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Calcium and Magnesium in Groundwater of Okene and Environs, Central Nigeria

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ABSTRACT

Calcium and magnesium are lithophile elements that play pivotal roles in groundwater composition and are essential for human health. Calcium, the most abundant mineral in the human body, plays a crucial role in bone and teeth formation, muscle activity, nerve impulse transmission, blood coagulation, cardiac function, and enzyme production. When combined with magnesium, it supports the proper functioning of the human heart. The aim of this work is to evaluate the content of Ca and Mg in shallow groundwater in parts of Okene and environs and to deduce if the level consumes meets the WHO daily recommended limits. Thirty-two groundwater samples were collected randomly spanning over an area of 35km^2 and analyzed. The HACH DR 1900 Spectrophotometer was used to analyze sulphate, nitrate and phosphate. The BWB XP Flame Photometer was used to analyze sodium, potassium and calcium. Magnesium, chloride, bicarbonate was analyzed by titrimetric methods. Results showed that calcium ranged from 14.1mg/l to 210mg/l and magnesium ranged from 19.2mg/l to 105.6mg/l. The total hardness ranged from 114.27mg/l to 801.10mg/l and percentage total hardness ranged from 1.18% to 8.28%. Three primary rock types constitute the aquifers from which water is abstracted for drinking in the study area (gneiss, migmatite, and older granite), exhibiting variations in their contents of calcium and magnesium. Averagely, content of calcium and magnesium are higher in the migmatite compared to the other rock types. Generally, the total content of calcium in the groundwater do not meet the recommended daily intake of 1000 mg for an adult. Also, about 90% of the groundwater have adequate magnesium content, as daily recommended intake is 200 – 400 mg. With a few exceptions, most groundwater samples are within permissible limits and suitable for drinking purposes. The use of groundwater for drinking may assist in increasing the level of mineral nutrient uptake in the local population, however, it must also be augmented by foods rich in calcium and magnesium in order to satisfy normal human dietary requirements.

***Keywords*:** Calcium, Magnesium, Hardness, Okene, Groundwater.

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1. INTRODUCTION

Calcium and magnesium are essential elements for human health. Calcium, the most abundant mineral in the human body, plays a crucial role in the formation of bones and teeth, muscle activity, nerve impulse transmission, blood coagulation, cardiac function, and enzyme production. Together with magnesium, it supports the proper functioning of the human heart. A deficiency in calcium can increase the risk of high blood pressure and heart failure, while prolonged deficiency may lead to osteoporosis. Magnesium also plays diverse roles in the body, directly influencing neuromuscular function, supporting the normal activity of vitamins C and B, participating in enzymatic processes for energy production, reducing coagulation levels, protecting blood vessel walls from fibrosis, and catalyzing the utilization of fats, proteins, and carbohydrates (Teofilovic et al., 1999; Cotruvo et al., 2009).

In terms of geological presence, calcium is the most abundant alkaline earth metal in the Earth's crust and is a primary constituent in many minerals and rocks, including calcite, aragonite, dolomite, gypsum, apatite, clinopyroxenes, plagioclases, hornblende, and epidote (Clare & Rhodes, 1999). As rocks weather, calcium readily dissolves and enters the hydrosphere, with carbonate equilibrium being the main driver that restricts calcium migration in natural waters.

Magnesium, a significant component of most rock formations, is an essential ingredient in various petrogenic minerals, including dark ferromagnesian minerals like olivine, pyroxenes, and amphiboles, as well as minerals such as serpentinite, talc, brucite, chlorite, biotite, tourmaline, dolomite, magnesite, and spinel (Jovic & Jovanovic, 2004). During the weathering of rocks, magnesium typically enters the hydrosphere by degrading dark ferromagnesian minerals like chlorite, Mg-calcite, and dolomite.

Recent research has indicated the potential beneficial or protective roles of calcium and magnesium in certain diseases across various regions worldwide. These studies have shown calcium's impact on neurological disturbances (Jacqmin et al., 1994; Emsley et al., 2000), the involvement of both calcium and magnesium in amyotrophic lateral sclerosis (Yasui et al., 1997), magnesium's importance in preeclampsia in pregnant women (Melles and Kiss, 1992), and calcium's association with high blood pressure (Rubenowttz, 1999). Furthermore, magnesium has been linked to both high blood pressure and metabolic syndrome (Rasic Miutinovic, 2012). According to Cost et al., (1999), maintaining a consistent lifelong daily intake of drinking water with highly bioavailable calcium could be crucial for preserving calcium balances and enhancing spinal bone mass.

In a study by Cepollaro et al., (1996), supplementing with calcium mineral water for one year resulted in an increase in bone mass density in postmenopausal women. In Spain, Verd Vallespir et al., (1992) found a correlation between low calcium content in drinking water and a higher rate of bone fractures in children.

In the late 1990s, several epidemiological studies, primarily combined with ecological case-control studies conducted in Taiwan, explored the relationship between drinking water hardness and mortality from various cancers, revealing significant geographical variations. Magnesium showed a protective effect against cerebrovascular diseases (Yang, 1998) and hypertension (Yang and Chui, 1996). Kuo et al., (2010) reported an increased risk of rectal cancer from trihalomethanes (THMs) in areas with low magnesium levels in drinking water. Similarly, the risk of kidney cancer from THMs was higher in areas with soft water (Liao et al., 2012). Regions with magnesium levels exceeding 17 mg/L recorded fewer deaths from diabetes (Yang et al., 1998).

In Finland, the protective effect of magnesium in drinking water against the incidence of Type 2 diabetes among young adults was confirmed (Kousa et al., 2012).

Kozisek (2005) suggested that optimal levels of magnesium and calcium in drinking water should range from 20-30 mg/L for magnesium and 40-80 mg/L for calcium, with a recommended hardness (the sum of calcium and magnesium) of around 2-4 mmol/L. Typical dietary recommendations suggest an intake of approximately 1000 mg of calcium and 200-400 mg of magnesium per day (Ong, Grandjean et al., 2009).

This study aims to evaluate the content of calcium and magnesium in shallow groundwater in parts of Okene and the surrounding areas, assessing whether the levels consumed meet the WHO's recommended daily limits. The following objectives will guide this evaluation:

- To map the distribution of calcium and magnesium using GIS in parts of Okene, central Nigeria.
- To use multivariate analysis to explain the variation of these ions in the aquifers in the area.

