

Relevance of water quality index for groundwater quality evaluation: Thoothukudi District, Tamil Nadu, India

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Abstract The present hydrogeochemical study was confined to the Thoothukudi District in Tamilnadu, India. A total of 100 representative water samples were collected during pre-monsoon and post-monsoon and analyzed for the major cations (sodium, calcium, magnesium and potassium) and anions (chloride, sulfate, bicarbonate, fluoride and nitrate) along with various physical and chemical parameters (pH, total dissolved salts and electrical conductivity). Water quality index rating was calculated to quantify the overall water quality for human consumption. The PRM samples exhibit poor quality in greater percentage when compared with POM due to dilution of ions and agricultural impact. The overlay of WQI with chloride and EC corresponds to the same locations indicating the poor quality of groundwater in the study area. Sodium (Na %), sodium absorption ratio (SAR), residual sodium carbonate (RSC), residual sodium bicarbonate, permeability index (PI), magnesium hazards (MH), Kelly's ratio (KR), potential salinity (PS) and Puri's salt index (PSI) and domestic quality parameters such as total hardness (TH), temporary, permanent hardness and corrosivity ratio (CR) were calculated. The majority of the samples were not suitable for drinking, irrigation and domestic purposes in the study area. In this study, the analysis of salinization/freshening processes was carried out through binary diagrams such as of mole ratios of $\text{SO}_4^{2-}/\text{Cl}^-$ and Cl^-/EC that clearly classify the sources of seawater intrusion and salt-pan contamination. Spatial diagram BEX was used to find

whether the aquifer was in the salinization region or in the freshening encroachment region.

Keywords Water quality index · Irrigation quality · Domestic quality · Drinking purposes · Seawater intrusion

Introduction

Freshwater is limited, but its demand is increasing day by day. Where surface water is not available, sufficient, convenient, or feasible for consumption, but groundwater potential is suitable in quantity or quality, groundwater consumption has great importance. Groundwater is a renewable natural resource, which is replenished annually by precipitation. Groundwater quality plays an important role in its protection and quality conservation. Hence, it is very important to assess the groundwater quality not only for its present use, but also from the viewpoint of a potential source of water for future consumption (Kori et al. 2006). In India, most of the population is dependent on groundwater as the only source of drinking water supply. The quality of groundwater is as important as its quantity, owing to the suitability of water for various purposes. Variation in groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities (Subramani et al. 2005; Chin 2006). The chemical characteristics of groundwater play an important role in classifying and assessing water quality. Geochemical studies of groundwater provide a better understanding of possible changes in quality. The quality of groundwater depends on various chemical constituents and their concentration, which are mostly derived from the geological data of the particular region. Groundwater occurs in the

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weathered portion, along the joints and fractures of the rocks. Numerous studies have concentrated on groundwater quality monitoring and its suitability for drinking, domestic and agricultural uses in the recent decade (Bahar and Reza 2009; Chidambaram et al. 2010; Zhao et al. 2011; Subba Rao et al. 2012; Singaraja 2015). Among the sources of contamination, agriculture has both direct and indirect effects on groundwater chemistry (Jalali and Kolahchi 2008; Thivya et al. 2013b).

The study area, Thoothukudi District, a hard rock terrain receives the major part of rainfall from the northeast monsoon. The surface water sources are generally precarious during the monsoon seasons, and during no monsoonal periods people have to largely depend on groundwater resources for their domestic, agricultural, and industrial activities. About 70% of the study area is dominated by local human activities and agricultural activities, the rest by industries manufacturing chemicals, petrochemicals, thermal power plant, heavy water plant (HWP), chloralkali, HCl, trichloroethylene, cotton and staple yarn, caustic soda, polyvinyl chlorine resin, fertilizers, soda ash, carbon dioxide gas in liquid form and aromatics which dispose industrial and hazardous wastes near agricultural lands and pose a major threat to the adjoining groundwater environments. Salt is produced on a widespread scale in Tuticorin District; it constitutes 70% of the total salt production of the state and meets almost 30% of the requirement of the country. The salt pan area has increased at the expense of agricultural land, coastal sand with/without vegetation, sand dunes, scrub and mudflats and this has seriously affected the groundwater (Gangai and Ramachandran 2010; Singaraja et al. 2016).

Few researchers have worked on the variation analysis and assessment of chemical characteristics of groundwater quality in Tuticorin District, Tamil Nadu. However, spatial variations of irrigation groundwater quality parameters and their interrelationship have not been included. Further, it is observed that the concentration of major ions in groundwater of the area is high at many locations leading to unsuitability of groundwater for drinking, irrigation and domestic purposes. Many researchers had worked on the groundwater of Tuticorin District on various concepts, such as the land use and land cover pattern along the metal pollution in groundwater, to highlight the effect of the industrial (SIPCOT) effluents on Thoothukudi City (Puthiyasekar et al. 2010), trace element concentration in the groundwater in Tuticorin City (Ravichandran 2003), coastal transformation of Tuticorin City (Ramanujam and Sudarsan 2003), hydrological influences on the water quality in Tamirabarani basin, depositional environment in and around Tamirabarani estuary of Tuticorin (Solai et al. 2012) and hydrochemical characteristic of the coastal aquifer and aquifer characteristic along with its modeling around an industrial complex of Tuticorin district (Mondal

et al. 2009). Mondal et al. (2008), Singaraja et al. (2013), Singaraja (2015) and Selvam et al. (2016) identified the groundwater quality to be rapidly deteriorating. Increase in population and rapid urbanization have made groundwater the major source of water supply; hence, it is very essential to understand the hydrogeochemical processes that take place in the aquifer system.

Therefore, the study of behavior of aquifer in the study area is of great importance. Hence, it has been proposed to characterize the hydrogeochemical processes activated in the study area, with reference to natural and manmade activities and to classify water on the basis of sodium percentage (Na %), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), residual sodium bicarbonate (RSB), permeability index (PI), magnesium hazard (MH), potential salinity (PS), Kelly's ratio (KR), Puri's salt index (PSI), total hardness, permanent hardness, temporary hardness and corrosivity ratio (CR) and water quality index (WQI). A complete test to determine the WQI of a local body is vital to establish a continuing record for possible water remediation. The main objective of the present study is to evaluate the groundwater quality and its suitability for drinking, irrigation and domestic purpose in Thoothukudi District, as the groundwater is the only major source of water for drinking, irrigation and domestic purposes due to the lack of surface water in this region.

Study area

The present study area is situated in the southeast coast of Tamil Nadu, India. It is located between 8°19' and 9°22' N latitude and 77°40' and 78°23' E longitude (Fig. 1) covering an area of about 4621 km² and is distributed in 462 villages. The population is about 15,72,273 and depends mostly on irrigation. The area experiences a hot tropical climate. The average annual temperature is from 23 to 29 °C and the annual rainfall is about 570–740 mm. The district receives rain under the influence of both northeast monsoons. Geologically, three major units exist in this area, hornblende biotite gneiss (HBG), alluvio-marine and fluvial marine (Fig. 1). The HBG is the dominant formation and, however, alluvial deposits occur on both sides of the river, which are composed of clay, silt, sand and gravel. Alluvial marine and fluvial marine are dominant in the eastern part of the study area. Charnockite patches are noted in the study area, in the central part of the study area and along the western margin. The study area is also represented by intrusions of granite, quartzite and patches of sandstone.

