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Trace elements geochemistry of fractured basement aquifer in southern Malawi: A case of Blantyre rural

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ABSTRACT

In this study, twenty one (21) trace elements in the basement complex groundwater of Blantyre district, Malawi were analyzed. The majority of the analyzed trace elements in the water were within the standards set by World Health Organization (WHO) and Malawi Standards Board (MSB). But, iron (Fe) (BH16 and 21), manganese (Mn) (BH01) and selenium (Se) (BH02, 13, 18, 19 and 20) were higher than the WHO and MSB standards. Factor analysis (FA) revealed up to five significant factors which accounted for 87.4% of the variance. Factor 1, 2 and 3 suggest evaporite dissolution and silicate weathering processes while the fourth factor may explain carbonate dissolution and pH influence on trace element geochemistry of the studied groundwater samples. According to PHREEQC computed saturation indices, dissolution, precipitation and rock-water-interaction control the levels of trace elements in this aquifer. Elevated concentrations of Fe, Mn and Se in certain boreholes are due to the geology of the aquifer and probable redox status of groundwater. From PHREEQC speciation results, variations in trace element species were observed. Based on this study, boreholes need constant monitoring and assessment for human consumption to avoid health related issues.

1. Introduction

Groundwater is the main domestic water source in developing countries. It is reliable, convenient and cleaner compared to surface water. Since most communities in rural areas have easy and direct access to groundwater, they use it with little or no treatment. This fact makes it hazardous in cases of high loading of undesirable elements. Most of such elements exist entirely from the geochemical activities since water is a profound chemical reaction media and solution. As such, it is very likely that any element existing in the aquifer can dissolve and react under special circumstances such as oxidation/reduction conditions (redox), pH variations and optimal temperature. Some elements may mobilize under reducing conditions while others are more prevalent under oxidizing conditions. Besides, chemical reactions and speciation may influence the potency of certain elements. For instance, ionic barium and its soluble compounds are toxic to humans while the insoluble barium sulfate ($BaSO_4$) is harmless (Nogueira et al., 2010). Mobile elements are more hazardous than precipitated elements. As such, the extent to which elements affect humans and living organisms depends on the chemical characteristics/species, concentration, exposure duration and bioaccumulation potential of the element.

Complex processes control the distribution of trace elements in groundwater, which has a large range of chemical composition (Chen et al., 2007). Trace elements composition of, and their associated elevations in groundwater, depends on various natural factors (Chen et al., 2007; Helena et al., 2000). As well, human activities can change groundwater composition, either by polluting it or by changing the hydrological cycle (Helena et al., 2000).

To find out the quality of groundwater for rural communities, the analytical and field data was assessed using World Health Organization (WHO, 2011) and Malawian standards (MSB, 2005) maximum permissible levels (MPL). The trace elements geochemistry was evaluated using statistical techniques especially multivariate's factor analysis. Furthermore, trace element speciation studies were done using PHREEQC geochemical modeling.

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Therefore, this paper discusses the hydrochemistry of trace elements in basement complex aquifers of southern Malawi. There are very limited studies so far on trace elements in the groundwaters of the Blantyre district (Mapoma and Xie, 2014). The field sampling and analytical work were done in the months of September and October, 2013.

2. Geological setting of the study area

Blantyre district is located within latitudes 15.350–16.015° S and longitudes 34.725–35.125° E. The district covers an area of 1792 km^2 with undulating topography ranging from an elevation of about 780–1612 m above sea level. Blantyre district is underlain by an extensive Precambrian crystalline basement complex made up of metamorphic and igneous rocks that include syenitic granites, charnokites and ultra-basic gneisses, schists, granulites and quartzites (Mkandawire, 2004). The main lithofacies within the bounds of the Blantyre district are dark grey gneisses enriched in amphibole and pyroxene.

3. Materials and method

3.1. Field sampling and field parameter measurement

Twenty-one community boreholes within Machinjiri area in Blantyre (Fig. 1) were selected for study. Preliminary analyses included immediate in situ measurements of pH (Wagtech pH meter, S/N 297046), dissolved oxygen (HANNA, Model HI9743), temperature, electric conductivity (EC) and total dissolved solids (TDS) (Wagtech EC/TDS/°C meter, S/N 303178) and turbidity (Wagtech Turbidity meter, Model No. WT3020) while ALPHA titration technique was used to determine bicarbonate (HCO_3) in the Department of Physics and Biochemical Sciences chemistry laboratory of the University of Malawi. A portable hand held GPS (Global positioning system) was used to record borehole collar elevation and location coordinates. Furthermore, water samples for laboratory analysis were collected in two sets of 21 samples. During collection, the water samples were filtered through a 0.45 μm millipore filter into 100 mL high density polyethylene (HDPE) bottles washed with distilled water. The pH for twenty one samples intended for cation (major and trace elements) analysis was controlled to pH < 2 using 6 M HNO_3. The samples for laboratory analysis were kept in refrigerator for preservation.

3.2. Analytical techniques

The laboratory analysis was done at State Key Laboratory of Biogeology and Environmental Geology of China University of Geosciences (Wuhan) within one week of sampling. Unacidified aliquots were analyzed for fluorides (F), chlorides (Cl), nitrates (NO_3), nitrites (NO_2), sulfates (SO_4) and bromine (Br) by Ion Chromatography model DX-1100 (Dionex). Major water quality cations and trace elements were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) (ICAP6300). The major and trace elements analyzed were calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), silica (Si), silver (Ag), arsenic (As), aluminium (Al), gold (Au), boron (B), barium (Ba), beryllium (Be), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lithium (Li), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn), strontium (Sr), vanadium (V) and zinc (Zn). The average analytical error for major and trace chemical constituents using ICP-OES is less than ±5%.

