

# Application of Chemometric Techniques in Groundwater Quality Investigation in Angware Area Jos North-Central Nigeria

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**Abstract:** Twenty water samples were collected and analyzed using DR2000 spectrophotometer, flame photometer and titrimetric method. The results indicate that the relative abundance of the cations were in the order of  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Fe}^{2+} > \text{K}^+ > \text{Pb}^{2+}$  while those of the anions were  $\text{HCO}_3^- > \text{Cl}^- > \text{F}^- > \text{SO}_4^{2-}$ . Correlation of the mean values of the chemical parameters with the World Health Organization standards indicates that  $\text{Pb}^{2+}$  and  $\text{F}^-$  exceeded the maximum allowable limit. Principal Component Analysis identified three factors that account for 74.55% of the total variance. Factor 1 is characterized by high positive loadings with respect to  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TH,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ . This factor is related to soil/rock-water interaction and also represents Na-Mg-Ca-Cl- $\text{HCO}_3$  facies. Factor 2 includes high positive loading for pH and TDS and factor 3 has high loading for only  $\text{SO}_4^{2-}$  which may be related to anthropogenic activities. Cluster analysis identified two clusters that are related to natural mineralization and anthropogenic contamination. Cluster 1 has close similarities for  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , TH and included  $\text{K}^+$ ,  $\text{Fe}^{2+}$  and  $\text{F}^-$  in the same cluster and is related to natural mineralization. Cluster 2 comprised of pH and TDS in close similarities followed by  $\text{SO}_4^{2-}$  and  $\text{Pb}^{2+}$  and included temperature in the same cluster and is related to anthropogenic pollution. PCA and CA indicate that the variables responsible for groundwater composition are related to natural and anthropogenic sources.

**Keywords:** Angware area, Principal Component and Cluster Analyses and Groundwater quality

## Introduction:

Groundwater quality is controlled by combined effects of the composition of water that enters groundwater reservoir and reactions with minerals in the aquifers to different levels of anthropogenic effects. A part from natural effects of rock-water interaction, anthropogenic influences resulting from domestic, agricultural and industrial activities play an important role in the degradation of groundwater quality. Due to the long residence time of groundwater in the invisible subsurface environment, the effects of pollution may first become apparent ten to hundreds of years after introduction of pollutant (Appelo and Postma, 1996). The ever-increasing demand for potable water requires knowledge of the quality of stored water as well as of the natural and anthropogenic processes that influence it (Machado et al., 2008). The

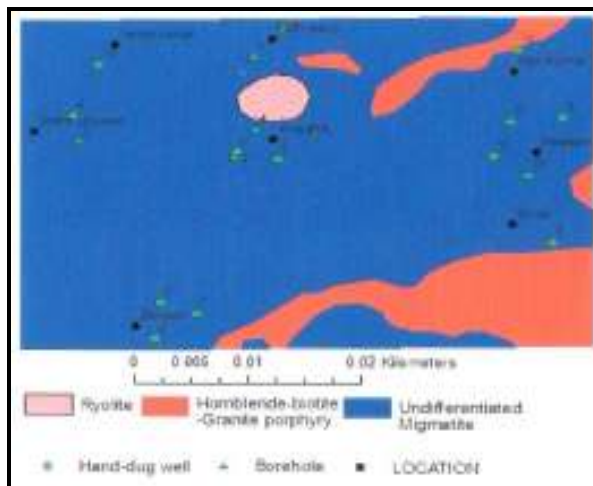
authors went further to stress that water stored in some aquifers can differ in their chemical composition due to internal and external processes, and suitable methodologies are needed for their identification. In this study, groundwater quality investigation in Angware area has been performed using two multivariate techniques (Principal Component Analysis and Cluster Analysis). PCA and CA are the two most important tools of the multivariate techniques that are applied to determine the dominant interrelationship among variables to understand the processes that may be responsible in controlling the groundwater chemistry (Shrestha and Kazama, 2007).

