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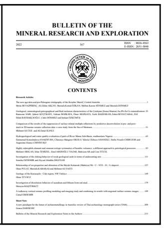

Hydrogeological and water quality evaluation of parts of River Mamu Sub-Basin, southeastern Nigeria

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ABSTRACT

The water sources in parts of the River Mamu sub-Basin, southeastern Nigeria were evaluated for domestic and agricultural purposes using hydrogeology and water quality. Thirty water samples from both surface water and groundwater were analysed for hydrochemical and biological parameters. The average depth to aquifers and their thicknesses are 109.9m and 11.8m respectively. The concentration of the major ions, TDS and EC are within the DSÖ permissible guidelines for drinking water. Heavy metals concentration ranges in mg/L for Cd^{2+} (0 - 0.06), Cr^{3+} (0 - 0.19), Hg^{2+} (0 -1.0), As^{3+} (0 - 0.14) and total Fe (0 - 2.4) which in some of the samples exceed the permissible guideline values. The fecal coliform range in 100ml/L of samples (0 - 36) exceeds the guideline values in some of the samples. The water is Ca-Mg-Cl-SO$_4$ type with the dominant ions as Ca^{2+} and SO$_4^{2-}$ for both groundwater and surface water. The dominant geochemical processes are rock-water interaction in the groundwater, which is a major contributor of dissolved ions and precipitation in the surface water. The WQI (17.84 - 301.99) connotes some samples as very poor quality for domestic purposes. Irrigation indices depict most of the water as good to excellent for agriculture.

1. Introduction

Water is vital to the existence and substance of life. The quality and quantity constitute major factors in the supply of water for drinking, domestic, agricultural, and other important activities. Rivers are vital resources as sources of water supply; the study area the River Mamu Sub-Basin is heavily dependent on the rivers for water supply. The surface water bodies are used for drinking, domestic and agricultural activities and the populace rely on natural resources as their major source of livelihood. According to Amadi et al. (2016), the groundwater is being an alternative to the surface water has been highly exploited for human, industrial and agricultural purposes across the world including the study area, in order to meet the persistent increase in water demand. The water is essential for both natural and anthropogenic activities and it is the engine of most lives on earth, thus, it is necessary to mitigate activities that degrade water in order to improve the quality (Ashun and Bansah, 2017). Agriculture is the major occupation of the people in the study area and it is heavily dependent on the availability of the water. It is also the main source of employment for the majority of Nigerians (Odetola and Etumnu, 2013; Pavelic et al, 2012). Thus, the need for potable water and water for agriculture is of paramount importance.

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Environmental pollution is one of the largest threats facing Nigeria and other parts of the world today. It occurs in several ways and affects many spheres of the environment most importantly the water sources. The deterioration of surface water and groundwater qualities has been attributed to both natural processes and anthropogenic activities (Yan et al., 2015, Okolo et al., 2018, Udoh et al., 2021). These dissolved constituents in water may affect soil fertility. Part of the River Mamu Sub-Basin studied is metamorphosing into an urban area since the creation of the Anambra State. The study area consists of the new satellite towns that sprang up as a result of the rapid increase in population, industrialization, and urbanization of the nearby Awka, the capital city of Anambra State. This has increased the demand for water resources. More so, rapid economic development and urbanization in many countries of the world have resulted in water pollution and degradation of the aquatic ecosystem which in turn has caused massive damage to the function and integrity of water sources (Song et al., 2011).

In the last few years, water sources especially surface water has been under serious threat due to increased human activities. These activities concentrate more in the upstream of the River Mamu catchment area and include slump settlements beside the River Mamu at Amansea/Ugwuoba area, with associated poor hygiene and sanitation with the river serving for bathing and waste disposal. Cattle and goat markets with abattoirs are also situated in the wetland of Amansea area, which serves as a source of recharge in the hydrologic system. There has been adequate water supply to the area in view of the annual rainfall amount (1750 - 2050 mm) as noted by Ayogu et al., 2020. However, they observed a decrease in rainfall amount for some of the years in the past 50 years. The decline could be attributed to climatic changes. The danger is that no measures (dams) are in place to store the excess water and runoff. This may result in water scarcity in the future.

In view of the above, it is essential to evaluate the quality of water sources as a prelude to developing environmental strategies for future proper management of water resources in the area. The present study therefore will identify the major aquifers and examine the various physio-chemical and bacteriological characteristics of the major water sources in parts of the River Mamu Sub-Basin concerning drinking, domestic and irrigational purposes based on existing local and international guidelines, in addition to the hydrogeochemical process responsible for the contribution of the ionic species.

1.1. Geographical Setting

River Mamu is one of the major watersheds in south-eastern Nigeria and together with its numerous tributaries become a major tributary to the Anambra River. The river maintains the natural border between Anambra and Enugu States and the Sub-basin area of the Mamu River is shared between riparian states of Anambra (84%) and Enugu (16%). The study area is located between latitudes 6^{o} 14’ 0” and 6^{o} 26’ 0” N and longitudes 6^{o} 57’ 30” and 7^{o} 10’ 0” E (Figure 1). It covers an area of about 373 km^2 and is majorly drained by the River Mamu and its tributaries. The Mamu River serves as a sink for wastewater from agriculture and runoff in the sub-basin.

The area is generally low lying with elevation ranging from 32 - 102 meters. There are two main climatic seasons, namely the rainy and dry seasons. The rainy season starts from April to October with peaks in July and August and a break of one week in August known as the August break. In the months of September and October, the intensity of rain increases with the number of rainy days decreasing. In these months, the rain is accompanied by lightning and thunderstorms.

The dry season has little or no rain. The month of January is very dry and cold in the mornings, nights and very hot in the afternoons. The major occupation of the people in the study is subsistent farming, fishing, and trading except for the population that works in the government offices in the nearby state capital. The Mamu River has many tributaries with a drainage pattern that is considered to be dendritic (Figure 1), underscoring the uniformity of the underlying lithology—mostly shale, which supports tall trees and bushes descriptive of a rain forest.

1.2. Geological Setting

The study area is underlain by the Palaeocene Imo Formation and the Ebenebe sandstone member which is overlain by the Eocene Nanka Formation (Figure 1). The Imo Formation is the basal unit of

