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THEMATIC ISSUE

Isotopic differentiation of groundwater recharge processes in a semi-arid region of southern India

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Abstract
Ensuring the availability of adequate quantity and quality of water to meet demands of domestic sector has become the prime objective for the developing countries like India. The coastal and the nearby inland region are the places of intense human activity due to urbanisation and industrialization leading to the depletion and degradation of environmental resources. The present investigation on the coastal and inland aquifers of Tuticorin, Gulf of Mannar, Tamil Nadu aims to better understand the recharge characteristics, factors controlling recharge, effect of weather parameters on recharge, source of recharge water, differences between inland and coastal recharge processes and climatic signature in groundwater isotopic composition from the hydrochemical and stable isotope data. Different mechanisms of salinization in the coastal aquifers were deduced as direct influence of the sea water and concentrations of ions by evaporation. The dissolution or leaching from the aquifer material is also imparting salinity to groundwater in this area.

Keywords Groundwater recharge source · Different recharge processes · Coastal and inland aquifers · Stable isotopes · Tuticorin

Introduction

According to Safriel and Adeel (2008), semi-arid regions cover ~ 15% Earth's terrestrial surface area. The complex climatological and geomorphological features define the groundwater dynamics in the semi-arid regions. As these regions support 14.4% of world's population, the ever-increasing demand for water turns the semi-arid regions into very critical eco-hydrological zones. Moreover, coastal areas around the globe are the most populated and urbanised areas. Exploitation of the available surface and groundwater resources are often manifold than the recharge potential of these reserves, resulting in lowering of groundwater table, making the coastal zones, and in particular those in the semi-arid regions, susceptible to seawater intrusion (Girish et al. 2013; Jesiya and Gopinath 2019a, b). In addition to the withdrawal for domestic and agricultural purposes, uncertainty in rainfall pattern and intensity disturb groundwater recharge in

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semiarid regions. The combined effect of anthropogenic and varying climatologic parameters exerts multiple pressures on semiarid regions. As per the estimates of IAEA, a major part of groundwater presently being used in the semi-arid and arid zones is fossil water, which is non replenishable (Scanlon et al. 2006). Hence to manage groundwater in the semiarid coastal regions scientifically, accurate estimates of recharge to meet the domestic and ecological requirements are necessary.

In semiarid regions, several techniques were used to determine the groundwater recharge such as physical (groundwater level fluctuation method, Darcy's Law, water budget method), chemical (tracers), isotopic (stable and radioactive) and modelling (groundwater flow models, contaminant transport models) (Lerner et al. 1990; Hendrickx and Walker 1997, Zhang and Walker 1998; Kinzelbach et al. 2002; Scanlon et al. 2002; Laluraj and Gopinath 2006; Laluraj et al. 2006; Jesiya and Gopinath 2020). Isotope techniques are extremely useful in groundwater studies in the semi-arid regions especially to determine the groundwater origin, mixing of groundwater in different aquifers, and residence time (Verhagen et al. 1991; Zhu 2000; Zhu et al. 2007; Palmer et al. 2007; Bouchaou et al. 2008; Swetha et al. 2020; Jesiya et al. 2021a, b). Isotopic differences between the different hydrological components owing to the hydrometeorological conditions form the basis of such studies. In addition to this, common salinization problems encountered in the coastal groundwater can also be delineated with isotopic techniques (Bergelson et al. 1999; Kim et al. 2003; Marimuthu et al. 2005; Schiavo et al. 2009; Jørgensen et al. 2008; Ghabayen et al. 2006; Marimuthu et al. 2005; Kim et al. 2003; Mukherjee et al. 2007; Saravana Kumar et al. 2009; Schiavo et al. 2009; Pulido-Leboeuf 2004; Carol et al. 2009; Li et al. 2008; Girish et al. 2020). Previous studies have shown that salinization in coastal aquifers can happen in many pathways such as direct ingress of sea water, from mineral salts, dissolution of evaporites, seepage from contaminated surface water, irrigation return flows often mixed with sewage, seepage of industrial/domestic effluents, deep brines or upward flow from deep saline water and fossil seawater (Pulido-Leboeuf et al. 2003; Aunay et al. 2006; Vengosh et al. 1999; Yamanaka and Kumagai 2006; Gopinath and Resmi 2011).

In India, semi-arid regions occupy 37% of the total geographical area of the country spread over in 10 states. In southern India, except Kerala, all other states have either arid or semi-arid regions. In Tamil Nadu, 95,250 km^2 (10%) is under semi-arid condition (Kalsi 2007). The Tuticorin coast, in the Gulf of Mannar is one such area in Tamil Nadu, where the fragile groundwater system is under severe anthropogenic pressure due to exploitation for human, agricultural and industrial needs. The groundwater quality of the shallow aquifers of this region has been studied extensively (Selvam et al. 2013; Mondal et al. 2011; Singaraja et al. 2014, 2018; Pandian and Sashikkumar 2013; Pandian et al. 2016; Ravindran et al. 2016) and Kumar et al. (2016) found that the groundwater potential of the area was limited. The natural groundwater velocity at a site inside the industrial complex of Tuticorin determined by borehole tracer studies indicated that velocity is 0.034 m/day (Mondal et al. 2009) and according to Rangarajan et al. (2009), only 10.6% of seasonal rainfall recharged the groundwater system. Hence, this paper focuses on stable isotopic variations of hydrogen and oxygen in groundwater from open well, tube well and bore wells from the coastal and inland aquifers, rainwater, river water and seawater to better understand the groundwater–seawater interaction in the of Tuticorin district.

