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Evaluation of hydro-chemical facies and surface water quality dynamics using multivariate statistical approaches in Southern Nigeria

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The geochemical and chemical constituents of river water quality could be influenced by human activities and organic processes like water interacting with the lithogenic structure that the river flows through. Evaluating evidence based primary root of the predominant pollutant ions, their interactions as well as the factors controlling their dominance is crucial in studies regarding water environment and hydrology especially as most studies focus on theoretical methods. In order to understand the water cycle, safeguard surface water resources, and preserve the human environment, this study evaluated surface water hydro-chemical facies, quality dynamics, and portability in southern Nigeria using multivariate statistical approaches by analyzing selected hydro-chemical characteristics as indicators of pollution along the river during wet and dry seasons. Twenty water samples were taken, analyzed, and subjected to mathematical statistics: Gibbs plot, trilinear piper analysis, stiff pattern analysis, ionic scatter analysis, correlation, and principal component analysis. Result of surface water recorded mean pH ranges from 4.8 for wet season and 5.3 for dry season, above the WHO, and during dry season TDS, $Mg^{2+,}$ Pb, and Cd were above the WHO limits, respectively. Abundance of cation and anion in surface water was in a decreasing trend of: $HCO_3 > Ca^{2+} > Mg^{2+} > Cl^- > Na^+ > SO_4^{2-} > K+ > NO_3^-$. Trilinear plot, stiff pattern, and Gibbs ratio indicated hydrochemical facie of water dominated by calcium bicarbonate ($Ca\text{-}HCO_3$) water type. From plots and ionic ratio, the major hydrochemical process of water chemistry during wet and dry seasons was rock-water interaction arising majorly from weathering processes. Ionic ratios of Ca^{2+} and Mg^{2+}[1], Ca^{2+} and HCO^{2-} [1:2], $Ca^{2+} + Mg^{2+}$ and $HCO^{3-} + SO4^{2-}$ [1:1], revealed dissolution of dolomite as their common origin, with total cations in wet and dry seasons ranging between 43 and 57% and total anions: 37.3–62.7, with dry season dominance. The overall WQI of the river seemed good quality due to rapid flow and self-purification of the river but may be harmful in the future. It was recommended that constant surveillance and monitoring of human activities along waterways be enforced in order to ensure that undesirable pollution levels don't occur in the river.

Keywords Hydrochemical facies, Anion and Cation, Anthropogenic Action, Multivariate Analysis

Surface water includes waters in the stream or stream waters, river water, and even spring water. It also includes lake water, even pond water, as well as water in reservoirs originating from events of atmospheric precipitation/rainfall on watershed catchments flowing through river channels and streams and eventually flushing into ponds and lakes[1] The rivers are one of the examples of surface water that constitutes a source of water for the purposes of agriculture, human consumption, industry, and domestic use globally[2–4]. However, global water quality has been on the decline over decades due to natural and human impacts[5].

The river quality is reduced by both natural and human interactions with the river. Such human endeavors as the discharge of domestic, industrial, and agricultural drainage waters into the river system[6], remain the main causes of river pollution[7–9]. Human activities influence the geochemical parameters, chemical constituents of river basins[10], and organic processes like water interacting with the lithogenic structure that the river flows through[3,11], thereby degrading river surface water quality and making it unfit for human consumption[12–14].

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Thus, it is always pertinent to evaluate river surface water quality in order to ensure the safety of human consumption and health. The evaluation aims to pinpoint the causes of water pollution and create a plan for managing water sources sustainably while preserving and advancing human health and other forms of social and economic development[15]. Therefore, the evaluation of hydrochemical, hydrological, and hydrodynamic characteristics of river water quality becomes veritable indicators of assessment of river water quality.

Hydro-chemical characteristics include those of hydrology and hydrodynamics, particularly in water systems such as lakes and lagoons, as well as overall coastal water systems[16,17] as well as in streams and rivers[16–18]. Hydrochemical evaluation of river water entails investigation into the likely relationship that exists among chemical constituents, natural environment, man's influence, land degradation, climate change, and spatio-temporal variations in water quality. Accordingly[19–25], suggested the use of hydrochemical indices such as ions to evaluate geogenic or anthropogenic inputs to the surface water chemistry of river basins, which provides ecosystem function to man and ensures aquatic life survival. In order to understand the water cycle, safeguard surface water resources, and preserve the human environment, it is crucial to study the hydrochemical properties of rivers and lakes. Additionally, revealing the primary root of the predominant ions and the factors controlling their dominance is also of paramount importance in studies regarding water environment and hydrology[26], especially as many of the studies[19–22] emphasize the use of approaches that employ theoretical methods, but studies of this dimension are scarce. Therefore, evaluating evidence based primary root and source of the predominant ions and their interactions using multiple analytical tools such as Stiff, Gibbs, Ionic scatter etc. could help gain more understanding of river pollution dynamics.

Thus, there is a need for up-to-date/regular and conventional hydrological monitoring and assessment of river systems so as to ensure adequate guard against deterioration, control, and management of river systems[9,27], given their substantial ecosystem services to humans, and the environment generally, especially for their use in agricultural and food production as well as human consumption[28]. Thus, thorough surface river water quality assessment and monitoring is a veritable procedure that could be adopted in the evaluation of river systems for suitability of purpose such as irrigation purposes, consumption, and other purposes, as well as effective water resource management and safe guarding of aquatic life[29,30]. Hence, the objective of this study, which focused on the evaluation of the hydrochemical parameters of the Ethiope River and the susceptibility of river water quality to pollution using a conventional multi-statistical method of evaluation in the study area, and intended to investigate the underlying questions including: what are the predominant ions and where is their primary root? are they significantly interacting with river dynamics and flow to cause pollution in the study area?

Materials and methods

Study area

The River studied traversed between Ukwuani and Ethiope East Local Government Areas and lies within the central north part of Delta State in the south-south geopolitical zone of Nigeria. The coordinates in this part of Nigeria read between latitudes 5°40'6"N, 6°00'N and longitudes 5°39'5"E, 6°10'9"E (Fig. 1). The area, which is part of the Niger Delta region, is a hub for oil exploration and exploitation, together with the characteristic gas flaring activities and visibly seen pockets of industrialization all over the region. The tributaries flowing into and making up the river Ethiope together make up the main river servicing the area as it flows towards the south-west path all the way down to Igun before changing flow pathways towards the northwest into the Benin-Sapele river at Sapele before summarily draining into the Atlantic Ocean[19]. The river discharge is reflective of the rainfall pattern in the area with a lagging time of about 3months without any record of flood event in the upper and middle courses of the river implying that precipitation around the area produces significant infiltration rather than run-off. Ethiope river is located within the equatorial region, having two main significant climatic regimes namely the dry and wet seasons. The wet season usually runs from April to October while the dry season runs from November to March[25]. The mean yearly rainfall in the study area reads about 2800 mm, with varying optimum high temperatures ranging between 23°C and 37°C during the noontime and a minimum temperature ranging between 18°C and 22°C during the night time. The percentage amount of precipitation in the cloud (relative humidity) hovers around a high of 50–75%[25]. The geology of the Niger Delta, where the Ethiope River is located, has been described as comprising three (3) lithostratigraphic units: the Agbada, Akata, and Benin Formation. Six major geomorphic units have been identified (Fig. 2). Sediments of the Ethiope River belong to the Warri-Sombreiro Deltaic Plain. The groundwater level in this deltaic plain is typically between 0 and 5 m, and the soil is made up of a top layer of silty clay that is no thicker than 6 m[31]. Unregulated sand mining activities are also prevalent with the use of sand dredging machines for small-scale industries. Tourism and religious number of visitors to the area.

Economically, river Ethiope serves as a means of occupation and recreation in the area with significant activities like fishing, swimming, cloth washing and bathing going on the area. The river banks are dumped with substantial waste products which subjects the river to potential contamination especially during the raining season when it overflows its banks, bringing in agricultural by-products and chemical fertilizers and pesticides from the surrounding farmlands.

Surface water sampling techniques

The Ethiope river water samples were taken on purposive sampling bases bearing in mind locations with visible, varying kinds of human interactions with the river that may have an impact on the water chemistry (Table 1). Ten (10) locations were sampled and georeferenced (Table 1). A total of 200 samples were collected over the 10-month period of study, comprising 20 samples monthly. The samples were taken during dry and rainy periods of the year. The dry season sampling covered a period of 5 months (December 2022 to April 2023) while the wet season covered 5 months (June to October 2022). Sampling points were selected in towns along the river course where the river channel is accessible by foot as no canoes or boats traverse the river in its upper course.

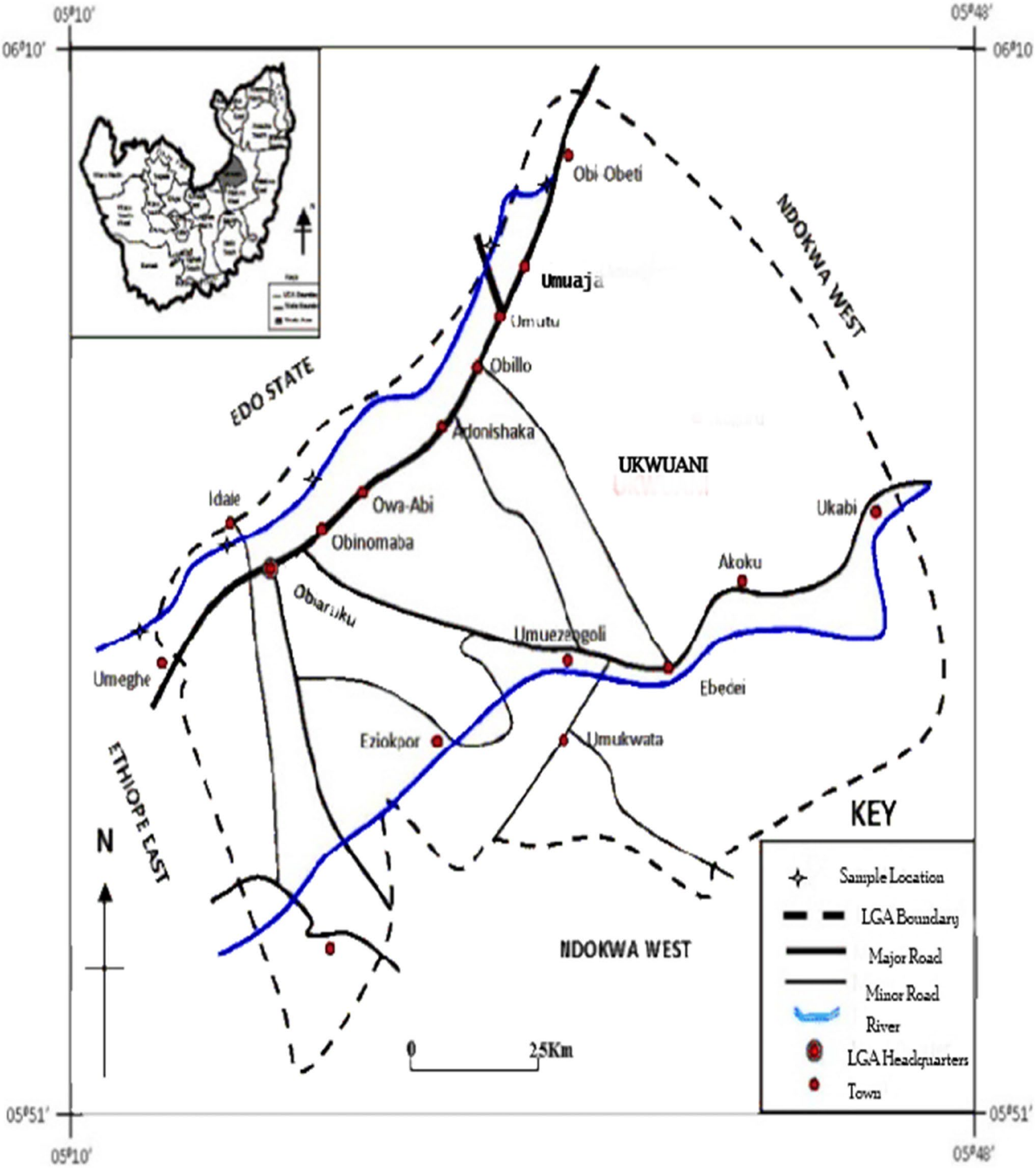


Figure 1. Map showing the study location and sampling points. (adapted from Nigerian Geological Agency[22]).

