Statistical Analysis of the Hydrogeochemical Evolution of Groundwater in the Rangampeta area, Chittoor District, Andhra Pradesh, South India

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Abstract Multivariate statistical techniques involving factor analysis (FA) and R-mode hierarchical cluster analysis (HCA) were performed on 30 groundwater samples from Rangampeta, Chittoor District, Andhra Pradesh, South India to extract principal processes controlling the water chemistry. The groundwater samples were analyzed for distribution of chemical elements Ca, Mg, Na, K, Si, HCO₃, CO₃, Cl, and SO₄. It also includes pH, and electrical conductivity (EC). Gibbs diagrams were also constructed to identify the processes that are responsible in controlling the water chemistry. Factor analysis extracted for four factors consisting of F1 (with high loading factor of Cl, EC, Mg and Na), F2 (with high loading factor of K, (HCO₃+CO₃) and Ca), F3 (with high loading factor of pH and Si) and F4 (with high loading factor of SO₄). The varifactors obtained from Factor analysis indicated that the parameters responsible for groundwater quality variations are mainly related to groundwater-rock interaction (particularly weathering of silicate minerals), agriculture and anthropogenic sources. With HC analysis the water samples have been classified into 4 clusters. Cluster I (13 wells) and cluster II (8 wells) have shown moderate salinity. However, cluster IV (4 wells) had the lowest concentrations of ions and classified as fresh water. Cluster III (5 wells) shows mid salinity between (I and II) and IV clusters. The distribution of these groundwater types and their quality has been found to be an in direct relation with the host rocks of the area. The results showed that the method was comprehensive and efficient in analyzing the dynamics of water quality.

Keywords: factor analysis, cluster analysis, groundwater quality, Rangampeta, South India

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1. Introduction

Water is a valuable, limited resource and is essential for life. Groundwater is one of the earth's most widely distributed and important renewable perennial resources occurring beneath the earth surface. Also, groundwater is the essential component of the hydrological cycle, which facilitates that unique behavior of the water on the continent [1,2]. It is well known that water is a universal solvent and dissolves minerals from the rock with which it comes in contact. So that, water during the course of its flow, acquires the properties of its surrounding conditions and becomes a source of elements present in the areas through which it flows. On the other hand, in some areas groundwater resources are at risk from the results of point and non-point source pollutants such as agricultural and industrial activates, animal waste and household chemicals run-off, failing septic systems, etc. [3,4,5,6].

The quality of groundwater is very important in evaluating its utility in various fields such as domestic,

public water supply and agriculture. The utilizable water resource in India is not enough to irrigate the cultivatable area. Hence, efforts are needed to maximize the chances of water for irrigation in agriculture [7]. Water management in agriculture is aiming for better tools to estimate risk assessment due to stricter legislation on soil and groundwater contamination, together with increasing population and demand in food production [8]. Therefore, in order to preserving the availability and quality of water resource, the monitor and assessment of water quality on regular basis is extremely important.

For a better understanding of water quality characteristics of a study area is the use of multivariate analysis for data extrapolation. A number of multivariate statistical techniques, such as cluster analysis (CA), principal component analysis (PCA), factor analysis (FA) and discriminant analysis (DA) offer significant assistance in the interpretation of complex data matrices. The outcome is thus a generally improved understanding of the water quality status of the studied systems. The application of multivariate statistical techniques also enhances the identification of possible factors that influence water systems. These techniques undoubtedly offer a valuable tool for reliable and sustainable management of water resources [9-13]. Earlier studies indicate that the multivariate statistical techniques have successfully assisted in characterizing the surface and freshwater quality [14,15,16].

These techniques provide the identification of possible sources that affect the water environmental system and offer a valuable tool for reliable management of water resources [11,17,18]. The multivariate analysis, which provides a representative and reliable estimation of the quality of groundwaters by explaining the correlation amongst large number of variables in terms of small number of factors without losing much information [19,20,21]. Hence, the specific objective of the present study is to extract the principal processes that are most important in assessing variations in groundwater quality by using of multivariate statistical analysis in groundwater of Rangampeta area.

