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Hydrochemistry in integration with stable isotopes (δ^{18} O and δ D) to assess seawater intrusion in coastal aquifers of Kachchh district, Gujarat, India



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ABSTRACT

Coastal aquifers are highly vulnerable to salinization, especially by seawater intrusion. This problem is exacerbated by increasing demands for freshwater in coastal zones due to urbanization and industrialization. This paper investigates seawater intrusion in coastal aquifers of Kachchh district in Gujarat, an economic hub of the country in western India. A total of 26 groundwater samples were collected from various villages of the district from Kandla to Mandavi. In this study hydro-chemical, stable isotope ($\delta^{18}O$ and δD) and GIS analysis were used to infer salinization processes. The origin of salinity and mixing of various water masses has been studied through the integration of major ions chemistry with stable isotopes $\delta^{18}O$ and δD . Most of the samples were showing Na-Cl type water facies. It was observed that besides natural processes (such as water-rock interaction, ion exchange, dissolution/precipitation dynamics and evaporation) which are governing the groundwater quality, current land use practices have augmented the salinization in this poorly drained semi-arid area. Various ionic ratios (such as Mg^{2+}/Ca^{2+} , Na^+/Cl^- , SO_4^{2-}/Cl^- , K^+/Cl^-) and isotopic composition ($\delta^{18}O$ and δD) of groundwater suggest that while in coastal areas seawater intrusion and formation of saline plumes is taking place, due to upconing of underlying natural saline water which is enhanced by overexploitation. In inland areas groundwater quality is deteriorating due to infiltration of wastewater and irrigation return flow. The continued stress on land and water resources has shifted the natural balance and accelerated the salinization process in this water scarce region. For securing freshwater in future, the integrated water resources management is required which should also include calculation of groundwater budget in the coastal aquifer.

1. Introduction

Most of coastal areas are economic hub worldwide due to abundance of natural resources and navigational facilities and currently supporting two third of the population. Industrialization and urbanization often led to overexploitation of various natural resources in the coastal region, especially groundwater. Indiscriminate withdrawal of groundwater to meet the growing demand for various purposes leads to a decrease in piezometer level, which induces seawater intrusion. Seawater intrusion induced deterioration of groundwater quality and salinization has been reported throughout the world, e.g. Mediterranean region (Gimenez and Morell, 1997; Pulido-Bosch et al., 1999), Croatia (Biondic et al., 2006), Mexico (Escolero et al., 2007), Israel (Kafri et al., 2007), and Greece (Panagopoulos, 2008). This makes groundwater resources highly vulnerable, especially in an arid and semi-arid region where due to limited availability of surface water groundwater is the only source of potable drinking in the coastal region. Salinization also reduces agricultural productivity and limits the choice of a crop (Van Dam, 1999; Arslan and Demir, 2013). Salinization of aquifers may lead to serious consequences and jeopardize the environment and the economy of the region.

The extent of saline water intrusion in coastal area is governed by coastal topography, aquifer lithology, sea to the inland hydraulic gradient and the rate of recharge and withdrawal of groundwater (Freeze and Cherry, 1979). The variations in sea level and changes in aquifer recharge control the processes at the interface between the freshwater and seawater. Changes in the interface position trigger ion exchange and redox reactions, dissolution–precipitation (Appelo, 1994; Appelo, 1996).

Salinization in coastal regions is frequently observed in both confined and unconfined aquifers (Gilboa, 1966; Ikeda, 1985). In the case of unconfined aquifers, excessive pumping of groundwater leads to a decline in the piezometric level induced seawater intrusion. In confined aquifers, the groundwater is generally isolated from seawater by

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confining bed of argillaceous sediments, which have frequently deposited in the latest transgression, due to such isolation, the water salinization process in the confined aquifer system is more complicated.

In various part of India also, salinization of coastal aquifers has been reported by various authors: Digha, West Bengal (Choudhury et al., 2001), Godavari Region (Surinaidu et al., 2014), Chennai (Nair et al., 2016), Gujarat (Desai et al., 1979; Rina et al., 2013a, 2013b). Various approaches are used to study seawater intrusion, such as geophysical (Rao et al., 2011; Werner et al., 2013; Akpan et al., 2013), numerical (Bobba, 2002; Abudawia and Rosier, 2015), and various isotopic approaches (Khaska et al., 2013; Gemitzi et al., 2014; Mahlknecht et al., 2017; Kanagaraj et al., 2018), conventional geochemical methods such as the use of chemical concentrations of major and trace elements (Mondal et al., 2011) which may help to elucidate the mixing of end members. Mechanism of SW–GW mixing has been extensively studied through an array of environmental isotopes and chemical tracers (Nair et al., 2015; Zamora et al., 2017). The δ D and δ ¹⁸O stable isotopes are known to be potential markers of the water origin.

Situated in the west coast, State Gujarat is one of the fast-growing economies among Indian states and having 4th highest GDP in India. In coastal areas of Gujarat, the problem of groundwater salinity was first detected in the late sixties and seventies after large-scale pumping by farmers. Over the years, the problem of salinity ingress has affected 12 coastal districts in the state. A total of 2542 village are affected either by dynamic salinity or inherent salinity. Salinization is one of the major environmental concerns in the coastal region of the area. The present study has been done in the lower reaches of Kachchh district, which is experiencing an industrial boom also. Approximately 40 medium and several large industrial units along with two major ports at Mundra and Mandvi and seven minor ports has been established in the lower reaches of Kachchh district.

In this context, the present study is an effort to understand the geochemical processes governing the groundwater salinization in this water-scarce region. Hydro-chemistry in integration with stable isotope (δ^{18} O and δ D) has been used to study seawater intrusion in the area.

2. Material and methods

2.1. Study area

2.1.1. Geohydrology and climate of the study area

Kachchh is the largest district of Gujarat, which is bounded in the north by the Sindh Province of Pakistan, northeast by Rajasthan state, while its southern margin is shared with the Gulf of Kachchh and western and in southwestern side Arabian Sea is present.

