



A Multivariate Statistical Analysis of Bore Well Chemistry Data - Nashik and Niphad Taluka of Maharashtra, India

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Abstract:

Pearson correlation matrix, Hierarchical cluster and principal component analysis (PCA) were simultaneously applied to groundwater hydro chemical data of 31 bore well locations in post monsoon 2007 from Nashik and Niphad taluka. Using the Kaiser criterion, principle component (PC) was extracted from the data and rotated using varimax normalization, for 31 locations. The combined use of both technique resulted in more reliable interpretation of the hydrochemistry. From the analysis, concentration of total dissolved solids (TDS), electrical conductivity (EC), total hardness (TH), calcium (Ca), magnesium (Mg), sodium (Na), chloride (Cl), bicarbonate (HCO_3) at most of the sampling stations in agricultural area having higher values. Computational analysis of data set of hydro chemical constituents in the groundwater suggests that the aquifer is mainly controlled by Cl, Na, EC and TDS; there is strong positive relationship between TDS - EC, TDS- Cl, TDS - TH and TDS - Na. It indicates that, there is strong evidence of anthropogenic activities on major ions present in the groundwater and weathering of sodium, potassium minerals in the study area. The high Na and Cl contents detected in certain samples may suggest the dissolution of chloride salts. The dissolution of halite in water release equal concentrations of Na and Cl into the solution.

Keywords: Dendrogram, Groundwater, Hydro chemical Data, Hierarchical Cluster, Multivariate Analysis, Principal Component analysis.

1. Introduction

The early study of the characterization of groundwater facies utilized graphical representations of the major compositions of groundwater. These classical classification techniques such as Stiff and Piper diagrams only consider selected major water constituents in determining the groundwater type (Hem, 1989). Multivariate statistical techniques were used to interpret complex data matrices to better understand the water quality and ecological status of the studied system and suggested that, the extent of salinity appears to be as a function of magnesium salts rather than calcium salt (Farooq *et al.*, 2010). The ground water quality depends not only on natural factors such as the lithology of the aquifer, the quality of recharge water and the type of interaction between water and aquifer, but also on human activities, which can alter these groundwater systems either by polluting them or by changing the hydrological cycle (Abdulmuhsin and Abdul Baqi, 2010). These multivariate statistical analysis methods were used with a remarkable success in evaluation of trace elements in groundwater (Kouping *et al.*, 2006). The groundwater quality is depleting rapidly with change in human life style i.e. massive industrialization, urbanization and more agricultural activities. The rapid industrialization,

urbanization and agricultural expansion pose high pressure on groundwater resources (Yadina *et al.*, 2008), therefore it is necessary to monitor and evaluate the groundwater quality. The effect of discharge of tannery effluents in the Palar river basin was studied using factor analysis and geostatistics (Sajil Kumar *et al.*, 2011).

In present study, at certain places various parameters exceed the Indian standards of potable water. Groundwater quality of 31 water samples of bore well has been statistically researched by using multivariate technique. In this principal component analysis (PCA), cluster analysis and parameters correlation analysis are used to categorize the spatial variation. These methods are also giving a better understanding of the physical and chemical properties of the groundwater system (Subba rao *et al.*, 2001; Subyani and Masoud, 2009; Chenini and Khemiri, 2009 and Belkhiri *et al.*, 2010). Groundwater is the main source of potable water of Nashik and Niphad taluka. The main source for groundwater contamination is from industrial, domestic and agricultural waste. The industrial waste is directly added in the Nasardi River, which is flowing in industrial area. Domestic waste from effluent treatment plant (ETP) at Tapovan, added in Godavari River, which flowing through irrigated area.