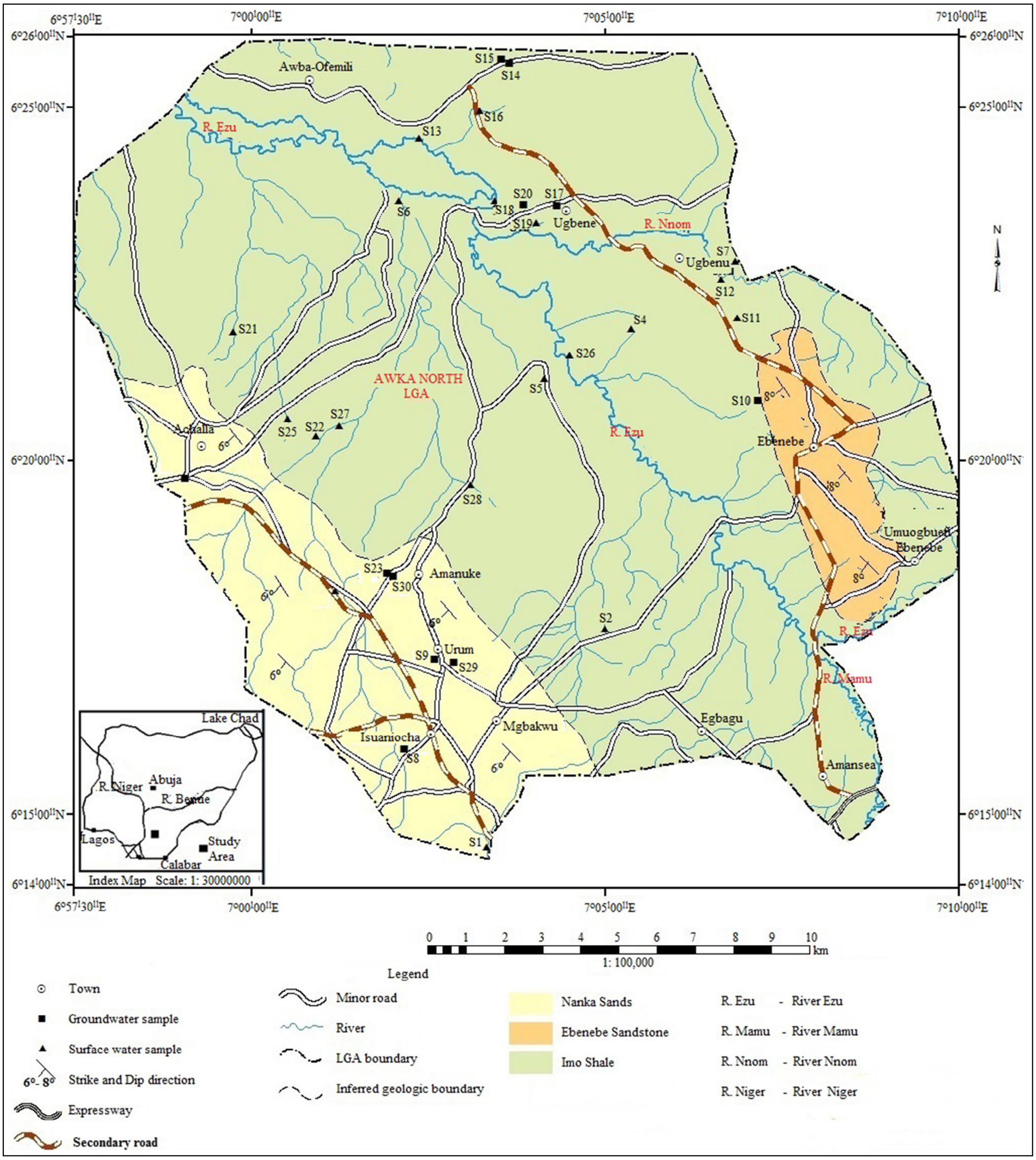


Figure 1- The location and geologic map of the study area.

the Niger Delta Basin (Nwajide, 1980; Whiteman, 1982; Nwajide, 2013). A formation is essentially a mudrock unit consisting of dark grey to bluish-grey shale, with occasional admixtures of clay, ironstone, thin sandstone bands, and limestone intercalations. The Ebenebe Sandstone Member is fine-grained, flat-bedded, and thickening upwards. At Ebenebe town, the outcrop exposure is about 25 meters high and dips northwest. It is composed of quartzose sand with little or no feldspar. The Nanka Formation overlies the Imo Formation in the southwestern part of the study area. The formation has an upper unit, which is composed of loose sand with fine to medium grains and mudrocks. The lower subunit consists of well-sorted, clayey, fine-grained, unconsolidated sandstone, with very thin claystone towards the top.

2. Materials and Methods

Field studies, included identification of various aquiferous units and collection of water samples, were carried out during the wet season (April - July 2018). Thirty water samples comprising surface water (18) and groundwater (12) were collected from different points (Figure 2). The samples were collected with prewashed plastic bottles, which were rinsed severally with the samples to be collected at the point of collection. The samples were collected in duplicate at each point and labelled A and B. The samples labelled A were filled in the field with Whiteman filter paper, preserved with a few drops of nitric acid, and were used for the analysis of cations. The samples were transported to the laboratory on ice and stored in a refrigerator until analysis. The water samples were analyzed according to APHA (2005) standard methods at Springboard Laboratory in Awka, Anambra State, Nigeria.

AAS (Varian AA 240) was used for the analysis of cations, titration methods were used to analyse some anions, and the membrane filter method was used to analyze the biological parameters. The pH and turbidity were tested in the field with the Hanna pH/turbidity meter. The pH/turbidity meter was calibrated daily before going to the field. The pH meter was calibrated with pH standards. A three-point calibration was conducted using buffered standards of pH 4.00, pH 7.00, and pH 9.00 according to the manufacturer's manual. The reagents used for the analysis of physico-chemical parameters were AR grade, and double-distilled water was used for the preparation of solutions. The Na^+, Mg^{2+}, Ca^{2+}, and K^+ Agilent AAS detection limit was 0.001ug/ml, Fe detection limit was 0.003ug/ml, and Hg^{2+}, Cr^{2+}, As^{3+} and Cd^{2+} detection limit was 0.0002ug/ml. For nitrate and sulphate, UV-VIS spect detection limit was 0.01mg/l. The analytical precision for the measurements of the major ions was determined by calculating the ionic balance error that was observed to be within the acceptable range of 5 - 10%. The hydrochemical analysis result was subjected to interpretation using different graphical methods, ionic ratios, and water quality and irrigation indices to determine the usefulness of water sources for domestic, drinking, and agricultural purposes.

Furthermore, the weighted arithmetic was used to calculate the water quality index (WQI). All the

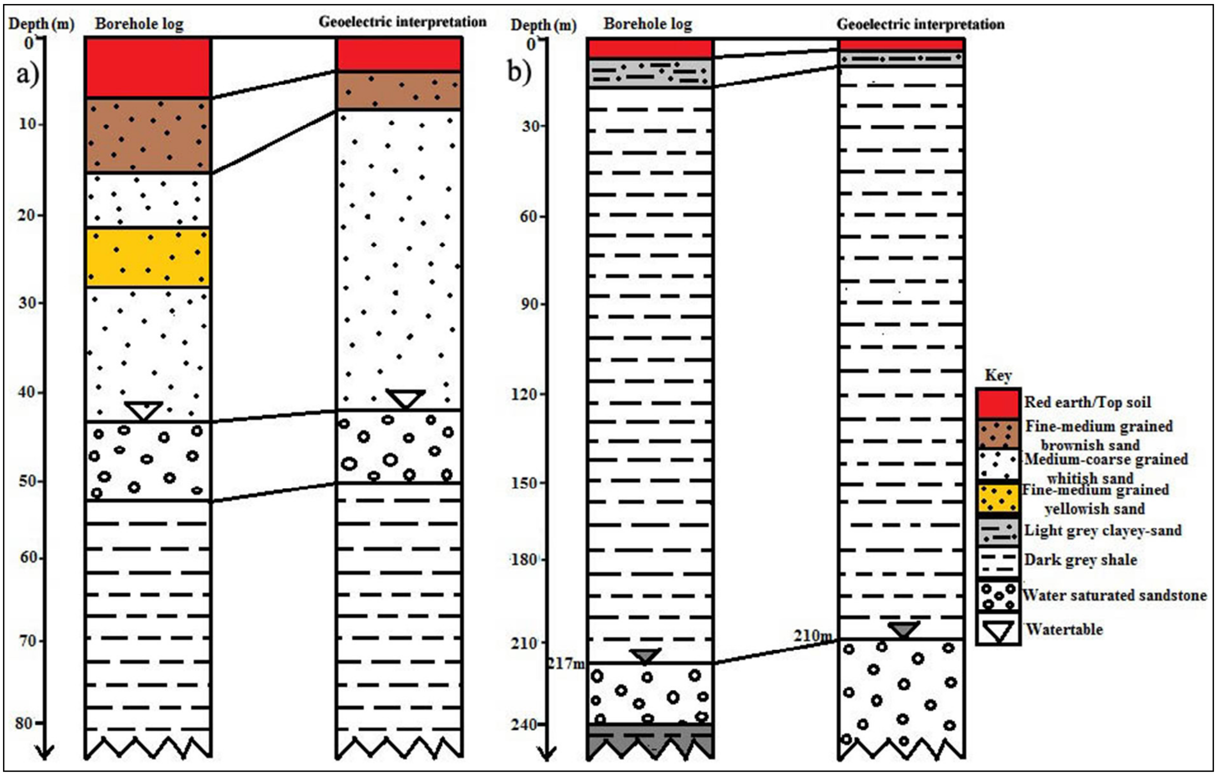


Figure 2- The correlation between the borehole log and geoelectric section in the area; a) Achalla area, and b) Ebenebe /Amansea area.

parameters used in the calculation were assigned a weight (w_i) according to its relative importance in the overall quality of water for drinking purposes (Srinivasamoorthy et al., 2008) as displayed in Table 1. The relative weight (W_i) was obtained from Equation 1. The weighted arithmetic was used to calculate the water quality index (WQI). The chemical parameters used for the calculation of WQI include; pH, Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^-, Cl^-, TDS, NO_3^-, SO_4^{2-} and Fecal Coliform. The relative weight (W_i) was obtained by dividing individual weight (w_i) by the total weight (w_t) as shown in Equation 1 (Horton, 1965).

$$W_i = w_i / w_t \qquad (1)$$

Where w_i is the weight assigned to the individual water quality parameter, w_t is the total weight of the individual parameters.

The quality rating scale q_i is obtained from the concentration (C_i) of the individual parameters in each water sample divided by guideline value (S_i) for each parameter multiplied by one hundred as shown in Equation 2. The WHO 2011 guidelines were applied in the calculation (Gebrehiwot et al., 2011).

$$qi = (C_i/S_i) \times 100 \qquad (2)$$

The sub-index (*SI*) for each parameter was calculated by multiplying the relative weight W_i by quality rating scale qi as shown in Equation 3.

$$SI_i = W_i \times q_i \qquad (3)$$

Where SI_i is the sub-index for the ith parameter, W_i is the relative weight of the ith parameter, q_i is the quality rating based on the concentration of the ith parameter. Finally, the WQI was determined by the summation of the sub-index (SI_i) for each parameter in each water sample as shown in Equation 4 (Reza and Sigh, 2010).

$$WQI = \sum SI_i \qquad (4)$$

Table 1- Descriptive statistic weight, relative weight and WHO Standard for some determined parameters in groundwater samples in the area.