Surface water samples were collected by lowering a clean 1.5-liter sterilized plastic can in an upstream direction of the river and at a surface water layer depth of about 5 cm and allowing the can to fill after the plastic cans were neatly washed and disinfected using chromic acid. Afterwards, Whatman filtering was used in conjunction with 45 micrometer fiber glass to filter the retrieved samples. To preclude the possibility of adsorbed metals, 3.3 ml of HNO_3 was added to the water samples at the site to bring their pH down to 1.5 and for preservation. The samples were then shaken to combine, and they were left to stand for at least 15 h before taken to laboratory for analysis. Some of the water hydrochemical parameters viz. pH, Electrical conductivity (EC), temperature, alkalinity, total dissolved solid (TDS) were measured in-situ by immersion using portable

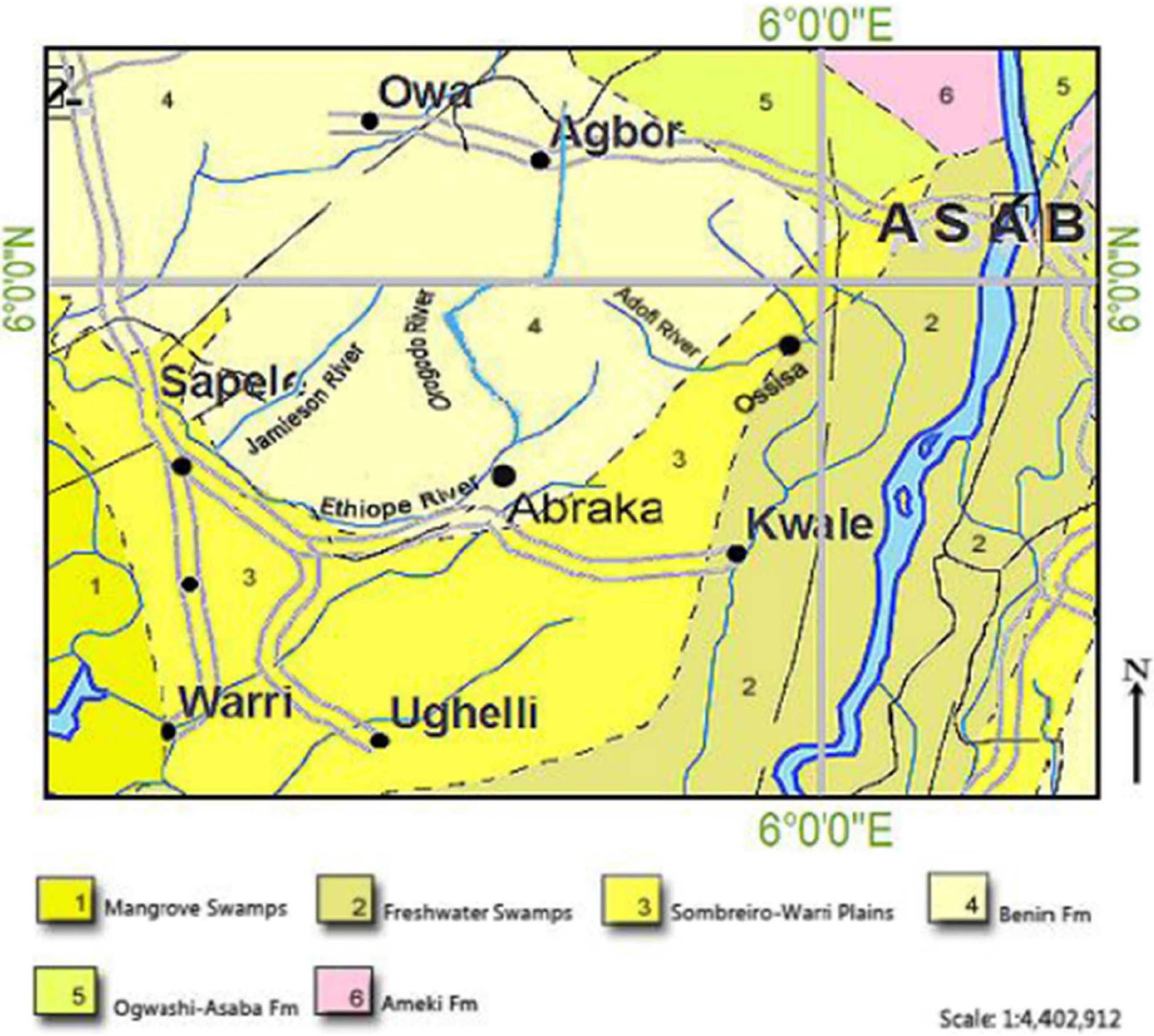


Figure 2. Map showing the geologic layout. (adapted from Nigerian Geological Survey Agency[22]).

Sample No	Sample Code	Location	Latitude/longitude	Activities
1	UMJ-1	Umuaja	Lat:5.94197;Long:6.23274	Tourism; Religious activity
2	UMT-1	Umutu	Lat:5.92376;Long:6.22156	Sand mining; Domestic waste dumping; Industrial activity
3	NNB-1	Obinomba	Lat:5.86627;Long:6.17509	Sand mining. Fish farming, Crude pipeline installation
4	OBK-1	Obiaruku	Lat:5.85321;Long:6.14523	Domestic activity(washing of clothes)
5	ABK-1	Abraka	Lat:5.82407;Long:6.10828	Sand mining
6	UMJ-2	Umuaja	Lat:5.94197;Long:6.23274	Tourism; Religious activity
7	UMT-2	Umutu	Lat:5.92376;Long:6.22156	Sand mining; Domestic waste dumping; Industrial activity
8	NNB-2	Obinomba	Lat:5.86627;Long:6.17509	Sand mining. Fish farming, Crude pipeline installation
9	OBK-2	Obiaruku	Lat:5.85321;Long:6.14523	Domestic activity (washing of clothes)
10	ABK-5	Abraka	Lat:5.82407;Long:6.10828	Sand mining

Table 1. GPS coordinates for the river water samples during dry and wet seasons events.

handheld multi-meter device. Samples were then transported upright to the laboratory in coolers packed with ice. Analytical procedures were in accordance with[32] specifications. Since there is considerable human activity at the source/origin of the Ethiope River[33], standard was considered as a control value for water samples.

Laboratory analysis for surface water samples

The hydro chemical parameters measured include anions, cations, water quality parameters and heavy metals. The anions determined include nitrates (NO_3^-), sulfates (SO_4^{2-}), chloride (Cl⁻), carbonates (CO_3^{2-}), and bicarbonates (HCO_3^-). Water quality parameters measured in situ include pH, electrical conductivity (EC), total dissolved solute (TDS), and total hardness, while major cations, viz., calcium (Ca^{2+}), sodium (Na^+), magnesium (Mg^{2+}), and potassium (K+), were also determined. In addition, heavy metals viz. lead (Pb), iron (Fe), zinc (Zn), chromium (Cr), and cadmium (Cd) were also determined. All parameters were measured using standard procedures. Nitrate ion (NO_3^-) determination was **by** HCl (Kjeldhal method;[34]; method no. 973 – 48) and reading 470 nm wavelength on a spectrophotometer (Turbedimetric method;[34] method no. 973 – 57). Chloride ion (Cl^-) was determined by $AgNO_3$ till the disappearance of the pink color is noticed. (Meranic nitrate method;[34] method no. 973 – 51). pH by fisher centromatric tetrameter (model 36-pH meter;[34] method no. 973.41). Electrical conductivity was determined using an EC meter (model LF-91). Total dissolved solids were filtered through a standard glass-fiber filter, and total hardness (TH) was computed in line with the procedure described by[35].

Cations and heavy metals determination

The cations determined in the study, viz., sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), were analyzed using a prepared standard solution. During standard solution preparation, 1 gram of the uncontaminated metal feed stock was diluted in 20 mil of hydrochloric acid and then dissolved in one liter inside a volumetric flask together with deionized water to make up the metal stock solution to 100 mg/l. Every metal that was examined underwent this process again. According to Allen's procedure, multiple dilutions of the feed metal solution were used to create solutions with concentrations of 4 mgl^{-1}, 6 mgl^{-1}, and 8 mgl^{-1}[36]. For heavy metal determination, Parkinson absorption spectrometer model 403 was utilized to perform analyses on heavy metals, along with the necessary lamps. Nitric acid was used to stabilize water samples in situ for analysis of heavy metals. A volume of 100 mL each of river water samples from all locations was analyzed for heavy metals. Among the heavy metals and minerals, lead, iron, zinc, magnesium, and calcium were determined by an atomic absorption spectrophotometer (model: Perkin Elmer 2380), while sodium and potassium were determined by a flame photometer.

Quality assurance and control

Throughout this investigation, the use of Analytical Research-grade (AR) chemicals (Merck and Sigma-Aldrich, Germany) was guaranteed; the reagents used were in their purest form (99.9%), requiring no additional purification or modification. The two main chemicals utilized are HCl and HNO_3. The plastic bottles were first cleaned with approximately 1.15 M of diluted HNO_3 and then washed with distilled water. Prior to analysis, all reagents and calibrations were made using Milli-Q water standards. Before being used, all stock solutions and references were kept at 4 °C. All analyses were performed in three duplicates. Every step of the quality assurance process was carried out, including the thorough cleaning and washing processes and the blank levels of equipment monitoring.

Hydrochemistry examination

Groundwater chart software USGS (GW_ Chart Software version; GW_Chart v.1.30.0; https://www.usgs.gov/software/gwchart-program-creating-specialized-graphs-used-groundwater-studies) was utilized to analyze the hydrochemistry of the sample water and also to divide the water types into two seasons. Meanwhile, the Piper trilinear analysis method was employed by creating a Piper diagram[37,38].

Water Quality Index (WQI)

WQI is used in analyzing both surface and ground water quality, providing a reliable outlook on the quality of water for domestic purposes[39,40], and/or its fitness for drinking purposes[41–43]. WQI provides a rating that shows the collective impact of known water quality parameters[44]. WQI is an arithmetical summary of a number of water quality parameters in a single value expression. It is computed with the assumption that low values denote less deviation from the parameters' recommended values and are therefore suitable and acceptable water quality for human consumption and vice versa. In this study, a total of 18 hydrochemical characteristics were used to compute the WQI. They were given a relative weight (wi) based on their relative importance in the overall quality of the water and their perceived impacts on primary health. The mathematical expression for the quality rating or sub-index (qn) was computed as follows:

$$Qn = 100\frac{(Vn - Vid)}{Sn - Vn)} \tag{1}$$

Qn stands for the nth water quality parameter's quality rating, Vn depicts an estimate value of the nth water quality parameter at specific sampling georeferenced location, Sn means the regulatory acceptable value of the nth parameter while the Vid means the model value of nth parameter in pure water.

The unit weight was computed by a value that is proportionally inverse to the suggested standard value S_n of the corresponding parameter.

$$Wn = \frac{K}{Sn} \tag{2}$$

Wn stands for the unit weight for the nth water quality parameter; S_n means recommended value for the nth parameter while K is the constant for proportionality.

The unit weight and quality rating were aggregated linearly to determine the overall WQI.

$$WQI = \frac{\sum QnW_n}{\sum W_n} \tag{3}$$

WQI stands for water quality index; Σ means summation sign, Qn is quality rating for the nth water quality parameter; while W_n equals unit weight for the nth water quality parameter.

Multivariable analytical statistics

When many different factors are affecting the quality of both surface and ground water, a multivariable statistic is a helpful tool for assessing the quality of the water. The most popular statistical methods for determining the prevailing elements and origins of the differences in quality of water and their effects on aquatic environments are factor analysis/principal component analysis (FA/PCA), correlation matrix analysis, and hierarchical cluster analysis. Multivariate techniques are included in cluster analysis and are used to identify actual data groups. When objects are clustered, they are arranged so that they belong to the same class[45]. Adopting the most comparable homogeneous groups to one another when considering certain properties is the primary goal of the cluster analysis. The most similar observations are joined, followed by the subsequent most comparable observations, using hierarchical clustering[45]. With the goal of reducing the number of interconnected variables in a large set and converting them into a reduced form of discrete (uncorrelated) variables, PCA is a potent pattern recognition technique[46].

All sample results were submitted to both inferential (ANOVA) and descriptive (mean, standard deviation, and ranges) statistics, with $P < 0.05$ being regarded as statistically significant[47]. A Mann-Whitney test was utilized to contrast the means for the wet and dry seasons. Hydrochemical analyses were carried out through the determination and representation of facies, the Piper's trilinear plot, Stiff diagram, Gibbs plot of Na+/Na + Ca and Cl/Cl + HCO_3 ratios versus TDS on a logarithmic scale, and ionic relationship/molar ratios. Softwares used for data analysis include Microsoft Excel (2013) and XLSTAT (2022).

Chemical analysis accuracy

It is imperative for water quality data to be of high accuracy. The accuracy of the water quality data for hydrochemical analysis was examined by determining the ratio of positive to negative ions. An error of up to ± 5% is tolerable. The formula was used to determine the data's degree of error[48]:

$$Electrical\ Balance\ (E.B.\%) = \frac{Sum\ of\ cations - Sum\ of\ anions}{Sum\ of\ cations + Sum\ of\ anions} \times 100 \tag{4}$$

where cations Na^+, K^+, Mg^{2+} and Ca^{2+}, and anions Cl^-, HCO_3^-, SO_4^{2-} and NO_3^- are expressed as mEq/L

Results and Discussion

Physicochemical characteristics of Ethiope river

Hydrogen ion (pH)

Values of pH varied from 4.50 to 5.47, with an overall wet/dry mean value of 5.08. The surface water of the Ethiope River therefore indicates a slightly acidic to acidic nature. During the rainy season, pH values ranged from 4.5 to 5.13 mg/l, with a mean value of 4.80, and 5.17 to 5.47, with an average value of 5.28 in the dry season, meaning that the river was more acidic in the wet season than the dry season (Tables 2 and 3). With the event of gas flaring activities, oil exploration, and industrializations visibly characterized by the study area, river acidification is probable. Through wet depositions and dissolution of sulfur dioxide, carbon dioxide, and nitrogen dioxide[49,50], low pH values recorded in both dry and wet seasons in the study area may be justified. However, despite the presence of rainfall with atmospheric dilution capability[50], the pH during the wet season exceeded the dry season. During the rainy season, runoffs from agricultural fields surrounding the river could introduce some organic matter[51] into the river, which inhibits dilution and subsequently increases the pH of the river even further during the rainy season. pH has a strong cascading effect on aquatic amphibians, fish, and other animals by altering their metabolism, reproduction, and livelihood[52]. Many other aquatic plants, including the planktons and benthic invertebrate animal species like the snails, are pH-sensitive, in which high acidity in water may drastically reduce their richness and evenness[53], thereby threatening their survival and plunging them to likely extinction. In addition, low pH in surface water, especially with such lithostratigraphic underlying rock formations found in river ethiope, could dissolve certain heavy metals (such as cadmium, iron, mercury, aluminum, etc.)[54], sequestered in surrounding and underlying rocks and soil, which subsequently could be bioaccumulated by aquatic animals. Thus, when pH is in such a biodiversity-threatening range, the dynamics of aquatic ecosystems and food chains may be affected, which has an anthropocentric effect, especially for people of the Niger Delta region whose major occupation is fishing and farming. The recorded pH in the study disagrees with pH (7.0–7.5) in the Rupsha Upazila, Bangladesh[55], 6.7–7.8 in the Indian River[56], and 7.1–7.7 in Algeria[57], but agrees with the results found by[58] and [59]. The result of pH is against the acceptable standards (6.5–8.5) for pH in surface water according to the US EPA[60] and WHO[33], indicating that the river is acidic throughout the

Water tracer for wet season	Min	Max.	Mean	Standard Deviation	WHO(2011)
pH	4.500	5.140	4.872	0.242	6.5–8.5
Electrical Conductance.EC ($\mu S/cm^3$)	21.200	111.500	50.060	38.505	1500
Total Dissolved Solids, TDS (NTU)	140.700	422.100	272.020	111.972	1000
Bicarbonate, HCO_3^- (mg/l)	227.200	530.980	361.340	130.861	600
Total Hardness, TH (mg/l)	239.900	499.790	351.852	106.356	500
Calcium, Ca^{2+} (mg/l)	48.100	100.204	70.545	21.322	100
Magnesium, Mg^{2+} (mg/l)	29.184	60.800	42.803	12.939	50
Sodium, Na^+ (mg/l)	1.009	2.011	1.369	0.391	200
Potassium, K^+ (mg/l)	0.396	0.573	0.453	0.071	100
Chloride, Cl^- (mg/l)	37.900	51.690	44.794	6.895	250
Sulphate, SO_4^{2-} (mg/l)	0.084	3.701	1.526	1.397	250
Phosphate, PO4	0.069	1.426	0.589	0.532	1
Nitrate, NO_3^- (mg/l)	0.000	0.014	0.003	0.006	50
Zinc, Zn	0.006	0.280	0.090	0.111	3–5*
Iron, Fe	0.000	0.023	0.005	0.010	0.3*
Chromium, Cr	0.000	0.013	0.003	0.006	0.05
Lead, Pb	0.000	0.000	0.000	0.000	0.01
Cadmium Cd	0.000	0.000	0.000	0.000	0.003

Table 2. Hydrochemical characteristics of Ethiope river in wet season. *based on taste and aesthetics; not of health significance in drinking water.