2. Study Area

The study area lies between at latitude $19^{\circ} 33'$ and $25^{\circ} 53'$ North and longitude $73^{\circ} 16'$ and $75^{\circ} 6'$ East in Northern Maharashtra and covers total area of 476 sq.km. Agriculture is main occupation of the people of the area. The drainage on the whole area is fine to medium the amount of precipitation, permeability, topography and structure in the area. The structure and lithology have played major role in the evolution of the topography and drainage pattern in the area. Average rainfall is approximately 650mm, most of which is during period June-September (Santech system). The whole taluka is covered by Deccan

trap. As regards the soil of Niphad taluka is filled with disintegrated basalts of various shades from gray to black. This is favorable for the grapes, onions, vegetables, flowers and sugarcane. The black soil contains high alumina and carbonates of calcium and magnesium with variable amount of potash, low nitrogen and phosphorus (Santech system). In the developing country like India, the drinking water supply is carried out through surface as well as groundwater. Niphad gets water supply mainly from Groundwater that is dug wells and bore wells. These water sources are used for drinking, irrigation and industrial purpose. Location of study area is shown in figure a

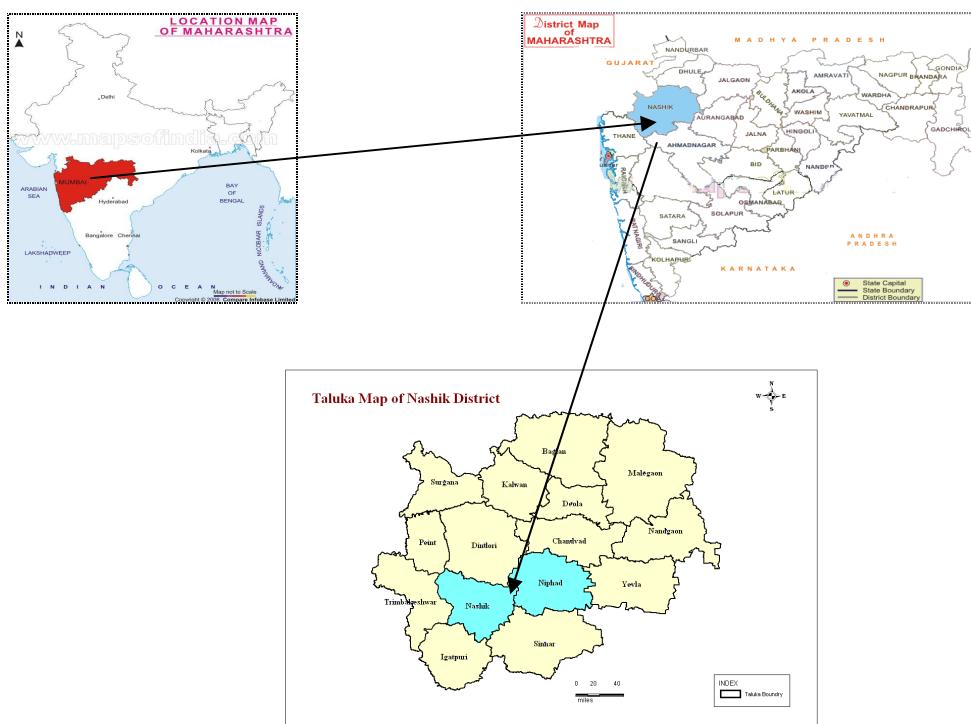


Figure a: Location map of Nashik and Niphad Taluka of Maharashtra, India

3. Methodology

The study area was divided in several grids and representative groundwater samples were taken from each grid. The grids were of $10 \times 10 \text{ km}^2$ and samples were collected from each grid. While selecting each sampling station, drainage pattern and type of activity present in the specific area were considered. All underground water samples are collected from bore wells in different parts of the study area during post-monsoon 2007 season and analyzed for their chemistry. The containers used for sample collection are polythene containers of capacity two liters. These containers were thoroughly cleaned, washed and rinsed before collection. During the present study

physical and chemical parameters were determined (APHA, 2005). The measurement of temperature, conductivity, pH and total dissolved solids were taken in the field, immediately after the collection of samples using portable water quality analyzer (Elico PE-136). Chloride, hardness, calcium, total alkalinity were analyzed by titrimetry. Sodium and potassium were estimated by flame photometer (Elico). Nitrate, fluoride, and iron were done by the UV 2201 spectrophotometer (Systronics). Turbidity and sulphate were determined by nepheloturbidimeter. Standard procedures used in groundwater analysis is given in Table 1 and location of sampling stations were given in Table 2

