



HYDROGEOCHEMICAL ASPECTS IN COASTAL AQUIFERS - A CASE STUDY FROM CUDDALORE DISTRICT, SOUTH INDIA

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ABSTRACT

This paper examines the hydrogeochemical processes due to the over exploitation of groundwater, which results in decline of water levels, leading to intrusion of salt water along the coastal region of the Cuddalore District, Tamilnadu, South India. Major cations and anions (pH, EC, TDS, Ca^+ , Mg^+ , Na^+ , K^+ , Cl^- , HCO_3^- , H_4SiO_4 , F^- , SO_4^- and NO_3^-) were analyzed for 54 groundwater samples collected in two seasons, post monsoon and pre monsoon of 2007. The groundwater chemistry commonly found to be mixed with sea water composition. Interpretation of analyzed data showed that cations were mainly contributed by natural weathering process and NO_3^- , F^- and PO_4 were contributed from anthropogenic sources. $\text{Na}^+ - \text{Cl}^-$, $\text{Ca}^+ - \text{Cl}^-$ and $\text{Mg}^+ - \text{Cl}^-$ were the dominant water facies in the study area. Water quality shows that increase of ionic strength from recharge to discharge area with few anomalous values in the central part of the Cuddalore region.

Keywords: Hydrogeochemistry, Weathering, Salt water intrusion, Coastal aquifers, south India.

1. INTRODUCTION

The hydrogeochemical process reveals the zone and quality of water that are suitable for drinking, agriculture and industrial purposes. Hydrogeochemical studies are to understand the changes in water quality due to rock – water interaction as well as anthropogenic influences. Many of the ground waters in the coastal aquifer are suffering from seawater intrusion both by the natural processes and anthropogenic activities like over – extraction, urbanization and agricultural activities (Ozler, 2003). Hydrogeochemical study is useful tool to identify the processes that are responsible for groundwater chemistry (Elango L, et al 2003). The chemical composition of groundwater, which

moves from the recharge area to the discharge area, reflects changes by various geochemical processes. Saline water is the most common type of pollution in fresh ground water displaces or mixes with fresh water in an aquifer (Todd, 1980). Hydrogeochemical data helps in estimating the extended of mixing, the circulating pathways and residence time of groundwater (Edmunds, 1995). The type and concentration of salts in groundwater depend on the geological environment and movement of groundwater (Ragunath, 1987). Salt water intrusion is a major hazard in the coastal aquifers in different parts of India especially Tamilnadu. Cuddalore region covers different litho units and forms of complex

hydrogeochemical environments. The Tertiary sandstone aquifers having groundwater potential in Cuddalore region, the sandstone is separated from the upper alluvial formation by impervious clay layer and hence, the groundwater occurs under confined condition in the sandstones and in phreatic condition in the shallow alluvial aquifers. The location of Neyveli mining region and Veeranam Lake from which groundwater extraction is at its maximum falls in the environment (Anandan 2005). The present study mainly focused on evaluates the chemistry of groundwater in aquifers systems, hydrogeochemical facies and seasonal variation in groundwater quality.

2. STUDY AREA

Area chosen for study is Cuddalore region, which is located in southern part of Cuddalore district in the east coast of India (Figure 1). It lies in

between $79^{\circ} 29'E$ to $79^{\circ} 54'E$ longitude and $11^{\circ} 20'N$ to $11^{\circ} 45'N$ latitudes (Figure 1). Long term average rainfall of the district is 1160.36mm. Groundwater in this area is overexploited for agriculture and industrial purposes are predominant land use in this area, which induces salinity in the coastal aquifers, and coastal stretch of Cuddalore district is about 10km. The geology of the area plays a significant role in the determination of the groundwater potential of the region. The area lies between the various geological formations ranging in age from the oldest Archaean rocks to recent sediments. The most common outcrops in the area are limestone, sandstone and clays. These are covered in places by lateritic, kankar and alluvium. The tertiary formation having good potential groundwater covered by sandstone argillaceous and pebble bearing grits, clays (variegated) with lignite seams and pebble beds.

