

ASSESSMENT OF GROUNDWATER QUALITY DURING DRY SEASON IN SOUTHEASTERN BRAZZAVILLE, CONGO

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ABSTRACT: Groundwater samples collected from southeastern Brazzaville, Congo, during July 2008 (dry season) were analyzed for pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), sodium (Na^+), Potassium (K^+), Chloride (Cl^-), Sulfate (SO_4^{2-}), Bicarbonate (HCO_3^-), Fluoride (F^-) and Nitrate (NO_3^-) using standard procedures (APHA, 1985). The results revealed that all the groundwater samples were below the limits, accordingly to the WHO standards (2004). Except pH of the samples were below the limit (6.5 to 8.5). EC of all the samples were below $300\mu\text{S}/\text{cm}$. A comparison of the groundwater quality in relation to drinking water quality standards revealed that pH is the disqualifying parameter. The correlation studies and R-mode factor analysis were carried out on the hydrochemical data set. Factor analysis has revealed the factors controlling the hydrochemistry of the groundwater. Four principal factors were extracted by using Kaiser normalization: (1) dissolution of magnesium bearing minerals; (2) mineralization; (3) dissolution of calcium-bearing minerals (silicate and carbonate); (4) impact of domestic waste water and septic tank.

Keywords: Groundwater, hydrochemistry, factor analysis, hierarchical cluster analysis

INTRODUCTION

Suitability of groundwater for drinking, irrigation and industrial purposes depends upon its quality. Changes in groundwater quality are due to variation in climatic conditions, residence time of water with aquifer materials and inputs from soil during percolation of water (Mitra et al., 2007; Krishna Kumar et al., 2008). Application of uncontrolled fertilizers and manure is one of the main sources of groundwater pollution, especially in developing countries, like Brazzaville, where domestic sewage contributes pollutants to groundwater. Understanding the groundwater characteristics is important for groundwater management in the study area. Many hydrogeochemical processes have been highlighted in the control of the chemical composition of groundwater, like carbonates and silicates weathering, ion exchange (Giridharan et al., 2008; Subba Rao, 2008). In this study, an attempt is made to assess the quality of the groundwater in dry season for drinking purpose and to examine the controlling factors of hydrogeochemical processes for taking management measures for sustainable development. For this, factor analysis was used to highlight the controlling factors (Reeve et al., 1996).

MATERIALS AND METHODS

Study area

The study area is located between 15°13'53" to 15°14'10" East and longitude and 4°15'7.2" to 4°15'28.8" South latitude (Figure 1). The area is in the equatorial climate zone, with two seasons of rainy (October to May) and dry (June to September). Temperature varies from 25°C to 36°C in rainy season, while it is between 18°C and 24°C in dry season. The mean annual rainfall is 147 mm. The vegetation is of savanna type (*Loutetia demeusi*) and presents a formation to sparse gramineous carpet, with a shrubby layer of *hymenocardia acida*. The soils are of type ferralitic, which have been derived from Tertiary Silicate. Aquifer is shallow. Generally, the deep wells do not exceed 2 m depth. The main natural recharge to groundwater is from precipitation (rainfall). Farming activities are present around some well water sites and also agricultural activities near the River Mfilou. The southeastern Brazzaville is made of sedimentary deposits with recent alluvium formations covering the bed rock. The formation of Inkisi is classically joined to the schisto-sandy group.

