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Analysis of the Seasonal Variation of Groundwater Quality in a Highly Cultivated Catchment, Northern Benin

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Abstract This study assesses groundwater quality in the Dassari watershed, a highly cultivated catchment area in Northern Benin, West Africa. Four sampling campaigns were conducted and the groundwater samples were analyzed using the standardized methods of the American Public Health Association. Descriptive and multivariate statistics were applied to describe and group the water samples into categories. The water samples were also compared to the World Health Organization (WHO) norms and those of the Republic of Benin. Boxplot comparison method and variance analysis were used to analyze the seasonal variation of groundwater parameters in both rainy and dry seasons. The hydro-chemical facies of the sampled groundwater were investigated through Piper and Chadha diagrams, and the general type of groundwater in the catchment was found to be as calcium-rich and magnesium-rich water based on the identification of the dominant cations. The major anion in the samples was Hydro-carbonate HCO_3^-, thus the groundwater in the study catchment can be considered as carbonate-rich water. Comparing the concentrations of analyzed parameters to WHO and the Republic of Benin guidelines for drinking water, the whole catchment was found to have potable groundwater. Comparing the nitrate concentration in the samples to a natural limit of 10 mg/L, we show that all samples had a nitrate concentration above that limit, thus indicating an anthropogenic pollution due to high fertilizer use. However, these concentrations are still under the permissible limit of WHO (50 mg/L). The analysis of the seasonal change in hydro-chemical parameters revealed no significant change at 5% level of these parameters from rainy season to dry season. In the Dassari catchment, groundwater is still potable although we found a slight sign of pollution due to high fertilizer use.

Keywords: *groundwater quality, hydro-chemical Facies, Dassari catchment, Republic of Benin, seasonal variation*

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1. Introduction

Groundwater is a key resource which is very solicited to solve water scarcity problems worldwide in semi-arid and arid regions in particular. Groundwater is an important source of water supply because of its abundance and stable quality [1]. It is a renewable natural resource and a valuable freshwater source provided by hydroecosystem [2]. In comparison to surface water, groundwater is more solicited for drinking water supply because it is in general less susceptible to contamination and pollution [3]. Despite its deep location in the substratum, it is also exposed to natural and human impacts [2].

The groundwater chemical composition is influenced by the geochemistry of aquifers and the leaching of soils, the dissolution of aerosol particles and other human activities such as mining and conventional agriculture [4,5].

In Sub-Saharan Africa, agriculture is the backbone of economy. Due to the decreasing soil fertility, the use of fertilizer became a solution for securing crop productivity. The intensive use of fertilizer occurs in this region where policies are put in place by governments for cash crop production like fibre crop or cotton. By the way a strong interest is given to fertilizer use in sub-Saharan African countries it is observed an intensive use of fertilizers, which might be a source of groundwater pollution because of soil leaching processes that are inevitable. Thus, it is necessary to investigate the variation of groundwater quality as cultivated lands are increasing over the years and more attention is given to the use of chemical fertilizers.

Groundwater contamination from nitrate in particular is the most frequent emerging issue in many countries with both human and ecosystem health consequences. Agriculture stands as the primary source of nitrogen contamination in groundwater. Due to its high water solubility, nitrate has a high leaching potential [6]. The use of groundwater sources for drinking and other domestic purposes is a common feature of many low-income communities. Therefore, groundwater quality is very important to human health. Investigations to understand the hydrochemical characteristics of groundwater and its quality change under natural water circulation processes in a dominant agricultural area not only help in envisaging the alteration of this valuable resource [5], but also aid to offset the impact of the intensive use of fertilizers on groundwater.

Studies on groundwater quality in the Republic of Benin are very few and have been highly localised [7]. Groundwater quality has not been investigated yet regarding the probable consequence of fertilizer use. Geochemical composition of an aquifer is not the only factor determining groundwater quality as human factors also play an important role [8]. The general chemical nature of groundwater and variation in hydrochemical facies can be understood by analysing major cation and anion concentrations at different time periods.

The main objective of this study was to determine the degree of change in the chemical parameters of groundwater in a small highly cultivated catchment in northern Benin. A groundwater quality survey on a small catchment where more and more attention is given for cotton production with an intensive use of fertilizer, is important as a first step in the development of a groundwater management strategy for similar catchments in the Republic Benin.

2. Description of the Study Site

2.1. Geographic Location and Climate

The study site 'Dassari catchment' is a nested catchment of the Pendjari River basin or Volta basin in the Republic of Benin. It is located in North-West Benin and stretches over the coordinates 10°40’ N and 11° N and 1° E and 1°15’ E. It covers an area of approximately 192 km^2. The study site is fully located in the Sudanian zone characterized by a semi-arid climate with a dry season from November to April and a rainy season from Mai to October. The mean annual rainfall amounts to 919.77 mm and the mean near-surface air temperature is about 34°C [9].

The people living in this catchment area are predominantly farmers and use various water sources for drinking and other domestic proposes.

2.2. Geology and Hydrogeology

The Dassari catchment area is composed of one drainage system. Groundwater is one of the major water resources in Dassari catchment and is most used during the dry season. This catchment is characterized by a relatively flat topography. Elevation in the area is varying from 153 m to 234 m above sea level. The entire catchment lays on the low metamorphic sedimentary rocks of Proterozoic (Cambrian) belonging to the Pendjari series [10] which are made up of silts, argillites and fine green sandstones [11].

