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ORIGINAL ARTICLE

Hydrochemical Facies and Ionic Exchange in Coastal Aquifers of Puducherry Region, India: Implications for Seawater Intrusion

M. Sridharan[1] · D. Senthil Nathan[1]

Abstract

Purpose Salinization of groundwater by seawater intrusion is a major concern for the coastal aquifers worldwide. Seawater intrusion occurs mainly due to overpumping of freshwater and sea-level rise which causes lateral and vertical movements of seawater into the coastal aquifers.

Methods There are several methods to identify and assess the extent of seawater ingress towards land. In the present study, a hydrochemical approach is adopted to understand the status of intrusion. The ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^{2-}, and in-situ parameters namely TDS, pH, and EC were determined for 174 water samples collected both in pre- and post-monsoon in Puducherry region, India.

Results Ionic ratios such as HCO_3^{2-}/Cl^-, Na^+/Cl^-, Ca^{2+}/Cl^-, Ca^{2+}/Na^+, Mg^{2+}/Cl^-, K^+/Cl^-, SO_4^{2-}/Cl^-, and Cl^-/Br^- were calculated and correlated with total dissolved solids (TDS) to evaluate seawater intrusion. The ionic ratios such as HCO_3^{2-}/Cl^-, Ca^{2+}/Cl^-, Mg^{2+}/Cl^-, K^+/Cl^-, and SO_4^{2-}/Cl^- vs. TDS shows negative correlation indicating salinization of groundwater. Cl^-/Br^- ratio is used to distinguish the causes of salinity in groundwater. The Hydrochemical Facies Evolution diagram (HFE-diagram) and heat maps generated out of it have been very well used to understand evolution of seawater intrusion and freshening process in the coastal aquifer to time. The majority of samples in pre-monsoon fall under the facies $Na–HCO_3/SO_4$, followed by $Na–mixHCO_3/mix SO_4$, $Mix Na–HCO_3/Mix SO_4$, and $MixNa–MixHCO_3/mix SO_4$ facies indicating direct cations exchange process, whereas, in post-monsoon, $Na–Cl$, $Mix Na–Cl$, and $Mix Ca–Cl$ facies are dominant indicating reverse ion exchange process. In the study area, five locations, viz. Ariyankuppam, Kariambattur, Kalapet, Mutialpet, and Parikalpet, fall under $Na–Cl$ and $Ca–Cl$ facies in pre- and post-monsoon which indicates consistent seawater intrusion. The hydrochemical changes that take place during seawater freshwater interaction along coastal aquifer are determined by ionic exchange.

Conclusion About 24.2% of samples in pre-monsoon and 13.5% of samples in post-monsoon show mixing of seawater. The highly negative ionic exchange values of sodium during pre-monsoon indicate increased amount of seawater fraction in groundwater.

1 Introduction

Coast is a landform where land and sea meet each other. Throughout the world, coasts are the regions thickly populated with large-scale development. In the coastal region, groundwater is major source of water supply. Coastal aquifers which hold groundwater are said to be most virgin. Its virginity is always tested by deterioration of groundwater quality. The major problem affecting quality of coastal groundwater is salinization. Salinization of groundwater is controlled by factors like seawater intrusion, rock–water interaction, over exploitation, rise in sea level, climatic changes, hydrogeological setting of the study area, salt panning, improper sewage disposal, use of chemical fertilizers and pesticides, marine formations, etc. (Nair et al. 2015; Batayneh et al. 2014; Anders et al. 2013;

✉ M. Sridharan
  msridharansri@gmail.com

1 Department of Earth Sciences, Pondicherry University, Puducherry 605014, India

Amiri et al. 2015). Among all these factors, seawater incursion is considered to be a major threat to coastal aquifers globally.

Seawater intrusion is a phenomenon caused by movement of seawater into the fresh water coastal aquifer either by natural or anthropogenic means (Christina et al. 2014). Freshwater floats over the seawater due to less density without any distinct boundary called transition zone. Due to overpumping, the decrease in freshwater level results in invasion of seawater. Overexploitation of bore wells at transition zone or at deeper depths along coast leads to salinization of groundwater (Ayolabi et al. 2013). Tsunamis, and Tidal and estuarine activities cause infiltration of seawater into coastal aquifers of shallow depth (Mondal et al. 2010a; Longe et al. 1987; Saxena et al. 2003; Lee and Song 2006; Mondal et al. 2007; Kim et al. 2008; Todd 1953). Thus, groundwater and seawater together play an important role in the hydrological system of coastal aquifers (Mondal et al. 2010a, b).

To assure safe drinking water to all living community and to save our prosperous environment, it is necessary to manage water resources. There are several methods that can be adopted for studying salinization of groundwater like hydrochemical facies evolution method (Giménez-Forcada 2014); freshwater–seawater interaction (Mondal et al. 2010a, b); isotopic techniques (Anders et al. 2013); ionic ratios (Batayneh et al. 2014; Chen and Jiao 2007); and geophysical surveys (Ayolabi et al. 2013). The main purpose of this study is (1) to understand theevolution of hydrochemical facies during intrusion and freshening phase using hydrochemical facies evolution—diagram and (2) to determine the amount of seawater incurred into groundwater using empirical hydrochemical data, by which seawater ingress into the coastal aquifers of Puducherry region can be traced out spatially and temporally.

2 Materials and Methods

2.1 Study Area

Puducherry, a union territory, lies along Coromandel coast of India between the latitudes 11°45′ and 12°03′N, and longitudes 79°37′ and 79°53′ (CGWB 2007). Enclaves of study area are bounded by Cuddalore and Villupuram districts of Tamil Nadu on north, west, and south, with Bay of Bengal on the east. It covers an area of about 293 sq. km geographically. The annual rainfall is about 1272.70 mm on an average. Topographically study area is a flat terrain with mean elevation of 15 m above mean sea level (MSL). River Gingee and River Ponnaiyar are the two major rivers run across the study area and drain into Bay of Bengal.

2.2 Geology and Hydrogeology

The study area is geologically covered entirely by sedimentary formations of marine and non-marine origin, whose ages range from Cretaceous to Recent with Archaean charnockite as basement (CGWB 2007; Table 1.). Here, the major aquifers that hold groundwater are Cuddalore sandstone, Vanur sandstone, and Ramanathapuram formation, under confined condition (Fig. 1; CGWB 2007). Groundwater is the main source of water supply for domestic, agricultural, and industrial purposes in Puducherry and is extracted by bore wells (Thilagavathi et al. 2012).

2.3 Methodology

For the current study, 175 groundwater samples were collected from bore wells covering all the lithology of Puducherry region. Groundwater samples were collected in and around Puducherry region (Fig. 2) and analyzed using standard procedures (APHA 2005). Bore wells were pumped out for 10–15 min to remove the stagnated water. Prior to sampling, polyethylene bottles were acid washed and rinsed with water to be sampled. The hydrogen ion concentrations (pH), electrical conductivity (EC), total dissolved solids (TDS), and salinity were measured in situ condition using Hanna portable water analyzer. Ions such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), sulphate (SO_4^{2-}), and bromide (Br^-) were analyzed using ion chromatography (ICS DIONEX 1100) and bicarbonate using volumetric titration (sulphuric acid method). The ionic balance error was found to be ±10%. Locations of sampling sites were identified using Garmin GPS device. The analytical results of hydrochemistry are tabulated in Table 2.

