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Hydrogeochemical Assessment of Groundwater Quality and Geological Influence in Igarra and environs, Southwestern Nigeria

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ABSTRACT The impact of Geology on groundwater is not fully appreciated in many Nigerian groundwater quality literature. This study investigates the influence of Geology on the hydrogeochemical makeup of groundwater in Igarra and environs, Nigeria. Igarra and environs is underlain by metasediments intruded by Pan African Granites. Ten water samples were collected and analyzed in the laboratory to determine their chemical composition. The results revealed that the pH of most samples was slightly acidic to mainly alkaline, with high electrical conductivity (EC) and total dissolved solids (TDS) values. Correlation and regression analyses showed that the TDS, EC, salinity, chemical oxygen demand, dissolved oxygen, and major and minor constituents positively influenced the pH of the groundwater. Hierarchical cluster analysis demonstrated that the water samples had different compositions and concentrations based on local geological influences. The water samples from Granite, Quartzites, Migmatites and Gneiss rock types shared similar characteristics and had a lower concentration of minerals than the water samples taken from the Quartz Mica Schists and Metaconglomerates. The water in Igarra was predominantly Magnesium Bicarbonate type. However, some of the water samples exceeded the drinking standards for TDS, EC, Cl, Fe, Cr, Cd, and Pb. The study recommends the inclusion of biological parameters to gain a clearer picture of the water quality, particularly from the anthropogenic point of view.

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Nigeria has an enormous quantity of groundwater contained in both Basement and Sedimentary aquifers. Akujieze *et* al., (2003) estimated the total amount of groundwater resources to be 50 million trillion litres/year, although revised to 43 million trillion litres by Kazemi, (2004). Groundwater plays a crucial role in the social and economic life of Nigerians, in terms of its utility for domestic, industrial and agricultural purposes, (Edet *et al.*, 2011). The rocks making up an aquifer will impart a chemical signature to the water, in the form of a specific set of dissolved ions. This is useful to us because we can use the groundwater chemistry to infer where the water is coming from and to link the groundwater to specific geologic units (Uliana, 2012). The chemistry of groundwater is due to several processes such as, soil/rock interaction during recharge and groundwater flow, prolonged storage (residency) in the aquifer, dissolution of mineral species and anthropogenic inputs (Hem, 1985; Sekabira *et al.*, 2010). The focus of previous research on groundwater chemistry and quality has primarily been on comparing analytical data against established national and international standards for drinking, domestic, and agricultural purposes. In this approach, the geological factors affecting water quality have been given less attention (Edet *et al.*, 2011). However, this current study takes a different approach by examining how Geology impacts the chemistry and quality of groundwater.

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MATERIAL AND METHODS

The study area is located between Longitude 6°3'30" and 6°8'0" and Latitude 7°14'50" and 7°22'5" with an area of about 85.68km² (Fig. 1). The major towns in the study area include Igarra, Aiyetoro, Semorika, Ayegunle, Ugboshi Ele and Enwan. The study area can be accessed by Igarra-Auchi road as the major road which connects towns like Auchi, Ibillo, Igarra, Ayegunle to each other. There are also several other minor roads that sprout from the major road like the Okpe road. The study area also has several well utilized paths that serve the local people as means of accessing their farms and these paths greatly aid in increasing the accessibility of the study area. The climatic condition of the study area is tropical and favours rock weathering and soil formation. There are two major seasons: wet and dry seasons. The wet season starts in March and persists till October during which rainfall is low to medium. The dry season starts in November and ends in March. Temperature ranges from 25°C during the brief harmattan period to about 35°C at the peak of the dry season (Obiadi et al., 2012). The vegetation falls within the guinea savannah grassland with lush vegetation of tall trees, shrubs and grasses. The vegetal distribution reflects the underlying geology with the schist area of the study area being heavily forested while the Granite area is sparsely forested. The surface of the study area is entirely drained by several networking surface streams (Fig.1). The drainage pattern is sub-angular. Streams and rivers are structurally controlled since they take advantage of the fractures of the basement rocks. The streams are generally shallow (less than 2m deep) and in places flow on the bedrock, therefore the underlying Geology is usually exposed by the streams.

