

Groundwater contamination due to salt-panning activity and seawater intrusion at Tuticorin coastal zone, southern Tamil Nadu, India

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Abstract

An attempt was made for the first time in the state of Tamil Nadu to assess the impact of saltpan and salt water intrusion effluent on available water sources existing in and around salt pans. A total of 48 water samples from different sampling sites were collected along coastal line and analyzed for physicochemical parameters such as Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ during Pre-monsoon. Results indicate both higher Cl⁻ and SO₄²⁻ concentration in water samples from salt pans than in water samples from other sources. In addition to ratio of Cl⁻/HCO₃⁻ and Na⁺/Cl⁻ were clearly indicated that relationships of salt pan contamination and seawater intrusion. It is also clearly evident that moles ratio of SO₄²⁻/Cl⁻ vs Cl⁻ and ternary plot differentiated the salt pan and seawater contaminated in the study area. The result obtained conclusively suggests the detrimental impact of saline effluent on water quality in Tuticorin coastal area, rendering it unsuitable for the propagation of life and unfit for agricultural purpose. And this indicates a worse condition of salt pan vicinities, as the ground water is only source of drinking water in those places.

Keywords: Saltpan; Seawater Intrusion; Physicochemical.

1. Introduction

Salinization of coastal fresh water aquifers by seawater intrusion, geomorphic changes, tidal waves, cyclonic storms and man-made hazards are major causes of the ground water pollution in the coastal areas of the Tamil Nadu, India. Studies of groundwater salinization by sea water intrusion in coastal areas in general, But Differentiating salt pan contaminated area from those of seawater incursion area is difficult. Very few literature are available for salt pan contaminated region such as Deuterium and oxygen-18 isotopes study on groundwater salinization of adjoining salt pans in Porbandar coast, Gujarat, India (Chandrasekharan et al. 1997), groundwater contamination due to salt pan along Mumbai coastal zone (Chandrasekharan et al. 2000). Singaraja et al. (2013b) preliminary find out the salt pan contaminate in Tuticorin coastal region. Many of the groundwater in the coastal aquifer is suffering from seawater intrusion by over-abstraction and water quality degradation due to urbanization and agricultural activities. Groundwater pollution has been reported in megacities, as well as in agricultural lands (Burt et al. 1993; Appelo and Postma, 2005; Singaraja et al. 2013a). Intrusion of saline waters in coastal regions occurs naturally, and can be exacerbated due to exploitation of coastal aquifers as water sources (Ozler, 2003; Prasanna et al. 2010; Thilagavathi et al. 2012).

In this scenario salinity problem in the coastal hard rock aquifers has gained its importance due to the lesser quantity of available fresh groundwater. This situation becomes more critical if the region has industrial estates, with urban cities, salt pans, and

aquaculture ponds and with extensive agriculture activities. One such region is the area considered for study, Tuticorin falling on south eastern part of the India. Tuticorin coast attracts various wetland features like creek, coastal sand dune, and mangrove ecosystem. Extensive beach sand dunes enriched with deposits of black sand are seen (Chandrasekar et al. 2011). Industrial area has also been slowly increasing with a number of major and small-scale industries coming up in Tuticorin. The types of industries found here include petrochemicals, thermal power plant, Heavy Water Plant (HWP), chlor-alkali, HCl, trichloro-ethylene, cotton and staple yarn, caustic soda, poly vinyl chlorine resin, fertilizers, soda-ash, and aromatics. Salt is produced on an extensive scale in Tuticorin as the district constitutes 70% of the total salt production of the state and meets almost 30% of the requirement of the country. Climate, soil and availability of brine make it conducive for salt production, and salt pans form the second largest land use class in this region. Within a span of twelve years, salt pan area has increased at the expense of agricultural land, coastal sand with/without vegetation, sand dunes, scrub and mud- flats (Gangai and Ramachandran, 2010). This trend is a cause of concern as these pans are fed by both bore wells and sea brine, and this has seriously affected the groundwater table. Further, once agricultural land has been converted into salt pans, the fertility of the soil is lost.

