


# Hydrogeochemical assessment of groundwater quality and drinking-water suitability in the Killi River Basin, Thiruvananthapuram, India

Arunima M. Lal <sup>1,\*</sup>, Rajesh Reghunath<sup>2</sup>

<sup>1</sup>Department of Geology, University College, Thiruvananthapuram 695034, Kerala, India

<sup>2</sup>Department of Geology, University of Kerala, Kariavattom, Thiruvananthapuram 695581, Kerala, India

## ABSTRACT

The Killi River, an important tributary of the Karamana River, flows through the densely populated city of Thiruvananthapuram. Over the past few years, rapid urbanisation, population growth, and unplanned waste disposal have significantly degraded the quality of both surface and groundwater resources. This study attempts to assess the groundwater quality of the Killi River basin. Water samples were collected from twenty-nine open dug wells in February 2024 and subjected to physicochemical analysis following standard methods. The analysis results show that, at many locations, pH values fall below or exceed the permissible limits set by BIS (2012) and WHO (2011) standards. EC and TDS values are within the permissible limits. Elevated phosphate concentrations in many samples indicate anthropogenic pollution from sewage discharge, detergents, and agricultural runoff. Nitrite concentrations in all groundwater samples exceed permissible limits, suggesting significant contamination of the groundwater system. Groundwater facies is mainly Ca–Cl type, with some samples showing a tendency towards a mixed Ca–Mg–Cl water type. This suggests that alkaline earth metals dominate over alkali metals, and strong acidic anions exceed weak acidic anions. This reflects the influence of rock–water interaction, along with potential anthropogenic inputs, on groundwater chemistry. The groundwater chemistry of the study area is primarily controlled by water–rock interaction processes, as indicated by the Gibbs diagram. It can be concluded that the groundwater resources of the Killi river basin are suitable for domestic use, except for nitrite and phosphate. Hence, periodic monitoring is recommended to ensure long-term water quality and to detect any potential contamination.

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## 1. Introduction

Groundwater is a major component of global freshwater resources, supplying nearly half of the world's drinking water and a substantial share of irrigation water for agriculture (United Nations, 2022). The chemical composition of groundwater is primarily shaped by natural processes, including rock weathering, mineral dissolution, ion exchange, and water–rock interactions as water moves through aquifers (Hem, 1985). Rapid population growth, urbanisation, industrial expansion, and intensified agricultural activities have significantly increased human

pressure on groundwater resources, leading to excessive exploitation and contamination (Biju et al., 2025). Groundwater quality refers to the physical, chemical, and biological characteristics of groundwater that determine its suitability for uses such as drinking, irrigation, and industrial purposes.

In India, groundwater is a major source of water supply, meeting approximately 80% of domestic water needs and contributing more than 45% of the total water used for agriculture, thereby supporting irrigation over nearly 39 million hectares (Kumar et al., 2005). In Kerala, groundwater is the principal source

\*Email: [arunima@universitycollege.ac.in](mailto:arunima@universitycollege.ac.in) (AML), [rajeshgeologist@gmail.com](mailto:rajeshgeologist@gmail.com) (RR)

of water for domestic, industrial, and commercial purposes (Kumar and Panakkal, 2012). Previous investigations have documented elevated concentrations of nutrients, heavy metals, and microbial contaminants across the state, indicating growing pressure on water resources in Kerala (Aju et al., 2024; Prasad and Narayana, 2004). Variation in groundwater quality within a region is governed by physical and chemical parameters, which are strongly influenced by geological formations as well as anthropogenic activities (Rajani, 2015; Subramani et al., 2005).

The present study aims to assess groundwater quality and its suitability for drinking in the Killi River basin, Thiruvananthapuram, Kerala, by comparing the observed values with the WHO drinking water standards (2011). The study also investigates the hydrochemical characteristics and the mechanisms controlling groundwater chemistry in the study area. The primary objective is to evaluate the hydrochemical nature of groundwater resources and to understand the influence of both natural processes and anthropogenic activities on groundwater quality within the basin.

Although several studies have reported the overall groundwater quality of the Killi River Basin, detailed hydrochemical investigations of the basin remain limited. Most previous studies have focused on basic physicochemical characteristics such as drinking water suitability, sanitation aspects, pollution indices, river morbidity profiles, degradation volume development, macroinvertebrate assemblage, and aquatic insect diversity (Dinesh et al., 2017; Dinesh et al., 2018; Jyothylakshmi and Abraham, 2020; Sukanya and Joseph, 2020; Vijayan et al., 2018; Waheed et al., 2024), while comprehensive interpretations of groundwater chemistry using integrated hydrogeochemical approaches have received less attention. In particular, the dominant geochemical processes controlling groundwater composition and the combined influence of natural factors and anthropogenic activities have not been clearly addressed. Therefore, the present study aims to fill this research gap by combining water-quality assessment with detailed hydrochemical interpretation to better understand groundwater-quality variations and their controlling factors in the Killi River Basin. This integrated approach also provides important baseline information for sustainable groundwater management and environmental planning in the study area.

## 2. Study Area

The Killi River is an important tributary of the Karamana River, located in Thiruvananthapuram District in southern Kerala, India. It originates from elevated terrain near Panavur in Nedumangad Taluk and flows through several rural, peri-urban, and densely urbanized regions before merging with the Karamana River at Thiruvallam, Thiruvananthapuram. The river basin lies between latitudes  $8^{\circ}40'30''$  N and  $8^{\circ}27'0''$  N and longitudes  $76^{\circ}57'$  E and  $77^{\circ}2'0''$  E in Thiruvananthapuram District, Kerala. The Killi River is the sixth-order and largest tributary of the Karamana River. It flows predominantly north–south for more than 24 km before joining the Karamana River, with a drainage area of 102 km<sup>2</sup>. The Killi River flows through the panchayats of Panavur, Anad, Karakulam, Kudappanakkunnu, and Vattiyoorkavu, the Nedumangad Municipality, and the Thiruvananthapuram City Corporation, supporting a large population living along its banks. According to the 2011 Census, about 16.8 lakh urban residents live within the Thiruvananthapuram City Corporation area, many of whom directly or indirectly depend on the river. The Killi River serves as a major source of freshwater for domestic use, drinking, irrigation, household activities, and agricultural purposes, while also supporting local livelihoods and maintaining ecological balance in the region (Waheed et al., 2024).

Geologically, the river basin lies within the Kerala Khondalite Belt, composed of high-grade Precambrian metamorphic rocks, with younger Tertiary and Quaternary sediments occurring in the lower reaches. The major rock types in the basin include Khondalite, Charnockite, associated gneissic formations, and younger sediments. Variations in rock formations affect groundwater storage and movement, while differences in soil properties influence vegetation development and land-use patterns within the basin. The basin is characterized by undulating terrain, including uplands, midlands, lowlands, lateritic plains, and alluvial deposits, which influence groundwater movement and recharge. These physiographic features play a significant role in controlling hydrological processes, recharge patterns, and the overall hydrochemical characteristics of groundwater in the basin.

