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MULTIVARIATE STATISTICAL ANALYSIS OF GROUNDWATER CHEMISTRY DATA FROM HADEJIA LOCAL GOVERNMENT AREA OF JIGAWA STATE, NIGERIA

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ABSTRACT

The multivariate statistical tools cluster analysis (CA) and principal component analysis (PCA) were simultaneously applied to groundwater hydrochemical data of Hadejia Local Government area Jigawa State, Nigeria to extract principal processes controlling water chemistry. The combined use of both techniques resulted in more reliable interpretations of the hydrochemistry. They revealed 2 processes responsible for water chemistry which is an anthropogenic activities and natural (mineralization and weathering of geological deposits). A total of 20 sampling points were selected for the study, the groundwater samples were collected in triplicate and analyzed for physicochemical and trace metals values. Test of significance of the observed correlation coefficients have been tested and shows high positive correlation between TDS and NO_3^- , as $r = 0.835$, TDS and Cu as $r = 0.866$, NO_3^- and Cu as $r = 0.75$, while marked/moderate positive correlations between Mg and Cl^- as $r = 0.585$, Cl and Cu as $r = 0.550$, TDS and Mn as $r = 0.551$, Mg and Mn as $r = 0.557$, Cu and Mn as $r = 0.560$ were observed, this suggest that the aquifer chemistry is mainly controlled TDS, Mg, NO_3^- , Cu, Cl, and Mn which indicates the origin of major cations to be dissolution/precipitation processes (Kwatiwada et al., 2002), these strong positive correlations are an indication of common source. Cluster analysis results grouped the 20 sampling points into five statistically significant clusters based on their similarities. PCA was used to investigate the origin of each water quality parameters and yielded five Varimax factors/components with 75.28% total variance, indicating the major variations are related to anthropogenic activities and natural processes.



Keywords: Groundwater Chemistry, Hadejia, Cluster Analysis, Principal Component Analysis

1. INTRODUCTION

Water is the essence of life and safe drinking water is a basic human right essential to all (Versari, *et al.*, 2002). It is essential for the wellbeing of mankind and for sustainable development. Though, necessary for human survival, many are denied access to sufficient potable drinking water supply and sufficient water to maintain basic hygiene. The effects of drinking contaminated water results in thousands of deaths every day, mostly in children under five years in developing countries (WHO, 2004). Thus, access to safe clean water and adequate sanitation is a fundamental right and a condition for basic health (Palamuleni, 2002). The use of shallow ground water sources for drinking and other domestic purposes is a common feature for many low income communities in developing countries.

Pollution of ground water refers to any deterioration in the quality of the water resulting from the activities of man. This definition also includes apparently natural processes like salt water encroachment into freshwater- bearing aquifers in coastal areas resulting from the artificial lowering of ground-water heads. Most pollution of ground water results from the disposal of domestic, municipal and industrial wastes on the land surface, in shallow excavations including septic tanks, or through deep wells and mines; the use of fertilizers and other agricultural chemicals; leaks in sewers, storage tanks, and pipelines; and animal feedlots. The magnitude of a pollution problem depends on the size of the affected area, the amount of the pollutant involved, the solubility, toxicity, and density of the pollutant, the mineral composition and hydraulic characteristics of the soils and rocks through which the pollutant moves, and the effect or potential effect on ground-water use. The use of physic-chemical properties of water to assess water quality gives a good impression of the status, productivity and sustainability of such water body (Mustapha, 2008).

The term multivariate analysis, as usually applied by chemometricians, defines any statistical, mathematical or graphical approach which considers multiple variables simultaneously. This is slightly different from the standard statisticians' definition of multivariate analysis, which requires that multiple dependent variables be considered simultaneously in the analysis.

Chemometrics is broadly defined as the application of mathematical and statistical methods to chemistry, because the mathematical and statistical aspects of chemistry require measured values. Analytical chemists have been at the forefront of the chemometrics revolution (Stanley, 1986). As such, chemometrics represents an exciting dynamic field that contributes to a better understanding and improved application of chemistry.

Multivariate techniques such as factor analysis, principal component analysis, and cluster analysis are powerful techniques to identify the underlying processes that control groundwater chemistry, grouping of samples of similar composition and origin, and to predict the variables that differentiate the sampling stations temporally and spatially. These techniques have widely been used as unbiased methods in the analysis of groundwater quality data to characterize groundwater composition influenced by natural and anthropogenic factors (Lambrakis *et al.*, 2004; Ruiz *et al.*, 1990; Dragon, 2006). The principal component analysis was carried out to identify factors influencing the quality of groundwater. The 15 variables were taken into account for PCA, and were carried out on the normalized data set to eliminate the effect of the data measurement scale (Mohapatra *et al.*, 2011).

