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Characterization of the Hydrochemistry, Scaling and Corrosivity Tendencies, and Irrigation Suitability of the Water of the Rivers Karawa and Iyiaji

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Abstract: Assessing water quality is necessary to ascertain its viability for domestic, industrial, and agricultural purposes. A total of 48 water samples were, respectively, drawn from the Rivers Karawa and Iyiaji located in Ezeagu and Uzo-uwani which are typical rural areas in Enugu State, Nigeria. These samples were taken in two seasons (early rainy season and late dry season). Physicochemical properties were determined using standard methods. The scaling and corrosivity potentials of the water were evaluated using the Larson-Skold index, aggressive index, Puckorius scaling index, and Ryznar stability index models. Additionally, seven irrigation evaluation criteria, as well as spatial distribution maps, were used to determine the suitability of the river waters for irrigation purposes and to interpolate the spatial distribution of the river water quality parameters. Major ion chemistry was used in the assessments. The physicochemical properties of river waters fell within the recommended standard values. However, NO_3^- greatly exceeded the recommended range in both rivers. The cations and anions from River Karawa were $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ and $NO_3^- > Cl^- > SO_4^{2-} > HCO_3^- > CO_3^- > PO_4^-$, while those from River Iyiaji were $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $Cl^- > SO_4^{2-} > NO_3^- > PO_4^- > HCO_3^- > CO_3^-$. A piper plot showed the predominance of Ca^{2+} and Mg^+, as well as SO_4^{2-} and Cl^-, in both rivers. The seven irrigation assessment indices indicated that the water of the Rivers Karawa and Iyiaji is suitable for irrigation purposes. In addition, the scaling and corrosivity models predicted that the river waters have high scaling and corrosivity potentials. Specifically, while the aggressive index suggested that it is severely corrosive, the Langelier saturation index suggested that the water from both rivers is supersaturated and, thus, has potential to scale.

Keywords: physicochemical parameters; industrial water quality; irrigation water assessment; river water; statistical analysis; water quality assessment

1. Introduction

Water is used primarily for four purposes: household, agricultural (irrigation), industrial, and in-stream usage [1,2]. Among these significant water uses, agriculture consumes the majority of water globally and accounts for more than 80% of water usage in North America [3,4]. Baker et al. [5] and Fellman and Getis [6] also noted that just a tiny percentage of the tremendous amount of water that is present on the earth's surface is usable and fit for use by people, plants, and animals. Irrigated agriculture uses 90% of the world's fresh water and roughly 73% of that in the world's poorest countries. Therefore, irrigation utilizes around 16% of the world's cropland to generate more than a third of the global yield. FAO [7] also noted that only 241.5 million hectares of the world's total arable land and land used for permanent crops are covered by irrigation, or 15.98% of the total. Humans use water resources in a variety of ways, and in the process, they bring waste into the natural drainage system that is unable to be easily disposed of through the process of natural recycling because of its volume, composition, or both. In the course of natural processes, aquatic creatures can break down, absorb, and spread chemicals in quantities in which they naturally occur, and it is only in rare instances that pollutants overwhelm the cleansing abilities of the recipient waters. Human activities however have added significant amounts of chemicals to water-receiving sources at higher intensities than a particular body of water can purify [8]. The type of contaminants, such as metals or inorganic chemicals, has an impact on the purifying processes as well since they take a longer time to break down or cannot break down at all through natural mechanisms. When such compounds are present in water, they lower the quality of the water and may eventually cause the buildup of hazardous ions and bio-amplification [9].

Rivers have played a significant role among other surface waterways as one of the main sources of water for irrigation application in most developing nations, especially in arid and semi-arid regions. Surface water quality is a very sensitive and global environmental issue that is important for long-term economic development and environmental sustainability [10]. In recent years, there has been a rise in global awareness of the quality of irrigation water, and new strategies have been created to manage water resources sustainably [11]. As a result of the ongoing population increase, intensified industrialization, rapid urbanization, and a changing environment, the lack of water resources has become a major issue in many nations [12]. As a result, producing enough food to meet the needs of the population has become a global problem for sustainable agricultural development. Water shortages and sustainable irrigation water management are two such challenges [13].

In the present study, the hydrochemistry, corrosivity and scaling tendencies, and irrigation suitability of the water of the Rivers Karawa and Iyiaji in southeastern Nigeria were assessed. These rivers are used extensively for irrigation of farmland along the river banks. They are also used for some domestic purposes such as washing of cloths, washing of cars, and washing of cassava to mention but a few. The objectives of the study are to (1) evaluate the river water for irrigation application resulting from the growing need and interest in dry seasons' agro-farming, (2) assess the storageability and corrosivity of the river water, and (3) evaluate the hydrochemistry of the cations and anions available in the river water. Statistical analyses, graphical plotting, and indexical methods were integrated to better achieve the aim of the study. The novelty of the current study centers on the fact that establishing the irrigation suitability of Karawa and Iyiaji river water is paramount considering the rate of its use by peasant farmers living around the banks of the river. It is hoped that the findings of this research would significantly contribute to the effective management of the water body for agricultural purposes besides its domestic application status.

2. Materials and Methods

2.1. Study Area

Ezeagu and Uzo-uwani, being the major towns around the sampling locations, form the major agricultural belts in eastern Nigeria [14]. As typical of rural areas in Nigeria, there is a lack of modern basic infrastructures, and the economy is principally peasant farming. The study area is rich in many agricultural products such as cassava, yam, maize, plantain, cowpea, etc. These rivers were cherry-picked owing to their vulnerability to nonpoint sources of pollution such as free grazing of cattle, cassava processing, open defecation, sharp sand/soil mining, and rice and tapioca processing which are massive agricultural activities [15]. The main water supply sources are the rivers, ponds, hand-dug wells, and, in very few cases, community boreholes. Water from these sources is not treated and hence has some health risks associated with them [15,16].

The study area has two notable climatic seasons: wet and dry seasons. The wet season starts from around April to September while the dry season starts from around October to March [15]. These seasons are caused by the north–south fluctuations of discontinuity between the dry Sahara (continental) air and the humid Atlantic air. The dry period is characterized by cold, dry, and windy weather while the wet season is characterized by heavy, intense rainfall [15]. The most frequent types of sewage disposal methods are open defecation and pit toilets. The major agricultural products in the area are yam, maize, rice, banana, pineapple, okra, and cassava. Identifiable sources of pollution include soft drink and brewery factories as well as other industrial activities that happen within the 9th-mile corner in Enugu, Nigeria. Pollutants can be transported to distant places from their point sources through run-off water and atmospheric deposition [17]. Agro-wastes such as indiscriminate household waste disposal, food processing and farm wastes, emissions from vehicles, open defecation, the use of modern chemical products in homes, and fertilizers and pesticides also increase the water pollution in the area. Most of these wastes also harbor organic pollutants and pathogens. In terms of sanitation, pit toilets and surrounding bushes are in common use in the area [18].

2.2. Geo-Hydrology of the Study Area

Three underlain geologic formations (Imo, Nsukka, and Ajali Formations) are known in Ezeagu and Uzo-uwani, and these are part of the Niger Delta and Anambra sedimentary basins [15,19]. Two main aquifer systems characterize the area which is shallow unconfined and deep semi-confined. The shallow unconfined aquifer systems are found in fractured, jointed, and weathered shale. The deep semi-confined aquiferous systems are found in the area underlain by Nsukka and Ajali formations whereas the weathered shale beds provide an impermeable layer that hinders the downward flow of infiltration water. The thickness range of the superficial unconfined spring framework is from 10 to 60 m [3,20,21]. The genuine thickness of the profound semi-limited spring frameworks could not be resolved from borehole logs since the whole thickness of Ajali formation was not fully penetrated [3,22].

2.3. Sample Collection

Water samples were collected from two locations (Table 1) in each of the rivers (Aguobu Iwollo, Olo for the Karawa river and Ogbosu, Adaba for the Iyiaji river). A total of forty-eight (48) water samples were collected from the two rivers, comprising three samples from each sampling point, section, and sampling season (2019 and 2020). Water samples were collected during the early dry season (November–December) and late dry season (March–April), which are the periods when these river water are actually used by farmers for irrigation purposes (Figure 1). In collecting samples from the rivers, the polyethylene sampling containers were dipped just below the surface (about half the depth of the river) to reduce the contamination of sampled water by surface films. The samples were collected about 5 m away from the river banks where the farmers are known to insert their pipes used in taking water from the rivers. The samples from the same river were collected about 100 ft away from each other and mostly from places closer to the point collection of river water for irrigation water.

Table 1. Sampling and GPS locations.

Water Type	Sample Location	GPS Location	Elevation (m)
River Karawa (RK1)	Aguobu Iwollo (sp4)	6°25′39.1476″ N, 7°14′27.06″ E	219
River Karawa (RK2)	Oguluogu (sp3)	06°25′868″ N, 007°11′732″ E	200
Iyiaji River (RI1)	Ogbosu (sp1)	6°28′38″ N, 7°4′0″ E	22
Iyiaji River (RI2)	Adaba (sp2)	6°27′50.39″ N, 7°1′57.78″	85

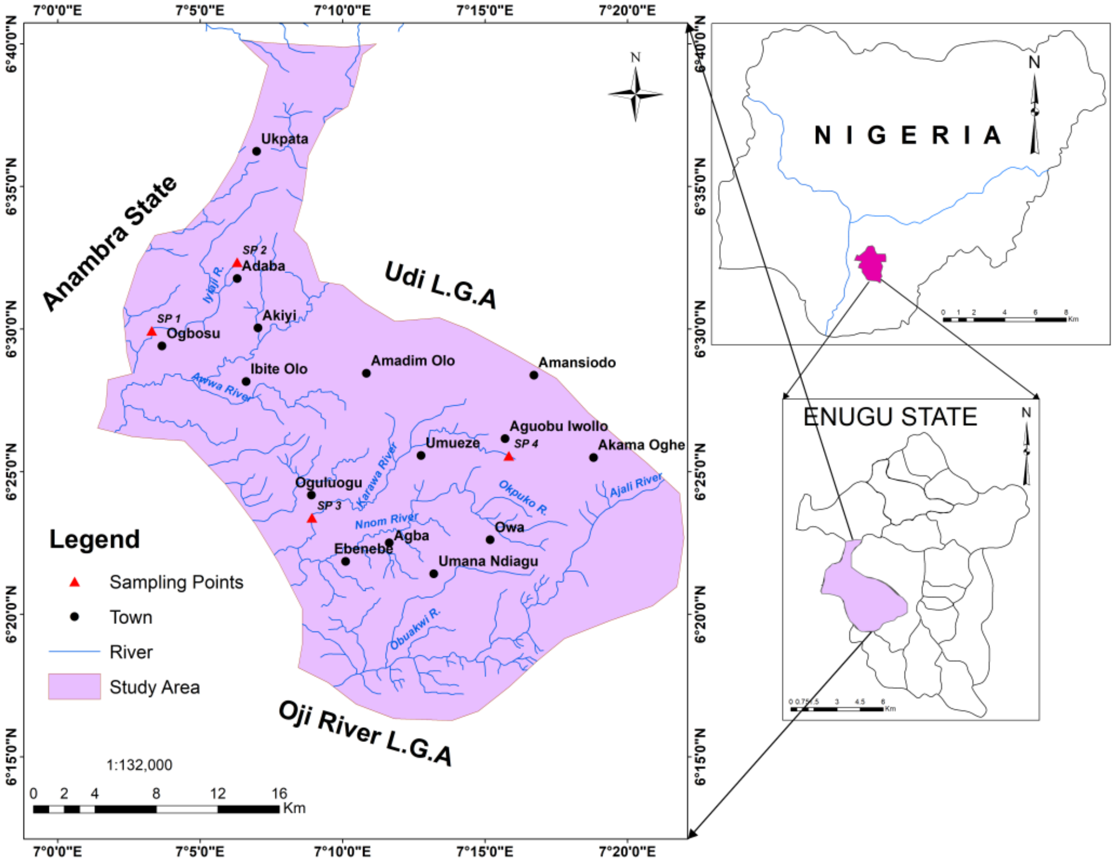


Figure 1. Map of Ezeagu and Uzo-uwani local government areas showing sampling locations.

2.4. Sample Analysis

The samples were analyzed on-site for pH (Jenway, 3510, Cole-Parmer, USA), electrical conductivity, and total dissolved solids (WTW Conductivity Meter LF90 Burladingen/Germany). Additionally, potassium and sodium were ascertained with a flame photometer (Searchtech, FP640, England). Sulphate was determined by the turbidimetric method (APHA-AWWA-WEF, 1999). Phosphate was determined by the colorimetric method using ascorbic acid as reported by Murphy and Riley [23]. Alkalinity was measured using the titrimetric method. The cadmium reduction method was used to determine the nitrate content [24]. In the nitrate determination method, the samples were passed through a copper-coated cadmium reduction column. Nitrate in the sample was reduced to nitrite in a buffer solution. The nitrite was then ascertained by diazotizing with sulfanilamide and coupling with N-1- naphthylethylenediamine dihydrochloride to form a color azo dye. The absorbance was measured at 540 nm which is directly proportional to the concentration of nitrate plus nitrite in the water sample. The nitrate concentrations was then calculated by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrate plus nitrite values [25]. Total hardness as well as Ca^{2+} and Mg^{2+} were determined with titrimetric method using EDTA [26]. Sodium and potassium ions were ascertained by flame photometer (Jenway PFP7/PFP7/C). In the determination of chloride and carbonate ions (Cl^- and HCO_3^-), in line with APHA, [27] argentometric and potentiometric titration procedures were used, respectively. A mean value of each analysis parameter resulting from the triplicate results obtained are presented in Table 2. Standard methods according to APHA et al. [28] were used to determine all other parameters.

2.5. Irrigation Water Quality Evaluation Criteria

The irrigation evaluation indices used in the assessment of river Karawa and Iyiaji for irrigation purposes.

1. Soluble sodium percent (SSP) evaluates sodium hazard [29]. SSP is given in Equation (1). A water sample with an SSP value greater than 60% is not advisable for irrigation application because it can cause sodium accumulation which could lead to a breakdown in physical properties of the soil.

$$SSP = \frac{Na^+ + K^+}{Na^+ + Ca^{2+} + Mg^{2+} + K^+} \times 100 \quad (1)$$

2. The permeability index (PI) of water is a function of calcium, magnesium, sodium, and carbonate in the soil [30]. According to Doneen [29], the PI is given as in Equation (2):

$$PI = \left((Na^+ + \sqrt{HCO_3^-} \right) / Na^+ + Mg^{2+} + Ca^{2+}) \times 100 \quad (2)$$

3. Kelly [31] defined irrigation water according to Equation (3):

$$Kelly's\ Ratio\ (KR) = Na^+ / \left(Ca^{2+} + Mg^{2+} \right) \quad (3)$$

4. The sodium absorption ratio (SAR) which indicates the level to which irrigation water undergoes cation exchange reaction in soil is given in Equation (4) as proposed by Richards [32].

