# Speciation, Saturation Indices and Inverse Modelling Studies in the Metasedimentary Crystalline Limestone Terrain Pandalgudi, Aquifer Region, Viruthunagar District, Tamilnadu, India

## Kaliammal M[a], Udayanapilai A. V[b]

[a]Research Scholar, P.G Studies and Research Centre, Department of Geology, V.O.Chidambaram College, Tuticorin, Tamilnadu, India, Reg No: 9373, Affiliated toManonmaniam Sundaranar University, Tirunelveli-12, Tamilnadu, India

[b]India. Visiting Fellow, Department of Geology, Alagappa University, Karaikudi, Tamilnadu, India

## Abstract

Pandalgudi aquifer region lies between the latitudes from N 9° 15' to N 9° 30' and longitudes from E 78° 0' to E 78° 15'. The physico-chemical parameter results of two groundwater samples from the villages Kosukundu (A) and Raghuramapuram (A1) crossing meta-sedimentary crystalline limestone terrain of Pandalgudi aquifer area are given. The piper analysis of the two samples A and A1 in the flow path of Melakarandai stream represents the geochemical facies of Mixed CaMgCl and $CaHCO_3$ respectively. The speciation character, saturation indices and inverse modelling study of the samples performed through PHREEQC computer software programme in the flow path are interpreted. The speciation analysis through the above software represents the predominance of chemical ionic species of the samples. The chemical mechanisms of dissolution and precipitation activities across the flow path are controlled by saturation indices of the minerals. The inverse flow mineral models of the two samples crossing crystalline limestone terrain established through the software represents eight aqueous geochemical models and these models indicates the dissolution and precipitation activities.

KEYWORDS: Piper analysis, PHREEQC, Speciation, Saturation Indices, Inverse flow mineral model, Dissolution and Precipitation

## Introduction

Modelling is a systematic description of an object or phenomenon that provides important characteristics with the object or phenomenon. The scientific models can be material, visual, mathematical or computational and are often utilised in the construction of scientific theories. Models generally represent the simplified version of a concept. All models are normally solved by using a computer. Groundwater modelling is a tool which helps to analyze many groundwater problems. Before doing modelling concept, one must analyse the model usage and modelling limitations. Numerical modelling study is widely applied in groundwater analysis since mid of 1980 (Charles R. Faust James and W. Mercer, 1980). Some hydro geologists disappointed and exaggerated about the numerical modelling and lastly conclude that numerical models are worthless. The conceptual modelling of groundwater is generally based on mathematical models which have been classified as analytical model and numerical model. Groundwater model can be classified as groundwater flow model, solute transport model, heat transport model and transport model and deformation model (Charles R. Faust James and W. Mercer, 1980). All groundwater models are performed and solved by using a computer. They also have many

groundwater modelling codes. Each modelling code has its own characteristics and limitations. A logical sequential study is adopted in the groundwater models. In each model, it includes model objectives, hydro geological characterisation, modelling software selection, model design (input parameters), model calibration, sensitivity analysis, model verification, predictive simulation and performance monitoring plan (Kaliammal and Udyanapillai 2018). Aqueous geochemical models are generally based on chemical thermodynamics, chemical kinetics or both. The PHREEQC computer software programme has been written in 'C' programming language and is applied for study of speciation, saturation indices, reaction path, advective geochemical reaction and inverse geochemical models. Many researchers have applied various aqueous geochemical models (Helgeson et al., 1970; Plummer et al., 1976; Wolery, 1979; Felmyet al., 1984; Parkhurst et al., 1990; Elangovan et al., 1999; Prasanna et al., 2006; Chidambaram et al., 2012; Suma et al., 2015; Kaliammal and Udayanapillai 2018). PHREEQC and WATQ4F aqueous geochemical models are generally applied by the hydrologist. The WATQ4F is used only for finding out the saturation indices, whereas PHREEQC is widely applied for many applications in geochemical modelling. The geochemical modelling through PHREEQC software demarcates the main geochemical factors and controlling mechanism of geochemistry of groundwater. Notwithstanding the applications of PHREEQC software are more, the speciation character analysis, saturation indices calculation and inverse modelling programme were studied in the flow path of the groundwater samples of the study area.

