Article

Hydrochemistry of groundwater from Sarabanga Minor Basin, Tamilnadu, India

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Abstract

The study area Sarabanga, forms an important Minor river basin of river Cauvery, situated in Salem district. The study area being a hard rock terrain with minimal rainfall and large extraction of groundwater for domestic, irrigational and industrial purposes have threatened the groundwater environment both in the terms of quality and quantity. Hence an attempt has been made to identify the major geochemical process activated for controlling the ground water chemistry. Groundwater was generally alkaline with higher EC values. The dominance of anions and cations were of the order of $Cl > HCO_3 > SO_4 > NO_3 > PO_4$ and $Na > Ca > Mg > K$. The plot for Na/Cl to EC indicates Na released from silicate weathering and Cl from anthropogenic activities. The plot for $Ca+Mg$ to SO_4+HCO_3, indicates ion exchange process. The plot of $Na-Cl$ to $Ca+Mg-HCO_3-SO_4$ confirms that Ca, Mg and Na concentrations in groundwater are derived from aquifer materials. Thermodynamic plot indicates that groundwater is in equilibrium with kaolinite, muscovite and chloride minerals. In general, water chemistry is guided by complex weathering process, ion exchange along with influence of Cl ions from anthropogenic impact.

Keywords groundwater; hydrochemistry; Sarabanga Minor Basin.

1 Introduction

Groundwater quality appraisal is gaining importance, due to intense urbanisation, industrialization and agricultural activities putting the soil and groundwater to greater risk of contamination (Ackah et al., 2011; Sayyed and Wagh, 2011; Tiwari, 2011). Water pollution also threats human health, economic development and social prosperity (Milovanovic, 2007). The chemical composition of groundwater is controlled by many factors, including the composition of the precipitation, geological structure, mineralogy of the watersheds, aquifers, geological processes within the aquifer along with influence of external pollution agencies like effluents from agricultural return flow, industrial and domestic activities. An understanding the geochemical evolution of groundwater is important for a sustainable development of water resources in the present state of art. Demarcating the character of the groundwater in varied space, was proved to be an important technique in solving different geochemical problems (Chebotarev, 1955; Hem 1959; Back and Hanshaw, 1965; Srinivasamoorthy et al., 2011). Calculation of minerals saturation index and thermodynamic equilibrium studies (Garrels and Christ, 1965) to decipher the possible reactant and product minerals. The study area gains its own importance by its location in hard rock terrain, frequent failure in monsoon, highly industrialized and

urbanized zone all of which contributes for a proper appraisal of the chemical quality of groundwater in the study area.

2 Study Area

The Sarabanga sub basin lies between north latitudes 11° 30′ to 11° 55′ N and east longitudes 77° 40′ to 78° 13′ E with a total spread of 1089 sq. km. It originates at Shevaroy hills at the altitudes of 1200m in Salem district and configures river Cauvery at Pudupalayam in Namakkal district. The total river course of the river is about 65.69 km towards northwest and southwest of Salem town. The geology is composed of Granites like Charnockites, Magnetite Quartzite and Peninsular gneiss along with Syenites. Hills, undulating plains, plateaus, pediments and bazadas are the mixture of geomorphic units. Northern parts of study area include hill ranges and high land where eastern and southeastern parts are low lying due to the configuration of the river into river Cauvery. Groundwater in study area occurs in weathered portion of rock along joints and fratures. Weathered layer thickness in gneissic terrain ranges from 2.2 to 50 m. In charnockite weathered layer, thickness was between 5.8 and 55m. Groundwater occurs under semi-confined conditions in the alluvium along the river course. Water table fluctuation in the study area ranges from 0.2 to 13.05m BGL (Below Ground level) (Srinivasamoorthy et al., 2009).
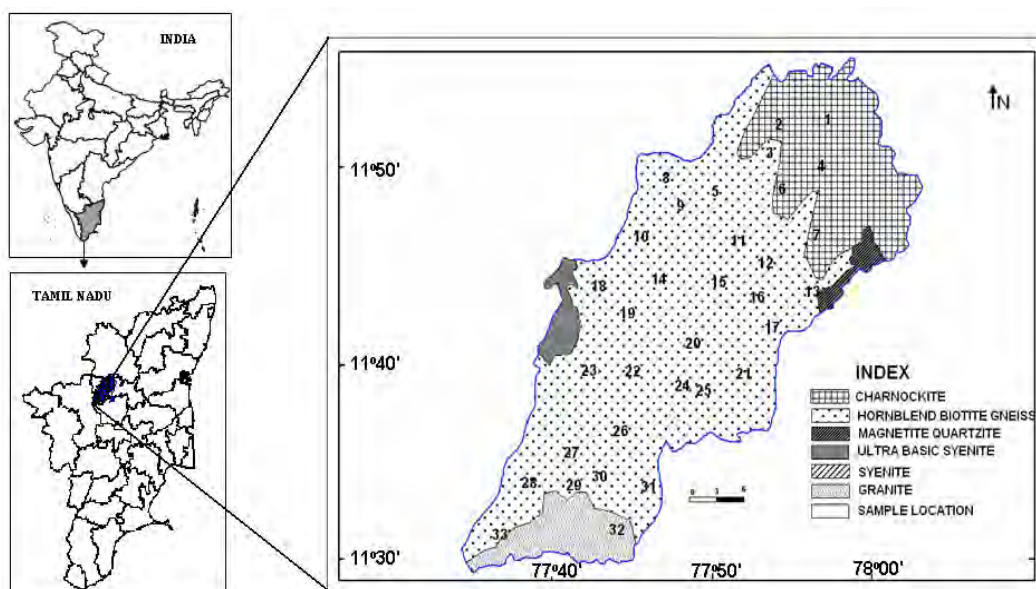

Fig. 1 Location, geology and sampling points of the study area.