A holistic study to derive behavior of the groundwater chemistry and its differentiated to salt pan contamination and sea water intrusion of the study area has not been attempted. This study aims to determine the status of the salt pan contamination and sea water intrusion by using the major cations and anions and also to derive

the other possible mechanism responsible for the groundwater chemistry of the region.

climate. The average annual temperature from 23°C to 29°C and the annual rainfall is about 570 mm to 740 mm.

2. Study area

The present study area is, situated in the southeast coast of Tamil Nadu, India. It is located between 8° 19' to 9° 10' N latitude and 77° 04' to 78° 23' E longitude (Fig.1) covering an area of about 1115Km². The salt pans in the basin have been use for salt manufacture for the past 70 years. The area experiences a hot tropical

2.1. Geomorphology of the area

The salt pans are located in the coastal depression of Tuticorin coastal region which extends from a nearby, many villages like Mullakkadu, Mudukkadu, Veppalodai, Toppasipatti, near

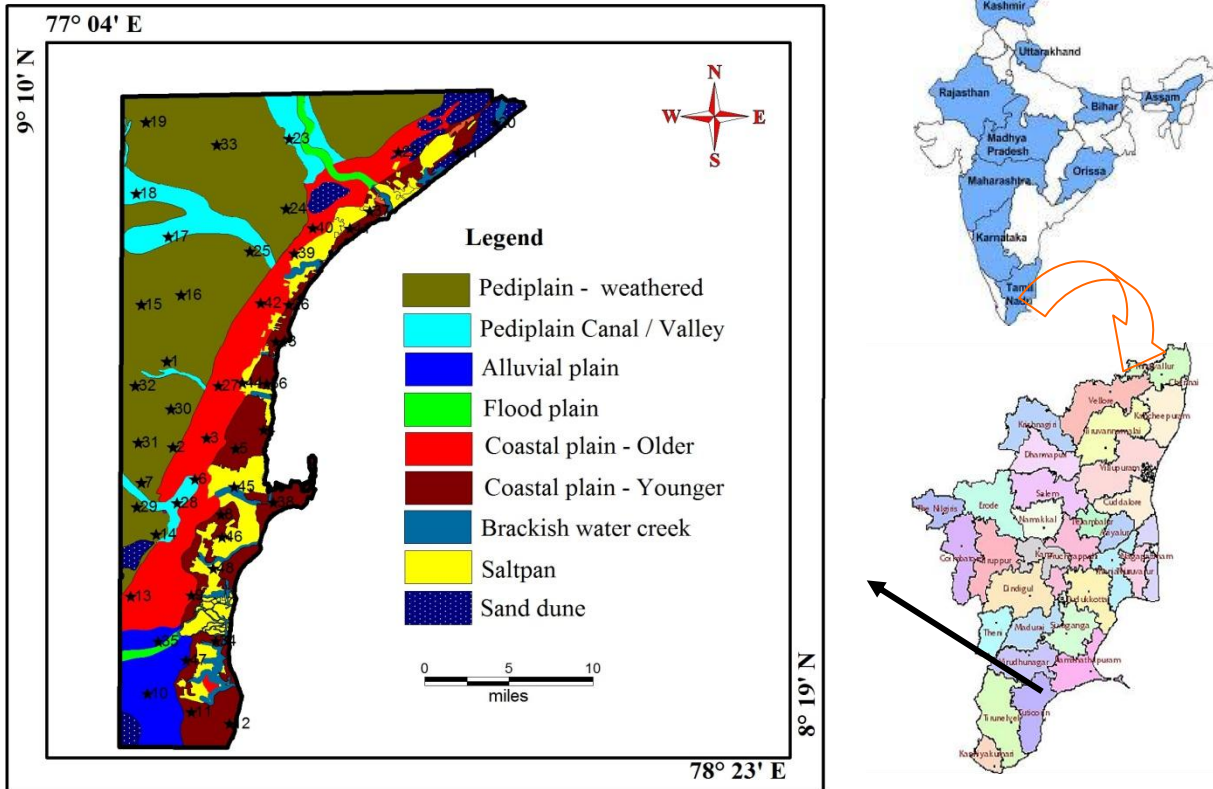


Fig. 1: Sample location and Geomorphology map of the study area

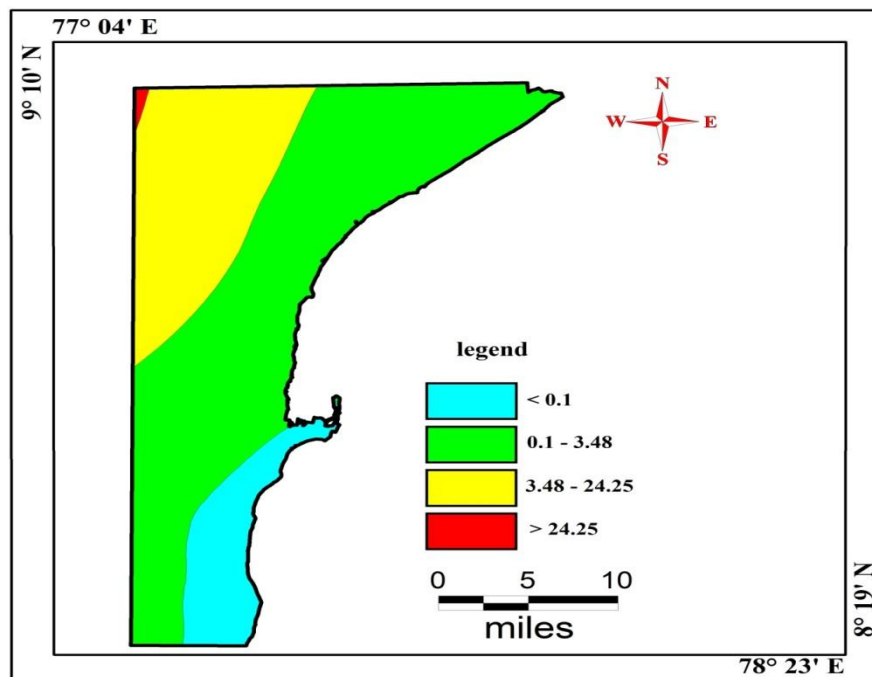


Fig. 2: Water level map of the study area during study period (All values in m AMSL)

Taruvaikulam, Panaiyur and Kallurani. There are older, younger, alluvial plain deposits along the sea coast. Pediplain presented in northwestern part followed by few batches of sand dune covered in the study area (Fig. 1).

2.2. Hydrological features

The area adjacent to salt works is covered by a thin layer of soil along the coast line, groundwater conditions were determined by an inventory of 20 open wells. The depth to water level in the study area varied between -4.70 to 24.25m AMSL. It is also noted that most of the wells range from -4.70 to 3.48m AMSL along coastal region, except a few which have deeper water levels apart from coast (Fig. 2). Groundwater generally moves from land side towards salt pans and also from coastal side although there are local changes in the flow direction.

