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Hydrogeochemistry of the Geologic Profiles of Enwan and Environs, Akoko Edo, South South Nigeria

IZEZE, E. O.^{1,} (D)*, *OSEMELE, W.*¹

¹Department of Earth Sciences, Federal University of Petroleum Resources, Effurun

ABSTRACT

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Granites, Groundwater, Pegmatites, Piper plot, Schist Hydrogeochemical investigation as well as petrographic examination of rock samples was carried out in Enwan and environs, in Akoko Edo, South South Nigeria. Ten (10) water samples and two (2) rock samples were collected from study area for analyses. All of the samples collected were subjected to geochemical and petrographic analysis respectively, Physical parameters such as pH, TDS, Electrical conductivity and temperature were measured in-situ using standard equipments and the analysis for the chemical parameters was carried out with Atomic Absorption Spectrometer (AAS). The concentration of metals in the samples was determine through geochemical analysis the correlation of physical and chemical parameters. Ca²⁺, Mg²⁺, K⁺, Na²⁺, Fe²⁺ and Cu²⁺ were the cations analyzed for while the anions included HCO3, NO3 and Cl⁻. The results were compared with the world Health Organization (WHO) and Nigerian Industrial Standard (NIS) standards to determine the quality of the groundwater. ENW4 had the relatively highest calcium and magnesium ions concentration. ENW3 and ENW4 have the relatively highest chloride ion concentration, but all the samples have extremely high chloride concentration. The anthropogenic sources from which the high concentration of these parameters such as Chloride, Iron, Electrical conductivity and pH were found could either be as a result of the human activities in this study area or weathering of rock forming minerals such as Biotite, Quartz, plagioclase. The source of contamination of Iron in the groundwater is from weathering of surrounding rocks and subsequent leaching into the aquifer. During weathering, because feldspars are not resistant to weathering unlike

quartz that are very resistant, it gives off Na⁺ and K⁺ which are then washed down into the groundwater through percolation. The Piper plot shows that the all the samples belong in the Ca²⁺-Mg²⁺-Cl⁻ hydrochemical facies which results to an area of hardness because of the magnesium and chloride ions.

1. INTRODUCTION

Water is the most common substance on earth. It covers more than 70% of the earth's surface and free water (i.e. that not bound up in minerals) comprises only about 0.02% of the Earth's mass, but without it

life could not exist (NIS 2008 and Jonathan et al 2012). It fills the oceans, rivers, streams and lakes (surface water, Ajibade et al. 1987). It is in the ground (groundwater) and in the air we breathe. Groundwater and surface water are important resources for abstraction for beneficial use and irrigation purposes and also important features of the natural environment. Groundwater has a strong interaction with many surface water features such as rivers, wetlands and with the wider environment, which leads to environmental problems and may in some cases offer a medium for environmental solution (Ajibade 1976 and Chaanda 2019). Despite the vital importance of groundwater and surface water to man, his animal and is subject pollution plant, it to (Nwankwoala 2013).

Groundwater is the world's largest accessible freshwater and important resource for drinking water supply, irrigation and industrial purposes as well as for global food security. Approximately one-third of the world's population depends on groundwater for drinking purpose. Geology of an area, the degree of chemical weathering of various rock types and anthropogenic factors affect the chemistry of groundwater (Omo-Irabor et al. 2018, Oyaware 1964, and Woakes et al. 187). The combination fertile, low-lying of topography with shallow water table and widespread of aquifer with easy accessibility of water makes the groundwater, and is the main source of water among the residents in Enwan. About 75% of the state populations living in Akoko-Edo L.G.A are relied on groundwater for domestic water supply, agricultural and industrial activities. Almost the entire population of Enwan and environs rely on either treated or untreated groundwater. However, the low-lying coastal aquifers are generally fragile, easily depleted due to anthropogenic activities and over exploitation of groundwater. With the growing demands due to increasing number of population spreading, industry and agriculture, there has been increasing concern on the quantity and quality of groundwater resources. To manage and protect precious groundwater resources in a sustainable manner, the characterization and understanding of the natural evolution of groundwater chemistry is crucial to elucidate their geochemical nature and its relation. Presently, the hydro geochemical study of groundwater in this area has not been investigated in depth on a basin-wide scale and poorly understood. The aim of this study is to characterize the groundwater quality in the Lower Kelantan Basin multilayered aquifer using geochemical analysis.

