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Assessment of hydrochemistry and heavy metal contamination in the groundwater around an abandoned Copper Mine area in Klein Aub, Namibia

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Abstract

The long mining history in Namibia has resulted in numerous abandoned mining sites scattered throughout the country. Past research around the Klein Aub abandoned Copper mine highlighted environmental concerns related to past mining. Considering that residents of Klein Aub depend solely on groundwater for their domestic, irrigation and other uses, there is a need to thoroughly investigate groundwater quality in the area to ascertain the extent of the contamination. This study characterises groundwater quality using a comprehensive quality assessment approach. On-site parameters reveal that pH ranges between 6.82-7.8, electrical conductivity ranges between 678 - 2270 $\mu\text{S}/\text{cm}$, and dissolved oxygen ranges between 1.4 -5.77 mg/L. With the exception of two samples, the onsite parameters indicate that water is of excellent quality according to the Namibian guidelines. The stable isotopic composition ranges from -7.26 to -5.82‰ and -45.1 to -35.9‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The groundwater plots on and above the Global Meteoric Water Line, and the best-fit line is characterised by a slope of 4.9, implying the evaporation effect. Hydrochemical analyses indicate bicarbonate and chloride as dominant anions, while calcium and sodium are dominant cations, indicating groundwater dissolving halite and mixing with water from a recharge zone. The Heavy Metal Pollution Index suggested that the water samples are free from heavy metal pollution. The Heavy Metal Evaluation Index clustered around 3, implying that heavy metals moderately affect groundwater. The groundwater quality is suitable for irrigation purposes. The findings offer valuable insights into the area's hydrochemistry and highlight potential environmental risks; hence, groundwater monitoring is recommended.

1. Introduction

1.1. Background

The Klein Aub settlement in central Namibia has a long copper and silver mining history. Mining operations began in 1966, and the mine was abandoned in 1987 [1]. Mining operations ceased without any remedial measures [2]. Mine waste, such as tailing dams, concrete structures, and foundations, occurs around the mine area and poses a potential health risk to the inhabitants. Abandoned mine sites, such as the Klein Aub mine, represent a major outstanding international environmental problem related to mining [3]. In Namibia, most abandoned mines have not been

rehabilitated, and little research has been done to assess possible environmental problems [4,5]. Environmental risks posed by abandoned mines include contamination of soil and groundwater by heavy metals such as Arsenic (As), Lead (Pb), Mercury (Hg), and Silver (Ag), Cadmium (Cd), which can be potentially toxic at low concentrations [6–8]. Consumption of crops grown on contaminated soils and drinking contaminated groundwater can cause adverse health impacts. Several studies have emphasised the need for urgent groundwater management and protection,



especially in arid and semi-arid regions such as Namibia [9].

Previous research in the Klein Aub area highlighted environmental concerns related to past mining, including air pollution through dust blown from tailings, soil pollution, surface and groundwater pollution, and water erosion of tailings [1,5,10]. These studies, particularly that of [10], focused on soil and surface water samples with only one borehole to assess underground water quality. The results of their study indicate the potential risk of groundwater contamination. Considering that residents of the Klein Aub settlement depend solely on groundwater for all purposes, there is a need to investigate and understand groundwater quality in the area to ascertain the extent of groundwater contamination. This study makes considerable effort to characterise groundwater quality using a comprehensive approach of quality assessment, geostatistical analysis, and health risk assessment.

1.2. Studied location

The study area is located at Klein Aub, as indicated in Figure 1. The study area is about 90 km southwest of Rehoboth. The topography of the area has been described by [11] as generally flat with hilly ridges and peaks. It has a subtropical desert climate. The highest rainfall is usually recorded from January to February, with an average of 406.1 mm. Relative humidity during the rainy season is around 59%. There is little rainfall between April and December, with an average of 2.5 – 3.1 mm. Relative humidity during the dry period is approximately 16% [12]. The temperature ranges from 33 °C in summer to 8 °C in winter. November is the warmest month, whereas the lowest temperatures are usually experienced in June [12]. The dominant wind direction in the area is usually the easterly wind, which transports dust from the tailings dump [2] with an average wind speed of 16.3 kmph. The strongest wind is usually experienced in October, whereas the weak winds are recorded in March, with an average of 9.7 kmph [12].

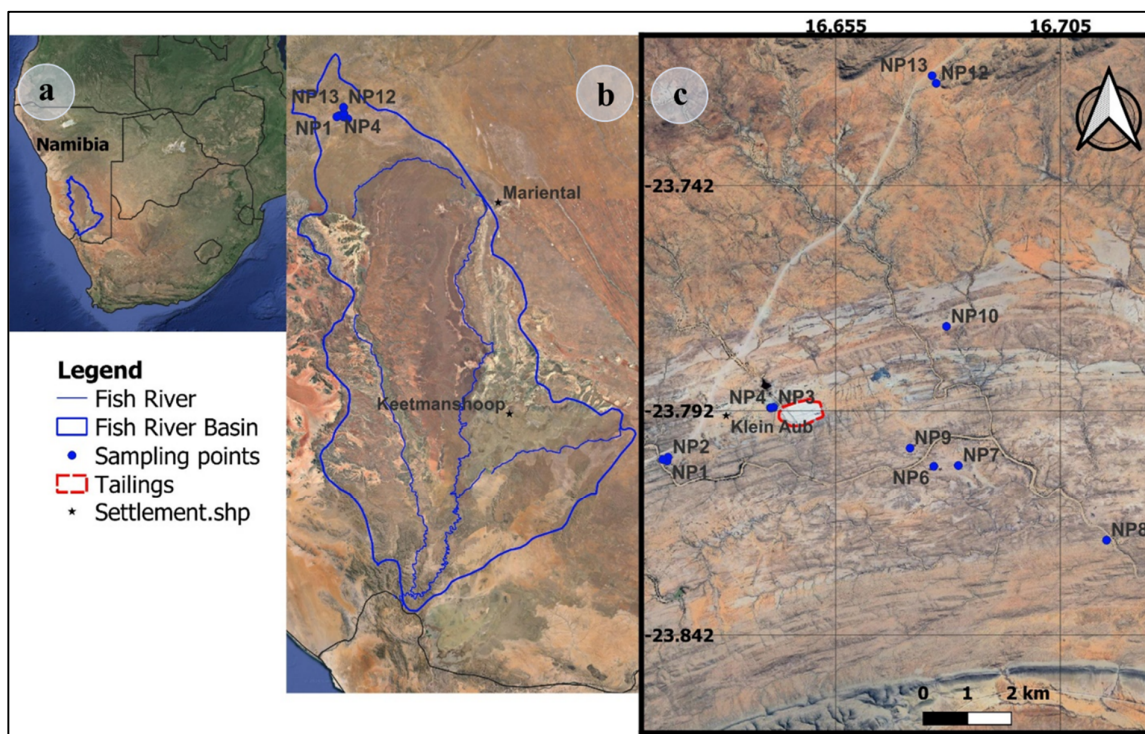


Figure 1. Location of the study area (a) google Earth used as a base layer; (b) & (c) the drainage network of the Fish River basin. The circles represent the sampling points in the studied area.