Sample collection and analysis

Twenty one samples of wells water and one sample of spring water were collected in three times in dry season (July 2008) from the study area (Figure 1). The samples were analyzed for different parameters as pH, EC, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , F^- and NO_3^- following standards methods of APHA (1995). Before water sampling, all the polyethylene bottles were cleaned and rinsed thoroughly with water to be analyzed. All reagents used were of analytical grade. Samples were unfiltered and the concentration of the different parameters could correspond to the total concentration if the groundwater was used by the consumers for drinking. Hydrogen ion concentration (pH), Electrical Conductivity (EC), Total Dissolved solids (TDS) were measured on-site using Consort C933 multi-parameters portable. The groundwater samples were stored at 1-4°C temperature prior to analysis in the laboratory. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) were analyzed titrimetrically using standard EDTA, Sodium (Na^+) and Potassium (K^+) were determined by flame photometer, Chloride (Cl^-) was determined using standard AgNO_3 titration, Sulphate (SO_4^{2-}) was analyzed by nephelometric method, Bicarbonate (HCO_3^-) was estimated titrimetrically from total alkalinity using HCl, Fluoride (F^-) and nitrate (NO_3^-) were determined by spectrophotometry. The Statistica (Statsoft) computer program was used to perform all statistical analysis.

RESULTS AND DISCUSSION

Water chemistry

The chemical composition of the groundwater samples collected in the study area during dry season is presented in Table 1. The results revealed that pH ranged from 3.40 to 6.37. Minimum pH was observed from the spring water sample S. Figure 1 shows the percentage of observations (groundwater samples) versus pH. A percentage of 9% of the all groundwater samples has a pH value between 3-3.5 (Figure 2). These waters were more acidic. The groundwater samples of the other wells were slightly acidic with a range of 3.58-6.37. All groundwater samples were found to be below the WHO (2004) limit of pH, with a mean of 4.64 and acidic in nature. The numerical expression of ability of an aqueous solution to carry electric current is EC. The values of EC ranged from 53.58 to 283.20 $\mu\text{S}/\text{cm}$, with a mean of 169.07 $\mu\text{S}/\text{cm}$. The percentage of groundwater samples related to EC (Figure 3) shows that low values of EC (<100 $\mu\text{S}/\text{cm}$) were observed in 13.6% (S, P2 and P9) of all the groundwater samples. TDS varied from 33.92 to 150.20 mg/L, with a mean of 89.76 mg/L. The concentration (mg/L) of individual ions varied as Ca^{2+} from 8 to 32; Mg^{2+} 3 to 15; Na^+ 0.13 to 25.08; K^+ 2.5 to 10.1; Cl^- 2 to 42; SO_4^{2-} to 12; HCO_3^- 10.98 to 86.62; F^- 0.18 to 1.16 and NO_3^- 0.55 to 2.47. The groundwater samples have low levels of potassium. This is due to the tendency of potassium to be fixed by clay minerals and to participate in the formation of secondary minerals (Mathess, 1982). Individual ions as Na^+ , K^+ , Cl^- , HCO_3^- and F^- exhibited difference of the coefficients of variance higher than 40%. The content relative of a cation or anion is defined as the percentage of the milliequivalent per liters (meq/L) of the total cations or the total anions (Sen and Al-Dakheel, 1986). Pie diagram of median concentration of cations and anions in percentage of milliequivalents are plotted (Figure 4).