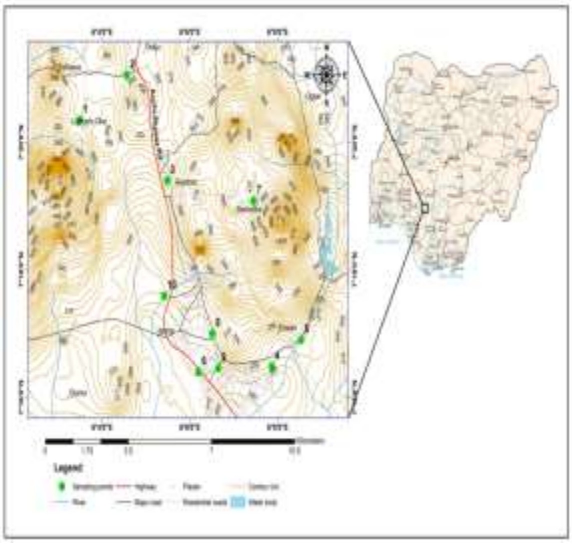


Fig 1: *Topographic map of Igarra and environs showing sample points*.

Local Geology: Igarra falls within the Igarra schist belt, which is part of the Southwestern Nigerian Basement Complex rocks and can be classified into four main lithologies (Oyawoye, 1972), namely: The Migmatite Complex; the Metasediment series, Miscellaneous rock types and the Older Granites (Fig. 2).

The contacts between the Metasediments are fault bound in most areas and this has made it difficult to identify the basal unconformities, however, in the western flank of the area, the Metasediments gently overlie the underlying Gneisses (Odeyemi, 1976).

Using fracture analysis, Akperi *et al.*, (2015) found out that the metasedimentary rocks in Igarra have undergone at least three phases of deformation while the Older Granite which intruded the Metasedimentary rocks have experienced a single phase of deformation history which is represented on the rocks as a dominant East - West fracture trend which conforms well with the major East-West compression of the Pan African Orogeny that led to the syn-tectonic emplacement of the Older Granites of the Nigerian Basement Complex (Oden *et al.*, 2012; Oden, 2014).

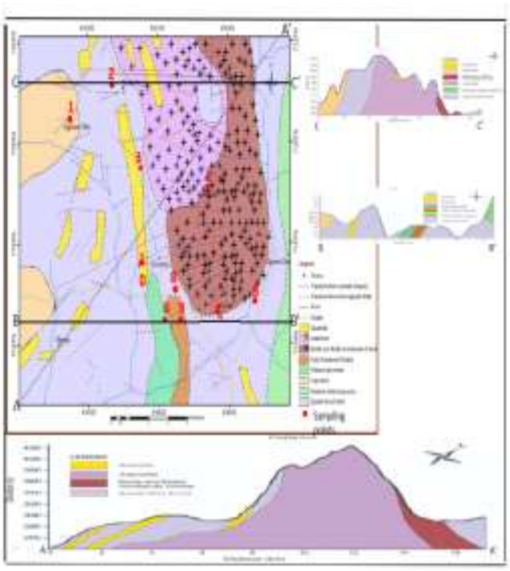


Fig 2: Geologic map and cross section of Igarra and environs showing sample points.

The study area was partially mapped using a Global Positioning System (GPS) device. This was used to determine the longitude and latitude as well as the elevation of the locations of the boreholes and other places of interest for the map production. Eight (8) groundwater samples (boreholes and wells) and two (2) surface water samples were selected for geochemical analysis. The samples were collected in 1.5 L high-density, cleaned polythene containers, 300mL BOD and 300mL DO bottles and rinsed 3–4 times before sampling using the water to be sampled. Collected samples were stored in a cool environment before being transported to the laboratory for analysis in less than twenty four hours after collection.

Plate 1: Groundwater sample collection at Igarra

Plate 2: Surface water sample collection at Igarra.

