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Hydrochemical Characteristics, Controlling Factors and Water Quality Evaluation of Groundwater Quality in Kono, Sierra Leone

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Abstract

Groundwater is a major source of drinking water and is considered an imperative component of the accessible water assets across Sierra Leone and many parts of the world. The degradation of groundwater can jeopardize drinking water availability and human health. 29 groundwater monitoring samples with 16 water quality parameters were analyzed. Descriptive statistics, Piper plots, Arc GIS spatial interpolation, Gibbs plots, ion ratio analysis, Wilcox diagram, water quality index (WQI), and entropy-weighted water quality index (EWQI) were used to investigate the hydrochemical characteristics, controlling factors and evaluate the groundwater quality in the study area. The results revealed that the groundwater mean concentration of NO_3^- in the mining concession was 34.00 mg/L which was above the permissible limit, Ca^{2+} and HCO_3^- are higher in the Koidu community compared to the mining concession water, indicating weakly alkaline with dominant anions and cations of HCO_3^- and $Na^+ + K^+$ respectively, and the hydrochemical types were mainly $HCO_3^- \cdot Ca^{2+}$ and $HCO_3^- \cdot Na^+$. The order of anion concentration in groundwater was $HCO_3^- > NO_3^- > SO_4^{2-} > Cl^-$ and $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$ in the mining concession and the Koidu community respectively. Cations were $Ca^{2+} > Na^+, K^+ > Mg^{2+} > Fe^{2+}$, and $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > Fe^{2+}$ in the mining concession and the Koidu community respectively. The interpretation of WQI and EWQI analysis exhibits 55.17% excellent, 17.24% good, 20.69% medium, 6.90% very poor, and 27.59% excellent, 24.14% good, 34.48% medium, 3.45% poor, and 10.34% very poor water respectively. Most of the sampling sites display similar trends to the WQI and EWQI. The solute source of groundwater was mainly controlled by water-rock interaction, cation exchange and the weathering of silicate and carbonate rocks were jointly the main contributors to the formation of the chemical components of groundwater in the study area, among which the main controlling factors of the groundwater were leaching, precipitate concentration and anthropogenic activities, and sulfate rock and carbonate rock dissolution. The overall water quality in the study area was suitable for human consumption but was polluted to an insignificant extent by mining activities. This study provides theoretical support and a decision-making basis for developing, utilizing, and protecting water resources in the study area.

Keywords: Diamond Mining, Controlling factors, Hydrochemical facies, Water Quality Index

Introduction

Globally, groundwater is a substantial and crucial component of the hydrological cycle that sustains communities and ecosystems (Cairano, 2020). Water is the source of life, the necessity of production, and the foundation of ecology. With the high-quality development of the socio-economy, surface water resources are far from meeting production and livelihood needs living demand (Zhang et al., 2019). And groundwater has abundant water content and good water quality (Tang et al., 2019). Making it an important source of drinking water, agricultural irrigation, and industrial water (Peng et al., 2021). In recent years, due to the unreasonable development and utilization of groundwater, a series of ecological and environmental problems such as reduced water volume and deterioration of water quality have occurred (Cui et al., 2020; Li et al., 2022). The chemical evolution characteristics of groundwater are a concentrated reflection of changes in the groundwater environment (such as deterioration of water quality), and clarifying its formation mechanism is also an important content of groundwater resource and quality evaluation (Cui et al., 2020). The formation of groundwater hydrochemistry is mainly controlled by factors such as stratigraphic lithology, geological structure, topography, and human activities (Kou et al., 2018; Li et al., 2022; Xiao et al., 2016; Zhang et al., 2017). Therefore, it is of practical significance to systematically study the spatial distribution characteristics of groundwater quality and carry out evaluation for the development and utilization of water resources and ecological environmental protection.

At present, research methods for groundwater characteristics and evaluation mainly include the hydrochemical type method, descriptive statistical method, ion proportion coefficient method, saturation index method, etc. (Tang et al., 2019), especially the emergence of classic hydrogeochemical research methods such as Gibb's plot (Gibbs, 1970; Huang et al., 2014), Piper plot (Piper, 1944), and Na terminal element diagram (Gaillardet et al., 1999).which provide convenience for qualitative analysis of groundwater components and sources (Li et al., 2022; Liu et al., 2018). In recent years, techniques such as multivariate statistical analysis (Chen et al., 2007). hydrogeochemical simulation (Pu et al., 2013; Liu et al., 2019). And 3S technology (Machiwal & Jha, 2015). Have also been widely used in the study of groundwater characteristics. In addition, water quality evaluation is also a hot topic in current groundwater research. The methods for water quality evaluation mainly include fuzzy comprehensive evaluation, fuzzy mathematics, multivariate statistical analysis, Nemero index, and water quality index (WQI), etc. (Ali et al., 2021) especially the WQI has been widely used in groundwater quality evaluation (Mthembu et al., 2022). The entropy-weighted water quality index (EWQI) is a modified version of the traditional WQI, aimed at addressing the subjective influence of human factors in the weight assignment of the WQI and improving the reliability of evaluation (Li, 2016) At present, many scholars widely use the EWQI for water quality evaluation. In many parts of the world, groundwater pollution has grown to be a serious environmental concern, regardless of whether it is caused by human activity or natural processes and whether it has numerous social repercussions (Kouassy Kalédjé et al., 2023). Heavy metal contamination of groundwater is one of the major issues facing mining communities worldwide today. Groundwater naturally contains heavy metal contaminants that may pose a health risk. These contaminants include manganese, lead, cadmium, mercury, cyanide, and arsenic (Chapagain et al., 2009; Rakotondrabe et al., 2017). Globally, mining activities have been proven to be a major cause of groundwater contamination that has been well documented (Fallahzadeh et al., 2017; Fazi et al., 2016). Water resources are crucial for human consumption, plant growth, and mine exploitation in mining areas, so their sensible development has always been a significant topic deserving of discussion (Wu et al., 2014). Additionally, water pollution and various mining activities can also influence the concentrations of major ions in surface and groundwater in and around a mine (Singh et al., 2012).

In many regions, groundwater is an essential resource that is used for industrial, agricultural, and drinking purposes. It is crucial to comprehend how diamond mining affects Koidu's groundwater quality for the sake of both the local communities whose livelihoods depend on it and the preservation of this vital resource. Kono District, eastern Sierra Leone, a predominantly diamond mining region of the Country, has one of the largest mining companies. Koidu Limited is a Kimberly diamond mining company. As required for a project of this nature, the company carried out an Environmental Impact Assessment in 2012 and was issued with an EIA License. As required by the Sierra Leone Environmental Protection Agency Act (Act and Regulations - EPA-SL) performance Standard #1 of the International Finance Corporation, Koidu Limited is required to carry out environmental compliance monitoring to monitor environmental impacts resulting from operations and monitor environmental and social performance against environmental baseline conditions, objectives, and targets (https://Koidulimited.Com/). Mining and agriculture are the two major occupations in the study area.

This research aims to evaluate and characterize the hydrochemistry of shallow groundwater for human consumption. Furthermore, the implications for the environment and human health were sought considering the effectiveness of existing mitigation measures and exploring potential improvements in mining practices to reduce their environmental footprint. Regarding groundwater research, scholars have paid more attention to the spatial distribution pattern of groundwater quality (Zhang, 2019), while there is a slight lack of research on the evolution of groundwater hydrochemical characteristics and water quality evaluation. Because of this, to protect consumer satisfaction and avoid health risks for people, groundwater quality assessments are crucial and a systematic analysis was conducted using mathematical statistics, graphical methods, and spatial distribution of parameters using geographic information systems (GIS). The hydrochemical characteristics and the evaluation groundwater quality around the mining concession and Koidu city are evaluated based on the Entropy Weighted Water Quality Index, to provide a scientific basis for the rational development, utilization, and protection of the groundwater resources in the study area.

According to (Zhang et al., 2022), industrial operations are normally the main cause of high pollution loading in the vicinity of the cities in their investigation of the risk of groundwater contamination. Water quality is given by the concentration of dissolved solids, temperature, and the absence of toxic (Saravanan et al., 2022) or biological pollutants (Tröger, 2020). In actuality, accessibility to clean and safe water is vital for human health. In this regard, the Sierra Leone National standards established for drinking water quality safeguards were used for this study.

