

Significance of saturation index of certain clay minerals in shallow coastal groundwater, in and around Kalpakkam, Tamil Nadu, India

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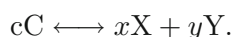
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The saturation index of clay minerals like Gibbsite, Kaolinite, Illite, Montmorillonite and Chlorite in groundwater were studied in detail by collecting 29 groundwater samples from the shallow coastal aquifers in and around Kalpakkam. The samples collected were analysed for major cations, anions and trace elements by using standard procedures. The study reveals that pH has a significant role in the saturation index (SI) of minerals. It also shows that the relationship of electrical conductivity to the SI of these minerals is not significant than that of the ionic strength, log pCO₂ values, and alumina silica ratio have significant relation to the SI of these clay minerals. The SI of these clay minerals was spatially distributed to identify the areas of higher SI. Silica has good correlation to SI of Kaolinite, Gibbsite and Montmorillonite and Al has good correlation to SI of all the minerals except to that of Chlorite.

1. Introduction

Thermodynamic stability of a groundwater is characterized by the state of SI with respect to a particular mineral. Since most of the earth materials are alumino-silicates, the SI of water in contact with these minerals helps us to understand/predict the reaction pathways.

The value of ionic activity product (IAP) for a mineral equilibrium reaction in a natural water may be compared with the value of K_{sp} , the solubility product of the mineral. The mineral may be actively dissolving for the case where the mineral C is being dissolved according to the reaction



IAP is given by Fetter (1988) as:

$$\text{IAP} = (\alpha_x)^x (\alpha_y)^y.$$

Solubility products for a number of compounds are given by different authors and in this study, the data from the WATEQ4F database has been used, where $\alpha = \gamma m$; m is the mole concentrate for the specific ion in question and

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + a_iB\sqrt{I}},$$

where γ_i is the activity coefficient of ionic species i , Z_i is the charge of ionic species i , I is the ionic strength of the solution, A is a constant equal to

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0.5085 at 25°C, B is a constant equal to 0.3281 at 25°C, and a_i is the effective diameter of the ion.

At standard condition, the standard Gibbs free energy of a reaction ΔG_r° is the difference between the sum of the free energy of the products and the sum of the free energy of the reactants:

$$\Delta G_r^\circ = \sum \Delta_r^\circ \text{ products} - \sum G_r^\circ \text{ reactants.}$$

It is related to the equilibrium constant by the formula

$$\Delta G_r^\circ = RT \ln K_{sp},$$

where R is the gas constant, which is a conversion factor equal to 0.00199 kcal/(mole·°K), T is the temperature in degrees Kelvin, and ΔG_r° is in kcal/mole.

This is a useful relationship. Since the values of ΔG_r° have been measured for many reactions, the value of K_{sp} can be computed if ΔG_r° is known (Fetter 1988). At 1 atmospheric pressure and 25°C, $K_{sp} = -\Delta G_r^\circ/1.364$.

If the value of $\log \text{IAP}$ is $\geq \log K_{sp}$, the natural water is saturated or supersaturated with respect to the mineral. If IAP is $< K_{sp}$, the solution is undersaturated with respect to the mineral.

This indices $\log(\text{IAP}/K_{sp})$ were calculated to know if;

SI = $\log \text{IAP}/K_{sp} = 0$; equilibrium state

SI = $\log \text{IAP}/K_{sp} < 0$; undersaturation state
(mineral dissolution condition)

SI = $\log \text{IAP}/K_{sp} > 0$; oversaturation state
(mineral precipitation condition).

Among the aluminosilicate SI of certain clay minerals like Gibbsite, Kaolinite, Illite, Chlorite and Montmorillonite are discussed in the present paper. The possibilities of Na^+ , K^+ , Ca^{2+} and Mg^{2+} and H_4SiO_4 , in the silicate minerals make up nearly 70% of groundwater when in contact with rocks (Bricker 1965). Silicate sheets (Si_2O_5) bonded with aluminum oxide/hydroxide layers ($\text{Al}_2(\text{OH})_4$) are called Gibbsite layers. Gibbsite is an aluminum oxide mineral that has the same structure as these aluminum layers in Kaolinite, but for the presence of silica. This mineral generally forms from the alteration (mostly weathering) of aluminum rich silicate minerals like Feldspars (Chidambaram et al 2009). The molecular formula is common for the Kaolinite group (Kaolinite, nacrite, dickite) that is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Grim 1968). Illite is a serial name for dioctahedral interlayer-deficient mica with composition $\text{K}_{0.65}(\text{Al}_2)(\text{Si}_{3.35}\text{Al}_{0.65})\text{O}_{10}(\text{OH})_2$ (Rieder et al 1998). The aluminium in octahedral positions can be partially substituted by Mg^{2+} , Fe^{2+} and Fe^{3+} . The Chlorite mineral is represented with Mg, Fe hydroxyl aluminosilicate

(Mg Al Fe) $_{12}$ [(Si Al) $_8$ O $_{20}$] (OH) $_4$ H $_2$ O. The molecular formula for Montmorillonite is usually given as $(\text{M}_x^+ \cdot n\text{H}_2\text{O})(\text{Al}_{2-y}\text{Mg}_x)\text{Si}_4\text{O}_{10}(\text{OH})_2$, where $\text{M}^+ = \text{Na}^+$, K^+ , Mg^{2+} , or Ca^{2+} (Brindley and Brown 1980) and x is generally 0.33. Comparative chemical compositions of aqueous extracts from representative clays showed that the concentration of a 'dissolved element' in an extract depends not only on the amount present in the sample but also on its aqueous solubility, the pH and Eh of the system, its possible combination with other ions present, the effect of organic matter as a component and complexes, the ion-exchange effect and dispersibility of colloidal clay particles (Keller et al 1989). The groundwater plays a significant role in the disintegration and decomposition of rock masses and minerals to soil and then to clay particles; during the process the aqueous system attains equilibrium with the composition of these clay minerals which decides the fate of dissolution of minerals and the chemical evolutionary pathways (Venturelli et al 2003; Gomez et al 2006; Chidambaram et al 2007a; Prasanna et al 2008). In reality, a number of kinetic reasons exist that may cause systems to behave differently than predicted (Nordstrom and Ball 1989; Busby et al 1991). However, the SI of these clay minerals can be useful for examining potential secondary phases and the dissolution of the mineral of interest in aquifer system. This paper discusses the interrelationship of SI of clay minerals and also with various other geochemical parameters which will help to understand the hidden geochemical processes.

