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Hydrochemical characteristics and groundwater assessment of a multi-aquifer system in Alappuzha area, South India

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ABSTRACT

A hydrogeochemical investigation was carried out in a multi-aquifer in the Alappuzha area, Kerala, South India. Quality assessment of groundwater for both drinking and irrigation purposes was carried out to understand its hydrogeochemical evolution. Quaternary alluvium (phreatic aquifer) and Tertiary sediments (confined aquifer) forms the major aquifer system in this area. The topmost Tertiary aquifer namely, the Warkalli aquifer is extensively developed through tube wells. For the present study, 74 water samples were collected from dug wells, tube wells, and surface water bodies, during June 2021 and analysed for major ion chemistry. The analysis of hydrochemical components indicates that the groundwater is alkaline in nature and all the parameters with in the permissible limit, except hardness and fluoride. The hydrochemical composition primarily reflects the interplay between precipitation-recharged groundwater and the surrounding geological formations. The presence of bicarbonate ions in the groundwater can be attributed to both root zone respiration and the breakdown of silicate minerals through weathering processes. On the other hand, chloride and sulfate ions predominantly stem from the marine source within the unsaturated zone, as well as marine aerosols. The groundwater samples collected from the deeper aquifer near Alappuzha town show high fluoride (<2 mg/L). Improper waste disposal and lack of waste management facilities contribute pollutants leaching into the phreatic aquifers, necessitating control measures to protect them from contamination. Groundwater from the phreatic aquifer was generally good and suitable for irrigation, but sustainable agricultural practices required consideration. The study emphasizes the need for proper management and protection measures to ensure the availability of safe and suitable groundwater for various uses.

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1. Introduction

Groundwater is a fundamental component of the earth's hydrological cycle, playing a crucial role in meeting the water demands of various sectors, including agriculture, industry, and domestic use. With approximately half of the global population relying on groundwater as their primary source of drinking

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water, its significance cannot be overstated (Jia et al., 2019). However, escalating anthropogenic pressures, coupled with the effects of climate change, are exerting unprecedented stress on this finite resource. The over-exploitation of groundwater reserves is resulting in the rapid depletion of major aquifers worldwide. This has become a pressing concern as replenishment rates fail to keep pace with extraction rates (Gleeson et al., 2016). Studies have highlighted the alarming state of 21 out of 37 major aquifers in the world, which are no longer sustainable due to the unsustainable rates of groundwater extraction (Wada et al., 2016). Such conditions are especially critical in regions such as India, Pakistan, and North Africa, where agriculture forms the backbone of the economy, leading to adverse consequences for both water availability and agricultural productivity (Dalin et al., 2017). The increasing strain on groundwater resources threatens the sustainability of these vital ecosystems, and immediate action is imperative. In addition to depletion, groundwater faces another significant challenge — pollution. Uncontrolled groundwater abstraction for irrigation in agricultural areas has led to both depletion and contamination (Wang et al., 2018). Industrial discharges, improper waste disposal, and the use of fertilizers and pesticides are contributing to the degradation of groundwater quality (Khan et al., 2013, Massoud et al., 2016). Coastal regions, undergoing rapid urbanization and intensive agricultural practices, are particularly vulnerable to groundwater pollution, with detrimental implications for the environment and human health (Narany et al., 2018). To mitigate the escalating threats to groundwater resources, immediate action is required. Researchers worldwide have investigated groundwater quality and pollution sources, highlighting the pressing need for improved monitoring and management (Nasrabadi and Abbasi Maedeh, 2014, Khan et al., 2017). Sustainable development and the protection of crucial ecosystems and communities that rely on clean groundwater necessitate robust strategies to ensure its long-term viability (Famiglietti, 2014).

The demand for freshwater has led to the exploitation of coastal freshwater reserves, causing saline intrusion and adversely affecting the aquifers. Consequently, the groundwater quality in the coastal aquifers has deteriorated (Venkatramanan et al., 2015, 2019). The main factor behind this degradation is the intrusion of seawater into the coastal aquifer, which is primarily attributed to extensive overexploitation (Gallardo and Marui, 2007). The vulnerability of the coastal aquifer to seawater contamination renders the groundwater unsuitable for drinking purposes. Numerous studies have inferred that once seawater intrudes into the fresh groundwater of a coastal aquifer system, restoring its original fresh groundwater condition becomes challenging (Jeen et al., 2001; Chidambaram et al., 2022; Keesari et al., 2016; Thilagavathi et al., 2015; Chung et al., 2019). India is the largest user of groundwater in the world, with around 60% of the country's irrigated agriculture depending on groundwater. However, the groundwater resources in India are depleting at a faster rate, and this has serious implications for the sustainability of groundwater for agriculture and the livelihoods of farmers. Groundwater is a major source for domestic and agricultural purposes in Kerala. As the population in Kerala continues to grow and viable locations for surface reservoirs become scarcer, the extraction of groundwater is anticipated to increase. Therefore, it is essential to study and document the groundwater resource potential of the state and its sustainability. Thomas and Duraisamy (2018) conducted a thorough hydrogeological mapping in Ahmednagar district, Maharashtra, India. Employing a geospatial methodology, they aimed to demarcate regions facing significant strain as a result of extensive exploitation. The foremost challenge confronting humanity in this century pertains to the consequences of global warming on water resources, with a particular emphasis on coastal aquifer systems, (Foster et al., 2016, Unnikrishnan et al., 2006; Sheffield and Wood, 2008). Groundwater is being extracted on large scale from the coastal aquifers of Kerala, especially from Alappuzha. Domestic water requirements of the area are being met by pumping of groundwater from both the shallow and deep aquifers. Hence, it is highly essential to understand the groundwater availability in the area and its quality for its sustainable development. (Kunhambu, 2003; Shaji et al., 2009). Therefore, this hydrogeochemical investigation of multi-aquifers of the Alappuzha area, Kerala, was undertaken to understand the hydrogeochemical properties of groundwater.

Various hydrogeochemical methods are used by researchers around the world to study the water quality and understand the hydrogeochemical evolution of groundwater in different hydrogeological settings (Birkle, 2006; Sherif and Kacimov, 2008; Mondal et al., 2010; Thilagavathi et al., 2012;). Correlation analysis was conducted to explore the relationships among different parameters (Mahlknecht et al., 2004; Farnham et al., 2003; Singh et al., 2017). Factor analysis was employed by researchers like Liu et al. (2003) for groundwater pollution studies, while Das and Nag (2017) utilized multivariate and principal component analyses to identify correlations between cations and anions. Numerous studies have employed GIS techniques to map groundwater quality, particularly evaluating sulphate and phosphate contamination from anthropogenic sources (Anbazhagan and Nair, 2004; Pandian and Sankar, 2007; Vennila et al., 2008; Chowdhury et al., 2009; Vasanthavigar et al., 2010; Singh et al., 2011; Kshetrimayum and Bajpai, 2012; Belkhiri and Narany, 2015; Zahedi, 2017).

Coastal plains in many continents contain subsiding basins with thick Cenozoic sediments, characterized by distinct aquifers separated by aquitards and aquicludes. The Alappuzha district in Kerala, India, is known for its complex groundwater scenario with shallow water conditions, wetlands, and multi-aquifer systems. Many researchers have adopted various approaches to understanding the hydrogeology and hydrochemistry of coastal aquifer systems in this region (Vinayachandran, 2017; Narayan et al., 2002a, 2002b; Narayana and Priju, 2006). The present research work focuses on groundwater quality assessment in the multi-aquifer system in the Alappuzha region, specifically, the Recent alluvium and Tertiary sediments (Warkalli), unravelling the various hydrogeochemical processes involved in its evolution. The spatial variation of groundwater quality parameters in Alappuzha, South India, was plotted using GIS tools for assessing the water quality.

2. Study area

The study area, ‘Alappuzha’ is part of the western coastal plains located in the southern part of India in the state of Kerala. The major town of the study area include Alappuzha municipality, Punnappara north, Punnappara south and Ambalapuzha etc. The coastal aquifers in Kerala are seen as an elongated band with thick accumulation of Tertiary and Quaternary sediments below the surface with different aquifers separated by aquitards and aquicludes. The study area is situated within the longitudinal range of 76° 18’ to 76° 23’ 30” E and the latitudinal range of 09° 24’ 30” to 9° 30’ 30” N (Fig. 1). The area consists of a flat coastal plain frequently connected with sand ridges that can reach heights of up to 6 m above the mean sea level (amsl). The eastern part features the presence of Vembanad Lake, which significantly influences the coastal drainage system in the area. Alappuzha has a hot and humid climate with relatively stable temperatures throughout the year. The annual average temperature varies between 24°C and 33°C. The average annual temperature ranges from 24°C to 33°C, the region experiences high humidity due to its proximity to the Arabian Sea. Alappuzha experiences a tropical monsoon climate with abundant rainfall throughout the year, with an average annual precipitation ranging from 2500 to 3000 millimetres. The land cover consists of diverse coastal, backwater, and agricultural areas, with paddy cultivation being the prominent land use activity, (Kannan and Joseph, 2010).

Alappuzha (Alleppey) is one of the well-developed coastal districts in the southern part of Kerala State covering an area of 1,414 sq. km. Kuttanad, also known as the “rice bowl of Kerala” is located in the district and has a predominant position in the production of rice for the state. The primary drainage of Alappuzha district occurs through the Pamba River and its tributaries. Alappuzha district consists of coastal alluvium comprising sand and clay along the coastal region and floodplain deposits in Kuttanad region. Residual laterite formations are encountered in the south-eastern parts of the district and granites are encountered in and around Chengannur area. Charnockite, khondalite and granite form the basement. They are overlain by Tertiary sedimentary formations. The laterite/alluvial sediments of Quaternary period overlay the Tertiaries. The aquifer system in the study area can be broadly classified into Tertiary and Alluvial aquifers.

The Tertiary formation of the Kerala coast is further divided into four distinct beds viz. Alleppey, Vaikom, Quilon and Warkalli (CGWB, 1992) in succession from the bottom to top. The Alleppey coastal region is where the most substantial thickness of Tertiary sediments is recorded. The Quilon beds display restricted aquifer characteristics, as documented by CGWB (1992) and CGWB (2003). Among the tertiary group, the most potential aquifers are constituted by the Vaikom and Warkalli beds. Deeper boreholes, reaching 200 meters beneath the surface, have the presence of the Alleppey beds.