1.3. Geology and hydrogeology

The Geology of the site consists of the Middle Proterozoic Klein Aub Formation, Sinclair sequence; the ore body is hosted in Kagas Member

strata, which consist of a basal quartzite interbedded with green slate, green argillite and a calcareous sandstone at the top of the succession [13] (Figure 2). The Kagas Member strata belong

to the Tsumis Group, which disconformably overlies Neoproterozoic strata of the Damara sequence and unconformably overlies the Paleoproterozoic to Mesoproterozoic rocks of the Rehoboth Inlier [13]. The sediments were deposited in a lacustrine or shallow marine environment. The Klein Aub Formation, mainly composed of medium to fine clastic sedimentary rocks and subordinate carbonates, represents a sag phase of basin development [14]. The Klein Aub Formation, which spans the upper half of the Sinclair Sequence and is 920 Ma old (Upper Mokolian to Lower Namibian), contains quartzite, conglomerate, and argillite. The rocks of the Klein Aub Formation have experienced lower greenschist facies metamorphism [13]. The Tsumis Group strata generally dip southward in the Klein Aub region, away from the Rehoboth Inlier's basement rocks.

The primary mineral in the Klein Aub ore body is chalcocite (CuS), while the secondary minerals are Bornite, Chalcopyrite, Djulerite, and Silver

[14]. The mineralisation occurs as strata-bound copper-silver deposits in calcareous argillites associated with the subordinate faults of the Klein Aub wrench fault system [14]. The Klein Aub Mine has exploited these deposits since 1964.

The Klein Aub area falls under the Fish River Basin and covers an extensive part of southern Namibia, draining an area of nearly 120,000 km² [15]. The Sinclair Complex is hydrogeologically insignificant mainly due to the impermeable nature of the Mesoproterozoic volcano-sedimentary rocks and associated granitoid and the absence of extensive fracture networks limiting the infiltration and movement of groundwater within the complex [15]. Hence, the area's aquifers are primarily associated with fractured rock systems, particularly within the Nama Group's metamorphic and sedimentary formations. The historical Klein Aub Copper Mine underscores the area's complex geology, with mining activities highlighting potential pathways for groundwater flow.

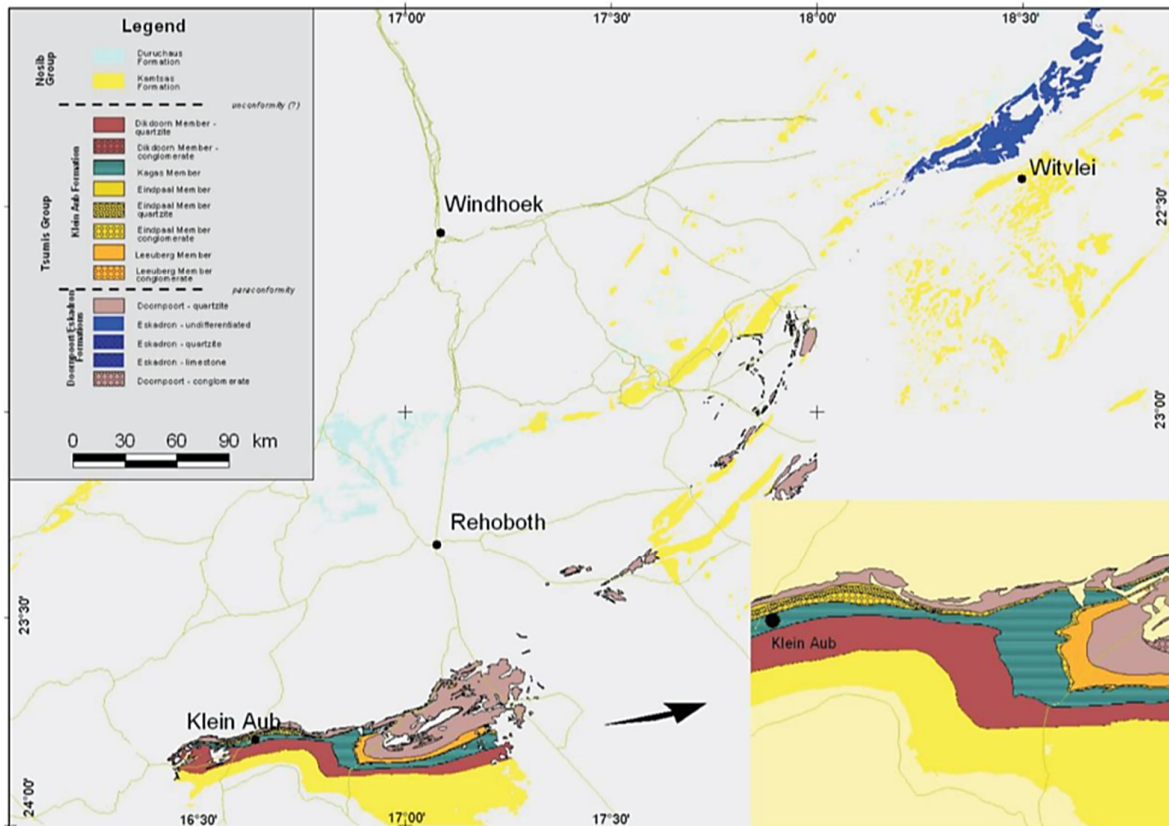


Figure 2. The geology of the studied area [13]. The studied area consists of the Klein Aub Formation units of the late Mesoproterozoic Tsumis Group.

2. Materials and methods

2.1. Sampling and *in-situ* measurements

Sampling was undertaken in August 2022, where 13 groundwater samples were collected at locations shown in Figure 1. The recommended standard operating procedure for collecting, storing, transporting and analysing samples was adopted. The samples were analysed for their physical and chemical properties, heavy metals content, and stable isotopes. The water levels were measured in boreholes with a contact gauge dip meter. Temperature (T), pH, electrical conductivity (EC), and dissolved oxygen (O₂) were measured *in situ* with a portable field water analysis box (Multi 3630 ID SET G probes).

2.2. Chemical analysis

The chemical analysis was performed at the Analytical Laboratory Services in Windhoek, Namibia; anions were estimated using titrimetric methods, while the concentration of cations was determined using ion chromatography and inductively coupled plasma optical emission spectrometry (ICP-OES). The accuracy of the analysis or result discrepancies was calculated by the charge balance error (% CBE) according to Equation 1:

$$\% \text{ CBE} = \left(\frac{\Sigma \text{cation (meq/L)} - \Sigma \text{anion (meq/L)}}{\Sigma \text{cation (meq/L)} + \Sigma \text{anion (meq/L)}} \right) \times 100 \quad (1)$$

where Σcation is the sum of the concentration of cations and Σanion is the sum of the concentration of anions, all measured in meq/L.

2.3. Statistical analysis

The Spearman's rank correlation was carried out on the water quality data to assess the strength and direction of the association between variables using IBM SPSS Statistics version 21. The strength and significance of the correlation coefficients were interpreted based on conventional thresholds. Hierarchical cluster analysis (HCA), a multivariate statistical technique employed to group subjects exhibiting similar characteristics [16] was also carried out. In hydrogeochemical research, HCA is applied to categorise samples (Q-mode) or parameters (R-mode) into clusters based on their degrees of (dis)similarity, which are visually represented in a dendrogram [16].

2.4. Stable isotopes analysis

The stable isotopes were analysed at the University of Namibia using an off-axis integrated cavity output spectroscope (Los Gatos DLT100) to

determine the ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen isotopes ($\delta^2\text{H}$). The results were expressed as δ values, reported in parts per thousand (‰), and plotted against the international Vienna Standard Mean Ocean Water (VSMOW). The δ value is calculated using Equation 2:

$$\delta = \left[\left(\frac{R_{\text{sa}}}{R_{\text{st}}} \right) - 1 \right] \times 1000 \quad (2)$$

R_{sa} represents the ratio of the stable isotope amount in the sample, and R_{st} indicates the ratio of the stable isotope amount in the standard. Using Microsoft Excel, the groundwater samples of $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ were plotted against the Global Meteoric Water Line (GMWL). The stable isotope effects were also evaluated.

