EVALUATION OF GRAPHICAL AND MULTIVARIATE STATISTICAL METHODS FOR CLASSIFICATION AND EVALUATION OF GROUNDWATER IN ALATHUR BLOCK, PERAMBALUR DISTRICT, INDIA

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(Received 22nd Jul 2016; accepted 20th Dec 2016)

Abstract. This paper assesses the quality of water using different graphical and statistical methods like Durov, Schoeller, Piper – Tri linear diagram, Box and Whisker plot for three seasons in the study area Alathur block, Perambalur District. The graphical representation provides limitations compared with the multivariate method for large data sets. A total of 10 groundwater samples were collected from hand dug wells in this area and they were analyzed for various physical and chemical parameters. The sequence of the dominance of the major ions are in the following order $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- > SO_4^{2-} > HCO_3^- > NO_3^-$. The dominating hydrochemicals of facies of groundwater are Ca-Cl and mixed Ca-Mg-Cl and alkaline earth metals (Ca^{2+}, Mg^{2+}) and strong acids (SO_4^{2-}, Cl^-) that dominate over alkalis (Na^+, K^+) and weak acids like HCO_3^-, CO_3^-. Based on the analytical result, groundwater in the study area is generally hard to very hard, slightly alkaline to brackish in nature. This indicates that leaching of salts, rock weathering and evaporation are among the most dominant processes in controlling water quality. For industrial purposes, the quality of water was assessed by using the Langeliner saturation index (LSI) and Ryznar saturation index (RSI). Seasonal variations in different parameters were also determined.
Keywords: *graphical representation, hydrochemical analysis, Durov, Schoeller plot, Piper diagram*

Introduction

The need to maintain environmental quality through sustainable use of resources has been emphasized by environmentalists. The overall human activities are designed and implemented for the economic growth of a country and societal needs, would directly or indirectly have a bearing on the environment especially to water (Joseph and Nagendran, 2004). Several water sources are affected due to the rapid growth of population industrialization and urbanization. Concerns and consequence related to the environment are inextricable and are lined to economic issues such as poverty which drive people to indulge in destructive activities like cutting of trees and over exploitation of water

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1503_105116

resources. These activities lead to changes in the hydrological cycle, change in climatic conditions, rainfall patterns, etc. The study is undertaken to analyze the above said parameters. The quality of groundwater has been studied in several basins by many researchers (Ramesh and Jagadeewari, 2012; Cobbian et al., 2012). The knowledge of hydrochemistry is essential to determine the origin of chemical composition of groundwater (Zaporozec, 1972). The hydrogeochemical evaluation study is becoming very important to determine the processes involved in the chemical evolution of groundwater (Andrade and Stigter, 2011; Singh et al., 2012a). People also mostly depend upon the groundwater as the water resource for all the activities like drinking, agriculture and domestic use. The study area is predominantly agricultural zone with dense agriculture activities going on throughout the year. Hence, in the present study baseline attempt has been made to study the subsurface water quality in various seasons.

Materials and Methods

Study Area

Perambalur district of India mainly depends upon agriculture as a main source of gross income of the people. The major crops of the district are small onion. Onion is cultivated in more than 22 thousand hectares. Other crops are paddy, sugar, maize, millet, etc. The district receives rainfall mostly during the northeast monsoon season as 908 mm which is lesser when compared to other districts. The district is predominantly covered by red loam and black soil. Using the software Arc GIS 9.3.1, we got a picture presented in *Figure 1* which shows different types of rocks present in the Alathur zone. It consists of coarse sandstone with day, argillaceous sandstone, sandstone & shales, charnockites, Shales with bands of limestone, Sandstone with calcareous gritstone, sandstone, pebbly sandstone & clay, gypseterous clay, sand and silt. Alathur is a major block in Perambalur district, which lies from 11°10’ N, 78°41’ E to 11°10’N, 79°05’E (*Figure 1*).

