Geochemical characterization of groundwater and water quality assessment for sustainable management of hard rock aquifer in South India

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Abstract

Hydrogeochemical investigation was carried out in groundwater of Virudhunagar district, Tamil Nadu, India. Geologically the study area is occupied with Archaean, Charnockite, Unclassified Genesis and Pleistocene Laterite formations. A total of 72 groundwater samples were collected spatially during North East Monsoon (NEM) in 2019 based upon the coverage of geological formations. The collected samples were studied for different physio-chemical parameters like pH, TDS and EC, major cations (Ca, Mg, Na, K) and major anions (Cl, HCO₃, SO₄, PO₄). EC and TDS ranges from 273 to 5869 mg/L and 194 to 4159 mg/L. The ionic dominance of the hydrochemical parameters follows in the order of Na > Ca > Mg > K and Cl > HCO₃ > SO₄ > PO₄. The data represents two major hydrogeochemical facies of Ca-HCO₃ and mixed Ca-Mg-Cl in the study region. The USSL classifications of samples signifies low alkali hazard and high to very high salinity hazard. The higher concentration of TDS and EC in the samples reflects the unsuitability of groundwater. According to the WHO drinking water quality standards and the value of SAR, RSC, Na% reflects the groundwater in the study region is more suitable for irrigation than drinking purpose. The statistical method also adopted to understand the major factors influencing the variation in hydrochemistry of the region. Weathering, leaching of salts and anthropogenic activities were identified to be the key governing factor in the varied groundwater chemistry of this region.

Introduction

The quality of water is the dynamic concern for mankind, meanwhile it is openly connected with human welfare. Mostly the groundwater (about 20 to 40%) is utilized for the drinking purposes in world (Morris et al. 2003). It is also playing a vital role in the agricultural activities and its development. Increasing the population leads to increasing the need of more groundwater resources for agricultural and every day household needs. Still, maximum of the aquifers is not of sufficiently functioning for good quality water due to the impact of various factors like natural or anthropogenic impact (Epule et al. 2011). Hence, Deprived water quality will distress the human health and also agricultural development (Olajire and Imeokparia 2001), hence it is directly and badly affecting economic growth and social wealth of the country (Milovanovic 2007). The chemical characteristics of groundwater is mainly processed by natural and anthropogenic factors (Garcia et al. 2001; Nur et al. 2011; Fakir et al. 2002; Kim et al. 2005). Recent researchers are more concern on the hydrogeochemical studies (Chidambaram et al. 2011, Thilagavathi et al. 2012, Thilagavathi et al. 2020; Kumaresan and Riyazuddin 2006; Thivya et al. 2013; Adithya et al. 2016 Tatawat and Singh 2008; Panda et al. 2017; Semwal and Jangwan 2009; Dinesh and Singh 2010; Biswajeet and Saied 2011; Senthil et al. 2014; Devaraj et al. 2018). The groundwater quality and its movements is dependent on the properties of nearby lithology and also by the varies activities by the human (Jayaalakshmi et al. 2012). The spatial and sequential assessment of most important ions in groundwater is a broadly recognized tool to afford an imminent around the aquifer's heterogenetic and connectivity, moreover the processes that control the ground water interaction (Panda et al. 2017; Chidambaram et al. 2012).

Ground Water quality and geochemistry plays a significant character in groundwater defense and also quality management. Since, it is most important to assess the quality of groundwater for the present-day and future usage (Kori et al. 2006). Many researchers have recommended different methodology for analyzing quality of groundwater (Bassam and Rumikhani 2003; Hameed et al. 2010, Selvam 2017, Singaraja et al. 2015). The groundwater quality of Virudhunagar district and its taluks were reported by Nageswari et al. (2007), Magesh et al. (2013) Udayanapillai, et al. (2016), Muthulakshmi et al. (2009, 2010), Ponmanickam et al. (2007). The heavy metal level in groundwater and its health hazard were studied by Raja et al. (2021).

Therefore, it is very necessary to evaluate about the current status of groundwater quality and its suitability for drinking and irrigation. Agriculture is a principal practice in the in Virudhunagar, as it is the foremost source of requirements for the majority of the people. The study area also predominantly depends on the agricultural and small to large scale industries of fireworks, [printing](#), ginning factories, Oil and spinning mills, power and hand loom industries and Cement industries. Since it is most significant to study the groundwater quality and the factors governing the hydrochemical variation towards the groundwater resource management. Monitoring of variation in hydrochemical parameters has proved to be advantageous in solving many groundwater quality problems and is being used as a powerful tool by the hydrologists. To derive a proper management strategy a detailed study on the suitability of groundwater for irrigation and also for the drinking purposes and its spatial variation is essential. Hence, present study attempts to evaluate the groundwater suitability for both drinking and irrigation purpose. Also the study describes the processes in control of groundwater geochemistry of this region.

Study Area

The current study area is positioned in Virudhunagar district, at the Southern part of the Tamilnadu state, India. It covers an area of about 4,234 square kilometers and lies between the latitude 9°24'27.85" N to 9°11'10.19" N and longitude of 78°24'9.55" E to 78°5'24.45" E (Fig. 1). It is bounded by the Western Ghats in the West, Madurai district in the North, Sivagangi district in North East, Ramanathapuram district in the East and Thothukudi district in the South. Study area comprises eight taluks such as 1. Aruppukottai, 2. Kariapatti, 3. Srivilliputhur, 4. Rajapalayam, 5. Virudhunagar, 6. Sivakasi, 7. Sattur and 8. Tiruchuli taluks. The total population of the district is about 17,51,301. The Vaippar, The Gundar, and The Arjunanadi are the three major rivers flows in the district and the drainage pattern is dendritic. The climatic condition is generally hot, dry with less humid. The normal yearly rainfall of the study region is 987 mm. The annual temperature is between 23.78°C and 33.95°C and the temperature rise up to 40.2°C during the daytime.

