

Hydrogeochemistry of Artesian and Controlled shallow Wells' Water: a case study of Ikere-Ekiti, Southwestern Nigeria

Abstract

Hydrochemistry of water from artesian and controlled shallow wells at Ikere-Ekiti was carried out to elucidate the wells' water quality status and hydrochemical evolution. Water samples from fifteen wells (5 artesian wells and 10 controlled shallow wells) were collected in duplicates into pre conditioned polyethylene bottles. The samples for cations analysis were acidified with concentrated HNO_3 to a pH of 2 and cations and anions determinations were carried out employing Atomic Absorption Spectrophotometer and Colorimetric method using Spectrophotometer respectively. Prior to sampling, at each location, in-situ parameters (pH, temperature ($^{\circ}\text{C}$), EC ($\mu\text{S}/\text{cm}$) and TDS (mg/L) were obtained using Multiparameter portable Meter. Results of this study revealed that all water samples in the area have $\text{pH} < 7$ and are acidic. The Total Hardness indicated that all water samples from artesian wells fell into the very hard water category while eight (80%), one each of the water samples from the controlled shallow wells were in the moderately hard, hard and very hard water classes respectively. All the measured chemical parameters had concentrations within approved standard of drinking water except for the NO_3^- values that were above $50\text{mg}/\text{L}$ for all water from the controlled shallow wells. The order of increased cations concentrations in the Artesian Wells' water was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ as against $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ in the controlled shallow wells' water. As for the anions, order of concentrations ($\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^-$) was the same. Differences in the order of ionic concentrations were due to lithologic variations as well as differential weathering. The hydrochemical evolution of groundwater in the study area was controlled solely by weathering and water in the study area was the CaCl type. The physico-chemical parameters were both positively and negatively correlated among themselves and ions in the groundwater of the study area are both from the geogenic and anthropogenic sources. There is no significant difference between water from the artesian and controlled shallow wells as water from them are low mineralized with most physico-chemical parameters falling below approved standards for drinking water. However, the acidic nature of all sampled water as well as high NO_3^- concentrations call for caution and further investigations.

Keywords: chemical parameters, ionic concentrations, hydrochemical evolution, low mineralized

Introduction

Artesian well signifies well from which water gushes out naturally without pumping. When the water level from a well in a confined aquifer rises above the level of the ground surface and flows freely without pumping, it is called artesian well (Price, 1996, Wheeler, 1980). Most occurrences of Artesian Wells are located at the bottom of slopes in hilly environment, where water heads within the uplands can generate strong upward hydraulic gradients (Price, 1996). Sources of water derived in wells include storage release, decreased discharge to surface water (also called baseflow reduction) and various forms of induced recharge (Zhang, et al.2022; Kpegli, et al. 2022).

Water services by government are not within the control of companies and households apart from the growing cost of the water utilities. Drilling into aquifers hoisting artesian water provide water utilization

for domestic and industrial activities. It reduces reliance on external supplies and provides freedom of controllable water resources utilization by companies and individual.

Majority of artesian aquifers worldwide are replenished continuously by groundwater and rainfall. The water flows down from the porous aquiferous materials (gravel and sand). Continuous percolation is interjected by impermeable materials (aquifuge and aquiclude), to forestall escape of the water. There is sufficient positive pressure within the confined aquifer pushing the water out without any pumping (Fitts, 2013, Ezugwu et al., 2019).

Unlike wells that are dug by hand or drilled deep into the ground, artesian wells may require less digging because of how close the groundwater is to the surface. It is dug wherever a gently dipping permeable rock layer receives water along its outcrop at a level higher than the level of the surface of the ground at the well site.

One of the major importances of the water from artesian well is its high mineral content such as calcium, magnesium, potassium and sulphur, which are believed to help in repairing damaged tissue and help fight illness when absorbed into the skin. It is important to note that the source of the well can affect the risk of drinking the artesian water. Some sources of artesian water could be in poor quality environment, and could contaminate the confined aquifer. Poor quality water could contain contaminants that are dangerous to human health (Johnson et al., 2016).

