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ORIGINAL ARTICLE

Hydrochemical characteristics of coastal aquifers of Kadaladi, Ramanathapuram District, Tamilnadu, India

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Abstract Geochemical signatures of groundwater in the coastal aquifers of Kadaladi block of Ramanathapuram District, Tamilnadu, India were used to identify the chemical processes that control hydrochemistry. The parameters such as pH, EC, TDS and major ion concentrations Na, K, Ca, Mg, Cl, HCO_3, SO_4, PO_4 and NO_3 of the groundwater were analyzed. Abundances of these ions are in the following order $Na > Ca > Mg > K$ and $Cl > HCO_3 > SO_4 > NO_3 > PO_4$. Na–Cl is the dominant hydrochemical facies of the study area. Interpretation of the hydrochemical data suggests that hydrochemistry of the study area is controlled by mixing of fresh water with relict saline water, ion-exchange processes, silicate weathering and evaporation are responsible for the groundwater chemistry of the study area. Above statement is further supported by Gibbs plot where most of the samples fall within the evaporation zone. Good quality groundwater is restricted to coastal sand dunes running parallel to the coast and it is important to conserve these dunes.

Keywords Groundwater · Geochemical facies · Ionic ratios · Kadaladi · Tamilnadu

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Introduction

Groundwater is the backbone of Indian agriculture and drinking water security. It is a common pool resource, used by millions of farmers across the country. Due to the ever increasing demand for potable and irrigation water and inadequacy of available surface water, the importance of groundwater is increasing exponentially every day (World Bank 2010; Selvam and Sivasubramanian 2012). Groundwater remains the only drinking water source in most of Indian rural household. With an estimated 30 million groundwater structures, India is fast hurtling towards a serious crisis of groundwater overuse and quality deterioration (World Bank Report 2010). Groundwater is threatened by several factors related to its mismanagement. Degradation of groundwater quality in coastal region generally occurs due to natural processes such as saline water intrusion, wind driven sea spray and marine aerosols deposited on the top soil, evaporation and interaction of groundwater with brines and sedimentary formation (Sanford et al. 2007). Apart from the natural process, anthropogenic contaminations such as industrial effluents, agricultural fertilizers, municipal waste water, septic tank effluent and landfill are other major causes of water quality deterioration (Mondal et al. 2008; Mondal and Singh 2011; Selvam et al. 2013).

Seawater intrusion is one of the most common problems in almost all coastal aquifers around the globe (Melloul and Goldenberg 1997, 1998; Sivakumar and Elango 2008; Chidambaram et al. 2009; Mondal et al. 2010, 2011; Srinivasamoorthy et al. 2011). This phenomenon can be explained by the variety of conditions like gentle coastal hydraulic gradients, tidal and estuarine activity, sea level rises, low infiltration, excessive withdrawal and local hydrogeological conditions (Sarma et al. 1982; Longe et al.

1987; Rajmohan et al. 1997, 2000; Barret et al. 2002; Saxena et al. 2004; Kacimov et al. 2009). The common method for assessing seawater intrusion through an aquifer in coastal belts is a periodic analysis of groundwater (Todd 1980; Kim et al. 2009; Mondal et al. 2010, 2011 and Krishnakumar et al. 2012). Chemistry of groundwater is an important factor determining its use for domestic, irrigation and industrial purposes. Interaction of groundwater with aquifer minerals through which it flows greatly controls the groundwater chemistry. Hydrogeochemical processes that are responsible for altering the chemical composition of groundwater vary with respect to space and time. The hydrogeochemical processes of groundwater system help to obtain an insight into the contributions of rock/soil–water interaction (Senthilkumar and Elango 2013). Very few research works have been conducted with the aim of assessing the chemical composition of groundwater in the coastal regions of Tamilnadu. When considering the present study area, so far there is no scientific publication available related to groundwater quality. In this work, a detailed investigation has been carried out to evaluate the geochemical process regulating groundwater quality.

Study area

Kadaladi block of Ramanathapuram district, Tamilnadu, India lies between the latitude 9° 6′–9° 21′ N and longitude 78° 18′–78° 45′ E and covered by the Survey of India Toposheets 58 K/7, 58 K/8, 58 K/11 and 12 (Fig. 1). Total areal extent of the present study area is 623 km^2. Presently, Ramanathapuram district is divided into 11 blocks and Kadaladi block is further divided into 60 Panchyat villages. Kadaladi block is mainly covered by sedimentary formation and about 70 % of the study area is covered with Fluvial, Fluvio-Marine, Aeolian and marine sediments of Quaternary age. The Fluvial deposits are made up of sand, silt and clay. The western side of the study area is exposed with Archaean rocks such as Garnetiferous Biotite Gneiss, Quartzite and Charnockites which are intruded later by Pink Granite. The Aeolian deposits are made up of red sands and they are in the form of ancient sand dunes. These dunes run ~10 km parallel to the coast and extend up to 3 km across. These sand dunes are separated by marshy deposits of black clays from the sea coast. The sands are underlain by calcareous hardpan. The study area enjoys a tropical climate.

