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Hydrochemical characteristics of rural community groundwater supply in Blantyre, southern Malawi

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ABSTRACT

The purpose of this research was to characterize the quality of groundwater for drinking and irrigation in Blantyre, Malawi as well as identify some geochemical processes governing mineralization of major and some minor elements. The aquifer studied is part of the extensive crystalline basement complex. The suitability and classification involved confirmatory analysis of the results with World Health Organization and Malawi Standards Board groundwater guideline values. The water samples were analyzed for major descriptors (pH, Temperature, turbidity, major ions, total dissolved solids and electrical conductivity (EC), using standard methods. Besides, arsenic, iron and fluoride were analyzed as well. Multivariate statistics (especially Hierarchical Cluster Analysis and Factor Analysis), hydrographical methods (i.e. Piper diagram) and geochemical modeling programs (AquaChem and PHREEQC) were used to characterize the quality and explain the sources and evolution of groundwater. Suitability of groundwater for irrigation was assessed using Wilcox method which identified BH01, BH16 and BH21 as high salinity areas. Incidentally, the three boreholes had relatively higher sulfate and nitrate concentrations than the rest. Nevertheless, the groundwater was found to be within acceptable limits for drinking quality except elevated concentrations of nitrate, fluoride and iron in some boreholes compared with WHO standards, despite meeting the national standards. Borehole BH01, BH02, BH07, BH13 and BH18 exhibited nitrate concentrations greater than national standards (45 mg/L) an indication of groundwater contamination. Furthermore, the groundwater is slightly acidic to slightly above neutral with total dissolved solids less than 500 mg/l. Generally, groundwater was undersaturated with respect to both calcite and dolomite while oversaturated with respect to halite, goethite and hematite. Silicate and carbonate weathering were identified as main mineral sources for major ions in groundwater. There is a dire need for more studies and monitoring of the groundwater in this area to safeguard the resource and human health.

1. Introduction

Groundwater quality has recently gained significant attention in rural water supply due to its reliability and dependable nature. Even though groundwater contributes only 0.6% of the total water resources world over (Meenakshi and Mehshwari, 2006), rural communities largely depend on it due to intermittent and inadequate piped water supply. Groundwater provides a relatively clean, reliable and cost effective resource (Bovolo et al., 2009) with good natural quality that is adequate enough for potable supplies while demanding minimal treatment attention (Yidana, 2010). However, natural factors and anthropogenic activities degrade some of the aquifers rendering them unfit for human consumption (Epule et al., 2011).

Globally, about 25–40% of the drinking water is derived from groundwater (Morris et al., 2003). While the quantity of freshwater has dwindled appreciably (Pritchard et al., 2008), groundwater quality is threatened from liquid waste (von der Heyden and New, 2004) and fertilizer application. Thus, the current generation faces the challenge to conserve water resources in the wake of global

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change.

Developing countries are currently facing major challenges in terms of inadequate and safe drinking water supply (DeGabriele, 2002) aggravated by high population growth. It is postulated that at least 44% of the population in sub-Saharan Africa does not have access to clean and reliable water supply (Dungumaro, 2007). This condition threatens human health and plant growth (Olajire and Imeokparia, 2001), thereby adversely affecting economic development and social prosperity (Milovanovic, 2007). Therefore it is of noble cause to assess the groundwater quality and ascertain its suitability for drinking and irrigation purposes.

In Malawi, 85% of rural people have some form of access to safe drinking water (World Bank, 2013 data, http://data.worldbank.org/indicator/SH.H2O.SAFE.RU.ZS) of which about 37% use boreholes as their main source (Staines, 2002) and consumed without any form of treatment (Pritchard et al., 2007, 2008). According to Environmental Affairs Department (EAD, 2004), about 46% of people in the rural area of Malawi have access to potable water in the form of tap (10%), borehole (29%) and protected wells (7%). The rest of the population in the rural areas draw from hand dug wells (Pritchard et al., 2008), providing raw water supplies which contributes to high water borne disease incidences. School children are vulnerable to contaminated drinking water since they are not easily monitored when taking water in rural areas.

In the wake of such worries, scientists locally and elsewhere have studied and assessed the quality of groundwater in the aquifers. Various elements ranging from essential to health threatening have been determined. Variations have been attributed to mainly the geologic input of the aquifer strata (Mapoma et al., 2014). However, in some instances human activities, such as agriculture and irrigation, have contributed significantly to increased loads of minerals as well as their mobilization such as heavy metals, fluoride and arsenic. The health implications of such loading are numerous, especially on human health, such as fluorosis, arsenicosis, cancer and many more.

Guidelines based on health implications offer assurance to communities using groundwater. Various studies on aquifers in specific areas present facts on the quality of groundwater assuring communities of its quality. In some instances results from adjacent aquifers are used as standards to certify safety of groundwater to be abstracted. However, analysis of groundwater on the site to be exploited is the best assurance a community can get. In Blantyre, Malawi, a study done in Lunzu Area (adjacent to Machinjiri) indicated that the water quality of the aquifer is good (Palamuleni, 2002). However, it is expected that groundwater quality can vary in such aquifers within meters of each sampling point. As such, this study was carried out to assess the groundwater suitability for domestic and irrigation in Machinjiri based on both WHO and Malawi Standards. Furthermore, a multivariate analysis was perfumed to evaluate the sources and geochemical controls. The results of the study will provide baseline data on groundwater geochemistry in the area as well as incite on groundwater management and monitoring. Above all, the paper will assist in understanding of the geochemical processes governing groundwater as a starting point of future research in the area.

2. Geomorphology and hydrology of the study area

Machinjiri is a rural setting consisting of various villages within Blantyre District. Blantyre District hosts the largest commercial and industrial city of Malawi. It is the geopolitical capital of Southern Region of the country located in the Shire Highlands at 15° 42″S and 35°E coordinates (Fig. 1). The district is 1792 km^2 in area with undulating topography ranging from an elevation of about 780 to 1612 m above sea level comprising of hills, plateau and ridges and the natural drainage system (Geohive, http://www.geohive.com/cntry/malawi.aspx). In terms of geology, the district is part of the crystalline basement complex that formed during the late Precambrian and lower Paleozoic age. Carter and Bennett (1973); Chilton and Smith-Carington (1984) have both described the geology of Malawi as mainly underlain by the basement complex that is divided into weathered (comprising of plains and plateau areas) and fractured basement (mainly occupying the highlands and hilly places). Machinjiri area thus belongs mainly to the fractured basement system whose extensive rock formation consists of impenetrable pyroxene granulite and syenitic gneiss. Luckily, since Blantyre is on the eastern edge of the southern branch of the East African Rift Valley where prominent faults occur, the basement is fractured enough for potential aquifers to exist for groundwater exploitation (Mapoma and Xie, 2014; Mapoma et al., 2014).

3. Materials and methods

3.1. Sampling and sample analysis

In this study, groundwater was sampled from 21 running hand pumped boreholes (coded as BH01 – BH21) within Machinjiri Traditional Authority. The sampling and subsequent analysis took place in September, 2013. The water samples were filtered on site using 0.45 μm membrane filters. Twenty one samples for cation analyses were stored in 100 ml polypropylene bottles and acidified to pH $\leq$ 2 using HNO_3. The other set of 21 samples for anion analysis were not acidified. The samples were immediately stored in a refrigerator at the Department of Physics and Biochemical Sciences of University of Malawi, The Polytechnic. Preliminary analyses included immediate in situ measurements of pH (Wagtech pH meter), temperature, electric conductivity (EC) and total dissolved solids (TDS) (Wagtech EC/TDS/°C meter) and turbidity (Wagtech Turbidity meter). Bicarbonate (HCO_3) was analyzed in the Department of Physics and Biochemical Sciences' chemistry laboratory via APHA titration technique. Borehole site elevation and coordinates were measured using a portable hand held global positioning system (GPS).