2. Study area

The study area falls between the geographical coordinates, 12°60'–12°45'N latitude and 80°00'–80°15'E longitude (figure 1). The river Palar with its tributaries, drain into the sea in the study area. This coastal region is chiefly composed of alluvium, which helps in easy infiltration of the surface water. The geomorphic features such as dunes and beach ridges are found along the coastal part of the study area. Apart from its importance as a coastal region it is also significant to note that the natural calamities like cyclones are frequently disturbing the normal ecosystem. The aquifer behaviour and its response to natural calamities in this region will help us to identify the region for natural/artificial recharge. The brackish backwater is noted in the northeastern part of the study area south of Mahabalipuram and north of Kalpakkam (figure 1). The historically famous Mahabalipuram limits the northeastern boundary and the Palar river bounds the southern part of the study area with bay of Bengal in the east. The average annual

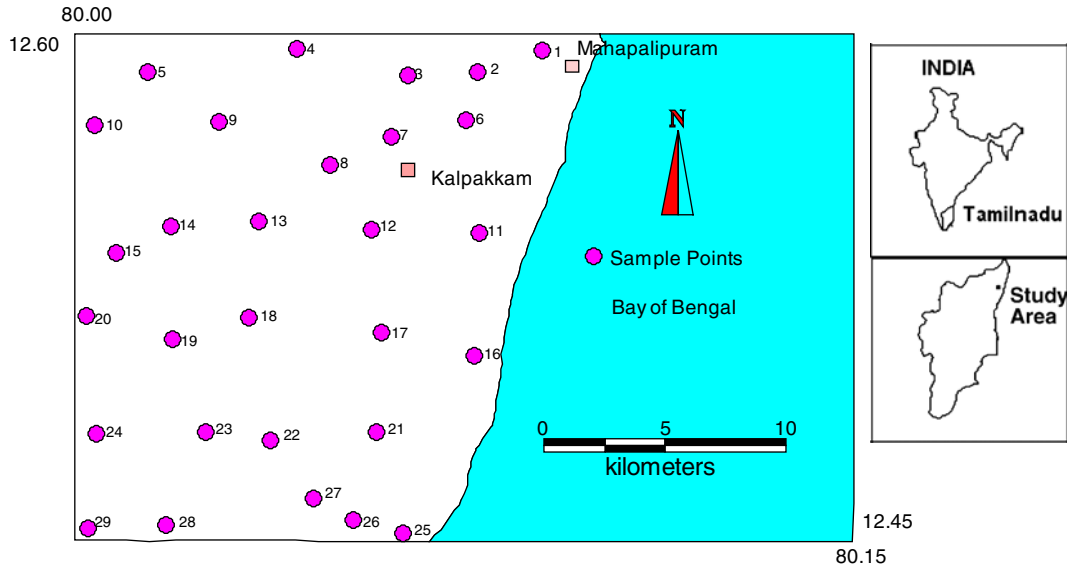


Figure 1. Sample location map of the study area.

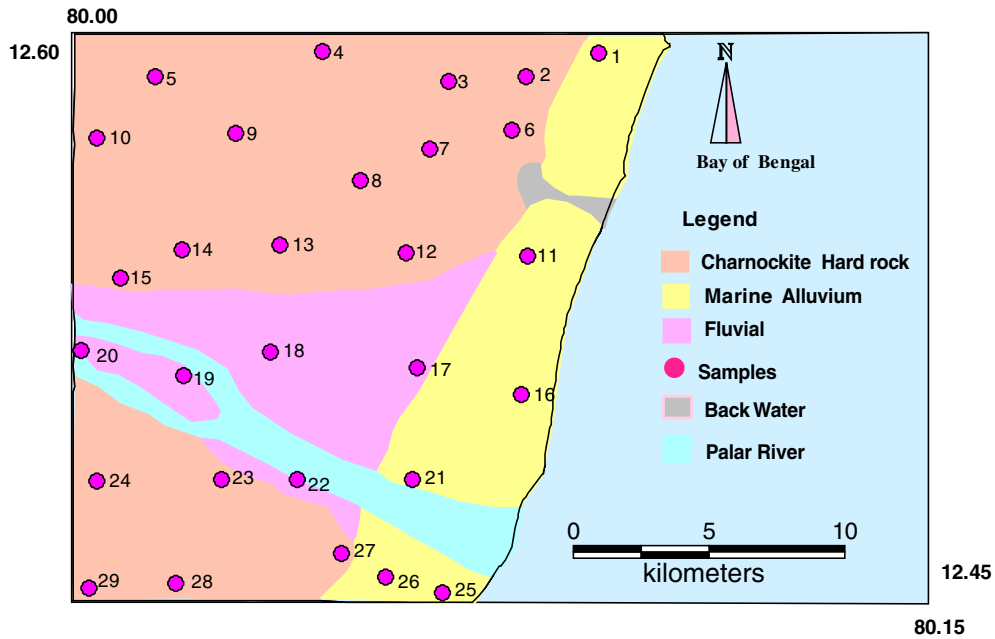


Figure 2. Geology of the study area.

rainfall in the study area is 1237 mm, the water table in the alluvial formation is shallow and in the hard rock it is deeper. There is a wide range in the depth to water table from 1 to 20 m below the ground level (mbgl).

3. Geology

The study area reveals that there are two major lithologies, i.e., Charnockite (hard rock) and alluvium formation (fluvial and marine). The Palar river flows from the northwest to southeastern part

of the study area fringed by this Quaternary alluvium (flood plain). The Quaternary formation is found along the river course of the Palar and it spatially divides the charnockites into northern and southern parts (Chidambaram *et al* 2011). Marine alluvial formation is found parallel to the coast (figure 2). The subsurface lithology of the study area shows six types of geological formations which include sand, clayey sand, clay in the east and sandy clay in the east with weathered Charnockite in west. Earlier studies by Gurumoorthy *et al* (2004); Karmegam *et al* (2010); Arumugum *et al* (1997) have revealed that the Charnockite rock

Table 1. The chemical constituents in groundwater (all values in $mg\ l^{-1}$ except EC in $\mu s/cm$ and pH).

