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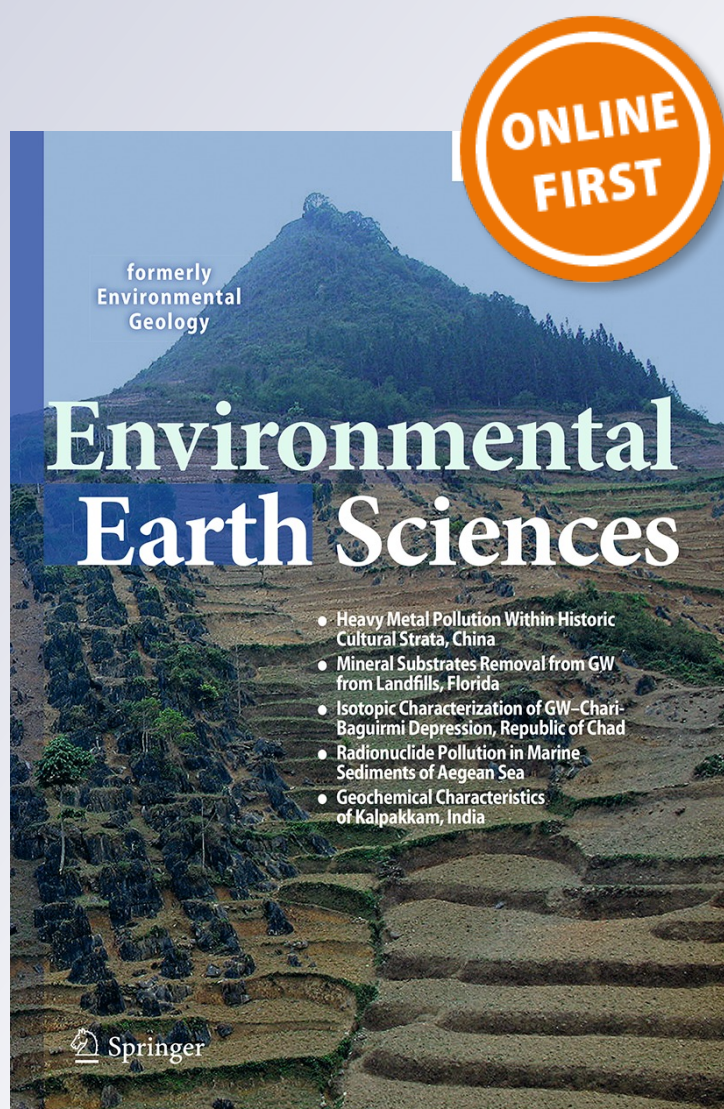
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Assessment of groundwater quality in and around Vedaraniyam, South India

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Abstract Groundwater from 47 wells were analyzed on the basis of hydrochemical parameters like pH, electric conductivity, total dissolved solids, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , CO_3^{2-} , HCO_3^- , NO_3^- , PO_4^{3-} and F^- in the Cauvery delta of Vedaraniyam coast. Further, water quality index (WQI), sodium percentage (Na %), sodium absorption ratio, residual sodium carbonate, permeability index and Kelley's ratio were evaluated to understand the suitability of water for drinking and irrigation purposes. The result shows significant difference in the quality of water along the coastal stretch. The order of dominance of major ions is as follows: $\text{Na}^+ \geq \text{Mg}^{2+} \geq \text{Ca}^{2+} \geq \text{K}^+$ and $\text{Cl}^- \geq \text{HCO}_3^- \geq \text{CO}_3^{2-} \geq \text{PO}_4^{3-} \geq \text{F}^-$. Na/Cl, Cl/ HCO_3^- ratio and Revelle index confirmed that 60–70 % of the samples were affected by saline water intrusion. WQI showed that 36 % of the samples were good for drinking and the remaining were poor and unsuitable for drinking purpose. The degradation of groundwater quality was found to be mainly due to over-exploitation, brackish aquaculture practice, fertilizer input from agriculture and also due to domestic sewage.

Keywords Groundwater · Land use · Hydrochemistry · Coastal · Spatial analysis · South India

Introduction

Basically, groundwater is an integral part of the environment, and hence it is a major life-sustaining resource for all living beings. In India, as also in certain parts of the world, water crisis is becoming a regular phenomenon, perhaps due to improper scientific management of water resources leading to continued environmental degradation. In the last few decades, there has been a tremendous increase in the demand for freshwater resource due to rapid population growth and industrialization (Ramakrishnaiah et al. 2009). It is estimated that approximately one-third of the world population depends on groundwater for drinking (Nickson et al. 2005). At the same time, geographical location and land use pattern have a significant influence on the quality and quantity of groundwater. Since it plays an important role in determining the various hydrological phenomena such as infiltration rate, overland flow, evaporation and interception, a number of researchers (Gilliom et al. 1995; Fianko et al. 2009; Kim 2010; Jiang and Yan 2010) have determined the link between land use and groundwater quality. There are various ways by which groundwater may be contaminated, such as from discharge of treated and untreated sewage, aquaculture, salt pans, solid waste and industrial activity (Vengosh and Keren 1996; Kumar et al. 2010). Further, overextraction of groundwater in the coastal areas is a reason for the seawater migrating inland into the coastal aquifer. The quality of groundwater deteriorates as the salt concentration increases (Giménez-Forcada et al. 2010). Therefore, understanding the groundwater quality is important to determine its suitability

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for drinking, agricultural and industrial use (Subramani et al. 2005; Chidambaram et al. 2011). Measures to prevent and control groundwater pollution at the source and along pathways need to be advocated. Multivariate statistical technique provides significant information on critical aspects of water quality and indicates the need to secure water quality and also promote microlevel planning and management in a particular area (Das et al. 2010; Belkhiri et al. 2010; Chapagain et al. 2010). Few studies were attempted to evaluate the groundwater chemistry in Vedaraniyam region (Mary et al. 2012; Ramkumar et al. 2010). A systematic study is required to evaluate the water quality and to determine the factors affecting the water chemistry of the region. Hence, an attempt has been made to assess the same and evaluate the hidden hydro-geochemical process.

Study area

Vedaraniyam is located in Nagapattinam District and lies between 10°15' and 11°30'N latitude and 79°30' and 79°55'E longitude. It has medium tropical transition climate, characterized by monthly average temperature of above 27 °C. The major activities are agriculture, salt pan, fishing and aquaculture, which engage almost 75 % of the workforce of the study area. The major rivers are Mulliyar, Koraiyar and Valvanar which pass through the long agricultural belt before draining into the Vedaraniyam wetlands (Fig. 1). The study area occupies an area of about 1,066 km² which includes the great Vedaraniyam wetland swamp (Muthupet mangrove and Seruthalaikadu creek) and dry evergreen Kodiyakarai reserved forest, which falls under the Ramsar convention site. Numerous small-scale aquaculture farms have been established along the Cauvery River tributaries and adjacent to the Vedaraniyam canal during the 1990s (Ravichandran 2005). A number of domestic and industrial salt works operate around the Vedaraniyam wetlands.

Land use/land cover

The Vedaraniyam coast consists of the following land use categories such as settlement, agriculture land, mangroves, river, land with and without scrub, plantation, scrub forest, salt-affected land, waterlogged area, marshy/swampy land, creek, mud/tidal flat, aquaculture and salt pan (Fig. 2). The study on the P6 LISS III satellite image of 2007 shows that the dominant land use category was agricultural land, occupying 319.64 km², followed by plantation (172.30 km²) and settlement (63.96 km²). Further, aquaculture and salt pan cover an area of 17.58 sq. km and

44.75 km², respectively, which also contribute to the increase of salt-affected land (33.2 km²).

Materials and methods

Groundwater samples were collected randomly from bore wells from 47 locations of the study area during February 2009 (Fig. 1; Table 1). Before taking a sample, water was pumped for 10–15 min to ensure complete homogeneity. Then the extracted water samples were collected in pre-cleaned polythene bottle and analyzed for various water quality parameters as per standard procedure. pH, EC and TDS were measured in the field itself using water analysis kit (Deep Vision -191). Na⁺ and K⁺ were analyzed using flame photometer (Systronic 128). Ca²⁺, Mg²⁺, Cl⁻ and HCO₃⁻ were determined by volumetric titration method. Nitrate, phosphate and fluoride were determined using a spectrophotometer (Shimadzu UV-1800). The charge balance of the analyzed cations and anions are well within ±10 %. Descriptive statistics were carried out using the SPSS package (Khan 2011). Spatial distributions of geochemical parameters were prepared on Arc-GIS software by interpolation method called inverse distanced weighted (IDW) method (Lee et al. 2006).