3.2. Laboratory analysis

Chemical analysis of the samples was done at State Key Laboratory of Biogeology and Environmental Geology of China University of Geosciences (Wuhan) within one week of sampling. All cations, namely Arsenic (As) calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na), were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (ICAP6300). The average analytical error for major and trace chemical constituents using ICP-OES is less than ±5%. In contrast, major anions (chlorine, Cl and sulfate, SO_4) as well as fluorides (F), nitrates (NO_3) and nitrites (NO_2) were determined by ion chromatography (IC) (Dionex ICS 1100) with a detection limit of 0.01 mg/L. Total hardness of water was determined using empirical method (EPA, http://www.epa.ohio.gov/portals/35/permits/IndustrialStormWater_Final_GP_AppJ_dec11.pdf) (Equation (1)).

$$TH(\text{mg } CaCO_3/l) = 2.497[Ca] + 4.118[Mg] \quad (1)$$

3.3. Data analysis and interpretation

The data obtained from laboratory analysis was used to analyze the quality of groundwater for both domestic (mainly drinking) and irrigation purposes. This was achieved through multi-comparison

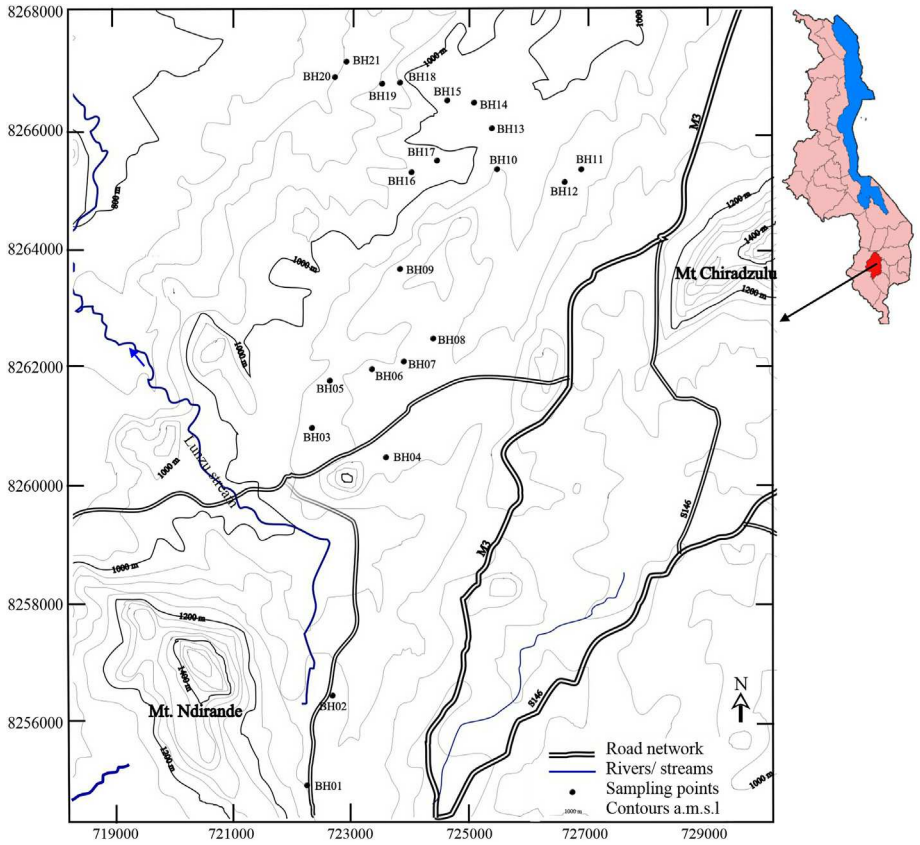

Fig. 1. The study area within Blantyre District of Malawi including sampling points and average mean sea level elevation (a.m.s.l).

of results obtained with local (Malawi Standards Board (MSB), 2005) and international standards (WHO, 2008) as well as calculation of Sodium Adsorption Ratio (SAR) (Equation (2)).

$$SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}} \quad (2)$$

where the ionic concentrations are in mmol/l.

The computed SAR values and field EC data were used to explain the suitability of groundwater for irrigation purposes. In this study the Wilcox Diagram for classifying water quality suitability for irrigation purposes was adopted and graphical output implemented through AquaChem software (Schlumberger Water Services, 2014, http://www.swstechnology.com/groundwater-software/water-quality-analysis/aquachem). The diagram relates sodium adsorption ratio (SAR), which expresses the sodium or alkali hazard, to EC (a salinity hazard). The EC in irrigation water can be classified into low (C1), medium (C2), high (C3) and very high (C4) salinity zones. Zones (C1–C4) have the value of EC less than 250, 250–750, 750–2250 μS/cm and more than 2250 μS/cm, respectively. The sodium hazard is expressed, in terms of classification of irrigation water, as low (S1:<10), medium (S2:10–18), high (S3:18–26) and very high (S4:>26).

The geochemical modeling program PHREEQC v2.8 (Parkhurst and Appelo, 1999), implemented with MINTEQ.v4 database (Allison et al., 1991), was used to calculate saturation indices (SI) as the log of the ratio between ion activity product and the equilibrium constant (Güler and Thyne, 2004; Belkhiri et al., 2012). The Langelier Saturation Index (LSI) was computed to evaluate scaling potential of groundwater in the area. Whenever the computed Langelier Saturation Index (LSI) is less than 0, the water is recognized to be undersaturated with respect to calcium carbonate. The undersaturated water has a tendency to remove existing calcium carbonate protective coatings in pipelines and equipment. However an LSI = 0 is where water is considered to be neutral and devoid of neither scale-forming nor scale removing. In contrast, an LSI > 0 is observed in supersaturated water with respect to calcium carbonate ($CaCO_3$) and scale forming may occur.

Extrapolation of hydrochemical water facies was achieved by computation using AquaChem 2012.1 and observation made from piper diagram (using USGS GW-Chart software).

Concentration of silica and TDS together with various parameter ratios (Table 1) (extracted from AquaChem 2012.1) guided us to present self explanatory graphs and meaningful interpretation of results.

In this study a multivariate statistical approach together with Pearson's correlation analysis were used to analyze data using IBM SPSS statistics version 20 (IBM, http://www-01.ibm.com/software/analytics/spss/). All chemical variables determined in the 21 samples were analyzed using Hierarchical Cluster Analysis (HCA) and Factor Analysis (FA). The HCA and FA were used as a quantitative and independent approach for groundwater classification allowing grouping of the groundwater samples and making of correlations between chemical parameters and groundwater samples, respectively. In this case the objective of HCA was to examine and classify boreholes based on distribution of the hydrochemical dataset. The Euclidian distance was used as a similarity/dissimilarity measure, whereas the Ward's linkage method was used to link clusters (Yidana, 2010).

The FA technique was considered useful in this study in order to identify underlying variables that explain the pattern of correlations within the observed physico-chemical elements. The aim was

Table 1
Silica, TDS and various parameter ratios used to interpret results (Extracted from AquaChem 2012.1 software).