Uncontrolled flows from poorly constructed and uncapped artesian well can cause deterioration of the quality of shallow groundwater and surface water. Uncontrolled flows can cause erosion and land subsidence, damage structures and waste groundwater. This study therefore highlights hydrochemistry of artesian wells' water in Ikere-Ekiti basement terrain of southwestern Nigeria focusing on its hydrochemistry as well as their peculiarities vis-à-vis the controlled shallow wells' water in the study area.

Location of study

The study area is at Ikere-Ekiti as shown in Fig.1. The area lies in the tropic and is located within Longitudes 5°10'E to 5°20'E and Latitudes 7°30'N to 7°35'N (Fig.1). The study area has good road network and minor roads that facilitate easy sampling of the water. The area has rainy and dry seasons with the former covering March to November while the latter spans from ending of November to early March. The recent effects of climate change could warrant little variation in the mentioned periods. The annual rainfall is about 1500mm, high relative humidity between 70 and 85% while the annual temperature is 28°C. In terms of geology, the area belongs to the Archean-Early Proterozoic basement complex of southwestern Nigeria. The lithologic units comprise of the migmatite gneiss – quartzite complex, the most abundant into which other rock units intruded (McCurry, 1976; Rahaman, 1988, Ayodele and Akinyemi, 2014). The other rocks include the Older Granites and Charnockites. The Older Granites occur as rising hills (Olosunta and Orole hills) while the charnockites outcropped as oval or semi-circular hills or boulders (5m – 10m height) along the margins of the Older Granites (Talabi, 2017).

Groundwater occurrence in the study area is erratic due to variations in structures and overburden thickness. Response of rocks to weathering varies in view of the differences in mineralogy and chemical composition. Therefore rocks that are more susceptible to weathering/fracturing could serve as a better groundwater aquifer. River Osun that rose from the hills at the western end of the area with highest topographical point of 598m above main sea level is the major surface water in the study area. River Owururu is a major tributary to River Osun though there are other minor streams meandering through intersecting valleys. River Osun is noted for its prominent nuisance to the community as it causes flooding of its environment especially during the rainy season. Volume of water in the rivers and streams

