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ORIGINAL ARTICLE

Hydrochemical characteristics and GIS-based assessment of groundwater quality in the coastal aquifers of Tuticorin corporation, Tamilnadu, India

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Abstract Tuticorin corporation stretches geographically from 8°43′–8°51′N latitude and 78°5′–78°10′E longitude, positioned in the East–West International sea routes on the South–East coast of India. The rapid urban developments in the past two decades of Tuticorin have caused depletion of groundwater quantity, and deterioration of quality through excessive consumption and influx of pollutants from natural and anthropogenic activities. The water samples collected in the field were analyzed for electrical conductivity, pH, total dissolved solids, major cations like calcium, magnesium, sodium, potassium, and anions SUCH AS bicarbonate, carbonate, chloride, nitrate and sulfate, in the laboratory using the standard methods given by the American Public Health Association. In order to assess the groundwater quality, 36 groundwater samples had been collected in year 2011. The geographic information system-based spatial distribution map of different major elements has been prepared using ArcGIS 9.2. The Piper plot shows that most of the groundwater samples fall in the field of Ca^{2+}-Mg^{2+}–Cl^{-}-$SO_4{}^{2-}$ and Na^{+}-K^{+}–Cl^{-}-$HCO_3{}^{-}$ by projecting the position on the plots in the triangular field. The cation concentration indicate that 83, 39 and 22 % of the K^{+}, Na^{+}, Ca^{2+} concentrations exceed the WHO limit. As per Wilcox's diagram and US Salinity laboratory classification, most of the groundwater samples are not suitable for irrigation due to the presence of high salinity and medium sodium hazard. Irrigation waters classified based on sodium absorption ratio, have revealed that 52 % groundwater are in general safe for irrigation, which needs treatment before use. permeability index also indicates that the groundwater samples are suitable for irrigation purpose.

Keywords Groundwater quality · Geographic information system · Wilcox's diagram · Permeability index · Tuticorin corporation · WHO

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Introduction

Water is the most important natural resource, which forms the core of ecological system. Recently there has been overall development in various fields such as agriculture, industry and urbanization in India. This has lead to increase in the demand of water supply which is met mostly from exploitation of groundwater resources. Hydrochemical study is a useful tool to identify the suitability of the groundwater. The physical parameters taken into consideration in the present study are color, odor, turbidity and temperature. The chemical parameters taken into consideration are hydrogen ion concentration (pH), specific conductance (EC), total dissolved solids (TDS), total hardness (TH) and all major cations and anions. Various workers in our country had carried out extensive studies on water quality have studied groundwater chemistry of shallow aquifers in the coastal zones of have concluded that groundwater present in the shallow aquifers are poor in quality and beyond potable limit as per the standard set by WHO (Amer 1995; Chidambaram et al. 2009; Dar et al. 2010). In many coastal towns or cities, groundwater seems to be the only source of fresh water to meet domestic, agricultural and industrial needs. But groundwater is under constant threat of saline water incursion, which seems to have become a worldwide concern (Rajmohan et al. 1997; Dar et al. 2011). The rapid growth in population in India enhanced the groundwater salinity through excessive consumption of groundwater for agricultural, domestic and industrial purposes due to the lack in surface water sources and high water demand. Moreover, high evaporation and low and erratic rainfall depleted the groundwater level and available groundwater quantity, especially in the coastal areas, and resulted in seawater intrusion (Adepelumi et al. 2009; Rajmohan et al. 2003; Todd 1959). Consequently, several agriculture farms near to the coast are abandoned due to groundwater salinity. Further, many inland farms have also been abandoned and groundwater in most of the farms is even not supporting date palms though date palms are very tolerant to salinity (Rajmohan et al. 2003; Selvam and Sivasubramanian 2012). Hence, it is apparent that recent studies firmly argue the effect of natural and anthropogenic contamination sources on groundwater composition, especially in coastal aquifer, and also imply the necessity of groundwater contamination studies in coastal aquifer. In the present study, a detailed investigation was carried out to evaluate the geochemical processes regulating groundwater quality in coastal aquifers of Tuticorin region since the groundwater has been impaired by natural as well as anthropogenic activities. Anthropogenic activities can alter the relative contributions of the natural causes of variations and also introduce the effects of pollution (Whittemore et al. 1989).

Geographic information system (GIS) has emerged as a powerful tool for storing, analyzing and displaying spatial data, and using these data for decision making in several areas including engineering and environmental fields (Goodchild 1993). The purpose of the study is to understand the groundwater quality in the coastal area and prepare the spatial distribution map of the various physico-chemical parameters using the GIS. In this study, GIS is utilized to locate groundwater quality zones suitable for different usages such as irrigation and domestic.

Study area

Tuticorin is located on the southeast coat of Tamilnadu, India. Historically, Tuticorin is famous for its maritime activity and pearl culture. It was the seaport of the Pandyan kingdom; it was later taken over by the Portuguese in 1548,