The study region is mostly covered by the physiographic units of plains, uplands, hills and valleys. The landuse of the study area comprise by built-up land, agricultural land, forest, wastelands, and water bodies (Magesh and Chandrasekar 2013). Paddy is the predominant crop type in this area

followed by the Sugarcane, Groundnut and Pulses are the major cultivation in the study region. Foremost soil types of the study region are Black soil, Red sandy soil and Deep red loam soil. Geologically the Virudhunagar district can be mostly categorized into hard rock and sedimentary formation (alluvium and tertiary) (Fig. 1). The major part of the region covered by a gneissic group of rocks which include feldspathic gneiss, Charnokite follows in the western part of the area around Srivilliputtur. The pink granite occurs south of Watrap and around Mangalam. The eastern part of the region is covered by alluvial formation in Narikudi and Thiruchuli block. Tertiary formation occupies the eastern region covered Narikudi, Thiruchuli and Kariyapatti block. Limestone, Limekanker and Granite are the major minerals occurred in this region (Magesh and Chandrasekar 2013).

The average water level during pre-monsoon is 12 m below ground level (bgl) and during post monsoon is 8 m bgl. The groundwater potential varies among the porous and fissured formation. Groundwater in porous formation occurs in phreatic to semiconfined condition with the average thickness of 25 m bgl. The aquifers in hard crystalline formation are highly heterogeneous in nature with the thickness of 4 to 15 m bgl in weathered zone and 10 to 15 m bgl in dug wells. Hard rock in this region yields 40–110 lpm (liters per minute) and sediments well yield 40–150 lpm. Transmissivity and Storability of fractured crystalline formation is about 1-548 m²/day and 3.41X10⁻⁵ to 7.0X10⁻³ and specific yield is about < 2%.

The study area is one of the foremost in overall nation for the match industries, fireworks and printing production, it is generally focused in all over the place of Sivakasi taluk (which is called as small Japan). Virudhunagar district also produce oil, chicory, coffee seeds, dry chillies and pulses. Ginning factories, spinning mills, power and hand loom industries are also existing in the district of Rajapalayam and it is one of the biggest weaving town in all over the state. The cement plants are located in RR Nagar and Alankulam of Virudhunagar and Sivakasi Taluk.

Materials And Methods

Sampling of Groundwater is carried out during NEM (November 2019). An aggregate of 72 groundwater samples was collected from various hand pumps in different part of the Virudhunagar District. One-liter sample was collected and filtered by using vacuum filtration unit with the Millipore filter paper (0.45-µm) to remove the suspended sediments. The collected groundwater samples were analyzed for physical parameters (EC, pH, TDS), using the field wings multi-parameter (PCSTestr™ 35). The major cations like Ca and Mg were determined by titration method. Na and K were analysed using Flame photometer (CL 378). Similarly, anions like Cl and HCO₃ was analysed by titration, SO₄, PO₄, and SiO₂ were analyzed by using spectrophotometer (UV 1800 spec). The different analyses were carried out by following the standard procedures (APHA, 1998). At the time of sampling the water temperature varies between 26 and 32°C. The analytical accuracy for the results of cations and anions was measured by computing the ionic balance represents about 5–10 % (Freeze and cherry, 1979). The data produced to find the quality index to calculate Sodium absorption ratio (SAR), Sodium Percentage (Na%), Residual sodium Carbonate (RSC), Magnesium Hazard (MH), Kelly Ratio (KR) (Table 1) and USSL were plotted using CHIDAM software. Spatial diagram was plotted using ArcGIS. The multivariate analysis was adopted to categorized the chemical and physical variables of big data by using (SPSS) version 17.0.

Result And Discussion

The analytical outcomes suggest the physicochemical parameters and its maximum, minimum and average value for the groundwater samples are represented in Table 2 and 3 respectively. The values of hydrochemical parameters were compared with the WHO standard (2014). Based on average value of the parameters the dominance of major cations is arranged in the order of Na>Ca>Mg>K and anions are Cl >HCO₃> SO₄>PO₄.

Suitability of drinking water quality:

The pH values in the groundwater samples ranges between 6.75 and 8.38, indicating the nature of groundwater is alkaline and it is due to the existence of carbonic acid which is produced by the CO₂ and HCO₃ in water and it affects the level of pH in the groundwater (Azeez et al 2000; Ramesh and Elango, 2012). The basicity is also due to the limestone rock dissolution and limestone mining (Essumang et al,2011; Marzouk 2018) and the pH level is within the acceptable limits of the WHO standards. Spatially most of the higher pH sample with alkaline nature is observed in the Eastern and North western part of the study region which is occupied by the geology of Alluvium and Feldspathic Gneiss (Fig 2).

The Electrical Conductivity (EC) and Total Dissolved Solids (TDS) of groundwater is directly related to level of dissolved salt in groundwater. The EC value of the samples varies from 273 to 5870 µm/cm with an average value of 1593 µm/cm (Fig. 3). About 36% of samples are above the permissible limit of WHO standards (Table 3). Total Dissolved solids (TDS) value in the groundwater samples are ranging between 194 and 4160 mg/l (Table 2). The maximum value of EC and TDS is observed at Sattur followed by the Virudunagar, Varagnur and Velanoorni. The great difference in EC is mostly related to the lithological composition, dissolution of salts as an outcome of limestone quarrying undertakings (Prowse 1987; Eugene et al. 2014) and other anthropogenic activities like waste outlet from the small and large firework, cement, ginning factories in Sattur and Virudhunagar and dumping of manure beside the riverbeds is predominant in the study region. The lower level of EC is due to lesser groundwater residence time in the aquifer and also by the less dilution process (Kortatsi 2006; Chidambaram et al. 2011; Thivya et al. 2013). The higher values of EC are observed in central, east and southern part of the study region (Fig 3).

