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Characterization of Groundwater Hydrochemistry using Multivariate Statistical Techniques

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Abstract: **Pennagaram block of Dharmapuri district was taken our study. In our study area groundwater is a major water system for household and agricultural improvement. During the year of 2013, eighty groundwater samples were collected from various locations in the study area. The various ground water parameters were analyzed and computing various statistical tools using SPSS software version 16.0. The descriptive statistics shows, the average of cations are Ca^{2+} > Na^{+} > Mg^{2+} > K^{+} and anions are Cl^{-}> HCO_3^{-}> SO_4^{2-}>NO_3^{-} > F^{-}. It shows the cations and anions are highly adjustable with water constituents. The major ions are mainly influenced by EC. Based on dendrogram, the more significant parameters modify the value of EC and TDS. It might be caused by change in spatial and temporal variation. Correlation and Factor analysis shows the impact of alkaline and alkaline earth chlorides are dissolution from the soil. At higher pH ionic exchange occurs between F^{-} and OH^{-} ions resulting in increase of F^{-} ions in groundwater. This result identifies the water quality factors and spatial variations of water quality for resourceful water quality management.**

Keywords: **Groundwater, Pennagaram, Correlation, Factor analysis, Cluster analysis.**

I. INTRODUCTION

Groundwater is an essential source of water for rural and urban backgrounds. Groundwater is utilized as a major water system for household and agricultural improvement. Human prosperity is weakened by unhygienic surroundings open sewage conveying and positioning waste water into normal water bodies. Fast growth of urban areas, particularly in developing countries, has affected the availability and nature of underground water because of its dishonorable wastage transfer, especially in urban areas (Shivasharanappa et al. 2011).

Nearby 80% of the infections in human beings are caused by unclean aquatic resources. Better quality of water will resolve the social – financial advancement, as the administration need is moved to different segments of the economy. The superiority of water is depending on its physico-chemical and biological parameters. It is measured with the assistance of different parameters to show the contamination levels. With the use of directories to gather and compress huge measurements of water quality information has progressively picked up response to mirror the composite impact of those parameters (Al Meini, A.K. 2010).

It is essential to apply appropriate statistical methodology for analyzing water quality data to draw valid conclusions and hence provide useful advice in water management (Liya Fu et. al 2012). The water quality monitoring can produce large set of data, understanding those data sets cannot be easy. For accurate analysis of data, requires large range of chemical parameters (Lalitha et. al 2012).

In this context, multivariate statistical technique is an efficient way to display complex relationships among the parameters. They can be an effective means of managing, interpreting and representing data about groundwater constituents and geochemistry (Belkhiri et. al. 2010). The objective of this study was using multivariate statistics to understand the mechanisms potentially affecting the quality of water.

II. PROFILE OF THE STUDY AREA

The study area, lies between $77^0$46' to $78^0$04' East Longitude and 11^0 53' to $12^0$19' North Latitude. The study area falls in Pennagaram block, Dharmapuri district, Tamil Nadu and it forms a part of the Government of India Topo sheets 57H/15. In these, Plain area covers an area of 633.67 km^2 and it is situated in an altitude on 450 meters above mean sea level. The study area goes through a hot climate during the summer upto 36^0C and in winter between 16^0C - 12^0C. The Iron composite (red sandy) soil is most common and it is generally derived from Archean crystalline rock. Approximately 33% of the study area identified as agricultural land. The usual rainfall in this area is around 850 mm. The Ground water level varies from 3.65 to 13.45m.

III. MATERIALS AND METHODS

During the year of 2013, eighty groundwater samples were collected from various places in the study area at different seasons. Sampling stations covers the overall area of Pennagaram block villages. The groundwater samples were received in a pre-cleaned two liter polythene bottles without air bubbles. The different physico-chemical parameters were analyzed according to standard techniques prescribed by APHA (1995). The groundwater parameters are expressed in ppm or mg/L, but EC in µs/cm and pH is no unit. To study the Descriptive analysis, Correlation analysis, Factor analysis and Cluster analysis of various water quality parameters was carried out using SPSS software version 16.0.

