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Hydrogeochemical Characteristics of Groundwater Influenced by Seawater Intrusion in Coastal Aquifer of Guhagar, Ratnagiri District, Maharashtra (India)

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ABSTRACT

Groundwater is the main source of drinking in coastal areas and the gradually decline in its quality is a most important issues. The aim of present study is to assess the groundwater quality and its deterioration in coastal aquifer in Guhagar area of Ratnagiri District, Maharashtra (India) by examining the hydrogeochemical characteristics. A total 25 water samples were collected from three different zones from the study area viz. seawater, backwater and groundwater, apart from this one surface water sample during the winter season. Samples were analyzed for its physicochemical parameters (i.e., pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, CO_3^{2-} and HCO_3^{-}) and selective trace elements such as Cd and Pb. The majority of the observed chemical parameters of all groundwater samples are within the permissible limit of the BIS water quality standards except pH, potassium and lead while WQI values indicate that the water quality is very poor to unsuitable category. The Cd and Pb concentrations in seawater and backwater are observed beyond the permissible limits. Generally established plots such as USSL plots, Gibbs plot, Bivariate plots and molar ratios such as sodium/chloride and chloride/bicarbonate were used to identify the seawater intrusion into the coastal aquifers. The suitability of groundwater for irrigation was evaluated based on sodium adsorption ratio (SAR), soluble sodium percentage (SSP), residual sodium carbonate (RSC), Permeability index (PI), Corrosivity ratio, sodium percentage (Na %) suggests that the most of the groundwater is suitable for irrigation purposes. Seawater ingression, ionic ratios and difference in groundwater geochemistry during the high and low tides indicate that the moderate effect of seawater.

KEYWORDS: *Seawater intrusion, groundwater, coastal aquifer, Guhagar, India.*

INTRODUCTION

Coastal aquifers are important source of freshwater supply in coastal regions. Excessive groundwater extraction has led to seawater intrusion and water quality degradation in many coastal aquifers (Bear et al., 1999; Saxena et al., 2003; Mondal et al. 2010, 2011). The salinization of coastal aquifers will deteriorate with the increasing demands for freshwater resources in coastal areas and predicted international sea level rise by 0.1 m to 2 m before 2100 (Pfeffer et al., 2008). Better understanding of seawater intrusion in coastal aquifers and the ability to more precisely prediction of the extent of aquifer salinization is very important for improving water resources planning, development and management in coastal areas. Seawater intrusion in a coastal aquifer is a natural phenomenon that occurs due to flow and salt transportation driven by the density variation between the seawater and fresh groundwater. The seawater intrusion is increased by groundwater extraction and potentially sea level rise as these processes reduce the hydraulic gradient that drives fresh groundwater discharge in to the ocean (Werner and Simmons, 2009; Chang et al., 2011).

As a natural factor, the ocean tide has a greater impact on seawater intrusion (Kim et al., 2005). Therefore, it is essential to determine whether groundwater has been contaminated due to seawater intrusion in the coastal areas. Because domestic and irrigation source in coastal area is groundwater due to the inadequate geographical features. Groundwater quality is drastically decreasing due to seawater intrusion into groundwater. The present study was carried out to identify the seawater ingress in the Guhagar area of Ratnagiri District and its impact on groundwater quality. The main source of drinking water supply in the studied regions is groundwater except one small dam situated near Guhagar Town. Small rivers are flowing in this area but during the dry seasons the most of the rivers were dried. In this situation, water quality assessment and the study of hydrogeochemical processes affecting the groundwater quality in coastal areas will be helpful to promote sustainable development and the management of water resources.

Study Area

The study area is a coastal territory which lies between Guhagar Town in the South (Latitude 17°30′31′′ N and Longitude 73°10′58′′ E) and Anjanvel village in the North (Latitude 17°34′05′′ N and Longitude 73°09′18′′ E). The total distance from Anjanvel to Guhagar is ~ 12.5 km (Figure 1). The present study area is receives rainfall from southwest monsoon during the period of June to September, July being the recipient of maximum rainfall. October and November months receive late showers from retreating monsoon. Such variation in rainfall has an important bearing on groundwater level fluctuations. The average annual rainfall of the Guhagar area is 2745 mm. The hottest month is May, its mean monthly temperature being 32.7°C and the coldest month is January, its mean monthly temperature being 18.6°C. The annual average evaporation is 158 mm. The maximum humidity of over 80% is experienced in the rainy months that seldom lower down to 60% due to proximity of sea. The data thus suggests that the area experiences per-humid to humid type of climate (IMD 1972; NBSS 1995; Uamrikar and Thigale, 2007).

Geology of the Area

The study area is mostly covered by the basaltic lava flows of the Continental Tholeiitic Province of India (Deccan Volcanic Province), of the upper Cretaceous to Miocene Period. At a number of places, laterite cappings on basalt occur at various altitudes. The basalt is massive, compact and fine grained with occasional presence of vesicles. The Quaternary (Holocene) sediments were found along the coast. These sediments are found in consolidated and unconsolidated calcareous sands and contain molluscan shells in varying proportions. These sediments are fine grained to medium grained and rounded to sub rounded in character (Herlekar and Sukhatnkar, 2011). Beaches are represented by sand, spit by beach rock, flats by mud and uplifted abrasion platforms by colluvium and alluvium (Uamrikar and Thigale, 2007). Geological map of the study area is depicted in Figure 1.

