Hydrochemical Characterization of Coastal Groundwater in Porbandar Region, Gujarat, India

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Abstract— The hydrochemical data of groundwater samples from a coastal region in Porbandar district, Gujarat, India have been examined using factor analyses to determine the main factors controlling the groundwater chemistry and salinity. A total of seventy groundwater samples were collected from the study area and analysed for pH, EC, Ca^{2+}, Mg^{2+}, Na^{+}, K+, HCO_3^{-}, Cl-, NO_3^{-}, and SO_4^{2-}. Factor analysis has revealed that different hydrogeochemical processes such as saltwater encroachment from sea, saltwater upconing, ion exchange, inherent salinity of rocks / marine sediments, carbonate and silicate weathering of rocks, and leaching of salts/minerals are the key factors regulating the groundwater chemistry of the region.

Keywords— Coastal groundwater, hydrogeochemistry, factor analysis, salinity, total dissolved solids, groundwater quality

INTRODUCTION

Groundwater is a vital resource for communities and ecosystems thriving in the coastal regions. Salinization is the most widespread form of groundwater quality deterioration, especially in the coastal areas, and is represented by the increase of total dissolved solid (TDS) and other related chemical constituents [1,2]. Besides encroachment of saltwater from the sea, the composition of coastal groundwater is influenced by many other processes viz., saltwater upconing, ion exchange, wet and dry deposition of atmospheric salts and water rock interactions. Because of the complexities of the regional hydrogeological conditions and hydro chemical process, advanced techniques are required to interpret observed relationship among different chemical constituents / variables. Hydro chemists have thus applied factor analysis to interpret these relationships and assess controlling factors behind groundwater composition [3-7]. Factor analysis is a technique of quantitative multivariate analysis with the goal of representing the inter-relationship among a set of variables or objects. Factor analysis provides a simple interpretation of a given body of data and affords fundamental description of particular set of variables related to hydro chemical processes beyond strict litho logical controls [8]. Factors are constructed in such a way that they reduce the overall complexity of the data by taking advantage of inherent interdependencies. It is useful for interpreting commonly collected groundwater quality data and relating these data to specify the involved hydrogeologic processes.

STUDY AREA

The study area is a coastal region located in south-western part of the Saurashtra peninsula with its major portion falling in the Porbandar district of Gujarat state in India. It lies between latitudes 21°30’ and 22°0’ N and longitudes 71°22’ and 72°22’E with a geographical area of about 1750 km^2. Porbandar district falls under semi-arid climate zone with annual rainfall of 634 mm. Agriculture is the main occupation of the local population and groundwater is the major resource for irrigating the crops. The geology of the region mainly comprises of milliolitic limestone, clays, laterites and alluvium in the coastal plains, while in the upper inland areas weathered/ hard basalt is present. Groundwater is highly saline near the coast, but it is generally fresh in inland areas. For hydrochemical characterization of groundwater, the study area is divided into four zones based on the distance of the respective zone from the sea coast (Fig. 1): (i) Zone I (region 0-3 km from coast), (ii) Zone II (region 3-6 km from coast), (iii) Zone III (region 6-12 km from coast) (iii) Zone IV (region more than 12 km from coast).

