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CORSO DI LAUREA IN SCIENZE E TECNOLOGIE
PER L'AMBIENTE E IL TERRITORIO

IRRIGATION WITH SALINE WATER: PREDICTION OF SOIL SODICATION AND MANAGEMENT

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LIST OF SYMBOLS

Symbol	Description	Unit measure
Chapter 1		
EC	Electrical conductivity	mS/cm
EC_e	Electrical conductivity of extracting water	mS/cm
ESP	Exchangeable sodium percentage	
SAR	Sodium adsorption ratio	$(mmol/L)^{1/2}$
Chapter 2		
γ_+	Amount of monovalent cation present in the adsorbed phase	$mmol_c/100g$
γ_{2+}	Amount of divalent cation present in the adsorbed phase	$mmol_c/100g$
CEC	Cation exchange capacity	$mmol_c/100g$
Na^+	Concentration of sodium in solution	mol/L
Ca^{2+}	Concentration of calcium in solution	mol/L
$C_{+,k}$	Generic concentration of a general cation in solution	$mmol_c/ml$
C_{tot}	Total electrolyte concentration	$mmol_c/ml$
K_G	Gapon exchange constant	$(mol/L)^{-1/2}$
ESP*	New exchangeable sodium percentage	
f_{Na}	Sodium fraction in soil solution	
r	Water added in the soil system	ml/100g
R_D	Distribution ratio for a general ion between solid and solution phase	
w	Moisture of the soil	ml/100g
x	Shift of a general cation between solid and solution phase	$mmol_c/100g$
Chapter 3		
j	Infiltration water that enters the root zone	$L/m^2/y$

j_a	Infiltration water that enters the root zone during accumulation	$\mathrm{L/m^2/y}$
j_l	Infiltration water that enters the root zone during leaching	$\mathrm{L/m^2/y}$
C_{in}	Salt concentration of irrigation water	$\mathrm{mol_c/L}$
C	Initial salt concentration in the soil solution	$\mathrm{mol_c/L}$
f	Calcium fraction in soil solution	
f_a	Calcium fraction of irrigation water during accumulation	
f_l	Calcium fraction of irrigation water during leaching	
N	Calcium fraction in exchange complex	
V	Constant volume of soil moisture	$\mathrm{L/m^2}$
M	Dry mass of the soil	$\mathrm{kg/m^2}$
γ	Cation exchange capacity	$\mathrm{mol_c/kg}$
τ	Fraction of water that evapotranspires from the root zone	

Chapter 4

C_{Ca}	Calcium concentration	$\mathrm{mmol_c/L}$
C_{Na}	Sodium concentration	$\mathrm{mmol_c/L}$
C_{dw}	Total salt concentration of drainage water at field capacity	$\mathrm{mmol_c/L}$
C_{iw}	Total salt concentration of irrigation water	$\mathrm{mmol_c/L}$
C_{tot}	Total salt concentration in the water	$\mathrm{mmol_c/L}$
D_{cw}	Amount of consumptive water	$\mathrm{cm^3/cm^2}$
D_{dw}	Amount of drainage water	$\mathrm{cm^3/cm^2}$
D_{iw}	Amount of irrigation water	$\mathrm{cm^3/cm^2}$
EC_{dw}	Electrical conductivity of drainage water	mS/cm
EC_{FC}	Electrical conductivity at field capacity	mS/cm
EC_{iw}	Electrical conductivity of irrigation water	mS/cm
f_{dw}	Calcium fraction of drainage water	
f_{iw}	Calcium fraction of irrigation water	
FC	Moisture content at field capacity	$\mathrm{cm^3/100g}$

SP	Average moisture content of the saturated paste	$cm^3/100g$
ρ_b	Average bulk density	g/cm^3

RESUME

This thesis has been conducted in the context of an internship through an Erasmus scholarship at Wageningen University (The Netherlands), Department of Environmental Sciences, Soil Physics, Ecohydrology and Groundwater Management Group, under the supervision of Prof. Sjoerd van der Zee.

The need of crop production and withdrawal of water are increasing globally due to the growth of world population and its wellbeing. Consequently the use of poor quality water could be useful to limit the consumption of water, but negative consequences could arise. Especially when lands are irrigated with wastewater, and even more in arid and semiarid regions, agronomists need to control the soil salinity and sodicity to avoid the loss of fertility, soil structure and permeability (in the particular case of high sodium levels), and eventually erosion.

The thesis studies the evolution of the rate of soil sodicity in the root zone as a consequence of the irrigation with saline water. Hence three different aspects were studied in depth to have a global vision of the soil sodication as a result of periodical salinity.

The chapter 1 analyzes problems related with the use of water in agriculture and technical measures to calculate salinity and sodicity. It gives also a general framework of the common water parameters to evaluate the quality of irrigation water. Finally the chapter focuses on the soil structure and reactions that involve its solid and solution phases.

Results obtained during the internship are proposed in three following chapters. In chapter 2 it is analyzed the sensitivity of the ESP parameter to initial soil conditions. In fact there are evidences that several experiments are not made under the same initial conditions and, consequently, ESP values are not standardized. It has been concluded that there are not big differences assuming different initial conditions. Hence different inputs, as the dilution or concentration processes of the soil solution that are in equilibrium with the solid phase, have negligible effect in the exchangeable sodium.

The aim of the chapter 3 is to model the relationship between seasonal irrigation using saline water and the evolution of sodication processes in the soil. The first part of the chapter refers to the explanation of the theoretical assumptions that have been made, the

implementation of differential equations, both for salt and calcium fraction in the soil solution, and the link with the solid phase. Such a relationship has been made possible by the introduction of the Gapon exchange equation. Because of the non linearity of the expression the analytical solution was not possible, therefore the classical 4th order Runge-Kutta method has been used to do numerical simulations. The second part discusses the obtained results. The model considers a period of salt accumulation, due to a 6-months use of wastewater and the complete evapotranspiration of the infiltration water, followed by a semester in which the same soil has been irrigated with good quality water. Scenarios were conducted both in short-term (1 year) and long term (50 and 90 years). It has been concluded that, according to the simulations, an accumulation of sodium can be expected in the soil even if salt balance is kept null. Such an accumulation seems to be independent from the soil characteristics, especially the cation exchange capacity (CEC).

Chapter 4 analyzes the leaching requirement as a possible technique to avoid the sodium accumulation in the soil, using the mentioned technique applied to sodicity instead of salinity. Thus it has been implemented an expression that calculates the request of leaching to maintain the soil in good conditions with respect to the sodium concentration. Final conclusions underline that there are different requests of leaching if salinity or sodicity are considered.

Hence the problem found and discussed in chapter 3 may be solved with the leaching requirement technique, introduced in chapter 4. The conclusions we obtained are quite clear: the necessity of using poor quality water is increasing globally and there is the possibility to use it for irrigation. However the complete comprehension of the mechanisms that are involved in the soil is fundamental to determine the good management of it. It has been proposed a real, simple and useful technique to deal these problems. The data set we need to apply good management practices are limited, hence our approach may be a powerful instrument to allow the use of poor quality water avoiding the soil sodication.

RIASSUNTO

Il lavoro di tesi è stato condotto per buona parte durante un periodo di studio presso la Wageningen University (Olanda), Dipartimento di Scienze Ambientali, gruppo di Fisica del Suolo, Ecoidrologia a Gestione delle Acque Sotterranee, con il coordinamento del Prof. Sjoerd van der Zee e reso possibile nell'ambito del progetto Erasmus.

La crescita globale della popolazione e il conseguente bisogno di aumentare la produzione alimentare mondiale impongono la necessità di cercare fonti alternative di risorse idriche. Inoltre le risorse idriche potabili, o comunque acque di buona qualità per quanto riguarda il loro basso contenuto salino, sono oggetto di uno sfruttamento via, via crescente a causa della maggior richiesta di acqua per le varie attività produttive. L'uso di acque di scarsa qualità in agricoltura può quindi essere un'utile alternativa alla mancanza di approvvigionamento idrico. Nonostante le ottime potenzialità non vanno dimenticati i problemi che possono sorgere: specialmente in aree aride e semiaride il controllo del livello salino e sodico del suolo è una priorità, evidenziata maggiormente se si utilizzano acque salmastre. Infatti possono sorgere problemi dovuti a un'eccessiva concentrazione di sali, e in particolar modo sodio, nel terreno per evitare problemi di perdita di fertilità, perdita di struttura del suolo e dispersione delle particelle colloidali, diminuzione della permeabilità; tutto questo si traduce nel rischio di erosione dei suoli.

L'elaborato ha, quindi, per oggetto lo studio delle caratteristiche di salinità e sodicità del suolo nella zona vadosa in seguito all'utilizzo di acque irrigue salino-sodiche. Sono stati perciò studiati tre differenti aspetti, proposti in tre differenti capitoli.

Nel capitolo 1 sono introdotti i problemi dominanti relativi all'utilizzo di acque salino-sodiche in agricoltura e le principali metodologie di misura e classificazione delle acque. Sono quindi proposti i parametri chimici essenziali, riferiti a salinità e sodicità, utilizzati. Infine è sottolineata l'importanza della matrice suolo, la struttura e le reazioni di equilibrio che avvengono tra fase solida e fase in soluzione.

I risultati del lavoro effettuato sono proposti nei tre capitoli seguenti. Il primo studio è introdotto nel capitolo 2. Si è stimata la sensibilità dell'ESP (percentuale di sodio scambiabile) assunte differenti condizioni iniziali di un suolo, come umidità e capacità di

scambio cationico. Spesso, infatti, ricerche e studi consultabili in letteratura dimostrano come le condizioni iniziali non siano quasi mai le medesime, ovvero non siano standardizzate. Si è potuto constatare che le differenze dovute a fenomeni di diluizione o concentrazione nella soluzione suolo hanno effetti trascurabili a livello di siti di scambio.

Nel capitolo 3 è proposto un modello analitico, il quale rappresenta il lavoro principale effettuato. L'obiettivo che si è voluto raggiungere consta nello spiegare l'influenza dell'irrigazione con acqua salina sullo sviluppo di processi di sodicazione del suolo. È stato preso in esame un periodo di irrigazione di sei mesi con acque di scarsa qualità, in cui si è assunto un accumulo salino nel suolo dovuto a completa evapotraspirazione dell'acqua apportata tramite irrigazione, seguito da un secondo periodo semestrale caratterizzato da irrigazione con acque di buona qualità, così da garantire la lisciviazione dei sali e, quindi, un accumulo salino annuale pari a zero. Se da un lato il suolo così gestito soddisfa i criteri di salinità totale, dall'altro potrebbe non rispettare il bilancio del sodio. Inizialmente è stato simulato il comportamento nel suolo dei sali totali, calcio e sodio, in un anno; nella seconda fase si è simulata la stessa gestione del medesimo suolo in un arco di tempo di 50 anni o più, sino a 90. La prima parte del capitolo chiarisce i presupposti teorici che sono alla base del modello e le assunzioni adottate; vengono inoltre descritte le principali equazioni sviluppate sia per il bilancio salino, sia per il bilancio del calcio. Il modello, a causa della non linearità delle equazioni differenziali, è stato risolto numericamente utilizzando il metodo di Runge-Kutta. La seconda parte del capitolo espone i risultati della simulazione. È stato dimostrato che l'utilizzo delle acque salmastre avvia un processo di accumulo di sodio nel suolo sebbene il bilancio salino sia in pareggio. Si è potuto constatare che l'accumulo di sodio nel suolo è indipendente dalle caratteristiche del complesso di scambio del suolo stesso (CEC).

La conclusione del lavoro è presentata nel capitolo 4. In una prima fase è stato introdotto il concetto di "richiesta di lisciviazione" rispetto al problema sodio, partendo dallo stesso concetto sviluppato per il problema salino. È stato così sviluppato un algoritmo che permette di gestire l'irrigazione rispetto al problema della sodicità. Utilizzando entrambe le equazioni, riferite a salinità e sodicità, per la stessa acqua di irrigazione, si è osservato che in alcuni casi la richiesta di lisciviazione è maggiore per il problema di accumulo salino, altre volte per il problema di accumulo sodico.

Si è concluso che il problema dell'utilizzo di acqua salmastre e sodiche può trovare una soluzione soddisfacendo la "richiesta di lisciviazione", sviluppata nel capitolo 4. Le conclusioni che si possono trarre sono perciò sufficientemente chiare: la necessità di utilizzare acque di scarsa qualità è in aumento e c'è la possibilità di valorizzare queste acque in agricoltura. Nondimeno la completa comprensione dei meccanismi con cui avvengono gli scambi cationici nel suolo è comunque un passaggio obbligato per la corretta gestione del suolo stesso. Il lavoro di tesi qui proposto cerca di spiegare solamente una piccola parte di questi problemi; allo stesso tempo è stata proposta una tecnica semplice, fattibile e in definitiva utile per affrontare questi problemi, considerando il numero minimo di parametri richiesti per essere applicata.

1. INTRODUCTION

1.1. A worldwide scale overview: future problems in the future society

In less than fifty years the world population has doubled, world food supplies have decreased and energy, land, biological and water resources have become under great pressure. The United Nations (2001) estimate that approximately 9.4 billion people will be present by 2050. So world's natural resources become more stressed for the large expansion of world population. In face of this element the problem of malnourished is increasing, and the World Health Organization reports there are 3.7 billion people who are undernourished. Since 1984 food production has been declining per head because of growing numbers of people, shortages of energy in crop production and freshwater (Pimentel and Pimentel, 2008). As a result the problem of the supplies of water for humankind is one of the major we have now and we will have in future. Even if water is considered a renewable resource because of hydrologic cycle and natural depuration, we do not have to forget that approximately 70% of water withdrawn is consumed and is unrecoverable worldwide in quick times. If it is considered the problem of the growth of population and the need of food and resources, like water, that are increasing, we do not have to forget that this is related with the increasing welfare in which many people are going. States like China and India, but also Brazil and some African states, are increasing their power and their lifestyle that is even more similar to Europe, U.S.A. and all other countries that we call advanced. The ecological footprint is an important index that can be used to analyze the human natural demand. It compares human consumption of natural resources with the earth's capacity to regenerate them. It considers seven parameters to evaluate the global resources request:

- built-up land;
- nuclear energy;
- CO_2 from fossil fuels;
- fishing ground;
- forest;
- grazing land;
- cropland.

So that it is possible to estimate how many natural resources are used and if the world can provide human requests. The Living Planet Report (2006) confirms that we are using the planet's resources faster than they can be renewed, and the latest data available (2003) indicate that humanity's ecological footprint has more than tripled since 1961. Our footprint now exceeds the world's ability to regenerate by about 25%. Almost half of the global footprint becomes from energy needs, i.e. fossil fuels. In 2003 the global ecological footprint was 2.2 hectares per person, but the total supply of productive area was 1.8 global hectares per person. People consume resources from all over the world, thus the footprint considers all of these areas. We can see in the figure 1.1 the regional differences between advanced and third-world countries.

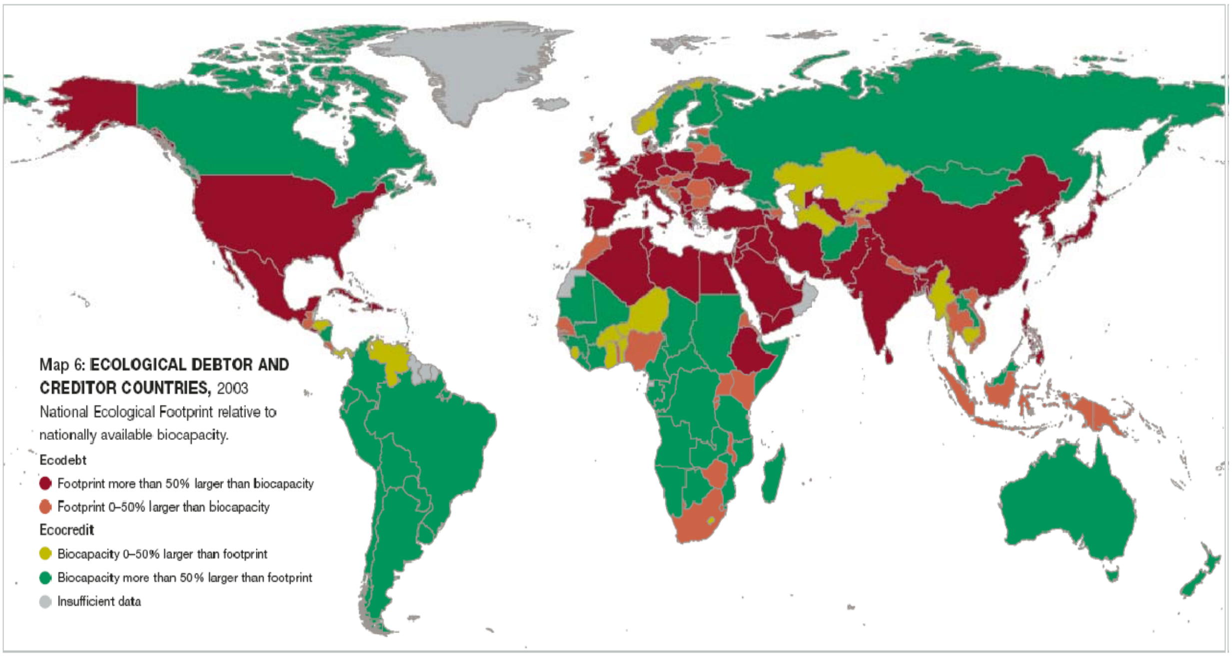


Figure 1.1: Ecological debtor and creditors. Source Living Planet Report, 2006.

In table 1.1 we can see some ecological footprint indexes: important differences we note from "northern" and "southern" world countries.

Freshwater is not included in the ecological footprint because it cannot be expressed in terms of global need hectares that make up this index. It is nonetheless critical to ecosystems and human population.

Country	**Population (millions)**	**Ecological footprint per capita**
World	*6301.5*	*2.23*
United Arab Emirates	3	11.9
U.S.A.	294	9.6
United Kingdom	59.5	5.6
Greece	11	5
Russian Federation	143.2	4.4
Italy	57.4	4.2
Brazil	178.5	2.1
China	1311.7	1.6
Egypt	71.9	1.4
Morocco	30.6	0.9
India	1065.5	0.8

Table 1.1: Ecological footprint (global hectares per person in 2003). Source Living Planet Report, 2006.

Freshwater is far from equally distributed around the world, and many countries withdraw more water than can be sustained without having placing pressure on the land and ecosystems. A useful indicator is the withdrawals-availability ratio, that measures the annual water use by the population against the annual renewable water resource. The higher the ratio, the greater the stress places in freshwater resource. Withdrawals of 5-20% represent mild stress, 20-40% represent moderate stress, more than 40% severe stress (Hails, 2006). For instance the U.S.A. freshwater withdrawals, including that for irrigation, total about 5500 L/person/day. Worldwide, the average withdrawal is 1700 L/person/day for all purposes (Gleick *et al.*, 2002).

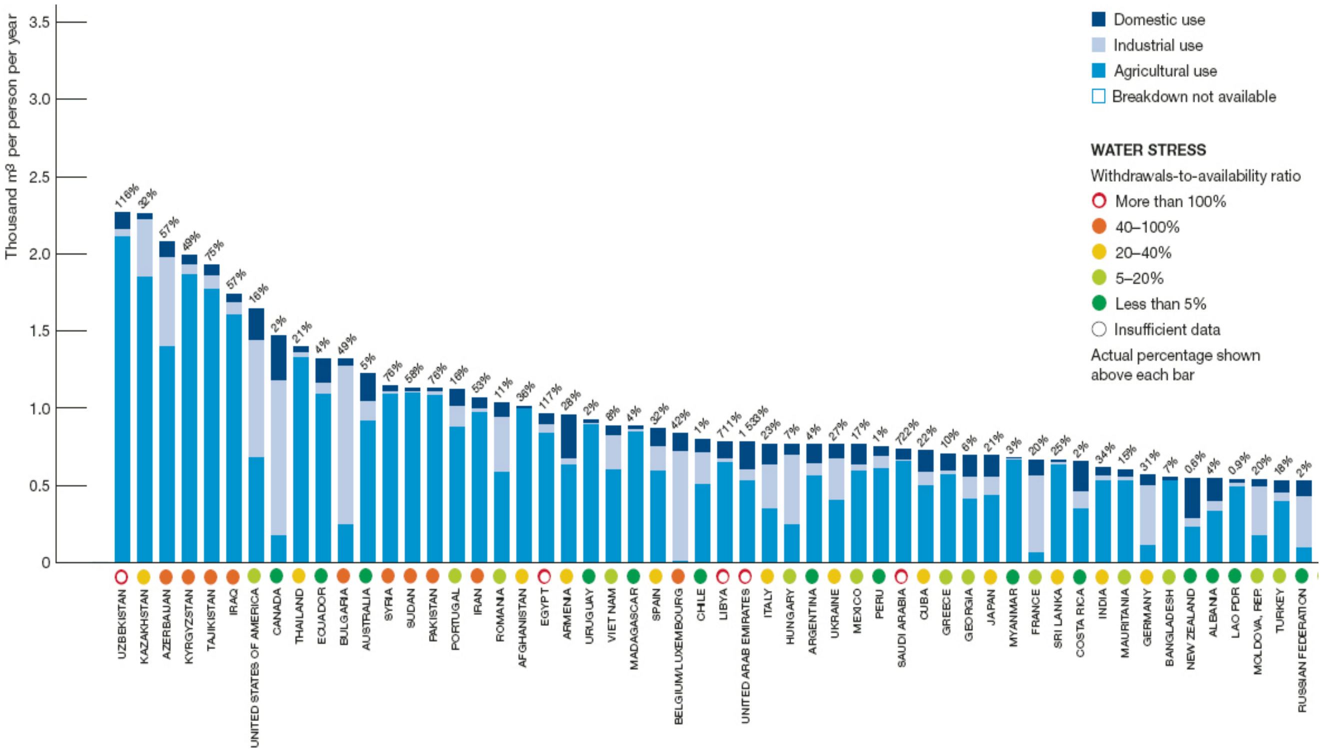


Figure 1.2: Annual water withdrawals per person, by country, 1998-2002.
Source Living Planet Report, 2006.

