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Research Paper

A STUDY ON THE SPATIAL ANALYSIS OF DISSOLVED SILICA IN GROUNDWATER OF VILLUPURAM DISTRICT OF TAMIL NADU

Nepolian M[1]*, Chidambaram S[1], Thivya C[2], Thilagavathi R[1],
Rakesh Roshan Gantayat[1], Paramaguru P[1] and Pradeep K[1]

*Corresponding Author: Nepolian M ✉ geonepolian87@gmail.com

Some studies on discrepancy of silica concentrations in groundwater of hard rock aquifers of lower permeability stipulates the increase in residence time, which mainly leads to increase in assemblage of ions. In order to understand the hydrogeochemistry of the groundwater of a hard rock aquifer and its relation with silicates, 120 groundwater samples were collected and analyzed to demonstrate spatial coverage and represent different litho units in Villupuram district. This analysis has been carried out mainly for of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (Cl, HCO^{3-}, SO_4^{2-}, PO^{4-}, NO^{3-}, H_4SiO_4) present in the water samples. Physico-chemical parameters like pH, TDS (Total Dissolved Solids), Temperature and EC (Electric Conductivity) were also analyzed to determine the water quality. The results of silica showed different ranges of concentrations and were plotted in different formations. To understand the reason behind this dissimilarities, different techniques like Thermodynamics, Statistics and GIS were adopted.

Keywords: Silica, Groundwater, Hard rock aquifer, Hydro-geochemistry, Villupuram

INTRODUCTION

Silica in ground water can be found in two forms, dissolved silica and particulate matter. Silica dissolved in natural waters is considered to be a good indicator of weathering and water circulation conditions (Dobrzynski, 2005). Silica released as a result of chemical weathering of silicate minerals in rocks and sediments has been acquired by circulating groundwater and therefore the source of silica (SiO_2) in groundwater is mainly from water rock interaction (Hem, 1986). The amount of silica released into the water is conditioned by different factors, such as water saturation deficit of the aeration zone, seasonal fluctuations of precipitation and temperature, bedrock reactivity, and mineral stability (Dobrzynski, 2005). Dissolved silica in water is normally measured as SiO_2 despite the fact that the exact form of dissolved silica is not known (Al-Rehaili, 2003). Average concentration of silica in natural water ranges between1.0 and 30.0 mg/L (Davis, 1964).

The solubility limit for silica in water is estimated at approximately 120 mg/L at 25°C (Stumm and Morgan, 1981). Solubility of silica in water is

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[1] Department of Earth Sciences, Annamalai University, Tamilnadu, India.
[2] Department of Geology, University of Madras, Guindy Campus, Tamilnadu, India.

directly proportional to temperature (Fournier, 1983) has studied and reported that temperature–solubility relationship of silica and they concluded that at least a temperature of about 300°C is used as a geo-thermometer in the studies of deep groundwater and geothermal systems. Another study (Marchand, 2002) demonstrates that silica content of groundwater increases due to increased contact with silicate rocks and that the silica content is directly proportional to the residence time of water in host rock. They also showed that water ascending from deeper reservoirs had higher silica values than in groundwater of shallow origin.

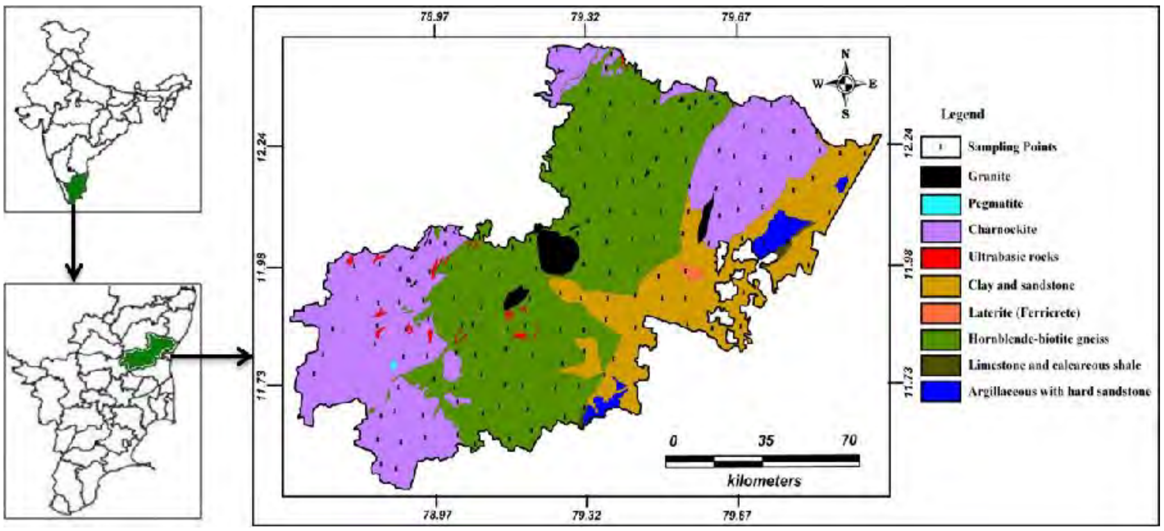
The current research focuses mainly to understand the relationships between bedrock and groundwater chemistry. Groundwater chemistry has been investigated in Archean, LateArchean to Proterozoic, Quaternary, Proterzoic, Tertiary and Cretaceous formations. The paper deals with various conditions that favor the silica concentration in groundwater, with a special emphasis on silica solubility in terms of the stability diagrams. Further, it also focuses on variation in the spatial distribution of silica concentration in groundwater of Archean LateArchean to Proterozoic, Quaternary, Proterzoic, Tertiary and Cretaceous formations.

STUDY AREA

Villupuram district forms the eastern part of Tamil Nadu state surrounded by Cuddalore District in the East and South, Salem and Dharmapuri districts on the West, and Thiruvannamalai and Kanchipuram districts on the North, covering an area of about 7.223 sq km. It is located between north Latitude of 11°49' and 12°47' and East Longitude of 78°61' and 80°03'. The climate is sub-tropical and the temperature varies from 26.1 to 35.2°C in the district. The relative humidity varies from 20 to 70% and is high during PRM monsoon.

