

Hydrogeochemistry Of Thirumanimuttar Basin: An Indication Of Weathering and Anthropogenic Impact

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ABSTRACT: A total of 148 groundwater samples were collected from bore wells from Thirumanimuttar sub-basin for two seasons to identify major geochemical process activated to alter groundwater chemistry. The study revealed relationships with the lithology and anthropogenic process. Groundwater in the region was dominated by Na – Ca – Mg and Cl and HCO₃ types. The (Ca +Mg) Versus TZ⁺ plot for both seasons reveals higher Ca and Mg due to leaching due to silicate mineral weathering from aquifer matrix of the study area. The plot for (Na + K) versus TZ⁺ indicates weathering process of both alkali and alkali earth from feldspars along with additional sources like contribution from alkali/saline soil and residence time. Saturation index of silicate, carbonate and fluoride minerals indicates oversaturation and equilibrium state and sulfate minerals were at undersaturated state during both the seasons. Lithology and Anthropogenic activity plays a significant role in controlling groundwater chemistry of the study area.

Key words: Thirumanimuttar, Groundwater, Ion exchange, Anthropogenic impact, Saturation index

INTRODUCTION

Water resource evaluation is gaining importance in the present scenario due to increasing in population, industries and increasing agricultural practices, which severely alters the chemical composition of water. Hence it is essential to demarcate the processes involved in chemical evolution of groundwaters for better understating its suitability for various purposes. Groundwater chemistry is largely a function of the mineral composition of the aquifer through which it flows. As groundwater moves along its path from recharge to discharge areas, a variety of hydrogeochemical processes alter its chemical composition. The relationship between geological matters and groundwater quality has attracted many researches (Freeze and Cherry, 1979, Ophori and Toth, 1989, Domernico and Schwartz,

1990). (Ahmad Zaharin Aris, *et al.*, 2007) Indicated high Na-Cl Concentration derived from Salt water Intrusion by using Piper diagram and PHREEQC from Manukan Island Sabah. (Jayasena, *et al.*, 2007) Studies about Groundwater chemistry and identified Groundwater from mafic rocks have high dissolved solids, while quartzose metaclastic rocks yield water with low dissolved solids. Similar studies were also put forth by (Cleaves, 1974). The character of groundwater in different aquifers over space and time proved to be an important technique in solving different geochemical problems (Chebotarev, 1955, Hem, 1959, Back, *et al.*, 1966, Srinivasamoorthy, *et al.*, 2005). Calculation of mineral saturation index and thermodynamic equilibrium studies initiated by (Garrels and Christ, 1965) to decipher the possible reactant and product minerals and indication of

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the equilibrium state of groundwater and the surrounding materials.

Thirumanimuttar Sub-basin lies between North Latitudes and $11^{\circ}48'$ and East Longitudes $77^{\circ}53'$ and $78^{\circ}28'$ with a total drainage area of about 2030 km^2 . It originates at Manjavadi pass at Salem district and configures river Cauvery at Paramathi in Namakkal district (Fig. 1). Surface water flow is precarious due to vagaries in monsoon and generally people has to largely depend on groundwater resources for their various utilities. The geology of the study area is composed of rock types represented by metasediments with Charnockites, granitic gneiss, calc granulite, syenite and ultra basic as major exposures (Fig. 2). Hills, undulating plains, pleatues, pediments and bazadas are the mixture of

geomorphic units of the study area. Normal annual rainfall over the study area is about 1590 mm . Groundwater generally occurs in weathered portions of the rocks along joints and fractures. Groundwater flow was noted due North East direction and along downstream flow is due West to East which generally coincides with the topography of the study area. Thickness of aquifers ranges from 3 to 30m in general.

MATERIALS & METHODS

A total of 148 groundwater samples were collected for two different seasons Pre (May-2008) and Post (January-2008) monsoon Seasons. The samples were analyzed for Bicarbonate, Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Sodium, Potassium, Calcium, and Magnesium

