83	2.80	1.22	0.11	10.04
W6	3.01	0.20	7.05	150.50	13.92	10.19	1.33	0.22	19.80
W7	2.88	0.08	2.69	141.88	5.30	3.88	1.22	0.11	10.04
W8	3.13	0.32	11.34	155.42	18.84	13.80	1.42	0.31	27.94
Min	2.38			111.49			0.64		
Max	3.23			155.42			1.42		
Mean	2.81			136.58			1.11		

above 1, and so they fall into the category of medium pollution (Figure 6). Therefore, to better and more accurately assess heavy metal contamination in groundwater samples of the Konaro area, the average approach presented by Edet and Offiong (2002) was employed to modify the present water quality design for the indicators. Table 5 presented the pollution indicators values suggested by this method. As can be seen, pollution indicators are categorized as low for samples having indicators lower than the average value, medium for those locating between the average and two times the average, and high for samples having the value higher than two times the average values (Jahanshahi & Zare, 2015).

Table 5. Classification of groundwater quality using the modified pollution indices

Indexing method	Class of pollution	Degree of pollution	No. of samples in the class	% of samples in the class
Cd	<1	Low	3	37.5
	1–2	Medium	5	62.5
	>2	High		
HPI	<136	Low	3	37.5
	136–272	Medium	5	62.5
	>272	High		
HEI	<2.8	Low	3	37.5
	2.8–5.6	Medium	5	62.5
	>5.6	High		

According to the calculated values of the HEI index, 37.5% of the samples are in the low-risk level with an index of less than 2.8 and 62.5% of the samples are in the medium risk level with an index of between 2.8 to 5.6 (Table 5 and Figure 7a). According to the calculated values of the HPI index, 37.5% of the samples are in the low-risk level with an index of less than 136 and 62.5% of the samples are in the medium risk level with an index of between 136 to 272 (Table 5 and Figure 7b). According to the calculated values of the C_d index, 37.5% of the samples are in the low-risk level with an index of less than 1 and 62.5% of the samples are in the medium risk level with an index of between 1 to 2 (Table 5 and Figure 7c). Therefore, based on the results of the Pollution indices, the Konaro ophiolitic area is mainly at medium-risk level, and only a small portion is in the low risk zone.

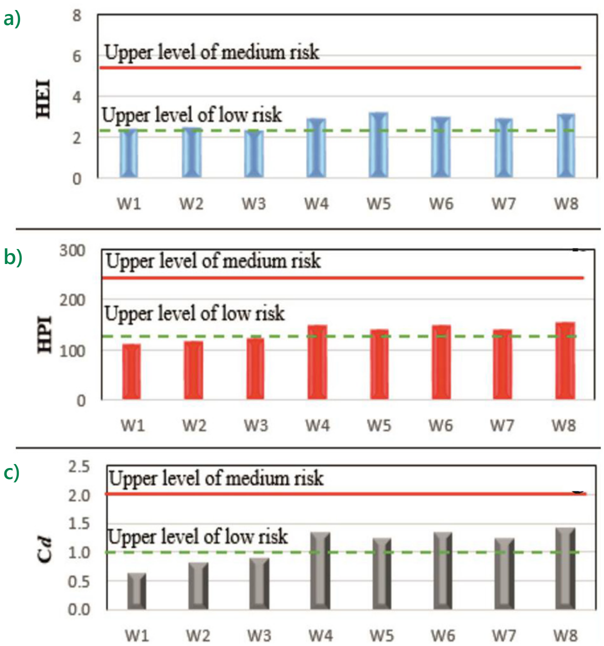

Figure 7. Pollution evaluation indices of groundwater samples indicating the samples with low, medium, and high risk level

In general, the concentration of heavy metals in water is low since their solubility is limited (Jahanshahi & Zare, 2015). According to Table 2, in the Konaro area, the pH of groundwater is neutral to slightly alkaline since pH is always higher than 7. There are probably two factors involved: (1) the low concentration of metal sulfides in ophiolitic rocks and (2) the existence of carbonate minerals that can quickly neutralize acid production (Jahanshahi & Zare, 2015). Calcite mineral is a key neutralizing agent due to its occurrence in the lithology unites of the studied area as well as its rapid reaction rate. In the Konaro ophiolitic zone, both of the above factors probably contributed to the lack of groundwater acidification.