## Geology of the Area:

The study area is Angware in Jos north central local government area. It is located between latitudes  $9^{\circ}58'N$  to  $10^{\circ}00'N$  and longitudes  $9^{\circ}05'E$  to  $9^{\circ}08'E$ , and covers an

area of about 19.4Km<sup>2</sup> (Fig. 1). Water supply to the people of the area is from hand-dug wells, boreholes and surface water obtain from streams and ponds. These sources of water supply have questionable quality due to anthropogenic activities such as agricultural activities and indiscriminate waste disposal practice. The population of the area is about 2500 (National Population Commission, 2005). The area falls within the Savannah wood land (Du Preeze and Barber, 1965) with mean annual rainfall ranging from 1250 mm to 2500 mm (Offodile, 2002). The area is largely drained by River Saradam. The altitude of the area ranges from 100 m to 1500 m (Offodile, 2002).

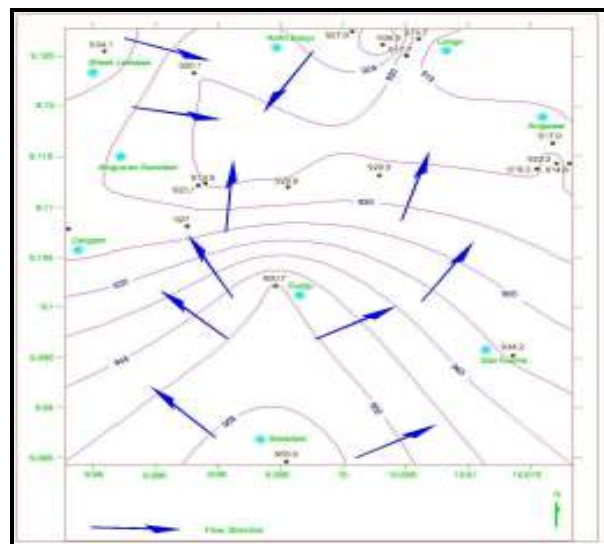
The Plateau province is underlain by the younger granite suite, which includes granites, syenites and rhyolites (Du Preeze and Barber, 1965) and metasediments and volcanic rocks of different petrology (Offodile, 2002). The study area lies within the Plateau province, and is underlain by the undifferentiated migmatites, hornblende-biotite granite porphyry and rhyolites (Fig. 1).



**Figure 1:** Geologic Map of the Study area Showing Sample Locations

The areas underlain by the undifferentiated migmatites are relatively flat, low-lying and occur in massive forms. They are characterized by leucocratic and melanocratic banding caused possibly by metamorphism. The mafic minerals are characterized by fine crystals while the felsic minerals have larger crystals. The

phenocrysts of the feldspars range from 0.3 cm to 0.5 cm. The undifferentiated migmatites form the dominant rock types and covers extensive areas. Minerologically, the rocks consist of quartz, feldspars and mafic minerals. The hornblende-biotite granite porphyry occurs as elongate ridge with a relatively high topography of about 1234 m in the southern part of the study area. It is exposed in the north-eastern and northern parts of the study area. Minerologically, the rocks consist of hornblende, biotite, quartz and feldspars. The feldspars range in size from 1 cm to 1.6 cm and quartz phenocrysts range from 0.1 cm to 0.6 cm. The biotites are fine grain in texture and form the groundmass. The rhyolites outcrop in the northern part of the study area. It is extrusive in nature, and characterized by fine grain texture. It occurs at an elevation of about 1034 m. Figure 2 indicates that regional groundwater flow takes place from the recharge area at Saradam in the south, and flows towards Dan Kurma and Zangam in the southwest. Another flow zone takes place from Shere Jankasa in the northwest and flows towards the northern part of the study area.



**Figure 2:** Hydraulic Head Distribution in Unconfined Aquifer

A minor recharge zone occurs between Rafin Sanyi and Lenge areas in the north and flows towards the north-eastern part. The major discharge area occurs between Anguwan Saradam and Angware areas.