Name	pH	EC	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	PO ₄	SO ₄ ²⁻	Al	Fe	NO ₃ ⁻	H ₄ SiO ₄
Punjari	7.6	1408	706.5	28	57.6	143.6	13	248.2	402.6	0.3	9.4	0.15	0.14	166	64
Vadakadambadi	7.7	809.8	405.5	40	36	172.3	4.7	188.6	305	0.2	3.4	0.212	0.26	23.3	75.5
Kuchchikadu	7.8	1072	541.8	40	48	164.4	4.4	144.7	414.8	0.2	7	0.168	0.21	3.36	61.5
Pulikkudram	7.4	1009	510.5	52	38	165	4.4	198	308.6	0.25	5.6	0.039	0.03	30.6	52.5
Edayilur	7.6	1440	726.9	56	57.6	137.7	4.5	301.3	305	0.2	7.3	0.046	0.06	72.5	35
Manamai	8	742.7	373.8	48	52.8	128	3.6	188.6	317.2	0.15	2	0.274	0.39	39.8	60.5
Nallur	7.6	3273	1643	110	90	72.2	4.5	175	489	0.3	22.5	0.113	0.16	13.8	86
Mullikulottur	7.9	998.9	499.8	40	58.2	176.5	9.3	217	329.4	0.35	29.8	0.028	0.08	27.2	86
Therukazhikundram	7.4	1097	556.4	56	40.8	110	3.2	143	305	3.3	6	0.033	0.05	16.2	59.5
Mambakkam	7.7	352.6	176.2	12	24	150	9.6	85	346.4	0.15	0.2	0.021	0.03	10.4	90
Nanamedu	8.1	2992	1499	44	48	46.6	4.5	120	402.6	0.4	7.3	0.003	0.01	24.6	32.5
Velangadu	7.7	1192	607.6	36	52.8	154.8	23.9	177.2	427	0.3	6	0.018	0.05	10.9	36
Naduvalkkarai	7.6	2260	1122	48	50.4	212	4.5	389.9	475.8	0.35	8.2	0.024	0.08	9.4	44
Kilappakkam	7.9	1012	509.1	32	36	124	38.9	70.9	439.2	0.15	5.8	0.026	0.09	104	34
Velagam	7.6	2140	1068	80	86.4	111.6	4.4	389.9	402.6	0.3	7.7	0.022	0.05	37.4	50
Kalpakkam	7.4	748.2	374.8	12	16.8	146	4.9	124.1	219.6	0.1	8.8	0.31	0.26	3.39	27
Ayappakkam	7.3	840.2	419.7	20	26.4	98	4.8	106.4	246.4	0.1	11	0.087	0.1	50.9	56
Nerumbur	7.3	367.4	184.1	16	16.8	160.1	4.4	177.2	158.6	0.3	2.2	0.018	0.08	65.5	44
Sevur	8	1735	867.5	56	50.4	167.8	11.2	336.7	341.6	2	9.4	0.019	0.02	9.3	66
Nilamangalam	7.6	587.4	294.4	32	31.2	135	4.4	153.2	341.6	0.35	1.1	0.019	0.04	17.9	68.5
Veppancheri	8.1	1028	513.7	8	36	187.5	4.4	88.62	451.4	3.4	1	0.282	0.28	8.36	94.5
Anaikattu	7.5	2798	1401	120	96	104.3	4.5	455.8	462.6	0.4	10.3	0.106	0.14	18.2	75
Surpilaiyarkuppam	7.4	315.5	158	8	16.8	32.1	4.3	35.45	109.8	0.4	2.5	0.164	0.18	4.02	95
Agaram	7.2	1573	787.4	44	48	139.8	4.5	248.2	183	0.45	7.8	0.017	0.06	15.7	68
Kanathur	6.9	265.6	133.7	20	14.4	154.7	4.6	134.9	223.2	1.8	2.5	0.019	0.02	6.64	63
Kuvathur	7.2	1354	677.2	36	40.8	130.6	9.5	159.5	292.8	2.35	17.5	0.096	0.1	3.79	77.5
Nedumaram	6.9	255.7	129.3	8	19.2	57	4.3	46.2	148	0.4	1.5	0.186	0.2	5.28	67.5
Akkimpattu	7.2	441.8	221.4	24	2.4	45.2	4.6	35.45	134.2	0.4	6.5	0.134	0.14	16.6	72.5
Tiruvadur	7.6	272.5	132.9	4	19.2	51.7	4.8	35.45	146.4	0.35	2.2	0.03	0.02	4.24	54

mass in this area is hard, compact and groundwater occurs at depths greater than 15–20 m below ground level.

4. Materials and methods

Twenty nine groundwater samples were collected, systematically using clear acid-washed polythene bottles. Sampling was carried during February 2008 and analysis was carried out using standard procedures (APHA 1998). The parameters such as temperature and pH were measured in the field. Electrical conductivity and total dissolved solids were measured in the laboratory by using electrodes. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^- were determined by ion chromatograph (Metrohm IC 861). HCO_3^- was determined by volumetric titration. WATEQ4F was used to derive the saturation index (SI) and SPSS was used for correlation analysis. Log pCO_2 values were not measured in the field, they were obtained from the WATEQ4F output.

Aqueous speciation computed with WATEQ4F program (Ball and Nordstrom 1992) was used to define possible chemical reactions in the aquifer system and to assess the state of equilibrium between groundwater and minerals present. It is an equilibrium speciation code, which can calculate complexes, activity coefficient equilibrium with mineral composition, saturation index and gas pressures, all as a function of temperature and for all kinds of hydrochemical conditions.

5. Result and discussion

Groundwater in the study area is generally alkaline in nature with pH ranging from 6.85 to 8.1 with an average of 7.55 (table 1). Sodium is the important and most abundant alkali metal which is highly mobile and soluble in groundwater. The order of dominance of cations are $\text{Na}^+ > \text{Ca}^{2+} >$

$\text{K}^+ > \text{Mg}^{2+}$ and that of anions are $\text{HCO}_3^- > \text{Cl}^- > \text{H}_4\text{SiO}_4 > \text{SO}_4^{2-}$.

5.1 pH and SI

The SI of clay minerals observed shows (figure 3) three different groups.

