The Hydrochemical Characteristics of Groundwater in the Tarkwa Mining Area, Ghana

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Abstract: A study has been carried out on the groundwater in the Tarkwa mining area to establish the hydrochemistry of groundwater in the community. The groundwater was found to vary considerably in terms of chemical and physical properties. Generally, the water was mildly acidic (pH 4.3 to 6.7), moderately mineralized and fresh. Chemical constituents are generally low. The order of relative abundance of major cations in the groundwater is $Na > Ca > Mg > K$ while that of anions is $HCO_3 > Cl > SO_4$. The majority of groundwater clustered toward $Ca–Mg–HCO_3$ with the remaining being $Na-Cl$ and $Na-HCO_3$ water types. Weathering and ion exchange are probably the main processes through which major ions enter the groundwater system.

INTRODUCTION

In 1999 the United Nations Environment Programme (UNEP) reported that 200 scientists in 50 countries had identified water shortage as one of the two most worrying problems for the new millennium (UNEP, 1999). The reasons for the water crisis may be the rise in population, the desire for better living standards and the inefficiency of the way we use much of our water. Pollution is making more of the water that is available unfit for use. Both the people and governments are increasingly, seeking to solve the water problems by using subterranean supplies of groundwater instead. Groundwater has thus become the major source of water supply for domestic, industrial and agricultural sectors of many countries including Ghana. It is estimated that approximately one third of the world's population use groundwater for drinking (UNEP, 1999).

The exploitation of groundwater for the water supply needs of many rural communities in Africa has been on the increase in the last decade and, in Ghana, groundwater continues to play an important role in the socioeconomic development of the country. Realizing that most surface water resources are polluted, the government of Ghana has shifted attention from developing surface water resources to groundwater resource development and to supply communities in rural communities because of the anticipated high cost of treating polluted surface water resources (Kortatsi, 2007). Consequently, groundwater has become the principal source of potable water supply for the communities within the country. From an exploration survey carried out in Ghana by the Water Research Institute (WRI, 1993), about 90% of the rural and 25% of the urban communities depend largely on groundwater for their domestic water needs.

There are about 56,000 abstraction systems made up of about 10,500 boreholes, 45,000 hand-dug wells, and some other dugouts in the country (WRI, 1993). The emphasis or reliance on groundwater supplies for rural communities stems from the fact that groundwater sourcing is not only feasible but also the most economic source of potable water. It is perceived to be a safer source of drinking water with adequate protection and excellent microbial and chemical quality that requires minimum treatment. Processes such as cation exchange, dissolution of weathered mantle and mixing with existing water within the unsaturated zone during recharge normally determines the chemistry of groundwater. Even though the quest for clean and potable water has led to the exploitation of groundwater, it is prudent to note that this also comes with some form of pollution. Chemical and microbiological activities are the major threats to the effect of total reliance on groundwater as source of drinking water. Underground water comes into contact with ore-bearing rocks resulting in dissolution of elements into the water course.
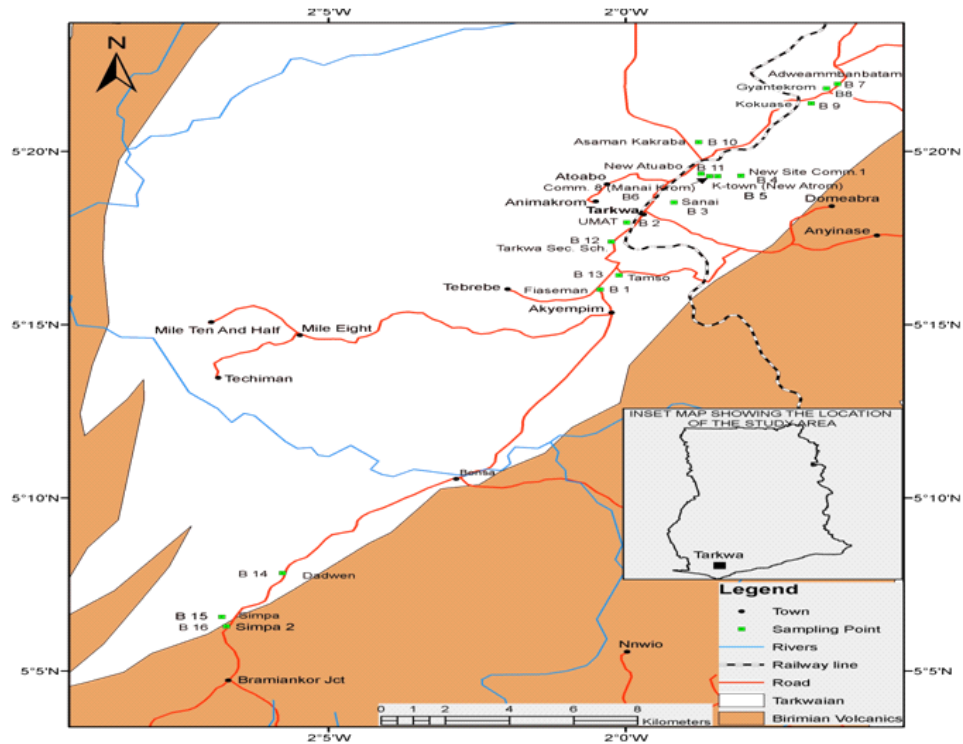
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Fig. 1: Map of study area showing location of sampling points

