EFFECT OF CHEMICAL AND MINERALOGICAL COMPOSITION OF ROCKS ON THE GROUNDWATER CHEMISTRY OF HEWANIE AND ITS SURROUNDING AREAS, SOUTHERN TIGRAY, ETHIOPIA.

Abraha Nigusse[1], *Abraham Bairu[2], Nata Tadesse[3], and K. Bheemalingeswara[3]

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Abstract

The study was conducted in Hewanie and its surrounding areas of 169.82 km^2 with a major objective of identifying the effect of chemical and mineralogical composition of rocks on the chemistry of the groundwater quality. This was conducted by taking 11 groundwater and 5 rock samples from the main geological units of the study area. Water samples were analyzed for major cations and anions, trace elements, TDS, total hardness, pH, electrical conductivity, and alkalinity the rock samples for major cations and anions and trace elements using AAS. The data was used to qualify and assess the quality of groundwater in the study area. Concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-} of groundwater samples in mg/l varied from 84 to 412, 96 to 211.2, 19.09 to 43.93, 2.34 to 51.09, 244 to 585.6, 71 to 340.8 and 49.49 to 122.5, respectively. Concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-} of rock samples in ppm varied from 2586.4 to 28540, 2575.8 to 5289.6, 28.83 to 6134.9, 190.3 to 2379, 293.74 to 3717.6, 433.1 to 1143.1, 2787.8 to 27849.6, respectively. The predominant cations trend in both the groundwater and rock samples the study area was $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$. Therefore, it is concluded that the local rock chemistry is seriously affecting the groundwater chemistry.

Key words: *Rock-water interaction, groundwater, rock, mineralogical composition, quality, Hewanie, Ethiopia.*

Introduction

Some of the substances that find their way naturally into groundwater are unhealthy to us or to other life forms. Groundwater is essential for human and all other living things as food. In addition to groundwater uses for drinking, humans need groundwater for various other purposes like bathing, washing, and cooking, industrial, agricultural and recreational activities. Thus, the availability of adequate groundwater supply in terms of its quantity and quality is essential for the existence of life. It should be free from pathogens-disease causing microbes and toxic or physiologically undesirable chemicals or biological materials. Groundwater is available in nature in the form of groundwater and surface water. Discharge of wastes poses problem for surface, while seepage of chemicals from dumpsites may affect groundwater depending on the nature of the underlying rocks in the area. Hence, groundwater requires physical, chemical and biological treatment, depending on the nature of existing pollutants, before being supplied for domestic uses .To plan and implement the type and extent of treatment, natural groundwater must be analyzed for physical, chemical and microbiological parameters. After appropriate treatment in a groundwater treatment plant, the quality of groundwater is again tested to ensure its suitability for human consumption. The suitability of groundwater is judged on the basis of modern drinking groundwater standards set up by different governmental and health agencies. Groundwater resource protection is a universal problem for the continued existence of mankind, and the management of this problem requires cooperation between governmental and nongovernmental organizations. The importance of groundwater for man and his environment has been clearly defined in 12 items of the European charter on groundwater declared by European council on May 6, 1948 in Strasbourg (Tolgyessy, 1993).

Inhabitants of Hewanie and its surroundings are predominantly using groundwater for domestic purposes. Water of acceptable quality is scarcely

[1]*Department of Civil Engineering, Institute of Science and Technology, Ambo University, Ambo, Ethiopia.*

[2]*Research and Technology Development Directorate, Tigray Science and Technology Agency, Mekelle, Tigray, Ethiopia.*

Corresponding author email: abrahambairu@ymail.com

[3]*Department of Earth Sciences, Mekelle University, Mekelle, Tigray, Ethiopia.*

available and hence they are suffering from hardness and salinity□ hazards due to the inappropriate concentration of ions in the groundwater. The groundwater quality problems which are observed in the study area may also cause various health problems for the peoples of that area. It is expected that the dissolved solids in the groundwater may exceed the standards, which are set by the World Health Organization (WHO). Therefore, performing the qualitative analysis of this groundwater is vital to recommend solutions. The Tigray Regional Government has also aimed at providing quality groundwater to the people of the region. In line with that an effort present paper tries to address the problems in terms of groundwater quality and help finding solutions.

The results of the investigation conducted in and around Hewanie in Hintalo Wejjerat Wereda, southern Tigray, Ethiopia carried out with an objective of identifying the effect of chemical and mineralogical composition of rocks on the chemistry of the groundwater quality are presented.

Methodology

Location

The study area is geographically located between 1445000 to 1453000m N and 551000 to 556000m E with an aerial extent of 169.82 sq. km. The area is surrounded by mountains where the drainage pattern is mainly dense and shows dendritic pattern. The streams generally flow towards the northwestern part (Figure 1).

