Evaluation of long-term nitrate and electrical conductivity in groundwater system of Peninsula, India

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Abstract
We have investigated the impact of rainfall and temperature on nitrate and electrical conductivity (EC) in groundwater of the seven taluks of Kancheepuram district of Tamil Nadu, India using statistical framework. Total 34 years long-term data of period 1985–2018 of nitrate and EC was used for the analysis in order to identify impact of climate parameters over agrichemicals loading in groundwater. It was found that pattern of climatic parameters are also act as co-factors for loading of agrichemicals concentration in groundwater. Result show an increase of average temperature and rainfall and it does not show a direct effect on nitrate contamination in groundwater. Further, two taluk, namely Chengalpattu and Tirukalukundram have an increasing trend of nitrate loading in groundwater during non-monsoon and monsoon season due to change in land use and anthropogenic acts. The EC show rising trend for Maduranthakam and Sriperumbudur during non-monsoon season and Chengalpattu, Maduranthakam, Sriperumbudur and Tirukalukundram during monsoon season.

Keywords Nitrate load · Agrichemicals · Land use · Electrical conductivity · Groundwater

Introduction
Nitrogen is a vital nutrient for aquatic organisms; however, it is a pollutant if present beyond permissible limit in water systems. Its concentration and form in the groundwater environment generally reflect the integration of different sources from soil to aquifer factors including anthropogenic contributions (Wade et al. 2001). Nitrogen contamination is already raised as a global environmental issue (Steffen et al. 2015; Gautam et al. 2021). It is accepted that the nitrogen losses will be more from agricultural areas because of climate change (Bindi and Olesen 2011; Zessner et al., 2017; Nemčík-Jureč et al. 2019; Rawat et al. 2018). Understanding the impact of climate change on water quality is crucial to ensure the sustainability of future water resources. Whitehead et al. (2009) reviewed potential impacts of climate change on UK surface water quality. Bloomfield et al. (2006) reviewed the fate and transport of pesticides in ground and surface water. In UK, nitrate is present in elevated concentration and few locations show a higher value compared to WHO drinking water limits (Rivett et al., 2007). Many studies show a statistical correlation between increasing mode of nitrate contamination in groundwater and applied fertilizers in crops (Spalding and Exner, 1993; Almasri and Kaluarachchi, 2007; Rawat et al. 2018; Karmakar et al. 2021; Gautam et al. 2021).
Non-point sources are major contributor of nitrate in groundwater of rural areas because agriculture activity is main in rural areas. The agriculture activities include fertilizers, manure, leguminous crops and irrigation return-flows (Psaroulou and Karatzas 2014; Serio et al. 2018; Gemitz et al., 2009; Lockhart et al., 2013; Camargo et al., 2005; Dupas et al., 2016) are main activities for livelihood, which increased nitrogen level in groundwater due to leaching processes. Within groundwater system, nitrogen trioxide (NO$_3$) and nitrogen dioxide (NO$_2$) are generally the dominant nitrogen fraction (Lockhart et al., 2013; Camargo et al., 2005; Dupas et al., 2016) are main activities for livelihood, which increased nitrogen level in groundwater due to leaching process. Change in temperature regime and, particularly, an increase in intensive rainfall events change in rainfall patterns, affects nitrogen leaching processes from agricultural land to groundwater systems (Bindi and Olesen 2011; Ficklin et al. 2010; Hansen et al. 2017; Huno et al. 2018; Mas-Pla and Menció, 2019). Change in temperature regime also influence chemical and biological activities which result into a decrease in oxygen solubility, and rise in pH, hence provide a favorable condition to develop microorganisms.

Electrical conductivity (EC) is a significant physical factor in water quality assessment for drinking as well as irrigation (Singh et al. 2013; Singh et al. 2015). Since the nature of mineral influences the EC of groundwater, it is necessary to understand trend of EC in aquifer. The existence of ion particles in the groundwater raises its conductivity. Even standard water quality classification method such as the Wilcox (1948) and Salinity Laboratory (USA, 1954) uses EC as main input parameter.

The main objective was to investigate impact of the change in climate parameters (rainfall and temperature) on EC and nitrate load using statistical tools. This study provides an overview of the effect of three decades change in nitrate and EC loads in Kancheepuram district.

Materials and methods

Study area

The Kancheepuram district is situated (11° 00' to 12° 00' North latitudes and 77° 28' to 78° 50' East longitudes) on the north east coast of Tamil Nadu and adjacent to Chennai a state capital of Tamil Nadu state. The district has a total geographical area of 1704.79 km$^2$ with 87.2 km coastline and divided into 10 taluks namely Alandur, Chengalpattu, Sholinganallur, Sriperumbudur, Kancheepuram, Tambaram, Madurantakam, Cheyyur, Tirukalukundram, and Uthiramerur) with 520 revenue villages (Fig. 1). The temperature varies from 21 to 39 °C and maximum temperature (April and May) and minimum temperature (November and December). Agriculture is the main economic activity and major crops are, namely paddy, groundnut, sugarcane, and gram (black and green). The district lies under Eastern Ghats Tamil Nadu uplands eco-sub region (8.3) and Eastern Ghats and Tamil Nadu uplands eco-sub region (18.2). It has two types of monsoon as southwest monsoon (June-Sept, with an average rainfall 462 mm), and north east monsoon (Octo-December, an average rainfall 697 mm) while an average annual rainfall is 1420 mm (https://agritech.tnau.ac.in/district_contingency_plan/df/TN1Kancheepuram%203.2.2011.pdf). Forest area (23,900 ha), permanent pastures (18,300 ha), cultivable wasteland (10,700 ha), land under miscellaneous tree crops and groves (12,900 ha), barren and uncultivable land (10,900 ha), current fallows (14,900 ha), and other fallow (56,500 ha) are the major land use categories. Major source of irrigation are tanks (total no. 1942), open wells (no. 63411) and bore wells (no. 12249).

