Revista Minelor – Mining Revue
ISSN-L 1220-2053 / ISSN 2247-8590
vol. 31, issue 3, pp. 118-126, selected paper from the First International EnviroMining Virtual Conference 2025

HYDROGEOCHEMICAL AND ANTHROPOGENIC CONTROLS ON GROUNDWATER QUALITY IN THE TALENSI DISTRICT, NORTHERN GHANA: IMPLICATIONS FOR ARSENIC CONTAMINATION

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DOI: 10.2478/minrv-2025-0035
received – 23.01.2025 / revised – 11.02.2025
accepted – 18.02.2025 / published – 22.09.2025

Abstract: *Talensi District is mainly a rural area in the Upper East Region of Ghana, which relies heavily on groundwater for drinking and irrigation purposes. However, there are several artisanal and small-scale mining (ASM) activities in the district, which pose a serious threat to groundwater quality in the area. Therefore, the current study assessed the hydrogeochemical and anthropogenic controls that influence the quality of the available groundwater sources in the areas dominated by ASM activities in the Talensi District. The study utilized hydrogeochemistry, chemometric analysis, and geographic information system to assess the sources of the groundwater constituents. A total of ten (10) groundwater samples were collected from the ASM- dominated areas in the Talensi District. The aquifer is dominated by Na-SO4-HCO3 and Na-SO4 hydrogeochemical facies. These water types are derived from water-rock interaction, forward ion exchange reaction, and dissolution of rocks containing gypsum, halite, calcite, and aragonite. The mean concentrations of the potentially toxic elements (PTEs) vary in the order Fe > Pb > As > Mo > Cr > Ni > Cd > Sb > Cu. All the samples showed concentrations above the guideline values set by the World Health Organization for Fe, Pb, As, Mo, Cr, and Ni. The As concentrations in the groundwater samples are in the range of 2.90 to 6.5 mg/L with a mean concentration of 4.5 mg/L. The weathering and dissolution of ore minerals and leaching of chemicals used in processing gold in the area during the ASM activities are the causes of arsenic enrichment and mobilization in the groundwater.*
Keywords: *hydro-geochemistry, groundwater quality, artisanal and small-scale mining, potentially toxic elements, arsenic contamination, northern Ghana*

1. Introduction

Gold mining in the Talensi District in the Upper East Region started in the early 1930s with the first exploration work being done in the village of Nangodi by a German mining firm [1]. Cardinal Namdini gold mine is a large-scale mining company in the area, which practices open-pit mining. Open-pit mining can impact groundwater by altering the natural flow of the surface water, that recharges aquifers. Moreover, the Kulubiliga River runs through most of the Talensi District's settlements, and many residents there depend on it for drinking water. The quality of the river is significantly impacted by the introduction of toxic substances from the effluent of artisanal and small-scale mining (ASM) activities. The ASM activities are widely recognized as the most water polluting activities, which deplete Kulubiliga River's water supply. The district's mining operations affect the quantity and quality of groundwater supply to the inhabitants as well as the health of the people.

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In view of this, it is crucial to investigate the hydrogeochemistry and factors that influence the quality of domestic water supply in the district. Therefore, this study assessed the hydrogeochemical and anthropogenic controls that influence the quality of the available groundwater sources in the areas dominated by ASM activities in the Talensi District.

2. Methods

2.1. Study area

The study was carried out in the Talensi District, which is situated in the Upper East Region of Ghana. Approximately 75% of the district is made up of crystalline Precambrian rocks (metavolcanic rocks) from the Birimian Supergroup (Fig. 1). Granitoids from the Eburnean and Tamnean Plutonic Suites have intruded these rocks. Granites and monzonites with a high K-feldspar concentration (also known as the Bongo type) make up the majority of the intrusions associated with the Birimian in the study area [2]. The Kwahu-Bombouka Group of the Voltaian Supergroup covers the district's lower and eastern portions. Along with the Tarkwaian Group, these group of rocks are mostly composed of shales, medium-grained mudstones, and fine-grained micaceous sandstones.

2.2. Sample collection and analysis

Ten groundwater samples were collected from active boreholes located within the Talensi District. Ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS) were the laboratory instrumentation used for the quantification of anions and potentially toxic elements (PTEs), respectively. Duplicates and Simulated Rainwater (standard reference material) were used as measures to guarantee quality control and assurance of the analysis. The hydrochemical data was interpreted by plotting Piper, Gibbs, and bivariate diagrams using AquaChem software. The mineral phase saturation was also calculated using PHREEQC in the AquaChem software. Sources of arsenic and other hydrochemical parameters were interpreted from multivariate statistical analysis involving factor and principal component analyses.