## Study area

Pandalgudi aquifer region covers 750 sq km, which lies between the latitudes from N 9° 15' to N 9° 30' and longitudes from E 78° 0' to E 78° 15'. Major outcrops in the study area are calc-granulite and crystalline limestone, hornblende-biotite gneiss, charnockite and granite of Proterzoic age and a small part of Tertiary calcareous sandstone. Proterozoic and Tertiary formations are followed by thick calcrete profile of 1 metre thickness of Sub-Recent age. This calcrete zone is overlain by black soil, sandy loamy soil and river alluvium of recent deposits. Upparu stream, Melakarandai stream, a part of Gundar River and Vaippar Rivers are remarkably significant drainages in the study area. The two groundwater samples located in Melakarandai stream section crossing meta-sedimentary crystalline limestone outcrop are undertaken for aqueous geochemical modelling study in the aquifer area (Figure 1).
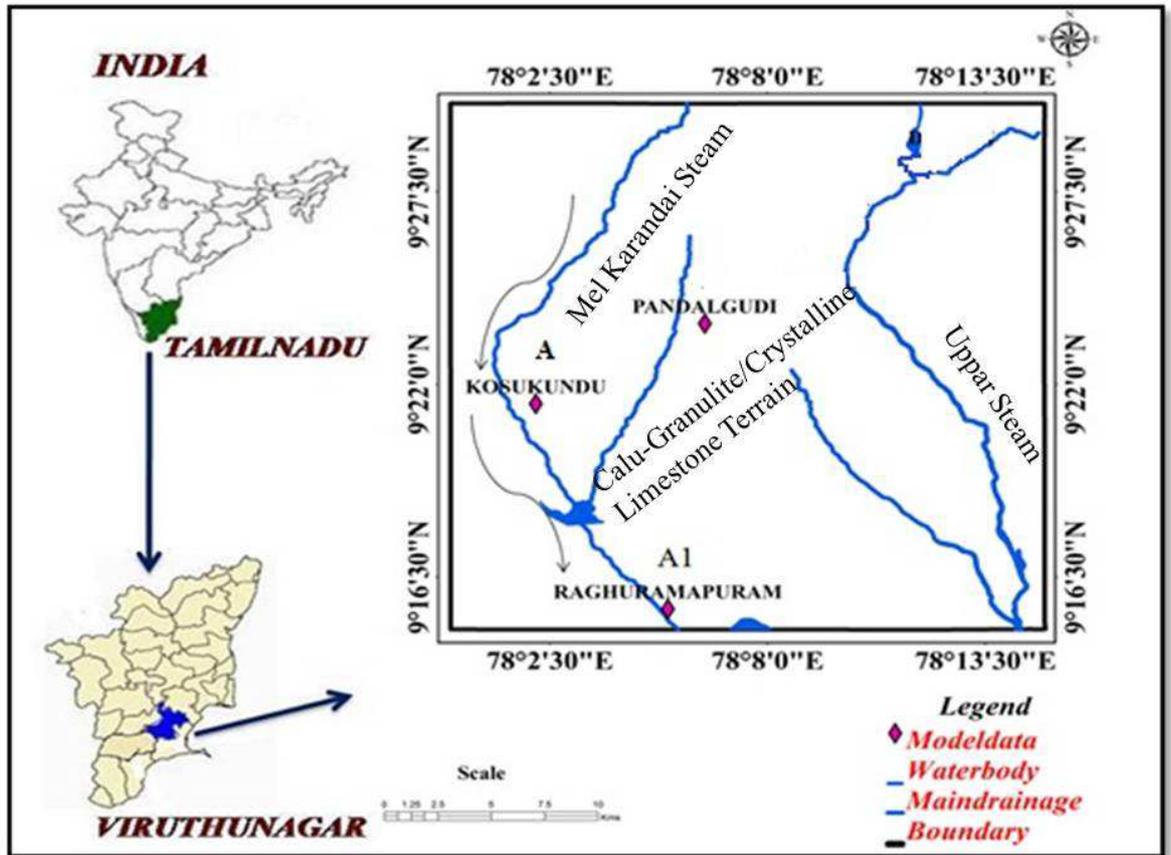
Figure 1.Location and drainage map of the study area.

## Materials and Methods

The selected two representative groundwater samples collected in the flow path direction of Melakarandai stream crossing meta-sedimentary crystalline limestone terrain were subjected to major ion analysis. The major ion such as $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $HCO_3^-$, $Cl^-$, $SO_4^{2-}$, $NO_3^-$ and $F^-$, were analyzed by adopting the standard procedure APHA (1995). But $SiO_2$ analyses of the groundwater samples were estimated through spectrophotometric method. Speciation, Saturation Indices and Inverse modelling studies were carried out by using PHREEQC software program (Patkhrust and Appelo 1999).

## Results and discussion

The analytical results of the two groundwater samples from Kosukundu (A) and Raghuramapuram (A1) in the flow path of Melakarandai stream crossing crystalline limestone terrain are given in the (Table 1). The Piper (1944) geochemical facies diagram of the sample A and A1 plotted, are also given in the (Figure 2). These above two samples falls on the two different geochemical facies of CaMgCl and CaHCO₃ respectively in the diamond shaped plot of Piper diagram. The CaMgCl facies of the 'A' samples before crossing crystalline limestone terrain is changed into CaHCO₃ rich geochemical facies after crossing crystalline limestone terrain. Based on the results obtained from the flow path, speciation character, saturation indices and inverse geochemical models were established by the computer software programme PHREEQC.