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}} \quad (4)$$

5. Raghunath, based on Mg and Ca, proposed Magnesium Absorption Ratio (MAR) for the classification of irrigation water as shown in Equation (5) [33].

$$MAR = (Mg^{2+} / \left(Ca^{2+} + Mg^{2+} \right)) \times 100 \quad (5)$$

6. Chloro-alkaline indices (CAI) explain the ion exchange between rock and the water [20].

$$CAI = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \quad (6)$$

7. Residual sodium carbonate (RSC), also known as residual alkalinity (RA), is also used to classify irrigation water according to Equation (7) [32,34,35].

$$RSC = (HCO_3^- + CO_3) - \left(Ca^{2+} + Mg^{2+} \right) \quad (7)$$

2.6. Prediction of Scaling and Corrosion Potential of the River Water

Five indices were used to predict the calcium carbonate scaling and corrosion potential of the two rivers. Several indices that reasonably predict the likelihood of calcium carbonate precipitating from water to in turn cause corrosivity and discourage storability of the water do exist [36]. Corrosion being electrochemical in nature is a physicochemical interaction between the surrounding and metal which leads to a change in the properties of the metal [37]. As corrosion occurs in pipe, it releases particles from the pipe into the water/fluid leading to contamination. Some of the models are the following.

(A) Langelier saturation index model (LSI): this model is perceived to be the most widely accepted indicator of scaling potential in water networks and water supply [37]. It incorporates the water master variable-pH which is the driving force for scaling potential. It predicts that when the LSI value is greater than zero, the water is super-saturated and has the potential to scale. When LSI = 0, the water is saturated and has no tendency to scaling, but when LSI < 0, the water is not saturated and has a tendency to corrode [37]. It is calculated using Equation (8).

$$LSI = pH - pHs \tag{8}$$

pH = normal water pH, pHs = pH at saturation of $CaCO_2$

$$pHs = (9.3 + A + B)\ x\ (C + D) \tag{9}$$

$$A = (Log_{10}\ (TDS) - 1\ x\ 10 \text{ in mg/L} \tag{10}$$

$$B = -13.12\ x\ Log_{10}(^{\circ}\text{C} + 273) + 34.55 \text{ in } ^{\circ}\text{C} \tag{11}$$

$$C = Log_{10}\left(Ca^{2+} as\ CaCO_2\right) - 0.4 \text{ in mg/L} \tag{12}$$

$$D = Log_{10}(Alkalinity\ as\ CaCO_2) \text{ in mg/L} \tag{13}$$

(B) Ryznar Stability Index (RSI): an alternative method for computing calcium carbonate scale formation to Langelier saturation index is the Ryznar stability index which is given in Equation (14).

$$RSI = 2pHs - pH \tag{14}$$

The water is scaling rigorously if the RSI < 5.5 and scaling if the RSI < 6.2 but >5.5. At 6.2 < RSI < 6.8, water is neutral-balanced (water is not corrosive or scaling properties). When 6.8 < RSI < 8.5, the water is corrosive, and when RSI is >8.5 water is rigorously corrosive [37].

(C) Larson-Skold Index (LS): this explains the ratio of the concentration of sulphate ions and chloride ions to the concentration of carbonate and bicarbonate ions. The index has proven to be an essential tool in predicting the aggressiveness of water through cooling waters [38], and it is expressed in Equation (15).

$$LS = \left(C\ Cl^- + C\ SO_4^{2-}\right) x \left(C\ HCO^{3-} + C\ CO_3^{2-}\right) \tag{15}$$

The water will have a tendency to scaling. The corrosion rate may be higher, and the water shows a high rate of localized corrosiveness when the LS < 0.8, 0.8 < LS < 1.2 and LS > 1.2, respectively [37]. When the Larson-Skold value is lower than 0.8, chloride and sulphate are unlikely to interfere with the formation of protecting film, or water has a tendency to scaling [36].

(D) Puckorius Scaling Index (PSI): PS is calculated from Equation (16).

$$PSI = 2pHs - pHeq \tag{16}$$

$$pHeq = -1.465Log_{10}(TAlk) + 4.54 \tag{17}$$

where pHeq = pH of water at equilibrium, and Talk = total alkalinity as $CaCO_3$.

When the value of PS is greater than 7, the water is likely corrosive and may dissolve the scale, but scaling is unlikely to occur when PS is less than 6.1 [37]. Among all the index models, PS is the only one that uses the driving force calcium carbonate scale formation [37,38].

(E) Aggressive Index (AI): Equation (18) was applied to calculate the AI. An AI value of 12 and above indicates that the water has scaling property (non-aggressive) while a value of AI < 10 shows that the water is severely corrosive (very aggressive). When the AI is <12 but >10, it shows that the water is approximately corrosive which implies being moderately aggressive. AI is a suitable index for Asbestosis-cement pipelines [38].

$$AI = pH + Log_{10} TAlk\ x\ Hardness \tag{18}$$

2.7. Statistical Analysis and Spatial Modeling

Pearson's correlation between the sampled rivers parameters at 0.05 significant levels was determined, while the relationship between the parameters was evaluated using the hierarchical cluster Dendrogram. All the statistical analyses were performed with SPSS version 16.0. Water types, percentage difference of anion–cation balance, and salinity hazard were determined using the Rock ware Aq.QA, 1.5.0.Origin Pro9 version which was used to create a piper plot, Wilcox diagram, Hierarchical Cluster Dendrogram, Gibbs, Doneen, Pie plots, and trilinear draws, for hydrochemical classifications.

An extended ArcGIS 10.2 module for spatial modeling was used to interpolate the spatial distribution of the river water quality parameters. The Inverse Distance Weighted (IDW) interpolation approach has been applied in creating several spatial distribution maps of river water [39,40].

3. Results and Discussion

The acceptability of surface water for agricultural and domestic applications is in direct relation to the different physiochemical parameters and their concentrations. The descriptive values of the determined parameters are presented in Tables 2 and 3. The pH values of all the river water samples were slightly acidic except the EDSs in both sampling years of the River Iyiaji 1 which were slightly alkaline (7.5 and 8.1). The pH values were within the recommended limit (6.5–8.4) for irrigation water [7]. Carbonate ion concentrations increase with increasing pH, and when more CO_2 dissolves in river water it becomes more acidic. When CO_2 from the atmosphere reacts with seawater, it immediately forms carbonic acid (H_2CO_3), which in itself is unstable. This further dissociates to form CO_3^- and HCO_3^-. The CO_3^- and HCO_3^- ions are responsible for the buffering capacity of the river water (river water can resist drastic pH changes even after the addition of weak bases and acids). The CO_3^- ion can react with Ca^{2+}, which are in excess in river water, to form $CaCO_3$, the material out of which the shells of mussels, the skeleton of corals, and the exoskeletons of some microalgae are made of. The total dissolved solid (TDS), total hardness (TH) and electrical conductivity (EC) were within the acceptable limit of the FAO [7] and WHO [41]. TDS concentration delineates the presence of inorganic salts and small amounts of organic matter in water, and EC is the measure of water ability to conduct electrical current [42]. The sources of material leading to higher EC and TDS can come from nature, such as the geological conditions of the water, and from human anthropogenic activities, such as industrial and domestic waste as well as agriculture [43]. The relationship between EC and TDS is not always linear, and this situation is highly dependent on the water material contents and salinity. The higher the material contents or the salinity levels, the more complex it is to describe these parameters [42].

Table 2. Descriptive values of the determined parameters in Karawa river.

River	Sample	Year of Sampling	T (°C)	pH	EC	TDS	TA	TH	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	PO_{42}-	SO_{42}^-	K^+	Na^+	HCO_3^-	CO_3^-
K1	EDS	2019	27 ± 1.3	5.8 ± 0.3	160 ± 23.5	80 ± 2.7	1.2 ± 0.0	38 ± 0.5	24 ± 2.4	14 ± 1.2	16.8 ± 1.4	41 ± 3.9	1.4 ± 0.1	14.33 ± 1.2	3.2 ± 0.1	1.2 ± 0.2	3.5 ± 0.3	2.68 ± 0.1
	LDS	2019	28 ± 1.7	6 ± 0.8	225.4 ± 21.6	153 ± 2.5	1.86 ± 0.1	37.5 ± 0.4	18.3 ± 5.6	19.2 ± 1.9	16.8 ± 1.2	47 ± 4.3	0.34 ± 0.2	13.8 ± 1.4	0.8 ± 0.0	1.3 ± 0.1	8.02 ± 0.5	4.05 ± 0.3
	EDS	2020	27 ± 1.2	5.9 ± 0.4	192.7 ± 12.8	116.5 ± 11.6	1.53 ± 0.1	37.75 ± 0.9	21.15 ± 2.1	16.6 ± 0.4	16.8 ± 1.6	44 ± 2.5	0.87 ± 0.1	14.07 ± 1.2	2 ± 0.2	1.25 ± 0.2	5.76 ± 0.1	3.37 ± 0.1
	LDS	2020	28 ± 2.0	5.2 ± 0.1	184.9 ± 13.2	112.3 ± 3.6	1.72 ± 0.0	37.5 ± 1.1	19.1 ± 3.4	18.4 ± 2.6	15.7 ± 1.8	42 ± 3.5	0.83 ± 0.1	13.92 ± 1.1	2.6 ± 0.2	1.4 ± 0.2	7.4 ± 0.2	2.88 ± 0.2
		Mean	26	5.73	190.75	115.45	1.58	37.68	20.64	17.05	16.53	43.5	0.86	14.03	2.15	1.29	6.17	3.25
		Min	27	5.2	160	80	1.2	39	18.3	14	15.7	41	0.34	13.8	0.8	1.2	3.5	2.68
		Max	28	6	225.4	153	1.86	44	24	19.2	16.8	47	1.4	14.33	3.2	1.4	8.02	4.05
K2	EDS	2019	26 ± 1.4	5.9 ± 0.7	180 ± 18.7	108 ± 7.8	0.5 ± 0.0	30 ± 0.2	18 ± 1.1	12 ± 0.8	14 ± 0.4	16 ± 1.7	2.1 ± 0.0	12 ± 1.6	2.04 ± 0.3	2 ± 0.0	7.28 ± 1.0	3.35 ± 0.2
	LDS	2019	27 ± 1.2	6.9 ± 0.8	162 ± 20.4	110 ± 4.7	1.4 ± 0.1	34 ± 0.4	20 ± 2.1	14 ± 0.7	12 ± 0.2	18 ± 0.7	1.2 ± 0.2	10 ± 0.6	1.2 ± 0.0	1.2 ± 0.0	6.25 ± 1.0	2.91 ± 0.1
	EDS	2020	27 ± 1.9	6.4 ± 0.4	171 ± 22.4	109 ± 3.9	0.95 ± 0.1	32 ± 0.8	19 ± 2.1	13 ± 0.5	13 ± 0.1	17 ± 0.9	1.65 ± 0.1	11 ± 1.1	1.62 ± 0.1	1.6 ± 0.0	6.76 ± 0.3	3.13 ± 0.3
	LDS	2020	28 ± 1.7	5.7 ± 0.1	167 ± 21.4	113.1 ± 9.2	2.1 ± 0.2	38.8 ± 0.2	21.3 ± 0.9	17.5 ± 1.1	14.2 ± 0.6	19.5 ± 1.7	1.53 ± 0.2	13.3 ± 1.3	3.8 ± 0.1	2.2 ± 0.1	9.5 ± 1.1	5.5 ± 0.4
		Mean	27	6.23	170	110.03	1.24	33.70	19.58	14.13	13.3	17.63	1.62	11.58	2.17	1.75	7.45	3.73
		Min	26	5.7	162	108	0.5	24	18	12	12	16	1.2	10	1.2	1.2	6.25	2.91
		Max	28	6.9	180	113.1	2.1	40	21.3	17.5	14.2	19.5	2.1	13.3	3.8	2.2	9.5	5.5
FAO (1994)				6.5–8.4	3000	600–1000 *	-	200–500 *	0–400	0–60	0–1065	0–10	-	0–960	-	0–920	0–610	0–3

K2 = Karawa 2, K1 = Karawa 1, EDS—early dry season, LDS—late dry season, * WHO [41], NA—not available, SD—standard deviation, all parameters are in mg/L except EC (µS/cm) and pH which does not have unit.

Table 3. Descriptive values of the determined parameters in Iyiaji river.