2.1.2. Climate

Kachchh region is characterized by an arid climate; summer is very hot, and sandstorms are common with the maximum temperature of about 44–46 °C, whereas in winter the maximum temperature generally varies from 10 to 14 °C. The monsoon prevails for a very short period (June–August) with a meager and erratic rainfall. The average rainfall in the area is 456.61 mm. Diurnal variation in temperature may be as large as 20 °C. Potential evapotranspiration varies between 3.4 and 9.2 mm/d (CGWB, 2013). Due to scanty rainfall and an ephemeral river system, the entire study area depends heavily on groundwater for its domestic, agriculture and industrial requirements. An acute shortage of water is exacerbated by the inferior water quality in terms of salinity.

2.1.3. Hydrogeological setup of the area

The Kachchh Basin is a western margin pericratonic rift basin of India. The geology of Kachchh Peninsula is very intruding; it shows three major formations-Mesozoic, Tertiary and Quaternary. The Mesozoic formation comprises Late Triassic (Rhaetic) Continental, Middle to Late Jurassic marine and Late Jurassic to Early Cretaceous fluvio-deltaic sediments. Mesozoic sediments are the rift filled sediments and constitute the major part of the basin. The Tertiary sediments, on the other hand, are mostly shallow marine shelf sediments in the peripheral and intervening structural lows bordering Mesozoic uplift areas. The Quaternary formation consists of a wide variety of sediments ranging from marine to fluvial, lacustrine and aeolian. Maximum stratigraphic succession is exposed in Kachchh mainland situated at the depocentral region. Sedimentary rocks of middle Jurassic to Recent period of marine and non-marine origin formed under different environmental conditions are present in the district. The tertiary rock of the Kachchh Basin is economically important - they produce good quality limestone, clay, lignite and bauxite deposits. Rann of Kachchh is known for salt and brine producing capabilities.

The region is conspicuously featured by uplands surrounded by lowlands. The uplands are rugged, hilly terrain exposing the Mesozoic rocks bordered by thin strips of gently dipping Cenozoic rocks which form coastal plains. The lowlands are extensive plains, alluvial or mud and salt flats (Rann) and grassy undulations (Banni). The highlands are the areas of uplifts and the plains are intervening basins. The Kachchh mainland can be broadly divided into the following regions: (i) The Great Rann, (ii) Mainland, consisting of planes, hills and dry river beds, (iii) The Coastline along the Arabian Sea in the South and (iv) The Grasslands of Banni. The drainage of the Kachchh is largely governed by lithology and tectonics, sea level changes also affect the drainage of the area. In general, drainage pattern of the area is dendritic in nature.

Semiarid climate, erratic rainfall and presence of limited surface water body and frequent drought make the region's water scarce. The groundwater occurrence and movement depend on the hydrogeological setup of the area; hydro-geologically, the study area can be divided into - 1. Mesozoic formations, 2. Deccan trap (Hard Rock) as the aquifer, 3. Tertiary formations and 4. Quaternary sediments (CGWB, 2013).

Despite huge investments in piped water supply, this region of Gujarat reels under a severe drinking water crisis throughout the year. Modern and traditional technologies are failing, wells and bores are drying up rapidly and drinking water quality is deteriorating. Groundwater in most of the area is brackish to saline. Central, eastern and western part of the district, yield potable water, and the southern area yields potable to brackish water from confined aquifers. The central and southern part of the district is occupied by Basaltic formation and yield limited quantity of potable water from unconfined aquifer.

2.2. Sampling and analytical procedure

For sample collection, an extensive field survey was done based on topographic sheets, Garmin GPS and satellite images of the area. The study area was divided into several grids $(5 \text{ km} \times 5 \text{ km})$ on satellite images and representative groundwater samples were collected based on the spectral signature. A total 26 groundwater samples were collected during October 2015 from the following villages-Tuna, Rampar, Chandrapar, Vira, Bhadreshwar, Vadala, Mokha, Gundala, Mundra, Maska, Undhiyari, Bhadia, Nani Khakkar, Navinal, Dhrab, Toda, Chhasara, Chandroda, Khedoi, Nagalpar, Dhabra, Anjar, Varshamedi, Mithi Rohar, Gandhidham, Galpadar covering Kandla to Mandvi talukas of the Kachchh district. Sampling location map and Elevation Map of the area is given in Fig. 1.

At each site, groundwater samples were collected in three separate, clean high-density polypropylene bottles (Tarsons; 250 ml and 125 ml) one each for the anions, cations and isotopic analysis. Sampling bottles were soaked for 24 h in 1:1 diluted HCl solution and washed with deionized water and oven dried. The samples were collected mostly from bore wells and dug wells. Before sample collection bore wells were left running for a few minutes to minimize the impact of iron pipe and bottles were rinsed two or three times at each site. A bottle containing 125 ml of water sample was acidified with Pure HNO₃ (pH < 2) to stabilize the trace metals and was used for the determination of major cations and trace metals. The bottle containing 250 ml of water was used for anion analysis and another unacidified bottle (125 ml) water



Fig. 1. Study area with sampling locations and elevation of the area.

samples were used for stable isotopes (δ^{18} O and δ D) analysis. The sampling bottles were properly labeled and immediately sealed after sample collection to avoid reaction with the atmosphere. The physical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), oxidation-reduction potential (ORP), and turbidity were measured in-situ using Horiba multi-parameter probe (Model U-50). The samples were stored in Styrofoam boxes containing ice, brought to the laboratory and preserved at 4 °C for further analysis. For isotopic analyses, a sealed aliquot of the sample was sent to the IWIN division, Physical Research Laboratory (PRL), Ahmedabad. Samples were vacuum filtered with 0.22 µm millipore filter paper for the analysis of various parameters. A total of 13 hydrochemicals parameter and stable isotopes (δ^{18} O and δ D) were analyzed. Methods of sample collection, handling, preservation and analysis were done according to standard procedures of APHA (American Public Health Association, 2012) to ensure data quality consistency.

Analysis of major anions (F^- , Cl, $SO_4^{2^-}$ and NO_3^-) was done using standard protocols of APHA (2012). Major cations (Ca^{2^+} , Mg^{2^+} , Na^+ , K^+) were analyzed using atomic absorption spectrophotometer (Thermo Fisher, M Series). The instrument was calibrated using elemental standard (Merck). Dissolved silica was analyzed by the molybdo-silicate method (APHA, 2012). A total of 18 water quality parameters have been studied using graphical plots and statistical analyses. The analytical precision of the measured ion was determined by calculating the Ion balance error, which was within 5%.