Shoeneich and Aku (1996) identified two groundwater zones into fractured aquifer and soft overburden aquifer with yield exceeding 10 m<sup>3</sup>/hr. The soft overburden aquifer consists of clay lenses, sandy clay and gravels with effective porosity ranging from 2.0 to 2.5 (Shoeneich and Aku, 1996). Bulus (2010) carried out geophysical investigation in the area and discovered that most of the fractures vary between the depth ranges of 5 m to 25 m and are isolated fractures with average weathered overburden thickness of 19.4 m.

**Methodology:**

Twenty (20) water samples were collected consisting of 14 samples from the hand-dug wells and 6 samples from boreholes (Fig. 1). The samples were collected from existing wells use for water supply according to Chilton (1992) method. All samples were filtered through 0.45 µm membrane filter immediately after sampling. The samples were collected in two polythene bottles. One of the samples was dedicated to cation analysis, and trace metal analysis was acidified with nitric acid to discourage bacterial action and oxidation process. The second sample was used for the analysis of

anions. Before the collection of the samples, field parameters such as pH, temperature and TDS were determined in the field using pH meter (Wagtech), and conductivity/TDS meter (HACH). The sample containers were rinsed twice with the sample to be collected according to Barcelona et al (1985) method. The chemical parameters were analyzed using flame photometer (ELE International), spectrophotometer (Model DR2000, USA) and titrimetric method. The water samples were analyzed at the Acts laboratory, Canada. The results were analysed using Multivariate statistical analysis (PCA and CA)

**Results and Discussions:**

The summary of physical and chemical parameters is presented in Table 1. From the results, the ranges and means of the physical and chemical parameters reveal temperature range from 19.1°C to 28°C and mean of 22.2°C, pH ranges from 5.8 to 7.6 with an average of 6.5, thus indicating acidic to neutral, and mean value indicates slightly acidic condition. TDS and total hardness vary from 3.3 mg/l to 1900 mg/l and 15.9 mg/l to 62.89 mg/l with mean values of 548.5 mg/l and 20.4 mg/l, respectively.

**Table 1:** Summary of Physical and Chemical Parameters in the Area

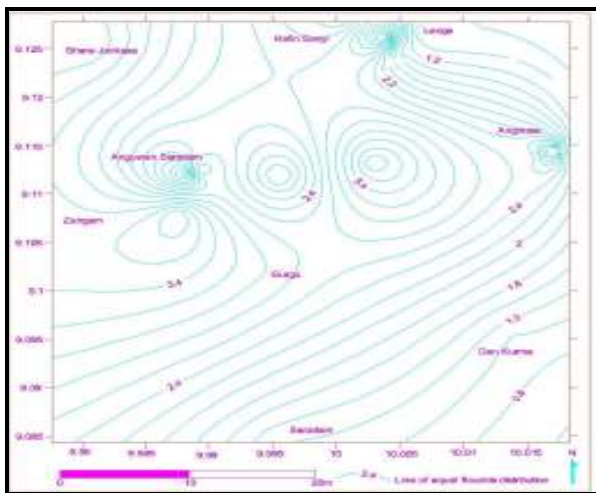
	Minimum	Maximum	Mean	Std. Deviation	WHO(2004)
Temperature	19.10	28.00	22.2000	3.21968	
pH	5.80	7.60	6.5316	0.63162	6.5-9.2
TDS (mg/l)	3.27	1900.00	548.5135	604.46925	500
Sodium (mg/l)	1.70	38.10	9.7150	10.98713	200
Potassium (mg/l)	0.20	7.10	1.6100	1.58443	150
Calcium (mg/l)	4.40	18.20	8.2450	4.33729	75
Magnesium (mg/l)	1.00	4.70	2.1300	1.23122	50
Iron (mg/l)	0.10	3.80	1.9500	1.31449	1.0
Lead (mg/l)	0.03	0.14	0.0670	0.03147	0.01
Bicarbonate (mg/l)	19.60	318.40	74.7550	85.12062	500
Sulphate (mg/l)	0.10	6.00	1.4000	1.269989	250
Chloride (mg/l)	1.10	28.40	7.5000	7.66365	200
Fluoride (mg/l)	4.00	4.00	2.4350	1.19441	1.5
TH (mg/l)	62.80	62.80	29.3600	15.37306	

