



Assessment of hydrogeochemical status of groundwater in a coastal region of Southeast coast of India

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Abstract

A study was conducted in a coastal region of Cuddalore district of Tamil Nadu, India, to identify the hydrogeochemical processes controlling the groundwater chemistry. The major geological units of the study area are sandstone, clay, alluvium, and laterite soils of Tertiary and Quaternary age. A total of 64 groundwater samples were measured for major ions and stable isotopes. Higher electrical conductivity values indicate the poor quality groundwater along the coastal region. Saline water intrusion mainly affects the hydrochemical composition of the aquifer water reflected by Na–Cl-type waters. $Cl^- / (Cl^- + HCO_3^-)$ ratio also indicates the mixing of fresh groundwater with saline water. The results of δD and $\delta^{18}O$ analyses show that isotopic compositions of groundwater ranges from -7.7 to -2.1% for $\delta^{18}O$ and from -55.6 to -18.5% for δD . Correlation and factor analysis were carried out to find the association of ions and to determine the major factors controlling the groundwater chemistry of the region. The study indicates that ion exchange, weathering, salt water intrusion along the coast, and anthropogenic impacts are the major controlling factors for the groundwater chemistry of the region.

Keywords Coastal aquifers · Salt water intrusion · Weathering · Isotopes · Cuddalore

Introduction

The quality of coastal aquifers is controlled by the variations of hydrogeochemical processes like salt water intrusion, geogenic process (weathering, ion exchange and rock-water interaction), and anthropogenic activities (agriculture, industry and urbanization). Table 1 explains the various controls of hydrogeochemical processes in the coastal aquifers worldwide. Every part of the country has its own causative factors for the variation of groundwater quality. So, it is important

to determine the chemistry of groundwater quality for its sustainable development (Subba Rao et al. 2012). The area chosen for this study is in a such complex environment, occupied by the river Uppanar, Perumal lake, industries, and agricultural field.

Groundwater is the only dependable water resource for human consumption, as well as for drinking, irrigation, domestic, and industrial uses for many people around the world. Rapid depletion of groundwater supplies due to continuous populace growing and industrial development threatens the quality of water in many aquifers. Many researchers have stated that rapid urbanization along the coastline aquifers openly or secondarily affects the groundwater quality and quantity (Boukari et al. 1996; Lambrakis 1998; Zilberbrand et al. 2001; Foppen 2002; Faye et al. 2004). The process of assessing the suitability of groundwater for various purposes requires a proper thought on the hydrochemistry of an area. Further, it is important to understand how water–rock interaction (weathering) or any type of anthropogenic impact affects groundwater quality (Todd 1980; Kelley 1940). Much of the groundwater in coastline aquifers in India is affected from seawater intrusion due to over-extraction. However, hydrogeochemical patterns are

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Table 1 List of studies carried out worldwide on coastal aquifers

S. no.	Researchers	Year	Study areas	Controls of hydrogeochemical processes
1.	Laluraj et al.	2005	Coastal zones of Cochin, India	Influence of saline water incursion
2.	Ahmad et al.	2008	Coastal region of Oman	Saltwater intrusion and agricultural activities
3.	Carol et al.	2009	Samborombon Bay, Argentina	Salinization processes
4.	Silva-Filho et al.	2009	Rio de Janeiro coastal aquifer, SE–Brazil	Domestic wastewater and not by marine water encroachment
5.	Olufemi et al.	2010	Lagos Metropolis, Nigeria	Impact of saline intrusion
6.	Giménez-Forcada	2010	Coastal plains of Elba Island (Tuscany, Italy)	Seawater intrusion
7.	Karmegam et al.	2010	Coastal Aquifer in and around Kalpakkam, South India	Ion exchange processes, recharge processes and saline water intrusion
8.	Chidambaram et al.	2010	Portnova to Pumpuhar, southeast coast of India	Seawater intrusion
9.	Mohapatra et al.	2011	Puri city in Orissa State, India	Organic matter degradation/Fe(III) reduction and anthropogenic pollution, seawater intrusion
10.	Bhuvana Jagadeeswari and Ramesh	2012	Chennai, India	Seawater intrusion
11.	Thilagavathi et al.	2012	Coastal aquifers of Pondicherry regions	Rock weathering processes, agricultural influences and seawater intrusion
12.	Wang and Jiao	2012	Pearl River Delta, China	Ion exchange processes and mixing of seawater
13.	Mongelli et al.	2013	North-western Sardinia, Italy	Seawater intrusion and water–rock interaction
14.	Anis et al.	2013	coastal flood plain: Cap Bon, Tunisia	Seawater intrusion
15.	Fengshan et al.	2014	Coastal Region of Tangshan, China	Rock water interaction and saline water intrusion
16.	Singaraja et al.	2015	Coastal region of Thoothukudi district, Tamil Nadu, India	Seawater intrusion
17.	Barut	2015	Coastal karst aquifer, Mandalia Bay (southeastern Aegean Sea coasts)	Saline water intrusion
18.	Surinaidu	2016	Central Godavari delta, India	Seawater intrusion, dissolution of evaporites in the groundwater and ion exchange process
19.	Papazotos et al.	2016	Marathon coastal plain, Greece	Seawater intrusion, reverse ion exchange and nitrate concentration
20.	Singh et al.	2017	Tuticorin town, Southeast coast of India	Seawater intrusion due to high rate of withdrawal of groundwater
21.	Subba Rao et al.	2017	Coastal region of Andhra Pradesh, India	Rock–water interaction, sluggish drainage conditions due to influences of geogenic, anthropogenic and marine sources

complex because of the input from different water sources (Subba Rao 2006; Sanford and Pope 2010). Generally saline water intrusion in coastal regions occurs naturally, but it can be aggravated due to the exploitation of coastal aquifers as water sources (Martinez and Bocanegra 2002; Ozler 2003). In addition to the natural salinity of groundwater, anthropogenic activities contribute significantly to the deterioration of water quality (Egun 2010). Thus, the main objective of the study was to identify the factor controls the groundwater chemistry in the coastal region.

Study area

The study area is situated in a coastal region of Cuddalore district, Tamil Nadu, India, which lies between north latitudes 11°44'34" and 11°29'59" and east longitudes 79°35'06" and 78°46'11" (Fig. 1). The region is chiefly

composed of Tertiary and Quaternary formations. Tertiary formation includes sandstone, clay, and grit sand, whereas Quaternary formation mostly covered by fluvial sediments of silt, clay, fine- to coarse-grained sand, and laterite. Tertiary formation gently dips towards east–southwest direction and it occurs at the depth of 100–457 m, and Quaternary formation occurs at the depth less than 30 mbgl (Arogyasami 1967; Sundaram 1979). In some locations, sandstones intervene with clay lenses that underlie the alluvial sand up to a depth of 50 m bgl. Soils in these regions are of oxysol type with the thickness greater than 3 m (Subramaniam 1969).