Result

The minimum, maximum, mean and standard deviation of physicochemical parameters of groundwater quality such as pH, EC, TDS and major elements (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, CO₃²⁻, HCO₃⁻, NO₃⁻, PO₄³⁻ and F⁻) are presented in Tables 1 and 2. Among this, pH is a very important indicator of its quality and controlled by the amount of dissolved CO₂, carbonate and bicarbonate in groundwater (Ghandour et al. 1985). In the studied samples, the pH value ranged from 7.3 to 8.2 indicating that the groundwater was of alkaline nature due to bicarbonate form of dissolved carbonate (Nagarajan et al. 2010). Generally, carbonate concentrations are low in groundwater at near neutral pH, and at pH values above 8, carbonate exists in groundwater. However in the present study, carbonate was present in some sample locations even with high pH value due to the presence of carbonate rocks (Rizk et al. 1988; Ramkumar et al. 2010). The EC value of groundwater varies from 530 to 6,300 µS/cm with a mean value of 1,500 µS/cm. A higher EC value is noticed in the eastern part of the study area. The TDS value ranged from 340 to 4,120 mg/L and the highest TDS was found in sample 27. According to Davis and DeWiest (1966), TDS is classified into four different categories based on drinking and irrigation suitability (Fig. 3). Table 3 shows that

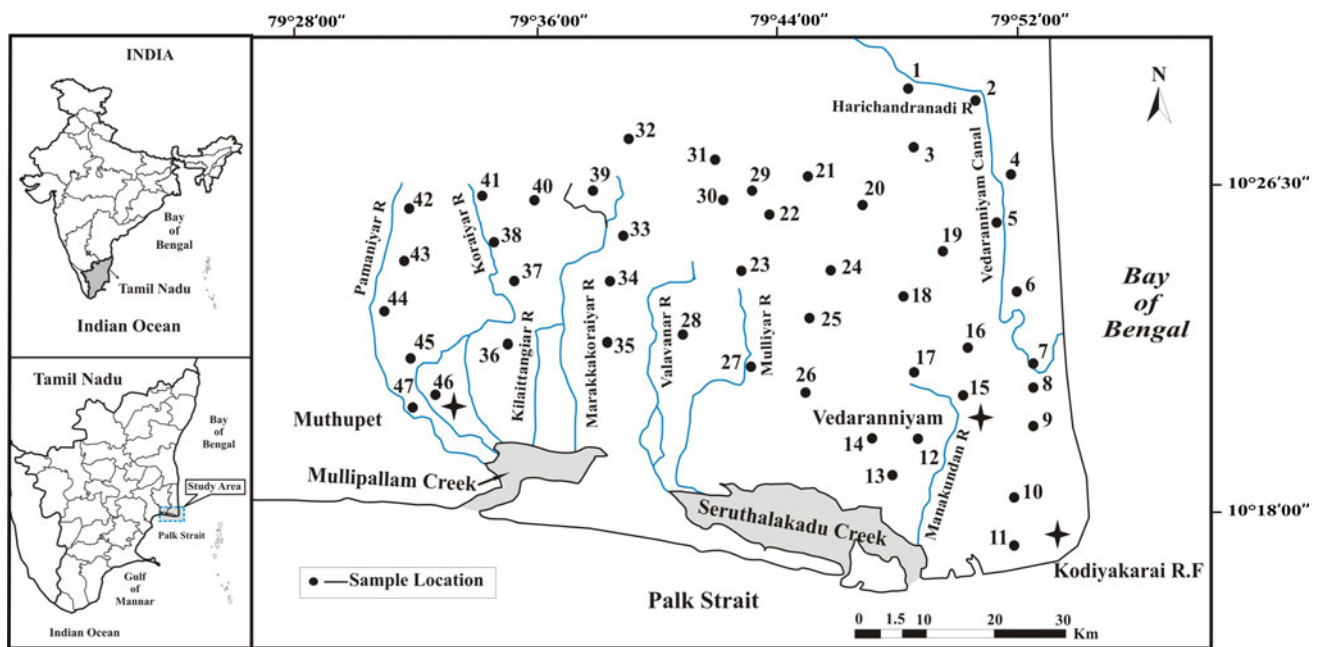


Fig. 1 Study area and sample location map. The numbers in the map indicate different sample locations

Fig. 2 Land use/land cover of the study area (LISS-III-2007)

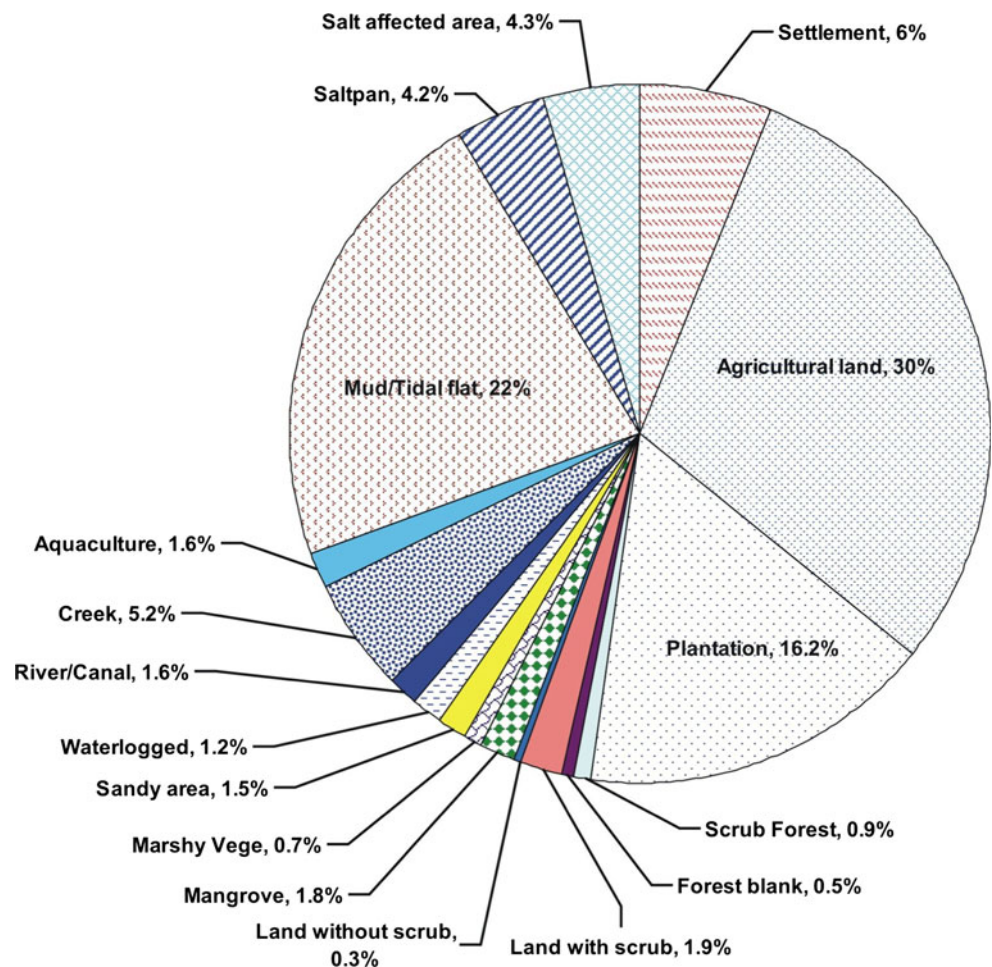


Table 1 Chemical composition of groundwater samples collected from the study area