Hydrology

The study area is underlain by porous and fissured formations. The unconsolidated and semi-consolidated

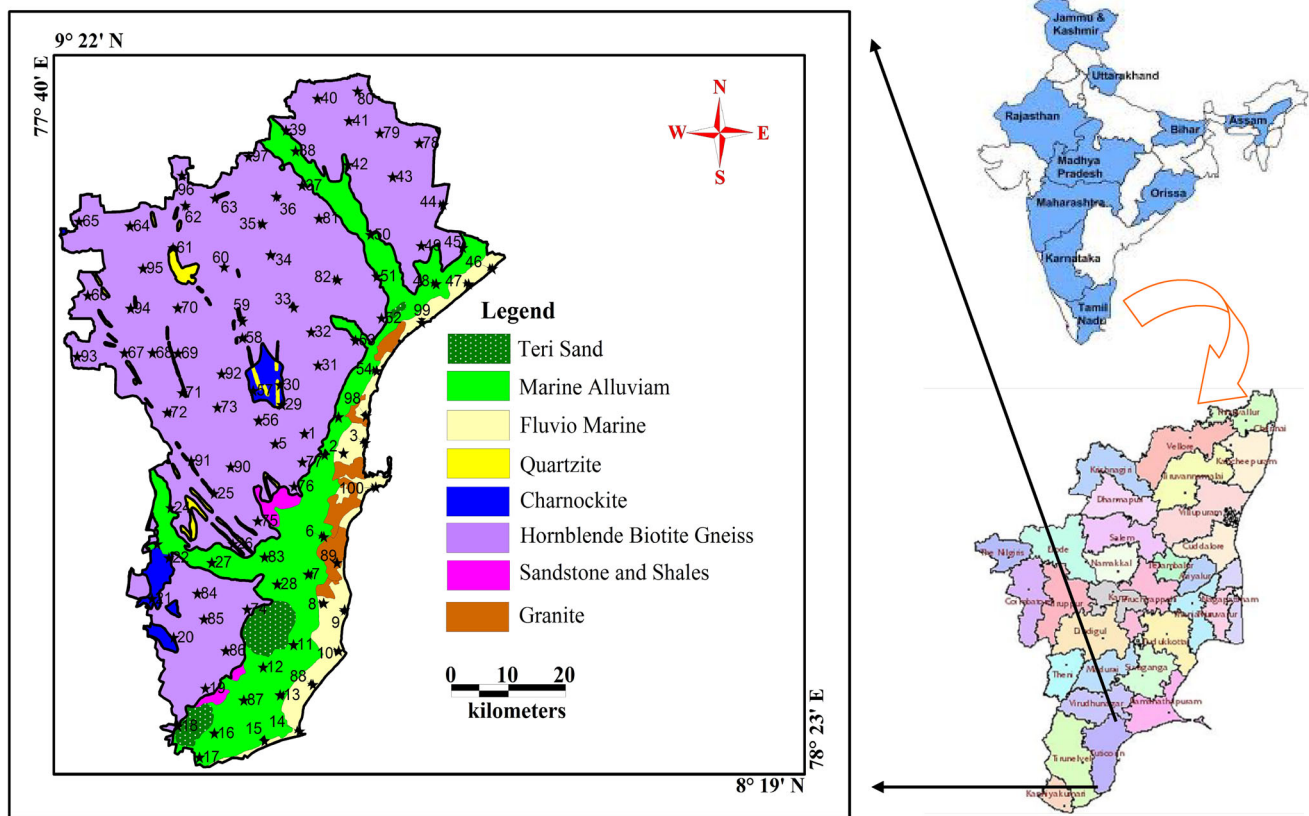


Fig. 1 Sampling location and geology map of the study area

formations and weathered and fractured crystalline rocks are important aquifer systems in the district. The porous formations in the study area include sandstones and clays of recent to sub-recent Quaternary and Tertiary age. The general study area stratigraphic succession is presented below (Table 1). The recent formations contain mainly sand, clay and gravel, confined to the major drainage-covered regions. The maximum thickness of alluvium is 45.0 m bgl, whereas the average thickness is about 25.0 m. Groundwater occurs under water table and confined conditions in these formations and is developed by means of dug wells and filter points (CGWB 2009). Alluvium, which forms a good aquifer system along the Vaippar and Gundar riverbed, is one of the major sources of water supply to the surrounding villages. The morphotectonic analysis of the crystalline tract indicates

the presence of deep-seated tensile and shear fractures, particularly along the fold axes. These tension joints, fractures and shear fractures at deeper depth of 30–100 m have been acting as conduits for groundwater movement (CGWB 2009). Limited freshwater availability is noted in sedimentary areas, and the floating lenses of freshwater make the coastal tract vulnerable to water quality changes. Groundwater from alluvial/tertiary aquifer present in the eastern part of the district is in hydraulic connection with the sea and hence vulnerable to saline water ingress (CGWB 2009). The general aquifer parameters show that the transmissivity ranges from less than 7 to 135 (m²/day), with a storativity range of $1.32 \times 9 \times 10^{-3}$ to $1.88 \times 9 \times 10^{-3}$ the parameters vary in the denudation areas, structurally controlled regions and highly weathered regions (CGWB 2009).

Table 1 The stratigraphic succession in Tuticorin District

Period	Age	Formation	Lithology
Quaternary	Holocene to recent	Alluvium colluvium	Marine alluvium, fluvio marine, teri sand, sandstone, shales
Tertiary	Mio-Pliocene	Panamparai sandstone	Hard, compact, sandstone, shales
Proterozoic	Precambrian	Crystalline complex	Charnockite, hornblende biotite genesis, granite, quartzite

Land use/land cover

The spatial land uses were classified based on NRSA (National Remote Sensing Agency 2013) guidelines with slight modifications and derived 19 land use classes (Level III), suitable to the local condition. This map clearly classified the land as built-up lands, agricultural lands, forests, mangroves forest, wastelands, water bodies (Rivers/Tanks) and salt pan in the Tuticorin District (Fig. 2). Majority of the study area covered by agricultural land area apart from the coastal tract. Forest areas are spatially represented in the southern, central and northwestern part of the study area, and mangroves forest in the eastern part. Water bodies occupy the rivers, tanks, and streams. The saltpan covered the coastal region along the eastern part of the study area.

Materials and methods

A total of 100 groundwater samples (Fig. 1) were collected during PRM and POM in 2013. The sample bottles were labeled, sealed and transported to the laboratory under standard preservation methods. The major anionic and cationic concentrations were determined in the laboratory using the standard analytical procedures as recommended by the American Public Health Association (APHA 1995). Alkalinity and physical parameters such as temperature, pH, EC and TDS were measured in the field. Na^+ and K^+

were determined using flame photometer. Ca^{2+} , Mg^{2+} , Cl^- and HCO_3^- were determined by volumetric titration methods. Anion concentrations were determined for SO_4^{2-} , NO_3^- and PO_4^- using ion chromatography (IC); also, H_4SiO_4 was analyzed using UV–Vis spectrophotometry (Eaton et al. 1995). The accuracy of complete chemical analysis of a groundwater sample was checked by computing the cation–anion balance (Eq. 1), where the total concentrations of cations, $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ (TCC) in milliequivalents per liter, should equal the total concentrations of anions, $\text{HCO}_3^- + \text{Cl}^- + \text{SO}_4^{2-} + \text{NO}_3^- + \text{F}^-$ (TCA), expressed in the same units.

$$\text{Cation – anion balance} = [(\text{TCC} - \text{TCA}) / (\text{TCC} + \text{TCA})] \times 100. \quad (1)$$

The reaction (cationic and anionic balance) error (E) of all the groundwater samples was less than the accepted limit of $\pm 10\%$, an added proof for the precision of the data (Matthess 1982; Domenico and Schwartz 1990).

Results and discussions

Hydrogeochemistry

The pH indicates the strength of the water that reacts with the acidic or alkaline material present in the water. pH was found to be acidic to alkaline in nature in most of the samples ranging between 6.80 and 9.20 and 6.80 and 9.40 during the PRM and POM seasons, respectively (Table 2). It controls the carbon dioxide, carbonate and bicarbonate equilibrium. The combination of CO_2 with water produces carbonic acid, which affects the pH of the water, and higher pH is noted in the salt water-intruded regions and along the regions covered by salt pans.

The TDS, which indicates total dissolved ions in the water, is between ranges 194.50 and 16,685.61 mg l^{-1} during PRM and 300 and 12,727 mg l^{-1} during POM, respectively. Electrical conductivity is the measure of charged ions in groundwater; it is found to vary from 308.80 to 28,140 $\mu\text{S/cm}$ in PRM and 461 to 19,872 $\mu\text{S/cm}$ in POM.