The analytical data represents the Calcium and Magnesium concentration varies from 20 to 892 mg/L and 4.8 to 450 mg/L. Samples of about 22% to 11% are above the permissible limit of WHO standards (Table 2 and 3). The higher concentration of Ca which is in the not permissible category is observed in isolated patches near North, South east and South west part of the study region (Fig 4). Maximum value of Mg is noted in Eastern,

Northern and Southern part of the study area (Fig 4). Since the higher concentration of Ca and Mg in groundwater is due to the dissolution of limestone, granulite and other alkaline metamorphic rocks weathering (Chandrasekhar et al. 2012; Ayyandurai et al. 2011; Udayanapillai and Kaliammal, 2016; Marzouk 2018). Maximum value of Ca and Mg is noted at Varagnur and Virudhunagar locations.

Both Sodium and Potassium concentration ranges from 9 to 944 mg/L, 3 to 296 mg/L respectively. 24% and 17% of groundwater samples higher than the WHO standard for Na and K respectively (Table 3). Higher concentration of Na is observed as an isolated patch in northern, eastern and southern part of the study region. Southern and south eastern part of the region shows high concentration of K. Higher concentration of Na and K (Fig 5) is observed at Virudunagar, Varagnur, Muthaneri, Velanoorni and Panaiyur locations. Weathering of minerals are the major source of higher level of Sodium and Potassium in groundwater of the study region (Udayanapillai and Kaliammal 2016). The study area is mostly occupied by the Feldspathic Gneiss. Wells closer to the quarries are also shows increasing level of K in groundwater which infiltrates the pollutants in the groundwater (Marzouk, 2018).

The maximum and minimum concentration of Cl, HCO₃, PO₄ and SO₄ ranges from 53 to 2980 mg/L, 134 to 1198 mg/L, 5 to 23mg/L and 4 to 35mg/L respectively. 19% and 35% of total samples have Cl and HCO₃ concentration above the permissible limit of WHO drinking water standards (Table 3 & Fig 6). PO₄ and SO₄ concentration for all the groundwater samples are within the permissible limit (Fig 7). Higher level of Cl is observed at Northern, Eastern and southern region of the study area (Fig 6). Maximum of HCO₃ (Fig 6) is noted at Sattur, Annikuttam and Mil Krishnapuram locations. Spatially most of the region showed not permissible zone of HCO₃ (Fig 6). Anthropogenic waste like agricultural fertilizers, animal waste, municipal and small- and large-scale crackers industries sewage that infiltrates into groundwater leads to the higher concentration of Cl (Thilagavathi et al. 2014; Thivya et al.2013) and the black soil in the region may also the source for higher Cl (Udayanapillai and Kaliammal 2016). The silicate minerals weathering and also the dissolution of the minerals enriches the HCO₃ level in groundwater (Gastmans et al.2010; Khashoggi and El Maghraby 2013)

The water quality map was prepared for the parameters of Ca, Mg, Na, K, Cl, HCO₃, and SO₄. These parameters were divided into two (1 and 0) based on the WHO drinking quality index. The individual maps for all these 7 parameters were integrated in the ArcGIS platform to plot the final water quality map. Later the total of 7 maps were prepared and categorized into four classes as Excellent, Moderate, Poor and Unsuitable. The final water quality map shows that most of the groundwater samples are falling in Excellent and Good category. Isolated patches of the samples from north, south and east represents the poor and unsuitable category for drinking water (Fig 8). Unsuitable area of groundwater is mainly due to the industrial effluents in the north and southern part of the region and agriculture used fertilizers in the eastern part. The higher level of TDS, Na and Cl in the study region lead to the unsuitable of ground water quality.

According to the Richards (1954), TDS classification represents that 62% of samples are below the 1000mg/L and useful for the drinking purposes. However, 8% of samples falls in hazardous category and not useful for the drinking and irrigation purpose. Based on the Total hardness all the groundwater samples fall under the moderately to very hard category (Table 4). More hardness of groundwater is owing to the availability of alkaline earth like Ca and Mg which is mostly from the geogenic source and dissolution of composed rocks like limestone and dolomite (Chaudhary et al. 2018).

Suitability of Irrigation quality:

The groundwater suitability for irrigation purpose is studied from Sodium adsorption ratio (SAR) and salinity ratio. The SAR and EC values variation (Chidambaram et al.2020) has been identified from the USSS plot. High level of SAR, reflects the vulnerability of sodium replacing Calcium and Magnesium into the soil and affects its permeability, fertility of the soil and reduce the agricultural activities (Tahmasebi et al.2018).

All the samples falls in the category of good to excellent based on their SAR value (Fig 9) which represents the irrigation water are with low sodium hazard. Groundwater with less sodium can be utilized for agriculture (Jeon et al. 2020). The wilcox plot shows that 21% of samples have low sodium and are falling in medium salinity hazard field of S1-C2 followed by 33% of groundwater samples with higher salinity and falling in low sodium hazard of S1-C3 category. 21% of samples are falling in S1- C4 class of low sodium hazard and very high salinity hazard. Based on the wilcox classification all the samples have medium to very high salinity with low sodium hazards which signifies that maximum of the samples are appropriate for irrigation purposes of high salt tolerant crops (Zhu 2002). Higher salinity water for the agriculture leads to the salt accumulation in the root and make destruction the plant and lead to drought plant situation (Greenway and Munns 1980; Zhu 2002)

The Na% is also assisted to evaluate the suitability of groundwater for irrigation purpose. From Table 4 it is evident that the order of dominance of Na% in groundwater samples are Excellent (43%) > Good (38%) > Permissible (15%) > Doubtful (3%) > Unsuitable (1%). Samples from Mennakualm, Thamaraiklam and Sattur are not suitable for the irrigation. Dissolution and weathering of various minerals and usage of highly chemical fertilizer leads to high Na% (Rao 2002; Bhat 2016). Most of the samples are represented in permissible to excellent category point toward the suitability of groundwater for irrigation (Table 4).

The Residual Sodium Carbonate (RSC) is the sum of excess CO₃ and HCO₃ over the sum of Ca and Mg influences the irrigation quality of water (Eaton,1950) and (Richards, 1954). Table 4 shows that 80.5 % of samples are suitable for agriculture purpose, 8 % of samples are represented in moderate category and 11% of groundwater samples are not safe for agriculture purpose. The regular use of the higher RSC groundwater for the

agriculture purposes leads to decreasing the permeability of soil and blazing of the plants and less yield of the crops (Toumi et al.2015; Ramesh and Elango 2012).