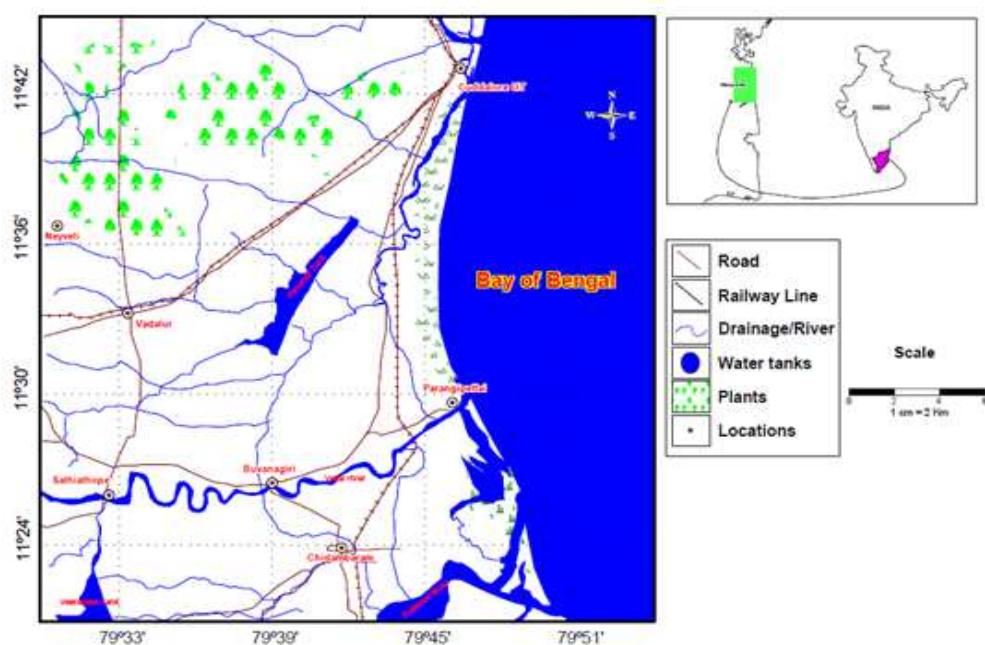


Figure 1: Location map of the study area.

3. METHODOLOGY

A total of 54 groundwater samples were collected during post monsoon (POM) and pre monsoon (PRM) in year 2007 mostly covered by the shallow aquifers in this region. The samples collected after 10 minutes pumping and stored in polyethylene bottles. pH, electrical conductivity (EC) and total dissolved solids (TDS) were

measured by handheld pH, EC and TDS meter in the field. The collected samples were analyzed for major cations, like Ca^+ and Mg^+ by Titrimetry, Na^+ and K^+ by flame photometry (AIMIL); anions, like Cl^- and HCO_3^- by Titrimetry, SO_4^{2-} , PO_4^{3-} , NO_3^- and H_4SiO_4 by Spectrophotometer (JENWAY 6505). The analyses (APHA 1998) were done by adopting standard procedures.

Table 1: Summary of Geochemical Data

Param eters	POM 07		PRM 07	
	Min	Max	Min	Max
pH	6.60	8.10	6.40	7.80
EC	578.90	3104.15	495.99	2833.56
TDS	320.50	2152.00	331.27	1973.05
Ca	26.90	125.36	20.85	101.48
Mg	12.20	66.60	7.47	81.67
Na	22.50	421.25	16.60	504.10
K	15.70	76.00	7.18	57.89
Cl	74.50	856.24	68.36	984.25
HCO₃	81.70	394.20	75.24	331.72
SO₄	1.40	27.36	2.86	41.20

4. RESULT AND DISCUSSION

4.1 Groundwater chemistry

The minimum, maximum and average values in mg l^{-1} are given in Table 1. The total cations (TZ^+) and total anions (TZ^-) balance shows the charge balance error percentage (Edmond JM et al 1995). Calculating the normalized inorganic charge balance which is defined as $\{\sum_{\text{cation}} - \sum_{\text{anion}} / \sum^+ + \sum^-\}$ and represents the fractional difference between the total cations and anions (Freeze RA 1979). As exemplified by Huh et al the measured major ions (Na^+ , Ca^+ , Mg^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- , HCO_3^-) are generally give a charge balance. More than 98% groundwater samples showed a charge excess, but some inversely with a negative charge deficit. Maximum charge imbalance that was calculated was 17% and minimum charge

