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Geochemical Impact Assessment of Groundwater Quality Along a Coastal District of Andhra Pradesh, India

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ABSTRACT

Coastal groundwater has always been circumspect with severe geochemical impacts which impart qualitative fluctuations from time to time. The Bay of Bengal coast of Srikakulam district in Andhra Pradesh, India has witnessed many geomorphological changes in the recent times and there was a severe concern over the groundwater quality. A geochemical assessment was carried out for two seasons along the coast to investigate the contributing factors for these qualitative deviations. Twenty nine groundwater samples of bore and open wells of pre and post monsoon seasons were analysed for various physico-chemical parameters. The chemical, geological and geophysical interpretations of the data revealed mechanisms controlling the origin of the chemical ions in the groundwater. The flow patterns, geochemical facies and zones, intrusion zones along with the present status were examined during the assessment. The geochemical factors imparting the qualitative changes of the groundwater were quantified.

INTRODUCTION

Groundwater being the most dependent source of drinking water in many parts of the world has been under discussion regarding its qualitative aspects. May be the forms of pollution might change with place and time, but the mere term refers to its status for consumption or to discard. A wide range of ecological and human crises result from inadequate access to, and the inappropriate management of, freshwater resources (Gleick 1998). Rodell et. al. (2009), felt that the improper management of the groundwater would not only lead to shortage of the potable water, decrease in agricultural outputs, but also create socioeconomic stress. The extent and ease of these pollutions depend on the geological nature of the groundwater and it is a well known fact that coastal groundwater do circumspect more readily than the plain and the elevated one. May be the slope in the geology of the land can segregate the pollutants in these regions, or the drainages being directed into the coast leading to this pollution (Wang et al. 1999). The principles of weathering and leaching of the ions which control the chemical mechanisms of the groundwater constitution are being challenged by the environments of the coastal groundwater.

Most of the earlier groundwater studies were used to mere qualitative perspective and subjected to a single parameter reports. But now-a-days coastal groundwater studies have a range from pollution levels, usage, groundwater levels, intrusion zones, etc., which signify the cause to protect this precious natural resource. Llamas & Martinez (2005) even felt that, intensive groundwater slowly generates social conflict and lead to water wars between communities and countries. Even the use of GPS enabled software and satellite images were being part of the modern technology in reporting the coastal groundwater studies (Anbazhagan & Nair 2004, Stieglitz 2010). These new trends clearly show the socio-economical impacts besides knowing the mechanisms controlling the groundwater in any given region. It would be wise enough to monitor the aspects of groundwater on periodical basis to foresee any impinging dangers with time and space. This even more suits for the coastal groundwater than that of the plains, as these are more vulnerable to all kinds of influences.

Based on the above observations, a study was conducted along the coast of Srikakulam district of Andhra Pradesh, India to identify the geochemical impacts on the groundwater. Other studies in India include the coastal parts like Odisha's Rajnagar by Das et al. (2016), potability of groundwater by Prasanth et al. (2012), GIS based assessment by Selvam et al. (2013), along Cochin port by Laluraj et al. (2005), etc. Earlier studies in the area included the report of geophysical studies like influencing factors by Rao et al. (1996), usage of thermic maps for groundwater quality (Murthy 2003), GIS study by Kumar et al. (20101) and groundwater for irrigation by Reddy & Reddy (2011). It was observed that the earlier studies have been reported mainly based on the geophysical assessments, single parameter based and had not covered the whole district. The limitations in the sample collection included, the source should be the nearest one to the coast at any given area, the source should be a potable one and might be an open or bore well. In places where a cluster of wells were present, the sample with the average of the EC and pH was considered as the sample. For the better understanding of the seasonal effects, pre monsoon (April, 2015) and post monsoon (November, 2015) were analysed.

STUDY AREA

Srikakulam, the northernmost district in Andhra Pradesh, was a part of Visakhapatnam district till it was bifurcated in 1950. It is the extreme northeastern district of Andhra Pradesh situated within the geographic co-ordinates of 18°-20' and 19°-10' of northern latitude and 83°-50' and 84°-50' of eastern longitude. A portion of Srikakulam district is a plain terrain with intense agriculture and another portion of the district is rocky and hilly terrain covered with forests. The district is skirted to a distance by Kandivalasagedda, Vamsadhara and Bahuda at certain stretches of their courses, while a line of heights of the great Eastern Ghats run from northeast. Vizianagaram district flanks in the south and west while Orissa bounds it on the north and Bay of Bengal on the east .The total area of the district is 5837 sq. km. It has a population around thirty thousand according to the 2001 census. Some extent of Mahendragiri hills also covers Srikakulam district. It enjoys a semi-humid to semiarid climate with an average temperature of 17°C in winter to 39°C in summer. It comes under the southwest monsoon (June-September) with an average rainfall of 900 mm. The map showing the sampling stations is depicted in Fig. 1.

