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Hydrogeochemical Characterization of Groundwater from Fissured Aquifers in the Angovia Mine Operating Permit Area (Central-West Côte d'Ivoire)

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Abstract

The main objective of this study is to determine the hydrogeochemical specificities of the groundwater of the Angovia mine operating permit, located in the Yaouré mountains in the center-west of Côte d'Ivoire. To do so, descriptive and multivariate statistical analysis methods with the SOM (Self Organizing Maps) algorithm were applied to the physicochemical parameters of 17 boreholes using the calcite (ISC) and dolomite (ISD) saturation indices. The results obtained have shown that the groundwater in the Angovia mine operating permit area has an average temperature of 27.52˚C (long rainy season) and 27.87˚C (long dry season) and has an average pH of 7.09 ± 0.35 during the main rainy season and 7.32 ± 0.35 during the main dry season. They are mineralized with an average electrical conductivity of 505.98 ± 302.85 µS/cm during the long rainy season and with 450.33 ± 233.74 µS/cm as average during the long dry season. The main phenomena at the origin of groundwater mineralization are water residence time, oxidation-reduction and surface inflow. The study of the relative age of the water shows that the groundwater in the Angovia mine operating permit area is mainly undersaturated with respect to calcite and dolomite. They are therefore very old in the aquifer with a slow circulation speed during the long rainy season and the long dry season.

Keywords

Hydrogeochemistry, Mineralization, Fissure Aquifers, Operating Permits, The Angovia Mine

1. Introduction (Heading 1)

Water is an essential element, even primordial to life on earth. The history of water and that of men are closely linked [1]. Just like air, drinking water is vital; having it in sufficient quantity and quality contributes to maintaining health and directly contributes to the quality of the environment [2]. It is estimated that each year, more than 842,000 people, including 361,000 five-year-old children, die from diarrhea due to unsafe drinking water and lack of sanitation and hygiene. Water has today become a global strategic issue whose management must be integrated into a political perspective of sustainable development [3].

In Côte d'Ivoire, the lack of water increases during dry periods in certain localities and forces populations to travel long distances to obtain supplies from permanent water points (surface water), generally of dubious quality and vectors of many diseases such as diarrhea, dysentery, cholera, etc [4]. Faced with this situation, it is therefore important to use groundwater which constitutes the main source of drinking water supply for populations in most regions of the world [5]. However, this resource, which was once of good quality, is currently threatened by various point and diffuse contamination sources of anthropogenic origin such as domestic wastewater, urbanization, agricultural and mining exploitation. If the impact of agricultural exploitation on water resources is not too marked in Côte d'Ivoire, this is not the case of mining which today constitutes one of the most important sources of pollution of natural resources in general and water in particular. The Angovia mine operating permit area, which is one of the most important deposits in the gold sector in Côte d'Ivoire, is no exception to the rule. This permit is located in a rural area, with a population of approximately 2,400 inhabitants [6]. In this area, the population is generally supplied with drinking water from boreholes [7]. However, mining, whether at the ores extraction level, their transformation or their transport, generates damage to the natural environment, particularly to water resources. The quality of water resources remains threatened by chemicals used for mineral processing. Faced with this threat to the quality of groundwater, it is necessary to know the real impact as well as the probable origin of these pollutants that could be found in these waters. It is in this context that the present study entitled: "Hydrogeochemical characterization of groundwater from fissured aquifers in the Angovia mine operating permit area (Central-West of Côte d'Ivoire)" has been carried out.

The main objective of this study is to determine the hydrogeochemical specificities of groundwater in the Angovia mine operating permit area.

2. Material and Methods

2.1. Presentation of the Study Site

The study site of the Angovia gold project is located in the center-west of Côte d'Ivoire between 5˚19' and 5˚31' West longitudes and 6˚53' and 7˚65' North latitudes (**Figure 1**). It is located in the Marahoué region, at 25 km from the Bouaflé town. This gold zone is also located 6 km from the Kossou hydroelectric dam.

The relief of the Marahoué region is made up of plateaus and plains which occupy most of the region which is very uneven with an average altitude of 250 m. The vegetation appears as a mosaic of semi-deciduous forest and savannah. The savannah in this region resembles an intermediate zone between grassy savannah and tree and shrub savannahs [8]. The average rainfall in the Marahoué region recorded in Bouaflé over the period 2000 to 2018 is 1106 mm. The geological formations are dominated by volcanic rocks which begin with a tholeitic basaltic series (in the Yaouré region) and continue with a calc-alkaline series which constitutes the Upper Birimian. The aquifers are of the alteritic and fractured type. Alteritic aquifers are surface formations resulting from processes of physicochemical alteration and erosion of the base.

2.2. Material

The material consists of hydrochemical data from boreholes and software for processing.