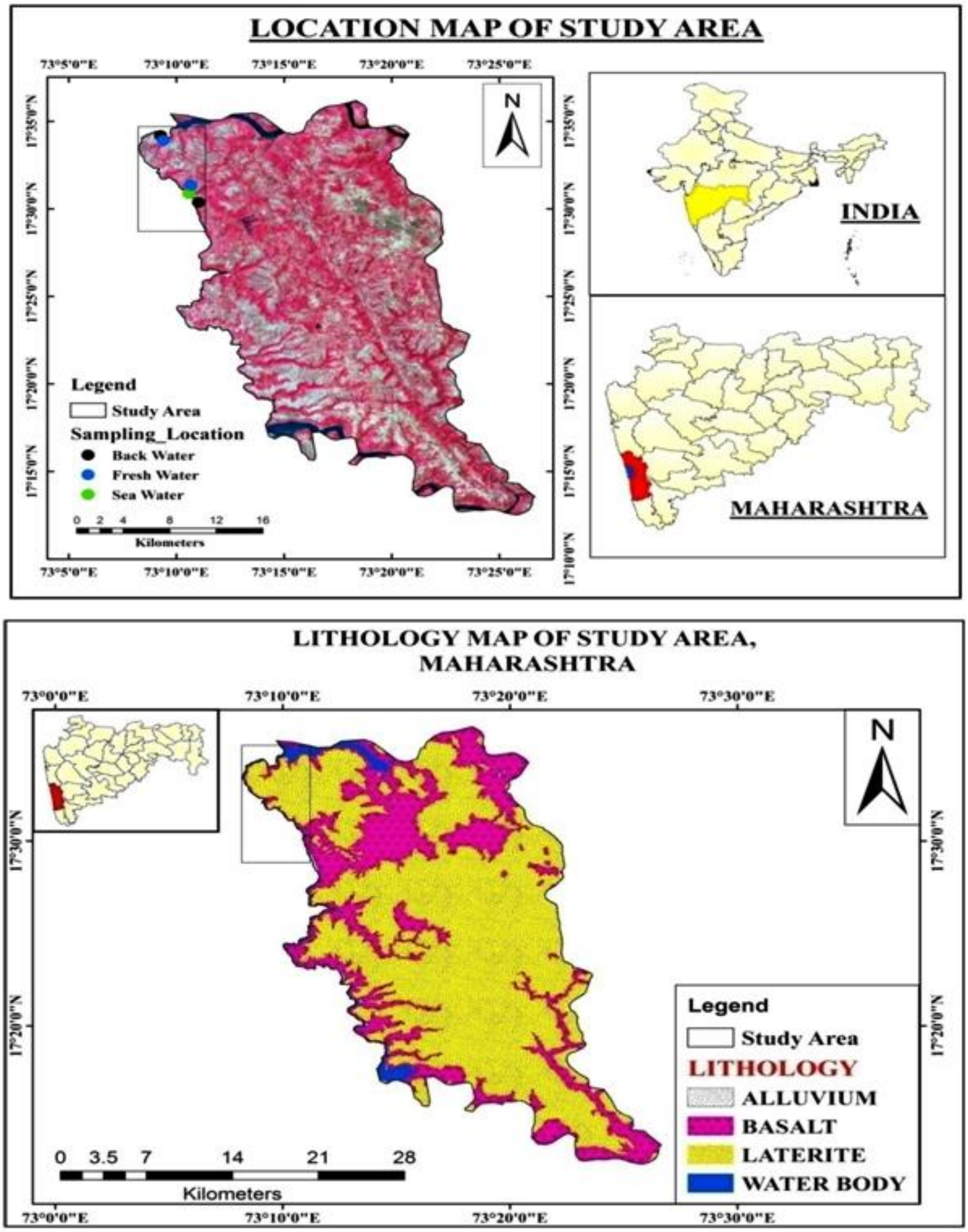


Figure 1: Location map of the study area

Hydrogeology of the Area

The top unconfined aquifer is distributed in the entire area. Water bearing rock formation in the top section is more often weathered basalts while higher altitude areas usually have hard basalts. In general, the aquifer consists of weathered jointed and fractured basalts. Groundwater level in the study areas was shallow and some of the wells groundwater level below the mean sea level (Uamrikar and Thigale, 2007). In the field investigation, it was found that total depth of the wells is shallow and it is around 6 meters below ground level (bgl). According to the results, there is a clear variation of the groundwater table during dry and wet seasons. Elevation of the groundwater table varies from 2 to 7 m above the mean sea level (m, amsl) in the study area.

MATERIALS AND METHODS

Sampling and Chemical Analysis

A total seven locations have been fixed for water sampling and depicted in Table 1 along with its co-ordinates. For the purpose of present study, a total of 25water samples were collected, out of which 12 water samples from Town Guhagar, twelve water samples from village Anjanvel and one surface water sample (Water sample number 25) was collected from the perennial stream which is flowing towards Arabian Sea near Guhagar town, Ratnagiri District, Maharashtra (India). The samplings had been carried out on 17th and 18th December 2020. Water samples were taken from four different zones viz. fresh water (Groundwater), back water (Estuarine) and seawater from selected sites twice in a day during high and low tide conditions while one water sample collected from stream. In this regard, it is difficult to specify the exact sampling depth so that we assumed groundwater samples are mixed over the whole vertical section where wells are selected as sampling sites (James, 2020).

The analysis of the influence of seawater on the groundwater quality was based on physicochemical parameters such as electrical conductivity (EC), total dissolved solids (TDS) and pH. A dissolved ion analysis was conducted to evaluate the hydrochemical properties of the aquifers. The pH measured with a with pH meter (Hach), the EC and TDS measured on EC meter. To analyze cations, samples were collected in 500 ml plastic water bottles and acidified to less than a pH 2 of with ultra-pure HNO_3.The alkalinity measurement was carried out in a laboratory using an automatic titrator and measured by acid titration to pH 4.5. The major cations were measured using inductively coupled plasma-optical emission spectrometry (Perkin Elmer) and major anions were analyzed using ion chromatography (Dionex). The Cadmium (Cd) and Lead (Pb) were measured using Atomic Adsorption Spectrophotometer. This analysis was carried out at Precise Analytics Laboratories A Division of Meyer Organics Private Limited, Thane, Maharashtra (India). The USSL plot of groundwater samples was drawn on Aqua Chem 4.0 scientific software.

Table 1: Sampling location sites from Guhagar area of Ratnagiri District., Maharashtra (India)

Locations Sr. No.	Category	Location	Latitude	Longitude
1	Groundwater	Anjanvel	17°34´06´´ N	73°09´25´´ E
2	Back water	Anjanvel	17°34´05´´ N	73°09´18´´ E
3	Sea water	Anjanvel	17°34´04´´ N	73°09´24´´ E
4	Groundwater	Guhagar	17°31´01´´ N	73°10´38´´ E
5	Back water	Guhagar	17°30´24´´ N	73°10´52´´ E
6	Sea water	Guhagar	17°30´57´´ N	73°10´32´´ E
7	Surface Water	Guhagar	17° 30' 31"N	73° 10' 58"E

RESULTS AND DISCUSSION

Hydrochemical Characterization

All analytical results of the water samples from the study area are depicted in Table 2. Obtained results of water quality parameters have been compared with Bureau of Indian Standards (BIS) for drinking water.

Table 2: Physico-chemical parameters of the water samples from Guhagar area of Ratnagiri District., Maharashtra (India)

Sample ID	Sampling Date	Category	Location	Tide	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	CO_3^{2-}	HCO_3^{-}	Cd	Pb
1	17-Dec-20	Groundwater	Anjanvel	Low tide	7.23	216.6	171.1	12.3	12.1	21.2	8	46	5.4	0	91.1	0	0
2	17-Dec-20	Back water	Anjanvel	Low tide	7.36	33400	24158	308.1	840.9	9038	316.3	24392.4	934.7	0	109.4	0.1	5
3	17-Dec-20	Sea water	Anjanvel	Low tide	8.02	47600	37058	446.8	1177.2	11030	330	38987.9	1473.1	182.3	0	0.1	0.7
4	17-Dec-20	Groundwater	Guhagar	Low tide	6.34	183.7	139.6	10	12.6	9.2	3.2	30	0	0	54.7	0	0.5
5	17-Dec-20	Back water	Guhagar	Low tide	7.04	13490	8992	154.1	355	2903	118.2	8597.3	270.2	0	72.9	0	0.2
6	17-Dec-20	Sea water	Guhagar	Low tide	8.05	48500	38162	462.2	1233.3	6680	536.8	38588	1365.9	182.3	0	0.1	0.7
7	17-Dec-20	Groundwater	Anjanvel	High tide	7.35	217.2	167.2	12.3	11.7	44.1	8.1	45	6.4	0	91.1	0	0
8	17-Dec-20	Back water	Anjanvel	High tide	7.21	19810	13940	200.3	485.8	3158	205.4	13995.7	675.7	0	91.1	0.1	0.2
9	17-Dec-20	Sea water	Anjanvel	High tide	7.83	40500	31396	339	1009	9540	431.6	30590.5	2150.8	72.9	0	0.1	0.6
10	17-Dec-20	Groundwater	Guhagar	High tide	6.32	144.8	110	10.8	12.6	17.8	1.3	25	69.2	0	72.9	0	0.3
11	17-Dec-20	Back water	Guhagar	High tide	7.28	5860	3674	77	233.6	856	52.8	2599.2	193.3	0	54.7	0.1	0.4
12	17-Dec-20	Sea water	Guhagar	High tide	7.93	48600	36956	477.6	1205.2	12730	459	38987.9	974.5	218.7	0	0.1	1.4
13	18-Dec-20	Groundwater	Anjanvel	Low tide	7.43	155.8	115.3	10	9.3	29.1	4	37	0	0	54.7	0	0
14	18-Dec-20	Back water	Anjanvel	Low tide	7.19	30500	23172	261.9	775.5	4235	318.7	23792.6	974.5	0	91.1	0.1	0.1
15	18-Dec-20	Sea water	Anjanvel	Low tide	7.9	45900	34890	369.8	1083.8	4847.5	218.5	37388.4	1015.7	145.8	0	0.1	0.1
16	18-Dec-20	Groundwater	Guhagar	Low tide	6.25	143.3	110.3	9.2	9.3	29.2	1.3	31	0	0	72.9	0	0
17	18-Dec-20	Back water	Guhagar	Low tide	7.25	13250	9396	123.3	317.7	3266	114.3	10996.6	380.7	0	72.9	0.1	0.6
18	18-Dec-20	Sea water	Guhagar	Low tide	7.99	48200	37780	400.6	1252	11835	600.8	39987.6	2059.7	182.3	0	0.1	0.3
19	18-Dec-20	Groundwater	Anjanvel	High tide	7.12	247.8	185.9	15.4	12.1	29.3	10.3	55	6	0	109.4	0	0.1
20	18-Dec-20	Back water	Anjanvel	High tide	7.18	14550	10224	154.1	355	3129	132.6	9397.1	556.3	0	91.1	0	0.1
21	18-Dec-20	Sea water	Anjanvel	High tide	7.92	42500	32362	400.6	1065.1	8955	500.6	32589.9	1305.8	0	145.8	0.1	0.3
22	18-Dec-20	Groundwater	Guhagar	High tide	6.34	152.6	119	9.2	8.4	8.2	1.2	30	0	0	72.9	0	0.1
23	18-Dec-20	Back water	Guhagar	High tide	7.1	8440	5836	107.9	233.6	624	462.2	5398.3	316.7	0	72.9	0	0.2
24	18-Dec-20	Sea water	Guhagar	High tide	7.88	48200	37966	477.6	1252	9950	572.4	36988.5	1348.4	182.3	0	0.1	0.5
25	18-Dec-20	Surface Water	Guhagar	Low tide	6.85	124.4	80.4	9.8	9.7	17.0	6.4	36.8	4.3	0	72.9	0.0	0.0