Sample number	pH	EC ($\mu\text{S/cm}$)	TDS (mg/L)	Na ²⁺ (mg/L)	K ⁺ (mg/L)	Ca ⁺ (mg/L)	Mg ²⁺ (mg/L)	NO ₃ ⁻ (mg/L)	PO ₄ ⁻³ (mg/L)	CO ₃ ⁻² (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	F ⁻ (mg/L)	Error (%)
1	7.54	2,870.00	1,880.00	312.80	1.60	72.00	113.70	1.50	2.40	24.00	219.60	936.00	0.50	-7.25
2	7.80	4,470.00	3,070.00	536.00	46.00	48.00	105.00	7.40	0.60	0.00	451.40	1,131.60	0.60	-5.13
3	7.64	1,840.00	1,210.00	391.00	32.00	56.00	88.50	0.40	1.30	0.00	366.00	617.00	0.50	8.83
4	7.88	970.00	640.00	179.40	5.90	44.00	35.00	0.70	0.80	0.00	307.40	229.00	0.50	6.15
5	7.63	1,700.00	1,120.00	184.00	0.60	60.00	65.60	0.10	0.40	0.00	196.40	427.00	0.50	3.76
6	7.53	980.00	640.00	65.86	0.40	64.00	52.50	3.80	0.80	0.00	213.50	199.00	0.50	6.15
7	7.48	750.00	490.00	80.20	7.80	60.00	45.00	7.60	0.40	0.00	234.00	179.00	0.40	6.96
8	7.68	1,170.00	770.00	138.00	0.60	48.00	43.00	19.50	3.10	36.00	115.90	229.00	0.50	8.61
9	7.70	3,510.00	2,310.00	199.00	0.50	60.00	111.80	0.20	7.30	0.00	231.80	694.80	0.50	-5.88
10	7.64	1,330.00	870.00	358.80	28.10	28.00	66.10	12.30	1.70	48.00	356.00	426.00	0.40	8.02
11	7.68	4,020.00	2,640.00	312.80	58.50	36.00	124.90	25.40	0.70	0.00	353.80	913.20	0.40	-8.11
12	7.25	810.00	530.00	70.15	9.90	44.00	3.90	5.40	1.30	0.00	312.00	29.80	0.50	-2.57
13	7.26	530.00	340.00	76.00	1.20	36.00	30.10	3.20	3.10	0.00	364.20	69.50	0.50	-2.97
14	7.55	3,190.00	2,100.00	17.48	0.30	108.00	101.00	1.80	0.30	0.00	244.00	456.40	0.20	-7.40
15	7.60	2,020.00	1,330.00	161.00	1.40	52.00	86.00	0.30	0.80	0.00	268.40	376.00	0.40	5.53
16	7.46	1,460.00	960.00	138.00	46.80	36.00	66.60	0.10	0.60	0.00	246.80	286.50	0.50	8.94
17	7.67	2,910.00	1,910.00	75.90	0.60	44.00	113.20	18.70	0.80	0.00	268.40	466.50	0.30	-9.25
18	7.69	4,620.00	3,160.00	659.74	0.10	32.00	93.00	27.60	0.50	0.00	36.60	1,081.90	0.50	9.04
19	7.75	3,810.00	2,500.00	531.10	19.50	64.00	52.50	1.30	0.40	24.00	250.10	843.70	0.40	4.07
20	7.72	1,770.00	1,180.00	133.40	1.60	32.00	26.20	4.20	2.10	24.00	213.50	129.00	0.40	8.56
21	7.62	1,620.00	1,070.00	147.20	1.60	28.00	57.00	0.30	0.30	0.00	256.20	248.20	0.50	5.70
22	7.62	1,010.00	660.00	61.27	1.00	36.00	29.00	0.10	2.30	54.00	115.90	89.30	0.40	4.57
23	7.52	3,560.00	2,340.00	598.00	95.20	72.00	78.30	82.60	1.20	0.00	445.30	804.00	0.30	9.56
24	7.62	1,430.00	940.00	239.20	19.90	28.00	43.40	1.80	0.20	0.00	164.70	467.00	0.40	0.02
25	7.80	3,860.00	2,530.00	184.00	49.90	64.00	140.00	0.10	2.20	0.00	250.10	704.70	0.50	0.22
26	7.75	3,950.00	2,590.00	285.20	50.70	68.00	170.60	68.20	1.20	0.00	555.10	684.90	0.50	2.20
27	7.62	6,300.00	4,120.00	487.60	78.00	96.00	236.70	40.10	17.00	0.00	207.40	1,340.00	0.50	5.75
28	7.58	970.00	640.00	896.00	101.40	40.00	75.30	13.50	0.70	0.00	329.40	1,299.00	0.50	8.13
29	7.50	1,100.00	720.00	24.15	0.20	40.00	70.50	0.10	1.40	0.00	366.00	139.00	0.50	-5.57
30	7.54	780.00	510.00	119.60	24.00	28.00	14.40	0.10	0.10	0.00	140.30	219.60	0.50	-0.60
31	8.20	2,660.00	1,740.00	404.80	11.10	32.00	45.70	0.10	0.50	12.00	329.40	526.10	0.60	5.97
32	7.80	910.00	590.00	847.00	201.20	40.00	45.00	0.10	0.70	0.00	353.80	1,201.00	0.40	9.22
33	7.53	3,200.00	2,100.00	119.60	0.60	64.00	169.10	8.90	0.50	0.00	457.50	536.00	0.40	-0.72
34	7.69	5,600.00	3,880.00	692.00	25.70	44.00	91.40	0.40	9.40	0.00	219.60	1,191.10	0.40	4.00
35	7.43	530.00	340.00	154.10	0.60	52.00	38.40	0.10	4.60	0.00	250.10	239.00	0.40	6.52
36	7.53	1,310.00	860.00	179.50	0.10	28.00	19.90	11.90	0.40	30.00	164.70	188.60	0.30	7.74
37	7.78	2,420.00	1,580.00	124.50	4.10	36.00	64.20	2.20	0.80	0.00	152.50	387.10	0.30	-3.15
38	7.95	890.00	580.00	68.93	0.50	32.00	48.10	3.30	0.60	0.00	250.10	199.00	0.80	-6.61
39	7.77	1,120.00	740.00	138.00	3.50	32.00	45.70	0.10	0.60	0.00	250.10	196.50	0.50	8.58
40	7.88	1,300.00	850.00	145.52	10.90	36.00	53.30	0.80	0.30	0.00	335.50	186.70	0.40	8.63
41	7.50	1,120.00	730.00	144.90	13.10	32.00	63.20	0.10	0.20	0.00	274.50	239.50	0.30	9.01
42	7.93	2,170.00	1,420.00	171.30	3.60	32.00	60.30	11.40	0.20	0.00	359.90	337.50	0.40	-5.10
43	8.10	2,190.00	1,440.00	368.00	0.80	24.00	47.60	0.10	0.40	30.00	475.80	415.00	0.60	1.56
44	7.50	1,630.00	1,040.00	108.10	1.80	28.00	95.30	0.10	0.20	18.00	640.50	188.60	0.40	-7.71
45	7.59	4,120.00	2,840.00	279.15	22.80	56.00	168.60	81.80	0.30	0.00	280.60	764.30	0.50	2.76
46	7.62	1,050.00	690.00	24.15	1.00	44.00	69.50	10.30	0.10	0.00	323.30	109.20	0.50	2.45
47	7.47	1,880.00	1,230.00	135.70	0.10	40.00	67.20	0.10	0.40	0.00	207.40	307.70	0.40	5.47

36.2 % of samples are within the permissible limit for drinking and 46.8 % of samples useful for irrigation purpose. However, 8.5 % of samples are unfit for drinking as well as irrigation. Freeze and Cherry (1979) also classified

the TDS, based on fresh, brackish, saline and brine water type (Table 3). This classification shows about 44.7 % of the groundwater to be under freshwater condition and the remaining samples as brackish water type (Fig. 4).

Table 2 Minimum, maximum, mean and standard deviation of physicochemical parameters

S. no	Parameters	Min	Max	Mean	Std. deviation
1	pH	7.25	8.2	7.6	0.2
2	EC ($\mu\text{S}/\text{cm}$)	530.0	6,300.0	2,200.0	1,500.0
3	TDS (mg/L)	340.0	4,120.0	1,455.7	959.8
4	Ca^{2+} (mg/L)	24.0	108.0	46.3	18.0
5	Mg^{2+} (mg/L)	3.9	236.7	84.1	46.3
6	Na^+ (mg/L)	17.48	956.8	200.6	205.8
7	K^+ (mg/L)	0.1	201.2	21.0	37.0
8	Cl^- (mg/L)	29.8	1,340.0	388.8	345.9
9	CO_3^{2-} (mg/L)	0.0	54.0	27.3	15.3
10	HCO_3^- (mg/L)	36.6	640.5	277.9	117.8
11	NO_3^- (mg/L)	0.1	82.6	10.2	19.8
12	PO_4^{3-} (mg/L)	0.1	17.0	1.6	2.9
13	F^- (mg/L)	0.2	0.8	0.5	0.1

The relative tendency of major ions in groundwater is in the following order $\text{Na}^+ \geq \text{Mg}^{2+} \geq \text{Ca}^{2+} \geq \text{K}^+$ and $\text{Cl}^- \geq \text{HCO}_3^- \geq \text{CO}_3^{2-} \geq \text{PO}_4^{3-} \geq \text{F}^-$. The sodium concentration in the present samples ranged from 17.5 to 958.8 mg/L. The BIS (1998) guideline shows the maximum permissible limit for sodium in drinking water to be 200 mg/L. In most of the samples, Na^+ concentration was within the permissible level and only 13 samples exceeded the permissible limit (Fig. 5a–h). The magnesium concentration of the studied samples ranged from 3.9 to 236.7 mg/L. As per the standard, 30 mg/L is the maximum

permissible and 100 mg/L is the allowable limit of magnesium for drinking purpose, but Mg^{2+} concentrations in the studied samples showed that about 27.7 % exceeded the allowable limit. Higher concentration of Mg^{2+} is toxic and affects the crop yields (Joshi et al. 2009); also it combines with sulfate to produce laxative effect. The calcium value of groundwater samples ranged from 24 to 104 mg/L; all the samples were within the permissible limits (75–200 mg/L) of BIS (1988) for drinking purpose. The potassium ion concentration varied from 0.1 to 202.2 mg/L with mean value of 37 mg/L; about 57 % of the samples were within the permissible limit (10 mg/L) and the remaining samples (43 %) exceeded the limit.

