AQUEOUS GEOCHEMICAL MODELING IN THE GRANITE TERRAIN OF PANDALGUDI AQUIFER REGION, VIRUTHUNAGAR DISTRICT, TAMILNADU, INDIA

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Abstract : Pandaludi aquifer area is bounded within the latitudes from N 9° 15' to N 9° 30' and longitudes from E 78° 0' to E 78° 15'. The analytical results of two groundwater samples from the villages Aladipatti (A) and Koppuchittampatti (A1) crossing granite terrain of Pandalgudi aquifer region are given. The piper analysis of the two samples A and A1 in the flow path of Uppar stream represents the geochemical facies of CaMgCl and CaCl respectively. Speciation character, Saturation Indices and Inverse modelling study of the samples through PHREEQC software programme in the flow path are interpreted. The speciation represents the predominance of ionic species of the samples. The dissolution and precipitation activities across the flow path are represented by the saturation indices of the minerals. The inverse flow mineral models of the two samples crossing granite terrain show eight aqueous geochemical models and these models represents the dissolution and precipitation activities.

Keywords - **Piper geochemical facies, PHREEQC, Speciation, Saturation Indices, Inverse flow mineral model, Dissolution, Precipitation.**

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I. INTRODUCTION

Groundwater modelling is a tool which analyzes many groundwater problems. Generally, models are useful for reconnaissance studies of proceeding field investigation, for interpretive studies of following the field program and for interpretation study of future field behavior. In addition, models are useful for studying various flow type bahaviors by examining hypothetical aquifer problem. Before doing modelling concept, model usage and modelling limitations are to be known. Numerical models are extensively used for groundwater analysis since mid of 1980 (James and Mercer, 1980). Some hydrologists disillusioned and overreacted about numerical modelling and finally conclude that models are worthless. Conceptual modelling in groundwater study based on mathematical models is classified as analytical model and numerical model. The groundwater models types are generally classified as groundwater flow model, solute transport model, heat transport model and deformation model (James and Mercer, 1980). All models are normally solved by using a computer. There are many different groundwater modelling codes available. Each code has their own capabilities, operation characteristics and limitations. Groundwater models are developed in a logical sequence such as model objective, hydrogeological characterisation, modelling software selection, model design (input parameter), model calibration, sensitivity analysis, model verification, predictive simulation and performance monitoring plan. Geochemical modelling is the practice of using chemical thermodynamics, chemical kinetics or both. Geochemical modelling techniques using PHREEQC software will help in demarcating the main factors and mechanism controlling the geochemistry of groundwater. This computer programme has been written in 'C' programming language. This has been applied for the study of speciation, saturation indices calculation, reaction path and advective geochemical calculations and inverse geochemical modelling. Numerous researchers in various part of the world have applied various geochemical models for the aqueous geochemical studies (Helgeson *et al.,* 1970; Plummer *et al.,* 1976; Shannon *et al.,* 1977; Spostigo and Mattigod, 1979; Wolery, 1979; Felmy *et al.,* 1984; Parkhurst *et al.,* 1990). The universal problems, demands and scientific priorities of geochemical modeling were discussed elaborately by the (Jenne 1981). He described the simulation model of calcite dissolution and porosity changes in saltwater mixing zone in coastal aquifer by using PHREEQC. The same model was used by (Elangovan *et al.,* 1999). WATQ4F geochemical reaction model proposed by (Truesdell and Jones, 1973, Plummer *et al.,* 1976), has been utilised to determine the solubility equilibrium for the groundwater of Gadilam river basin (Prasanna *et al.,* 2006). WATQ4F is used only for finding out the saturation indices. Despite the PHREEQC software (Parkhurst and Appello 1999) applications are more in the geochemical modelling, speciation character, saturation indices and inverse modelling programm were studied in the flow path of the groundwater samples.

