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# Controls of evaporative irrigation return flows in comparison to seawater intrusion in coastal karstic aquifers in northern Sri Lanka: Evidence from solutes and stable isotopes

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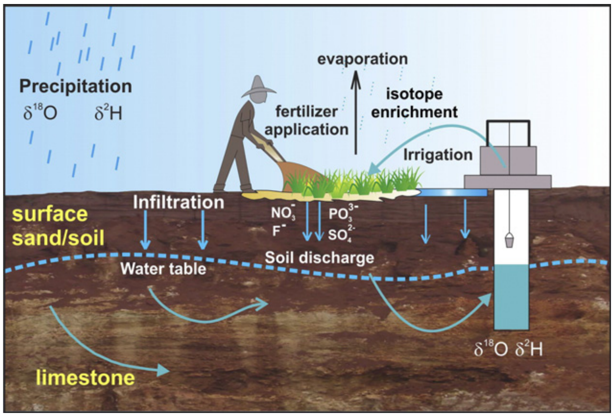
## HIGHLIGHTS

- Miocene limestone aquifers are the main source of drinking water in the Jaffna region, Sri Lanka.
- This work investigated the processes governing the groundwater composition.
- Major solute geochemistry and isotopes of $\delta^{18}O$ and $\delta^{2}H$ were employed.
- Groundwater quality is degraded and highly modified by human activities.
- Stable isotopes and water chemistry indicate that evaporation dominates over seawater intrusion.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Groundwater in Miocene karstic aquifers in the Jaffna Peninsula of Sri Lanka is an important resource since no other fresh water sources are available in the region. The subsurface is characterized by highly productive limestone aquifers that are used for drinking and agriculture purposes. A comprehensive hydrogeochemical study was carried out to reveal the processes affecting the groundwater quality in this region. Major and trace element composition and environmental isotope ratios of oxygen and hydrogen ($\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$) were determined in 35 groundwater samples for this investigation. The ion abundance of groundwater in the region was characterized by an anion sequence order with $HCO_3^- > Cl^- > SO_4^- > NO_3^-$. For cations, average $Na^+ + K^+$ contents in groundwater exceeded those of $Ca^{2+} + Mg^{2+}$ in most cases. Ionic relationships of major solutes indicated open system calcite dissolution while seawater intrusions are also evident but only close to the coast. The solute contents are enriched by agricultural irrigation returns and associated evaporation. This was confirmed by the stable isotope composition of groundwater that deviated from the local meteoric water line (LMWL) and formed its own regression line denoted as the local evaporation line (LEL). The latter can be described by $\delta^{2}H_{H2O} = 5.8 \times \delta^{18}O_{H2O} - 2.9$. Increased contents of nitrate-N (up to 5 mg/L), sulfate (up to 430 mg/L) and fluoride (up

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Groundwater quality
Selenium

to 1.5 mg/L) provided evidences for anthropogenic inputs of solutes, most likely from agriculture activities. Among trace elements Ba, Sr, As and Se levels in the Jaffna groundwater were higher compared to that of the dry zone metamorphic aquifers in Sri Lanka. Solute geochemistry and stable isotope evidences from the region indicates that groundwater in the area is mainly derived from local modern precipitation but modified heavily by progressive evaporative concentration rather than seawater intrusion.

## 1. Introduction

Groundwaters in karstic terrains are important because nearly 25% of the world population rely on karst aquifers for potable water supply (Ford and Williams, 2007). However, karst aquifers are also highly vulnerable due to usually short residence times of groundwater in the system. Such karstic aquifers are often complex and heterogeneous (Bakalowicz, 2005; Romanov et al., 2003; White, 2002; Wu et al., 2009). They are often characterized by open conduits that provide low resistance pathways to water infiltration as well as various solutes originating from anthropogenic or natural sources. In karst aquifer systems, the geochemical evolution of groundwater is controlled mainly by the composition of recharge water, while characteristics of the aquifer material and contaminations from surface activities also play a role (White et al., 1995; Wu et al., 2009). Groundwater is a vital water source in karst areas, where surface water resources are often absent. Therefore, an improved understanding of geochemical evolutions of groundwater in such regions is important.

Only 9% of the land area of Sri Lanka consists of Miocene limestone sequences that are confined to the north and northwestern part of the island (Fig. 1). These limestone formations are characterized by shallow confined karstic aquifers that occur in channels and cavities of carbonate rocks (Panabokke and Perera, 2005). In this Miocene carbonate belt, groundwater resources occur as a series of several isolated hydrological basins (Basnayake, 1988; Davis and Herbert, 1988) with four main karstic confined aquifers. They are known as Chunnakam (formerly Valikamam), Thenmaradchi, Vadamarachchi and Kytes, which encompass the northern Jaffna peninsula (Davis and Herbert, 1988). Since the region is characterized by a semi-arid climate, these groundwater resources play an increasingly important role in agriculture and domestic water supply.

These Miocene aquifer systems were therefore subject to several earlier studies with particular attention to pollution (Dissanayake and Weerasooriya, 1987; Gunaalan et al., 2015; Hidayathulla and Karunaratna, 2013; Joshua et al., 2013; Nanthini et al., 2001; Nishanthiny et al., 2010; Thushyanthy and De Silva, 2012). Most of these studies, however, considered only few geochemical parameters such as nitrate and phosphate that are attributed to anthropogenic activities such as fertilizer applications and septic tank leaching (Dissanayake and Weerasooriya, 1987; Joshua et al., 2013). In recent years, the Jaffna region was subject to substantial land-use changes. Therefore an improved understanding of geochemical processes that govern the composition of groundwater becomes apparently important for water resource management and environmental protection in the region. Moreover, most of the terrain is surrounded by the Indian Ocean (Fig. 1) and intrusion of saline waters becomes a realistic threat to aquifers, in addition to the anthropogenic pollution. So far little is known about the natural processes such as rock-water interaction or seawater intrusion that could strongly influence the geochemical compositions of karst aquifer water in this region.

In this study, karstic groundwater resources in the semi-arid Jaffna peninsula were investigated by hydrogeochemical and stable isotope data. These techniques help to outline various processes such as timing of recharge, water-rock interactions and mixing of different water types (Bakalowicz, 2005; Chandrajith et al., 2014; Kanduč et al., 2012; Lang et al., 2006; Thilakerathne et al., 2014; van Geldern et al., 2015; Yousif et al., 2016; Zavadlav et al., 2013). In addition to geochemical characterization of the groundwater, we also investigated the geochemical processes and factors that control the composition of groundwater in this karstic terrain. Such information is important for future groundwater management in the area where surface water resources are extremely scarce. This study is also representative for other near-shore karst areas worldwide where seawater intrusion and water scarcity constrain groundwater resources that are already under pressure from anthropogenic pollution impacts.