Land use is dominated by mixed dryland cultivation and built-up areas, with increasing urbanisation

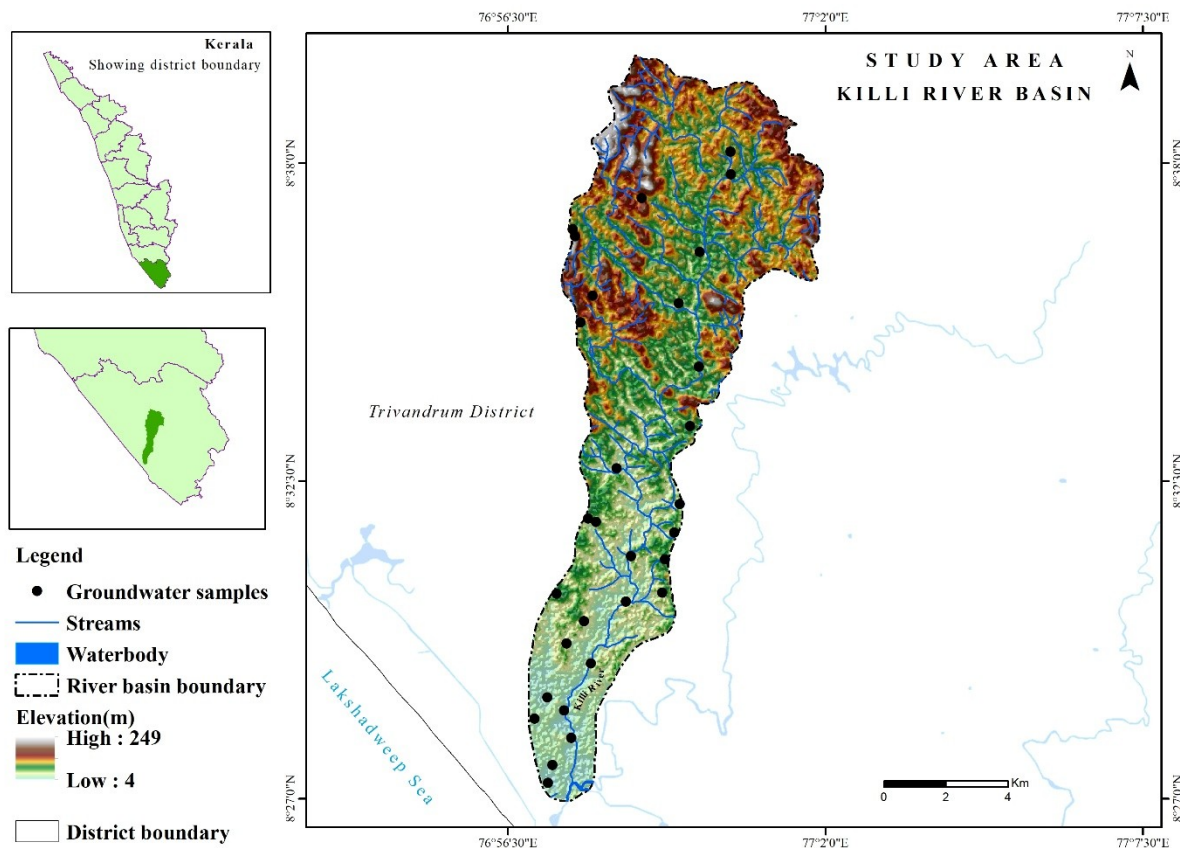


Fig. 1. Map showing the sampling locations within the study area.

towards the southern region and town areas. The densely populated catchment has undergone significant land-use changes, marked by the expansion of settlements and a decline in open spaces and mixed tree-crop areas.

### 3. Materials and Methods

To understand the hydrogeochemistry of the study area, 29 groundwater samples were collected from randomly selected open dug wells during February 2024 (Fig. 1). The samples were collected in pre-cleaned one-litre polyethylene bottles following standard procedures outlined by APHA (1985). Prior to sampling, each bottle was rinsed with the respective sample water to avoid contamination. After collection, the bottles were properly sealed and labelled on site. A few parameters, such as pH, EC, and TDS, were analysed in situ during sampling using a potable instrument (EUTECH 650), with an accuracy of 0.01 for pH and 0.01 for conductivity. Nutrients were analysed using 0.45  $\mu\text{m}$  cellulose nitrate filter paper, and all calorimetric estimations were measured using a

UV-visible spectrophotometer (SYSTRONICS 2203). Total alkalinity, total hardness, calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), and chloride ( $\text{Cl}^-$ ) were determined using titrimetric methods, including EDTA and argentometric titrations. Sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) were analysed using a flame photometer. Sulphate ( $\text{SO}_4^{2-}$ ), phosphate ( $\text{PO}_4^{3-}$ ), and nitrate ( $\text{NO}_3^-$ ) were determined using spectrophotometric methods. Major ions were analysed in the chemical laboratory of the Department of Geology, University of Kerala. Laboratory procedures strictly followed standard operating procedures (APHA, 2012). The accuracy of the analytical data was ensured through the implementation of standard quality control procedures throughout the study. All instruments were calibrated using appropriate standard reference solutions prior to analysis, and calibration was periodically verified to maintain accuracy. Spatial analysis of the hydrochemical data was carried out using ArcGIS software, which enabled the preparation of thematic maps for effective visualization and interpretation of groundwater quality distribution patterns.