2.4 Hydrochemical Facies Evolution during Freshening and Intrusion Process

There are several types of graphical representation to understand hydrochemical characteristics and facies of water system. To understand freshening and intrusion phases than happens for a period of time in coastal aquifer, Hydrochemical Facies Evolution Diagram has been proposed by Giménez -Forcada (2010). Based on the distribution of anion and cation percentages, the process which interrupt in coastal aquifer and the stages involved during ingress/regress of sea water into the coastal aquifers can be understood. In the HFE-diagram, the abscissae indicate evolution of $\%Na^+ + \%K^+$ and $\%Ca^{2+} + \%Mg^{2+}$ in meq/L and ordinates indicate evolution of $\%Cl^-, \%HCO_3^-$ and $\%SO_4^{2-}$. As freshening and intrusion in coastal aquifers are more complex, some considerations are made,

Table 1 Stratigraphic succession of Puducherry region (CGWB 2007)

Era	Period	Formations	Lithology
Quaternary	Recent	Alluvium, laterite	Sand, clay, silts, kankar, gravels, and laterite
	Mio-Plicocene	Cuddalore formation	Pebblyand gravely and coarse grained sandstones with minor clays and siltstones with thin seams of lignite
Unconformity			
Tertiary	Paleocene	Manaveli formation	Yellow and yellowish brown, grey calcareous siltstone, and claystones and shale with thin bands of limestone
		Kadaperikuppam formation	Yellowish white-to-dirty white sand. Hard fossiliferrous limestone, calcareous sandstone, and clays
Unconformity			
Mesozoic	Upper cretaceous	Turuvai formation	Highly fossiliferrous limestone, conglomerate at places, calcareous sandstone, and clays
		Ottai claystone	Grey-to-greyish green claystones, silts with thin band of sandy limestone, and fine grained calcareous sandstone
	Lower cretaceous	Vanur sandstone	Quartzite sandstone, hard coarse grained, occasionally feldspathic, or calcareous with minor clays
		Ramanathapuram formation	Black carbonaceous silty clays and fine-to-medium grained sands with bands of lignite and medium to coarse grained sandstone
Unconformity			
Archean		Eastern Ghat complex	Charnockite and biotite hornblende gneisses

which includes ignorance of ions such as Mg^{2+}, K^+, and SO_4^{2-} because they occupy secondary position in freshwater and groundwater. As the concentration of K^+ is lesser, it is incorporated/substituted by Na^+, and hence, Na^+ is added with K^+. The concentration of bicarbonate and sulphate ions is not added up, because both the ions are present in larger concentration in freshwater.

In HFE-diagram, based on the percentage of ions, there are four major heterotopic facies, namely $Ca–HCO_3$ (freshwater), $Ca–Cl$ (salinizing water indicating reverse cation exchange reaction), $Na–HCO_3$ (salinized water undergoing direct cation exchange reactions), and $Na–Cl$ (seawater). The two major phases are freshening (FW) and intrusion (SW). When seawater ingress takes place in the coastal aquifers, hydrochemical facies evolve from $Ca–HCO_3$ facies to $Na–Cl$ facies via intermediate $Ca–Cl$ facies and other sub-facies characterizing the intrusion. This intrusion phase is associated with reverse cation exchange process stimulated by sodium rich seawater. When aquifer is recharged by freshwater, the hydrochemical facies evolves from facies $Na–Cl$ to $Ca–HCO_3$ via intermediate facies $Na-HCO_3$, and this phase is said to be Freshening phase. Freshening phase is associated with direct cation exchange stimulated by infiltration of freshwater through rainfall. The line which separates freshening and intrusion phase is designated as conservative mixing line. Freshening phase lies above the conservative mixing line, whereas intrusion phase lie below conservative mixing line.

Groundwater samples are grouped into particular hydrochemical facies based on highest percentage (greater than 50%) of both cation and anion. In addition, based on the above consideration, each of nine major heterotopic facies, viz., $Ca–HCO_3$, $Ca–SO_4$, $Ca–Cl$, $Mg–HCO_3$, $Mg–SO_4$, $Mg–Cl$, $Na–HCO_3$, $Na–SO_4$, and $Na–Cl$ facies, are further classified into four isotopic facies. For example, $Ca–HCO_3$ encompasses four isotopic facies such as MixCa–MixHCO_3, Ca–mixHCO_3, MixCa–HCO_3, and $Ca–HCO_3$. If the ion does not exceed 50%, such type of facies is defined with prefix 'mix'. Freshening and intrusion fields of HFE-diagram have been classified into sub-stages for freshening and are designated as f1, f2, f3, and f4, and FW and intrusion sub-stages are designated as i1, i2, i3, i4, and SW.

During the freshening phase, the salinized aquifer gets freshened from inland towards coast by recharge. This freshening process continues until there exist equilibrium between salinized $Na–Cl$ water and recharging freshwater. The initial sub-stage f1 is characterized by Mix Na–Cl facies followed by Mix Na–Mix Cl facies as f2 sub-stage, Mix Ca–Mix HCO_3 and Ca–Mix HCO_3 as f3 sub-stage, and $Ca–HCO_3$ as f4 sub-stage. Ultimate freshening phase is characterized by heterotopic facies $Ca-HCO_3$. Freshening hydrochemical facies evolution series indicates direct cation exchange process. An aquifer which holds completely freshwater ($Ca-HCO_3$) is salinized by intrusion of seawater through sub-stages from i1—Ca–MixHCO_3 and then to sub-stage i2—MixCa–Mix Cl, Ca–Mix Cl followed
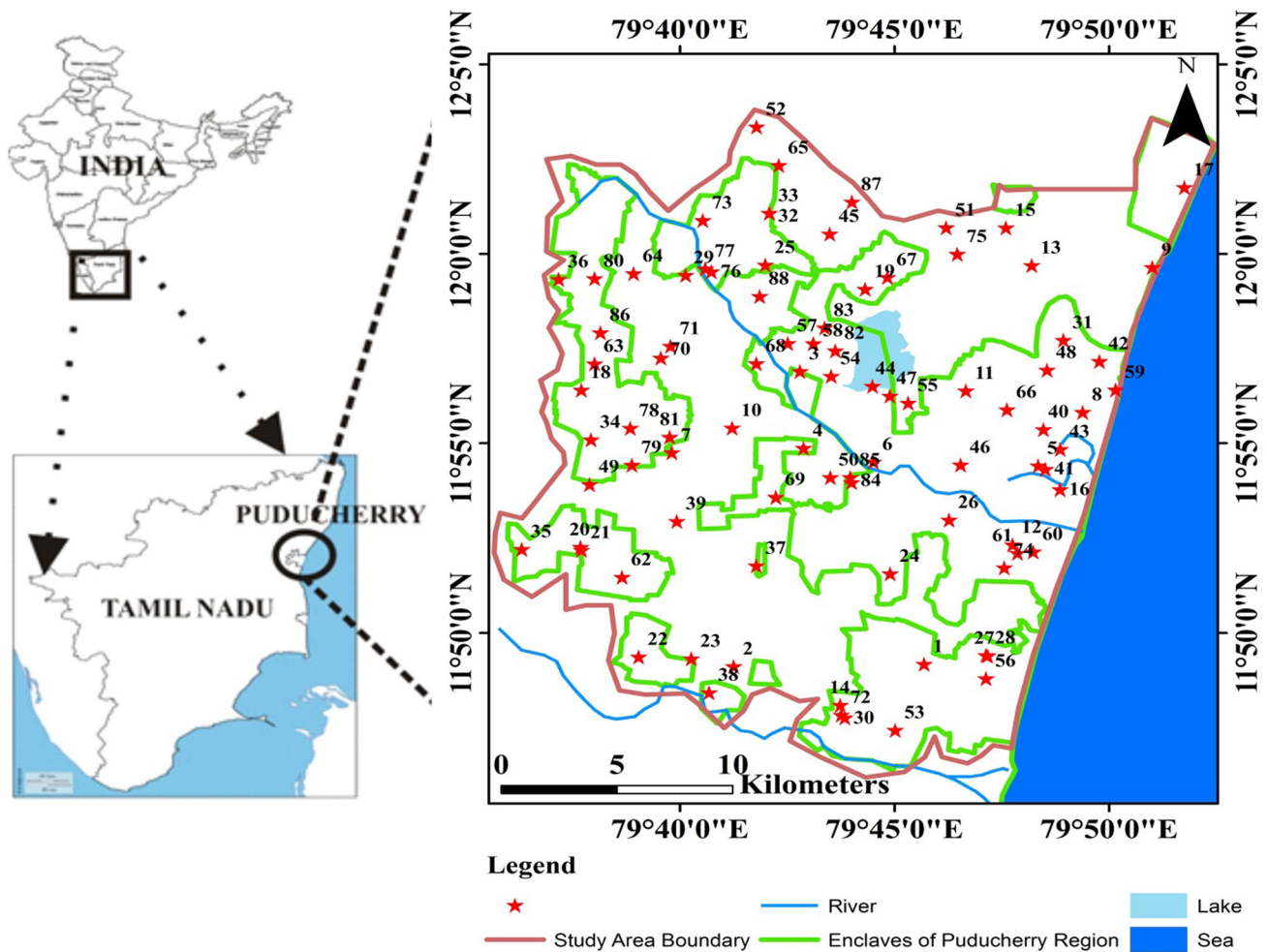
Fig. 1 Study area map with sample locations