Water tracer for Dry season	Min	Max.	Mean	Standard Deviation	WHO(2011)
pH	5.170	5.470	5.284	0.137	6.5–8.5
Electrical Conductance.EC (µS/cm3)	9.810	18.740	12.448	3.711	1500
Total Dissolved Solids, TDS (NTU)	930.400	1471.000	1155.440	213.276	1000
Bicarbonate, HCO_3^- (mg/l)	429.660	577.400	501.076	55.030	600
Total Hardness, TH (mg/l)	419.520	519.860	467.344	41.920	500
Calcium, Ca^{2+} (mg/l)	84.168	104.210	93.788	8.312	100
Magnesium, Mg^{2+} (mg/l)	51.072	63.232	56.809	5.132	50
Sodium, Na^+ (mg/l)	1.760	2.166	1.977	0.205	200
Potassium, K^+ (mg/l)	0.221	0.491	0.363	0.105	100
Chloride, Cl^- (mg/l)	44.790	55.120	50.300	5.222	250
Sulphate, SO_4^{2-} (mg/l)	0.000	3.142	1.348	1.258	250
Phosphate, PO_4	0.000	0.292	0.097	0.118	1
Nitrate, NO_3^- (mg/l)	0.008	0.055	0.028	0.022	50
Zinc, Zn	0.000	0.025	0.008	0.010	3–5*
Iron, Fe	0.024	0.316	0.191	0.120	0.3*
Chromium, Cr	0.000	0.014	0.007	0.006	0.05
Lead, Pb	0.000	0.097	0.037	0.038	0.01
Cadmium Cd	0.000	0.038	0.013	0.016	0.003

Table 3. Hydrochemical characteristics of Ethiope river in dry season. *based on taste and aesthetics; not of health significance in drinking water.

season. The pH mean result for wet and dry seasons is far above the safe limit of pH for agricultural irrigation: 6.0 − 8.4[61], 6.0–8.5[62]), 6.5 − 8.5[63].

Electrical conductivity (EC)

EC ranges from 9.81 to 111.5 $\mu S/cm^3$, with an overall wet/dry average value of 31.25 $\mu S/cm^3$, with wet season > dry season but below detection limit. EC is usually influenced by the dissolution of salts to produce positively charged and negatively charged ions. The higher the concentration of dissolved salts, the higher the conductivity of water[64]. In association with EC levels found in the study, it could be observed (Tables 2 and 3) that most ions investigated in the study, viz., sulfate, chloride, sodium, potassium, and nitrate, were all at minimal levels except for calcium, magnesium, phosphate, and bicarbonate, which may indicate the reason for the minimal EC levels in the study river. However, the wet season had more dissolved salts than in the dry season, suggesting the fact that agricultural and industrial runoffs[54] emanating from the surrounding area of the study area may have been responsible for higher EC during the rainy season, which results in higher dissolution and enrichment of mineral salts or dissolved ions in the surface water. Meanwhile, the lower EC levels during the dry season might be due to a higher evaporative tendency[65]. The result agrees with the finding that, during wet season, electrical current is transported by the ions in solution. Electrical conductivity can be categorized into type 1 when the dissolved salt is below 1,500 μS/cm^3, type 2 when the dissolved salt is medium and between 1,500 and 3,000 μS/cm^3, and type 3 when the dissolved salt is high, i.e., above 3,000 μS/cm^3[66,67]. Thus, water samples of the Ethiope River are classified as Type I with a low concentration of salts. The mean results of EC during wet and dry seasons in (μS/cm^3) are far below the allowable limits (0.70 dS m^{-1};[63]), (0.75 dS m^{-1};[62], or (1.2 dS m^{-1};[68]) when converted.

Total dissolved solids (TDS)

TDS in the study area ranged from 140.70 to 1,471.70 mg/l with dry/wet mean values of 713.73 mg/l. A higher TDS value of 1471 above WHO (1000 mg/l) was recorded during the dry season, more than 140 mg/l recorded during the wet season (Tables 2 and 3). The causative chemical species of TDS have been linearly associated with conductivity. Accordingly, the conductivity-causing dissolved salts of sulfate, phosphates, chloride, sodium, potassium, nitrate, calcium, magnesium, bicarbonate, and carbonates together are also accused of contributing to TDS in surface water[64]. From the present study, the positively charged calcium and magnesium ions and the negatively charged bicarbonate ion were chiefly in high concentrations above and near WHO limits, indicating a major contribution to the high TDS value recorded during the dry season. During the dry season, there is usually a facilitated and intense salt dissolution, ion exchange capacity, reverse absorption/adsorption or desorption, and rock weathering due to higher temperature[69], and also higher river evaporative tendencies leading to an increase in salt and other ion concentrations, perhaps the reason for the higher TDS in the dry season. The low TDS values of the Ethiope River water samples observed during the rainy season could be attributed to the fact that its catchment lies on the outcrop of the Benin Formation, which is directly recharged perennially by rainfall[22]. A lower mean of TDS values indicates the influence of rock-water interactions during recharge. Natural waters contain mainly dissolved solids such as Na^+, Ca^{2+}, K^+, Mg^{2+} and Cl^-, SO_4^{2-}, PO_4^{3}-, HCO^{3-}, and $H_4SiO_4^{2-}$[70]. The source of TDS value could be associated with anthropogenic activities such as agriculture or rock-water interactions. Anthropogenic activities and other human interferences within the cities and especially around rivers could increase the number of dissolved solids into water bodies and subsequently may increase conductivity[71,72].

TDS has been accused of increased salt toxicity and ionic composition changes of individual ions[73]. This could lead to disbalance in the aquatic community, shortening of animal and plant biodiversity by eliminating the intolerant species, and causing acute/chronic effects at the life stages of the animals. High TDS (especially high concentrations of Na^+, Mg^{2+}, $SO4^{2-}$, HCO^{3-}, and CO_3^{2-}) has also been accused of low chlorophyll content of aquatic plants and subsequently low primary productivity leading to altered feeding relationships within the aquatic ecosystem[74]. Additionally, the use of water high in TDS level, particularly salt, for irrigation purposes in dry areas raises the amount of dissolved salt that is transferred to the soil, which may have negative effects on the quality of the soil and crop yield[75]. Again, surface water rich in dissolved salts and minerals is capable of reducing dissolved oxygen, leading to algal bloom and excessive enrichment of surface water[76]. Furthermore, higher amounts of dissolved salts in waters can potentially result in the taste of water[77]. However, the suitability of drinking water based on the amount of TDS can be categorized as excellent (less than 300 mg/l), good (between 300 and 600 mg/l), fair (between 600 and 900 mg/l), poor (between 900&1200 mg/l), and unacceptable (above 1200 mg/l). Meanwhile, water having a minimal level of TDS is not suitable for drinking due to its flat, insipid taste[40]. Values of TDS in this study are significantly higher than values (9.8 to 17.0 mg/l) obtained by[25] and (43.77 to 62.0 mg/L) by[25] in Ethiope River. This could be as a result of sand dredging activities and intensified anthropogenic activities currently going on in the study area. River quality may be categorized into fresh (when the TDS is below 1,000 mg/l); brackish (when the TDS falls within the range of 1,000 and 10,000 mg/l); saline (when the TDS falls between 10,000 and 1,000,000 mg/l); and brine (when the TDS is above 1,000,000 mg/l)[78,79]. According to this classification scheme, the average value of samples in the study was classified as freshwater. The outcome agrees with the conclusions of[58] and [80], respectively.

Bicarbonate$\left(HCO_3^-\right)$

In the wet season, bicarbonate ranged from 227 to 530.980 mg/l, with a mean value of 361.340 mg/l. In dry season, it ranged from 429.660 to 577.40 mg/l, with a mean value of 501.076 mg/l, indicating a negligible variation of bicarbonates in both seasons, although wet season is slightly higher than dry season (Tables 2 and 3). The amount of bicarbonates in the surface water of the study area was near the WHO limit of 600 throughout the study period. Generally, bicarbonate salts in water sources have geologic origin and are the product of weathering of carbonaceous rocks and sediments[81]. Specifically, the presence of bicarbonates in surface and groundwater is principally caused by the dissolution or weathering of rock minerals of carbonate and alumino-silicate origin. Such rock mineral origins as Kyanite or andalusite, limestone, or the shell of coral reefs are catalyzed by carbon dioxide and water[82], where the carbon dioxide could come from aquatic biological respiration, wet deposition, atmospheric absorption, and gas flaring from oil production activities within the Ethiopian River study area. Additionally, due to the lithostratigraphic nature of the bedrocks in the river of study area, which is primarily made up of such carbonate-rich rocks as calcite and dolomite[83], part of the high concentration of bicarbonates in the river of study may be explained. Subsequently, the process of carbon dioxide dissolution in water results in the formation of carbonic acid, which is responsible for the weathering of carbonate-rich rocks[83], within and around the river to produce bicarbonates. More so, urban and agricultural runoffs containing lime applied to the soil as a buffer or carbonate-containing construction materials such as cement, gravel, and stones could also be another source of the elevated bicarbonates. The slightly higher level of bicarbonates in wet season may be partly due to high river dissolution in rainy season. The presence of bicarbonates in drinking water has been associated with alkalinity regulation of water, but only at moderate levels. Consuming bicarbonate mineral-regulated water, according to[84], has the potential capability to prevent or improve type 2 diabetes by changing the metabolism of the patient. However, consuming excessively bicarbonate water/alkalinity close to 11 has been accused of causing the same health effects as those highlighted in acidic water. It could lead to gastrointestinal problems, vomiting, nausea, skin and eye irritation, cardiovascular and kidney problems, dehydration, and bone health issues[85]. Increased bicarbonate levels can also cause increased pH. Levels that could affect intolerant species and biodiversity reduction[53]. Concentrations of HCO^{3-} as anion in both seasons are greater than the normal ground and surface waters, ranging from 25 to 400 ppm[86], 73 to 201 mg/l Lhasa river[87], 12.4–85.5 mg/l in river India[56], but lower than 204–708 mg/l in Rupsha Upazila, Bangladesh[55].

Total Hardness (TH)

TH ranges from 239.90 to 499.790 mg/l in the wet season and 419.92 to 519.86 mg/l in the dry season. Mean values are 351.85 mg/l and 467.34 mg/l in the rainy and dry periods, respectively. The TH of the river ethiope was high throughout the seasons and was above the WHO limit of 500 mg/l, particularly in the dry season (Tables 2 and 3). Although several dissolved metals with divalent or multivalent cation nature, such as aluminum, iron, zinc, manganese, strontium, and barium, can cause TH in water[88], TH is a primary function of $CaCO_3$ and $MgCO_3$ in water. The dissolution of rock minerals rich in $CaCO_3$ and $MgCO_3$ frees up the ions causing hardness (Ca^{2+}, Mg^{2+})[89,90]. The geological nature of river ethiope is suspected to be rich in dolomite and limestone, as can be seen in the above limit results of Ca^{2+and} Mg^{2+} (Tables 2 and 3). Due to the high acidity level of the river ethiope throughout the seasons (Tables 2 and 3), the accused carbonates of TH ($CaCO_3$ and $MgCO_3$) may have been weathered by carbonic acid to loosen up the ions, which are responsible for hardness. This may be connected to the high TH levels of the river. The TH of the Ethiopian River, which showed a higher value during the dry season, may be due to a higher temperature that increases weathering intensity, which dissolves the associated minerals, as well as reduced water flow during the fraught dry season[69]. Hard water has been associated with alteration of balance in aquatic ecosystems by increasing the pH of water and affecting sensitive species[53]. Hardness of water has also been accused of scaling in water pipes, heating kettles, laundry, and kitchen problems where it challenges lathering with soap or detergent[91]. Although hard water has no clearly known adverse health effect as posited by WHO in its conference at Geneva, drinking water with excessive levels (250 mg/l) each of magnesium and sulfate is capable of altering bowel habits or causing laxative effects in humans[88]. One of the most prevalent signs of hard water is persistently dry skin, the development of ezcema, and irritation. Hard water's high mineral concentration has been accused of contributing to dry skin by depriving one's skin of its natural oils, which would otherwise keep it hydrated and healthy[92]. However, a number of large-scale studies have reported an inverse tie between drinking hard water and risk of cardiovascular diseases in men with reference to regional socioeconomic and climatic differences[93–96]. The maximum value during the dry season is above the maximum allowable limit of total hardness for drinking purposes (500 mg/l), and the most desirable limit is 100 mg/l according to the WHO[33] standard. Hence, the water is classified as very hard based on average values[89,90], which is at variance with the observation that water hardness parameters of[97], indicate laundry and industrial friendly. Thus, the users of the Ethiope River may have challenges with laundry, kitchen, and scaling but are not likely to experience diarrhea from drinking the water since the sulfate concentration (Tables 2 and 3) is very low.