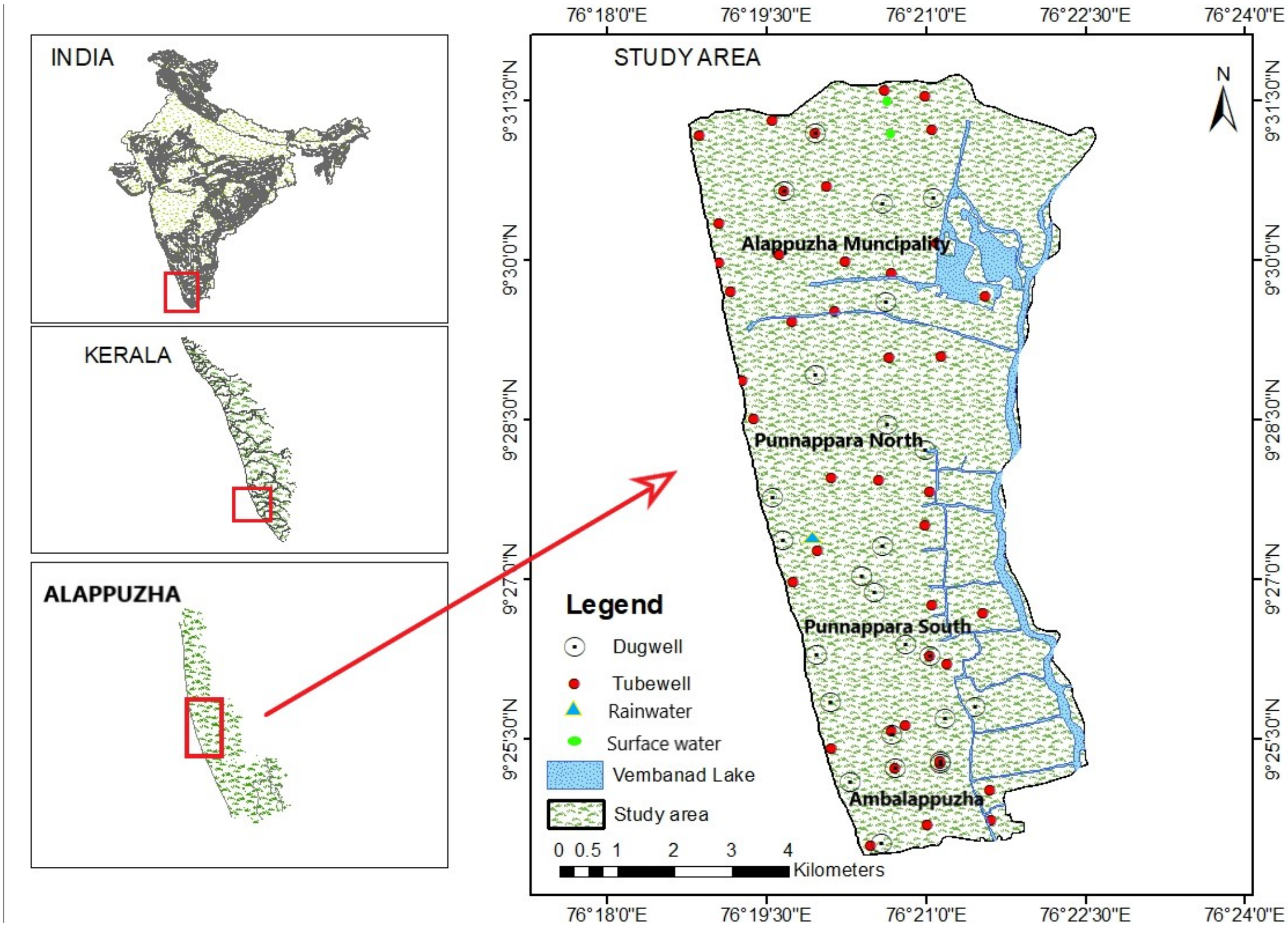


Fig. 1. Location map of the study area with sample location.

3. Water sampling and analytical methods

Sampling of groundwater took place in June 2021, resulting in the collection of a total of 74 samples (Fig. 1), which include 25 dug wells, 42 tube wells, one rainwater and two pond water samples. The groundwater samples were collected after purging the wells for 30 minutes. The groundwater samples were filtered using Whatman membrane filters with a pore size of 0.45 µm. Subsequently, these filtered samples were preserved in polyethylene bottles that had been thoroughly cleaned with concentrated suprapure nitric acid (HNO_3, 65%) prior to use. The water samples were collected in 1-liter polythene bottles for hydrochemical analysis. Within the study area, the depth of both dug wells and tube wells ranged from 1.5 to 4 meters and 9 to 140 meters below the ground level respectively. To assess various chemical parameters such as pH, Electrical Conductivity (EC), and Total Dissolved Solids (TDS), on-site handheld water quality meters from Hanna were employed during the groundwater sampling process. Specifically, separate water samples were collected for cation and anion analysis. The sampling location details and in-situ parameters are given in (Table 1). Major cations, viz., Na^+, K^+, and Ca^{2+} were analysed by Systronics flame photometer 128, and major anions, viz SO_4^{2-}, NO_3^- and F^- were analysed by Double beam spectrophotometer 2203 in Geochemical Laboratory, Dept. of Geology, University of Kerala.

To assess whether the groundwater is suitable for irrigation, we considered various indicators such as Sodium Absorption Ratio (SAR), Residual Sodium Carbonate (RSC), Percentage of sodium (Na%), Magnesium Absorption Ratio (MAR), and Permeability Index (PI). Additionally, we used USSL and Wilcox diagrams as tools to determine if the groundwater is appropriate for irrigation.

4. Results and discussion

The pH levels of samples collected from phreatic aquifer ranged from 6.2 to 8, while those from confined aquifer ranged from 5.8 to 8.8, observed during the season (Fig. 2b). The Electrical Conductivity (EC), which indicates the total dissolved ions, exhibited a range of 128 to 911 µS/cm in the phreatic aquifer and confined aquifer, and a broader range of 42 to 2180 µS/cm across the entire study area (Fig. 2a). The sodium in the phreatic aquifer varied from 13.5 to 241 mg/L and in the confined aquifer, it varied from 12 to 1606 mg/L. The potassium concentration varied from 1.86 to 61.5 mg/L (phreatic aquifer) and 4.6 to 73.2 mg/L (confined aquifer) (Table 1).

The Ca^{2+}in the samples from the phreatic aquifer varied from 11 to 287 mg/ L and confined aquifer 16 to 256.5 mg/ L are within the allowed limits of BIS (2012) and Mg^{2+} from 0.47 to 16.9 mg/L and 0.47 to 154.5 mg/L for the phreatic aquifer and the confined aquifer, respectively (Table 1). Cl^- concentration in phreatic aquifers varied from 16 to 413.8 mg/L and confined aquifers varied from 19.9 and 1979 mg /L (Fig. 2a), SO_4^{2-} varied from 5 to 109 mg /L (open well) and 0.94 to 259.6 mg /L (tube well) (Table 1) and HCO_3^- concentration in open well samples varied from 4.88 to 268 mg/L and 9.8 to 736.8 mg/L in confined aquifer (Table 1). The presence of bicarbonate ions in groundwater can be attributed to two primary sources: root zone respiration and the erosion of silicate minerals, as highlighted in the study by Keesari et al. (2007). Additionally, it is worth noting that human activities, specifically industrial and domestic waste, are responsible for elevated levels of sulphate and chloride in groundwater. This fact has been documented in several studies, including those conducted by Singh et al. (2008), Satyanarayana et al. (2017), and Nadikatla et al. (2020).

The measured TDS values of the groundwater in the phreatic aquifer ranged from 70 to 501 mg/L and in the confined aquifer ranged from 23 to 1199 mg/L (Fig. 2c). All of the collected samples fall within the permissible limits for drinking water quality, which is set at 1000 mg/L (according to WHO, 2011 and (BIS, 2012), except for a single sample that has a Total Dissolved Solids (TDS) value of 1199 mg/L and also the assessment of water domestic usability involves the consideration of total hardness. Hardness arises from the presence of dissolved calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}). High Total Hardness (TH) levels in drinking water have the potential to contribute to various health issues such as arterial calcification, urinary stone formation, kidney or bladder-related ailments, and gastrointestinal disorders (see Table 1). TH values in phreatic aquifers ranged from 42 to 860 mg/L and in confined aquifer it ranged from 66 to 1348 mg/L. The classification of groundwater according to Total Hardness (TH) as outlined by Durfor and Becker (1964) reveals that the majority of the collected samples belong to the "very hard" category (Fig. 3).

Among the inorganic contaminants, In the study area, fluoride (F^-) is a prevalent contaminant, and the permissible limit for F^- according to the World Health Organization (WHO) guidelines from 2011 is 1.5 mg/L. Groundwater samples from open wells within the area exhibited F^- concentrations ranging from 0.012 to 0.59 mg/L, while in tube wells, F^- concentrations ranged from 0.012 to 2 mg/L, as illustrated in Fig. 2d and detailed in Table 1. Groundwater in phreatic aquifers has fluoride concentrations within the permissible range of 0.06 to 0.1 mg/L. However, a few tube wells tapping deeper aquifers around the urban study area have fluoride concentrations in the range of 2 mg/l.

4.1. Groundwater quality zonation map for domestic use

The groundwater quality zonation map is mainly used for drinking water quality analysis. The study area is divided into four zones such as good, moderately good, poor and very poor based on the water quality index values (Table 2) (Rekha et al., 2013). The parameters taken into consideration for the preparation of groundwater quality zonation map for drinking include pH, EC, TDS, Cl^- and F^- . These parameters show comparatively higher concentration than the other parameters. Based on the quality of water, the study area can be divided into four categories such as very good, good, moderate and poor. These integrated parameters like pH, EC, TDS, Cl and F^- were given rank and weightage which do have unambiguous influence on the quality of water in this region. Based on the rank and weightage water quality zonation map were prepared. F^- is taken to as a key parameter for the preparation of water quality zonation map. The rank and weightage of each parameter is used for the preparation of water quality zonation map. The groundwater in the zones depicted as good and moderately good water can be directly used for domestic purposes. Groundwater within the zones identified as having poor quality should undergo treatment before being utilized for

Table 1. Statistical data of various hydrochemical parameters measured in the phreatic and confined aquifers of the study area.