Groundwater development in the Wassa West District, which is home to major mining communities have often been hampered among other problems by contaminants from mining and mining related activities, improper waste disposal, leakage of underground storage tanks, and seepage of agrochemicals from munincipal and agricultural fields (Akabza, 2000). Groundwater in the Wassa West District run a high risk of pollution with industrial chemical from mining, municipal, industrial, and domestic waste because of the high density of mining companies, intensive small scale mining activities and urbanization. Pollutants released on the ground surface from mining activities may rapidly reach the aquifer and travel long distance in a very short time through preferential pathways (Tazioli *et al.*, 1995). Groundwater is, therefore, equally vulnerable to contamination from many sources. It has, therefore, become imperative to aim at identifying the various sources of contaminants and assessing the physical and chemical quality of the groundwater to ascertain their wholesomeness as well as the health impacts of the contaminants in groundwater on the communities.

MATERIALS AND METHODS

The study area: The Wassa West District, of which Tarkwa is part, is one of the Districts in the Western Region of Ghana. It is located between Latitude 5.00'N and 5.00 40'N and Longitudes 1.0 45′ W and 2.0 10′ W (Fig. 1). It is bounded to the north by the Wassa Amenfi District, the south by the Ahanta West District, the West by the Nzema East District and the East by Mpohor Wassa East District. The District has a total land area of 2354 km². The District is part of the Birimian and Tarkwaian geological formations which are regarded as the most economically important formations due to its mineral potentials (Kesse, 1985). It accounts for the existence of many gold and the only manganese mining companies in the country.

The climate of the study area is typically equatorial, generally with high temperatures and two tropical wet seasons from March to July and September to November. The harmattan dry and dust-laden winds that blow from the Sahara (North-East) and the southwesterly moist monsoon air mass from the south Atlantic Ocean influence climate in the area. These air masses meet at the Inter-Tropical Convergence zone (ITCZ), which moves north and south with the season once each year. From March to October when the ITCZ is far from the north of the area, the climate is cool and wet. From November to February, when it is just north of the area, however the climate is dry (Dickson and Benneh, 1980).

Annual rainfall data for the area indicates minimum and maximum values of 1449 and 2608 mm, respectively

with an annual average of about 1874mm (Bogoso Gold Ltd., 2002). The major wet season occurs from March to July with a peak in June and a minor wet season from September to October and a main dry season between December and February. The average relative humidity ranges from 70-90% (Bogoso Gold Ltd., 2002). The period of highest relative humidity occurs in May and June during the major wet season whilst the lowest relative humidity occurs in December to February, the main dry season. The soil in the area is heavily leached as a result of the high rainfall and is acidic in nature (pH of 4-6.5). In-situ chemical weathering which predominated over physical weathering produce these soils. The vegetation of the area is described as tropical rain forest, characterized by evergreen and a transition zone between the wet evergreen and moist tropical forest.

