International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2013): 4.438

Geochemistry of Natural Water Systems in Ugwulangwu, Ebonyi State, Nigeria

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Abstract: ***The study area is underlain by Albian (Asu River Group) and Turonian (Ezeaku Formation) sediments which consists of calcareous sandstones with subordinate siltyshales and black carbonaceous shales respectively. The hydrogeochemistry of the groundwater and surface water system was evaluated by analysing 25 water samples drawn from 15 bore holes/ hand-dug wells and 10 surface waters locations. The analytical results showed that for both groundwaters and surface water bodies the pH range is from 5.50 to 8.0 which indicates mildly acidic to mildly alkaline environments. Both the groundwater and surface waters have low solute concentrations which suggest small residence time of recharge water in the rocks. For the groundwater samples, total hardness ranges from 20-160mg/l with most values being greater than 100mg/l which indicates waters that are moderately hard to hard. The surface waters are generally softer than the groundwater with total hardness being mostly under 100mg/l in the groundwater. In the groundwaters, cation concentrations are in the order Mg^{2+}>Na^{+}> Ca^{+} while anions follow the order HCO_3^->Cl^->SO_4^{2-} but for the surface waters, it is Na^+ >Mg^{2+}>Ca^{2+} and anions have the order, HCO_3^->Cl^-> SO_4^{2-}. The difference in cationic chemistry between groundwater and surface waters is attributed to cation exchange reactions in the aquifer. The average value of manganese in the groundwater is 105.85mg/l but only few surface water samples had manganese. The indication is that manganese carbonates are reacting with water to release pyrolusite (MnO_2) into the water. The application of ionic ratios to the interpretation of the geochemical analysis result showed that important processes such as dolomite dissolution, carbonate weathering and dissolution of ferromagnesian minerals and cation exchange are responsible for the chemical composition of the natural waters.***

Keyword: Ugwulangwu; ionic ratios; dolomite dissolution; carbonate weathering

1. Introduction

Ugwulangwu and environs are enclosed by latitudes 6^0 00'N and 6^0 05'N and longitudes 7^0 50'E and 7^0 55'E covering an area of about 82.35 square kilometres. It is part of the southern flank of the Abakaliki anticlinorium in the Cross River plains (Ofodile, 1976). It is also part of Ohaozara local government area in Ebonyi State, a sub-region with important geological features such as brine fields in Uburu-Okposi area; Amasiri – which is the type locality for Amasiri sandstone and Asu River – which also is the type locality for Nigeria's oldest sedimentary rocks. Ugwulangwu has a mean annual rainfall of 1850mm/year and a mean annual humidity of over 80% (Iloeje, 1981). Over 70% of the rains fall within the months of April and September which corresponds to the rainy season of the year. Rainy season last from April to October while dry season range from November to March. Vegetation ranges from savannah grasslands to subtropical rainforests. The drainage pattern is trellis and is effected by Asu River and its tributaries. The main tributaries are Onwor, Isinkwo, Ugwulangwu, Umuke, Mgbom and MmiriEziUkawu. Topographically, Ugwulangwu and environs has a set of ridges and hills at the northeastern part of the map but the rest of the area is low-lying. Fig. 1 shows a topographical section through the area. This shows that the area is divided into two by the valley of the Asu River and its tributaries.