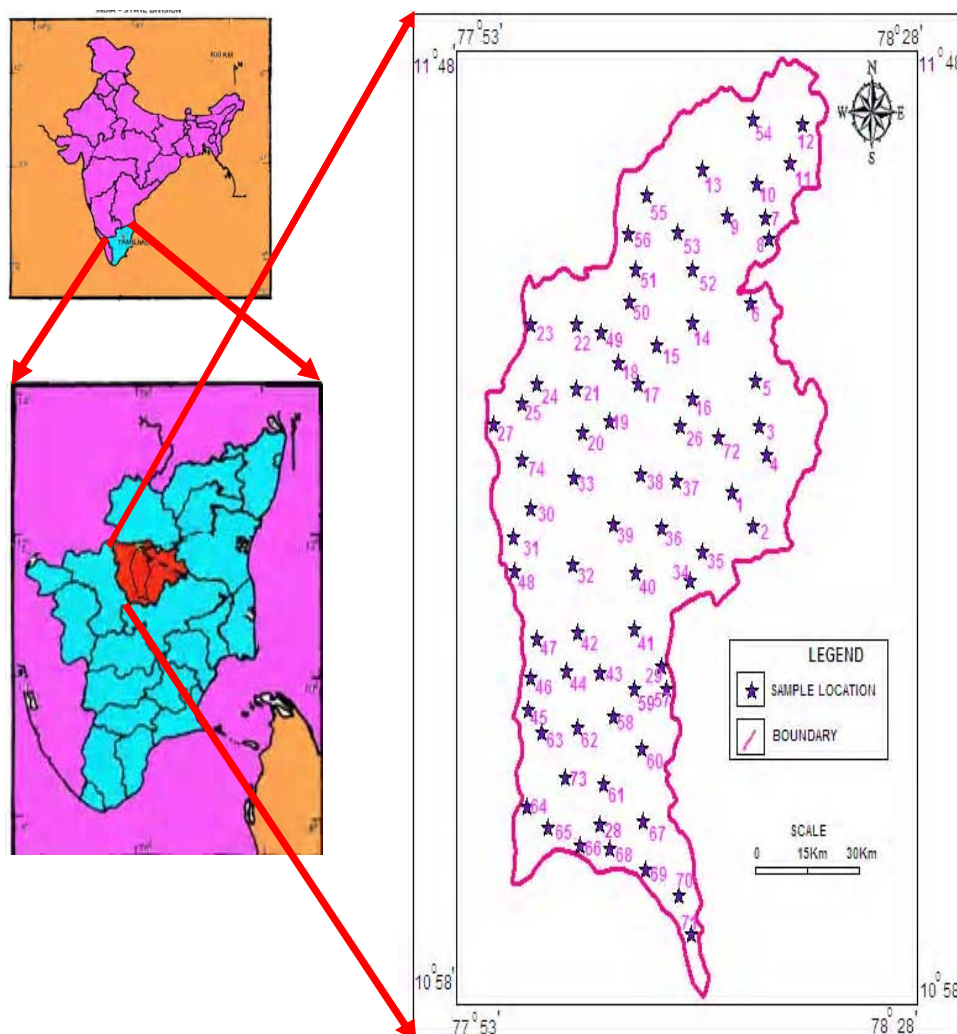


Fig. 1. Groundwater Sample and Location Map of the Study Area

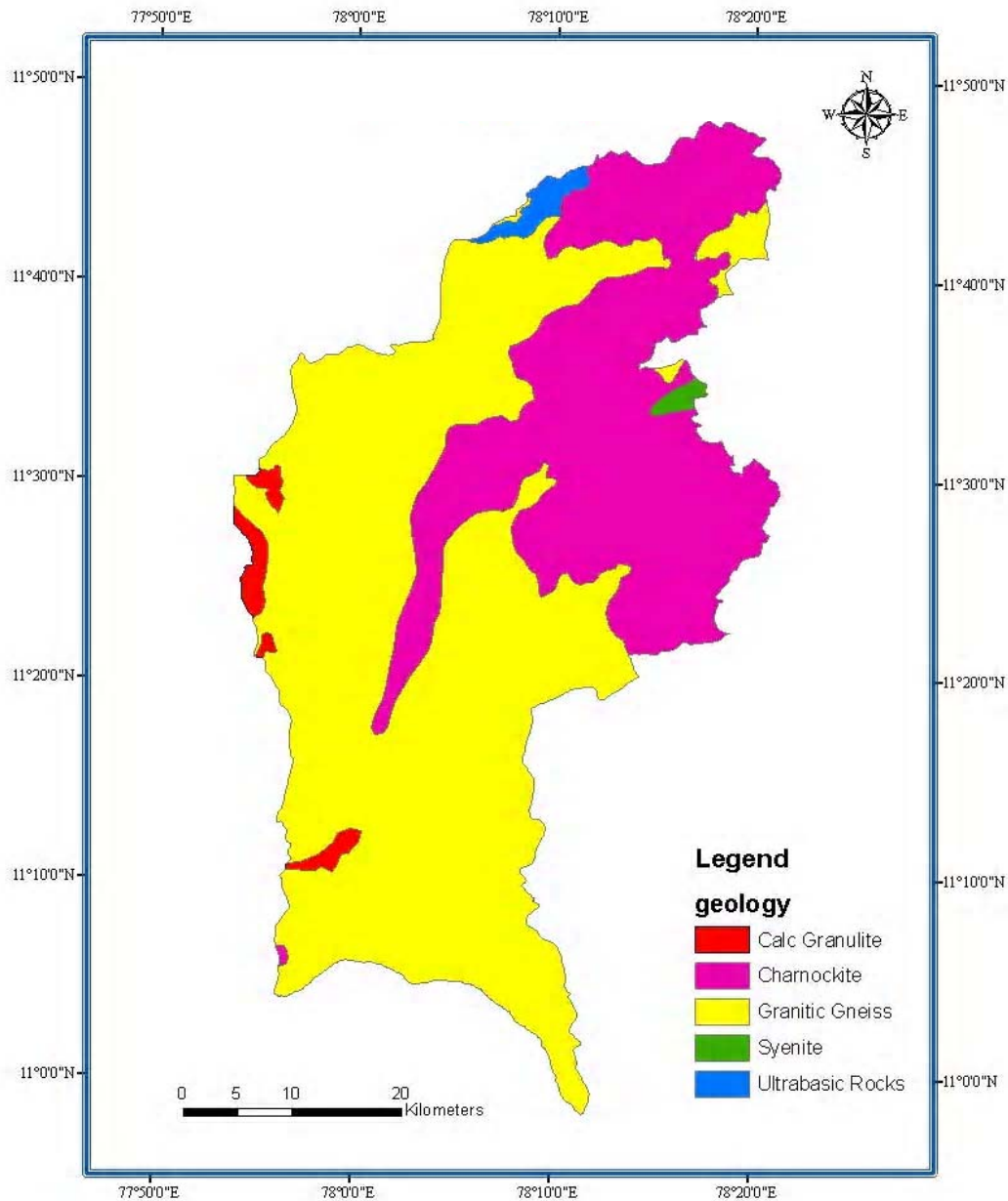


Fig. 2. Geology map of Thirumanimuttar Sub basin

using standard procedures by (APHA, 1995). pH, TDS and EC were measured by Systronics Water Quality Analyzer 371. F was analyzed using Orion fluoride ion electrode model (94-09, 96-09). SO_4 , PO_4 , H_4SiO_4 was determined by digital spectrophotometer model GSS 700A (Electronic corporation of India). Na and K were determined by using flame photometer (Systronics mk-1/mk-III). Ca^{2+} and Mg^{2+} , HCO_3 were analyzed by titrimetric method. The charge balance calculated was generally $< 10\%$ and ratio of TDS/EC are within acceptable limits (0.8), confirming the reliability of the analytical results.

RESULTS & DISCUSSION

Statistics of groundwater chemistry is represented for two different seasons (Table 1 and 2). Groundwater in general is acidic to alkaline during Pre monsoon season and alkaline during Post monsoon season with pH ranging from 6.9 to 9.22 and 7 to 8 during pre and post monsoon seasons. EC values ranges from 473 to 5453 and 638 to 5826 during Pre and post monsoon season respectively. Higher EC was recorded during Post monsoon season along Northsouth direction. HCO_3 was noted high during post monsoon season (1068 ppm) may be due to action of CO_2 upon the

Table 1. Statistics of ground water chemistry during Pre Monsoon Season (all values in mg/L except pH and EC)

Parameters	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃	PO ₄	H ₄ SiO ₄	Cl ⁻	SO ₄	NO ₃	F ⁻	TDS	EC
Max	9.22	179	158.4	1497.0	277.0	893.8	1.5	33.0	1602.3	126.8	133.0	4.2	3490	5453