Study area

Geological and hydrogeological setting

Tuticorin coastal belt, which is part of the Gulf of Mannar Biosphere Reserve, is an Ecologically Sensitive Zone (Environmental Information System 2008) and consists of highly productive ecosystems of great biological diversity. The study area is located in the Tuticorin district of Tamil Nadu state in India (Fig. 1). The region has a total area of 980 km^2, with Veppilodai in the Northern end and Tiruchendur on the southern tip. The eastern side of the study area comprises of Tuticorin port which formulates one of the major ports in India, being the same it attracts a major population settle across this coast. Thamaraibharani River drains into the Bay of Bengal through the study area resulting in the formation of a deltaic region in the same. The area is famous for its salt pans, and, all along the coast numerous private and Govt owned saltpans are present.

The geological units in the study area are fluvial sediments /fluvial marine deposits along the coast, pink and grey granite/pegmatite, charnockite, Hornblende Biotite Gneiss in the consolidated formations (Fig. 2). The coastal areas are prominent in marine geomorphic units, which comprises of most of the saltpans in the area. Black Cotton soil with isolated red soil patches in high ground covers the district in the west. The sandy soil is present in the alluvial coastal tract. Alkaline and saline soils are also noticed at places. The number of red sandy tracts formed of the sand dunes locally known as Teri sand complex is the important feature in the coast (CGWB 2009).

Climatic and hydrological background

Major part of precipitation received in the area is during the northeast monsoon season by the cyclonic storms caused due to the depressions in Bay of Bengal. The

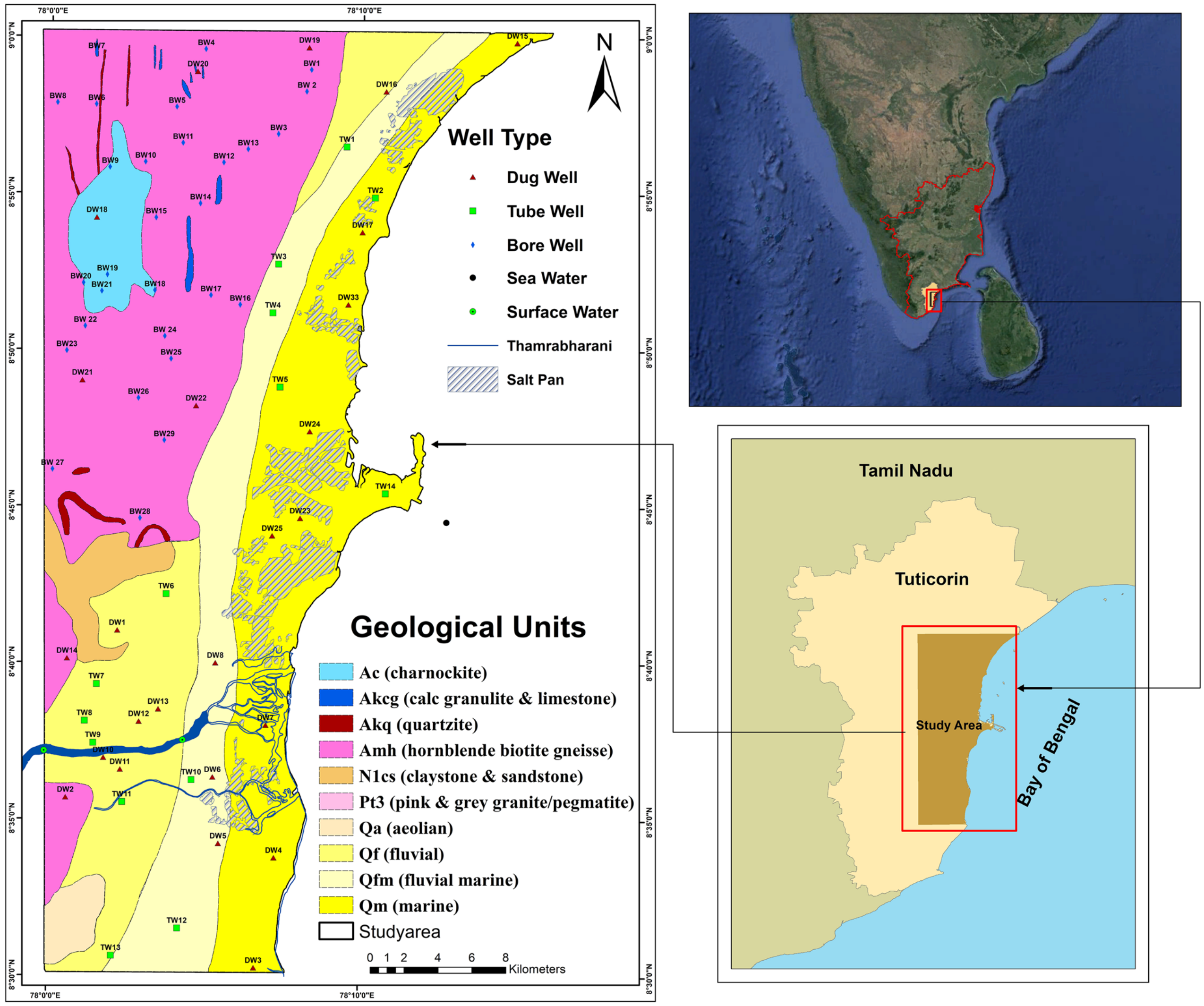

Fig. 1 Location map of the Tuticorin coast with geological units

southwest monsoon rainfall is highly erratic and summer rains are negligible. The normal annual rainfall over the district varies from about 570–740 mm (CGWB 2009).

The study area is underlain by both porous and fissure formations. The main aquifer system seen in the study area is consolidated and unconsolidated systems. The porous formations include sandstones and clay from Recent to sub Recent and Tertiary age (CGWB 2009). The aquifer parameter in the study area comprise of mainly hard rock and alluvium with a mean depth to water level ranging between 5 and 20 m. As the saltpans acquire the coastal regions of the study area, agricultural lands are seen across the deltaic region which comprises of mainly paddy, banana and beetle leaf plantations. There are a number of rainwater storage tanks in the study area which serves as one of the major water supply for irrigation and drinking purpose.