1.1.1. Water resources and hydrologic cycle

The water present on the Earth is estimated in 1.4 x 10^{18} m^3, and about 97% is in the ocean. Earth's freshwater, held in rivers, lakes and reservoirs is about 0.3% (35 x 10^{15} m^3). Some two thirds of this freshwater is locked up in glaciers and permanent snow cover (UNESCO, 2003). The Earth's atmosphere contains about 13 x 10^{12} m^3 of water, and it is the source of rains. The solar energy causes about 577 x 10^{12} m^3 of water evaporation yearly, and the 86% of this becomes from ocean. Thus the 14% of water evaporates from land, but about the 20% of water precipitations fall on lands (Shiklomanov and Rodda, 2003). This is an important aspect of the hydrologic cycle that allows the existence of terrestrial's ecosystems and human life.

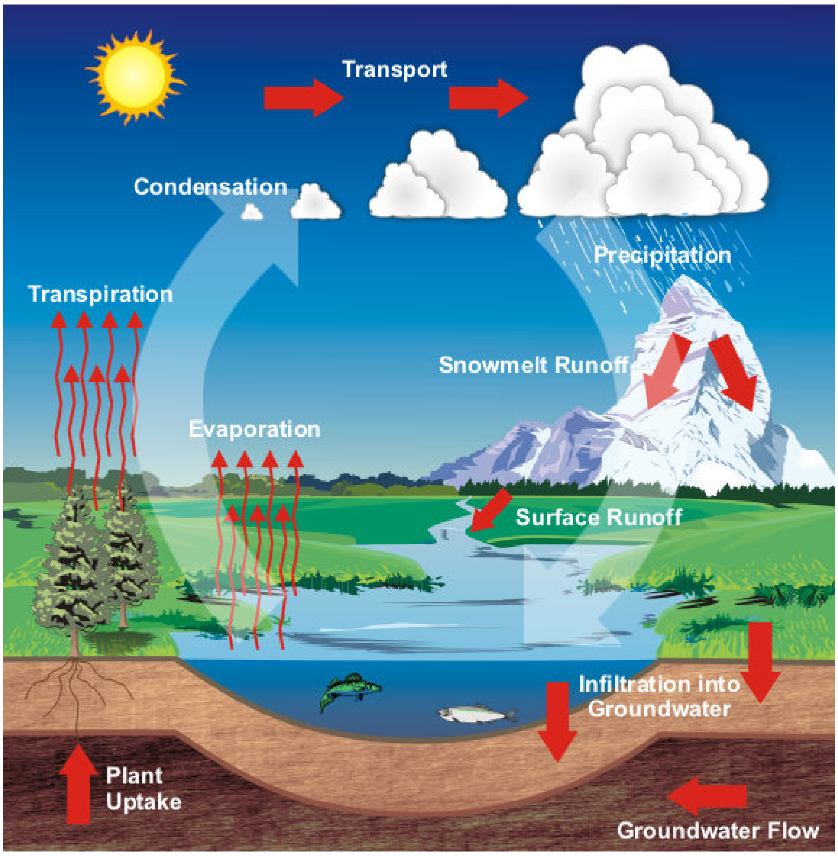


Figure 1.3: Qualitative overview of the hydrologic cycle.

However water availability is different among regions, with huge differences in different parts of the world and wide variations in seasonal and annual precipitation in many places. The average precipitation for most continents is about 700 mm/y, but this mean varies among and within them. In fact if we consider the African continent, we observe that has an average rainfall of 640 mm/y, but there is a great variability between arid and non arid zones (Pimentel *et al.*, 2004). Regions that receive less 500 mm/year usually have problems of water shortages and inadequate crop yields. Moreover a nation that has less than 1,000,000 L/head/year is considered with problems of water scarcity (Engelman and Le Roy, 1993). For example many states of Middle Eastern countries have insufficient freshwater. The UNESCO 1st World Water Development Report (2003) confirms the difficulties of many countries around the world (table 1.2). Thus we need to manage water resources and we need to consider agricultural, environmental and societal systems all together because they need great quantities of water.

Region	**Water availability per capita (m^3/year)**
Canada	94353
Congo, Dem. Republic	25183
France	3493
Italy	3325
Morocco	971
Egypt	859
Israel	276
Jordan	179
Saudi Arabia	118

Table 1.2: Quantity of water available per person/year. Source UNESCO 1st World Water Development Report, 2003.

1.1.2. Water use in the world

The increase of population and of its wellbeing gives serious problems at water resources. Now we use water for all aspects of our life. Even if agriculture worldwide consumes most of freshwater, also urban agglomerations and industries give several problems to water resources. Presently 48% of world's population lives in towns and cities; by 2030 this will rise to about 60%. Moreover countries that most urbanized in the past forty years are generally those with the largest economic growth. Urban areas generally provide the economic resources to install water supply and sanitation, but they also concentrate wastes. Where good waste management is lacking, urban areas are among the world's most life-threatening environments (UNESCO, 2003). Also industry, fundamental part of the global economy, requires adequate resources of good water. Global annual water use by industry is expected to rise from an estimated 725 km^3 in 1995 to about 1170 km^3 by 2025, by which time industrial water usage will represent 24% of all water abstractions. There are some differences in water use for different part of the world, in fact it is assumed that industry is more present in developed countries. Figure 1.4 shows industrial, domestic and agricultural usage for similar regions of the world (UNESCO, 2003):

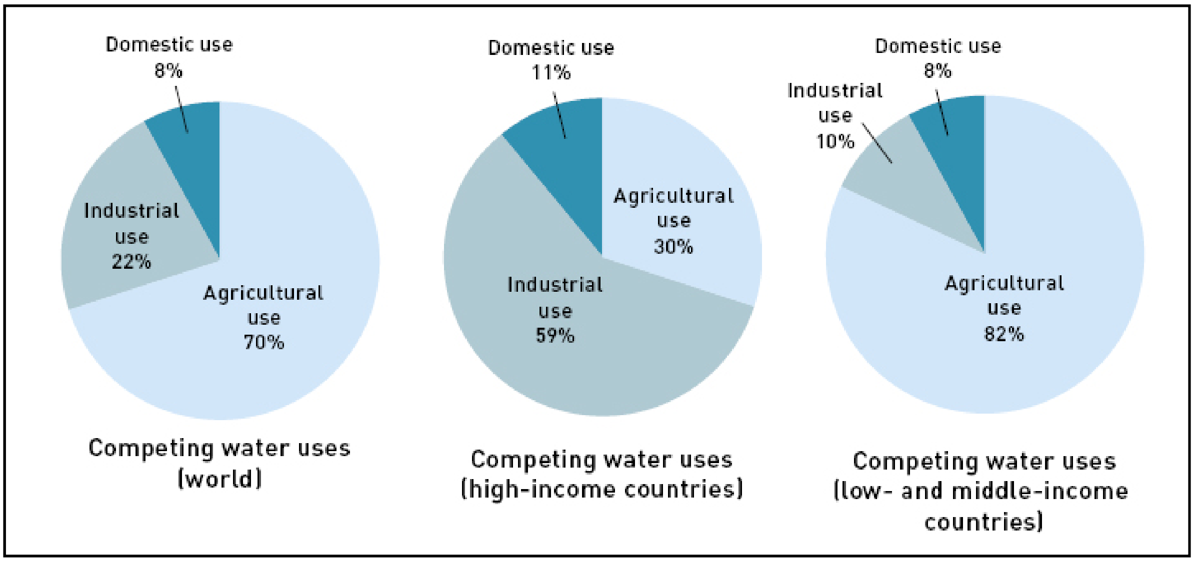


Figure 1.4: Water distribution uses in the world. Source UNESCO, 2003.

Problems with water pollution by industry are not restricted only to freshwater, but the threats are also for coastal zones that are increasing concentration of industry and population. So that habitats and water of coastal areas are under great stress. In addition air emissions of persistent organic pollutants, for example, may pollute waters far removed from industrial centers (UNESCO, 2003).

At last we can say that water needs for human activities is in great increase and the main problems are pollution and reduction of water resources due to its major request.

1.2. Agriculture and irrigation water

Humans obtain all their nutrients from crops and livestock and these nutrient resources require energy, land and water for the productions. The importance of irrigation in agriculture is underlined when we consider that approximately 17% of croplands worldwide are irrigated and they produce about 40% of the world's food (FAO, 2002). Because of the increasing of world population we need to increase the irrigated areas, and this is possible if we rise the efficiency of water use. In fact water is already in very short supply in several countries, and many others also suffer locally from severe shortages (FAO, 2002). When we deal with water shortages and crop productions it should be useful to consider even that livestock requires a great quantity of energy and thus water resources, because of the passage from one step to another in the "trophic pyramid", where trophic pyramid means the flux of matter and energy from one organism to another. In fact it is estimated that in each level passage the energy available reduced on a factor 10. Hence, the loss of energy as it passes from producers to primary consumers even explains the increasing quantity of water requested. This aspect involves that the energy requirement for the production of a certain quantity of meat is comparable as ten times the energy for the production of forages. Table 1.3 summarizes the request of water to produce 1 kg of forage crops (Pimentel *et al.*, 1997). The last line of the table refers to the water demand to produce 1 kg of beef meat:

Crop productions	**L/kg dry mass**
Potatoes	500
Wheat	900
Alfalfa	900
Sorghum	1100
Corn	1400
Rice	1900
Soybeans	2000
Beef	*43000*

Table 1.3: Request of water for different crop productions. The last line refers to the quantity of water requested to product 1 kg of beef. Source Pimentel *et al.,* 1997.

It is important to understand the large quantity of water used in livestock systems because it allows to evaluate these productions in terms of water needed for the soil. In fact producing 1 kg of beef requires about 43 times more water than producing 1 kg of grain (Pimentel and Pimentel, 1996). If we consider the quantity of water directly required from livestock we need only 1.3% of the total use in agriculture. But if water for crop productions requested by livestock is included, this dramatically increases the water requirement. Producing 1 kg of fresh beef requires 13 kg of grain (USDA, 2001) and 30 kg of forage (Heischmidt, 1996). So that the sum of water requested for both grain and forage is 43,000 L and it becomes relevant to find alternatives at good quality water and to increase the efficiency of irrigation systems. For instance reducing pollution of water used by industries, farms and urban areas would enable much more of it to be re-used in agriculture. In fact there are enormous potential benefits from use of wastewater in agriculture. As an example we can consider that the water of a city that reaches the public sewerage system is more or less 80% of water used. If it is well treated there are many possibilities of using carefully this water. The fertilizer value of the effluent is almost as important as the water itself. Typical concentrations of nutrients in treated wastewater effluent from conventional sewage treatments are: nitrogen, 50 mg/L; phosphorus, 10 mg/L; and potassium, 30 mg/L (FAO, 2002). If we consider the Italian law limit of 170 kg/ha of nitrogen per hectare, we can use a quantity of water that is 3400 m^3/ha. Considering a city of 500,000 inhabitants that use generally 120 L per day of water, we obtain totally 48000 m^3/day; finally we could irrigate 5000 hectares. In addition we can consider that most of these nutrients should be adsorbed from crops, with obvious advantages for quality rivers (FAO, 2002). We can conclude that the correct use of water resources, that means also the possibility to use saline or non conventional water, such as domestic or zootechnical wastewater, subdued to different depurative process, should be one of the key to guarantee the water necessity and maintaining good quality of the soil and ecosystems.

On the other hand agricultural ecosystems, that allow to maintain the food production, need to be well protected to guarantee crop yields; the closer the agricultural system is to the natural ecosystem, the more sustainable it is, because less environmental degradation takes place in the less intensively managed system. This aspect becomes important when we deal with water management, because water can be best conserved in the fields, as nutrients, by controlling soil erosion and water runoff and by maintaining a good quantity of organic matter in the soil. A better water management also means less input of energy. It is estimated, for example, that United States invest large amounts of fossil energy input in agricultural productions into supplying irrigation water – more or less 20% (Pimentel and Dazhong, 1990), but if water is maintained in the soil we need less quantity of it for crop productions. Moreover if we have the possibility to use poor quality water it gives important alternatives to the freshwater used. So that it results that a good quality and good management of the agricultural ecosystems is fundamental to maintain water quantity. Not only water management is important for maintaining agricultural ecosystems stability. We may think about the importance of a correct percentage of organic matter in the soil, or the importance of species diversity that allows the natural equilibrium of all organisms that live the same field. In other words, to keep in good conditions the ecosystem can give important results in terms of land need and steady productions. This aspect involves the hope to guarantee to the future generations the food needs and productivity of agricultural soils safeguarding the environment.

1.2.1. Consequences of using wastewater in agriculture

The possibility of using poor quality water for irrigation is important and in many countries it has already done and continues to be an important source (van der Zee and Shaviv, 2002). Wastewater is charged with elevated concentrations of chemical compounds in ionic forms and as suspended soil materials, called dissolved organic matter. Irrigation with wastewater is associated with a concentrating of compounds due to the loss of part of the water from the soil system by evapotranspiration, whereas chemicals cannot. This aspect is particularly underlined in arid and semiarid regions, where the ratio of water that evaporates is high. The difference between soil and water mechanisms is correlated with the different time in which processes become. In fact changes in the soil, different from atmosphere and water, occur slower because the buffering mechanisms that oppose changes are much more profound. It implies that we can obtain good results of maintaining in good conditions the soil quality, on the other hand a bad wastewater management can have disastrous consequences with impossibility to remedy in short times. Using wastewater can get advantages in more water for the crops and also can improve fertilization of soil and crop at the same time. Moreover we remove pollutants from water that are adsorbed by the soil and used by plants, and we also create economic value of something that was considered only a cost (van der Zee and Shaviv, 2002). On the other hand crop requests may be different from water composition, so that we can find problems of chemicals accumulation. Soil accumulation of such monovalent ions compromises soil properties due to the deterioration of its structure. The problem becomes great when we deal with sodicity. In wastewater, especially if it arises from domestic wastewater, a relatively high Na^+ content may be expected. Sodicity problems arise slowly, but once soil deterioration occurs within short times and reasonable economic costs sodic soils are rarely remedied. The unbalance between monovalent and divalent cations causes swelling and shrinking behavior of soils with a certain quantity of clay. Swelling causes a major non permeable behavior that does not allow good quality water to enter the soil. It means that the problem of supplies of water increases. When this problem become evident the necessity of leaching is almost impossible because of the loss of permeability. Another problem of using this kind of water deals with heavy metal accumulation, with bad consequences for both crop growth inhibition and soil pollution (van der Zee and Shaviv, 2002). This can even imply the possibility to pollute groundwater resources. Nowadays water treatments avoid this problem and metal contents are usually reduced to such a degree, so that the problems are not expected, but it does not mean we need to pay less attention at all water parameters.

1.2.2. Salinity problems in irrigation

The consequences for present and future times of salt accumulation in the soil use are significant, even more if we consider that often salinity problems can be correlated with sodicity ones. Consequences of salinization include (Monatanarella, 2006):

- loss of soil fertility due to toxic effects of high salt contents;
- reduced water infiltration and retention resulting an increase water run-off;
- damage to transport infrastructure from shallow saline groundwater;
- damage to water supply infrastructure;
- loss of biodiversity;
- land value depreciation.

Many agricultural practices cause alteration of soil attributes that result in soil malfunction and degradation, and soil quality is a critical component of sustainable agriculture. The use of non conventional water resources can give serious consequences to crop productions and soil if management is not correct. Soil salinity problems and irrigation with saline water are widespread and it is estimated that include one third of all irrigated lands. Both humid and arid, semiarid regions are involved in this problem, even if it is more present in the second one. For example there is salinity soil hazard in Australia, India, Middle East, Southwestern U.S.A., that are commonly arid and semiarid; nevertheless we have the same problems in Sweden, Holland and Hungary. Also the Mediterranean basin is interested in this matter (Yaron, 1981). It has been estimated that 100,000 acres per year of land (nearly 250,000 ha) are no more productive due to salinity problems (Evans, 1974). This aspect will be discussed better in the section 1.3.

The salinity problem is more acute in arid and semiarid regions due to the need of extensive irrigation, low annual rainfall that is not enough to meet evaporative need crops and relative scarcity of good quality water. Thus, even with relatively good quality water, the permanent irrigation practice causes the irrigated soil to be affected by an excess of soluble salts (Bresler, 1982). Moreover, world prospects indicate that the quality of the irrigation water tends to deteriorate, so there is the necessity of using poor quality water. In this situation there is an accumulation of salts in the land and the soil becomes saline. It is demonstrated that problems related to salt concentrations are often present in areas with drainage problems (Yaron, 1982). In this case water, that hardly drains, evapotranspires and salts accumulate in the field.

1.2.3. Effect of salinity in crop productions

Crops generally suffer from high salinity levels of irrigation waters because of high osmotic pressure that inhibits water suction. Crops symptoms from high salinity are generally the same as symptoms of moisture stress from dry conditions. Dissolved salts cause plant cell dehydration by decreasing the osmotic potential of soil water. Figure 1.5 shows a qualitative behavior of plants growth at different soil solution concentrations.

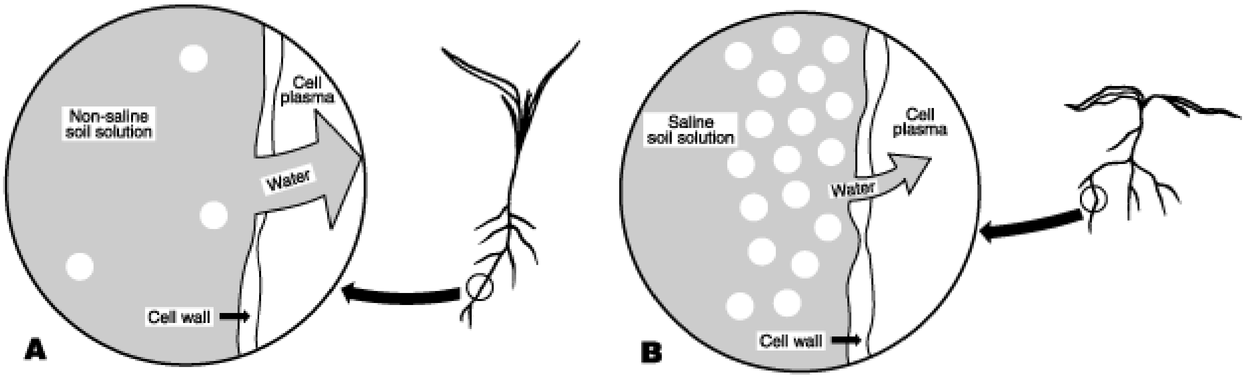


Figure 1.5: Different water extraction with low salinity (A) and high salinity (B) in soil solution.

Table 1.4 summarizes crop forages and vegetables that suffer from salinity. Salt sensitive species produce great yield reductions over a very narrow range of soil salinities. For instance bean production reduces of 10% at only 1.5 mS/cm of extracting water, while 3.5 mS/cm is enough to reduce of 50% the production. Others are more tolerant, as wheat (*Triticum eastivum* L.) and tall fescue (*Festuca aruninacea* Schreb.). The examples show that is possible and helpful to use saline water, but it must be pay attention. Since salinity of the soil will not be less than that of the irrigation water, the range of irrigation water salinity that allows maximum yield is restricted for sensitive crops.