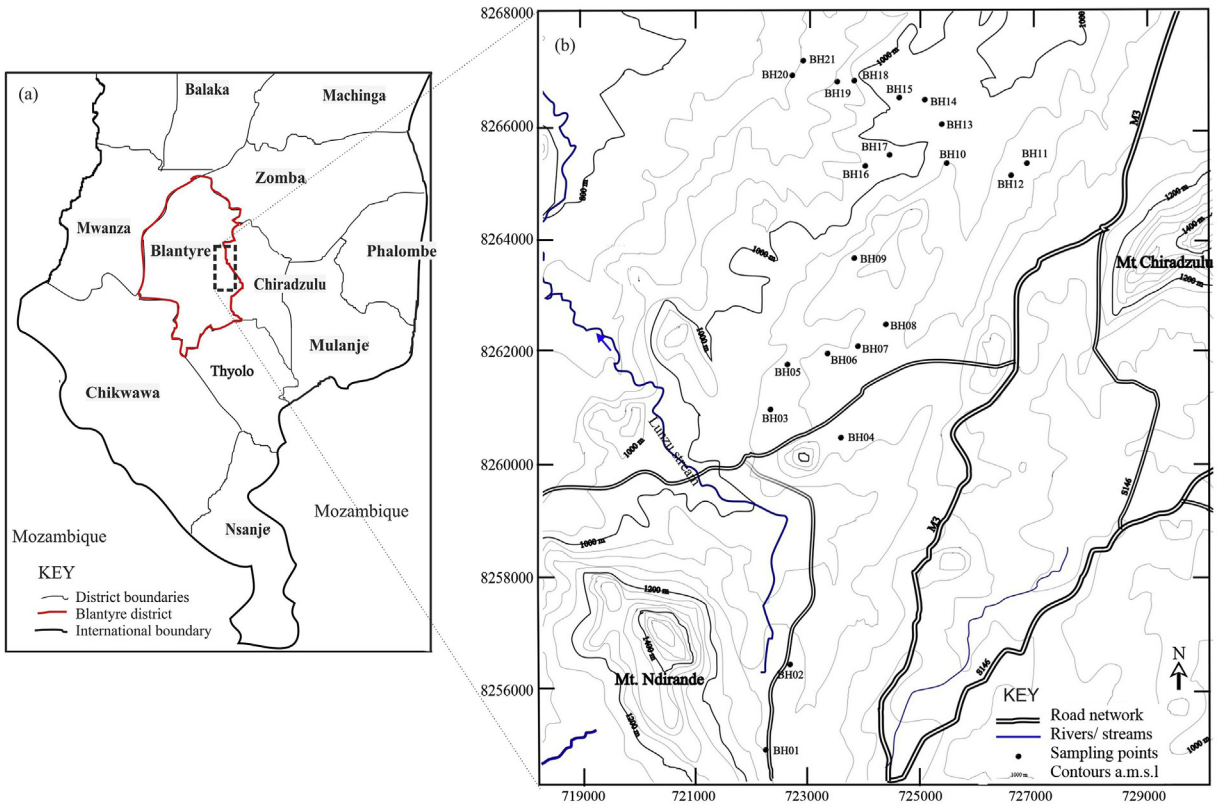

Fig. 1. Map showing the location of Blantyre district in southern Malawi (a) and the specific study area within the district (b) including sampling points and contours representing average mean sea level elevation (a.m.s.l).

3.3. Data analysis

To elucidate the interrelationships between elements, factor analysis (FA) approach together with Pearson's correlation using IBM® SPSS® statistics version 20 were used. Factor analysis explained the associations amongst variables (physico-chemical), by reducing the dimensionality of the data table (Helena et al., 2000). The aim was to find factors that explained most of the variance observed in variables and explicate the relationships amongst the parameters. Principal component analysis (PCA) was the extraction technique selected whereas the rotation method was Varimax with Kaiser Normalization.

The geochemical modeling program PHREEQC version 2.8 (Parkhurst and Appelo, 1999), implemented with LLNL (Lawrence Livermore National Laboratory) database V8.R6230 calculated saturation indices (SI) as the log of the ratio between ion activity product and the equilibrium constant (Belkhiri et al., 2012). The same program was used to provide speciation results.

4. Results and discussion

4.1. Hydrochemical characteristics

The results of physical measurement and trace element analysis of groundwater samples from the Blantyre district are presented in Table 1. A schoeller diagram (Fig. 2) provides a summary of the distribution of major chemical descriptors in groundwater of the study area. The groundwater is dominated by calcium (Ca) and magnesium (Mg) and bicarbonate (HCO_3). Previous studies show that iron (Fe) concentration in the basement complex is high (Dill et al., 2005). Thus, Fe is also an important descriptor of the quality of groundwater in this region. Dissolved oxygen, temperature and pH values range from 0.77 to 4.82 mg/L, 22.50–25.30 °C and 6.10 to 7.21, respectively. Total dissolved solids and electric conductivity values are 79.9–438.0 mg/L and 159.7 to 873.0 μS/cm, respectively.

4.2. Trace elements geochemistry

4.2.1. Alkali and alkaline earth metals

Lithium (Li) is the only alkali metal that was analyzed in this group. Although Li was detected in all of the 21 water samples, the concentrations were low (Li_{range} = 1.4–8.1 μg/L; Li_{mean} = 3.4 μg/L). Lithium is a reactive element and therefore combines with other elements in groundwater. Li is present in aluminosilicates and mineral bearing rocks containing other alkali metals (such as Na and K) suggesting that Li is derived from rock-water interaction in the same way as K (Witherow and Lyons, 2011). Lithium interacts with Al through displacement mechanism; as such presence of Li influences Al dissolution from aluminosilicate such as biotites and muscovites found in granite, gneisses and schist.

Barium (Ba_{range} = 25.3–616.5 μg/L), beryllium (Be_{range} = 0–0.4 μg/L) and strontium (Sr_{range} = 137–1132 μg/L) are the trace elements that were detected in the alkaline earth metals group (Table 1). Beryllium being the most electronegative of the alkaline earth elements tends to form more covalent compounds than ionic compounds. At pH values recorded in this research (Table 1), beryllium tends to exist as $Be(OH)_2(s)$. This reason can explain the low concentrations of Be detected in the samples. The higher concentrations of Ba and Sr detected relative to Be in this group could be explained from the fact that Ba and Sr form more ionic compounds than Be. Both barium and strontium closely resemble calcium more than magnesium. The two elements may displace calcium in human tissue which requires close monitoring of the groundwater in this area.

4.2.2. Transitional metals

Eleven transitional metals were analyzed i.e. vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), silver (Ag), cadmium (Cd) and gold (Au). Relatively, the sampled groundwater is more enriched in V (11.6–74.3 μg/L) than Cr (nd to 14.1 μg/L). It was identified that relatively higher Cr concentrations were found in BH14 and BH20 (Table 1). Frequent monitoring and assessment of these two boreholes is necessary.

Apart from major groundwater quality elements, Fe and Mn, the redox sensitive elements, are important parameters used to define rural groundwater quality. High concentration of Fe or Mn in groundwater is the principal factor in well abandonment because elevated Fe and/or Mn is unpleasant to groundwater users. This study revealed that Fe content in the samples ranged from 4.6 to 1096 μg/L while excluding BH15 (*nd* value), Mn values were between 0.2 and 797 μg/L. The elevated Fe content observed in BH16 and BH21 (Table 1) may undermine the integrity of these two boreholes due to formation of rusty hydroxides leading to well abandonment. Also, the groundwater sample for BH01 had Mn concentrations higher than WHO recommended value (Table 1). High oral exposure to Mn can result in increased intellectual impairment and reduced intelligence quotients in school-aged children (Bouchard et al., 2011).

