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Long-term geochemical assessment of groundwater in a hardrock aquifer system

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■ ABSTRACT : Groundwater is one of the most vital natural resource supporting the survival of human civilization. Lowering of groundwater levels accompanied by deteriorating groundwater quality worldwide has created a serious concern about sustainability of water supply in the 21st century. Rapid urbanization and unplanned management of day-to-day activities has led to the release of harmful substances to groundwater resources depleting the qualitative aspect of groundwater. In this study, the concentration of 13 groundwater-quality parameters for the confined aquifer of 14 blocks in the study area located in South India were analyzed critically using premonsoon and post-monsoon groundwater-quality data for 34 years. Both statistical and graphical methods were employed to analyze the spatial and temporal variability in the concentration of groundwater-quality parameters. Two groundwater quality diagrams (Piper diagram and Schoeller diagram) were prepared for the geochemical classification of groundwater of the aquifer. Groundwater quality was also analyzed for irrigation suitability. The results indicated statistically significant long-term variation in the concentration of pH, F⁻, Ca²⁺, Mg²⁺ and K⁺. Also, a majority of the groundwater-quality parameters' concentration was found to be spatially significant. Piper diagram revealed that groundwater in the study area is mainly of Na-Cl⁻ and Ca-Mg-SO₄⁻² types with Na⁺, and Cl and HCO, as dominant cation and anions, respectively. It was found that the concentration of Total Dissolved Solids and Total Hardness in the confined aquifer exceed their maximum permissible limits for drinking water. The US Salinity Laboratory diagram revealed high salinity in the groundwater with low sodium hazard. In terms of magnesium hazard, groundwater of the entire area is unsuitable for irrigation.

■ KEY WORDS : Groundwater quality, Geochemical classification, Spatio-temporal variation, Hydrochemical facies

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roundwater plays a major role in supporting life of human beings and also for the socio-economic development of a country. It is estimated that approximately one third of the world's population use groundwater for drinking (UNEP, 1999). India uses about

230 km³ of groundwater per year, which is over a quarter of the global total (World Bank, 2010). About 0.05 per cent of water available in India is trapped as soil moisture and 30.1 per cent is groundwater (Shiklomanov, 1993). Apart from drinking, India also uses largest amount of groundwater for irrigation (Tushaar, 2009). Particularly, the three states of Andhra Pradesh, Rajasthan and Tamil Nadu, together accounts for over half of India's threatened groundwater resources (World Bank, 2010). Availability of groundwater in the state of Tamil Nadu is limited due to comparatively less storage capacity of weathered crystalline formations which occurs all over the state. However, around 37 per cent of the administrative units (blocks) in Tamil Nadu are over exploited; 33 and 57 blocks are under critical and semicritical stage, respectively (CGWB, 2010).

Salinization, growing contamination of groundwater by point and non-point sources of pollution, groundwater contamination by Arsenic and Fluoride and seawater intrusion into the freshwater aquifers are the salient groundwater issues in Tamil Nadu. Aquifer waters suffer from pervasive contamination. Unlike rivers, the damage is generally irreversible. Rate of groundwater renewal is very slow in comparison with that of surface water. Since water in aquifers moves at a very slow rate, the pollutants continue to accumulate (Nag and Suchetana, 2016). Variation of groundwater quality in an area is a function of physical and chemical parameters that are generally influenced by geological formations and anthropogenic activities (Subramani et al., 2005). Hydrogeochemical study reveals the zones and quality of water that is suitable for drinking, agricultural and industrial purposes (Anbazhagan and Nair, 2004). In general, colour and taste of the water are the two basic criteria for a consumer to decide the suitability of given water for drinking without considering other lethal chemical contaminations like Arsenic, Nitrate, Fluoride and other heavy metal contaminations (Kumar et al., 2007). Soil and water are in direct contact with each other and the possible contamination in any one medium would be transferable to the other. Therefore, it is very necessary to evaluate the water quality of resources prior to irrigation in order to prevent complications in the agricultural area.

Some of the past studies used different techniques to evaluate groundwater. Stigter *et al.* (1998) investigated hydrogeological and hydrochemical composition of groundwater under irrigated land in a Mediterranean environment of Portugal by applying a mixing cell model. Five different water types could be discerned from the Piper plot, based on various chemical parameters (e.g. EC, Cl⁻, NO₃⁻, Na⁺, Cl⁻ ratio) and well characteristics (e.g., location and depth). Güler et al. (2002) evaluated the performance of graphical and statistical methodologies used to classify water samples including: Collins bar diagram, pie diagram, Stiff pattern diagram, Schoeller plot, Piper diagram, Q-mode hierarchical cluster analysis, K-means clustering, principal components analysis and fuzzy k-means clustering. The use of graphical techniques was proved to have limitations compared with the multivariate methods for large datasets. Liu et al. (2003) applied factor analysis to 28 groundwater samples collected from wells in the coastal blackfoot disease area of Yun-Lin, Taiwan. Correlations among 13 hydrochemical parameters were statistically examined. A two-factor model was suggested and explained over 77.8 per cent of the total groundwater quality variation. Park et al. (2005) evaluated salinization in the western coastal area of South Korea by performing regional hydrochemical study on 356 shallow groundwater samples collected within 10 km from the coastline. The geochemical data were used for multivariate statistical analyses such as ANOVA, t-test, and discriminant analysis suggesting that the hydrochemistry is controlled by several intermixed processes. Moral et al. (2008) characterized spring water and analyzed factors affecting spatial variability of groundwater quality parameters in the carbonate aquifers of Sierra de Segura situated in the central part of Betic Cordillera (Southern Spain). A model of groundwater geochemical evolution was proposed. Ahmad and Qadir (2011) found very high concentration of EC, TDS, TH, HCO₃⁻, SO₄⁻²⁻ and Na⁺ near a sugar mill based on a study on groundwater quality evaluation in the Dera Ismail Khan area of Pakistan.

Bjerg and Christensen (1992) performed a geostatistical analysis using STAT-GRAPHICS software package on the spatio-temporal variability of groundwater quality in an aquifer of Denmark collecting 350 groundwater samples and found large vertical and horizontal variations in the concentration of parameters. Babiker *et al.* (2004) studied the extent and variation of nitrate contamination in groundwater in the Kakamighara Heights of Japan and also established suitable relationships with different land use types by making use of GIS. Singh *et al.* (2004) applied different multi-variate statistical techniques to evaluate the spatio-temporal variations in the quality of Gomti River water, India. The groundwater quality map showed groundwater zones that