For example, discharges of municipal wastewater can be a major source of pathogens (Izeze and Uzokwe 2019, Odeyemi 1976); urban runoff and livestock can contribute substantial microbial load; body contact recreation can be a source of faucal contamination; and agricultural runoff can lead to increased challenges to treatment. As a consequence, changes in groundwater levels or quality can have detrimental environmental impacts. The threat to human population may occur drinking the water through from contaminated or polluted wells or rivers. Even as the trend of population increases and industries develop, greater and industrial quantities of water are being required all over the globe with respect to Man's use for life sustenance. In a bid to promoting healthy living amongst the inhabitants of any defined geological region, an adequate supply of clean wholesome water is highly essential. Good quality water better referred to as potable water is the one that is safe to drink, pleasant to the taste and useable for domestic purposes.

However, if groundwater and surface water

are to continue to play an important role in the development of the world's water resources potential, then it will have to be protected from the increasing threat to subsurface and surface pollutants.

The study tends to determine the geochemical analysis using the correlation of physical and chemical parameters, and the groundwater concentration of the study area due to the activities of rock blasting, weathering, debris run-off and their effects in the environment as well as municipal drinking water.

2. MATERIAL AND METHODS

The Study Area

Enwan lies between latitude 7⁰16'30"N and $7^{0}19'00''$ N and longitudes $6^{0}06'30''$ E and $6^{0}08'30''E$. It is situated at the northern flank of Akoko-Edo, Southwest Nigeria. Bush burning and farming done in some areas also helped in making the area quite accessible. The study area has a market situated at a strategic location which could also serve as a landmark for easy accessibility and movement. Enwan lies 7⁰16'30"N between latitude and $7^{0}19'00$ "N and longitudes $6^{0}06'30$ "E and $6^{0}08'30''E$. It is one of the major towns in Akoko-Edo, South-south Nigeria. It covers an area of 121km^2 and forms the upper middle quadrant of 1:50000 GSN Sheet 266 (Auchi N.W) The area under study relatively has a high relief. The highest area is at the North Western portion with an average height of about 459m above sea level, while the relatively lower portions occur at the Southern and Central portion with an average height of about 306m above sea level. There lief of the area consists of isolated hills and batholiths. The elevations of these vary from 266m to 277m with an average elevation of 270m.

The highlands are however separated by sometimes extensive lowlands. The valley has a general "V" to "U" shape. This is shown in Figures 1 and 2.







Figure 2: Map overview of Igharra



Plate 1: Water sample collection from a hand-dug well.

A ten water samples were collected in one litre polythene bottles as shown in plate 1; one from surface water, and nine from groundwater including five from hand-dug well and four from boreholes to broadly cover the groundwater variations. The selected wells are used for domestic and agricultural purposes. Tables 1 and 2 show the different locations with their ph., TDS, EC, Temperature and anion concentrations.

S/N	SAMPLE_ID	рН	TDS (ppm)	EC (^{μs})	TEMP.(⁰ C)
1	ENW1	5.4	60	117	29.1
2	ENW2	5.6	110	221	28.1
3	ENW3	6.7	658	1318	33.1
4	ENW4	7.1	417	837	33.4
5	ENW5	6.6	169	337	29.5
6	ENW6	7.0	226	456	33.5
7	ENW7	7.3	238	475	31.0
8	ENW8	7.2	190	381	30.8
9	ENW9	7.3	114	224	29.7
10	ENW10	7.2	104	210	29.5

Table 1: In-situ water sam	ple parameters	collected at the field
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Table 2:	Concentration	of Anions in	n mg/l of the	water samples
	Concentration	or r mono n		mater builtpres

S/N	LOCATION	HCO3 (mg/l)	Cl ⁻ (mg/l)	NO3 (mg/l)
ENW1	ENWAN	ND	1060	0.05
ENW2	ENWAN	ND	1100	0.08
ENW3	ENWAN	ND	1520	0.03
ENW4	ENWAN	ND	1240	0.16
ENW5	ENWAN	ND	1170	0.04
ENW6	ENWAN	ND	1210	0.13
ENW7	ENWAN	ND	993	0.06
ENW8	ENWAN	ND	1060	0.08
ENW9	ENWAN	ND	1130	0.07
ENW10	ENWAN	ND	1240	0.06