	EC_e x 10^3 mS/cm at 25° C at which yields decreased by:		
Crop	**10%**	**25%**	**50%**
***Allium cepa* L.**	2	3.5	4
***Beta vulgaris* L.**	10	13	16
***Daucus carota* L.**	1.5	2.5	4
***Festuca arundinacea* Schreb.**	7	10.5	14.5
***Lactuca sativa* L.**	2	3	5
***Lolium perenne* L.**	8	10	13
***Lycopersicon esculentum* Mill.**	4	6.5	8
***Oryza sativa* L.**	5	6	8
***Phaseolus vulgaris* L.**	1.5	2	3.5
***Solanum tuberosum* L.**	2.5	4	6
***Trifolium pretense* L.**	2	2.5	4
***Triticum aestivum* L.**	7	10	14
***Zea mais* L.**	5	6	7

Table 1.4: Salt tolerance of plants; EC_e refers to electrical conductivity of extracting water. Source Bernstein, 1982.

When poor soil conditions prevent adequate leaching or when water management is not good, much lower irrigation of poor quality can eventually cause salt accumulation in the soil. Sodicity is another problem connected with salinity. Often the two problems are linked, in fact usually salinity and sodicity problems are in the same kind of water. Sodic soils inhibit plant growth because of unfavorable soil conditions and potential deficiencies of calcium and magnesium (Bernstein, 1982). The first of the two aspects above is correlated with the loss structure of the soil and it means lack of oxygen because of the occlusion of pores by the soil particles. All plants reduce their production with loss of soil structure as a result of high sodium content. On the other hand, even if high salt level can inhibit crop production, it keeps and improves soil structure by promoting flocculation and tends to maintain certain levels of calcium and magnesium. The measurable effect is an adequate keeping of exchangeable divalent cations.

1.2.4. Salinity water parameters

The most important parameter for saline water and its management is the total concentration and total quantity of dissolved salts. One of the first used parameter to this aim is called Total Dissolved Solids (TDS), which considers the total amount of all organic and inorganic compounds contained in a liquid and that are present in molecular or ionized form. It is determined by evaporating from a water sample to dryness and weighing the quantity of salts remaining. The U.S. Salinity Laboratory Staff (1954) collected a representative sample of surface water and groundwater, and it seems to be a clear method of water classification. But several remained salts often contain a variable amount of water. Values were usually reported in ppm (parts per million) TDS, although now sometimes is preferred milligrams per liter (mg/L). There are no relevant differences between the two sets of units when we deal with irrigation waters, although numerically mg/L are somewhat larger than ppm because of different solution densities. In fact salt water is heavier than pure water. Groundwater and surface water have generally different range of dissolved solids. The U.S. Salinity Laboratory Staff (1954) reported lowest values for irrigation waters equal approximately 75-100 mg/L, found in the western U.S.A. The total quantity of dissolved solids normally increases with increasing distance from the river’s head, as a result of mineral weathering. Even for high quality river salts concentration are commonly 10-20 times greater than those present in precipitation. More typical levels of dissolved solids measure approximately 250-900 mg/L. Water with high concentration of dissolved salts becomes more dangerous for crop productions and fine-textured soils. However, irrigation waters used in Salt River Valley of central Arizona sometimes approach TDS values from 2,000 to 3,000 mg/L, and also in Texas has been used water with 4,000 mg/L of TDS (McNeal, 1982). More saline waters must be used carefully and it should be guaranteed the correct management. For instance the practice of leaching requirement could be one of the solution to the problem. Groundwater used for irrigation usually contains higher TDS levels than to river water of the same region. The lowest reported TDS value commonly 200-300 mg/L, with well waters levels till 2,000-3,000 mg/L. The higher levels are due to selective withdrawals of water by plants in the groundwater recharge area and to dissolution of minerals in the soil and rocks when water flows (McNeal, 1982).

Another method to evaluate the total quantity of dissolved salts is the electrical conductivity (EC) of the water. This method is now preferred because TDS is more ambiguous and requires time and technologies that now are out-of-date. The determination of EC involves placing two electrodes in a sample of water, imposing an electrical potential difference. It is so measured the resistance of the solution. As the salt concentration increases also the ability to transmit electricity increases. Results are usually converted from electrical resistance to electrical conductance and they are usually referred to temperature equals

25°C. The unit measure is usually mS/cm, which is equal to mmhol/cm, that is referred to resistance (ohm). The U.S. Salinity Laboratory Staff (1954) gave an approximate relation between TDS and mho/cm: TDS (mg/L) ≈ 640 x EC (mmho/cm). From this it results that commonly irrigation waters would occur in the range of 0.15-1.5 mmho/cm (equals 96-960 mg/L). Another important conversion that we can usually use to find the total cation or anions in water is: cations - or anions - (meq/L) ≈ 10 x EC (mmho/cm). The U.S. Salinity Laboratory Staff proposed the following water classification (table 1.5) that highlights whether there is salinization hazard (Bolt and Bruggenwert, 1976):

	EC (mS/cm)
Low salinization hazard	< 0.25
Medium salinization hazard	0.25 < X < 0.75
High salinization hazard	0.75 < X < 2.25
Very high salinization hazard	> 2.25

Table 1.5: Classification of irrigation water with respect to salinity.
Source USDA Handbook No. 60, 1954.

Another important aspect to evaluate the water quality is the osmotic pressure. In fact plants behavior to salinity is the expression of osmotic properties and it is linked to it. The osmotic pressure (OP) is produced by the presence of salts; those salts that produce large numbers of ions and that remain most completely dissociated into individual ionic components are those that produce the greatest osmotic effects. If we consider that water usually has a mixed salts solution, even we assume that the differences of OP are less pronounced than for single salt solution (McNeal, 1982). So that we can consider sufficiently valid the relationship there is between osmotic pressure and electrical conductivity: OP (atm) = 0.36 x EC (mS/L). This value is nearly valid to osmotic pressure expressed in bar (1 atm = 1.013 bar).

1.2.5. Sodicity problems in irrigation

Aside from their influence on the concentration of the soil solution, the addition of salts to the soil profile may also lead to an alteration of the composition of the exchange complex. Such an alteration is typically in the direction of an increase of the percentage of exchangeable sodium ions, because their salts are the most soluble occurring in nature. The gradual increase in the sodium saturation of the exchange complex is called the process of sodication or alkalinization. Generally alkalinization means increase of pH, but it can be used even for sodium accumulation due to the sodium salts effect of rising pH values. The rate of sodication process depends on the composition and concentration of the water supplied to the profile, the amount of water added with irrigation per year and the CEC of the soil. CEC is the cation exchange capacity, that is defined as the total quantity of cations that may be retained in the surface layer by electrostatic attraction. Usually it is expressed in mmol_c/100g of soil. This property is typical of clay soils, which are composed by a great number of layers characterized by residual electrical charges. The sodication effect generally occurs because of the high solubility of sodium salts, and it is more present if there is an excess of CO_3^{2-} and HCO_3^- over Ca^{2+} and Mg^{2+} (Bolt and Bruggenwert, 1976). The most important phenomena that involve sodium in the soil are swelling, dispersion (So and Aylmore, 1993) and in consequence erosion. In addition sodic soils become less permeable even at low salt concentration and water availability for plants reduces. Thus this problem becomes relevant if we consider the soil quality and its potential crop production. From antiquity farmers know that sodic soils develop a dark brown surface crust of salts mixed with dispersed organic matter (Szabolcs, 1989). This condition results from an accumulation of adsorbed sodium on exchange sites of soil mineral layers and organic matter, which causes the problems that here are above.

1.2.6. Sodicity water parameters

Irrigation water can create sodic soils and various methods have been proposed to classify them and their capability to produce sodic soils. Considering the simple Na^+ concentration cannot give good results because at low concentrations sodium can represent alone the 90% of total cations and can imply sodicity (McNeal, 1982). As a result we will measure low sodium concentrations, even if the sodicity hazard should be high. The U.S. Salinity Laboratory Staff (1954) proposed SAR (Sodium Adsorption Ratio) as a useful index for sodium hazard. This parameter is given by the following relation:

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \tag{1.1}$$

Where the cations are concentrations expressed in mmol/L. If we consider that the most common cations in the water are Ca^{2+}, Mg^{2+}, Na^{+}, while K^{+} is usually relatively small, we can conclude that salinity and sodium hazard of a given water can be estimated from any two of the three parameters: EC, Na^{+}, and ($Ca^{2+} + Mg^{2+}$) concentration. Instead we cannot consider pH as a considerable measure of sodic water because, even if soils with high values of sodium tend to have pH ≥ 8.5, particularly at low salts concentration this is not a reliable indicator (U.S. Salinity Laboratory Staff, 1954). Here below (table 1.6) it is schematized the classification of irrigation water with respect to sodicity:

	SAR (mmol/L)$^{1/2}$
Low sodification hazard	< 7
Medium sodification hazard	7< X < 13
High sodification hazard	13 < X <20
Very high sodification hazard	> 20

Table 1.6: Classification of irrigation water with respect to sodicity.
Source USDA Handbook No. 60, 1954.

At last we can consider the Residual Sodium Carbonate (RSC) as another useful parameter to classify irrigation waters, because it determines the alkalinization hazard (usually linked with Na^{+}). When all the Ca^{2+} and Mg^{2+} added by irrigation precipitate in the soil as carbonates, the excess of CO_3^{2-} and HCO_3^{-} will be present as dissolved Na^{+} (and K^{+}). In the long period all divalent cations exchanged from the soil will precipitate until the almost totality of the adsorption complex is saturated with Na^{+} (Bolt and Bruggenwert, 1976).

1.3. Salt affected soils and classification

Nowadays salt affected soils are naturally present in more than 100 countries of the world and many of these regions are also affected by irrigation-induced salinization (Rengasamy, 2006). Based on the FAO/UNESCO Soil Map of the world (2003), table 1.7 emphasizes the regional distribution of salt affected soils. All the areas shown in the table are not necessarily arable but cover all salt affected soils around the world.

Region	**Total area**	**Saline soils**	**%**	**Sodic soils**	**%**
Africa	1899.1	38.7	2.0	33.5	1.8
Asia, Pacific & Australia	3107.2	195.1	6.3	248.6	8.0
Europe	2010.8	6.7	0.3	72.7	3.6
Latin America	2038.6	60.5	3.0	50.9	2.5
Near East	1801.9	91.5	5.1	14.1	0.8
North America	1923.7	4.6	0.2	14.5	0.8
Total	12781.3	397.1	3.1	434.3	3.4

Table 1.7: Regional distribution of salt affected and sodic soils. Source FAO, 2003.

Soil degradation processes occurring in Europe include erosion, loss of organic matter, landslides, compaction, contamination by pollutants and salinization. Many recent studies suggest that there has been in the last decades a significant increase in soil degradation processes and there are evidences that these processes will increase in the next years if no action is taken (Montanarella, 2006). The salinity accumulation and sodic problems are relevant in different grounds; however the problem is even more present in predominant clay texture soils (Bolt and Bruggenwert, 1976).

The classification of salt affected soils, as presented by the USDA salinity laboratory staff (1954), is widely used. This classification was created principally for purposes of reclaiming salt affected soils. It is a simple system based on two criteria:

- salinity of the soil, which is expressed as electrical conductivity;
- sodium percentage, which is expressed as ESP (Exchangeable Sodium Percentage).

ESP represents the ratio between Na^+ adsorbed in the solid phase and the cation exchange capacity, which is the maximum quantity of exchangeable cations of a soil and it is usually expressed in $mmol_c/100g$ of soil. There is an important relationship that links SAR and ESP, hence sodium in the soil solution and in the adsorbed phase (U.S. Salinity Laboratory Staff, 1954):

$$\frac{ESP}{(1-ESP)} = 0.015\,SAR \qquad (1.2)$$

Different ranges of ESP were proposed to define sodic soils: for instance the U.S. Salinity Laboratory Staff (1954) proposed sodic soils with ESP more than 15, while in Australia it considers ESP ≥ 5. There are also studies that show how even soils with ESP ≤ 1% exhibit sodic behavior (Sumner, 1993). In fact this parameter is related with soil properties and the EC of irrigation water. However usually SAR and ESP are similar, and the higher is SAR value the more similar is ESP. Finally we can say that the classification of irrigation water should consider at least EC and SAR to define a good management of all, and especially non conventional, waters. In fact the problem of sodicity arises when it occurs water with low EC values, either through good water applications or rainwater falls (Halliwell *et al.*, 2001):

SAR	**EC (mS/cm)**		
	No problem	**Slight to moderate**	**Severe problem**
0-3	> 0.9	0.9-0.2	< 0.2
3-6	>1.3	1.3-0.25	< 0.25
6-12	> 2.0	2.0-0.35	< 0.35
12-20	> 3.1	3.1-0.9	< 0.9
> 20	> 5.6	5.6-1.8	< 1.8

Table 1.8: Guidelines for interpretation of water quality for irrigation. Source Halliwell *et al.*, 2001.

At low concentration adverse physical effects of a high ESP value will appear early, while the opposite conditions we have with high salinity of irrigation water.

Due to its simplicity, the USDA classification of salt affected soils does not be applied for all situations and all soils indiscriminately, because there are variations occurring in nature that here are not considered, for instance there are not references about the soil texture. However the major part of soils have characteristics that can allow us to use this classification with a certain confidence.

1.3.1. Saline soils

Saline soils have a conductivity of the saturation extract more than 4 mS/cm at 25° C and ESP is less than 15% (U.S. Salinity Laboratory Staff, 1954). When adequate drainage is established the excessive soluble salts may be removed by leaching and they again become normal soils. They are recognized by the presence of white crusts of salts on the surface. The chemical characteristics are mainly determined by the kinds and amounts of salts present. Owing to the presence of excess salts and the absence of significant amounts of exchangeable sodium, saline soils generally are flocculated. As a consequence permeability is equal to, or higher than, that of similar non saline soils.

1.3.2. Saline-alkali soils

Saline-alkali is applied to soils for which the conductivity is more than 4 mS/cm at 25° C and the exchangeable sodium percentage is greater than 15%. These soils form when salinization and sodication processes combined together. As long as excess salts are present, the appearance and properties of these soils are generally similar to those of saline soils (U.S. Salinity Laboratory Staff, 1954). The pH is seldom higher than 8.5 and the particles remained flocculated. If the excess soluble salts are leached downward, the properties may change and become similar to those non saline-alkali soils. As the concentration of the salts in the soil solution is lowered, some of the exchangeable sodium hydrolyzed and forms sodium hydroxide. This can change to sodium carbonate upon reaction with carbon dioxide adsorbed from the atmosphere. In any event, upon leaching, the soil may become strongly alkaline (pH more than 8.5), the particles disperse and the soil becomes unfavorable for the entry and movement of water and for tillage. The management of saline-alkali soils continues to be a problem until the excess of salts and exchangeable sodium are removed from the root zone and a favorable physical condition of the soil is reestablished.

1.3.3. Nonsaline-alkali soils

Nonsaline-alkali is applied to soils for which ESP is more than 15% and the electrical conductivity is less than 4 mS/cm at 25° C (U.S. Salinity Laboratory Staff, 1954). The pH value is usually more than 8.5, sometimes till 10. These kind of soils usually occur in arid and semiarid regions. The drainage and leaching of saline-alkali soils usually lead to the formation of nonsaline-alkali soils. Dispersed and dissolved organic matter present in the soil solution of highly alkaline soils may be deposited on the soil surface by evaporation, thus causing darkening and giving rise to the term “black alkali”. The ESP present in nonsaline-alkali soil may have a marked influence on the physical and chemical properties. As the proportion of exchangeable sodium increases, the soil tends to become more dispersed. The pH can also increase as high as 10. At these pH values the composition of soluble salts in solution may vary a lot from that of normal and saline soils. While the anions present consist mostly of chloride, sulfate and bicarbonate, small amounts of carbonate often occur. In fact at high pH calcium and magnesium with carbonate ions are precipitated, hence the soil solution of these soils usually contains a few quantities of these cations and sodium is predominant. Sometimes large quantities of soluble potassium may occur in these soils.

1.3.4. Salinity and sodicity problems in Europe

The problem of land degradation concerning salinity and alkalinity in Europe limits the satisfactory utilization of soil in many regions and causes planning problems in both agricultural and environmental aspects. Frequently soils become salinized and/or alkalinized because of human activities such as inadequate irrigation management of agricultural lands. Salinization affects around 3.8 million ha in Europe and most affected are Campania in Italy, the Ebro valley in Spain and the Great Alföld in Hungary, but also areas in Greece, Portugal, France, Slovakia and Austria (Monatanarella, 2006). There are also evidences that the occurrence of salt affected soils in Italy is located along the coasts of mainland and some regions of Sardinia and Sicily (Szabolcs, 1989). The problem certainly exists even due to the widely irrigation practices occurring in the territory.

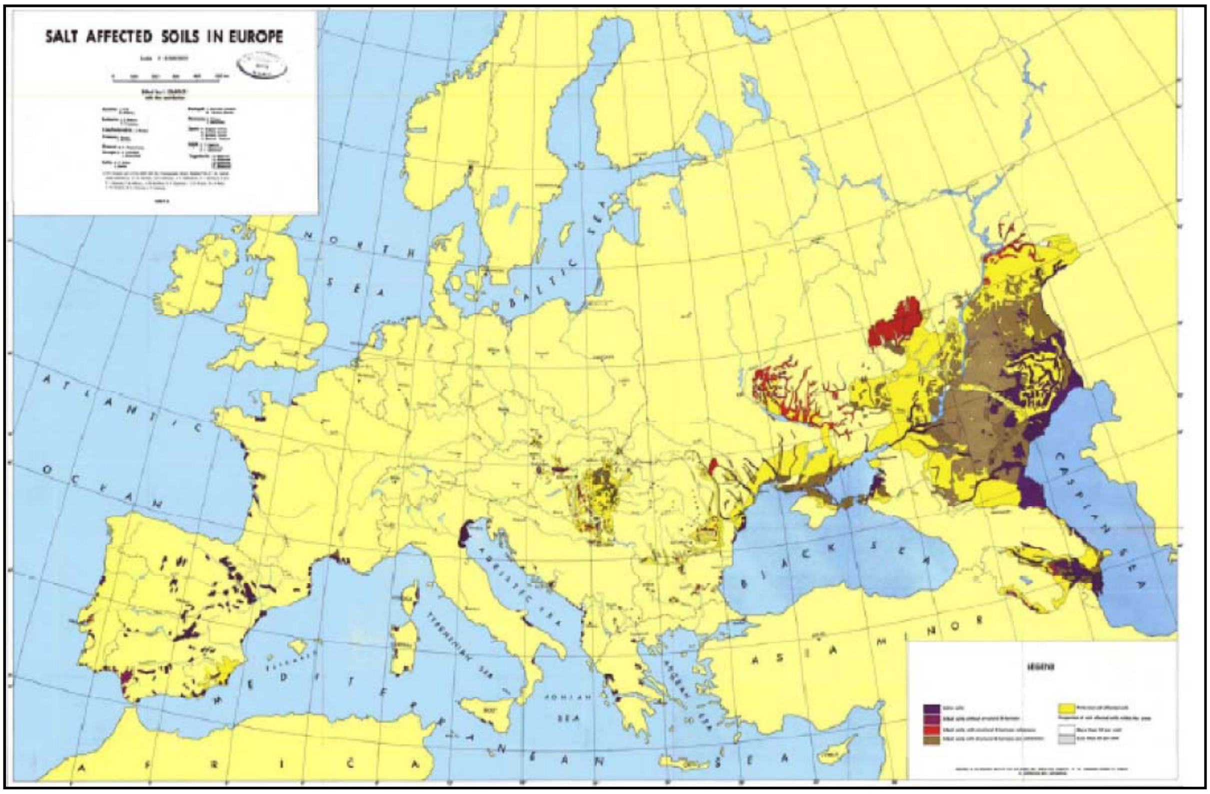


Figure 1.6: Salt affected soils in Europe. Source Szabolcs, 1989.

1.3.5. Salinity problems in Italy

Salinity of soils in Italy is not a widespread phenomenon now, but there are some aspects that may be decisive for the arise of this problem in large scale. At first the overexploitation of the groundwater may cause the fall of water table level and the consequent intrusion of seawater, especially along the coasts. This aspect may cause the presence of saline water and the following withdrawals. Hence the problem arises because that saline water is used for irrigation and it should be particularly marked in regions with high percentage of agricultural lands.

