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A STATISTICAL APPROACH ON HYDROGEOCHEMISTRY OF GROUNDWATER IN MUTHUPET COASTAL REGION, TAMILNADU, INDIA

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Abstract: Seventy two groundwater samples were collected from February to September 2007 covering in three seasons for delineating hydrochemical nature in Muthupet coastal area. Dominance of cations are in the following order Na>Ca>K>Mg and Cl>SO4>HCO3>NO3 by anions in three seasons. From the Piper trilinear diagram, it is observed that the majority of groundwater samples are Na-Cl and Ca-Mg-SO4 facies clearly indicates seawater incursion. The statistical treatment of the data (cluster, factor analysis) indicates that seawater incursion is the dominant process that influences the quality of the groundwater in the coastal region.

Keywords: Hydrogeochemical facies, Correlation materix, Cluster analysis, Factor analysis, Seawater Incursion.

1. INTRODUCTION

Water is a finite resource and it is becoming a scarce commodity in many parts of the world. Competition amongst agriculture, industry, and domestic uses for limited water supplies is a constraining factor for economic development in countries with scarce water resources. These undesirable effects are expected to become more serious as climatic changes cause more desertification, greater erosion in watersheds, and sea level elevation in coastal areas. In the last 20 years, groundwater salinization has become an urgent environmental problem worldwide and constitutes one of the most widespread forms of water contamination. The problem is particularly serious in coastal areas, where rapid population growth and intensive economic activity has increased the need for fresh-water supplies. This need is mainly being satisfied by pumping groundwater from coastal aquifer systems. However, in coastal regions, groundwater quality patterns are complex because of the input from many different water sources. These include precipitation (possibly polluted or saline due to strong evaporation), seawater, ascending deep groundwater, and anthropogenic sources such as wastewater or irrigation return flow (Steinich et al. 1998). Proper management of available groundwater reserves is impossible without knowledge of the spatial distribution of fresh and saline groundwater and the processes that determine their evolution (Glynn & Plummer 2005). Over exploitation of the groundwater has become a common issue with many coastal region in the world, now experiencing extensive seawater intrusion in aquifers resulting in severe deterioration in groundwater quality, and hence from a use point of view, quality as well (Paniconi et al., 2001, Ma et al., 2005; Karahanoglu & Doyuran, 2003, Venkatramanan et al., 2009, Ramkumar et al., 2011). In this study, the groundwaters of an alluvium where intensive agricultural activities take place were geochemically investigated to evaluate the factors regulating the groundwater quality. The results show that the clustered groups are well correlated to the aquifer conditions and adequately represent the levels of groundwater contamination by seawater intrusion and agricultural activities, suggesting that the clustering approach based on chemical data can be applied to the assessment of groundwater.

2. STUDY AREA

The study area, Muthupet is situated in Tiruvarur district of Tamilnadu (Fig.1). The study area is located between latitude 10°16'00'' to 10°34'00'' North and longitude 79°26'30'' to 79°42'00'' East in the survey of India toposheets number 58N/7, N/10, and N/11. The geological formations include mixture of sand, silt, clay, and natural levee complexes. The entire block comes under recent quaternary formation. The area forms part of Cauvery delta with gentle slope towards Bay of Bengal. No surficial older formations are exposed except for small area around Mannarkudi (1040; 7929) covered by lateritic soil over the Cuddalore formations of Mio-Pliocene age. The quaternary deposit represents the rest of the areas. The thickness of the quaternary sediments increases south of the Kollidam rivers.

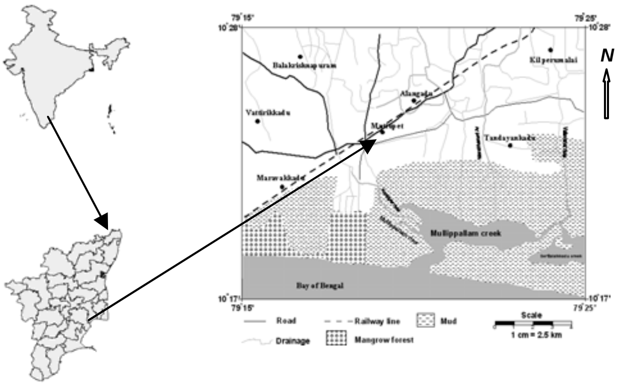

Figure 1. Location map of Study area

These sediments have been delineated as alluvial plain deposit. Cauvery formation of the Cauvery river and its distributaries, narrow fluvio-marine deltaic plain deposits (East coast formation). The fluvial deposits comprise flood plain, flood basin, point bar, channel bar and palaeo-channels with admixtures of sand, silt, clay and gravel. The ground water is extracted by filter point wells, tube wells, shallow bore wells and infiltration wells especially in the sandy aquifers. The premonsoon declining trends are compensated by subsequent monsoon recharge. During summer water level goes down from 6 to 7m below ground level.