Min	6.9	16	11.91	0.8	0.8	73.22	0.475	2	86.84	1	4	0.03	303	473
Average	7.29	70.8	48.27	312.27	26.39	413.7	0.649	17.068	475.91	28.69	38.03	1.14	1433	2239
Std. Dev.	0.35	34	28.89	330.71	55.53	164.1	0.162	5.7703	356.64	27.9	29.08	0.78	754	1179

Table 2. Statistics of ground water chemistry during Post Monsoon Season (all values in mg/L except pH and EC)

Parameters	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃	PO ₄	H ₄ SiO ₄	Cl ⁻	SO ₄	NO ₃	F ⁻	TDS	EC
Max	8	464	377	598	322	1068	3	37	1730	758	136	1	3729	5826
Min	7	8	5	6	1	92	0	7	24	25	1	0	408	638
Average	8	57	113	234	50	376	1	19	429	218	38	1	1535	2399
Std. Dev.	0	58	90	165	61	224	1	6	357	180	40	0	764	1193

basic material of soil and granitic rock. Cl was higher in post monsoon season (1730 mg/L) due to leaching from upper soil layers due to industrial and domestic activities and dry climates (Srinivasamoorthy, 2008). SO₄ was higher in Post monsoon season (758 ppm) may be due to action of leaching and anthropogenic process in metamorphic environment by release of sulphur gases from industries and utilities get oxidized and enter into the groundwater (Saxena, 2004). PO₄ was within the permissible limit during both the seasons. Fluoride was higher during pre monsoon (4.2 ppm) due to leaching from fluoride rich rocks and easier accessibility of rain water to weathered rock, long term irrigation processes, semi arid climate and long residence time of groundwater. The effect of dilution was well noted during post-monsoon season. NO₃ was higher in post monsoon season (136 ppm) and along highly agricultural areas may be due to leaching from plant nutrient and nitrate fertilizers (Freeze and Cherry, 1979, Madison and Brunett, 1984).