2. DESCRIPTION OF THE STUDY AREA

The study area is situated between latitudes 7°32′ and 7°38′N and longitudes 6°10′ and 6°18′E (Fig. 1). It encompasses approximately 35 km² and includes Okene, Adavi, and parts of Okehi Local Government Areas in north-central Nigeria.

This region features a climate typical of the tropical woodland and tall grass savannah zone due to its geographical location. It is characterized by two distinct seasons: the rainy season and the dry season. The temperature ranges from 18.4°C to 36.9°C, with an annual rainfall of about 1500 mm (Ogbonna et al., 2006). Relative humidity is low during the dry season and high during the wet season, which begins around March and ends in October. The dry season commences in November and lasts until early March of the following year (Aremu et al., 2014). Heavy rainfall usually occurs in June and July, followed by a short break in August and another downpour in September, leading to two distinct peaks of rainfall in the area.

The landscape is predominantly covered by grasses, shrubs, and trees ranging from medium to tall heights, while the shrubs comprise various species. This diversity in vegetation is influenced by both natural processes and human activities, such as bush burning and poor forestry practices (Ogbonna et al., 2006). The valleys surrounding the study area are blanketed with thick vegetation, evidenced by the flow of water down the ridges throughout most months of the year.

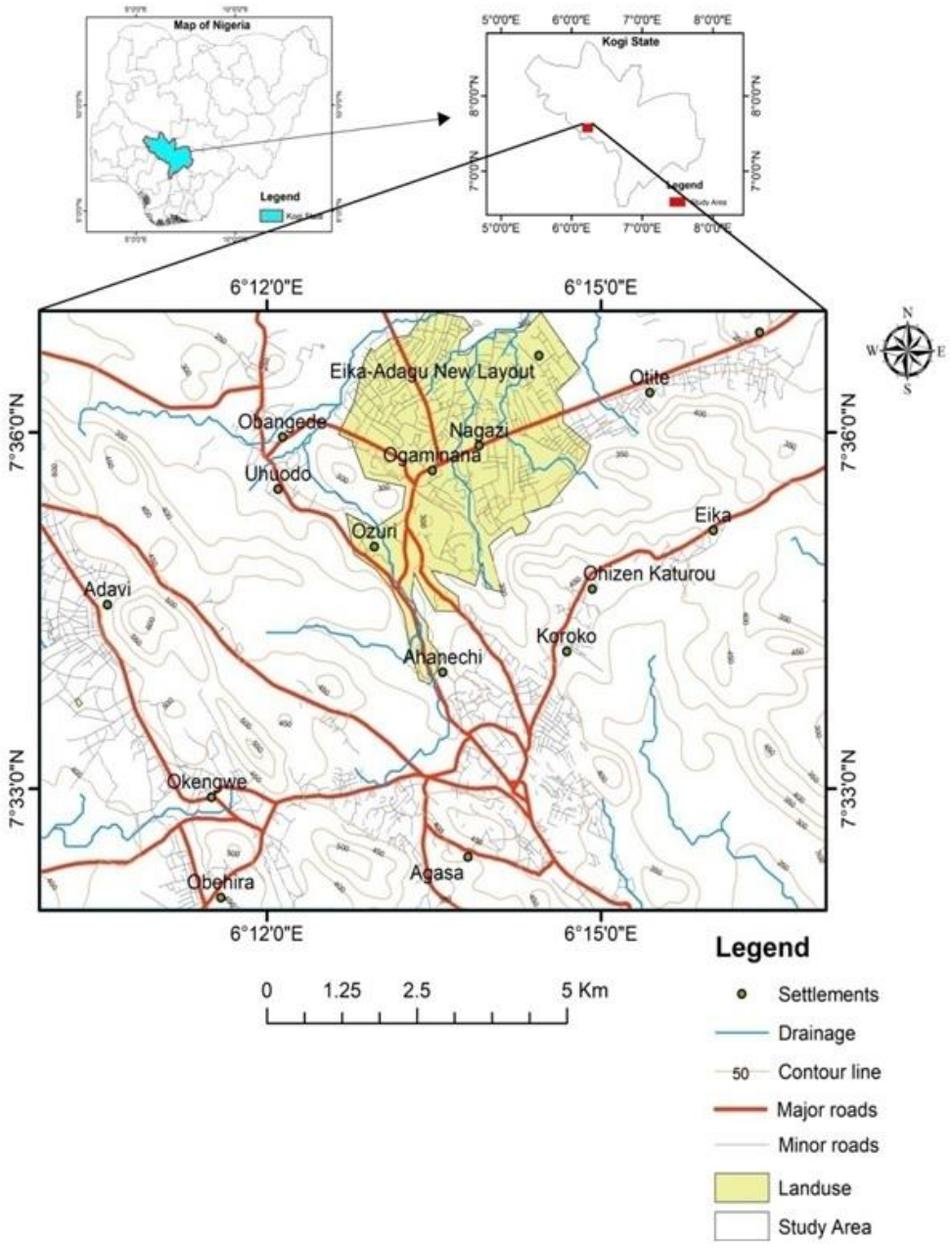


Figure 1. Location Map of the Study Area.