are desirable and undesirable for drinking and irrigation purposes. Raju (2007) assessed the hydrogeochemical characteristics of groundwater and evaluated it for domestic, irrigation and industrial purposes using seasonal groundwater quality data in the upper Gunjanaeru River Basin, Andhra Pradesh, India. Higher chemical concentrations were found in the post-monsoon season due to dissolution of surface pollutants added through agricultural and domestic activities. Anbazhagan and Nair (2004) and Yammani (2007) made use of GIS applications to identify the suitability of groundwater for domestic and agricultural purposes. Mondal et al. (2008) carried out hydrochemical study on groundwater samples collected from 42 sites from Potharlanka Island, India in December 2001 and October 2006. Discussions were made on the impacts of flood caused due to heavy rainfall and improvement of groundwater due to artificial recharge structures. Tyagi et al. (2009) investigated hydrochemistry of groundwater and its suitability for irrigation uses in Muzaffarnagar district of Uttar Pradesh, India. A total of 104 groundwater samples were used for GIS analysis and for plotting Piper diagram, Gibbs diagram, Wilcox diagram, and US salinity diagram. Barring a few locations, most of the groundwater samples were found suitable for irrigation uses. Nas and Berktay (2010) provided an overview of the present groundwater quality and determined the spatial distribution of groundwater quality parameters in the Konya city, Turkey using GIS. Ghosh and Kanchan (2014) carried out geochemical and multi-variate analysis on 78 groundwater samples collected from the alluvial tract in Bengal during the pre-monsoon season of May 2011 and found probable relation of arsenic concentration with over extraction of groundwater. Madhnure (2016) carried out a detailed hydrochemical study to aid sustainable development and management in Precambrian Province, India by exploring the hydrometeorologic, geomorphologic, hydrogeologic, geophysical and groundwater characteristics and suggested both supply-side and demand-side measures. A number of studies have also been carried out to evaluate the potability of groundwater and its suitability for irrigation considering short-term data (Aksoy and Scheytt, 2007; Kumar et al., 2007; Arumugham and Elangovan, 2009; Sharma et al., 2012; Bozdag and Gocmez, 2013; Agca, 2014; Jassas and Merkel, 2015 and Sojobi, 2016).

From the literature reviewed, it is clear that several

METHODOLOGY

Study area:

The study area, Tiruchirappalli district, also known as Trichy, is located in the central part of Tamil Nadu in South India (Fig. A). It encompasses a geographical area of about 4403.83 km² falling within 10°16' and 11°22' N latitude and 78°15' and 79°16' E longitude. The district is delineated into 14 administrative units (blocks) namely, Anthanallur, Lalgudi, Manachchanallur, Manapparai, Manikandam, Marungapuri, Musiri, Pullambadi, Tattayengarpettai, Tiruverumbur, Thottiyam, Thuraiyur, Uppliyapuram and Vaiyampatti. Tiruchirappalli is characterized by subtropical climate with hot and dry summer during the months of April, May and June and pleasant monsoon weather from November to January. The normal annual rainfall varies from 730 mm to 900 mm with an average daily rainfall of 820 mm. The minimum and maximum temperature of the district ranges from 29.3°C to 38.5°C.

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studies on the assessment of groundwater have been reported from different parts of the globe, but relatively less number of studies on groundwater-quality is reported from India. The past studies on groundwater-quality evaluation used short-term water-quality data (mostly yearly or a few years' time-series data). Groundwater quality being highly dynamic in nature needs to be monitored at a regular interval for longer period. Longterm water-quality data are helpful in understanding the dynamics and trend of quality variation in groundwater, which in turn can help in formulating sustainable groundwater management plans. Therefore, the main goal of this study is to analyze and evaluate the quality of groundwater for drinking and irrigation purposes using 34 years (1981-2014) groundwater-quality data obtained from a hard-rock aquifer system of Cauvery Basin, Tamil Nadu, India. Considering this broad goal, specific objectives of this study are: (a) to explore the long-term temporal and spatial variability of the concentrations of salient groundwater-quality parameters, (b) to investigate geochemical characteristics of groundwater and (c) to assess groundwater suitability for drinking and agricultural purposes. This study is first of its kind in the study area. The methodology and findings of this study could be useful for the efficient planning and management of groundwater resources in other hard-rock aquifer systems of India and other regions of the world.



The Cauvery River flows through the center of the study area draining the north and south of the district with Ayyar, Uppar and Koraiyar being its major tributaries. Due to the Cauvery River dispute, in the nonmonsoon season, sufficient water is not available in the river and so the river and its tributaries get dried up. This causes severe surface water demand for both domestic and irrigation purposes forcing the farmers here to rely on groundwater for irrigation and this highlights the importance of groundwater in this area.

There are five major geological formations *viz.*, alluvium, sandstone, limestone, charnockite and granite gneiss. The depth to water level varies from 1.95-9.49 m to 1.60-15.15 m during the pre-monsoon and post-monsoon seasons, respectively. As such, the annual rise and fall of groundwater level in the study area ranges from 0.0271-0.8567 m/year and 0.0066-0.7136 m/year, respectively (CGWB, 2008).

About 54 per cent of the total area of Tiruchirapalli is agricultural land. Paddy, cereals, fruits and vegetables, oil seeds, sugarcane and pulses accounts to be the mostly cropped agricultural produce in the study area (CGWB, 2008). As such, mineral fertilizers used in agricultural activities leads to the release of NO_3^- and K⁺ to groundwater. Forest area comprises of 10.5 per cent of the total area and 6 per cent is water body. A total of 3.8 per cent of the study area is under settlement. Leaking urban sewer lines, septic system drainfields, garbage dump sites and municipal treatment plants are the potential threats to groundwater contamination. However, domestic waste water discharge and livestock wastes also accounts for the most probable anthropogenic contaminant sources. Mining activities are prominent in many places of Tiruchirapalli, covering about 0.2 per cent of the study area. A number of growing steel/iron fabrication industries, cement factories and leather tanneries acts as a supplier of toxic chemicals to the groundwater. Food process industries and sugar mills are also located in the study area.

Groundwater sampling and analyses:

A total of 63 piezometers were present in the confined aquifer underlain in the study area (Fig. B). Seasonal (pre-monsoon and post-monsoon) water-quality data of 13 groundwater-quality parameters namely, Cl⁻, pH, TDS, TH (Total Hardness), F⁻, NO₃⁻ as N, Na⁺, Mg²⁺, Ca²⁺, K⁺, SO₄⁻²⁻, HCO₃⁻ and CO₃⁻²⁻ were obtained from Institute for Water Studies, Chennai, Tamil Nadu. The data was available for a period of 34 years from 1981 to 2014.

Statistical analyses:

As an initial step of investigating the quality of groundwater present in the study area, a descriptive



statistical analysis (mean, standard deviation, co-efficient of variation, minimum and maximum) was carried out for 11 groundwater-quality parameters (TDS, Cl⁻, pH, EC, TH, F⁻, NO³⁻, Na⁺, Mg²⁺, Ca²⁺ and K⁺) for 34 years period from 1981-2014 which plays a major role in drinking water quality. Correlation matrices were also prepared to know the relationship between a pair of groundwater-quality parameters in terms of correlation co-efficient (Mehta, 2010). All the statistical analyses were done block-wise for pre-monsoon and postmonsoon seasons separately using MS-Excel.

Statistical significance of variation in groundwater quality:

The seasonal concentrations of the groundwaterquality parameters were analyzed to understand their long-term temporal and spatial variability using one-way ANOVA test, block-wise. The significance of the test was assessed by comparing the computed p-value (probability of a value of F greater than or equal to the observed value) against the α -value (probability of getting an extreme) and the results were considered significant if the computed p-value was less than the α -value. The observed test-statistic (F) is given by:

$$F = \frac{\left(\frac{SS}{p}\right)}{\left(\frac{SSE}{n-p-1}\right)} = \frac{MS}{MSE} \qquad \dots \dots (1)$$

where, SS = Sum of squares, SSE = Sum of squared error, SST = Total sum of squares, MS = Mean square, MSE = Mean squared error, p = No. of independent variables and n = No. of observations.