Increasing level of Ca and Mg in the groundwater will increase the level of pH in soil and reduces the infiltration quality of the soil which is directly affects the crop growth. The Magnesium adsorption ratio (Lloyd and Heathcoat 1985) calculated for the study area's groundwater samples representing 58% of samples are unsafe for the irrigation and 42% of sample are in safe category (Table 4).

Estimation of irrigation suitability of the groundwater samples proposed by Kelley (1940) and Paliwal (1967) is depends on the Ca and Mg with Na value. The Kelly ratio of <1 are not suitable for the irrigation. About 91% of samples are in safe zone for irrigation and remaining 9 % of samples are in unsafe zone for the groundwater samples. About 39% of samples are fresh, 17% of samples are Fresh brackish, 36% of samples are Brackish and 8% of samples are from Brackish salt category based on Cl classification (Table 4). Long residence time and anthropogenic pollutants infiltration (Subba Rao et al. 2007) are the main source for higher chloride level in the groundwater samples of the study area.

Hydrogeochemical evaluation from Piper diagram:

Hydrogeochemical facies shows the processes of chemical behavior of the groundwater samples. Based on the cation triangle majority of the samples represent the dominance of Ca-Mg type and few of the groundwater shows the dominance of Na+K type. 40% of samples fall in Calcium-Magnesium facies and 60% of samples are in Calcium-Sodium Facies (Table 4). According to the anionic triangle all the samples show the predominance of HCO₃ and Cl. Chloride-sulfate and Bicarbonate facies is represented by 92% of samples and 8% of samples are from Chloride facies. In the diamond field represents the abundance of the water type in the study area is in the order of Ca-HCO₃ > mixed Ca-Mg-Cl > Ca-Cl > Ca-Na-HCO₃ > Na-Cl (Fig 10). 49% of samples falls in Ca-HCO₃ facies representing recharge zone and mainly influenced by the rock water interaction processes (Bricker et al 2003; Devaraj et al. 2018). Followed by that 32 % of samples represented in mixed Ca-Mg-Cl and 8.3% of samples in Ca-Cl facies indicating the transition zone and influenced by irrigation process due to agricultural activities and other anthropogenic factors like quarries and crackers industries (Thilagavathi et al.2016; Devaraj et al. 2018). 8% samples shows the Ca-Na-HCO₃ facies and 2.7 % of samples represented in Na-Cl field indicating the dissolution and anthropogenic impact (Krishnakumar et al.2016). The chemical constituents of the samples is predominantly influenced by the the dissolution and also precipitation of minerals during groundwater recharge.

Gibb's Hydrogeochemical evaluation:

Gibbs plots is used to demonstrate the ratio between the cation and anion along with TDS to categorize the process liable for the variation in groundwater chemistry. Based on the Gibbs diagram (Fig 11) maximum of the samples are influenced by rock-water interaction which signifying the influence of local geological sources, weathering of minerals. However few samples shows the dominance of the manmade activities (Chidambaram et al.2008; Manikandan et al.2011). Samples with higher TDS values, and Na/(Na+Ca) and Cl/(Cl+HCO₃) ratio signifies control of evaporation. It specifies that the evaporation-sedimentation is the main factor of the variation in chemical composition of groundwater of the study area (Udayanapillai and Kaliammal 2016).

Correlation matrix:

The correlation matrix of the samples represents both positive and negative co-relationship between the variables (Thivya et al.2015). A strong positive correlation (>0.5) noted between Cl - Ca, Mg, Na; Ca - Mg, K, Cl; Mg - Na, Cl, HCO₃; Na - Cl, HCO₃. A strong correlation between EC and TDS with Ca, Mg, Na, Cl and HCO₃ (Table 5). Positive and good correlation of Cl with other parameters indicates the impact of anthropogenic activities and ion exchange process (Thilagavathi et al. 2012; Thivya et al.2013;). HCO₃ with Ca, Na and Mg reflects the weathering of limestone in the study region (Marzouk 2018). Good correlation of EC with other parameter indicates that the Ca, Mg, Na, Cl and HCO₃ are the substantial ions for higher EC in groundwater of the study area.

Factor analysis:

Factor analysis is a multivariate arithmetic technique, offers the overall connection among the measured chemical variables by displaying the multivariate patterns that could help to categorize the original data (Table 6). The factor analysis has generated three significant factors with the total variance of 70.3%. Factor I, represents 38.6 % of total variance with a strong positive loading of Mg, Na, Cl, HCO₃, EC and TDS, in the study area demonstrating the leaching of secondary salts, and anthropogenic activities (Prasanna et al. 2010, Thivya et al.2013; Devaraj et al.2016). About 23% of the groundwater samples in the study area obtained from the Factor 1, spatially most of the positive loading samples of factor I represented on isolated patches of North east, western and southern part of the study area (Fig 12). Factor II shows strong representation of Ca, Mg, K, Cl with a negative loading of pH with total variance of 20.6% and 33% of samples represents in this factor II. Dominance of Ca and Cl indicates the influence of anthropogenic activities in limestone quarries and other industries like cement factories, paper plants and crackers industries. Positive loading of Mg and K with negative pH represents the ion exchange leads to the rock water relations and also the weathering activities (Chidambaram et al. 2007). Positive score of Factor II represented in the western and south western part of the study region (Fig 12). Factor III elucidates 11% of total variance and 35% of samples. This factor shows the positive loading of SO₄ and PO₄ which may be influenced from anthropogenic impacts like agriculture (fertilizer) activities (Vengosh and Keren 1996). Most of the Western and isolated patches of the eastern and northern part of the study area shows the dominance of the factor III (Fig 12). Comparing the percentage of samples with positive loading shows that Factor III shows 35%, factor II obtained

33% and Factor I obtained 23% of samples signifying dominance of anthropogenic activities to the variation in groundwater chemistry of the study area.