3. METHODOLOGY

In total, 72 groundwater samples were collected from February to September 2007, covering the postmonsoon, summer, and premonsoon seasons. Samples were collected in good quality polyethylene bottles of 1-l capacity. Sampling was carried out without adding any preservatives in rinsed bottles directly for avoiding any contamination and brought to the laboratory. Samples were analysed in the laboratory for the major ions/compounds using standard methodologies. The pH and electrical conductivity (EC) were measured on pH and electrical conductivity meters, respectively. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using standard EDTA; chloride (Cl^{-}) was determined by standard $AgNO_3$ titration; carbonate (CO_3^{2-}) and bicarbonate (HCO_3^{-}) were determined by titration with HCl; sodium (Na^{+}) and potassium (K^{+}) were measured by flame photometry; sulphate (SO_4^{2-}) was determined by spectrophotometric turbidimetry; nitrate (NO_3^{-}) was determined by UV-visible spectrophotometer (Rowell, 1994). Total dissolved solids (TDS) were computed by multiplying the EC (dS m) by a factor of 640. Care was taken that the pH and EC and the HCO_3^{-} and Ca^{2+} ions were analysed within 24 h of sampling. The depth of the water table varies from 4.6 m to 5.38 m in winter and 2.40 m to 3.85 m in summer below ground level (Table 1).

Table 1. Physico–chemical parameters of the groundwater samples

Water quality parameter in mg/l	***Concentration in study area mg/l***		
	Postmonsoon	Summer	Premonsoon
	Min-Max.	Min-Max.	Min-Max.
pH	6.2-7.2	7.2-8.5	6.5-8.0
Electrical conductivity (µS/cm)	1014-1927	2421-3227	1517-2265
Total dissolved solids	649.4-1233	1549.5-2065.3	971.4-1449.6
Calcium	19-31	69.6-136.3	37.3-64
Magnesium	14-29	23.2-55.8	19.2-33
Sodium	142.6-352-4	336.4-620	265.1-522.9
Potassium	18-50.2	32.3-130	28.6-98
Bicarbonate	26-46	69-92	34.6-73
Sulphate	151.5-512.3	337.8-713	232-443.9
Chloride	209.5-309.4	519.5-702	294.4-503
Nitrate	1.9-2.8	5.8-7.8	3.73-4.98

4. RESULTS AND DISCUSSION

4.1. Major ion geochemisty

Generally, pH is controlled by acidity and total alkalinity of groundwater. The value of pH ranged from 6.3 to 7.25, 7.2 to 8.6 and 6.5 to 8.0 in post monsoon, summer and pre monsoon seasons respectively. These variations are slightly higher than the permissible limit of drinking water standard. The general increase of pH in a sedimentary terrain is relates to weathering of plagioclase feldspar in the sediments, aided by dissolved atmospheric carbon dioxide resulting in the release of sodium and calcium which progressively increases the pH and alkalinity of the groundwater.

The importance of electrical conductivity in the coastal water refers to the measure of salinity in the water which greatly affects the taste and thus has a significant impact on the user's acceptance of the water as potable. Electrical conductivity was low when the freshwater recharge during pre monsoon and post monsoon and progressively increases during summer along the coastline. The electrical conductivity values were found between 1014 and 3227 µS/cm at 25°C in the study area. The relatively higher values of electrical conductivity in the study area can be attributed to the higher amount of total dissolved salts in groundwater and the source for that may be the salts from the seawater. The concentration of total dissolved solids ranged from 139.91 to 516.13 mg/l in the study area. Normally, total dissolved solids in water may originate from natural sources and sewage discharges. In groundwater, several processes may cause an increase in the dissolved solids content. These include movement of water through sediments containing higher soluble mineral matter and also by contamination due to influx of industrial and municipal waste disposal along with incursion of seawater. Calcium and magnesium concentration generally derived from leaching of limestone, dolomites, gypsum and anhydrites (Garrels 1976, Ramkumar et al. 2010). Calcium concentration ranged from 19 to 31 mg/l, 69.6 to 136.3 mg/l and 37.3 to 64 mg/l in post monsoon, summer and pre monsoon seasons respectively. Despite the seasonal fluctuations, these calcium concentrations were well within the drinking water standard. The concentration of magnesium ranged from 14 to 55.83 mg/l during the study period, with an average value of 34.91 mg/l. This may be due to the enrichment by mineral dissolution or by ion exchange process. Sodium concentration varies from 142.6 to 620.1 mg/l in the study area. Sodium might have been derived from dissolution of evaporate minerals and subsequent mixing with groundwater; since in these regions large number of saltpans are in operation. Potassium content ranged from 18.05 to 130.53 mg/l in the study period. It indicates the entry of more saline water to the groundwater and also from agricultural sources.

