Identification of major sources controlling groundwater chemistry from a hard rock terrain – A case study from Mettur taluk, Salem district, Tamil Nadu, India

K Srinivasamoorthy*, S Chidambaram, M V Prasanna, M Vasanthavihar,
John Peter and P Anandhan

Department of Earth Sciences, Annamalai University 608 002, Tamil Nadu, India.
**e-mail: moorthy_ks@yahoo.com*

The study area Mettur forms an important industrial town situated NW of Salem district. The geology of the area is mainly composed of Archean crystalline metamorphic complexes. To identify the major process activated for controlling the groundwater chemistry an attempt has been made by collecting a total of 46 groundwater samples for two different seasons, viz., pre-monsoon and post-monsoon. The groundwater chemistry is dominated by silicate weathering and $(Na + Mg)$ and $(Cl + SO_4)$ accounts of about 90% of cations and anions. The contribution of $(Ca + Mg)$ and $(Na + K)$ to total cations and HCO_3 indicates the domination of silicate weathering as major sources for cations. The plot for Na to Cl indicates higher Cl in both seasons, derived from Anthropogenic (human) sources from fertilizer, road salt, human and animal waste, and industrial applications, minor representations of Na also indicates source from weathering of silicate-bearing minerals. The plot for Na/Cl to EC indicates Na released from silicate weathering process which is also supported by higher HCO_3 values in both the seasons. Ion exchange process is also activated in the study area which is indicated by shifting to right in plot for $Ca + Mg$ to $SO_4 + HCO_3$. The plot of $Na - Cl$ to $Ca + Mg - HCO_3 - SO_4$ confirms that Ca, Mg and Na concentrations in groundwater are derived from aquifer materials. Thermodynamic plot indicates that groundwater is in equilibrium with kaolinite, muscovite and chlorite minerals. Saturation index of silicate and carbonate minerals indicate oversaturation during pre-monsoon and undersaturation during post-monsoon, conforming dissolution and dilution process. In general, water chemistry is guided by complex weathering process, ion exchange along with influence of Cl ions from anthropogenic impact.

1. Introduction

Groundwater contains minerals carried in solution, the type and concentration of which depends upon several factors like soluble products of rock weathering and decomposition in addition to external polluting agencies and changes in space and time. As a result of chemical and biochemical interaction between groundwater and contaminants from urban, industrial and agricultural activities along with geological materials through which it flows, it contains a wide variety of dissolved inorganic chemical constituents in various concentrations. The character of groundwater in different aquifers over space and time proved to be an important technique in solving different geochemical problems (e.g., Chebotarev 1955; Hem 1959; Back *et al* 1966; Gibbs 1970; Srinivasamoorthy *et al* 2005). Calculation of mineral saturation index and thermodynamic equilibrium studies were initiated by Garrels and Christ (1965) to decipher the possible reactant and product minerals and indication

Keywords. Groundwater; residence time; ion exchange; thermodynamics; saturation index.