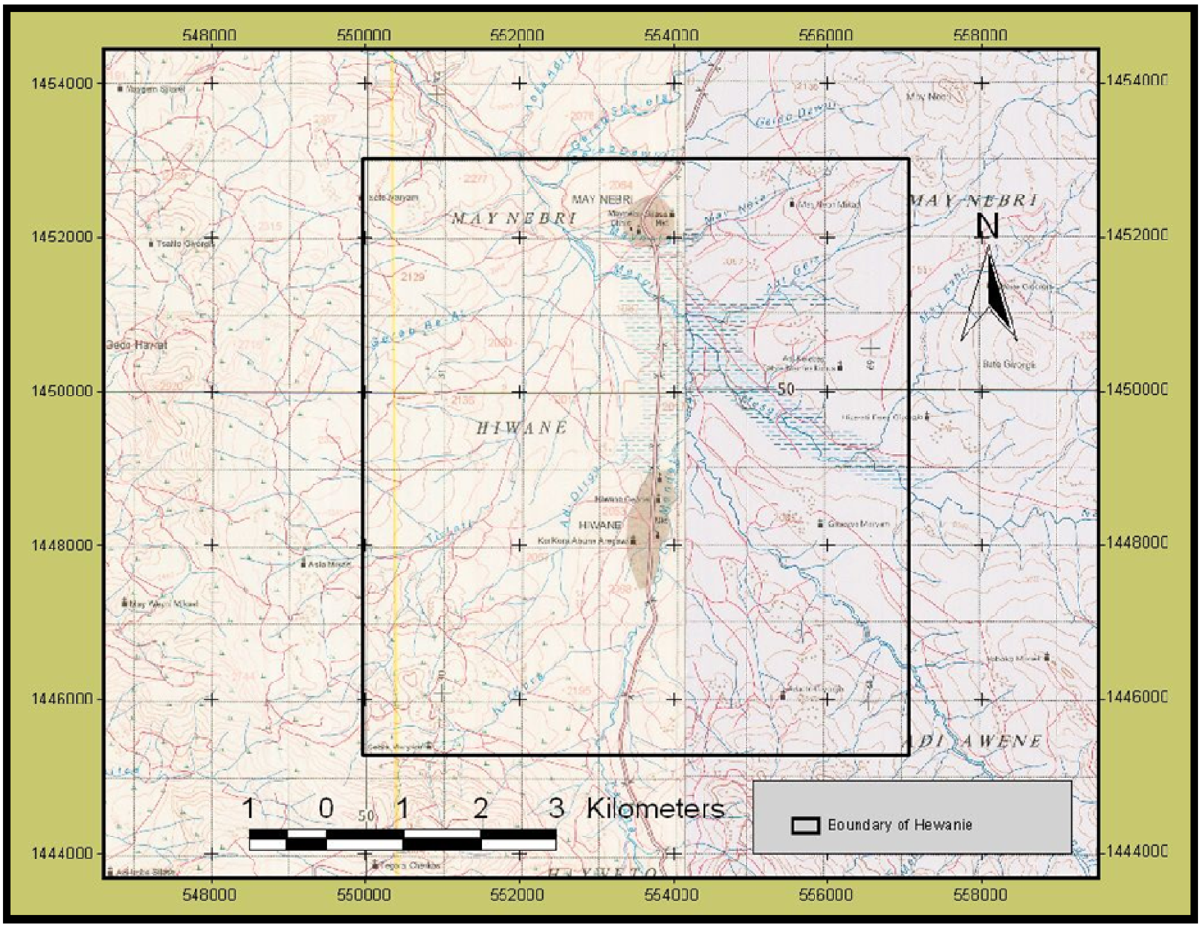

Figure 1 Location map of the study area

Sampling

Eleven groundwater and five rock samples were collected from the selected wells and selected main geologic units, respectively. All the groundwater samples were collected in pre-washed, numbered two liter plastic bottles using depth integrated sampling techniques. Care was taken not to take stagnant groundwater and also the ones which are protected free from surface water interaction and other surface contaminants. Further, the wells selection, well location and the local rock was also taken into consideration. The rock samples were also taken from the dominant geologic units and fresh samples greater than ½ a kilogram were taken in properly numbered plastic bags. The details of groundwater and rock samples are given below.

A total of ten groundwater samples were collected. One sample (MAHP1) from the basalt and shale and limestone intercalation, one sample (KUHP2) from the upper sandstone and limestone contact points, two samples (TSEHP3 and TSEHP4) from the thick Shale and thin limestone, two samples (GBHP5 and SWNT) form the shale and limestone intercalation, one sample (HTHP6) from the alluvial deposit, one sample (BW(FTC)) from the crystalline limestone and two samples (MSGSP1 and MSGSP2) from the micritic limestone. Similarly, one rock sample (MA) from the basalt and shale and limestone intercalation, one rock sample (TS) from the thick Shale and thin limestone, one rock sample (GB) from the shale and limestone intercalation, one rock sample (FTC) from the crystalline limestone and one rock sample (MSG) from micritic limestone totally five rock samples were collected from the study area (Figure 2).

Sample analyses

These rock samples were powdered, agitated and analyzed for major cations and trace elements Ca, Mg, Na, K, Fe, Mn, Co, Cu, Ni, Pb and the major anion constituents Cl, SO_4, and HCO_3 using Atomic Adsorption Spectrophotometer (AAS) and Ultra Violet Spectrophotometer (UVS) at Ezana Mining Development Analytical Laboratory PLC.

The groundwater samples were also analyzed for major and trace ions. The major cations and anions were analyzed using Atomic Adsorption Spectrophotometer (AAS) and Ultra Violet Spectrophotometer (UVS), respectively by Tigray Agricultural and Rural Development Bureau Soil and Groundwater Laboratory, and the trace cations and anions were detected using Atomic Adsorption Spectrophotometer (AAS) in Ezana Mining Development Analytical Laboratory PLC. as per the standard methods of APHA (2005) and Eaton *et al.* (1998).

The qualities of the groundwater were assessed in terms of total hardness, total dissolved solids, alkalinity, electrical conductivity (ECw), pH and concentration of major and minor and trace constituents. The total dissolved solid (TDS) was calculated from the electrical conductivity of the groundwater (ECw), the total hardness (TH), from the concentration of Ca and Mg. Alkalinity was calculated from the concentration of the HCO_3 as $CaCO_3$ and pH. The physical parameters such as the temperature, ECw and pH were measured in-situ using standard equipment (Century Water Analysis Kit).

$$\text{Total hardness (TH)} = 2.5Ca^{2+} + 4.1Mg^{2+} \ldots (1)$$

Where: TH, Ca and Mg are measured in milligrams per liter and the ratios in equivalent weights (Fournier, 1981).