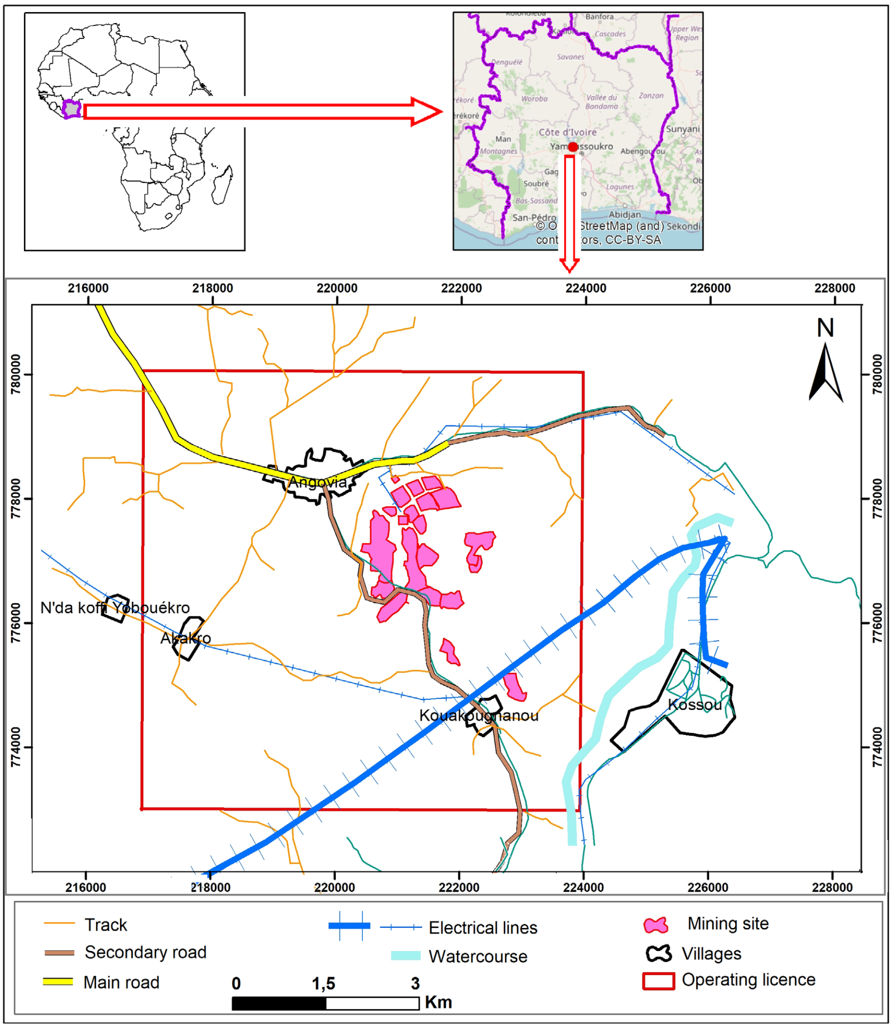


Figure 1. Location of the study site.

2.2.1. Hydrochemical Data

The hydrochemical data used come from physicochemical analyzes of groundwater samples of 17 boreholes taken over the period 2014-2015 (December 8, 2014 to January 20, 2015).

The physicochemical parameters used are T, pH, Turb, EC, O2dis, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, SO_4^{2-}, Cl^{-}, HCO_3^{-}, PO_4^{3-}, NO_3^{-}, NO_2^{-} and Trace metal elements (F, As, Ba, B, Cr, Co, Cu, Fe, Mn, Ni, Sr, Pb, Zn and Al) obtained during village and urban water projects carried out by the FORACO-CI companies. The analyze of the various samples were carried out in the laboratory of the Perseus Yaoure Company. Figure 2 shows the distribution of the different drilling operations in the Angovia mine operating permit area.

2.2.2. Data Processing Tool and Software

The data processing tool is a computer on which the following software are installed:

- Diagrams (version 5.1) which is a multi-language hydrochemical software for the interpretation of hydrochemical data;
- ArcGIS 10.5 for producing thematic maps;
- Matlab 6.1 for multivariate statistical analysis (SOM);
- Statistica 7.1 for descriptive statistical analysis;
- Microsoft Office Excel for creating graphs and curves.

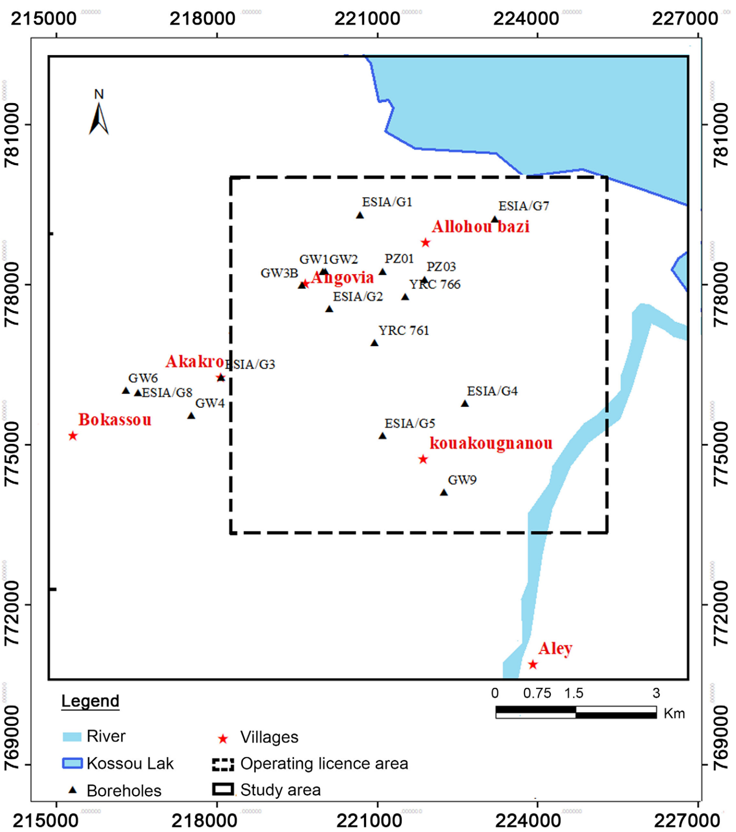


Figure 2. Distribution map of selected boreholes in the study area.

2.3. Methods

After validating the measurements by the ionic balance, the collected data were processed using a combination of multivariate statistical methods and hydrochemical methods.

2.3.1. Validation of Measurements

Ion balance calculation is used to check the reliability of chemical analysis results. The calculation of the ionic balance (IB) is done by checking the scale of anions and cations. In theory, the sum of anions expressed in meq/L must correspond exactly to the sum of cations also expressed in meq/L [1]. A perfectly balanced ionic balance is rarely obtained. There is always a percentage of errors (ERR) evaluated according to Equation (1):

$$\text{ERR}\left(\%\right)=\frac{\sum\text{Cations}-\sum\text{Anions}}{\sum\text{Cations}+\sum\text{Anions}}*100 \quad (1)$$

- If ERR < 5%, then the analysis is considered satisfactory;
- If 5% < ERR < 10%, then the analysis deemed acceptable;
- If ERR > 10%, then the analysis is doubtful and must be repeated for verification.

2.3.2. Physico-Chemicals Characteristics of Groundwater in the Study Area

The physicochemical characterization of groundwater requires the quantification of the different physicochemical parameters. This is based on descriptive statistics by calculating means, maximums, minimums, standard deviations and variation coefficients (CV) of physicochemical parameters compared to potability standards.

2.3.3. Multivariate Statistical Analysis Using the Self-Organizing Maps (SOM) Algorithm

Statistical methods of multivariate analysis are very effective for the global representation and interpretation of a large mass of data. They are increasingly used in studies of geochemical processes and support classical methods [9] [10]. They make it possible to highlight the relationships between the different parameters in a hydrogeological system where the evolution of the chemical composition of the water depends on several processes which may or may not interfere with each other and to better characterize the quality of groundwater [11].

The multivariate statistical method applied in this study uses the "Self-Organizing Maps" or "SOM" algorithm developed by [12]. This classification algorithm built on the model of a non-linear and non-hierarchical artificial neural network [12]. Works through cells connected to each other. It allows multidimensional data sets to be analyzed by grouping data (clusters) based on their similarity and visualizing them on a two-dimensional grid made up of neurons, called self-organizing maps.