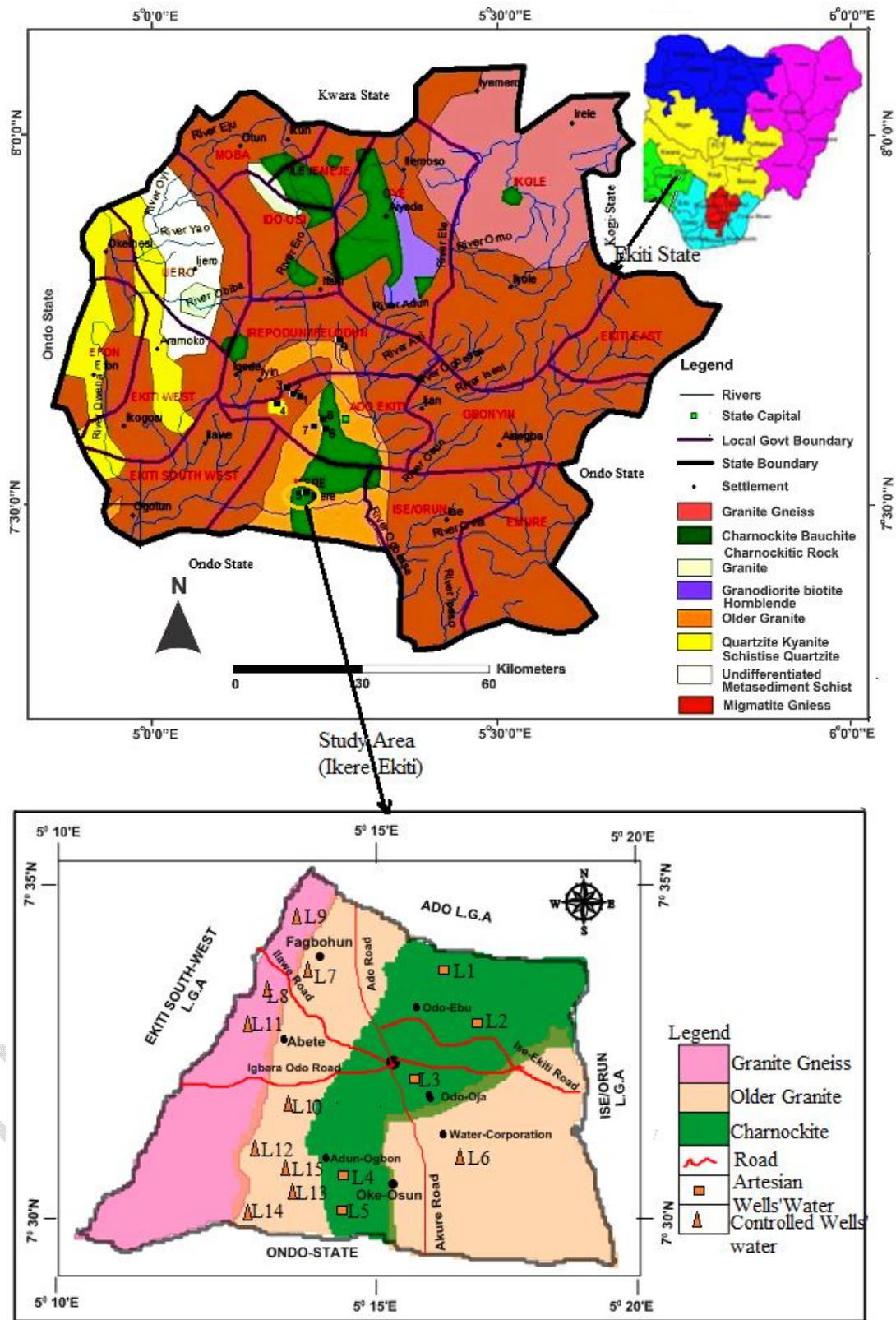


Fig. 1. Location of Study showing sampling points

vary considerably with seasons. The volumes of water are high during the rainy season while most tributaries dry off. Rainfall is the dominant means of recharging the shallow wells in the study area and volume of water in the wells reduces considerably during the dry season why some may dry off completely. In contrast, the artesian wells have water flowing in them throughout the year and they could provide the water requirements of the community especially during the dry season when shallow wells would have dried off.

Methodology

Water samples were taken from fifteen wells comprising of five artesian wells and 10 controlled shallow wells at varied distances from the artesian wells employing standard method (Stednick, 1991). Prior to sampling, at each location, in-situ parameters (pH, temperature (°C), EC (µS/cm) and TDS (mg/L) were obtained using Multiparameter portable Meter Testr™ 35 series S/N: 1382654. Total Hardness (TH (mg/L) was estimated employing $TH (mg/L) = 2:497 Ca^{2+} + 4:115Mg^{2+}$. The concentrations of the constituents are expressed in mg/L (UNESCO, 2007).

At each well, water was collected in duplicates into preconditioned polyethylene bottles. The sample meant for cations analysis was acidified with concentrated HNO₃ to a pH of 2 to avoid cations precipitation and absorption to the walls of the sampling bottles (United State Environmental Protection Agency (USEPA), 1983). All samples were kept at 4 °C in a refrigerator till analyses were carried out at the Federal University of Technology, Akure, Ondo State Nigeria. Cations determination was by Atomic Absorption Spectrophotometer (Varian – AA240) while the anions was by Colorimetric method using DR 5000 Spectrophotometer (Hach, USA).

Statistical analysis of the chemical data was carried out employing Microsoft Office Excel 2007. Correlation of the chemical parameters was obtained using Paleontological Statistics (PAST) Version 3.14 while Piper and Schoeller diagrams were obtained employing GW_Chart and Microsoft Office Excel 2007 respectively.