The average annual rainfall in these regions for the period 2003–2012 was about 138.70 mm. Uppanar is the major river in this region and it has developed a thick cover of alluvium with mixtures of sand, silt, and clay with the thickness varying from 10 to 15 m (Jeevanandam et al. 2006). It originates from the southern part of

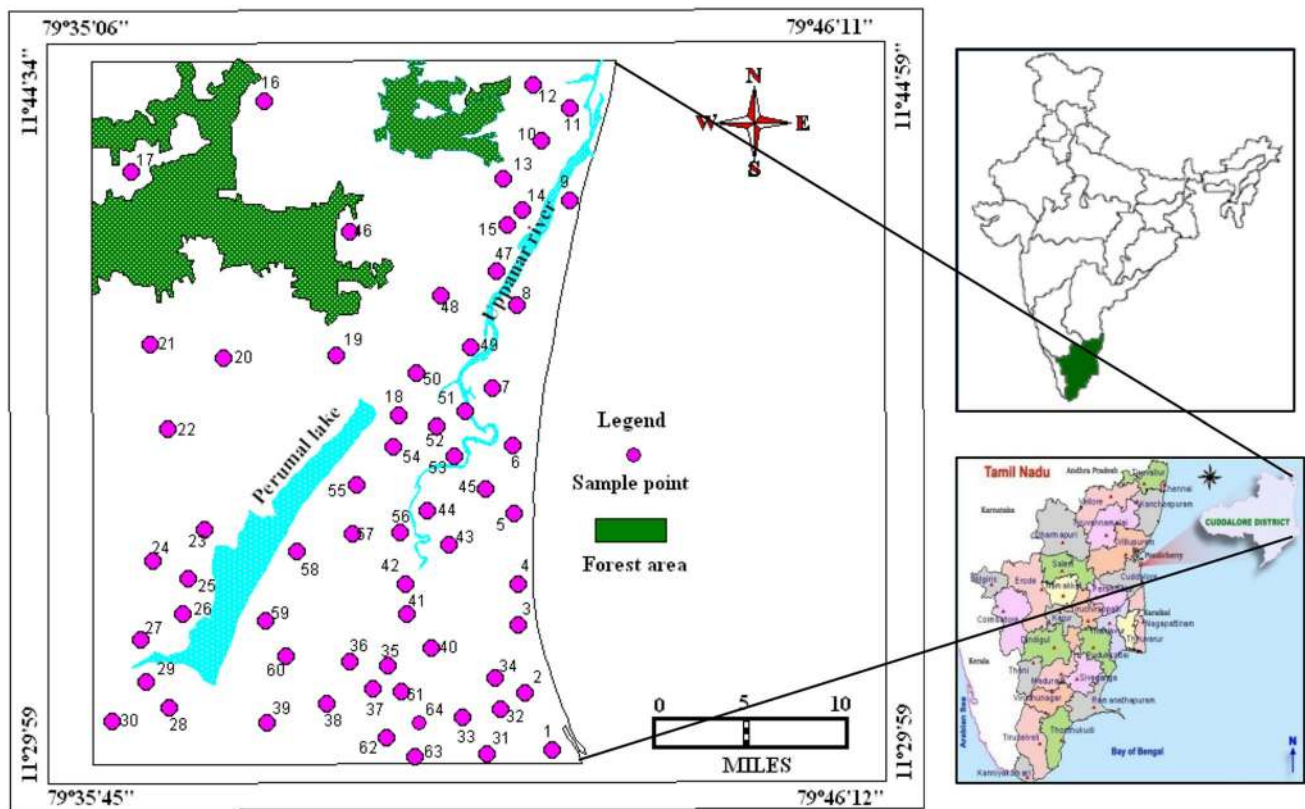


Fig. 1 Sampling location map of the study area

perumal Eri. It generally flows from south to north side and discharges into the Bay of Bengal. Subdendritic type of drainage pattern is noted in this region. The major occupation in the area is agriculture, with more than 60% of the population engaged in this activity. The study region lies in the coastline of less surface water resources. The level of groundwater development in this region is 89%, which is noted in the semi-critical stage (CGWB 2009), resulting in anthropogenic contamination by seawater intrusion. All the industries of SIPCOT (Small Industries Promotion Corporation of Tamil Nadu) are situated near the NE part of coastal region in the study area. The industries surrounding this region have continuously discharging chemicals like sulfur, lime, pesticides and it leads to the subsurface pollution in the northeastern side of the region (Sankaran et al. 2009).

The Cuddalore sandstone and unconsolidated Quaternary alluvium form the potential and principal aquifer systems in this region and it covers up to a depth of about 100 m bgl (CGWB 1997). Comparison of geoelectrical logging data (CGWB 1997) with depth-wise resistivity values at certain sites in the study area indicate discontinuous, unconfined and confined to semi confined aquifers constitute the major aquifer system in the study area.

Methodology

A total of 64 groundwater samples were collected from the study area during March 2011. The sample bottles are then labeled, sealed, and brought to the laboratory and conserved by adopting standard procedures by APHA (2005). Ca, Mg, Cl, and HCO_3 were measured by titration and SO_4 , NO_3 , PO_4 , and H_4SiO_4 were obtained by using Digital Spectrophotometer (ModelGS5 700A). Na and K were measured by flame photometer (Systronics mk-1/mk-III). The accuracy of chemical analysis was checked by computing the cation–anion balance and it is noted to be less than ± 5 to 10% (Domenico and Schwartz 1990). Oxygen ($\delta^{18}\text{O}$) and deuterium (δD) isotopes in the groundwater samples were measured with Isotopic Ratio Mass Spectrophotometer (FinniganDelta^{plus}Xp, Thermo Electron Corporation, Bermen, Germany). The standard deviation of the measurements is $\pm 1.72\%$ for oxygen and $\pm 0.8\%$ for hydrogen. The measurements of samples are periodically checked and calibrated with international isotope water standards recommended by IAEA (V-SMOW, GSIP and SLAP). The results are reported in terms of δ units (Permil

deviation of the isotope ratio from the international standard V-Smow), with δ being defined by

$$\delta = \left[\frac{(R_{\text{sample}} - R_{\text{SMOW}})}{R_{\text{SMOW}}} \right] \times 10^3,$$

where $R = D/H$ or $^{18}\text{O}/^{16}\text{O}$.

General parameters

pH varies from 5.2 to 9.8 with an average 7.1, indicating slightly acidic to alkaline nature. EC values ranged from 928 $\mu\text{S}/\text{cm}$ to 13,975 $\mu\text{S}/\text{cm}$ with an average of 4850 $\mu\text{S}/\text{cm}$ (Table 2). The spatial distribution of electrical conductivity (EC) values for groundwater samples is shown in Fig. 2. Higher EC values (> 5250 and $4250\text{--}5250$ $\mu\text{S}/\text{cm}$) occur in the north eastern and south-western region of the study area which lies along the coastline, with an aerial extent of about 116 sq km. EC values range from 3000 to 4250 $\mu\text{S}/\text{cm}$ in the central part of the region along the Uppanar river mouth, covering an area of about 104 sq km. EC values from 2250 to 3000 $\mu\text{S}/\text{cm}$ cover an area of about 95 sq km in the north western and south-eastern part of the study area followed by the ranges from 1750 to 2250 $\mu\text{S}/\text{cm}$, covering a region of about 63 sq km in north western part. EC values (< 1750 $\mu\text{S}/\text{cm}$) cover an area of about 34 sq km in western part of the study area. Overall higher values were noted in the eastern part of the study area indicating the leaching of secondary salts and anthropogenic impact by agricultural activities and aquaculture apart from sea water intrusion. This may also be due to anthropogenic impacts from an industrial estate SIPCOT (Small Industries Promotion Corporation of Tamil Nadu), which is located close to the study area. The long-term extraction of this coastal aquifer leads to the impact of the effluents generated by them.