Table 1: Unit, Method of Analysis of Each Parameter

Sr. No	Parameter	Unit	Method
1	Temperature	^o C	Thermometer
2	pH	-	Potentiometric
3	EC	μ S/cm	Potentiometric
4	TDS	mg/l	Potentiometric
5	Na	mg/l	Flame Emission Photometric
6	K	mg/l	Flame Emission Photometric
7	TH	mg/l	EDTA Titrimetric
8	Ca	mg/l	EDTA Titrimetric
9	Mg	mg/l	Calculation from TH and Ca
10	Total alkalinity	mg/l	Titrimetric
11	Cl	mg/l	Argentometric Titration
12	NO ₃	mg/l	Spectrophotometric
13	F	mg/l	Spectrophotometric
14	Fe	mg/l	Spectrophotometric
15	SO ₄	mg/l	Nephelometric
16	Turbidity	NTU	Nephelometric

Table 2: Location of Sampling Stations

Stn. No	Location	Land Use	Stn. No	Location	Land Use
1	Satpurgaon	Industrial	17	Eklahare	Urban
2	Satpur	Industrial	18	Eklahare	Urban
3	Satpur	Industrial	19	Eklahare	Urban
4	Ambad	Industrial	20	Lakhalgaon	Urban
5	Ambad	Industrial	21	Chehadi.Khurd	Agricultural
6	Ambad	Industrial	22	Chitegaon phata	Agricultural
7	Ambadgaon	Industrial	23	Shimpi takli	Agricultural
8	Untawadi	Industrial	24	Chandori	Agricultural
9	Kailasnagar	Urban	25	Chandori	Agricultural
10	Dasak	Urban	26	Kasbesukene Phata	Agricultural
11	Madsangavi	Urban	27	Kherwadi	Agricultural
12	Madsangavi	Urban	28	Kherwadigaon	Agricultural
13	Madsangavi	Urban	29	Ozarshivar	Agricultural
14	Shilapur	Urban	30	Ozarshivar	Agricultural
15	Azadnagar	Urban	31	Oane	Agricultural
16	Odha	Urban	Total = 31 sampling sites		

4. Multivariate Analysis

Multivariate statistical approaches allow driving hidden information from the data set about their possible influences of the environment on water quality. Multivariate analysis was performed on matrix of hydro-geochemical data. The statistical analysis was performed using SYSTAT 13 software package. PCA aims to transform the observed

variables to a new set of variables, which are uncorrelated and arrange in decreasing order of importance to simplify the problem. Principal components analysis was performed on correlation matrix of the raw data in which a water sample is described by sixteen physical and chemical parameters. In recent times, multivariate statistical methods have been applied widely to

investigate environmental phenomenon (Gajendran and Thamrai, 2008) the combined use of principle component analysis (PCA) and cluster analysis enabled the classification of groundwater samples into distinct groups on the basis of their hydro chemical characteristics. Multivariate statistical tools have been used to study and classify different sediment types (Huisman, and Kiden, 1998) , and hydro geochemical processes (Cameron., 1996) , used cluster analysis and PCA to identify the temporal and spatial variations of water chemistry in New York. Multivariate statistical techniques, cluster and principal component analysis were applied to the data on groundwater quality of Ain Azel plain (Algeria), to extract principal factors corresponding to the different sources of variation in the hydrochemistry, with the objective of defining the main controls on the hydrochemistry at the plain scale (Belkhiri *et al.*, 2010). A grouped characteristic of the groundwater quality helps the

local government and industries to plan the use and protection of groundwater resources (Liu *et al.*, 2008). Not only groundwater but also analyses of the quality of surface water were done by multivariate techniques (Singh *et al.*, 2008).

