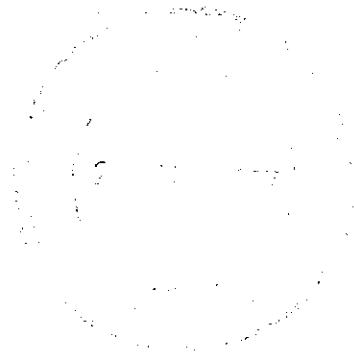REPORT NO. C-9

SALINIZATION OF THE IRRIGATED SOILS IN THE PUNJAB (PAKISTAN)

Consultancy Report

by

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FOREWORD

This consultancy report is an output of a collaborative research program with CEMAGREF the French national research organization for agriculture, water and forests. This research is also an important part of our program under the project *"Managing Irrigation for Environmentally Sustainable Agriculture in Pakistan"* funded by the Government of The Netherlands.

This collaborative salinity research was done during 1996 at IIMI field sites in southeastern Punjab with Mr. Marcel Kuper as the principal investigation. The advisor for this collaborative research was Dr. Serge Marlet of the Centre for International Cooperation in Agricultural Research for Development (CIRAD) in Montpellier; he had spent five years in Niger doing similar salinity research. An M.S. student, Mr. Nicolas Condom, has reported the field research results (IIMI Report No. R-22). Both of them are now working together in West Africa.

This consultancy report is a significant scientific contribution to our understanding of the geochemical processes and their effects on soil salinity. We greatly appreciate the efforts of Serge Marlet, Nicolas Condom and Marcel Kuper in undertaking this work.

Gaylord V. Skogerboe
Director, Pakistan National Program
International Irrigation Management Institute

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SALINIZATION OF THE IRRIGATED SOILS IN THE PUNJAB (PAKISTAN)

Irrigation water quality is currently evaluated from indicators such as electrical conductivity (EC), pH and sodium adsorption ratio (SAR). Water quality is then classified with respect to the salinization, alkalinization and sodification hazard . But this classification doesn't consider the geochemical process, while models allow this to be taken into account.

The geochemical mechanisms of soil salinization and sodification for some irrigated schemes in the Punjab have been modeled according to the analytical data. They include precipitation and dissolution of a few minerals and cation exchanges. This model has been used to:

- explain the origin of grounwater quality from a mixing of increasing amounts of fresh river water with initial saline goundwater;

- predict how water changes when it concentrates and to suggest a new classification of water quality assessment for irrigation with respect to the residual alkalinity concept; and

- predict the soil salinity, alkalinity and sodicity when the geochemical model is coupled with a very simple water balance model based on a knowledge of the leaching fraction.

The use of such a geochemical model could provide many applications in IIMI's program in Pakistan:

- to prospect and to spatialize for the best water quality of additional water supplies according to the residual alkalinity concept and EC; and

- to evaluate to salinization and sodification hazard according to water quality, soil type and water management when irrigation and drainage performances are known.

Such a geochemical model could be coupled with any kind of model, from a simple evaluation of irrigation performance to a more sophisticated water and solute transport model as it was realized in Niger [Marlet, 1996] and Pakistan [Condom, 1996].

The soils of the Punjab in Pakistan are often threatened by salinization, sodification or alkalinization, both in irrigated or barren soils. In barren soils, capillary rise from a shallow water-table and salt concentration at the ground surface can be the lone cause of degradation. In irrigated soils, these phenomena are due to a rise in water table, use of low quality groundwater, or inadequate quantities of irrigation water. Due to a lack of irrigation water due to chronic shortages, tubewells have been drilled to provide additional irrigation water supply. Irrigation with tubewells leads to a fall of the water tables and a decrease in waterlogging. The materials of the Indus plains are issued from thick marine sediments and from alluvium of the river system. Thus, the groundwater is often saline and the shallow groundwater is pumped to avoid a salinization hazard. Neverthless, it contributes to the sodification process that becomes much more of a problem than salinity. Water quality varies greatly, so there is an interest in: (i) understanding their origin so as to improve the prospecting capability for obtaining the best irrigation water supply; and (ii) assessing water quality in order to predict how water chemistry changes when it concentrates.

In a first part, the theorical principle and mechanisms of soil salinization are presented. In a second part, the geochemical mechanisms involved in the salinization of the soil in the Punjab, including mineral precipitation and cations exchange, are studied and modeled. In a third part, the various groundwater qualities are studied and the geochemical model is used to simulate their origin from a mixing of increasing amounts of fresh river water with saline water. In a fourth part, the effect of various water qualities when it concentrates are simulated according to: (i) the residual alkalinity concept and the geochemical model; and (ii) water management. These topics suggests ways for evaluating or classifying water quality and how to manage different water sources.

1. Theory

1.1. Residual alkalinity concept

When water evaporates, precipitates occur and affect the composition of the soil solution. Common precipitates are: calcite, chert (colloïdal silica, chalcedony), gyspum, and clay minerals [*Appelo and Postma*, 1995]. The principle has been developed by *Eaton* [1950] and *Hardie and Eugster* [1970] in an evolutionary sequence for evaporating waters. It suggests that the composition of saline waters is a function of the concentration ratios in the starting solution, where alkalinity plays an important part.

Alkalinity (Equation 1) is equal to the sum of the concentrations of the weak bases multiplied by the number of protons that each base can neutralize, minus the concentration of the solution. For most soils and natural waters, alkalinity is due to the carbonate species.

$$Alkalinity = HCO_3^- + 2CO_3^{2-} + OH^- - H^+ + HS^- + 2S^{2-} + H_3SiO_4^- + ... = HCO_3^- + 2CO_3^{2-} \ (mol_c.l^{-1}) \quad (1)$$

When a solution is concentrated by evaporation to the point that calcite ($CaCO_3$) precipitates, alkalinity and calcium molality cannot increase together. In the case where Ca^{2+} equivalents exceed alkalinity equivalents in the original solution, alkalinity decreases and calcium molality increases. In a reverse situation, alkalinity increases and calcium molality decrease. This concept of Residual Alkalinity (RA) has been generalized to the succesive precipitation of several minerals [*Van Beek and Van Breemen*, 1973; *Al Droubi et al.*, 1980, *Vallès et al.*, 1989, 1991]. RA is calculated adding the cations charges and substracting the anions charges, which are involved in precipitates, to alkalinity. For example, with respect to calcite and sepiolite (Equation 2); and to calcite, sepiolite and gypsum (Equation 3), residual alkalinity can be written as:

$$RA-calc.+sep. \ (mol_c/l) = Alkalinity - 2Ca - 2Mg = RSC \qquad (2)$$

$$RA-calc.+sep.+gyps. \ (mol_c/l) = Alkalinity - 2Ca - 2Mg + 2SO_4 \qquad (3)$$

RA allows a prediction of how water chemistry changes with increasing concentrations. When RA>0, alkalinity increases while calcium and magnesium molalities decrease in the soil solution; they display a minority ion behavior according to the residual alkalinity concept. When RA<0, alkalinity decreases while calcium and magnesium molalities increases at a slower rate than the concentration factor; they display a majority ion behavior according to the residual alkalinity concept.

1.2. Model description

Numerous geochemical models based on purely thermodynamic laws allows the major geochemical processes to be simulated. Most of these models can take into account widely different temperature and pressure conditions and store a considerable amount of thermodynamic data relative to a large number of chemical species and reactions. Their use for practical purposes may be restricted due to costly computer resource requirements. So, a model derived from the thermodynamic model GYPSOL [*Vallès and Bourgeat*, 1988] was used, which accounts for speciation of the major chemical component, precipitation or dissolution of a few minerals, and cation exchanges. This model is sufficiently simplified so that its repeated use is not too expensive (CPU time), adaptable to conditions prevailing in cultivated soils, but also accurate and reliable for decision making in alkaline and saline soils management. GYPSOL has been validated for the ion behavior in natural waters up to an ionic strenght of 1.

The chemical composition of the soil solution, the activity of the aqueous species, the equivalent fraction of the cations adsorbed, and the mineralogical composition of the soil are calculated in the model. The Cationic Exchange Capacity (CEC), the temperature and the CO_2 partial pressure are considered as constant. Instantaneous equilibrium between the

minerals, the adsorbing complex, and the soil solution is assumed in every case and an iterative procedure is used to reach convergence. The presentation of the model is detailed in the annex.

2. Study and Modelization of the geochemical mechanisms

The soil solution is in equilibrium with respect to minerals through precipitation or dissolution and the exchange complex through cation exchanges.

These minerals are calcite and clay minerals like kaolinite, sepiolite, illite and a feasible precipitation of paragonite for the most concentrated soil solution. Gyspum and chert (amorphous silica) precipitates have not been proved; but their occurrence is probable. The undersaturation of the extracts with respect to amorphous silica was imputed to slow dissolving in the soil suspension. In this study, the irrigated soil samples were not very saline and no gypsum exists. But for most concentrated waters, the occurrence of gypsum precipitation or dissolution cannot be ignored.

Cation exchanges between sodium and calcium, calcium and magnesium, and sodium and potassium have been modeled.

2.1. Chemical analysis

Fifteen soil samples were obtained randomly from irrigated fields in the study area near Hasilpur. Suspensions of the fifteen soil samples in water were prepared with 1:1 and 1:20 soil-water ratios. For four of them, additional suspensions were prepared with 1:2, 1:5 and 1:10 soil-water ratios. The soil solution was extracted by centrifugation 24 hours later. K, Na, Ca, Mg, Cl, SO_4, Si and Al molalities were analyzed using ion chromatography. Al molality is very low and could not be determined. Alkalinity was determined by titration with acid using the Gran plot method. pH was measured before centrifugation and 2 hours, 7 hours, 4 days, 6 days and 10 days after centrifugation. The GYPSOL model was used to calculate ion activities and pCO_2 as a function of their molality and pH measured before centrifugation. Thus, the soil residue was dried and the cationic exchange capacity and the adsorbed K, Na, Ca and Mg were determined by the cobaltihexamine chloride method.

