Hydrochemical Characterization of Benin Formation in Benin-city and Environs, Nigeria using Multivariate Analyses

Joshua Oluwasanmi Owoseni (Corresponding author)
Department of Applied Geology, Federal University of Technology, Akure. Nigeria
PMB 704, Akure, Ondo State. Nigeria.
E-mail: joowoseni@futa.edu.ng

Yinusa Ayodele Asiwaju-Bello
Department of Applied Geology, Federal University of Technology, Akure. Nigeria
PMB 704, Akure, Ondo State. Nigeria.
E-mail: ayoasiwajubello@futa.edu.ng

Abstract

Multivariate statistics was applied to some hydrochemical data from Benin Formation in Benin-city metropolis, Southern Nigeria with a view to characterizing and determining the main structures underlying groundwater chemistry in the area. Laboratory chemical analysis followed standard laboratory analytical procedures stipulated by American Society for Testing and Materials (ASTM). Hydrochemical data were standardized to z-scores and screened for outliers, normality and linearity prior to statistical analysis at significant level of 5%. Q-mode Hierarchical Cluster Analysis (HCA) grouped the groundwater samples into distinct clusters to represent different hydrochemical facies. R-mode Principal Component analysis (PCA) reduced bulk hydrochemical data to discrete principal components indicating possible dominant processes responsible for groundwater chemistry. Results of PCA revealed six principal components (PCs) which together explain 86.84 % of the total variance in the dataset. The results of PCA implied that Ca, total hardness, Mg, total dissolved solids, chloride, electrical conductivity and Na are the most significant parameters controlling groundwater chemistry in the area. The extracted components also indicated that atmospheric controls and silicate mineral weathering processes are the main factors responsible for variation in groundwater chemical variations in the area. Results of HCA which identified six significant clusters indicated high degree of spatial, statistical and chemical coherence, and validated grouping of groundwater into chemical clusters in the study area. Results from this study showed PCA and HCA are useful tools for analyzing dominant processes responsible for variation in groundwater chemistry in the study area.

Keywords: Principal component analysis, cluster analysis, groundwater chemistry, coefficient of variation.

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1. Introduction

The coastal plain sand aquifer (Benin Formation) under investigation constitute the main source of water for various uses including domestic, industrial and agricultural purposes in the study area (Olobaniyi and Owoyemi, 2006). Much concerns have been raised in recent past over the chemical quality of groundwater in Benin-city and its environs (Igbinomwanhia, 2012; Ekong, 2015). The fears raised are in connection with unregulated and indiscriminate open dumping of solid wastes as well as flood control by injection of untreated storm water into the subsurface environment (Akpoborie, 2011; Oteze, 2011). Groundwater contamination has caused serious health implications in many parts of sub-Saharan Africa (Nwankwoala and Udom, 2011; Adewusi, 2012; Forstinus *et al.,* 2016). This often calls for investigation into chemical status of groundwater in the shallow aquifer serving as source of water for different uses in the sub-region.

The use of traditional approaches to study the chemistry of groundwater in Benin Formation aquifer have been reported (Erah *et al.,* 2002; Ukpebor and Unuigbe, 2003; Imasuen and Omorogieva, 2013; Idugboe *et al.,* 2014; Akpoborie *et al.,* 2015). There is need for the application of multivariate statistical approaches which have been validated in other places (Olobaniyi and Owoyemi, 2006; Balogun and Akoteyon, 2012; Zhang *et al.,* 2012; Yang *et al.,* 2015; Armanuos *et al.,* 2016; Zhang *et al.,* 2016; Orakwe and Chukwuma, 2017) for hydrochemical characterization of Benin Formation in Benin-city. A combination of hierarchical cluster analysis (HCA) and principal component analysis (PCA) were therefore employed in grouping groundwater samples on the basis of similarities in multidimensional space as well as reduction of bulk hydrochemical data into components which explain likely underlying structures existing among hydrochemical clusters. R-mode factor analysis by principal component extraction with varimax rotation and Kaiser normalization was adopted in the current study. The decision on the number of components to retain and interpret, is often based on some criteria, viz: (i) components within the sharp descent before eigenvalues level off on the scree plot, (ii) components accounting for at least 70% total variability, (iii) components with eigenvalues greater than 1 (Kaiser, 1958).