- Illite, Kaolinite, Montmorillonite,
- Gibbsite, and
- Chlorite.

The clay minerals were grouped with respect to the range of saturation index as group A (oversaturated), group B (near saturation) and group C (undersaturated to saturated).

Group A: The SI of the minerals in group 'A' shows oversaturation. There is a decreasing trend of SI with increase of pH. This increase of pH reduces the availability of H^+ for ion exchange.

Group B: The SI of Gibbsite ranges from near saturation to saturation. This may be due to the availability of Al or OH – for the saturation during the process of increase in pH. The water when recharged is initially saturated with Gibbsite (Chidambaram *et al* 2003). Further increase of pH and the ions acquired from the surrounding minerals either by ion exchange or by other process results in the decrease of SI of Gibbsite (Chidambaram *et al* 2006).

Group C: The undersaturated Chlorite increases to saturation and oversaturation with the increase of pH. This clearly shows that the H^+ is exchanged for the cations and these ions are made available which in turn help in the SI of Chlorite.

It is evident that the SI of group A minerals show oversaturation and most of them are concentrated around the pH range of 7.5. The SI of group

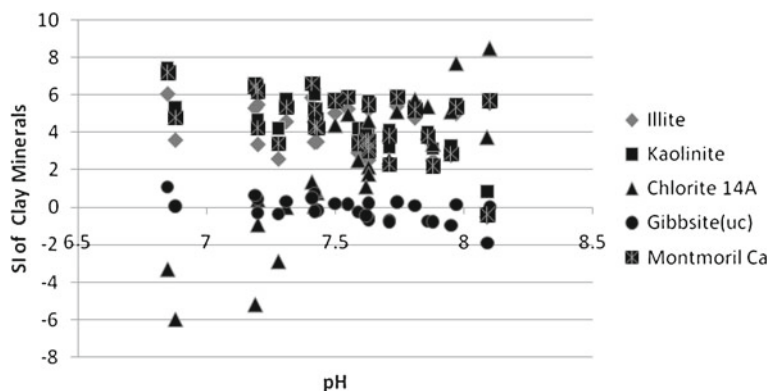
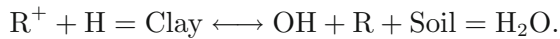


Figure 3. The relation between the SI of clay minerals in different samples and their respective pH.

B mineral Gibbsite falls between near saturation to undersaturation range; it is also noted that it becomes undersaturated above pH of 7.5. The SI of group C mineral Chlorite is undersaturated below pH of 7.5 above which it gradually gets saturated and further it becomes oversaturated. Hence, it is noted that there is an inverse relationship in the trend of SI of group A and B minerals to that of group C minerals. It is clearly evident that most of the cations are made available by ion exchange process of with H^+ ion Al, Si and available (OH^-) which aids in the saturation of Chlorite.

The cation exchange in acidic Kaolinite–iron oxide systems is complicated by the adsorption of anion as well as cations (Ayres and Hagihara 1953; Thomas 1960a). The exchange equation for the reaction of cation with such a system then becomes:



When H^+ ion arrive on the exchange surfaces they meet not only the clay, but also complex hydroxyl aluminum ions (Rich and Obenshain 1955; Thomas 1960b). The H^+ ion tend to neutralize some of the OH^- on the hydroxyl aluminum ion. This neutralization decreases the concentration of H in the system thereby increasing the pH. The available OH^- tends to combine with the aluminosilicates and cations to become saturated with Chlorite composition.

5.2 EC and SI

The electrical conductivity (EC) can be influenced by the presence of fine sediment (Fenn 1987), interaction of rock with water (Srinivasamoorthy 2007), anthropogenic (Prasanna *et al* 2008), sea water intrusion into the aquifers (Chidambaram *et al* 2005), etc. Moore *et al* (2008) discusses the factors that govern the spatial and temporal variability of electrical conductivity and illustrate how these

variations can be used as indicators of water chemistry and hydrologic process. EC ranges from 255.7 to 3273 $\mu\text{S}/\text{cm}$ with an average of 1185.56 $\mu\text{S}/\text{cm}$. The spatial distribution of EC (figure 4) shows that most of the samples representing the southwestern part of the study area range from 250–1250 $\mu\text{S}/\text{cm}$. The lesser value may be due to the infiltration/recharge of freshwater along the Palar river basin through Quaternary fluvial formation. The samples from the western part of the study area (hard rock) show EC less than 1500 $\mu\text{S}/\text{cm}$. Few samples above 1250 $\mu\text{S}/\text{cm}$ fall in the eastern part of the study area. Higher EC is noted in the eastern part of the study area along the coast. There may be three factors influencing this higher EC.

- It falls along the contact of the igneous and sedimentary terrain, hence it may result in mixing of groundwater of different geochemical types, or
- due to evaporated recharge from the surface water bodies, or
- saline water into this aquifer (Prasanna *et al* 2009).

The electrical conductivity enhances other anions present in water (chloride, sulfate, bicarbonate) which associates with the available cations and aids the saturation of chlorides, carbonates or sulfate minerals. Higher SI was noted (figure 5) in lower EC ($<1500 \mu\text{S}/\text{cm}$) for group A minerals, near saturation in group B and undersaturation to oversaturation in group C minerals. There is no definite trend noted with respect to EC. It is evident from the figure that EC is not the governing factor for the SI of Chlorite, since both oversaturated and undersaturated conditions were noted in lower EC. One limitation to the use of EC as an indicator is that EC does not respond to the presence of uncharged dissolved substances, such as silica, a common weathering product from igneous rock (Ericksson 1981). There is drop of SI values of all these minerals between 1750 and

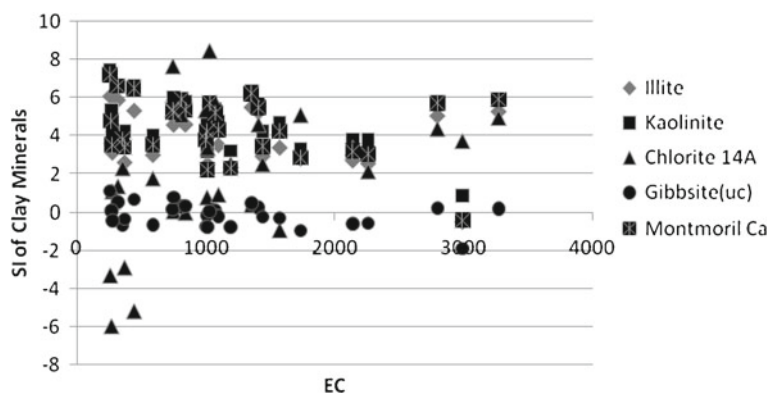


Figure 4. The relation between the SI of clay minerals in different samples and their respective (EC) electrical conductivity $\mu\text{S}/\text{cm}$.