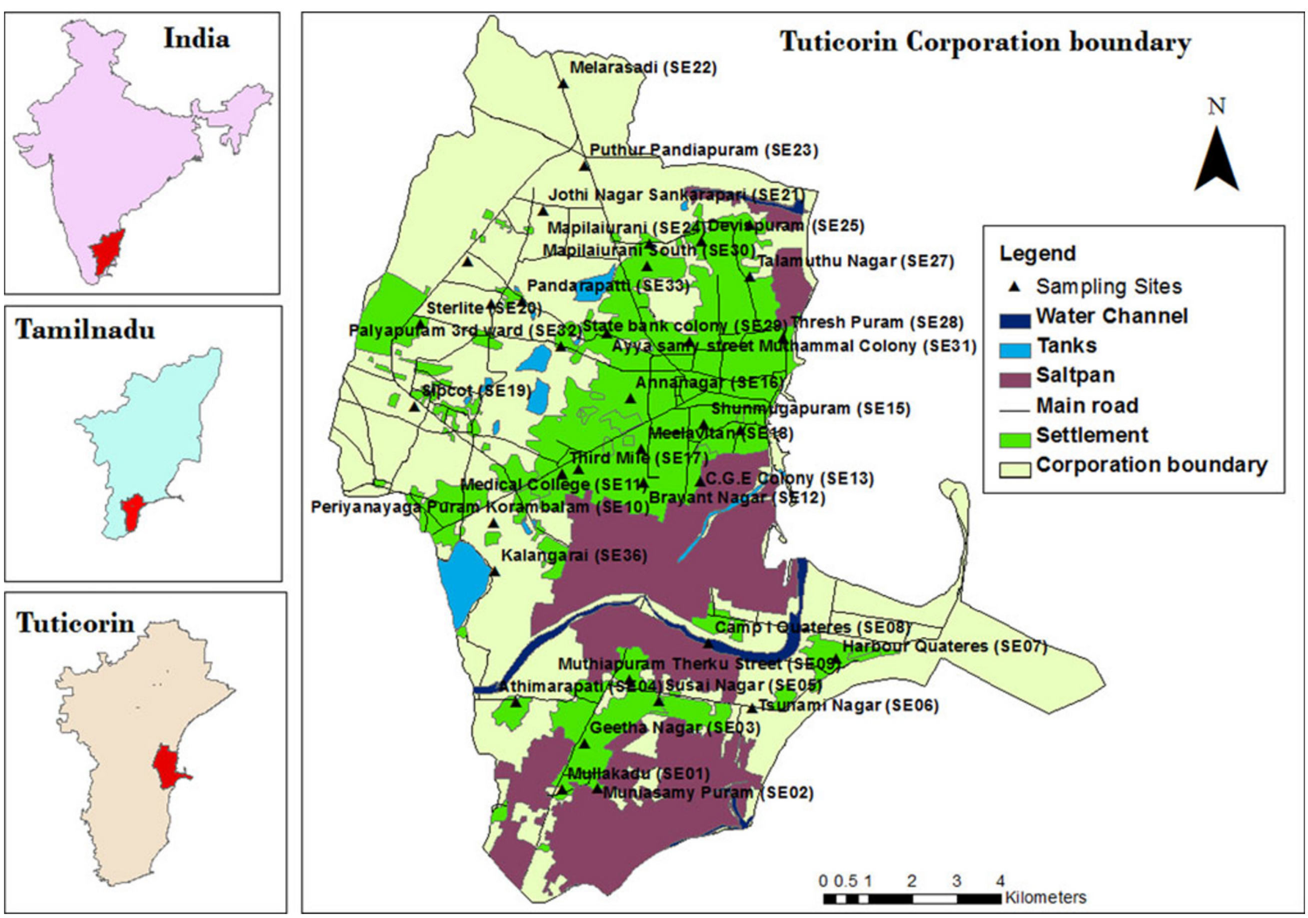


Fig. 1 Location map of study area

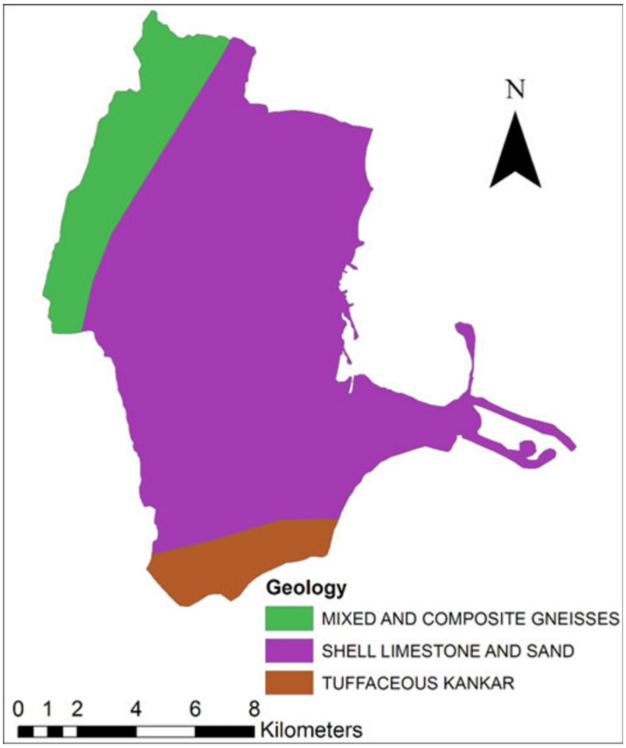


Fig. 2 Geology map of study area

captured by the Dutch in 1658, and ceded to the British in 1825. The lighthouse built in 1842 marked the beginning of the history of harbor development in the city. Tuticorin was established as a Municipality in 1866. It attained the status of Corporation on 5th August 2008 after 142 years. The city was industrially developed after the port construction and became district head quarters in the year 1986. After the formation of the district head quarters, the economic development was boosted and began to develop rapidly. Therefore, the urban expansion takes place in the different parts of the city during the study period. The study area covers geographical area of 154 sq km and lies between 8°43′–8°51′N latitude and 78°5′–78°10′E longitude (Fig. 1). Topographic elevation varies from few meters (near the coastline) to 27 m (amsl) in western part of the study area. The slope is gentle in the western and the central part, and nearly flat in the eastern part. Rainfall data from seven stations over the period of 1901–2008 were utilized and a perusal of the data shows that the normal annual rainfall over the district varies from about 570–740 mm. It is minimum around Arasadi (577.4 mm) and Tuticorin (582.8 mm) in the central eastern part of the district. The district is covered by Black Cotton soil in the west, with isolated red soil patches in high ground. The sandy soil is present in the coastal tract. Alluvial soil is restricted to river flood plain and coastal part. Alkaline and saline soils are also noticed at places. Tuticorin is covered by long and extensive sandy beach. It trends in north–south direction. Well-developed sandy beach is identified below south harbor breakwater. This beach is dominated by an admixture of quartz, feldspars and mica minerals.

Geology and hydrology

About 90 % of the study area is made up of sedimentary rocks of Tertiary to Recent age comprising Shell limestone and sand, tuffaceous kankar, sand (Aeolian deposits) etc., and the remaining area is covered by mixed and composite Genesis of Proterozoic age of crystalline rocks (Fig. 2). The Archean groups of formations are crystalline and metamorphic, and finely foliated with a general NW–SE trend described by Balasubramanaian et al. (1993) and Rangarajan et al. (2009).

The study area is covered with black soils in the western part (Sankarapari area), red soil (sandy loam to sandy soil) in the central part and alluvial sandy soils (Coastal area) in the eastern part. The maximum soil thickness is about 3 m. The sandy soils originated from sandstones and these have low soil moisture retentively. The alluvium soils are wind-blown sands and shells constitute beach sand and coastal dunes, which have very low soil moisture retentivity. The important aquifer systems in the district are constituted by unconsolidated and semi consolidated formations and weathered and fractured crystalline rocks. The porous formations in the district include sandstones of Tertiary age. The Recent formations comprising mainly sands, clays and gravels are confined to major drainage courses in the district. 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 being developed by means of dug wells and filter points. The productive zones are encountered in the depth range of 29.5–62.0 m bgl.

Materials and methods

A total of 36 groundwater samples had been collected from open wells and bore wells, well distributed within the study area during June 2011 and analyzed to understand the chemical variations of water quality parameters using standard methods (APHA 1995) (Table 1). The samples were collected in one liter high density polyethylene (HDPE) bottles pre-washed with dilute hydrochloric acid and rinsed three times with the water sample before filling and labeled accordingly. The samples were stored at a temperature 4 °C prior to analysis in the laboratory. Samples were analyzed in the laboratory for the physico-chemical attributes such as pH, electrical conductivity (EC), total hardness (TH), total dissolved solids (TDS) and major cations, such as calcium (Ca), magnesium (Mg),

Table 1 Well inventory and characteristics in the study area

Location name	Latitude	Longitude	Total depth (m)	Depth to water table (m)	pH	EC (µs/cm)	TDS
Mullakadu	78.1158	8.7241	12	7	7.8	2,430	1,450
Muniasamy Puram	78.123	8.7243	13.6	11.4	7.8	2,640	1,570
Geetha nagar	78.1204	8.7335	13	8.7	7.4	3,900	2,400
Athimarapati	78.1064	8.7418	10.3	7.1	7.8	1,080	710
Susai nagar	78.1356	8.7421	19.3	15.4	7.4	4,180	2,700
Tsunami nagar	78.1548	8.7407	13.6	9.5	7.7	1,520	980
Harbor quateres	78.1721	8.7509	9.2	5.5	7.7	1,280	790
Camp I quateres	78.1459	8.7541	19.6	13.1	7.6	10,000	6,000
Muthiapuram	78.1297	8.7466	19	16	7.4	2,720	1,620
Periyanayaga Puram	78.1016	8.7785	19.6	11.3	7.6	10,550	6,300
Medical college	78.1193	8.7895	18	12	7.6	2,350	1,470
Brayant nagar	78.1325	8.7869	16	13	7.7	1,840	1,840
C.G.E colony	78.1441	8.7872	22	17.5	7.7	10,470	6,500
Fisher colony	78.1525	8.7975	15.3	9	7.9	1,900	1,170
Shunmugapuram	78.1449	8.7987	16	8	7.4	2,570	1,570
Annanagar	78.1298	8.8041	9.3	5	7.5	2,490	1,560
Third mile	78.1159	8.7885	16.3	10.2	7.8	910	580
Meelavitan	78.1321	8.7937	19.8	15	7.1	8,720	5,300
Sipcot	78.0855	8.8024	29.5	25	7.8	1,830	1,150
Sterlite	78.0866	8.8192	70	30	8.8	4,810	3,100
Jothi nagar	78.1118	8.8423	50	28	10.2	2,000	1,290
Melarasadi	78.1161	8.8686	29	22	7.5	12,650	7,600
Puthur Pandiapuram	78.1203	8.8516	32.3	19	8	1,440	910
Mapilaiurani	78.1338	8.8357	16.9	9.5	8.1	350	2,300
Devispuram	78.1445	8.8361	46	18.5	7.5	6,200	3,800
Siluvaipatti	78.1545	8.8395	18	15	7.4	19,100	10,200
Talamuthu Nagar	78.1544	8.8289	20.3	13	7.7	12,820	7,600
Thresh puram	78.1613	8.8163	16.3	7.3	7.8	2,630	1,580
State bank colony	78.1419	8.8155	16.3	4.4	7.5	2,780	1,700
Mapilaiurani south	78.1333	8.8311	9.6	5.5	7.5	7,730	4,800
Ayya samy street	78.1251	8.8172	16.3	8	8	3,160	1,940
Palyapuram	78.1156	8.8146	19.6	8.1	7.9	7,500	4,500
Pandarapatti	78.1074	8.8237	49	27	7.9	2,600	1,570
Vijay company	78.0964	8.832	76	15	7.9	7,900	4,800
Sankarperi entrance	78.1012	8.8233	19.3	15	7.5	8,070	4,700
Kalangarai	78.1019	8.7688	25.4	11.2	7.9	840	530