Geology of the area: The rocks of the study area do not have adequate primary porosity. The Birimian and Tarkwaian rocks that underlie the area are largely crystalline and inherently impermeable, unless fractured or weathered. Groundwater occurrence is therefore associated with the development of secondary porosity and permeability. The zones of secondary permeability are often discrete and irregular and occur as fractures, faults, lithological contacts and zones of deep weathering (Kortatsi, 2002). Groundwater in the area is acknowledged to occur in two distinct hydraulically connected aquifer system; an upper weathered zone aquifer and a deeper un-weathered aquifer or fractured zones and dyke contacts (Junner *et al*., 1942). The weathered zone aquifer is generally phreatic and the principal groundwater flow occurs where relic's quartz veins are more abundant. The regolith is generally dominated by clay and silt, rendering the aquifer highly porous, with high storage, but low permeability. Thus, the aquifers here are either un-confined or semi-confined, depending on the clay and silt proportion. Aquifers are recharged by direct infiltration of precipitation through brecciate zones and the weathered outcrop (Kortatsi, 2002).

The Tarkwaian system is made up of a sequence of clastic sedimentary rocks, which comprises sandstones, conglomerates and phyllites. It is spatial association with 'belt' rocks of the Birimian. It is regarded as detritus of Birimaian rocks and granitoids that was uplifted and eroded in the Eburnean event. The rocks of the Tarkwaian system consist of the Kawere Group, The Banket Series, the Tarkwa Phyllite and the Huni Sandstone. The Kawere Group is the oldest group and the conglomerates consist of silicified Birimian greenstone and hornstone with minor jasper, quartz, quartz-porhyry, tourmaline-quartz rocks with Birimian phyllites and schists in a matrix with quartz, feldspar, chlorite, carbonate, epidote and magnetit. The Banket

conglomerate consists of 90% quartz and the rest is Birimian schist, quartzite, hornstone, chert and gondite. It represents a fluviatile series. The Tarkwa Phyllite consists of chloritoid and magnetite or hematite with sericite and chlorite. Huni Sandstone (a quartzite) consists of variable amounts of feldspar, sericite, chlorite, ferriferous carbonate, magnetite or hematite and epidote (Junner *et al*., 1942; Kesse, 1985; Kuma, 2001). The general topography of the study area consists of low-lying plains with prominent hills and ridges usually less than 200 meters in height. A major topographical feature of the area is the abrupt change in the nature of the country at the boundaries between the Birimian and Tarkwaian system. Faulting and jointing, dips and scarp slopes of these beds determine the transverse valleys and gaps in ridges. The Huni sandstones and the Kawere conglomerates define low-lying swamps in this area.

Sampling: Groundwater samples were collected individually from a combination of domestic and municipal boreholes in Tarkwa (Fig. 1) into acid-cleaned high-density 1-L linear polyethylene sampling bottles with strict adherence to the sampling protocol as described by Gale and Robins (1989) and analyzed independently. Water samples from boreholes were pumped out using the existing infrastructure for over 20 min before samples were taken. Samples were filtered using Sartorius polycarbonate filtering apparatus and a 0.45 μm cellulose acetate filter membrane. At each point, two samples were collected for major ions and trace metal analyses. Samples for trace metal analyses were acidified to pH <2 after filtration with 10% analytical-grade HNO_3. On-site analyses of temperature, electrical conductivity, total dissolved solids (TDS), and pH were conducted using portable HACH conductivity meter and Metrolin model 691-pH meter, respectively. Before taking readings, all equipments were adequately calibrated. Water samples were transported in ice cooler on ice to the laboratory and stored at 4ºC prior to analyses.