Methodology

Preliminary data were collected through a reconnaissance survey and based on the hydrogeology of the area, water samples at different coastal and inland aquifers during pre and post-monsoon period of 2013 along a 980 km^2 area in the Tuticorin coast belt, Tamil Nadu, India were monitored for major ion chemistry and stable isotopes. 29 groundwater samples from dug wells (DW, ~ 8 to 10 m bgl), 15 from tube wells (TW, ~ 60 to 70 m bgl) and 29 from bore wells (BW, ~ 30 to 100 mbgl), sea water and two surface water samples were collected. Rainwater samples were also collected from the area as monthly composites. Physicochemical parameters were determined in the field. Major ion, chloride was measured by argentometry against standard $AgNO_3$ and after subtracting the background value as per the standard

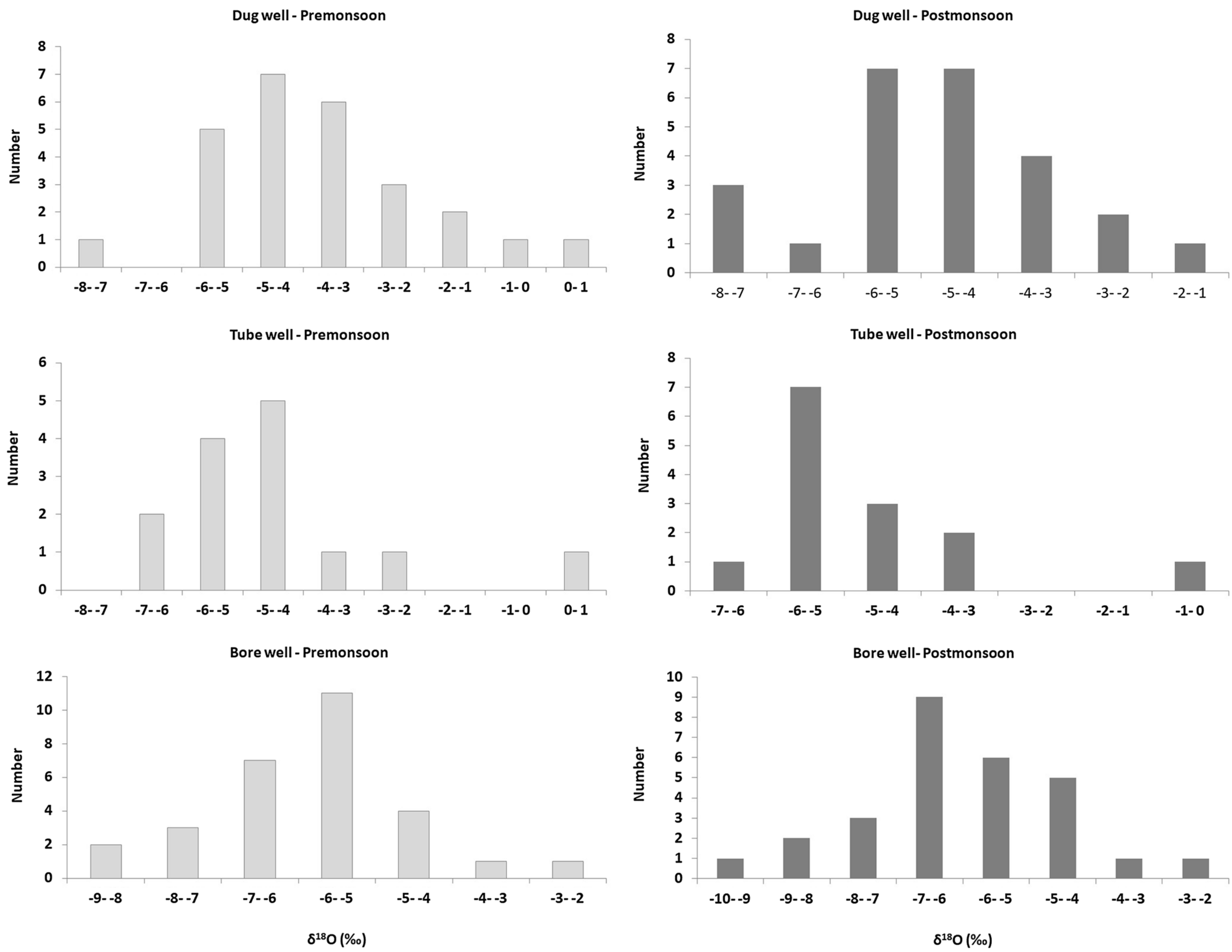

Fig. 2 Frequency analysis of δ^{18}O of dug well, tube well and bore well samples in premonsoon and postmonsoon seasons

procedure (APHA 2012). The isotopic analyses (δ^{18}O and δD) were done by standard equilibration method (Epstein and Mayeda 1953) in which water samples (300 µl) are equilibrated with CO_2 and H_2 at the Physical research Laboratory, Ahmedabad. The equilibrated CO_2 and H_2 gases were analysed in Delta V Plus isotope ratio mass spectrometer in continuous flow mode using Gas Bench II for $^{18}O/^{16}O$ and *D*/*H* ratios (Maurya et al., 2009). The reproducibility of the measurement was better than 0.1‰ for δ^{18}O and 1‰ for δD.

Result and discussion

Isotope geochemistry

The summary statistics of stable isotope composition of groundwater collected from dug wells (DW), tube wells (TW) and bore wells (BW) of the study area in the premonsoon and postmonsoon seasons are presented in Table 1.