**Table 1.The selected representative samples data of A and A1, in the flow path of crystalline limestone terrains respectively**

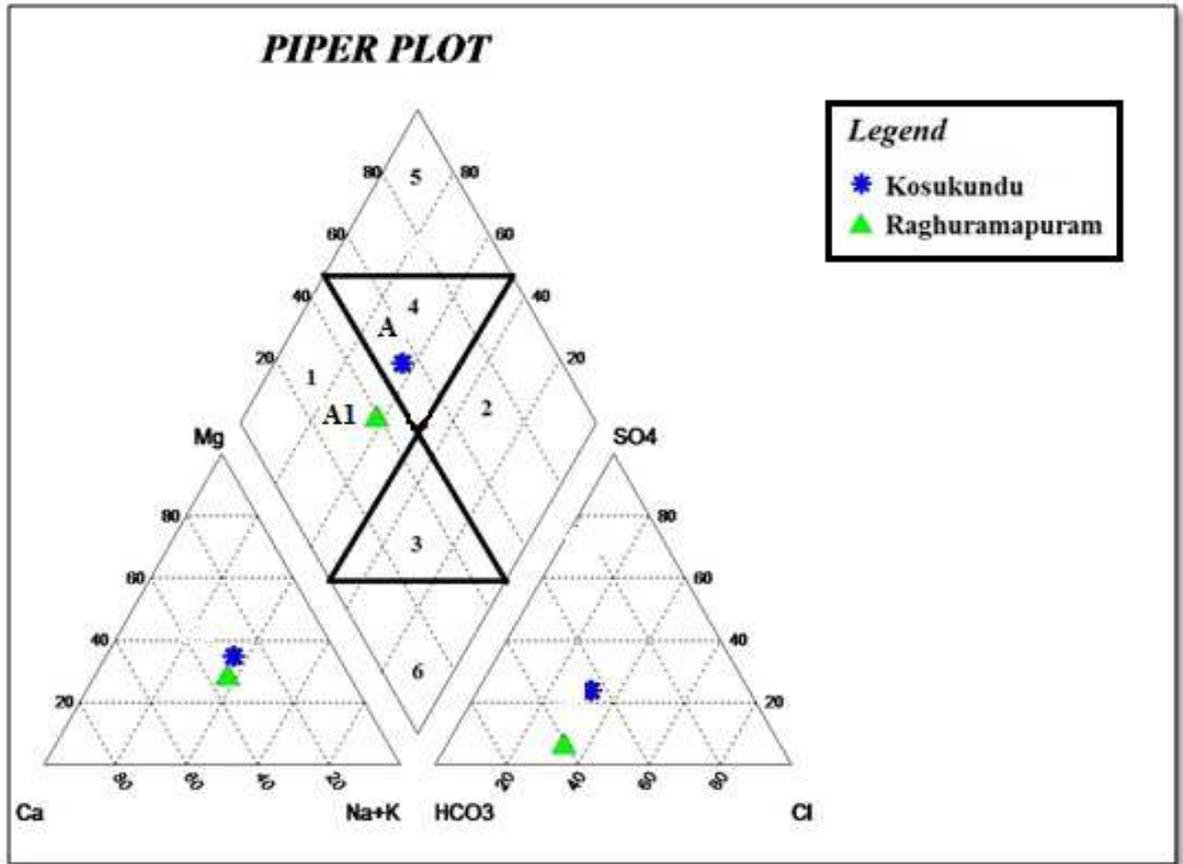| Solution | Village/Terrains | TDS | EC | pH | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $HCO_3^-$ | $SO_4^{2-}$ | $Cl^-$ | $NO_3^-$ | $F^-$ | $SiO_2$ | TH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Kosukundu | 500.2 | 809 | 7.5 | 51.2 | 35.99 | 65 | 11 | 207.4 | 84.4 | 85.02 | 2 | 0.22 | 22.3 | 87.19 |
| A1 | Raghuramapuram | 697 | 1180 | 7.3 | 80 | 40 | 87 | 24 | 403 | 32 | 128 | 0.14 | 0.19 | 5.5 | 119.88 |



Figure 2. Geochemical facies diagram of the sample A and A1 of the study area.

**Speciation**

 The speciation result of groundwater solution (A) before crossing meta-sedimentary crystalline limestone terrain and the groundwater solution (A1), after crossing limestone terrain are tabulated in the (Tables 2 a and b). Speciation describes the chemical reactivity of element in ion form in the groundwater and its values are represented in molality. The molality illustrates how much number of moles per solute per kilogram of solvent. Molality unit is mentioned as mole/kg. In every speciation study through PHREEQC, the activity of solution can also be measured. Speciation study represents not only species distribution but also provides its molality, activity, log molality and log-gamma values. Distributions of species are represented in the oxidation state.

