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Hydrochemical Signatures for Identification of Fresh and Saline Water Resources, along Visakhapatnam-Bhimunipatnam Corridor

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ABSTRACT
Phenomenal increase in the demand for potable water to meet the basic needs of the ever increasing population has led to significant increase in the exploitation of groundwater, especially in many segments of our country where surface water availability is meager. One such segment includes the urban conglomeration in and around Visakhapatnam. To ensure that many localities along and across Visakhapatnam-Bhimunipatnam corridor get potable water free from saline water pollution it has been decided to first identify the patches of fresh and saline water sources and then categorize them quality wise. As a part of this important societal problem, a hydrogeochemical study has been carried out in Visakhapatnam and Bhimunipatnam district situated along the East coast of India to primarily identify the influence of saline water on fresh water aquifers and then categorize quality wise the suitability of groundwater for drinking and domestic purposes. Limited investigations in this coastal region have reported signs of seawater intrusion, pollution due to industrial effluents and natural weathering process. A total of 63 groundwater samples have been collected and analyzed for major anions and cations for post and pre-monsoon seasons of 2015. The geochemical parameters have been compared with World and Indian quality standards. The study has revealed that most of the samples are suitable for drinking purpose. Gibb's plot revealed that the mechanisms responsible for controlling the chemical composition of the groundwater include both the rock water interaction and evaporation. The correlation of laboratory analysis of different proportions (%) of seawater to freshwater and to the field electrical conductivity indicates that 84% of samples are of type I category (low salts) and are safe for drinking. Out of the remaining, 13% of samples belong to type II (medium salts) and 3% to Type III (high salts) categories, respectively. The ionic ratios show that 8% of the samples indicate the transformation of the fresh groundwater aquifer system to saline.

Key words*:* Groundwater, Visakhapatnam-Bhimunipatnam, hydro-geochemical study, anions and cations, weathering, seawater intrusion, electrical conductivity.

INTRODUCTION

Distribution of fresh water resources is uneven throughout the World and the fresh water availability is becoming scarce day by day owing to population growth and diverse human activities. In the absence of fresh surface water resources, groundwater is exploited to meet the demand exerted by the various sectors. Variation in the water quality of groundwater in response to local geological set-up and anthropogenic factors warrants the evaluation of the quality of the groundwater for any purposes including that for human consumption. Many researchers across the globe (Babiker and Mohamedm, 2007; Vennila et al., 2008; Shomar et al., 2010 and Magesh et al., 2013) have carried out studies with spatial technologies and interpreted the quality of groundwater.

Groundwater of an aquifer in any given area has a unique chemistry acquired as a result of chemical alteration of meteoric water recharging the system (Back, 1966; and Drever, 1982). Water is the prime natural resource for Man`s survival and overall development of the country. Water is flowing in two forms, namely, surface water and groundwater. Rapid urbanization, especially in developing countries like India, has affected the availability and quality of groundwater due to its overexploitation, improper waste disposal, irrigation return water and lack of recharge. The quality of groundwater is the function of its physical and chemical parameters, which depend on the soluble products of weathering, decomposition and the related changes that occur with respect to time and space (Bhargava and Killender 1988; Prasad et al., 1984, Srinivasamoorthy 2011). Water pollution not only affects water quality but also threatens human health, economic development and social prosperity (Milovanovic 2007). The dependence on groundwater has increased tremendously in recent years in many parts of India. Hence, physico-chemical analysis of water is important to assess the quality of groundwater that influences the suitability of water for domestic, irrigation, and industrial needs (Prasanna et al., 2011; Chidambaram et al., 2011; Singaraja et al., 2013b; Ackah et al., 2011; Sayyed and Wagh,2011; Tripathi, 2011). Generally, groundwater quality depends on the quality of recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes (Twarakavi and Kaluarachchi 2006, Singaraja et al., 2013b).The present study pertains to the evaluation of the physico-