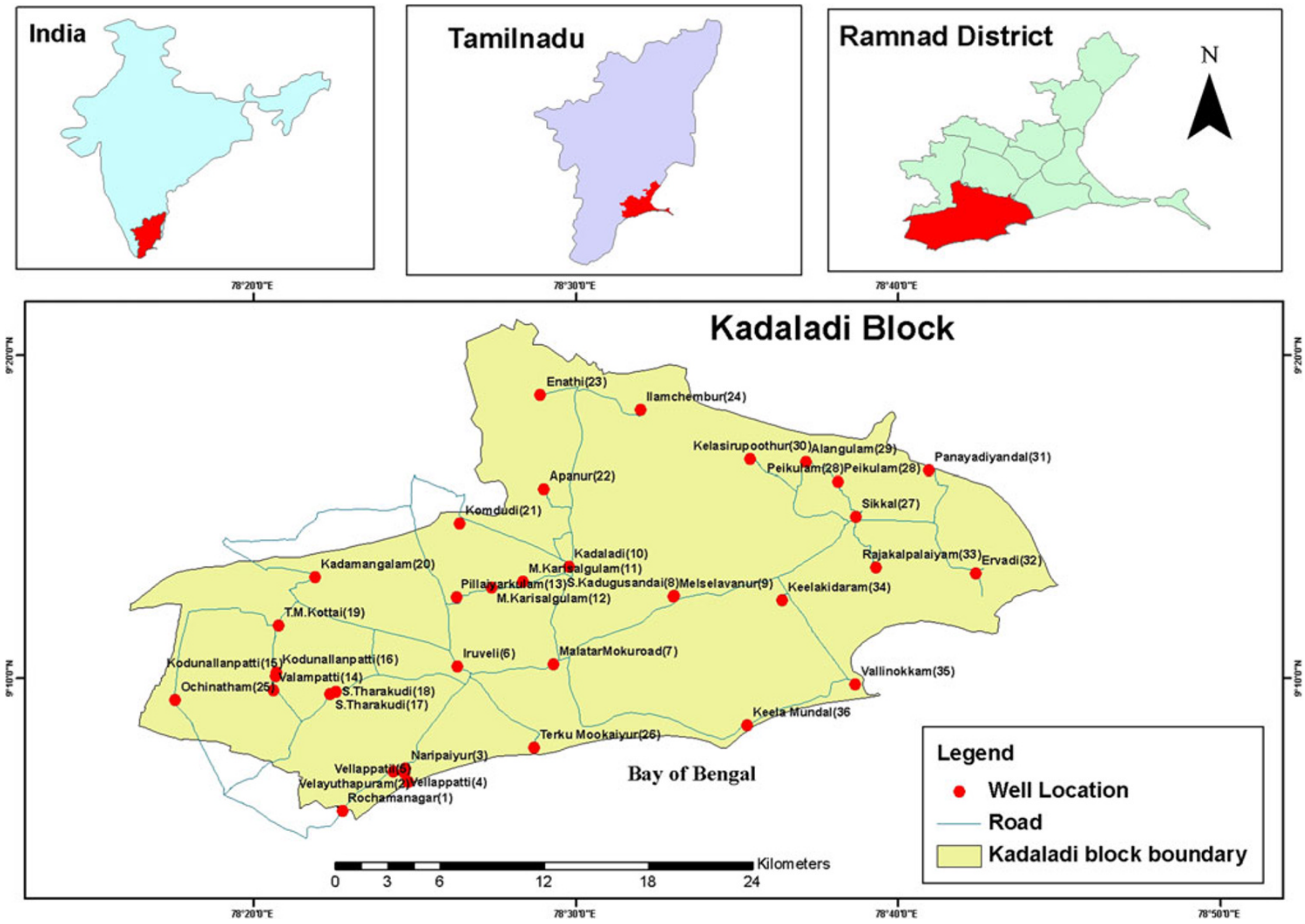

Fig. 1 Location map of the study area

In the plains, the maximum and minimum temperatures recorded are 39 and 29 °C, respectively. Heat becomes intense in March to September and shoots further up unless interfered by rains. Humidity is relatively high as 79 % on an average and ranges between 80 and 90 % in coastal regions. Coastal areas are flanked by beach ridge complex, swales, swamps and backwater. The sand flat is another feature of the coast comprising clay, silt and often inundated by seawater and encrusted with salt. Major rivers flowing through the study area are Gundar River and Palar River. They flow from northwest to southeast within the study area and enter into Bay of Bengal. The drainage pattern, in general, is dendritic. Both the rivers are seasonal and flow only during monsoon season. In addition to this, a small Kadugusandai Odai also flows through the study area.

The district receives rain under the influence of both southwest and northeast monsoons. The northeast monsoon chiefly contributes to the rainfall in the district. Most of the precipitation occurs in the form of cyclonic storms caused due to the depressions in the Bay of Bengal. The southwest monsoon rainfall is highly erratic and summer rains are negligible. Rainfall data from two stations over the period 1901–2000 were utilized and a perusal of the data shows that the normal annual rainfall over the district is 827 mm and decreases toward inland. The general practice of people in the study area is to store rain water in tanks and use them for their needs throughout the year (Fig. 2). But most monsoons fail. To cater the need of the people, Tamilnadu Government has established a desalination plant at Naripayur located within the study area. This plant produces good quality drinking water from sea water and supplies them to the surrounding villages.