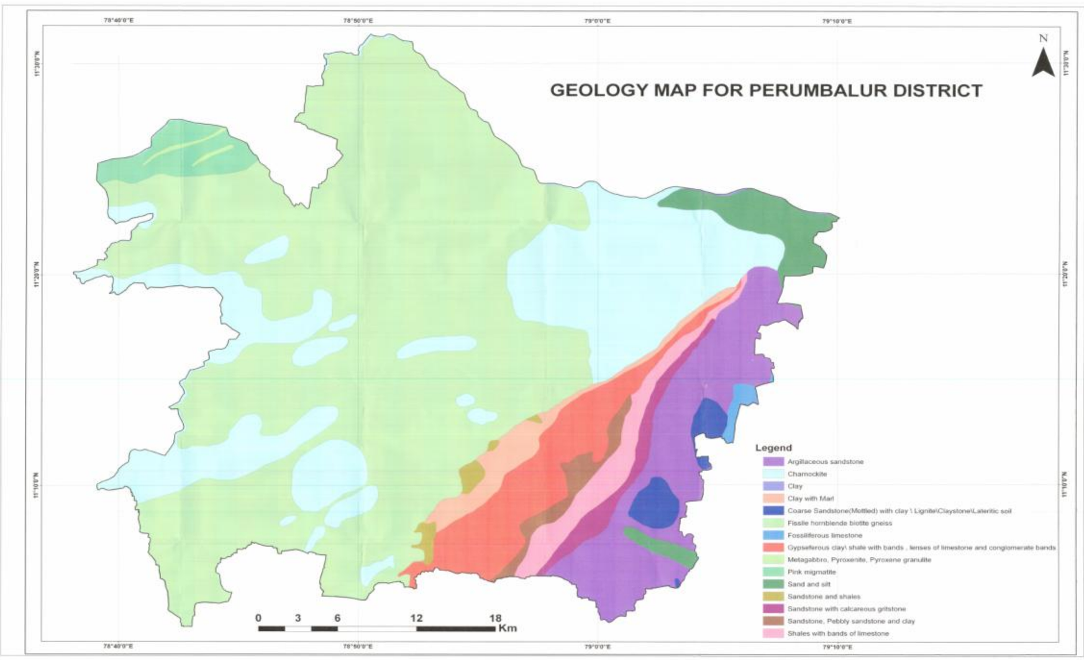

Figure 1. *Map of the study area*

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DOI: http://dx.doi.org/10.15666/aeer/1503_105116

Methodology

From bore well, ten groundwater samples were collected in different seasons through the year 2012-2013: November 2012 (Monsoon), February 2013 (Post-monsoon), and May 2013 (summer). The samples were analyzed using standard procedures (APHA, 2005). Major cation such as Ca and Mg were analyzed titrimetrically, Na and K by flame photometer, major anions Cl and HCO_3 titrimetrically and chloride was determined by $AgNO_3$ titration (Vogel 1968) method. SO_4 and PO_4 were analyzed using a spectrophotometer. EC and pH were determined in the field itself using multi-parameter water quality probe (Elico PE 138).

Result and Discussion

It is very essential to understand the quality of groundwater for different purposes. Nowadays, due to man-made activities, like frequent climatic change and rainfall pattern year by year, precipitation quantity is reduced due to above mentioned reasons. The physicochemical parameters of all water samples for all the three seasons were analyzed and presented in the *Table 1*.

Principle of graphical and numerical presentation of chemically analyzed water is based on the relationships of group of ions forming a chemical type of water. A single graph will not give all of the information such as concentration of ions, comparison of the proportions of the ions, classification of water type and identification of mixed waters of different composition identification of any of the chemical process that may take place in groundwater circulation or the relationship of chemical composition to rock type.

General Parameters

The physicochemical characteristics of groundwater of to ten stations are presented in *Table 1* for all three seasons. The pH values vary from 7.04 to 8.38 indicating the alkaline nature of groundwater samples. All pH values are within the permissible limit (6.5 - 8.5) of the Bureau of Indian Standards (BIS, 1998). The Electrical conductivity (EC) varies from 808 to 5207 μS/cm. The station S7 exceeds the BIS permissible limit of 3000 μS/cm in two seasons. In natural waters the dissolved solids are mainly concentration of carbonates, bicarbonates, chlorides, sulfates, phosphates and nitrates of calcium, magnesium, sodium and potassium with traces of iron, manganese and other minerals. Organic matter and various dissolved gases are also present in small amounts (Jain, 2010) The TDS value lies between 565 to 3645 mg/L. The station S7 exceeds the permissible limit of 2000 mg/L (BIS, 1998). Water having high TDS values is used for drinking purposes and it induces unfavorable physiological reaction, in the transient consumer and gastrointestinal irritation (Shankar et al., 2008). The total hardness in our study area varies from 219 to 697 mg/L. The sample S7, in two seasons the TH exceeds BIS permissible limit. The total hardness is due to the presence of cation in the water as primary causes for excess of hardness do not give lather to soap solutions.

