Impact of monsoon shower on the hydrogeochemistry of groundwater along the lithological contact: a case study from South India

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Abstract
Groundwater chemistry is mainly governed by lithological variations, space and resident time. In addition, hydrogeochemical characteristics of groundwater in the lithological contact zones are too complex. Hence, Cretaceous–Tertiary (KT) boundary from Ariyalur district, Tamilnadu, India, was selected for this study to identify the hydrogeochemistry of groundwater. This study includes 284 groundwater samples from four different seasons (pre-monsoon, post-monsoon, southwest monsoon and northeast monsoon). Groundwater samples were collected and analysed for major cations and anions, including physical parameters using standard procedures. High electrical conductivity (EC) showed the longer residence time of groundwater in hard rock region at the central and southern part of the study area. Ca2+, Na+, Cl− and HCO3− are the dominant ions in all the four seasons. The seasonal composition migration was observed from Na–Ca–Cl–HCO3 type to Na–Mg–Cl–HCO3 type, and Ca-HCO3 is the predominant water type in piper plot. Interpretation of data reveals that the groundwater quality was unsuitable for domestic and irrigation purposes during pre- and southwest monsoon seasons. Rock–water interaction and dissolution of minerals are the main sources of groundwater chemistry. Agriculture activities during monsoonal seasons also play a role in controlling the hydrogeochemistry of groundwater in this region.

Keywords Hydrogeochemistry · Cretaceous–Tertiary (KT) boundary · Lithology · Weathering · Monsoon · South India

Introduction
The dissolved ions in groundwater aid to recognize the major geochemical processes and help to determine the utility of water for various purposes. In regulating the contribution of the various geochemical factors during every stage shows a complex process. The vast extent of the ecosphere’s irrigation and agriculture relies on subsurface water. The groundwater quality of a region is determined by precipitation, geological materials, geographic, land-use geomorphology and accessibility of recharge sources. The dependence on surface water in many regions had increased rapidly due to insufficient surface water sources, non-perennial rivers, and frequent monsoon failures. In the recharge zone, hydrochemistry is affected by water chemistry and by various reactions before recharge and reactions between the groundwater and aquifer matrix (Li et al. 2008). Chemical characteristics of the adjoining rocks, the qualitative and measurable characteristics of moving water bodies, and the human interaction with the subsurface aquifers govern the utility of water. The spatial variability of water chemistry results from rock–water interaction under different subsurface migration conditions (Prasanna et al. 2013).

Scientists have recognized many other factors that influence groundwater chemistry, such as the amount of pores in the aquifer, waste water penetration from shallow salt water, water level rise and seawater incursion (Araguas 2003; Carol
Several authors have claimed that geological heterogeneities influence hydrogeochemical processes on different scales (Singh et al. 2013; Chidambaram et al. 2010; Adithya et al. 2016; Thilagavathi et al. 2017; Olofinlade et al. 2018; Devaraj et al. 2018, 2020). In recent decades, groundwater quality concerns have become a major concern, and groundwater quality assessment and health risk assessment have been extensively studied around the world (Zhang et al. 2020a, b; Adimalla and Qian 2021; Adimalla et al. 2020a, b). This present study is more significant due to the difference in the adjoining lithologies, intensity of weathering, water level fluctuation, surface water–groundwater interaction, permeability and porosity of these aquifers (Archaean, Cretaceous, Tertiary and Quaternary).

Hydrogeochemical methods and the study of principal component analysis provide confidence in the degree of water–rock interactions and processes of mixing (Xu et al. 2019a, b, c; Adimalla 2020; Adimalla et al. 2020a, b). There are few studies on the hydrogeochemical status to determine the dissolved ion concentration in the adjoining region of the study area (Mehra et al. 2016; Thiyya et al. 2015, 2018; Saravanan et al. 2016; Loganathan and Ahamed 2017; Kumar et al. 2017). Irrigation water quality plots are the major keys to classify the groundwater quality (Zhang et al. 2019; Adimalla 2019). An investigation has been done to identify the hydrogeochemical characterization of groundwater (shallow aquifer) for irrigation purpose (Xu et al. 2019a, b, c).

The study about groundwater chemistry and its relation with local geology are important in groundwater management (Xu et al. 2019a, b, c). Also, Groundwater is one of the key sources of drinking water, and its use and protection as drinking water faces challenges as water tables decline (Zhang et al. 2020a, b). In order to recognize the geochemical processes accountable for the discrepancy in hydrogeochemical characters of groundwater along Cretaceous–Tertiary boundary, many studies have previously been conducted globally, though hydrogeochemical research on groundwater to ascertain the suitability for different purposes are scarce especially along the KT boundary of Trichinopoly, Tamil Nadu, India. Therefore, the current study has attempted with an intense sampling campaign representing four different seasons and adopting even distribution, to determine the water quality for various purposes, its spatial and temporal variation and to identifying chief hydrogeochemical process in the region.

**Study area**

The major city, Ariyalur is in the central portion of Trichinopoly district in southern Tamil Nadu, India (Fig. 1). The present study region lies between the latitude of 78° 80′ E and 79° 27′ E, the longitudes 11° 44′ N and 10° 97′ N representing survey of India toposheets 58-I-15, 58-I-16, 58-M-3 and 58-M-4. The mean elevation of the area is 50 m above mean sea level. Physiographically the north-western portion is elevated and slopes towards the south-east with a spatial extent of 1774 km². Temperature varies from 21 to 40 °C in January and June, respectively. Average yearly rainfall of 1096 mm and the highest amount of rainfall is generally recorded during NEM (i.e. 45.9% of total rainfall), followed by SWM (39.6%), winter (2.8%) and summer (11.7%). The river Vellar is the major drainage flowing from the northern part and; another minor tributary is River Marudiyar moving transversely from southwest to southeast. The river Marudiyar is ephemeral and there is no flow during non-monsoon periods.

The geology the region is covered by charnockites, sandstones, migmatic gneiss and calcareous stones. The surface marine structure is characteristic of the Cauvery basin's cretaceous succession with a rich Albian-Maastrichtian era faunal sequence (Rangaraju et al. 1993). Lithological, there are 3 foremost groups classified as Ariyalur, Uttatur and Trichinopoly formations. The Ariyalur formation is the major outcrop than the other two (Sastry et al. 1972), and it outcrops on the eastern and northeastern part of the Ariyalur district. It is the most prominent fossiliferous cretaceous formations of the Cauvery basin in the south India and characterizes the Mesozoic progression. Tectonics, paleontology, stratigraphy, paleoclimatic and topographic sequence have been addressed and inferred by various scholars (Banerji 1979; Sundaram and Rao 1986; Ramanathan 1979; Ramasamy and Banerji 1991; Govindan et al. 1996; Madhavaraju and Ramasamy 1999, 2001; Ayyasami 2006; Devaraj et al. 2018, 2020). The major land-cover and land-use features are agricultural terrestrial, water supplies, leftover land, scrubland and farm/plantation. The spatial coverage of these features shows, aquatic bodies (21.45%), left over terrestrial (6.88%), farmstead/coprice (6.29%) and scrubland (3.1%) representing minor portion. Agricultural land occupies 62.17% of the entire area (Devaraj et al. 2018).

Groundwater in weathered and fractured zones in semi-confined conditions depending on the interconnection between the weaker structures, and its development. In Ariyalur region, thickness of aquifer varies from 15 to 35 MBGL. The Alluvium formation is good water bearing region with a highest thickness of 37 m and this formation is very porous and permeable zone. Water table in the study
area fluctuates from 10.0 to 15.0 m MBGL in the hard rock aquifers.