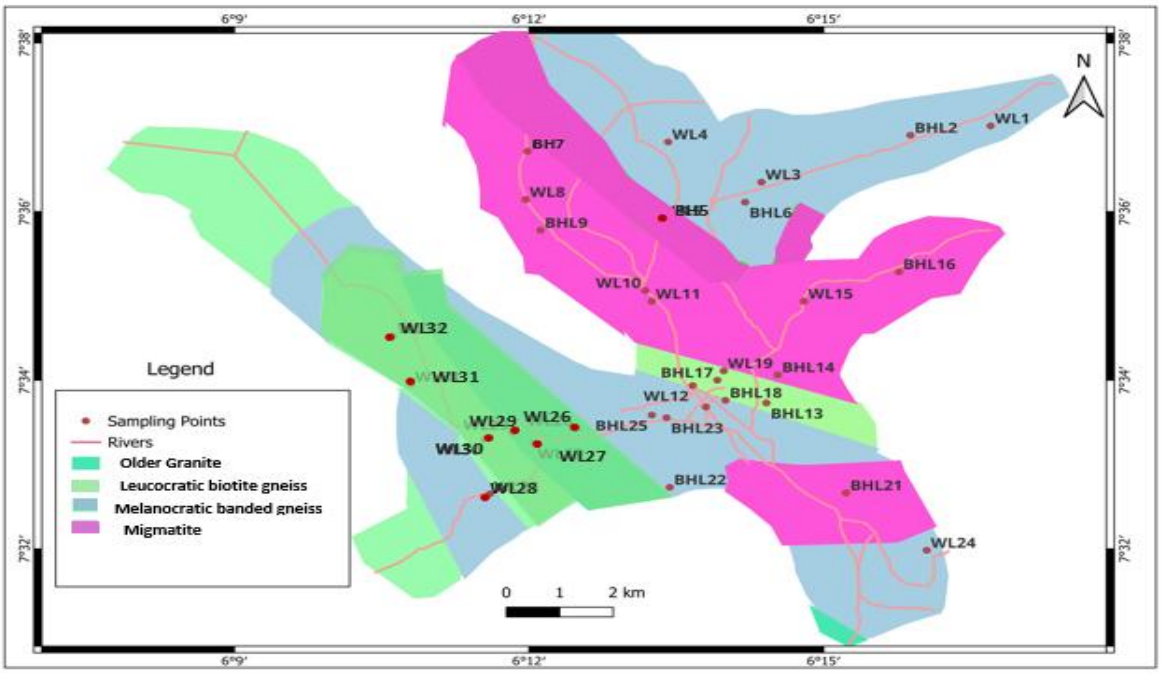


Figure 2. Geologic Map of the Study Area Showing Sample Location.

2.1. Relief and Drainage

The physical features of the area are characterized by hills and rocky formations, along with undulating highlands. Notable hills include Anyioke, Atami, Odunmi, Okunchi, and Oborenyi. The region is rich in mineral resources, such as iron ore and precious stones.

The landscape is predominantly covered by grasses, shrubs, and a variety of trees ranging from tall to medium height. These trees come in different sizes, and the shrubs consist of various species. However, this diverse vegetation is being threatened by degradation caused by natural factors and human activities, such as bush burning and poor forestry practices (Ogbonna et al., 2006).

The valleys in the study area are blanketed with thick vegetation, supported by the consistent flow of water from the ridges throughout most months of the year. There are four main rivers in the area: the Obuburu, Ohaovo, Ogede, and Esomi (Fig. 2). These rivers are perennial and flow in different directions due to the unique topography and geological structures of the region. Consequently, the drainage pattern of the area can be described as radial (Gideon, 2019).

3. METHODOLOGY

Thirty-two water samples were collected from various sources, including hand-dug wells and boreholes, at different locations. These samples were gathered in clean 250 ml plastic containers that had been rinsed with the water being sampled. Hand pumps were operated for several minutes to ensure that fresh water was obtained directly from the aquifer. For each location, two sets of samples were collected in 250 ml plastic containers. One of these samples was acidified with two drops of concentrated nitric acid to preserve the cations and prevent the adsorption and precipitation of ions. GPS coordinates were recorded for each location, and temperature, pH, and electrical conductivity (EC) were measured for all samples in the field using a conductivity/pH meter.

3.1. Laboratory Preparation and Analysis

The water samples collected were stored in ice-filled coolers and transported to the laboratory. The samples were divided into 60 ml sterilized plastic bottles and sent to the laboratory for analysis of the major and minor cations using the Atomic Absorption Spectrophotometer (AAS). The anions, chloride (Cl^-) and bicarbonate (HCO_3^-), were analyzed through titration, while sulfate (SO_4^{2-}), nitrate (NO_3^-), and phosphate (PO_4^{3-}.) were analyzed using the Flame Spectrophotometer

Statistical Evaluation of Data

Field data was evaluated using the Statistical Package for the Social Sciences (SPSS) Version 16 software to determine the median, mean, mode, maximum, minimum, and standard deviation and Arc GIS 10.0 was used to produce maps.

4. RESULT AND DISCUSSION

Summary of chemical composition for shallow ground water in the study area is presented in Table 1. The results revealed an average pH of 5.54, indicating slightly acidic conditions. The mean TDS was 326.47 mg/L, EC was 599.12 µS/cm, temperature was 29.32°C. The order of cation abundance was $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. Calcium made up approximately 45% of total cation concentration, ranging from 14.1 to 210 mg/L. Magnesium levels ranged between 19.2 and 105.6 mg/L (mean: 45 mg/L), sodium from 7 to 200.1 mg/L (mean: 58.13 mg/L), and potassium from 0 to 23 mg/L (mean: 3.92 mg/L). The average total hardness (TH) was 302.21 mg/L, with higher concentrations of alkaline earth metals than alkali metals. Anion concentrations show $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > PO_4^{3-}$. Chloride concentrations reached up to 250 mg/L (mean: 92.91 mg/L).

The variation of the anions and physicochemical parameters in the water are further represented in Table 2 according to the geologic environment and groundwater bearing rock (aquifer). These average values are within permissible limits when compared with the WHO standards for drinking water (Table 3).

Table 1. Summary of Chemical Composition (Mg/l) of Water in the Study Area. Conductivity Is In Ms/Cm

Elements	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3	PH	TDS	Cond.	TH
Mean	46.82	45	35.06	3.92	93.22	33.44	83.29	6.9	5.5	328.01	602.39	302.2
Median	29.39	38.4	34.9	2.3	67	27	76.18	5.75	5.5	308	558	269.7
Std.Deviation	49.2	19.27	58.06	5.25	63.24	30.59	31.23	4.16	0.19	141.62	262.53	165.6
Skewness	2.5	1.2	1.9	2.7	1.3	3.0	0.5	0.6	0.2	0.85	0.92	1.7
Minimum	14.1	19.2	18.3	0.2	26	5.0	38.08	1.3	5.0	137	250	114.3
Maximum	210	105.6	200.1	22.5	260	174	164.98	15.27	6.5	701	1350	806

Table 2. Hydrochemical Parameters for Waters Sampled in the Different Aquifers.

