Statistical analysis of seasonal variations and hydrogeochemical evolution of groundwater in Nannilam block, Thiruvarur district, Tamil nadu, India

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Abstract

The identification of factors accountable for hydrogeochemistry of groundwater is essential to quantify the chemical characteristics of groundwater. In order to obtain an insight into the seasonal variations in hydrogeochemistry along Nannilam taluk in Thiruvarur district in the Indian state of Indian state of Tamilnadu; which is a complex geological terrain with varied of sedimentary formations (recent); 100 ground water samples were collected during different seasons viz; South West Monson (SWM) and North East Monsoon (NEM). Groundwater samples were collected spatially from hand pumps and physical parameters like pH, temperature, TDS, and electrical conductivity (EC) were measured in field. Major ions were analysed for major ions like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3, Cl^{-}, SO_4^{2-}, NO_3, PO_4 and H_4SiO_4. Statistical analysis of the data has been attempted to unravel the hidden relationship between ions. Correlation analyses and factor analyses were applied to classify the groundwater samples and to identify the geochemical processes controlling groundwater geochemistry. Factor analysis indicates that followed by leaching of secondary salts, weathering and anthropogenic impacts are the dominant factors controlling hydrogeochemistry of groundwater in the study area. Factor score overlay indicate major active hydrogeochemical regimes are spread throughout the Southeastern, parts of the study area. The dominant ions controlling the groundwater chemistry irrespective of season are Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, HCO_3 and SO_4. An attempt has also been made to note the seasonal variation of the factor representations in the study area. This study also illustrates the usefulness of statistical analysis to improve the understanding of groundwater systems and estimates of the extent of weathering and ion exchange processes along with anthropogenic activities and salt water intrusion.

1. Introduction

The Ground water quality that is in uninterrupted motion through the aquifer frame work, acquires various physical, chemical and biological characteristics as it flows from recharge area to the discharge area. Geochemical characteristics of aquifers are one of the major controls of ground water chemistry. Rock-water interaction is the casual mechanism behind a variety of geogenic contamination in India. In arid to semiarid regions like Tamilnadu, hydrogeochemistry could be controlled by the interplay of several geochemical processes such as evaporation, transpiration, ion exchange, rock- water interactions and microbial activities (Abdulrahman Shuaibu et al. 2025). Interpretations on the water chemistry data has been significant in coastal areas and at the same time there has been misleading results by adopting standard diagrams, which may work good for uniform lithologies. But in the present study diagrams, significant changes have been selectively used in the study area consists of hard and sedimentary rocks; Fluvial and Marine alluvial formations and sand dunes. Multivariate statistical analysis has been successfully applied in a number of hydrogeochemical studies. This technique will help to simplify and organize large data sets to provide meaningful insight (Laaksoharju et al. 1999). This is a broadly used technique in geochemistry; useful for interpreting groundwater quality and relating them to identify major hydrogeological and hydrogeochemical processes (Mahamuda Abu et al.2024). brought out the seasonally variable species and the spinal species, which are responsible for the groundwater chemistry of a region by using correlation analysis of the hydrogeochemical data. The factor analysis which forms an integral part of the statistical interpretation has been successfully applied to the sort out of hydrogeochemical processes from commonly collected/analysed ground water quality data (Remy Rumuri et al.2020; Kai Chen et al.2022). Factor analysis can be applied to investigation of groundwater contamination (Pintu Prusty et al 2020). When the hydrogeochemical interpretation is combined with the knowledge of the geological and hydrogeological setting, multivariate statistical methods can also help to understand groundwater flow in complex aquifer systems (Farnham et al. 2003). The factor score analysis to interpret the hydrogeochemically active regimes and to know the spatial variation of a particular factor with season was also attempted by (Karmegam et al. 2010). All the hydrogeochemical studies mentioned above show that multivariate statistical analyses significantly help to classify groundwater and identify major mechanisms influencing groundwater chemistry. Few disseminated geochemical studies were carried out in the Nannilam taluk in Thiruvarur district by several. There has been no attempt made to study the statistical nature of these data sets for the groundwater of the entire district. Hence, the main objective of this study is to bring out the usage of factor score in identification of the hydrogeochemically active regimes represented by the major factors; to bring out the hidden relationship among dissolved ions present in water which may vary with season.

