A study on variation in dissolved silica concentration in groundwater of hard rock aquifers in Southeast coast of India

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Abstract. Ground water of hard rock aquifers due to its lesser permeability results in the increased residence time, which leads to the higher concentration of ions. Hence in order to understand the hydro-geochemistry of the groundwater of a hard rock aquifer in India, 23 groundwater samples were collected from different locations of the study area and subjected to analysis of major cat ions and anions. The results of silica showed different range of concentration and was plotted in different groups. In order to understand the reason for this variation, different techniques like Thermodynamics, Statistics and GIS were adopted and it was inferred that the concentration was mainly governed by lithology and land use pattern of the study area.

1. Introduction

Silica in ground water can be found in two forms as dissolved silica and in particulate matter. Silica dissolved in natural waters is considered to be a good indicator of weathering and water circulation conditions [13]. Silica released as a result of chemical weathering of silicate minerals in rocks and sediments acquired by circulating groundwater and therefore the source of silica (SiO2) in groundwater is mainly from water– rock interaction [15]. 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 [13]. Dissolved silica in water is normally measured as SiO2 despite the fact that the exact form of dissolved silica is not known [1]. Average concentration of silica in natural water ranges between1.0 and 30.0 ml/L [12].

The solubility limit for silica in water is estimated at approximately 120 mg/L at 25°C [40][37]. Solubility of silica in water is directly proportional to temperature [16]. Fournier and Giggenbach et al. (1985) 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 geothermometer in the studies of deep groundwater and geothermal systems. Another study [26] 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 and Quarternary 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 and Quarternary formations.
2. Study area

The study area is located in Tindivanam Taluk, of Villupuram district in figure 1. The study area is in the northern part of Tamil Nadu and close to the State capital of Chennai at a distance of about 100 Kms. Tindivanamtaluk is a hard rock region covering an area of 574.3 sq.km which lies between Latitude 12º 22’ - 11º 53’N and longitude 79º 29’ - 80º1’E. It falls in survey of India Toposheet No. 58-M-6. The Tindivanam in general is having an average elevation of about 42.39 m above the mean sea level (MSL). The elevation map is show in the figure.2 higher elevation >85 m is in Northwestern part and lesser elevation of 13.89 m is in Southeastern region, Tindivanam had a population of 72,796 (Census, 2011) with a sex-ratio of 1,003 females for every 1,000 males, much above the national average of 929. Most of the study area is covered by agricultural lands which is main source of income for people in this taluk shown in figure.3. Numerous small surface water bodies can be seen and which are mainly helps to irrigation activities. It is also can be seen in figure.3 that salt pan activities in south western part of the study area. Salt exploration from back waters for domestic purpose is another source of income for the people at coastal area.

Figure 1. Land use and land cover map for the study area

Figure 2. Surface elevation contours of the study area

Figure 3. Land use and land cover map for the study area

Figure 4. Spatial distribution of water level in the study area
2.1 Climate and Rainfall

The area falls under tropical climate with higher temperature in the summer months of March to May. The average temperature varies from 26 to 41°C [5]. Study area receives rainfall from southwest monsoon (June – September), and northeast monsoon (October – December). The higher rainfall is observed during the northeast monsoon period. The normal annual rainfall is 986 mm of decade. The average groundwater level varies from 1.47 m to 62.83 m above mean sea level (MSL) in the study area [5]figure 4.

2.2 Geology

Figure.1 shows the sampling points and spatial variation of geology in the study area. The study area predominantly comprises of Charnockite, and Hornblende-biotite gneiss in the western part of the study area. Pegmatites contain feldspar and smaller amount of quartz in some locations. Eastern part is mainly composed of quaternary formations. Northeastern part is covered by Clayey sand. Southern part is covered by Argillaceous and calcareous sandstones along with small amount of sand and silt deposits.

3. Methodology

A total of about 23 groundwater samples were collected as figure 1 from hand pumps representing entire Tindivanam Taluk during the monsoon season. The parameters such as temperature and pH were measured in the field. Electrical conductivity (EC) and total dissolved solids (TDS) were measured in the laboratory by using standard electrodes. Collected groundwater samples were analyzed for its major anions and cations using standard procedures [3][34][35].

Calcium, magnesium, bicarbonate, and chloride were determined by trimetric method. Sodium and potassium were analyzed through flame photometry (ELICO CL 378). Silica, phosphate, and sulfate were determined by spectrophotometry (HACH Spectrophotometer). The reliability of the results were determined by the ionic balance of groundwater samples and a 5–10 % of percentage error was noted [14].

An aqueous model program WATEQ4F [4] was used to derive the Log pCO 2 and Ionic strength of groundwater samples. The statistical software SPSS-20 was used for correlation and factor analysis. Thermodynamic stability diagrams were plotted using WATCLAST program.