Parameter	Attention value	Conclusion
SiO_2 (mmol/L)	>0.5	Volcanic Glass or hydro thermal water possible
HCO_3/SiO_2	>10	Carbonate weathering
	>5 and <10	Ambiguous
	<5	Silicate weathering
SiO2/(Na + K−Cl)	<1	Cation exchange
	>1 and <2	Albite weathering
	>2	Ferromagnesian Minerals
(Na + K−Cl)/(Na + K−Cl + Ca)	>0.2 and <0.8	Plagioklase weathering possible
	<0.2 or >0.8	Plagioklase weathering unlikely
Na/(Na + Cl)	>0.5	Sodium source other than halite − albite, ion exchange
	=0.5	Halite solution
	<0.5, TDS >500	Reverse Softening, seawater
	<0.5, TDS <500 and >50	Analysis Error
	<0.5, TDS <50	Rainwater
Mg/(Ca + Mg)	=0.5 and HCO_3/Si >10	Dolomite Weathering
	<0.5	Limestone-dolomite weathering
	>0.5	Dolomite dissolution, calcite precipitation or seawater
	<0.5 and HCO_3/Si < 5	Ferromagnesian Minerals
	>0.5	Granitic weathering
Ca/(Ca + SO_4)	=0.5	Gypsum dissolution
	<0.5, and pH < 5.5	Pyrite oxidation
	<0.5, and pH neutral	Calcium removal - ion exchange or calcite precipitation
	>0.5	Calcium source other than gypsum - carbonate or silicates
TDS	>500	Carbonate weathering or brine or seawater
	<500	Silicate weathering
Cl/∑Anions	>0.8 and TDS>500	Seawater or brine or evaporites
	>0.8 and TDS<100	Rainwater
	<0.8	Rock weathering
HCO_3/∑Anions	>0.8	Silicate or carbonate weathering
	<0.8 sulfate high	Gypsum dissolution
	<0.8 sulfate low	Seawater or brine

to identify a small number of factors that essentially explained most of the variance observed in variables. The extraction method was principal component analysis (PCA) whereas the rotation method was Varimax with Kaiser Normalization.

4. Results and discussion

4.1. General hydrochemistry

The hydrochemical characteristics of groundwater in the study area are presented in Table 2. In the same Table 2 acceptable drinking water standards by MSB and WHO have been provided for. The conductivity values were all within the acceptable limits for MSB standards, however three sampling areas were above the acceptable WHO limit. Conductivity is indicative of the amount of total dissolved solids (TDS) that in turn suggests the extent of mineralization of the water. TDS values were all less than 500 mg/L which is within the freshwater classification of TDS <1000 mg/L. Moreover, other parameters measured were all within the acceptable MSB limits except for a few cases with respect to NO_3 (24%). Therefore, the majority of the groundwater samples are suitable for domestic purposes. However, the MSB standard is less stringent in some parameters than the WHO guidelines (WHO, 2008). As such it is observed that 10% of samples had F and Fe values slightly higher than the WHO respective benchmarks. These observations are consistent with studies elsewhere within the region (Palamuleni, 2002; Pritchard, 2007; Mkandawire, 2008).

The predicted mean total hardness (Equation (1)) is 164.87 ± 19.94 mg $CaCO_3$/l ranging from a minimum value of 44.22 mg $CaCO_3$/l to a maximum of 356.83 mg $CaCO_3$/l. The median value obtained from the calculation is 127.65 mg $CaCO_3$/l. The range was within the acceptable MSB and WHO limit value.

The SAR computation (Equation (2)) to assess suitability of groundwater for irrigation purposes in the study area suggested the water to be of good quality. This was because the SAR calculation was lower than 10 indicating the suitability for irrigation purposes. This observation was also confirmed in Fig. 2 where all borehole SAR values were within S1 which implies low sodium hazard (USSL, 1954). However, groundwater for all boreholes indicated a medium salinity hazard under C2 class except for BH06 which was under C1 (low salinity hazard) while BH01, BH 16 and BH21 plot under high salinity hazard (C3). Thus there is a need to monitor the salinity of groundwater in this cluster prior to irrigation.

In terms of scaling potential, the groundwater in the study area had LSI values ranging from −4.49 to −2.46. Thus there was no evidence to suggest scale forming potential of groundwater in the studied samples.

4.2. Groundwater types and sources of minerals

The computed hydrochemical water types (Table 2) and observations from piper diagram, revealed some variations in hydrochemical water types. Along the gradient, it is apparent that the groundwater is dominated by Mg−Ca−Na cations (61%) while HCO_3 dominating the anion group with a mixture of Cl−HCO_3 (23.8%) and SO_4−HCO_3 (9.5%) apparent in some cases (discussion on this in next section). Conversely, a discernible decrease in pH value upgradient inversely consistent with water facie changes down-gradient. Borehole site elevation significantly correlated with Na ($r = 0.55$; $p = 0.010$), Si ($r = 0.44$; $p = 0.044$), SO_4 ($r = -0.53$; $p = 0.013$), F ($r = -0.740$; $p< 0.001$) and NO_3 ($r = 0.49$; $p = 0.024$). The correlation results offer insight into the variations and trends in the water type especially with respect to the role played by Na and SO_4 in influencing the transition.

The observed SiO_2 values in all borehole samples were greater than 0.5 mmol/l, thus granitic rocks that are part of the crystalline

Table 2
A general statistical summary of physico-chemical quality of groundwater in Machinjiri Area with their corresponding local and international maximum permissible levels (MPL) for a total of 21 pairs of samples (see Materials and Methods).