Conclusion

Sodium and Calcium are the principal cation and Chloride and Bicarbonate are the dominant anions in the groundwater of the study area. Groundwater samples of the study area are mostly alkaline with the higher TDS and EC due to the varied lithology and intense industrial and agriculture activities. 22%, 11%, 24%, 17%, 19% and 35%, of samples are directly above the acceptable limit for Ca, Mg, Na, K Cl and HCO_3 respectively. The increasing trend of the concentration of the hydrochemical parameters in groundwater are mostly due to dissolution of minerals and intensive anthropogenic activities (both industrial and agricultural activities). The USSL classification for TDS reveals that 62% of the samples are within good category and useful for drinking purpose. It is inferred from the water quality map shows that isolated patches from north, south central and eastern parts are representing poor to unsuitable category of drinking water Groundwater samples from Virudhunagar, Vadamalapuram, Varaganur, Idayakulam, Sattur, Menakulam, Muthaneri, Velanoorani and Tuttinattam represents the poor to unsuitable category, due to the impact of industries and limestone queries nearby locations. SAR of all the samples represent good to excellent category. RSC, MH, KR and Na% exposes that greater than 80% of samples are suitable for irrigation. Gibbs diagram shows the major controlling factor area evaporation and rock water interaction. Piper diagram represents the dominance of the Ca-HCO_3 and mixed Ca-Mg-Cl water type. Leaching of salts, weathering and influence of manmade activities are foremost factors influencing the groundwater chemistry of the study area. Thus, it is inferred from the study that the groundwater is appropriate for irrigation and drinking purposes except certain places in north, south and eastern part of the study region.

Declarations

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Ethics Data Availability: The manuscript, Data are the authors' original work and the manuscript has not received prior publication and is not under consideration for publication elsewhere. The manuscript now submitted is not copied or plagiarized version of some other published work.

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Tables

Table. 1 Chemical, analytical and data calculated methods for groundwater samples-

Parameters	Method and Materials
pH	multi-parameter (PCSTestr TM 35).
EC $\mu\text{S}/\text{cm}$	
TDS (mg/L)	
Ca (mg/L)	Titrimetric using Burette, Flasks
Mg(mg/L)	
Cl(mg/L)	
HCO ₃ (mg/L)	
SO ₄ (mg/L)	Spectrophotometer/ HACH (DR 6000)
PO ₄ (mg/L)	
H ₄ SiO ₄ (mg/L)	
Na and K(mg/L)	Flame photometer/ Elico CL 378
Sodium Adsorption Ratio (SAR) (meq)	$\text{Na} / (\sqrt{\text{Ca} + \text{Mg}} / 2)$
Residual Sodium Carbonate (RSC) (meq)	$(\text{CO}_3 + \text{HCO}_3) - (\text{Ca} + \text{Mg})$
(Sodium percentage) Na% (meq)	$\text{Na} + \text{K} / (\text{Ca} + \text{Mg} + \text{Na} + \text{K}) \times 100$
Magnesium Hazard (MH) (meq)	$\text{Mg} / \text{Ca} + \text{Mg} \times 100$
Kelly Ratio (KR) (meq)	$\text{Na} / \text{Ca} + \text{Mg} \times 100$

Table. 2 Chemical Composition of groundwater Samples (All Values in mg/l except pH and EC($\mu\text{S}/\text{cm}$))