Laboratory results which included: physical parameters (Electrical Conductivity, Total Dissolved Solids, Salinity, Chemical Oxygen Demand, Biochemical Oxygen Demand, Dissolved Oxygen and pH); basic cations (Calcium and Magnesium, Sodium and Potassium) and anions (Chloride, Bicarbonate, Sulphate and Nitrate) alongside Phosphorus, Nitrate, Nitrite, Ammonium, Iron, Manganese, Zinc, Copper, Chromium, Cadmium, Nickel, Lead and Vanadium were subjected to descriptive and graphical statistical analysis using Microsoft Excel package, SPSS software, Piper and Durov components of GW_Chart software (mean, median, minimum and maximum values, standard deviation, correlation analysis, regression analysis, piecharts, histograms, radar plots, piper plots, hierarchical cluster analysis dendograms). The results were also compared against the WHO standards and Nigerian standards to ascertain the suitability of the water for domestic uses.

RESULTS AND DISCUSSION

Table 1 presents the statistical summary of the surface and groundwater physic-chemical parameters from Igarra. It is observed that the pH of both the surface water and groundwater samples in Igarra and environs are slightly acidic to alkaline (Table 1), with pH ranges of 6.7 - 8.4 and 6.5 - 8.3 and median values of 7.55 and 7.5 respectively and this is similar to what Isewede et al., (2020) found in Igarra but different from the findings of Lawani and Dirisu (2019), who had water samples with acidic trends and this might have been because their samples were taken from contaminated sources.

The standard deviations show that there is a considerable variance in the pH of the water samples from Igarra and environs and this variance in pH is interpreted to be as a result of the inhomogeneity of the rock types (Migmatites, Schistose Quartzite, Granite, Quartz Mica Schists, Metaconglomerates). The Electrical Conductivity (EC), Salinity, Total Dissolved Solids (TDS) and Hardness values of the water samples (surface water and groundwater) from Igarra range from 368-5570 µmhos/cm, 0.166-2.52 g/L, 184-2780 mg/L, and 17.776 - 132.99 mg/L respectively.

The dissolution of minerals from the Basement rocks is interpreted to have led to the higher amount of dissolved constituents in the water samples. The standard deviation values also show here that there is a high variance of the EC, Salinity, TDS and Hardness values in Igarra and environs due to the inhomogeneity of the rock types. The Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) values for both surface water and groundwater samples are observed to be similar but the groundwater samples have higher COD values. As noted for the other parameters discussed above the standard deviation values suggest inhomogeneity in Igarra and environs.

The values of the Major, Minor, and Trace ions have a high variance from one rock type to another, further buttressing the point that the water chemistry is influenced by the Geology.

Table 1: Statistical Summary of the Surface and Groundwater Physico-chemical Parameters in Igarra.