The alluvium with alternate layers of sand and clay with a thickness of 15–25 m and are characterized by floating freshwater lenses limited to a depth of 6–7 m below ground level. It can sustain a pumping of up to 2 h and can yield about 2–5 l/s. So people prefer dug wells of 3–6 m depth than the bore wells of 30 or 50 m and extract good quality groundwater which floats as lens on the saline water. Comparatively good quality of water is available in the narrow strip of land between red sand dunes running roughly 10 km parallel to the coast and the coastline (Fig. 3). Natural recharge from rainfall elevates the groundwater level and replenishes the fresh water lens of these sand dune areas. In the study area, there are no deep aquifer has been reported so far. During our reconnaissance survey, we have visited the drilling sites of Mineral Exploration Corporation Ltd (MECL) who were in search of lignite beds. They have not encountered any hard rock or lignite up to the depth of 400 m.

Materials and methods

Collection of groundwater samples

Totally 36 wells were identified during our reconnaissance survey for the collection of water samples to carry out chemical analysis. Due care was given to the distribution of wells throughout the study area during well selection. Dug well and bore well samples were collected during the

Fig. 2 “Oorani” in the study area

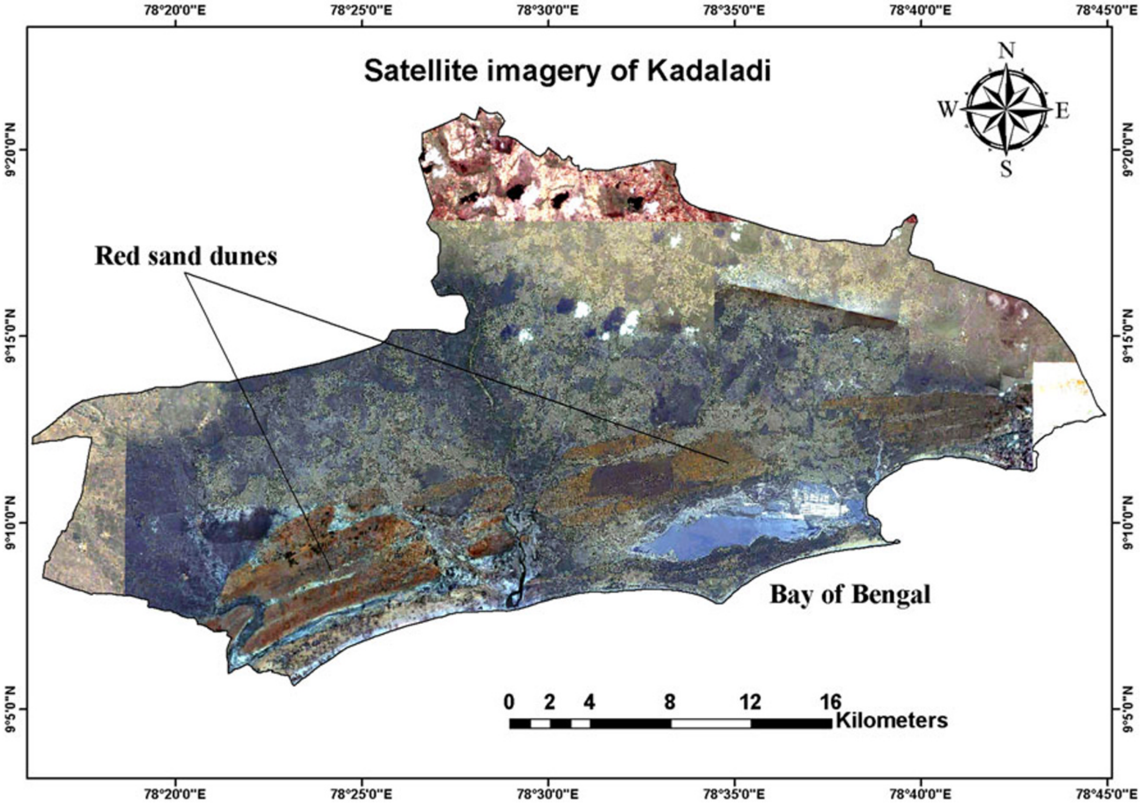

Fig. 3 Satellite image of the study area

pre-monsoon (PRM) period of 2012 (June 2012). Methods of collection and analysis of groundwater samples were essentially the same as given by Brow et al. (1983), APHA (1995). The samples were collected in 1 l capacity polythene bottles. Prior to the collection, bottles were thoroughly washed with diluted HNO_3 acid, and then with distilled water in the laboratory before filling the bottle with the sample. Portable Eco-testers were used to measure TDS, EC and pH on-site. The precise locations of the sampling points were also determined in the field using GARMIN 12 Channel GPS. The well locations of the groundwater samples are given in Fig. 1.

Chemical analysis of groundwater

The groundwater samples collected were analyzed for various physicochemical parameters as described by the American Public Health Association (APHA 1995). Calcium (Ca) and Magnesium (Mg) were determined titrimetrically using standard EDTA; Chloride(Cl) was determined by standard $AgNo_3$ titration; bicarbonate (HCO_3) was determined by titration with HCL; sodium (Na^+) and potassium (K^+) were determined by Flame Spectrometer; Sulphate (SO_4) was determined by spectrophotometric turbidimetry. Majority of the analyzed samples show ion balance errors within ±5 %, indicating the results are generally acceptable. All concentrations are expressed in milligrams per liter (mg/l), except pH, EC and TDS. The EC concentrations were expressed in µS/cm and TDS concentrations were expressed in ppm. Concentration of chemical parameters of water samples are given in Table 1.

