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Multivariate Statistical Analysis for the Assessment of Hydrogeochemistry of Groundwater in Upper Kambo Watershed (Douala-Cameroon)

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Abstract

The determination of the processes responsible for the mineralization of groundwater requires a large number of samples and physicochemical data, the treatment of which proves to be tedious. Many statistical methods are developed to facilitate the treatment of a certain volume of data. In this study, multivariate statistical analysis including principal components analysis (PCA) and hierarchical cluster analysis (HCA) have been applied on the groundwater physicochemical data of the upper Kambo watershed. The aim is to simplify the data in order to evaluate the relationships between the parameters and also to detect the factors that influence the water chemistry. For the PCA, three factors were retained representing 70% of the total inertia. Factor 1 shows the heterogeneity of sources of acquisition of the mineralization by the positive correlation with all the variables. Factor 2 indicates the dissolution of carbonates and anthropogenic input. Factor 3 highlights the silicate, anthropogenic and atmospheric or marine origin. The HCA enables to differentiate 4 groups of water according to the degree of mineralization. Groups 1 and 2 represent the most mineralized waters, dominated by calcium. The poor mineralized waters are groups 3 and 4 with the rather close contents in calcium and sodium.

Keywords

Principal Component Analysis, Cluster Analysis, Groundwater, Upper Kambo Watershed, Douala

1. Introduction

Groundwater is one of the major water resources. If for a certain part of the world, such as the arid zones, this resource represents a rare commodity [1], it is nevertheless available in significant amount in equatorial zone [2]. Groundwater is widely used for irrigation, industrial activities, drinking water and domestic needs based on bacteriological and chemical composition [3]. Several factors influence water chemistry including water-rock interaction, water dynamics, aquifer lithology, anthropogenic activity [4] [5] [6] [7]. This field of research increasingly interests more researchers because of the importance of water in human activities. In Douala, groundwater has already been the subject of several studies focusing on quality assessment [8] [9] [10] [11]. Very few of them have used statistical methods for interpretation of data. However, multivariate statistical analyses are, in recent decades, more and more used to the contaminant data processing [12] [13] [14] [15] [16] because they allow treating a significant number of data for maximum information. Principal component analysis allows showing differences on the chemical characterization of the different poles of acquisition of the mineralization [14]. HCA gives the similarity between two samples and the distance can be represented by the difference between analytical values from the samples [17].

This study used application of multivariate statistical techniques for assessment of hydrogeochemistry of groundwater in upper Kambo watershed.

2. Materials and Methods

2.1. Study Area

The study area is located in sub urban zone in Douala lying between 4°00'29" to 4˚02'08"N; and 9˚46'11" to 9˚48'06"E (**Figure 1**). It covers an area of about 5000 square meters. The main activities are small trade, breeding cattle and poultry. The density of the population is between 26 and 150 inhabitants per square kilometer [18]. The climate is coastal equatorial-type with two seasons: a rainy season running from March to November and a dry season that runs from December to February. The annual average rainfall is 4000 mm for an average annual temperature of 26.5˚C. The driest month is February and the wettest is August.

Geologically, the study area is located in the sedimentary basin of Douala. This basin is made up of several formations (**Figure 2**) which go from Albo-Aptien to the Quaternary [19] [20] [21]. From the bottom to up, there are several formations constituted of basal sandstones which included conglomerates with basement elements, coarse and medium arkosiques sandstone, fine micaceous, carbonaceous and carbonated, sandstones, micaceous black shale, mudstones, limestone and marls [22]. Logbajeck formation consists of micro-conglomérats, sands, coarse and middle sandstones, rare intercalations of fossiliferous limestone and sandy clays, sandstone and sands with intercalations of marls and limestone [22]. Logbaba formation consists mainly of sandstone, Sands and fossiliferous sandy clays [20] [22]. Matanda formation is dominated by coarse Sands at the base and thin at the top, alternating with pockets of variegated clays,