ID	Elev.	pH	Temp. (°C)	EC (μS/cm)	TDS (mg/l)	Turbidity (NTU)	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	F (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	As (mg/l)	Fe (mg/l)	Water type
BH01	1118	6.44	23.30	825*	413	0.30	80.24	1.38	38.07	22.08	33.71	0.53	144.95	166.09**	21.08	91.5	nd	0.00	Ca–Mg–Cl–HCO_3
BH02	1111	6.54	22.50	639	319	0.00	53.07	3.04	34.98	14.85	31.75	0.33	74.39	116.85**	15.18	85.4	nd	0.04	Mg–Ca–Cl–HCO_3
BH03	1088	6.44	23.20	279	139	0.00	20.35	0.68	14.05	11.65	36.73	0.70	12.44	15.70	7.04	103.7	nd	0.01	Mg–Ca–Na–HCO_3
BH04	1070	6.35	23.20	307	155	0.00	24.07	1.07	14.34	13.25	36.51	0.66	16.54	31.08	7.99	97.6	nd	0.03	Ca–Mg–Na–HCO_3
BH05	1058	6.32	23.40	265	134	0.00	15.51	0.79	13.17	14.48	34.74	0.24	21.87	6.78	7.95	103.7	0.0032	0.03	Mg–Ca–Na–HCO3–Cl
BH06	1101	6.10	23.10	160	80	0.02	8.35	0.88	5.69	12.81	29.33	0.25	8.73	7.96	4.80	42.7	0.0045	0.02	Na–Mg–Ca–HCO_3
BH07	1093	6.35	23.30	422	211	0.01	27.48	1.73	21.15	14.33	35.31	0.32	38.66	83.76**	9.39	61	nd	0.02	Mg–Ca–Na–Cl–HCO_3
BH08	1102	6.33	23.30	248	125	0.20	16.08	0.71	11.83	11.44	37.18	0.46	10.83	15.75	5.85	79.3	nd	0.01	Mg–Ca–Na–HCO_3
BH09	1106	6.45	23.50	301	150	0.00	21.04	0.79	14.44	11.94	28.11	0.46	13.88	18.08	8.50	134.2	nd	0.01	Mg–Ca–HCO_3
BH10	1037	6.43	23.80	307	153	0.00	21.37	0.99	16.26	13.62	39.79	0.99	11.51	7.74	9.57	24.4	nd	0.01	Mg–Ca–Na
BH11	1059	6.61	23.40	290	146	0.00	22.12	0.77	17.62	12.71	38.21	1.14	12.74	22.10	8.28	97.6	0.0022	0.01	Mg–Ca–Na–HCO_3
BH12	1050	6.57	23.30	304	148	0.14	20.33	0.81	14.05	14.61	32.47	0.69	18.87	16.11	9.27	61	0.0007	0.01	Mg–Ca–Na–HCO_3–Cl
BH13	1021	6.40	23.80	403	204	0.00	34.64	1.75	19.83	12.88	42.53	0.88	16.87	49.33**	8.02	109.8	nd	0.01	Ca–Mg–HCO_3
BH14	1031	6.34	23.80	280	142	0.00	18.57	0.95	13.81	11.43	43.36	1.00	14.45	33.49	5.47	61	nd	0.02	Mg–Ca–Na–HCO_3
BH15	1071	6.64	24.00	266	132	0.00	20.20	1.06	14.09	10.06	43.77	0.88	7.39	10.85	5.53	79.3	nd	0.01	Mg–Ca–Na–HCO_3
BH16	960	7.10	24.40	873*	438	0.09	58.06	1.68	50.33	27.85	37.00	1.55*	12.54	nd	210.75	91.5	0.0027	1.08*	Mg–Ca–SO4–HCO_3
BH17	985	7.13	23.80	379	191	0.15	21.40	1.02	19.42	11.79	37.92	1.25	8.27	18.51	9.50	109.8	0.0016	0.01	Mg–Ca–HCO_3
BH18	944	6.97	24.40	414	206	0.19	29.91	0.54	20.05	20.56	37.35	1.02	16.21	50.37**	25.91	91.5	nd	0.01	Mg–Ca–Na–HCO_3
BH19	938	6.81	25.20	371	187	0.28	34.29	0.71	15.58	16.32	39.65	1.19	9.04	33.42	19.12	85.4	nd	0.01	Ca–Mg–Na–HCO_3
BH20	890	6.91	25.10	554	277	0.00	38.87	2.17	38.12	15.00	42.99	0.77	13.61	39.17	9.30	176.9	0.0042	0.02	Mg–Ca–HCO_3
BH21	886	7.21	25.30	873*	417	0.06	75.98	1.28	33.39	32.96	35.19	1.51*	20.38	nd	207.65	91.5	nd	1.10*	Ca–Mg–SO4–HCO_3
WHO		6–8.5		750	1000	5	200	100	50	200		1.5	600	45	400		0.05	1.0	
MSB		6–9.5		3500	2000	25	250		200	500		6.0	750	45	800	400	0.05	3.0	
Exc'd.				14.3%								9.5%		23.8%				9.5%	

ID = borehole number, Elev. = borehole site elevation above mean sea level (m), Exc'd = exceedence, *exceeding WHO benchmark, **exceeding MSB and WHO benchmark.

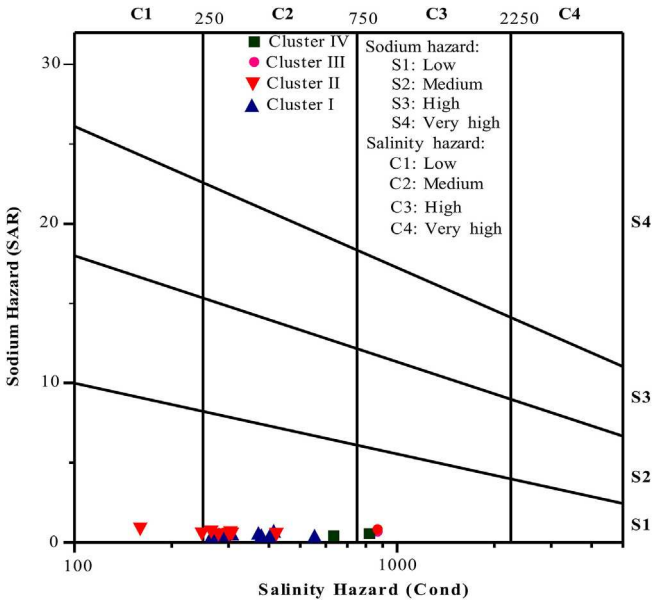

Fig. 2. Wilcox diagram illustrating the quality of groundwater fitness for irrigation in Machinjiri area based on SAR and salinity hazard criteria.

basement aquifer may have contributed to the origin of minerals in the aquifer. Ferromagnesian minerals such as pyroxene, amphibole, biotite, hornblende, plagioclase (e.g. albite) and cation exchange might be the controls in mineralization of the groundwater in this study area. Halite solution, albite, ion exchange and rainwater injection may be the sources of Na into the groundwater. Mg mineralization may be contributed from granitic weathering besides ferromagnesian minerals and dolomite (Table 1). Carbonates, silicates and evaporites (e.g. gypsum and anhydrite) contribute most of the calcium in groundwater while ion exchange and precipitation may attenuate groundwater Ca content in the studied samples.

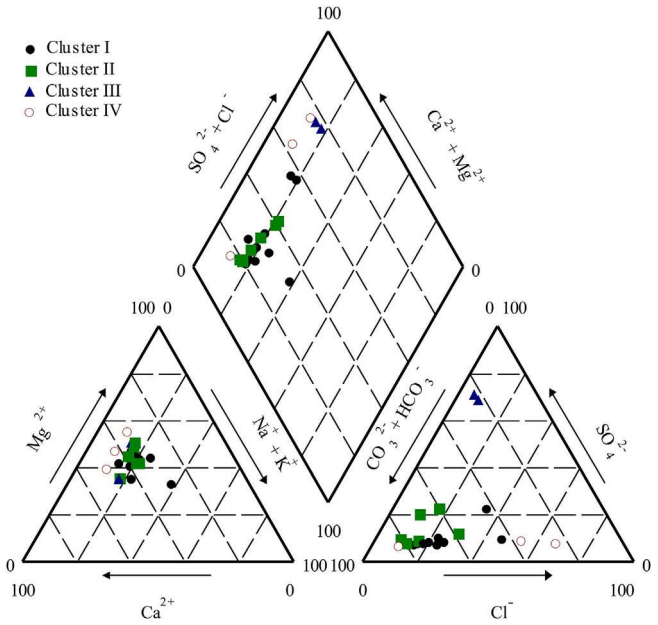

Fig. 3. Piper diagram for groundwater samples from the study area labeled according to clusters (identified from HCA; Fig. 4).

The results of Cl content with respect to total anions indicate strongly that rock weathering of evaporites is the main source of Cl mineralization in the studied aquifer because the calculated ratio of Cl/total anions was less than 0.8 (Fig. 4a). Similarly, the ratio of HCO_3 to total anions indicates the value less than 0.8 which is consistent with brine water (Fig. 4b). This is explained by presence of NO_3 and SO_4 that elevates the total anion content compared to HCO_3 ions. In boreholes (BH16 and BH21) where NO_3 was not detected (Table 2), it was observed that the concentration of SO_4 and F was very high relative to the rest of the samples. Equally noted was higher TDS values and EC for the same boreholes where NO_3 was not detected. In contrast the relatively higher NO_3 values paired well with relatively high Cl levels (BH01 and BH02) with similar effect observed on TDS and EC. It is suspected that nitrate fertilizers may well be the source of some elevated nitrate levels in groundwater through leaching process. An integrated approach to water supply management is needed to minimize anthropogenic input of nitrate and sulfate into groundwater emanating from fertilizer application.