Table -1 : Chemical composition of groundwater in dry season

Code	pH	EC	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	F ⁻	NO ₃ ⁻
S	3.40	83.98	44.72	13	11	13.37	2.5	8	5	37.82	0.36	0.55
P1	3.49	283.20	150.20	16	13	2.68	8.7	19	6	69.54	0.50	1.25
P2	3.58	63.86	33.92	11	15	3.32	4.3	14	4	68.32	0.29	0.97
P3	3.60	144.00	76.36	10	8	1.06	3	10	6	46.36	0.18	1.07
P4	4.88	147.54	78.50	15	11	18.73	4	12	7	23.18	0.40	1.00
P6	4.04	186.60	99.18	17	10	20.09	11	17	11	17.08	0.49	2.47
P8	3.81	190.48	101.16	31	15	24.68	6.2	2	12	85.40	0.25	1.20
P9	4.85	53.58	28.50	14	12	16.71	5.6	10	11	30.50	0.33	1.00
P10	4.09	176.96	93.82	8	9	7.68	8	12	7	26.84	0.48	1.50
P11	4.06	151.72	80.58	32	12	15.70	4.5	6	12	86.62	0.39	0.96
P12	4.52	200.72	106.28	20	9	25.08	10.1	3	8	35.38	0.51	1.14
P13	4.83	180.46	95.92	12	9	1.73	4.1	10	8	48.80	1.16	1.27
P14	4.89	164.32	87.12	20	10	8.55	7	7	9	67.10	0.30	2.00
P15	4.29	182.40	96.96	16	8	0.13	5.4	6	10	65.88	0.29	2.06
P16	3.78	195.26	103.48	16	5	17.16	5	4	11	12.20	0.27	2.20
P17	4.85	164.82	87.56	15	6	21.41	5	2	10	8.54	0.3	2.01
P19	5.82	183.12	97.12	14	3	14.74	4	1	5	14.64	0.11	2.20
P21	5.27	167.82	89.14	13	7	2.97	4	25	9	12.20	0.28	0.87
P22	5.43	226.6	119.80	16	5	6.72	4	20	7	13.42	0.4	1.00
P23	6.24	197.16	105.14	16	7	9.04	3.2	20	8	14.64	0.15	1.40
P24	5.94	180.48	95.70	20	9	3.78	5	42	9	10.98	0.15	0.96
P27	6.37	194.46	103.50	19	6	11.21	5.1	20	7	17.08	0.16	0.97
Mean	4.64	169.07	89.76	16.55	9.09	11.21	5.44	12.27	8.27	36.93	0.35	1.37
S.D	0.89	49.54	26.25	5.65	3.10	7.79	2.19	9.36	2.28	25.42	0.21	0.53
C.V (%)	19.20	29.30	29.24	34.13	34.13	69.48	40.23	76.28	27.56	68.83	60.00	38.46
WHO (mg/L)	6.5-8.5	300	500	75	50	200	20	200	200	250	1.5	50

Except pH and EC ($\mu\text{S}/\text{cm}$), the others parameters are expressed in mg/L.

The concentration of earth alkalis elements (Ca and Mg) represents less than 15% of the total cations, which show a low rock/water interaction. No cation exceeded 50% of the total cation in all the groundwater samples. The order of the relative abundance of major cations in the groundwater was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^{+} > \text{K}^{+}$, while that of the anion was $\text{HCO}_3^{-} > \text{Cl}^{-} > \text{SO}_4^{2-}$ with HCO_3^{-} the dominant anion. The availability of carbonate minerals in the recharge areas and silicate weathering are the main factors, which led to the increase of carbonate and bicarbonate concentration in the groundwater (Elango et al., 2003).

Taking in account the median values in percentage of major cations and anions, the following hydrochemical facies identified the groundwater: Ca-Mg-HCO₃. Some groundwater samples were enriched with Cl⁻ ions (27.27%) and Na⁺ ions (13.63%).

Figure 1 : Location of the sites water in the study area (S: spring water, P: well water)