Bicarbonate ion varied from 26 to 46; 69 to 92; and 34.66 to 73.33 mg/l in the groundwater samples during post monsoon, summer and pre monsoon seasons. A low bicarbonate concentration during postmonsoon indicates the influence of freshwater addition to the groundwater during monsoon period where as these area received a monsoonal of 1327.1mm. Chloride concentration of groundwater samples in the study ranged between 209.5 and 702.46 mg/l. Relatively, higher Cl concentration in groundwater in the coastal region is attributed to influence of seawater on the coastal aquifer which was highly visible during summer due decline water table. Sulphate ion varied from 151.45 to 713.4 mg/l during the study period and nitrate ion varied from 1.9 to 7.8 mg/l in the study area. The conspicuous variation observed for this parameter was mainly by the influence of agricultural activity and by the influence of seawater into the shallow aquifer system. To ascertain the suitability of groundwater for drinking and public health purposes, hydrochemical parameters of the study area are compared with the guideline recommended by world health organization (WHO, 1984) which shows that groundwater has partial suitability for drinking purposes.

4.2. Hydrogeochemical facies

Hydrogeochemical facies are distinct zones that possess cation and anion concentration categories (Freeze and Cherry 1979). The interpretation of distinct facies from the 0% to 10% and 90% to 100% domains on the diamond-shaped cation and anion graph is more helpful than using equal 25% increment. This is useful to understand the total chemical character of water samples in terms of cation–anion pairs. The percentage reacting values at the three cation groups Ca, Mg, and (Na + K) are plotted as a single point in the left triangular field and the three anion groups (HCO_3+CO_3), SO_4, and Cl similar on the right triangular field. Piper (1953) classification is used to express similarity and dissimilarity in the chemistry of different water samples based on the dominant cations and anions. Major cations and anions such as Ca, Mg, Na, K, HCO_3, SO_4, and Cl in meq/l were plotted in Piper's trilinear diagram to evaluate the hydrochemistry of groundwater of Muthupet coastal region with the help of Aquachem 4.1 software (Fig. 2). The plot shows that most of the groundwater samples fall in the field of Na–Cl facies. The remaining samples fall in Ca Mg SO4 facies, it clearly indicates the presence of seawater incursion and hard water in the study area.

4.3. Correlation matrix

Correlations between major cations and anions were carried out using Pearson's correlation. A correlation analysis is a bivariate method applied to describe the degree of relation between hydrochemical parameters. A high correlation coefficient (near 1 or 21) means a good relationship between two variables, and a value near 0 means there is no relationship between them at a significance level of, 0.05. More precisely it can be said that parameters showing r. 0.7 are considered to be strongly correlated, whereas when r has a value between 0.5 and 0.7, moderate correlation is said to exist (Kim et al. 2002; Helena et al. 2000).