Factor analysis (FA) as a data reduction technique is widely used, being capable of detecting similarities among samples and/or variables [22,23,24]. In summary, the goal is to explain a portion of their variance in a set of variables input into the analysis by identifying certain underlying common dimensions called the factors. The factor analysis

will be used to interpret the observed relationships among the variables. This will provide simpler relationships that offer insight into the underlying structure of the variables and also to evaluate the composition of groundwater [25].

The main objective of this study is to identify the factors that affect on groundwater in the Rangampeta area using FA as an effective multivariate statistical technique. The water quality data were incorporated to FA to understand and define the mechanisms, processes (natural) and specific source of water quality deterioration and contamination in this area.

2. Study Area

The study area is located on north latitude from $13^{\circ} 36'$ 05" to $13^{\circ} 37' 10$ " N and east longitude from $79^{\circ} 15' 00$ " to $79^{\circ} 17' 60$ " E in Chandragiri mandal, Chittoor district, in Andhra Pradesh [Figure 1]. This area is included in the survey of India top sheet No. 57 O/6. This area is covered by Precambrian granites in the form of domes. The granite is migmatised and fully crystalline (holocrystalline) igneous rock, formed by crystallisation of molten rock (magma) at depths. It is composed of grey or pink feldspar, quartz and muscovite mica.



Figure 1. Map of the study area with water sample locations

Sample No	Latitude	Longitude	Sample No	Latitude	Longitude
1	13° 36' 11"	79° 15' 28"	16	13° 36' 52"	79° 17' 13"
2	13° 36' 06"	79° 15' 32"	17	13° 36' 08"	79° 16' 01"
3	13° 36' 07"	79° 15' 38"	18	13° 36' 10"	79° 15' 59"
4	13° 36' 08"	79° 15' 45"	19	13° 36' 13"	79° 15' 53"
5	13° 36' 12"	79° 15' 34"	20	13° 36' 12"	79° 16' 49"
6	13° 36' 12"	79° 16' 17"	21	13° 36' 11"	79° 17' 30"
7	13° 36' 07"	79° 16' 16"	22	13° 36' 10"	79° 17' 17"
8	13° 36' 12"	79° 16' 28"	23	13° 36' 13"	79° 16' 14"
9	13° 36' 06"	79° 16' 25"	24	13° 36' 20"	79° 16' 04"
10	13° 36' 13"	79° 16' 39"	25	13° 36' 28"	79° 16' 20"
11	13° 36' 11"	79° 16' 44"	26	13° 36' 36"	79° 16' 42"
12	13° 36' 12"	79° 16' 54"	27	13° 36' 53"	79° 17' 32"
13	13° 36' 08"	79° 16' 56"	28	13° 36' 42"	79° 17' 21"
14	13° 36' 24"	79° 17' 00"	29	13° 36' 24"	79° 17' 22"
15	13° 36' 40"	79° 16' 58"	30	13° 36' 37"	79° 17' 50"

3. Materials and Methods

Groundwater samples were collected during January-February 2013 from 30 locations from Rangampeta surrounding area (Figure 1 and Table 1). The dug wells are circular or rectangular in shape with 30 to 60 sq.m.. The depth of the wells is upto 30 m. The average discharge of energized wells ranges from 18 to 30 cu.m/day. However, during monsoon period, the discharge varies from 80 to 200 cu.m/day and during summer months, 10 to 50 cu.m/day. The collected water samples were transferred into precleaned polythene containers for analysis of chemical characters. To know the suitability of waters for irrigation, chemical parameters like pH, electrical conductivity (EC), Ca, Mg, Na, K, Si, Cl, HCO₃, CO₃, and SO₄, were analyzed by adopting the standard procedures of water analysis. The availability of data on field parameters such as electrical conductivity (EC), pH were measured. The major cations and anions were determined adopting the analytical techniques, which are based on the methods proposed by APHA [26].

In Rangampeta area, the highest day temperature is in between 34° C to 43° C. The humidity levels of around 68%. The climate is tropical in Rangampeta area, in winter there is much more rainfall in Rangampeta than in summer. The average annual temperature in Rangampeta is 30° C. The average annual rainfall is 870 mm.

Soils

The major portion of the area is covered by red soils with portions of alluvial soil. In this area, 60% of the soils are red loamy and 28% red sandy. The remaining 10% is covered by black clay, black loamy, black sandy and red clay.