Soil

There are six types of soils namely deep black soils (19%), moderately deep black soils (14.1%), moderately deep red soils (12.9%), deep red soils (12%), very deep red soils (9%), and shallow black soils (6.1%). Soil is mostly clay, sandstone and shale, along the coasts and the river banks are sandy in nature and in these areas, water percolates quickly thorough the soil. Few parts of study area also comprise hard rock surface (Fig. 2).

Geology, hydrogeology and fissured formation

The geological formations are beach sand of quaternary and recent period, Cuddalore sandstone of Mio-pliocene age, shale and sandstone of Upper Gondwannas and charnockite of Archaean era (Fig. 3). The district is underlain by both sedimentary and fissured formations. The important aquifer systems are constituted by unconsolidated and semi-consolidated formations, and weathered, fissured and fractured crystalline rocks (Fig. 4) (http://cgwb.gov.in/district_profile/tamilnadu/kancheepuram.pdf). Gondvana sandstones and shales and Tertiary mottled clays and sandstones represent the porous, semi-consolidated sediments. Groundwater occurs under water table conditions to confined conditions in inter granular spaces of sandstones, sands and in the bedding planes and thin fractures of shales. The depth of the wells ranges from 5 to 10 m bgl and specific capacity of porous formation range from 1.00 to 80.00 lpm/m/dd.

The unconsolidated formations occur mainly along the banks of Palar and Cheyyar rivers. Between Walajabad and Kancheepuram small diameter dug wells tap the alluvium with depths ranging between 6 and 12 m bgl and yield ranges from 25 to 35 m$^3$/hr. Along the coast, windblown sand acts as aquifer zones and groundwater extraction is by means of shallow dug wells with radial arms.
The movement of groundwater in fissured crystalline is principally controlled by joints, fissured, fractures and their inter-connections. The wells depth ranges between 6 and 17 m bgl. The depth of dug cum bore wells ranges from 25 to 45 m bgl. The specific capacity in the fissured formation ranges from 10 to 250 lpm/m/dd.

Data collection and management

The groundwater nitrate and EC data were collected of period 1985–2018 from the State Ground and Surface Water Resources Data Centre, Taramani, Chennai. These data are maintained on a pre- and post-monsoon basis from 01/1972 to 12/2018 for 125 wells of Kancheepuram district. The number of observational wells increased from 23 in 1972 to 125 in 2018, respectively. In present study total 52 wells data were considered from 1985–2018 to maintain constant wells for studied taluks. These 52 wells fall under the seven taluk (Chengalpattu, Cheyyur, Kancheepuram, Maduranthakam, Sripurumbudur, Tambaram and Tirukalukundram) remaining three Alandur, Sholinganallur, and Uthiramerur taluk were not considered due to lack of number of wells.

We aggregated number of wells as they are existing in taluk (13 wells aggregated for Tambaram, 10 wells aggregated for Kancheepuram, 8 wells aggregated for Maduranthakam, 6 wells aggregated for Cheyyur and Tirukalukundram, 5 wells aggregated for Chengalpattu, and 4 wells aggregated for Sripurumbudur).

Daily rainfall (mm) and maximum and minimum temperature (°C) data of period 1985–2018 were downloaded from NASA web site (https://giovanni.gsfc.nasa.gov/giovanni). We have aggregated the daily weather data into monthly and monthly data arranged into pre- and post-monsoon because nitrate and EC data are also in the format of pre- and post-monsoon.

Methodology

In present study the Analysis of Variance (ANOVA) (single factor) test was applied for identification of significant differences in taluk’s aquifer, Tukey’s HSD test was also used for further analysis of ANOVA. Mann–Kendall trend test (MK test) was applied after pre-whitening test to decipher the trend in long term water quality data.
**Analysis of variance (ANOVA)**

The statistical test ANOVA was applied to know the existing variability within a group and between groups. ANOVA suggest that if \( F_{\text{critical}} = F_{\text{calculated}} \) with P level and if \( F_{\text{calculated}} > F_{\text{critical}} \) then the null hypothesis will be rejected.