Parameters	Mean	Min	Max	STDEV	WHO STD	Weight (wi)	Relative Weight (Wi)
pH	5.88	5.41	6.11	0.23	6.5 - 8.5	5	0.128
NO_3^-	4.73	2.48	6.97	2.84	50	5	0.128
Mg^{2+}	2.15	1.54	3.26	0.45	50	3	0.076
Na^+	0.68	0.21	1.18	0.26	200	3	0.076
Ca^{2+}	6.81	3.31	9.94	1.99	75	3	0.076
Cl^-	45.42	25	67	13.24	250	2	0.051
SO_4^{2-}	96.85	93.49	197.1	3.13	250	4	0.103
HCO^{3-}	20	5	40	11.08	150	4	0.103
TDS	96.22	10.19	390.9	54.05	1000	5	0.128
Fecal Coliform	10.33	0.00	36.00	13.21	0.00	5	0.128
Total						36	1.00
Parameter s	Mean	Min	Max	STDEV	WHO STD	Weight (wi)	Relative Weight (Wi)
pH	5.96	5.38	6,42	0.26	6.5 - 8.5	5	0.128
NO_3^-	5.57	0.72	14.21	4.18	50	5	0.128
Mg^{2+}	2.38	1.32	6.11	1.17	50	3	0.076
Na^+	0.73	0.27	1.31	0.33	200	3	0.076
Ca^{2+}	6.32	3.17	12.8	1.67	75	3	0.076
Cl^-	40.72	27	58	8.32	250	2	0.051
SO_4^{2-}	107.77	91.4	130	1.48	250	4	0.103
HCO_3^-	25	15	35	5.94	150	4	0.103
TDS	20.85	10.12	80.28	17.95	1000	5	0.128
Fecal Coliform	3.50	0.00	22.00	7.04	0.00	5	0.128
Total						39	1.00

More so, the suitability of the water sources for agricultural use was evaluated using Na%, Magnesium Ratio (MAR), Permeability Index (PI), and SAR. The values were calculated differently for groundwater and surface water (Table 5). The sodium percentage for each sample was calculated using Equation 5 as suggested by Wilcox (1955):

$$\text{Na\%}=\frac{\text{Na+K}}{\text{Ca+Mg+Na+K}}\text{ x100 AV} = \frac{\Theta_{600}}{2} \tag{5}$$

Where, Na, K, Ca, and Mg represent the concentrations of dissolved sodium, potassium, calcium, and magnesium for each water sample in mg/L.

Magnesium Ratio (MAR) was calculated with Equation 6 according to Paliwal (1972).

$$\text{MAR}=\frac{\text{Mg}}{\text{Ca+Mg}}\text{ x100} \tag{6}$$

Permeability Index was obtained from Equation 7 by Doneen (1964).

$$\text{PI}=\frac{\text{Na}+\sqrt{\text{HCO}_3}}{\text{Ca+Mg}}\text{ x100} \tag{7}$$

The Sodium Absorption Ratio (SAR) was calculated using Equation 8.

$$\text{SAR}=\frac{\text{Na}^{+}}{\sqrt{\frac{\text{Ca}^{2+}+\text{Mg}^{2+}}{2}}} \tag{8}$$

3. Findings

3.1. Hydrogeology of the Area

The River Mamu Sub Basin is underlain by the Quaternary (alluvial plain and coastal plain sand), and the Pre-Paleogene - Cretaceous sedimentary sequence (Kogbe, 1981; Nwajide, 2013). The area is underlain by the Nanka Formation (Eocene) which overlies the Imo Formation and the Ebenebe sand member (Palaeocene). The geologic materials show that the sands are majorly poorly sorted and consist of mixed grains that range from fine - coarse. The shale of the Imo Formation is very thick in most parts of the study area except in the southwestern part that is underlain by the Nanka Formation. The Nanka Formation consists of clayey sand: sand consisting of fine to coarse grains, poorly sorted to well-sorted (Table 1 and Figure 2). The implication is the paucity of boreholes in the northern and central parts of the study area, especially where the Ebenebe sandstone and the Nanka Formation were not encountered. In the western part, a multi-aquifer system exists, the Nanka Formation constitutes unconfined to semi-confined aquifers (Figure 2a) which occur at shallower depths. However, the Ebenebe sandstone constitutes semi-confined to confined aquifers (Figure 2b) with some boreholes existing under artesian to sub-artesian conditions and greater depths to aquifers. These artesian to the sub- artesian aquifer are cost-effective, as they will need little or no energy to bring the water to the distribution point. The aquiferous units are the Ebenebe sandstone and the Nanka Formation while the Imo Shale constitutes the aquitard (Figure 2). This is in agreement with the result obtained by Nwajide (2013), and Offodile (2012). The aquifer thicknesses range from 10 to 20 meters and the depth to water table varies between 45 to 200 meters (Figure 2). This also conforms to the results obtained by Anakwuba et al. (2014), Chinwuko et al. (2015), and Chinwuko et al. (2016). The calculated aquifer parameters range for hydraulic conductivity (K) (0.137 - 0.328m/day) and transmissivity (T) (1.874 - 5.389m^2/day) which is displayed in Table 2. These values according to Freeze and Cherry (1979) show the aquifer material has very good vertical and horizontal conductive and transmissive properties. Thus, the values of K, T, b obtained in the present study will ensure good yield for the boreholes. Similar results were obtained in the area by Offodile (2012).

Table 2- Calculated aquifer parameters for the study area using geophysical data.

VES Name	VES Point	Aquifer Resistivity (Ohm-m)	Aquifer Thickness (b)(m)	Depth to aquifer (m)	Hydraulic Conductivity (m/day)	Transmissivity (m^2/day)
Achalla Amukabia	1	1100.00	9.4	44.0	0.328	3.080
Achalla Odawa	2	1500.00	7.8	56.4	0.240	1.874
Achalla Centre	3	1433.07	11 .0	42.0	0.252	2.767
Amansea Town	4	2341.00	35 .0	210.0	0.154	5.389
Holy Family Amansea	5	2630.00	28 .0	197.0	0.137	3.837
Average		1800.81	18.2	109. 9	0.222	3.390

3.2. Characterisation of the Water Quality Parameters

The result from the water analysis was compared with the WHO permissible guideline (2011) (Table 3). Turbidity of the surface water (22.8-198.7) and the groundwater (80.3-120.6) samples were above the stipulated guideline value implying the presence of particulate substances. Fine materials (clay) and unconsolidated, non-plastic sand were major parts of the lithology of the area, which may contribute particulate materials to the water, coupled with the fact the samples were collected during the wet season with further addition from runoff. The presence of microorganisms also contributes to cloudiness in the water, hence preventing light from passing through (WHO, 2011). The groundwater sources are generally slightly acidic (5.38-6.42) with no sample meeting the guideline value for pH. The dissolution of atmospheric CO_2 in rainwater forms carbonic acid, which through acid rain and other geological processes may result in the acidic pH of water. Carbonic acid acts as a catalyst in weathered rocks, minerals, and other chemical processes in the presence of water, resulting in the leaching of dissolved chemical substances into the water. The concentration of the major ions Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, $HCO3^{-}$, SO_4^{2-}, Cl^{-} and NO_3^{-} in groundwater are within the permissible guideline values (Figure 4a and Table 1). These results are conformable to those of Ezeabasli et al. (2014) and Nwajinaka et al. (2019). The ionic species are released from weathering processes within the study area, which dominantly comprises of weathering of silicates minerals, and dilution of NO_3^{-}, that have originated from anthropogenic sources such as domestic wastes and leachate from nitrate fertilizers (Omonona et al., 2017). The low concentration of the major ions may be a result of adsorption ions to clay-rich layers. The elevated concentration of SO_4^{2-} and Cl^{-} can be attributed to the leaching of salts (NaCl, $CaCl_2$, and $MgCl_2$), (Ayogu et al., 2020, Dinka et al., 2015), while Okogbue et al. (2012) trace their source to the anthropogenic activities (agriculture and domestic wastes). A high concentration of SO_4^{2-} can be because is more mobile than other ions in water. Considering the peculiarities of the study area, the present study will align to the sources being both geology and anthropogenic. The major ions contribute to the EC and TDS. Hence, these values were not significant in the present study. It points to the fact that we are dealing with freshwater.