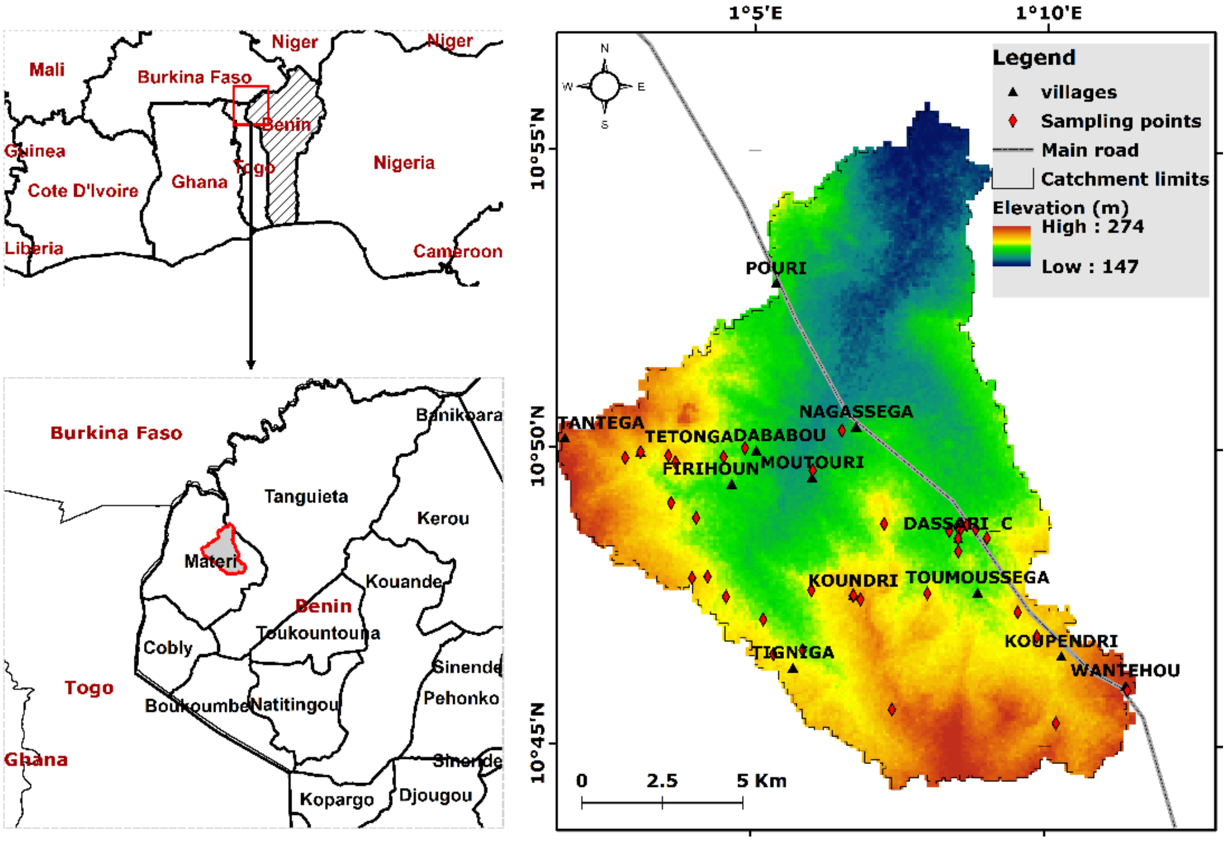

Figure 1. Map the Dassari catchment area

Groundwater flowing through the Pendjari series is hydrocarbonate-sodic or hydrocarbonate-sodium-chloride, hydrocarbonate-sulphated, calcium-magnesium rich. The predominant cations are those of alkaline metals (60.6 mg/L). In general, the calcium and magnesium ion content in groundwater in this region does not exceed 82.3 and 30.3 mg/L, respectively. The pH is close to neutral (6.1 to 7.3) and the hardness is 0.14 to 5.26 mg equivalent/L. The dominant ions are those of calcium and magnesium with a concentration of 46 and 10.6 mg/L respectively, followed by those of sodium and potassium with a concentration of 26.9 mg/L for both [11].

The hydrogeology within the study catchment is based on geological materials and the groundwater is derived primarily from crust alteration or fractures [11,12].

Groundwater associated with alluvium and weathering crusts is the most commonly used by the population. It is generally captured by large hand-dug wells that may dry up during the dry season depending on their position and rainfall.

As for the water of the fractures, it is confined in the tectonized zones and accumulates mainly in the faults. It is perennial for the most part and captured by boreholes or hydraulic boreholes [11].

2.3. Soil and Land Use

Soils in the Dassari catchment are mainly ferruginous soils with crust. Some Gleysoils are found in lowlands and river channels around the catchment, indicating the hydromorphic conditions. The catchment is characterized by temporary river streams [9].

The natural vegetation of the catchment is dominated by a mosaic of savannas with degraded gallery forests along rivers. In terms of land use, the area is dominated by agricultural lands (food crop and cotton production). The rural residential areas occupy the lowest percentage of the whole catchment area.

3. Material and Methods

3.1. Groundwater Sampling and Analysis

To reach the goal of this study, boreholes inside the Dassari catchment were first selected by overlapping the geographical coordinates of the existing boreholes with the catchment shapefile. Thus, a total of thirty-five (35) groundwater sources points or boreholes were identified. These coordinates were obtained from The Benin General Directorate of Water (Direction Génerale de l'Eau) that is in charge of water supply in rural area.

Four sampling campaigns (March and September 2015; March and September 2016) were conducted in both dry and rainy seasons. March represents the dry season while September represents the rainy season. Groundwater samples were collected in polyethylene bottles (1.5 L) for the physico-chemical analysis in laboratory. A total of 140 samples were collected during the four sampling campaigns.

In situ, water temperature, pH, conductivity and dissolved oxygen were measured using a compact precision handheld meter Multi 340i. Alkalinity, calcium, hydrocarbonate, sulphate, magnesium, chloride ion, total iron, nitrite, nitrate, ammonium, phosphate, fluorides and sulphate were analysed in the laboratory within 24 hours of sampling using the standard recommended analytical methods of the American Public Health Association [13]. The volumetric method was applied for the quantitative analysis of calcium, magnesium, chloride and hydrocarbonate. The calcium and magnesium in the samples were determined using the Complexometric titration with EDTA (Ethylene-Diamine Tetra Acetic acid). The chlorides were determined by titration with silver nitrate (Mohr's method). The spectrophotometry method was used to estimate the concentrations of nitrate, nitrite, ammonium, sodium, potassium, phosphate, total iron and fluorides. Sulphate concentration was determined using the colorimetric method. The spectrophotometer used is DR/2400 HACH with operating wavelengths ranging between 400 and 800 nm.

The suitability of groundwater for domestic purposes was evaluated by comparing the values of various water quality parameters with those of the World Health Organisation (WHO 2017) and Benin standard specification guidelines values for drinking water.

3.2. Statistical Analysis

With the goal of evaluating significant changes in groundwater quality used for drinking in a highly cultivated area, the data obtained from the water samples were statistically analysed. Descriptive statistics were used to retrieve information on the major ion concentrations in groundwater per season. Pearson correlation and Student *t*-test were used for describing the significance of the relationship that might exist or not among water quality parameters.

Piper diagrams were plotted using GW_Chart 1.29.0.0 software while Microsoft Excel 2013 was used to build the Chadha's diagram. Moreover, the data used to generate the analytical results shown in Table 1 were submitted to principal component analysis. Cluster analysis (CA) was used to group the water samples based on their similarity.