The isotopic analysis (δ^{18} O and δ D) was done using the standard calibration method in which water samples (300 µl) are equilibrated with CO₂ and H₂. The equilibrated CO₂ and H₂ gases were analyzed in Delta V Plus isotope ratio mass spectrometer in continuous flow mode using Gas Bench II for ¹⁸O/¹⁶O and D/H ratios. The reproducibility of the measurement was better than 0.1‰ for δ^{18} O and 1‰ for δ D. The δ^{18} O and δ D values obtained in the laboratory were corrected using an integrated calibration curve based on VSMOW2, GISP and SLAP2 (obtained from the International Atomic Energy Agency, Vienna) measurements. The calibration equations used for the reported values are (Maurya et al., 2011)

 $\delta^{18}O_{(corrected)} = 1.0025(\pm 0.0009) \times \delta^{18}O_{(measured)} + 0.0156(\pm 0.0302)$

 $\delta D_{(corrected)} = 1.0025(\pm 0.0006) \times \delta D_{(measured)} + 0.0044(\pm 0.1710)$

Spatial distribution of water quality parameters was generated using the IDW algorithm in spatial analyst module of Arc GIS 10.1.

2.3. Hierarchical cluster analysis

This is a classification method, where objects are grouped into the classes or clusters based on similarities within a class and dissimilarities between different classes. Clusters are formed sequentially by starting with the most similar pair of objects and forming higher clusters step by step. Hierarchical agglomerative CA was performed on the normalized data set (mean observations over the whole period) by means of Ward's method using squared Euclidean distances as a measure of similarity.

Based on geochemical characteristics, cluster analysis helps us to find similar sampling location in a region, which helps in future sampling strategy in an optimal manner in the monitoring network. Thus, it reduces the cost of sampling in water resource management. In various studies (Simeonova et al., 2003; Kim et al., 2005), this approach has been used successfully to water quality assessment and monitoring program.

3. Results and discussion

3.1. Distributions of major ions

Details of the physico-chemical analysis of groundwater samples along with their statistical distribution are given in Table 1. A very wide and skewed variation in most of the parameters suggests multiple sources are governing the groundwater hydrochemistry in the area.

Groundwater temperature ranges from 24° to 29 °C. The pH value ranged from 8.1 to 10.5, with an average pH 8.8 suggests the alkaline nature of groundwater. Maximum pH 10.5 was observed in the western part, Undhiyari village. Higher pH, concentration suggests a more dissolution of salts due to interaction between soil and rain water (Subramanian and Saxena, 1983) as well as a semiarid climatic condition of the study area. Electrical conductivity in groundwater samples ranged from 1870.0 to 15,900.0 µS/cm with average 5897.6 µS/cm, whereas TDS ranged from 413.0 to 9850.0 mg/l which suggests highly saline groundwater in the area. Results suggest that no groundwater samples are coming under freshwater (EC < $500 \,\mu$ S/cm) and under marginal water (500–1500 μ S/cm), 50% of samples have an EC value between 1500 and 5000 μ S/cm and rest 50% of the sample have EC value > 5000 µS/cm (Davis and Dewiest, 1966). Semiarid climate and high evaporation rate contributing to the high salt concentration in groundwater. The degree of salinization is indicated by an increase in TDS which is also observed in an increase in cation and anion. The abundance of cation has shown the following trend: Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ whereas the variability of anions in groundwater has been observed as: $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$.

Chloride concentration in groundwater samples ranged from 169.1 to 2662.5 mg/l with average value of 748.7 mg/l. The present area is formed by marine transgression in the geological past; a thick

Table 1

Details of statistical data of different water quality parameters analyzed. All concentrations are in mg/l except EC (μ S/cm) and pH.

	Min	Max	Average	Stdv
pН	8.10	10.50	8.82	0.57
EC	1870.00	15,900.00	5897.69	3561.43
TDS	413.00	9850.00	3594.73	2261.79
CO_3^-	0.00	72.00	26.87	17.57
HCO ₃ ⁻	101.63	488.00	255.09	110.79
F -	0.60	2.05	1.43	0.47
Cl ⁻	149.10	2662.50	748.70	623.24
NO ₃ ⁻	0.55	128.87	36.84	39.64
SO_4^{2-}	49.74	230.78	154.70	45.68
Na ⁺	172.68	1229.61	502.45	255.30
K ⁺	0.09	35.93	11.10	10.24
Ca ²⁺	6.20	236.69	80.62	63.03
Mg^{2+}	5.86	174.88	53.27	45.32

depositional environment is present in the area. Along with spray of marine salt, evaporite dissolution could be the reason of high chloride concentration in the study area. Due to low recharge, prolonged entrapment of groundwater and poor subsurface drainage resulting from relatively low permeability of the aquifer material (at shallow depths) leads to high chloride concentration in the aquifer of the study area.

 $\rm HCO_3^-$ is second most abundant anion in the study area, which ranged from 113.8 to 488.0 mg/l with average concentration 258.2 mg/l. Dissolution of carbonates and reaction of silicates with carbonic acid account for the addition of $\rm HCO_3^-$ to the groundwater. Sulphate concentration in groundwater samples varied from 49.74 to 230.8 mg/l with average concentration 151.0 mg/l. Besides dissolution of gypsum and anhydrite minerals, higher sulphates suggest breaking of organic substances and other human influences such as agrichemical pollutants and industrial discharge. A possible source of elevated SO₄²⁻ could also be from the oxidation/dissolution of SO₄²⁻ relict sulphide and sulphate-rich marine clay and silt deposits present in the area.

Nitrate concentrations in groundwater samples varied from 0.5 to 129.0 mg/l with average concentration 37.0 mg/l, approximately 25% of groundwater samples in area NO_3^- concentration was higher than suggested by the Bureau of Indian Standards and World Health Organization. High nitrate concentration in aquifers suggests the impact of nitrogenous fertilizers, biological oxidation of nitrogenous substances which come from sewage and industrial wastes as well as irrigation return flow due to intensive agriculture in the area. Waste from two agricultural port and from different food processing unit is also contributing high nitrate concentration in the area. Atmospheric precipitation is also augmenting nitrate concentration (Rina et al., 2012). Spatial variation of some water quality parameter is given in Fig. 2.