Results and discussion

General characteristics

The results of chemical analysis for the groundwater samples collected in June, 2012 are listed in Table 1. Groundwater in the study area is generally alkaline in nature with pH ranging from 7.2 to 8.2, with an average of 7.8. EC is an indirect measure of ionic strength and mineralization of natural water. EC of groundwater samples of the study area ranges from 190 to 47,600 µS/cm, with an average of 8,226 µS/cm. Total dissolved solids (TDS), which is generally the sum of dissolved ionic concentration varies between 116 and 33,320 mg/l with an average of 5,406 mg/l. Table 1 clearly shows that about 89 % of samples collected falls under brackish water category. Lower pH (7.2), EC (190 µS/cm) and TDS (116 ppm) has been recorded in the samples collected from Roachmanagar, Velayuthapuram, Vellapatti, M. Karisalkulam and Terku Narippaiyur. Higher

Table 1 Chemical concentration of major ions

Sample no	pH	EC	TDS	Na	K	Ca	Mg	CO_3	HCO_3	Cl	SO_4	PO_4	NO_3
1	7.2	390	238	33	12	38	13	12	183	43	22	0.38	0.1
2	7.6	670	409	50	5	69	20	12	220	99	41	0.27	0.18
3	7.8	4420	2696	500	210	168	87	24	500	937	252	1.1	0.42
4	7.8	720	439	58	15	64	26	24	256	85	35	0.43	0.15
5	7.8	530	323	47	6	43	20	12	183	85	28	NA	0.14
6	7.9	2470	1507	234	6	61	34	24	464	440	121	0.73	0.22
7	7.6	4900	2989	530	10	131	125	12	354	1276	230	0.92	0.32
8	7.7	4900	2970	440	10	134	117	12	354	1276	221	0.91	0.27
9	7.8	610	372	56	10	34	15	24	268	57	41	0.7	0.17
10	7.7	2320	1415	144	22	90	57	NA	476	425	182	0.24	0.3
11	7.5	6900	4209	550	10	394	232	NA	293	2028	227	0.21	0.22
12	7.9	290	177	16	16	24	14	NA	49	28	19	0.7	0.19
13	8	490	299	37	13	26	34	24	220	43	17	0.7	0.22
14	7.4	47600	33320	6500	100	1872	1818	NA	342	22880	1392	0.81	0.24
15	7.4	47600	33300	6300	100	1872	1838	NA	244	22865	1363	0.38	0.26
16	7.9	190	116	16	5	11	10	NA	98	43	40	0.27	0.23
17	7.9	2450	1495	130	16	120	85	NA	366	525	162	1.1	0.26
18	7.9	2450	1465	128	16	112	88	NA	366	496	153	0.92	0.1
19	7.5	46700	32690	4500	100	1860	1737	NA	366	22334	1374	0.91	0.14
20	8.2	620	378	30	9	35	35	12	293	43	49	0.7	NA
21	7.6	8620	5258	1050	210	182	292	NA	390	2311	445	0.43	0.1
22	7.9	1640	1000	188	8	40	27	12	268	241	226	0.34	NA
23	7.9	13740	8381	1760	20	131	249	NA	647	3276	1238	0.24	0.1
24	7.4	730	445	75	15	48	20	NA	317	85	61	1.4	0.1
25	7.7	11150	6802	980	30	832	473	NA	220	1574	1756	0.6	3.9
26	8	4730	2885	510	80	75	106	NA	464	1120	178	0.76	NA
27	7.8	8680	5295	1140	10	189	179	NA	525	2255	508	0.6	0.14
28	8.2	25200	16632	3600	300	480	577	12	415	9394	1887	0.46	0.11
29	8.1	8420	5136	1030	20	110	165	NA	378	2240	422	0.1	NA
30	8	9160	5588	980	60	130	191	NA	427	2623	536	0.3	NA
31	7.6	2880	1757	300	14	120	72	NA	427	624	220	0.43	NA
32	7.9	11660	7113	1500	310	280	246	NA	512	2879	488	0.76	1.2
33	7.9	640	390	90	10	24	19	12	293	57	44	0.35	NA
34	7.8	4580	2794	360	114	149	98	NA	256	1248	155	0.92	1.51
35	8	3390	2068	270	134	146	74	NA	342	567	301	0.38	12.3
36	8	3710	2263	280	110	120	83	NA	427	780	204	0.92	5.7
Rainwater	NA	NA	NA	0.4	0.7	0.4	0.1	NA	0.4	0.7	1.8	NA	0.4
Seawater	NA	52480	33588	9350	688	381	1270	NA	141	19300	2450	NA	8

pH (8.2), EC (47,600 μS/cm) and TDS (33,320 ppm) has been recorded from Valamppatti, T. M. Kottai, Peikulam, Enathi, Komboothi and Ervadi.

Among the cations, the minimum concentration of Na, Ca, Mg and K are 16, 11, 10 and 5 mg/l and the maximum concentrations are 6,500, 1,872, 1,838 and 310 mg/l respectively. The averages of these cations are 956, 284, 258 and 59 respectively. The order of abundance of these cations is Na > Ca > Mg > K.

Geochemical classification

Trilinear plotting systems are used to study water chemistry and quality (Piper 1944). On conventional trilinear diagrams sample values for three cations (Calcium, Magnesium and Alkali metals-Sodium and Potassium) and three anions (Bicarbonate, Chloride and Sulfate) are plotted relative to one another. These ions are generally the most common constitutions in unpolluted groundwater.