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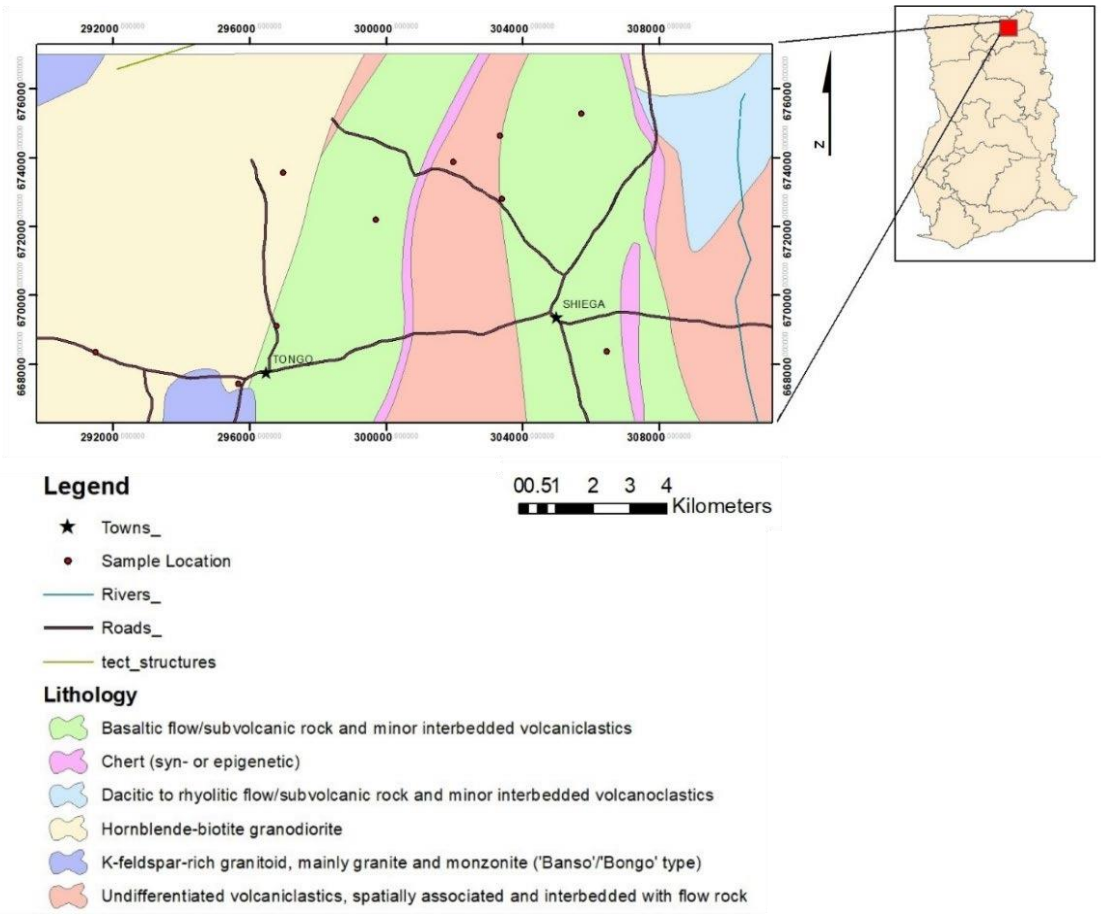

Fig. 1. Location and geological map of the study area

3. Results and Discussion

3.1. Hydrochemistry

Table 1 presents descriptive summary statistics of the hydrochemical parameters. The pH values range from 6.85 to 7.29. The World Health Organization (WHO) permissible pH range is 6.50 to 8.50 [3]. All ten borehole samples analyzed fall within this range, indicating homogeneity in geochemical processes. Sample temperatures range from 28.2 to 29.5°C, with a mean of 28.51°C, suggesting no hydrothermal influence [4], possibly attributed to depth-related variations. Electrical conductivity (EC) values range from 247 to 504 µS/cm, with a mean of 358 µS/cm. These values are within WHO limits of 2500 µS/cm. The total dissolved solids (TDS) values range from 123 to 252 mg/L, with a mean of 178 mg/L, which is below the WHO [3] 1000 mg/L limit. This implies limited charged species and groundwater-mineral interaction. For major cations, Na^+, concentrations range from 9.00 – 31.0 mg/L, with a mean of 20.3 mg/L falling within the 200 mg/L limit. Potassium (K^+) levels range from 0.20 to 5.40 mg/L, with a mean of 1.80 mg/L, which is much lower than the

30.0 mg/L guideline value. Magnesium (Mg^{2+}) and calcium (Ca^{2+}) range from 0.01 to 0.14 mg/L with a mean value of 0.20 mg/L and 0.40 to 1.80 mg/L with a mean value of 0.90 mg/L, respectively. Calcium (Ca^{2+}) appears to be enriched in the water due to carbonate mineral dissolution.