River	Sample	Year of Sampling	T (°C)	pH	EC (µS/cm)	TDS (mg/L)	TA	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	SO_4^{2-} (mg/L)	K^+	Na^+	HCO_3^-	CO_3^-
I1	EDS	2019	24.8 ± 1.2	8.1 ± 0.3	1313 ± 39.5	580 ± 29.5	75 ± 2.1	110 ± 12.7	74 ± 2.5	36 ± 1.6	160 ± 27.1	50 ± 2.9	1.8 ± 0.4	146 ± 17.9	2.2 ± 0.7	12 ± 2.1	3.2 ± 0.1	1.82 ± 0.0
	LDS	2019	25 ± 1.4	5.7 ± 0.8	1374 ± 48.4	640 ± 34.2	64 ± 2.4	108 ± 13.4	76 ± 4.6	32 ± 2.5	162 ± 22.1	50 ± 5.3	4 ± 0.7	146 ± 12.7	7.2 ± 0.9	11.5 ± 1.3	2.8 ± 0.1	3.65 ± 0.2
	EDS	2020	26 ± 1.7	7.9 ± 0.3	1343.5 ± 43.5	610 ± 39.7	69.56.4	109 ± 17.1	75 ± 7.9	34 ± 1.3	161 ± 19.7	50 ± 2.6	2.9 ± 0.6	146 ± 14.8	4.7 ± 0.2	11.75 ± 1.1	3 ± 0.2	2.74 ± 0.1
	LDS	2020	25.8 ± 2.5	5.2 ± 0.7	973.4 ± 28.6	730 ± 30.6	78.42.2	121.3 ± 15.6	82.1 ± 7.5	39.2 ± 2.8	180.2 ± 23.7	52.1 ± 7.8	3.2 ± 0.1	149 ± 19.5	8.6 ± 0.3	13.2 ± 2.1	4.8 ± 0.1	3.2 ± 0.1
		Mean	25.4	6.72	1250.98	640	71.73	112.08	76.78	35.3	165.8	50.53	2.98	146.75	5.68	12.11	3.45	2.85
		Min	24.8	5.2	973.4	580	64	86	74	32	160	50	1.8	146	2.2	11.5	2.8	1.82
		Max	26	8.1	1374	730	78.4	177	82.1	39.2	180.2	52.1	4	149	8.6	13.2	4.8	3.65
I2	EDS	2019	26 ± 1.9	6.8 ± 0.2	1233 ± 38.9	540 ± 22.8	1.7 ± 0.01	54 ± 6.7	32 ± 2.6	22 ± 1.8	66 ± 3.1	48 ± 1.7	0.22 ± 0.1	40±	1.68±	1.2±	4.51±	1.404±
	LDS	2019	27 ± 2.1	5.7 ± 0.2	1002 ± 28.6	548 ± 29.6	1.86 ± 0.4	46 ± 5.7	34 ± 4.9	12 ± 2.0	78 ± 2.6	32 ± 1.9	0.22 ± 0.1	102±	2.42±	2.02±	3.88±	2.246±
	EDS	2020	27 ± 2.8	6.7 ± 0.3	1117.5 ± 41.0	544 ± 37.5	1.78 ± 0.2	50 ± 8.6	33 ± 3.7	17 ± 1.5	57 ± 3.5	40 ± 0.9	0.22 ± 0.1	71±	2.05±	1.61±	4.195±	1.825±
	LDS	2020	26 ± 1.9	5.3 ± 0.1	1013 ± 44.9	632 ± 33.2	63.3 ± 3.8	124 ± 5.8	87 ± 4.3	37 ± 2.1	82 ± 2.5	63 ± 2.0	2.4 ± 0.2	139±	3.2±	12.4±	5.3±	3.1±
		Mean	26	6.125	1091.38	566	17.16	68.5	46.5	22	70.75	45.75	0.765	88	2.3375	4.3075	4.47125	2.14375
		Min	26	5.3	1002	540	1.7	46	32	12	57	32	0.22	40	1.68	1.2	3.88	1.404
		Max	27	6.8	1233	632	63.3	57.4	87	37	82	63	2.4	139	3.2	12.4	5.3	3.1
FAO (1994)				6.5–8.4	3000	600–1000 *	NA	200 –500 *	0–400	0–60	0–1065	0–10	NA	0–960	NA	0–920 mg/L	0–610 mg/L	0–3 mg/L

I1 = Iyiaji 1, I2 = Iyiaji 2, EDS—early dry season, LDS—late dry season, * WHO [41], NA—not available, SD—standard deviation. All parameters are in mg/L except EC (µS/cm) and pH which does not have unit.

With the exception of NO_3^-, other parameters assessed (Na^{2+}, Mg^{2+}, Ca^{2+}, K^+, Cl^-, HCO_2^-, CO_3^-, PO_4^-, and SO_4^{2-}) were within the recommended limit of the FAO [7] and WHO [41]. NO_3^- ranged from 16 to 47 in the Karawa River and 32 to 63 in the River Iyiaji with the FAO recommended value being 0–10 mg/L. Since both rivers are situated around farms settlements, the presence of elevated levels of NO_3^- in the river water samples could be due to pesticide run-offs from the surrounding farms applied to boost crop yield. Similarly, the discharge of industrial wastes into River Iyiaji levels may have led to high SO_4^{2-} concentrations. The mean pHs of the River Karawa sampling locations are 5.73 (K1) and 6.23 (K2). Similar observations were noted in the I1 (6.72) and I2 (6.13) sampling sites of the River Iyiaji. Generally, the low pH observed in both rivers could be ascribed to the high concentrations of NO_3^-, SO_4^{2-} and other contributors present in both river waters.

The irrigation values of both River Karawa and River Iyiaji are seen in Tables 4 and 5. Seven parameters were used to evaluate the suitability of both rivers for irrigation purposes. The calculated values of PI, SSP, KR, MAR, RSC, CAI, and SAR, respectively for the River Karawa at early dry season and late dry season in both years under consideration are seen below.

Table 4. Irrigation analysis of the River Karawa.

River	Sample	PI	SSP	KR	MAR	RSC	CAI	SAR
Karawa 1	EDS 2019	7.830	10.377	0.032	36.842	−31.820	0.739	0.389
	LDS 2019	10.650	5.303	0.035	51.200	−25.430	0.875	0.425
	EDS 2020	9.360	7.927	0.033	43.974	−28.620	0.807	0.407
	LDS 2020	10.590	9.639	0.037	49.067	−27.220	0.745	0.457
Karawa 2	EDS 2019	14.680	11.869	0.067	40.000	−19.370	0.711	0.730
	LDS 2019	10.510	6.594	0.035	41.176	−24.840	0.800	0.412
	EDS 2020	12.500	9.143	0.050	40.625	−22.105	0.752	0.566
	LDS 2020	12.880	13.393	0.057	45.103	−23.800	0.577	0.706

Table 5. Irrigation analysis of the River Iyiaji.

River	Sample	PI	SSP	KR	MAR	RSC	CAI	SAR
Iyiaji 1	EDS 2019	11.302	11.433	0.109	32.727	−104.980	0.911	2.288
	LDS 2019	11.024	14.759	0.106	29.630	−101.550	0.885	2.213
	EDS 2020	11.165	13.113	0.108	31.193	−103.265	0.898	2.251
	LDS 2020	11.443	15.234	0.109	32.317	−113.300	0.879	2.397
Iyiaji 2	EDS 2019	6.021	5.063	0.022	40.741	−48.086	0.956	0.327
	LDS 2019	8.309	8.803	0.044	26.087	−39.874	0.943	0.596
	EDS 2020	7.088	6.821	0.032	34.000	−43.980	0.936	0.455
	LDS 2020	10.779	11.175	0.100	29.839	−115.600	0.810	2.227

When placed in comparison with Table 6 which is a summary of sample points delineation according to Adegbola et al. [44], we can see that the PI values in both the River Karawa and River Iyiaji at the different sampling times and seasons fall below expectation with values less than 25. This means the water sources are unsuitable for irrigation with respect to permeability index. The SSP values in both the River Karawa and River Iyiaji were below 50 meaning that they are safe. The KR values in both the River Karawa and River Iyiaji were below 1 which means that both rivers are good due to non-alkali hazards in the water [45]. The MAR values in both rivers were less than 50 making them suitable although the value from late dry season 2020 (LDS 2020) in the River Karawa (49.067) came close to the benchmark value of 50. The RSC values from both rivers were suitable as they had values less than 1. The CAI values in both rivers were all positive meaning there was no ion exchange in the water samples. Lastly, the SAR values in both rivers were less than 10 meaning that the rivers were excellent for irrigation with respect to sodium adsorption ratio.

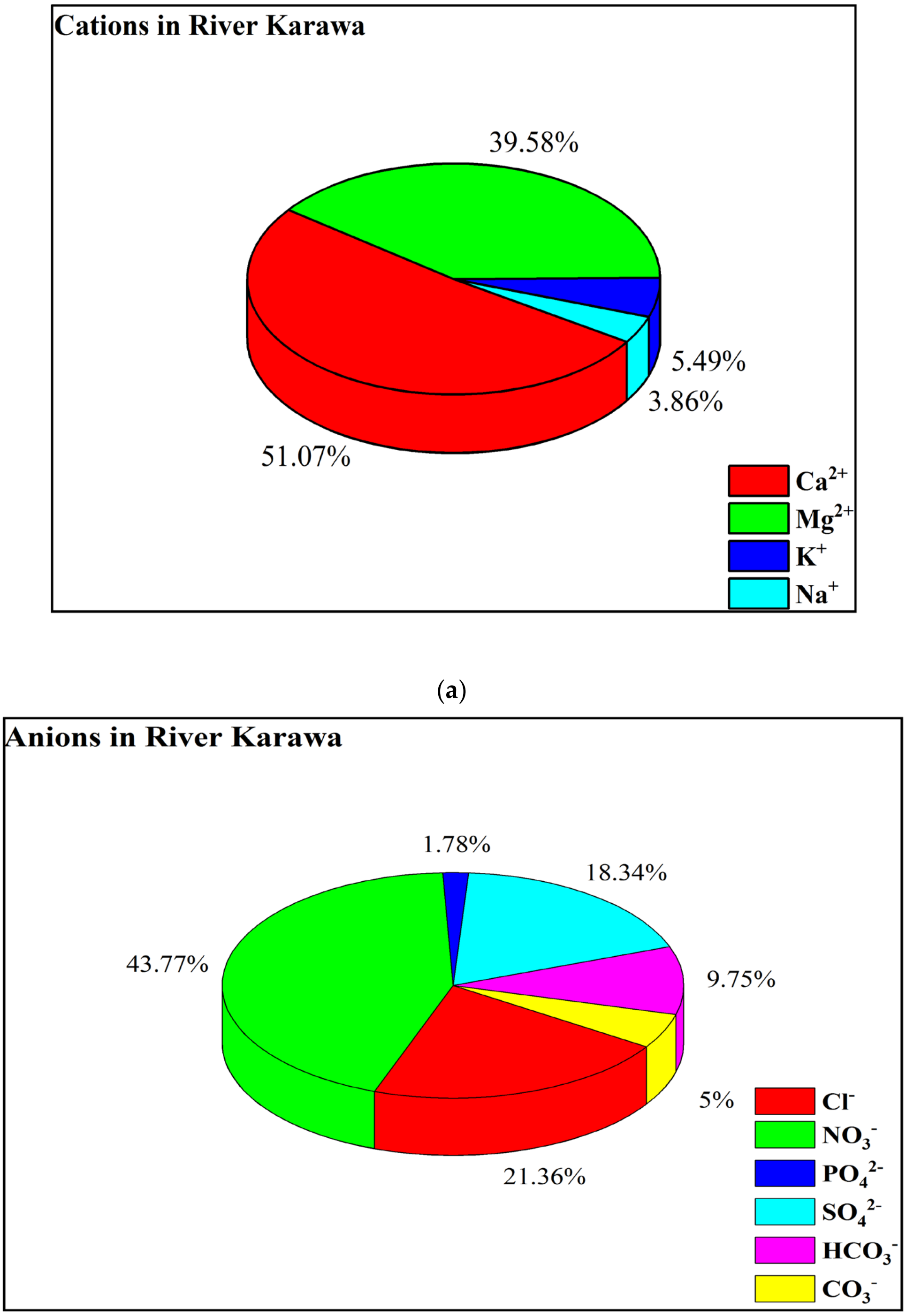
Table 6. Sample points delineation under different limits (meq/l).

PI	Class	SSP	Class	KR	Class	MAR	Class	RSC	Class	CAI	Class	SAR	Class
<25	Unsuitable	<50	Safe	<1	Good	<50	Suitable	<1.25	Suitable	Positive	No ion exchange	<10	Excellent
25–75	Good	>50	Unsuitable	>1	Unsuitable	>50	Unsuitable	1.25–2.50	Doubtful	Negative	Ion exchange	10–18	Good
>75	Excellent							>2.50	Unsuitable			18–26	Fair
												>26	Unsuitable

Source: Adegbola et al. [44].

3.1. Ion Chemistry

For the River Karawa, the major ions (anions and cations) present in water samples from the River Karawa are $Ca^{2\,+}$, Mg^{2+}, K^+, Na^+, Cl^-, $NO_3{}^-$, $PO_4{}^-$, $SO_4{}^{2-}$, $HCO_3{}^-$, and $CO_3{}^-$. It is expressed in percentage and represented in a pie chat in Figure 2a,b. For the cations, calcium ions had the most contribution at 51% while sodium ions had the least contribution at 4%. The order of contribution for the cations is $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. For the anions, nitrate ions had the most contribution at 44% while phosphate ions had the least contribution at 2%. Higher nitrate content was observed in the late dry season sample from Iyiaji 2 (I2). Around this sampling station, there were noticeable clusters of farming activities and the main point through which free ranging cattle drink water from the river. Nitrate in water bodies mainly comes from manure and sewage, fertilizers, and atmospheric rainfall as $NH_4{}^+$ from fertilizers and rainfall and as nitrogen in soil organic matter [46]. Land use types can affect the spatial variation in nitrate sources [47]. Water samples are likely to have alterations in chemical composition due to microbial activities and chemical reactions [48]; hence, maintaining the pH by adding nitric acid prevents metabolic processes and adsorption within the samples. The surroundings of these rivers are dominated by informal settlements, which lack proper sewage disposal systems. As a result, nitrate ions, phosphates, and chloride are substantially introduced into these rivers, which contributes to the high nitrate values observed even during the rainy seasons. A high nitrate concentration also suggests that the river contamination is due to wastewater, sewage, and industrial discharge. Additionally, the decomposition of organic matter and free ranging cattle which come to drink water from the rivers within the area could have led to the high levels of nitrates. This observation was also made by Ngatia et al., [48]. According to Fadiran and Mamba [49], the major sources of accumulated nitrate and nitrite are non-point sources from excessive fertilizer usage or inadequate or untreated sewage. The nitrate value obtained is comparable to the report of Fadiran and Mamba [49] in the assessment of nitrates and nitrites in some water and factory effluents in Swaziland. The order of contribution for the anions is $NO_3{}^- > Cl^- > SO_4{}^{2-} > HCO_3{}^- > CO_3{}^- > PO_4{}^-$. The major ions in the River Iyiaji are Cl^-, $NO_3{}^-$, $PO_4{}^-$, $SO_4{}^{2-}$, $HCO_3{}^-$, $CO_3{}^-$, Ca^{2+}, Mg^{2+}, K^+, and Na^+. It is expressed in percentage and represented in a pie chat as seen in Figure 3a,b. For the cations, calcium ions had the most contribution at 60% while potassium ions had the least contribution at 4%. The order of contribution for the cations was $Ca^{2+} > Mg^{2+} > Na^+ > K^+$. For the anions, chloride ions had the most contribution at 41% while phosphate ions, bicarbonate ions and trioxocarbonate ions had the least contribution at 1% each. The order of contribution for the anions is $Cl^- > SO_4{}^{2-} > NO_3{}^- > PO_4{}^- > HCO_3{}^- > CO_3{}^-$.