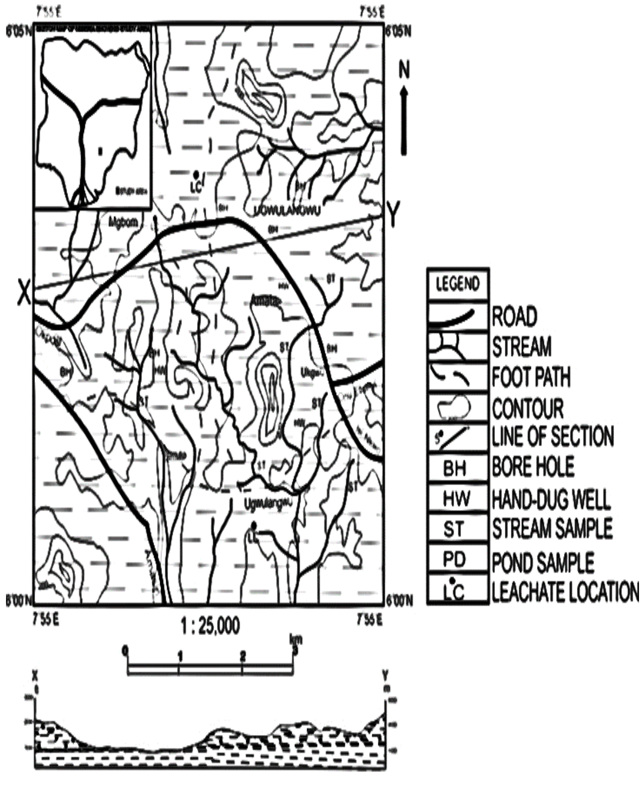

Figure 1: Topographic map of Ugwulangwu (Note the topographic section)

A lot of geological investigations have been carried out in communities close to the study area. Much of the early foundation was laid by Nwachukwu (1972) who investigated the tectonic evolution of the southeastern part of the Benue trough. This led to the discovery of lead-zinc mineralisation in the Albianshales of Asu River Group. Nwachukwu (1975) did more work on hydrothermal fluids in the area. It was also established at the time, that the brine fields in Okposi and Uburu had very high salinity levels more than in any other area. This attracted more work on the brine fields by Olade (1976); Offodile (1976) and Egboka and Uma (1986).

The aim of the present study is to determine the geochemical characteristics of the groundwater and surface water bodies that exist in the study area. Moreover, there is need to establish if the geochemistry of these water systems has been influenced in any way by the chemistry of the brine fields located in nearby communities.

2. Geology and Hydrogeology

The study area is underlain by sediments of Asu River Group and EzeAku Formation (Figure 2). The Asu River Group in Ugwulangwu is represented by a calcareous sandstone with subordinate silty shale lenses. This unit is poorly bedded but has massive outcrops in the northeastern and southeastern parts of the area. It is fine to medium grained with colours ranging from buff to white. The dips range from 2^0 to 6^0 in the southeast direction.