Sources of fluoride may well be recognized from fluorite (CaF_2) which is the principal mineral of fluorine occurring as accessory minerals in granitic rocks formed mostly during the late hydrothermal stage (Kundu et al., 2001). Other sources include rock-forming minerals such as fluoroapatite ($Ca_5(PO_4)_3F$), cryorite

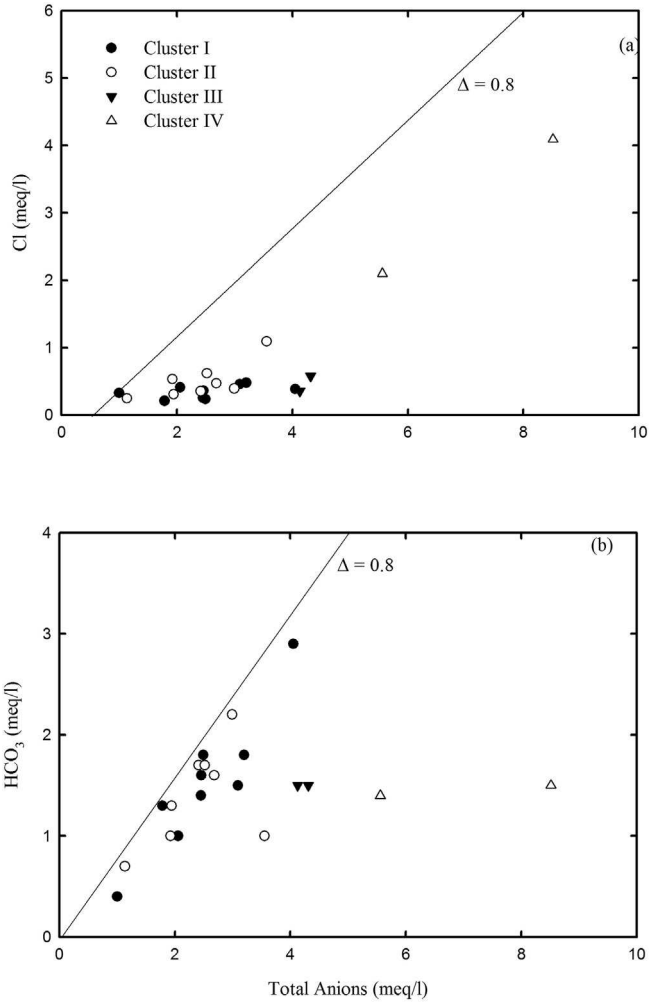

Fig. 4. Illustration of the ratios between (a) Cl vs Total anions and (b) HCO_3 vs Total anions in meq/L.

(Na_3AlF_6), villiaumite (NaF), topaz ($Al_2SiO(F,OH)_2$) and silicates. The silicates include phyllosilicates of mica, illite and amphibole group minerals in which F ion substitutes for the hydroxyl group because of their similarity in ionic radius (Chae et al., 2006; Rafique et al., 2008). Therefore, percolation of groundwater in the basement aquifer may dissolve these minerals to enrich fluoride concentrations. Various factors may play a role in enrichment of fluoride in groundwater, including pH, availability of complexing agents and presence of fluoride mineral bearing rocks. High fluoride groundwater are commonly found where there is identifiably low Ca^{2+}, alkaline pH and usually of the Na–HCOs type (Gomez et al., 2009; Wang et al., 2009; Chae et al., 2007). In our study the water was of slightly acidic to neutral pH and of Mg–Ca–Na–HCO (-mixed Cl or SO_4) type. Thus, the low concentration of fluoride detected in most of the samples may be due to the slightly acidic to neutral pH of the groundwater, lower Na concentrations relative to bivalent anions, anion exchange and probably low fluoride mineral bearing rocks.

As regards to iron, pump corrosion may enrich iron content in underlying groundwater besides geogenic influence and rock–water interaction. However, mordern pumps are made of stainless steel. As such there is an insignificant possibility of iron corrosion being the source of iron contamination. Mostly, iron combines with oxygen to form iron oxide minerals such as hematite (Fe_2O_3) and magnetite(Fe_3O_4) that can release iron when in contact with water. The dissolution of iron-bearing minerals (e.g. hematite and magnetite) may be the plausible cause of enriched iron in the groundwater of the study area.

4.3. Multivariate analysis

4.3.1. Hierarchical cluster analysis

Fig. 5 is a manifest of the hierarchical cluster analysis (HCA) that was done to reveal natural groupings (or clusters) within the data set that would otherwise not be apparent. The analysis yielded 4 clusters when the phenon line was drawn at rescaled distance of 10. The choice of phenon line was based on semi-objective observation of the dendrogram. Cluster I is composed of boreholes BH10, BH11, BH13, BH14, BH15, BH17, BH18, BH19 and BH20. Cluster II is made up of BH03, BH04, BH05, BH06, BH07, BH08, BH09 and BH12. Cluster III consists of boreholes BH16 and BH21 while Cluster IV is a grouping of BH01 and BH02. Some boreholes did not register As and

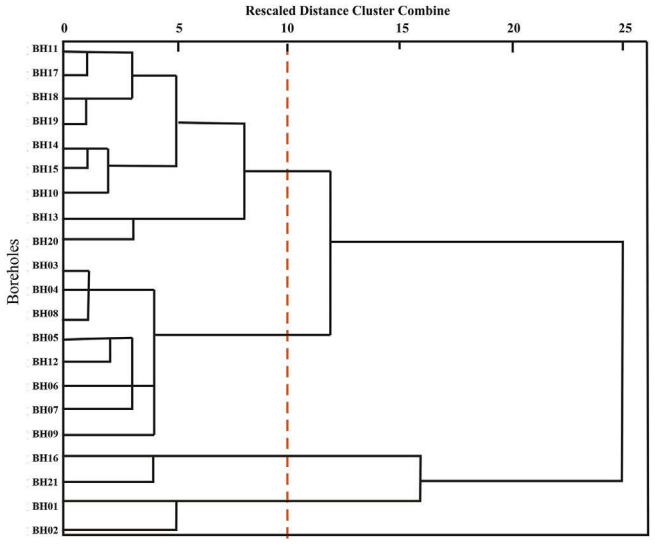

Fig. 5. A dendrogram realized from Hierarchical Cluster Analysis showing the four clusters based on pheno line drawn at a rescaled distance of 10.

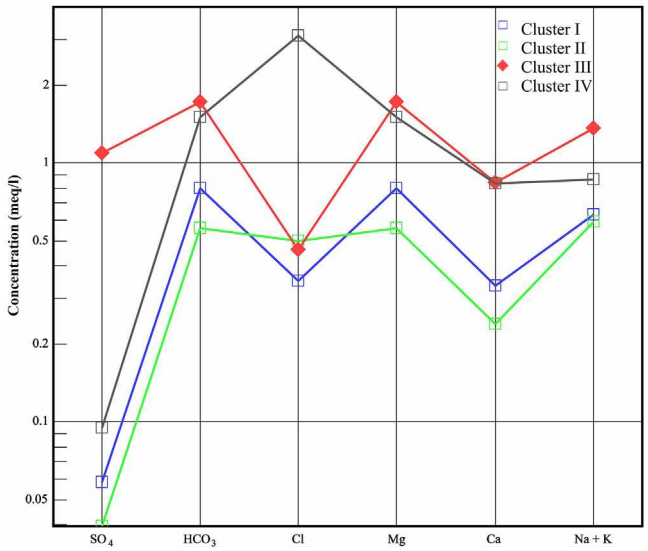

Fig. 6. Shoeller diagram showing average composition of groundwater.