Figure 3: Map	showing wa	ter sample points	in the study area
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S/N	LOCATION	Na ⁺ (mg/l)	K ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Fe ²⁺ (mg/l)	Cu ²⁺ (mg/l)
ENW1	ENWAN	< 0.001	0.5	0.78	< 0.001	< 0.001	0.05
ENW2	ENWAN	0.07	7.2	2.73	0.03	< 0.001	< 0.001
ENW3	ENWAN	0.16	1.4	< 0.001	0.94	0.6	0.06
ENW4	ENWAN	7.04	7.2	10.37	1.84	1.4	0.05
ENW5	ENWAN	< 0.001	1.5	3.6	0.1	3.0	0.03
ENW6	ENWAN	< 0.001	0.69	4.32	0.34	0.2	0.09
ENW7	ENWAN	< 0.001	0.57	8.12	0.77	< 0.001	0.07
ENW8	ENWAN	< 0.001	7.2	5.08	0.41	3.3	0.08
ENW9	ENWAN	< 0.001	0.83	2.48	0.36	< 0.001	0.05
ENW10	ENWAN	0.12	7.2	0.7	< 0.001	< 0.001	0.08

Table 3: Concentration of cations in mg/l of the water samples.







Figure 5: Chart showing the distribution of the TDS in the water samples.

	ENW1	ENW2	ENW3	ENW4	ENW5	ENW6	ENW7	ENW8	ENW9	ENW10
Ca2+	0	0.03	0.94	1.84	0.1	0.34	0.77	0.41	0.36	0
Mg2+	0.78	2.73	0	10.37	3.6	4.32	8.12	5.08	2.48	0.7
Na+	0	0.07	0.16	7.04	0	0	0	0	0	0.12
K+	0.5	7.2	1.4	7.2	1.5	0.69	0.57	7.2	0.83	7.2
Fe2+	0	0	0.6	1.4	3	0.2	0	3.3	0	0
Cu2+	0.5	0	0.06	0.05	0.03	0.09	0.07	0.08	0.05	0.08

Table 4: Concentration of Different Parameters

 Table 5: Comparison of the results with WHO and NIS standards

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe ²⁺	Cu ²⁺	pН	EC	TDS	Tem p
	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)			(ppm)	(⁰ C)
WHO	75.0	50.0	20.0	3000	0.1	2.0	6.5	500	500	_
STANDARD										
(2012)							-9.2			
NIS	_	_	200	_	??	??	6.5	1000	500	Amb
STANDARD										ient
(2007)							-8.5			
ENW1	< 0.001	0.78	< 0.001	0.50	< 0.001	0.5	5.4	117	60	29.1
ENW2	0.03	2.73	0.07	7.20	< 0.001	< 0.001	5.6	221	110	28.1
ENW3	0.94	<0.001	0.16	1.40	0.6	0.06	6.7	1318	658	33.1
ENW4	1.84	10.37	7.04	7.20	1.4	0.05	7.1	837	417	33.4
ENW5	0.10	3.60	< 0.001	1.50	3.0	0.03	6.6	337	169	29.5
ENW6	0.34	4.32	< 0.001	0.69	0.2	0.09	7.0	456	226	33.5
ENW7	0.77	8.12	< 0.001	0.57	< 0.001	0.07	7.3	475	238	31.0
ENW8	0.41	5.08	<0.001	7.20	3.3	0.08	7.2	381	190	30.8
ENW9	0.36	2.48	<0.001	0.83	< 0.001	0.05	7.3	224	114	29.7
ENW10	< 0.001	0.70	0.12	7.20	< 0.001	0.08	7.2	210	104	29.5