Sample ID	*Rock type	pH	TDS (mg/L	Cond. (µS/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	Cl^{-} (mg/L)	HCO_3^{-} (mg/L)	SO_4- (mg/L)	NO_3- (mg/L)	TH
WL1	MBG	6.0	277	500	43.6	57.6	25.4	0.9	154	63.46	40.67	1.93	346.07
BHL2	MBG	5.5	355	661	24.7	48	63.9	0.8	50	126.91	18	5.93	259.34
WL3	MBG	6.5	294	558	63.3	38.4	41.4	4.1	56	38.07	27	7.67	316.19
WL4	MBG	5.7	308	521	22.9	28.8	106.8	1.1	38	114.22	14	3.83	175.78
BHL5	M	5.5	650	1200	29	105.6	171.3	4.5	180	126.92	67	8.77	507.27
BHL6	MBG	5.9	193	395	21	38.4	35.5	1.2	78	50.77	21	7.73	210.57
BHL7	M	5.6	413	770	44.9	57.6	64.9	1.5	90	114.22	36	10.23	349.31
WL8	M	5.2	421	790	51.2	48	113	2.4	74	63.46	49	8.13	325.51
BHL9	M	5.7	433	800	40.6	57.6	120.8	3.4	144	101.53	33	2.83	338.58
WL10	M	4.9	423	798	103.5	28.8	178.7	22.5	66	88.84	49.33	11.2	377.04
WL11	M	5.3	186	350	17.3	19.2	25.3	4.5	26	63.5	9	2.3	122.26
WL12	LBG	5	215	375	22.1	28.8	30.1	3.6	54	63.46	18	2.2	173.78
BHL13	LBG	5.8	530	970	192	38.4	103.2	5.3	210	114.22	62.33	5.57	637.56
BHL14	M	6	701	1300	210	67.2	200.1	20.7	260	88.82	65	11.47	801.10
WL15	M	5.4	221	400	22.4	19.2	36	6.4	58	63.46	12.03	5.43	135
BHL16	M	5.6	220	395	29.7	28.8	27.1	1.5	42	76.15	10.67	1.3	192.76
BHL17	LBG	5.4	180	345	26.2	48	31.1	0.5	54	50.76	23	4.87	263.09
WL18	MBG	5.4	371	650	42.9	38.4	34.3	4.7	70	101.52	24.27	15.27	265.25
WL19	LBG	5.2	183	348	15.5	28.8	18.3	0.4	42	76.2	20	2.1	157.30
BHL20	LBG	5.7	500	940	156	86.4	53.2	1.3	246	114.22	170	15.3	745.33
BHL21	OG	5.6	330	600	22.8	57.6	44.3	2.2	124	88.84	40	5.1	294.13
BHL22	MBG	6.2	363	635	30.6	48	103.8	1	130	126.9	52	6.1	274.07
BHL23	MBG	5.3	300	550	16.7	38.4	25.5	0.2	52	164.98	15	1.47	199.83
BHL24	OG	4.6	157	280	18.6	28.8	19	1.5	68	88.83	27	9.17	165.04
BHL25	MBG	6.2	380	665	37.2	57.6	29.7	0.4	146	50.77	47	9.17	330.09
WL26	LBG	5.4	137	250	14.1	19.2	6.8	0.3	30	76.15	5	2.73	114.27
WL27	LBG	5.5	300	548	31.7	57.6	28.5	6.1	84	38.1	30.67	13.9	316.35
WL28	MBG	5.6	265	430	28.1	38.4	24	0.2	53	38.07	28	5.1	228.30
WL29	LBG	5.3	168	329	20.7	28.8	12.7	2.8	54	50.77	5	5.17	170.29
WL30	LBG	5.4	401	750	38.3	67.2	54.2	11.1	156	101.52	34	14.5	372.36
WL31	LBG	5.5	390	726	41.7	48	22.4	5.6	58	63.46	10	9.27	301.79
WL32	LBG	5.4	182	345	18.8	38.4	8.7	2.8	36	76.15	7	5.3	205.07

*MBG – Melanocratic Banded Gneiss, OG - Older Granite, M - Migmatite, LBG – Leucocratic Biotite Gneiss, Cond. – Electrical Conductivity

Table 3. Comparison of Samples With Drinking Water Guideline.

Parameters	Range mg/l	Mean mg/l	WHO (2022) Permb. Max	(NSDWQ 2022)	Remarks
pH	5 – 6.5	5.54	6.5 8.5	6.5 – 8.5	Pipe corrosion, impaired taste
EC (mg/l)	288 - 1747	599.05	900 1250	1000	Salty taste
TDS (mg/l)	147 - 873	326.67	<600 1000	500	Salty taste, pipe scaling
Ca (mg/l)	14.1 - 210	46.82	100 500	100	Furring of kettles, waste soap
Mg (mg/l)	19.2 – 105.6	45	60 170	100	
Na (mg/l)	18.3 – 200.1	58.13	200 300	200	High blood pressure
K (mg/l)	0.2 – 22.5	3.92	-	-	-
HCO_3 (mg/l)	38.08– 164.98	83.29	550 1000	100	-
Cl (mg/l)	26 - 260	93.22	250 -	100	Salty taste
SO_4 (mg/l)	5 - 174	33.44	250 1000	100	Laxative effect
NO_3(mg/l)	1.3 – 15.27	6.91	50 50	50	Methemoglobinemia blue baby syndrome
TH (mg/l)	114.3 - 806	302.2	200	200	Furring of kettles, waste soap, pipe scaling

4.1. Drinking Water Quality Assessment

Groundwater quality in Okene and its environs was evaluated by comparing the measured physicochemical parameters with the World Health Organization (WHO 2022) guideline values for drinking water. As shown in Table 3, only two sampling locations recorded pH values within the WHO permissible range (6.5–8.5), while the remaining thirty samples were slightly below this range, indicating slightly acidic groundwater conditions across most parts of the area. Both electrical conductivity (EC) and total dissolved solids (TDS) values were generally below 600 mg/L**,** which is considered acceptable and indicative of good palatability. However, elevated EC values were observed in several locations, including BHL2 (661 µS/cm), BHL5 (1200 µS/cm), BHL7 (770 µS/cm), WL8 (790 µS/cm), BHL9 (800 µS/cm), WL10 (798 µS/cm), BHL13 (970 µS/cm), BHL14 (1300 µS/cm), WL18 (650 µS/cm), BHL20 (940 µS/cm), BHL22 (635 µS/cm), BHL25 (665 µS/cm), WL30 (750 µS/cm), and WL31(726µS/cm)**.** Similarly, TDS values exceeded the 600 mg/L threshold in BHL5 (650 mg/L) and BHL14 (701 mg/L)**.** Groundwater with EC and TDS values above 1,000 mg/L is typically regarded as unpalatable and may indicate mineralization or contamination influences.

