Geosciences 2011; 1(1): 16-25
DOI: 10.5923/j.geo.20110101.02

Use of Hydrochemistry and Stable Isotopes as Tools for Groundwater Evolution and Contamination Investigations

Srinivasamoorthy Krishnaraj[1,*], Vasanthavigar Murugesan[2], Vijayaraghavan K[2], Chidambaram Sabarathinam[2], Anandhan Paluchamy[2], Manivannan Ramachandran[2]

[1]Department of Earth Sciences, Pondicherry University, Puducherry, 605014, India
[2]Department of Earth Sciences, Annamalai University, Annamalainagar, Tamilnadu, 608002, India

Abstract Hydrochemical and isotopic studies in groundwater was attempted in a basin to gain knowledge on geochemical evolution and water quality status. The results of the chemical analysis indicate the sources of ions into the groundwater are from dissolution and leaching from source rocks, cation exchange and anthropogenic activities. The saturation index calculated specify oversaturation of carbonate species and undersaturation of amorphous silica indicating groundwater chemical evolution controlled by water rock interactions. Water type alters from Ca-HCO_3 to Na-Cl indicating groundwater chemistry controlled by rock-water interaction and anthropogenic activities. The plots of various ionic ratios point out groundwater chemistry affected by ion exchange process, silicate and carbonate weathering along with anthropogenic activities. The isotopes of δ^2H versus $\delta^{18}O$ signify ionic concentration increases along the groundwater flow direction along lower elevations. The water type's classification designate 5 distinct groups ranging from low EC and highly depleted isotopes to very high EC with enriched stable isotopic composition indicating longer residence time of groundwater.

Keywords Ionic Ratios, Stable Isotopes, Hydrogeochemistry, WATEQ4F, Thirumanimuttar

1. Introduction

Groundwater is a valuable resource in many areas, and it commonly plays a key role in the economic development. Recently, water demand has increased rapidly with the construction of energy, development of industry, agriculture, urbanization, improvements in living standards and eco-environment construction. The chemical composition of groundwater is controlled by many factors, including the composition of the precipitation, geological structure and mineralogy of the watersheds and aquifers and the geological processes within the aquifer. The interaction of all factors leads to various water types. In many areas, particularly arid and semi-arid zones, groundwater quality limits the supply of potable fresh water. To utilize and protect valuable water resources effectively and predict the change in groundwater environments, it is necessary to understand the hydrochemical characteristics of the groundwater and its evolution under natural water circulation processes (Lawrence *et al.,* 2000; Edmunds and Ma, 2006. The study area Thirumanimuttar sub basin, a hard rock terrain receives major part of rainfall from northeast monsoon. The surface water sources are generally precarious to get their supply during monsoon seasons and in non monsoonal periods people have to largely depend on groundwater resources for their domestic, agricultural and industrial activities. Although aquifers in the study area are intensively exploited prior to the present study, little was known about the major hydrogeochemical process that controls the observed water chemistry. Similarly the origin of elevated concentrations of elements and the vulnerability of the aquifer to pollution were equally unclear. A growing population and increased agricultural and industrial activities in the area have resulted in deterioration of water resources. In the present study, a detailed investigation was carried out with the objective of identifying hydrochemical processes and their relation to groundwater quality Zongyu Chen et al., 2006; Franco Cucchi et al., 2007; Guangxin Zhang et al., 2007; Aji et al., 2008; Prasanna et al., 2009; Janza, M. 2010; Kebede et al., 2010; Latifa et al., 2011; Dickson et al., 2011 Ruiqiang et al., 2011.

2. Materials and Methods

Study Site Description

Thirumanimuttar basin lies between North Latitudes 10°58′ and 11°48′ East Longitudes 77°53′ and 78°21′ with a

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* Corresponding author:
krishnarajsrinivasamoorthy@gmail.com (Srinivasamoorthy Krishnaraj)

total drainage of about 2438 km^2 (Fig. 1).

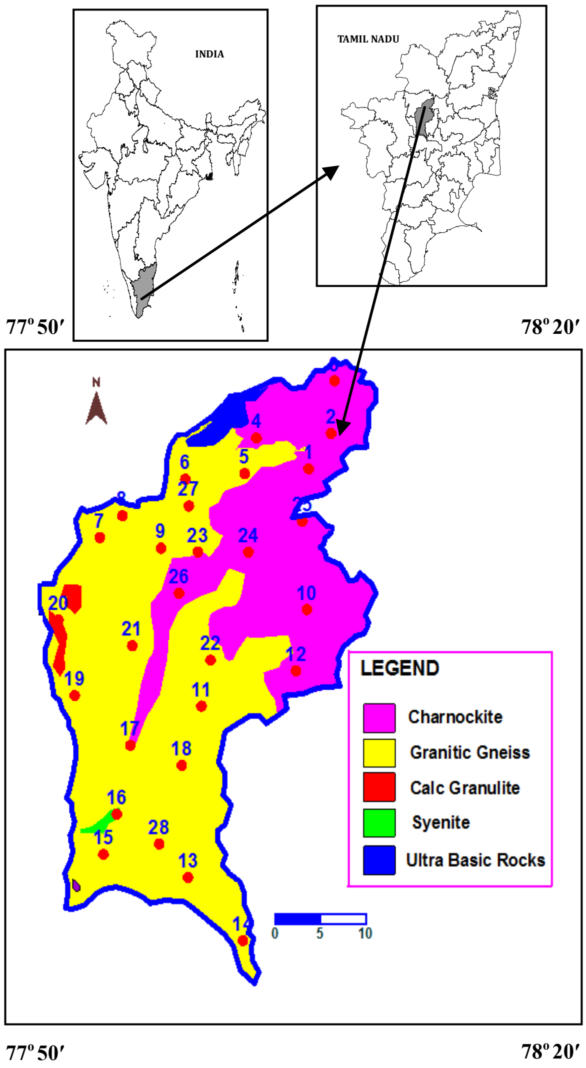

Figure 1. Geology and sampling location map of the study area

It originates at Salem district and configures river Cauvery at Namakkal district in Tamilnadu state, India. The mean temperature varies from 20°C to 45°C. The normal annual rainfall over the study area is about 900 mm. The basin is characterized by hills (986m amsl) in the northern parts and slopes towards south (104m amsl). The geology of the study area is underlined by rocks representing metasediments of Archaean age with major litho units encompassing Charnockites, granitic gneiss, calc granulites, syenite and ultra basic as major exposures. Geomorphology of the study area is dominated by Alluvial plain, Bajadas, colluvial plain, deep pediment, hill, pedeplain and structural hills. Drainage is mostly of dentritic and trellis type. Groundwater occurrence in the study area is mainly associated with development of secondary porosity as a result of weathering and fissures along with development of fractures. The distinct dry and wet season have facilitated deep weathered and regolith under semi arid climatic conditions. The depth of weathering ranges from 2.2 to 50 m, while the fractures in rocks extend to 100 m depth. Most of the dug wells are confined to the weathered zone, while the bore wells extends into the fractured zone. Water table depth reaches low 0.2 m during monsoon (August-January) and decline below 13.5m during summer (March-July) (Vasanthavigar *et al.,* 2010). Groundwater occurs in the weathered residium under unconfined conditions as well as in the fractured rocks under semi confined conditions. Groundwater development is by shallow open wells and deep bore wells.