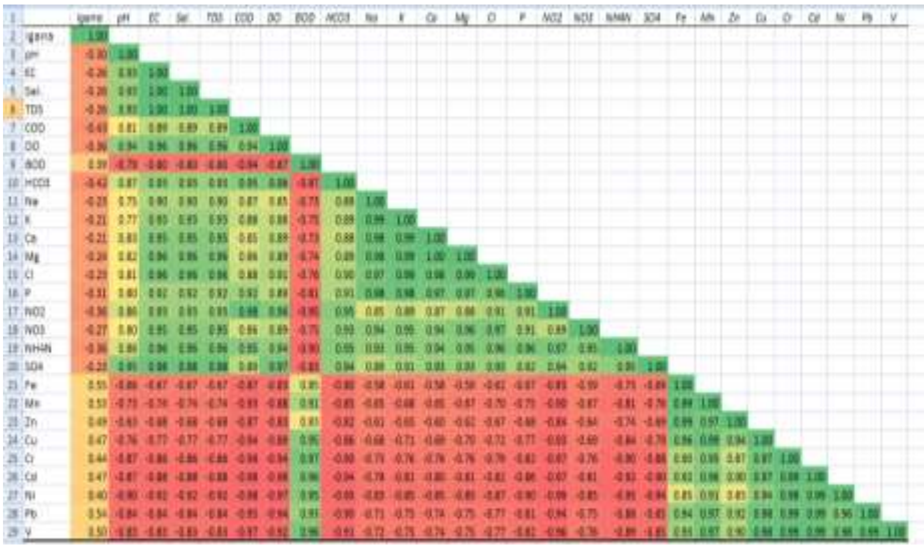
		Surface water (n = 2)					**Groundwater (n = 8)**				
Parameters	**Unit**	**Mean**	**Median**	**Min**	**Max**	**Std Dev**	**Mean**	**Median**	**Min**	**Max**	**Std Dev**
pH		7.55	7.55	6.7	8.4	1.202082	7.4625	7.5	6.5	8.3	0.825
EC	**µmhos/cm**	2969	2969	368	5570	3678.369	2051.89	1485.5	517.4	3940	1567.162
Sal.	**g/L**	1.343	1.343	0.166	2.52	1.664529	0.92813	0.672	0.234	1.782	0.709
TDS	**mg/L**	1482	1482	184	2780	1835.649	1025.45	742.6	258	1970	782.605
Hardness	**mg/L**	76.46	76.46	19.93	132.99	79.94478	42.067	34.993	17.776	71.756	22.26102
COD	**mg/L**	31.6	31.6	12	51.2	27.71859	32.4	33.6	19.2	44.8	7.850
DO	**mg/L**	3.35	3.35	1.2	5.5	3.040559	3.425	3.25	2.3	4.8	1.106
BOD	**mg/L**	1.45	1.45	0.4	2.5	1.484924	1.1875	1	0.4	2.2	0.636
HCO_3	**mg/L**	268.4	268.4	140.3	396.5	181.1608	263	252.9	201.3	390.4	65.613
Na	**mg/L**	3.315	3.315	0.51	6.12	3.966869	1.555	1.405	0.63	3.28	0.917
K	**mg/L**	1.755	1.755	0.18	3.33	2.227386	0.86	0.745	0.27	1.72	0.541
Ca	**mg/L**	13.39	13.39	4.3	22.48	12.8552	7.64875	6.855	3.65	12.04	3.566
Mg	**mg/L**	10.485	10.485	2.24	18.73	11.66019	5.59625	4.355	2.11	10.16	3.270
Cl	**mg/L**	256.4	256.4	35.5	477.3	312.3998	143.875	97.5	53.2	277.3	94.752
P	**mg/L**	0.1645	0.1645	0.054	0.275	0.156271	0.11338	0.122	0.061	0.166	0.037
NO_2	**mg/L**	0.054	0.054	0.027	0.081	0.038184	0.05438	0.054	0.033	0.074	0.014
NO_3	**mg/L**	2.033	2.033	0.053	4.013	2.800143	1.00538	0.3355	0.151	3.221	1.151
NH4N	**mg/L**	0.4155	0.4155	0.251	0.58	0.232638	0.36725	0.3575	0.263	0.491	0.081
SO_4	**mg/L**	0.328	0.328	0.046	0.61	0.398808	0.24263	0.2225	0.053	0.472	0.184
Fe	**mg/L**	0.3075	0.3075	0.082	0.533	0.318905	0.15988	0.146	0.084	0.234	0.056
Mn	**mg/L**	0.0715	0.0715	0.029	0.114	0.060104	0.049	0.046	0.031	0.071	0.014
Zn	**mg/L**	0.168	0.168	0.062	0.274	0.149907	0.10613	0.112	0.063	0.133	0.025
Cu	**mg/L**	0.0535	0.0535	0.02	0.087	0.047376	0.03825	0.035	0.025	0.061	0.013
Cr	**mg/L**	0.036	0.036	0.011	0.061	0.035355	0.02775	0.0245	0.013	0.05	0.014
Cd	**mg/L**	0.018	0.018	0.003	0.033	0.021213	0.014	0.013	0.005	0.024	0.007
Ni	**mg/L**	0.011	0.011	0.002	0.02	0.012728	0.01025	0.0095	0.004	0.018	0.005
Pb	**mg/L**	0.0275	0.0275	0.007	0.048	0.028991	0.01913	0.017	0.009	0.032	0.009
V	**mg/L**	0.008	0.008	0.001	0.015	0.009899	0.00538	0.0045	0.001	0.011	0.003