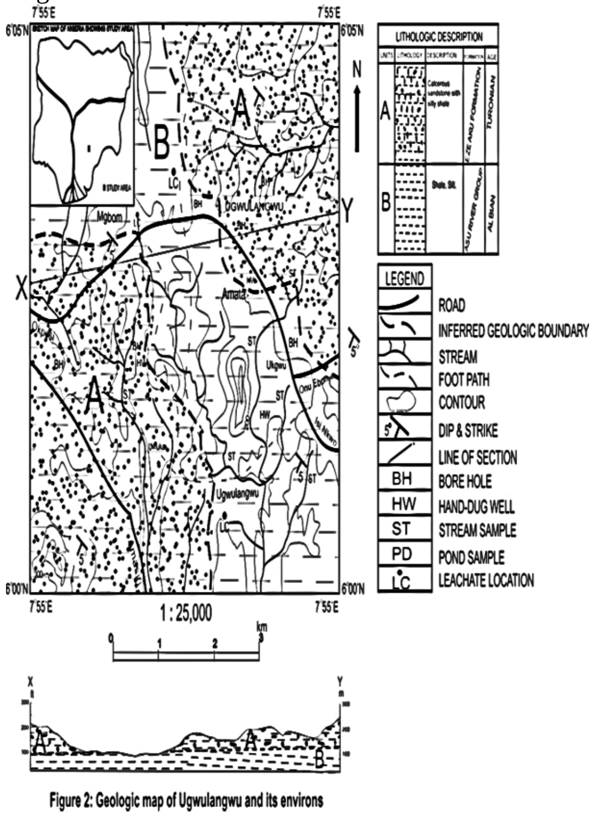

Figure 2: Geologic map of Ugwulangwu and its environs

This unit is uncomformably overlain by black, carbonaceous shales of Ezeaku Formation. The shales are occasionally interbedded with siltstones and mudstone. It outcrops at Amata and Ukawu. The colour ranges from bluish grey to olive brown. There is evidence that both formations have calcareous cements and high percentages of feldspars and clay minerals. The two aquifer systems in the area are the shallow, unconfined aquifers and the slightly deeper confined aquifer. The shales yield small volumes of water wherever they are fractured. They sustain hand-dug wells where the static water level is about 8m at the end of the dry season. The unconfined aquifers consist of fractured shales. They are thin but laterally extensive. The confined aquifer is made up of poor-yielding indurated fine to medium grained sandstones. Flow is enhanced by jointing and fracturing of the rocks. Uma and Loenhert (1992) reported that at Okposi, these confined aquifers yield free flowing wells with a head of 0.7m above the ground surface and a yield of 67ml/hr. From the work of Uma and Loenhert (1992), there is an indication of hydraulic connectivity between the aquifers at Ugwulangwu and Okposi. If there is a connectivity, then it can be expected that the brine fields at Okposi would impact the water composition at Ugwulangwu.

3. Materials and Methods

Samples were taken from 15 boreholes and hand-dug wells and also from 10 surface water bodies. The water samples were filtered with 0.45μmcellulose acetate filters and portions were acidified on site to stabilise chemical species that could alter before laboratory analysis. Measurements of temperature, electrical conductivity and pH were taken in situ during the field work using portable multi-parameter water quality meter (Hach 93130). In taking the samples, each container was rinsed with the water to be sampled before the sampling was done. In the laboratory, the cations were analysed with Atomic Absorption Spectrophotometer while the anions were analysed with standard methods prescribed by American Public Health Association in Clesceri et al, (1998).

4. Results and Discussion

Table 1 presents the results of the chemical analyses for the boreholes and hand-dug wells. For the boreholes and hand-dug wells, pH ranges from 5.50 to 8.0. Acidic pH values occurred in 8 of the 15 samples while 7 samples showed mildly alkaline to alkaline pH values. Total dissolved solids are quite low (from 46.00 mg/L at BH10) to 260mg/L (Ukawu village borehole) which is an indication of small residence time. Total hardness ranges from 20mg/L to 167mg/L. Calcium (Ca^{2+}) ranges from 0.80mg/L at HW1 to 90mg/L at BH9 while magnesium (Mg^{2+}) ranges from 9.70mg/L at HW1 to 94mg/L at BH3. Sodium (Na^+) ranges from 32.0mg/L at BH9 to 124mg/L at BH6 while potassium (K^+) ranges from 10.40mg/L at BH10 (Mgbom village) to 44.00mg/L at HW2 (Ukawu School). Bicarbonate (HCO_3^-) ion has the largest concentration value among the anions. It goes from 8.0mg/L at HW1 to 171.0mg/L at Ukawu village, BH1. It is closely followed by the chloride ion (Cl^-) which goes from 5.40mg/L at BH8 to 18.90 (HW1). Sulphate (SO_4^{2-}) ion is the least ion. It ranges from 0.00mg/L to 12.00mg/L.

Iron (Fe^{2+}) ranges from 0.10mg/L to 0.73mg/L which is slightly higher than the recommended limit (0.3mg/L). Manganese (Mn) is however much higher than iron. It ranges from trace to 124.50mg/L at BH3. Infact, manganese is the largest cation which suggests that the mineral pyrolusite (MnO_2) is in the water solution. This may be due to the oxidation of manganese carbonates

Table 1: Results of Chemical Analyses for Boreholes and Hand-Dug Wells (in mg/l)