imbalance in 2%. The average water temperature at the time of sampling varies from 23°C to 33°C. In general, pH of the water is alkaline in nature with an average of 7.4 in POM and 7.17 in PRM. The pH is controlled by total alkalinity of the ground water and partially by sea water mixing. pH in the study area varies from 6.6 to 8.1 with an average of 7.4 in post monsoon (February) and in pre monsoon (August) it ranges from 6.4 to 7.8 with an average of 7.17. EC varies from 578 to 3104 $\mu\text{s/cm}$ in post monsoon and 495 to 2833 $\mu\text{s/cm}$ in pre monsoon. Total dissolved solids (TDS) ranges vary from 320 to 2152 mg/l in post monsoon and 331 to 1973 mg/l in pre monsoons. The water samples of the study area are classified as fresh to brackish in nature⁵. Bicarbonate is the dominant anion followed by chloride, sulfate, nitrate and phosphate in post monsoon season and

in pre monsoon bicarbonate is the dominant anion followed by chloride, sulfate and phosphate. The dominant cations are as follows: calcium followed by sodium, potassium and magnesium during post monsoon and calcium followed by magnesium, sodium and potassium in pre monsoon.

4.2 Mechanism of Weathering

Gibbs 1970, proposed a diagram to understand the relationship between the chemical components of waters from their respective aquifers lithologies. Three distinct fields namely, Precipitation dominance, Rock dominance and Evaporation dominance are shown in the Gibbs diagrams (Figure 2 and 3). The Gibbs Ratio I – $\text{Cl}/(\text{Cl}+\text{HCO}_3)$ for anion and Ratio II – $\text{Na}+\text{K}/(\text{Na}+\text{K}+\text{Ca})$ for cation of the samples have been plotted separately against the respective values of TDS. During post monsoon, 6 samples (23%) fall

in the Rock dominance category indicating the role of weathering of rocks as the minor mechanism of controlling the groundwater chemistry. The 3 to 12 samples (40%) fall in Precipitation dominance, and the remaining samples (37%) fall in outside the field indicating that various other process also exist in controlling the water chemistry. During pre monsoon, 8 samples (34%) fall in Rock dominance and 6 to 8 samples (31%) fall in Precipitation dominance. The remaining samples (35%) fall in outside the field. It is also supported by Edmond (1995) using ternary classification based on the $\text{SiO}_2(\text{Cl}+\text{SO}_4)-\text{HCO}_3$ to identify the principle factors controlling water chemistry as from rock dominance or from intensity of weathering. During post monsoon, 80% of samples fall in carbonate weathering and in pre monsoon, 20% of samples move to weathering limited silica field (Figure 4).

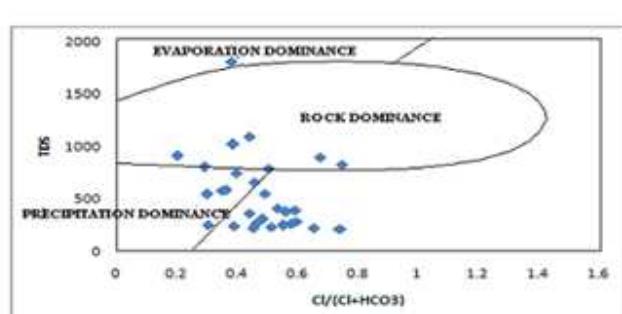
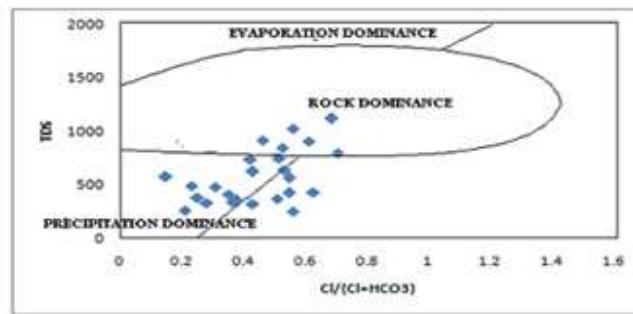
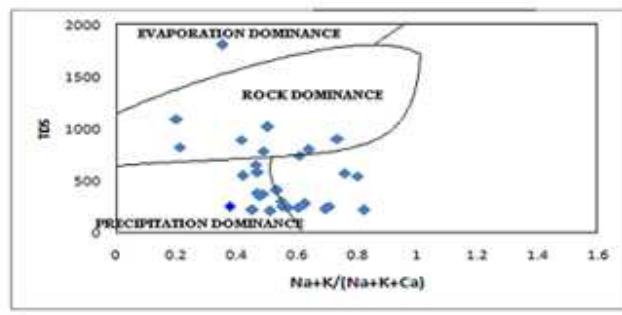
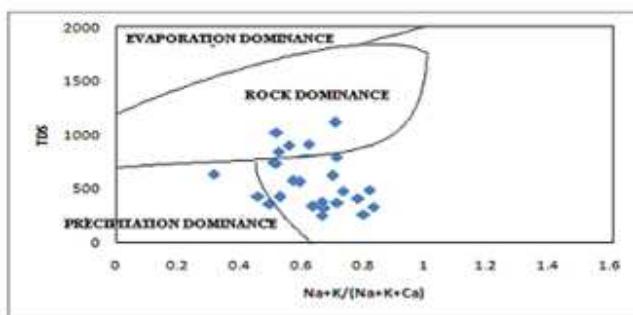