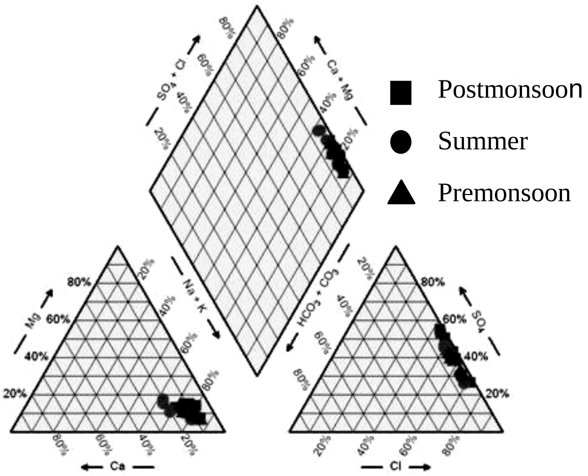

Figure 2. Distribution of the water samples on Piper diagram

In this study, the statistical approach was used to define the origin of the chemical elements by identifying hydro chemical processes. Statistical analyses are used for to get an overall idea of water chemistry of the region. During postmonsoon season K with No_3 in the groundwater show good correlation. Total dissolved solids having correlation with K, Na, SO_4, No_3 and Cl. The positive correlation between Ca and Mg is attributed to the precipitation of aragonite, dolomite and calcite, precipitation taken place during the cation exchanging process which is the later effect from the seawater intrusion into the aquifer. The lower concentration of Ca compared to Na is a result from the cation exchange process that occurs naturally when seawater intrudes in to the aquifer system (Appelo and Willemsen, 2005).

The Na is positively correlated with Ca, Mg and TDS. The correlation between Na and Cl however shows around (0.72) which in interpreted as a result of seawater intrusion. The Na-Cl correlation shows the influence of seawater and groundwater mixing. According to Mandel & Shiftan (1981), the average of (0.66) is less than that of seawater (0.87). In this study, the Na-Cl signature is around (0.60) which is not as clear as theoretical correlation, this is means that seawater as a result of aquifer recharge from infiltration. Potassium shows positive and significance correlation with all analyzed parameter except HCO_3 with a significance level of more than (0.08), such correlation is interpreted as arising from the fact that most of these components are derived from the interaction of groundwater with the aquifer matrix (high-Ca-calcite), which is very common in the coastal aquifer (Appelo 2005), part of which are certainly derived from seawater intrusion in the study area. The positive and significance correlation of K with both Cl and SO_4^{2-} which generally very high in the sea may be interpreted in the light of seawater intrusion (Al-Agha 2004).

In summer season TDS is positively correlated with Na, K, and SO_4. The Na-Cl correlated positively Ca, Mg, K, it reveals the highly affected saline from the coastal and saline soils (Ahamad Zaharin et. al, 2007) Cl correlated with Na, K, SO_4 may be due to the leaching and higher concentration of sulphate minerals in the area and seawater intrusion (Abdullah et. al, 2002). During premonsoon season Na is positively correlated with Ca, Mg, SO_4^{2-} then Mg correlated with Ca, Na, and SO_4^{2-}. The same kind of results observed during postmonsoon and summer seasons. The correlation matrix of the three seasons clearly indicates seawater incursion present in the aquifer (Table 2a, b and c).

Table. 2a. Correlation Coefficients of hydrochemical data of groundwater (Postmonsoon)

	pH	**TDS**	**Ca**	**Mg**	**Na**
pH	1.00				
TDS	0.07	1.00			
Ca	0.23	-0.23	1.00		
Mg	-0.11	0.49	0.53	1.00	
Na	0.28	0.62	0.20	0.14	1.00
	K	**HCO_3**	**NO_3**	**SO_4**	**Cl**
K	1.00				
HCO_3	0.36	1.00			
NO_3	0.78	0.56	1.00		
SO_4	0.52	-0.01	-0.24	1.00	
Cl	0.62	-0.37	-0.91	0.29	1.00

Table.2b. Correlation Coefficients of hydrochemical data of groundwater (Summer)

	pH	**TDS**	**Ca**	**Mg**	**Na**
pH	1.00				
TDS	0.00	1.00			
Ca	-0.10	0.09	1.00		
Mg	0.18	-0.32	0.58	1.00	
Na	0.10	0.55	0.52	-0.57	1.00
	K	**HCO_3**	**NO_3**	**SO_4**	**Cl**
K	1.00				
HCO_3	0.31	1.00			
NO_3	0.06	0.78	1.00		
SO_4	0.46	-0.17	0.12	1.00	
Cl	0.41	0.33	0.32	0.56	1.00

Table.2c. Correlation Coefficients of hydrochemical data of groundwater (Premonsoon)

	pH	TDS	Ca	Mg	Na
pH	1.00				
TDS	0.70	1.00			
Ca	0.03	-0.46	1.00		
Mg	0.03	-0.06	0.31	1.00	
Na	0.48	0.39	0.52	0.62	1.00
	K	**HCO_3**	**NO_3**	**SO_4**	**Cl**
K	1.00				
HCO_3	-0.20	1.00			
NO_3	0.52	-0.19	1.00		
SO_4	0.12	0.21	0.80	1.00	
Cl	-0.17	0.26	0.26	0.63	1.00

Table.3a. Varimax rotated factor loadings (Postmonsoon)