	Location	pH	EC ($\mu mhos$)	TDS	Ca^{2+}	Mg^{2+}	Fe^{2+}	Na^{+}	K^{+}	Mn^{2+}	SO_4^{2-}	Cl^{-}	HCO_3^{-}	CO_3^{2-}	NO_3^{-}	Total Hardness
1	Ukawu Village Sq. BH1	8.00	0.49	260.00	25.70	68.10	0.12	62.00	20.00	109.90	0	11.50	171.00	0	0	154.00
2	Nwafor's House Amata HW1	6.50	0.08	60.00	0.80	9.70	0.10	54.00	19.60	Trace	0	18.90	8.0	0	0	20.00
3	School Area Ukawu HW2	6.66	0.43	50.00	24.50	68.20	0.11	102.00	44.00	94.40	0	9.30	162.00	0	0	152.00
4	Opp. Amata Pri. Sch. HW3	8.00	0.48	120.00	70.00	64.50	0.27	70.00	32.00	102.50	1.20	7.40	118.00	0	0	167.00
5	Pri. Sch/Mkt Sq. Amata BH2	5.75	0.14	230.00	25.00	42.30	0.62	70.00	24.00	114.80	1.40	12.00	112.00	0	0	124.00
6	Pri. Sch/Mkt Sq. Amata BH3	8.00	0.11	60.00	23.00	94.00	0.52	84.00	22.40	124.50	0.40	7.20	124.00	0	0	125.00
7	Pri. Sch/Mkt Sq. Amata BH4	7.44	0.47	70.00	45.00	34.00	0.12	42.00	18.60	103.40	0	6.00	118.00	0	0	119.00
8	Mgbom School BH5	7.55	0.34	70.00	80.00	32.40	0.73	62.00	34.40	109.20	0.60	7.40	98.00	0	0	124.00
9	Ukwu Oji Umuka BH6	6.00	0.07	64.00	43.00	73.00	0.20	124.00	13.40	102.60	12.00	6.20	124.00	0	0	118.00
10	Pri. Sch/Mkt Sq. Amata BH7	7.45	0.08	124.00	32.00	74.00	0.32	70.00	19.00	105.40	10.00	6.40	102.00	0	0.10	154.00
11	UmukaPri. Sch. BH8	5.50	0.18	60.00	72.00	32.00	0.42	86.00	24.30	104.60	9.00	5.40	74.00	0	0.20	155.00
12	Grace of God Umuka BH9	6.40	0.73	80.00	90.00	54.40	0.16	32.00	18.70	94.80	8.30	9.20	120.00	0	0	164.00
13	Okoye's Compd. Umuka HW4	6.87	0.04	64.00	82.00	43.00	0.13	64.00	18.10	92.70	0	11.60	112.00	0	0	134.00
14	UgwuNwali's House HW5	6.45	0.82	54.00	45.00	32.50	0.16	92.00	13.40	102.00	0.70	11.00	142.00	0	0	122.00
15	MgbomVillageSq BH10	7.25	0.07	46.00	32.00	90.00	0.10	62.00	10.40	121.21	0.40	8.05	162.00	0	0	117.00

Most of the pH values fall within the neutral to mildly alkaline range of (6.5 to 8.0) which indicates an environment where the dominant anion would be bicarbonate. It serves as a good buffer for acids. Here, the soil would easily form carbonate concretions.

Table 2 shows the results of chemical analyses of surface waters at Ugwulangwu. Ten samples were analysed. The pH range is from 5.80 at Isi Nkwo stream to 7.90 at MmiriEziUkawu (mildly acidic to mildly alkaline). The total dissolved solids varies from 58mg/L at Umuka stream to 130mg/L at Isi Nkwo stream while total hardness goes from as low as 2.0mg/L at Mgbom pond II to 136.00mg/L at OnuUgwulangwu stream.