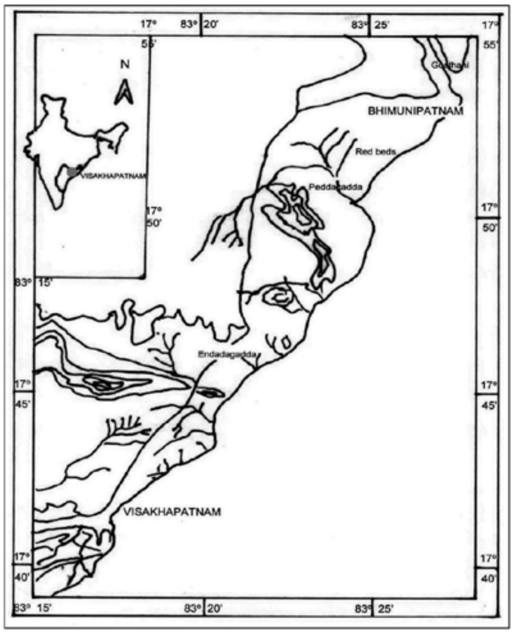

Figure 1. Map of the Study Area

chemical characteristics of the groundwater, since people are mainly dependent on the groundwater for their needs. The manuscript covers the suitability of the groundwater for drinking purposes, along and across Visakhapatnam-Bhimunipatnam corridor.

STUDY AREA

The study area, Visakhapatnam and Bhimunipatnam stretch is a 27km coastal strip situated along the East coast of India. It lies between North latitudes 17°30′- 18°0′ and East longitudes 83°15′-83°30′.(Figure 1). The area under study is situated on either side of the beach road and it is characterized by Eastern Ghat mobile belt. This area is covered with denudational hills of height range between 30 to 540m above mean sea level. In the Visakhapatnam-Bhimunipatnam area, agriculture is the most important economic activity. Since agriculture depends on chemical fertilizers and pesticides that can degrade the quality of shallow aquifers through seepage of chemicals and also as the shallow aquifers in the coastal corridor under study can be affected by saline water intrusion, to ensure good quality of groundwater in the coming decades through large scale preventive measures it has been decided to take up hydro-geochemical investigations to obtain area specific groundwater chemistry. Such information, cross checked through seasonal monitoring, would help in proper planning of quality enhancement projects.

The prominent geological formations include Khondalites, Granite gneiss and Charnockites and Coastal alluvium of recent age. The major rock types exposed between Visakhapatnam and Bhimunipatnam along the coast mainly belong to the Khondalitic group. Leptynites are found to exist in abundance. Minor quantities of Charnockites and Pegmatites occur at places. The red sediments (Rao, 1978) are found to occur as predominant land masses along the Visakhapatnam and Bhimilipatnam coast. These red sediments overlie Khondalites and Leptynites. The plain areas in the region are normally found to occur between two successive hill ranges. The plain areas mostly occupied by red sediments of varying thickness. It is further observed that one or more streams are found to flow through these plains to join the sea.

Pedda gedda, the largest stream along the coast exhibits dendritic pattern of drainage. These streams normally discharge excess rainwater from the inland areas and adjoining hills into the sea. Most of the streams discharge quickly because of the steep slope of the hills in the area.

MATERIALS AND METHODS

Groundwater samples have been collected in polyethylene bottles at 63 groundwater sampling sites during pre-monsoon and post-monsoon seasons (Figure 1) from open and bore wells. Physico-chemical parameters, such as Electrical Conductivity (EC) and pH have been measured in the field immediately after the collection of the samples using portable field meters. TDS has been calculated from EC by an empirical formula TDS=0.64*EC. Chloride, hardness, calcium, magnesium, carbonate and bicarbonate have been determined by titration. Flame photometer has been used to calculate the sodium and potassium. Sulphate has been determined by spectrometer. Analytical precision has been maintained throughout the experiments.