Fe/Mn-oxide and hydroxide minerals such as hematite (Fe_2O_3), magnetite (Fe_3O_4) and manganite (MnO(OH)) are potential sources of Fe and Mn in this aquifer through rock-water interaction, for example:

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe^{2+} + 3OH^- \quad (1)$$

Cobalt (Co) concentrations ranged from 0.4 to 5.2 μg/L while that of Ni was 0.8–16.5 μg/L. Existence of laterite soils in Blantyre district (Dill et al., 2005) may explain the presence of nickel in groundwater. Laterite soil mineral ores such as nickeliferous limonite (Fe, Ni)O(OH) and garnierite (a hydrous nickel silicate) (Ni, $Mg)_3Si_2O_5(OH)_4$ are potential sources of nickel. Presence of laterite soils can explain the coexistence of Ni and Fe in the studied groundwater while Co is frequently associated with Ni.

The concentration of copper (Cu) was 0.2–25.8 μg/L. In nature, copper (Cu) exists as a trace constituent of Ag-Au alloy (electrum). However, the principal sources of Cu in groundwater are chalcopyrite ($CuFeS_2$) chalcocite (Cu_2S) and cuprite (Cu_2O) while the use of $CuSO_4$ as a fungicide contaminates groundwater with Cu.

Zinc (Zn) is used as an anti-corrosion agent to fortify iron pipelines against corrosion. Any pipeline or pump material fortified with zinc may contaminate water through oxidation processes. But, the low concentration of Zn (28.5% non detects) observed in the samples (Zn_{max} = 112.4 μg/L) suggest interaction between aquifer strata and groundwater as the mechanism controlling Zn enrichment rather than human activities.

Evidence of silver (Ag) in seven (7) out of twenty one (21) boreholes was found, with a maximum value of 21.8 μg/L for BH01. The rest of the boreholes had Ag concentrations less than 10.4 μg/L and minimum being 2.8 μg/L. In nature, Ag is found in native form as an alloy with gold (electrum) and in ores containing sulfur (argentite, Ag_2S and pyrargyrite, Ag_3SbS_3), arsenic, antimony or chlorine (chlorargyrite, AgCl). Therefore, coexistence of Ag and Au may strongly suggest electrum dissolution as the source of Ag of which Au concentration ranged from 80.7 to 139.8 μg/L.

From the samples, traces of cadmium (Cd_{range} = 0.1–0.9 μg/L) in 14 out of 21 boreholes were detected (Table 1). Cadmium can be found as a constituent of fertilizers, coating materials, paint, plastics and fungicides (Syers et al., 1986; Taylor, 1997). Cd is rare in the earth's crust but nearly always associated with sphalerite (ZnS), the

Table 1
The values of physical parameters and trace element constituents[a] of groundwater samples collected from 21 borehole samples.

ID	Elev.	pH	Temp.(°C)	EC (μS/cm)	TDS (mg/L)	Ag	Al	As	Au	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	Se	Sn	Sr	V	Zn
BH01	1118	6.44	23.3	825[b]	413	21.8	*nd*	*nd*	96.1	38.9	616.5	*nd*	0.5	5.2	1.7	25.0	4.6	7.9	797[b]	1.9	10.1	6.5	1.6	721.9	63.5	*nd*
BH02	1111	6.54	22.5	639	319	2.8	3.6	*nd*	96.2	34.8	581.8	0.1	0.9	1.4	0.6	2.1	38.9	5.6	1.0	14.5	11.6	*nd*	0.3	619.4	55.7	0.8
BH03	1088	6.44	23.2	279	139	*nd*	*nd*	*nd*	111.0	25.8	80.1	0.4	*nd*	0.4	1.8	5.1	8.2	2.2	9.5	6.3	16.5	20.5[b]	*nd*	204.8	32.1	*nd*
BH04	1070	6.35	23.2	307	155	7.6	*nd*	*nd*	111.7	25.1	74.2	*nd*	*nd*	4.7	1.3	2.6	31.0	3.3	0.6	*nd*	16.3	3.7	0.9	194.6	31.5	9.3
BH05	1058	6.32	23.4	265	134	*nd*	*nd*	3.2	106.1	18.4	61.1	0.2	*nd*	3.6	0.5	6.1	26.7	1.4	1.4	*nd*	4.0	8.5	4.6	180.9	24.5	13.1
BH06	1101	6.10	23.1	160	80	9.0	*nd*	4.5	92.6	24.2	33.7	*nd*	0.2	1.0	2.1	4.8	15.5	1.8	4.3	*nd*	3.7	*nd*	1.2	136.7	11.6	112.4
BH07	1093	6.35	23.3	422	211	*nd*	5.4	*nd*	112.9	23.7	108.6	0.3	0.8	2.6	1.3	3.4	16.6	2.7	0.2	2.1	6.9	1.4	4.9	270.6	37.0	3.0
BH08	1102	6.33	23.3	248	125	*nd*	*nd*	*nd*	113.5	24.0	65.5	0.1	0.3	2.1	3.0	6.9	7.0	1.8	0.2	7.5	6.5	3.0	4.2	204	23.4	0.8
BH09	1106	6.45	23.5	301	150	*nd*	*nd*	*nd*	80.7	25.4	72.2	*nd*	*nd*	1.9	1.1	4.3	7.6	1.6	10.8	2.3	*nd*	6.9	3.1	245.5	28.7	37.2
BH10	1037	6.43	23.8	307	153	5.4	*nd*	*nd*	128.7	20.6	46.6	0.1	0.2	1.1	1.9	25.8	8.0	3.2	0.7	10.6	8.9	*nd*	5.1	263.2	32.2	6.4
BH11	1059	6.61	23.4	290	146	*nd*	*nd*	2.2	117.4	20.7	74.6	*nd*	0.8	3.4	4.1	1.3	5.8	2.9	10	12.6	6.4	*nd*	1.5	292.8	31.9	7.9
BH12	1050	6.57	23.3	304	148	*nd*	*nd*	0.7	91.8	18.4	97.8	0.2	0.1	3.7	2.3	0.5	9.7	3.8	117	12.4	6.1	*nd*	3.6	314.1	28.0	*nd*
BH13	1021	6.40	23.8	403	204	*nd*	*nd*	*nd*	139.8	23.0	478	*nd*	*nd*	4.4	1.5	4.5	6.7	3.6	0.5	*nd*	12.0	12.6[b]	3.8	627.6	44.2	29
BH14	1031	6.34	23.8	280	142	*nd*	*nd*	*nd*	132.0	20.9	119.6	0.3	0.4	2.1	12.2	0.9	18.6	2.0	0.3	2.2	11.0	*nd*	6.0	343.1	29.4	*nd*
BH15	1071	6.64	24.0	266	132	*nd*	*nd*	*nd*	130.9	20.2	170.6	0.1	*nd*	2.6	1.4	4.6	7.8	2.4	*nd*	13.1	10.1	1.4	*Nd*	331.4	36.4	3.5
BH16	960	7.10	24.4	873[b]	438	*nd*	*nd*	2.7	108.6	15.2	25.3	0.2	0.4	4.0	0.2	1.4	1080	6.4	69.9	8.6	8.7	1.2	3.6	1113	72.7	*nd*
BH17	985	7.13	23.8	379	191	10.4	7.3	1.6	115.5	20.1	222.9	*nd*	*nd*	2.1	1.1	5.0	14.5	1.5	3.9	0.8	11.0	*nd*	3.1	230.8	57.8	15.1
BH18	944	6.97	24.4	414	206	*nd*	*nd*	*nd*	111.6	15.0	44.2	0.2	0.6	5.0	1.7	3.6	10.3	1.8	110	15.7	11.7	12.6[b]	1.0	237.5	34.8	22.9
BH19	938	6.81	25.2	371	187	*nd*	*nd*	*nd*	118.4	15.9	50	*nd*	0.2	4.5	*nd*	10.2	6.6	2.9	0.8	*nd*	7.8	10.8[b]	4.9	218	32.7	67.1
BH20	890	6.91	25.1	554	277	7.0	*nd*	4.2	131.9	26.8	325.6	0.2	0.8	3.2	14.1	1.1	24.2	3.7	0.6	16.5	12.1	14.3[b]	2.0	320.8	74.3	0.1
BH21	886	7.21	25.3	873[b]	417	*nd*	*nd*	*nd*	103.3	16.5	27.5	*nd*	0.5	3.3	3.4	0.2	1096	8.1	89.9	*nd*	9.7	*nd*	2.4	1132	47.3	*nd*
WHO		6–8.5		750	1000	–	200	50.	–	50	700	–	10	–	50		1000	–	400	–	50	10	–	–	–	1500
MSB		6–9.5		3500	2000	–	500	50	–	50	–	–	10	–	–	2000	3000	–	1500	–	50	10	–	–	–	1500