Table 2: Chemical Analyses Result for Surface Water Bodies in the Study Area (in mg/l)

S/no	Locations	pH	EC ($\mu mhos$)	TDS	Ca^{2+}	Mg^{2+}	Na^{2+}	K^{+}	Mn^{2+}	SO_4^{2-}	Cl^{-}	HCO_3^{-}	CO_3^{2-}	NO_3^{-}	Fe^{2+}	Total Hardness
1	Onwor Stream, Amata	6.2	0.12	80	3.2	9.7	63	11.5	Trace	10	24	20	0	0	0.37	18
2	Onwor Stream between Amata and Ukawu	6.56	0.09	70	3.4	12.3	44	20	Trace	11.5	18	23	0	0	0.53	38
3	Amata Stream	6	0.12	72	2.2	72.3	65	22	108	0	11	113	0	0	0.45	112
4	Mgbom Pond I	6	0.1	80	2.8	4.9	45	22	Trace	0.2	5	11	0	0	0.26	24
5	Mgbom Pond II	6	0.34	70	1.6	9.2	46	12	0.24	13	12	9	0.2	0	0.11	2
6	Umuka stream	7.1	0.23	58	26.3	5.8	22	9.8	0.13	0.4	18	120	1.42	0	0.23	18
7	Ugwulangwu stream at Girls School	7.4	0.34	90	0.9	3.6	48	26	Trace	8	4.6	130	0	0.2	0.13	30
8	Isi Nkwo Stream	5.8	0.07	130	0.8	9.7	121	12.4	101	0	13	9	0	0	0.12	114
9	OnuUgwulangwu Stream	6.6	0.07	64	2.4	52	94	18.6	0.24	50	12	13	0.4	1	0.11	136
10	MmiriEziUkawu	7.9	0.14	110	26.7	62	52	11.6	112	0	9	45	0.12	0	0.01	30

Values of calcium (Ca^{2+}) go from 0.80mg/L at Isi Nkwo stream to 26.70mg/L while magnesium (Mg^{2+}) goes from 3.60mg/L at Girls' School Ugwulangwu to 72.30mg/L at Amata Stream. The cation with the highest concentration is sodium (Na^+). It ranges from 22.0mg/L at Umuka stream to 121mg/L at Isi Nkwo stream. Potassium (K^+) varies from 9.80mg/L at Umuka stream to 26mg/L at Girls' School Ugwulangwu. Unlike the boreholes/hand-dug wells that had high values of manganese in virtually all the sampled locations, manganese in the surface waters ranges from trace to 108.00mg/L. In other words, some processes are acting as manganese sinks in the surface waters. Iron (Fe) ranges from 0.01mg/L to 0.03 and is on the average slightly higher than the levels found in the boreholes. Bicarbonate (HCO_3^-) has the largest anion concentration and it varies from 9mg/L to 130mg/L while chloride (Cl^-) ion follows closely from 4.60mg/L at Girls' School Ugwulangwu to 24.0mg/L at Onwo Stream, Amata. Sulphate (SO_4^{2-}) values are low, which is a possible indication of sulphate reduction processes. It ranges from 0.0mg/L to 50mg/L. For the groundwater samples, total hardness ranges from 20-160mg/l with most values being greater than 100mg/l which indicate waters that are moderately hard to hard. The surface waters are generally softer than the groundwater with total hardness being mostly under 100mg/l in the groundwater. In the groundwaters, cation concentrations are in the order $Mg^{2+}>Na^+> Ca^+$ while anions follow the order $HCO_3^->Cl^- >SO_4^{2-}$ but for the surface waters, it is $Na^+ >Mg^{2+}>Ca^{2+}$ and anions have the order, $HCO_3^->Cl^-> SO_4^{2-}$. The difference in cationic chemistry between groundwater and surface waters is attributed to cation exchange reactions in the aquifer.