Data Treatment

To detect outliers data, all variables were analyzed by formula namely Z-score. The formula for calculating of the Z-score is:

$$\mathbf{Z} = (\mathbf{x} - \boldsymbol{\mu}) / \boldsymbol{\delta}$$

Where:

- Z = Z-score
- x = individual data value
- μ = arithmetic mean
- δ = sample standard deviation

If the Z-score is < - 4 or > 4, the sample should be presumed to be outlier, because it is at least four standard deviations greater or less than the arithmetic mean. Based on the cutoff point for the Z-score, none of the survived variables were outliers in this study. Subsequently, the normality of the physical and chemical data was checked by Kolmogorov–Smirnov (K-S) method that confirms the result of Z-score analysis. Furthermore, the basic statically analysis, factor analysis and R-mode hierarchical cluster analysis was performed with the help of SAS 9.2, and MINITAB 15 softwares. The spatial distribution ions in surveyed wells were analyzed using the program SURFER 9 (Golden Software Inc.). The ions concentrations were first interpolated with the Kriging method.

4. Results and Discussion

4.1. Groundwater Chemistry

 Table 2. Minimum, maximum, standard deviation and average

 values of different constituents of water samples

S. No.	Constituents	Min	Max	Average	S.D
1	Calcium (Ca) (mg/l)	7	52	26	14
2	Magnesium (Mg) (mg/l)	7	60	29	15
3	Sodium (Na) (mg/l)	8	138	66	37
4	Potassium (K) (mg/l)	2	168	28	49
5	Bicarbonate (HCO ₃) (mg/l)	10	327	113	67
6	Carbonate (CO ₃) (mg/l)	2	72	19	16
7	Sulphate (SO ₄) (mg/l)	10	61	31	14
8	Chloride (Cl) (mg/l)	39	306	148	69
9	Silicon (Si) (mg/l)	3	11	7	2.1
10	pH	7.90	8.60	8.30	0.23
11	Specific conductance (µmhos/cm)	230	1190	683	244
12	Chloroalkaline indices 1	-0.55	0.59	0.12	0.35
13	Chloroalkaline indices 2	-0.38	1.61	0.30	0.54
14	Gibbs Ratio I	0.38	0.98	0.68	0.15
15	Gibbs Ratio II	0.31	0.93	0.70	0.18

The major physicochemical properties of groundwater from studied area was statistically analyzed and the results summarized by minimum, maximum, mean in a Table 2. From the Table, it is observed that the pH values of the water samples ranged from 7.9 to 8.6 with a mean value of 8.3 in the study area. Eighty-seven percent of the water samples fall in the safe limit of pH standard (6-8.5) for irrigation purpose [27]. The amounts of EC varied from 230.0 to 1190.0 with an average value of 683.0 µmhoscm According to the EC grading standards as suggested by Wilcox [28], 3.30% of the water samples are classified as excellent, 63.3% of the water samples are classified as good and 33.3% as permissible. Among the cations, the concentrations of Ca^{2+} , Mg^{2+} , Na^+ and K^+ ions ranged from 7 to 52, 7 to 60, 8 to 138 and 2 to 168 ppm with a mean of 26, 29, 66 and 28 ppm, respectively. Among the anions, the concentrations of HCO_3^- , CO_3^{2-} , CI^- and SO_4^{2-} ions lie in between 10 and 327, 2 and 72, 39 and 306, 10 and 61 ppm with a mean of 113, 19, 148 and 31 ppm, respectively. The order of abundance of the major ions is as follows: Na > Mg \approx K > Ca > Si and Cl > HCO₃ > $SO_4 > CO_3$. It should be noted that we did the water sampling in the monsoon season. Thus, the groundwater quality of the study area may show seasonal variation.

The spatial distribution patterns of the concentration of different ions in surveyed wells using Kriging method are shown as contour map in Figure 2. Spatial distribution patterns of Na, Cl, Mg, particularly EC, to a lesser extent Si, Ca, HCO₃ and K indicated that the highest concentrations of the surveyed ions were found in central, southwest and northern parts of the studied area. On the other word, a strip of salinity has been extended from SW to NE of the studied area. In agreement to FA and CA results, the similar distribution patterns were found for EC, Na, Cl and Mg suggests that the increase of these ions probably came from a common anthropogenic source. Furthermore, the nearly smooth spatial distribution of Ca, K, Si, HCO₃, and SO₄ suggests that their distribution pattern could be mainly controlled by parent material.



