



Evaluation of Factors Influencing the Groundwater Chemistry of Part of Kancheepuram Taluk, Tamilnadu

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Abstract

Groundwater is the major source for domestic and irrigation activities in urban regions. A study was carried out in the part of Kancheepuram taluk of Tamil Nadu, to identify the factors that influencing the groundwater chemistry. Totally 24 samples were collected by representing the whole region which is underlain by both sedimentary and hard rock aquifers. The samples have been analysed for major ions Ca, Mg, Na, K, Cl, HCO₃, SO₄ NO₃ and pH, TDS. Geochemical plots such as Piper and Chadha has been used to identify the hidden geochemical processes. Multivariate statistical methods such as Correlation and factor analysis were used as predictive and effective tool for groundwater evolution which also supports the geochemical plots. The results suggest that different hydrogeochemical processes, like weathering (recharge processes), ion exchange processes, and anthropogenic activities (like sewage infiltration and agriculture), has predominant impact in the study area.

1. Introduction

Groundwater resources are dynamic in nature. In many countries groundwater is used for irrigation, domestic and industrial purposes. Further the quality depends upon the geochemistry of groundwater. Geochemical signatures is controlled by several factors such as rock types, soil characteristics, topography, salinization in coastal areas and anthropogenic activities (Das Brijraj and Kaur, 2007; Cloutier et al., 2008). The characteristics of groundwater in different types of aquifers over space and time have been proved to be a significant technique for solving different geochemical problems (Chebotarev, 1955; Hem, 1959; Back et al., 1965; Gibbs, 1970; Srinivasamoorthy et al 2005). The knowledge of hydrochemistry is important to determine the origin of chemical composition of groundwater (Zaporoze, 1972). The hydrology and geochemistry of waters have been further discussed in the classic works of Stumm and Morgan (1996), Hem (1991), Drever (1988) and Domenico and Schwartz (1998).

The hydrogeochemical investigation is combined with statistical methods for better understanding the geochemical evolution of groundwater. Multivariate statistical analysis such as correlation and factor analysis using principal component analysis have been applied in number of hydrogeochemical studies (Prasanna et al., 2010; Thivya et al., 2013; Chidambaram et al., 2008) to identify the geochemical evolution. Melloul and Collin (1992) used principal component analysis (PCA) and classical geochemical methods such as Scholler and Piper diagrams and the study identified major water groups and factors which affecting groundwater quality in an aquifer. The present study area Kancheepuram district is predominantly depends upon the groundwater for all purposes which lie in both hard and sedimentary aquifers. Some of the previous studies carried out in Kancheepuram district, Tamil Nadu which include groundwater quality monitoring and pumping tests by Public Works Department (2000), groundwater flow model-

ing by Senthil Kumar and Elango (2001), hydrogeochemical processes using inverse mass-balance modeling by (Lakshmanan et al., 2003). But the study on hydrogeochemical processes combined with statistical methods has not been attempted yet in these regions. Hence a study has been proposed to understand the factors which are influencing the groundwater chemistry with statistical analysis in the Kancheepuram taluk.

2. Study area

Kancheepuram district is bounded by $12^{\circ} 47' 10''\text{N}$ and $12^{\circ} 55' 20''\text{N}$ and $78^{\circ} 57' 20''\text{E}$ and $80^{\circ} 6' 25''\text{E}$ (Fig. 1). It is endowed with a flat topography with occasional undulations due to the presence of residual hills and scattered outcrops. The district is underlain by both sedimentary and fissured formations. The important aquifer systems in the district are constituted by the unconsolidated and semi consolidated formations with weathered, fissured and fractured crystalline rocks. The normal annual rainfall over the district varies from 1105 mm to 1214mm. It generally experiences hot and humid climatic conditions. It is part of the composite east flowing river basin and spread over a part of Palar and Cheyyar sub-basin. The sedimentary formations covers in northern and southern part and the hard rock formation Charnockite have been observed in central part of the region (Fig. 2).