**Materials and methods**

The samples representing the different litho units and land use were collected during four different season ($n = 284$) South West monsoon (SWM), Pre-monsoon (PRM), North East monsoon (NEM) and Post-monsoon (POM) (Fig. 1). Subsequently the samples were sealed and transported for analysis to the laboratory; they were stored at a temperature of 4 °C and filtered before analysis with a 0.45-micron filter. And the samples were analysed for chemical constituents as per the standard procedure (APHA 1995). The instruments and their specifications which were used for hydrogeochemical parameters are given (Table 1). In situ analysis such as electrical conductivity (EC), pH, total dissolved solids (TDS) and ($\text{HCO}_3$) bicarbonate were measured in the sampling site and cross-checked again in the laboratory. The samples obtained were analysed in the laboratory for important cations and anions. Titrimetric method was adopted for determining Ca, Mg, HCO$_3$, and Cl. Na and K were determined by flame photometer (ELICO CL 378).

![Image](Fig_1.png)

**Fig. 1** Lithology map of the study area with the location of the groundwater samples

| Sl No | Parameters | Chemical/Instrument used | Model/Provider | Detection limit/Accuracy and specifications |
|-------|------------|--------------------------|----------------|-------------------------------------------|
| 1     | Ca$^{2+}$  | 0.02 m EDTA/Burette      | 50,018/Riviera | GI: 0.1 mL, Volume: 50 mL, Accuracy/Tolerance: ±0.05 mL |
| 2     | Mg$^{2+}$  | 0.02 m EDTA/Burette      | 50,018/Riviera | GI: 0.1 mL, Volume: 50 mL, Accuracy/Tolerance: ±0.05 mL |
| 3     | Cl$^{-}$   | 0.06 N Silver nitrate solution/Burette | 50,018/Riviera | GI: 0.1 mL, Volume: 50 mL, Accuracy/Tolerance: ±0.05 mL |
| 4     | HCO$_3^-$  | 0.02 N H$_2$SO$_4$/Burette | 50,018/Riviera | GI: 0.1 mL, Volume: 50 mL, Accuracy/Tolerance: ±0.05 mL |
| 5     | Na$^+$; K$^+$ | FLAME PHOTOMETER       | CL 378 /Elco Limited, Hyderabad, India | 1–100 ppm |
| 6     | SO$_4^{2-}$ | UV–VIS SPECTROPHOTOMETER | DR6000/HACH, UK | 420 nm | 0.70 mg/L |
|       | PO$_4^{3-}$ |                          |                | 880 nm (OD) | 0–25 mg/L |
|       | NO$_3^-$   |                          |                | 275 nm | 0–10 mg/L |
|       | H$_4$SiO$_4$ |                         |                | 810 nm | 00–10 mg/L |
Fluoride was measured by the ion electrode (Orion 94–09, 96–09). UV-double beam spectrophotometer (DR 6000, HACH) was used to analyse NO₃, PO₄, SO₄ and H₄SiO₄ adopting standard techniques (APHA 1995, 1998). Each sample was analysed three times and the average was accounted. The precision of major ion analysis was calculated by using Eq. 1 (Freeze and Cherry 1979) by determining ionic balance error (IBE), and it was found that values fell within 5–10% (Fig. 2).

\[
\text{IBE} = \left[\frac{(\text{TA} - \text{TC})}{(\text{TA} + \text{TC})}\right] \times 100
\]

(1)

The detailed specifications of the analytical methodology are provided in the table. Values greater than the limit of detection are diluted and measured subsequently multiplied by the dilution factor. The PCA (Factor analysis) and the Pearson correlation analysis were determined by Social Sciences Statistical Package (SPSS) version 17.0. Vertical mapper along with Map info software (Professional 8.5) was used to prepare the spatial distribution maps. The calculation on water quality indices was obtained by the programme 'WATCLAST' (Chidambaram et al. 2003). The software includes Ca²⁺, Mg²⁺, K⁺, Na⁺, HCO₃⁻, Cl⁻, SO₄²⁻, H₂SiO₄, PO₄³⁻ (mg/l) concentrations, and other parameters, including TDS, EC and pH.

**Result and discussion**

**Water chemistry**

**pH**

The pH of the water governs the solubility and thereby the geochemical equilibrium. The pH is a metric of the availability (activity) of hydrogen ions (H⁺). The hydrogen ion is very small and can penetrate and destroy mineral structures so that dissolved components are added to the groundwater. pH varies from acidic to alkaline in nature, ranging from 5.54 to 8.41 (Table 2). In PRM, lowest pH was observed and highest during SWM.

![Analytical values were cross checked by plotting total cations and anions for all the four seasons](image)
Electrical conductivity (EC)

Higher the salt content, greater the electrical current flow would be. Electrical conductance is directly related to the abundance of charged ionic compounds (Hem 1985). The study area has electrical conductivity (EC) ranging from 326 to 15,550 μs/cm. Compared with other seasons, the highest EC value observed during SWM, it may be due to dissolution or leaching of the aquifer content, saline water influence or anthropogenic sources (Devaraj et al. 2018).

The attribute values of the specific locations were used to study the spatial variation. The general pattern of the dissolved ions in water is reflected by the spatial data of electrical conductivity. This provides us initially with first-hand data on the geochemically active regimes (Chidambaram et al. 2000; Anandhan et al. 2005; Srinivasamoorthy et al. 2004). The spatial variation of electrical conductivity with respect to samples from different seasons shows distribution of the higher values in the central part of the study area especially near the lithological contact and the hard rock region (Fig. 3).

Higher values of EC during PRM were observed along the SW and central portion of the study area. The EC ranges from 326 to 15,550 μs/cm during SWM and higher values were noted in the southern and NW part of the study area. The spatial distribution during NEM shows higher values in the NW region of the study area and in POM higher EC concentration was noted in the southern and SW parts. Season distribution of the values shows that the spatial coverage of EC values > 3000 μs/cm was observed in NEM. The higher EC values stretch along the Vellar River during NEM due to the dissolution and infiltration of domestic sewage and landfill leachates (Saxena et al. 2003). In general, seasonal variation of EC spatial representation shows that the southern part of the study area (PRM, SWM, NEM and POM) has higher values. The categorization of the seasonal variation in samples with respect to season is observed in Table 3. Also the fluctuation of EC irrespective with seasons showed in (Fig. 4) according to Richards (1954).

The percentage of groundwater samples in each category based on this classification indicates that 36.6% of PRM samples, 80% of SWM, 26.7% of NEM and 18.3% of POM samples represent “Fresh” category. Greater percentage of samples belonging to “Brackish” category was observed during PRM, followed by SWM, NEM and POM.

Total dissolved solids (TDS)

TDS is known as the residue of filtered water samples after evaporation. Bicarbonates, sulphate, chloride, calcium, magnesium, sodium, potassium, silica and nitrate are the major dissolved solids. TDS varies between 200 and 8710 mg/l with an average of 1626 mg/l during NEM. NEM shows higher TDS followed by SWM, POM and PRM, indicating groundwater dilution during the monsoon season. Samples were categorized into four classes based on Carroll (1962). Almost 47.8% of the SWM and POM samples represent “Fresh water” category and lesser percentage of samples represented this category during PRM, followed by SWM, NEM and POM.