Results and Discussion

The summary of the results of the physico-chemical parameters of water from the artesian and shallow wells is presented in Table 1. Measured physic-chemical parameters are in Table 2. The study area has tropical climate with temperature ranging from 23°C - 28°C (Talabi, 2017). The temperatures (°C) of water from artesian wells varied from 24.60°C – 32.60°C (av. 28.82°C) while that of the controlled shallow wells was from 23.90°C – 30.50°C (av. 28.36°C). There is no significant change in temperature compared to the range of annual temperature of the study area. The values of the temperatures show that there is no thermal pollution in the water of the area. As indicated in Tables 1 and 2, pH in the artesian wells' water ranged from 6.26 – 6.72 (av.6.47) while that of the controlled wells' water were between 5.30 and 6.82 (av. 5.54). This observed trends of pH showed that all water from the artesian wells fall within approved standard of drinking water compared to the controlled wells' water in which 60% of the samples fell outside the range (WHO, 2011). Water from both wells was acidic. However, water from the controlled wells posed more risks to consumers. Acidic water constitutes health risks to consumers as its taste is pungent apart from the fact that the water can corrode and leach plumbing materials as well as causing acid reflux and frequent heartburn (Nordberg et al., 1985, Hansen et al., 2018). Acidic water can be corrected employing acid neutralizing filters. Electrical conductivity (EC (µS/cm)) represents the ability of water to conduct electricity. The higher the EC (µS/cm) values, the higher the electrolytes in the water. In this study, the EC (µS/cm) of the artesian wells' water ranged from 475 – 509 (av. 492.00) while that of shallow wells' water were from 155 – 916 (av. 300.60). The EC values revealed that there were

more solutes dissolved into the artesian wells' water, however, the values in the shallow wells indicated that there was localized anthropogenic sources causing EC values to be as high as 916 ($\mu\text{S}/\text{cm}$) at a location (Location 6).

Water hardness represents the total calcium and magnesium ions concentrations in a water sample i.e. the concentration of calcium carbonate in the water. Other divalent ions like iron can cause hardness of water but calcium and magnesium are most prevalent (Wurts, 1993).

Table 1. Summary of Physico-chemical Parameters of Artesian Wells' and Controlled Shallow Wells'' Water in the study area.

Parameters	Artesian Wells' Water					Controlled shallow Wells' Water			
	Min	Max	Mean	Stdev	WHO 2011	Min	Max	Mean	Stdev
Temp ($^{\circ}\text{C}$)	24.6	32.6	28.82	4	-	23.9	30.5	28.36	2.12
pH	6.26	6.72	6.47	0.22	6 - 9	5.3	6.82	5.84	0.53
EC ($\mu\text{S}/\text{cm}$)	475	509	492	15.94	1500	155	916	300.6	222.57
TDS (mg/L)	219	267	244.8	17.22	1000	74	468	160.9	121.46
TH	172.16	272.23	197.91	50.41	500	64.06	280.28	107.76	63.55
Ca (mg/l)	48.1	65.73	56.43	8.44	100	16.03	83.37	32.25	20.55
Mg (mg/l)	12.65	26.27	20.64	5.76	50	1.95	17.51	7.17	4.46
Na (mg/l)	1.5	9	4.6	3.42	200	2.7	9	5.33	1.97
K (mg/l)	5.28	9.74	7.59	1.72	20	1.48	6.47	3.95	1.73
HCO ₃ (mg/l)	0.5	4	2.94	1.4	125 – 350	3.7	6	4.57	1.25
SO ₄ (mg/l)	10.67	42.67	29.34	13.42	250	53.33	405.33	133.08	108.99
Cl ⁻ (mg/l)	10.93	18.22	13.85	3.05	250	21.56	546.75	123.32	171.07
NO ₃ (mg/l)	263.97	363.63	303.03	41.51	50	134.68	247.81	176.44	40.51
Fe (mg/l)	0.22	0.22	0.22	0	0.3	0.04	0.16	0.11	0.05
Mn(mg/l)	0.02	0.06	0.04	0.02	0.1 – 0.5	0.01	0.07	0.03	0.02
Zn (mg/l)	0.01	0.03	0.02	0.01	0.01 – 3	0.01	0.08	0.04	0.02
Cd (mg/l)	0.01	0.01	0.01	0	0	0.01	0.01	0.01	0

According to Kumari (2016) Soft water has hardness (mg/L) less or equal to 60, moderately hard (61 – 120), hard (121 – 180) and very hard ≥ 181 . In the water samples from artesian wells, the TH (mg/L) ranged from 172.16 – 272.23 (av. 224.22) while that of controlled shallow wells were between 64.06 and 280.23 (av.110.03). The result showed that all water samples from artesian wells fall into the very hard water category. As for the water samples from the controlled shallow wells, eight samples (80%) of the water samples fall into the moderately hard water class while in the hard and very hard categories only one sample fall in the classes respectively. Hard water is generally not harmful to humans' health (WHO, 2003) but it could pose severe problems in the industry. Soap does not readily produce good lathers in hard water. Hard water could be harmful to boilers and hot water pipes as salts could be deposited in them causing reduction in efficiency (Akram, 2018).