Sample Number	Location Name	Longitude	Latitude	Ca	Mg	Na	K	Cl	HCO3	PO4	SO4	SiO2	pH	EC	TDS	Ionic Balance
1	V.Puthur	78°22'9"	9°35'31"	44.0	45.6	129.0	5.5	195.0	512.4	5.5	18.1	39.0	7.6	1070.0	750.0	10.0
2	Mennakulam	78°20'56"	9°29'19"	20.0	34.0	399.3	3.6	326.8	1009.8	9.5	8.6	55.2	7.8	2680.0	1890.0	10.0
3	Irunchirai	78°20'17"	9°38'10"	42.0	34.4	148.5	4.0	141.8	549.0	5.7	6.8	39.9	8.1	808.0	570.0	7.3
4	Tachanental	78°13'28"	9°43'43"	40.0	19.2	39.8	3.4	124.1	134.2	14.1	4.2	64.7	7.9	342.0	242.0	7.1
5	Cinimatai	78°17'32"	9°39'3"	72.0	64.8	160.1	5.3	390.0	512.4	5.7	3.7	39.1	7.6	1130.0	799.0	10.0
6	Narikudi	78°7'36"	9°35'37"	160.0	141.6	239.7	4.0	709.0	634.4	5.7	10.5	50.8	7.3	2560.0	1800.0	0.8
7	Muthaneri	78°17'59"	9°31'55"	316.0	292.8	203.5	10.3	1187.6	536.8	6.1	7.2	58.8	7.4	3400.0	2390.0	-7.2
8	Velanoorni	78°4'27"	9°27'59"	348.0	338.4	452.3	23.4	1664.8	622.2	5.7	5.8	37.3	8.2	4610.0	3260.0	-6.8
9	Sengulam	78°17'32"	9°19'51"	396.0	136.8	49.6	22.6	755.8	366.0	10.1	7.4	54.1	6.9	2080.0	1450.0	-9.9
10	Tuttinattam	78°16'33"	9°19'50"	512.0	62.4	269.7	14.3	1097.2	353.8	5.9	10.9	62.3	7.3	3520.0	2470.0	-7.1
11	Therkunatham	78°16'0"	9°20'22"	104.0	45.6	17.9	20.1	124.1	280.6	5.7	11.4	62.5	7.1	420.0	275.0	-9.4
12	Suthamadam	78°12'49"	9°21'6"	200.0	103.2	81.0	5.2	501.3	353.8	6.9	9.6	56.6	7.1	1541.0	1100.0	-4.4
13	Kathalampatti	78°11'31"	9°26'27"	52.0	44.0	79.7	3.9	141.8	463.6	6.0	7.9	58.2	7.7	790.0	560.0	9.8
14	Panaiyur	78°13'46"	9°30'34"	224.0	230.4	405.5	4.7	1169.9	695.4	6.0	5.5	48.5	6.9	4130.0	2930.0	-3.7
15	Tiruchuli	78°12'22"	9°32'2"	28.0	46.4	110.0	3.4	70.9	561.2	5.8	8.7	64.1	7.9	865.0	614.0	6.6
16	Tamaraikulam	78°11'43"	9°40'11"	38.0	99.8	596.3	5.8	963.5	1012.2	7.0	8.6	64.6	7.9	4350.0	3310.0	9.8
17	Chokkandal	78°14'21"	9°40'11"	96.0	38.4	53.1	3.1	106.4	500.2	5.8	15.2	33.8	7.6	686.0	483.0	6.0
18	Avarankulam	78°13'28"	9°42'9"	52.0	40.8	18.8	3.4	124.1	158.6	6.5	7.4	79.1	7.1	423.0	301.0	-3.3
19	Naganathal	78°6'35"	9°43'31"	124.0	64.8	56.8	4.3	195.0	463.6	6.3	15.4	64.6	7.2	997.0	702.0	-2.0
20	Kariyapatti	78°6'10"	9°41'8"	68.0	52.8	77.3	4.8	106.4	585.6	6.4	5.8	53.6	7.4	885.0	630.0	6.8
21	Srirampoor	78°10'6"	9°39'43"	60.0	64.8	141.3	5.0	195.0	683.2	7.1	6.9	22.2	8.4	1106.0	784.0	7.6
22	Namasivayapuram	78°10'6"	9°39'43"	52.0	28.8	9.6	4.2	70.9	219.6	5.9	7.1	9.9	8.1	273.0	194.0	3.6
23	Aruppukkottai	78°6'8"	9°30'23"	124.0	55.2	101.7	12.2	230.4	463.6	5.9	8.9	48.3	8.2	1215.0	858.0	-3.5
24	Savasapuram	78°7'16"	9°30'2"	156.0	50.4	31.6	4.7	159.5	475.8	6.1	13.5	59.5	8.3	901.0	636.0	-2.7
25	Muthuramalingapuram	78°9'33"	9°27'1"	20.0	33.6	108.2	4.3	53.2	500.2	6.1	9.8	40.3	8.4	663.0	474.0	8.0
26	Ramachandrapuram	78°8'17"	9°22'38"	76.0	60.0	85.1	3.7	70.9	622.2	6.0	7.5	46.3	7.2	762.0	533.0	-0.2
27	Kosukondu	78°2'29"	9°21'37"	32.0	33.6	63.7	3.5	70.9	353.8	7.4	14.9	50.5	7.9	506.0	362.0	7.0
28	Kurundhamadam	78°2'26"	9°25'47"	72.0	52.8	9.1	2.8	70.9	341.6	6.0	5.7	32.0	7.4	435.0	308.0	-3.4
29	Ramalingapuram	77°59'51"	9°31'14"	68.0	50.4	10.1	4.2	53.2	292.8	6.2	9.2	36.2	7.7	375.0	266.0	-9.8
30	Mallankinru	78°1'10"	9°34'59"	48.0	67.2	92.2	3.5	53.2	573.4	6.1	9.2	48.2	7.8	785.0	560.0	-3.5
31	Vadagarai	78°4'47"	9°38'52"	80.0	129.6	214.3	3.4	283.6	768.6	6.0	18.6	45.1	7.5	1380.0	1940.0	-6.7
32	D.kadampankulam	78°5'1"	9°44'0"	260.0	81.6	95.7	7.5	496.3	488.0	6.2	9.9	34.2	6.9	1766.0	1280.0	-3.7
33	Virudhunagar	77°56'43"	9°35'2"	816.0	450.4	944.4	4.0	2980.2	780.8	5.9	23.7	49.4	6.8	5670.0	3950.0	-10.1
34	Kuppampatti	77°57'47"	9°29'4"	32.0	86.4	20.5	3.4	106.4	317.2	6.0	18.2	50.7	7.7	684.0	403.0	-5.4
35	Appayyanayakkanpatti	77°59'30"	9°25'10"	156.0	40.8	13.4	3.2	190.9	378.2	5.9	17.7	41.5	7.1	706.0	500.0	1.2