**The Mann–Kendall test (MK test)**

MK test is based on an assumption that used time series is uncorrelated. In this work the serial correlation was removed by applying pre-whitening test. MK test is based on statistics \( S \), it can be calculated using formula given below:

\[
S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \text{sgn}(x_j - x_k)
\]

where

\[
\text{sgn}(x_j - x_k) = \begin{cases} 
+1 & \text{if } x_j - x_k > 0 \\
0 & \text{if } x_j - x_k = 0 \\
-1 & \text{if } x_j - x_k < 0 
\end{cases}
\]

where \( n \) = number of observed data series, \( x_j \) and \( x_k \) are the value in period \( j \) and \( k \), \( j > k \). For \( n \geq 10 \), the sampling distribution of \( S \), \( Z \) follows the standard normal distribution where,

The standardized test statistic \( Z \) is computed as follow:

\[
Z = \begin{cases} 
\frac{S-1}{\sqrt{\text{VAR}(S)}} & \text{if } S > 0 \\
0 & \text{if } S = 0 \\
\frac{S+1}{\sqrt{\text{VAR}(S)}} & \text{if } S < 0
\end{cases}
\]

The null hypothesis, \( H_0 \) = no significant trend is present, is accepted. If the test statistic \( Z \) is not statistically
significant, i.e., \(-Z_{\alpha/2} < Z < Z_{\alpha/2}\), where \(Z_{\alpha/2}\) is the standard normal deviate.

**Sen’s estimator**

The trend magnitude was estimated using the Theil and Sen slope estimator test (Sen, 1968; Theil, 1950). The slopes \((T_i)\) of all data pairs are first calculated by:

\[
T_i = x_j - x_k / (j - k) \quad \text{for } i = 1, 2, \ldots, N
\]

where \(x_j\) and \(x_k\) are data values at times \(j\) and \(k\) \((j > k)\), respectively. The median of these \(N\) values of \(T_i\) is Sen’s estimator of slope. It is calculated using following formula:

\[
\beta = T_{N+1/2} \quad \text{if } N \text{ is odd}
\]

\[
\beta = 1/2(T_{N/2} + T_{N+2/2}) \quad \text{if } N \text{ is even}
\]

An upward trend \((+\beta)\) and downward trend \((-\beta)\) present in the time series.

The statistical analysis was performed in MS-Excel and SPSS.

**Results and discussion**

**Descriptive statistics**

The detailed descriptive statistics of non monsoon nitrate concentration is given in Table 1. The maximum value of nitrate concentration in last 34 year’s NM period is less than recommended value (45 mg/l) of Bureau of Indian Standards (BIS, 2012). But within seven taluks, Kancheepuram taluk has a maximum value of 20.73 mg/l while second highest as 20.46 mg/l in Tambaram taluk. It is due to agriculture and industrial activities which are involved in both taluk. However, minimum value was found in Cheyyur taluk. The low value of nitrate may be due to dilution of aquifer during NM. Comparing the mean value of nitrate concentration within study area, we found that Tambaram has a highest mean level of nitrate in last 34 year’s NM. The second highest mean value is 9.49 mg/l for Kancheepuram. However, Cheyyur has lowest NM mean value of 4.78 mg/l. The Cheyyur taluk show least variation in nitrate concentration within study area because it has least value of Standard Deviation (StD) and Standard Error (StE). Whereas...
Fig. 4 Hydrogeology map of the study area

Source: http://cgwb.gov.in
Kancheepuram show highest variability in nitrate concentration in last 34 year’s non-monsoon due to high value of StE and StD. Except at Kancheepuram and Tambaram all other taluk’s boundary touches to the sea and it may be a reason for low value of nitrate in last 34 year’s NM. The nitrate distribution as per 34 year’s NM data is as follows: Cheyyur < Sriperumbudur < Tirukalukundram < Maduranthakam < Chengalpattu < Kancheepuram < Tambaram. The maximum average NM rainfall within study area was 167.34 cm. However, 34 years maximum average NM temperature was 31.17 °C. The distribution and variation in average NM rainfall within study area is high while low for average NM temperature.

Table 2 has demonstrated last 34 year’s monsoon characteristics of nitrate. In study area nitrate concentration never cross the BIS limit in last 34 years monsoon period. It may be due to significant amount of rainfall during monsoon (112.31 cm). The maximum value of nitrate concentration within study area was 14.05 mg/l for Tambaram taluk. While during the NM Kancheepuram was also highly sensitive to mean and maximum nitrate concentration. In the monsoon period low temperature also play an important role because during low temperature percolation rate will be less as compared to NM period when temperature is high. The Tirukalukundram has low nitrate concentration during both monsoon and NM period. Based on mean value of nitrate concentration in taluk, it show distribution as Tirukalukundram < Sriperumbudur < Maduranthakam < Cheyyur < Chengalpattu < Kancheepuram < Tambaram. The Kancheepuram taluk show a maximum variability (due to high StD value) in distribution of nitrate concentration in last 34 year’s monsoon.

The box-plot results of the nitrate concentration (as independent variable) of NM represent the nitrate characteristics (Fig. 5A). It show a nitrate variation in different aquifer. The Chengalpattu has higher range of nitrate distribution from median value of nitrate.

In Tirukalukundram and Kancheepuram the mean value of nitrate concentration of monsoon is almost equal (Fig. 5B). However, Tambaram taluk has less range of median value of the nitrate in monsoon. From box plot, it is evident that during monsoon period nitrate has unequal distribution over the study area. The each box is of different size (length wise shape) for NM and monsoon. Whereas each taluk has some difference. This difference means a high spatial and temporal variation in nitrate concentration within study area at taluk level as well as this variation found in NM and monsoon level.