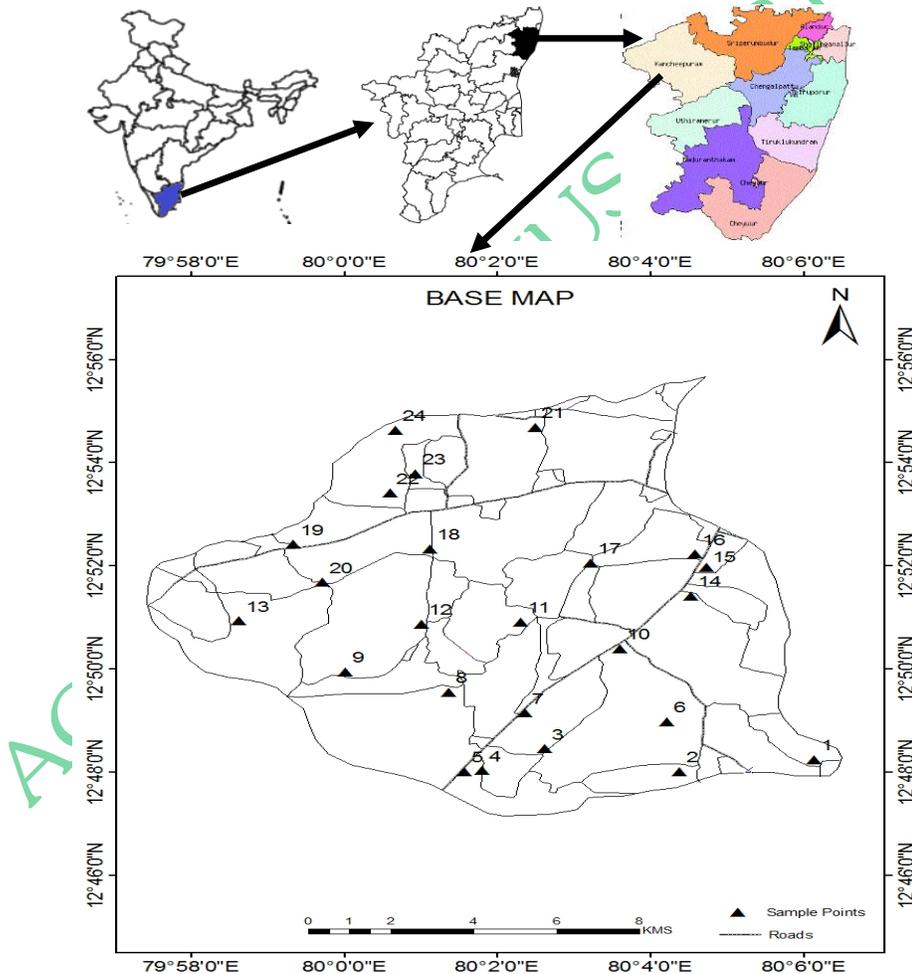


Fig.1. Location map of the study area with sampling points

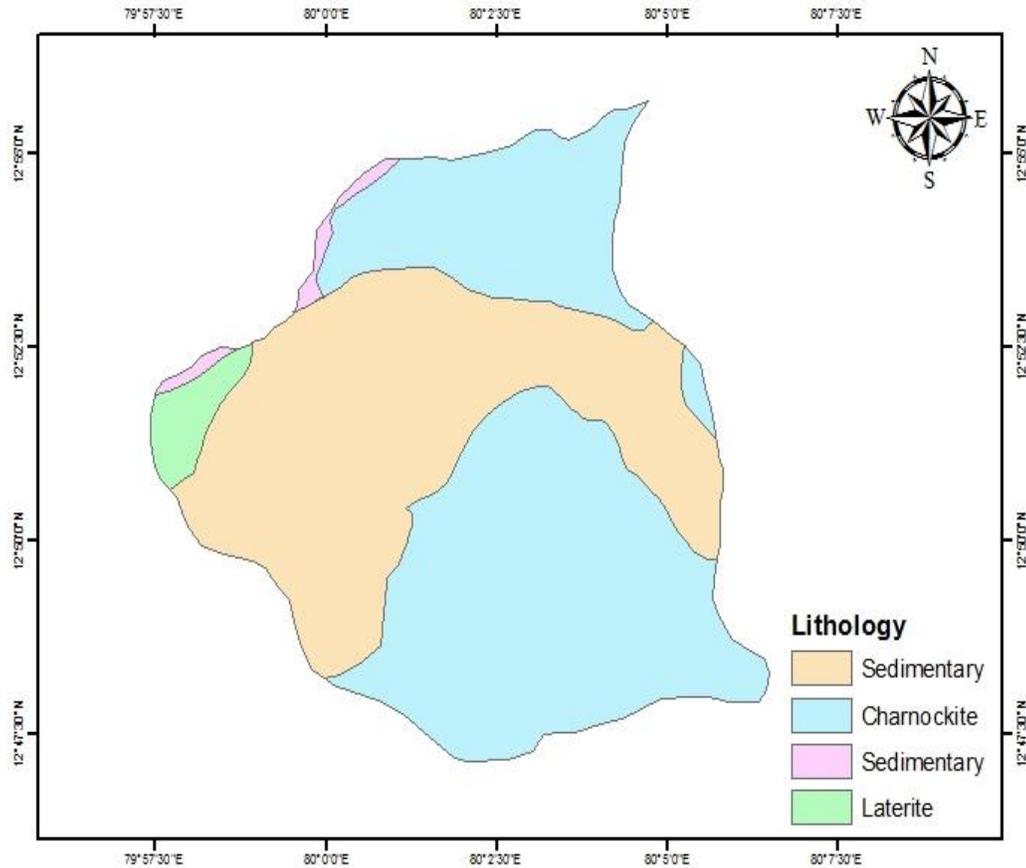


Fig. 2 Lithology map of the study area

3. Methodology

A total of 24 groundwater samples were collected in the post monsoon (January 2014) representing the region (Fig. 1). Sampling and analysis were carried out using standard procedures (Ramesh and Anbu 1996; APHA 1995). 500 ml of water samples were collected in polyethylene bottle. pH and electrical conductivity (EC) were determined in the field using Field Analysis Kit. The collected groundwater samples were analyzed for major ions. Calcium, magnesium, bicarbonate, and chloride were determined by titrimetric method. Sodium and potassium were analyzed through flame photometry. Silica, phosphate, and sulfate were determined by spectrophotometry. The reliability of the results was determined by the ionic balance of groundwater samples and a 5–10 % of percentage error was noted. Then, the results were processed in Statistical Package for the Social Sciences (SPSS) 16.0 package software using multivariate statistical techniques such as the factor analysis. The principal component analysis with orthogonal rotation of the initial factors was done by using Kaiser's varimax rotation.

4. Results and Discussion

The maximum, Minimum and Average concentration of chemical constituents of groundwater are given in Table. The order of dominance of ions is as follows



