

Identification of Hydrogeochemically Active Regimes in Groundwaters of Erode District, Tamilnadu —A Statistical Approach

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Abstract: Water chemistry plays a notable role in determining the quality and utility. There are several factors influencing the water chemistry in the hard rock terrain of Erode district. Samples were collected in four different seasons and analysed for the major and minor ions. The results obtained were subjected to statistical analysis like correlation, factor and factor score analysis. In order to get the interrelationship of these ions and the dominant sources representing the water chemistry, correlation and factor analysis were carried out. The correlation analysis helps in the determination of the spinal and the seasonal species/ions. Na, Mg, Cl, Ca and SO₄ were determined as the spinal species and F, NO₃, K and PO₄ as the seasonal species. The factor analysis reveals that the anthropogenic sources play a significant role in the water chemistry. As it is a complex geochemical system, and represented by several factors, the first three dominant factors were spatially distributed by their factor scores, in order to get the dominant hydrogeochemical regimes.

Key words: Hydrogeochemistry, correlation, factor and factor score.

Introduction

Hydrogeochemical system of an area is governed by several factors. They vary spatially and temporally. The physical and chemical properties do not directly reveal the governing process. As the study area is a hard rock terrain, the groundwater potential is governed by several factors like weathering, fracture and shear zone. The samples were collected and analysed for major ions in different seasons. In order to handle this large data set and to get a reliable interpretation, application of statistics is essential. Correlation between ions reveals the interrelationship among the number of observable quantitative variables. The factor analysis technique explains the observed relation among the several variates in terms of simpler relation that can provide an insight

into the underlying structure of the variates (Matalas and Reihner, 1967; Usunoff and Guzman-Guzman, 1989). The use of cluster analysis was also highlighted to determine the hydrogeochemical regimes (Colby, 1993). The application of factor score for cluster analysis was done by Heejun Suk and Kang-Kun Lee (1999) in order to reduce the clustering error caused by data error of multicollinearity. The results of cluster analysis were compared with the results of geochemical interpretations (Cho et al., 1997; Lee, 1997). The main objective of the present study is to enumerate the usage of factor score in identification of the hydrogeochemically active regimes represented by the major factors. Relationship of the ions present in water may vary with season. Certain ions maintain the relationship with season and some don't. Such relationships have been enlightened by the use of

the correlation analysis. An attempt has also been made to note the seasonal variation of the factor representations in the study area.

Study Area

The area chosen for study is Erode district located in the NW part of Tamilnadu, India. It lies between N latitudes $10^{\circ}35'00''$ and $11^{\circ}58'00''$ and E longitude $76^{\circ}05'00''$ and $77^{\circ}57'00''$. The major part of the study area is covered by Archean crystalline metamorphic complex (Figure 1). Acid charnockite, gneiss, and granite are the major rock types of this region. Abundant minerals include quartz, feldspars, amphibole, mica and apatite. Soil type in the area includes black cotton soil, red lateritic soil and alluvial soil. The rocks of these areas are highly weathered, jointed and covered with recent valley fills and soil cover at some places. The area receives rainfall in both NE and SW monsoon. NE monsoon is more effective than the SW. The major river running is Bhavani flowing along the east and mixes with river Cauvery. Cauvery flows South along Eastern boundary of the district. Two other rivers noted in the district are the Noyil and Amaravathi flowing towards east in the southern part of the study area.

Hydrogeology

Permeability values vary from 1.15 to 48.38 m/day. Permeability values are higher near the surface water bodies and in wells ending in highly weathered formations. The range of transmissivity in the area varies from 10.7 to 106.5 m^2/day . Water table fluctuation on seasonal observation shows that the maximum fluctuation is observed at the southeast part of the area (Moolanur) and fall is noticed in water levels in the centre (Vijayamangalam and Arachalur). The long-term record of 25 years indicates rising trend of water levels, in major parts of the district ranging from 0.17 m to 6.54 m, the maximum at Kangayam. Fall was noticed at Kundadem, Kannivadi and Erode. The water table fluctuation in the canal command areas are within the limit of equilibrium.

Methodology

Groundwater samples have been collected in entire Erode district in a definite pattern. The location of the samples in the study area is as shown in Figure 2. The samples were collected in Polyethylene bottles during the four respective seasons—SW monsoon (SWM) (July 1998),

NE monsoon (NEM) (October, 1998), postmonsoon (POM) (January, 1999) and summer (March, 1999)—broadly to cover the seasonal variations. A total of 160 samples were collected at the rate of 40 samples/season. Each sample was analysed for the major and minor species (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , F^- and H_4SiO_4) by standard procedures (APHA, 1998; Ramanathan, 1993). Flame photometer was used for analysis of Na^+ and K^+ ; titration for Ca^{2+} , Mg^{2+} , Cl^- and HCO_3^- ; and spectrophotometer for SO_4^{2-} , NO_3^- , PO_4^{3-} and H_4SiO_4 ; Orion ion electrode for F^- . The pH and electrical conductivity were measured in the field.