Elements/Parameters	Phreatic aquifer		Confined aquifer		Average	Desirable limit	Permissible limit	Effects
	Minimum	Maximum	Minimum	Maximum				
pH	6	8	5.8	8.8	7	6.5	8.5	Taste
EC (µS/cm)	128	911	42	2180	530.8	750	1500	-
TDS (ppm)	70	501	23	1199	291.9	500	2000	Gastrointestinal irritation
Bicarbonate (mg/l)	5	268	9.8	737	141.4	300	500	Temporary hardness
Carbonate (mg/l)	4.8	52.8	4.8	77	18.2			
Total alkalinity (mg/l)	14.5	282.6	24	770.5	159.7	200	600	Rice on cooking turns yellow
Total hardness (mg/l)	42	860	66	1348	277.8	300	600	Cardiovascular diseases
Calcium (mg/l)	11	287	16	256.5	83.8	75	200	Scale formation
Magnesium (mg/l)	0.5	17	0.5	155	10.1	30	100	Scale formation
Chloride (mg/l)	16	414	20	1979	117	250	1000	Salty taste
Sulphate(mg/l)	5	109	0.9	260	38	200	400	Laxative effective
Sodium(mg/l)	13.5	241	12.5	1606	134.8	50	200	Salty taste
Potassium (mg/l)	1.8	61.5	4.6	73	18	-	12	Bitter taste
Nitrate (mg/l)	0.07	0.33	0.07	3.3	0.5	45	100	Blue baby diseases in children
Fluoride (µg/L)	0.01	0.6	0.01	2	0.28	-	1.5	Fluorosis
Silicate(mg/l)	45	245	48	345	135			

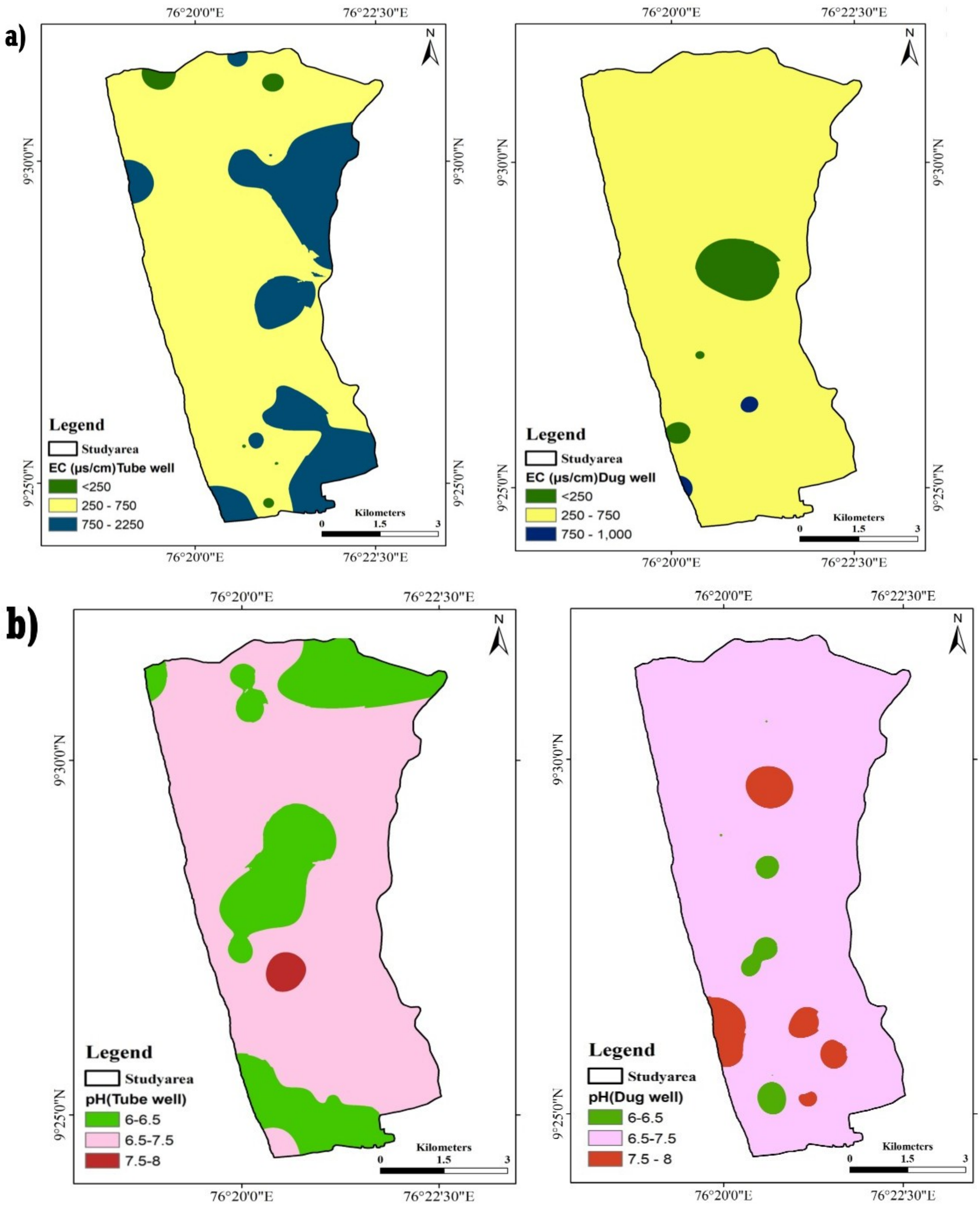
domestic purposes. In the phreatic aquifer, most of the groundwater samples from the study area come under the poor and very poor category (Fig. 4), because the water table is very shallow, thus, making them more vulnerable to surface contaminants like pesticides, fertilizers, industrial pollutants, and sewage. Also, in general, the phreatic aquifer is having a higher rate of recharge compared to the confined aquifers. Therefore, improper waste disposal and lack of proper waste management facilities can result in pollutants leaching into the soil and eventually reaching the phreatic aquifers at certain areas. Other area includes good and moderately good zones (Fig. 4). In the case of the confined aquifer, north-western part the study area falls under good to moderately good category zone. The poor-quality zones are found in the north-eastern part, mainly in the Alappuzha municipal area and the southern part (Ambalapuzha) of the study area.

4.2. Hill Piper diagram

The hydrochemical data was represented on a Piper diagram, following the method developed by Piper (1944). This diagram revealed a unique and recognizable pattern, in the central area of the diamond field, 50% of the samples displayed a lack of dominance in either cation or anion pairs. Around 35% of the samples fell within the realm of permanent hardness, with the remainder falling into the category of temporary hardness (Fig. 5). The water samples from the phreatic aquifer (dug well samples) are clustered closer to the bicarbonate (HCO_3^-) vertex of the triangle. They are found to be influenced by the chemistry of the overlying soil and the surface water, leading to a dominance of bicarbonate (HCO_3^-) ions and lower concentrations of other major ions are observed. This indicates a dominance of HCO_3^- in the water chemistry. Groundwater in the confined aquifer (tube well samples) show a more diverse distribution across the Hill Piper diagram, indicating a mix of different ions and hydrochemical facies. They have a more complex hydrochemical composition, influenced by different geochemical processes that occur over time. However, the hydrogeochemical observations are not supporting that the groundwater samples have a marine signature, via direct seawater ingression. Therefore, the potential sources of salt contributions could originate from marine aerosols. This could potentially be altering the water chemistry in such locations. The major facies found were Ca^{2+}–HCO_3^-, Na^+–Cl^-, and Na^+–HCO_3^-–Cl^-

4.3. Gibbs diagram

The interrelationship among hydrochemical constituents and the relative influence of hydrogeological processes can be assessed using Gibbs plot (Singh et al., 2020). Three major processes affect the chemical quality of water, viz., the influence of precipitation, water-rock interactions and evaporation, and these processes can be deciphered with the help of Gibbs diagram (Gibbs, 1970). Gibbs diagram was constructed for both anions and cations by correlating with TDS (Fig. 6). The plots show that the tube well sample data fall in the rock-dominant field and the dug well samples extends towards the precipitation field. Based on this interpretation, it seems that the tube well samples are primarily influenced by the geology of the aquifer materials (rock-dominant field), while the dug well samples are more influenced by precipitation and atmospheric processes (precipitation field). The distinction between the two fields suggests the different hydrogeochemical processes and sources of water for the phreatic and confined aquifers. Thus, it can be inferred that the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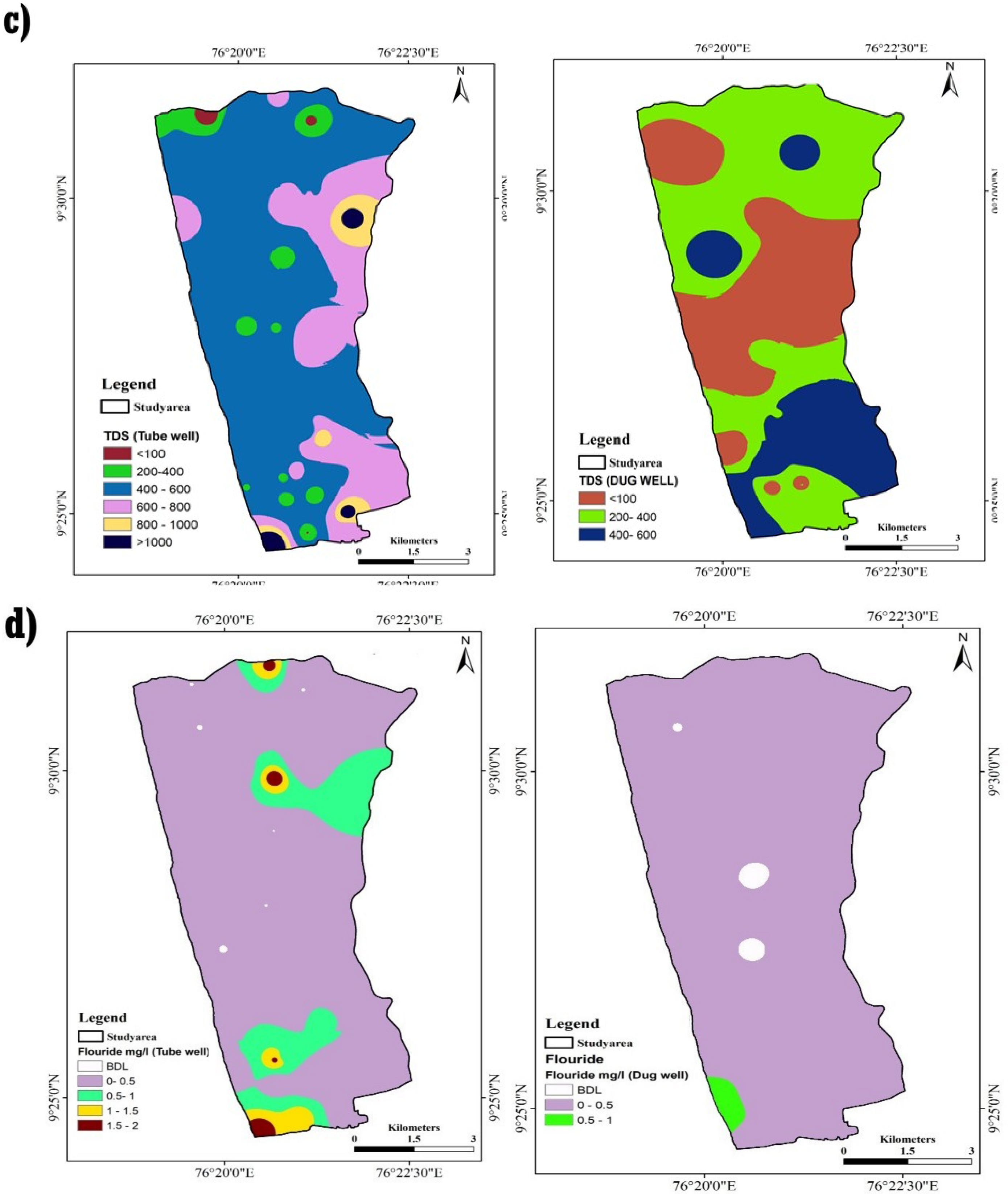

Fig. 2. Spatial variation maps of **a**) EC, **b**) pH, **c**) TDS and **d**) F^- in groundwater of confined and phreatic aquifers of Alappuzha area.