Major cation abundance follows this order: $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$. and could be a result of ion exchange reaction [5]. The predominant anion is bicarbonate (HCO^-), which has a mean value of 14.1 mg/L and the concentration ranges from 4.10 to 32.6 mg/L. It might originate from the rock formations in the study region, attributable to the carbonate lithology prevalent in the area. According to [6], infiltration, which forms carbonic acids dissolves feldspars, releasing HCO^- into groundwater. The chloride (Cl^-) and sulphate (SO^{2-}) concentrations vary from 3.00 to 19.7 mg/L (average of 9.40 mg/L) and 1.10 to 25.9 mg/L (average of 12.3 mg/L), respectively. Both the Cl^- and SO^{2-} concentrations are below the 250 mg/L and 400 mg/L allowable limits, respectively. The order of anion dominance is $HCO^- > SO^{2-} > Cl^-$.

The median concentrations of critical PTEs in the water vary in the following order: Fe > Pb > As > Mo > Cr > Ni > Cd > Sb > Cu (Fig. 2). All the samples show concentrations above the guideline values for Fe, Pb, As, Mo, Cr, and Ni. The As concentrations in the groundwater are in the range of 2.90 to 6.50 mg/L (Fig. 2) with a mean concentration of 4.50 mg/L, which exceeds the maximum permissible level set by the World Health Organization. The mobilization of PTEs in the groundwater is attributed to the weathering and dissolution of ore minerals [7], and the leaching of chemicals used in processing gold in the area during the ASM activities.

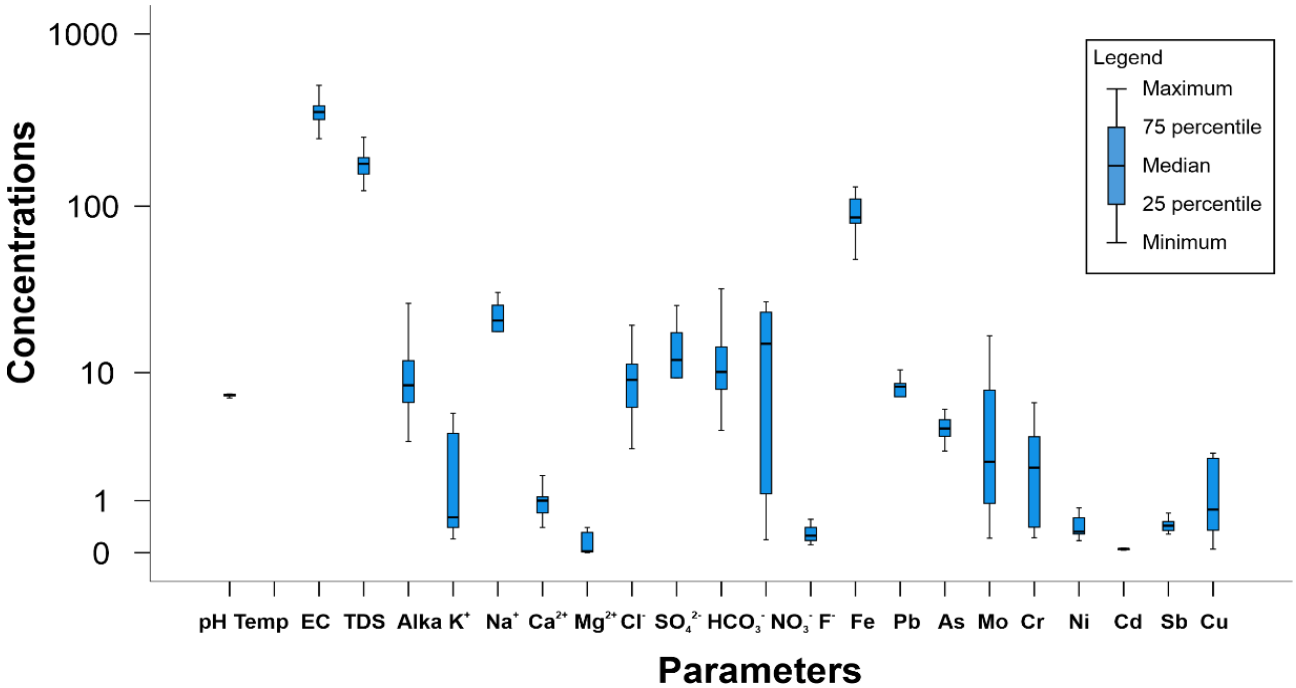

Fig. 2. Box and whisker plot showing the concentrations of hydrochemical parameters in groundwater of the Talensi District (Temp in ˚C, EC in µS/cm and all hydrochemical parameters in mg/L)

Table 1. Descriptive data about the hydrochemical characteristics of the Talensi District's groundwater