Generally, a critical examination of Table 1 shows that both Artesian Wells' water and that of the controlled shallow wells are low mineralized with most physico-chemical parameters falling below approved WHO (2011) standards except for NO₃⁻ concentrations that were above approved standard of 50mg/L in all controlled shallow Wells' locations. This clearly indicated that water from the Artesian Wells was of better quality than the controlled shallow wells' water. Nitrate pollution is often associated with surface anthropogenic activities and thus the nitrate contamination of the shallow wells' water was from surface anthropogenic activities (Adeyemi et al., 2003). The order of increased cations concentrations in the Artesian Wells' water is Ca²⁺>Mg²⁺>K⁺>Na⁺ as against Ca²⁺>Mg²⁺>Na⁺>K⁺ in the controlled shallow wells' water. As for the anions order of concentrations, both for the Artesian Wells'

and controlled shallow wells' water maintained the same order ($\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^-$). Differences observed in the order of ionic concentrations were consequent of lithologic variations as well as differential weathering.

Mechanism controlling the Groundwater Chemistry of the Study Area.

Groundwater chemistry is controlled by many hydrochemical processes. Included in these processes are; evaporation, weathering, precipitation, mixing, ion exchange, redox reactions and dissolution (Krishna et al., 2016). The chemistry of groundwater is very important in determining the suitability of the water for different uses. In this study, Gibb's Plot (Gibbs, 1970), Schoeller diagram (Schoeller, 1977) and Piper Diagram (Piper, 1944) were employed to ascertain the water-interactions characteristics as well as deciphering the groundwater into different hydrochemical facies respectively.

Table 2. Physico-chemical Parameters of Artesian and controlled Wells' water from the study Area

Loc	Temp (°C)	PH	EC (µS/cm)	TDS (mg/L)	TH (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	NO ₃ (mg/L)
1	27.7	6.69	475	242	216.31	48.1	23.38	1.50	8.67	0.5	32	10.93	321.89
2	32.6	6.42	475	219	220.18	48.1	24.32	9.00	9.74	3.1	42.67	14.58	266.67
3	24.6	6.72	509	267	248.21	56.11	26.27	2.00	7.49	3.5	ND	18.22	263.97
4	29.9	6.26	502	248	220.21	64.13	14.6	7.50	5.28	3.6	10.67	14.58	363.63
5	29.3	6.26	499	248	216.18	65.73	12.65	3.00	6.78	4.0	32.0	10.93	298.99
Min	24.6	6.26	475	219	172.16	48.10	12.65	1.50	5.28	0.50	10.67	10.93	263.97
Max	32.6	6.72	509	267	272.23	65.73	26.27	9.00	9.74	4.00	42.67	18.22	363.63
Mean	28.82	6.47	492	244.8	224.22	56.43	20.24	4.60	7.59	2.94	29.34	13.85	303.03
Stdev	4	0.22	15.94	17.22	46.45	8.44	6.17	3.42	1.72	1.40	13.42	3.05	41.51
6	23.9	6.82	916	468	280.23	83.37	17.51	5.30	4.18	6	405.33	51.1	247.81
7	28.2	6.43	247	124	72.07	17.64	6.81	3.50	1.48	ND	96	36.4	138.72
8	26.9	5.55	155	74	68.05	16.03	6.81	3.00	4.84	ND	96	21.87	202.02
9	27.1	5.41	159	78	64.06	16.03	5.84	7.00	1.97	ND	53.33	273.5	184.51
10	27.1	5.48	233	113	104.11	38.48	1.95	7.00	2.52	ND	90.67	29.15	134.68
11	30.5	6.29	305	140	108.07	24.05	11.67	5.00	6.47	ND	192	546.75	137.37
12	30.1	6.12	201	94	76.03	22.44	4.86	9.00	2.93	ND	80	182.25	158.92
13	30.1	5.3	250	241	145.71	46.34	7.29	5.50	3.85	3.7	ND	21.56	235.56
14	29.8	5.54	315	117	94.57	32.55	3.23	5.30	4.96	ND	78.42	23.65	168.13
15	29.9	5.49	225	250	87.43	25.54	5.75	2.70	6.34	ND	106	46.88	156.72
Min	23.9	5.3	155	74	64.06	16.03	1.95	2.70	1.48	3.70	53.33	21.56	134.68
Max	30.5	6.82	916	468	280.23	83.37	17.51	9.00	6.47	6.00	405.33	546.75	247.81
Mean	28.36	5.84	300.6	169.9	110.03	32.25	7.17	5.33	3.95	4.85	133.08	123.31	176.44
Stdev	2.12	0.53	121.46	121.46	69.67	20.54	4.46	1.97	1.73	1.63	108.99	171.07	40.51