An approximate relation for most natural groundwater in range of 100 to 5000 micro siemens per centimeter are stated below were used to determine the total dissolved solids (TDS) of the groundwater samples (Todd, 2005).

$$1\text{meq/l of cations} = 100\mu S/cm \text{ and } 1mg/l = 1.56\mu S/cm \ldots\ldots (2)$$

If all of the alkalinity in the sample is a result of inorganic carbon species, the distribution of these species between bicarbonate and carbonate can be calculated using the equilibrium constants for the speciation reaction and the measured pH of the solution with the following equation (Deutsch, 1997).

Alkalinity (mg/l $CaCO_3$) = [HCO_3^-] mg/l x (1 + $\frac{2x10^{-10.3}}{10^{-pH}}$) x 50 / 61…………………… (3)

Data analyses

SPSS 15.0 version software was used to carry out standard statistical analysis for: minimum, maximum, mean, standard deviation and also to produce graphs of the chemical parameters of the groundwater and rock samples.

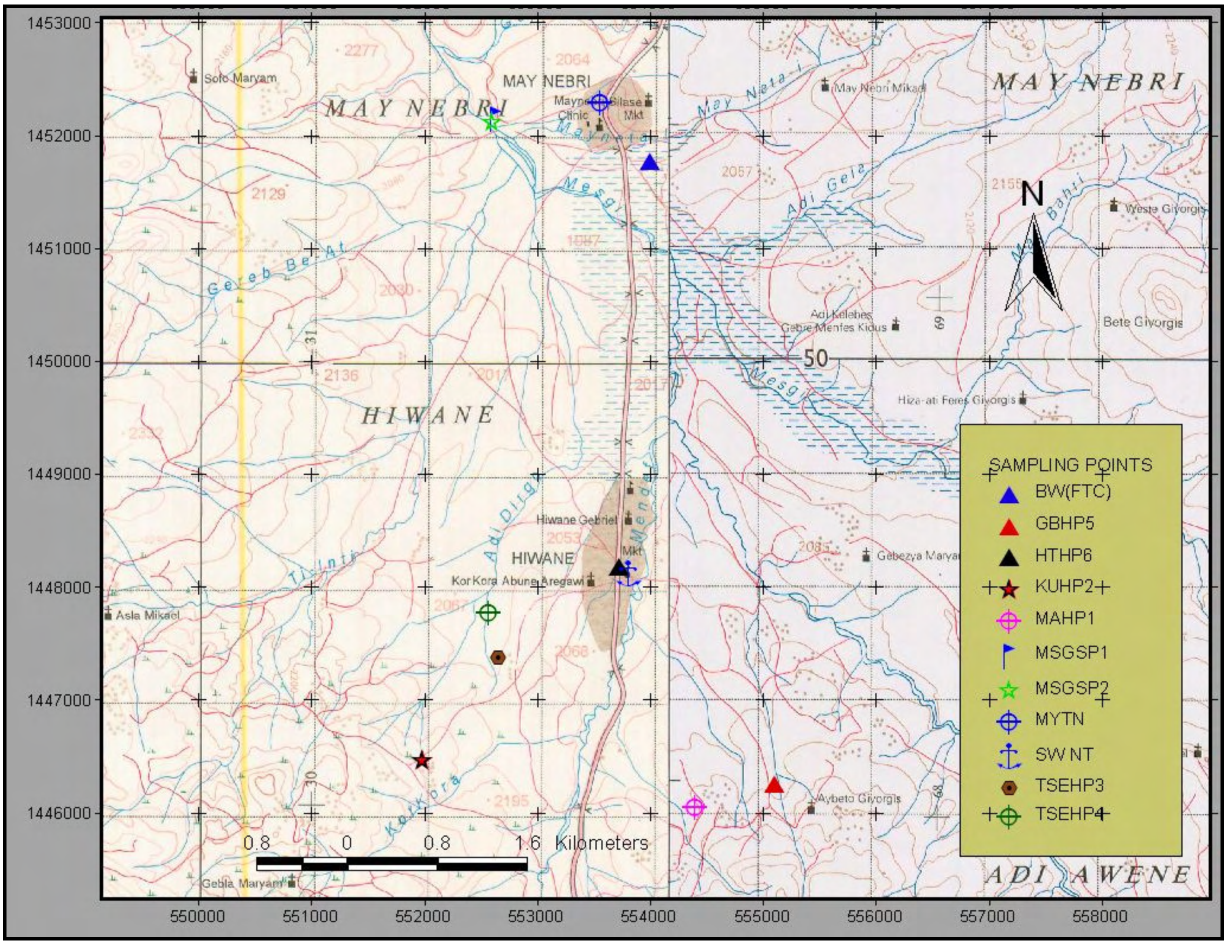

Figure 2 Sampling locations of groundwater and rock samples

Result and Discussion

Groundwater analysis
Cations and Anions of the Groundwater Samples

The concentration of the major cations and anions varied widely. Concentration of Ca^{2+}, Mg^{2+}, Na^+ and K^+ varied from 84 mg/l at SWNT to 412 mg/l at GBHP5 and MSGSP2, from 96mg/l at KUHP2 to 211.2mg/l at MSGSP1, from 19.09mg/l at KUHP2 to 43.93mg/l at MSGSP1, from 2.34mg/l at MAHP1 to 51.09mg/l at GBHP5, respectively (Table 1 and Figure 3). Concentrations of major anions also varied largely. Concentrations of HCO_3^- varied from 244mg/l of MSGSP2 to 585.6 mg/l at HTHP6, Cl^- varied from 71mg/l at MAHP1 to 340.8 mg/l at

MSGSP2, SO_4^{2-} ranged from 49.49mg/l in MAHP1 up to 122.5 mg/l of BW(FTC) (Table 1 and Figure 4).