The study is aimed at analyzing the physic-chemical parameters and trace metals levels in groundwater samples (boreholes) from twenty (20) sampling locations in Hadejia L.G.A. of Jigawa State and to analyze the results using Chemometrically using Multivariate Statistical Techniques: Principal Component Analysis (PCA) and Cluster Analysis (CA) to detect the factors influencing the quality of groundwater and detect the similarity among the variables and different sampling sites.

2. MATERIALS AND METHODS

2.1 Study Area

Hadejia local government lies on the northern-bank of the River Hadejia which drained into lake Chad, it lies in the north eastern corner of Jigawa state ($12^{\circ} 13' - 13^{\circ} 60'N$ latitude and $9^{\circ} 22' - 11^{\circ}00'E$ longitude). The area is underlain by rock and younger sediments of the Chad formation, which are of quaternary age. The topography of the area is dominated by the river which at some points is 1-2 metres above the surrounding plains including the town. The relief is generally undulating, usually below 400 metres above sea level. The climate of the area is semi arid. It is characterized by long dry season and a short wet season from June to September. The climatic variables vary considerably during the year. However, the micro- climate is modified by the local effect of the



Hadejia River system, making the temperature slightly cooler in the southern parts. The mean annual temperature is about 25°C but the mean monthly values range between 21°C in the coolest month and 31°C in the hottest month. The total annual rainfall ranges from 600 mm in the northern part to 762 mm in the southern areas. The regional vegetation falls within the Sudan Savannah type. Extensive open grasslands with few scattered trees are characteristic of the vegetation.

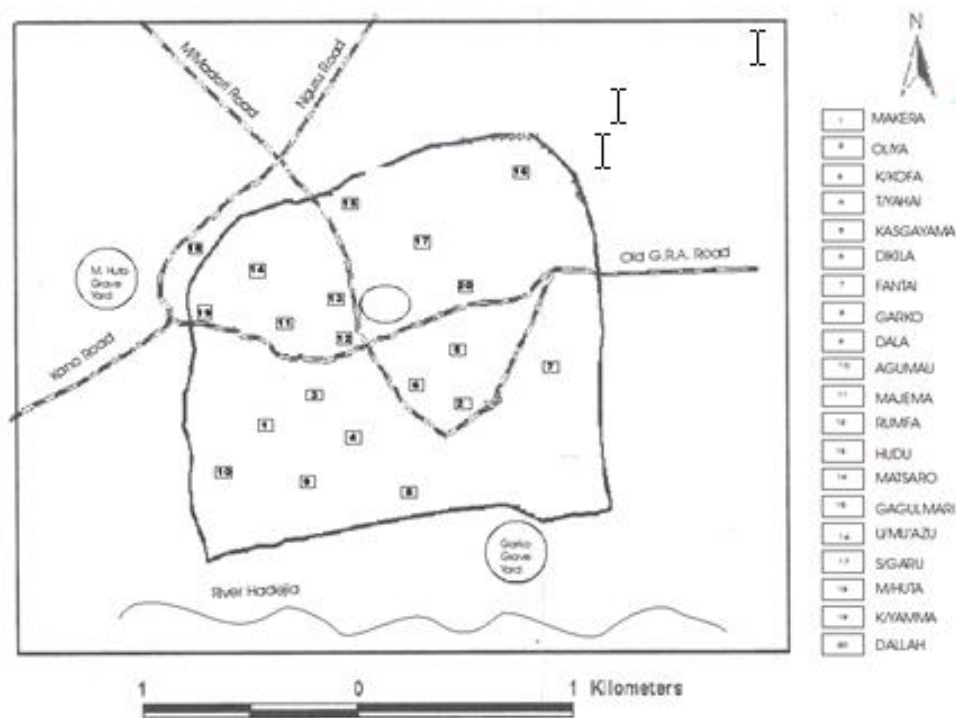


Fig. 1: Map of Hadejia local government area showing sampling sites

Groundwater samples for the analysis were collected from 20 different sites monthly in June, July, and August 2013 during the wet season. All the samples were collected and treated in accordance with the (APHA, 2005, ASTM, 2004). The boreholes were allowed to flow for about 3 minutes before the water is collected.