Approximately 69% (22 samples) exhibited total hardness (TH) values above the WHO guideline value of 200 mg/L**,** which may cause scaling and encrustation in pipes, tanks, and distribution systems, particularly when interacting with high pH or alkalinity. Concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, and Cl^- generally fell within acceptable limits, except for sample BHL14**,** which showed unusually high concentrations of TDS (701 mg/L), EC (1300 µS/cm), Ca^{2+} (210 mg/L), Na^+ (200.1 mg/L), Cl^- (801 mg/L), and HCO_3^- (114.22 mg/L) all exceeding both WHO and NSDWQ limits. No health-based guideline exists for K^+, but its measured concentrations were within normal ranges.

4.2. The Basement Aquifer

Migmatite (M)

Groundwater samples derived from the migmatite aquifer include those from the College of Nursing, Obangede 1 (BHL7); Obangede 2 (WL8); Ogaminana (BHL5); Uhuodu (BHL9); Ozuri (WL10); Okunchi (WL11); Inozoimi 2 (BHL4); Koroko (WL15); and Eika Ohizen (BHL16). These constitute 28.13% of the study area. These locations exhibit notable spatial variations in the physicochemical composition of groundwater. At Ogaminana (BHL5), the water shows relatively high TDS (650 mg/L) and electrical conductivity (1200 µS/cm), accompanied by elevated concentrations of Mg^{2+} (105.6 mg/L), Na^+ (171.3 mg/L), Cl^- (180 mg/L), HCO_3^- (126.92 mg/L), and total hardness **(**TH = 507.27 mg/L), indicating significant mineralization and prolonged water–rock interaction.

Across the other migmatite localities, TDS values range from 186 mg/L (Okunchi) to 423 mg/L (Ozuri), and electrical conductivity varies from 350 µS/cm (Okunchi) to 798 µS/cm (Ozuri). Major ions also fluctuate considerably, with Ca^{2+} ranging from 17.3 mg/L (Okunchi) to 103.5 mg/L (Ozuri); Mg^{2+} from 19.2 mg/L (Okunchi) to 57.6 mg/L (Obangede); Na^+ from 25.3 mg/L (Okunchi) to 178.7 mg/L (Ozuri); K^+ from 1.5 mg/L (Obangede 1) to 22.5 mg/L (Ozuri); Cl^- from 26 mg/L (Okunchi) to 144 mg/L (Uhuodu); and NO_3^- from 2.3 mg/L (Okunchi) to 11.2 mg/L (Ozuri). Total hardness also shows large variations, ranging from 122.26 mg/L (Okunchi) to 349.5 mg/L (Obangede). Significant compositional differences are also observed between BHL14 and WL15, with Ca^{2+} (210–22.4 mg/L), Mg^{2+} (67.2–19.2 mg/L), Na^+ (200.1–58 mg/L), K^+ (20.7–6.4 mg/L), TDS (701–221 mg/L), and EC (1350–400 µS/cm) showing pronounced spatial variability. Inozoimi 2 (BHL4) recorded the highest total hardness (801 mg/L) and calcium concentration (210 mg/L) within the entire study area, reflecting intense weathering of Ca-bearing minerals such as plagioclase, biotite, and hornblende. In contrast, Eika Ohizen (WL16) exhibited relatively stable concentrations across most measured parameters, indicating limited hydrochemical variation.

4.3. Gneissic Aquifers

Gneiss underlies a major portion of the study area and occurs in three principal variants: melanocratic banded gneiss (MBG), leucocratic biotite gneiss (LBG), and quartzofeldspathic gneiss. These rock types form important aquifer units that exert significant control on groundwater chemistry through mineralogical composition and degree of weathering.

4.4. Melanocratic Banded Gneiss (MBG)

The melanocratic banded gneiss constitutes approximately 31.25% of the study area. Groundwater samples tapping this aquifer include WL1, BHL2, WL3, WL4, BHL6, BHL18, BHL22,BHL23,BHL25, and WL28.

At Otite (WL1), the groundwater exhibits a relatively high Mg^{2+} concentration (86.4 mg/L), while the lowest value (19.2 mg/L) was recorded at WL12, located behind the Okene Water Works. Similarly, elevated Ca^{2+} concentrations were noted around Inozoimi, whereas the lowest (16.7 mg/L) occurred at Agassa Junction (BHL23). At Agassa Uvette (BHL22), Ca^{2+} and Mg^{2+} concentrations were 30.6 mg/L and 48 mg/L, respectively. Other wells and boreholes situated within this lithological unit show only minor variations in major ion chemistry, suggesting relatively uniform mineralogical control and moderate groundwater circulation within the aquifer.

4.5. Leucocratic Biotite Gneiss (LBG)

The leucocratic biotite gneiss underlies about 34.38% of the study area, hosting several wells and boreholes, including WL12, BHL13, BHL17, WL19, BHL20, WL26, WL27, WL29, WL30,WL31,andWL32.Among these, BHL13 (Inozoimi 1**)** stands out, exhibiting significantly elevated ionic concentrations: Ca^{2+} (192 mg/L), Mg^{2+} (38.4 mg/L), Na^{+} (103.2 mg/L), Cl^{-} (210 mg/L), HCO_3^{-} (114.22 mg/L), SO_4^{2-} (62.33 mg/L), TH (637.56 mg/L), TDS (530 mg/L), and electrical conductivity(970µS/cm).Moderate concentrations of Mg^{2+} (28.8 mg/L) and HCO_3^{-} (76.2 mg/L) were observed in wells such as WL19 (Anyoke), WL29 (Okengwe 1), WL31 (AdaviEba1),andWL32(AdaviEba2).At WL30 (Ozuma), groundwater shows notable enrichment with Mg^{2+} (67.2 mg/L), Cl^{-} (156 mg/L), HCO_3^{-} (101.52 mg/L), NO_3^{-} (14.5 mg/L), accompanied by TH (372.36 mg/L), TDS (401 mg/L) and EC (750 µS/cm).

At WL27 (Obehera 1), Ca^{2+} and Mg^{2+} were recorded as 31.7 mg/L and 57.6 mg/L, respectively, while WL26 (Oro) had the lowest values of Ca^{2+} (14.1 mg/L), Mg^{2+} (19.2 mg/L), and TH (114.27 mg/L) across this aquifer zone.