Concentrations of Na^+ and SO_4^{2-} of all the groundwater samples were <200mg/l and <300mg/l and concentrations of Mg^{2+} and Cl^- were >50mg/l and >10mg/l of the concentration levels in natural water. One, three and four groundwater samples had concentration values of Ca^{2+}, HCO_3^- and K^+, respectively found < 100mg/l, <500mg/l and <10mg/l the concentration levels in natural water while the remaining groundwater samples were above concentration levels in natural water Todd (2005).

Electrical conductivity of groundwater (ECw)

The electrical conductivity of the groundwater samples ranged from 0.88dS/m to 3.01dS/m at 25°C through the sample codes KUHP2 to GBHP5, respectively (Table 1). The high ECw in the GBHP5 indicates that, there are high amounts of dissolved solids. These dissolved solids come from the soluble rocks particularly Shale and the Micritic limestone which are dominant in the area. Since EC is directly related to TDS, the locations showing minimum and maximum values were observed at KUHP2 and GBHP5 for both parameters EC and TDS. Hence, according to Driscoll (1986), the ECw of 6 groundwater samples were found within the good water class while the remaining 4 groundwater samples were found within the fair water class for the ECw between 0.7 – 1.5dS/m and 1.5 – 3.7dS/m, respectively.

Total dissolved solids (TDS)

The Total Dissolved Solids in the groundwater samples ranged from 564.10 mg/l to 1929.48mg/l at KUHP2 and GBHP5, respectively (Table 1 and Figure 5). Based on the WHO (2004), the groundwater samples are classified in to four categories. Out of the 11 groundwater samples only 1 is categorized as good (300 – 600mg/l), 4 are fair (600 – 900mg/l) and 1 is poor (900-1200mg/l) and the remaining 4 are unacceptable (>1200mg/l).

The minimum amount is observed at KUHP2 which was taken from a spring originating from basalt and limestone contact point and the maximum amount is observed at GBHP5 which was taken from Shale and Micritic limestone intercalation. These dissolved solids are results of the soluble rocks.

According to Freeze and Cherry (1979), six groundwater samples were considered as fresh groundwater and 4 groundwater samples were considered as brackish groundwater.

Total Hardness

The total hardness of groundwater samples varied from 683.44 mg/l to 1768.32mg/l (Table 1 and Figure 5). The lower value at MAHP1 was found from the contact spring of the basalt and limestone and the higher value at GBHP5 was found from the thick shale and thin limestone intercalation. Due to the chemical composition of the micritic limestone dominantly found in this area the Ca and Mg content of the groundwater becomes high hence it is very hard. Generally, all the groundwater samples of the study area were found within the class of very hard water as TDS values ≥ 300mg/l, Sawyer and McCarty, 1967. Unlike to this study 12 out of 14 groundwater samples analyzed were found soft while the remaining 2 were hard water in the study conducted in Gubrunde and Environs, Northern Nigeria (Arabi *et al.*, 2010).

Alkalinity

Alkalinity was calculated using the above formula and the computed values ranged from 200.65mg/l of CaCO3 at MSGSP1 – 480.12mg/l of CaCO3 at HTHP6 (Table 1 and Figure 5). All the groundwater samples of the study area exhibit alkalinity values above the permissible limit of 120 mg/L (WHO, 2008). This may be due to the dissolution of crystalline limestone in the in the study area. It may also be noted that in polluted waters, other negative ions like PO4, NO3 may contribute to alkalinity (NAS, 1974).

pH

The groundwater of the study area was found basic its pH values ranged from 6.84 to 7.43. The lowest pH was measured at HTHP6 and the highest pH was measured at sample MSGSP2 (Table 1). The groundwater samples were found within the Secondary Maximum Contaminant Level (SMCL) for pH is 6.5 to 8.5 on pH scale as established by the APHA, (2005).

Groundwater Types

Totally four groundwater types were identified: Mg-Ca-HCO_3, Mg-Ca-HCO3-Cl, Ca-Mg-HCO_3 and Mg-HCO_3 type. Out of these the dominant one is Mg-Ca-HCO_3. This groundwater type was found in 7 of the groundwater samples out of the 11. Generally, the groundwater of the study area is dominated by the major ionic components. Unlikely, two water types Ca – Mg – HCO_3 and Ca – Mg – SO_4 – Cl were found in the groundwater samples of Port Harcourt City, Southern Nigeria (Nwankwoala and Udom, 2011).

Trace constituents of the groundwater samples

Trace elements are contributed to groundwater from a variety of natural and anthropogenic sources. Once liberated into groundwater, element distributions are continually modified by complex geochemical and biological processes (Newcomb and Rimstidt, 2002).

The concentrations of Pb, Co, Cu, Zn, and Mn of groundwater samples varied from undetectable to 0.06mg/l at two samples TSEHP3 and HTHP6, from undetectable to 0.12mg/l at GBHP5, from 0.06mg/l at MAHP1 and BW (FTC) to 0.09mg/l at KUHP2, MSGSP1 and MSGSP2, from undetectable to 0.29mg/l at KUHP2 and from undetectable to 0.13mg/l at GBHP5, respectively (Table 2).

The concentration of the trace elements Cu, Ni and Mn for the groundwater samples of the study area were found within the maximum permissible limit of drinking water, which is 2mg/l, 0.07mg/l and 0.4mg/, respectively. However , 60% of the Pb concentration of the groundwater samples was found within the permissible limit, 0.01gm/l while the remaining 40% was found above the maximum permissible limit of drinking water set by WHO (2008).