J. Earth Syst. Sci. **117**, No. 1, February 2008, pp. 49–58

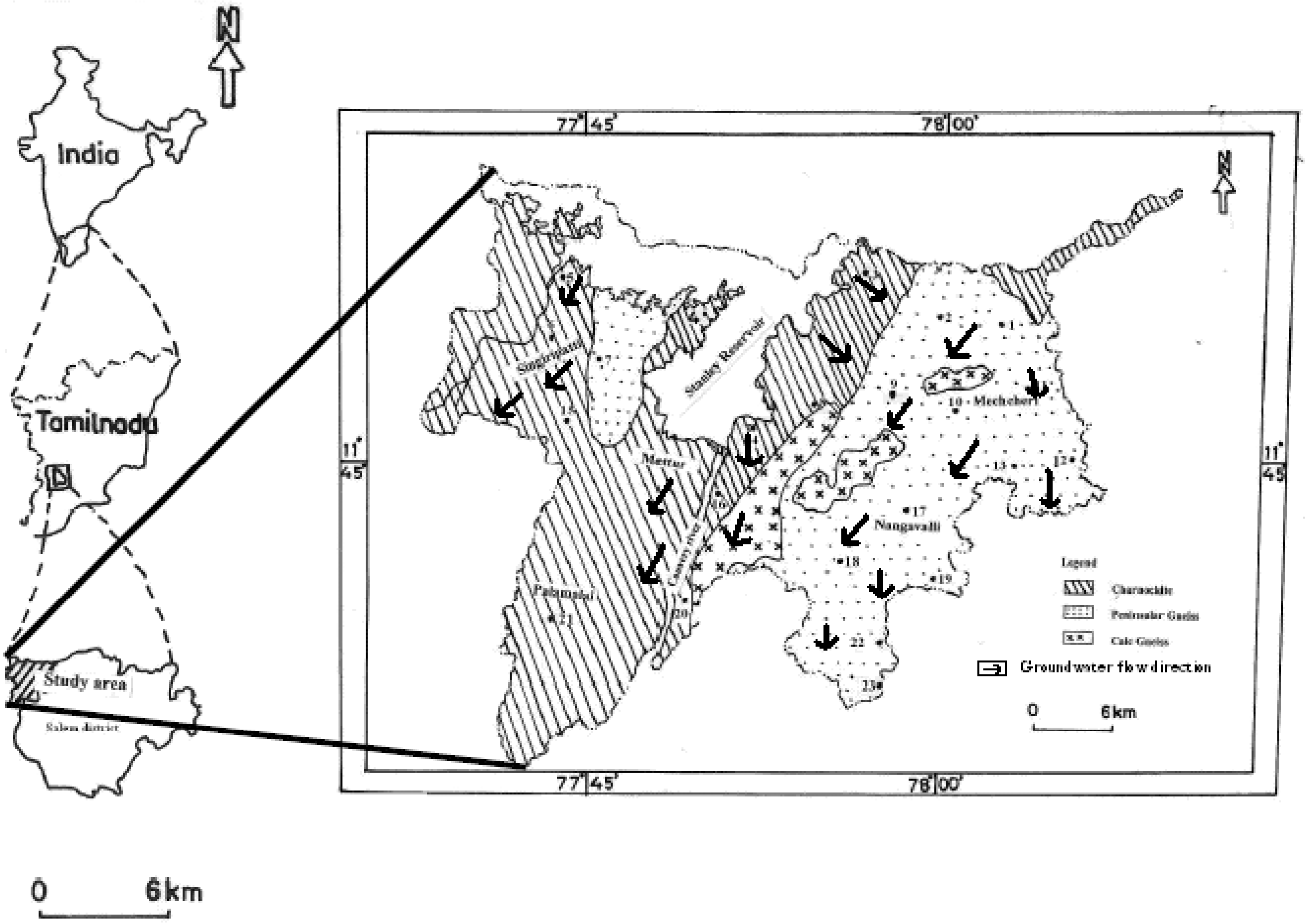

Figure 1. Location, geology and sampling locations of the study area.

of the equilibrium state of groundwater and the surrounding materials. Nandakumar and Murthy (1997) attempted for groundwater quality variation in shallow basaltic aquifers and identified Base Exchange reaction in canal command areas. The study area gains its own importance by its location in a hard rock terrain, frequent failure in monsoon, highly industrialized and urbanized zone all of which contributes for a proper appraisal of the chemical quality of groundwater in the study area.

2. Study area

The study area (figure 1) occupies northwestern part of Salem district in Tamil Nadu and lies between north latitudes 11°30′ and 12°00′ and east longitudes 77°45′ and 78°00′ with a total extent of 777.15 km^2. The average rainfall of the study area is about 804.3 mm which is meager when compared with the district average of 1019 mm (TWAD 2002). The geology is composed of granites like charnockites, basic granulites and magnetite quartzite. Peninsular gneiss and calc gneiss of metasedimentary group are also exposed in the study area. Ultramafic and basic intrusives like pyroxenite, peridotite, anorthosite and dolerite dykes along pegmatoidal granites are exposed all around the study area. Hills, undulating plains, plateaus, pediments and bazadas are the mixture of geomorphic units. Northern and southwestern parts of the study area include hill ranges and high lands where eastern and southeastern parts are low lying due to the flow of river Cauvery. The main drainage of the study area is by river Cauvery which flows from north to south with a sub-dentric drainage pattern. Groundwater in the study area occurs in weathered portions of rocks along joints and fractures. Groundwater flow was noted along NS and NW direction which coincides with the topography of the study area (Srinivasamoorthy 2005). Weathered layer thickness in gneissic terrain ranges from 2.2 to 50 m. In charnockite weathered layer, thickness was between 5.8 and 55 m. Groundwater occurs under semi-confined conditions in the alluvium along the river course. Water table fluctuation in the study area ranges from 0.2 m to 13.5 m BGL (Below Ground Level).

Table 1. *Chemical composition of groundwater during pre-monsoon season (all values in meq/I except pH, EC, H_4SIO_4 and TDS).*

Location	Lithology	pH	EC (μs/cm)	Cl	HCO_3	SO_4	PO_4	NO_3	F	H_4SiO_4 (mg/l)	Na	K	Mg	Ca	TDS Mg/l
Tettiguipetti	Peninsular gneiss	7.2	1930	10.51	6.73	3.42	0.00	0.77	0.04	17.5	7.58	0.58	3.84	7.62	1410.02
Mallikundam	Peninsular gneiss	7.6	1420	9.22	5.66	1.85	0.00	0.53	0.03	21.7	5.78	0.36	7.60	2.59	1106.39
Koonandiyur	Charnockite	7.5	1490	4.01	4.98	0.70	0.00	0.44	0.07	1.6	5.62	0.31	2.57	1.00	702.24
Tinnapatti	Peninsular gneiss	7.4	1540	7.00	6.32	3.09	0.00	0.07	0.03	14.3	6.55	0.18	7.79	1.79	1089.08
Kaveripuram	Charnockite	7.1	2550	5.36	6.62	1.20	0.00	1.23	0.03	8.6	7.29	0.51	7.12	1.00	1038.28
Singipatti	Charnockite	7.3	920	5.29	3.81	0.66	0.00	1.03	0.03	14.2	7.99	0.28	1.78	1.39	743.84
Kolathur	Peninsular gneiss	7.2	1755	4.26	6.64	0.41	0.00	1.06	0.02	18.4	6.67	0.43	4.04	2.39	928.64
Gonur	Charnockite	7.8	1233	3.00	5.28	0.61	0.00	0.74	0.10	13.2	3.32	0.05	5.43	1.00	682.57
Pottaneri	Peninsular gneiss	7	670	1.00	7.19	0.41	0.00	0.12	0.02	16.8	3.14	0.05	3.75	2.20	682.67
Mecheri	Peninsular gneiss	8	1700	3.76	5.31	2.12	0.00	0.66	0.03	22.2	4.37	0.36	4.08	1.80	823.31
Pukkampatti	Peninsular gneiss	7.8	1580	3.74	4.72	3.70	0.00	0.58	0.15	16.4	5.56	0.03	3.71	2.80	883.62
Aranganur	Peninsular gneiss	7.6	1447	9.75	7.28	2.75	0.00	0.54	0.03	17.2	5.92	0.66	10.49	2.57	1314.22
Periyasathapadi	Peninsular gneiss	7.6	1347	10.25	4.86	1.69	0.00	0.98	0.02	22.4	4.48	0.09	11.16	0.82	1082.83
Kunjandiyur	Charnockite	7.3	1870	4.74	5.59	2.06	0.00	0.02	0.07	19.8	4.45	0.15	4.33	3.08	853.47
Alamarathupatti	Charnockite	7.4	1730	9.26	6.72	3.07	0.00	0.60	0.04	14.4	6.42	1.01	4.21	7.18	1320.56
Mettur	Charnockite	7.7	1300	7.24	3.84	3.90	0.11	0.58	0.03	19	5.11	0.21	3.93	4.67	1001.06
Nangavalli	Peninsular gneiss	7.2	4900	8.24	5.75	3.65	0.00	0.92	0.04	20	11.55	0.15	3.86	2.69	1266.77
Ollapatti	Peninsular gneiss	7.6	1370	8.48	3.35	4.57	0.00	0.12	0.07	13	5.75	0.19	9.41	0.29	1004.83
Periyasoragai	Peninsular gneiss	7.6	1810	23.22	7.33	0.99	0.01	0.55	0.18	16.6	10.73	1.26	14.53	3.11	1903.45
Kalnayakanpatti	Charnockite	7.2	1877	6.23	5.82	1.03	0.09	0.93	0.06	16.4	4.72	0.72	6.71	1.09	939.45
Kannamuchi	Charnockite	7.1	1750	22.49	4.87	0.93	0.00	0.47	0.02	19.3	9.91	1.18	9.95	6.78	1717.78
Dooramapuram	Peninsular gneiss	7.9	4090	17.72	4.72	4.50	0.00	0.53	0.09	16.2	17.48	0.61	9.68	0.70	1738.76
Pappampatti	Peninsular gneiss	7.9	1954	11.30	4.76	4.37	0.00	0.41	0.07	18	6.41	0.69	5.13	3.29	1039.75