Parameters	Unit	Min	Max	Mean
pH		6.90	7.30	7.14
Temp.	°C	28.2	29.5	28.5
EC	µs/cm	247	504	358
TDS	mg/L	123	252	178
Alkalinity	mg/L	3.40	26.7	11.6
Na^+	mg/L	9.00	31	20.3
K^+	mg/L	0.20	5.40	1.80
Mg^{2+}	mg/L	0.01	0.40	0.20
Ca^{2+}	mg/L	0.40	1.80	0.90
Cl^-	mg/L	3	19.7	9.40
SO_4^{2-}	mg/L	1.10	25.9	12.3
HCO_3^-	mg/L	4.10	32.6	14.1
NO_3^-	mg/L	0.01	27.2	12.0
F^-	mg/L	0.10	2.30	0.50
Al	mg/L	10.8	23.1	15.3
Ag	mg/L	0.04	0.70	0.10
As	mg/L	2.90	6.50	4.50
Cd	mg/L	0.03	0.10	0.05
Co	mg/L	0.04	1.00	0.70
Cr	mg//L	0.20	6.40	2.10
Cu	mg//L	0.05	3.20	1.50
Fe	mg//L	48.8	129.5	89.1
Mo	mg//L	0.20	17.0	4.30
Ni	mg//L	0.20	0.80	0.40
Pb	mg//L	2.00	15.4	8.20
Sb	mg//L	0.02	0.70	0.40
Sr	mg//L	0.02	695	385
V	mg//L	0.90	28.5	7.50
Zn	mg//L	0.01	0.01	0.01
SI Calcite		-3.70	-2.65	-3.14
SI Aragonite		-3.84	-2.79	-3.32
SI Anhydrite		-3.70	-3.90	-4.49
SI Gypsum		-5.05	-3.69	-4.29
SI Halite		-9.08	-7.83	-8.35
SI Dolomite		-7.94	-5.32	-6.76

3.2. Hydrochemical facies

A Piper diagram (Fig. 3) was employed to decipher the specific groundwater compositions in the study area. Notably, Na-SO4-HCO3 and Na-SO4 water types emerged as the dominant water types constituting a substantial 40% each of the sampled water (Fig. 3). Additionally, Na-HCO3 water type contributes to around 20% of the sampled groundwater in the region. The prevalence of Na^+ in these water types is likely attributed to ion exchange reactions and mineral dissolution [8]. The interaction between meteoric water and soil bicarbonates leads to the formation of weak acid solutions, contributing to the gradual breakdown of carbonate minerals, which resulted in the HCO^- enrichment in the groundwater [9]. The significant levels of HCO^- concentrations in all the analysed samples, as well as within these water types, serve as evidence of the existence of carbonate rock formations within the aquifers of the Talensi District, aligning seamlessly with the local geological setting. The existence of SO^{2-} in the mixed waters provides information about the impact of atmospheric precipitation and ion exchange reactions [8]. This further emphasizes the intricate web of geochemical processes at play within the aquifer system.

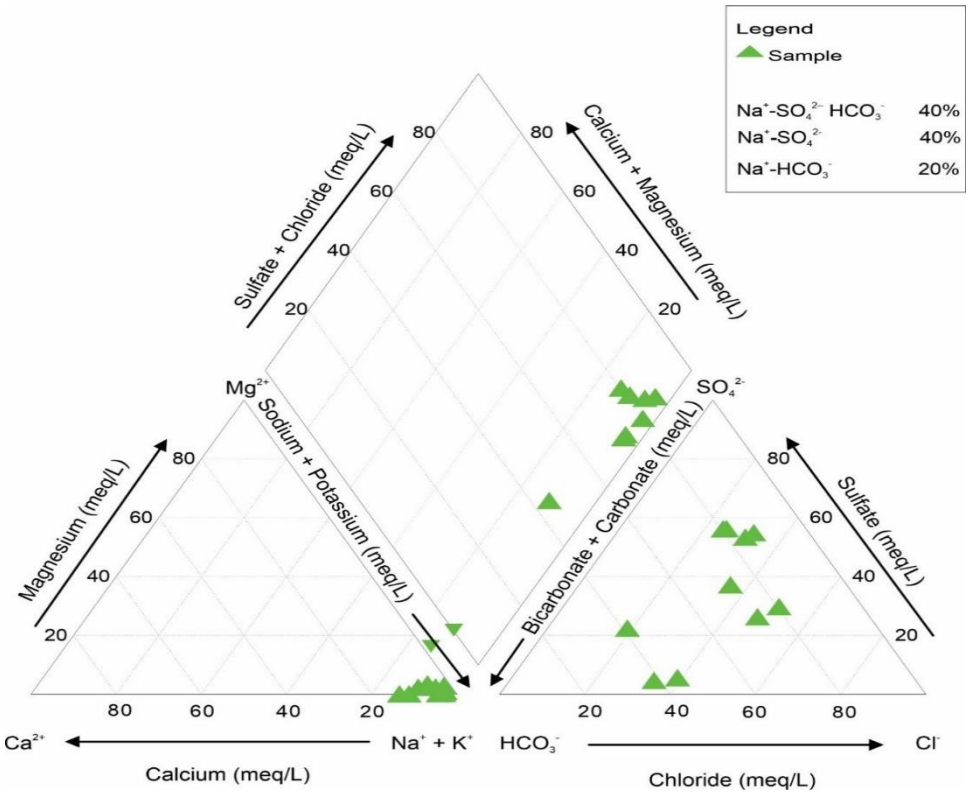

Fig. 3. Piper diagram illustrating the groundwater evolution and hydrochemical facies