36	Maniyampatti	77°57'51"	9°24'14"	56.0	60.0	77.8	3.4	70.9	524.6	6.4	24.1	41.8	7.5	731.0	526.0	0.2
37	Subramaniyapuram	77°56'27"	9°16'49"	88.0	67.2	144.5	4.9	90.9	627.0	6.3	31.1	58.2	7.9	1466.0	1040.0	-9.0
38	Thottailovanpatti	77°53'40"	9°12'42"	352.0	98.4	109.5	18.3	744.5	414.8	9.0	32.7	53.8	6.9	2520.0	1780.0	-3.8
39	Subbiyapuram.N	77°53'40"	9°15'44"	88.0	86.4	48.0	4.7	88.6	493.6	6.3	32.5	50.8	7.5	790.0	565.0	-9.2
40	Sattur	77°54'56"	9°21'21"	68.0	120.0	903.2	3.6	833.1	1198.0	6.5	23.6	84.2	7.7	5870.0	4160.0	-9.2
41	Vadamalapuram	77°52'43"	9°22'2"	40.0	40.8	47.6	3.6	53.2	402.6	6.7	29.8	64.9	7.6	485.0	344.0	8.3
42	E.Kumaralingapuram	77°54'8"	9°25'44"	104.0	129.6	310.5	3.9	619.1	768.6	6.1	26.9	61.2	7.4	2800.0	1960.0	2.0
43	Kattanur	77°53'39"	9°30'43"	200.0	81.6	72.8	14.1	336.8	500.2	6.2	30.1	72.1	7.3	1340.0	940.0	-4.6
44	Kumaralingapuram	77°55'18"	9°34'50"	116.0	148.8	327.5	3.8	514.0	695.4	7.0	29.1	64.6	7.8	2500.0	1780.0	-9.8
45	Puthukottai	77°45'48"	9°35'13"	220.0	136.8	118.0	5.1	514.0	414.8	6.9	31.5	31.7	7.6	1380.0	978.0	-11.0
46	Sukravarampatti	77°47'57"	9°30'54"	100.0	163.2	261.7	5.2	478.6	719.8	7.0	26.4	64.0	7.8	1732.0	1200.0	-7.2
47	Sivakasi	77°48'0"	9°27'36"	216.0	86.4	100.6	6.4	383.6	512.4	6.8	27.2	53.4	7.0	1167.0	803.0	-5.9
48	Anaikuttam	77°48'52"	9°24'27"	264.0	192.0	233.6	76.5	673.6	854.0	22.7	26.7	68.6	7.2	2550.0	1790.0	-9.2
49	V.Duraiswamipuram	77°47'56"	9°20'57"	172.0	122.4	90.7	5.5	401.3	463.6	6.7	26.1	66.7	7.3	1320.0	936.0	-7.5
50	Elayirampennai	77°48'59"	9°16'21"	100.0	50.4	10.8	3.7	70.9	329.4	6.2	25.3	44.8	7.4	483.0	345.0	-9.1
51	Varanganur	77°43'31"	9°16'26"	892.0	345.6	481.8	296.4	2466.2	824.6	6.2	22.1	68.6	7.0	5200.0	3680.0	-9.7
52	Muthu swamipuram	77°44'23"	9°20'40"	72.0	144.0	57.4	4.3	224.1	573.4	7.6	30.4	15.3	7.6	984.0	694.0	-4.6
53	Idiyankulam	77°43'12"	9°25'21"	100.0	96.0	48.3	3.7	141.8	488.0	6.2	22.4	65.1	7.2	830.0	580.0	-9.1
54	Kunampatti	77°42'31"	9°31'18"	128.0	43.2	11.7	3.7	90.9	353.8	6.1	19.4	57.0	8.0	402.0	284.0	-8.4
55	Nathampatti	77°45'5"	9°35'45"	60.0	76.8	87.7	3.5	124.1	658.8	6.4	24.3	50.8	8.0	823.0	587.0	6.0
56	Tailapuram	77°46'37"	9°39'39"	72.0	156.0	47.3	3.1	268.2	451.4	6.1	26.4	47.1	8.0	816.0	578.0	-8.8
57	Mavuoothu	77°40'27"	9°40'43"	36.0	40.8	10.7	3.6	53.2	256.2	6.3	25.2	45.8	7.0	295.0	207.0	5.5
58	Sundarapandiam	77°40'35"	9°36'41"	64.0	122.4	36.3	3.5	53.2	622.2	6.2	25.0	38.3	7.5	784.0	556.0	-9.6
59	Srivilliputtur	77°37'43"	9°30'30"	160.0	76.8	50.3	27.3	260.4	402.6	6.2	30.3	45.7	7.6	1308.0	928.0	-7.8
60	Pazhaya chennelkulam	77°38'3"	9°25'56"	76.0	52.8	10.7	3.3	70.9	305.0	6.8	29.3	42.9	7.6	417.0	293.0	-5.5
61	Sivalingapuram	77°38'19"	9°20'34"	260.0	93.6	153.4	137.8	549.5	658.8	6.5	33.8	47.9	7.0	1903.0	950.0	-6.4
62	Ramarajapuram	77°38'23"	9°17'49"	72.0	32.0	25.1	3.5	88.6	353.8	6.3	29.2	48.4	7.5	504.0	356.0	10.1
63	Vijayarangapuram	77°35'7"	9°18'29"	404.0	9.6	71.4	3.5	439.5	475.8	6.4	31.4	46.0	7.1	1120.0	780.0	-6.9
64	Asilapuram	77°33'53"	9°21'34"	236.0	4.8	184.2	6.7	514.0	512.4	6.2	34.5	31.3	7.6	1616.0	1120.0	7.8
65	Mill krishanapuram	77°34'4"	9°26'13"	304.0	50.4	210.6	6.9	904.0	549.0	6.3	35.0	47.9	7.7	3150.0	2230.0	10.4
66	Rajapalayam	77°33'36"	9°27'39"	188.0	67.6	155.0	8.2	531.8	671.0	6.5	29.2	21.2	7.4	1668.0	1340.0	9.9
67	Mamsapuram	77°35'19"	9°29'45"	88.0	61.2	92.9	3.2	177.3	585.6	6.3	26.4	41.1	7.5	934.0	661.0	6.0
68	Kansapuram	77°36'9"	9°37'38"	136.0	41.2	172.9	2.9	336.8	671.0	6.6	28.8	42.6	7.2	1656.0	1170.0	8.9
69	Nedungulam	77°35'54"	9°39'18"	152.0	57.6	46.6	3.1	177.3	622.2	6.6	26.5	54.2	7.1	1008.0	708.0	4.8
70	Nallamangalam	77°28'1"	9°23'3"	136.0	65.6	138.1	3.4	336.8	744.2	6.8	28.7	50.4	7.0	1445.0	1010.0	10.2