All parameters were expressed in mg/l except EC in µS/Cm and pH; ND= no data replace "0" by Not detectable"

Groundwater geochemistry

The analytical results of the groundwater samples showed that pH ranges from 6.25 to 7.43 with an average value is 6.80. EC was found ranged from 143.3 to 247.8 µS/cm with an average value is 182.7 µS/cm. TDS concentration ranges between 110.0 and 185.9 mg/l with average of 139.8 mg/l (Table 2). The pH, EC and TDS values were observed in all groundwater samples within the permissible limit (BIS, 2003). Detay and Carpenter (1997) has been categorized drinking water based on values of electrical conductivity which shows level of mineralization (Table 3). According to this classification groundwater samples from the study area falls under weakly and slightly mineralized water category. This suggests that the water needs to add some minerals before the drinking purpose. Ca^{2+} concentration ranges from 9.2 to 15.4 mg/l with an average of 11.2 mg/l (Table 2). Calcium concentrations in all the groundwater samples were observed within the permissible limits (BIS, 2003) (Table 2). Mg^{2+} concentration ranges from 8.4 to 12.6 mg/l, with an average of 11.0 mg/l (Table 2). Na^+ concentration ranges from 8.2 to 44.1 mg/l with an average of 23.5 mg/l (Table 2). However, groundwater sample Nos. 19 exceeds the K^+ concentration in the study area which ranges from 1.2 to 10.3 mg/l with an average of 4.7 mg/l (Table 2). All the groundwater samples have Na^+ concentrations were observed within the permissible limits (BIS, 2003). Cl^- concentration in the groundwater samples ranges from 25.0 to 55.0 mg/l with an average of 37.4 mg/l (Table 2). Cl^- concentration in all groundwater samples was found to be lower than permissible limit. SO_4^{2-} ranges from 5.4 to 69.2 mg/l with an average of 21.8 mg/l (Table 2). SO_4^{2-} concentration is also observed with the permissible limits. HCO_3^- influences the hardness and alkalinity of water. The bicarbonate was sourced from the weathered material of parent rocks. The maximum permissible limit of HCO_3^- in drinking water is 300 mg/l (BIS, 2003). HCO_3^- concentration in the groundwater samples varied from 54.7 to 109.4 mg/l with an average of 77.5 mg/l (Table 2). This suggests that the all groundwater samples HCO_3^- concentration from the study area is within the permissible limit.

Cd concentration in all groundwater samples was observed within the permissible limit (0.01 mg/l, BIS 2003); this suggests that the groundwater is suitable for drinking purposes in the study area according to cadmium concentration. Pb concentration in groundwater samples is varied from 0.1 to 0.5 ppm (average 0.125 mg/l). The lead concentration in 50 % groundwater samples were observed beyond the permissible limit (0.05 mg/l, BIS 2003); this suggests that these groundwater samples (water sample number 4, 10 , 19 and 22) were not suitable for drinking purposes in the study area according to the Pb concentration. Lead is naturally present in trace amounts in all biological materials, i.e. in soil, water, plants and animals. The main source of lead contamination is due to transport burning fossil fuel (Smirjakova et al., 2005; Mondal et al., 2010).

Table 3: Relation between water conductivity and mineralization (After Detay and Carpenter, 1997)

EC (µS/ cm)	Mineralization	% of samples
< 100	Very weakly mineralized water	Nil
100-200	Weakly mineralized water	05
200-400	Slightly mineralized water	03
400-600	Moderately mineralized water	Nil
600-1000	Highly mineralized water	Nil
> 1000	Excessively mineralized water	Nil

Surface water geochemistry

In the present study 01 surface water sample has been collected (river water) and analysed its psychochemical parameters (Table 2). The obtained results of surface water showed that pH (6.85), EC (124.4 µS/cm), TDS (80.4 mg/l), Ca^{2+} (9.8 mg/l), Mg^{2+} (9.7 mg/l), Na^+ (17 mg/l), K^+ (6.4 mg/l), Cl^- (36.8 mg/l), SO_4^{2-} (4.3 mg/l), CO_3^{2-} (0 mg/l), HCO_3^- (72.9 mg/l), Cd (not detected)and Pb (not detected). The psychochemical results of surface water samples seen that all parameters are within permissible limit of drinking water standard.

Seawater geochemistry

Similarly, in the seawater samples (Table 2) pH were observed between 7.83 to 8.05, EC, TDS, Ca^{2+} , Mg^{2+} , Na^+, K^+, Cl^-, SO_4^{2-}, CO_3^{2-} and HCO_3^- ranged from 40500.0 to 48600.0 µS/cm, 31396.0 to 38162.0 mg/l, 339.0 to 477.6 mg/l, Mg^{2+} 1009.0 to 1252.0 mg/l, Na^+ 4847.5 to 12730.0 mg/l, 218.5 to 600.8 mg/l, 30590.5 to 39987.6 mg/l, 974.5 to 2150.8 mg/l, 72.9 to 218.7 mg/l, and 0 to 145.8 mg/l, respectively, as presented in Table 2. The seawater samples have pH between 2.6 and 7.5 with average of 6.51, suggesting generally acidic to mild alkaline in nature. Cd concentrations in all eight seawater samples were observed within the permissible limit (0.01 ppm, BIS 2003). Pb concentrations in most of seawater samples except one seawater samples were observed beyond permissible limit (0.1 ppm, BIS 2003).

Backwater geochemistry

The physicochemical characteristics of back water samples (Table 2) are as follows; pH: 7.04 to 7.36, EC: 5860.0 to 33400.0 µS/cm, TDS: 3674.0 to 24158.0 mg/l, Ca^{2+} : 77.0 to 308.1 mg/l, Mg^{2+} : 233.6 to 840.9 mg/l, Na^+: 624.0 to 9038.0 mg/l, K^+: 52.8 to 462.2 mg/l, Cl^- : 2599.2 to 24392.4, SO_4^{2-}: 193.3 to 974.5 mg/l and HCO_3^- : 54.7 to 109.4 mg/l (Table 2). Whereas two trace elements also analysed from water samples i.e. cadmium and lead. Cd concentration in 05 water samples out of 08 back water samples were observed above the maximum permissible limit (0.01 mg/l, BIS 2003). Pb concentrations in the 6 water samples, out of eight water samples, were observed beyond permissible limit (0.1 mg/l, BIS 2003). Cadmium and lead is not essential for plants, animals and humans. The coastal regions peoples mostly depend on fishing business and also most of the population in coastal region use fish as its diet and these cadmium and lead concentration found beyond the permissible limits in backwater samples which is threaten to the fishes and ultimately its impact on human health hazards due to the consumption of fish available in this highly contaminated water. Long-term exposure (over years or decades) to cadmium in drinking water and or food may be a cause of kidney damage (BIS, 2003) and can also lead to anaemia, cardiovascular disease and hypertension (Mielke et al., 1991; Robards and Worsfold, 1991; Golekar et al., 2013). The earlier researchers reported that the cadmium's effect on the cardiovascular system (Schroeder, 1965).