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Table 1. *Physicochemical characteristics of groundwater samples*

Station	EC	TDS	pH	TH	Ca	Mg	Na	K	NO_3	Cl	F	SO_4	PO_4	HCO_3
November (Monsoon)														
S1	1732	1212	7.32	287	57	35	136	42	13	202	0.6	157	0.08	323
S2	1458	1021	7.16	382	77	45	185	24	16	182	0.2	162	0.01	251
S3	1292	904	7.21	314	64	37	125	35	11	129	0.4	43	0.07	485
S4	1399	980	7.57	326	66	39	101	46	13	133	0.2	124	0.34	343
S5	1814	1270	7.12	306	62	36	175	55	14	273	1	82	0.03	416
S6	808	565	7.8	271	56	32	66	22	0	40	0.6	32	0	323
S7	5190	3633	7.47	677	119	91	675	175	39	899	0.6	934	0.06	545
S8	1767	1237	7.23	219	43	27	212	67	16	172	0.4	135	0.07	444
S9	1968	1378	7.52	338	68	40	254	61	26	253	0.8	167	0.28	384
S10	2387	1671	7.04	470	96	55	312	54	21	434	0.4	193	0.31	416
February (Post monsoon)														
S1	1834	1283	7.13	291	56	36	140	51	16	230	0	189	0	343
S2	1458	1021	7.08	505	78	74	191	31	26	158	0	179	0.1	255
S3	1516	1061	7.6	489	76	72	126	39	3	186	0	92	0	440
S4	1215	851	7.15	218	53	21	124	52	17	113	0	105	0.1	279
S5	1873	1311	7.19	444	80	59	182	58	17	295	1	81	0	408
S6	815	571	8.16	380	76	46	60	19	1	44	0	35	0	327
S7	5207	3645	7.67	697	119	96	698	179	47	899	1	512	0	537
S8	1617	1132	8.07	291	43	44	235	61	23	149	0	58	0.3	440
S9	1985	1389	7.53	202	41	24	268	66	26	311	1	69	0	364
S10	2286	1600	7.04	485	97	58	326	50	22	434	0	175	0.1	444
May (Summer)														
S1	1717	1202	7.44	384	92	37	163	67	15	250	1	118	0.15	291
S2	1557	1090	7.22	590	178	35	98	21	14	182	0.8	238	0.05	198
S3	1562	1094	7.45	598	99	86	89	37	14	250	0.8	29	0.16	404
S4	1445	1012	7.72	372	91	35	124	47	12	214	0.4	144	0.02	206
S5	1792	1254	7.51	513	92	68	154	60	18	283	1	102	0.17	315
S6	1948	1363	7.96	566	124	61	187	66	22	218	1.2	355	0.03	327
S7	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S8	1525	1068	7.78	356	54	53	147	54	17	194	0.6	98	0.15	307
S9	1996	1397	8.38	392	68	53	214	61	25	271	0.8	124	0.53	376
S10	1716	1202	7.96	354	96	28	187	45	15	293	0.4	105	0.36	323

All the values are in mg/L except pH and EC. EC is expressed in µS/cm

Cation Chemistry

The concentrations of various cations analyzed in groundwater for three seasons are presented in *Table 1*. The major cations present in most of the ground waters have highest concentrations (all >1mg/L). They are calcium, magnesium, sodium and

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DOI: http://dx.doi.org/10.15666/aeer/1503_105116

potassium (Younger, 2007). Calcium and magnesium concentrations vary from 41 to 124 mg/Land 24 to 89 mg/L respectively. In groundwater the calcium content, generally exceeds the magnesium content in accordance with their relative abundance in rocks. All the samples in three seasons are within the BIS permissible limit of 200 mg/L. Sodium and potassium concentrations vary from 60 to 698 mg/L and 19 to 179 mg/L, respectively except one sample in two seasons which exceeds the BIS permissible limit 200 mg/L. Potassium in all the samples in three seasons exceeds the BIS permissible value of 10 mg/L. High Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} concentrations are mainly due to their mineralogical origin in the soil weathering of feldspar and montmorillonite. It generates the water soluble Na^{+} and K^{+} ions. In addition, cation exchange processes and agricultural, industrial activities also contribute for high Na^{+} and K^{+} concentration in the study area (Naidu et al., 1985; Singh et al., 1997; Singh et al., 2006).

Anion Chemistry

The concentrations of various anions analyzed in the groundwater samples are presented in Table 1 for three seasons. The major ions having highest concentrations (all > 1mg/L) in groundwater are bicarbonates, sulphates and chlorides (Naidu et al., 1985). In the present study, groundwater contains predominant anion is chloride, which varies from 40 to 899 mg/L and the desirable limit recommended by WHO is 250 mg/L. Above 30% of samples exceeds the desirable limits in all three seasons and however, no adverse health effects on human being have been reported by the use of water having high chloride contents (Jain, 2010). The sulphate concentration in groundwater is due to the presence of soluble salts like calcium, magnesium and sodium. Rainfall infiltration and groundwater recharge gives significant change in sulphate concentration (Jain, 2010). The sulphate concentration in our study area varies from 29 to 934 mg/L. The station S7 exceeds the BIS permissible limit of 400 mg/L in two seasons. Sulphate present alone may not give any adverse health effects while presence of sulphate in excess of greater than 400 mg/L with sodium or magnesium may lead to gastrointestinal irritations (Shankar et al., 2008). The permissible limit for bicarbonate is 250 mg/L, in all three seasons, bicarbonate ranges from 206 to 545 mg/L. India is an agricultural based country. Many parts of India are reported to have high nitrate concentration in the groundwater, due to over usage of nitrogen fertilizers which changes the natural drainage patterns.