Parameters such as Temperature, pH, Electrical conductivity, Total Hardness, Ca, Mg, were determined using standard methods for the examination of water samples quality (ASTM, 2004). Temperature, pH, Electrical Conductivity, and Total Dissolved Solids were measured using Hanna pH 210 model microprocessor, EQ-660 digital conductivity meter and Hatch 446600 model TDS meter respectively. Total Hardness, Ca, mg were determined using titrimetric method. NO₃⁻, Cl⁻, Fe, Cu, Zn, Mn, Cr and Pb were determined using CHEMetrics Vacu-Visual self filling ampoules water testing kits with CHEMetrics Photometric Multi Element Analyzer model V-2000. The samples were chemically analyzed at the Centre for Energy, Research and Training, ABU Zaria.

2.2 Data Analysis

These data generated was analyzed using IBM SPSS® (statistical software for social science)(released- 21.0 for widows evaluation standard version), and XLSTAT® 2010 (Microsoft Office). The well founded techniques of Pearson Correlation Analysis, Principal Component Analysis (PCA) and Cluster Analysis (CA) was jointly used, the first affording a direct measure of interdependence of the set of variables under investigation while the latter two provide the data reduction, pattern recognition and visual grouping of the data to help understand interrelated parameters and site clusters produced.



3. RESULTS AND DISCUSSION

Table 1: Physico-chemical parameters of groundwater of Hadejia

Parameter	Range	NSDWQ, 2007	WHO, 2011
pH	6.12 - 7.97	6.5 - 8.50	6.5 - 8.50
Temperature(°C)	26.90 - 27.60	Ambient	Ambient
Conductivity (µs/cm)	163 – 1706	1000	1000
Total hardness(mg/L)	112 – 553	150	150
TDS(mg/L)	98 – 799	500	500
Fe(mg/L)	0.19 - 0.89	0.30	0.30
Cu(mg/L)	0.03 - 5.59	1.0	1.0
Zn(mg/L)	0.02 - 2.39	3.0	3.0
Mn(mg/L)	0.33 - 19.79	0.20	0.20
Cr(mg/L)	0.09 - 0.30	0.05	0.05
Pb(mg/L)	0.02 - 2.99	0.01	0.01
Ca(mg/L)	22.0 – 136.0	NS	75
Mg(mg/L)	19.0 – 76.00	50-150	50-150
Cl ⁻ (mg/L)	2.05 – 27.11	250	250
NO ₃ (mg/L)	1.71 - 47.70	50	50

3.1 Pearson Product Moment Correlation Analysis

Correlation coefficient is commonly used to measure and establish the relationship between two variables. It is a simplified statistical tool to show the degree of dependency of one variable to the other (Belkhiri *et al.*, 2011).

Test of significance of the observed correlation coefficients have been tested as shown in Table2.



Table 2: Pearson Product Moment Correlation Analysis

	pH	Temp	EC	TH	TDS	Ca	Mg	Cl	NO ₃	Fe	Cu	Zn	Mn	Cr	Pb
pH	1	0.19	-0.108	-0.17	-0.117	0.026	-0.31	-0.217	0.134	0.053	0.003	-0.3	0.068	0.083	0
Temp		1	0.217	0.034	-0.14	-0.31	0.077	0.014	-0.272	0.045	-0.134	-0.01	0.076	0.172	0.218
EC			1	0.355	-0.192	-0.27	-0.3	-0.225	-0.341	-0.22	-0.305	-0.08	-0.116	.488*	-0.4
TH				1	.453*	0.157	-0.12	-0.137	0.41	-0.195	0.282	-0.13	0.117	-0.05	-0.08
TDS					1	0.143	0.175	.478*	.835**	-0.125	.866**	-0.17	.551*	-0.29	-0.22
Ca						1	-0.11	0.062	0.224	-0.08	0.114	0.331	-0.185	-0.18	0.131
Mg							1	.585**	-0.023	0.379	0.319	0.213	.557*	-.472*	0.126
Cl								1	0.207	.458*	.550*	0.141	0.424	-.499*	-0.05
NO ₃									1	0.003	.751**	-0.28	0.28	-0.36	-0.18
Fe										1	-0.092	-0.1	-0.072	-.555*	0.332
Cu											1	-0.19	.560*	-0.38	-0.21
Zn												1	-0.093	-0.11	0.201
Mn													1	-0.14	-0.1
Cr														1	-0.34
Pb															1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