Among the anionic (Cl^- , NO_3^- , PO_4^{3-} , CO_3^{2-} , HCO_3^- and F^-) concentrations, chloride plays a predominant role in the studied groundwater samples. The chloride value ranged from 29.8 to 1,340 mg/L, but 46 % of samples exceeded the permissible limit (250 mg/L). Nitrate is another important anionic groundwater parameter, and the concentration range is 0.1 to 82.6 mg/L. According to the BIS (1998) guideline (45 mg/L), all the samples are within the permissible limit, except those from the following stations: 23, 26, 27 and 45. Higher concentration of nitrate may produce methanoglobinemia and gastric cancer (Naidu et al. 1998; Olaniya et al. 1978). Figure 6 indicates that the Cl^- versus NO_3^- trend line represents the mixing with saline water and the progressive pollutant load of NO_3^- enrichment (Re et al. 2011). Phosphate concentration ranged from 0.1 to 17.0 mg/L; higher concentration of PO_4^{3-} is indicative of pollution and the major sources are

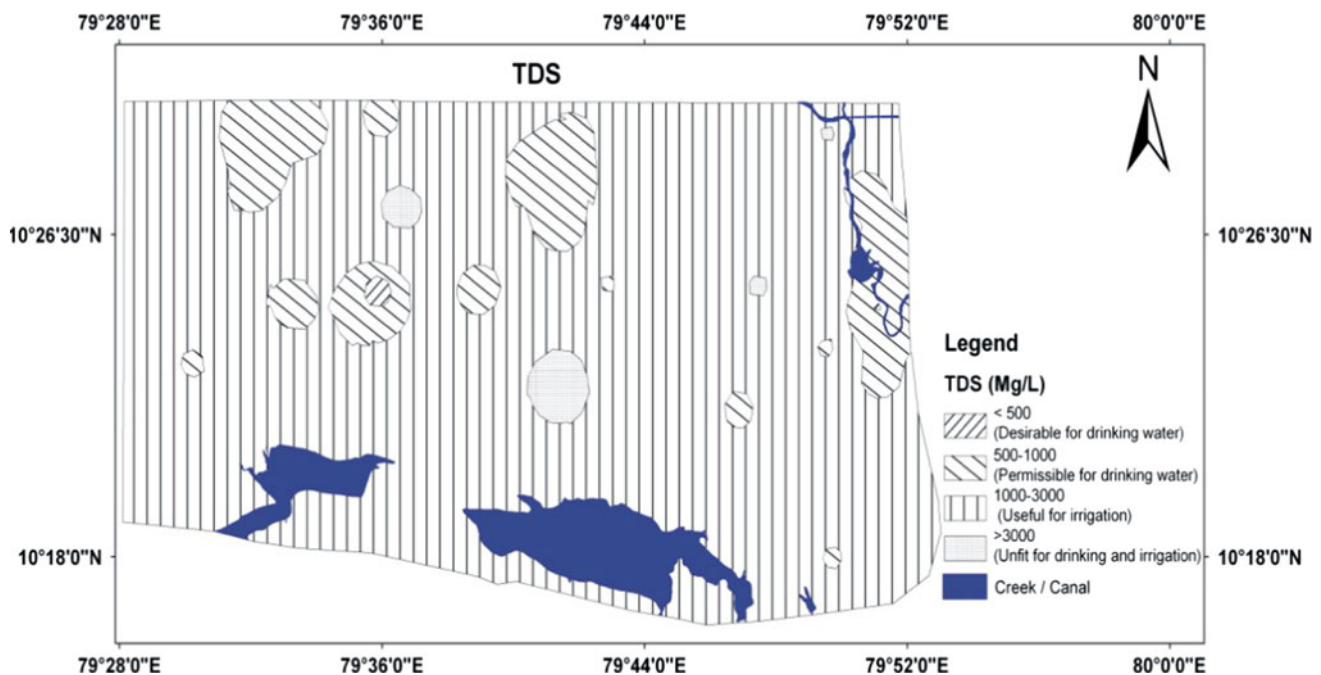
**Fig. 3** Spatial distributions of TDS (Davis and DeWiest 1966)

Table 3 Groundwater quality based on TDS

Parameter	Range	Classification	Sample numbers	No. of samples	% of samples
Davis and DeWiest (1966)					
TDS (mg/L)	<500	Desirable for drinking water	7, 35	2	4.3
	500–1,000	Permissible for drinking water	4, 6, 8, 10, 12, 13, 16, 22, 24, 28, 29, 30, 32, 36, 38, 39, 40, 41, 46	17	36.2
	1,000–3,000	Useful for irrigation	1, 3, 5, 9, 11, 14, 15, 17, 19, 20, 21, 23, 25, 26, 31, 33, 37, 42, 43, 44, 45, 47	22	46.8
	>3,000	Unfit for drinking and irrigation	2, 18, 27, 34	4	8.5
Freeze and Cherry (1979)					
TDS (mg/L)	<1,000	Freshwater	7, 4, 6, 8, 10, 12, 13, 16, 22, 24, 28, 29, 30, 32, 35, 36, 38, 39, 40, 41, 46	21	44.7
	1,000–10,000	Brackish water	1, 2, 3, 5, 9, 11, 14, 15, 17, 18, 19, 20, 21, 23, 25, 26, 27, 31, 33, 34, 37, 42, 43, 44, 45, 47	26	55.3
	10,000–100,000	Saline water	Nil	–	–
	>100,000	Brine water	Nil	–	–

Table 4 Factor analysis-rotated component matrix-varimax with Kaiser normalization

Component	1	2	3	4	Communalities
pH	0.15	0.08	0.82	0.11	0.714
EC	0.97	0.03	0.13	−0.01	0.955
TDS	0.97	0.03	0.13	−0.01	0.955
Ca ²⁺	0.60	0.12	−0.44	−0.14	0.597
Mg ²⁺	0.84	0.04	−0.16	0.09	0.742
Na ⁺	0.02	0.95	0.12	0.09	0.928
K ⁺	0.13	0.94	−0.03	0.09	0.908
Cl [−]	0.94	0.07	0.15	−0.05	0.921
HCO ₃ [−]	0.10	0.23	0.07	0.78	0.672
NO ₃ [−]	0.55	0.21	−0.21	0.42	0.573
PO ₄ ^{3−}	0.53	0.21	−0.04	−0.62	0.714
F [−]	−0.05	0.03	0.72	−0.06	0.522
Eigenvalues	4.63	1.98	1.49	1.09	
Cumulative %	37.34	53.68	66.42	76.67	

Bold values indicate the factor loadings higher than 0.5, which are significant contributors to the variance in the groundwater chemistry

domestic sewage, detergents, agricultural effluents and fertilizers. The concentration of fluoride observed in this study ranged from 0.2 to 0.8 mg/L with a mean value of 0.5 mg/L.

Discussion

Saline water intrusion

Groundwater salinization in coastal aquifer was observed based on the chloride with carbonate–bicarbonate and sodium–chloride interaction. The Cl[−]/HCO₃[−] ratio is

classified into three, such as <0.5 for no intrusion, 0.5–6.6 for slight to moderate intrusion and >6.6 for strong intrusion. Based on this Cl[−]/HCO₃[−] ratio, it is inferred that 70 % of the samples are affected with slight to moderate seawater intrusion and only three samples are affected with strong seawater intrusion (Fig. 7). According to the Revelle index (RI) (Cl[−]/CO₃^{2−} + HCO₃[−]), the studied samples ranged from 0.2 to 50.9, which indicates 70 % of samples exceeded the RI ratio (>1) due to possible seawater mixing. Further, Na⁺/Cl[−] weight ratio (0.85) was used to confirm the mixing of freshwater and seawater (Re et al. 2011). Figure 8 shows that half of the studied samples have less than the Na⁺/Cl[−] reference value maybe due to possible seawater mixing.

Factor analysis

Factor analysis is very useful to interpret the groundwater quality data and to understand specific hydro-geochemical processes. The R-mode factor analysis is a most widely used statistical method. Hence, varimax with Kaiser normalization rotated factor loading matrix was performed. In the analysis, four principal components were extracted accounting for 76.67 % of variance, which shows the major effective controlling agents in the groundwater (Table 4). Factor 1 accounted for about 37.34 % of variance, which is positively contributed by EC, TDS, Cl[−], Ca²⁺, Mg²⁺, PO₄^{3−} and NO₃[−]. EC and TDS have loadings of 0.97, and control the overall mineralization, while Cl[−] has a loading of 0.94. It is derived from saline water intrusion, salt pan deposits or agricultural return flow into groundwater (Ramkumar et al.

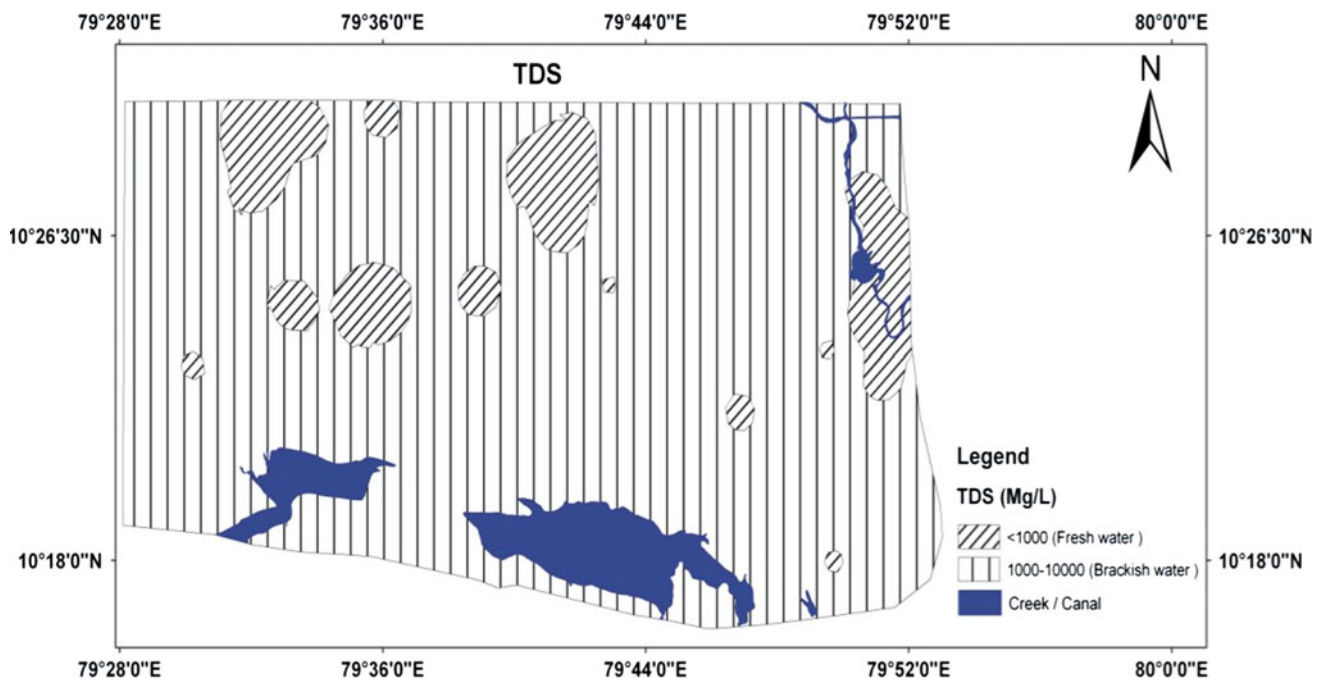


Fig. 4 Spatial distributions of TDS (Freeze and cherry 1979)