Fig 2: Mechanism controlling the chemistry of groundwater during Post monsoon 2007 (after Gibbs, 1970)

Fig 3: Mechanism controlling the chemistry of groundwater during Pre monsoon 2007 (after Gibbs, 1970)

Figure 5 shows Na^+/Cl ratio in post and pre monsoon seasons. Na^+/Cl ratio should be approximately equal to 1, whereas ratio greater than 1 is typically interpreted as Na released from silicate weathering reaction⁹. In this study, Na^+/Cl ratio of groundwater sample varying from 0.16 to 1.33 in post monsoon and 0.05 to 1.21 in pre monsoon. In post monsoon, 5 samples and in pre monsoon, 1 sample fall above 1 in Na^+/Cl ratio, that indicates the Na released from the silicate weathering. The remaining sample fall less than 1 that indicates the sodium might have come from irrigation return flow and anthropogenic activity.

A general frame of chemical process affecting the groundwater can be determined by the Ca^+ / ($\text{Ca}^+ + \text{Mg}^+$) vs. $\text{SO}_4^- / (\text{SO}_4^- + \text{HCO}_3^-)$ diagram shown in Figure 6. Most of the samples fall within the Calcite-Anhydrite-Dolomite field (CAD) in both the seasons. The composition of the samples

within the CAD triangle is essentially controlled by calcite, dolomite and gypsum dissolution, which are the main minerals of carbonate rocks hosting the aquifers. Low $\text{SO}_4^- / (\text{SO}_4^- + \text{HCO}_3^-)$ values suggest that interaction with sulphate minerals are negligible (Schiavo MA et al 2006).

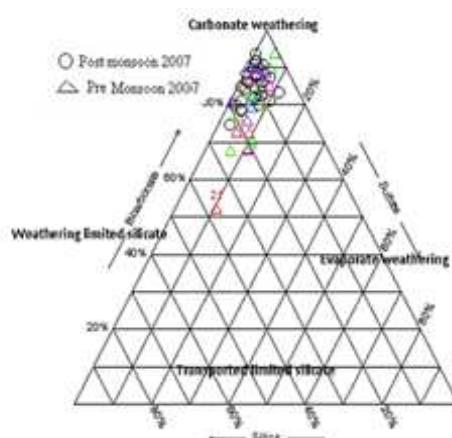


Fig 4: Ternary diagram post Monsoon 2007 and pre monsoon 2007

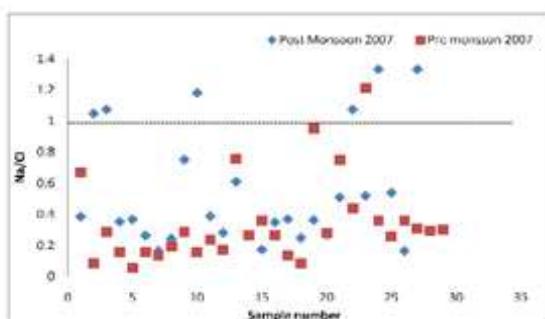


Fig 5: Na/Cl ratio meq/l in Post and Premonsoon seasons (2007)