Sodium is dominant cations, its concentration ranged from 172.7 to 1229.6 mg/l with an average concentration 502.4 mg/l. The highest concentration of sodium was observed in Dhrav (1229.6 mg/l) and Undhiyar (1216.0 mg/l) western part of the study area which is at lower elevation and lowest concentration was observed in Muska (172.7 mg/l) village. Besides weathering and dissolution of minerals, various agricultural activities, industrial waste as well as marine spray, salt pan from the adjoining area may possibly be contributing high sodium concentration in the area. The continuous evaporation, prolonged dry spells and various processes such as ion and reverse ion exchange are augmenting high concentration of Na⁺ ion in the aquifer. Potassium concentration ranged from 0.1 to 35.9 mg/l with an average concentration 11.1 mg/l. The highest concentration of potassium was found in the western part of Undhiyari (35.9 mg/l) and southern part Bhadreshwar (35.7 mg/l) of the investigated area. Besides weathering of K-feldspar minerals, irrigation return flow also contributes high K⁺ in groundwater. The K⁺ is attributed to the presence of some isolated pockets of old saline water or connate water.

The magnesium concentration in groundwater samples ranged from 5.9 to 174.9 mg/l with an average concentration 53.3 mg/l. The highest concentration was observed in eastern part Tuna (174.9 mg/l) and western part Undhiyari (165.8 mg/l) of the study area and the lowest was observed at Gundala (5.9 mg/l) middle southern part of the study area. The weathering of ferromagnesium minerals, ion exchange, precipitation of CaCO₃ and marine environment (Rao et al., 2012) may result into high magnesium concentration in groundwater. Gundala, Maska, Mundra, Nani khakkar, Navinal, Toda, Chhasara, Khedoi, Dhabra, Galpadar villages are within the permissible limit (30 mg/l) recommended by BIS (2012) and rest sampling site beyond the permissible limit. Calcium concentration ranged from 6.2 to 236.7 mg/l with an average concentration 80.6 mg/l; its higher concentration is observed at western part Undhiyari and lowest concentration was observed at southern part Gundala (6.2 mg/l).



Fig. 2. Spatial variation of water quality parameters (A) pH (B) EC (C) TDS (D) chloride (E) sulphate (F) sodium.

3.2. Correlation of physicochemical parameters of groundwater

Correlation matrix of various physico-chemical parameter is given in Table 2. Both EC and TDS are strongly correlated with Na⁺, Ca²⁺, Mg^{2+} , Cl⁻ and SO₄²⁻. Na⁺, Mg²⁺ and Ca²⁺ are strongly correlated with Cl⁻, suggests common origin of these ions. Na⁺, Mg²⁺, Ca²⁺ and Cl⁻ ions are moderately correlated with SO₄²⁻. Very high correlation ($r^2 = 0.93$) between Na⁺ and Cl⁻ suggests that both seawater intrusion and evaporites dissolution are the important factors contributing to groundwater enrichment by these chemical elements indicates the presence of highly saline water in the study area. The positive correlation between Ca²⁺ and SO₄²⁻ suggests that besides the dissolution of

Table 2	
Correlation matrix of different water quality parameters.	

	pH	EC	TDS	CO_3	HCO_3	F ⁻	Cl ⁻	NO_3	SO_4	Na	К	Ca	Mg
pН	1.00												
EC	0.94	1.00											
TDS	0.91	0.95	1.00										
CO_3	0.22	0.00	0.06	1.00									
HCO ₃	0.08	0.00	-0.04	0.27	1.00								
F ⁻	0.10	-0.09	-0.11	0.52	0.34	1.00							
Cl ⁻	0.90	0.97	0.91	-0.04	-0.13	-0.16	1.00						
NO_3	0.14	0.12	0.11	-0.09	-0.09	0.30	0.13	1.00					
SO ₄	0.58	0.69	0.63	-0.26	-0.12	-0.17	0.66	0.02	1.00				
Na	0.94	0.95	0.91	0.16	0.10	-0.06	0.93	-0.04	0.64	1.00			
K	0.32	0.44	0.39	-0.30	0.34	-0.41	0.42	-0.13	0.38	0.42	1.00		
Ca	0.67	0.78	0.75	-0.18	-0.33	-0.26	0.87	0.25	0.63	0.71	0.36	1.00	
Mg	0.73	0.83	0.75	-0.23	-0.10	-0.08	0.84	0.45	0.57	0.69	0.46	0.76	1.00

Parameters showing r > 0.7 are considered as strongly correlated whereas r between 0.5 and 0.7 shows moderate correlation.





anhydrite and/or gypsum, anthropogenic activity is also responsible for the presence of these ions in groundwater. The moderate correlation between Mg⁺-NO₃⁻ and Mg⁺-SO₄²⁻, Ca-SO₄²⁻ and Cl⁻-NO₃⁻ suggests the possible impact of leaching of excess fertilizers and due to irrigation return water that may create a long-term risk of groundwater pollution. The moderate correlation between Cl⁻-SO₄²⁻ suggests a common origin of these ions.

3.3. Geochemical evolution of groundwater

To understand the hydro-geochemical processes operating in groundwater system of the study area, Piper (1944) trilinear plot and Chadha's diagram (Chadha, 1999) is used. The Piper trilinear diagram (Fig. 3.A) suggests that among cations Na⁺, Ca²⁺, Mg²⁺ whereas among anions Cl^- , HCO_3^- and SO_4^{2-} are dominant species present in the aquifer. Most of the samples were Na^+-Cl^- type and only a few samples were Na⁺-HCO₃⁻. Chadha's plot (Fig. 3.B) is expressed as the difference between alkaline earth $(Ca^{2+} + Mg^{2+})$ and alkali metals (Na⁺-K⁺) for cations, and the difference between weak acidic anions $(HCO_3^- + CO_3^-)$ and strong acidic anions $(Cl^- + SO_4^{2-})$. The data were converted to percentage reaction values (milliequivalent percentages) and is expressed in four quadrants which is subdivided into eight fields: (1) Alkaline earths exceed alkali metals, (2) alkali metals exceed alkaline earths, (3) weak acidic anions exceed strong acidic anions, (4) strong acidic anions exceed weak acidic anions, (5) alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively, (6) alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions, (7) alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions (9) alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. It was observed that most of the groundwater samples belong to sub-field (7), such water generally creates salinity problems, both in irrigation and drinking purposes. The positions of data points in the proposed diagram represent Na⁺-Cl⁻ type, Na₂SO₄-type, Na⁺dominant Cl⁻-type, or Cl⁻ dominant Na⁺-type waters. Few samples fall in the sub-field 2, which also suggests alkali metals exceed alkaline earth. The higher concentration of alkali ions present in the water may influence ion-exchange reactions between the solid and aqueous phases, resulting in sodium-enriched sediments.