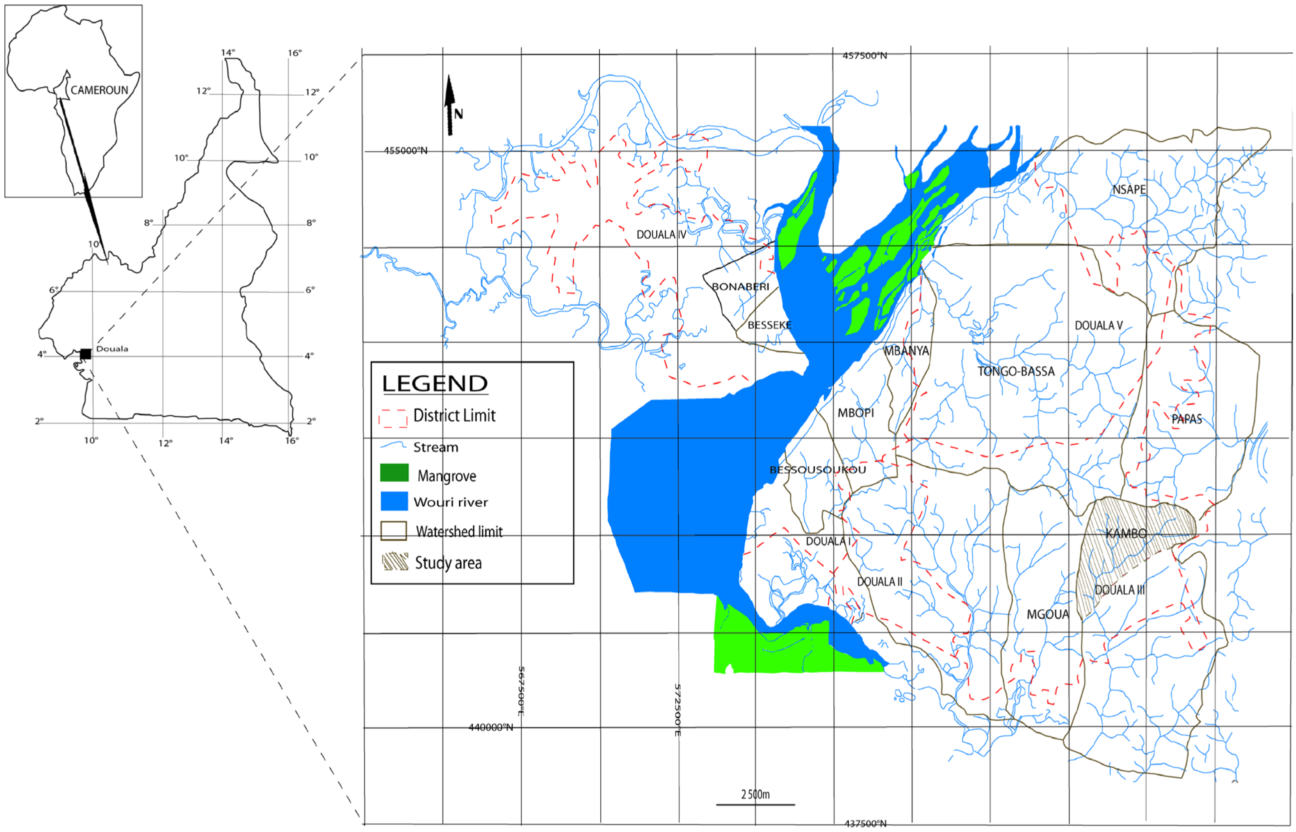


Figure 1. Geographic location of study area.

sometimes interstratified with basalts [19]. Wouri formation is characterized by gravels and coarse sands with argillaceous matrix [22].

In this area, soil is heterogeneous. It is noticed the ferralitic soils which are dominant, hydromorphic soils, little evolved soils and raw minerals soils [20] [23]. The mineralogical contents of these soils reveal many alteration products such as kaolinite, gibbsite, quartz, illite, goethite, anatase, feldspar alkali and hematite [24] [25].

In hydrogeological terms, two aquifer systems constitute the sedimentary basin of Douala [26] [27]. The deep aquifer system made up of the basal sandstone aquifer and paleocene sands aquifer of thickness 200 m. The shallow aquifer system includes the aquifer of the mio-pliocene and quaternary alluviums aquifer. The mio-pliocene aquifers mainly consist of sandstone and clay sands that are the ones concerned in this study.

2.2. Sampling and Analyses

A total of 34 samples (**Figure 3**) were collected from 27 wells, 4 springs and 3 Drillings (bore wells) during 3 campaigns (February, 2013, August 2013, and March 2014). For points sampled 2 or 3 times, the mean of the results was considered. The samples were taken according to the mode of conservation for groundwater sampling [28]. Water samples were kept in polyethylene bottles in capacity 1.5 liters. Before filling the bottles, they have been rinsed with water to