4.6. Older Granite

The Older Granite aquifer underlies approximately 6.25% of the study area and is represented by two boreholes, BHL21 (Checkpoint 1) and BHL24 (Checkpoint 2)**.** Groundwater chemistry within this lithologic unit shows moderate variability. Calcium concentrations range from 18.6 to 22.8 mg/L, while magnesium ranges from 28.8 to 57.6 mg/L, indicating limited dissolution of carbonate-bearing silicate minerals. The concentrations of other major ions show no significant deviation across the two boreholes, suggesting relatively uniform water–rock interaction. The total dissolved solids (TDS) values range from 157 to 330 mg/L**,** and electrical conductivity (EC) from 280 to 600 µS/cm**,** reflecting moderately mineralized groundwater**.** Total hardness (TH) values fall between 165.04 and 294.13 mg/L**,** classifying the groundwater as moderately hard to hard water.

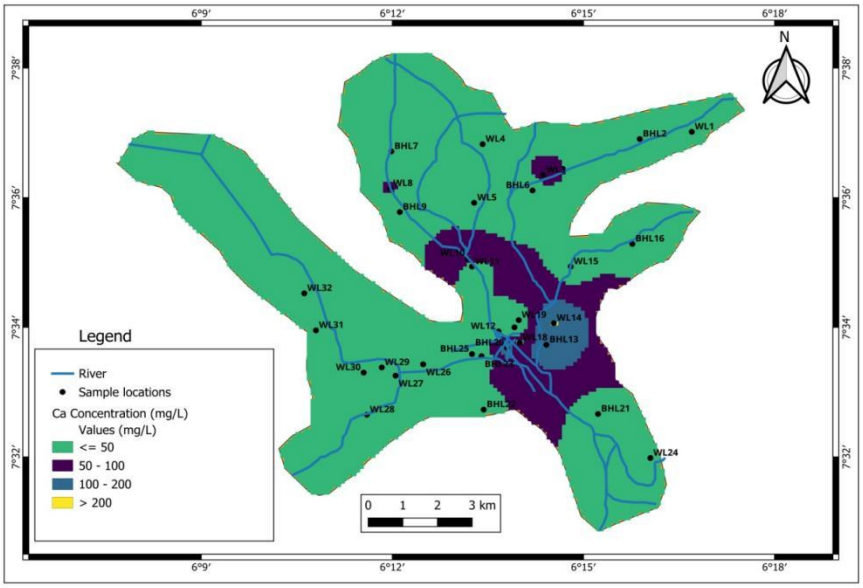


Figure 3. Ca Concentration Distribution (mg/L)

Calcium (Ca^{2+}) concentrations are generally below 50 mg/L across most of the sampling points**,** while relatively higher concentrations ranging from 50 to 200 mg/L occur mainly in the central and eastern parts of the study area. The distribution suggests that calcium is predominantly derived from natural geochemical processes**,** particularly the weathering and dissolution of calcium-bearing minerals in basement rocks such as migmatite and gneiss**.** However, the elevated concentrations observed at some locations may also be influenced by anthropogenic activities**,** including the leaching of domestic wastewater and agricultural runoff into the groundwater system.

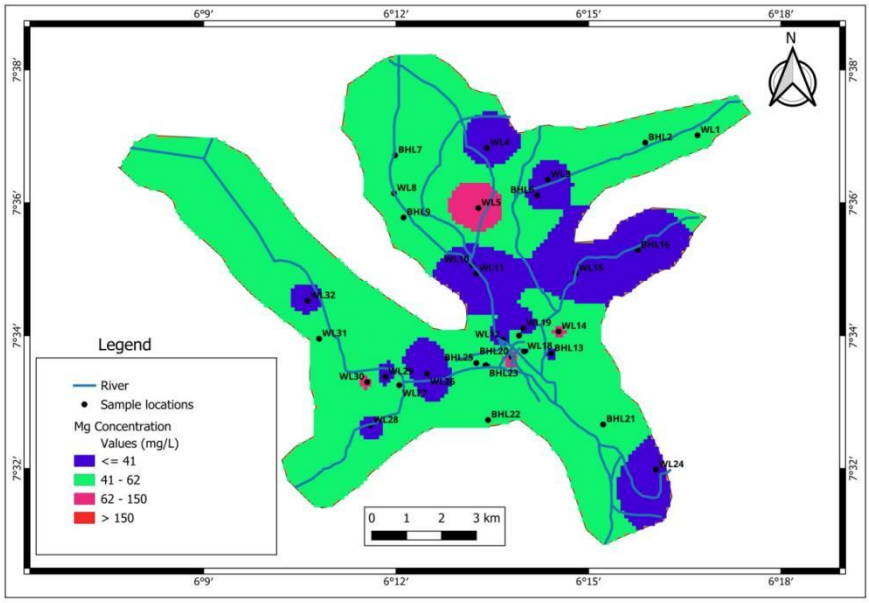


Figure 4. Mg Concentration Distribution (mg/l)

Magnesium (Mg) levels range from 19.20 to 105.57 mg/L, with higher concentrations near magnesium rich rocks like melanocratic banded gneiss, migmatite, and biotite gneiss all within the study area. Most samples exceed 60 mg/L, according to the World Health Organization (WHO,2022). Elevated magnesium in groundwater result in water hardness and potential laxative effects when combined with sulfate.

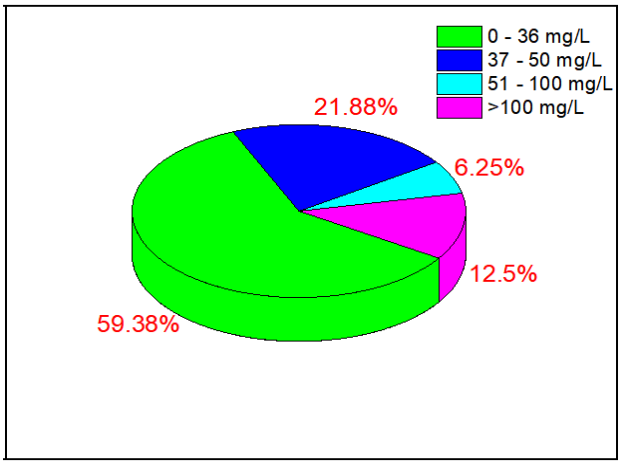


Figure 5. Pie Chart for Concentration of Ca In Water Samples (World Health Organization (2022) Permissible Limit of 100 Mg/L).