pH ranges from acidic to alkaline in nature. EC ranges from 420 to 4650 $\mu\text{s}/\text{cm}$ in groundwater. Ca concentration ranges from 6 to 296 mg/l which may be from minerals like calcite, plagioclase and hornblende. The principal source of Mg^{2+} in the natural waters is magnesium bearing minerals in the rocks and secondary source are animals, domestic and industrial wastes (Garcia et al., 2001) and it ranges from 9 to 122 mg/l. Na ranges from 9 to 656 mg/l may be due to the weathering of plagioclase feldspar and clay minerals may also release large amount of exchangeable sodium whereas K ranges from BDL to 20 mg/l due to weathering in the formation of secondary minerals (Mathews et al. 1982) (Table.1).

The presence of Cl indicates a longer distance of migration of groundwater along the flow path or anthropogenic impact or greater residence time where it is ranges from 28 to 993 mg/l. Excessive chloride concentration leads to salinity, which deteriorate the soil (Purushotham et al., 2011). SO_4 ranges from 6 to 205 mg/l and they are probably derived from weathering of sulfate and gypsum-bearing sedimentary rocks (Elango et al. 2003; Jeevanandam et al. 2006) and also due to application of sulphate bearing fertilizers (Karanth, 1997). NO_3 may be released to groundwater by usage of fertilizers and domestic wastes as they contain nitrogen-containing compounds (Nolan and Hitt 2003) and it is ranges from 3 to 151 mg/l (Table. 1). F ranges from 0.03 to 1.46 mg/l mainly occurs in groundwater as a natural constituent derived by weathering of rocks (Nayak et al., 2008).