Nitrate concentration > 45 mg/L in drinking water has adverse health effects on human’s results in methaemoglobinaemia which generally affects the infants (Jain, 2010) and gastriccarcinona (Tank and Chandel, 2010). The nitrate concentration ranges from 0 to 47 mg/L. The phosphate concentration is very low in the study area in all the three seasons. The fluoride concentrations in all three seasons are well within the permissible limit of 1.5 mg/L. In India, due to high fluoride concentration geo-environmental problems are present and generally fluoride concentration is due to natural process (Singh et al., 2012b).

Correlation analysis

Person Correlation analysis is a useful method in hydrogeochemical studies since the produced correlation matrix can indicate the associations between individual parameters demonstrating the overall coherence of the data set and revealing the links between individual parameters and various controlling factors (Wang and Jiao, 2012). In the

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current study, the statistical software package SPSS 17.0 is used to calculate Pearson correlation coefficient. The result obtained for all the three seasons are presented in *Table 2*. From the data's, all major cations and anions with the exception of PO_4 were positively correlated with TDS. Theses correlation coefficient are large 0.9 for all three season for Na and > 0.5 for Ca, Mg, and Cl and all are significant at the 0.01 level. It can be judged from the analysis that during groundwater flow, the following reaction has likely taken place:

$$NaCl = Na^{+} + Cl^{-} \quad (E_1)$$

$$Na_2SO_4 = 2Na^{+} + SO_4^{2-} \quad (E_2)$$

$$CaSO_4 = Ca^{2}{}_{+}\ SO_4^{2-} \quad (E_3)$$

$$MgSO_4 = Mg^{2\ +} + SO_4^{2-} \quad (E_4)$$

Table 2. *Correlation matrix for the water quality parameters*

Parameters	EC	TDS	PH	TH	Ca	Mg	Na	NO_3	Cl	F	SO_4	PO_4	HCO_3
(a)November													
EC	1												
TDS	1.00	1											
PH	-0.05	-0.05	1										
TH	0.89	0.90	-0.05	1									
Ca	0.83	0.83	-0.10	0.99	1								
Mg	0.93	0.93	0.00	0.99	0.96	1							
Na	0.98	0.98	-0.08	0.90	0.85	0.93	1						
NO_3	0.91	0.91	-0.17	0.81	0.77	0.82	0.92	1					
Cl	0.99	0.99	-0.12	0.93	0.88	0.95	0.98	0.89	1				
F	0.17	0.17	0.07	-0.02	-0.06	0.00	0.14	0.13	0.19	1			
SO_4	0.97	0.97	0.10	0.89	0.82	0.94	0.95	0.85	0.94	0.07	1		
PO_4	0.02	0.02	0.04	0.11	0.18	0.05	0.02	0.24	0.04	-0.21	-0.06	1	
HCO_3	0.66	0.66	-0.15	0.47	0.41	0.51	0.65	0.56	0.64	0.26	0.56	0.00	1
(b)February													
EC	1												
TDS	1.00	1											
PH	-0.01	-0.01	1										
TH	0.64	0.64	-0.03	1									
Ca	0.66	0.66	-0.11	0.94	1								
Mg	0.62	0.62	0.03	0.98	0.85	1							
Na	0.97	0.97	0.03	0.61	0.63	0.59	1						
NO_3	0.83	0.83	-0.16	0.37	0.36	0.38	0.89	1					
Cl	0.99	0.99	-0.08	0.65	0.71	0.60	0.96	0.81	1				
F	0.60	0.60	0.00	0.20	0.23	0.20	0.57	0.55	0.62	1			
SO_4	0.93	0.93	-0.14	0.70	0.72	0.67	0.88	0.78	0.89	0.355	1		
PO_4	-0.20	-0.20	0.19	-0.24	-0.35	-0.16	-0.04	0.14	-0.25	-0.429	-0.219	1	
HCO_3	0.73	0.73	0.30	0.54	0.51	0.54	0.71	0.41	0.74	0.421	0.507	-.006	1
(c)**May**													
EC	1												
TDS	1.00	1											
PH	0.97	0.97	1										
TH	0.79	0.79	0.78	1									
Ca	0.63	0.63	0.63	0.85	1								
Mg	0.68	0.68	0.66	0.79	0.36	1							
Na	0.90	0.90	0.84	0.45	0.33	0.41	1						
NO_3	0.93	0.93	0.86	0.66	0.44	0.66	0.91	1					
Cl	0.92	0.92	0.91	0.69	0.49	0.65	0.83	0.79	1				
F	0.79	0.79	0.67	0.81	0.61	0.72	0.61	0.77	0.62	1			
SO_4	0.53	0.53	0.46	0.54	0.70	0.17	0.47	0.54	0.23	0.61	1		
PO_4	0.48	0.48	0.42	0.06	-0.09	0.21	0.64	0.57	0.59	0.10	-0.193	1	
HCO_3	0.88	0.88	0.86	0.72	0.37	0.84	0.76	0.84	0.89	0.68	0.199	0.586	1