	Cl- (mg/l)	HCO3- (mg/l)	NO3- (mg/l)	рН	EC	TDS (ppm)	Temp. (0C)
WHO STANDARD (2012)	250	_	50	6.5 – 9.2	500	500	-
NIS STANDARD (2007)	_	-	??	6.5 - 8.5	1000	500	Ambient
ENW1	1060	ND	0.05	5.4	117	60	29.1
ENW2	1100	ND	0.08	5.6	221	110	28.1
ENW3	1520	ND	0.03	6.7	1318	658	33.1
ENW4	1240	ND	0.16	7.1	837	417	33.4
ENW5	1170	ND	0.04	6.6	337	169	29.5
ENW6	1210	ND	0.13	7.0	456	226	33.5
ENW7	993	ND	0.06	7.3	475	238	31.0
ENW8	1060	ND	0.08	7.2	381	190	30.8
ENW9	1130	ND	0.07	7.3	224	114	29.7
ENW10	1240	ND	0.06	7.2	210	104	29.5

Table 6: Comparison of the results with WHO and NIS standards

From the tables 4,5 and 6, the Calcium is the most correlated parameter being strongly related with itself and five (5) other parameters including EC, TDS, NO3, Na and Mg. Copper and pH are the least correlated as deduced from the table, Iron and Potassium are not correlated to any of the parameters also. This implies that these parameters are from the same source.

ENW1, ENW5, ENW6, ENW7 and ENW9 in the Enwan axis have relatively high magnesium ion concentration; this indicates that the water in these areas are Alkaline. ENW4 has the highest calcium ion concentration which is also Alkaline, ENW10 is high in Na + K concentration, and all the samples have extremely high chloride concentration. The waters of the study area can therefore be classified as a Ca^{2+} - Cl^- water.

Only the ENW3 has TDS values higher than the WHO regulated standard for drinking water which is 500 mg/l. All the analysed water samples gave pH values that were within the WHO standards which range between 6.5-8.5 mg/l, except ENW1 and ENW2.

The plot shows that areas with high TDS values equally have high concentration of Ca, Mg and Cl are shown in Figures 4, 5 and 6.

Geospatial Interpolation and mapping using Arc-GIS

Geospatial maps were generated for each of the analyzed parameters in the surface area

using Arc-GIS so as to determine the probability of the presence of the parameters

in unsampled points within the surface area.

	pН	EC	TDS	Cl	NO3	Na	K	Mg	Ca	Fe	Cu
pН	1	0.25183	0.251093	0.117765	0.251619	0.180362	0.050657	0.421119	0.411359	0.201297	0.647805
		0.241374	0.242037	0.372966	0.241563	0.309022	0.444735	0.11276	0.118792	0.288538	0.021415
EC	0.25183	1	0.99998	0.784125	0.069877	0.380674	-0.05969	0.144903	0.733182	0.102163	0.152934
	0.241374		3.19E-19	0.003627	0.423944	0.138909	0.434951	0.344798	0.007917	0.389418	0.336586
TDS	0.251093	0.99998	1	0.783313	0.066274	0.379382	-0.06321	0.143713	0.733056	0.101779	0.151215
	0.242037	3.19E-19		0.003678	0.42783	0.139794	0.431139	0.34602	0.00793	0.389826	0.338338
Cl	0.117765	0.784125	0.783313	1	-0.0741	0.18204	-0.00886	-0.34198	0.34289	-0.03879	0.104796
	0.372966	0.003627	0.003678		0.419398	0.307362	0.490312	0.166719	0.166035	0.457634	0.38663
NO3	0.251619	0.069877	0.066274	-0.0741	1	0.724401	0.370793	0.686324	0.541647	0.012793	0.158601
	0.241563	0.423944	0.42783	0.419398		0.008907	0.145755	0.014201	0.052923	0.48601	0.330828
Na	0.180362	0.380674	0.379382	0.18204	0.724401	1	0.414407	0.678835	0.832393	0.14252	-0.07997
	0.309022	0.138909	0.139794	0.307362	0.008907		0.116889	0.015449	0.001403	0.347247	0.413089
К	0.050657	-0.05969	-0.06321	-0.00886	0.370793	0.414407	1	0.209438	0.143549	0.268198	-0.14104
	0.444735	0.434951	0.431139	0.490312	0.145755	0.116889		0.280713	0.346188	0.226864	0.348771
Mg	0.421119	0.144903	0.143713	-0.34198	0.686324	0.678835	0.209438	1	0.690371	0.270932	0.088574
	0.11276	0.344798	0.34602	0.166719	0.014201	0.015449	0.280713		0.013556	0.224479	0.403879
Ca	0.411359	0.733182	0.733056	0.34289	0.541647	0.832393	0.143549	0.690371	1	0.117753	0.132989
	0.118792	0.007917	0.00793	0.166035	0.052923	0.001403	0.346188	0.013556		0.372979	0.357089
Fe	0.201297	0.102163	0.101779	-0.03879	0.012793	0.14252	0.268198	0.270932	0.117753	1	0.00643
	0.288538	0.389418	0.389826	0.457634	0.48601	0.347247	0.226864	0.224479	0.372979		0.492968
Cu	0.647805	0.152934	0.151215	0.104796	0.158601	-0.07997	-0.14104	0.088574	0.132989	0.00643	1
	0.021415	0.336586	0.338338	0.38663	0.330828	0.413089	0.348771	0.403879	0.357089	0.492968	