### Table 2

| Parameters | PRM Max | PRM Min | PRM Avg | SWM Max | SWM Min | SWM Avg | NEM Max | NEM Min | NEM Avg | POM Max | POM Min | POM Avg | WHO 2011 Max | WHO 2011 Min |
|------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------------|---------------|
| Ca\(^{2+}\) | 304     | 16.0    | 74.1    | 272     | 8.00    | 59.5    | 328     | 28.0    | 113     | 380     | 14.0    | 113     | 75.0          |               |
| Mg\(^{2+}\) | 242     | 12.0    | 42.9    | 154     | 4.8     | 38.8    | 156     | 12.0    | 55.3    | 139     | 9.6     | 55.9    | 50.0          |               |
| Na\(^{+}\) | 1342    | 44.0    | 353     | 2471    | 53      | 359     | 227     | 11.8    | 96.9    | 347     | 11.0    | 72.3    | 200           |               |
| K\(^{+}\) | 235     | 4.00    | 31.9    | 352     | 1.3     | 44.7    | 86.2    | 1.1     | 13.4    | 68.5    | 0.20    | 9.05    | 12.0          |               |
| F\(−\) | 4.00    | 0.07    | 0.67    | 0.06    | 0.01    | 0.03    | 4.0     | 0.04    | 0.68    | 4.00    | 0.04    | 0.70    | 1.50           |               |
| Cl\(^{−}\) | 3172    | 53.2    | 446     | 4165    | 35.4    | 459     | 1205.3  | 53.2    | 346     | 869     | 30.45   | 209     | 250           |               |
| HCO\(_3\)^− | 878     | 183     | 366     | 750     | 89      | 387     | 788     | 137     | 411     | 1135    | 130.60  | 495     | 500           |               |
| NO\(_3\)^− | 475     | 3.00    | 120     | 380     | 5.00    | 94.2    | 321     | 0.13    | 25.5    | 120     | BDL     | 18.8    | 45.0          |               |
| PO\(_4\)^{3−} | 0.68    | BDL     | 0.05    | 1.53    | 0.01    | 0.12    | 22.9    | 0.04    | 4.07    | 0.51    | BDL     | 0.03    |               |               |
| SO\(_4\)^{2−} | 18.0    | 0.20    | 4.53    | 18.4    | 1.22    | 3.51    | 0.05    | BDL     | BDL     | 11.0    | 0.30    | 2.59    | 250           |               |
| H\(_2\)SiO\(_4\) | 231     | 5.20    | 120     | 242     | 18.0    | 174     | 174     | 22.0    | 102     | 170     | 26.00   | 87.7    |               |               |
| pH | 7.87    | 6.14    | 7.01    | 8.41    | 6.78    | 7.27    | 8.03    | 5.54    | 6.84    | 7.81    | 6.42    | 7.07    | 6.5–8.5       |               |
| EC | 13,430  | 436     | 2402    | 15,550  | 326     | 2644    | 15,400  | 668     | 3754    | 14,430  | 440     | 2657    | 500           |               |
| TDS | 5666    | 266     | 1232    | 7810    | 200     | 1405    | 8710    | 307     | 1626    | 5983    | 248     | 1167    | 500           |               |
| Temp˚C | 41.1    | 27.3    | 33.6    | 33.5    | 29.1    | 31.4    | 29.5    | 29.1    | 32.5    | 38.0    | 25.9    | 30.2    | 33.0          |               |

BDL below detection limit
Nearly 54.9% of the PRM samples fall in the “Fresh water” category.

Hydrogeochemical parameters

The average concentration of ions is observed in the order as depicted in Table 5. The calcium concentration ranges between 8 and 380 mg/l with an average of 113.35 mg/l; it is observed to be higher during POM. Mg$^{2+}$ varies between 4.80 and 242.40 mg/l, with an average of 55.90 mg/l and highest value was observed during PRM (Chidambaram 2000). The leaching of magnesium from mafic rocks, or even hypersthene found in charnockite, is primarily the source of magnesium in groundwater. Mg is important for plant and animal nutrition and serves as the key source of water hardness is magnesium, along with calcium in groundwater (Matthess 1982). The sodium concentration ranged from 11 to 2471 mg/l in the samples, with an average of 358.6 mg/l. Sodium concentration is higher in SWM and lower in NEM, suggesting the contribution from the sodium feldspar weathering along with dissolution and anthropogenic sources. In most fresh water aquifers, potassium is less in groundwater due to its mobility (Hens 1985) or due to ion exchange processes (Chidambaram 2000). K$^+$ varies between 0.20 and 352 mg/l and higher concentrations were noted in SWM, averaging 44.72 mg/l. Potassium is well within the prescribed limit and in most of the samples, with few anomalies due to urban landfill and fertilizer leaching, regardless of the seasons.

Cl$^-$ ranges from 30.5 to 4165 mg/l in samples, and higher concentrations were noted in SWM samples with an average of 458.85 mg/l. Some locations show that the chloride in groundwater originates from both natural and anthropogenic sources, exceeding the allowable limit. The use of inorganic fertilizers, leachate from landfills, and septic tank effluent and runoff may be due to this anomalies (Freeze and Cherry

![Fig. 3](https://example.com/fig3.png)

Fig. 3 The temporal variation of Electrical conductivity in the groundwater samples and their spatial distribution (all values in µs/cm)

| EC Values in µs/cm | PRM ($n = 71$) | SWM ($n = 71$) | NEM ($n = 71$) | POM ($n = 71$) |
|-------------------|----------------|----------------|----------------|----------------|
| Fresh             | $< 1500$       | 26             | 19             | 13             |
| Brackish          | 1500–3000      | 26             | 35             | 22             |
| Saline            | $> 3000$       | 19             | 17             | 36             |

| EC Values in µs/cm | PRM ($n = 71$) | SWM ($n = 71$) | NEM ($n = 71$) | POM ($n = 71$) |
|-------------------|----------------|----------------|----------------|----------------|
| Fresh             | $< 1500$       | 26             | 19             | 13             |
| Brackish          | 1500–3000      | 26             | 35             | 22             |
| Saline            | $> 3000$       | 19             | 17             | 36             |
In water, alkalinity is the indicator of its neutralization power (Chapelle et al. 1987), bicarbonate in water was attributed to $\text{H}_2\text{CO}_3$ dissociations. It is also produced due to the organic decomposition of atmospheric $\text{CO}_2$ released. Bicarbonate varies between 89 and 1134.6 mg/l, averaging 494.5 mg/l. Average $\text{HCO}_3^-$ values were observed to be in the following order of dominance POM, PRM, NEM and SWM, suggesting the contribution of the chemical weathering of silicate and carbonate as major source (Mondal and Singh 2004). The nitrate accumulation in groundwater is primarily due to the infiltration of sewage and leaching of animal dung and leakage from septic tanks through the soil to groundwater (Chidambaram 2000). Nitrogen is also from the household, fertilizer or nitrogen fixing bacteria. The nitrate concentration ranged from Below Detection Limit (BDL) to as high as 475 mg/l during PRM. In the monsoon season and also by agricultural activity, they accumulated and decomposed. Sulphate is generally found in small amounts (Singh et al. 1994) in groundwater, with the maximum acceptable limit is 400 mg/l (WHO 2004). The $\text{SO}_4^{2-}$ concentration varies between BDL and 18.4 mg/l and the mean concentration is 4.5 mg/l, with higher values observed during SWM. The dissolved sulphate ion contribution may also be attributable mineral dissolution, and other sources or due to bacterial fixation, fertilisers, and other anthropogenic sources (Anandhan 2005; Chidambaram et al. 2012).

The phosphate concentration ranges from BDL to 22.9 mg/l with higher concentration observed during NEM. $\text{PO}_4^{3-}$ has fluctuated without a clear pattern, regardless of space and time.

**Table 4** Water quality classification based on TDS Content by Carroll (1962)

| TDS in ppm   | Water quality     | No. of samples |
|--------------|-------------------|----------------|
|              |                   | PRM  | SWM  | NEM  | POM  |
| 0–1000       | Fresh water       | 39   | 34   | 29   | 34   |
| 1000–10,000  | Brackish water    | 32   | 37   | 42   | 37   |
| 10,000–100,000 | Salt Water     | –    | –    | –    | –    |
| > 100,000    | Brine             | –    | –    | –    | –    |

**Table 5** The order of dominance of cations and anions in different seasons

| Seasons | Cations | Anions                   |
|---------|---------|--------------------------|
| PRM     | $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ | $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{F}^- > \text{PO}_4^{3-}$ |
| SWM     | $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ | $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{F}^-$ |
| NEM     | $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ | $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{F}^- > \text{PO}_4^{3-}$ |
| POM     | $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ | $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{F}^- > \text{PO}_4^{3-}$ |
Groundwater fluoride toxicity is a result of many variables, such as fluorine-bearing mineral availability and solubility, temperature, $\text{Ca}^{2+}$ and $\text{HCO}_3^-$, pH concentration etc (Chandra et al. 1981). Groundwater with higher fluoride is common globally, and it is governed by composition minerals and physical properties of the aquifer matrix, pH, temperature, and the interaction with other ions (Tahaikt et al. 2008). In groundwater, F varies from 4 to 0.01 mg/l, least was observed during PRM, NEM and POM. Silica is an integral component of nearly all minerals. The silica concentration in the region varies from 5.2 to 242 mg/l with an average of 174 mg/l. In SWM, higher $\text{H}_4\text{SiO}_4$ concentrations were observed and least during PRM, NEM and POM, suggesting dissolution from source rock.