Materials and Method

Study Area

Location and Climate

Kono District, in the Eastern Province of Sierra Leone, lies within latitude 8°37ˈ55.2" N and longitude 10°58ˈ8.4" W as shown in Figure 1. There are 14 chiefdoms in this district, two of which were covered in this study namely Tankoro and

Gbense. These chiefdoms have been predominantly diamond mining chiefdoms for over three decades attracting countless youths, engaged primarily in the artisanal small-scale mining of the highly precious diamond and gold minerals (Simbo et al., 2023). The Koidu mining concession is situated within the Tankoro Chiefdom. It is approximately 2 km south of the district capital, Koidu, and approximately 330 km east of Freetown, the capital city (https://reliefweb.int/report/sierra-leone/sierra-leone-kono-district-profile).

The climate in the region is described as wet tropical monsoon, with a single wet season each year between mid-May and mid-November. The average rainfall is approximately 2,540 mm, with the wettest month usually in August and rivers attaining maximum discharge in mid-September. This region is part of the tropical rainforest belt of Sierra Leone. The normal temperature range is 20°C to 33°C, although it can drop as low as 10°C at night during the harmattan season in January. Day temperatures average 31°C in the dry season and 28°C in the wet season (https://slmet.gov.sl/warnings-5).

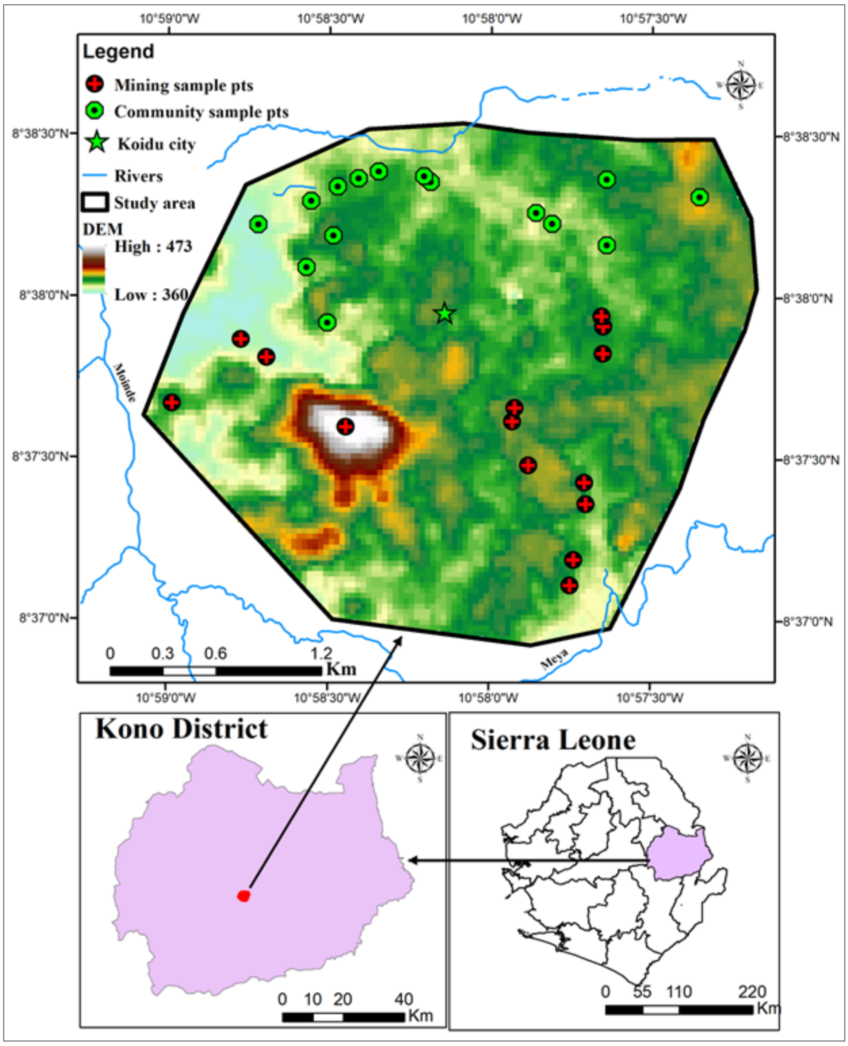


Figure 1: Map of the study area showing DEM and groundwater sampling points

Topography and Drainage (Geological settings)

Topographically, the Koidu limited diamond fields consist of the undulating coastal plains and the dissected margins of the inland plateau, which are embayed by the broad valleys of the major rivers. Approximately 0.36 km^2 of the mining lease area is occupied by Monkey Hill, which reaches a height of just over 500 m, surrounded by gently undulating topography (between 365 m and 391 m) where the kimberlites occur. Monkey Hill forms a watershed, with the northern tributaries draining into the Woyie River and those to the south joining up with the Meya River. The current mining lease area (Fig. 2) measures 4.9873 km^2 and the beacon coordinates of the concession boundary.

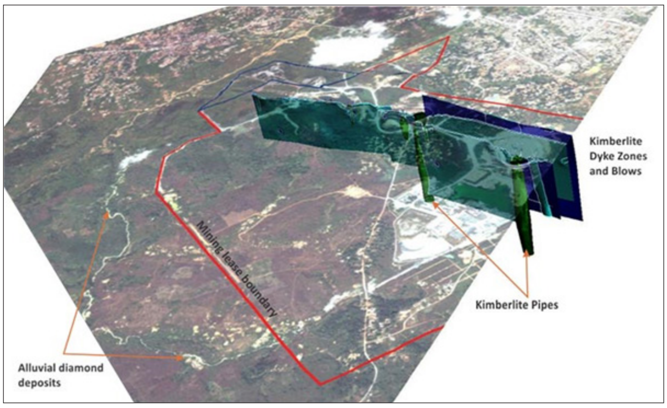


Figure 2: Geological basement of the mine concession Kimberlite dyke zone of Diamonds – Koidu Limited {Accessed January 2024 from KL website}

Sample Collection and Analysis

A total of 29 groundwater samples, including 14 from the mining concession and 15 from the Koidu community were procured from the mechanically-drilled hand-pumped, pipe-borne, and hand-dug wells with depths ranging from 28 to 90 m in June 2022 and analysed. Before sampling, each bottle was thoroughly cleaned three times using the groundwater that was to be collected. Groundwater was analysed in a specialized laboratory for physical and chemical parameters (NUQC Laboratory-Sierra Leone). A stringent quality control system was incorporated according to standard procedures of the American Public Health Association (APHA et al., 2017) and the national standards were in place at the testing facility. Subsequently, the following parameters were measured in-lab: chemical oxygen demand (COD), total hardness (TH), total dissolved solids (TDS), total alkalinity (TA), major ions (Ca^{2+} Na^+ Fe^{2+} Mg^{2+} K^+ NO_3^- SO_4^{2-} HCO_3^- Cl^-) except for pH, electrical conductivity (EC), and turbidity (NTU) which were done in-situ.

Using portable, multiparameter instruments, the temperature and pH of the water were measured on-site (Hanna HI9811-5). Samples were collected, sealed, and kept at 20°C until analysis. Using flame atomic absorption spectrophotometry, Na^+, Fe^{2+}, and K^+ were found. HCO_3^- and CO_3^{2-} were measured using a conventional titrimetric technique. We used EDTA titrimetric techniques to analyse Ca^{2+}, Mg^{2+}, and TH. A spectrophotometer (ICS-1500) was used to analyse NO_3^- and SO_4^{2-}. The titration method was utilized to ascertain the Cl^- concentration using a standard solution of $AgNO_3$. Using a drying and weighting method, TDS was determined. The COD was examined using the dichromate method. ArcGIS 10.7.1, and MATLAB 2023b software were employed to create spatial maps, and Piper, Gibbs, and box plots of water quality parameters to visualize the distribution patterns. Data were compared to the National water quality standards of Sierra Leone, 2014.

Correlation Analysis

The physicochemical indices of the water were correlated by calculating the Pearson correlation coefficient (r). The formula is expressed as:

$$r = \frac{\sum_i^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i^n (x_i - \bar{x})^2}\sqrt{\sum_i^n (y_i - \bar{y})^2}} \qquad (1)$$

where r is the correlation coefficient between two variables (x and y), $\bar{x}$ and $\bar{y}$ are the means of the variables. Before determining the correlation of x and y, the value of r should pass the significance test.