2. Study Area

Study area lies in Nannilam taluk Thiruvarur district of Tamil Nadu which extends over 241.3 sqkm. The present study area falls in between 10º48'' and 11º00'' North latitude and 79º33''and 79º45 (Fig:1). The district receives precipitation from both the Southwest and Northeast monsoons, with the average annual rainfall ranging between 1100 and 1260 mm. Rainfall distribution shows a gradual increase towards the eastern and southern parts of the district, reaching its peak near Thiruvarur in the east. The predominant geological formations of Thiruvarur district are mainly Recent and Tertiary formations. The hydrogeology is mainly based on major water bearing formation viz., Alluvium, sand stone, sand. The pre-monsoon depth of ground water table is ranged from 3.07 to 7.01 m bgl and post-monsoon depth of ground water table is ranged from 0.37 to 4.71 m bgl. In the sedimentary, ground water occurs under water table and confined conditions. Two main aquifer systems are encountered in the region such as Porous formations, viz., alluvium, sandstone.

3. Methodology

A total of 100 samples were collected spatially from hand pumps and bore wells of study area based on spatial coverage and lithology during four different seasons viz; South West Monson (SWM) and North East Monsoon (NEM). The pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC) of the water samples were measured in the field using a portable water-analysis kit. Sampling and analysis were carried out using standard procedures (APHA 1998). Major ions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, CO_3^{-}, HCO_3^{-}, NO_3, H_4SiO_4, PO_4^{-} and SO_4^{2-} were analyzed in lab. Cations such as Ca^{2+}, Mg^{2+}as well as anions such as Cl^{-}, CO_3^{-} and HCO_3^{-}, were analysed by titrimetry method. Na^{+} and K^{+} was analysed using flame photometer (ELICO CL 378). SO_4^{2-}, NO_3^{-}, H_4SiO_4, and PO_4^{-} were analysed with the help of UV-VIS Spectrophotometer, Model DR 6000 (HACH, UK).

Precision of analysis was checked by error percentage calculation.

$$Error\% = \frac{(TC - TA)}{(TA + TC)} x100 \qquad \text{Eq. (1)}$$

(Where TA- total anions and TC- total cations) The percentage of error is found to vary between ±1 to ±10 % (Hem, 1985). In this study, correlation analyses and factor analyses were carried out by using Statistical Package of Social Studies (SPSS) version 16 and the summary of hydrogeochemical statistics data is listed in Table 1.