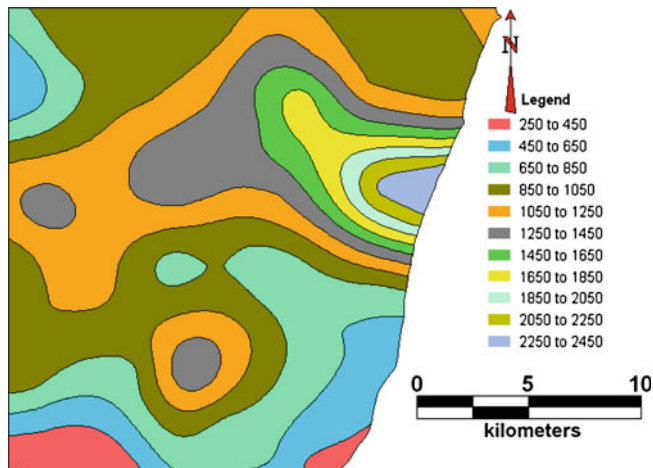


Figure 5. Spatial distribution of electrical conductivity ($\mu\text{s}/\text{cm}$) in the study area.

2250 $\mu\text{s}/\text{cm}$, again there is a further increase of SI beyond 2250 $\mu\text{s}/\text{cm}$.

5.3 Ionic strength

Ionic strength (IS) is a measure of total concentration of ions in solution which emphasizes increased contribution of species with charges greater than one to solution non-ideality (Domenico and Schwartz 1990).

$$I = 0.5 \sum m z^2,$$

where m is the concentration of a given ion in moles per liter and z is the charge on that ion. The terms in the summation include one for each ionic species present.

The approximate value of IS can be computed from the specific conductance of the solution if it has been measured (Lind 1970). However, calculation should not be made unless one has some knowledge of the principal dissolved species present in the solution. If the composition is unknown for water with a specific conductance of

1000 μmhos , calculated value of IS could range from 0.0085 to 0.027. The relationship of the IS of samples and SI of these minerals clearly show (figure 6) negative relationship to SI of group A and group B minerals and positive relation to that of the SI of group C minerals. This clear relation is not witnessed with the electrical conductivity of the samples.

5.4 $p\text{CO}_2$ and SI

An increase in the carbon dioxide partial pressure during water–rock interaction influences the process of mineral dissolution. Carbon dioxide may be generated by several processes. In absence of calcite in the mineral assemblage, saturation in calcite and high pH may be easily reached during dissolution of plagioclase in water with dissolved CO_2 coming from atmosphere and soil, and under condition, for instance, of Kaolinite saturation (Venturelli *et al* 2003).

Although the concentration of CO_2 in the gas mixture is low, interaction with ground waters could be sufficient to increase the silicate dissolution. The SI of group A minerals generally increases with increase of $\log p\text{CO}_2$ values. Low $\log p\text{CO}_2$ values show higher SI for all the minerals except that of Gibbsite which shows near saturation, but SI of Chlorite decreases with $p\text{CO}_2$, many of the waters with $p\text{CO}_2$ less than $10^{-1.5}$ bar, having low salinity ($\sum \text{ions} < 40 \text{ mEq}/\text{L}$), commonly with high pH (up to 9.7) and with moderate-to-very low sulphate and chloride concentrations will have extreme composition with very low calcium, magnesium, and potassium contents (Toscani *et al* 2001). This low concentrations of cations may result in lesser values of SI of Chlorite in groundwater samples. There is a slight decrease in the SI of group A minerals around -2 , the samples falling in this region represent the hard rock terrain.

Higher $p\text{CO}_2$ values are noted in the hard rock terrains of the study area (figure 7). High $p\text{CO}_2$

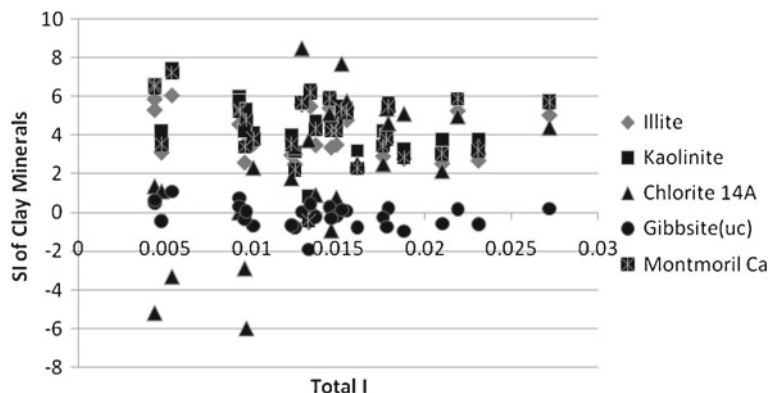


Figure 6. The relation between the SI of clay minerals in different samples and their respective ionic strength.

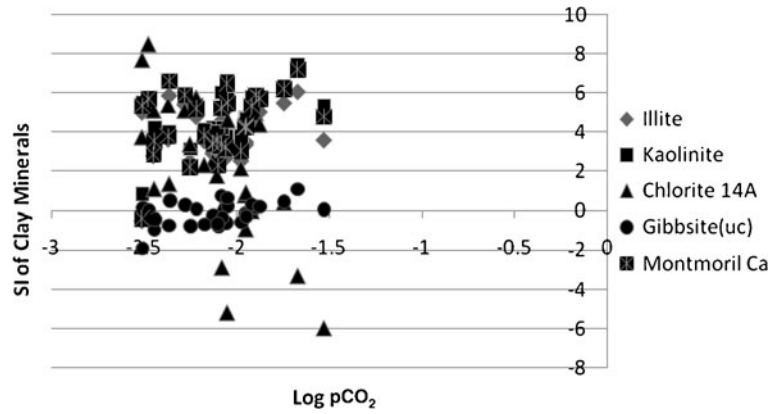


Figure 7. The relation between the SI of clay minerals in different samples and their respective log pCO₂.