Results and Discussion

The summary of the analytical results of groundwater in the study area is represented in Table 1, which shows the average, maximum, minimum and standard deviation values for different seasons. The analytical precision for the measurement of major ions is about $\pm 6\%$ to $\pm 9\%$. The total cations (TZ^+) and total anions (TZ^-) balance (Allan Freeze and Cherry, 1979) shows the charge balance error (E%) percentage. The error percentage ranges from $\pm 2\%$ to $\pm 10\%$ with exceptions of few ions in different seasons, due to abnormally high concentration occurring locally in different seasons. The correlation coefficient between TZ^+ and TZ^- is generally occurring around 0.6 to 0.9. TDS/EC ratio ranges from 0.5 to 0.9. The role played by the other ions than those studied here for the cation and anion charge balance is lesser. The groundwater in the study area is colourless and odourless in most of the places. Results of the four seasons were processed by WATCLAST (Chidambaram et al., 2003). Here the dominant facies are $\text{Na} + \text{K} - \text{Cl}$ and SO_4 and $\text{Na} + \text{K} - \text{Ca} - \text{Mg} - \text{Cl} + \text{SO}_4 - \text{HCO}_3$ hydrogeochemical facies (Chidambaram et al., 2002).

In view of the limitation of the existing graphical methods, and increasing number of chemical parameters now being measured in groundwater chemistry studies, there is a need for wide range of statistical analysis of data. Delineating the relationship between the geochemical water type is difficult, while it is almost impossible to visualise the impact of both the physical and chemical variables on the water. Statistical methods, especially factor analyses and correlation analyses are often used to achieve the above objectives.

Correlation

The correlation analysis for groundwater of different seasons of the Erode district is studied in detail. Figure 3 represents the correlation matrix.