The correlation analysis between TDS and Cu, TDS and NO₃⁻, NO₃⁻ and Cu shows high positive correlation as $r = 0.866$, 0.835 and 0.751 respectively, while Mg and Cl⁻, Cu and Mn, Mg and Mn, TDS and Mn, Cl⁻ and Cu, shows marked/moderate positive correlation as $r = 0.585$, 0.560 , 0.557 , 0.551 and 0.550 respectively. This suggests that the aquifer chemistry in the wet season also is mainly controlled by TDS, Mg, NO₃⁻, Cu, Cl⁻, and Mn, which indicates the origin of major cations to be dissolution/precipitation processes (Khatriwada *et al.*, 2002), while presence of higher Cl⁻ contents detected in certain samples may suggest the dissolution of chloride salts. Presence of high NO₃⁻ result from the filtration, percolation and seepage and could be as a result of nearness of some of the boreholes to the landfill and refuse dumping site, this agreed with the findings of Srinivasamoorthy *et al.*, (2009) in their study.

These strong positive correlations are an indication of common source. Correlation analysis reveals similarities or differences in the behaviour of pairs of ions and does not conveniently identify groups of ions that behave similarly (Akoteyo and Sokadoye, 2011).

3.2 Principal Component Analysis

PCA techniques allow the association between the variables to be identified, thus reducing the dimensionality of the datasets. It is a powerful technique for pattern recognition that attempt to explain the variance of a large set of interrelated variables. The principal component analysis has emerged as a useful tool to better understanding the relationship among the variables.

In this study, a factor with an eigenvalue > 1.0 was considered for subsequent discussion. The results in Table 2 shows that five (5) principal components were extracted and rotating using the

varimax normalization (Kaiser, 1960) which accounts for more than 78% of the total variance, which is quite good and can be relied upon to identify the main sources of variation in the hydrochemistry. The factor loading were sorted according to the criteria of (Liu *et al.*, 2003) by which strong, moderate and weak loadings corresponds to absolute loading values of > 0.75 , $0.75 - 0.50$, and $0.50 - 0.30$ respectively



Table 2: PCA Rotated Component Matrix with Kaiser Normalization

	VF1	VF2	VF3	VF4	VF5
pH	0.024	-0.086	0.061	-0.815	-0.232
Temp	-0.041	-0.034	-0.213	-0.071	0.069
EC	-0.292	-0.378	-0.580	0.207	0.447
TH	0.235	-0.093	0.031	0.052	0.915
TDS	0.882	0.022	0.082	-0.022	0.339
Ca	0.025	-0.045	0.788	0.065	0.142
Mg	0.453	0.435	-0.080	0.505	-0.326
Cl ⁻	0.575	0.478	-0.084	0.376	-0.210
NO ₃ ⁻	0.688	0.136	0.216	-0.358	0.358
Fe	-0.113	0.915	-0.136	-0.029	-0.104
Cu	0.917	0.081	0.080	-0.064	0.123
Zn	-0.133	-0.131	0.519	0.661	-0.192
Mn	0.802	-0.061	-0.175	0.087	-0.178
Cr	-0.302	-0.783	-0.301	-0.094	-0.041
Pb	-0.246	0.451	0.507	-0.037	-0.008
Eigen values	4.020	2.658	1.828	1.579	1.176
% of Variance	27.015	17.718	12.188	10.524	7.838
Cumulative %	27.015	44.733	56.921	67.445	75.284

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

Rotation converged in 10 iterations.

The first principal factor VR1 explained for 27.01% of the total variance, which represent higher loading for TDS, Cl⁻, NO₃⁻, Cu and Mn with significance contribution from Mg. The dissolution and weathering process of the mineral is mainly responsible for the release of Mn, however, the activities is also controlled by the redox level of the groundwater.

It is reasonable to observe a strong positive correlation of TDS with NO₃⁻ and, TDS with Cu, Mg with Cl⁻ represented the abundant mineral elements in the groundwater. Therefore VR1 is accordingly defined as the salinization factor. The higher Cl⁻ and TDS is an indication that there is a possibility that the groundwater is polluted by sewage, or waste from refuse dumping site (Liu *et al.*, 2003), high chloride has health



implication on human and could impart taste in water. High NO_3^- concentration in water causes blue-baby syndrome (methaenoglobaemia) (Khatiwada et al., 2002).