Table 2 shows a strong positive relationship in Igarra and environs between the pH and Electrical Conductivity (EC), Salinity, Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), and the Major and Minor ions but it shows a moderate to strong negative relationship with the Biochemical Oxygen Demand (BOD) and the Heavy metals (Iron, Manganese, Zinc, Copper, Chromium, Cadmium, Nickel, Lead, and Vanadium).

A strong positive relationship also exists between the BOD and Heavy metals. We can postulate from this that the parameters that have a strong positive relationship with the pH influence it strongly and are also influenced by it; this would mean for example, that the higher the concentration of Magnesium (which has a correlation coefficient of 0.82), the higher would be the pH and vice versa but this does not apply to the BOD and heavy metals, which have their own relationship (a strong positive relationship with themselves but a moderate to strong negative relationship with the pH and parameters that have a positive relationship with the pH); we can observe from their relationship, that the higher the BOD, the higher the concentration of Heavy metals and vice versa. Heavy metals are important for the growth of organisms in water and the absence of sufficient quantities of them could limit their growth (Mittal and Ratra, 1999), therefore it is understandable that they have a strong positive relationship. Due to the moderate to strong negative relationship between the Heavy metals and the other parameters (except for BOD), it can be postulated that they are from different sources. Based on the piper and radar plots (Fig. 4, 5, 6, & 7), the water samples from Igarra and environs are dominated by Magnesium Bicarbonate type, but range from Magnesium Bicarbonate type to Calcium Chloride type depending on the rock type the water has interacted with (Fasunwon *et al.*, 2010; Edet *et al.*, 2011; Obiefuna and Orazulike, 2011; Danhalilu *et al.*, 2018; Nwankwo*et al.*, 2020). The Calcium Chloride types are generally found in or close to the Quartz Mica Schist rocks, while the Magnesium Bicarbonate type are generally found in the other rocks such as Migmatite, Schistose Quartzite, Metaconglomerates and Calc Gneiss and Marble.

A positive relationship is observed between the pH and Magnesium concentration, with an R^2 value of 0.8697 (Fig. 3), indicating that, the Magnesium concentration influences the pH by about 87% and this relationship is similar for the other major and minor ions, but it is not the case for the Heavy metals; the scatter plot of pH against Zinc values (right) shows that there is a negative relationship between the pH and Zinc values with an R^2 value of 0.6597, which suggests that the higher the heavy metals, the lower the pH.

Table 2: Correlation Analysis of the Physicochemical Parameters of Water Samples (surface water and groundwater) from Igarra and environs.



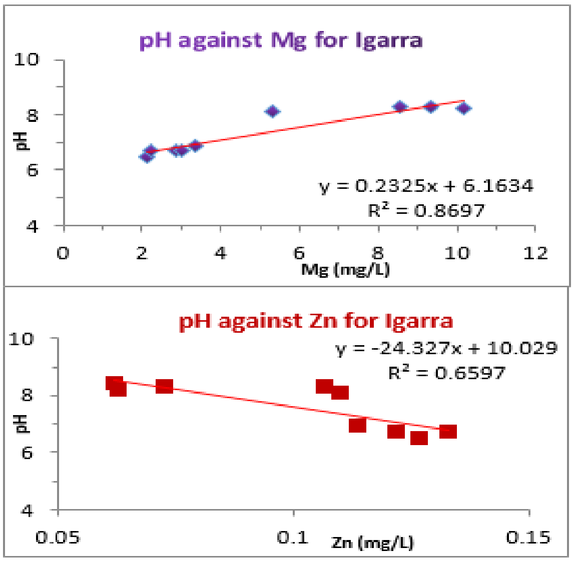


Fig 3: Scatter plot of pH against Magnesium values (left) and Zinc values (right) for Igarraand environs.