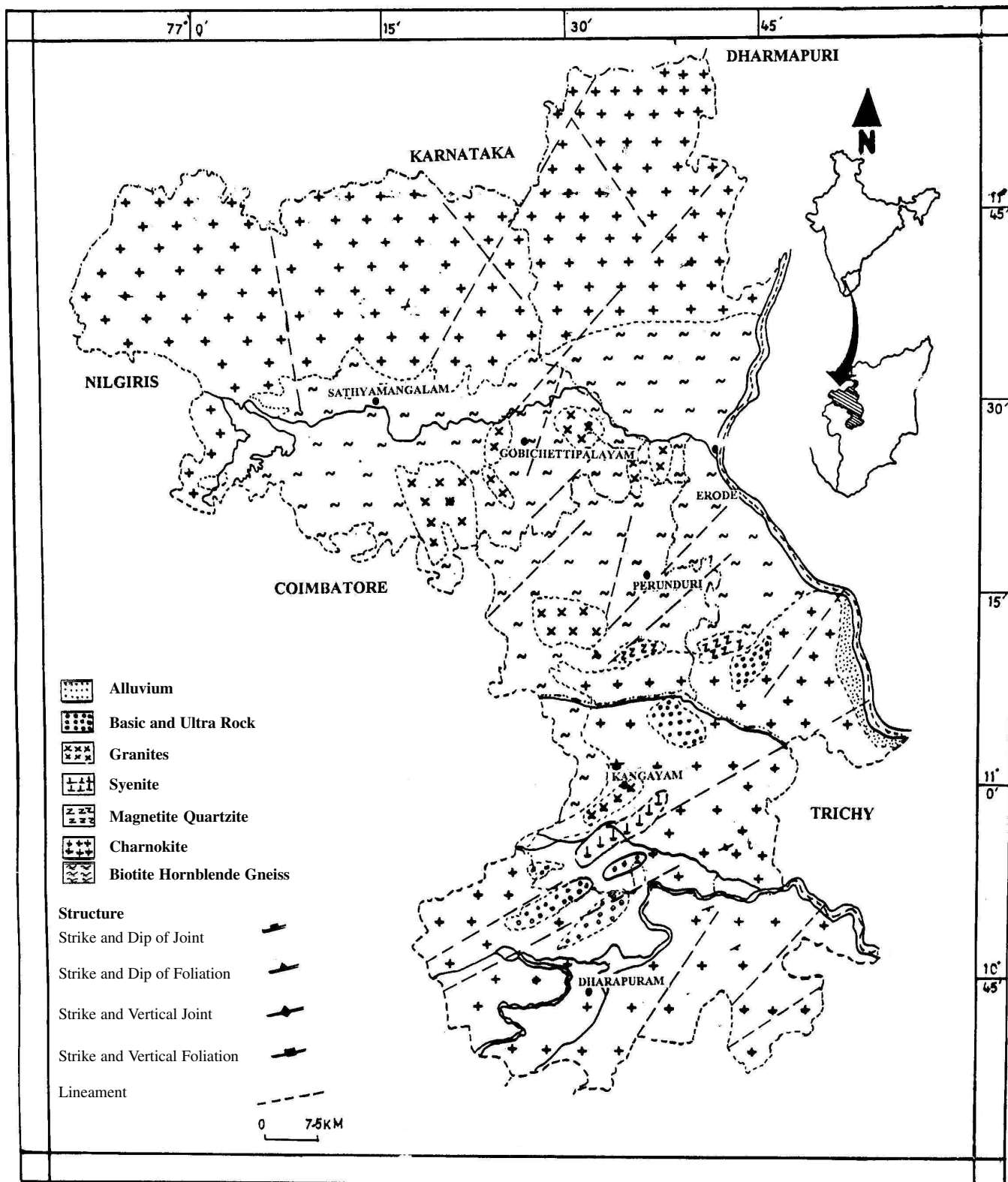


Figure 1: Location map of the study area.