2.5. Hydrochemical data analysis

The correlation between ions was analysed using Microsoft Excel to determine the dominant process controlling the chemical composition based on the dissolved species, e.g. Na⁺ and Cl⁻, Ca²⁺ and HCO₃⁻. Hydrochemical diagrams, including Gibbs, Piper, Schoeller and Stiff, were generated with Diagrammes software version 8.6 developed by the laboratory of hydrogeology at the Université d'Avignon to interpret the water chemistry and are freely available on <https://terre-et-eau.univ-avignon.fr/equipements-de-terrain-et-de-laboratoire/logiciels/#1>.

2.6. Assessment of heavy metals contamination

Two methods, the Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI), were used to evaluate the contamination concerning heavy metal concentrations.

2.6.1. Heavy metal pollution index (HPI)

The Heavy Metal Pollution Index (HPI) model was first developed by [17] to assess the level of heavy metal presence in water samples and to determine the overall quality of water, whether it is polluted or not polluted with heavy metals. It is based on the weighted arithmetic quality mean method. The method evaluates water quality first by establishing a rating scale for each selected parameter, giving weightage, and second by selecting the pollution parameter on which the index is to be based. The rating system is an arbitrary value between zero and one, and its selection depends upon the importance of individual quality considerations comparatively, or it can be assessed by making values inversely

proportional to the recommended standard for the corresponding parameter [17].

Generally, HPI is evaluated using the empirical relationship given in Equation 3:

$$HPI = \frac{\sum_{i=1}^n Q_i W_i}{\sum_{i=1}^n W_i} \quad (3)$$

where:

W_i – unit weightage of the i th parameter,

n – number of parameters considered, and

Q_i – sub-index of the i th parameter.

The unit weight/weightage (W_i) as expressed in Equation 4:

$$W_i = \frac{K}{S_i} \quad (4)$$

Where

k – constant, usually 1, and

S_i – recommended standard (S_i) guideline value of the corresponding parameter (17). Thus, Equation 5:

$$W_i = \frac{1}{S_i} \quad (5)$$

The sub-index (Q_i) of the parameter is calculated using Equation 6:

$$Q_i = \sum_{i=1}^n \frac{(M_i(-)I_i)}{(S_i - I_i)} * 100 \quad (6)$$

where:

M_i – monitored value of the heavy metal of the i th parameter, I_i is the ideal value of the i th parameter, and

S_i – standard value of the i th parameter.

This study uses the World Health Organization (WHO), 2011 guideline values of the metals (Table 1). The sign (–) indicates a numerical difference between the two values, ignoring the algebraic sign. HPI has no classification when calculated. According to [18], the value of the HPI result is either <100 (indicating that water is free from heavy metal pollution and potable or >100 (indicating that water is polluted with heavy metals). All metal concentration values were converted from mg/l to µg/l before the computation of HPI.

2.6.2. Heavy metal evaluation index (HEI)

The Heavy Metal Evaluation Index (HEI) proposed by [19] determines the level and degree of heavy metal presence in surface water or groundwater. It is a quick indicator of the overall status of water quality regarding heavy metal contamination.

HEI is expressed in Equation 7:

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{max}} \quad (7)$$

where:

H_c – concentration (mean values) of i th parameter in the sample analysed and

H_{max} – maximum allowable concentration of i th parameter (obtained from WHO, 2011 water quality guidelines).

The HEI classification of [20] indicates that the degree of pollution of water with heavy metals worsens as the HPI value increases. A HEI value of 1 is a threshold of warning. If $HEI < 1$, water is safe/free from metal contamination, but HEI value > 1 indicates potable water.

Table 1. Applied parameters and constants for calculation of HPI and HEI using the WHO, 2011 guidelines.

Metal	MCL* (µg/l)	W_i	I_i	S_i	H_{max}
As	50	0.02	10	50	50
Zn	5000	0.0002	3000	5000	5000
Pb	1.5	0.7	10	100	1.5
Cd	3	0.3	3	5	3
Cr	50	0.02	50	1	50
Cu	1000	0.001	2000	1000	1000
Mn	50	0.02	500	100	50

2.7. Irrigation water quality

To determine the quality of groundwater for use in agriculture, especially irrigation, the Sodium

percentage (%Na), Sodium absorption ratio (SAR), Sodium soluble percentage (SSP), Magnesium hazard (MH), and Kelley index (KI) were determined, as shown in Table 2.

Table 2. Standards for determination of water quality for irrigation

Index	Formula	Rating & suitability for irrigation	Agricultural implication
Sodium Ratio (SR)	$(\text{Na}^+ + \text{K}^+) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)$	<20 excellent 20-40 good 40-60 permissible 60-80 doubtful >80 unfit	In irrigation water classification, sodium is considered an important ion because of its soil reactivity [21]. The ion exchange of Ca^{2+} and Mg^{2+} ions is induced and controlled by sodium concentration. The reduction in soil permeability is a result of this process, resulting in poor internal drainage.
Sodium Absorption Ratio (SAR)	$\text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na})/2}$	0-10 excellent 10-18 good 18-26 doubtful >26 unfit	High SAR values may reduce plant osmotic action and cause the accumulation of sodium to toxic levels.
Sodium Soluble Percentage (SSP)	$\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)$	<50 good >50 not good	Sodium ion exchanged by Mg^{2+} and Ca^{2+} ions present in clay particles reduces the permeability of soil [22] and cause soil hardening. Salinity and alkalinity resulting from a combination of sodium with chloride and carbonates retard plant growth and crop productivity.
Magnesium Hazard (MH)	$((\text{Mg}^{2+} / (\text{Mg}^{2+} + \text{Ca}^{2+})) \times 100)$	<50 suitable >50 unsuitable	In an undisturbed natural condition/scenario, alkaline earth (Ca^{2+} and Mg^{2+}) usually exists in an equilibrium groundwater state. Although essential to crops, they are also linked with soil friability and aggregation. An excess of magnesium ions in groundwater affects the soil quality by increasing its alkalinity and reducing crop yield [23,24].
Kelley's Index (KI)	$\text{N}^{2+} / (\text{Mg}^{2+} + \text{Ca}^{2+})$	<1 good >1 not good	It shows the suitability of water for irrigation based on the sodium quantity in the water [21]. Water with KI >1 is not suitable for irrigation due to alkali hazards

3. Results and Discussion

3.1. Field *in-situ* physico-chemical parameters

The physicochemical parameters are shown in Table 3. The onsite parameters reveal that pH ranged between 6.82 and 7.80, with an average of 7.30, implying that the water is alkaline. All the samples meet the [25] WHO guideline value of 6.0-8.5 for pH in drinking water.

The EC, which evaluates the ionic composition in water, ranged between 678 and 2270 $\mu\text{S}/\text{cm}$ and had an average value of 1153.42 $\mu\text{S}/\text{cm}$. The WHO guideline value is 1500 $\mu\text{S}/\text{cm}$, which was exceeded by six of the water samples. They tend towards slightly saline water with 1000-3000 $\mu\text{S}/\text{cm}$ EC.