Groundwater Quality Index Analysis

The groundwater water index was carried out to determine the groundwater quality for drinking and domestic purposes. The entropy-based water quality index, as regarded one of the most acceptable methods (Zhang et al., 2007) and the weighted arithmetic mean water quality index followed for the evaluation of analytical data for meeting criteria for drinking purposes (Krishna & Achari, 2023). The WQI is a dimensionless scale that communicates information on water quality in an enormously easier, lucid, and consistent form (Adak et al., 2001; Gupta et al., 2003; Masood et al., 2022). For this study, the weighted arithmetic index approach has been adopted to perform the quantitative assessments of water quality. 16 key water quality parameters were computed (pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, NO_3^-, SO_4^{2-}, EC, NTU, TH, Cl^-, TDS, HCO_3^-, COD and $CaCO_3^-$). The generic equation for computing WQI as described below:

$$WQI = \sum_{i=1}^{n} w_i q_i \qquad (2)$$

where,

WQI represents a numeric value between 0 and 100; q_i is the water quality score of the i^{th} water quality parameter, w_i is the unit weight of the ith water quality parameter, n represents parameter count. The quality score q_i is computed using the following relation:

$$q_i = \left[(v_i - v_o) / (v_s - v_o) \right] \qquad (3)$$

where, v_i and vo are the true and the ideal values of the i^{th} parameter, mostly v_o=0, but for certain parameters like pH (v_o= 7) and DO (v_o=14.6 mg/L). vs denotes the standard permissible value for the ith parameter. The unit weight wi is worked out with the equation:

$$w_i = \frac{k}{v_s} \qquad (4)$$

Which is

$$k = \frac{1}{\frac{1}{s_1} + \frac{1}{s_2} + \frac{1}{s_3} \ldots + \frac{1}{s_n}} = \frac{1}{\sum_{n=1}^{n} \frac{1}{s_n}} \qquad (5)$$

where, k represents the proportionality constant; S_n = Standard desirable value of the nth parameters; on summation of all selected parameters unit weight factors, W_n = 1

Entropy based water quality index

Shannon originally introduced the idea of entropy in 1948 to describe the degree of uncertainty surrounding a random event or the information content of a parameter (Shyu et al., 2011; Alfaleh et al., 2023). The uncertainty of anticipated data from a likely event is indicated by the Shannon entropy. In terms of mathematics, the probability of an event and the data values are inversely related. An event's probability will be high and its Shannon entropy will be low if it is accurately predicted. Consequently, the two components of information gained are explained by information and uncertainty, which are indirectly calculated by lowering the degree of uncertainty (Crutchik et al., 2020). The theory of entropy is now used in many disciplines, including ecology, hydrology, and water quality (Alfaleh et al., 2023).

In order to calculate EWQI, the following procedure based on Shannon information entropy has been adopted (Amiri et al., 2014; Egbueri et al., 2020; Masood et al., 2022). In the initial stage, the entropy weight of each parameter is computed through the following steps: Let the number of water samples be "*s*" (*i*= 1,2,3,4…*s*) and the number of hydrochemical variables be "*p*" (*j*=1, 2, 3, 4…, *p*). Subsequently, the Eigen value matrix *X* can be generated using Eq. 6:

$$X = \begin{Bmatrix} x_{11} & x_{12} & \cdots & x_{1p} \\ x_{21} & x_{22} & \cdots & x_{2p} \\ \vdots & \vdots & \vdots & \vdots \\ x_{S1} & x_{S2} & \cdots & x_{SP} \end{Bmatrix} \quad (6)$$

A normalized matrix, *Y*, is created by applying a normalizing function to Eigen value matrix, *X*, in order to eliminate the impact of various units and dimensions of water quality variables. The normalized matrix *Y* is developed as shown below:

$$Y = \begin{Bmatrix} y_{11} & y_{12} & \cdots & y_{1p} \\ y_{21} & y_{22} & \cdots & y_{2p} \\ \vdots & \vdots & \vdots & \vdots \\ y_{S1} & y_{S2} & \cdots & y_{SP} \end{Bmatrix} \quad (7)$$

The index's effectiveness of risk for parameter *j* in the sample number i is determined using Eq. 8:

$$P_{ij} = \frac{y_{ij}}{\sum_{i=1}^{s} y_{ij}} \quad (8)$$

The expression used for estimating information entropy (ej) is as follows:

$$e_j = -\frac{1}{\ln s}\sum_{i=1}^{s} p_{ij} \ln P_{ij} \quad (9)$$

An inferior value of entropy signifies a greater impact of *j* index. The entropy weight (*wj*) for the variable j is computed using Eq. 10.

$$w_j = \frac{1-e_j}{\sum_{j=1}^{P}(1-e_j)} \quad (10)$$

In the next phase, the qualitative ranking criteria (Q_j) is determined for every variable using the following equation (Eq. 11):

$$Q_j = \frac{C_j}{S_j} \times 100 \quad (11)$$

Cj is the concentration of jth parameter in mg/L, and Sj is the Sierra Leone standards for groundwater quality in mg/L.

The final phase involves computation of EWQI and is given by the following relation:

$$EWQI = \sum_{j=1}^{n} w_j Q_j \quad (12)$$

Based on EWQI, the groundwater quality is characterized into five classes as shown in Table 2.

Results and Discussion:

Hydrochemical Characteristics and Distribution Patterns

The hydrochemical characteristics of groundwater are highly intricate and contingent upon numerous factors, including but not limited to rock weathering, cation exchange, recharge water quality, river water leakage, evaporation, and human influences (Li et al., 2018; Ren et al., 2021). Table 1 lists the statistical characteristics of the groundwater hydrochemical data needed to interpret the hydrochemistry of the groundwater in the study area. The groundwater in the study area is weakly alkaline with only one (B_3) above the permissible limit Low hardness. The descriptive statistics of the data for all the 16 physicochemical parameters considered for the groundwater samples and their corresponding permissible limits have been shown in Table 1 and Figure 3.

The pH value of the groundwater ranges from 5.2 to 6.8 and 6.0 to 6.8 for the mining concession water and the Koidu limited respectively with an average value of 6.33 signifying slightly acidic groundwater in nature. In the majority of the sites, the pH was within the permissible limit for drinking as specified by the National standard (6.5–8.5) apart from the sites A_2, A_3, A_4, A_5, A_6, A_8, B_1, B_2, B_8, and B_15 which were below the permissible limit. The concentrations of TDS and TH range from 17.0 to 317/ mg/L and 5 to 175.00 mg/L, respectively. As shown in Table 1, the concentration of Na^{+} ranges from 2.40 to 14.00 mg/L with a mean of 8.50 mg/L in the mining concession water, whereas that in the Koidu community water varies from 1.80 to 61.80 mg/L with a mean of 21.95 mg/L. The concentration of Mg^{2+} ranges from 2.00 to 9.00 mg/L in the mining concession water, but in the Koidu community water, it varies from 2.00 to 6.00 mg/L. The concentration of Fe^{2+} ranges from 0.01 to 1.00 mg/L in both the mining concession water and the Koidu community water, with sites A_3, A_4, A_8, A_11, B_9, and B_10 above the permissible level. The other ions (K^+, NO3−, SO42−, Cl^-, $CaCO_3^-$, and NTU) have similar trends in that the concentrations in the mining concession water are higher than those in the Koidu community water. The cause of this phenomenon is that the mining concession water is more susceptible to pollution compared with the Koidu community water. Particularly, the mean concentration of NO_3^- in the mining concession water is 34.00 mg/L which is above the permissible limit, Ca^{2+} and HCO_3^- are higher in the Koidu community water as compared to the mining concession water, indicating the presence of alkaline. However, there is an opposite finding for the concentration of COD. Groundwater with high COD levels is concentrated in the urban land and other construction land (Ren et al., 2021). It can be inferred that domestic and industrial sewage lead to a high concentration of COD.