Geochemical classification of groundwater:

The 'Piper's Trilinear diagram' or simply 'Piper diagram' were plotted for defining the hydrochemical facies of groundwater present in the study area for both pre- and post-monsoon seasons. It is an important tool for determining chemical relationships and geochemical evolution of groundwater in more definite terms in comparison to other plotting methods (Walton, 1970). The Piper plot allows comparisons of 6 parameters between a large number of samples. Like all trilinear plots, it does not portray absolute ion concentrations. The main purpose of Piper plots is to show clustering of samples based on their chemical relationships. In this plot, major ions are plotted as cation and anion percentages of milliequivalents in two base triangles. The data points in the two triangles are then projected onto the diamond grid. The diamond-shaped field indicates the type of groundwater and two triangular fields shows the major cations and anions present in the groundwater samples (SWS, 2014).

In addition to this, a pair of Schoeller diagrams were plotted to have a better understanding of the combination of major and minor constituents of groundwater in the study area. Schoeller diagram is a helpful tool which represents the cation and anion compositions of a number of samples on a single graph in which minor trends or groupings can be identified visually (Machiwal and Jha, 2010). It is a semi-logarithmic plot to represent major ion analyses and to demonstrate different hydrochemical water types on the same plot. Unlike trilinear plots, the main advantage of Schoeller diagram is that it displays the actual parameter concentrations (Schoeller, 1962 and SWS, 2014).

Evaluation of groundwater quality for drinking purpose:

Groundwater in the study area was evaluated to assess its suitability for drinking purpose. The spatial variation in the average seasonal concentration (premonsoon and post-monsoon) of 11 groundwater-quality parameters (Cl⁻, pH, TDS, TH, F⁻, NO₃⁻ as N, Na⁺, Mg²⁺, Ca^{2+} , K⁺ and SO₄²⁻) of 14 blocks were plotted in scatter diagrams. These concentrations were then compared with the World Health Organization (WHO) guidelines for drinking water. Box and Whisker plots were placed sideby-side to compare and contrast groups of groundwaterquality data. Box and Whisker plot provides an excellent summary of five important statistical aspects (spread of central 50 per cent of the data, stretch of the tail of distribution, sample median, symmetry of the data and extremes) of water quality parameters along with the identification of outliers (USEPA, 1996). In this way, they are very useful for comparing individual waterquality constituents among different settings (Alley, 1993). Groundwater - quality parameters having higher concentration than the corresponding maximum permissible limits and recommended limits were analyzed using Box and Whisker plots. STATISTICA software was used for preparing seasonal Box and Whisker plots.

Evaluation of groundwater quality for irrigation :

Water quality, soil types and cropping practices play an important role for a suitable irrigation practice. The important chemical constituents that affect the suitability of water for irrigation are the total concentration of dissolved salts, relative proportion of bicarbonate to calcium, magnesium and relative proportion of sodium to calcium. Water quality problems in irrigation include salinity and alkalinity (Kumar *et al.*, 2007).

Classification of groundwater for agricultural purposes:

A high salt content, that is, high Electrical Conductivity (EC) leads to the formation of saline soil. Also, sodium concentration is important in classifying irrigation water because sodium reacts with soil to reduce its permeability. Sodium content is usually expressed in terms of percent sodium or soluble-sodium percentage (%Na) (Raju, 2007). Sodium Adsorption Ratio (SAR) is a measure of the degree to which irrigation water tends to enter into cation-exchange reactions in soil. Sodium replaces the adsorbed calcium and magnesium in soil. Due to this, the soil structure is damaged and it becomes compact and impervious. Residual sodium carbonate (RSC) determines the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purpose (Eaton, 1950). Several classes of groundwater to assess its suitability for irrigation were obtained from literature and are summarized in Table A. In this study, seasonal groundwater-quality maps of the study area were prepared based on electrical conductivity, sodium adsorption ratio, percentage sodium and residual sodium carbonate using ArcGIS software.

US salinity laboratory (USSL) diagram:

The 'USSL diagram' is used to evaluate the suitability of water for irrigation purpose. It classifies water into four classes based on each of salinity (Electrical conductivity) and sodium hazards (Sodium adsorption ratio). These four classes of salinity and alkalinity are 'Low', 'Medium', 'High' and 'Very High', thus giving a total of 16 classes of irrigation water (USDA, 1954). Groundwater can be classified into these 16 categories based on which position they fall in the diagram. In this study, USSL diagrams were plotted using the average value of 34 years (1981-2014) groundwater-quality data for 14 blocks by using AquaChem 2014.2 software. The diagrams were prepared for pre-monsoon and post-monsoon data separately.

Permeability index (PI):

Long term use of sodium rich irrigation water leads to the replacement of Ca^{2+} which remains adsorbed over the clay particles by Mg^{2+} . The clay particles tends to swell up reducing the permeability of soil (Ayers and Westcot, 1989). Permeability index (PI) is a measure of assessing the suitability of groundwater for irrigation in terms of soil permeability. PI can be defined as (Doneen, 1964 and Ragunath, 1987):

PI =
$$\frac{\left(Na^{+} + \sqrt{HCO_{3}^{-}}\right)}{\left(Ca^{2+} + Mg^{2^{+}} + Na^{+} + K^{+}\right)}x 100$$
(2)

Concentrations are expressed in meq/L.:

Based on the PI values, groundwater can be classified into three classes, namely Class I (> 75%), Class II (25-75%) and Class III (< 25%). Groundwater falling in Classes I and II are considered to be good and suitable for irrigation whereas, Class III indicates that the water is unsuitable for irrigation with 25 per cent or less of maximum permeability.

Magnesium hazard (MH):

Elevated levels of Mg^{2+} in soils result in severe structural degradation that leads to lower infiltration rates

Table A : Guidelines for classifying groundwater for irrigation										
Sr. No.	Water-quality classes	EC* (µS/cm)	SAR [#]	% Na [*]	RSC [#] (meq/L)					
1.	Excellent	< 250	< 10	0-20	-					
2.	Good	250-750	10-18	20-40	< 1.25					
3.	Permissible	750-2000	-	40-60	-					
4.	Doubtful	2000-3000	18-26	60-80	1.25-2.5					
5.	Unsuitable	> 3000	> 26	> 80	> 2.5					

Note: * Source:- Wilcox, 1955; # Source:- USDA, 1954.

and hydraulic conductivities (*http://publications.iwmi*. *org*). It reduces the permeability of soil by forming massive clods of soil after ploughing. It also affects calcium availability increases toxicity effects leading to defoliation of plant leaves. Magnesium Hazard (MH) or Magnesium ratio (MR) is defined as (Szabolcs and Darab, 1964):

$$MH = \frac{Mg^{2+}}{(Ca^{2+} + Mg^{2+})} x100 \qquad \dots (3)$$

Concentrations are expressed in meq/L.:

MH is classified into two groups: MH > 50% (Unsuitable for Irrigation) and MH < 50% (Suitable for Irrigation).

The PI and MH were calculated for each of the 14 blocks during pre-monsoon and post-monsoon seasons.