The water level depth varies from 76 to 450 m below ground level. It receives 1119.8 mm rainfall (1902-1980) annually and highest in coastal region. The development of the groundwater in

Fig: 1 Lithology And Sampling Points Of The Study Area



this region is through dug wells and bore wells (JnNURM, 2009). Granular rock bodies overlies on the crystalline sedimentary contact regions, where wells of 40 to 60 mbgl depth, having 7 to 10 lps discharge capacity are found. The study area is represented by Hornblende-biotite gneiss, Charnockite, Clay and sandstone, Laterite, pegmatite, Granite, Limestone with calcareous shale and argillaceous with hard sandstone lithologies (Figure 1).

The Villupuram in general is having an average elevation of about 175.44 m above the Mean Sea Level (MSL). The elevation map is shown in the (Figure 2) higher elevation >894.05 m is in Southwestern part and lesser elevation of 103.77 m is in Eastern region

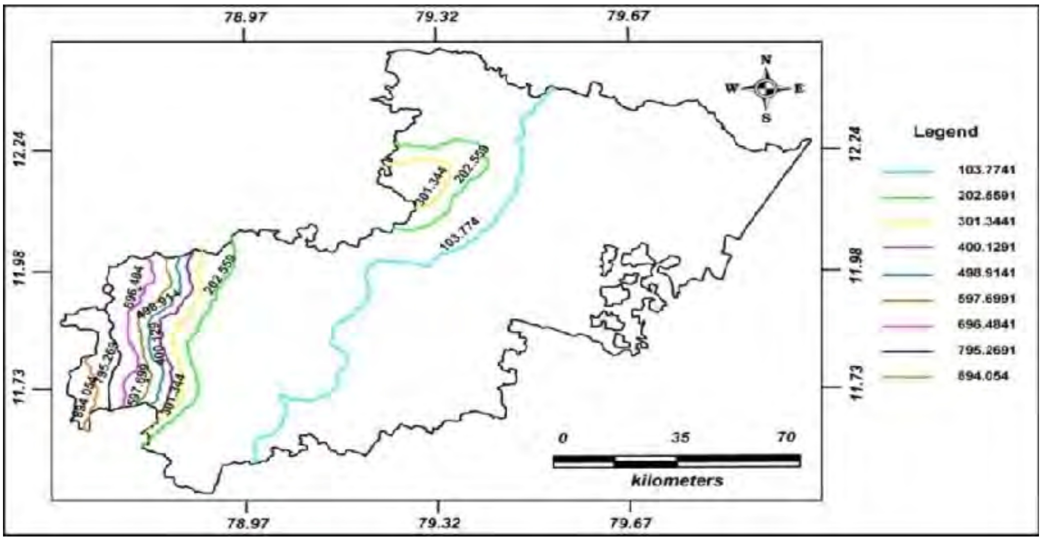
METHODOLOGY

170 water samples were collected from different hand pumps covering throughout the study area during Pre monsoon (PRM). Parameters like pH, TDS, Temperature and conductivity were analyzed in field itself by using water analysis kit. Sampling and analysis was carried out using standard (APHA, 1998, Ramanathan, 1992; Ramesh and Anbu, 1996). The collected sample were measured for major ions like Ca^{2+},Mg^{2+}, by titrimetric; Na^+, K^+ by flame photometry (CL 378);Cl, HCO_3^- by titrimetric and SO_4^{2-}, PO_4^-, NO_3^- and H_4SiO_4 by using Spectrophotometer(DR 6000, HACH).The Ionic balance of groundwater samples ranges between 5–10% (Domenico and Schwartz, 1998; Freeze and Cherry, 1979). The software Aquachem 4.0 has been used for piper plot (Piper, 1953). A computer program WATCLAST in C++ was used for calculation and graphical representations (Chidambaram, 2003).

HYDRO-GEOCHEMICAL PROCESSE

In piper plot the concentration of major cations (Ca, Mg, Na and K) and anions (CO_3^+ HCO_3, Cl and SO_4) are plotted on two separate triangular diagrams and combined information displayed on a quadrilateral. The position of diagrams signifies the composition of groundwater. The geochemical

Fig: 2 Elevation Map Of The Study Area



evolution can be understood from the Piper plot, (Ca-Mg-Cl mixed type, Na-Cl type, Ca- HCO_3 type). Maximum number of samples have Ca-Mg-Cl and Na-Cl water type corresponding to mixed water type. This may be due to anthropogenic impact (Srinivasamoorthy *et al.,* 2011). Some Na-Cl type water samples are also found in coastal region may be due to seawater infiltration into the aquifer (Prasanna *et al.,* 2011, Thilagavathi *et al.,* 2012).Along the eastern part above diagram shows that the alkali (Na) exceeds the alkaline earth (Ca and Mg) and strong acids Cl exceed the week acids (HCO_3 and SO_4). Some Samples having Ca-HCO_3 water type signifies the predominance of infiltration of freshwater into the aquifer (Thivya *et al.,* 2013a). Higher Ca and Mg occurring in groundwater may be due to weathering of primary mineral sources of rock–water interaction (Srinivasamoorthy *et al.,* 2008) (Figure 4).

RESULTS AND DISCUSSION

pH value ranges from 6.15 to 8.23 which shows the alkaline nature of groundwater. EC ranges from 252 to 7360 µs/cm with an average of 1542.89 µs/cm. Total Dissolved Solids (TDS), is the sum total of dissolved ions which ranges between 108.2 to 1810 mg/L (Table. 1). The order of dominance is given as

$Na > Ca > Mg > K = Cl > H_4SiO_4 > HCO_3 > NO_3 > SO_4 > PO_4 > F$

A higher value of EC was noted in the southern part nearby Gomuki River and it may be due to the infiltration of sewage effluents along the river (Thivya *et al.,* 2013a; b). A lower value of EC was observed in the north eastern part (Figure 5). In majority of the groundwater samples EC varies from 252 and 7360 µS/cm.