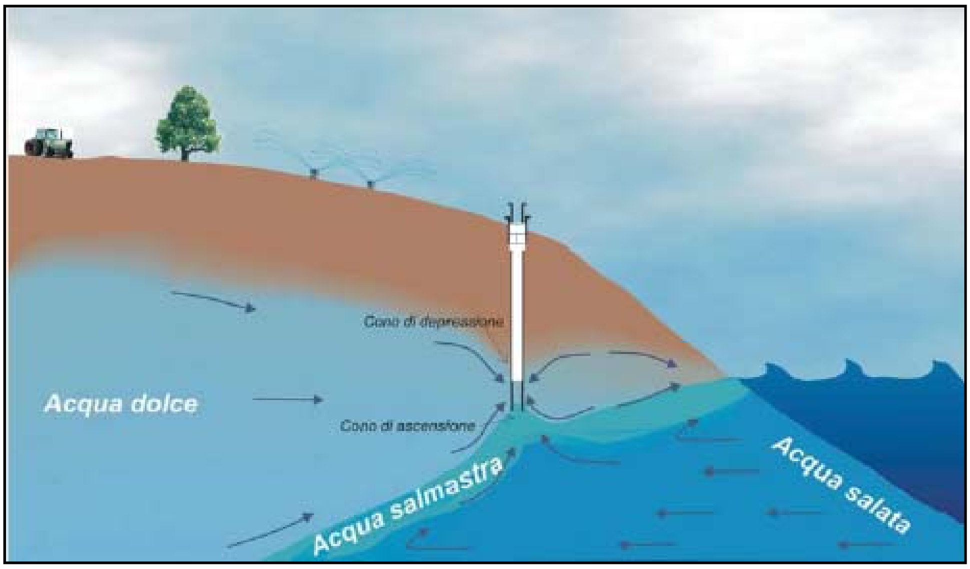


Figure 1.7: Intrusion of seawater due to excessive withdrawals. Source APAT, 2007.

On the second hand the need of using wastewater is increasing globally, especially in agriculture, thus the contribution of salts is clearly more than using freshwaters. At last arid lands will increase due to the effects of climate change (Malhi *et al.*, 2002), hence there will be less leaching and more evapotranspiration with the consequent arise of new saline soils. The geographical position of Italy allows to predict the possibility of growing salinity and sodicity problems. Nowadays there are evidences that the problem is in the low Po valley, Tyrrhenian and Adriatic coasts and major islands, i.e. Sardinia and Sicily (APAT, 2007). Seawater intrusion is also one of the main problems of coastal alluvial plains, which are used intensively for agriculture and industry purposes (Tedeschi and Dell'Aquila, 2005). As a consequence of the effect of seawater they are all saline soils dominated by effect of sodium chloride. Hence the salinity problem becomes more dangerous even due to sodic accumulation (Szabolcs, 1989).

Figure 1.8: Distribution of saline soils. Note that 10% of Sicily lands has problems of salt accumulation. Source APAT, 2007.

1.3.6. The Veneto region situation

In the Veneto Italian region there are problems due to the loss of organic matter, erosion, pollution and salinization. The presence of salt affected soils in Veneto is caused by subsidence of brackish and lagoon areas, and even due to the withdrawals of great quantity of groundwater for industry, civil use and agriculture (APAT, 2007). Studies demonstrated that the major problem is along the coast, where the seawater intrusion causes salinization due to the natural and man-induced subsidence (Tedeschi and Dell'Aquila, 2005).

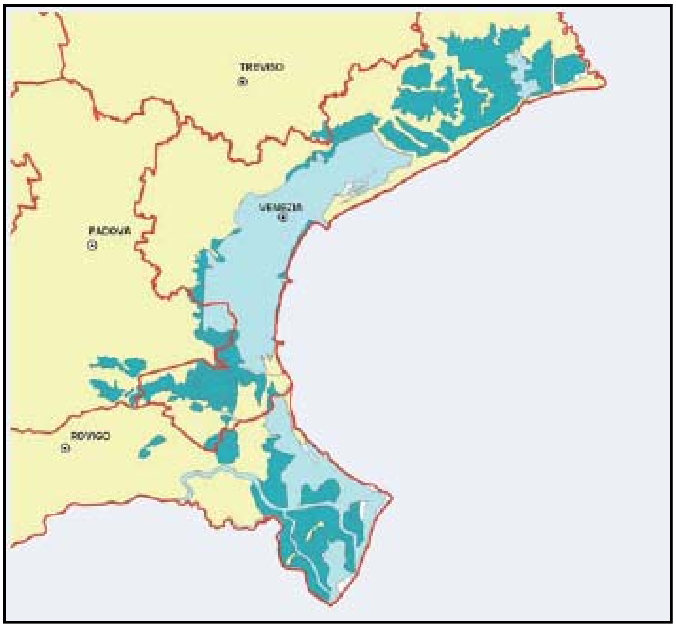


Figure 1.9: Veneto region areas characterized by saline soils or with major salinization hazard. Source APAT, 2007.

2. STUDY OF SENSITIVITY OF ESP TO DIFFERENT SOIL CONDITIONS

2.1. Introduction

Measurements on sodication soil processes usually are not made under the same initial conditions. Different countries and different studies often have not the same standard state; for instance it is not used the same solid:solution ratio, or studies have been done at field capacity, but the soil moisture can change because of different physical soil conditions. Thus there could be not harmonization on results of experiments and assumptions that have been made, such as values on the exact adsorption ratio of the major monovalent and divalent cations that is settled by the exchange equilibrium (in our case, in fact, we will consider Na^+ and Ca^{2+}). The exchange equations are the main point to predict changes in the soil system as a result of external inputs, such as fertilizers, ion uptake by plants, irrigation practices and possible wastewater use.

The problem arises when the initial conditions, such as soil moisture, or the addition of water and cations in the soil, are not the same. There are evidences that experiments are sometimes made with a certain solid:solution ratio (USDA, 1954; White, 1966; Puls *et al.*, 1991), or at field capacity and in the saturated paste (Stivens and Khan, 1966; Bolt and Bruggenwert, 1976; Everest and Seyhan, 2006); these last two are soil characteristics that can change from one site to another and may have effect in the soil measures that we need to do. Other times different salt concentrations or CEC are used (McKenzie, 1951; Bayens and Brandbury, 2004). Hence we need a relationship between the exchange complex and the soil solution to determine the exact exchange equilibrium between monovalent and divalent cations that are involved in the adsorption processes. At last we need to assess how big differences there are between ESP* (a new estimated value of ESP) and the ESP value that is given as initial parameter, after changing inputs that are CEC, water added in the soil system (r, ml/100g), the moisture of the soil (w, ml/100g) and the total salt concentration in the soil solution (C_{tot}, $mmol_c/ml$). Hence different initial conditions could have different effects in the exchange complex and soil solution. In our case we have a simplified situation where, as mentioned before, we consider only the principle monovalent and divalent cations, i.e. sodium and calcium.

2.2. The Gapon equation

Before explaining the scheme of calculations and results that have been obtained, it is fundamental to introduce the Gapon exchange equation. In fact the rate of the different cations that are in the solid and solution phases is balanced by exchange equations. In our particular case we will consider an heterovalent exchange, in fact we will assume the exchange equilibrium between the most common monovalent and divalent cations in a soil system, i.e. Na^+ and Ca^{2+}. Experimental data have shown that for most soils the mono-divalent equilibrium is characterized by the following equation:

$$\frac{\gamma_+}{\gamma_{2+}} = K_G \frac{Na^+}{\sqrt{Ca^{2+}/2}} \qquad (2.1)$$

where K_G is the empirically determined Gapon exchange constant and γ_+ and γ_{2+} refer to the monovalent and divalent cations adsorbed in the solid phase (in our case sodium and calcium), while Na^+ and Ca^{2+} refer to sodium and calcium in the soil solution phase. The Gapon constant K_G has the $[\text{concentration}]^{-1/2}$ dimension. Hence, if the concentration both for monovalent and divalent cations is expressed in terms of moles, usually soils exhibit a $K_G = 0.5\ (\text{mol/L})^{-1/2}$.

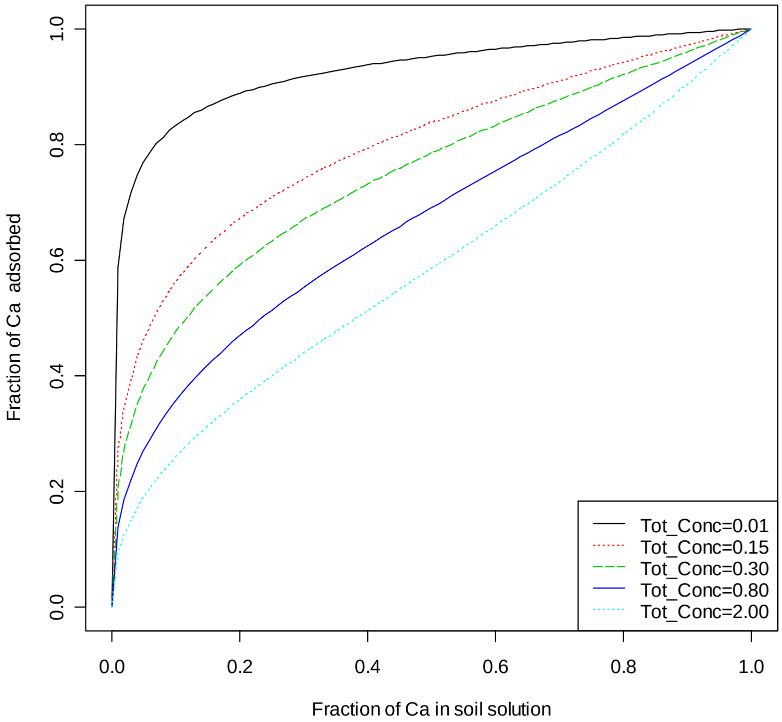


Figure 2.1: Gapon equation with different salt concentrations (mol_c/L). The figure shows different divalent-monovalent soil affinity changing the total concentration in soil solution.

The main limitations are underestimation of the exchangeable Na^+-percentage in the high range (> 40% Na) and in montmorillonitic soils, where K_G tends to be close to unity (Bolt and Bruggenwert, 1976). The Gapon equation is the simplest and reliable mono-divalent exchange equation which may be used in all those cases where no information is available as to the particular conditions locally.

2.3. Calculations of ESP*

The solid phase particles of the soil often carry a negative surface charge. The overall electroneutrality of the system is maintained by the presence of an excess of cations close to the solid surface. It is possible to exchange these cations against others, while maintaining the electroneutrality of the system by means of the replacing cations. The total amount of the cations exchangeably adsorbed by the complex system is the CEC, which is expressed in $mmol_c/100g_{soil}$. All cations are adsorbed in different concentrations by the negative surface charge and the exchange reactions on surfaces are very high. Once the equilibrium has been reached there exists a relationship between the composition of the exchange complex and the soil solution. In soil science history many studies have attempted to generalize this relationship using exchange equations, but no one has found an exchange equation valid for all different exchange materials in the soil; however it states that often a reasonable accuracy is found with equations that only depend on one empirical parameter. As highlighted in paragraph 2.2 experimental data have shown that for the most soils the mono-divalent exchange equilibrium follows the Gapon equation, that here we will write in terms of fraction of sodium (f_{Na}) and C_{tot} ($mmol_c/ml$), i.e. total salt concentration:

$$\frac{\gamma_+}{\gamma_{2+}} = K_G \frac{C_{tot}\, f_{Na}}{\sqrt{C_{tot}\,(1-f_{Na})/_2}} \tag{2.2}$$

where γ_+ and γ_{2+} refer respectively to the quantity of monovalent and divalent cations in the adsorbed phase (expressed in $mmol_c/100g$ soil) and the Gapon empirical constant is expressed in $(mmol/ml)^{-1/2}$. Changes occurring in the field that influence the exchange equilibrium may be summarized as additions (positive and negative) of ions and/or water. In our special case we consider only the addition of water. Hence the Gapon equation can be written as (Bolt and Bruggenwert, 1976):

$$\frac{\gamma_{+}}{\gamma_{2+}} = K_G \frac{wC_{tot}f_{Na}/_{w}}{\sqrt{w\,C_{tot}\,(1-f_{Na})/_{2w}}} \tag{2.3}$$

where w is the moisture content of the soil (ml/100g soil), thus wC_{tot} equals the amount of cations present in the solution of a certain quantity of soil ($mmol_c$/100g). Inputs generate inequality from left and right hand side of the expression. In this case the input is the addition of water (r, ml/100g soil) in the soil system, thus we have:

$$\frac{(\gamma_{+})+x}{(\gamma_{2+})-x} = K_G \frac{(w\,C_{tot}f_{Na}-x)/(w+r)}{\sqrt{w\,C_{tot}\,(1-f_{Na})+x/_{2(w+r)}}} \tag{2.4}$$

where x ($mmol_c$/100g) is the shift of monovalent and divalent cations between solid and solution phase. We can use x both for monovalent and divalent cations due to the same unit measure ($mmol_c$/100g) that we consider. Using milligrams or moles instead of millimoles charge would involve changes in the main equation.

The above equation (2.4) is valid for all cases in which we have addition or extraction of water; hence the exchange equilibrium, which is present between the solid phase and soil solution, is reversible and the equilibrium in the soil system can be reestablished as before the alteration. In this particular case it may be used to calculate the new exchange equilibrium after irrigation or plant uptake, even if our purpose is to evaluate the variations in the sodium and calcium fractions in solid and solution phases. The shift of x is settled by physical conditions (Bolt and Bruggenwert, 1976):

$$w\,C_{tot}\,f_{Na} > x > -[w\,C_{tot}\,(1-f_{Na})] \tag{2.5}$$

The physical meaning of this range is simple: in fact x cannot be more than the real quantity of monovalent cations that are present in solution, whereas it must be even more than the initial quantity of divalent cations present in the soil solution. In this special case we assume that the soil system is characterized by a shift of x ($mmol_c$/100g soil) of monovalent cations from solution to complex, accompanied by a reverse shift of x ($mmol_c$/100g) of divalent ions from complex to solution. The opposite argument is for the second range, in which we have the same shift of monovalent and divalent ions, but in the reverse way:

$$\gamma_{2+} > x > \gamma_{+} \tag{2.6}$$

As said before, in our case we assume only an addition of water (r), which means that x is always negative, due to the dilution phenomenon; in consequence divalent ions move towards the complex. If we assume now a soil with a certain high CEC value, and considering only the movement of divalent cations, we have also that the distribution ratio ($R_D = \gamma_{+,k}/C_{+,k}$) is large, where $C_{+,k}$ is a generic concentration of a general cation in solution and $\gamma_{+,k}$ is a generic cation in the soil adsorbed phase. It means that the maximum relative change, i.e. $1/R_D$, is limited because x must be inside the physical range of equation (2.5). Moreover the net movement of divalent cations is towards the complex, but there is a low amount of them respect to the quantity in the complex. The conclusion is that the exchangeable ratio (left hand side of the equation) is maintained constant. The same argument, but in the opposite way, is for sodium.

Values of f_{Na} of the main expression (2.4) are obtained from the ESP value, given as initial parameter, assuming a reasonably ESP range 1-30% (Bolt and Bruggenwert, 1976; Halliwell *et al.*, 2001). Thus we have:

$$ESP = \frac{\gamma_+}{CEC}100 \qquad \rightarrow \gamma_+ = \frac{ESP\ CEC}{100} \tag{2.7}$$

And assuming that ($\gamma_+ + \gamma_{2+}$) = CEC we have:

$$\rightarrow \gamma_{2+} = CEC\frac{1-ESP}{100} \tag{2.8}$$

Finally f_{Na} is found from:

$$f_{Na}^2 + f_{Na}\left(\frac{\gamma+}{\gamma 2+}\right)^2 \frac{1}{2\,K_G^2\,C_{tot}} - \left(\frac{\gamma+}{\gamma 2+}\right)^2 \frac{1}{2\,K_G^2\,C_{tot}} = 0 \tag{2.9}$$

We assume two possible initial moisture contents (w) equals 1 ml/100g (i.e. considering dry soil) and 25 ml/100g. In this case we referred to Bolt and Bruggenwert (1976), in which 25 is a reasonable value of soil moisture at field capacity. Generally we keep it constant (equals 25) to compare different results and due to the fact that for low w values differences are less evident. Hence we prefer to consider the bigger one to stress how the ESP*/ESP ratio changes.

Solving equation number (2.4) with respect to x seems to be difficult, in fact it is a 4th order polynomial equation. However with a different approach, that consists of comparing the right hand side with the left hand side (for instance plotting graphically the two different parts of the equation together), it is easier to obtain the same results of x (Bolt and Bruggenwert, 1976). Finally the new estimated ESP* is found with the following equation:

$$ESP^* = \frac{(\gamma_+ + x)}{CEC}100 \tag{2.10}$$

Table 2.1 summarizes the data set used for the simulations.

Simulations	Line	r (ml/100g)	w (ml/100g)	CEC ($mmol_c$/100g)	C_{tot} ($mmol_c$/ml)	ESP (%)
ESP*/ESP after changing r, water added in the soil	I	50	25	30	0.01	1-31
	II	100	25	30	0.01	1-31
	III	200	25	30	0.01	1-31
ESP*/ESP after changing the initial salt concentration						
	I	50	25	1-100	0.01	5
	II	50	25	1-100	0.002	5
ESP*/ESP after changing the soil moisture w						
	I	50	1	1-100	0.01	5
	II	50	25	1-100	0.01	5
ESP*/ESP after changing the initial given ESP						
	I	2-500	25	30	0.01	15
	II	2-500	25	30	0.01	5

Table 2.1: Initial values used for the simulations to find ESP* value, i.e. the new estimated ESP index.

2.4. Results and discussion: the ESP*/ESP ratio

Figure 2.2 shows the evolution of ESP*/ESP ratio with respect to the initial ESP value in three different dilution conditions, which corresponds to an addition of water equals 50 ml/100g, 100 ml/100g and 200 ml/100g. In this case we keep as constant w = 25 ml/100g, $C_{tot} = 0.01$ $mmol_c$/ml and CEC = 30 $mmol_c$/100g. What we can see is that the bigger is r the smaller is ESP* with respect to the initial ESP, due to the more evident effect of dilution. With respect to this we consider that we have an extreme situation that arises with excessive input of the r parameter, corresponding to a large amount of irrigation water. Now the solution phase is dominant and the soil system will adjust to the composition of the leaching solution (Bolt and Bruggenwert, 1976). We can also see that for high ESP values the differences are decreasing till to have no effect of water dilution. This second aspect refers to the low Ca^{2+} concentration that is present in the soil-solution system; it means that there is low flux of divalent cations towards the complex, hence the differences we note are very small. This consideration is valid for all samples in which there is a comparison between different initial ESP values.

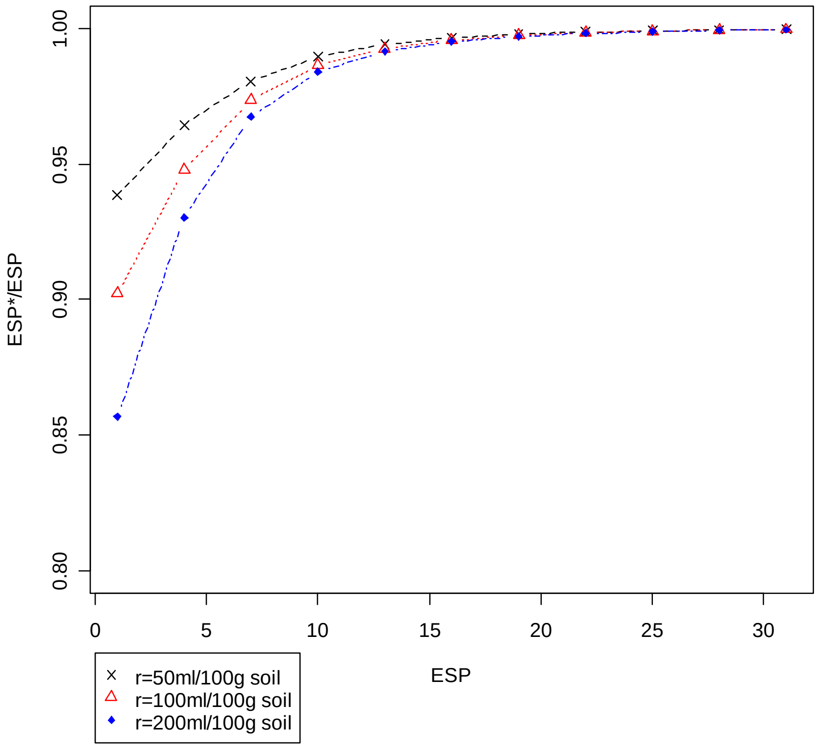


Figure 2.2: Relationship between ESP*/ESP and initial ESP for different r and keeping constant C_{tot} = 0.01mmol$_c$/ml, CEC = 30mmol$_c$/100g and w = 25 ml/100g.

The figures below (figures 2.3 and 2.4) demonstrate the same trend, however something changes. In both cases we can see how the ESP*/ESP ratio changes with the CEC range, but for two different conditions. We consider reasonable values of CEC in the range of 1:100 (mmol$_c$/100g) as expressed in McKenzie (1951), Bolt and Bruggenwert (1976), Bayens and Brandbury (2004).