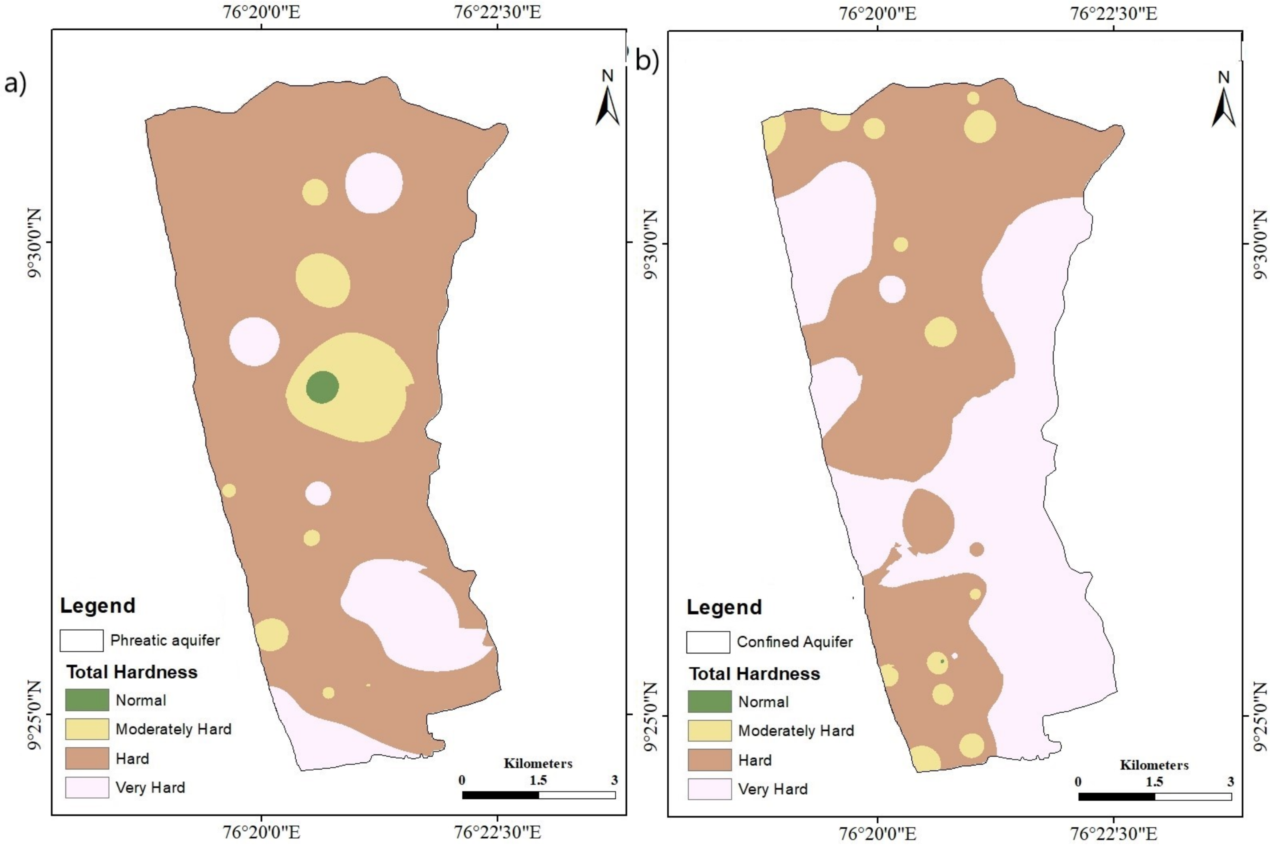

Fig. 3. Spatial variation map of Total Hardness in phreatic and confined aquifer of Alappuzha area.

Table 2. Rank and weightage applied for groundwater quality zoning.

Parameter	Phreatic aquifer				Confined aquifer			
	Class	Rank	Weightage	Index	Class	Rank	Weightage	Index
EC	130–280	3	15	45	42–470	6	20	120
	290–440	10		150	480–900	10		200
	450–590	8		120	910–1300	4		80
	600–740	2		30	1400–1800	3		60
	750–900	1		15	1900–2200	1		20
TDS	70–150	3	15	45	23–260	6	10	60
	160–240	10		150	270–490	10		100
	250–320	8		120	500–730	4		40
	330–410	2		30	740–960	2		20
	420–490	1		15	970–1200	1		10
F	0.012–0.122	10	25	250	-0012–0.396	10	40	40
	0.12–0.23	5		100	0.4–0.78	5		200
	0.24–0.35	3			0.79–1.2	3		120
	0.36–0.48	2		50	1.3–1.6	2		80
	0.49–0.6	1		25	1.7–2	1		40
Cl	16–96	10	25	250	20–410	10	20	20
	97–180	4		100	420–800	4		80
	190–250	3		75	810–1200	3		60
	260–330	2		50	1300–1600	2		40
	340–410	1		25	1700–2000	1		20
pH	6.2–6.6	1	20	20	8.3–8.8	1	10	10
	6.7–6.9	4		80	7.7–8.2	2		20
	7–7.3	10		200	7.1–7.6	8		80
	7.4–7.6	3		60	6.5–7	6		60
	7.7–8	2		40	5.8–6.4	3		30

chemistry of the groundwater is mainly controlled by the interactions of precipitation-recharged groundwater with local rock formations. The impact of evaporation on water chemistry seems to be

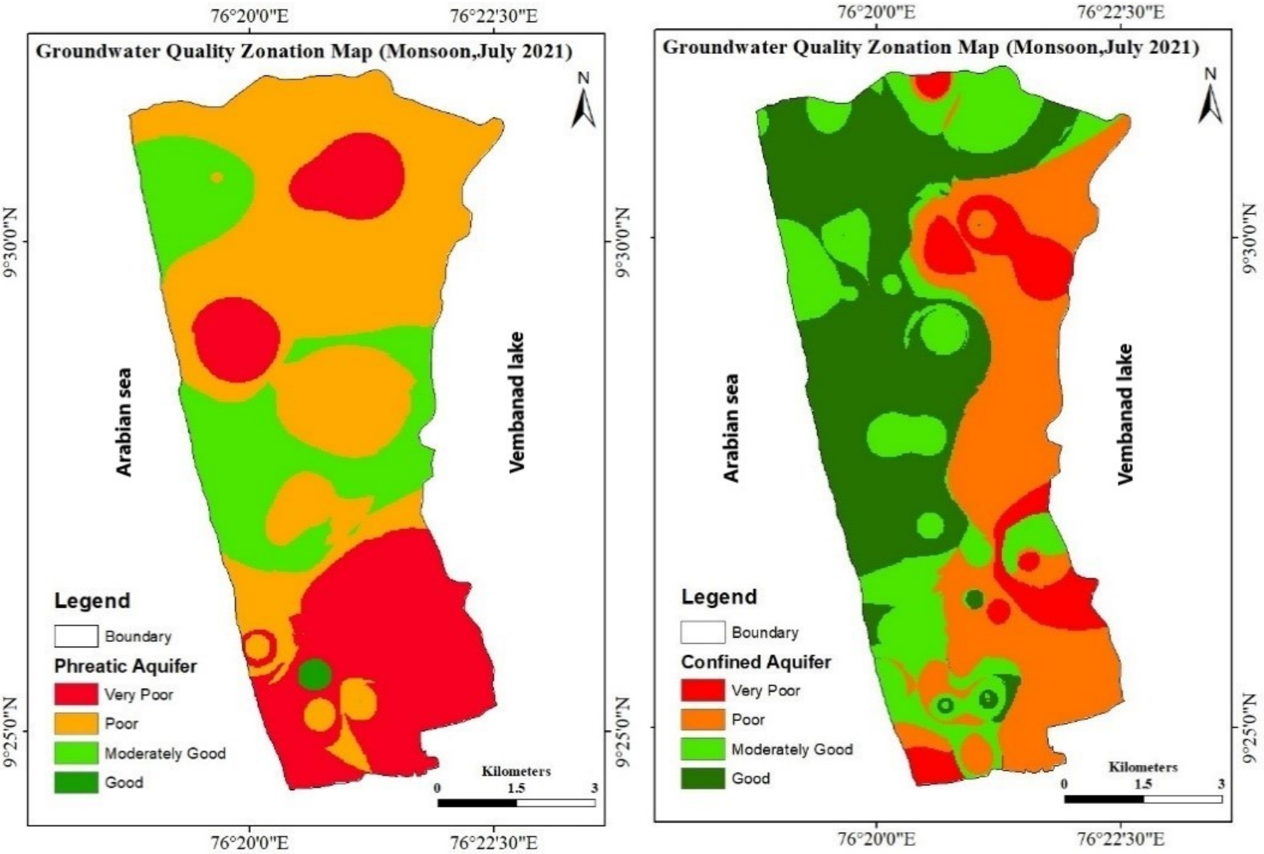

Fig. 4. Groundwater quality zonation map of phreatic and confined aquifers of Alappuzha area.