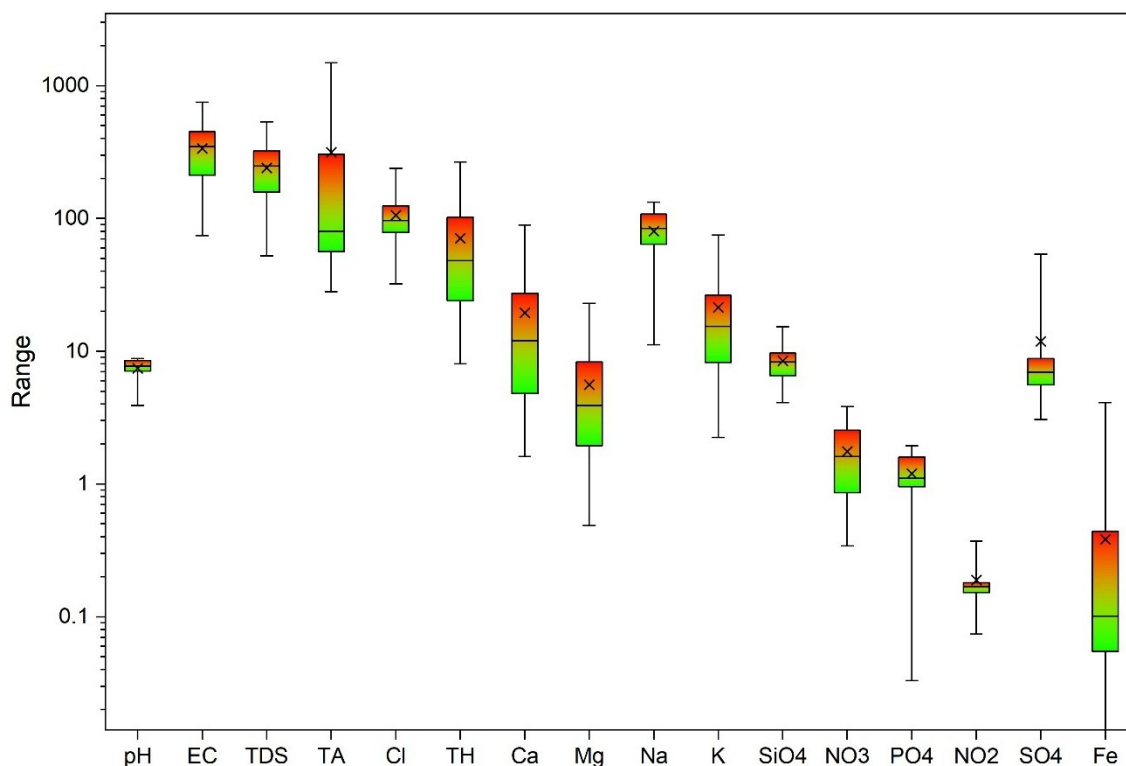


Fig. 2. Box plot representing the distribution of physicochemical parameters, indicating minimum, maximum, and mean values.

## 4. Result and Discussion

### 4.1. Groundwater chemistry of the Killi River basin

The groundwater samples were analysed for various chemical parameters, including pH, EC, TDS,  $\text{Ca}^+$ ,  $\text{Mg}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^-$ ,  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^-$ , Total alkalinity (TA), and Total hardness (TH). The estimated values are given in Table 1 and are also represented as a box plot (Fig. 2).

Table 1. Descriptive statistics of major chemical parameters in water samples from the study area.

Parameter	Range	Mean
pH	3.9–8.8	7.4
EC	74.3 to 749 $\mu\text{S}/\text{cm}$	337.39
TDS	52.3 to 535 $\text{mg}/\text{L}$	240.39
Ca	1.6–89 $\text{mg}/\text{L}$	19.45
Mg	0.48–22.85 $\text{mg}/\text{L}$	5.60
Na	10.11–132 $\text{mg}/\text{L}$	80.28
K	2.2–74 $\text{mg}/\text{L}$	21.43
Cl	32.0–238.26 $\text{mg}/\text{L}$	105.84
Fe	0.001–4.09 $\text{mg}/\text{L}$	0.3828
$\text{SO}_4$	2.9–53.8 $\text{mg}/\text{L}$	11.88
$\text{NO}_2^-$	0.07 to 0.37 $\text{mg}/\text{L}$	0.1890
$\text{NO}_3^-$	0.34 to 3.811 $\text{mg}/\text{L}$	1.759
SiO	4.11 to 15.32 $\text{mg}/\text{L}$	8.48
$\text{PO}_4^{3-}$	1.09–1.94 $\text{mg}/\text{L}$	1.19
TH	8 to 266 $\text{mg}/\text{L}$	70.82
TA	28–1480 $\text{mg}/\text{L}$	314.62

The pH values of the groundwater samples from the Killi River basin range from 3.9 to 8.8. The lowest value is observed at Anad (3.9), and the highest at Oolanpara and Attakulangara (8.8). It may be noted that nearly 42% of the groundwater samples fall outside the permissible drinking water range of 6.5–8.5 (WHO, 2011). The extremely acidic pH observed in Anad (3.9) may be attributed to the intensive use of fertilisers for agricultural activities, which can enhance groundwater acidification (Srinivasamoorthy et al., 2014). Similar acidic conditions in Anad have also been reported by previous studies, such as Vijayan et al. (2018). These low pH also been attributed by the presence of laterites and lateritic soil. In contrast, the lower stretches exhibit comparatively alkaline groundwater, particularly in highly urbanised areas, likely due to the leaching of dissolved constituents and increased anthropogenic inputs into the groundwater system.

EC values in the study area range from 74.3 to 749  $\mu\text{S}/\text{cm}$ . As per WHO (2011) guidelines for drinking water quality, the desirable limit for electrical conductivity in drinking water is less than 400  $\mu\text{S}/\text{cm}$ . Higher EC values are observed at places like Thycaud (749  $\mu\text{S}/\text{cm}$ ) and Karamana (621  $\mu\text{S}/\text{cm}$ ). In the case of EC distribution, nearly 33% of samples

exceed the permissible limit. The total dissolved solids (TDS) in the groundwater samples range from 52.3 to 535 mg/L, with the highest concentration recorded at Thycaud (535 mg/L). In the case of TDS, all samples fall within the maximum permissible limit. The total hardness (TH) values in the groundwater samples range from 8 to 266 mg/L. As per the guidelines of WHO (2011), the highest desirable limit for total hardness (TH) in drinking water is 200 mg/L, and all groundwater samples fall within the desirable limit except at Attakulangara (266 mg/L). According to WHO (2011), the desirable limit of total alkalinity (TA) is 200 mg/L, and the TA values in the study area fall between 28 and 1480 mg/L. Nearly 30% of the samples exceed the desirable limit of TA, and the values exceeding the permissible limit are observed in highly urbanized and polluted areas, including Poonthura (772 mg/L), Manacaud (852 mg/L), Attakulangara (1036 mg/L), Attukal (1412 mg/L), Iranimuttam (1480 mg/L), and Killippalam (1480 mg/L). According to WHO (2011), the recommended calcium limit in drinking water is 75 mg/L. The study area shows a variation of Ca values from 1.6 to 89 mg/L, in which most of the samples fall within the desirable limit and all samples fall within the permissible limit. The highest value of Ca is recorded at Attakulangara (89 mg/L). Magnesium values in the study area vary from 0.48 to 22.85 mg/L. According to the WHO (2011) guidelines, the permissible limit for magnesium in drinking water is 50 mg/L, and all groundwater samples from the study area fall within the acceptable limits. Sodium values show spatial variation from 10.11 to 132 mg/L. All samples fall within the recommended limit of WHO (2011) in drinking water, which is 150 mg/L. Potassium values show variation from 22.2 to 74 mg/L in the Killi basin. Around 60% of the samples exceed the desirable limit of potassium (12 mg/L) as per WHO (2011). Maximum values were recorded at Attakulangara (61.73 mg/L), Vazhayila (71.73 mg/L), and Pazhakutti (74.79 mg/L). Chloride values in the study area vary from 32.0 to 238.26 mg/L. As per WHO (2011), the maximum permissible limit for chloride in groundwater is 200 mg/L. In the study area, only one sample exceeds this limit (at Thycaud, 238.26 mg/L). The sulfate values in the basin vary from 22.9 to 53.8 mg/L. As per WHO (2011) drinking water quality standards, the maximum permissible concentration of sulfate is 200 mg/L, and all the samples fall within the permissi-