To analyse the significance of changes in water quality parameters between rainy season and dry season, the boxplot comparison method was used. A one-way analysis of variance (ANOVA) was further used at 5% level of significance to test the significance level of the seasonal change of the parameters.

4. Results and Discussion

4.1. Electrical conductivity (EC), Total Dissolved Solids (TDS) and Hardness (Hd) Values

The physical and chemical parameters of groundwater in the studied catchment are summarized in Table 1. In Dassari catchment, average pH was 7.66 with a minimum and maximum between 6.98 and 8.87, thus indicating the neutral to slightly alkaline nature of the water samples. Only two samples among 140 samples have a pH value slightly exceeding the World Health Organization permissible upper limit of 8.85.

Table 1. Descriptive statistics of chemical parameters in borehole water

Descriptive Statistics									
Parameters	Seasons	Number of samples	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
pH	Rainy season	70	7.76	0.48	0.08	7.59	7.92	7.02	8.87
	Dry season	70	7.57	0.44	0.07	7.41	7.72	6.98	8.50
	Total	140	7.66	0.47	0.06	7.55	7.77	6.98	8.87
EC [µS/cm]	Rainy season	70	594.16	363.80	61.49	469.19	719.12	56.65	1520.80
	Dry season	70	612.58	373.51	63.14	484.27	740.89	55.93	1599.00
	Total	140	603.37	366.12	43.76	516.07	690.67	55.93	1599.00
Hd [mg/l]	Rainy season	70	168.29	69.59	11.76	144.39	192.20	58.54	359.87
	Dry season	70	178.32	71.51	12.09	153.75	202.88	60.03	380.02
	Total	140	173.31	70.23	8.39	156.56	190.05	58.54	380.02
TDS [mg/l]	Rainy season	70	401.06	245.56	41.51	316.70	485.41	38.24	1026.54
	Dry season	70	413.49	252.12	42.62	326.89	500.10	37.75	1079.33
	Total	140	407.27	247.13	29.54	348.35	466.20	37.75	1079.33
Ca^{2+} [mg/l]	Rainy season	70	39.64	15.65	2.64	34.27	45.02	8.76	89.49
	Dry season	70	41.67	16.39	2.77	36.04	47.29	9.53	93.51
	Total	140	40.65	15.94	1.90	36.85	44.45	8.76	93.51
Mg^{2+} [mg/l]	Rainy season	70	16.83	10.51	1.78	13.22	20.45	0.99	41.99
	Dry season	70	18.04	10.69	1.81	14.37	21.71	1.54	44.00
	Total	140	17.44	10.55	1.26	14.92	19.95	0.99	44.00
Na^{+} [mg/l]	Rainy season	70	8.00	2.46	0.42	7.15	8.85	4.57	13.16
	Dry season	70	8.53	2.48	0.42	7.68	9.38	4.81	13.73
	Total	140	8.27	2.47	0.30	7.68	8.85	4.57	13.73
K^{+} [mg/l]	Rainy season	70	1.20	1.88	0.32	0.56	1.85	0.09	8.37
	Dry season	70	1.24	1.87	0.32	0.59	1.88	0.04	8.54
	Total	140	1.22	1.86	0.22	0.78	1.66	0.04	8.54
CO_3^{2-} [mg/l]	Rainy season	70	53.96	73.57	12.44	28.69	79.23	0.64	355.92
	Dry season	70	29.32	31.00	5.24	18.67	39.97	0.63	117.84
	Total	140	41.64	57.40	6.86	27.95	55.33	0.63	355.92
HCO_3^{-} [mg/l]	Rainy season	70	171.21	83.02	14.03	142.69	199.73	21.28	349.05
	Dry season	70	174.45	83.94	14.19	145.62	203.29	21.94	347.55
	Total	140	172.83	82.89	9.91	153.07	192.60	21.28	349.05
Cl^{-} [mg/l]	Rainy season	70	12.34	3.80	0.64	11.03	13.64	7.05	20.30
	Dry season	70	13.16	3.82	0.65	11.84	14.47	7.41	21.17
	Total	140	12.75	3.81	0.46	11.84	13.65	7.05	21.17
SO_4^{2-} [mg/l]	Rainy season	70	31.01	79.67	13.47	3.64	58.37	0.01	409.50
	Dry season	70	30.79	80.39	13.59	3.17	58.40	0.01	414.50
	Total	140	30.90	79.45	9.50	11.95	49.84	0.01	414.50
PO_4^{2-} [mg/l]	Rainy season	70	0.98	1.52	0.26	0.46	1.50	0.08	6.78
	Dry season	70	1.00	1.51	0.26	0.48	1.52	0.04	6.91
	Total	140	0.99	1.50	0.18	0.63	1.35	0.04	6.91
NO_3^{-} [mg/l]	Rainy season	70	22.50	13.70	2.31	17.79	27.20	0.01	55.47
	Dry season	70	23.63	14.12	2.39	18.78	28.48	0.02	59.70
	Total	140	23.07	13.82	1.65	19.77	26.36	0.01	59.70
NO_2^{-} [mg/l]	Rainy season	70	0.13	0.21	0.03	0.06	0.21	0.01	0.80
	Dry season	70	0.17	0.25	0.04	0.08	0.26	0.02	1.04
	Total	140	0.15	0.23	0.03	0.10	0.21	0.01	1.04
NH_4^{+} [mg/l]	Rainy season	70	0.18	0.28	0.05	0.08	0.28	0.01	1.54
	Dry season	70	0.21	0.31	0.05	0.10	0.31	0.01	1.69
	Total	140	0.19	0.30	0.04	0.12	0.26	0.01	1.69
Fluoride [mg/l]	Rainy season	70	0.62	0.65	0.11	0.40	0.84	0.00	3.24
	Dry season	70	0.86	1.43	0.24	0.37	1.35	0.01	8.20
	Total	140	0.74	1.11	0.13	0.47	1.00	0.00	8.20
Fe^{2+}	Rainy season	70	0.82	1.96	0.33	0.14	1.49	0.00	10.20
	Dry season	70	0.89	2.16	0.37	0.15	1.64	0.01	11.27
	Total	140	0.86	2.05	0.25	0.37	1.34	0.00	11.27

[14] which is the same with the standard in the Republic of Benin. This difference of 0.02 is not significant to need a focus of attention.