Geochemical processes

Piper plot

Groundwater chemical data were processed on a Piper diagram (Piper 1944) to govern the compositional trends in groundwater, and this is shown in Fig. 3. This diagram indicates that samples plot in a range of hydrochemical facies, but the dominant facies observed are of Ca–Mg– SO_4 –Cl, Ca– HCO_3 , and Na–Cl types. Groundwater in the study area indicates a pattern of hydrogeochemical trends, which starts from a Ca–Mg– SO_4 –Cl type via Na– HCO_3 type to Na–Cl type; or from Ca– HCO_3 type directly to Na–Cl type (Fig. 5). The path of mixing/migration of the groundwater composition (evolutionary path) with the seawater/end solutions can be obtained (Varma et al. 1996) from the Piper plot.

The effect of mixing of groundwater and its behavior on the Piper plot is well explained by Karmegam et al. (2011) and Singaraja et al. (2012). The observed pattern of compositional change suggests that cation exchange reactions are taking place when saltwater intrusion occurs (Jeen et al. 2001; Richter and Kreitler 1993). Most of the groundwater samples indicated a chemical composition dominated by sodium and chloride ions, which usually specifies a strong seawater influence (Pulido-Leboeuf 2004). The Ca– HCO_3 type of water probably signifies the partly flushed water or confined saline water source, in which HCO_3 is higher than the alkaline earth cations (Ca + Mg) in equal concentrations (Mercado 1985). This is more prominent in Alluvial aquifer due to frequent flushing or recharge of groundwater. These excess HCO_3 ions release the alkali ions (usually Na^+) which enter into the groundwater by ion exchange processes (Jeen et al. 2001), whereas it results in the domination of Na^+ in groundwater.

Chadda's hydrogeochemical process evaluation

Generally, anionic composition of groundwater changes systematically from bicarbonate dominance to chloride dominance as groundwater flows from a recharge zone to a discharge area (Appelo and Postma 1996). The factors that influence the change of chemical composition of groundwater can be investigated graphically by plotting the difference in milli equivalent concentrations between alkaline earths (calcium + magnesium) and alkali metal elements (sodium + potassium) on the x -axis and the difference in milli-equivalent concentrations between weak acids (bicarbonate) and strong acids (chloride + sulfate) on the y axis (Fig. 4). Samples falling in Field 2 (Ca–Mg–Cl) are prominent between western side of the region and the coastal region possibly represents ion exchange reactions or an hydrochemical evolutionary path from Ca–Mg–Cl type water to Na–Cl mixed sea water, whereas Ca–Mg–Cl represents the reverses ion exchange processes. Samples represent Na–Cl type in Field 3 indicates the sea water mixing, which are mostly constrained in the coastal region and recharge characteristics was noted in Field 1.

Relationship of $\text{Cl}^-/\text{HCO}_3^-$ ratio

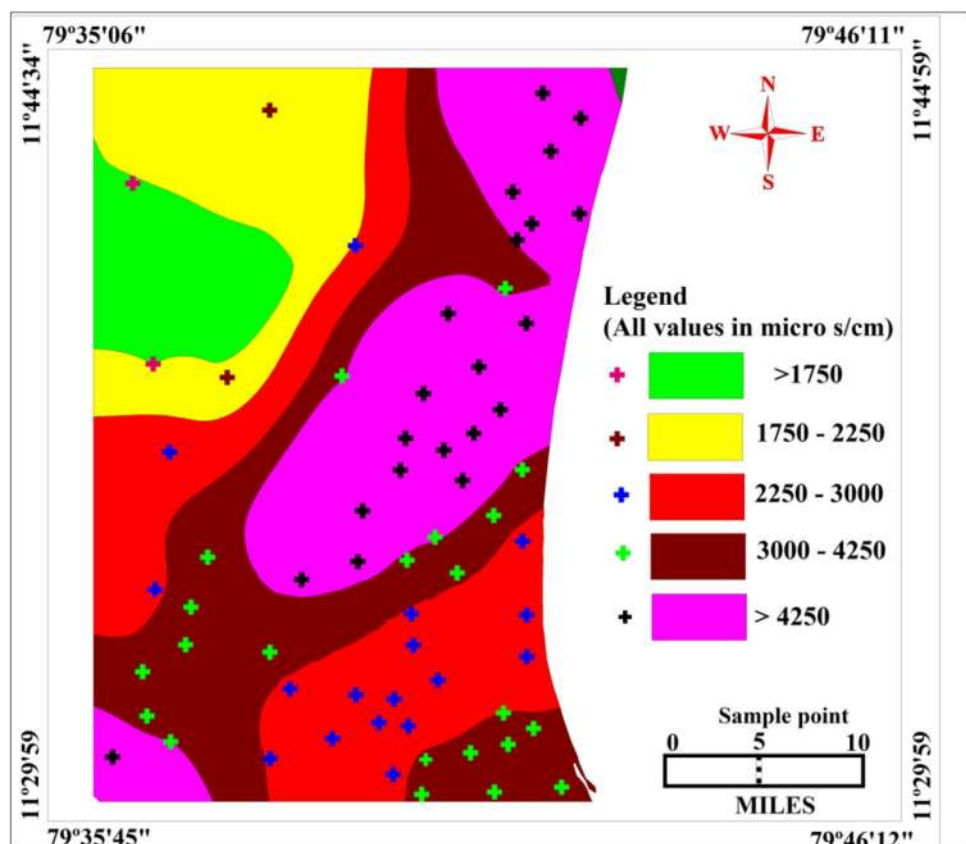
The $\text{Cl}^-/\text{HCO}_3^-$ ionic ratios were also studied to characterize the origin of salinity in groundwater. Ionic ratios of groundwaters are often used to assess the seawater intrusion in coastal regions (Sanchez-Martos et al. 1999; Kim et al. 2003). As previously noted in this study, TDS is an often a good surrogate for Cl^- and thus the ratio is the good indicator of salinization due to the seawater encroachment (Nwankwoala and Judom 2011). The ratios of Cl/HCO_3 in the study area range between 0.28 and 13.47 and had

Table 2 Chemical concentrations of groundwater samples collected in the study area (all values in mg/L and except EC in $\mu\text{S}/\text{cm}$ and pH)