Table 1. Maximum, Minimum and Average concentration of chemical constituents of groundwater (All values are in mg/l except EC in $\mu\text{s}/\text{cm}$ and pH)

Parameters	Maximum	Minimum	Average
Ca	296.00	6.00	93.75
Mg	122.00	9.00	42.67
Na	653.00	9.00	146.38
K	20.00	0.00	2.42
Cl	993.00	28.00	225.83
HCO_3	708.00	177.00	394.25
NO_3	151.00	3.00	40.63
SO_4	205.00	6.00	66.08
F	1.46	0.03	0.61
EC	4650.00	420.00	1462.08
pH	7.9	6.6	7.2

4.1 Hydrogeochemical process evaluations

Piper diagrams (Piper 1944) are drawn by plotting the proportions (in equivalents) of the major cations (Ca, Mg, Na, K) on one triangular diagram, the proportions of the major anions ($\text{CO}_3 + \text{HCO}_3$, Cl, SO_4) on another, and combining the information from the two triangles on a quadrilateral. It is used for classification of groundwater (Wen et al. 2005; Thilagavathi et al. 2012) to evaluate the hard rock geochemistry (Srinivasamoorthy et al. 2008; Thivya et al. 2013) and also to identify the hydrogeochemical facies (Chidambaram et al. 2008). The plot have been classified to six fields viz. Field 1 (Ca- HCO_3 type); 2 (Na-Cl type); 3 (Mixed Ca- Na- HCO_3 type); 4 (Mixed Ca-Mg-Cl type); 5 (Ca-Cl type) and 6 (Na- HCO_3 type). Most of the samples falls in Ca- HCO_3 type indicates the freshwater recharge into the aquifers (Prasanna et al., 2010). Some of the samples fall in mixed Ca-Mg-Cl and Na-Cl type indicating the predominance of anthropogenic impact and also saline intrusions. Samples fall in Mixed Ca- Na- HCO_3 type and Ca-Cl

type reflect the ion exchange process and mixing type of cations and anions which may be due to additional leachate (Chidambaram et al. 2012) (Fig.3).

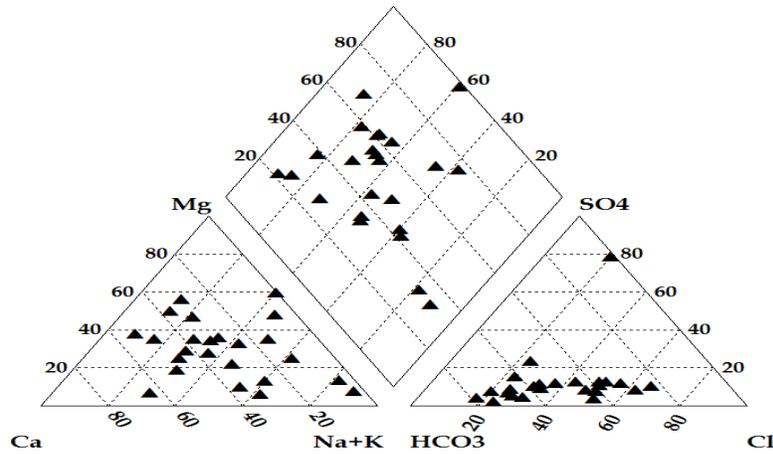


Fig.3 Piper plot to decipher the hydrogeochemical processes

The piper plot is further classified based on the dominant cations or anion. The waters are classified into two types based on the dominance of alkaline earth group (Ca + Mg) and alkalis (Na + K). Based on the concentration of cations most of the groundwater samples (83.4%) belong to the type in which alkaline earths dominate over alkalis and in the remaining samples alkalis dominate. Among the anions, Cl and SO₄ are classified as strong acids and carbonate and bicarbonate are considered as weak acids. In the present study, majority of the samples (66.40%) belong to the category in which strong acids exceed weak acids due to alkalinity (Table. 2). Majority of the groundwater samples belong to the Mixed type (50%) in which no cation or anion exceed 50% followed by Magnesium bicarbonate type (25%), Calcium Chloride type (16.6%) and Sodium Chloride type (8.34%). Sodium bicarbonate type is not found.

Table 2. Characterization of groundwater on the basis of Piper tri linear diagram

Subdivision of the diamond	Characteristics of corresponding subdivisions of diamond shaped fields	Percentage of samples in this category
1	Alkaline earth (Ca+Mg) exceed alkalis (Na+K)	83.40
2	Alkalis exceeds alkaline earths	16.60
3	Weak acids (CO ₃ +HCO ₃) exceed strong acids (SO ₄ + Cl)	33.40
4	Strong acids exceeds weak acids	66.40
5	Magnesium bicarbonate type	25.00
6	Calcium-chloride type	16.60
7	Sodium-Chloride type	8.34
8	Sodium-Bicarbonate type	0
9	Mixed type (No cation-anion exceed 50%)	50.00