2.2. Results

2.2.1. Saturation diagram

The activities of the solute species provide an indication about the degree of saturation of the sample solutions with minerals likely to dissolve or precipitate. In this section all of the analyses will be considered. The minerals are presented in Table 1.

Table 1. Dissolution reaction of minerals - thermodynamic data [*Fritz*, 1981].

Mineral	Dissolution reaction	pK
Calcite	$CaCO_3 \leftrightarrow Ca^{++} + CO_3^-$	- 8.73
Gypsum	$CaSO_4.2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	- 4.84
Amorphous silica	$H_4SiO_4 \leftrightarrow H_4SiO_4^*$	- 2.71
Sepiolite	$Si_6Mg_4O_{15}(OH)_2.4H_2O + 8H^+ + 3H_2O \leftrightarrow 4Mg^{++} + 6H_4SiO_4^*$	+31.00
Illite:	$Si_{3.5}Al_{2.3}Mg_{0.25}O_{10}(OH)_2K_{0.6} + 8H^+ + 3H_2O \leftrightarrow 0.6K^+ + 2.3Al^{3+} + 0.25Mg^{++} + 3.5H_4SiO_4^0$	+10.34[b]
Kaolinite	$Si_2Al_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{+++} + 2H_4SiO_4^* + H_2O$	+ 7.43[b]
Paragonite	$Si_3Al_3O_{10}(OH)_2Na + 10H^+ \leftrightarrow Na^+ + 3Al^{3+} + 3H_4SiO_4^*$	+18.47[b]
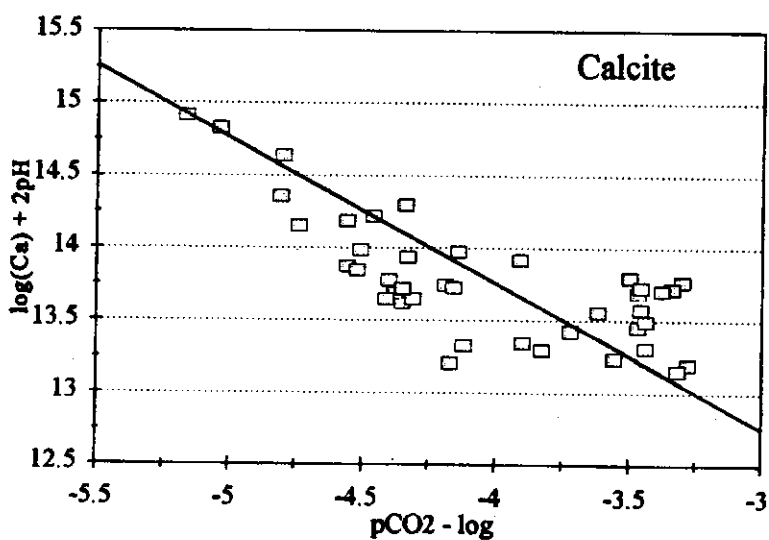
Figure 1. Saturation diagram for calcite.
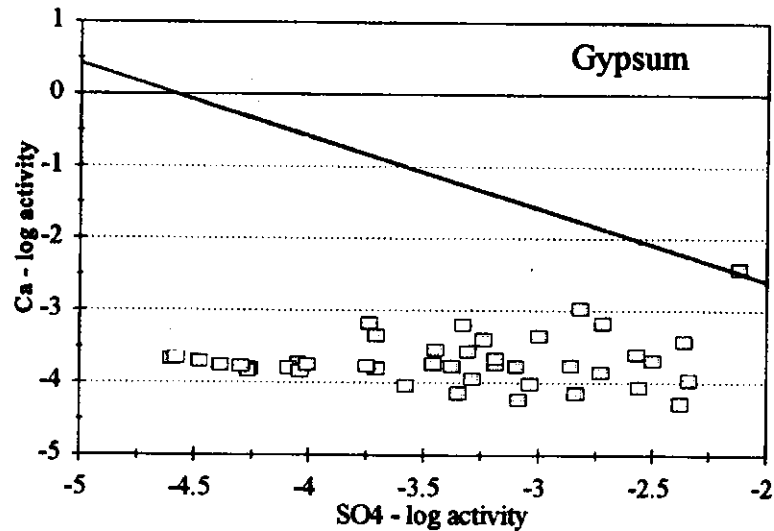
Figure 2. Saturation diagram for gypsum.

The saturation diagram in which the analytical result are plotted against calcite (Figure 1) indicates that this mineral achieves saturation, whereas the soil solution remains undersaturated with respect to gypsum (Figure 2). One soil sample is in equilibrium with respect to gypsum. Neverthless, gypsum could precipitate at higher concentrations. Note that the partial pressure of CO_2 (pCO_2) in the soil solution is very low (Figure.1), which is less than the atmospheric pressure. This phenomenom may be imputed to mineral dissolution in the soil suspension that produces alkalinity and consumes CO_2 for calcite dissolution, which can be writen as:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^-$$ (4)

This leads to a fast increase in pH that is linked to alkalinity and pCO_2, which under these circumstances can be writen as:

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O , \quad pH \approx 7.81 + \log(alkalinity) - \log(pCO_2)$$ (5)

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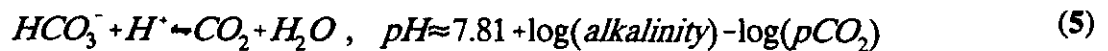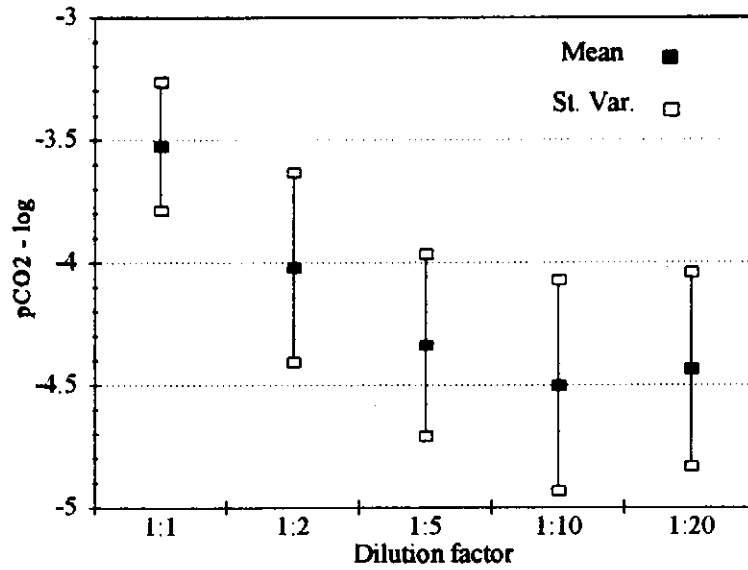
Figure 3. Effect of the dilution factor of the soil suspension on pCO_2 before centrifugation.
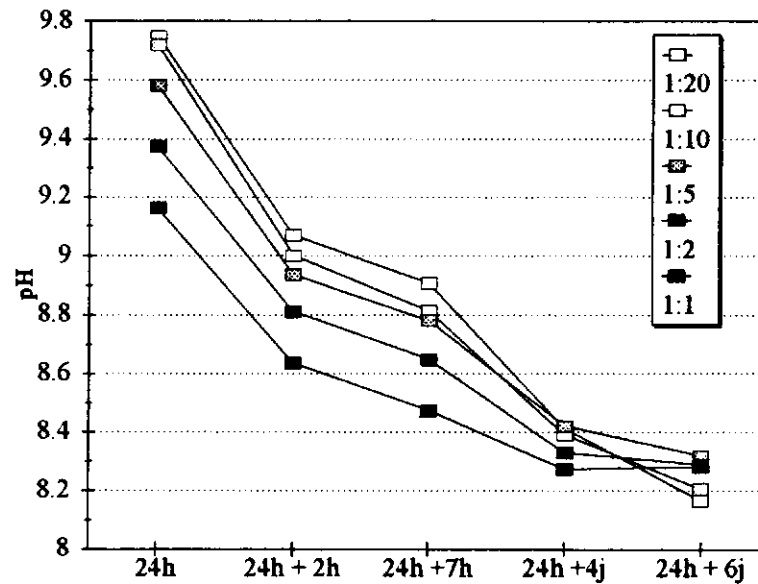
Figure 4. Evolution of the pH of the extract with time after centrifugation.

pCO_2 has been plotted against the dilution factor in the soil suspensions (Figure. 3); while decreases with high dilution because a larger amount of minerals dissolve to achieve equilibrium. pH has been monitored for 6 days after centrifugation (Figure 4); which decreases continuously due to CO_2 diffusion that tends towards the equilibrium. Despite these variations, the extracts achieve equilibrium with respect to minerals; but, the extract cannot be considered as representative of the composition of the soil solution because pCO_2 is very much lower than that in the soil solution.