The total dissolved solids (TDS) ranged from 433.92 to 1452.80 mg/L, with an average of 738.19 mg/L. In 7 of the 13 boreholes, the TDS exceeded the WHO guideline value of 500 mg/L. TDS is an important determinant of water quality for drinking (500—1000 mg/L) and agricultural applications. Water with a TDS greater than 3000 mg/L is considered unfit for drinking and irrigation.

For the evaluation of drinking water quality for human consumption regarding chemical, physical and bacteriological quality in Namibia, [26] classified water into four groups: Group A (Water with excellent quality), Group B (Water with acceptable quality), Group C (Water with low

health risk), and Group D (Water with a high health risk, or water unsuitable for human consumption). Ten samples of the groundwater indicated that the water is potable. However, samples 3, 5, and 13 fell under the D water class and did not meet the Namibian water quality safety standards for human consumption.

3.2. Hydrochemical facies

The Piper Trilinear diagram in Figure 3 shows the hydrochemical water types for the collected groundwater samples. The cations in the chemical components of the groundwater samples are mainly calcium ions, of which 83.3% were calcium water type, and the remaining 16.7% of samples located at the centre of the ternary plot are regarded as no dominant type. The alkaline earth metal Ca^{2+} and Mg^{2+} concentrations range from 71.0 to 258.0 mg/l and 12.0 to 45.0 mg/l, with a mean of 121.7 mg/l and 22.4 mg/l, respectively. The concentrations of alkaline metals Na^+ and K^+ are 34.0 to 178.0 mg/l and 1.8 to 5.8 mg/l, as well as a mean of 85.4 mg/l and 3.3 mg/l, respectively.

For the anions, HCO_3^- accounts for the majority, with concentrations ranging from 244.0 to 378.2 mg/l with a mean of 316.7 mg/l. Concentrations of the anions Cl^- and SO_4^{2-} range from 23.0 to 346.0 mg/l and 25.0 to 253.0 mg/l, respectively, with mean values of 112.0 and 103.2 mg/l, respectively. The abundance of major ions is then grouped in the

order $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ for cations and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ for anions. Two main hydrochemical facies are observed in Figure 2, CaMgHCO_3 and mixed CaMgCl . CaMgHCO_3 is the dominant water type at 58.3%, and the CaMgCl water type at 41.7%. The different chemical facies may be related to rock-water interaction, causing the dissolution of the calcareous argillites in the area, which host the primary minerals chalcocite (CuS) and the secondary minerals bornite and chalcopyrite [14].

3.3. Factors affecting groundwater chemistry

Figure 4 shows a Gibbs diagram representing some key processes controlling water chemistry. The plot shows the relationship between water composition and lithological characteristics of aquifers. In [27], which describes the mechanisms controlling world water chemistry, the plot has three dominant fields that control groundwater chemistry: rock weathering, precipitation, and evaporation. The Gibbs diagram suggests that the factor controlling the chemistry of most of the samples falls under evaporation, tending towards rock dominance.

This may be due to the arid climatic conditions of the area, which have high evaporation and low precipitation. This is supported by the sparse rainfall in the study area, which lies in the Namib Desert. Rainfall peaks in January, February, and March, and mean monthly rainfall averages approximately 62 mm, 66 mm, and 55 mm, respectively. High solar radiation, low humidity, and high temperature lead to remarkably high evaporation rates of about 3,800 mm per annum [28]. Evaporation concentrates dissolved solids and may increase the total salinity in water.

On the other hand, of the 51 % of samples plotted in the region of rock dominance, chemical weathering is the main driving mechanism where groundwater dissolves rocks and releases constituents that affect water quality. Similar results were obtained by [29–31], highlighting water-rock interaction as the most important process controlling groundwater chemistry. Although the Gibbs diagram was initially developed to interpret surface water chemistry, it has been routinely applied in groundwater studies. [32] cautioned against the oversimplification of the diagram when evaporation is discussed, where the water table occurs deeper than a few meters, thus making the contribution of evaporation to

groundwater chemistry negligible or insignificant. In the study area, neither the groundwater table nor discharges are near the surface.

However, carbonates are reported in the area's stratigraphy [33], which is confirmed by the ion concentrations in Table 3. Where evaporites occur, rock-water interaction is the primary mechanism governing groundwater quality over evaporation [34] such that the changes in groundwater chemistry are due to the dissolution of evaporite minerals. Generally, rock-water interaction leads to the precipitation and/or dissolution of some minerals, which affects the groundwater chemistry [35,36]. We align with this position concerning the study area. Groundwater within the study area is of deep meteoric type. Findings obtained from ion exchange revealed that groundwater is influenced mainly by silicate weathering.

Using interpretations linked to the original Gibbs diagram to define groundwater geochemical processes may oversimplify the interpretation of aquifer systems and overlook important processes. Thus [32] suggested that approaches to understanding groundwater's hydrochemical processes should include using other more sophisticated diagrams (e.g., the Piper plot) and analytes (e.g., isotope geochemistry). Analysing the Gibbs diagram alongside other hydrochemical assessments like the Piper plot and water quality indices can give insights into the hydrogeochemical processes shaping groundwater quality for drinking and irrigation purposes.

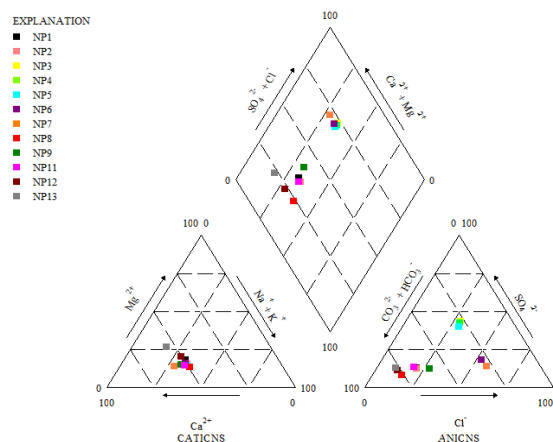


Figure 3. Piper diagram showing the hydrochemical facies in the studied area. The groundwater samples are mainly calcium ions, of which 83.3% were calcium water type. for the anions, CaMgHCO_3 and CaMgCl are the dominant water types.

Table 3. Physico-chemical results of water samples in the studied area.