The Pollution index maps were produced based on the calculated values of each index, and the degree of contamination for each of them was determined in the maps (Figure 8).

The C_d, HPI, and HEI increase toward the northwestern part of the study area. According to Figure 8, the northwestern part of the study area and along the ophiolitic rocks has moderate indices values. According to Figure 8, the C_d, HPI, and HEI demonstrate more comparable distribution patterns having an increasing tendency towards the southeastern to northwestern orientation, showing the presence of similar point sources.

3.5. Multivariate statistical processes

Multivariate statistical processing through principal component analysis (PCA), correlation analysis, and cluster analysis (CA) to determine the interdependence between the various heavy metals as well as the most influential factor affecting groundwater quality assessment were performed.

3.5.1. Principle component analysis (PCA)

PCA was carried out with Varimax rotation and Kaiser Normalization on groundwater samples data that clarified the observed relationship of cluster variables by simple methods, represented in variance and covariance patterns and the similarity between observations. The application of parameters having higher eigenvalues than one was suggested by Kaiser proposed (Liu et al., 2003). As can be seen in Figure 9a and 9b, three parameters were extracted for groundwater quality data sets having eigenvalues higher than 1 expressed 81.758% of the

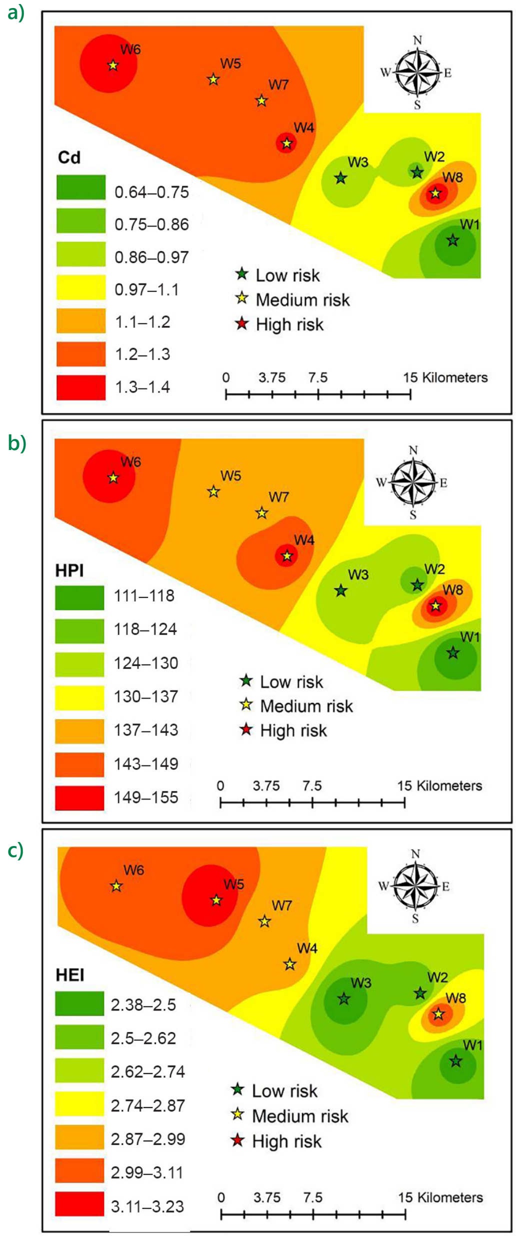

Figure 8. Maps showing the spatial distribution of three indices scores obtained by quality evaluation indices of the groundwater samples: a) C_d; b) HPI; c) HEI

total variance in the Konaro area. Furthermore, to determine the number of retained PCs for understanding the underlying factors structure, the scree plot (Figure 9a) was applied.