**Table 2a. Distribution of Species or Speciation of the solution Kosukundu (A) sample before crossing crystalline limestone terrain**

| B Solution Element Oxidation State | Molality Mmol/Kgw | No. of Species | % of Major Species |
|---|---|---|---|
| C(4) | $4.381 \times 10^{-3}$ | 9 | 31.17% |
| Ca | $1.278 \times 10^{-3}$ | 7 | 9.94% |
| Cl | $2.399 \times 10^{-3}$ | 1 | 17.07% |
| F | $1.159 \times 10^{-5}$ | 7 | 0.05% |
| H (O) | $1.412 \times 10^{0}$ | 1 | 0.00% |
| K | $2.815 \times 10^{-4}$ | 3 | 2.94% |
| Mg | $1.481 \times 10^{-3}$ | 6 | 10.54% |
| N (5) | $1.429 \times 10^{-4}$ | 1 | 0.05% |
| Na | $2.829 \times 10^{-3}$ | 6 | 20.11% |
| O (O) | $0.000 \times 10^{0}$ | 1 | 0.00% |
| S (6) | $8.791 \times 10^{-4}$ | 7 | 1.59% |
| Si | $3.714 \times 10^{-4}$ | 4 | 0.44% |

**Table 2b. Distribution of Species or Speciation of the solution Raghuramapuram (A1) sample after crossing crystalline limestone terrain**

| A Solution Element Oxidation State | Molality Mmol/Kgw | No. of Species | % of Major Species |
|---|---|---|---|
| C(4) | $7.214 \times 10^{-3}$ | 9 | 12.81% |
| Ca | $7.759 \times 10^{-3}$ | 7 | 13.78% |
| Cl | $5.772 \times 10^{-3}$ | 1 | 10.25% |
| F | $1.267 \times 10^{-5}$ | 7 | 0.02% |
| H (O) | $8.816 \times 10^{0}$ | 1 | 0.00% |
| K | $1.539 \times 10^{-4}$ | 3 | 0.27% |
| Mg | $1.155 \times 10^{-2}$ | 6 | 20.51% |
| N (5) | $7.878 \times 10^{-6}$ | 1 | 0.01% |
| Na | $3.927 \times 10^{-3}$ | 6 | 6.97% |
| O (O) | $4.117 \times 10^{0}$ | 1 | 0.00% |
| S (6) | $1.948 \times 10^{-2}$ | 7 | 34.58% |
| Si | $4.391 \times 10^{-4}$ | 4 | 0.80% |

In speciation data output, the 'C (4)' indicates the total molality values of ions of $HCO_3^-$, $CO_2$, $CaHCO_3^+$, $MgHCO_3$, $NaHCO_3$, $CaCO_3$, $CO_3^{-2}$, $MgCO_3$ and $NaCO_3$, while the 'Ca' data includes the total molality values of $Ca^{+2}$, $CaHCO_3^+$, $CaSO_4$, $CaCO_3$, $CaF^+$, $CaOH^+$ and $CaHSO_4^+$. The 'Cl' data mentions the sole molality values of $Cl^-$ only. The 'F' data contains the total molality values of $F^-$, $MgF^+$, $CaF^+$, $NaF$, $HF$, $HF_2^-$ and $SiF_6^{-2}$. The H (O) data points out the sole molality values of $H_2$ only. The data 'K' represent the sum molality values of $K^+$, $KSO_4^-$ and $KOH$. The data 'Mg' consists of the sum molality values of $Mg^{+2}$, $MgHCO_3^+$, $MgSO_4$, $MgCO_3$, $MgF^+$ and $MgOH^+$. The data 'N (5)' indicates the sole molality values of $NO_3^-$ only. The data 'Na' represents the sum molality values of $Na^+$, $NaHCO_3$, $NaSO_4^-$, $NaCO_3^-$, $NaF$ and $NaOH$. The data 'O (O)' points out solely the molality values of $O_2$ only. The data S (6) represents the total molality values of $SO_4^{-2}$, $CaSO_4$, $MgSO_4$, $NaSO_4^-$, $KSO_4^-$, $HSO_4^-$ and $CaHSO_4^+$. The data 'Si' includes the sum of the molality values of ions of $H_4SiO_4$, $H_3SiO_4^-$, $H2SiO_4^{-2}$ and $SiF_6^{-2}$.

**Speciation results of the study area**

In the flow model before crossing meta-sedimentary crystalline limestone terrain, the A solution (Kosukundu) (Table 2a) reports the predominance of ionic species of C (4), Cl, Na and Mg with the percentage values of moles 31.17%, 17.07%, 20.11% and 10.54% respectively than the other species. But A1 solution at Raghuramapuram after crossing meta-sedimentary crystalline limestone outcrop reveals the predominance of ionic species of C (4), Ca, Mg and S(6) with the percentage of 12.81%, 13.78%, 20.51% and 34.58% respectively. The predominance of Ca and Mg in the A1 solution may be derived from the dissolution from limestone and calcrete sources. The drainage of Melakarandai stream is fully covered by calcrete deposits. The dissolving Ca and Mg ion from groundwater derived from the source rocks of calc-alkaline nature, forms calcrete (Udayanapillai et al., 2014, Perumal Velmayil and Udayanapillai, 2015, Perumal Velmayil et al., 2015, 2017). The predominant sources of S(6) in A1 solution may be obtained from the sulphides and sulphates of heavy metal, gypsum, anhydrite and pyrite derived from the source rocks and also from secondary sources like, the excessive uses of fertilizer in agriculture field.