Major Ion Chemical Analysis

To assess water chemistry values under natural conditions twenty four groundwater samples in the study area were collected during Pre monsoon (PRM) May season from long-term groundwater observation wells and drinking wells. Each sample was collected in acid-washed polyethylene 1000 ml bottle with strict adherence to the sampling protocol as described by Gale and Robins (1989). Samples were filtered using a 0.45 lm cellulose acetate filter membrane. The bottles were tightly capped to protect samples from atmospheric CO_2, adequately labeled, and preserved in the refrigerator until they were taken to the laboratory for measurement. Precaution was also taken to avoid sample agitation during transfer to the laboratory. Deuterium and Oxygen –18 samples were collected unfiltered in 30 ml glass bottles with poly-sealed lids during PRM. Before taking readings, pumping was carried out until the meter readings were stable for each parameter. Samples were analyzed in the laboratory for the major ions chemistry using standard methods (APHA, 1995). Calcium (Ca) and magnesium (Mg) were determined titrimetrically using standard EDTA. Chloride (Cl) was determined by standard $AgNO_3$ titration. Bicarbonate (HCO_3) by titration with HCl. Sodium (Na) and potassium (K) by flame photometry. Electrical Conductivity (EC), pH, and Total Dissolved Solids (TDS) were measured by Water Quality Analyzer. Sulphate (SO_4), Phosphate (PO_4) and Silicate (H_4SiO_4) was determined by spectrophotometer. Nitrate (NO_3) and Fluoride (F) were analyzed by using ion sensitive electrode. Stable isotope analyses were performed at Indian Institute of Technology, Kharakpur, India. Care was taken that the pH, EC, HCO_3 and Ca were analyzed within 24 hours of sampling. The quantity controls of the measurements consisted of duplicate samples.

3. Results and Discussion

Statistics

In the groundwater samples pH value ranges from 6.4 to 8.0 with an average of 7.4. The increase in pH is explained by the consumption of dissolved CO_2 gas by organisms and aquatic plants (Njitchoua *et al.,* 1997) whereas the decrease of this parameter is primarily due to oxidation of organic matter and also due to human induced pollution (Table 1). Higher pH was noted in locations like 6, 13, 24 and 27 indicating pollution sources. Concentration of TDS, a measure of quality ranged from 488.3 to 3441.0 mg/l with an average of 1499.9 mg/l.

According to TDS classification 84% of the samples belonged to brackish type (TDS > 1000 mg/l) and the remaining 14% represented fresh water (TDS < 1000 mg/l). The electrical conductivity values range from 763.0 to 5,376 µs/cm at 25°C, averaging 2336 µs/cm. Anomalous high value noted in location 27, is noticed near the channels carrying industrial discharge and urban sewage disposals and accumulation of leaching chemicals. Sodium is the most abundant cation in groundwater, it varies from 5.1 to 1061 mg/l with an average of 232.8 mg/l. Calcium varies in concentration ranging from 15.9 to 147.9 mg/l, with average of 77.3 mg/l. The sources of sodium and calcium in the groundwater are from the minerals like silicates, feldspars, pyroxenes and amphiboles identified in the rock types of the study area. High concentration of Na and Ca in the groundwater is attributed to cation exchange among minerals (Subramanian and Saxena, 1983). Magnesium concentration ranges from 22.0 to 170.2 mg/l with an average of 65.4 mg/l. The sources of magnesium are due to leaching of minerals like Dunite, Olivine, Augite, Biotite and Hornblende from the major litho units of the study area. Potassium ranges from 1.5 to 325.0 mg/l with an average of 34.3 mg/l. Due to the resistance of potassium bearing minerals (Orthoclase, Microcline and Biotite), Potassium is generally lower in groundwater, but abnormal concentrations in certain locations may be due to human intervention (Subbarao *et al.,* 1999). The chloride in groundwater ranges from 79.7 to 1453.5 mg/l, with average value of 437.7 mg/l. Due to the absence of chloride bearing minerals in the study area anomalous high Cl might have been derived from anthropogenic sources (Srinivasamoorthy *et al.,* 2008). The bicarbonate ion ranges from 183.0 to 854.2 mg/l with an average value of 403.3 mg/l. Due to the lack of carbonate rocks in the study area, the possible sources of bicarbonate include weathering from silicate minerals in addition to cations such as Ca, Mg and HCO_3 along with presence of organic matter in the groundwater which is oxidized to produce carbon dioxide, which in turn promotes dissolution of minerals. Nitrate ion in the study area ranges from 17.5 to 527.0 mg/l with an average of 170.5 mg/l. Sulphate ion ranges from 1.0 to7.7 mg/l with an average of 4.11 mg/l. Fluoride ions ranges from 0.1 to 4.3 mg/l with an average of 1.7 mg/l. Concentrations of NO_3 are the result of different pollution processes involving municipal wastewaters, fertilizers and the application of agricultural pesticides, among others. The highest NO_3 concentration levels were found in areas where large amounts of N fertilizers (commonly urea, nitrate or ammonium compounds) are used due to intensive agricultural practices (Srinivasamoorthy *et al.,* 2009). Sources of fluorides are from leaching of fluoride bearing minerals like apatite, hornblende and mica identified in the source rocks of the study area along with intensive irrigation, high rate of evapotranspiration and long residence time of waters in the aquifers (Wodeyar and Sinivasan, 1996; Subbarao, 2006). Silica in the groundwater ranges from 33.0 to 75.0mg/l with an average of 56.0 mg/l, higher concentration is mainly due to presence of silicate minerals from the litho units of the study area. The abundance of the major cations and anions in the groundwater are of the following order: Na>Ca>Mg>K and $Cl>HCO_3>NO_3>SO_4>F>PO_4$ respectively.