Figure 2. Spatial distribution of the analyzed major ions, pH and EC in wells of studied area (blue circle symbols is the locations of groundwater samples)

4.2. Multivariate Analysis

The multivariate statistical tools comprising of R-mode hierarchical cluster analysis (HCA) and principal

component analysis (PCA) i.e. factor analysis were simultaneously applied to groundwater hydrochemical data of the studied area to extract principal processes controlling the water chemistry.

4.2.1 Factor Analysis (FA)

Factor analysis is a multivariate statistical technique that can be applied to any kind of scientific data to establish the pattern of variation among variables or summarize information in a smaller set of factors or components for easy handling and interpretation [29]. Scree plot of eigenvalues is the most acceptable method of this analysis [Figure 3]. The plot shows the eigenvalues (Y axis) sorted from large to small as a function of the factor number (X axis). Only factors with eigenvalues greater than or equal to 1 will be accepted as possible sources of variance in the data [30]. Parameters were grouped based on the factor loading and following factors were indicated (Table 3). The first factor, F1 with 30.5% of total variance of water quality among the studied wells, is the most important of all followed by factors F2, F3 and F4 with respectively with 19.6%, 13.8% and 10.8% of total variance. These factors variance exceeded 70% and they are sufficient to explain the mechanisms controlling groundwater chemistry.

 Table 3. Rotated Factor Loading Matrix, eigenvalues, % variance and cumulative variance values

Variable	Factors				
	1	2	3	4	
EC	0.863	0.236	-0.054	-0.167	
pH	-0.185	-0.295	0.715	-0.055	
Si	0.389	-0.200	0.623	0.382	
Ca	0.027	0.585	0.233	0.419	
Mg	0.676	-0.135	0.071	-0.275	
Na	0.584	-0.623	0.095	-0.104	
Κ	0.424	0.771	-0.160	-0.023	
HCO ₃ +CO ₃	0.355	0.597	0.543	-0.272	
Cl	0.866	-0.255	-0.226	-0.074	
SO_4	0.520	-0.114	-0.198	0.752	
Eigenvalue	3.0	1.9	1.4	1.1	
Variance (%)	30.5	19.6	13.8	10.8	
Cumulative (%)	30.5	50.1	63.9	74.7	



Figure 3. Scree plot of factor analysis of the studied groundwaters

Four of water quality parameters were significantly loaded on factor I. These parameters included Cl, EC, Mg and Na. This indicated more variation in these parameters among the studied wells than the parameters loaded on factor II. This appears that this factor reflects the variations in the geological formations of the study area and inconsistent distribution of anthropogenic activities (agricultural activities such as irrigation practices and fertilizations) on some of the studied wells. The high concentration of Na+ and Cl⁻ in the groundwater mostly can be attributed to the human activities. It is well known that, Na+ and Cl⁻ ions are mostly derived from agricultural fertilizers, animal waste, and municipal and industrial sewage [31]. These factors can be related to the TDS variation and can be used to indicate the influence of human activities on the water chemistry [31,32]. There were strong correlation between TDS and Cl⁻ (r = 0.70) and nearly good correlation between TDS and Na⁺ (r =0.40), indicating the influence of human activities on the water chemistry. Earlier studies have indicated that the high concentrations Cl⁻ in groundwaters can result from the excessive application of manure and inorganic fertilizer [33,34]. To enhance the feed flavors and maintain cation–anion balance in the diet, salts are commonly added to animal feed [35]. The result is supported by that the Na-Cl is one of the major water facies in the surveyed groundwater samples. Thus, factor 1 can be termed as anthropogenic or salinization factor.

Potassium, $(HCO_3 + CO_3)$ and Ca were loaded on factor II with lesser percentage of variation among the wells. This may be due to the high stability of potassium [36]. Also, lesser percentage of variation of Ca and $(CO_3 + HCO_3)$ among the studied wells is probably due to the presence of the carbonate minerals.