3 Material and Methods

A total of 33 representative groundwater samples were collected (Fig. 1) during Pre Monsoon Season, covering the enter litho units of the study area. The sample were filtered 0.45 m Millipore filters and immediately stored in polyethylene bottles and analyzed for major and minor cations and anions using standard procedures (APHA, 1995). The pH and conductivity were measured *in situ* by pH conductivity meter model CONSORT C425. Ions like bicarbonate, Chloride, Calcium and Magnesium were analyzed using Titration. Fluoride 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). Sodium and Potassium were determined by using flame photometer (Systronics mk-1/mk-III).The analytical precision for

the measurements of ions was determined by calculating the ionic balance error that varies by about 5–10%. TDS/EC ratio is 0.50/1.0 (with excess of anions in water).

4 Results and Discussion

Groundwater in general was alkaline in nature and with higher EC values (Avg.2136.65). HCO_3 ranges from 195.2 to 2013.42 with an average of 507.2 mg/l. SO_4 ranges from 1.13 to 128.9 with an average of 27.3 mg/l. Fluoride and NO_3 were ranging from 0.0 to 2.8 and 0 to 133 mg/l with averages of 1.02 and 61.8 respectively (Table 1). The general dominance of anions were in the order of Cl > HCO3 > SO_4 > NO_3 > PO_4. For cations Na ranges from 19.9 to 2870 with an average of 403.4 mg/l. K was lesser with 0.4 to 450.9 with an average of 36.6 mg/l. Ca and Mg ranges from 16.0 to 86.26 and 4.8 to 140.94 with averages of 45.0 and 43.2 mg/l respectively. The general dominance of cations was in the order of Na > Ca > Mg > K. Silica ranges form 9.9 to 144.6 with an average of 67.9 mg/l.
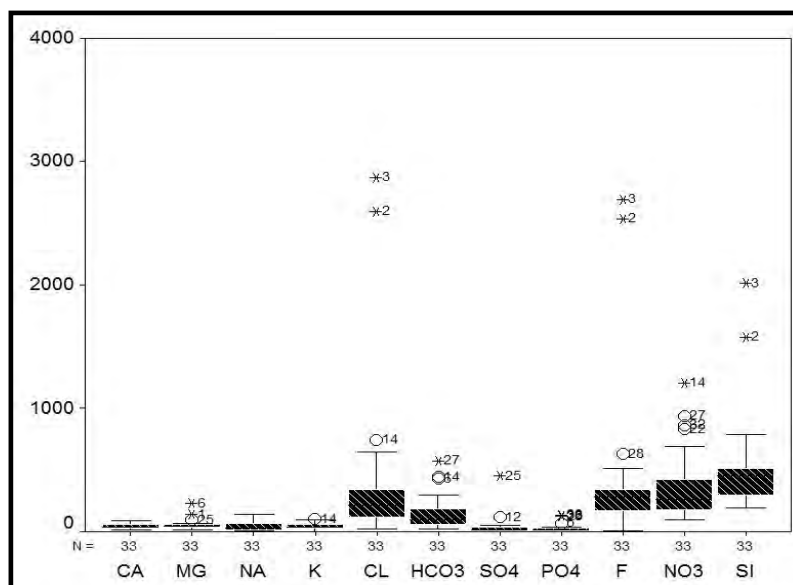

Fig. 2 Box plots for the major ion constituents in groundwater

Box plots were used to represent temporal concentration of the major ions (Fig. 2). The upper and lower quartiles of the data define the top and the bottom of a rectangle box. The line inside the box represents the median value and the size of the box represents the spread of the central value (Taheri and Voudouris, 2008). The ions like Cl, F, HCO_3, NO_3 and Si shows increasing trend due to the effective leaching from rock matrix along with anthropogenic activities (Srinivasamoorthy et al., 2008). HCO_3 is mainly formed due to the action of atmospheric CO_2 and CO_2 released from organic decomposition (Bouwer, 1978). The concentration of Silica is due to weathering of feldspar and sources for chloride is due to leaching from soil due to industrial, domestic activities and dry climate (Stallard and Edmond, 1983). The sources of SO_4 is known to be derived from industrial effluents, automobile emissions, and phosphatic fertilizers in urban environments (Subbarao et al., 1996), since no lithogenic sources of sulfate noted in the study area (Srinivasamoorthy et al., 2009). Nitrogen in groundwater derived from organic industrial effluents, fertilizer or nitrogen-fixing bacteria, leaching of animal dung, sewage, and septic tanks through soil and water matrix to groundwater. In general,

increase of nitrate in groundwater may be an indicator of bacterial pollution (Sundaray et al., 2009). The statistics of the chemical components of the groundwater chemistry is given along with comparison from WHO (1993) and its desirable health effects. The large variations in mean, median and standard deviation values of ions suggest that the water chemistry in the study region is heterogeneous and influenced by complex hydrogeochemical process and complex contaminant sources (Vasanthavigar et al., 2012).