Seawater intrusion

Quantification of seawater ingression

The fraction of seawater present in groundwater can be estimated by using the concentration of Cl^- ion (Appelo and Postma, 2005). It is assumed that the entire Cl^- ion originated from the seawater and the seawater percentage (SW%) in groundwater samples can be calculated using the formula:

$$SW\ \% = \frac{ConcCls - ConcClf}{ConcClsea - ConcClf} \times 100 \quad (1)$$

Where,

ConcCls: is average Cl^- ion concentration in the groundwater samples

ConcClf: is average Cl^- ion concentration in the backwater samples and,

ConcClsea: is average Cl^- ion concentration in the seawater sample (all in meq/l)

SW% for surface water (stream water) was 0% and for the seawater was 100%.

The SW % in groundwater samples from the study is ranged from 0.00% (U20, U34) to 0.05 (sample number 19). If the SW% of >5% indicates mixing between brine and groundwater. None of the samples from the study area have SW% >5%. This suggests that there is no clue about the mixing of seawater into the groundwater based on SW %.

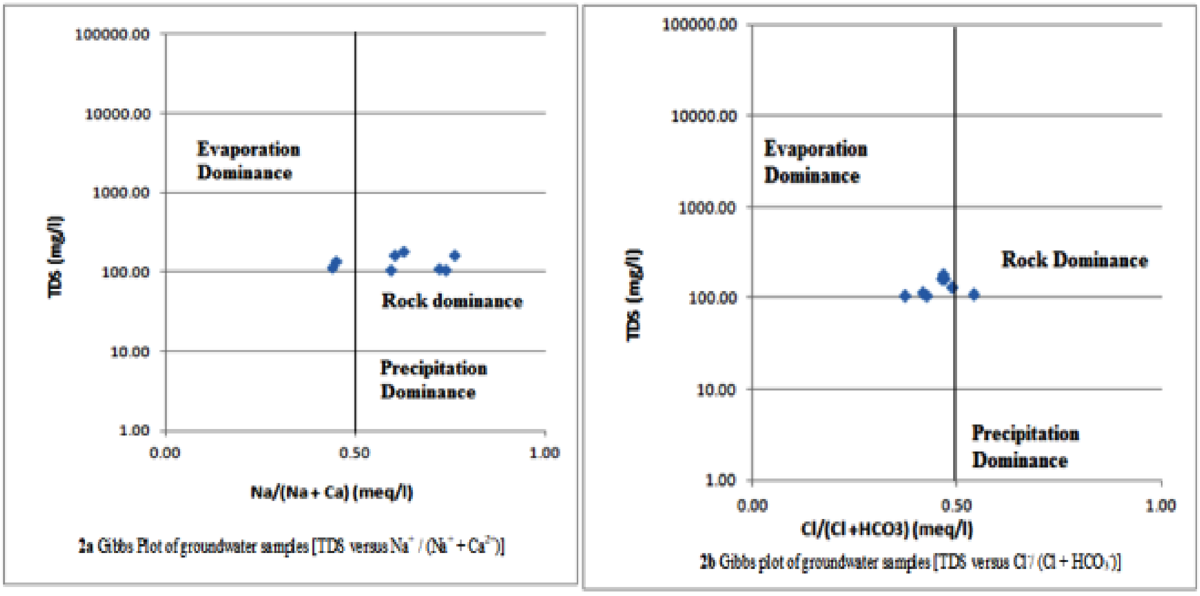
Groundwater - rock interaction

The mechanism of water rock interactions has been interpreted by using Gibbs diagram (Gibbs, 1970). Gibbs (1970) proposed a process that allows us to understand ion contribution to the water by precipitation, rock weathering and evaporation. A simple plot of TDS versus the weight ratio of $Na^+ / (Na^+ + Ca^{2+})$ (Figure

2a) or $Cl^- / (Cl^- + HCO_3^-)$ (Figure 2b) provides information on the relative importance of the three major mechanisms that controls water chemistry.

1. Evaporation processes dominated, with Na^+ and Cl^- as the major ions
2. Rock weathering dominated, with Ca^{2+} and HCO_3^- as the major ions
3. Precipitation (rain) dominated, with Na^+ and Cl^- as the major ions

In the present study all the groundwater samples show rock dominance. These results suggest that the chemical weathering of rock forming minerals, interaction between groundwater and the weathered material and ion-exchange reactions controlled the composition of groundwater.



2a Gibbs Plot of groundwater samples [TDS versus $Na^+ / (Na^+ + Ca^{2+})$]

2b Gibbs plot of groundwater samples [TDS versus $Cl^- / (Cl + HCO_3)$]

Figure 2: (a) Gibbs Plot of groundwater samples [TDS versus $Na^+ / (Na^+ + Ca^{2+})$] and (b) Gibbs plot of groundwater samples [TDS versus $Cl^- / (Cl + HCO_3^-)$]

Bivariate analysis

Various molar ratios/bivariate plots between ions were generally used to understand the geochemical process to reveals the significant impact of geogenic processes such as ion exchange, water-rock interaction, evaporation, and anthropogenic inputs on groundwater chemistry. The Na^+ vs. Cl^- plot has been widely used for the investigation of seawater intrusion (Jones et al., 1999; Kim et al., 2003). Molar ratios of Na^+/Cl^-less than the theoretical seawater molar ratio (0.84) indicate the mixing of seawater with groundwater (Vengosh et al., 1999; Mondal et al., 2011). If the molar ratio of $Na^+/Cl^-$is very low, then the groundwater samples are considered to be influenced by the inverse cation exchange processes. The mixing of seawater with the groundwater in the aquifer system was due to the seawater intrusion. The higher molar ratios of $Na^+/Cl^- > 1$ suggest that the possible dissolution of halite in the aquifer contributed to the groundwater salinization (Appelo and Postma, 2005). In the present study, about 50 percent groundwater samples shows molar ratios of Na^+/Cl^- is less than 0.84, indicating the mixing of seawater with groundwater (Figure 3a). While remaining 50 percent groundwater samples shows molar ratios of $Na^+/Cl^- > 1$ this suggest that the Na^+ and Cl^- ions in groundwater from the study area were found due to the mineral dissolution, water-rock interaction and ion exchange in the aquifer (Andersen et al., 2005).

The strong positive correlation ($R^2=0.81$) of the TDS and Cl^- bivariate plot shows that most of samples the derived from a common source and indicated seawater intrusion (Figure 3b). Also salinity of groundwater was due to mixing of seawater with groundwater as well as the water-rock interaction (Ghiglieri et al., 2012). Strong positive correlation ($R^2=0.77$) of the Na^+/Cl^- bivariate plot suggests that most of the samples were derived from a common source and indicated seawater intrusion (Fig. 3a). The relation between SO_4^{2-} and Cl^- suggest that $SO_4^{2-}$was mostly derived from seawater mixing with the groundwater system (Mohanty and Gurunadhara Rao, 2019). The linear pattern between SO_4^{2-} and Cl^- shows slightly positive correlation (R^2=0.14) and it indicates that SO_4^{2-} in groundwater was mostly from the seawater intrusion (Figure 3c). Slightly positive correlation (R^2=0.07) between Mg^{2+} and Cl^- indicates that the groundwater composition is slightly influenced by ion exchange (Fig. 3d). Correlations of Ca^{2+} with Cl^- (R^2=0.77) and Ca^{2+} with SO_4^{2-}(R^2=0.001) are moderate and slight, respectively (Figures 3e and 3f). They indicate poor dissolution of gypsum compared to the calcite dissolution. The relationship between Ca^{2+} and SO_4^{2-} however, suggests that the dissolution of gypsum is poor compared to the dissolution of calcite. In the present study, average molar ratio of $Na^+/Cl^-$was 0.39 for the seawater sample, and it was 0.71 for surface water sample (25) collected from the perennial stream. The groundwater samples have Na^+/Cl^-between 0.70 and 1.55, with an average of 0.32. Strong positive correlation (R^2=0.32) of the Na^+/Cl^-bivariate plot suggests that most of the samples were derived from a common source and indicated seawater intrusion (Figure 3a). The higher concentrations of Na^+ and Cl^- ions in groundwater were due to mixing of seawater. More Na^+ ion compared to the ratio of hypothetical seawater mixing line suggests additional sources and other processes. High values of Na^+ and Cl^- ions in the groundwater were due to the minerals dissolution caused by water–rock interaction and ion exchange processes.