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Total hardness (TH) also positively correlated with Ca, Mg and SO_4 which is logical since TH is a measurement of the first two elements and is approximately equal to their sum. The positive correlation between TH and SO_4 can then be explained by reaction E_3 and E_4 (Li et al., 2013).

Graphical Presentation of Data

Most of the graphical methods are designed simultaneously to represent the total dissolved solids concentration and the relative proportion of certain major ionic species (Hem, 1989). Piper diagram are drawn by plotting the proportions (in equivalents) of major cations (Ca^{2+}, Mg^{2+}, Na^{+} + $K^{+)}$ on one triangular diagram (Piper, 1944). The proportion of major anions (CO_3^-, HCO_3^-, Cl^- and SO_4^{2-}) represents another triangular diagram. From the quadrilateral diagram the nature of cation and anion can be judged. Based on the observations, the major cation is Na+K and anion is Cl^- and HCO_3^- is found in all three seasons. The quadrilateral diagram shows that majority of water samples are of mixed Ca-Mg-Cl type which is presented in the *Figure 2*.

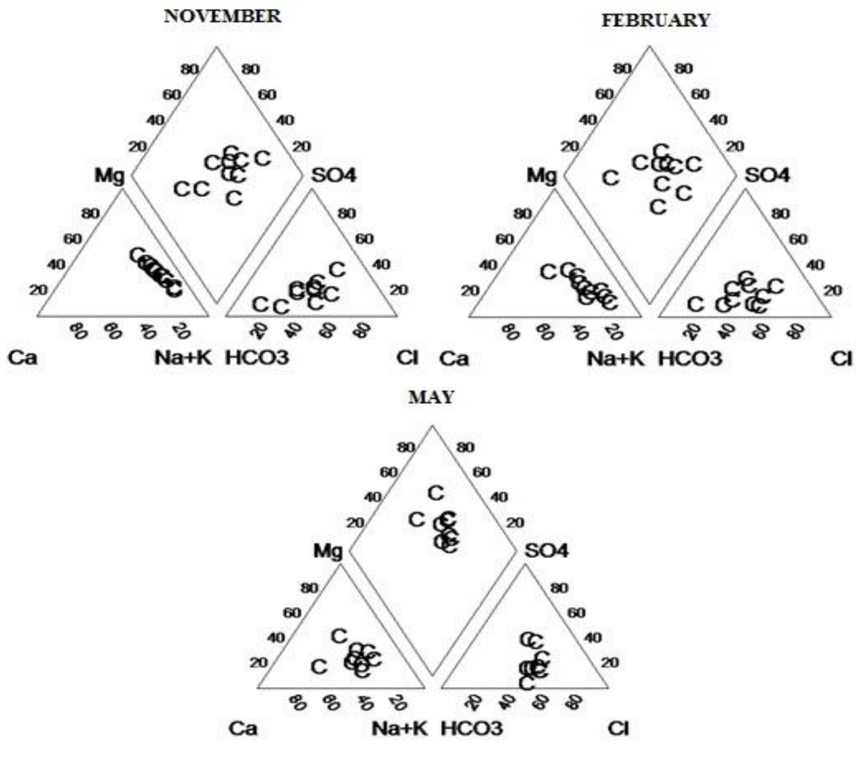

Figure 2. *Piper trilinear diagram for groundwater samples*

The Schoeller diagram represent the combination of major and minor constituents of groundwater in the study area in three seasons (Schoeller, 1967) which is presented in the *Figure 3* and the result obtained indicates that Na, Cl is dominant and SO_4 is in low concentration. The orders of ions are Na, Cl, Ca+Mg, HCO_3 and SO_4. The box and whisker plot is a powerful statistical tool as it identifies the chemical parameters influencing the water chemistry in the study area. It demonstrates the median, range and shape of the data distribution (*Figure 4*).