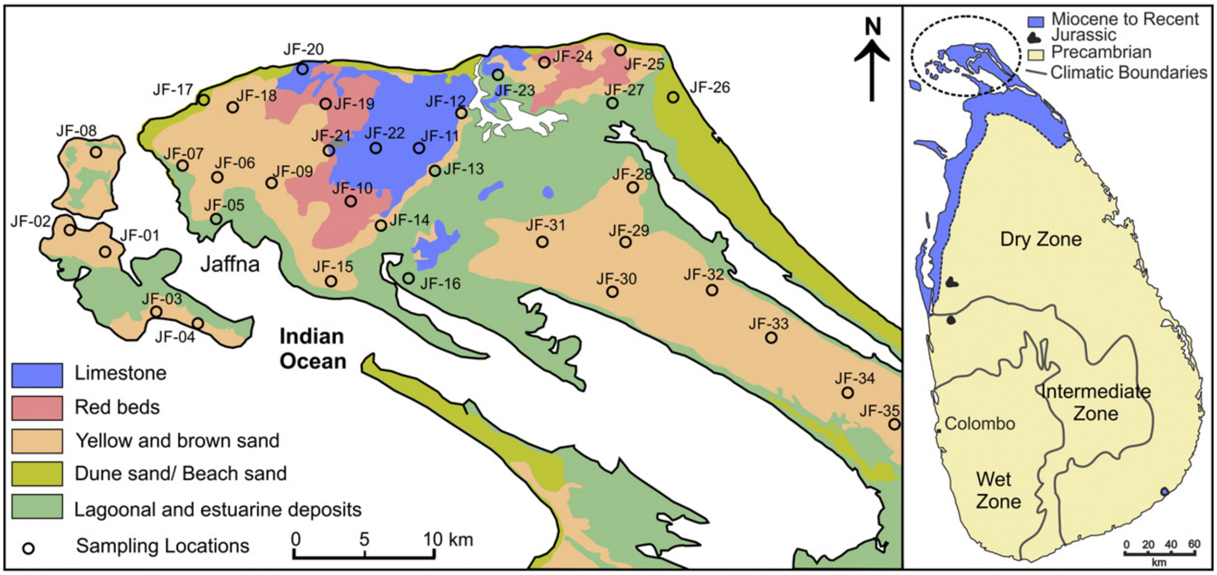

**Fig. 1.** Simplified geological map of the study area and sampling locations.

### *1.1. Geological and hydrogeological setting*

The Miocene sedimentary basin that is located in the northern and north-western coastal belt of Sri Lanka extends over an area of about 5000 km$^2$. This is the only sedimentary region in Sri Lanka. These karstic sedimentary beds are surrounded by the ocean in the North and by high-grade metamorphic rocks from the landward side. The studied Jaffna peninsula covers an area of about 1100 km$^2$ and is connected to the main land by a narrow land bridge (Fig. 1). The area is entirely underlain by Miocene limestone sequences that slightly dip westwards. The vertical thickness of the Miocene limestone beds exceeds 90 m and is underlain by thick sandstones (Cooray, 1984). On top of the fossiliferous limestone beds is a patchwork of unconsolidated marine and non-marine Quaternary deposits such as red earth, yellow-brown sands, dune and beach sands and lagoonal deposits (Fig. 2). Associated soils in the region are dominated by highly permeable calcareous-red-yellow latosols, alluvial soil and red loams (Panabokke, 1996). Tectonically, the NW-SE and NE–SW running joint systems in the limestone beds are important for recharging of the aquifers and provide the most important conduits for water infiltration. These karst features with interior cavern systems in the region have hardly been explored so far.

Climatologically, the Jaffna region receives 950 mm of average annual rainfall that is fairly low compared to the rainfall in the rest of the island. For comparison, the wet zone of Sri Lanka receives over 2500 mm annual rainfall while the dry zone region receives about 1000 mm of annual rain (Fig. 1)(Domrös, 1979). Most of the precipitation in the region occurs through north-east monsoons that bring rains from mid-October to January. The recharge of groundwater in the Jaffna Region occurs mostly during this time and most of the precipitation readily percolates through thin loose sandy layers that are overlain by fractured limestone. Evapotranspiration rates of about 2000 mm prevail throughout the year (Thushyanthy et al., 2012). Groundwater in the study region is mainly extracted through dug wells with depths of up to 10 m. Some of the sinkholes in the limestone beds have also been converted to water wells. Such wells are often deeper than 10 m and serve domestic and agricultural activities. The agriculture activities in the region entirely depend on groundwater resources and the total groundwater usage is estimated as 147 million m$^3$ per year (Punthakey and Gamage, 2006).

## 2. Material and methods

Groundwater samples were collected from 35 water supply wells covering the entire Jaffna peninsula (Fig. 1). Depths from groundwater level to the surface varied from 2.6 m to 9.5 m except for two wells with groundwater levels of 21 m and 39 m below ground (m bgl). These two deep wells are natural sinkholes in limestone beds. Groundwater samples were collected after pumping the wells for 10–15 min by a submerged pump. Electrical conductivity (EC) and pH were measured using a field portable EC/pH meter (Hach® SensION + MM150). The total alkalinity was determined directly in the field using the Hach® Digital Titrator with bromocresol green-methyl red indicator. For cation analysis, samples were filtered with a 0.45 μm pore size nylon filter and subsequently acidified with 1% *v*/*v* $HNO_3$. Filtered and unacidified samples were used for anion analysis. For oxygen and hydrogen stable isotope analyses of the water ($\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$), 15 mL of water were collected from each location into screw capped high-density polyethylene (HDPE) tubes that were secured with Parafilm™ around the cap to avoid evaporation after sampling. All samples were kept in the dark at 4 °C until analyses were performed.

Water samples were analyzed using the methods described by the American Public Health Association (APHA, 2012). Filtered and unacidified samples were used to analyze chloride, nitrate-N, fluoride and sulfate contents by a spectrophotometer (Hach® DR 4700). Major ions and trace metals in groundwater samples were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Scientific® iCAPQ). Instrumental calibrations were performed using commercial standards and the instrumental internal drift was corrected using Be, Rh and Re internal standards. In addition, in-house water standards were used as controls. The analytical precision was determined by calculating the cation-anion balance error that was within 10% for most of the samples. A few samples showed higher charge balance errors up to 20%, possibly due to contributions from other trace elements or organic material that were not determined. Water isotope compositions were determined with a Picarro L1102*i* (Picarro Inc., Santa Clara, CA, USA) wavelength-scanned cavity ring-down infrared spectrometer that was coupled with a vaporization module. The quality assurance was maintained according to the procedure described by van Geldern and Barth (2012). The isotope results are expressed in the standard per-mille (‰) notation (Coplen, 2011). It reports values as relative differences (δ values) with respect to the Vienna Standard Mean Ocean Water (V-SMOW) where $\delta = (R_{sample} - R_{standard}) / R_{standard}$. The term R is the ratio of $^2H/^1H$ and $^{18}O/^{16}O$, respectively. External reproducibility was better than 0.1 and 1.0‰ ($\pm 1\sigma$) for $\delta^{18}O$ and $\delta^2H$, as determined by the standard deviation of control standards. More details of the analytical procedures are given in van Geldern and Barth (2012).