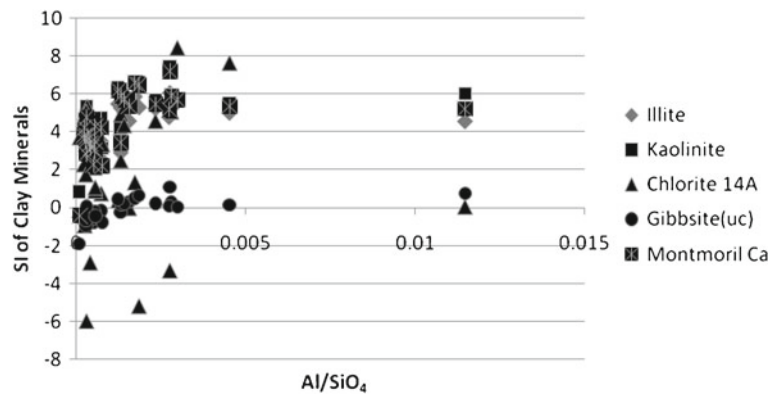


Figure 8. The relation between the SI of clay minerals in different samples and their respective aluminosilicates.

acts as a source of H⁺ through the dissociation of H₂CO₃, for chemical weathering of felsic and mafic silicates in weathered and hard rock terrains of the study area. The total absence of carbonate minerals in the region eliminates the possibility of carbonate dissolving under higher pCO₂. The lack of such a reactive geochemical sink is undoubtedly an important factor in the occurrence and persistence of high pCO₂.

5.5 Al:Si and SI

Paces (1978) put forward a hypothesis about the existence in natural waters of solid compounds representing reversible metastable states in the chain of breakdown of primary minerals into thermodynamically stable secondary minerals. These metastable reversible solids determine the apparent equilibrium states in solution, the irreversible reactions being too slow to influence the metastable equilibrium to any noticeable degree. Aluminium occurs in primary minerals (e.g., Feldspars, Micas, Hornblendes, etc.). Aluminium released will be found either in hydroxides or in secondary so called clay minerals of Kaolinite or Montmorillonite type.

The Al/H₄SiO₄ ratio increases with the SI of minerals in groups A and B upto 0.003 and becomes almost stable beyond. Though the Chlorite shows undersaturation and saturation in this range, there is an increasing trend with increase of this ratio. The Al³⁺ activity depends both on pH and the concentration of soluble silica (figure 8), SiO₂. The undersaturation of Chlorite even with respect to equivalent ratio may be due to nonavailability of cations for those samples. It is conceivable that the activities of aluminium and silica in groundwater can be controlled by HAS (hydroxy aluminosilicates). Ion activity quotients of HAS in groundwater is calculated according to the scheme given by Schneider *et al* (2004). It proved that equilibrium with HAS can be maintained in groundwaters that have values below pH of 9.5 and above 6.7. Hence, pH plays a significant role in the release of Al and Si into the medium which in turn governs the SI of these minerals.

5.6 Spatial distribution of SI

The spatial distribution of the Gibbsite shows a minimum of -1.892 to a maximum of 1.089. Higher values indicating oversaturation is noted in the