The calcium concentration results (Fig.5 & 6) show that 59.38% of the groundwater samples recorded Ca^{2+} concentrations between 0 and 36 mg/L, while 21.88% had concentrations ranging from 37 to 50 mg/L. About 6.25% of the samples fell within the 51–100 mg/L range, and 12.50% had concentrations above 100 mg/L. Overall, the findings indicate that calcium levels in most of the groundwater samples are relatively low to moderate, suggesting limited to moderate contribution of calcium from the surrounding aquifer materials.

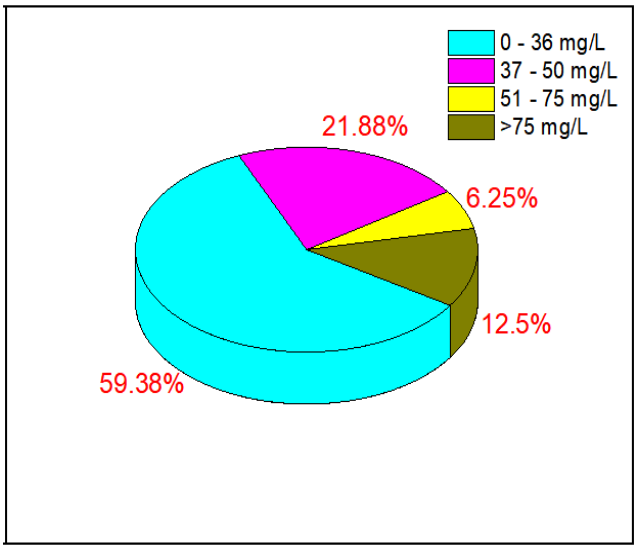


Figure 6. Pie Chart for Concentration of Ca In Water Samples (Nigerian Standard for Drinking Water Quality (Nsdwq 2022) Permissible Limit of 75 Mg/L).

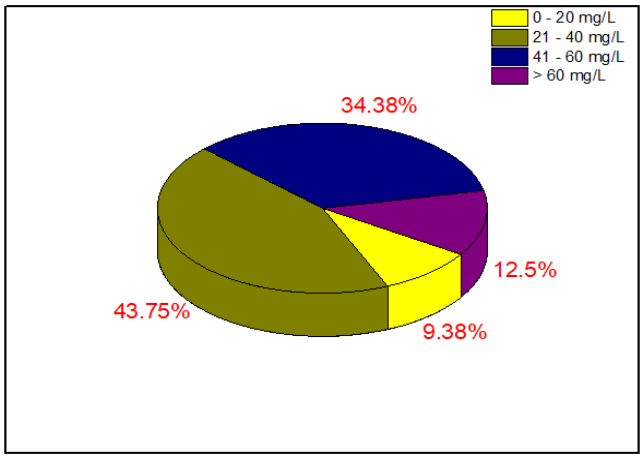


Figure 7. Pie Chart for Concentration of Mg In Water Samples (World Health Organization (2022) Permissible Limit > 60 Mg/L).

The magnesium concentration distribution (Fig. 7) indicates that 9.38% of the groundwater samples recorded Mg^{2+} concentrations between 0 and 20 mg/L, while 43.75% fell within the 21–40 mg/L range. About 34.38% of the samples had concentrations between 41 and 60 mg/L, whereas 12.50% recorded concentrations above 60 mg/L. Generally , the results show that the majority of the groundwater samples (78.13%) had magnesium concentrations between 21 and 60 mg/L, indicating generally moderate levels of magnesium in the groundwater.

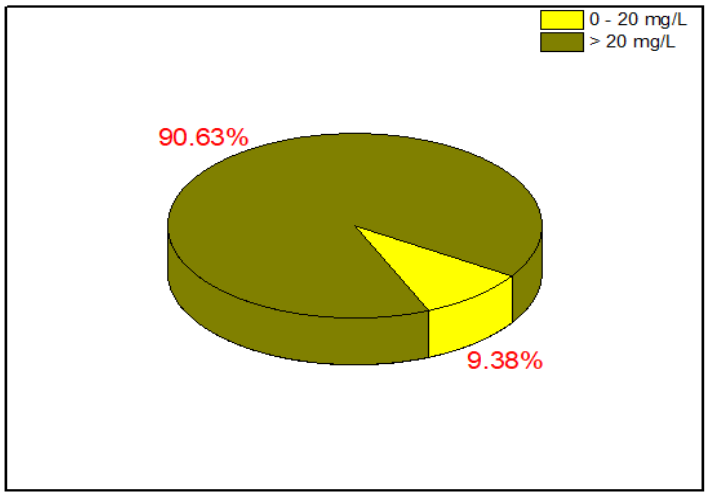


Figure 8. Pie Chart For the Concentration Of Mg In Water Samples (Nigerian Standard For Drinking Water Quality (Nsdwq 2022) Permissible Limit Of 20 Mg/L)

The chart (Fig.8) shows that 9.38% of the groundwater samples recorded magnesium concentrations within the permissible range of 0–20 mg/L**,** while a much larger proportion**,** 90.63% of the samples, had concentrations above the NSDWQ permissible limit of 20 mg/L**.** This indicates that the vast majority of the groundwater samples exceeded the Nigerian standard for magnesium.