Fe	0.10	0.09	0.17	0.04	0.22	0.18	0.42	0.71	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.71	0.17
Mn ²⁺	0.01	0.04	0.03	0.02	0.02	0.03	0.04	0.01	0.10	0.01	0.01	0.13	0.01	0.10	0.04	50	
Ca ²⁺	72.00	74.00	129.00	130.00	129.00	233.00	258.00	80.00	117.00	71.00	74.00	93.00	71.00	258.00	121.67	75	
Mg ²⁺	16.00	14.00	22.00	22.00	22.00	45.00	38.00	13.00	20.00	12.00	18.00	27.00	12.00	45.00	22.42	50	
K ⁺	2.90	4.10	3.10	3.10	3.10	5.80	3.20	1.80	1.80	3.70	3.80	2.90	1.80	5.80	3.28	10	
Na ⁺	53.00	57.00	102.00	104.00	102.00	178.00	147.00	68.00	80.00	52.00	48.00	34.00	34.00	178.00	85.42	200	
NO ₂	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.28	<0.01	<0.01	<0.01	<0.01	<0.01	0.28	0.28	0.28	1.0	
NO ₃	10.00	3.00	<0.5	<0.5	<0.5	42.00	67.00	5.60	14.00	6.70	15.00	10.00	3.00	67.00	19.26	45	
SO ₄ ²⁻	35.00	35.00	248.00	253.00	224.00	147.00	114.00	25.00	52.00	37.00	29.00	39.00	25.00	253.00	103.17	400	
F ⁻	0.40	0.30	0.40	0.50	0.50	0.40	0.40	0.40	0.30	0.40	1.30	1.30	0.30	1.30	0.55	1.5	
Cl ⁻	44.00	46.00	124.00	127.00	124.00	323.00	346.00	36.00	88.00	39.00	23.00	24.00	23.00	346.00	112.00	200	
Total Hardness	246.00	242.00	413.00	415.00	413.00	767.00	801.00	253.00	375.00	227.00	259.00	343.00	227.00	801.00	396.17	500	
HCO ₃ ⁻	286.70	298.90	244.00	262.30	262.30	378.20	359.90	372.10	366.00	286.70	311.10	372.10	244.00	378.20	316.69	300	
Total Alkalinity	235.00	245.00	200.00	215.00	215.00	310.00	295.00	305.00	300.00	235.00	255.00	305.00	200.00	310.00	259.58	250	
Temp (°C)	22.10	22.40	23.60	23.80	24.50	23.30	25.00	23.00	22.20	20.40	21.00	22.50	20.40	25.00	22.82	28	
DO	2.37	2.86	5.77	4.85	5.34	3.52	2.73	3.79	2.02	2.35	1.40	3.86	1.40	5.77	3.41		
TDS	483.20	469.76	810.24	804.48	808.32	1452.80	1440.00	496.00	689.28	433.92	460.80	509.44	433.92	1452.80	738.19	500	
EC (uS/cm)	755.00	734.00	2166.00	1257.00	1263.00	2270.00	2250.00	775.00	1077.00	678.00	720.00	796.00	678.00	2270.00	1153.42	1500	
pH	7.40	7.32	7.80	7.74	7.64	7.02	7.00	7.26	7.15	7.46	7.00	6.82	6.82	7.80	7.30	6.5-8.5	
SWL (m)	7.23	8.97	19.70			19.55		9.44	15.86	3.80	19.40	21.73	3.80	19.70	13.96		
Sample Number	NP1	NP2	NP3	NP4	NP5	NP6	NP7	NP8	NP9	NP11	NP12	NP13	Minimum	Maximum	Average	WHO (2011)	

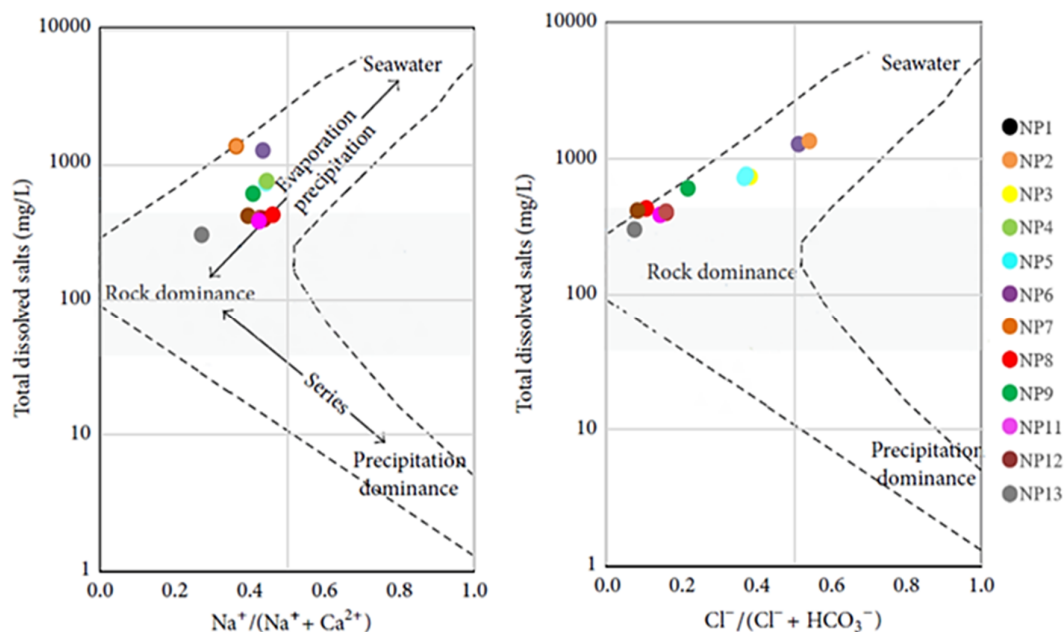


Figure 4. Gibbs plot showing factors controlling groundwater chemistry. The diagram suggests that evaporation and rock-water interaction control the chemistry of most of the samples.

The stiff diagram classifies waters according to the anion and cation facies, and the geometry of each polygon depends on the hydrochemical elements and infers the dominant species and its chemical relationship. In Figure 5, boreholes NP6 and NP7 have higher HCO_3^- and Ca^{2+} concentrations. These boreholes also have the highest EC values (2250 and 2270 $\mu\text{S}/\text{cm}$) compared to the 678 to 1266 $\mu\text{S}/\text{cm}$ range for the others. These other boreholes have different hydrochemical water types based on their chemical composition. They are more loaded with anions than cations.

3.4. Heavy metals

Heavy metal contamination in the groundwater was assessed using the concentration of six heavy metals. The concentrations for the heavy metals, Cu, Zn, Pb and As range from <0.01 to 1.1 mg/l , <0.01 to 2.1 mg/l , <0.01 to 0.01 mg/l , and 0.01 to 0.02 mg/l , respectively. The concentrations of Hg in all the samples are $<0.01 \text{ mg/l}$. According to the Namibian water quality standards, all samples are below the threshold value of 100 mg/l for groups A and C, indicating that the water samples are not contaminated. However, the concentration of the heavy metals in the water samples is above the [25] guideline values for each metal except in samples NP3, NP5 and NP13.

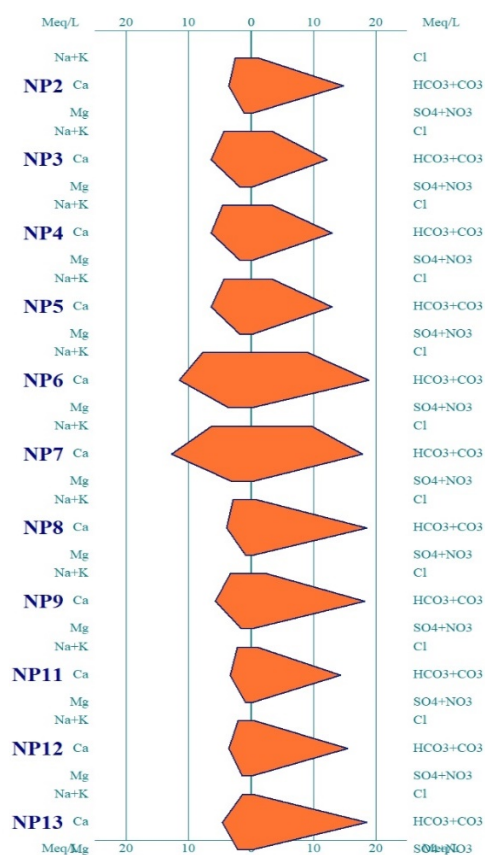


Figure 5. Stiff diagram for the groundwater samples. Higher HCO_3^- and Ca^{2+} concentrations are observed in boreholes NP6 and NP7.