S. no	pH	EC	TDS	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	H ₄ SiO ₄	NO ₃	PO ₄
1	7.1	6490	4111	130.00	75.00	57.00	6.00	468.00	230.00	15.00	29.50	1.30	0.01
2	7.9	2365	1452	124.00	14.80	10.00	4.00	220.00	110.00	27.50	40.00	1.67	0.01
3	7	3085	2014	98.00	17.10	116.00	28.00	250.00	112.00	68.40	69.50	1.98	1.70
4	7.7	3465	2198	44.00	14.40	136.00	19.00	125.00	210.00	62.50	84.00	1.80	1.00
5	7.8	928	587	40.00	18.00	21.00	3.00	97.00	67.09	36.00	112.50	1.84	0.69
6	7.6	1365	857	42.00	19.50	36.00	5.00	135.00	65.00	34.50	104.00	1.69	0.23
7	6.8	7020	4452	85.00	40.00	147.00	78.00	474.00	42.70	58.00	164.00	2.40	1.17
8	6.6	4460	2798	75.00	35.00	125.00	105.00	420.00	35.00	46.00	168.00	22.15	2.20
9	9.8	4210	2598	85.00	80.80	85.00	49.00	384.00	165.00	38.40	72.00	19.18	0.01
10	6.4	4910	3125	66.00	26.00	31.00	2.00	415.00	36.60	22.70	112.50	7.90	0.01
11	7.7	10,315	6687	120.00	62.00	60.00	10.00	365.00	125.00	2.50	39.00	6.30	0.01
12	6.8	5130	3157	135.99	20.30	40.00	5.00	421.00	103.70	41.50	74.00	34.80	0.00
13	6	6070	3745	220.00	85.00	178.00	15.00	480.00	310.00	24.00	164.00	19.60	0.52
14	7.2	5580	3498	185.00	65.00	46.00	4.00	450.00	210.00	35.00	102.00	24.10	0.19
15	7.1	6700	4278	112.00	80.00	62.00	5.00	327.00	156.00	30.50	42.00	8.26	1.19
16	6.7	2600	1598	150.00	121.20	92.00	4.00	358.00	254.00	43.00	82.00	18.70	1.38
17	5.7	2215	1386	128.00	69.00	29.00	2.00	320.00	156.00	42.60	192.00	1.67	0.01
18	6.9	13,975	8949	86.00	25.60	85.00	6.00	575.00	439.20	19.50	191.00	34.40	0.01
19	5.3	1655	1047	30.00	12.00	45.00	1.00	79.00	101.00	33.50	192.00	18.60	0.23
20	5.7	1895	1250	57.99	31.00	10.00	2.00	110.00	97.60	48.30	134.00	13.00	0.01
21	5.3	1515	898	39.00	18.00	7.00	1.00	70.89	48.80	35.50	62.00	18.00	0.01
22	6.6	4885	3124	52.00	26.00	160.00	56.00	286.00	146.00	16.80	232.00	12.80	0.01
23	5.7	3100	1945	37.00	16.00	106.00	8.00	124.00	207.40	28.50	222.00	9.80	0.01
24	7.3	4360	2750	56.00	18.00	86.00	9.00	399.00	75.00	15.50	120.00	13.50	0.01
25	7.2	4185	2600	50.00	16.00	120.00	3.00	410.00	140.30	24.50	144.00	62.20	0.01
26	5.6	4960	3118	62.00	27.50	96.00	17.00	289.00	75.00	24.00	211.00	46.00	0.01
27	6.3	2370	1524	50.00	16.00	64.00	12.00	203.83	36.60	18.10	170.00	19.40	0.01
28	6	6545	4145	32.00	13.00	40.00	3.00	124.07	42.70	38.40	98.50	7.90	0.01
29	5.3	1610	998	57.00	23.00	87.00	3.00	177.20	178.00	53.00	231.00	27.70	0.01
30	5.2	11,530	7289	102.00	52.00	60.00	5.00	561.00	138.20	26.00	134.00	2.80	0.01
31	7	3105	1954	97.00	48.00	119.00	15.00	385.00	143.80	45.00	99.00	7.10	0.14
32	6.5	7090	4521	38.00	20.00	86.00	3.00	168.38	67.10	29.50	42.00	18.70	0.41
33	6.6	4295	2722	55.00	16.00	84.00	56.00	194.97	103.70	31.70	113.00	37.80	0.76
34	7	4925	3150	112.00	12.00	35.00	5.00	150.66	134.20	43.00	111.00	9.88	0.01
35	6.6	4510	2789	33.00	14.00	106.20	42.00	168.39	73.20	45.30	86.00	10.80	2.30
36	7.2	1850	1120	24.00	10.00	94.00	6.00	124.07	152.50	11.00	132.00	7.70	0.53
37	6.9	1490	899	32.00	11.00	31.00	91.00	112.00	88.20	38.10	71.00	15.10	0.01
38	6.8	1625	999	86.00	22.00	75.00	12.00	145.00	186.00	28.40	73.00	60.60	0.01
39	7.8	5240	3245	20.00	16.00	83.00	4.00	97.00	160.00	32.50	20.00	27.80	0.01
40	9.1	2315	1400	50.00	18.00	65.00	8.00	79.76	158.60	44.00	41.00	67.40	0.01
41	9.2	4150	2598	26.00	8.00	94.50	19.00	81.00	153.00	22.00	162.00	48.00	0.01
42	8.2	2405	1485	34.00	18.00	57.00	7.00	124.07	48.80	36.00	32.00	34.80	0.01
43	9.3	1745	1108	53.00	20.00	44.00	5.00	150.60	115.70	15.20	44.00	86.40	0.01
44	8.2	8250	5200	46.00	18.00	45.00	18.00	97.48	207.40	21.50	29.50	40.80	0.41
45	9.1	1730	1000	76.00	37.00	38.00	9.00	79.76	179.00	40.50	28.00	78.20	0.01
46	8.8	2320	1504	50.00	12.00	87.00	10.00	115.21	140.30	30.50	108.00	77.50	0.26
47	9.5	1500	1005	74.00	53.00	61.00	25.00	97.49	350.00	34.50	114.00	50.60	0.01
48	8.7	4475	2756	36.00	12.00	128.00	40.00	210.00	56.40	53.60	24.00	7.86	2.10
49	8.7	13240	8542	35.00	17.00	40.00	25.00	97.49	69.40	33.50	39.00	28.40	0.19
50	8.8	8615	5487	38.00	25.00	145.00	9.00	499.00	178.00	56.50	76.00	4.76	0.44

Table 2 (continued)

S. no	pH	EC	TDS	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	H ₄ SiO ₄	NO ₃	PO ₄
51	8.9	3005	1954	44.00	35.00	283.00	6.00	564.00	85.40	26.00	42.00	5.86	0.08
52	7.5	4330	2689	37.00	18.00	46.00	9.00	150.66	36.60	48.50	32.00	6.54	0.13
53	5.9	12,245	7798	68.00	18.00	66.00	9.00	125.00	87.80	56.00	99.00	37.00	0.01
54	8.1	2110	1400	38.00	17.50	66.00	13.00	82.00	123.00	25.00	46.00	41.00	1.00
55	6.1	6925	4402	47.00	18.00	97.00	3.00	159.52	134.20	69.00	103.00	19.70	0.01
56	5.7	4680	2890	48.00	18.00	115.00	38.00	186.50	95.70	39.00	101.00	31.80	0.01
57	6.5	9055	5654	41.00	20.00	129.00	5.00	221.55	152.50	49.50	141.00	8.74	0.01
58	6.7	6940	4452	48.00	22.00	54.00	3.00	212.70	42.70	10.50	40.00	4.84	0.01
59	7.2	8370	5400	30.00	15.00	216.00	5.00	407.67	146.40	15.50	30.00	3.74	0.01
60	5.9	2215	1452	28.00	13.00	245.00	8.00	274.74	439.20	4.56	70.00	2.84	0.01
61	7.7	3555	2230	29.00	16.00	141.00	12.00	168.39	158.60	28.00	44.50	28.50	0.40
62	7.5	5780	3542	37.00	19.00	40.00	3.00	141.80	97.60	15.70	103.20	10.80	2.00
63	7.8	2715	1804	49.00	23.00	174.00	5.00	325.00	48.80	6.50	71.00	7.74	0.01
64	7.5	8825	5674	68.00	27.00	136.00	3.00	524.00	132.52	15.80	430.00	23.00	0.01