Saturation Indices

Mineral equilibrium calculations for groundwater are useful in predicting the thermodynamic control on the composition of groundwater and the approximate degree to which the groundwater has equilibrated with the various carbonate mineral phases such as Calcite, Dolomite, and Magnesite (Deutsch, 1997). By using the saturation index approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch, 1997). The saturation indices were determined using the hydrogeochemical equilibrium model, WATEQ4F for Windows (Ball and Nordstrom, 1991). The saturation index (SI) of a given mineral is defined as: $SI = \log_{10} (IAP/K_{SP})$ (Lloyd and Heathcode, 1985)

Table 1. Statistics of chemical parameters (all in mg/l, pH and EC in µS/cm)

Parameters	Max	Min	Avg	Std.Dev
Ca	147.9	16.0	77.3	31.4
Mg	170.2	22.0	65.5	28.9
Na	1061.0	5.1	232.8	249.5
K	325.0	1.5	34.3	68.0
HCO_3	854.3	183.0	403.4	158.0
PO_4	5.5	0.2	1.7	2.0
H_4SiO_4	75.0	33.0	56.0	10.3
Cl	1453.5	79.8	437.8	364.8
SO_4	7.8	1.0	4.1	1.8
NO_3	527.0	17.5	170.6	164.1
F	4.3	0.2	1.7	1.0
TDS	3441.0	488.3	1500.0	704.7
EC	5376.0	763.0	2336.9	1101.9
pH	8.0	6.4	7.4	0.4
$\delta^{18}O$	-1.1	-5.1	-2.9	1.1
$\delta^{2}H$	-4.5	-35.7	-20.3	7.8
Quartz	0.8	0.2	0.5	0.1
SiO_2 (a)	-0.4	-1.1	-0.8	0.2
Calcite	0.9	-4.4	0.2	0.9
Dolomite	2.0	-2.6	1.0	1.0
Anhydrite	-0.9	-5.9	-2.1	0.9
Gypsum	-0.7	-2.5	-1.7	0.5
PCO_2	-0.6	-2.8	-1.9	0.5

The IAP represents ion activity product and *K*sp is the solubility product at a given temperature. The thermodynamic data used in this computation were those contained in the default database of the 'WATEQ4F for Windows'. Supersaturation (SI > 0) indicates that precipitation is thermodynamically favorable in spite of the fact that slow rates of reaction can inhibit precipitation. On the other hand, undersaturation (SI < 0) signifies that dissolution is favored. The summary statistics of saturated indices of some of the common mineral phases is presented in Table 1. Nearly all of the water samples were oversaturated with respect to calcite and dolomite and undersaturated with respect to gypsum, suggesting that these carbonate mineral phases may have influenced the chemical composition of the study area. The results also indicate that the waters are likely to precipitate calcite and dolomite, while they are undersaturated with respect to gypsum mineral. As the saturation state indicates the direction of the process, precipitation is expected for calcite and dolomite and dissolution is expected for gypsum (Appelo and Postma, 1996). Taking into the consideration the semi arid climate and the result of evaporation are the sources for these ions into the groundwater environment (Srinivasamoorthy *et al.,* 2011). The groundwater is uniformly supersaturated with respect to quartz but undersaturated with respect to amorphous silica (Table 2) suggesting that amorphous silica possibly controls the silica concentration in the groundwater.

Hydrogeochemical Facies

The Hydrochemical water type of the groundwater samples from the study area is represented in Hill Piper diagram Fig. 2.

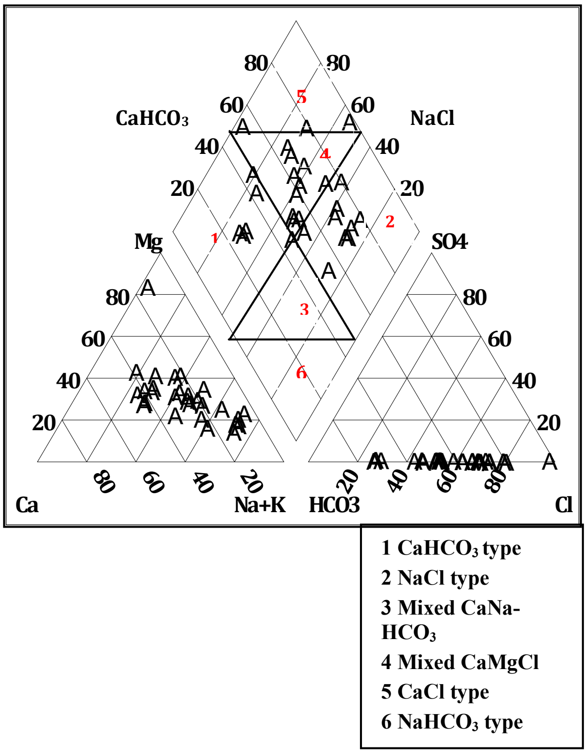

Figure 2. Piper trilinear diagram for Facies classification

The groundwater on the diamond diagram shows that the nearly all groundwater have a water type of alkali soil member are bigger than the alkali elements (Ca + Mg > Na + K). Weak acidic roots are bigger than the strong acidic roots (HCO_3 > Cl + SO_4) and Carbonate hardness is bigger than the 50%. Majority of groundwater samples represents Ca-HCO_3, mixed CaMgCl, CaCl, and NaCl types. The groundwater showed paths of hydrochemical evolution, from Ca– HCO_3 type via Ca–Cl type to Na–Cl type; or from Ca–HCO_3 type directly to Na–Cl type. This suggests that the groundwater hydrochemistry is controlled by water– rock interaction and anthropogenic pollution. Typical classification of hydrochemical Facies for groundwater is shown in Fig. 3.

The Ca-HCO_3 type occurred near the hilly terrains indicating the recharge zones. The concentration of TDS in the groundwater is mostly less than 1,000 mg/l, belonging to fresh water. The HCO_3 and Cl are the major anions and Ca is the major cation in the groundwater. In the intermediate zone of groundwater recharge and discharge areas, water type transformed into mixed Ca-Mg-Cl and Ca-Cl types. This type of water represented high TDS water in the central and southern parts of the study area ranging from 1,000 to 2,000 mg/l (sample nos. 13–15). The groundwater belonged to the slightly saline or the moderately saline water. The major anions in the groundwater were Cl, NO_3 and HCO_3 and the major cations were Na and K. (3) The Na-Cl type of water was dominant in the north eastern and north western part of the study area. The groundwater had strong evapotranspiration, and this groundwater type represented the high TDS, more than 2,000 mg/l belonging to the very saline water. The major anion and cation in the groundwater are Cl and Na respectively.