ble range. The nitrate concentrations in the study area range from 0.34 to 3.811 mg/L and are well within the recommended limit. The nitrite concentrations in the groundwater samples range from 0.07 to 0.37 mg/L. According to WHO (2011) drinking water guidelines, the acceptable limit for nitrite is less than 0.1 mg/L. Approximately 80% of the samples exceed this recommended limit, indicating elevated nitrite concentrations in most of the groundwater samples. Phosphate values of the river basin vary from 1.09 to 1.94 mg/L. Though there is no specified guideline value for phosphate in drinking water, concentrations above 0.1 mg/L indicate anthropogenic contamination (Badamasi et al., 2019; Kim et al., 2013; Kumar et al., 2012; Zhang et al., 2023). In the present study, all samples fall above 0.1 mg/L phosphate. The iron concentration in the study area falls between 0.001 and 44.09 mg/L. Nearly 24% of samples exceed the limit of 0.3 mg/L as prescribed by WHO (2011). Bicarbonate values in the study area show variation from 34.16 to 1805.6 mg/L. The recommended bicarbonate concentration in drinking water is 300 mg/L. Nearly 24% of samples in the study area surpass the desirable bicarbonate limit at many places such as Oolanpara (370.88 mg/L), Nanthanacaud (649.04 mg/L), Poonthura (941.84 mg/L), Manacaud (1039.44 mg/L), Attakulangara (1263.92 mg/L), Attukal (1395.68 mg/L), Manacaud (1722.64 mg/L), and Killippalam (1805.6 mg/L).

Elevated electrical conductivity indicates a higher concentration of dissolved ions in groundwater, reflecting increased mineralization or possible contamination. The elevated total hardness observed at the urban sampling location is likely due to localized anthropogenic influences, including sewage leakage, septic system infiltration, and leaching from cemented structures, which contribute calcium and magnesium ions to groundwater. This is further supported by the concurrent increase in electrical conductivity (EC) and chloride ( $\text{Cl}^-$ ) at the same or nearby location in lower stretches of the river, indicating enhanced dissolved ionic content and possible contamination. Anthropogenic inputs have been identified as the primary contributors to chloride ( $\text{Cl}^-$ ) concentrations (Roy et al., 1999). The presence of nitrite ( $\text{NO}_2^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ) also suggests recent and continuous input from domestic wastewater and urban runoff, reinforcing the role of anthropogenic activities in modifying groundwater chemistry. Similar localized groundwater quality de-

terioration in urban settings has been reported from Thiruvananthapuram district, where increased hardness, salinity, and nutrient concentrations were linked to land-use practices and sewage contamination.

The physico-chemical characteristics of groundwater in the Killi River Basin have been widely studied, indicating that water quality is strongly influenced by both natural and anthropogenic factors. Most physicochemical parameters, including pH, electrical conductivity, total dissolved solids (TDS), total hardness (TH), nitrate, nitrite, phosphate, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and dissolved oxygen (DO), were reported to exceed permissible limits in previous studies (Anukumar, 2006; Jyothylakshmi and Abraham, 2020). Elevated concentrations of certain ions in downstream and urban-influenced zones are associated with increasing built-up areas and anthropogenic inputs such as domestic wastewater and agricultural runoff. Land use changes, particularly the expansion of settlements, have further contributed to spatial variations in water quality across the basin (Vijayan et al., 2018). These studies also revealed that the concentrations of these parameters progressively increased from the upstream to the downstream sections of the river. The midstream and downstream segments were found to be unsuitable for drinking, domestic use, and bathing, particularly during the pre-monsoon season (Jyothylakshmi and Abraham, 2020). Anukumar (2006) further reported a similar pattern of nutrient fluctuations and highlighted the deteriorating health status of the Killiyar due to increasing anthropogenic pressure and pollution load.

The spatial distribution maps illustrate the variation in different physicochemical parameters across the study area, highlighting their spatial variability and distribution patterns (Figs. 3–5).

#### 4.2. Hydro geochemical facies

Hydrogeochemical facies (Chebotarev, 1955) describe the evolution of groundwater chemistry along its flow path within an aquifer system. They help to understand the origin, evolution, and spatial variation of groundwater chemistry. The Piper diagram (Piper, 1944) is a graphical method that facilitates the interpretation of the diverse chemical characteristics of water samples.

Most groundwater samples in the study area cluster towards the  $\text{Ca}^{2+}$  apex, indicating calcium as the dominant cation.  $\text{Mg}^{2+}$  is the second most abundant

cation, whereas  $\text{Na}^+$  and  $\text{K}^+$  occur at comparatively lower concentrations. In the anion triangle, the samples cluster mainly towards the  $\text{Cl}^-$  apex, with moderate contributions from  $\text{HCO}_3^-$ . The water type is Ca–Cl, while a few samples show a transitional trend towards mixed Ca–Mg–Cl facies (Fig. 6). The hydrochemical facies analysis suggests a dynamic geochemical system involving various geological components, such as rock-water interaction and ion exchange processes, along with possible anthropogenic inputs, including septic tank leakage, domestic sewage infiltration, and urban runoff, which affect groundwater chemistry (Singh et al., 2018; Subba Rao, 2006).

The Schoeller diagram (Schoeller, 1967) presents the relative concentrations of groundwater constituents. The major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) and major anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ) are arranged along the horizontal axis, while their concentrations in milliequivalents per litre (meq/L) are shown on the logarithmic vertical axis. In the present study area, calcium ( $\text{Ca}^{2+}$ ), bicarbonate ( $\text{HCO}_3^-$ ), and chloride ( $\text{Cl}^-$ ) generally show higher concentrations than other ions, indicating their dominance in the groundwater chemistry of the study area. Sodium ( $\text{Na}^+$ ) also shows comparatively higher values among the cations, whereas potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), and sulphate ( $\text{SO}_4^{2-}$ ) display relatively lower concentrations (Fig. 7). The dominance of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$ , along with relatively higher  $\text{Na}^+$  and lower  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  in the Schoeller diagram indicates that groundwater chemistry in the study area is mainly controlled by water–rock interaction, with additional influence from anthropogenic inputs.

The dominance of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  reflects silicate and carbonate weathering in crystalline and lateritic terrains during groundwater recharge, whereas elevated  $\text{Na}^+$  suggests ion exchange processes and minor anthropogenic contributions. Higher  $\text{Cl}^-$  levels indicate contamination from domestic sewage and urban runoff (Hem, 1985). Low  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  suggest limited evaporite dissolution and weak agricultural or industrial influence (Todd and Mays, 2004).