Table 7: showing the Correlation matrix and relationship between the parameters



Figure 6: Durov plot showing a graphical representation of the chemistry of the water samples

3. RESULTS

The values of K^+ in the analyzed water samples ranges from 0.5mg/l to 7.2mg/l but no recorded permissible limit by WHO and NIS, also no consumption effect.

The values of Fe in the analyzed water samples ranges from <0.001mg/l to 3.3mg/l. The recorded permissible limit by WHO for Iron is 0.1mg/l and not all the analyzed samples fall within this value. Samples ENW3, ENW4, ENW5, ENW6 and ENW8 exceeded the permissible limit hence contains high concentration of Fe.

Figure 7: Spatial Distribution Map for Fe





Figure 8: Spatial Distribution Map for Cu

Concentration

The values of Cu in the analyzed water samples range from <0.001mg/l to 0.09mg/l. The recorded permissible limit by WHO for Copper is 2.0mg/l and all the analysed samples fall within this value.

The values of Cl⁻ in the analyzed water samples gave values which ranges from 993mg/l to 1520mg/l, both of which are higher than the permissible limits (250mg/l) set by WHO standard for portable drinking water. The values gotten are extremely higher than this limit.



Figure 9: Spatial Distribution Map for Cl⁻ concentration

The values of NO_3^- analyzed in the water samples gave values which ranges from 0.03mg/l to 0.16mg/l.The recorded permissible limit by WHO for Nitrate is 50mg/l and all the analyzed samples fall within this value.



Figure 10: Spatial Distribution Map for NO₃⁻ Concentration

TDS was observed on all samples except ENW3 were found to be in concurrence with the WHO and NIS standards for portable drinking water hence the water is considered good for drinking. The value of the ENW3 sample exceeded the WHO and NIS standard, hence not suitable for consumption. The values of Ca ²⁺analyzed in the water samples gave values which range from<0.001mg/l to 1.84mg/l, both of which

from<0.001mg/l to 1.84mg/l, both of which are lower than the permissible limits set by WHO (2012) and NIS (2008) standards for portable drinking water.

The EC observed on all water samples except ENW3 and ENW4 were found to be in line with the WHO and NIS standards for portable drinking water hence the water is considered good for drinking. The value of the ENW3 and ENW4 sample exceeded the WHO and NIS standard, hence not suitable for consumption.

3.1. Discussion

The concentration of cautions on the water samples from the study area is moderate as all the parameters fall within the limit established for portable drinking water by WHO except Iron. In the study area, ENW1, ENW2, ENW7, ENW8 and ENW10 have low Iron concentration while ENW3, ENW4, ENW5, ENW6 and ENW9 have high Iron concentration. The spatial concentrations are shown on Figures 7, 8, 9 and 10

Health Effect of Iron in Drinking Water: Most minerals from groundwater, including iron, will be absorbed by water. Large amounts of iron in drinking water can give it an unpleasant metallic taste. Iron is an essential element in human nutrition, and the health effects of iron in drinking water may include warding off fatigue and anemia. The EPA cautions that although iron in drinking water is safe to ingest, the iron sediments may contain trace impurities or harbor bacteria that can be harmful. Iron bacteria are naturally occurring organisms that can dissolve iron and some other minerals. These bacteria also form a brown slime that can build up in water pipes. Iron bacteria are most commonly problematic in wells, where water has not been chlorinated.