Ca^{2+} and Mg^{2+}(calcium & magnesium)

Ca^{2+} and Mg^{2+}ions can be quickly associated with water hardness as they are readily abundant in surface water and arising from their compounds in bicarbonates, sulfates, and chloride forms when dissociated. The mean values of calcium concentration in wet season in the surface water sampled for the study varied from 70.55 to 100.2 mg/l within the 100 mg/l WHO[33] limit for domestic water supply, while magnesium concentrations varied between 42.80 and 60.8 mg/l. In the dry season, the mean calcium varied from 84 mg/l to 104 mg/l within the 100 mg/l WHO limit, while magnesium varied from 51 mg/l to 63 mg/l above the 50 mg/l WHO limit with the wet period < dry period. The sources of these ions are not farfetched from the dissolution of rocks containing their carbonates, as discussed earlier in the previous pages. The low value of calcium in the river during the wet season is in tandem with the finding of[80], who reported low calcium in rivers in Itu and Uruan, Akwa Ibom, Nigeria. This low calcium could be as a result of current water removal or sediment absorption. The value agrees with those reported by[98] and [99]. It is noted that higher content of Mg in drinking water can lead to reduction of cardiovascular disease (CVD) and other benefits in population[100].

Sodium and potassium (Na, K)

During the wet and dry seasons, the mean values of Na ranged from 1.37 to 1.98 mg/l, with wet season < dry season, while K ranged from 0.450 − 0.363 mg/l, with wet season > dry season, all below 200 and 100 mg/l WHO[33] permissible limits, respectively. Higher content of K during the wet season may be due to silicate weathering and/or dissolution from the basement complex during the rainy season.

Chloride (Cl^-): The chlorine ion ranged from 37.18 to 51.69 mg/l and 44.79 to 55.12 mg/l, with average concentrations of 44.79 mg/l and 50.30 mg/l in the corresponding rainy and dry seasons, with the dry season greater than the rainy season. The chloride ion is extremely stable in water and originates mainly from anthropogenic activities such as city effluents/leachates carrying drainages into the rivers, sedimentary rock/soil weathering and leaching, etc[66]. The mean values for both seasons are well within WHO limits for drinking water. The required threshold for chloride is 250 mg/l[33].

Sulphate $\left(SO_4^{2-}\right)$ *and Nitrate* (NO_3)

The mean values of sulfate during wet and dry seasons ranged from 1.35 to 1.53 mg/l, with wet season > dry season, all below the 400 mg/l of the WHO[33] standard. Sulfates in water originate from the dissolution of gypsum and anthropogenic activities, respectively. The average nitrate values are 0.003 mg/l and 0.03 mg/l in the wet and dry seasons, respectively, with the dry season > the wet season, all far lower than the WHO recommended value of 45 mg/l. The nitrates are suspected to come from indirect/non-point anthropogenic sources originating mainly from agricultural practices and from other widespread contaminants in subsurface environments[101–104]. ADB (Asian Development Bank)[63]. recommended limit value (30 mg/L).

Phosphate $\left(PO_4^{3-}\right)$

The mean values of PO_4^{3-}during wet season events ranged from 0.069 to 1.426 mg/l with an average of 0.589 and 0.00 to 0.292 with a mean of 0.097 in dry season with wet season > dry season. The maximum value in wet season is above the 1.00 mg/l WHO limit. Natural waters contain phosphates. The high level of phosphates in the river Ethiope may have come from a wide range of non-point sources, such as agricultural runoff from fertilizer application, animal rearing, detergents, dissolution of portions of rocks containing phosphate compounds, industrial effluent, and waste water releases into the surface water[64,70,75,105]. In the wet season, increased rainfall intensity and runoffs could have emptied substantial amounts of phosphorous picked up from the surrounding farms in the study area, perhaps the reason for the high value in the rainy season (Tables 2 and 3). High phosphates in water can lead to eutrophication and algal bloom, thereby reducing the amount of dissolved oxygen required by aquatic animals. This can substantially reduce biodiversity for intolerant species[53]. WHO[33] states that the maximum amount of phosphate that can be present in drinking water is less than 1 milligram per liter. Phosphate (PO3 – 4) levels in the water samples of the present study are within the range of 0.08 to 2.3 mg/L, with a mean value of 0.48 mg/L in surface water in Bangladesh[40].

Hydro-chemical facies of the Ethiope River during wet and dry season events

Hydrochemical processes in surface water depict the chemical quality of water, and most especially their source or origin[106], in decreasing order[48,107]. These facies are commonly represented with the stiff pattern, Gibb's diagram, piper's plot, and ionic scatter diagram/molar ratios. Gibbs diagram expresses the association between water make-up and bedrock characteristics. Usually, three key fields of dominant areas of interest, viz., rock-water interaction, precipitation, and evaporation dominance, are designated for water chemistry[108]. The chief samples lie in the rock-water interaction dominance field (in the middle field of the Gibbs diagrams) (Fig. 3), reflecting Gibbs plot, TDS vs. Na/(Na ÷ Ca), and TDS vs. Cl/(Cl + HCO3). Among the processes of rock-water interactions are weathering and dissolution, ion exchange, oxidation, and reduction. From the interpretation of results, where the salts are of geologic origin, the major hydrochemical process occurring with the wet season group and dry season group of Ethiope River samples is rock-water interaction, and dry season was the evaporation

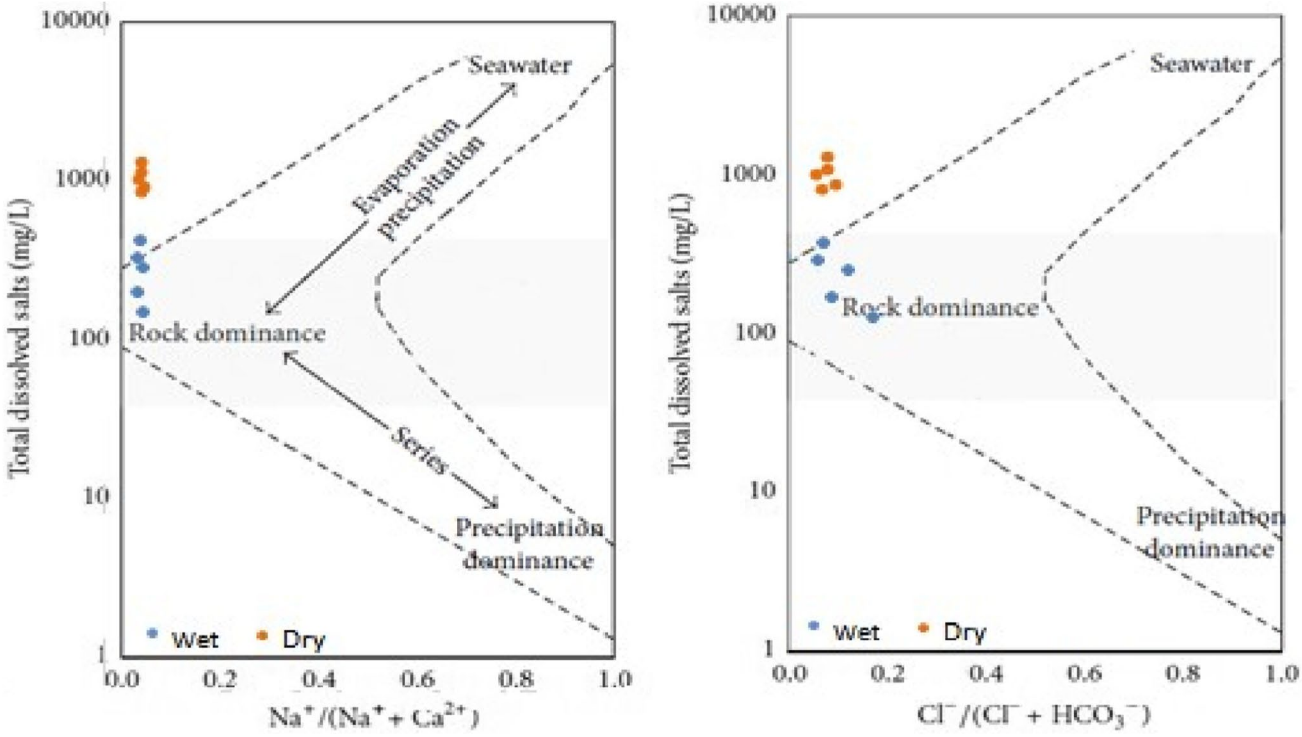


Figure 3. Gibbs diagram showing rock-water interaction processes and evaporative dominance defining chemistry of Ethiope river.

dominance processes (Fig. 3). This result corroborates the elevated levels of bicarbonates (Tables 2 and 3) found throughout the study period. This means that the bicarbonates actually emanate from rock-water interactions and river evaporative phenomena in river ethiope. The outcome agrees with the discovery of[109], who inferred that rainfall and river water are the Ca-HCO_3 water type in south-western China, and Gibb's plot and molar ratios explain that geochemical weathering was suggested as the chief regulatory factor for the geochemical make-up of this natural water. Accordingly, it is reported that climatic, fluvio-geomorphic, and anthropogenic processes support the influence of water use in a river regime[110], because of the fact that the weathering of rock minerals, dry season evaporation, and wet season precipitation, as well as other anthropogenic activities, make up the main sources of ions in river waters[27]. The modified Gibbs[108] diagrams shown in this study implicate rock-water interaction as the chief factor affecting river water chemistry of the Ethiope River (Fig. 3).

Water type and geochemical controlling mechanisms in Ethiope river

The Piper diagram explains the geochemical evolution of surface water and indicates water type[111]. This plot contains two ternary diagrams below and a diamond for depicting cations and anions ratios expressed in mEq/L. The dual triangles located at the bottom of the plot depict and represent the predominant cation and anion contents of the river. The diamond-shaped structure above represents the interaction of the cations and anions and reveals the hydrochemical facies of the water. Six 'hydrogeochemical' facies, including HCO^{3-}Ca, mixed HCO_3-Na·Ca, $HCO_{3_}$Na, mixed Cl^-Mg·Ca, Cl-Ca, and Cl-Na, are spelled out by the Piper trilinear plot[37,112]. The overall hydrochemical characteristics of surface water are represented by the hydrochemical facies, which is usually depicted by the Piper's trilinear diagram (Fig. 4). The diagram (Fig. 4) indicates that Ca-HCO_3 (calcium bicarbonate) is the predominant compound in the Ethiope River constituting calcium bicarbonate water type. It also shows that alkaline-earth metal ions (Ca^{2+} and Mg^{2+}) exceed alkali metal ions (Na^+ and K+), and the total concentration of weak acids is greater than that of strong acids ($Cl^- + SO_4^{2-}$). The abundance of Ca-HCO_3 and Ca2+/Mg2+ (alkaline earth metals) indicates that there is a carbonate-dominated underlying rock[113]. These results corroborate the high TH, TDS, HCO3, and Ca^{2+} found in the study (Tables 2 and 3).

Stiff diagrams present a swift pictorial evaluation between different surface water samples[87]. Figure 5 shows higher concentrations of calcium and bicarbonate ions with respect to other anions and cations in both the wet and dry seasons water samples of the Ethiope River. More so, the Stiff[114] diagram (Fig. 5) revealed that hydrochemical characteristics of the Ethiope River varied from one sampling point to the next, as noticed from the different forms of each succeeding polygon (Fig. 5), indicating spatial differences in bedrock bicarbonate-rich rock makeup of the river leading to spatial differences in carbonic acid dissolution of the rock. This means that river users from locations with higher bicarbonates stand more risk of the effect of higher bicarbonate contamination in water than others. The diagram also shows the dominance of bicarbonate in the river, especially in the wet season, which is due to the processes of dissolution. The result is at variance with the finding of[115], who observed the dominance of magnesium and sulphate in the water during the rainy season by dissolution processes in the Mamu River basin, south-eastern Nigeria.

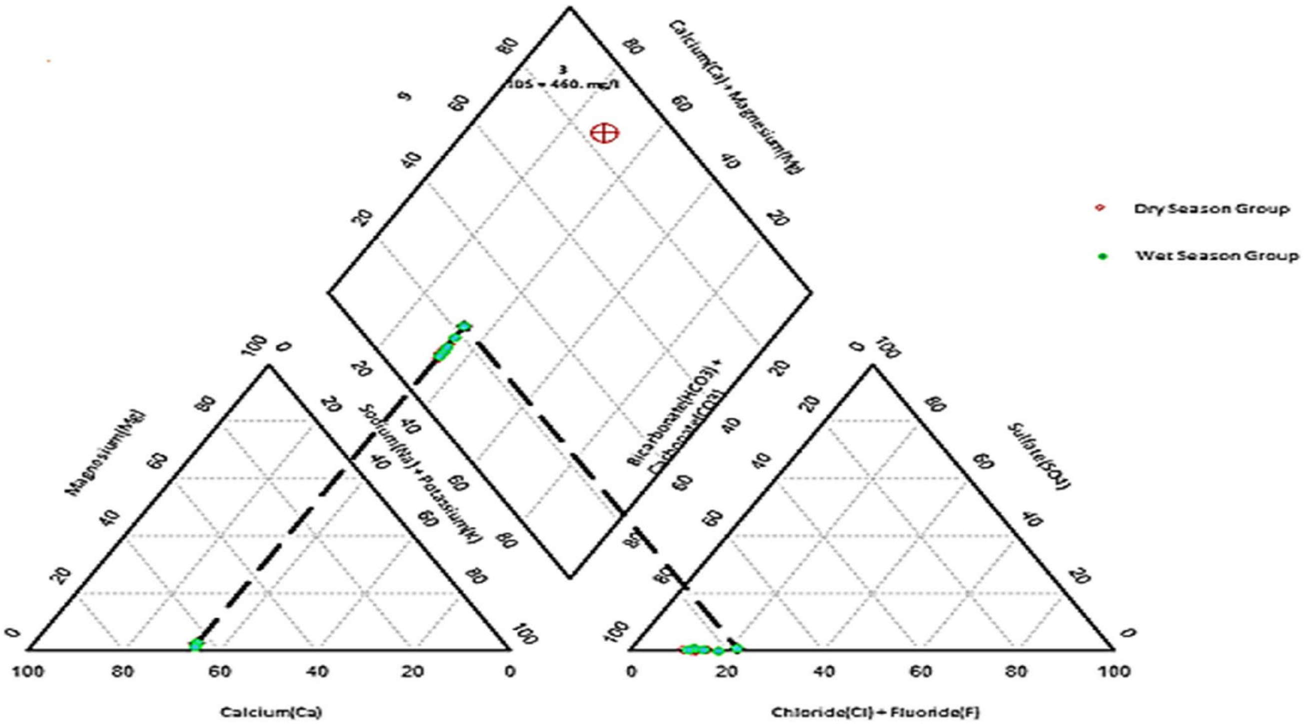


Figure 4. Trilinear (Piper) plot showing hydrochemical facies and interpretation of Ethiope river surface water chemistry.