Na was higher in pre monsoon season (1497 ppm) indicating weathering from plagioclase bearing rocks and also due to over exploitation (Hem, 1985). K is higher in Post monsoon season (322 mg/L) may be due to weathering of feldspar and clay from aquifer matrix. Ca was higher during post monsoon season (464 mg/L) may be due to dissolution of precipitates of CaCO₃ and Ca Mg (CO₃)₂ during recharge (Datta and Tyagi, 1996,

Lakshmanan *et al.*, 2003). Mg concentration of the study area was higher during postmonsoon season (377 mg/L); which might have been derived from dissolution of magnesium calcite, gypsum and/or dolomite from source rock (Garrels, 1976). Trilinear plot developed by Hill (1940) and Piper (1944) is used to delineate variability and trends in water quality have contributed extensively to understand groundwater flow and geochemistry (Dalton and Upchurch, 1978). Aquachem version 4 was used for plotting the Piper diagram. The plot shows majority of water samples irrespective of seasons fall in the field of mixed Na-Cl types of water (Fig. 4) with minor representations also from Mixed Ca-Mg-Cl, Mixed Ca-Na-HCO₃, Ca-Cl and Ca-HCO₃ types for pre and post monsoon seasons. From the plot alkalis (Na and K) exceeds alkaline earths (Ca and Mg) and Strong acids (Cl and SO₄) exceeds weak acid (HCO₃).

The results from the water analysis were used as a tool to identify the sources and mechanisms activated in the study area. The (Ca +Mg) Versus TZ⁺ plot (Fig. 5) for both seasons lie far below equiline with minor indications along alkaline earth also but 90% of the groundwater of the study area was found to be enriched with alkalis, which might have been enriched in groundwater from silicate dissolution from aquifer matrix. In the plot for (Ca +Mg) versus HCO₃+SO₄ (Fig. 6). the data point irrespective of seasons falls below equiline

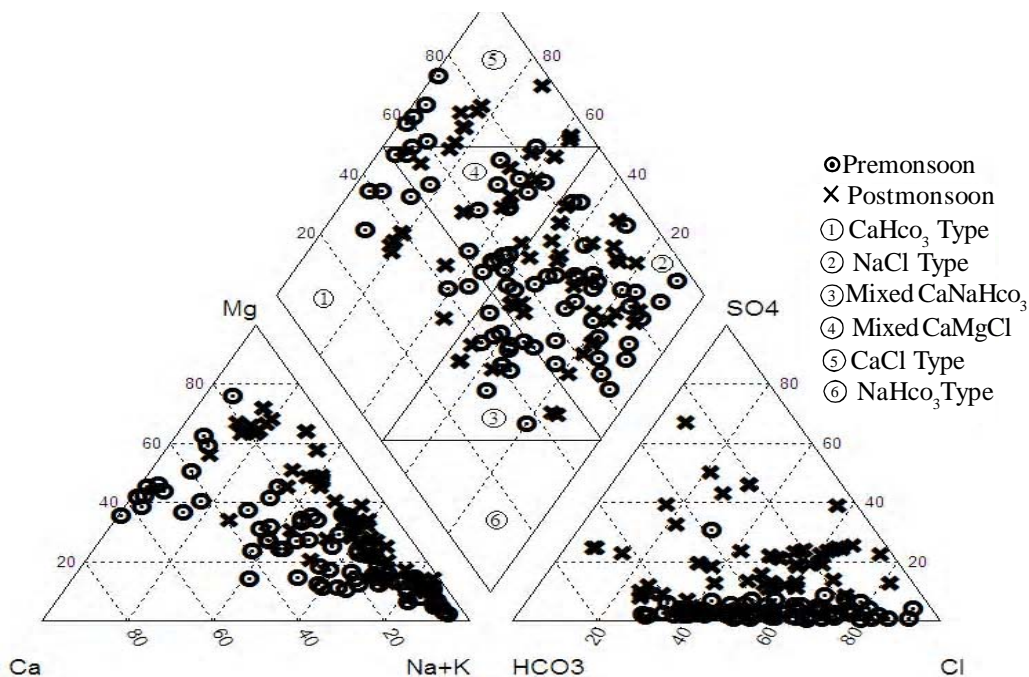


Fig. 3. Chemical facies of groundwater in piper diagram for pre and post monsoon season

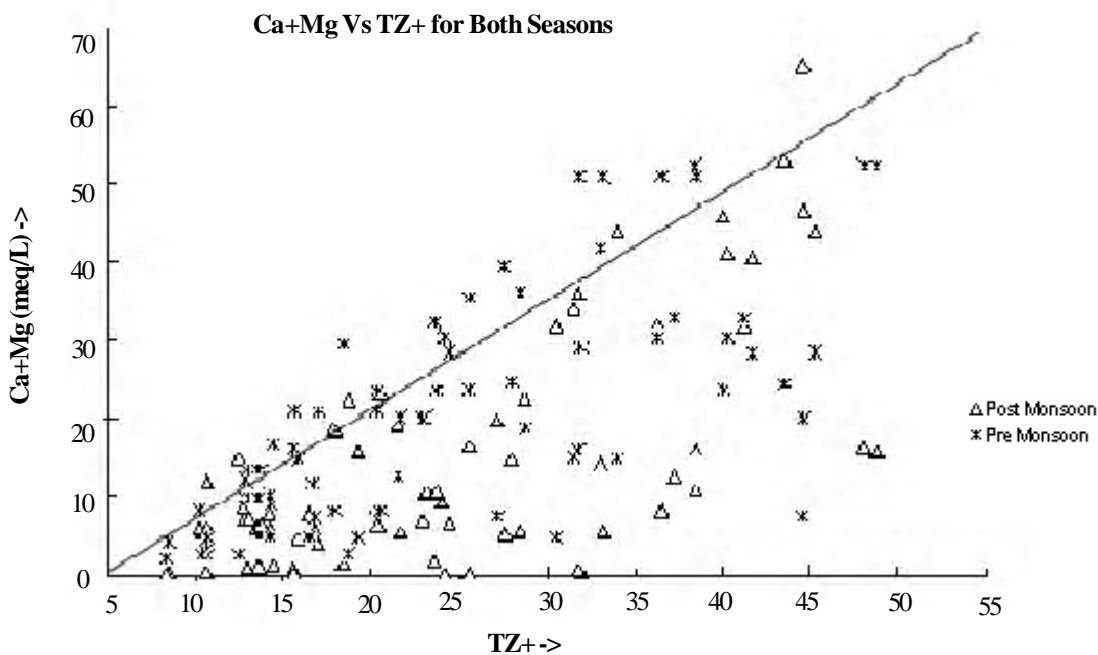


Fig. 4. The plot of Ca+Mg Vs TZ+ for Both Seasons

indicates $\text{HCO}_3 + \text{SO}_4$ as dominant factor which might be due to reaction of feldspar minerals with carbonic acid in the presence of water, which releases HCO_3 . The plot for (Na + K) versus TZ+ (Fig. 7) reveals 90% of the samples falls below the equiline, indicates Ca + Mg is the dominant factor that is responsible for hardness in water.

