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

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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 (SiO₂) 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 SiO₂ despite the fact that the exact form of dissolved silica is not known (Al-Rehaili, 2003). Average concentration of silica in natural water ranges between 1.0 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...
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

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Fig: 1 Lithology And Sampling Points Of The Study Area

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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$_4^{3-}$, NO$_3^-$ and H$_2$SiO$_4$ 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 PROCESSES**

In piper plot the concentration of major cations (Ca, Mg, Na and K) and anions (CO$_3^{2-}$, 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
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$_2$SiO$_4$ > 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
Cation + Al-silicate + H$_2$CO$_3$ + H$_2$O = HCO$_3^-$ + H$_4$SiO$_4$ + cation + Al-silicate(s)

Essentially, a primary mineral is converted into a secondary mineral. The secondary minerals are...
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\textsubscript{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 Montmorillonite 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 metastable 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 [H₄SiO₄]. 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 H₄SiO₄ as the other.

The reactions and their equilibrium constants are as follows:

\[
\begin{align*}
3\text{KA1Si}_3\text{O}_8 \text{(c)} + 2\text{H}^+ \text{(aq)} + 12\text{H}_2\text{O} &= \text{KA1}_2\text{Si}_3\text{O}_{10} \text{(OH)}_2 \text{(c)} + 6\text{H}_4\text{SiO}_4 \text{(aq)} + 2\text{K}^+ \text{(aq)} \quad \alpha 2 \\
2\text{KA1Si}_3\text{O}_8 \text{c} + 2\text{H}^+ \text{(aq)} + 9\text{H}_2\text{O} &= \text{H}_4\text{A1}_2\text{Si}_2\text{O}_9 \text{(c)} + 2\text{K}^+ \text{aq} + 4\text{H}_4\text{SiO}_4 \text{(aq)} \quad \alpha 3 \\
2\text{KA1}_2\text{Si}_3\text{O}_{10} \text{(OH)}_2 \text{(c)} + 2\text{H}^+ \text{(aq)} + 3\text{H}_2\text{O} &= 3\text{H}_4\text{A1}_2\text{Si}_2\text{O}_9 \text{(c)} + 2\text{K}^+ \text{(aq)} \quad \alpha 4 \\
2\text{KA1}_2\text{Si}_3\text{O}_{10} \text{(OH)}_2 \text{(c)} + 2\text{H}^+ \text{(aq)} + 18\text{H}_2\text{O} &= 3\text{A1}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \text{(c)} + 2\text{K}^+ \text{(aq)} + 6\text{H}_4\text{SiO}_4 \text{(aq)} \quad \alpha 5 \\
\text{H}_4\text{A1}_2\text{Si}_2\text{O}_9 \text{(c)} + 5\text{H}_2\text{O} &= \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \text{(c)} + 2\text{H}_4\text{SiO}_4 \text{(aq)} \quad \alpha 6
\end{align*}
\]

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

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**Figure 6: Thermodynamic Stability Plot Of K System**

![Figure 6: Thermodynamic Stability Plot Of K System](http://www.ijges.com/current-issue.php)
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 / evapotranspiration 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 (CO₂) AND IONIC STRENGTH**

Partial pressures of CO₂ (pCO₂) in water were calculated from measured pH and alkalinity of groundwater samples using the program WATEQ4F (Plummer et al., 1976).

Log pCO₂ were studied for six different formations exist in the study area. The log pCO₂ 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 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 pCO₂ 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
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 (Figure 10). 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, Thivy 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, HCO$_3$ concentration ranges between 30 and 426 with an average of
196.71 mg/L (Figure 12). The higher HCO₃⁻ 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 hydrogeochemical nature is 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⁺, Ca²⁺, 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, Kallakurichi Taluck 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 Ca²⁺, may have originated from carbonate and silicate weathering or due to reverse ion exchange process (Subramani et al., 2009). Mg²⁺ 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⁺, NO₃⁻ and PO₄³⁻ (Table 2). Nitrate concentration occurs
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$_4$SiO$_4$ and TDS with total variance of 10.40% (Table. 2). The North and Southwestern part representing more loadings of H$_4$SiO$_4$, 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$_4$SiO$_4$ 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$_4$SiO$_4$ 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 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

<table>
<thead>
<tr>
<th>Rotated Component Matrix</th>
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<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
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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 activities. 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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