ND: Not detected

The Gibb's plot (Fig. 2) shows that the hydrochemical evolution of groundwater in the study area was controlled solely by weathering. The differences in hydrochemical evolution of water from both the artesian and controlled shallow wells were still revealed as shown by the clustering of the water samples in the Gibb's plot (Fig. 2). The weathering (principally chemical weathering) depends on the intensity of rock-water interactions. The intensity of rock-water interactions varies temporally and spatially depending on the chemical composition of the initial precipitation, the lithologic units and residence time. The Piper diagram (Piper, 1994) was proposed to present hydrochemical data so that the sources of the dissolved salts in water can be revealed. The relative abundance of common ions in water can be

visualized. The Piper diagram (Fig.3.) revealed that both water from artesian wells and controlled wells fell into the CaCl water type, alkaline dominant and strong acids were superior, indicating high salinity of water. This observation was reflected in the water hardness observed in the study area. The high concentrations of Ca^{2+} and Mg^{2+} in water from both the artesian and controlled shallow wells reflected the high level of anthropogenic activities that accompanied runoff in the area (Bogart et al., 2018).

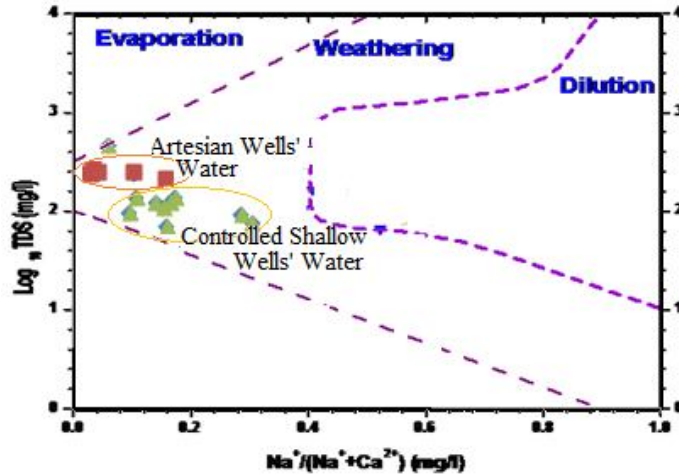


Fig. 2. Gibb's Plot (Gibbs, 1970)

The Schoeller diagram (Schoeller, 1977), was also used to present average chemical composition of both the water from the artesian and controlled shallow wells. Though, the water from the artesian wells was not separated from those from the controlled well's water, the order of ionic concentrations in meq/l shows $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{NO}_3 > \text{Cl} > \text{SO}_4 > \text{HCO}_3$ (Fig. 4.).