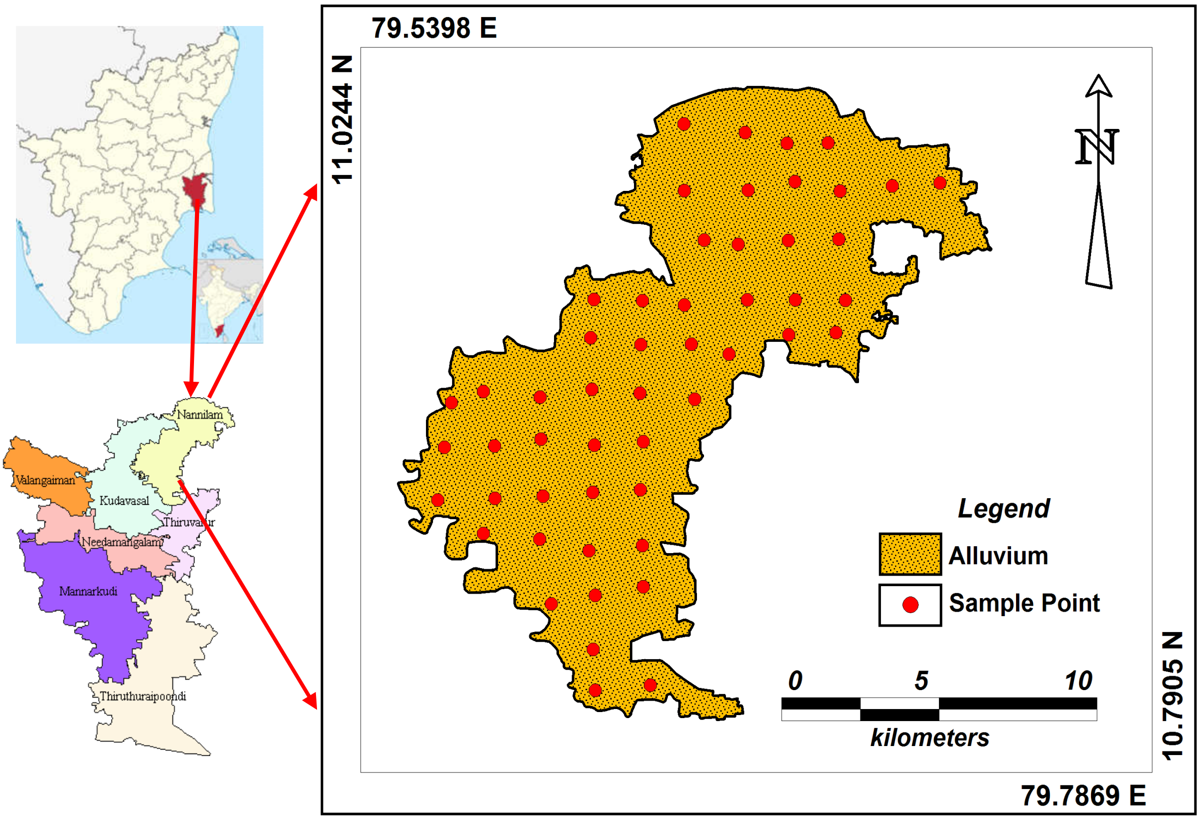


Fig 1: Location map of the study area with the major lithology

4. Results and Discussion

4.1 Groundwater geochemistry

The statistics of the water chemistry is represented in Table 1. The Groundwater of the region is generally acidic to alkaline with pH ranging from 7 to 6.8 and 6.8 to 7.8 during SWM and NEM seasons, respectively. The higher pH is noted in the salt water intruded regions and along the regions covered by salt pans. The EC is a measure of an ability to conduct current so that the higher EC indicates the enrichment of salts in the groundwater. Thus, the EC can be classified as type I, if the enrichments of salts are low (EC\1,500 μS/cm); type II, if the enrichment of salts are medium (EC: 1,500 and 3,000 μS/cm); and type III, if the enrichments of salts are high (EC:1500 μS/cm) (Subba Rao et al. 2012). The EC values ranges from 356.0 to 2360.0 μS/cm and 298.0 to 4039.0 μS/cm during SWM and NEM, respectively. According to the classification of EC, 84 and 76 % of the groundwater samples are under the type I (low enrichment of salts) during SWM and SWM, respectively. EC showed an increasing trend along the groundwater flow direction and was noted to be higher during SWM. The TDS values ranges from 254.0 to 1690.0 and 259.0 to 2019.5 during SWM and NEM, respectively. This may be due to the influence of anthropogenic sources, such as domestic sewage, septic tanks and agricultural activities (Xianbin Zhu et al.2022). The samples tend to fall in the evaporation dominance in the study area. Ca^{2+} Concentration ranges from 26.0 to 79.0 with an average of 52.7 during SWM and 23.0 to 117.0 with an average of 60.2 during NEM. The concentration of magnesium in groundwater samples in the study area varies from 32.4 to 89.6 with an average of 61.2 and 12.0 to 87.6 with an average of 39.7 during SWM and NEM, respectively. The results of these comparisons are supported by correlation and factor analysis. In many locations Mg^{2+} and Ca^{2+}, this may be due to anthropogenic contamination of water (Stanislav Rapant et al 2017). Na^{+} Concentration varies from 19.5 to 289.2 with an average of 109.1 and 70.1 to 405.8 with an average of 150.3 during SWM and NEM. Sodium concentration also exceed the permissible limit, the increasing sodium in groundwater is likely due to seawater influence or salt pan deposits or ionic exchange process (Indu et al. 2020). K^{+} concentration ranges between 2.5 and 35.4 with an average of 6.7 and 3.7 to 54.9 with an average of 11.4 during SWM and NEM respectively. It may be due to weathering of feldspar and presence of clay minerals in the aquifer matrix. In fact, the Cl- is derived mainly from the non-lithological source and its solubility is generally higher (Arif Ahamad et al,. 2019). Cl- concentration ranges from 53.2 to 369.5 with an average of 158.4 during SWM and 70.9 to 726.7 with an average of 211.5 during NEM. The increase of chloride in groundwater is likely due to salt pan deposits and agricultural return flow in groundwater (Monica Chakraborty et al,. 2022). Higher Cl- concentration may also be due to the leaching from upper soil layers derived from industrial and domestic activities (Lulu Wu et al,. 2024). HCO_3^- was higher during SWM (763.8 mg/l) may be due to action of CO_2 upon the basic material of soil and lithology. SO_4 values ranges from 0.4 to 13.0 with an average of 6.1 and 3.4 to 19.1 with an average of 8.3 during SWM and NEM may be due to the action of leaching and anthropogenic activities in a metamorphic environment by release of sulphur gases from industries and urban utilities get oxidized and enter into the groundwater system (Hazir et al. 2025). Salt pans/sea water intrusion can be responsible for most of SO_4 inputs into the groundwater samples (Ismail abd elaty et al., 2018)