by sub-stage i3—Mix Na–Cl, Mix Ca–Cl, Ca–Cl, and sub-stage i4—Mix Na–Cl. Finally, complete salinization is characterized by facies Na–Cl which indicates reverse cation exchange process. Each sub-stages are quantified assigning values from 1(lowest value to freshwater) to 10 (highest value to saline water). Values from 2 to 5 indicate sub-stages of freshening phase f1, f2, f3, and f4, respectively. Similarly, values from 6 to 9 indicate sub-stages of intrusion phase i1, i2, i3, and i4. Value 5.5 indicates boundary separating freshening and intrusion phases.

2.5 Ionic Changes

The groundwater along the coastal aquifers often shows fluctuations in its chemistry due to mixing of fresh groundwater and saline seawater (Mondal et al. 2010a, b; Giménez-Forcada 2014; Pulido-Lebeuf 2004; Appelo and Postma 2005). Such fluctuations can be calculated using hydrochemical ionic changes (Δ) by comparing theoretical conservative mixing values of freshwater and seawater

with measured concentration of ions in the sampled groundwater as follows:

$$\Delta C_i = C_{i\,sample} - C_{i\,mixed} \qquad (1)$$

where ΔC_i is the changes in concentration of ion i, $C_{i\,sample}$ is the measured concentration of ion i in the collected sample, and $C_{i\,mixed}$ is the theoretical concentration of ion in the mixing zone of freshwater and groundwater. The theoretical mixing concentrations of ions are determined by considering seawater contribution based on concentration of chloride ion in freshwater, seawater, and sample. Following is the expression which aids us to determine the contribution of seawater, i.e., seawater fraction in groundwater of coastal aquifers:

$$f_{sea} = \left(C_{cl,sample} - C_{cl,fresh}\right) / \left(C_{cl,sea} - C_{cl,fresh}\right) \qquad (2)$$

where f_{sea} is the seawater contribution and $C_{cl,\,sample}$, $C_{cl,\,fresh}$, and $C_{cl,\,sea}$ are the concentration of chloride ions in sample, freshwater, and seawater, respectively. Using
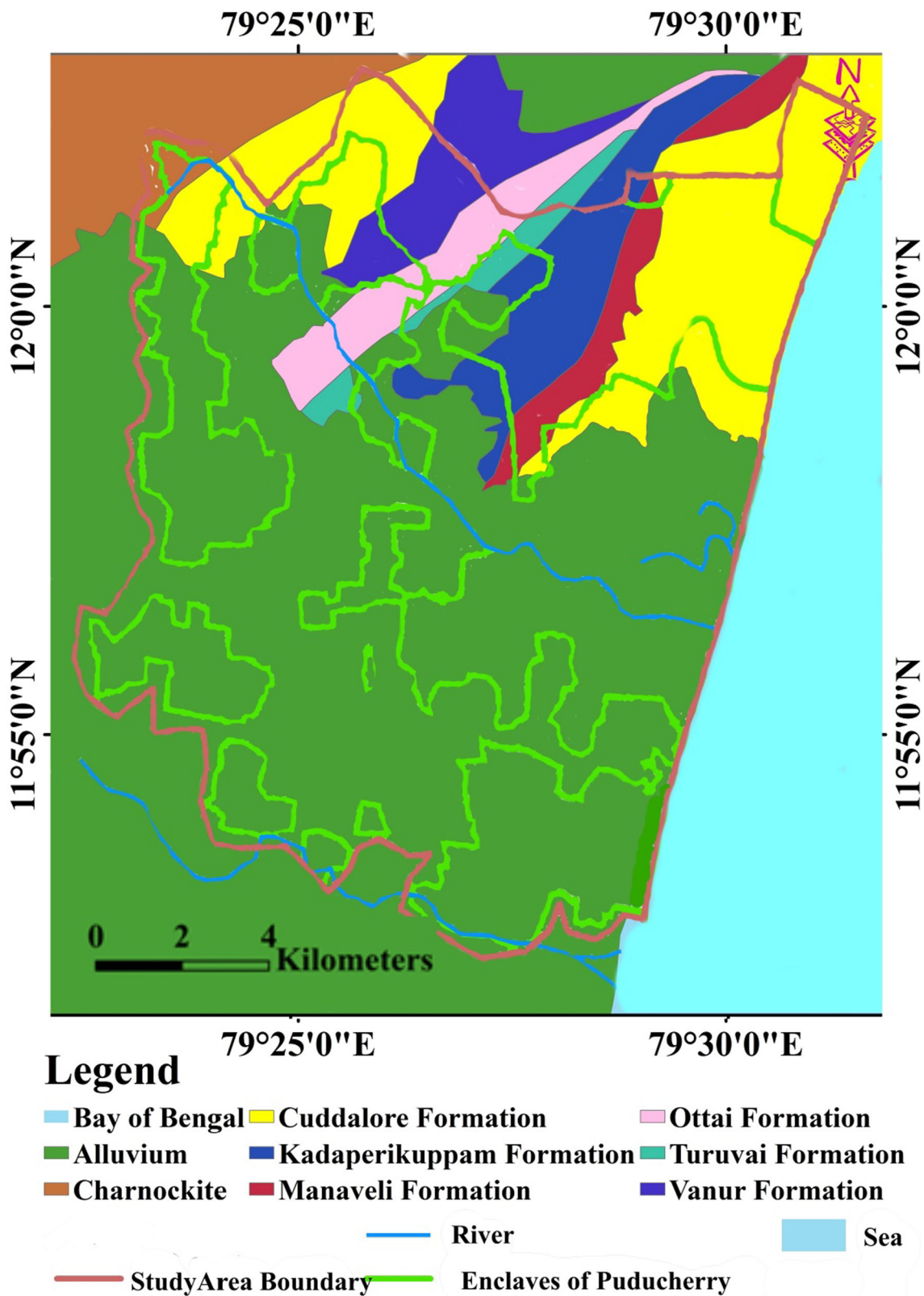
Fig. 2 Geological map of Puducherry region

Table 2 Hydrogeological properties of Aquifers in study area (CGWB 2007)

Aquifer	Aquifer condition	Transmissivity (m^2/day)	Storability	Specific yield	Porosity
Alluvial	Unconfined	275–770	–	6–15%	Highly porous (Alluvium and Cuddalore formation)
Tertiary	Discontinuous patches occur as unconfined aquifer and mainly occur as confined aquifer	1000–2000	9.583×10^{-5} to $8.9 \times 10^{-4.}$	–	
Cretaceous	Discontinuous patches occur as unconfined aquifer and mainly occur as confined aquifer	100–2000	$2.93 \times 10-5$ to $1.36 \times 10-4$	–	Highly porous (Vanur and Ramanathapuram formations)
Weathered crystalline	Occurs as unconfined aquifer in weathered mantle and semi-confined to confined aquifers in fracture	<1–5	–	1.5–2.2%	

Eqs. 1 and 2, the theoretical concentration of individual ion in the groundwater samples is determined as follows:

$$C_{imixed} = f_{sea} \times C_{isea} + (1 - f_{sea}) \times C_{i,fresh} \quad (3)$$

While determining the theoretical concentration of ions and seawater fraction in groundwater, Cl^- ion is considered as a conservative tracer element as its concentration remains stable for longer time and also its high solubility nature. The sources for Cl^- ion in groundwater may be either seawater ingress or aquifer materials or both. Here, the concentrations of ions are expressed in meq/L.