**Saturation Indices**

The aim of the study of saturation indices is used to foretell the relative mineralogy of the litho unit from the groundwater without collecting and analyzing the mineralogy of solid samples (William J. Duetsch et al., 1997). The aqueous solution model established through PHREEQC (Parkhurst and Appelo, 1999) helps to calculate Saturation Indices of the minerals.

When the saturation indices are greater than zero or less than zero or in the zero level, it indicates the mineral precipitation in the flow path and in oversaturated state or dissolution in flow path and in under saturated condition or equilibrium state of mineral constituent in solution respectively. The saturation indices of the mineral in the flow path model vary depending upon topography and geology of the terrain (Suma et al., 2015; Kaliammal and Udayanapillai 2018). The calculated saturation indices of the samples A and A1 crossing limestone terrain are given in (Tables 3 a and b).

**Table 3a. The saturation indices of the groundwater sample Kosukundu (A) before crossing limestone terrain**

| Mineral Phase | SI Log | IAP Log | KT | Chemical Composition |
|---|---|---|---|---|
| Anhydrite | -2.09 | -6.45 | -4.36 | CaSO4 |
| Aragonite | -0.05 | -8.39 | -8.34 | CaCO3 |
| Calcite | 0.09 | -8.39 | -8.48 | CaCO3 |
| Chalcedony | 0.12 | -3.43 | -3.55 | SiO2 |
| Chrysotile | -3.22 | 28.98 | 32.20 | Mg3Si2O5(OH)4 |
| CO2(g) | -2.12 | -20.27 | -18.15 | CO2 |
| Dolomite | 0.38 | -16.71 | -17.09 | CaMg(CO3)2 |
| Fluorite | -2.54 | -13.14 | -10.60 | CaF2 |
| Gypsum | -1.87 | -6.45 | -4.58 | CaSO4:2H2O |
| H2(g) | -23.00 | -23.00 | 0.00 | H2 |
| H2O(g) | -1.51 | -0.00 | 1.51 | H2O |
| Halite | -6.85 | -5.26 | 1.58 | NaCl |
| O2(g) | -37.12 | 46.00 | 83.12 | O2 |
| Quartz | 0.55 | -3.43 | -3.98 | SiO2 |
| Sepiolite | -2.16 | 13.60 | 15.76 | Mg2Si3O7.5OH:3H2O |
| Sepiolite (d) | -5.06 | 13.60 | 18.66 | Mg2Si3O7.5OH:3H2O |
| SiO2(a) | -0.72 | -3.43 | -2.71 | SiO2 |
| Talc | 0.72 | 22.12 | 21.40 | Mg3Si4O10(OH)2 |

**Table 3b. The saturation indices of the groundwater sample Raghuramapuram (A1) after crossing limestone terrain**

| Mineral Phase | SI Log | IAP Log | KT | Chemical Composition |
|---|---|---|---|---|
| Anhydrite | -0.53 | -4.89 | -4.36 | CaSO4 |
| Aragonite | 0.69 | -7.65 | -8.34 | CaCO3 |
| Calcite | 0.83 | -7.65 | -8.48 | CaCO3 |
| Chalcedony | 0.20 | -3.35 | -3.55 | SiO2 |
| Chrysotile | -0.76 | 31.44 | 32.20 | Mg3Si2O5(OH)4 |
| CO2(g) | -2.06 | -20.21 | -18.15 | CO2 |
| Dolomite | 1.95 | -15.14 | -17.09 | CaMg(CO3)2 |
| Fluorite | -2.21 | -12.81 | -10.60 | CaF2 |
| Gypsum | -0.31 | -4.89 | -4.58 | CaSO4:2H2O |
| H2(g) | -23.20 | -23.20 | 0.00 | H2 |
| H2O(g) | -1.51 | -0.00 | 1.51 | H2O |
| Halite | -6.42 | -4.84 | 1.58 | NaCl |
| O2(g) | -36.72 | 46.40 | 83.12 | O2 |
| Quartz | 0.63 | -3.35 | -3.98 | SiO2 |
| Sepiolite | -0.39 | 15.37 | 15.76 | Mg2Si3O7.5OH:3H2O |
| Sepiolite (d) | -3.29 | 15.37 | 18.66 | Mg2Si3O7.5OH:3H2O |
| SiO2(a) | -0.64 | -3.35 | -2.71 | SiO2 |
| Talc | 3.33 | 24.73 | 21.40 | Mg3Si4O10(OH)2 |

In the flow path model of crystalline limestone terrain between A and A1 samples, the saturation indices of minerals were analyzed. The sulphate mineral such as anhydrite and gypsum are in under saturated condition in both solutions and represent the dissolution activities in the flow path. Among the carbonate minerals such as aragonite, calcite and dolomite, the aragonite is in under saturated condition in A solution and oversaturated in A1 solution and shows both dissolution and precipitation in the flow path. But the calcite and dolomite are in oversaturated in both the solution and shows precipitation only. The low saturation indices of carbonates causes for dominant scaling properties (Demoel et al., 2013).