Table 1. Minimum, maximum and mean of physico chemical parameters and comparison of chemical composition of water with WHO (2022) in milligrams per litre (except EC - µS/cm and TDS ppm)

*The Below Detectable Limit * No health based guideline value have been proposed by either WHO or BIS for these ions in drinking water.*

Season	**SWM**			**NEM**			**WHO(2022) BIS(2012)**
Parameter	**Max**	**Min**	**Avg**	**Max**	**Min**	**Avg**	
Ca^{2+}	79.0	26.0	52.7	117.0	23.0	60.2	70-200
Mg^{2+}	89.6	32.4	61.2	87.6	12.0	39.7	30-100
Na^{+}	289.2	19.5	109.1	405.8	70.1	150.3	*
K^{+}	35.4	2.5	6.7	54.9	3.7	11.4	*
Cl^{-}	369.5	53.2	158.4	726.7	70.9	211.5	250-1000
HCO_3^{-}	763.8	256.2	519.5	713.8	170.8	428.4	*
CO_3^{-2}	12.0	0.0	2.4	11.0	0.0	2.0	*
NO_3^{-}	62.1	20.4	38.5	74.8	19.5	45.8	45-50
PO_4^{2-}	2.4	-5.9	-1.0	3.4	-3.4	0.3	*
SO_4^{2-}	13.0	0.4	6.1	19.1	3.4	8.3	200-400
H_4SiO_4	210.0	45.4	116.2	263.1	89.0	165.8	*
pH	8.6	7.0	7.9	7.8	6.8	7.2	6.5-8.5
EC	2360.0	356.0	1112.5	4039.0	298.0	1330.9	*
TDS	1690.0	254.0	791.6	2019.5	259.0	684.5	500-2000
Temp˚C	38.2	27.8	29.7	32.4	26.6	29.4	*

4.2 Statistics

Multivariate statistical methods such as correlation, Factor analysis and Principal Component Analysis (PCA) were performed to quantitatively classify the groundwater samples and to correlate between the chemical parameters and groundwater samples.