In interpreting chemical analyses of water, ratios between various ions are often used to discern the actual sources of those ions or the processes that released them into the aquifers. Hem (1992) used Mg^{2+}/Ca^{2+} and Na^+/Cl^- to determine waters with sea water composition. Sonnenfeld (1984) have been able to differentiate various evaporite deposits on the basis of K^+/Br^- ratios. Other important ratios used as tools for hydrogeochemical interpretation include Na^+/Cl^- ratio(Bojarski, 1970; Collins, 1972); SO_4^{2-}/Cl^- ratio (Hem, 1992), Br^-/Cl^- ratio (Rittenhouse, 1967) and brine differentiation plots (Hounslow, 1995).

Table 3 shows the various ratios calculated on the basis of milliequivalents per litre. The Mg^{2+}/Ca^{2+} ratio values is between 0.67 to 19.95. According to Meisler and Becher (1967), high Mg^{2+}/Ca^{2+} ratios occur in sedimentary aquifers if there is dolomite dissolution and if the TDS (total dissolved solids) is about 500mg/L. In Ugwulangwu, the value of TDS is mostly between 100 – 260mg/L which means that the high Mg^{2+}/Ca^{2+} ratio is likely due to the dissolution of ferromagnesian minerals (Hounslow, 1995).

Table 3: Various chemical ratios calculated for the boreholes and hand-dug wells (based on Table 1)

S/N	*Location*	*Mg^{2+}/Ca^{2+}*	*Na^+/Cl^-*	*Ca^{2+}/SO_4^{2-}*	*Na^+/Ca^{2+}*	*$Mg^{2+}/Ca^{2+} + Mg^{2+}$*	*$Ca^{2+}+Mg^{2+}/SO_4^{2-}$*	*Na^+/Na^++Cl^-*	*$Ca^{2+}/Ca^{2+}+SO_4^{2-}$*
1	Ukawu Village BH1	4.37	8.32	-	2.10	0.81	-	0.89	1.0
2	Nwafor's House, Amata, HW1	19.95	4.41	-	58.73	0.95	-	0.81	1.0
3	School Area, Ukawu, HW2	4.59	16.94	-	3.63	0.82	-	0.94	1.0
4	Opp. Amata Primary School, HW3	1.52	14.57	137.97	0.87	1.52	352.04	1.07	0.99
5	Primary School/ Market Square, Amata, BH2	2.79	8.98	43.03	2.44	0.74	163.07	0.90	0.98
6	Primary School/ Market Square, Amata, BH3	6.74	18	143.5	3.18	0.87	1110.38	0.94	0.99
7	Primary School/ Market Square, Amata, BH4	1.25	28.82	-	2.17	0.55	-	0.96	1.0
8	Mgbom School, BH5	0.67	12.90	332.67	0.68	0.40	554.83	0.93	0.99
9	Ukwu Oji, Umuka BH6	2.80	30.82	8.58	2.51	0.74	32.59	0.97	0.90
10	Ukwu Oji, Umuka BH7	3.81	16.82	7.68	1.91	0.79	36.95	0.94	0.88
11	Umuka Primary School, BH8	0.73	24.61	19.21	1.04	0.42	33.29	0.96	0.95
12	Grace of God Church, Umuka, BH9	1.0 Calcite ppt abs	5.35	25.96	0.31	0.50	51.84	0.84	0.96
13	Okoye's Compound Umuka, HW4	0.86	8.51	-	0.68	0.46	-	0.89	1.0
14	UgwuNwali's Compound HW5	1.190	12.91	149.73	1.78	0.54	328	0.93	0.99
15	Mgbom Village Square BH10	4.64	12.84	199.62	1.83	0.82	1125.37	0.93	1.0
		↓ Dissolution of Ferromagn	Another Source for Na^+	$Ca^{2+}> SO_4^{2-}$ = Gypsum is not the	↓ Carbonate weathering	↓ Dolomite dissolution	Not useful	Sodium source is not from halite - albite	

		esium minerals If TDS < 260.		source of Ca^{2+}					dissolution -ion exchange	

NB: The concentration values in Table 1 were converted from mg/L to meq/L before these ratios were computed.