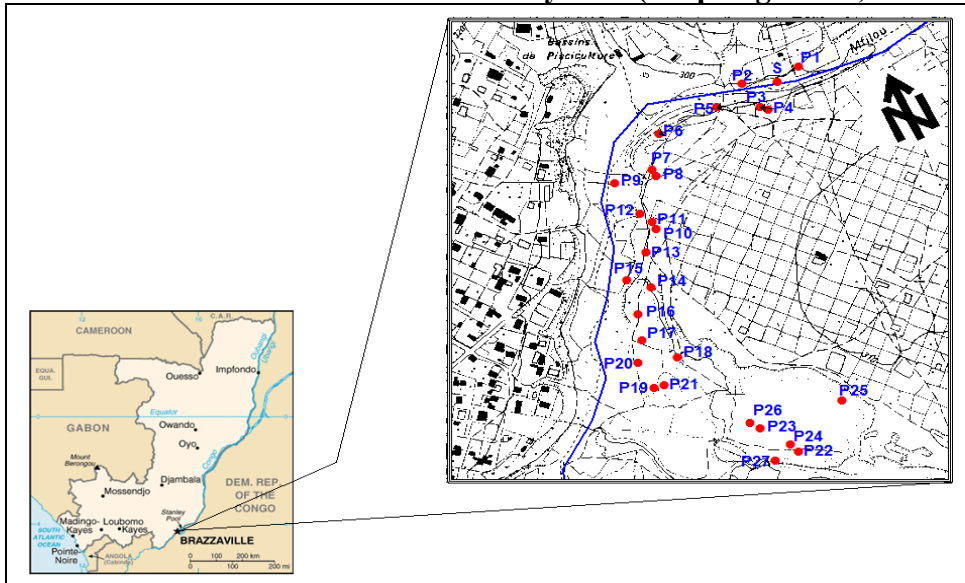


Figure 2 : Percentage of observations (groundwater samples) related to pH

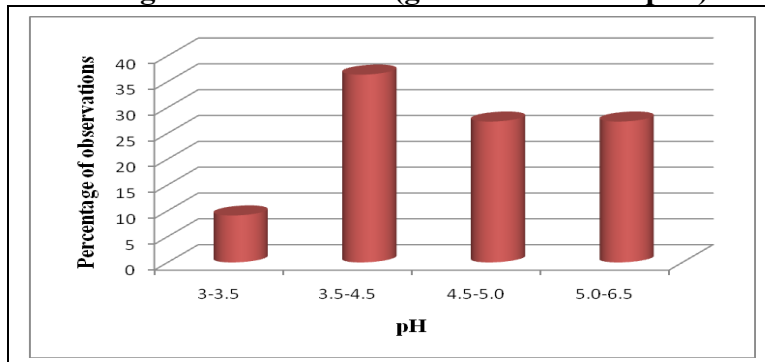


Figure 3 : Percentage of observations (groundwater samples) related to EC

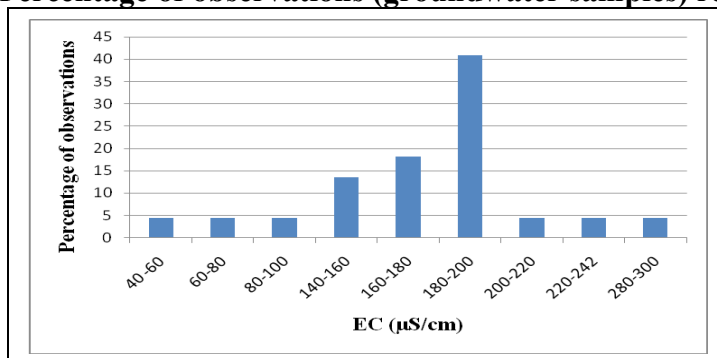
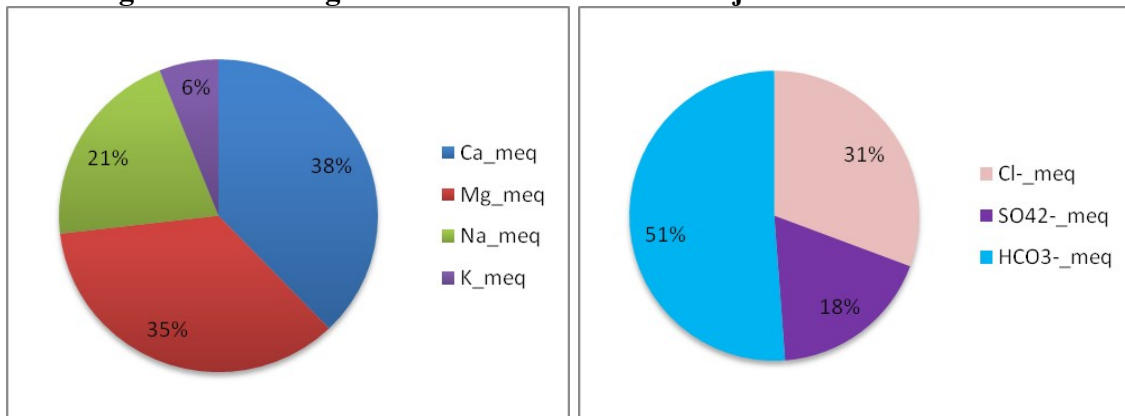
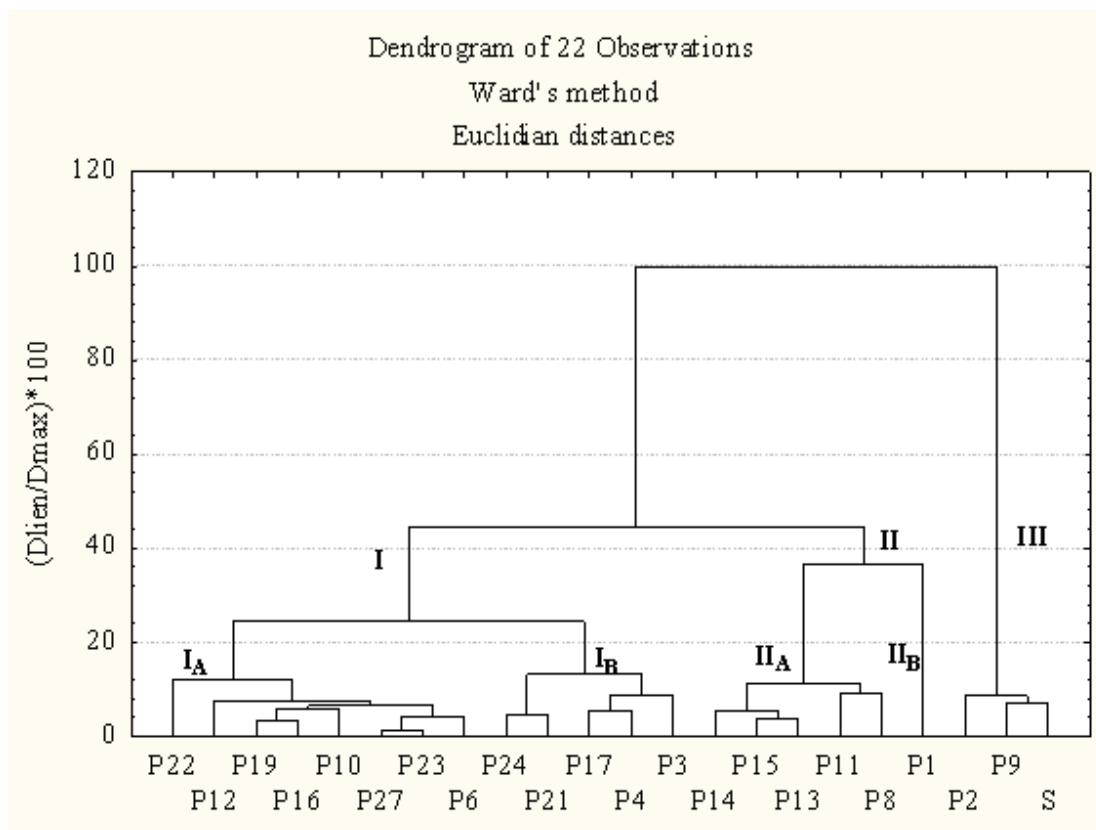


Figure 4 : Pie diagrams of median values of major cations and anions



The simultaneous enrichment with Na⁺ and Cl⁻ was observed in 18.18% of the total groundwater samples. The groundwater samples with high percentage of sodium and chloride would indicate that complex hydrochemical processes occur in the groundwater, such as cation exchange process, anthropogenic activity (domestic waste water).