Water hardness is caused primarily by the presence of cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup> and anions such as carbonate, bicarbonate, chloride and sulphate in water (Sadashivaiah et al., 2008). According to Sawyer and McCarty (1967) classification; hardness ranging from 0-75 mg/l is classified as soft;

75-150 mg/l as moderate; 150-300 mg/l as hard and >300 mg/l as very hard. Based on the above classification, the water can generally be classified as soft. The ranges and means of the cations indicate the following Na<sup>+</sup> (1.7 mg/l-38.1 mg/l) 9.7 mg/l, K<sup>+</sup> (0.2 mg/l-7.1 mg/l) 1.6 mg/l, Ca<sup>2+</sup>

(4.4 mg/l-18.2 mg/l) 8.2 mg/l,  $Mg^{2+}$  (1 mg/l-4.7 mg/l) 2.1 mg/l,  $Fe^{2+}$  (0.1 mg/l-3.8 mg/l) 2 mg/l and  $Pb^{2+}$  (0.03 mg/l-0.1 mg/l) 0.07 mg/l. The results of the anions indicate that  $HCO_3^-$  (19.6 mg/l-318.4 mg/l) 74.8 mg/l,  $SO_4^{2-}$  (0.1 mg/l-6 mg/l) 1.4 mg/l,  $Cl^-$  (1.1 mg/l-28.4 mg/l) 7.5 mg/l and  $F^-$  (1 mg/l-4 mg/l) 2.4 mg/l. Based on the mean values of the chemical parameters, the relative abundance of the cations is in the order of  $Na^+ > Ca^{2+} > Mg^{2+} > Fe^{2+} > K^+ > Pb^{2+}$  while those of the anions are  $HCO_3^- > Cl^- > F^- > SO_4^{2-}$ . The correlation of the mean values of the groundwater quality data with the World Health Organization (WHO) standards indicate that the cations, TDS and total hardness are all below the maximum recommended limit,  $Pb^{2+}$  range above the maximum recommended limit while the anions,  $F^-$  range above WHO recommended limit.  $Pb^{2+}$  has been classified as potentially hazardous and toxic to most forms of life (USEPA, 1986); it causes a number of ailments in humans such as neurological disorder in fetuses and children (Orebiyi et al., 2010).

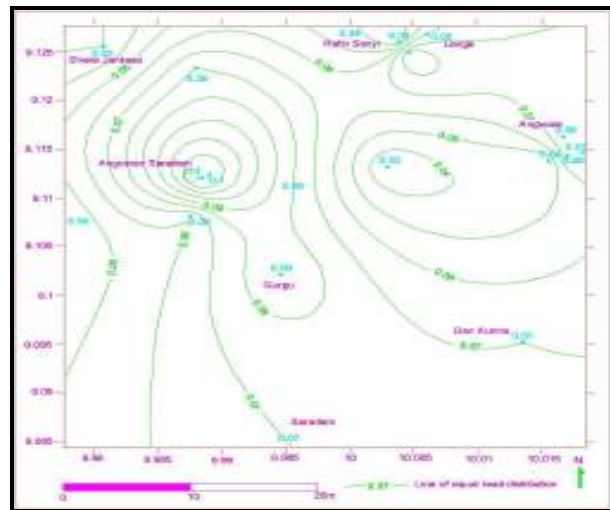
Fluoride content in drinking water is responsible for human and animal health problems causing dental and skeletal fluorosis (Nanni et al., 2008).