1.1 Study Area

Benin-city and environs (5º32′E - 5º43′E, 6º17′N - 6º28′N) is situated within western Niger Delta in southern Nigeria (Fig. 1). It is underlain by coastal plain sand aquifers (Fig. 2) consisting of highly porous massive continental sands and gravels, with poorly developed discontinuous interbeds of thin clay units at various depths. The Formation is of Miocene to Recent age (Short and Stauble, 1967; Weber and Daukoru, 1975).

The aquifer in the study area is categorized into: (i) the Benin Formation consisting of freshwater continental friable sands and gravels with occasional intercalation of clay, (ii) the Ogwashi-Asaba Formation (consisting of sands, grits, lignite and clays) which grades upwards into the overlying Benin Formation exposed along stream channels around Ekiadolor and Uzalla in the north eastern part of the study area, and (iii) alluvium which are recent deposits made up of clayey sands, silts, sands and gravels occurring along Ikpoba and Ovia flood plains.

Figure 1. Location map of the study area (Modified after Digun-Aweto *et al.*, 2018).

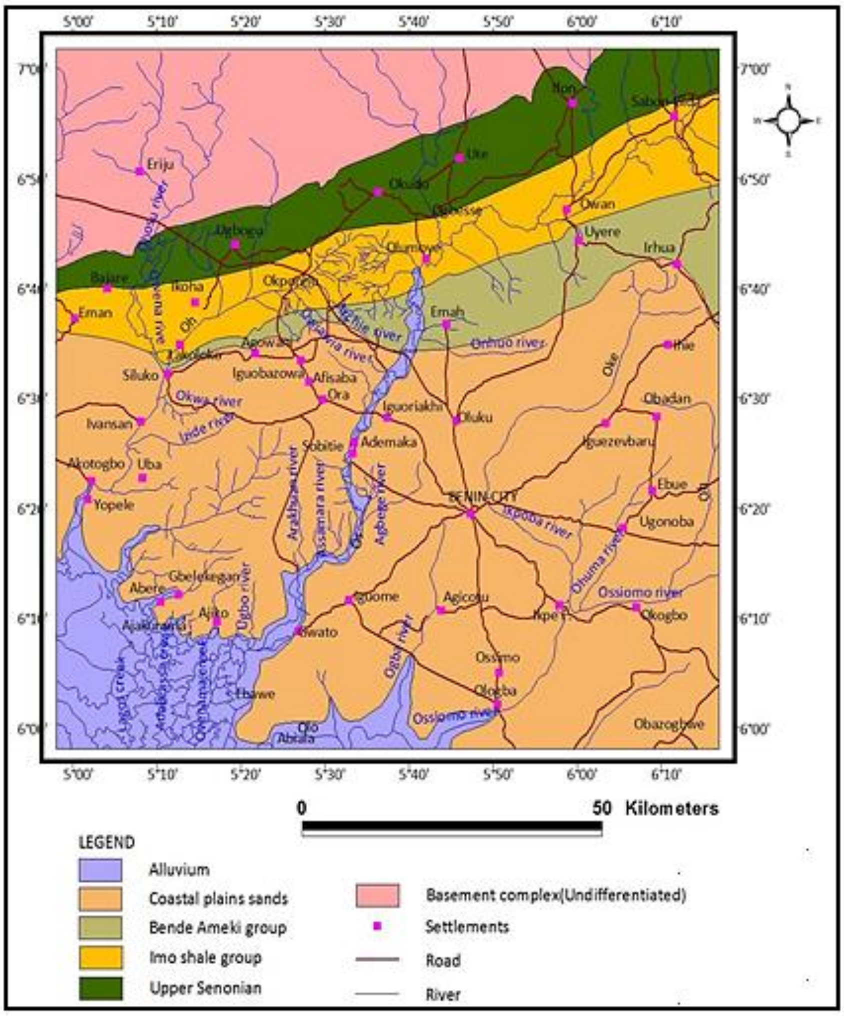

Figure 2. Geologic map of the study area (Modified after Olatunji *et al.*, 2014).