F, as such the two variables were not used in the HCA.

Samples in clusters I and III have a cationic composition that is dominated by Mg, with abundance orders Mg > Na > Ca ≫ K (meq/L) and anionic composition dominated by bicarbonates (meq/L). However, the clusters differ in abundance order of anions as can be observed from Fig. 6(Cluster I: HCO_3 > Cl > SO_4; Cluster III: HCO_3 > SO_4 > Cl). Thus their chemical composition is characterized by Ca–HCO_3 and mixed cation-HCO_3 type (Fig. 3; Table 2). Comparatively, cluster III water samples have highest salinity of all clusters (TDS = 312 mg/L, EC = 644 μS/cm) while samples in Cluster I have relatively low salinity (TDS = 182 mg/L, EC = 363 μS/cm). Then again, the samples in Cluster I also have relatively higher values of silica (SiO_2 = 41 mg/L) compared to all four clusters. However, samples in Cluster II are dominated by Na in the order of Na > Mg > Ca ≫ K (meq/L) while the anionic composition is similar to that of Cluster I (Fig. 6). The salinity for Cluster II is relatively the lowest of all clusters (TDS = 143 mg/L, EC = 286 μS/cm). Samples in Cluster IV are also characterized by cationic composition dominated by Mg similar to Clusters I and III, however the abundance order is different (Mg > Ca ≈ Na ≫ K (meq/L)) (Fig. 6). At the same time, their anionic composition is dominated by chlorides (abundance orders (meq/L): Cl^- ≫ HCO_3- > SO4) (Fig. 6). Thus their median chemical composition is characterized by Mg–Cl (Fig. 6), but also contains some Ca–HCO_3 and mixed cation-Cl types (Fig. 3; Table 2).

4.3.2. Factor analysis

Similarity relationships among water samples were examined using factor analysis (FA). The analysis yielded 13 principal components of which three were significant because of their high eigen values (≥1) and their high cumulative variance of 82.72%. The results are shown in Table 3. The first factor which accounts for 55.95% of the total variance is characterized by very high loadings of Fe, Na, SO_4 and moderate to high EC, TDS, Ca and TH. This reveals that the EC and TDS are due to mainly Ca, Fe, Na, SO_4 and suggesting the mineral composition mainly of $CaSO_4$, $NaSO_4$, $FeSO_4$ and $CaCO_3$ system. The second factor accounting for 17.14% of the total variance is associated with high loading of EC, TDS, TH, Ca, K, Mg and Cl. The system is more of chloride/carbonate type. The third factor accounting for 9.02 percent of total variance is characteristic mainly of pH, Si and F. Sulfate and Fe mineralization is explained by the

Table 3
Factor analysis's Varimax rotated component matrix achieved with Kaiser Normalization as the rotation method.

Parameter	Factor 1	Factor 2	Factor 3
pH	0.311	0.170	**0.631**
EC	0.636	**0.762**	0.094
TDS	0.619	**0.774**	0.095
Ca	0.555	**0.789**	0.023
Fe	**0.934**	0.153	0.152
K	−0.090	**0.819**	0.139
Mg	0.479	**0.801**	0.233
Na	**0.890**	0.376	0.014
Si	−0.221	−0.032	**0.821**
F	0.607	−0.087	**0.691**
Cl	−0.065	**0.792**	−0.454
SO_4	**0.949**	0.183	0.151
Total Hardness	0.539	**0.827**	0.130
HCO_3	0.271	0.318	0.358
Eigenvalue	7.834	2.400	1.348
% of variance	55.954	17.144	9.626
Cumulative %	55.954	73.097	82.723

Note: Bold values indicate highest significant factor loadings for the physical-chemical parameters that explains the strong relationship among variables within a principal component.

first factor while the second factor accounts for the total hardness, total dissolved solids and Cl elevation. The last factor explains the fluoride levels in the system.

A bivariate Pearson correlation for all samples indicate that Ca significantly correlated with Cl ($r = 0.65$; $p = 0.001$), SO_4 ($r = 0.65$; $p = 0.002$) and NO_3 ($r = 0.064$; $p < 0.001$) suggesting a significant contribution from sulfates (anhydrite, gypsum) cation exchange with respect to halite. Similarly, Mg strongly correlated with SO_4 ($r = 0.65$; $p = 0.001$), a weak correlation with Cl ($r = 0.46$; $p = 0.037$) and NO_3 ($r = 0.50$; $p = 0.020$) whereas Na correlated significantly with SO_4 ($r = 0.89$; $p > 0.001$) and F ($r = 0.51$; $p = 0.018$). No significant correlation with F observed for Ca and Mg reducing the significance of fluorite and MgF dissolution, while a medium correlation between Na and F was observed ($r = 0.5$; $p = 0.02$). The relationship between TDS and anions (F, SO_4 and NO_3) is illustrated in Fig. 7. Weak relationship between TDS and F is apparent while strong relationship is exhibited with respect to SO_4 ($R^2 = 0.55$) and NO_3 ($R^2 = 0.84$). This confirms the low concentrations of fluorides observed in this research compared to SO_4 and NO_3. Presence of trace amounts of arsenic in some boreholes (BH05, 06, 11, 12, 16, 17 & 20) may be explained by mild Fe concentration and lightly acidic groundwater.

Cluster I is explained by Factor 2 where Ca, K and Mg are strongly correlated with Cl and Total hardness (TH) followed by positive relationships with HCO_3 and SO_4 consistent with the water type observed (Table 1; Fig 3). Carbonates and silicate weathering (Fig. 8b) is the dominant control of Ca mineralization in this cluster with silicate weathering predominating over carbonate. Moreover, the inverse modeling results indicates undersaturation with respect to carbonates (aragonite, calcite and dolomite) and evaporites (anhydrite and gypsum) (Table 4). According to Fig. 8a, only one sample aligned on the dolomite weathering line, however the computation with respect to $HCO_3/SiO_2 < 10$ implies that dolomite dissolution is not significant. As such, silicate weathering followed by carbonate weathering and to a lesser extent evaporites are dominant sources of Ca. Moreover, granitic weathering predominates over ferromagnesian minerals in controlling the mineralization of Mg and Ca (Fig. 8a).