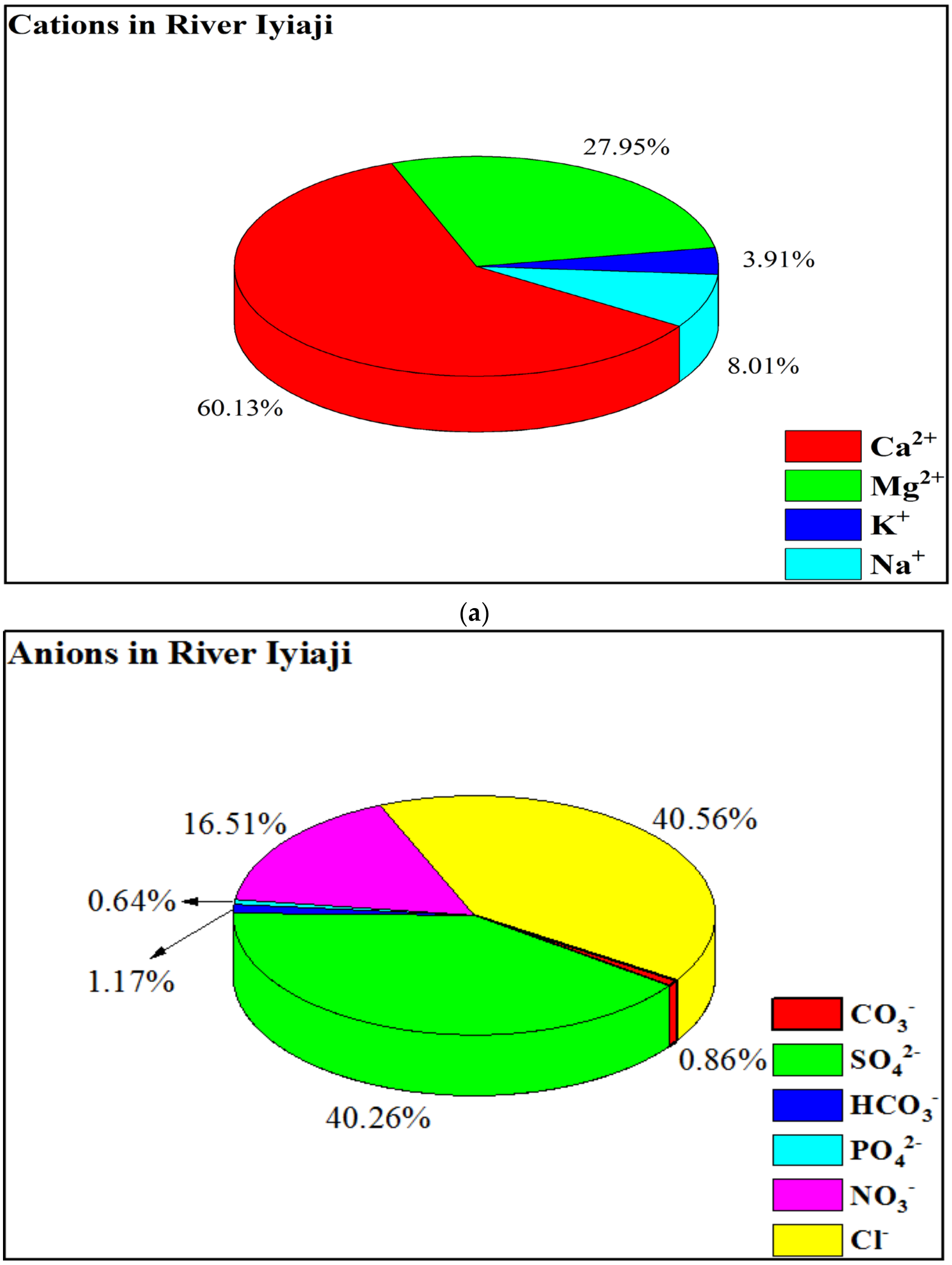


(**a**)

(**b**)

Figure 2. (**a**) Cation contribution in the River Karawa (**b**) Anion contribution in the River Karawa.

A piper plot in Figure 4 was used to show the hydrochemical properties or concentrations of both the River Karawa and River Iyiaji. It was used to understand the similarities and differences in the classification and composition of surface water into chemical types [50]. The percentage of ion levels expressed in milli-equivalent per liter (mEq/L).



(**a**)

(**b**)

Figure 3. (**a**) Cation contribution in the River Iyiaji. (**b**) Anion contribution in the River Iyiaji.

According to the findings, the main cations in both rivers were Ca^{2+} and Mg^+, as well as SO_4^{2-} and Cl anions. Surface water samples from both rivers revealed that the no dominant zone of the cation triangle had the greatest cation content. The anion triangle indicates that the surface water with a mixture of HCO^{3-} and Cl ions has the maximum anion concentration in the chloride type section. Furthermore, a sizable portion of the quaternary diagram’s data clearly implies that the Cl-Ca facial type corresponds to surface water from both rivers. This demonstrates that strong acids exceeded weak acids and that alkaline earth metals exceeded alkali metals. This dominance of strong acids over weak acids as observed in the current study rivers is in agreement with results documented for the Heihe River in China [51]. Only one sample from the River Karawa indicated the Cl-Na type.

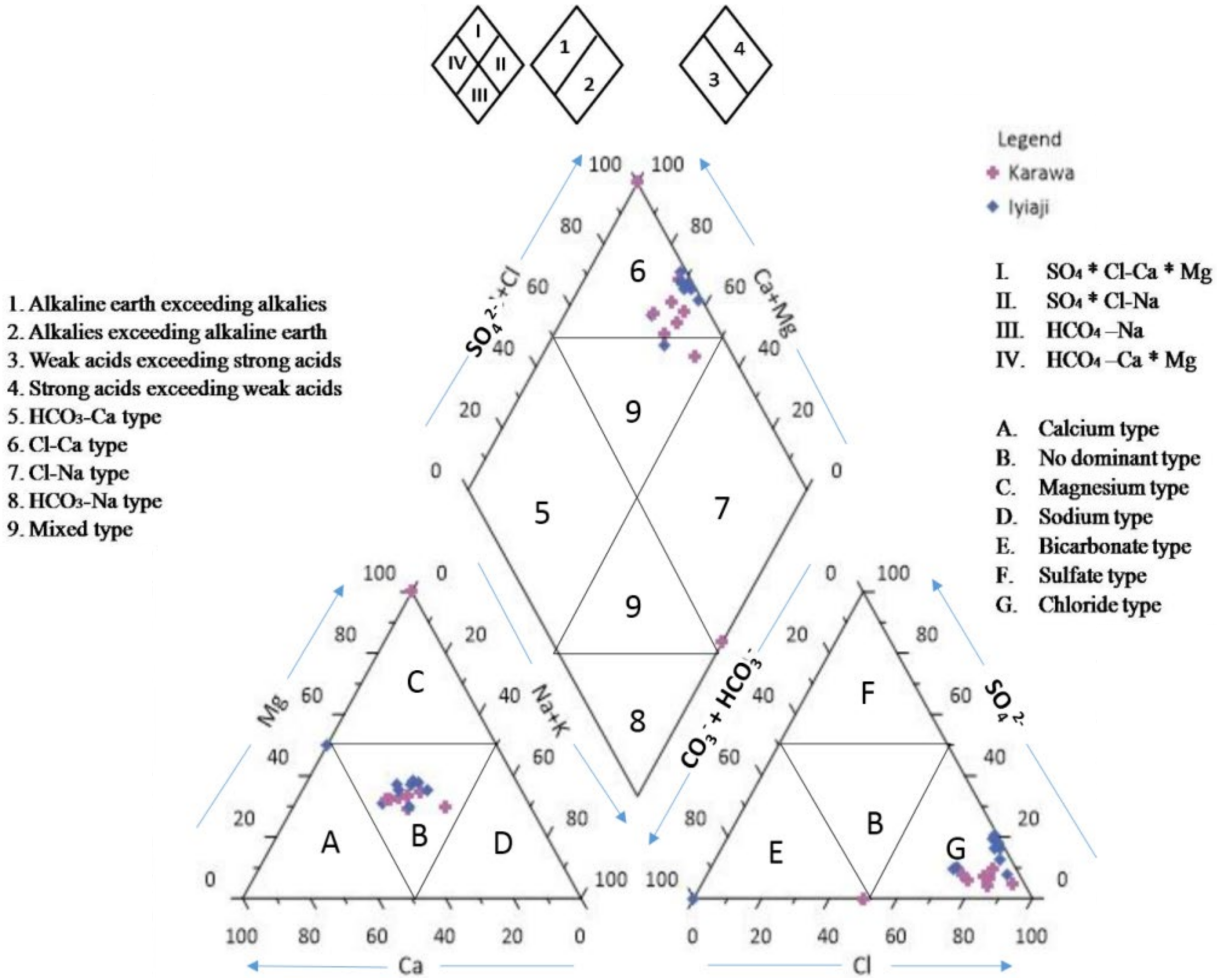


Figure 4. Piper plot showing the hydrochemical properties of the Rivers Karawa and Iyiaji.

In Figure 5a,b, a Gibbs diagram was used to represent some of the key processes controlling surface water chemistry [52]. The Gibbs plot is made up of three different fields namely, the evaporation dominance, the rock or rock water dominance, and the precipitation or rainfall dominance. Outside these three regions is the undefined region. A plot of total dissolved solids (TDSs) versus cations (Na/(Na+Ca)) and total dissolved solids (TDSs) versus anions ($Cl/(Cl+HCO_3)$) gives us the Gibbs cation ratio and Gibbs anion ratio, respectively. The Gibbs diagram in Figure 5a shows that samples from the River Iyiaji and most samples from the River Karawa fell within the rock dominance field with few samples from the River Karawa edging toward the undefined region. This indicates that interaction of the water with surrounding rock is the main process influencing the water chemistry [53].

In Figure 5b, the Gibbs diagram shows that samples from the River Iyiaji fell in the undefined region and samples from the River Karawa all fell in the precipitation dominance indicating probable low salinity of the River Karawa resulting from high volume of last rainfall that is yet to have sufficient contact time with minerals for geochemical modification [52]. The levels of the main ions in the undefined regions could have been adjusted due to factors like cation exchange, anthropogenic impacts, or even precipitation [54].

A Doneen plot of total concentration was made for both rivers under consideration as seen in Figure 6 [3,55]. A prolonged application of water which is rich in Ca^{2+}, HCO_3^-, Mg^{2+}, and Na^+ affects soil permeability. In a bid to find out the suitability of water, the Doneen plot used the PI and classified irrigation water in three different classes: Class-I, Class-II, and Class-III. Only Class-I and -II types of water are suitable for irrigation [3,55–57]. From the plot below, 100% of water samples from both the River Karawa and River Iyiaji fell under

Class-I. This means that the water from both rivers is suitable for irrigation purposes having a maximum permeability value over 75%.

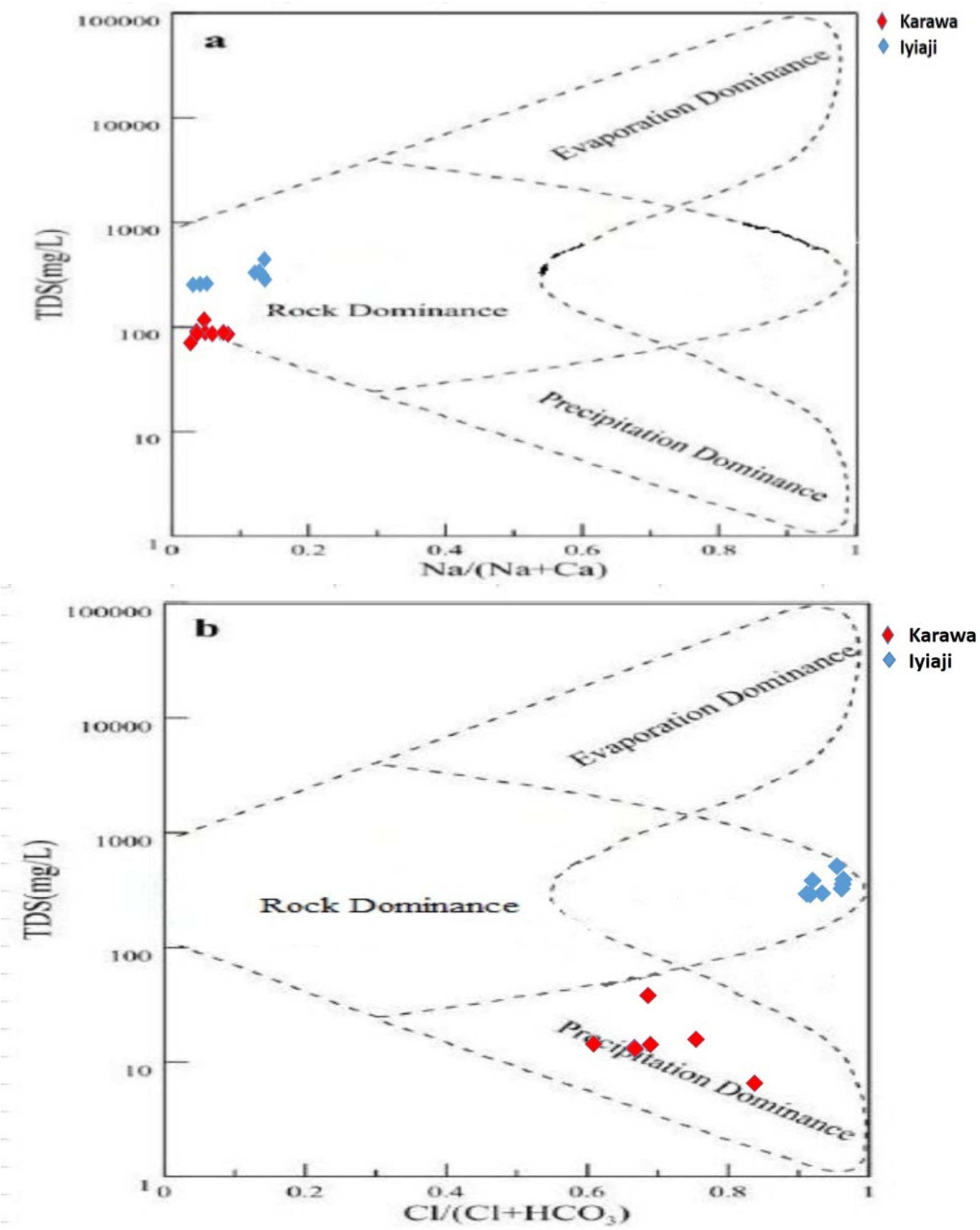


Figure 5. (**a**) Gibbs diagram of TDS vs. cations of the River Karawa and River Iyiaji hydrochemical facies. (**b**) Gibbs diagram of TDS vs. anions of the River Karawa and River Iyiaji hydrochemical facies.