**Figure 3:** Distribution of Fluoride in the Study Area

Figure 3 indicates fluoride plumes having concentrations of 4 mg/l occur around Zangam, and between, Anguwan Saradam

and Angware and Rafin Sanyi areas. Shoeneich and Aku (1996) attributed the source of fluoride to be leached from the basement rocks. Figure 4 shows the distribution of lead with a minor plume occurring at Anguwan Saradam having concentration of 0.1 mg/l. This plume decreases down gradient towards Shere Jankasa and Angware areas. The source of lead is attributed to anthropogenic activities associated with mining activities as well as indiscriminate waste disposal practices in the area.



**Figure 4:** Distribution of Lead in the Study Area

**Principal Component Analysis.**

PCA was applied to the groundwater quality data to examine the relationship between water properties analyzed and to identify the factors that influence the concentration of each factor. The factor loadings were sorted out according to Liu et al (2003) into strong, moderate and weak which corresponds to loading values >0.75, 0.75-0.50 and 0.50-0.30. Principle component analysis rendered three significant factors (Table 2) explaining 74.55% of the total variance of the groundwater quality data. Factor 1 explain 47.7% of the variance and is characterized by the strong positive loadings with respect to  $Na^+$  (0.97), TH (0.96),  $Mg^{2+}$  (0.94),  $Ca^{2+}$  (0.93),  $Cl^-$  (0.90) and  $HCO_3^-$  (0.90).

**Table 2:** Factor Loading Matrix for Groundwater Chemistry Data in the Area

	Component		
	1	2	3
Temperature	.142	-.693	-.219
pH	-.090	.877	.281
TDS (mg/l)	.051	.799	-.358
Sodium (mg/l)	.970	-.013	.064
Potassium (mg/l)	.690	.147	-.052
Calcium (mg/l)	.931	.203	.025
Magnesium (mg/l)	.938	-.049	-.014
Iron (mg/l)	.539	.421	-.355
Lead (mg/l)	-.514	.026	-.414
Bicarbonate (mg/l)	.895	-.276	.091
Sulphate (mg/l)	-.271	.053	.872
Chloride (mg/l)	.904	-.326	.052
Fluoride (mg/l)	.559	.225	.198
TH (mg/l)	.964	.127	.014
%variance	47.73	17.03	9.80
%cumulative variance	47.73	64.76	74.55

These strong positive loadings are confirmed by the strong positive correlations (Table 3) between  $Ca^{2+}$ - $Na^{+}$  ( $r=0.93$ ),  $Mg^{2+}$ - $Na^{+}$  ( $r=0.88$ ),  $HCO_3^{-}$ - $Na^{+}$  ( $r=0.89$ ),  $Cl^{-}$ - $Na^{+}$  ( $r=0.90$ ) and  $TH$ - $Na^{+}$  ( $r=0.94$ ) (Table 4). Others include  $Cl^{-}$ - $Mg^{2+}$  ( $r=0.81$ ),  $TH$ - $Mg^{2+}$  ( $r=0.93$ ) and  $Cl^{-}$ - $HCO_3^{-}$  ( $r=0.99$ ),  $TH$ - $HCO_3^{-}$  ( $r=0.80$ ) and  $TH$ - $Cl^{-}$  ( $r=0.81$ ). These strong positive correlations are an indication of a common source. Factor 1 therefore can be ascribed to the signatures of natural water recharge and water-soil/rock interaction. Surface water charged with atmospheric  $CO_2$  infiltrates into subsurface and aggressively attack aluminosilicates including feldspars and micas (Olobaniyi and Owoyemi, 2006) liberating cations such as  $Na^{+}$ ,  $Ca^{2+}$  and