71	Sundhararajapuram	77°30'1"	9°25'52"	176.0	9.6	163.5	5.3	354.5	427.0	7.0	32.6	45.2	7.8	1724.0	1230.0	3.1
72	Devipattanam	77°25'40"	9°22'27"	96.0	75.6	276.9	5.0	443.1	915.0	17.6	27.9	40.0	7.4	1503.0	1040.0	10.4

Table. 3 Maximum, minimum and average values for the analytical results of groundwater samples.

Parameters	Max	Min	Avg	WHO 2014	% of samples >WHO 2014
Ca (mg/L)	892.0	20.0	153.9	200.0	22%
Mg (mg/L)	450.4	4.8	90.7	150.0	11%
Na (mg/L)	944.4	9.1	151.6	200.0	24%
K (mg/L)	296.4	2.8	16.6	10.0	17%
Cl (mg/L)	2980.2	53.2	441.8	600.0	19%
HCO ₃ (mg/L)	1198.0	134.2	539.7	500.0	35%
PO ₄ (mg/L)	22.7	5.5	7.1	NG	
SO ₄ (mg/L)	35.0	3.7	19.5	400.0	Nil
SiO ₂ (mg/L)	84.2	9.9	49.6	NG	
pH	8.4	6.8	7.5	6.5-8.5	
EC μ S/cm	5870.0	273.0	1593.0	1500.0	36%
TDS (mg/L)	4160.0	194.0	1136.0	1500.0	21%

Table. 4 Suitability of groundwater for drinking and irrigation (Results from CHIDAM software, Chidambaram et al 2020)

Category	Range	Number of Samples	Percentage of Samples	Category	Range	Number of Samples	Percentage of Samples
Na% (Wilcox,1955)				Indices of Base Exchange (IBE) Schoeller (1965)			
Excellent	0-20	30	42%	Exchange between Na and K in rock with Mg or Ca in groundwater		17	24%
Good	20-40	27	38%	Exchange between Na and K in groundwater with Mg or Ca in rock		55	76%
Permissible	40-60	12	17%	TDS Classification(USSI 1954)			
Doubtful	60-80	2	3%	<200		1	1%
Unsuitable	>80	1	1%	200-500		15	21%
Na% (Eaton,1950)				500-1500		39	54%
Safe	<60	69	96%	1500-3000		11	15%
Unsafe	>60	3	4%	>3000		6	8%
Kelly Ratio, (Kelly,1946)				Chloride Classification (Stufzand 1989c)			
Safe	<1	66	92%	Extremely Fresh	<0.141	0	
Unsafe	>1	6	8%	Very Fresh	0.141-0.846	0	
Magnesium Adsorption Ratio (Lloyd& Heathcoat (1985)				Fresh	0.846-4.231	28	39%
Safe	<50	30	42%	Fresh Brackish	4.231-8.462	12	17%
Unsafe	>50	42	58%	Brackish	8.462-28.206	26	36%
Sodium Adsorption Ratio (Richards 1954)				Brackish salt	28.206-282.064	6	8%
Excellent	0-10	69	96%	Salt	282.064-564.127	0	
Good	10-18	3	4%	Hyperhaline	>564.127	0	
Fair	18-26	0		CATION FACIES			
Poor	>26	0		Calcium-Magnesium Facies		29	40%
Residual Sodium Carbonate (Richards,1954)				Calcium-Sodium Facies		43	60%
Good	<1.25	57	79%	Sodium-Calcium Facies		0	
Medium	1.25-2.5	7	10%	Sodium Facies		0	
Bad	>2.5	8	11%				
Electrical Conductivity (Wilcox,1955)				ANION FACIES			
Excellent	<250	0		Bicarbonate Facies		0	
Good	250-750	18	25%	Bicarbonate-Chloride-Sulfate Facies		0	
Permissible	750-2250	39	54%	Chloride-Sulfate-Bicarbonate Facies		66	92%
Doubtful	2250-5000	12	17%	Chloride Facies		6	8%
Unsuitable	>5000	3	4%				
Sawyer and McCarty Hardness							
Soft	<75	0					
Slightly Hard	75-150	0					
Moderately Hard	150-300	11	15%				
Very Hard	>300	61	85%				

Table. 5 Correlation matrix for the variable in groundwater

Parameters	Ca	Mg	Na	K	Cl	HCO ₃	PO ₄	SO ₄	H ₄ SiO ₄	pH	EC	TDS
Ca	1.00											
Mg	0.67	1.00										
Na	0.46	0.63	1.00									
K	0.59	0.40	0.21	1.00								
Cl	0.87	0.85	0.78	0.49	1.00							
HCO ₃	0.14	0.39	0.74	0.21	0.41	1.00						
PO ₄	0.03	0.05	0.06	0.12	0.03	0.21	1.00					
SO ₄	0.15	-0.01	0.00	0.11	0.02	0.14	0.09	1.00				
H ₄ SiO ₄	0.12	0.15	0.27	0.18	0.17	0.17	0.15	0.01	1.00			
pH	-0.47	-0.23	-0.07	-0.23	-0.32	0.004	-0.09	-0.21	-0.21	1.00		
EC	0.65	0.72	0.91	0.36	0.88	0.65	0.06	0.02	0.29	-0.20	1.00	
TDS	0.63	0.72	0.91	0.34	0.87	0.66	0.05	0.00	0.28	-0.18	0.99	1.00

Table. 6 Factor analysis for the chemical composition of Groundwater.

Parameter	Factor I	Factor II	Factor III
Ca	0.44	0.84	-0.05
Mg	0.69	0.49	-0.09
Na	0.96	0.06	0.09
K	0.22	0.64	0.15
Cl	0.77	0.59	-0.09
HCO ₃	0.77	-0.18	0.38
PO ₄	0.05	-0.03	0.73
SO ₄	-0.13	0.26	0.54
H ₄ SiO ₄	0.24	0.10	0.47
pH	0.06	-0.71	-0.28
EC	0.93	0.30	0.06
TDS	0.93	0.27	0.05
Total Variance	39.00	21.00	11.00

Figures

Figure 1

Lithology, Drainage and Groundwater water sampling locations of the study. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Spatial distribution of pH in groundwater samples

Figure 3

Spatial distribution of EC ($\mu\text{S/cm}$) in groundwater samples

Figure 4

Spatial distributions of Ca and Mg (mg/L) in groundwater samples

Figure 5

Spatial distribution of Na and K (mg/L) in groundwater samples

Figure 6

Spatial distribution of Cl and HCO₃ (mg/L) in groundwater samples

Figure 7

Spatial distribution of SO4 (mg/L) in groundwater samples

Figure 8

Suitability for drinking water quality map for the groundwater sample

Figure 9

Classification of ground samples in relation to salinity hazard and sodim hazard.

Figure 10

Piper facies diagram for groundwater samples

Figure 11

Gibbs plot to identify the mechanism of groundwater chemistry (after Gibbs et al.1970)

Figure 12

Spatial distribution of factor score for the groundwater samples