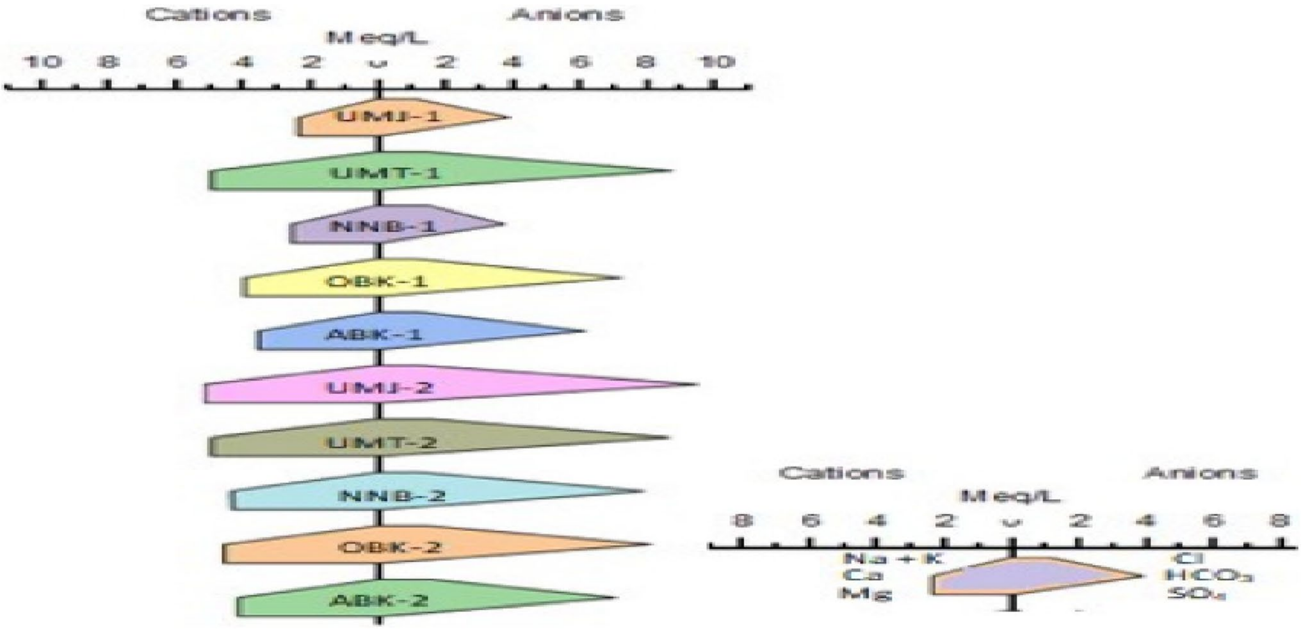


Figure 5. Stiff diagram for surface water samples of Ethiope river (Dry Season Group).

Ionic dominance pattern, ionic ratios and other chemical indices

Spatial patterns of ions in surface water are determined by oxidative reactions in host rock[115], differences in water chemistry, and human interferences[116].

Calcium, Ca^{2+} (50% of total cations), and bicarbonates, HCO_3^- (84% of total anions), are the dominant cations and anions in the water samples for both wet and dry seasons in the Ethiope River. The order of abundance of cations in the surface water samples of the Ethiope River is $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, while the order of anion abundance is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3$. The cations were slightly less dominant (49%) than the anions in the water sample. Water dominated by precipitation contains a lot of Na^+ and Cl^- ions; weathering-dominated water contains a lot of Ca^{2+} and HCO^{3-} ions; and evaporation-crystallization-dominated water has a lot of Na^+ and Cl^- ions[117]. Hence, water samples for the Ethiope River for both wet and dry seasons are weathering dominated with relatively high Ca^{2+} and HCO_3^- concentrations as compared to other ions. The presence of HCO_3^- is usually linked with the organic dissolution of carbonic acid (H_2CO_3) content of carbonate rocks (limestone magnetite and dolomite), as well as the combination of CO_2 with rainwater (Dinka et al. 2015). In the same vein, Ca_2^+ and Mg^{2+} arise from variations in both cationic and anionic levels as a result of leaching and human activities[115,118].

The end-member diagram showing ionic ratios could help to analyze and determine the rock types and weathering sources associated with the hydrochemical facies of surface water in an area of study[87,119]. The chemical composition of the river surface water in the area of study is mainly in the carbonate region (Fig. 6), suggesting that the surface water chemical composition originates from the weathering carbonic rocks. In general, for most fresh surface water, Ca^{2+} and $Mg^{2+}$and HCO_3^- arise from the breakdown of carbonates, evaporites (Na^+ and K^+), silicates, and weathering of silicates, while SO_4^{2-} and Cl^- come from evaporates, sulfates, and anthropogenic inputs. The $Ca^{2+} + Mg^{2+}$ scatter diagram in relation to total cations (Fig. 7a) showed that the data plots along the equiline, demonstrating a higher contribution of $Ca^{2+} + Mg^{2+}$ to increasing TDS values than Na^+ and K^+ (Fig. 7b). Figure 7c showing the ratio of $(Ca^{2+} + Mg^{2+})/ (HCO_3^- + SO_4^{2-})$, indicates the bimodal process of Ca enrichment and breakdown process (carbonate vs. silicate). If Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} ions are from the dissolution of dolomite, gypsum, and calcite, a 1:1 stoichiometry of $(Ca^{2+} + Mg^{2+})$ to $(HCO_3^- + SO_4^{2-})$ may occur[120,121]. The water samples plot along the 1:1 equilibrium, which indicates that Ca^{2+} and Mg^{2+} essentially arise from the dissolution of dolomite, gypsum, and calcite. A high ratio of $(Na^+ + K^+)$/total cation (Fig. 7a) and $(Ca^{2+} + Mg^{2+})/Na^+ + K^+$ (Fig. 7j) establishes that the chemical characteristics of the Ethiope River basin were primarily predisposed by carbonate weathering. The Ca^{2+} +Mg^{2+}/HCO_3^- plot (Fig. 7d) showed that $Ca^{2+} + Mg^{2+}/HCO_3^-$ increased with increasing concentrations of HCO_3^-, indicating $Ca^{2+} + Mg^{2+}$ and HCO_3^- are of a common origin. The Na^+/Cl^- ratio (Fig. 7g) is less than 1. This could imply that Na^+ comes from halite dissolution rather than ion exchange. The Ca^{2+}/Mg^{2+} ratio is usually used to assess the source of Ca^{2+} and Mg^{2+} in river systems. The ratio of 1 indicates dissolution of dolomite; a ratio greater than 1 (> 1) signifies calcite role; and a ratio greater than 2 (> 2) signifies dissolution of silicate minerals[109,122]. Every one of the water samples has a Ca^{2+}/Mg^{2+} ratio of 1 (Fig. 7i), indicating dolomite dissolution as their source in the water. The findings of the ionic ratio diagrams (Fig. 7a-j) indicate the predominant influence of carbonate weathering on the hydrochemical characteristics of Ethiope River surface water samples from the wet and dry seasons.

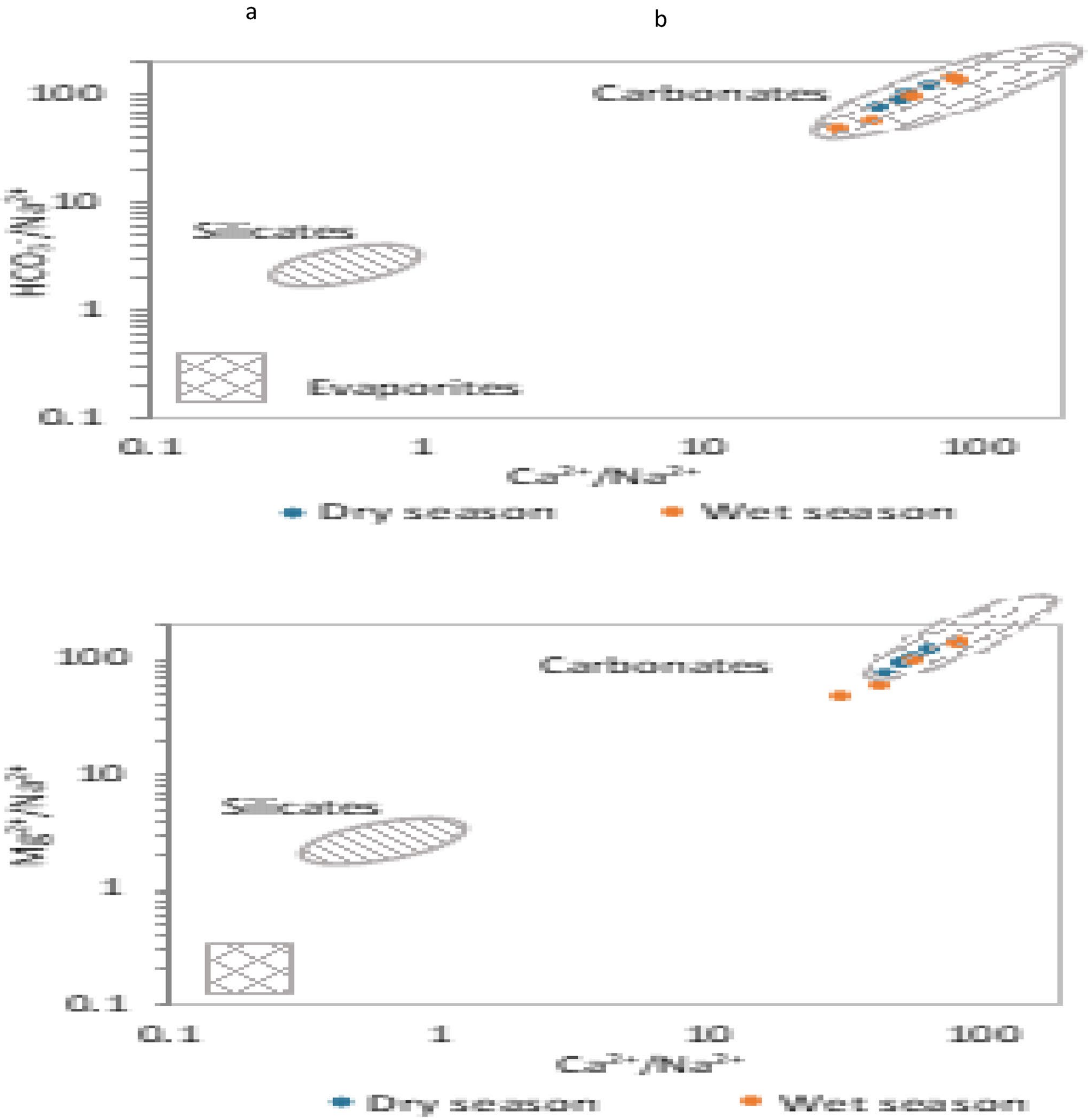


Figure 6. Diagram showing combination of Na-normalized ionic ratios of (**a**) Ca^{2+} versus HCO_3^- and (**b**) Ca^{2+} versus Mg^{2+}, for Ethiope river (wet and dry season).