5. Results and Discussion

The descriptive statistics of the analyzed groundwater quality parameters are depicted in Table 3. Values of electrical conductivity (EC), total dissolved solids (TDS), sodium (Na), chloride (Cl), total hardness (TH), calcium (Ca), magnesium (Mg), Total alkalinity (T.alk) are increases as Industrial < Urban < Agriculture. It is interesting to note that higher values of most of the parameters are found in agricultural area, while lower values of parameters are observed in industrial area. This shows clear impact of irrigation activities in study area on groundwater.

Table 3: Basic Statistics of Groundwater in Post Monsoon 2007

Sr. No.	Parameters	No. Sampling Sites	Minimum	Maximum	Mean	Standard Error	Standard Deviation	Variance
1	Temp.	31	18.7	34.4	25.6	0.5	2.9	8.3
2	pH	31	7.14	8.4	7.6	0.0	0.3	0.1
3	EC	31	551.0	3,059.0	1,386.4	115.7	644.2	415,018.4
4	TDS	31	358.2	1,988.4	901.1	75.2	418.7	175,345.3
5	Na	31	15.6	310.0	122.2	16.3	90.8	8,243.5
6	K	31	0.1	40.8	3.5	1.8	9.9	98.3
7	TH	31	189.9	896.4	411.5	27.8	155.1	24,049.7
8	Ca	31	22.4	286.8	90.4	9.9	54.9	3,014.3
9	Mg	31	14.7	109.4	44.4	4.5	25.2	634.5
10	Total alkalinity	31	154.0	642.4	348.0	21.5	119.6	14,304.9
11	Cl	31	22.0	586.9	185.0	25.6	142.5	20,316.2
12	NO ₃	31	5.2	183.1	40.6	6.8	38.0	1,446.7
13	F	31	0.1	0.8	0.3	0.0	0.2	0.0
14	Fe	31	0.0	0.5	0.2	0.0	0.1	0.0
15	SO ₄	31	16.8	152.5	72.2	6.3	34.9	1,221.2
16	Turbidity	31	0.1	9.0	1.1	0.3	1.8	3.1

5.1 Pearson Correlation

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.*, 2010). From Sixteen variables have been considered in analysis and a curve fit procedure for linear mode has been adopted to find out the possible correlation between selected parameters. The scattering data in the block is an indication of inadequate relationship between selected variables in the study area. From matrix plot, strong ($r = 0.8$ to

1.0), moderate ($r = 0.6$ to 0.8) and low ($r = 0.5$ to 0.6) correlation between selected variables was found out. To know this objective r - values correlation probability value were calculated. To nullify the effect of missing data, pair wise missing data deletion technique has been adopted. The generated simple matrix plots are presented from figure b to d. The calculated correlation table and correlation r - value are compiled in Table 4.