Physicochemical analyses: Water samples collected were analyzed by both classical and automated instrumental methods prescribed by the standard methods for the analyses of water and wastewater and EPA (Standard Methods, 1998; EPA, 1983). The concentrations of the major ions sulphate (SO_4^{2-}) and nitrate (NO_3^-) were determined by ion chromatography (DIONEX ICS-90, Australia) whilst that of alkalinity, total hardness, HCO_3^- and chloride (Cl^-) were determined by the titration method. Sodium (Na) and potassium (K) were determined using the flame photometer (Sherwood, Model 420, UK). The ionic balance for the analyses was within ±5. All reagents used were of analytical grade and instruments were pre-calibrated prior to measurement. Replicate analyses were carried out for each determination to ascertain reproducibility and quality assurance.

Table 1: Physicochemical parameters, major ion constituents and saturation indices

Name	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16
Temp	28.30	27.4	27.5	26.8	27.8	26.7	27.2	27.2	27.1	27.7	27.7	27.5	27.4	26.1	25.8	26.7
pH	5.70	5.9	6.2	4.4	5.3	5.3	5.7	5.3	6.7	5.6	6.6	4.3	5.8	5.7	6.0	6.2
E.C µS/cm	211.0	95.6	140.6	354	107.3	107.3	194	391	421	132.7	49	420	148.7	147.5	232	129.8
TDS mg/L	94.70	41.5	61.5	152.8	45.6	45.6	83.3	203	181.7	69.2	25.2	180.1	65	64.5	102.4	56.3
TH mg/L	48.00	22.0	16.0	136.0	36.0	20.0	60.0	196.0	176.0	8.0	20.0	176.0	12.0	36.0	72.0	16.0
TA mg/L	33.00	43.0	10.0	125.0	41.0	23.0	30.0	199.0	198.0	7.0	23.0	172.0	4.0	57.0	92.0	9.0
Ca^{2+} mg/L	13.24	8.8	3.86	45.81	10.35	5.16	15.14	62.28	58.79	1.26	5.16	55.79	2.56	10.35	26.03	3.86
Na^+ mg/L	26.16	21.74	21.5	19.82	11.1	20.52	18.86	39.26	34.02	24.12	9.36	31.68	21.22	19.84	34.84	19.96
Mg^{2+} mg/L	7.29	3.55	2.46	24.32	6.1	3.19	6.47	35.25	31.6	1.2	3.19	31.6	1.73	7.1	9.66	2.46
K^+ mg/L	9.10	6.40	6.20	7.50	5.40	4.50	5.60	5.50	5.20	8.50	4.40	5.70	5.60	4.70	8.60	7.80
HCO_3^- mg/L	75.55	93.77	21.79	272.38	89.34	50.12	70.73	433.66	431.52	15.18	50.12	374.72	8.75	124.13	200.4	19.65
Cl^- mg/L	25.36	29.59	33.25	13.74	10.57	25.36	21.95	33.82	15.85	39.43	10.57	19.02	39.1	14.79	46.74	33.09
SO_4^{2-} mg/L	25.80	0.75	3.25	54.75	4.5	1.28	16.5	32	17.5	1.25	2.5	42.5	0.75	11.5	1.85	4.25
NO_3^- mg/L	1.220	0.42	2.11	0.34	0.13	0.84	0.21	0.42	0.46	2.83	0.51	0.25	2.07	0.34	0.46	1.48
Sat. indices																
Gypsum	-2.73	-4.39	-4.08	-2.02	-3.55	-4.36	-2.85	-2.19	-2.45	-4.98	-4.05	-2.09	-4.89	-3.17	-3.63	-3.96
Calcite	-2.86	-2.75	-5.16	-1.37	-3.25	-3.8	-2.82	-0.67	-0.58	-6.19	-3.78	-1.09	-5.96	-2.79	-1.91	-5.28
Halite	-7.81	-7.82	-7.76	-8.22	-8.55	-7.9	-8.01	-7.55	-7.93	-7.64	-8.62	-7.89	-7.7	-8.16	-7.43	-7.82
Dolomite	-5.63	-5.54	-10.2	-2.67	-6.38	-7.47	-5.65	-1.24	-1.07	-12.1	-7.43	-2.08	-11.8	-5.39	-3.88	-10.4