2.3.4. Relative Age of Groundwater

Saturation indices allow us to know the degree of saturation of the water in relation to the minerals present or likely to precipitate in the aquifer. The saturation index (SI) of a mineral was obtained from the following Equation (2) [13] [14]:

$$IS = \log\left(\frac{PAI}{Kps}\right) \quad (2)$$

where PAI is the ionic activity product of the chemical species dissociated in solution, Kps the equilibrium solubility product for the chemical involved at the sample temperature:

- when IS < 0, the solution is under saturated relative to the mineral (dissolution of the mineral). In this case, water is capable of dissolving the mineral;
- when IS = 0, the solution is saturated with respect to the mineral;
- when IS > 0, the solution is supersaturated relative to the mineral (precipitation of the mineral).

It is important to note that the saturation index directly depends on the validity of the ionic content measurements and the pH measurement, in particular for saturation with respect to carbonate minerals.

3. Results

3.1. Validation of Measurements

The study of the validation of chemical analysis measurements carried out on groundwater samples from the study area reveals that the chemical analyzes are satisfactory. This satisfaction with the chemical analyzes is due to the fact that for all the samples ERR < 5% with values varying from (−5.799%) to (4.493%) respectively at the ESIA/G5 and ESIA/G2 level.

3.2. Groundwater Physico-Chemical Parameters in the Study Area

Basic Statistics of Physicochemical Parameters

Physical parameters

Table 1 gives the statistics of the physical parameters of the study area. The analysis of this table shows that the groundwater of the study area has temperatures which vary from 26.12˚C to 29.32˚C with an average of 27.52˚C ± 0.91˚C during the long rainy season. During the long dry season, temperatures range from 26.43˚C to 29.55˚C with an average of 27.87˚C ± 0.97˚C. The sampled waters' pH varies from 6.35 (GW2) to 7.58 (GW4) with an average of 7.09 ± 0.35 during the long rainy season and from 6.69 (GW3B) to 7.96 (PZ03) with an average of 7.32 ± 0.33 during the long dry season. Overall, 75% of waters have pH > 7 while the remaining 25% have pH ≤ 7 during the long rainy season. During the long dry season, 82.35% of waters have pH > 7, while 17.65% have pH < 7. Waters with pH values < 7 are said to be aggressive and those with pH > 7 are called encrusting. The groundwater turbidity of the fissured aquifers in the Angovia permit area ranges from 0.23 NTU (GW1) to 168.46 NTU (ESIA/G5)

Table 1. Physical parameters basic statistics of groundwater in the Angovia mine operating permit area.

Parameter	Unit	Long rainy season					Long dry season					WHO standards (2011)
		Min	Max	Avg	σ	CV (%)	Min	Max	Average	σ	CV (%)	
T	(˚C)	26.12	29.32	27.52	0.91	3.31	26.43	29.55	27.87	0.97	3.48	25˚C à 30˚C
pH		6.35	7.58	7.09	0.35	4.94	6.69	7.96	7.32	0.33	4.51	6.5 < pH < 8.5
Turb	(NTU)	0.23	168.46	24.70	42.19	170.81	0.23	1866.78	142.69	448.03	313.99	<5
CE	(µS/cm)	108.30	1404.00	505.98	302.85	59.85	97.50	1060.00	450.33	233.75	51.91	≤500
O_2dis	(mg/L)	17.78	44.90	24.47	7.36	30.08	20.90	61.60	34.78	10.71	30.79	-

Min: Minimum, **Max**: Maximum, **Avg**: Average, ***σ***: Standard deviation, **CV**: Coefficient of Variation.

with an average of 24.70 ± 42.19 NTU during the great rainy season. During the long dry season, turbidity values vary from 0.23 NTU (GW6) to 1866.78 NTU (ESIA/G5) with an average of 142.69 ± 448.03 NTU. Electrical conductivity (EC) values vary from 108.30 µS/cm (ESIA/G2) to 1404 µS/cm (GW6) with an average of 505.98 ± 302.85 µS/cm during the long rainy season and from 97.50 µS/cm (ESIA/G2) to 1060 µS/cm (GW9) with an average of 450.33 ± 233.75 µS/cm during the long dry season. Waters with good mineralization are characterized by conductivity values lower than 500 µS/cm (10 boreholes, or 58.82%) during the long rainy season and 11 boreholes, or 64.70% during the long dry season. The highly mineralized waters which have electrical conductivities greater than 500 µS/cm are distributed in 7 boreholes, *i.e.* 41.18%, during the long rainy season and 6 boreholes, *i.e.* 35.29%, during the long dry season. Dissolved oxygen (O2dis) levels vary from 17.78 to 44.90 mg/L with an average of 24.47 ± 7.36 mg/L during the long rainy season and from 20.90 to 61.60 mg/L with an average of 34.78 ± 10.71 mg/L during the long dry season. The physical parameter data (T, pH and O2dis) are homogeneous because (CV < 50%). Turbidity and EC data are scattered (CV > 50%). It emerges from this analysis that all the parameters present values generally lower than the WHO standards (2011) with the exception of Conductivity where values of 1404 and 1060 µS/cm respectively during the rainy and dry seasons. As for pH, all water resources have pH values below 8.5.

Chemical parameters

Table 2 presents the chemical parameters statistics of the study area. The chemical parameters taken into account in this study are the major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-) and the nutrient salts (NH_4^+, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, F^-).

The calcium ion (Ca^{2+}) contents vary from 12 mg/L (ESIA/G2) to 142.40 mg/L (GW6) with an average of 51.74 ± 30.82 mg/L during the long rainy season and 11.50 mg/L (ESIA/G2) to 138.50 mg/L (GW9) for an average of 48.15 ± 30 mg/L during the long dry season. Magnesium (Mg^{2+}) in groundwater in the Angovia gold mine operating license area has concentrations ranging from 7.17 mg/L

Table 2. Groundwater chemical parameters basic statistics in the Angovia mine operating permit area.