II. STUDY AREA

Pandalgudi aquifer area extends over about 750 sq km, bounded between the latitudes from N 9° 15' to N 9° 30' and longitudes from E 78° 0' to E 78° 15'. Major lithounits are calc-granulite and crystalline limestone, hornblende-biotite gneiss, charnockite and granite of Proterozoic formation and a small part of Tertiary calcareous sandstone. The Proterozoic and Tertiary formations are overlain by calcrete black soil, sandy loamy soil and river alluvium of Recent and Sub-recent deposits. Uppar stream, Melakarandai stream, a part of Gundar river and Vaippar river are the important drainages. The two groundwater samples located in the Uppar stream section crossing granite outcrop are undertaken for aqueous geochemical modelling study in the aquifer area (Figure 1).
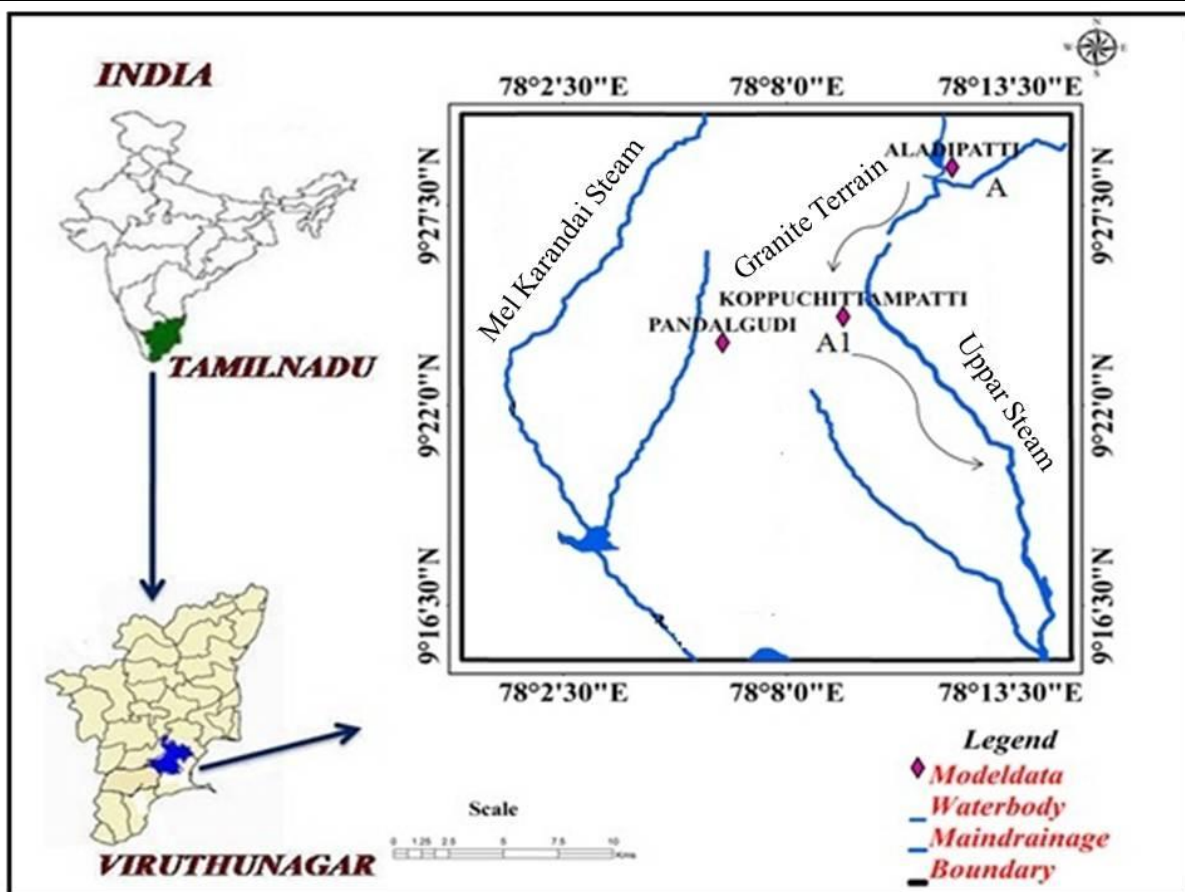
Figure 1. The drainage map of the study area.

III. MATERIALS AND METHODS

The selected two representative groundwater samples in the flow path direction of Uppar stream crossing in granite terrain were selected to major ion analysis, such as Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and F^-, by adopting the standard procedure of APHA (1995). But SiO_2 analysis of groundwater is estimated through spectrophotometric method. Speciation, Saturation Indices and Inverse modelling were performed by using PHREEQC software program (Patkhrust and Appelo 1999).

IV. RESULTS AND DISCUSSION

The analytical results of the groundwater samples. Aladipatti (A) and Koppuchittampatti (A1) in the flow path of upparu stream terrain crossing granite terrain are given in the (Table 1). The Piper (1944) geochemical facies diagram of the sample A and A1 are also given in the (Figure 2). These two samples falls on the two discrete zones of geochemical fcies of CaMgCl and CaCl respectively in the diamond shaped plot of Pipers diagram. The CaMgCl facies of the 'A' samples before crossing granite terrain is changed into CaCl rich geochemical facies after crossing granite terrain. Based on the results obtained from the flow path, speciation character, saturation indices and inverse geochemical models were established by the computer software programm PHREEQC.