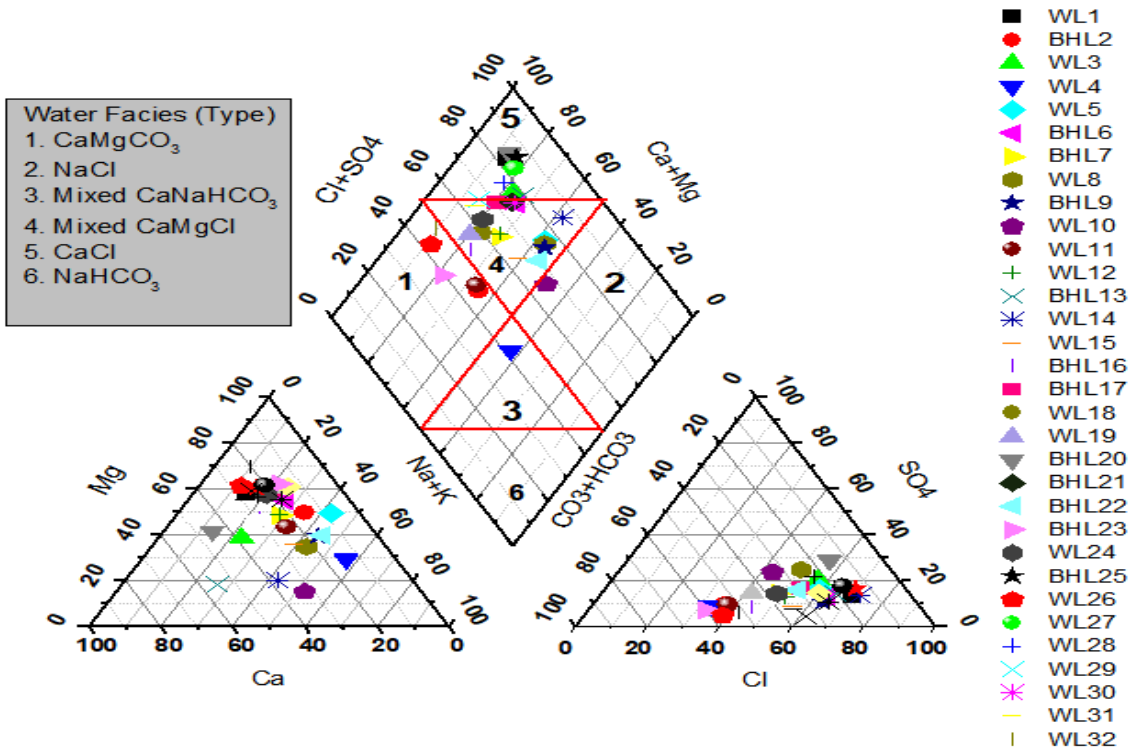


Figure 9. Piper Trilinear Diagram of the Water Types in the Study Area.

The central diamond field shows that most samples fall within mixed Ca–Na–HCO_3 and mixed Ca–Mg–Cl facies**.**

5. POSSIBLE SOURCES OF CALCIUM AND MAGNESIUM

Groundwater in the Okene area generally exhibits consistent concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) across various bedrock types, although localized increases in calcium are sometimes observed in densely populated zones, likely reflecting anthropogenic influences such as leaching from cement materials, domestic wastewater, and agricultural runoff. Both calcium and magnesium are lithophile elements, naturally abundant in the Earth's crust and integral to groundwater chemistry (Jovic & Jovanovic, 2004). Their presence in the unconfined aquifer system primarily reflects mineral weathering and dissolution processes within the crystalline basement rocks that dominate the region.

Calcium in the Okene groundwater is mainly derived from the weathering of calcium-bearing minerals such as apatite, hornblende, biotite, magnesite, and spinel (Clare & Rhodes, 1999). Within the basement complex, plagioclase feldspars, especially the calcium-rich varieties (anorthite and labradorite), are the principal contributors of calcium to solution (Lekmang, 2015). In areas influenced by volcanic lithologies or hydrothermal alteration, olivine and clinopyroxene also contribute to the calcium load through progressive dissolution under slightly acidic conditions.

Magnesium, on the other hand, originates primarily from the decomposition of ferromagnesian minerals such as olivine, pyroxenes, amphiboles, and biotite**,** which are common in both the migmatite gneiss and granitic bedrocks of Okene. According to Gideon (2019), the mineralogical assemblage of the Okene basement rocks comprising quartz, biotite, muscovite, microcline, plagioclase, and hornblende provides abundant sources of both calcium and magnesium. The combined weathering of these minerals under warm, humid tropical conditions enhances cation release into groundwater, thus explaining the dominance of Ca^{2+} and Mg^{2+} observed in hydrochemical analyses. On the whole, the distribution of these cations reflects a geogenic origin, with minor modification by human-induced inputs in built-up areas.

5.1. Intake of Calcium and Magnesium in Drinking Water of the Study Area

In the Okene area, the assessment of calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations in groundwater reveals varying degrees of nutritional adequacy relative to recommended health standards. Only about 34% of the sampled well points specifically WL1, WL3, BHL7, WL8, BHL9, WL10, BHL13, WL14, WL18, BHL20, and WL31 fall within the optimal calcium concentration range of 40–80 mg/L, which is considered beneficial for human health (Kozisek, 2005). This finding implies that most groundwater samples contain suboptimal calcium levels, falling below the recommended daily intake of approximately 1000 mg/day set by the World Health Organization (WHO, 2011). Consequently, calcium intake from drinking water in the area is inadequate to meet dietary requirements.

In contrast, the magnesium content of groundwater in the study area appears to be sufficiently adequate, with about 90% of the sampled wells falling within the optimal range of 20–30 mg/L (Kozisek, 2005). Only three wells (WL11, WL15, and WL26) recorded slightly lower magnesium concentrations of 19.2 mg/L, which are marginally below the optimal threshold. Given this, the estimated daily magnesium intake (200–400 mg/day) from drinking water is considered adequate for maintaining physiological balance and metabolic functions.

Overall, while magnesium levels in the groundwater of Okene are largely within acceptable health limits, calcium concentrations are notably deficient, which may limit the mineral's nutritional contribution from drinking water alone. It is therefore recommended that residents supplement their diet with calcium-rich foods such as dairy products, leafy vegetables, and fortified grains to offset the low calcium levels, ensuring a balanced intake of these two essential hardness minerals.

6. CONCLUSION

The study area is underlain by banded biotite gneiss, migmatite, and older granite, which form part of the Precambrian Basement Complex of North-Central Nigeria. These rocks, rich in silicate minerals, govern the hydrogeochemical composition of groundwater. The sources of calcium and magnesium are mainly the weathering of calcium plagioclase feldspars in basement and volcanic rocks, and ferromagnesian minerals such as olivine and clinopyroxene. Variations in Ca^{2+} and Mg^{2+} concentrations among wells reflect differences in mineral composition, water–rock interaction, residence time, and human influences.

Although no direct link was found between mineral intake from groundwater and diseases such as hypertension or cardiovascular disorders, low calcium levels, combined with poor dietary intake, may contribute to calcium deficiency-related health risks. Hydrochemically, the dominant groundwater facies are CaMgCl (53.13%), CaCl (25%), and $CaMgCO_3$ (15.63%), indicating strong mineral weathering and ion exchange processes. The prevalence of chloride-rich water explains the salty taste, hardness, and scaling effects observed in domestic use.

In general, while magnesium intake from water is adequate, calcium levels remain deficient, highlighting a nutritional and water-quality concern. Further integrated studies combining isotopic, hydrogeochemical, and medical data are recommended to clarify the links between groundwater composition and public health in Okene.

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