3.3. Spatial distribution of groundwater arsenic concentrations

Arsenic (As) is the only carcinogen of concern among the trace elements, which shows extremely high concentrations in all the samples, in contrast to the recommended threshold of 0.01 mg/L. Thus, much attention has been given to the distribution of the As concentrations in this study. The northern and eastern parts of the district show higher As concentrations (Fig. 4), highlighting potential health effects. The As enrichment in groundwater might be related to gold ores that are rich in arsenopyrites [10]. The dominance of ASM practices in the area is another cause for elevated As levels in the groundwater. Ingestion of inorganic arsenic from contaminated water can have negative effects on humans [7]. Low doses and extended exposure to arsenic cause a range of health problems collectively referred to as "arsenicosis" [11].

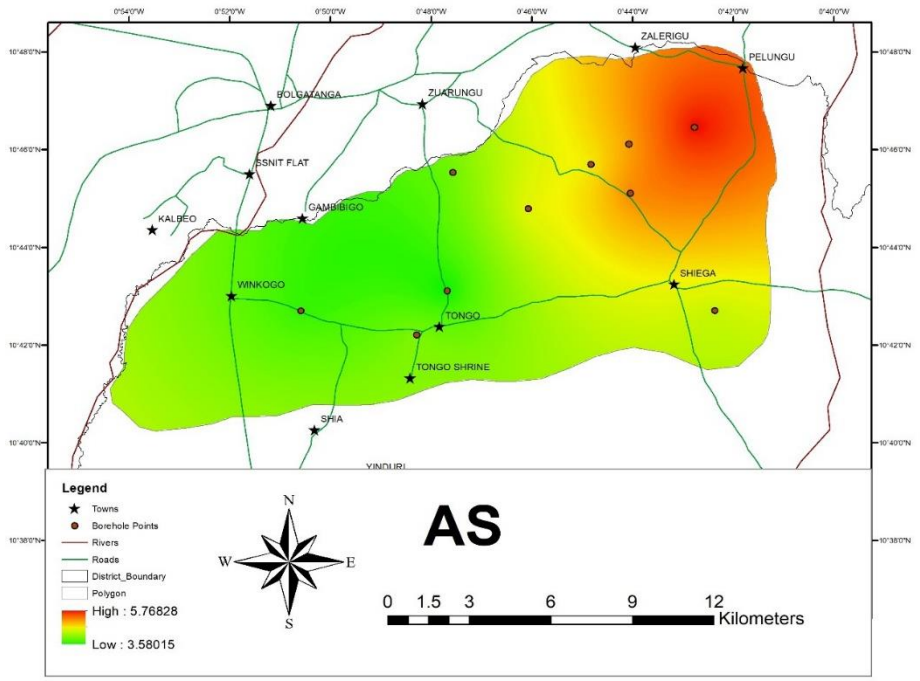

Fig. 4. Spatial distribution of groundwater arsenic concentrations in the study area

3.4. Factors controlling groundwater chemistry

The intricate relationships between many natural processes that impact the chemistry of groundwater, such as evaporation, precipitation, and rock weathering (rock-water interaction), are made clear using Gibbs diagrams [12]. Ion dissolution in groundwater mostly results from chemical reactions, nearby rock formations, and complex water-rock interactions [13]. The examination of these diagrams confirms that groundwater chemistry in the Talensi District is primarily defined by rock weathering dominance (Fig. 5). The Gibbs plots show a link between higher TDS values and the Na/ (Na^+ + Ca^{2+}) ratio, which suggests that cation exchange reactions involving Na^+ and Ca^{2+} play a substantial role in the variations in groundwater chemistry [14].