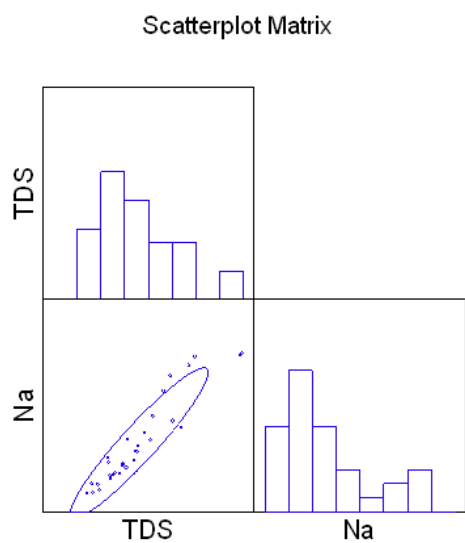


Figure b: Correlation between TDS and Na in Bore Well source

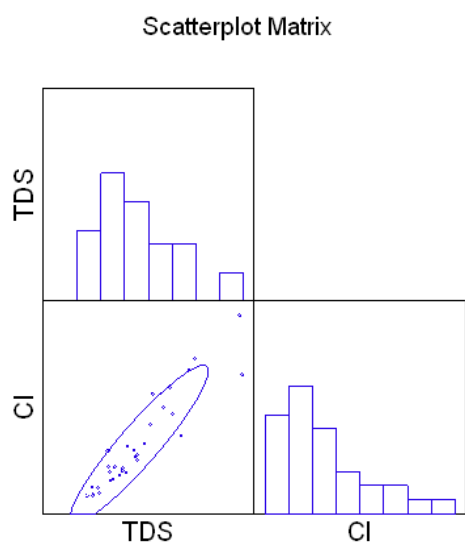


Figure c: Correlation between TDS and Cl in Bore Well source

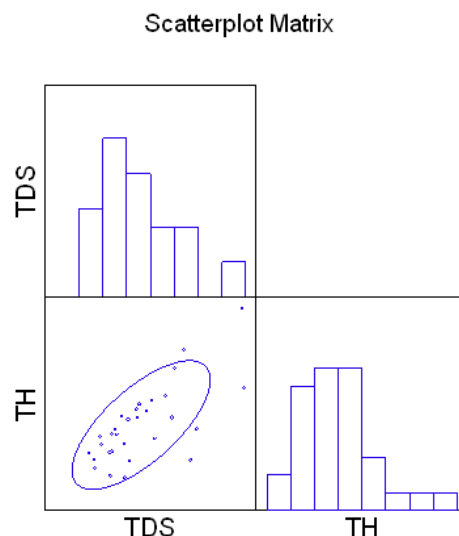


Figure d: Correlation between TDS and TH in Bore Well sources

The correlation analysis between EC and TDS, TDS and Na, TDS and Cl shows strong positive relationship as $r = 1.0, 0.94, 0.92$ respectively and moderate correlation between TDS and chloride $r = 0.7$ and very low positive correlation ($r = 0.2$ to 0.4) with Ca, Mg, Talk, suggesting that aquifer chemistry is mainly controlled by TDS, EC, Na and Chloride (Figure b to d, Table 4). Good, medium and low correlation between chemical parameters (Table 4) indicates that electrical conductivity and total dissolved solids is the most appropriate variable in explaining more than 60% variation in hardness, sodium, magnesium, sulphate, chloride and bicarbonate (Pattanaik., 2007).

These strong associations could primarily be put into two distinct groups: firstly, the elements contributing to the conductivity of water as of the strong dependency between EC, TDS, Mg, Cl, Ca, and Na. Secondly, the strong associations between NO_3 , HCO_3 and Fe indicated the parameters contributing to the typical characteristics of the non-rechargeable and stagnant groundwater (Khatiwada *et al.*, 2002). The major exchangeable ions, EC and Na (0.9), Na and Cl (1.0), TDS and Na (0.9), Ca and Total Hardness (0.8), were found to be correlated positively indicating the origin of major cations to be dissolution/precipitation processes (Khatiwada *et al.*, 2002). There are two outliers, which may be related to different soil parent materials or geology of the sampling sites. Cl and Na possess a very good positive correlation (0.91) between each other. The high Na and Cl contents detected in certain samples may suggest the dissolution of chloride salts. The dissolution of halite in water release equal concentrations of Na and Cl into the solution (Belkhiri *et al.*, 2010).