3. Materials and methods

A total of 48 groundwater samples (Fig.1) were collected in during PRM. The sample bottles were labeled, sealed, and transported to the laboratory under standard preservation methods. The major anionic and cationic concentrations were determined in the laboratory using the standard analytical procedures (Table 1).

4. Results and discussions

4.1. Hydro geochemistry

Groundwater from the study area is neutral to alkaline with pH ranging from 6.30 to 9.20. Maximum value was noted that salt pan region eastern part of the study area, the similar trend was observed from darling pans (Smith et al. 2004). EC values ranges from 308 μ S/cm to 37500 μ S/cm and TDS ranges from 194mg/l⁻¹ and 23699mg/l⁻¹ respectively. Higher concentration was noted that study area indicating effective leaching of ions into the groundwater system during recharge and seawater intrusion, similar trend was also observed in Cuddalore coastal region (Singaraja et al. 2012a).

Among the cations, the concentrations of Na⁺, Ca²⁺, Mg²⁺ and K⁺ ions ranged from 22.70 to 6896.00, 4.00 to 680.00, 4.80 to 1248.00 and 0.50 to 255.00 mg/l⁻¹, with an average of 1732.55, 138.77, 267.56 and 73.48 mg/l⁻¹, respectively. The order of abundance is Na⁺ > Mg²⁺ > Ca²⁺ > K⁺. For the anions, the concentrations of Cl⁻, HCO₃⁻, and SO₄²⁻ falls between 53.18 to 12658.78, 24.40 to 431.00 and 0.50 to 3096.00 mg/l⁻¹ respectively, with an average of 1767.30, 178.36 and 766.70 mg/l⁻¹. The order of their abundance is Cl⁻ > HCO₃⁻ > SO₄²⁻. The maximum, minimum, and average values of groundwater chemical constituents are given in Table 2.