THERMODYNAMIC STABILITY

Most important among the weathering reactions is the incongruent dissolution of aluminum silicates which may schemati-cally be represented by

Figure 3: Piper diagram

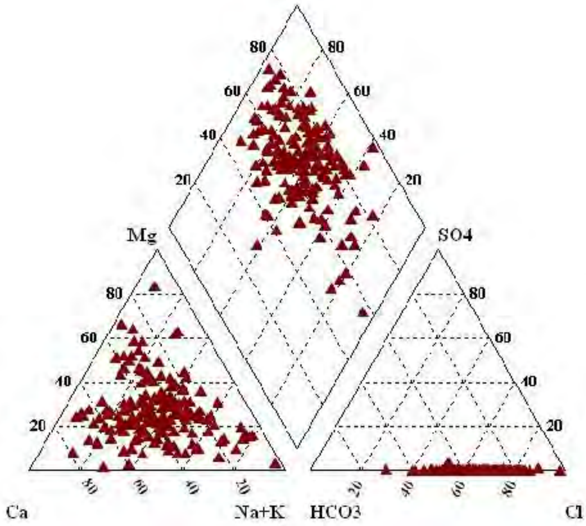


Figure 4: Spatial Distribution Of Electrical Conductivity Of Groundwater Samples

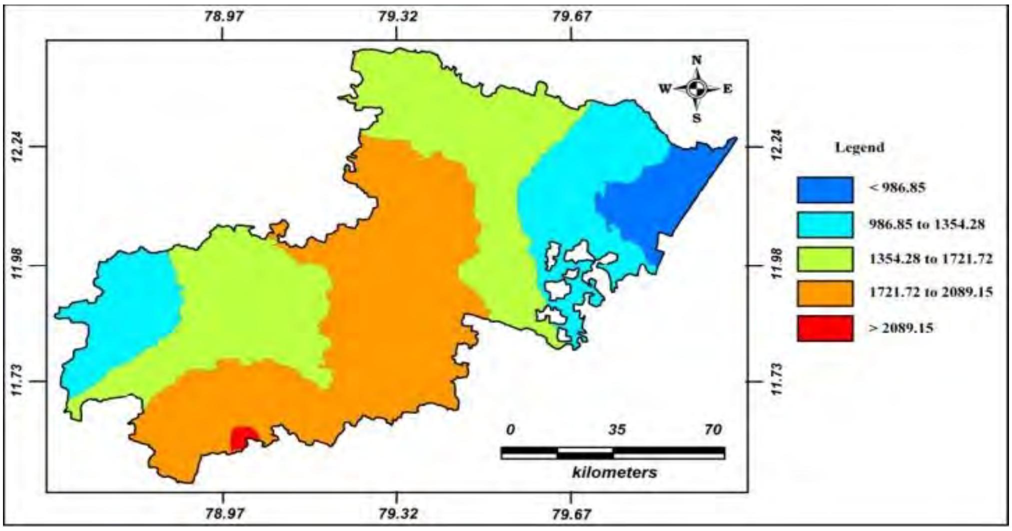


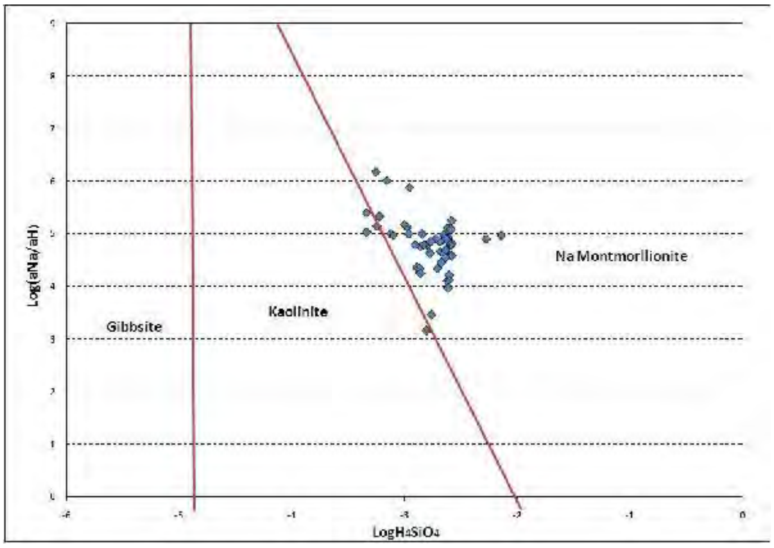
Table 1: The Maximum, Minimum and Average Chemical Constituent's of Groundwater (All values are in mg/L except pH and Electrical conductivity (EC) in µS/cm)

Parameter	Minimum	Maximum	Average
Ca	6	256	76.89
Mg	2.4	123.6	34.89
Na	4.9	762	90.20
K	BDL	116.8	10.95
Cl	35.45	1807.95	273.35
HCO_3	30	426	196.71
NO_3	BDL	267.54	28.56
PO_4	BDL	4.09	0.22
SO_4	0.06	7.74	1.06
H_4SiO_4	24	500	118.62
F	0.04	3	0.55
pH	6.15	8.23	7.41
EC	252	7360	1542.89
TDS	108.2	1810	627.49

Cation+ Al-silicate + H_2CO_3 + H_2O = HCO_3^- + H_4SiO_4 + cation + Al-silicate(s)

Essentially, a primary mineral is converted into a secondary mineral. The secondary minerals are

Figure 5: Thermodynamic Stability Plot Of Na System



frequently structurally ill-defined or X-ray amorphous. The structural breakdown of aluminum silicates is accompanied by -release of cations and usually of silicic acid. As a result of such reactions alkali in it get imparted to the dissolved phase from the bases of the minerals. In most silicate phases. Al is conserved during the reaction, the solid residue being higher in Al than the original silicates. Because the alkalinity of the solution increases during the weathering processes, the solid residue has a higher acidity than the original aluminum silicate.

The stages of structural breakdown of minerals can be established by the stability field of the silicate minerals. Hence standard stability diagrams were evolved for the thermodynamic studies (Stumm and Morgan, 1970). In spite of these limitations, a major application of these diagrams is that samples can be plotted to understand the appropriate ion activities for a given sample of water on these standard fields and evaluate the position of water composition in terms of mineral-water equilibria. Similar studies were adopted for composition of well waters in the black soil zone over weathered Deccan basalt of Malwa Plateau, Madhya Pradesh (Lunkad and Raymahashay, 1978). Studies were also reported to understand the ground water composition in lateritic soil profiles of Kerala is consistent with occurrence of Gibbsite, Kaolinite and Halloysite (Raymahashay *et al.*, 1987; Chidambaram *et al.,* 2011).