Table 1. The selected representative samples of analytical data of A and A1, in the flow path of Granite terrains respectively

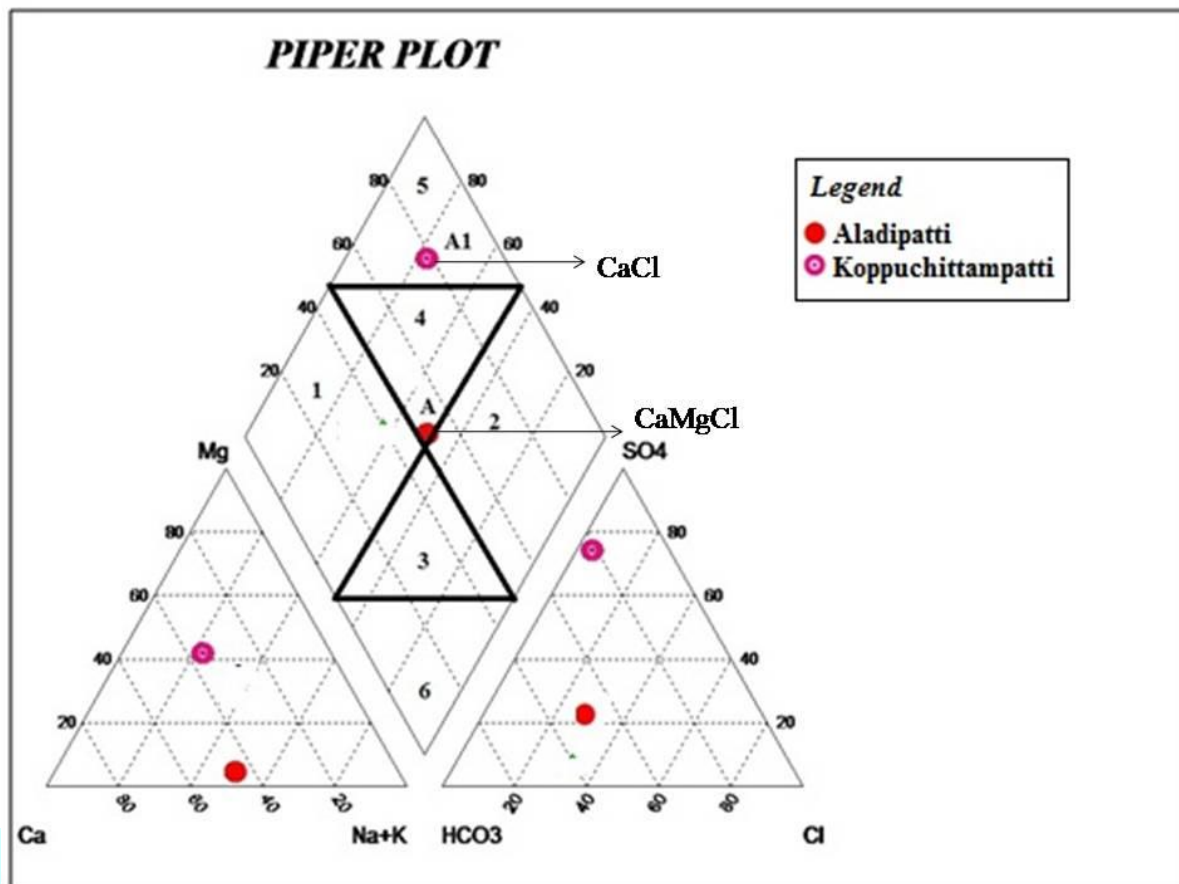| Solution	Village/Terrains	TDS	EC	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	F^-	SiO_2	TH
A	Aladipatti	3764	4300	7.5	285	16	350	20	293	101	103	0.38	0.2	20.2	300
A1	Koppuchittamaptti	536	1835	7.9	61	43	38	11	366	990	43	0.26	0.21	28.2	104

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

4.1 Distribution of Species or Speciation

The distribution of species or speciation character of the groundwater solution of (A) before crossing granite terrain and the groundwater solution (A1), after crossing granite terrain are tabulated in the (Tables 2 a and b). The speciation defines the chemical reactivity of the element in ion forms in the groundwater and its values are in molality. Molality is defined as number of moles per solute per kilogram of solvent. The SI unit for molality is mole/kg. In the speciation study through PHREEQC, the activity of solution is also measured. The speciation study represents the species distribution and its molality, activity, log molality and log-gamma values. The speciation tables obtained from PHREEQC software provides the distribution of species in the oxidation state.