2010). The positive loadings on chloride with Ca^{2+} and Mg^{2+} may also represent the salinity of groundwater (Akoteyon and Soladoye 2011). PO_4^{3-} and NO_3^- have moderate loadings (0.55 and 0.53) in factor 1 and may attribute to anthropogenic activities. Application of potassium fertilizers Potash and NPK (nitrogen–phosphorus–potassium, mixed fertilizer) and gypsum seems to be contributed well in potassium and sulfate concentrations in addition with domestic wastewater (sewage, septic tank effluent, etc.) (Nagarajan et al. 2010). Representation of PO_4^{3-} , Ca^{2+} and Mg^{2+} in the first factor is indicative of anthropogenic impact from agricultural practices (Prasanna et al. 2009, 2010). The second factor explains about 16.34 % of the variance and contains Na^+ and K^+ . This may be due to the process of ion exchange between the aquifer matrix and the groundwater (Chidambaram et al. 2007). The third factor is represented by pH and F; the representation in this factor indicates the lowering of pH values or the addition of H^+ to the system along with K and Mg. This may be due to the normal mica weathering process which releases these ions and H^+ into the system (Chidambaram et al. 2007). Factor 3 extracted about 12.74 % of the total variance represented by pH and F^- . In addition, calcium was negatively loaded in the third factor, which is consistent with fluoride influence. Normally, fluoride ions help in dissolution of the calcium ion concentration in groundwater (Dutta et al. 2010; Kumar et al. 1992). Fluoride is a strong electro-negative ion and it easily attracts Ca^{2+} from the mineral matrix. The fourth factor is positive loading of HCO_3^-

due to carbonate dissolution, accounting for 10.25 % of the total variance.

Cluster analysis

Cluster analysis is also another data reduction method that is used to classify entities with similar properties (Pathak et al. 2008). Through hierarchical cluster analysis (HCA), the associations among the stations were obtained using Ward's method with Euclidian distance as a similarity measure with dendrogram plots (Fig. 9). The physico-chemical parameter concentrations were used as variables to show the spatial heterogeneity among the stations as a result of sequence and their relationship in the level of contamination. There were two major groups of cluster obtained from the sampling, while sample yielded groups are summarized below. Group I, clustered with a limited number of stations, interprets the spatial similarity in the physicochemical composition, as influenced by human interference and extent of pollutants received by salt pan and aquaculture activity. Group I is further subdivided into two subgroups, Ia and Ib (Table 5). Ia is typically represented by the first factor (Group I— Ca^{2+} , Mg^{2+} , Cl^- , PO_4^{3-} and NO_3^-) group of samples; the stronger relation between the groups are due to anthropogenic impact and also agricultural practices (Prasanna et al. 2009, 2010). Ib under this subgroup is represented by the 27th sample site grouped alone; F^- dominance is due to the weathering of minerals. Fluoride from this region is mainly obtained from

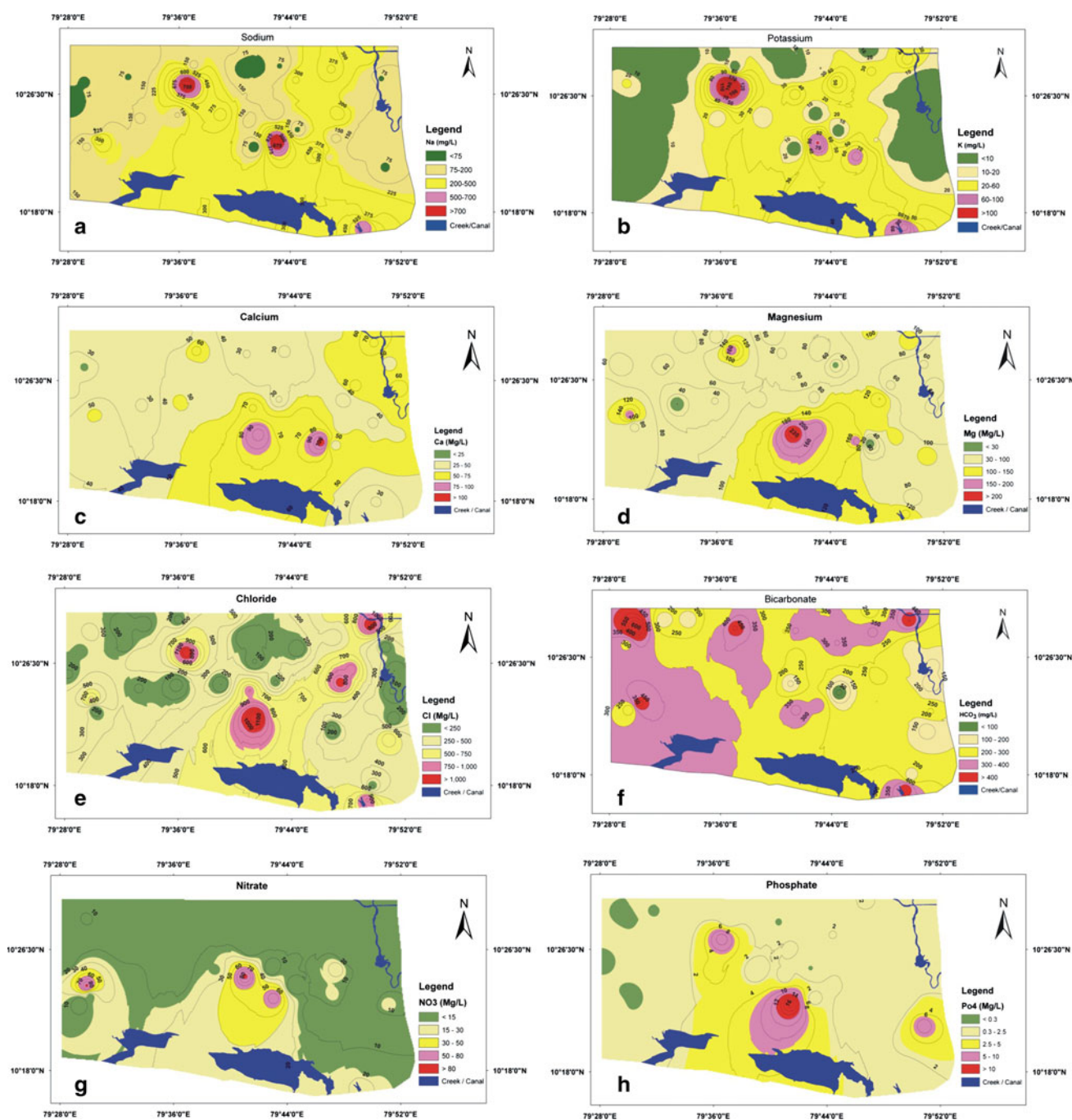


Fig. 5 a–h Spatial distribution of physicochemical parameters

the weathering of mica present in the alluvium sand. Hence it is inferred that dominance of F^- is due to the weathering of minerals. This fact is also supported by spatial distribution of the result (Figs. 11, 12). The Group II cluster samples showing ion exchange of Na and K (Chidambaram et al. 2007) consists of 66 % of samples distributed around the western part of the study area. Also, Group II cluster could be categorized as less polluted compared to Group I.

Water quality index

Water quality index provides the overall influence of individual water quality for drinking purpose. It is classified into five, such as excellent (<50), good (51–100), poor (101–200), very poor (201–300) and unsuitable for drinking (>300). Based on the importance of water quality parameters, maximum and minimum weight was assigned.