Among the silicates minerals such as chalcedony, chrysotile, sepiolite and sepiolite'd', the chalcedony is in oversaturated condition in both solution, whereas crystotile, sepiolite and sepiolite 'd' are in under saturated condition. These mineral shows both precipitation (chalcedony) and dissolution activities (chrysotile, sepiolite and sepiolite'd') in the flow path.

The quartz mineral shows oversaturated condition which indicates precipitation. The amorphous silica ($SiO_2$ (a)) shows under saturated in both solution which indicate dissolution activities. The talc mineral shows oversaturated condition which shows precipitation activity in the flow path. The chloride mineral halite shows under saturated condition in both solution and represents the dissolution activities in the flow path. The variation in saturation indices may be due to time of contact of water and rock interaction (Kaliammal and Udayanapillai 2018).

In general, the saturation indices, precipitation and dissolution activities are controlled by weathering activities of minerals from the source rock and also by influx of water by recharge and drain out by the process of evaporation and evapo-transpirtation (Srinivasamoorthy et al., 2012, Kaliammal and Udayanapillai, 2018).Saturation indices of minerals in the flow path of crystalline limestone terrain represent their dissolution and precipitation activities of the minerals in the flow path.

**Inverse modelling**

Inverse geochemical modelling is used to infer the geochemical reactions that prove the change in chemical composition of water along a flow path. Two chemical analysis of groundwater data from two locations crossing a lithological outcrop in the flow path are needed to find out the different set of phases of potential reactive models. A mole balance model is a set of mole transfer of phases and reactions that causes for the change in composition along the flow path (Suma et al., 2015, Kaliammal and Udayanapillai, 2018). Here, the flow model was run between the samples Kosukundu (A) and Raghuramapuram (A1) crossing crystalline limestone through Melakarandai stream flow path of the study area. There are eight models of aqueous solutions or groundwater that were derived by PHREEQC software in the limestone terrain of the study area (Table 4). Such similar inverse models were derived in the granite terrain of Chinnar river basin (Suma et al., 2015) and Upparu basin, Pandalgudi (Kaliammal and Udayanapillai, 2018). From the eight models, different set of mineral phases of mole transfer values were identified. The incorporation and removal of phase mole values are defined as dissolution and precipitation of mineral phases respectively. The positive mole transfer value is considered as dissolution activities, whereas negative phase mole transfer values

represent as precipitation (Chidambaram et al., 2012; Suma et al., 2015, Kaliammal and Udayanapillai, 2018).

**Table 8.4. The Inverse flow model of the groundwater samples Kosukundu (A) and Raghuramapuram (A1) in the limestone terrain of the study area**

| Mineral Name | Model I | Model II | Model III | Model IV | Model V | Model VI | Model VII | Model VIII |
|---|---|---|---|---|---|---|---|---|
| Anhydrite | 1.58E-02 | -1.97E+01 | - | 1.58E-02 | 1.47E-02 | - | 1.58E-02 | 1.58E-02 |
| Aragonite | -2.33E-02 | -2.33E-02 | -2.33E-02 | -2.33E-02 | -1.79E-02 | - | -2.33E-02 | - |
| Calcite | - | - | - | - | - | -1.02E-02 | - | -2.33E-02 |
| Chalcedony | - | - | - | - | - | - | - | - |
| Chrysotile | 3.08E+00 | -4.94E+00 | -1.71E+01 | 3.08E+00 | -2.11E+00 | -9.14E+00 |  | 3.08E+00 |
| Dolomite | 1.53E-02 | 1.53E-02 | 1.53E-02 | 1.53E-02 | 8.88E-03 | - | 1.53E-02 | 1.53E-02 |
| Gypsum | - | 1.97E+01 | 1.58E-02 | - | - | 1.29E-02 | - | - |
| Halite | 3.93E-03 | 4.04E-03 | 4.04E-03 | 4.04E-03 | - | -5.48E-03 | 4.04E-03 | 4.04E-03 |
| Quartz | - | -1.24E+01 | -4.27E+01 | - | - | - | 6.53E+00 | - |
| Sepiolite | - | 7.41E+00 | 2.56E+01 | 1.85E+01 | -1.27E+01 | -5.49E+01 | 1.96E+01 | - |
| Sepiolite d | 1.85E+01 | - | - | - | - | - | - | 1.85E+01 |
| SiO$_2$ | - | - | - | - | - | - | - | - |
| Talc | -1.54E+01 | - | - | -1.54E+01 | 1.06E+01 | 4.57E+01 | -1.31E+01 | -1.54E+01 |

In the above eight models, the anhydrite mineral occurs in the models I, II, IV, V, VII and VIII. It represents the uniform positive phase mole transfer values, except in the model II. It generally shows dissolution activity in the flow path and II model shows negative phase mole transfer values which represent precipitation activity.