Table 2. *Chemical composition of groundwater during post-monsoon season (all values in meq/I except pH, EC, H_4SIO_4 and TDS).*

Location	Lithology	pH	EC (μs/cm)	Cl	HCO_3	SO_4	PO_4	NO_3	F	H_4SiO_4 (mg/l)	Na	K	Mg	Ca	TDS Mg/l
Tettiguipetti	Peninsular gneiss	7.3	1060	10.32	4.48	3.68	0	0.09	0.03	27.9	5.40	3.27	1.81	6.76	978.21
Mallikundam	Peninsular gneiss	7.4	1350	13.32	6.48	1.92	0	0.44	0.04	32.4	4.88	1.05	6.61	9.09	1189.29
Koonandiyur	Charnockite	7.7	800	4.84	5.78	0.68	0	0.17	0.17	34	5.44	0.64	3.15	3.48	771.14
Tinnapatti	Peninsular gneiss	7.7	2605	29.83	7.99	3.63	0	0.12	0.02	17.4	12.91	0.68	3.35	22.34	1994.48
Kaveripuram	Charnockite	7.9	656	2.24	5.75	3.39	0.04	0.10	0.02	24.8	4.06	0.03	5.25	1.00	638.4
Singipatti	Charnockite	7.2	631	5.24	3.75	1.11	0	0.06	0.03	14	3.23	0.84	2.76	2.50	583.7
Kolathur	Peninsular gneiss	7.8	1392	14.52	4.49	3.67	0	0.11	0.03	32.8	7.05	0.15	7.37	9.83	1124.05
Gonur	Charnockite	7.2	742	5.00	5.04	2.48	0	0.12	0.15	36.5	3.61	0.05	5.95	2.01	704.68
Pottaneri	Peninsular gneiss	7.6	1002	5.64	6.29	0.50	0	0.09	0.08	16.5	5.67	0.82	1.71	3.07	798.82
Mecheri	Peninsular gneiss	8.0	1547	7.02	6.43	1.70	0	0.10	0.06	10.8	4.24	0.27	4.60	5.41	841.65
Pukkampatti	Peninsular gneiss	7.4	600	4.00	3.84	1.64	0	0.12	0.04	22	3.63	0.53	2.44	2.08	551.9
Aranganur	Peninsular gneiss	8.1	912	7.50	5.21	1.91	0	0.11	0.06	18.2	7.02	0.10	3.34	3.48	831.96
Periyasathapadi	Peninsular gneiss	7.3	884	11.32	3.61	1.70	0	0.10	0.07	17.9	5.92	0.24	0.72	8.32	824.58
Kunjandiyur	Charnockite	7.8	811	8.77	3.29	2.70	0	0.12	0.21	14	3.67	0.64	7.51	3.49	758
Alamarathupatti	Charnockite	7.6	919	8.24	4.16	1.38	0	0.09	0.03	34.4	4.69	0.80	2.97	4.31	776.13
Mettur	Charnockite	7.7	789	7.50	4.0	0.49	3.54	0.14	0.06	21.8	6.76	0.14	4.04	2.69	762.64
Nangavalli	Peninsular gneiss	7.2	812	7.01	4.32	3.62	0	0.11	0.03	35.5	5.06	0.19	4.49	4.08	757.44
Ollapatti	Peninsular gneiss	8.4	1460	8.01	2.33	1.39	0	0.11	0.06	22	4.35	0.77	1.29	4.41	616.82
Periyasoragai	Peninsular gneiss	7.4	1265	8.01	7.20	3.03	0.41	0.09	0.15	27.2	7.12	0.93	5.72	3.85	1050.2
Kalnayakanpatti	Charnockite	7.7	1540	12.32	8.88	3.15	2.72	0.06	0.09	23.2	6.39	1.05	7.47	8.04	1319.41
Kannamuchi	Charnockite	7.3	1468	19.98	5.27	1.40	0	0.31	0.03	27.3	6.99	1.44	4.38	11.81	1375.89
Dooramapuram	Peninsular gneiss	8	800	5.29	4.28	1.68	0	0.09	0.07	27.2	3.84	0.69	6.10	2.10	684.34
Pappampatti	Peninsular gneiss	7.7	1325	9.42	4.35	3.26	0	0.16	0.09	33	11.94	1.13	2.57	3.40	1014.21