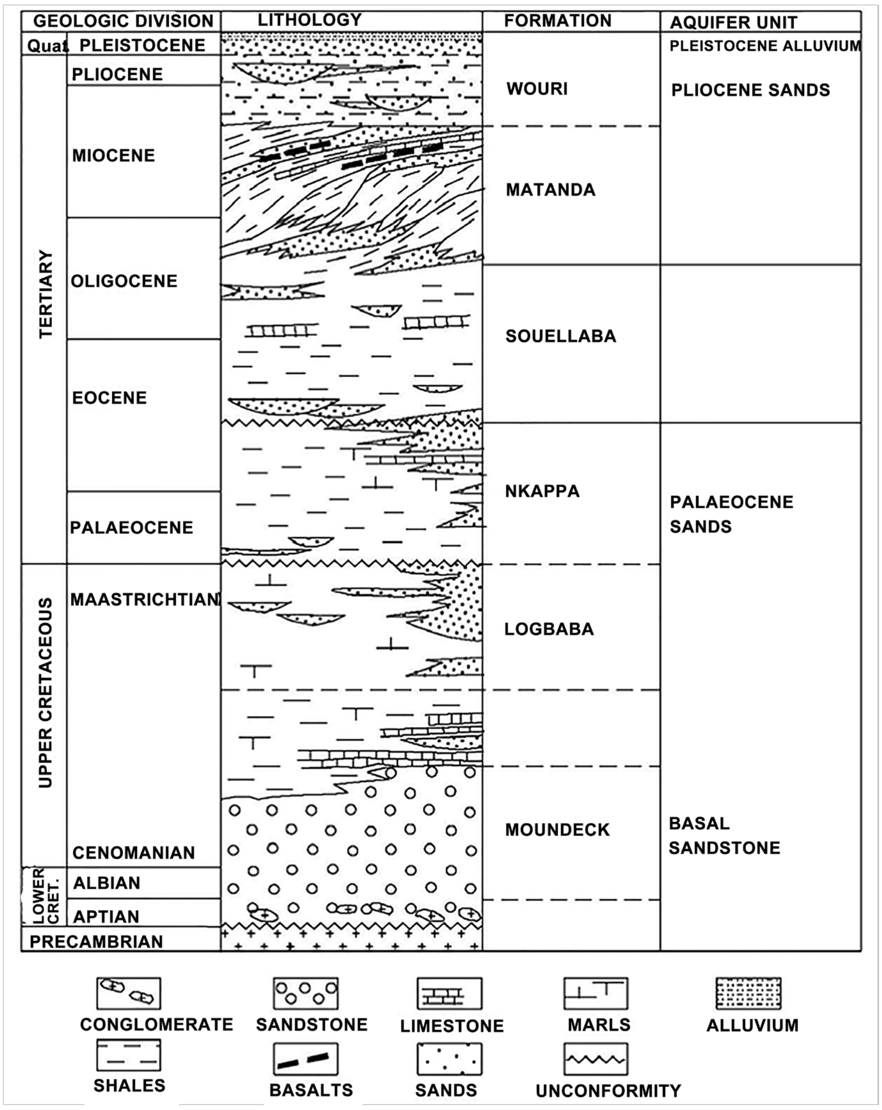


Figure 2. Chronostratigraphic column of the Douala basin and major aquifer units [28].

remove. The filling was made to the brim before being closed. Samples were preserved in iceboxes in 4˚C before the routing in the laboratory. The physical parameters (temperature, pH, electrical conductivity (EC)) were measured in the field using a portable multiparameter, mark ANNA Hi 98128.

Chemical analyses were performed in the laboratory of soils and waters of the Institute of Agronomic Research for Development (IRAD) of Cameroon. The cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) were analyzed by spectrophotometer of atomic absorption with flame. Bicarbonates (HCO_3^-) and chloride (Cl^-) were analyzed by titrimetry, Nitrates (NO_3^-) and sulphate (SO_4^{2-}) have been determined by colorimetry.

Principal Component Analysis (PCA) is used for the recognition of reasons that can explain the variance of the important number of data and variables inter-correlated, and transform them into smaller series of variables in depended (principal components). In the study context, PCA is used to determine the