Table 4: Pearson Correlation Matrix

	pH	EC	TDS	Na	K	TH	Ca	Mg	T Alk	Cl
pH	1									
EC	-0.2	1.0								
TDS	-0.2	1.0	1.0							
Na	-0.1	0.9	0.9	1.0						
K	-0.1	-0.1	-0.1	-0.2	1.0					
TH	-0.5	0.7	0.7	0.5	-0.3	1.0				
Ca	-0.3	0.5	0.5	0.4	-0.1	0.8	1.0			
Mg	-0.3	0.3	0.3	0.2	-0.2	0.5	-0.2	1.0		
Total alkalinity	-0.6	0.5	0.5	0.3	-0.2	0.8	0.4	0.6	1.0	
Cl	0.0	0.9	0.9	1.0	-0.2	0.6	0.5	0.1	0.3	1.0
NO₃	-0.2	0.4	0.4	0.4	-0.1	0.4	0.2	0.3	0.2	0.3
F	0.3	0.6	0.6	0.7	0.0	0.2	0.3	-0.2	0.0	0.7
Fe	0.1	-0.2	-0.2	-0.2	-0.1	0.0	0.0	-0.1	-0.2	-0.1
SO₄	-0.3	0.6	0.6	0.6	-0.1	0.5	0.5	0.1	0.3	0.5
Turbidity	-0.2	0.4	0.4	0.3	-0.1	0.1	0.0	0.2	0.2	0.2

5.2 Factor Analysis

Kaiser criterion (Kaiser, 1960) applied to determine the total number of factors for each dataset in this analysis. Under this criterion, only factor with eigenvalues greater than or equal to one will be accepted as possible sources of variance in the data, with the highest priority ascribed to factor that has the highest eigenvector sum. The rationale for choosing 1 is that a factor must have a variance at least as large as that of a single standardized original variable to be acceptable.

Five principle components (PC) were extracted and rotating using the varimax normalization (Kaiser, 1960). An initial run using the Kaiser criterion resulted in eight principle components. However it was observed that the sixth, seventh and eighth factor would not constitute a unique source of variance in the hydrochemistry since it had only three loading greater than 0.50. It was therefore dropped and five factors were chosen for varimax rotation. The results (Table 5, figure e) shows that the five PC account for more than 86% of the total variance, which is quite good and can be relied upon to identify the main sources of variation in the hydrochemistry.

PC 1 has high loadings (> 0.50) for EC, TDS, Na, TH, Ca, Mg and accounts for 85.6 % of the variance in the hydrochemistry in the area. EC, TDS, Na, TH, Ca and Mg showing positive loadings under PC 1 and derived from industrial, domestic and agricultural waste in the study area. PC 2, which accounts for 11.1 % of the total variance, contains high loadings for EC, TDS, Na and K, and represents the contribution of agricultural activities and weathering of K - feldspar from underlying geology, a process is accompanied by rise in pH.

PC 3 has high loadings of TH, Na, EC and TDS representing 2.2 % of the total variance in the hydrochemistry. PC 3 represents weathering of dolomite from underlying sedimentary material. PC 4, which accounts for 0.8 % of the total variance in the hydrochemistry, shows positive loadings for EC, TDS, and TH represents the contribution of domestic wastes. PC 5, which accounts for 0.3 % of the total variance in the hydrochemistry, shows positive loadings for Na, K, and TH, representing the weathering of minerals of Na and K in the study area (Liu, 2008). Rotated loading matrix and factor loading plot of parameter is shown in Table 5 and figure e respectively.

Table 5: Rotated Loading Matrix (VARIMAX, Gamma = 1.000000)

	1	2	3	4	5
PH	-0.008	-0.155	-0.093	0.000	0.054
EC	606.325*	189.813*	85.774*	57.478*	26.434*
TDS	394.111*	123.379*	55.753*	37.361*	17.182*
Na	89.228*	6.724*	2.104*	-13.347	7.352*
K	-0.744	-0.274	-0.927	0.004	-9.841
TH	67.618*	127.795*	46.451*	1.760*	31.386*
Ca	19.403*	46.213*	-21.335	0.490	6.835*
Mg	4.478*	2.593*	24.415	0.120	3.410*

The values with * indicate absolute component loadings higher than 0.5, which are considered significant contributors to the variance in the hydrochemistry

'Variance' Explained by Rotated Components				
1	2	3	4	5
535,883.945	69,770.628	13,679.963	4,881.091	2,188.366