4.3 Correlation analysis

In SWM, high positive correlation (> 0.5) has been obtained between Cl-Mg^{2+}, Cl-Na^{+}, HCO_3-Mg^{2+}, HCO_3-Na^{+}, HCO_3-Cl, NO_3-Na^{+}, NO_3- Cl, NO_3- HCO_3 and SO_4 - HCO_3; SO_4- NO_3. In general, most of the ions are positively correlated with Cl^{-}, especially Mg^{2+}, Na^{+} (Table 2) shows strong correlation with Cl-, indicating that such ions are derived from the same source of saline waters (Avinash Kumar Bairwa et al,. 2024), chemical weathering along with leaching of secondary salts (Prasanna et al. 2010). It is evident that most of the ions were significantly correlated to HCO_3 during the seasons, which suggests the occurrence of complex processes such as ion exchange, rock water interaction and weathering, making HCO_3 a dominant ion in the hydro geochemistry of the region (Subba Rao et al. 2012) There is a wide distribution of samples noted in the study area with a broader range of Cl- and SO_4 values (Singaraja et al. 2012).

In NEM, good correlation exhibits between Mg^{2+}-Ca^{2+}, Cl-Mg^{2+}, Cl-Na^{+}, Cl-K^{+}, HCO_3-Ca^{2+}, HCO_3-Mg^{2+}, (Table 2). Poor correlation is exhibited by HCO_3-NO_3-, HCO_3-SO_4, H_4SiO_4 and PO_4 with other ions indicating effective leaching of these ions due to percolating rain water to the aquifer matrix (Paramaguru Palanivel et al. 2022). The concentration of Na^{+} and Cl^{-} can be ascribed to the intrusion of seawater into the aquifer system, which increases the concentration of these ions. Very high Na^{+}/Cl^{-} ratios may be indicative of anthropogenic contamination, like salt pans and fertilizers (Jones et al. 1999). In general, most of the ions are positively correlated with Cl^{-}, and especially Na^{+}, Mg^{2+}, Ca^{2+} and K^{+}. The study on the correlation between Na^{+} and Cl^{-} ions shows that samples of SWM fall near the equiline indicating almost equal concentration of Na^{+} and Cl^{-}. Further during NEM, samples fall just below the equiline showing that there is a decrease in Na^{+} concentration compared to Cl^{-} indicating the influence of other sources like leaching of salt from the surface or recharge due to evaporated/saline waters (Chidambaram et al. 2010). Na^{+} exhibited a high positive correlation with Cl^{-} in the collected water samples. It showed that the dissolution of halite was important in regulating the concentration between Na^{+} and Cl^{-} in water samples during SWM and NEM (Devaraj et al.2020). There was also a positive and significant correlation of mineral is not reported in the study area, it may be due to the process of ion exchange (Prasanna et al. 2010).

Table 2: Correlation coefficients of geochemical parameters for (a) SWM (b) NEM

SWM	Ca	Mg	Na	K	Cl	HCO_3	NO_3	PO_4	SO_4	H_4SiO_4	pH	EC
Ca	1.000											
Mg	.380	1.000										
Na	.403	.362	1.000									
K	.121	.368	.031	1.000								
Cl	.440	**.643**	**.844**	.080	1.000							
HCO_3	.465	**.648**	**.787**	.306	**.685**	1.000						
NO_3	.342	.234	**.601**	.154	**.492**	**.516**	1.000					
PO_4	.107	.164	.229	.267	.244	.168	.368	1.000				
SO_4	.300	.324	.430	.214	.289	**.546**	**.580**	.203	1.000			
H_4SiO_4	-.220	.016	-.231	.104	-.247	-.070	.015	.165	-.001	1.000		
pH	.258	.259	.019	-.071	.128	.052	-.101	-.044	.169	-.269	1.000	
EC	.469	**.615**	**.931**	.156	**.923**	**.830**	**.558**	.283	.436	-.202	.080	1.000
NEM												
Ca	1.000											
Mg	**.881**	1.000										
Na	.153	.263	1.000									
K	.193	.376	.452	1.000								
Cl	.468	**.618**	**.859**	**.559**	1.000							
HCO_3	**.751**	**.702**	.380	.055	.440	1.000						
NO_3	.059	.033	.249	.048	.127	.101	1.000					
PO_4	.036	.137	.407	.321	.360	.135	.093	1.000				
SO_4	-.033	.019	.138	-.023	.057	.135	.169	-.237	1.000			
H_2SiO_4	.234	.177	-.044	-.037	-.051	.420	.054	-.056	.225	1.000		
pH	-.578	-.622	-.034	-.267	-.254	-.457	-.055	-.270	-.023	-.093	1.000	
EC	**.559**	**.667**	**.754**	.433	**.870**	**.623**	.178	.274	-.019	.019	-.363	1.000