2. Materials and Methods

2.1 Sampling and Laboratory Analysis

A total of 29 boreholes tapping from shallow Benin Formation were sampled within the study area. Some physicochemical parameters were measured on the field due to their easy susceptibility to change on storage. These parameters include temperature, total dissolved solids (TDS) and hydrogen ion concentration (pH) using HANNA COMBO pH/TDS/EC/Temperature meter (HI98129 model) which was calibrated prior to use. Major cations (Ca, Mg, Na and K) and anions (Cl, HCO_3, NO_3, SO_4, and PO_4) were measured through standard laboratory analytical techniques stipulated by American Society for Testing and Materials (ASTM). Sodium and potassium concentrations were determined using atomic absorption spectrophotometer (AAS). Also, Ca, Mg, Cl and HCO_3 were measured by EDTA titrimetric method while SO_4, PO_4 and NO_3 were analyzed by ultra-visible spectrometry technique.

2.2 Statistical Analysis

Both univariate and multivariate statistics were adopted for data analysis in this study. The SPSS Statistics 17.0 software package (SPSS, 2008) was used for the analyses.

2.2.1 Data Preparation

Prior to statistical data analyses, hydrochemical datasets were standardized to z-scores and rendered dimensionless to minimize any effects of difference in units of measurement and variance of parameters as required (Singh *et al.,* 2004). Also, in bid to ensure the quality of component solution, the datasets were screened for outliers and assessed for normal distributions as well as linearity among all pairs of variables before statistical analysis was performed at significance level of $p = 0.05$ (Mertler and Vannatta, 2005).

2.2.2 Principal Component Analysis

This study employs the Principal Component Analysis (PCA) which is an exploratory procedure that reveals all (unique, shared and error) variability for each measured variable (Mertler and Vannatta, 2005). The underlying mathematical aim of PCA is to determine uncorrelated linear combinations of the original variables that accounts for as much of the total variance in the original variables as possible (Johnson and Wichem, 1998). The total variance is often partitioned into as many principal components (PC) as possible and extracted sequentially with each subsequent PC uncorrelated with the previous one. Each principal component gives the linear combination of variables that accounts for the maximum amount of variance in the system of original variables which describes the underlying structure that explains any shared variability existing among the set of variables being examined. This enables easy examination of how individual variables reflect the possible sources of variability (Williams, 1992; Agresti and Finlay, 1997). Each PC is obtained as:

$$C_{mn} = b_{m1}x_{1n} + b_{m2}x_{2n} + b_{m3}x_{3n} + \cdots b_{mz}x_{zn}$$

where C is the specific component score, b is the component loading, x is the measured value of the original variable, m is the component number, j is the sample number, and z is the total number of original variables (Mertler and Vannatta, 2005; Shrestha and Kazama, 2007). The analytic operation begins with extraction of the first linear combination that accounts for the largest amount of variance. Then, the second linear combination (uncorrelated with the first) which accounts for the next biggest amount of variance (after removing the one attributed to the first component) is extracted. The process continues until all variance has been accounted for by extracting all components regarded as significant in the dataset (Orakwe and Chukwuma, 2017). The number of principal components retained and interpreted in the current study was based on the following criteria (Mertler and Vannatta, 2005), (i) Kaiser's rule on eigenvalue (ii) the scree test (iii) assessment of model fit, and (iv) components accounting for at least 70% total variability.

2.2.3 Hierarchical Cluster Analysis

In classifying the datasets into significant groups, the current study adopted the hierarchical cluster analysis (HCA) which groups samples based on similarities in multidimensional space. It is obtained as,

$$C_{ij} = \left(\frac{x_{ij}}{x_{max}}\right)^{-1}$$

where x_{ij} is the distance between two clusters and x_{max} is the highest x_{ij} (Forina *et al*., 2002). The HCA was performed with assumptions of homoscedasticity of variables (Mertler and Vannatta, 2005) using group average linkage and squared Euclidean distance methods.