Factor III, with lesser loading of Si and pH explained with 13.8% of variance. pH of most of the water samples was greater than 7. Alkalinity of water may be due dissolution of carbonate mineral in the studied area. Silicon was loaded on the third factor with small percentage of variation among the studied wells due to the presence of Si in most of the rocks of the study area. The result is supported by that the granitic rocks in the studied area consist of feldspars (plagioclase and orthoclase), pyroxene, and quartz. According to all that mentioned above the factor II and factor III can be denoted as groundwater-host rock interaction factor. Factor IV was loaded with $SO_4^{2^\circ}$. It may represent the variations in agricultural management such as using different fertilizers in the studied area.

4.2.2. Hierarchical Cluster Analysis (HCA)



Figure 4. Dendogram for 30 samples from cluster analysis in R-mode

Cluster analysis is a method for placing objects into more or less homogeneous groups so that the relation between the groups is revealed [37]. So there are two types of cluster analysis (Q-mode and R-mode): The Rmode HCA was done to classify the parameters into groups based on their similarity with each other, whereas the Q-mode was performed to classify the parameters into groups based on their dissimilarity with each other [29,38]. It is also possible to evaluate whether water quality samples at various locations can be combined into homogenous regions. Ward's method is the most popular hierarchical algorithm and is recommended as distance measures of clustering. Plot of R-hierarchical cluster with Ward's linkage is portrayed in Figure 4 and the mean values of chemical constituents for each cluster are showed in Table 4. On the basis of the cluster analysis wells of studied area are clustered as follows:

Table 4. Mean values of chemical constituents for each cluster				
Variable	Cluster I	cluster II	Cluster III	cluster IV
well	(13 wells)	(8 wells)	(5 wells)	(4 wells)
EC	730.8	879.6	552.2	298.0
pH	8.3	8.3	8.2	8.3
Si	8.0	7.7	5.4	5.7
Ca	20.0	35.2	30.6	19.7
Mg	32.8	36.2	20.4	16.2
Na	97.9	49.2	55.0	12.7
K	8.9	85.7	3.8	5.2
HCO ₃ +CO ₃	99.7	224.9	107.8	84.0
Cl	190.8	154.5	109.0	45.2
SO_4	39.8	31.5	22.8	12.7

Cluster I is composed of the wells 6, 8, 12, 14, 15, 16, 20, 21, 22, 27, 28, 29 and 30, and concerns 43% of the water samples. This type of water with a mean EC of 730.8 μ mhoscm⁻¹, has high salinity in compared to the clusters III and IV. This cluster is basically Cl⁻ and Na⁺ dominated, however; CO₃²⁻ + HCO₃⁻ and SO₄²⁻ are also present (Table 4).

Cluster II is represented by the wells 2, 3, 4, 10, 17, 18, 23 and 26, and it occupies 27% of the water samples. This cluster of water with a mean EC of 879.6 μ mhoscm⁻¹, also has higher salinity in compared to the clusters III and IV. This water cluster II is being dominated by CO₃²⁻ + HCO₃⁻, Cl⁻ and K⁺. It also has higher concentrations of Ca²⁺, Mg²⁺ in compared to other clusters, which is the characteristic of mixed water (Table 4).

Cluster III includes wells: 1, 5, 19, 24 and 25, and concerns 17% of the water samples. The mean EC of the cluster is 552.2 μ mhoscm^{-1,} which has lesser salinity in compared to clusters I and II. Cl⁻ and CO₃²⁻ + HCO₃⁻ content are middle, which is also the characteristic of blended water.

Cluster IV is composed of the wells 7, 9, 11 and 13, and concerns 13% of the water samples. This type of water is fresh with a mean EC of 298 μ mhoscm⁻¹, which is the characteristic of less saline water. The concentration of all ions in this cluster is basically low. This water type can be interpreted as the first step of water-rock interactions occurring in dilute solutions. As a result water samples in clusters I and II are higher concentrated in compared to water samples in clusters und IV, indicates the groundwater quality in the clusters I and II is slowly getting to degradation.