The electrical conductivity (EC) in the study region exhibits large variations, and its value ranges from 34.60 to 634.00 µs/cm with an increase in the mining concession for most sites. Elevated levels of EC in groundwater may be a sign of water circulation, surface infiltration, and cation exchanges. Based on electrical conductance, groundwater could be ranked into four classes; low conductivity class (EC3000 µs/cm) (Sarma & Swamy, 1981). Based on this categorization of EC, only A_5, A_6, A_7, A_8, and A_12 sites were within the permissible levels of the mining concession water, and sites B_3, B_4, B_5, B_10, and B_11 were above the permissible limited.

The fluctuation amplitude of groundwater hydrochemical concentration is significant in different hydrogeological zones (Peng et al., 2021; Liu et al., 2023). The order of anion concentration in groundwater in the mining concession is: $HCO_3^- > NO_3^- > SO_4^{2-} > Cl^-$, while in the Koidu community is: $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$. The relationship between the concentration of groundwater cations in the mining concession is as follows: $Ca^{2+} > Na^+, K^+ > Mg^{2+} > Fe^{2+}$, while in the Koidu community, it is as follows: $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > Fe^{2+}$. In almost all water samples, HCO3− and Ca2+ were the dominant ions in the study area. Generally, ion concentration showed a horizontal change with increased Ca2+ and a decrease in Na+ with depth, where HCO_3^- and SO_4^{2-} decrease overall. To examine the predominant hydrochemical facies in the water samples, a piper trilinear diagram was also drawn (Figure 5).

Table 1: Statistical analysis of groundwater quality parameters and its coherence with the Sierra Leone National standards (Mine concession and Koidu Community *n=29*)

Parameters	Mining Concession water				Koidu Community water				SLS 43:2014 Standard
	Min	Max	Mean	Std Dev	Min	Max	Mean	Std Dev	
Ca^{2+}	2.00	53.00	19.50	16.92	2.00	85.00	17.80	24.28	100
Na^+	2.40	14.00	8.50	4.32	1.80	61.80	21.95	19.89	90
Fe^{2+}	0.02	1.00	0.28	0.26	0.05	1.00	0.18	0.26	0.3
Mg^{2+}	2.00	9.00	3.57	2.28	2.00	6.00	2.80	1.26	NA
K^+	1.10	14.00	5.84	4.91	1.10	4.10	1.77	0.74	NA
NO_3^-	5.30	34.00	21.16	7.72	0.44	25.00	5.52	8.02	10
SO_4^{2-}	5.00	30.00	8.64	9.05	5.00	30.00	7.13	6.47	250
pH	5.20	6.80	6.17	0.52	6.00	6.80	6.49	0.29	6.5 - 8.5
EC	34.60	634.00	315.46	198.70	14.89	418.00	168.03	134.64	250
NTU	0.10	84.70	7.17	22.34	0.10	84.70	6.34	21.68	75
TH	5.00	175.00	70.00	59.23	5.00	175.00	69.67	59.84	500
Cl^-	0.40	7.60	2.07	2.71	0.40	0.60	0.43	0.07	250
TDS	17.10	317.00	146.73	100.96	7.44	317.00	110.84	86.64	2500
HCO_3^-	15.00	190.00	58.93	50.69	25.00	285.00	104.33	92.93	250
$CaCO_3^-$	5.00	140.00	43.57	45.25	10.00	140.00	50.33	41.81	250
COD	18.00	150.00	58.00	34.39	10.00	95.00	58.00	23.15	NA

All the units of parameters presented are in mg/L, except for pH and EC (µs/cm); Max represents the maximum value, Min represents the minimum value, and Std Dev represents the standard deviation

Water Quality Assessment – Methods

Groundwater hydrochemical characteristics are very complex and depend on multiple factors, such as weathering of rocks, cation exchange, recharge water quality, river water leakage, evaporation, and anthropogenic factors (Li et al., 2018; Ren et al., 2021). To interpret the hydrochemistry of the groundwater in the study area, the characterization of groundwater quality based on EWQI and WQI as listed in Table 2. Generally, the study area exhibits 55.17% excellent, 17.24% good, 20.69% medium, and 6.90% very poor for the WQI and 27.59% excellent, 24.14% good, 34.48% medium, 3.45% poor, and 10.34% very poor.

Table 2: Quality characterization of groundwater based on WQI and EWQI

EWQI range	WQI range	Rank	Water quality category	EWQI (% of samples)	WQI (% of samples)	Remarks
EWQI <25	WQI <50	1	Excellent	27.59%	55.17%	Beneficial for health and well-being
25 ≤ EWQI < 50	50≤ WQI < 100	2	Good	24.14%	17.24%	Acceptable for potable use
50 ≤ EWQI < 100	100 ≤ WQI < 150	3	Medium	34.48%	20.69%	Impure and quality unacceptable
100 ≤ EWQI < 150	150 ≤ WQI < 200	4	poor	3.45%	0.00%	Treatment before use
EWQI ≥ 150	WQI ≥ 200	5	very poor	10.34%	6.90%	It needs too much attention

The computed results of both EWQI and WQI methods in both the mining concession and Koidu Community portray higher excellent values in both methods in the Koidu community as compared to the mining concession in the classified spatial analysis (Figure 3). Generally, the majority of the sampling sites display similar trends to the groundwater samples (Figure 4).

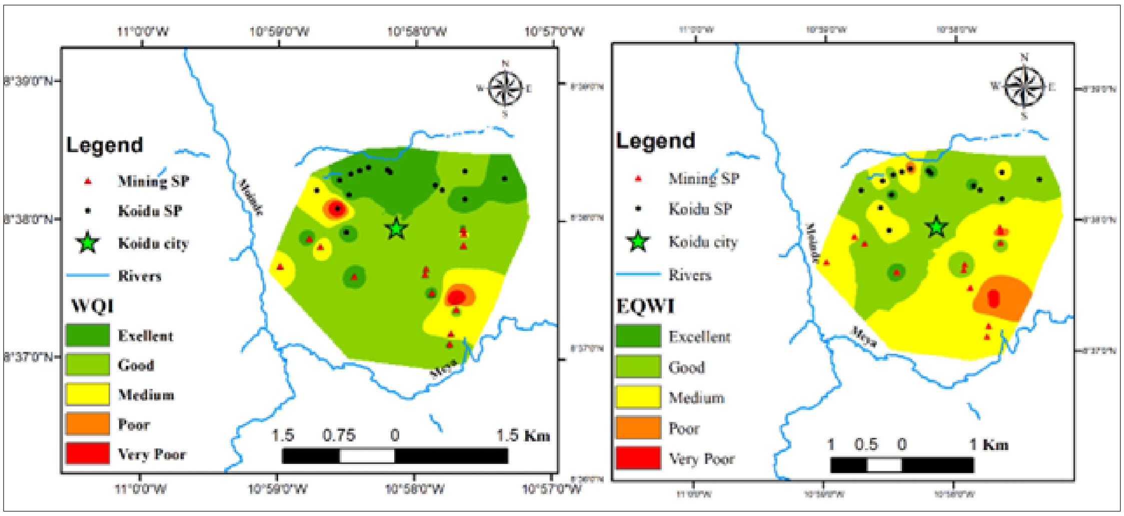


Figure 3: Classified spatial distribution maps based on IDW for WQI and EWQI of the study area

As shown in Figure 4 and Table 2, based on the WQI category groundwater samples belonging to A_1, A_5, A_10, A_12, A_13, B_1, B_2, B_3, B_4, B_5, B_6, B_7, B_11, B_12, B_14, and B_15 sites had "excellent" water quality; A_2, A_6, A_14, B_8, and B_13 showed "good water" quality; A_3, A_7, A_8, A_9, A_11, and B_9 indicated "medium water" quality; and unfortunately, A_4 and B_10 showed "very poor water" quality and none of the samples represented the "poor water" category.

Similarly, the EWQI-based category of groundwater samples belonging to sites A_5, A_6, A_7, A_8, A_12, A_14, B_1, B_2, B_6, B_7, B_8, B_9, B_12, B_14 and B_15 had shown "excellent" water quality; A_1, A_9, A_10, A_11, A_13, B_4, B_5, B_10, B_11 and B_13 showed "good water" quality; B_3 indicated "medium water" quality; and A_2, A_3, and A_4 sites indicated "poor" water quality and none for "very poor water" quality.