Aggressive water, high in CO_2 and low in dissolved solids encounter silicates high in cations and silica leaving Alumino-silicate residue with an increase in Al-Si ratio (Garrels and Mackenzie, 1967). As water continues to attack feldspar, pH rises with increase in cation and silica. Kaolinite forms until cations and silica contents rise high enough so that Montmorllionite initiates its formation.

Stability diagram have been widely used for understanding the geochemical behavior between minerals and water phase. In Na system, samples are stable with Kaolinite and it tends to move towards Montmorillonite due to the excess supply of silica (Figure 6). There are two distinct groups identified with lesser and greater silica falling in Kaolinite Montmorillonite field respectively and also indicating the movement of ions along the groundwater flow path. However, as shown by Siever (1957) maximum silica solubility at low temperature is controlled by amorphous silica rather than by quartz. The rate of crystallization of quartz is slow that amorphous silica, a met stable phase, should be looked upon as the upper limit of dissolved silica content of natural waters for most low-temperature processes.

In K system (Figure 7), samples are stable with Kaolinite and tend to move towards K-feldspar field, indicating the abundance of cations which may be associated with the mineral like Montmorillonite, Chlorite and Illite present in the aquifer system (Prasanna *et al*,. 2010; Chidambaram, 2011).

When reactions are written for the mineral compatibilities, it has been discovered that only three variables need be considered: $[K^+]$, $[H^+]$, and $[H_4SiO_4]$. Furthermore, the ratio of $[K^+]$ to $[H^+]$ in the various equilibrium constants is always unity. Therefore, all the mineral relations can be described in two-dimensional representations involving the ratio of $[K^+]$ to $[H^+]$ as one axis, and the activity of H_4SiO_4 as the other.

The reactions and their equilibrium constants are as follows:

$3KA1Si_3O_8$ (c) + $2H^+$ (aq) + $12H_2O$ = $KA1_3Si_3O_{10}$ $(OH)_2$ (c) + $6H_4SiO_4$(aq) + $2K^+$(aq) α 2 $2KA1Si_3O_8$c + $2H^+$ (aq) + $9H_2O$ = $H_4A1_2Si_2O_9$ (c) + $2K^+$aq + $4H_4SiO_4$ (aq) α 3

$2KA1_3Si_3O_{10}$ $(OH)_2$(c) + $2H^+$(aq) + $3H_2O$ = $3H_4A1_2Si_2O_9$(c) + $2K^+$(aq) α 4

$2KA1_3Si_3O_{10}$ $(OH)_2$(c) + $2H^+$(aq) + $18H_2O$ = $3A1_2O_3.3H_2O$(c)+ $2K^+$(aq)+ $6H_4SiO_4$(aq) α 5

$H_4A1_2Si_2O_9$(c) + $5H_2O$ = $Al_2O_3.3H_2O$(c) + $2H_4SiO_4$ (aq) α 6

Among all the aspects of interesting fact is that most ground and stream waters fall into the Kaolinite field of stability. Also, they have dissolved silica contents ranging between the solubility of

Figure 6: Thermodynamic Stability Plot Of K System

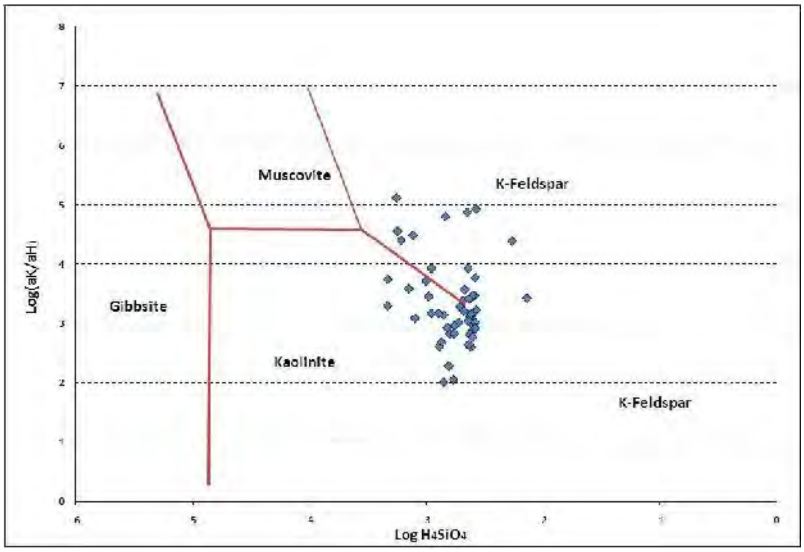
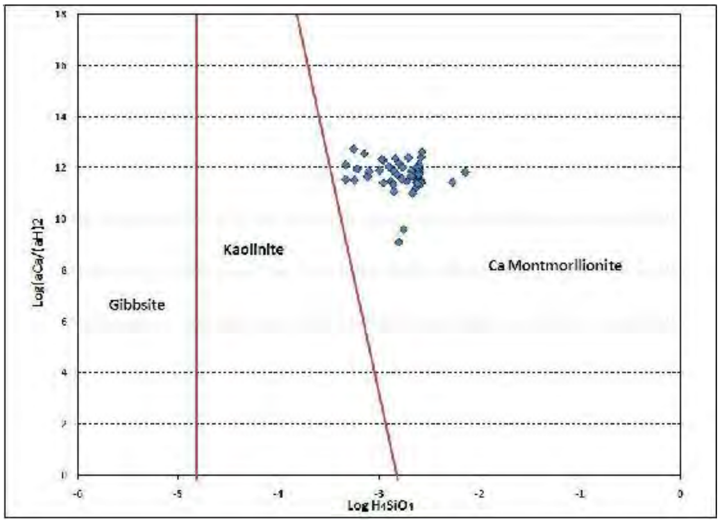


Figure 7: Thermodynamic Stability Plot Of Ca System



quartz and that of amorphous silica. The presence of silica in most waters in excess of that predicated for reactions with K-mica and K-feldspar can be attributed to the presence of other minerals that equilibrate more rapidly than K-feldspar.

In Ca system, samples tend from Montmorillonite field (Figure 8). This indicates that the formation of new clay minerals in the area is mainly due to the supply of excess cations and silica to the pre-existing Kaolinite which appears to be formed owing to evaporation / evapo-transpiration process, as suggested by Jacks (1973). This may happen due to a long residence time of water in the aquifer matrix (Srinivasamoorthy *et al.*, 2008).