TA = total alkalinity; TH = total hardness

RESULTS AND DISCUSSION

Hydrochemistry: The result of the chemical analysis of the groundwater is presented in Table 1. The Groundwater in the studied area showed a wide range of characteristics in terms of physicochemical parameters and elemental concentrations. The groundwater temperature varied from 25.8 to 28.3ºC. The pH of the groundwater ranges from 4.3 to 6.7 with a mean and median value of 5.67 and 5.70, respectively. The pH of the groundwater in the study area could thus be described as acidic. As much as 87.5% of the groundwater sampled had their pH values outside the recommended range of 6.5-8.5 for potability (WHO, 2004).

The Electrical Conductivity (EC) of groundwater ranges between 49-421µS/cm with a mean and median value of 205.1 and 148.1 µS/cm, respectively. The electrical conductivity of most fresh waters ranges from 10 to 1000 µS/cm but may exceed 1000 µS/cm (Chapman, 1992). The low concentration of ions in the groundwater may probably be due to short residence times in that there is not enough time for the water to interact with the host rocks to cause dissolution. These low and varied values could also be attributed to the discrete nature of the aquifers in the study area.

The electrical conductivity was strongly correlated with the concentration of Ca, Mg, and HCO_3^- as indicated by a linear relationship (Fig. 2a) between Ca + Mg and electrical conductivity for groundwater samples. These ions are generally derived from the dissolution of carbonate minerals. A plot of the EC versus TDS for the aquifers (Fig. 2b) gives a high correlation coefficient of 0.977, thus confirming the linear relationship of these parameters and the efficacy of the field measurements.

Alkalinity values ranged from 4.0 to 199.0 mg/L. A plot of these values against Ca+ Mg/Na (Fig. 3) shows a classical relationship where low alkalinity values are associated with calcium and magnesium. High HCO_3^- alkalinity could exist in the presence of Na dominance,
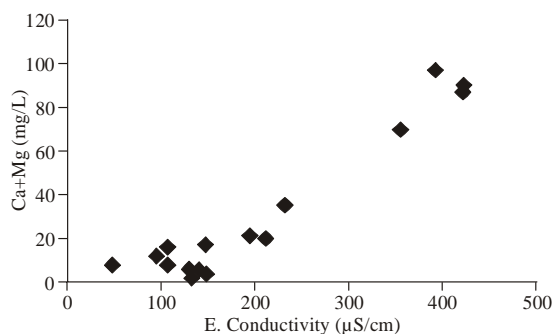

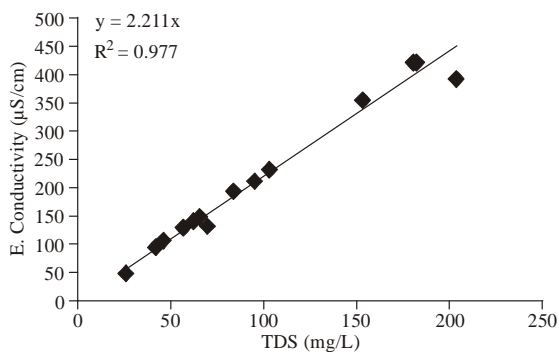Fig. 2a: Correlation between EC and Ca + Mg