The data in VR1 suggests that process such as mineral dissolution, weathering and pollution from anthropogenic activities are occurring in the groundwater. These ions in the component are related to weathering (Mohapatra *et al.*, 2011). These parameters are reactive components of partial anthropogenic origin and are indicators or reflect the status of inorganic pollution. This factor can be labeled or interpreted as a measurement of mineral component of the groundwater (Vega *et al.*, 1998). High NO_3^- concentration in the sample may originate from a number of sources, geological deposits, natural organic matter decomposition and deep percolation of nitrate from organic compounds (Matthess, 1982).

The high TDS values observed in the groundwater samples may be due to pollution discharges from pits and ponds e.t.c. This factor can be labeled as the salt or hardness component because it is mainly saturated with hardness including calcium.

The second principal factor VR2 accounted for 17.72% of the total variance, which also represent higher loading for iron and negative higher loading for Cr with significance contribution from Mg, Cl and Pb. These could be conceived to mainly originate from the ionic dissolution in the course of groundwater migration.

The third principal factor VR3 accounted for 12.18% of the total variance and represents a higher loading for Ca and negative higher loading for EC with significance contribution from Zn and Pb. The group variables expresses water natural mineralization thus the degree of rock weathering and in other way, the residual time of water and the water-rock interaction.

The fourth principal factor VR4 accounted for 10.52% of the total variance which represent higher loading for Zn and Mg and negative higher loading from pH with significance contribution from Cl^- . Zinc can come from natural sources and acidic water tends to leach it out of rocks.

While the fifth principal factor VR5 for wet season accounted for 7.84% of the total variance which represent higher loading from T/Hardness with significance contribution from EC, TDS and NO_3^- . It is reasonable to observe a strong positive correlation of TDS with Cl^- and T/Hardness. TDS represented the abundant mineral elements in the groundwater and T/Hardness increases with TDS.

3.3 Cluster Analysis

Cluster analysis is applied to detect the similarity among the different sampling sites. The clustering procedure generates either cluster or groups on the basis of similarity or dissimilarity of variables (Demirel, 2004). Cluster analysis classifies a set of observations into 2 or more unknown groups based on combination of internal variables.

The dendrogram, a tree for visual classification of similarity, does not provide cluster assignments by itself, therefore the number of clusters to be formed must be interpreted by the user. One informal method cited by (Everitt, 2001) consists of making an examination of the difference between fusion level in the dendrogram, and cutting the dendrogram when large changes are observed (Demirel, 2004).

A classification scheme using the Euclidean distance for dissimilarity measures from dendrogram of 15 indexes based on the cluster analysis is depicted in figure below.

