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Evaluation of the Hydrochemistry and Pollution Levels in Groundwater of Njahasang, Southeast Nigeria

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Abstract: *This study assesses groundwater quality, chemistry, and pollution levels in Njahasang, southeastern Nigeria, by evaluating physicochemical parameters. Fifteen (15) groundwater samples were collected and analyzed using standard laboratory techniques. Physical parameters were measured using the HANNA Instrument multi-parameter probe (model HI9813). Major anions were analyzed using volumetric methods (HCO_3^-, Cl^-), colorimetric methods (SO_4^{2-}), and ultraviolet (UV) spectrophotometry (NO_3^-), while major cations and heavy metals were determined using an Atomic Absorption Spectrophotometer (Bulk Scientific model 210VGP).*

Results showed that major cations followed the order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, anions followed $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$, and heavy metals followed Mn > Fe > Zn > Cr > Cd > Pb. The Water Quality Index (WQI) indicated that all groundwater samples were of excellent quality for domestic use. Hydrochemical facies identified Ca^{2+}-Mg^{2+}-HCO_3^- and Ca^{2+}-Mg^{2+}-SO_4^{2-} water types. Chloro-alkaline indices (CAI-1 and CAI-2) revealed a dominant reverse ion exchange process, as all values were positive. Cluster analysis suggested both geogenic and anthropogenic sources of ion contamination, while Gibbs plots indicated that rock-water interaction and host rock weathering were the primary processes controlling groundwater chemistry.

The degree of contamination (Cd) indicated low contamination overall, except for Mn, which exhibited moderate levels based on the contamination factor (Cf). According to the Pollution Load Index (PLI), 27% of the samples showed progressive deterioration, likely due to elevated Mn concentrations from shales, while 73% exhibited no pollution. Plots, tables, and models based on major ionic constituents provide an effective visualization of groundwater quality and chemistry.

Keywords: *Major cations, major anions, heavy metals, hydrochemistry, contamination, pollution*

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1.0 Introduction

Water is important to mankind because their survival depends on it. The utilization of this natural resource comprises domestic, agricultural, and industrial puposes (Roșca *et* *al.*, 2020). About three-quarters of the earth's surface area is covered by water, and 97% of the earth's water resources which are locked in the sea and ocean are saline (Cidu *et al.*, 2011). Fresh water occurs in the form of surface and groundwater, and they constitute the remaining 2.5%. Of this amount, 1.3% are surface water, 30.1% occur as groundwater and 68.6% occur in the form of glaciers and ice caps (Shiklomanov, 1993). Groundwater is located in the interstitial spaces of rocks within an aquifer (Ochelebe and Kudamnya, 2022). Shallow aquifers are explored by means of open wells usually below twenty meters (20 m) deep, and shallow boreholes which are generally below 60 m deep. The deep aquifer is usually tapped using boreholes greater than sixty meters (Edet, 2018).

Fresh groundwater resource is vital, and it is under continuous pressure in most developing cities, owing to population surge, unplanned and haphazard infrastructural development and urbanization, and industrialization (Ostad-Ali-Askari and Shayannejad, 2021; Kudamnya and Edet, 2024; Omorogieva *et al.*, 2024). Moreover, the demand for groundwater for drinking and domestic activities continues to rise, as it is perceived to be safer for consumption compared to surface water in terms of quality (Kudamnya *et al.*, 2021). Monitoring and protecting groundwater is crucial because its pollution can lead to significant environmental concerns (Jones *et al.*, 2014; Battista and Vollaro, 2017; Yan *et al.*, 2016). According to WHO/UNICEF (2000), over two million people die annually from consuming contaminated water. Consequently, the quality of groundwater in poorly managed towns is a growing concern.

To ensure its safe use, groundwater must periodically be monitored to meet quality standards. Poor groundwater quality can result in reduced agricultural productivity, heightened health risks for humans, and biodiversity loss. These issues are influenced by a range of factors, including precipitation, overexploitation of mineral resources, weathering, and geological, mineralogical, and geochemical processes in the saturation zone (Abdelshafy *et al.*, 2019; Karunanidhi *et al.*, 2020; Mohammed *et al.*, 2022).

As groundwater flows, its quality naturally evolves over time and space due to the hydrological cycle and the influence of human activities (Ochelebe *et al.*, 2020). These processes can modify the chemistry of major ionic constituents - Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, HCO_3^{-}, and Cl^{-} - with concentrations exceeding 0.5 mg/L, thereby potentially affecting groundwater quality (Merkel and Planer-Freidrich, 2002). These ions, along with physical parameters such as pH, electrical conductivity (EC), and total dissolved solids (TDS), play a vital role in assessing water quality and predicting environmental changes (Amah *et al.*, 2012; Li *et al.*, 2016).

Previous studies suggest that ions present in groundwater are predominantly geogenic (Musa *et al.*, 2014; Busico *et al.*, 2018; Ekwere *et al.*, 2023; Okereke and Edet, 2023). They indicate that rock weathering and ion-exchange reactions are key processes influencing groundwater chemistry. Yidana *et al.* (2012) and Chegbeleh *et al.* (2020) demonstrated that groundwater residence time, pH, and temperature govern the rate of rock weathering and ion-exchange reactions. Furthermore, some authors (Abanyie *et al.*, 2020; Sunkari *et al.*, 2021; Sunkari *et al.*, 2025; Lermi and Sunkari, 2023) have linked anthropogenic activities such as agriculture, mining, and unplanned developments to groundwater contamination.

In Nigeria, many communities rely on groundwater because it is more reliable in quality than surface water, which is easily contaminated by human activities (Khudair *et al.*, 2022). However, groundwater can also be polluted through natural and human processes (Ochelebe and Kudamnya, 2022). About 52% of households in Nigeria have access to improved drinking water sources (NBS, 2014).

Furthermore, 42.9% of households in Cross River State depend on groundwater (NBS, 2017). Farming is common in the study region and relies heavily on groundwater, especially during the dry season, to meet food demands for the growing population. Major ions are often used to study groundwater chemistry and can come from mineral dissolution (Edet, 2016; Ghalib, 2017). Studies on the hydrochemistry of surface water within and around the Calabar Flank have been investigated (Edet Offiong, 2002; Ephraim, 2003), while Nganje *et al.* (2017) suggested local recharge of the aquifers by recent rain and surface water.

The aim of this research is to assess the hydrochemistry and potential contamination of groundwater in parts of the Calabar Flank, southeast Nigeria. The approach is to holistically incorporate physical parameters, major ions, and heavy metals for analysis. The results will evaluate groundwater quality and provide baseline data for sustainable groundwater resource development and future management.