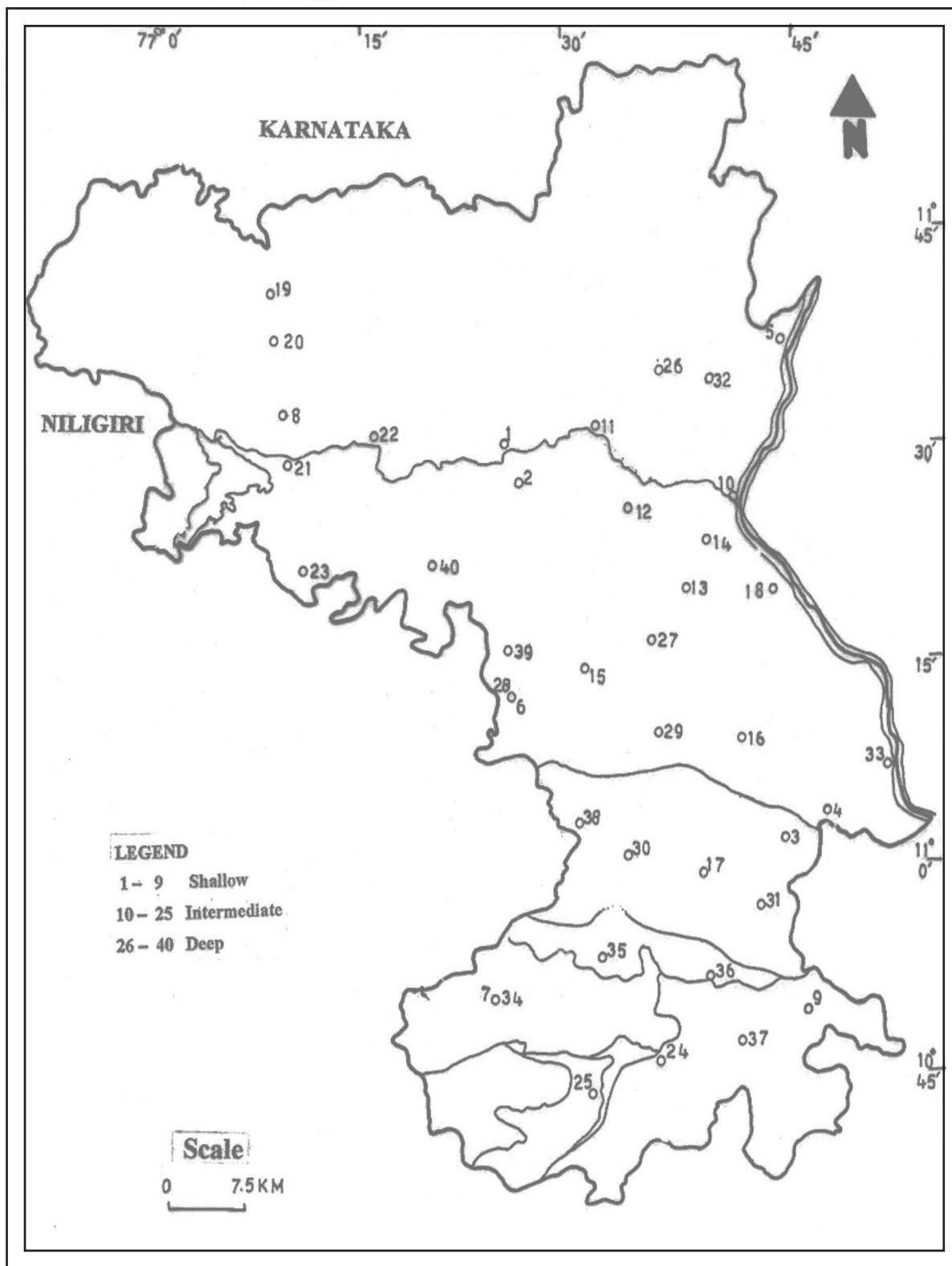


Figure 2: Sample location map.

Table 1: Average chemical composition of the groundwater samples of Erode district

<i>SW Monsoon</i>					<i>NE Monsoon</i>				
	<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Stdev</i>		<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Stdev</i>
pH	8.27	6.49	7.51	0.35		8.50	6.70	7.44	0.36
EC	7270.00	577.00	1887.67	1360.80		6010.00	530.00	1979.67	1523.67
Cl	2508.00	29.92	366.67	406.60		1595.00	35.45	409.83	428.43
HCO ₃	568.80	80.40	203.93	77.61		322.10	91.50	192.03	59.41
SO ₄	1100.00	4.00	127.03	194.33		693.00	6.03	139.37	105.95
PO ₄	1.86	0.10	0.45	0.39		2.71	0.01	1.24	0.52
NO ₃	337.50	1.00	118.67	88.52		340.00	10.75	99.47	70.41
F	1.30	0.04	0.42	0.30		2.40	0.03	0.68	0.50
H ₄ SiO ₄	9.85	1.50	5.28	1.97		18.40	5.10	12.23	2.51
Na	1034.00	34.00	191.27	171.83		564.00	11.00	165.50	151.27
K	340.00	4.00	48.69	78.33		145.00	2.00	25.08	35.79
Mg	190.80	13.20	43.08	36.99		174.00	12.00	47.87	36.33
Ca	194.40	20.00	52.00	36.82		228.00	20.00	78.55	57.10
TDS	383.00	371.32	1157.33	886.50		3067.00	326.00	1172.00	790.40

<i>Post Monsoon</i>					<i>Summer</i>				
	<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Stdev</i>		<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Stdev</i>
pH	8.52	6.41	7.61	0.35		8.00	6.75	7.16	0.25
EC	5450.00	620.00	2068.33	1372.33		5200.00	194.00	2152.67	1412.33
Cl	1595.00	48.60	368.03	383.43		1283.00	26.58	406.20	348.90
HCO ₃	408.70	40.30	243.60	74.27		373.30	43.92	223.37	77.53
SO ₄	257.00	6.00	118.40	73.86		300.00	0.10	121.96	79.35
PO ₄	5.00	0.02	0.74	0.76		3.78	0.01	1.61	0.78
NO ₃	600.00	5.00	81.12	82.99		315.70	6.13	115.93	76.16
F	7.00	0.07	1.12	1.37		3.20	0.05	0.67	0.66
H ₄ SiO ₄	12.30	1.20	8.24	2.40		17.30	3.40	12.14	3.31
Na	700.00	29.00	193.10	168.47		507.00	15.00	184.20	132.67
K	384.00	5.00	50.04	74.17		131.00	1.00	25.14	36.33
Mg	164.40	1.20	41.69	34.73		156.00	4.80	46.84	30.54
Ca	216.00	22.00	77.48	44.15		190.00	10.00	69.92	48.03
TDS	3159.00	377.88	1183.67	749.50		2708.00	122.65	1208.00	638.20

The correlation figure (Figure 3a) of the southwest monsoon indicates good correlation of Mg with other ions like Na, Cl, SO₄ and Ca. It is also established that K has poor positive correlation with Na, NO₃ and Mg. Similarly NO₃ is related to K, Na, Cl, Ca and H₄SiO₄. Jacks (1972) noted the higher concentrations of nitrogen in the study area and grouped the main sources of nitrogen. They constitute nitrobacters, cropping of certain nitrogen-fixing plants and fertilizers.