Gibbs diagrams (Gibbs, 1970), plotting  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  vs TDS and  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$  vs TDS, were used to identify the mechanisms controlling groundwater chemistry (Gibbs, 1970). In both diagrams, most groundwater samples fall within the rock dominance field (Fig. 8), indicating that

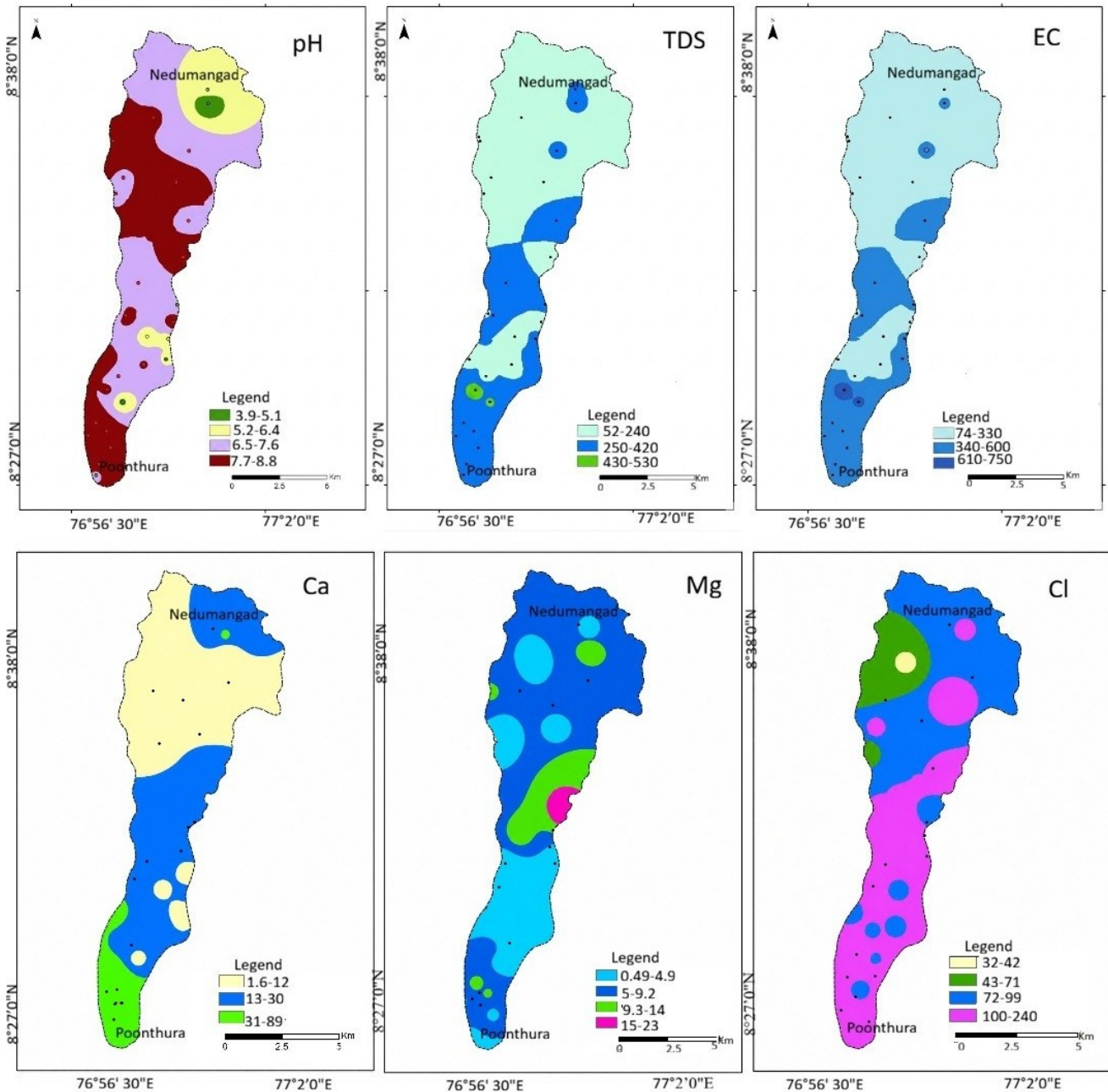


Fig. 3. Spatial distribution of pH, TDS, EC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^{-}$  across the study area.

rock-water interaction is the principal process governing the hydrochemical characteristics of groundwater in the study area (Adimalla and Venkatayogi, 2018; Subba Rao, 2008). The moderate TDS values and the distribution of ionic ratios suggest that dissolution and weathering of aquifer minerals significantly contribute to the ionic composition of groundwater.

Correlation analysis of hydrochemical parameters provides significant insight into the water chemistry of the study area. A strong positive correlation between EC and TDS ( $r = 1.00$ ) indicates that groundwater conductivity is primarily controlled by the dis-

solved ionic content (Fig. 9). This pattern can be driven by increased salinity and waste-contaminated water, as higher concentrations of dissolved minerals immediately increase EC (Srinivasamoorthy et al., 2014; Rusydi, 2018). Similarly, a strong positive correlation between  $\text{Na}^{+}$  and  $\text{Cl}^{-}$  ( $r = 0.76$ ) suggests anthropogenic inputs such as wastewater discharge and agricultural runoff. The strong association between TH and Ca ( $r = 0.92$ ) suggests that hardness is mainly governed by calcium-bearing minerals through rock-water interaction processes (Subba Rao, 2006). EC and  $\text{Cl}^{-}$  also show higher val-