Water ability of to conduct electricity is measured by the electrical conductivity (EC). Water with a high value of EC indicates its enrichment in salts/dissolved matter.

According to WHO guidelines reported by Ebrahime et al. [15] EC up to 1500 µS/cm is the maximum permissible for drinking water. The EC values recorded in Dassari catchment ranged from 55.93 to 1599 µS/cm, with a mean of 603.37 µS/cm. This indicates that most of the groundwater samples collected between 2015 and 2016 were in the permissible limit. Only about 5.7% of the samples (8 samples) have EC values slightly greater than the permissible upper limit (1516 to 1599 µS/cm). This means that these eight samples have medium enrichment of salts.

Total dissolved solids (TDS) content represents the total amount of inorganic substances, mainly salt, in the water [15]. In the study area, TDS values ranged from 18.17 to 1100.5 mg/L with an average value of 101.45 mg/L. According to WHO [16] the classification of drinking water based on TDS level is as follows: excellent, less than 300 mg/L; good, between 300 and 600 mg/L; fair, between 600 and 900 mg/L; poor, between 900 and 1200 mg/L; and unacceptable, greater than 1200 mg/L. Water with extremely low concentrations of TDS may also be unacceptable because of its flat, insipid taste. Based on this classification, 37.1% of the samples are excellent while 51.4% of the samples are good, 2.9% are fair and 8.6% are poor. None of the samples is classified as unacceptable water. The samples with the highest value of EC also have the highest value of TDS but they do not exceed the limits of 3000 µS/cm and 1200 mg/L.

Water hardness is the traditional measure of the capacity of water to react with soap [16]. Groundwater Hardness (Hd) is mainly controlled by calcium and magnesium ions which are in general produced by the dissolution of carbonated rock. According to WHO, there is no health- based limits for hardness of drinking water. The sampled boreholes hardness values ranging from 58.5 to 380 mg/L with a mean value of 173.3 mg/L in Dassari catchment. Based on the WHO classification about 77.2% of the samples were found to be hard and very hard (see Table 2).

Table 2. Groundwater classification based on Electrical Conductivity, Total Dissolved Solids and Total Hardness

Parameters	Classification	Sample percentage
EC (µS/cm)		
0 - 800	Good	78.6
800 - 3000	Acceptable	21.4
3000 -10,000	Not recommended	0.0
>10,000	Not suitable	0.0
TDS (mg/L)		
< 300	Excellent	37.1
300 - 600	Good	51.4
600 - 900	Fair	2.9
900 -1200	Poor	8.6
>1200	unacceptable	0.0
Hardness (mg/L)		
<60	Soft	1.4
60 - 120	Moderately hard	21.4
120 - 180	Hard	38.6
>180	Very hard	38.6

4.2. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) Values

Naturally, calcium and magnesium are the most abundant elements in surface and ground water. In Dassari catchment Ca^{2+} concentrations vary from 8.76 to 93.51 mg/L with a mean of 40.65 mg/L (Table 1). The highest concentration of Ca^{2+} (93.51 mg/L) is observed in the dry season while in the rainy season the highest concentration of Ca^{2+} observed is 89.49 mg/L. Though there are a little bit high these concentrations of Ca^{2+} did not exceed the maximum allowable concentration of 200 mg/L recommended by WHO. But 2.9% (4 samples) of the samples had Ca^{2+} concentrations exceeding the maximum acceptable limit of 75 mg/L [16]. Regarding Benin standard specification guidelines values for drinking water, the permissible concentration of Ca^{2+} is 100 mg/L. This means that 100% of the groundwater samples collected for this were good for consumption regarding calcium concentration.

In both rainy and dry seasons, magnesium content in the sampled groundwater ranged from 0.99 to 44 mg/L with a mean of 17.44 mg/L. The acceptable limit of Mg^{2+} concentration in drinking water is specified as 50 mg/L according to Benin and WHO standards and the maximum allowable concentration of Mg^{2+} is 150 mg/l (WHO 2004).

Regarding these standards on Mg^{2+} concentration, all samples were suitable for consumption.

4.3. Sodium (Na^{+}) and Potassium and (K^{+}) Values

In most natural water sources sodium is in general found in lower concentration than calcium and magnesium [2]. During the rainy and dry seasons in Dassari catchment, the concentration of Na^{+} ranged from 4.57 to 13.73 mg/L with a mean of 8,27 mg/L. The permissible limit of sodium is 200 mg/L according to WHO standards [14]. Regarding this value, none of the samples did not exceed the permissible limit of Na+ concentration. Thus, the groundwater in the study site is suitable for domestic purposes.

Naturally, potassium (K^{+}) concentration is quite lower compared with Ca^{2+}, Mg^{2+} and Na^{+} despite its natural availability. Its concentration in drinking water seldom reaches 20 mg/L [2]. The concentration of K^{+} during the rainy and dry seasons in Dassari catchment ranged between 0.04 and 8.54 mg/L with a mean of 1.22 mg/L. The maximum permissible limit of potassium in the drinking water is 12 mg/l and it was found that all samples are below the permissible limit of WHO reported by Sarath Prasanth et al.[2].

4.4. Ammonia (NH_4^{+}) and iron (Fe^{2+}) values

Ammonia in the environment originates from metabolic, agricultural and industrial processes. Natural levels in groundwater are usually below 0.2 mg/L. Anaerobic groundwater may contain up to 3 mg/L [14]. In the study area the concentrations of ammonia ranged from 0.01 mg/L to 1.69mg/L with a mean of 0.19 mg/L. Considering these values groundwater in Dassari catchment are not ammonia-rich water. Since ammonia in drinking-water is not immediate health relevant, there is no health-based guideline value recommended.

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%. Iron is most commonly found in nature in its oxides' form. According to WHO [14] the taste threshold value is 0.12 mg/L. In the water samples from wells, iron concentrations below 0.3 mg/L were characterized as unnoticeable whereas levels of 0.3-3 mg/L were found acceptable. In the groundwater samples from Dassari catchment Fe^{2+} concentrations vary from 0 mg/L to 11.27 mg/L with a mean of 0.86 mg/L. 12 samples (5.6% of all samples) exceed the maximum acceptable limit of 3 mg/L [14].