## 3. Results and discussion

### *3.1. Hydrogeochemical characteristics*

The pH of the groundwater from the karstic region of Jaffna ranges between 7.2 and 7.8 with an average value of 7.7 (Table 1). The electrical conductivity (EC) varies from 0.31 mS/cm to 10.51 mS/cm with a mean value of 2.53 mS/cm. These values are comparatively high with respect to groundwater in the dry zone high grade metamorphic aquifer systems in rest of the island that is characterized by EC values of about 1000 μS/cm (Jayasena et al., 2008). This indicates higher amounts of dissolved solids in the groundwater of the Jaffna limestone region. Conductivity values were generally higher at locations where precipitation directly infiltrate the limestone beds (mean = 2.83 mS/cm) than water that seeps through sand dunes (1.67 mS/cm).

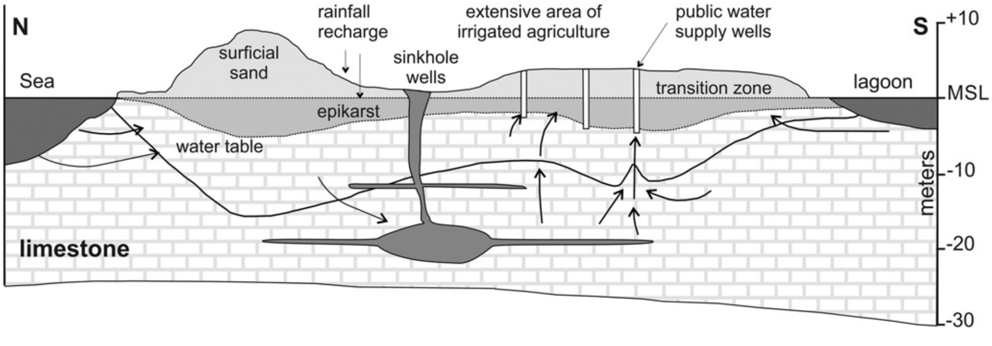

**Fig. 2.** Generalized hydrogeological cross-section of the Jaffna peninsula. Arrows indicate pathways of recharge water (modified after Joshua et al., 2013).

The major solute composition of Jaffna groundwater was dominated by $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $Cl^-$ and $SO_4^{2-}$. In most wells, ion abundances were in the concentration sequence order of $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ and the average $Na^+ + K^+$ (13.7 mmol/L) contents in groundwater exceed those of $Ca^{2+} + Mg^{2+}$ (5.06 mmol/L). The $SO_4^{2-}$ content in Jaffna groundwater varied from 13 to 430 mg/L with a mean of 87 mg/L. From the collected well samples 13% had $SO_4^{2-}$ contents higher than 100 mg/L. For comparison, the average $SO_4^{2-}$ contents of metamorphic rock aquifers in the dry zone terrains of Sri Lanka was 29 mg/L (Rubasinghe et al., 2015). Similarly, the nitrate-N content in groundwater of Jaffna region is higher than that in the metamorphic terrain of Sri Lanka. Nitrate-N in the study area varies from 0.40 to 5.9 mg/L with the mean value of 1.76 mg/L. However, the dry zone metamorphic aquifers showed a mean nitrate-N content of 0.98 mg/L (Rubasinghe et al., 2015). Some early studies on the groundwater quality of this region also recorded similarly elevated nitrate-N contents, but most wells showed lower contents than the World Health Organization (WHO) recommended limit of 10 mg/L (Joshua et al., 2013; Thushyanthy et al., 2012).

Agriculture is the main industry in the study region in which 65% of the populations is involved. About 34% of land area of the peninsular is utilized for commercial agriculture (Thushyanthy and De Silva, 2012). The main source of sulfate and nitrate in the area was most likely contributed from fertilizer application and septic tank leachates (Dissanayake and Weerasooriya, 1987; Joshua et al., 2013). Such contaminants can easily leach through the highly permeable aquifer material. Fluoride is another important solute that was considered in this study since this element is known to cause serious health problems in the dry zone regions of Sri Lanka (Chandrajith et al., 2012). Not only for dental and/or skeletal fluorosis, fluoride is also considered as one of the major contributors to chronic kidney diseases with uncertain etiology (CKDu) in certain parts of the dry zone of Sri Lanka (Chandrajith et al., 2011). In the Jaffna region, the fluoride content varied from 0.08 to 1.54 mg/L that is comparatively lower than other dry zone metamorphic aquifer regions of Sri Lanka. Only 15% of studied wells in the region exceeded the recommend level of fluoride for drinking water in Sri Lanka (0.6 mg/L). High fluoride levels in the metamorphic terrain of Sri Lanka are often associated with dissolution of fluoride-bearing minerals, mainly micas and amphiboles but such minerals are absent in limestones. Therefore, the human activities, mainly the application of phosphate-bearing fertilizer and agricultural runoffs are responsible for the elevated fluoride in some of the wells in the region. This is plausible because phosphate minerals contain higher amounts of fluoride and thus fertilizer produced from such minerals can contribute this element (Edmunds and Smedley, 2013; Ozsvath, 2009). Further increases of salinity of soil solutions due to evapotranspiration can also enhance the concentration of fluoride in recharge water (Edmunds and Smedley, 2013).

Hydrogeochemical data in particular major cations and anions obtained from the Jaffna region were used to determine the geochemical evolution of groundwater. A Piper diagram (Fig. 3) was used to determine the geochemical characteristics of groundwater in the Jaffna region. Accordingly, dominant water types are in the order Na–Cl > mixed Ca–Mg–Cl > Ca–$HCO_3$ > mixed Ca–Na–$HCO_3$. The presence of Na–Cl and Ca–Mg–Cl water types in this succession indicates the admixture of saline water that may be caused by seawater intrusion, irrigation return flows or septic tank leachates. In our study mixed Ca–Na–$HCO_3$ and Ca–$HCO_3$ waters are mostly a result of dissolution of calcite and dolomite.