**Irrigation quality**

Groundwater suitability for agriculture purpose is primarily governed by Sodium Adsorption Ratio, Sodium percent, and Residual Sodium carbonate. Apart from these parameters, total sodium concentration and EC are considered as significant (Wilcox 1955).

**Sodium adsorption ratio**

The appropriateness of groundwater for irrigation depends on the impact on both plants and the soil and their mineral constituents in water. The effects of salts on soils have an indirect influence on plant growth due to changes in soil composition, permeability, and aeration. The alkali hazard is stated as “Sodium Adsorption Ratio” (SAR) and is commonly utilized to determine irrigation water quality. If the water quality is high in Na$^+$ and low in Ca$^{2+}$, the ion exchange sites that become saturated with Na$^+$ damage the soil structure due to the dispersion of the clay particles that decreases plant growth. The SAR is determined by using the following formula (Richard 1954).

\[
\text{SAR} = \frac{\text{Na}^+}{\sqrt{\left(\text{Ca}^{2+} + \text{Mg}^{2+}\right)/2}} \quad \text{(Concentrations are in meq/L)}
\]

(2)

In (Table 6), the classification is provided by categorizing it into excellent, good, reasonable, and bad. All samples were found to fall into excellent categories in all seasons, with the exception of a few PRM and SWM samples.

**Salinity hazard**

The water salinity hazard as calculated by electric conductivity (EC) is extremely powerful parameter in determining the utility of water on crop productivity. Salinization can be caused by water with high electrical conductivity (Ghaffor et al. 1990, 1993). High salinity is unsafe water and is harmful to plants. Soils with high overall salinity levels are known as saline soils. High salt concentrations in the soil can result in a state of "physiological" drought. The salinity of water is normally determined by either TDS (total dissolved solids) or EC (electrical conductivity).

Salinity is also increases concentration of specific ions and osmotic pressure for growth and controls the plant yield (Fracios 1989). Studies of waters are categorized into four key groups (Richard 1954) based on electrical conductivity. The USSL groundwater classification for irrigation purposes (Fig. 5) was used by the United State Salinity Laboratory to acquire the irrigation water classification. This plot exhibits that majority of samples are represented in categories C3-S2, C3-S3, and C4-S4 (high salinity hazard) during the PRM and SWM and other seasonal samples of NEM, POM vary from C3-S1 and C4-S1 (low to very high salinity risk) of which the highest salinity is observed in PRM and SWM may be due to the leaching of secondary salts.

**Sodium percentage**

Classification of sodium percent is categorized as excellent, fine, acceptable, questionable, and unsuitable (Wilcox 1955). The content of Na is an important factor for evaluating appropriateness for farming purposes. The combination of sodium with CO$_3$ contributes for the development of alkaline soils, and the combination of Na with Cl leads to the formation of saline soils. The development of these soil types hinders the plant growth (Karmegam et al. 2010; Thiyva et al. 2013; Devaraj et al. 2016). An upper limit of 60% of sodium in water is permitted for agricultural purposes. The higher percentage of sodium is mainly owing to greater water residence time, dissolution of minerals, and due to the leaching of the fertilizers applied (Qiyan and Baoping 2002; SubbaRao et al. 2002). Na percent is classified into two categories, as safe and dangerous (Table 6). Groundwater classification for agricultural purpose using Na% was determined by,

\[
\text{Na}\% = \left[\left(\text{Na} + \text{K}\right) / \left(\text{Ca} + \text{Mg} + \text{Na} + \text{K}\right)\right] \times 100 \quad \text{(Concentrations are in meq/L)}
\]

(3)

Similarly, in PRM, 26% of samples, 18% of samples during SWM, 98% of NEM samples and 100% of samples during POM fall into the safe category. Most of the samples from PRM and SWM are unsuitable for irrigation purposes.

The Wilcox diagram displays against Na% and EC values (Fig. 8). The figure demonstrates approximately, 85% of the
| Category                      | Grade   | PRM N=71 | SWM N=71 | NEM N=71 | POM N=71 |
|-------------------------------|---------|----------|----------|----------|----------|
| Na% Wilcoxr (1955)           |         |          |          |          |          |
| Excellent                    | 0–20    | 0        | 0        | 14       | 28       |
| Good                         | 20–40   | 4        | 0        | 42       | 42       |
| Permissible                  | 40–60   | 15       | 13       | 14       | 1        |
| Doubtful                     | 60–80   | 39       | 45       | 1        | 0        |
| Unsuitable                   | > 80    | 13       | 13       | 0        | 0        |
| Na%                          |         |          |          |          |          |
| Safe                         | <60     | 19       | 13       | 70       | 71       |
| Unsafe                       | > 60    | 52       | 58       | 1        | 0        |
| S.A.R. Richards (1954)       |         |          |          |          |          |
| Excellent                    | 0–10    | 52       | 51       | 71       | 71       |
| Good                         | 10–18   | 16       | 15       | 0        | 0        |
| Fair                         | 18–26   | 3        | 3        | 0        | 0        |
| Poor                         | > 26    | 0        | 2        | 0        | 0        |
| R.S.C. Richards(1954)        |         |          |          |          |          |
| Good                         | < 1.25  | 51       | 36       | 68       | 63       |
| Medium                       | 1.25–2.5| 9        | 10       | 3        | 4        |
| Bad                          | > 2.5   | 11       | 25       | 0        | 4        |
| EC Wilcox (1955)             |         |          |          |          |          |
| Excellent                    | < 250   | 0        | 0        | 0        | 0        |
| Good                         | 250–750 | 23       | 4        | 17       | 6        |
| Permissible                  | 750–2250| 43       | 39       | 40       | 35       |
| Doubtful                     | 2250–5000| 4        | 18       | 10       | 22       |
| Unsuitable                   | > 5000  | 1        | 10       | 3        | 7        |
| USGS Hardness                |         |          |          |          |          |
| Soft                         | < 75    | 0        | 1        | 0        | 0        |
| Slightly Hard                | 75–150  | 5        | 14       | 0        | 0        |
| Moderately Hard              | 150–300 | 31       | 32       | 10       | 10       |
| Very Hard                    | > 300   | 203      | 256      | 229      | 229      |
| IBE Schoeller (1965)         |         |          |          |          |          |
| (Na + k)rock- > Ca/Mg g.w    | 60      | 61       | 5        | 14       |          |
| (Na + k)g.w.- > Ca/Mg rock   | 11      | 10       | 66       | 57       |          |
| Schoeller Classification (1967) |   |          |          |          |          |
| Type I                       | 71      | 71       | 71       | 71       |          |
| Type II                      | 0       | 0        | 0        | 0        |          |
| Type III                     | 0       | 0        | 0        | 0        |          |
| Type IV                      | 0       | 0        | 0        | 0        |          |
| Corrosivity Ratio (1990)     |         |          |          |          |          |
| Safe                         | < 1     | 43       | 37       | 33       | 14       |
| Unsafe                       | > 1     | 28       | 34       | 38       | 57       |
| Chloride Classification      |         |          |          |          |          |
| Extremely fresh              |         |          |          |          |          |
| Very fresh                   | 0       | 0        | 0        | 0        | 0        |
| Fresh                        | 0       | 0        | 0        | 0        | 0        |
| Fresh Brackish               | 8       | 18       | 15       | 34       |          |
| Brackish                     | 24      | 17       | 22       | 22       |          |
| Brackish-salt                | 33      | 29       | 29       | 15       |          |
| Salt                         | 6       | 7        | 2        | 0        |          |
| Hyperhaline                  | 0       | 0        | 0        | 0        | 0        |
Table 6 (continued)