The Aragonite occurs in all models, except in the model VI and VIII. It shows all negative phase mole transfer values and represents the precipitation activity. The calcite concentrations occur only in the model VI and VIII, with varying negative phase mole values and represent precipitation activity in the flow path.

The dolomite minerals occur in all the models except in the model VI. All models show positive mole transfer values and represents dissolution activities. It shows generally uniformity in the phase mole transfer values except in the V. Dissolution of dolomite accompany with the weathering process of the CaMg bearing minerals (dolomite, biotite and hornblende etc) from the litho unit took place in the flow path (Udayanapillai et al., 2012).

The halite mineral model is available in all models, except in V with varying positive and negative phase mole values. This models represent both dissolution and precipitation activities. When evaporation exceeds rainfall, the level of precipitation will be available more (Grzegors S. Kyzypelz et al., 2013).

The mineral chalcedony is not available in all models. The mineral chrysotile occurs in all models except in VII, with varying positive and negative phase mole transfer values representing both dissolution and precipitation activities in the flow path.

The mineral gypsum occurs in the models of II, III and VI with varying positive phase mole transfer values representing dissolution activities. The mineral quartz occurs only in the model II, III and VII with varying negative and positive mole transfer values. It represents both precipitation and dissolution activities in the flow path.

The mineral sepiolite clay mineral occurs in all models except in I and VIII models, with varying positive and negative phase mole transfer values. It represents both dissolution and precipitation activities in the flow path. The occurrence of sepiolite clay mineral in calcrete indicates arid environments (Udayanapillai et al., 2014).

The solubility of sepiolite and sepiolite (d) are significantly different. The sepiolite (d) is the disordered form of sepiolite. It occurs only in the model I and VIII with uniform positive phase mole transfer values, representing dissolution activities. The amorphous $SiO_2$ is not available in all models in the flow path. The mineral talc is available in all models except in II and III. It shows varying both positive and negative phase mole transfer values. It represent both dissolution and precipitation activities in the flow path. The dissolution and precipitation activities of the minerals are also indicated by saturation indices along the flow path from recharge to discharge area (Kaliammal and Udayanapillai, 2018). The discharging and discharging activities depends upon the rainfall, evaporation and evapo-transpirtation.

## Conclusion

In the flow model of limestone terrain established through PHREEQC software, the following salient features are observed. The speciation character expresses the predominance of ionic species of the samples. In the flow path, the A1 solution after crossing limestone terrain, shows the predominance of ionic species of C(4), S(6) Mg and Ca with the percentages of 12.81%, 34.58%, 20.51% and 13.78% respectively. The saturation indices represent dissolution and precipitation activities of mineral and controlling mechanism. Eight inverse mineral models were derived in the flow path which shows precipitation and dissolution activities in the flow path.

## Acknowledgement

## References

1. **APHA, (1995).** "Standard methods for the examination of water and waste water". 19th Ed., Washington, DC: APHA.
2. **Charles R Faust James and W. Mercer (1980).** "Ground-water Modeling: Numerical Modelsa". NGWA, Vol. 18 (4), pp. 395 – 409.
3. **De Moel P. J, Vander Helm A. W. C, Van Riji M and Van Dijk J. K, (2013).** "Assessment of calculation methods for calcium carbonate saturation in drinking water DIN 38404-10 compliance". Drinking water Engingerring Science. Vol. 6, pp. 115 – 124.
4. **Elangovan, K., Balasubramanian, A., ThirugnanaSambandam, R., Rengarajan, R., Satish, P. N and Janardhan, A. S. (1999).** Geochemical modeling of crystalline aquifers of Salem district, Tamil Nadu. Indian J Geochem. Vol. 14, pp. 1–17.
5. **Felmy, A. R., Bervin, D. C and Jenne, E. A. (1984)**. MINTEQ. A computer program for calculating aqueous geochemical equilibria. US EPA 84-032, Athens GA.
6. **Gbadebo, A. M., Taiwo, A. M and Adeola, A. J (2013).** "Assessment of dissolved silica content of groundwater from Southwestern Nigeria". Journal of Human Ecology. Vol. 43 (3), pp. 273 – 279.
7. **Grzegorz S. Kyzypetz, ShawanDogramaci and Pauline F. Grierson, (2013).** "Geochemical and hydrogeochemical processes controlling groundwater salinity of large Inland, Wetland of Northwest Australia". Chemical Geology. Vol. 357, pp. 164 – 177.
8. **Helgeson, H. C., Brown, T. H., Nigrini, A., and Jones, T. A. (1970).** "Calculation of mass transfer in geochemical processes involving aqueous solutions". GeochimicaetCosmochimicaActa. Vol. 34, pp. 569–592.
9. **Kaliammal M and Udayanapillai A.V (2018).** "Aqueous Geochemical Modeling in the Granite Terrain of Pandalgudi Aquifer Region, Viruthunagar District, Tamilnadu, India". International Journal of Creative Research Thoughts (IJCRT). Vol. 6 (2), ISSN:2320-2882, pp. 442 – 448.
10. **Parkhurst, D. L., Thorstenson, D. C and Plummer, L. N. (1990).** PHREEQE—A computer program for geochemical calculation. USGS water resources investigations report. Vol. 195, pp. 80 – 96.
11. **Parkhurst, D.L and Appelo, C.A.J. (1999).** User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport,

and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99–4259, pp. 312.