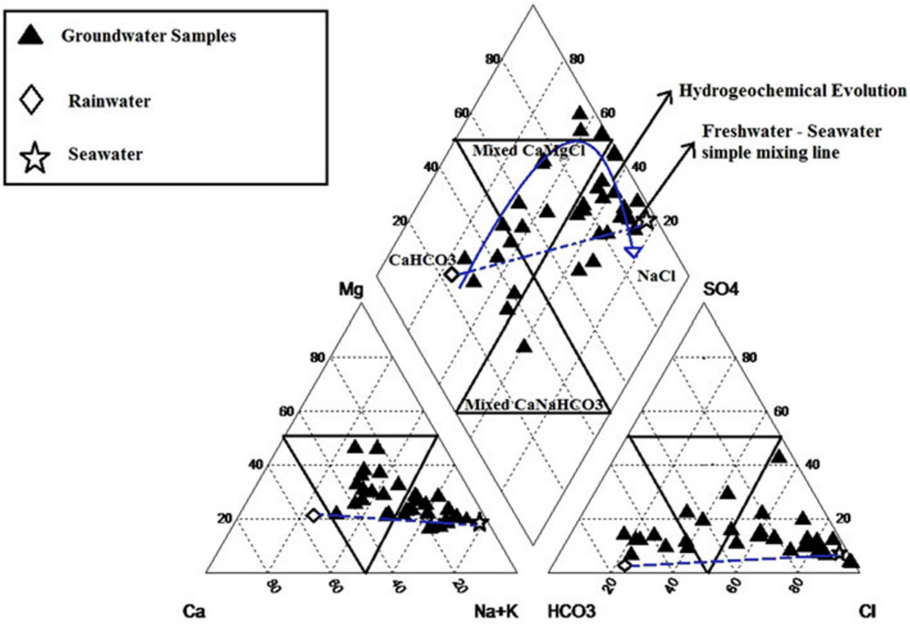

Fig. 4 Pipper plot for the groundwater samples

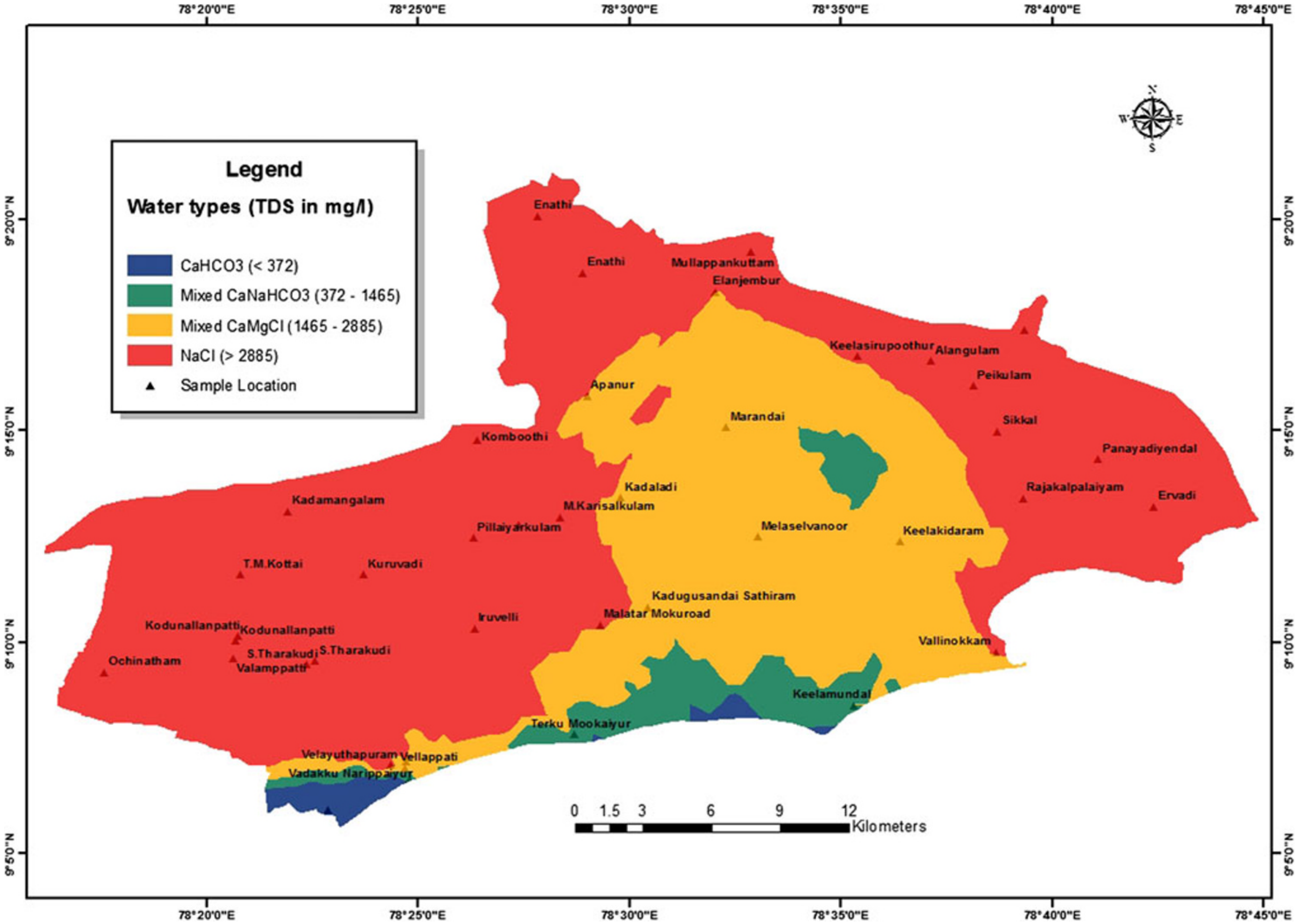

Fig. 5 Spatial distribution of water types

Fundamental interpretations of the chemical nature of water samples are based on the location of the sample ion values.