Rock Analysis

Major cations and anions of rock samples

Concentrations major cations of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} of rock samples of the study area varied from 2586.4ppm at TS to 28540ppm at FTC, from 2575.8ppm at TS to 5289.6ppm at FTC, from 28.83ppm at MA to 6134.9ppm at GB, from 190.3ppm at MA to 2379ppm at GB, respectively (Table 3 and Figure 6). Concentrations major anions of HCO_3^- varied from 293.74ppm at MSG to 3717.6ppm at TS, Cl^- varied from 433.1ppm at TS to 1143.1ppm at MSG, SO_4^{2-} ranged from 2787.8ppm at TS to 27849.6ppm at FTC (Table 3 and Figure 7).

Trace elements of rock samples

The concentrations of Pb, Co, Cu, Zn, Mn, Ni and Fe varied from undetectable to 2ppm at two samples GB and FTC, 9ppm at all samples to 198ppm at MSG, from 5ppm at FTC – 25ppm at MSG, from 5ppm at MA to 60ppm at FTC and from 36ppm at MA to 421ppm at FTC, from less than 2ppm at MA to 105ppm at MSG and from 1190ppm at MA to 42400ppm at TS, respectively (Table 3). According to Klimasauskas *et al.*, (2007) the concentration of Pb, Cu and Ni, ranged from 0.5 – 10,000ppm, the concentration of Co ranged from 0.1 – 10,000ppm, the concentration of Zn ranged from 1 – 10,000ppm and the concentration of Mn ranged from 5 – 10,000ppm hence the concentrations of these elements in the study area were found within this bound.

Rock – Water Interaction

The predominant major cations trend in the study area was $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and the abundance of the major anions was in the following order: $HCO_3^- > Cl^- > SO_4^{2-}$ while carbonates remain nil throughout the groundwater samples. Similarly the abundance of cations in Port Harcourt City, Southern Nigeria was in the following order of $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and anions were also in the order of $HCO_3^- > Cl^- >$

$SO_4^{2-} > NO_3^-$ where calcium is the dominant cation while bicarbonate dominates the anionic components of the groundwater (Nwankwoala and Udom, 2011). Similarly, the carbonate concentrations of the study area remains zero as in the groundwater samples of Hantebet watershed in the application of water quality index to assess suitability of groundwater quality for drinking purposes, Tigray, Northern Ethiopia Gebrehiwot *et al.*, (2011).

The results of the chemical and mineralogical analysis of the rock samples show that the dominant major cations were found in the order of $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and the predominance of major anions were in the of $HCO_3^- > SO_4^{2-} > Cl^-$ (Table 1 and 3).

Conclusion

The predominant major cation trends in both the groundwater and rock samples of the study area was found similar in the order of $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and also similar major anion trends in both the groundwater and rock samples was observed. Therefore, from the results obtained it is possible to conclude that the high concentration of cations, anions, trace elements and dissolved solids in the groundwater samples come from the soluble rock units and hence the chemistry of the groundwater samples was affected by the chemical and mineralogical composition of the rocks.

From the results obtained from the rock sample analysis a large amount of calcium, magnesium and bicarbonate were found in the limestone both in the crystalline and micritic while relatively small amount of sodium and potassium were obtained. But in the shale samples relatively large amounts of sodium and potassium were found. Then, it was concluded that the source for large amount total hardness, TDS and alkalinity were largely the micritic limestone and some extent the crystalline limestone. But in the shale the dominant components are silica and iron which are less soluble in groundwater.

The sulphate in the groundwater is limited, because of the limited amount of gypsum and its less solubility.

Recommendation

The causes for the quality problems are the micritic and to some extent the crystalline and shale units. Therefore, any type of drilling for domestic purposes should be done outside of these geologic units. Hence, to supply adequate and good quality of groundwater for the people of Hiwanie town and its surrounding areas it is better to construct wells in the sandstone, basalt and dolerite because these units have considerable good quality, because of the less solubility nature of the rocks.

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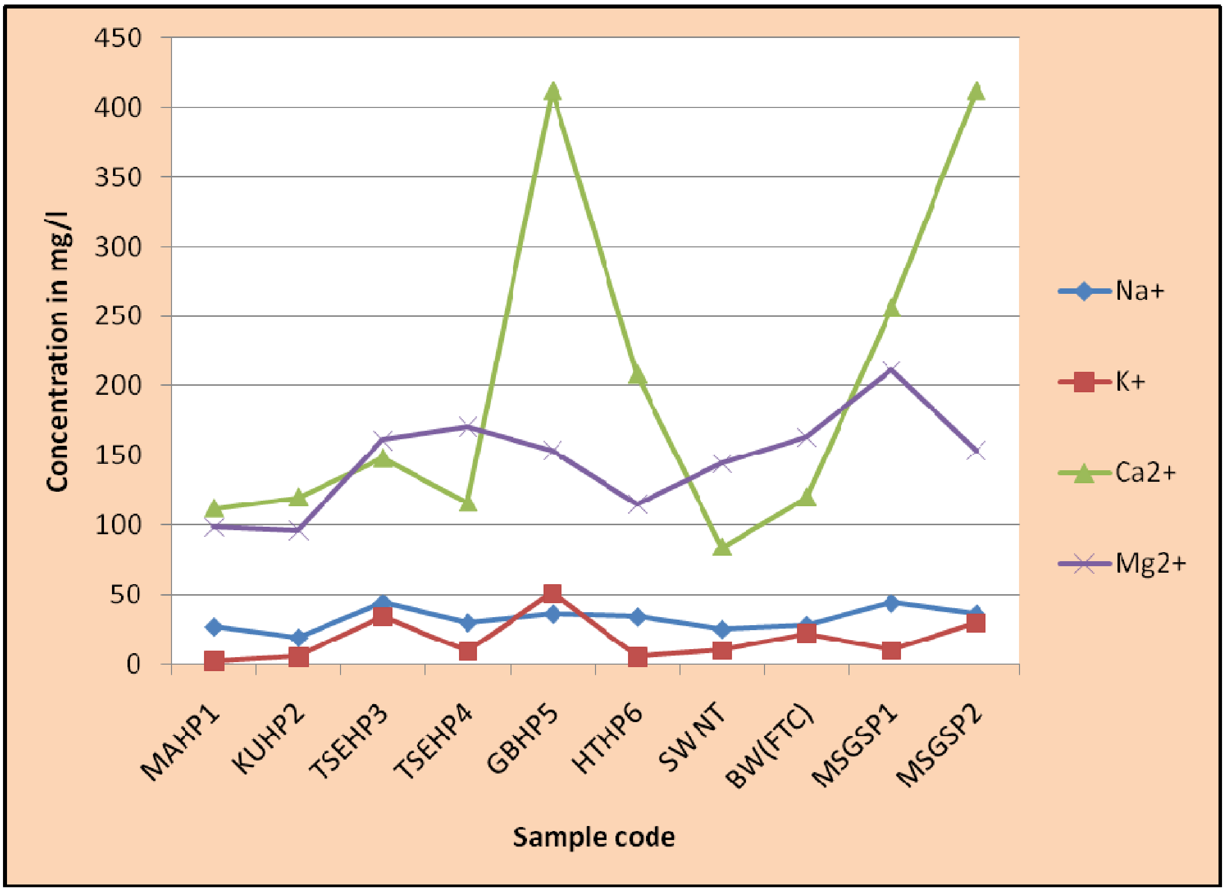