4.4 Factor Analysis

This multivariate analytical technique is used as a data reduction tool that derives a subset of uncorrelated variables called factors that explain the variance observed in the original dataset (Loganathan et al.2017). Factor analysis helps to establish observed relationship between numerous variables in term of simpler relations thereby simplifying interpretation and to evaluate the composition of groundwater (Mohamed Gad et al.2024). The varimax rotated factors that were extracted with Eigen values >1and their total data variance (TDV) are given in Table 3. The factors extracted were categorized according to factor loadings. The first factor, F1 with highest total data variance among the sample points, is chosen for SWM and NEM (TDV- 46.328 and 42.551 respectively) and factor scores were computed for all samples corresponding to this predominant factor. The major factor scores for different seasons were spatially showed. The dominant factor during SWM is constituted by Na, HCO_3 and NO_3 accounts for the major factor during NEM; whereas Na, K, Cl and PO_4.

Table 3. Rotated Component Matrix of the hydro-geochemical analysis for SWM and NEM

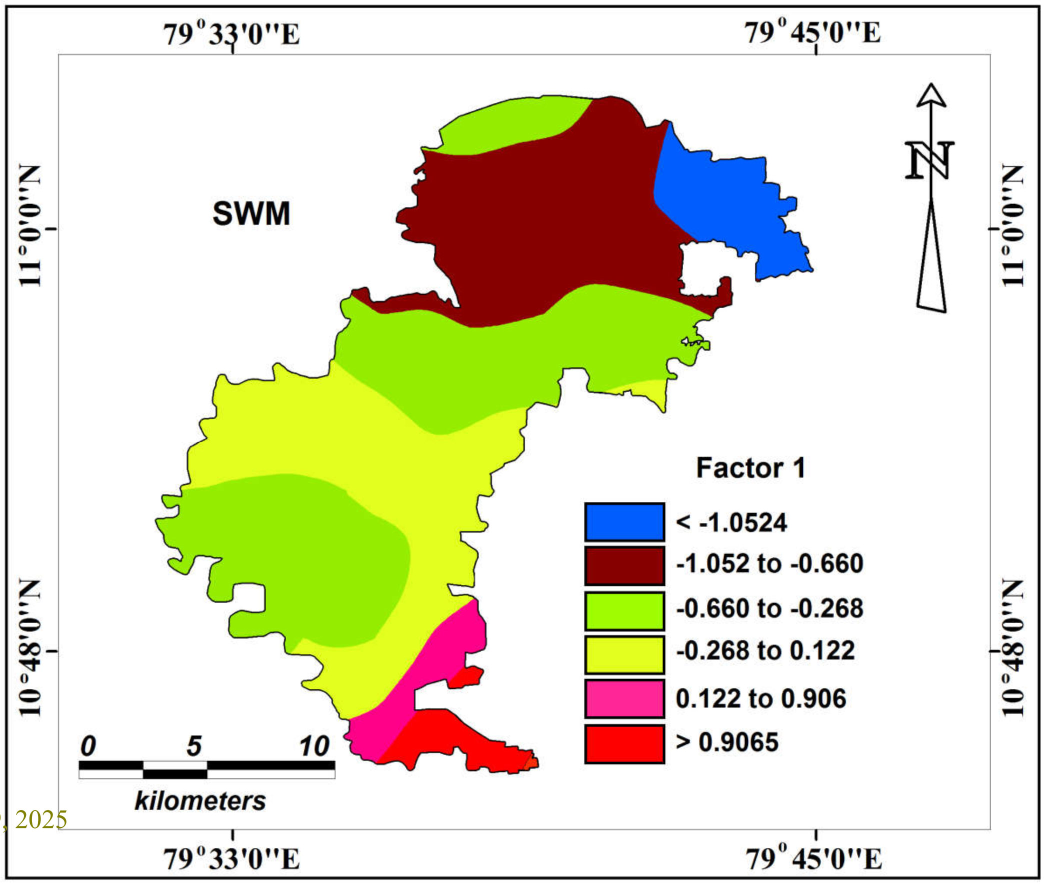
Parameters	SWM			NEM		
	1	2	3	1	2	3
Ca	.462	.082	.483	.166	.914	.012
Mg	.479	.428	.529	.338	.873	-.023
Na	.964	-.063	-.001	.913	.010	.271
K	.034	.768	.196	.626	.117	-.175
Cl	.896	-.013	.210	.890	.318	.091
HCO3	.809	.290	.220	.238	.802	.305
NO3	.688	.296	-.210	.258	-.071	.478
PO4	.280	.526	-.206	.527	.020	-.344
SO4	.471	.407	.159	-.048	-.008	.778
H2SiO4	-.228	.563	-.413	-.245	.403	.494
pH	-.038	-.093	.818	-.114	-.722	.198
EC	.960	.084	.160	.804	.485	.115
TDV%	46.328	12.403	9.622	42.551	15.218	10.774