Fig. 2b: Correlation between EC and TDS

which develops through cation exchange, calcite precipitation both of which decreases the Ca+Mg/Na ratio, and evapotranspiration enrichment of all ions (Hayashi et al. 2004). The relationship between total cation and alkalinity (Fig. 4) could be used to indicate the influence of mineral weathering on water chemistry (Kim *et al*., 2004). The plot of total cation against alkalinity showed some deviation from the 1:1 line (Fig. 3). The observed deviation could be due to other chemical processes, such as oxidation of ammonium and/or organic matter. The oxidation of ammonium and
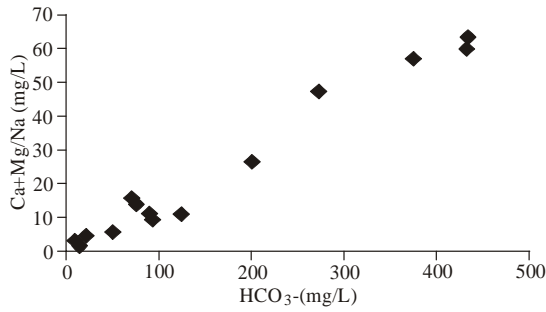
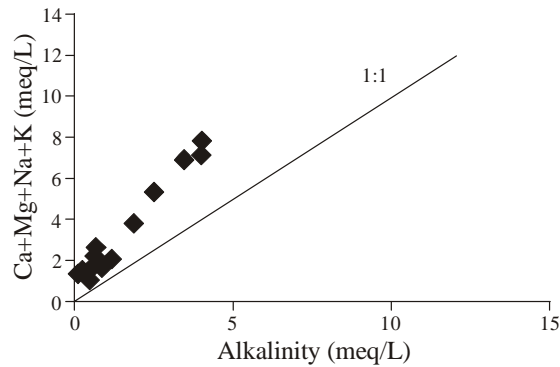Fig. 3: Plot of Ca+Mg/Na against HCO_3^-

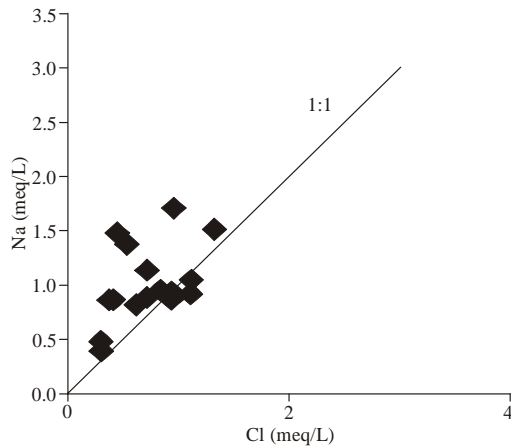Fig. 4: plot of total cation against alkalinity

Fig. 5: Plot of Na^+ as a function of Cl^-

organic matter decreases alkalinity and therefore, the total cation concentrations become unbalanced by alkalinity (Kim *et al*., 2004).

The Na-Cl relationship was used to identify the mechanisms for acquiring salinity and saline intrusions (Dixon and Chiswell, 1992; Sami, 1992). A plot of Na^+ as a function of Cl^- (Fig. 5) in the groundwater samples indicate that there is deviation from the expected 1:1 relation and leaned towards the Na^+ side, implying some of the Na^+ is derived from other processes. This is corroborated with the poor correlation between the two ions (r = 0.47). The low concentrations and poor correlation of Na^+ and Cl^- in water samples suggests that the dissolution of halite might not be an important factor regulating the concentration of these ions in groundwater. Furthermore, most of the groundwater samples deviated from the 1:1 line, indicating thus that Cl^- salt influence may not be an important process regulating water chemistry in the Tarkwa area. This assertion is confirmed by the low Cl^- to sum of anions ratio with a low mean and median value of 0.11 and 0.082 respectively. Thus ion exchange reaction is more plausible reason accounting for the excess Na over Cl.

Saturation indices: The saturation state of the groundwater was reviewed with respect to the major carbonate minerals in order to investigate the thermodynamic controls on the composition of the groundwater and the approximate degree to which the groundwater has equilibrated with the various carbonate mineral phase. The quality of groundwater also depends on the mineralogy, reactivity of drift materials and the degree of equilibrium that has been attained between water and rock (Robins, 2002).