sodium (Na), potassium (K), and anions, such as bicarbonate (HCO_3), carbonate (CO_3), chloride (Cl), nitrate (NO_3) sulfate (SO_4), and phosphate (PO_4) in the laboratory using the standard methods given by the American Public Health Association (APHA 1995). These parameters are tabulated in Table 2. pH, EC and TDS were measured using portable water quality analyzers. Major cations (Ca, Mg, Na, and K) were determined using ICP-mass spectrometer while the anions were determined as follows: bicarbonate (HCO_3), and total hardness (TH) were analyzed by volumetric method and sulfate (SO_4) was estimated by the spectrophotometric technique and nitrate(NO_3) was determined by ion chromatography. Chloride (Cl) by volumetric titration using $AgNO_3$ and K_2Cr, HCO_3 and carbonate (CO_3) was determined by Portamess using HCl, phenolphthalein, methyl orange by titration method. Fluoride was estimated using an ion-selective electrode (ISE) with a pH/ISE meter (Orion 4-Star meter). All concentrations are expressed in milligrams per liter (mg/l), except pH and EC. The results were evaluated in accordance with the drinking water quality standards given by the World Health Organization (WHO 2004).

Table 2 Descriptive statistics of the groundwater samples in Tuticorin corporation area

Water quality parameters	Units	Minimum concentration	Maximum concentration	Average	SD
pH	–	7.1	10.2	7.6	7.8
EC	µS/cm	350	19,100	4,887.778	4,332.83
TDS	mg/l	530	10,200	3,016.111	2426.35
Na	mg/l	27	1,400	408.777	430.13
K	mg/l	5	400	63.41667	80.11
Ca	mg/l	11	570	139.6667	111.03
Mg	mg/l	15	442	118.0833	109.41
HCO3	mg/l	0	756	293.25	153.23
CO3	mg/l	0	168	46	34.12
Cl	mg/l	36	5,885	899.4167	1175.19
SO4	mg/l	19	1,272	354.7222	344.26
PO4	mg/l	0.1	0.1	0.1	0.1
NO3	mg/l	0	14	5.658333	5.30
F	mg/l	0.16	4.8	0.76	0.83
TH	mg/l	138.18	2,642.46	835.07	662.47
SAR	–	0.99	20.03	5.74	4.99

GIS analysis

The base map of Tuticorin coastal area was digitized from survey of India toposheet no 58L/1&2 and 58L/5 using ArcGIS 9.2 software. The precise locations of sampling points were determined in the field GARMIN 12 Channel GPS and the exact longitudes and latitudes of sampling points and imported in GIS platform. The spatial distribution for groundwater quality parameters such as hardness, pH, TDS, HCO_3, SO_4, NO_3, Ca, Mg, Cl and F were done with the help of spatial analyst modules in ArcGIS 9.2 software.

Result and discussion

Hydrochemistry

Understanding the groundwater quality is important as it is the main factor determining its suitability for drinking, agricultural and industrial purposes (Subramani et al. 2005). Table 2 summarizes results of the various physical and chemical parameters including statistical measures such as minimum, maximum, average and standard deviation analyzed groundwater samples from the study area. Results of the descriptive statistics of physical and chemical parameters for the groundwater samples result were compared with the standard guideline values recommended by the World Health Organization. The classifications are desirable, maximum permissible and the values exceed maximum permissible limit are termed as not permissible. The cation concentration indicate that 83, 39 and 22 % of the K^+, Na^+, Ca^{2+} concentrations exceed the WHO limit. Nitrate (NO_3) concentration of all the water samples within the study area is within the desirable limit (Table 3).

pH is the measure of the acidity or alkalinity of a solution. A pH of 7 is neutral; lower numbers indicate acidity, and higher numbers indicate alkalinity. During the present investigation, pH values ranges from 7.1 to 10.2 with an average value 7.7. The pH value as low as 7.1 was recorded in Meelavitan and the highest was found in Jothi nagar near Sankarapari with a value of 10.2. This shows that the groundwater of the study area is dominantly of alkaline in nature (Fig. 3).

Total dissolved solids

The distribution of TDS values clearly shows that the entire study area ranges from 530 to 10,200 mg/l, with an average value is 3,016 mg/l. To ascertain the suitability of groundwater of any purposes, it is essential to classify the groundwater depending upon their hydrochemical properties based on their TDS values (Davis and DeWiest 1966; Freeze and Cherrey 1979), which are represented in Tables 4 and 5 respectively. In the study area, 19 % of the groundwater samples are freshwater and rest of the sample represents brackish water type based on the report by Freeze and Cherrey (1979). According to WHO standards, 64 % of the samples has exceeds the permissible limits and only 36 % of the samples are within the permissible limit. Higher value of TDS can be attributed to the contribution of salts from the subsurface lithology and further due to higher residence time of groundwater in contact with the aquifer body. Most of the samples exceed the 1,500 ppm

Table 3 Groundwater samples of study area exceeding the permissible limits prescribed by WHO 2004 for domestic purposes

Water quality parameters	Units	WHO (2004)		Number of samples exceeding allowable limits	Percentage of samples exceeding allowable limits	Undesirable effects
		Most desirable limits	Maximum allowable limits			
pH	–	6.5	8.5	02	5.56	Taste
EC	μS/cm	780	3125	16	36.48	
TDS	mg/l	500	1500	23	63.94	Gastrointestinal irritation
Na	mg/l	–	200	14	38.92	
K	mg/l	–	10	30	83.31	Bitter taste
Ca	mg/l	75	200	8	22.24	Scale formation
Mg	mg/l	30	150	11	30.58	
HCO_3	mg/l	–	300	12	33.36	
Cl	mg/l	200	600	13	36.14	Salty taste
SO_4	mg/l	200	400	11	30.58	Laxative effective
NO_3	mg/l	45	–	Nil	0	Blue baby
F	mg/l	–	1.50	03	8.4	Flurosis