3.4. Salinization of groundwater

Subsurface geology, weathering, saturation state or degree of equilibrium of different mineral with water is governing the geochemical evolution of groundwater. To infer the geochemical evolution the hydro-chemical data were subjected to various conventional graphical plots to understand the mechanism controlling the groundwater chemistry of the area.

3.4.1. Provenance and water-rock interaction

The scatter diagram of $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$ (Fig. 4.A) shows that most of the samples fall below the equiline (1:1) which suggests that silicate weathering and ion exchange is the dominant process governing the groundwater quality. Only a few samples lie above the equiline suggesting carbonate mineral dissolution and reverse ion process is also taking place in the area. The scatter plot between (Na⁺ + K⁺) and Cl⁻ (Fig. 4.B) shows that most of the samples (89%) fall above the equiline, suggests that the excess of the cation is either due to silicate weathering or due to salts present in the soil (Stallard and Edmond, 1983). Na⁺ + K⁺ vs Cl⁻ plot shows that abundant alkalis are available to form alkali carbonates or alkali sulphate.

Scatter plot $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$ (Fig. 4.A) suggests an excess of Ca and Mg at sampling locations (G1, G11, G18). Variation in the cation composition is perhaps more difficult to analyze, because it is governed by three factors namely (i) characteristics of

freshwater, (ii) seawater intrusion and (iii) secondary processes such as cation exchange. The ion exchange reaction of Na⁺ and Ca²⁺ often occurs when seawater intrudes freshwater. When seawater intrudes a freshwater aquifer the following ionic exchange reactions represent cationic behavior:

$$2Na^{+}(K^{+}) + Ca - X2 = 2Na(K^{+}) - X + Ca^{2+},$$

$$2Na^{+}(K^{+}) + Mg - X2 = 2Na(K^{+}) - X + Mg^{2+},$$

Typically, cation exchangers in aquifers are clay minerals, organic matter, oxyhydroxides and fine-grained rock materials, which have mainly Ca^{2+} adsorbed on their surfaces. When seawater intrudes into a coastal freshwater aquifer, Na^+ replaces part of the Ca^{2+} on the solid surfaces. Thus, Na^+ is taken up by the solid phase, Ca^{2+} is released.

3.4.2. Evaporites dissolution in the area

The Gibbs (1970, 1971) plot of log TDS against $Na^+/(Na^+ + Ca^+)$ (Fig. 5.A) and $Cl^-/(Cl^- + HCO_3^-)$ (Fig. 5.B) also suggests that evaporation and crystallization are playing a major role in controlling the chemistry of the groundwater due to arid climatic condition. Evaporation increases all forms of ions in groundwater.

 Na^+/Cl^- vs EC scatter plot (Fig. 6.A) is another effective indicator of evaporation. If the evaporation process is dominant, assuming that no mineral species are precipitating, the Na⁺/Cl⁻ ratio would be unchanged (Jankowski and Acworth, 1997), the plot of Na⁺/Cl⁻ versus EC would give a horizontal line, which would then be an effective indicator of concentration by evaporation and evapotranspiration. Fig. 6.A suggests that Na^+/Cl^- exhibited a decreasing trend as EC increased, which suggests besides evaporation excess of Na⁺ is derived from the silicate weathering process or salt in the soil (Stallard and Edmond, 1983). In the study area the excess of sodium may also be present due to spray of marine salt. Na/Cl molar ratio in groundwater samples varies from 0.66 to 3.07. The Na⁺/Cl⁻ molar ratio greater than one reflects the release of Na⁺ from silicate weathering (Stallard and Edmond, 1983). The scatter plot of Na⁺ vs Cl⁻ (Fig. 6.B) also indicates only a few samples are lying on equiline, which suggests a dissolution of halite whereas samples above equiline suggests the presence of an excess of sodium contents. Excess of the sodium salt is due to various anthropogenic activities as well as the contribution of marine salt.

Due to less solubility, minerals such as calcite and gypsum become precipitates with the evaporation of water. This will lead a decreased in Ca⁺/Na⁺ ratio accompanied with decreased HCO₃⁻. In the study area, a negative correlation exists between Ca/Na ratios and TDS and a positive correlation between Ca⁺/Na⁺ ratios and HCO₃⁻. This confirms the influence of evaporation on groundwater quality of the area. Thus, Na-normalized HCO₃⁻ and Ca²⁺ of shallow fresh groundwater are used to illustrate the behavior of Ca²⁺ and bicarbonate. Fig. 7 shows most of the samples were within an evaporative dissolution domain with few samples in the lowermost part of evaporation dominance. The excessive evaporation from unsaturated zone and the leaching of these salts during precipitation in subsequent years increases salinization of groundwater in the study area.

3.5. Ionic ratios to infer seawater intrusion

In coastal aquifers, groundwater chemistry depends largely on the freshwater component, which is intimately linked to the geology of the recharge areas as well as land use pattern. So, it is important to understand the relationships between freshwater and surrounding saline water. Over-exploitation accelerates the rate of flow and salinization process. Each potential source of salinization can be characterized by a distinguishable chemistry and well-known ionic ratio (Table 3) associated with different geochemical processes (Vengosh and Ben-Zvi, 1994; Vengosh and Rosenthal, 1994; Raghunath, 2005).

Ionic ratio of sampling locations is given in Table 4. In general,



Fig. 4. Scatter plot (A) Ca + Mg vs $HCO_3 + SO_4$ (B) Na + K vs Cl⁻.



Fig. 5. Scatter plot (A) $Na^+/(Na^+ + Ca^+)$ and TDS; (B) $Cl^-/(Cl^- + HCO_3^-)$ and TDS.



Fig. 6. Scatter plot (A) EC and Na^+/Cl^- (B) Na^+ and Cl^- .