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The soil solutions were not analyzed for aluminium; hence, the degree of saturation of magnesian aluminium silicates could not be determined precisely. However, Figure 5 indicates that sepiolite achieves saturation; thus, it is likely that closely related magnesian aluminium silicates (montmorillonite) do precipitate. These soils are rich in illite that could explain the potassium control. Thus, the Al^{3+} activity in the extracts were assessed, supposedly in equilibrium with kaolinite (Table 1). Figure 6 indicates that illite achieves saturation. $H_4SiO_4^0$ molality remains surprisingly undersaturated with respect to amorphous silica (Table 1), which commonly precipitates when fresh water evaporates. Slow dissolving of silica could explain this phenomenom and the apparent disequilibrium of the extracts with amorphous silica. H_4SiO_4 should mainly be issued from the dissolution of silicates.
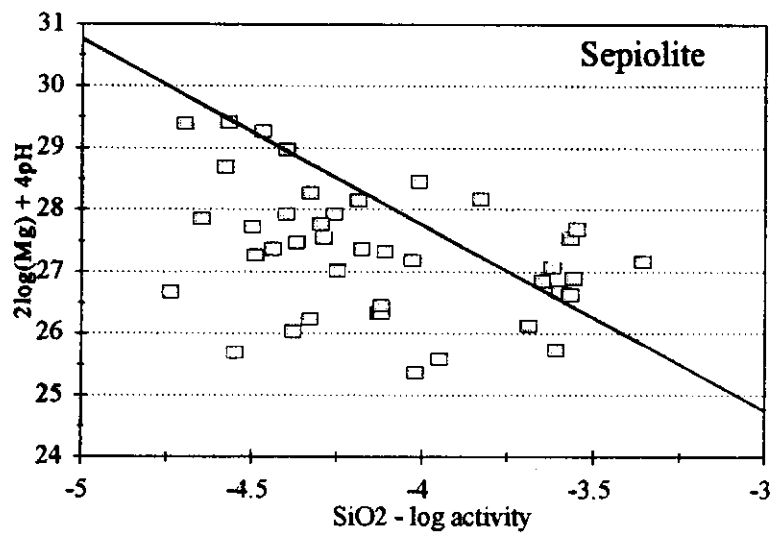
Figure 5. Saturation diagram of sepiolite.
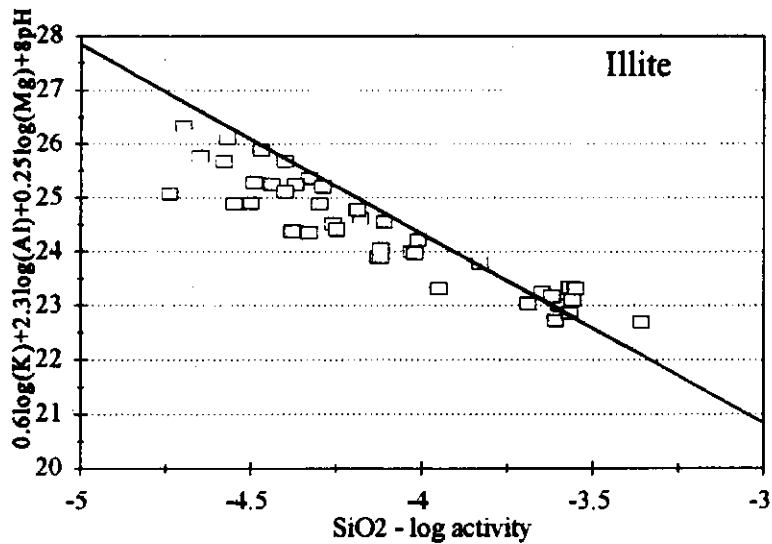
Figure 6. Saturation diagram of illite.
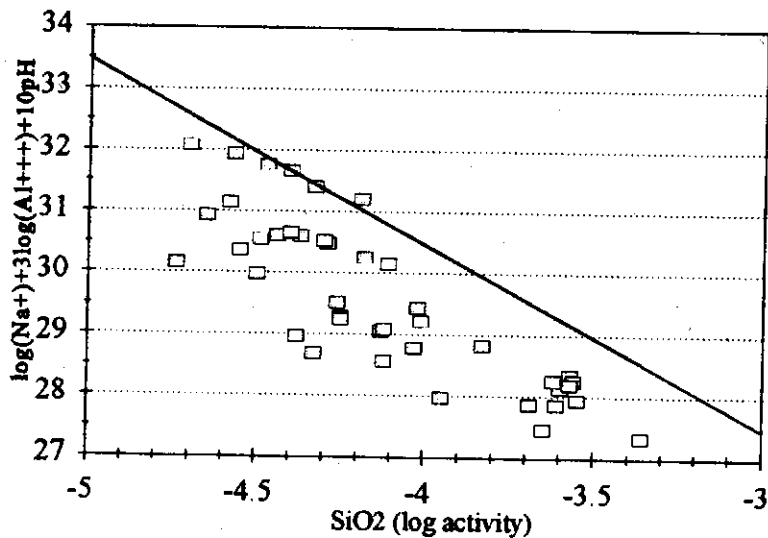
Figure 7. Saturation diagram of paragonite.

The saturation diagram (Figure 7) indicates that paragonite achieves saturation for one soil sample whatever the five dilution factors. The other soil samples are undersaturated with respect to paragonite. But the trend of the analysis parallels that of the theorical equilibrium. Such a phenomenom has already been observed by *Marlet et al.* (1996), but paragonite precipitation has not been proven.

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2.2.2.   Cation exchanges

In order to model the Na^+-Ca^{2+}, Ca^{2+}-Mg^{2+} and Na^+-K^+ exchanges, the parameters α and β were fitted from the activities of dissolved cations and the charge fraction of adsorbed cations (Equations 16, 17 and 18). The results showed good agreement with the model (Figures 16,17 and 18) and the parameters were fitted as follows:
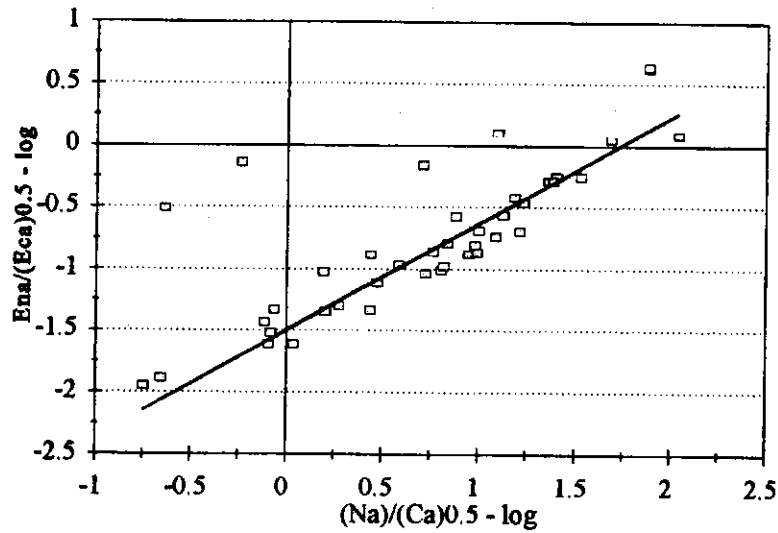
Figure 8. Na-Ca exchange [line is Eq. (6)].

$$\frac{E_{Na}}{\sqrt{E_{Ca}}} = 0.0317[\frac{(Na)}{\sqrt{(Ca)}}]^{0.867} \tag{6}$$
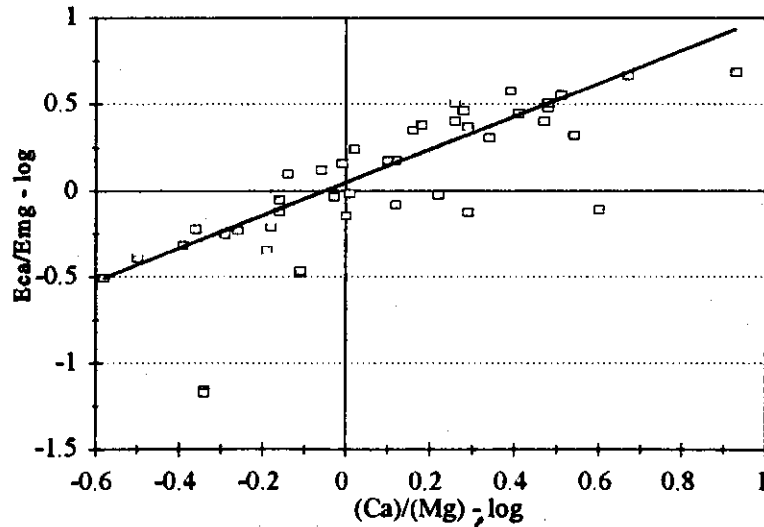
Figure 9. Ca-Mg exchange [line is Eq. (7)].

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$$\frac{E_{Ca}}{E_{Mg}} = 1.118[\frac{(Ca)}{(Mg)}]^{0.953} \tag{7}$$
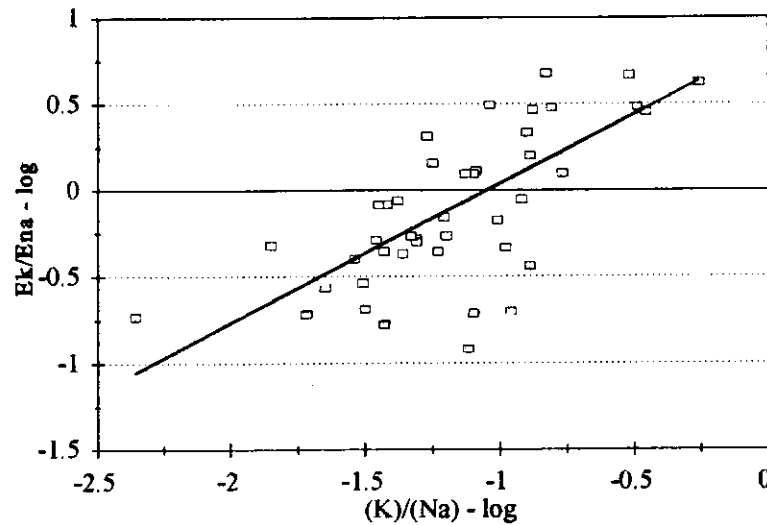
Figure 10. K-Na exchange [line is Eq. (8)].

$$\frac{E_K}{E_{Na}} = 6.974[\frac{(K)}{(Na)}]^{0.804} \tag{8}$$

3.   Groundwater origin and quality

The various groundwater qualities are issued from the same process that takes into account geochemical equilibrium of the groundwater with respect to the dissolution of minerals and ionic exchanges, along with the progressive dilution of the initial saline water due to marine sediments, with fresh river water. This process has been simulated according to the geochemical model and is consistent with the analytical data.