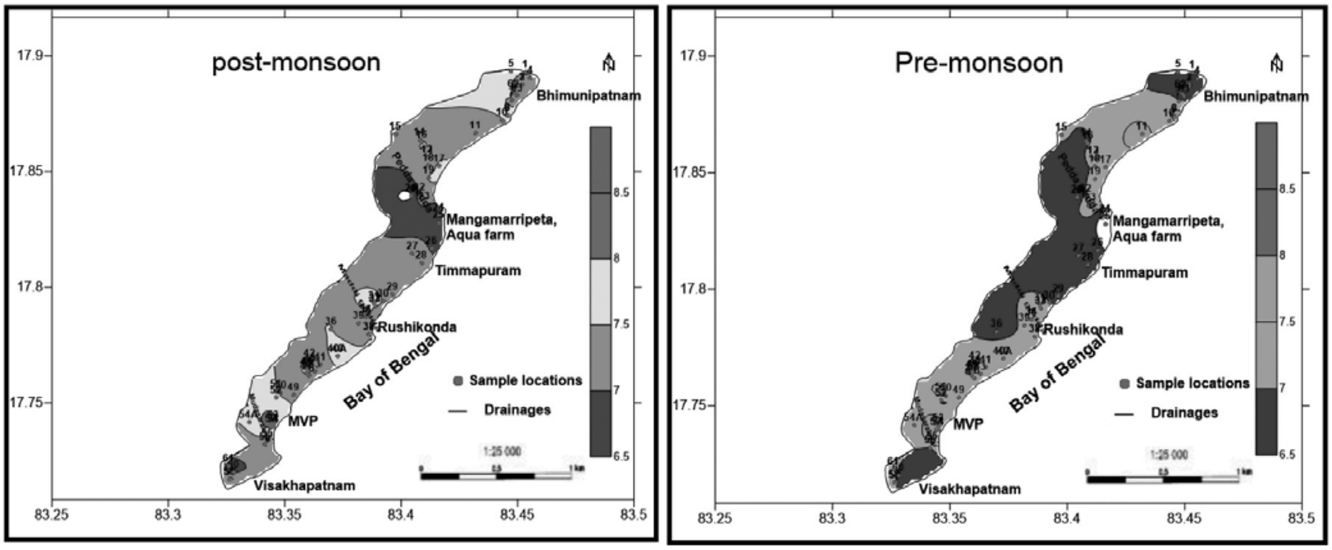

Figure 2. Distribution of pH in groundwater (Post and Pre monsoon).

Standard methods have been adopted for the analysis of the water samples (APHA 1995). The study area map has been prepared from the soft copy of the topographic map published by the Survey of India produced on a scale 1:25000.

RESULTS AND DISCUSSION

Potential Hydrogen (pH):

The pH of water is an important indicator for its quality and provides important information on geochemical equilibrium or solubility calculation (Hem 1985). The acceptable limit value for drinking water is specified as 6.5-8.5(WHO 2011; ISI 2012). The Distribution of lesser value of pH indicates presence of CO_2 in water. The pH value of most of the groundwater samples in the study area for both post and pre-monsoon periods varies from 6.1-8.1(Figure 2), which shows that the groundwater in the study area is slightly acidic and moderately alkaline in nature.

Electrical Conductivity

Electrical Conductance is a measure of the ability of water to conduct an electrical current-specific conductance. It is directly proportional to the saltiness (Salinity) or dissolved salt contents in water. The electrical conductivity of water is a measure of the conductance of cubic centimeter of water at 25 °C in micro-Siemens. The most desirable limit of EC in drinking water is 1,500μs/cm (WHO 2011). Electrical Conductivity has been used as a criterion for the classification of drinking and irrigation waters (Erguvanli and Yuzer, 1987). The EC of groundwater in the study area is varying from 275-6300μs/cm and 3970 μs/cm during post and pre-monsoon periods, respectively (Figure 3). Higher EC in 3% of the study area indicates the enrichment of salts in the groundwater. Such higher concentration depends upon temperature, concentration and types of ions present (Hem 1985).

The EC can be classified as type I, if the enrichments of salts are low (EC<1500μs/cm); type II, if the enrichments of salts are medium (EC 1500 and 3000μs/cm) and type III, if the enrichments of salts are high (EC>3000μs/cm). According to the above classification of EC, 84% of the total groundwater samples come under the type I (low enrichment of salts); 13% under type II (medium enrichment of salts) and 3% under type III (high enrichments of salts).While major parts of the study area come under good quality groundwater zones, the effect of saline water intrusion may be the reason for medium enrichment of EC in 13% of the study area and high percentage of salts in 3% of the study area. The conductivity of the groundwater sources varied in the total study area from 275-6300μs/cm (post-monsoon) and 323-3970μs/cm (pre-monsoon).

This shows that during the post-monsoon period, despite the groundwater dilution by precipitation, the EC increased significantly to 6300μs/cm in 3% of the study area. Large variation in EC is mainly attributed to geochemical process like ion exchange, reverse exchange, evaporation, silicate weathering, rock water interaction, sulphate reductions and oxidation processes (Ramesh 2008). In the study area the enrichment of salt in groundwater, in 16% of the area, may be due to evaporation and anthropogenic activities. In general if proper precautionary measures are not taken at the earliest there is a possibility of increased salinity around such zones that are already polluted by saline water intrusion. The effect of pH may also increase the dissolution process, which eventually increases the EC value.