3.5. Spearman's rank correlation and hierarchical cluster analysis

The results of the Spearman's rank correlation matrix heatmap with values rounded to 2 decimal places and enhanced for clarity are shown in Figure 6. Strong positive correlations (e.g. EC vs Ca, total hardness, TH vs Ca) show up as deep red, while strong negative correlations (e.g. pH vs HCO_3 , pH vs total alkalinity, TA) show as deep blue. Weak or no correlation trends sit near the centre colour on the scale. EC vs TDS shows perfect correlation, where one increase leads to a corresponding increase in the other. Positive correlations are observed between the following pairs: TH vs Ca ($\rho = 0.99$), TH vs Mg ($\rho = 0.95$), suggesting that calcium and magnesium are the key contributors to total hardness in the water samples; EC/TDS vs Na ($\rho \approx 0.90$), Cl ($\rho \approx 0.90$), SO_4 ($\rho \approx 0.87$), contribute significantly to water salinity; Ca vs Cl ($\rho = 0.91$), Ca vs SO_4 ($\rho = 0.87$), Ca vs Na ($\rho = 0.90$) indicate co-migration or shared sources; and Temp vs EC, TDS ($\rho \approx 0.85$) suggesting temperature enhanced ion solubility in minerals. Moderate positive correlations exist between Fe vs Mn ($\rho \approx 0.63$), suggesting geogenic source contributions from

rocks rich in these minerals or anaerobic groundwater zones. Negative correlations are notable between pH vs HCO_3 and pH vs TA pairs ($\rho \approx -0.74$), indicating an inverse relationship, which suggests water with higher alkalinity may be buffering acidic inputs, which in turn lowers water pH.

Hierarchical Cluster Analysis was applied to group similar water quality parameters based on their statistical similarities. Two major super-clusters (Figure 7) are formed, one dominated by salinity and hardness-related parameters (Cluster A), and the other by redox-sensitive and nutrient variables (Clusters B and C). The former had Ca, EC, Cl, Na, Mg and K, forming the tightest and earliest merging, suggesting strong interdependence among these ions. Cluster B comprises DO, SO_4 , Temp., pH, and F with moderate similarity. DO may vary with temperature, and fluoride solubility is pH dependent. Cluster C comprises transition metals and nutrients (Mn, Fe, HCO_3 , and NO_3), although Fe shows slightly weaker similarity. This cluster suggests redox-sensitive species or geochemical weathering processes.

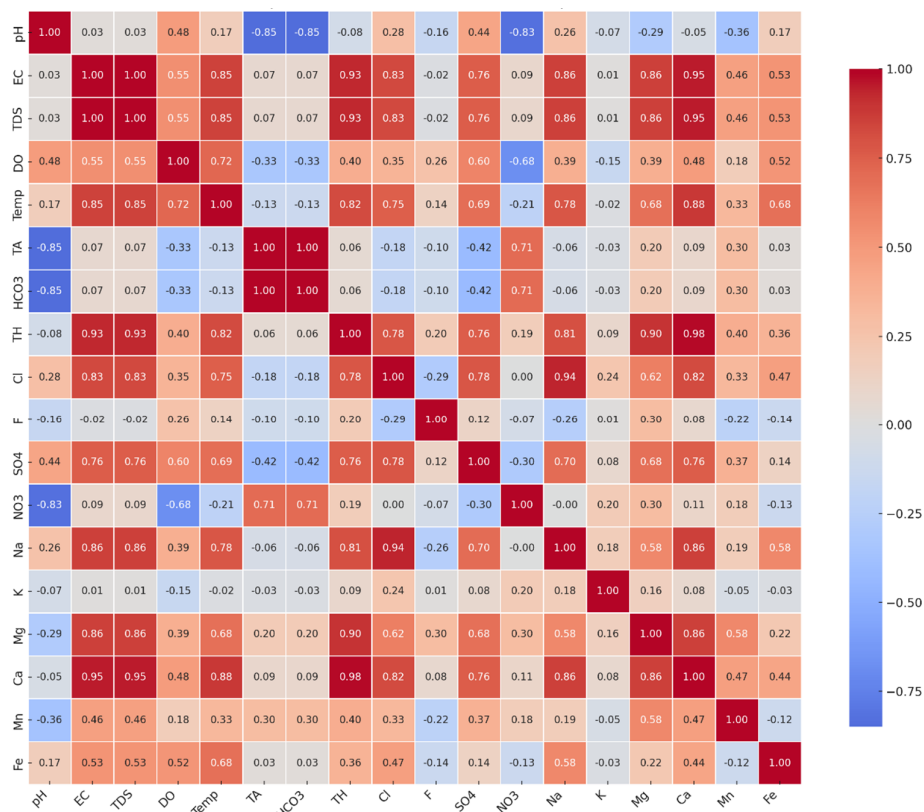


Figure 6. Spearman's rank correlation heatmap. Deep red colors show strong positive correlations (e.g. EC vs Ca, total hardness, TH vs Ca), deep blue colours show strong negative correlations (e.g. pH vs HCO_3 , pH vs total alkalinity, TA)

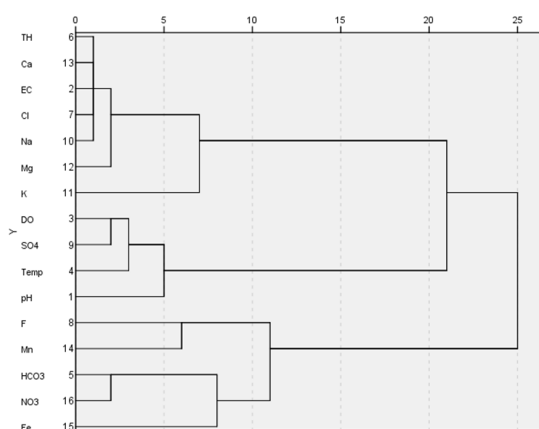


Figure 7. Dendrogram of Hierarchical Cluster Analysis. Two main clusters, where Cluster A is dominated by salinity and hardness-related parameters (Cluster A), and Cluster B is dominated by redox-sensitive variables.

3.6. Heavy metals pollution monitoring

Tables 4 and 5 summarises the calculated values of HPI and HEI, respectively. The water samples are, therefore, potable and relatively free from heavy metal pollution. The relative absence of pollution shown by the HPI results agrees closely with the HEI values, indicating that heavy metals moderately affect groundwater. Overall, Cu contributes most to the HPI values. However, our findings contradict those of [10], who used hydrochemical data from only one borehole water sample and obtained an average HPI value of 115, indicating high-risk water unsuitable for human consumption. Data from the present study, obtained from 13 boreholes spread across the area, better represent the overall groundwater chemistry in the area.

Table 4. Groundwater Quality in the study area using HP.

Sample	Cu	Zn	Pb	As	HPI	Pollution level
NP1	<0.01	0.3	0.01	0.02	1.46	Not polluted
NP2	0.02	0.06	0.01	0.02	1.46	Not polluted
NP3	0.14	0.01	<0.01	0.01	0.49	Not polluted
NP4	0.17	0.01	<0.01	0.02	0.97	Not polluted
NP5	1.1	0.01	0.01	0.01	0.98	Not polluted
NP6	0.01	0.05	<0.01	0.02	0.98	Not Polluted
NP7	0.01	2.1	0.01	0.02	1.48	Not Polluted
NP8	0.02	0.15	0.01	0.02	1.49	Not polluted
NP9	0.01	0.06	0.01	0.02	1.46	Not polluted
NP11	0.02	0.05	0.01	0.02	1.46	Not polluted
NP12	0.01	<0.01	0.01	0.02	1.97	Not polluted
NP13	<0.01	0.19	<0.01	0.01	0.49	Not polluted

The concentrations of the heavy metals are in $\mu\text{g/}$

Table 5. Groundwater Quality using HEI [19] in the studied area.