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Despite the negative residual alkalinity of both the initial saline water, as well as river or canal water, groundwater residual alkalinity becomes positive during the dilution process due to calcium and magnesium adsorption on the exchange complex. This can explain the occurrence of soil sodification due to the use of such groundwaters as additionnal water supply for irrigation as will be shown in the following section. This can also explain why the alkalinity of some barren soils, such as the so called "Satghara series", is high while others are issued from a neutral salinization process. The spatialization of the groundwater quality should be of significant interest when prospecting for the best irrigation water supplies.

3.1.   Chemical analysis

Groundwater samples (132) were collected from exploratory drilling that was carried out in part of the Bahawalpur area during 1957-58. During the course of the investigations, 37 test holes were drilled to depths of about 600 feet. Water samples for chemical analysis were collected from all permeable beds penetrated by the boreholes to depths of about 450 feet, which is the limit of effective recovery for the airlift device used in sampling. The data from shallow aquifers, at 80 feet in depth or less, were generally ignored because they are likely to show the effects of local recharge from irrigation; in any event, the shallow data were not assessed to be representative of an appreciable proportion of the grounwater currently in storage. No systematic study has been made of the quality of the shallow grounwater; but data suggested that it may be of tolerable quality for irrigation with respect to salinization hazard. The area between the Sutlej River and the Fordwah Canal offers the only possibilities for large scale exploitation of deep grounwater for irrigation supplies. This pattern is chiefly due to the effect of seepage from the Sutlej River, which is the principal natural source of groundwater recharge; and to a lesser extent to seepage from the Fordwah Canal and its distributaries, which are the principal sources of artificial recharge. The groundwater quality deteriorates continuously southward from the Sutlej River, especially south of the Fordwah Canal. The water samples were analyzed for calcium, magnesium, sodium, chloride, sulfate and carbonates.

During this period, a tubewell program was implemented in the shallow aquifer of the study area for obtaining additional irrigation water supply. Grounwater samples (438) were collected from tubewells: (i) 394 water samples were analyzed for 'calcium plus magnesium', sodium, chloride, sulfate and carbonates; and (ii) 44 water samples were analyzed for calcium, magnesium, sodium, potassium, chloride, sulfate and carbonates. The composition of the sea water and Sutlej River water, that have been considered in this study, are presented in Table 2.

Table 2. Water composition of river water and sea water(* from *Appelo and Potsma* [1995]).

(mmoles/l)	sea water *	river water
Calcium	10.7	0.35
Magnesium	55.1	0.45
Sodium	485.0	0.20
Potassium	10.6	0.01
Chloride	566.0	1.00
Sulfate	29.3	0.15
Alkalinity	2.4	0.51
Residual alkalinity:calcite+sepiolite	-129.2	-1.09
Residual alkalinity:calcite+sepiolite+gypsum	-70.6	-0.79

3.2.   Simulation

The progressive dilution of the seawater with fresh river water has been simulated according to the geochemical model, which accounts for speciation of the major chemical component, precipitation or dissolution of a few minerals, and cation exchanges. The cation exchanges have been modeled according to equations (16), (17) and (18). The initial composition of the exchange complex (Table 3) is supposed to be in equilibrium with the sea water. A pCO_2 of $10^{-2.5}$, a cationic exchange capacity of 0.05 mol./kg and an initial gypsum amount of 0.014 moles/kg was chosen for the simulation. The soil solution was supposed to be in equilibrium with respect to calcite, sepiolite, illite and amorphous silica throughout the dilution process (Table 1).

Table 3. Initial composition of the exchange complex (% CEC).

Exchangeable cations	K	Na	Ca	Mg
(%CEC)	1.34	66.12	20.71	11.83

3.3.   Results

The results have been plotted against chloride molality. Chloride supposedly does not interact with its environnement and is used as a tracer. Points represent sample analysis, the line results from the simulation, and sea water is plotted as SW. The simulation shows a good agreement with the chemical analysis. The geochemical mechanisms involved in the origin of various water qualities are explained below.
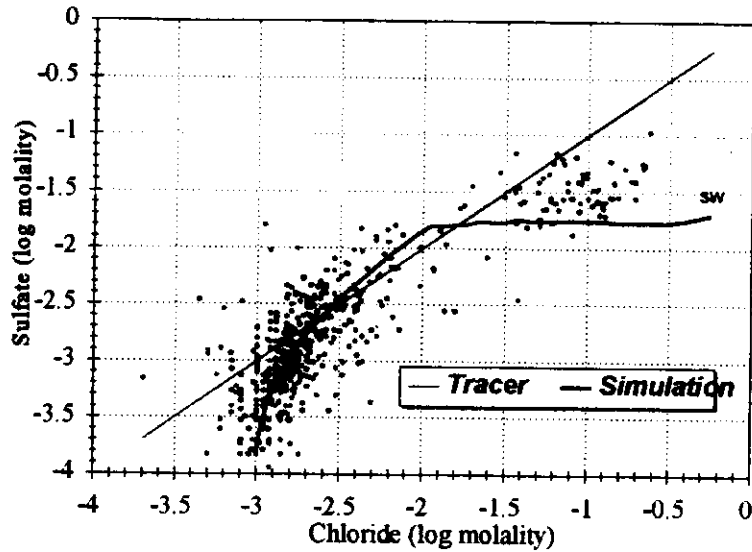
Figure 11. Chemical analysis and simulation with sulfate plotted against chloride as a tracer.
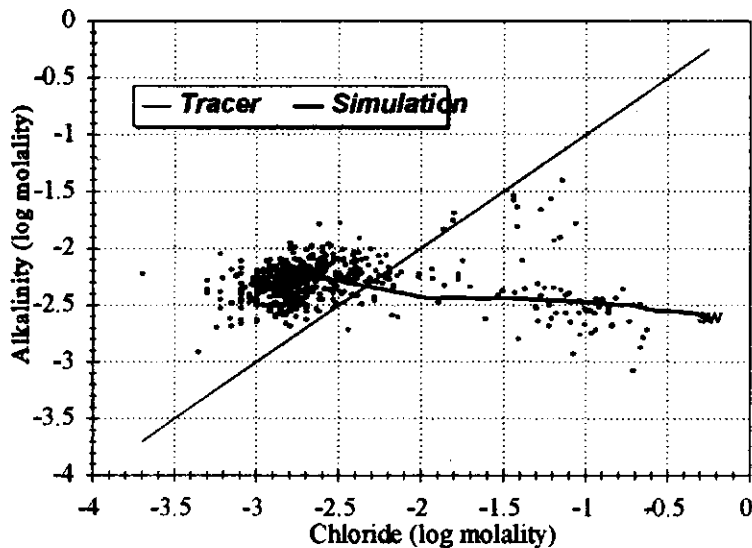
Figure 12. Groundwater analysis with alkalinity plotted against chloride as a tracer.

As the groundwater concentration decreases, sulfate decreases first at a very low rate, then at a very faster rate than chloride (Figure 11). This behavior could be attributed to gypsum dissolution whose presence is likely. But when gysum is dissolved, sulfate molality decreases faster than that of chloride because it is less abundant in river water. Alkalinity (Figure 12) tends to increase with dilution, then decrease for the less concentrated grounwaters. The increase is due to calcite, sepiolite and, to a lesser extent, illite dissolution. This trend is followed by a weak decrease because the mixing with fresh water is not balanced by the dissolution of minerals.

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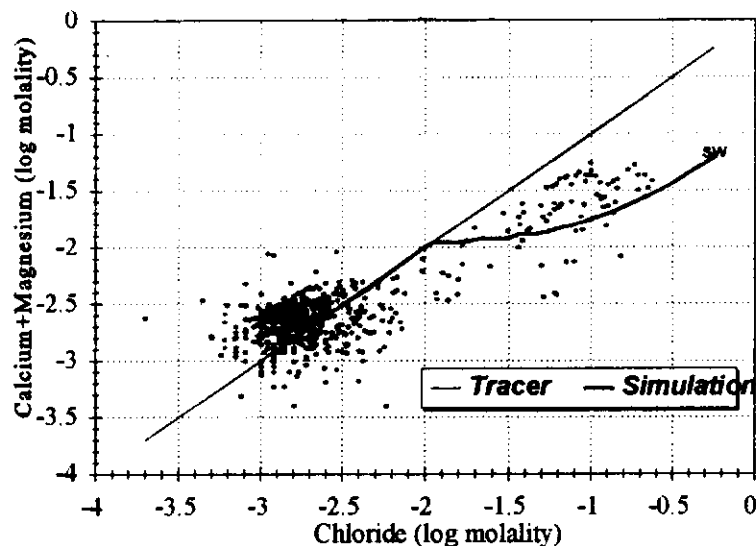
Figure 13. Chemical analysis and simulation of calcium+magnesium against chloride as a tracer.
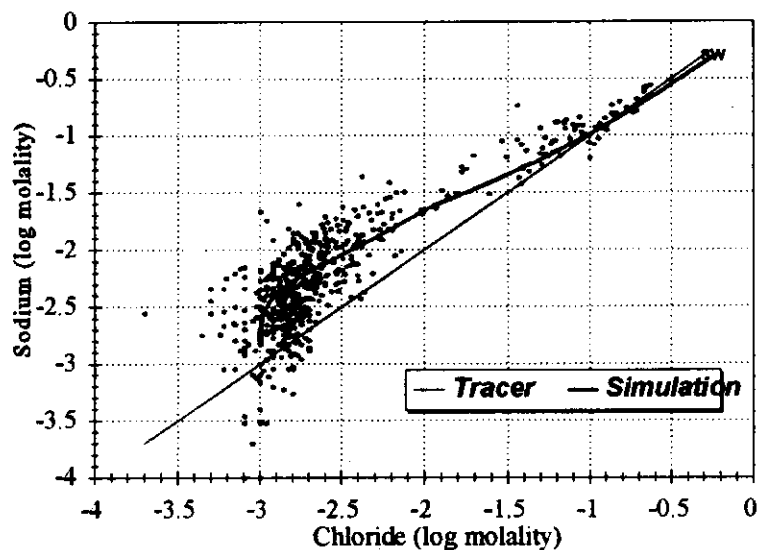
Figure 14. Chemical analysis and simulation of sodium against chloride as a tracer.