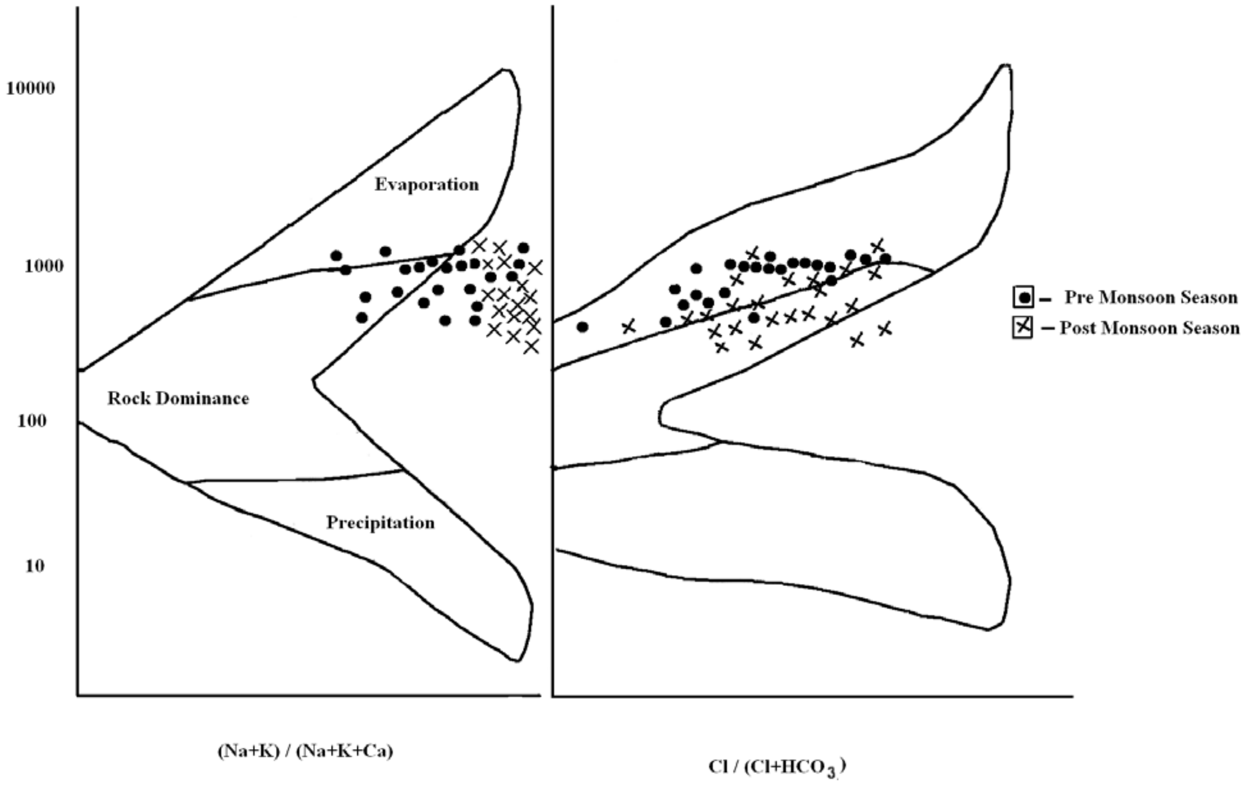

Figure 2. Gibbs plot for pre- and post-monsoons.

3. Materials and methods

A total of 46 representative groundwater samples were collected (figure 1) for two different seasons, viz., pre-monsoon (June) and the post-monsoon (December) along with a maximum representation covering the entire study area. The samples were filtered using 0.45 μm Millipore filters and immediately stored in polyethylene bottles and analyzed for major and minor cations and anions using standard procedures (see APHA 1995). pH and EC were measured *in situ* by pH conductivity meter model CONSORT C425. HCO_3, Cl, Ca and Mg were analyzed using titration. F was analyzed using Orion fluoride ion electrode model (94-09, 96-09). SO_4, PO_4, H_4SIO_4 was determined by digital spectrophotometer model GSS 700A (Electronic Corporation of India). Na and K were determined by using flame photometer (Systronics mk-1/mk-III). The analytical precision for the measurements of ions was determined by calculating the ionic balance error that varies by about 5–10%. TDS/EC ratio is 0.50/1.0 (with excess of anions in water).

4. Results and discussion

Groundwater in general was alkaline in nature and higher EC values were noted during the pre-monsoon season. HCO_3 in the study area was higher in pre-monsoon season due to weathering of silicates. Cl was higher in post-monsoon season indicating leaching from upper soil layers due to industrial and domestic activities and dry climates (Herman Bouwer 1978). SO_4 was higher in pre-monsoon season indicating breaking of organic substances from topsoil/water, leachable sulphate preset in fertilizer and other human influences (Miller 1979; Craig and Andeson 1979). Fluoride and NO_3 was higher in pre-monsoon indicating leaching of fluoride rich rocks and organic substances from weathered soil (tables 1 and 2). The general dominance of anion was in the order of $Cl > HCO_3 > SO_4 > NO_3 > PO_4$. For cations Na was higher in pre-monsoon season indicating weathering from plagioclase bearing rocks. K was lesser in both the seasons indicating its lower geochemical mobility. Ca and Mg were higher in pre-monsoon indicating the weathering from primary mineral sources. The general dominance of cations was in the order of $Na > Ca > Mg > K$. H_4SIO_4 was higher indicating the existence of alkaline environment and abundance of silicate minerals in the study area.