Table 1: Summary of the methods, instruments and make, critical reference materials along with their brands used for the analysis of ions in the given study

Chemical Parameter	Units	Methods and Instrument (make)	Reagents (make)	Methodology References
pH		pH meter (SYSTRONICS)	pH 4.1, 7.0, and 10 (buffer solutions) THERMO ORION	APHA (1992)
EC	μ S/cm	EC meter (SYSTRONICS)	1413 ms/cm Orion application solution, THERMO ORION	APHA (1992)
TDS	mg/l ⁻¹	TDS meter (HANNA)	692 ppm Orion application solution, THERMO ORION	APHA (1992)
Ca ²⁺	mg/l ⁻¹	Volumetric	EDTA, Sodium hydroxide and Murexide (MERCK)	APHA (1992)
Mg ²⁺	mg/l ⁻¹	Volumetric	EDTA, Sodium hydroxide, Ammonia buffer and Erichrome black -T (MERCK)	APHA (1992)
Na ⁺	mg/l ⁻¹	Flame photometer	Sodium chloride (NaCl), KCl and (ELICO)	APHA (1992)
K ⁺	mg/l ⁻¹	Flame photometer (ELICO)	Calcium carbonate (CaCO ₃) (MERCK)	APHA (1992)
HCO ₃ ⁻	mg/l ⁻¹	Volumetric	NaCl, KCl and CaCO ₃ (MERCK)	APHA (1992)
Cl ⁻	mg/l ⁻¹	Volumetric	Hydrosulfuric acid (H ₂ SO ₄), Phenolphthalein and Methyl orange (MERCK)	APHA (1992)
SO ₄ ²⁻	mg/l ⁻¹	UV- Vis Double Beam Spectrophotometer (ELICO)	Silver nitrate, Potassium chromate (MERCK)	APHA (1992)
			Glycerol, HCl, Ethyl alcohol, NaCl, Barium chloride and Sodium sulphate (MERCK)	Eaton et al. (1995)

4.2. Evident for salt pan contaminant and seawater intrusion

4.2.1. Cl⁻/HCO₃⁻ ratio

The ratios of Cl⁻/HCO₃⁻ ranged between 0.41 and 152.50 and had strong positive linear relation with Cl⁻ concentrations with R² value of 0.82 (Fig. 3). This linear relationship indicates simple mixing of fresh groundwater with salt pan and saline waters. It's also interesting to note that there is slight deviation in the linear relationship at the lower range of the mole ratios this is mainly due to the variation in the HCO₃⁻ values. The decrease of this HCO₃⁻ ion represents in the increase of the Cl⁻/HCO₃⁻ ratio even at the lower values of the Cl⁻ represented in the 'X' axis. This decrease of HCO₃⁻ value or increase of Cl⁻ relatives to HCO₃⁻ ions, ie mainly may be due to land use patter (percolation of salt pans) along the coast region of the study area.