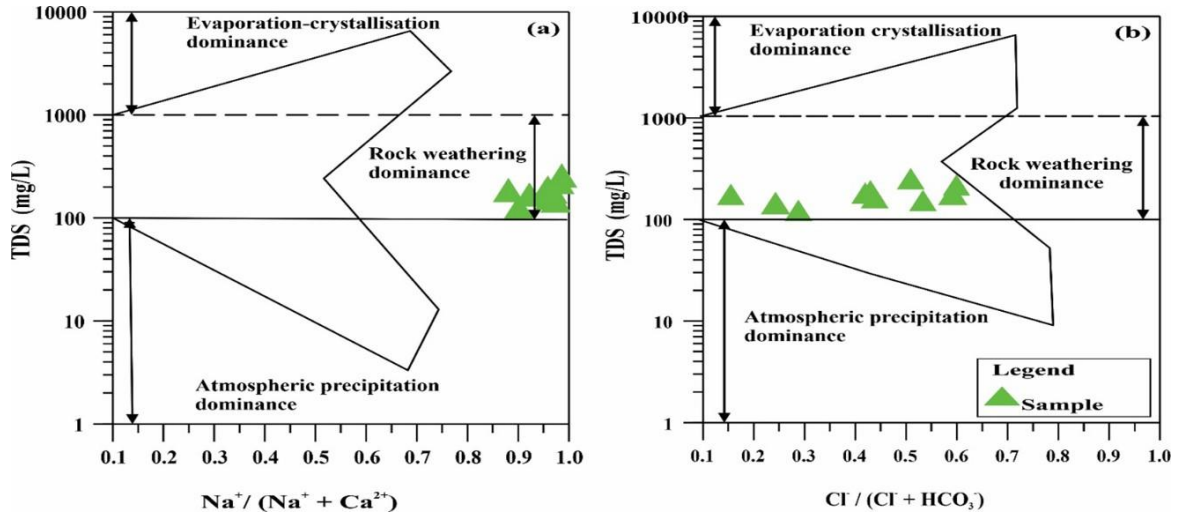

Fig. 5. Gibbs diagrams illustrating the main factors influencing the chemistry of groundwater in the research area

A bivariate analysis was used in addition to Gibbs plots to evaluate significant ion connections, highlighting the main sources of these hydrogeochemical parameters. Ions such as Ca^{2+}, Na^+, Mg^{2+}, Cl^-, and SO42- were used in the bivariate plots (Fig. 6). The aquifer's dominant hydrogeochemical processes are revealed by the plots close to a 1:1 equiline. Samples tend to group along the 1:1 equiline, indicating that weathering processes including calcite, halite, gypsum, and carbonate are dominant. In contrast, samples that diverge above and below the equiline are more likely to undergo reverse ion exchange processes or forward ion exchange reactions, respectively [15]. All samples are below the 1:1 equiline on the Ca^{2+} vs HCO3- plot (Fig. 5a), which indicates that the ions were enriched through forward ion exchange reaction. Similarly, the Ca^{2+} vs SO42- plot (Fig. 6b) shows that the majority of samples plot below the 1:1 equiline, demonstrating the significant impact of forward ion exchange on groundwater chemistry. However, one sample is close to the equiline, pointing to gypsum dissolution enriching the ions in that particular water sample. Also, the Na^+ vs Cl^- plot (Fig. 6c) shows that most of the samples are above the 1:1 equiline, indicating silicate weathering and reverse ion exchange are largely enriching the ions in the water and where ions of different charges can substitute each other as a result of complex geochemical processes. The samples that fall on a 1:1 equiline also indicate halite dissolution [16], which influences the quality of that water sample as the study area contains salt-bearing minerals. The bivariate plot of Ca^{2+} + Mg^{2+} vs SO42- + HCO3- (Fig. 6d) shows that all the samples fall below the 1:1 equiline, indicating that anions enriched in the water are predominately from forward ion exchange reaction.

The summary statistics shows computations of the groundwater's mineral phase saturation index (SI) (Table 1). The SI values range from -3.70 to -2.65 for calcite, with an average of -3.14. Anhydrite SI values range from -3.84 to -2.70 with an average of -3.32 while gypsum SI values fall between -5.05 to -3.69, with a mean of -4.29, aragonite SI values vary from -3.84 to -2.79, with a mean of -3.32. Similarly, the range of dolomite SI values is between -7.94 to -5.32, with an average of -6.76, and halite saturation indices are between -9.08 to -7.83, averaging at -8.35. However, all mineral types are undersaturated in the studied samples (Fig. 7), indicating a tendency for calcite and aragonite to precipitate under the current aquifer conditions [17]. In addition, the undersaturation identified in the samples for calcite and aragonite suggests that the early rapid dissolution of dolomite aided in the precipitation of calcite and aragonite. The complex geochemical process of de-dolomitisation emphasises the complex interaction between precipitation dynamics and mineral dissolution within the aquifer system [6].