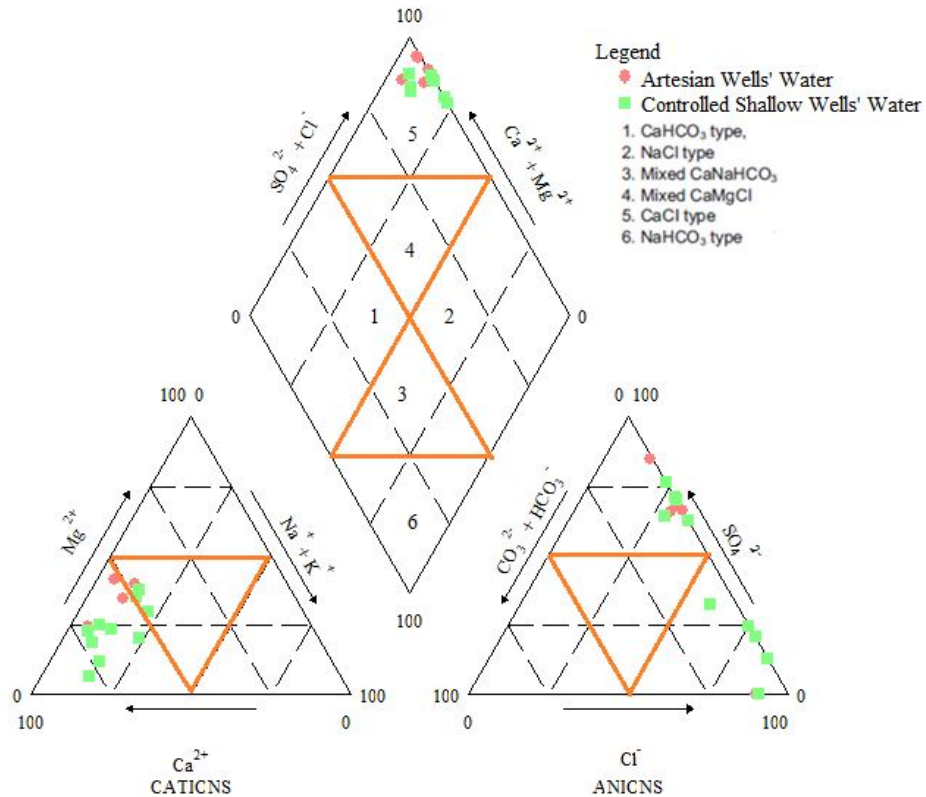


Fig. 3. Piper Diagram

Pearson's Correlation Analysis

The Pearson's correlation coefficients for nine important parameters (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- and EC) were calculated using Paleontological Statistics (PAST) Version 3.14 as presented in Table 3. The correlation table revealed a positive correlation between Ca^{2+} and HCO_3^- , Mg^{2+} and HCO_3^- , K^+ and HCO_3^- , EC and Ca^{2+} , EC and Mg^{2+} , EC and K^+ , EC and HCO_3^- , EC and SO_4^{2-} , EC and NO_3^- , Mg^{2+} and K^+ , Mg^{2+} and HCO_3^- , Mg^{2+} and SO_4^{2-} , K^+ and SO_4^{2-} , HCO_3^- and SO_4^{2-} . Those ions that are positively correlated was an indication that they had related source of origin. Though, this depends on the value of the correlation coefficient that ranged from -1 to +1. In this study, Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} and NO_3^- contributed significantly to EC with correlation coefficient, $r \geq 0.5$. It also implied that the ions contributed significantly to total dissolved solids (TDS) of the groundwater. Research by Adeyemi et al. (2003), indicatee that NO_3^- concentrations were often associated with surface anthropogenic activities. By implication, surface anthropogenic activities contributed to those ions that had significant positive correlation. Chloride ions have negative correlation with other ions except NO_3^- ($r = 0.22$), Na^+ ($r = 0.20$) and very weak correlation with HCO_3^- ($r = 0.07$). Contributions of Cl^- to the groundwater solute of the area were mainly from anthropogenic activities. The correlation table showed clearly that the physico-chemical parameters were both positively and negatively correlated among themselves and ions in the groundwater of the study area were from both geogenic and anthropogenic sources.

Conclusion

This study examined the hydrochemistry of water from artesian wells and controlled shallow wells at Ikere-Ekiti, Nigeria. Results of this study indicates that all water samples in the area have $\text{pH} < 7$ and are acidic. All water samples from the artesian wells fall within WHO approved standard of drinking water while 60% of the water samples from the controlled shallow wells fall outside the standard.