Ca^{2+} concentration ranges from 4 to 1600 mg l^{-1} during PRM and 29 to 500 mg l^{-1} during POM. The concentration of magnesium in groundwater samples in the study area varies from 4.80 to 1248 mg l^{-1} and 9 to 895 mg l^{-1} during PRM and POM, respectively. Higher Ca^{2+} and Mg^{2+} are noted in PRM compared to POM. In many locations, $\text{Mg}^{2+} > \text{Ca}^{2+}$, due to the influence of seawater Mondal et al. (2008) and higher contribution of Mg^{2+} than the contribution of Ca^{2+} , is caused by the influences of ferromagnesium minerals, ion exchange

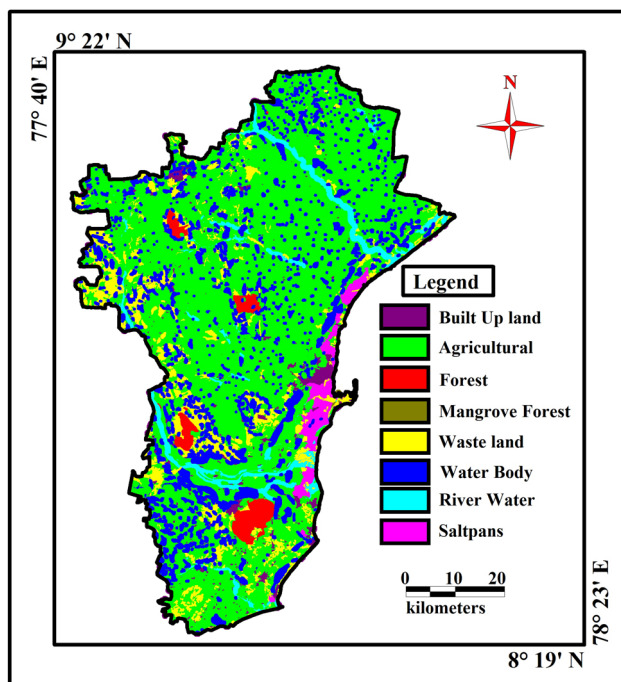


Fig. 2 Land use/land cover map of the study area

Table 2 Range of chemical ions during PRM and POM (all values are in mg l⁻¹ except for those of pH and EC which are in μS cm⁻¹)

	pH	TDS	EC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	F ⁻	Cl ⁻	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ²⁻	H ₄ SiO ₄	PO ₄ ⁻
Pre-monsoon														
Minimum	6.80	194.50	308.80	4.00	4.80	14.80	0.50	0.00	35.45	12.20	0.51	0.50	1.25	0.00
Maximum	9.20	16,685.61	28,140.00	1600.00	1248.00	4488.00	520.50	2.90	10,812.25	536.80	148.00	456.00	125.00	12.00
Average	7.58	2025.59	3307.00	114.30	88.87	477.10	49.02	0.45	1004.21	162.68	8.34	74.91	61.78	0.72
Post-monsoon														
Minimum	6.80	118.00	198.00	29.00	9.00	4.00	2.00	0.00	35.45	50.40	0.71	2.00	1.30	0.00
Maximum	9.40	15,724.00	31,550.00	500.00	895.00	4250.00	213.00	2.42	9052.50	683.20	148.20	312.00	295.00	1.02
Average	7.83	1715.20	3253.27	112.72	101.67	285.77	27.62	0.39	726.13	268.72	8.54	74.99	155.01	0.15

between Na⁺ and Ca²⁺, precipitation of CaCO₃, and marine environment (Subba Rao et al. 2012). The Na⁺ concentration varies from 14.80 to 4488 mg l⁻¹ and 4 to 4250 mg l⁻¹ during PRM and POM. The sodium concentration also exceeds the permissible limit, and the increasing sodium in groundwater is likely due to seawater influence or salt pan deposits or ionic exchange process. Na⁺ is also attributed to be released by weathering of the sodic feldspar. This is because of the silicate weathering and/or dissolution of soil salts stored by the influences of evaporation and anthropogenic activities (Subba Rao et al. 2012), in addition to the agricultural activities and poor drainage conditions. In contrast to the concentrations of Ca²⁺, Mg²⁺ and Na⁺ ions among the cations, a lower concentration of K⁺ is observed between 0.5 and 520 mg l⁻¹ during PRM and 2 and 213 mg l⁻¹ during POM in the groundwater, because the potash feldspars are more resistant to chemical weathering and are fixed on clay products.

In fact, the Cl⁻ is derived mainly from the non-lithological source and its solubility is generally high. It ranges from 35.45 to 10,812.25 mg l⁻¹ during PRM and 35.45 to 9052.50 mg l⁻¹ during POM. A higher concentration of chloride in the coastal region may be due to seawater intrusion (Chidambaram et al. 2007; Singaraja et al. 2013) and also leaching from the upper soil layers derived from industrial and domestic activities (Srinivasamoorthy et al. 2008). The value of HCO₃⁻ is observed from 12.2 to 536 mg l⁻¹ during PRM and 50.4 to 683 mg l⁻¹ during POM, respectively. The higher concentration of HCO₃⁻ in the water shows a dominance of mineral dissolution weathering (Stumm and Morgan 1996). The SO₄²⁻ values range from 0.50 to 456 mg l⁻¹ and 2 to 312 mg l⁻¹ during PRM and POM, and higher sulfate noted in PRM due to salt pans/sea water intrusion can be responsible for most of the SO₄²⁻ inputs into the groundwater samples (Barbecot et al. 2000). The value of NO₃⁻ in the groundwater is observed between 0.51 and 148 mg l⁻¹ and 0.7 and

148.20 mg l⁻¹ during PRM and POM, respectively. The groundwater shows a very low content of NO₃⁻ near the coast and also NO₃⁻ is a non-lithological source. In natural conditions, the concentration of NO₃⁻ does not exceed 10 mg l⁻¹ in the water (Cushing et al. 1973) so that the higher concentration of NO₃⁻, beyond 10 mg l⁻¹, is an indication of anthropogenic pollution. It is mainly due to influences of poor sanitary conditions and indiscriminate use of higher fertilizers for higher crop yields in the study area. Nitrate in groundwater is mainly derived from organic industrial effluents, fertilizer or nitrogen-fixing bacteria, leaching of animal dung, sewage and septic tanks through soil and water matrix to groundwater (Richards 1954). The concentration of PO₄⁻ shows that lesser values are noted in both the seasons. In the groundwater, there is a higher concentration of F⁻ during PRM (3.2 mg l⁻¹) when compared with POM. Hence, it is clearly evident that there is a decrease in the concentration of F⁻ ions during the POM, indicating a dilution effect and a similar trend was observed in the Dindigul region (Manivannan et al. 2010).

The geochemical trend of groundwater in the study area demonstrates that sodium is the dominant cation (Na⁺ > Ca²⁺ > Mg²⁺ > K⁺) and (Na⁺ > Mg²⁺ > Ca²⁺ > K⁺) during PRM and POM. Chloride is the dominant anion (Cl⁻ > HCO₃⁻ > SO₄²⁻ > H₄SiO₄ > NO₃⁻ > F⁻) and (Cl⁻ > HCO₃⁻ > SO₄²⁻ > H₄SiO₄ > NO₃⁻ > F⁻) during PRM and POM seasons, respectively.

Piper diagram

Hill Piper plot (Piper 1953) is used to infer the hydro-geochemical facies of groundwater (Fig. 3). In PRM, the samples are clustered in the fields of 1, 2, 3, 4 and 5, and the majority of the samples are concentrated in the Na–Cl type (Fig. 3), indicating the saline nature in the groundwater (Prasanna et al. 2010) with minor representations from mixed Ca–Mg–Cl, mixed Ca–Na–HCO₃, Ca–Cl, and Ca–HCO₃ types. From the plot, alkalis (Na⁺ and K⁺)

exceed alkaline earths (Ca^{2+} and Mg^{2+}) as well as strong acids (Cl^- and SO_4^{2-}) exceed weak acid (HCO_3^-). In the groundwater of Na–Cl type, Na^+ is considered to be derived from mixing with seawater. The dominance of Na in this water could also be caused by the water's increased alteration capacity due to the high CO_3 concentration that favors the solubility of alkaline elements from silicic rocks. Hence, sodium can also be attributed to the seawater ingress/dissolution of sodium-rich feldspars. However, ion exchange phenomena between Na^+ and Ca^{2+} could also be responsible for sodium and calcium concentrations (Lambrakis and Kallergis 2005) or due to seawater intrusion (Chidambaram et al. 2007).

In POM, samples are clustered in the fields of 1, 2, 3, 4 and 5, and the majority of the samples are concentrated in the Ca–Mg–Cl type and mixed Ca–Cl type. Ca and Mg are major cations and Cl is the major anion in this groundwater. This facies is characterized by a low concentration of HCO_3^- and relatively higher concentration of Cl^- and Ca^{2+} , which are mainly distributed among the marine sediments and occur in the intermediate zone of the groundwater discharge area; a similar trend was observed in Cuddalore District (Prasanna et al. 2010). It is observed from the Piper plot that groundwater samples shows alkalis (Na^+ and K^+) exceed alkaline earths (Ca^{2+} and Mg^{2+}) as well as strong acids (Cl^- and SO_4^{2-}) exceed weak acid (HCO_3^-) (Udayalaxmi et al. 2010) and Ca^{2+} – Cl^- type water may be a leading edge of the seawater plume (Jeen et al. 2001). Few samples represented the fields 1 and 2. From the plot, a strong seawater influence is clearly evident in PRM compared to POM and a clear shift from Ca– HCO_3^- to Na–Cl, Ca–Cl and mixed Ca–Mg–Cl types during POM (Rasouli et al. 2012; Singaraja et al. 2014).