Distinct zones within aquifers having defined water chemistry properties are referred to as hydrochemical facies (Vasanthavigar et al. 2010). Determining the nature and distribution of hydrochemical facies can provide insight into how groundwater quality changes within and between aquifers. In Fig. 4, the HCO_3–Cl–SO_4 anion triangle shows groundwater samples plotted between the bicarbonate type and chloride type end member and Sulfate (SO_4) is not present in any significant proportion. In Ca–Mg–Na cation triangle samples clustered off-center towards Sodium type groundwater. These two triangles projected onto the main diamond field. If the groundwater is simply mixed with seawater, groundwater composition should be plotted on a straight line connecting the background freshwater and seawater. However, the groundwater in the study area shows a curved path (arrow) of hydrochemical evolution, which starts from the $CaHCO_3$ type via the mixed CaMgCl type and ends to the NaCl type. This is a typical pattern which indicates the cation exchange reaction when seawater incursion occurs (Richter et al. 1993). This pattern suggests that the groundwater chemistry in the study area changes due to the cation exchange reaction as well as the simple mixing with seawater as a result of seawater incursion. Figure 5, showing the spatial distribution of groundwater type within the study areas reveals that groundwater available in the coastal sand dunes is comparatively fresh and come under $CaHCO_3$ and mixed $CaNaHCO_3$ type. This type of groundwater may have resulted due the recent recharge of the coastal sand dunes by rainwater. Majority of the groundwater within the study area comes under NaCl and mixed CaMgCl type. The higher salinity of the groundwater of the present study area may be due to the mixing of fresh water with relict saline water from a high stand of sea level in past geological time. Since the study area comes under a semi-arid climate, the absence of effective natural flushing activity enhances accumulation of salts and saline water (Cardona et al. 2004).

In addition to Piper diagram, Gibbs plots were also used to gain better insight into hydrochemical processes such as precipitation, rock water interaction and evaporation on groundwater chemistry in the study area. Gibbs (1970) demonstrated that if TDS is plotted against Na/(Na + Ca) and Cl/Cl + HCO_3, this would provide information on the mechanism controlling the chemistry of waters. Figure 6a, b displays that groundwater samples were plotted mostly in the evaporation zone and few samples in the rock water interaction zone. Cation points are scattered. But the anion shows some linear trend because the increase in Cl and HCO_3 may due to the level of mixing of sea water and evaporation. It is expected that as evaporation greatly increases the concentration of ions formed by chemical weathering of subsurface lithology, leading to higher

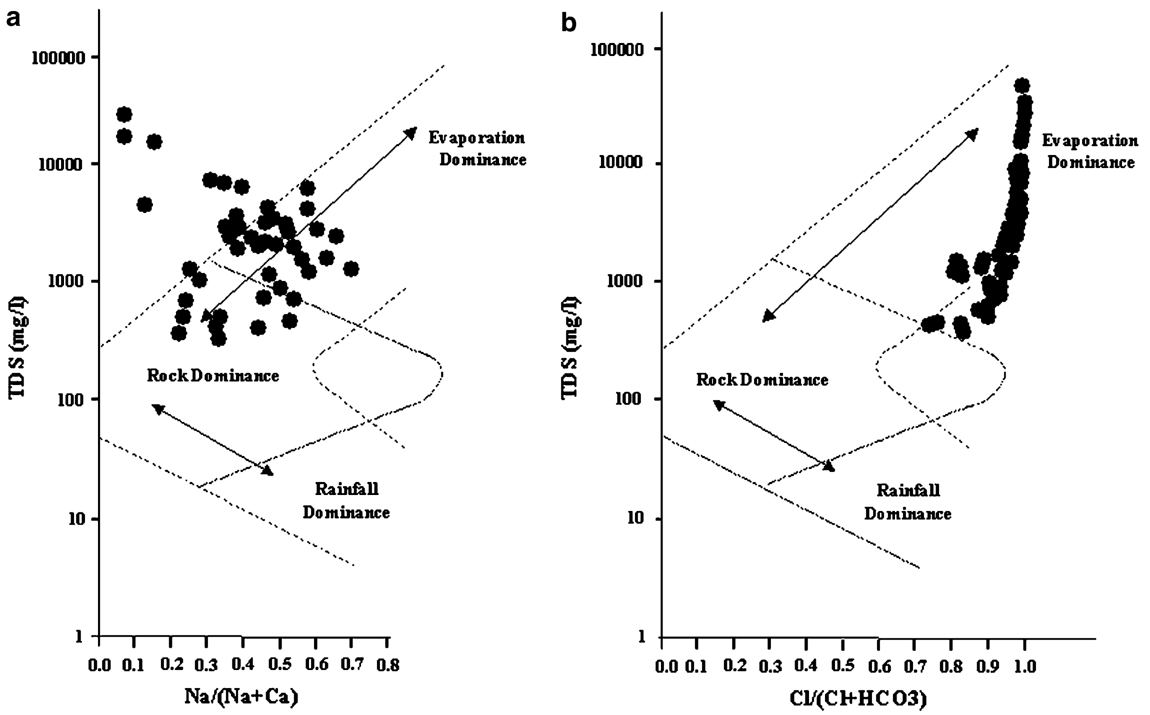

Fig. 6 **a**, **b** Mechanism controlling groundwater chemistry

salinity (Volker 1961; Stuyfzand P 1993). Both Piper and Gibbs suggest that groundwater chemistry is mainly regulated by mixing of high saline water and evaporation.