Fig. 6 Relationship between Cl^- and NO_3^- concentration (Re et al. 2011)

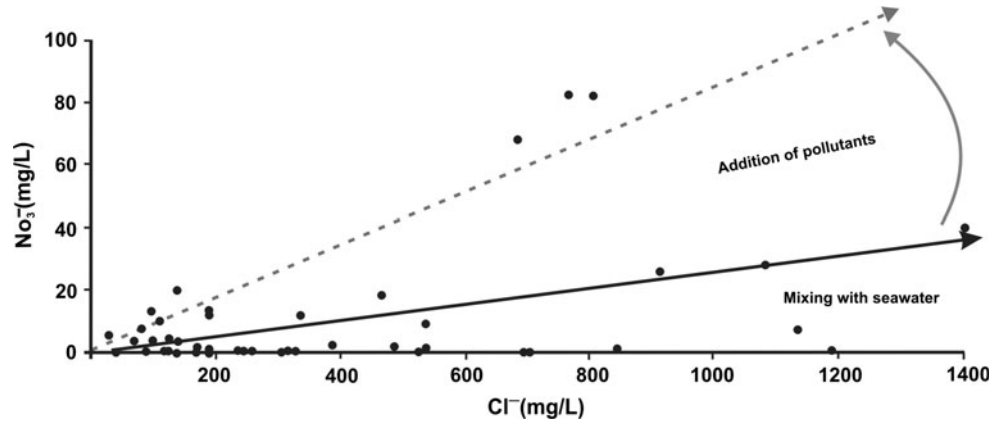


Fig. 7 Relationship between Cl^- and Cl/HCO_3 ratio

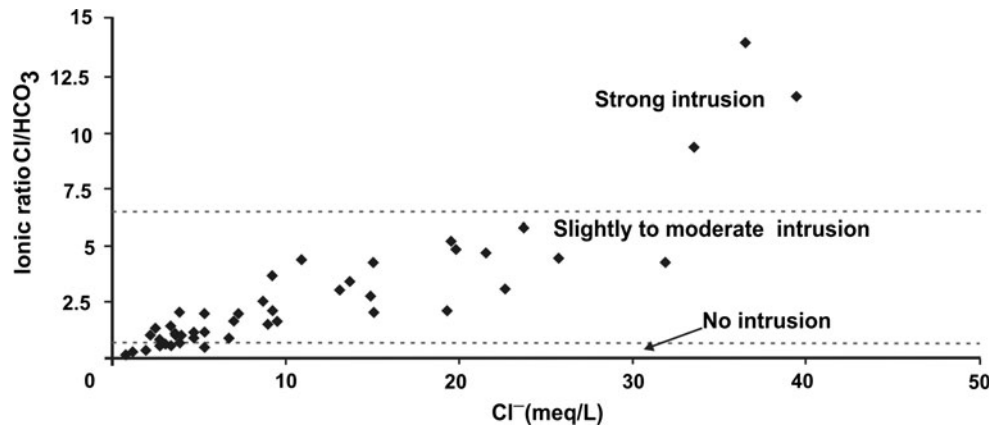
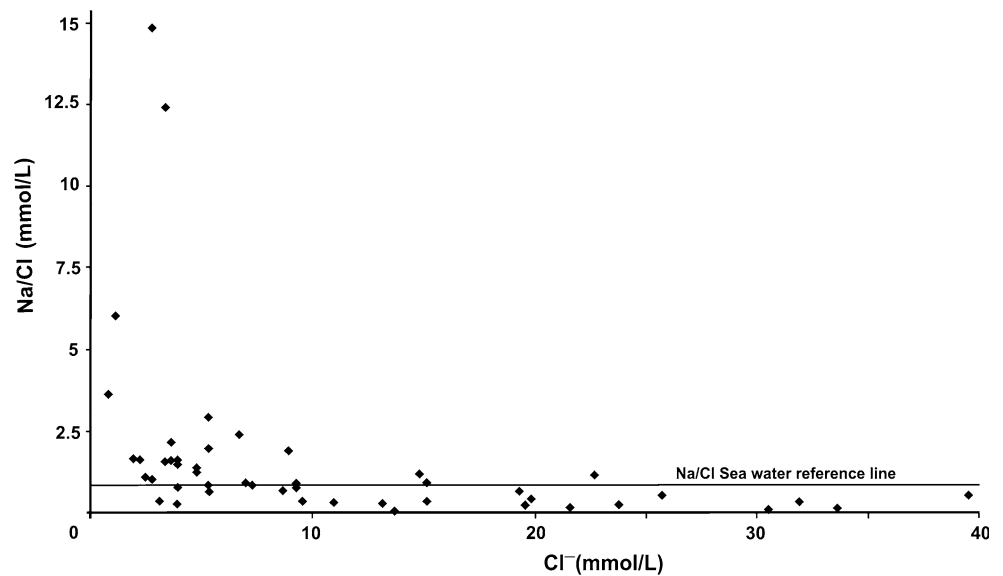


Fig. 8 Relationship between Cl^- and Na/Cl ratio



Maximum weight of 5 was assigned for the parameters: TDS, chloride, nitrate and fluoride, because they play a vital role in groundwater quality (Vasanthavigar et al. 2010; Srinivasamoorthy et al. 2008). Other parameters such as bicarbonate, sodium, potassium, calcium and magnesium were assigned weight 1–4 depending on their

importance in water quality evaluation. After assigning the weight for each parameter, the relative weight was calculated (Table 6). Further, quality rating (q_i) is assigned in each parameter based on concentration of the sample (C_i) divided by drinking water quality standard (S_i) using the following equation:

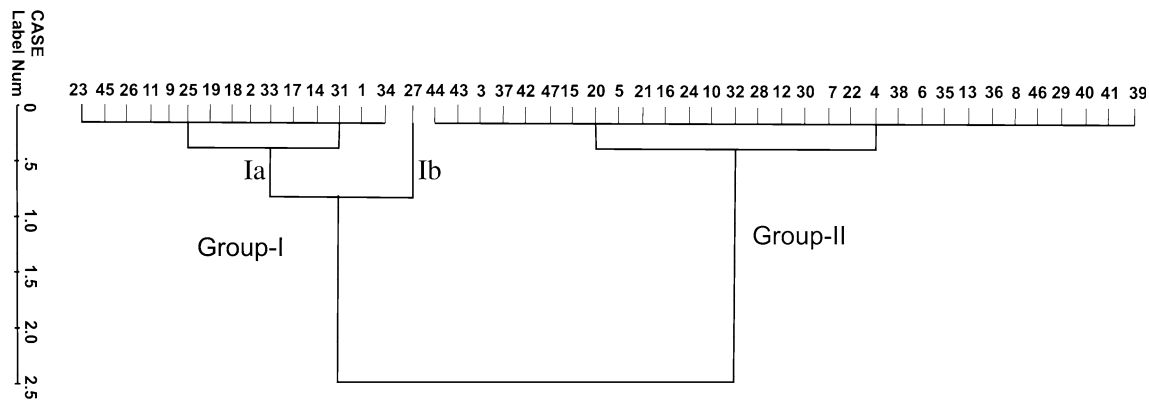


Fig. 9 Dendrogram refers to the map showing the location of the samples (Fig. 1)

Table 5 Different water groups in Vedaraniyam region using cluster analysis

Cluster	Sample no.
Group Ia	1, 2, 9, 11, 14, 17, 18, 19, 23, 25, 26, 31, 33, 34, 45
Group Ib	27
Group II	3, 4, 5, 6, 7, 8, 10, 12, 13, 15, 16, 20, 21, 22, 24, 28, 29, 30, 32, 36, 37, 38, 39, 40, 41, 42, 43, 44, 46

Table 6 Water quality index and relative weight

Chemical parameters	BIS:10500 1,991	Weight (W_i)	Relative weight $W_i = \frac{w_i}{\sum_{i=1}^n w_i}$
TDS (mg/L)	500	5	0.152
Bicarbonate (mg/L)	120 ^a	1	0.030
Chloride (mg/L)	250	5	0.152
Nitrate (mg/L)	45	5	0.152
Fluoride (mg/L)	1	5	0.152
Calcium (mg/L)	75	3	0.091
Magnesium (mg/L)	30	3	0.091
Sodium (mg/L)	200 ^b	4	0.121
Potassium (mg/L)	10 ^b	2	0.061
		$\sum w_i$ 33	$\sum w_i$ 1.000

^a US Public Health Service value

^b BIS 1998

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

Finally, WQI is computed based on the following equation:

$$SI_i = W_i/q_i$$

$$WQI = \sum SI_i$$

where SI_i is the sub index of i th parameter.

Therefore, the water quality rating of the studied samples obtained ranges from 52 to 397. About 36 % of the

samples were found to be good for drinking purpose, 43 % were poor, 19 % were very poor and the remaining 2 % unfit for human consumption.

Irrigation water quality

Periodical monitoring of groundwater quality is necessary for planning, design and operation of irrigation systems to ensure a minimum of deleterious salts or compounds in the irrigation water (Sangodoyin and Ogedenbe 1991). The irrigation suitability was based on the salinity, Na %, SAR, RSC, PI, Kelly ratio and Wilcox diagram. Excess salinity reduces the osmotic activity of plants and thus interferes with the absorption of water and nutrients from the soil (Saleh et al. 1999; Thorne and Peterson 1954). Salinity, sodicity and toxicity generally need to be considered for evaluation of the suitable quality of groundwater for irrigation (Shainberg and Oster 1978).

EC is a good measure of salinity hazard to crops. According to Raghunath (1987), EC were classified into five major types (Fig. 10). Table 7 shows that 25 samples (53.2 %) are within the permissible limits and can be used for irrigation on almost all types of soil, 7 samples are in a doubtful class and 13 samples (27.7 %) are of unfit category.