It can be seen from the frequency analysis (Fig. 3) that δ^{18}O of majority of the samples from the dug wells ranged between − 3 and − 5‰ and samples from tube wells ranged from − 4 to − 5‰ and bore well samples in the range − 5 to − 6‰. In general, there is a depletion of 1‰ in δ^{18}O of groundwater as we go deeper from DW to TW and again 1‰ depletion from TW to BW, in the Tuticorin area during the premonsoon period. The same observation holds good in the postmonsoon season also with an overall decrease of 1‰ in each of the sample sets (dug well: − 4 to − 6‰; tube well: − 5 to − 6; and bore well: − 6 to − 7‰). The dug wells in the study area are mostly in the depth range 8–10 m bgl and the tube wells are much deeper up to 60–70 m bgl. The bore wells in the region are ~ 30 to 100 m bgl. The decrease in δ values of dug well samples to tube well samples to bore well samples may be actually the evaporative enrichment of heavier isotopes in the shallow well water samples.

Seasonal variation of δ^{18}O by taking the average for each sample sets are shown in Fig. 3. After monsoon, depletion

Table 1 Summary statistics of stable isotope composition of groundwater of the study area in the premonsoon and postmonsoon seasons

	Dug well			Coastal tube well			Inland bore well		
	δ¹⁸O (‰)	δD (‰)	d-excess (‰)	δ¹⁸O (‰)	δD (‰)	d-excess (‰)	δ¹⁸O (‰)	δD (‰)	d-excess (‰)
Premonsoon									
Mean	− 3.77	− 28.06	2.01	− 4.51	− 32.11	3.87	− 5.85	− 41.46	5.25
Standard deviation	1.78	12.29	5.87	1.86	13.98	3.05	1.39	9.22	3.16
Minimum	− 7.20	− 52.90	− 10.20	− 6.90	− 54.70	− 1.90	− 8.90	− 64.70	− 6.00
Maximum	0.70	− 4.70	10.40	0.70	3.80	8.10	− 2.20	− 23.40	8.60
Postmonsoon									
Mean	− 4.82	− 35.68	2.80	− 4.96	− 33.72	6.02	− 6.08	− 43.75	4.89
Standard deviation	1.41	10.00	4.05	0.82	6.64	2.13	1.37	9.53	2.85
Minimum	− 7.50	− 56.60	− 4.50	− 6.20	− 43.30	2.80	− 9.20	− 67.60	− 4.80
Maximum	− 1.40	− 15.30	8.90	− 3.80	− 24.70	10.50	− 3.30	− 30.80	10.90

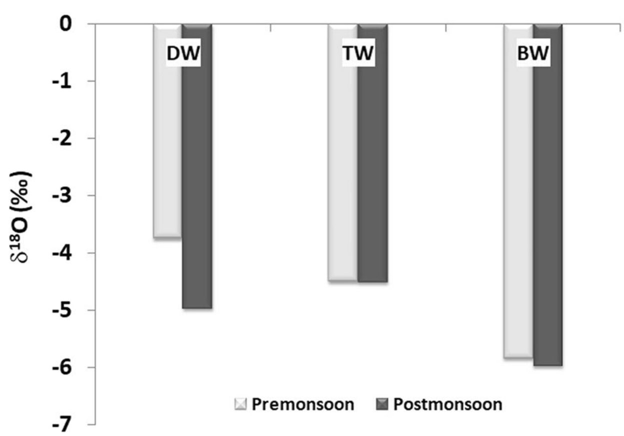

Fig. 3 Seasonal variation of averaged $\delta^{18}O$ of groundwater from dug well and tube well and bore well of Tuticorin region

in $\delta^{18}O$ can be visualised in all sample sets in varied extents. The rainwater during the northeast winter monsoon period is found to be depleted in heavier isotopes in this region and correspondingly the groundwater also showed depleted δ values than the premonsoon period. Groundwater abstracted from dug wells showed more seasonal variation than the tube well and bore well samples may be due to the difference in evaporation rate from the shallow dug wells and deeper tube wells and bore wells.

The groundwater in the area can be further classified as coastal and inland based on the distance from the shore. Wells up to approximately 8 km from the coast are considered as coastal, which are in the coastal marine or fluvial marine lithology. Wells beyond 8 km from coast are considered as inland, which include mainly, fluvial and hornblend biotite gneisse. Dug wells in the coastal region are found to be more depleted than those of the inland. During premonsoon, the depletion of ~ 2‰ is observed, and in the postmonsoon, it is reduced to ~ 1‰ between the coastal and inland samples. This can be an imprint of less evaporation in coastal zone where relative humidity is high. On the contrary, the tube well samples showed similar isotopic composition irrespective of the distance from the shore/lithology in the two seasons (Fig. 4a, b). Seasonal variation in isotopic composition in the hard rock aquifer (bore well) is random compared to the other aquifers (Fig. 5). Deeper waters are not influenced by processes in the shallow surface. In fact, seasonal fluctuations are attenuated beyond a certain depth and hence there is not much seasonal variation in bore well samples. The bore wells sampled in the study area were located in/near the fractures, faults etc. as can be ascertained from the lineament map (not shown). In hard rock aquifers, there are preferential migratory pathways through faults, fractures and fissures which quickly transport waters of different origins, both laterally and vertically.

δD–δ¹⁸O relationship and recharge condition

The δD and $\delta^{18}O$ in the water resources of the area co-varied in the two seasons as shown Figs. 5 and 6. Regression lines were computed separately for the coastal and inland regions for each well type. Groundwater and surface water data points were plotted below the local meteoric water line due to evaporative enrichment. The slope, *y*-intercept and regression coefficients in the premonsoon and postmonsoon periods are given in Table 2.