The trace elements chromium (0-0.17), iron (0-1.72), mercury (0-0.82) and arsenic (0-0.17) in surface water and cadmium (0-0.13), Chromium (0-0.17), iron (0-1.72) and arsenic (0-0.14) all in mg/l exceed the permissible guideline values (Figure 3b and Table 3). Heavy metals together with SO_4^{2-} released from fertilizer and manure application can lead to very high concentrations above the permissible limit for drinking water (Appelo and Postma, 2005). The chemical weathering of detrital silicates like amphiboles and biotite and, clay minerals may also release the heavy metals (Edmunds et al., 1992). The atmospheric input of the heavy metals is important. The heavy metals remain fixed by sorption, but in the acid water, they can be mobilised. This may be true for the study area, which is located very close to the industrial estate in Awka, the water being slightly acidic, would be an added advantage. The arsenic may substitute for sulphide in pyrite and oxidation of pyrite can be one of the causes of the high arsenic content of the groundwater (Smedley and Kinniburgh, 2002). Appelo et al. (2002), have proposed that displacement of adsorbed arsenic by the dissolved carbonate could be the cause of the arsenic mineralization. On the basis of the foregoing, the increased concentration of the heavy metals in the water source can be traced to the fertilizer and manure application, weathering of silicate minerals, oxidation of pyrites, displacement by the dissolved carbonate, and atmospheric input. The presence of iron can be attributed to rock-water interaction, oxidation of the pyrites, dissolution of iron-containing minerals, and reduction and dissolution of the iron oxides. The iron in drinking water is not harmful and may even be beneficial. However, iron may impart a bitter taste to water, increase turbidity, which may affect the aquatic biota, clog distribution system and, stain clothing and sanitary installations. The heavy metals can be attributed to geology especially the presence of clay, rock-water interaction, and partly to anthropogenic sources majorly from agriculture in the study area.

The biological parameters considered include the total coliform (8-68), (4-26) and the fecal coliform (0-36), (0-22) in 100ml/l of sample in the surface water and groundwater, respectively (Table 3 and Figure 3). The total coliform serves as an indicator of biological pollution. The WHO guideline stipulated nil for drinking water, but all the water samples show the presence of total coliform. The presence of fecal coliform in some water samples confirms that

Table 3- The result of chemical and bacteriological analysis of surface water samples in the study area.

S	Cd^{2+} mg/l	Hg^{2+} mg/l	Cr^{2+} mg/l	Fe mg/l	Mg^{2+} mg/l	Na^{+} mg/l	K^{+} mg/l	Ca^{2+} mg/l	As^{3+} mg/l	pH	BOD mg/l	Cl^{-} mg/l	Hd mg/l	NO$_3^-$ mg/l	SO$_4^{2-}$ mg/l	HCO$_3^-$ mg/l	DO mg/l	Tb NTU	EC µsm	TDS mg/l	T C 100 mg/l	F C 100 mg/l
1	0.00	0.00	0.06	0.29	6.11	1.18	3.98	7.48	0.00	5.62	510.00	39.00	54.00	5.57	97.95	25.00	47.40	33.30	8.20	10.20	12.00	0.00
2	0.00	0.23	0.07	0.00	3.57	0.99	2.98	5.38	0.08	5.38	298.00	58.00	96.00	0.72	103.90	25.00	36.10	25.80	31.9	40.14	8.00	0.00
3	0.00	0.82	0.00	0.44	2.92	1.07	2.47	12.80	0.04	5.73	386.00	30.00	38.00	1.78	98.02	20.00	35.40	36.60	8.40	10.12	34.00	10.00
4	0.00	0.70	0.00	0.00	2.62	0.16	3.01	5.85	0.01	5.78	242.00	35.00	16.00	0.77	101.20	25.00	31.30	39.60	11.20	10.12	24.00	20.00
5	0.06	0.00	0.11	0.83	2.64	0.81	0.38	4.37	0.00	5.81	520.00	58.00	18.00	7.76	112.80	20.00	42.80	35.70	7.40	20.02	22.00	0.00
6	0.00	0.00	0.16	0.76	2.98	0.78	1.84	3.17	0.03	5.91	314.00	59.00	22.00	8.15	95.43	25.00	29.70	43.60	57.80	80.28	16.00	0.00
7	0.00	1.00	0.00	0.63	2.78	0.83	2.01	6.46	0.00	6.17	262.00	49.00	48.00	8.09	91.40	20.00	28.60	40.60	27.50	30.18	52.00	24.00
11	0.00	0.00	0.11	0.42	2.24	0.68	3.89	6.63	0.02	6.03	152.00	36.00	24.00	7.48	104.70	25.00	21.40	101.10	9.60	10.17	20.00	0.00
12	0.04	0.00	0.06	0.00	1.94	0.46	4.31	5.94	0.00	6.07	88.00	34.00	14.00	6.07	96.20	20.00	18.80	98.10	8.20	10.87	8.00	0.00
13	0.00	0.00	0.15	0.39	1.80	0.54	4.19	5.38	0.01	5.94	204.00	39.00	28.00	1.03	119.80	30.00	19.20	165.60	28.90	10.22	22.00	0.00
18	0.00	0.00	0.17	0.72	2.01	0.49	2.87	7.39	0.09	5.95	226.00	29.00	22.00	0.90	110.30	20.00	18.30	149.30	12.10	10.29	36.00	0.00
19	0.02	0.00	0.13	1.16	1.62	0.78	2.99	8.41	0.05	5.98	4.00	27.00	18.00	0.77	125.00	20.00	16.10	148.40	10.90	20.49	12.00	0.00
21	0.04	0.00	0.08	0.31	1.81	0.76	2.87	5.29	0.00	6.04	236.00	35.00	12.00	5.66	114.00	15.00	22.70	126.70	8.20	10.67	14.00	0.00
22	0.00	0.00	0.03	1.72	1.35	0.21	2.91	8.88	0.08	5.92	58.00	44.00	10.00	13.33	96.40	25.00	21.00	198.70	20.10	30.29	60.00	30.00
25	0.00	0.00	0.12	1.70	1.71	0.61	2.39	8.39	0.14	6.42	136.00	43.00	56.00	4.89	114.70	30.00	24.90	124.80	48.10	10.34	26.00	36.00
26	0.02	0.00	0.14	1.04	1.35	0.62	2.19	7.31	0.03	6.42	8.00	30.00	18.00	1.67	104.20	35.00	1.40	145.00	12.00	20.12	46.00	20.00
27	0.02	0.00	0.14	2.40	1.54	0.63	2.09	8.07	0.12	6.22	202.00	43.00	22.00	6.34	123.60	35.00	21.10	169.30	38.60	30.38	68.00	30.00
28	0.05	0.00	0.07	1.58	1.32	0.63	2.84	4.27	0.11	5.83	102.00	45.00	34.00	14.21	130.00	35.00	15.90	94.20	9.50	10.38	18.00	0.00
Min	0.00	0.00	0.00	0.00	1.32	0.21	0.38	3.17	0.00	5.38	4.00	27.00	10.00	0.72	91.40	15.00	1.40	25.80	7.40	10.12	8.00	0.00
Max	0.06	0.83	0.17	2.40	6.11	1.18	3.98	12.80	0.14	6.42	520.00	58.00	96.00	14.21	130.00	35.00	47.40	198.70	57.80	80.28	68.00	36.00
Mean	0.014	0.015	0.09	0.71	2.38	0.68	2.79	6.32	0.06	5.96	219.33	40.72	30.56	5.57	107.77	25.00	25.12	96.69	19.94	20.85	27.67	10.33
SD	0.02	0.42	0.04	0.47	1.17	0.26	0.95	1.67	0.04	0.26	151.24	8.32	15.85	4.18	1.48	5.94	10.87	57.11	15.45	17.95	18.04	13.21
WHO STD	0.05	0.01	0.05	0.3	50	200		75	0.07	6.5-8.5		250	500	50	250	150	5	5	1000	Nil	Nil	Nil

Key: S-Samples; H-Hardness; Tub-Turbidity; TC-Total Coli; FC-Fecal Coli.

Table 3- (continued).