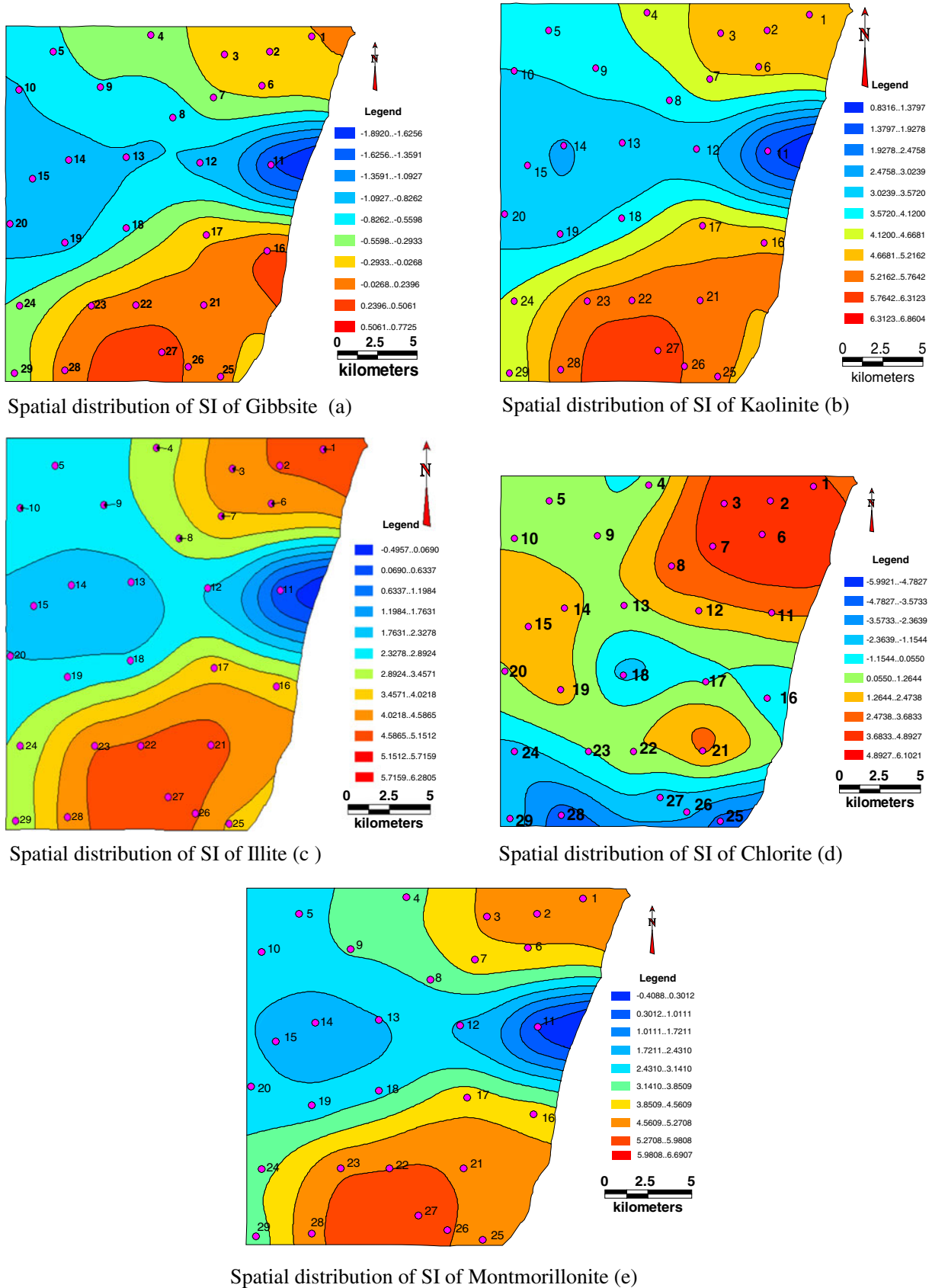


Figure 9. Spatial distributions SI of clay minerals along with sampling location.

Table 2. Correlation analysis for groundwater samples.

	Gibb.	Kaoli.	Illite	Chlorite	Mont.	pCO ₂	Al	H ₄ SiO ₄	Ca	Mg	Na	K	pH	Fe
Gibb.	1.00													
Kaoli.	0.98	1.00												
Illite	0.90	0.96	1.00											
Chlorite	-0.29	-0.24	0.02	1.00										
Mont.	0.95	0.99	0.98	-0.15	1.00									
pCO ₂	0.45	0.42	0.24	-0.65	0.37	1.00								
Al	0.70	0.67	0.73	0.27	0.67	-0.16	1.00							
H ₄ SiO ₄	0.32	0.50	0.63	0.18	0.60	-0.01	0.24	1.00						
Ca	-0.16	-0.13	-0.08	0.36	-0.08	0.16	-0.19	0.02	1.00					
Mg	-0.25	-0.22	-0.10	0.61	-0.16	-0.01	-0.13	0.03	0.88	1.00				
Na	-0.18	-0.18	-0.11	0.29	-0.16	-0.01	-0.03	-0.08	0.01	0.13	1.00			
K	-0.30	-0.34	-0.24	0.14	-0.35	-0.12	-0.23	-0.28	-0.08	0.03	0.13	1.00		
pH	-0.60	-0.57	-0.33	0.88	-0.49	-0.84	0.06	-0.05	0.16	0.38	0.27	0.27	1.00	
Fe	0.76	0.75	0.81	0.23	0.75	0.02	0.83	0.30	-0.03	0.02	0.05	-0.07	-0.06	1.00

southern and southeastern parts of the study area. Lower values are noted in the eastern and the central parts of the study area. The hard rock terrain and the flood plain along the Palar river show undersaturation to saturation. Most of the samples show spatially undersaturated nature. The SI ranges of Kaolinite ranges from 0.831 to 7.446. The spatial distribution of Kaolinite indicates a similar trend of that of Gibbsite, but all the samples spatially show saturation to over-saturation, though the trend remains the same. SI of Illite ranges from -0.495 to 6.056. Higher SI noted is in the southeastern and the northeastern parts of the study area (figure 9). Similar trend was also observed in the spatial distribution of SI of Montmorillonite.

The Chlorite SI ranges from -5.992 to maximum of 8.476. This shows higher SI when compared with SI of other minerals (Gibbsite, Kaolinite, Illite and Montmorillonite). Saturation to oversaturation is noted in the central and the northeastern parts of the study area. This may be due to the backwater intrusion or due to mixing solution derived from hard rock weathering and that of the Quaternary formation.

In general, hard rock region shows lower SI for Gibbsite, Kaolinite, Illite and Montmorillonite.

Higher SI is noted along the contact of the different formations and lower values are noted in the regions with higher EC along the coast. This may be due to the nonavailability of ions for saturation of clay minerals. This region with low SI of these minerals may correspond to high SI of calcite, Aragonite, Gypsum, Halite, etc.

6. Correlation

Application of statistics helps us to identify the hidden relationship between the parameters observed. In this context correlation analysis was applied to find out the linkages between the SI of minerals, pH and the other ions (table 2). The diagram depicting (figure 10) the species relation (Chidambaram *et al* 2007b) shows that the excellent correlation exist between SI of group A and B minerals, Al shows good correlation with these groups. But H₄SiO₄ has good correlation with group A minerals only and not with SI of Gibbsite, as the composition of Gibbsite is independent of H₄SiO₄ ion. Fe has excellent correlation with Al, Gibbsite and group A minerals, probably this may suggest a common source of Al and Fe as iron-alumina coating on clay (Thomas 1960b). SI of

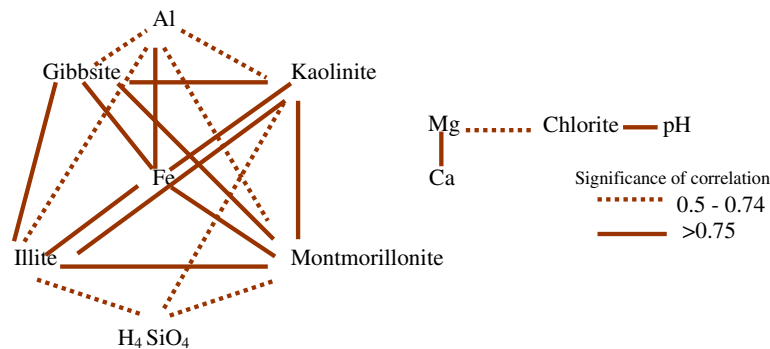


Figure 10. Diagram depicting the correlation between different dissolved silica pH with SI of clay minerals.

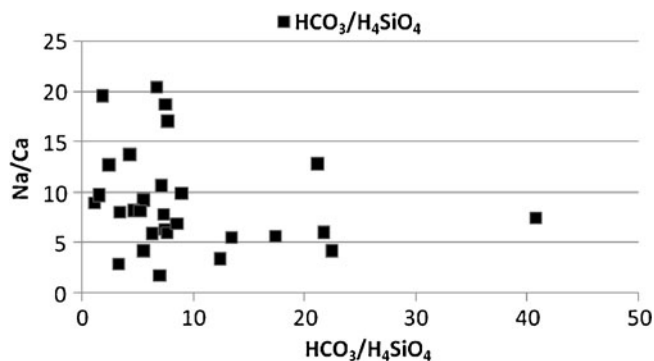


Figure 11. The relation between the SI of clay minerals in different samples and their respective Na/Ca vs. $\text{HCO}_3^-/\text{H}_4\text{SiO}_4$.