Figure 3 Concentration of major cations of the groundwater samples

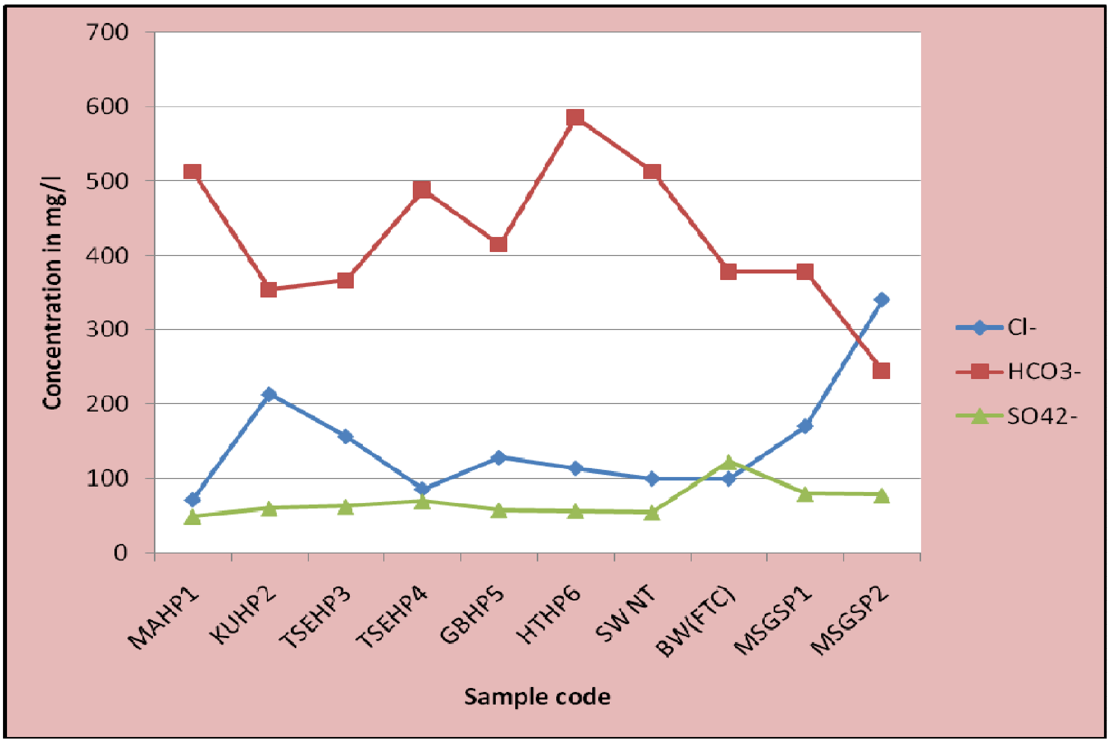

Figure 4 Concentration of major anions of groundwater samples

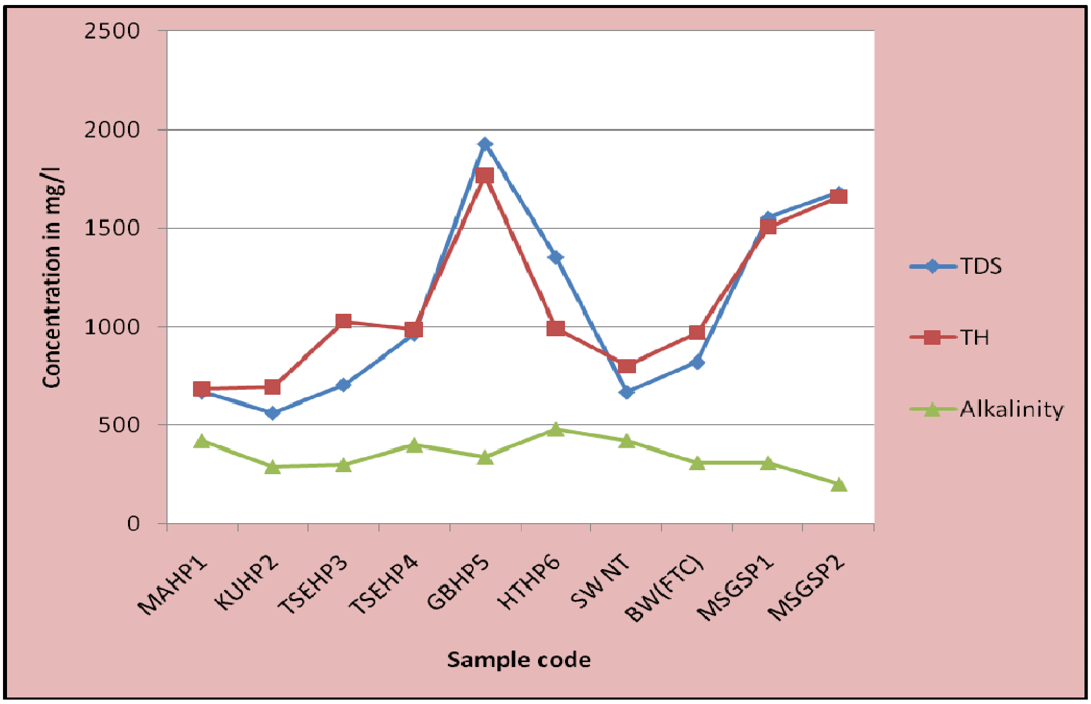

Figure 5 Graph representing the total hardness, alkalinity and TDS of the groundwater samples