$Mg^{2+}$  into water leaving clay minerals. The dominant cation in factor 1 is  $Na^{+}$  followed by  $Mg^{2+}$  and  $Ca^{2+}$ , and the dominant anion is  $Cl^{-}$  followed by  $HCO_3^{-}$ . Factor 1 therefore represents  $Na$ - $Mg$ - $Ca$ - $Cl$ - $HCO_3$  facies. Possible water types could be classified into  $Na$ - $HCO_3$ ,  $Na$ - $Cl$ ,  $Ca$ - $Cl$  and  $Ca$ - $Mg$ - $HCO_3$  and the water types could have been evolved through cation exchange ( $Na$ - $HCO_3$ ), saline water (fossil water) ( $Na$ - $Cl$ ), reverse cation exchange ( $Ca$ - $Cl$ ) and represents water of intermediate composition between  $Ca$ - $Mg$ - $HCO_3$  and  $Na$ - $Cl$  waters, and recently recharged water (meteoric water) due to the dissolution of aluminosilicates ( $Ca$ - $Mg$ - $HCO_3$ ).

**Table 3** Correlation Matrix of Some Chemical Parameters in the Area

	Temp	pH	TH	TDS	Sulfate	Potassium	Calcium	Magnesium	Iron	Lead	Bicarbonate	Sulphate	Chloride	Fluoride
Temp	1													
pH	-.440	1												
TH	.112	.082	1											
TDS	-.219	.417	.177	1										
Sulfate	.124	-.089	.042	-.088	1									
Potassium	-.375	-.073	.041	.142	.821	1								
Calcium	.383	.118	.065	.279	.828	.521	1							
Magnesium	.376	-.048	.430	-.038	.818	.818	.593	1						
Iron	-.288	.188	.823	.288	.427	.352	.428	.588	1					
Lead	-.028	-.071	-.452	.368	-.407	-.238	-.418	-.484	-.107	1				
Bicarbonate	.246	-.321	.860	-.172	.804	.828	.777	.788	.333	-.400	1			
Sulphate	-.138	.323	-.210	-.277	-.086	-.190	-.359	-.204	-.344	.812	-.188	1		
Chloride	-.388	-.321	.867	-.198	.801	.828	.766	.812	.328	-.882	.881	-.458	1	
Fluoride	-.088	.178	.874	.255	.821	.828	.841	.808	.217	-.224	.488	-.852	.438	1

TH= Total hardness, TDS= Total dissolved solids

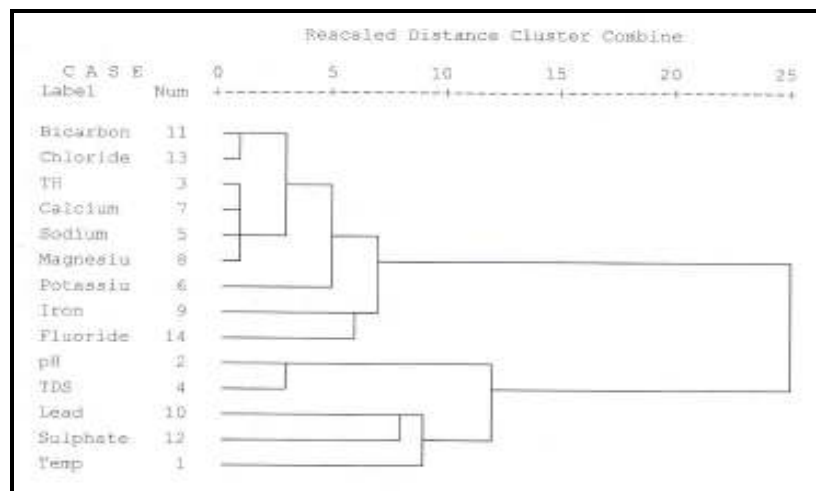
Factor 2 explains 17.03% of the variance and has strong loading for pH (0.88) and TDS (0.80). Table 2 indicates moderate loading between TDS and pH ( $r=0.62$ ) and insignificant loading between TDS, pH,  $Fe^{2+}$  (0.19-0.27). Table 2 further reveal moderate negative correlation between pH-temperature ( $r=-0.54$ ) and insignificant negative correlation between TDS-pH ( $r=-0.22$ ). TDS comprises of inorganic salts majorly  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $HCO_3^-$  and  $SO_4^{2-}$  and small amounts of organic matter dissolved in it (Amadi et al., 2010). TDS therefore is controlled by the dissolution of these ions in the water through geogenic or anthropogenic inputs. Factor 2 explains the relationship between ions dissolved in water and the influence of pH on the reactions that take place between them. Factor 3 explains 9.80% of the variance and has high loading for only  $SO_4^{2-}$  (0.87). Table 2 indicates insignificant correlation with the chemical parameters and insignificant positive correlation with pH. These suggest  $SO_4^{2-}$  may have been derived from anthropogenic sources. It can be deduced that factor 1 contains hydrochemical variables originating from weathering process and formation