Their presence is the result of dissolution of carbonate minerals such as calcite and dolomite. Few samples fall in above the equiline that indicates Na+K are dominant. In the plot for Na Versus Cl (Fig. 8) majority of samples during Pre monsoon season fall in Cl zone indicating Cl derive from anthropogenic sources like leaching from fertilizer,

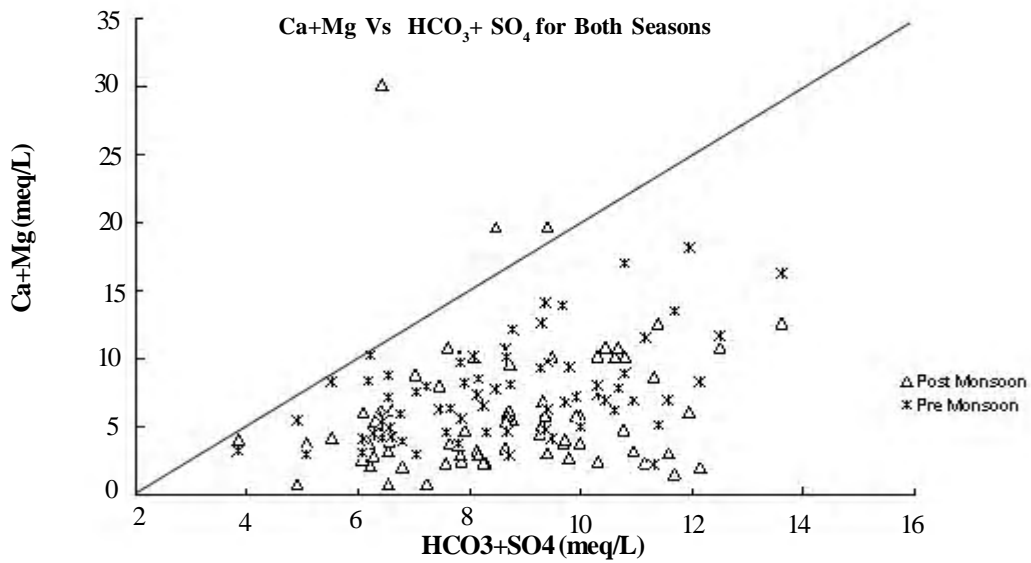


Fig. 5. The plot of Ca+Mg Vs HCO₃+SO₄ for Both Seasons

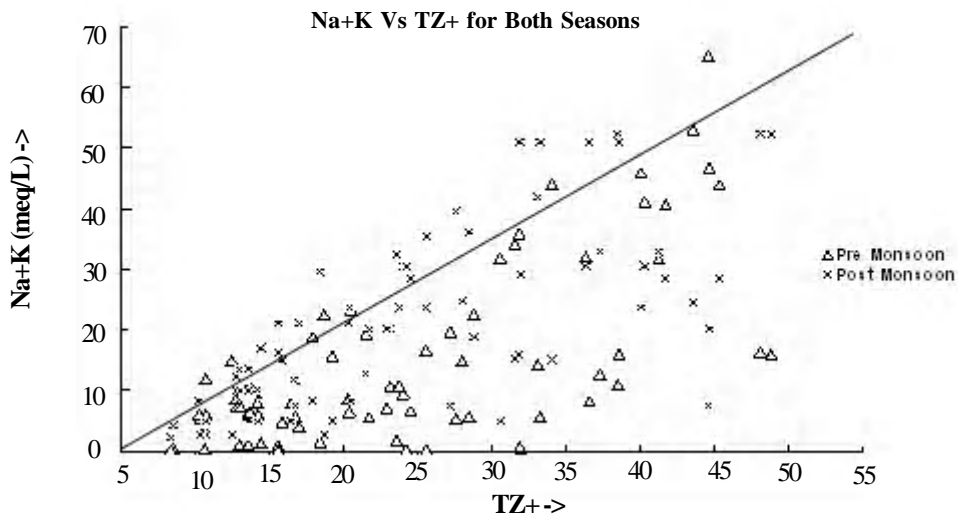


Fig. 6. The plot of Na+K Vs TZ⁺ for Both Season

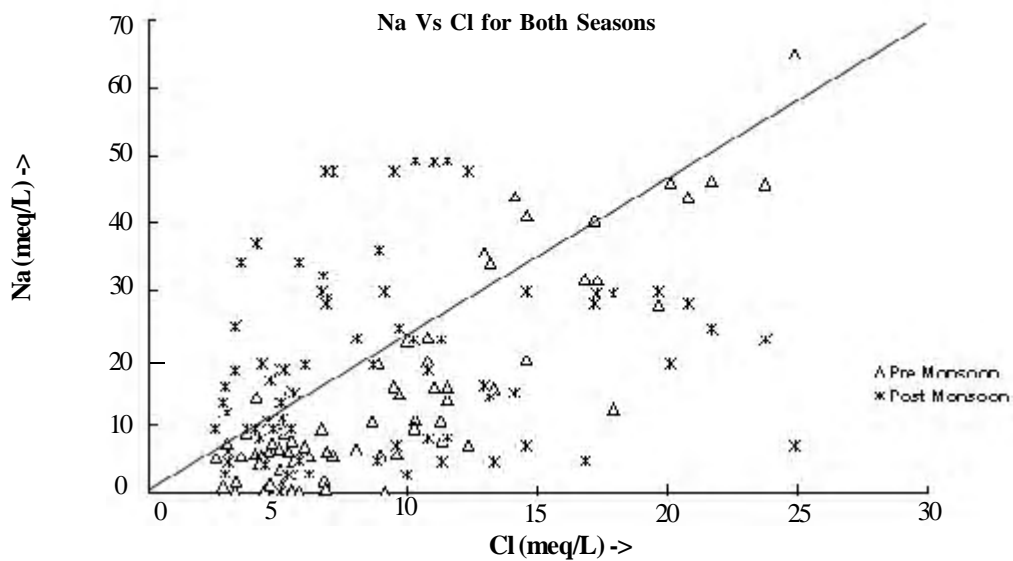


Fig. 7. The plot of Na Vs Cl for Both Seasons

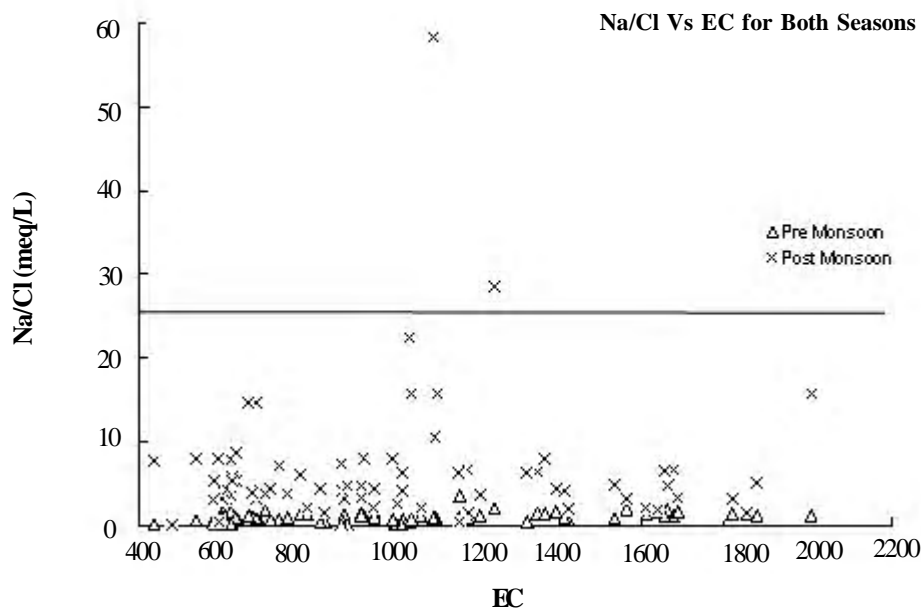


Fig. 8. The plot of Na/Cl Vs EC for Both Seasons

road sal, human, animal waste and industrial applications. These sources can result in significant concentrations of chloride in groundwater because chloride is readily transported through the soil (Stallard and Edmond, 1983). Minor indications during post monsoon season is also noted in Na zone indicating Na released from silicate weathering process.

In the plot for Na/Cl Versus EC (Fig. 9) shows Na is an increasing trend with Cl along with higher and lower Na/Cl ratio, indicates Sodium and chloride are produced by the solution of halite (sodium chloride) which can occur as grains disseminated in unconsolidated and bedrock deposits. Chloride also occurs in bedrock cementing material, connate fluid inclusions, and as crystals deposited during or after deposition of sediment in sea water. High sodium and chloride levels can result from upward movement of brine from deeper bedrock in areas of high pumpage, from improper brine disposal wells, and from the use of road salt (Hem, 1985). The plot of $\text{Ca}+\text{Mg}''\text{HCO}_3''\text{SO}_4$ versus $\text{Na}''\text{Cl}$ confirms that Ca, Mg concentrations are derived from aquifer materials and Silicate weathering process (Fig. 10). Disequilibrium indices $\log(IAP/KT)$ was calculated by using PHREEQC geochemical model software for those minerals and other solids stored in the model data book for which the dissolved constituents are reported in groundwater analysis.

Disequilibrium indices $\log(IAP/KT)$ were calculated to determine, if water is in thermodynamic equilibrium $\log(IAP/KT=0)$, oversaturated $\log(IAP/KT>0)$, or undersaturated $\log(IAP/KT<0)$, with respect to certain solid phases (Trusdell and Jones, 1973).

The disequilibrium indices of Carbonate minerals figure (Fig. 11.a & b) Aragonite, calcite, dolomite and Magnesite, were represented from the data bank of PHREEQCI. The samples in pre-monsoon season are near-oversaturated to equilibrium with aragonite, calcite, dolomite and magnetite with minor indications in undersaturation state. The samples in post monsoon season follow the same trend as in pre monsoon, in general carbonate results shows that calcite, dolomite and magnetite are saturated to oversaturated which is indicated by excess input of Ca and Mg ions mainly derived from silicate weathering process.

The disequilibrium indices of Fluoride (Fig. 12.a & b) Fluorapatite, FCO_3 apatite and Hydroxyapatite were represented and the status of groundwater in premonsoon indicates that all the minerals are in the state of near equilibrium to oversaturation during both the seasons which indicates greater dissolution of Fluoride rich minerals from aquifer matrix. The disequilibrium indices of Silicate minerals (Fig. 13.a & b) Chalcedony, Quartz, $\text{SiO}_2(\text{a})$ and Cristobalite were represented for