1.1 The Geologic setting and Hydrogeology of the study area

The study area is situated within the Calabar Municipal area, southeastern Nigeria (Fig. 1). It is located within latitudes 5° 8' 20" to 5° 14' 20" and longitudes 8° 14' 00" to 8° 22' 10". The Calabar area belongs to the lowland and swampland of South-eastern Nigeria (Iloeje, 1991). Elevations, here are generally less than 100m above the mean sea level. Monthly temperature is between 23.10C and 28.70C with an average precipitation between 26.7mm in February to 459.1mm in July (Edet & Okereke, 2002).

The Calabar Flank, is a significant geologic province that stretches from the eastern part of the Niger Delta to the Cameroun Volcanic Line. The area is bounded by the Oban Massif to the north and the Atlantic Ocean to the south. The geology of the Calabar Flank is largely characterized by Cretaceous to Tertiary sedimentary sequences of continental fluviatile sands and clays, known as the Coastal Plain Sands. This formation is characterized by alternating sequence of loose gravel, sand, silt, clay, lignite and alluvium (Short & Stauble, 1967).

The Calabar Flank contains several aquifer systems which range from unconfined and semi-confined to confined aquifers. Hydrogeologic unit of the study area is mainly coastal plain sands and alluvium which receives a significant amount of recharge from precipitation as well as the network of rivers around. Hence, the basin has important implications for both groundwater exploration and environmental management due to its distinct hydrogeologic characteristics. Investigation within the study area show three aquiferous units with a depth range of 120-180m (Ekwere & Ekwere, 2015) The Coastal Plain Sands (Benin Formation) is by far the most prolific aquiferous hydrogeologic unit in the area and all the water boreholes are located in this Formation (Esu & Amah, 1999). Alluvial aquifer overlies the Benin Formation in the Southern parts of the study area. Recently, (Edet & Okereke, 2002; Amah & Esu, 2008) identified two water bearing units within the Coastal Plain Sand of the area. These are upper gravelly sand aquifer (UGSA) and lower fine sand aquifer (LFSA).

2.0 Materials and methods

2.1 Sampling and laboratory analysis

A total of fifteen (15) groundwater samples were collected during the dry season from the study area, when the effect of dilution was presumed to be lowest. During sampling, the samples were collected using two (2) 0.75-cl plastic containers, and thoroughly rinsed with the water to be sampled. The sample bottles were labeled to ensure easy identification. One bottle was designated for collecting samples for major anion analysis, while the other was used for collecting samples for major cation and heavy metal analysis. Few drops of dilute nitric acid (HNO_3^-) was added to each sample collected for the cation and heavy metal analysis.

The procedure performed is to ensure that representative groundwater samples was obtained. The locations of sampling points were determined in the field using the GARMIN-eTrex 20x global positioning system (GPS).

Physical parameters (electrical conductivity (EC), total dissolved solids (TDS) and pH) were measured in-situ by means of a portable HANNA Instrument multi-parameter probe model no. HI9813. The samples collected were filtered using the ash-less WHATMAN filter paper (110 mm diameter) and labeled properly for identification, and subsequently sent to the laboratory for analysis. Volumetric methods were used to analyze major anions such as bicarbonate (HCO_3^-) and chloride (Cl^-); calorimetric methods were used to determine SO_4^{2-}; and an ultraviolet (UV) spectrophotometer screening method was used to analyze NO_3^-. The major cations and heavy metals were analyzed using the Atomic Absorption Spectrophotometer (Bulk scientific model 210VGP) at the Department of Soil Sciences, Kogi State University, Anyigba.

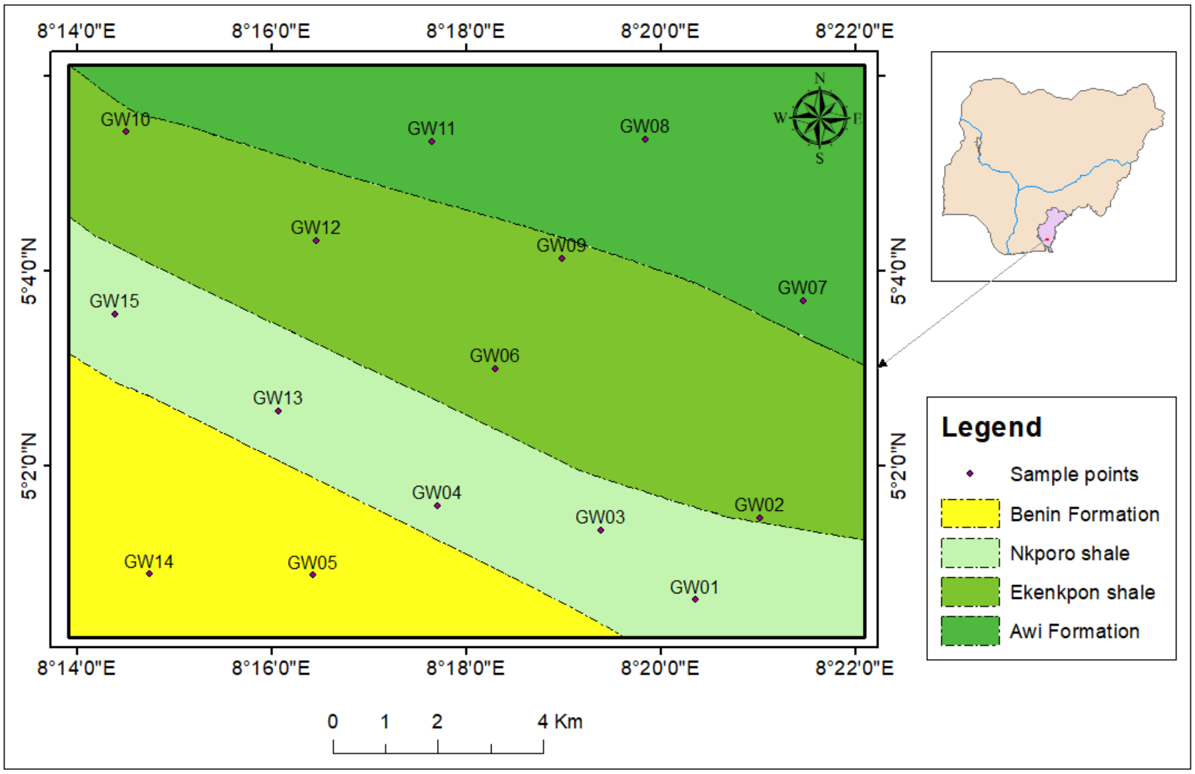

Fig. 1: Geological map of the study area with sample points

2.2 Data interpretation

In this study, interpretation of data obtained from laboratory analysis was presented in the form of tables, plots, and numerical equations. Also, computation of statistical summaries (minimum, maximum and mean) was executed with Microsoft Excel spreadsheet. The Pearson correlation matrix was used to explain relationships between physicochemical parameters analyzed in the study's groundwater, while the dendrogram visually illustrates these relationships by grouping them based on their similarities or differences. The correlation coefficients were computed, and the dendrogram was produced with the MINITAB-16 software. The interpretations for strength of the relationship between the correlated parameters (Bahar and Reza, 2010, Ochelebe and Kudamnya, 2022) was adopted. Rock-ware 15.0 software was used to produce the Piper plot for classifying the hydrochemical facies of the groundwater from the study area. A dendrogram was used in cluster analysis to explain the arrangement of cluster based on similarities or differences between data points. Gibbs plot was produced using the software Grapher 16, from which interpretation of ion sources was derived. Furthermore, indexical approaches were used to compute the following:

Water quality index (WQI):

The groundwater quality for domestic purposes was computed using the WQI model. The weighted arithmetic WQI model was adopted to reveal the influence of individual quality parameters. Water quality score, comparative weight, and the general WQI were computed using the model equations that follow:

$$q_i = \left(\frac{C_i}{S_i}\right) x100 \qquad (1)$$

$$w_i = \frac{1}{S_i} \qquad (2)$$

where q_i is the quality rating of the ith parameter within the given number of samples, n; C_i, is the measured concentration of respective ions; S_i is the standard value of the ith parameter within the given number of samples, n, and w_i represents the relative weight of the ith parameter within the given number of samples, n. Finally, the overall WQI was computed using the following:

$$WQI = \frac{\sum_1^n q_i w_i}{\sum_1^n w_i} \qquad (3)$$

The WQI values computed in this study were compared with the classification according to Akter et al. (2016): < 50 (Excellent), 50-100 (Good), 101-200 (Poor), 201-300 (Very poor), > 300 (Unsuitable).

i. *Contamination Factor (C_f):*

$$C_f = \frac{C}{C^o} \qquad (4)$$

where C is the measured concentration of each metal in the sample, while C^o is the background value of the metal. The interpretations are as follows: $C_f < 1$ (low contamination), $1 \leq C_f \leq 3$ (moderate contamination), $3 \leq C_f \leq 6$ (considerable contamination), $C_f \geq 6$ (very high contamination).

ii. *Degree of Contamination (C_d):*

$$C_d = \sum_{i=1}^{n} C_{fi} \qquad (5)$$

All variable is as defined. The interpretation of results is based on the following classification: $C_d < 8$ (low contamination), $8 \leq C_d \leq 16$ (moderate contamination), $16 \leq C_d \leq 32$ (considerable contamination), $C_d \geq 32$ (very high contamination).

iii. *Pollution Load Index (PLI):*

$$PLI = \left(C_{f1} + C_{f2} + C_{f3} + \cdots + C_{fn}\right)^{1/n} \qquad (6)$$

where n is the number of metals and C_f is the contamination factor. PLI = 0 indicates no pollution (perfection), PLI = 1 indicates only baseline levels of pollutants present, and PLI > 1 indicates progressive deterioration of the groundwater quality.

iv. *Chloro-alkaline Index (CAI):*

$$CAI - 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \qquad (7)$$

7

$$CAI - 2 = \frac{Cl^- - (Na^+ + K^+)}{(SO_4^{2+} + HCO_3^- + CO_3^{2-} + NO_3^-)} \qquad (8)$$

8

2.0 Results and Discussion

Results of the in-situ measurements and laboratory analysis obtained for the physicochemical parameters are presented (Table 1 and 2). Thus, pH has no unit; EC is measured in µS/cm; TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^- and NO_3^- are measured in mg/l; Pb, Cd, Mn, Fe, Zn, and Cr are measured in µg/l.

3.1 Physical and chemical parameters

The statistical summary of physical parameter (EC, TDS and pH) for the groundwater samples from the study area is presented (Table 3). EC of the groundwater ranges from 29.10 to 213.00 µS/cm, with a mean value of 90.61 µS/cm. TDS values range between 18.00 and 121.00 mg/l, with a mean value of 64.40 mg/l.

The pH values are in the range of 5.80 to 6.90, and an average of 6.41. Based on their mean values, physical parameters measured from the samples analyzed in situ are below the permissible standard according to WHO (2022). Since EC values are < 1000 µS/cm, groundwater within the area under investigation indicates 'very weakly mineralized water' (Detay and Carpenter 1997).

Table 1: Results of laboratory analysis on physical parameters and major ions in groundwater

Sample code	EC	TDS	PH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_3^{-}
GW01	135.10	84.00	6.60	40.00	30.00	0.15	3.50	208.00	27.00	816.00	6.35
GW02	134.90	57.00	6.30	48.00	10.00	5.15	1.80	180.00	27.00	720.00	7.70
GW03	213.00	110.00	6.60	48.00	12.00	1.51	1.70	454.00	24.80	1520.00	0.39
GW04	204.00	121.00	6.50	40.00	17.00	0.70	6.00	320.00	27.00	960.00	0.39
GW05	33.70	101.00	6.40	56.00	8.00	1.10	5.20	265.00	31.00	120.00	0.38
GW06	49.00	102.00	6.30	64.00	11.00	0.50	3.60	170.00	33.00	152.00	0.35
GW07	60.10	106.00	6.80	68.00	12.00	1.30	6.38	150.00	41.00	336.00	0.34
GW08	59.20	18.00	6.90	31.00	8.00	1.84	5.70	179.00	41.60	296.00	0.37
GW09	29.10	19.00	6.70	44.00	20.00	2.01	3.50	189.00	40.50	416.00	0.97
GW10	40.20	23.00	6.50	45.00	16.00	1.38	2.70	511.00	42.80	240.00	0.70
GW11	43.10	32.00	6.10	24.00	14.00	1.17	2.60	504.00	31.00	1000.00	1.73
GW12	54.30	19.00	6.00	42.00	12.00	1.82	2.00	142.00	32.60	368.00	0.62
GW13	56.00	18.00	5.80	55.00	13.00	1.83	3.18	236.00	24.00	488.00	1.42
GW14	60.30	37.00	6.20	54.00	13.00	1.91	2.70	224.00	25.00	624.00	1.42
GW15	187.20	119.00	6.50	40.00	12.00	1.38	10.30	340.00	27.00	1360.00	0.39

Table 2: Results of laboratory analysis on heavy metals in groundwater

Code	Pb	Cd	Mn	Fe	Zn	Cr
GW01	0.00001	0.00006	0.00064	0.01620	0.00020	0.00001
GW02	0.00002	0.00009	0.00078	0.00490	0.00020	0.00006
GW03	0.00001	0.00005	0.00068	0.01240	0.00008	0.00011
GW04	0.00004	0.00031	0.00081	0.01420	0.00041	0.00049
GW05	0.00002	0.00032	0.00030	0.00980	0.00007	0.00055
GW06	0.00004	0.00003	1.00012	0.01170	0.00001	0.00031
GW07	0.00004	0.00004	0.00083	0.01380	0.00031	0.00003
GW08	0.00004	0.00009	0.00073	0.01460	0.00055	0.00001
GW09	0.00002	0.00010	1.00030	0.00990	0.00009	0.00010
GW10	0.00003	0.00011	1.00013	0.01520	0.00003	0.00002
GW11	0.00001	0.00039	0.00093	0.01050	0.00121	0.00004
GW12	0.00002	0.00004	0.00095	0.00800	0.00117	0.00001