3 Results and Discussion

3.1 Ionic Ratios

For comprehensive study of seawater ingress along the coastal aquifers, ionic ratios are widely used (Batayneh et al. 2014; Barbecot et al. 2000; El Moujabber et al. 2006; Kim et al. 2003; Sanchez Martos et al. 1999). Apart from chemistry of groundwater, mineralogy of rocks can also be utilised to some extent (Nwankwoala and Udom 2011). In the current study, ionic ratios such as HCO_3^{2-}/Cl^-, Na^+/Cl^-, Ca^{2+}/Cl^-, Ca^{2+}/Na^+, Mg^{2+}/Cl^-, K^+/Cl^-, and SO^{2-}_4/Cl^- were calculated and plotted. Total dissolved solids (TDS) are very good proxy for chloride (Fig. 3c) which can be very well used to study ingress of seawater (Batayneh et al. 2014; Nwankwoala and Udom 2011; Lee and Song 2006). The ratio of HCO_3^{2-}/Cl^- in almost all the samples analyzed was greater than that of seawater ratio 0.0069. However, this ratio of samples is gradually approaching seawater ratio with increasing TDS level (Fig. 3b) indicating intrusion of seawater. Ca^{2+}/Na^+ ratio shows similar trend as HCO_3^{2-}/Cl^-, i.e., ratio shows decreasing trend with increasing TDS (Fig. 3d). It indicates that high TDS is associated with high Cl^- and higher Na^+ concentration

(Saxena et al. 2003). Na^+/Cl^- ratio does not show any correlation with TDS indicating co-existence of both the ions during event of intrusion phase (Fig. 3e; Batayneh et al. 2014). Similar to HCO_3^{2-}/Cl^- ratio, other ionic ratios such as Ca^{2+}/Cl^-, Mg^{2+}/Cl^-, K^+/Cl^-, and SO^{2-}_4/Cl^- show negative trend indicating enhancement in concentration of chloride, i.e., increase in TDS with decrease in ratio (Fig. 3f–i).

The plot $Na^+ + K^+$ vs. TDS shows very good positive correlation in pre-monsoon (PRM) when compared to post-monsoon (POM) indicating signature of salinization of groundwater (Fig. 3j; Saxena et al. 2003). $Ca^{2+} + Mg^{2+}$ vs. TDS exhibits moderate correlation in post-monsoon, whereas in pre-monsoon, it does not show any relationship (Fig. 3k). This may be due to recharge of groundwater during post-monsoon by which groundwater gets freshened.

Groundwater may acquire salinity by various means like agriculture, industries, salt panning, improper sewage disposal, domestic wastewater, ocean marine sediments, seawater intrusion, etc. Being the most conservative element, bromide (Br) and Chloride (Cl) ions are used widely as a tracer for seawater intrusion in coastal aquifers and to distinguish other modes of salinization from seawater intrusion (Fig. 3a; Table 1; Morris and Riley 1966; McCaffrey et al. 1987; Davis et al. 1998; Nair et al. 2015). These two ions do not take part in redox or adsorption–desorption reaction. The Standard Mean Ocean Water (SMOW) value of Cl/Br ratio ranges from 288 to 292. The locations having Cl/Br ratio falling closer to the SMOW line in Fig. 3a are affected by seawater intrusion. If Cl/Br ratio is more than SMOW value, groundwater salinity is considered to be influenced by domestic waste water and below SMOW value suggests the influence of agricultural waste. In the study area, 23.2 and 16.4% of water samples show signature of intrusion during pre- and post-monsoon, respectively.
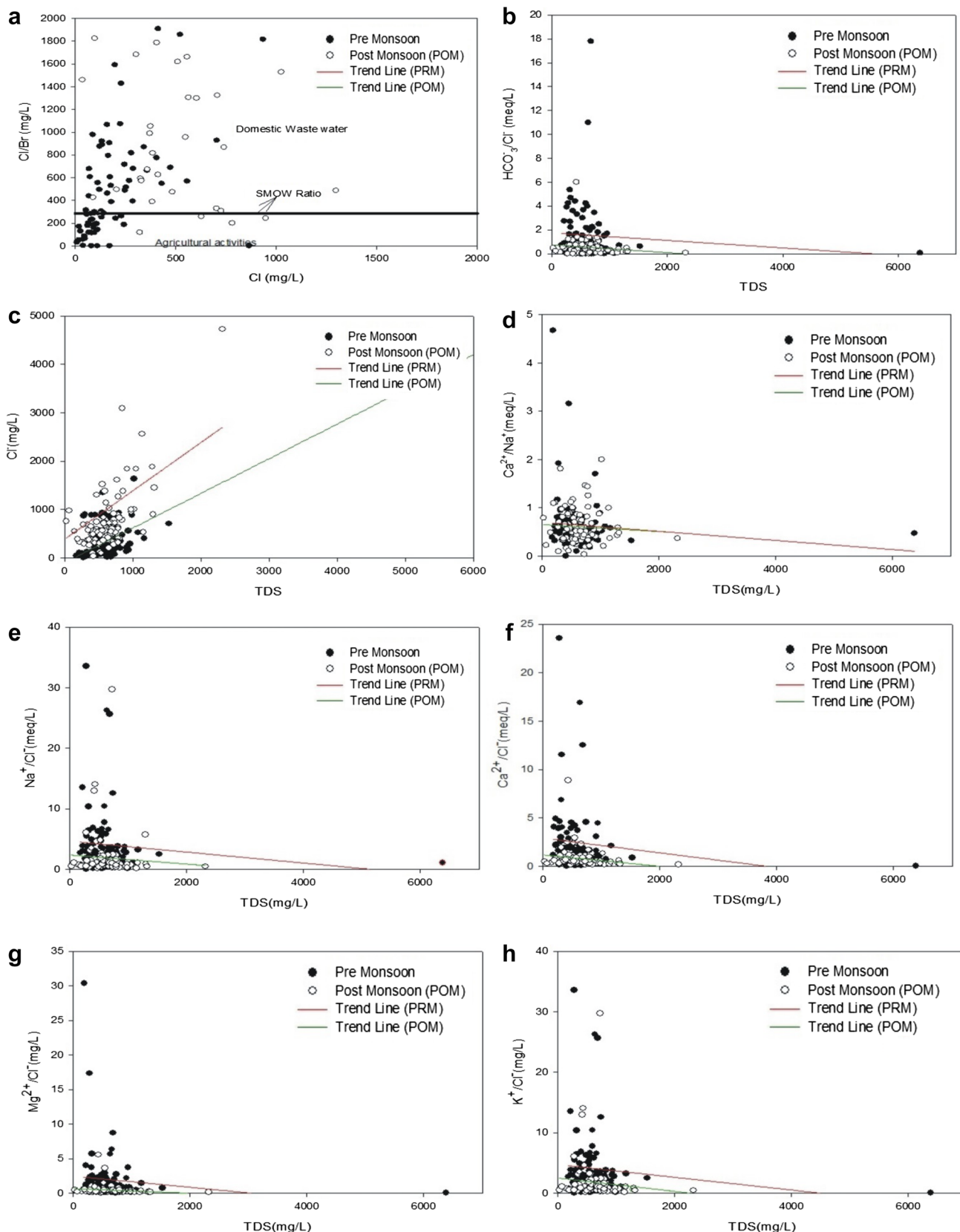
Fig. 3 a, b, c, d, e, f, g, and h ionic ratio plot with respect to TDS. i and j Ionic ratio plot of SO_4^{2-} vs. TDS and $Na^+ + K^+$ vs. TDS. k Ionic ratio plot of $Ca^{2+} + Mg^{2+}$
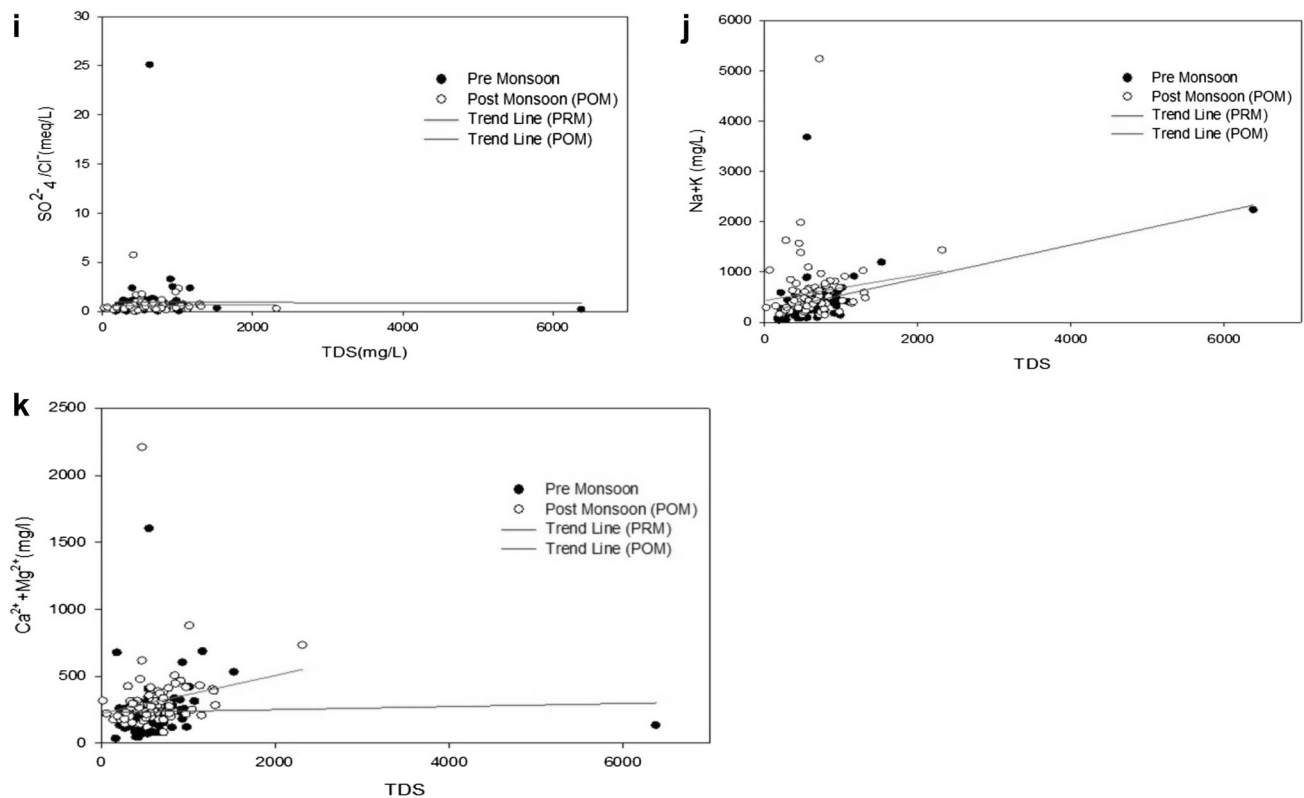
Fig. 3 continued