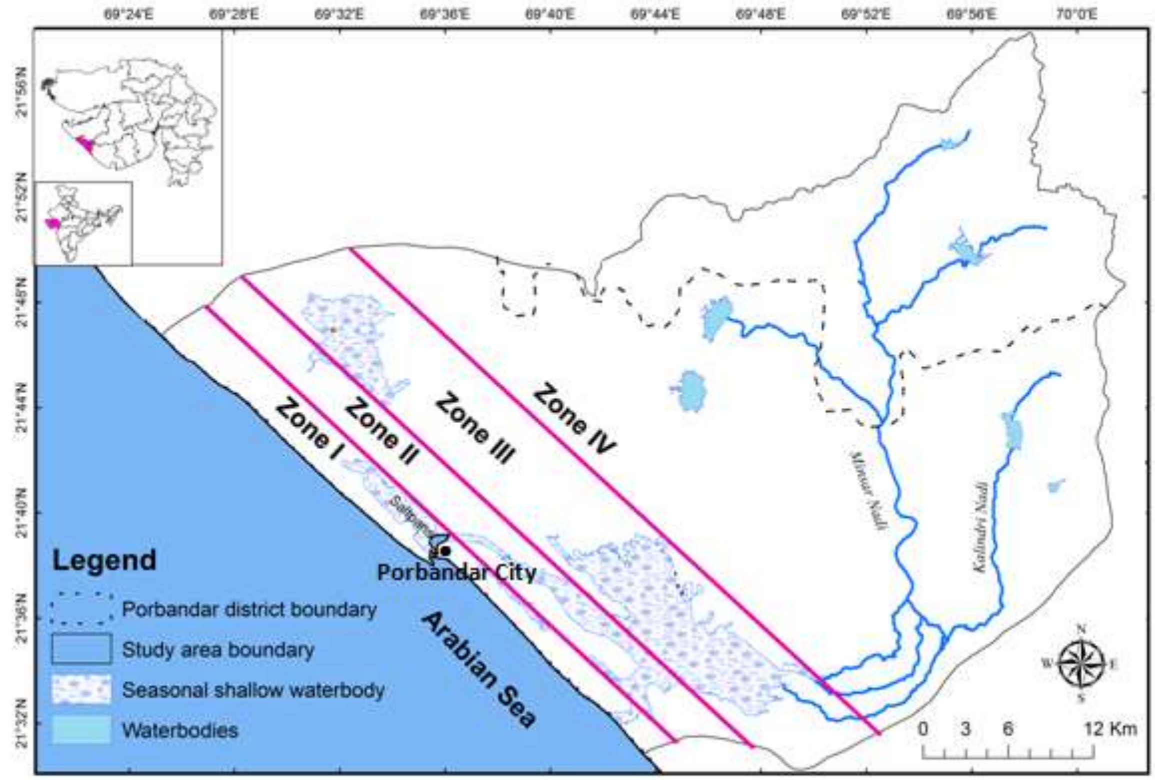

Fig. 1: Location map of study area with zone positions

MATERIAL AND METHODS

A total of 70 groundwater samples were collected during post monsoon period in 2013 from dug wells and piezometers in the study area. The water samples were preserved in polyethylene bottles of 1000 ml. Samples were analyzed in the laboratory for the physico-chemical attributes like pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), major and minor ions i.e. Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^{+}), Potassium (K^{+}), Chloride (Cl^{-}), Bicarbonate (HCO_3^{-}), Nitrate (NO_3^{-}), and Sulphate (SO_4^{2-}). These parameters were analyzed using standard methods [9,10]. EC and pH were measured using digital meters immediately after sampling in the field. Ca^{2+}, Mg^{2+}, Cl^{-} and HCO_3^{-} were determined by titration; Na^{+} and K^{+} were measured by flame photometry; NO_3^{-} by colour development with absorption method; SO_4^{2-} by turbidity method; and F^{-} by SPADNS method. The accuracy of the chemical analysis was verified by calculating ion balance errors which were found to be within ± 10%.

In the present study factor analysis is applied to obtain correlations among the hydrochemical constituents of groundwater samples. The general mathematical solution to represent number of factors has been explained as follows [11,12]:

$$Z_{kj} = a_{1j}F_{k1} + a2_{j}F_{k2\ldots\ldots+}\ a_{mj}F_{km+}\ a_{nj}F_{kn}$$

The a's are factor loadings, coefficients that reflect the importance of each variable j, in the factors represented by the aF terms. Thus, where factor loadings are high, it can be assumed that the variable contributes to that factor. The F's are factor scores. The scores indicate the importance of each factor with respect to each sample k. Z's are original variables in standard form. The sum of the squares of the factor loadings for each variable is the communality and reflects the proportion of the total variability accounted for by the factoring. The sum of squares of factor loadings within each factor before rotation or other manipulation to maximize loadings is the eigen value for that factor. Factor loading is the measure of the degree of closeness between the variables and the factor.

According to Kaiser criterion, the factors with eigen value greater than 1 are selected. The first three highest factors *viz.* Factor 1 (F1), Factor 2 (F2), and Factor 3 (F3) are extracted to carry out the analysis. In order to maximize the variance of the principal axes, the varimax rotation can be applied. The objective of varimax rotation is moving each factor axis to positions so that projections from each variable on to the factor axes are either near the extremities or near the origin. The largest loading, either positive or negative, suggests the variance of the factor loading of the variables; positive loading indicates that the contribution of the variables increases with the increasing loading in a dimension; and negative loading indicates a decrease [8].

The above methodology was used to identify the source of dissolved ions and the chemical processes which lead to groundwater salinization. Factors were interpreted as different sources of delivering/receiving ions to/from waters. The variables used for factor analysis were pH, Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, EC and TDS.

RESULTS AND DISCUSSION

The pH of groundwater in the four zones was found to vary in the range 6.70 - 8.46 with an average pH of 7.63. Average value of TDS in Zones I, II, III and IV was found to be 2085.49 mg/L, 2019.04 mg/L, 1584.58 mg/L and 770.41 mg/L, respectively. Thus, the groundwater salinity, in general, decreases as distance from the coast increases.