Table 8.2a. Distribution of Species or Speciation of the solution Aladipatti (A) sample before crossing granite terrain

A Solution Element Oxidation State	Molality Mmol/Kgw	No.of Species	% of Major Species
C(4)	8.806×10^{-3}	9	42.11%
Ca	1.998×10^{-3}	7	9.94%
Cl	3.613×10^{-3}	1	17.28%
F	1.001×10^{-5}	7	0.05%
H (O)	3.544×10^{0}	1	0.00%
K	6.143×10^{-4}	3	2.94%
Mg	1.647×10^{-3}	6	7.88%
N (5)	1.000×10^{-5}	1	0.05%
Na	3.787×10^{-3}	6	18.11%
O (O)	0.000×10^{0}	1	0.00%
S (6)	3.334×10^{-4}	7	1.59%
Si	9.161×10^{-5}	4	0.44%

Table 8.2b. Distribution of Species or Speciation of the solution Koppuchittampatti (A1) sample after crossing granite terrain

A1 Solution Element Oxidation State	Molality Mmol/Kgw	No.of Species	% of Major Species
C(4)	1.963×10^{-1}	9	59.91%
Ca	1.200×10^{-2}	7	3.66%
Cl	4.000×10^{-3}	1	1.22%
F	1.800×10^{-4}	7	0.05%
H (O)	3.429×10^{0}	1	0.00%
Mg	8.000×10^{-3}	6	2.44%
Na	7.500×10^{-2}	6	22.89%
O (O)	2.515×10^{0}	1	0.00%
S (6)	4.000×10^{-3}	7	1.22%
Si	2.820×10^{-2}	4	8.61%

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

4.2 Speciation Result of the Study Area

In the flow model before crossing granite terrain, the 'A' solution (Aladipatti) (Table 8.2a) shows the predominance of ionic species of C (4), Cl and Na with the percentage of moles 42.11%, 17.28% and 18.11% respectively than the other species. But A1 solution after crossing granite outcrop shows predominance of ionic species of C (4), Na and S(i) with the percentage values of 59.91%, 22.89% and 8.61% respectively than the other species. In both solutions, C4 is the predominant species. The occurrence of carbonate rich calcrete deposit in Koppuchittampatti village is more evident for the supporting of predominance of C4 species (alkalinity) in the groundwater samples of study area.

4.3 Saturation Indices

The purpose of the study of saturation indices is used to prognosticate the relative mineralogy of the stratigraphy unit from the groundwater without collecting and analyzing the mineralogy of solid samples (Duetsch *et al.,* 1997). The aqueous solution groundwater speciation model through PHREEQC (Parkhurst and Appelo, 1999) helps to calculate saturation indices of the minerals.

If saturation indices are greater than zero, it indicates the mineral precipitation in the flow path and the solution is oversaturded. If saturation indices are less than zero, it indicates the mineral dissolution in the flow path and the solution is undersaturated in nature. The saturation indices zero indicates equilibrium state of mineral constituents in solution. The saturation indices of mineral in the flow path models vary, depending upon topography and geology of the area (Suma *et al.,* 2015). The calculated saturation indices for the samples A and A1 crossing granite terrain are given in (Tables 3 a and b).

Table 8.3a. The saturation indices for the groundwater sample Aladipatti (A) of before crossing granite terrain

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----------------------------Saturation indices--------------------

Phase        SI log    IAP log     KT

Anhydrite    -2.38     -6.74     -4.36 CaSO4
Aragonite     0.20     -8.13     -8.34 CaCO3
Calcite       0.35     -8.13     -8.48 CaCO3
Chalcedony   -0.49     -4.04     -3.55 SiO2
Chrysotile   -5.54     26.66     32.20 Mg3Si2O5(OH)4
CO2(g)       -1.64    -19.79    -18.15 CO2
Dolomite      0.75    -16.34    -17.09 CaMg(CO3)2
Fluorite     -2.51    -13.11    -10.60 CaF2
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Gypsum        -2.16    -6.74    -4.58 CaSO4:2H2O
H2(g)        -22.60   -22.60     0.00 H2
H2O(g)        -1.51    -0.00     1.51 H2O
Halite        -6.56    -4.97     1.58 NaCl
O2(g)        -37.92    45.20    83.12 O2
Quartz        -0.06    -4.04    -3.98 SiO2
Sepiolite     -4.72    11.04    15.76 Mg2Si3O7.5OH:3H2O
Sepiolite(d) -7.62    11.04    18.66 Mg2Si3O7.5OH:3H2O
SiO2(a)       -1.33    -4.04    -2.71 SiO2
Talc          -2.81    18.58    21.40 Mg3Si4O10(OH)2
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Table 8.3b. The saturation indices for the groundwater sample Koppuchittampatti (A1) after crossing granite terrain