In addition to these factors, dyeing industries which have been recently established also play a major role. In the northeast monsoon season (Figure 3b) K ion shows good correlation with Ca, SO₄, Na, Cl, Mg and NO₃. In this season HCO₃ shows correlation with Na and SO₄, and SO₄ with silica. The post-monsoon (Figure 3c). also

indicates the same trend of Mg with that of the SW monsoon. But meagre correlation is established with Na and Mg. Correlation was also established between K and PO₄, HCO₃ and SO₄. In the summer season, silica and bicarbonate shows relationship to Na and with each of them indicating the role of weathering.

Moreover the relation of F is indicated with Na and HCO₃ in summer (Figure 3d). When water passes through soil containing decomposing organic matter, it absorbs large amount of CO₂. The carbon dioxide is then converted to HCO₃ in weathering reactions. The weathering reactions are brought about by the release of cations and silica from silicates.

NO₃ does not show any correlation with other ions in the summer. Similar case was observed in the non-

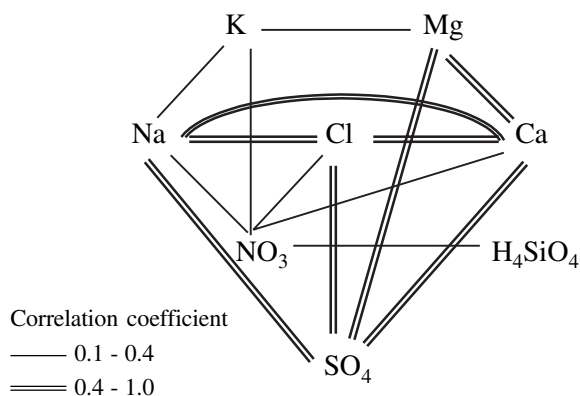


Figure 3a: SW monsoon.

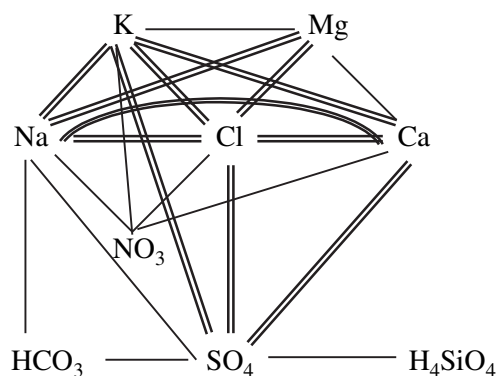


Figure 3b: NE Monsoon.

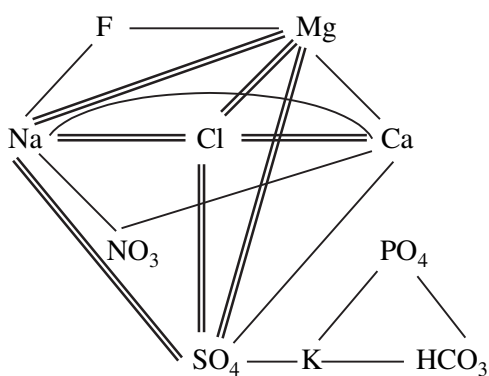


Figure 3c: Post monsoon.

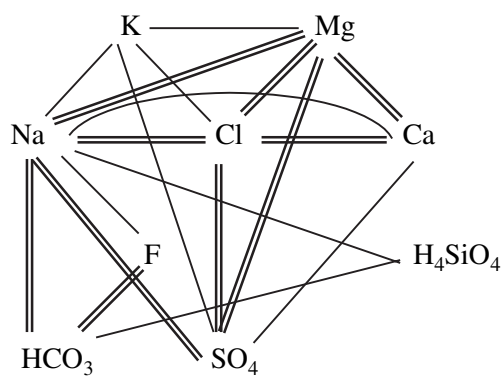


Figure 3d: Summer.

irrigated areas of the Bundelkand gneiss (Chourisa and Tellam, 1992). Agricultural practices in this region are mainly monsoon dependent. So, it may be interpreted that NO_3 was not correlated with other ions because of lesser intensities of agriculture activities during this season.

Na, Mg, Cl, Ca and SO_4 have good positive relationships in all seasons. It signifies that these ions are dominant determinants of water chemistry of the region. Hence they are termed as the “Spinal species”. There are no correlations of silica with other ions in the post-monsoon season as that of nitrogen in summer. There is no relationship of fluoride with other ions in the monsoon season; this may due to effect of dilution. Certain species are correlated with other ions in specific seasons alone and they are termed as “Seasonal species”. Although there are well known problems in examining correlation in constant-data sets. Factor and factor score analyses may yield useful information in the influence of the local conditions.