Sodium percentage

Sodium percentage is widely used to assess the groundwater quality, because a higher level of sodium in irrigation water may increase the exchange of sodium content of irrigated soil and affect soil permeability, structure and create toxic condition for plants (Bangar et al. 2008; Durfer and Backer 1964; Todd 1980). Hence, Na % is assessed based on Raghunath (1987), using the following equation

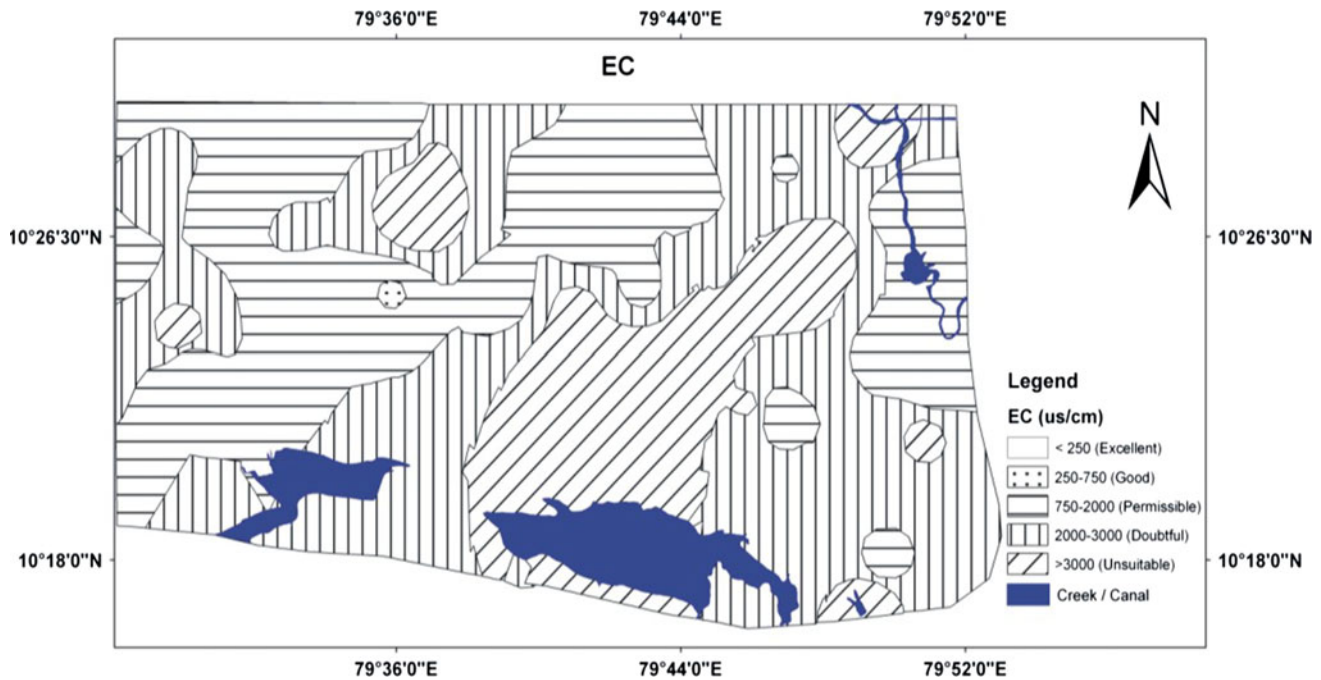


Fig. 10 Spatial distribution of suitability of groundwater for irrigation based on EC

$$\text{Na \%} = \frac{(\text{Na}^+ + \text{K}^+) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} (\text{meq/l})$$

Based on the relative proportions of cation concentration, 40.4 % of samples were within the permissible limits, 10.6 % were excellent, 29.8 % were good, 14.9 % were doubtful and 4.3 % were unsuitable for irrigation (Fig. 11; Table 7). Excess sodium in waters produces the undesirable effects of changing soil properties and reducing soil permeability. Hence, the assessment of sodium concentration is necessary while considering the suitability for irrigation (Nishanthiny et al. 2010). The sample locations fall along the coastal regions and Na might have been acquired from the seawater by saline intrusions (Chidambaram et al. 2007).

Sodium absorption ratio

Sodium absorption ratio (SAR) has been extensively used as an indicator of sodium hazard in irrigation water (Gholami and Srikantaswamy 2009). Richard (1954) has classified water quality based on the following equation

$$\text{SAR} = \frac{\text{Na}^+}{(\text{Ca}^{2+} + \text{Mg}^{2+})^{1/2}} (\text{meq/l})$$

According to Richard's classification, the computed SAR value shows that 91.4 % of samples are excellent, 4.3 % are good and 4.3 % are doubtful for irrigation (Fig. 12). Wilcox's (1955) diagram relating to sodium

percentage and electrical conductivity of the particular sample shows that 10.5 % samples fall under the excellent to good class, 36 % under good to permissible, 12.8 % under permissible to doubtful and doubtful to unsuitable class, respectively, and the remaining samples (27.7 %) are unsuitable for irrigation (Fig. 13). High concentrations of sodium ion in irrigation water have a tendency to be easily absorbed by clay particles due to exchange of calcium and magnesium ion. These exchange processes decrease the soil permeability and reduce internal drainage.

Residual sodium carbonate

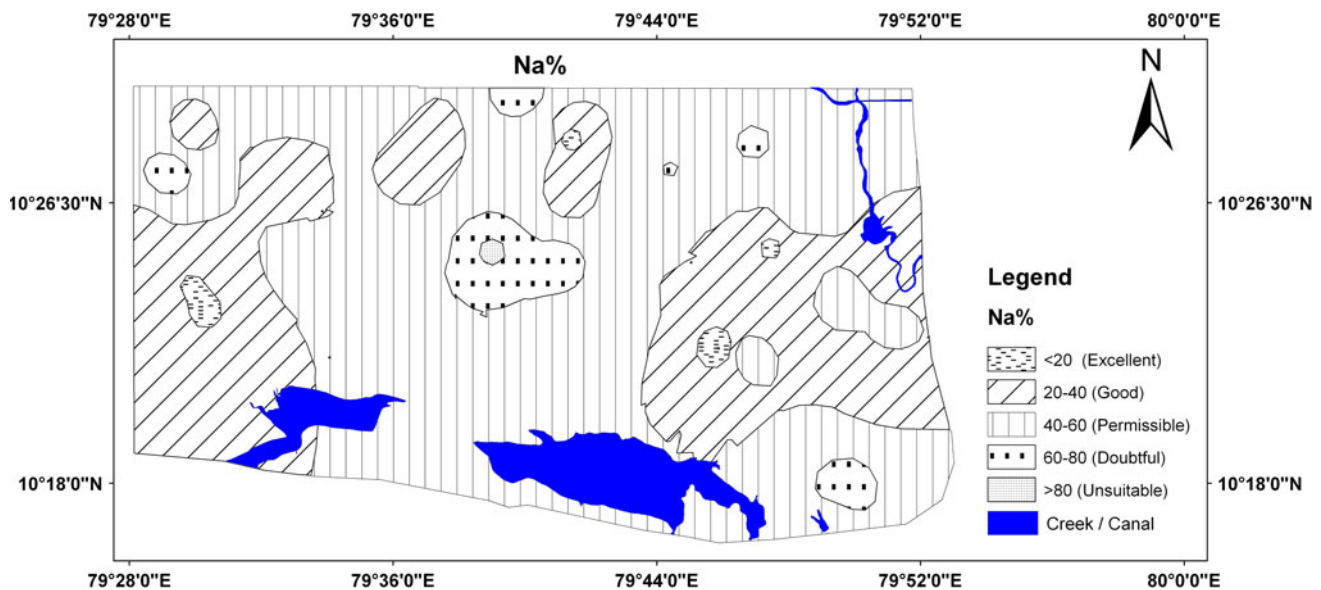
RSC is another parameter to identify the irrigation water quality, assessed based on the presence of carbonate and bicarbonate, along with the sum of calcium and magnesium ions, which is calculated using the following equation (Lloyd and Heathcote 1985):

$$\text{RSC} = (\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+}) (\text{meq/l})$$

The unfit water samples (containing excess of carbonate and bicarbonate) for irrigation will precipitate calcite in soil from solution and increase sodium in solution, resulting in soil dispersion (Emerson and Bakker 1973) as well as impaired nutrient uptake by plants (Kanwar and Chaudhry 1968). According to the RSC classification, 91 % of the samples (<1.25) are suitable for irrigation, 4.5 % of samples are marginal (1.25–2.5) and the remaining samples are not suitable for irrigation (>2.5). The samples show

Table 7 Irrigation quality of groundwater based on EC, SAR and Na % value

Parameter	Range	Classification	Sample numbers	No. of samples	% of samples
Raghunath (1987)					
EC ($\mu\text{S}/\text{cm}$)	<250	Excellent	Nil	–	–
	250–750	Good	7, 35	2	4.3
	750–2,000	Permissible	3, 4, 5, 6, 8, 10, 12, 13, 16, 20, 21, 22, 24, 28, 29, 30, 32, 36, 38, 39, 40, 41, 44, 46, 47	25	53.2
	2,000–3,000	Doubtful	1, 15, 17, 31, 37, 42, 43	7	14.9
	>3,000	Unsuitable	2, 9, 11, 14, 18, 19, 23, 25, 26, 27, 33, 34, 45	13	27.7
Richards (1954)					
SAR	<10	Excellent	1–22, 24–27, 29, 30, 33–42, 44–47	42	91.4
	10–18	Good	23, 31	2	4.3
	18–26	Doubtful	28, 32	2	4.3
	>26	Unsuitable	Nil	–	–
Raghunath (1987)					
Na %	<20	Excellent	14, 18, 29, 45, 46	5	10.6
	20–40	Good	6, 7, 9, 15, 17, 22, 25, 33, 34, 37, 38, 42, 44, 47	14	29.8
	40–60	Permissible	1, 2, 4, 5, 8, 11–13, 16, 19, 21, 24, 26, 27, 30, 35, 36, 40, 41	19	40.4
	60–80	Doubtful	3, 10, 20, 23, 31, 39, 43	7	14.9
	>80	Unsuitable	28, 32	2	4.3

**Fig. 11** Spatial distribution of suitability of groundwater for irrigation based on Na %

comparatively lesser concentration of CO_3^{2-} and HCO_3^- reflecting lesser impact of weathering and the release of Ca and Mg by the ion exchange process (Thivya et al. 2013).