IV. RESULTS AND DISCUSSION

A. Descriptive Statistics

The descriptive statistics (Table I) shows a data set to minimum and maximum values, mean or average and standard deviation. The pH values in the groundwater samples mostly vary within the permissible limit of 6.5 to 8.5 (WHO 2011). Electrical conductivity (EC) of water is considered to be an indication of the total dissolved salt content (Hem, 1985). The values of EC and TDS are mostly attributed to the geochemical process; such as ion exchange silicate weathering, interaction of rocks with water and also anthropogenic activities (Priya et. al 2012). During, post-monsoon (POM) 18.75% and pre-monsoon (PRM) season 6.25% of the samples shows that the EC values exceeds the permissible limit in the study area. The TDS content of the samples 80.25% in PRM and 88.75% in POM were measured and found within the WHO limit (1500 mg/l).

TABLE I: DESCRIPTIVE STATISTICS OF THE GROUNDWATER SAMPLES

Parameters		Pre-Monsoon (PRM)				Post-Monsoon (POM)			
Variable	**Unit**	**MIN**	**MAX**	**MEAN**	**STD**	**MIN**	**MAX**	**MEAN**	**STD**
pH	**-**	6.95	8.14	7.43	0.27	6.92	8.21	7.386	0.288
EC	**µs/cm**	1264	2381	1905	277	1222	2490	1735	286.4
TDS	**mg/l**	877	1652	1322	192	847.8	1728	1204	198.7
TH	**mg/l**	560	1022	768	108	510	1022	696.9	111.6
TA	**mg/l**	125	319	191	35.8	120	296	179.2	36.44
Cl^-	**mg/l**	318	686	526	100	276	659	466.2	97.25
SO_4^{2-}	**mg/l**	33	109	70.1	16.7	30	110	68.44	18.35
Ca^{2+}	**mg/l**	154	353	257	41.5	156	333.2	241.4	39.19
Mg^{2+}	**mg/l**	8.403	63.85	31.28	12.52	5.144	71.11	22.96	10.98
NO_3^-	**mg/l**	14.2	49.3	33.4	6.98	13.4	45	29.95	6.559
PO_4^{3-}	**mg/l**	0.79	3.1	1.21	0.39	0.24	2.45	1.024	0.439
F^-	**mg/l**	0.24	3.33	1.44	0.78	0.32	2.98	1.347	0.682
K^+	**mg/l**	3	35	8.41	5.65	3	40	8.1	5.444
Na^+	**mg/l**	91	271	150	39.9	80	222	142.2	35.85

Magnesium was in the range of around most of the samples exceeds the desirable limit of 50 mg/l (WHO 2011). The potassium values ranges from the maximum permissible limit of 12 mg/l (WHO 2011) exceeds 17.5% of the samples in PRM and 16.25% of the samples POM seasons. Similarly, the sodium ranges from the maximum permissible limit of 200 mg/l (WHO 2011) exceeds 16.25% of the samples in PRM and 8.75% of the samples in POM seasons. The excess of sodium, potassium and magnesium constituents shows that evidence of granite-water interaction, i.e. the ions exchanging from granite and water (Naseem S et al. 2010). In hydrochemistry, the increased Ca^{2+} ion concentration with increasing total dissolved solids is due to the gradual dissolution of carbonate minerals or Ca^{2+} bearing minerals in aquifer (Sujatha 2003). According to WHO 2015, Calcium values are slightly higher in both the seasons. The WHO limits of calcium between 75 - 200 mg/L.

The total hardness (TH) values shows most of the samples are not within the allowable limit 300 to 600 mg/l. It is due to the presence of alkaline earth metals such as calcium and magnesium. Chloride, sulphate and phosphate contents are within the permissible limits in both the seasons. The high nitrate contamination of the sample implies the anthropogenic impact of pollution in the area (Vikas 2008).The fluoride concentration in groundwater nearly 50% of the samples were above the maximum allowable limit 1.5mg/l. The sources of fluoride were the major rocks that occur in the study area which has the presence of fluoride bearing minerals. Fluoride for higher concentrations in drinking water may cause health impact (dental and skeletal fluorosis).

B. Correlation Analysis

Correlation is a wide class statistical connection between two or more variables. This study is very helpful to find a conventional relationship which can be exploited in practice (Dissanayake C B, 1991). The correlation study was conducted among the values of an array of groundwater quality parameters showed in table II. The positive correlation coefficient between two sets of an array shows that there is a close association with the properties of parameters. Similarly, the negative correlation coefficient between any two sets of the array shows that the parameter in one array is independent of the parameter in the other array.