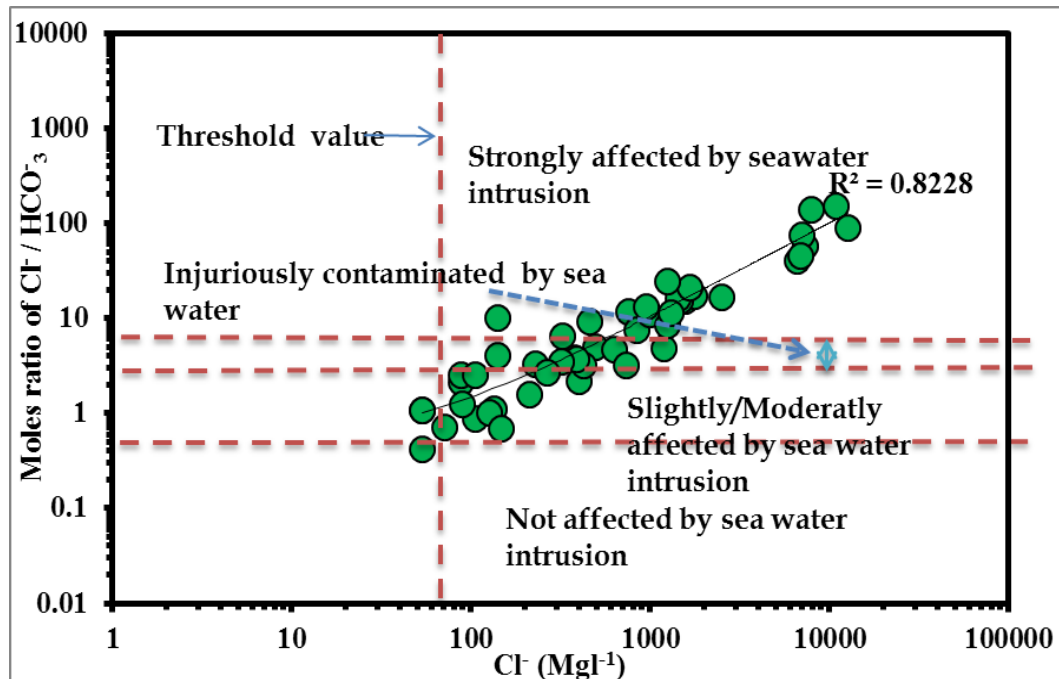
Simpson classification includes five classes: <0.5 for good quality water, 0.5 to 1.3 for slightly contaminated water, 1.3 to 2.8 moderately for contaminated water, 2.8 to 6.6 injuriously contaminated and >15.5 for highly contaminated water. Considering the threshold value of Cl⁻ concentration (63 mg/l) and the ratio of Cl⁻/HCO₃⁻, it was found that about 29% of the groundwater was strongly affected by the saline water, 15% were slightly, 54% moderately affected and 2% of samples were not affected by sea water. The most of the ground waters show the strong contamination with sea water. It is also interesting point note that lesser amount of HCO₃⁻ is also contributed to the groundwater through oxidation of organic matter as a byproduct of SO₄²⁻ reduction (Lyons et al. 1984; Compton, 1988; Last, 1990). As chloride is the dominant ion found in salt pan and seawater while bicarbonate is present only in very small amounts (Singaraja et al. 2013b; Singaraja et al. 2014).

4.2.2. Na⁺/Cl⁻ moles ratio

Moles ratios of Na⁺/Cl⁻ versus Cl⁻ concentrations indicate that ratio values of groundwater falling near the seawater ratio (0.86) indicate that fresh groundwater were contaminated with the saline waters. The Na⁺/Cl⁻ ratios ranged from 0.33 to 8.32 in the present study area. The ratio of Cl⁻ to Na⁺ and Mg²⁺ indicate a predominant seawater source for these ions. Water near to the coast often has a composition similar to seawater from wet and dry deposition of cyclic salts from the salt pan regions that originate as sea-spray or vapour, or from dissolution of salt formed by evaporation of a remnant of seawater (Herczeg and Lyons, 1991). The amount of Na⁺ released into solution by feldspar weathering is relatively minor compared to the large contribution from coastal rainfall, but enrichment is observed in dilute ground waters with Na⁺/Cl⁻ >1.

Table 2: Maximum, Minimum and Average of the chemical constituents in groundwater samples (All values in mg l^{-1} Except EC in $\mu\text{s/cm}$ and pH.)

	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-
Max	9.20	37500	23699	680.00	1248.00	6896.00	255.00	12658.75	3096.00	431.00
Min	6.30	308	194	4.00	4.80	22.70	0.50	53.18	0.50	24.40
Avg	7.05	6523	3855	138.77	267.56	1732.55	73.48	1767.30	766.70	178.36