| Category                  | PRM N = 71 | SWM N = 71 | NEM N = 71 | POM N = 71 |
|---------------------------|------------|------------|------------|------------|
| TDS Classification(USSL,1954) |            |            |            |            |
| < 200                     | 0          | 0          | 0          | 0          |
| 200–500                   | 1          | 6          | 0          | 10         |
| 500–1500                  | 25         | 42         | 13         | 43         |
| 1500–3000                 | 26         | 15         | 22         | 16         |
| Cation Facies             |            |            |            |            |
| Ca–Mg Facies              | 0          | 0          | 16         | 27         |
| Ca–Na Facies              | 67         | 65         | 55         | 44         |
| Na–Ca Facies              | 4          | 6          | 0          | 0          |
| Na Facies                 | 0          | 0          | 0          | 0          |
| Anion Facies              |            |            |            |            |
| HCO3 Facies               | 0          | 0          | 0          | 0          |
| HCO3–Cl–SO4 Facies        | 0          | 0          | 0          | 0          |
| Cl–SO4–HCO3 Facies        | 60         | 58         | 66         | 71         |
| Cl Facies                 | 11         | 13         | 5          | 0          |
| Hardness Classification (Handa 1964) |            |            |            |            |
| Permanent Hardness (NCH)  |            |            |            |            |
| A1                        | 3          | 0          | 17         | 34         |
| A2                        | 3          | 1          | 37         | 18         |
| A3                        | 33         | 26         | 2          | 0          |
| Temporary Hardness (CH)   |            |            |            |            |
| B2                        | 15         | 28         | 1          | 0          |
| B2                        | 15         | 28         | 1          | 0          |
| B3                        | 16         | 15         | 0          | 0          |

Fig. 5  USSL diagram representing irrigation quality of groundwater samples for the four seasons
groundwater samples are fall into excellent to good condition, 13% of the samples fall in the permissible to doubtful condition and 2% sample belongs to the good to a permissible field.

Residual sodium carbonate (RSC)

The excess carbonate will increase the precipitation tendency of CaCO$_3$ in the sediments, which in turn will enhance the Na concentration in water. In addition, it is possible that Na will be controlled during the ion dispersion process (Emerson and Bakker 1973). RSC also impacts the absorption nutrients by the plants (Kanwar and Chaudhry 1968). Thus, the alkaline land affects the utility of groundwater for irrigation.

RSC is categorized into three groups as “Good”, “Medium”, and “Poor”, according to Richard (1954) (Table 6). 72% of samples fall in good category during PRM, 12% fall in medium and 15% fall in the poor category. In SWM, 51% of samples fall into good and 14% fall in poor categories. During NEM, 35% of samples represent “good”, 95% in “medium” and 4 percent of samples reflect a “poor” class. In POM, 89% of samples fall in “good category”, 6% in “moderate” and 6% of samples are poor.

Corrosivity ratio

Water is being brought through metal pipelines for many purposes to the study area. The appropriateness of the groundwater for transport is based on the sample’s corrosive nature. The value of $< 1$ is safe and the value of $> 1$ is dangerous. The CR is calculated by the following formula:

$$\text{CR} = \left\{ \left( \text{Cl}/35.5 \right) + \left( \text{SO}_4/96 \right) \right\}/2(\text{HCO}_3) \times 100. \text{(Concentrations are in meq/L)}$$  \hspace{1cm} (4)

$$\text{CA I} = \text{Cl} - (\text{Na + K})/\text{Cl}. \text{(Concentrations are in meq/L)} \hspace{1cm} (7)

and

$$\text{CA II} = (\text{Na + K})/(\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3). \text{(Concentrations are in meq/L)} \hspace{1cm} (8)$$

61% of samples during PRM, 52% of samples of SWM, 46% of samples of NEM, and 20% of samples in POM are in safe category.

Chloro-alkaline indices

The “Chloro-Alkaline Indices” (Schoeller 1977) unravels the geochemical interaction between aquifer matrix and the groundwater media during residence time in the aquifer and along the groundwater flow.

61% of samples during PRM, 52% of samples of SWM, 46% of samples of NEM, and 20% of samples in POM are in safe category.

Permeability index

A water quality infiltration problem is reported when the penetration rate for the water decreases or even after the rainfall event water stays on the soil surface for a long period of time or infiltrates too slowly to provide the crop with enough water to sustain appropriate yields. Doneen (1948) derived the permeability index (PI) parameter of determining the suitability of water for irrigation as:

$$\text{PI} = \left\{ \left[ \{\text{Na} + (\sqrt{\text{HCO}_3})\} / (\text{Ca + Mg + Na}) \right\} \times 100. \text{(Concentrations are in meq/L)} \right.$$  \hspace{1cm} (6)

The Permeability Index is an important factor for evaluating the soil-related quality of irrigation water for agricultural improvement (Thilagavathi et al. 2012; Adimalla and Venkatayogi 2018). If there is a micronutrient deficiency, it can lead to an increase in toxicity associated with HCO$_3$. The Permeability Index of the groundwater sample calculates the cumulative intensity of the total cation content of Na and HCO$_3$. Permeability Index values were plotted along with sodium adsorption ratio. Most samples irrespective of the seasons represent Class I (Figs. 6, 7 and 8) representing the permissible category, with only a few samples PRM, SWM and NEM and SWM in Class II and one SWM sample representing Class III, (poor category). It is important to note that there is a linear distribution in Class I between SAR and PI and it increases in Class II and III.
To explain the groundwater metasomatism, Schoeller (1977) suggested “Index of Base Exchange” (IBE). There are some minerals capable of adsorption and cation exchange with those in groundwater (clay minerals, glauconite, zeolite and organic substances). The exchange of cations plays a

\[ \text{Na}^+ + \text{K}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} \]

Fig. 6 Modified Doneen’s plot for determining the appropriateness of groundwater for different seasons (after Manivannan 2011)

![Modified Doneen’s plot for determining the appropriateness of groundwater for different seasons](image_url)

Fig. 7 Doneen’s plot for determining the appropriateness of groundwater for different seasons

![Doneen’s plot for determining the appropriateness of groundwater for different seasons](image_url)

Fig. 8 Wilcox diagram representing irrigation quality of groundwater samples for the four seasons

![Wilcox diagram representing irrigation quality of groundwater samples for the four seasons](image_url)
major role in the Na+ K in the groundwater. The positive ratio reflects the probability of Ca+ Mg (water) exchange to Na+ K (mineral) as 84%, 85%, 7% and 20% of samples are represent this process during PRM, SWM, NEM and POM respectively.

Piper plot

According to the seasonal variation, the water type of the sample migrates corresponding to the variation in composition with respect to seasons (Fig. 9). Na–Ca–Cl–HCO₃ (PRM) to Na–Cl (SWM) to Ca–HCO₃ (NEM) to Mixed Na–Mg–Cl–HCO₃ (POM). In order to understand groundwater flow and geochemistry (Dalton and Upchurch 1978) is planned to delineate variability. In the POM season, sample persistence in the field of Ca²⁺–Mg²⁺–HCO₃⁻ type can be seen indicating natural recharge phase, mainly owing to interaction between groundwater and the aquifer matrix, Chidambaram 2000, Drever 1997). Majority of the POM samples show dominance of Ca²⁺–Na⁺–HCO₃⁻–Cl⁻-facies. Due to irrigation and over-exploitation processes, these samples can be affected by farming processes (Thivya et al. 2013) during this period. Subsequently, in PRM and SWM, Na⁺–Ca²⁺–HCO₃⁻–Cl⁻ type was inferred due to the integrated process like ion exchange process and natural weathering (Thivya et al. 2015). Lesser Ca²⁺ and Mg²⁺ in the groundwater samples reflect ion exchange of Na⁺ from aquifer matrix during pre-monsoon season.