4. Results and Discussion

The analytical results along with maximum, minimum, and average values of chemical constituents are given in the Table1. Further the dominance orders of the ions are as follows:

$$Ca^{2+} > Na^+ > Mg^{2+} > K^+ = Cl^- > HCO_3^- > H_2SiO_3 > NO_3^- > SO_4^{2-} > PO_4^{3-}$$

Groundwater occurs in the acidic to alkaline environment with a minimum pH value of 7.21 to a maximum value of 7.79. Higher electrical conductivity value noted along the course of the Gadilam River may be due to sewage infiltration [42]. Higher Ca²⁺ and Mg²⁺ occurring in groundwater may be due to weathering of primary mineral sources of rock water interaction [39]. Higher Na⁺ may be due to the weathering of plagioclase-bearing rocks [20]. K⁺ occurs in less quantity in groundwater which may be due to ion exchange or weathering process [10].

Piper diagram [30] was drawn by plotting the proportions (in equivalents) of the major cations (Ca²⁺, Mg²⁺, Na⁺ + K⁺) on one triangular diagram, the proportions of the major anions (CO₃⁻ + HCO₃⁻, Cl⁻, SO₄²⁻) on another, and combining the information from the two lower triangular fields for cations, anions and a central diamond-shaped field shown in figure-5.

The groundwater can be classified into following category based on the location of points in diamond shaped field. In TindivanamTaluk, majority of the groundwater samples fall in Ca-Mg-Cl type and Ca-HCO₃ type, normal alkaline earth water with prevailing bicarbonate and chloride water type. The most of the samples fall in the Ca–Mg–HCO₃ type indicating the natural recharge and weathering from river or rain source or this facies may be due to rock – water interaction [33]. The most of the samples fall in the Ca–HCO₃ facies indicating the dominance of freshwater recharge. This third type is predominantly due to Ion Exchanges [19] [23].
Table 1. Maximum, minimum and average of the chemical constituents in groundwater representing all samples
(All values in mgL-1 except EC in μScm-1 and pH)

| Parameter | Maximum | Minimum | Average |
|-----------|---------|---------|---------|
| pH        | 7.79    | 7.21    | 7.54    |
| EC        | 4010    | 421     | 1590.8  |
| Ca        | 92      | 28      | 57.1    |
| Mg        | 61.2    | 15.6    | 32.5    |
| Na        | 72.2    | 2.9     | 27.1    |
| K         | 10      | 0.3     | 3.3     |
| Cl        | 135.3   | 31      | 85.31   |
| HCO₃⁻     | 274.5   | 81.5    | 167.3   |
| SO₄²⁻     | 37.1    | 16.3    | 21.9    |
| PO₄³⁻     | 86.548  | 6.422   | 15.489  |
| H₂SiO₄⁻   | 108.82  | 0.044   | 30.38   |
| TDS       | 1850    | 220     | 720.5   |

4.1 Electrical Conductivity

The spatial distribution of EC gives three general trends in water as figure 6. Higher concentration of EC was noted in the southern part nearby Varahanadi River. This may be due to the infiltration of saline water from salt pan activities in this region. Lower concentration of EC was observed in the northern part. EC values for majority of the groundwater samples were varies between 1139 and 1857 μS/cm.

Most important among the weathering reactions is the incongruent dissolution of aluminium silicates which may schematically be represented by

\[ \text{Cation} + \text{Al-silicate} + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}_4\text{SiO}_4 + \text{cation} + \text{Al-silicate(s)} \]  

(1)

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 aluminium silicates is accompanied by release of cations and usually of silicic acid. As a result of such reactions alkali in it is 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 aluminium 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 [17] and [40]. 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 [25]. 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 [36] [8].

Minerals of the Kaolinite group are the main alteration products of weathering of feldspar. Besides Kaolinites and Montmorillonites, micas are possible products or intermediates. Mica (illite) has been identified as an intermediate in the decomposition of Na/K-feldspar.

Aggressive waters, high in CO₂ and low in dissolved solids encounter silicates high in cations and silica leaving Alumino- silicate residue with an increase in Al-Si ratio [5]. The initial water yields and attacks the Gibbsite residue which is evidenced by few points in Gibbsite field. 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 7. 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 figure 4. However, as shown by [38] 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 8 shows that 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 [33][8].

When reactions are written for the mineral compatibilities, it is discovered that only three variables need be considered: \([\text{K}^+]\), \([\text{H}^+]\), and \([\text{H}_4\text{SiO}_4]\). Furthermore, the ratio of \([\text{K}^+]\) to \([\text{H}^+]\) in the various equilibrium constants is always unity. Therefore, all the mineral relations can be described in two-dimensional representations involving the ratio of \([\text{K}^+]\) to \([\text{H}^+]\) as one axis, and the activity of \(\text{H}_4\text{SiO}_4\) as the other.