Tables 3 and 4 represent spatial and temporal characteristics of EC during NM and monsoon period. Study area received a high amount of rainfall (112.31 cm) and low temperature during monsoon hence EC value during the monsoon is less than NM period. Kancheepuram has high average value (1531.22 µS/cm) of EC distribution from WHO (2004)
desirable limit (1400 µS/cm) in both NM and monsoon period. Based on increasing order of mean value of EC during last 34 year’s NM period, seven taluks are arranged such as Sriperumbudur < Cheyyur < Maduranthakam < Chengalpattu < Tambaram < Tirukalukundram < Kancheepuram (Table 3). During monsoon the distribution is changed as Chengalpattu < Maduranthakam < Cheyyur < Sriperumbudur < Tirukalukundram < Tambaram < Kancheepuram (Table 4).

Box plot reveal outliers at the upper whisker for the variable, which means that the variable is right-skewed. This represent that spatial and temporal series of EC in groundwater do not follow a normal distribution. The length of the upper whisker at Chengalpattu, Maduranthakam, Sriperumbudur during NM (Fig. 6A), and Cheyyur, Maduranthakam, Sriperumbudur, Tirukalukundram during monsoon (Fig. 6B) show a longer than the lower whisker. Which represent that the density of the first 25% of the data sets are more compared to density of the data in the last quartile (75–100%). After comparison of median value of EC and distribution of middle (as indicated by size of the boxes) 40% of the data set of the EC over NM and monsoon, that length wise shape of the each boxes are not similar for NM and monsoon in each taluk nearby Peninsula area. Non-similar boxes of EC variable indicate that EC variable must be required for intensive monitoring of EC in groundwater due to high spatial and temporal variation. The median value of EC or box size of EC value of almost all aquifer of each taluk remain low in monsoon compared to NM. It is attributed to good amount of rainfall which facilitates groundwater recharge during each monsoon, and further dilute the concentration of the each variable in the aquifer.

**Fig. 5** A and B. Box-plot of variation of nitrate concentrations in borehole water of seven taluk of Kancheepuram district aquifer

**Table 3** Summary statistics of EC concentration (µS/cm) of groundwater for non-monsoon (1985–2018)

| Tests | Chen | Chey | Kan | Mad | Sri | Tam | Tir | NMAR | NMAT |
|-------|------|------|-----|-----|-----|-----|-----|------|------|
| Me    | 954.63 | 921.79 | 1531.22 | 933.65 | 920.35 | 1248.59 | 1188.28 | 88.11 | 29.96 |
| SdE   | 36.25 | 38.86 | 31.28 | 24.14 | 36.61 | 32.49 | 20.68 | 4.78 | 0.15 |
| Med   | 987.60 | 884.41 | 1511.77 | 923.13 | 887.48 | 1215.66 | 1191.51 | 84.35 | 30.36 |
| StD   | 211.34 | 226.58 | 182.41 | 140.79 | 213.48 | 189.47 | 120.56 | 27.85 | 0.90 |
| Ra    | 944.00 | 1013.32 | 1031.00 | 584.49 | 815.00 | 1016.55 | 513.83 | 118.29 | 2.78 |
| Min   | 440.00 | 623.33 | 1149.00 | 692.50 | 615.00 | 928.84 | 961.67 | 49.06 | 28.39 |
| Max   | 1384.00 | 1636.66 | 2180.00 | 1276.99 | 1430.00 | 1945.38 | 1475.50 | 167.34 | 31.17 |

**Table 4** Summary statistics of EC concentration of groundwater for monsoon (1985–2018)

| Tests | Chen | Chey | Kan | Mad | Sri | Tam | Tir | MAR | MAT |
|-------|------|------|-----|-----|-----|-----|-----|-----|-----|
| Me    | 803.48 | 824.06 | 1502.28 | 823.58 | 860.53 | 1259.68 | 988.60 | 112.31 | 26.20 |
| SdE   | 49.67 | 43.75 | 33.11 | 28.72 | 32.98 | 20.02 | 20.78 | 7.63 | 0.06 |
| Med   | 789.88 | 780.69 | 1491.84 | 811.92 | 818.71 | 1271.31 | 989.25 | 105.86 | 26.11 |
| StD   | 289.63 | 255.11 | 193.05 | 167.46 | 192.28 | 116.75 | 121.15 | 44.47 | 0.36 |
| Ra    | 1228.00 | 1105.00 | 930.25 | 708.34 | 717.50 | 492.28 | 464.74 | 196.65 | 1.68 |
| Min   | 364.00 | 551.67 | 1116.00 | 581.61 | 535.00 | 1016.15 | 796.67 | 32.68 | 25.68 |
| Max   | 1592.00 | 1656.67 | 2046.25 | 1289.95 | 1252.50 | 1508.43 | 1261.41 | 229.33 | 27.35 |
Nitrate trend

Trend analysis show the statistically increasing (+) and decreasing (-) trend of nitrate and EC. During NM nitrate concentration show a rising trend in Chengalpattu (Fig. 7A) with 0.06 mg/l per year while Cheyyur (Fig. 7B), Kancheepuram (Fig. 7C), Maduranthakam (Fig. 7D), Sriperumbudur (Fig. 7E), Tambaram (Fig. 7F), and Tirukalukundram (Fig. 7G) also follow an increasing trend with 0.01, 0.05, 0.04, 0.01, 0.03, and 0.1 mg/l per year, respectively. It seems that nitrate in all taluk show an increasing trend in NM period but increasing rate was very slow while average increasing rate of study area was 0.03 mg/l per year in last 34 year’s NM period.