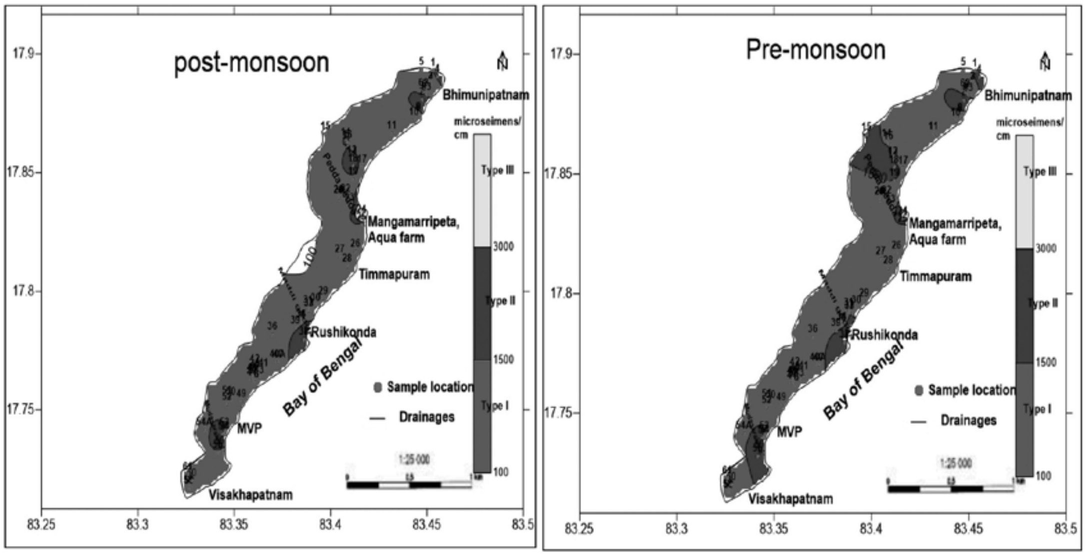

Figure 3. Distribution of EC in groundwater (Post and Pre- monsoon).

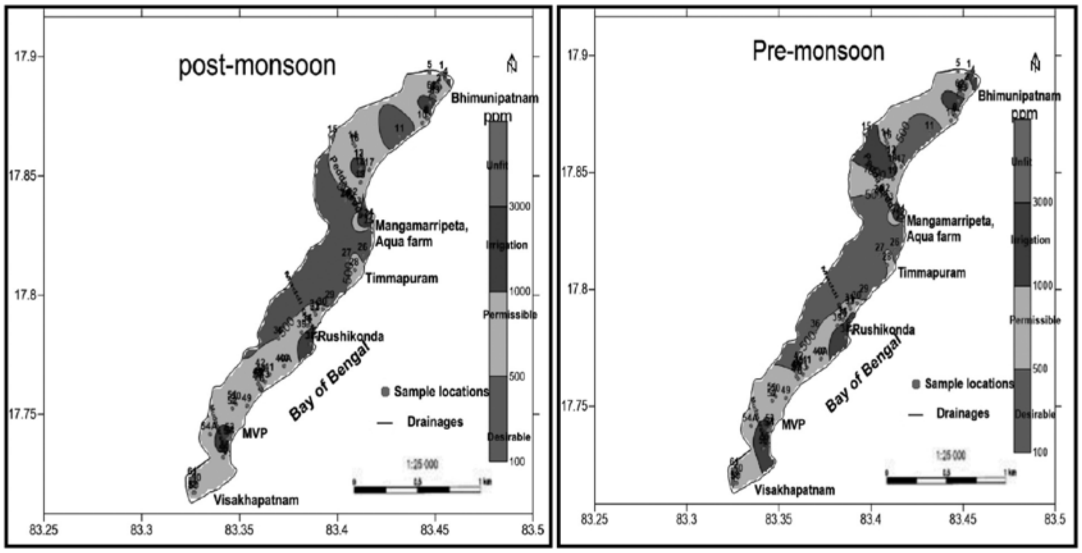

Figure. 4. Distribution of TDS in Ground Water (Post and Pre Monsoon).