3.2 Hydrochemical Facies Evolution for identifying Seawater Intrusion Process

To evaluate the series of hydrochemical facies changes during intrusion and freshening processes, Hydrochemical Facies Evolution-Diagram (HFE-D) can be used to extract detailed information (Giménez -Forcada 2010).

In HFE-diagram (Fig. 4a, b), a field below the conservative mixing line (Intrusion phase) shows increase in salinity with gradual exchange of Ca by Na. Evolution of hydrochemical facies starts from $Ca-HCO_3$ facies (freshwater) to Na–Cl (seawater) facies via characteristic Ca–Cl (intermediate salinizing) facies (Giménez-Forcada 2010). Here, the exchange of Na by Ca indicates occurrence of reverse cation exchange reaction. Ca–Mix HCO_3/Mix SO_4, Mix Ca–Mix Cl, Mix Ca–Cl, and Mix Na–Cl are the hydrochemical facies of evolution during pre-monsoon. The evolution of hydrochemical facies in post-monsoon is Mix Ca–Cl, Ca–Cl, and Mix Na–Cl. About 24.1% of water in pre-monsoon and 18.8% of water samples in post-monsoon falls under intrusion field indicating reverse cation exchange process (Table 3) (Appelo and Postma 2005).

In freshening stage, above conservative mixing line in HFE-diagram (Fig. 4a, b), there will be freshening of groundwater slowly from Na–Cl facies to Ca-HCO₃ facies (Giménez-Forcada 2010). Na–Mix Cl, Na–Mix HCO_3/Mix SO_4, Mix Na–Mix HCO_3/Mix SO_4, Na–HCO_3/SO_4, Mix Na–HCO_3/SO_4, and Mix Ca–HCO_3/SO_4 are the facies achieved during pre-monsoon. Na–Mix Cl, Na–Mix HCO_3/ Mix SO_4, and Na–HCO_3/SO_4 is the dominant facies in post-monsoon. About 75.9 and 76.4% of samples fall under freshening field indicating replacement of Na by Ca indicating direct cation exchange process in pre- and post-monsoon, respectively. Samples of both pre- and post-monsoon which fall along the conservative mixing line depict that there is no base exchange reactions; instead, there occurs mixing of freshwater and seawater (Table 4) (Fig. 4a, b; Giménez-Forcada 2010).

Freshening and intrusion events of the study area during pre- and post-monsoon are brought to focus by heat maps using Arc-GIS software. Kriging interpolation method was used in Arc-GIS tool to prepare spatial distribution maps (Fig. 5a, b). Kriging method is an interpolation technique which weighs values of neighbor location and anticipates value for location where measurement is not done. Figure 5a, b shows the spatial distribution maps for seawater intrusion at Puducherry region during pre- and post-monsoon.