The results from the water analysis were used as a tool to identify the process and mechanisms affecting the chemistry of groundwater from the study area. Gibbs (1970) plot was used to

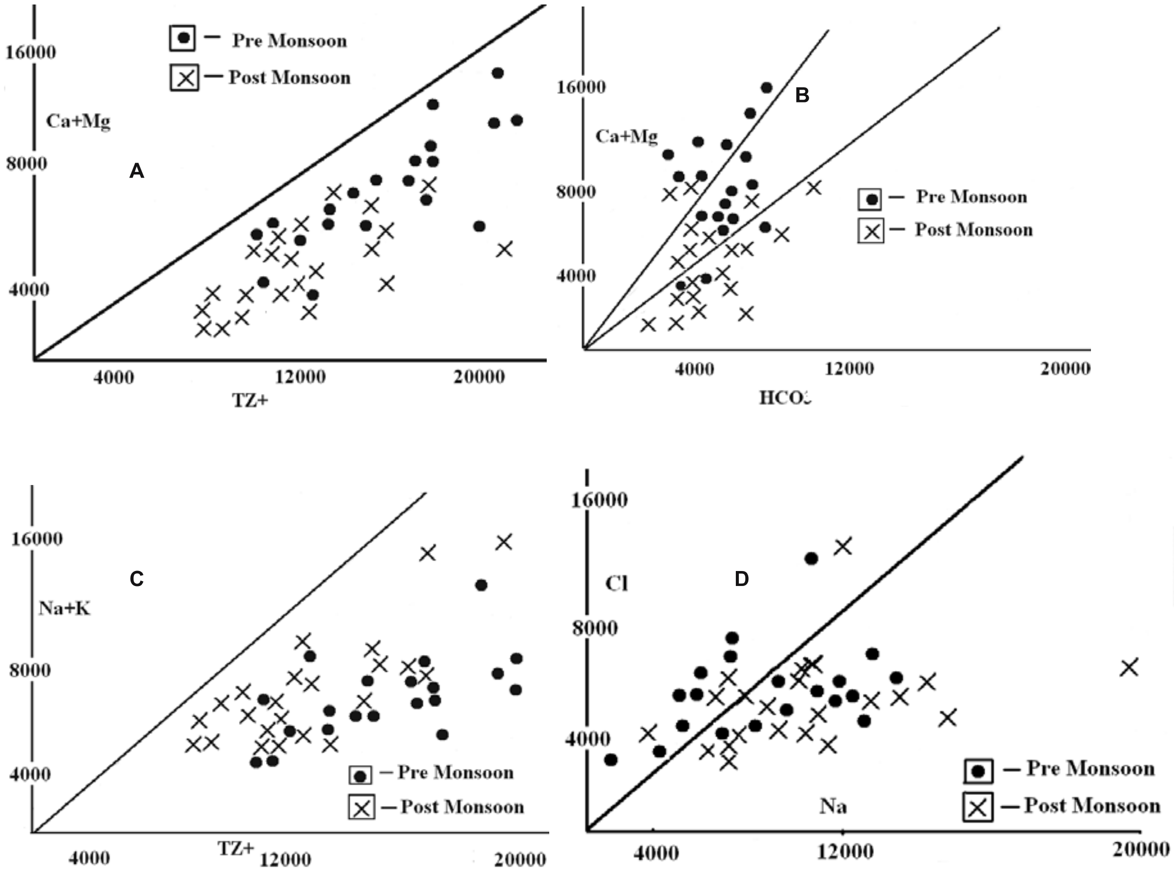

Figure 3. **(A–D)** Plot for relationship of ions during pre- and post-monsoon seasons.

determine the mechanism controlling the water chemistry (figure 2). Samples from both seasons fall in rock dominance zone suggesting precipitation induced chemical weathering along with dissolution of rock forming minerals.

The (Ca + Mg) *versus* TZ^+ plot (figure 3A) for both seasons lie far below equiline with average equilibrium ratio of 0.40 to 0.35 indicating that alkalis are enriched twice to thrice the amount of Ca and Mg due to leaching from silicate weathering which is dominant in the aquifer materials of the study area. In the plot for (Ca + Mg) *versus* HCO_3, the data point irrespective of seasons fall away from equiline 1:1 to 2:1, indicating predominance of alkali earth by silicate weathering over bicarbonate. Minor representations are also noted in bicarbonate zone due to the reaction of the feldspar minerals with carbonic acid in the presence of water, which releases HCO_3 (Elango *et al* 2003) (figure 3B). The plot for (Na + K) *versus* TZ^+ (figure 3C) indicates weathering process of both alkali and alkali earth from feldspars alongwith additional sources like contribution from alkali/saline soil and residence time are major contributing sources for ions in groundwater irrespective of seasons. The plot for Na *versus* Cl (figure 3D) shows that, majority of samples for both the seasons fall near Cl and Na zones indicating Na derived from weathering from silicate bearing minerals. Since Cl is abundant in both the seasons and due to rare Cl bearing minerals in silicate terrain, it might have derived from Anthropogenic (human) sources of chloride include fertilizer, road salt, human and animal waste, and industrial applications. These sources can result in significant concentrations of chloride in groundwater because chloride is readily transported through the soil (Stallard and Edmond 1983). This is well evidenced from Cl levels of the study area which is a major industrial town of Salem district.