The results from the water analysis were used as a tool to identify the process and mechanisms affecting the chemistry of groundwater from the study area. Gibbs (1970) plot is used to determine the mechanism controlling the water chemistry (Fig. 3). The Samples represents in rock dominance and precipitation zones indicating chemical weathering of rock-forming minerals and evaporation are the primal factors influencing the groundwater quality suggesting precipitation induced chemical weathering along with dissolution of rock forming minerals.

Table 1 Comparison of water quality parameters with WHO (1993) and statistics of water chemistry

| Parameters	WHO International Standard (1993)		Results of chemical analysis of groundwater samples (all values in mg/l except pH and EC in μs/cm)			Undesirable effects
	Most desirable limit	Maximum allowable limit	Max	Min	Avg	
pH	7-8.5	9.2	8.6	7.3	8.0	Taste
TDS (mg/l)	500	1,500	4380.0	247.0	1395.9	Gastrointestinal irritation
Na (mg/l)	-	200	2870.0	19.9	403.5	-
Ca (mg/l)	75	200	86.3	16.0	45.1	Scale formation
Mg (mg/l)	50	150	140.9	4.8	43.2	
Cl (mg/l)	200	600	2694.1	10.6	418.3	Salty taste
SO_4 (mg/l)	200	400	128.9	1.1	27.3	Laxative effect
NO_3 (mg/l)	45	-	133.0	0.0	61.9	Blue baby
F (mg/l)	-	1.5	2.8	0.0	1.0	Fluorosis
HCO_3 (mg/l)	384	-	2013.4	195.2	507.3	Corrosion of pipes
K (mg/l)	-	30	450.9	0.4	36.7	Depression, muscle weakness, heart rhythm disorder and confusion
Si (mg/l)	-	-	144.6	9.9	67.9	disturb phosphorilation
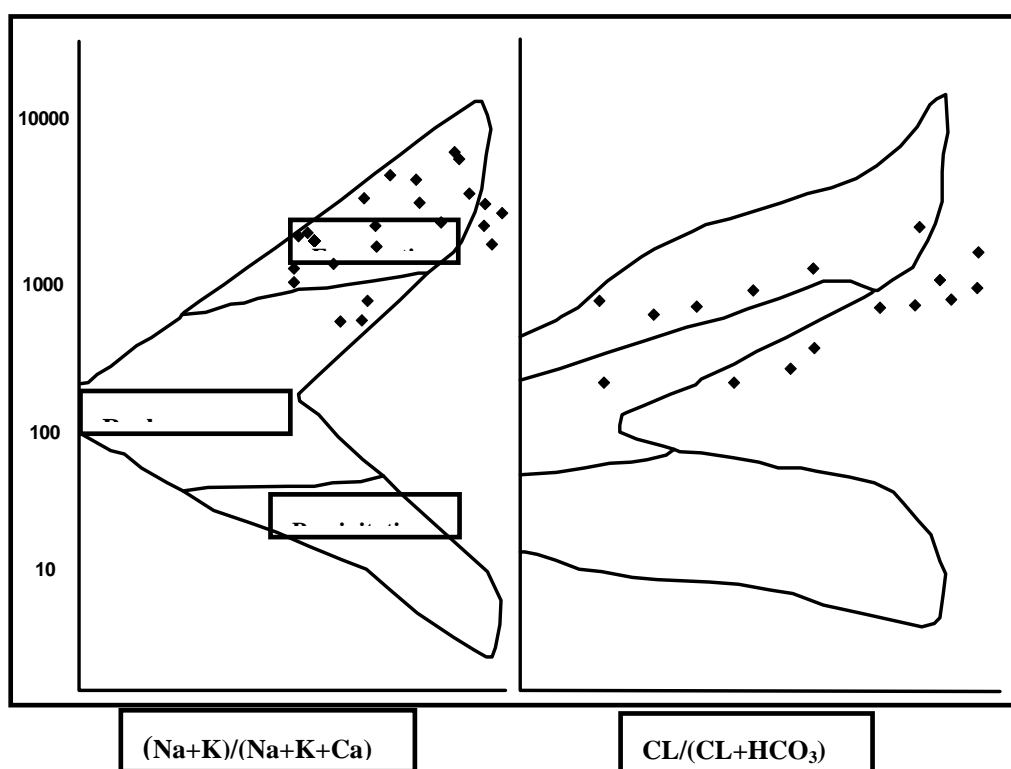
Fig. 3 Gibbs plot for the groundwater samples.