Statistical analysis

Correlation matrix

Correlation analysis and PCA were adopted for the statistical interpretation. This PCA analysis is used to identify the source of a particular ion by correlating each other (Chidambaram et al. 2014). The correlation shows that there is an excellent correlation observed between Ca–Mg, Ca–Na, Ca–Cl, Mg–Cl, Na–Cl and SO₄ in PRM. There is a weak association between other parameters like pH, F, PO₄, SO₄ and H₂SiO₄. Cl displays a strong correlation with Ca, Mg and HCO₃, suggesting secondary salt leaching, and chemical weathering suggest major correlation of HCO₃ with Ca, Mg and pH (Chidambaram et al. 2008). The weak positive association between SO₄, PO₄, NO₃ and H₂SiO₄ demonstrates the effect of farming activities.

The connection between Ca and Mg, Na, Cl, SO₄, EC, between Mg and Na, SO₄, EC, between Na and Cl, NO₃, SO₄, EC, between Cl and SO₄, EC, between NO₃ and EC also between SO₄ and EC, show strong to excellent correlation during SWM (Table 8) suggesting the processes of leaching and weathering. Chloride demonstrates a strong association with Mg, and Na reiterating the process of secondary salt leaching. Chemical weathering is demonstrated by the important association of HCO₃ with Mg and K (Srinivasamoorthy et al. 2009). The effect of dilution may be due to a weak positive correlation between SO₄, PO₄, NO₃ and other ions.

There is a strong correlation between Ca and Cl, Mg, EC; Mg with Cl; EC with Na and Cl (Table 7) during NEM. There is a weak correlation with all the other ions between SO₄, PO₄ and H₂SiO₄. Cl displays a strong correlation with Ca, Mg, Na and HCO₃, suggesting secondary salt leaching and correlation of HCO₃ with other ions (Ca, Mg, Na and K) reflect chemical weathering (Karmegam et al. 2012). There is a strong correlation between Ca and Na, Cl, HCO₃, PO₄, EC; Mg with Na, Cl and EC; Na with Cl, HCO₃, PO₄ and EC; Cl with PO₄, EC, HCO₃ and PO₄ showing a positive correlation with EC. Cl shows a good correlation with Ca, Mg, Na and HCO₃ suggesting secondary salt leaching and correlation between HCO₃ and Ca, Mg, Na, and K suggests chemical weathering. A strong correlation with Ca, Cl, HCO₃, Na, K and PO₄ suggests the impact of anthropogenic sources on the system.

Factor analysis (pre-monsoon)

FA has resulted in four important variables that explain 64.2% of the pre-monsoon dataset’s total data variability (TDV). The ion association in Factor I represents Ca, Mg, Na, and Cl with a TDV of 30.9%, suggesting secondary salt leaching. This aspect clearly demonstrates that the influence
Table 7  Correlation matrix of hydrogeochemical parameters for northeast and post-monsoon seasons

|       | Ca   | Mg   | Na   | K    | F    | Cl     | HCO₃  | NO₃  | PO₄  | SO₄  | H₂SiO₄ | pH   | EC     | Temp  |
|-------|------|------|------|------|------|--------|-------|------|------|------|--------|------|--------|-------|
| NEM   |      |      |      |      |      |        |       |      |      |      |        |      |        |       |
| Ca    | 1    |      |      |      |      |        |       |      |      |      |        |      |        |       |
| Mg    | 0.68 | 1    |      |      |      |        |       |      |      |      |        |      |        |       |
| Na    | 0.34 | 0.39 | 1    |      |      |        |       |      |      |      |        |      |        |       |
| K     | 0.22 | 0.18 | 0.46 | 1    |      |        |       |      |      |      |        |      |        |       |
| F     | −0.13| −0.13| 0.08 | −0.01| 1    |        |       |      |      |      |        |      |        |       |
| Cl    | 0.79 | 0.82 | 0.69 | 0.429| −0.01| 1      |       |      |      |      |        |      |        |       |
| HCO₃  | 0.24 | 0.13 | 0.03 | −0.05| 0.43 | −0.08  | 1     |      |      |      |        |      |        |       |
| NO₃   | 0.25 | 0.32 | 0.06 | 0.191| −0.05| 0.11   | 0.43  |      |      |      |        |      |        |       |
| PO₄   | 0.29 | 0.37 | 0.25 | 0.143| 0.19 | 0.34   | 0.08  |      |      |      |        |      |        |       |
| SO₄   | 0.02 | −0.18| 0.04 | −0.04| 0.14 | 0.00   | −0.21 |      |      |      |        |      |        |       |
| H₂SiO₄| −0.33| −0.35| −0.21| 0.005| −0.04| −0.30  | −0.10 |      |      |      |        |      |        |       |
| pH    | −0.12| −0.19| −0.15| −0.07| 0.01 | −0.19  | 0.17  |      |      |      |        |      |        |       |
| EC    | 0.56 | 0.69 | 0.60 | 0.185| −0.07| 0.72   | 0.18  |      |      |      |        |      |        |       |
| Temp  | −0.05| −0.06| −0.17| −0.04| 0.19 | −0.09  | −0.04 |      |      |      |        |      |        |       |
| POM   |      |      |      |      |      |        |       |      |      |      |        |      |        |       |
| Ca    | 1    |      |      |      |      |        |       |      |      |      |        |      |        |       |
| Mg    | 0.28 | 1    |      |      |      |        |       |      |      |      |        |      |        |       |
| Na    | 0.58 | 0.57 | 1    |      |      |        |       |      |      |      |        |      |        |       |
| K     | 0.49 | 0.13 | 0.51 | 1    |      |        |       |      |      |      |        |      |        |       |
| F     | −0.02| 0.04 | 0.25 | 0.02 | 1    |        |       |      |      |      |        |      |        |       |
| Cl    | 0.68 | 0.66 | 0.80 | 0.39 | 0.03 | 1      |       |      |      |      |        |      |        |       |
| HCO₃  | 0.54 | 0.49 | 0.67 | 0.39 | 0.21 | 0.42   | 1     |      |      |      |        |      |        |       |
| NO₃   | 0.37 | 0.08 | 0.30 | 0.26 | 0.06 | 0.23   | 0.28  |      |      |      |        |      |        |       |
| PO₄   | 0.63 | 0.21 | 0.59 | 0.43 | 0.17 | 0.56   | 0.42  |      |      |      |        |      |        |       |
| SO₄   | 0.19 | 0.26 | 0.41 | 0.33 | −0.02| 0.35   | 0.19  |      |      |      |        |      |        |       |
| H₂SiO₄| −0.03| −0.18| −0.21| −0.02| 0.20 | −0.16  | −0.13 |      |      |      |        |      |        |       |
| pH    | −0.28| −0.02| 0.21 | −0.02| 0.29 | −0.10  | 0.15  |      |      |      |        |      |        |       |
| EC    | 0.70 | 0.58 | 0.91 | 0.53 | 0.11 | 0.83   | 0.60  |      |      |      |        |      |        |       |
| Temp  | 0.07 | −0.04| 0.25 | 0.11 | 0.25 | 0.02   | 0.04  |      |      |      |        |      |        |       |
| POM   |      |      |      |      |      |        |       |      |      |      |        |      |        |       |
| Ca    | 1    |      |      |      |      |        |       |      |      |      |        |      |        |       |
| Mg    |      | 1    |      |      |      |        |       |      |      |      |        |      |        |       |

NEM
Ca
Mg
Na
K
F
Cl
HCO₃
NO₃
PO₄
SO₄
H₂SiO₄
pH
EC
Temp

POM
Ca
Mg
of domestic sewage source (Ruiz et al. 1990; Voudouris et al. 1997). This may also be due to the influence of high Na+, as calcareous and dolomite has Na+ as a result of deposition during the shallow marine conditions and due to the existence of skeletal remains (Billings and Ragland 1968). In the hydrogeochemical setting, factor II indicates (Table 9) the effect of Na, NO3 and SO4. The loading of nitrate and sulphate concentration is primarily due to the weathering of the gypsum found in the cretaceous formation. Factor III with 11.3% of total data variability demonstrates positive loading of K, PO4 indicating human influence such as septic tanks, residential water softeners, and fertilizer (Vengosh and Keren 1996). Factor IV shows F and HCO3 enrichments with TDV 7.87% (Table 9). The loading of HCO3 and F is due to the high alkaline water, favouring release mechanism and enhancing the mobility of F ions in the groundwater.