RESULTS AND DISCUSSION

The results obtained from the present investigation as well as relevant discussion have been summarized under following heads :

Results of groundwater chemistry based on statistical analysis:

The results of descriptive statistics obtained from the statistical analysis of the concentration of salient groundwater-quality parameters are presented in Table 1 and 2. The main point of focus in Table 1 is the coefficient of variation (CV) of Cl⁻ which is maximum in all the blocks except Manapparai. However, the same value of CV is found for TH, F⁻, NO₃⁻, Ca²⁺ and K⁺ in some blocks. In contrast, the scenario changes a bit in the post-monsoon season (Table 2). The CV value of Cl⁻ is maximum in five of the blocks. The results in 2 blocks (Lalgudi and Pullambadi) during pre-monsoon and 4 blocks (Anthanallur, Lalgudi, Pullambadi and Tiruverumbur) during post-monsoon season could not be presented due to lack of data.

The correlation matrices for 11 groundwater-quality parameters (TDS, Cl⁻, pH, EC, TH, F⁻, NO³⁻, Na⁺, Mg²⁺, Ca²⁺ and K⁺) were prepared for both pre- and postmonsoon seasons (Tables 3 and 4). The results indicate significant positive correlation (r \geq 0.5) for the following pair of parameters: EC, TH, Na⁺ and Ca²⁺ with TDS; TH, Mg²⁺ and Ca²⁺ with EC; Mg²⁺ with TH and Ca²⁺ with Na⁺ in both the seasons. In contrast, in the postmonsoon season significant positive correlation ($r \ge 0.5$) is also seen between 14 other pairs of groundwaterquality parameters as compared to that in the premonsoon season and they are: Cl⁻ and Na⁺ with TDS; EC, TH, NO₃⁻, Mg²⁺ and Ca²⁺ with Cl⁻; F⁻ and NO₃⁻ with EC; F⁻ and Ca²⁺ with TH; NO₃⁻ and Mg²⁺ with F⁻ and K⁺ and NO₃⁻. However, negative correlations between parameters are also found between some pairs in both the seasons.

Spatio-temporal variability of groundwater-quality parameters:

The long-term temporal variation in the concentration of groundwater-quality parameters are shown in Table 5 and 6. The concentration of pH in Marungapuri block is showing statistically significant temporal variation at 1 per cent significance level whereas in Tattayengarpettai, Uppliyapuram and Vaiyampatti blocks at 5 per cent significance level in the pre-monsoon season. Also, the temporal variation of F-in Manikandam and Marungapuri, Mg²⁺ in Tattayengarpettai and Tiruverumbur and K⁺ in Uppliyapuram blocks are statistically significant at 1 per cent significance level. However, the temporal variation of F⁻ concentration in Uppliyapuram block is found to be statistically significant at 5 per cent significance level. Unlike the pre-monsoon season, the temporal variation of pH in Vaiyampatti, F in Thuraiyur, Ca²⁺ in Uppliyapuram and K⁺ in Manapparai are statistically significant at 1 per cent significance level and that of pH in Manikandam block at 5 per cent significance level are found in the post-monsoon season. Agriculture being the dominant land use in the study area, the use of lime and chemical fertilizers adds to the Mg^{2+} , Ca²⁺ and K⁺ content, respectively. Percolation of toxic substances released from industries increases the pH of groundwater. However, increasing mining activities and effluents of phosphate fertilizer are the major anthropogenic causes of significant rise in F⁻ content of groundwater. The variability in concentration of the groundwater-quality parameters for Lalgudi and Pullambadi blocks in pre-monsoon season and Anthanallur, Lalgudi, Pullambadi and Tiruverumbur blocks in the post-monsoon season could not be presented due to lack of data.

Like temporal variation, the spatial variation in the concentration of groundwater-quality parameters is presented in Table 7. The spatial variation of Cl⁻, TDS,

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Table 1 : Descriptive	statistics of	concentra	tion of sali	ient gro	oundwater-	quality par	ameters in	pre-monso	on season			
Blocks	Statistics	TDS (mg/L)	Cl ⁻ (mg/L)	pН	EC (µS/cm)	TH (mg/L)	F (mg/L)	NO ₃ ⁻ (mg/L)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	K ⁺ (mg/L)
Anthanallur	Mean	682.7	218.3	8.2	1201.0	325.2	0.6	17.6	118.7	43.8	53.3	12.2
	SD	284.3	105.3	0.1	420.8	144.5	0.1	8.4	17.9	8.1	13.6	4.6
	CV	0.4	0.5	0.0	0.4	0.4	0.2	0.5	0.2	0.2	0.3	0.4
	Min	459.5	126.0	8.1	840.0	205.0	0.4	3.0	91.5	33.0	29.8	4.5
	Max	1238.5	419.0	8.3	2130.0	606.0	0.6	49.0	188.5	76.0	105.7	30.0
Manachchanallur	Mean	893.7	264.6	8.2	1588.6	373.3	0.7	21.7	147.7	50.1	71.1	33.2
	SD	112.6	87.5	0.1	214.4	81.7	0.1	3.0	12.7	2.0	5.6	6.9
	CV	0.1	0.3	0.0	0.1	0.2	0.1	0.1	0.1	0.0	0.1	0.2
	Min	696.8	141.8	7.9	1264.0	211.0	0.5	8.3	115.0	44.7	55.3	22.8
	Max	1094.6	462.9	8.3	1988.0	486.0	0.9	38.4	188.7	56.7	85.2	60.4
Manapparai	Mean	1533.8	584.8	8.3	2705.6	527.7	0.9	12.0	302.8	58.7	94.7	12.7
	SD	91.5	46.8	0.1	160.1	129.4	0.1	1.6	7.2	10.6	13.2	2.0
	CV	0.1	0.1	0.0	0.1	0.2	0.1	0.1	0.0	0.2	0.1	0.2
	Min	1457.8	532.0	8.2	2554.0	371.7	0.7	5.8	282.7	38.5	64.7	7.5
	Max	1697.0	658.4	8.4	2956.0	765.0	1.1	20.5	323.4	95.5	139.3	17.8
Manikandam	Mean	829.6	293.5	8.1	1441.9	354.4	0.6	5.3	180.1	52.8	54.0	9.4
	SD	262.7	154.7	0.2	457.7	105.7	0.2	0.9	17.8	5.9	5.5	1.7
	CV	0.3	0.5	0.0	0.3	0.3	0.3	0.2	0.1	0.1	0.1	0.2
	Min	304.5	35.5	7.8	535.0	150.0	0.3	0.5	35.5	16.0	16.0	3.0
	Max	1196.5	578.0	8.6	2045.0	517.5	1.0	14.0	280.5	89.0	83.0	21.0
Marungapuri	Mean	1077.8	400.6	8.1	1947.3	633.5	0.8	13.7	166.1	76.0	107.6	9.3
	SD	412.6	184.4	0.4	744.9	287.9	0.3	2.5	17.9	13.5	13.6	3.2
	CV	0.4	0.5	0.0	0.4	0.5	0.4	0.2	0.1	0.2	0.1	0.3
	Min	324.5	85.0	7.2	620.0	215.0	0.4	3.0	40.0	19.0	25.5	1.5
	Max	1713.5	753.5	8.6	3185.0	1195.0	1.5	34.5	253.0	169.0	198.5	46.5
Musiri	Mean	1223.1	374.4	8.1	2094.3	508.1	0.8	25.5	188.1	66.0	84.0	77.1
	SD	437.3	196.8	0.2	672.3	221.5	0.3	6.0	24.7	8.9	11.9	20.7
	CV	0.4	0.5	0.0	0.3	0.4	0.4	0.2	0.1	0.1	0.1	0.3
	Min	509.5	142.0	7.9	1020.0	220.0	0.5	2.0	58.5	27.0	36.5	3.5
	Max	1855.5	815.5	8.8	3235.0	935.0	1.5	91.0	297.0	132.0	166.5	259.5
Tattayengarpettai	Mean	711.8	196.6	8.2	1256.5	331.7	0.6	16.8	134.3	37.6	56.8	25.3
	SD	224.0	86.6	0.3	385.8	112.1	0.2	2.7	16.8	4.7	8.6	5.8
	CV	0.3	0.4	0.0	0.3	0.3	0.3	0.2	0.1	0.1	0.2	0.2
	Min	208.0	33.5	7.7	390.0	160.0	0.3	1.5	4.5	18.0	21.0	4.0
	Max	1087 5	374.0	89	1870.0	590.0	0.8	33.5	277.0	70.0	119.0	57.5
Thottivam	Mean	755 /	23/ 1	82	1338.8	311.7	0.8	91	168 1	44 9	48 5	10.8
Inotayum	SD	150.7	78.2	0.2	258 0	872	0.0). 1 1	15.0	37	63	10.0
	CV	0.2	0.2	0.2	230.0	02.3	0.2	0.1	0.1	0.1	0.5	0.1
		0.2	0.5	0.0	0.2	0.5	0.3	0.1	0.1	0.1	0.1	0.1
	M1n	527.5	124.0	1.1	955.0	225.0	0.5	2.0	64.0	25.0	21.5	5.0
	Max	1148.5	434.5	8.5	2080.0	555.0	1.1	16.5	245.5	76.0	113.0	17.5