Fig. 7. Bivariate plots of Na-normalized HCO_3^- and Ca^{2+} .

Table 3

The comparative ionic ratio of potential salinization sources given by different authors.

Ionic ratio	Seawater intrusion	Deep saline upcoming	Agriculture return flow	Wastewater infiltration
$\begin{array}{c} Na^{+}/Cl^{-} \\ SO_{4}^{2-}/Cl^{-} \\ K^{+}/Cl^{-} \\ Mg^{2+}/Ca^{2+} \\ Ca^{2+}/(HCO_{3}^{-} + SO_{4}^{2-}) \end{array}$	$\begin{array}{l} 0.86{-1}^{a} \\ 0.05^{a,c} \\ 0.019 \\ > 5^{b} \\ 0.35{-} < 1 \end{array}$	$< 0.8^{b}$ ~0.05 ^{c,d} $< 0.019^{f}$ > 1 ^a > 1 ^a	- ≫0.05 ^e - -	1.1 ^c 0.09 ^d ≫0.02 –

Source: a) Vengosh and Rosenthal (1994); b) Vengosh and Ben-Zvi (1994), c) Vengosh et al. (1994), d) Mercado (1985), e) Vengosh et al. (2002) and f) Vengosh et al. (1999).

freshwater is dominated by calcium, whereas seawater by magnesium, the Mg^{2+}/Ca^{2+} ratio can provide an indicator of seawater intrusion. The Mg^{2+}/Ca^{2+} ratio > 5 is a direct indicator of seawater contamination (Metcafe and Eddy, 2000). Likewise, seawater and seawater diluted with freshwater have distinguished geochemical characteristics (Metcafe and Eddy, 2000; Ghabayen et al., 2006). At the lower reaches sampling locations G1, G2, G3, G4, G5, G6, G7, G8, G1, G11, G12, and

Table 4

lonic	ratio	at	different	sampling	sites.
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G13 were showing $Mg^{2+}/Ca^{2+} > 1$ suggests deep brine upconing is taking place in the area.

Sodium and chloride are the dominant ions in seawater with a longer residence time, which gives a characteristic Na⁺/Cl⁻ ratio = 0.86 to 1 for seawater intrusion. Seawater solutes are specifically characterized by an excess of Cl⁻ over the alkali ions (Na⁺ and K⁺). Thus, even at an early stage of salinization processes, Na⁺/Cl⁻ ratios when combined with other geochemical parameters can be an indicator of the origin of the salts. The Na⁺/Cl⁻ ratios 0.8–1.0 at sampling locations G3, G4, G15, G22, G23, G24 suggests seawater intrusion, however with G22, G23 and G24 being located far away from the coast, direct contamination by seawater can be ruled out. At sampling locations G1, G11, G18 and G20, Na⁺/Cl⁻ < 0.8, which shows possibilities of deep brine upconing. At rest other locations Na⁺/Cl⁻ > 1 suggests salinization of aquifers due to wastewater infiltrations.

The value of the ionic ratio of $K^+/Cl^- = 0.019$ indicates seawater intrusion. At sampling sites G2, G5, G9, G17, G19, G25 and G26 ionic ratio of $K^+/Cl^- \gg 0.02$ indicates wastewater infiltration. At sampling location G1, G3, G4, G6, G7, G8, G10, G11, G12, G13, G14, G15, G16, G18, G20, G21, G22, G23, G24 deep saline upcoming taking place as indicated by an ionic ratio of K^+/Cl^- . The ionic ratio of groundwater is nearly similar to seawater due to the prolonged abstraction of groundwater. The ionic ratio of $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ is 0.35- < 1shows seawater intrusion. At sampling site G1, G2, G4, G7, G9, G16, G19, G21, G23 G24 found between 0.35 and < 1 indicate seawater intrusion and sampling sites G11, G15, G18, G20, G22 deep saline upcoming in the sites.

The ionic ratio of $SO_4^{2^-}/Cl^- = 0.05$ suggests sea water intrusion (Vengosh et al., 1994; Vengosh et al., 1999; Lagudu et al., 2013). Ionic ratio $SO_4^{2^-}/Cl = 0.05$ at sampling site G11 (Undhiyari) suggests seawater intrusion, whereas at all other sites $SO_4^{2^-}/Cl^- < 0.05$ ratio suggests contamination from anthropogenic sources. A high $SO_4^{2^-}/Cl^-$ ratio is attributed to the application of gypsum fertilizers (Vengosh et al., 2002).

The salinization problem is related to natural recharge mechanisms and that seawater intrusion has a more local Influence (Rina et al., 2013a, 2013b). However rapidly changing land use/land cover in

Sample ID	Mg^{2+}/Ca^{2+}	Na ⁺ /Cl ⁺	SO_4^{2-}/Cl^{-}	K^+/Cl^-	$Ca^{2+}/(HCO_3^- + SO_4^{2-})$
G1	2.27	0.68	0.11	0.011	0.97
G2	2.21	1.52	0.24	0.036	0.24
G3	1.35	0.96	0.16	0.007	0.82
G4	1.84	0.86	0.13	0.005	0.43
G5	2.57	1.50	0.24	0.057	0.16
G6	1.61	1.54	0.24	0.008	0.26
G7	1.43	1.41	0.24	0.002	0.46
G8	1.57	4.04	0.44	0.004	0.03
G9	0.59	1.83	0.19	0.037	0.35
G10	1.55	1.79	0.32	0.003	0.18
G11	1.17	0.70	0.05	0.012	1.41
G12	1.27	1.23	0.14	0.001	0.29
G13	1.04	1.70	0.27	0.000	0.15
G14	0.62	1.38	0.22	0.011	0.33
G15	0.92	0.90	0.08	0.003	1.14
G16	0.43	1.32	0.19	0.008	0.47
G17	0.51	3.07	0.54	0.080	0.22
G18	0.70	0.66	0.11	0.003	1.55
G19	1.00	1.28	0.49	0.028	0.40
G20	0.66	0.78	0.13	0.018	1.28
G21	0.53	1.47	0.43	0.001	0.68
G22	0.68	0.89	0.17	0.016	5.00
G23	0.55	0.93	0.17	0.017	0.92
G24	1.91	0.80	0.12	0.014	0.40
G25	1.41	1.32	0.25	0.044	0.31
G26	0.76	1.57	0.22	0.033	0.24



Fig. 8. (A) Water table map of 2008. (B) Water table map of 2013.