Parameter	Unit	Long rainy season					Long dry season					WHO standards (2011)
		Min	Max	Avg	σ	CV(%)	Min	Max	Moy	σ	CV(%)	
HCO_3^-	(mg/L)	66.50	495.17	278.46	137.68	49.44	68.52	476.57	258.83	120.68	46.62	-
SO_4^{2-}	(mg/L)	1.00	77.20	10.25	21.91	213.76	1.00	76.25	9.26	19.42	209.72	<250
Cl^-	(mg/L)	0.44	122.48	12.40	28.89	232.98	0.83	119.70	13.07	27.98	214.08	<250
NO_3^-	(mg/L)	0.06	330.88	22.36	79.94	357.51	0.11	318.37	22.33	76.69	343.44	≤50
NO_2^-	(mg/L)	0.05	0.48	0.08	0.10	125	0.05	0.44	0.08	0.09	112.5	≥3
PO_4^{3-}	(mg/L)	0.02	0.12	0.05	0.02	40	0.02	0.12	0.03	0.03	100	≤5
F^-	(mg/L)	0.10	0.40	0.14	0.09	64.28	0.12	0.14	0.08	0.07	87.50	<5
NH_4^+	(mg/L)	0.02	0.32	0.07	0.07	100	0.10	0.20	0.12	0.04	33.33	≤1.5
Ca^{2+}	(mg/L)	12.00	142.40	51.74	30.82	59.57	11.50	138.50	48.15	30.00	62.30	≤100
Mg^{2+}	(mg/L)	7.17	71.14	25.22	16.19	64.19	6.98	74.00	25.70	16.77	65.25	≤50
Na^+	(mg/L)	6.74	47.12	20.71	12.96	62.58	5.28	46.40	20.54	12.26	59.69	≤200
K^+	(mg/L)	0.28	2.68	0.88	0.66	75	0.28	4.88	1.07	1.14	106.54	≤12

Min: Minimum, **Max**: Maximum, **Avg**: Average, σ: Standard deviation, **CV**: Coefficient of Variation.

(ESIA/G2) to 71.14 mg/L (GW6) with an average of 25.22 ± 16.19 mg/L during the long rainy season. During the long dry season, its content varies from 6.98 mg/L (ESIA/G2) to 74 mg/L (GW9) with an average of 25.70 ± 16.77 mg/L. The concentration of sodium (Na+) in the Angovia mine operating permit area groundwater varies between 6.74 mg/L (ESIA/G3) and 47.12 mg/L (ESIA/G1) with an average of 20.71 ± 12.96 mg/L during the long rainy season and between 5.28 mg/L (ESIA/G2) and 46.40 mg/L (ESIA/G1) giving an average of 20, 54 ± 12.26 mg/L during the long dry season.

Trace metal elements in groundwater

Table 3 presents the statistics of metallic trace elements in the study area. The metallic trace elements considered in this study are As, Ba, B, Cr, Co, Cu, Fe, Mn, Ni, Sr, Pb, Zn and Al. Barium (Ba) contents in groundwater vary from 0.00 to 0.18 mg/L with an average of 0.03 ± 0.04 mg/L during the long rainy season and from 0.00 to 0.06 mg/L with an average of 0.02 ± 0.02 mg/L during the long dry season. Chromium (Cr) contents vary from 0.00 to 0.03 mg/L with an average of 0.01 ± 0.01 mg/L during the long rainy season and from 0.01 to 0.05 mg/L with an average of 0.01 ± 0.01 mg/L during the long dry season. Copper (Cu) contents are between 0.00 and 0.01 mg/L during the long rainy season and from 0.00 to 0.13 mg/L with an average of 0.01 ± 0.03 mg/L during the long dry season. Lead (Pb) contents vary from 0.00 to 0.33 mg/L with an average of 0.05 ± 0.09 mg/L during the long rainy season and from 0.00 to 0.17 mg/L presenting an average of 0.04 ± 0.05 mg/L during the long dry season. Manganese (Mn) contents vary from 0.00 to 1.64 mg/L, the estimated average is about 0.31 ± 0.46

Table 3. Trace metal elements in groundwater basic statistics of the Angovia mine operating permit area.

Parameter	Unit	Long rainy season					Long dry season					WHO standards (2011)
		Min	Max	Avg	σ	CV (%)	Min	Max	Avg	σ	CV (%)	
As	(mg/L)	0.00	0.01	0.00	0.00	-	0.00	0.10	0.01	0.02	200	0.01
Ba	(mg/L)	0.00	0.18	0.03	0.04	133.33	0.00	0.06	0.02	0.02	100	0.7
B	(mg/L)	0.02	0.56	0.06	0.13	216.67	0.02	0.21	0.04	0.06	150	0.7
Cr	(mg/L)	0.00	0.03	0.01	0.01	100	0.01	0.05	0.01	0.01	100	-
Co	(mg/L)	0.00	0.01	0.00	0.00	-	0.00	0.01	0.00	0.00	-	-
Cu	(mg/L)	0.00	0.01	0.00	0.00	-	0.00	0.13	0.01	0.03	300	2
Pb	(mg/L)	0.00	0.33	0.05	0.09	180	0.00	0.17	0.04	0.05	125	0.01
Mn	(mg/L)	0.00	1.64	0.31	0.46	148.39	0.01	1.59	0.25	0.38	152	<0.5
Ni	(mg/L)	0.00	0.03	0.01	0.01	100	0.00	0.06	0.01	0.01	100	0.07
Sr	(mg/L)	0.06	1.29	0.28	0.31	110.71	0.03	1.37	0.26	0.31	119.23	-
Zn	(mg/L)	0.02	0.92	0.13	0.21	161.54	0.01	10.61	0.67	2.56	382.09	3
Al	(mg/L)	0.03	4.03	0.47	0.95	202.13	0.03	19.95	1.87	4.90	262.03	0.2
Fe	(mg/L)	0.10	8.94	1.30	2.17	166.92	0.10	46.40	4.66	11.55	246.78	<0.3

Min: Minimum, **Max**: Maximum, **Avg**: Average, σ: Standard deviation, **CV**: Coefficient of Variation.

mg/L during the long rainy season. Manganese (Mn) contents vary from 0.01 to 1.59 mg/L too with an average of 0.25 ± 0.38 mg/L during the long dry season. Nickel (Ni) contents vary from 0.00 to 0.03 mg/L with an average of 0.01 ± 0.01 mg/L during the long rainy season and from 0.00 to 0.06 mg/L giving an average of 0.01 ± 0.01 mg/L over the long dry season. As for Iron (Fe) contents, they vary from 0.10 to 8.94 mg/L giving an average of 1.30 ± 2.17 mg/L during the great rainy season. Over the long dry season, they vary from 0.10 to 46.40 mg/L, with an average of 4.66 ± 11.55 mg/L. According to the results obtained, one notes that the iron contents values are very high (46.40 mg/L) in the ESIA/G5 borehole waters. Zinc (Zn) contents evolve from 0.02 to 0.92 mg/L screening an average of 0.13 ± 0.21 mg/L over the long rainy season and from 0.01 to 10.61 mg/L with an average of 0.67 ± 2.56 mg/L during the long dry season. Strontium (Sr) contents vary from 0.06 to 1.29 mg/L with an average of 0.28 ± 0.31 mg/L during the long rainy season and from 0.03 to 1.37 mg/L with an average of 0.26 ± 0.31 mg/L during the long dry season. The data for trace metal element contents are mostly scattered (CV > 50%). Analysis of the data in Table 3 shows that, like the chemical data, ETMs have contents generally lower than WHO standards with the exception of Fe, Pb and Al.