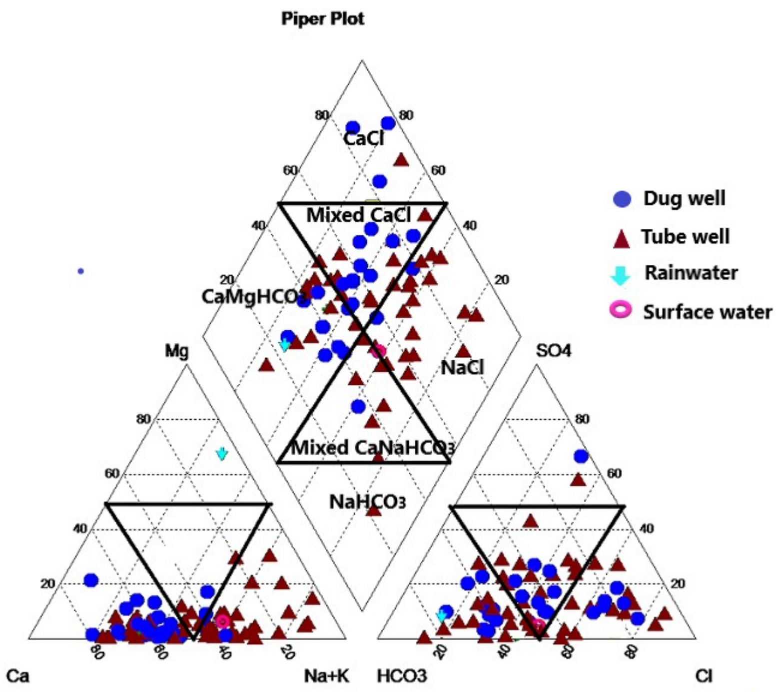

Fig. 5. Piper diagram used for geochemical classification of shallow and deep groundwater samples collected from the study area during June 2021.

negligible. Since the region experiences normal temperatures (24°C to 27°C) during monsoon period, it can be expected that the evaporation effects are minimal.

4.4. Irrigation water quality

The quality of water plays a vital role in the domain of irrigated agriculture. The appropriateness of water for irrigation relies on the impact of water's mineral constituents on both plant life and soil health (Hill, 1942; Anon, 1946). Key factors determining water's suitability for irrigation encompass salinity, sodium percentage, Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), and permeability index. Salinity correlates broadly with parameters such as Total Dissolved Solids (TDS) and Electrical Conductivity (EC). Elevated TDS and electrical conductivity levels in irrigation water have the potential to elevate soil salinity. The salts present in water not only directly affect plant growth but also exert an indirect influence on soil structure, permeability, and aeration, subsequently impacting plant growth dynamics (Todd, 1959). Water exhibiting electrical conductivity below 250 µS/cm is classified as excellent, while the range of 250 to 750 µS/cm is considered good, 750 to 2250 µS/cm as medium, 2250 to 4000 µS/cm as poor, and exceeding 4000 µS/cm as highly unsuitable for irrigation (Fipps, 2003). The electrical conductivity of the majority of the groundwater samples collected from the study area during the monsoon period are in good category for irrigation (Table 3).

The significance of sodium concentration in the classification of irrigation water lies in its interaction with soil, leading to decreased permeability. The groundwater's sodium content within the study area is quantified using the sodium percentage (Na%), with all ionic concentrations measured in milliequivalents per liter (epm). In accordance with the Wilcox classification (Wilcox, 1955), sodium percentage (Na%) values below 20% are categorized as excellent, while those falling between 20% and 40% are good. Additionally, levels between 40% and 60% are considered permissible, ranging from 60% to 80% are considered doubtful, and values exceeding 80% are classified as unsuitable, In the phreatic aquifer of the study area, 92% of the groundwater samples fall within the very good to good category, 8% of the samples under good to permissible category (Fig. 7b). Only one sample is in permissible to doubtful category for irrigation purposes and, in the case of groundwater samples from the confined aquifer, 57% of samples fall within the very good to good category, only 4% (2 samples) were in good to permissible category and 26% of the samples in permissible to doubtful and one sample (location name: Vandanam) falls in doubtful to unsuitable category. The location, Vandanam, is situated near the beach area and the groundwater is having high electrical conductivity values, hence, not suitable for irrigation due to the risk of soil salinity problems. The calculated values of SAR in the study area varies from 0.64 to 4.5 in phreatic aquifer and 0.52 to 25 in the confined aquifer. The USSL (1954) plot indicates that only 12% of the groundwater samples from the phreatic aquifer is categorized predominantly as C1S1 (characterized by low salinity and low sodium levels), while approximately 80% of the samples are classified within the C2S1 category as shown in Fig. 7a. This suggests that the phreatic aquifer in the study region possesses moderate salinity levels combined with low sodium content, rendering it suitable for irrigation across various soil types. Conversely, about only 8% of the phreatic aquifer samples, fall into the C3S1 classification, indicating a high salinity-high sodium profile. The water from the phreatic aquifer falls within the "C1" category on the USSL diagram. It has low SAR and sodium content, indicating that it is suitable for irrigation without significant risk of soil dispersion. The USSL diagram representing groundwater samples obtained from the confined aquifer reveals that only 10% of the samples are categorized as C1S1 (low salinity–low sodium type), while 55% of the samples belong to the C2S1 category (Fig. 7a).

This indicates that a majority of the groundwater within the confined aquifer possesses moderate salinity levels with low sodium content, making it suitable for irrigation across various soil types. Approximately 11% of the groundwater samples obtained from the confined aquifer are situated within the C3S1 category. Indicating a high salinity-high sodium type. Only 16% of the samples fall in the medium salinity to high sodium category (C3S2), and one sample in the C2S4 and C2S3 category. This type of water can be used to irrigate salt-tolerant and semi-tolerant crops under favourable drainage conditions. Analysis of the USSL plot concerning groundwater samples derived from the confined aquifer reveals insightful findings. Among these samples, a

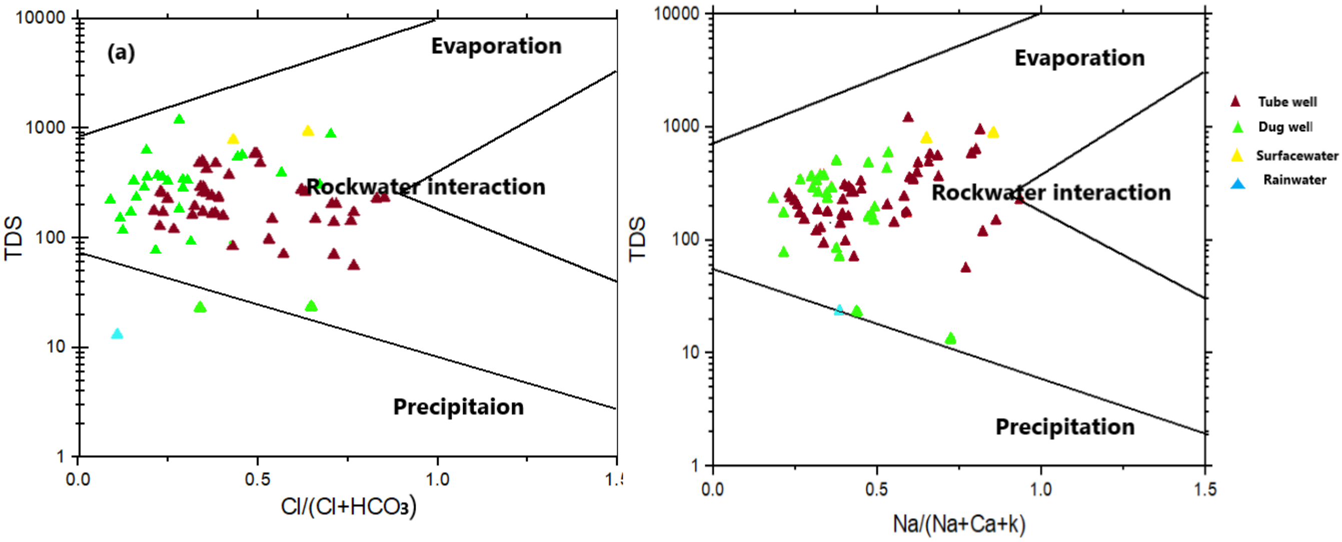

Fig. 6. Gibbs diagram showing the mechanisms controlling the groundwater chemistry of phreatic and confined aquifers of Alappuzha area during June 2021.

Table 3. Irrigation water quality.

Parameters	Phreatic aquifer		Confined aquifer	
	Minimum	Maximum	Minimum	Maximum
SAR	0.64	4.6	0.54	25.07
SSP	19.45	61.7	23.16	85.26
MAR	0.48	32.5	0.5	81.95
K-RATIO	0.21	1.51	0.24	5.41
RSC	-10.59	-0.19	-9.00	9.80
RSBC	-10.16	-0.12	-8.24	10.12
PI	20.49	75.77	37.62	103.59
Na%	0.19	0.62	0.23	0.85

mere 10% align with the C1S1 classification denoting low salinity and low sodium content, while a significant 55% are categorized under C2S1, representing medium salinity combined with low sodium levels (Fig. 7a). This distribution underscores that the majority of groundwater within the confined aquifer holds medium salinity characteristics, complemented by low sodium concentrations, rendering it suitable for irrigation across diverse soil types. Further examination indicates that approximately 11% of the confined aquifer's groundwater samples correspond to the C3S1 zone, indicating a high salinity-high sodium composition. Additionally, around 16% of the samples belong to the C3S2 classification, representing medium salinity coupled with elevated sodium content. Notably, a solitary sample occupies the C2S4 and C2S3 categories. These specific water compositions find applicability in irrigating crops capable of tolerating higher salt levels, with favourably managed drainage conditions. The groundwater from the confined aquifer falls within the "C4" category on the USSL diagram. It has a higher SAR and sodium content, suggesting that it may pose some risk of soil dispersion when used for irrigation. Overall, the analysis of water quality using the Wilcox and USSL diagrams shows that the water from the phreatic aquifer in the Alappuzha region is generally more suitable for irrigation compared to water from the confined aquifer. However, it's essential to consider other factors like crop type, soil characteristics, and irrigation practices to make more comprehensive decisions regarding water use in agriculture (Gowd, 2005).