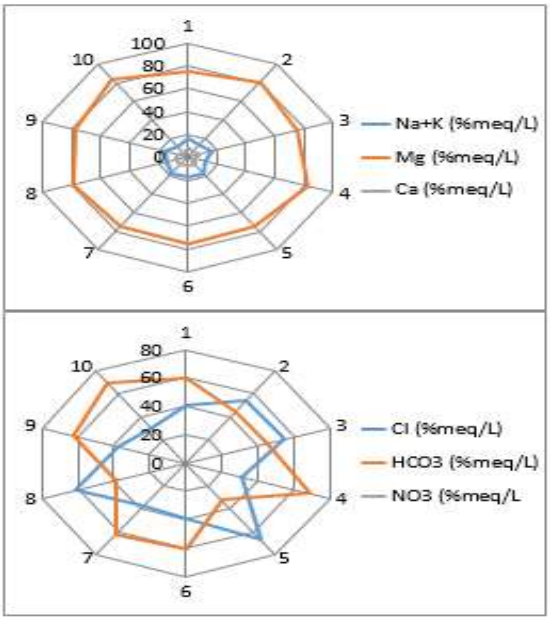


Fig 4: Radar diagram of Cation (left) and Anion (right) variation in Igarra and environs (% meq/L)

The concentration of the ions in the water is stronger in the Quartz Mica Schist rocks (Fig. 5 & 7). It should be noted that the Quartz Mica Schists are metasediments, thus, they were once sediments rich in Shales, which were deposited in a marine environment and would therefore be richer in Chloride ion, when compared with the other rock types such as the Schistose Quartzite or Metaconglomerates, which would have been metamorphosed from sediments closer to the coastline or on land (Sandstone and Conglomerates). The Quartz Mica Schists are also observed to be friable and highly weathered (Megwara and Egesi, 2017), thus they would impact the water chemistry more than the other more resistant rock types.

The water sample five (5) is interpreted to have an especially high concentration of ions compared with the other water samples because it was collected from the Onyami River which flowed almost exclusively on Quartz Mica Schist rocks before the location of sample five (5) and is dammed at Ojirami (Fig. 1, 2, 4 & 5). The implication of this is that the river has been able to dissolve ions over its course through the highly weathered Quartz Mica Schist rocks. In addition to this factor, the samples were collected at the end of the dry season, when river discharge was low due to low recharge from precipitation and this further increased the concentration of the ions in sample five (5), therefore demonstrating the influence of Geology on water chemistry. The cluster plot (Fig. 7) shows that the water samples taken from Granite, Quartzites, Migmatitites and Gneiss rock types have similar chemical characteristic, while all the samples taken from Quartz Mica Schists share similar chemical characteristics with themselves and the water samples from the Metaconglomerates at a higher level. Although the chemical characteristics of Igarra sample five (5) (which was a water sample taken along the Onyami River which flowed on Quartz Mica Schist) are similar to the other Quartz Mica Schist rocks. It also exhibits a marked difference with other water samples taken from Quartz Mica Schist rocks which could be due to the higher concentration of the ions as discussed above. The values of Electrical Conductivity (EC) and Total Dissolved Solid (TDS) for Igarra samples 2, 3, 5, 6 and 8 all exceed established drinking water standards (Table 3), with most of these implicated samples taken from water in or close to Quartz Mica Schist rocks; since the Schists are inferred to be formed from marine sediments (Shales), they would have had clay minerals which usually have high CEC and it is expected that the higher the CEC, the higher the Electrical Conductivity (Henry, 1997), thus the high Electrical Conductivity. The ability of the Quartz Mica Schists to be easily broken down might be the cause of the high TDS. Although EC and TDS have no significant health impacts, they might be tell-tale signs that some other ions in the water that might have health impacts might be in excess.