Percent of Total Variance Explained				
1	2	3	4	5
85.549	11.138	2.184	0.779	0.349

Scree Plot

Factor Loadings Plot

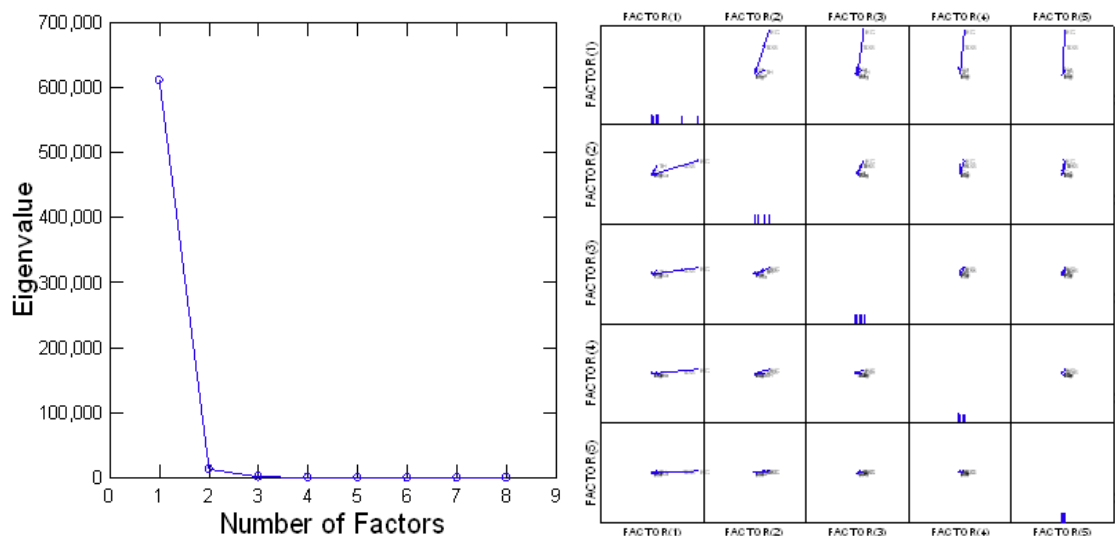


Figure e: Factor Loading Plot of Correlation between Parameters in Bore Well Sources

5.3 Cluster analysis

Cluster analysis comprises a series of multivariate methods that are used to find true groups of data. In clustering, the objects are grouped such that similar objects fall into the same class (Danielsson *et al.*, 1999). Hierarchical cluster analysis is the most widely applied techniques in the earth sciences and is used in this study. Hierarchical clustering joins the most similar observations, and then successively the next most similar

observations. The levels of similarity at which observations are merged are used to construct a dendrogram. Some measure of similarity must be computed between every pair of objects. In this study, a standardized m-space Euclidian distance (Davis,1986). Cluster analysis groups variables into clusters on the basis of similarities (or dissimilarities) such that each cluster represents a specific process in a system (Yadina *et al.*, 2008). For cluster analysis single linkage method was

used. In this method the distance between the clusters was determined by the distance of the two closest objects (nearest neighbor) in the different cluster (Systat Software Incorporated), as shown in Table 6

In this study, the hierarchical cluster analysis (HCA) was applied to the raw data for 31 different locations, using SYSTAT 13 (Systat Software Incorporated). HCA is a powerful tool for analyzing water quality data. A classification scheme using the Euclidean distance for similarity measures (Guler *et al.*, 2002). from dendrogram of 16 indexes based on the cluster analysis is depicted in figure f. On the basis of dendrogram of 16 indexes can be grouped into three main clusters. First cluster group shows close association between TDS and EC. This group associated with group second to a lesser degree having Total alkalinity and Total hardness indexes. Group third shows close association between chloride and sodium. This finding corroborates the result of correlation and cluster analysis. The enrichment of Na and Cl ions in groundwater is due to the interaction of water with rocks and secondly association of TDS with higher concentration of Na and Cl ions. This indicates anthropogenic activities such as discharge of sewage and agricultural runoff, which support the contamination of groundwater. Yidana (2008) observed similar results for surface water.