Table 6 presents the measured factor loadings, each parameter cumulative percentages and percentages of variance. According to the PC1, PC2, and PC3 for groundwater quality data, the total variance of 37.617%, 22.822%, and 21.318%, were calculated, respectively. It is evident that PC1 is profoundly highly positively loaded on Zn, Cu, Cr, and Ni. The sources of which are either natural from geogenic through weathering and leaching of minerals from ophiolitic rocks. PC2 is influenced by very highly positively loaded Fe and pH, their sources could be from oxidation processes induced by rain or percolating water. PC3 is influenced by very highly positively loaded with Pb while highly negatively loaded with Cr, meaning that the origin of these two elements is different. It is assumed that PC1 and PC2 are indicative of the water-rock interaction and natural processes. PC3 is highly positively loaded with Pb (0.980). Sources of the Pb are mainly from anthropogenic origin activities.

Table 6. Principal component analysis of heavy metals

Parameters	Components		
	1	2	3
Zn	**0.948**		
Cu	**0.901**	–0.391	
Ni	**0.887**		
EC	–0.391		
pH		**0.872**	–0.368
Fe		**0.833**	
Pb			**0.980**
Cr	**0.565**	0.355	**–0.722**
Eigen values	3.009	1.826	1.705
% of variance	37.617	22.822	21.318
Cumulative %	37.617	60.439	81.758

Note: Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 5 iterations.

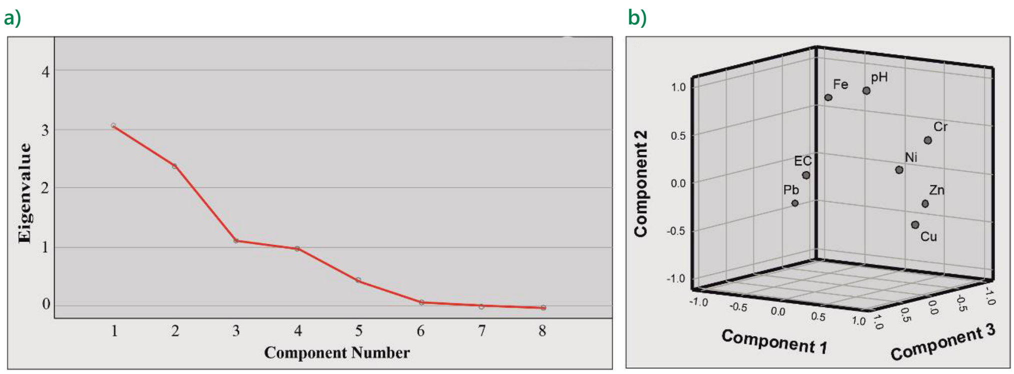

Figure 9. Principal component analysis by (a) scree plot of the characteristic roots (eigenvalues), and (b) component plot in rotated space

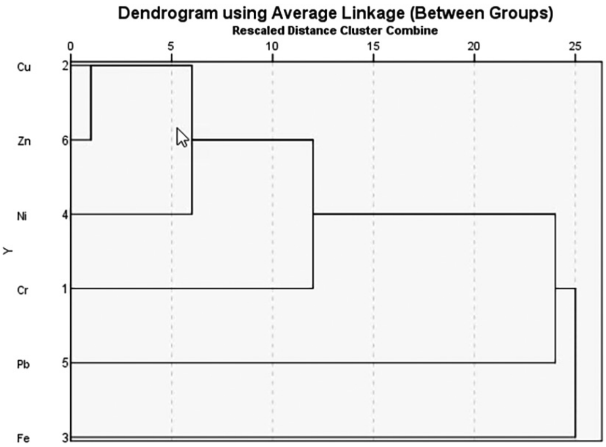

Figure 10. Heavy metal group cluster analysis tree

3.5.2. Cluster Analysis (CA)

TCluster analysis of the R mode is conducted to describe various groupings of elements in the dataset affecting the total quality of groundwater. As can be seen in Figure 10, cluster analysis reveals that Cu, Zn are categorized in a single cluster, then, in the next steps, Ni and Cr are added to them. Pb and Fe are added to the stairs farther away. According to the mentioned heavy metals clustering, all heavy metals except Pb and Fe have the same origin in the region and are probably from geogenic sources. Pb may be from anthropogenic inputs and Fe from oxidation.