S	Cd^{2+} mg/l	Hg^{2+} mg/l	Cr^{2+} mg/l	Fe mg/l	Mg^{2+} mg/l	Na^{+} mg/l	K^{+} mg/l	Ca^{2+} mg/l	As^{3+} mg/l	pH	BOD mg/l	Cl^{-} mg/l	Hd mg/l	NO_3^{-} mg/l	HCO_3^{-} mg/l	DO mg/l	SO_4^{2-} mg/l	Tb NTU	EC µsm	TDS mg/l	T C 100 mg/l	F C 100 mg/l
8	0.03	0	0.09	0.96	1.92	0.95	2.25	8.53	0.01	6.03	294	47	58	6.64	35	30.3	93.49	97.9	44.5	30.12	22	0
9	0.03	0	0.07	0.01	2.16	0.52	2.89	8.83	0	5.41	440	40	28	2.48	5	36.7	132.4	83.7	11.7	10.54	4	0
10	0	0	0.05	0	2.45	0.53	3.29	6.64	0.02	5.8	454	50	28	6.97	20	46.1	97.36	80.3	56.9	40.28	6	8
14	0.03	0	0.07	0.30	3.26	0.61	6.98	5.91	0.11	5.82	104	67	18	5.18	5	18.6	197.1	100.8	229	390.9	8	12
15	0.02	0	0.06	0	2.45	1.23	3.29	5.85	0.02	6	172	34	20	3.9	20	19	128	89.7	61.9	50.12	10	0
16	0	0	0.10	0.77	1.81	0.59	3.11	8.49	0.11	6.22	112	25	8	8.46	20	17.6	100.8	112.4	32.7	40.32	18	0
17	0	0	0.11	0	1.54	0.51	3.84	9.94	0.07	5.86	54	28	22	7	5	17.4	125.2	113.4	26.2	10.19	14	0
20	0	0	0	0	1.87	0.51	2.37	7.49	0.03	5.78	48	52	22	1.54	20	20	123.6	87.1	67.7	100.8	12	0
23	0	0	0.14	0.94	2.18	0.27	2.64	3.89	0.11	6.01	76	58	10	0.64	25	21.7	110.5	120.6	92.5	140.2	26	22
24	0	0	0.12	0	1.97	1.05	2.51	6.97	0.06	6.11	190	41	36	1.18	40	22.6	99.69	81.7	102.5	150.45	20	0
29	0.01	0	0.12	0.27	2.33	0.64	1.09	3.31	0.17	5.74	22	40	26	6.56	20	16	118.8	80.7	29	40.48	24	0
30	0.02	0	0.19	0.92	1.86	1.31	1.98	5.81	0.11	5.78	58	63	10	6.23	25	17.1	124.6	104.1	88.7	150.28	14	0
Min	0.00	0	0.00	0.00	1.54	0.27	1.09	3.31	0.00	5.41	22.00	25.00	8.0	2.48	5.00	16.00	93.49	80.30	11.70	10.19	4.00	0
Max	0.03	0	0.19	0.96	3.26	1.31	3.29	9.94	0.17	6.11	454.00	67.00	58.00	6.97	40.00	46.10	197.10	120.60	229.00	390.9	26.00	22.00
Mean	0.02	0	0.10	0.65	2.15	0.73	3.02	6.81	0.07	5.88	168.7	45.42	23.83	4.73	20.00	18.3	96.85	96.03	70.28	96.22	14.83	3.50
SD	0.01	0.00	0.04	0.41	0.45	0.33	1.44	1.99	0.05	0.23	150.4	13.24	13.63	2.84	11.08	9.35	3.13	14.22	57.58	54.05	7.21	7.04
WHO STD	0.05	0.01	0.05	0.3	20	200		75	0.07	6.5-8.5		250	500	50	500	5	250	5	1000	1000	NIL	NIL

Key: S-Samples; H-Hardness; Tub-Turbidity; TC-Total Coli; FC-Fecal Coli

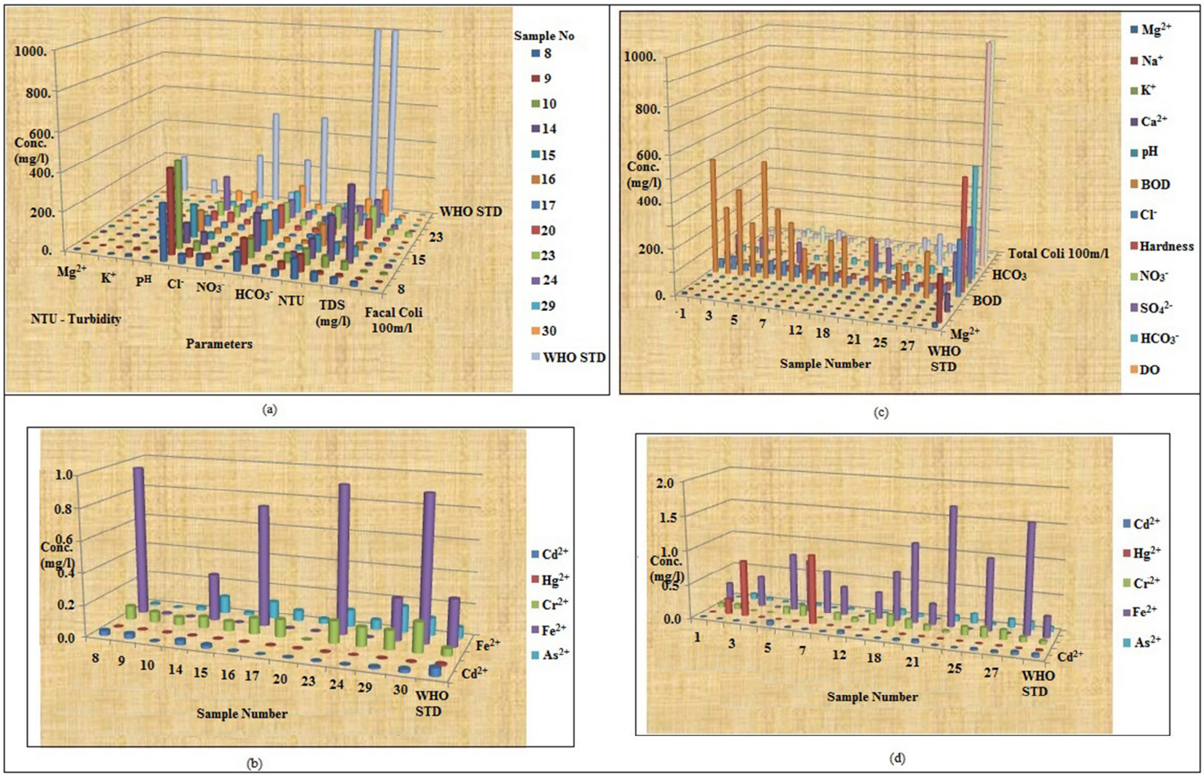


Figure 3- Bar - chart showing the measurement parameters and trace elements compared to WHO guideline in the area; a) measured parameters in groundwater samples, b) trace elements in groundwater samples, c) measured parameters in surface water samples, and d) trace elements in surface water samples.

some of the samples are biologically polluted. High Coliform count in addition to increased Cl^- and NO_3^- connotes poor sanitation and influx of human waste through runoff (WHO, 2011). The fact that most of the communities in the study area do not have toilet facilities and use the nearby bushes, bath in the river which all attest to poor hygiene, may have contributed to the biological pollution. Therefore, there is a need for disinfecting the water and boiling it before drinking.

These trace elements may be attributed to geology and anthropogenic activities. Though there is paucity of industries in the study area, the area is located in downstream of the River Mamu. In upstream of the river is located a major industrial layout in Awka the capital of Anambra State. The industries discharge their waste effluents directly into the river, which may be a source of the trace elements in surface water sources. Another source could be from agricultural activities especially fertilizers and herbicides used in the farms and fishery. The previous studies in Imo Shale and Nanka Formation recorded a high concentration of trace elements especially iron (Okolo et al., 2018; Ezeabasli et al, 2014) hence, linking them to the geology. The presence of these trace elements is a serious source of concern as the populace in the area drinks the water directly without treatment. Metals are known to have great health implications for humans and aquatic organisms, as they are known to accumulate in the human organs (WHO, 2004). In general, the water sources can be said to be polluted because of the presence of these trace elements and biological parameters.