nd = not detected.
Elev. = Site elevation above mean sea level (m).
Temp. = Temperature (°C).
MSB = Malawi Standards Board (MSB, 2005) limit values.
[a] Concentration in μg/L.
[b] Exceeding WHO (2011) maximum permissible levels.

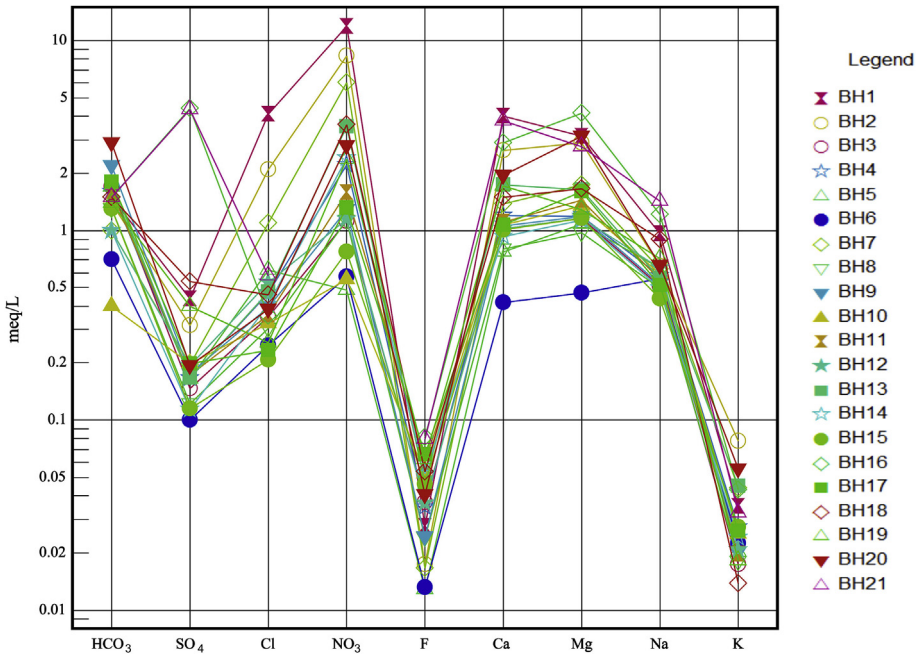

Fig. 2. Schoeller diagram illustrating major ion balance for Machinjiri area.

latter being more abundant. This suggests that association of Greenockite (CdS) and sphalerite may be a probable reason for the coexistence of Zn and Cd in boreholes where both elements were detected (Table 1).

4.2.3. Poor metals

In this group of metals, the analytical study identified aluminium (3.6–7.3 μg/L), lead (3.7–16.5 μg/L) and tin (0.3–6 μg/L) in 14.5%, 95.2% and 90.5% of the total samples, respectively. From the overall data compiled in this study, aluminium (Al) was the least detected trace element (3 out of 21 samples) (Table 1).

The low concentration of lead (Pb) (Table 1) rules out anthropogenic contamination of the studied groundwater. Presence of galena (PbS), which has 86.6% Pb by weight, and other common minerals found naturally in the studied aquifer e.g. cerussite ($PbCO_3$) and anglesite ($PbSO_4$), are sources of the detected Pb levels.

Table 2
A rotated component matrix[a] extracted using principal component analysis.

Groundwater quality parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH		0.35	0.46	**0.70**	
EC	**0.92**		0.32	0.21	
TDS	**0.92**		0.32	0.21	
Ca	**0.92**		0.34		
K	**0.70**	0.11	−0.19	0.14	*0.58*
Mg	**0.86**	0.12	0.18	0.39	0.14
Na	0.50	−0.15	**0.77**		−0.13
Cl	**0.89**	−0.26	0.23	−0.17	
SO_4	0.37		**0.85**		−0.12
Si		**0.95**		0.11	
HCO_3	0.15			**0.86**	0.14
F	−0.22	**0.70**	0.25	0.28	*−0.38*
NO_3	**0.90**	−0.10			
Au		**0.95**	−0.14		
B	**0.88**	−0.26	−0.26		0.10
Ba	**0.91**	0.10		0.12	0.13
Co	0.10		**0.74**		
Cr	0.13	0.41	−0.34	**0.42**	
Cu	0.41		0.14	−0.40	**−0.60**
Fe	0.15				**0.91**
Li	**0.93**		0.17		
Mn	**0.70**	−0.21	0.35	−0.11	*−0.45*
Pb	0.28	**0.66**	0.15		0.31
Sr	**0.88**	0.14			
V	**0.73**	0.30	0.11	0.55	
% of variance explained for Initial Eigenvalues	43.50	15.45	11.83	7.50	4.88

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

[a] Varimax with Kaiser Normalization was used as the rotation method.