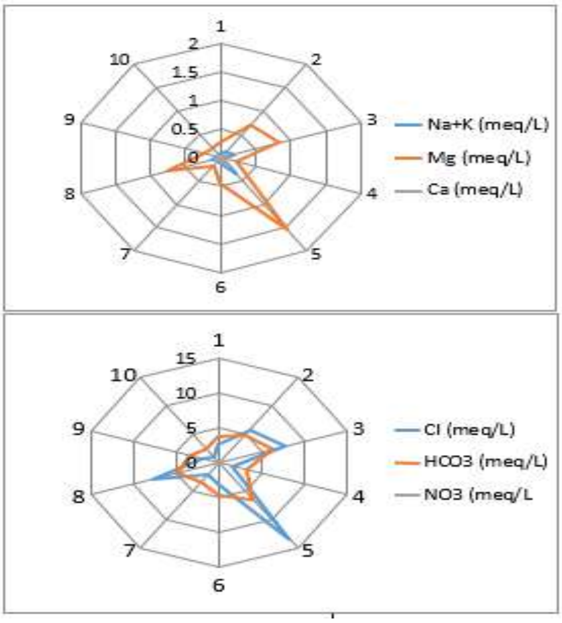


Fig 5: Radar diagram of Cation (left) and Anion (right) variation in Igarra and environs (meq/L).

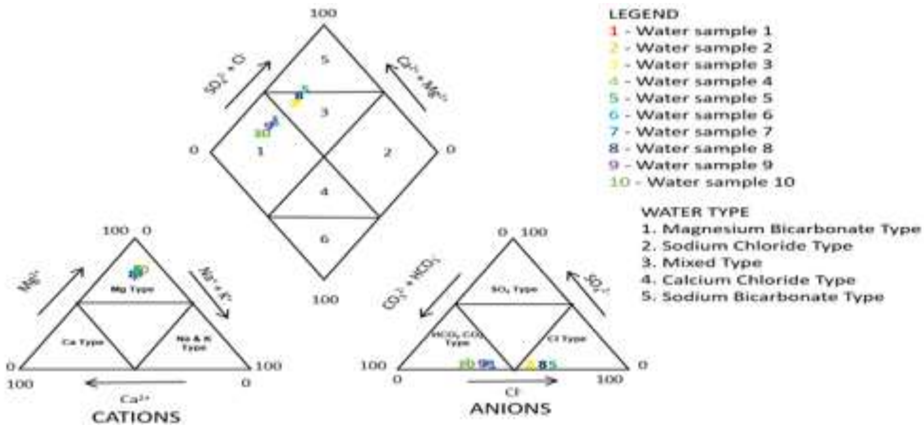


Fig 6: Piper diagram of Water samples (surface water and groundwater) from Igarra and environs (Adapted from Piper, 1944).

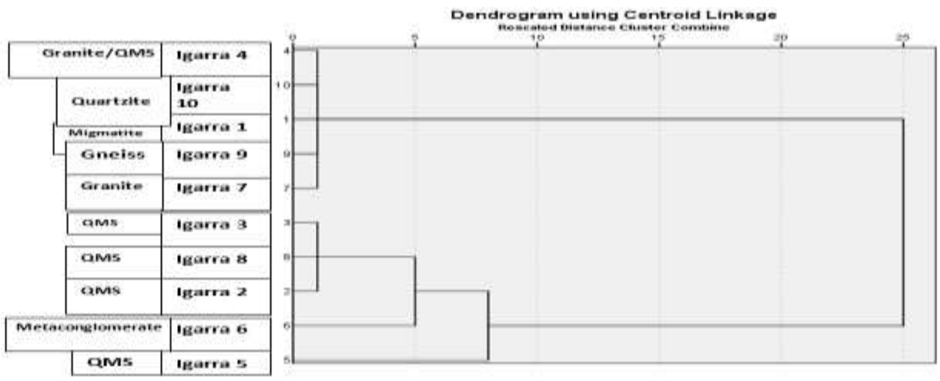


Fig 7: Hierarchical cluster analysis for data from Igarra and environs.