A hydrochemical diagram proposed by Chadha (1999) has been applied to evaluate and interpret the representation of the factors in the four fields which are responsible for groundwater geochemistry. In first stage data were converted to percentage reaction values (milliequivalent percentages) and expressed as the difference between alkaline earths (Ca + Mg) and alkali metals (Na + K) for cations, and the difference between weak acidic anions (HCO₃ + CO₃) and strong acidic anions (Cl + SO₄). These are broadly summarized as: The four fields of the Chadha plot explains

- Field 1—Ca–HCO₃ type recharging waters
- Field 2—Ca–Mg–Cl type reverses ion exchange waters
- Field 3—Na–Cl type end-member waters (seawater)
- Field 4—Na–HCO₃ type base ion exchange waters

Most of the samples fall in field 1 which exhibits the recharging processes in groundwater (Karmegam et al. 2010). Samples fall in reverse ion exchange and mixing are the predominant processes (Manivannan 2010). These groundwater represents the Ca + Mg is in excess to Na + K due to release of Ca and Mg from the weathering of mineral in bedrocks or due to reverse base cation exchange reactions of Ca + Mg into groundwater and subsequent adsorption of Na into the mineral surfaces (Karmegam et al. 2010; Thilagavathi et al. 2012). Field 3 indicates the salinization processes and field 4 indicates the base ion exchange where the samples have less representation in these fields (Fig.4).

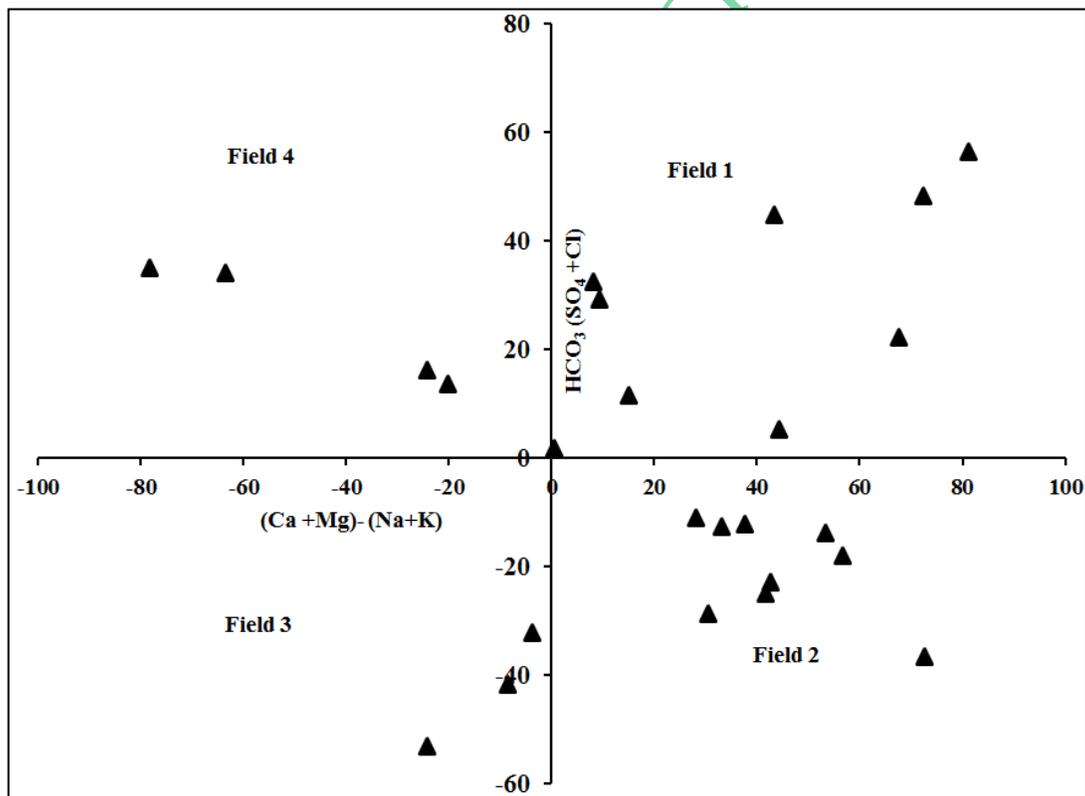


Fig. 4 Chadha's geochemical process evolution plot

4.2 Relationship Diagram

In order to specify the likely origin of the each major element participating to the groundwater salinisation, plots of Na versus Cl, Ca versus SO₄ and Mg versus SO₄ are constructed. The Na–Cl relationship has often been used to identify the mechanism for acquiring salinity and saline intrusions in semi-arid or arid regions (Sami 1992; Herczeg et al. 2001). The Na/Cl displays a well-defined correlation (Fig. 5) indicating that Na and Cl ions have probably the same origin, which is the likely dissolution of halite deposits. Samples have more Na relative to Cl which is due to rock water interaction involving feldspar weathering.