Nitrate concentration in monsoon fluctuate due to significant amount of rainfall. Only three taluk Chengalpattu, Cheyyur and Tirukalukundram show an increasing nitrate trend for monsoon. Chengalpattu (Fig. 8A) was single taluk which has highest loading of nitrate in NM period. While Cheyyur (Fig. 8B) show an increasing trend but it is almost same as NM period trend for Cheyyur and Tirukalukundram. Except Kancheepuram (Fig. 8C), Maduranthakam (Fig. 8D) and Sriperumbudur (Fig. 8E), Tambaram (Fig. 8F) taluk show a decreasing trend due to excess water during monsoon. Tirukalukundram (Fig. 8G) show an increasing trend but it is almost same as NM period trend for Tirukalukundram Four taluk can be arranged as Maduranthakam (−0.05 mg/l per year), Kancheepuram (−0.05 mg/l per year), Sriperumbudur (−0.04 mg/l per year), and Tambaram (−0.03 mg/l per year).

EC Trend

EC trend in groundwater during non-monsoon (Fig. 9A–G) and monsoon (Fig. 10A–G) of seven taluk. The EC trend for NM show Chengalpattu (Fig. 9A), Maduranthakam (Fig. 9D), Sriperumbudur (Fig. 9E) and Tirukalukundram (Fig. 9G), have a positive slope (17.9, 10.8, 12.4 and 5.3, respectively), which reflects the statistically rising trend of EC for NM period. EC in Sriperumbudur aquifer has an increasing trend of 12.4 mg/l per year which is highest EC steepness within study area during last 34 year’s NM period. Second highest steepness value of EC in Chengalpattu aquifer, this taluk has steepness for nitrate loading during NM and monsoon it may be due to high use of fertilizers in the agricultural field for increase of crop productions. Similarly for Maduranthakam and Tirukalukundram have an increasing trend of nitrate loading during NM and monsoon. Except these four (Chengalpattu, Maduranthakam, Sriperumbudur and Tirukalukundram) remaining other taluk’s aquifer show a declining slope for EC.

An increasing trend was observed for Chengalpattu, followed by Maduranthakam, Sriperumbudur and Tirukalukundram for EC in monsoon period but rate of increment is less than from NM period (6.1, 4.5, 12.4 and 1.6 mg/l per year, respectively) due to dilution of aquifer. Remaining aquifers were also found in a decreasing trend but very low during monsoon period.

Rainfall and temperature effect on nitrate and EC

Rainfall and temperature effect on nitrate and EC in seven taluk is graphically represented using Fig. 11A–D and Fig. 12A–D. It is seemed that there is no direct link between the NM and monsoon rainfall and temperature with NM and monsoon nitrate and EC. The climatic parameters effects on agrichemical (nitrate and EC) suggest that indirect rainfall effect is observed like dilution process in aquifer after NM season. The value of site-specific nitrate loading was assessed by a number of researchers (Buczko et al. 2010; Lord and Anthony 2002; Schroeder et al. 2004). Schroeder et al. (2004) found that similar agricultural inputs can give different outputs result as deviation in soil salt, crop characteristics, even when choose a common type of crop. de Ruiter et al. (2007) found that how surplus nitrate in soil can leach into groundwater as nitrate contamination.
Fig. 7 A–G Nitrate trend in groundwater during non-monsoon of seven taluk
Fig. 8  A-G Nitrate trend in groundwater during monsoon of seven taluk
Fig. 9  A-G EC trend in groundwater during non-monsoon of seven taluk
Fig. 10  A-G EC trend in groundwater during monsoon of seven taluk
Fig. 11  A–D Impact of change in rainfall concentration on nitrate and EC
### Table 5 ANOVA (Single Factor) summary for non-monsoon (NM) and monsoon (M) nitrate

| Groups               | Count | Sum NM/M | Sum NM | Sum M | Average NM/M | Average NM | Average M | Variance NM/M | Variance NM | Variance M |
|----------------------|-------|----------|--------|-------|--------------|------------|------------|----------------|--------------|------------|
| Chengalpattu (Cu)    | 34    | 244.78   | 192.45 | 52.33 | 7.199        | 5.66       | 10.57      | 4.85           |             |            |
| Cheyyur (Cr)         | 34    | 162.66   | 184.13 | 21.47 | 4.784        | 5.42       | 3.34       | 4.80           |             |            |
| Kancheepuram (K)     | 34    | 322.74   | 232.69 | 90.05 | 9.492        | 6.84       | 12.70      | 3.37           |             |            |
| Maduranthakam (M)    | 34    | 226.81   | 180.52 | 46.29 | 6.671        | 5.31       | 6.02       | 3.48           |             |            |
| Sripurumbudur (S)    | 34    | 171.02   | 171.87 | 0.85  | 5.030        | 5.05       | 4.36       | 5.55           |             |            |
| Tambaram (Ta)        | 34    | 356.12   | 314.64 | 41.48 | 10.474       | 9.25       | 8.49       | 5.40           |             |            |
| Tirukalukundram (Th) | 34    | 193.54   | 149.81 | 43.73 | 5.692        | 4.41       | 4.28       | 2.37           |             |            |