Sample Number	HEI	Class	Characteristic of water with heavy metal.
NP1	3.00	IV	Moderately affected
NP2	3.01	IV	Moderately affected
NP3	1.07	III	Slightly affected
NP4	4.01	V	Strongly affected
NP5	2.55	IV	Moderately affected
NP6	2.005	IV	Moderately affected
NP7	3.005	IV	Moderately affected
NP8	3.01	IV	Moderately affected
NP9	3.005	IV	Moderately affected
NP11	3.01	IV	Moderately affected
NP12	3.05	IV	Moderately affected
NP13	1.00	I	Pure

3.7. Water stable isotopes

The stable isotopic composition ranges from -7.26 to -5.82‰ and -45.1 to -35.9‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The groundwater plots on and above the GMWL (Figure 8). The best-fit line indicates a slope of 4.9 with a correlation coefficient of 0.75. The observed slope is much lower than the one representing the meteoric water

without significant evaporation. The slope of the evaporation line typically ranges from 2.5 to 5, depending on the aridity of the area and the atmospheric isotopic composition [37,38]. Hence, the slope of 4.9 in the study area indicated an evaporation effect, corresponding to the observation made in Figure 4, where most of the samples plotted on the evaporation section of the

Gibbs diagram. Evaporation from shallow aquifers is common and an important component of the hydrological cycle, particularly in semi-arid and arid areas [39,40]. The static water level in the study area, ranging from as low as 3.8 m to 25.94 m, indicates that the groundwater samples came from a relatively shallow aquifer susceptible to evaporation.

The correlation coefficients for the latitude effect, for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, are 0.0206 and 0.0978, respectively. For the longitude effect, they are 0.0337 and 0.1969, respectively. The latitude and longitude effects do not exhibit statistical significance or correlation with the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the groundwater in the study area. Such observations correspond to some of the isotopic studies in Namibia, such as that of [41,42], indicating no statistical significance for latitude and continental effects.

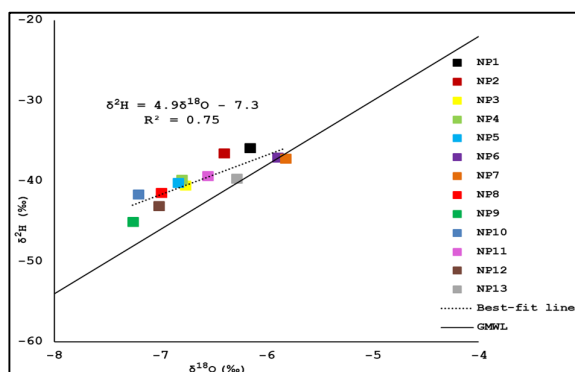


Figure 8. Dual plot of stable isotopes in the study area with an observed slope of 4.9 from the best-fitting line through the points.

3.8. Assessment of water quality for irrigation

An assessment of the suitability of the water quality in the various locations for irrigation was undertaken. The area lies in an arid climate with sparse rainfall, which makes irrigation the only viable option for crop farming. The quality of the water for irrigation is expressed in the results of the indices summarised in Table 6 and Figures 9 and 10. The high sodium concentration in irrigation waters can give rise to sodicity waters. Sodicity is the amount of Na^+ present in irrigation water. It can alter the chemical and physical properties of the soil due to an accumulation of Na^+ . Irrigation waters with excessive amounts of Na^+ can deteriorate the structure of the soil and stunt plant growth, which has a concomitant effect on crop

yield. It also adversely impacts the physical properties of soils in the form of clay dispersion, which deteriorates aggregate stability, decreases permeability in soils and soil aeration, and increases the susceptibility to soil erosion problems [43]. The Sodium Absorption Ratio (SAR) showed that the groundwater was good to excellent and, therefore, suitable for irrigation since it was below the maximum threshold for that category. SAR also influences the infiltration time of water in soils. Electrical conductivity, another important parameter in the suitability of water for irrigation, fell within the WHO guideline (2011) value of $1000 \mu\text{S}/\text{cm}$. The water also satisfies the WHO TDS values of $1000\text{--}3000 \text{ mg}/\text{L}$, which is useful for irrigation.

Schoeller diagrams are used to show the relative concentrations of and to distinguish patterns in the ratios of anions and cations whose concentration in groundwater is influenced by the chemical composition and geochemistry of the aquifer rock material. In Figure 9, all the water samples fall into the acceptable to good range for irrigation. Although some studies cited by [44] reported changes in soil physico-chemical properties with long-term irrigation, the alterations are site-specific and may be positive or negative. Some of these long-term effects are described in Table 2. The implication of irrigation on agriculture is described in Table 2. Beneficial outcomes include enhanced soil organic carbon content due to increased inputs from crop residues [45] and increased income from those involved in irrigation [46]. Conversely, continuous irrigation facilitates soil erosion and reduces soil fertility [47]. Also, excessive irrigation water accentuates aquifer recharges through percolation from excess irrigation water in addition to other sources of groundwater recharge [48]. [49] also list solodisation (reduction in soil exchangeable Na content), salinisation (accumulation of soluble salts) and solonisation (increased soil exchangeable Na content) as other environmental impacts of irrigation in arid and semi-arid areas like the present study area.

On the Wilcox diagram in Figure 10, the samples are classified as follows: NP 13 – C3-S1 class; NP 1,2,11,12 – C2-S2 class; NP 3, 5, 8, 9 – C3-S2 class; and NP 6, 7 – C3-S3 class. The waters are generally suitable for irrigation. Overall, the parametric indices classify the water as good to excellent and suitable for irrigation.

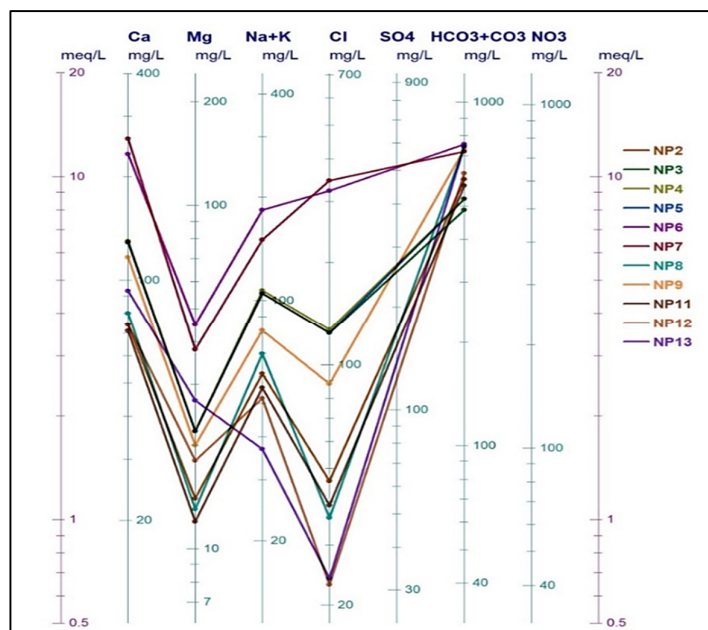


Figure 9. Schoeller diagram for the groundwater samples in the study area. Water samples fall in the acceptable-good-for-irrigation region.