3. Results and Discussion

3.1 Groundwater Chemistry

Groundwater chemical characteristics are presented in form of descriptive statistics (Table 1). The predominant cations and anions in the groundwater are Ca/K and Cl/HCO_3 (averaging 7.04/8.04 mg/L and 49.46/17.25 mg/L) respectively. Among the fifteen variables investigated, electrical conductivity (EC) has the highest standard deviation (SD) while PO_4 has the least value of SD. However, the degree of dispersion among the variables measured in different units is better understood by the coefficient of variation (CV) which indicated that SO_4 and temperature have the largest and smallest coefficient of variations of 197.59 % and 4.97 % respectively. The major cations and anions account for 28.81% and 71.19% of mean TDS.

3.2 Principal Component Analysis

Six (6) components were retained as the optimal number of principal component factors and interpreted following the Kaiser's rule on eigenvalues being greater than one (Kaiser, 1958), scree test plot (Fig. 3) and, cumulative loading accounting for minimum of 70% of total variability. The first to sixth components accounted for 41.40%, 13.61%, 8.57%, 8.02%, 7.66% and 7.62% of the total variance respectively with a cumulative loading of about 86.84% (Table 2). The level of variation reduced drastically from the seventh to the fifteenth components thereby rendering their cumulative contribution too low to be reckoned with as statistically significant.

Table 1. Descriptive statistics of groundwater hydrochemistry

Parameter	Units	n^a	Min.	Max.	Mean	SD	CV (%)
TDS	mg/L	29	1.00	152.00	41.21	44.80	101.66
pH	-	29	4.21	5.54	4.72	0.38	8.01
TH	mg/L	29	3.20	216.42	39.72	49.22	121.90
K	mg/L	29	0.56	20.39	8.04	6.20	75.35
Na	mg/L	29	0.43	17.08	6.71	5.09	74.58
Mg	mg/L	29	0.39	28.20	5.40	6.37	113.46
Ca	mg/L	29	0.64	40.32	7.04	9.47	127.57
SO_4	mg/L	29	0.00	0.78	0.10	0.23	197.59
NO_3	mg/L	29	0.00	1.28	0.27	0.36	135.69
HCO_3	mg/L	29	12.20	24.40	17.25	4.33	25.99
Cl	mg/L	29	28.40	113.60	49.46	20.65	41.76
EC	µS/cm	29	1.49	244.78	82.30	120.64	101.95
SAR	-	29	0.03	1.96	0.54	0.39	72.78
PO_4	mg/L	29	0.00	0.80	0.10	0.17	186.39
Temp	°C	29	26.80	32.60	29.66	1.43	4.97

^{a} indicates number of samples, Min. indicates minimum, Max. indicates maximum, SD indicates standard deviation, CV indicates coefficient variation

Table 2. Total variance explained

component	Extraction Sums of Squared loadings			Rotation Sums of Squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.689	44.572	44.572	6.205	41.369	41.369
2	1.841	12.274	56.846	2.041	13.610	54.979
3	1.220	8.131	64.977	1.286	8.571	63.550
4	1.178	7.856	72.833	1.203	8.018	71.569
5	1.097	7.316	80.149	1.148	7.656	79.224
6	1.004	6.694	86.843	1.143	7.618	86.843