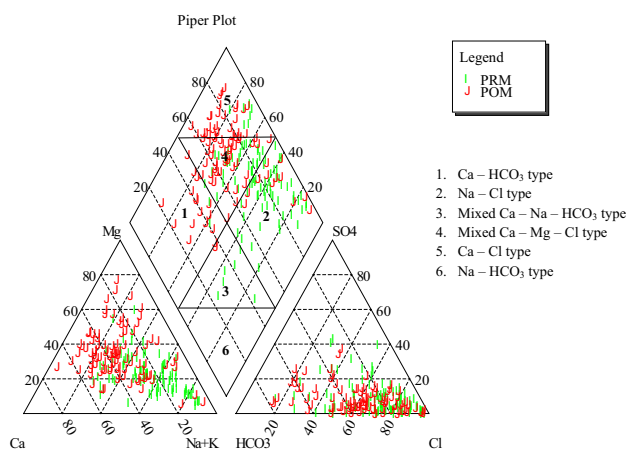


Fig. 3 Piper facies diagram for groundwater samples representing PRM and POM

Groundwater quality parameters

Water quality for drinking purposes

The quality of groundwater is important because it determines the suitability of water for drinking, and domestic and irrigation purposes (Raju et al. 2011; Manikandan et al. 2012; Singaraja et al. 2013). WQI is an essential parameter for demarcating groundwater quality and its suitability for drinking purposes (Tiwari and Mishra 1985; Mishra and Patel 2001; Avvannavar and Shrihari 2008). WQI is defined as a technique of rating that provides the composite influence of individual water quality parameters on the overall quality of water (Mitra and ASABE Member 1998) for human consumption. The standards for drinking purposes as recommended by WHO (2004) have been considered for the calculation of WQI. For computing WQI, four steps are followed.

In the first step, each of the 11 parameters (pH, TDS, Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- , F^- , Ca^{2+} , Mg^{2+} , Na^{2+} and K^+) has been assigned a weight (w_i) according to its relative importance in the overall quality of water for drinking purposes (Table 3). A maximum weight of 5 has been assigned to parameters like total dissolved solids, chloride, fluoride and sulfate due to their importance in water quality assessment (Srinivasamoorthy et al. 2008). Bicarbonate and potassium are given a minimum weight of 2, as these play an insignificant role in the water quality assessment. Other parameters like calcium, magnesium, sodium, pH and nitrate were assigned weights between 1 and 5 depending on their importance in water quality determination.

In the second step, the relative weight (W_i) was computed from the following equation:

$$W_i = w_i / \sum_{i=1}^n w_i,$$

where W_i is the relative weight, w_i the weight of each parameter and n the number of parameters.

The calculated relative weight (W_i) values of each parameter are given in Table 3.

In the third step, a quality rating scale (q_i) for each parameter is assigned by dividing its concentration in each water sample by its relevant standard according to the guidelines laid down in the WHO (2004) and multiplying the result by 100:

$$q_i = (C_i/S_i) \times 100,$$

where q_i is the quality rating and C_i the concentration of each chemical parameter in each water sample in milligrams per liter.

Table 3 Relative weight of chemical parameters

Parameters	WHO Standard	Weight (w_i)	Relative weight (W_i)
pH	6.5	3	0.073
TDS (mg l^{-1})	500	5	0.122
Ca^{2+} (mg l^{-1})	100	3	0.073
Mg^{2+} (mg l^{-1})	50	4	0.098
Na^+ (mg l^{-1})	200	4	0.098
K^+ (mg l^{-1})	20	2	0.049
HCO_3^- (mg l^{-1})	125	1	0.024
Cl^- (mg l^{-1})	250	5	0.122
SO_4^{2-} (mg l^{-1})	200	5	0.122
NO_3^- (mg l^{-1})	45	4	0.098
F^- (mg l^{-1})	1.5	5	0.122
Total of weight = 41			Total of relative weight = 1

S_i is the world drinking water standard for each chemical parameter in milligrams per liter according to the guidelines of the WHO (2004).

In the fourth step, for computing the WQI, the SI is first determined for each chemical parameter, which is then used to determine the WQI according to the following equation:

$$SI_i = W_i \times q_i,$$

$$WQI = \sum SI_i,$$

where SI_i is the sub-index of the i th parameter and q_i the rating based on concentration of the i th parameter.

Water quality types were determined on the basis of WQI. The computed WQI values range from 23.67 to 1373.81 and 30.02 to 934.45 for PRM and POM, respectively. The WQI range, type of water and calculation of WQI for percentage samples can be classified in Table 4. During PRM, 19% of groundwater samples represent “excellent water”, 31% indicate “good water”, 29% shows “poor water”, 12% shows “very poor water” and 9% indicates water unsuitable for drinking purposes. During POM, 28% sample signifies “excellent water”, 39% shows “good water”, 20% shows “poor water”, 6% shows “very poor water” and the remaining 7% of the samples are unsuitable for drinking purposes. The PRM samples show signs of poor quality in drinking purpose compared to POM. This may be due to dilution of ions after monsoon, overexploitation of groundwater, direct discharge of effluents and agricultural impact (Singaraja et al. 2013; Thivya et al. 2013a; Thilagavathi et al. 2012).

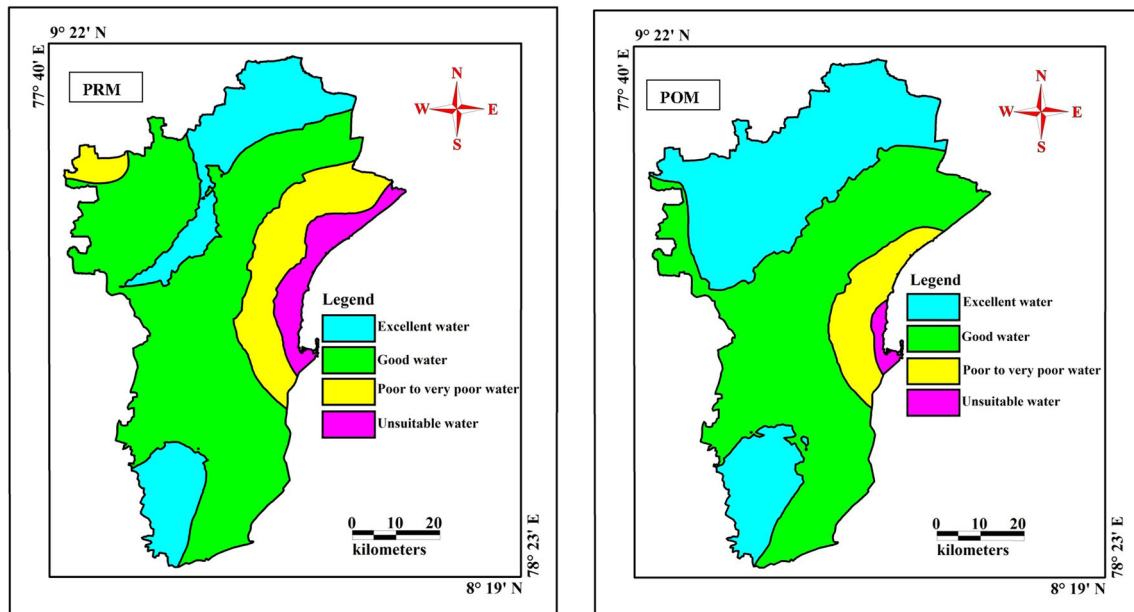
Spatial distribution of WQI (Fig. 4) shows that four zones are clearly indicated: excellent, good, poor to very poor and water unsuitable for drinking purpose during both seasons. The water in Zone 1, the eastern part of the study area along the coast, covering a region of about 265.6 and 50.30 km^2 during PRM and POM, is unsuitable for

drinking purpose. Zone 2 covers an area of 689.05 and 368.1 km^2 during PRM and POM; it is parallel to the coast and bounds Zone 1 in the eastern part of the study area with poor to very poor water. Zone 3 covers an area of 2691.39 and 2307.39 km^2 during PRM and POM, followed by Zone 2 and the central part of the study area in both seasons. Zone 4 falls on the northern and southwestern part of the study area, covering an area of about of 944.5 and 1863.1 km^2 during PRM and POM.