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------------------------Saturation indices------------------------

Phase        SI log    IAP log    KT

Anhydrite    -1.44     -5.80     -4.36 CaSO4
Aragonite     2.64     -5.69     -8.34 CaCO3
Calcite       2.79     -5.69     -8.48 CaCO3
Chalcedony    2.00     -1.55     -3.55 SiO2
Chrysotile    5.83     38.03     32.20 Mg3Si2O5(OH)4
CO2(g)       -1.35    -19.50    -18.15 CO2
Dolomite      5.60    -11.49    -17.09 CaMg(CO3)2
Fluorite     -0.05    -10.65    -10.60 CaF2
Gypsum       -1.22     -5.80     -4.58 CaSO4:2H2O
H2(g)       -24.60    -24.60      0.00 H2
H2O(g)       -1.51     -0.00      1.51 H2O
Halite       -5.40     -3.82      1.58 NaCl
O2(g)       -33.92     49.20     83.12 O2
Quartz        2.43     -1.55     -3.98 SiO2
Sepiolite     7.01     22.77     15.76 Mg2Si3O7.5OH:3H2O
Sepiolite(d)  4.11     22.77     18.66 Mg2Si3O7.5OH:3H2O
SiO2(a)       1.17     -1.55     -2.71 SiO2
Talc         13.54     34.94     21.40 Mg3Si4O10(OH)2
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The sulphate minerals such as anhydrite and gypsum are in undersaturated condition in both A and A1 solution, where as the carbonate minerals such as aragonite, calcite and dolomite are in the state of supersaturated condition in both solutions. The low saturation indices of carbonate mineral causes for dominant scaling properties (Demoel *et al.,* 2013). The chloride mineral 'halite' is also in the state of undersaturated condition in both solutions. The large negative saturation indices values for halite reflect the high solubilities of Na^+, K^+ and Cl^- in water.

The silicates minerals includes chalcedony, chrysotile, quartz, sepiolite, sepiolite 'd', SiO_2 and talc. Among the above silicate minerals, the sepiolite, sepiolite 'd' and amorphous silica are in undersaturated condition in both solutions. But the chalcedony, chrysotile, quartz and talc mineral changes from undersaturated condition to supersaturated condition in the final solution.

The negative saturation indices represent dissolution activities in the flow path, whereas positive saturation indices represent the precipitation activities in the flow path (Suma *et al.,* 2015). The sulphate minerals such as anhydrite and gypsum undergo dissolution activities in the flow path, whereas the carbonate mineral such as aragonite, calcite, dolomite, proceeds precipitation activities in the flow path. But the silicate minerals such as chalcedony, chrysotile and quartz causes for both dissolution and precipitation activities in the flow path, whereas sepiolite, SiO_2 (a) and talc minerals undergo dissolution activities in the flow path of the granite terrain. The halite also causes for dissolution activities in the flow path. The dissolution and precipitation activities classification based on saturation indices have already applied on the flow path models of granite terrain of Chinnar river basin (Suma *et al.,* 2015). The precipitation and dissolution tendency may be increased or decreased due to the evaporation and recharge of water in the groundwater flow movement. The variation of saturation indices may also be due to the time of contact of water and rock interaction.

In general, saturation indices, dissolution and precipitation activities are controlled by weathering activities of minerals from source rock and also by influx of water by recharge and drain out by the process of evaporation and evapotranspiration. Thus saturation index of the minerals in the flow path of granite terrain represent their dissolution and precipitation activities of the minerals.