Isotopic values of rainwater in Tuticorin region ranged from − 0.4 to − 8.41‰ in oxygen isotope ratios and from 0.05 to − 55.1‰ in hydrogen isotope ratio. In this region, during the study period, only north east winter monsoon (October–January) was active. Accordingly, due to rain-out of the air masses carrying moisture, the first rains are depleted and has d-excess value above 10‰. However, the rains showed progressive enrichment in heavier isotopes as the season advances from October to December. Evaporative enrichment of heavier isotopes in the falling raindrops is very obvious from the low d-excess ($\delta D - 8 \times \delta^{18}O$) value

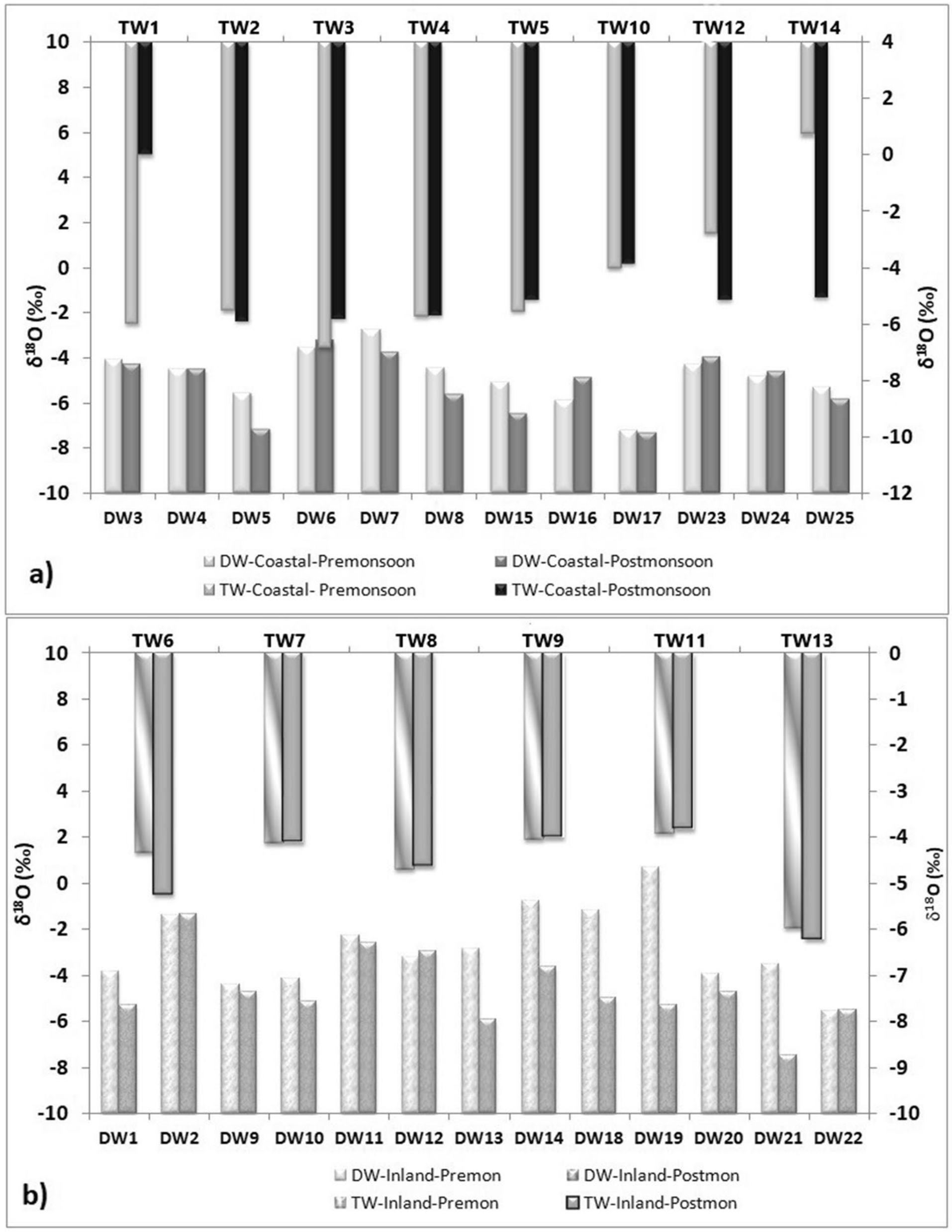

Fig. 4 **a** $\delta^{18}O$ variation of the groundwater from dug well and tube wells in the coastal region of the study area during premonsoon season, **b** during postmonsoon season

(3.3‰) and enriched $\delta^{18}O$. The slope and y-intercept of the regression line of the LMWL also emphasises that evaporative enrichment and rain from the progressively depleted air masses are the main controls over the isotopic evolution of precipitation in this region (Table 2, Figs. 6 and 7). Contribution from the recycled vapour to the precipitation is not significant enough to impart any isotopic modification of rain water or in other words, evaporation from the rain drops is so intense that, in effect, the resultant rain is highly enriched in heavier isotopes.

The main recharge source for the groundwater and surface water for the region is rain water as can be seen from the regression plots (Figs. 5, 6). However, the groundwater and surface water samples were found to plot below/on the LMWL, showing different degrees of evaporation. In addition, each of the sample types is characterised by different slope values in different seasons. The surface water samples had slope values much less than that of LMWL in the two seasons. The surface water was enriched during postmonsoon season either due to evaporative enrichment/saline water intrusion in the downstream area.