Chemical analysis accuracy/charge balance error

The charge balance error for water samples of the Ethiope River for both wet and dry seasons ranges from −1.3 to 0.5 (Tables 4 and 5, and Fig. 10). Total cations values range from 4.891 to 10.493 mEq/L, while total anion values range from 4.946 to 10.766 mEq/L. It is observed that in 90% of samples (1, 2, 4, 5, 6, 7, 8, 9, 10), the sum of total anions is greater than the sum of total cations. Ideally, in a chemically balanced equation for freshwater, the sum of cations and the sum of anions in mEq/L should be equal. For analyses of Ethiope River water samples, the sum difference between cations and anions is negative, suggesting missing minor cation(s) (Table 4; Fig. 8). This corresponds with the exclusion of minor cations such as the trace metals and silica in the charge balance calculations. From Table 4. Total cations ranged from 35.62 to 47.29, constituting 43–57%, while total anions ranged from 28.69 to 48.30, constituting 37.3–62.7%, with the dry season having the highest concentrations, respectively. The result was in disagreement with the finding of[123], who reported that spatially, the ion concentrations were obvious in the wet season, and cations in water serve an important physiological purpose in humans. Juxtaposing total anions and charge balance error (Table 5) against acceptable percent for

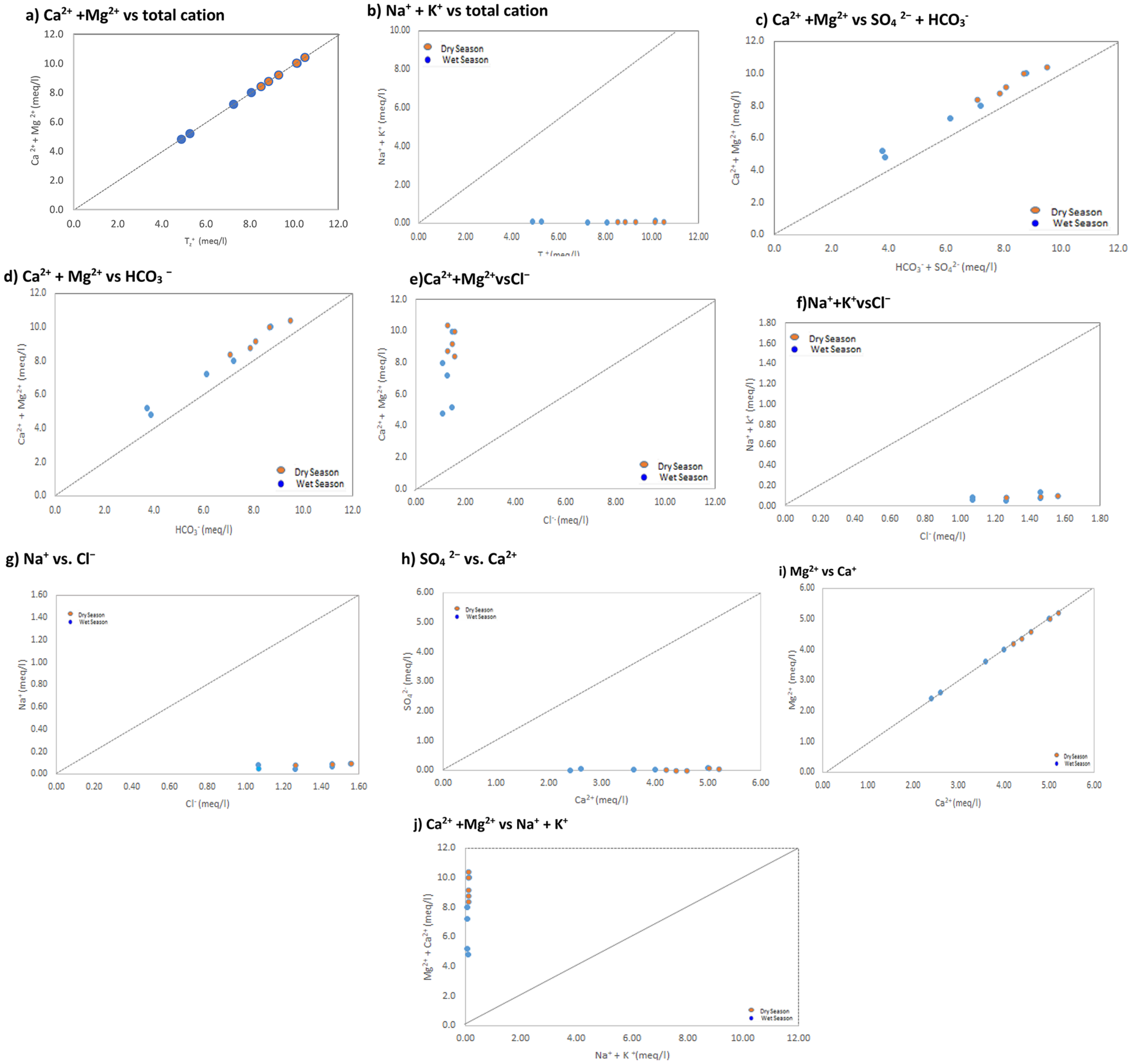


Figure 7. (**a-j**): Ionic scatter diagram of the Ethiope river water samples for wet and dry seasons.

sum difference (Table 4; Fig. 8), the charge balance error is less than or equal to 2; hence, the data analyzed was sufficient chemical accuracy or good quality for all the sampled locations.

Correlation matrix for surface water samples of Ethiope river during the season

The color-coded correlation matrix table (Table 6) revealed positive correlation for green-colored cells and negative correlation for red-colored cells. The color gradient and intensity show the strength of positive/negative correlations. Also, the correlation matrix shows a strong inverse link when values are close to -1 and a strong positive association when values are close to 1. Zero (0) in the matrix indicates that there is no association at all, while values of 1 in the matrix indicate that the parameters are the same and there is no quantitative or qualitative difference[124].

Correlation of wet season

pH showed a strong negative correlation with all other parameters except for the chloride ion (where it exhibited weak negative correlation), indicating that the dissolved ions may have contributed to the low pH or high acidity. TH, K, Ca, Mg, NO_3, and HCO_3 ions show strong positive correlation with each other, indicating they are of the same source, and weak correlation with the SO_4 ion. Ca and Mg ions show a positively significant correlation ($r = 1.000$, $p < 0.0001$), signifying the role of dolomite in their concentrations in the surface water. The chloride ion shows weak correlation with TH, Ca, and Mg ions and a negative correlation with pH. It,

Label	Sample ID	Group	Total Cations	Total Anions	Charge Balance Error
1	UMJ-1	Wet Season	4.891	4.946	-0.6
2	UMT-1	Wet Season	10.139	10.239	-0.5
3	NNB-1	Wet Season	5.274	5.224	0.5
4	OBK-1	Wet Season	8.062	8.279	-1.3
5	ABK-1	Wet Season	7.255	7.404	-1.0
	%	-	43 (%)	37.3(%)	
6	UMJ-2	Dry Season	10.493	10.766	-1.3
7	UMT-2	Dry Season	10.118	10.249	-0.6
8	NNB-2	Dry Season	8.845	9.120	-1.5
9	OBK-2	Dry Season	9.299	9.539	-1.3
10	ABK-2	Dry Season	8.503	8.629	-0.7
	%		57 (%)	62.7 (%)	

Table 4. Determination of chemical analysis accuracy/charge balance error for Ethiope river water samples (wet and dry seasons).

Anion Sum	Acceptable Percent
mEq/L	Sum Difference (%)
0–3	±0.2
3–10	±2
10–800	±2–5

Table 5. Acceptable difference for anion-cation balance. **Source**: [32]

however, is positively correlated with Na and K ions in the water samples of the Ethiope River during the wet season. The strong correlation between Ca and Mg ions with TH signifies that the former are the chief cause of water hardness. The positive correlation of chloride with sodium and calcium ions also demonstrates that soluble salts are predominant. NO_3 ions show a strong positive relationship with SO_4 ($r = 0.870$, $p = 0.0001$) and PO_4 ($r = 0.879$, $p = 0.0001$). The strong association between NO_3 and SO_4 ions represents evaporation's impacts and marine sources, agricultural practices, and inadequate drainage on the surface water system[121].

Correlation of dry season

For the dry season, pH is strongly positively correlated with Ec, Ca, K, TH, Mg, HCO_3, and SO_4 ions; it exhibits weak correlation with NO_3 ions and weak negative correlation with Na and Cl ions. TDS, TH, Ca, Mg, K, HCO_3, SO4, and NO_3 ions are all positively correlated to each other, implying a simultaneous increase or decrease in concentrations of the variables in the water sample during the dry season. Ca and Mg ions also show significant positive correlation ($r = 0.999$, $p < 0.0001$) as their wet season counterparts, demonstrating the dolomite's role to their concentrations in the surface water. Na and K ions show weak negative correlation to TDS, TH, Ca, Mg, K, HCO_3, SO_4, and NO_3, signifying an inverse relationship in their concentrations in the water samples: an increase in Na and K ions will result in a decrease in Ca, Mg, K, HCO_3, SO_4, and NO_3 ions, and vice versa.

Principal Component Analysis (PCA)

By removing some irrelevant data, PCA was used to analyze the compositional pattern of the variables over the full dataset and narrow it down to a few key variables[125,126], as presented in Table 7. Scree plots of two different seasons (Figs. 9, 10, 11 and 12) have also been employed to illustrate how the eigenvalues of each component have changed[127,128].

PCA during wet season

Analyzing PCA for wet season, a varimax rotated PCA is displayed in Table 7. Software used for data analysis includes Microsoft Excel (2013) and Grapher™ (2022) Version 14 (Golden Software, LLC) to determine the source allocation of chemical species detected in and to define the relationship between the main ions in Ethiope surface water. Three factors with high eigenvalues > 1 were taken out, accounting for a total of 65.08% of the variance, reflecting the scree plot (Figs. 9 and 10).

The first factor (PC1) shows 56.2% of the variance overall, with high positive loading in decreasing order: Cr/Fe > NO_3 > K > Na > Mg/Ca/TH > SO_4 > PO_4 > pH, supposed to elucidate mixed sources affected by crustal as geo-genic and human practices such as agriculture, mining, and solid wastes[129].

The second factor (PC2) shows a high loading of Zn > Cl, accounting for 18.59% of the total variance, suspected to come from natural sources[130], which functions as a neutralizer in Nigeria's coastal oil settlements[131] Accordingly, part of the reason for increased bulk Cl − and Zn in urban-industrial environments is human activity. especially inorganic wastes[132].

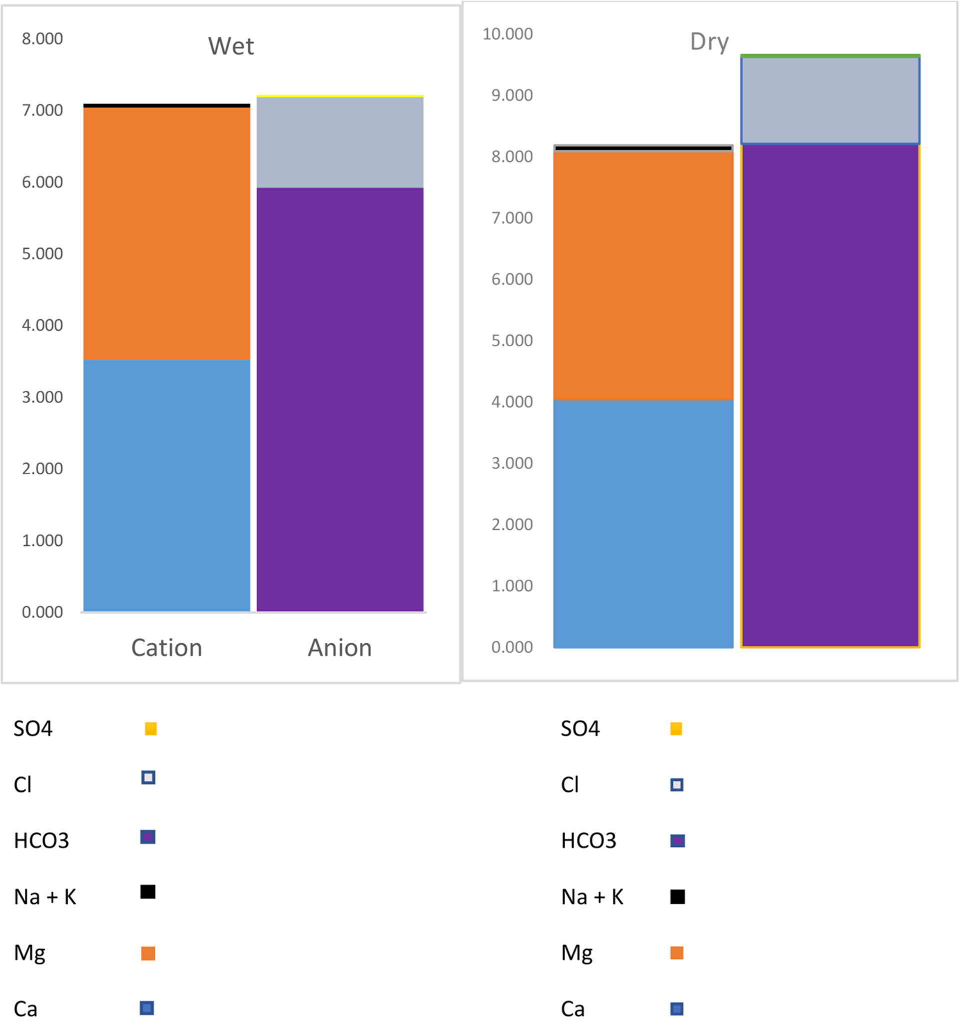


Figure 8. Ion balance diagram of the Ethiope river water samples (wet and dry seasons).

The third factor (PC3) is highly loaded by EC with a variation of 15.200%, which is closely related to inorganic salts and small amounts of organic matter from human activities[78].

The factor loading is classified as’strong’,‘moderate”, ‘moderate’ and ‘weak’ on the basis of their absolute loading values > 0.75–0.50 and 0.50–0.30, respectively [126,133].