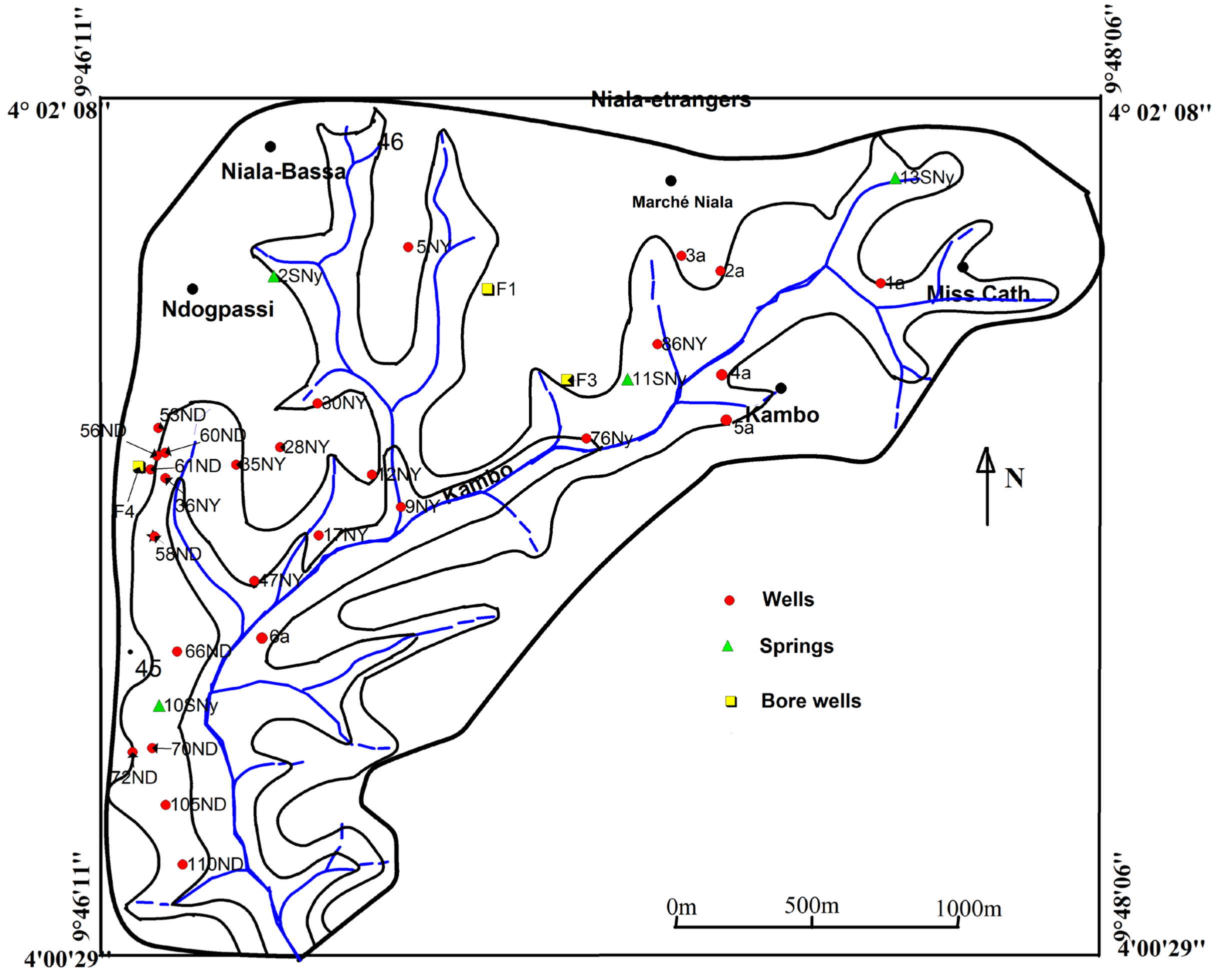


Figure 3. Location of sampling sites.

possible contributing factors in the waters samples hydrochemistry [14] [29].

Hierarchical Cluster Analysis was used to classify the samples into distinct hydrochemical groups. The Ward's linkage method [30] was used in this analysis. This method used a standardized space Euclidian distance [12]. A low distance shows that the two objects are similar or closer, whereas a large distance indicates dissimilarity. In clustering, the objects are grouped such that similar objects fall into the same class Ten parameters (variables) measured (consisting of EC, pH, Ca, Mg, Na, K, Cl, SO_4, HCO_3, NO_3) were used in this analysis and 34 points.

Multivariate statistical analysis was applied to 10 observations and 34 sample points. The statistical analysis was performed using R software.

3. Results and Discussion

3.1. Hydrochemistry

The hydrochemical analysis shows that (Table 1): temperature of water in the study area varies between 25˚C and 27˚C for an average of 25.48 ± 0.46. The pH is ranged from 4.23 to 6.22 for an average of 5.01. The pH of the set of waters allows giving to these waters an acid character. This pH tends towards neutrality in certain wells and bore wells. It should be noted that the pH values encountered in the different water points reflect those of the waters in the Douala sedimentary zone. Conductivity in the water varies between 29.45 µS/Cm and 404 µS/Cm for an average of 177. Conductivity for the whole of water is low and water is thus not very mineral-bearing.