The $Na^+/Cl^-$ molar ratios are widely used as an indicator for seawater intrusion, particularly in coastal aquifer systems (Möller, 1990). In the study region, $Na^+$ and $Cl^-$ ratio (Fig. 4) varied from 0.42 to 2.09 with a

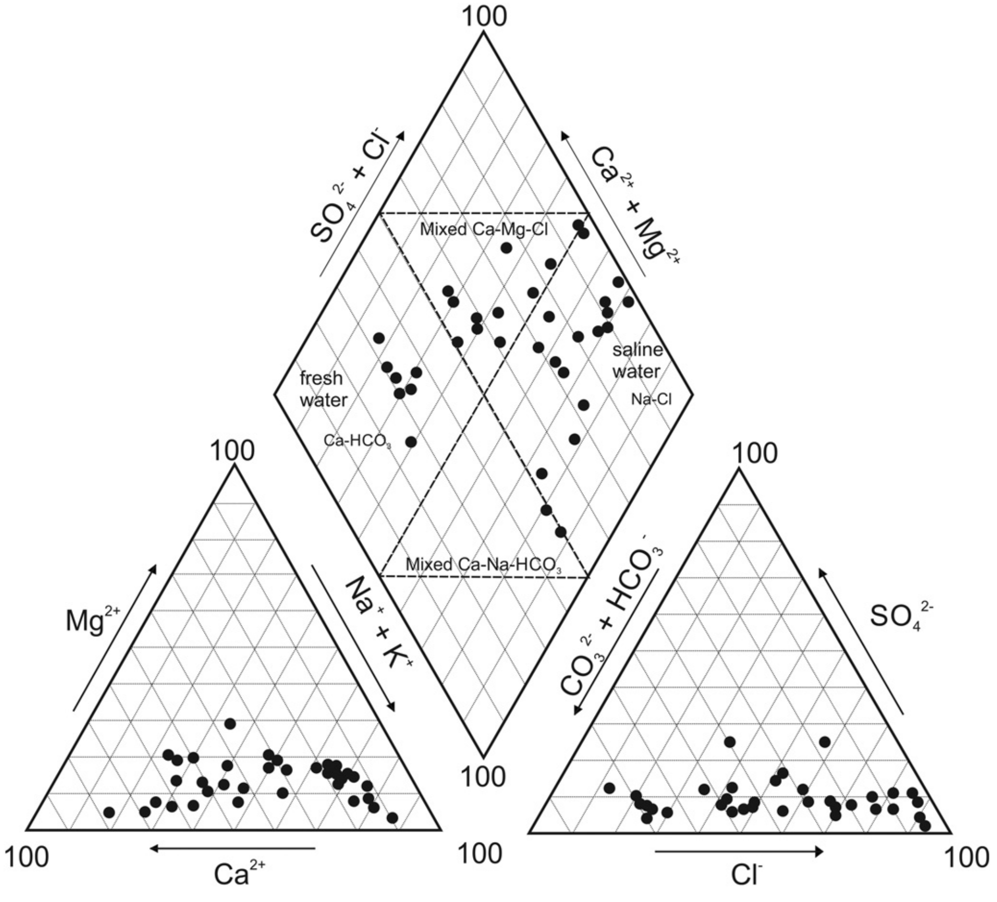

**Fig. 3.** Piper diagram of the geochemical composition of Jaffna groundwater.

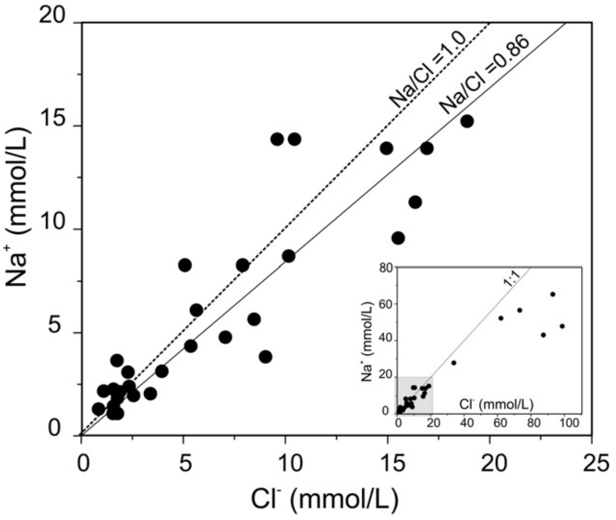

**Fig. 4.** Relationships between $Na^+$ and $Cl^-$ for groundwater from the Jaffna Peninsula.

strong positive correlation ($r = 0.96$). A few samples from the study region plot on the 1:1 line that represents halite dissolution. Another set of samples plots close to the seawater dilution ratio of 0.86. Lower $Na^+/Cl^-$ ratios than the seawater ratio indicate the mixing of ocean water with freshwater (Lee and Song, 2007). In addition, ion exchange processes that occur in the aquifer material could also modify the $Na^+/Cl^-$ ratios. During the ion exchange process, $Na^+$ replaces $Ca^{2+}$, leading to depletion of $Na^+$ in groundwater relative to $Cl^-$ (Appelo and Postma, 2005; Vengosh et al., 1997). Higher $Na^+/Cl^-$ ratios than the lines for halite and seawater sources indicate anthropogenic influences such as fertilizers applications and leachates from septic tanks (Jones et al., 1999; Vengosh et al., 1997; Zghibi et al., 2014).

### 3.2. Trace elements in groundwater

In this study, 17 trace elements (Li, B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Ba, Pb, U) were measured in each groundwater sample using ICP-MS (table 2). In general, trace element levels in groundwater of the Jaffna Peninsula were lower than the standards of water quality prescribed by World Health Organization (2011) and US-EPA (2012). In most samples, dissolved Co, Cd and Pb were either at or below their analytical detection limit (0.1 μg/L) and hence are not discussed further. Only the sample from well JF-25 showed slightly higher Pb contents of 1.23 μg/L. The well JF-35 also showed a higher Co content of 2.28 μg/L. Among the studied trace elements, Sr showed higher concentrations and varied from 28 μg/L to 21,000 μg/L with a median of 580 μg/L. In addition, Ba contents varied from 8.6 μg/L to 710 μg/L with a median of 98 μg/L. Both Sr and Ba are usually derived from the weathering of carbonates (Shand et al., 2009; Szramek et al., 2011). The arsenic content in Jaffna groundwater varied from 0.07 μg/L to 15.1 μg/L with a median of 0.7 μg/L. Only two wells (JF-03 and JF-33) had As contents that were higher than the recommended value of 10 μg/L by the WHO.