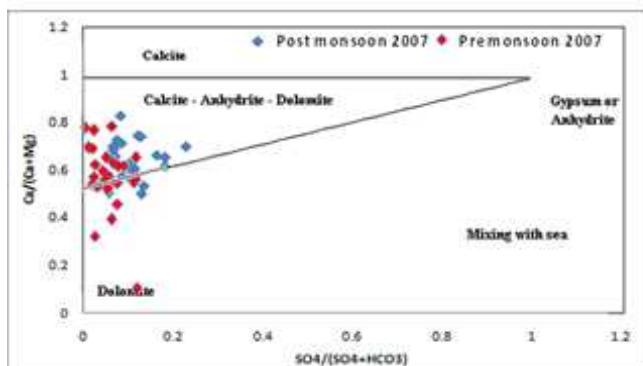


Fig 6 : Diagram of $\text{Ca}/(\text{Ca}+\text{Mg})$ VS. $\text{SO}_4/ (\text{SO}_4 + \text{HCO}_3)$ concentration in Post,Pre monsoon 2007

4.3 Piper facies

The geochemical evolution of groundwater can be understood by plotting the concentration of major cations and anions in the piper (1944) trilinear diagram. The Figure 7 represent 30% of the groundwater samples fall in $Mg^+ - Cl^-$ type of water and followed by $Ca^+ - Cl^-$ (22%), $Na^+ - Cl^-$ (18%), $Na^+ - HCO_3^-$ (18%) and $Ca^+ - HCO_3^-$ (8%) in post monsoon season. In pre monsoon, 63% of samples fall in $Mg^+ - Cl^-$ type and followed by $Ca^+ - Cl^-$ (22%), $Na^+ - HCO_3^-$ (15%), $Na^+ - Cl^-$ (6%) and $Ca^+ - HCO_3^-$ (6%). From the plot, alkaline earths (Ca and Mg) exceeds the alkali (Na^+) and strong acid (Cl^-) exceeds the weak acids (HCO_3^- and SO_4^{2-}) (Manish Kumar et al 2006).

4.4 Sea water contamination

Coastal aquifers have their end boundaries in

contact with sea water and are always under dynamic equilibrium. The abundance of Na^+ , Cl^- , and SO_4^{2-} over other ions in the groundwater at few locations indicates the possible sea water contamination in this area. These ions increasing the EC and total dissolved solids (Table 1). The total cations vs. chloride illustrate the seawater influence as well (Figure 8) by samples which have been plotted along the seawater mixing line. The upward deviation from the mixing line seems to be caused by other chemical reactions providing cations without changing chloride concentration. In post monsoon, 3 samples fall below the sea water mixing line and in pre monsoon, 8 samples fall below the sea water mixing line. Because of the influence, it's likely that the chemistry of these samples is highly affected by cation exchange.