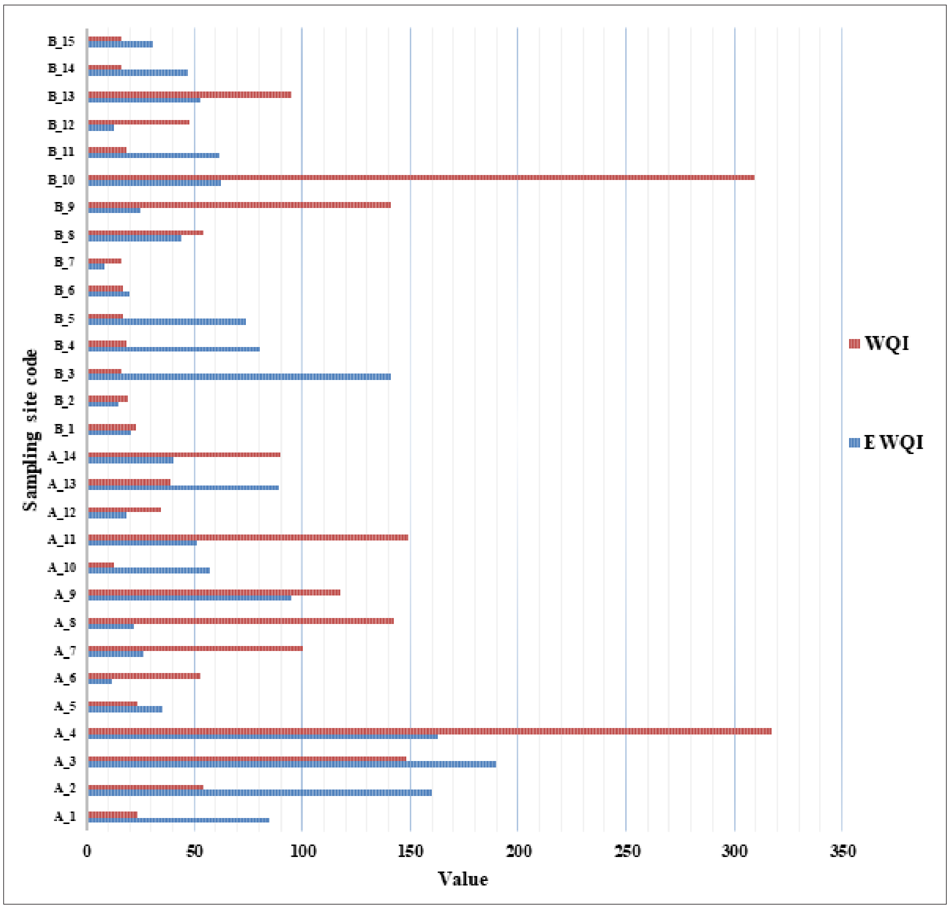


Figure 4: Comparison of WQI and EWQI based on groundwater quality of the different sites

Piper Plot

A Piper diagram (Piper, 1944) was used to study the hydrochemical types of groundwater. Based on the Piper three-line diagram, the types and evolutionary characteristics of shallow groundwater hydrochemistry can be intuitively reflected (Liu et al., 2023). As shown in Figure 5, most of the Mining concession and Koidu community water samples are classified as, HCO_3^-– Na^+ or HCO_3^-– Ca. $Na^+ + K^+$ and Ca^{2+} types and several water samplings can be classified as HCO_3^-. Na^+–Ca^{2+} types. The anions were plotted mainly in zones E (bicarbonate type) and F (Sulphate type). The cations, however, fall into zones A (Calcium type), B (No dominant type), and D (Sodium type). It suggests that carbonate hardness exceeding 50% with alkaline earth and weak acids predominated in the mine concession and hardness exceeding 50% and mixed type predominant in the Koidu community. The high sodium and calcium concentrations may come from cation exchange and water percolation which introduces sodium from the vadose zone into groundwater. Cations are mainly distributed at the Ca^{2+} terminal, while there is a small amount of distribution at the $Na^+ + K^+$ terminal. The dominant anion is HCO_3^-, followed by SO_4^{2-}, indicating that the hydrochemical formation of shallow groundwater around the study area is mainly controlled by the dissolution of carbonate rocks (Ren et al., 2021). The Piper diagram observation suggests that rock weathering and the water-rock interaction may control groundwater chemistry.

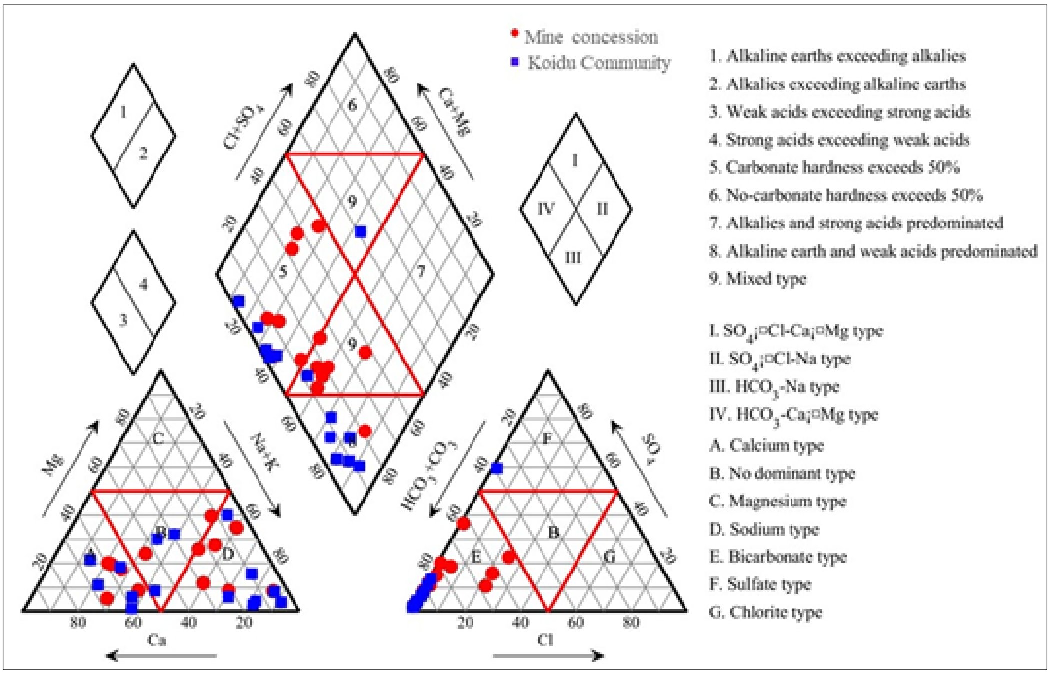


Figure 5: Piper diagram showing the hydrochemical characteristics of the Mine concession and the Koidu Community

Mechanism of Water-rock Interaction (Gibbs Plot)

The Gibbs diagrams are a commonly utilized instrument for comprehending the natural formation mechanism of groundwater. It identifies three mechanisms: rock dominance, precipitation dominance, and evaporation dominance (Gibbs, 1970). Figure 6 shows that most of the water samples are plotted in the middle section of the diagrams. This observation suggests that rock weathering is the most significant natural mechanism governing the groundwater evolution in the study area. Through water-rock interactions, minerals and salts like calcite, dolomite, and halite dissolve and find their way into the groundwater (Ren et al., 2021).

Additionally, it demonstrates that the mining concession water has a higher rock dominance tendency than the Koidu community water. This indicates that, in comparison to deeper subsurface water sources to a shallow one. Consequently, it is clear that significant rock weathering and modest evaporation jointly affect the geochemistry of mining concession water in the study area. Nevertheless, only the natural process can be analysed using the Piper and Gibbs diagrams. Other methods should be used to assess the anthropogenic processes to conduct additional research.