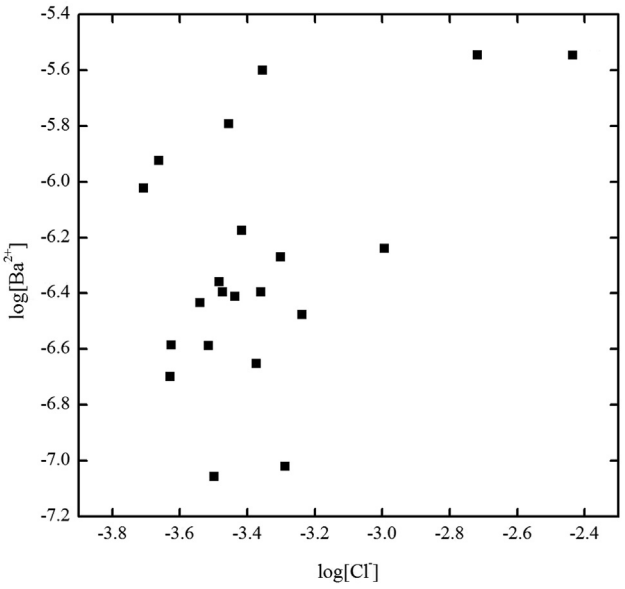

Fig. 3. Log-activity of Ba^{2+} versus log-activity of Cl^{-} (mmol/kg).

The other poor metal, tin (Sn), is found in trace amounts in granite intrusions containing cassiterite (SnO_2) mineral responsible for Sn in groundwater.

4.2.4. Metalloids (boron and arsenic) and selenium

In this study, concentrations of B were between 15.0 and 38.9 μg/L. Ionic B is favored at higher pH. However, the pH range observed in this study (Table 1) limits ionization of B, hence lower values detected. Agricultural activities (especially fertilizer application) can contribute to levels of B observed in this groundwater.

Out of 21 samples analyzed, 7 yielded traces of arsenic (As) between 0.7 and 4.5 μg/L (Table 1). The results were consistent with groundwater quality in the region (Mapoma and Xie, 2014; Mkandawire, 2008).

Lastly, 13 out of 21 groundwater samples in this study had Se ranging from 1.0 to 20.5 μg/L (Table 1). As shown in Table 1, 5 out of the 13 samples where Se was detected had values higher than WHO MPL (Se_{max} = 20.5 μg/L). In large quantities Se is toxic to human beings which calls for frequent monitoring of the boreholes identified to have such high values than recommended. Selenium is an impurity in metal sulfide ores (Fordyce, 2007), where it partially replaces sulfur. As such Se is associated with gypsum ($CaSO_4$) mineral occurrence in the area.

4.3. Factor analysis

Factor analysis (FA) was used to elucidate the relationships amongst the dataset. The FA isolated five (5) significant factors based on their Eigenvalues > 1 that explained 87.4% of the variance amongst the dataset (Table 2).

The positive relationship between major elements/TDS/EC and trace elements (Li, Ba, V, Sr, B and Mn), infer the significant role of major solutes on dissolution of these trace elements in the investigated groundwater samples (see Table 2). For example, the activity of Cl (Fig. 3), can influence dissolution of Ba from $Ba(NO_3)_2$ or $BaSO_4$ end-members by anion exchange. Factor 2 suggests that silicate end members may play a role in presence of dissolved gold and lead in the samples deduced from the relationship between silica and these two trace elements.

The results show a strong relationship between Co and Na while Na had a significant correlation with SO_4 (Factor 3). Thus, processes involved in dissolution of sulfate containing minerals (such as mirablilite and gypsum) and cation exchange with Na potentially increases concentration of Co in basement complex.

Groundwater pH has a controlling effect on trace element mobility and solubility (Paschke, 2007; Welch and Stollenwerk, 2003) despite the degree of chemical evolution of the water sample. Groundwater pH is influenced by many factors, with HCO_3 being one of its main controls. pH and HCO_3 displayed positive relationships with Cr as indicated by Factor 4 (Table 2). Chromium exhibits a wide range of oxidation states dependent on pH evolution. Thus, changes in HCO_3 concentration in the groundwater influence the oxidation state and Cr concentration in the aquifer.

Fe showed a negative relationship with Cu and F, yet positive with K (Factor 5). FeF_2 and CuF_2 minerals are sources expected to increase presence of Fe and Cu in groundwater, respectively. FeF_2 is slightly soluble in water (Greenwood and Earnshaw, 2012) while CuF_2 is hygroscopic. It follows that presence of K in groundwater and other alkali metals induce the dissolution of Fe while cation exchange controls the concentration of Cu in the aquifer. The Pearson's correlation matrix (Table 3) supports the factor analysis results.

Table 3
Pearson's correlation matrix showing the relationships amongst trace elements.

	B	Ba	Be	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	Se	Sn	Sr	V	Zn
Au	−0.25	0.06	0.20	0.08	0.42	0.04	−0.13	−0.19	−0.31	0.22	0.31	0.18	0.37	−0.08	0.16	−0.37
B		**0.77**	−0.05	−0.16	0.08	0.34	−0.37	0.29	*0.52*	−0.19	0.27	0.06	−0.43	0.01	0.25	−0.19
Ba			−0.04	0.16	0.07	0.25	−0.24	0.43	*0.50*	0.01	0.29	0.15	−0.26	0.28	***0.55***	−0.28
Be				−0.29	0.32	−0.27	0.09	−0.07	0.18	−0.23	0.09	0.41	−0.02	0.08	0.10	−0.50
Co					−0.09	0.02	0.16	0.35	*0.44*	0.18	0.03	−0.17	0.03	0.29	0.29	−0.09
Cr						−0.23	−0.08	−0.05	−0.09	0.15	0.15	0.32	0.12	−0.06	0.20	−0.23
Cu							−0.24	0.17	***0.57***	−0.23	−0.06	−0.02	0.16	−0.06	0.03	0.04
Fe								***0.65***	0.03	0.01	−0.03	−0.34	0.01	**0.84**	0.41	−0.22
Li									***0.59***	0.08	0.13	−0.20	−0.22	**0.88**	***0.63***	−0.29
Mn										−0.25	0.02	−0.06	−0.20	0.35	0.35	0.04
Ni											0.01	0.28	−0.42	0.01	0.09	−0.37
Pb												0.47	−0.44	0.09	0.36	−0.40
Se													−0.49	−0.26	0.00	0.42
Sn														−0.06	−0.17	−0.07
Sr															***0.63***	−0.30
V																−0.49

Bold = Correlation is significant at the 0.001 level.
Bold Italicized = Correlation is significant at the 0.01 level.
Italicized = Correlation is significant at the 0.05 level.