GW13	0.00001	0.00051	0.00087	0.01210	0.00083	0.00002
GW14	0.00002	0.00004	0.00094	0.01120	0.00044	0.00061
GW15	0.00004	0.00005	0.00080	0.01090	0.00068	0.00003

Table 3: Statistical summaries for the analyzed physicochemical parameters

Group	**Parameter**	**Minimum**	**Maximum**	**Mean**	**WHO (2022)**
Physical parameters	EC	29.10	213.00	90.61	**1000.00**
	TDS	18.00	121.00	64.40	**500.00**
	PH	5.80	6.90	6.41	**7.00**
Major cations	Ca^{2+}	24.00	68.00	46.60	**200.00**
	Mg^{2+}	8.00	30.00	13.87	**50.00**
	Na^{+}	0.15	5.15	1.58	**200.00**
	K^{+}	1.70	10.30	4.06	**12.00**
Major aions	Cl^{-}	142.00	511.00	271.47	**250.00**
	SO_4^{2-}	24.00	42.80	31.69	**250.00**
	HCO_3^{-}	120.00	1520.00	627.73	**500.00**
	NO_3^{-}	0.34	7.70	1.57	**50.00**
Heavy metals	Pb	1.00E-05	4.00E-05	2.00E-05	**0.01**
	Cd	3.00E-05	5.10E-04	1.50E-04	**0.00**
	Mn	3.00E-04	1.00E+00	2.01E-01	**0.08**
	Fe	4.90E-03	1.62E-02	1.17E-02	**0.30**
	Zn	1.00E-05	1.21E-03	4.20E-04	**3.00**
	Cr	1.00E-05	6.10E-04	1.60E-04	**0.05**

Note: All values are measures in µg/l

Also, variation in the EC may be due to factors such as ion exchange, precipitation, dissolution, evaporation, silicate weathering, carbonate weathering, redox processes, and anthropogenic activities (Ekwere *et al.*, 2023). The amount of Ca^{2+} in the groundwater samples varies between 24.00 to 68.00 mg/l with a mean value of 46.60 mg/l, while for Mg^{2+} it ranges from 8.00 to 30.00 mg/l with an average value of 13.87 mg/l. The concentration of Na^{+} varies from 0.15 to 5.15 mg/l with a mean of 1.58 mg/l, while K^{+} varies from 1.70 to 10.30 mg/l, with a mean value of 4.06 mg/l. Hitherto, the concentration values obtained for the major cation (Table 3) revealed that they are all below the permissible limit of WHO (2022). Also, Cl^{-} ranges between 142.00 and 511.00 mg/l, with a mean of 271.47 mg/l, while the concentration of HCO_3^{-} ranged from 120.00 to 1520.00, mg/l with a mean concentration of 627.73 mg/l. The concentration of SO_4^{2-} ranged from 24.00 to 42.80 mg/l, and a mean value of 31.69 mg/l, while NO_3^{-} concentration varied between 0.34 and 7.70 mg/l, with mean value of 1.57 mg/l. Concentration values of the major anions (Table 3) showed that only Cl^{-} and HCO_3^{-} recorded mean values that exceeded the permissible limit as prescribed by the World Health Organization. According to Abugu *et al.* (2021), the higher concentrations of Cl^{-} and HCO_3^{-} ions resulted from the relatively weak acid nature of the groundwater as recorded by the pH values obtained.

A descriptive statistical analysis of heavy metal concentrations in groundwater from the study area is presented in Table 3. The results indicate that the relative abundance of heavy metals in groundwater samples from parts of

Calabar follows the order: Mn > Fe > Zn > Cr > Cd > Pb, based on mean concentrations (Table 3). The analysis shows that only manganese (Mn) exceeded the permissible limit set by WHO (2022), while the concentrations of Fe, Zn, Cd, and Pb remained well below the acceptable standard. According to Takeda (2003), excessive concentrations of Mn can impair neurological function. Evidence from occupational exposure shows that miners and welders exposed to airborne manganese for extended periods developed neurological disorders such as Parkinson's disease. The distribution of these heavy metals across the study area is illustrated (Fig. 2).

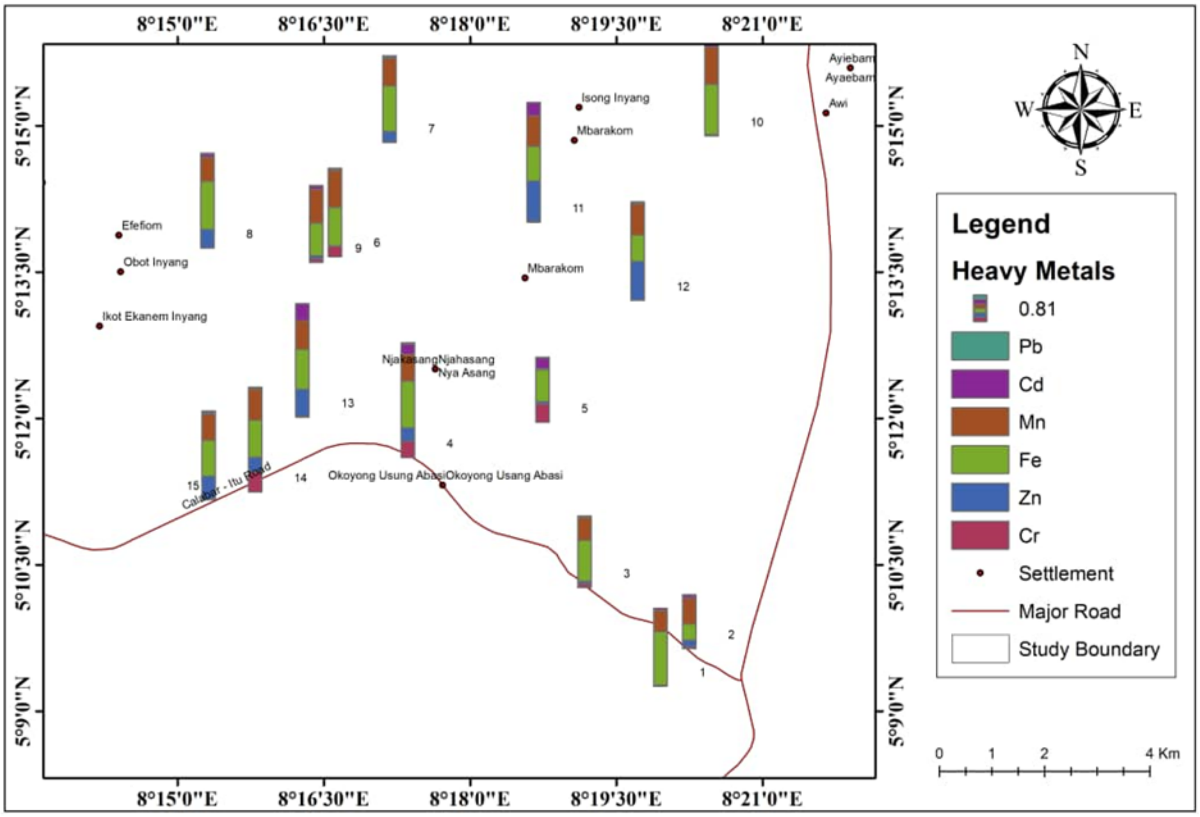

Figure 2: Concentration point map of analyzed groundwater sample across the study area