Table 6: Euclidean Distance using Single Linkage Method between chemical parameters

	Clusters Joining	Euclidean Distance	Members in Group
Fe	F	0.334	2
Turbidity	Fe	1.869	3
pH	Turbidity	6.692	4
pH	K	10.245	5
pH	Temp.	18.241	6
Mg	pH	31.587	7
Mg	NO ₃	38.240	8
Mg	SO ₄	48.508	9
Ca	Mg	51.605	10
Cl	Na	85.773	2
Cl	Ca	89.219	12
Total alkalinity	TH	108.288	2
Total alkalinity	Cl	223.760	14
TDS	EC	533.519	2
TDS	Total alkalinity	586.861	16

The first component is associated with a combination of various hydro chemical processes that contribute to enrich more mineralized water (high value of TDS), as suggested by Hem (Hem, 1989), which supports the contamination in groundwater from human and animal waste. Similar observations have also been reported by Yidana *et al.*, 2008. The concentration of total alkalinity in the groundwater is nothing but the result of reaction of soil CO₂ that originates from H₂CO₃. The negative loading of pH suggests that decrease of pCO₂ and H₂CO₃ values during the out gassing of CO₂ decreases there is sharp rise in pH value which shifts the water towards alkaline side and concentration of H₂CO₃ increases. Minerals of bedrock are subjected to weathering and subsequently affected by leaching, which contribute dissolved salts to groundwater, resulting in an increase in TDS and EC.

6. Conclusions

In general the groundwater of the Nashik and Nipahd taluka is alkaline in nature and hard, but at some places the groundwater is relatively soft and falls within the safety limits as prescribed by Indian Standards. Multivariate statistical techniques are efficient ways to display complex relationships among many objects. The concentration of TDS, EC, TH, Ca, Mg, Na, Cl, HCO₃ at most of the sampling stations in agricultural area having higher values. Computational analysis of data set of hydro chemical constituents in the groundwater suggests that the aquifer (TDS) is mainly controlled by Cl, Na, EC and TDS; there is strong positive relationship between TDS - EC, TDS- Cl, TDS - TH

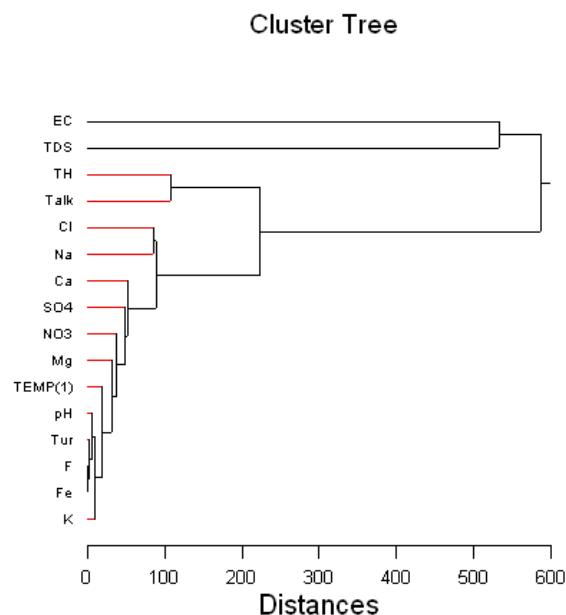


Figure f: The Dendrogram Showing the Clustering of Chemical Parameters

and TDS - Na. The Dendrogram of 16 chemical parameters are plotted and grouped into three main clusters. It is interesting to note that higher values of most of the parameters are found in agricultural area, while lower values of parameters are observed in industrial area. This shows clear impact of irrigation activities in study area on groundwater. Cl and Na possess a very good positive correlation (0.91) between each other. The high Na and Cl contents detected in certain samples may suggest the dissolution of chloride salts.

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