Spatial distribution heat map (Fig. 5b) displays the progression of seawater from sub-stage i4 (navy blue) to i1 (olive green) via sub-stages i3 (sky blue); i2 (bluish green)
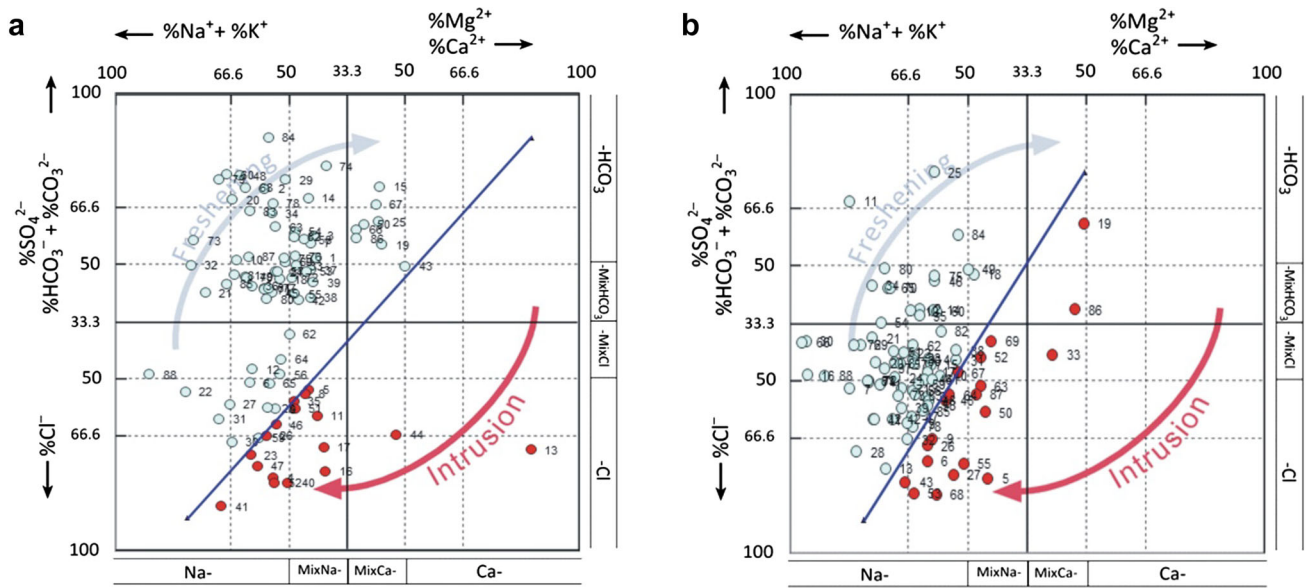
Fig. 4 a, b Hydrochemical facies evolution diagram for freshening and intrusion processes during pre- and post-monsoon

Table 3 Analytical results of hydrochemistry for pre- and post-monsoon season

Parameters	Pre-monsoon				Post-monsoon				Water from Bay of Bengal (Gurumoorthy et al. 2004)
	Min	Max	Mean	SD	Min	Max	Mean	SD	
pH	5.99	8.56	7.03	0.34	6.09	7.45	5.84	0.46	8.05
TDS (mg/L)	173	6380	1187	501.18	110	3980	1143	557.58	40860
EC (µS/Cm)	341	3080	646	668.34	110	3980	641.9	313.79	63850
Na (mg/L)	26.2	3588	34.7	39.87	120	5201	56.2	66.30	13572
K (mg/L)	ND	353	49.1	46.79	ND	417	64.09	69.19	254
Ca (mg/L)	ND	881	159.8	110.22	63	1683	6.4	184.64	238
Mg (mg/L)	7	719	76	95.38	7.4	524	2.5	60.44	918
Cl (mg/L)	8	470	360.5	579.66	35.4	2351	1009.8	2517.48	14455
SO$_4$ (mg/L)	ND	948	218.7	302.64	ND	414	10.09	525.82	2500
HCO$_3$ (mg/L)	ND	902	343.14	254.18	ND	317		39.94	–
Br (mg/L)	ND	11.57	0.516	1.23	ND	5.37	0.535	0.93	–

during pre-monsoon, but there is a small patch of area with less intense intrusion. It is due to continuous fresh water recharge by major River Sankarabarani in the study area where several check dams lie across the river and vegetative cover with less dense concrete structures facilitates the infiltration. During the post-monsoon, there is a significant regression of seawater due to precipitation and recharge, especially in the southern part of study area, while in northern and eastern part, it shows constant influx of seawater. Highly developed city, lesser recharge, industrialization, overpumping, etc., are the major factors responsible for intrusion. Though there is a significant decrease in area of intrusion in southern part during post-

monsoon, complete freshening of groundwater is lacking. In addition, the groundwater quality of this region is still identified to be influenced by ingress of seawater. Along the northwestern part of the study area, we can find hydrochemical facies showing signature of seawater intrusion but are actually due to cretaceous marine formations namely Ottai claystone and Turuvai formation. Apart from it, some chemical industries release their waste products and other effluents into the ground without treatment at Sedarapet, Karasoor, Tondamanatam, Madagadipet, etc. Apart from it, garbage dumping sites such as nearer to locations Lawspet and Perambai also shows deterioration in quality of groundwater.
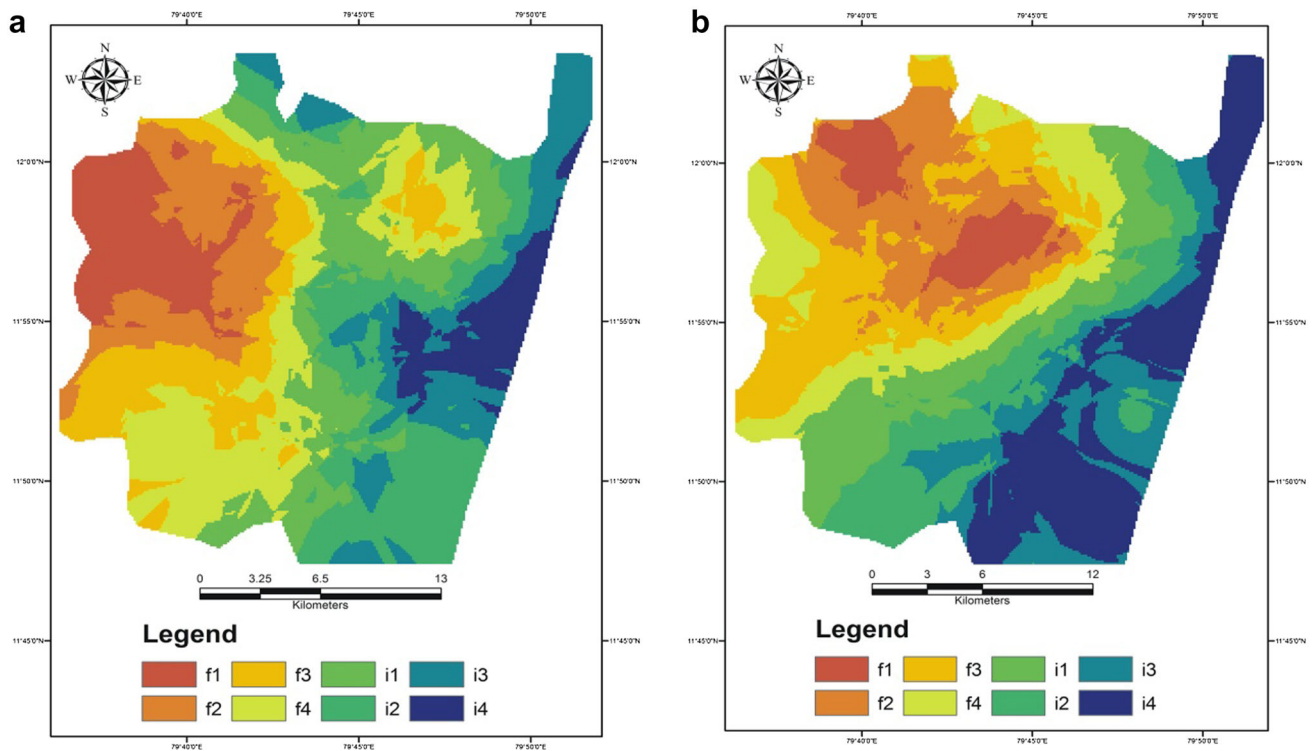
Fig. 5 **a**, **b** spatial distribution map of hydrochemical facies with respect to intrusion and freshening sub-stages in pre- and post-monsoon (f_1, f_2, f_3 and f_4—freshening facies, whereas i_1, i_2, i_3, and i_4—intrusion facies)