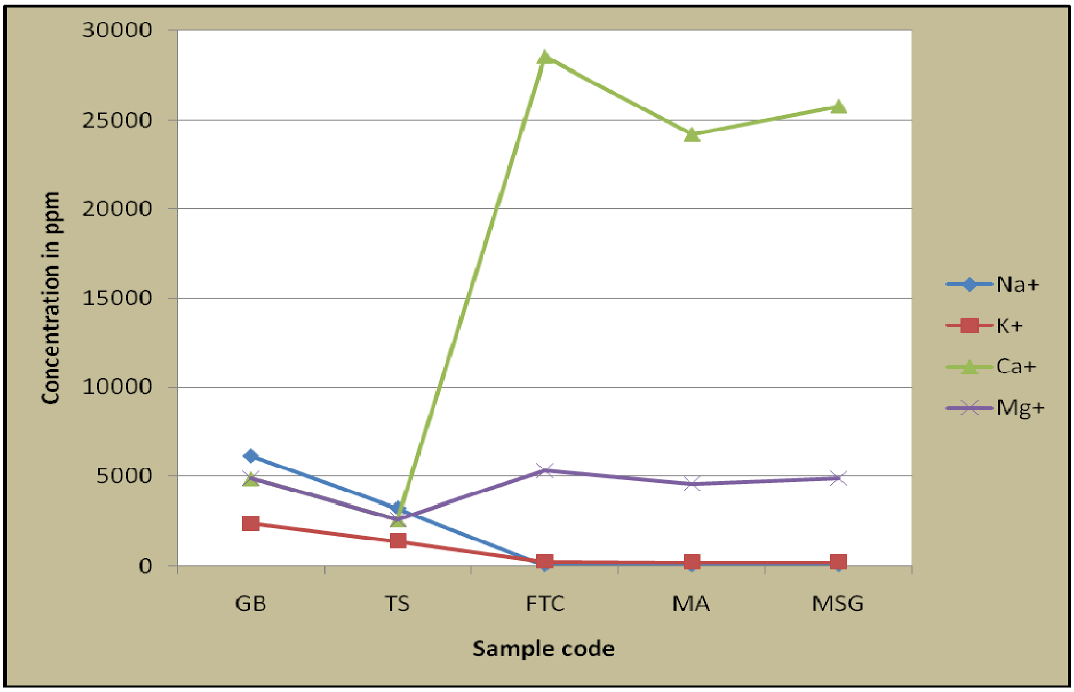

Figure 6 Concentration of major cations of rock samples

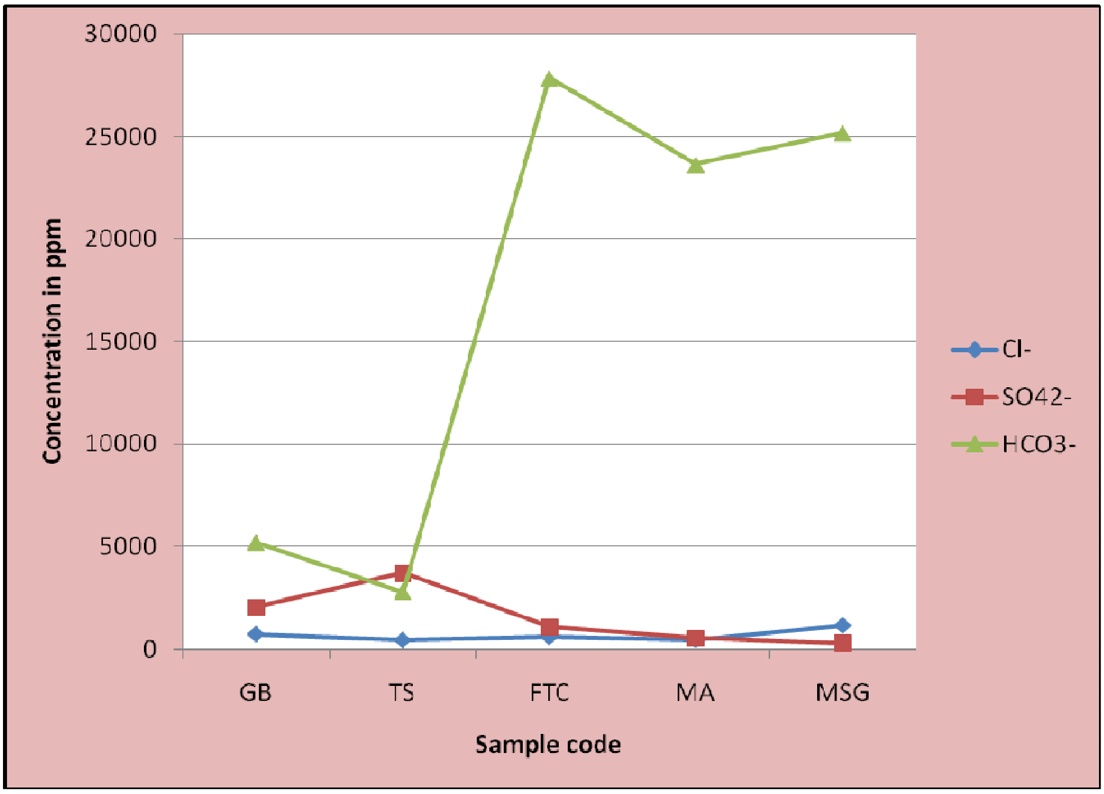

Figure 7 Concentration of major anions of rock samples

Table 1 The major and minor ions, pH, TDS and ECw determined in the groundwater samples of study area

Sample code	GPS location (in UTM)			EC (dS/m)	pH	Temp (°C)	Na^+ mg/l	K^+ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Cl^- mg/l	HCO_3^- mg/l	SO_4^{2-} mg/l	TDS (mg/l)	TH mg/l	Alkalinity mg/l
	UTME (m)	UTMN (m)	Elev (m)													
MAHP1	554398	1446044	2215	1.04	7.1	21.3	26.91	2.34	112	98.4	71	512.4	49.49	666.66	683.44	420
KUHP2	551983	1446472	2232	0.88	7.39	21.1	19.09	5.46	120	96	213	353.8	60.27	564.1	693.6	290.6
TSEHP3	552652	1447377	2074	1.1	7.19	22	43.93	34.32	148	160.8	156.2	366	62.72	705.12	1029.28	300.72
TSEHP4	552568	1447769	2087	1.5	7.37	22.3	29.9	9.36	116	170.4	85.2	488	69.58	961.53	988.64	400.78
GBHP5	555107	1446263	2064	3.01	6.89	23.1	36.11	51.09	412	153.6	127.8	414.8	57.82	1929.48	1768.32	340.13
HTHP6	553729	1448177	2061	2.11	6.84	22.6	34.04	5.46	208	115.2	113.6	585.6	56.84	1352.56	992.32	480.12
SW NT	553812	1448121	2025	1.04	7.25	21.4	25.07	10.14	84	144	99.4	512.4	54.39	666.66	800.4	420.16
BW(FTC)	554000	1451777	2016	1.28	7.2	21.2	28.06	22.23	120	163.2	99.4	378.2	122.5	820.51	969.12	310.51
MSGSP1	552633	1452152	1968	2.42	7.09	23.3	43.93	10.14	256	211.2	170.4	378.2	79.87	1551.28	1505.92	310.74
MSGSP2	552601	1452117	1965	2.62	7.43	23.5	36.11	30.01	412	153.6	340.8	244	77.91	1679.48	1659.76	200.61