3.3. Multivariate Statistical Analysis of Groundwater

3.3.1. Kohonen Self-Organizing Maps (SOM)

The physicochemical parameters of the boreholes were processed using the Kohonen self-organizing map (S.O.M). Based on the quantification (QE) and topography (TE) errors (Table 4), a Kohonen map of 20 cells (5 rows × 4 columns) is chosen to project the 17 samples.

Table 4. Estimated quantification (QE) and topography (TE) errors of the different sizes of Kohonen maps (the matrix retained is in bold).

N	$5\sqrt{N}$	Possible matrix	QE	TE
17	21	**5 × 4**	**1.041**	**0.000**
		7 × 3	0.957	0.059
		6 × 3	1.011	0.059

Figure 3 presents the samples according to physicochemical parameters distribution during the two main seasons (rainy and dry) in each grouping it defined by the hierarchical classification analysis used. Drillings belonging to the same family have the same physicochemical parameters contents.

3.3.2. Mineralization of Groundwater in Contact with Geological Formations

Long rainy season

Figure 4 analysis revealed that family 1 waters are characterized by high values of dissolved oxygen, pH, temperature, PO_4^{3-}, HCO_3^- and Zn. It is noted that family 2 includes waters with a strong gradient of conductivity and pH, marked with Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, F^-, As, B, Mn, Sr and HCO_3^-. Family 3 includes waters marked with Ca^{2+}, Mg^{2+}, NH_4^+, Pb, Ba, Cr, Co, Cu, Mn, Ni, Al, Fe and HCO_3^-. Family 4 is characterized by waters marked with NH_4^+, PO_4^{3-}, As, Ba, Cr, Co, Cu, Pb, Mn, Ni and Zn.

The abundance of Ca^{2+}, Mg^{2+} and HCO_3^- in the waters of families 2 and 3 highlights a phenomenon of acid hydrolysis linked to water-rock contact. The presence of NO_3^- and NO_2^- in the waters of family 2 shows a supply of nutrient salts in the environment, just like families 1 and 4 marked by high PO_4^{3-} contents.

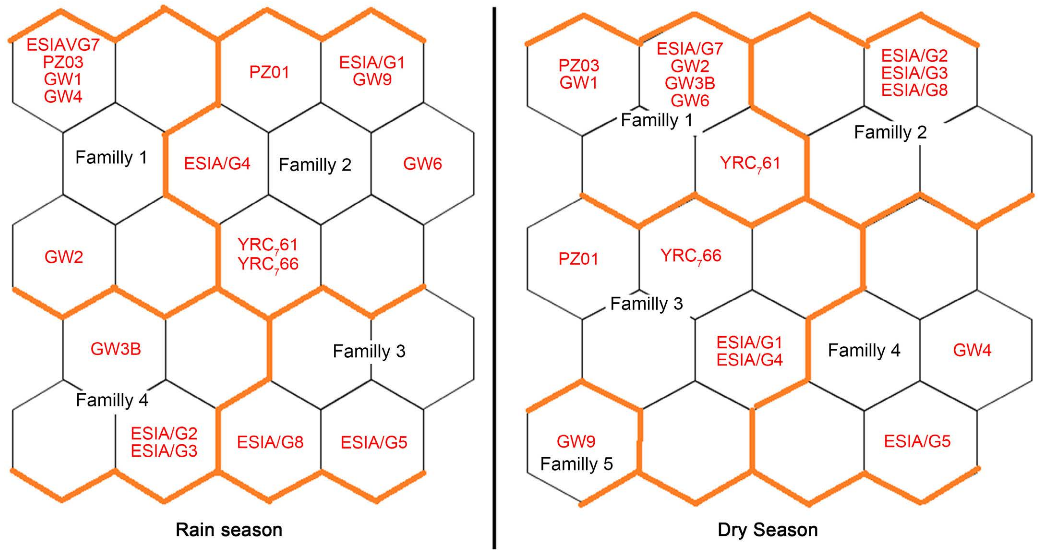
Long dry season

The analysis of Figure 5 shown that the waters of family 1 are characterized by high values of temperature, pH, Na^+, HCO_3^- and Ba. We see that family 2 includes waters marked with NH_4^+, F^-, Ba and Pb. Family 3 includes waters marked with Ca^{2+}, Mg^{2+}, Na^+, K^+, PO_4^{3-}, F^-, HCO_3^-, Ba, B and Pb Family 4 is characterized by waters marked with Fe, Al, Sr, Ni, Cr, Co, Cu, As, HCO_3^-, PO_4^{3-}, B and Na^+. We see that family 5 includes waters marked with Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, HCO_3^-, Co and Mn. The abundance of Ca^{2+}, Mg^{2+} and HCO_3^- in family 3 and 5 waters highlights a phenomenon of acid hydrolysis linked to water-rock contact. For the waters of family 5, the high gradients of EC, NO_3^- and NO_2^- obtained show a supply of nutrient salts in the environment, just like family 3 marked by high PO_4^{3-} contents.

3.3.3. Spatial Distribution of Kohonen Families in the Study Area

Long rainy season

Family 2 waters are the most widespread in the study area (Figure 6). The waters of families 1 and 3 are less distributed and are found more in the center of the study area. The drillings of family 4 are grouped together in the center of the Angovia mine operating permit zone.



(a) (b)

Figure 3. Distribution of samples on the Kohonen map (Rainy season (a) and long dry season (b)).