The calcium which is the more represented cation varies from 0.97 with 56.21 mg/l (average 12.83 ± 14.04) in the whole of samples. A significant dispersion is to be noted between the results of the various analyses. Magnesium is represented in these water samples in small proportion. Its content varies from 0.75 with 13.2 mg/l (average 3.93 ± 2.46). Sodium varies from 1.58 and 16.64 mg/l (average 7.72 mg/l ± 3.99 mg/l). The potassium contains contents closer to those of sodium in the whole samples which lies between 0.97 and 16.4 mg/l (average 4.71 ± 3.28).

The analysis of the contents of cations shows that the importance order for the cations is $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$. In certain samples, sodium dominates. However the alkaline earth has a broad predominance on the alkaline ones. The bicarbonate contents vary from 1.72 and 181 mg/l (average 29.32 ± 37.36). With regard to chlorides, the contents as a whole lie between 0 and 78 mg/l (average 13.95 ± 14.72). In small proportion, the contents of nitrates lie between 0.1 with 9.89 mg/l (average 4.02 ± 2.75). Sulphates are the anions most slightly represented. In whole samples analyzed, their contents go from 0 to 10.3 mg/l (average 3.58 ± 2.38). By considering the average of the contents in the whole water, bicarbonates largely dominate the others followed anions by chlorides, nitrates and finally sulfates ($HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$).

3.2. Correlation Coefficient Analysis

The correlation matrix (Table 2) established between the different parameters and the thirty four (34) samples, several observations were made: The higher positive values specify good correlation (>70%) between the parameters pH-Calcium, sodium-potassium. A significant correlation (>60%) is observed between pH-magnesium, pH-bicarbonate, CE-calcium, CE-magnesium, calcium-bicarbonates. Poor correlation or negative correlation is noticed between the other parameters. Among them, temperature is negatively correlated with other parameters.

Table 1. Descriptive statistics for the groundwater physical and chemical parameters of sampling sites.

Parameters	pH	EC.	T˚C	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^-
Units		(µS/Cm)	˚C	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Maximum	6.22	404	27.5	56.21	13.215	16.64	16.4	9.885	78.01	10.29	180.97
Minimum	4.23	29.45	25	0.975	0.745	1.58	0.97	0.1	0	0	1.72
Average	5.01	177.19	25.48	12.83	3.93	7.72	4.71	4.02	13.95	3.58	29.32
SD	0.49	87.1	0.46	14.04	2.46	3.99	3.28	2.75	14.72	2.38	37.36

Table 2. Correlation matrix of the physic and chemical parameters of the study area.

	T˚C	pH	EC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-
T˚C	1										
pH	−0.38	1									
EC	−0.37	0.56	1								
Ca^{2+}	−0.29	0.79	0.65	1							
Mg^{2+}	−0.42	0.61	0.61	0.55	1						
Na^{+}	−0.29	0.42	0.53	0.48	0.61	1					
K^{+}	−0.23	0.26	0.24	0.3	0.45	0.75	1				
HCO_3^-	−0.26	0.61	0.3	0.65	0.43	0.23	0.13	1			
Cl^-	−0.19	0.18	0.16	0.26	0.04	0.15	0.1	−0.06	1		
SO_4^{2-}	−0.09	0.12	−0.02	0.14	0.25	0.12	0.29	−0.05	0.17	1	
NO_3^-	−0.13	−0.14	0.21	−0.11	0.16	0.26	0.29	−0.27	−0.06	0.32	1

Due to the negative correlation between temperature and others, the temperature was excluded from PCA and HCA for good visibility of the results.