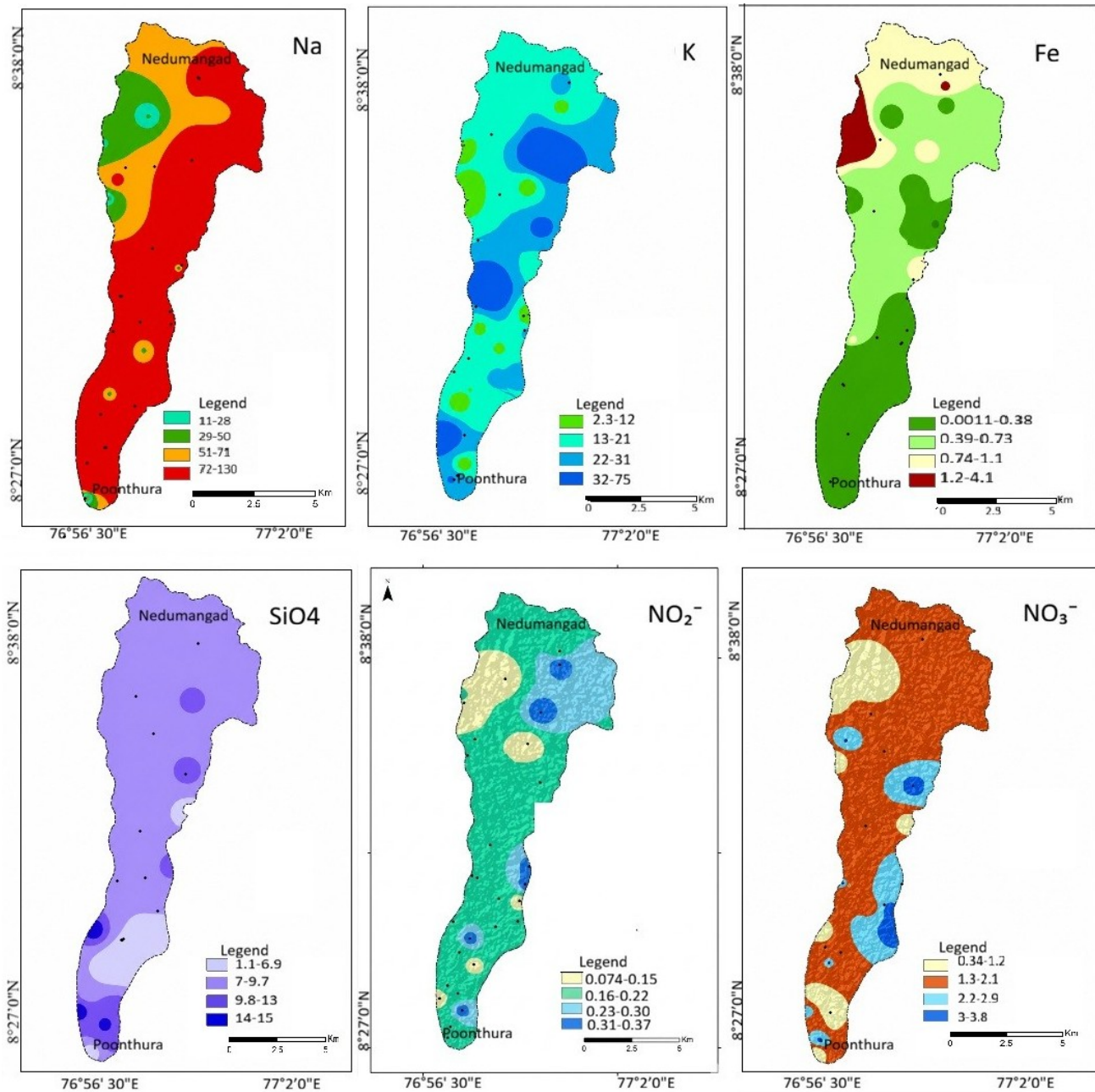


Fig. 4. Spatial distribution of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}$ ,  $\text{SiO}_4$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  across the study area.

ues, indicating that chloride significantly controls and enhances groundwater conductivity through its high solubility and contribution to ionic strength. The negative correlation of  $\text{NO}_3^-$  with pH and TH suggests localized anthropogenic contamination, particularly from agricultural runoff and domestic wastewater.

## 5. Conclusion

The assessment of groundwater quality parameters against the World Health Organization (2011)

drinking water standards indicates that several parameters exceed the recommended limits in the study area. The pH of certain groundwater samples falls outside the permissible range, while electrical conductivity (EC) exceeds the acceptable limit in some locations. Similarly, total alkalinity (TA) and potassium ( $\text{K}^+$ ) concentrations surpass the recommended limits in several samples. Elevated nitrite ( $\text{NO}_2^-$ ) levels are also observed in many samples, suggesting potential sources of contamination. In addition, phosphate ( $\text{PO}_4^{3-}$ ) concentrations remain above the recommended limit throughout the study

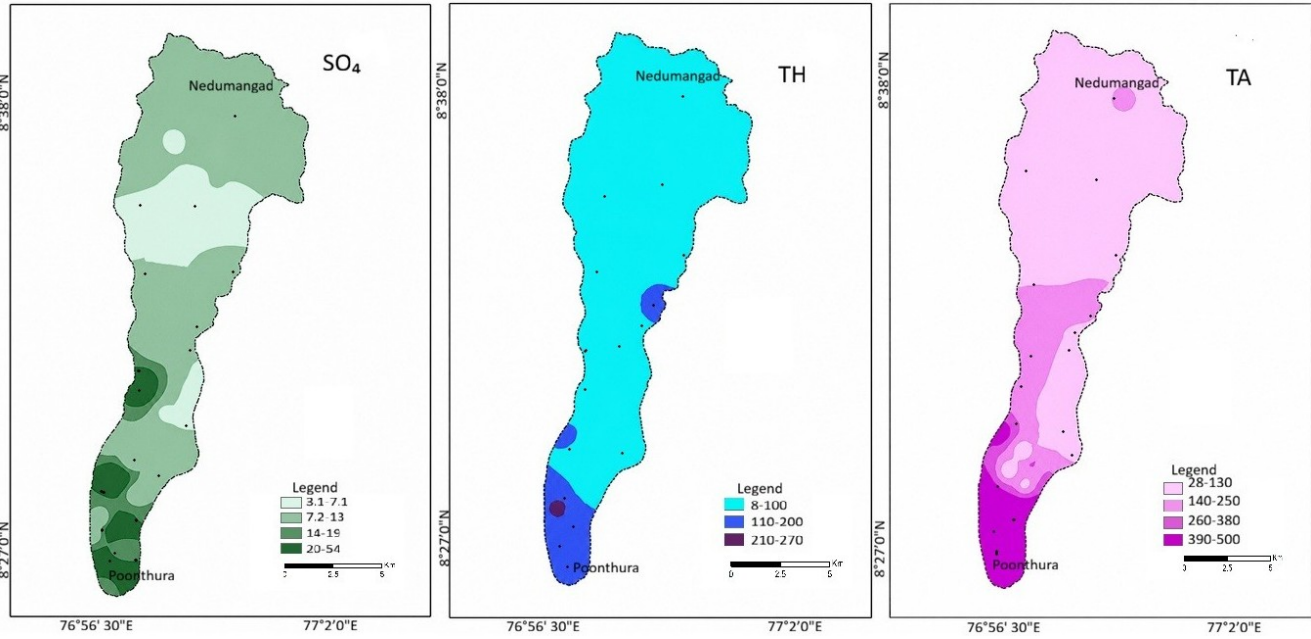


Fig. 5. Spatial distribution of  $\text{SO}_4^{2-}$ , total hardness, and total alkalinity across the study area.