Factor Analysis

After computation of the correlation matrix and the correlation coefficient, measures of interrelationship for all pairs of constituents are determined. Then by the examination of the factor loadings, factors are interpreted by rotation. In this study principal component method is used as a parameter estimation method to transform a set of observed independent variables into an orthogonal set of variables called principal components. The first principal component accounts as much as possible of variance of the observed variates. The second principal component accounts for as much as possible of the residual variances not accounted by the first principal component. Each succeeding principal component accounts for as much as possible for the residual variance not accounted for by all the previous principal components. Initial factor loadings are unlikely to reveal the underlying structure of the observed variates because of certain mathematical conditions such as the variance properties of the principal components. To have a more clear view of this structure, common factors associated with initial set of loadings are linearly transformed into a new set of common factors, associated with new set of loadings, factor rotation. Though numerous schemes have been proposed, Kaiser scheme called varimax rotation is used in this study. Varimax rotation yields sets of loadings, such as the variance of loadings are maximum.

The factor analysis of four seasons were carried out and the results (Table 2) indicate that five factors were extracted with Eigen value greater than one, during the

Table 2: Factor analyses results of the groundwater chemistry of different seasons

<i>SW Monsoon</i>					
	1	2	3	4	5
Ca	0.836	0.073	-0.178	-0.051	0.057
Cl	0.911	-0.097	0.287	-0.056	0.012
EC	0.917	0.180	0.240	-0.014	0.016
F	0.022	0.152	0.085	0.841	-0.201
H ₄ SiO ₄	0.014	0.060	0.871	0.147	0.088
HCO ₃	0.041	0.787	0.077	0.322	0.201
K	0.300	0.392	0.130	-0.567	-0.277
Mg	0.935	-0.005	0.192	-0.049	0.093
Na	0.897	-0.020	0.290	0.010	-0.089
NO ₃	0.358	0.146	0.614	-0.198	-0.119
pH	0.057	0.117	0.023	-0.089	0.923
PO ₄	0.014	0.833	0.065	-0.155	-0.010
SO ₄	0.776	0.112	-0.336	-0.107	-0.066

<i>Post Monsoon</i>				
	1	2	3	4
Ca	0.502	-0.085	-0.496	0.519
Cl	0.961	0.050	0.024	0.088
EC	0.961	0.156	-0.087	0.105
F	0.439	-0.262	0.011	-0.487
H ₄ SiO ₄	0.062	0.025	0.954	-0.010
HCO ₃	0.012	0.707	-0.353	-0.111
K	0.209	0.735	0.205	0.125
Mg	0.907	-0.033	0.139	-0.050
Na	0.938	0.094	0.010	0.048
NO ₃	0.283	0.213	-0.095	0.606
pH	-0.005	0.510	-0.223	-0.601
PO ₄	0.035	0.702	0.101	0.132
SO ₄	0.769	0.158	-0.098	0.162

<i>NE Monsoon</i>					
	1	2	3	4	5
Ca	0.803	0.327	-0.162	0.021	-0.082
Cl	0.967	0.177	-0.003	-0.008	0.028
EC	0.947	0.262	0.033	0.017	-0.004
F	-0.062	-0.141	0.872	0.122	-0.054
H ₄ SiO ₄	0.277	0.167	0.328	0.624	0.099
HCO ₃	0.085	0.566	0.617	-0.266	0.001
K	0.452	0.660	-0.169	0.071	-0.171
Mg	0.916	-0.016	0.034	-0.009	-0.031
Na	0.708	0.450	0.174	-0.091	0.066
NO ₃	0.369	0.189	0.016	0.259	-0.639
pH	0.233	-0.007	0.115	-0.811	-0.017
PO ₄	0.200	0.105	-0.042	0.279	0.802
SO ₄	0.225	0.849	-0.005	0.183	0.061

<i>Summer</i>				
	1	2	3	4
Ca	0.820	-0.171	-0.170	0.050
Cl	0.965	0.093	0.141	0.037
EC	0.952	0.192	0.042	0.129
F	0.123	0.890	-0.051	-0.072
H ₄ SiO ₄	0.119	0.403	0.633	-0.269
HCO ₃	0.120	0.836	0.100	0.099
K	0.339	-0.161	0.306	0.645
Mg	0.883	0.174	-0.078	-0.074
Na	0.740	0.486	0.279	0.164
NO ₃	-0.065	0.072	-0.236	0.768
pH	0.094	0.225	-0.790	0.130
PO ₄	0.043	0.144	0.655	0.210
SO ₄	0.587	0.215	0.136	0.452