The Selenium (Se) level in the study region varied from 0.3 μg/L to 4.6 μg/L with a mean of 0.86 μg/L. For comparison, the values reported here are higher than Se levels recorded in CKDu affected regions (mean = 0.19 μg/L; range 0.10 μg/L to 1.14 μg/L; $n = 36$) in the dry zone of the metamorphic terrain (Nanayakkara et al., 2014). For Sri Lanka Fordyce et al. (2000) indicated that Se in groundwater in the dry zone varied from 0.06 μg/L to 0.21 μg/L with the average of 0.11 μg/L while in the wet zone regions it was 0.06 μg/L to 0.09 μg/L with an average of 0.07 μg/L. Selenium is an important parameter due to its dual role as an essential trace nutrient and a toxic element. It is an essential trace element in mammals and plays an important role in the antioxidant enzyme glutathione peroxidase. It protects cells against effects of free radicals that are produced during normal oxygen metabolism (Rayman, 2012). Fordyce et al. (2000) noted that 24–40% of the Sri Lankan female population suffer from Se deficiency. Moreover, association between low Se intake and chronic kidney diseases with uncertain etiology (CKDu) that are widespread in the dry zone areas of Sri Lanka has also been recognized (Jayatilake et al., 2013). Therefore our results suggest that the Jaffna region is less prone to CKDu when judged by groundwater geochemistry.

### 3.3. Oxygen and hydrogen stable isotopes

The $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$ values of groundwater from the Jaffna region varied from −7.1 ‰ to −2.5 ‰ and from −46 ‰ to −20 ‰ (Table 1). Fig. 5 shows the relationship between $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$ of groundwater from the Jaffna peninsula compared to the Local Meteoric Water Line (LMWL). The latter has a regression of $\delta^2H_{H2O} = 8.5 \times \delta^{18}O_{H2O} + 15.0$ (Edirisinghe et al., 2013). When compared to the isotope composition of local precipitation, the groundwater isotope values deviate at a lower slope from the LWML. Therefore the groundwaters are either affected by mixing with ocean water or else by evaporation prior to infiltration in the shallow unsaturated zone. If evaporation is the cause, the regression defines a local evaporation line (LEL) with a slope of 5.8. The least squares fit regression for the isotope composition of Jaffna groundwater is $\delta^2H = 5.8 \times \delta^{18}O_{H2O} - 2.9$ ($r^2 = 0.98$). The intersection of the Jaffna groundwater regression with the LMWL gives a crossover point $\delta_p$ with values of −6.6 ‰ and −41.4 ‰ for $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$, respectively. These values can be regarded as the mean isotopic composition of the local groundwater in the region (Gibson et al., 2008; van Geldern et al., 2014). Although it should also match the weighted mean average of the local precipitation, the weighted mean isotope compositions of rain water in the region were reported as −5.9 ‰ and −34.7 ‰ for $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$ (Edirisinghe et al., 2013). This discrepancy may be explained by the fact that individual rain events during the monsoon time have a stronger influence on groundwater. This preferential recharge would shift the groundwater average value from the weighted annual mean of the local precipitation.

The $\delta^{18}O_{H2O}$ and $\delta H_{H2O}$ values of −0.04 ‰ and −1.2 ‰ were obtained for the near shore coastal waters of Sri Lanka (Chandrajith et al., 2014). These values were used for creating a mixing line between the original groundwater value, derived from the intersection of the LMWL and the Jaffna groundwater regression, and seawater (Fig. 5). This mixing line runs close to the regression of the Jaffna region groundwater samples. This renders isotope mass balances difficult since both processes (i.e. evaporation and mixing of seawater and groundwater) evolve towards more enriched $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$ values. The influence of evaporation of agricultural return flows is currently regarded here the more likely process than mixing with seawater. This is because $\delta^{18}O_{H2O}$ values do not show a linear relation with the chloride contents in groundwater for most samples (Fig. 6). A positive correlation of chloride concentrations and $\delta^{18}O$ values would be expected for seawater-groundwater mixtures. Only a few wells located close to the coast (JF-01, JF-02, JF-05, JF-07 and JF-17) showed enriched contents of chloride along with enriched $\delta^{18}O_{H2O}$ values. This indicates possible admixture of seawater with freshwater for these five specific locations (van Geldern et al., 2013; Chandrajith et al., 2014). On the other hand, chloride can also enter via other pathways such as from anthropogenic activities. These include leaking septic tanks and fertilizer applications. Higher chloride contents are usually not removed from the aquifer system due to its high solubility (Appelo and Postma, 2005). Therefore, the isotope modification that was observed in groundwater relative to the LMWL provides evidences for evaporation processes rather than seawater intrusion except some wells along the shoreline. Similar observations were also made in semi-arid regions by Murad and Krishnamurthy (2008). They demonstrated that groundwater samples plotted below the LMWL with a higher intercept and interpreted this

**Table 1**
Major element composition (in mg/L otherwise specified) of groundwater from the Miocene Limestone region of Jaffna, Sri Lanka.