3.3. Classification of Water Using Major Ions

Piper's (1944) trilinear diagrams were used for classifying the groundwater and surface water into major water types and to assess the dominant ions and geochemical processes in the study area. Using Langguth (1966) classification of the Piper diagram, the water type is Ca-Mg-Cl-SO_4 type (domain i) (Figure 4) for both the groundwater and surface water. The dominant ions are Ca^{2+} and $SO4^{2-}$ depicting calcium and sulphate rich groundwater and surface water. This is a water type dominated by earth alkaline metals with increased portions of alkalis with prevailing SO_4^{2-} and

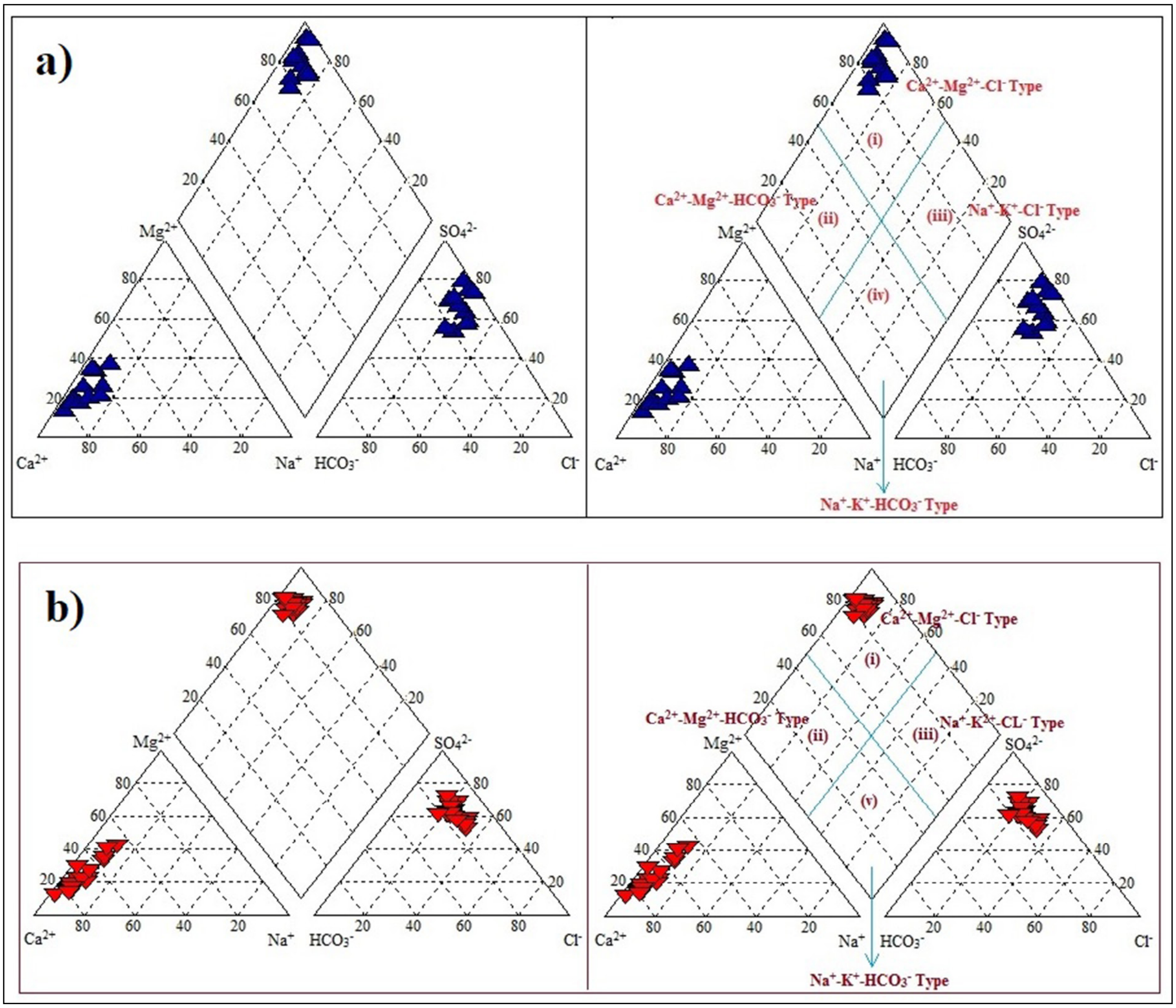


Figure 4- Graphical representation of hydrochemical facies in both groundwater and surface water; a) groundwater, b) surface water.

Cl^- ions. Therefore, the groundwater and surface water sources within the study area are composed of normal earth alkaline (Ca^{2+} and Mg^{2+}) along with strong acids ($SO4^{2-}$ and Cl^-) that are dominant in nature. This water type is not affected by the mixing of water from different sources. It denotes water with secondary hardness. The distribution of geochemical facies or water type tells the geochemical flow path. Utom et al., (2013) and Poehls and Smith (2009) observed that the geochemical flow path begins with $CaHCO_3$ type through $NaCO_3$ to $CaCl_2$ type. This depicts that the water type in the present study is the end water in the flow path.

3.4. Hydrogeochemical Processes

The water quality of an area is influenced by climatic, anthropogenic, and geologic processes (Ayogu et al., 2020; Okolo et al., 2020; Nganje et al., 2015; Appelo and Postma, 2005). Rock and mineral weathering, evaporation, precipitation, and anthropogenic are the main sources of dissolved ionic species in the water (Singh et al., 2005). Different ionic ratio plots were applied in modeling and understanding the hydrogeochemical processes responsible for contributing the major ions in water sources using Hounslaw (1995) classification. The plots of Ca^{2+}+Mg^{2+} versus HCO^{3-} +SO_4^{2-} , Ca^{2+}+Mg^{2+} versus total cations and TDS versus Na^++K^+/Na^++K^++Ca^{2+} (Figure 5) were applied in the present study. The plot of Ca^{2+}+Mg^{2+} versus HCO^{3-} + SO_4^{2-} shows that the points fell under the 1:1 line (Figure 5a). This depicts that silicate weathering is the dominant chemical process responsible for the contribution of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- to groundwater. The plotted points

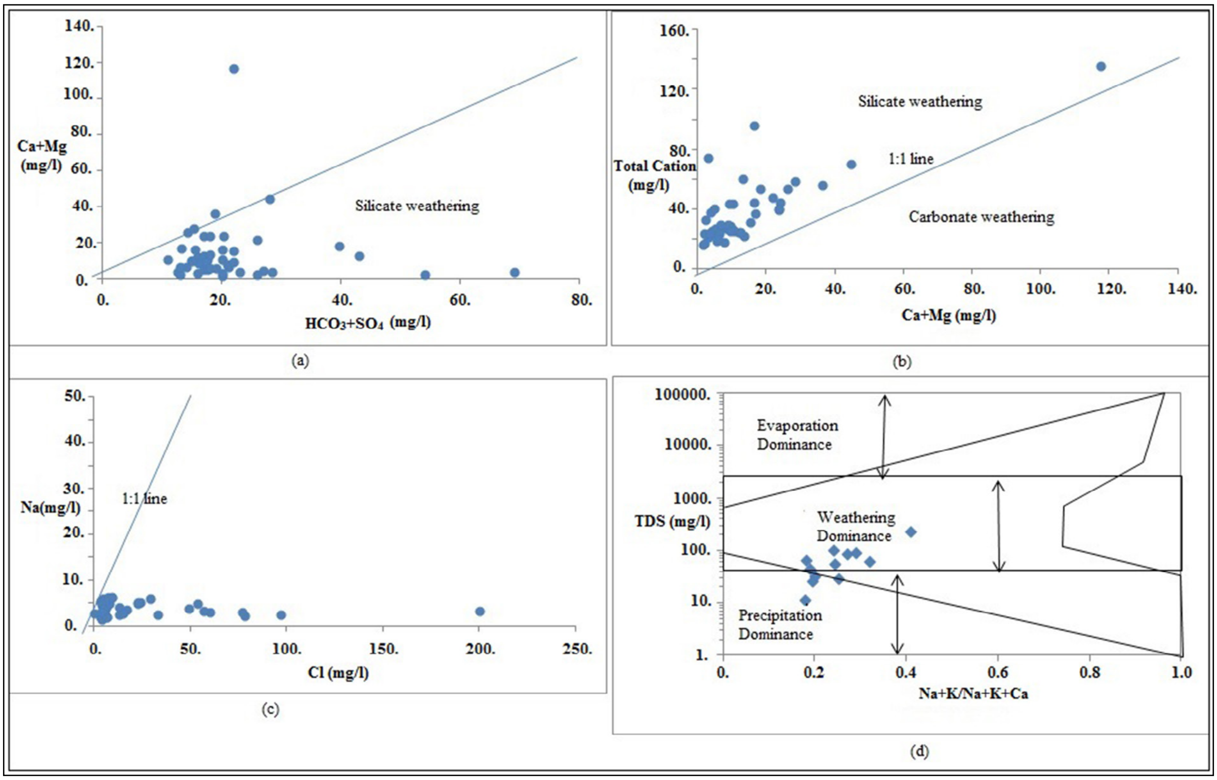
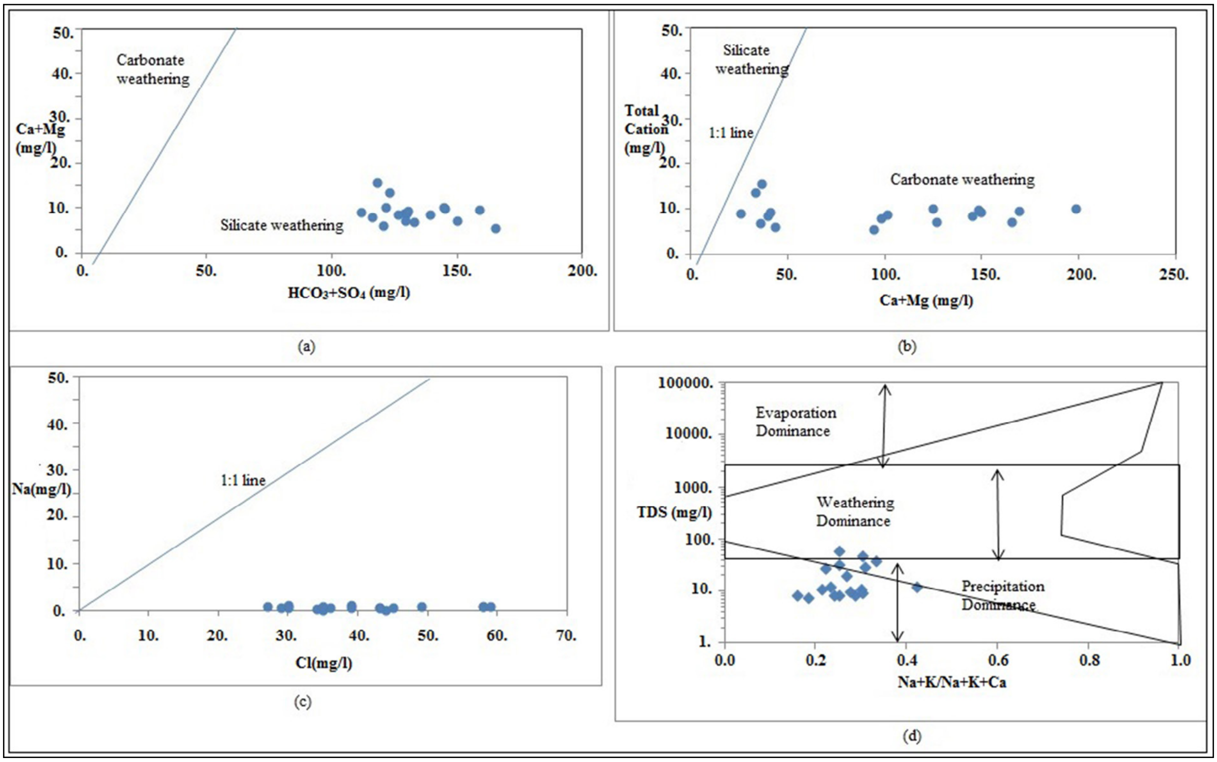