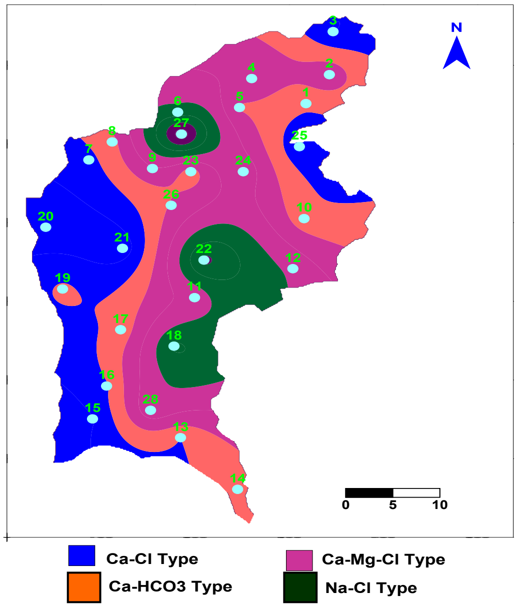

Figure 3. Spatial distribution pattern of hydrochemical Facies

Sources of Ionic Constituents in Groundwater

The concentrations of carbonates are caused by the CO_2 present in the soil zone formed from the weathering of parent materials. The weathering is caused by alternate wet and dry conditions, characterizing the semi-arid climate of the area. The values of PCO_2 is higher in groundwater (-0.50) that in atmosphere (-3.50) as a result of decay of organic matter and root respiration in the soil zone. The CO_2 in turn combines with rainwater to form carbonates as explained below:

$$CO_2 + H_2O = H_2CO_3$$
$$H_2CO_3 = H + HCO_3$$
$$H_2CO_3 = 2H + CO_3$$

The HCO_3 may also be derived from the dissolution of silicate minerals, Orthoclase, Plagioclase, Hornblende, Diopside, Hypersthene, Olivine and Biotite of country rocks of the area by the carbonic acid (Tesoriero *et al.,* 2004). A general reaction for the weathering of silicate rocks with carbonic acid is as follows:

(Cations) silicates + H_2CO_3 = H_4SiO_4+HCO_3+cations +solid products (mostly clay minerals)

Binary plots of (Ca + Mg) versus (HCO_3 + SO_4) (Fig.4) were examined to study the relative importance of ion exchange and different weathering processes. If Ca, Mg, SO_4 and HCO_3 are derived from a simple dissolution of Calcite, Dolomite and Gypsum, a 1:1 stoichiometry of (Ca+Mg) to (SO_4+HCO_3) should exist (McLean *et al*., 2000). When ion exchange takes place the points shift right due to excess Ca + Mg over SO_4 + HCO_3. If reverse ion exchange is the process, it will shift the points to the left due to a large excess of Ca+ Mg over SO_4 + HCO_3. The plot shows that 60% of the groundwater samples are clustered below the 1:1 line representing reverse exchange and 40% of the samples clustered above point toward ion exchange process indicating, portion of the HCO_3 + SO_4 must be balanced by Na and K by calcium and magnesium in clay material.

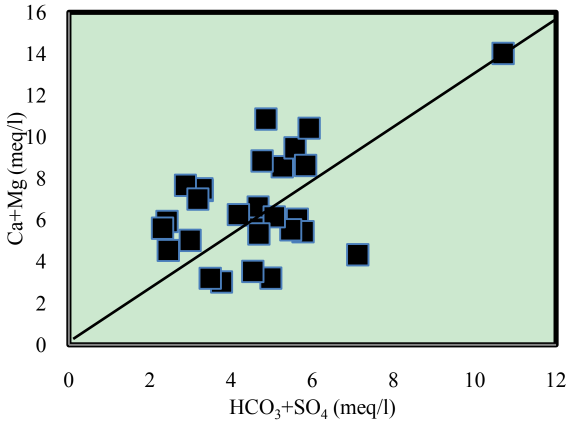

Figure 4. The plot for (Ca + Mg) versus (HCO_3 + SO_4)

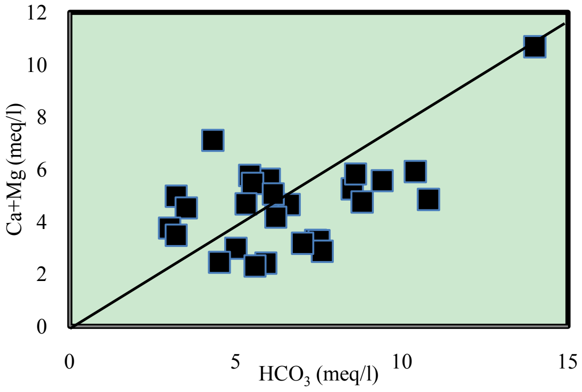

Figure 5. The plot for (Ca+Mg) versus HCO_3

The plot (Ca+Mg) versus HCO_3 (Fig.5) shows that data cluster around 1:1 equiline although two locations approach this line. Evaluation of the slopes of Ca and Mg with HCO_3 gives valuable information about the stochiometry of the process. The dissolution of carbonate minerals is the major source of Ca and Mg in the groundwater, whereas HCO_3 is produced by weathering of silicate and carbonate minerals (Srinivasamoorthy *et al.,* 2011). The most common weathering reaction in the case of carbonate is simple dissolution Zhang et al. (1995), giving a 1:2 ratio of Ca:HCO_3 or aCa+Mg:HCO_3 equivalence ratio of 1:1. The low molar ratio(<0.5) of Ca/HCO_3 measured in the groundwater was due to the exchange of calcium and magnesium in water by sodium bound in clay and/or cation exchange or HCO_3 enrichment possibly from silicate weathering (Drever, 1997). High ratios,(>0.5) suggests other sources for Ca and Mg, such as reverse ion exchange, which is observed in hard rock formations with an increase in salinity.

Silicate weathering is one of the key geochemical processes controlling the major ions chemistry of the groundwater, especially in hard rock aquifers (Mackenzie and Garrels, 1965; Rajmohan and Elango, 2004; Kumar *et al*., 2006). Silicate weathering can be understood by estimating the ratio between Na + K and total cations (TZ^+). The relationship between Na + K and total cations (TZ+) of the area indicate that the majority of the samples are plotted near the Na + K = 0.5TZ+ line (Fig. 6) indicating the involvement of silicate weathering in the geochemical processes, which contributes mainly sodium and potassium ions to the groundwater (Stallard and Edmond, 1983). Furthermore, weathering of soda Feldspar (Albite) and Potash Feldspars (Orthoclase and Microcline) may contribute Na^+ and K^+ ions to groundwater. Feldspars are more susceptible for weathering and alteration than Quartz in Silicate rocks.