| Well ID | Well depth (m) | Temp °C | pH | EC mS/cm | $Cl^-$ | $F^-$ | $HCO_3^-$ | $NO_3$-N | $PO_4$ | $SO^{2-}{}_4$ | Na | K | Ca | Mg | $\delta^{18}O$ ‰ | $\delta^2H$ ‰ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JF_01 | 4.2 | 29.8 | 7.84 | 8.78 | 2600 | 0.83 | 145 | 0.5 | 0.35 | 380 | 1300 | 39 | 240 | 150 | −2.94 | −20.5 |
| JF_02 | 4.9 | 29.8 | 7.33 | 9.66 | 3100 | 0.38 | 250 | 0.4 | 0.34 | 150 | 990 | 28 | 530 | 200 | −3.82 | −25.8 |
| JF_03 | 6.0 | 29.6 | 7.16 | 7.95 | 250 | 1.54 | 149 | 0.6 | 0.53 | 37 | 110 | 11 | 68 | 28 | −5.73 | −35.9 |
| JF_04 | 3.0 | 30.1 | 7.96 | 0.92 | 83 | 0.40 | 380 | 0.5 | 0.41 | 21 | 55 | 2.5 | 120 | 27 | −4.80 | −30.7 |
| JF_05 | 3.5 | 30.2 | 7.66 | 9.87 | 3300 | 1.42 | 166 | 0.6 | 0.33 | 430 | 1500 | 44 | 370 | 190 | −2.80 | −19.3 |
| JF_06 | 2.9 | 30.0 | 7.81 | 1.40 | 320 | 0.42 | 190 | 0.6 | 0.35 | 28 | 88 | 4.1 | 84 | 41 | −3.46 | −22.0 |
| JF_07 | 3.4 | 29.8 | 8.20 | 1.13 | 2200 | 0.68 | 601 | 0.5 | 0.29 | 370 | 1200 | 23 | 250 | 140 | −3.54 | −22.7 |
| JF_08 | 3.9 | 30.2 | 7.54 | 4.58 | 1200 | 0.61 | 373 | 0.4 | 0.33 | 120 | 640 | 33 | 150 | 73 | −3.29 | −21.2 |
| JF_09 | 21 | 30.2 | 7.32 | 2.55 | 580 | 0.47 | 341 | 2.0 | 0.36 | 81 | 260 | 18 | 130 | 45 | −5.72 | −34.5 |
| JF_10 | 5.3 | 30.1 | 7.46 | 0.82 | 67 | 0.12 | 317 | 3.0 | 0.30 | 26 | 49 | 6.2 | 94 | 6.4 | −6.27 | −38.6 |
| JF_11 | 39 | 30.2 | 7.28 | 0.94 | 140 | 0.09 | 198 | 5.8 | 0.13 | 30 | 72 | 3.7 | 100 | 7.3 | −6.66 | −42.8 |
| JF_12 | 3.4 | 30.4 | 7.43 | 1.18 | 190 | 0.20 | 279 | 4.1 | 0.37 | 35 | 100 | 5.8 | 120 | 16 | −6.63 | −41.7 |
| JF_13 | 2.6 | 30.4 | 7.40 | 1.90 | 360 | 0.35 | 176 | 2.3 | 0.29 | 210 | 200 | 4.8 | 160 | 27 | −4.79 | −30.2 |
| JF_14 | 3.9 | 30.5 | 7.39 | 1.20 | 200 | 0.32 | 196 | 0.6 | 0.34 | 81 | 140 | 14 | 79 | 14 | −2.47 | −18.5 |
| JF_15 | 4.6 | 30.6 | 7.80 | 2.00 | 370 | 0.21 | 294 | 5.4 | 0.41 | 96 | 330 | 25 | 50 | 31 | −4.82 | −28.8 |
| JF_16 | 4.0 | 31.0 | 7.79 | 0.74 | 63 | 0.20 | 281 | 0.5 | 0.32 | 23 | 25 | 6.7 | 120 | 4.6 | −4.00 | −23.1 |
| JF_17 | 2.7 | 31.2 | 7.91 | 10.51 | 3500 | 0.43 | 258 | 1.1 | 0.56 | 68 | 1100 | 24 | 660 | 220 | −3.88 | −25.1 |
| JF_18 | 2.8 | 31.2 | 6.81 | 0.48 | 55 | 0.25 | 99 | 5.3 | 0.25 | 20 | 25 | 0.9 | 45 | 10 | −3.26 | −21.7 |
| JF_19 | 5.7 | 31.5 | 7.81 | 1.30 | 180 | 0.14 | 346 | 0.9 | 0.80 | 50 | 190 | 21 | 41 | 12 | −3.99 | −26.3 |
| JF_20 | 2.5 | 31.8 | 7.19 | 2.19 | 550 | 0.46 | 92 | 0.5 | 0.38 | 96 | 220 | 27 | 52 | 34 | −1.98 | −14.9 |
| JF_21 | 3.5 | 30.8 | 7.79 | 0.79 | 63 | 0.08 | 313 | 2.5 | 0.35 | 26 | 42 | 8.8 | 110 | 5.9 | −6.12 | −37.1 |
| JF_22 | 7.9 | 30.8 | 7.95 | 1.98 | 340 | 0.71 | 381 | 3.1 | 0.36 | 120 | 330 | 2.3 | 52 | 20 | −5.55 | −35.0 |
| JF_23 | 4.6 | 31.2 | 7.59 | 0.82 | 120 | 0.23 | 192 | 3.1 | 0.44 | 20 | 47 | 1.1 | 100 | 7.3 | −5.46 | −36.1 |
| JF_24 | 7.1 | 31.3 | 7.68 | 1.63 | 300 | 0.13 | 315 | 1.8 | 0.40 | 42 | 130 | 38 | 150 | 24 | −6.00 | −37.1 |
| JF_25 | 9.5 | 30.5 | 7.98 | 2.55 | 530 | 0.45 | 419 | 2.7 | 0.37 | 92 | 320 | 16 | 99 | 49 | −6.24 | −39.8 |
| JF_26 | 3.0 | 30.8 | 7.40 | 0.63 | 91 | 0.13 | 166 | 0.7 | 0.25 | 14 | 45 | 2.8 | 58 | 9.2 | −5.47 | −34.7 |
| JF_27 | 4.8 | 30.9 | 7.79 | 1.42 | 280 | 0.55 | 218 | 0.7 | 0.32 | 49 | 190 | 12 | 53 | 28 | −4.58 | −30.2 |
| JF_28 | 4.2 | 30.7 | 7.80 | 2.56 | 670 | 0.21 | 136 | 0.6 | 0.28 | 71 | 350 | 8.7 | 84 | 37 | −4.44 | −29.4 |
| JF_29 | 4.4 | 31.0 | 7.80 | 0.56 | 56 | 0.19 | 198 | 0.6 | 0.28 | 13 | 33 | 5.2 | 53 | 13 | −5.08 | −29.9 |
| JF_30 | 4.6 | 31.3 | 7.97 | 0.77 | 56 | 0.10 | 303 | 0.6 | 0.48 | 32 | 52 | 3.3 | 90 | 13 | −6.51 | −40.5 |
| JF_31 | 4.0 | 30.4 | 7.50 | 2.49 | 600 | 0.44 | 268 | 0.5 | 0.19 | 77 | 320 | 9.8 | 84 | 48 | −3.56 | −23.8 |
| JF_32 | 4.3 | 30.6 | 7.40 | 0.67 | 30 | 0.16 | 266 | 0.5 | 0.31 | 33 | 30 | 36 | 51 | 13 | −6.10 | −39.9 |
| JF_33 | 4.3 | 30.3 | 7.20 | 0.50 | 62 | 0.21 | 125 | 1.4 | 0.37 | 14 | 84 | 11 | 10 | 1.9 | −2.53 | −20.4 |
| JF_34 | 4.3 | 30.1 | 7.30 | 0.76 | 81 | 0.20 | 150 | 5.9 | 0.26 | 76 | 71 | 7.6 | 66 | 6.7 | −6.48 | −41.9 |
| JF_35 | 5.5 | 30.0 | 6.80 | 0.31 | 39 | 0.14 | 96 | 1.4 | 0.52 | 17 | 50 | 2.0 | 7.6 | 2.2 | −7.10 | −45.5 |
| Mean | 5.9 | 30.5 | 7.57 | 2.53 | 646 | 0.38 | 248 | 1.8 | 0.36 | 87 | 305 | 14.5 | 129 | 44 | | |
| Median | 4.3 | 30.5 | 7.59 | 1.30 | 250 | 0.25 | 250 | 0.7 | 0.35 | 49 | 130 | 9.8 | 90 | 24 | | |

finding as evidence of the evaporation of return flows resulting from intense agricultural activities.