Calcium plus magnesium (Figure 13) and sodium (Figure 14) molalities decrease at a lower rate than that of chloride. This means that they are supplied by the soil through the dissolution of minerals or cation exchanges. Because sodium desorbs from the exchange complex, the calcium and magnesium supply must be attributed to calcite, sepiolite and gypsum dissolution that do not balance with calcium and magnesium adsorption on the exchange complex. The rate of decrease in calcium plus magnesium increases when gypsum is fully dissolved. The faster decrease in sodium molality than that of chloride for the less concentrated water is imputed to the lower sodium molality in the river water.

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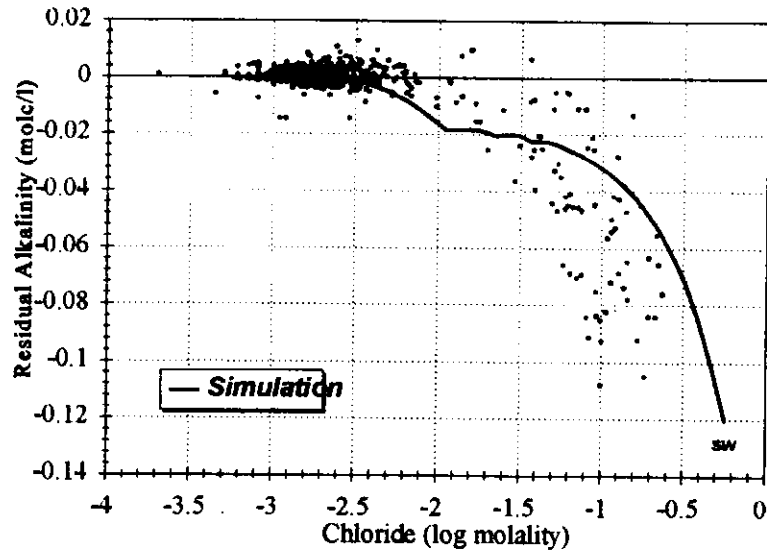
Figure 15. Chemical analysis and simulation of residual alkalinity applied to the precipitation of calcite and sepiolite.
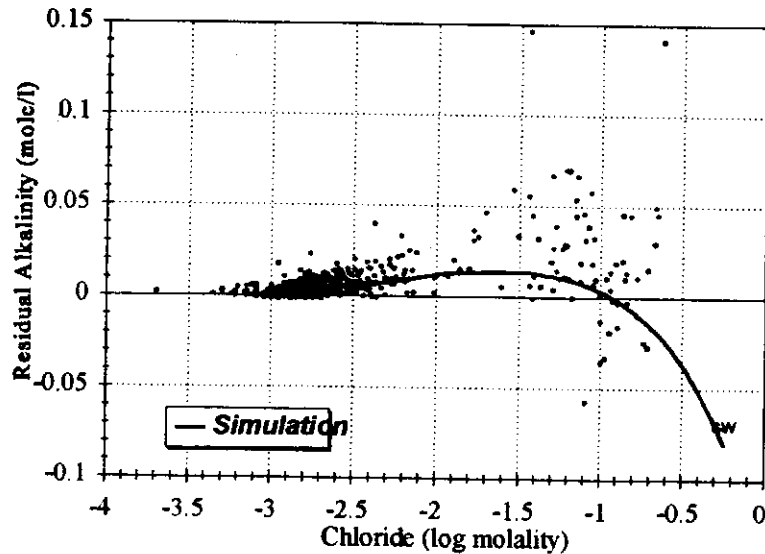
Figure 16. Chemical analysis and simulation of residual alkalinity applied to the precipitation of calcite, sepiolite and gypsum.

Residual alkalinity is considered as an invariant criteria because it varies at the same rate as the concentration factor when minerals precipitate or dissolve. Though residual alkalinity is negative for sea or river water (Table 2), chemical analysis show positive residual alkalinity that can not be explained by the precipitation or dissolution of minerals.. This behavior is imputed to calcium and magnesium adsorption on the exchange complex (Figure 17) that leads to a disequilibrium between calcium and magnesium evolution and that of alkalinity, which are not affected by ionic exchange. Residual alkalinity will become more positive as the cationic exchange capacity increases.

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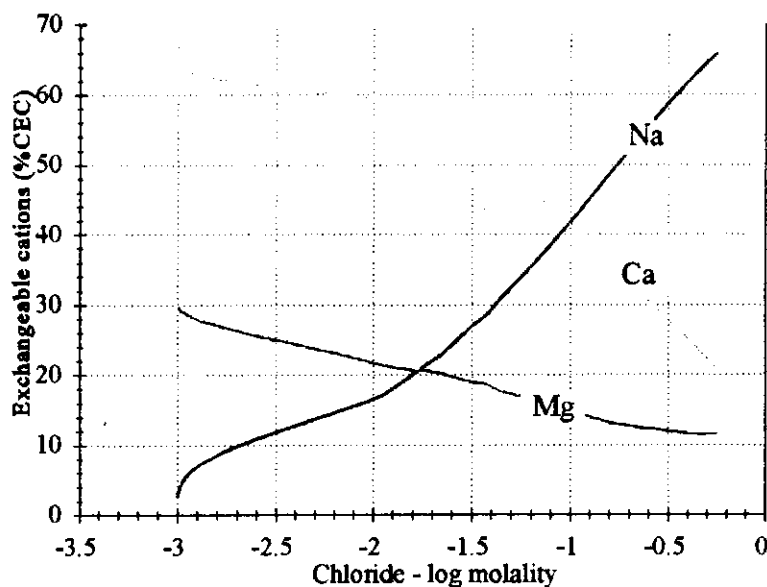
Figure 17. Simulation of exchangeable cations against chloride.

4. Water quality assessment

The geochemical model allows the prediction of how water chemistry changes as the water becomes more concentrated. This model has significant importance for irrigation water quality assessment. Neverthless, a simplified classification for water quality assessment is being proposed according to the residual alkalinity concept that is a good indicator for water quality assessment with respect to the alkalinization and sodification hazard.

When residual alkalinity with respect to calcite and sepiolite (or Residual Sodium Carbonates) is positive, the sodification and alkalinization hazard is high and the water is not suitable for irrigation unless large leaching fraction are used with moderate residual alkalinity. Regardless of the EC value, this water type must be mixed with fresh canal water to reverse the sign for the residual alkalinity. Its use for irrigation can lead to soil surface degradation, even after one irrigation event. The cationic exchange capacity acts as a buffer with respect to alkalinization and sodification. Thus, the sandy soils with low value of Cationic Exchange Capacity are more sensitive than the clayey soils.

When calcite and sepiolite residual alkalinity is negative, the quality must be assessed according to calcite, sepiolite and gypsum residual alkalinity.

When calcite, sepiolite and gypsum residual alkalinity is positive, the sodification and, to a lesser extent, alkalinization hazard exist if the concentration becomes high. This depends on the initial value of EC and the leaching fraction.

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When calcite, sepiolite and gypsum residual alkalinity is negative, the sodification hazard is low and there is no alkalinization hazard. The salinization hazard must be assessed according to EC and the leaching fraction.

But the evolution of chemical properties depends also on the water management practices, including irrigation and drainage or leaching fraction. The geochemical model has been coupled with a simple water balance model. The results show that the salinization hazard is linked with water management, while water quality plays an important role with respect to the sodification hazard. Such a geochemical model provides a tool for evaluating the trend in salinity and sodicity over time when the irrigation and drainage performances are known.

4.1. Mechanisms of soil salinization

4.1.1. Simulations

In order to illustrate the various geochemical mechanims involved in soil salinization, the evaporation of the canal water and two tubewell waters were simulated according to the residual alkalinity concept:

- the canal water is very fresh and is considered as being low with respect to the salinity and sodicity hazard in the USSL classification, which is characterized by a negative residual alkalinity with respect to calcite, sepiolite and gypsum precipitation;

- the Tubewell 1 water is considered as medium to high with respect to the salinity hazard and low with respect to the sodicity hazard in the USSL classification, which is characterized by a negative residual alkalinity with respect to calcite and sepiolite precipitation and positive residual alkalinity with respect to calcite, sepiolite and gypsum precipitation; and

- the Tubewell 2 water is considered as being medium to high with respect to the salinity hazard and as low to medium with respect to the sodicity hazard, which is characterized by a positive residual alkalinity with respect to calcite and sepiolite precipitation.

In order to illustrate the influence of cation exchanges, the evaporation without any cation exchange and with a cationic exchange capacity of 0.05 mol$_c$/kg were simulated. A pCO$_2$ of 10$^{-2.5}$ was chosen for the simulations. The soil solution was assumed in equilibrium with respect to the exchange complex, calcite, sepiolite, illite and amorphous silica throughout the concentration process. The simulations provide the evolution of alkalinity, calcium, magnesium, sodium, chloride and sulfate molalities with concentration. For each simulation, the results were plotted against the concentration factor. The properties are presented in Table 4.