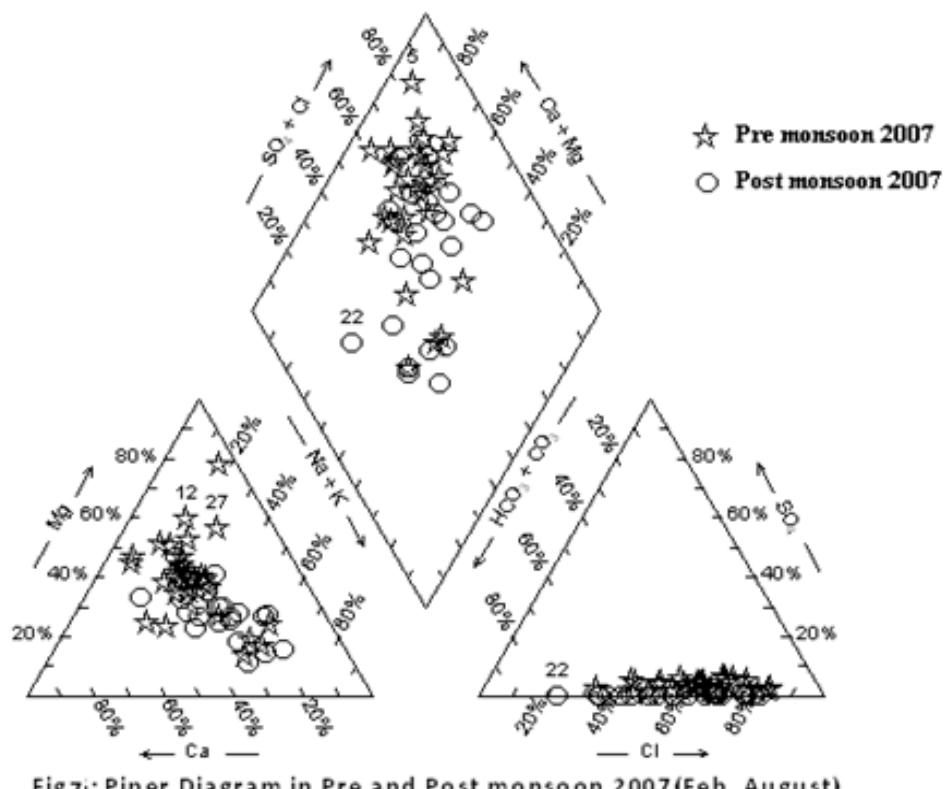


Fig 7: Piper Diagram in Pre and Post monsoon 2007 (Feb, August)

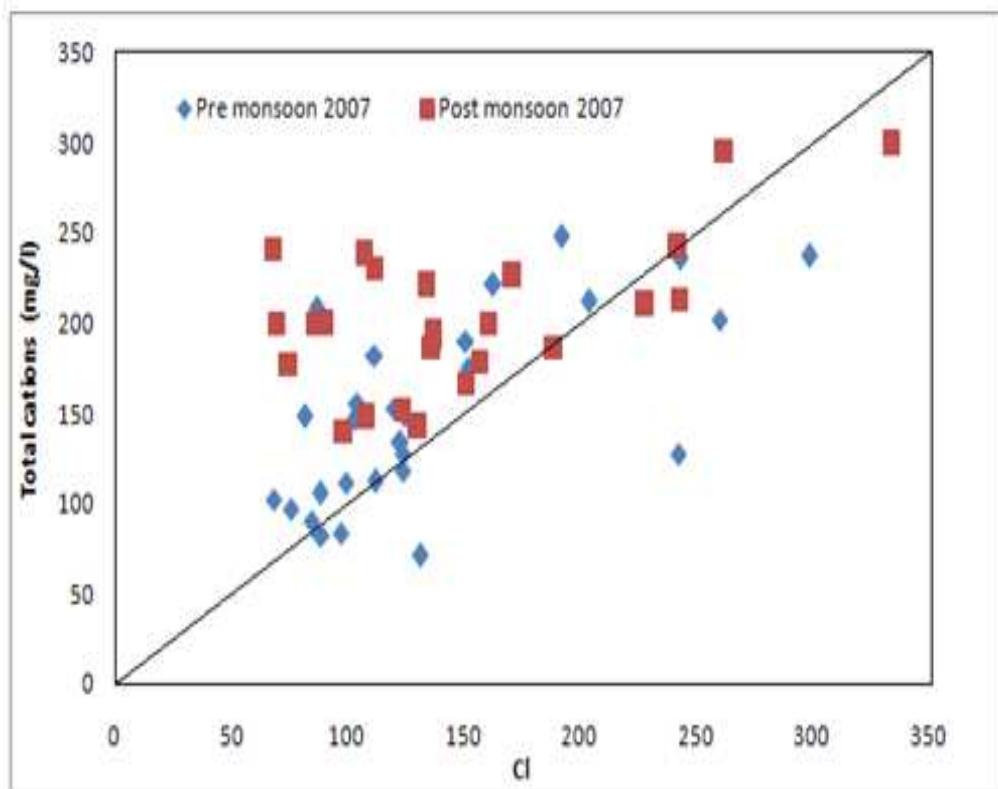
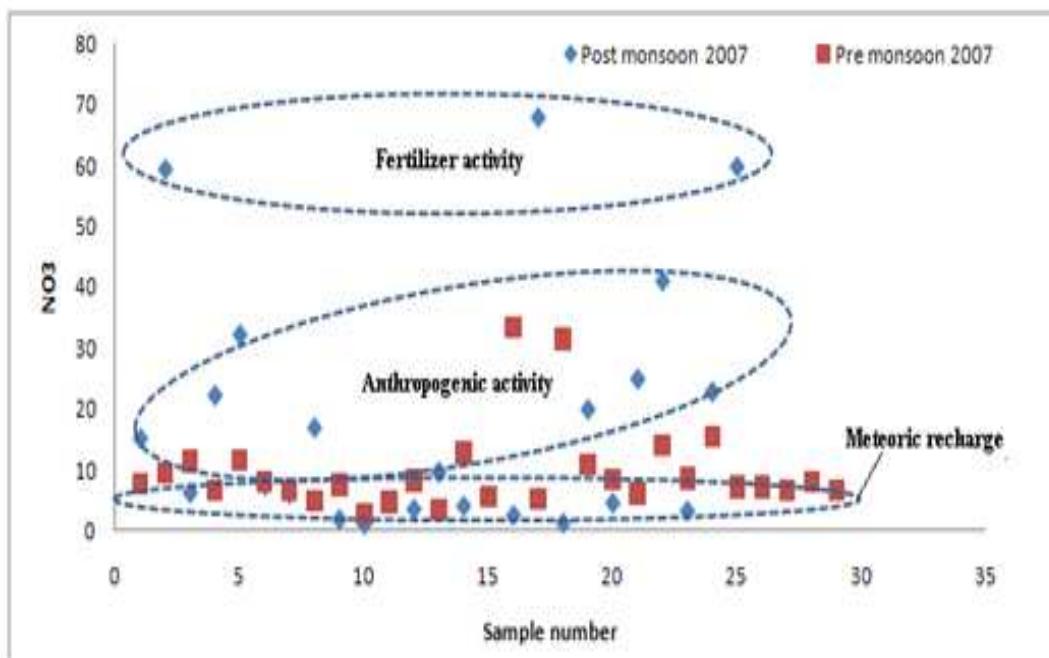
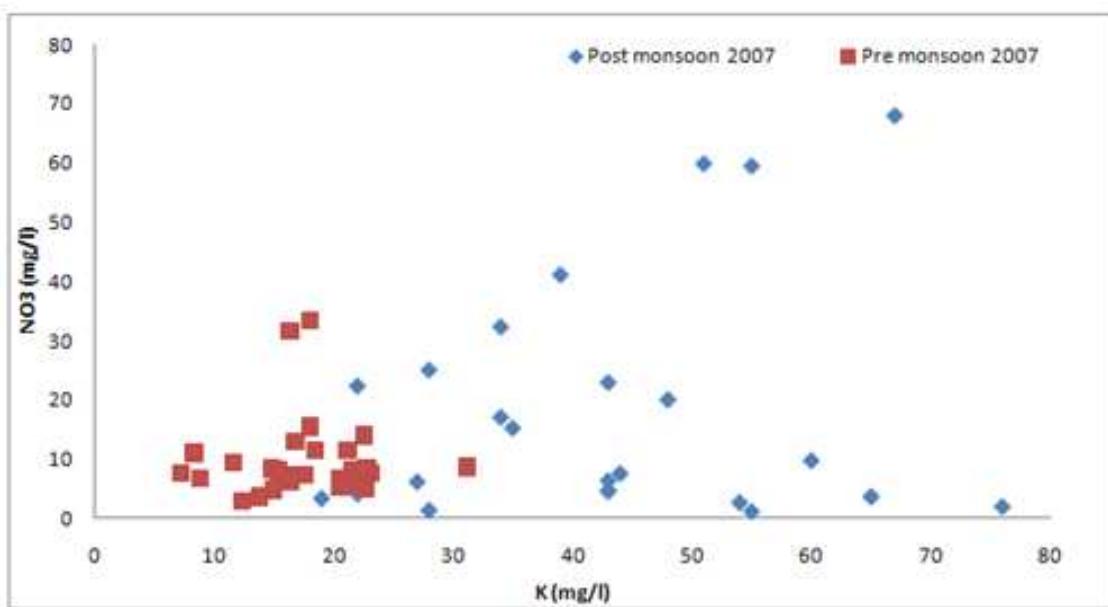