4.1 Ionic ratios

The (Ca+Mg) v*ersus* TZ$^+$ plot (Fig. 4A) lie far below the equiline with average equilibrium ratio of 0.40 to 0.35 indicating the contribution of alkalis (Na and K) as like that of alkaline earth (Ca and Mg) due to leaching from silicate weathering, from the aquifers of the study area . In the plot for (Ca +Mg) *versus* HCO$_3$, the data points fall away from equiline 1:1 to 2:1, indicating the predominance of alkali earth over bicarbonate due to silicate weathering. Minor representations in bicarbonate is also due to the reaction of the feldspar minerals with carbonic acid in the presence of water, releasing HCO$_3$ (Elango et al., 2003) (Fig. 4B). The plot for (Na + K) *versus* TZ$^+$ (Fig. 4C) indicates weathering of both alkali and alkali earth from Feldspars along with additional sources from alkali/saline soil and residence time. The plot for Na *versus* Cl (Fig. 4D) shows that, majority of samples fall near Cl and Na zones indicating Na derived from silicate bearing minerals and Cl from anthropogenic sources including fertilizer, road salt, human and animal waste, and industrial applications, since due to the rare Cl bearing minerals in silicate terrain and rapid transportation of chloride through soil into the groundwater environments (Stallard and Edmond, 1983), which is evidenced from Cl levels of the study area. The plot for Na/Cl *versus* EC (Fig. 5A), the Na/Cl decreases when EC increases with higher Na/Cl ratio, indicating Na released from silicate weathering process. This is also supported by higher HCO$_3$ values in groundwater due to reaction of feldspar minerals with carbonic acid, as one of the reasons for increase in EC (Jankowski and Acworth, 1997). The plot Ca +Mg *versus* SO$_4$+HCO$_3$, the pointer of ion exchange process shifts the points to the right side of the plot due to excess SO$_4$+HCO$_3$. If reverse ion exchange is the process, points shift left due to excess Ca+Mg. In the present study, the point clusters around the equiline 1:1 and falls in SO$_4$ +HCO$_3$ indicating the ion exchange process due to excess bicarbonate (Fig. 5B). The plot of Na−Cl

versus Ca+Mg−HCO$_3$−SO$_4$ confirms that Ca, Mg and Na concentrations in the groundwater is derived from aquifer materials (Fig. 5C) (Srinivasamoorthy et al., 2008).
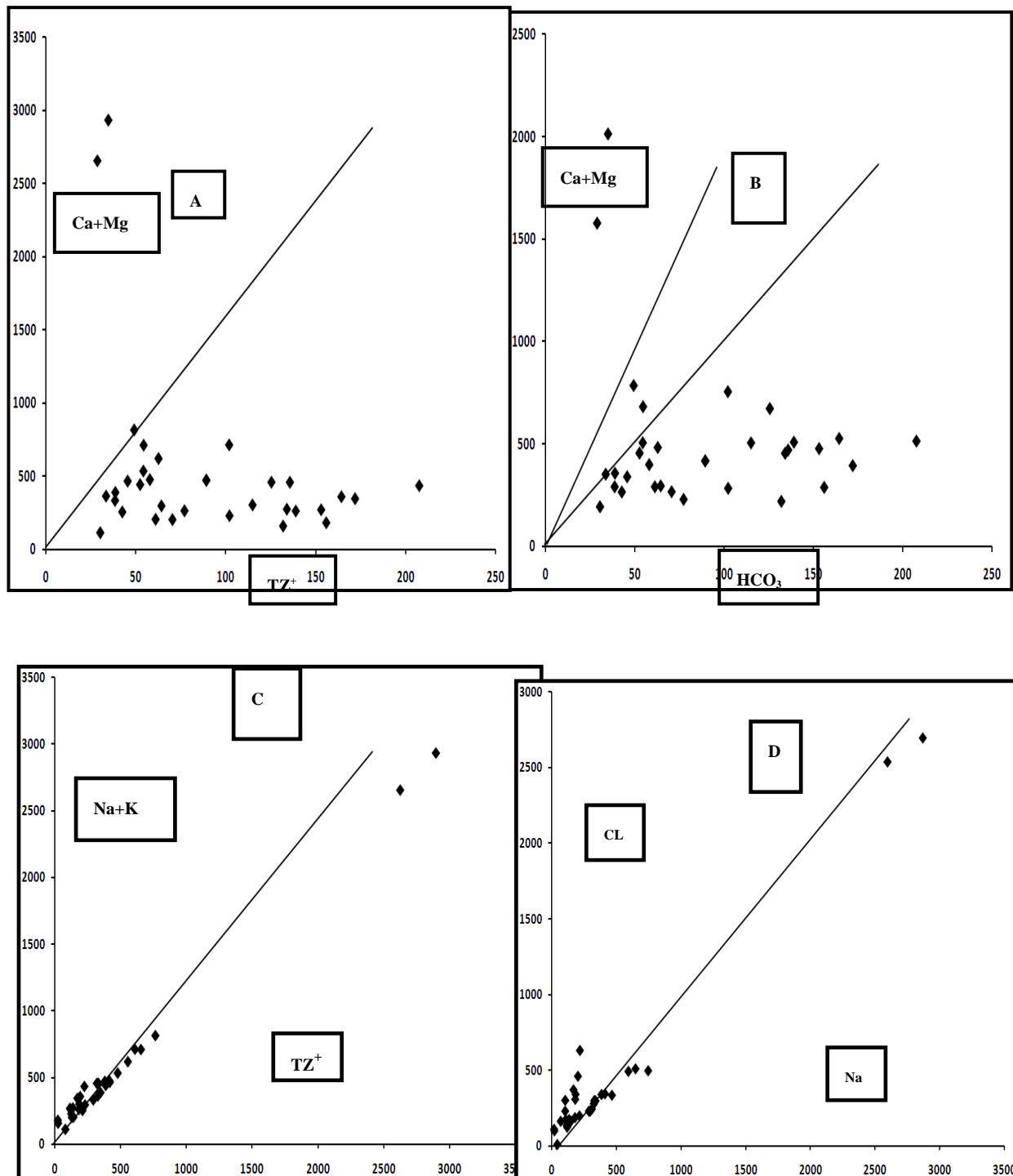