Postmonsoon				
Variables	Factor 1	Factor 2	Factor 3	Communality
pH	0.44	0.51	0.69	0.93
Electrical conductivity (µS/cm)	0.74	0.33	0.56	0.94
Total dissolved solids (TDS)	0.74	0.33	0.56	0.94
Calcium (Ca)	0.28	0.35	0.85	0.86
Magnesium (Mg)	0.70	0.44	0.40	0.82
Sodium (Na)	0.51	0.23	0.70	0.80
Potassium (K)	0.34	0.90	0.18	0.80
Bicarbonate (HCO_3)	0.33	0.64	0.60	0.84
Sulphate (SO_4)	0.60	0.22	0.71	0.90
Chloride (Cl)	0.87	0.33	0.24	0.86
Nitrate (NO_3)	0.30	0.74	0.56	0.92
Eigen values	8.74	0.74	0.55	
Total % of variance	79.46	6.69	5.05	
Cumulative % of variance	79.46	86.15	91.19	

4.4. Factor analysis

Factor analysis is a frequent statistical technique in hydrochemical studies (Subbarao et al., 1996; Adami et al., 1997, Davis, 1986, McCuen & Snyder, 1986) applications. The main goals of factor analysis are: (1) to reduce the number of 'variables' and (2) to detect structure in the relationships between 'variables' (analytical parameters) and/or 'cases' (sampling points in our study). The mathematical base of factor analysis and a review of the chemical aspects can be found in Mermet et al., (1998). Nowadays, the calculations of factor analysis and graphical results are performed with the appropriate software are described in detail by Davis (1986). Factor analysis is performed in this study using statistical programme named STATISTICA.

The Varimax rotated factor loadings are given in table 3. The proportion of the total variance explained by the extracted factors from the post monsoon, summer and pre monsoon data are 91.19%, 93.53% and 89.95% respectively. The communalities of the variables in the data sets are near to the range 0.8-0.9 which explains that the factor analysis model is assumed to represent adequately the overall variance of the data set.

Table.3b. Varimax rotated factor loadings (Summer)

Summer				
Variables	Factor 1	Factor 2	Factor 3	Communality
pH	0.65	0.45	0.56	0.92
Electrical conductivity (µS/cm)	0.50	0.61	0.57	0.94
Total dissolved solids (TDS)	0.50	0.61	0.57	0.94
Calcium (Ca)	0.38	0.27	0.86	0.89
Magnesium (Mg)	0.49	0.16	0.77	0.80
Sodium (Na)	0.56	0.71	0.30	0.88
Potassium (K)	0.27	0.91	0.14	0.78
Bicarbonate (HCO_3)	0.73	0.49	0.43	0.92
Sulphate (SO_4)	0.71	0.33	0.57	0.91
Chloride (Cl)	0.19	0.69	0.67	0.87
Nitrate (NO_3)	0.66	0.45	0.56	0.93
Eigen values	9.15	0.81	0.33	
Total % of variance	83.14	7.35	3.04	
Cumulative % of variance	83.14	90.49	93.53	

Table.3c. Varimax rotated factor loadings (Premonsoon)

Premonsoon				
Variables	Factor 1	Factor 2	Factor 3	Communality
pH	0.59	0.46	0.61	0.93
Electrical conductivity (µS/cm)	0.70	0.53	0.41	0.94
Total dissolved solids (TDS)	0.70	0.53	0.41	0.94
Calcium (Ca)	0.29	0.28	0.89	0.86
Magnesium (Mg)	0.65	0.10	0.69	0.91
Sodium (Na)	0.28	0.79	0.44	0.87
Potassium (K)	0.24	0.89	0.08	0.66
Bicarbonate (HCO_3)	0.76	0.26	0.25	0.62
Sulphate (SO_4)	0.87	0.18	0.34	0.89
Chloride (Cl)	0.82	0.42	0.23	0.88
Nitrate (NO_3)	0.63	0.54	0.47	0.92
Eigen values	8.38	0.90	0.61	
Total % of variance	76.16	8.21	5.59	
Cumulative % of variance	76.16	84.36	89.95	

First factor accounts for 79.46% of the total variance and represents permanent hardness (Mg, Ca, and SO_4^{2-}) and salinity (Na, Cl). These parameters indicate large residence time of groundwater, greater solubility of minerals and application of fertilizers in Muthupet coastal area. The second factor is represented by K, HCO_3, and NO_3 explain 6.69% of the total variance. High concentration of HCO_3 is derived from calcareous materials on the reaction of atmospheric CO_2. Factor 3 is represented by pH, Ca, Na, Cl and HCO_3. It explains 5.05% of the total variance. It is indicated the dissolution of leaching of secondary minerals (3a, b and c).