3.5.3. Correlation matrix (CM)

According to Table 7, Pearson's correlation coefficient matrix was applied for identifying the relationship between various metals. To understand the relationships between inter-parameters, a comparison was made between the correlation analysis results and the results of PCA analysis. There was a significant positive correlation of Zn with Cu (0.968), Ni (0.720) and Cr (0.530), indicating the similar sources for PC1, Fe with pH (0.562) similar to sources reported for PC2 and there was a significant negative correlation of Pb with Cr (0.685) similar to sources reported for PC3. Correlations between heavy metal pollution indicators show that HPI with HEI (r = 0.876) and C_d (r = 0.995) and, also HEI with C_d (r = 0.894) have a strong correlation. This suggests that these three indicators can be employed for the assessment of the risk of heavy metal contamination in the Konaro area. Therefore, it was found that CM, PCA, and CA approaches are strongly correlated for categorizing the causative parameters in the studied dataset.

4. Conclusions

Multivariate statistical approaches and heavy metal pollution indices were employed to investigate heavy metal contamination in the ophiolitic area of Konaro. The average concentrations of selected heavy metals for the groundwater samples in the study area were in descending order: Fe > Cr > Ni > Zn > Cu > Pb. The mean concentrations of none of the heavy metals studied had values lower than the MAC values for potable water. HPI, HEI, and C_d indices were employed to assess the amount of heavy metal pollution owing to ophiolitic rocks on groundwater of the Konaro area. The overall conclusion, despite the large outcrops of ophiolite rocks in the region, is the mentioned indices show that this area is moderate to low risk. The medium to low concentration of heavy metals in groundwater in the Konaro area may be owing to the existence ophiolitic rocks such as ultramafic, mafic and pelagic limestone together. The presence of calcite minerals in the soils of the region from the surrounding pelagic limestones, which quickly neutralizes sulfide by producing an acidic compound due to the oxidation process. Furthermore, there the adsorption and exchange of heavy metals may be resulted from clays. Nevertheless, the difference in heavy metal enrichment in groundwater samples can be resulted from the dominant lithological units around each sample. To determine the contribution of each metal to the calculated indices, CM, CA, and PCA was conducted for heavy metals and heavy metal pollution indices (HEI, HPI, and C_d). The HEI was strongly correlated with HPI and

Table 7. Correlation analysis of heavy metals and pollution indices (sources: Kabata-Pendias & Mukherjee, 2007; WHO, 2011)

	pH	EC	Cr	Cu	Fe	Ni	Pb	Zn	HEI	HPI	Cd
pH	1										
EC	0.023	1									
Cr	0.634	–0.181	1								
Cu	–0.325	–0.294	0.367	1							
Fe	0.562	–0.065	0.109	–0.420	1						
Ni	0.179	–0.121	0.452	0.684	–0.093	1					
Pb	–0.407	0.027	–0.685	0.088	–0.157	0.311	1				
Zn	–0.124	–0.375	0.530	**0.968****	–0.219	**0.720***	–0.041	1			
HEI	**0.768***	–0.196	**0.893****	0.227	0.506	0.503	–0.519	0.447	1		
HPI	0.597	–0.182	**0.995****	0.434	0.044	0.529	–0.620	0.584	**0.876****	1	
Cd	0.634	–0.184	**1.000****	0.370	0.108	0.458	–0.679	0.534	**0.894****	**0.995****	1

Notes: Significant values are in bold typeface. *. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

C_d, indicating that the index was reliable enough for assessing pollution. The data and results presented herein from the Konaro area, although obtained only during one springtime, obviously show that ophilitic rocks in the Konaro area are the geogenic source for heavy metals (Ni, Cu, Cr and Zn).

Acknowledgements

The authors wish to acknowledge the Islamic Azad University of Zahedan Branch and Sistan & Baluchestan Regional Water Authority for financial support.

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