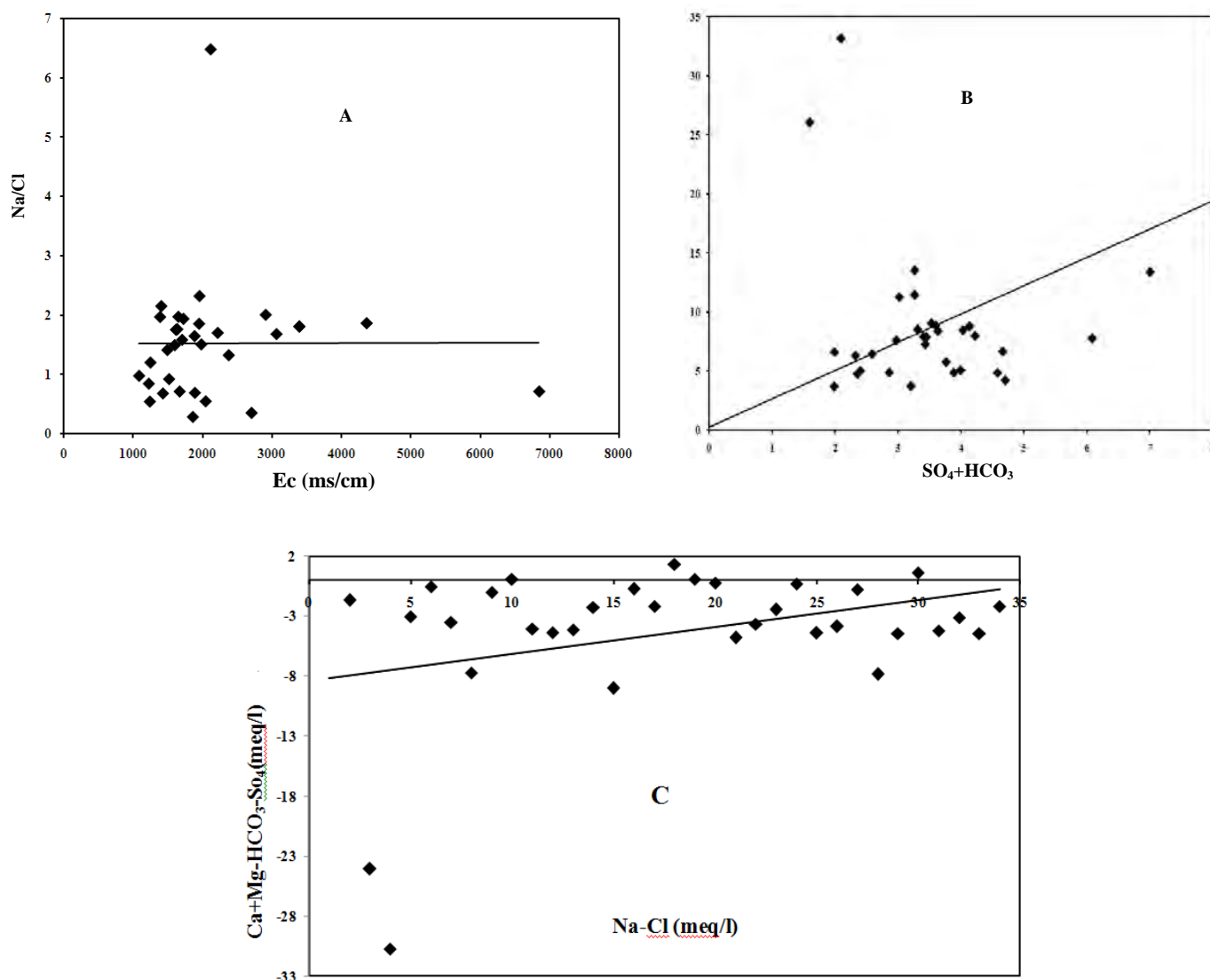
Fig. 4 (A-D) Plot for relationship of ions.