The electrical conductivity (EC) measures the capacity of a solution to conduct an electric current. This depends on the presence of ions, their total concentration, their mobility, their valence and the temperature at which measurement was taken. Spatial distribution of the EC of the groundwater samples of Tuticorin District was carried out for different seasons (Fig. 5). In Zone 1, a higher concentration was observed in the northeastern and southwestern part of the study area, covering a region of about 1770.29 and 1439 km^2 during PRM and POM with water unsuitable for drinking purpose. Zone 2 covers an area of 1642.51 and 1325 km^2 during PRM and POM, it is parallel to the coast and bounds Zone 1 in the eastern part of the study area. Zone 3 covers an area of 1055.8 and 1855.6 km^2 during PRM and POM, followed by Zone 2 and its central part of the study area in different seasons. Zone 4 falls on the northern part of the study area, covering an area of about of 152.7 and 4.55 km^2 during PRM and POM. A higher concentration of EC in the northeast part of the study area may be due to seawater intrusion along the coast (Prasanna et al. 2011; Singaraja et al. 2013). In general, a lower concentration of EC is noted in the north, northwestern and southern part due to the infiltration of Tamirabarani, Karamanaiyar and Vaippar river basins. A similar trend was also observed in the groundwater samples around the Gadilam river basin (Prasanna et al. 2010). The spatial distribution of electrical conductivity (EC) for

Table 4 The WQI range, type of water and percentage of the water samples during PRM and POM

Range	Type of water	Percentage of the samples	
		PRM	POM
<50	Excellent water	19	28
50–100.1	Good water	31	39
100–200.1	Poor water	29	20
200–300.1	Very poor water	12	6
>300	Water unsuitable for drinking purposes	9	7

**Fig. 4** Spatial distribution of WQI in the study area during PRM and POM

groundwater samples: higher EC was noted in the north-eastern and central part of the study area due to seawater intrusion, salt pans, agricultural return flow and industrial area. EC showed increasing trend along the groundwater flow direction. This indicates the leaching of secondary salts and anthropogenic impact by fertilizers used for agricultural activities apart from seawater intrusion. This may be due to anthropogenic impacts from the nearby industry SIPCOT (Prasanna et al. 2008).

Stuyfzand (1989) proposed the chloride classification in epm values such as extremely fresh, very fresh, fresh, fresh brackish, brackish, brackish-salt, salt and hyperhaline categories (Table 5). More than 30 and 24% of the samples fall under the fresh categories during PRM and POM, 14 and 25% of samples under fresh brackish, 42 and 40% under brackish, 13 and 11% under brackish salt and only 1 sample falls under the saltwater categories during PRM and POM, respectively (Table 5). It is also interesting to note that the majority of the water samples are unfit for drinking

purpose during PRM compared to POM. Cl^- concentration apart from coastal region derived from Anthropogenic sources include fertilizer, human and animal waste and industrial applications. These sources can result in significant concentrations of chloride in groundwater because chloride is readily transported through the soil (Stallard and Edmond 1987). Increasing Cl^- concentrations toward the coastline are good indicators of seawater intrusion. In the process of seawater intrusion, mixing between saline and freshwater and water–rock interaction may influence groundwater salinity (Appelo and Postma 1999; Vengosh et al. 2002; Appelo and Postma 2005). Spatial distribution of Cl^- (Fig. 6) Zone 1 has values $>1250 \text{ mg l}^{-1}$ with an area covering about 412.71 and 57.68 km^2 during PRM and POM respectively. Zone 2 has values $750\text{--}1250 \text{ mg l}^{-1}$, covering an area of about 382.5 and 281.5 km^2 during PRM and POM, followed by Zone 3 with $250\text{--}750 \text{ mg l}^{-1}$, covering an area of about 1971.69 and 1124.9 km^2 during PRM and POM, respectively. Zone 4,

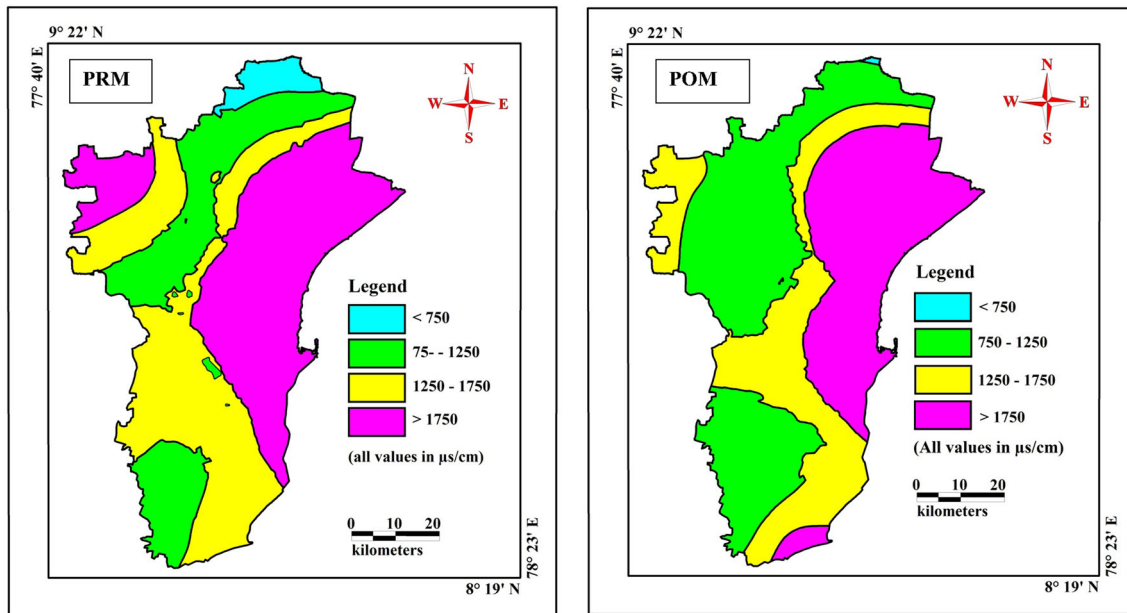


Fig. 5 Spatial distribution of EC in the study area during PRM and POM (all values in mg l^{-1})

the values $<250 \text{ mg l}^{-1}$ was represented in these regions covering an area of about 1281.02 and 541.56 km^2 during PRM and POM. The higher concentration of chloride in the coastal region may be due to seawater intrusion (Chidambaram et al. 2007). Low Cl^- ($<250 \text{ mg l}^{-1}$) concentration shows in center and western part of study area which covers about 1854.1 and 3156.92 km^2 during PRM and POM seasons respectively.

The observed high values of chloride and EC correspond to the same WQI, indicating the poor quality of groundwater in the study area. The same is also confirmed with seawater intrusion in same locations identified by WQI, EC, and Cl. Poor water quality is observed in the eastern part of the study area along the coastal region during PRM and POM. It is also interesting to note that most of the water is unsuitable for drinking purpose during PRM compared to POM due to the dilution effect after monsoon (Figs. 4, 5, 6).

Classification of water use for irrigation and domestic purpose

The suitability of groundwater for irrigation purpose is mainly based upon factors as soil texture and composition, crops grown and irrigation practices in addition to the chemical characteristics of water. Parameters such as sodium percent, SAR, RSC, permeability index, MH, PS, KR, PSI, TH and CR were calculated using the equations in Table 6.

Sodium percentage

The sodium in irrigation waters is also expressed as percent sodium or soluble sodium percentage ($\text{Na} \%$) and can be determined using the equation in Table 6, where all ionic concentrations are expressed in milliequivalents per liter. According to Wilcox (1955), 25 and 52% of the samples fall under the good class during PRM and POM, 31 and 18% in permissible class, 34 and 5% in doubtful class and 10 and 2% in unsuitable class during PRM and POM for irrigation (Table 5). A high percentage of Na^+ with respect to (Ca^{2+} , Mg^{2+} and Na^+) in irrigation water causes deflocculating and impairing of soil permeability (Singh et al. 2008). According to Joshi et al. (2009), a high percentage of sodium in the water for irrigation purpose can potentially stunt plant growth and reduce soil permeability.

Sodium absorption ratio (SAR)

The distribution of SAR was plotted using Richards (1954) classification, where concentration is expressed in equivalent per million (epm). It was found that samples fall in all categories (Table 5). More than 88 and 93% of samples fall under excellent class during PRM and POM, 6 and 4% under good category, 4 and 1% under fair category and the remaining 6 and 2% under poor category during PRM and POM.