Hydrochemical Facies and ion sources

The Piper diagram (Fig. 3) revealed that the hydro-chemical facies for groundwater in this study is predominantly Ca^{2+} - Mg^{2+} - HCO_3^- water type, and Ca^{2+} - Mg^{2+} - SO_4^{2-} water type. This explains that the groundwater in the study area is of meteoric origin and fresh, probably due to the infiltrating rain water during recharge that results in the dissolution of the underlying carbonate rock (Appelo and Postma, 1993; Musa *et al.*, 2014; Edet and Okereke, 2022; Kudamnya *et al.*, 2025). Other means could probably be a result of weathering, leaching, and cation exchange (Farid et al. 2015). The dominance of Ca^{2+} over Na^+ results from reverse ion exchange (Akanbi, 2016). The ions Na^+, K^+, Ca^{2+}, Mg^{2+}, and HCO_3^- are derived from the weathering of minerals such as feldspars and other silicate minerals. Additionally, the presence of limestone and dolomite rocks in the Calabar Flank contributes to the release of Ca^{2+}, Mg^{2+}, and bicarbonate (HCO_3^-) ions. The use of fertilizers can sometimes increase the levels of nitrate (NO_3^-) and potassium (K^+) in groundwater. Computed values of the chloro-alkaline index (CAI) revealed that both CAI-1 and CAI-2 values were consistently positive across all sampled locations during the study. This indicates that reverse ion exchange processes are occurring, wherein Na^+ and K^+ are entirely exchanged for Ca^{2+} and Mg^{2+} in the groundwater (Agyemang, 2020).

The Gibbs diagram was produced using the major anion and cation constituents, respectively (Fig. 4a and b), revealed that the majority of the samples analyzed plotted within the rock-water dominance field, while the others were released during recharge by precipitation.

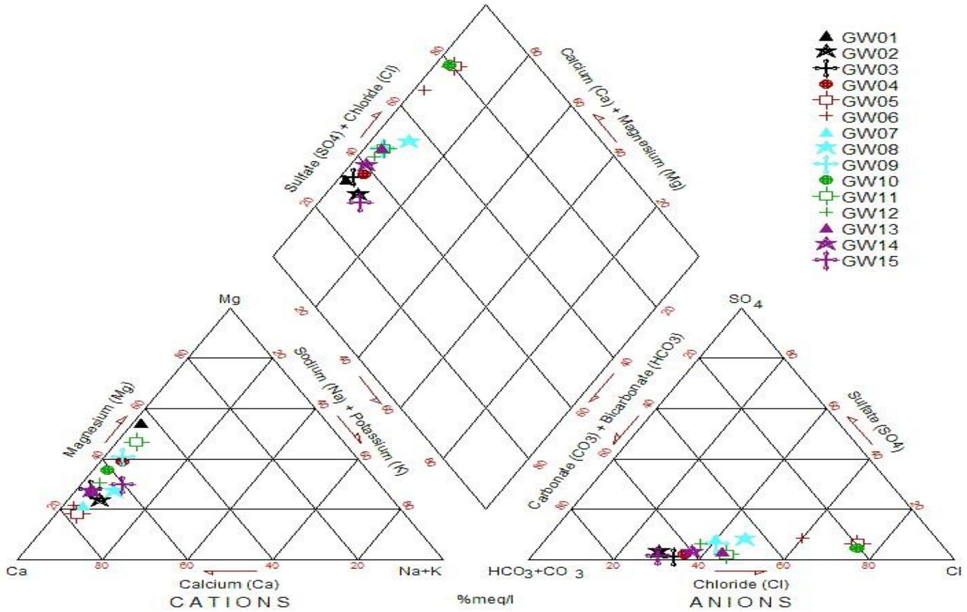

Figure 3: Piper Diagram for identifying hydrochemical facies in the study area

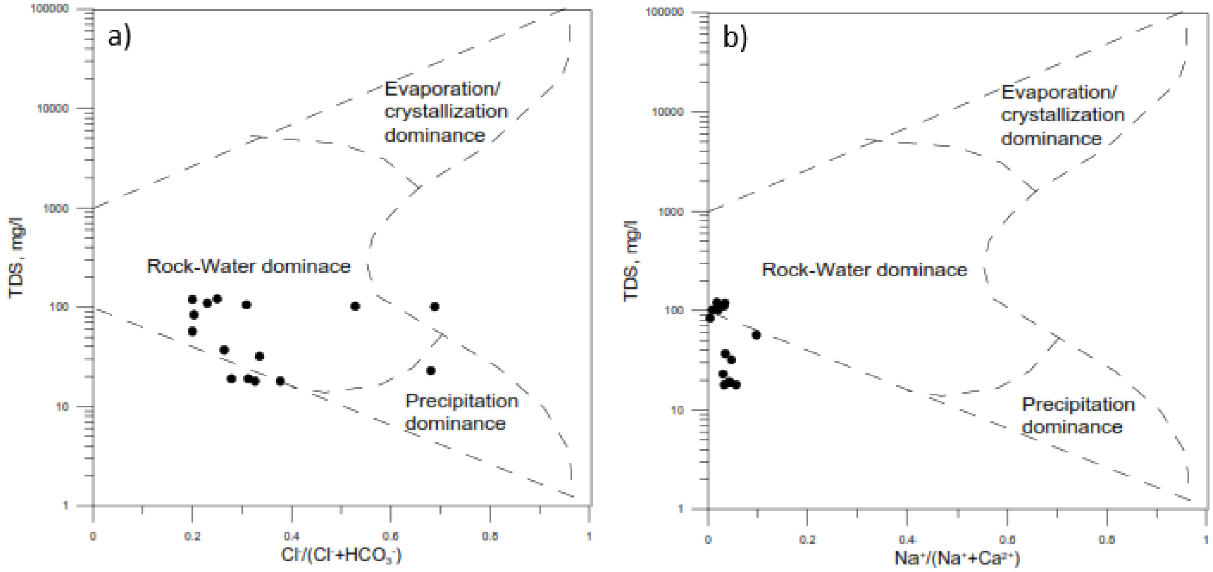

Figure 4: Gibbs Plot for the groundwater samples a. – TDS vs Cl-/(Cl-+HCO3-); b. – TDS vs Na+/(Na++Ca2+)

Therefore the primary process responsible for the release of ions into the groundwater, as identified in this study, is the weathering of the host rock through rock-water interactions. This process leads to the enrichment of ion constituents along the groundwater flow path within the subsurface (Ochelebe and Kudamnya, 2022). The contribution of rainfall to the water's chemistry indicates that these anions may originate from the dissolution of carbon dioxide (CO_2) within the soil zone and the atmosphere (Abugu et al., 2021; Edet and Okereke, 2022).