4.5. Principal component analysis

The hydrochemical data can undergo statistical analysis using a correlation coefficient, which serves as an indicator of the degree to which one variable can predict another. (Nie, 1975; Davis and Sampson, 1986). Correlations among 16 hydrochemical parameters were statistically examined in the present study. A high correlation coefficient signifies a strong connection between two variables, whereas a correlation coefficient nearing zero indicates a weak or insignificant relationship. Positive r^2 values indicate a

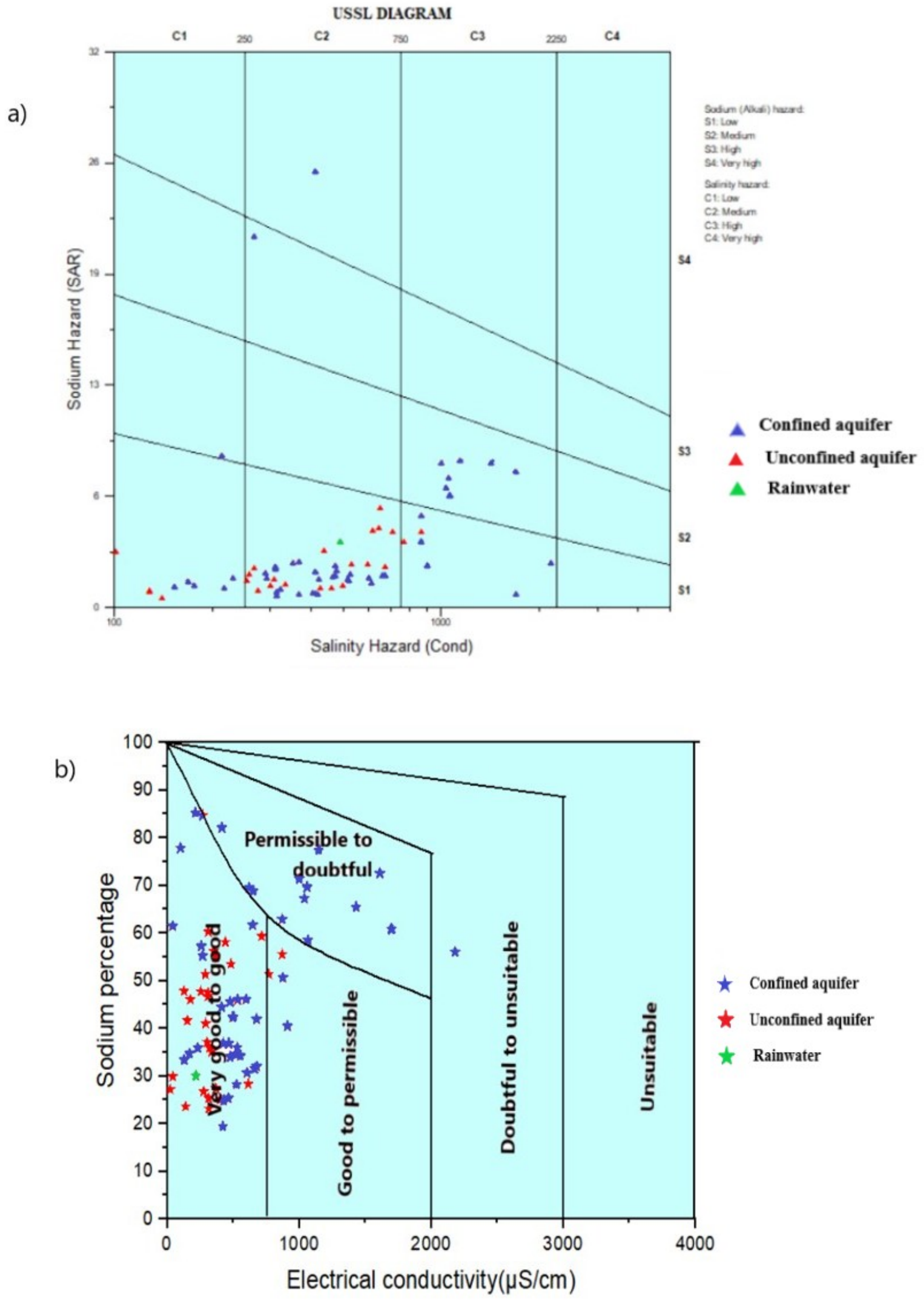

Fig. 7. Irrigation water quality diagrams (**a**) USSL diagram, used for the categorization of irrigation water quality based on salinity and sodium hazard (**b**) Wilcox diagram (water quality classification based on percent sodium and electrical conductivity (after Wilcox, 1955).

positive relationship, while negative values suggest an inverse relationship. The correlation coefficient matrices for the analysis are presented in Table 4 and 5. These matrices were obtained via linear regression analysis. The analysis reveals three discernible correlation patterns: (i) a highly competitive relationship among ions possessing identical charges but differing valence numbers, such as Cl^- with SO_4^{2-} ($r^2 = 0.6$; $p < 0.01$) and confined aquifer ($r^2 = 0.5$; $p < 0.01$), (ii) a strong chemical affinity between ions of opposing charge, sharing equal valence numbers, like Cl^- with Na^+ under phreatic conditions ($r^2 = 0.816$; $p < 0.01$) and confined conditions ($r^2 = 0.98$; $p < 0.01$), and (iii) a non-competitive correlation among ions of identical

Table 4. Correlation matrix of chemical constituents in groundwater of phreatic aquifer of Alappuzha region June 2021.

	EC	PH	TDS	CO_3^-	HCO_3^-	CL^-	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	NO^{3-}	PO_4^{3-}	SiO_3^{2-}	F^-
EC	1															
PH	.177	1														
TDS	1.000**	.177	1													
CO_3^-	.546**	.243	.546**	1												
HCO_3^-	.546**	-.048	.546**	.271	1											
CL^-	.348	.153	.348	.499*	.524**	1										
TH	.601**	.116	.601**	.523**	.652**	.847**	1									
Ca^{2+}	.664**	.084	.664**	.531**	.710**	.780**	.984**	1								
Mg^{2+}	.010	.195	.009	.134	.182	.794**	.577**	.436*	1							
Na^+	.691**	.091	.691**	.736**	.692**	.810**	.803**	.809**	.394	1						
K^+	.671**	.076	.671**	.662**	.507**	.584**	.582**	.630**	.175	.791**	1					
SO_4^{2-}	.465*	.158	.465*	.586**	.259	.596**	.744**	.722**	.426*	.585**	.449*	1				
NO^{3-}	-.007	-.015	-.007	.177	.334	.754**	.420*	.363	.562**	.571**	.370	.199	1			
PO_4^{3-}	.268	-.044	.268	-.268	.350	-.048	.047	.129	-.176	.087	.393	-.218	.055	1		
SiO_3^{2-}	.650**	.011	.650**	.240	.462*	.247	.451*	.493*	.097	.487*	.504*	.549**	.032	.367	1	
F^-	.448*	.074	.448*	.275	.376	.178	.168	.167	.076	.509**	.224	.065	.190	.033	.466*	1

charge and equivalent valence numbers, such as K^+ with Na^+ under phreatic conditions ($r^2 = 0.8$; $p < 0.01$) and in confined condition ($r^2 = 0.7$; $p < 0.01$). It was found that EC of groundwater and the major components of seawater (Na^+, Cl^-, and SO_4^{2-}) showed significant correlations between them, viz., EC Vs Na^+, in phreatic aquifer, $r^2 = 0.69$, but less correlation in confined aquifer, $r^2 = 0.2$; EC Vs Cl^-, in phreatic aquifer, $r^2 = 0.35$, and in confined aquifer, $r^2 = 0.09$; and EC Vs SO_4^{2-}, in phreatic aquifer, $r^2 = 0.47$, and in confined aquifer, $r^2 = 0.27$; $p < 0.01$). Confined aquifers, by definition, are confined by impermeable layers of rock or clay, which restrict the direct exchange of water and solutes with adjacent water bodies but phreatic aquifers, being shallow and in direct contact with the overlying soil and surface water bodies, are more vulnerable to seawater intrusion in coastal regions. The fluctuations in these relationships might signify the intricate nature of the hydrochemical constituents within groundwater. A four-factor model is extracted for both phreatic and confined aquifers and it explains the total groundwater quality variations of over 71% and 73% respectively. (Table 2).

The bellow mentioned factors have been computed for the hydrochemical aspects of the different aquifers.

In phreatic aquifer:

Factor 1: EC, TDS, Na^+, K^+, Ca^{2+}, SiO_3^{2-}, CO^-_3, SO_4^{2-}, TH

Factor 2: Cl^-, NO_3^-, Mg^+, Na^+, Ca^{2+}, TH

Factor 3: CO^-_3, SO_4^{2-}, pH

Factor 4: F^-

In confined aquifer:

Factor 1: Na^+, K^+, Mg^+, Cl^-, CO^-_3, SO_4^{2-}, TH

Factor 2: Ca^{2+}, $PO\ _3\ ^-$, SiO_3^{2-}, pH

Factor 3: EC, TDS, F^-

Factor 4: EC, TDS, NO_3^-, SiO_3^{2-}

In phreatic aquifer, a total of 79% of the samples explain the variation in the data. Factor 1 accounted 36.3% (Table 6) of the total variance and was characterized by the association of EC, TDS, Na^+, K^+, Ca^{2+}, SiO_3^{2-}, CO^-_3, SO_4^{2-} and TH. Strong correlations are exhibited by these elements. A positive correlation of these ions (i.e., EC, TDS, Na^+, K^+, Ca^{2+}, SiO_3^{2-}, CO^-_3, SO_4^{2-}, and TH) indicates the mixing of water of different types namely precipitation, infiltration, saltwater intrusion etc. Among these, Na^+ and EC displays a strong positive correlation indicating evidence of saltwater intrusion. High Na^+ values are obtained from water samples collected from the dug well located at the place named Vandanam. Sodium is often found in groundwater of phreatic aquifer, as a result of anthropogenic activities like agricultural practices etc.

In the confined aquifer, the total of 73% samples explains the variation in the data. The factor 1 accounted 33.3% (Table 6) of the total variance and was characterized by the association of Na^+, K^+, Mg^+, Cl^-, CO^-_3, SO_4^{2-} and TH. Strong correlations are exhibited by these elements. A positive correlation of these ions (i.e., Na^+, K^+, Mg^+, Cl^-, CO^-_3, SO_4^{2-} and TH) indicates the mixing of water of different types by rock-water interactions, infiltration, saltwater intrusion etc. Among these, Na^+ and Cl^- displays a strong positive correlation indicating evidence of saltwater intrusion, the tube well sample from the location Chirayil, exhibits high Cl^- ion content. Tube well samples collected from the Chirayil area is characterized by having high total hardness and Mg concentration. In this area, where there is hydraulic connectivity between the lagoon and the

Table 5. Correlation matrix of chemical constituents in groundwater of confined aquifer of Alappuzha region during June 2021.