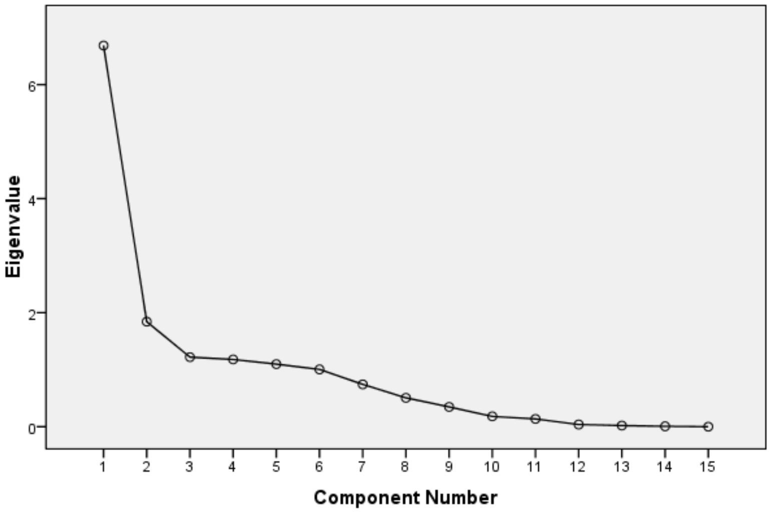

Figure 3. The Scree Plot

From the rotated component matrix (Table 3), the first principal component (PC1) exhibited strong positive loading (Liu *et al.*, 2003 and Nabeel *et al.*, 2012) for calcium ion concentration, total hardness, magnesium ion concentration, total dissolved solids and chloride ion concentration while it showed moderate positive loadings for sodium ion concentration. This is indicative of silicate weathering and anthropogenic impact. The second principal component (PC2) exhibited strong positive loadings for SAR and potassium ion concentration, and moderately positive loading for sodium ion concentration. PC3 had moderate positive loading for nitrate ion concentration, indicating impact of some human activities, possibly agriculture. PC4 had strong positive loading for temperature, signifying unconfined aquifer condition with direct thermal connection of the groundwater with the atmosphere. PC5 showed strong and moderate positive loadings for sulphate ion concentration and pH respectively indicating fairly acidic nature of the water. PC6 showed strong positive loading for phosphate ion concentration, implying possible anthropogenic impact especially from domestic wastewater.

Table 3. Principal component and varimax rotated component matrix

Var.	Component matrix						Rotated component matrix[a]						Com.
	1	2	3	4	5	6	1	2	3	4	5	6	
Ca	**0.963**	-0.185	0.021	-0.026	0.051	0.062	**0.978**	0.062	0.056	0.018	-0.057	0.048	0.969
TH	**0.967**	-0.143	-0.027	-0.093	0.038	0.042	**0.968**	0.077	0.131	0.074	-0.048	0.040	0.969
Mg	**0.950**	-0.102	-0.069	-0.151	0.026	0.022	**0.937**	0.089	0.195	0.123	-0.039	0.032	0.941
TDS	**0.959**	-0.076	0.026	0.106	0.002	0.031	**0.934**	0.212	0.005	-0.005	-0.125	0.075	0.939
Cl	**0.838**	-0.261	0.177	-0.075	0.009	0.192	**0.896**	-0.049	-0.004	-0.077	0.099	0.151	0.844
EC	**0.809**	-0.163	-0.061	0.193	0.121	0.111	**0.832**	0.121	-0.160	0.033	-0.110	-0.061	0.750
Na	**0.872**	0.412	-0.074	0.088	-0.035	0.047	**0.726**	**0.622**	0.143	0.107	-0.020	0.019	0.947
SAR	0.131	**0.861**	0.142	0.201	-0.048	-0.029	-0.097	**0.872**	0.148	-0.146	0.090	-0.003	0.822
K	**0.602**	**0.608**	-0.105	0.327	0.017	0.083	0.425	**0.813**	-0.040	0.073	-0.033	-0.083	0.857
HCO3	-0.133	-0.459	0.065	**0.720**	0.048	0.279	0.011	-0.170	-0.864	-0.162	-0.170	0.016	0.831
NO3	**0.526**	-0.120	0.378	-0.296	0.258	-0.501	0.516	-0.133	**0.541**	-0.457	-0.206	-0.096	0.838
Temp	0.160	-0.067	-0.878	-0.283	-0.227	0.101	0.133	-0.082	0.126	**0.945**	-0.077	-0.047	0.942
SO4	-0.040	0.336	0.294	-0.488	0.018	**0.599**	-0.017	0.115	0.176	-0.033	**0.861**	0.107	0.799
pH	-0.421	-0.097	0.018	-0.103	**0.542**	0.458	-0.248	-0.275	-0.258	-0.067	**0.517**	-0.474	0.701
PO4	0.070	-0.209	0.371	-0.043	-0.812	0.175	0.058	-0.100	-0.074	-0.045	0.084	**0.922**	0.879
% Var	**44.672**	**12.274**	**8.131**	**7.856**	**7.316**	**6.694**	**41.369**	**13.610**	**8.571**	**8.018**	**7.656**	**7.618**	**86.843**