During SWM, Na is found associated with HCO_3 and NO_3 which is characterized by impact of fertilizer leaching by infiltrating rainwater during Monsoon and is represented mostly in the North-Eastern side of the study area characterised predominantly by agricultural land respectively as shown in (Fig 2).

During NEM, Na^+& K^+ are found in association with Cl and HCO_3. It can be assumed that the complexity and variations in the geological formations of the study area and inconsistent distribution of anthropogenic activities (agricultural activities such as irrigation practices and fertilizations) are reflected by this factor. Higher levels of Na^+ and Cl^- in the groundwater mostly can be linked to the human activities such as use of agricultural fertilizers, animal waste, and municipal and industrial sewage (Rajesh Kumar et al.2024). Earlier studies report that Cl^- in groundwater can be the consequence of the excess application of manure and inorganic fertilizers (Adimalla et al. 2020)

4.5 Factor scores

Factor scores are used to reveal the spatial variation of chemical processes. It is also used to identify positive zones of each factor in the study area by regression method (Adimalla et al. 2020). The spatial variation by using the factor score values of each sampling points were plotted by Gis software. Figure 2 shows the spatial distribution of factor scores for factor I during SWM period, indicating the probable zones of the agricultural landscape and inland irrigation. The values ranging from 0.122 to 2.38 fall in the South Eastern part of the study area the spatial distribution of factor score shows that agricultural activity and fertilizer is higher in the SWM compared to the NEM. It may be also due to higher amount of groundwater exploration in this area due to occurs in unconfined alluvial formations, with deeper fracture/jointed aquifers in the underlying hard rock (gneiss/charnockite) formations, which prevails in this region during this sampling period. In NWM, factor I (Fig. 2) is well represented in regions roofed by saltwater intrusion activities along the coast and also with high fertilizer activity. Further high concentration of Cl- in water samples may be attributed to contamination by anthropogenic sources such as industrial discharge (Nishmitha et al.2025). Another source of high Cl- in shallow groundwater is the evaporation of surface water and moisture in the unsaturated zone (Richter and Kreitler 1993). The spatial distribution of the factor score show that the intensity of salt water activity is well noted along the coastal area ranging from 0.122 to 2.38, falling in the Eastern part of the study area. It is interesting to note that same trend was observed during SWM and NEM.