The saturation indices were determined using the hydrogeochemical equilibrium model, Phreeqc for Windows (Apello and Postma, 1999). The saturation index (SI) of groundwater samples with respect to mineral precipitation is expressed by:

$$SI = \log_{10}(IAP/Ksp)$$

where IAP is the ion activity of the solution and Ksp is equilibrium constant which is the solubility product at a given temperature. The thermodynamic data used in this computation were those contained in the default database of the Phreeqc for Windows.

Supersaturation (SI > 0) indicates that precipitation is thermodynamically favorable in spite of the fact that slow rates of reaction can inhibit precipitation. Undersaturation (SI < 0) on the other hand signifies that dissolution is favored. The saturation indexes indicate that the groundwater in the study area is undersaturated with respect to calcite, dolomite, gypsum and halite (Fig. 6).

Groundwater characteristics: The chemical composition of groundwater from the studied area is shown on the phase diagram in Fig. 7. The water samples could be divided into three distinct types with two end-members: (Ca+Mg)-rich and (Na+K)-rich waters

The ionic dominance for water bodies according to Stumm and Morgan (1981) are: Ca > Mg > Na > K and $HCO_3 > SO_4 > Cl$ for fresh waters, and Na > Mg > Ca > K and $Cl > SO_4 > HCO_3$ for waters of marine origin. Major cation and anion concentrations dominance pattern observed in this study were generally in the order: Na > Ca > Mg > K and $HCO_3 > Cl > SO_4$ and thus indicating partial cationic and anionic characteristics of fresh water.
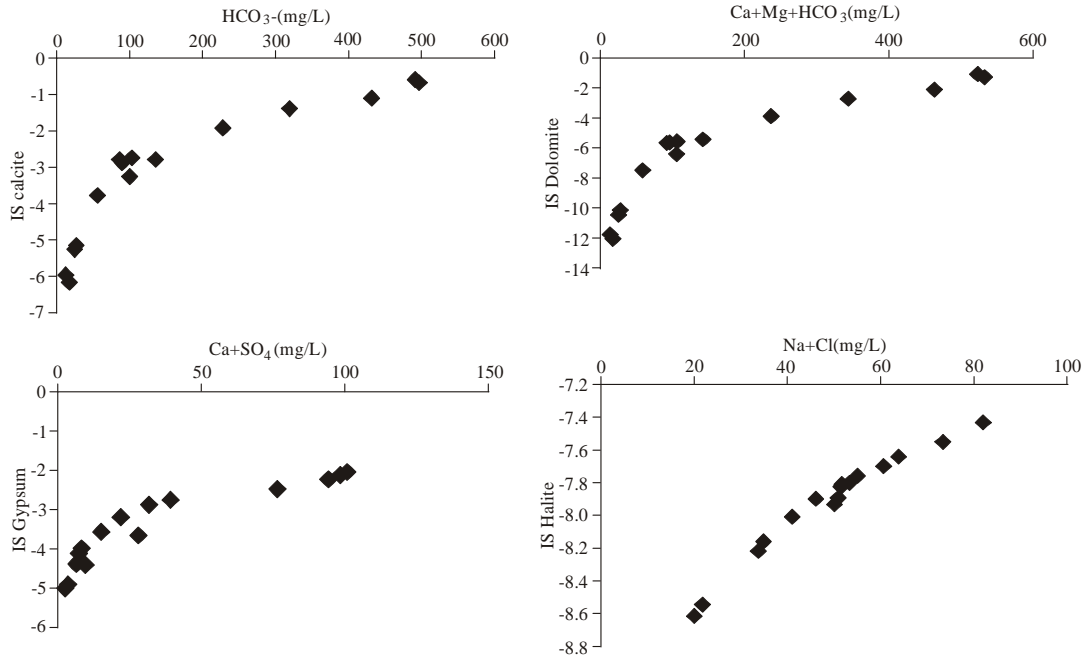
Fig. 6: Saturation Indices (calcite, dolomite, gypsum and halite) of groundwater samples
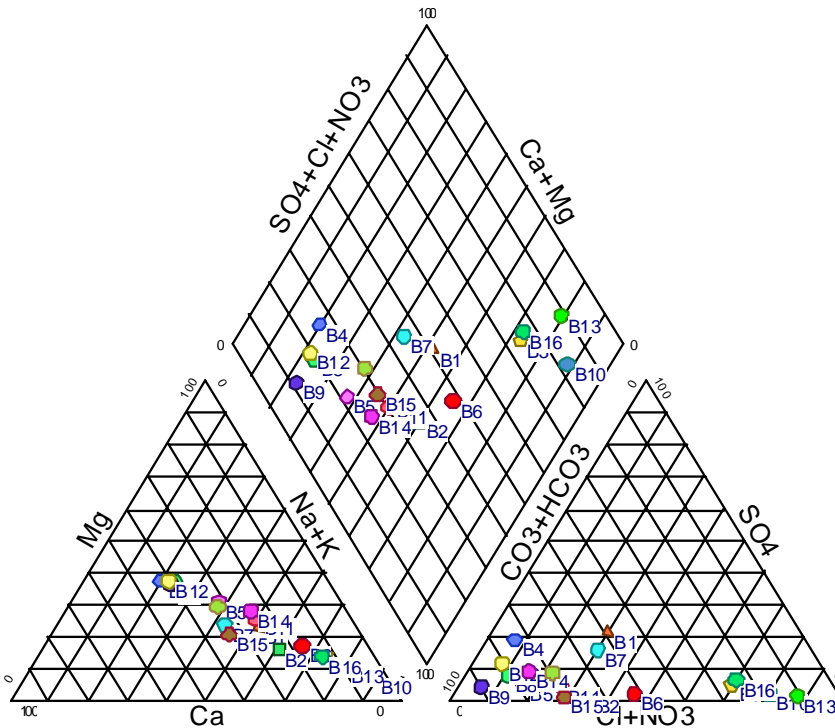