APPLIED ECOLOGY AND ENVIRONMENTAL RESEARCH 15(3):105-116.
http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
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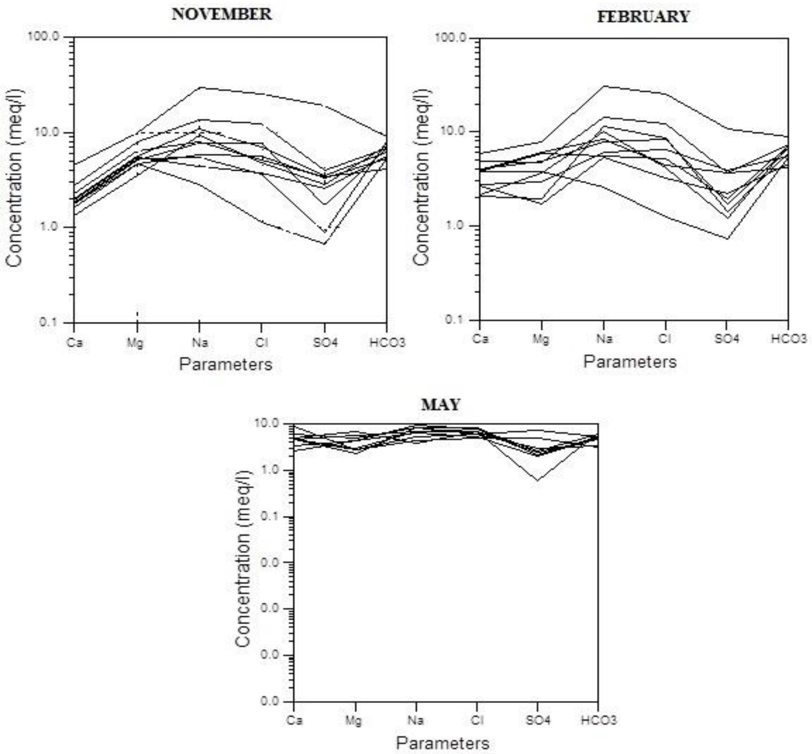