The reactions and their equilibrium constants are as follows:

\[
3\text{KA}_1\text{Si}_3\text{O}_8 (c) + 2\text{H}^+ (aq) + 12\text{H}_2\text{O} = \text{KA}_1\text{Si}_3\text{O}_{10}(\text{OH})_2 (c) + 6\text{H}_4\text{SiO}_4(aq) + 2\text{K}^+(aq)
\]  

(2)
2KA1Si3O8c + 2H⁺(aq) + 9H₂O = H₄A1₂Si₂O₉(c) + 2K⁺(aq) + 4H₄SiO₄(aq)  (3)

2KA1₃Si₃O₁₀(OH)₂(c) + 2H⁺(aq) + 3H₂O = 3H₄A1₂Si₂O₉(c) + 2K⁺(aq)  (4)

2KA1₃Si₃O₁₀(OH)₂(c) + 2H⁺(aq) + 18H₂O = 3A₁₂O₃.3H₂O(c)+ 2K⁺(aq)+ 6H₄SiO₄(aq)  (5)

H₄A1₂Si₂O₉(c) + 5H₂O = Al₂O₃.3H₂O(c) + 2H₄SiO₄(aq)  (6)

Among the aspects of interest 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 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 to move from Kaolinite to Montmorillonite field figure 9. 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 [22]. This may happen due to a long residence time of water in the aquifer matrix [39].

**4.2 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.

Log pCO₂ were studied for two different formations exist in the study area. The log pCO₂ is ranges between -2.65 to -2.09 with an average of -2.43 in Archean formations. It ranges between -2.86 to -2.27 with an average of -2.60 in the Quaternary formations. 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 [9]. Most of the groundwater samples from Archean formations shown in figure 10 exhibits ionic strength greater than 0.01 and ranges between 0.01 and 0.0143 which shows the considerable interactions with host rock. The ionic strength of the Quaternary aquifer samples ranges from 0.005 to 0.01 which indicates that longer residence time or due to influence of salt pan activity and it is more in the topographic lows where water is stagnant due to surface elevations.

**4.3 Dissolution of Silica minerals**

4.3.1 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 circumneutral region; they increase with decreasing pH in the acid region, and increase with increasing pH in the alkaline region [15]. It was observed that there is a correlation with pH and silica in certain
groundwater samples from Archean formations figure.11. The alkaline nature of groundwater in Archean regions favors the dissolution of secondary minerals.

4.3.2 Phosphate and Silica
In Archean formations the PO4 concentrations are ranges between 6.75 and 86.55 with an average of 15.19 mg/L figure 12. The higher PO4 concentration of 86.55 mg/L was observed in groundwater from Illamangalam village. Majority of the samples from both formations show least amount of silica weathering whereas groundwater samples from topographically higher elevations in the western region show higher silica concentration.

4.3.3 Bicarbonate (HCO3) and Silica
Weathering of silicate minerals leads the higher concentration of HCO3 in groundwater [38] and it also indicates the process of recharge [28] [41] [42]. Figure13 shows that there is no definite relationship between HCO3 and silica in groundwater from Archean formations. But in few samples HCO3 concentration is increasing with increasing silica concentration. It can be noted from “Fig. 12 and 13” that concentration of PO4 and HCO3 for majority of the samples lies within the 20 mg/L of silica in groundwater.

4.3.4 Statistical Analysis
The need for statistical analysis of 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 [10].

4.3.4.1 Factor analysis
Factor analysis was carried out using SPSS-20 software package and the results reflect the complexity in chemistry. The factors were extracted with Eigen values >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 Na⁺, HCO3, and Mg²⁺ with 23.03% of the total variance shown in Tables 2 and 3. The Na⁺ is the dominant ion factor which is falls on the south eastern south western regions as figure 14. The higher Na⁺ value is observed in the Idayanchavadi village. The representation of Na⁺ in groundwater is may be due to leaching of secondary salts from backwater region [20] [8].
Factor 2 samples have strong positive loadings of Ca²⁺, Mg²⁺, and HCO3 with a total variance of 21.79 % Table 2 and 3. The dominant ions, Ca²⁺ and Mg²⁺, observed in northwestern and south central part which may have originated from carbonate and silicate weathering along the contact between Charnockite and Hornblende-Biotite gneiss formations figure 14. Mg²⁺ in groundwater also liberated from the Mg-rich minerals like Enstatite–Hypersthenes, which is a more
The common mineral in Charnockites / Gneissic formations [7] [10]. The representation of HCO$_3^-$ is due to the weathering of silicates and it also indicates the process of recharge [39] [28] [41] [42].