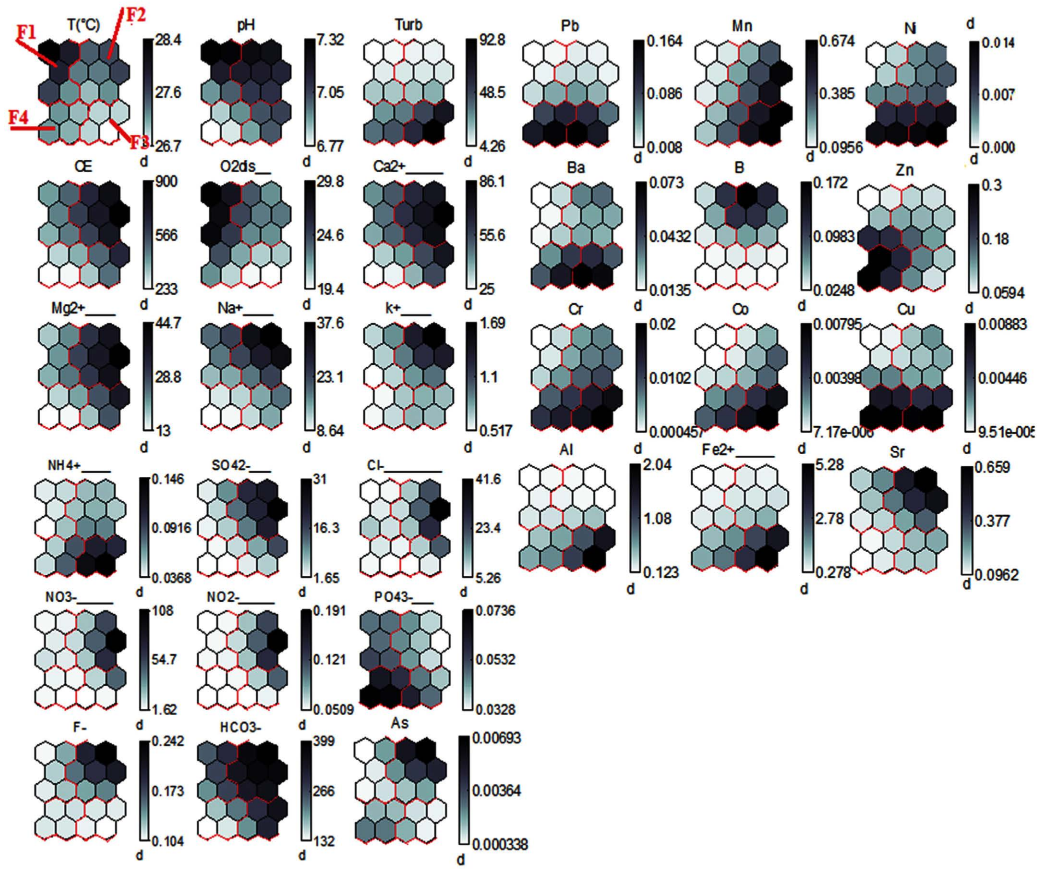


Figure 4. Gradient value of each parameter on the Kohonen map over the long rain season.

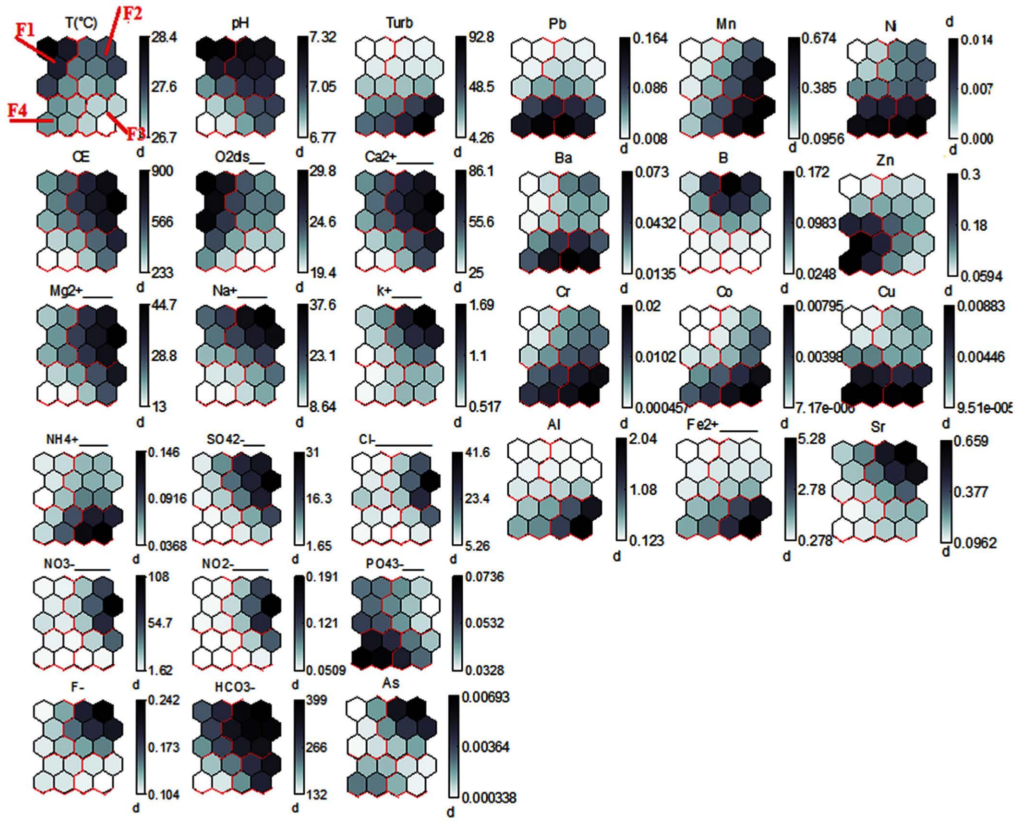
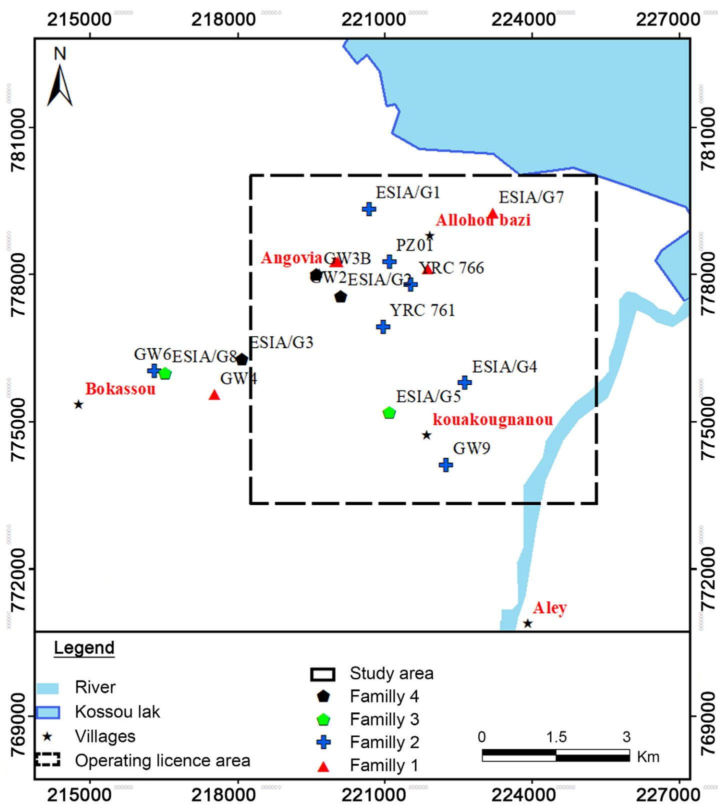
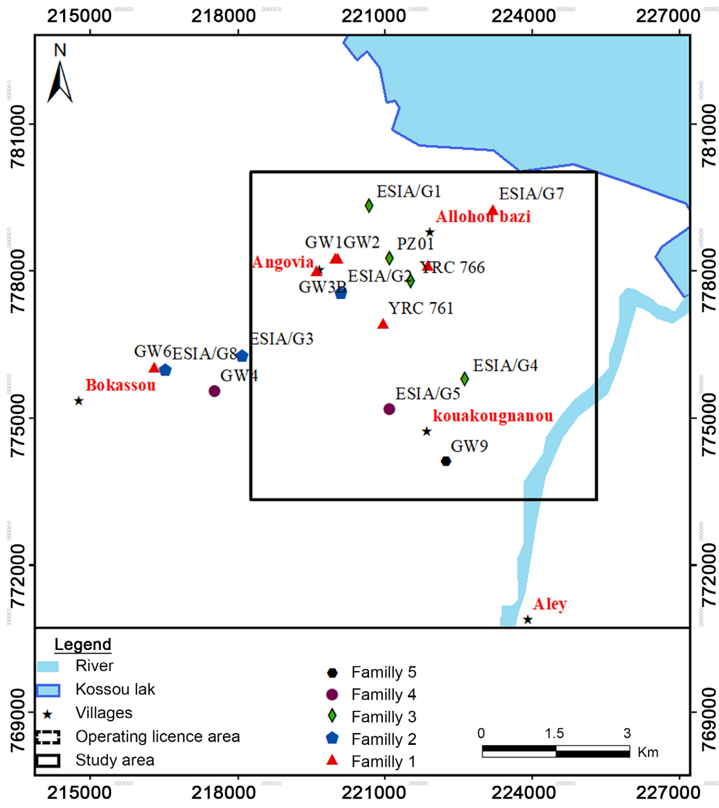