Table 5 Geochemical classification of groundwater samples collected during POM and PRM

Category	Grade	PRM (<i>N</i> = 100)	POM (<i>N</i> = 100)	Category	Grade	PRM (<i>N</i> = 100)	POM (<i>N</i> = 100)
<i>EC Wilcox (1955)</i>				<i>S.A.R. Richards (1954)</i>			
<250	Excellent	0	1	Excellent	0–10	88	93
<250–750	Good	22	19	Good	10–18	8	4
750–2000	Permissible	49	39	Fair	18–26	4	1
2000–3000	Doubtful	18	30	Poor	>26	6	2
>30,000	Unsuitable	11	10	<i>R.S.C. Richards (1954)</i>			
<i>TDS classification (USSL 1954)</i>				<i>Hardness (Todd 1980)</i>			
<200	Freshwater	1	2	Soft	<75	3	0
200–500	Brackish water	23	18	Slightly hard	75–150	20	0
500–1500	Saline water	50	50	Moderately hard	150–300	23	22
>1500	Brine water	26	30	Very hard	>300	54	78
<i>Chloride classification (Stuyfzand 1989)</i>				<i>Hardness classification (Handa 1964)</i>			
Extremely fresh	<0.14	0	0	<i>Permanent hardness (NCH)</i>			
Very fresh	0.14–0.84	0	0	A1		2	8
Fresh	0.84–4.23	30	24	A2		37	71
Fresh brackish	4.23–8.46	14	25	A3		49	13
Brackish	8.46–28.21	42	40	<i>Temporary hardness (CH)</i>			
Brackish-salt	28.21–282.1	13	11	B1		0	6
Salt	282.1–564.1	1	0	B2		5	2
Hyperhaline	>564.3	0	0	B3		7	0
<i>Na % Wilcox (1955)</i>							
Excellent	0–20	0	23				
Good	20–40	25	52				
Permissible	40–60	31	18				
Doubtful	60–80	34	5				
Unsuitable	>80	10	2				

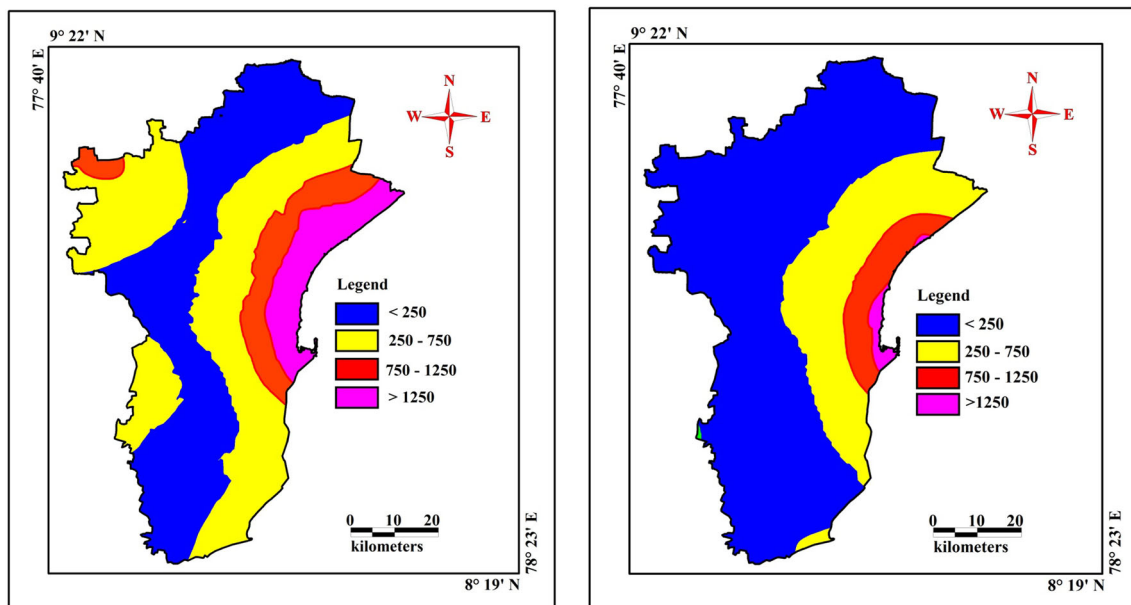
**Fig. 6** Spatial distributions of chloride in the study area representing PRM and POM (all values in mg l^{-1})

Table 6 List of formula different in parameters

Equation	Parameters	References
Na %	$(\text{Na} + \text{K})/(\text{Ca} + \text{Mg} + \text{Na} + \text{K}) \times 100$	Wilcox (1955)
SAR	$\text{Na}/\sqrt{\text{Ca} + \text{Mg}/2}$	Richards (1954)
RSC	$(\text{CO}_3 + \text{HCO}_3) - (\text{Ca} + \text{Mg})$	Richards (1954)
RSBC	$\text{HCO}_3 - \text{Ca}$	Gupta and Gupta (1987)
PI	$\{(\text{Na} + \text{HCO}_3)/[\sqrt{(\text{Ca} + \text{Mg} + \text{Na})}]\} \times 100$	Doneen (1964)
MH	$\text{Mg} \times 100/(\text{Ca} + \text{Mg})$	Raghunath (1987)
PS	$\text{Cl} + 1/2\text{SO}_4$	Doneen (1964)
KR	$\text{Na}/(\text{Ca} + \text{Mg})$	Kelly's (1963)
PSI	$(\text{Total Na}^+ - 24.5) - ((\text{Total Ca} - \text{calcium in CaCO}_3) \times 4.85)$	Puri (1949)
TH	$2.497\text{Ca} + 4.115 \text{Mg}$	(Todd 1980)
CR	$\{(\text{Cl}/35.5) + (\text{SO}_4/96)\}/2(\text{HCO}_3)/100$	Ryznes (1944)

Residual sodium carbonate (RSC)

Residual sodium carbonate (RSC) value considers the bicarbonate content of the water. High concentration of bicarbonate leads to an increase in pH value of water that causes dissolution of organic matter. An increase in RSC value leads also to precipitate calcium and magnesium that can cause an increase in sodium content in the soil. The high concentration of bicarbonate ion in irrigation water leads to its toxicity and affects the mineral nutrition of plants. According to Richard's classification, water with RSC greater than 2.5 epm is considered unsuitable for irrigation. Water with RSC of 1.25–2.5 is considered as marginal and that with a value less than 1.25 is safe for irrigation purpose. All the water samples analyzed had RSC values fall on all categories such as 95 and 98% of the water samples less than 1.25, suggesting that the water can be used for irrigation purpose during PRM and POM. 3 and 2% of the water samples indicate medium categories during both seasons. 2% of the PRM groundwater samples are unfit for irrigation purpose (Table 5).

Residual sodium bicarbonate (RSBC)

Generally, the concentration of bicarbonate and carbonate within the soil influences the suitability of water for irrigation purpose, because water samples with high RSBC value tend to have relatively high pH values. Therefore, land irrigated with such water becomes infertile owing to deposition of sodium carbonate (Eaton, 1950). The RSBC was calculated by an equation in Table 6. The residual sodium bicarbonate (RSBC) values of the water samples were found between (–) 1380.4 and 508.8 mg l⁻¹ during PRM and –151.2 and 596.4 mg l⁻¹ during POM. The positive RSBC value indicates that the dissolved calcium and magnesium ions are less than those of carbonate and bicarbonate contents. The RSBC of the samples was not

satisfactory (<5 mg l⁻¹) according to the criteria set by Gupta and Gupta (1987). 16 and 10% of the samples were not satisfactory during PRM and POM.

Permeability index (PI)

Based on the permeability index (PI), a water suitability classification for irrigation water was developed by Doneen (1964). The PI was calculated by an equation in table (Table 6), where all the ions are expressed in meq/l. The PI values in the study area vary from 57.94 to 1246.76 during the PRM and 79.48 to 1312.90 during POM. According to the PI values, 99% of the samples come under Class III (PI >75%) and the remaining 1% of the samples under classes I and II (PI ranges from 25 to 75%) category during PRM and all the samples fall in class III during POM. In general, the groundwater samples from the study area indicate that they are not suitable for irrigation purposes during both seasons.

Magnesium hazard (MH)

The magnesium content of water was considered as one of the most important qualitative criteria in determining the quality of water for irrigation. Generally, calcium and magnesium maintain a state of equilibrium in most waters, but increasing amount of magnesium in water will increase the salinity of the water and therefore decline the crop yield (Joshi et al. 2009). The presence of magnesium in soil and water would adversely affect their quality and render the soil unfit for cultivation (Chidambaram et al. 2013; Chandu et al. 2008). If magnesium ratio of the samples are >50% of the water sample, it will make the water poisonous to plants (Rajmohan and Elango 2005). In most waters, calcium and magnesium maintain a state of equilibrium. A ratio, namely index of magnesium hazard, was developed by Raghunath (1987) (Table 6). According to this, a high

magnesium hazard value (>50%) has an adverse affect on the crop yield as the soil becomes more alkaline.