4.4. Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) values

Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions are the main form of carbonate compounds in freshwater [17]. They are often derived from the dissolution of carbonate minerals in soil. They also control the alkalinity in most groundwater. In Dassari catchment, the observed values of CO_3^{2-} ranged from 0.63 to 355.92 mg/L and HCO_3^- ranged from 21.28 to 349.05 mg/L, with average values of about 41.64 mg/L and 172.83 mg/L respectively. The carbonate and bicarbonates are probably derived from the weathering of the geological material in the catchment which is mainly composed of rocks of Proterozoic (Cambrian) belonging to the Pendjari series [10] that is a carbonate-rich rock. There is no drinking water standard established for carbonate and bicarbonate.

4.5. Chloride (Cl^-) and Fluoride (F^-) Values

Chlorides are present in water at low concentrations (less than 100 mg/L) unless the water is classified as brackish or saline [15]. In groundwater chloride might come from diverse sources such as weathering, leaching of sedimentary rocks and soils. There is no health-based guideline for chloride in drinking-water issued from WHO. But it was recommended a taste threshold of 200-300 mg/L. During the four campaigns all water samples from the study area under the WHO's taste threshold. Cl^- concentrations ranged from 7.05 to 21.17 mg/L with a mean value of 12.75 mg/L.

In the sampled water, the concentration of F^- varied from 0 to 8.20 mg/L (Table 1) with a mean value of 0.74 mg/L. The highest concentration of F^- is obtained during the dry season. The maximum acceptable concentration of Fluoride in drinking water is 1.5 mg/L according to the Republic of Benin and WHO standards. Concentrations between 0.6 and 1.7 mg/l in drinking water have a beneficial effect on the structure and resistance to decay of children's teeth, but excess levels may cause mottling of teeth [14]. In the study catchment about 7.14% (10 samples) of the samples exceed the acceptable limit. According to Subba Rao et al. [18] the key factors that determine the concentration of F^- in groundwater are the sources of geogenic (apatite, biotite, and clays) and anthropogenic (chemical fertilizers), with a combination of higher rate of evaporation and longer interaction of water with the aquifer materials under alkaline environment.

4.6. Sulphate (SO_4^{2-}) and Phosphate (PO_4^{3-}) Values

According to WHO [14] high concentration of sulfate do not cause health issues for humans. But concentrations exceeding 250 mg/L result in a bitter taste in drinking water and may cause a laxative effect for some consumers. WHO specifies the maximum permissible concentration of sulfate in drinking water as 500 mg/L because of the gastrointestinal effects. The sulfate concentrations of the samples from the study catchment ranged between 0.01 and 414.50 mg/L with a mean value of 30.90 mg/L. None of the samples did exceed the WHO limit, thus indicating that groundwater in the catchment is still good for drinking.

Phosphate concentrations in the samples varied from 0.04 to 6.91 mg/L with a mean value of 0.99 mg/L (Table 1). The highest concentration of phosphate is observed in dry season. Kipngetich et al. [19] reported that the recommended limit of phosphate concentration by WHO is 5 mg/L. Based on this threshold, only 5.7% (8 samples) of the samples had their phosphate values greater than the maximum limit.

4.7. Nitrate (NO_3^-) and Nitrite (NO_2^-) Values

Nitrate (NO_3^-) is found naturally in the environment and is an important plant nutrient. It can reach both surface water and groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures) [14]. The value of NO_3^- in the groundwater samples ranged from 0.01 to 59.70 mg/L, with a mean value of 13.82 mg/L (Table 1). 94.3% of the samples had their NO_3^- concentration below the recommended value for drinking water by WHO (50 mg/L) while 5.7% of the samples had NO_3^- concentration above the recommended limit. NO_3^- is a of non-lithological source. In natural conditions, the concentration of NO_3^- does not exceed 10 mg/L in water so that a high concentration of NO_3^- above 10 mg/L is an indication of anthropogenic pollution [18]. 84.3% of the samples had NO_3^- concentrations higher than 10 mg/L, indicating the impact of a high fertilizer use on groundwater in the study area.

Nitrite (NO_2^-) is not usually present in significant concentrations except in a reducing environment, because nitrate is the more stable oxidation state. It can be formed by the microbial reduction of nitrate and in vivo by reduction from ingested nitrate. The groundwater shows a very low content of NO_2^- from 0.01 to 1.04 mg/L, with a mean value of 0.15 mg/L. 100% of the water samples had their NO_2^- concentration below the recommended limit for drinking water that is 3 mg/L.

4.8. Hydro-geochemical Facies

Hydro-chemical parameters in groundwater can be understood by plotting the concentration of major cations and anions in a Piper trilinear diagram [15,20]. It is a graphical presentation of the major ions that helps to quickly determine the hydro-chemical facies of groundwater [15]. The major cation and anion concentrations are presented in the bottom triangles on the left and right, respectively. The diamond in the top centre of the diagram presents the composition of both ions. The Piper trilinear diagram for the groundwater samples in rainy and dry season is shown in Figure 2 which explains clearly the variations of the major cation and anion concentration in Dassari catchment.