Geochemical process

The compositional relations among the dissolved ions can be used to assess the origin of solutes and the processes that results in water composition. The chemical data of groundwater samples are plotted on Na Versus Cl scatter plot. The Na/Cl relationship has often been used to identify the mechanism for acquiring salinity and saline intrusions. Sodium and Chloride show a good correlation (Fig. 7a), indicating groundwater are probably controlled by water–rock interaction, most likely derived from the weathering of calcium–magnesium silicates, chiefly from calcite, plagioclase, gypsum and feldspar (Srinivasamoorthy et al. 2011). However, increased concentration of HCO_3 compared to Na concentration (Fig. 7b) in groundwater suggests that silicate weathering also occurs (Fisher and Mullican 1997).The evolution of the slopes of Ca and Mg with HCO_3 gives valuable information about the sources of Ca and Mg in groundwater (Richter et al. 1993). Ca + Mg Versus HCO_3 plot (Fig. 7c) shows a horizontal trend line

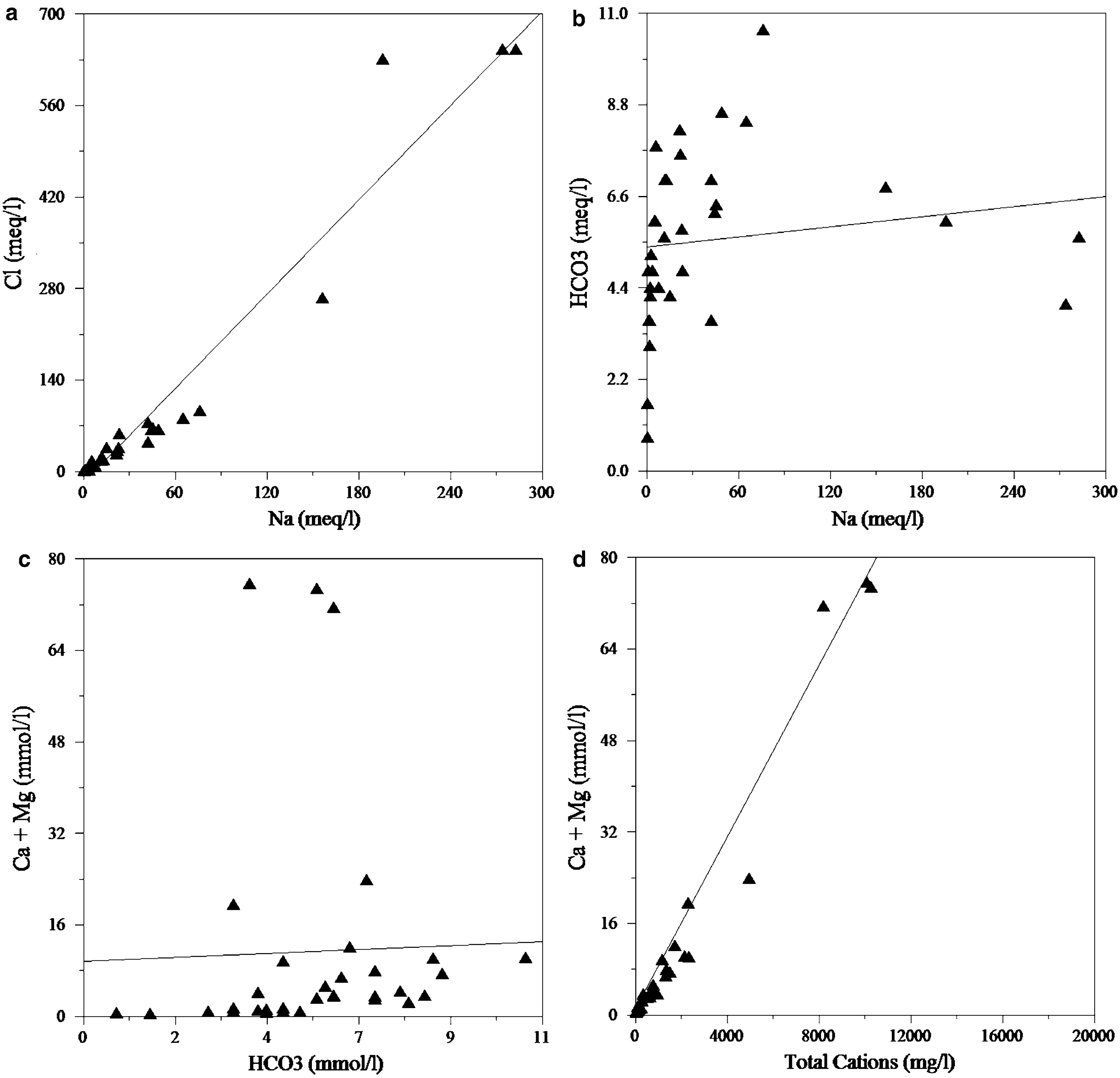

Fig. 7 Ionic scatter diagram of groundwater in the study area

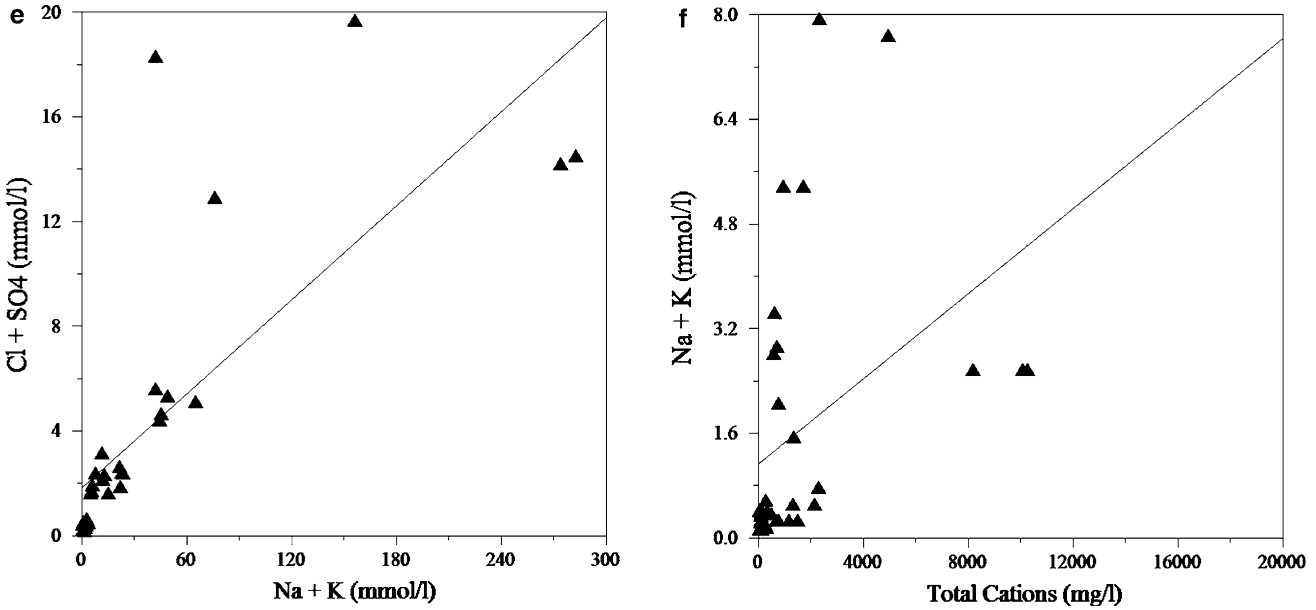

Fig. 7 continued

indicating that Ca + Mg/HCO_3 ratio does not change during the increase of HCO_3. This indicates contribution of Ca + Mg and HCO_3 are from different sources. Feldspars present in the sand and the clay minerals in the black soil may be the source for Ca and Mg. Higher HCO_3 may because of the higher evaporation and the presence of Kankar. Enrichment of HCO_3 and depletion of Ca + Mg may be due to cation exchange (Spears 1986). The plot of Ca + Mg versus total cations shows that the data falls on the 1:1 trend line, reflecting Na and K as the major contributor for the increase of TDS (Fig. 7d). From Fig. 7e, increase in Alkalinity corresponds to the simultaneous increase of Cl + SO_4 suggesting a common source for these ions. The increased Na content which is an index of weathering suggests that ions result from silicate weathering or dissolution of soil salts, the excess of Na + K over Cl suggests silicate weathering and also suggests the higher concentration of Alkalis is from sources and precipitation (Singh et al. 2011). The Na + K versus Total cations scatter diagram (Fig. 7f) of the study area shows most of the sample points falling below the trend line. This suggests that the cations in the groundwater might have been derived from silicate weathering.