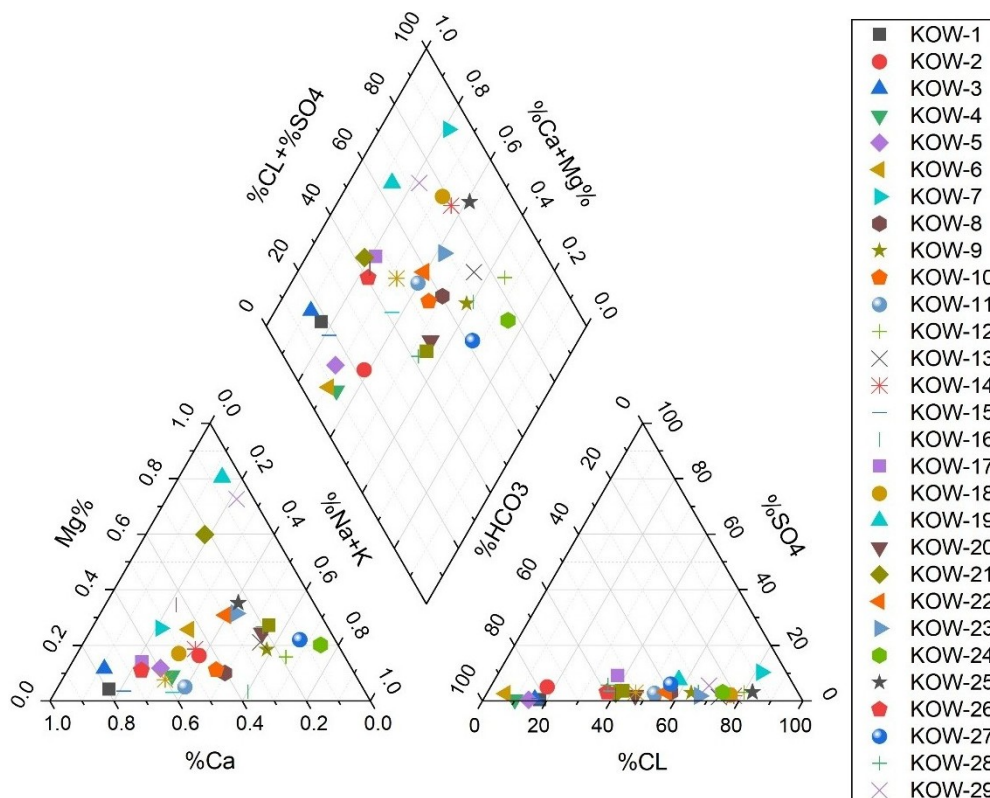


Fig. 6. Groundwater classification of the study area using Piper diagram.

area, likely due to anthropogenic influences, including agricultural runoff and domestic waste discharge. Furthermore, calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), iron (Fe), and bicarbonate ( $\text{HCO}_3^-$ ) concentrations exceed the permissible limits in certain groundwater

samples. In contrast, total dissolved solids (TDS), total hardness (TH), magnesium ( $\text{Mg}^{2+}$ ), sulphate ( $\text{SO}_4^{2-}$ ), and nitrate ( $\text{NO}_3^-$ ) remain within the permissible limits for all analysed groundwater samples. The hydrogeochemical facies analysis indicates

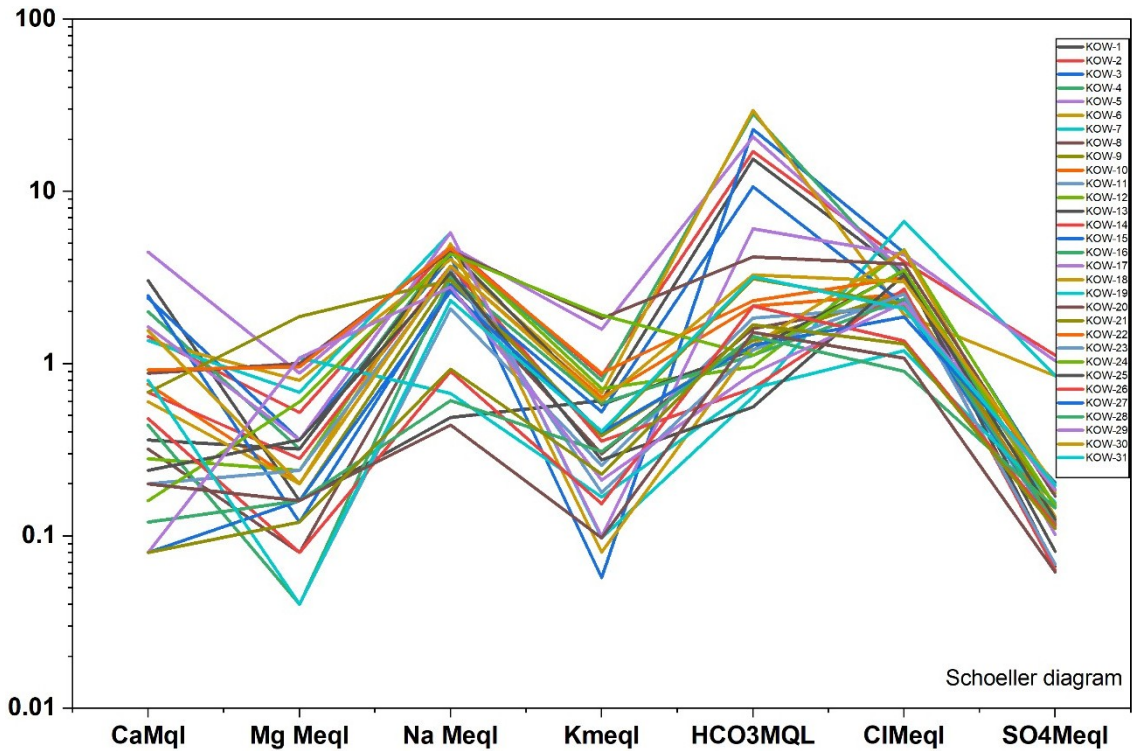


Fig. 7. Schoeller diagram representing the major ion distribution of the study area.