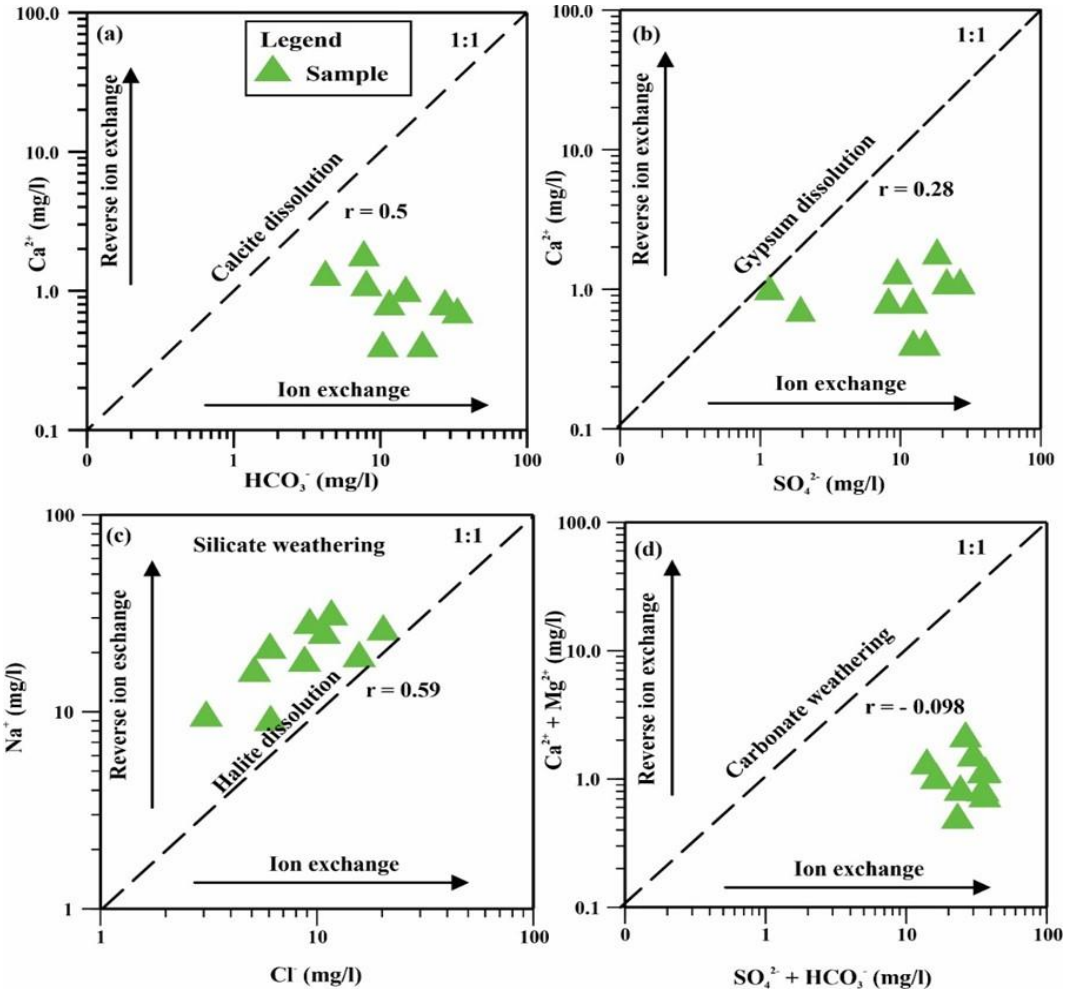

Fig. 6. Major element relationship depicting primary processes influencing groundwater chemistry