3.2 Water quality for domestic use

Groundwater quality determines its suitability for use based on specific criteria. The physical and chemical parameters of groundwater in the study area were compared with the WHO standard guideline values recommended for drinking and other domestic uses. Additionally, the Water Quality Index (WQI) was determined and classified. The WQI was computed using an indexical approach that applied the weighted arithmetic index method to approximately fifteen (15) physicochemical parameters, including EC, TDS, pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Pb, Cd, Mn, Fe, Zn, and Cr. The order of abundance for the major ionic species was observed as follows:

- **Cations:** $Ca^{2+} > Mg^{2+} > K^+ > Na^+$
- **Anions:** $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$

From the computed WQI values, groundwater quality in all sampled locations was categorized as "excellent." The WQI ranged from 1.07 (GW14) to 36.00 (GW10). The analysis of physicochemical parameters showed that all concentration levels were below the permissible limits established by WHO (2022), confirming the suitability of groundwater for consumption and domestic purposes (Table 2).

The findings reveal that the WQI model effectively determined the water quality status of all the samples. The dominance of Ca^{2+} and Mg^{2+} among cations, along with HCO_3^- and Cl^- among anions, reflects the geochemical processes influencing groundwater chemistry, such as rock-water interactions and mineral dissolution. The observed deviations in the order of anion abundance at specific locations (GW05, GW06, and GW10) suggest localized variations in groundwater chemistry, possibly due to differences in geological formations or anthropogenic influences.

The WQI classification further substantiates the excellent quality of groundwater in the study area, with all samples falling well within the acceptable limits for drinking and domestic use. The low WQI values highlight the absence of significant contamination and the effectiveness of natural filtration processes within the aquifer system. These results underscore the reliability of the WQI model in assessing groundwater quality and provide a robust framework for future groundwater quality monitoring.

Table 3: Major ionic constituents in groundwater and computed WQI and their classes

Code	Water type	Order of dominance for major ions		CAI 1	CAI 2	WQI	
		Cation	Anion			Value	Class
GW01	Groundwater	Ca2+ > Mg2+ > K+ > Na^+	$Cl^- > HCO_3^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.98	0.24	0.24	Excellent
GW02	Groundwater	$Na^+ > Ca^{2+} > Mg^{2+} > K^+$	$Cl^- > HCO_3^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.96	0.23	0.24	Excellent
GW03	Groundwater	$Na^+ > Ca^{2+} > Mg^{2+} > K^+$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.99	0.29	0.29	Excellent
GW04	Groundwater	$Na^+ > Ca^{2+} > Mg^{2+} > K^+$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.98	0.32	0.32	Excellent

GW05	Groundwater	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	$Cl^- > HCO_3^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.98	1.71	1.75	Excellent
GW06	Groundwater	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	$Cl^- > HCO_3^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.98	0.90	0.92	Excellent
GW07	Groundwater	$Na^+ > Ca^{2+} > Mg^{2+} > K^+$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.95	0.38	0.40	Excellent
GW08	Groundwater	$Na^+ > Ca^{2+} > Mg^{2+} > K^+$	$Cl^- > HCO_3^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.96	0.51	0.53	Excellent
GW09	Groundwater	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	$Cl^- > HCO_3^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.97	0.40	0.41	Excellent
GW10	Groundwater	$Ca^{2+} > Mg^{2+} > Na^+ > K^+$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.99	1.79	1.80	Excellent
GW11	Groundwater	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.99	0.48	0.49	Excellent
GW12	Groundwater	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.97	0.34	0.35	Excellent
GW13	Groundwater	$Na^+ > Ca^{2+} > Mg^{2+} > K^+$	$Cl^- > HCO_3^- > NO_3^- > CO_3^{2-} > SO_4^{2-}$	0.98	0.45	0.46	Excellent
GW14	Groundwater	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.98	0.34	0.34	Excellent
GW15	Groundwater	$Ca^{2+} > Na^+ > Mg^{2+} > K^+$	$HCO_3^- > Cl^- > CO_3^{2-} > NO_3^- > SO_4^{2-}$	0.97	0.24	0.25	Excellent

3.3 Groundwater chemistry

The correlation matrix was employed to assess the strength and direction of the linear relationships between pairs of variables. Key findings include TDS and EC (+0.64): A strong positive correlation, indicating that EC is significantly influenced by TDS; EC and HCO_3^- (+0.83): A very strong correlation, suggesting HCO_3^- as a major contributor to groundwater ion content; TDS and K^+ (+0.51): A strong relationship, highlighting K^+ as a contributor to TDS; SO_4^{2-} and NO_3^- (+0.46): A moderate positive correlation, suggesting a shared source, such as agricultural runoff or industrial pollution; NO_3^- and Na^+ (+0.50): A strong association, likely stemming from agricultural activities, including fertilizer application; Pb and pH (+0.48): A positive correlation, indicating higher Pb solubility at elevated pH levels; Pb and SO_4^{2-} (+0.46): A moderate correlation, hinting at geogenic and anthropogenic origins; Zn and Mn (-0.49): A negative correlation, suggesting differing behaviors or sources; Zn and pH (-0.55): A negative relationship showing decreased Zn solubility at higher pH levels; Pb and NO_3^- (-0.42): A negative correlation, suggesting different sources or processes influence these parameters.

The correlations reveal important insights into the sources and processes influencing groundwater chemistry. The strong relationships among TDS, EC, K^+, and HCO_3^- indicate that these ions are largely derived from the chemical weathering and dissolution of underlying carbonate or felsic rocks. In some cases, human activities may also contribute (Abugu et al., 2021; Edet and Okereke, 2022; Ochelebe and Kudamnya, 2022). Also, the strong correlation between SO_4^{2-} and NO_3^- suggests agricultural runoff and industrial pollution as common sources of these ions, with fertilizer use being a significant contributor. The relationship between NO_3^- and Na^+ further emphasizes the role of agricultural practices, particularly fertilizer application, in influencing groundwater quality. A correlation between Pb and pH implies that Pb becomes more soluble at higher pH levels, potentially due to geogenic or anthropogenic factors. Similarly, the relationship between Pb and SO_4^{2-} suggests a combination of natural and human-induced sources. The negative correlations observed between Zn and Mn, and HCO_3^- and SO_4^{2-}, highlight distinct geochemical behaviors, competitive processes, or variations in environmental conditions. For instance, the solubility of Zn decreases as pH increases, leading to precipitation at higher pH levels. The negative relationship between Pb and NO_3^- suggests different sources or mechanisms influencing these parameters, possibly separating natural geogenic processes from anthropogenic contributions. The findings underscore the combined effects of natural geochemical processes and human activities, such as indiscriminate open defecation, fertilizer application, and pesticide use, on groundwater chemistry (Eldaw et al., 2021; Edet and Okereke, 2022). These correlations help to elucidate the complex interplay of factors affecting water quality in the study area.