Fig. 2 Spatial distribution of electrical conductivity (EC) in the study area

a strong positive direct relation with Cl⁻ concentrations (Fig. 5). It shows the mixing of fresh groundwater with saline water. Based on Cl/HCO₃ ratios groundwater can be classified into unaffected (< 0.5), slightly or moderately affected (0.6–6.6), and strongly affected (> 6.6) by salinization process. (Revelle 1941; Todd 1959). On the basis of the ratio of Cl⁻/HCO₃⁻, 84.3% of the groundwaters were

considered to be strongly influenced by the saline water, and 9.3% were slightly or moderately affected by industrial activities. Similar observations were made by Demirel (2004) to categorize the saline water intrusion by Chloride enrichment in Mersin-Kazanli coastal region of Turkey. A combined effect of seawater and urban wastewaters may also be a reason for the poor quality of groundwater, which

Fig. 3 Geochemical classification of groundwater in the study area

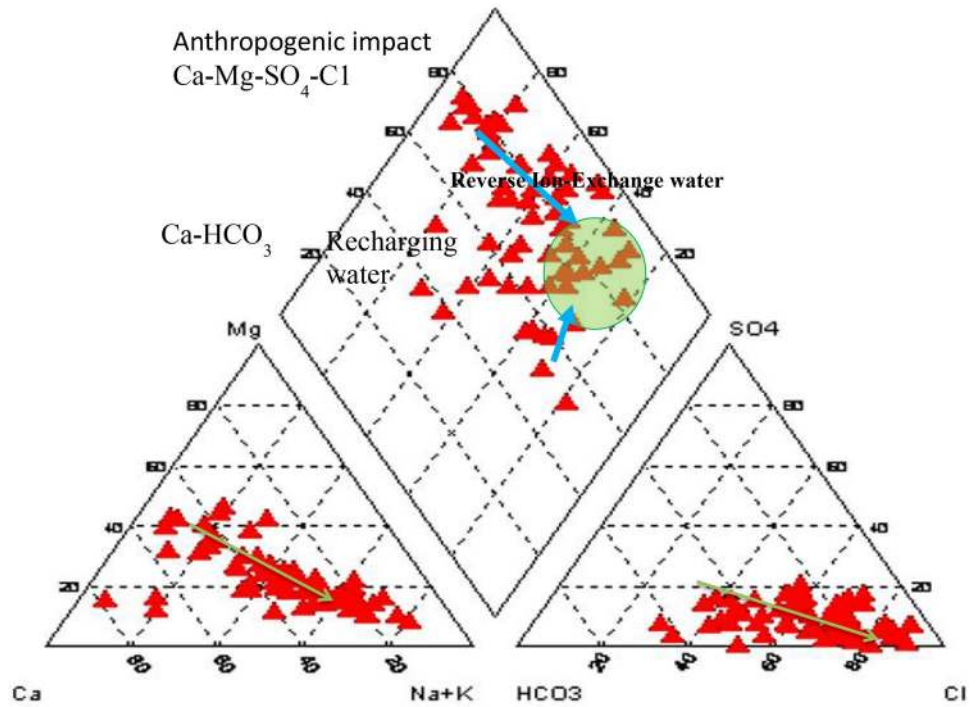
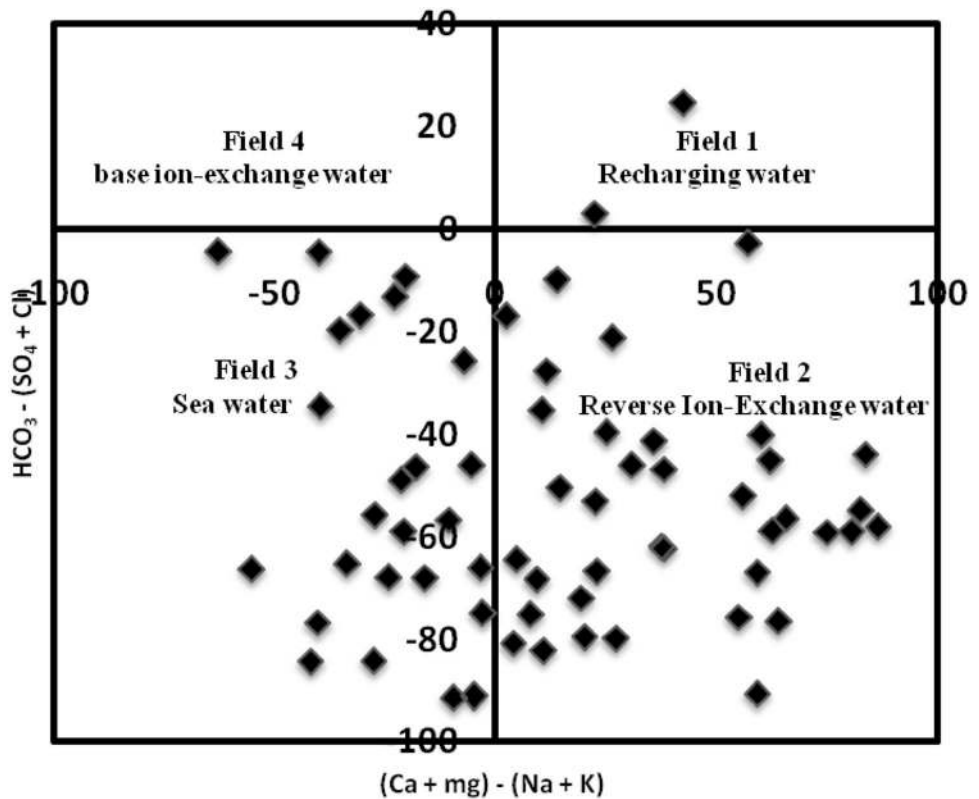


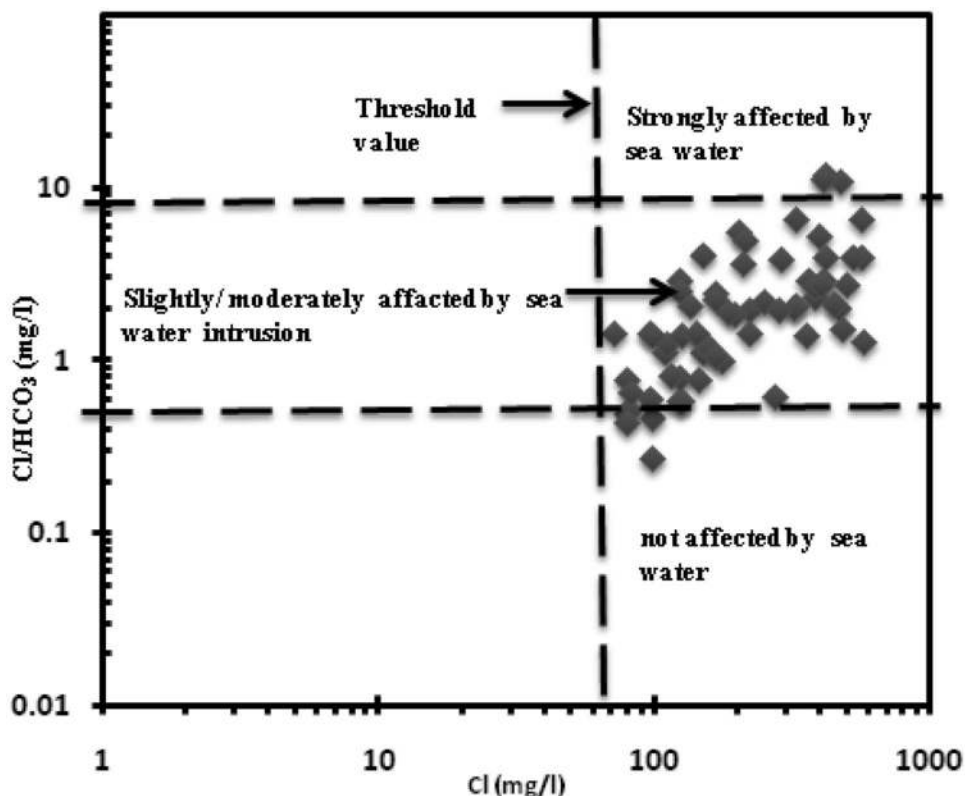
Fig. 4 Chadda's plot for groundwater samples to determine the chief chemical processes



is influenced by topographic low close to the coastal area (Subba Rao et al. 2001). It was also interesting to note that 6.2% of the samples unaffected by salinization was located near Perumal Lake in the study area, which may be due to

the dilution effect from the surface water recharged into the aquifer or lesser extraction of groundwater due to the increased usage of surface water.