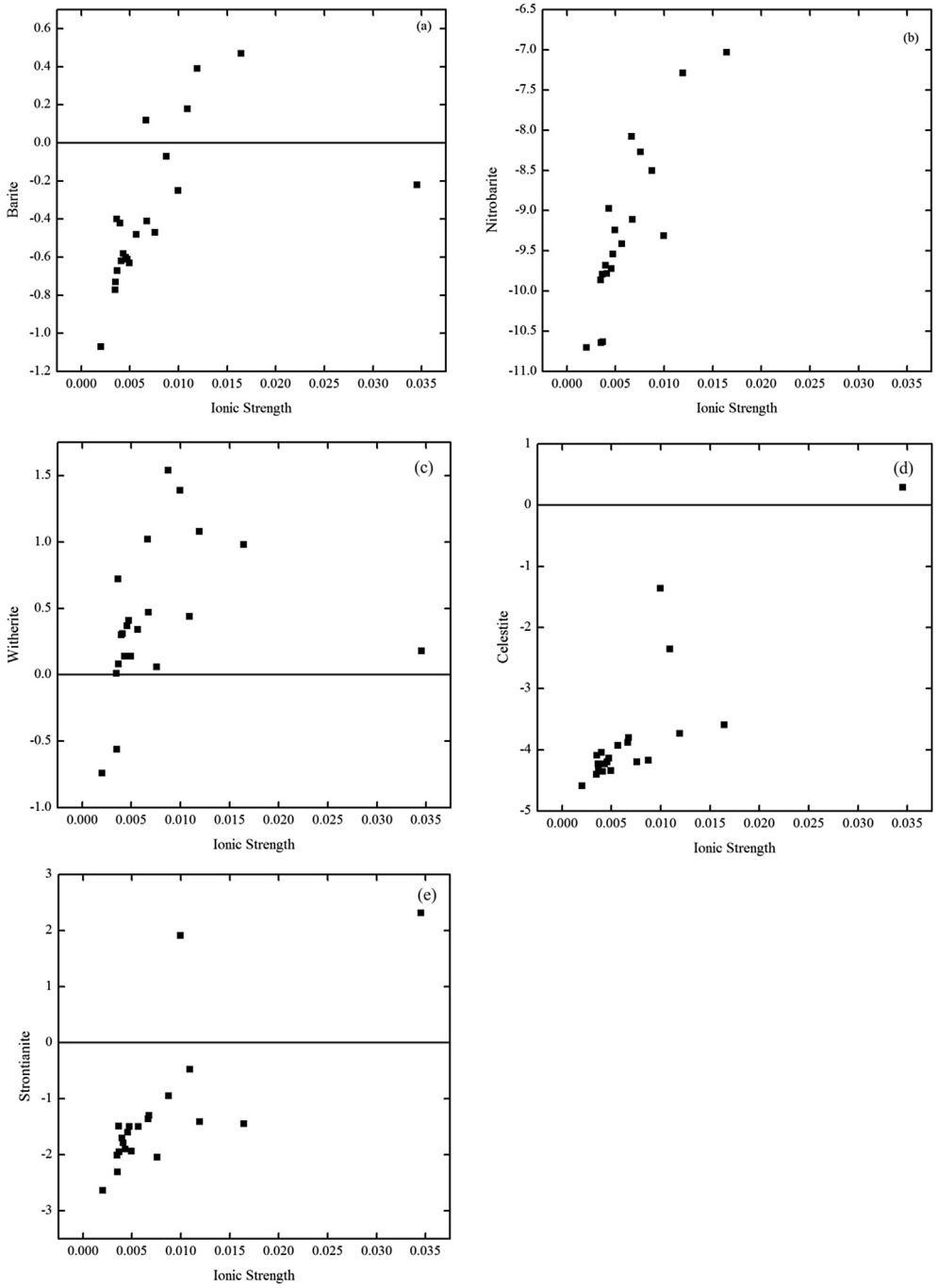

Fig. 4. Variation of saturation indices for barite (a), nitrobarite (b), witherite (c), celestite (d) and strontianite (e) with ionic strength (unitless).

4.4. Geochemical modeling

4.4.1. Saturation indices

Trace element hydrochemistry is controlled by mineral phase end-members existing within the aquifer, although, human activities may also play a key role in elevating the levels. Precipitation reactions taking place in groundwater is one way of attenuating dissolved trace elements. Inverse geochemical modeling using PHREEQC identified the saturation state of each end-member for the trace elements analyzed.

In the alkali and alkaline earth metals group, barite ($BaSO_4$), witherite ($BaCO_3$) and nitrobarite ($Ba(NO_3)_2$) end-members are sources of dissolved Ba. Yet, Ba dissolution is mostly controlled by barite (Underwood et al., 2009). All twenty one groundwater samples varied between undersaturated to saturated with respect to barite (Fig. 4a) while undersaturated with respect to nitrobarite (Fig. 4b), indicating possible mixed dissolution/precipitation controls. Furthermore, the studied samples were saturated with respect to witherite except for BH16 and BH21 that displayed an undersaturation with respect to the mineral phase (Fig. 4c). High concentrations of SO_4 and anion exchange with NO_3 favors barite formation over the more soluble nitrobarite.

The inverse model showed that the groundwater was undersaturated with respect to celestite ($SrSO_4$) end-member (Fig. 4d),

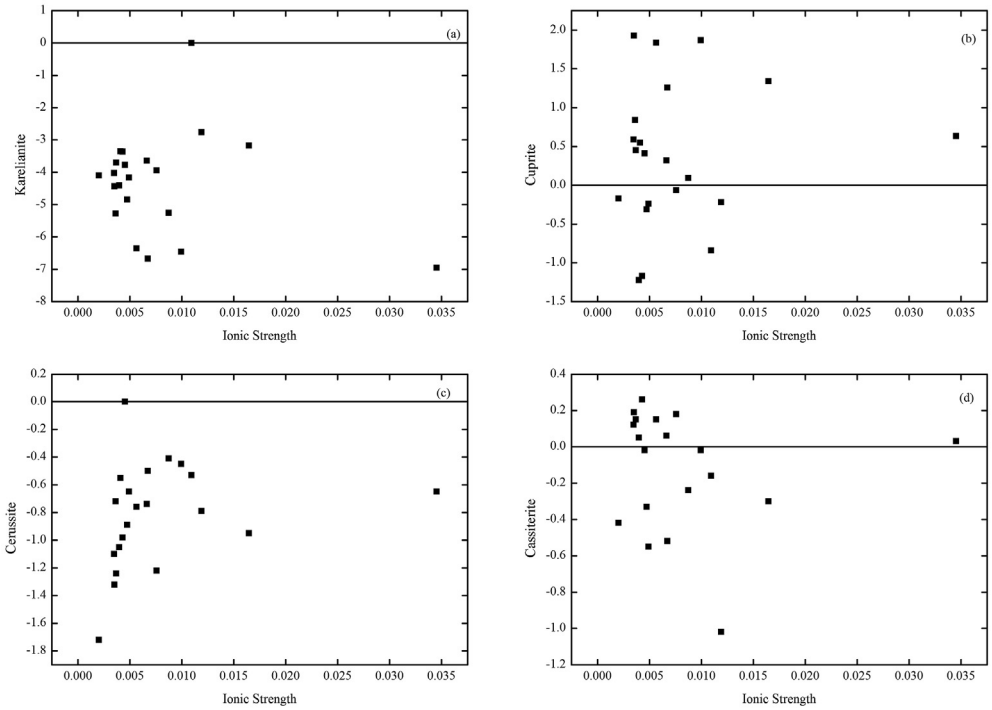

Fig. 5. Variation of saturation indices for karielianite (a), cuprite (b), cerussite (c) and cassiterite (d) plotted against ionic strength (unitless).

suggesting that dissolution of evaporite minerals (e.g. celestite) could be the prominent source of Sr. But, the undersaturation of Sr with respect to strontianite ($SrCO_3$) (Fig. 4e) is a sign of mixed evaporite dissolution and carbonate weathering processes releasing strontium into the groundwater. Conversely, the model identified two boreholes (BH16 and BH21) whose groundwater was oversaturation with respect to strontianite (Fig. 4e). Incidentally, BH16 and BH21 have relatively higher concentrations of strontium (Table 1). In these two groundwater samples, formation of strontianite in the system equilibrates strontium concentrations in the system.