Figure 3. *Schoeller diagram for groundwater samples*

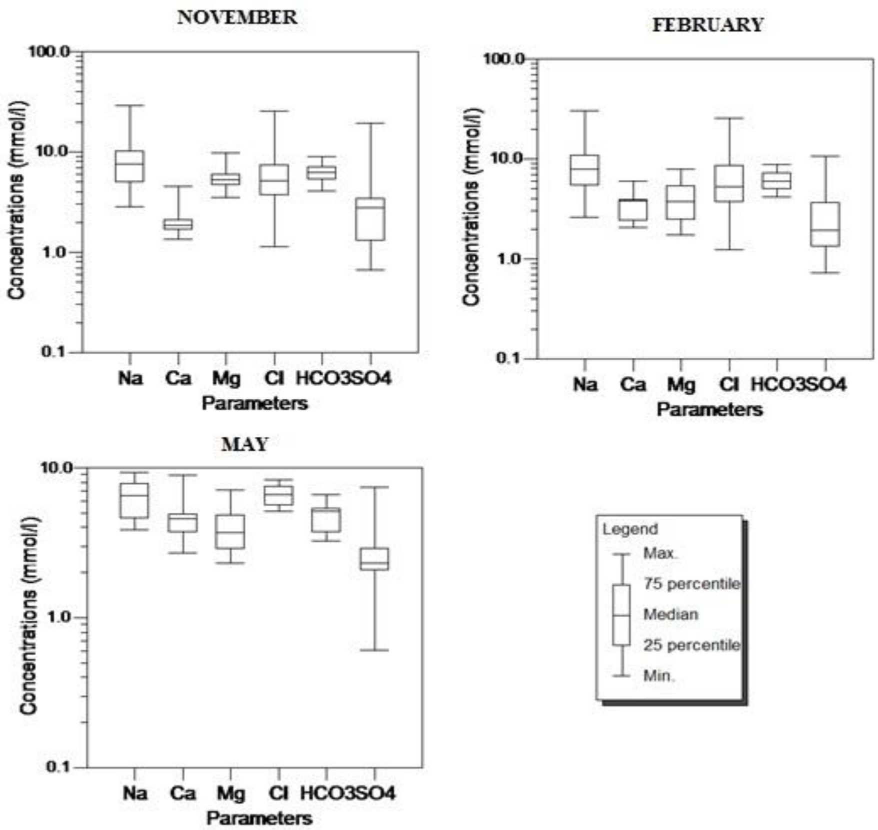

Figure 4. *Box and whisker plot for groundwater samples*

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The central box represents the values from the lower to upper quartile (25th to 75th percentile) and the vertical line extends from the minimum to the maximum values A. (Tizro and Voudouris, 2008). The plot clearly shows Na^+, Ca^{2+}, K^+, Cl^-, SO_4^{2-} and HCO_3^- ions that influence indication dominance of weathering and anthropogenic activities (Chidambaram et al., 2011). In all three seasons, Na, Ca, Mg is elevated and it may be due to cation exchange process. Durov diagram shows the type of water in the study area S.A. (Durov, 1948) which is showed in *Figure 5*. Durov diagram also shows that the dominant water type is Na + K, Ca + Mg and mixed Na-Ca-Mg-Cl type of water. In an anion region Cl^- is most dominant type followed by HCO_3^- and SO_4^{2-} type.

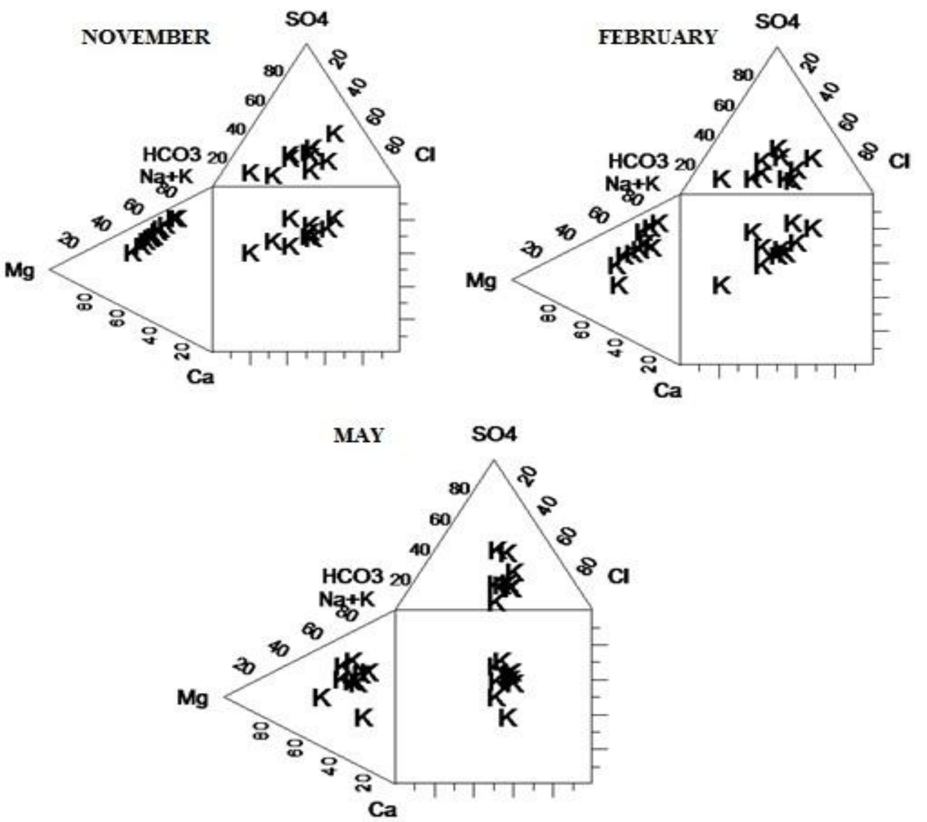

Figure 5. *Durov diagram for groundwater samples*

Suitability of Industrial Purpose

The water saturation index can be used to predict if water is precipitating out or dissolving or in equilibrium with calcium carbonate. A negative LSI value indicates the solution is under saturated with $CaCO_3$. A positive value is supersaturated with $CaCO_3$ and scaling may occur.

The Langelier saturation index (Degremont, 1991; Langelier, 1936) and the Ryznar saturation index (Ryznar, 1944) were determined to establish water suitability for industrial purpose. Langelier saturation index (LSI) can be calculated by taking difference saturation pH for $CaCO_3$ using the following equation:

$$LS1 = pH_w - pH_s \quad \text{(Eq.1)}$$

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where pH_s denotes the pH at saturation in calcium carbonate can be calculated using the equation (2):

$$pH_s=(9.3 + A+B) - (C+D) \quad \text{(Eq.2)}$$

where constant A = ($\log_{10}$ [TDS] - 1/10), B = -13.12 x $\log_{10}$(°C+273)+34.55, C=log 10 [Ca^{2+} as $CaCO_3$] - 0.4 and D=$\log_{10}$ [Alkalinity as $CaCO_3$].