TABLE II: CORRELATION MATRIX OF THE GROUNDWATER SAMPLES

	pH	EC	TDS	TH	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	NO_3^-	F^-	K^+	Na^+
PRM													
pH	1	0.081	0.081	.123	.160	.060	.002	.045	.171	-.099	.693**	-.062	.084
EC		1	**1.000****	**.853****	.395**	**.960****	.696**	**.811****	.202	**.705****	.013	.493**	**.819****
TDS			1	**.853****	.395**	**.960****	.696**	**.811****	.202	**.705****	.013	.493**	**.819****
TH				1	.480**	**.840****	.520**	**.881****	**.375****	.456**	.025	.268*	.560**
HCO_3^-					1	.254*	.033	.378**	.267*	.121	.328**	.029	.252*
Cl^-						1	.658**	**.799****	.199	.659**	-.044	.456**	**.808****
SO_4^{2-}							1	.558**	-.001	.527**	-.121	.496**	**.703****
Ca^{2+}								1	-.109	.525**	-.03	.303**	.614**
Mg^{2+}									1	-.07	.112	-.032	-.028
NO_3^-										1	-.16	.418**	.690**
F^-											1	-.021	.017
K^+												1	.535**
Na^+													1
POM													
pH	1	.251*	.251*	.267*	.147	.257*	.089	.256*	0.104	0.162	.667**	-0.07	0.152
EC		1	**1.000****	**.986****	.554**	**.934****	.638**	**.919****	.447**	.484**	0.194	.322**	.654**
TDS			1	**.986****	.554**	**.934****	.638**	**.919****	.447**	.484**	0.194	.323**	.654**
TH				1	.543**	**.923****	.648**	**.916****	.488**	.487**	0.211	.307**	.633**
HCO_3^-					1	.347**	0.114	.450**	.367**	0.182	.323**	0.031	0.188
Cl^-						1	.606**	**.902****	.329**	.437**	0.138	.369**	**.749****
SO_4^{2-}							1	.629**	.239*	.449**	0.065	.381**	.645**
Ca^{2+}								1	0.096	.462**	0.134	.380**	**.718****
Mg^{2+}									1	0.202	.233*	-0.06	0.01
NO_3^-										1	0.065	.225*	.541**
F^-											1	-0.09	0.062
K^+												1	.507**
Na^+													1

The strong correlation between EC and TDS (r = 1.000) in both the seasons, which may cause from which may cause the conductivity increases at the concentration of all the dissolved constituent increases. In both the seasons, the EC and TDS also illustrate the strong significant positive correlation ($r \leq 0.8$) with TH, Cl^- , Ca^+ and Na^+. These interactions are clearly identifying the foremost elements contributing the salinity of groundwater and their tendency to follow a similar trend. Similarly, the same strong positive correlation between TH-Cl^-, TH-Ca^{2+} and Cl^--Na^+. This shows the presence of alkaline chlorides and alkaline earth chlorides are leaching from the soil in the study area (Udayalaxmi et al. 2010). On the other hand, the strong positive correlation ($r = 0.8 - 0.5$) between EC and TDS with SO_4^{2-} and NO_3^-. Similarly the same strong positive correlation ($r = 0.8$ to 0.5) between pH-F^-, TH-SO_4^{2-}, TH-Na^+, Cl^--SO_4^{2-}, Cl-NO_3^-, SO_4^{2-}-Ca^{2+}, SO_4^{2-}-NO_3^-, SO_4^{2-}-Na^+, Ca^{2+}-Na^+, NO_3^--Na^+ and K^+-Na^+. Chloride, nitrate and Sulphate are generally associated with sodium, calcium and magnesium (Nagarju et al. 2011).

The negative correlation ($r = 0.0$ to -0.1) between the parameters F^--Cl^-, F^--SO_4^{2-}, F^--Ca^{2+}, Mg^{2+}-SO_4^{2-}, Mg^{2+}-Ca^{2+}, Mg^{2+}-K^+, Mg^{2+}-Na^+ and F^--K^+. Fluoride shows the correlation with pH and Bicarbonate. High fluoride in groundwater is generally associated with high concentration bicarbonate ions (Handa, 1975). The process of weathering rocks releases fluoride in soil and groundwater. The alkaline water can activate fluoride from fluoride bearing minerals with precipitation of calcium carbonate because the solubility of CaF_2 increases with increase in $NaHCO_3$ rather than with other salts (Saxena and Ahmed 2001).