MATERIALS AND METHODS

Srikakulam district has the longest coast in the Andhra Pradesh State and extends over 193 km. It took considerable time in fixing the sampling stations with due representation of the entire area under study and 29 stations were finalized. The interactions with the Groundwater Board gave a clear idea of the stations they monitor and the ground level realities in collecting the samples along the coast. The initial marking of the coordinates from the district top sheets for the coordinates varied from the onsite marking using the GPS. Triple distilled water was used in the preparation of the solutions made from the AR and GR grade reagents during the analysis. Surfer 8.0 was used to generate the base map with the limits of the coordinates and later the sampling stations were posted accordingly on the map.

The values of pH and EC were noted along with the date, sample tag with other local surroundings of the sample on the site itself in 2 L plastic bottles. Care was taken in filling up the bottle up to the neck without air bubbles after double rinse with the sample water. All the samples were analysed for the following parameters using standard groundwater methods (APHA 1995). The parameters are total dissolved solids (TDS) and the anionic species include carbonates (CO_3^{2-}), bi-carbonates (HCO_3^-), chlorides (Cl^-), nitrates (NO_3^-), phosphates (PO_4^{3-}) and sulphates (SO_4^{2-}). Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) analysis included the cationic species. The water quality assessment was made in the dilute solutions it best fits the expression in parts per million (ppm) rather than per cent, hence, all the calculations were done with respect to ppm.

RESULTS AND DISCUSSION

The pH of the groundwaters fell in the range of 7.22 to 8.25 in the pre monsoon (PRM), and 7.28 to 8.42 in the post monsoon (POM) in the study area. The electrical conductivity (EC) values of the water samples range from 624 to 2672 in PRM and 562 to 2658 µ Siemens/cm^2 in the POM. The total dissolved solids (TDS) of PRM and POM range from 462 to 1712 and 294 to 2015 ppm respectively. The concentrations of the cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) of the PRM in the area are 24 to 162, 14 to 88, 51 to 556 and 1 to 44 ppm respectively. The same in POM are 24 to 122, 18 to 84, 36 to 332 and 2 to 110 ppm. The anionic (CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and PO_4^{3-}) concentrations of PRM and POM in the groundwater samples range from 0 to 40, 152 to 570, 50 to 588, 8 to 260, 2 to 35 and 0.01 to 1.82 ppm and 0 to 40, 166 to 435, 52 to 520, 10 to 126, 2 to 35 and 0.01 to 2.04 ppm respectively. The chemical analysis of all the parameters of the two seasons has been statistically summarized in Table 1.

Dominance of higher pH values indicates that the groundwater has alkaline nature in the study area. The higher mean in the post monsoon indicate the dilution of the groundwater even more than in the pre monsoon, and the possible reason would be the mixing of the fresh rainwater and also due to the alkalies. The TDS and EC values are interrelated and are evident of having higher values in the post monsoon than that of the pre monsoon. This usually is due to the dissolved alkali and alkaline earths with respect to their bicarbonate and chlorides in these waters. Other small amounts of dissolved organic matter do reflect the EC and TDS values as well. With respect to pH, calcium, carbonate, bicarbonate and sulphate, the mean in the post monsoon is less when compared to the pre monsoon. This can be attributed to several local geological fluctuations during the seasonal change added to the local environments of the groundwater. No major concentrations of nitrate and phosphate were observed.