	EC	**pH**	**TDS**	**CO_3^-**	**HCO_3^-**	**CL^-**	**TH**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**SO_4^{2-}**	**NO^{3-}**	**PO_4^{3-}**	**SiO_3^{2-}**	**F^-**
EC	1															
PH	.312*	1														
TDS	1.000**	.312*	1													
CO_3^-	.284	.385*	.284	1												
HCO_3^-	.362*	.482**	.362*	.575**	1											
CL^-	.098	.130	.098	.653**	.498**	1										
TH	.389*	.222	.389*	.653**	.409**	.737**	1									
Ca^{2+}	.183	.324*	.183	.299	.260	.010	.339*	1								
Mg^{2+}	.320*	.056	.320*	.514**	.322*	.768**	.843**	-.206	1							
Na^+	.201	.193	.201	.720**	.593**	.977**	.754**	.073	.758**	1						
K^+	.291	.175	.291	.543**	.485**	.615**	.651**	.271	.551**	.701**	1					
SO_4^{2-}	.270	.110	.270	.586**	.422**	.506**	.689**	.234	.611**	.576**	.519**	1				
NO^{3-}	.413**	.171	.413**	.250	.451**	.119	.310*	-.076	.379*	.192	.239	.334*	1			
PO_4^{3-}	.093	.247	.093	.237	.101	-.087	.053	.285	-.112	-.054	.223	-.083	.002	1		
SiO_3^{2-}	.372*	.204	.373*	.120	.341*	-.004	.185	.351*	.013	.054	.337*	.133	.427**	.412**	1	
F^-	.446**	.119	.446**	.129	.058	.050	-.037	-.087	.009	.122	.026	-.137	.046	-.026	.080	1

Table 6. Results of the principal component analyses with Varimax rotation.

Rotated Component Matrix								
	Component (phreatic)				**Component (confined)**			
	1	2	3	4	1	2	3	4
EC	.929	-.025	.134	.172	.179	.134	.762	.515
pH	.088	.007	.502	.095	.193	.577	.349	-.023
TDS	.929	-.025	.134	.172	.179	.134	.762	.515
CO_3^-	.543	.226	.631	.111	.768	.346	.179	-.026
HCO_3^-	.635	.403	-.298	.204	.556	.371	.195	.257
CL^-	.359	.909	.160	-.013	.936	-.068	.040	-.137
TH	.671	.647	.138	-.211	.858	.115	.060	.238
Ca^{2+}	.754	.554	.074	-.206	.117	.780	-.037	.027
Mg^{2+}	-.022	.829	.180	-.101	.838	-.313	.088	.255
Na^+	.697	.591	.178	.285	.955	.005	.122	-.072
K^+	.747	.326	-.022	.113	.719	.283	.022	.199
SO_4^{2-}	.575	.379	.452	-.371	.718	.030	-.100	.338
NO^{3-}	-.028	.871	-.120	.267	.225	-.061	.112	.807
PO_4^{3-}	.393	-.093	-.776	.095	-.058	.701	-.041	.080
SiO_3^{2-}	.767	.010	-.099	.114	.005	.518	.064	.637
F^-	.332	.078	.139	.844	-.027	-.057	.851	-.147
% of Variance	36.313	23.919	10.869	7.853	33.287	13.737	13.353	12.397
Cumulative%	36.313	60.232	71.101	**78.954**	33.287	47.024	60.377	**72.774**

underlying aquifer, the lagoon water can seep into the aquifer during the periods of low water table conditions or due to changes in lagoonal water levels. This process can be termed as lagoonal water intrusion. As the lagoonal water mixes with the groundwater, it introduces higher chloride concentrations, causing an increase in the chloride content in the groundwater. High values of CO_3^- found in tube wells of the locations Ponagirichira and Chirayil areas. CO_3^- ions in groundwater are a product of the process of dissolving carbonate minerals such as calcite and dolomite. Samples collected from the tube wells of the Ambalapuzha area show a high concentration of SO_4^{2-}. SO_4^{2-} is often present in the confined aquifer due to the weathering of sulphide minerals and the oxidation of organic matter (Table 5).

Factor 2 explains 23.9% of the total variance in groundwater samples from the phreatic aquifer, that includes Cl^-, NO_3^-, Mg^{2+}, Na^+, $Ca^{2+}$and TH. This implies that there is a strong positive correlation between Cl^-, NO_3^-, Mg^{2+}, Na^+, Ca^{2+} and TH (Table 4). Alappuzha coastal region is characterized by intensive agricultural activities, hence, excessive use of fertilizers and pesticides can result in elevated nitrate (NO_3^-) concentrations in the groundwater. Agricultural runoff can also contribute to the increased levels of other ions like Ca^{2+} and Mg^{2+}. This factor reflects the signature of saline water intrusion and hence shows evidence of seawater or lagoonal water ingression due to excessive groundwater pumping. High values of Ca^{2+} (287 mg/L) are obtained for groundwater samples from the dug wells of the

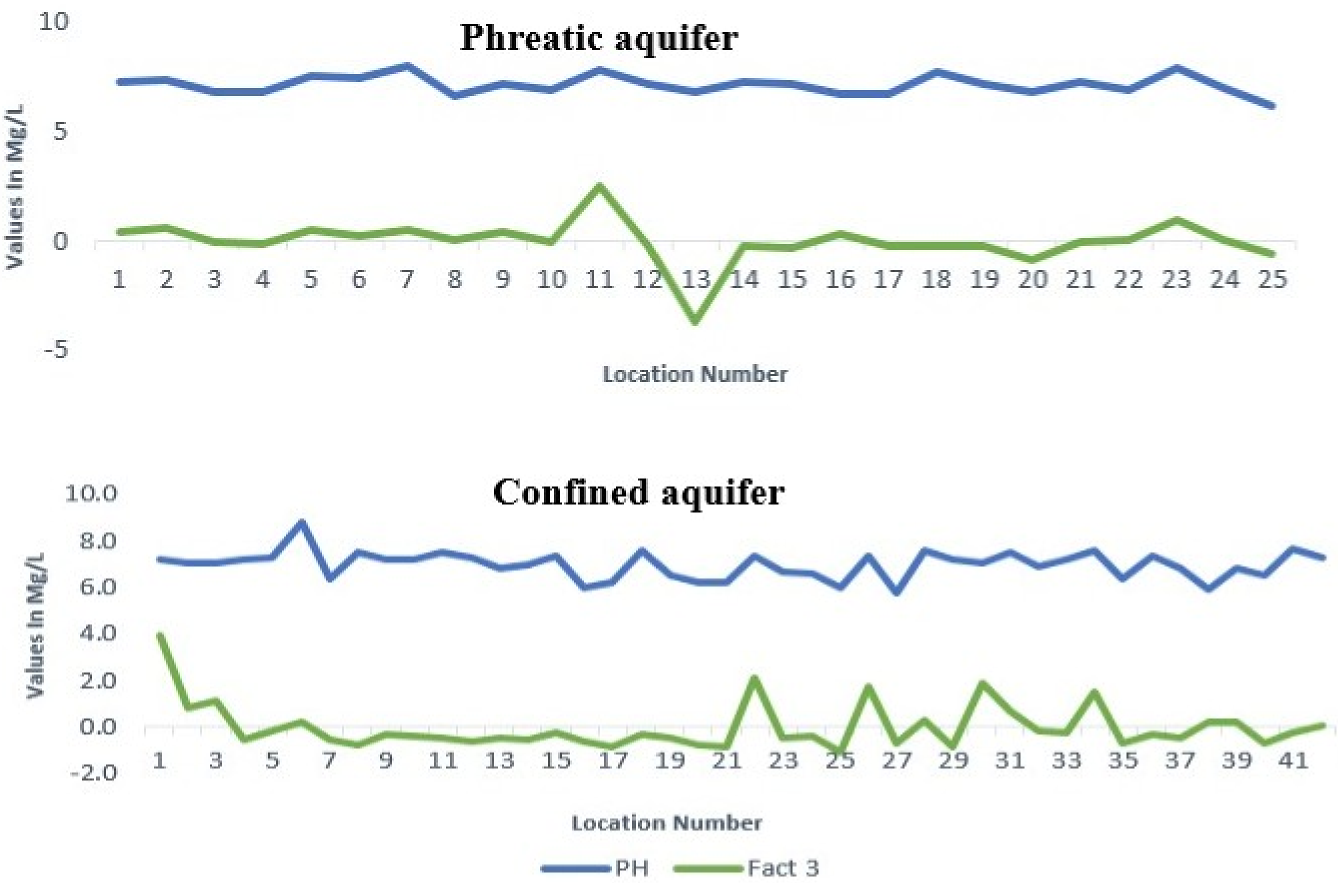

Fig. 8. The relation between average F3 score and pH of groundwater in phreatic and confined aquifers.

location Vandanam. In the confined aquifer, Factor 2 explains 13.74% of the total variance including Ca^{2+}, PO_4^{3-} $SiO_3^{2-}$and pH. The pH of the groundwater can be influenced by redox conditions in the subsurface. Certain redox reactions can affect the solubility of various ions, including calcium, phosphates, and silica, leading to their co-occurrence in the groundwater. And also, various geochemical reactions, including mineral precipitation and ion exchange processes, have the potential to impact the levels of calcium, phosphates, silica, and pH within groundwater. Water samples gathered from Thumpoli area's tube wells exhibited a notably elevated pH of 8.8, signifying an alkaline nature. Tube wells of Paravur, Vazhicheri contains water with high PO_4^{3-} (4.5 mg/L) and SiO_3^{2-}concentrations compared to the rest of the samples collected from the study area.