The geochemical data obtained from this study indicate that the evolution of groundwater in the region is currently marked by processes such as carbonate dissolution and irrigation return flows that were subject to evaporation prior to infiltration as evident from stable isotope measurements and major solute composition. Excess $Na^+$ and $Cl^-$ in the groundwater could stem from agricultural activities such as application of chemical fertilizers such as ammonium chloride and animal manure. The observed enriched stable isotope compositions in the samples are potentially related to the high degree of evaporation prior to infiltration rather than seawater intrusion as $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$ values do not correlate with groundwater chloride concentrations.

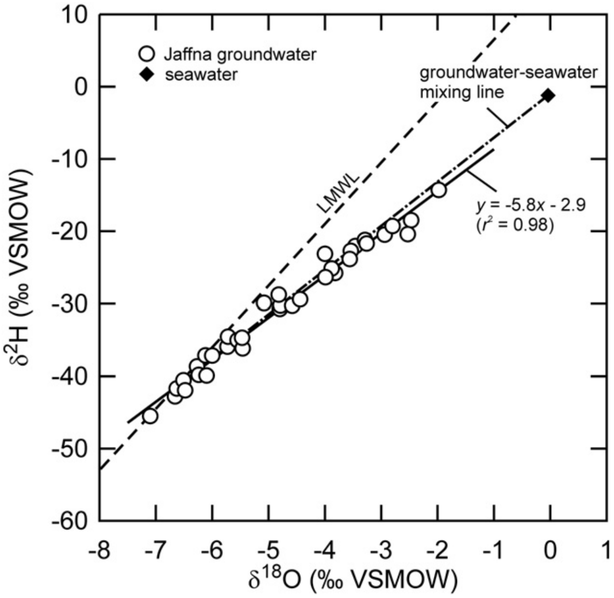

**Fig. 5.** $\delta^2H_{H2O}$ versus $\delta^{18}O_{H2O}$ for groundwater from the Miocene aquifer systems of the Jaffna Peninsula relative to the Local Meteoric Water Line (LMWL). Possible local evaporation line (LEL) and groundwater-seawater mixing line are also shown.

## 4. Conclusions

This study helped to narrow down sources of solute composition in groundwater and their behaviors in the aquatic systems in the Jaffna Peninsula, Sri Lanka. It is representative for a typical tropical coastal region that is underlain by limestones. The quality of groundwater in the region is mainly impacted by geogenic factors but also modified by anthropogenic activities such as irrigation and fertilizer applications. The stable isotope composition of Jaffna water indicates that groundwater is mainly derived from local modern precipitation. The enriched $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$ groundwater values are mainly the result of progressive evaporative concentration of the heavier isotopes prior to water infiltration and groundwater recharge. This process mainly occurs during irrigation under warm ambient temperatures. Simultaneously, the irrigation return flow also led to evaporative concentration of solutes in groundwater. This process is even more pronounced if parts of the groundwater water are pumped a cycle for agricultural irrigation purposes and the evaporative concentration occurs consecutively during each pumping cycle. However, some wells located near the coast show indications for seawater intrusion. At present, the quality