In the first case (figure 2.3) we assume two different initial concentrations. The graphic shows that differences between ESP and ESP* values are bigger when C_{tot} is high. In this case w does not change and equals 25 ml/100g. Hence, the bigger is C_{tot} the smaller is the distribution ratio for each ion $R_D = \gamma_{+,k}/(wC_{+,k})$ and so the maximum relative change for divalent cations (equals $1/R_D$) towards the complex becomes bigger than for low C_{tot} values (here equals 0.002 mmol$_c$/ml). On the other hand, if this effect is clear for low CEC values, it becomes less evident when CEC is increasing. In fact the system goes to a complex-dominated exchange adjustment (Bolt and Bruggenwert, 1976), in which the maximum relative change is limited. Hence there are less differences between the two situations expressed above.

In figure 2.4 there are the same initial conditions of figure 2.3 (initial ESP = 5 and r = 50 ml/100g), but in this case w changes and C_{tot} = 0.01 mmol$_c$/ml. In this case the trend seems to be the same, even if we have some differences at low CEC values. In fact here the ESP*/ESP ratio has more differences considering low w, while for increasing CEC we have the same conditions of figure 2.3. We would expect, as in figure 2.3, that due to the bigger value of 1/R_D, for high w, the maximum change of divalent cations should also be large. However this is not true when we have low CEC values. Here the comparison between the two lines gives opposite results, so it should mean that the main process is opposite.

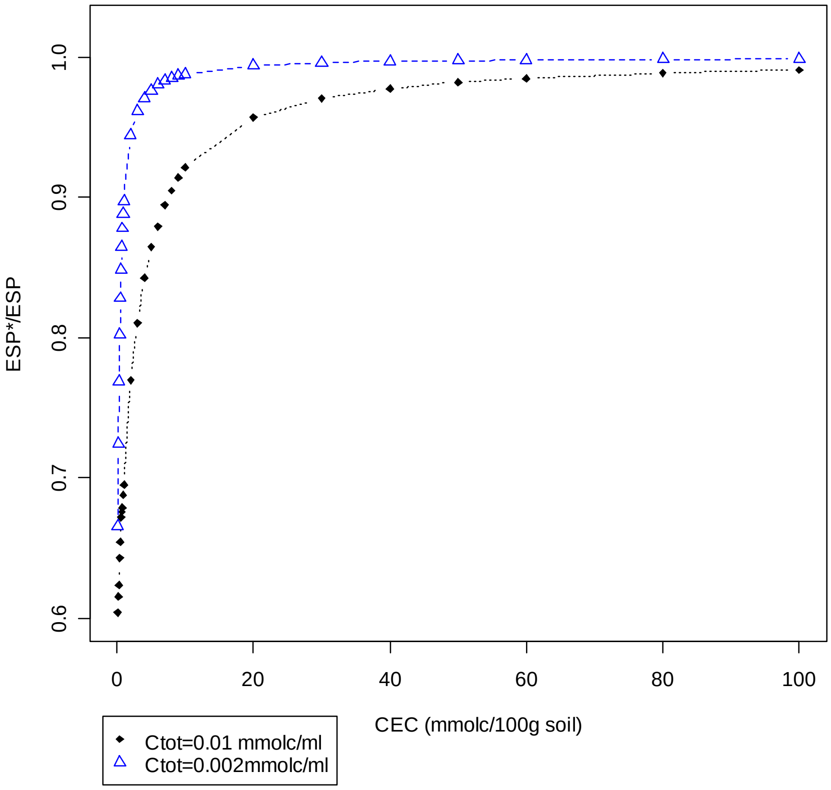


Figure 2.3: Relationship between ESP*/ESP and CEC for different C_{tot} and keeping constant r = 50ml/100g, CEC = 30mmol$_c$/100g and w = 25ml/100g.

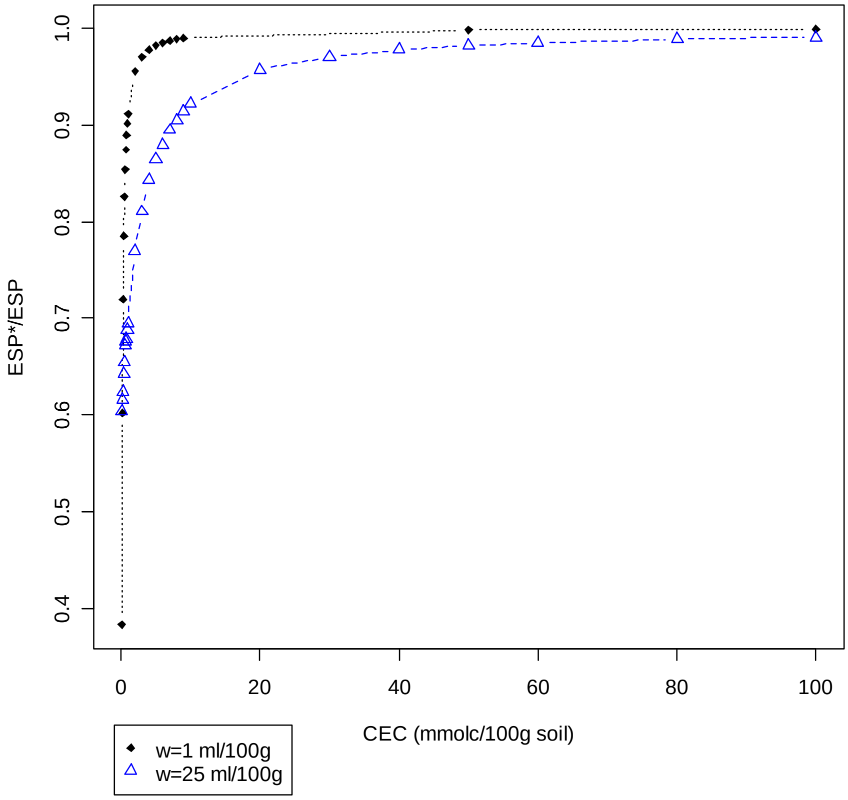


Figure 2.4: Relationship between ESP*/ESP and CEC for different w and keeping constant r = 50ml/100g, CEC = 30mmol$_c$/100g and C$_{tot}$ = 0.01 mmol$_c$/ml.

At last we consider figure 2.5, in which ESP*/ESP is shown in a range of r; ranges of r are different in different experiments and countries (USDA, 1954; White, 1966; Puls *et al.*, 1991), but a mean range we consider from 2 to 500 (ml/100g). We assume C_{tot} = 0.01 mmol$_c$/ml, w = 25 ml/100g and CEC = 30 mmol$_c$/100g. We chose this CEC value because it is in the range of typical agricultural soils. In fact, as mentioned in Bolt and Bruggenwert (1976), heavy clay soils exhibit CEC values of up to 40 mmol$_c$/100g.

We can note that for increasing r values the differences in the exchangeable sodium percentage ratios are more evident, though small and with a minimum of 0.93 for initial ESP = 5%. On the contrary, with ESP = 15% the ratio is never smaller than 99.3. This extreme situation arises with excessive input of a parameter. In our case we assume an increase quantity of water added to the soil system, and, as in figure 2.2, we can assume it as a particular case in which we have a big quantity of irrigation water. Hence the solution phase is dominant and the soil system will develop to the composition of the leaching solution.

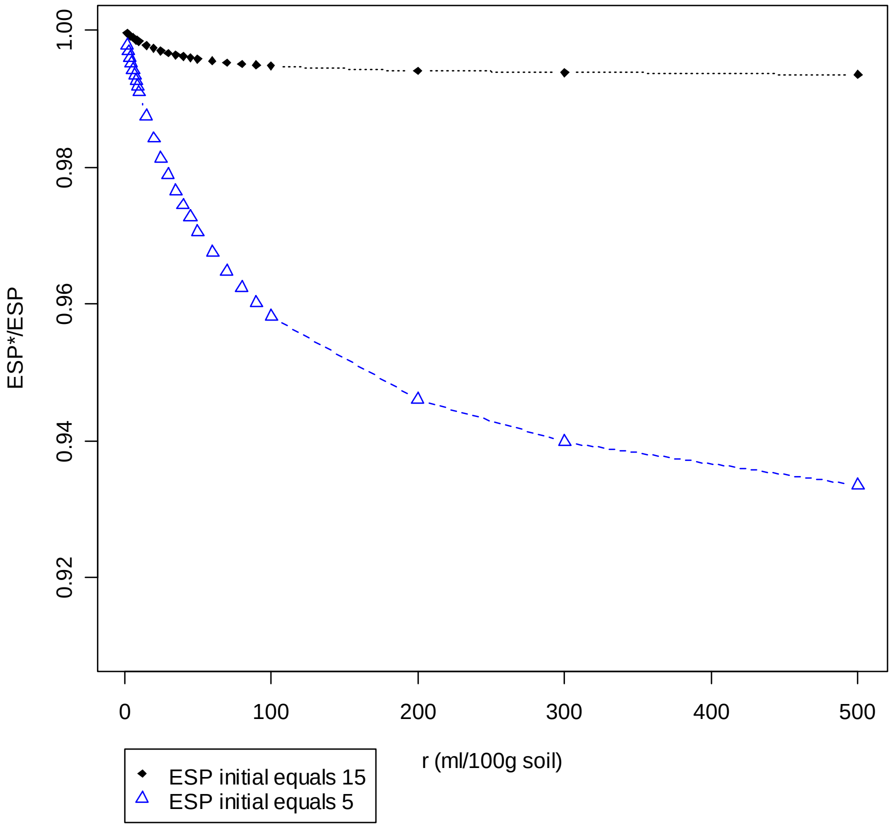


Figure 2.5: Relationship between ESP*/ESP and r for different initial ESP keeping constant w = 20ml/100g, CEC = 30mmol$_c$/100g and C_{tot} = 0.01 mmol$_c$/ml.

2.5. Conclusions

It is important to determine the exact ESP, from which we can obtain the fraction of sodium and calcium, because it allows to use reliable data. In fact, as said before, in different studies usually are used different parameters. Hence it is decisive to understand whether we can use them directly or where we need to obtain new data. The work here present gives us important results over this theme. Generally we can say that differences are low and this is due to the fact that we consider only dilution, thus the range of shifting of ions keeps low. The introduction of monovalent and divalent cations would give more differences in terms of shifting of them from the complex to the soil solution and vice versa. It also means that x is always negative, and it implies that the fraction of sodium in the exchangeable complex decreases, while calcium is increasing. The main differences we have if we consider low initial ESP or low CEC. On the contrary, in figure 2.3 and 2.4, if we consider a general CEC value of 30 mmol$_c$/100g, we note that ESP* has differences almost negligible.

Figure	r (ml/100g)	W (ml/100g)	C_{tot} (mmol$_c$/ml)	CEC (mmol$_c$/100g)	ESP	ESP*
2	50	25	0.01	30	5	4.853
2-3	50	25	*0.002*	30	5	4.980
3	50	*1*	0.01	30	5	4.985
4	*100*	25	0.01	30	5	4.791
4	*300*	25	0.01	30	5	4.699

Table 2.2: Comparison between different conditions keeping constant certain parameters.

Small differences we note also in figure 2.5 (see table 2.2), but here the high r value influences more ESP* than in the first three cases. Actually these two last conditions consider amounts of water added of 100% and 300% in weight respect to the soil. It means that are out of real conditions. However they can suggest how the soil behaves and how big differences there are for different case studies. At last we can suggest that under extreme conditions it should be important to check how big are the differences. Using very high quantity of water or very high saline waters generally implies differences that should be decisive to understand the problem. Usually it is under these extreme conditions that we have more evidences about what we are studying. On the other hand, under real conditions, differences in ESP*/ESP ratio are very small and we can assume that ESP parameter is in steady state conditions. We can also conclude that sodium and calcium fractions does not suffer big consequences by different initial conditions. At last we can say that differences in ESP values under different conditions are usually negligible. The study suggests that the values of ESP we find in literature are quite harmonized even if the initial conditions are not the same. Hence the comparison among different sodic soils usually can be done without allowing for the initial parameters.

3. SOIL SODICATION AS A RESULT OF PERIODICAL SALINITY

As mentioned in chapter 1, soil sodication significantly threatens agriculture in arid and semiarid regions in the world. Sodicity limits the production potential of soils due to affect on soil structure (So and Aylmore, 1993), such as swelling, dispersion and decrease of permeability that also involves the loss of water infiltration. As a result plant water uptake is more difficult and all these aspects mentioned before imply the soil degradation. Sodium is generally recognized to play a key role in sodication due to the possible high presence of it in water accompanied by a medium or low level of electrical conductivity, as shown in table 1.8 (Halliwell *et al.*, 2001). The decrease of water resources and quality will be one of the most problems in the future (UNESCO, 2003) and to use poor quality water, such as in irrigation, may give problems of salinization and even more of sodication. Seasonal salinity already occurs in many arid and semiarid regions because of accumulation of salts in the root zone unless extra water is added to the soil to leach down the salts. Studies demonstrate that the problem can arise also in non arid regions (Armstrong *et al.*, 1996; Tedeschi and Dell'Aquila, 2005). Usually this is mended by leaching requirement during or after the growing period, but much attention is paid as how to leach the salts (Howell, 1988); on the contrary little attention is paid to possible connection of such a practice to sodication of soils.

3.1. Materials and methods

The analytical model that we propose has the aim to describe the behavior both for sodicity and salinity in a homogeneous root zone, as a result of periodical irrigation with saline water. The main purpose of the analytical model is to determine and explain the relationship between salinity and sodicity and to pinpoint the origin of this relation. Hence keeping in view such a relation we want to describe how the soil sodication process deals with the soil structure. Using poor quality water we can increase the problem of salinity and sodicity even where rainfall is quite enough, thus problems may occur also in non arid regions. In fact the soluble salts that occur in soils consist mostly of various proportions of the cations sodium, calcium and magnesium, while the anions are usually chloride and sulfate. Potassium ordinarily occur in minor amounts, as nitrate and carbonate (USDA, 1954). Hence we assume a simplified situation in which salinity is due to the presence of sodium (also representing potassium) and calcium (also representing magnesium). Changes in salt concentration and distribution of calcium and sodium are calculated as the result of infiltration, drainage and evapotranspiration. Thus we have four sections that schematize the analytical model and that are represented in the figure 3.1.

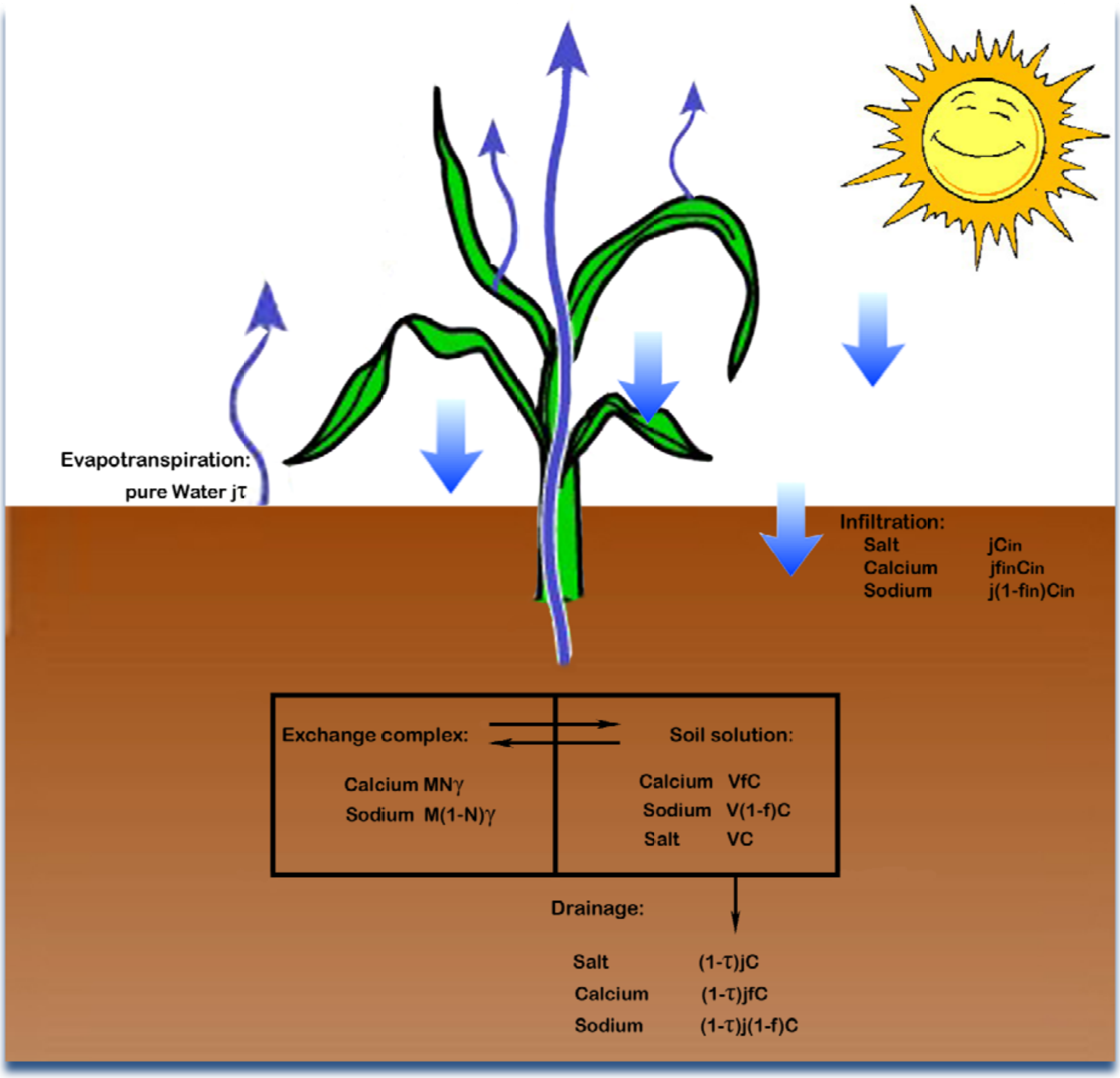


Figure 3.1: Visual representation of the model in which salt concentration C, calcium fraction in soil solution (f) and calcium fraction in the exchange complex (N) change in time as the result of infiltration, evapotranspiration and drainage.

During one season the different components of figure 3.1 will reach an equilibrium given by the initial conditions we assume:

1. infiltration: infiltration water enters the root zone at rate j ($L/m^2/y$) with a certain salt concentration C_{in} (mol_c/L). Infiltration water contains $f_{in}C_{in}$ mol_c/L of Ca^{2+} and $(1-f_{in})C_{in}$ mol_c/L of Na^+, where f represents the fraction of calcium in solution and (1-f) the fraction of sodium. Part of the water will evapotranspires at rate τj, where τ represents the fraction of infiltrating water that evaporates from the root zone. We reasonably assume that neither sodium nor calcium leave the soil with water that evaporates. Because the analytical model considers a constant volume of soil moisture V (L/m^2), water drains from the root zone at rate (1-τ)j;
2. soil solution: salts in soil solution we consider VC, where C represents the totals salt concentration in the soil solution, thus calcium in soil solution is VfC and sodium V(1-f)C. The salt concentration and composition in the drainage water are assumed to be identical to those in the soil-solution system;
3. exchange complex: in the exchange complex calcium equals MNγ, where M is the dry mass of the soil (kg_{soil}/m^2), N is the fraction of calcium in the complex, (1-N) represents the Na^+ fraction and γ (mol_c/kg_{soil}) the soil exchange capacity. Infiltration causes the change of the salt concentration C, and as a consequence it changes even fC and (1-f)C, calcium and sodium respectively in the solution. Because of the cation exchange the equilibrium immediately changes, hence Nγ and (1-N)γ change;
4. drainage: water drains at rate (1-τ)j. There is no difference between infiltration from the top or from the bottom of the root zone, in the form of poor quality water or capillary rise. In order to calculate the effect of evaporation we select $\tau = 1$, so that all the water entering the root zone will evaporate.

Thus the model develops in two different conditions: in the first half year we assume accumulation of salts. In this condition we assume no drainage and $\tau = 1$. On the contrary, in a second time we have leaching without evaporation, hence $\tau = 0$. Moreover the model was implemented considering the balance of total salts in the root zone, followed by the calcium balance.