Chlorite has an excellent correlation with pH and good correlation with Mg^{2+} . Log pCO_2 is negatively related to Chlorite and has strong negative correlation with pH. Hence, it is clear that lesser values of pCO_2 and higher values of pH favour the SI of Chlorite. Hence Mg^{2+} and pH are the deciding parameters for the SI of Chlorite. But for the SI of group A and B minerals, they depend on Fe, Al and H_4SiO_4 . Cations Na^+ and K^+ lack correlation with SI of all the clay minerals studied.

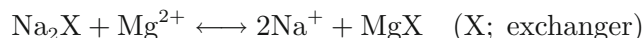
Chemical weathering reaction can release HCO_3^- . This mechanism can be grouped into two principal ways:

- Congruent dissolution of carbonate minerals.
- Incongruent dissolution of silicate minerals to Kaolinite.

In both type of reactions, weathering accumulation of HCO_3^- results, though there is a main difference in stoichiometry of the two reactions. For weathering of carbonate minerals, the HCO_3^- ion concentration is balanced by cations on an equivalent basis. Kaolinisation of silicate minerals results ' SiO_2 ' in solution which is related to the HCO_3^- ion concentration through the composition of primary silicates (Garrels 1967). The silica concentration in groundwater seems to be controlled by the equilibrium with respect to amorphous silica (silica gel) and by the alteration of Feldspars, especially Albite, which are transformed to Kaolinite, preferably in the superficial zones (Gomez *et al* 2006).

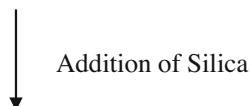
Figure 11 shows that Na^+ is higher than Ca^{2+} and HCO_3^- is greater than H_4SiO_4 . Moreover, the ratio of $\text{Na}^+/\text{Ca}^{2+}$ is higher, when the $\text{HCO}_3^-/\text{H}_4\text{SiO}_4$ ratio is lesser and *vice versa*. This indicates that plagioclase weathering is not the main contributor for the cation. The other possibility for the increase of Na^+ is by ion exchange or seawater intrusion into the coastal aquifer.

This variation of the relative concentration of the cation can be considered as normal, taking into account that the behaviour of Na^+ is more conservative than Ca^{2+} and Mg^{2+} , since the latter can disappear from the solution by irreversible processes (precipitation: formation of Saleite, neof ormation of Apatite, Ca silico-phosphates, etc.) or by 'reversible' processes such as an ion exchange. The ion exchange, i.e., the process that governs the concentration of cations may be as follows:



has been suggested by Venturelli *et al* (2000) and criticized by Toscani *et al* (2001). But based on the exchange reaction, for each exchanged mol of Ca^{2+} or Mg^{2+} , 2 moles of Na and K are released to the solution. The molar concentration of Na in the Na- HCO_3 type water is approximately equal to the concentration of bicarbonate, which agrees with the complex of the clay minerals. Dissolution of Na^+ feldspars could be a process that increases the sodium concentration in the waters (Gomez 2002), but the relative concentration of Ca^{2+} , Mg^{2+} and Na^+ are mainly controlled by processes of ion exchange with rock matrix.

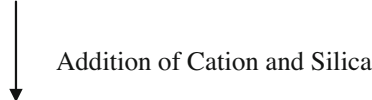
Gibbsite $\text{Al}_2(\text{OH})_4$



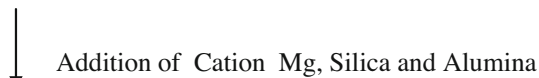
Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



Illite $\text{K}_{0.65}(\text{Al}_2)(\text{Si}_{3.35}\text{Al}_{0.65})\text{O}_{10}(\text{OH})_2$



Montmorillonite ($\text{M}_x^+ \cdot n\text{H}_2\text{O}$) ($\text{Al}_{2-y}\text{Mg}_y$) $\text{Si}_4\text{O}_{10}(\text{OH})_2$, where $\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{or } \text{Ca}^{2+}$



Chlorite (Mg Al Fe) $_{12}[(\text{Si Al})_8 \text{O}_{20}] (\text{OH})_4 \text{H}_2\text{O}$

It is observed that the SI of group A minerals in the groundwater samples decreases with the increase of ionic strength, ionic strength includes

a measure of valency. The increase of neutral compounds like silica would not affect the ionic strength. But the addition of cations like Mg^{2+} , Al or Ca^{2+} will increase the IS. Hence there is an increase of SI of Chlorite with increase in the concentration of such cations. During the process of saturation of Chlorite the H in the water might have been exchanged for Mg^{2+} present in the host rock thereby increasing the OH concentration and a decrease in the H concentration in the groundwater which has resulted in increase of pH. This may also be due to the weathering of the hypersthene present in the Charnockite as:



The low pCO_2 values of the groundwater samples indirectly indicate the recent recharge or interaction with atmosphere. Hence, the groundwater recharged along the contact between the different litho units (between the Charnockite and alluvium) has also aided the decrease in pCO_2 values and increase in the intensity of weathering releasing the Ca^{2+} and Mg^{2+} to the groundwater, which favours the saturation of Chlorite and other HAS.

7. Conclusion

The study on the SI of these hydroxyl aluminum silicates (clay minerals) shows that:

- There is an inverse relation between the composition of Chlorite with that of other minerals considered for the study.
- There is a clear exhibit of the relation between the SI of clay minerals and that of the ionic strength of the samples than that of the electrical conductivity.
- The partial pressure of carbon dioxide and pH also govern the SI of clay mineral.
- The Al/ H_4SiO_4 ratio in the water samples has lesser impact on the SI of Chlorite than SI of other clay minerals.
- The correlation of the Mg^{2+} and pH has positive relation to SI of Chlorite. SI of other clay minerals have association with H_4SiO_4 , Al and Fe.

Hence the study on the state of SI of clay minerals reveals their relationship with pH, ionic strength pressure of carbon dioxide and major ions, which in turn helps in the identification of hidden hydrogeochemical process.

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