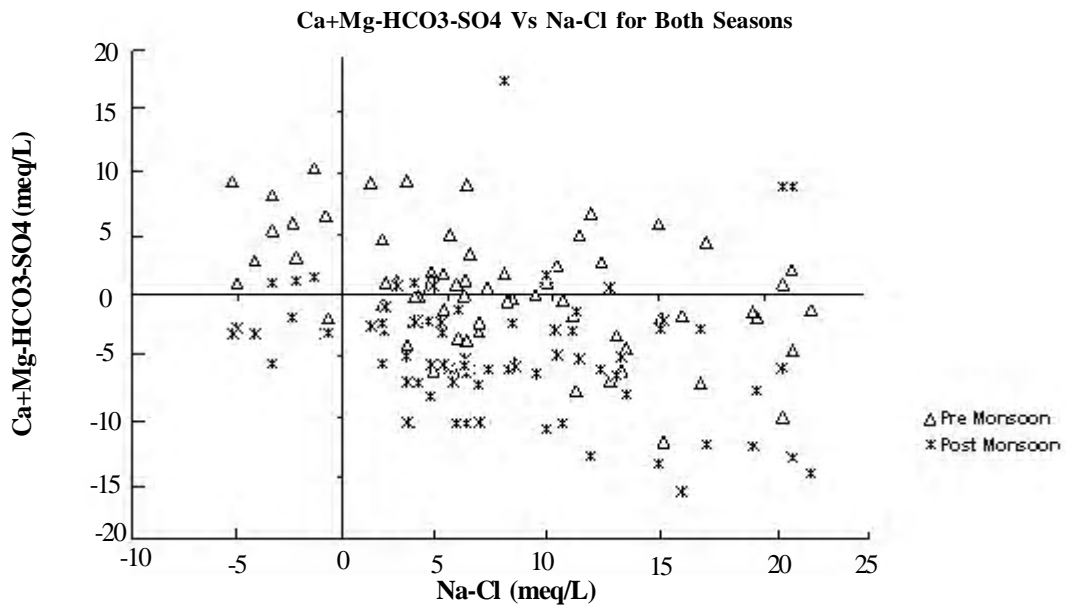


Fig. 9. The plot of $Ca+Mg''HCO_3''SO_4$ Vs $Na''Cl$

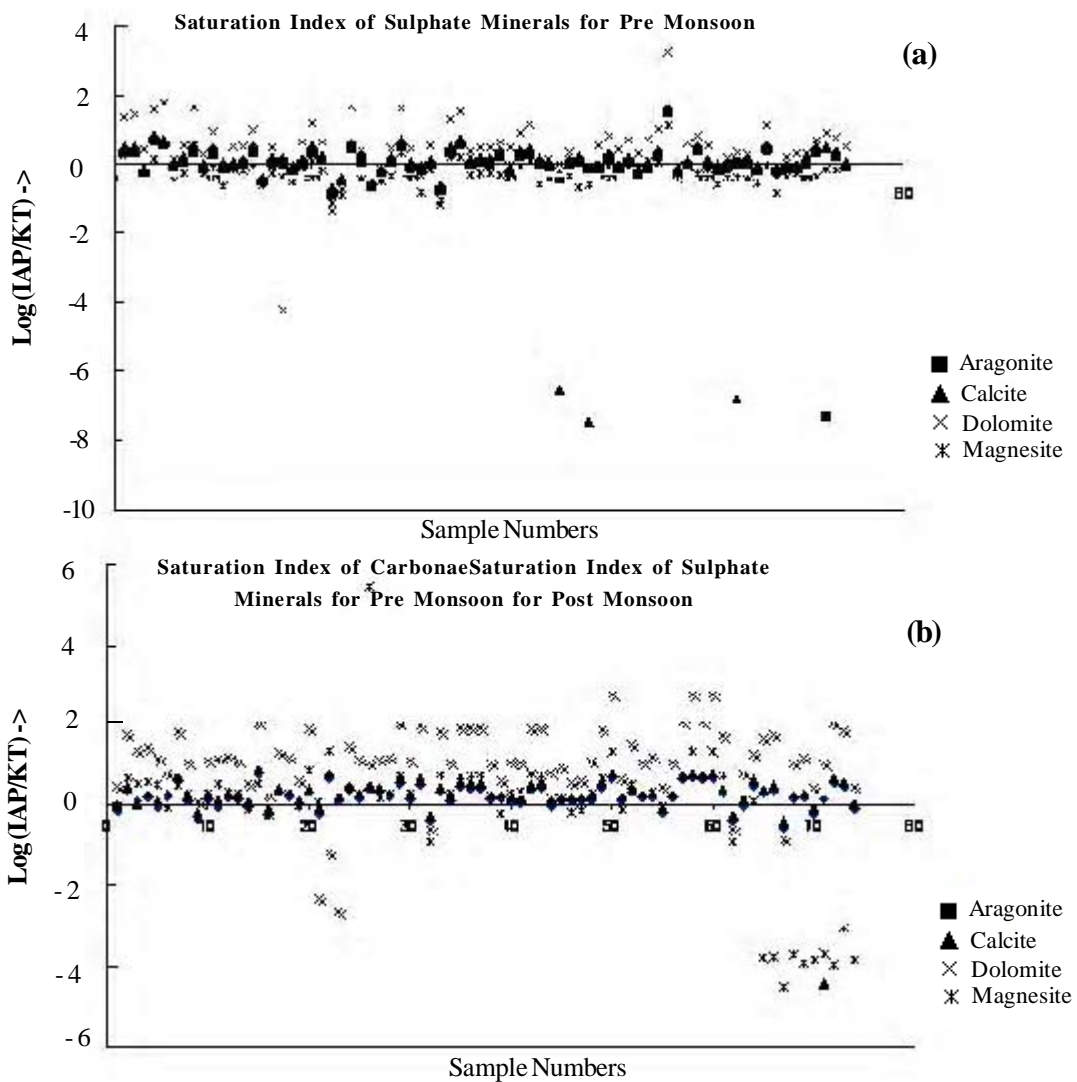


Fig. 10. (a & b) Saturation Index of Carbonate Minerals for Pre and Post Monsoon Season

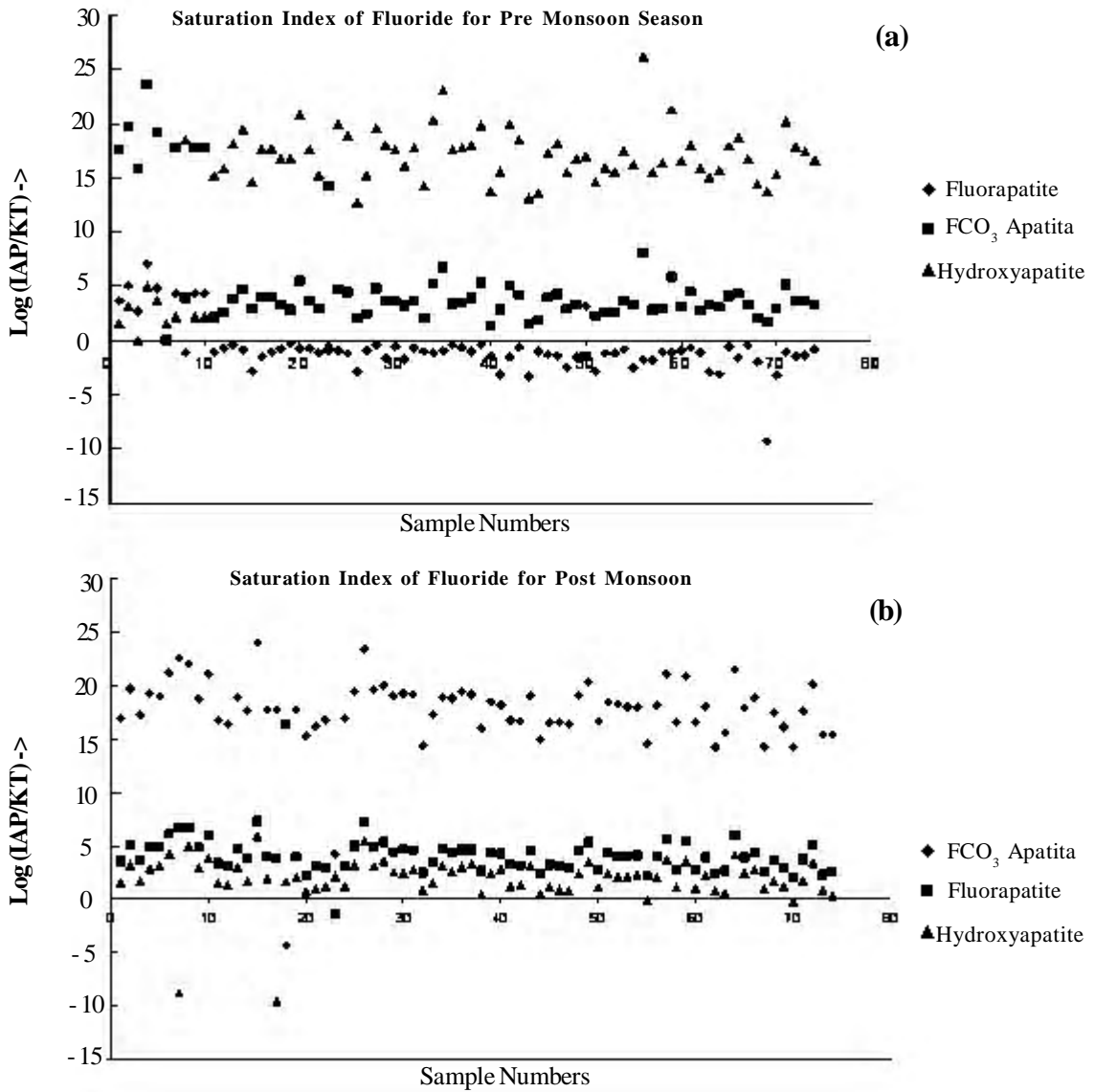


Fig. 11. (a & b) Saturation Index of Fluoride Minerals for Pre and Post Monsoon Season