**Fig. 3:** Molar ratios of $\text{Cl}^-/\text{HCO}_3^-$ versus Cl^- concentration for the study area

The Na^+/Cl^- ratio show that 56% of the samples (Fig. 4) were above the seawater ratio, indicating a large proportion of groundwater was affected by seawater intrusion to certain degrees. It is also evident that very high Na^+/Cl^- ratios may be indicative of anthropogenic contamination, like salt pans (Jones et al. 1999). It is also interesting to note that good correlation exists between SO_4^{2-} and Cl^- and in certain locations they fall above and below the equiline. But samples are also fall above the equiline (Fig. 5), which may also be due to the influence of the salt pans activity in these regions (Smith et al. 2004) such as Mullakkadu, Mudukkadu, Veppalodai, Toppasipatti, near Taruvaikulam, Panaiyur and Kallurani. This process may be enhanced in the study area mainly due to the leaching of the salts after the monsoon from the dried salt pans. The samples falling below the equiline of SO_4^{2-} and Cl^- indicate sea water intrusion (Singaraja et al. 2013b) like Diraspurm, harbor beach, Sippikulam and Sakkamalpurm. It also evident that negative water level (-4.70m AMSL) observed along the coastal region may be due to saltwater intrusion (Fig. 2).

Seawater has distinct ionic ratios such as $\text{Na}^+/\text{Cl}^- = 0.86$, $\text{SO}_4^{2-}/\text{Cl}^- = 0.05$; $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})$ and $\text{Mg}^{2+}/\text{Ca}^{2+} = 5.2$ (Vengosh et al. 2002; Vengosh and Rosenthal 1994). The minimum and maximum values of these ratios in the samples of the study area are given in (Table 3). The Na^+/Cl^- ratio is greater than unity in about 67% of the samples of the study area. The Na^+/Cl^- molar ratio could reach unity due to the mixing of seawater and freshwater (Vengosh and Rosenthal 1994). Relative to seawater, the groundwater has relatively low Na^+/Cl^- ratios in many samples (0.20–3.73), high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios and high $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratios

(greater than unity) (Vengosh et al. 2002, Mondal et al. 2010). The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ionic ratio greater than 5 is a direct indicator of seawater contamination as noted in few samples of the study area.

High $\text{SO}_4^{2-}/\text{Cl}^-$ ratio is attributed to the application of gypsum fertilizers (Vengosh et al. 2002). Higher SO_4^{2-} values comparative to the Cl^- values may also due to the influence of the salt pans in the region (Smith et al. 2004). It is also clearly find that ternary plot (Fig. 6) distributed the salt pan contaminated region and saltwater intrusion region in the study area. Lesser values of K^+/Cl^- and $\text{SO}_4^{2-}/\text{Cl}^-$ indicate aquifers with relatively lesser anthropogenic impact. K^+ seems to be also contributed from anthropogenic sources, this finding get strengthen by the comparison of K^+/Cl^- ratio that found quite higher and equivalent to waste water infiltration. $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio depicts Sea water intrusion process in most of the samples and but still the ratios may also result from several complex reactions in the aquifer (Kumar et al. 2006). When an aquifer has an underlying layer of saline water and is pumped by a well penetrating only the upper freshwater portion of the aquifer, a local rise of the interface below the well occurs. This phenomenon is known as upconing (Singaraja 2011). The interface is near horizontal at the start of pumping. With continued pumping, the interface rises to progressively higher levels until eventually it reaches the well. This generally necessitates the well to be shut down because of the degrading influence of the saline water. When pumping is stopped, the denser saline water tends to settle downward and to return to its former position. Observations of all these ratios (Table 3) indicate that there is also a possibility of saline upconing conditions in the study area.