Table 4: Pearson correlation matrix of the physicochemical parameters analyzed in groundwater samples

	EC	**TDS**	**pH**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**Cl^-**	**SO_4^{2-}**	**HCO_3^-**	**NO_3^-**	**Pb**	**Cd**	**Mn**	**Fe**	**Zn**	**Cr**
EC	1																
TDS	**0.64**	1															
PH	0.21	0.32	1														
Ca^{2+}	-0.18	0.34	-0.25	1													
Mg^{2+}	0.16	-0.01	0.15	-0.23	1												
Na^+	0.02	-0.34	-0.15	0.01	-0.38	1											
K^+	0.27	**0.51**	**0.41**	-0.01	-0.12	-0.3	1										
Cl^-	0.24	0.06	-0.05	**-0.42**	0.05	-0.21	-0.08	1									
SO_4^{2-}	**-0.57**	-0.32	**0.54**	-0.01	-0.07	-0.07	0.10	-0.09	1								
HCO_3^-	**0.83**	**0.40**	0.03	**-0.40**	0.18	0.01	0.14	**0.49**	**-0.60**	1							
NO_3^-	0.19	-0.08	-0.10	-0.13	**0.40**	**0.50**	-0.35	-0.20	-0.33	0.14	1						
Pb	0.07	0.35	**0.48**	0.19	-0.32	-0.15	**0.68**	-0.21	**0.46**	-0.24	**-0.42**	1					
Cd	-0.15	-0.16	**-0.51**	-0.18	-0.07	-0.09	-0.04	0.30	-0.27	-0.02	-0.09	-0.34	1				
Mn	**-0.41**	-0.20	0.15	0.20	0.17	-0.13	-0.18	0.08	**0.55**	**-0.43**	-0.20	0.22	-0.23	1			
Fe	0.10	0.17	**0.46**	0.05	**0.45**	**-0.73**	0.26	0.23	0.25	-0.01	-0.27	0.24	-0.01	0.1	1		
Zn	-0.11	-0.39	**-0.55**	**-0.49**	-0.15	0.01	0.03	0.06	-0.19	0.19	-0.12	-0.19	0.37	**-0.49**	-0.21	1	
Cr	0.01	0.33	-0.10	0.32	-0.18	-0.18	0.04	-0.07	-0.31	-0.13	-0.23	0.12	0.13	-0.04	-0.06	-0.29	1

The cluster analysis revealed that there are several key hydrogeochemical processes influencing the physicochemical parameters, they include mineral dissolution, ion exchange and anthropogenic influences. Furthermore, EC, TDS and HCO_3^- clustering may suggest a possible control by a common process like dissolution of minerals (weathering). The cluster of EC, TDS, K^+, Pb, Cl^-, SO_4^{2-}, NO_3^- and pH is likely an indication of anthropogenic inputs (industrial waste and agricultural runoff) which may result in pollution of the groundwater. The presence of Pb suggests industrial contamination, while K^+, SO_4^{2-} and Cl^- may be controlled from agricultural practices or natural weathering processes. These ions can possibly be mobilized from mineral weathering in soils or rock, especially in silicate minerals. The pH influences cation exchange processes, as well as the solubility and mobility of metals like Pb, and may result in processes altering the chemical balance. Also, the clustering of Na^+, Mn, Fe, Mg^{2+} and NO_3^- could be related to both natural mineral dissolution and anthropogenic sources such as agricultural runoff or industrial activities. These assertions were corroborated by previous studies (Ekwere et al. 2023; Thomas 2023). The isolated groups of heavy metals Cd, Zn, Cr suggests localized contamination or pollution sources influencing the groundwater chemistry.

3.4 Extent of groundwater deterioration

The results obtained from the laboratory results was used to compute contamination factor (C_f) and hereby presented (Table 5). In addition, values of the degree of contamination (C_d) was also evaluated for each water samples with respect to the heavy metals (Pb, Cd, Mn, Fe, Zn, and Cr) analyzed using the values obtained for the C_f. Generally, in-terms of the C_f, groundwater samples revealed *low contamination* with respect to the heavy analyzed in all the locations. Similarly, in-terms of the C_d, it was observed that the entire groundwater samples analyzed revealed low degree of contamination. However, C_f computed for Mn revealed higher values at few locations which indicated *moderate contamination* at GW06, GW09 and GW10 with respect to the metal. Interestingly, the PLI computed revealed elevated levels at same locations (GW06, GW09 and GW10) where C_f indicated moderate degree of contamination with respect to Mn. The PLI indicated values 0.5633, 0.5448 and 0.5225 respectively for the locations, as they tend towards baseline pollution level (Table 6).