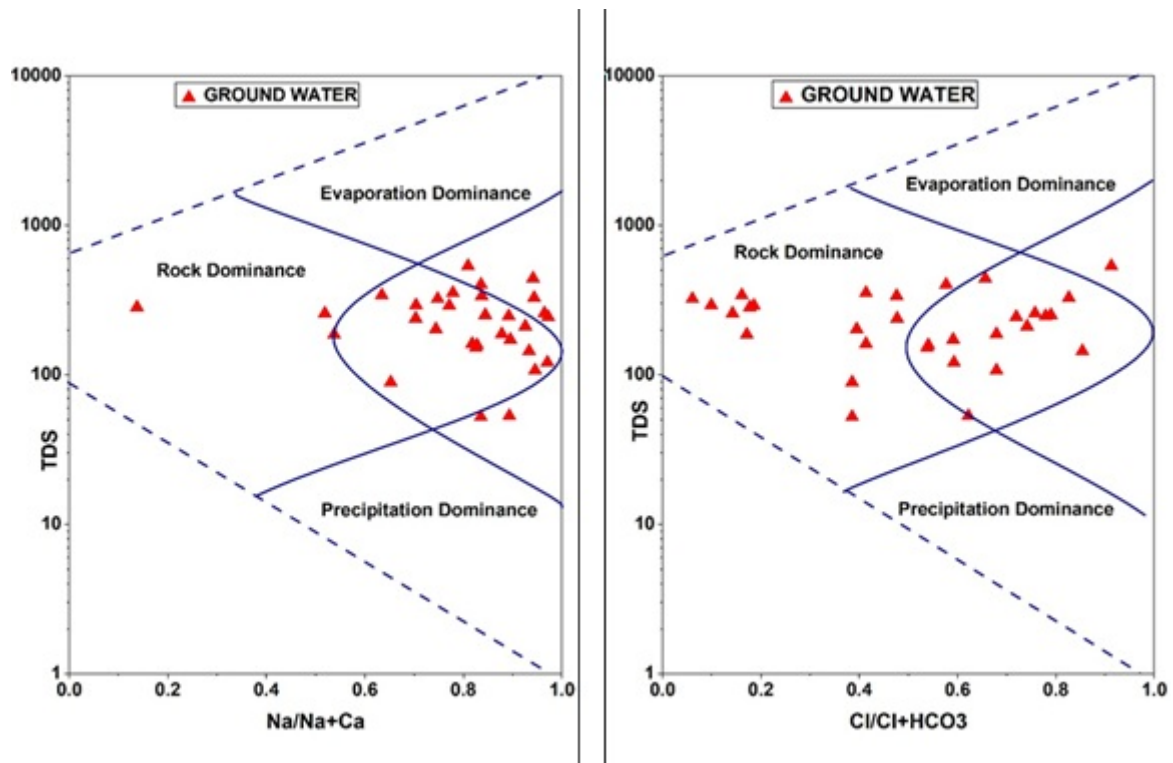


Fig. 8. Gibbs diagram of the study area.

that groundwater in the study area is predominantly of the Ca–Cl type, with a few samples showing a transitional trend towards mixed Ca–Mg–Cl facies. The majority of groundwater samples fall within the

rock dominance field, suggesting that water–rock interaction is the principal factor controlling the hydrogeochemical characteristics of groundwater in the study area. Moreover, the distribution of

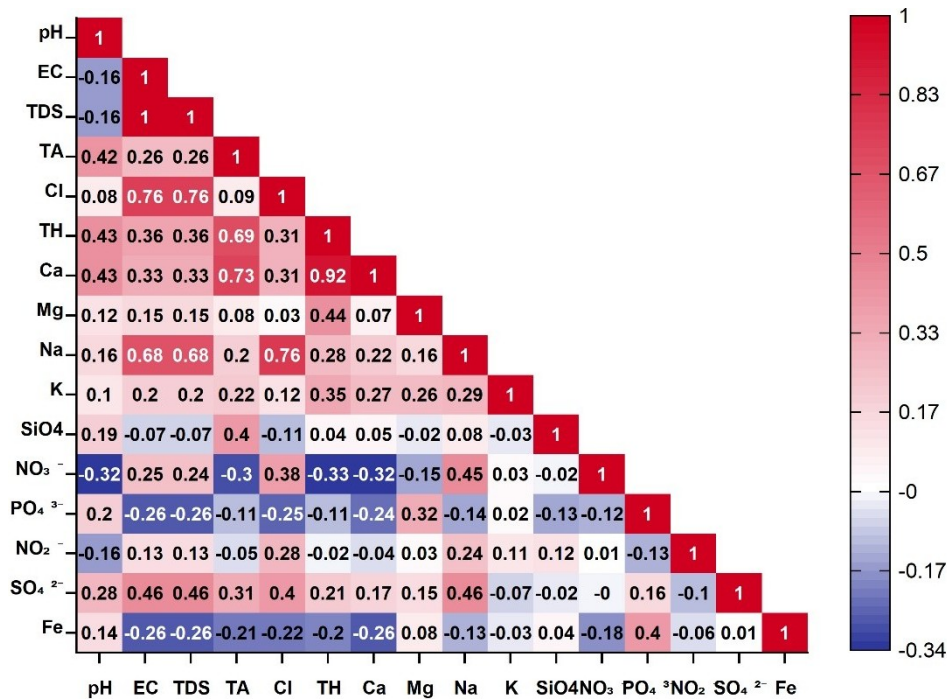


Fig. 9. Pearson correlation matrix showing the interrelationships among groundwater physicochemical parameters in the study area.

major ions suggests that groundwater chemistry is predominantly characterised by  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , followed by  $\text{Na}^+$  and  $\text{Cl}^-$ , whereas  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{K}^+$  occur in relatively lower concentrations. Overall, the hydrochemical characteristics of groundwater are largely governed by natural geochemical processes, particularly rock–water interaction, with additional influences from localized anthropogenic activities. The majority of ions exhibit higher concentrations in the lower reaches of the river basin, especially in urbanised areas such as Attakulangara, Thycaud, Oolanpara, Manacaud, and Killipalam, indicating intense anthropogenic pollution, high population density, limited natural recharge, and poor drainage conditions. Pearson correlation analysis of groundwater quality revealed strong correlations among various parameters. A strong positive correlation between EC and TDS ( $r = 1.00$ ) indicates that conductivity is controlled by dissolved ions and may reflect increased salinity and contamination. Similarly, the positive correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.76$ ) suggests anthropogenic inputs such as wastewater and agricultural runoff. The strong association between TH and Ca ( $r = 0.92$ ) indicates that hardness is governed by calcium-bearing minerals, while the correlation between EC and  $\text{Cl}^-$  ( $r = 0.76$ ) highlights the role of chloride in enhancing groundwater conductivity due to its high solubility.

Overall, the study offers important scientific insights into the groundwater quality of the Killi River Basin and supports sustainable groundwater management by identifying key hydrogeochemical processes, anthropogenic impacts, contamination-prone areas, and areas requiring protection and monitoring.

## 6. Limitation of the Study

The present study is limited to groundwater samples collected during a single sampling period, which may not fully capture seasonal variations in water quality. The analysis focused primarily on physicochemical parameters and hydrochemical interpretation using standard diagrams, while microbial and detailed heavy metal assessments were excluded. Source identification relied on hydrochemical and land-use evidence rather than direct tracing methods. Further studies involving seasonal monitoring, microbial analysis, isotopic techniques, and advanced source apportionment are recommended for a more comprehensive understanding of groundwater quality in the Killi River Basin.

## 7. Future Recommendations

Future studies should address the limitations of the present work and provide a more comprehensive understanding of groundwater quality in the Killi

River Basin. Therefore, continuous monitoring and appropriate groundwater management strategies, including proper management of domestic wastewater, improved septic systems, and prevention of direct waste discharge, are essential to reduce contamination. Controlled use of fertilisers in agriculture, along with the promotion of rainwater harvesting and artificial recharge, should be encouraged to improve groundwater sustainability. In addition, public awareness and strengthened groundwater management policies are necessary to ensure the sustainability and safe utilisation of groundwater resources in the Killi River Basin.

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### CRedit statement

Arunima M. Lal: conceptualization, data curation, methodology, software, formal analysis, validation, and writing—original draft. Rajesh Reghunath: supervision, conceptualization, and writing—review and editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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