PARTIAL PRESSURE OF CARBON DIOXIDE (CO_2) AND IONIC STRENGTH

Partial pressures of CO_2 (pCO_2) in water were calculated from measured pH and alkalinity of groundwater samples using the program WATEQ4F (Plummer *et al.*, 1976).

Log pCO_2 were studied for six different formations exist in the study area. The log pCO_2 is ranges between -3.23 to -1.46 with an average of -2.25 in Archean formations. It ranges between -2.83 to -1.59 with an average of -2.13 in the Late Archean to Proterozoic formation. It ranges between -2.69 to 1.48 with an average -2.03 Quaternary formations. It ranges between -2.09 to -1.97 with an average -2.03 Proterozoic formation. It ranges between -2.09 to -1.19 with an average 1.71 Tertiary formation. It ranges between -2.19 to -2.17 with an average -2.18 Cretaceous formation. It was observed that higher ranges of log pCO_2 in hard rock aquifers.

The higher ionic strength indicates longer residence time or greater interaction with the host rock (Chidambaram *et al.*, 2007). Most of the groundwater samples from Archean formations (Figure 9) exhibits ionic strength greater than 0.0037 and ranges between 0.0037 and 0.0133

Figure 8: Relationship Between Log Pco2 Vs. Ionic Strength

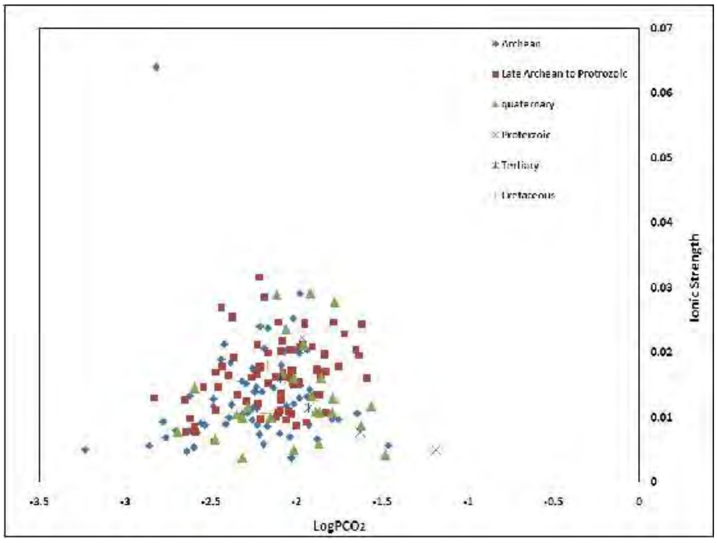
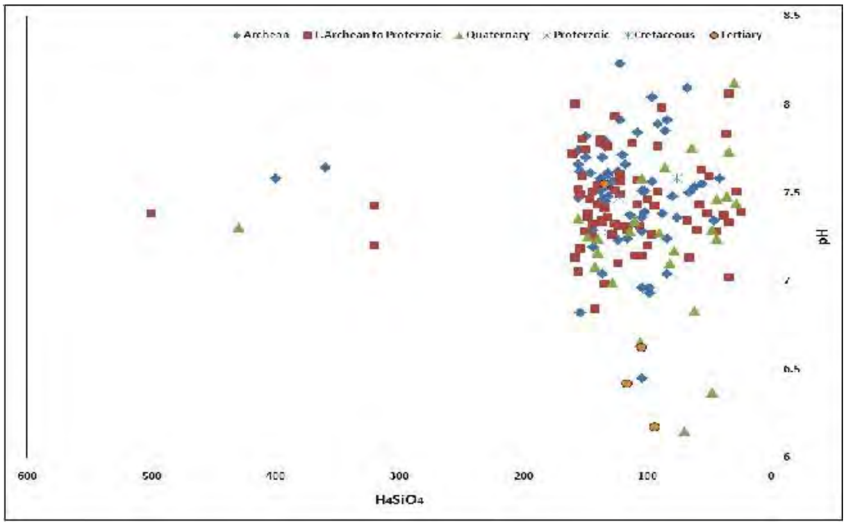


Figure 9: Relationship Between H_4sio_4vs Ph



which shows the considerable interactions with host rock. Average value of it is in formation show that 0.013 in Archean, late Archean to Proterozoic 0.016 and the highest is noted in 0.064 that of lowest in 0.0037.

DISSOLUTION OF SILICA MINERALS

pH and Silica

Hydrogen percentage plays an important role in rock weathering. The dissolution rates of most silicate minerals are independent of pH in the circum-neutral region. They increase with decreasing pH in the acid region and increase with increasing pH in the alkaline region (Drever, 1994). It was observed that there is a correlation of pH and silica in most of the groundwater samples from Late Archean to Proterozoic formations some groundwater samples from Quaternary, Proterozoic, Tertiary and Cretaceous formations (Figure10). The alkaline nature of groundwater in Archean region favors the dissolution of secondary minerals. Higher silica is noted in Archean and late Archean to Proterozoic formation with pH above neutral to Alteration conditions.

Phosphate and Silica

In Archean formations, the PO_4 concentration ranges between 0 and 4.09 with an average of 0.222 mg/L (Figure 12). The higher PO_4 concentration of 4.09 mg/L was observed in groundwater of Rangappanur village. Majority of the samples from Archean and Late Archean to Proterozoic formations show least amount of silica weathering, whereas groundwater samples from topographically higher elevations in the western region show higher silica concentration. There is not much correlation of SiO_2 concentration to $PO_{4.}$

Bicarbonate (HCO_3) and Silica

Weathering of silicate minerals leads the higher concentration of HCO_3 in groundwater (Srinivasamoorthy *et al.,* 2008) and it also indicates the process of recharge (Ophori and Toth, 1989; Subba Rao, 2007, Thivya *et al.,* 2013). Figure 12 shows that there is no definite relationship between HCO_3 and silica in groundwater in six different formations. But in few samples, HCO_3 concentration is increasing with increase in silica concentration. It can be noted from Figure 11 and 12 that concentration of PO_4 and HCO_3 for majority of the samples lies within the 20 mg/L of silica in groundwater.