In the study area, the magnesium hazard values range from 9.09 to 84.38 during PRM and 14.75 to 84.50 during POM. In the study area, 69% of the samples collected showed MH ratio <50% (suitable for irrigation), while 31% falls in the unsuitable category with magnesium hazard >50% during PRM, 26% in the unsuitable category and 74% in the suitable category during POM. The evaluation illustrates that 31 and 26% samples can cause adverse effect on the agricultural yield during PRM and POM.

Kelly's ratio (KR)

Kelly's ratio is used to determine the suitability of groundwater for irrigation. Sodium measured against calcium and magnesium was considered by Kelly (1963) for calculating the Kelly's ratio equation (Table 6). Groundwater having Kelly's ratio more than one (1) is generally considered unfit for irrigation. Kelly's ratio (KR) was found in the ranges from 0.39 to 11.92 during PRM and 0.04 to 14.26 in the POM samples of the study area. 31% and 78% of the samples were found to be less than the permissible value of 1.0, showing a good balance of sodium, calcium and magnesium ions during PRM and POM, respectively. 69 and 22% of the samples were not suitable for irrigation in the study area during PRM and POM.

Potential salinity (PS)

This is defined as the chloride concentration plus half of the sulfate concentration. It is expressed in milliequivalents per liter. The PS was calculated by the equation in Table 6. Doneen (1964) pointed out that the suitability of water for irrigation is not only dependent on the concentration of soluble salts. He found that low solubility salts precipitate in the soil and accumulate with successive irrigation, whereas the concentration of highly soluble salts increases the salinity of the soil (Doneen 1964). The huge amount of potential salinity in the coastal region is due to the presence of chlorides, which are derived from the saline waters of sea. The potential salinity of the water samples varied from 1.60 to 306.33 meq/L during PRM and 1.71 to 257.48 meq/L during POM.

Puri's salt index (PSI)

Puri (1949) established an index to interpret the quality of irrigation water. The PSI was calculated by an equation in Table 6. The value varies from -24.5 to 0 for good waters and 0 to +ve values for poor-quality waters. The PSI values varied from -6858.50 to 3087.53 during PRM and

-1438.2 to 3682.3 during POM. 73 and 92% of the samples showed negative values during PRM and POM and 27 and 8% of the sample showed positive values. Positive values indicate free Na^+ ions in the irrigation water. Free Na^+ ions are prevalent in many samples. Continuous irrigation with the groundwater having excess free Na^+ will lead to Na^+ accumulation in soils.

Classification of water use for domestic purpose

Total hardness (TH)

Hardness is a very important property of water for domestic purposes. Hard water causes problem in boilers in industries. Hardness of the water is attributable to the presence of alkaline earths, i.e., Ca^{2+} and Mg^{2+} . Hardness has no known adverse effect on health, but it is mainly an esthetic concern because of the unpleasant taste. But Durvey et al. (1991) showed that long-term consumption of extremely hard water might lead to an increased incidence of urolithiasis, anencephaly, parental mortality, some types of cancer and cardiovascular disorders.

Hardness can prevent formation of lather with soap, increase the boiling point of water and may cause encrustation in water supply distribution systems. Ca^{2+} and Mg^{2+} ions are largely responsible for water hardness and in addition higher Mg^{2+} concentrations has a laxative effect, maybe cathartic and diuretic (WHO 2004). Hardness of water is usually expressed as total hardness (TH) given by Table 6, where TH is the total hardness as CaCO_3 in mg l^{-1} ; Ca^{2+} the Ca^{2+} concentration in mg l^{-1} ; and Mg^{2+} the Mg^{2+} concentration in mg l^{-1} (Todd 1980).

Table 5 classifies groundwater in the study area according to their hardness (Durfor and Becker 1964). 3% of groundwater samples of the study area represent the soft category, 20% the moderately hard category during PRM and just 23 and 22% is hard water and 54 and 78% is very hard category during PRM and POM that may be a potential health risk factor. The hardness in the study area generally increases due to leaching of Ca^{2+} and Mg^{2+} ions into groundwater. In addition, a high range of TH in water may also cause corrosion in pipes in the presence of certain heavy metals (Garg et al. 2009).

Permanent hardness and temporary harness

Handa (1964) classified the groundwater based on hardness into permanent and temporary. Permanent hardness includes three categories such as A1, A2 and A3, and temporary hardness also has three categories such as B1, B2 and B3.

2 and 8% of the groundwater samples fall under the A1 category during PRM and POM. 37 and 71% of the

samples fall in the A2 category during PRM and POM. 49 and 13% of the groundwater samples fall in the A3 category during PRM and POM, representing permanent hardness (Table 5). 6 and 2% of the samples fall in the B1 and B2 category during POM, 5 and 7% of the samples fall under the B2 and B3 category in the study area during PRM representing temporary hardness.

Corrosivity ratio (CR)

Groundwater extracted from the study area has been utilized for various purposes and is transported by metallic pipes that may or may not be suitable for transport. This fact is highlighted using corrosivity ratio proposed by

Ryznes (1944), in Table 5. According to the corrosivity ratio, 89 and 81% of the groundwater samples fall in less than one category during PRM and POM, indicating that the majority of the groundwater samples of the study area are noncorrosive.

Indication of seawater intrusion

It is clearly obvious that the SO_4^{2-}/Cl^- mole ratios range from 0.005 to 1.45 during PRM, 0.004 to 1.43 during POM (Fig. 7) and most of the samples fall above the seawater value (0.1). It is also indicate that higher values (0.86) of SO_4^{2-}/Cl^- were above the sea water standard (0.1 to 0.86). In salt pan region groundwater samples enhance in SO_4^{2-} when compared to Cl^- may be due to organic dimethyl sulfide gas (DMS), which enhance the SO_4^{2-} in groundwater and excess of sulfate may be due to the presence of the dissolution of gypsum from salt pan region (Chandrasekharan et al. 1997; Singaraja et al. 2013). It is fascinating that there is a higher level of SO_4^{2-}/Cl^- mole ratios during both seasons (Fig. 7). It also clearly indicates that the depth of water level in the study area varied between -4.70 and 209.08 m AMSL during PRM and between -0.25 and 208.25 m AMSL during POM. The spatial distributions (Fig. 8) of water level show that regional groundwater flow is from northwest to southeast and that the high permeability generates a high groundwater flow toward the coast that minimizes the mixing with seawater during both seasons. Hence, we expected to find a gradual mixing of freshwater with seawater, using the chloride concentrations as a conservative tracer. However, our results