Total Dissolved Solids

The principal ions contributing to TDS are bicarbonate, carbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium (US EPA 1983). According to (WHO, 2011) specification, TDS upto 500 mg/l is the highest desirable and upto 1000 mg/l is the maximum permissible. In the study area the TDS value varies between a minimum of 122mg/l and a maximum of 4089 mg/l (Fig 4) indicating most of the ground water samples lie within the maximum permissible limit. According to the Davis and De Wiest (1966) (Table 1) classification of groundwater based on TDS, 24% of the total groundwater samples are desirable for drinking (TDS<500mg/l), 58% permissible for drinking (500-1000 mg/l) and 19% is suitable for irrigation purposes. High concentration of TDS in groundwater is due to leaching of salts from the soil and also domestic sewage may penetrate into the groundwater, which may lead to increase in TDS values. The spatial distribution of TDS in groundwater (pre and post monsoon) shows that major part of the study area comes under a mixed category of desirable cum permissible for drinking and good for irrigation. So, in reality even though major part of the study area comes under good quality groundwater zone, as per pH and EC values the higher TDS shows considerable impact due to anthropogenic activity. As such, even in the 84 % good quality zone it is better to distill TDS content to avoid probable ill effects due to direct drinking of groundwater.

Table 1. Classification of Groundwater samples of the study area

TDS (mg/l)	Class	Number of Samples		In Percentage	
		Post-Monsoon	Pre-Monsoon	Post-Monsoon	Pre-Monsoon
up to 500 mg/l	Desirable for drinking	15	15	24	24
500-1000 mg/l	Permissible for drinking	37	35	58	55
Up to 3000 mg/l	Useful for irrigation	10	12	16	19
Above 3000 mg/l	Unfit for drinking and irrigation	1	1	1.58	1.58

Calcium and Magnesium (Ca and Mg)

Calcium and magnesium are the most abundant elements in both surface and groundwaters.They exist mainly as bicarbonate and to a lesser degree in the form of sulphate and chloride. Calcium concentrations are varying from 141 to 2.1 mg/l. The higher concentration of calcium observed is 141 mg/l, from the groundwater samples collected from 3% of the study area. The desirable limit of calcium concentration for drinking water is specified as 75mg/l (ISI 2012).On an average in the good quality zone the percentage of calcium concentration hovers around 50 to 60 mg/l. This shows that all the groundwater samples in major part of the study area are within the permissible limit. Magnesium usually occurs in lesser concentrations in groundwater than calcium (Nilufer Arshad, 2009). Magnesium content is varying from 2.15 to 354 mg/l. The maximum permissible limit of magnesium concentration of drinking water is specified as 100mg/l (ISI 2012) and 150 mg/l (WHO 2011).Out of total 63 samples, Sample numbers 7, 15, 24, 37,38, 56, 57 exceeds the ISI limit as they show values of 110, 106, 124, 112, 223,354 mg/l. This shows that only about 10 % of samples are beyond permissible level.

The seawater has high Mg concentration than Ca. The ionic ratios Mg/Ca, HCO_3/Cl were plotted against the samples to evaluate the groundwater chemistry of the wells used in the present study. Fig.5 shows that 8% of the samples are showing extremely low HCO_3/Cl and variably high Mg/Ca during pre- monsoon season indicating the transformation of the fresh groundwater aquifer system to saline.

Sodium and Potassium (Na and K)

Sodium ranks sixth among the elements in order of abundance and is present in most of the natural waters. Sodium is generally found in lower concentration than calcium and magnesium in freshwater. The concentration of sodium is varied from 15 to 538mg/l. The maximum permissible limit of sodium is 200mg/l. Processed samples reveals that a few samples are exceeding the permissible limit of WHO and ISI. Since groundwater with high sodium content is not suitable for agriculture, as it tends to deteriorate the soil, the zones that contain high concentration of sodium be left out for conventional agriculture. If experimental cultivation yields good results these patches of land could be used for growing saline resistant varieties of rice.

Potassium is a naturally occurring element; however its concentration remains quite low compared to calcium, magnesium and sodium. Its concentration in drinking water seldom reaches 20mg/l. The concentration of potassium in both post-monsoon and pre-monsoon seasons is found to vary from 0.82 to 87.2mg/l. The maximum permissible limit of potassium in the drinking water is 30mg/l. Higher concentrations are found only in 4 samples. The low concentration of potassium found in some samples is due to high resistance of potash feldspars to chemical weathering in the study area.

Bicrabonate (HCO_3)

The value of bicarbonate ranges from 57 to 765 mg/l. Bicarbonate is the dominant ion, except in the groundwater, occurs near the coast. The higher concentration of bicarbonate in the water points to the dominance of mineral dissolution (Stumm and Morgan 1996).