In Archean formations, HCO3 concentration ranges between 30 and 426 with an average of

Figure 10: Relationship Between H_4Sio_4vs Po_4

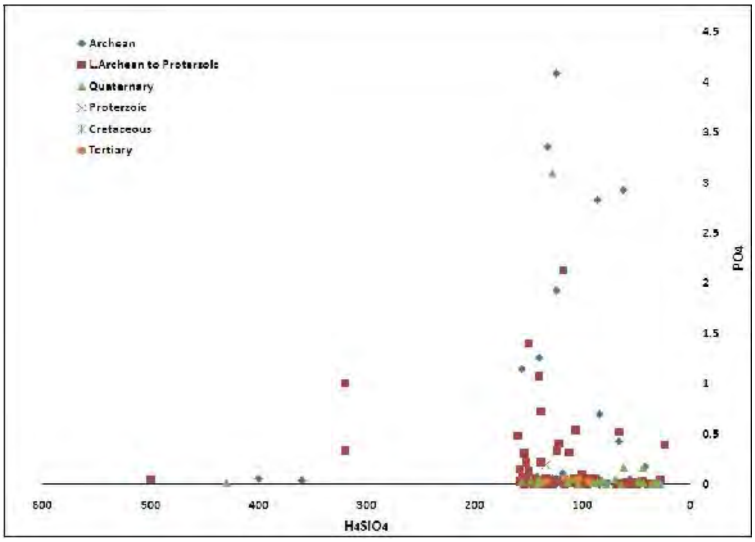
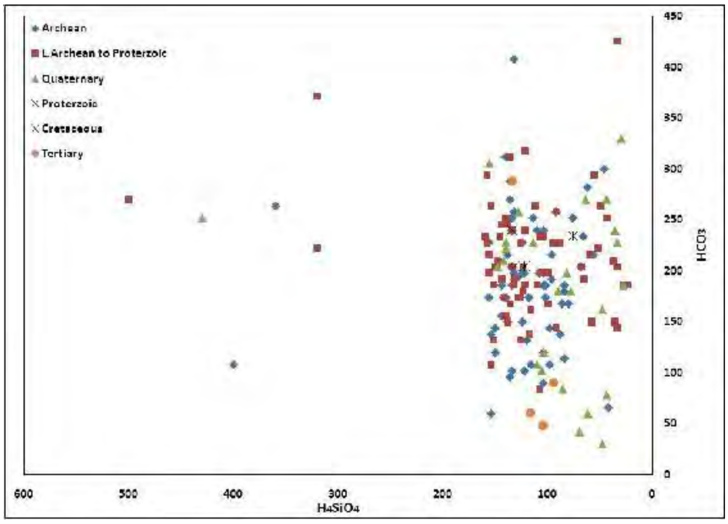


Figure 11: Relationship Between H_4sio_4vs Hco_3



196.71 mg/L (Figure 12). The higher HCO_3 concentration of 426 mg/L was observed in groundwater of Mampazhapattu village.

Statistical Analysis

The need for statistical analysis of the data for determining its hydrogeochemicalnatureis essential. Statistical data generally have better representation than graphical representations because (a) there are a finite number of variables that can be considered (b) variables are generally limited by convention to major ions and (c) superior relationships may be introduced by use of certain procedures (Chidambaram, 2000).

Factor Analysis

Factor analysis was carried out using SPSS 16.0 software package and the results reflect the complexity present in the chemistry. The factors were extracted with Eigenvalues >1 and their percentage of variance and cumulative percentage of variance of hydrogeochemical parameters of the groundwater are given in Table 2.

Factor 1: Samples show strong positive loadings of Cl^-, EC, Na^+, Ca^{2+} and Mg with 25.58% of the total variance (Table 2). The dominant ion for this factor is Cl^-. The higher Cl^- value is observed in the Kilnaraipur, KallakurichiTaluck of Villupuram district which is situated along the banks of the Gamuki River. Saravanan *et al.* (2011) also discussed about the deterioration of quality of groundwater around this region. The representation of higher EC in the study area, which is mainly due to the dissolution of the ions (Narmatha *et al.,* 2011). The other dominant ions, Na^+ and Ca^{2+}, may have originated from carbonate and silicate weathering or due to reverse ion exchange process (Subramani *et al.,* 2009). Mg^{2+} in groundwater also liberated from the Mg-rich minerals like enstatite-hypersthene chlorite, which is more common mineral in gneiss and shear zone (Chan, 2001; Chidambaram, 2000).

Factor 2: Samples accounts for 11.152% of total variance with the high positive loadings of K^+, NO_3 and PO_4 (Table 2). Nitrate concentration occurs

Table 2: Saturation index Formation wise Maximum Minimum Average

Formation	Minimum	Maximum	Average
Archean	0.0037	0.064	0.013315
Late Archean to Protrozoic	0.0063	0.0317	0.0163
Quaternary	0.0038	0.0292	0.013396
Proterzoic	0.0174	0.0223	0.01985
Tertiary	0.005	0.0161	0.010075
Cretaceous	0.0106	0.018	0.0143

in groundwater due to the industrial effluents or sewage infiltration or nitrate fertilizers from intensive agricultural activities (Freeze and Cherry, 1979). PO_4 also indicates impact of anthropogenic activities due to agricultural wastes and phosphate fertilizers (Prasanna *et al.,* 2008).

Factor 3: Samples account for 10.52% of total variance with the high positive loading of HCO_3 and pH (Table. 2) indicating the dissolution of weathering process. The representation of HCO_3^- is due to the weathering of silicates and also indicates the process of recharge (Srinivasamoorthy *et al.*, 2008; Thivya *et al.,* 2013; Subba Rao, 2007).

Factor 4: Samples have strong positive loadings of H_4SiO_4 and TDS with total variance of 10.40% (Table. 2). The North and Southwestern part representing more loadings of H_4SiO_4, this is mainly due to the dissolution of silicates, where the land is mainly used for agricultural purpose.The Central part shows small amount of H_4SiO_4 loadings. This is due to anthropogenic impacts from the agricultural practices (Prasanna *et al.*, 2009, Thivya *et al.*, 2013). It can be observed that the H_4SiO_4 is dominantly occurring in topographically elevated regions (western parts) in the study area.