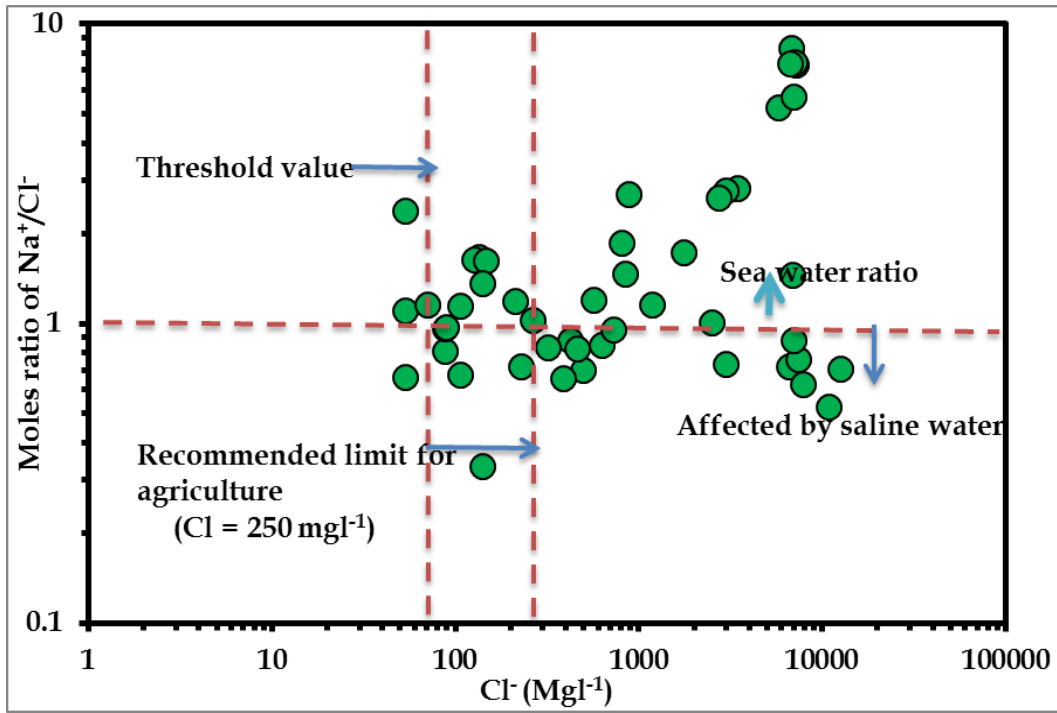


Fig. 4: Molar ratios of Na^+/Cl^- versus Cl^- concentration

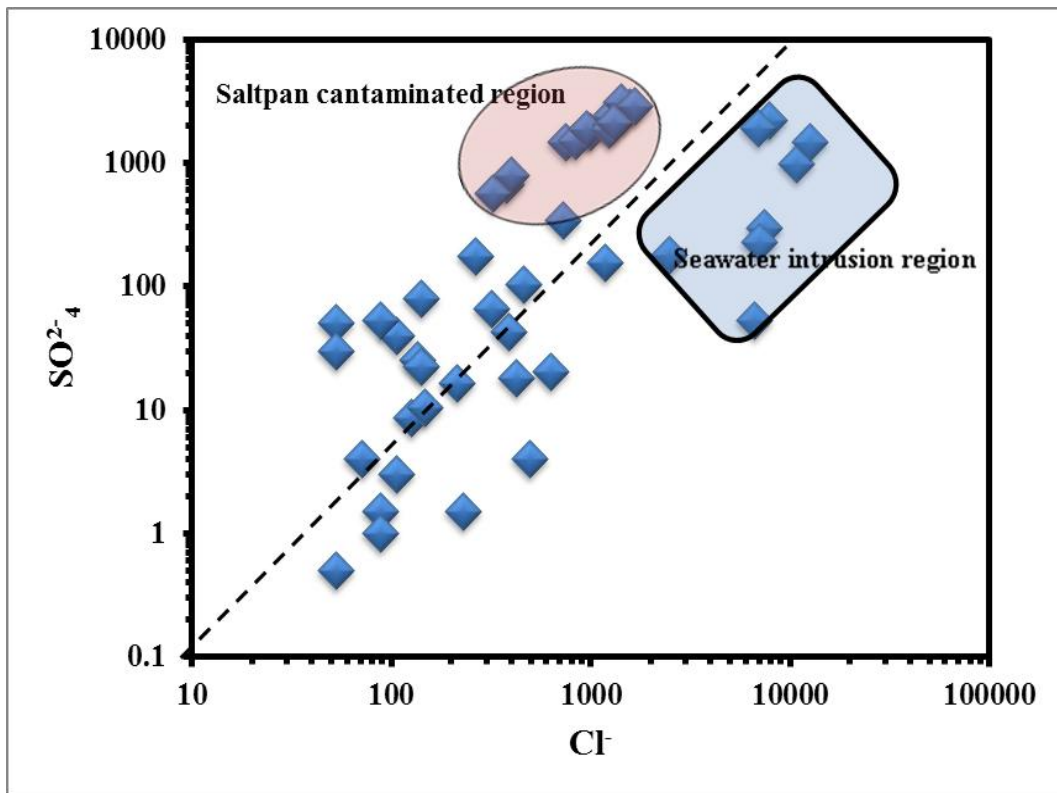


Fig. 5: Relationship between Cl^- and SO_4^{2-}

Table 3: The comparative ionic ratio of potential salinization sources and study area groundwater parameter for seawater intrusion