Figure 5- Ionic plots for groundwater in the area showing sources of ionic species.

also shift to the left indicating a reverse ion exchange process resulting in excess of Ca^{2+} and Mg^{2+}. The plot of Ca^{2+}+ Mg^{2+} versus total cations (Figure 5b) shows silicate weathering as a major source of cations in the groundwater. However, in the plot of Na^{+} versus Cl^{-}, the plotted points fell below the 1:1 line (Figure 5c), which indicates a smaller concentration of Na^{+} to Cl^{-} and can be attributed to halite solution and other evaporates (Walker et al., 1997). Nevertheless, Gibbs's (1970) plot (Figure 5d) illustrates the natural mechanism controlling groundwater chemistry in the study area. These include evaporation dominance, rock-weathering dominance, and precipitation dominance. The majority of the plotted points are within the rock-weathering domain with a few in the precipitation dominance domain. These indicate that rock-weathering is the main contributor of the major ionic species in groundwater with minor imputes from precipitation. Ayogu et al. (2020) and Okogbue et al. (2012) reached similar conclusions.

Furthermore, in the ionic ratio plots for the surface water, the plot for Ca^{2+}+Mg^{2+} versus SO_4^{2-} +HCO_3^{-} shows plotted points are below the 1:1 line (Figure 6a), indicating silicate weathering. The points are shifted to the left indicating an ion exchange process with an excess of SO_4^{2-} and HCO_3^{-} ions, which is in agreement with Datta et al. (1996). The plot of Ca^{2+}+Mg^{2+} versus total cations indicates that carbonate weathering also contributes to the presence of dissolved major ions in the surface water (Figure 6b). However, Na^{+} versus Cl^{-} plot (Figure 6c) shows that the source of Na^{+} is from silicate weathering and dissolution of other related evaporates as suggested by Elango and Kannan (2007). Consequently, the Gibbs plot indicates that 85% of the plotted points are in the precipitation dominance domain and 15% in the rock weathering dominance domain (Figure 6d).

Therefore, Gibbs (1970) diagram and the ionic plots identified the rock-water interaction, silicate weathering and ion exchange reactions in the groundwater, and the precipitation and silicate weathering in the surface water as the most dominant factors that influence the water chemistry in the study area. They are the main sources responsible for the changing concentration of ions in the water sources in the study area.



(a) (b) (c) (d)

Figure 6- Ionic plots for surface water in the area showing sources of ionic species.

3.4.1. *Classification of Drinking Water Using Water Quality Index*

The calculated WQI for the groundwater samples is (17.84 - 184.05) and in the surface water (17.97 - 307.2) (Table 5). These values indicate that 75% of the samples of groundwater and 61% of the surface water are of excellent quality for drinking, while others range from very poor to unfit for drinking (Table 4). The percentage distribution of WQI in the groundwater and surface water is shown in Figure 7.

3.4.2. *Suitability of Water Resources for Agricultural Use*

The suitability of water for agricultural use is determined by the dissolved chemical constituents in water. Four different indices such as Na%, SAR, MAR, and PI were calculated in order to ascertain the suitability of water for agriculture in the area. The calculated values for all the indices are shown in Table 5. The percentage distribution and the suitability for agriculture are displayed in Table 6. The result indicated that 100% of all the samples of both the surface water and groundwater are excellent for agriculture based on SAR and MAR. However, using Na%, 100% for the surface water, and 91.7% for the groundwater range from good to excellent for agriculture. The PI indicated that 72.2% of the surface water and 66.7% of the groundwater are within Class1 and Class 2 range, which depict water that is good to excellent for agriculture. These values are very

Table 4- WQI and corresponding water quality status and possible use of water of Mamu Sub-Basin.

WQI	Status	Number of Samples		Possible Use
		Surface water	Groundwater	
0 - 25	Excellent	11	9	Drinking and all other use
25 - 50	Good	Nil	Nil	Domestic, and all other use except drinking
51 - 75	Fair	Nil	Nil	Agriculture and some industrial use
76 - 100	Poor	Nil	Nil	Agriculture
101 - 150	Very Poor	1	1	Use with caution/Treatment
> 150	Unfit for drinking	6	2	Treatment before any use

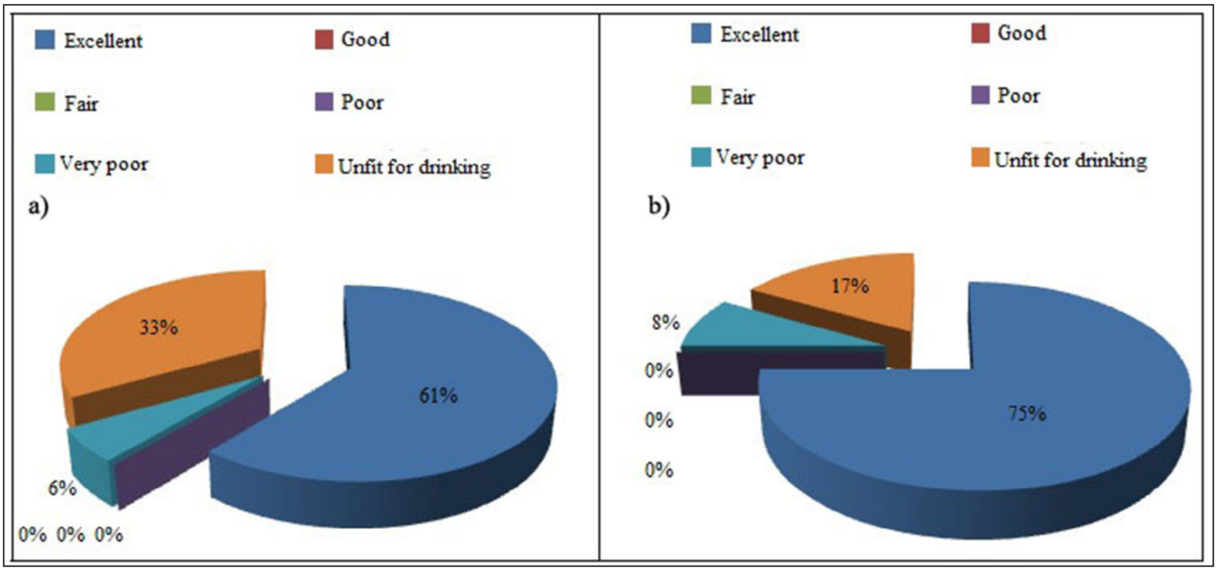


Figure 7- Pie chart showing the distribution of WQI in the study area; a) surface water, b) groundwater.