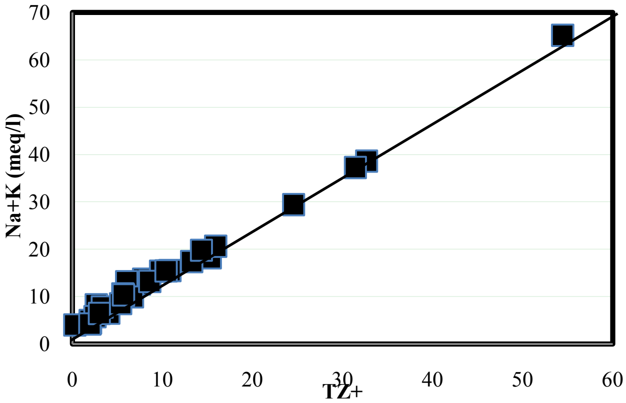

Figure 6. The plot for Na+K versus TZ+

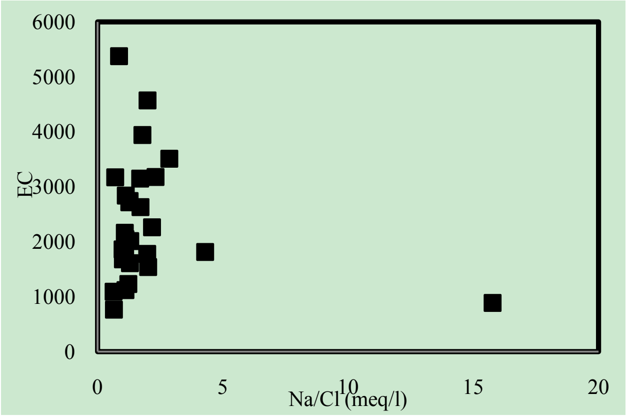

Figure 7. The plot for Na/Cl versus EC

Weathering of Silicate rocks is one of the major processes responsible for the high concentration of Na. In general, evaporation causes an increase in the concentrations of all species in the water. If the evaporation process is dominant, and no mineral species are precipitated, the Na/Cl ratio is unchanged (Jankowski and Acworth, 1997). Hence, a plot of Na/Cl versus Ec would give a horizontal line, which would indicate concentration by evaporation and evapotranspiration (Fig. 7).

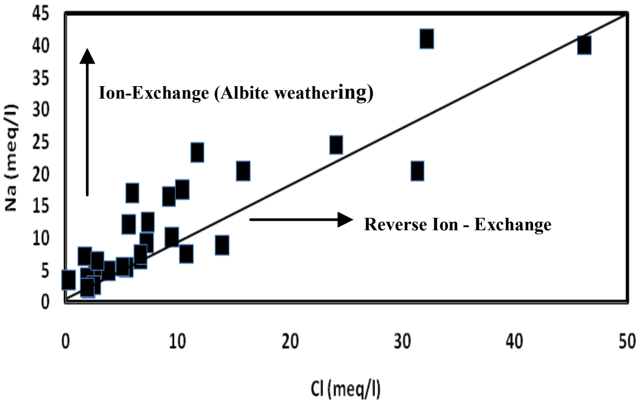

Figure 8. The plot for Na versus Cl

If halite dissolution is responsible for the sodium, the Na/Cl molar ratio is approximately one, whereas a ratio greater than one is typically interpreted as Na released from a silicate weathering reaction (Meybeck, 1987). In the present study, the molar ratio of Na/Cl for groundwater samples of the study area generally ranged from 0.64 to 15.77. Majority of the samples have molar ratio greater or equal to 1 indicating ion exchange is the major process which is replaced by silicate weathering. When sodium is plotted against chloride (Fig. 8), most of the groundwater samples lie above the 1:1 trendline.

The excess of Na can be attributed to silicate weathering (Stallard and Edmond, 1983) from feldspars or due to anthropogenic activities like waste water. Usually wastewater is enriched in Na relative to Cl (Vengosh and Keren, 1996). Therefore, even if halite is the dominant source of Na and Cl in the groundwater, the molar ratio will vary spatially as a result of cation exchange (Wayland *et al.,* 2003). This ratio should also decrease due to the cation exchange of Na as water moves through the aquifer, which would explain Cl enrichment in most water samples.

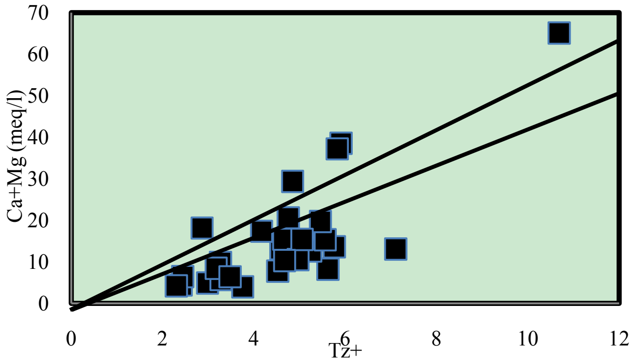

Figure 9. The plot for (Ca+Mg) Versus TZ^{+}.

The (Ca + Mg) Versus TZ^{+} plot (Fig. 9) for both seasons lie far below equiline with average equilibrium ratio of 0.40 to 0.35 indicating that alkalis are enriched twice to thrice the amount of Ca and Mg due to leaching from silicate weathering which is dominant in the aquifer materials of the study area. Significantly the increase in alkalis corresponds to a simultaneous increase in (Cl+SO$_4$) suggesting a common source for these ions and the presence of Na$_2$SO$_4$ and K$_2$SO$_4$ in the soils (Datta and Tyagi, 1996).

Stable Isotopes of Water

The stable isotope ratios of oxygen and hydrogen in the water molecule can be used as an indicator of various sources of ions to groundwater. Different environmental processes influence the isotopic composition of a substance through fractionation, or preferential incorporation, of a particular isotope of an element in one species or phase over another. The fractionation of stable isotopes is due largely to the associated mass differences, related bond vibration frequencies, and zero point energies (Criss, 1999). Additionally, fractionation processes generally result in isotopically lighter molecules statistically favoring the less dense phase and the heavier molecules favoring the denser phase, often in a predictable manner. In water, isotopically light molecules have a higher zero point energy, therefore requiring less energy Input for phase change from liquid to vapor than that of heavier water. Accordingly, during evaporation the water molecule with the least significant energy barrier for phase change will preferentially evaporate, resulting in residual water that becomes progressively heavier or enriched in δ^{18}O and δ^{2}H. Similarly, the heavy isotopes of water are the first to fall as rain, resulting in water vapor masses that become progressively lighter as one moves inland (continental effect) from a water source or to a higher elevation (Orographic rainout effect). Other factors that can influence the fractionation of δ^{18}O/ δ^{16}O and δ^{2}H/ δ^{1}H generally include temperature, diffusion, and the kinetic effects of humidity (Clark and Fritz, 1997). It should however be noted that plants take up water indiscriminately and thus further fractionation due to crop uptake of soil water does not appreciably occur (Appelo and Postma, 2005). Stable isotopes are useful in hydrogeological investigations for the very fractionation effects discussed above, which enable one to trace environmental phenomena. Additionally, the stable isotopes of water are useful tracers as they are conservatively transported in most groundwater environments, due to the fact that they represent the water molecule itself and not a dissolved solute, which can be significantly influenced by water rock interactions, biotransformation, sorption, exchange-reactions, etc.