![Figure 13. Relationship between H$_2$SiO$_4$ Vs HCO$_3^-$](image)

Factor 3 samples have strong positive loadings of H$_2$SiO$_4$ with total variance of 20.33% Table 2 and 3. The western part representing more loadings of H$_2$SiO$_4$, this is mainly due to the dissolution of silicates where the land is mainly used for agricultural purpose figure 14. The northern part also shows small of amount of H$_2$SiO$_4$ loadings this also due to anthropogenic impacts from the agricultural practices [32][42]. It can be observed that the H$_2$SiO$_4$ is dominantly occurring in topographically elevated regions (western and northern parts) in the study area figure 2 and figure 15.

Factor 4 samples have strong positive loadings of K$^+$, SO$_4^{2-}$ and PO$_4^{3-}$ with a total variance of 20.17 %. The higher loadings of above factors were observed in the southern and eastern parts mainly due to agricultural impact on groundwater [41]. Sulfate and Phosphate in the groundwater system in this region is mainly due to use of considerable amount of Potash fertilizers [27] [11] [29] [2] [42].

The spatial representation of factors 1 to 4 shows that more number of factors (factor 1,2 and 4) were observed in south eastern part of the study area as figure 14 which are mainly influenced by leaching of secondary salts, weathering process and agricultural activities. Similarly, north western part also influenced three types of factors (factor 2, 3 and 4) predominantly by weathering process and agricultural activities. Groundwater flows mainly from western to eastern

![Figure 14. Contour map for factors observed in the study area](image)

![Figure 15. Comparison of Factor 3 with Land use and Land cover in the study area](image)

| Factor | Eigen values | Percentage of Variance | Percentage of Cumulative Variance |
|--------|--------------|------------------------|-----------------------------------|
| 1      | 2.072        | 23.025                 | 23.025                            |
| 2      | 1.961        | 21.790                 | 44.815                            |
| 3      | 1.829        | 20.327                 | 65.143                            |
| 4      | 1.816        | 20.173                 | 85.316                            |
direction figure 4. Water is tapped in the lower part due to salt pan activity and backwater regions which are greatly helps to leaching of secondary salts.

| Table 3. Rotated component matrix |
|----------------------------------|
|       | 1    | 2    | 3    | 4    |
| Ca    | .067 | .893 | -.282| -.091|
| Mg    | .589 | .630 | -.113| .286 |
| Na    | .900 | -.075| -.109| -.088|
| K     | -.218| .037 | .041 | .885 |
| Cl    | .454 | .424 | -.682| .042 |
| HCO₃  | .659 | .599 | .288 | -.044|
| SO₄   | .425 | -.131| -.185| .805 |
| PO₄   | -.186| .441 | .484 | .530 |
| H₄SiO₄| .086 | -.102| .952 | -.043|

Figure 16. Spatial distribution of H₄SiO₄

It was observed from spatial distribution map for silica content in groundwater that higher silica in western and small patches of north eastern regions fig 16. It was observed from the study that three different factors (i.e natural and anthropogenic processes) are helping the increase the amount of silica in groundwater. It is mainly due to the weathering of the hard rock aquifer in the elevated region aided by the agricultural activity. The higher PO₄ and silica in figure 12 from high land in Archean formations show that there is dissolution of silica due to agricultural activities. Opaline silica from the rice plants provides a readily soluble source of silica and frequent oxidation and reduction cycles of paddy soil may accelerate weathering, thereby making silica more soluble [9].

5. Conclusion

Groundwater in Tindivanam Taluk occurs in the near neutral to alkaline environment with a minimum pH value of 7.21 to a maximum value of 7.79. The most of the samples fall in the Ca–Mg–HCO₃ type indicating the natural recharge from surface water or this facies may be due to rock–water interaction. In Na system, samples are stable with Kaolinite and it tends to move towards Montmorillonite due to the excess supply of silica, and also indicating 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 PO₄ and silica from high land in Archean formations show that there is dissolution of silica due to agricultural activities. The weathering enhances the HCO₃ concentration along with increasing silica concentration. The spatial representation of factors 1 to 4 shows that more number of factors (factor 1, 2 and 4) are represented in south eastern part of the study area which are mainly influenced by leaching of secondary salts, weathering process and agricultural activities. Similarly, north western part is also influenced by three types of factors (factor 2, 3 and 4) like weathering process and agricultural activities. The dominant hydrogeochemical process in the study area is as weathering processes, leaching of secondary salts, and agricultural impact. The study concludes that three different factors (lithology, elevation and agricultural activity) are helping to increase the amount of silica in groundwater in Tindivanam Taluk.
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