Factor analysis (southwest monsoon)

Four factors with eigenvalue greater than 1 were extracted during this season. The total data variability of 39.9% was observed for first factor with loadings of EC, Ca, Mg, Na, Cl, SO4 suggesting secondary salt leaching (Tables 8, 9). Factor II (11.2% TDV) has a loading of F and HCO3. Higher positive loading of F and HCO3 and negative loading of pH and temperature show that the pH of the carbonate rocks regulates the release of F during this season. Factor III shows 8.8% TDV with loadings of H4SiO4 and temperature reflecting the thermodynamic constrains on the release of silica to the groundwater. 7.7% of TDV with positive loading of PO4 and K was observed in factor IV, which suggests anthropogenic sources as discussed in the previous season (Vengosh and Keren 1996).

Factor analysis (northeast monsoon)

The season data shows four prominent factors and the Factor I is expressed by a TDV of 31.3% with a positive loading of electrical conductivity, Ca2+, Mg2+, Na+ and Cl measured in groundwater suggest that the adsorbed or other types of solid solution within the geological matrix join the aqueous media upon dissolution of the matrix. It could also be because that the Cl in groundwater is leached from the sediments deposited in marine environments. However, the connate sea water may be washed out due to several reasons within marine sediments, including the aquifer properties like permeability and porosity, the sedimentary basin structure, and distance from the region of recharge (Johns 1968). A TDV of 11.8% was observed for factor II (Table 9) with a positive NO3− loading suggesting mixing of domestic wastewater or other anthropogenic activity. The positive loading of Na and K suggesting intense weathering in Factor III (Prasanna et al. 2009). The positive loadings of F and pH were observed as fourth factor; similar process was discussed in previous season.

Factor analysis (post-monsoon)

The maximum number of factors was extracted in this season due to the geochemical complexity with a TDV of 72.43%. Ca, Na, K, Cl, HCO3, PO4 and EC (Table 9) reflect Factor I and as discussed earlier the factor explains the dissolution of secondary salts. Mg, Cl, EC with 11.5% of TDV is loaded in Factor II, which represents diffuse groundwater pollution due to agricultural practices (especially in the areas utilizing dolomite as neutralizers, agricultural additives). SO4 and temperature, indicating the temperature controlled factor, are expressed by factor III with 9.2% TDV. The pH shows the dominance in the factor IV representing the base ion exchange and Factor V was loaded with H4SiO4 reflecting
Table 8 Correlation matrix of hydrogeochemical parameters for pre- and southwest monsoon seasons

|     | Ca    | Mg    | Na    | K     | F     | Cl     | HCO₃   | NO₃   | PO₄   | SO₄   | H₂SiO₄ | pH     | EC     | Temp   |
|-----|-------|-------|-------|-------|-------|--------|--------|-------|-------|-------|--------|--------|--------|--------|
| **PRM** |       |       |       |       |       |        |        |       |       |       |        |        |        |        |
| Ca  | 1     |       |       |       |       |        |        |       |       |       |        |        |        |        |
| Mg  | 0.71  | 1     |       |       |       |        |        |       |       |       |        |        |        |        |
| Na  | 0.52  | 0.64  | 1     |       |       |        |        |       |       |       |        |        |        |        |
| K   | 0.18  | 0.13  | 0.10  | 1     |       |        |        |       |       |       |        |        |        |        |
| F   | −0.17 | −0.09 | 0.22  | −0.15 | 1     |        |        |       |       |       |        |        |        |        |
| Cl  | 0.76  | 0.83  | 0.88  | 0.05  | 0.00  | 1      |        |       |       |       |        |        |        |        |
| HCO₃| −0.03 | 0.17  | 0.39  | 0.07  | 0.29  | 0.19   | 1      |       |       |       |        |        |        |        |
| NO₃ | 0.15  | 0.20  | 0.48  | 0.21  | 0.28  | 0.25   | 0.20   |       |       |       |        |        |        |        |
| PO₄ | 0.06  | 0.02  | 0.04  | 0.42  | −0.06 | −0.01  | −0.04  |       |       |       |        |        |        |        |
| SO₄ | 0.38  | 0.30  | 0.53  | 0.21  | 0.32  | 0.41   | 0.14   |       |       |       |        |        |        |        |
| H₂SiO₄| 0.00 | −0.07 | −0.16 | 0.09  | 0.12  | −0.16  | −0.04  |       |       |       |        |        |        |        |
| pH  | −0.59 | −0.40 | −0.12 | −0.18 | 0.24  | −0.31  | −0.01  |       |       |       |        |        |        |        |
| EC  | 0.45  | 0.44  | 0.57  | 0.07  | 0.10  | 0.59   | 0.07   |       |       |       |        |        |        |        |
| Temp| 0.09  | −0.01 | −0.06 | −0.06 | −0.13 | 0.02   | −0.05  |       |       |       |        |        |        |        |
| **SWM** |     |       |       |       |       |        |        |       |       |       |        |        |        |        |
| Ca  | 1     |       |       |       |       |        |        |       |       |       |        |        |        |        |
| Mg  | 0.65  | 1     |       |       |       |        |        |       |       |       |        |        |        |        |
| Na  | 0.65  | 0.65  | 1     |       |       |        |        |       |       |       |        |        |        |        |
| K   | 0.29  | 0.12  | 0.01  | 1     |       |        |        |       |       |       |        |        |        |        |
| F   | 0.07  | 0.18  | 0.27  | −0.19 | 1     |        |        |       |       |       |        |        |        |        |
| Cl  | 0.78  | 0.76  | 0.95  | 0.10  | 0.17  | 1      |        |       |       |       |        |        |        |        |
| HCO₃| 0.00  | 0.18  | 0.26  | −0.11 | 0.32  | 0.10   | 1      |       |       |       |        |        |        |        |
| NO₃ | 0.41  | 0.42  | 0.61  | 0.20  | 0.23  | 0.53   | 0.30   |       |       |       |        |        |        |        |
| PO₄ | −0.07 | −0.11 | −0.08 | 0.23  | −0.09 | −0.10  | 0.11   |       |       |       |        |        |        |        |
| SO₄ | 0.68  | 0.70  | 0.86  | 0.10  | 0.29  | 0.87   | 0.15   |       |       |       |        |        |        |        |
| H₂SiO₄| −0.16| −0.24 | −0.36 | 0.13  | 0.01  | −0.32  | −0.07  |       |       |       |        |        |        |        |
| pH  | −0.52 | −0.43 | −0.26 | −0.20 | −0.01 | −0.37  | −0.01  |       |       |       |        |        |        |        |
| EC  | 0.76  | 0.79  | 0.93  | 0.15  | 0.27  | 0.95   | 0.19   |       |       |       |        |        |        |        |
| Temp| 0.15  | 0.14  | 0.05  | 0.07  | −0.05 | 0.09   | 0.07   |       |       |       |        |        |        |        |

|     | NO₃   | PO₄   | SO₄   | H₂SiO₄ | pH    | EC    | Temp   |
|-----|-------|-------|-------|--------|-------|-------|--------|
| **PRM** |       |       |       |        |       |       |        |
| Ca  | 1     |       |       |        |       |       |        |
| Mg  |       | 1     |       |        |       |       |        |
| Na  |       |       | 1     |        |       |       |        |
| K   |       |       |       | 1      |       |       |        |
| F   |       |       |       |        | 1     |       |        |
| Cl  |       |       |       |        |       | 1     |        |
| HCO₃|       |       |       |        |       |       | 1      |
| NO₃ | 0.06  | 1     |       |        |       |       |        |
| PO₄ | 0.48  | −0.12 | 1     |        |       |       |        |
| SO₄ | −0.02 | 0.35  | −0.28 | 1      |       |       |        |
| H₂SiO₄| −0.01| −0.09 | −0.07 | −0.23  | 1     |       |        |
| pH  | 0.29  | −0.04 | 0.48  | −0.24  | −0.01 | 1     |        |
| EC  | −0.18 | −0.07 | −0.12 | −0.06  | −0.09 | −0.12 | 1      |
| Temp|       |       |       |        |       |       |        |