Fig. 5 (A-C) Plot for relationship of ions

4.2 Thermodynamic stability

Thermodynamic plotting of [Na]/H, [K]/H,[Ca]/H and [Mg]/H, for groundwater from study area are plotted on the stability diagram as a function of [H_4SiO_4]. In plot for Ca, the samples (Fig. 6A) clusters in Kaolinite field indicating impact of dilution. In the plot for Magnesium (Fig. 6 B) shift of stability from Kaolinite to Chlorite is noted, indicating the formation of new clay minerals due to supply of excess cations and Silica to pre-existing Kaolinite from aquifer materials. The plot of Na falls in the Kaolinite stability field, indicating Na–Feldspar incongruent dissolution produces Kaolinite (Fig. 6 C) (Jacks, 1973). The plot of K silicates (Fig. 6D) indicates incongruent dissolution of Kaolinite and formation of Muscovite. Majority of samples fall in Kaolinite and Muscovite field. When the Ionic Activity Product (IAP) of Potassium increases, the pH remains constant, resulting in the shift of plots from Kaolinite to Muscovite field along with release of H+ ions which combines with HCO_3 to form CO_2 (Karanth, 1997).
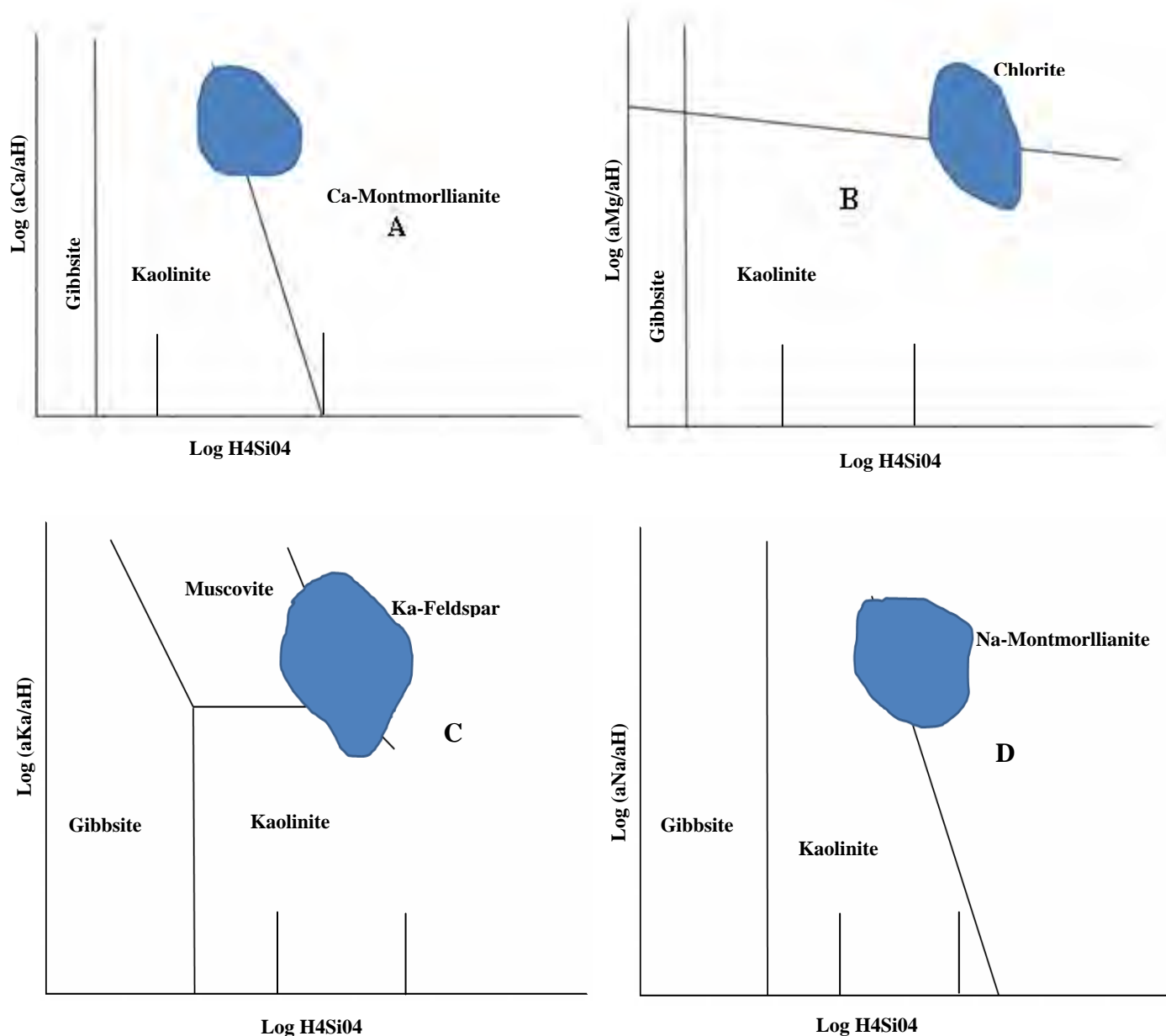
Fig. 6 Thermodynamic stability plot for (A) Ca, (B) Mg, (C) Na and (D) K System.

4.3 Disequilibrium indices

Disequilibrium indices log (IAP/KT) was calculated by WATEQ4F geochemical model for the minerals and other solids stored in the model data bank for which the dissolved constituents are reported in groundwater analysis. Disequilibrium indices of log (IAP/KT) indicate: if the groundwater is in thermodynamic equilibrium, the log (IAP/KT = 0), and when it is oversaturated log (IAP/KT > 0) and during under saturated log (IAP/KT < 0) with respect to certain solid phases (Trusdell and Jones, 1973; Drever, 1988). The disequilibrium indices of silicate minerals (Fig. 7) Chalcedony, Christobalite and Quartz were represented from the data bank of WATEQ4F to represent the dissociation factors in the study area. The status of groundwater in the study area indicates all the minerals phases are in the state of oversaturation to equilibrium.