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Table 4. Water composition of canal water and tubewell waters.

| (mmoles/l)	canal water	tubewell-1	tubewell-2
Calcium	0.35	1.55	0.45
Magnesium	0.45	1.20	0.30
Sodium	0.20	2.50	6.70
Potassium	0.01	0.20	0.20
Chloride	0.50	1.30	1.00
Sulfate	0.15	2.20	1.60
(meq/l)	canal water	tubewell-1	tubewell-2
Alkalinity	1.01	2.50	4.20
RA:calcite+sepiolite	-0.59	-3.00	+2.70
RA: calcite+sepiolite+gypsum	-0.29	+1.20	+5.90
(%CEC) calculated *	canal water	tubewell-1	tubewell-2
Potassium *	1.61	1.88	2.02
Sodium*	0.44	3.68	11.29
Calcium*	66.32	69.61	61.89
Magnesium *	31.57	24.83	24.83
EC (dS/m)	0.19	0.82	0.84
SAR	0.2	1.5	7.7

4.1.2. Evaporation of the canal water
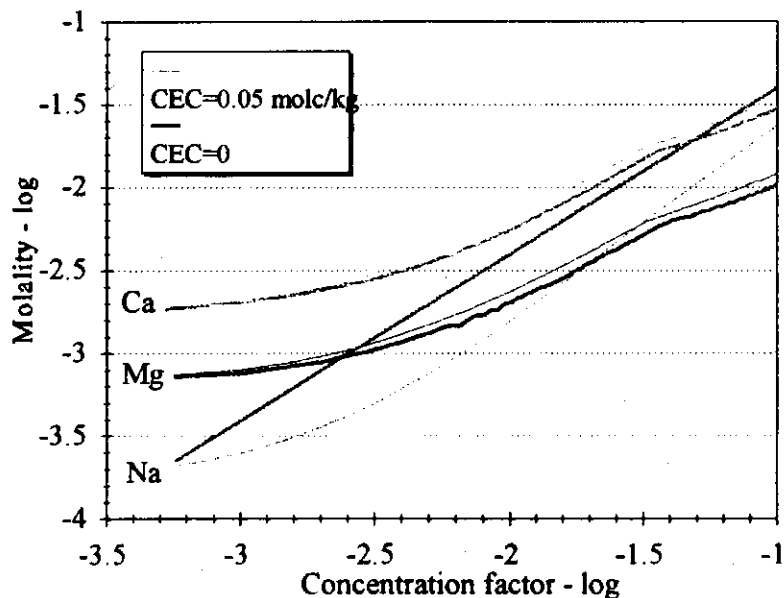
Figure 18. Evaporation of the canal water as irrigation supply with sodium, calcium and magnesium against the concentrtion factor.

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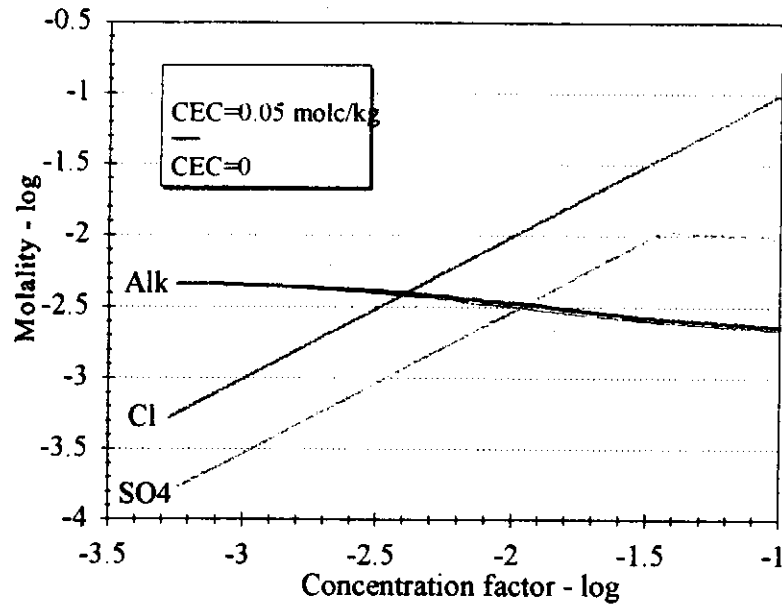
Figure 19. Evaporation of the canal water as irrigation supply with chloride, sulfate and alkalinity against the concentration factor.

During the first stage of the concentration process, chloride, sulfate and sodium are not involved in any precipitation and increase at the same rate as the concentration factor. Calcium and magnesium increase at a lower rate than the concentration factor due to calcite and sepiolite precipitation, whereas alkalinity decreases that displays a minority ion behavior according to the residual alkalinity concept with respect to the precipitation of calcite and sepiolite.

Gypsum precipitates from a concentration factor of about 100. According to the negative residual alkalinity with respect to the precipitation of calcite, sepiolite and gypsum:

- The decrease in alkalinity continues at a lower rate, while the increasing rate of calcium slows down due to gypsum precipitation;

- The sulfate molality decreases, related to the increase in calcium molality; and

- The rate of increase in magnesium slows down, related to alkalinity.

When the cation exchanges are considered, sodium adsorbs while calcium and magnesium desorbs on the exchange complex. Thus, sodium increases at a lower rate , while calcium and magnesium increases at a faster rate than without any cation exchanges. Calcium and magnesium contribute to neutralizing alkalinity that decreases at a faster rate through calcite and sepiolite precipitation.

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4.1.3. Evaporation of the Tubewell 1 water

Figure 20. Evaporation of the Tubewell 1 water as irrigation supply: evaluation of calcium, magnesium and sodium with concentration.
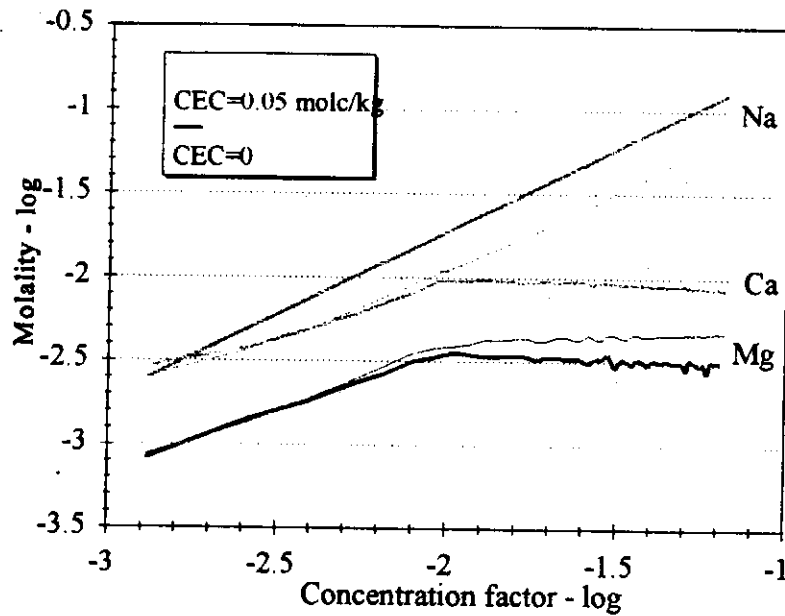

Figure 21. Evaporation of the Tubewell 1 water as irrigation supply: evolution of alkalinity, chloride and sulfate molalities with concentration.

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During the first stage of the concentration process, the mechanisms are similar with the previous simulation. Calcite and sepiolite precipitates; due to the negative residual alkalinity with respect to calcite and sepiolite, an increase in calcium and magnesium molalities and a decrease in alkalinity is observed. They display majority and minority ionic behavior according to the residual alkalinity concept, respectively.

Gypsum precipitates from a concentration factor of about 10. Thus, residual alkalinity with respect to calcite, sepiolite and gypsum becomes positive and the trend in molalities differs: calcium and magnesium molalities decrease, wheras alkalinity increases. Sulfate molality, related to calcium molality, increases but the rate slows down due to gypsum precipitation.

The influence of cation exchanges is similar with the previous simulation and leads to an increase in calcium and magnesium molalities, and a decrease in alkalinity and sodium molalities. Sulfate molality also decreases according to gypsum precipitation and calcium molality.