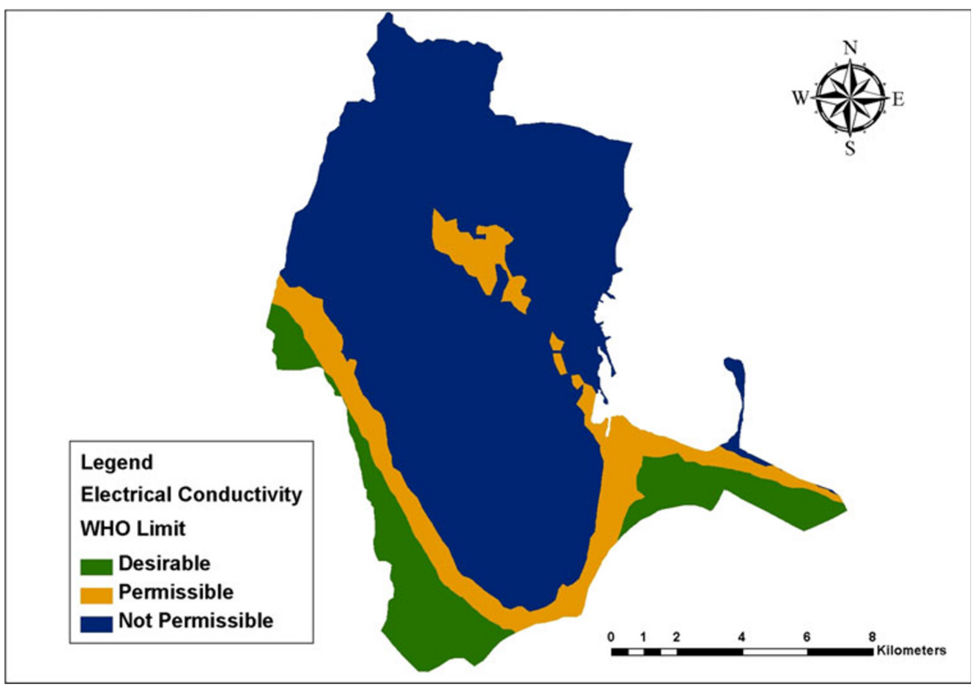


Fig. 3 Spatial distribution of EC

indicates may be attributed to infiltration from the sewage canals unprotected drainages and industrial wastes. The groundwater samples collected from Mappilaiurani, Kalangarai and Thirdmile are within the desirable limit and suitable for drinking purpose without any risk.

Electrical conductivity

Electrical conductivity (EC) is measure of salt content of water in the form of ions. The EC value is measured in micro-semens per centimeter and is a measure of salt content of water in the form of ions. The EC values ranges from 350 to 19,100 μs/cm with an average value 4,887 μs/cm. Electrical conductivity of groundwater within Tuticorin Corporation is given in Table 6. It is found that 16 % of the samples are within the desirable limit and 39 % of the samples have crossed the permissible limit, but saline waters in 44.3 % of the sample location were dominant in the area according to the WHO standard 2004. Higher EC value may be the indication of seawater intrusion. These

Table 4 Groundwater classification of all groundwater (TDS- Davis and Dewiest 1966)

Total Dissolved Solids (mg/l)	Classification	Sample numbers	Number of sample	Percentage of samples
<500	Desirable for drinking	24	1	2.78
500–1,000	Permissible for drinking	4, 6, 7, 17,23,36	6	16.66
1,000–3,000	Useful for irrigation	1, 2, 3, 5, 9, 11, 12, 14, 15, 16, 19, 20, 21, 28, 29, 31, 33	17	47.23
>3,000	Unfit for drinking and irrigation	8, 10, 13, 18, 22, 25, 26, 27, 30, 32, 34, 35	12	33.33
Total		36	36	100

Table 5 Groundwater classification of all groundwater (TDS-Freeze and Cherrey 1979)

Total dissolved solids (mg/l)	Classification	Sample numbers	Number of sample	Percentage of samples
<1,000	Fresh water type	4, 6, 7, 17,23, 24, 36	7	19.42
1,000–10,000	Brackish water type	1, 2, 3, 5, 8, 9, 10, 11, 12, 13, 14, 15, 16, 19, 18, 20, 21, 22, 25, 27, 28, 29, 30, 31, 32, 33, 34, 35	28	77.80
10,000–100,000	Saline water type	26	1	2.77
>100,000	Brine water type	Nil	Nil	Nil
Total		36	36	100

Table 6 Groundwater classification based on electrical conductivity

Electrical conductivity (mg/l)	Classification	Sample numbers	Number of sample	Percentage of samples
<1,500	Permissible	4, 7, 17, 23, 24, 36	6	16.67
1,500–3,000	Not permissible	1, 2, 6, 9, 11, 12, 14, 15, 16, 19, 21, 28, 29, 33	14	38.99
>3,000	Hazardous	3, 5, 8, 10, 13, 18, 20, 22, 25, 26, 27, 30, 31, 32, 34, 35	16	44.44
Total		36	36	100

groundwater samples had been classified in a more systematic manner using dominating cations and anions. The spatial distribution of EC within the study area has been given the Fig. 3.

Total hardness

Total hardness (TH) ranges from 138.18 to 2,642.46 mg/l with an average value of 835.07 mg/l. According to WHO standards, the maximum allowable limit of TH for drinking is 600 mg/l and the most desirable limit is 300 mg/l. The classification of groundwater based on TH shows that a majority of the groundwater sample of the study area fall in the very hard water category (Fig. 4). The TH in mg/l is determined by the following equation (Todd and David 1959).

$$\text{TH mg/l} = 2.497\,\text{Ca}^{2+} + 4.115\,\text{Mg}^{2+} \quad (1)$$

Total hardness of the groundwater samples were calculated and classified according to Sawyer and McCarthy (1967), and the calculated values are given in the Table 8. Among the 36 groundwater sample, 5.5 % of the samples are under moderately hard, 11 % samples are fall under hard and 83 % sample fall under very hard class in the study area (Table 7). This reveals that the study area experiences very hard water and high hardness level is noticed. According the WHO standards, 16 groundwater sample out of 36 collected exceeds the maximum allowable limit (600 mg/l). High levels of hardness may effected water supply system, excessive soap consumption, calcification of arteries and cause urinary concretions, diseases of kidney of bladder and stomach disorder (CPCB 2008).

Sulphate

Sulphate (SO_4) concentration varies from 19 to 1,272 mg/l with an average value of 354.72 mg/l. The concentration of sulphate is likely to react with human organs if the value exceeds the maximum allowable limit of 400 mg/l will

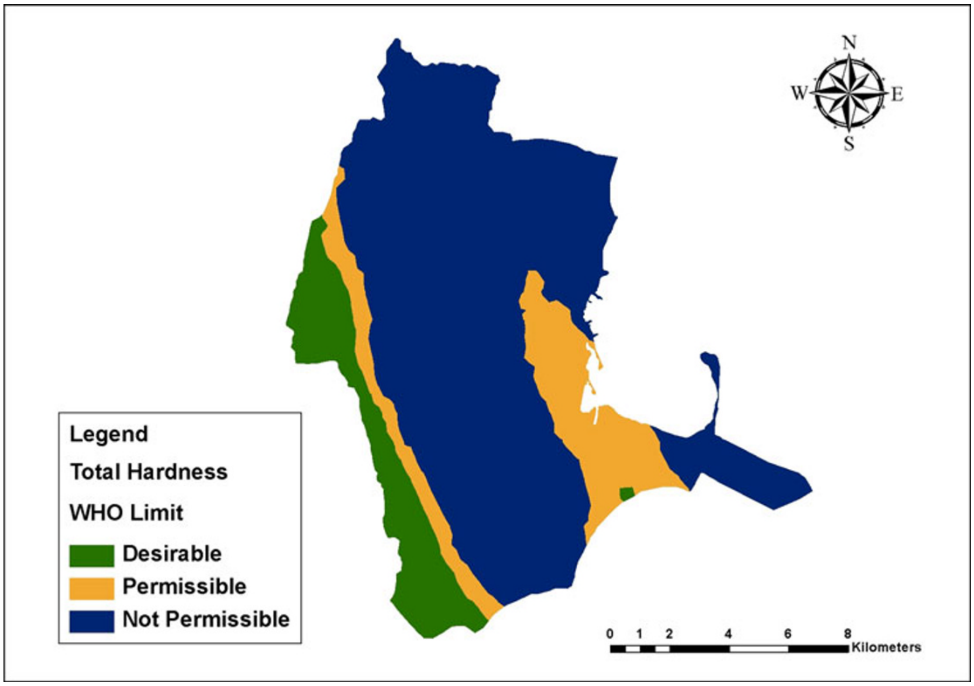


Fig. 4 Spatial distribution of TH

Table 7 Groundwater classification based on hardness (Sawyer and McCarthy 1967)

Total Hardness as $CaCO_3$ (mg/l)	Classification	Sample numbers	Number of sample	Percentage of samples
<75	Soft	–	–	
75–150	Moderately high	20, 24	2	05.55
150–300	Hard	17, 19, 21, 36	4	11.10
>300	Very hard	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 22, 23, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35	30	83.35
Total		36	36	100

cause a laxative effect on human system with the excess magnesium in groundwater. The sulphate of groundwater of the study area is given Table 2 and it is found that 30.58 % of the samples exceed permissible limits. Most of the samples (53.6 %) fall in the desirable limit in the study area. The spatial distribution map of sulphate ion concentration in groundwater is presented in Fig. 5.