Fig. 9. Scatter plot between δ^{18} O and δ D.

coastal region leads to exploitation of aquifers which in turns exacerbates the deterioration of groundwater quality.

From the elevation map of the area (Fig. 1), it is clear that elevation is low in southern and western part of the area. In any natural condition, the groundwater usually follows the surface topography of the area. From the water table contour maps (Fig. 8.A), it is also clear that there is not much change in the hydraulic gradient in pre-monsoon (May 2008), and post-monsoon (November 2008). The hydraulic gradient of the groundwater flow is from the western part to central part of the region. Throughout the study area there is lowering of groundwater table during pre-monsoon both in May 2008 and 2013, possibly induced by over-pumping in summer. Also, there is a significant decline in water level from 2008 to 2013. Highest water level was observed in westernmost region of the study area. From pre to post-monsoon, due to further decline in groundwater level, quite likely that hydraulic gradient changed from sea to inland area. These are low lying areas, where there is possibility of induced seawater intrusion. However, in inland area overexploitation is inducing salinity. Water level map of premonsoon and monsoon of 2008 and 2013 has been given in Fig. 8.A and B.

3.6. Agricultural practices

Economic development and agricultural practices also play an important role in controlling the groundwater quality of a region. Poor agricultural practices pose a potential threat to groundwater quality by playing an important role in the movement of solutes. Intensive use of fertilizers, as well as recycling of irrigation water, results in leaching of nutrient constituents from the surface to shallow aquifers, thereby exerting a strong polluting effect. The situation becomes vulnerable, especially in arid areas, it significantly affects hydro-chemical evolution, particularly groundwater salinization. This result suggests that poor agricultural practices, excessive application of fertilizers and irrigation return flow increase Cl^- , NO_3^- , SO_4^{2-} and K^+ ions in the aquifers.

3.7. Origin of saline water

The water stable isotope when combined with the ionic content of the water, it offers a powerful tool to study the mixing between water masses of different salinities and therefore to trace back the salinity origin (Fritz and Fontes, 1980). Stable isotopes δ^{18} O and δ D is used to assess the genesis and evolution of groundwater.

3.7.1. Isotopic signature of groundwater in the area

In groundwater samples of the area, isotopic composition varied from [$\delta^{18}O = -1.48$ to -6.06% with average -3.32%, and $\delta D = -46.04$ to -17.83% with an average -29.49%]. Depleted $\delta^{18}O$ is observed in the northeastern part of the area, whereas enriched $\delta^{18}O$ is observed in some locations of the western part as well as in the southern part of the area and it's moving towards the northern part. Depleted δD is observed in the northeastern part, whereas the enriched



Fig. 10. Spatial variation (A) δ^{18} O (B) δ D.



value in southwestern and the northern part. *d*-*Excess* in the groundwater varied from -13.95% to 4.06% with an average -2.96%. The relationship trend between δD and $\delta^{18}O$ (Fig. 9) was compared with the equation of a local meteoric water line (LMWL) calculated from the following relation for North Gujarat (Gupta and Deshpande, 2005).

$$\delta D = (7.6 \pm 0.6) * \delta^{18} O - (2.9 \pm 2.2) [R^2 = 0.89].$$

It was observed that all samples were below the LMWL which suggests that these groundwater samples were originated from local precipitation, however, due to the prevailing climatic condition of the area significant evaporation has taken place. Of the 26 samples, only 5 samples (G19, G22, G23, G24, and G25) were in the lower region of LMWL, showing the depleted value rest other samples are highly enriched. The study area is in arid zones, extensive evaporation from the unsaturated zone or even evaporative losses from the water table (Allison et al., 1994; Dincer et al., 1974, Deshpande et al., 2013) leads to significant deviations from precipitation.

From the δ^{18} O contour map (Fig. 10.A) and δ D contour map (Fig. 10.B), it can be seen that a very high gradient exists within a very small distance between sampling locations G18 to G19, G25 and G1 which suggest presence of some impervious boundary in the geological formation in between these points. Because of the presence of an impervious boundary, lateral mixing of groundwater is not occurring.

3.7.2. Regression line of $\delta^{18}O$ and δD

The regression line of δ^{18} O and δD (Fig. 11.A) groundwater samples of the area is $\delta D = 5.33$ (± 0.45) $\delta^{18}O - 11.82$ (± 1.63), when compared with LMWL, lesser slope suggests significant evaporation, due to combined effect of both local atmospheric and ground surface processes which results in minor to significant evaporation of water before groundwater recharge (Gupta and Deshpande, 2005). High temperature, less rainfall, significant evaporative modification during passage through the soil zone in the area will be the reason for lower slope in the area. Most of the samples are around the regression line, suggesting a common origin; however, very large scatter is seen in the observed samples indicating differently evolved groundwater possibly due to various land use activity.

 $\delta^{18}\text{O}$ –d-excess scatter plot (Fig. 11.B) depicts two important isotopic signature of groundwater samples in the area - Region A showing $\delta^{18}\text{O} < -2\%$ to -4% and d-excess -5 to -15%, this isotopic signature is observed at lower elevation. Enriched $\delta^{18}\text{O}$ and lower d-excess indicates there is a significant kinetic evaporation of the precipitated water before groundwater recharge, as well as post-precipitation evaporation from surface water and/or soil moisture in response to high PET of the region. Due to high temperature and wind speed, primary precipitation in these regions may already have evaporated from falling raindrop which results in characteristics isotopic signature in the area. Most of these sampling locations are in Mundra to Mandvi which has high industrial activities including various ports. Enriched values of these sampling locations are possibly also due to declining water table which has been observed in last two decades and aridity of climate further intensify the enriched isotopic signature.

Region B showing isotopic signature $\delta^{18}O > -4\%$ and *d-excess* 0 to 5‰ at higher elevation at sampling locations (G19, G22, G23, G24, G25). Depletion of heavy isotopes ($\delta^{18}O > -4\%$) accompanied by high *d*-excess (0 to 5‰), indicates a limited modification due to evaporation before groundwater recharge. This may partly be facilitated by the relatively thick alluvial soil that covers this region.