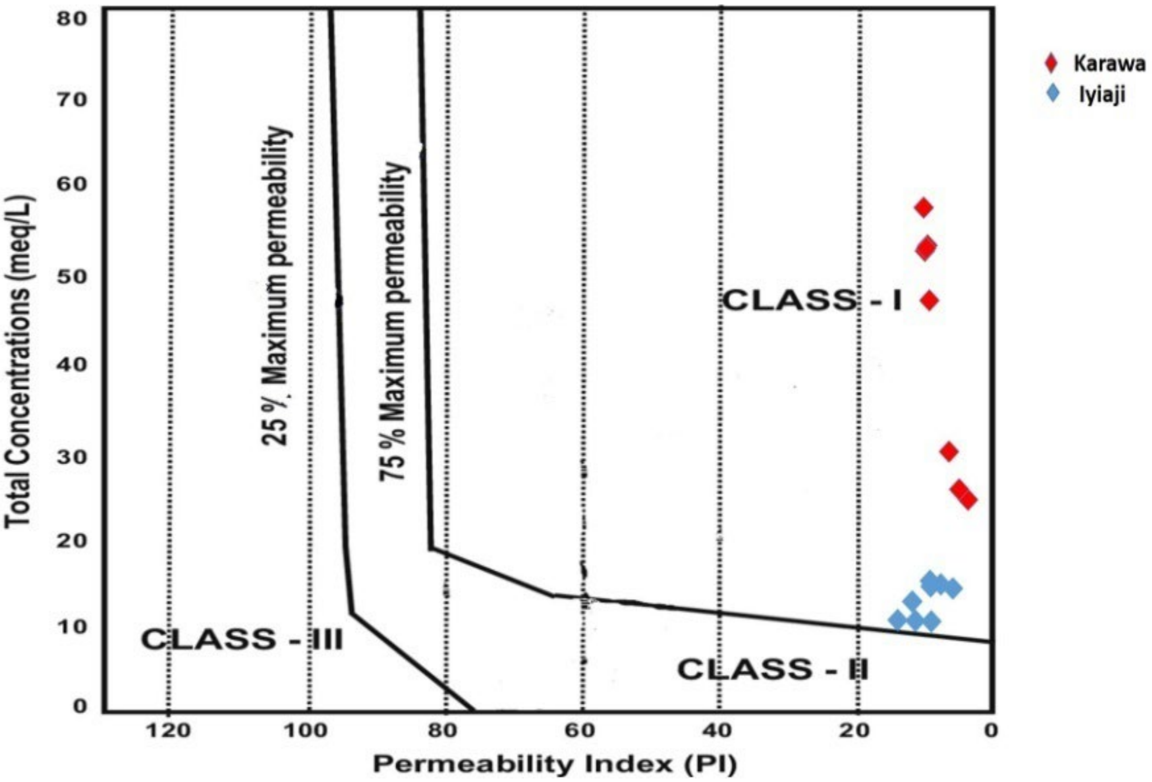


Figure 6. Doneen plot of total concentration (TC in meqL^{-1}) PI for the Rivers Karawa and Iyiaji.

The USSL (United States Salinity Laboratory) graphical diagram plots the SAR versus the salinity hazard values as seen in Figure 7. A typical USSL plot has water divided into CI, CII, CIII, and CIV types on the basis of salinity hazard and SI, SII, SIII, and SIV types on the basis of sodium hazard [58]. The C1 water type with low salinity is considered suitable for irrigation whereas the C4 water type with very high salinity is not suitable for irrigation. Additionally, while the low sodium water S1 is considered good for irrigation purposes, very high sodium water S4 is unsuitable for irrigation [59].

From the USSL plot of the River Karawa and River Iyiaji, water samples from the River Karawa lies in the CI-SI region while water samples from the River Iyiaji lies within the CIII-SI region. This means that although the River Iyiaji fell within the low salinity-high sodium water region hence needing remediation through drainage and control of salinity before being applied for irrigational purposes, the River Karawa is most suitable for irrigation.

Wilcox [60] proposed a system for categorizing groundwater for agricultural use based on electrical conductivity and percent sodium in the form of a diagram. Wilcox [60] classified the water in five respective degrees of applicability for irrigation purposes: excellent to good, good to permissible, permissible to doubtful, doubtful to unsuitable, and unsuitable. From Figure 8, the River Karawa showed that it is an excellent to good type of water for irrigation and the River Iyiaji showed that it is good to permissible type of water for irrigation purpose.

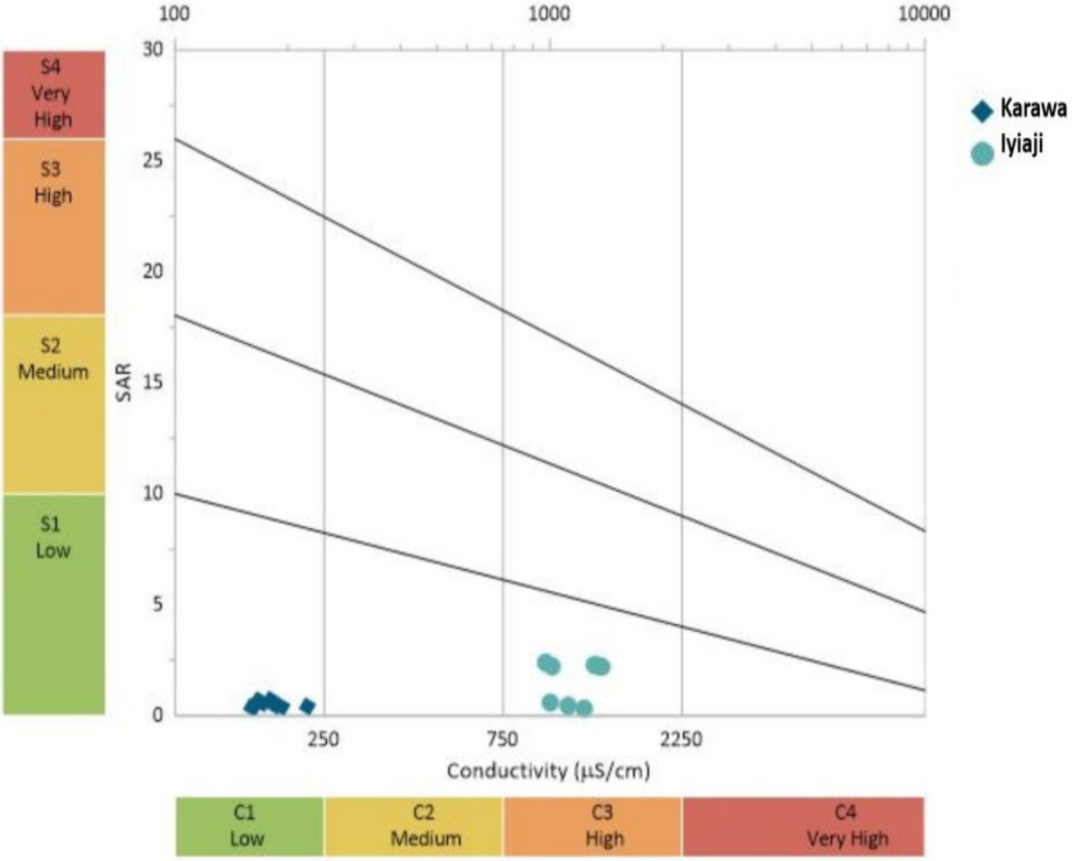


Figure 7. USSL plot of the River Karawa and River Iyiaji.

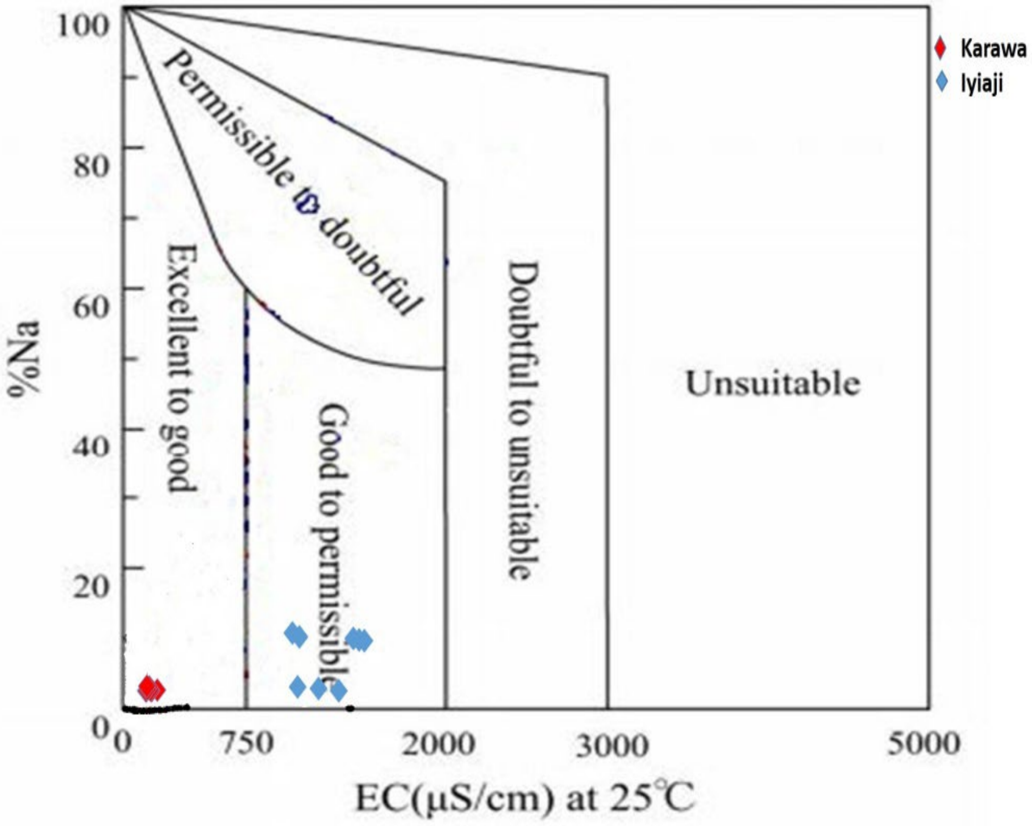


Figure 8. Wilcox rating plot of the River Karawa and River Iyiaji.

3.2. Correlation and Cluster Analysis

The physic-chemical properties and major ion concentrations of both the Rivers Karawa and Iyiaji were subjected to statistical analysis using a hierarchical cluster dendrogram to detect the relationships and differences in the various water samples. Cluster analysis is a multivariate statistical analysis commonly used to separate water chemistry parameters into two or more (Figure 9) related groups with similar characteristics [61]. Taking a distance of 0.5 in the cluster analysis (Figure 9), three distinct clusters were observed (pH and carbonates in two separate clusters) while all other parameters were grouped into one cluster. This indicated that almost all parameters, except pH and carbonates, influence each other.

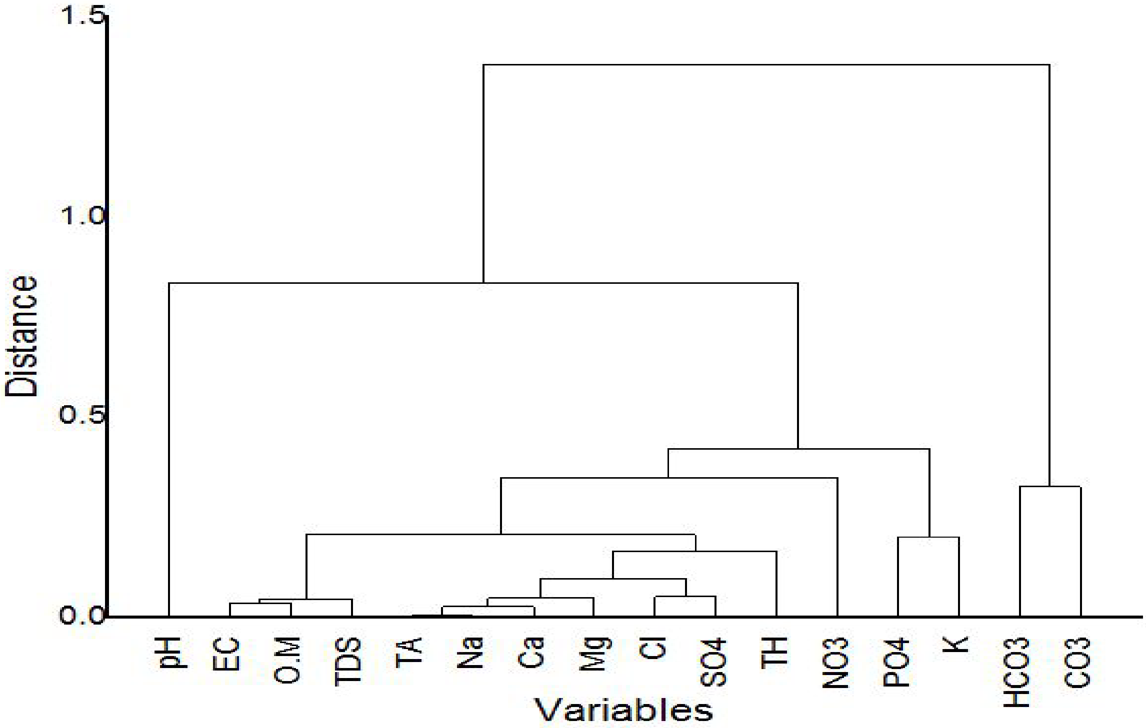


Figure 9. Hierarchical cluster dendrogram of the Rivers Karawa and Iyiaji.

The correlation results showed that there was a significant positive correlation between most of the parameters analyzed in the early dry season and late dry season samples indicating that there is not much difference in the use of the water either in the early rainy season or late dry season. A similar observation was made by [3] for the correlation between the two different years studied.

3.3. Scaling and Corrosivity Tendencies and Spatial Distribution of Water Parameters

Scaling and corrosivity of pipes and water storage facilities for domestic and irrigations purposes form part of the key issues that require attention in agriculture. The corrosivity and scaling propensity are often swayed by the changes in the chemical and physical parameters in water [36]. Common among these parameters are electrical conductivity, pH, total dissolved solids, temperature, Calcium, Chloride, sulphate, and carbonates.

When the value of LSI is greater than zero, it shows the water is supersaturated and has the potential to scale as well as tends to precipitate $CaCO_3$ [62]. The calculated LSI value of the Rivers Karawa and Iyiaji in both EDS and LDS revealed that the water has the potential for scaling (Table 7). This is against the observation of Omeka et al. [36] in the assessment of water in an agrarian area (Nigeria) of which they attributed the low scaling tendency to the geology of the study area with the alluvium deposit being the major lithostratigraphic unit underlying the area, with silty-clean alluvial sands constituting the major aquifer material. They also opined that the breakdown of rocks especially sandstone may have led to the release of orthosilicic acid (H_4SiO_4) in the groundwater [63], thereby elevating the acidic nature of the water and by implication the corrosivity potential. According to Egbueri [64], water saturation by CaCO3 is mostly controlled by the chemical reactions occurring between the major cations (Mg and Ca), number of carbonate rocks (for example, limestones and dolostones) within the underlying rock/aquifer system, and the pH and temperature of the water. The low concentration of carbonate rocks reported (from the geology of the area) within the underlying rock is directly related with the low saturation of $CaCO_3$ in the water.