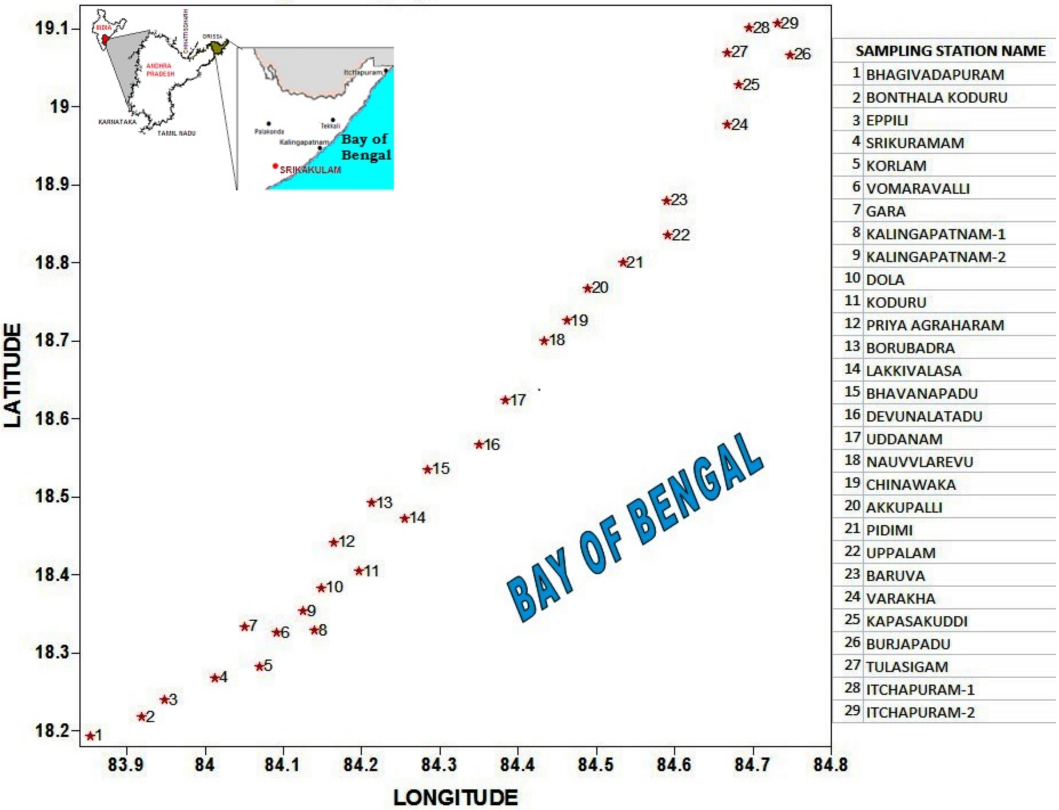

Fig. 1: Map of the study area.

Geochemical assessment for groundwater evolution: The Piper's trilinear diagram was used to assess the geochemical evolution and the possible sources for the dissolved salts in the groundwater of the present study area (Piper 1994). It was obtained by the combination of the percentages of the total of cations and anions and the zones represent their natural composition (fresh, marine and mixed) type in the study area. The pre and post monsoon geochemical classification of the zones are shown in the Figs. 2a and 2b. The freshwater type (Zone 5) of the pre monsoon with samples 6, 8, 9, 12, 13, 15, 20, 21, 27 and 28 comprised of 34%. Whereas, in post monsoon it was observed as 17% with samples 10, 15, 18, 21 and 23. The mixed water type (Zone 9) in PRE and POM are 1, 4, 10, 11, 14, 16, 18, 19, 23 and 25 with 34% and 2, 4, 13, 19, 25, 27 and 28 with 24% of the total samples, respectively. The marine water type (Zone 7) of PRE and POM included the samples 3, 5, 17, 22, 24 and 26 with 21% and 1, 5, 7, 11, 12, 14, 16, 22, 26 and 29 with 34% share.

These zones were represented in the Piper diagrams in Figs. 2a and 2b. It is evident from the predominant presence of the mix water type followed by the marine water type, that the carbonate and non-carbonate alkali dominate in these areas. The freshwater environment can be attributed to the carbonate hardness resulted from the dominance of the alkaline earths (Ca^{2+} and Mg^{2+}) and that of the weak acids (CO_3^{2-} and HCO_3^{-}) indicating the interaction of soil on the groundwater. In case of mixed water, it was evident that the cations and anions, that are not excessive of 50% in their total concentration, with due dominance of various geochemical interactions and local variations in the geology. Whereas, dominance of the marine type water can be attributed to the non-carbonate alkali originated from the abundance of alkalis (Na^{+} and K^{+}) and strong acids (Cl and SO_4^{2-}) interaction, coupled with the topographic low lying effects along the coastal environment of the study area.

It was observed that there are many stations where the groundwater showed anomalies with respect to the above criteria. As of the TDS value greater than 1000 ppm should fall under the marine water type, but deviations were seen in this regard and also with the criteria for the lesser value as well. In the pre monsoon season station 2 had the criteria of over 1000 ppm in its TDS value but could be seen falling in the marine zone and the same with stations 6 and 8 in the post monsoon season. In cases where the value is less and the stations falling under the marine zone are station 7 in

Table 1: Statistical summary of the physico-chemical parameters.