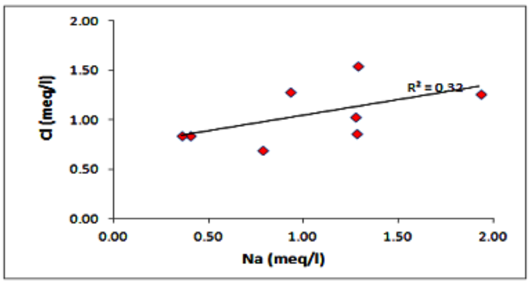


Fig. 3 a Bivariate plot Na^+ vs. Cl^-

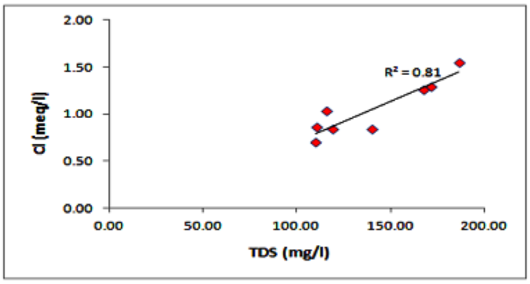


Fig. 3 b Bivariate plot TDS vs. Cl^-

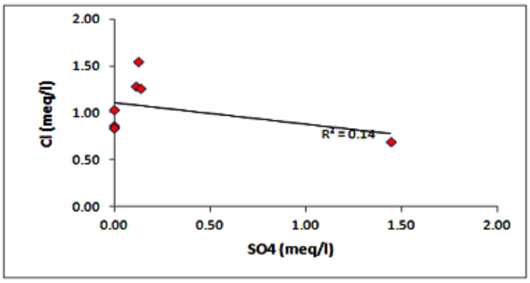


Fig. 3 c Bivariate plot SO_4^{2-} vs. Cl^-

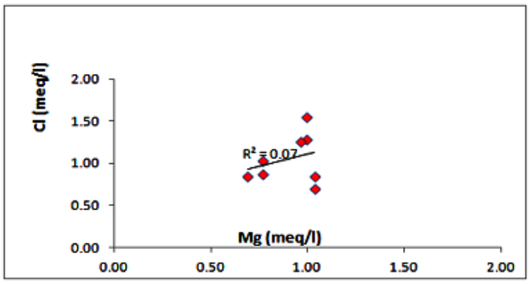


Fig. 3 d Bivariate plot Cl^- vs. Mg^2

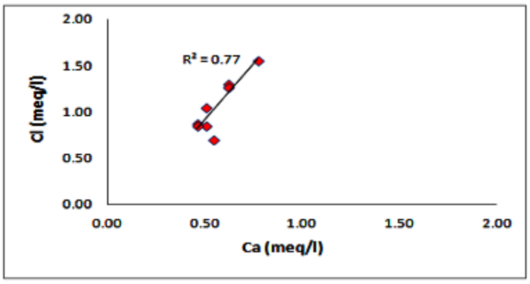


Fig. 3 e Bivariate plot Cl^- vs. Ca^{2+}

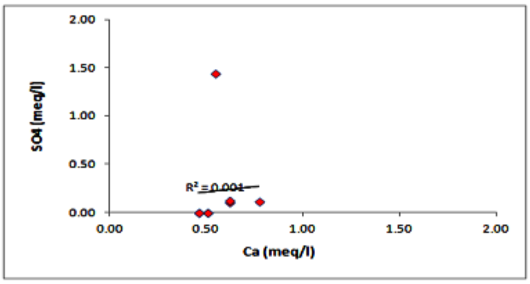


Fig 3 f Bivariate plot SO_4^{2-} vs. Ca^{2+}

Figure 3a to 3f: Bivariate plots

Ionic exchange

The ionic ratios between different chemical species have been commonly used to evaluate the seawater intrusion in coastal areas (Vengosh, and Rosenthal, 1994; Saxena et al., 2003; Mondal et al., 2010; Argamasilla et al., 2017). To understand the effect of seawater intrusion, the results of the dissolved ion analysis were classified according to the Cl^-/HCO_3^- molar ratio and water quality type in this study. The value of r (Cl^-/HCO_3^-) has been used as an effective factor to determine the effect of seawater. Less than 0.5 means that there is no effect of seawater, more than 0.5 and less than 1.3 means there is a slight effect, more than 1.3 and less than 2.8 means a moderate one, 2.8 to 6.6 means a severe effect, and 6.6 or more can be interpreted as the seawater effect is very severe (Revelle, 1941). In the present study, a value of r (Cl^-/HCO_3^-) is more than 0.5 and less than 1.3, indicating a moderate seawater effect, was present in all the 08 groundwater samples (100 % of the total).

The relationship between ratio of (Cl^-/HCO_3^-) and the (Na^+/Cl^-) molar ratio is shown in Figure 4. In this case, samples with ratio of (Cl^-/HCO_3^-) of less than 1.3 (not subject to seawater contamination) showed a very wide range of Na^+/Cl^-molar ratios, but those with ratio of (Cl^-/HCO_3^-) of 2.8 or more (significant seawater pollution) attained an Na^+/Cl^- molar ratio close to the composition of seawater (i.e., 0.84). It can be concluded that more than half of the groundwater samples in the study area have been affected by seawater.

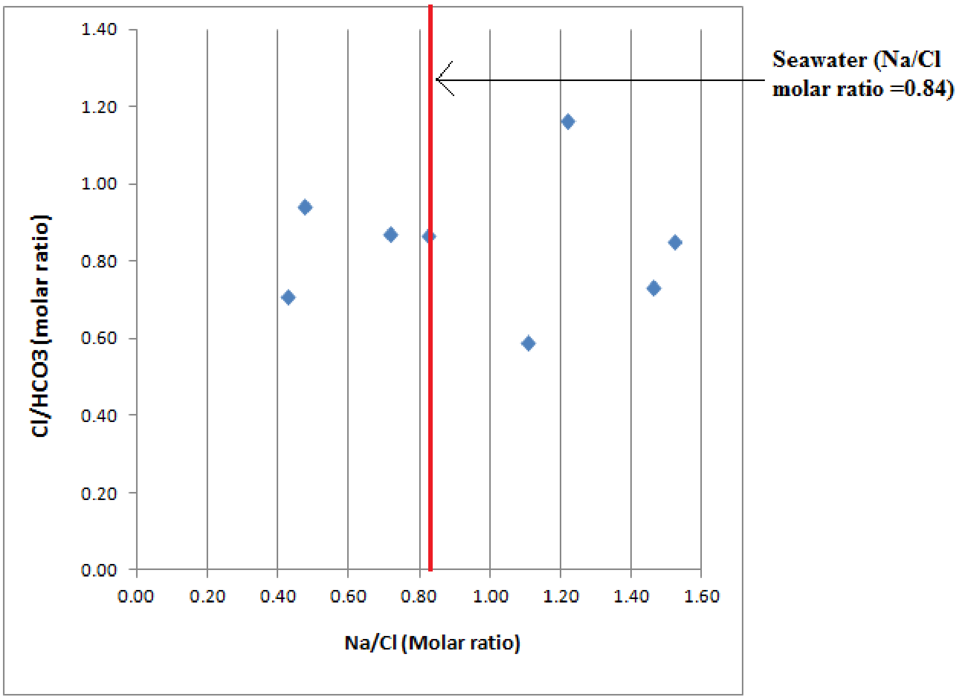
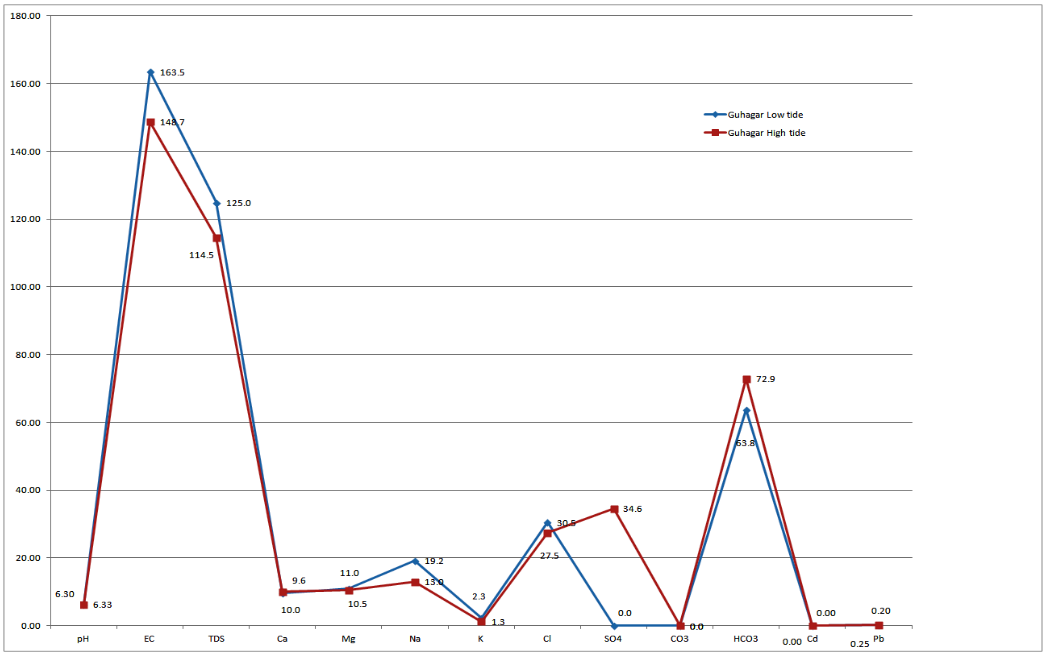