monsoon seasons and four in the other two non-monsoon seasons. This reflects the influence of monsoon in the groundwater chemistry of the region. The results of the SWM shows that five factors explains about 79% of the total sample variance and communalities are generally higher than 0.74. The NWM is also represented by five factors with 78% of variance with communalities >0.6. POM and summer are represented by four factors with 72% and 74% respectively and with communalities >0.5. Representations in the percentage of variance points out that the monsoon season are more significant in influencing the water chemistry than the other seasons. The hydrogeochemical system is complex and it is not possible to list out all factors responsible. So, the dominant factors responsible are extracted by this method in all four seasons. The first factor is represented by Ca, Cl, Mg, Na and SO₄. NO₃ is also represented except in

summer. This indicates the anthropogenic influence over the area mainly may be due to the dyeing industry.

The representation of the second factor is K, HCO₃, PO₄ (SWM); K, HCO₃, Na (NEM), K, HCO₃, PO₄ (POM) and F, HCO₃, H₄SiO₄, Na (Summer); the second factor significantly shows the influence of bicarbonate. HCO₃ is the predominant anion in most of the fresh waters. The weathering of feldspar in the pegmatites may contribute PO₄ from the apatites. The possibility of this association was also noted in the irrigated areas of the Bundelkand massif (Chourisa and Tellam, 1992). But in NEM and summer the second factor represents weathering of feldspars. The pegmatite weathering and the release of F from (OH,F) molecules of the micaceous and amphibole minerals were established by the earlier studies (Chidambaram, 2001).

The third factor is represented by H_4SiO_4 , K, NO_3 (SWM), F, H_4SiO_4 , HCO_3 (NEM), K, H_4SiO_4 (POM) and K, H_4SiO_4 , PO_4 (summer). The third factor is represented by silica. Alumino-silicates yield cations and silica and are transformed to secondary clay minerals. The weathering of feldspars would yield Na and silica. The incongruent dissolution of the alumino-silicates may schematically be represented (Stumm and Morgan, 1970) by



Weathering of silicate mineral adds HCO_3^- , H_4SiO_4 and cation into the solution, leaving clay mineral as residue.

The silica in the SWM is associated with nitrate ions. This may be due to the agricultural practices done along the flood plains of the rivers. Opaline silica from the rice plants provides a readily soluble source of silica and frequent oxidation-reduction cycles of paddy soil may accelerate weathering of smectite, thereby making silica more soluble (Wang et al., 1993). Weathering of silicate minerals is mainly represented by third factor.

Factors 4 and 5 do not play important roles as 1, 2 and 3 in determining the whole groundwater chemistry. In many cases factor loading patterns of minor factors tend to compensate for the gap between the actual water chemistry and that composed by the combinations of major factors (Heejun Suk and Lee, 1999). Therefore, it is difficult to explain by one specific chemical reaction as it is a complex hydrogeochemical process.

Factor Scores

The factor scores were also estimated to find out the spatial variation of the factor representation and to identify the zone of representation of each factor. They are commonly obtained by two-approached weighted

least square method and the regression method. The regression method (Johnson and Wichern, 1992) is used in the study to compute the factor scores. The positive zones indicate the dominance of that factor (hydrogeochemical regime). The spatial variation by using the factor score values of each sampling points were plotted by Idrisi GIS software. The first factor of all the four seasons were overlayed (Figure 4) to get the active zone representing the first factor. The figure shows that the representations are in the southern part of the study area covered by charnockites and along the regions of the dyeing industries. Though there are few dyeing industries in the northern gneissic region there is frequent flushing by the river Bhavani and Cauvery. So significant representations of the first factor is not seen in the northern part.

The spatial representations of the second factor score indicate (Figure 5) that they are dominantly represented in the northern part of the gneissic region along the flow path of the river Bhavani and in the region where it confluences with river Cauvery. This factor is mainly marked by the signature of the bicarbonate mainly due to weathering. It is also represented in the charnockite region where the Noyil and Amaravathi river flows. So the influences of rivers are noted in the second factor.

The spatial distribution of the factor scores for the third factor (Figure 6) indicates the influence of the silica either by weathering or by agriculture according to the season. They are well represented in the charnockitic terrain. A good representation of this factor is seen in the gneissic region only near the Bhavani Sagar reservoir. This may be due to the dominance of the agricultural practices.