The spatial representation of factors 1 to 4 shows that more number of factors (factor 1, 2 and 3) were observed in south western part of the study area (Figure 13) which are mainly influenced by leaching of secondary salts, weathering process and agricultural activities. Similarly, Southwestern part also influenced three

Figure 12: Contour Map For Factors Observed In The Study Area

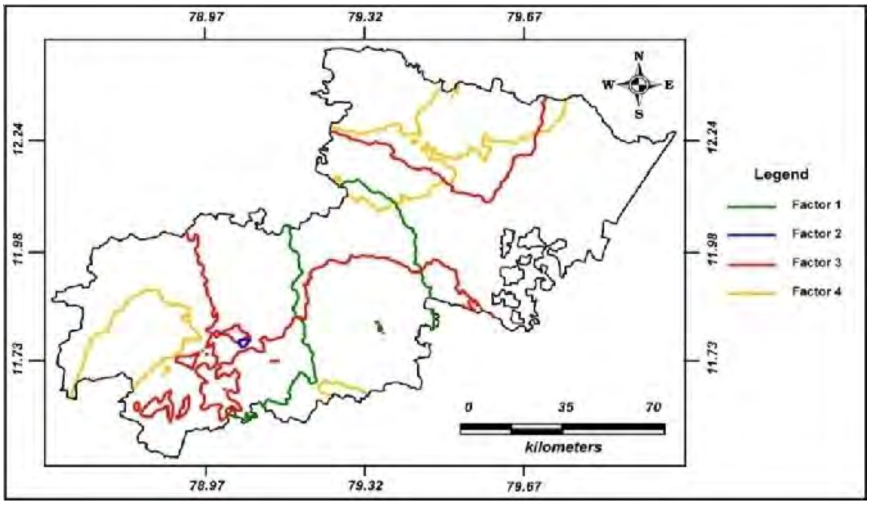


Figure 13: Spatial Distribution Of H_4SiO_4

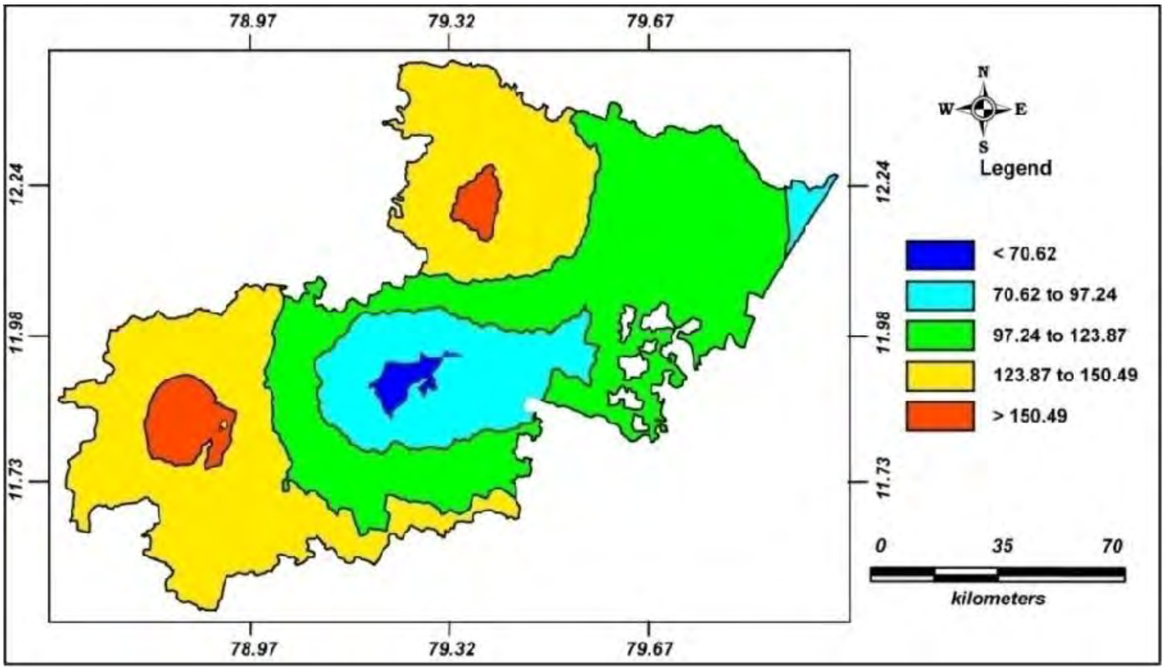


Figure 14: Land Use And Land Cover Map For The Study Area

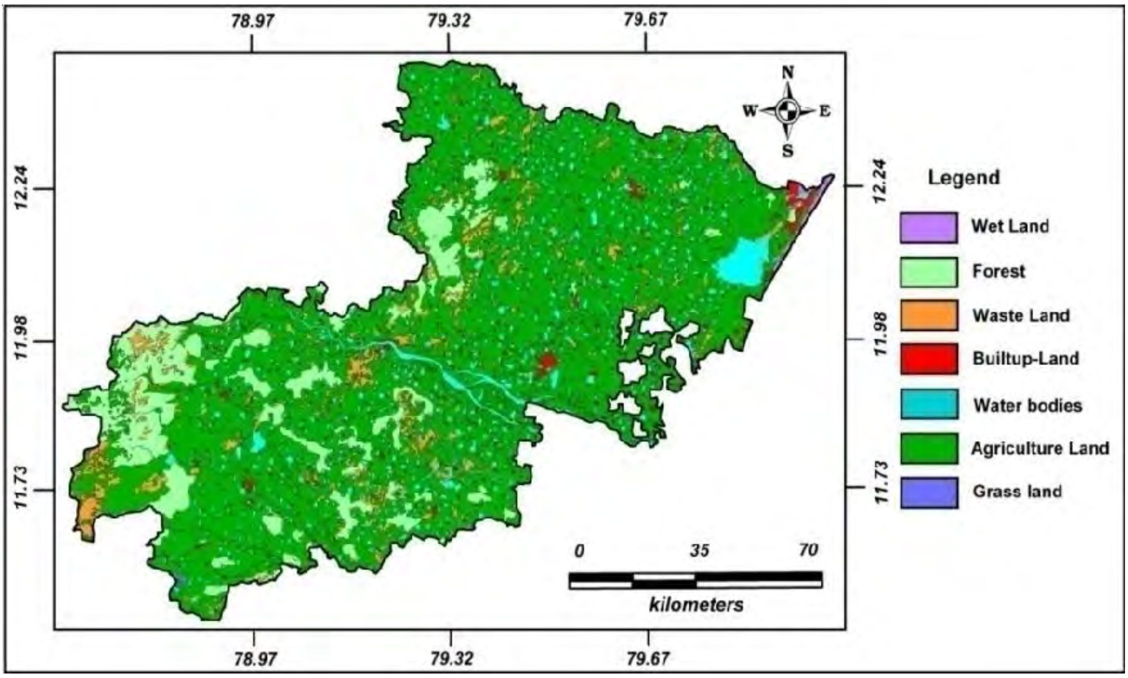


Figure 15: Comparison Of Factor-4 with land Use And Land Cover In The Study Area

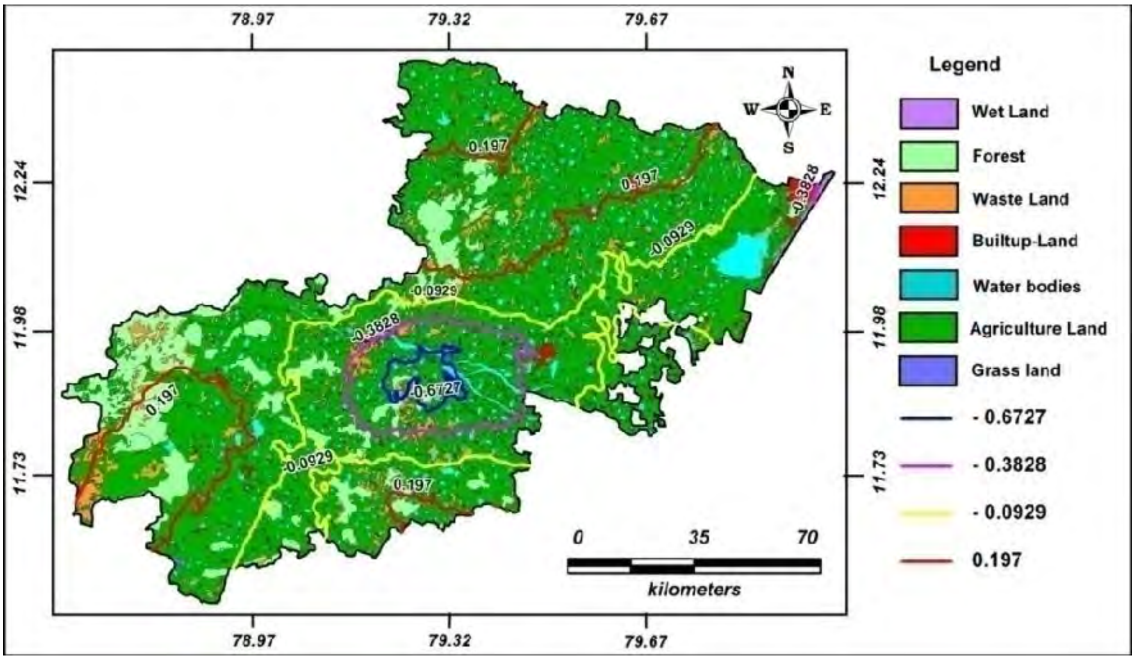


Table 3: Rotated Component matrixes

Rotated Component Matrix				
	Factor 1	Factor 2	Factor 3	Factor 4
Varimax rotated (n = 170) (RPM)				
Ca	**.627**	.118	-.373	.400
Mg	**.592**	-.195	.187	.316
Na	**.817**	.069	.206	-.333
K	.126	**.761**	.249	-.109
F	.251	-.307	.197	.033
Cl	**.969**	-.017	.006	-.007
HCO_3	.292	.327	**.645**	.295
NO_3	.175	**.450**	-.251	.181
SO4	.094	-.062	.048	.274
Po4	-.066	**.631**	.070	-.088
H_4SiO_4	-.111	-.015	.028	**.782**
ph	.012	-.021	**.782**	.053
EC	**.889**	.121	.018	.211
TDS	.470	.323	.238	**.459**
Eigenvalues	3.581	1.561	1.473	1.456
Variance (%)	25.578	11.152	10.520	10.403
Cumulative (%)	25.578	36.730	47.250	57.653

types of factors (Factor 1, 2 and 3) predominantly by weathering process and agricultural activities. Groundwater flows mainly from Eastern to western direction (Figure 3).

The spatial distribution map for silica in groundwater shows that higher silica is found in North and Southwestern regions (Figure 14). It is observed from the study that four different factors (i.e., natural and anthropogenic processes) are helping to increase the amount of silica in groundwater and it is mainly due to the weathering of the hard rock aquifer in the elevated region aided by the agricultural activites. The higher silica (Figure 