### Table 6 ANOVA (Single Factor) summary non-monsoon (NM) and monsoon nitrate

| Source of Variation | SS   | df   | MS   | F    | P-value | F crit |
|---------------------|------|------|------|------|---------|--------|
| Between Groups      | 983.04 | 532.71 | 6    | 163.84  | 23.05 | 1 × 10^{-16} | 2.13 |
| Within Groups       | 1642.20 | 984.10 | 231  | 7.11   | 4.26    |         |
| Total               | 2625.24 | 1516.80 | 237  |        |         |         |

### Table 7 ANOVA (Single Factor) summary for non-monsoon (NM) and monsoon EC

| Groups               | Count | Sum NM/P | Sum NM | Sum M | Average NM/P | Average NM | Average M | Variance NM/P | Variance NM | Variance M |
|----------------------|-------|----------|--------|-------|--------------|------------|------------|----------------|--------------|------------|
| Chengalpattu (Cu)    | 34    | 32,457.42 | 27,318.36 | 5149.06 | 954.63       | 803.48     | 4.5 × 10^4 | 8.4 × 10^4     |             |            |
| Cheyyur (Cr)         | 34    | 31,340.79 | 28,017.89 | 3322.90 | 921.79       | 824.06     | 5.1 × 10^4 | 6.5 × 10^4     |             |            |
| Kancheepuram (K)     | 34    | 52,061.52 | 51,077.60 | 988.42  | 1531.22      | 1502.28    | 3.3 × 10^4 | 3.7 × 10^4     |             |            |
| Maduranthakam (M)    | 34    | 31,744.2  | 28,001.63 | 3742.57 | 933.65       | 823.58     | 2.0 × 10^4 | 2.8 × 10^4     |             |            |
| Sripurumbudur (S)    | 34    | 31,291.86 | 29,258.17 | 1933.69 | 920.35       | 860.53     | 4.6 × 10^4 | 3.7 × 10^4     |             |            |
| Tambaram (Ta)        | 34    | 42,451.94 | 42,829.19 | 3787.25 | 1248.59      | 1259.68    | 3.6 × 10^4 | 1.4 × 10^4     |             |            |
| Tirukalukundram (Th) | 34    | 40,401.43 | 33,612.50 | 6788.93 | 1188.28      | 988.60     | 1.5 × 10^4 | 1.5 × 10^4     |             |            |

### Table 8 ANOVA (Single Factor) summary non-monsoon (NM) and monsoon EC

| Source of Variation | SS     | df | MS     | F    | P-value | F crit |
|---------------------|--------|----|--------|------|---------|--------|
| Between Groups      | 11,174,444 | 6  | 1,862,407 | 53  | 7E-41   | 2.14     |
| Within Groups       | 8,088,424 | 231 | 35,014.82 | 237 |         | 1E-45     |
| Total               | 19,262,867 | 237 |        |      |         |         |

### Table 9 Tukey Test for non-monsoon (NM) and monsoon (M) EC and nitrate

| Nitrogen | Significant_{PM} | Significant_{M} | EC | Significant_{PM} | Significant_{M} |
|----------|------------------|-----------------|----|------------------|-----------------|
| T        | 1.97             | 1.97            |    | 1.97             | 1.97            |
| Df       | 231              | 231             |    | 231              | 231             |
| MSE      | 7.12             | 4.26            |    | 35,014.82        | 39,937.27       |
| Tukey Test (CV) | 0.90            | 0.69            |    | 63.23            | 67.52           |
Fig. 12 A–D Impact of change in temperature on nitrate and EC within study area
ANOVA and MK test analysis

ANOVA Tables 5, 6, 7 and 8 suggest that how aquifers of different taluk act in EC and nitrate load response. A null hypothesis (H0) for the test mean that different taluk’s aquifers are equal. If there is a statistically significant result, then it means that the two taluk’s aquifers are different (or unequal). When it will clear how each independent aquifer’s EC and nitrate mean load is different from the others aquifer, then we can understand behavior of aquifer for EC and nitrate. Test returns a significant F-statistic, we may use a post hoc test (or Tukey test, Table 9) to identify the corrected