In the plot for Na/Cl *versus* EC (figure 4A, U and V) the Na/Cl shows a decreasing trend with increasing EC along with higher Na/Cl ratio, indicates Na released from silicate weathering process. This is also supported by higher HCO_3 values in groundwater due to reaction of feldspar minerals with carbonic acid might be one of the reasons for increase in EC (Jankowski and Acworth 1997) in both the seasons.

The plot for Ca + Mg *versus* SO_4 + HCO_3 is a major indicator to identify ion exchange process activated in the study area. If ion exchange is the process, the points shift to right side of the

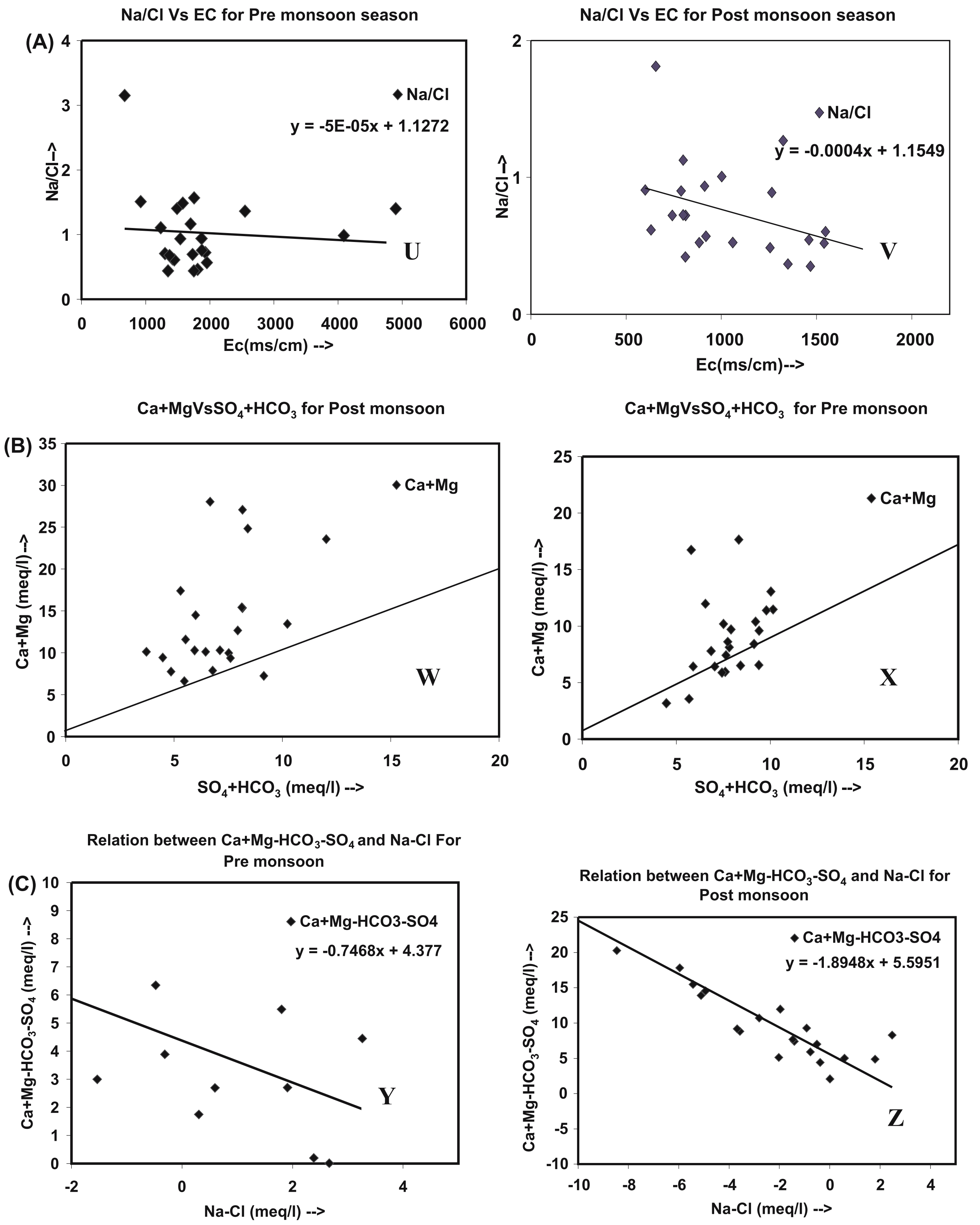

Figure 4. (**A**) Na/Cl *vs.* EC; **U** – pre-monsoon, **V** – post monsoon. (**B**) Ca + Mg *vs.* $SO_4 + HCO_3$; **W** – pre-monsoon, **X** – post-monsoon and (**C**) Na–Cl *vs.* Ca + Mg–HCO_3–SO_4; **Y** – pre-monsoon, **Z** – post-monsoon.

plot due to excess $SO_4 + HCO_3$. If reverse ions exchange is the process, points shift left due to excess Ca + Mg. In pre-monsoon, the point clusters around the equiline 1:1 and falls in $SO_4 + HCO_3$ indicating the ion exchange process which may be due to the excess bicarbonate (figure 4B, W and X). In post-monsoon season, the plot points Ca + Mg indicating excess calcium and