Concentrations of Cl^-, Na^+, Ca^{2+} and Mg^{2+} were found to generally decrease away from the coast. Ca^{2+} and Mg^{2+} were found to be dominant cations present in groundwater next to Na^+. Similarly, HCO_3^- anion was also present in considerable amounts next to Cl^-. Average values of major cations in Zones I, II, III and IV were found, respectively, as Na^+ : 564.85mg/l, 396.73mg/l and 186.59mg/l; Ca^{2+} : 147.08 mg/l, 252.18 mg/l, 172.61 mg/l and 77.34 mg/l ; Mg^{2+} : 52.64 mg/l, 37.76 mg/l, 31.61 mg/l and 22.72 mg/l. Average values of major anions in Zones I, II , III and IV were found, respectively, as Cl^- : 796.83 mg/l, 767.24 mg/l, 603.67 mg/l and 172.85mg/l; HCO_3^- : 386.91mg/l, 337.21mg/l, 302.34 mg/l and 404.29 mg/l; SO_4^{2-} : 144.67 mg/l, 123.07 mg/l, 170.06 mg/l and 39.54 mg/l; NO_3^- : 8.99 mg/l, 17.73 mg/l, 13.20 mg/l and 9.10 mg/l . As revealed by average values from different zones, these parameters varied in wide ranges across the groundwater samples collected from the area.

Factor analysis was applied to obtain correlations among the hydrochemical constituents of groundwater samples. According to Kaiser criterion, the factors with eigen value greater than 1 were selected. In order to maximize the variance of the principal axes the varimax rotation was applied.

For the purpose of factor analysis, the above four zones (i.e. Zone I, II, III and IV; refer Fig. 1) were regrouped into three zones: Zone A comprising Zone I; Zone B comprising Zone II and III; and Zone C comprising Zone IV. The discussion in the following paragraphs is based on the above three regrouped zones: Zones A, B and C.

For post monsoon season of the year 2013, three factors were identified *viz.* Factor 1 (F1), Factor 2 (F2) and Factor 3 (F3), which control the groundwater chemistry. For factor loadings, high positive loading was defined as greater than 0.75 and moderate loading was defined as 0.5-0.75. Loadings of less than 0.3 were considered insignificant.

The analysis reveals that for Zone A, the three factors (F1, F2 and F3) explain 80.01% of the total variance in post monsoon. Table 1 presents the eigen values, the percentage of variance, the cumulative eigen value and the cumulative percentage of variance associated with each other for Zone A during post monsoon.

In Table 1, F1 has a high positive loading of TDS, EC, Cl^-, Na^+, K^+ and SO_4^{2-} accounting for 40.19% of the total variance in Zone A. The high loading of these ions indicates salinity originating from seawater. F2 explains total variance of 17.30% and has a negative loading of HCO_3^- and NO_3^-. The leaching of salts due to rainfall recharge and irrigation water takes place in monsoon and post monsoon. Therefore, this factor can be related to anthropogenic inputs. F3 explains total variance of 22.52% and has positive loading of Cl^-, Ca^{2+} and Mg^{2+}. The negative loading of pH also contributed to the factor. The positive loading of Cl^-, Ca^{2+} and Mg^{2+} can be attributed to ion exchange process and dissolution of halite salts and calcite minerals in post monsoon. The negative loading of pH may be caused by the biogenic or organic control from marine sediments of the pH value [13,14].

Table 1: Results of factor analysis with varimax rotation for Zone A (2013)

Variable	F1	F2	F3
pH	-0.146	0.338	-0.731
EC	0.864	0.047	0.494
TDS	0.864	0.047	0.494
HCO_3^-	-0.066	-0.711	-0.208
Cl^-	0.827	0.118	0.538
SO_4^{2-}	0.891	-0.106	0.217
NO_3^-	-0.1	-0.851	0.153
Na^+	0.928	0.015	0.309
K^+	0.751	-0.21	-0.222
Ca^{2+}	0.488	0.202	0.681
Mg^{2+}	0.192	0.04	0.807
Cumulative eigen value	5.493	-1.071	2.532
Variability %	40.19	17.3	22.52
Cumulative %	40.19	57.49	80.01

For Zone B, the first three factors explain 77.79% of the total variance in post monsoon season. Table 2 presents the eigen values, the percentage of variance, the cumulative eigen value and the cumulative percentage of variance associated with each other for Zone B during post monsoon.