Sources of K in the area may be attributed to possible aluminosilicate weathering such as K-feldspar ($KAlSi_3O_8$). Halite dissolution is possible for BH12 and 19 as the possible sources of Na while ion exchange controls mineralization of Na (Fig. 9c). However, the saturation index indicates the groundwater is saturated

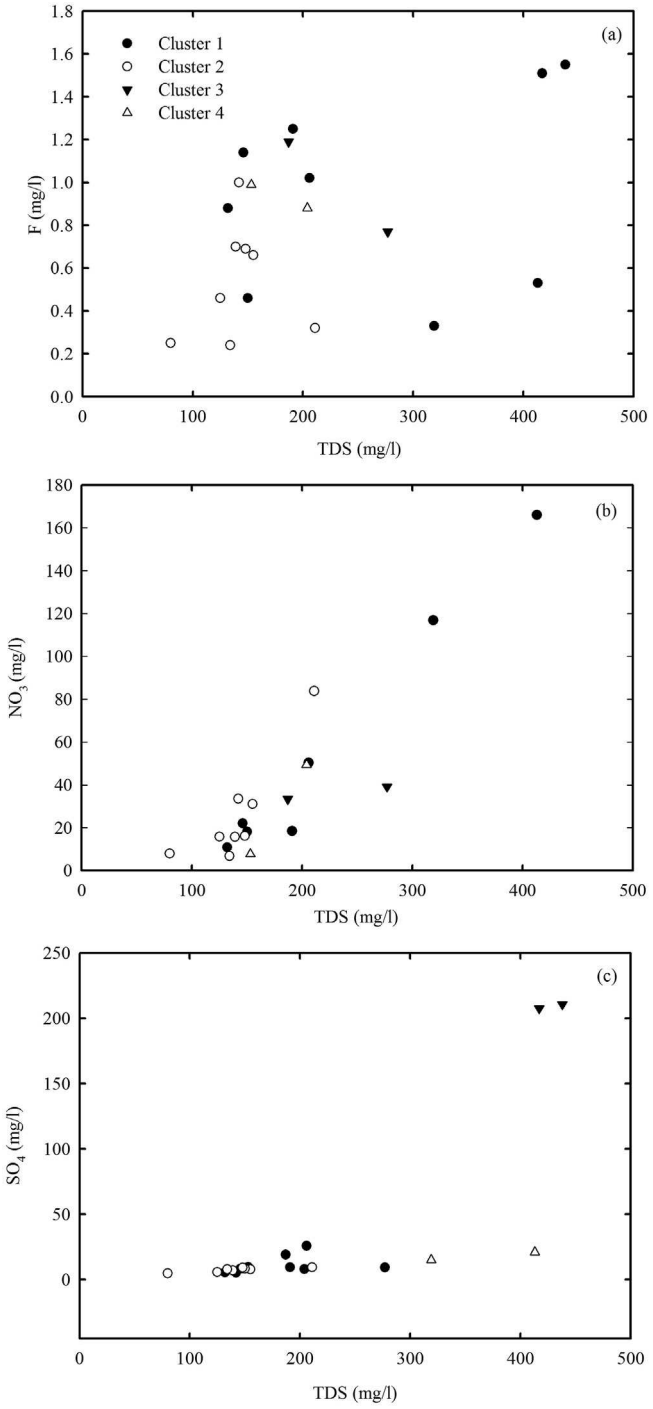

Fig. 7. Illustration of the relationship between TDS and anions in groundwater (a) TDS vs F, (b) TDS vs SO4 and (c)TDS vs NO_3.

with respect to halite (Table 4). Yet the main control of Na mineralization is cation exchange implying that sources other than halite play a significant role in Cl dissolution most notably chlorides of calcium, magnesium and potassium. Total hardness is explained by high loadings of Ca and the positive relationship between Ca and HCO_3. The water hardness in the studied area is below the maximum permissible limit (MPL) values for both WHO and Malawian Standards.

Cluster II is explained by Factor 3 where ferromagnesian mineral sources, and to a lesser extent albite weathering (BH07 and BH09) (Fig. 9a) and cation exchange BH08 (Fig. 9a and b), control the

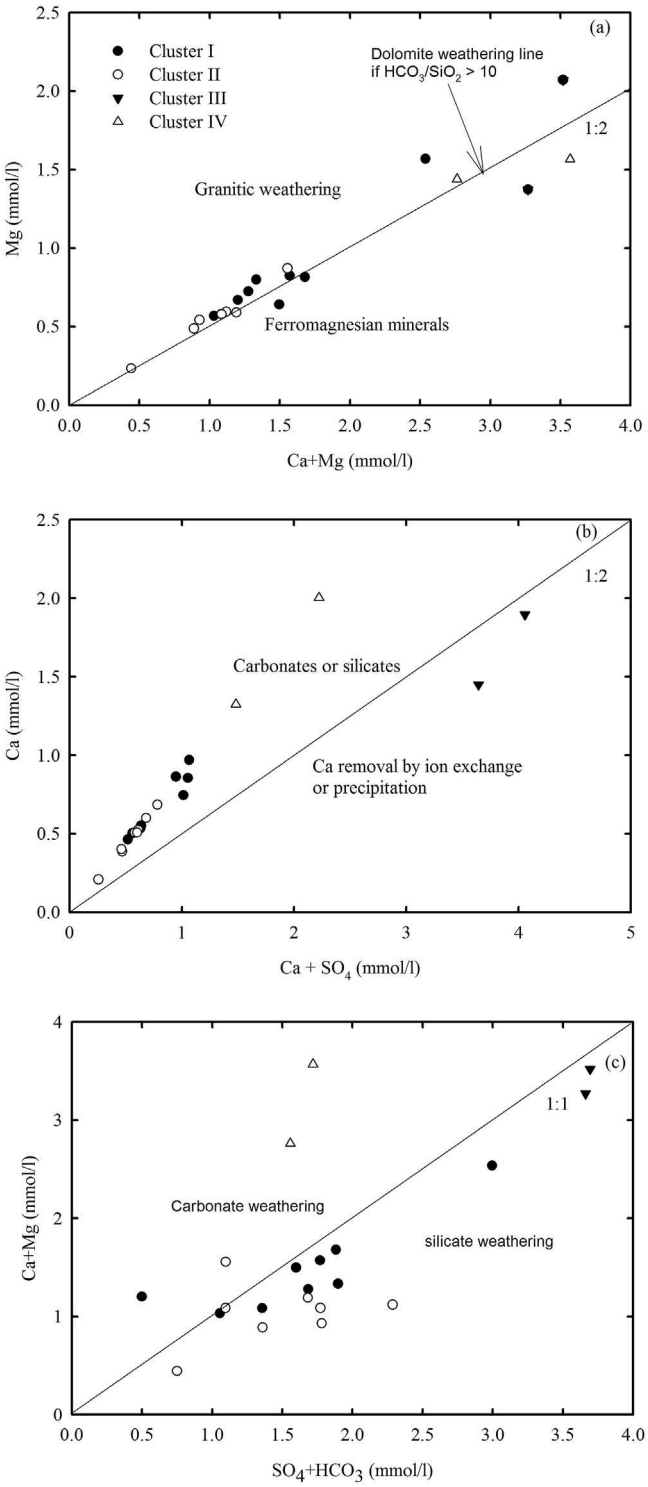

Fig. 8. Scatterplots of (a) Mg vs (Ca + Mg) (b) (Ca) vs (Ca + SO_4) and (c) Ca + Mg) vs (SO_4 + HCO_3) to illustrate the dominant sources of minerals.

mineralization of Na. Just the same granitic weathering (Fig. 8a), silicates and carbonates (Fig. 8b and c) control Na, Ca, K and Mg mineralization in the groundwater. On the contrary, the saturation index (Table 4) indicates an undersaturated condition with respect to fluorite (CaF_2) that could explain the presence of F in the groundwater. Due to CaF_2 solubility control (Factor 2), as well as very strong relationship between F and Na (Factor 1) and poor

Table 4
Saturation indices of the four principal water clusters.