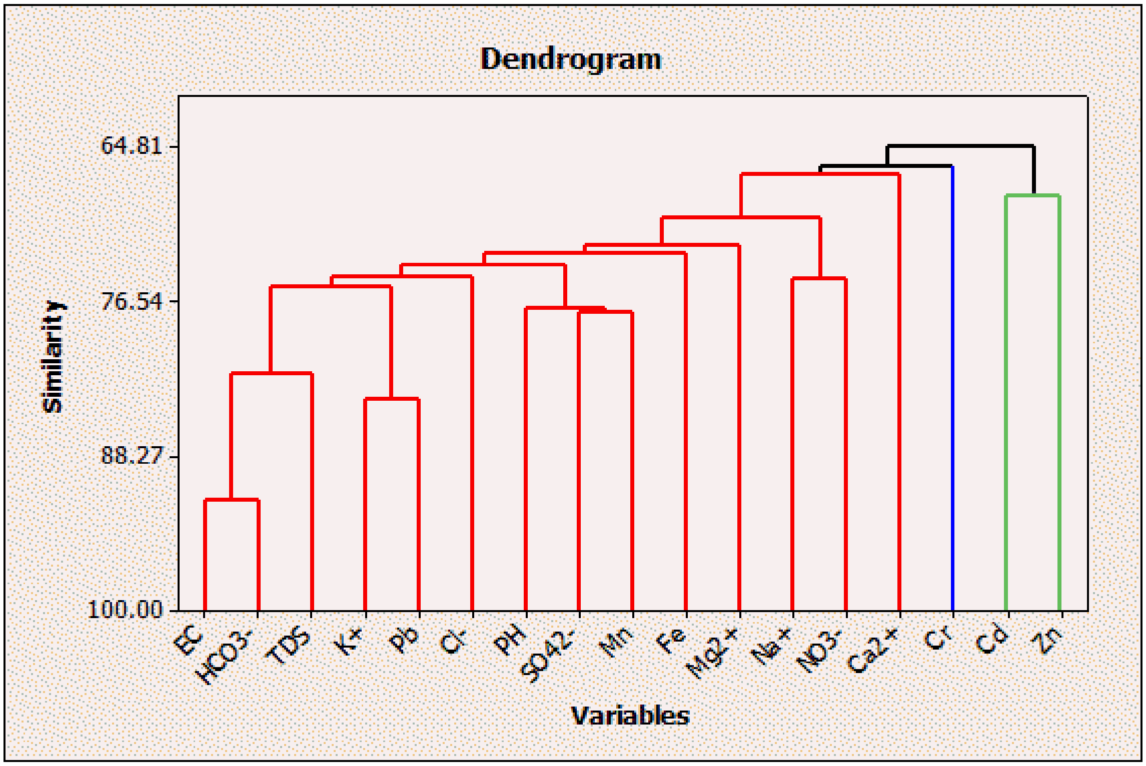

Figure 3: Dendrogram of cluster analysis for the analyzed groundwater physicochemical parameters

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Table 5: Computed contamination factor (C_f) in groundwater from the study atrea

Code	**Contamination Factor, C_f**					
	Pb	**Cd**	**Mn**	**Fe**	**Zn**	**Cr**
GW01	0.0010	0.0200	0.0080	0.0540	0.0001	0.0002
GW02	0.0020	0.0300	0.0098	0.0163	0.0001	0.0012
GW03	0.0010	0.0167	0.0085	0.0413	0.0000	0.0022
GW04	0.0040	0.1033	0.0101	0.0473	0.0001	0.0098
GW05	0.0020	0.1067	0.0038	0.0327	0.0000	0.0110
GW06	**0.0040**	**0.0100**	**12.5015**	**0.0390**	**0.0000**	**0.0062**

GW07	0.0040	0.0133	0.0104	0.0460	0.0001	0.0006
GW08	0.0040	0.0300	0.0091	0.0487	0.0002	0.0002
GW09	**0.0020**	**0.0333**	**12.5038**	**0.0330**	**0.0000**	**0.0020**
GW10	**0.0030**	**0.0367**	**12.5016**	**0.0507**	**0.0000**	**0.0004**
GW11	0.0010	0.1300	0.0116	0.0350	0.0004	0.0008
GW12	0.0020	0.0133	0.0119	0.0267	0.0004	0.0002
GW13	0.0010	0.1700	0.0109	0.0403	0.0003	0.0004
GW14	0.0020	0.0133	0.0118	0.0373	0.0001	0.0122
GW15	0.0040	0.0167	0.0100	0.0363	0.0002	0.0006
Minimum	0.0010	0.0100	0.0038	0.0163	0.0000	0.0002
Maximum	0.0040	0.1700	12.5038	0.0540	0.0004	0.0122
Mean	0.0025	0.0496	2.5082	0.0390	0.0001	0.0032
Class	**LC**	**LC**	**MC**	**LC**	**LC**	**LC**

***Note**: LC – Low contamination; MC – Moderate contamination*

Table 6: Evaluated values of degree of contamination (C_d) with their corresponding pollution load index (PLI)

Code	C_d		PLI	
	Values	Class	Values	Class
GW01	0.0438	Low degree of contamination	0.6665	No pollution
GW02	0.0334	Low degree of contamination	0.6370	No pollution
GW03	0.0303	Low degree of contamination	0.6267	No pollution
GW04	1.0199	Low degree of contamination	1.1262	Progressive deterioration
GW05	0.0338	Low degree of contamination	0.6382	No pollution
GW06	0.0720	Low degree of contamination	0.7240	No pollution
GW07	1.0542	Low degree of contamination	1.1324	Progressive deterioration
GW08	1.0452	Low degree of contamination	1.1308	Progressive deterioration
GW09	0.0596	Low degree of contamination	0.7014	No pollution
GW10	0.0517	Low degree of contamination	0.6851	No pollution
GW11	0.0465	Low degree of contamination	0.6732	No pollution
GW12	0.0474	Low degree of contamination	0.6752	No pollution

GW13	0.0458	Low degree of contamination	0.6714	No pollution
GW14	3.4330	Low degree of contamination	1.3786	Progressive deterioration
GW15	0.0000	Low degree of contamination	0.0000	No pollution

4.0 Conclusion

In this study, an attempt was made to analyze the physicochemical constituent of groundwater in parts of the Calabar Flank, southeast Nigeria, in order to evaluate it chemistry and also to investigate the extent of pollution of the water source (if any). The constituent analyzed are EC, TDS, pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-}, Pb, Cd, Mn, Fe, Zn, and Cr. Groundwater in the study area was observed to be weakly acidic, since pH values ranges from 5.80 to 6.90. Major cations analyzed revealed that their concentration are below the permissible limit of the World Health Organization, while this observation was similar with respect to the anions except for Cl- and HCO3-. The findings of the study indicate that Ca^{2+} and HCO_3^{-} are respectively the dominant major cation and anion in the area. The relative abundance the major cations is in the order $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$; the major anionic constituents dominantly occur in the order $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$, although it was different in few locations in which the order was $Cl^{-} > HCO_3^{-}$ $SO_4^{2-} > NO_3^{-}$; in-terms of the heavy metals analyzed, they occur in the order Mn > Fe > Zn > Cr > Cd > Pb. The hydrochemical facies/groundwater type in the study area include Ca^{2+}–Mg^{2+}–HCO_3^{-} water type, and Ca^{2+}-Mg^{2+}-SO_4^{2-} water type. The WQI revealed that the groundwater in the study area is excellent for drinking and other domestic use. CAI-1 and CAI-2 showed that the reverse ion exchange process is dominant since all the values obtained were positive.

Generally, reverse ion exchange processes, anthropogenic pollution (industrial waste and agricultural runoff) and weathering of rocks are the significant regulating factors controlling groundwater chemistry in the study area. Heavy metal contamination of the groundwater is low, except for Mn which showed moderate contamination. Pollution load index (PLI) revealed that 73% of the sampled analyzed had ‘no pollution’, while 27% indicated progressive deterioration probably due to elevation concentration of the Mn. It is recommended that the water should be treated before they are utilized, and seasonal monitoring during both wet and dry seasons should be done, since this study only sampled the water in the dry season.

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Compliance with Ethical Standards Declaration

Ethical Approval

Not Applicable

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Authors' Contribution

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