12. **Perumal V and Udayanapillai. A.V. (2015)** "Petro-Mineralogy and Major Elements Geochemistry of Regolith profile of Calcrete deposits at Pandalgudi, ViruthunagarDistrict, Tamilnadu, INDIA". Published a paper in International Research Journal of Earth Science (ISCA-IRJES)-2015-039.

13. **Perumal V, Udayanapillai A.V, John S. Armstrong-Altrin and Satyanarayanan M (2017)** "Major element geochemistry and depositional environment of Regolithcalcrete deposit of Nedungkulam village, near Sathankulam area Tuticorin district, Tamilnadu, India". Published a paper in International Journal of Outreach, Vol-9, 2017, pp. 307-313.

14. **Perumal V, Udayanapillai A.V, John S. Armstrong-Altrin and Satyanarayanan. M (2015)** "Micromorphology and GIS based Evaluation of Major Element Geochemistry of Calcrete Deposits in and around Nedungulam village, near Sathankulam, Tuticorin District, Southern Tamilnadu, India" Published a paper in International Journal of Frontier Geoscience, American V-King Scientific Publication, Vol-3 Issue-2, 2015, pp. 11-19.

15. **Piper A. M, (1944).** "A graphic procedure in the geochemical interpretation of water analysis". Journal of Transactions – American Geophysical Union. Vol. 25, pp. 914 – 923.

16. **Plummer, L. N., Jones, B. F., and Truesdell, A. H. (1976).** "WATEQF—Afortran IV version of water, a computer program for calculating chemical equilibrium of natural waters". US Geol Survey water resources investigations report. Vol. 76, pp. 1361.

17. **Prasanna, M. V., Chidambaram, S., Srinivasamoorthy, K., Anandhan, P and John Peter, A. (2006).** A study on hydrogeochemistry along the ground water flow path in different litho units in Gadilam river basin, Tamil Nadu (India). International Journal of Chemical Sciences. Vol. 2 (2), pp. 157–172.

18. **S. Chidambaram, P. Anandhan, M. V. Prasanna, A. L. Ramanathan, K. Srinivasamoorthy and G. Senthil Kumar (2012).** "Hydrogeochemical Modelling for Groundwater in Neyveli Aquifer, Tamil Nadu, India, Using PHREEQC: A Case Study". Journal of Natural Resources Research. Vol. 21 (3), pp. 311 – 324.

19. **Srinivasamoorthy K, Vasanthavigar M, Chidambaram S, Anandhan P, Manivannan R and Rajivgandhi R, (2012).** "Hydrochemistry of groundwater from Sarabanga Minor Basin, Tamilnadu, India". Proceedings of the International Academy of Ecology and Environmental Sciences. Vol. 2 (3), pp. 193 – 203.

20. **Suma CS, Srinivasamoorthy K, Saravanan K, Faizalkhan A, Prakash R and Gopinath S (2015).** "Geochemical Modeling of Groundwater in Chinnar River Basin: A Source Identification Perspective". International Conference on Water Resources, Coastal and Ocean Engineering (ICWRCOE 2015). Vol. 4, pp. 986 – 992.

21. **Udayanapillai A.V, Thirunanasambandam R, Venkataraman P, Thangavel M, Kaliammal M, Perumal V and Amar Kumar Dash, (2014).** "GIS based evaluation of major element geochemistry of calcrete deposit in and around Sivalarpatti village, near Pandalgudi, Virhthunagar District, Tamlinadu, India". Journal of Outreach. Vol. VII, pp. 136 – 141.

22. **Udayanapillai A. V, Venkataraman P, Jeyaranjeetham J and Perumal V, (2012).** "Geochemistry of Groundwater in and around Vilathikulam and OttaipidaramTaluks, Thoothukudi District, Tamilnadu, India". Journal of Outreach. Vol. 5, ISSN: 0975 1246, pp. 113 – 116.

23. **William J. Deutsch and Randy Siegel (1997).** Groundwater Geochemistry: Fundamentals and Applications to Contamination.

24. **Wolery, T. J. (1979)**. Calculation of chemical equilibrium between aqueous solutions and minerals: The EQ3/EQ6 software package (41 pp.). Livermore, University of California, Lawrence Livermore Laboratory (UCRL 52658).