In the transitional metals group, V was modeled to be undersaturated with respect to Karelianite (V_2O_3) (Fig. 5a) as one important mineral dissolving to increase V in groundwater. Also, the present study showed that groundwater was undersaturated with respect to hematite (Fe_2O_3; SI < -1.42) and siderite ($FeCO_3$; SI < -1.74) while Fe levels being buffered by saturation with respect to goethite (FeO(OH); SI > 0.68). The undersaturated to saturated state of groundwater with respect to cuprite (Cu_2O) (Fig. 5b) explains the variations in Cu levels while undersaturated state with respect to willemite (Zn_2SiO_4) end-member (SI < -3) suggest a silicate dissolution processes controlling the concentration of Zn in groundwater in this area.

Of the poor metals, it was found that Pb was undersaturated with respect to cerrusite ($PbCO_3$) (Fig. 5c), anglesite ($PbSO_4$; SI < -3) and alamosite ($PbSiO_3$; SI < -2) implying that carbonate weathering, evaporite dissolution and silicate weathering are processes controlling Pb levels in the studied aquifer. Lastly, the state of groundwater samples varied between undersaturated to saturated with respect to cassiterite (SnO_2) (Fig. 5d) suggesting a mixed dissolution/precipitation mechanism controlling the availability of dissolved Sn in the studied aquifer.

4.4.2. Equilibrium speciation analysis

PHREEQC speciation analysis was done to show the predominant ionic state of each trace element within the pH conditions of the studied groundwater samples. The analysis showed that 99% of Li was in free ionic form (Li^+) in the groundwater samples studied and $LiSO_4^-$ dominated the remaining 1%. The dissolved Ba and Sr (*alkaline earth metals*) exist in form of free ions (>95% and >90%, respectively) in this aquifer. The remaining percent comprises of $BaNO_3^+$, $SrNO_3^+$ and $SrSO_4$ complexes (Fig. 6a and b, respectively) probably due to high concentration of NO_3 and SO_4 in the groundwater studied relative to Cl and F.

In the *transitional metals* group, the dominant species of Cr was $Cr(OH)_2^+$ followed by $Cr(OH)^{2+}$ and $Cr(OH)_3$ (Fig. 6c) and traces of Cr^{3+}. Similarly, 8 vanadium species were identified with $H_2VO_4^{2-}$, $VO_2(OH)_2^-$ and VO_3OH^{2-} dominating, in that order (Fig. 6d). One sample (BH21) showed dominance of $VO_3(OH)_2^-$ followed by $VO_2OH_2^-$. In general, the investigated groundwater has prevalence of vanadium (V) over other forms of vanadium. After all, Cr and V tend to form oxyanions mostly, which supports these speciation results.

Free Mn^{2+} is the most dominant species that was identified through PHREEQC geochemical modeling (Fig. 6e). High concentrations of SO_4 in BH16 and BH21 samples increased the percentage of $MnSO_4$ in the aquifer compared to other species in these two boreholes. As well, the predominant species of Fe were Fe^{2+} ($\approx$> 60%) and $FeHCO_3^+$. Nevertheless, traces of $FeCO_3^+$ and $FeSO_4$ were observed (Fig. 6f).

Co(II) is predominant over Co(III) in the investigated samples, and the most predominant ionic species observed through modeling was Co^{2+} with high percentage of $HCoO_3^-$ especially for boreholes BH16, 17, 18 and 21 samples (Fig. 7a). Above 99% of the modeled species of Ni occurred as Ni^{2+} followed by traces of $NiNO_3^+$, $NiSO_4$, $NiCl^+$ and $Ni(NO3)_2$. Nevertheless, the sample obtained from BH16 had significant concentrations of $NiSO_4$ (9.12%) relative to Ni^{2+} (90.48%) explained by lack of NO_3 in the samples.

Within the same transitional metal group, the dominant species of Cu were $CuCO_3$, $CuCl_2^-$ and Cu^{2+} (Fig. 7b). Presence of Cl promotes the concentration of $CuCl_2^-$ through ion exchange (Equation (2)).