| Comparison | Nitrogen | EC |
|------------|----------|----|
|            | Significant(NM) | Significant(M) | Significant(NM) | Significant(M) |
| Cu Vs Cr   | √        | X  | √           | X            |
| Cu Vs K    | X        | X  | X           | X            |
| Cu Vs M    | X        | X  | X           | X            |
| Cu Vs S    | √        | X  | √           | X            |
| Cu Vs Ta   | X        | X  | X           | X            |
| Cu Vs Th   | √        | √  | X           | X            |
| Cr Vs Cu   | X        | X  | X           | X            |
| Cr Vs K    | X        | X  | X           | X            |
| Cr Vs M    | X        | X  | X           | X            |
| Cr Vs S    | X        | X  | √           | X            |
| Cr Vs Ta   | X        | X  | X           | X            |
| Cr Vs Th   | X        | √  | X           | X            |
| K Vs Cu    | √        | √  | √           | √            |
| K Vs Cr    | √        | √  | √           | √            |
| K Vs M     | √        | √  | √           | √            |
| K Vs S     | √        | √  | √           | √            |
| K Vs Ta    | X        | X  | √           | √            |
| K Vs Th    | √        | √  | √           | √            |
| M Vs Cu    | X        | X  | X           | √            |
| M Vs Cr    | X        | X  | X           | √            |
| M Vs M     | X        | X  | X           | X            |
| M Vs S     | X        | X  | √           | X            |
| M Vs Ta    | X        | X  | X           | X            |
| M Vs Th    | √        | √  | X           | X            |
| S Vs Cu    | X        | X  | X           | √            |
| S Vs Cr    | X        | X  | X           | √            |
| S Vs K     | X        | X  | X           | X            |
| S Vs M     | X        | X  | X           | X            |
| S Vs Ta    | X        | X  | X           | √            |
| S Vs Th    | X        | X  | X           | X            |
| Ta Vs Cu   | √        | √  | √           | √            |
| Ta Vs Cr   | √        | √  | √           | X            |
| Ta Vs K    | √        | √  | X           | X            |
| Ta Vs M    | √        | √  | √           | X            |
| Ta Vs S    | √        | √  | √           | X            |
| Ta Vs Th   | √        | √  | √           | X            |
| ThVs Cu    | X        | X  | √           | √            |
| ThVs Cr    | √        | X  | √           | √            |
| ThVs K     | X        | X  | X           | X            |
| ThVs M     | X        | X  | √           | √            |
| ThVs S     | X        | X  | √           | X            |
| ThVs Ta    | X        | X  | X           | X            |
Table 11  Mann–Kendall test for nitrate and EC during non-monsoon and monsoon

| Time series (1985 to 2018) of taluks | Mann–kendall trend | Sen's slope estimate |
|-------------------------------------|--------------------|---------------------|
|                                     | Test Z | Signific | Q | Qmin99 | Qmax99 | Qmin95 | Qmax95 | B | Bmin99 | Bmax99 | Bmin95 | Bmax95 |
| **Non-monsoon (Nitrate)**           |        |          |   |        |        |        |        |   |        |        |        |        |
| Chengalpattu                        | 0.62   | -0.07    | 0.024 | -0.108 | 0.207  | -0.071 | 0.145  | 5.08 | 12.65  | -4.29  | 10.23  | -1.19  |
| Cheyyur                             | -0.07  | -0.002   | -0.086 | 0.076  | -0.064 | 0.053  | 4.70   | 9.45  | 0.52   | 8.01   | 1.74   |
| Kancheepuram                        | 1.25   | 0.066    | -0.091 | 0.216  | -0.053 | 0.175  | 5.64   | 14.12 | -3.93  | 12.15  | -1.11  |
| Maduranthakam                       | 0.15   | 0.005    | -0.109 | 0.117  | -0.077 | 0.071  | 5.94   | 12.63 | -0.16  | 10.91  | 2.31   |
| Sriperumbudur                       | 1.07   | 0.042    | -0.064 | 0.124  | -0.038 | 0.104  | 2.50   | 8.43  | -2.40  | 6.87   | -1.38  |
| Tambaram                            | 0.71   | 0.041    | -0.091 | 0.156  | -0.065 | 0.124  | 7.94   | 16.36 | 0.73   | 14.90  | 2.81   |
| Tirukalukundram                     | 0.56   | 0.022    | -0.086 | 0.120  | -0.051 | 0.094  | 4.20   | 10.61 | -1.31  | 8.33   | 0.24   |
| **Monsoon (Nitrate)**               |        |          |   |        |        |        |        |   |        |        |        |        |
| Chengalpattu                        | 1.868  | +        | 0.069 | -0.038 | 0.177  | -0.005 | 0.144  | 1.788 | 7.664  | -4.415 | 5.635  | -2.439 |
| Cheyyur                             | -0.089 | -0.002   | -0.064 | 0.085  | -0.049 | 0.056  | 5.013  | 8.417 | 0.558  | 7.595  | 1.996  |
| Kancheepuram                        | -1.141 | -0.033   | -0.111 | 0.064  | -0.091 | 0.037  | 8.910  | 13.053| 2.870  | 12.015 | 4.767  |
| Maduranthakam                       | -1.423 | -0.03    | -0.119 | 0.027  | -0.096 | 0.014  | 7.361  | 12.030| 3.701  | 10.832 | 4.343  |
| Sriperumbudur                       | 0.356  | 0.009    | -0.088 | 0.081  | -0.056 | 0.064  | 3.960  | 9.772 | -0.257 | 7.916  | 0.778  |
| Tambaram                            | -0.296 | -0.01    | -0.138 | 0.103  | -0.105 | 0.072  | 10.844 | 18.210| 3.176  | 15.990 | 5.286  |
| Tirukalukundram                     | 0.385  | 0.007    | -0.053 | 0.082  | -0.035 | 0.060  | 3.834  | 7.0312| -0.239 | 6.018  | 0.971  |
| **Non-monsoon (EC)**                |        |          |   |        |        |        |        |   |        |        |        |        |
| Chengalpattu                        | 1.305  | -0.741   | 5.500 | -6.946 | 16.707 | -3.444 | 13.643 | 667.234| 1383.44| 54.84  | 1181.10| 219.83 |
| Cheyyur                             | -0.652 | -1.430   | -9.413 | 4.932  | -7.640 | 3.469  | 1603.18| 2080.05| 1206.69| 1968.31| 1296.72|
| Kancheepuram                        | 2.520  | *        | 5.366 | -0.302 | 10.793 | 1.501  | 8.984  | 632.66 | 938.06 | 332.36 | 841.72 | 434.63 |
| Maduranthakam                       | 3.765  | ***      | 13.702 | 5.652  | 21.160 | 7.525  | 19.391 | 573.76 | -272.41| 7.916  | 0.778  |
| Sriperumbudur                       | -1.542 | -2.860   | -7.357 | 2.533  | -5.985 | 1.292  | 1396.17| 1649.45| 193.875| 899.675| 272.366|
| Tambaram                            | 0.741  | 1.605    | -5.326 | 7.786  | -3.149 | 6.594  | 1084.64| 1490.57| 719.02 | 1355.30| 786.53 |
| **Monsoon (EC)**                    |        |          |   |        |        |        |        |   |        |        |        |        |
| Chengalpattu                        | 3.528  | ***      | 18.727 | 7.101  | 29.655 | 10.581 | 26.869 | -319.11| 373.030| -869.788| 174.401| -727.062|
| Cheyyur                             | 1.305  | 3.013    | -5.560 | 9.895  | -2.356 | 8.395  | 592.80 | 1095.024| 193.875| 899.675| 272.366|
| Kancheepuram                        | -0.978 | -3.288   | -12.709| 6.132  | -10.698| 3.339  | 1690.34| 253.013 | 1136.408| 2137.373| 1317.026|
| Maduranthakam                       | 3.765  | ***      | 11.077 | 4.320  | 16.330 | 6.048  | 15.218 | 178.32 | 567.117 | -91.990 | 469.512 | -38.600 |
| Sriperumbudur                       | 3.618  | ***      | 11.937 | 4.058  | 20.341 | 5.639  | 17.880 | 192.84 | 611.313 | -310.315| 528.974| -145.388|
| Tambaram                            | -0.682 | -1.867   | -6.955 | 3.998  | -5.737 | 2.700  | 1381.30| 1681.098| 1024.850| 1605.277| 1105.008|
| Tirukalukundram                     | 2.253  | *        | 5.371  | -0.478 | 7.786  | -3.149 | 6.594  | 1084.64| 1490.57| 719.02 | 1355.30| 786.53 |