The Ca/SO₄ of Ca versus SO₄ shows a moderate correlation (Fig.5.27), indicating that the dissolution of gypsum and/or anhydrite is relatively limited. The Mg/SO₄ of Mg versus SO₄ (Fig. 5) exhibits a well-defined relationship which indicates an origin of Mg and SO₄ related to either the dissolution of MgSO₄ evaporitic minerals (Adams et al. 2001) or the contribution of MgSO₄ fertilizer commonly used in the agricultural areas.

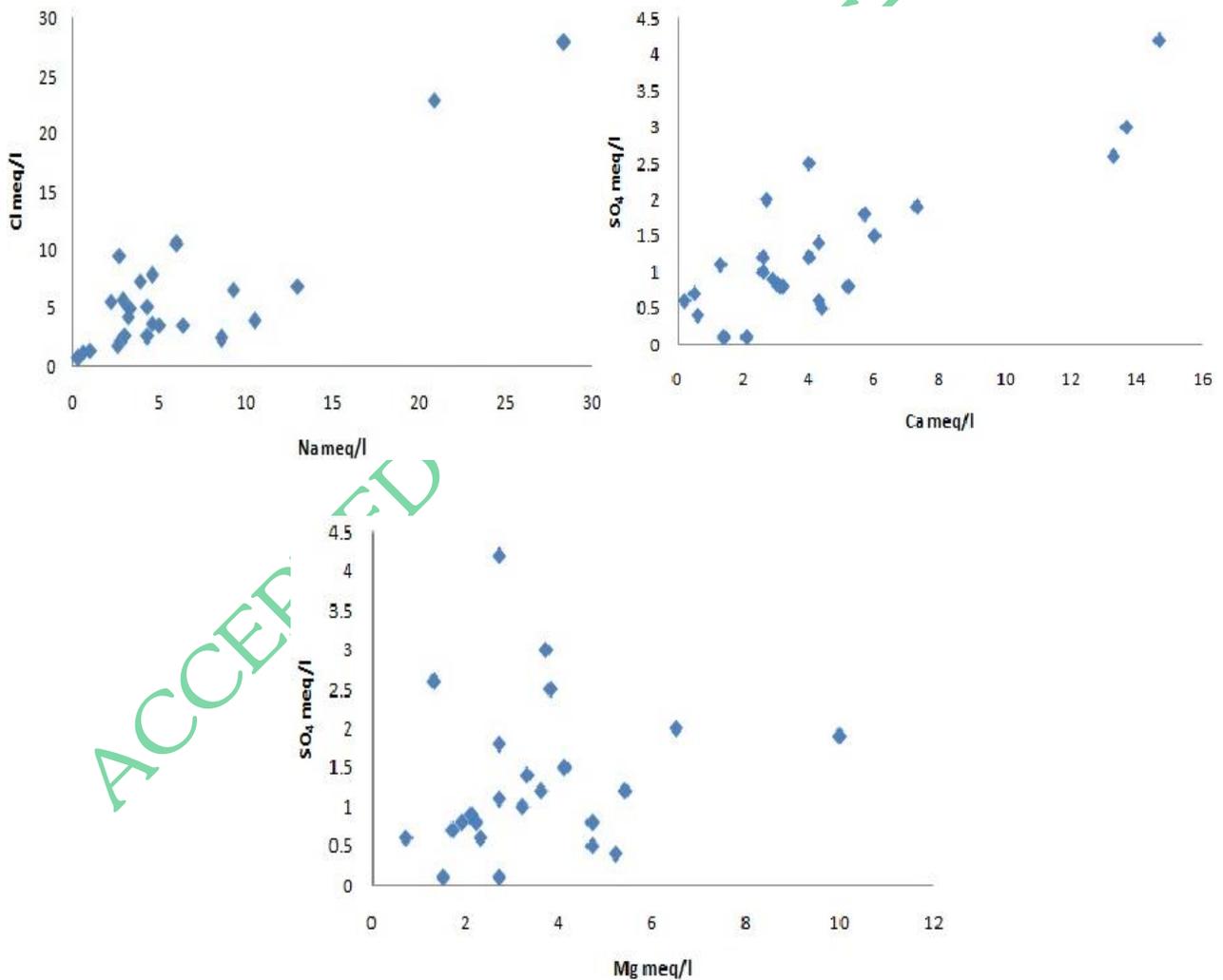


Fig. 5 Relationship plot for Na - Cl, Ca - SO₄ and Mg - SO₄

4.3 Multivariate Statistical Method

The preliminary step in the multivariate statistical analysis is calculation of correlation matrix, which provides the interrelations among the set of variables. Correlation coefficient of <0.5 exhibit poor correlation, 0.5 indicate good correlated and >0.5 represent excellent correlation. The correlation matrix (Table. 3) shows high values of positive and negative correlations among various elements.

EC exhibits good correlation with HCO₃, SO₄, Cl, NO₃, Ca and Na which implies that they are the substantial ions for the increase of EC in groundwater (Thivya et al. 2015). pH shows good correlation with F which resembles the fluoride dissolution in groundwater. The good correlation between HCO₃ - SO₄, Cl, Na indicates weathering and agricultural processes; SO₄- Cl, NO₃, Ca, Na exhibits the anthropogenic processes; Cl- NO₃, Ca, Na resembles anthropogenic and ion exchange processes (Subramani et al. 2009); Ca- Na reveals the reverse ion exchange process.

Table 3. Correlation analysis for groundwater samples

	EC	pH	HCO ₃	SO ₄	Cl	NO ₃	F	Ca	Mg	Na	K
EC	1										
pH	-0.06	1									
HCO ₃	0.73	0.19	1								
SO ₄	0.88	-0.20	0.57	1							
Cl	0.98	-0.10	0.59	0.84	1						
NO ₃	0.67	-0.05	0.46	0.64	0.59	1					
F	-0.13	0.65	0.15	-0.14	-0.22	-0.04	1				
Ca	0.85	-0.37	0.47	0.84	0.88	0.48	-0.42	1			
Mg	0.17	-0.08	-0.02	0.18	0.16	0.41	-0.03	0.06	1		
Na	0.92	0.17	0.80	0.74	0.87	0.59	0.08	0.64	-0.09	1	
K	0.41	0.16	0.21	0.38	0.41	0.27	0.00	0.28	-0.14	0.46	1