Table 7. Storability and corrosivity evaluation models.

Sample	LSI	RSI	LS	PSI	AI
Karawa 1	18.497	31.695	286.180	15.431	7.114
Karawa 2	18.374	30.517	278.158	17.137	6.922
Iyiaji 1	20.634	34.547	1969.065	20.699	9.282
Iyiaji 2	21.098	36.070	1049.337	18.599	8.249

LSI = Langelier saturation index.

The RSI obtained in the rivers were all above 8.5 (RSI > 8.5) indicating that the water is rigorously corrosive [37]. The neutral zone of the Ryznar index is more or less the numerical value six according to Wojtkowska et al. [65]. Generally, any value above six indicates that the water is likely to form a $CaCO_3$ scale. A value below the number 6 indicates that the water will dissolve $CaCO_3$ formations. The Ryznar stability index (RSI) has also been found very useful as a predictive model for scaling and corrosivity tendency in a water distribution network. Following the RSI classification criteria [62], 100% of the water samples indicated rigorous corrosive tendencies ($RSI \geq 8.5$). This observation negatively correlates with the obtained results of Omeka et al. [36]. It can therefore be inferred that the high contributions from Mg and Ca from the aquifer units or underlying rock led to the high scaling tendencies noted in the water samples.

The Larson-Skold Index result revealed that all the water types assessed were severely corrosive (LS > 1.2) and the ratio of the concentration of chloride and sulfate ions to the concentration of bicarbonate and carbonate ions will interfere with natural film formation (LS > 0.8) according to Wojtkowska et al. [65] and Omeka et al. [36]. In this river waters, 0% of the samples showed a value less than 0.8, indicating high corrosion and a high scaling tendency.

The Larson-Skold Index is usually used in determining the relationship between weak (CO_3^{2-} and HCO_3^-) and strong acidic anions (Cl^- and SO_4^{2-}). Due to the anaerobic reduction of sulphates by sulphate reducing bacteria in water to sulfides, the increased concentration of bicarbonates and sulphates has been revealed to sway water corrosivity and scaling tendencies [66]. This exposes water distribution and storage facilities that are made of metallic materials to scaling and encrustation challenges [67]. Usually, this is followed by two circumspections (a) the sulfate-reducing bacteria present in the organic matter as carbon act as an electron donor and facilitate the conversion of sulfate to sulfide thereby enhancing encrustation, if organic matter is present in the water [67,68], and (b) the increased amount of sulfide-producing bacteria will result in the corresponding increase in the amount of H_2S gas which may react with the water storage metallic surfaces causing (Equation (19)) encrustation [69]. In a similar manner, bicarbonates reacting with sulfide minerals within the underlying rocks could sway the acidity of water leading to the formation of strong acid (H_2SO_4) and so elevating the water corrosivity potentials [64,66,69,70].

$$SO_4^{2} + \text{Organic matter} \rightarrow S_2 + CO_2 + H_2O \tag{19}$$

Egbueri [71] reported in a fast-developing suburb (Nigeria) that the corrosivity and scaling evaluation indices record the majority of the samples with low to insignificant scaling potentials which is against our findings in this study. Egbueri et al. [72], in their assessment of water in the Umunya area, southeastern Nigeria, unveiled that the natural waters are severely corrosive, having the tendency to damage domestic, irrigational, and industrial water distribution systems. According to Eyankware et al. [73], in a modeling approach to the investigation of groundwater corrosion and scaling potential at Benue State, Nigeria, obtained from PSI, revealed that 37.5% of drinking water was considered not prone to scaling, while 62.5% of groundwater is likely prone to scaling. This was attributed to fluctuation in pH and TDS values within the study area. The results obtained in this study revealed that the surface water is in a strong saturated atmosphere and could precipitate $CaCO_3$ in the system and as well shows a tendency to dissolve $CaCO_3$ in water.

3.4. Statistical Analysis and Spatial Distribution Map of the Water Parameters

From the study area, the Mg concentration ranged from 12 to 32 Mg/L in the LDS sample of 2019 with the highest concentration around the Adaba and Oguluogu sampling sites of the River Karawa. Ca, which ranged between 18.3 and 76 mg/L in the 2019 LDS samples, had its highest concentration around the Ebenebe, Aguobu Iwollo, and Oguluogu areas while its least concentration was around the Ogbosu sampling area. For the total alkalinity in the LDS, of 2019, it fell between 1.401 mgL and 63.99 mg/L. Table 8 presents the sampling regions where the concentration of each of the analyzed parameters were higher and lower (peak and valley values) and predicted the direction of concentration movement. The spatial distribution map (Figure 10a–x) clearly revealed that the water quality levels at some places were poor with respect to the measured quality parameter. The spatial distribution map as presented in Figure 10a–x revealed that Mg, Ca, total hardness, total alkalinity, total dissolved solids, potassium, sulphate, phosphate, chloride, and electrical conductivity had a peak value around the Ogbosu sampling station during the late dry seasons (Table 8). The pH and nitrate recorded their peak values within the Aguobu Iwollo/Ogbosu sampling points in the late dry seasons. Meanwhile, the valley value of Mg, pH, and phosphate were observed to be around the Adaba sampling point. For Ca, total hardness, total alkalinity, total dissolved solids, electrical conductivity, potassium, and nitrate, their valley values were found around the Oguluogu, Ebenebe, and Aguobu Iwollo areas of the rivers during the late dry seasons. During the early dry seasons (EDSs), the peak values of these parameters were also observed at the Ogbosu sampling station except for sulphate and phosphate which had their peak values around Adaba and Oguluogu, respectively (Figure 10i,j). Calcium, TH, TA, K, sulphate, and nitrate had their valley value around Oguluogu in the River Iyiaji while Mg, chloride TDS, EC, and pH had their valley value around Aguobu Iwollo in Karawa.

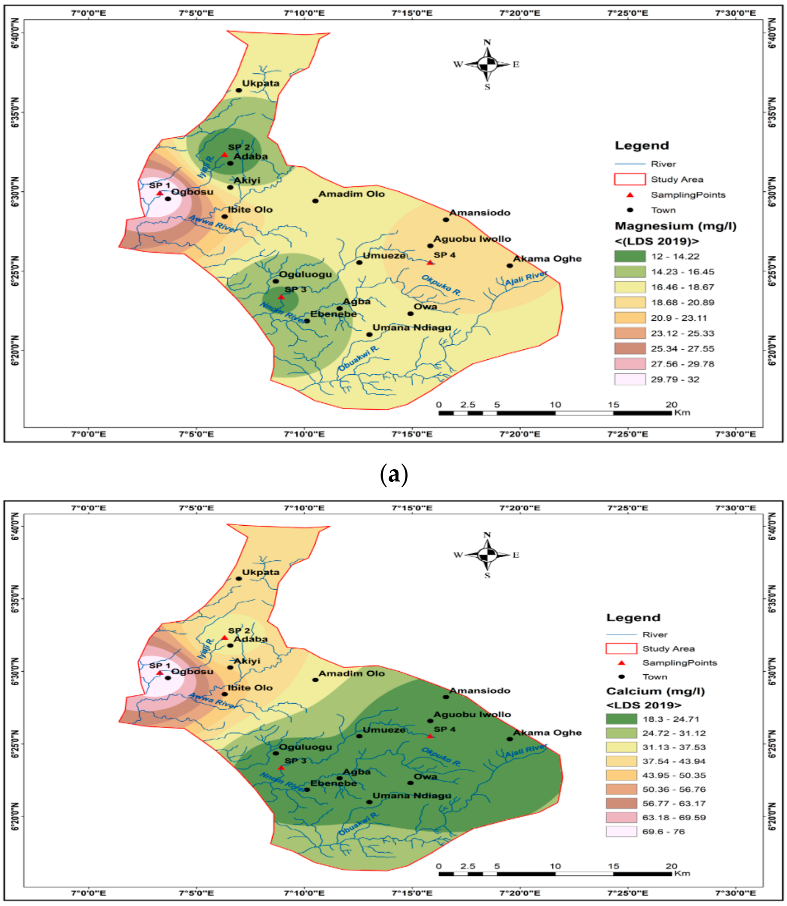
Table 8. Peak and valley value locations of some water parameters.

Parameter	Peak	Valley	Season
Mg	Ogbosu	Adaba	LDS
	Ogbosu	Oguluogu	EDS
Ca	Ogbosu	Oguluogu/Aguobu Iwollo	LDS
	Ogbosu	Oguluogu	EDS
TH	Ogbosu	Ebenebe	LDS
	Ogbosu	Aguobu Iwollo	EDS
TA	Ogbosu	Oguluogu	LDS
	Ogbosu	Aguluogu	EDs
TDS	Ogbosu	Oguluogu/Aguobu Iwollo	LDS
	Ogbosu/Adaba	Aguobu Iwollo/Oguluogu	EDS

Table 8. *Cont.*

Parameter	Peak	Valley	Season
EC	Ogbosu	Oguluogu/Aguobu Iwollo	LDS
	Ogbosu/Adaba	Oguluogu/Aguobu Iwollo	EDS
pH	Oguluogu	Ogbosu/Adaba	LDS
	Ogbosu	Oguluogu/Aguobu Iwollo	EDS
Potassium	Ogbosu	Aguobu Iwollo/Oguluogu	EDS
	Ogbosu	Oguluogu/Aguobu Iwollo	LDS
Sulphate	Adaba	Ogbosu	EDS
	Ogbosu	Oguluogu/Aguobu Iwollo	LDS
Phosphate	Oguluogu	Adaba	EDS
	Ogbosu	Adaba/Aguobu Iwollo	LDS
Nitrate	Ogbosu/Adaba	Oguluogu	EDS
	Ogbosu/Aguobu Iwollo	Oguluogu	LDS
Chloride	Ogbosu	Oguluogu	EDS
	Ogbosu/Aguobu Iwollo		LDS

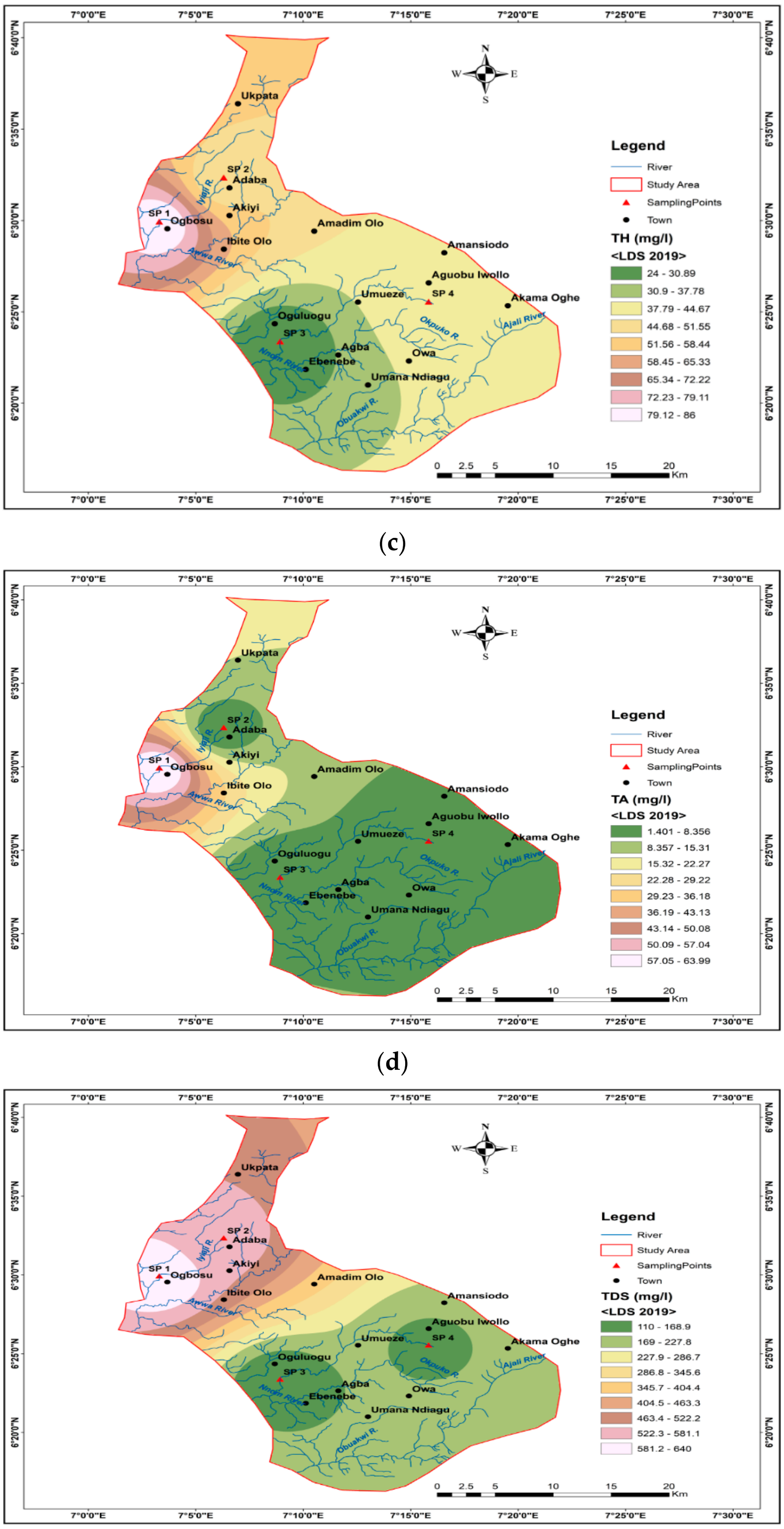
LDS = Late dry season, EDS = early dry season.