Groundwater from the tube wells were found to behave differently from rest of the samples in that the slope values were considerably different in the pre and postmonsoon seasons. In the premonsoon season (May, 2013), the value was close to that of GMWL (7.4), and in the postmonsoon season

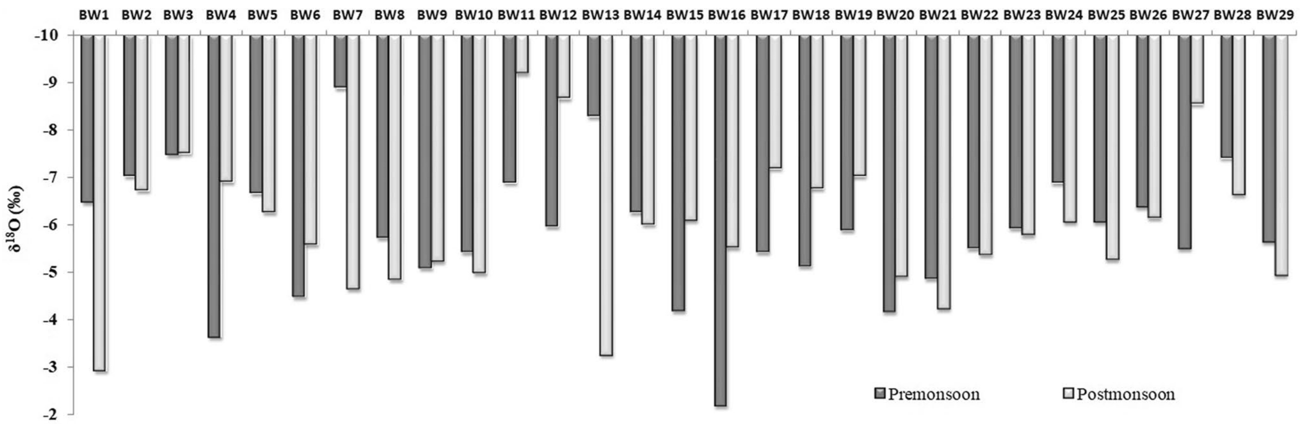

Fig. 5 Seasonal variation of $\delta^{18}O$ of the groundwater of bore wells in the study area

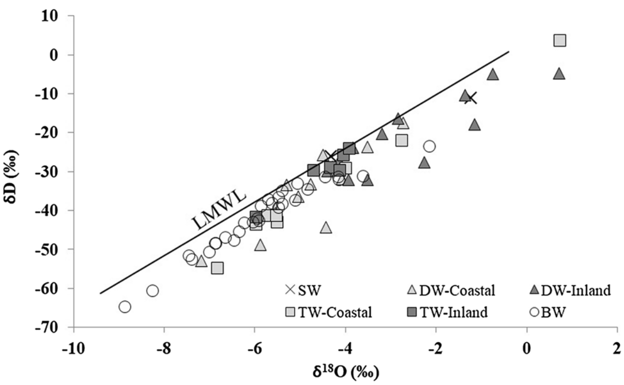

Fig. 6 Relationship between δD and $\delta^{18}O$ of groundwater and surface water in the Tuticorin region in the pre-monsoon season

(Dec, 2013), drops to 4.8. It may be noted that the rainwater, which was mainly from the northeast monsoon (Oct–Dec) had a slope value of 6.9. Hence it can be assumed that the groundwater was recharged by the rains occurred in the previous north east monsoon (slope value probably between 6.5 and 7) and correspondingly the slope obtained for the groundwater during the premonsoon period (May, 2013) of the study, corresponds to that of the rainwater. It can further be assumed that during the non-rainy period of June to September in the study area, the groundwater is mixed with water with different isotopic composition, probably seawater and the groundwater sampled during the postmonsoon season has lower slope value. In the case of dug well samples, the slope was similar in both seasons and close to that of LMWL. The shallow groundwater even though showed evaporative enrichment, is being recharged rapidly by the infiltrating rainwater. The deeper groundwater (bore well) on the other hand showed more depleted isotopic composition than the rainwater and the slope is not changing over seasons.

On a closer look, it can be seen that the slope values increases from 4.9 for surface water, 6.3 for dug well samples, 6.4 for bore well samples and 7.4 for tube well samples, which clearly indicates progressively greater extent of evaporation from surface water (SW) to dug well samples (DW) to bore well samples (BW) to tube well samples (TW). The source water for SW, DW and BW seems to be local contemporary precipitation with slope 6.9 because SW, DW and BW have lower slope than LMWL. The TW has slope > LMWL which indicates that deep water of TW may be of different origin (old water of different climate regime or recharged from different precipitation regime or long distance transport of water).

Deuterium excess (d-excess) is a derived secondary parameter which shows the magnitude of evaporative enrichment of heavier isotopes in a water body. Seasonal

Table 2 Regression parameters of the different groundwater, surface water and LMWL of the study area

	Slope (m)		*y*-intercept		R^2	
	Premonsoon	Postmonsoon	Premonsoon	Postmonsoon	Premonsoon	Postmonsoon
LMWL	6.9		3.5		0.998	
SW	4.9	2.4	−4.8	−18.5	1	1
DW	6.3	6.8	−4.1	−3.2	0.829	0.889
TW	7.4	4.8	1.1	−10.3	0.959	0.892
BW	6.4	6.5	−3.9	−4.6	0.938	0.935

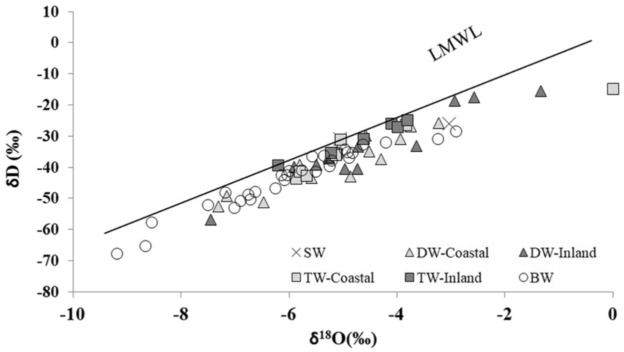

Fig. 7 Relationship between δD and $\delta^{18}O$ of groundwater and surface water in the Tuticorin region in the post-monsoon season