Figure 5 : Hierarchical classification of water sites



Statistical analysis

The correlation coefficient matrix between the examined parameters, which was calculated using linear regression analysis, as illustrated in Table 2. Samples showing $r > 0.7$ are considered to be strongly correlated whereas r between 0.5 and 0.7, and $r < 0.5$ show moderate correlation and low correlation, at a significance level of $p < 0.05$, respectively. Table 2 shows perfect correlation between EC and TDS, which indicates that EC is a measure of dissolved solids in the groundwater. Moderate correlation ($r = 0.61$) between Ca^{2+} and SO_4^{2-} highlight the contribution of evaporitic salt CaSO_4 . The oxidation of in situ pyrite and the reaction of sulfuric acid with carbonate under evaporative condition could be the processes operative in the formation of the gypsum deposits (Cole and Vorster, 1999). Sulfate ions would proceed from the oxidation of pyrite FeS_2 (Banton and Bangoy, 1997) as shown below:

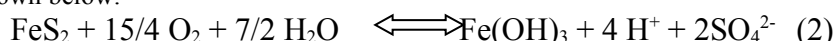


Table – 2 : Linear correlation of the different hydrochemical parameters of the area

	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
pH	1.00											
EC	0.20	1.00										
TDS	0.20	1.00	1.00									
Ca^{2+}	0.02	0.22	0.22	1.00								
Mg^{2+}	-0.58	-0.35	-0.35	0.30	1.00							
Na^+	-0.06	-0.07	-0.07	0.46	0.07	1.00						
K^+	-0.23	0.38	0.38	0.17	0.23	0.33	1.00					
Cl^-	0.43	0.17	0.17	-0.12	-0.02	-0.49	-0.05	1.00				
SO_4^{2-}	-0.02	0.08	0.09	0.61	0.09	0.42	0.28	-0.13	1.00			
HCO_3^-	-0.57	-0.09	-0.09	0.46	0.72	-0.12	0.11	-0.35	0.11	1.00		
F^-	-0.25	0.12	0.12	-0.15	0.20	-0.09	0.24	-0.13	0.02	0.19	1.00	
NO_3^-	-0.01	0.30	0.30	-0.05	-0.39	0.19	0.40	-0.36	0.31	-0.15	-0.05	1.00

* Significant at $p < 0.05$ (two Tailed)

This reaction would explain also the acidic nature of the groundwater.

The ions Ca^{2+} have a low positive correlation ($r = 0.46$) with HCO_3^- . The correlation is strong ($r = 0.72$) between Mg^{2+} and HCO_3^- , that would suppose a more significant water/rock interaction with Mg-bearing minerals. The major exchangeable ions Na-Ca correlate positively ($r = 0.46$) and Na-Mg shown no significant correlation ($r = 0.07$). Here, the possible negative correlation brought about by cation exchange dependencies is not evident. The pH is negatively correlated with Mg^{2+} ($r = -0.58$) and HCO_3^- ($r = -0.57$). The decay of soil organic matter increases the partial pressure of carbon dioxide ($p\text{CO}_2$) in the infiltrating water. Subsequently, an increase in $p\text{CO}_2$ causes a drop in pH (Adams et al., 2001).

Cluster analysis is an exploratory method which encompasses a number of different methods which organize not only observations, but also variables into groups called clusters. Observations within the clusters are similar whereas observations in different clusters are dissimilar. The data structure is arranged into a tree diagram, usually called a dendrogram. The utilized methods, algorithms, and similarity/dissimilarity measures are described elsewhere in the literature (Everitt, 2001). In this study, the Ward's clustering method and Euclidean distance were used. The dendrogram generated is given at Figure 5. Based on the results of cluster analysis and locations of the sampling sites, it is concluded that:

Cluster 1 (P3, P4, P6, P10, P12, P16, P17, P19, P21, P22, P23, P24 and P27): sites from the upstream and downstream of the Mfilou River are included in this cluster. These sites predominantly located in the most urbanized part of the basin.