Fig. 5 Relationship between $\text{Cl}^-/\text{HCO}_3^-$ vs Cl^- concentration in the study area

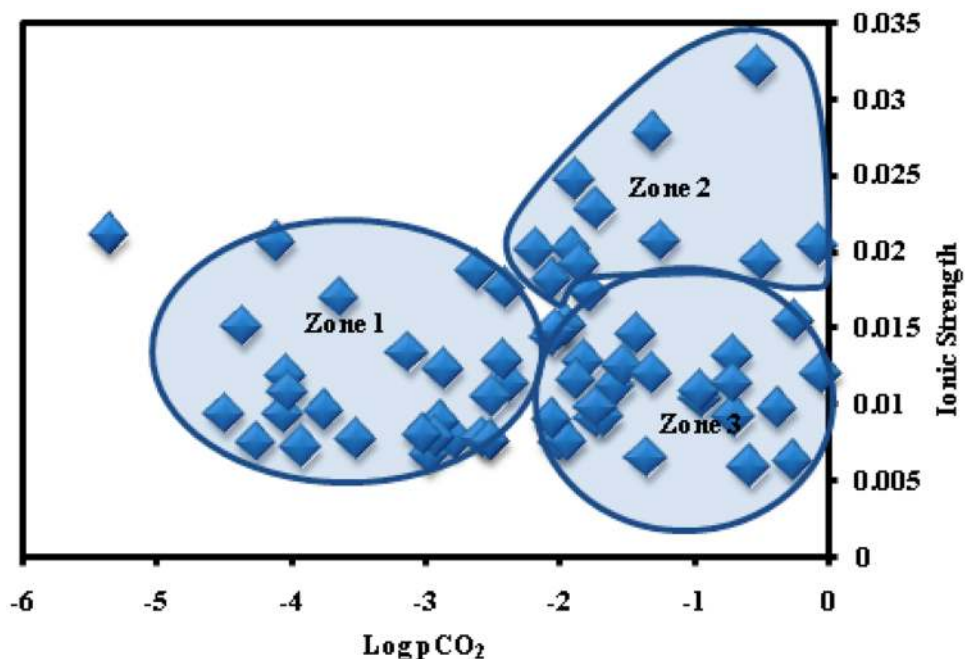


Log pCO₂

Log pCO₂ values for samples were calculated to determine the recharge processes (Prasanna et al. 2009; Raymahashay 1986). Log pCO₂ value ranges from - 5.34 to - 0.05

(Fig. 6). The distribution of the ionic strength (IS) values in the samples varied from < 0.006 to > 0.032. There is a linear relationship between IS and Log pCO₂. The increase of IS values reflects the long residence time of the saline water or due to the recharge of evaporated saline water (zone

Fig. 6 Relationship of log pCO₂ to ionic strength in the study area



2). Low ionic strength and lower Log pCO₂ values were noted in most of the samples (zone 1), which likely indicates inflow of fresh water to the aquifer (Prasanna et al. 2007). The lesser Log pCO₂ values with higher ionic strength indicate closed system (Chidambaram et al. 2011). Hence it is understood that three basic environments are prevailing in the study area: frequent flushing region/open system, may be shallow groundwaters; groundwaters of the closed environment with long residence time and sea water intrusion regions. Samples are more prominently represented in zone 1 and zone 3.

Table 3 shows an extensive research on groundwater quality and its chemistry in the coastal aquifers at different parts of the world and compared with the present study area. Results from this study show that the mean value of Ca, Mg, Na, K, HCO₃ and SO₄ is comparatively lower than the other parts of the world except few locations. Interestingly, EC and TDS mean values are higher compared to other places except at Tuticorin, India. The mean value of pH is almost same as in other places. Overall, it indicates the ionic concentration in the coastal aquifers of present study is comparatively lower than in the other parts of the coastal aquifers worldwide.

Environmental isotopes

The local meteoric water line (LMWL) for Tamilnadu state exhibits an equation of $\delta D = 7.89 \delta^{18}O \pm 10.38$ (Chidambaram et al. 2009), which is closer to the global meteoric water line (GMWL) derived by Rozanki et al. (1993). The slight variations are due to the different climatic influences which include air temperature, secondary evaporation, variation in precipitation, and moisture (Clark and Fritz 1997). The rain water isotope data for the region nearby the study area were taken from Chidambaram et al. (2009). It exhibits an LMWL (Fig. 7) of

$$\delta D = 7.6 \delta^{18}O + 3.2.$$

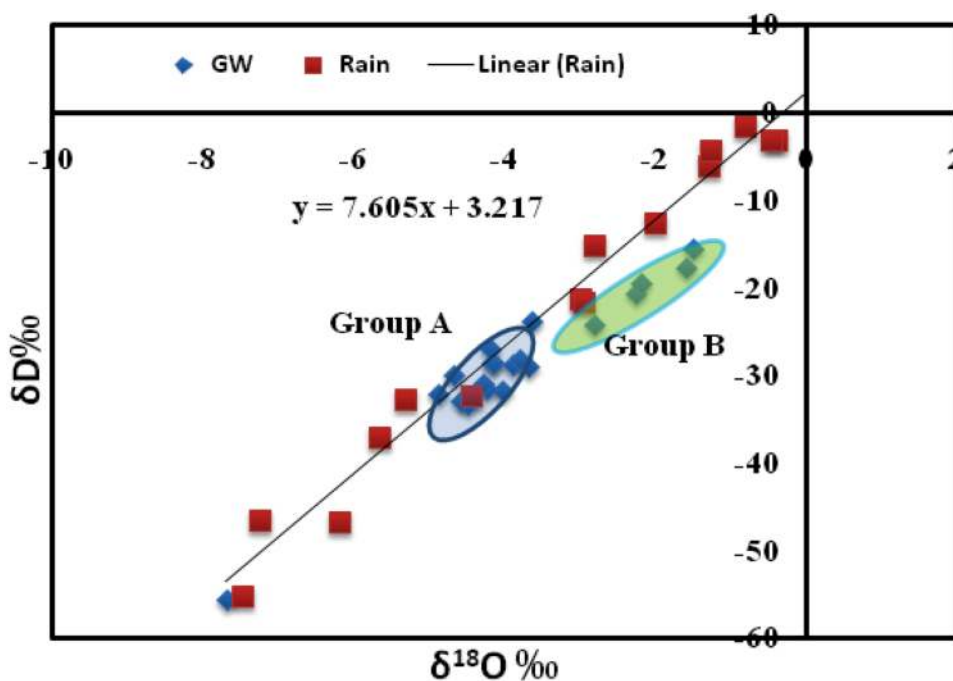
The results of δD and $\delta^{18}O$ analyses show that isotopic compositions of groundwater range from -7.7 to -2.1% for $\delta^{18}O$ and from -55.6 to -18.5% for δD . The comparison of the stable isotopes of the rain water with the groundwater samples show that most of the samples (Group A) fall in line with the LMWL indicating the recharge from the local rainfall recharge. There are few samples (Group B) indicative of evaporative enrichment/sea water intrusion. It is also observed that the heavier isotopes are more in five samples which may be due to the precipitation near the shore or that of saline water intrusion (Prasanna et al. 2009). The origin of salinization in ground water is generally distinguished by using $\delta D-\delta^{18}O$ relationship, because the stable isotope fractionation is mostly related to temperature