Figure 4: A plot of the relationship between the Cl^-/HCO_3^- and Na^+/Cl^-molar ratios

Relationship high tide and low with groundwater geochemistry

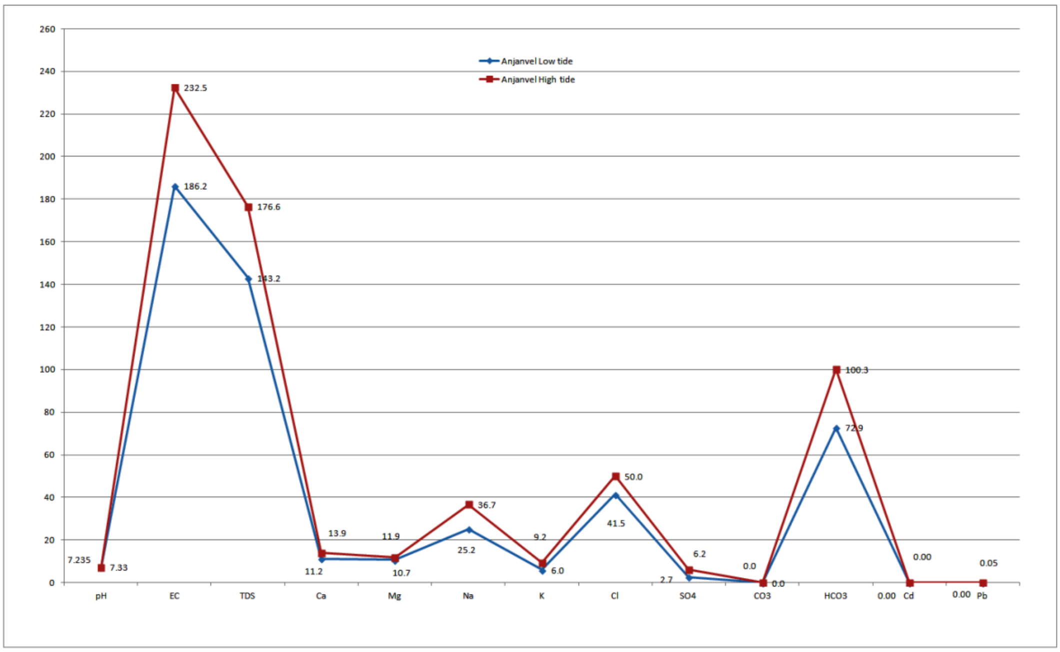
Earlier researchers reported that the rise in groundwater levels (0.5 to 0.9 m) due to seawater intrusion under high tide condition in the beach rock, mud and basaltic aquifers from the Guhagar area of Ratnagiri district (Uamrikar and Thigale, 2007). Therefore, it cannot be denied that rise in groundwater levels due to seawater ingress under high tide condition may affect groundwater quality of the present study area. The present sampling sites is belonging to the mud and basaltic aquifers and therefore its one of the possibility of seawater intrusion in groundwater. In the present study, the groundwater samples were collected during both low and high tide conditions from the same locations, and quantifying the relationship of seawater intrusion under high tide condition. For this purpose, two groundwater sampling sites had been selected viz. (1) Guhagar and (2) Anjanvel, and determined physicochemical parameters. The line plot was drawn based on ionic concentrations during low and high tide conditions from Guhagar and Anjanvel groundwater samplings sites (Figures 5 and 6).

It is seen that the sulphate and bicarbonate concentrations at both sites were extremely high during high tide than the low tide condition this suggest that seawater intrusion may be happened under high tide condition in the present study area.



All parameters were expressed in mg/l except EC in µs/cm and pH

Figure 5: Ionic variations in groundwater samples during high tide and low tide (Guhagar site)



All parameters were expressed in mg/l except EC in µs/cm and pH

Figure 6: Ionic variations in groundwater samples during high tide and low tide (Guhagar site)

Evaluation of the Groundwater Quality

Water Quality Index

The derivation of WQI involves weight assign for each parameter, normalization of the weights, standardization of the parameters, calculation of individual WQI scores and aggregation of the scores. Weights for the parameters (pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, Cd and Pb) given in Table 4 were adapted from previous studies (Alastal et al., 2015; Ketata, et al., 2012; Moustafa et al., 2020). The weights values range from one to five based on their importance for water quality assessment. Cd and Pb concentration were given the maximum weight of five because these are important indicators for assessment of the overall water quality, while potassium, magnesium and bicarbonate were given the minimum weights of one because it poses little risk to consumer health. Other chemical parameters were assigned a weight between one and five depending on their importance in determining the water quality. A factor of four was assigned to EC and TDS because of the indication of salinity. A factor of three was assigned to pH because of the indication of alkalinity and effect on hardness and to sodium, chloride and sulphate because of their indication of salinity and effect on taste. Calcium, sodium, chloride and sulphate were given a weight of two because of their effect on hardness.