Health Effects of Iron Overload: It is possible for you to get too much iron through your diet, but ingesting too much iron through your drinking water is not associated with adverse health effects. However, while chronically consuming large amounts of iron can lead to a condition known as iron overload; this condition is usually the result of a gene mutation that afflicts about one million people in the United States. Left untreated, iron overload can lead to hemochromatosis, a severe disease that can damage the body's organs. Early symptoms include fatigue, weight loss, and joint pain, but if hemochromatosis is not treated, it can lead to heart disease, liver problems and diabetes. A blood test can identify iron overload.

The concentration of the anions also falls within the limit except Chloride (Cl) of which all the values extremely exceeded the permissible limit of 250mg/L. From the analysis data gotten, the study area has an average Chloride concentration of 1172mg/L.

Chloride in surface and groundwater from both natural and anthropogenic sources, such as run-offs containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, irrigation drainage and seawater intrusion in coastal areas. Chlorides are leached from various rocks into soil and water by weathering, the chloride ion is highly mobile and is transported to closed rivers, basins or oceans. Chloride levels in unpolluted waters are often below 10mg/litre.

A normal adult human body contains approximately 81.7g chloride. Chloride toxicity has not been observed in humans except in the special case of impaired chloride Sodium metabolism e.g in congestive heart failure. Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a concomitant of fresh Hypertension intake water. associated with sodium chloride intake appears to be associated with the sodium rather than the chloride ion.

Chloride increases the Electrical conductivity of water and thus increases its corrosiveness. Chloride concentration in excess of about 250mg/litre can give rise to detectable taste in water.



Plate 2: Total Dissolved Solids (TDS)

Plate 2 shows the Total dissolved solids, or TDS, refers to inorganic and organic material present in water in a suspended molecular, ionized, or micro-granular form. These tiny particles can make water look cloudy or muddy, affect water taste, and in some cases, cause disease. A wide range of metals, salts, and organic minerals, compounds can make up TDS, including copper, cadmium, nitrate, calcium, arsenic magnesium, potassium, chlorides, sulfates, lead, bacteria, viruses, plankton, and other microorganisms. Some of these substances are harmless, others provide minerals the body needs, and some are harmful, such as arsenic, cadmium, nitrate, and lead. The EPA considers TDS levels of 500 milligrams per liter safe. TDS levels higher than 1000 mg/L are not fit for human consumption.

Effects of Total Dissolved Solids: Elevated levels of TDS, while not necessarily bad for your, can give water a bitter, salty, or brackish taste. Calcium and magnesium, two minerals commonly found in TDS, can cause water hardness, scale formation, and staining. Water lacking in TDS is more corrosive, and can leach harmful metals such as lead or copper from plumbing pipes and hardware. People who drink water with low levels of total dissolved solids often complain the water has a flat, pleasant taste. Drinking water with moderate amounts of TDS may be the best water of all. In taste tests, water with moderate TDS ranks higher than water with low or elevated TDS levels.

The TDS of all the analyzed water samples are moderate except for ENW3 which exceeds the permissible limit by WHO standard having 658mg per litre as its value.

4. CONCLUSION

The analyzed water samples, the groundwater is found to be alkalinic, though with a high concentration of Chloride. The source of this Chloride as observed is anthropogenic i.e. an effect resulting from human activities within the study area. These human activities here are causing environmental degradation which is the deterioration of the environment through the depletion of resources such as air, water and soil.

The anthropogenic sources from which the high concentration of these parameters such as Chloride, Iron, Electrical conductivity and pH were found could either be as a result of the human activities in this study area. These activities include Oil milling, farming, Bush burning, fishing.

The major minerals present in all rock types found in the studied area were Biotite, Quartz, plagioclase. The source of contamination of Iron in the groundwater is from the surrounding rocks. During weathering, because feldspars are not resistant to weathering unlike quartz that are very resistant, it gives off Na^+ and K^+ which are then washed down into the groundwater through percolation.

The Piper plot shows that the all the samples belong in the $Ca^{2+}-Mg^{2+}-Cl^{-}$ hydrochemical facies which results to an area of hardness because of the magnesium and chloride ions.

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