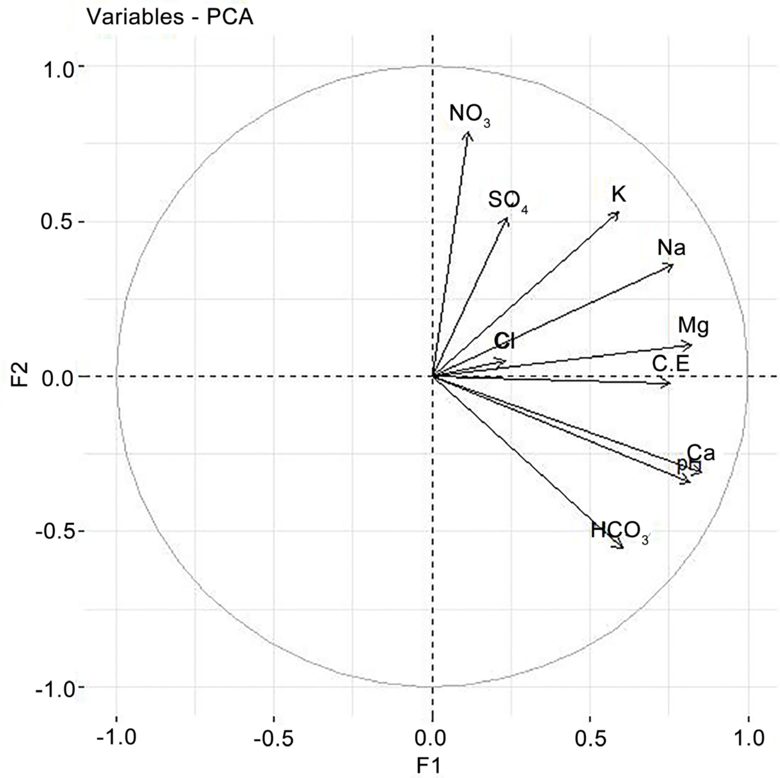
3.3. Principal Component Analysis

Principal component analysis (PCA) focused on the following variables: pH, Conductivity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, HCO_3^-, NO_3^-, SO_4^{2-}, temperature is excluded from this analysis because it is negatively correlated with the other parameters (Table 2). The factor analysis generated three significant factors which explained 70% of the variance in data sets (Figure 4).

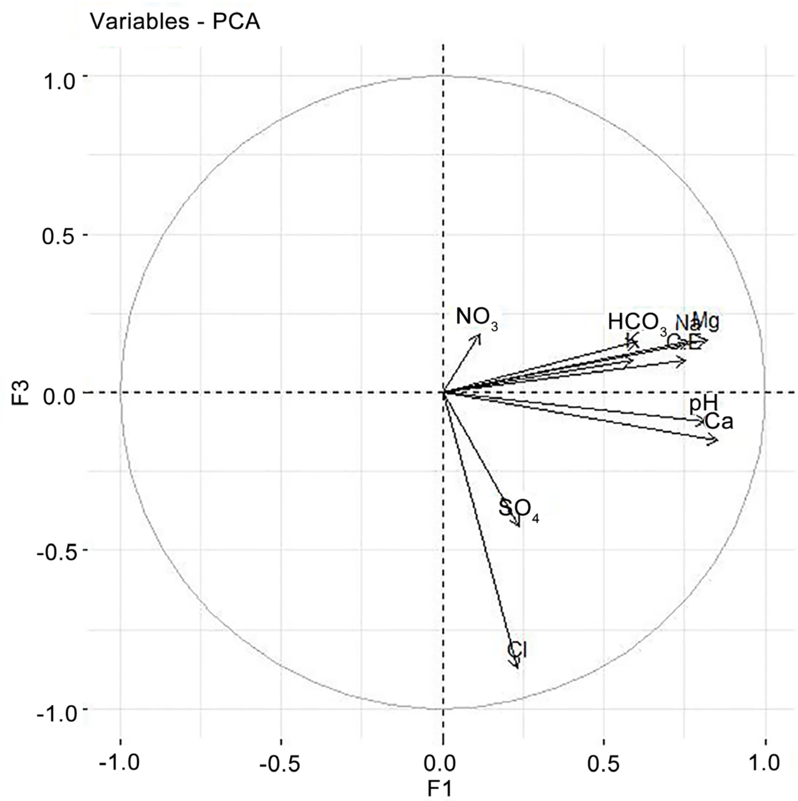
Factor1 (F1) accounts for 40% % of the variance in water quality of groundwater within the study area. It positive correlated with all variables. This shows that changes in dissolved ionic charges are entirely or partly related to variation in levels of these different ions. However, pH, EC, Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, HCO_3^- (Table 3), are highly correlated to this factor 1. Those five chemical elements (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, HCO_3^-) considered to be elements that control the mineralization.

Factor 2 (F2) accounts for 18% of the variance in water chemistry, positive correlated with Mg^{2+}, Na^{+}, K^{+}, NO_3^-, Cl^{-}, SO_4^{2-} and mainly dominated by NO_3 correlated negatively to pH, Ca^{2+}, EC, et HCO_3^- (Table 3). This shows an opposition of carbonated pole to chloride pole. Certain proximity is noted between nitrates and sulfates indicate a common origin of these two ions which can be anthropogenic or atmospheric. This proximity is also noted between Na and K and to a lesser extent with chlorides indicates an origin related to the dissolution of halite.

Factor 3 (F3) accounts for 11% of the variance in water correlated negatively to Ca^{2+}, Cl^{-}, SO_4^{2-}, and correlated positively to EC, Mg^{2+}, Na^{+}, K^{+}, et HCO_3^-, NO_3^- (Table 3). There is a grouping between EC, pH, Mg^{2+}, Na^{+}, K^{+}, et HCO_3^-, indicate a silicate origin. Chlorides as opposed to nitrate indicate an opposition of marine origin to anthropogenic origin.