Table 4: List of physico-chemical parameters with corresponding unit, WHO standard (Si), WQI weight (Wi), and normalized weight (wi)

Chemical Parameter	Unit	Standard (Si)	Weight (Wi)	Relative Weight (wi)
pH	-	6.5–8.5	3	0.094
EC	µS/cm	1400	4	0.125
TDS	mg/l	200	4	0.125
Ca^{2+}	mg/l	75	2	0.063
Mg^{2+}	mg/l	30	1	0.031
Na^+	mg/l	200	2	0.063
K^+	mg/l	10	1	0.031
Cl^-	mg/l	250	2	0.063
SO_4^{2-}	mg/l	200	2	0.063
HCO_3^-	mg/l	300	1	0.031
Cd	mg/l	0.01	5	0.156
Pb	mg/l	0.1	5	0.156

The normalized weight of each parameter is obtained as:

$$wi = \mathrm{Wi} / \sum_{i=1}^{n}(\mathrm{Wi}) \qquad (2)$$

where wi is the normalized weight for parameter i, Wi is the assigned weight for parameter i, and n is the total number of parameters. Water quality observations are then standardized by dividing the values by their corresponding water quality standard:

$$q_i = C_i / S_i \qquad (3)$$

where qi is the partial WQI score for parameter i, Ci is the observed concentration for parameter i (pH:7.00 for acidity), and Si is the water quality standard for parameter i. For the water quality standards, we use the WHO 2011 (WHO, 2011) guidelines for drinking-water. The overall WQI score is obtained by summation of the scores of each parameter multiplied by their normalized weight:

$$WQI = \sum_{i=1}^{n}(wiqi) \qquad (4)$$

A WQI value less than one indicates that the water can be used without any precaution, while higher values indicate poor quality of the water. WQI scores make it possible to classify the suitability of water for human consumption into categories such as excellent, good, poor, very poor and unsuitable for use as shown in Table 5 (Aish, 2013-missed ref in the list; Tyagi et al., 2013; Sahu and Sikdar 2008; Mondal, 2020). The WQI scores and associated water quality classes are given in the last columns of Tables 6. All WQI scores were all larger than 3, except water samples 16 and 25, which indicates that the water quality is unsuitable for drinking use. The water samples number 16 and 25 which collected from wells and river, respectively the results of these samples had shown WQI less than 3 indicating very poor water quality and remaining all groundwater samples WQI values greater than three, indicating that the groundwater is unsuitable for human consumption.

Table 5: Classification of the water quality according to the WQI score

WQI Range	**Water Quality Class**
< 0.5	Excellent
0.5 - 1.00	Good
1.00 - 2.00	Poor
2.00 - 3.00	Very Poor
> 3.00	Unsuitable

Table 6: WQI score and water quality classification of groundwater and surface waters samples from the study area

Sample Code	**Sampling Date**	**Category**	**Location**	**Tide**	**WQI**	**WQC**
1	17-Dec-20	Groundwater	Anjanvel	Low tide	3.96	Unsuitable
4	17-Dec-20	Groundwater	Guhagar	Low tide	7.90	Unsuitable
7	17-Dec-20	Groundwater	Anjanvel	High tide	4.07	Unsuitable
10	17-Dec-20	Groundwater	Guhagar	High tide	5.97	Unsuitable
13	18-Dec-20	Groundwater	Anjanvel	Low tide	3.00	Unsuitable
16	18-Dec-20	Groundwater	Guhagar	Low tide	2.56	Very poor
19	18-Dec-20	Groundwater	Anjanvel	High tide	5.46	Unsuitable
22	18-Dec-20	Groundwater	Guhagar	High tide	3.48	Unsuitable
25	18-Dec-20	Surface Water	Guhagar	Low tide	2.99	Very poor

Irrigation water quality

Assessment of suitability of groundwater for the irrigation purpose was calculated based on Sodium Adsorption Ratio, Salinity Hazard, Soluble Sodium Percentage, Residual Sodium Carbonate, Permeability Index, Na Percentage and Corrosivity Ratio. Irrigation water quality parameters of the groundwater samples from the study area are depicted in Table 7.

Table 7: Irrigation water quality parameters of groundwater samples of coastal aquifer in Guhagar area of Ratnagiri District, Maharashtra, India

Sample ID	**SAR**	**RSC**	**% Na**	**CR**	**SSP**	**PI**
1	1.03	-0.11	33.82	0.47	41.30	49.18
4	0.46	-0.64	19.92	0.47	23.98	49.35
7	2.17	-0.08	51.95	0.47	57.54	36.84
10	0.88	-0.38	32.61	0.90	34.01	47.29
13	1.60	-0.37	48.22	0.58	52.10	38.65
16	1.63	-0.03	50.39	0.37	51.70	45.05
19	1.36	0.03	38.72	0.47	46.69	45.31
22	0.47	0.05	23.29	0.35	25.29	72.92
Minimum	0.46	-0.64	19.92	0.35	23.98	36.84
Maximum	2.17	0.05	51.95	0.90	57.54	72.92

Sodium Absorption Ratio

The relative activity of sodium ion in the exchange reaction with soil is expressed in terms of Sodium Absorption Ratio (Srivastava and Parimal, 2012). It determines the suitability of irrigation water, because the same is considered as a measure of alkali/sodium hazard for crops. High SAR values indicate the risk of displacement of alkaline earths. It also adversely affects the soil structure. Adverse effect caused by high concentration of sodium on soil is known as sodium hazard. The Sodium Absorption Ratios in the water samples from the study area were calculated by using following equation (Richard, 1954).

$$SAR = \frac{Na}{\sqrt{(Ca+Mg)/2}} \qquad (5)$$

Where Na^+, Ca_2^+ and Mg_2^+ concentrations are in meq/l

Irrigation water had been classified into three category based SAR ratio is as follows (Raghunath, 1987). (1) Excellent: SAR ratio is less than 6, (2) Increasing problem: SAR ration between 6 to 9 and, (3) Severe problem: SAR ratio greater than 10. In the study area, SAR values were observed between 0.46 to 2.17. This suggests all groundwater samples from the study area is belonging to the excellent category.

Salinity Hazards

Electrical conductivity depends on water's capacity to convey an electric current, which is used for indicating the total concentration of ionized constituents present in natural water. Electrical conductivity is a good measurement of salinity hazard to crops as it reflects the TDS in groundwater. EC values was found ranged from 143.3 to 247.8 µS/cm with an average value is 182.7 µS/cm. Saxena et al (2004) and Mondal et al. (2005) have suggested a classification based on EC values for irrigation purpose is as (1) Fresh (<1500 µS cm−1), (2) Brackish (1500-3000 µS cm−1) and, (3) Saline (>3000). Based on this classification, all groundwater water samples from study area shows fresh water category.

The SAR value is an important parameter for determining suitability of groundwater for irrigation use because it is a measure of alkali/sodium hazards (Richard, 1954). The Sodium Hazard Diagram (USDA, 1954) drawn with the help of Electrical conductance and SAR values, different areas as (1) C 1- Low salinity water: Good for irrigation, (2) C2 - Moderate salinity water: Good for soils of medium permeability and the most Plants, (3) C3- Medium High salinity water: Satisfactory for plants having moderate salt tolerance and soils of moderate permeability and leaching, (4) C4 - High salinity water: Satisfactory for salt tolerant crops on soil of good permeability with special leaching, (5) S1 - Low sodium water: Good, (6) S2 - Medium sodium water: Good for coarse-grained permeable soils, unsatisfactory for highly clayey soils with low leaching, (7) S3 - High sodium water: Suitable only with good drainage, high leaching and organic material addition and, (8) S4 - Very high sodium water: Unsatisfactory.

The data plotted on the USSL diagram (Fig. 7) indicates the type of salinity hazards. It is observed that, most of groundwater samples fall under category C1S1 which suggest that low sodium and low salinity hazards conditions. Only 01 groundwater samples (sample number 19) plots in C2S1 suggesting low sodium and medium salinity hazards.