The plot of ionic ratio of bicarbonate/ chloride versus TDS is shown in Figure 6, for both post and pre-monsoon seasons. The plot shows that the values of HCO_3/Cl(meq/l) are <1 in the high TDS concentration (>2000) range of the analyzed samples, while its slope is positive in the low TDS concentration range (<2000mg/l). This result indicates that groundwater with high TDS concentrations is enriched with chloride due to sea water intrusion and the groundwater with low TDS concentrations is less affected by seawater. Only few samples of the study area are affected by seawater intrusion.

Sulphate (SO4)

Sulphate is one of the major anions occurring in surface waters. A decline in a Sulphate ion frequently is associated with an increase in bicarbonate ions (Fred Bell, 1998). The upper limit for sulphate concentration for drinking water is 200mg/l (ISI 2012). The sulphate concentration in the study area ranges between 0.9 to 166 mg/l during post

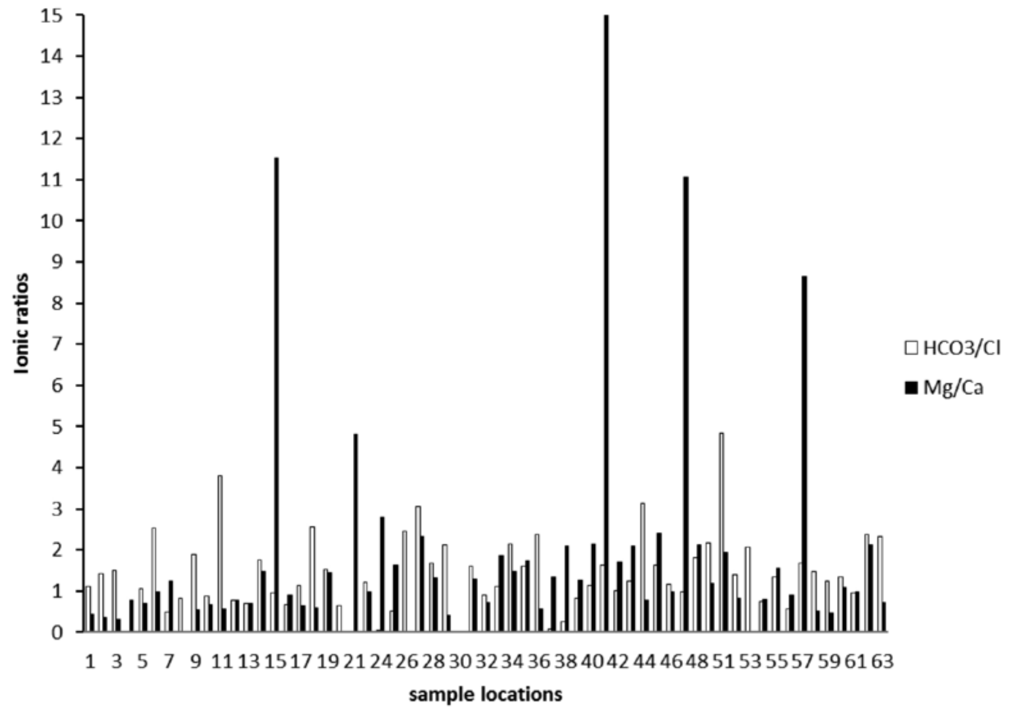

Figure 5. Ionic ratios of HCO_3/Cl and Mg/Ca.