**Table 2**
Trace element composition (in μg/L) of groundwater from Jaffna Region in Sri Lanka measured by ICP-MS.

| Well ID | Li | B | Al | Cr | Mn | Fe | Ni | Cu | Zn | As | Se | Sr | Ba | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JF_01 | 53 | 580 | 9.7 | 0.3 | 2.9 | 18 | 2.6 | 2.2 | 130 | 1.8 | 0.5 | 12,000 | 110 | 15 |
| JF_02 | 33 | 200 | 9.0 | 0.3 | 85 | 20 | 2.8 | 1.1 | 49 | 0.3 | <0.3 | 7200 | 710 | 2.6 |
| JF_03 | 2.6 | 190 | 7.7 | 0.3 | 130 | 34 | 0.9 | 1.0 | 15 | 15.1 | <0.3 | 950 | 140 | 0.1 |
| JF_04 | 5.3 | 83 | 5.9 | 0.4 | 54 | 400 | 19 | 0.9 | 11 | 3.3 | <0.3 | 3204 | 15 | 0.2 |
| JF_05 | 60 | 910 | 7.9 | 0.4 | 3.1 | 18 | 3.1 | 1.6 | 68 | 0.4 | 0.9 | 6800 | 160 | 4.4 |
| JF_06 | 4.4 | 180 | 8.1 | 0.5 | 1.1 | 14 | 1.3 | 2.4 | 23 | 0.2 | 0.3 | 860 | 300 | 3.5 |
| JF_07 | 45 | 280 | 3.3 | 0.2 | 130 | 110 | 2.9 | 0.5 | 36 | 6.1 | <0.3 | 8800 | 120 | 2.0 |
| JF_08 | 17 | 470 | 9.4 | 0.5 | 8.8 | 18 | 19 | 3.7 | 13 | 0.7 | 0.7 | 3500 | 200 | 3.6 |
| JF_09 | 8.4 | 160 | 23 | 0.8 | 16 | 35 | 2.8 | 2.5 | 130 | 0.6 | <0.3 | 1301 | 190 | 4.0 |
| JF_10 | 0.5 | 15 | 4.0 | 0.5 | 1.7 | 6.6 | 0.7 | 0.7 | 56 | 0.1 | 3.3 | 310 | 45 | 0.8 |
| JF_11 | 0.7 | 35 | 7.0 | 2.3 | 0.5 | 11 | 1.0 | 0.7 | 12 | 0.1 | 0.4 | 220 | 11 | 0.5 |
| JF_12 | 1.8 | 56 | 18 | 1.2 | 1.3 | 23 | 1.4 | 2.0 | 62 | <0.1 | 0.9 | 580 | 28 | 2.8 |
| JF_13 | 3.6 | 130 | 7.4 | 0.5 | 3.5 | 12 | 7.5 | 2.5 | 18 | 0.2 | 0.9 | 840 | 9 | 3.8 |
| JF_14 | 2.3 | 61 | 8.5 | 0.6 | 1.6 | 15 | 14 | 2.7 | 25 | 0.7 | 0.7 | 450 | 110 | 2.7 |
| JF_15 | 6.3 | 190 | 16 | 0.7 | 0.8 | 21 | 5.2 | 4.3 | 17 | 1.0 | 1.6 | 710 | 86 | 2.3 |
| JF_16 | 2.7 | 35 | 9.1 | 0.4 | 62 | 17 | 1.0 | 1.2 | 20 | 0.9 | <0.3 | 520 | 41 | 0.3 |
| JF_17 | 28 | 180 | 14 | 0.7 | 510 | 120 | 7.9 | 1.7 | 19 | 4.1 | <0.3 | 21,000 | 450 | 0.7 |
| JF_18 | 0.4 | 79 | 9.8 | 0.6 | 1.0 | 20 | 2.6 | 2.1 | 17 | 0.6 | 0.8 | 380 | 61 | 1.0 |
| JF_19 | 0.9 | 64 | 15 | 0.5 | 2.2 | 28 | 3.8 | 5.2 | 24 | 7.4 | <0.3 | 360 | 63 | 0.5 |
| JF_20 | 7.8 | 120 | 8.4 | 0.8 | 0.5 | 8.9 | 2.7 | 2.1 | 8.3 | 2.5 | <0.3 | 950 | 40 | 2.1 |
| JF_21 | 0.3 | 27 | 5.7 | 0.4 | 1.0 | 9.0 | 2.5 | 1.7 | 110 | 0.1 | 0.8 | 330 | 64 | 1.3 |
| JF_22 | 1.1 | 330 | 5.8 | 0.6 | 0.6 | 7.4 | 0.8 | 4.1 | 55 | 0.9 | 4.6 | 360 | 28 | 1.9 |
| JF_23 | 2.2 | 64 | 8.3 | 0.5 | 4.9 | 13 | 2.3 | 2.4 | 12 | 0.3 | 0.6 | 410 | 25 | 4.3 |
| JF_24 | 1.9 | 69 | 3.5 | 0.3 | 0.5 | 6.3 | 1.8 | 1.4 | 20 | 0.2 | 2.7 | 870 | 210 | 1.3 |
| JF_25 | 11 | 190 | 50 | 1.0 | 4.9 | 68 | 2.2 | 3.8 | 65 | 0.8 | 1.2 | 880 | 120 | 3.2 |
| JF_26 | 0.8 | 53 | 12 | 0.6 | 1.7 | 19 | 1.6 | 0.8 | 16 | 2.7 | <0.3 | 450 | 14 | <0.1 |
| JF_27 | 1.7 | 290 | 12 | 0.9 | 1.8 | 12 | 2.7 | 2.2 | 19 | 0.2 | 1.3 | 420 | 160 | 0.4 |
| JF_28 | 6.5 | 130 | 11 | 0.5 | 1.8 | 13 | 1.4 | 1.9 | 16 | 0.8 | <0.3 | 580 | 190 | 0.9 |
| JF_29 | 0.5 | 100 | 17 | 1.0 | 200 | 63 | 7.6 | 3.9 | 31 | 1.7 | 0.6 | 250 | 350 | 0.1 |
| JF_30 | 1.6 | 38 | 7.8 | 0.5 | 120 | 27 | 2.5 | 1.1 | 18 | 1.1 | <0.3 | 270 | 120 | 0.1 |
| JF_31 | 8.3 | 220 | 8.7 | 0.6 | 3.4 | 14 | 1.9 | 1.2 | 14 | 0.5 | <0.3 | 840 | 98 | 3.3 |
| JF_32 | 0.4 | 37 | 7.9 | 0.4 | 4.4 | 24 | 3.3 | 2.0 | 23 | 0.4 | <0.3 | 340 | 430 | 0.3 |
| JF_33 | 2.0 | 130 | 20 | 0.8 | 1.4 | 23 | 1.8 | 2.0 | 9.7 | 11 | <0.3 | 70 | 42 | <0.1 |
| JF_34 | 2.3 | 45 | 14 | 0.7 | 160 | 17 | 3.6 | 3.8 | 280 | 0.3 | 2.1 | 240 | 97 | 0.3 |
| JF_35 | 9.6 | 54 | 6.0 | 1.9 | 190 | 8.9 | 5.5 | 2.8 | 140 | 0.5 | 3.0 | 28 | 56 | <0.1 |
| Mean | 9.5 | 166 | 11.2 | 0.66 | 48.9 | 36.4 | 4.1 | 2.2 | 45.2 | 2.0 | 0.86 | 2208 | 140 | 2.0 |
| median | 2.6 | 120 | 8.7 | 0.5 | 3.1 | 18 | 2.6 | 2.0 | 20 | 0.7 | 0.5 | 580 | 98 | 1.3 |
| Min | 0.3 | 15.0 | 3.3 | 0.2 | 0.5 | 6.3 | 0.7 | 0.5 | 8.3 | 0.1 | 0.2 | 28.0 | 9.0 | 0.1 |
| Max | 60 | 910 | 50 | 2.3 | 510 | 400 | 19 | 5.2 | 280 | 15.1 | 4.6 | 21,000 | 710 | 15 |

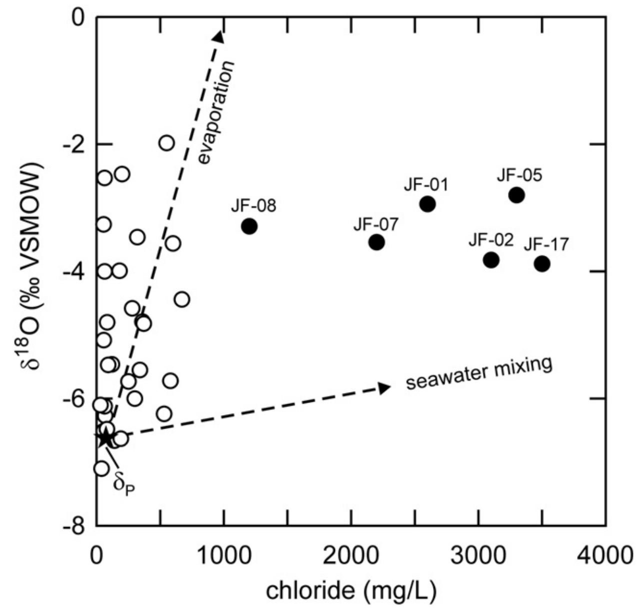

**Fig. 6.** Relationship between chloride concentrations and $\delta^{18}O_{H2O}$ in the study region. Filled circles indicate wells that are potentially influenced by seawater intrusion. Open symbols–groundwater wells with $Cl^- < 1200$ mg/L; closed circles–near shore wells with $Cl^- > 1200$ mg/L; star symbol — average annual mean of precipitation ($\delta_P$) derived from intersection of LEL with LMWL (see Fig. 5).

of groundwater in many of the wells is acceptable for drinking purposes. The currently most imminent vulnerability of groundwater in the region occurs through anthropogenic pollution, and particularly so due to agricultural activities. Extensive groundwater use in the peninsula may also further add concerns of active seawater intrusion after intense abstraction. The area should remain under close monitoring for both quality and quantity in order to protect groundwater as a vulnerable resource.

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