C. Cluster Analysis

Cluster analysis (CA) is a technique used for classifying large information into manageable meaningful small terms. It is a data reduction tool that creates subgroups from a big data set. This is the major statistical method for finding relatively homogeneous clusters of cases, based on measured characteristics. Hierarchical Cluster Analysis (HCA) is deals with intrinsic structure or underlying behavior of dataset without making a-prior assumption about the data, to classify the objects of the system into categories or clusters based on their nearness or similarity (Vega et al 1998). The CA results figure I and II established that the parameters were principally separated into two big clusters.

- Cluster 1 (9 parameters included pH, K^+, F^-, Mg^{2+}, NO_3^-, SO_4^{2-}, HCO_3^-, Na^+ and Ca^{2+})
- Cluster 2 (2 parameters, Cl^- and TH)

A careful consideration of the content of clusters reveals that during the PRM and POM the first cluster included dominant chemical parameters (K^+, F^-, Mg^{2+}, NO_3^-, SO_4^{2-}, HCO_3^-, Na^+ and Ca^{2+}) and one physical parameter (pH). The second cluster consisted of one chemical parameter (Cl^-) and one physical parameter (TH). In both the seasons, the physical parameter TDS and EC were seen clustering as independently.

For instance, within a group of water samples, there is a stronger relation between the groups (group 1) of parameters with other parameters in group 2. The possible salts combinations like NaCl, $CaCl_2$ and Ca-$NaHCO_3$ were derived from weathering and dissolution of rocks salts (Krishna kumar et al. 2014). The nitrate concentration was mostly derived from anthropogenic activities.

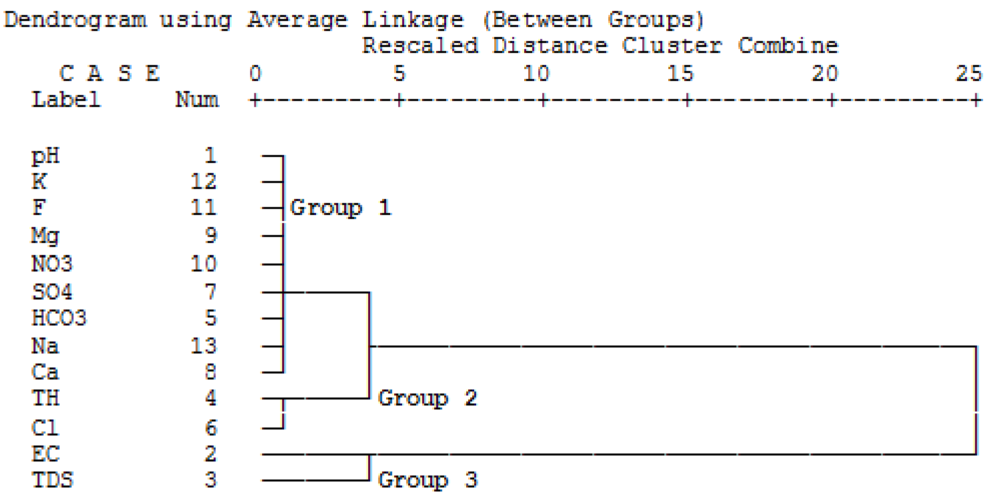

FIGURE I: DENDROGRAM FOR CLUSTER ANALYSIS OF GROUNDWATER FOR THE PRM

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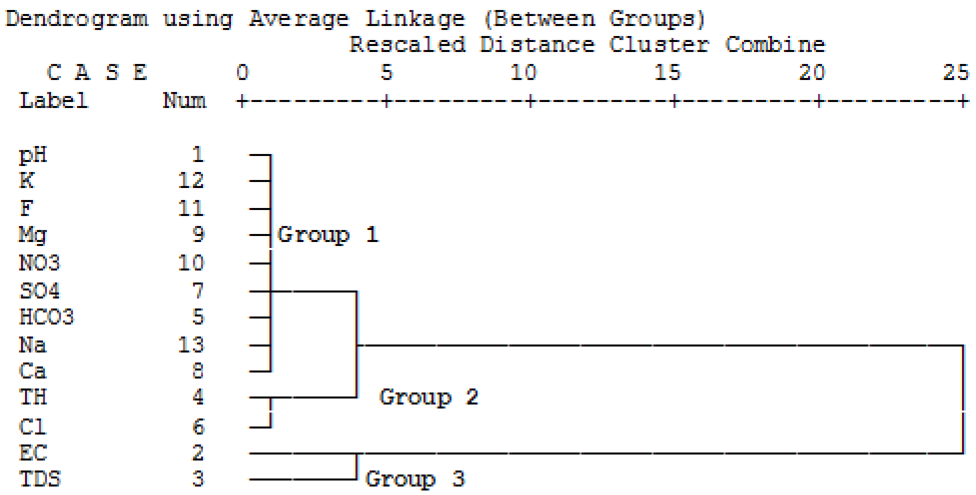