Chloride

The chloride (Cl) concentration varies from 36 to 5,885 mg/l with an average value of 899.41 mg/l. The maximum allowable limit of Cl is 600 mg/l. The Cl of groundwater in study area is found that 36.14 % samples exceed permissible limit and 60.4 % sample fall in the maximum allowable limit. Thus, high levels of Na and Cl ions in coastal groundwater may indicate a significant effect of seawater mixing (Mondal et al. 2010). High concentration of Cl may be injurious to some people suffering from diseases of the heart and kidneys, taste, indigestion, corrosion and palatability are effected (CPCB 2008). The spatial distribution map of chlorite ion concentration in groundwater of the study area is shown in Fig. 6.

Nitrate

The nitrate (NO_3) concentration varies from 0 to 14 mg/l with an average value of 5.65 mg/l. The NO_3 ions concentrations of all the groundwater samples are within the desirable limit of 45 mg/l as per WHO 2004 standard. The concentration of nitrogen derived from the biosphere (Saleh et al. 1999). Nitrogen is originally fixed from the atmosphere and then mineralized by soil bacteria into ammonium. The high concentration of NO_3 in drinking water is toxic and cause blue baby disease/methemoglobinemia in children and also gastric cancer and adversely effects [NS and cardiovascular system (CPCB 2008)].

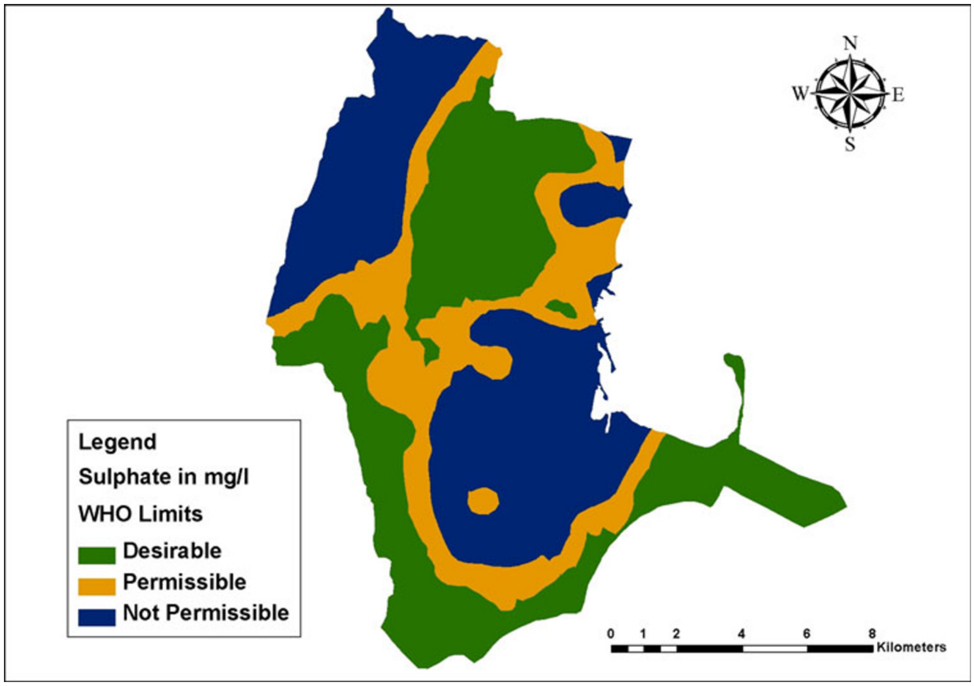


Fig. 5 Spatial distribution of SO_4

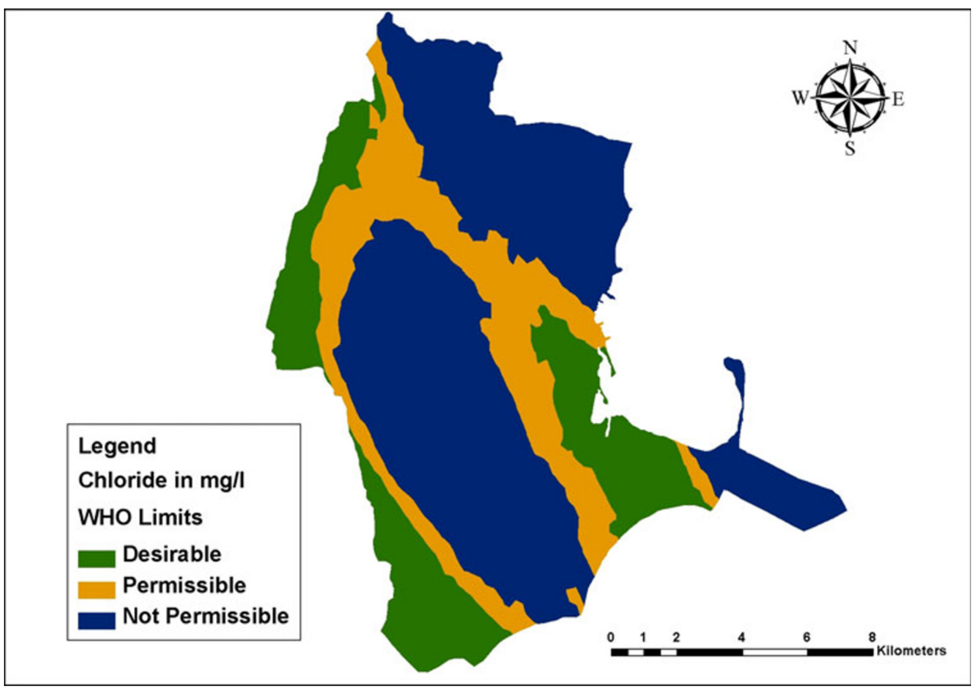


Fig. 6 Spatial distribution of Cl

Calcium

The calcium (Ca) ion concentration varies from 11 to 570 mg/l with an average value 139.6 mg/l. The maximum allowable limit of calcium ion concentration in groundwater is 200 mg/l as per WHO 2004 classification. 77.56 % samples fall in the maximum allowable limit of 22.24 % sample exceed the permissible limit. The spatial distribution map of potassium ion concentration in groundwater is of the study area shown in Fig. 7.

Magnesium

The magnesium (Mg) ion concentration varies from 15 to 442 mg/l with an average value 118 mg/l. The maximum allowable limit is magnesium ion concentration in groundwater is 150 mg/l as per WHO 2004 classification. 66.48 % samples fall in the maximum allowable limit of 30.58 % samples exceed the permissible limits. The spatial distribution map of potassium ion concentration in groundwater of the study area is shown in Fig. 8.