Parameter*1	Minimum		Maximum		Mean		Standard Deviation	
	PRM	POM	PRM	POM	PRM	POM	PRM	POM
pH	7.22	7.28	8.25	8.42	7.80	7.77	0.30	0.34
E.C.	624	562	2672	2658	1245.07	1381.86	502.71	468.01
TDS	462	294	1712	2015	860.21	967.24	359.10	370.96
Ca^{2+}	24	24	162	122	65.62	60.69	35.43	21.74
Mg^{2+}	14	18	88	84	38.86	43.48	18.13	16.51
Na^{+}	51	36	556	332	160.21	176.45	111.07	81.07
K^{+}	1	2	44	110	13.17	21.90	12.75	25.77
$C0_3^{2-}$	0	0	40	40	5.52	4.83	11.83	10.22
$HC0_3^-$	152	166	570	435	284.52	270.93	105.59	70.18
Cl^-	50	52	588	520	178.10	207.66	134.93	120.61
SO_4^{2-}	8	10	260	126	50.10	41.83	46.98	26.64
NO_3^-	2	2	35	35	11.38	12.31	7.87	8.28
PO_4^{2-}	0.01	0.01	1.82	2.04	0.46	0.44	0.49	0.53

*All parameters are expressed in mg/L, except pH and E.C.; TDS = Total Dissolved Solids, E.C. = Electrical Conductivity (μSiemens/cm^2)
1 = All values are rounded to nearest number.

Table 2 : Hydro-geochemical facies classification of water samples.

Hydro-geochemical facies	Distribution of groundwater samples	
	Pre Monsoon	Post Monsoon
$Na^+ > Ca^{2+} > Mg^{2+} : HCO_3^- > Cl^- > SO_4^{2-}$	3, 4, 6, 7, 10, 11, 12, 13, 14, 16, 19, 20, 22, 24 and 27	2, 6, 9, 10, 13, 16, 17, 22, 24, 25 and 26
$Na^+ > Mg^{2+} > Ca^{2+} : HCO_3^- > Cl^- > SO_4^{2-}$: $Cl^- > HCO_3^- > SO_4^{2-}$	1, 8, 9, 15, 18, 28 and 2917	3, 11, 15, 18, 19 and 287

PRM and stations 3, 9, 17, 20 and 24 in the POM. The possible reasons for this would be the under saturation environment towards the new environment, and thus in due course of time shifting to the old compositions generally yield these type of characteristics besides the over exploitation.

Hydro-geochemical facies with groundwater flow pattern: Zhang et al. (2012), reported that hydro-geochemical facies grows up into a conception being pregnant with the meaning in recent years according to the extended meaning in lithofacies and geochemical facies. They further said that, these are important in knowing the circulation pattern under which the groundwater is being accumulated underground. The hydro-geochemical facies with the flow pattern of the groundwater system was correlated by Ophori & Toth (1989). According to them, low TDS, Mg^{2+} : Ca^{2+} ratio and SO_4^{2-} and high HCO_3^- occur in the recharge areas. Whereas, the opposite conditions, such as high TDS, Mg^{2+}: Ca^{2+} ratio and SO_4^{2-} and low HCO_3^-, are associated with the discharge areas. They further stated that the groundwater's of Ca^{2+}-Mg^{2+}-HCO_3^- and Na^+-HCO_3^- types are dominant in the recharge areas, while Ca^{2+}-Mg^{2+}-SO_4^{2-}-HCO_3^- and Na^+-HCO_3^- types occur in the discharge areas.