+ Positive increment
* Significance level (0.05)
*** Significance level (0.001)
aquifers that have a difference in means. Tukey’s test, also known as Tukey’s HSD (honestly significant difference) test or Tukey’s range test, having ability to compare numbers of groups (or aquifer) in a single-step (Table 10). In present study Tukey's HSD test is used to find means that are significantly different from each other aquifer. From Table 10 and result from Tukey test, it seem that Kancheepuram taluk’s aquifer has more significantly (or √) different with respect to other aquifer behavior for EC and nitrate load during both non-monsoon and monsoon. While other aquifers have significant (or √) different with respect to other aquifer behavior during non-monsoon or monsoon. The Mann–Kendall trend show a negative trend for nitrate during non-monsoon season at Cheyyur and at rest station it show positive trend whereas in case of monsoon Cheyyur, Kancheepuram, Maduranthakam and Tambaram show a negative trend. The significant positive trend was reported at Chengalpattu. For the case of EC during non-monsoon season the significant positive trend was observed at Maduranthakam and Sriperumbudur. During the monsoon season significant positive trend was observed at Chengalpattu, Maduranthakam Sriperumbudur and Tirukalukundram (Table 11).

Conclusion

Excess nitrate loading in groundwater is a serious problem for any groundwater system. Under present climate change high pressure on agricultural sector for more yields hence farmers are changing cropping method and using excess fertilizer. It is an important reason of high nitrate loading in groundwater system. This has been well-studied in terms of crop production and potential changes in cultivars. However, the effect of climate change on the nitrate source is still difficult to model. Overall, it is observed that only Chengalpattu and Tirukalukundram taluk is showing an increasing trend for both agrichemical EC and nitrate over the 34 year in non-monsoon and monsoon season. Increasing trend of both agrichemical in these area, revealing that under both taluk agricultural and non-agricultural (urban and industry chemical output) activities are more compared to other remaining taluk. Other taluk are showing a fluctuation after non-monsoon. Because during monsoon a dilution process occurring in all types of aquifers and after dilution process aquifer is showing an increasing trend that mean leaching of agrichemical into aquifer is high. Fertilizer management must be scientific, and applying the correct dose of nitrogen at the most favorable time will reduce nitrate losses, use perennial crops as alternative cropping systems because it reduces nitrogen losses.

If adverse activity in agricultural and non-agricultural (miss-management of urban sewer) and industrial chemicals output is not minimized, then a continuous increment of agrichemicals in aquifer of Chengalpattu and Tirukalukundram will not arrest during non-monsoon and monsoon season. The study revealed that the nitrate loading in aquifer of Chengalpattu and Tirukalukundram are concerned with land-uses and anthropogenic acts.

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Declarations

Conflict of interest This research is in compliance with the ethical standard and conduct of the journal.

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