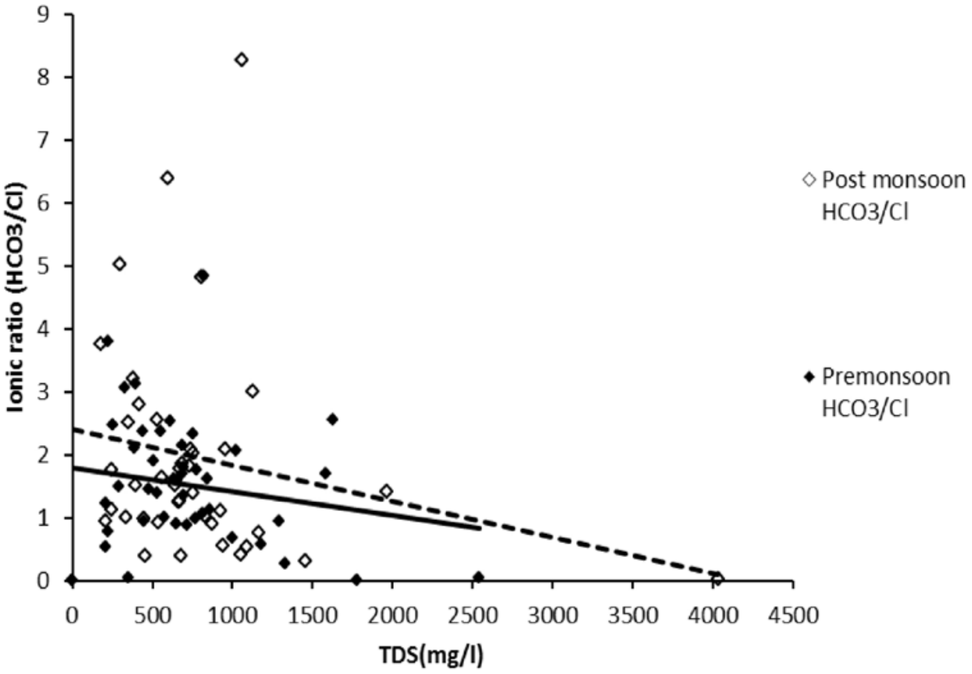

Figure 6. Cross plot of TDS versus HCO_3^-/Cl^- for post and pre monsoon seasons.

and pre-monsoon seasons. All the samples fall within the desirable limits. Higher concentration of Sulphate could cause a cathartic action on human beings and also cause respiratory problems (Maiti, 1982; Subba Rao and Prathap Reddy, 1999; and Subba Rao et al., 2002).

Chloride (Cl)

The origin of chloride in groundwater may be from diverse sources such as weathering, leaching of sedimentary rocks and soils, intrusion of saltwater, domestic and industrial

Table 2. Stuyfzand (1989) classification of groundwater

S.No	Main type	Cl(mg/l)	No. of samples
1	Oligohaline	5-30	1
2	Fresh	30-150	37
3	Fresh-Brackish	150-300	19
4	Brackish	300-1000	6

Table 3. Classification of groundwater

Percentage of seawater mixing			
1%	955	Type I<1500	Low salts
2%	1450		
4%	2910	Type II 1500-3000	Medium salts
6%	4200	Type III >3000	More salts
8%	5510		
10%	6760		
14%	9380		
18%	12000		
20%	12900		
40%	24000		
60%	34400		
100%	56000		

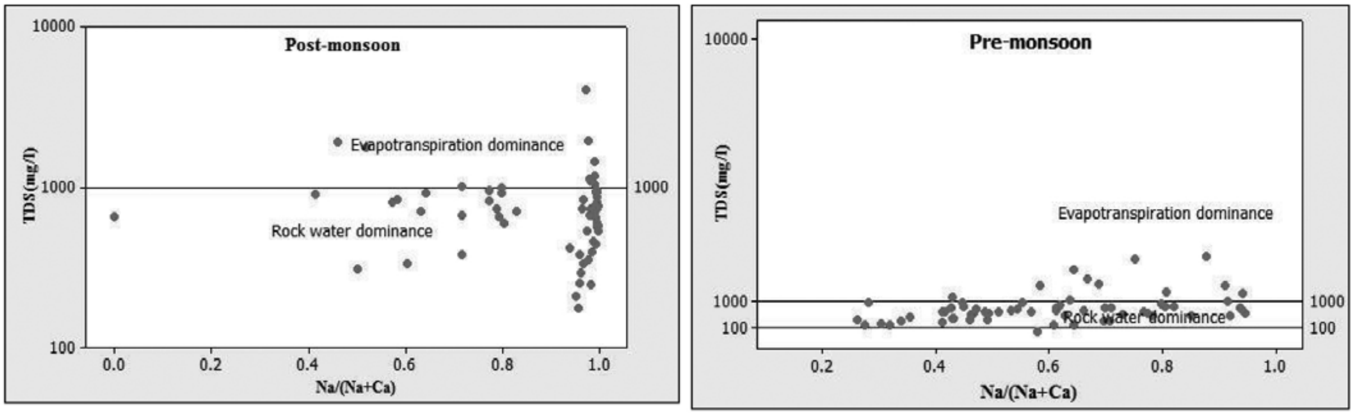

Figure 7. Gibb's diagram for post- monsoon and pre-monsoon seasons.

waste discharges, municipal effluents etc. (Karanth 1987). In the study area, the concentration of chloride is between 21 to 2769 mg/l. relatively high concentration of chloride is observed for the groundwater samples 7, 13, 15, 18, 24, 37, 38, 57. A desirable limit of chloride for drinking water is specified as 250mg/l (ISI 2012). The excess of chloride in the water is usually taken as an index of pollution and considered as tracer for groundwater contamination (Loizidou and Kapetanios 1993). In natural waters, the concentration of Cl bears strong correlation with the sodium content and specific conductance. High levels of Na and Chloride ions in coastal water may indicate a significant effect of seawater mixing (Mondal et al., 2008). According to Stuyfzand (1989) classification (Table 2) 59% of samples are fresh waters, 30% of samples belong to a mixture of fresh and brackish waters and 10% of samples are completely brackish.