Table 5- Summary of evaluation result of the different indices.

Sample Identification No		Water Quality Criteria				
	Su Kaynağı	WQI	Na%	SAR	MAR	PI
1	Surface water	19.43	27.5	0.16	44.96	45.47
2	Surface water	18.17	30.7	0.17	39.89	66.92
3	Surface water	146	18.4	0.13	18.58	35.25
4	Surface water	273	27.2	0.1	30.93	60.92
5	Surface water	17.97	14.5	0.02	37.66	75.35
6	Surface water	20.95	29.9	0.16	48.46	93.98
7	Surface water	307.2	23.5	0.01	30.9	57.38
8	Groundwater	20.74	23.4	0.15	18.37	65.7
9	Groundwater	17.84	23.7	0.08	20.21	25.08
10	Groundwater	121.98	29.6	0.09	26.95	55.02
11	Surface water	20.13	34	0.11	25.25	64.04
12	Surface water	19.02	37.7	0.08	24.62	62.59
13	Surface water	19.16	39.7	0.1	25.07	83.8
14	Groundwater	184.09	45.3	0.01	35.55	31.04
15	Groundwater	22.22	35.3	0.21	29.52	68.7
16	Groundwater	20.5	26.4	0.09	17.57	49.15
17	Groundwater	19.25	27.5	0.07	13.41	23.92
18	Surface water	18.09	26.3	0.08	21.38	52.36
19	Surface water	18.87	27.3	0.12	16.15	52.36
20	Groundwater	20.13	23,5	0.08	19.98	53.23
21	Surface water	19,18	33.8	0.14	25.49	65.25
22	Surface water	405.62	23.4	0.03	13.2	50.93
23	Groundwater	301.99	32.4	0.05	39.14	86.82
24	Groundwater	20.97	28.5	0.18	22.04	82.49
25	Surface water	481.99	22.9	0.1	16.93	60.27
26	Surface water	275.92	24.5	0.11	15.59	75.47
27	Surface water	406.07	24.9	0.1	16.02	68.12
28	Surface water	22.18	38.3	0.13	23.61	117.1
29	Groundwater	19.79	23.5	0.13	41.31	90.64
30	Groundwater	20.06	30	0.24	24.25	75.39

Table 6- Classification of water of Mamu Sub-River Basin agriculture using Wilcox (1955), and Todd (1980).

Indices	Range	Class	Number of Samples		Percentage of Samples	
			Surface water	Groundwater	Surface water	Groundwater
N%	< 20	Excellent	2	Nil	11.1	0
	20 - 40	Good	16	11	88.9	91.7
	40 - 60	Permissible	Nil	1	0	8.3
	60 - 80	Doubtful	Nil	Nil	0	0
	> 80	Unsafe	Nil	Nil	0	0
MAR	< 50	Suitable	18	12	100	100
	> 50	Unsuitable	Nil	Nil	0	0
SAR	< 10	Excellent/Good	18	12	100	100
	10 - 18	Permissible	Nil	Nil	0	0
	18 - 26	Doubtful	Nil	Nil	0	0
	> 26	Unsuitable	Nil	Nil	0	0
PI	< 75	Excellent (Class 1)	Nil	1	0	8.3
	25 - 75	Good (Class 11)	13	7	72.2	58.4
	> 75	Unsuitable (Class 3)	5	4	27.8	33.3

significant considering that the people in the study area depend heavily on agriculture for their livelihood.

3.5. Implication of Analyzed Parameters in Water Resources

The Pearson correlation matrix for the groundwater reveals mostly weak positive and negative relationships for parameters at the significance level of 0.05 (Appendix I). However, some parameters have a strong positive relationship at the significance level of 0.05. These include chromium and iron (0.6202) and chromium and arsenic (0.5961). The implication is that these trace elements have similar input sources. The main source is geology because of the rock-water interaction, weathering of silicates, oxidation, and dissolution. The positive relationship between turbidity and iron implies that iron is the major contributor to the turbidity in the groundwater in the study area. In addition, electrical conductivity and total dissolved solids were mainly inputted to the groundwater by the major ions (magnesium, potassium, chloride, and sulphate), hence their strong positive correlation. The dissolved major ions are attributed to the silicate weathering as classified by Gibbs (1970) diagrams and anthropogenic activities. The total hardness was strongly positively related to magnesium and sodium with a weak positive relationship to chloride implying that the groundwater has permanent hardness. This was also collaborated by the water type as classified by Piper's (1944) diagrams.

On the other hand, the correlation matrix for the surface water shows a strong positive relationship at the significance level of 0.05 for the following parameters. Iron, nitrate, and turbidity are positively related which implies similar sources and influence on cloudiness in the surface water. The sources of permanent hardness in the surface water is linked to sodium, magnesium, and chloride and indicated by their positive relationship. The biochemical oxygen demand is positively correlated to dissolved oxygen, magnesium, and sodium indicating their importance in plant nutrient and growth. Chloride is implicated in the presence of the total dissolved solids and electrical conductivity in the surface water. It is worthy to note that most of the trace elements are not strongly correlated in the surface water implying diversity in the input sources.

4. Results

This study evaluated the hydrogeological, water quality, and suitability of the water for drinking and agricultural use of parts of the River Mamu Sub-Basin, Southeastern Nigeria. The Nanka Formation and Ebenebe Sandstone constitute the aquiferous units while the Imo Shale, is the aquitard. The aquifer parameters K and T indicate the aquifer with good horizontal and vertical transmissive properties. The major cations and anions, electrical conductivity, and total dissolved solids are within the stipulated drinking water guideline values in both the groundwater and surface water. Their values in the surface water and groundwater range for Na^+ (0.21-1.31); Mg^{2+} (1.32-6.11); K^+ (0.38-3.98); Ca^{2+} (3.17-12.8); Cl^- (25-67); SO_4^{2-} (91-197); NO_3^- (0.72-8.46); HCO_3^- (5-40); EC (7.4-57.8); and TDS (10.19-390.9); all measured mg/l. The major ions control both EC and TDS in the water sources. The trace elements (chromium (0-0.19; arsenic (0-1.17) and iron (0-0.96)) in the groundwater and (chromium 90-0.17); arsenic (0-0.14); mercury (0-0.83) and iron (0-2.4)) in the surface water are above the guideline values. The increased concentration of these metals has been traced to weathering, the presence of clay minerals, and human activities. The biological parameters (total coliform (4-68) and fecal coliform (0-36)) in both the groundwater and surface water exceed the permissible limits of nil in 100ml/l of sample. Their presence in the water has been attributed to poor hygiene and sanitation. Thus, some of the groundwater and surface water in the study area are chemically and biologically polluted because of the biological parameters and the high concentration of some heavy metals.

The WQI (17.84-307.2) was used to ascertain the suitability of the water sources for drinking. It describes 61% of surface water and 75% of groundwater as excellent for drinking, but 33% of surface water and 17% of groundwater are unfit for drinking. The suitability for agriculture was determined using Na% which depicted 100% of the surface water as good-excellent and 91.7% and 8.3% of the groundwater as good and permissible, respectively. SAR and MAR show that 100% of the surface water and groundwater are excellent for agricultural use. The PI classified 72.2% of the surface water as good (Class 2) and 66.7% of the groundwater as good to excellent (Classes 1 and 2), but 27.8% of the surface water and 33.3% of the groundwater were described as unsuitable.

Piper's (1944) diagrams classified the groundwater and the surface water as Ca-Mg-Cl-SO_4 water type, which has normal earth alkaline (Ca^{2+} and Mg^{2+}) with strong acids (SO_4^{2-} and Cl^-) dominating. The dominant ions are Ca^{2+} and SO_4^{2-}. Gibbs's (1970) diagrams and the ionic ratio plots identified the dominant geochemical processes responsible for the input of ionic species and the changing water chemistry. They include weathering of the silicate minerals, the rock-water interaction, the presence of clay minerals, ion exchange, and precipitation. The Pearson's correlation indicates that the turbidity in the surface water and groundwater is influenced by the presence of iron and nitrate. The magnesium, sodium, and chloride are responsible for hardness in all the water sources indicating the permanent hardness. The heavy metal in the groundwater is strongly positively correlated alluding to similar input sources while the same metals in the surface water are very weakly positively correlated implying variable sources.

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