4.1.4.   Evaporation of the Tubewell 2 water

Figure 22.   Evaporation of the Tubewell 2 water as irrigation supply: evolution of calcium, magnesium and sodium molalities with concentration.
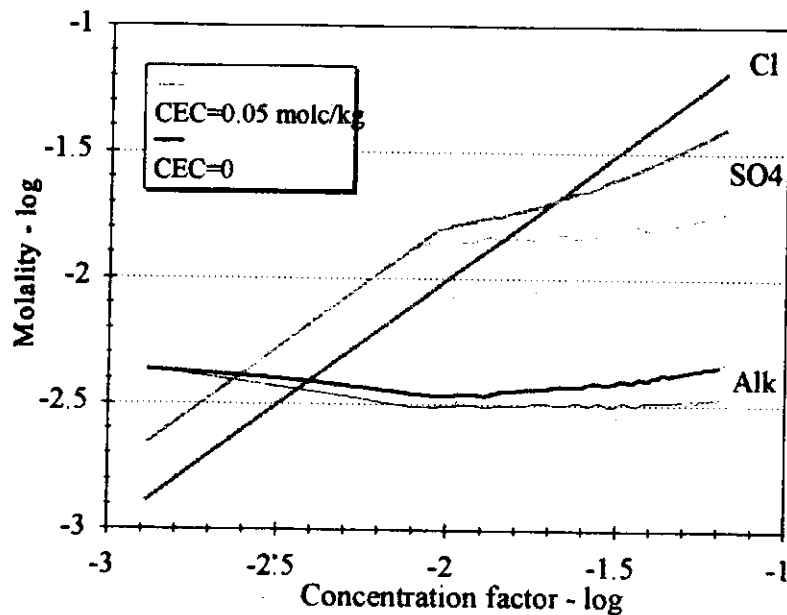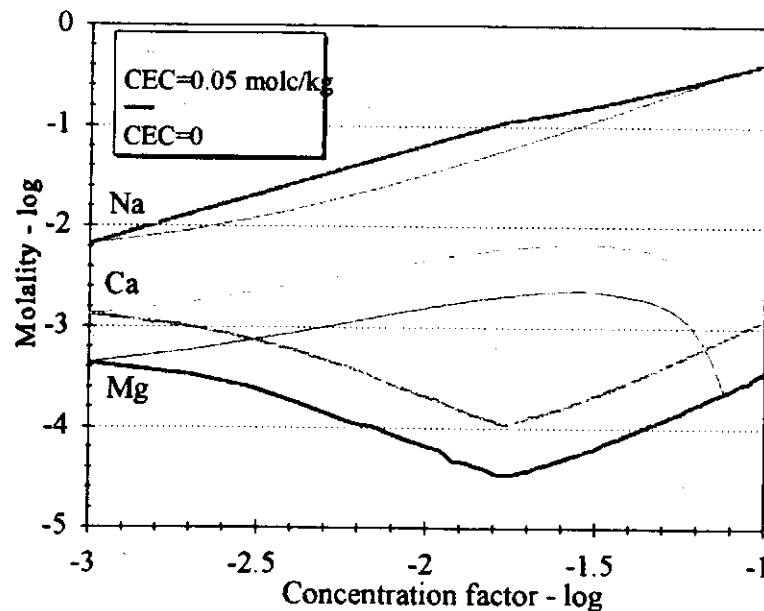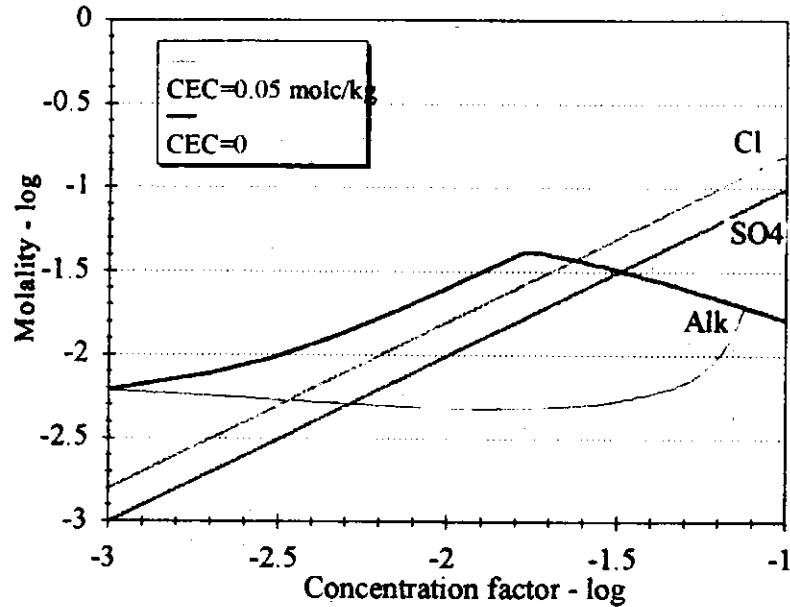
Figure 23. Evaporation of the Tubewell 2 water as irrigation supply: evaluation of chloride and sulfate molality and alkalinity with concentration.

Residual alkalinity with respect to calcite and sepiolite is positive and the evolutions differ from the other simulations. Alkalinity increases while calcium and magnesium molalities decrease. Due to the decrease in calcium molality, gypsum doesn't achieve saturation.

The trend in molalities differs because paragonite was allowed to precipitate from a concentration factor of about 30. Thus, due to the negative value of residual alkalinity with respect to calcite, sepiolite and paragonite precipitation, alkalinity decreases while calcium and magnesium molalities increase.

Due to a rapid desorption of calcium and magnesium, the exchange complex plays an important part in the alkalinization process. Calcium and magnesium desorption neutralizes alkalinity and can change the trend of the alkalinity as long as it can reverse the sign of residual alkalinity. Then, alkalinity increases consistently, while calcium and magnesium decreases, according to the residual alkalinity concept.

4.1.5.   Residual alkalinity and sodification

During the concentration process, cation exchanges play a role through calcium and magnesium desorption and sodium adsorption. The rate of these cation exchanges is due to an increasing disequilibrium between sodium and calcium + magnesium that becomes more important as the residual alkalinity becomes higher. Thus, the rate of sodification is related to residual alkalinity.

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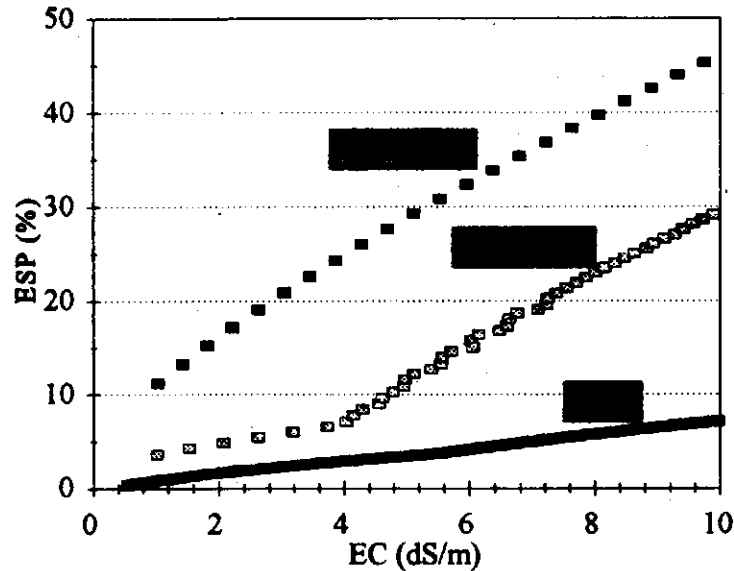
Figure 24. Evaporation of various water qualities: Exchangeable Sodium Percentage against the Electrical Conductivity.

This phenomenom is illustrated in Figure 24. For example, residual alkalinity of the Tubewell 1 water is - 3.0 at the beginning of the evaporation process, then becomes +1.20 when gypsum precipitates. That leads to a faster increase in ESP. Residual alkalinity is an illustration of chemical disequilibrium that lead to a faster sodium adsorption on the exchange complex. It could be a good indicator of sodification hazard.

4.2. Influence of water management

If residual alkalinity is a good indicator for water quality assessment with respect to alkalinization and sodification hazards, water management is the first cause of salt concentration in the soil and must be taken into account for prediction of soil salinization or sodification.

To illustrate the influence of water quality and management soil salinity and sodicity were simulated using two assumed values of leaching fraction (LF) of 0.01 and 0.1, where LF is defined as:

$$LF = \frac{I}{D} \qquad (9)$$

where I is the irrigation amount and D the drainage or deep percolation below the root zone. An irrigation amount, I, of 1000 mm/year and a water content (WC) of 200 mm in

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the root zone. Also, three water qualities were used: canal water; a mix of canal water and 10% of the Tubewell 1 water (Mix 1); and a mix of canal water and 10% of the Tubewell 2 water (Mix 2). Values for pCO_2 of $10^{-2.5}$ and a CEC of 0.05 $mol_c.kg^{-1}$ were used.

The evolution of EC and ESP is considered as homogeneous in the soil profile and are presented with respect to time. At each calculation step, the molality (M_i) of each chemical component is calculated as:

$$M_i.WC = M_{i-1}.WC + M_0.I - M_{i-1}.I.LF \qquad (10)$$

Where M_0 is the molality of the chemical component in the irrigation water and M_{i-1} the output of the previous calculation in the geochemical model. Then, the new composition of the soil solution is used as an input in the geochemical model.
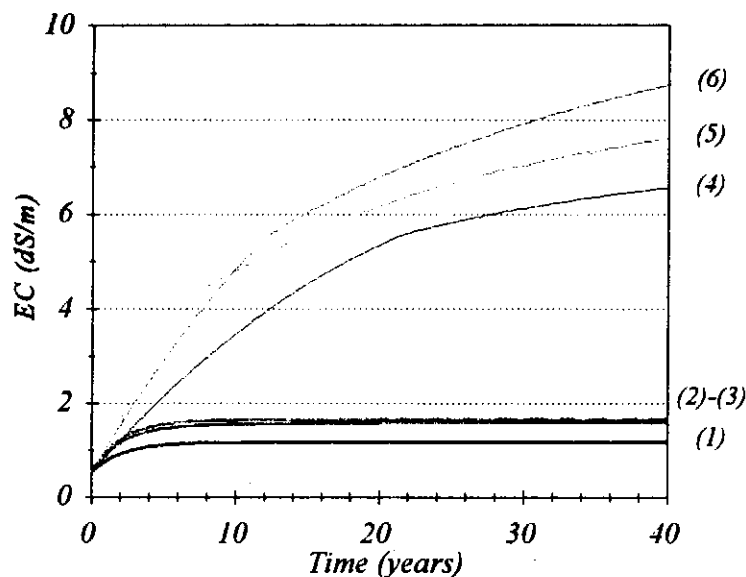
Figure 25. Evolution of the Electical Conductivity with respect to water quality and irrigation management: (1) canal & LF=0.1; (2) Mix 1 & LF=01; (3) Mix 2 & LF=0.1; (4) canal & LF=0.01; (5) Mix 1 & LF=0.01; (6) Mix 2 & LK=0.01.
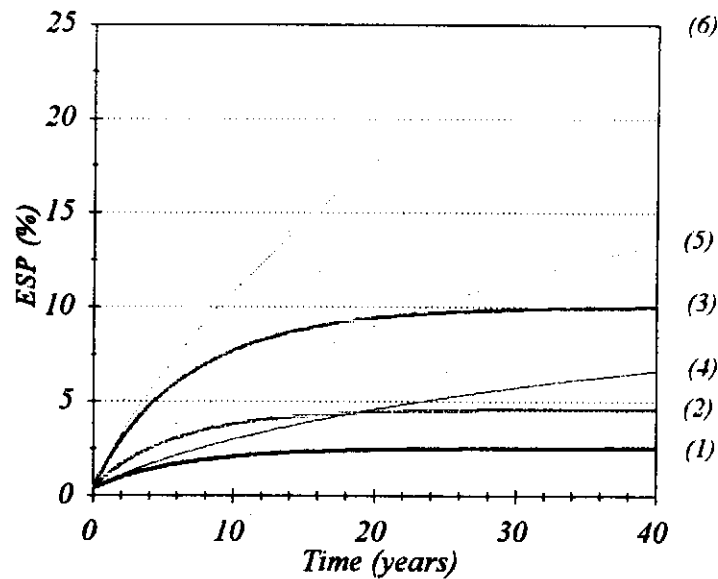
Figure 26. Evolution of the Exchangeable Sodium Percentage with respect to water quality and irrigation management: (1) canal & LF=0.1; (2) Mix 1 & LF=01; (3) Mix 2 & LF=0.1; (4) canal & LF=0.01; (5) Mix 1 & LF=0.01; (6) Mix 2 & LK=0.01.