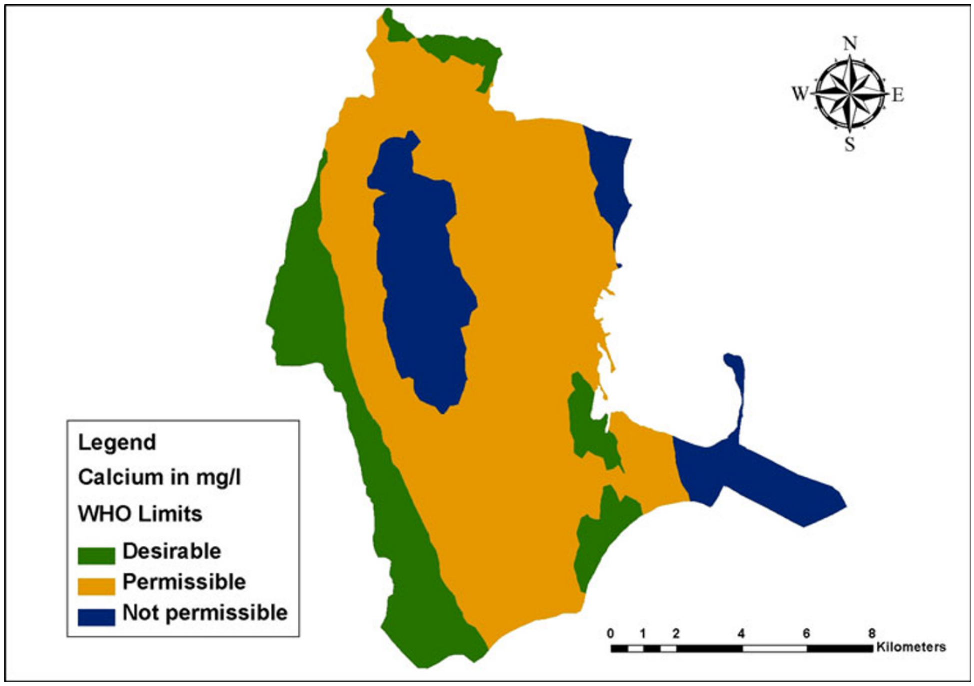


Fig. 7 Spatial distribution of Ca

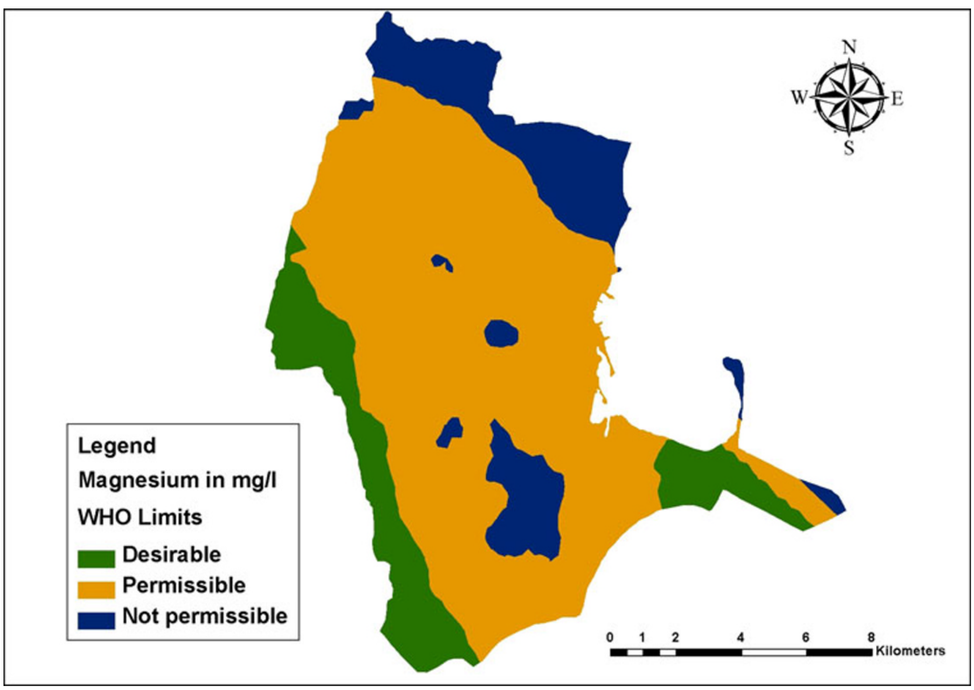


Fig. 8 Spatial distribution of Mg

Fluorite

The fluoride (F) concentration varies from 0.16 to 4.8 mg/l with an average value of 0.76 mg/l. One of the main trace elements in groundwater is fluoride, which generally occurs as a natural constituent. Bed rock containing fluoride minerals is generally responsible for high concentration of this ion in groundwater (Handa 1975).The fluoride concentration in groundwater of the study area is found that 91.6 % samples are within the maximum allowable limit (1.5 mg/l) and 8.4 % sample are exceed the permissible limit. The high fluoride content in groundwater leads to dental and skeletal fluorosis such as mottling of teeth and deformation of ligaments (CPCB 2008). The spatial distribution map of chlorite ion concentration in groundwater of the study area is shown in Fig. 9.

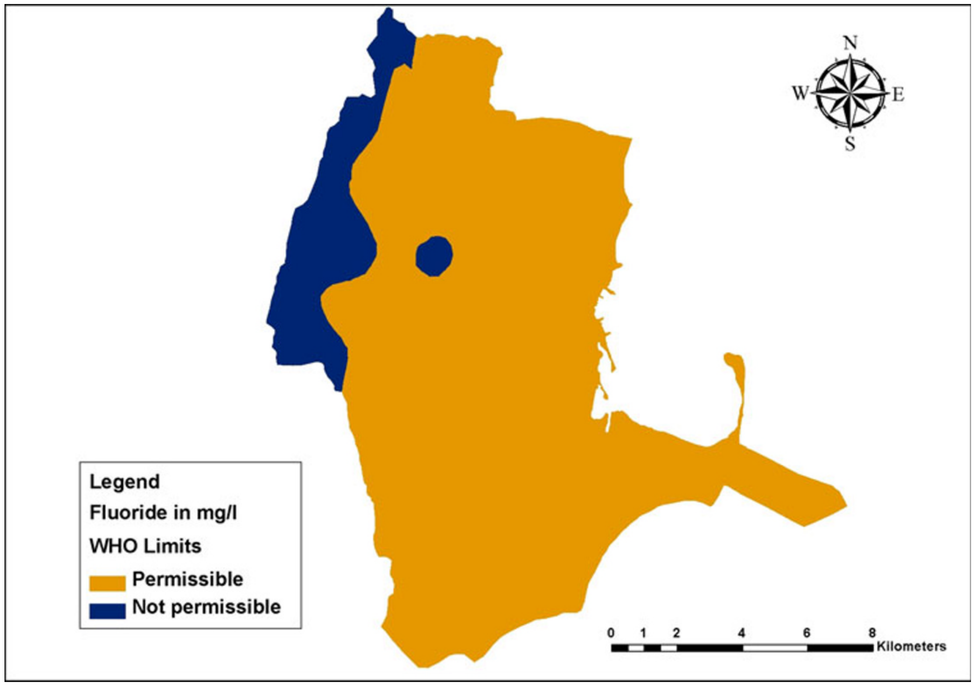


Fig. 9 Spatial distribution of F

Hydro-chemical facies

The piper diagram is extensively used to be understood by plotting the concentrations of major cations and anions in the Piper trilinear diagram (Piper 1994). On the basis of chemical analysis groundwater is divided into three distinct fields—two triangular fields and one diamond-shaped field. The percentage equivalents per mole values are used for plot. The Aquachem software is used for the plotting of Piper trilinear diagrams (scientific software group Utah, 1998). The overall characteristics of the water is represented in the diamond-shaped fields like namely Ca^{2+}-Mg^{2+}–Cl^{-}-$SO_4{}^{2-}$, Na^{+}-K^{+}–Cl^{-}-SO_4^{2-}, Na^{+}-K^{+}–Cl^{-}-$HCO_3{}^{-}$ and Ca^{2+}-Mg^{2+}-$HCO_3{}^{-}$ by projecting the position on the plots in the triangular field. In the study area majority of samples belong to Ca^{2+}-Mg^{2+}–Cl^{-}-SO_4^{2} and Na^{+}-K^{+}–Cl^{-}-$SO_4{}^{2-}$ type (Fig. 10). From the plot, it is observed that an alkali (Na^{+} and K+) exceeds the alkaline earths (Ca^{2+} and Mg^{2+}) and strong acids exceeds weak acids. The hydrochemical facies of groundwater is summarized in Table 8.