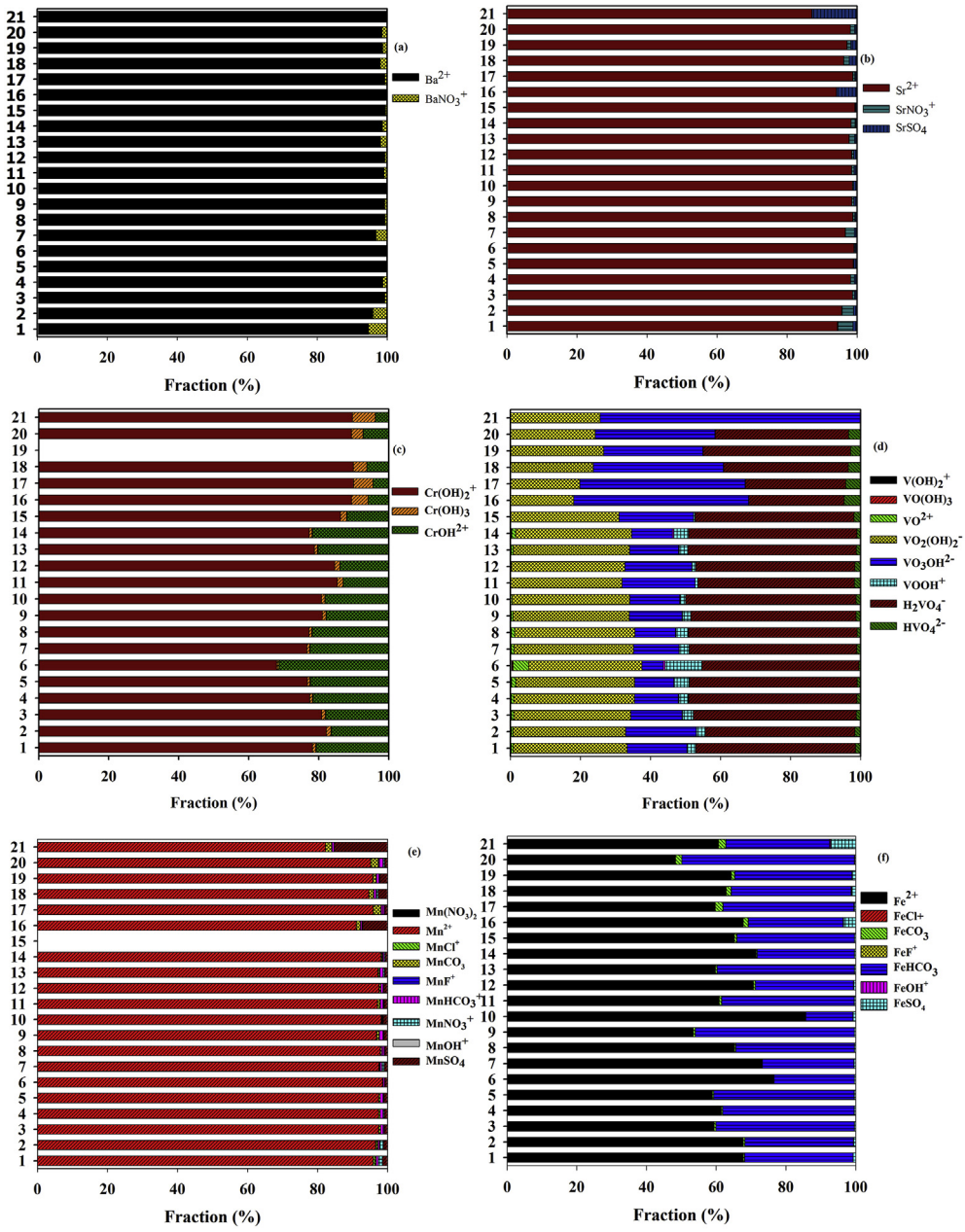

Fig. 6. Ba, Sr, Cr, V, Mn and Fe species modeled using PHREEQC. Samples without traces of elements are indicated by absence of bars.

$$CuSO_4 + M_xCl_2 \rightarrow CuCl_2^- + MSO_4 \quad (2)$$

where M may be Mg, Ca or Na.

As for poor metals and metalloids, the dominant Pb species identified in this study is Pb^{2+} followed by $PbCO_3$ (Fig. 7c). Also, boron species in this study are consistent with expectation at lower pH in the basement complex, as the predominant boron species observed from modeling analysis was $B(OH)_3^0$ (>98%) and traces of BO_2^- and $MgB(OH)_4^+$.

PHREEQC speciation modeling suggest that the dominant species of Se detected in the studied groundwater samples is HSe^- (>99.51%) followed by H_2Se (Fig. 7d). However, the model shows that the distribution of Se species in BH15, 16, 17, 19 and 20 is in the following order: $HSe^- > HSeO_3^- > SeO_3^{2-} > H_2Se$ (Fig. 7d).

5. Conclusions

The study highlights the levels of trace elements in rural groundwater supply of Blantyre district where the free ions of gold, barium, cobalt, iron, lithium, manganese, nickel, lead and strontium species (i.e. Au^+, Ba^{2+}, Co^{2+}, Fe^{2+}, Li^+, Mn^{2+}, Ni^{2+}, Pb^{2+} and Sr^{2+}, respectively) dominate the ionic species in this group while complex forms of B, Be, Cu, Cr and V were the dominant species for this group. In terms of standards, Fe, Mn and Se exceeded WHO drinking water guidelines in 9.52%, 4.76% and 28.57% of the samples, respectively. Although the main source of trace elements in this aquifer is presence of native minerals, it is possible that human activities in the area interfere with the levels of trace elements. From this study, it is recommended that routine studies and monitoring as part of the management plan of the boreholes in Blantyre district be carried out.

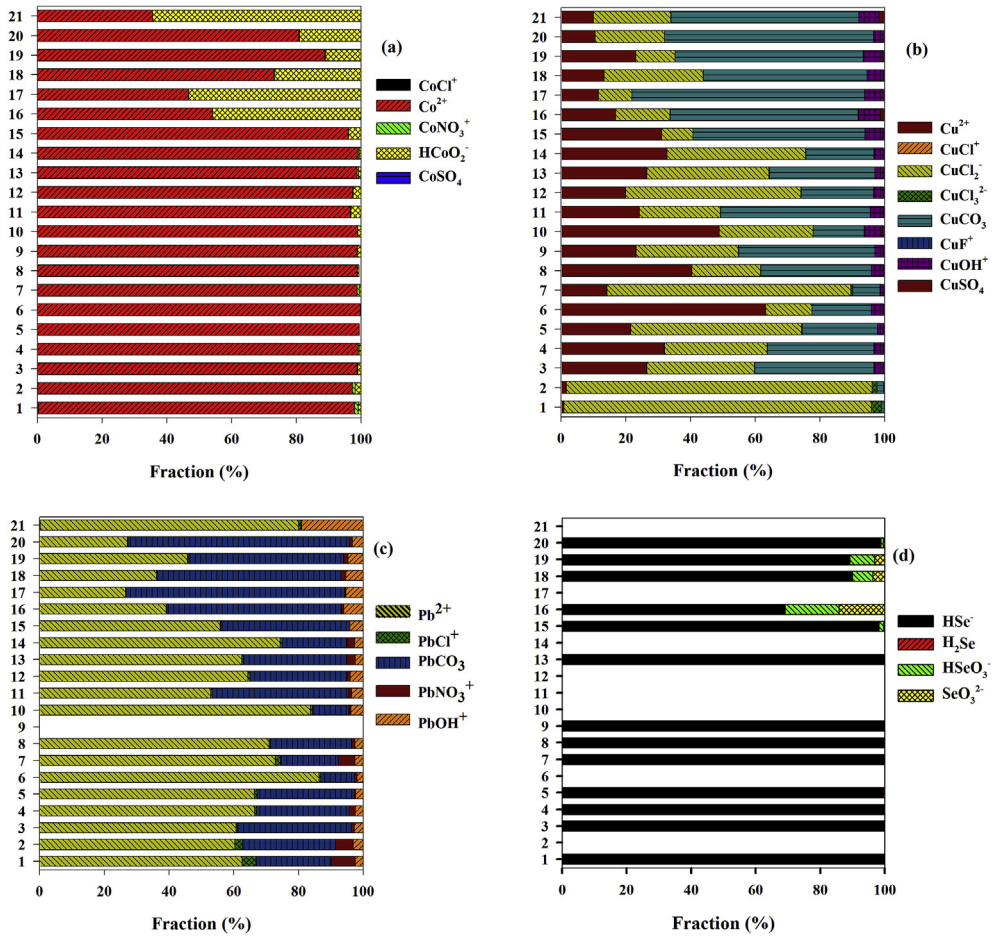

Fig. 7. PHREEQC speciation results for Co, Cu, Pb and Se. Samples without traces of elements are indicated by absence of bars.

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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.2017.04.011.

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