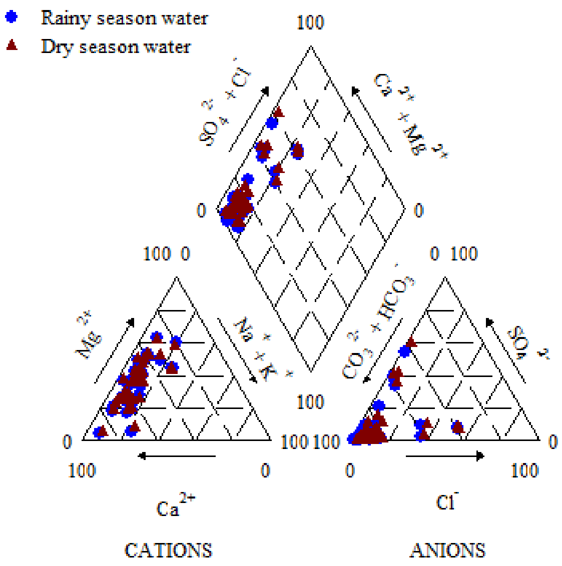

Figure 2. Piper diagram of the groundwater samples

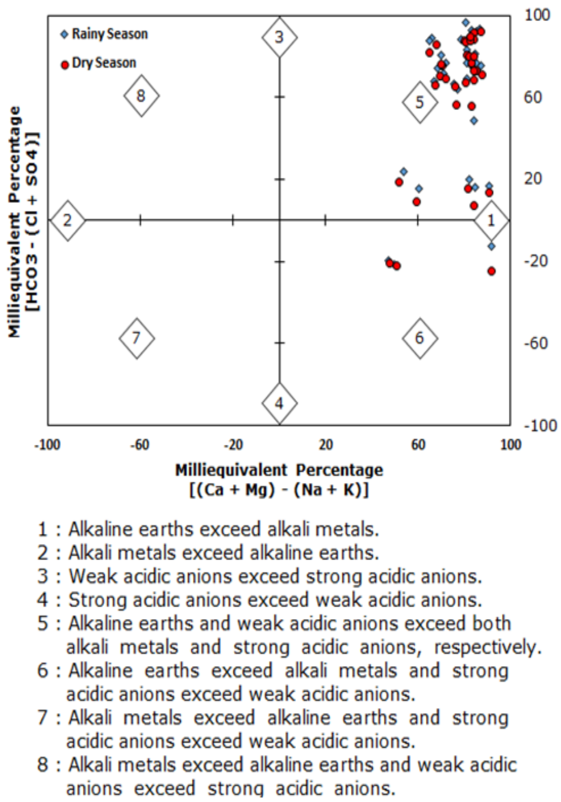

Figure 3. Chadha's plot of the groundwater samples

Looking at the bottom triangles on the left, it clearly comes out that all groundwater samples in the study area were calcium-rich water and 94.3% of the samples were magnesium-rich water. From the bottom triangles on the right, it is shown that 94.3% of the samples were carbonate-rich water while the remaining samples were moderate carbonate water. In the study area the majority of samples belongs to the Ca^{2+} – Mg^{2+} – HCO_3^- type in both rainy and dry seasons. Regarding the diamond in the top centre of the diagram, 11.4% of the samples were moderate strong acid water and cannot be identified as neither anion nor cation dominant.

In brief, groundwater in Dassari catchment is Calcium-Bicarbonate type and this is likely induced by the the rock/water interaction in the area.

The Chadha's plot (Figure 3) is conform with the Piper trilinear diagram (Figure 4). Based on the Chadha's plot, all the samples can be divided into two groups. In the first group, the alkaline earth metal cations exceed the alkali metals cations, viz. Ca2+ – Mg2+ > Na+ – K+ (field 1), 11.4% of the total samples fall into this group. The remain samples (88.6%) fall into the second group alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively viz. Ca2+ – Mg2+ – HCO3- > Na+ – K+ – Cl- – SO42- (field 5).

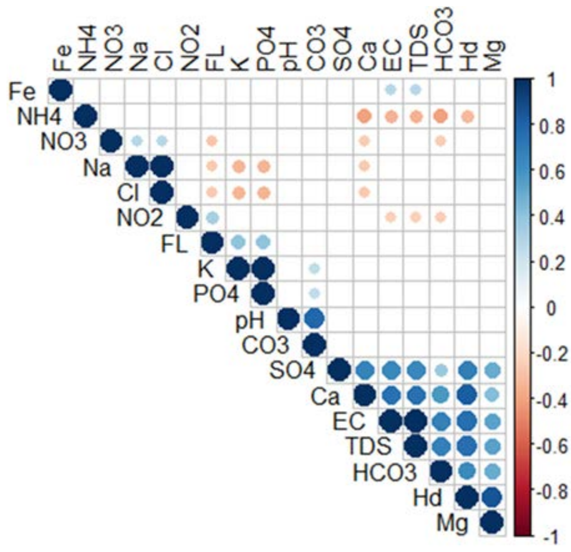

Figure 4. Correlogram of the hydro-chemical parameters

4.9. Interrelations of Chemical Parameters

The interrelations between chemical parameters have been analysed using Pearson's correlation plotted as a correlogram and presented in Figure 4. To examine the significance of a probable relationship between two water quality parameters the Student's *t-test* was used. In this Figure 4, the correlations with a p-value > 0.05 are considered as non significant and their values are not plotted.

This figure displays a strong positive and significant relationship between total hardness (Hd) and HCO_3 (r = 0.70), TDS (r = 0.80), EC (r = 0.8), Ca^{2+} (r = 1), SO_4^{2-} (r = 0.8) and Mg^{2+} (r = 0.8). This indicates that the groundwater quality in the study catchment is characterised by an alkaline environment and the groundwater is mainly controlled by Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}which leads to dissolve aquifer minerals. This finding is in good agreement with the Piper diagram and the Chadha's plot.

Significant and negative correlations existing between ammonia ($NH4^+$) and Ca^{2+}, EC, TDS, HCO_3^- , Hd; and between nitrate (NO_3^-) and Ca^{2+}, HCO_3^- and; between nitrite (NO_2^-) and EC, TDS and HCO_3^- indicate anthropogenic factors from agricultural activities in the catchment.

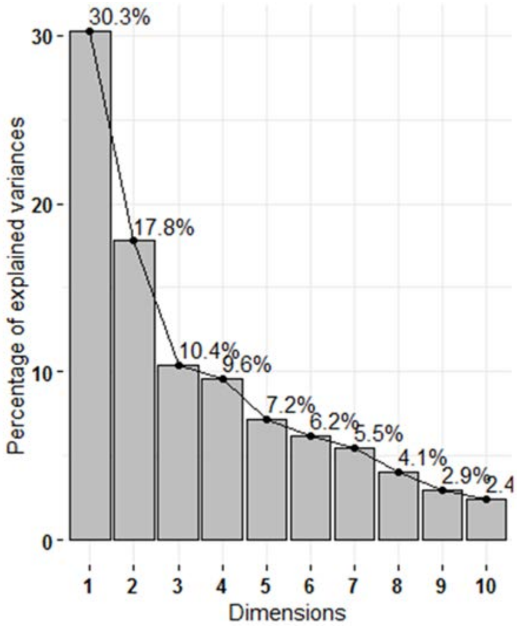

Figure 5. PCA scree plot of the percentage of explained variance

4.10. Principal component analysis

Principal component analysis (PCA) is a multivariate statistical analysis used to reduce the dimensionality of a data set without losing too much information [21,22]. Thus, PCA was applied to reduce the number of chemical parameters of groundwater for further assessment of the relationships between these parameters. In this study, the leading four principal components (PCs) were retained and summarised 68.1 % of the total variance. Figure 5 shows the percentage of the explained variance per component.

Figure 6 displays the correlation level between the leading two principal components and the analysed parameters. The first principal component is highly correlated with the ion concentrations of Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, EC, TDS and Hd while being negatively correlated with ammonia ($NH4^+$).