3.1.1. Salt balance

As suggested above, the first part of the analytical model is the salt balance. Hence we assume that the change of total salt contents in the root zone (calcium and sodium) $V\Delta C$

equals the mass of salt entering the soil $jC_{in}\Delta t$ and the mass of salt leaving the soil system $(1-\tau)jC\Delta t$. We can write this balance in terms of differential equation dC/dt:

$$\frac{dC}{dt} = \frac{jC_{in} - (1-\tau)jC}{V} \tag{3.1}$$

The two different conditions we assume are accumulation period and leaching period. The first one we assume with $\tau = 1$, hence the differential equation will become:

$$\frac{dC}{dt} = \frac{j\,C_{in}}{V} \tag{3.2}$$

Integration with respect to time means:

$$\int dC = \frac{j\,C_{in}}{V}\int dt$$

And finally the analytical solution is:

$$C(t) = Co + \frac{j\,C_{in}\,t}{V} \tag{3.3}$$

In leaching period we will have a different condition, i.e. $\tau = 0$:

$$\frac{dC}{dt} = \frac{j\,(C_{in} - C)}{V} = \frac{j\,C_{in}}{V} - \frac{j\,C}{V} \tag{3.4}$$

We can solve it analytically with the method of variations of constants. Thus the equation can be rewritten as:

$$\frac{dC}{dt} = b - aC \tag{3.5}$$

Where $a = \frac{j}{V}$ and $b = \frac{j\,C_{in}}{V}$

At first we take the homogeneous part and we solve the differential equation:

$$\frac{dC}{dt} = -aC \rightarrow \frac{dC}{C} = -a\,dt \rightarrow lnC = -at + k \rightarrow C(t) = U\exp(-at) \tag{3.6}$$

Where U is a constant. We make a trial solution and we assume that U is a function of time. Again we can find derivation with respect to U (this is because we have the non-homogeneous differential equation):

$$\frac{dC}{dt} = U'exp(-at) - aUexp(-at) \tag{3.7}$$

At last we consider the non-homogeneous part, in which we can combine equation (3.5) with equation (3.7):

$$b - aC = U' exp(-at) - aU exp(-at)$$

Combining again with equation (3.6) gives the following result:

$$b - aU exp(-at) = U' exp(-at) - aU exp(-at) \rightarrow b = U' exp(-at) \quad (3.8)$$

Now we can integrate to find the value of U:

$$U' = b \exp(at) \rightarrow U = b \int exp(at) = {}^{b}/_{a} \exp(at) + k \quad (3.9)$$

Where k is a constant. Finally, combining equation (3.6) and (3.9) we obtain:

$$C(t) = \left({}^{b}/_{a}\ exp(at) + k \right) \exp(-at) = {}^{b}/_{a} + k \exp(-at) \quad (3.10)$$

At time t = 0 we find that $k = C_0 - {}^{b}/_{a}$; hence the final analytical solution for the salt balance during leaching period is:

$$C(t) = {}^{b}/_{a} + \left(C_0 - {}^{b}/_{a} \right) \exp(-at) \quad (3.11)$$

As expressed above we assume two different conditions that give together one complete cycle. The values in this calculation have been chosen such that soil salinity at the end of the year is the same as that of the beginning of that year. Hence the soil is well managed with respect to soil salinity.

3.1.2. Calcium balance

The second part of the analytical model is the calcium balance. The total calcium content in the soil system is:

$$T = fCV + NM\gamma \quad (3.12)$$

As for the salt balance, also here the change of calcium content ΔT is the difference between the mass of calcium entering the root zone ($jf_{in}C_{in}\Delta t$) and the calcium leaving the soil system $j(1-\tau)fC\Delta t$. In terms of differential equation we have:

$$VC\frac{df}{dt} + Vf\frac{dC}{dt} + M\gamma\frac{dN}{dt} = jf_{in}\,C_{in} - j(1-\tau)fC \tag{3.13}$$

We can rewrite dN/dt in terms of df/dt and dC/dt. In fact N is the fraction of calcium in the exchange complex, and using an exchange equation it is expressed in terms of calcium in the soil solution. To do this we use the Gapon equation in which the Gapon constant $K_G = 0.5\ (\text{mol/L})^{-1/2}$ (Bolt and Bruggenwert, 1976). This equation shows a bigger affinity for divalent cations instead of monovalent ones, but this affinity decreases as soon as the fraction of monovalent ions becomes greater. The Gapon equation (2.1) in terms of N, f and C reads:

$$\frac{(1-N)}{N} = K_G\frac{(1-f)C}{\sqrt{fC/2}} \tag{3.14}$$

Hence we can explicit N:

$$N = \frac{1}{1+K_G\sqrt{2C}\left(\frac{1}{\sqrt{f}} - \sqrt{f}\right)} \tag{3.15}$$

If we differentiate with respect to time t we obtain:

$$\frac{dN}{dt} = N^2\left(\frac{K_G\sqrt{f}}{\sqrt{2C}} - \frac{K_G}{\sqrt{2fC}}\right)\frac{dC}{dt} + N^2\left(\frac{K_G\sqrt{C}}{\sqrt{2f}} + \frac{K_G\sqrt{f}}{\sqrt{2f^3}}\right)\frac{df}{dt} \tag{3.16}$$

Now we can combine equation number (3.13) with (3.16) which give:

$$\frac{df}{dt} = \frac{jf_{in}C_{in} - j(1-\tau)fC + \left[\frac{M\gamma N(1-N)}{2C} - Vf\right]\frac{dC}{dt}}{VC + M\gamma N^2K_G\sqrt{C/2}\left(\frac{1}{\sqrt{f}} + \frac{1}{f\sqrt{f}}\right)} \tag{3.17}$$

Equation 3.17 shows how the calcium fraction in solution changes with respect to time. We can find it numerically, while the evolution of the Gapon equation can be used to find N simultaneously (equation 3.16). At last total calcium, expressed in figure 3.1 as $\text{mol}_c/\text{kg}_{soil}$ is obtained from equation (3.13) dividing all by M, dry mass of the soil ($\text{kg}_{soil}/\text{m}^2$).

The integrations of equations (3.1) and (3.17), from which we obtain the salt and calcium balance respectively, has been made with the classical Runge-Kutta 4th order method using the R environment and particularly the “odesolve” package (Press *et al.*, 1992).

Combining following seasons gives the possibility to calculate salinization and sodication hazard and behavior during several years as shown in the next paragraph. Table 3.1 summarizes the data set used for all simulations.

Simulations	**Initial values**					**Accumulation period**					**Leaching period**				
	V **(l/m^2)**	**M** **(kg/m^2)**	**γ** **(mol_c/kg)**	**C** **(mol_c/kg)**	**f**	**j** **$(l/m^2/y)$**	**C_{in}** **(mol_c/kg)**	**f_{in}**	**t** **(y)**	**τ**	**j** **$(l/m^2/y$**	**C_{in}** **(mol_c/kg)**	**f_{in}**	**t** **(y)**	**τ**
1 year simulation	90	390	0.25	0.0098	0.98	300	0.02	0.05	0.5	1	300	0.002	0.25	0.5	0
1 year simulation. Accumulation and leaching are evaluated with different time	90	390	0.25	0.0098	0.98	300	0.02	0.05		1	300	0.002	0.25		0
									0.25					0.75	
									0.75					0.25	
50-90 years simulation, with different CEC values	90	390		0.0098	0.98	300	0.02	0.05	0.5	1	300	0.002	0.25	0.5	0
			0.03												
			0.10												
Initial parameters from which are obtained 64 different combinations		390		0.0098	0.98				0.5	1		0.002		0.5	0
	30		0.15			300	0.02	0.20			300		0.33		
	90		0.45			900		0.60			900		1		

Table 3.1: Data set for different simulations of the analytical model.

3.2. Results and discussion

Figure 5.2 shows the evolution of total salts, calcium and sodium as the result of periodical irrigation with poor quality water ($C_{in,a}$ = 20 mmol$_c$/L, SAR = 19 (mmol/L)$^{1/2}$) followed by a leaching period. Referring to the tables number 1.5 and 1.6 we can classify this water as dangerous for the soil and main crops, due to its high salinization and sodication hazard respectively. Hence one year is divided into two periods, each one of six months. In the leaching period water quality is characterized by low electrical conductivity (EC_w = 0.2 mS/cm) and lower SAR (equals 2.1 (mmol/L)$^{1/2}$) than in the first part of the year. We assume these values reasonably true and they can be compared with tables 1.5 and 1.6 (USDA, 1954). As shown in the figure number 3.2, the salt concentration increases during the accumulation period because saline water enters the root zone. Moreover we assume there is not leaching, while all water incoming in the soil evapotranspires (τ = 1). If we consider that water which leaves the root zone is pure, due to evaporation and plant uptake, we can easily understand that there is a net salt accumulation in the soil system. After half a year the accumulation period finishes and the leaching period begins. As a result, the salt concentration rapidly decreases till initial values. This is due to the assumptions we made, i.e. values have been chosen such that soil salinity at the end of an entire cycle (one year) is the same of that at the beginning of the same year. It means we have a good management of the field with respect to salinity.

Even though the salt concentration in the root zone has not increased at the end of the year, this is different for the ESP of the soil. As we find in literature (Bolt and Bruggenwert, 1976; Halliwell *et al.*, 2001) sodication hazard arises when, after a period of irrigation with high saline water, there is a following period characterized by water with low EC, such as rainfall. As a consequence swelling and dispersion will be the main problems of the soil system, though are buffered when wastewater remains in the soil over certain critical flocculation values. This is the situation in which we presumably are, even though here we focus in the sodication process and not in its consequences. The results of figure 3.2 demonstrates that sodium content both in soil solution as well as in the exchange complex increase, due to the high sodium fraction of irrigation water (1-f = 0.95). Also ESP increases: if at the beginning we have ESP = 0.14%, due to extreme initial conditions we assume, at the end of accumulation period ESP = 2.4 (with CEC = 25 mmol$_c$/100g). As a result of high salt concentration and high SAR, sodium added with irrigation water is exchanged with calcium content of the exchange complex. This is due to the decreasing affinity of the complex for divalent calcium with respect to monovalent sodium (Bolt and Bruggenwert, 1976; Appelo and Postma, 2005). In fact the higher charged ions are preferred more strongly when the total solute concentration decreases. This effect is a consequence of the exponent that is used in the mass action equation. The graph even shows how, at the leaching period starts, high concentrated soil solution is leached, whereas sodium remains almost constant. It means that the major part desorbed is represented by calcium. The lack of balance between monovalent and divalent cations content in the soil is even more clear when we focus in the calcium behavior: during accumulation period the total calcium content is almost constant, due to a limited amount that is present in the irrigation water that enters the soil system. However we can see that a large quantity of the divalent cation desorbes as a result of the decrease preference of the exchange complex for calcium, due to the increase of total salt concentrations. Figure 3.2 even shows that, as soon as leaching period starts, highly concentrated water rich of calcium leaves the root zone in order to guarantee leaching in the second part of the year. In fact good quality water is used for leaching purposes, characterized by low salinity and sodicity levels. At last water content in the soil solution that leaves the root zone has a quantity of calcium far more pronounced than the total calcium content. We can conclude that ESP has increased in the soil due to two main processes: first for the great input of sodium during accumulation period, and second for the net output of calcium during leaching. It appears that calcium changes from immobile to mobile phase during accumulation, while it is leached in the second period because of the addition of good quality water.

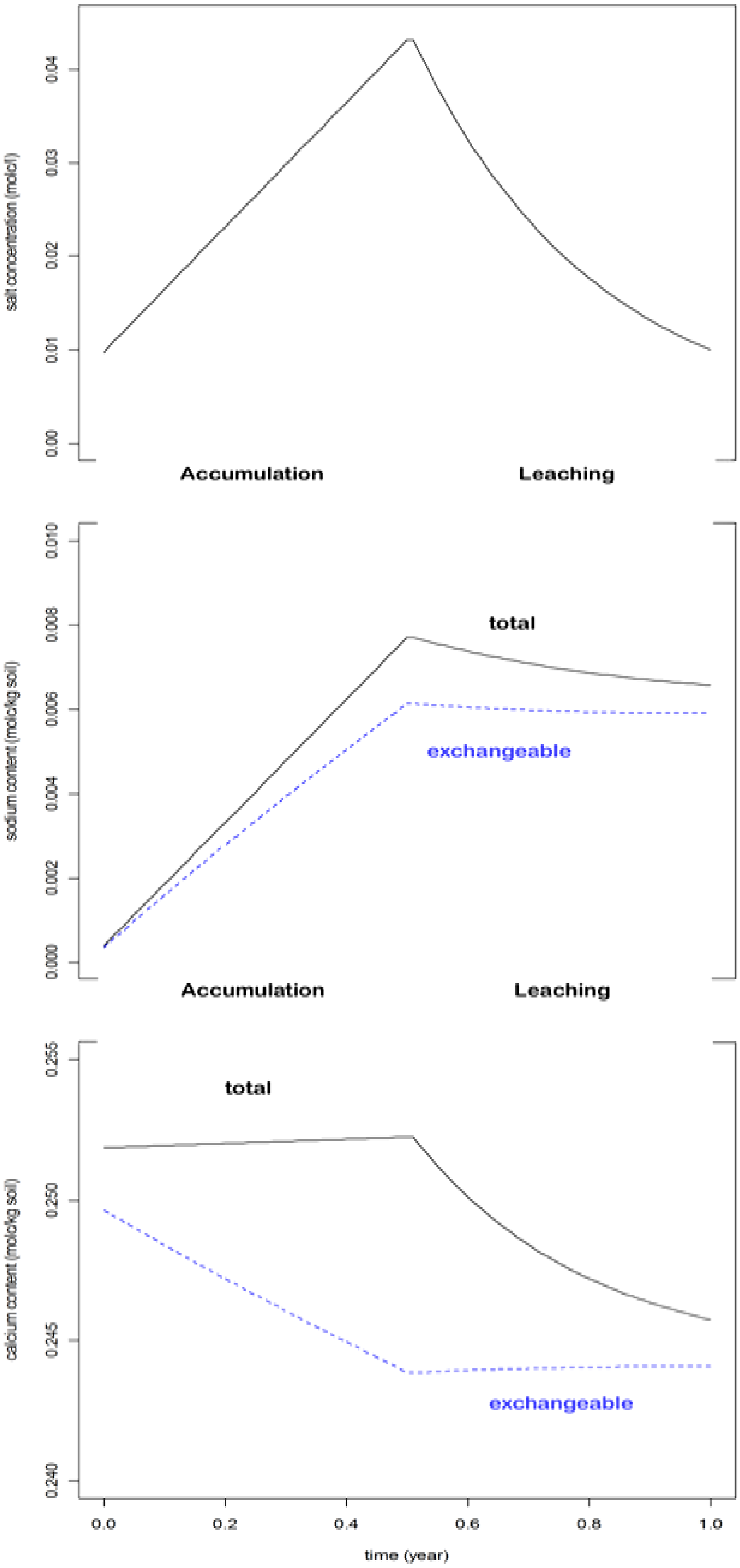


Figure 3.2: Evolution of salt, sodium and calcium contents during an accumulation period followed by a leaching period, both of half a year.

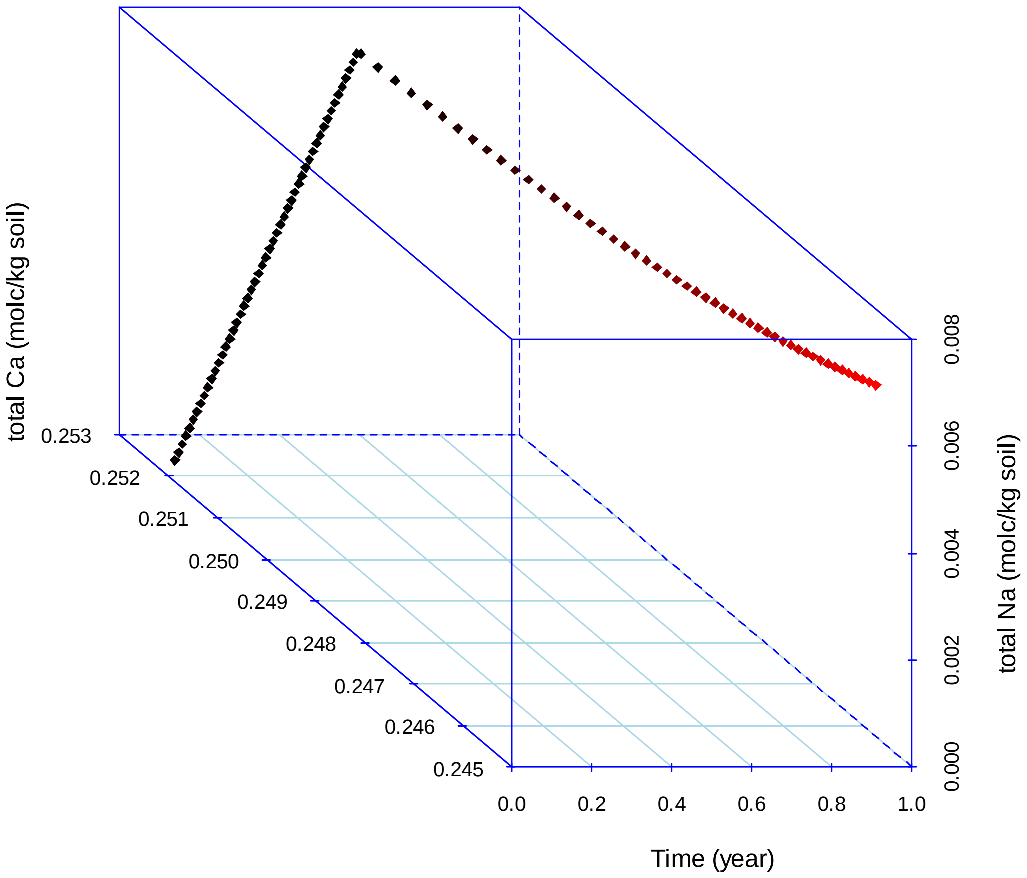


Figure 3.3: 3D representation of both cations (Ca^{2+} and Na^{+} in $mmol_c/kg_{soil}$) in the soil system with respect to time, during accumulation and leaching.

This is also proved when the calcium behavior has been compared in the three different scenarios below, in which the time of accumulation and leaching changes (figure 3.4). As explained before it states that the calcium content in the soil has been changed to the soil solution during the accumulation period.

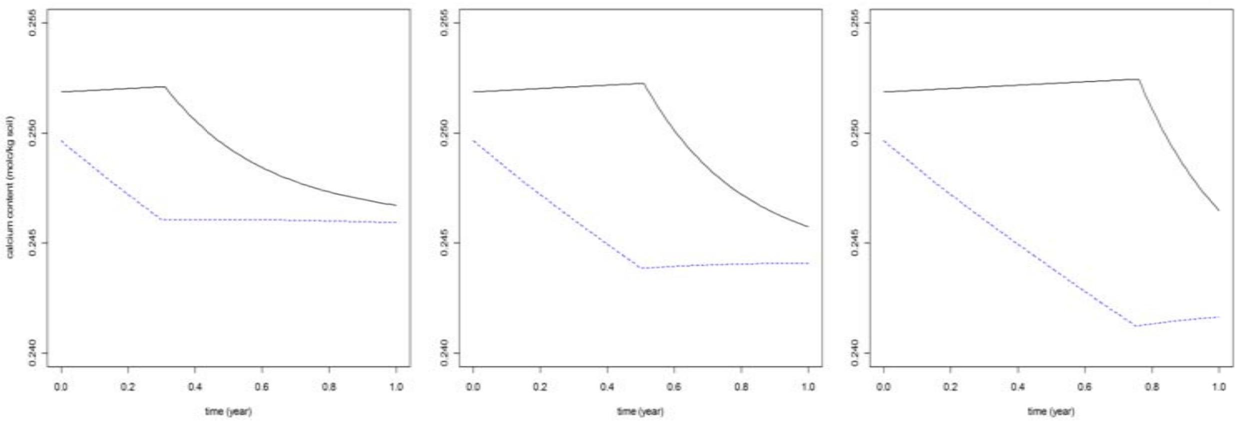


Figure 3.4: Total calcium (solid lines) and exchange complex (blue dotted lines) behavior with the changing time of accumulation and leaching. Initial data have been assumed the same of the figures 3.2 and 3.3.

The figure below (3.5) explains better the behavior of calcium between soil solution and exchange complex. In fact the major part of calcium in desorbed during accumulation, whereas the fraction in soil solution seems not to have a great increase, due to the high quantity of salts that is already present in the water. On the contrary in leaching period the fraction of calcium in the exchange complex is almost at steady state, while there is a great decrease in soil solution, due to the leaching effect. Eventually sodium has a great increase in the exchange complex during accumulation period, while it keeps almost constant in leaching. This is in agreement with the opposite calcium behavior.