In general, irrespective of the factors, the charnockitic terrain shows dominant hydrogeochemically active region (Figure 7). Except for few regions along the flow

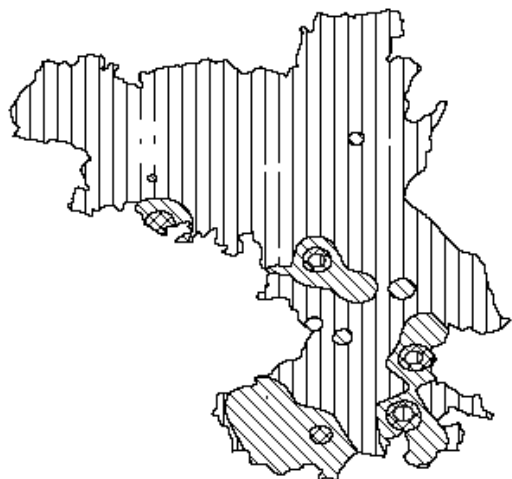


Figure 4: First factor representations in the study area.



Figure 5: Second factor representations in the study area.

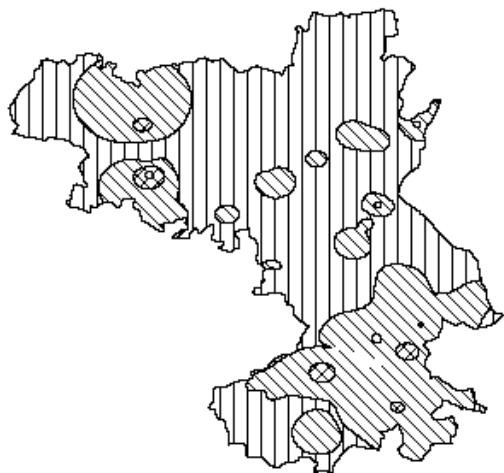


Figure 6: Third factor representations in the study area.

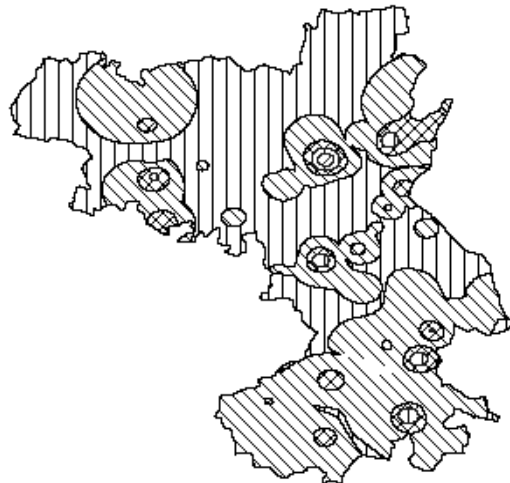
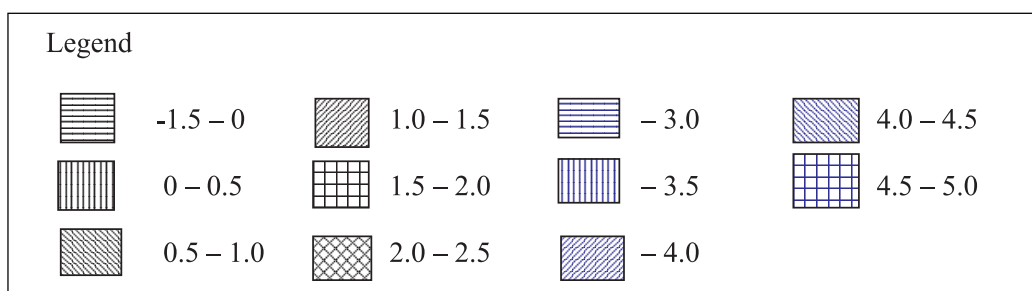


Figure 7: Spatial representation of hydrogeochemical active regimes.



path of the Bhavani river in the gneissic region other areas are not well represented by factors. The northernmost part of the study area does show any representation for the factors as the samples were restricted in these regions because of the presence of the western ghats (hilly region, reserve forest).

Conclusion

The results of the correlation analysis indicate that Na, Mg, Cl, Ca and SO_4 have good positive relationships in all seasons. It signifies that these ions are dominant determinants of water chemistry of the region. There are no correlations of silica with other ions in the post-monsoon season as that of nitrogen in summer. Representations in the percentage of variance points out that the monsoon season are more significant in influencing the water chemistry than the other seasons. The factor analysis indicates that first factor is represented by the anthropogenic influence, second factor by bicarbonate and third factor by dissolved silica. The spatial distribution of factor score shows that, irrespective of the factors the charnokitic terrain shows dominant hydrogeochemically active region. Except for few regions

along the flow path of the Bhavani river in the gneissic region, other areas are not well represented by factors.

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