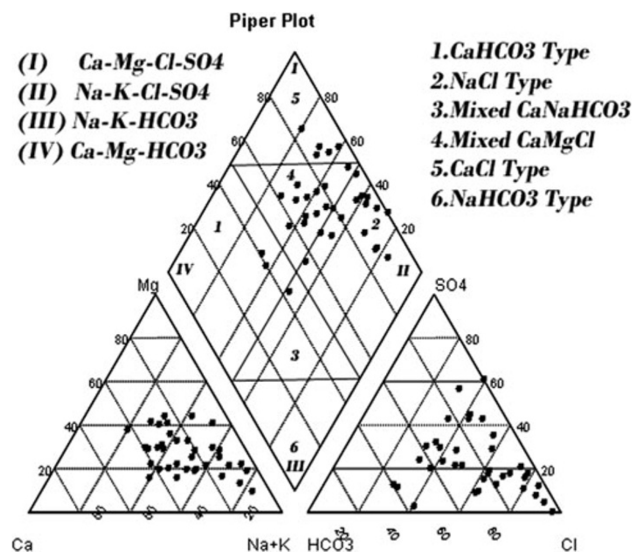


Fig. 10 Piper diagram depicting hydrochemical facies of groundwater

Classification of groundwater for irrigation water quality

Excessive amount of dissolved ion such as sodium, bicarbonate and carbonate in irrigation water affect plants and soil texture and reducing the productivity of agriculture. The physical effects of these ions are to lower the osmotic pressure in the plant structural cells, thus preventing water from reaching the branches and leaves. The chemical effects disrupt plant metabolism.

Sodium adsorption ratio

The relative activity of sodium ion in the exchange reaction with soil is expressed in terms of a ratio known as sodium adsorption ratio (SAR). It is an important parameter for determining the suitability of irrigation water, because it is a measure of alkali/sodium hazard for crops. SAR can be estimated by the formula:

Table 8 Hydrochemical facies of groundwater analytical data

Facies	Sample numbers	Number of samples	Percentage of samples
Ca^{2+} - Mg^{2+} – Cl^- - SO_4^{2-}	1, 2, 4, 5, 6, 9, 11, 14, 15, 17, 18, 23, 26, 31, 32, 33, 35, 36	18	49.99
Na^+ - K^+ – Cl^- - SO_4^{2-}	3, 8, 10, 12, 13, 19, 20, 21, 22, 25, 27, 28, 29, 30, 34	15	41.67
Na^+ - K^+ – Cl^- - HCO_3^-	16	01	2.78
Ca^{2+} - Mg^{2+}- HCO_3^-	7,24	02	5.56
Total	36	36	100

$$SAR = \frac{Na^+}{\sqrt{\frac{(Ca^{2+}+Mg^{2+})}{2}}} \quad (2)$$

There is a significant relationship between sodium adsorption ratio of irrigation water and the extent to which sodium is absorbed by the soils. If water used for irrigation is high in sodium and low in calcium content, then exchangeable calcium in soil may replace sodium by base exchange reaction in water. This can destroy the soil structure owing to dispersion of the clay particles. The SAR values in the study area range from 0.99 to 20.03 with an average of 5.74 (Table 2). None of the water samples exceeds the SAR value of 12. So the groundwaters within the study area are suitable for irrigation purpose (Table 9). Based on the Herman Bower classification (1978), all groundwater samples fall under no problem category of irrigation water quality (SAR < 6). If the SAR value ranges from 6 to 9, the irrigation water will cause permeability problems in shrinking and swelling types of clayey soils (Saleh et al. 1999).

The analytical data plotted on the US Salinity Laboratory Diagram (Richards 1954) illustrates that most of the groundwater samples (52.63 % samples) fall in the field of C3S1 and C4S1 (high to very high salinity with low sodium) waters, indicating very high salinity and low sodium water type, which can be used for irrigation on almost all types of soil with little danger of exchangeable sodium (Fig. 11). Among the water samples collected, 5.56 % of the groundwater fall in the field of C4S2 indicating very high salinity and medium sodium hazard. This can be suitable for plants having good salt tolerance, and restricts their suitability for irrigation, especially in soils with restricted drainage (Karanth 1989; Mohan et al. 2000). 2.78 % of the sample fall in the field of C2S1 indicating medium salinity and low sodium, C3S2, indicating high salinity and medium sodium, and C4S3 falls indicating very high salinity and high sodium hazard in the classification.

Percent sodium

Sodium concentration is important in classifying irrigation water, because sodium reacts with soil to reduce its permeability. Excess sodium in waters produces undesirable effects of changing soil properties and reducing soil permeability (Kelly 1951). Hence, the assessment of sodium concentration is of utmost importance while considering the suitability of irrigation water. In all natural waters percent of sodium content is a parameter to evaluate its suitability for agricultural purposes sodium combining with carbonate can lead to the formation of alkaline soils, whereas sodium combining with chloride form saline soils (Wilcox 1955). Both these soils do not help for the growth of plants. The sodium percentage (Na %) is calculated using the formula given below

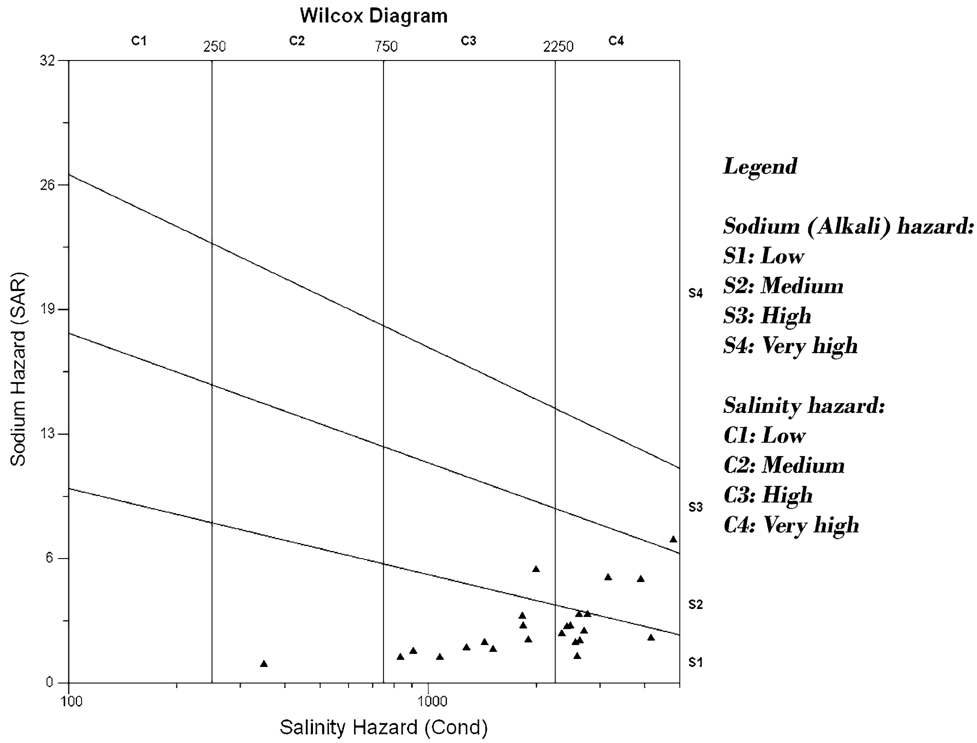
$$Na^+\% = \frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100 \quad (3)$$