Principal component (PC) analysis results show that the first two PCs, with 50.1% of total variance, have important role in the hydrochemical variability in the groundwater samples. As discussed above, PC1 mainly characterized by the effect of human activities and PC2 represents the natural process such as water-rock interaction. Therefore, the contribution of factors I and II (factor scores) on hydrochemical variability of the groundwater samples were computed and plotted in Figure 5. This plot depicts the contribution of factor I (X axis) and factor II (Y axis) on the water chemistry. If the water samples fall in the positive part of the factors, it means that the factor has an active role on quality of the groundwater. However, if the water samples fall in the

negative part of the factors, it means that the role of the quality of the groundwater is not significant. As shown in Figure 5, the most of the water samples of cluster I contributes to 43.0% of the total studied wells and is located in positive part of factor I, indicating that the quality of the groundwater mainly controlled by anthropogenic activates. Most of the water samples of cluster III and all water samples in cluster IV that respectively contributes to 17% and 13.0% of the total studied wells is located in positive part of factor II, indicating that the quality of the groundwater samples mainly controlled by water-host rocks interaction. The water samples fall in cluster II that contributes to 27.0% of the total studied wells is intermediate with regard to control quality, because factor scores of all water samples in this cluster is located in positive part of factor I and factor II, suggesting that both water-host rocks interaction and anthropogenic activates can have a significant effects on quality of the groundwater.



Figure 5. The Contribution of factors I and II (factor scores) in at each monitoring well

4.2.3. Mechanisms Controlling Groundwater Chemistry

Reactions between groundwater and the aquifer constituent minerals have a significant role on water quality. Further, these studies are useful to understand the genesis of groundwater [39,40]. To know the groundwater chemistry and the relationship of the chemical components of water to their respective aquifers such as chemistry of the rock types, chemistry of precipitated water, and rate of evaporation, Gibbs [41] has suggested these types of diagrams. In this diagram the ratio of dominant anions and cations are plotted against the value of TDS. These diagrams are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation, rock, and evaporation dominance.

The Gibbs ratios are calculated with the formulae given below:

Gibbs Ratio I (for Anion) = $Cl / (Cl + HCO_3)$

Gibbs Ratio II (for Cation) = (Na + K) / (Na + K + Ca)Where all ions ware expressed in meq/l.

In the present study area, the dominant anions (Cl and HCO_3) and cations (Na, K and Ca) are plotted against their respective total dissolved solids [Figure 6], in order to know whether the ground water chemistry is due to rock dominance, evaporation dominance or precipitation dominance. The Gibbs's plot suggest that most of the samples falls in weathering zone, which indicates the groundwater interaction between rock chemistry. Gibbs's diagrams suggest that chemical weathering of the rock,

which forms minerals. Gibbs ratio I values in the present study varies from 0.38 to 0.98 with a average value of

0.68 and Gibbs ratio II values varies from 0.31 to 0.93 with a average value of 0.70.



Figure 6. Mechanism controlling the chemistry frounfesyer (after Gibbs 1970)

5. Conclusions

Interpretation of analytical data showed that the abundance of the major ions is as follows: Na > Mg \approx K > Ca > Si and $Cl > HCO_3 > SO_4 > CO_3$. Factor analysis extracted four factors comprising F1 (with high loading factor of Cl, EC, Mg and Na), F2 (with high loading factor of K, (HCO₃+CO₃) and Ca), F3 (with high loading factor of pH and Si) and F4 (with high loading factor of SO₄), with a total variance of 74.7. The varifactors obtained from Factor analysis indicated that the parameters responsible for groundwater quality variations are mainly related to groundwater-rock interaction (particularly weathering of silicate minerals present in the granites), and anthropogenic sources (particularly agricultural activities). Soda - rich feldspars easily dissolve and contribute sodium to natural waters. The Gibbs's diagram support these factor analysis results and suggest that the main controlling mechanism of groundwater quality is due to the chemical weathering of rock forming minerals.

Based on HC analysis the water samples have been classified into 4 clusters. Cluster I (includes 13 wells with high concentration of Cl⁻ and Na⁺) and cluster II (includes 8 wells with high concentration of $CO_3^{2-} + HCO_3^{-}$, Cl⁻ and K^+) have shown moderate salinity. However, cluster IV (5 wells) had lowest concentrations of ions and classified as fresh water. Cluster III (4 wells) showed intermediate salinity between (I and II) and IV clusters. The results suggest that water samples in clusters I and II have shown higher concentration of ions when compared to water samples in clusters III and IV. This indicates that the groundwater quality in the clusters I and II is slowly getting to degradation. The results also showed that the potential salinity with regard to high concentration of Cl and Na, is the only problem with some of the water samples to use for irrigation usage in this area. Briefly, the results of this study demonstrate that the multivariate statistical analysis can be useful tool for effective groundwater quality management.

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