Fig 8: Relation between total cations and chlorine in Post and pre monsoon 2007

Fig 9: Sample VS. NO₃ in Pre and Post monsoon 2007(Feb, August)

Fig 10: K VS. NO₃ in Pre and Post monsoon 2007 (Feb, August)

4.5 Nutrients

Agriculture has direct and indirect effects on the rates and composition of groundwater recharge and aquifer biogeochemistry. Nitrate is the most typical chemical component of which groundwater chemistry has been significantly disturbed by agricultural activity (Hatim Elhatip et al 2003). The Figure 9 shows, in post monsoon, 7 samples (12%) fall in meteoric recharge (0.05 to 7 mg/l) and 8 samples (13%) mainly contributed by anthropogenic activity and 3 samples (4%) by fertilizer⁷. This may be due to the anthropogenic activity mixed with the groundwater through the percolation of freshwater due to rain (Prasanna MV et al 2009). In pre monsoon season, most of the samples fall in meteoric recharge (0.05 to 7 mg/l) and 5 samples (5%) contributed by anthropogenic activity. A plot between NO₃ vs. K was examined as higher NO₃ value should be associated with high K concentration, if the source is from fertilizer¹⁵. The plot indicates that in post-monsoon season, samples show an excess nitrate associated with high potassium content with few exceptions (Figure10), but in pre-monsoon this relationship did not hold well, perhaps due to meteoric effect.