Long-term geochemical assessment of groundwater in a hard-rock aquifer system

.5 76.0 113.0 17.5 Table 2: Contd.....

Table 1: Contd												
Thuraiyur	Mean	1185.4	432.2	8.2	1951.7	510.3	0.6	14.1	209.8	70.4	95.2	11.7
	SD	494.5	290.4	0.2	628.7	215.3	0.2	2.0	47.5	13.9	19.5	1.2
	CV	0.4	0.7	0.0	0.3	0.4	0.3	0.1	0.2	0.2	0.2	0.1
	Min	572.0	153.3	7.9	1040.0	350.0	0.2	3.5	73.0	27.3	40.3	7.7
	Max	2487.3	1243.5	8.5	3320.0	978.3	0.9	28.3	706.3	128.0	182.7	13.7
Tiruverumbur	Mean	585.9	125.7	8.2	1021.0	214.5	0.5	9.6	135.6	29.8	34.1	4.7
	SD	111.7	62.2	0.1	194.0	56.6	0.1	2.0	13.4	2.5	5.7	0.9
	CV	0.2	0.5	0.0	0.2	0.3	0.2	0.2	0.1	0.1	0.2	0.2
	Min	429.0	11.0	8.1	785.0	130.0	0.4	2.0	90.5	24.0	17.0	2.6
	Max	719.5	174.0	8.5	1280.0	280.0	0.6	13.0	164.0	36.0	46.8	7.5
Uppliyapuram	Mean	967.1	248.9	8.1	1679.2	543.6	0.7	21.5	168.3	60.5	95.1	7.8
	SD	335.3	99.5	0.2	509.4	213.7	0.3	3.6	19.6	8.4	11.6	1.4
	CV	0.3	0.4	0.0	0.3	0.4	0.4	0.2	0.1	0.1	0.1	0.2
	Min	459.3	104.0	7.8	850.0	185.0	0.4	3.3	69.0	11.0	19.0	1.5
	Max	1497.0	407.7	8.4	2276.7	780.0	1.2	43.3	309.0	110.0	163.5	16.0
Vaiyampatti	Mean	678.7	214.7	8.2	1213.1	364.8	1.2	9.9	116.1	45.9	60.7	8.5
	SD	266.0	122.1	0.2	457.8	103.3	0.3	1.3	20.7	4.9	5.1	2.0
	CV	0.4	0.6	0.0	0.4	0.3	0.3	0.1	0.2	0.1	0.1	0.2
	Min	333.7	62.7	7.8	546.7	181.0	0.6	1.3	36.3	19.3	32.3	1.3
	Max	1160.0	502.0	8.6	2093.3	538.3	1.9	17.3	272.7	90.0	90.7	27.3

Note: SD = Standard deviation; CV = Co-efficient of variation

EC and Na⁺ concentration are statistically significant at 1 per cent significance level in both the seasons. In addition, the concentration of TH, NO_3^- , Mg^{2+} and K⁺ are showing statistically significant spatial variation at 1 per cent significance level only during the pre-monsoon season.

Graphical representation of hydrochemical data:

The concentrations of groundwater-quality parameters were plotted in Piper's Trilinear diagram to classify groundwater based on the basic geochemical characters of constituent ionic concentrations with the help of Aqua Chem 2014.2 software and are shown in Fig. B (a-b). Piper's diagram revealed that Na⁺ is the major cation whereas Cl⁻ and HCO₂⁻ are the major anions constituting the groundwater of the study area. The dissolution of minerals rich in sodium in the aquifer materials can be the source of Na⁺. Furthermore, the dominant hydrochemical facies identified is of Na-Cland Ca-Mg-SO $_{_{\!\!\!\!\!\!\!\!\!\!\!\!\!\!}}$ type. Weathering of limestone and sandstone rocks give Ca²⁺ and Mg²⁺. This could be the possible reasons of the type of groundwater existing in the study area. However, it is also revealed that no clear changes are occurring in the hydrochemical facies of groundwater during pre- and post-monsoon seasons. The Schoeller diagrams Fig. 1 (a-b) revealed that TDS and F⁻ are having the highest and least concentration, respectively, in the entire study area following this order of concentrations: TDS>Cl⁻>HCO₃⁻>Na⁺>SO₄⁻>Mg²⁺>Ca²⁺>CO₃⁻>NO₃⁻>K⁺>F⁻.

Suitability of groundwater for drinking:

The spatial variation in the average seasonal concentration (pre-monsoon and post-monsoon) of 11 groundwater-quality parameters (Cl⁻, pH, TDS, TH, F⁻, $NO_{2^{-}}$, Na^{+} , Mg^{2+} , Ca^{2+} , K^{+} and $SO_{4^{-2}}$) in the study area along with the recommended level and maximum permissible level (wherever applicable) of WHO standards for drinking water is shown with the help of scatter plots Fig. 2 (a-k). It is found that the seasonal concentration of TDS and TH are exceeding the maximum permissible limits (1500 mg/L and 500 mg/L of CaCO₂) in Pullambadi and Musiri, Thuraiyur and Uppliyapuram blocks, respectively Fig. 2 (c-d). Also, the concentration of Cl⁻, NO₂⁻, Na⁺ and K⁺ are found to be exceeding their recommended limits (200,10, 200,10 mg/ L, respectively), posing some risk in the potability of groundwater. However, the rest of the parameters (pH, F⁻, Mg²⁺, Ca²⁺ and SO₄²⁻) are found to be well within the limits.