The Na^+/Cl^- ratio ranges from 4.41 to 30.82. The implication is that the Na^+ ion is not from halites. There is a contribution from albite dissolution or natural softening. The Ca^{2+}/SO_4^{2-} ratio range from nil to 332.67 which means that the source of Ca^{2+} is not only from gypsum but from other sources like carbonates. The ratio which establishes that carbonate weathering is responsible for the release of Ca^{2+} into the waters is the Na^+/Ca^{2+} ratio. It ranges from 0.68 to 58.73. Hounslow (1995) suggests that carbonate weathering is often responsible for low Na^+/Ca^{2+} ratios.

$Mg^{2+}/Ca^{2+} + Mg^{2+}$ ratio is useful in defining dolomite dissolution. Values greater than 0.5 usually indicate dolomite dissolution or calcite precipitation. From table 3, the indicated processes include carbonate weathering, sulphate reduction, dissolution of ferromagnesium minerals and dolomite dissolution. Sources for Na^+ is not from halite which suggests that the brine fields from Okposi is not influencing the ground water composition at Ugwulangwu.

Table 4 shows calculated ratios for Mg^{2+}/Ca^{2+}; Na^+/Cl^-; Ca^{2+}/SO_4^{2-}; Na^+/Ca^{2+} and $Mg^{2+}/Ca^{2+} + Mg^{2+}$. Indicated reactions from these ratios include dolomite dissolution; carbonate weathering and dissolution of ferromagnesiums just like the situation of the boreholes/hand-dug wells. In both the groundwater and surface water samples, it is clear that there are other sources for Na^+ other than the halite and for Ca^{2+} other than from gypsum. Sulphate reduction is indicated by the very low concentration values of SO_4^{2-}.

Table 4: Chemical ratios calculated for the surface waters in the study area (based on Table 3)

S/N	Location	Mg^{2+}/Ca^{2+}	Na^+/Cl^-	Ca^{2+}/SO_4^{2-}	Na^+/Ca^{2+}	$Mg^{2+}/ Ca^{2+} + Mg^{2+}$
1	Onwor Stream, Amata	4.99	4.05	0.77	17.13	0.83
2	Onwor Stream, between Amata &Ukawu	5.95	3.77	0.71	11.26	0.86
3	Amata Stream	54.09	9.12	-	25.71	0.98
4	Mgbom Pond I	2.88	13.88	35	13.99	0.74
5	Mgbom Pond II	9.46	5.90	0.29	25.01	0.90
6	Umuka Stream	0.36	1.88	164	0.73	0.27
7	UgwulangwuStrea at Girls' School	6.58	16.06	0.26	46.22	0.87
8	Isi Nkwo Stream	19.95	14.30	-	131.6	0.95
9	OnuUgwulangwu Stream	35.66	12.06	0.12	34.08	0.97
10	MmiriEziUkawu	3.83	8.91	-	1.70	0.79
		↓Dissolution of Ferromagnesium minerals If TDS < 260.	Another Source for Na^+	$Ca^{2+} > SO_4^{2-}$ = Gypsum is not the source of Ca^{2+}	↓ Carbonate weathering	↓ Dolomite dissolution

NB: The concentration values in Table 3 were converted from mg/L to meq/L before these ratios were computed.

5. Conclusion

The twenty five water samples from boreholes, hand-dug wells and streams of the study area represent the natural water systems in Ugwulangwu. The pH values indicate mildly acidic to mildly alkaline environment. Low solute concentrations is due to low residence time for the waters. The results of the chemical analyses were combined with the analysis of various chemical ratios to reveal the nature of geochemical processes responsible for the general water chemistry. Indicated reactions include carbonate weathering, dissolution of dolomites and ferromagnesian minerals and sulphate reduction. High values of manganese indicate the presence of magnesium carbonates being oxidised to manganese oxides such as pyrolusite. More geochemical data would need to be assembled in order to assess the carbonate processes occurring within the aquifer.

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