5 CONCLUSIONS

In the study area, groundwater quality is mainly controlled by weathering, precipitation, mixing of seawater, ion-exchange reactions, and anthropogenic inputs. The Mg⁺, Ca⁺ are derived mainly from dissolution of carbonate precipitates along with ion exchange process in the groundwater. NO₃ in groundwater is mainly derived from irrigation returns flow and anthropogenic activities. The dominant water facies is Mg⁺-Cl⁻, Ca⁺-Cl⁻, Na⁺-Cl⁻ in post monsoon Mg⁺-Cl⁻, Ca⁺-Cl⁻, Na⁺-HCO₃⁻ in pre monsoon season. The hydrogeochemistry of groundwater is mainly contributed by Rock dominance (23% in post monsoon and 34% in pre monsoon), Precipitation dominance (40% in post monsoon and 31% in pre monsoon) Evaporation dominance (2% in pre monsoon season). The sea water influence in post monsoon is around 4% and in pre monsoon around 7%. The nutrients are mainly by meteoric recharge (12% in post monsoon and 22% in pre monsoon) and anthropogenic activity in the groundwater (17% in post monsoon and 5% in pre monsoon).

REFERENCES

1. Anandhan P (2005). Hydrogeochemical studies in and around Neyveli mining region, Tamilnadu, India. Ph.D Thesis, Department of Earth Sciences, Annamalai University, 189p.
2. APHA (1998). Standard methods for the examination of water and wastewater (American Public Health Association), Washington DC, USASS, 19th edition.
3. Edmond JM, Palwer MR, Measures CF, Grant B, Stallard RF (1995). The fluvial geochemistry and denudation rate of the Guayana Shield in Venezuela, Colombia and Brazil, *Geochim Cosmochim Acta*. 59: 3301-3323.
4. Elango L, Kannan R, Senthil Kumar M (2003). Major ion chemistry and identification of hydrogeochemical processes of ground water in a part of Kanchipuram District, Tamil Nadu, India. *Environmental Geosciences*, 10(4): 157- 166.
5. Freeze AR, Cherry JA (1979). *Groundwater*, Prentice - Hall, Inc Englewood cliffs, New Jersey, 604p.
6. Gibbs RJ (1970). Mechanisms controlling world's water chemistry, *Science*, 170: 1088-1090.
7. Huh Y, Tsoi MY, Zaitiser A, Edward JN (1998), The fluvial geochemistry of the rivers of Eastern Siberia: III. Tributaries of the Lena and Anabar draining the basement terrain of the Siberian Craton and the Trans-Baikal, *Geochim Cosmochim Acta*, 62, 1657-1676
8. Manish K, Ramanathan AL, Rao MS, Bhishm K (2006). Identification and evalution of hydrogeochemical processes in the groundwater environment of Delhi, India *Environmental Geology*, 50: 1025-1039.
9. Ozler HM (2003). Hydrochemistry and saltwater intrusion in the Van aquifer, east Turkey. *Environ. Geol.*, 43: 759-775.
10. Piper AM (1944). A graphic procedure in the geochemical interpretation of water analysis.) *Trans Am Geophysical Union*, 25: 914 - 923.
11. Prasanna MV, Chidambaram S, Shahul Hameed A, Srinivasamoorthy K (2009). Study of evaluation of groundwater in Gadilam Basin using hydro geochemical and isotope data. *Environ. Monit. Assessment*, DOI 10.1007/s10661- 009-1092-5.
12. Ragunath HM (1987). *Geochemical survey and water quality*, *Groundwater* Wiley eastern limited, New Delhi, pp. 343-347.
13. Schiavo MA, Hauser S, Cusimano G, Gatto L (2006). Continental self recharge. 26: 826-834.
14. Todd DK (1980). *Ground Water Hydrology* - John Wiley and Sons New York, 535p.