The δ2H and δ^{18}O values of the groundwater range from -35.67 to -4.51 and -5.10 to -1.07%, with an average of -20.29 and -2.87respectively. Regular measurements of δ^{2}H and δ^{18}O in rainfall in the study area do not exist. So due to proximity to study area, heavy isotope ratios in rainwater from Tamilnadu (Chidambaram *et al.,* 2009) are also presented for comparison with the groundwater (Fig. 10).

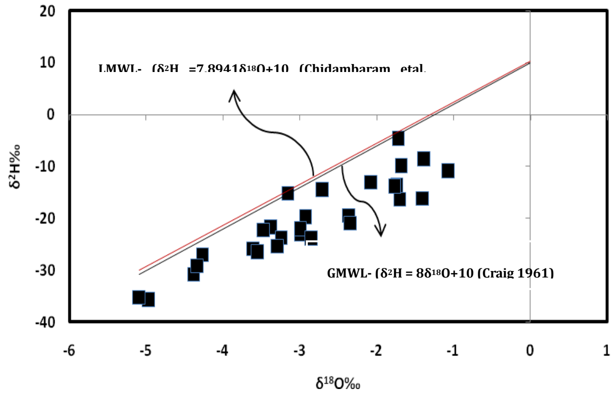

Figure 10. Relationship between $\delta^{18}O$ and δ^2H values

The global meteoric water line (GMWL) is also given as reference. The conventional δ D versus $\delta^{18}O$ diagram shows that the groundwater data plot to the right of the Global Meteoric Water Line of Craig (1961), defining a single trend with a slope of 5.3, which is consistent with evaporative slope of between 4 and 6 (Giggenbach, 1990; Clarke and Fritz, 1997; IAEA, 2007a, b) in semi-arid areas.

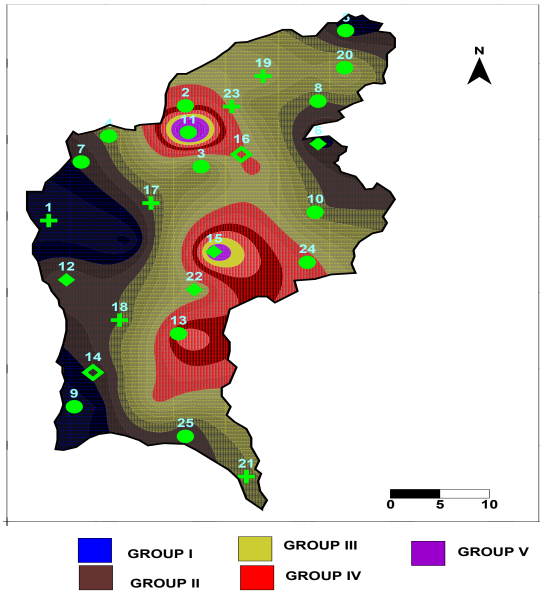

Figure 11. Spatial pattern of observed water types

The scatter plots in Fig. 11 also show very impressive patterns indicating different groundwater types, flows and sources. The ionic concentration increases generally in the direction of groundwater flow towards lower elevations. Local higher EC in the central part of the study area is related to pollution of some shallow wells from urban effluents. This is supported by a further higher concentration of Cl and NO_3 values indicating anthropogenic sources. Spatial analysis of hydrochemical data interpreted with isotopic signatures provided the existence of different water types and flow regimes (Criss *et al.,* 2001). The water types are categorized into spatial zones or groups. These spatial groups or patterns observed are summarized in Table 2 and discussed as follows.

The samples representing Group 1 are recharge waters with low EC< 1000 µS/cm and are relatively free from pollution. They are Ca-HCO_3 waters indicating young groundwater with low residence time and minimum rock water interaction noted along the NW part of the study area. The stable isotopes show highly depleted in nature. The Group 2 groundwater are intermediate between recharge and discharge areas evolved from group 1 with mixed Ca-HCO_3 and Ca-Mg-Cl types with intermediate EC <2000 µS/cm. With few exception of samples the groundwater showed lower concentrations of NO_3, Cl and SO_4 indicating the absence of pollution. These groups are prominently noted along north, NW and NE part of the study area with stable isotopic signatures showing moderately depleted. The groundwater representing Group 3 has EC values (EC < 2500 µS/cm). This group is dominantly Ca-Mg-Cl and Ca-Cl type water indicting stable isotopes are slightly enriched compared to other groups. Most of the samples in this group plot below the local meteoric water line of Tamilnadu (LMWL) and Global Meteoric Water Line (GMWL) showing relatively higher evaporation before recharge (Fig. 10). The relatively enriched isotopic composition shows recharge from evaporated surface water bodies such as rivers. This group is prominent along the central portion of the study area. The samples representing Group 4 is highly affected by pollution. As a result, they have a Ca-Cl, Na-Cl type waters with a relatively high EC values (EC < 3000 µS /cm). This group of groundwater is spatially distributed along the NW and NE part of the study area. They are characterized by enriched stable isotopic composition showing recharge from modern but highly polluted domestic and municipal wastewater from the study area (Criss RE, 1995). The Group 5 groundwater recorded with high EC (3000–5000 µS/cm) and Na-Cl type located at the centre and NE part of the study area associated with intensive polluted industrial wastewater. This group has highly depleted stable isotopic composition showing deep circulation and longer residence time (highly evolved group).

Table 2. Spatial patterns of groundwater in the study area

Groups	Group 1	Group 2	Group 3	Group 4	Group 5
Ca	82.7	69.5	72	44.4	147.9
Mg	69.7	61.1	59	41.7	170.2
Na	237.9	258.9	93.8	31.7	1061
K	23	14.3	8.7	1.7	325
HCO_3	411.4	457.7	195.3	294.3	854.3
PO_4	1	2.6	2.7	2	1.8
H_4SiO_4	57.9	54.3	56.9	60	46
Cl-	460.2	470.4	212.8	96	1418.4
d18O	-3.1	-1.6	-2.9	-4.3	-1.7
dD	-22.8	-12.7	-14.8	-29	-4.5
SO_4	4.7	3.9	1.4	3.8	2.7
NO_3	161.9	184.6	328	35.5	321
F	1.8	1.9	2.4	0.9	1.6
TDS	1579.9	1329.4	1609.6	688.2	3441
EC	2451.9	2077	2515	1079.3	5376
pH	7.4	7.5	7.6	7.6	6.4
Ca	82.7	69.5	72	44.4	147.9