Figure 5. Gradient value of each parameter on the Kohonen map over the long dry season.



(a)



(b)

Figure 6. Spatial distribution of the main groundwater families in the study area during: (a) (long rainy season); (b) (long dry season).

Long dry season

Family 1 waters are also the most widespread in the study area (**Figure 8**). The waters of family 2 are found more in the center of the study area. The waters of family 3 are less distributed and are found in the center and east of the study area. The drillings of family 4 are grouped together in the center of the Angovia mine operating permit zone. Finally, water from family 5 is found further south of the study area.

3.4. Relative Age of Groundwater in the Study Area

The ISD versus ISC diagram of the long rainy season (**Figure 7**) shows that 47.06% of the waters analyzed present under-saturation state, both with respect to calcite (ISC < 0) and dolomite (ISD < 0). As for the long dry season ISD function of ISC diagram (**Figure 8**), it shows that 41.18% of the waters analyzed present under-saturation state, both with respect to calcite (ISC < 0) and dolomite (ISD < 0).

Long rainy season

The representative points of the groundwater samples generally align along a regression line whose equation is: ISD = 1.945 * ISC + 0.0358.

The distribution of ISD values makes it possible to distinguish three (03) groups:

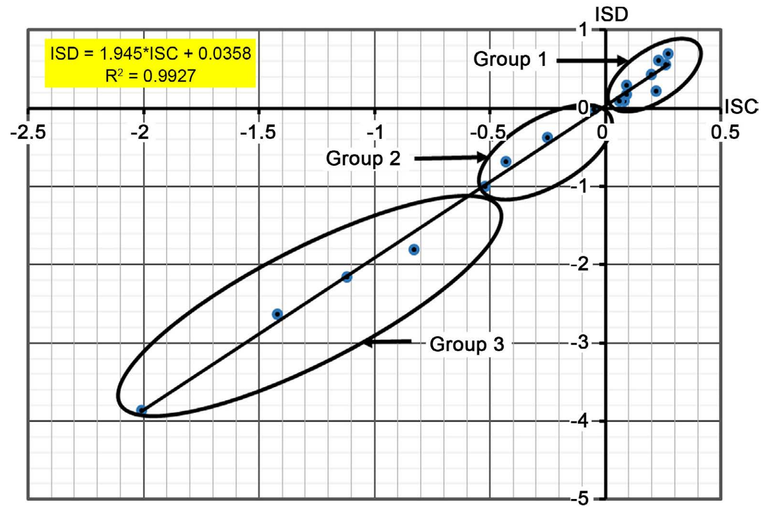


Figure 7. ISD = f (ISC) diagram of groundwater during the long rainy season in the Angovia mine operating permit area.

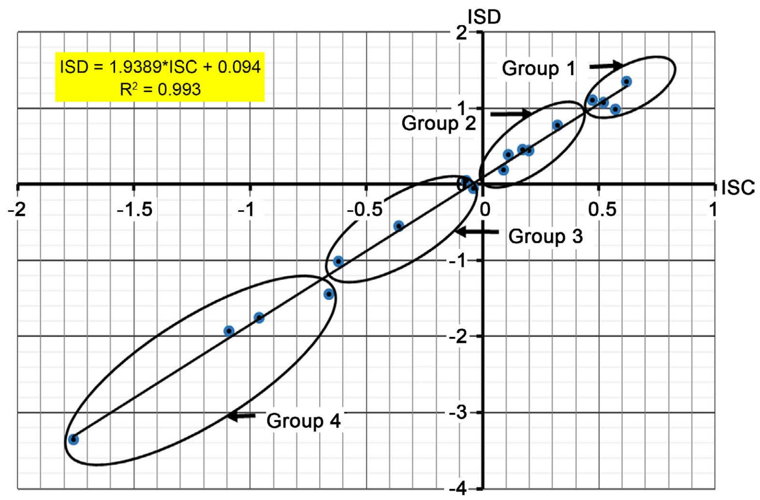


Figure 8. ISD = f (ISC) diagram of groundwater during the long dry season in the Angovia mine operating permit area.

- Group 1 (0 ≤ ISD < 1): These waters represent 52.94% of the samples (ESIA/G7, PZ01, ESIA/G5, PZ03, GW4, ESIA/G4, YRC 766, GW9, and ESIA/G1). Group 1 groundwater is saturated with respect to dolomite and calcite. These are very old waters in the aquifer with a long residence time and slow circulation speed.