The second principal component is highly and positively correlated with Na^+ and Cl^-, and weakly correlated with NO^{3-} and Fe^{2+}. This second principal component is also negatively correlated with PO_4^{3-}, K^+, F^-, pH, NO_2^- and CO_3^-.

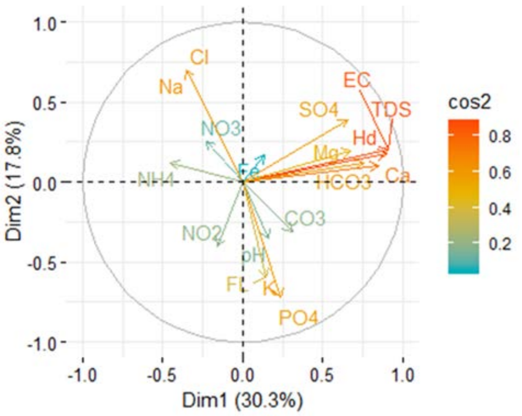

Figure 6. Plot of PCA loading scores for the groundwater chemical parameters

From Figure 5 and Figure 6 it comes out that the most important parameters controlling groundwater quality in rainy and dry seasons in the study catchment are Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, EC, TDS and Hardness(Hd).

4.11. Cluster Analysis

Cluster analysis (CA) is applied in this study to detect similarity and dissimilarity in the groundwater chemical parameters and to group the selected parameters into hydro-chemical groups or clusters. The hierarchical cluster analysis method was used to classify the water samples into clusters where hydro-chemical parameters in the same group or cluster are more similar to each other than to those in other groups or clusters. The application of CA on the water samples shows four groups based on the hydro-chemical composition (Figure 7 and Figure 8) for the rainy and dry seasons. In order to compare the hydrochemistry difference of each group and per season, the average values of the hydro-chemical parameters are shown in Table 3.

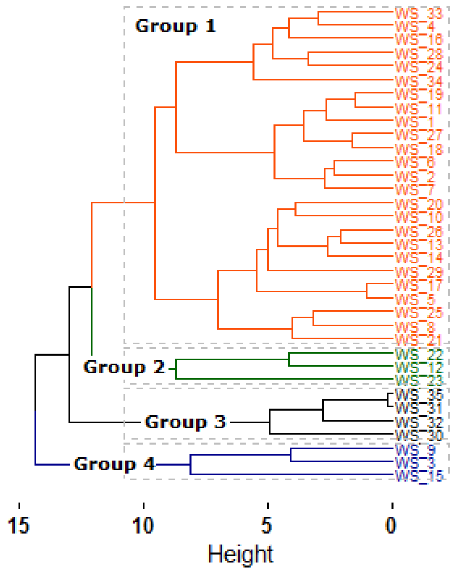

Figure 7. Dendrogram of the water sources in dry season

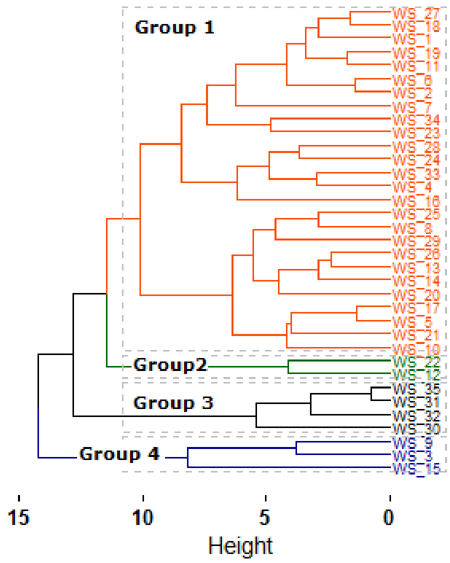

Figure 8. Dendrogram of the water sources in rainy season

Table 3. Average values of the hydro-chemical parameters per water groups

Parameters	Rainy season				Dry season			
	Group 1	Group 2	Group 3	Group 4	Group 1	Group 2	Group 3	Group 4
pH	7.8	8.1	7.3	7.7	7.6	7.6	7.2	7.39
EC [µS/cm]	554.7	805.5	87.7	1470.4	578.5	688.7	87.7	1520.27
Hd [mg/L]	162.8	229.6	72.5	302.6	174.2	211.3	75.4	317.05
TDS [mg/L]	374.4	543.7	59.2	992.5	390.5	464.9	59.2	1026.18
Ca^{2+} [mg/L]	39.7	46.7	13.7	69.2	42.2	44.1	14.2	71.66
Mg^{2+} [mg/L]	15.5	27.4	9.3	31.5	16.7	24.5	9.7	33.54
Na^{+} [mg/L]	7.9	5.9	10.1	7.6	8.5	6.0	10.7	8.17
K^{+} [mg/L]	0.9	7.6	0.2	0.7	0.8	6.4	0.2	0.72
CO_3^{-} [mg/L]	56.8	137.9	2.1	42.2	32.8	45.3	1.4	21.4
HCO_3^{-} [mg/L]	179.5	227.9	27.3	253.1	185.7	192.1	28.0	258.2
Cl^{-} [mg/L]	12.1	9.1	15.6	11.8	13.2	9.3	16.5	12.6
SO_4^{2-} [mg/L]	13.4	10.0	3.2	235.0	12.7	9.6	3.5	239.2
PO_4^{3-} [mg/L]	0.8	6.2	0.2	0.5	0.7	5.2	0.2	0.59
NO_3^{-} [mg/L]	21.5	14.7	29.2	27.4	23.1	13.9	30.4	28.87
NO_2^{-} [mg/L]	0.2	0.0	0.1	0.1	0.2	0.4	0.2	0.09
NH_4^{+} [mg/L]	0.1	0.2	0.7	0.2	0.1	0.2	0.9	0.19
F^{-} [mg/L]	0.7	1.6	0.0	0.4	0.7	3.8	0.0	0.47
Fe^{2+} [mg/L]	0.6	0.7	0.5	3.4	0.65	0.51	0.54	3.76

The analysis of the average values of the hydro-chemical parameters in the four groups reveals that in the rainy and dry seasons the group 4 was characterised by high values of the major cations and anions and high values of EC, Hd and TDS. The group 4 is followed by the group 2, group 1 and group 3 respectively. The group 3 has the lowest concentrations of the major cations and anions and of EC, Hd and TDS. This group 3 also has the highest concentration of Nitrate.

Considering the Hardness level presented in Table 1, groups 2 and 4 had a very hard water while groups 1 and 3 had a moderate hard water. Based on the TDS, group 3 was the group having excellent water, groups 1 and 2 were the groups having good water and group 4 was a poor water group. As well, considering EC groups 1 and 3 can be classified as having good water, while groups 2 and 4 can be classified as having acceptable water.