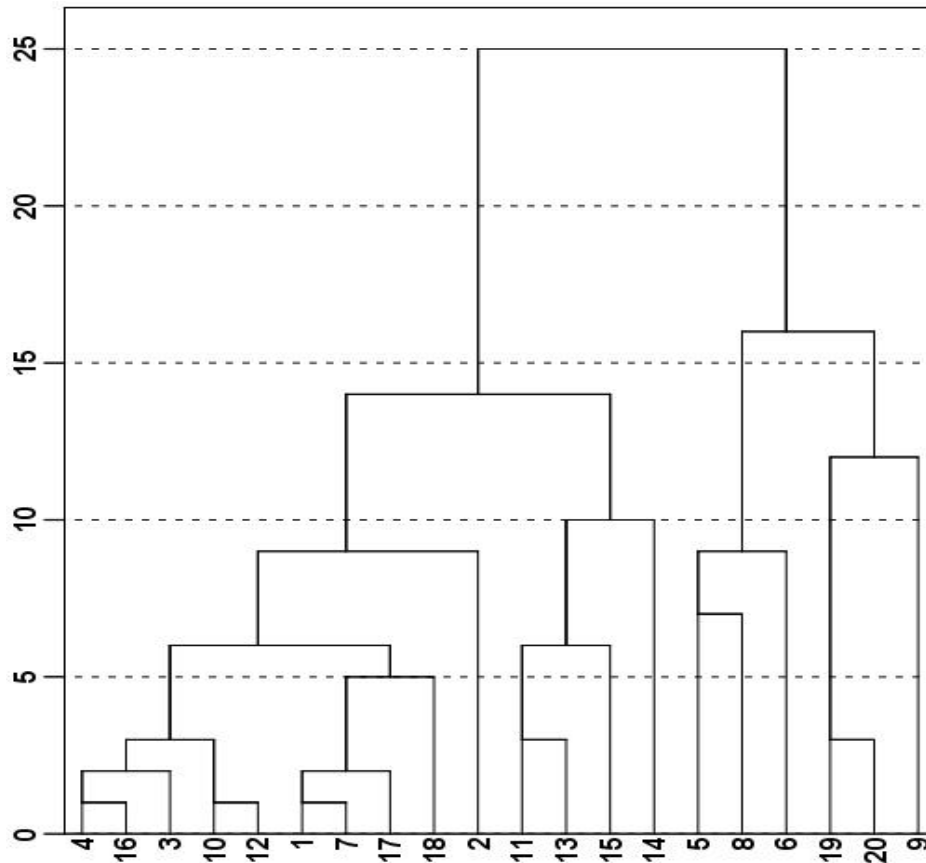


Figure 2 Dendrogram showing cluster analysis of sampling sites using Euclidean distance

However, in the wet season the results of cluster analysis generated 5 distinct clusters.

Cluster 1: consists of nine (9) boreholes which includes no. 4, 16, 3, 10, 12, 1, 7, 17, 18, and 2

Cluster 2: consist of one (1) borehole which include no. 2

Cluster 3: consists of four (4) boreholes which includes no. 11, 13, 15, and 14

Cluster 4: consists of three (3) boreholes which includes no. 5, 8, and 6

Cluster 5: consist of three (3) boreholes which includes no. 19, 20, and 9

It is possible in Cluster Analysis results that one single sample that does not belong to any of the group is placed in a group by itself. This unusual sample is considered as residue.



Table 3: Mean Parameters Values of the Four Principal Water Groups Determined from HCA

Cluster	pH	Temp °C	EC $\mu\text{S/cm}$	T/H mg/L	TDS mg/L	Ca mg/L	Mg mg/L	Cl ⁻ mg/L	NO ₃ ⁻ mg/L	Fe mg/L	Cu mg/L	Zn mg/L	Mn mg/L	Cr mg/L	Pb mg/L
1(n=9)	<u>6.05</u>	27.2	450	240	<u>255</u>	67.8	45	10.5	8.81	0.43	0.11	0.55	0.82	0.67	2.19
2(n=1)	6.76	27.1	<u>163</u>	<u>128</u>	352	51	45	21.3	12.5	0.56	1.8	0.37	<u>0.81</u>	0.14	2.01
3(n=3)	6.96	27.1	418	420	703	65	47	15.5	38.3	0.36	3.67	0.05	5.91	<u>0.13</u>	1.61
4(n=3)	6.78	27.3	1513	437	294	45.3	<u>35.3</u>	<u>9.49</u>	<u>5.57</u>	<u>0.28</u>	<u>0.00</u>	0.05	1.00	0.24	1.43
5(n=3)	7.10	27.0	1025	222	339	45.3	40.3	11.6	10.5	0.48	0.97	0.20	0.98	0.25	0.57

Samples from cluster I is composed of boreholes 1, 3, 4, 7, 10, 12, 16, 17 and 18 and constituted 45% of the water samples, and are characterized by high concentration of Ca, Cr, Zn and Pb and low concentration of TDS and pH in all clusters.

Samples from cluster II is composed of borehole 2 and constitute 5% of the water samples and is characterized by high concentration of Cl⁻ and Fe and low concentration of EC and T/Hardness and Mn in all clusters.

Samples from cluster III composed of boreholes 11, 13, 14 and 15 and constituted 20% of the water samples, and are characterized by higher concentration of TDS, Mg, NO₃⁻, Cu, Mn and low concentration of Cr in all clusters.

Samples from cluster IV is composed of boreholes 5, 6 and 8 and constitute 15% of the water samples, and are characterized by higher concentration of EC and T/Hardness and low concentration of Mg, Cl⁻, NO₃⁻, Fe, Cu in all clusters.

Samples from cluster V is composed of boreholes 9, 19 and 20 and constituted 15% of the water samples, and is characterized by having higher value of pH and lower concentration of Pb in the entire cluster.

It is possible in HCA results that one single sample that does not belong to any of the group is placed in a group by itself. This unusual sample is considered as residue.

4. CONCLUSION

The application of multivariate statistical methods both the cluster and principal component analysis has been more effective than the use of either one of them alone. They allow identifying the processes controlling the groundwater hydrochemistry. Two processes were identified indicating the major variations in groundwater chemistry in the study area are related to anthropogenic activities and natural processes.

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