Long-term geochemical assessment of groundwater in a hard-rock aquifer system	
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Table 2 : Descriptive	e statistics of	concentra	tion of sali	ent gro	oundwater-	quality par	ameters in	post-mons	oon season			
Blocks	Statistics	TDS (mg/L)	Cl ⁻ (mg/L)	pН	EC (µS/cm)	TH (mg/L)	F (mg/L)	NO ₃ ⁻ (mg/L)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	K ⁺ (mg/L)
Manachchanallur	Mean	787.9	221.8	8.2	1448.5	377.8	0.8	27.4	149.8	46.4	62.3	38.3
	SD	88.3	40.9	0.1	165.7	46.7	0.1	6.5	16.9	4.0	2.1	5.2
	CV	0.1	0.2	0.0	0.1	0.1	0.1	0.2	0.1	0.1	0.0	0.1
	Min	649.4	177.6	8.0	1188.0	317.0	0.6	13.8	101.4	32.4	56.1	25.0
	Max	944.4	307.2	8.3	1678.0	448.0	0.9	43.0	201.6	62.4	71.0	54.8
Manapparai	Mean	1198.3	383.5	8.1	2074.0	323.7	0.9	13.1	332.5	55.6	48.8	12.0
	SD	65.1	80.5	0.4	110.2	25.3	0.2	1.9	7.0	11.5	6.9	6.0
	CV	0.1	0.2	0.0	0.1	0.1	0.2	0.1	0.0	0.2	0.1	0.5
	Min	1092.0	289.0	7.4	1970.0	288.3	0.6	5.7	308.0	32.0	23.0	2.0
	Max	1282.0	521.0	8.5	2210.0	351.7	1.1	16.0	346.5	95.0	63.5	35.5
Manikandam	Mean	940.7	341.2	8.1	1665.0	450.5	0.5	8.6	188.9	54.4	76.4	16.2
	SD	134.1	79.1	0.3	222.4	63.6	0.3	1.3	22.4	5.6	10.3	4.6
	CV	0.1	0.2	0.0	0.1	0.1	0.6	0.2	0.1	0.1	0.1	0.3
	Min	727.0	202.0	7.6	1285.0	355.0	0.2	5.0	138.0	39.0	41.5	6.0
	Max	1102.5	434.5	8.5	1955.0	545.0	1.0	12.5	246.0	74.0	100.2	31.5
Marungapuri	Mean	878.1	279.1	8.1	1564.5	399.7	0.8	15.5	174.3	42.1	71.5	15.6
	SD	61.6	32.4	0.3	124.0	111.7	0.4	2.9	12.5	3.3	13.1	2.7
	CV	0.1	0.1	0.0	0.1	0.3	0.5	0.2	0.1	0.1	0.2	0.2
	Min	773.5	216.5	7.9	1377.5	256.3	0.5	11.0	151.3	35.0	40.8	8.0
	Max	941.5	306.8	8.3	1760.0	575.0	1.4	27.0	222.5	52.5	112.0	24.3
Musiri	Mean	1009.7	246.1	8.1	1846.7	411.7	0.7	18.3	224.9	59.7	63.8	42.2
	SD	185.4	114.2	0.2	396.2	190.2	0.1	2.2	19.8	12.2	14.2	15.4
	CV	0.2	0.5	0.0	0.2	0.5	0.1	0.1	0.1	0.2	0.2	0.4
	Min	813.5	88.5	7.7	1385.0	215.0	0.6	10.3	148.5	32.0	33.0	1.5
	Max	1245.0	429.0	8.3	2335.0	670.0	0.8	26.0	270.0	108.0	115.5	88.5
Tattayengarpettai	Mean	612.0	171.7	8.0	1100.0	284.2	0.7	21.5	123.6	40.8	44.2	11.6
	SD	76.3	44.1	0.1	129.1	27.0	0.2	4.3	13.8	4.4	3.6	2.7
	CV	0.1	0.3	0.0	0.1	0.1	0.3	0.2	0.1	0.1	0.1	0.2
	Min	466.5	94.0	7.7	865.0	232.5	0.2	7.3	69.0	29.5	36.5	1.0
	Max	678.0	218.0	8.2	1255.0	317.5	0.8	36.5	164.0	53.0	59.0	21.5
Thottiyam	Mean	758.7	254.2	8.1	1369.2	336.7	0.8	9.9	160.4	57.3	47.0	9.2
	SD	232.2	108.6	0.2	430.3	80.8	0.2	2.3	28.7	9.6	4.8	1.9
	CV	0.3	0.4	0.0	0.3	0.2	0.3	0.2	0.2	0.2	0.1	0.2
	Min	392.5	56.5	7.7	675.0	227.5	0.5	3.0	52.0	30.0	33.0	2.5
	Max	1028.5	365.0	8.4	1860.0	447.5	1.1	20.0	219.5	83.0	62.0	13.5
Thuraiyur	Mean	810.1	251.1	8.1	1507.5	454.7	0.7	23.1	155.3	45.6	66.8	6.0
	SD	105.1	65.6	0.2	253.6	97.0	0.1	2.6	16.3	2.8	5.2	1.9
	CV	0.1	0.3	0.0	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.3
	Min	695.8	178.0	7.8	1317.5	371.7	0.5	12.1	104.5	40.5	53.8	2.5
	Max	1007.0	379.3	8.3	2030.0	658.3	0.9	30.0	193.5	56.0	79.3	12.3

Table 2: Contd.....

Table 2: Contd												
Uppliyapuram	Mean	1010.5	330.9	8.0	1883.3	632.5	0.7	10.4	179.2	49.9	104.7	6.7
	SD	303.5	105.6	0.2	555.8	151.7	0.2	4.0	27.2	7.8	19.8	2.9
	CV	0.3	0.3	0.0	0.3	0.2	0.3	0.4	0.2	0.2	0.2	0.4
	Min	593.0	191.3	7.6	1130.0	392.5	0.5	4.7	107.3	31.0	53.0	0.3
	Max	1486.3	492.8	8.1	2772.5	805.0	1.0	30.0	292.3	71.0	152.3	17.3
Vaiyampatti	Mean	496.3	109.8	7.9	898.9	314.7	1.1	10.1	74.0	51.3	45.4	6.1
	SD	150.8	59.9	0.3	243.1	64.3	0.2	1.9	18.9	8.7	7.0	0.8
	CV	0.3	0.5	0.0	0.3	0.2	0.2	0.2	0.3	0.2	0.2	0.1
	Min	357.3	64.7	7.4	710.0	230.0	0.8	3.0	36.0	30.0	35.0	3.7
	Max	809.3	236.3	8.2	1423.3	416.7	1.3	14.7	135.7	82.0	72.3	8.3

Note: SD = Standard deviation; CV = Co-efficient of variation

Table 3 : C	Table 3 : Correlation matrix of groundwater-quality parameters during pre-monsoon season											
	TDS	Cl	pН	EC	TH	F	NO ₃ ⁻	Na^+	Mg^{2+}	Ca ²⁺	K ⁺	
TDS	1											
Cl	0.394	1										
pН	-0.226	-0.226	1									
EC	0.848	0.438	-0.595	1								
TH	0.681	0.424	-0.818	0.849	1							
F	0.431	-0.035	0.238	0.280	0.056	1						
NO ₃ ⁻	0.377	-0.524	-0.079	0.295	0.090	0.339	1					
Na^+	0.668	0.429	0.026	0.363	0.058	0.505	0.066	1				
Mg^{2+}	0.284	0.330	-0.708	0.553	0.828	-0.178	-0.050	-0.347	1			
Ca^{2+}	0.767	0.249	-0.357	0.649	0.489	0.363	0.231	0.643	-0.084	1		
K ⁺	0.467	0.152	-0.453	0.355	0.381	0.200	0.360	0.338	0.279	0.235	1	