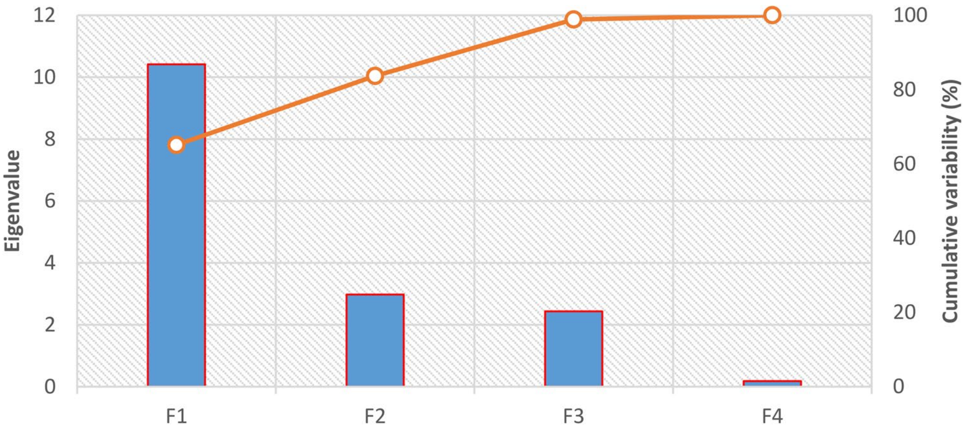
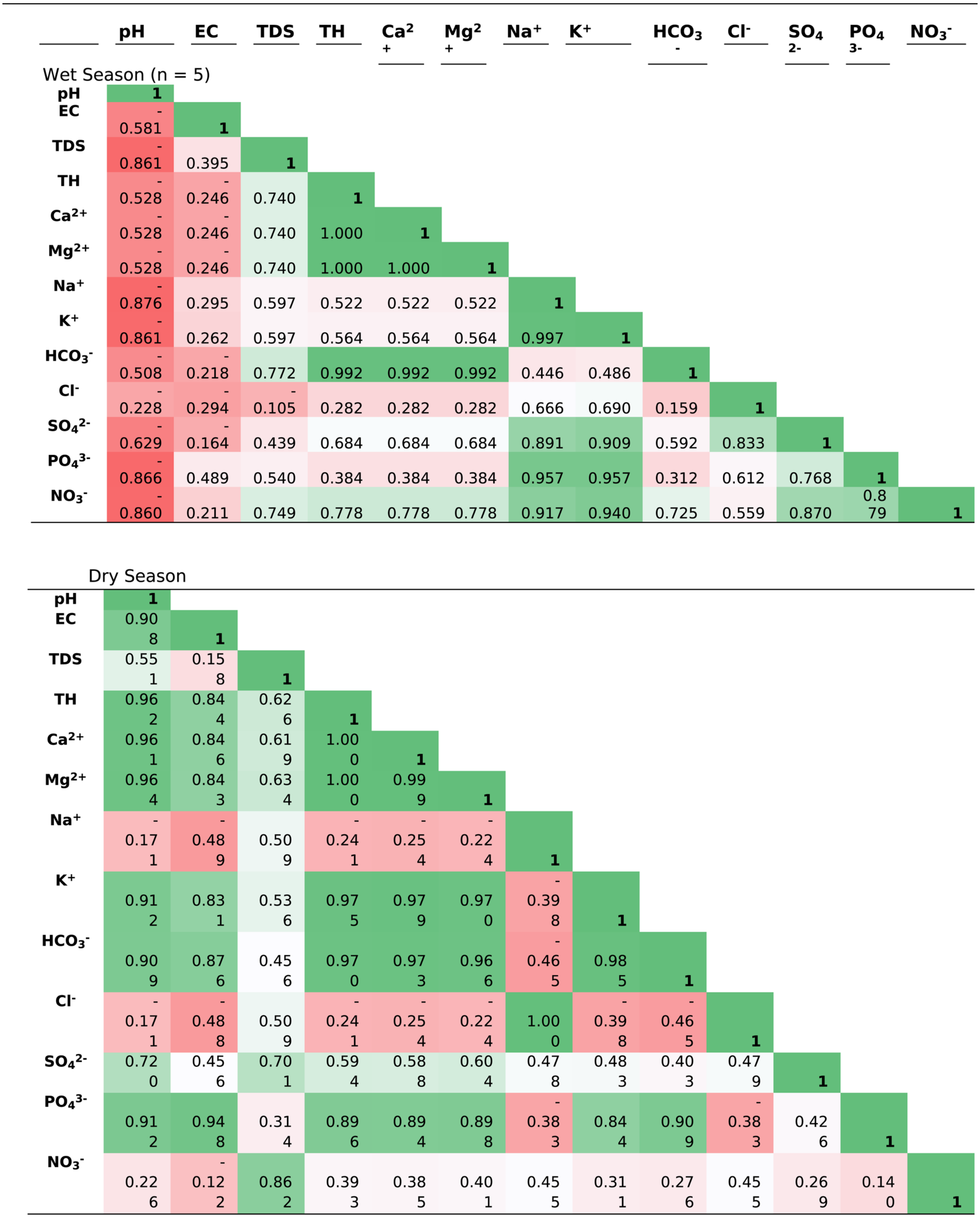


Figure 9. Scree plot showing eigenvalue and cumulative variability in wet season.



Wet Season (n = 5)

	pH	EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}	NO_3^-
pH	**1**												
EC	-0.581	**1**											
TDS	-0.861	0.395	**1**										
TH	-0.528	-0.246	0.740	**1**									
Ca^{2+}	-0.528	-0.246	0.740	1.000	**1**								
Mg^{2+}	-0.528	-0.246	0.740	1.000	1.000	**1**							
Na^+	-0.876	0.295	0.597	0.522	0.522	0.522	**1**						
K^+	-0.861	0.262	0.597	0.564	0.564	0.564	0.997	**1**					
HCO_3^-	-0.508	-0.218	0.772	0.992	0.992	0.992	0.446	0.486	**1**				
Cl^-	-0.228	-0.294	-0.105	0.282	0.282	0.282	0.666	0.690	0.159	**1**			
SO_4^{2-}	-0.629	-0.164	0.439	0.684	0.684	0.684	0.891	0.909	0.592	0.833	**1**		
PO_4^{3-}	-0.866	0.489	0.540	0.384	0.384	0.384	0.957	0.957	0.312	0.612	0.768	**1**	
NO_3^-	-0.860	0.211	0.749	0.778	0.778	0.778	0.917	0.940	0.725	0.559	0.870	0.879	**1**

Dry Season

	pH	EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}	NO_3^-
pH	**1**												
EC	0.908	**1**											
TDS	0.551	0.158	**1**										
TH	0.962	0.844	0.626	**1**									
Ca^{2+}	0.961	0.846	0.619	1.000	**1**								
Mg^{2+}	0.964	0.843	0.634	1.000	0.999	**1**							
Na^+	-0.171	-0.489	0.509	-0.241	-0.254	-0.224	**1**						
K^+	0.912	0.831	0.536	0.975	0.979	0.970	-0.398	**1**					
HCO_3^-	0.909	0.876	0.456	0.970	0.973	0.966	-0.465	0.985	**1**				
Cl^-	-0.171	-0.488	0.509	-0.241	-0.254	-0.224	1.000	-0.398	-0.465	**1**			
SO_4^{2-}	0.720	0.456	0.701	0.594	0.588	0.604	0.478	0.483	0.403	0.479	**1**		
PO_4^{3-}	0.912	0.948	0.314	0.896	0.894	0.898	-0.383	0.844	0.909	-0.383	0.426	**1**	
NO_3^-	0.226	-0.122	0.862	0.393	0.385	0.401	0.455	0.311	0.276	0.455	0.269	0.140	**1**

($p \leq 0.05$ except Ec and Cl not statistically significant; CI = 95%); All values in mg/l except pH and Ec (µS/cm^3**)**

Table 6. Correlation coefficient matrix (pearson) of hydrochemical parameters for Ethiope river for wet and dry seasons ($n = 10$).

Component for wet season event				**Component for dry season event**			
Variables	PC 1	PC2	PC3	P C1	PC2	PC3	PC4
pH	-0.853	0.011	-0.492	0.962	0.124	0.103	0.222
EC	0.138	-0.006	0.983	0.900	-0.286	0.063	0.324
TDS	0.786	-0.502	0.310	0.512	0.837	-0.038	-0.188
TH	0.833	-0.408	-0.373	0.990	0.137	-0.031	-0.016
Ca	0.833	-0.408	-0.373	0.992	0.125	-0.022	-0.027
Mg	0.833	-0.408	-0.373	0.988	0.151	-0.039	-0.001
Na	0.899	0.377	0.190	-0.361	0.891	0.052	0.269
K	0.920	0.360	0.145	0.983	0.001	0.049	-0.175
HCO3	0.786	-0.519	-0.337	0.988	-0.087	-0.078	-0.100
Cl	0.527	0.745	-0.385	-0.361	0.891	0.053	0.269
SO4	0.881	0.371	-0.276	0.535	0.614	0.442	0.376
PO4	0.826	0.411	0.372	0.921	-0.133	-0.217	0.294
NO3	0.991	0.065	0.064	0.272	0.760	-0.460	-0.372
Zn	-0.099	0.899	-0.405	0.470	0.550	0.668	-0.172
Fe	0.991	0.065	0.064	-0.623	0.715	-0.315	-0.038
Cr	0.991	0.065	0.064	-0.351	-0.854	0.349	0.160
Pb	0.741	0.411	0.132	-0.741	0.411	-0.132	0.514
Cd	0.593	0.327	0.143	0.593	-0.327	0.633	0.375
Eigenvalue	10.414	2.974	2.432	9.982	5.242	1.573	1.203
Variability (%)	65.084	18.588	15.200	55.453	29.124	8.738	6.685
Cumulative %	65.084	83.673	98.872	55.453	84.577	93.315	100.000

Table 7. Rotated component matrix of ionic species of the Ethiope river during wet and dry seasons.

Heavy metals

Biplot methods are a unique statistical tool for the inspection of data matrices and have been used in many scientific and technological domains because they have fewer limitations than conventional approaches[134], and have been applied in various fields of study[135–137]. In this study, the efficiency biplot was used to identify the current correlation between hydrochemical characteristics of the Ethiope River in southern Nigeria. During wet season, F1 was dominant with HCO_3, Mg EC, and NO_3, F2 was dominant with pH, and F1 and F2 were dominant with Zn, Cl, PO4, SO4, and TH, reflecting neutralization agents (Cl, Zn, PO_4, TH) and acidity (SO_4, NO_3), implying that the river Ethiope is neutralized by alkaline agents during wet season.

PCA during dry season

Four factors with high eigenvalues > 1 were taken out, accounting for a total of 100% of the variance, reflecting the scree plot (99.93%) (Figs. 11 and 12). The first factor (PC1) describes 55.453% of the overall variance, marked

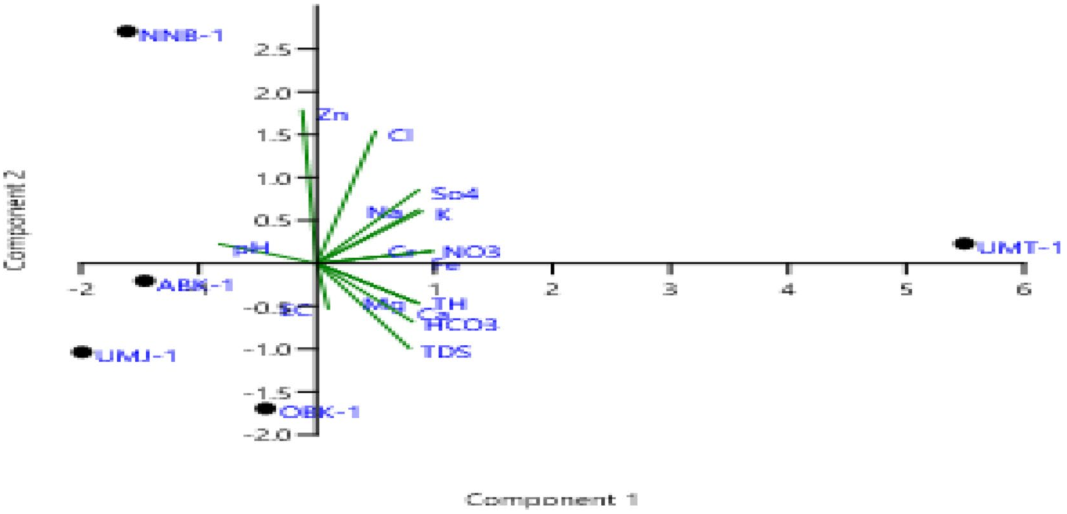


Figure 10. PC1 and PC2 of various water characteristics' (initial factor loading are represented by the green arrow lines for the wet season, the black solid circles reflect the values generated of each sample on the PC1 and PC2) of Ethiope river in wet season.

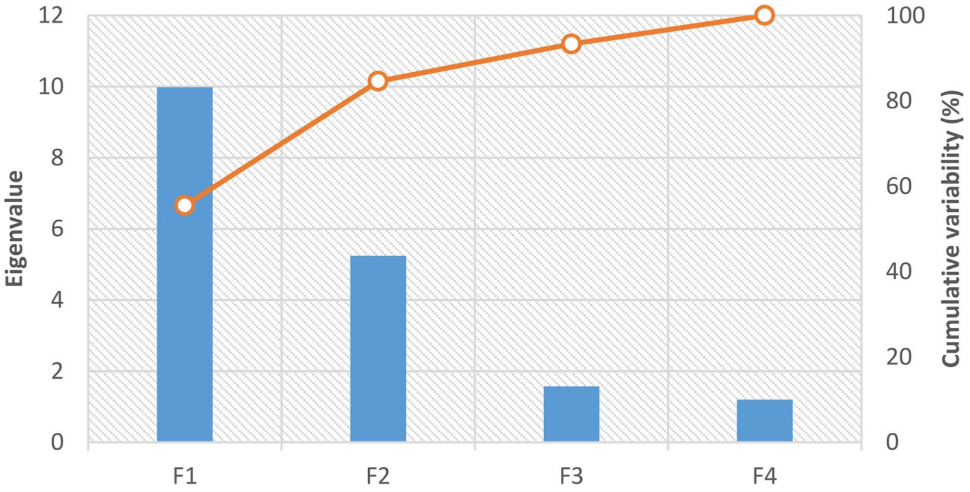


Figure 11. Scree plot showing eigenvalue and cumulative variability of Ethiope river during dry season.

by elevated positive loading in decreasing order: Ca > TH > HCO3/Mg > K > pH > PO4 > EC, the second factor (P2) explains 29.124%, which is characterized by positive loading in decreasing order: Na/Cl > TDS > NO3 and negatively loaded with Cr. The third factor (PC3) explains 8.74% that characterized by low positively loading in decreasing trend: Fe > Cd, and the fourth factor (PC4) explains 6.69% that characterized by low positively loading in decreasing trend of Pb > Cd > EC, respectively. Above all, the low and high positive loading could be regarded as coming from the same source, while negatively loading could be from other sources.

Based on biplot, during wet season, F1 was dominance with Cd, EC, PO4, HCO_3, and TH, F2 was dominance with Cr and F1 and F2 were dominance with NO3, TDS, Zn and SO4 reflecting acidity due to SO4 and NO3 in river Ethiope. The three main components—sulphate, nitrate, and phosphate—are typically caused by fertilizers (industrial and agricultural), showing human impacts[127]. The Cd, EC, TH and Cd The variables indicate geogenic sources since they are exclusively hydrochemical and are thought to have originated from the geological process. as observed by[128,138].