[a] Rotation method: varimax with Kaiser normalization, Var.: variables, Com.: communality

3.4 Hierarchical Cluster Analysis

The hierarchical cluster analysis (HCA) adopted to determine possible groupings of the groundwater samples generated six (6) significant hydrochemical clusters (Fig. 4). Ten (10) out of the twenty-nine (29) groundwater samples were classified as Cluster 1 and consist of water from boreholes BH51, BH52, BH67, BH68, BH69, BH70, BH72, BH73, BH74 and BH75. Cluster 2 comprises groundwater from six (6) boreholes which include BH46, BH49, BH56, BH57, BH60 and BH61. There were two boreholes each in cluster 3 (BH30 and BH53) and cluster 4 (BH63 and BH65). Cluster 5 comprises water samples from seven (7) boreholes which are BH02, BH50, BH55, BH59, BH62, BH64 and BH71. Cluster 6 consist of water samples from boreholes BH48 and BH58. There is high level of spatial, statistical and hydrochemical coherence (Tables 3 & 4; Fig. 5).

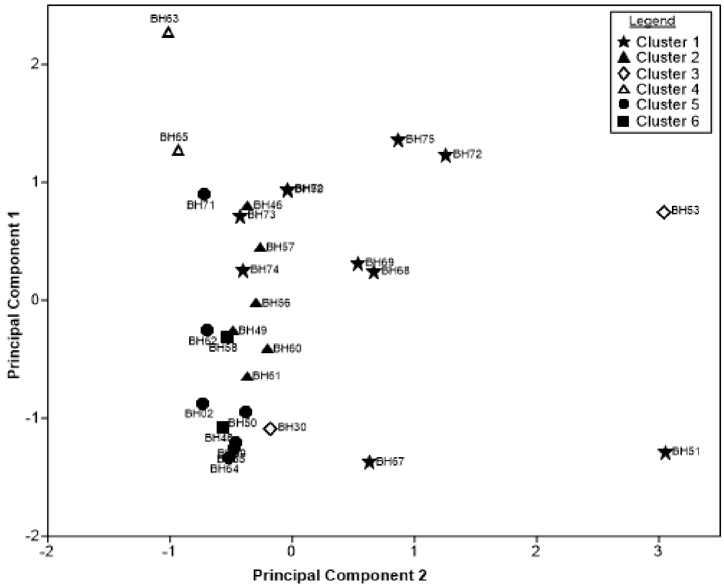

Figure 4. Distribution pattern of HCA-derived classification of samples from the plot of PC1 and PC2

Table 4. Mean groundwater chemistry of the clusters obtained from HCA

	Clusters					
	1	2	3	4	5	6
n^a	10	6	2	2	7	2
TDS	79.000	27.500	44.500	14.500	4.286	7.000
pH	4.558	4.488	4.73	4.915	5.059	4.880
TH	70.833	25.067	13.250	4.000	9.541	14.865
K	11.853	7.168	10.270	9.445	3.251	3.210
Na	10.655	5.513	7.900	7.265	2.501	2.470
Mg	9.266	3.895	3.555	0.390	1.641	2.260
Ca	13.137	3.638	9.730	0.960	1.124	2.240
SO_4	0.112	0.100	0.150	0.000	0.189	0.000
NO_3	0.410	0.270	0.250	0.150	0.151	0.060
HCO_3	16.470	18.300	15.250	15.250	15.686	24.400
Cl	59.640	44.967	71.000	35.500	42.600	28.400
EC	117.912	41.045	186.570	21.640	6.396	10.445
SAR	0.569	0.490	0.470	1.620	0.351	0.255
PO_4	0.092	0.117	0.000	0.050	0.120	0.060
Temp.	29.950	29.567	28.850	27.400	29.714	30.35