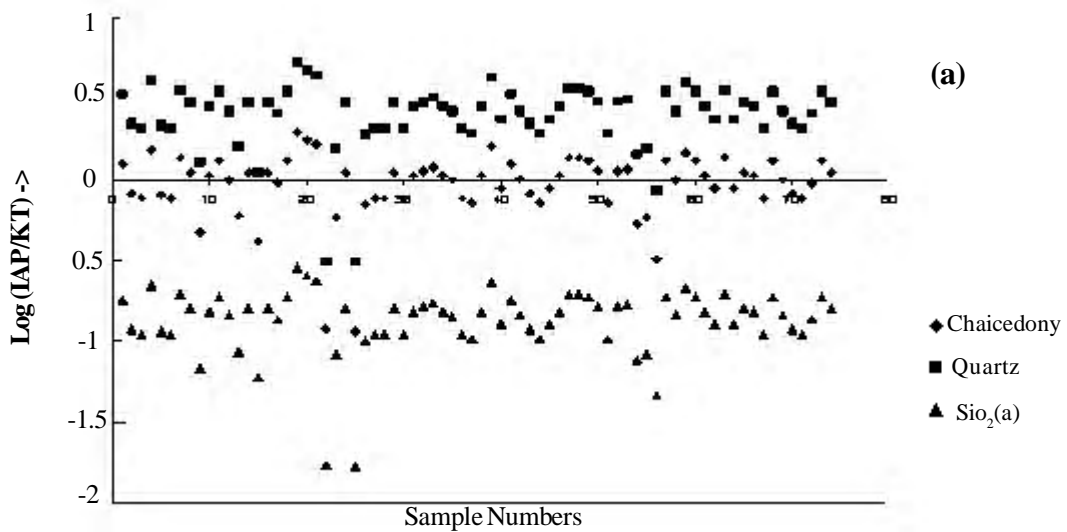


Fig. 12. a. Saturation Index of Silicate Minerals for Pre and Post Monsoon Season

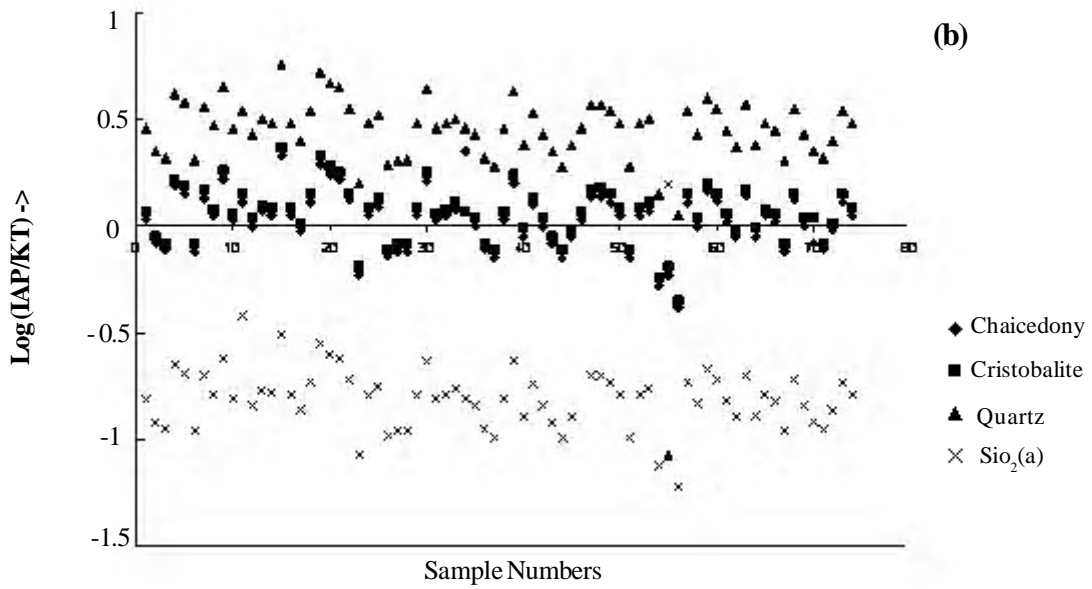


Fig. 12. b. Saturation Index of Silicate Minerals for Pre and Post Monsoon Season

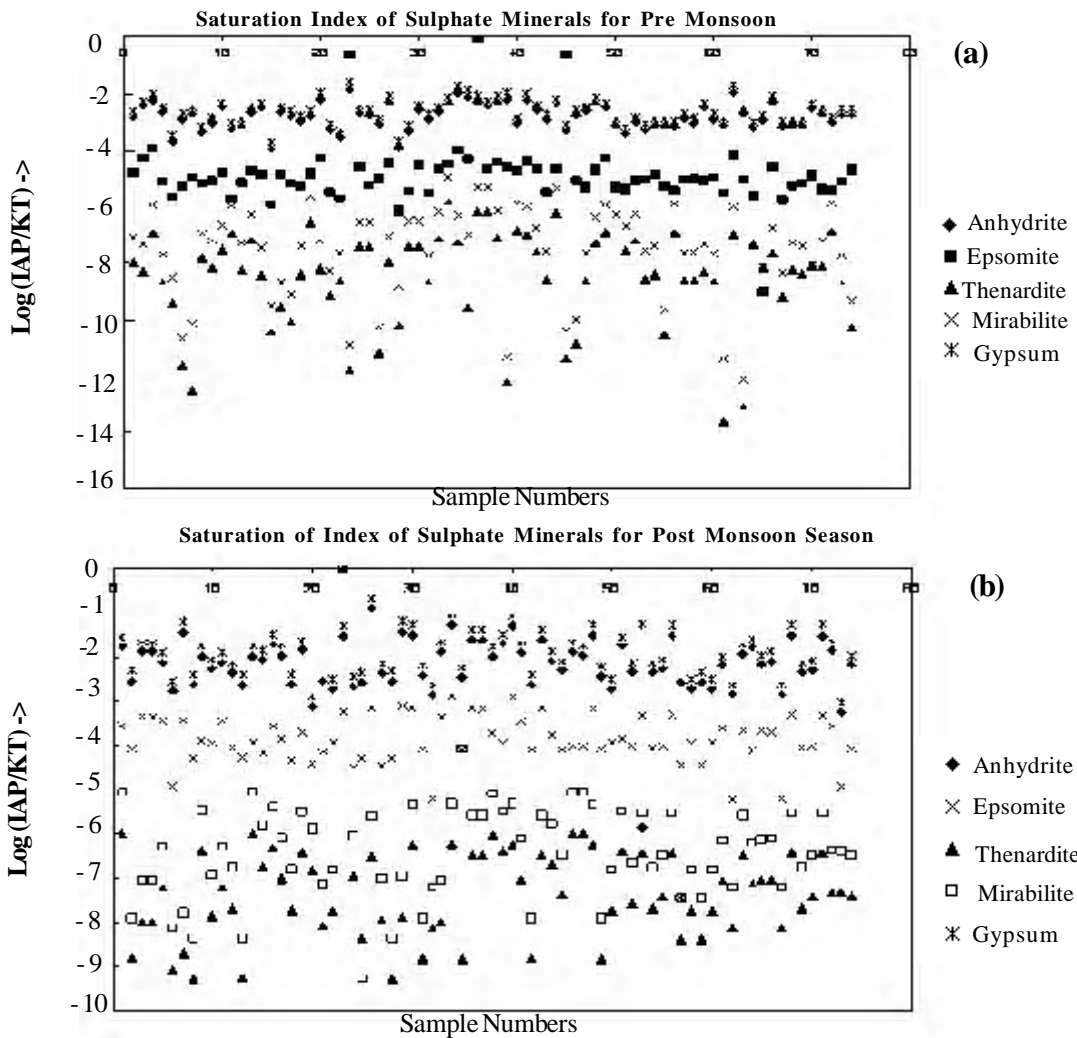


Fig. 13. (a & b) Saturation Index of Sulphate Minerals for Pre and Post Monsoon Season

dissociation factors in the study area. During both the seasons silicate minerals represents the state of undersaturation to oversaturation due to the Ca and Mg released from Silicate weathering process. The disequilibrium indices of Sulphate minerals (Fig. 14.a & b) Anhydrite, Epsomite, Thenandrite, Miralbite and Gypsum were represented and studied for dissociation factors in the study area. During both the seasons all the minerals falls in the state of undersaturation indicating lesser break down of sulfate minerals into the groundwater.