When the concentration of sodium is high in irrigation water, sodium ions tend to be absorbed by clay particles,

Table 9 Salinity and alkalinity hazard of irrigation water in US salinity diagram

Classification	SAR/EC	Sample numbers	Number of sample	Percentage of samples
C5-S4	SAR very high EC very high	–	–	–
C5-S2	SAR medium EC very high	–	–	–
C4-S1	SAR low EC high	1, 2, 5, 9, 11, 15, 16, 28, 29, 33	10	28.7
C4-S2	SAR medium EC high	13, 31	2	5.56
C4-S3	SAR low EC low-medium	20	1	2.78
C3-S1	SAR low EC medium–high	4, 6, 7, 12, 14, 17, 19, 23, 36	9	25.02
C3-S2	SAR medium EC medium -high	21	1	2.78
C2-S1	SAR low EC moderate	24	1	2.78

Fig. 11 US Salinity Laboratory diagram for classification of irrigation waters



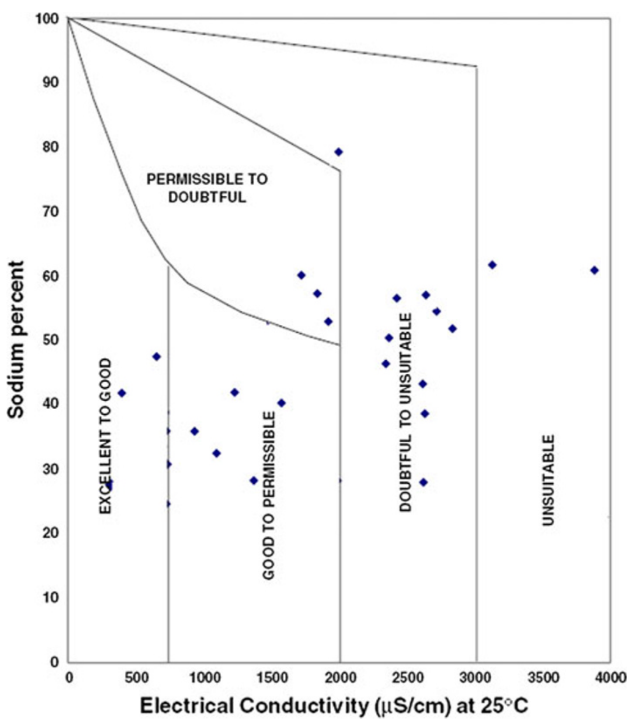


Fig. 12 Percent sodium and electrical conductivity plot (Wilcox 1955)

displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^{+} in water for Ca^{2+} and Mg^{2+} in soil reduces the permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation are restricted during wet conditions, and such soils become usually hard when dry (Saleh et al. 1999).

The classification of groundwater samples with respect to percent sodium (Fig. 12) is shown in Table 10. The groundwater for irrigation purposes by correlating percent sodium (i.e., sodium in irrigation waters) and electrical conductivity. A perusal of Wilcox's 1955 diagram shows that out of 36 samples, 20 (55.24 %) belong to the good to permissible; 3 (8.34 %), excellent to good; 16 (44.48 %), doubtful to unsuitable; and 4 (11.12 %), unsuitable categories.

Permeability index

The PI values also indicate suitability of groundwater for irrigation, as the soil permeability is affected by long-term use of irrigation water, influenced by the Na^{+}, Ca^{2+}, Mg^{2+} and HCO_3^{-} contents of the soil. The permeability index (PI), as developed by Doneen (1964) indicates the suitability of groundwater for irrigation. It is defined as follows:

$$\mathrm{PI} = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+} + Na^{+}} \times 100. \quad (4)$$

Where the concentrations are reported in milli equivalents per liter

According to permeability indices the groundwaters may be divided into Class I, Class II and Class III types. Class I and Class II water types are suitable for irrigation with 75 % or more of maximum permeability, and Class III types of water with 25 % maximum permeability. The

Table 10 Irrigation quality of groundwater based on sodium percentage

%Na	Classification	Sample numbers	Number of sample	Percentage of samples
<20	Excellent	–	–	–
20–40	Good	4, 33, 36	3	8.33
40–60	Permissible	1, 2, 5, 6, 7, 9, 11, 14, 15, 17, 18, 23, 24, 28, 29, 32, 35	17	47.24
60–80	Doubtful	3, 8, 10, 12, 16, 19, 22, 25, 26, 27, 30, 31	12	33.34
>80	Unsuitable	13, 20, 21, 34	4	11.09
Total		36	36	100

permeability index of the Tuticorin area ranges from 15.88 to 103.68 % with an average value of 51.15 %. Accordingly, all the 36 samples are categorized under classes 1 and 2 of Doneen's chart (Domenico and Schwartz 1990). World Health Organization uses a criterion for assessing the suitability of water for irrigation based on the permeability index. According to the permeability index values, 95.76 % of the samples fall under class 2 (PI ranged from 25 to 75 %) and 2.12 % belong to class 1 (PI > 7.5 %) in the pre-monsoon in 2011.

Conclusion

The present study has been carried out to evaluate hydrochemical characteristics of groundwaters of the coastal aquifers in Tuticorin, Tamilnadu. GIS has been applied to visualize the spatial distribution of groundwater quality in the study area. A total of 36 groundwater samples were collected and analyzed for various physico-chemical parameters. Very wide ranges and high standard deviations of hydrochemical parameters such as TDS, EC, Cl^-, K, SO_4, Mg suggest the groundwater in the coastal aquifers shows seawater mixing and anthropogenic contamination. Most of the water sample exceeds the maximum permissible limit of WHO standards. The abundance of the major cations and anions are in the following order, $Na^+ > Ca^{2+} > Mg^{2+} > K^+ = Cl^- > HCO_3^- > SO_4^{2-} > CO_3 > NO_3 > PO_4$. Results suggest that the groundwater in this study area is very hard and alkaline in nature. As represented by Piper trilinear diagram, Ca^{2+}-Mg^{2+}–Cl^--SO_4^{2-} facies are the dominant hydrochemical facies in the groundwater of Tuticorin Corporation. From the plot it is observed that an alkali (Na^+ and K^+) exceeds the alkaline earths (Ca^{2+} and Mg^{2+}) and strong acids exceeds weak acids. Regarding the TDS, 64 % of the groundwater sample of the study area exceeded the permissible limit. About 84 % of the groundwater sample of the study area exceeded the recommended limit of EC as per the WHO standard. The EC and TDS hydrochemical data clearly shows the consequences of seawater intrusion. The concentration of TH in two-third of the groundwater samples of the study area exceeded the permissible limit as per WHO 2004 standard. This revels that the study area experiences very hard water and high hardness level is noticed. Estimation of sulphate concentration shows 30 % of the groundwater samples exceed the permissible limit. 20 % Chloride ion concentration of the study area is beyond the maximum allowable limit for drinking purpose. The fluoride concentration of the maximum water sample are within the permissible.

Based on the USSL diagram, 52 % of the total sample of the present study area falls under the category of high to very high salinity with low sodium hazards. To overcome this problem we need to plan for better drainage. Based on SAR values 52 % of the groundwater samples are good for irrigation in almost all type of soil with little danger of exchangeable sodium. From the Wilcox Plot, it is observed that most of the samples fall in the permissible–doubtful classes for irrigation purpose. However, permeability index (PI) values indicate that almost all the groundwater sample fall under the class II and suitable for irrigation. It can also be drawn that Cl concentrations is the major factor that makes up the TDS in the groundwater, and plays an important role in the determination of the quality of groundwater in Tuticorin corporation. Finally, it is concluded that most of the groundwater sample collected within the study area are not suitable for dirking purpose. But it can be used for irrigation and industrial purposes.

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