^{a} Number of samples within each cluster

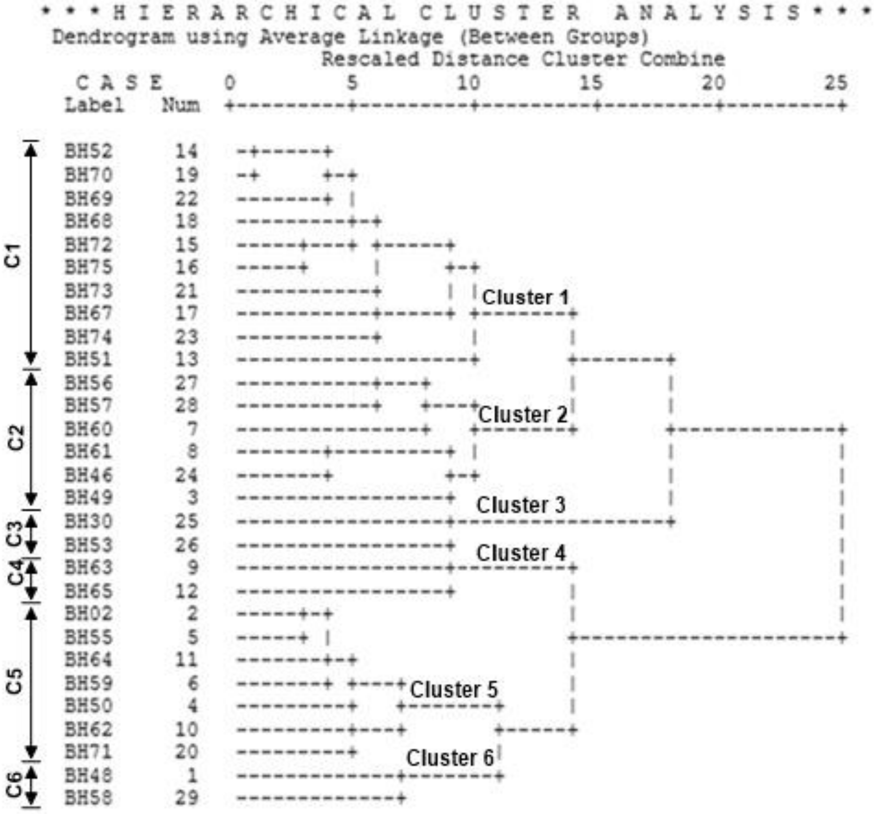

Figure 5. Dendrogram of the groundwater sample cluster

4. Conclusion

In this study, principal component analysis and hierarchical cluster analysis were employed to decomposed and classify hydrochemical variables to uncorrelated principal components that reveal underlying structures of the datasets. The following concluding remarks emanated from the current study:

(i) The principal component analysis indicated that six out of fifteen components accounted for a cumulative of 86.84% of the total variance and were the only ones retained and explained based on some standard statistical criteria. Other components (from the seventh to the fifteenth) were ignored because their contributions to variations in groundwater chemistry were not considered statistically significant.

(ii) Results of PCA revealed that Ca, total hardness, Mg, total dissolved solids, chloride, electrical conductivity and Na are the most significant parameters controlling variation in groundwater chemistry in the study area.

(iii) Comparison of hierarchical cluster analysis results (dendrogram) with score plots of principal components (PC1 and PC2) and mean groundwater chemistry indicated a generally high degree of spatial, statistical and hydrochemical coherence. This is a measure of validation of the grouping by PCA and HCA in the study area.

(iv) The study showed that atmospheric, geologic as well as hydrogeologic controls interplayed to account for groundwater chemical variations in the area.

(v) The study demonstrated PCA and HCA are useful tools for analyzing dominant processes responsible for variation in groundwater chemistry in the study area.

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