4. Summary and Conclusions

Hydrochemistry data from Thirumanimuttar basin has revealed groundwater is generally neutral to alkaline in nature. As per TDS classification 84% of the samples recorded higher TDS and the remaining 14% represented lower TDS. The abundance of the major cations and anions in the groundwater are of the following order: Cl>HCO_3>NO_3>SO_4>Br>F>PO_4 and Na>Ca>Mg>K. The sources of ions into the groundwater are from dissolution and leaching from source rocks, cation exchange and anthropogenic activities. The groundwater is generally over saturated with respect to major carbonate species namely calcite and dolomite and oversaturation was also noted for silicate species like quartz and undersaturation was noted for SiO_2(a). The groundwater showed paths of hydrochemical evolution, from Ca– HCO_3 type via Ca–Cl type to Na–Cl type; or from Ca– HCO_3 type directly to Na–Cl type. This suggests that the groundwater hydrochemistry is controlled by water– rock interaction and anthropogenic pollution. Higher PCO_2 was noted in groundwater due to decay of organic matter and root respiration in the soil zone along with loss of CO_2 during groundwater flow. The plot of (Ca + Mg) versus (HCO_3 + SO_4) indicates 60% of groundwater represents reverse exchange and 40% indicates ion exchange process. The plot (Ca+Mg)/HCO_3 indicate sources from silicate weathering. The plot for Na + K and total cations (TZ^+) indicates that the majority of the samples point out weathering and alteration of quartz in silicate rocks. The plot for Na/Cl indicates ion exchange due to enrichment of Na than Cl. The δ^2H versus $\delta^{18}O$ diagram shows that the groundwater data plot to the right of the Global Meteoric Water Line and LMWL. The water types were categorized into 5 spatial Groups. Group 1 represents indicates recharge waters with low EC and highly depleted isotopes. Group 2 are the intermediate between recharge and discharge areas with intermediate EC and moderately depleted isotopes. Group 3 represents higher EC values and enriched isotope values. Group 4 is highly affected by pollution with very higher EC and more enriched isotopic composition. The Group 5 represents very high EC and highly enriched stable isotopic composition showing deep circulation and longer residence time.

ACKNOWLEDGEMENTS

This work was supported by University Grants Commission, India Grant No.F.32-335/2006 (SR). The authors are grateful to Prof.Anindya Sarkar for isotope analysis at IIT, Kharakpur, India.

REFERENCES

[1] Aji, K, Tang, C, Song, S, Kondoh,A, Sakura,Y, Yu, J and Kaneko, S, 2008.Characteristics of chemistry and stable isotopes in groundwater of Chaobai and Yongding River basin, North China Plain, Hydrological Process. 22, 63–72. DOI: 10.1002/hyp.6640

[2] APHA–AWWA–WPCF, 1995, Standard Methods For The Examination Of Water And Waste Water (19th ed.). New York, USA

[3] C.A.J Appelo, D. Postma, Geochemistry, Groundwater And Pollution. Balkema, Rotterdam, 536, 1996

[4] C.A.J Appelo, D. Postma, Geochemistry, Groundwater And Pollution. 2nd edn. AA Balkema, Amsterdam, pp649, 2005

[5] Ball, J.W., Nordstrom, D.K., 1991. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open File Report 91-183, 92

[6] Chidambaram, S., Prasanna, M.V., Ramanathan, A.L., Vasu, K., Hameed, S., Warrier, U.K., Manivannan, R., Srinivasamoorthy, K., Ramesh, R., (2009). Precipitation of 2006 southwest monsoon of Tamil Nadu. Curr. Sci. 96-9, 1224-1229

[7] Clark, I.D., Fritz, P., 1997. Environmental isotopes in hydrogeology. Lewis Publishers, Boca Raton

[8] Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703

[9] Criss, R.E., 1995. Stable isotope distribution: variations from temperature, organic and water-rock interactions. In: Ahrens TJ (ed) Global earth physics: a handbook of physical constants, AGU Reference Shelf 1

[10] Criss, R.E., 1999. Principles of stable isotope distribution. Oxford University Press, New York; 254

[11] Criss, R.E., Davisson, M.L., Kopp, J.W., 2001. Nonpoint sources in the lower Missouri river. Journal of American Water Works Association. 93-2, 112–122

[12] Datta, P.S., Bhattscharya, S.K., Tyagi, S.K., 1996. 18O studies on recharge of phreatic aquifers and groundwater flow-paths of mixing in the Delhi area. Journal of Hydrolology, 176,25–36

[13] Deutsch, W.J., 1997. Groundwater geochemistry: fundamentals and application to contamination. CRC, Boca Raton

[14] Dickson Adomako, Abass Gibrilla, Tetteh T. Akiti, Richmond Fianko, Piotr Maloszewski, 2011. Hydrogeochemical Evolution and Groundwater Flow in the Densu River Basin, Ghana, Journal of Water Resource and Protection, 3, 548-561

[15] Drever, J.I., 1997. The geochemistry of natural waters (3rd ed.). New Jersey: Prentice Hall,436

[16] Edmunds, W.M., Ma, J.Z., Aeschbach-Hertig, W., Kipfer, R., Darbyshire, D.P.F., 2006. Groundwater recharge history and hydrogeochemical evolution in the Minqin Basin, North West China. Applied Geochemistry, 21, 2148–2170

[17] Franco Cucchi, Giuliana Franceschini and Luca Zini 2007. Hydrogeochemical investigations and groundwater provinces of the Friuli Venezia Giulia Plain aquifers, northeastern Italy, Environmental Geology, 55, 985–999. DOI 10.1007/s00254-007-1048-4

[18] Gale, I.N., Robins, N.S., 1989. The Sampling and Monitoring of Groundwater Quality. British Geological Survey. Hydrogeology Report, No. 89/37

[19] Giggenbach, W.F., 1990. Water and gas chemistry of Lake Nyos and its bearing on the eruptive process. J. Volc. Goethe. Res. 42, 337–362

[20] Guangxin Zhang,Wei Deng,1 Y. S. Yang and R. B. Salama, 2007. Evolution study of a regional groundwater system using hydrochemistry and stable isotopes in Songnen Plain, northeast China, Hydrological process. 21, 1055–1065

[21] IAEA a., 2007. Atlas of isotope hydrology. Africa–Vienna. ISBN 978- 92-0-1072707-8 ImesJL

[22] IAEA b., 2007. Global network of isotopes in precipitation (GNIP) Database IAEA/WMO, Vienna, Austria, http://www.isohis. iaea.org. Cited 22 April 2008

[23] Jankowski, J., Acworth, R.I., 1997. Impact of debris-flow deposits on hydrogeochemical processes and the development of dryland salinity in the Yass River catchment, New South Wales, Australia. Journal of Hydrology. 5-4, 71–88

[24] Janza, M. 2010. Hydrological modelling in the karst area, Rižana spring catchment, Slovenia. Environmental Earth Science Journal 61, 909-920

[25] Kebede, S., Travi, Y., Stadler, S. 2010, Groundwaters of the Central Ethiopian Rift: diagnostic trends in trace elements, δ18O and major elements. Environmental Earth Science, 61, 1641-1655