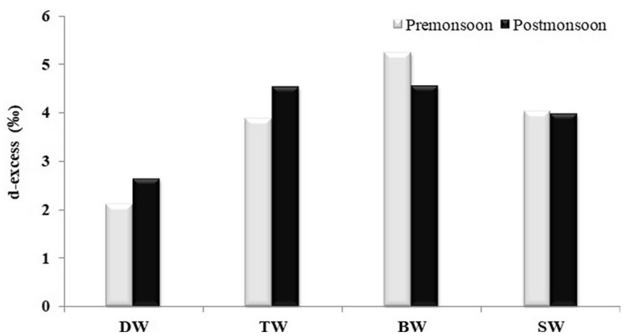

Fig. 8 Seasonally averaged d-excess values in the different water resources of the area

variation of d-excess in the groundwater and surface water of the study area are depicted in Fig. 8. The average d-excess values in all four types of samples, and in both the seasons, are < 6. In groundwater samples, there can be many reasons for such low d-excess values. Sea water has d-excess close to zero because its $\delta^{18}O$ and δD are close to 0. Admixture of sea water in groundwater can lower d-excess. Low d-excess in DW can be due to infiltration of sea water in shallow aquifers through back waters, high-tide waters or salinity ingression due to pumping of shallow waters in coastal areas. If evaporation is occurring from a water body, its d-excess will be less than 10‰. Lowest d-excess values obtained in the dug well samples for the two seasons and highest values obtained for the bore well samples indicates that evaporation was more in the shallow aquifers than either in the tube well or bore well samples. Seasonal variation was marginal in the surface water samples suggesting evaporative enrichment of heavier isotopes.

$\delta^{18}O$–Cl relationship

Environmental isotopes are used to find out the source of salinity in groundwater such as from the leaching of salts by percolating water from evaporitic deposits, intrusion of saline water from the sea/brackish surface water/brines etc. or by concentration of dissolved ions by evaporation. Stable isotopes, being conservative, do not change composition neither during transport in a unique groundwater system or in the leaching water by the dissolution of salts. However, when salinity is caused by the mixing of a source of saltwater with freshwater, the resultant water will have a different isotopic composition as well as salinity. This property is made use in this study to identify the sources of salinity. The $\delta^{18}O$ together with the conservative ion chloride is linearly correlated on a mixing line within the limits defined by the freshwater and saline water components (Payne 1983). In India, isotopes were used in a few studies in semi-arid regions such as Haryana (Krishan et al. 2020a, b).

The sea water of the Tuticorin coast has $\delta^{18}O$ value of 0.47‰ and chloride concentration of 21,993 ppm. The surface water of the Thamirabharani River draining through the area has a mean $\delta^{18}O$ of −2.79‰ and −4.05‰ in the premonsoon and postmonsoon seasons and chloride concentration of 102 and 180 ppm, respectively. The groundwater had mean $\delta^{18}O$ of −3.74, −4.5, and −5.84 for dug well, tube well and bore well samples in the premonsoon with corresponding chloride concentration of 2493, 4604 and 1463 ppm. During postmonsoon season, $\delta^{18}O$ values were −4.84, −4.61 and −5.97 ‰ and chloride concentration were 465, 923 and 353 ppm for dug well, tube well and bore well, respectively.

The scatter diagram of $\delta^{18}O$ and chloride concentration was plotted for groundwater and surface water for two seasons separately (Figs. 9, 10). The plot depicts different mechanisms of salinization in the coastal aquifers. As can be seen from the figure, apart from direct influence of the sea water, concentrations of ions by evaporation also contribute to the observed salinity in the area. The dissolution or leaching from the aquifer material is also imparting salinity to groundwater in this area. The tube well and dug well samples are found to be more affected by salinity than the

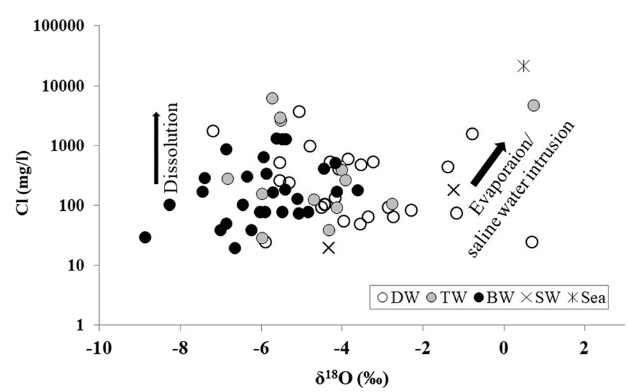

Fig. 9 $\delta^{18}O$ relationships with chloride in the premonsoon season

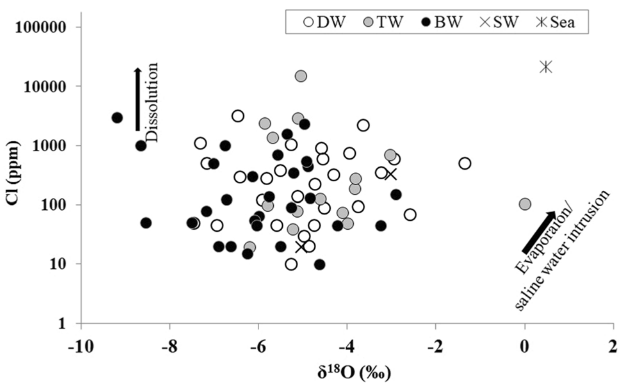

Fig. 10 $\delta^{18}O$ relationships with chloride in the postmonsoon season

bore well samples. The bore well samples are found to least interacting with sea water. Dissolution/leaching is the main mechanism for the salinity in deep groundwater. The deep groundwater is most depleted and showed only marginal seasonal variation. The chemical analysis showed the dominance of sulphate ion over chloride (data not shown). The observed high salt concentration in the deep groundwater can be due to the entrapped seawater. Spatial distribution of the salinization patterns for the study area shown in Fig. 11.