Regarding the concentration of NO_3^- which is an indicator of the impact of human activities (e.g. agriculture) on groundwater resources, all the four groups had their NO_3^- concentrations greater than 10 mg/L which is the natural limit of NO_3^- concentration in water [18]. But these NO_3^- concentrations were still under the permissible limit of 50 mg/L recommended by WHO for water consumption.

4.12. Seasonal Changes in Groundwater Parameters

The seasonal variation in groundwater parameters in Dassari catchment was analysed using the boxplot comparison method and one-way variance analysis (one-way ANOVA). Figure 9 shows boxplots of the analysed parameters for both rainy and dry seasons. It displays a slight variation of the groundwater parameters in dry season and rainy season. In the dry season, the concentrations of the analysed chemical elements seems to be a little bit higher than those obtained in the rainy season. The significance of this variation was tested by a one-way ANOVA considering the seasons as factors. The results of this test are summarised in Table 4.

The analysis of Table 4 reveals that there is no a significant change of the hydro-chemical parameters of groundwater in Dassari catchment from rainy season to dry season at a 5% level of significance. The slight variation that is noted might be due to dissolution and to the high evapotranspiration that characterises the geographical zone of the study area.

Table 4. Summary of one-way ANOVA test

Parameters	Rainy season	Dry season	F-Value	P-Value
pH	7.76	7.57	3.0851	0.083
EC [µS/cm]	594.16	612.58	0.0437	0.835
Hd [mg/L]	168.29	178.32	0.3531	0.554
TDS [mg/L]	401.06	413.49	0.0437	0.835
Ca^{2+} [mg/L]	39.64	41.67	0.2788	0.599
Mg^{2+} [mg/L]	16.83	18.04	0.2268	0.635
Na^{+} [mg/L]	8.00	8.53	0.8080	0.372
K^{+} [mg/L]	1.20	1.24	0.0046	0.946
CO_3^{-} [mg/L]	53.96	29.32	3.3335	0.072
HCO_3^{-} [mg/L]	171.21	174.45	0.0264	0.871
Cl^{-} [mg/L]	12.34	13.16	0.8068	11.80
SO_4^{2-} [mg/L]	31.01	30.79	0.0001	0.990
PO_4^{3-} [mg/L]	0.98	1.00	0.0043	0.948
NO_3^{-} [mg/L]	22.50	23.63	0.1164	0.734
NO_2^{-} [mg/L]	0.13	0.17	0.3941	0.532
NH_4^{+} [mg/L]	0.18	0.21	0.1341	0.715
F^{-} [mg/L]	0.62	0.86	0.7999	0.374
Fe^{2+} [mg/L]	0.82	0.89	0.0251	0.874

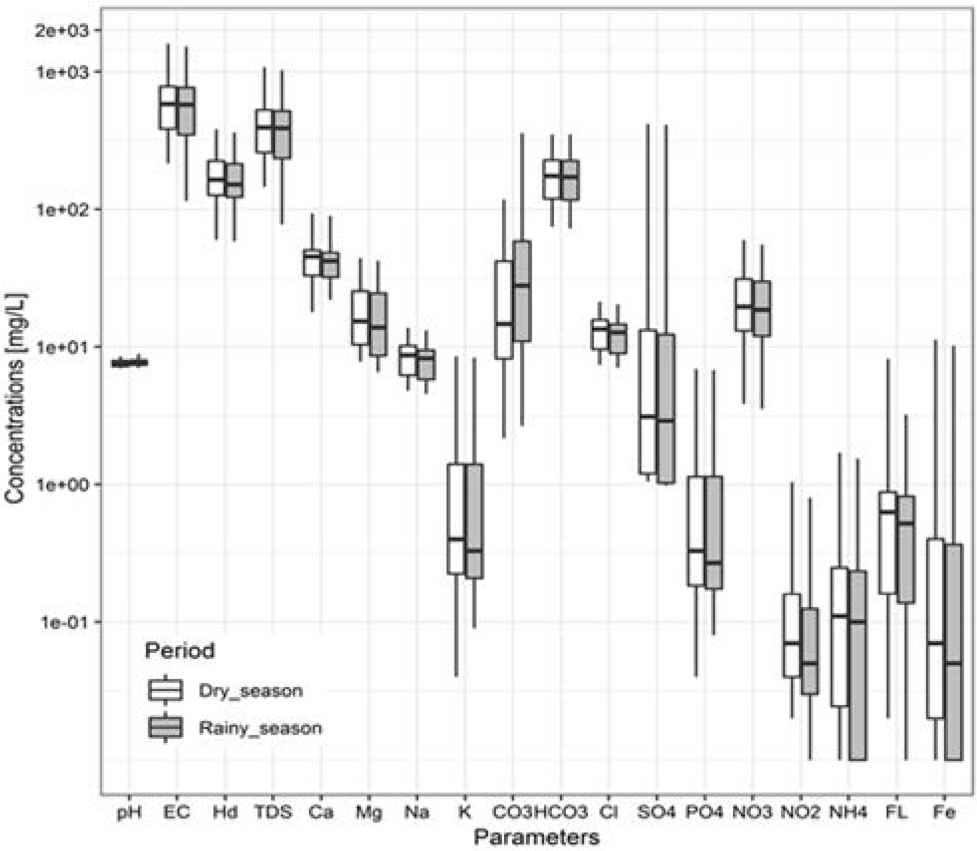

Figure 9. Boxplot of hydro-chemical parameters

5. Conclusion

The study has provided information on the quality of groundwater and its seasonal variation. The effects of anthropogenic activities such as agriculture on groundwater pollution in Dassari catchment in the North-Westof the Republic of Benin are also examined. The analysis of the chemical characteristics the water sampled from boreholes indicated that in the study catchment the groudwater is calcium-rich and magnesium-rich water and the dominant anion is hydro-carbonate (HCO3-). Regarding nitrate concentration in the water samples, groundwater in the study catchment is still good for consumption since the nitrate concentration was found under the permissible limit (50 mg/L) of WHO. But the nitrate concentrations of most samples (84.3%) were above the natural limit of 10 mg/L, thus indicating the impact of high fertilizer use on groundwater in the study area. Looking at the seasonal variation of the hydro-chemical parameters, there was no significant change of the parameters from rainy season to dry season.

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