Permeability index

Doneen (1964) has classified the irrigation water quality into three class based on permeability: class I and II having maximum permeability >75 % are suitable for irrigation;

class III having 25 % of maximum permeability is not suitable for irrigation. In the current study, the index ranged from 13.7 to 95.4 %. Based on the PI value, 83 % of the samples are under class I and II and are most suitable for irrigation and the remaining 13 % are unfit for irrigation.

$$\text{PI} = \frac{(\text{Na}^+ + \sqrt{\text{HCO}_3^-}) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)} (\text{meq/l})$$

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

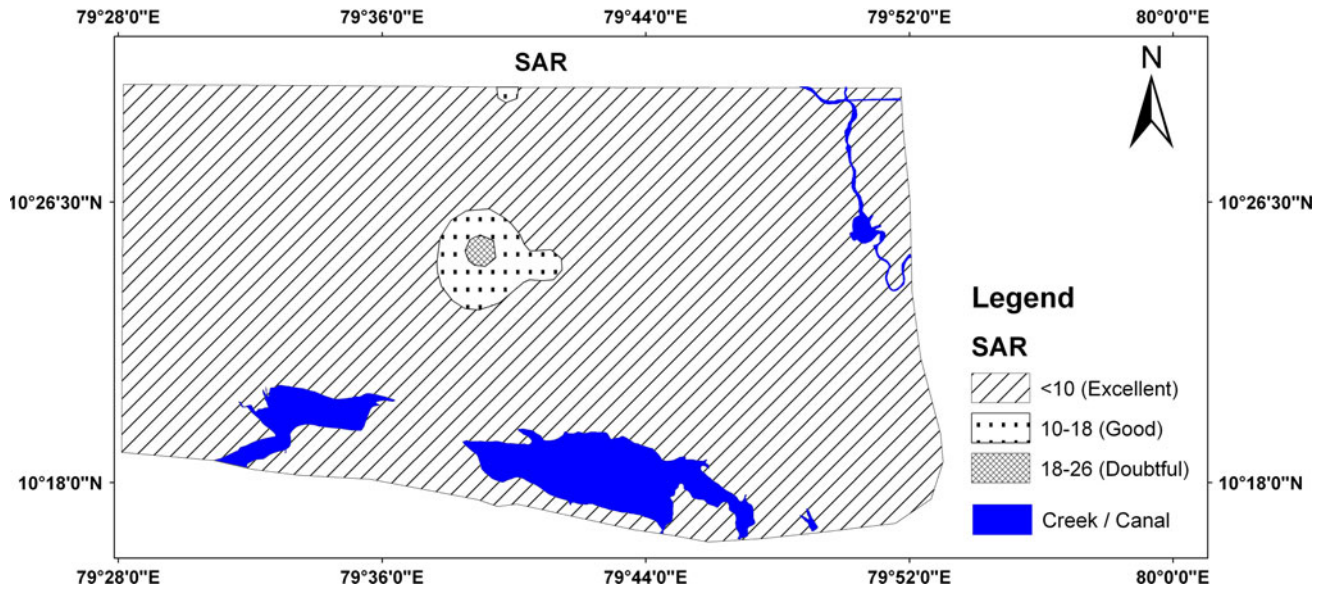
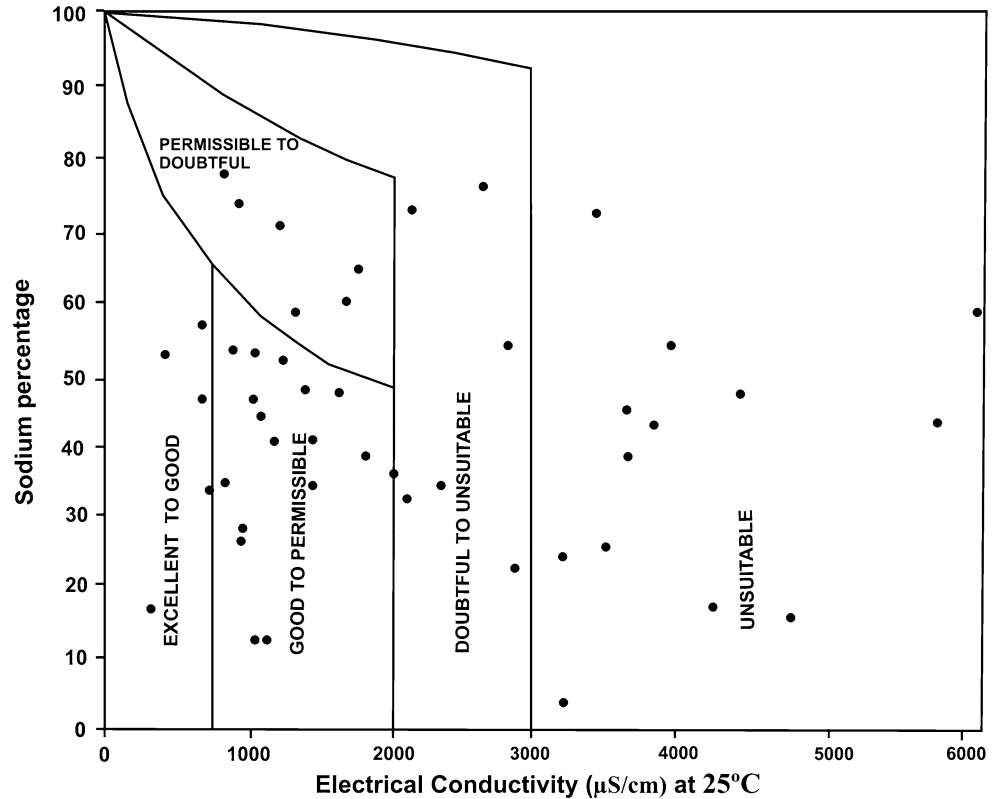


Fig. 12 Spatial distribution of suitability of groundwater for irrigation based on SAR

Fig. 13 Sodium percent and electrical conductivity plot



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. As represented in the factor analysis, the ion exchange process also plays a significant role in determination of PI. When air and water circulation is restricted during wet conditions, such soils become hard when dry (Collins and Jenkins 1996; Saleh et al. 1999).

Kelley's ratio

Kelley (1940) and Paliwal (1967) proposed the suitability of irrigation water quality based on the sodium concentration against calcium and magnesium. According to Kelley's ratio, 66 % samples (<1) are of good quality groundwater suitable for irrigation and the remaining samples are not suitable for irrigation (>1). Kelley's ratio is calculated as follows:

$$\text{Kelley's ratio} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}} (\text{meq/l})$$

Both cation exchange and reverse ion exchange are encouraged by aquifer materials and land use practices, in waterlogged area, marshy/swampy land, creek, mud/tidal flat represented by montmorillonite clays, which lead to the release of Na or Ca into groundwater and adsorption of Ca or Na, respectively (Alison et al. 1992; Blake 1989; Cerling et al. 1989; Foster 1950).

Conclusion

The present study of groundwater samples in Vedaraniyam coast shows that the water quality of the studied samples exceeded the BIS limits in some areas, which has the potential to affect human health adversely. The chemical composition of groundwater shows that sodium concentration was dominant in the cations and chloride in anions. Na/Cl and Mg/Cl ratios indicate that nearly 50 % of the samples are mixed with saline water intrusion. Anthropogenic input from salt pan and aquaculture practice increased salt-affected areas around 33.2 sq. km, which contributed to the increase in sodium and potassium concentration in groundwater. Elevated level of phosphate and nitrate concentrations is attributed mainly to the leaching of salts from agricultural runoff and domestic sewage such as ill-maintained septic tank and sewer lines. Further the calculated SAR, Na %, RSC and PI values show that around 80–90 % of water is useful for irrigation without any adverse impacts on the soil. It is obvious that Vedaraniyam aquifer has been moderately polluted and needs a long-term planning and implementation program for improving the groundwater quality. The study on the water quality parameters for drinking and irrigation shows that most of the groundwater samples are not suitable for drinking purpose and only few samples are unfit for irrigation purpose. The land use practices and the ion exchange process play a significant role in determining major geochemical processes of the study area. To ensure a sustainable management of this resource in this fragile ecosystem, proper management of the water extraction structures and maintenance of the surface water sources are needed.

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