Note: Bold values represent significant correlation

Table 4:	Table 4: Correlation matrix of groundwater-quality parameters during post-monsoon season											
	TDS	Cl	pН	EC	TH	F	NO ₃ ⁻	Na ⁺	Mg^{2+}	Ca ²⁺	\mathbf{K}^+	
TDS	1											
Cl	0.527	1										
pН	0.176	-0.014	1									
EC	0.632	0.956	-0.121	1								
TH	0.788	0.815	-0.266	0.913	1							
F	0.477	0.250	-0.112	0.508	0.585	1						
NO ₃ ⁻	0.485	0.753	0.323	0.771	0.492	0.519	1					
Na^+	0.902	0.136	0.347	0.276	0.472	0.371	0.386	1				
Mg^{2+}	0.589	0.770	-0.055	0.853	0.865	0.752	0.388	0.257	1			
Ca ²⁺	0.750	0.630	-0.429	0.714	0.848	0.054	0.456	0.537	0.468	1		
\mathbf{K}^+	0.101	-0.002	-0.513	0.059	0.092	0.228	0.548	-0.074	-0.047	0.225	1	

Note: Bold values represent significant correlation

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Table 5 : Temporal vari	Table 5 : Temporal variation of groundwater-quality parameters in pre-monsoon season using ANOVA										
				p-valu	ie						
Blocks	Cl ⁻	TDS	pН	EC	TH	F	NO ₃ ⁻	Na ⁺	Mg^{2+}	Ca ²⁺	K ⁺
Anthanallur	0.43	0.45	0.89	0.42	0.58	0.92	0.32	0.43	0.47	0.56	0.62
Manachchanallur	0.67	0.96	0.12	0.93	0.67	0.86	0.22	0.73	0.70	0.94	0.33
Manapparai	1.00	1.00	0.82	1.00	0.73	0.61	0.46	1.00	0.71	0.26	0.72
Manikandam	0.91	0.95	0.25	0.94	0.91	0.007*	0.12	0.95	0.77	0.84	0.85
Marungapuri	0.81	0.52	0.0006*	0.49	0.59	0.02*	0.49	0.57	0.72	0.38	0.68
Musiri	0.11	0.16	0.25	0.24	0.05	0.95	0.57	0.58	0.07	0.02	0.85
Tattayengarpettai	0.40	0.40	0.02**	0.39	0.05	0.61	0.92	0.57	0.03*	0.28	0.75
Thottiyam	0.80	0.39	0.08	0.73	0.62	0.98	0.95	0.03	0.43	0.68	0.73
Thuraiyur	0.75	0.81	0.15	0.83	0.55	0.28	0.41	0.58	0.70	0.20	0.88
Tiruverumbur	0.37	0.93	0.32	0.90	0.07	0.92	0.91	0.98	0.02*	0.68	0.90
Uppliyapuram	0.11	0.07	0.01**	0.08	0.28	0.04**	0.70	0.16	0.33	0.62	0.006*
Vaiyampatti	0.77	0.74	0.02**	0.75	0.75	0.28	0.26	0.69	0.82	0.41	0.15

Note: * and ** indicate significance of values at P=0.01 and 0.05, respectively

Table 6 : Temporal variation of groundwater-quality parameters in the post-monsoon season using ANOVA p-value Ca²⁺ TDS F Mg²⁺ Blocks Cl. EC TH NO₃⁻ \mathbf{K}^+ pН Na^+ Manachchanallur 0.95 0.96 0.49 0.95 0.61 0.74 0.25 0.64 0.98 0.56 0.17 Manapparai 0.94 1.00 0.24 1.000.98 0.50 0.61 1.00 0.76 0.59 0.001* Manikandam 0.97 0.98 0.04** 0.98 0.95 0.11 0.26 0.86 0.65 0.90 0.80 0.96 0.99 0.10 0.98 0.29 0.11 0.93 0.76 0.73 Marungapuri 0.69 0.24 Musiri 0.16 0.43 0.88 0.97 0.53 0.38 0.67 0.61 0.68 0.61 0.70 Tattayengarpettai 0.87 0.96 0.26 0.96 0.27 0.06 0.48 0.94 0.07 0.21 0.71 0.22 0.16 0.12 0.29 0.07 Thottiyam 0.34 0.16 0.19 0.80 0.56 0.88 Thuraiyur 0.87 0.93 0.34 0.83 0.61 0.002* 0.27 0.81 0.42 0.90 0.30 Uppliyapuram 0.55 0.14 0.04 0.12 0.32 0.08 0.06 0.25 0.07 0.03* 0.49 0.0002* 0.07 Vaiyampatti 0.39 0.57 0.28 0.68 0.28 0.15 0.43 0.54 0.74

Note: * and ** indicate significance of values at P=0.01 and 0.05, respectively

Table 7 : Spatial variation of groundwater-quality parameters using ANOVA									
Sr. No	Groundwater-quality parameters	Pre-monsoon	Post-monsoon						
51. 140.	Groundwater quanty parameters	p-value							
1.	Cl	0.00372*	0.00276*						
2.	TDS	0.00011*	0.00178*						
3.	pH	0.90719	0.52144						
4.	EC	0.00003*	0.00470*						
5.	TH	0.00028*	0.03392						
6.	F	0.18305	0.06834						
7.	NO ₃ ⁻	3.89×10 ⁻⁸ *	0.11694						
8.	\mathbf{Na}^+	1.53×10 ⁻⁵ *	$1.67 \times 10^{-5}*$						
9.	Mg^{2+}	0.0001*	0.00414						
10.	Ca^{2+}	0.0971	0.94105						
11.	\mathbf{K}^+	7.75×10 ⁻⁹ *	0.00297						

Note: * and ** indicate significance of values at P=0.01 and 0.05, respectively

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Table 8 : Block-wise variation of Permeability index and Magnesium hazard during pre- and post-monsoon seasons									
Blocks	Permeabilit	ty index (PI)	Magnesium	hazard (MH)					
Diocks	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon					
Anthanallur	57.77	67.93	73.68	60.35					
Lalgudi	66.41	58.34	65.33	65.92					
Manapparai	60.43	59.70	68.33	67.65					
Manikandam	65.87	68.29	70.74	67.70					
Manachchanallur	65.00	59.31	63.40	69.31					
Marungapuri	53.83	62.77	69.73	73.55					
Musiri	49.92	61.40	69.44	65.88					
Pullambadi	78.78	67.53	75.15	81.53					
Tattayengarpettai	58.07	65.01	66.18	67.79					
Thottiyam	64.48	65.44	66.92	60.62					
Thuraiyur	57.53	59.65	71.51	70.47					
Tiruverumbur	74.55	83.91	66.71	66.10					
Uppliyapuram	55.20	61.94	71.87	74.14					
Vaiyampatti	57.12	54.76	68.80	62.18					



Box and Whisker plots were prepared for all the parameters (TDS, TH, Cl⁻, NO₃⁻, Na⁺ and K⁺) for which the average concentration is exceeding the respective recommended limits but only that of TDS and TH are shown here Fig. 3(a-d). The length of box and length of whiskers decreases in the post-monsoon season as compared to that in the pre-monsoon season due to dilution effect. The median value exceeds the maximum permissible limit (1500 mg/L) in Pullambadi block and it

remains almost same in both the seasons. However, outliers are found in 5 blocks (Marungapuri, Pullambadi, Tattayengarpettai, Thottiyam and Tiruverumbur) during pre-monsoon, which increased to 6 blocks (Anthanallur, Manapparai, Marungapuri, Musiri, Uppliyapuram and Vaiyampatti) during post-monsoon season indicating extremes Fig. 3 (a-b). Like TDS, the concentration of TH also faced dilution effect in the post-monsoon season. The median value is exceeding the maximum permissible limit (500 mg/L) in Musiri block during premonsoon and in Pullambadi block during the postmonsoon season. However, the number of blocks having outliers reduces from 3 to nil Fig. 3(c-d).