According to the correlation of hydro-geochemical facies with the flow pattern of groundwater system, the low TDS (<1000 mg/L), low Mg^{2+} : Ca^{2+} ratio and SO_4^{2-} (<100 mg/L), and high HCO_3^- : Cl^- ratio (in stations PRM: 4, 6, 7, 10, 11, 12, 13, 14, 16, 19, 20, 21, 23, 25 and 27 with 52%; POM: 2, 4, 9, 13, 17, 21, 23, 24 and 25 with 31%) type hydro-geochemical facies observed in the parameters suggest that these areas lie in the predominated recharge zones. Nevertheless, in cases of high Mg^{2+} : Ca^{2+} ratio (PRM: 1, 8, 9, 15, 16, 17, 18, 28 and 29 with 31%; POM: 3, 7, 11, 15, 18, 19 and 24 stations with 24%, where it is >1.1) with the opposite to the above criteria indicate the association of these areas with discharge source. These fluctuations in some stations from the pre to post monsoon and the absence of other stations in neither of the classification indicate the mixed nature of the groundwater and can be caused by either the low concentrations of Ca^{2+} due to ion exchange between Ca^{2+} and Na^+ or by the preferential removal of Ca^{2+} by precipitation as carbonates (kankar and/or calcrete). This can also be confirmed by low mean values of the $Na^+ + K^+$ and $Ca^{2+} + Mg^{2+}$ with total cations and a slightly higher mean that of the Na^+ with Cl^-. Sami (1992) reported that, at high salinities this process reverses and sodium is adsorbed, re-

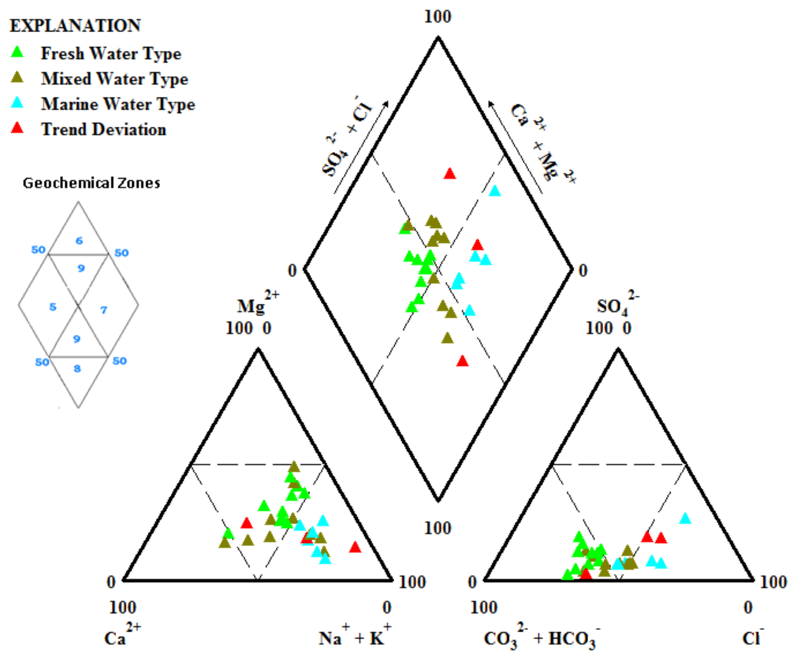

Fig. 2a: Geochemical classification of groundwater-pre monsoon.

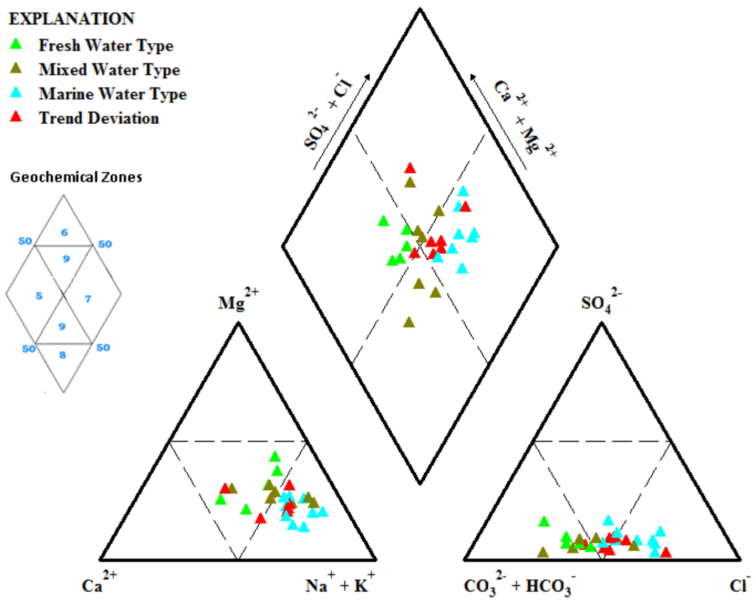

Fig. 2b: Geochemical classification of groundwater-post monsoon.

leasing calcium and magnesium.