Fig. 7: Trilinear piper plot of chemical composition of groundwater samples. These end members are distinct in anion chemistry. Type I waters consist of Na-Cl mainly and constituted 31.3% of the samples and were characterised by comparatively low electrical conductivities (mean conductivity 152.56 µS/cm). Type II waters belong to the Ca–Mg–HCO$_3$ type and constituted 62.5% of the samples

The analysis also showed an enrichment of Na^+ and depletion of Ca^{2+}. The observed ionic dominance pattern may have resulted from ion exchange reactions in which sodium displaces calcium and magnesium in the groundwater (Edmunds et al. 2003). Natural softening of groundwater could also involve ion exchange and be a possible cause of the observed trend. The natural softening process is given by the equation below:

$$CaCO_3 + H_2CO_3 + 2Na_{ex} \rightarrow Ca_{ex} + 2Na^+ + 2HCO_3^-$$
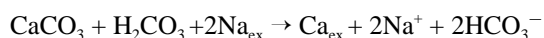
This being in accordance with the soft nature of the groundwater and the argillaceous nature of the soils in the Tarkwaian geological formation that favours ion exchange.

CONCLUSION

The results of the groundwater chemistry revealed generally low concentrations of physico-chemical parameters. The pH of the groundwater is acidic and acidification of the groundwater is for the most part due to natural biogeochemical processes. Nonetheless the majority of the samples (87.5%) fall within natural water pH range 4.5-7.0. The low pH and physico-chemical parameters coupled with bicarbonate dominance may be an indication of young aggressive groundwater. The major ion concentrations dominance pattern observed in this study were in the order of $Na > Ca > Mg > K$ and $HCO_3 > Cl > SO_4$ and indicated partial cationic and anionic characteristics of fresh water. The chemistry of groundwater is influenced by mineral weathering and cation exchange. The anthropogenic influence on the groundwater is at present minimal. Water quality is good for the majority of the groundwater as the majority of them were within the permissible drinking limits of World Health Organization (WHO, 2004).

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