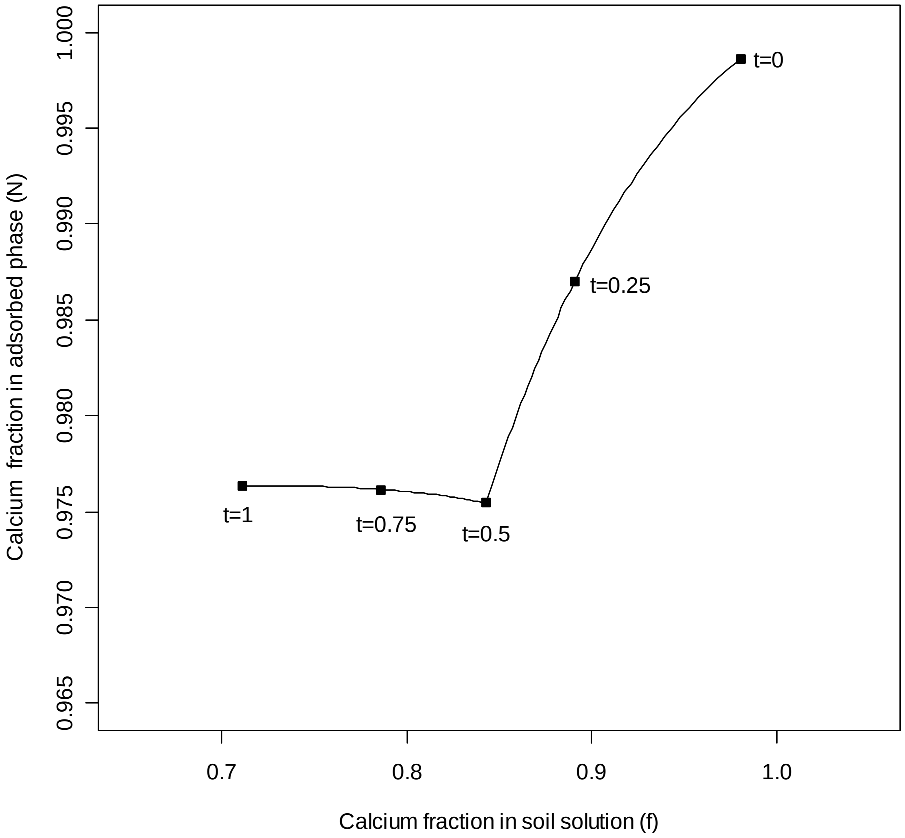


Figure 3.5: Relationship between calcium in adsorbed (N) and soil solution phase (f) during accumulation and leaching period.

Figure 3.7 shows two similar conditions that differ only CEC. In fact we can see the behavior of the soil system after several years. In accordance with the model we have, it is clear that salt concentration does not increase from one year to another, but there is an alternation between accumulation and leaching, as we expect. The parameters are identical to those of the figures 3.2-3.6, however we assume CEC of two different soil texture conditions, especially a low value (CEC = 3 $mmol_c/100g_{soil}$) and a higher one (CEC = 10 $mmol_c/100g_{soil}$). CEC has been chosen relatively small to obtain steady state for ESP within a short period of time, in fact assuming the same CEC of the figures above (CEC = 25 $mmol_c/100g$) the soil system does not reach steady state in a period of 90 years (figure 3.6).

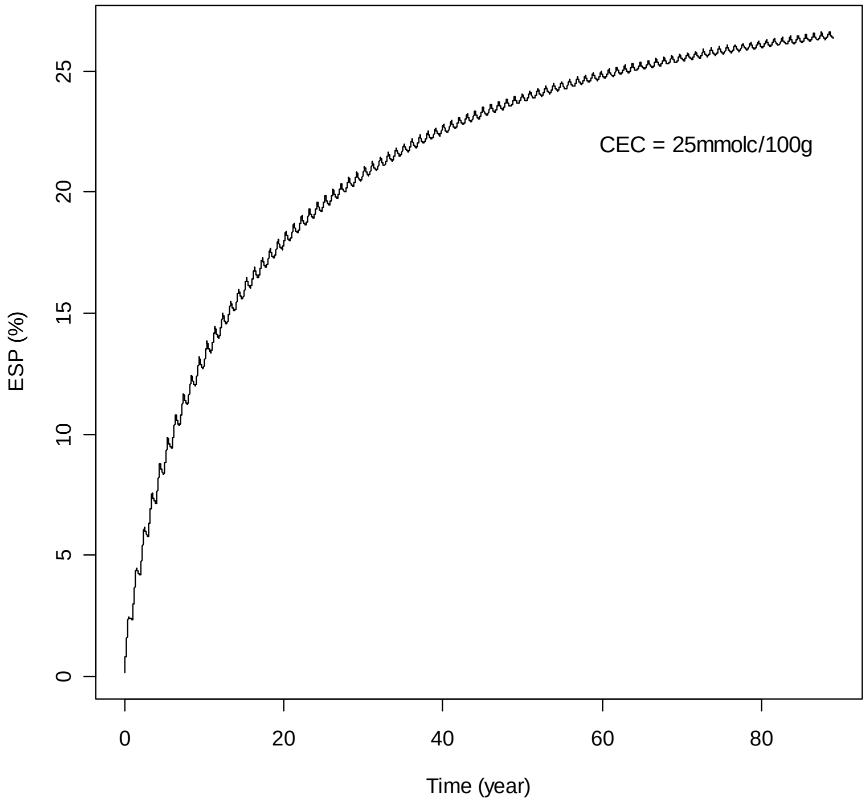


Figure 3.6: Sodium accumulation in the soil system for a 90 year time prediction.

Both cases (figure 3.7) eventually show a situation in which ESP, that is referred to two different CEC values, does not change from one year to another, while within the same year there is a variation due to the accumulation followed by the leaching period. We obtain these results assuming that the last values of each period must be the first of the next one. Hence in each period we have initial values, in terms of salt concentration and calcium fraction, that are the same of the last values of the period before. In this case, as in the calculations of the figures above (except for figure number 3.4), we consider that each period is of half a year, thus alternatively we have accumulation and leaching. The same management of the field is repeated for 50 years. The exchange complex in the soil steadily equilibrates to the saline and sodic solution which enters the soil in the accumulation period. In fact it states that in steady state there is a reduction of calcium desorption and sodium adsorption in the accumulation period as compared to the first few years. Hence there is less calcium leaching, but more sodium that is leached from the root zone in the drainage period. At last the soil system reaches steady state when the increase of calcium and sodium content in the accumulation is balanced by the same monovalent and divalent cations content during the leaching time.

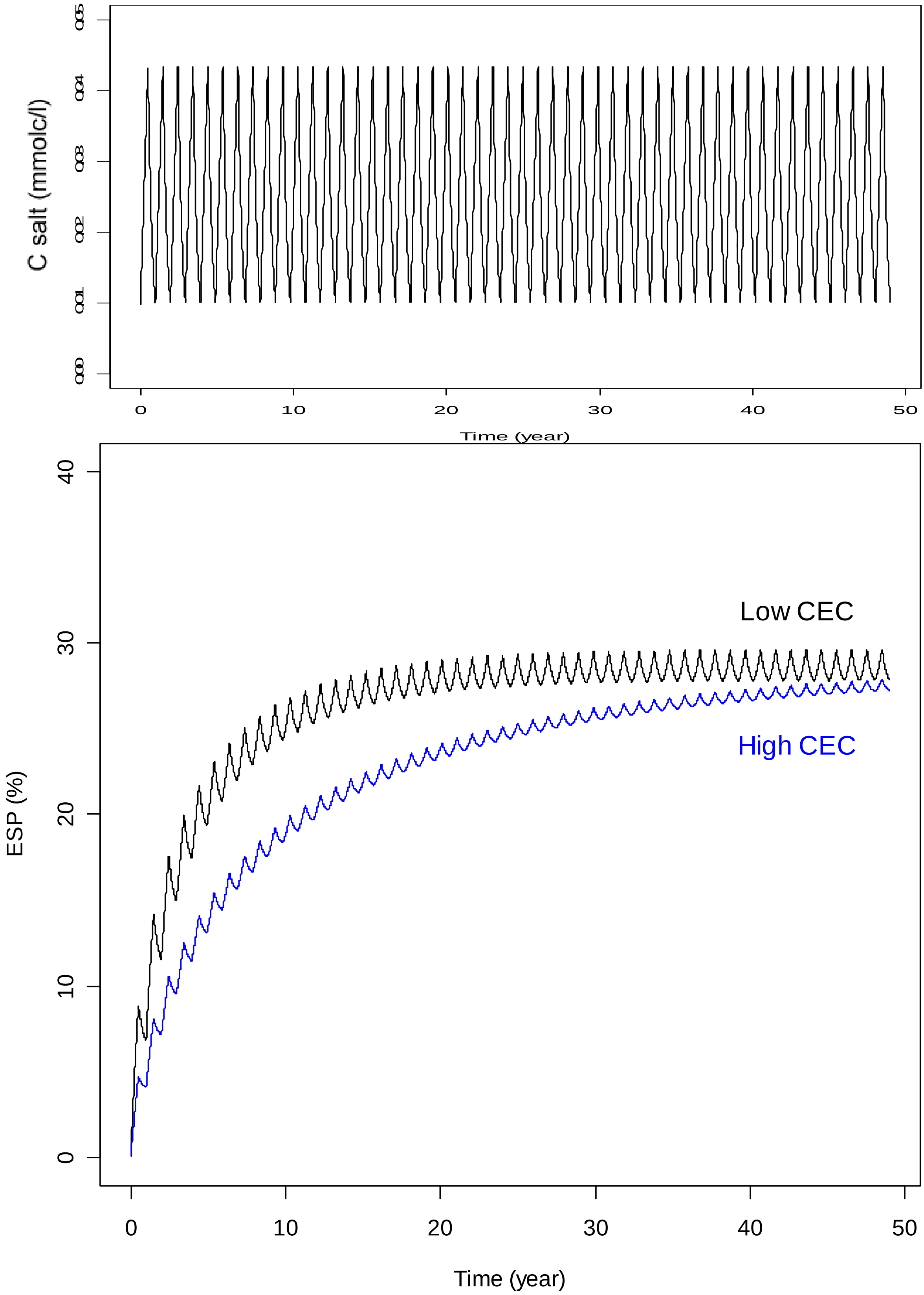


Figure 3.7: Salinization and sodication of two different root zone systems that differ only for CEC. Low CEC = 3 mmol$_c$/100g and high CEC = 10 mmol$_c$/100g.

There are others three aspects that need to be underlined:

1. variations within one year are more buffered with the higher CEC input. This may be explained if we consider that high CEC values means less percentage variations of ESP, assuming the same initial conditions;
2. as a result of the former, ESP takes a longer period of time to reach steady state with high CEC than with low CEC values;
3. it proves that CEC has not real effect on the final ESP as soon as the soil system has reached the steady state with respect to sodicity. As a consequence different soil textures could have the same problem on sodication due to this last aspect.

At last figure 3.7 even shows that a higher CEC value buffers the rate of sodication within one year, whereas it does not play a key role for the final ESP value after the soil system reaches a certain stability in terms of sodium accumulation. It seems that ESP is given by a concentrating process in the soil solution because of the negligible effect of CEC. Again, in figure 3.8 we can see the evolution of the sodium fraction in the soil solution (1-f) in a 3D representation, with the corresponding fraction in soil solution (1-f), whereas the time is 50 years, as in the figure above (3.7).

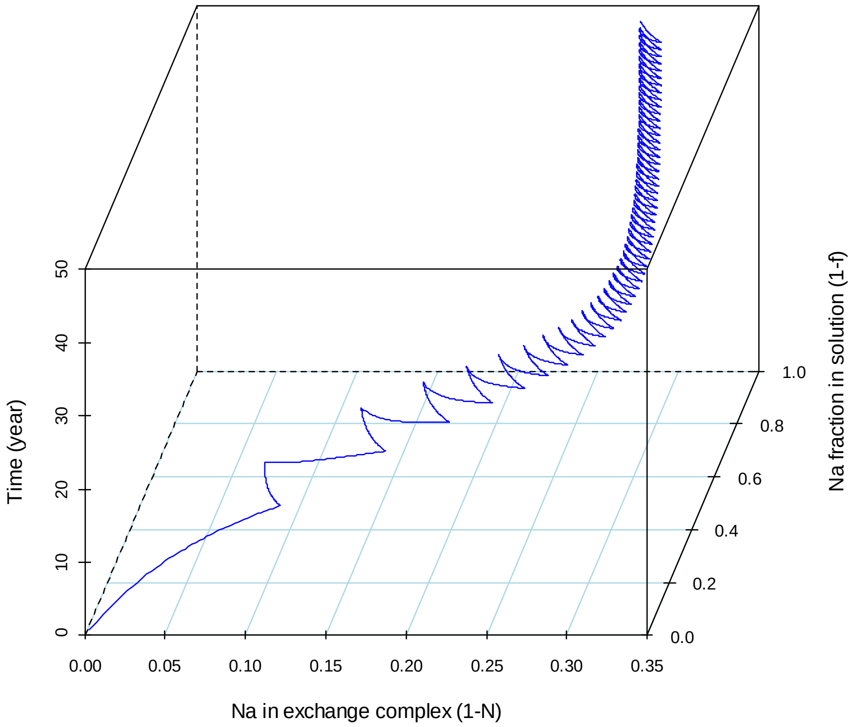


Figure 3.8: 3D graphic representation. The fraction of sodium in the exchange complex is related with its fraction in soil solution. CEC = 3 mmol$_c$/100g.

Figure 3.9 demonstrates the evolution of calcium fraction in accumulation and leaching period in 50 years. It is clear that in the exchange complex chemical reactions need more time to occur. In fact N (Ca^{2+} ratio in the exchange complex) is more buffered than f (Ca^{2+} ratio in soil solution). This aspect proves there are more fluctuations between monovalent and divalent cations in the soil solution compared to the exchange complex.

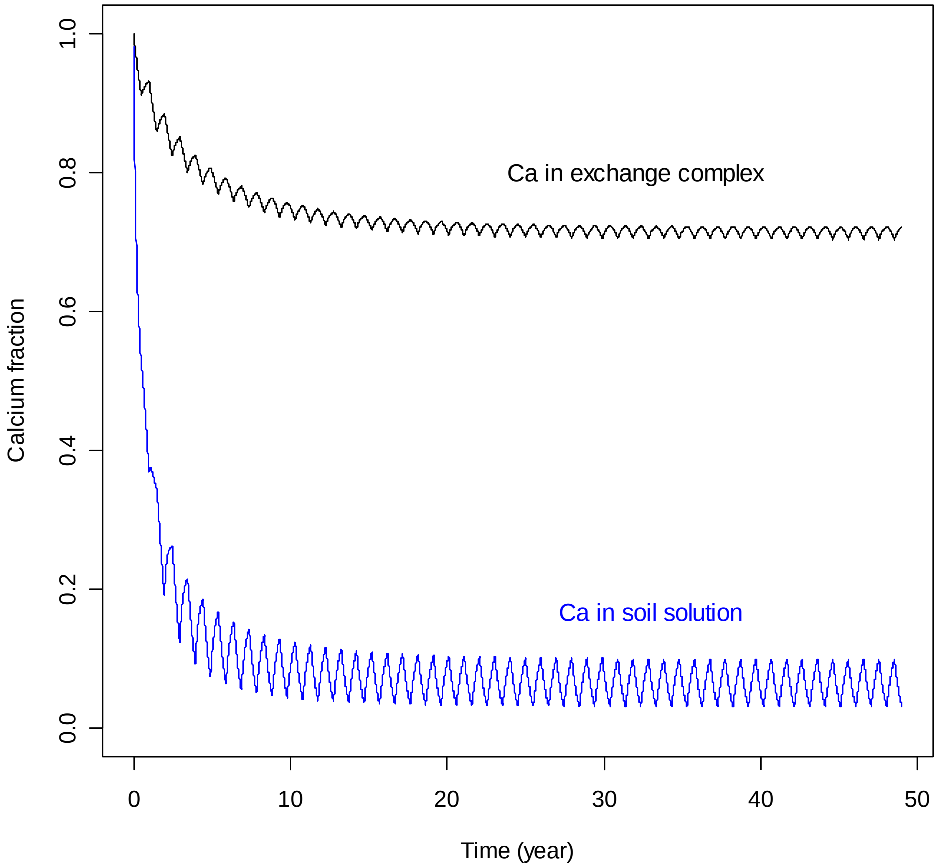


Figure 3.9: Calcium fraction in soil solution and in the exchange complex after 50 years. The figure has been obtained with the same initial conditions used for figure 3.7 at low CEC = 3 mmol$_c$/100g.

At last we define an upper limit for ESP_{final}, i.e. ESP_{max}, which is given by the following relation:

$$\frac{ESP_{max}}{100-ESP_{max}} = K_G \frac{x(1-f)C}{\sqrt{xfC/2}} \tag{3.18}$$

Where ESP_{max} is the maximum ESP value that can be reached in the soil and ESP_{final} the real one that is obtained with the simulation after several years, at steady state conditions.

This equation is the Gapon exchange equation (comparable with equation 2.1) that is expressed in terms of ESP (fraction of sodium in the exchange complex), fraction of sodium (1-f) and calcium (f) in soil solution and total salt concentration C. It can be used assuming that ESP_{max} is determined by concentration in the solution that enters the root zone in the accumulation period. The concentrating process accounts for concentration factor x, which is obtained from the ratio between the salt accumulation at the end of the accumulation period (C_a) and the concentration of poor quality water ($C_{in,a}$), thus we have:

$$x = \frac{C_a}{C_{in,a}} \tag{3.19}$$

This factor x is determined by two processes. To a high extent it is the result of accumulation during the accumulation period. The concentration at steady state with respect to salinity at the end of accumulation is calculated as:

$$C_a = C_l + \frac{j_a t_a C_{in,a}}{V} \tag{3.20}$$

Where j_a is the infiltration water during accumulation, t_a the time of accumulation, V the soil moisture and C_l the concentration at the end of the leaching period. It means that the same equation is valid even at the beginning of leaching period ($t = 0$, $\tau = 0$). The equation is found by integration of salt balance (3.1) with respect to time for $\tau = 1$. Additionally, salt concentration at the beginning of accumulation period is equal to that at the end of leaching period C_l.

At the end of leaching period is valid the following expression, found by integration of equation (3.1) with $\tau = 0$ and $C_{in,l}$ = salt concentration in leaching period :

$$C = C_{in,l} - \left[C_{in,l} - C_l - \frac{j_a t_a C_{in,a}}{V}\right] exp\left(-\frac{j_l}{V} t_l\right) \equiv C_l \tag{3.21}$$

Where j_l is the infiltration water during the leaching period and t_l the time of leaching. The identity says that the leached quantity (C_l in the right hand side of the identity) is approximately equal to the amount that is added in each accumulation period (C_l of equation 3.20). Moreover from the identity above we obtain that $C = C_l$ and it means that at the end of leaching period there is the same concentration of the next starting accumulation period; in fact we assume there is steady state, hence equilibrium. We can reorder this identity as:

$$C_l - C_{in,l} = \left(C_l - C_{in,l}\right) exp\left(-\frac{j_l}{V} t_l\right) + \frac{j_a t_a C_{in,a}}{V} exp\left(-\frac{j_l}{V} t_l\right) \tag{3.22}$$

Finally we can rewrite it again as:

$$C_l = C_{in,l} + \frac{j_a t_a C_{in,a}}{V}\left[\frac{exp\left(-\frac{j_l}{V} t_l\right)}{1 - exp\left(-\frac{j_l}{V} t_l\right)}\right] \tag{3.23}$$

Now we can find the x factor, combining equation 3.19 with equations 3.20 and 3.23:

$$x = \frac{C_a}{C_{in,a}} = \frac{C_{in,l} + \left(\frac{j_a t_a C_{in,a}}{V} - C_{in,l}\right) exp\left(-\frac{j_l}{V} t_l\right)}{C_{in,a}\left[1 - exp\left(-\frac{j_l}{V} t_l\right)\right]} + \frac{j_a t_a C_{in,a}}{V C_{in,a}} \tag{3.24}$$

Hence the concentration factor allows to determine which is the maximum level of ESP in the soil at the end of the accumulation period, thus ESP_{final} can be less or equal to ESP_{max}. In other words we can say that ESP_{max} is the sodium concentration of the soil if it is considered only accumulation. It is eventually possible because C_l, concentration at steady state at the end of leaching period, is exactly the same concentration at the beginning of accumulation. The development of these last calculations is expressed in figure 3.10. We consider an amount of 64 different combinations of parameters which determine 64 different scenarios (see table 3.2). Two values of $f_{in,a}$, $f_{in,l}$ (Ca^{2+} fraction of accumulation and leaching), j_a, j_l, V and γ have been used to obtain the figure below. The time parameter (t) is equal to 0.5 both for accumulation and leaching period due to the assumptions we made, i.e. the concentration factor x is obtained from concentration at the end of accumulation period, and C_l (see equation 3.21) is the salt concentration at the end of the leaching period (hence t = 0.5). Finally M = 390 kg/m^2, $C_{in,a}$ = 0.02 mol$_c$/L and $C_{in,l}$ = 0.002 mol$_c$/L. The x factor obtained from each scenario is constant.