Heavy metals in surface water in Ethiope river

The measured concentrations of heavy metals in the water samples are shown in Table 8. Results indicate overall mean and range values for the following metals: Pb (mean: 0.02 mg/l; range: 0.00–0.10 mg/l), Zn (mean: 0.05 mg/l; range: 0.00–0.28 mg/l), Fe (mean: 0.10 mg/l; range: 0.00–0.32 mg/l), Cd (mean: 0.01 mg/l; range: 0.00–0.04 mg/l), and Cr (mean: 0.00 mg/l; range: 0.00–0.01), respectively. The results from this study show relatively low levels of heavy metal accumulation in water samples. Values for wet season are generally lower

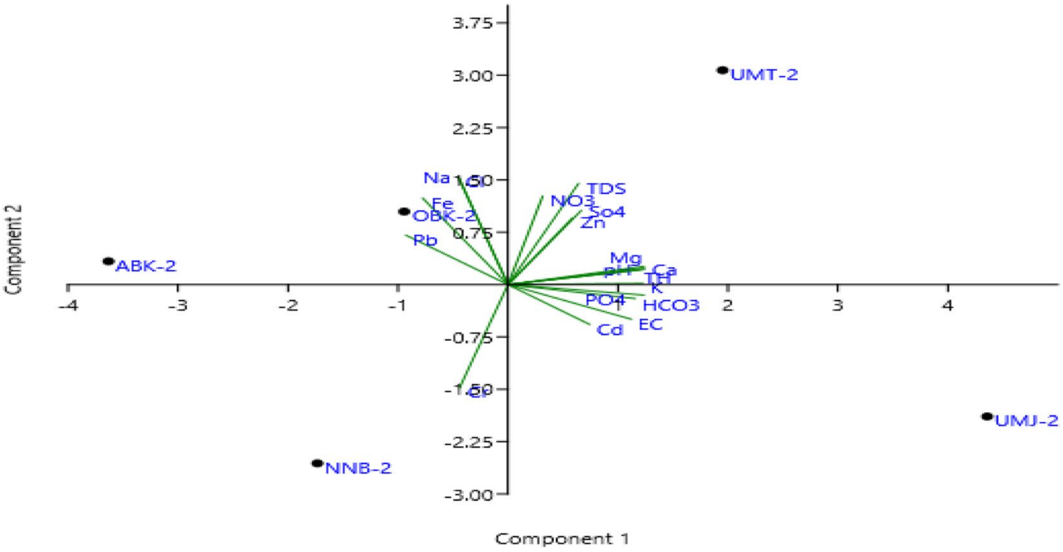


Figure 12. The first and second principal components of various water characteristics' (initial factor loads are represented by the green arrow lines for the dry season. The black solid circles reflects the values generated of each samples on the first and second principal component of Ethiope river in dry season.

S/*N*	Code	Group	Pb	Zn	Fe (mg/l}	Cd	Cr
1	UMJ-1	**Wet Season**	0.01	0.01	0.00	0.00	0.00
2	UMT-1		0.00	0.07	0.02	0.00	0.01
3	NNB-1		0.00	0.28	0.00	0.00	0.00
4	OBK-1		0.00	0.01	0.00	0.00	0.00
5	ABK-1		0.00	0.08	0.00	0.00	0.00
6	UMJ-2	**Dry Season**	0.00	0.01	0.02	0.04	0.01
7	UMT-2		0.03	0.03	0.23	0.00	0.00
8	NNB-2		0.01	0.01	0.11	0.00	0.01
9	OBK-2		0.05	0.00	0.32	0.02	0.00
10	ABK-2		0.10	0.00	0.28	0.01	0.01
Min			0.00	0.00	0.00	0.00	0.00
Max			0.10	0.28	0.32	0.04	0.01
Mean			0.02	0.05	0.10	0.01	0.01
Standard Deviation			0.03	0.09	0.13	0.01	0.01
WHO STDS			0.01	3–5	0.3	0.003	0.05

Table 8. Concentration of heavy metal in surface water samples of river ($n = 10$).

Variable\Subsamples	Dry Season - Wet Season
pH	**0.008**
EC	**0.008**
TDS	**0.008**
TH	0.095
Ca	0.095
Mg	0.063
Na	**0.032**
K	0.310
HCO_3	0.151
Cl	0.246
SO_4	0.841
NO_3	**0.024**

Table 9. Summary p-values for Mann-whitney test of Ethiope river wet and dry season samples.

and can be attributed to increased discharging and diluting capability of the river, while higher heavy metal values during dry season indicate human impacts and interactions with the river with low river discharging capability and evaporation[139]. The overall mean concentration of metals in the Ethiope surface water was in the decreasing trend of Fe > Zn > Pb > Cd/Cr, respectively, with Fe below the 0.03 mg/l WHO, Zn below the 5 mg/l WHO, Pb above the 0.01 mg/l, and Cd/Cr above the 0.05 mg/l WHO (1993) permissible limits for drinking water, respectively. The mean result of Pb in the present study was less than the range of 0.03–0.55 mg/l in Sirsa River, North Western Himalayas[140], which exceeded the allowable limits. In food and water, inorganic forms of poisonous Pb when in high concentrations have been accused of teratogenic effects in humans, inhibition of the procedure of hemoglobin synthesis, kidney dysfunction, gastrointestinal and urinary tract damage, as well as nervous system damage (central and peripheral nervous system)[141–143]. Similarly, Pb poisoning was also reported by[144] in the water of the Meenachil River at Kottayam, Kerala (India). Cd values in the present study were well within the Cd range of 0.01–0.07 mg/ reported in Sirsa River[140]. Cadmium, when consumed, can be irreversibly bioaccumulated throughout life in storage sites of the human organs, such as the kidney and bones, where it can cause damage to the kidney and reduction of bone minerals[145,146]. In addition, cadmium also disorganizes the human biological system even at relatively lower concentrations with other toxic heavy metals [129,147], causing significant occurrences and reoccurrences of headaches and vomiting.

Temporal variability of hydrochemical parameters for Ethiope river

The results of a two-tailed Mann- Whitney test indicates the p-values (Table 9) ranging from 0.008 to 0.841. According to the p-values ($p < 0.05$ is considered statistically significant), only pH ($p = 0.008$), Ec ($p = 0.008$), TDS ($p = 0.008$), Na(($p = 0.032$) and NO_3 ($p = 0.0024$) ions show temporal variability (Table 9).

Item	S_n	V_{id}	K	W_n	V_n	Q_n	W_nQ_n
pH	8.5	7	0.286	0.3400	5.06	56.4	19.1800
TDS	500	0	0.286	6.7300	31.25	6.67	44.8900
TH	300	0	0.286	0.0010	409.6	373.73	0.3700
Ca	75	0	0.286	0.0040	82.17	1,146.03	4.5800
Mg	30	0	0.286	0.0100	49.81	251.43	2.5100
Na	50	0	0.286	0.0060	1.67	3.46	0.0200
K	100	0	0.286	0.0036	0.41	0.41	0.0020
Cl	250	0	0.286	0.0010	47.55	23.49	0.0240
SO_4	200	0	0.286	0.0014	1.44	0.73	0.0010
NO_3	45	0	0.286	0.0060	0.02	0.04	0.0002
ΣWnqn	71.58						
ΣW_n	7.103						
$WQI = \Sigma W_n q_n / \Sigma W_n$	**10.077**						

Table 10. Calculated water quality index for Ethiope river for wet and dry seasons.

WQI	Interpretation
0 to 25	Excellent
26 to 50	Good
51 to 75	Poor
76 to 100	Very poor
> 100	Unfit for drinking

Table 11. Water Quality Index rating of the surface water in the study area. Source:[33].

Application of water quality index (WQI)

The overall water quality for sampled location is 10.08 (Table 10). Water quality index was calculated on the bases of ten (10) hydro-chemical parameters using the standard/threshold values of drinking water quality as recommended by WHO[33] and mean values of identified/sampled parameters using the weighted arithmetic index method[148].

The results indicate the water sample to be of excellent quality according to Table 11. The overall water quality index indicated about 10.01, found to be of excellent quality, far below the overall water quality range of 171.85 of River Landzu[149], and falls within WQI of the samples ranged from 10.23 to 63.64 of surface water, Dinajpur, Bangladesh[150].

Theoretical and practical implications of the study

This study has evaluated the water chemistry of Ethiope river and established the origin of the chemistry to come from mainly geological processes and anthropogenic activities of settlements around the river. The outcome of the study has helped in understanding theoretical scientific knowledge about the role of geological evolution, water-rock interactions, ion exchange, biogeochemical cycles (carbon, nitrogen etc.) and anthropogenic activities in influencing chemistry of river systems.

In practice, the results of the study have clearly helped to understand that ethiope river chemistry is potentially undesirable for portability purposes and aquatic life especially in wet season as it was reported to be acidic throughout the year but is best fit for irrigation. Although the river is currently self -purified which may account for the reason its yet to have exceeding water chemistry levels. However, with increasing populations and dependence on the river for wellbeing of the riverine people, the self-purification capability of the river may be overwhelmed causing more pollution and farther from portability. Thus, good sustainable water strategies and policy making that is proactive need to be put in place to control anthropogenic activities around the river areas.

Although there are limitations to the study which include spatio-temporal variability of water chemistry and inability to capture gradients of the river accurately where more significant pollution hotspots may be occurring. Again, it is also difficult to separate multiple ethiope water chemistry sources along rock water interactions, anthropogenic sources and geological processes using analytical method because of complexity of sources. These limitations may have impacted the findings and need to be bridged in future studies pertaining ethiope river.

Conclusions

The portability for drinking and domestic purposes of Ethiope surface water has been evaluated by examining the seasonal chemical characteristics and hydro chemical facies, their sources as well as the dominant chemical species makeup of the river using multivariate analysis (Gibbs plot, Trilinear piper analysis, Stiff pattern analysis, and Ionic scatter diagram). Result presented here has revealed an acidic surface water throughout the season ranging from 4.8 for wet season and 5.3 above WHO limits for dry season, making water acidic suspected to arise from wet deposition of acid anhydrides, dissolution of certain ions and organic matter inhibition from run off within the study area. The bicarbonate makeup of the river was also high throughout the season but more in dry season due to temperature, pH and evaporative effects on rock dissolution. TDS and TH were also high though not in adverse health causing levels and correlated with higher amounts of dissolved ions salts such as magnesium, bicarbonates and calcium. Based on Gibbs plot/Trilinear (Piper)plot, the Ethiope River was predominantly composed of Ca-HCO_3 (calcium bicarbonate) originating from rock-water interactions/weathering processes and is further supported by the evidenced high concentrations of alkaline earth metal ions (Ca^{2+} and Mg^{2+}) which were higher than the alkaline metal ions (Na^+ and K^+). In addition, it was found that the total concentration of weak acids was greater than that of strong acids ($Cl^- + SO_4^{2-}$). Results on Stiff pattern analysis revealed higher concentrations of calcium bicarbonate ions during wet season due to high river dissolution processes, and also showed varying concentrations of hydrochemical characteristics at different sampling points of Ethiope river suggesting spatial differences in concentrations of bicarbonates and alkaline earth metal ions (Ca^{2+} and Mg^{2+}). In line with results from ionic scatter analysis, Ca^{2+} constituted 50% of total Cations, T_z^+ and HCO_3^- constituted 84% of total anions, T_z^- corroborating the fact that the bedrock of Ethiope river and the chemical species are relatively predominated by calcium bicarbonate rock type. The order of abundance of cations in the river was in decreasing order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, while that of anion was in decreasing trend of $HCO_3^- > Cl^- > SO_4^{2-} > NO_3$, The cations were 49% greater than anions. While rainfall (evaporation-crystallization) is accused as the origin of presence of small amounts of Na^+ and Cl^-, weathering processes is accused of presence of large amounts of Ca^{2+} and HCO_3^- concentrations of Ethiope river. The strong correlation between NO_3 and SO_4 ions indicated influence of agricultural activities on the surface water system during wet season, while in dry season, SO_4 and NO_3 recorded inverse relationship due to other activities. PC1 recorded high positive loading in decreasing order: Ca > TH > HCO_3/Mg > K > pH > PO_4 > EC. PC2 recorded positive loading in decreasing order: Na/Cl > TDS > NO_3 and negatively loaded with Cr. PC3 showed low positive loading in decreasing trend: Fe > Cd, and PC4 recorded low positive loading in decreasing trend of Pb > Cd > EC respectively. Above all, the low and high positive loading could be regarded as coming from the same source, while negatively loading could be from other sources. The overall mean values of metals in water were in decreasing trend of Fe > Zn > Pb > Cd/Cr, with Pb, Cd above the permissible limits for drinking water. Despite human activities along the study location, the overall WQI of the river seemed of good quality which might be due to rapid flow and self -purification of the River. However, in the long run, the acidic nature of the water may harm aquatic life and pose potential human health effect as being depended on for drinking and other domestic purposes during water scarcity by the people especially with high TDS and TH level. With developing intensification of human activities within the study area the river purification may be overwhelmed. It is therefore of utmost importance to constantly mount surveillance and monitoring of human activities along water ways in order to ascertain good water quality for the teeming people of Southern Niger delta region through the prevention of water pollution.

Data availability

The data set generated for this study will be made available on request from the corresponding author: Nwogu F.U (fredianuchenna@gmail.com).

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Author contributions

Ubuoh provided methodology, result interpretation, discussion and supervised the work. Nwogu wrote the introduction and methodology, discussion, review, editing, interpretation, correspondence. Ossai-Abeh Conceptualized the topic, analysis, methodology, discussion, interpretation of results, software, resources. Ikwuemesi did project administration and investigation. Oke did the data curation, visualization, collaboration. Umoh: Resources, logistics, collaboration.

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Declarations

Competing interests

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Additional information

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