- Group 2 (−1 < ISD < 0): this group (GW3B, GW1, YRC 761 and GW6) represents under saturated waters with respect to calcite and dolomite (23.53% of sampled boreholes). These waters are old in the aquifer with an average residence time and average circulation speed.

- Group 3 (−4 < ISD < −1): this group (ESIA/G2, GW2, ESIA/G3, and ESIA/G8) represents waters under saturated with respect to calcite and dolomite. It also represents 23.53% of drilling. These waters are recent in the aquifer with a rapid circulation speed.

Long dry season

The representative points of the groundwater samples are generally aligned along a regression line whose equation is: ISD = 1.9389 × ISC + 0.094.

The distribution of ISD values distinguishes four (04) groups:

- Group 1 (SDI ≥ 1): Group 1 groundwater (PZ03, YRC 766, ESIA/G1 and ESIA/G4) are supersaturated with respect to dolomite and calcite and calcite (23.53% of boreholes sampled). This water is very aquifer with a very long residence time and a very slow circulation rate.

- Group 2 (0 < ISD < 1): this group (GW1, ESIA/G7, YRC 761, PZ01, ESIA/G5 and GW9) represents water saturated with respect to calcite and dolomite (35.29% of boreholes sampled). These waters are old, with a long residence time and slow circulation speed.

- Group 3 (−1 < ISD < 0): this group (GW2, GW4 and GW6) represents water that is undersaturated with respect to calcite and dolomite. It also represents 17.65% of the boreholes. These waters are old and have had an average residence time in the aquifer with an average circulation velocity.

- Group 4 (ISD < −1): this group (ESIA/G2, GW3B, ESIA/G3, and ESIA/G8) represents water that is undersaturated with respect to calcite and dolomite. It also represents 23.53% of the boreholes. These waters are recent and have had a short residence time in the aquifer with a high circulation velocity.

4. Discussion

The groundwater resources at the Angovia gold mine operating permit site hydrogeochemical characterization showed that groundwater is less sensitive to temperature variations than surface water with generally neutral pH. As for the slightly acidic values obtained, it could be attributed to the acidic character of the volcanic rocks encountered in the area. These are similar to those obtained by [2] [15] and [16] respectively in the Bondoukou, Tiassalé and N'zi-Comoé regions, which highlighted the acidic nature of the waters of Côte d'Ivoire's base aquifers. The waters of the study area are moderately mineralized with an average EC of 505.98 ± 302.85 µS/cm over all seasons. The high mineralization values that were observed during rainy seasons are probably due to rainwater intrusion. Indeed, electrical conductivity is influenced by various natural and anthropogenic factors including geology (the composition of rocks), groundwater inputs and surface inputs from anthropogenic activities. In fact, contaminated discharges also increase the electrical conductivity of water.

Overall, the chemical parameters (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^+, Cl^-, NO_2^-, NO_3^-, F^-, PO_4^{3-}, SO_4^{2-}, HCO_3^-) of the groundwater in the permit area operation of the Angovia mine complies with the recommendations World Health Organization standards. The high nitrate levels observed could come from ammonium nitrates contained in explosives used for rock blasting. Thus the concentrations of nitrates encountered in certain boreholes and wells can cause methemoglobinemia in infants and carcinogenic diseases in adults [17]. The presence of metallic trace elements such as chromium (Cr), cobalt (Co), copper (Cu), strontium (Sr), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn), boron (B) and arsenic (As) in water primarily represent an organoleptic (metallic taste) and aesthetic (color) nuisance. This nuisance can be felt by consumers at the average concentration of iron (1.30 ± 2.17 mg/L during the long rainy season and 4.66 ± 11.55 mg/L during the long dry season) and at the average concentration of manganese (0.31 ± 0.46 mg/L during the main rainy season and 0.25 ± 0.38 mg/L during the main dry season). An overload of the human body with iron can lead to primary hemochromatosis (poor regulation of iron absorption by the intestine) and even hepatic cancer (risk of liver cancer). Manganese can also cause irreversible neurological disorders because of its antagonism towards calcium. Iron and manganese give water an unpleasant taste, red-brown and black-brown appearance and color. This situation forces rural populations to turn to other sources of supply. These disorders generally occur when iron and manganese concentrations are greater than 10 mg/L and 2 mg/L, respectively [18].

Analysis using the SOM method shows us that the different families contain highly mineralized waters. They are especially characterized by high contents of HCO_3^-, Mg^{2+} and Ca^{2+}. The observation of these minerals in water would indicate dissolution phenomena by the mechanisms of acid hydrolysis of silicate minerals. Indeed, the studies carried out by [19] showed that in a carbonate environment, the simultaneous enrichment in Ca^{2+} and depletion in Mg^{2+} is mainly explained by the phenomenon of water-rock interaction. Family 3 is characterized by weakly mineralized waters marked by Fe, Mn, HCO_3^-, NO_3^-, NH_4^+ and O_2dis ions. The marking of this group by these ions shows that the mineralization of these waters is not only linked to the rock hydrolysis phenomenon of minerals but also to the phenomenon of oxidation-reduction mentioned by [20]. The presence of iron and manganese in the waters could also be attributed to the nature of the geological formations in the region as reported by [21] in the Baya watershed and [22] working on the groundwater of Martinique.

The presence of NO_2^-, NO_3^-, PO_4^{3-} and heavy metals would indicate pollution linked to anthropogenic activities in the process of water mineralization. This could be justified by the use of fertilizers during agricultural activities as highlighted by [23]. Indeed, nitrate ions resulting from the decomposition of organic waste infiltrate the groundwater and contaminate groundwater. These results corroborate those of [24].

The analysis of the ISD versus ISC graphs shows that the groundwater is under saturated at 89.58% and saturated at 10.42% with respect to the calcite dolomite. These waters are generally old in the aquifer.

5. Conclusions

The hydro geochemical study of groundwater in the Angovia mine operating permit area made it possible to characterize the physicochemical quality of groundwater in the study area. Physico-chemical analyzes showed that the groundwater in the study area is generally of good quality because the contents obtained are mostly below the WHO drinking water standard. However, the high NO_3^- levels could be attributed to the use of ammonium nitrate-rich explosives for rock blasting. The metallic trace elements found in drilling water have very low levels. The hydro geochemical characterization made it possible to show that the different processes responsible for the groundwater chemistry acquisition in the study area are: mineralization-residence time of water, oxidation-reduction, surface input and degradation and anthropogenic impact upon water quality.

The water relative age study showed that the groundwater in the Angovia mine operating permit area is mainly under saturated with respect to calcite and dolomite. They are very old with a long residence time and slow circulation speed during the two major seasons.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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