(**a**)

(**b**)

Figure 10. *Cont.*

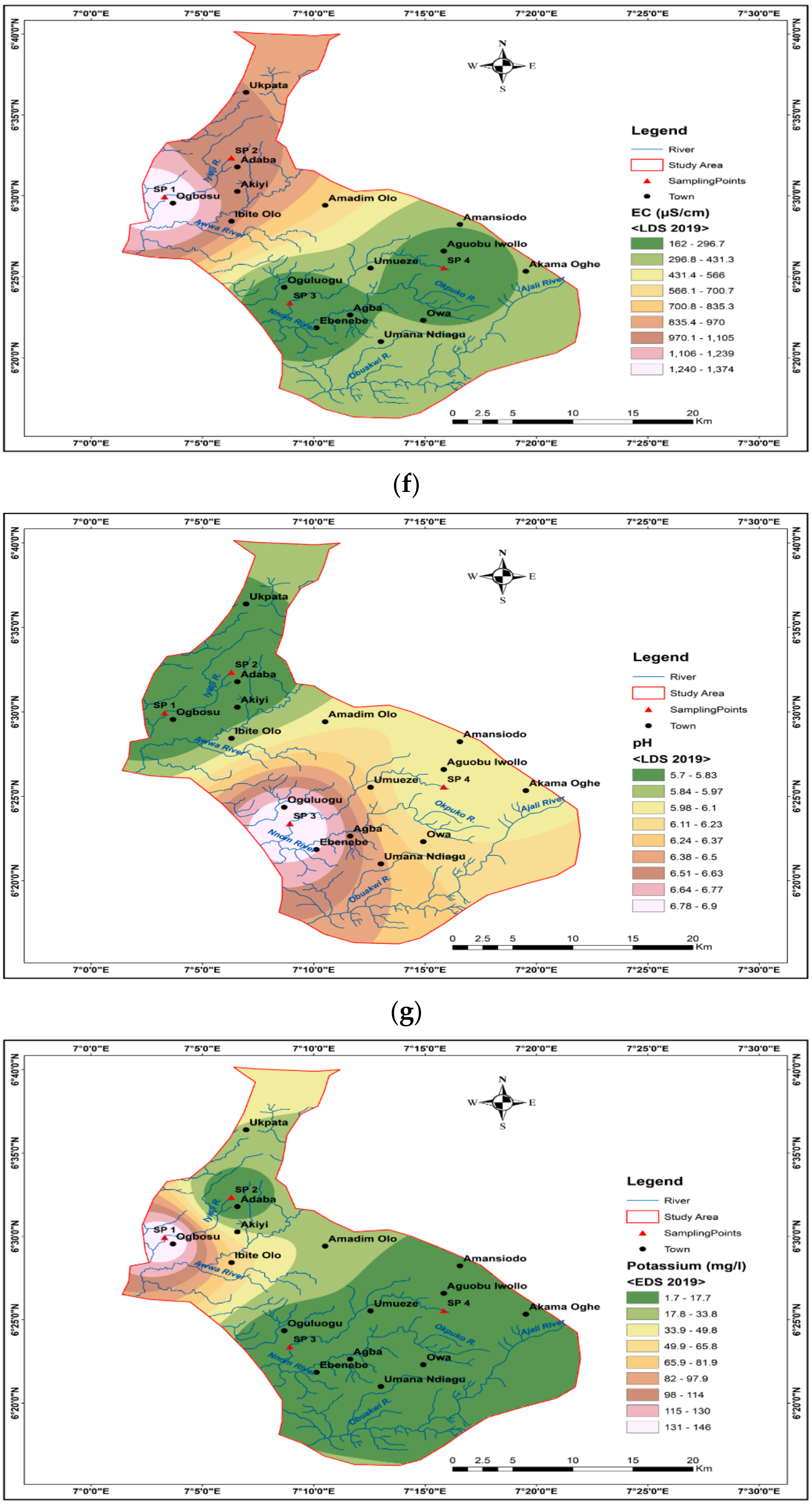


(**c**)

(**d**)

(**e**)

Figure 10. *Cont.*



(**f**)

(**g**)

(**h**)

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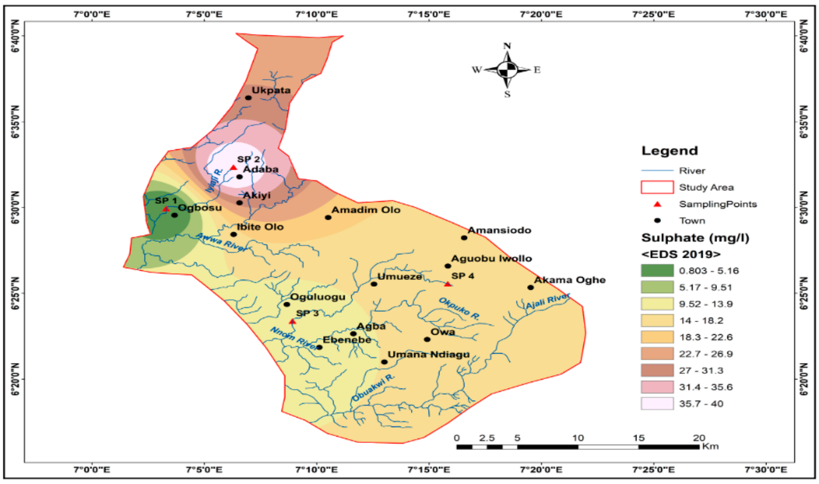
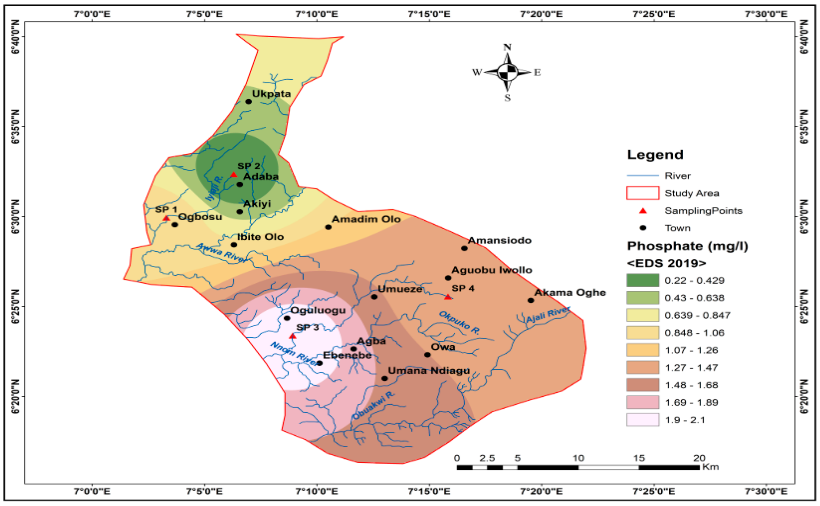
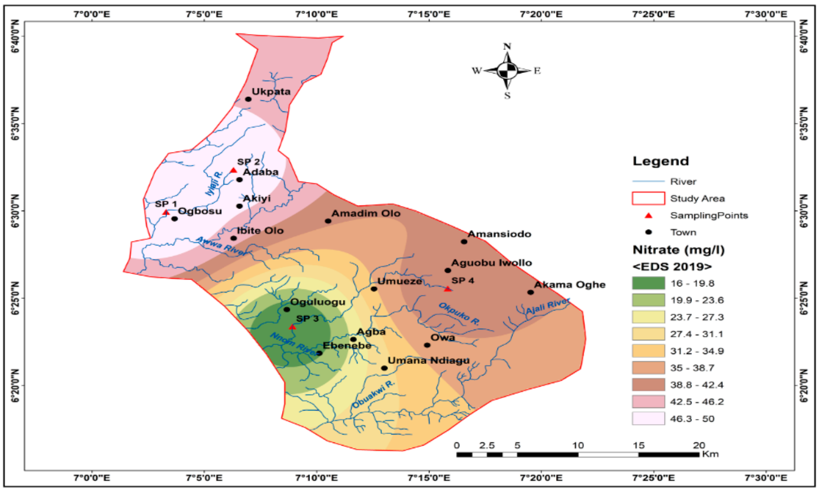


(**i**)



(**j**)



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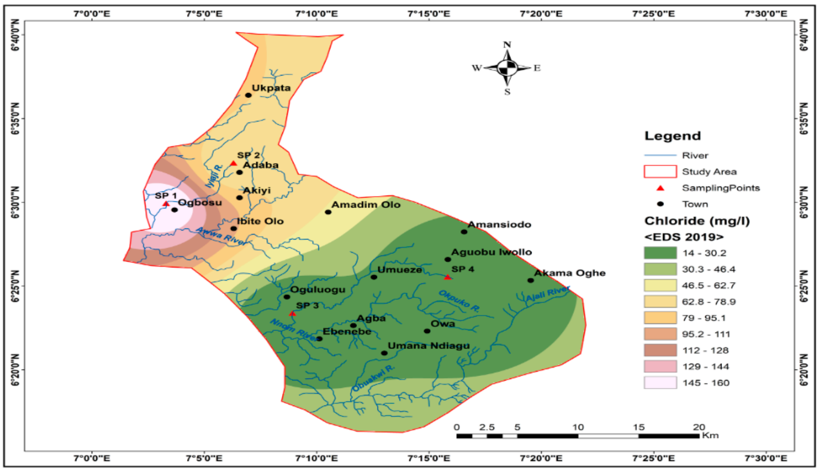
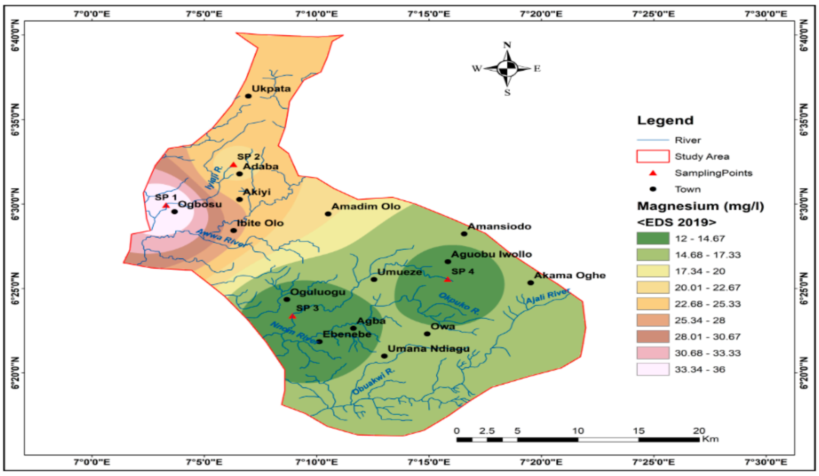


(**l**)



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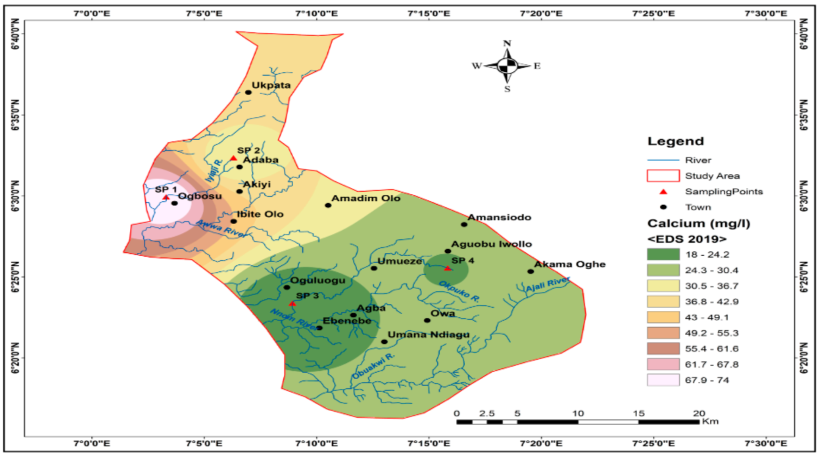
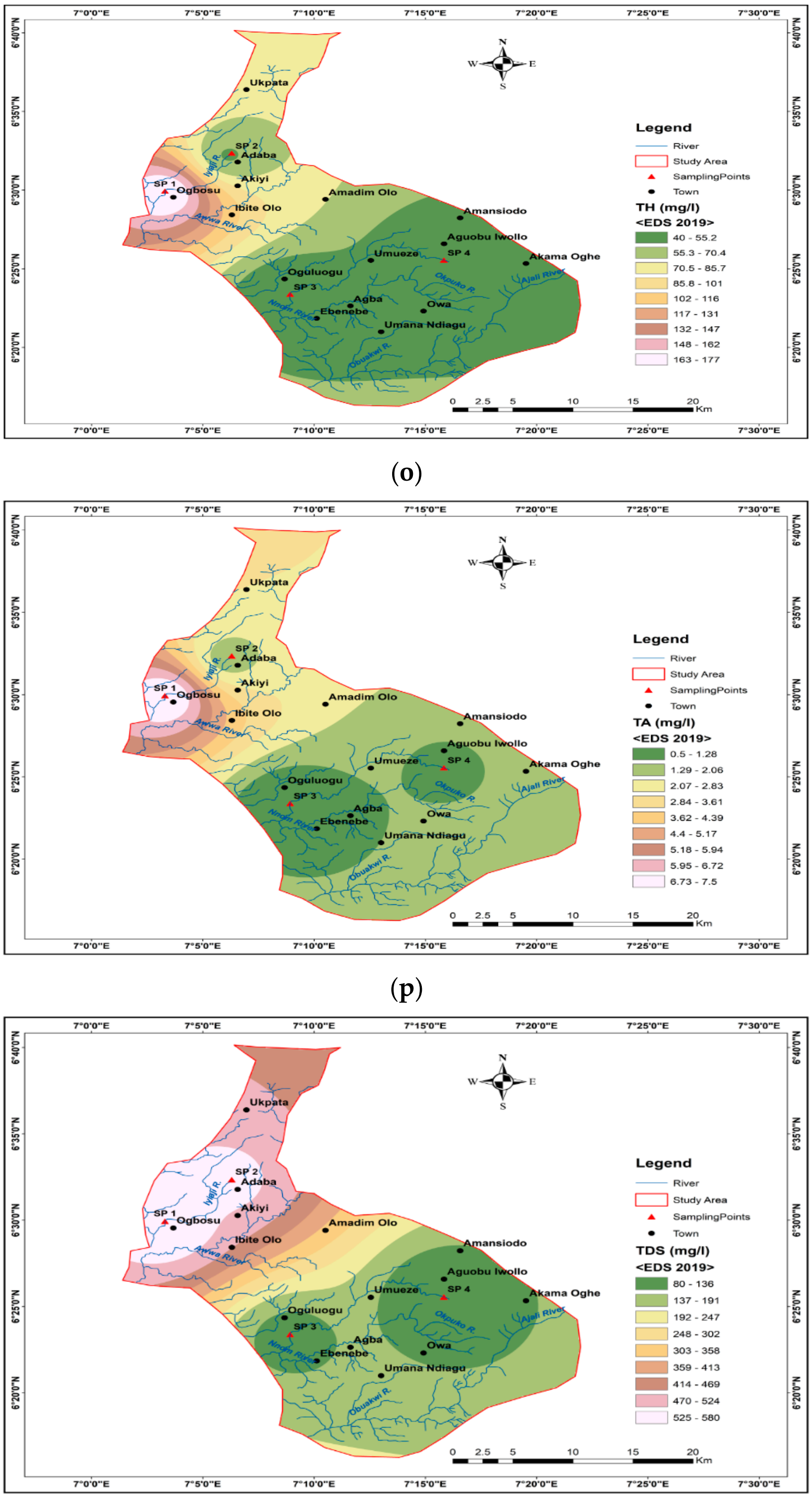


(**n**)

Figure 10. *Cont*.