Table 4 Number of samples falling in each sub-stage under intrusion and freshening phases

| Sub-stage	Freshwater +f4	f3	f2	f1	i1	i2	i3	Seawater + i4	Total samples	% of samples under intrusion
Pre-monsoon	20	9	13	7	2	1	15	21	88	24.1
Post-monsoon	4	14	28	16	2	4	5	16	89	18.8

Table 5 Calculated ionic changes and seawater fraction for study area

| Ions	Seawater (meq/L)	Freshwater (meq/L)	Pre-monsoon		Post-monsoon	
			Ionic changes (meq/L)		Ionic changes (meq/L)	
			Min	Max	Min	Max
Na	1126.00	0.04	−307.19	103.39	−143.49	32.61
K	10.96	0.12	−2.48	8.96	−0.04	10.66
Ca	21.05	3.04	−3.46	40.11	−2.61	2.93
Mg	32.30	0.99	−6.53	56.72	−0.91	0.53
Cl	461.1	4.82	−0.028	0.0001	−0.01	0.0001
SO_4	45.80	0.83	−3.68	26.78	−0.36	6.07
HCO_3	1.49	5.83	−5.87	8.98	−5.87	−0.04
f Sample (%)			24.2		13.5	

3.3 Hydrochemical Ionic Changes

When freshwater (groundwater) and saline water (seawater) interact each other, there occur certain chemical reactions. Such chemical reactions can be figured out explicitly by comparing theoretical mixing values of freshwater and seawater with concentration of ions determined from collected water samples. Based on the expressions 1, 2, and 3 (given in methodology), the fraction of seawater in water samples was estimated. Ionic
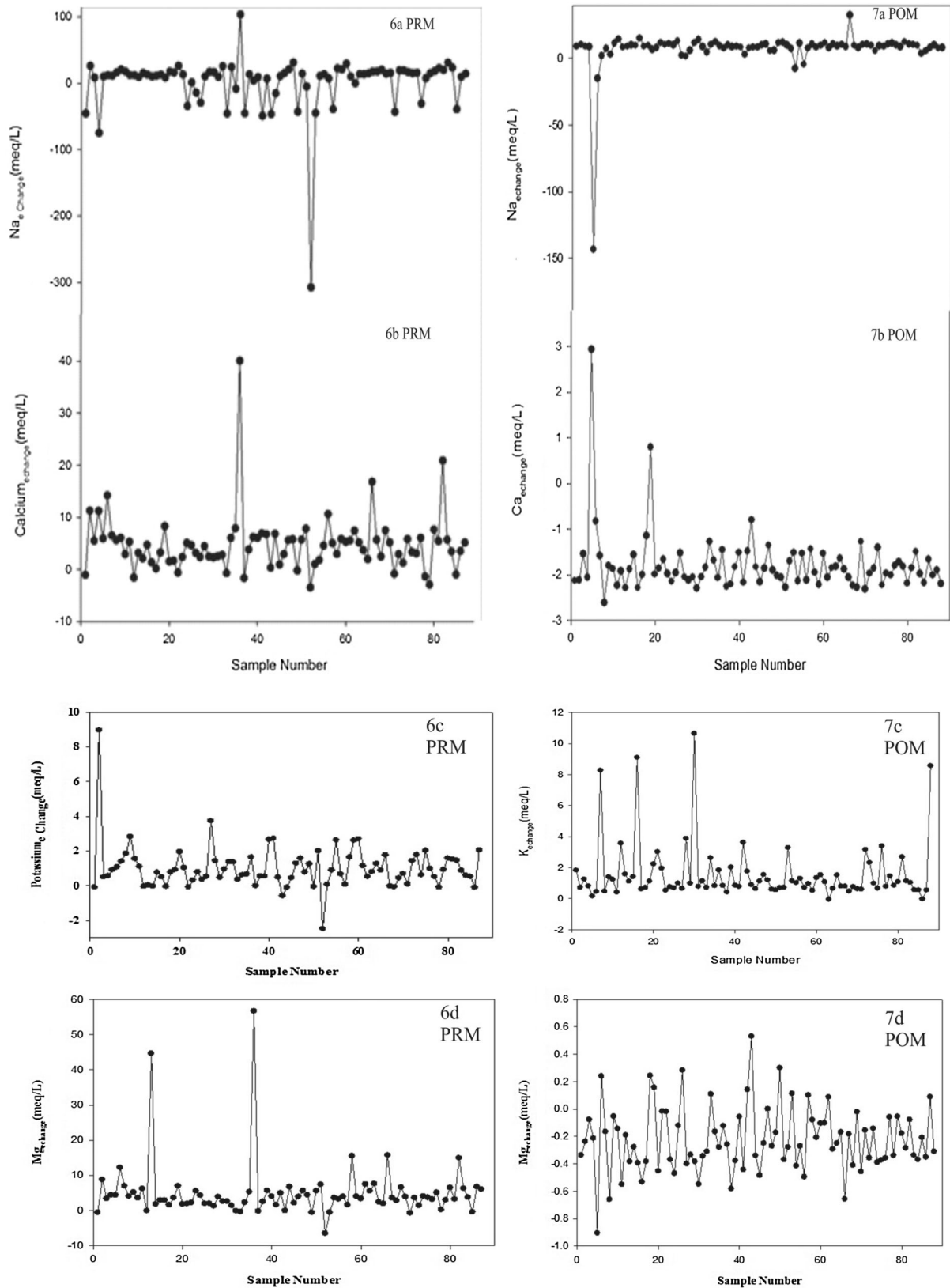
Figs. 6, 7 **Fig. 6a, b** Ionic changes plot of Na^+ and Ca^{2+} groundwater samples during pre-monsoon (PRM). **c–g** Ionic changes plot of K^+, Mg^{2+}, Cl^-, and SO_4^{2-} groundwater samples during pre-monsoon (PRM).