The Chloride concentration also exceeds established drinking water standards in samples 3, 5 and 8; these were also the samples with the highest EC and TDS values but Chloride concentrations have no health impact, although high Chloride concentrations give a salty taste to water (WHO, 2017; NIS, 2015). Sample 10 (Plate 2), which was a stagnant pool of water from an almost dried out stream (samples were taken at the end of the dry season in April), had values of Iron, Chromium, Cadmium and Lead exceeding established drinking water standards. Although Iron has no health impact, it can give an objectionable reddish-brown coloration to the water and also promotes the growth of 'iron bacteria' which deposits a slimy coating on piping. Chromium in high concentrations can cause cancer, while high concentrations of cadmium are toxic to the kidney and high concentrations of Lead can cause cancer. As it also interferes with vitamin D metabolism, it affects mental development in infants, and is toxic to the central and peripheral nervous systems. Therefore, Igarra sample 10 is unfit for drinking. Igarra samples 1, 2, 4, 6, 7, and 9 also have values of Lead that exceed drinking water standards, but these are much lower than in sample 10 and can be treated.

Table 3: Pollution index: Ratio of the hydrogeochemical parameters that exceed the standards to the standards (WHO, 2017; NIS, 2015).

	1	2	3	4	5	6	7	8	9	10
EC	0.79	3.64	3.94	0.52	5.57	2.18	0.65	3.93	0.77	0.37
TDS	0.79	3.64	3.94	0.52	5.56	2.18	0.65	3.92	0.77	0.37
Cl	0.35	0.83	1.11	0.21	1.91	0.43	0.28	1.11	0.28	0.14
Fe	0.52	0.46	0.28	0.78	0.27	0.45	0.77	0.35	0.67	1.78
Cr	0.56	0.36	0.26	1.00	0.22	0.42	0.86	0.30	0.68	1.22
Cd	0.50	0.30	0.17	0.80	0.10	0.37	0.73	0.27	0.60	1.10
Pb	1.80	1.10	0.90	3.20	0.70	1.60	3.00	1.00	2.70	4.80

Table 4: Suitability of water for irrigation comparison (Ayers and Westcot 1985; Wilcox 1948)

Class	TDS (mg/L)	RSC (mg/L)	SAR	SSP (%)	Sustainability for irrigation
I	<117.51	<1.25	<10	<20	Excellent
II	117.51–508.61	1.25–2.5	10–18	20–40	Good
III	>503.61	>2.5	18–26	40–80	Fair
IV	–	–	>26	>80	Poor

Igarra	1	2	3	4	5	6	7	8	9	10	Avg
TDS	395	1820	1970	258	2780	1090	327	1960	383	184	1117
RSC	3.38	4.04	5.48	3.05	4.79	4.12	3.21	4.05	3.13	2.11	3.74
SAR	0.12	0.14	0.21	0.08	0.29	0.15	0.10	0.15	0.10	0.07	0.15
SSP	16.77	12.78	16.84	12.08	17.07	16.91	17.41	13.83	15.25	12.17	15.60

There is a significant concentration of Lead in the southwestern Basement Complex rocks of which Igarra is a part of (Lapworth et al., 2012) and this is the possible reason for the high Lead values in these samples. Most of the water samples are poor for irrigation use (Table 4), apart from sample 10. Based on the physicochemical parameters, it can be postulated that the water samples in Igarra are moderately clean and can be fit for drinking except sample 10 which is unfit for drinking but fit for irrigation use, and this is similar to Isewede et al., (2020) but Lawani and Dirisu (2020) posited that the water samples they analyzed in Igarra and environs were unfit for human consumption but sample 10 is the only sample fit for irrigation use. Biological testing which is not part of the scope of this work can be done to gain a clearer picture of the water quality.

*Conclusion***:** The Geology of an area impacts the quality and chemistry of its groundwater. In Igarra, the water's alkaline nature is due to reactions between dissolved rock constituents and slightly acidic rainwater. The water is dominated by Magnesium Bicarbonate type, with Calcium Chloride types found in or near Quartz Mica Schist rocks. Water quality in Igarra is generally moderate for domestic use, but poor for irrigation and requires treatment.

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