Table. Assessment of the water quality for irrigation.

Sample	% Na	SAR	SSP	MH	KI
NP1	0.87	7.99	38.85	18.18	0.6
NP2	0.88	8.59	40.98	15.91	0.65
NP3	0.9	11.74	41.04	14.57	0.68
NP4	0.9	11.93	41.34	14.47	0.68
NP5	0.9	11.74	41.04	14.57	0.68
NP6	0.89	15.1	39.8	16.19	0.64
NP7	0.91	12.08	33.66	12.84	0.5
NP8	0.91	9.97	42.87	13.98	0.73
NP9	0.9	9.67	37.39	14.6	0.58
NP11	0.89	8.07	40.16	14.46	0.63
NP12	0.85	7.08	36.02	19.57	0.52
NP13	0.81	4.39	23.52	22.5	0.28
Minimum	0.81	4.39	23.52	12.84	0.28
Maximum	0.91	15.1	42.87	22.5	0.73
Average	0.88	9.86	38.06	16.23	0.6
Irrigation suitability	Excellent	Good to Excellent	Good	Suitable	Suitable

Sodium percentage (%Na), Sodium Absorption Ratio (SAR), Sodium soluble percentage (SSP),
Magnesium Hazard (MH), and Kelley Index (KI)

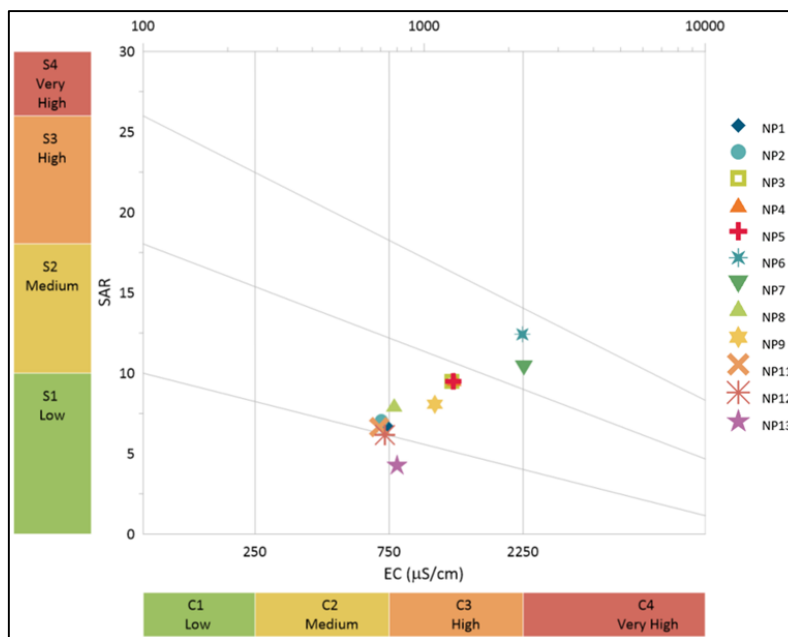


Figure 10. Wilcox plot for irrigation suitability assessment. most samples are classified as C2-S2 class and C3-S2 class.

4. Conclusions

The study successfully achieved its objectives by thoroughly characterising the groundwater and assessing potential contamination by heavy metals near the abandoned mine site. The findings provide critical insights into the area's hydrochemistry and identify potential environmental and public health risks. These results will play a pivotal role in shaping post-mining management strategies, ensuring the safe rehabilitation of the site, and protecting the Klein Aub community from the adverse effects of contaminated water sources.

Ensuring access to clean water and sanitation, as outlined in Sustainable Development Goal 6 (SDG 6), requires a comprehensive understanding of groundwater quality and proactive measures to address and mitigate contamination. Based on the findings of this study, the following recommendations are proposed: establishing a long-term groundwater monitoring system to assess heavy metal concentrations and other water quality parameters regularly. This will enable early detection of potential contamination and provide data to guide remediation efforts. Community education programs should be conducted to raise awareness about the risks of groundwater contamination and promote safe water usage practices. Engage local stakeholders in the planning and implementation of water management plans. Strengthening environmental regulations and enforcing strict compliance for abandoned mine site rehabilitation is also

proposed. Policies should mandate periodic assessments of legacy sites and ensure responsible parties contribute to mitigation efforts. Further research and collaboration with academic institutions and government agencies are encouraged, especially to include the soil and air characterisation for the Klein Aub area.

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ارزیابی هیدروشیمی و آلودگی فلزات سنگین در آب‌های زیرزمینی اطراف یک منطقه معدن مس متروکه در کلاین آب، نامیبیا

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چکیده

سابقه طولانی معدنکاری در نامیبیا منجر به وجود سایت‌های معدنی متروکه متعددی در سراسر کشور شده است. تحقیقات گذشته در اطراف معدن مس متروکه کلاین آب، نگرانی‌های زیست‌محیطی مربوط به معدنکاری گذشته را برجسته کرده است. با توجه به اینکه ساکنان کلاین آب صرفاً برای مصارف خانگی، آبیاری و سایر مصارف خود به آب‌های زیرزمینی وابسته هستند، نیاز به بررسی کامل کیفیت آب‌های زیرزمینی در این منطقه برای تعیین میزان آلودگی وجود دارد. این مطالعه کیفیت آب‌های زیرزمینی را با استفاده از یک رویکرد ارزیابی کیفیت جامع توصیف می‌کند. پارامترهای موجود در محل نشان می‌دهد که pH بین ۶.۸۲-۷.۸، رسانایی الکتریکی بین ۶۷۸-۲۲۷۰ میکروزیمنس بر سانتی‌متر و اکسیژن محلول بین ۱.۴-۵.۷۷ میلی‌گرم بر لیتر متغیر است. به استثنای دو نمونه، پارامترهای موجود در محل نشان می‌دهد که آب مطابق با دستورالعمل‌های نامیبیا از کیفیت عالی برخوردار است. ترکیب ایزوتوپی پایدار برای $\delta^{18}O$ و δ^2H به ترتیب از -۷.۲۶ تا -۵.۸۲‰ و -۴۵.۱ تا -۳۵.۹‰ متغیر است. نمودارهای آب‌های زیرزمینی روی و بالای خط جهانی آب‌های جوی قرار دارند و بهترین خط برازش با شیب ۴.۹ مشخص می‌شود که نشان‌دهنده اثر تبخیر است. تجزیه و تحلیل‌های هیدروشیمیایی نشان می‌دهد که بی‌کربنات و کلرید به عنوان آنیون‌های غالب، در حالی که کلسیم و سدیم کاتیون‌های غالب هستند، که نشان‌دهنده حل شدن هالیت در آب‌های زیرزمینی و مخلوط شدن با آب از یک منطقه تغذیه مجدد است. شاخص آلودگی فلزات سنگین نشان داد که نمونه‌های آب عاری از آلودگی فلزات سنگین هستند. شاخص ارزیابی فلزات سنگین در حدود ۳ قرار دارد که نشان می‌دهد فلزات سنگین به طور متوسط بر آب‌های زیرزمینی تأثیر می‌گذارند. کیفیت آب‌های زیرزمینی برای اهداف آبیاری مناسب است. یافته‌ها بینش‌های ارزشمندی در مورد هیدروشیمی منطقه ارائه می‌دهند و خطرات بالقوه زیست‌محیطی را برجسته می‌کنند. از این رو، نظارت بر آب‌های زیرزمینی توصیه می‌شود.

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