Minimum				0.88	6.84	21.1	19.09	2.34	84	96	71	244	49.49	564.1	683.44	200.61
Maximum				3.01	7.43	23.5	43.93	51.09	412	211.2	340.8	585.6	122.5	1929.48	1768.32	480.12
Average				1.7	7.18	22.2	32.32	18.06	198.8	146.6	147.7	423.3	69.14	1089.74	1109.08	347.437
Standard deviation				0.77	0.20	0.92	8.04	15.92	123.30	35.26	80.38	100.45	21.19	495.11	394.19	82.15

N.B.: TDS=Total Dissolved Solids, TH= Total Hardness, Elev = Elevation and Temp=Temperature

Table 2 Concentration of trace cations of the analyzed groundwater samples (mg/l)

Sample ID	Pb	Co	Ni	Cu	Zn	Mn
MAHP1	<0.02U	<0.02U	<0.02U	0.06	<0.02U	<0.02U
KUHP2	0.02	0.07	<0.02U	0.09	0.29	0.02
TSEHP3	0.06	0.02	<0.02U	0.08	0.02	<0.02U
TSEHP4	<0.02U	<0.02U	<0.02U	0.08	<0.02U	<0.02U
GBHP5	<0.02U	0.12	<0.02U	0.08	<0.02U	0.13
HTHP6	0.06	0.09	<0.02U	0.08	0.10	0.11
SWNT	<0.02U	0.10	<0.02U	0.08	<0.02U	0.02
BW(FTC)	<0.02U	<0.02U	<0.02U	0.06	0.03	0.02
MSGSP1	<0.02U	0.08	<0.02U	0.09	<0.02U	0.02
MSGSP2	0.02	0.08	<0.02U	0.09	<0.02U	0.02

N.B.: U=Undetectable (below 0.02mg/l)

Table 3. The major, minor and trace elements of rock samples collected from the study area (ppm)

Sample Code	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Cu	Zn	Ni	Co	Mn	Fe	Pb
GB	6134.9	2379	4837.3	4857.12	724.2	2050.08	5188	7	15	5	9	229	7930	2
TS	3228.7	1378.0	2586.4	2575.8	433.1	3717.6	2787.8	6	30	12	9	295	42400	<2
FTC	33.97	224.24	28540	5289.6	589.3	1083.36	27849.6	5	60	3	9	421	8460	2
MA	28.83	190.3	24220	4549.9	433.1	556.8	23633.9	8	5	<2	9	36	1190	<2
MSG	30.30	200.14	25800	4846.7	1143.1	293.74	25175.75	25	35	105	198	119	25100	<2