4.3.1 Factor Analysis

The purpose of factor analysis is to simplify the quantitative description of a system by determining the minimum number of new variables necessary to reproduce various attributes of the data. In this study totally three factors have been extracted from the factor analysis. A factor 1 sample shows strong positive loadings on EC, HCO₃, SO₄, Cl, NO₃, Ca and Na indicates the weathering, salinization and ion exchange processes. Factor 2 exhibits positive loadings on pH and F reflects the pH-enhanced dissolution of F due to weathering processes (Manikandan et al. 2011; Chidambaram et al. 2013) (Table. 4). Factor 3 shows positive loadings on NO₃ and Mg indicates the agricultural activities or anthropogenic activities (Cheong et al. 2012).

Table. 4 Rotated component matrix for groundwater samples

Parameters	Factor 1	Factor 2	Factor 3
EC	0.98	-0.09	0.12
pH	0.03	0.89	-0.11
HCO ₃	0.77	0.27	-0.01
SO ₄	0.88	-0.21	0.16

Cl	0.94	-0.19	0.08
NO₃	0.68	0.02	0.51
F	-0.06	0.89	0.04
Ca	0.81	-0.49	0.01
Mg	0.05	-0.03	0.93
Na	0.95	0.17	-0.11
K	0.52	0.11	-0.36

5. Conclusion

The chemical composition of groundwater of the study area is strongly influenced by weathering and ion exchange processes. Piper plot exhibits that most of the samples falls in Ca-HCO₃ type indicates the freshwater recharge into the aquifers. Some of the samples fall in mixed Ca-Mg-Cl and Na-Cl type indicating the predominance of anthropogenic impact and also saline intrusions and the same processes has also noticed in the Chadha plot. Samples have more Na relative to Cl which is due to rock water interaction involving feldspar weathering. EC exhibits good correlation with HCO₃, SO₄, Cl, NO₃, Ca and Na which implies that they are the substantial ions for the increase of EC in groundwater. Totally three factors were extracted from factor analysis mainly weathering, ion exchange, anthropogenic processes which controls and dominants the study area.

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