Parameter	Seawater intrusion	Deep saline up coning	Agriculture return flows	Wastewater infiltration	Study area
Na^+/Cl^-	0.86–1 ^a	< 0.8 ^b	–	1.1 ^c	0.33 – 8.32
$\text{SO}_4^{2-}/\text{Cl}^-$	0.05 ^{a,c}	*0.05 ^{c,d}	>> 0.05 ^e	0.09 ^d	0.005 – 1.60
K^+/Cl^-	0.019	< 0.019	–	>> 0.02	0.0 – 0.273
$\text{Mg}^{2+}/\text{Ca}^{2+}$	> 5 ^b	> 1 ^a	–	–	0.226 – 9
$\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})$	0.35 – <1	< 1 ^a	–	–	0.02 – 5.08

a) Vengosh and Rosenthal (1994), b) Vengosh and Ben-Zvi (1994), c) Vengosh et al.(1994), d) Mercado (1985) and e) Vengosh et al. (2002)

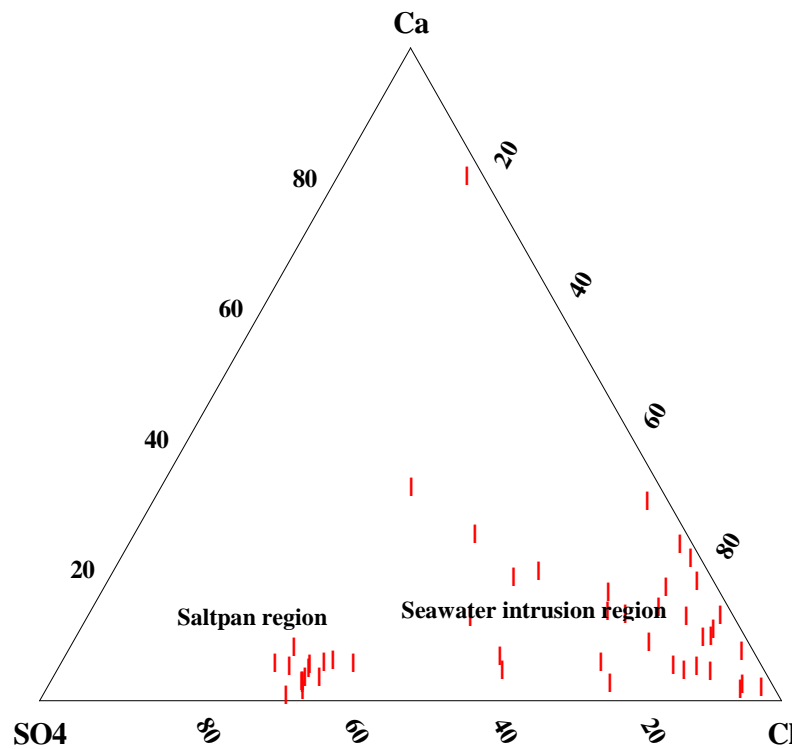


Fig. 6: Ternary plot for study area

5. Conclusion

The above study indicates the ratio of $\text{Cl}^-/\text{HCO}_3^-$ show that about 29% of the groundwater was strongly affected by the saline water. It is also noted that lesser amount of HCO_3^- is also contributed to the groundwater through oxidation of organic matter by product of SO_4^{2-} reduction may be due to salt pan contaminated in the study area. Na^+/Cl^- ratios may be indicative of anthropogenic contamination, like salt pans. Good correlation between SO_4^{2-} and Cl^- and in few locations they fall above the equiline which may be due to the influence of the salt pans activity in these regions. The samples falling below the equiline of SO_4^{2-} and Cl^- indicate sea water intrusion.

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