In Table 2, F1 has a high positive loading of TDS, EC, Cl^-, Na^+, K^+ and SO_4^{2-} accounting for 41.34% of the total variance in Zone B. The relatively low to moderate loading of HCO_3^- also contributes to F1. The high loadings of TDS, EC, Cl^-, Na^+, K^+ and SO_4^{2-} indicate salinization in local areas due to processes such as upconing of saline water due to pumping of groundwater for irrigation on account of dry spells in the monsoon season. The positive values of EC and HCO_3^- concentrations indicate carbonate weathering and silicate weathering. Thus, this factor relates to water rock interaction and salinization. F2 explains the total variance of 21.65 % and associated with high loading of NO_3^- and moderate loading of Ca^{2+} and Mg^{2+}. The positive values of Ca^{2+} and Mg^{2+} concentrations indicate strong carbonate weathering. The high positive loading of NO_3^- indicates leaching of fertilizer due to recharge processes in post monsoon season. Thus, this factor reflects water rock interaction and influence of anthropogenic activities. F3 explains total variance of 14.80% and associated with moderate positive loading of Ca^{2+} and HCO_3^-. High negative pH loading also contributed to factor. The positive values of Ca^{2+} and HCO_3^- concentrations indicate dissolution of calcite minerals. The negative loading of pH may be caused by the biogenic or organic control from marine sediments of the pH value. Thus, this factor reflects water rock interaction.

Table 2: Results of factor analysis with varimax rotation for Zone B (2013)

Variable	F1	F2	F3
pH	-0.008	0.093	-0.922
EC	0.932	0.322	0.106
TDS	0.932	0.322	0.106
HCO_3^-	0.469	-0.478	0.543
Cl^-	0.864	0.417	0.061
SO_4^{2-}	0.724	0.017	0.013
NO_3^-	0.004	0.894	-0.025
Na^+	0.958	-0.1	-0.091
K^+	0.817	-0.213	-0.162
Ca^{2+}	0.213	0.597	0.488
Mg^{2+}	0.211	0.825	0.022
Cumulative Eigen value	6.116	2.696	0.139
Variability %	41.34	21.65	14.8
Cumulative %	41.34	62.99	77.79

For Zone C, the first three factors explain 81.65% of the total variance in post monsoon season. Table 3 presents the eigen values, the percentage of variance, the cumulative eigen value and the cumulative percentage of variance associated with each other for Zone C during post monsoon.

In Table 3, F1 has a high positive loading of TDS, EC, Cl^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} and moderate loading of Na^+. The moderate negative pH loading also contributes to factor. The positive loading of TDS, Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+} indicate dissolution of halite salts and carbonate and silicate weathering. The factor also reflects salinity in Zone C due to the phenomenon of localized upconing of saline water from deeper depths. F2 explains the total variance of 20.51 % and associated with high loadings of Na^+ and HCO_3^-. The positive loading of Na^+ and HCO_3^- indicate the presence of freshwater which in turn indicates the presence of recharge zone in Zone C that is recharged due to rainfall during monsoon period. F3 explains total variance of 9.90% and associated with high loading of NO_3^-. The high positive loading of NO_3^- reflects widespread use of fertilizers for crop cultivation and indicates presence of leachates from agricultural fertilizers with rainfall recharge occurring in monsoon season in Zone C.

Table 3: Results of factor analysis with varimax rotation for Zone C (2013)

Variable	F1	F2	F3
PH	-0.568	0.099	-0.131
EC	0.949	0.245	0.145
TDS	0.949	0.245	0.145
HCO_3^-	0.201	0.892	0.105
Cl^-	0.946	-0.031	-0.038
SO_4^{2-}	0.947	0.041	0.156
NO_3^-	0.058	0.084	0.979
Na^+	0.669	0.612	0.315
K^+	0.458	-0.354	0.038
Ca^{2+}	0.915	-0.249	-0.041
Mg^{2+}	0.818	0.187	-0.175
Cumulative Eigen value	6.342	1.771	1.498
Variability %	51.24	20.51	9.90
Cumulative %	51.24	71.75	81.65

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CONCLUSION

The results indicate that average concentrations of TDS, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, decrease with increasing distance from the sea coast. No significant increasing or decreasing spatial trend is visible in the case of HCO_3^-, which shows higher concentration throughout the region due to presence of calcite minerals. From the factor analysis, it is evident that different hydrogeochemical processes and anthropogenic inputs affect the groundwater quality during post monsoon season, which are as follows: i) saltwater encroachment from sea, ii) localized upconing of saltwater due to pumpage, iii) ion exchange, iv) inherent salinity of rocks / marine sediments v) carbonate and silicate weathering of rocks, and vi) leaching of salts/minerals. Zones of major groundwater recharge exist in the inland area away from the coastal tract, which show presence of freshwater due to groundwater recharge in monsoon season. Overall, it is concluded that the groundwater salinity existing in the coastal area is principally controlled by a combination of factors which modify the concentration of constituent ions in the groundwater.

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