Conclusion

In this study, an attempt has been made to evaluate the geochemical processes regulating groundwater quality in the coastal region of Kadaladi block, Ramanathapuram district, Tamilnadu, India. For this study, 36 groundwater samples were collected and analyzed for pH, EC, TDS and major ions. The order of abundance of ions are $Na > Ca > Mg > K$ and $Cl > HCO_3 > SO_4 > NO_3 > PO_4$. Geochemical facies of classification of groundwater shows most of the samples are Na–Cl type and the remaining samples are mixed Ca–Mg–Cl type. This suggests mixing of high saline water which generally indicates a strong sea water influence. The scatter plot Na/Cl shows good correlation indicating the groundwater chemistry is probably controlled by rock–water interaction. The plot of Ca + Mg/HCO_3 shows enrichment of HCO_3 than Ca + Mg suggesting both are from different sources. In addition with Piper diagram and Scatter plots, Gibbs plots were also used to understand the hydrochemical processes. In the Gibbs plots, most of the samples fall in evaporation dominance zone. Present study describes a wide range of salinity values which are noticed in the study area. This is due to the wide range of sediment permeability that occurs in the coastal plain may result in the incomplete flushing of the relict salinity. Higher salinity of groundwater distributed within the study area may be due to mixing of fresh water with relict saline water due to a higher stand of sea level in past geological time. In addition to saline incursion, hydrochemistry is also controlled by rock–water interaction followed by the concentration of these ions by evaporation. The coastal sand dunes running parallel to coast for roughly 30 km are recharged with recent meteoric water. Hence, good quality of groundwater is restricted only to coastal dune within the study area and it is important to conserve these dunes. This is well reflected in the spatial distribution of hydrochemical facies map (Fig. 5). To further pin point the origin of the salinity, trace element and isotope studies are warranted.

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