A neutral LSI value indicates that the solution is at equilibrium with $CaCO_3$ and it is neither scale forming nor a scale removing. The LSI values of groundwater in the study area of three seasons are presented in *Figure 6*. It clearly shows that almost all the station shows negative value; except one sample in the month of May. The neutral LSI value indicates the solution is in equilibrium with calcium carbonate (Singh et al., 2006) So there is no chance of scale formation.

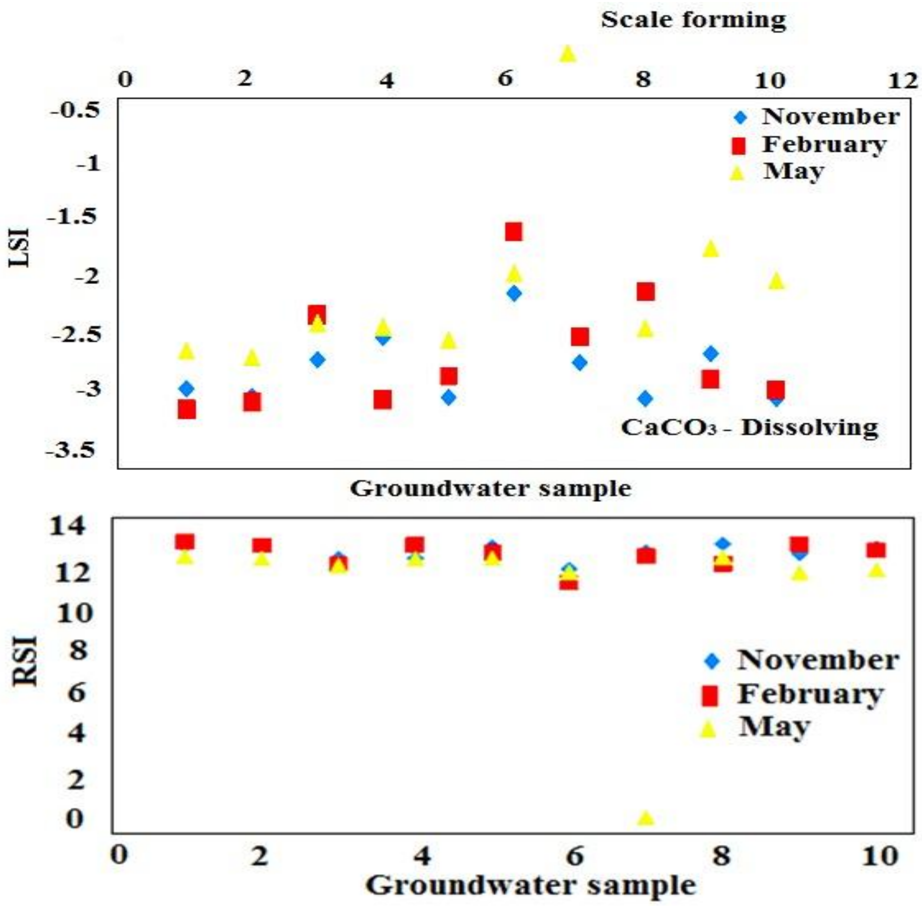

Figure 6. *LSI and RSI of groundwater samples*

John Ryznar changed the LSI in the year 1944. Like the LSI the Ryznar Saturation Index (RSI) is based on $CaCO_3$ saturation in water except that the RSI gives only positive values. RSI values are calculated using the expression (3):

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$$RSI = 2(pH_s) - pH_w \quad \text{(Eq.3)}$$

where pH_s is the saturation pH for calcium carbonate, pH_w is the measured pH of water. Three seasons RSI values are presented in *Figure 6*, which indicates that similar results obtained like LSI (*Table 3*).

Table 3. *RSI indicates the corrosion scale potential*

RSI rating	Indication
4-5	Heavy Scale
5-6	Light scale
6-7	Very light scale
>8	No scaling, corrosion

Conclusion

Water in Alathur block of Perambalur district shows slight alkaline to highly alkaline nature. All the graphical representation reveals that water is in mixed type of Na+K and Ca-Mg-Cl type. The station S7 exceeds severely with respect to the permissible limits prescribed by BIS in two seasons. LSI and RSI of different samples clearly show that samples are $CaCO_3$ dissolving type which indicates that there is no problem for industries. For drinking purposes some usual treatment has to be done before it is used. The alkaline nature of water yield of crop can be controlled by crop rotation policy.

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DOI: http://dx.doi.org/10.15666/aeer/1503_105116

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DOI: http://dx.doi.org/10.15666/aeer/1503_105116