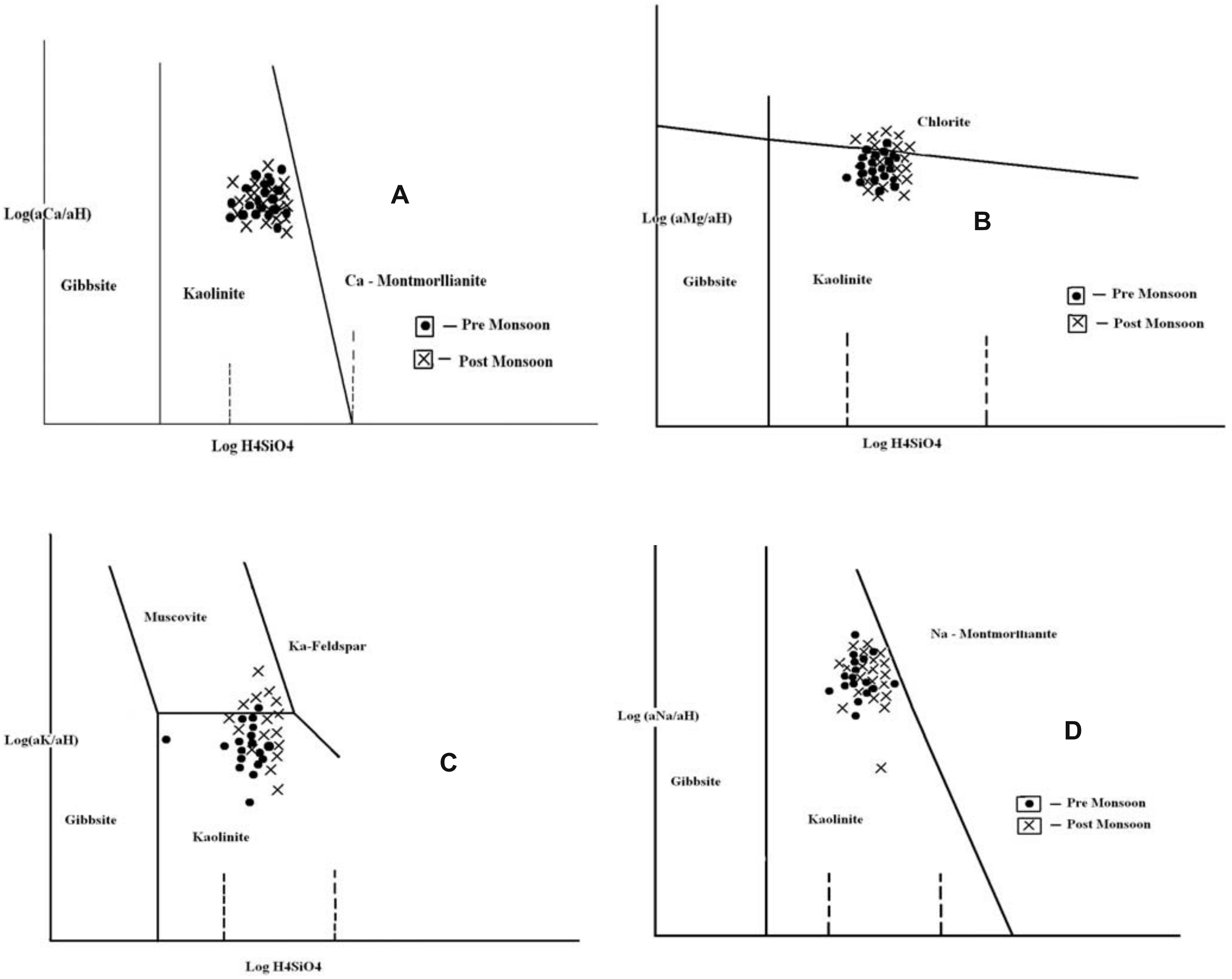

Figure 5. Thermodynamic stability plot for **(A)** Ca, **(B)** Mg system, **(C)** Na and **(D)** K system.

magnesium in groundwater exchanged with sodium from aquifer materials. The plot of Na − Cl *versus* Ca + Mg − HCO_3 − SO_4 confirms that Ca, Mg and Na concentrations in the groundwater is derived from aquifer materials (figure 4C, Y and Z).

Thermodynamic plotting of [Na]/H, [K]/H, [Ca]/H and [Mg]/H, for groundwater from study area are plotted on the stability diagram as a function of [H_4SiO_4]. In plot for Ca the samples (figure 5A) for both the seasons fall in Kaolinite field indicating impact of dilution. In plot for magnesium (figure 5B) shift of stability from kaolinite to chlorite is noted in both the seasons indicating the formation of new clay minerals due to supply of excess cations and silica to pre-existing kaolinite from aquifer materials.

The plot of Na falls in the kaolinite stability field irrespective of seasons, indicating Na–Feldspar will dissolve incongruently to produce kaolinite and dissolved products (figure 5C). As dissolution of feldspars continues the value of $Si(OH)_4$ and [Na]/[H] increases and water chemistry moves to Na–Montmorllianite during SUM.

The plot of K silicates (figure 5D) indicates incongruent dissolution of kaolinite and formation of muscovite. Majority of samples irrespective of seasons fall in kaolinite and muscovite field. When IAP of K increases as the result, the ratio of K increases and pH remains almost constant this variation result in shift of kaolinite to muscovite field along with release of H^+ ions which combines with HCO_3 to form CO_2.