3.7.3. Relationship of Cl and δ^{18} O

 δ^{18} O vs log Cl scatter plot (Fig. 12.A) and δ^{18} O vs Cl (Fig. 12.B) suggests that at most of the groundwater samples (except G19, G22, G23, G24, G25) are along the regression line with little deviation, also these points have highly enriched δ^{18} O values with high Cl⁻ content which suggests the possibilities of evaporative isotopic enrichment of accumulated saline water. These points are located mostly near the



Fig. 12. Scatter Plot (A) δ^{18} O vs log Cl (B) δ^{18} O vs Cl.



Dendrogram

Fig. 13. Dendrogram showing clusters of different sampling site.

Table 5

Cluster with similar site characteristics.

Class	1	2	3
Objects	11	13	2
Sum of weights	11	13	2
Within-class variance	5,125,033.537	1,504,665.157	3,801,724.314
Minimum distance to centroid	693.820	270.826	1378.718
Average distance to centroid	1966.517	1068.398	1378.718
Maximum distance to centroid	4076.734	1733.797	1378.718
	Obs1	Obs2	Obs11
	Obs3	Obs6	Obs15
	Obs4	Obs7	
	Obs5	Obs8	
	Obs12	Obs9	
	Obs16	Obs10	
	Obs18	Obs13	
	Obs20	Obs14	
	Obs23	Obs17	
	Obs24	Obs19	
	Obs26	Obs21	
		Obs22	
		Obs25	

coast, various small creeks, as well as rivulets, seawater ingression through these and subsequent leaching of such water which may also be contributing to salinization in the area.

Aquifers which are at lower elevation (G3, G4, G11, and G15) have

enriched $\delta^{18}O$ value as well as Na/Cl ratio (0.86–1) indicates seawater intrusion, which is also confirmed by the SO₄/Cl ratio as well as K⁺/Cl⁻. However, most of the aquifers in Mundra to Mandavi is showing enriched $\delta^{18}O$, but at some locations, Na/Cl >1 indicates salinization due to waste water infiltration. Greater Na than Cl in the region also attributed to meteoric waters salinized by the marine salts (Howard and Lloyd, 1983). Except at G11 & G15 where ionic ratio & $\delta^{18}O$ suggests seawater intrusion is taking place. Mg⁺/Ca⁺ ratio (>1) at most of locations G1 to G13 suggests deep saline up-coning is taking place. This suggests that besides the river, rivulets and small creek which is contributing salinization in the area, overexploitation will further aggravate this grim situation.

3.8. Cluster analysis

After data scaling by Z-transformation, cluster analysis was done using Ward's method. Cluster analysis is used to detect the similarity among different sampling sites. The significance of the clusters obtained was tested by Sneath's Index disjunction. The samples were found to be grouped into three clusters as seen in the dendrogram (Fig. 13) and Table 5. Electrical conductivity, Cl and pH seem to be a major distinguishing factor among these clusters. Cluster 1 encompasses a total of 11 samples; cluster 2 consisting of 13 samples and cluster 3 consisting of 2 samples, respectively. Each cluster represents a distinct signature which reflects the geochemical processes taking place in the subsurface, recharge processes as well as land use activities. Cluster I and cluster III includes wells that are mostly located in near the coast. However, these two cluster is also showing distinguished signature. Cluster I include those wells where electrical conductivity in these wells varied between 5000 and 10,000 $\mu S/cm$ and Cl^- concentration value varies between 500 and 1500 mg/l. Sampling locations in this cluster is showing ionic ratio similar either due to seawater intrusion or due to deep saline upconing, suggesting complex geochemical process is taking place in the area. Most of these sampling locations are near Kandla and Mundra Port, and overexploitation in these areas is producing upconing of underlying saline water or intrusion. Cluster III those wells where samples have electrical conductivity (10,000-16,000 µS/cm) and chloride concentration varies between 2115 and 2662 mg/l. Highest pH was also observed at these wells. This groundwater reflects chemical signature similar to seawater intrusion, which can be inferred from ionic ratio also. Human induced activities are inducing seawater intrusion at these locations which can be inferred from ionic ratio also. Cluster II is showing electrical conductivity < 5000 µS/cm and chloride concentration < 700 mg/l. Most of these sampling locations are in upper elevation where intensive agriculture is present. Ionic ratios at most of sampling locations are showing characters similar to waste water infiltration and irrigation return flow.

4. Conclusion

The seawater intrusion into coastal aquifer is well known problem worldwide but its protection has not been used in practice. Once seawater intrusion is started, restoration of water quality is generally an expensive or ineffective proposition. It requires a large amount of fresh water flushing for a long period of time. Monitoring and early detection of the origin of the salinity are crucial for water management and successful remediation.

The present study hydro-chemical analysis and stable isotopes ($\delta^{18}O$ and δD) is used to assess groundwater salinization processes in coastal aquifers of Kachchh district of Gujarat, an economic hub of the country. The results suggest that in the study area, a complex geochemical process is taking place, which results into three types of end-member with distinguished salinity and isotopic signature. Decline in water level in coastal aquifers are showing two different end members: either deep brine upconing or seawater intrusion like characteristics which is evident in cluster I and Cluster III. Over pumping which caused a decline in water level, leads to a deep depression in south western part hence the hydraulic gradient of the groundwater flow towards central part. Samples of cluster III are showing highest electrical conductivity and ionic ratio and isotopic composition suggests to seawater intrusion at these locations. If this rate of withdrawal continues samples in Cluster I will also get affected by saline water intrusion. It was observed that topography coupled with over-exploitation and variability of freshwater recharge causes the chemistry of the groundwater in the aquifers to vary widely, because of the intermixing between two or more water types. This situation becomes more complicated when seawater participates due to intrusion, because the mixing process can follow diverse evolution trends. Samples in cluster II is present on higher elevation in inland area is showing salinity either due to water infiltration or due to irrigation return flow. The salinization problem is related to natural recharge mechanisms and seawater intrusion has a more local influence induced by decrease in piezometer due to change in land use/land cover activities. Strategies are needed to reduce substantial gaps between seawater intrusion knowledge and management practice to the local people as well as for land use planners. Continuous evaluation of groundwater levels and quality are crucial for monitoring the impact of groundwater exploitation in this highly vulnerable coastal aquifer.

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