Hydro-geochemical facies: The concept of hydro-geochemical facies was introduced by Back (1960) to explain the distribution and genesis of principal groups or types of groundwater in a selected area. According to him, these facies indicate the major type of chemical processes in a lithologcial framework and a pattern of water flow in it. The hydro-geochemical facies are (a) $Na^+ > Ca^{2+} > Mg^{2+}$: $HCO_3^- > Cl^- > SO_4^{2-}$ and (b) $Na^+ > Mg^{2+} > Ca^{2+}$: $HCO_3^- > Cl^- > SO_4^{2-}$ and $Cl^- > HCO_3^- > SO_4^{2-}$ according to the classification. In the pre monsoon 76% of the total samples (1, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 19, 20, 22, 24, 27, 28 and 29) and 59% of the post monsoon samples (2, 3, 6, 9, 10, 11, 13, 15, 16, 17, 18, 19, 22, 24, 25, 26 and 28) belong to the Na^+ : HCO_3^- type, indicating the presence of similar sources of the origin and hence they are responsible for the similar environmental hydro-geological conditions. The occurrence of Na^+ : Cl^- type in the PRM constituted 4% (sample 17) and 4% (sample 7) can be attributed to their local variations of the geological conditions like clay horizons, low lying areas and backwater zones. The other samples which do not belong to the above classes can be considered as the mixed group of the above combinations. The various hydro-geochemical facies of the study area are shown in the Table 2.

Mechanisms controlling groundwater chemistry: It is a well established fact that geochemical ratios of the parameters do define their relation in the existence in the groundwater, and thus give valuable insight in knowing the origin. Sarin et al. (1989) reported that the source for the ions in the groundwater can be predicted using the HCO^-_3 : Cl^- ratio along with Ca^{2+} + Mg^{2+} : TC (total cations) and Na^+ + K^+ : TC ratios. They further stated that the cationic and anionic ratios of sodium and chloride also have to be included with the above in cases where their percentage of contribution in the total numbers is as significant as others. The mean HCO_3^- : Cl^- ratio in PRM and POM is more than unity with values of 2.14 and 1.76 respectively. The alkaline earths, Ca^{2+} + Mg^{2+} : TC (total cations) and alkalies, Na^+ + K^+ : TC ratios mean values are less than unity, which are 0.41 and 0.59 in PRM and in POM they are 0.37 and 0.63. The mean of Na^+ : Cl^- in the same order are 1.01 and 1.07, respectively. The means of these hydro-geochemical ratios are given in Table 3.

These values indicate the conditions in the study area, that the principal source for the chemical ions would be the rock weathering (Tardy 1971). As the sampling sources have coastal origin, it is obvious that the sodium and chloride ratio would contribute significant information for the assessment of the source of ions in the groundwater. In general, the ratios of alkaline earths and alkalies with their total numbers, their values should be more than unity in order to support the above prediction. But, the mean of sodium and chloride ratios of 0.94 and 0.91 in the two seasons are less than unity in the study area. Even though there are cases which validate the criteria, the overall scenario looks quite opposite, supporting the view that rock weathering is not the only source, but also other factors play their part in the genesis of the chemical ions in the groundwater, in the study area.

CONCLUSION

The geochemical assessment revealed various characteristics of the groundwater along the coast with possible sources and trends in the study area. The seasonal variations among various parameters had shown that these groundwaters are very fragile in keeping their identity. It was evident from the results that the post monsoon season samples does deviate more from the standards that those in the pre monsoon. As the study area being a topographically low lying area, it can be attributed to the mixing of the groundwater during the recharge period had certainly made the impact in losing the former's characteristics. The dominance of the hydro-geochemical of low TDS and Mg^{2+} : Ca^{2+} ratio in both seasons indicate that these are predominantly recharge areas, but the percentage was dropped in the post monsoon season. It can be understood that the soil chemistry of the local environment along the coast is the contributing factor for the presence of the alkaline earths (Ca^{2+} and Mg^{2+}) and that of the weak acids (HCO_3^-). The presence of the clay horizons and topographic lows is the reason for the mixed and marine stations where non-carbonate alkali is due to abundance of alkalies (Na^+, K^+) and strong acids (Cl^- and SO_4^{2-}).

Table 3: Means of hydro-geochemical ratios.

Hydro-geochemical ratio	Pre Monsoon	Post Monsoon
Mg^{2+} : Ca^{2+}	0.77	0.79
HCO_3^- : Cl^-	2.14	1.76
Ca^{2+} + Mg^{2+} : Total cations	0.41	0.37
Na^+ + K^+ : Total cations	0.59	0.63
Na^+ : Cl^-	1.01	1.07

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