Conclusions

The Tuticorin district of Tamil Nadu, India is selected for detailed stable isotopic study to identify the recharge mechanism and salinization in the shallow and deeper aquifers in the sedimentary and hard rock formations. The area faces severe freshwater inadequacy and the results drawn from the study can be summarised as:

In the study area, groundwater showed 1‰ reduction in $\delta^{18}O$ from the shallow to deeper aquifers in the coastal and inland regions. Seasonal variation of $\delta^{18}O$ in groundwater in the shallow aquifers of the coastal aquifers in the sedimentary formation and those of the inland aquifer were more compared to the deeper aquifers (tube well and bore well samples) may be due to the difference in the degree of evaporation. The northeast monsoon rains are the major recharge source to the groundwater of the region. Evaporative enrichment of heavier isotopes in the falling raindrops and rain formed from the progressively depleted air masses are the main controls over the isotopic evolution of precipitation in this region. Evaporation from the rain drops is so intense that, in effect, the resultant rain is highly enriched in heavier isotopes and the contribution of recycled vapour to the precipitation is not appearing significant enough to impart any isotopic modification of rain water. The regression analysis of $\delta^{18}O$ and δD showed that the source water for surface water and groundwater in the shallow (DW) and deeper (BW) aquifers seems to be the regional precipitation and the aquifers in the mid depth (TW) may be fed by water of different origin such as old water of different climate regime or recharged from different precipitation regime or long distance transport of water. Different mechanisms of salinization in the coastal aquifers were deduced as direct influence of the sea water and concentrations of ions by evaporation. The dissolution or leaching from the aquifer material is also imparting salinity to groundwater in this area. The results of the present investigation provide an outline of the geochemical processes controlling the groundwater chemistry of the fragile aquifer system of Tuticorin coast.

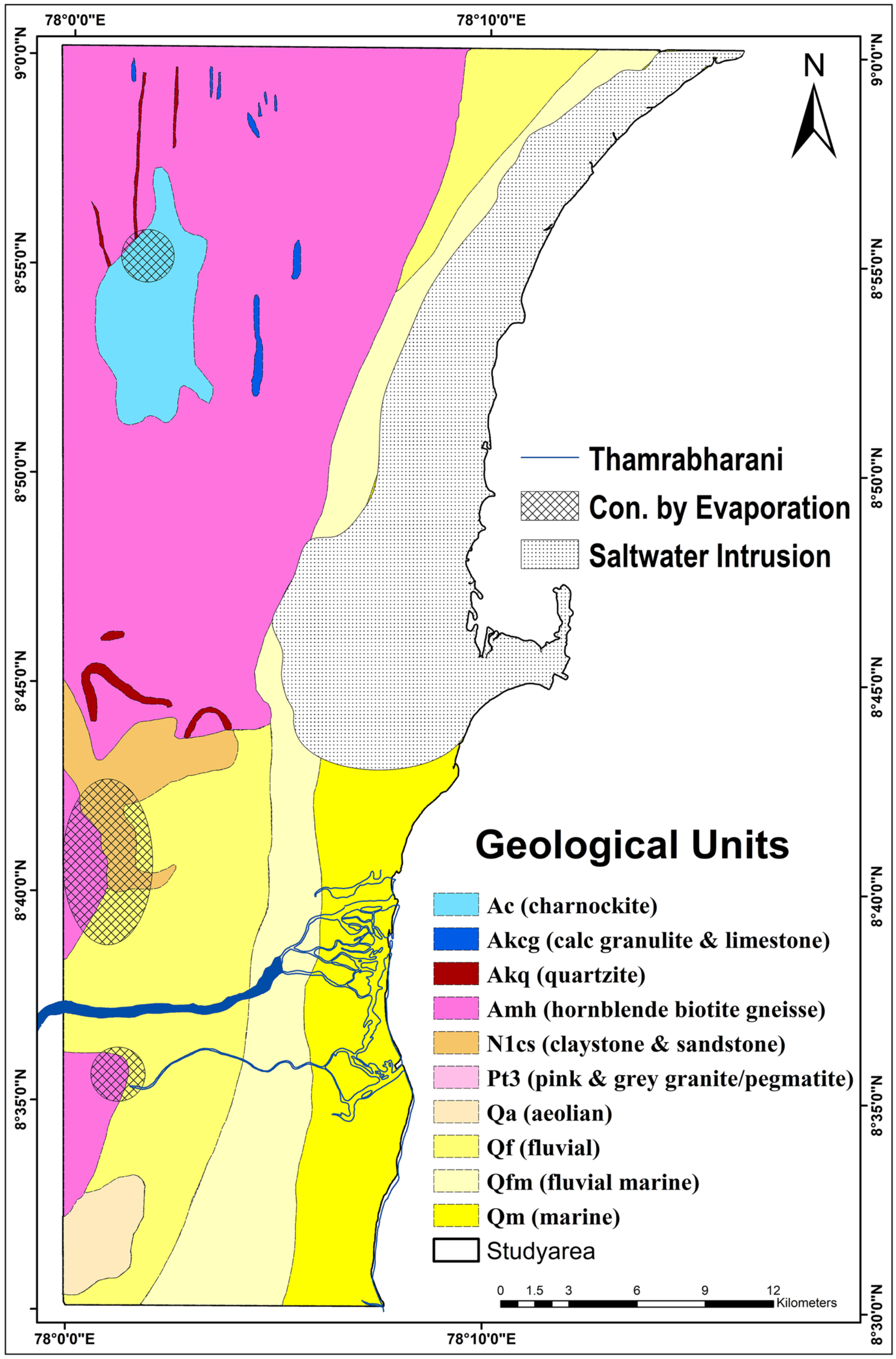

Fig. 11 Salinization pattern in groundwater of the study area

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Author contributions We hereby declare that authors have contributed equally to the collection, generation & interpretation of data and the preparation of manuscript.

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Availability of data and material We hereby declare that data associated with our manuscript will be available as per the request.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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