The disequilibrium indices of carbonate minerals (Fig. 8) Aragonite, Calcite, Dolomite and Magnesite were represented from the data bank of WATEQ4F. The samples are oversaturated to equilibrium with Aragonite, Calcite, Dolomite and Magnesite with minor indications in undersaturation state. In general, carbonate results show that Calcite, Dolomite and Magnesite are saturated to-oversaturated which is indicated by excess input of Ca and Mg ions from silicate weathering process.
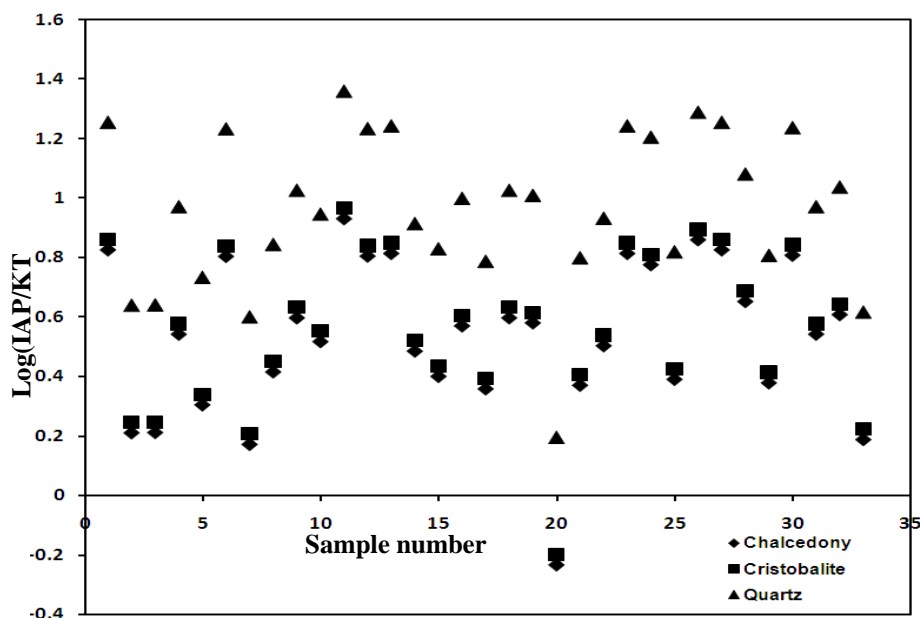

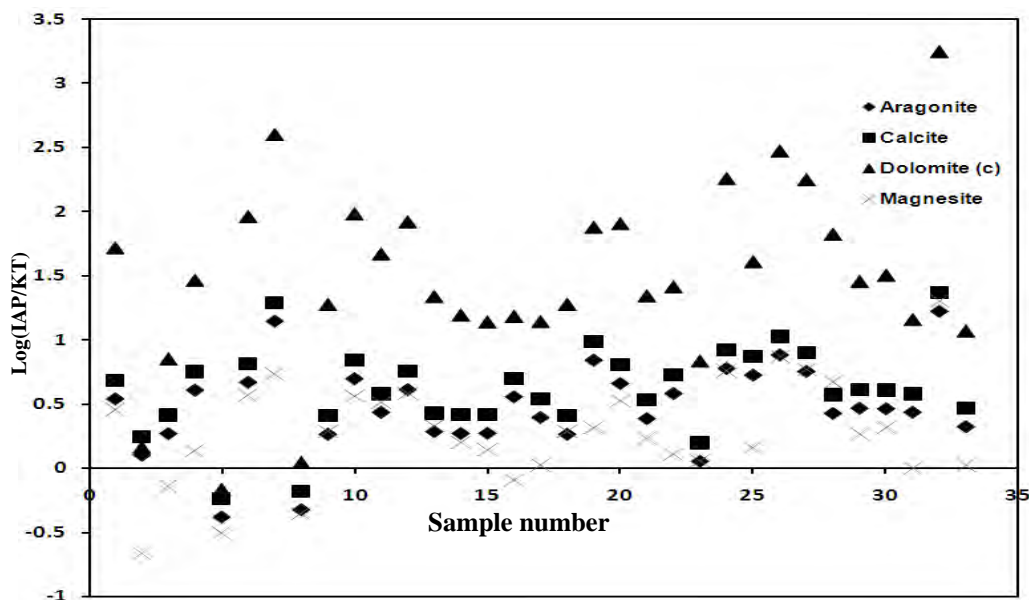**Fig.7** Disequilibrium indices for silicate minerals.

Fig. 8 Disequilibrium indices for carbonate minerals

5 Conclusions

The groundwater in Sarabanga region is a unique example for the impact of weathering, ion exchange and anthropogenic process controlling water chemistry. The chemical composition of groundwater of the study area is strongly influenced by rock water interaction, dissolution and deposition of silicates group of minerals. Weathering of silicate minerals controls the major ion chemistry of calcium, magnesium, sodium and potassium. Cl was dominant due to anthropogenic impact (human sources). The ion exchange and reverse ion exchange controls the water chemistry of the study area. Thermodynamic plot indicates, groundwater is in equilibrium with kaolinite, muscovite and chlorite minerals. SI of minerals indicates oversaturation and undersaturation of silicate and carbonate minerals with respect to pre-monsoon seasons. In general, water chemistry is guided by lithological influences on water chemistry by complex weathering process, ion exchange along with influence of Cl ions from anthropogenic impact.