(a)



(b)

Figure 4. Projection of the hydrochemical variables on the F1 × F2 axis (a) and F1 × F3 axis (b).

Through these analyses, it is noticed that the process of mineralization in this aquifer system would be very complex due to its geological mixed context (silicate and carbonate), its proximity to the sea and the rapid infiltration through the formation.

3.4. Cluster Analysis

Cluster analysis on the set of 34 samples is the dendrogram (Figure 5) where four groups are distinguished. The different clusters identified from the dendrogram with more or less distinct characteristics (Table 4)

1) Cluster 1

Cluster 1 contains four samples ((17Ny, 30Ny, 36Ny, 72ND) characterized by relatively high mineralization but lower than cluster 2 (mean of EC: 186 µS/Cm) and pH mean is 5.38. The dominating cation of this group is calcium while the bicarbonates dominate the other anions. The importance order of the ions is: Ca > Na > Mg > K and HCO_3 > Cl > NO_3 > SO_4. In this group, bicarbonates largely dominate chlorides. Water points are Ca-Mg-HCO_3 type.

2) Cluster 2

This group is represented by seven samples (28Ny, 35Ny, 60Ny, 56Ny,

Table 3. Factor Loadings for water quality parameter.

Parameters	F1	F2	F3
pH	0.82	−0.34	−0.09
EC	0.76	0.02	0.10
Ca^{2+}	0.85	−0.31	0.15
Mg^{2+}	0.82	−0.10	0.17
Na^{+}	0.67	0.36	0.16
K^{+}	0.59	0.53	0.10
NO_3^-	0.11	0.79	0.18
Cl^-	0.23	0.05	−0.87
SO_4^{2-}	0.24	0.51	−0.82
HCO_3^-	0.6	0.56	−0.16

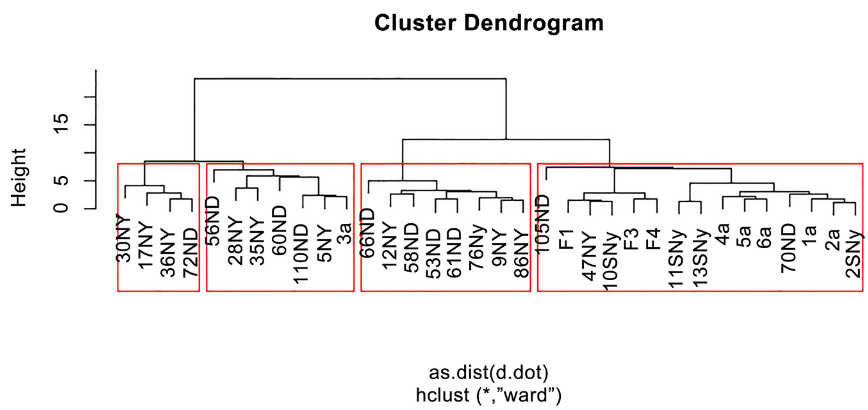


Figure 5. Dendrogram showing clustering of sampling sites.

Table 4. Physic and chemical characteristics mean for each group.

Parameters	Group 1	Group 2	Group 3	Group 4
pH	5.38	5.64	4.83	4.71
CE	186.5	278.25	179.62	44.25
Ca^{2+}	18.29	35.41	6.2	4.37
Mg^{2+}	5.76	6.28	4.45	2.06
Na^{+}	8.07	11.98	8.82	5.04
K^{+}	4.38	7.83	5.84	2.72
NO_3^-	1.4	4.19	6.25	3.43
Cl^-	4.67	21.59	13.82	12.75
SO_4^{2-}	1.55	4.49	6.02	2.38
HCO_3^-	100.53	50.02	15.09	8.25