Fig. 7a, b Ionic changes plot of Na^+ and Ca^{2+} groundwater samples during post-monsoon (POM). **c–g** Ionic changes plot of K^+, Mg^{2+}, Cl^-, and SO_4^{2-} groundwater samples during post-monsoon (POM)
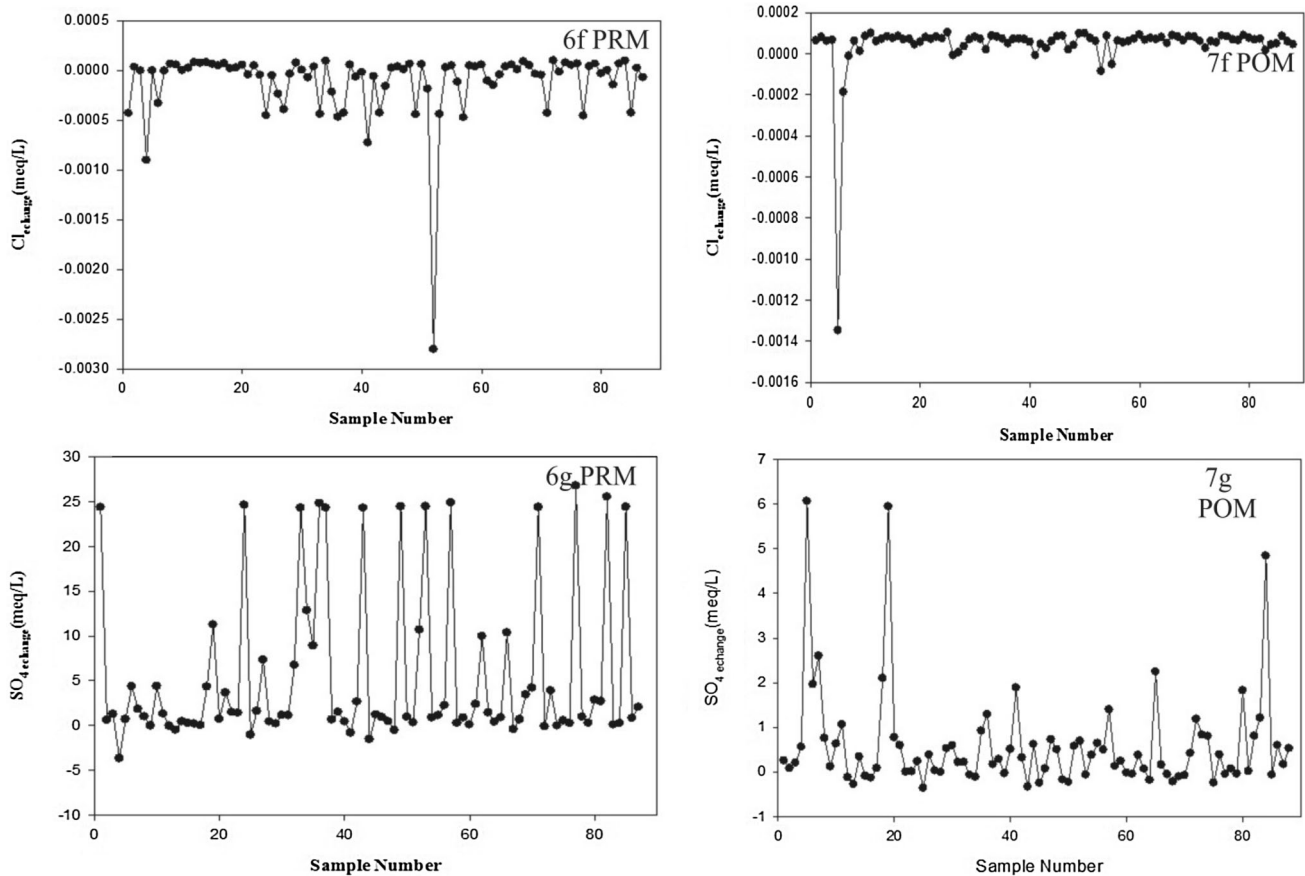
Figs. 6, 7 continued

changes were calculated for ions such as Na^+, Ca^{2+}, $Mg^{2+,}$ K^+, HCO_3^-, and SO_4^{2-} (Table 5). The average mixing rate of freshwater and seawater during pre-monsoon is 24.2%, whereas it is 13.5% in post-monsoon. The ionic change values clearly display the hydrochemical process that takes place along the seawater and freshwater mixing zone in coastal aquifers (Mondal et al. 2010a, 2010b). The hydrochemistry of groundwater along such coastal aquifers is very much intricate to study and it varies with respect to space and time (Mondal et al. 2010a).

Figures 6a–g, and 7a–g show calculated ionic change values for ions Na^+, Ca^{2+}, $Mg^{2+,}$ K^+, HCO_3^-, and SO_4^{2-} during pre- and post-monsoon. Among all the ions, sodium and calcium show a distinct pattern when compared to other ions (Figs. 6a, b, 7a, b). Such pattern is due to infuse of seawater into freshwater. Usually, the concentration of Na^+ in seawater and Ca^{2+} in freshwater is higher and so ionic change value is positive for sodium in groundwater and negative in seawater (Mondal et al. 2010a, b). However, some locations show negative Na^+ ionic exchange values for both pre- and post-monsoon. Such negative values indicate ingress of seawater. Higher sodium concentration denotes direct cation exchange process along mixing zone.

In general, the freshwater possesses higher concentration of calcium and bicarbonates due to dissolution of carbonates along the coastal aquifer (Mondal et al. 2010a). The dominant ions constituting seawater are Na^+ and Cl^- ions and the coastal aquifers showing signature of seawater ingress have Na^+ ions in aquifer materials (Appelo and Postma 2005). Seawater intrusion can be understood more clearly by the relationship between Na^+ and Ca^{2+} (Figs. 6a, b, 7a, b). The negative ionic exchange values of Na^+, K^+, and positive ionic exchange values of Mg^{2+} in samples of study area indicate seawater intrusion (Figs. 6a, c d, 7a, b, d; Mondal et al. 2010a). The ionic exchange values of sodium and potassium are highly negative and sulphate is highly positive (Figs. 6g, 7g; Mondal et al. 2010a) indicating seawater intrusion along the coast of Puducherry region.

4 Conclusion

Seawater intrusion is a major problem that exists along coastal aquifers. Puducherry is one of the coastal cities situated in the Southern East Coast of India. In the present investigation, hydrochemical techniques have been used to

study seawater intrusion in coastal aquifers of Puducherry region. The groundwater samples were collected and analyzed to understand the evolution of hydrochemical facies and ion exchange in response to seawater intrusion.

Ionic ratios are excellent tool to demarcate the areas affected by seawater intrusion. The relationship between TDS and ionic ratios, viz., HCO_3^{2-}/Cl^-, Na^+/Cl^-, Ca^{2+}/Cl^-, Ca^{2+}/Na^+, Mg^{2+}/Cl^-, K^+/Cl^-, SO^{2-}_4/Cl^-, and Cl^-/Br^- showed the signature of seawater influx along the coastal aquifers of study area.

HFE-diagram reveals that 24.1 and 18.8% of samples were affected by seawater intrusion in pre- and post-monsoon. Na–HCO$_3$/SO$_4$, Na–mixhco$_3$/MixSO$_4$, MixNa–HCO$_3$/MixSO$_4$, and MixNa–MixHCO3/Mixso$_4$ are the major facies indicating direct cations exchange process in pre-monsoon. Na–Cl, Mix Na–Cl, and Mix Ca–Cl facies are dominant facies indicating reverse ion exchange process during post-monsoon.

Heat maps generated from HFE-diagram display that there is continuous intrusion of seawater in northern and southern parts of study area both in pre- and post-monsoon. It is also identified that locations such as Ariyankuppam, Kariambattur, Muthialpet, Kalapet, and Parikalpet are intensely affected by seawater ingress. Because of urbanization, industrialization, overpumping, and lack of infiltration, the northeastern and eastern parts of the study area are intensely affected by seawater intrusion. However, along the coastal area, there are patchy zones which do not fall under intrusion facies due to freshening by river and check dams constructed across it as well as vegetal cover. Apart from coastal zones, there are locations at inland which fall under intrusion facies due to the aquifers containing sediments of marine origin, improper disposal of industrial and hospital wastes, and improper maintenance of garbage dumping sites.

Hydrochemical ionic exchange study reveals that the average mixing rate of seawater intrusion is 24.2 and 13.5% in both pre and post-monsoon. The ionic exchange values of sodium in groundwater samples were found to be highly negative in pre-monsoon when compared to post-monsoon. Similarly, negative ionic exchange values of potassium and positive ionic exchange values of magnesium and sulphate imply intrusion of seawater. Overall, the study area is found to be vulnerable to seawater ingression. To avoid major threat to life forms and other activities, regular monitoring of groundwater remedial measures is essential. Remedial measures include rainwater harvesting, afforestation, reduction in pumping, proper monitoring of waste disposal, modern agricultural practices, i.e., high productivity with less water usage, and most importantly individual awareness about the valuable asset "WATER".

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M. Sridharan has completed his post graduation studies in Applied Geology at Department of Earth Sciences, Pondicherry University, R.V Nagar, Kalapet, Puducherry-605014. Currently he is pursuing his Ph.D, in Earth Sciences. His research interests are Hydrochemisty, Sedimentology and Environmental Geology.

D. Senthil Nathan has finished his M.Sc., M.Phil., and Ph.D. His area of specialization/interest is Paleontology and Sedimentology. Currently he is Professor and Head of department, in Department of Earth Sciences, Pondicherry University, R.V Nagar, Kalapet, Puducherry-605014. He is having teaching experience of 21 years.