CONCLUSION

The groundwater of Thirumanimuttar region is a unique example for the impact of weathering, ion exchange and anthropogenic process controlling the groundwater chemistry. The chemical composition of groundwater of the study area is strongly influenced by rock water interaction, dissolution and deposition of silicate group of minerals. Weathering of silicate minerals controls the major ion chemistry of calcium, magnesium, sodium and potassium. The groundwater of the study area is dominated by Na, Ca and Cl ions. Na-Cl, Ca-Mg-Cl, Mixed Ca-Na-HCO₃, Ca-Cl and Ca-HCO₃ are the dominant hydrochemical facies present in the study area. The ion exchange process that controls the groundwater chemistry of the study area. Saturation index of minerals indicates oversaturation and equilibrium state of silicate, carbonate and fluoride minerals during both the seasons. Sulfate minerals revealed undersaturated during both the seasons. In general, water chemistry is guided by lithological influences on water chemistry by complex weathering process, ion exchange along with influence of ions from anthropogenic impact.

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REFERENCES

Aris, A. Z., Mohd. Harun Abdullah, M. H. and Kim, K. W. (2007). Hydrogeochemistry of groundwater in Manukan Island, Sabah. The Malaysian Journal of Analytical Sciences, **11**(2), 407- 41.

APHA, (1995). Standard methods for the examination of water and waste water. APHA.

Back, W. and Hanshaw, B. (1965). Chemical geo-hydrology advances in hydro-science. Academic Press, 49-109.

Back, W. Cherry, R. and Hanshaw, B. (1956). Chemical equilibrium between water and the minerals of a carbonate aquifer. Int. Speleo. Spc. Bull., **28**, 119-126.

Basch, M.E. and Funkhouser, R. V. (1985). Irrigation impacts on groundwater levels in Jasper and Newton Counties, Indiana, 1981-84: Indiana Department of Natural Resources, Division of Water, Water Resources Assessment, 85-1.

Bergeron, M.P. (1981). Effect of irrigation pumping on the ground-water system in Newton and Jasper Counties, Indiana: U.S. Geological Survey, Water-Resources Investigation 81-38

Cheboterev, I. I. (1955). Metamorphism of natural water in the crust of weathering-I. Geochim. Cosmochim. Acta, **8**, 22-48.

Cleaves, E. T. (1974). Petrologic and chemical investigation of chemical weathering in mafic rocks, eastern piedmont of Maryland. Maryland Geological Survey Report of Investigation, 25- 28.

Davis, S.N. and Dewiest, R. J. M. (1970). Hydrogeology: New York, John Wiley, 463.

Datta, P.S. and Tyagi, S. K. (1996). Major ion chemistry of groundwater in Delhi area: Chemical weathering processes and groundwater flow regime. J. Geol. Soc. India, 47: 179-188.

Dalton, M.G. and Upchurch, S.B. (1978). Interpretation of hydro-chemical facies by factor analysis. Groundwater, **16**(4), 228-233

Domenico, P.A. and Schwartz, F. W. (1990). Physical and chemical hydrogeology. Wiley, New York, 410-420.

Freeze, R.A. and Cherry, J. A. (1979). Groundwater. New Jersey, Prentice Hall.

Garrels, R.M. and Christ, C.L. (1965). Solutions minerals and equilibrium. New York, Harper and Row, 450.

Garrels, R.M. (1976). A survey of low temperature water mineral relations, in Interpretation of environmental isotope and hydrogeochemical data in groundwater hydrology. Vienna, International Atomic Energy Agency, 65-84.

Hem, J.D. (1959). Study and interpretation of the chemical characteristic of natural. USGS water supply, 269.

- Hem, J.D. (1985). Study and interpretation of the chemical characteristics of natural water (3d ed.). U.S. Geological Survey, Water Supply Paper 2254.
- Bouwer, H. (1978). Groundwater quality; Groundwater Hydrology. McGraw – Hill Kogakusha Ltd., 339-375.
- Hill, R.A. (1940). Geochemical patterns in Coachella Valley, California. American Geophysical Union Trans., **21**, 46-49.
- Jayasena, H. A. H., Chandrajith, R. and Dissanayake, C. B. (2007) Hydrogeochemistry of the groundwater flow system in a crystalline terrain: a study from the Kurunegala district, Sri Lanka. Environ. Geol. **55**, 723–730
- Lakshmanan, E., Kannan, K. and Senthil Kumar, M. (2003). Major ion chemistry and identification of hydrogeochemical process of groundwater in part of Kancheepuram district, Tamilnadu, India. J. Environ. Geosciences, **10(4)**, 157-166.
- Madison, R.J. and Brunett, J.O. (1984). Overview of the occurrence of nitrate in ground water of the United States, in National Water Summary 1984. U.S. Geological Survey, Water Supply Paper 2275.
- Ophori, D.U. and Toth, J. (1989). Patterns of groundwater chemistry, Ross Creek Basin, Alberta, Canada. Groundwater **27(1)**, 20–26.
- Pathak, J.K., Alam, M. and Sharma, Sh. (2008). Interpretation of Groundwater Quality Using Multivariate Statistical Technique in Moradabad City, Western Uttar Pradesh State. Indian Journal of Chemistry. **5(3)**, 607-619.
- Piper, A.M. (1944). A graphical procedure in the geochemical interpretation of water analysis. Am. Geophys. Union Trans., **25**, 914-928.
- Rosenshein, J.S. and Hunn, J.D. (1968). Geohydrology and ground-water potential of Lake County, Indiana: Indiana Department of Natural Resources, Division of Water, Bulletin 31.
- Saxena, V.K. (2004). Geothermal Resources of India, Allied Publishers, Pvt. Ltd., 48-70.
- Srinivasamoorthy, K. (2005). Hydrogeochemistry of groundwater in Salem district, Tamilnadu, India. Unpublished Ph.D. Thesis, Annamalai University, 355.
- Srinivasamoorthy, K., Chidambaram, M., Prasanna, M.V., Vasanthavigar, M., John Peter, A. and Anandhan, P. (2008). Identification of major sources controlling Groundwater Chemistry from a hard rock terrain – A case study from Mettur taluk, Salem district, Tamilnadu, India. J. Earth Syst. Sci. **117(1)**, 49-58.
- Stallard, R.F. and Edmond, J.M. (1983). Geochemistry of the Amazon river. The influence of geology and weathering environment on the dissolved load. *J. Geophysics. Res.*, **88**, 9671-9688.
- Trusdell A.H. and Jones, B.F. (1973). Wateq: A computer program for calculating chemical equilibria of natural waters. J. Research USGS., **2(2)**, 233-248.