11) from high land in Archean formations show that there is dissolution of silica due to agricultural activities. Opaline silica from the rice plants provide a readily soluble source of silica, frequent oxidation and reduction cycles of paddy soil may accelerate weathering, which is making silica more soluble (Chidambaram *et al.,* 2007).

CONCLUSION

Groundwater in Villupuram district occurs in the acidic to alkaline environment with a minimum pH value of 6.15 to a maximum value of 8.23. The most of the samples fall in the Ca^{2+}-Mg^{2+}-Cl and Na-Cl type indicates the mixed water type and which may be due to anthropogenic impact or may be due to seawater infiltration into the aquifer.

In Na system, samples are stable with Kaolinite and it tends to move towards Montmorillonite due to the excess supply of silica and also indicates the movement of ions along the groundwater flow path.

The alkaline nature of groundwater in Archean regions favors the dissolution of secondary minerals. The higher PO_4 and silica from high land in Archean formations show that there is dissolution of silica due to agricultural activities. The weathering enhances the HCO_3 concentration along with increasing silica concentration.

The spatial representation of factors 1 to 4 shows that more number of factors (factor 1, 2, 3 and 4) are represented in south western part of the study area which is mainly influenced by, weathering process and agricultural activities and Anthropogenic impact. Similarly, south western part is also influenced by various types of factors (factor 1, 2, and 3) like weathering process and agricultural activities. The dominant hydrogeochemical process in the study area is as weathering processes, leaching of secondary salts and agricultural activities. The study concludes that three different factors are helping the increase the amount of silica in groundwater in Villupuram district, Lithology, elevation and agricultural activity.

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