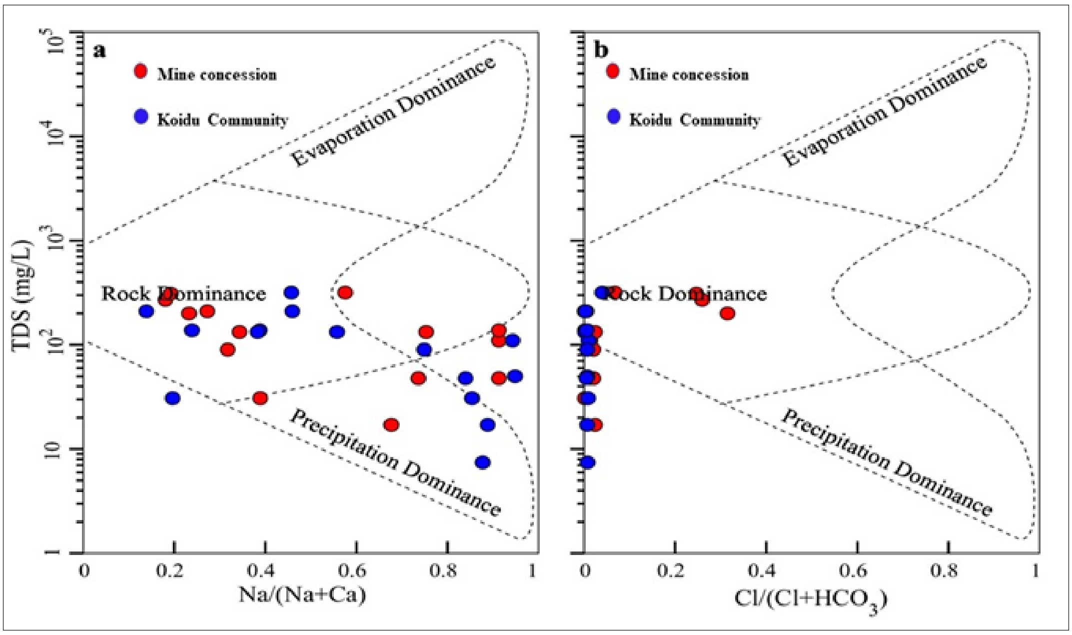


Figure 6: Gibbs plots for Mining concession and Koidu community of the study area.

The water-rock interaction between groundwater and surrounding media leads to changes in the chemical composition of groundwater (Marandi & Shand, 2018). And the water-rock interaction can reveal the mechanism of hydrochemical evolution (Wei et al., 2020; Qu et al., 2022). From Gibbs plots (Figure 6), it can be concluded that the cation Na^+ / Na^{++} Ca^{2+}) ranges from 0.1 to 0.98, and the anion Cl^- / $Cl^- + HCO_3^-$) ranges from 0.0 to 0.38. Most of the groundwater sample points point towards the end element of water-rock interaction (rock weathering control area), indicating that the hydrogeochemical process and hydrochemical characteristics of groundwater in the study area are mainly controlled by water-rock interaction (Liu et al., 2018; Marandi and Shand, 2018). A small number of samples fall in the precipitation dominance area, indicating that some groundwater in this area is also affected by precipitation concentration, but the influence is far less than that of water-rock interaction. The distribution of sample points is far from the rainfall control endpoint, indicating that atmospheric precipitation has a relatively small contribution to the main ion source of groundwater in the study area (Zhang et al., 2017).

The Wilcox diagram (Figure 7) indicated that all samples fell within the "excellent to permissible" zones. It also showed that 100% of samples within the Mining concession and Koidu Community were of healthier quality for consumption.

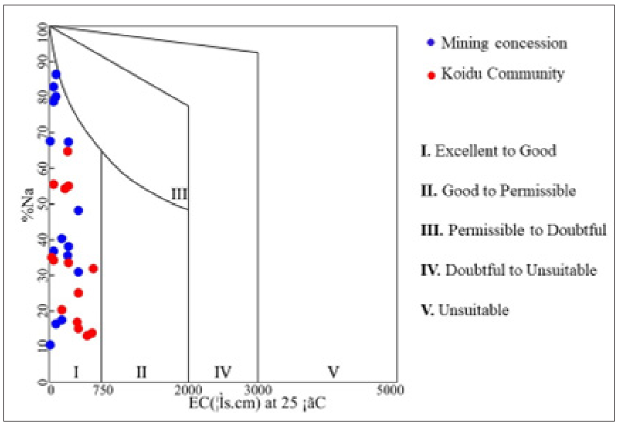


Figure 7: Water quality of samples as visualized in the Wilcox diagram

Factors Affecting Water Quality

Groundwater hydrochemical characteristics are very complex and depend on multiple factors, such as weathering of rocks, cation exchange, recharge water quality, river water leakage, evaporation, and anthropogenic factors (Li et al., 2018; Ren et al., 2021). Human activities such as mining and agriculture are the major causes of the evolution of groundwater hydrochemistry (Liu et al., 2023). Protecting groundwater quality and managing groundwater resources are just two of the many reasons why it's critical to have a thorough understanding of the primary variables influencing groundwater chemistry (Li et al., 2014). Composition diagram (rock weathering) and correlation analysis correlation analysis were performed (Figure 6 and Tables 3 & 4).

Correlation Analysis

The Pearson correlation coefficient (r) was used to represent the influence of different water quality parameters (Zhang et al., 2022; Qu et al., 2023). It can determine whether the ions in the hydrochemical components are from the same source (Liu et al., 2023), thus was carried out to explore the correlation between each pair of physicochemical indices. The major axis direction of the matrix represents blue and red as strongly/ moderately positive and negative correlation coefficients respectively. 29 samples with 16 physicochemical indices were used in the correlation analysis, resulting in a correlation coefficient matrix. Generally, strong and weak correlation values are used to infer the relationships of the chemical parameters. These values lie in the range between $r > 0.7$ and $r < 0.5$, respectively, while moderate correlations (r) values lie between 0.5 and 0.7. There is a significant positive correlation ($r > 0.6$, $P < 0.01$, in both the mining concession and the Koidu community but more so in the mining concession as shown in Tables 3 and 4.

In the mining concession, there is a strong correlation between TDS and K^+ (0.66), EC (0.95), Mg^{2+} (0.78), Cl^- (0.86), and TH (0.68) indicating that the above ions have a significant contribution to TDS, this indicates that these ions contributed to TDS. There is also a significant positive correlation between SO_4^{2-} and Na^+(0.54), Fe^{2+}(0.73); HCO_3^- and Fe_2^+(0.73), NTU (0.54) in the groundwater of the study area, indicating the dissolution of carbonates and iron in the groundwater ; (Luo et al., 2014; Liu et al., 2023). A noted weak correlation between Na^+ and Cl^- ($r = 0.35$) suggests low salinity groundwaters or silicate mineral dissolution other than halite as its origin (Okofo et al., 2021).

The strongly positive correlation between EC and TDS (0.95) also suggests that the concentration of dissolved solids in water directly contributes to its EC. When the TDS level increases, it leads to a corresponding increase in the EC of the water (Alfaleh et al., 2023). Therefore, changes in TDS levels can be reliably estimated or inferred by measuring EC. COD shows moderate correlations with various parameters (K^+, NTU, TDS, and Cl^-) suggesting potential associations.

Table 3: Correlation matrix of major ions of groundwater samples in the Mining concession

	Ca2+	Na+	Fe2+	Mg2+	K+	NO3-	SO42-	pH	EC	NTU	TH	Cl-	TDS	HCO3-	CaCO3-	COD
Ca2+	1															
Na+	0.25	1														
Fe2+	-0.29	0.34	1													
Mg2+	0.39	0.46	0.27	1												
K+	0.37	0.20	0.25	0.52	1											
NO3-	0.30	0.21	-0.26	0.45	0.16	1										
SO42-	-0.32	0.54	0.73	0.09	0.19	-0.23	1									
pH	-0.51	-0.05	-0.35	-0.53	-0.42	-0.03	0.02	1								
EC	0.21	0.31	0.42	0.70	0.71	0.37	0.30	-0.18	1							
NTU	-0.18	0.34	0.79	0.29	0.47	-0.01	0.67	-0.33	0.45	1						
TH	0.06	0.49	0.47	0.37	0.04	0.31	0.45	0.12	0.66	0.33	1					
Cl-	0.32	0.35	0.44	0.92	0.66	0.34	0.24	-0.58	0.81	0.46	0.41	1				
TDS	0.31	0.48	0.45	0.78	0.66	0.40	0.34	-0.28	0.95	0.47	0.68	0.86	1			
HCO3-	-0.33	0.17	0.75	-0.05	-0.05	-0.53	0.42	-0.19	0.00	0.54	0.13	0.07	0.03	1		
CaCO3-	-0.21	0.66	0.25	0.18	-0.19	0.08	0.50	0.19	-0.02	0.38	0.31	-0.02	0.08	0.20	1	
COD	0.19	0.26	0.42	0.4	0.71	0.23	0.33	-0.47	0.45	0.77	0.03	0.55	0.51	0.24	0.03	1