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Table 8 (continued)

|        | NO3 | PO4 | SO4 | H4SiO4 | pH  | EC  | Temp |
|--------|-----|-----|-----|--------|-----|-----|------|
| Na     |     |     |     | 1      |     |     |      |
| K      |     |     |     |        |     |     |      |
| F      |     |     |     |        |     |     |      |
| Cl     |     |     |     |        |     |     |      |
| HCO3   |     |     |     |        |     |     |      |
| NO3    |     | -0.04 |     | 1      |     |     |      |
| PO4    | 0.51 |     | -0.08 |       |     |     |      |
| SO4    |     | 0.16 |     | -0.35 |     |     |      |
| H4SiO4 | -0.15 |     |     |        |     |     |      |
| pH     | -0.24 | 0.17 |     | -0.11 |     |     |      |
| EC     | 0.62 |     | 0.82 | -0.33 | -0.38 |     | 1    |
| Temp   | -0.04 | 0.05 | 0.06 | 0.15  | -0.15 | 0.10 | 1    |

Table 9  Factor analysis of the PRM, SWM, NEM and POM samples (Varimax rotated)

|        | PRM     |       |       |       | SWM     |       |       |       | POM     |       |
|--------|---------|-------|-------|-------|---------|-------|-------|-------|---------|-------|
|        | 1       | 2     | 3     | 4     | 1       | 2     | 3     | 4     | 1       | 2     |
| Ca     | 0.85    | 0.29  | 0.10  | -0.17 | 0.83    | -0.18 | 0.26  | 0.06  |
| Mg     | 0.84    | 0.27  | -0.03 | 0.06  | 0.81    | 0.07  | 0.18  | -0.07 |
| Na     | 0.58    | 0.60  | -0.06 | 0.38  | 0.91    | 0.22  | -0.10 | -0.03 |
| K      | 0.05    | 0.31  | 0.72  | -0.20 | 0.21    | -0.32 | 0.25  | 0.66  |
| F      | -0.22   | 0.21  | -0.07 | 0.76  | 0.16    | 0.73  | 0.05  | -0.22 |
| Cl     | 0.82    | 0.44  | -0.13 | 0.11  | 0.96    | 0.02  | 0.01  | -0.03 |
| HCO3   | 0.16    | 0.06  | -0.06 | 0.69  | 0.11    | 0.77  | 0.02  | 0.15  |
| NO3    | 0.04    | 0.56  | 0.22  | 0.38  | 0.62    | 0.32  | -0.01 | 0.20  |
| PO4    | 0.03    | -0.02 | 0.80  | -0.02 | -0.12   | 0.12  | -0.07 | 0.84  |
| SO4    | 0.14    | 0.82  | -0.01 | 0.14  | 0.89    | 0.16  | -0.09 | -0.02 |
| H4SiO4 | 0.10    | -0.47 | 0.58  | 0.33  | -0.41   | 0.06  | 0.64  | 0.22  |
| pH     | -0.71   | 0.24  | -0.25 | 0.10  | -0.43   | 0.17  | -0.65 | 0.14  |
| EC     | 0.36    | 0.64  | -0.15 | 0.02  | 0.95    | 0.13  | 0.04  | 0.01  |
| Temp   | 0.18    | -0.20 | -0.20 | -0.23 | 0.06    | 0.10  | 0.62  | 0.029 |

|        | NEM     |       |       |       | POM     |       |       |       |        |       |
|--------|---------|-------|-------|-------|---------|-------|-------|-------|-------|-------|
|        | 1       | 2     | 3     | 4     | 1       | 2     | 3     | 4     | 1       | 2     |
| Ca     | 0.76    | 0.13  | 0.08  | -0.17 | 0.85    | 0.15  | 0.10  | -0.26 | 0.04    |
| Mg     | 0.83    | 0.24  | 0.10  | -0.22 | 0.28    | 0.85  | -0.05 | 0.09  | -0.09   |
| Na     | 0.51    | -0.13 | 0.67  | 0.00  | 0.72    | 0.47  | 0.26  | 0.33  | -0.14   |
| K      | 0.13    | 0.05  | 0.72  | -0.21 | 0.63    | -0.02 | 0.35  | -0.08 | -0.03   |
| F      | -0.14   | 0.11  | 0.32  | 0.71  | 0.19    | -0.09 | 0.06  | 0.68  | 0.31    |
| Cl     | 0.83    | -0.08 | 0.40  | -0.25 | 0.70    | 0.56  | 0.07  | -0.04 | 0.05    |
| HCO3   | 0.16    | 0.62  | -0.08 | 0.45  | 0.62    | 0.30  | 0.03  | 0.30  | -0.17   |
| NO3    | 0.13    | 0.83  | 0.10  | -0.18 | 0.38    | -0.18 | 0.47  | -0.11 | -0.49   |
| PO4    | 0.58    | 0.01  | -0.02 | 0.10  | 0.87    | -0.05 | -0.16 | 0.10  | -0.02   |
| SO4    | -0.03   | -0.70 | -0.02 | -0.04 | 0.12    | 0.28  | 0.81  | -0.06 | -0.05   |
| H4SiO4 | -0.58   | 0.07  | 0.30  | -0.03 | -0.05   | 0.15  | 0.11  | -0.02 | 0.86    |
| pH     | -0.02   | -0.07 | -0.16 | 0.69  | -0.14   | 0.00  | 0.05  | 0.82  | -0.21   |
| EC     | 0.82    | 0.08  | 0.27  | 0.01  | 0.73    | 0.50  | 0.33  | 0.08  | -0.09   |
| Temp   | -0.01   | -0.05 | -0.40 | -0.13 | 0.04    | -0.03 | 0.64  | 0.35  | 0.27    |
silicate dissolution during this season (Chidambaram et al. 2008).

Conclusion

In the study area, the chemical composition of groundwater is altered by hydrogeochemical processes and thus varies with space and time. The four-season spatial representation of the EC shows that higher concentrations were found in the central and southern parts of the studied region chiefly covered by hard rock region, reflecting greater residence time. Thus, the spatial distribution of the EC also reflects the influence of lithology variation. Since the study area is dominated by NEM monsoon rainfall, the flow in the river improves weathering and recharge along with domestic sewage and even along the river course due to the landfill leachates. The Piper plot reveals there is a compositional migration was observed by Ca–HCO₃ type in the predominant monsoon and the POM season. The utility of water for different purposes classified by adopting different indices show that PRM and SWM groundwater quality are generally poor with higher dissolved ions. Majority of the samples were inferred to be unsuitable for agricultural and domestic purposes during PRM and SWM. The major sources irrespective of the season were inferred to be the leaching and dissolution apart from silicate weathering and fluoride dissolution. Lithologically, the presence of clay in the sedimentary region has favoured the ion exchange process. There was an interplay of the anthropogenic factor on the hydrogeochemistry of the region, especially, during the monsoon periods due to the onset of the agricultural activities. Thus, the study of the groundwater in four prominent seasons provides a synoptic overview of the hydrogeochemical process in the study area, which can help in the sustainable management of the water resource.

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Compliance with Ethical Standards

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Consent for publication  This article submitted with consent of all the authors.

Human and animal rights  Also this research work involves only human participants not animals.

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