4.5. Cluster analysis

The dendrogram of the 11 indexes based on the cluster analysis is depicted in figures 3a, b and c. On the basis of dendrogram of all 11 indexes can be grouped into three main clusters. First cluster group shows close association between K, HCO_3, Mg, Ca, NO_3 and pH in post, summer and pre monsoon seasons respectively.

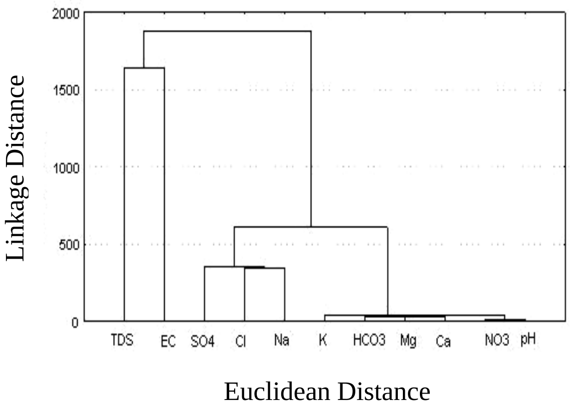

Figure 3a. Dendrogram of the 11 chemical parameters of 9 cases (postmonsoon)

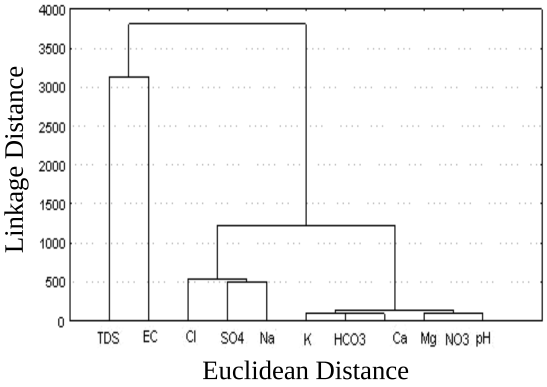

Figure 3b. Dendrogram of the 11 chemical parameters of 9 cases (summer)

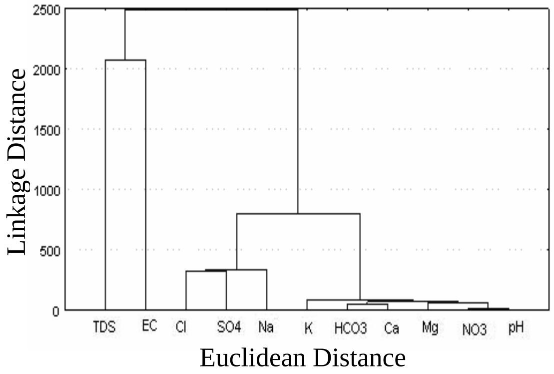

Figure 3c. Dendrogram of the 11 chemical parameters of 9 cases (premonsoon)

Group 2 and 3 shows the close association between Na, Cl, SO_4 and EC -TDS in the groundwater samples of during post, summer and pre monsoon seasons respectively. These indexes have high values in most of the sampling stations. These findings corroborate with the results of correlation analysis, cluster and factor analysis. These would be variables whose origin is found in natural mineralization and anthropogenic processes. The non-homogenous nature of the aquifer leads to different hydrochemical facies for groundwater Na and Cl. A close relationship is found between Na and Cl, this may be due to incursion of seawater into coastal aquifers (Figs 3a, b and c).

5. CONCLUSIONS

The problem of groundwater in Muthupet is rather complicated; it represents an over exploitation of an aquifer. The study area depends totally on the water derived from the aquifer for its domestic use. The over pumping for fresh water supply contributed to the deterioration of the water quality by exposing the deep saline water. Dendrogram of the 9 cases and 11 variables are plotted and grouped into three main clusters. The values of correlation coefficients and their significance levels will help in selecting the proper treatments to minimize the contaminations of groundwater of Muthupet. Factor analysis is useful over graphical representations to understand the chemical facies present in groundwater. The study reveals that the groundwater from Muthupet area has great influence from lithology and environmental factors in its genesis. A continuous monitoring program of the water quality will avoid further deterioration of the water quality in the coastal region.

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