In the Koidu community, the Pearson correlation coefficient (Table 4) relatively has limited strong positive correlation as compared to the mining concession. A moderate correlation of SO_4^{2-} were observed with Cl^- (0.60), NO_3^- (0.66), and TDS (0.68); TH and EC (0.67), Mg^{2+}(0.51); $CaCO_3$ and pH (0.54), EC (0.71), HCO_3^- (0.58), and TH (0.51). In the case of SO_4^{2-} and Cl^- (r = 0.60) moderate correlation in the Koidu community was caused by the dissolution of SO_4^{2-}, sulphate-bearing minerals, and the use of chemical fertilizer in agricultural fields (Samal et al., 2023; Kumari & Rai, 2020). The TDS in groundwater are mainly controlled by TH, Cl^-, HCO_3^-, SO_4^{2-}, and Ca_2^+. However, there were no obvious correlations between Mg_2^+ and HCO_3^-, and between Ca_2^+ and SO_4^{2-}, indicating that some chemical reactions might take place. For example, cation exchange, precipitation, and crystallization can disturb the ion contents (Li et al., 2019), which causes a weak correlation between TDS and Mg^{2+} as well as HCO_3^- for the Koidu community.

It can be concluded that anthropogenic activities, rock water interaction/weathering, ion exchange, evaporation, and human interventions are the main factors affecting the distribution of water quality in the city(Wagh et al., 2019; Hinge et al., 2022).

Table 4: Correlation matrix of major ions of groundwater samples in the Koidu community

	Ca2+	Na+	Fe2+	Mg2+	K+	NO3-	SO42-	pH	EC	NTU	TH	Cl-	TDS	HCO3-	CaCO3-	COD
Ca2+	1															
Na+	0.58	1														
Fe2+	-0.12	-0.31	1													
Mg2+	0.01	-0.24	0.28	1												
K+	-0.16	0.41	-0.08	-0.28	1											
NO3-	-0.13	0.10	-0.12	-0.24	0.45	1										
SO42-	-0.06	-0.16	-0.05	-0.05	-0.31	0.66	1									
pH	0.30	-0.03	0.10	-0.12	-0.20	-0.61	-0.54	1								
EC	0.19	0.05	0.29	0.19	-0.20	-0.17	0.00	0.40	1							
NTU	-0.13	-0.02	-0.14	-0.18	0.05	-0.03	-0.10	0.30	0.22	1						
TH	0.36	-0.08	0.34	0.51	-0.46	-0.12	0.15	0.18	0.67	-0.25	1					
Cl-	-0.17	-0.42	-0.07	-0.16	-0.24	0.35	0.60	-0.18	-0.08	-0.14	0.05	1				
TDS	0.21	-0.21	-0.16	0.22	-0.42	0.39	0.68	-0.16	0.17	-0.07	0.44	0.64	1			
HCO3-	0.36	-0.04	-0.16	0.33	-0.18	-0.30	-0.25	0.41	0.32	-0.16	0.37	0.18	0.47	1		
CaCO3-	0.31	0.12	-0.33	0.10	-0.24	-0.29	-0.17	0.54	0.71	0.36	0.51	0.01	0.29	0.58	1	
COD	-0.22	0.09	-0.01	-0.08	0.18	-0.18	-0.19	0.22	0.29	0.22	0.04	0.27	-0.19	0.00	0.36	1

The chemical composition of groundwater is formed by the water-rock interaction between groundwater and surrounding rocks in the study area. Therefore, the sources of ions in shallow groundwater and their interactions with hydrogeochemical processes can be roughly identified through the relationships between different ions (Zou et al., 2022; Wei et al., 2019).

The majority of groundwater samples in the study area are located above N (Na^++K^+)/N (Cl^-) [Figure 8 (a)], indicating that the hydrochemical components of groundwater are not only dissolved by rock salt but also by other sodium salts. The Na^++K^+ in groundwater deviates significantly from the 1:1 line, which may be affected by cation exchange, resulting in a concentration of Na^++K^+ greater than Cl^-.

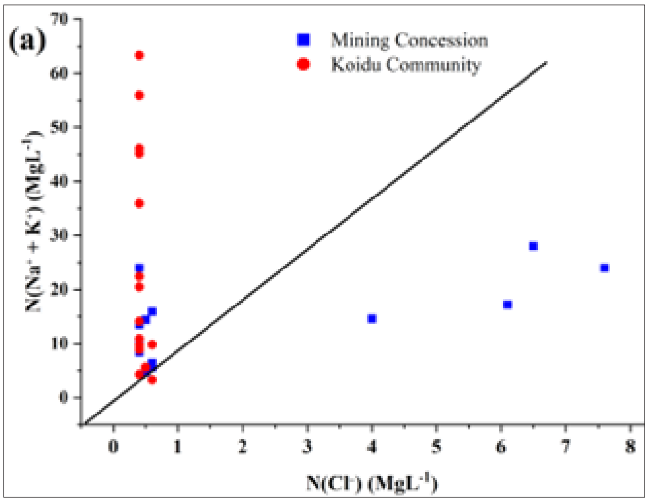
Most groundwater samples in the study area fall above the N (Na^+)/N (HCO_3^-) relationship, as shown in [Figure 8(b)]. This suggests that it is difficult for the Na+ produced by the dissolution of shallow groundwater minerals in the study area to balance the HCO_3^- content, suggesting that excess Na^+ is produced by the dissolution of sodium elements.

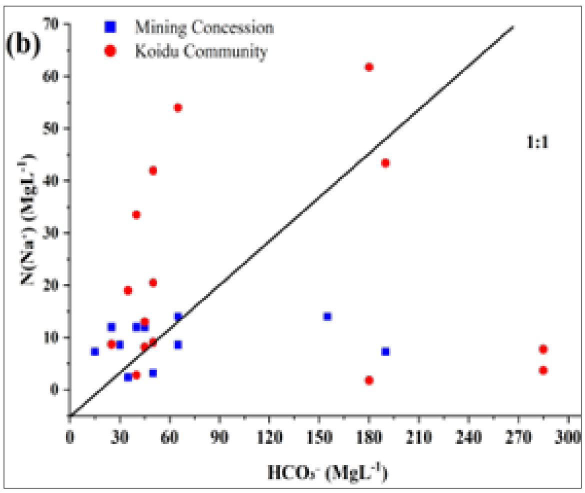
The value of N (Na^+)/N (SO_4^{2-}) can reflect whether the groundwater components are derived from the weathering process of mirabilite (Liu et al., 2015). Most groundwater samples in the study area have a ratio of Na^+ to SO_4^{2-} that is greater than or nearly equal to 1 [Figure 8(c)], suggesting that the primary source of both SO_4^{2-} and Na^+ may be nitrate weathering. In addition to nitrate weathering, cation exchange leads to an increase in Na+ (Zou et al., 2022).