Cluster II (P1, P8, P11, P13, P14 and P15): These sites are located in the least urbanized part of the basin.

Cluster III (S, P2 and P9): These sites are located nearby the Mfilou River.

Factor analysis has proved useful as an aid in the interpretation of geohydrological data (Schot and Van der Wal, 1992). Factor analysis is a multivariate statistical method, yields the general relationship between the measured chemical variables by showing multivariate patterns that may be help to classify the original data.

The first step was to standardize the raw data. The mean and variance of each variable are zero and one, respectively. This procedure eliminates the influence of different units of measurement, and makes the data dimensionless. The number of factors extracted was determined by applying the criterion proposed by Kaiser (1958). The second step was the use of R-mode factor analysis to find the main factors or processes responsible for the groundwater chemistry in the study area. Four factors account for 75.52% of the variance in the data set (Table 3).

Table -3 : Eigen values and factor loadings

Rotated Component Matrix				
Variable	Component			
	F 1	F 2	F 3	F 4
pH	-0.78	0.11	0.12	0.34
EC	-0.15	0.95	0.07	0.06
TDS	-0.15	0.95	0.07	0.06
Ca ²⁺	0.21	0.17	0.91	0.13
Mg ²⁺	0.85	-0.23	0.22	0.20
Na ⁺	-0.07	-0.12	0.64	-0.54
K ⁺	0.30	0.56	0.19	-0.37
Cl ⁻	-0.26	0.20	-0.12	0.78
SO ₄ ²⁻	0.03	0.14	0.75	-0.24
HCO ₃ ⁻	0.86	-0.02	0.22	0.08
F	0.48	0.30	-0.34	-0.16
NO ₃ ⁻	-0.24	0.37	0.04	-0.73
Eigen values	2.97	2.80	1.78	1.51
% Variance	24.73	23.36	14.87	12.56
Cumulative %	24.73	48.09	62.96	75.52

Absolute loading values > 0.70

The values of factor loading higher than 0.7. The hydrochemical aspects of the groundwater are given by the four factors. Factor 1 (F1) accounted for 24.73% of the total variance was characterized by the association of Mg²⁺, HCO₃⁻ and pH. Factor 1 is possibly the result of the water-rock interaction, interpreted as relating to the weathering of magnesium minerals. The negative factor loading of pH on F1 shows that a decrease of pH emphasizes the weathering process. Factor 2 (F2) accounted for 23.36% of the total variance, characterizes the mineralization of the groundwater in the study area, which is low. Factor 3 (F3) which explains 14.87% of the total variance shows the relationship between Ca²⁺ and SO₄²⁻. It is indicative of gypsum dissolution. Factor 4 (F4) account for 14.87% of the total variance and was characterized by the association of Cl⁻ and NO₃⁻. Factor 4 might be indicative of anthropogenic activities such as domestic waste water in the study area. The two main contributors for changing the geochemical composition of the groundwater are weathering processes and anthropogenic inputs (Chan, 2001).

CONCLUSION

Except pH values, all the others parameters of the groundwater quality are within the WHO (2004) limits for drinking purpose. The acidic nature of the groundwater and the concentrations of HCO₃⁻ are the results of the reaction of soil CO₂ with the dissolution of carbonates and silicate minerals.

The poor correlation of the ions Ca^{2+} , Na^+ , K^+ , SO_4^{2-} and F^- with pH reflects that the decreasing in the pH has no significant effect over the groundwater composition. Cluster analysis concluded that sites sampling can be grouped in three clusters of which the sites of cluster I and cluster II are under anthropogenic effects. The sites sampling of cluster III are under the influence of the Mfilou River. Results of the factor analysis revealed that 12 quality variables can be grouped under four factors namely: water-rock interaction, mineralization, gypsum dissolution and domestic waste water.

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