4.4 Inverse modelling

Inverse geochemical modelling has been utilised to infer the geochemical reactions that justify the change in chemical composition of water along a flow path. For this interpretation, two chemical analyses of groundwater data from two locations along a flow path crossing a geological outcrop are required 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 accounts for the change in composition along the flow path (Suma et al., 2015). Here, the flow model was run between the samples Aladipatti (A) and Koppuchittampatti (A1) crossing granite terrain through uppar stream flow path of the study area. There are eight mineral models of aqueous solutions groundwater which were derived through PHREEQC software in the granite 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). From the eight models, different set of mineral phases of mole transfer values were identified. The addition and removal of phase mole values are crossided as dissolution and precipitation of mineral phases respectively. The positive phase mole transfer value is noted as dissolution activities, whereas negative phase mole transfer values represent as precipitation (Chidambaram *et al.,* 2012; Suma et al., 2015).

Table 8.4. The Inverse flow model was run in the study area for the samples of Aladipatti (A) and Koppuchittampatti (A1) in granite terrain

Mineral Name	Model I	Model II	Model III	Model IV	Model V	Model VI	Model VII	Model VIII
Anhydrite	-1.44E-02	1.37E+03	1.37E+03	-	-	-	1.37E+03	-
Aragonite	1.87E-01	-	-	-	-	1.87E-01	1.87E-01	-
Calcite	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Chalcedony	-	-	-	3.23E+02	-	-	--	-
Chrysotile	-1.52E+02	1.12E-01	-	--	8.44E+02	-1.52E+02	1.02E-01	2.74E+03
Dolomite	-2.57E-01	-2.57E-01	-2.57E-01	-2.57E-01	-2.57E-01	-2.57E-01	-2.57E-01	-2.57E-01
Gypsum	-1.37E+03	1.37E+03	-	-	-	-1.44E-02	-1.37E+03	-
Halite	-1.72E-01	-1.72E-01	-1.72E-01	-1.72E-01	-1.72E-01	-1.72E-01	-1.72E-01	-1.72E-01
Quartz	-	-	-	-	-2.54E-01	-	-	-
Sepiolite	-6.69E-01	-	-5.99E-02	-9.69E+02	-1.27E+03	-	9.25E-02	-
Sepiolite d	-9.15E+02	-9.69E+02	-5.99E-02	-	-1.27E+03	-9.15E+02	-	-
SiO2	-	-	3.23E+02	-	2.11E+03	-	-	5.49E+03
Talc	7.62E+02	5.08E-01	6.46E+02	-4.99E-02	6.46E+02	7.62E+02	-	2.74E+03

In the eight granite terrain models of the study area, anhydrite, aragonite, calcite, chrysotile, SiO_2 and talc show the positive phase mole transfer values and represent dissolution activities in the flow path.

The calcite is always in the stable form which dissolves in the groundwater solution. The presence of more calcrete deposits over the granite basement indicate that the primary source rock aquifers of calc-alkaline and per-alkaline compositional aquifer in the depth of the study area (Udayanapillai *et al.,* 2014).

Dolomite occurs in all the eight models. It shows negative phase mole transfer value uniformly in the all models. So, the negative phase mole transfer values indicate the precipitation. The secondary dolomitization process involves $CaCO_3$ dissolution and dolomite precipitation (Amlan Banerjee, 2016). The formation of dolomite may also be due to microbial mediation and temperature of formation (Roberts *et al.,* 2017).

The halite mineral phase is available in all eight models and show uniform negative phase mole transfer values in the flow path. The negative values halite indicates the precipitation activity in the flow path. When the evaporation exceeds rainfall, the level of halite precipitation will be available more (Grzegors S. Kyzypelz *et al.,* 2013). The occurrence of sepiolite clay mineral in calcrete indicates arid environments (Udayanapillai *et al.,* 2014). The solubility of sepiolite and sepiolite (d) is significantly different. The sepiolite (d) is the disordered form of sepiolite. The amorphous SiO_2 indicates the dissolution activity in the flow path direction. In the alkaline water, SiO_2 dissolution will be more (Gbadebo *et al.,* 2013).

The gypsum and anhydrite occurs in certain models and shows both dissolution and precipitation activities in the flow path respectively by indicating positive and negative phase mole transfer values. The dissolution and precipitation activity of minerals are also indicated by saturation indices along the flow path from recharge to discharge area.

V. CONCLUSION

In the flow model of granite terrain established through PHREEQC software, the following results are obtained. The speciation character represents the predominance of ionic species of the samples. In both solution A and A1 groundwater samples in the flow path, C4 (alkalinity) is the predominant species. The saturation indexes of the minerals in the flow path of granite terrain represent their dissolution and precipitation activities of the minerals and controlling mechanism. Eight inverse mineral models were derived in the flow path of the terrain which also indicates the precipitation and dissolution activities in the flow path.

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