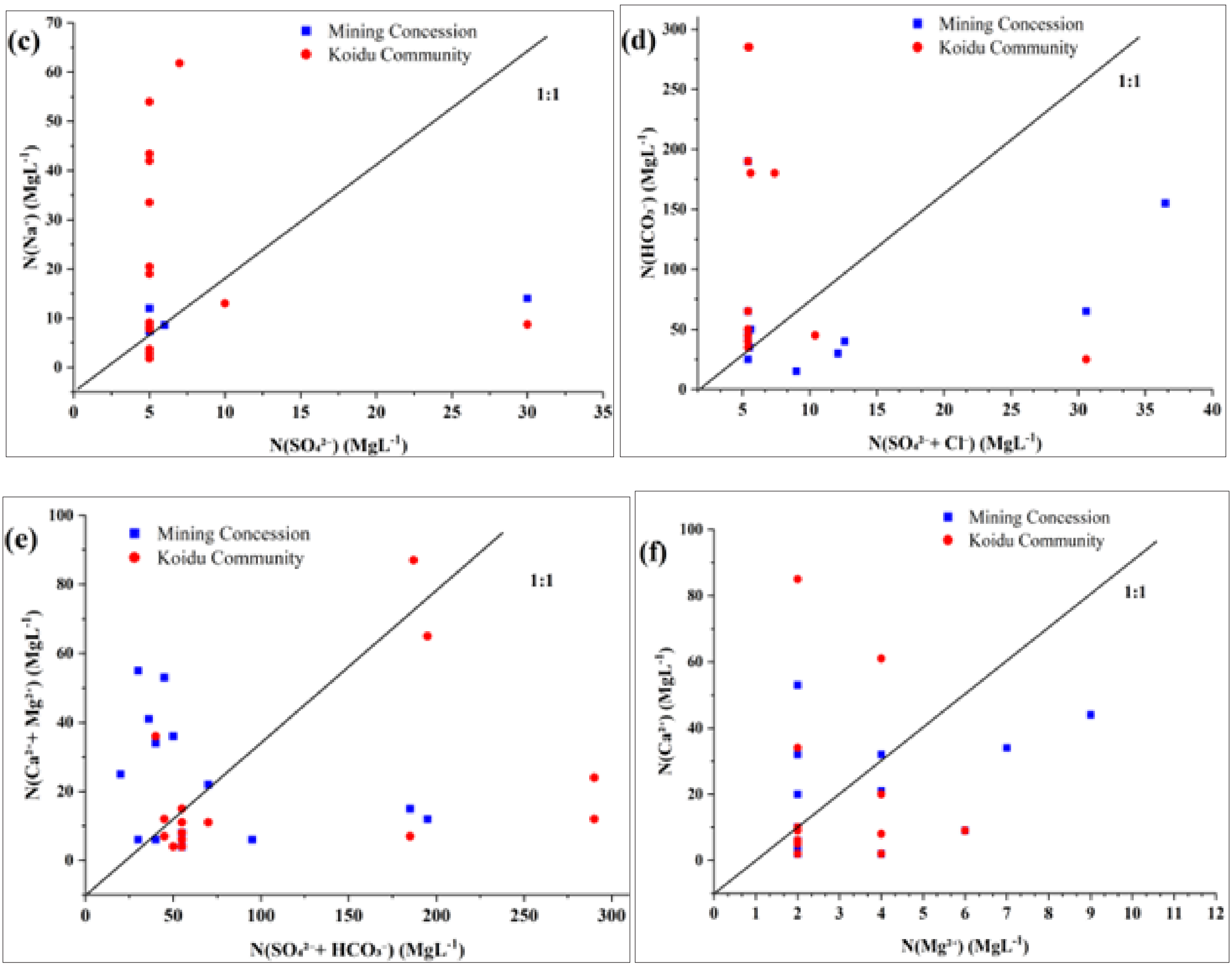
The contribution of the weathering and dissolution of evaporite and carbonate to groundwater ions can be judged based on the N(Cl^-+SO_4^{2-})/N(HCO_3^-) relationship (Zou et al., 2022; Wei et al., 2019). Most of the groundwater sample points in the study area fall above the straight line of N(Cl^-+SO_4^{2-})/N(HCO_3^-). This shows that the source of groundwater ion chemical components in the study area is controlled by the dissolution of carbonate rocks. Since pyrite minerals are commonly found in mountain strata in mining concession, the components of some water sample points are affected by the dissolution of pyrite [Figure 8(d)].

The N(Ca^{2+}+Mg^{2+})/N(HCO_3^-+SO_4^{2-}) value relationship can reveal whether ions in groundwater are controlled by the equilibrium between evaporite (gypsum) and carbonate rock (Ma et al., 2018). The groundwater in the study area has a linear relationship, and most sample points are distributed on both sides of the 1:1 equivalent line, indicating that the shallow groundwater water-rock interaction in the study area is complex. Most of the groundwater samples fall near the straight line of N(Ca^{2+}+Mg^{2+})/N(HCO_3^-+SO_4^{2-}), indicating that the groundwater studied is mainly controlled by the dissolution of carbonate rocks (calcite, dolomite) and evaporite minerals. Some shallow groundwater samples are located below and above the 1:1 equivalent line and far away from this line [Figure 8(e)]. It shows that the Ca^{2+} and Mg^{2+} contents in shallow groundwater in the study area are much fewer than HCO_3^- and SO_4^{2-}, and the missing part requires more Na^+ and K^+ to maintain the ion balance in the solute (Zheng et al., 2021).

N(Ca^{2+})/N(Mg^{2+}) can be used to determine whether the weathering and dissolution of carbonate minerals is controlled by dolomite or calcite (Guo et al., 2020). The N(Ca^{2+})/N(Mg^{2+}) value of groundwater in the study area is greater than 1 [Figure 8(f)], indicating that the carbonate rocks are dominated by calcite dissolution.







Figures 8: a-f Relationship between major ions of groundwater in the study area

Groundwater Quality Management

The increased awareness of the need to protect water quality has led to a global surge in research on hydrochemistry and water quality. Groundwater is the main source of drinking water in the study area. Mayer River, the biggest river running through the study area, has close contact with local groundwater. However, wastewater produced by upstream industry and downstream domestic sewage have polluted the river. This will further affect the groundwater quality through river water percolation. The local municipality authorities should prevent the river water from further pollution and enhance the treatment of industrial wastewater and domestic sewage. In addition, the rural toilet should be reformed to prevent the groundwater from the pollution of bacteria, nitrate, and sulphate. Perilous chemicals should be rationally used in the mining area, which will reduce non-point source pollution. For areas with high NO_3^- and total hardness caused by natural factors, the authorities in both the mining concession and the Koidu Community should organize drinking water source denitrification removal projects or install water purifiers to reduce potential human health risks. Meanwhile, regular groundwater monitoring in the Township is an indispensable part of groundwater management. Numerous factors, such as surface water percolation, human activity, land use change, climate change, and social development, all impact groundwater quality. Increasing sectoral cooperation is a critical step towards ensuring groundwater protection that works. Thus, groundwater research should be combined with natural sciences and social sciences, so that groundwater management can be more sustainable.

Conclusion

The study focuses on hydrochemical characteristics, controlling factors, and groundwater quality evaluation in Kono, Sierra Leone, which is crucial for populations residing in mining communities. It was conducted to assess the current status of groundwater quality in Koidu City based on 29 water samples collected in the mining concession and proximity communities within the mining concession using hydrogeochemical characterization, WQI, EWQI, and spatial assessment of the groundwater (GIS).

The physicochemical parameters viz., NO_3^-, EC, NTU, and Fe^{2+} of most water samples are not found within the National permissible limits. The concentration of cations in the study area is found in the following order: $Ca^{2+} > Na^+, K^+ > Mg^{2+} > Fe^{2+}$, whereas the concentrations of anions are in the order of $HCO_3^- > NO_3^- > SO_4^{2-} > Cl^-$.

The WQI indicates that 55.17% of the samples are in the "excellent" category, 17.24% "good" category, 20.69% in the "medium" category, and 6.90% "very poor" category and EWQI 27.59% in "excellent" category, 24.14% "good" category, 34.48% "medium" category, 3.45% "poor" and 10.34% " very poor" category. Based on both methods (WQI and EWQI), we can conclude that the groundwater at most of the locations in the study area is fit for drinking. The multivariate analysis results showed that the groundwater variation in the study area could be influenced by anthropogenic activities, ion exchange, and mineral dissolution due to rock weathering. Water–rock interaction, silicate dissolution, and cation exchange were the main hydrochemical processes regulating the hydrochemistry in the study area. Additionally, the groundwater residence time and mining operations were critical external factors that affected chemical variables. The overall quality of groundwater in the research area is not only good but excellent. However, it is polluted to a certain extent by mining activities, and some of the groundwater is not suitable for direct drinking.

Groundwater supplies must be available for human consumption, including drinking water, household use, and other economic explorations like mining and agriculture. This water needs to be in acceptable condition to be used for the above-mentioned purposes. Therefore, to ensure consumer safety and prevent natural or environmental mishaps, water quality monitoring is necessary. A management system is also necessary for the sustainability of water resources and the maintenance or improvement of water quality. Future research can investigate the temporal variation of dry season and wet season data, as well as the effect of well screen depth, bore well depth, and water depth on water quality.

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