dissolution, factor 2 explains the dependence of TDS on dissolved ions in water influenced by pH and factor 3 is related to anthropogenic contamination. The different factors revealed by PCA can be summarized as follows:

Factor 1 ( $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , TH,  $Cl^-$  and  $HCO_3^-$ )  
 Factor 2 (TDS and pH)  
 Factor 3 ( $SO_4^{2-}$ )

#### Cluster Analysis:

The hierarchical cluster analysis according to Ward (1963) with squared Euclidean distances was applied to detect multivariate similarities in groundwater quality. The dendrogram resulting from the cluster analysis (Fig. 4) displayed three clusters. Cluster 1 comprised of bicarbonate, chloride, calcium, TH, sodium and magnesium showing close similarities, and included potassium, iron and fluoride in the same cluster. This cluster represents the effect of water-rock interaction, leading to silicate mineral weathering. Cluster 2 comprised of pH and TDS showing close similarity followed by lead and sulphate and included temperature in the same cluster.



**Figure 4:** Dendrogram of Cluster Analysis of Groundwater Chemistry in the Study Area

Cluster 2 can be interpreted as anthropogenic contamination. Sulphate could have resulted from the application of sulphate fertilizer while lead could have been derived from paints, battery, car scraps, tire wears, insecticides and automobile exhaust. Cluster 2 can be

interpreted as resulting from the dissolution of sulphide bearing minerals such as galena, however, Table 3 indicated negative insignificant correlation between lead and sulphate ( $r=-0.1$ ), thus indicating different sources.

### Conclusions:

Twenty water samples were collected and analyzed using DR2000 spectrophotometer, flame photometer and titrimetric method. The results indicate that the relative abundance of the cations were in the order of  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Fe}^{2+} > \text{K}^+ > \text{Pb}^{2+}$  while those of the anions were  $\text{HCO}_3^- > \text{Cl}^- > \text{F}^- > \text{SO}_4^{2-}$ . The groundwater quality is unfit for human consumption without treatment due to high fluoride content and lead contamination.

Principal component analysis identified three factors that account for 74.55% of the total variance. Factor 1 includes high loadings for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TH,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  and is related to soil/rock interaction and also represents Na-Mg-Ca-Cl- $\text{HCO}_3$  facies. Factor 2 includes high positive loading for pH and TDS and factor 3 has high loading for only  $\text{SO}_4^{2-}$  which may be related to anthropogenic influence.

Cluster analysis identified two clusters that are related to natural mineralization and anthropogenic contamination. Cluster 1 has close similarities for  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , TH and included  $\text{K}^+$ ,  $\text{Fe}^{2+}$  and  $\text{F}^-$  in the same cluster and is related to natural mineralization. Cluster 2 comprised of pH and TDS in close similarities followed by  $\text{SO}_4^{2-}$  and  $\text{Pb}^{2+}$  and included temperature in the same cluster and is related to anthropogenic contamination. PCA and CA indicated that the variables responsible for groundwater composition are related to natural mineralization and anthropogenic sources. It is recommended that groundwater quality monitoring should be encouraged for the identified chemical parameters constituting groundwater quality problems.

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