FIGURE II: DENDROGRAM FOR CLUSTER ANALYSIS OF GROUNDWATER FOR THE POM

The study indicates, the clustering parameters were more or less same type in all the seasons. The clusters 1 and cluster 2 combine and bring one single cluster. It may be taken that wholly the parameters of cluster 1 are more significant parameters, which modify the value of EC and TDS in pre-monsoon and post-monsoon seasons in the study area.

D. Factor Analysis

Factor analysis (FA) is often used in data reduction to identify a small number of factors that explain most of the variance observed in a larger number of variables. Factor analysis (FA) was conducted after principal component analysis (PCA). Eigen value is the amount of variance explained by each factor. Factors with Eigen value greater than 1 explain more total variations in the data than individual effluent characteristics (Madhumita Das 2009). Eigen values of 1.0 or greater are considered significant. Liu et al. (2003) classified the factor loadings as 'strong', 'moderate' and 'weak', corresponding to the absolute loading values of >0.75, 0.75-0.50 and 0.50-0.30, respectively.

Pre-monsoon season

The results of the analysis table III and IV discovered that three factors accounted for 75.96% of the total variance. Based on the distribution of the Eigen value, factor 1 alone 47.46% of variance. EC, TDS, Cl^-, SO_4^{2-}, Ca^{2+}, NO_3^- and Na^+ are strongly correlated with factor 1. Mg^{2+} alone strongly correlated with factor 2. The pH and F^- were strongly correlated with factor 3. TH and K^+ exhibited moderately correlated with factor 1. On the other hand, TH and HCO_3^- are moderately correlated with factor 2 indicates the impact of fertilizer and the dissolution of limestone, which is mainly contributed in the geological formation of the study area (Majeda et al. 2013).

The Scree plot figure III exhibits, which also includes the percentage variances explained by each component and gives an idea of how the different principal components were extracted. This figure shows a pronounced change of slope after the 3rd Eigen value. Therefore, three components were retained, which have Eigen value > 1 and explain 75.96% of variance.

TABLE III: PCA OF PHYSICO-CHEMICAL VARIABLES DURING PRM SEASON

Component	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.599	50.765	50.765	6.170	47.463	47.463
2	2.051	15.776	66.541	1.955	15.038	62.500
3	1.225	9.421	75.962	1.750	13.462	75.962
4	.908	6.983	82.946			
5	.695	5.346	88.291			
6	.521	4.011	92.302			
7	.390	3.003	95.305			

8	.247	1.898	97.203			
9	.240	1.848	99.051			
10	.100	.766	99.816			
11	.024	.184	100.000			
12	6.094E-16	4.687E-15	100.000			
13	-4.780E-16	-3.677E-15	100.000			

Extraction Method: Principal Component Analysis.

TABLE IV: ROTATED COMPONENT MATRIX OF EIGEN VALUES DURING THE PRM SEASON

Rotated Component Matrix[a]

	Component		
	1	2	3
pH	.019	.107	.889
EC	.922	.349	.030
TDS	.922	.349	.030
TH	.705	.641	.006
HCO_3^-	.191	.663	.268
Cl^-	.900	.316	-.023
SO_4^{2-}	.807	-.079	-.044
Ca^{2+}	.794	.302	-.013
Mg^{2+}	-.074	.754	.038
NO_3^-	.785	-.053	-.137
F^-	-.066	.112	.923
K^+	.644	-.261	.039
Na^+	.896	-.006	.100