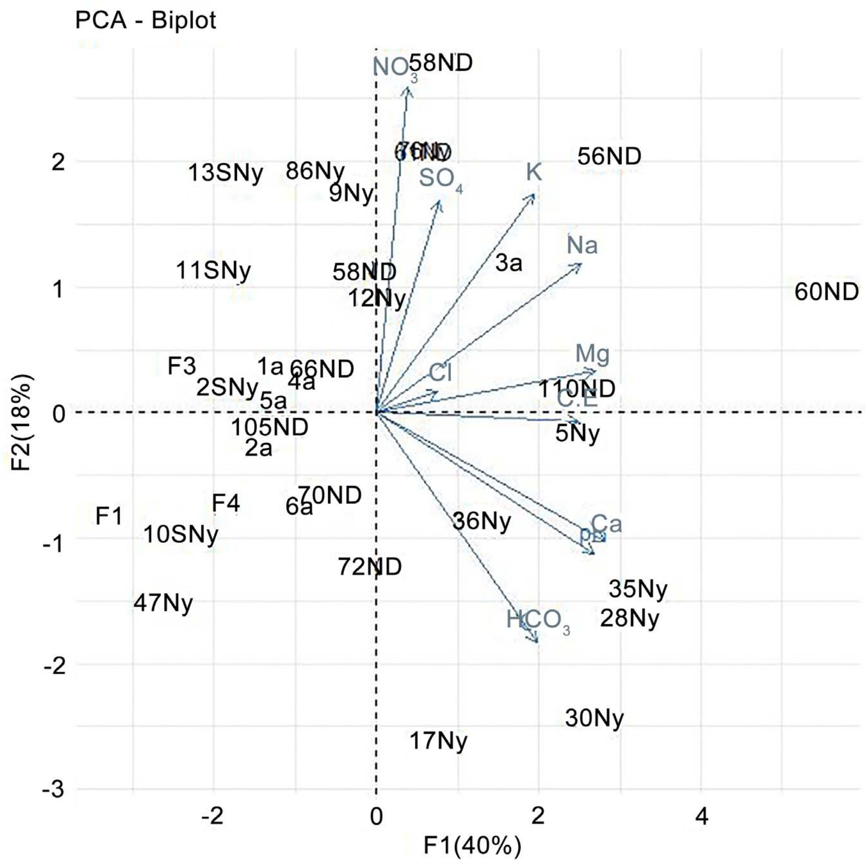


Figure 6. Projection of samples and parameters on the axis F1 and F2.

110ND, 3a, 5Ny). This group characterized by high mineralization. The electrical conductivity mean of this group is 278 µS/Cm and pH mean is 5.64. As the Cluster 1, Calcium is the dominant cation while the bicarbonates dominate the other anions (Ca > Na > K > Mg and HCO_3 > Cl > NO_3 > SO_4), but bicarbonate is less important than cluster 1 and in some samples dominated by chlorides. Water is mostly Ca-Mg-HCO_3-Cl type. We also have Ca-Mg-HCO_3 water type.

3) Cluster 3

This group includes eight samples (9Ny, 12Ny, 86Ny, 58ND, 53ND, 61ND, 66ND, 76Ny). The electrical conductivity mean is 179.62 µS/Cm and pH mean is 4.83. The mean rate of sodium for this group is more important than calcium, the mean for the bicarbonates is higher than the other anions (Na > Ca > K > Mg and HCO_3 > Cl > NO_3 > SO_4). Therefore, samples of this group are Ca-Na-Cl type.

4) Cluster 4

This group includes 15 samples (47Ny, 70ND, 105Ny, 1a, 2a, 4a, 5a, 6a, 10SNy, 2SNy, 11SNy, 13SNy, F1, F3, F4). The electrical conductivity mean is 126µS/Cm and pH mean is 4.71. This group characterized by low mineralization. Gap between sodium and calcium concentration is very low. However, sodium is more important in the majority samples than calcium. Order of importance of ions in water is Na > Ca > K > Mg and Cl > HCO_3 > NO_3 >SO_4. Samples of this group can be considered as mixed waters with regard to cations. For the anions, chloride dominates bicarbonates and exception made in five samples (47Ny, 70ND, 105Ny, 4a, F4) where bicarbonates are dominated. In this group Na-Ca-Cl or Na-Ca-HCO_3 water type are distinguished. Increase sodium concentration in this group may indicate cation exchange in aquifer.

The link between the results of Cluster analysis and those obtained from the Principal Component Analysis (**Figure 6**), shows that: Factor1 oppose high mineralized water to low mineralized water. Factor 2 axis allows identifying the chemical elements which determine mineralization in every group of water. In samples of the group 1, mineralization is controlled by Ca, Mg, HCO_3, group 2 controlled by Ca, Na et HCO_3, group 3 controlled by Na et Cl and group 4 controlled by Na, Mg, Ca, Cl or HCO_3.

4. Conclusion

Both applied statistical methods raised important information on the groundwater hydrochemistry of upper Kambo watershed. Principal Component Analysis shows that carbonate dissolution, silicates alteration, marine, air and anthropogenic input are the processes involved in the mineralization. HCA distributed water point into four groups according to the degree of water mineralization. Waters with low mineralization concern group 4 which include waters of springs, bore wells and the majority of wells. Waters of group 1 are influenced by Ca and HCO_3. Group 2 is influenced by HCO_3-Ca-Mg or Cl-Ca-Mg. Group 3 is under the influence of Cl-Na-Mg. In group 4, the facies are mixed; waters are HCO_3-Ca-Na or Cl-Mg-Na type.

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