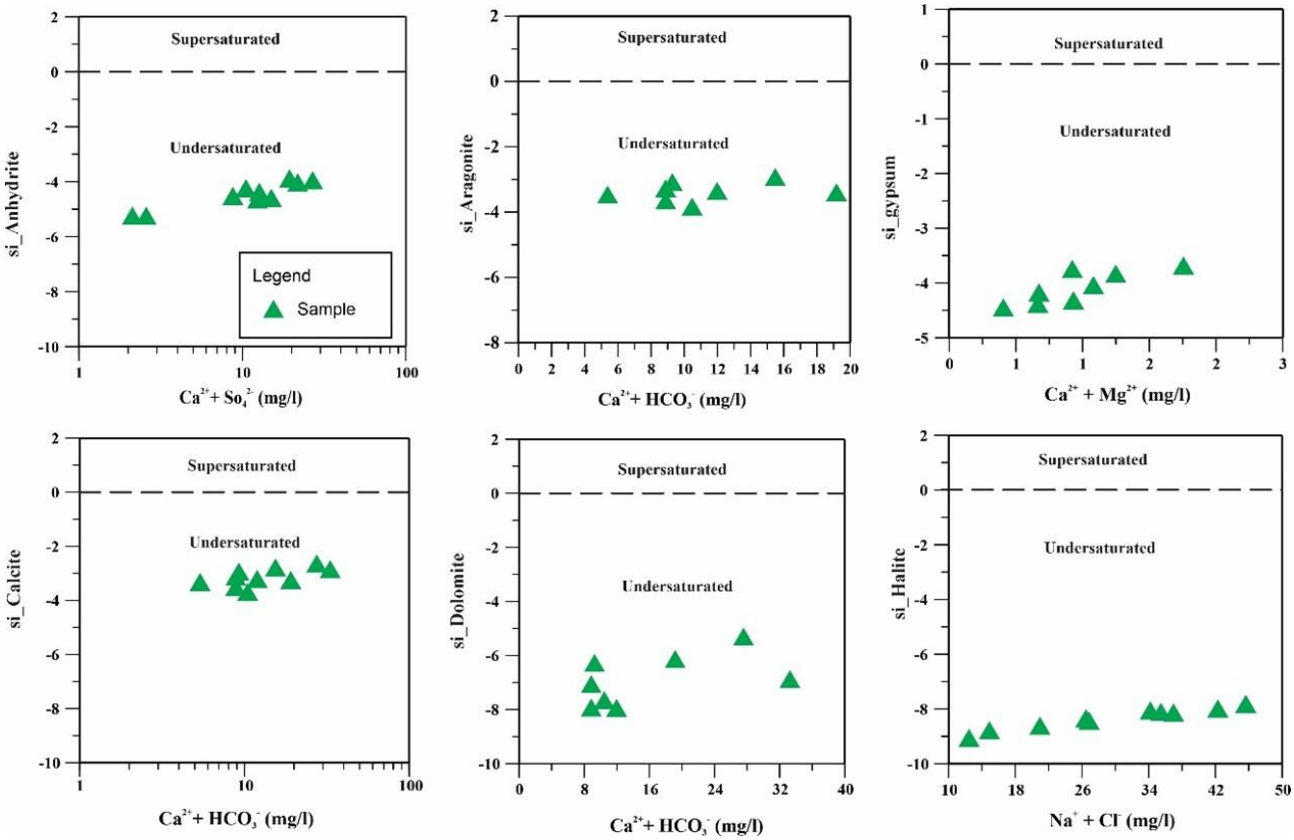

Fig. 7. Mineral phase saturation index in groundwater

3.5. Sources of groundwater constituents

The hydrochemical data was subjected to factor analysis using the principal component analysis criterion for component extraction. The dimensionality of the hydrochemical parameters was condensed into five components (Fig. 8) with eigenvalues above 1, which explained 94.65% of the total variance. The most important factor grouping is factor 2, which is strongly correlated with F^-, Cd, Cr, Al, Mo, Ag, V, As, K^+, Mg^{2+}, and Co (Fig. 8). Volcanic rocks in the study area contain these metals and ions and can release them into the groundwater during rock weathering [6]. Runoff and infiltration processes may cause As enrichment from the ore minerals like arsenopyrite and enargite, which comes from mined rocks and ore stockpiles that enter the groundwater [19].

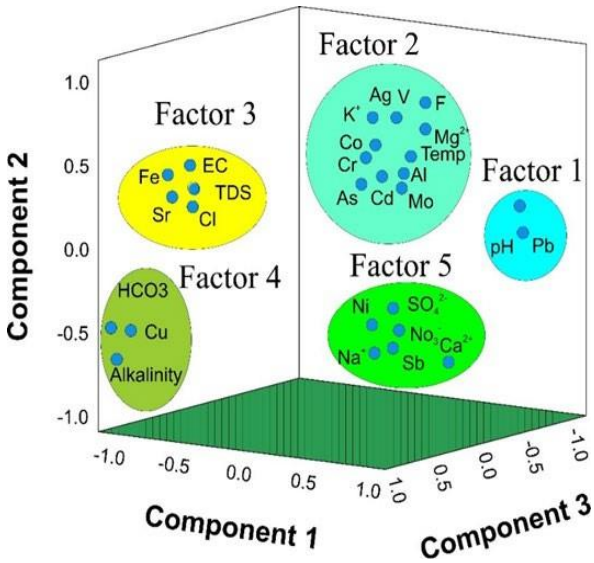

Fig. 8. Rotation plot of factor analysis using varimax rotation iteration

4. Conclusions

This study was aimed at examining the hydrogeochemical and anthropogenic factors influencing groundwater chemistry in the Talensi District. The findings suggest that the cation and anion concentrations follow the order: Na^+ K^+ > Ca^{2+} > Mg^{2+} and Cl^- > HCO^- > SO^{2-}. Furthermore, two main water types: Na-SO - HCO3 and Na-SO4 were found by evaluating the most prevalent water types in the study area. Concentrations of potentially toxic elements (PTEs) such as Fe, Pb, As, Mo, Cr, and Ni exceed the recommended levels in all samples. A mean concentration of 4.5 mg/L for As with a range between 2.90 to 6.50 mg/L was found in the groundwater. The localized weathering and dissolution of ore minerals during artisanal and small-scale mining (ASM) operations are the sources of arsenic mobilization in the groundwater.

Acknowledgements

This study is part of the BSc project work of the second author at the University of Mines and Technology, Ghana under the supervision of the first and third authors. The first author also acknowledges the Postdoctoral Research Fellowship Grant from the University of Johannesburg at the Department of Chemical Sciences

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