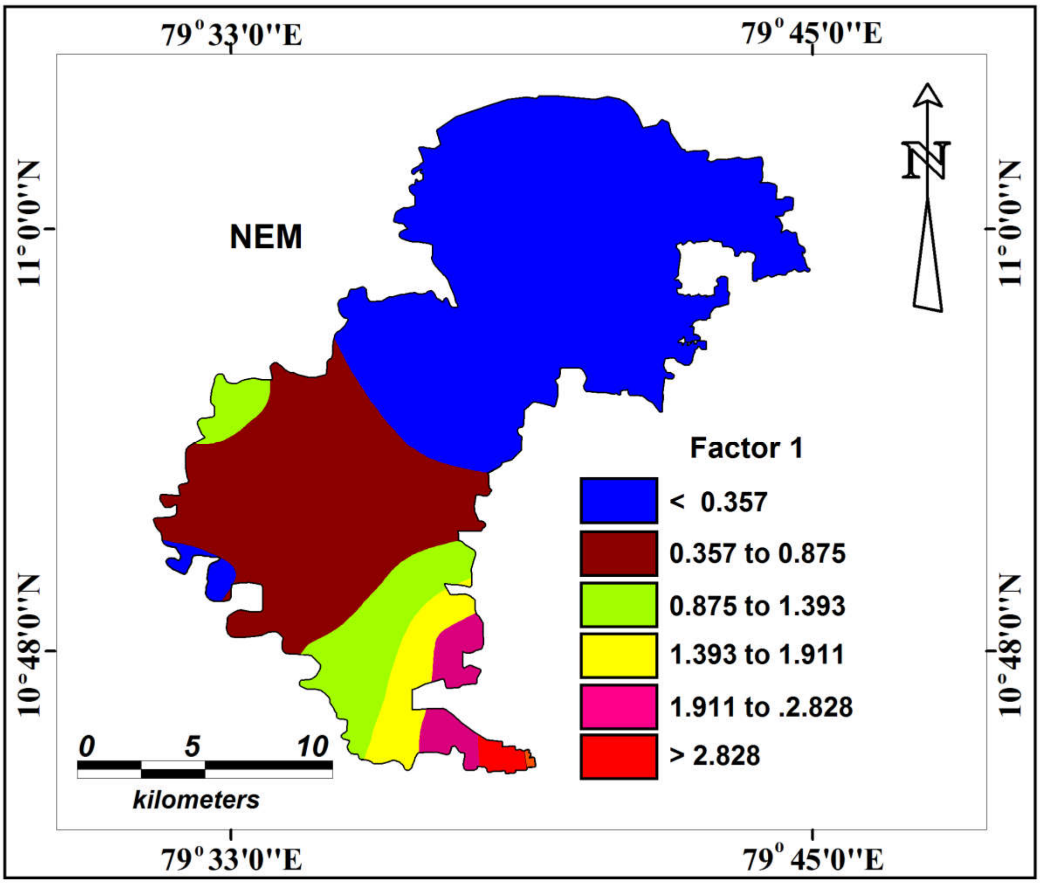


Fig 2: Spatial distribution of Factor 1 in groundwater during SWM and NEM

5. Conclusion

Multivariate statistical techniques were applied to ascertain the hydro geochemical nature of the complex aquifer systems in the study area for SWM and NEM periods. The groundwater chemistry is characterized by higher EC indicating the enrichment of salts and Cl-, Mg^{2+}, Na^{+}, Cl^{-}, HCO_3 and NO_3 exceed the permissible limit and is likely due to fertilizer or anthropogenic such as agricultural runoff and ionic exchange process The correlation of various parameters for SWM and NEM seasons indicate the occurrence of complex processes such as ion exchange, unconfined alluvial formations interaction weathering as well as anthropogenic sources in the study area. Factor analysis strongly evidences the influence of anthropogenic factors in the hydrogeochemistry of the region except during NEM where weathering and dissolution of deeper fracture/jointed aquifers in the underlying hard rock formations play the governing role in the water chemistry. Factor scores of the dominant factor for SWM and NEM seasons are spatially distributed along the South Eastern side covered mostly by agricultural land thereby favouring anthropogenic activities in the area. In general, the statistical relationship of major ions are weakened by the deep and shallow groundwater mixing, but these statistical results also imply that weathering and dissolution of the minerals such as sandstone and siltstone with lot of clay content, control the groundwater quality in aquifer system.

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