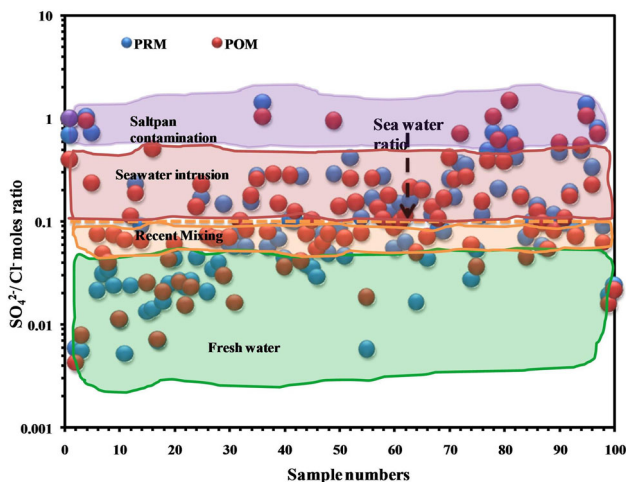


Fig. 7 Mole ratios of SO_4^{2-}/Cl^- versus sample numbers

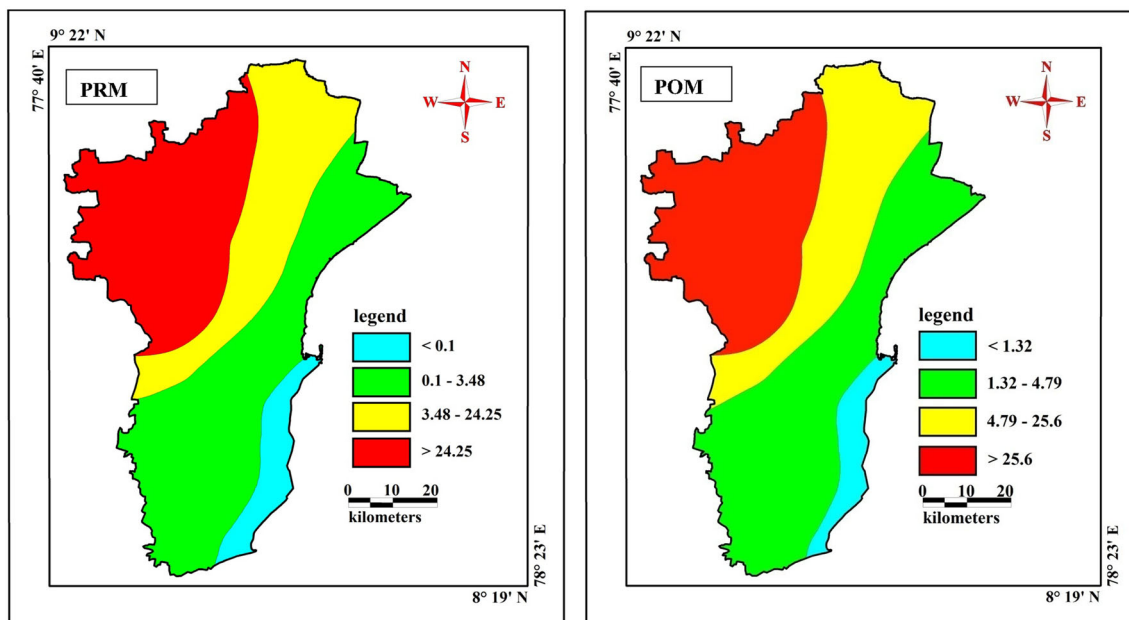


Fig. 8 Depth to water level during PRM and POM (m AMSL)

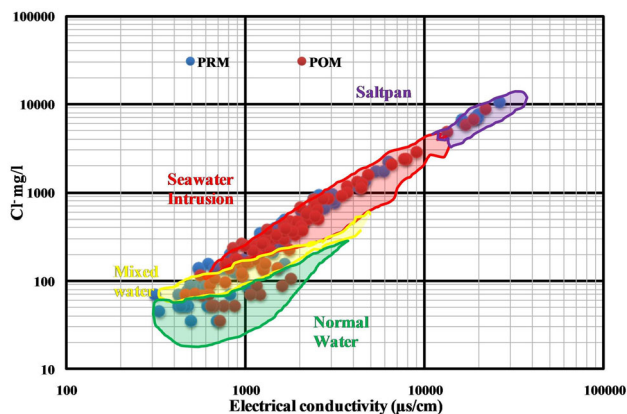


Fig. 9 Cl^- versus electrical conductivity showing normal groundwater conditions, saltwater intrusion, mixing between the two and salt pan contamination (from: Washington State Department of Ecology 2005)

show four zones on a plot of Cl^- vs EC: normal, mixed, SWI and salt pan (Fig. 9). Figure 9 shows that groundwater samples with Cl^- exceeding 4000 mg l^{-1} and EC exceeding more than $10,000 \mu\text{s/cm}$ are nearly influenced by salt pan contamination along the salt pan region (Fig. 9) Cl^- exceeding 200 mg l^{-1} and EC exceeding $\sim 1000 \mu\text{s/cm}$ are most likely influenced by SWI. Cl^- between 100 and 200 mg l^{-1} and EC between 600 and $2000 \mu\text{s cm}^{-1}$ show that they are clearly affected by seawater mixing (Washington State Department of Ecology 2005). An alternative approach, base exchange indices (BEX), can also be used to distinguish if an aquifer is undergoing salinization (negative BEX) or freshening (a positive BEX); according to Stuyfzand (2008). A

total of 35 and 30 samples were indicative of salinization during PRM and POM, respectively. Spatial distribution of BEX clearly differentiates that freshening and salinization zones. It clearly shows that the northeast part of the study area along the coast was strongly affected by salinization irrespective of season (Fig. 10).

Conclusions

The above study indicates that the groundwater of the study area is dominated by sodium and the following trends are noted: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ during PRM and POM, respectively. Chloride is the dominant anion and the following trend is noted: $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{H}_4\text{SiO}_4 > \text{NO}_3^- > \text{F}^-$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{H}_4\text{SiO}_4 > \text{NO}_3^- > \text{F}^-$ during PRM and POM, respectively. The type of water that predominates in the study area is Na–Cl during PRM and Ca–Mg– HCO_3^- during POM seasons, based on hydrochemical facies. It clearly indicates that strong seawater influence is noted during PRM compared to POM. The WQI calculated for PRM exhibits poor quality in greater percentage when compared with POM, indicating the effectiveness of dilution effect and the anthropogenic activities from the discharge of effluents from industrial, agricultural, and domestic uses. The WQI compared with Cl^- and EC observed high values similar to WQI, indicating the poor quality of groundwater along the northeastern parts of the study area dominated by seawater, agricultural, industrial and domestic activities. Higher TDS and Cl^- values were

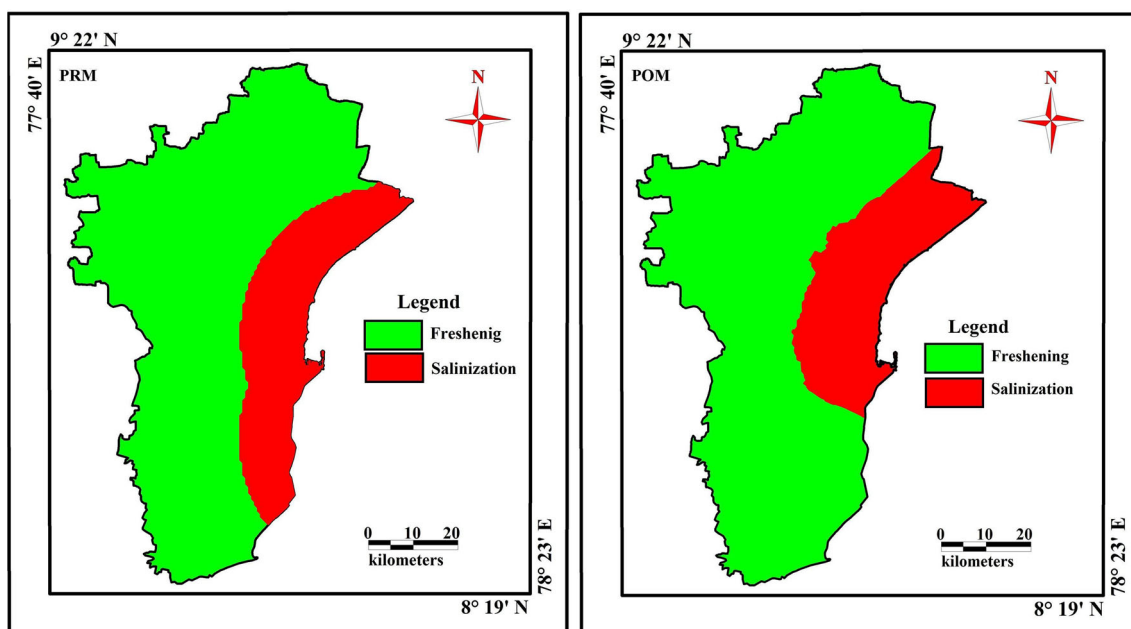


Fig. 10 BEX distribution in the groundwater of study area, according to Stuyfzand (2008)

observed in the northeastern part of the study area, owing to seawater intrusion, salt pan deposits and agricultural return flow in groundwater. Most of the water samples were not suitable for irrigation based on Na %, SAR, RSC, RSBC, PI, MH, KR, PS and PSI classification during PRM compared to POM. Total hardness shows that they range from moderately hard category to very hard category during PRM and POM. The depth of the water level map shows that the eastern part of the study area is in hydraulic connection with the sea and hence it is vulnerable to salt water intrusion. Higher level of $\text{SO}_4^{2-}/\text{Cl}^-$ mole ratios during PRM followed by POM is because of the dilution effect after rainfall. It is also point out that moles ratios values $\text{SO}_4^{2-}/\text{Cl}^-$ higher than sea water standard (0.1 to 0.86) due to organic dimethyl sulfide gas, which increase the SO_4^{2-} in groundwater. The plot of Cl vs EC shows four zones: normal, mixed, seawater intrusion and salt pan contamination. Spatial distribution of BEX shows clearly freshening along the western part and a salinization zone along the eastern part of the study area, irrespective of season. Hence, the study indicates that a considerable portion of the groundwater in this coastal environment has been deteriorated irrespective of season, but still seasonal influences in the water quality is noted by the process of recharge and further dilution of chemistry after the monsoon. This will help us to decide the utility purpose of water and to manage this commodity considering the seasonal variations.

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