5. Disequilibrium indices

Disequilibrium indices log(IAP/KT) was calculated by WATEQ4F geochemical model for those minerals and other solids stored in the model data book for which the dissolved constituents are reported in groundwater analysis. Disequilibrium indices log(IAP/KT) were

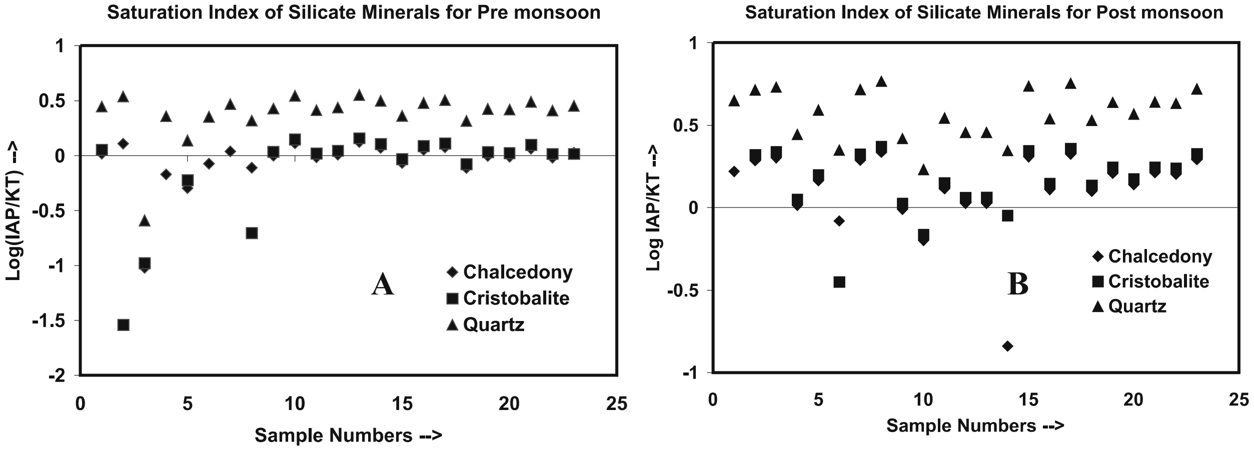

Figure 6. Disequilibrium indices for silicate minerals. **(A)** pre- and **(B)** post-monsoon seasons.

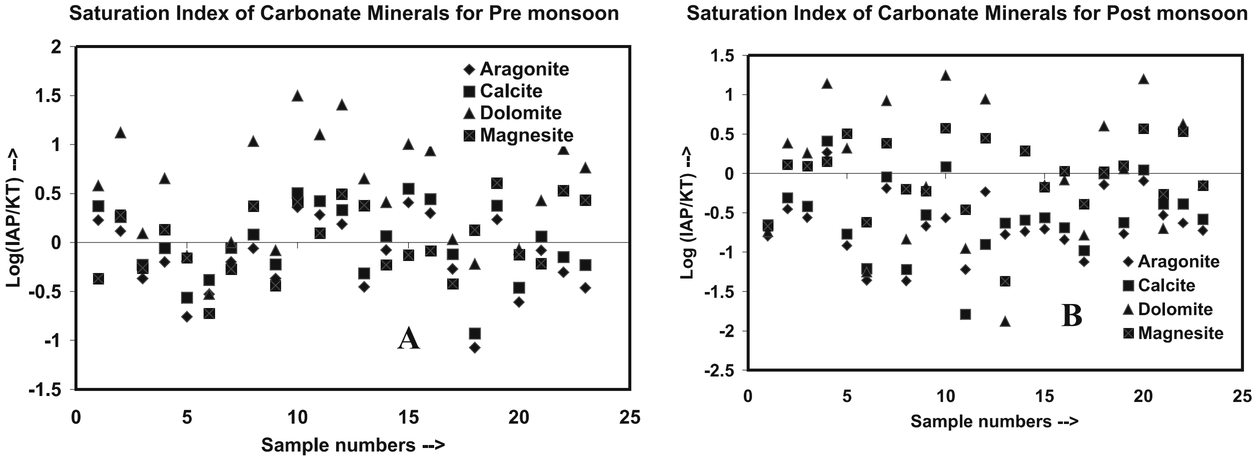

Figure 7. Disequilibrium indices for carbonate minerals. **(A)** pre- and **(B)** post-monsoon seasons.

calculated to determine, if water is in thermodynamic equilibrium log(IAP/KT $= 0$), oversaturated log(IAP/KT > 0) or undersaturated log(IAP/KT < 0) with respect to certain solid phases (Trusdell and Jones 1973).

The disequilibrium indices of silicate minerals (figure 6A and B) chalcedony, christobalite and Quartz were represented from the data bank of WATEQ4F and studied for dissociation factors in the study area. The data input was categorized on the basis of two seasons. The status of groundwater in pre-monsoon indicates that all the minerals are in the state of oversaturation to equilibrium. In post-monsoon, quartz follows the same trend of oversaturation but chalcedony and christobalite have neared saturation state indicating the effect of dilution.

The disequilibrium indices of carbonate minerals (figure 7A and B) aragonite, calcite, dolomite and magnesite were represented from the data bank of WATEQ4F. The samples in pre-monsoon season are near-oversaturated to equilibrium with aragonite, calcite, dolomite and magnesite with minor indications in undersaturation state. The samples in post-monsoon season follow the same trend as in pre-monsoon. In general, carbonate results show that calcite, dolomite and magnesite are saturated-to-oversaturated which is indicated by excess input of Ca and Mg ions from silicate weathering process.

6. Conclusions

The groundwater in Mettur region is a unique example for the impact of weathering, ion exchange and anthropogenic process controlling water chemistry. The chemical composition of groundwater of the study area is strongly influenced by rock water interaction, dissolution and deposition of silicates group of minerals. Weathering of silicate minerals controls the major ion chemistry of calcium, magnesium, sodium and potassium. Cl was dominant due to anthropogenic impact (human sources). The ion exchange and reverse ion exchange control the water chemistry of the study area. Thermodynamic plot indicates, groundwater is in equilibrium with kaolinite, muscovite and chlorite minerals. SI of minerals indicates oversaturation and undersaturation of silicate and carbonate minerals with respect to pre- and post-monsoon seasons. In general, water chemistry is guided by lithological influences on water chemistry by complex weathering process, ion exchange along with influence of Cl ions from anthropogenic impact.

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MS received 1 December 2006; revised 21 July 2007; accepted 6 September 2007