The results show that:

> the salinization hazard is due to irrigation management (or to the use of saline water that was not considered in this study) (Figure 25). Even if good water quality is used, salinization can occur if the leaching fraction is low (poor water management);

> the sodification hazard is mainly due to water quality. Even if the irrigation management is good, the use of poor water quality can lead to soil sodicity that becomes much more of a problem than salinity. Furthermore, when tubewell water is used without mixing, the soil surface tends towards an equilibrium with respect to the irrigation water quality after one irrigation event. The sodicity can reach very high values, 3.7% for Tubewell 1 and 11 3% for Tubewell 2 (Table 4), and lead to very fast soil degradation even if the soil is leached with fresh water during the next irrigation event. This has been pointed out in some fields of the irrigated schemes in Pakistan (Condom, 1996).

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5. Conclusions

Irrigation water quality is currently evaluated from such indicators as electrical conductivity (EC), pH and sodium adsorption ratio (SAR). Water quality is then classified with respect to the salinization, alkalinization and sodification hazard. But this classification doesn't consider the geochemical process, while models allow this to be taken into account.

The geochemical mechanisms of soil salinization and sodification in the irrigated schemes in the Punjab have been modeled according to the analytical data. They include precipitation and dissolution of a few minerals and cation exchanges. This model has been used:

- to explain the origin of grounwater quality from a mixing of increasing amounts of fresh river water with initial saline goundwater.

- to predict how water chemistry changes as it becomes concentrated and to suggest a new classification of water quality assessment for irrigation with respect to the residual alkalinity concept.

- to predict the soil salinity, alkalinity and sodicity when the geochemical model is coupled with a very simple water balance model based on a knowledge of the leaching fraction.

The use of such a geochemical model could provide many applications in IIMI's program in Pakistan:

- to spatialize and to prospect for the best water quality of additional water supplies according to the residual alkalinity concept and EC;

- to evaluate the salinization and sodification hazard according to water quality, soil type and water management when irrigation and drainage performances are known.

Such a geochemical model could be coupled with any kind of model, from a simple evaluation of irrigation performance to a more sophisticated water and solute transport model as was realized in Niger [Marlet, 1996] and Pakistan [Condom, 1996].

Annex: model presentation

1. Ionic activities

In this approach, an ion pair model using the Debye-Hückel's law extended to saline conditions is used to calculate ionic activity (a_i) as a function of their molality (m_i) :

$$a_i = \gamma_i . m_i \tag{11}$$

with:

$$\log \gamma_i = \frac{A \, z_i \, I^{0.5}}{1 + a^*_i \, B \, I^{0.5}} + C \, I \tag{12}$$

where γ_i is the activity coefficient of the charged species i, I is the ionic strength $I = \Sigma m_i z^2_i$, a_i is ion activity, m_i is ion molality, a^*_i is the ionic radius and z_i is the charge of the ionic species i. A, B and C are temperature dependent coefficients [*Valles and Bourgeat*, 1988].

The activity coefficient of neutral ion-pairs is assumed to be equal to that of aqueous CO_2 in a NaCl solution of the same ionic strength as the solution considered [*Helgeson*, 1969]. Water activity is calculated from the zero osmotic coefficient of a NaCl solution of the same ionic strength I as the solution considered [Fritz, 1981]. Despite variations of the solution considered which differs from a NaCl solution, these assumptions do not induce any differences in neutral ion-pairs and water activities because the ionic strenght remains low in such circumstances.

Seven chemical components (K, Na, Ca, Mg, Cl, SO_4 and Si) have been considered in the model. Alkalinity was calculated by assuming the electric neutrality of the solution:

$$\textit{Alkalinity } (mol c.l^{-1}) = 2Ca + 2Mg + Na + K - Cl - 2SO_4 \tag{13}$$

In a solution that is rich in divalent cations and weak in acid anions, ion pairs can form and 34 aquaeous species have been considered. Their activities have been calculated from their dissociation constants (Table A1). The law of mass action states that for a reaction of the generalized type:

$$a.A + b.B \rightleftharpoons c.C + d.D \tag{14}$$

the distribution at equilibrium between the species is described by:

$$K = \frac{(C)^c (D)^d}{(A)^a (B)^b} \qquad (15)$$

where K is the thermodynamic equilibrium or dissociation constant at a given temperature and pressure and the bracketed quantities denote activities.

Table A1: Dissociation constant of the aquaeous species (Vallès et Bourgeat, 1988).

Dissociation reactions	log K (25°C)	Dissociation reactions	log K (25°C)
$H_2O = H^+ + OH^-$	-14.0	$KCl^0 = K^+ + Cl^-$	+1.585
$HSO_4^- = H^+ + SO_4^{2-}$	-1.39	$KSO_4^- = K^+ + SO_4^{2-}$	-0.84
$HCO_3^- = H^+ + CO_3^{2-}$	-10.32	$KOH^0 = K^+ + OH^-$	-0.04
$H_2CO_3^0 = 2H^+ + CO_3^{2-}$	-16.70	$MgCO_3^0 = Mg^{2+} + CO_3^{2-}$	-3.40
$H_2CO_3^0 = CO_2 + H_2O$	+1.46	$MgHCO_3^+ = Mg^{2+} + HCO_3^-$	-0.90
$NaCl^0 = Na^+ + Cl^-$	+0.85	$MgOH^+ = Mg^{2+} + OH^-$	-2.58
$NaOH^0 = Na^+ + OH^-$	-0.719	$MgSO_4^0 = Mg^{2+} + SO_4^{2-}$	-2.75
$NaSO_4^- = Na^+ + SO_4^{2-}$	-1.06	$CaCO_3^0 = Ca^{2+} + CO_3^{2-}$	-3.20
$Na_2SO_4^0 = 2Na^+ + SO_4^{2-}$	-1.512	$CaHCO_3^+ = Ca^{2+} + HCO_3^-$	-1.26
$NaCO_3^- = Na^+ + CO_3^{2-}$	-1.269	$CaOH^+ = Ca^{2+} + OH^-$	-1.234
$Na_2CO_3^0 = 2Na^+ + CO_3^{2-}$	-0.672	$CaSO_4^0 = Ca^{2+} + SO_4^{2-}$	-2.31
$NaHCO_3^0 = Na^+ + HCO_3^-$	+0.25	$H_4SiO_4^0 = H_3SiO_4^- + H^+$	-9.80

2. Mineral precipitation and dissolution

When a generalized type mineral $A_a B_b$ dissolves into water, the ionic product Q is defined from the dissociation equation:

$$A_a B_b = a.A + b.B \qquad (16)$$
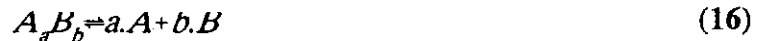
by:

$$Q = (A)^a (B)^b \qquad (17)$$

since the activity of the mineral $A_a B_b$ is equal to one by definition. When Q=K, the solution is in equilibrium with respect to the mineral which doesn't dissolve nor precipitate. When Q<K, the solution is undersaturated with respect to the mineral which may dissolve until the equilibrium Q=K is reached. When Q>K, the solution is oversaturated with respect to the mineral, which precipitates until the equilibrium Q=K is reached.

3.   Cation exchanges

The cation exchange isotherms are defined by a selectivity coefficient in the Gaines and Thomas convention [*Gaines and Thomas*, 1953]. The exchange reaction between a cation A of valence a, adsorbed on the exchanger soil, and a cation B of valence b can be writen as:

$$Soil-bA+aB^{b+} \rightleftharpoons Soil-aB+bA^{a+} \tag{18}$$
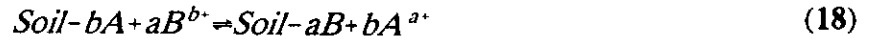
Thus, the selectivity coefficient (k_{GT}) can be writen as:

$$k_{GT(A-B)} = \frac{(A)^b E_B^a}{(B)^a E_A^b} \tag{19}$$

where (A) and (B) are the activities, a and b are the valences, and E_A and E_B are the charge (or equivalent) fractions of adsorbed ions A and B. The exchange between Ca^{2+}, Mg^{2+}, Na^+ and K^+ are considered in the model and the sum of the equivalent fraction of the cations adsorbed is equal to the Cationic Exchange Capacity (CEC). The selectivity coefficients are modeled according to an indirect method proposed by *Rieu et al.* [1991]. The relation between the exchangeable fraction ratio (EFR) and the activity fraction ratio is modeled as a power law function:

$$EFR = \frac{E_B^a}{E_A^b} = \alpha [\frac{(B)^a}{(A)^b}]^\beta \tag{20}$$

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S.No.	Title	Author	Year
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