Table 3 Comparison of hydrochemical parameters of the present study with other areas around the world (all average values in mg/L except pH, temperature (°C) and EC (µs/cm)

S. no.	Researchers	Study area	pH	EC	TDS	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	PO ₄	SiO ₂	NO ₃
1	Lalraj et al. (2005)	Cochin, India	7.4			75.4	10.9	186.9	42.7	233.9	213.6	2.1	NA	NA	NA
2	Silva-Filho et al. (2009)	SE-Brazil	6.1	453.5		27.7	10.1	56.5	11.6	68.1	100.3	28	NA	NA	NA
3	Olufemi et al. (2010)	Lagos Metropolis, Nigeria	6.4	778.3	389.2	89.5	NA	226.1	98.8	60.7	NA	37.9	0.02	NA	NA
4	Karmegam et al. (2010)	Kalpakkam, India	7.5	1185	594.5	38.9	41.7	126.8	7.3	178.4	314.8	7.3	0.67	NA	NA
5	Chidambaram et al. (2010)	SE coast of India	7.5	1373.1	1366.1	92.7	30.1	101.3	28.5	226.3	270.3	55.8	NA	NA	NA
6	Bhuvana Jagadeeswari and Ramesh (2012)	Chennai, India	7.2	NA	1120	67.5	24.7	316	10.9	315	276	111	NA	NA	13.6
7	Wang and Jiao (2012)	China	7.0	NA	NA	286.8	265.2	2551.5	82.8	5200.8	361.3	NA	NA	NA	193.9
8	Mongelli et al. (2013)	NW Sardinia, Italy	7.4	3092	3.7	114	128.4	594.5	30.8	1037.2	220.8	334.9	NA	NA	21.6
9	Anis Chekirbane (2013)	Cap Bon, Tunisia	5.7	2748.1	NA	160.9	38.6	551.5	38.6	759.8	419.8	156.3	NA	NA	129.6
10	Subba Rao et al. (2017)	Andhra Pradesh, India	7.8	2686.1	1745.8	48.6	80.9	399.1	29.3	623.3	429	NA	NA	NA	51.8
11	Singh et al. (2017)	Tuticorin, India	7.6	5158.3	3301.3	266.3	170	578.3	45	1110.9	326.6	806.7	NA	NA	20.8
12	Present Study	Cuddalore, India	7.1	4767.4	3015.6	65.2	28.5	86.9	15.6	247.4	135.3	32.9	0.3	102.9	22

NA not available

Fig. 7 Plot for $\delta^{18}\text{O}$ versus δD of groundwater samples



(Kendall and McDonnell 1998; Huddart et al. 1999). Group B samples also show that there is an end member of isotopic composition indicating sea water intrusion. It is evident that there is a clear mixing noted in between meteoritic samples and the sea water end member.

Relationship between $\delta^{18}\text{O}$ vs EC and Cl^-

The relationship of the stable isotopes with the groundwater quality in this region was studied by plotting $\delta^{18}\text{O}$, δD , EC, and Cl^- . Figures 8 and 9 show the connections

amongst $\delta^{18}\text{O}$ and EC, and Cl^- , respectively. The comparison of δD and EC shows that most of the samples (Zone I) fall in recharge region; the six samples (Zone II) fall in other sources of the region and five samples (Zone III) are indicative of seawater intrusion. So it indicates that during the mixing of fresh groundwater and highly mineralized brine, the water quality and $\delta^{18}\text{O}$ value rise with the quantity of the mixing waters. In zone III, it is evident that $\delta^{18}\text{O}$ increases with a linear logarithm relationship with Cl^- and EC in the mixing process (Dutkiewicz et al. 2000).

Fig. 8 Plot for $\delta^{18}\text{O}$ versus EC for groundwater samples

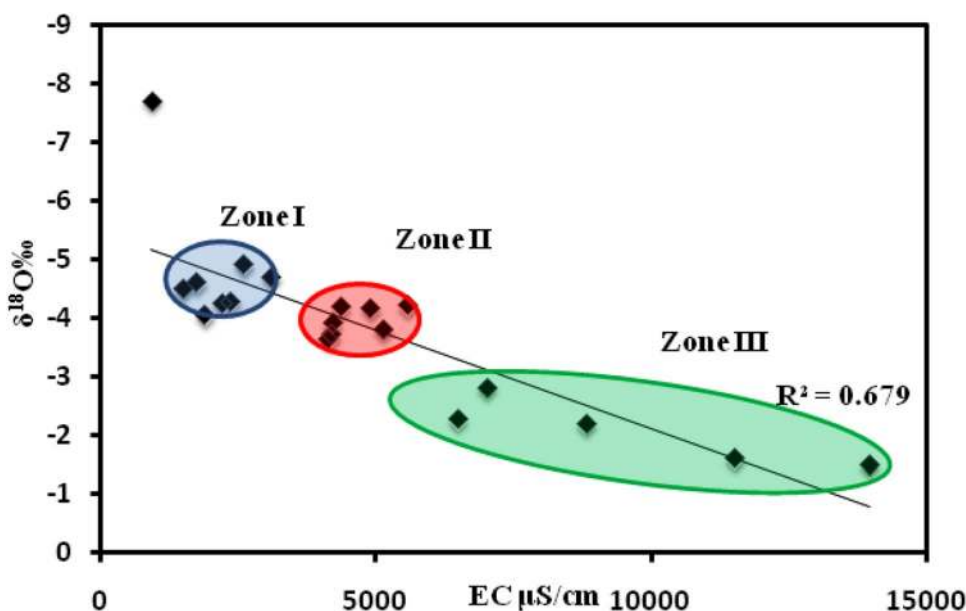
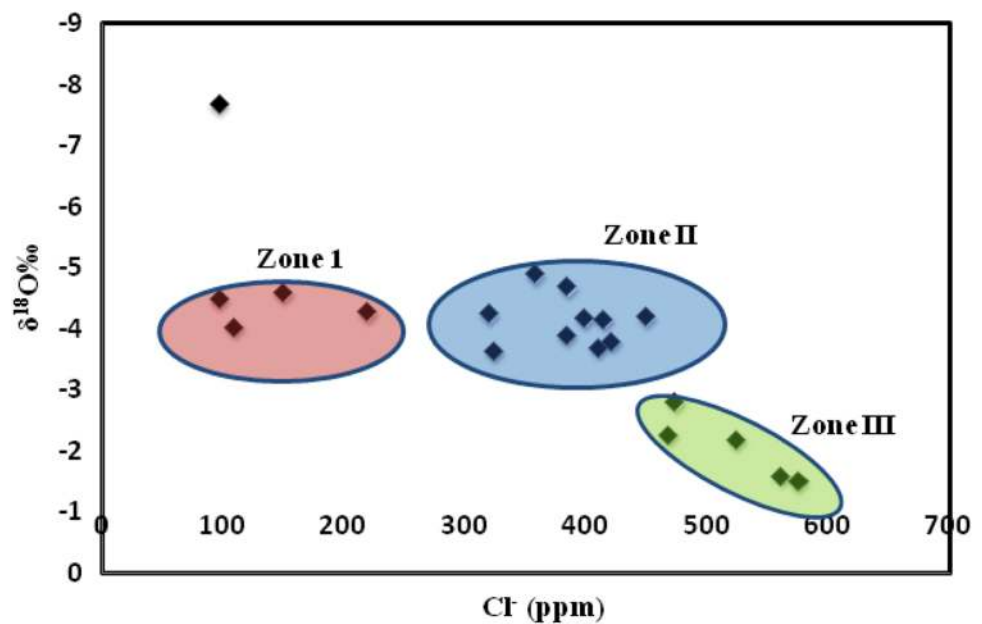