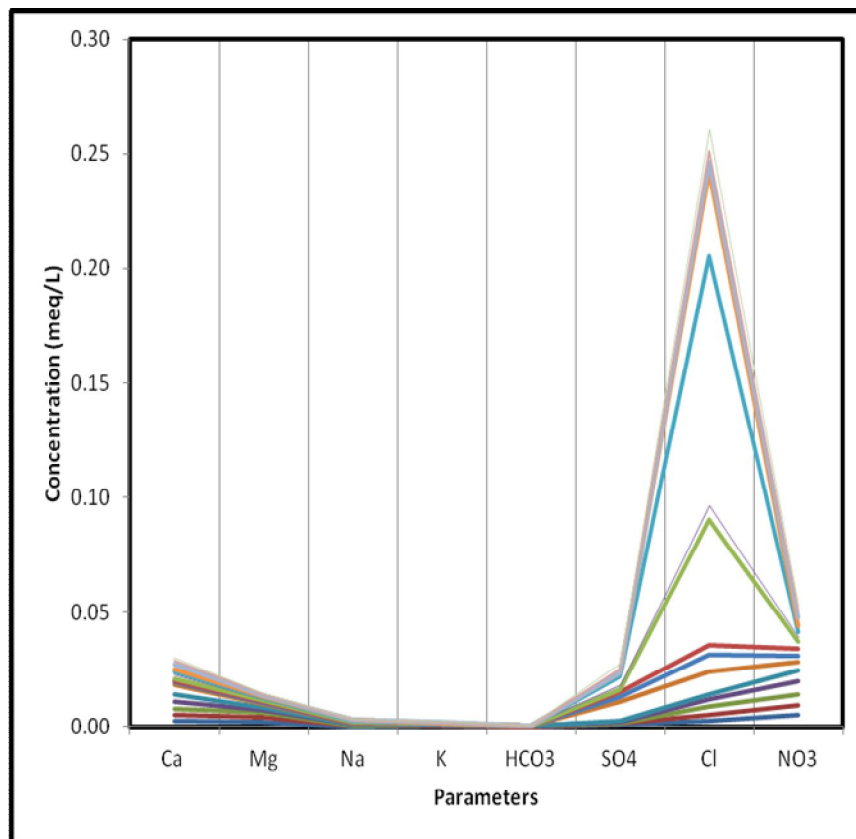


Fig. 4. Schoeller Diagram

The EC values reveal that there are more solutes dissolved into the artesian wells' water, however, there was a localized anthropogenic source that caused un-usual rise in EC value in location 6 of the controlled shallow wells. Furthermore, TH reveals that all water samples from artesian wells fall into the very hard water category while eight samples (80%) of the water samples from the controlled shallow wells fall into the moderately hard water class. In the hard and very hard categories only one sample falls in the classes respectively. Water from the artesian wells and controlled wells are low mineralized with most physico-chemical parameters falling below approved standards for drinking water.

Table. 3. Pearson Correlation of Nine Parameters of Artesian and Controlled Wells' Water in the study area.

Parameters	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	EC(μS/cm)
Ca ²⁺	1.00								
Mg ²⁺	0.62								
Na ⁺	-0.04	-0.20							
K ⁺	0.38	0.76	-0.27						
HCO ₃ ⁻	0.79	0.57	0.03	0.35					
SO ₄ ²⁻	0.73	0.73	-0.11	0.55	0.51				
Cl ⁻	-0.41	-0.18	0.20	-0.13	0.07	-0.44			
NO ₃ ⁻	0.22	-0.05	0.02	-0.19	0.34	-0.27	0.28		
EC (μS/cm)	0.90	0.70	-0.10	0.40	0.77	0.61	-0.24	0.50	1.00

Water from the Artesian Wells is of better quality than the controlled shallow wells' water as NO_3^- concentrations are above approved standard of 50mg/L in all controlled shallow Wells' locations. The order of increased cations concentrations in the Artesian Wells' water is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ as against $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ in the controlled shallow wells' water. As for the anions order of concentrations, both for the Artesian Wells' and controlled shallow wells' water maintained the same order ($\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^-$). Differences observed in the order of ionic concentrations are consequent of lithologic variations as well as differential weathering. The hydrochemical evolution of groundwater in the study area is controlled solely by weathering and water in the study area is the CaCl type. The physico-chemical parameters are both positively and negatively correlated among themselves and ions in the groundwater of the study area are from both geogenic and anthropogenic sources. There is no significant difference between water from the artesian wells and controlled shallow wells. However, the acidic nature of all sampled water as well as high NO_3^- concentrations, especially in the water from the controlled wells call for caution and further investigations.

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