In the groundwater samples from the phreatic aquifer, a total of 10.8% variance accounts for Factor 3 which contains CO_3^{-}, SO_4^{2-} and pH. These ions exhibit a positive correlation. Human activities, such as agriculture, industrial activities, or wastewater discharges, can introduce CO_3^{2-}, SO_4^{2-} and changes the pH of the groundwater. This factor reflects the signature of water-soil or water-rock interactions. Dissolution and weathering of the rocks on interaction with the water is described by this factor. A correlation between Factor 3 and pH is depicted in the graph (Fig. 8). In the groundwater samples from the confined aquifer, a total of 13.4% variance accounts for Factor 3, which contains EC, TDS, and F^-. This implies that there is a strong positive correlation between Electrical Conductivity (EC) and Total Dissolved Solids (TDS). EC and TDS are parameters employed to characterize the salinity levels of water. Punnappara dug well samples also displayed considerable EC and TDS values compared to other dug well samples. (Fig. 9) shows that there is a strong correlation between Total dissolved solids, Cl^- and Na^+ and (Fig. 10) depicts a moderate correlation between Electrical conductivity and Cl^- in the phreatic aquifer. Both these graphs imply saltwater intrusions

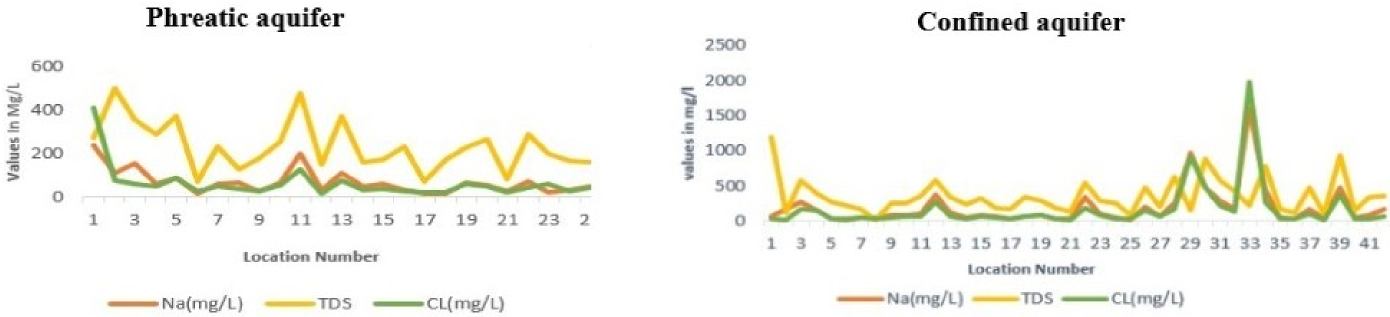

Fig. 9. Plots of TDS, Na and Cl in groundwater of phreatic and confined aquifers.

of the coastal aquifers.

This factor reflects the signature of saline water intrusion and hence shows evidence of seawater ingression or lagoonal water ingression due to excessive groundwater pumping. Water samples obtained from the tube wells of the Vandanam region shows high EC and TDS values.

In the groundwater samples from the phreatic aquifer, the Factor 4, which accounts for almost 8% of the total variance, constitute only F^-. The fact that Factor 4 consists only of fluoride (F^-) and does not correlate with any other parameters means that fluoride concentrations are not significantly influenced by the same underlying factor that affect the other parameters analysed. This suggests that fluoride behaves differently from the other variables in the phreatic aquifer and might be controlled by specific geochemical or hydrogeological processes unique to fluoride. In the groundwater samples from the confined aquifer, Factor 4, which accounts for almost 12.4% of the total variance, constitutes EC, TDS, NO_3^-, and SiO_3^{2-}. The concentrations of EC, TDS, NO_3^-, and SiO_3^{2-} in the groundwater can be influenced by water-rock interactions. As groundwater moves through the geological formations, it can interact with the minerals and rocks, leading to the release or retention of ions, including nitrate and silicate.

5. Conclusions

Hydrogeochemical parameters of the groundwater samples from the phreatic and confined aquifers of the Alappuzha district to assess the appropriateness of water for both drinking and irrigation purposes. The fundamental water quality parameters indicate distinctly that the groundwater possesses a slightly alkaline nature and is characterized by its fresh in quality. The predominant facies identified were Ca^{2+}–HCO_3^-, Na^+–Cl^-, and Na^+–HCO_3^-–Cl^-. The Gibbs plots indicate that the water chemistry is primarily influenced by the interplay between precipitation-recharged groundwater and the surrounding rock formations. The Wilcox diagram shows that above 90% of the groundwater samples in phreatic aquifer lie within the range of “very good” to “good” category, and approximately 50% of the groundwater samples obtained from the confined aquifer are classified within the range of “very good” to “good” quality and remaining samples are falling in permissible to doubtful category. The deterioration of groundwater quality is because of the influence of urban and industrial waste discharge, aquifer mineralogy and other anthropogenic activities. The USSL plot reveals that the phreatic aquifer within the study region displays medium salinity with low sodium levels, and it can be suitable for irrigation across various soil types. The water from the confined aquifer falls within the “C4” category on the USSL diagram and has a higher SAR and sodium content, suggesting that it may pose some risk of soil dispersion when used for irrigation. The correlation coefficient matrix developed for the groundwater from the phreatic aquifer show a positive correlation between EC, TDS, Na^+, K^+, Ca^{2+}, SiO_3^{2-}, CO^-_3, SO_4^{2-}, and TH, indicating the mixing of water of different types, viz., precipitation, infiltration, saltwater etc. Sodium is often found in phreatic aquifer as a result of anthropogenic activity like agricultural practices. In the confined aquifer, a positive correlation between Na^+, K^+, Mg^{2+}, Cl^-, CO^-_3, SO_4^{2-} and TH is observed and it indicates the mixing of water of different types, infiltration, saltwater and by rock-water interactions. The chemical composition and groundwater quality within the phreatic aquifers have been notably influenced by significant factors, primarily attributed to tidal inlets and the inputs arising from marine aerosols make significant contributions. The hydrogeochemical analysis carried out using factor analyses has unveiled a correlation

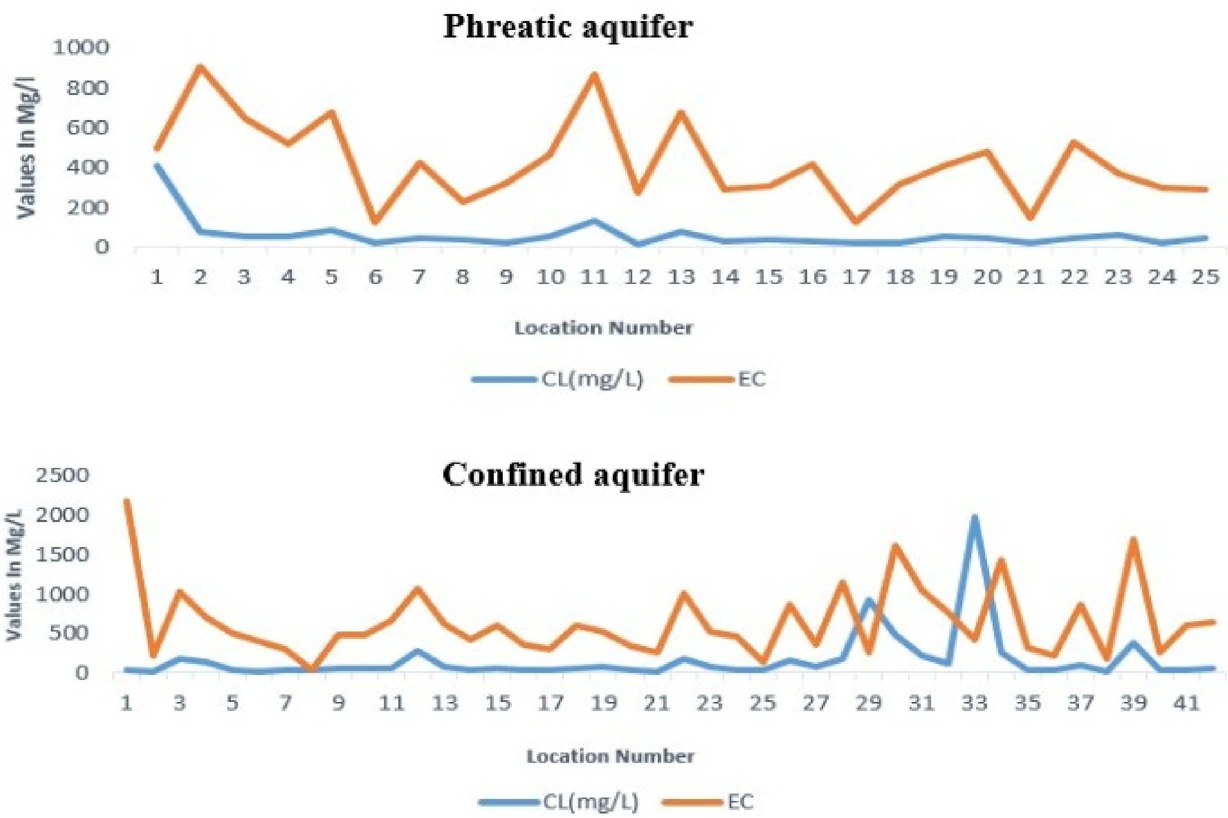

Fig. 10. The relationship between EC and Cl $^{-}$ in groundwater of phreatic and confined aquifers

between the results of these analyses and the hydrogeological characteristics in the area.

Thus, the study suggests that there are variations in groundwater quality across the study area, with certain regions being suitable for direct domestic use, while others require treatment to meet domestic water quality standards. Analysis of the hydrochemical data using the Piper diagram provides insights into the groundwater characteristics of the study area. It highlights the differences between the phreatic and confined aquifers in terms of dominant ions and hydrochemical composition. The absence of a marine signature in the groundwater samples suggests that marine aerosols are likely contributing to the salt content in certain locations. The presence of different hydrochemical facies indicates the influence of various geological and geochemical processes on the groundwater chemistry. The phreatic aquifers are generally located closer to the surface, making them more vulnerable to surface contaminants like pesticides, fertilizers, industrial pollutants, and sewage, and phreatic aquifers often have a higher rate of recharge compared to confined aquifers. In certain areas, improper waste disposal and lack of proper waste management facilities can result in pollutants leaching into the soil and eventually reaching the phreatic aquifers. Control measures are essential to protect the vulnerable phreatic aquifer from contamination. The projected irrigation parameters suggest that the groundwater within the phreatic aquifer is generally more suitable for irrigation purposes, but management practices must be considered for sustainable agricultural practices in the region. Since last ten years domestic needs for towns and panchayats are met from surface water (source Moovattupuzha and Pamba river) through the Japan International Cooperation Agency (JICA)-assisted Kerala Water Supply Project of Kerala Water Authority. Groundwater in the phreatic aquifers has fluoride concentrations within permissible ranges of 0.06 to 0.1 mg/L. however, a few tube wells tapping deeper aquifer around the urban study area have fluoride concentrations in the range of <2 mg/l. The hydrochemical analysis of the phreatic and confined aquifers reveals the influence of various factors on groundwater composition. It highlights the presence of saline water intrusion, lagoonal water intrusion, and anthropogenic influences affecting the water quality.

Ethical statement

Ethics approval and consent to participate: All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Availability of data

All data generated or analysed during this study are included in this published article and its supplementary information files (available by contacting the corresponding author).

Competing interests

The authors declare no competing interests.

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CRedIT statement

NSV: Investigation, Formal analysis, Visualization, Data curation, Writing–original draft. **RBB**: Project administration, Supervision, Methodology, Data Curation. **ES**: Project administration, Supervision, Data curation, Writing–review & editing. **JN**: Conceptualization, Supervision, Methodology, Writing–review & editing.

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