Suitability of groundwater for irrigation:

Spatial variability of EC, SAR, %Na and RSC:

The spatial concentration maps of EC, SAR, % Na and RSC in the study area for pre-monsoon and postmonsoon seasons are shown in Fig. 4 to 7. The EC concentration in the study area varies from 42.02 to 4795.29 μ S/cm in the pre-monsoon season and 4.49 to 3144.17 μ S/cm in the post-monsoon season. From the (Fig. 4) it can be seen that the EC concentration of most of the study area fall in the "Permissible" class and thus, it is suitable for irrigation. The SAR values vary from 0.11 to 10.94 mg/L (pre-monsoon) and 0.01 to 14.67 mg/L (post-monsoon). From the (Fig. 5), it can be seen that the SAR concentration in major portion of the study area

Confined Aquife • Pre-monsoon Post-mon ioon (a) Chloride 604 /gm 500 400 . . . Cone 300 Chloride 204 ded Limit • . Block **Confined** Aquifer + Pr = P (b) pH pH Concentratio . . 1 . 4 . . Fig. 2(a-b): Spatial variation of mean Cl⁻ concentration and pH during 1981-2014 period

is less than 10 and hence, fall in the "Excellent" class. Very small areas are found to be in the "Good" class with values lying in the range of 10-18 mg/L. The value of per cent Na ranges from 1.37 to72.02 mg/L (premonsoon) and 0.15 to 79.99 mg/L (post-monsoon) (Fig. 6). It mainly falls under the "Good" and "Permissible" classes for use in irrigation. In case of RSC, the concentration values ranges from 0.00003 to 3.76 mg/L (pre-monsoon) and 0.0001 to 8.10 mg/L (post-monsoon). Most part of the study area falls in the "Good" class (Fig. 7). However, the concentration of RSC in the eastern, central and southern parts of the study area is critical for use in agricultural fields as they fall in the "Doubtful" to "Unsuitable" classes.

Groundwater salinity and sodicity:

In order to analyze the suitability of groundwater for irrigation USSL diagrams were plotted for pre- and post-monsoon seasons and are shown in Fig. 8 (a-b).







The diagram reveals that groundwater of all the blocks falls in the C3-S1 class in the pre-monsoon season indicating high salinity and low sodium hazard in these blocks except Manapparai and Pullambadi. Manapparai block is having groundwater with high salinity and









Fig. 7(a-b): Spatial variation of RSC in groundwater in pre- monsoon and post-monsoon seasons



medium sodium content (C3-S2 class). Groundwater in the Pullambadi block is of greater cause of concern as it falls in the C4-S3 class indicating very highly saline and highly sodic conditions. In contrast, the groundwater in the Uppliyapuram block in the post-monsoon season is also found to fall in the C3-S2 class along with Manapparai block with high salinity and medium sodium content. The groundwater condition in the Pullambadi block still falls in the C4-S3 class. High dissolution of sodium-rich minerals like sandstone enhances the sodium content in the groundwater of these blocks. The scenario of the rest of the blocks remains almost same as compared to the pre-monsoon season.

Due to prolonged use of groundwater in the study area for irrigation purposes, its suitability was also checked in terms of permeability index (PI) and magnesium hazard (MH) and the results for the two seasons are presented in Table 8. It can be seen from the table that the PI values in all the blocks lie in Class II (25-75%) during pre- and post-monsoon seasons, which indicates safe groundwater quality. In contrast, the MH values higher than the threshold limit (<50% for irrigation suitability) in all the blocks during both the seasons. Prominent use of lime in the agricultural lands adds up to the magnesium content of groundwater. Thus, it can be inferred from the results obtained that the groundwater quality of the study area is good and safe for irrigation in terms of permeability index. However, the excessive magnesium in the groundwater makes it a cause of concern for irrigation posing problems of clod formation and soil impermeability.

Conclusion and Recommendations:

In this paper an easy and viable methodology is presented in order to analyze the quality of groundwater for its potability and use in agricultural purposes. The adopted methodology is described with the help of a case study in Tiruchirapalli District, Tamil Nadu, India. The long-term temporal and spatial variation of salient groundwater-quality parameters were explored using a statistical technique. Clustering of groundwater samples using two different types of graphical plots was done in order to classify the groundwater geochemically and compared to that of the WHO guidelines for drinking water. In addition, agriculture being the prime user of groundwater in the study area, the fitness of groundwater for use in irrigation was also evaluated. This was achieved by preparing seasonal spatial distribution maps of EC, SAR, per cent Na and RSC and also plotting EC and SAR in the well-known US Salinity Laboratory diagram. Moreover, potential hazard of reduction in soil permeability was investigated by computing the Permeability Index and Magnesium Hazard of groundwater.

Based on the analyses of the results of this study, the following conclusions could be drawn:

The temporal variations in the concentrations of pH, F^{-} , Mg^{2+} and K^{+} during the pre-monsoon season and that of pH, F^{-} , Ca^{2+} and K^{+} during the post-monsoon season are found to be statistically significant. In contrast, the spatial variation of the concentrations of pH, F^{-} and Ca^{2+} in pre-monsoon and that of pH, F^{-} , NO_{3}^{-} , TH, Mg^{2+} , Ca^{2+} and K^{+} in the post-monsoon season are not significant.

Groundwater in the study area is highly saline with hydrochemical facies of Na-Cl⁻ and Ca-Mg-SO₄²⁻ types. Na⁺ is the dominant cation, while Cl⁻ and HCO₃⁻ are the dominant anions in the groundwater.

The seasonal concentrations of Cl^- , TDS, NO_3^- , Na^+ , and K^+ exceed their recommended limits for drinking and that of TDS and TH exceed their respective maximum permissible limits.

The spatial variation of EC, SAR and %Na falls in the "Excellent" to "Permissible" classes for use in irrigation. However, the RSC concentration falls in the "Doubtful" to "Unsuitable" classes in some region.

In order to protect groundwater from contamination, treatment of industrial effluents must be carried out prior to releasing them. The reverse osmosis process is recommended in order to reduce the TDS concentration and TH in groundwater. The use of natural manures is preferred instead of using fertilizers and pesticides to limit the contribution of harmful substances to groundwater. The use of long-term groundwater-quality data employed in this study for groundwater-quality mapping is a robust and technically sound methodology to provide a scientific basis for the planners and managers of groundwater in order to achieve efficient planning and management. This is expected to improve the condition of groundwater through field investigation and analytical tools/techniques with a view to fight against the growing concern of groundwater quality deterioration. Thus, this approach is unique and can be easily employed in any study area world-wide.

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