Mechanism Controlling the Ground Water Chemistry

Gibb's Diagram

The mechanism controlling chemical relationships of groundwater based on aquifer Lithology and nature of

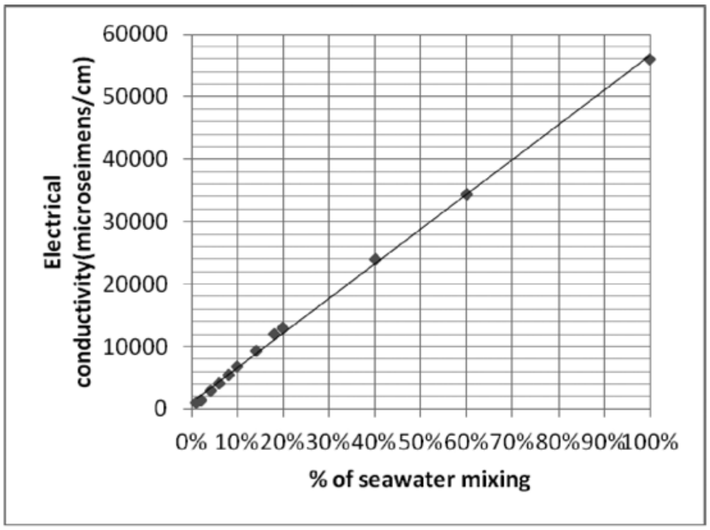

Figure 8. Plot of seawater mixing vs Electrical Conductivity.

geochemical reactions and solubility of interaction rocks has been studied following Gibbs (1970) and Viswanathaiah et al., (1978). The source of the dissolved ions in the groundwater can be understood by a Gibbs diagram (Gibbs, 1970). It is a plot of $(Na^+)/(Na^+ + Ca^{+2})$ vs. TDS. The Gibbs plot of data from the study area (Figure 7) indicates that interaction of rocks with the groundwater is the dominant process controlling the major ion composition of groundwater for both post-monsoon and pre-monsoon seasons. The plot indicates that the groundwater samples of the study area overlap in the rock-water interaction and evaporation dominance categories (Chidambaram et al., 2008; Srinivasamoorthy et al., 2008, Chowdhury and Srimanta Gupta 2011, Manikandan et al., 2011).

Laboratory studies: Mixing of seawater

Laboratory studies have been carried out to classify the groundwater based on Electrical Conductivity by mixing different proportions (%) of seawater to freshwater. The Figure 8 shows how concentration of EC is increasing for varying percentage of seawater mixing. Based on these laboratory results (Table 3) the samples of the study area are categorized as: 84 % of samples belong to type I and 13% to type II and 3% to type III.

CONCLUSIONS

The groundwater in the study area is slightly acidic and moderately alkaline in nature.

Based on EC and TDS, 84% of the total groundwater samples of the study area are desirable for drinking and good for irrigation.

Based on the hydrogeochemical parameters and their ionic ratios the seawater intrusion is noticed in few locations.

8% of the samples are showing extremely low HCO3/Cl and variably high Mg/Ca during pre-monsoon season indicating the transformation of the fresh groundwater aquifer system into saline.

The plot of bicarbonate/ chloride versus TDS for both post and pre-monsoon seasons shows the values of HCO3/Cl- were <1in the high TDS concentration (>2000) range of the analysed samples, while its slope was steeply negative in the low TDS concentration range (<2000mg/l), indicating that groundwater with high TDS concentrations was enriched with chloride due to seawater intrusion and the groundwater with low TDS concentrations is less affected by seawater.

Gibb's plot reveals that the mechanisms responsible for controlling the chemical composition of the groundwater are both rock water interaction and evaporation.

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Compliance with Ethical Standards

The author declares that she has no conflict of interest and adheres to copyright norms.

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