Fig. 9 Plot for $\delta^{18}\text{O}$ versus Cl for groundwater samples



$\delta^{18}\text{O}$ vs Cl diagram (Fig. 9) show similar trend to that of $\delta^{18}\text{O}$ vs EC. Relationship between $\delta^{18}\text{O}$ and Cl indicates the mixing trend with rainfall recharged fresh water and the sea water in Zone III samples and it is confirmed by the Cl- $\delta^{18}\text{O}$ relationship (Kim et al. 2003). In comparison with other groundwater samples, the sample numbers 1, 7, 18, 30, and 28 are enriched and noted to deviate significantly from the LMWL (Fig. 7), and also they have elevated Cl^- contents (Fig. 9). These five samples which fall along the line have slope 4.01, which is lower than LMWL (7.6), and it is recognized by evaporation and/or mixing of groundwater with seawater.

Correlation analyses

Cl^- - Ca^{2+} and Mg^{2+} - Ca^{2+} ions are positively correlated (> 0.5), which indicates the salinization near the industrial area due to the enrichment of some salts (CaCl_2 , MgCl_2 , and Na_2SO_4) including halite and gypsum. Then less significant correlation (0.3–0.5) was noted between Cl^- - Na^+ , Mg^{2+} ; HCO_3^- - Ca^{2+} , Mg^{2+} ; PO_4^{2-} - K^+ , SO_4^{2-} . Generally, almost all ions have a positive correlation with Cl^- , especially Ca^{2+} and Mg^{2+} (Table 4), revealing the derivation from similar source of salt waters (Kim et al. 2003). This correlation also signifies dissolution and leaching of secondary salts, with a significant correlation of HCO_3^- with Ca^{2+} , Mg^{2+} , PO_4^{2-} , K^+ , and SO_4^{2-} . Hence there may be interplay of the saline water intrusion and the leaching of the salts. NO_3^- , PO_4^{2-} , SO_4^{2-} , and H_4SiO_4 are poorly

Table 4 Correlation matrix for groundwater the chemical constitution present in groundwater of the study area

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HCO_3^-	NO_3^-	PO_4^{2-}	SO_4^{2-}	H_4SiO_4	pH
Ca^{2+}	1										
Mg^{2+}	0.749	1									
Na^+	-0.111	0.004	1								
K^+	-0.056	-0.007	0.166	1							
Cl^-	0.519	0.495	0.438	0.057	1						
HCO_3^-	0.317	0.336	0.263	-0.167	0.203	1					
NO_3^-	-0.072	-0.137	-0.171	-0.026	-0.299	0.145	1				
PO_4^{2-}	0.013	0.082	0.12	0.422	-0.004	-0.147	-0.202	1			
SO_4^{2-}	0.032	-0.018	-0.1	0.233	-0.175	-0.159	-0.069	0.303	1		
H_4SiO_4	0.078	0.008	0.115	0.077	0.255	0.1	-0.034	-0.096	-0.049	1	
pH	-0.14	-0.013	0.042	0.05	-0.101	0.055	0.367	0.05	-0.076	-0.395	1

correlated with other ions, indicating the individual complex processes (Briz-kishore and Murali 1992).

Factor analysis

Five factors were extracted with 75.29% of total data variability (TDV). Factor 1 represents Na^+ , Ca^{2+} , Mg^{2+} , and Cl^- (Table 5), which indicates the prevalence of reverse ion exchange induced by seawater intrusion (Kim et al. 2003). Factor 2 was characterized by K^+ , PO_4^{2-} , and SO_4^{2-} showing that anthropogenic signature comes from fertilizers. Factor 3 represented by Na^+ and Cl^- indicates the saline water intrusion to the aquifer increases the concentration of these ions. Factor 4 characterized by H_4SiO_4 indicate silicate weathering. The study area is principally consisting of alumino silicates, which undertake weathering and discharge silica into the solution. Poor representation of Ca^{2+} and HCO_3^- in this factor is due to the enrichment of silica by the precipitation processes of carbonate minerals from the system. Factor 5 is heavily loaded by NO_3^- indicating the impact of nitrate fertilizer. Nitrate is also probably the most wide-spread contaminant in groundwater which originates from both urban as well as agricultural activities (Nkotagu 1996; Stigter et al. 1998; Zilberbrand et al. 2001; Perez et al. 2003; Min et al. 2003). Hence, it is inferred that the reverse ion exchange, anthropogenic influence, and the sea water intrusion play a major role in determining the groundwater chemistry of the region.

Table 5 Factor analyses for the chemical composition of groundwater in the study area

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Ca^{2+}	0.93	0.00	-0.10	0.09	-0.01
Mg^{2+}	0.91	0.04	0.03	-0.07	-0.04
Na^+	-0.05	0.11	0.90	0.03	-0.05
K^+	-0.07	0.79	0.21	0.09	0.10
Cl^-	0.59	-0.03	0.57	0.17	-0.24
HCO_3^-	0.45	-0.23	0.35	0.07	0.45
NO_3^-	-0.11	-0.07	-0.18	-0.07	0.89
PO_4^{2-}	0.05	0.76	0.09	-0.19	-0.21
SO_4^{2-}	0.03	0.64	-0.38	0.07	-0.05
H_4SiO_4	0.03	0.02	0.18	0.89	0.12
pH	-0.06	0.06	0.16	-0.72	0.47
Eigen values	2.27	1.70	1.56	1.41	1.34
% of variance	20.67	15.45	14.16	12.85	12.17
Cumulative %	20.67	36.12	50.27	63.12	75.29

Conclusions

Groundwater is an important source of drinking water for many people around the world. In the present study, the relative concentrations of cations and anions occur in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{H}_4\text{SiO}_4 > \text{SO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{2-}$. The dominant hydrochemical facies of groundwater in the study area is $\text{Ca-Mg-SO}_4\text{-Cl}$, Ca-HCO_3 , and Na-Cl types indicating the geochemical variation along the groundwater flow path. The variation of $\log \text{pCO}_2$ and ionic strength reveals three different types of water: frequent flushing, sea water ingression, and long residence time of water in the aquifer system. δD and EC of the groundwater samples show that most of the samples fall in recharge region; six samples fall in other sources of the region and five samples are indicative for seawater intrusion. The $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$ ratios and statistical analysis reveal the fact that sea water ingression, silicate weathering, and ion exchange process govern the geochemistry of coastal groundwater in the study area.

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