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

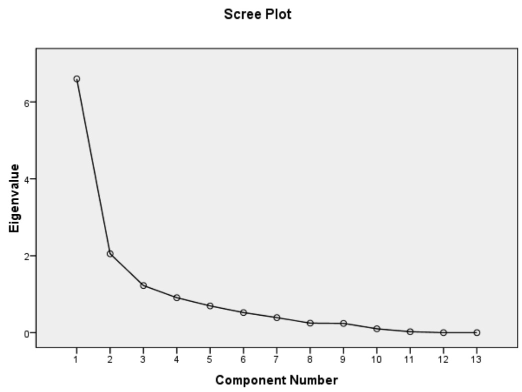

FIGURE III: THE SCREE PLOT REPRESENTS EIGEN VALUE FOR ALL STUDY STATIONS DURING PRM

Post-Monsoon Season

The results of the analysis table V and VI discovered that three factors accounted for 74.09% of the total variance. Based on the distribution of Eigen value, factor 1 alone accounts for 30.34% of the variance. SO_4^{2-} was strongly correlated with factor 1 and EC, TDS, TH, Cl^-, Ca^{2+}, Na^+, K^+ are moderately correlated. EC, TDS, TH and HCO_3^-, are strongly correlated with factor 2 and Cl^-, Ca^{2+}, Mg^{2+} are moderately correlated. F^- and pH are strongly correlated with factor 3. It is also interesting to note that the factor 3 of the PRM is represented as Factor 3 of the POM season indicates that, fluoride weathering factor is dominated. Fluoride concentration is a noticeable correlation exists between F^- and pH (Adriano 1986). At higher pH, ionic exchange occurs between F^- and OH^- ions resulting in increase of F^- ion concentration in groundwater.

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The Scree plot of POM season exhibited in figure IV, which also includes the percentage variances explained by each component and gives an idea of how the different principal components were extracted. This figure shows a pronounced change of slope after the 3rd Eigen value. Therefore, three components were retained, which have Eigen value > 1 and explain 74.61% of the variance.

TABLE V: PRINCIPAL COMPONENT ANALYSIS OF PHYSICO-CHEMICAL VARIABLES DURING POM SEASON

CComponent	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.552	50.397	50.397	3.945	30.344	30.344
2	1.941	14.928	65.325	3.817	29.365	59.710
3	1.208	9.294	74.619	1.938	14.909	74.619
4	.951	7.319	81.938			
5	.788	6.063	88.001			
6	.492	3.783	91.783			
7	.431	3.315	95.099			
8	.351	2.700	97.798			
9	.182	1.398	99.196			
10	.067	.514	99.709			
11	.038	.291	100.000			
12	3.131E-16	2.408E-15	100.000			
13	-2.505E-16	-1.927E-15	100.000			

Extraction Method: Principal Component Analysis.

TABLE VI: ROTATED COMPONENT MATRIX OF EIGEN VALUES DURING THE POM SEASON

Rotated Component Matrix[a]

	Component		
	1	2	3
pH	.199	.042	.910
EC	.618	.768	.060
TDS	.618	.768	.060
TH	.608	.765	.077
HCO_3^-	-.231	.827	.166
Cl^-	.634	.705	.107
SO_4^{2-}	.777	.191	-.181
Ca^{2+}	.639	.656	-.079
Mg^{2+}	.166	.522	.358
NO_3^-	.472	.184	.061
F^-	-.140	.178	.890
K^+	.733	-.044	.049
Na^+	.704	.249	.306

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

FIGURE IV: THE SCREE PLOT REPRESENTS EIGEN VALUE FOR ALL STUDY STATIONS DURING POM

V. CONCLUSION

The foremost descriptive statistics shows, the water constituents are highly adjustable with respect to cationic and anionic constituents. However, to summarize the average of cations is $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and anions are $Cl^{-} > HCO_3^{-} > SO_4^{2-} > NO_3^{-} > F^{-}$. The correlation matrix shows the presence of alkaline chlorides and alkaline earth chlorides are dissolution from the soil in the study area. The dissolved major cations are mainly influenced by EC might be the potential reason for the correlation values. The correlation between the parameters shows presence of high calcium and magnesium. These are absorbed by clay minerals and other exchanging mineral sites to exchanging the sulphate and chloride. Fluoride is generally associated with high concentration bicarbonate ions. According to the dendrogram, the wholly parameters of cluster 1 are more significant parameters, which modify the value of EC and TDS in PRM and POM seasons in the study area. It might be thought of as a change caused by spatial and temporal variation. Factor analysis results shows the impact of the dissolution of limestone, which is mainly contributed in the geological formation of the study area. At higher pH ionic exchange occurs between F^{-} and OH^{-} ions resulting in increase of F^{-} ion concentration in groundwater. This study is used to serve as a productive tool for analysis and interpretation of ground water samples in the study area. This result identifies the water quality factors and spatial variations of water quality for resourceful water quality management.

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