Phase	Stoichiometry	Cluster I	Cluster II	Cluster III	Cluster IV
Anhydrite	$CaSO_4$	−3.43	−3.17	−1.65	−2.85
Aragonite	$CaCO_3$	−1.69	−1.13	−0.44	−1.19
Calcite	$CaCO_3$	−1.51	−0.95	−0.26	−1.01
Chalcedony	SiO_2	−2.68	−2.62	−2.65	−2.62
Dolomite	$CaMg(CO_3)_2$	−2.82	−1.71	−0.36	−1.82
Fluorite	CaF_2	−2.19	−1.55	−0.93	−1.90
Goethite	FeO(OH)	0.68	1.97	2.81	1.85
Hematite	Fe_2O_3	−3.17	−2.91	−1.40	−2.59
Gypsum	$CaSO_4{:}2H_2O$	−8.29	−8.38	−7.93	−7.66
Halite	NaCl	3.36	5.95	7.62	5.70
Quartz	SiO_2	−2.22	−2.17	−2.20	−2.17
Siderite	$FeCO_3$	−2.48	−1.84	−1.78	−1.74

relationship with TDS (Fig. 7a), fluoride enrichment is very minimal in the crystalline basement aquifer. Also, the weak correlation observed between F and Ca offsets the possibility of fluorite controlling mineralization of F in the groundwater. Moreover, F dissolution is pH dependent as it may mobilize mostly in alkaline pH. Hydrolysis of F-bearing silicates such as muscovites ($KAl[AlSi_3O_{10}]F_2$) and biotites ($KMg_3[AlSi_3O_{10}]F_2$) may as well be the sources of F. The environmental conditions displayed by the sampled groundwater limits enrichment of F in the studied aquifer. This is explained further by the weak relationship with K and Mg. The strong relationship between SiO_2 and pH suggest probable controlling reactions of aluminosilicates for establishing pH conditions. The pH conditions can be instituted by increasing hydronium ions countering the HCO_3 ions through one such process like (Equation (3)):

$$3Al_2Si_2O_5(OH)_{4(s)} + 4SiO_{2(s)} + K + Ca + 15H_2O \leftrightarrow 2KCaAl_3Si_5O_{16}(H_2O)_{6(s)} + 6H_3O^+ \quad (3)$$

Besides, quartz is one of the minerals found in the crystalline basement complex even though its dissolution is very slow. The saturation index calculated for this cluster (Table 4) shows the groundwater is undersaturated with respect to quartz as one of the limiting control in dissolution and ion interactions of silica.

The strong positive correlations observed in Factor 1 (Table 3) describe the characteristics of water type for Cluster III with respect to symptoms of high SO_4 concentrations and higher Fe loadings. However, higher salinity values and total hardness are explained by Factor 2. This may suggest the significant influence of pyrite dissolution besides the system being undersaturated with respect to siderite. From Table 4, the supersaturation of goethite and hematite suggests Fe precipitation buffering the dissolution of siderite and (possibly) pyrite dissolution as well. Sulfate mineralization is suggested mainly by undersaturation with respect to anhydrite and gypsum end-member. However, gypsum mineralization is very minimal (Fig. 8b). It is equally important to note from Fig. 8b that Ca, for boreholes sampled under this cluster, plot below gypsum dissolution line and controlled by Ca removal processes such as ion exchange or precipitation. Instead, the possible sources may as well be the oxidation of pyrite (Equation (4)) and charcopyrite end-members as well as Na_2SO_4 considering the strong relationship between Na and SO_4 explained by Factor 1. Mineralization of Na in the cluster follows cation exchange process provided in Fig. 9a.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (4)$$

Cation/ion exchange controls both SiO_2 and Na mineralization in the groundwater sampled in Cluster IV (Fig. 8b and c). The anion group is excessively predominated by Cl ions over HCO_3 and SO_4 as

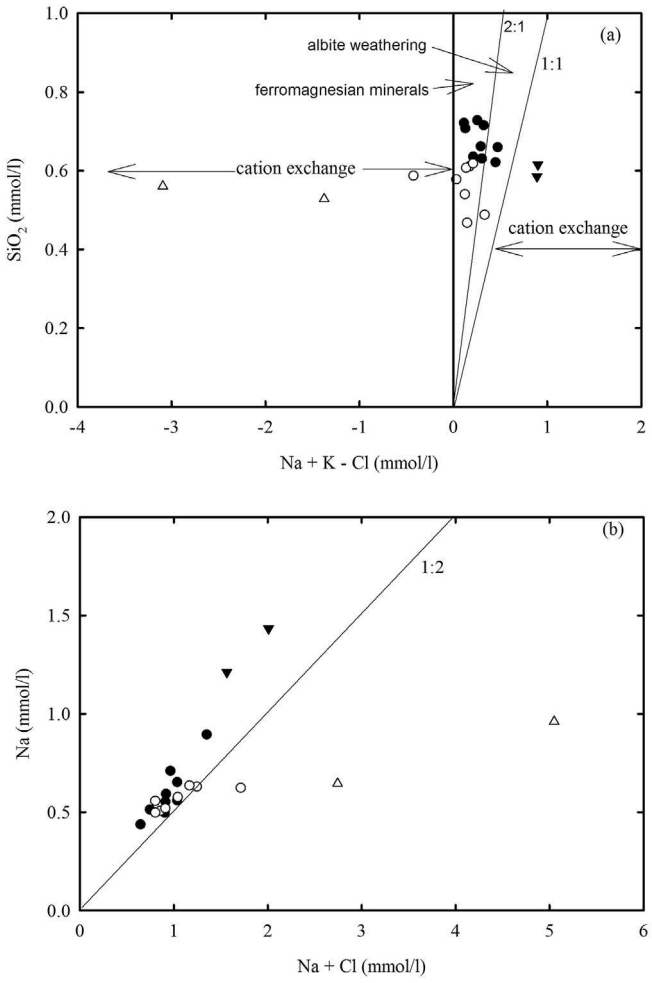

Fig. 9. Relationship between (a) SiO_2 vs (Na + K − Cl) and (b) Na vs (Na + Cl).

mentioned earlier in this section (Figs. 3, 6). This water type has a salty taste which was experienced in the field as well. The Na and Ca ions balance off while being dominated by Mg. The oversaturation of halite limits the dissolution of Cl suggesting other sources such as Chlorides of Ca, Mg and K minerals. Cluster IV is explained by Factor 2 where high loadings of Cl compare well with positive high loadings of Mg, Ca and K. The same Factor elucidates the higher total hardness observed in this cluster (316.56 mg/L).

5. Conclusion

The groundwater in Machinjiri, Blantyre which is part of the extensive crystalline basement aquifer, is suitable for irrigation and drinking purposes. This is confirmed by comparative analysis with chemical and physical quality standards (MSB and WHO). Sodium and Salinity hazard relationship confirmed that the groundwater in the study area is suitable for irrigation. However, there were some cases of elevated nitrates, sulfates and identified fluorides whose mere existence is cause for further studies and monitoring. Iron concentrations were found in all the samples despite meeting the quality criterion. In some boreholes the values of Fe, F and NO_3 were higher than the MPL set by WHO, however the values were lower than the MPL stipulated by the national standard guidelines except for nitrate (166.1 mg NO_3/l > MS733:2005 MPL). Contamination of groundwater is apparent in some boreholes in the area and this may be attributed to the use of inorganic fertilizers. As such groundwater management and constant monitoring is imperative to ensure sustainable rural water supply and water security.

Also noted is that groundwater geochemistry in the studied area is controlled by intrinsic factors such as granite weathering, cation exchange, pH and mineralization. More studies on geochemical controls governing groundwater evolution, sources as well as speciation modeling may significantly add value to understanding the geochemistry of the groundwater of the study area.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jafrearsci.2015.11.023.

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