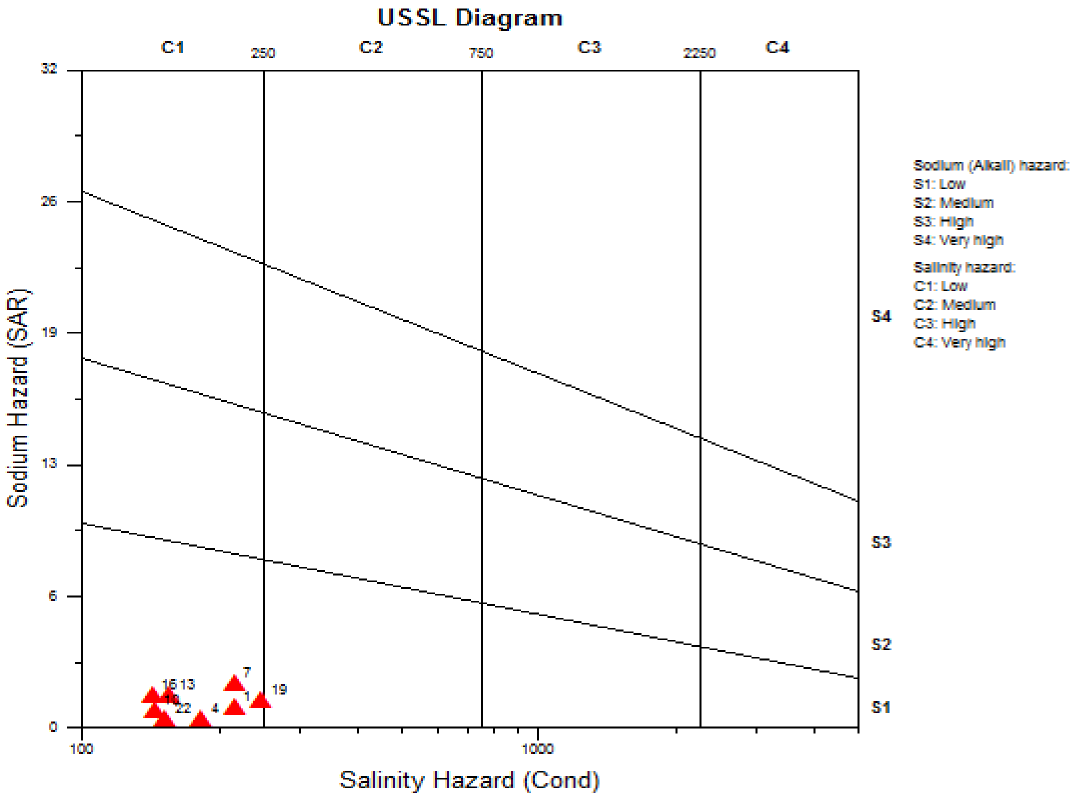


Figure 7: US Salinity Hazard Diagram of groundwater samples

Residual Sodium Carbonate (RSC)

Residual sodium carbonate (RSC) is an index used to determine the HCO_3^- hazard. High bicarbonate levels in groundwater can arrest plant growth and lead to calcite precipitation, decreased soil permeability, lowered infiltration capacity and an increase in erosion.

The value for RSC is calculated as per Eaton (1950),

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (6)$$

Where all ionic concentration expressed in meq/l

The groundwater having excess of CO_3^{2-} and HCO_3^- concentrations over the Ca^{2+} and Mg^{2+} in excess of limits have unfavourably effects on agriculture (Eaton, 1950). Lloyd and Heathcote (1985) have classified irrigation water based on RSC is as (1) Suitable: RSC values less than 1.25, (2) Marginal: RSC values between 1.25 to 2.5 and, (3) Not suitable: RSC values greater than 2.5. In the study area, the RSC values were observed between -0.64 to 0.05 this suggests all groundwater samples from the study area are belonging to the suitable category.

Sodium Percentage (Na %)

According to the percent sodium, the suitability of groundwater for irrigation use is determined because sodium concentration reacts with soil to reduce permeability. Sodium concentration is an important parameter for defining the type of water for irrigation. Sodium percentage (Doneen, 1962) is calculated by using following formula,

$$Na\ \% = (Na \times 100) / (Ca + Mg) \quad (7)$$

Where all ionic concentration is expressed in meq/l

Gopinath and Seralathan (2006) have suggested classification for water to be used for irrigation as (1) Excellent (<20%), (2) Good (20%-40%), (3) Permissible (40% - 60%) and, (4) Some doubtful (60%-80%). In the study area % of Na values were observed between 19.92 to 51.95, this suggests all groundwater samples from the study area is within the permissible limit.

Soluble Sodium Percentage (SSP)

SSP is used to evaluate sodium hazard. SSP is defined as the ratio of sodium and potassium content to the total cation content. Water with a SSP greater than 60% may result in sodium accumulations that will cause a breakdown the physical properties of the soil (Khodapanah et al., 2009). SSP has been calculated by using following equation (Todd, 1980)

$$SSP = \frac{(Na+K)\times 100}{(Ca+Mg+Na+K)} \qquad (8)$$

Where the concentration is expressed in meq/l

The value of SSP if less than 50 indicates good quality of water and higher values that the water is unsatisfactory for irrigation (USDA, 1954). It is observed that, the SSP values were greater than 50 in 03 groundwater samples (Sample ID 7, 13 and 16). This suggests that this water is not suitable for irrigation purpose.

Permeability Index (PI)

The soil permeability is affected by long term use of irrigation water and is influenced by sodium, calcium, magnesium and bicarbonate contents of the soil. The Permeability Index (PI) was calculated according to Doneen (1962) employing the following equation,

$$x = \frac{Na+\sqrt{HCO3}}{(Ca+Mg+Na)} \times 100 \qquad (9)$$

Where all ionic concentration expressed in meq/l

Doneen (1962) have classified irrigation water according to values of PI is as (1) Class I: waters are considered to be excellent and suitable for irrigation (PI >75%), (2) Class II: waters are considered to be good and suitable for irrigation (PI 25 -75%) and, (3) Class III: water is unsuitable for irrigation (PI < 25 %). The PI values in groundwater samples from study area were observed between 36.84 to 72.92. According to PI, all groundwater samples fallen under the class II category (25-75%). This suggests that the all water samples exhibit there is no permeability hazard.

Corrosivity ratio (CR)

Corrosivity ratio is calculated by using the formula expressed as, (Pandian and Sankar, 2007).

$$CR = \frac{(Cl+SO4)}{2\ (HCO3+CO3)} \qquad (10)$$

Where all ionic concentration expressed in meq/l

If CR value is greater than 1.0, their effect of corrosion leads to loss in carrying capacity of pipes (Pandian and Sankar, 2007; Mondal et al., 2016). Higher values of chloride promote corrosion of metal pipes as chloride increases the electrical conductivity of water (Gregory, 1990). In metal pipes, chloride reacts with metal ions to form soluble salts which corrode the pipe and therefore, PVC pipes are extensively used in agriculture. With changes in temperature of water, these PVC pipes reacts with water, Pb and other metals are released with water. In lead pipes, a defensive oxide layer is built up, but chloride enhances galvanic corrosion (Gregory, 1990). All the groundwater samples from the study area, the CR values were observed less than 1.0 suggests that water is good quality in terms of corrosion.

CONCLUSIONS

This work is demonstrated the hydrogeochemical characteristics of coastal aquifers of Guhagar area of Ratnagiri District in the State of Maharashtra, India. The Na^+/ Cl^- molar ratio (~0.84) close to the hypothetical seawater-freshwater mixing line recommended a significant influence of seawater along with water-rock interaction and ion exchange reaction in increasing the salinization. The groundwater of this region shows chiefly ion exchange characters. A few of the samples show seawater intrusion, and few represent recharge. The Cl^-/ HCO_3^- ratio in the groundwater from the study area is more than 0.5 and less than 1.3, indicating a moderate seawater effects. TDS/Cl^- ratio suggests water-rock interaction, while other ratios like SO_4^{2-}/Cl^-, Ca^{2+}/Cl^-, Mg^{2+}/Cl^-, and Ca^{2+}/SO_4^{2-} suggest that the seawater mixing, ion exchange, dissolution, and cation-exchange controlled the groundwater geochemistry.

The overexploitation of the coastal aquifers is allowed the salinization process at a faster rate and therefore affected the quality of soil and growth of plants and crops. Therefore, it is essential to have successful conservation and well managed plan to protect the coastal aquifers of this region from salinization process. Few conventional methods have been recommended for conservation and protection of the coastal aquifers of this region from salinization process. Reduction of pumping from wells is the simplest, direct and cost-effective method to maintain the groundwater balance in aquifers. Pumping wells are commonly relocated further inland away from the coast to provide a proper seaward hydraulic gradient, by keeping the groundwater levels above the sea level in the vicinity of the shoreline and reducing the excessive losses of fresh groundwater by outflows. It has also concluded that, coastal agricultural areas in the study area are more susceptible to salinization. New varieties of salinity tolerant crops should be introduced for cultivation in these areas. It is also needs to change the cropping patterns. Most of the farms are empty after harvesting of Kharif (Monsoon) crops and therefore, needs to Rabbi (winter) crops should be cultivated based on suitability of local climate and soil types.

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