[26] Kumar, M., Ramanathan, A.L., Rao, M.S., Kumar, B., 2006. Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India. Environmental Geology. 50, 1025–1039. DOI:10.1007/s00254-006-0275-4

[27] Lawrence, A.R., Gooddy, D.C., Kanatharana, P., Meesilp, M., Ramnarong, V., 2000. Groundwater evolution beneath Hat Yai, a rapidly developing city in Thailand. Hydrology Journal, 8, 564–575

[28] Latifa Bouragba, Jacques Mudry J, Lhoussaine Bouchaou, Youssef Hsissou and Tarik Tagma, 2011. Characterization of groundwater in the Souss upstream basin: Hydrochemical and environmental isotopes approaches, African Journal of Environmental Science and Technology, 5(4), 307-315

[29] Lloyd, J.W., Heathcote, J.A., 1985. Natural inorganic hydrochemistry in relation to groundwater, an introduction. Clarendon Press, Oxford

[30] Ma, J.Z., Ding, Z.Y., Edmunds, W.M., Gates, J.B., Huang, T.M., 2009. Limits to recharge of groundwater from Tibetan plateau to the Gobi desert, implications for water management in the mountain front. Journal of Hydrology 364 (1–2), 128–141

[31] Mackenzie, F.J., Garrells, R.H., 1965. Silicates: reactivity with water. Science Journal, 1505,57–58

[32] McLean, W., Jankowski, J., Lavitt, N., 2000. Groundwater quality and sustainability in an alluvial aquifer, Australia. In: Sililo O et al (eds) Groundwater, past achievements and future challenges. A Balkema, Rotterdam; 567–573

[33] Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. American Journal of Science, 287, 401–428

[34] Mohan Viswanathan Prasanna, Chidambaram, S., Shahul Hameed, A., Srinivasamoorthy, K., 2009. Study of evaluation of groundwater in Gadilam basin using hydrogeochemical and isotope data, Environmental Monitoring and Assessment, DOI 10.1007/s10661-009-1092-5

[35] Njitchoua, R., Dever, L., Fontes, J.C.H., Naah, E., 1997. Geochemistry, origin and recharge mechanisms of groundwaters from the Garoua Sandstone aquifer, northern Cameroon. Journal of Hydrology, 190, 123– 140

[36] Rajmohan, N., Elango, L., 2004. Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. Environmental Geology. 46, 47–61

[37] Rajmohan, N., Al-Futaisi, A., Al-Touqi, S. 2009. Geochemical process regulating groundwater quality in a coastal region with complex contamination sources: Barka, Sultanate of Oman. Environmental Earth Science,

DOI 10.1007/s12665-009-0037-1

[38] Ruiqiang Yuan, Xianfang Song, Yinghua Zhang, Dongmei Han, Shiqin Wang, Changyuan Tang, 2011.Using major ions and stable isotopes to characterize recharge regime of a fault-influenced aquifer in Beiyishui River Watershed, North China Plain, Journal of Hydrology, 405, 512–521

[39] Srinivasamoorthy, K., Chidambaram, S., 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. Journal of Earth System Science. 117(1), 49-58

[40] Srinivasamoorthy, K., Nanthakumar, C., Vasanthavigar, M., Vijayaraghavan, K., Rajivgandhi, R., Chidambaram, S., Anandhan, P., Manivannan, R., Vasudevan, S., 2009. Groundwater quality assessment from a hard rock terrain, Salem district of Tamilnadu, India, Arabian Journal of Geosciences, DOI 10.1007/s12517-009-0076-7

[41] Srinivasamoorthy, K.., Vasanthavigar, M., Vijayaraghavan, K., Sarathidasan, R., Gopinath, S., 2011. Hydrochemistry of groundwater in a coastal region of Cuddalore district, Tamilnadu, India: implication for quality assessment, Arabian Journal of Geosciences, DOI: 10.1007/s12517-011-0351-2

[42] Stallard, R.F., Edmond, J.M., 1983. Geochemistry of Amazon, the influence of geology and weathering environment on the dissolved load. Journal of Geophysical Research. 88, 9671–9688

[43] Subba Rao, N., 2006. Seasonal variation of groundwater quality in a part of Guntur district, Andhra Pradesh, India. Environmental Geology. 49, 413–429

[44] Subbarao, N., Srinivasa Rao, G.,Venkateswara Rao, S., Madhusudhana Reddy, P., John Devadas, D., 1999. Environmental control of groundwater quality in a tribal region of Andhra Pradesh, India. Journal of Geological Society of India. 71(4), 299–304

[45] Subramanian, V., Saxena, K.., 1983. Hydrogeochemistry of groundwater in the Delhi region of India, relation of water quality and quantity. In: Proceedings of the Hamberg symposium IAHS publication no. 146 , 307–316

[46] Tesoriero, A.J., Spruill, T.B., Eimers, J.L., 2004. Geochemistry of shallow ground water in coastal plain environments in the south-eastern United States: Implications for aquifer susceptibility. Applied Geochemistry. 19, 1471–1482

[47] Vasanthavigar, M., Srinivasamoorthy, K., Vijayaraghavan, K.. Rajivganthi, R.; Chidambaram, S., Anandhan, P., Mani-

vannan, R., Vasudevan, S., 2010. Application of water quality index for groundwater quality assessment: Thirumanimuttar sub-basin, Tamilnadu, India, Environmental Monitoring and Assessment. DOI: 10.1007/s10661-009-1302-1

[48] Vengosh, A., Keren, R., 1996. Chemical modifications of groundwater contaminated by recharge of treated sewage effluent. Journal of Contaminant Hydrology. 23, 347– 360

[49] Wayland, K.G., Long, D.T., Hyndman, D.W., Pijanowski, B.C., Woodhams, S.M., Haack Sh, K. 2003. Identifying relationships between base flow geochemistry and land use with synoptic sampling and R-Mode factor analysis. Journal of Environmental Quality. 32, 180–190

[50] Wodeyar, B.K., Sinivasan., K., 1996. Occurrence of Fluoride in the groundwaters and its impact in Peddavankahalla basin, Bellary district, Karnataka – a preliminary study. Current Science. 70-1, 71-74

[51] Zhang, J., Huang, W.W., Letolle, R., Jusserand, C., 1995. Major element chemistry of the Huanghe (Yellow River), China—weathering processes and chemical fluxes. Journal of Hydrology. 168, 173–203

[52] Zhu, G.F. , Li Z.Z , Su Y.H, Ma J.Z, Zhang, Y.Y, 2007. Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China, Journal of Hydrology, 333. 239– 251

[53] Zongyu Chen, Zhenlong Nie, Guanghui Zhang, Li Wan and Jianmei Shen, 2006. Environmental isotopic study on the recharge and residence time of groundwater in the Heihe River Basin, northwestern China, Hydrogeology Journal,14,1635–1651