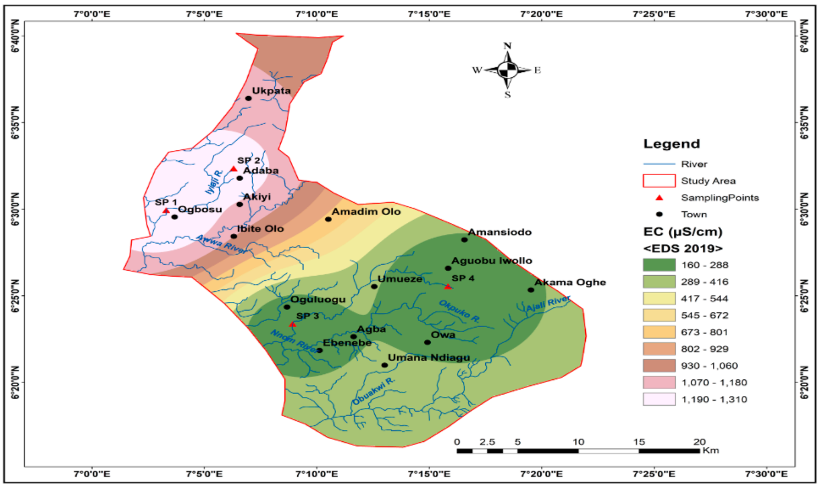


(**o**)

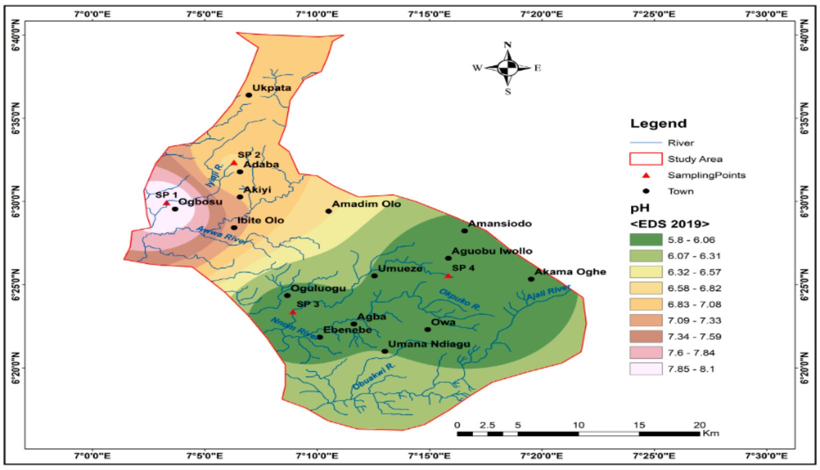
(**p**)

(**q**)

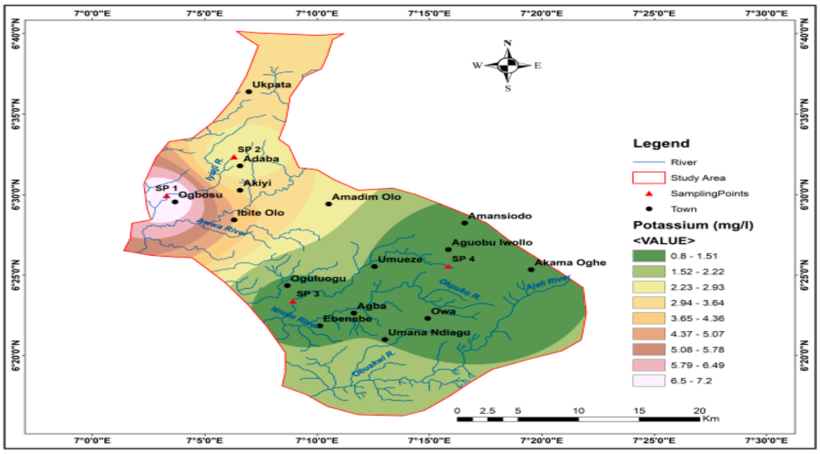
Figure 10. *Cont.*



(**r**)

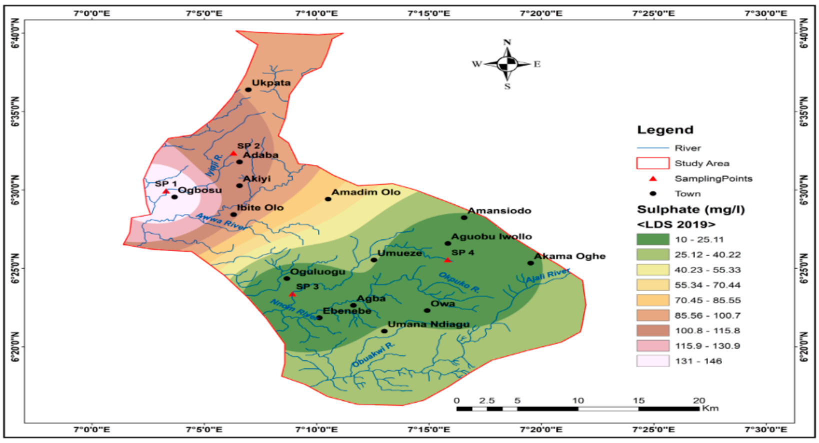


(**s**)

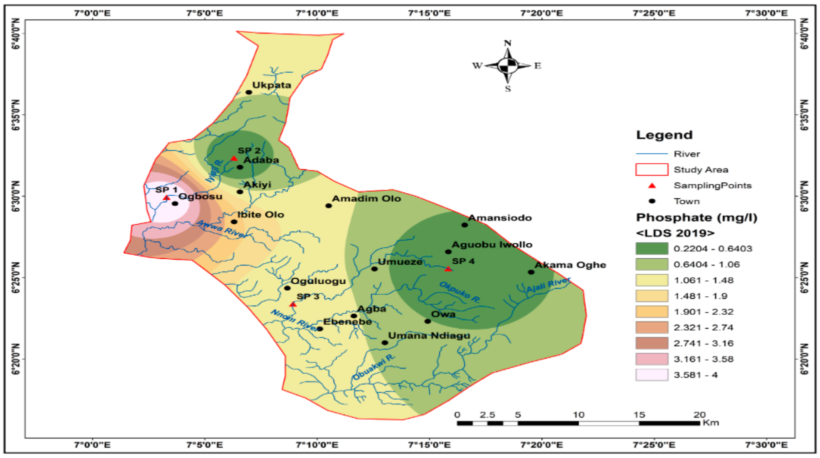


(**t**)

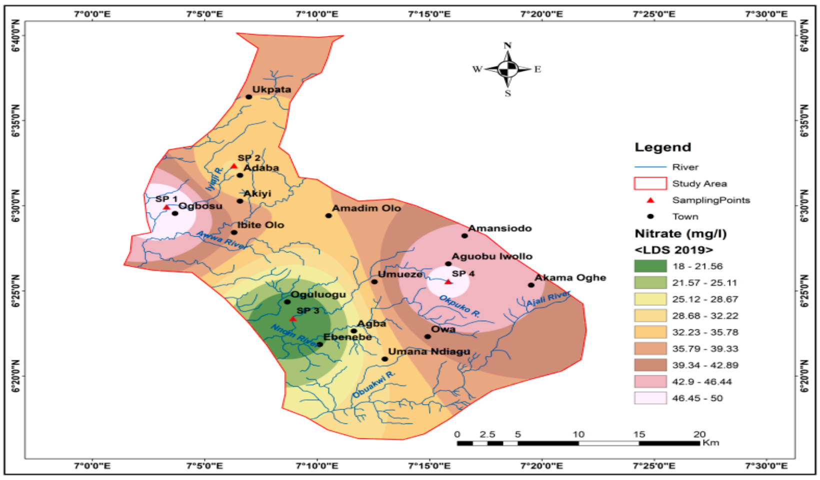
Figure 10. *Cont.*



(**u**)

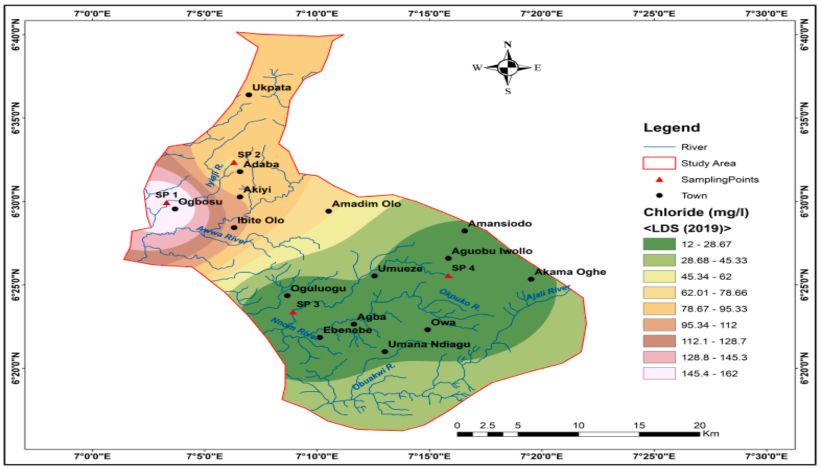


(**v**)



(**w**)

Figure 10. *Cont.*



(**x**)

Figure 10. (**a**) Spatial distribution of Mg in LDS. (**b**) Spatial distribution of calcium in LDS. (**c**) Spatial distribution of total hardness in LDS. (**d**) Spatial distribution of total alkalinity in LDS. (**e**) Spatial distribution of total dissolved solids in LDS. (**f**) Spatial distribution of electrical conductivity in LDS. (**g**) Spatial distribution of pH in LDS. (**h**) Spatial distribution of potassium in EDS. (**i**) Spatial distribution of sulphate in EDS. (**j**) Spatial distribution of phosphate in EDS. (**k**) Spatial distribution of nitrate in EDS. (**l**) Spatial distribution of chloride in EDS. (**m**) Spatial distribution of magnesium in EDS. (**n**) Spatial distribution of calcium in EDS. (**o**) Spatial distribution of total hardness in EDS. (**p**) Spatial distribution of total alkalinity in EDS. (**q**) Spatial distribution of total dissolved solids in EDS. (**r**) Spatial distribution of electrical conductivity EDS. (**s**) Spatial distribution of pH in EDS. (**t**) Spatial distribution of potassium in LDS. (**u**) Spatial distribution of sulphate in LDS. (**v**) Spatial distribution of phosphate in LDS. (**w**) Spatial distribution of nitrate in LDS. (**x**) Spatial distribution of chloride in LDS.

A paired sample *t*-test was used to determine if there were significant differences between the corresponding water parameters in both rivers. The *p*-values of the pH, potassium, and phosphate were greater than 0.05, indicating that there were no statistically significant differences between the means of the pH, potassium, and phosphate in the two rivers. For all other water parameters, the *p*-values were less than the 0.05 confidence level showing a statistically significant differences between the rivers.

Results of one-way Analysis of Variance (ANOVA) for the physicochemical parameters between the individual rivers and between the Rivers Karawa and Iyiaji were calculated. A statistically significant difference was recorded in the physicochemical parameters between sampling locations K1 and K2 ($p = 1.16 \times 10^{-13}$) of the River Karawa and I1 and I2 ($p = 2.44 \times 10^{-13}$) of the River Iyiaji. However, no significant difference was recorded in the physicochemical properties between the Rivers Karawa and Iyiaji ($p = 0.1699$) indicating that these two rivers are connected since both of them are tributaries to the River Niger (Nigeria).

Phosphate was the only water parameter that had its valley value around the Adaba sampling point in the River Iyiaji (Figure 10j). This observation showed that these parameters are higher down the river flow. A similar observation in parameter variations was made by Thomas [74] in the spatial evaluation of groundwater quality using factor analysis and geostatistical Kriging algorithm: a case study of Ibadan Metropolis, Nigeria.

4. Conclusions

This study assessed the hydrochemistry, corrosion and scaling tendencies, and suitability of the Rivers Karawa and Iyiaji for irrigation purposes. Samples were taken from both rivers with irrigational water quality indices and major ion chemistry. The River Karawa is quite safe for irrigation purposes. The values from the physicochemical analysis conducted on samples from both rivers fell within FAO [7] and WHO [41] standards except for the

NO_3^- detected in both rivers which was higher than the allowed standard range. The cations and anions analysis from the River Karawa showed $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ and $NO_3^- > Cl^- > SO_4^{2-} > HCO_3^- > CO_3^- > PO_4^-$ as the order of contribution, while that of the River Iyiaji showed $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $Cl^- > SO_4^{2-} > NO_3^- > PO_4^- > HCO_3^- > CO_3^-$. A piper plot showed that the main cations in both rivers were Ca^{2+} and Mg^+, as well as SO_4^{2-} and Cl anions. Furthermore, a sizable portion of the quaternary diagram's data clearly implied that the Cl-Ca facial type corresponds to surface water from both rivers showing that strong acids exceeded weak acids and that alkaline earth metals exceeded alkali metals. The water quality for irrigation was analyzed using water quality indices like sodium adsorption ratio (SAR), permeability index (PI), and soluble sodium percent (SSP) with the help of diagrams and plots like the USSL plot, the Wilcox rating plot, the Gibbs diagram, and the Doneen rating plot of total concentration. These indices suggested that the water from both rivers was suitable for irrigation purposes. The RSIs obtained in the rivers were all above 8.5 ($RSI > 8.5$) indicating that the water is rigorously corrosive [37]. The neutral zone of the Ryznar index is more or less the numerical value of six according to Wojtkowska et al. [65]. The Larson-Skold Index result revealed that all the water types assessed were severely corrosive ($LS > 1.2$) and the ratio of the concentration of chloride and sulfate ions to the concentration of bicarbonate and carbonate ions will interfere with natural film formation ($LS > 0.8$). The spatial distribution map revealed that Mg, Ca, total hardness, total alkalinity, total dissolved solids, potassium, sulphate, phosphate, chloride, and electrical conductivity had a peak value around the Ogbosu sampling station during the late dry seasons. The pH and nitrate recorded their peak value within the Aguobu Iwollo/Ogbosu sampling points in the late dry seasons. Meanwhile, the valley values of Mg, pH and phosphate were observed to be around the Adaba sampling point. For Ca, total hardness, total alkalinity, total dissolved solids, electrical conductivity, potassium, and nitrate, their valley values were found around the Oguluogu, Ebenebe, and Aguobu Iwollo areas of the rivers during the late dry seasons. During the early dry seasons (EDS), the peak values of these parameters were also observed at the Ogbosu sampling station except sulphate and phosphate which had their peak values around Adaba and Oguluogu, respectively.

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