References

Ackah M, Agyemang O, Anim AK, et al. 2011. Assessment of groundwater quality for drinking and irrigation: irrigation: the case study of Teiman-Oyarifa Community, Ga East Municipality, Ghana. Proceedings of the International Academy of Ecology and Environmental Sciences, 1(3-4): 186-194

APHA. 1996. Standard Methods for the Examination of Water and Waste Water. American Public Health Association, USA

Back W, Hanshaw B. 1965. Chemical Geohydrology Advances in Hydroscience (Back W, Hanshaw B, eds). Academic Press, USA

Bouwer H. 1978. Groundwater Hydrology. McGraw-Hill, USA

Cheboterev II. 1955. Metamorphism of natural waters in the crust of weathering-I. Geochimica et Cosmochima Acta, 8(1-2): 22-48

Drever JI. 1988. The Geochemistry of Natural Waters. Prentice Hall, New Jersy, USA

Elango L, Kannan R, Senthil Kumar M. 2003. Major ion chemistry and identification of hydrogeochemical processes of groundwater in part of Kancheepuram district, Tamil Nadu. Indian Journal of Environmental Geoscinces, 10(4):157–166

Garrels RM, Christ CL 1965. Solutions Minerals and Equilibria. Harper and Row, New York, USA

Gibbs RJ. 1970. Mechanisms controlling world water chemistry. Science, 170: 1088-1090

Hem JD. 1959. Study and interpretation of the chemical characteristic of natural water. Water Supply Paper 2254, USGS, USA

Jacks G. 1973. Chemistry of some groundwaters in igneous rocks. Nordic Hydrology, 4: 207-236

Jankowski J, Acworth RI. 1997. Impact of debris flow deposits on hydrogeochemical processes and the development of dry land salinity in the Yass river catchment, New South Wales, Australia. Hydrogeology, 5(4): 71–88

Karanth KR. 1987. Groundwater Assessment, Development and Management. Tata McGraw-Hill Publishing Company Limited, New Delhi, India

Milovanovic M. 2007. Water quality assessment and determination of pollution sources along the Axios/ Vardar River, Southeastern Europe. Desalination, 213: 159-173

Sayyed MRG, Wagh GS. 2011. An assessment of groundwater quality for agricultural use: a case study from solid waste disposal site SE of Pune, India. Proceedings of the International Academy of Ecology and Environmental Sciences, 1(3-4): 195-201

Srinivasamoorthy K, Chidambaram S, Prasanna MV, et al. 2008. Identification of major sources controlling Groundwater Chemistry from a hard rock terrain- A case study from Mettur taluk, Salem district, Tamilnadu, India. Journal of Earth System Sciences, 117(1): 49–58

Srinivasamoorthy K, Nanthakumar C, Vasanthavigar M, et al. 2011. Groundwater quality assessment from a hard rock terrain, Salem district of Tamilnadu, India. Arabian Journal of Geosciences, 4(1): 91-102

Srinivasamoorthy K, Chidambaram S, Vasanthavigar M. 2009. Application of multivariate statistical techniques in elucidation of hydrogeochemical data: a case study. International Journal of Ecological and Environmental Statistics, 14(S09): 98-109

Stallard RF, Edmond JM. 1983. Geochemistry of the Amazon River 2. The influence of geology and weathering environment on the dissolved load. Journal of Geophysical Research, 88: 9671-9688

Subbarao C, Subbarao NV, Chandu SN. 1996. Characterization of groundwater contamination using factor analysis. Environmental Geology, 28: 175-180

Sundaray SK, Nayak BB, Bhatta D. 2009. Environmental studies on river water quality with reference to suitability for agricultural purposes: Mahanadi river estuarine system, India—a case study. Environmental Monitoring and Assessment, 155: 227-243

Taheri TA, Voudouris KS. 2008. Groundwater quality in the semi-arid region of the Chahardouly basin, West Iran. Hydrological Processes, 22: 3066-3078

Tiwari RN. 2011. Assessment of groundwater quality and pollution potential of Jawa Block Rewa District, Madhya Pradesh, India. Proceedings of the International Academy of Ecology and Environmental Sciences, 1(3-4): 202-212

Trusdell AH, Jones BF. 1973. Wateq: A Computer Program for Calculating Chemical Equilibria of Natural Waters. National Technical Information Service, VA, USA

Vasanthavigar M, Srinivasamoorthy K, Rajiv Ganthi R, et al. 2012. Characterisation and quality assessment of groundwater with a special emphasis on irrigation utility: Thirumanimuttar sub-basin, Tamil Nadu, India. Arabian Journal of Geosciences, 5(2): 245-258

WHO. 1993. Guidelines for Drinking-water Quality (2nd edition) (Vol 1 Recommendations). World Health Organization, Geneva, Switherland