Scenario	**ESP_{final}**		**ESP_{max}**		**V (L/m^2)**	**γ (mol$_c$/kg)**	**j_a (L/m^2/y)**	**j_l (l/m^2/y)**	**f_{in} acc.**	**f_{in} lea.**	**t (y)**
	end acc.	**end lea.**	**end acc.**	**end lea.**							
1	16.25	15.53	22.17	21.26	90	0.15	300	300	0.2	0.33	90
2	15.91	15.66	21.73	21.41	90	0.45	300	300	0.2	0.33	90
3	06.06	05.50	08.64	07.88	90	0.15	300	300	0.6	0.33	90
4	05.88	05.67	08.40	08.11	90	0.45	300	300	0.6	0.33	90
5	25.93	24.13	46.70	44.32	90	0.15	900	300	0.2	0.33	90
6	25.36	24.70	45.96	45.08	90	0.45	900	300	0.2	0.33	90
7	09.72	08.15	21.22	18.17	90	0.15	900	300	0.6	0.33	90
8	09.27	08.62	20.36	19.11	90	0.45	900	300	0.6	0.33	90
9	13.70	12.91	19.25	17.88	90	0.15	300	300	0.2	1	90
10	13.55	13.17	18.70	18.21	90	0.45	300	300	0.2	1	90
11	05.11	04.37	07.33	06.29	90	0.15	300	300	0.6	1	90

12	04.89	04.61	07.02	06.63	90	0.45	300	300	0.6	1	90
13	24.61	22.46	44.97	42.02	90	0.15	900	300	0.2	1	90
14	23.98	23.18	44.12	43.03	90	0.45	900	300	0.2	1	90
15	09.22	07.47	20.25	16.81	90	0.15	900	300	0.6	1	90
16	08.72	08.00	19.30	17.88	90	0.45	900	300	0.6	1	90
17	20.15	19.40	36.39	35.29	30	0.15	300	300	0.2	0.33	90
18	18.87	18.61	34.52	34.12	30	0.45	300	300	0.2	0.33	90
19	07.25	06.62	15.05	13.84	30	0.15	300	300	0.6	0.33	90
20	07.04	06.81	14.64	14.21	30	0.45	300	300	0.6	0.33	90
21	32.09	30.22	64.81	62.81	30	0.15	900	300	0.2	0.33	90
22	31.45	30.79	64.14	64.43	30	0.45	900	300	0.2	0.33	90
23	11.85	10.04	34.38	30.32	30	0.15	900	300	0.6	0.33	90
24	11.27	10.60	31.11	31.61	30	0.45	900	300	0.6	0.33	90
25	20.85	20.13	37.27	36.35	30	0.15	300	300	0.2	1	90
26	16.66	16.27	31.18	30.57	30	0.45	300	300	0.2	1	90
27	06.03	05.16	12.69	10.98	30	0.15	300	300	0.6	1	90
28	05.79	05.48	12.21	11.62	30	0.45	300	300	0.6	1	90
29	30.45	28.18	63.05	60.47	30	0.15	900	300	0.2	1	90
30	29.77	29.00	62.30	61.38	30	0.45	900	300	0.2	1	90
31	11.16	09.11	32.88	28.08	30	0.15	900	300	0.6	1	90
32	10.56	09.80	31.52	29.77	30	0.45	900	300	0.6	1	90
33	12.33	11.39	15.80	14.63	90	0.15	300	900	0.2	0.33	90
34	12.04	11.71	15.44	15.03	90	0.45	300	900	0.2	0.33	90
35	04.98	04.44	06.53	05.84	90	0.15	300	900	0.6	0.33	90
36	04.79	04.59	06.29	06.03	90	0.45	300	900	0.6	0.33	90
37	21.07	19.00	37.70	34.70	90	0.15	900	900	0.2	0.33	90
38	20.51	19.76	36.90	35.82	90	0.45	900	900	0.2	0.33	90
39	07.74	06.12	15.98	12.87	90	0.15	900	900	0.6	0.33	90
40	07.25	06.62	15.05	13.84	90	0.45	900	900	0.6	0.33	90
41	08.11	06.34	10.53	08.28	90	0.15	300	900	0.2	1	90
42	07.71	07.09	10.03	09.23	90	0.45	300	900	0.2	1	90
43	03.17	02.15	04.19	02.85	90	0.15	300	900	0.6	1	90
44	02.90	02.52	03.83	03.34	90	0.45	300	900	0.6	1	90
45	17.96	14.83	33.16	28.29	90	0.15	900	900	0.2	1	90
46	17.15	16.01	31.92	30.17	90	0.45	900	900	0.2	1	90
47	06.59	04.36	13.78	09.36	90	0.15	900	900	0.6	1	90
48	06.02	05.16	12.69	10.98	90	0.45	900	900	0.6	1	90
49	17.34	16.24	32.14	30.45	30	0.15	300	900	0.2	0.33	90
50	16.77	16.39	31.27	30.69	30	0.45	300	900	0.2	0.33	90
51	06.56	05.81	13.68	12.24	30	0.15	300	900	0.6	0.33	90
52	06.32	06.06	13.22	12.70	30	0.45	300	900	0.6	0.33	90
53	30.21	27.95	62.71	60.12	30	0.15	900	900	0.2	0.33	90
54	29.47	28.66	61.88	60.96	30	0.45	900	900	0.2	0.33	90
55	11.08	09.10	32.63	28.00	30	0.15	900	900	0.6	0.33	90
56	10.39	09.66	31.05	29.36	30	0.45	900	900	0.6	0.33	90

Table 3.2: Data set and results of ESP$_{max}$ and ESP$_{final}$ obtained for 64 different scenarios.

As highlighted before, all figures show that ESP$_{max}$ is bigger than the corresponding ESP$_{final}$; this is the effect given by the x factor. In fact we assume it is a factor that allows to evaluate the maximum concentration of sodium in the exchange complex. Referring to the first of the six graphs, keeping constant $f_a = 0.2$ and $f_a = 0.6$ (figure 3.10A), we can say that for a high fraction of sodium (i.e. low f_a) ESP_{final} is generally high. So that also more sodium enters the root zone, hence more sodium is in the soil solution and more exchange will occur between soil solution and exchange complex. In the same graph we can see that points referred to the same f_a are almost on a straight line: it means that probably the x factor is quite affected by f_a. The graph even shows that the bigger is sodium ratio ($1-f_a$), the smaller is x factor; in fact points plotted with high ($1-f_a$) are close to the 1:1 line. It can be concluded that for high sodium concentration there is a decreasing affinity of the exchange complex for divalent cations (i.e. calcium) with respect to monovalent one (that is sodium) (Appelo and Postma, 2005). In fact the real ESP that we obtain after the accumulation and leaching process, i.e. ESP_{final}, is more similar to the maximum theoretical value, that is represented by $ESP_{max.}$ If we compare the same graph with the second (figure 3.10B) we can see different results: while in the first case (keeping f_a constant, figure 3.10A) there is a net difference in the behavior of ESP_{max} with respect to ESP_{final}, in the second graph (figure 3.10B) there is a sort of mixing between results of different f_l. Probably this is related with a less evident leaching effect in the exchange complex with respect to the accumulation period. In fact differences in f_l do not underline a different behavior on ESP_{final} and ESP_{max}. As explained before, probably calcium is replaced from the immobile to the mobile phase during the accumulation period, while during leaching it is removed from the root zone. Moreover there is a less salt concentration during leaching ($C_{in,l}$) and it probably limits the exchange effect because of a less Ca^{2+} quantity in leaching than in accumulation. The x factor is determined by a concentrating process during accumulation, hence different values of calcium ratio during leaching do not demonstrate variations in the relation between ESP_{max} and ESP_{final}. We can suppose the same soil behavior even for results referred to the fourth graph (keeping constant j_l, figure 3.10D).

The third graph (figure 3.10C) shows the behavior of ESP_{max} with respect to ESP_{final} keeping constant j_a, which is the quantity of water that is added in the root zone during the accumulation period. We note two different trends referred to two different quantity of water. In both cases the quantity of water during accumulation is characterized by high salt and sodium concentration; more water added to the soil system means also more sodium that enters the root zone, hence the accumulation of sodium is bigger than for low $j_a = 300$ mm.

The fifth graph (figure 3.10E) shows different ESP values if the moisture content of the soil is kept constant. It is clear that at lower soil moisture value ($V = 30$ L/m^2) there is a more concentrating process of sodium in the soil system, thus ESP becomes more than for V = 90 L/m^2. On the other hand for V = 30 L/m^2 the x factor generally seems to be bigger than for high V. We can conclude that in the first case the differences between ESP_{max} and ESP_{final} are more stressed. Probably this last aspect proves that, referring to the ESP exchange equilibrium, with high V it is more important the accumulation period instead of the leaching period.

At last we analyze the sixth graph (figure 3.10F): we can see that values of ESP are well mixed and it is in accordance with figure 3.7. In fact at steady state the effect of CEC is quite limited; we conclude, as highlighted before, that CEC has a negligible effect in the process of sodium accumulation.

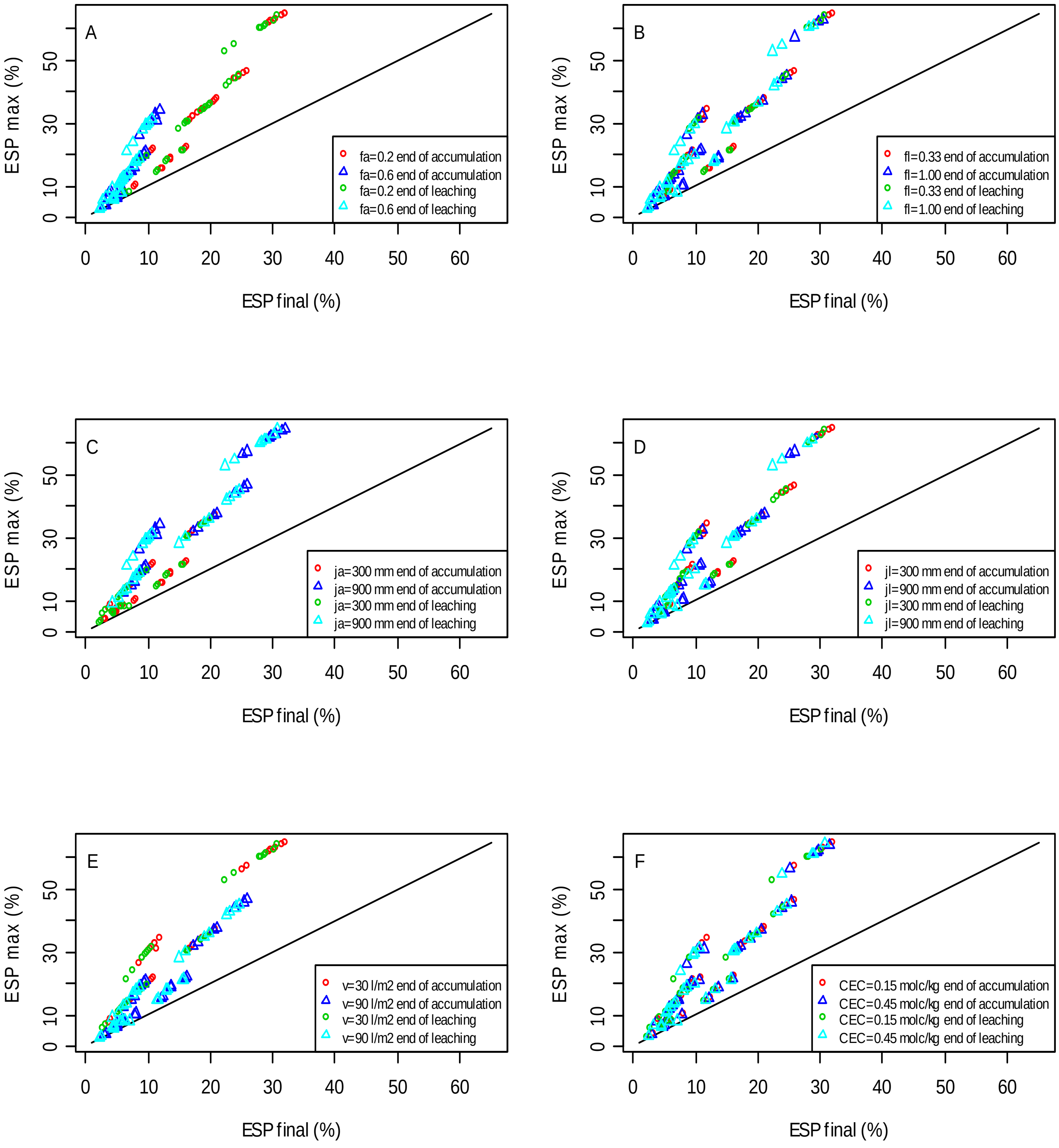


Figure 3.10: Relationship between ESP_{max} and ESP_{final} for different combinations at stedy state conditions. All six graphs show the same 64 scenarios, but different combinations determine different situations. End of accumulation and end of leaching refer to which points are plotted at steady state conditions.

3.3. Conclusions

To manage the soil in a good way is fundamental to avoid the loss of structure and maintain the soil fertility. The model demonstrates that even if salinity problems are under control, soil sodication is not avoided yet. There are also experimental evidences that bear out the same results (Minhas *et al.*, 2006). In fact in both cases (theoretical data and practical experiments) it states that an increase of ESP values tend to be maintained after several years. Other confirmations on field experiments come from Tedeschi and Dell’Aquila (2005): it states an increase of soil salinity and sodicity during a seven year cycle in which ESP shows less variations than the total salt concentration. The study takes into account the electrical conductivity of the extracting water and the ESP index. Due to the irrigation with poor quality water and the following natural leaching given by the annual rainfall is has been proved that ESP has a continuous increase during the seven year cycle. On the other hand EC_e shows a seasonal variability and such that measures of electrical conductivity plotted all together and related to autumn and spring (i.e. after irrigation and rainfall periods) have to be considered as belonging to two different populations. The comparison has been done evaluating all data of ESP and EC_e respectively in two different graphics finding the regression line and the correlated coefficient of determination. In addition the work highlights a very good relationship between ESP and the IASW index (index of aggregate stability in water), which determines the stability of a soil sample. It has been demonstrated one more time that the sodium ratio of the soil solid phase determines has a great effect on the soil structure.

Even in Miller and Pawluk (1994) has been proved the same conclusion that is highlighted by the model: in fact the fluctuation within the soil of the salt concentration is accompanied by the increase of sodium in the soil system. It can be concluded that, in both the theoretical model that has been developed and experimental results, the behavior of salinity and sodicity follows different paths: while soil salinity shows an alternation between high and low values, the sodication process is the result of a sort of accumulation effect that is affected by the lack of sodium, that leaches the root zone, and its accumulation when poor quality water has been added to the soil.

4. THE NECESSITY OF LEACHING REQUIREMENT: SALINITY AND SODICITY

4.1. Leaching Requirement: an introduction

The leaching requirement may be defined as the fraction of irrigation water that may be leached through the root zone to control soil salinity at any specified level. We must always express the leaching requirement as a fraction in order to check whether the fraction is not too high compared with the fraction for consumptive use and in view of the permeability of the soil. If leaching requirement is too high, we must choose a higher value of EC_{dw}, that means in practice shift towards more salt tolerant crops.

The leaching requirement depends on the salt concentration of the irrigation water and upon the maximum concentration permissible in the soil solution. The maximum concentration of the soil solution is the same as the concentration of drainage water from a soil where irrigation water is applied with areal uniformity and with no excess leaching (USDA, 1954). To explain the meaning of leaching requirement we can assume the simplest possible situation, in which we assume the following conditions:

- uniform areal application of irrigation water and uniformity of leaching;
- no rainfall;
- the amounts of salts exported by crops are negligible;
- all salts are highly soluble and do not precipitate;
- the calculation will be based on steady state water flow rates;
- bad management of the field, as water runoff and water uptake by shallow groundwater, are not included.

With these assumptions moisture, depth of the root zone, cation exchange reactions and drainage conditions of the soil do not need to be considered. Leaching requirement, hence, is simply the ratio of the equivalent depth of the drainage water to the depth of irrigation water and may be expressed as a fraction or as a percentage:

$$LR = \frac{D_{dw}}{D_{iw}} = \frac{EC_{iw}}{EC_{dw}} \tag{4.1}$$

Where D_{dw} (cm^3/cm^2) is the amount of drainage water, D_{iw} (cm^3/cm^2) the amount of irrigation water, EC_{iw} and EC_{dw} (mS/cm) the electrical conductivity of irrigation and drainage water respectively. The value we obtain and that we will consider as the requirement of leaching will be the amount of water we need to provide in addition.

Information about the consumptive use of water (D_{cw}) by the crops is necessary if the leaching requirement concept is to be used for determining either the depth of irrigation water that must be applied or the minimum depth of water to be drained, in order to keep the soil salinity from exceeding a specified value. Thus we have:

$$D_{iw} = D_{cw} + D_{dw} \tag{4.2}$$

Problems can arise when drainage is inadequate, hence water applied for leaching may cause the rise of water table, so that soluble salts can return to the root zone with any positive effect.

4.1.1. Drainage of irrigated lands related to salinity control

Drainage in agriculture is the process of removal of excess water in the soil. The terms “artificial drainage“ and “natural drainage” indicate whether or not man has changed or influenced the drainage process. Drainage is linked with leaching requirement. In fact we can have leaching of salts or of a particular ion when we have drainage conditions. The adequacy of drainage for agricultural purposes depends on different conditions. For example inadequate aeration of the soil can have severe consequences and limitation to the growth of the plants; even particular salinity conditions, as outlined above, can have negative effect on crops and soil. Especially in irrigated regions the adequacy of drainage is related to salinity. Salts in irrigation water or in shallow groundwater increase the drainage requirements (USDA, 1954). Finally we can say that irrigation water quality, leaching and soil management, that involves salinity control, are important in establishing drainage requirements. Thus if we need to maintain a favorable salt balance in the soil and we know the consumptive use of water, we can use the two expressions above, i.e. number (4.1) and (4.2) together, to have the following result:

$$D_{dw} = \frac{D_{cw}}{1-LR} LR \tag{4.3}$$

Drainage water D_{dw} does not include drainage water that moves in laterally from adjacent areas and that must pass into and through the drainage system; on the contrary it represents the quantity of water that exceeds the consumptive use. Thus for any specified EC_{dw}, that depends arbitrary in which tolerance level we consider, the depth of drainage water (D_{dw}) is the minimum depth of water that is required to be drained. From this simple relation we can see that leaching and drainage are well correlated.

4.2. Leaching requirement parameters: saturated paste and field capacity

The concentration of the soluble salts in the soil solution is influenced by the moisture content. With the purpose to characterize the salt content of the soil it is logical to measure this concentration at a standardized moisture content of the soil. Thus the salinity is usually characterized by means of electrical conductivity of the saturation extract (EC_e, mS/cm). This extract is usually obtained by suction-filtration of a water-saturated paste of the soil (Bolt and Bruggenwert, 1976), which depends on the pores percentage of the soil. From these criteria the U.S. Salinity Laboratory (1954) proposed a classification of saline soils with respect to expected salt damage to crops:

EC_e (mS/cm)	**0-2**	**2-4**	**4-8**	**8-16**	**> 16**
Effect on crop	Salinity effect mostly negligible	Yields of very sensitive crops may be restricted	Yields of many crops restricted	Only tolerant crops yield satisfactorily	Only a few very tolerant crops yield satisfactorily

Table 4.1: Expected salt effect on crop growth as a function of the concentration in the saturation extract. Source USDA Handbook No. 60, 1954.

Another important moisture parameter is called field capacity, that is the quantity of water held in the soil after excess of water has drained away; it means that water that moves for gravity is all drained. The physical definition of field capacity is the bulk water content retained in the soil at -0.33 bar. Measurements of salt water concentration may be done even at field capacity.

4.3. The extension of the leaching requirement to sodicity

To solve sodicity problems of a soil we can develop the leaching requirement technique referring to sodicity. The study that is presented here aims to analyze two different cases of leaching requirement (LR), related with saline and sodic waters. In fact there are studies that find a relationship between sodication and salinization of soils (Kaledhonkar *et al.*, 2001), and as the model proposed in chapter 3 shows. The good management of the soil needs to evaluate more than only one aspect. The harmonization of salinity and sodicity and the consequent extension of leaching requirement to sodicity problems may be useful:

1. to evaluate whether salinity or sodicity is the main problem to control;
2. as a consequence to operate in the soil with respect to the major problem, that can be salinization or sodication.

The first step is to consider the balance of the annual increase of EC-value of the profile of the soil, which equals (Bolt and Bruggenwert, 1976):

$$\Delta EC = \frac{(EC_{iw}\, D_{iw} - EC_{dw}\, D_{dw})}{D_{soil}\, SP\, \frac{\rho_b}{100}} \tag{4.4}$$

Where ΔEC (mS/cm) is the variation of electrical conductivity of soil solution, SP (cm^3/100g) the average soil moisture content at saturated paste and ρ_b (g/cm^3) the average bulk density. From this equation, if we assume that $EC_{dw} \approx EC_{FC}$ (field capacity) and considering that salinization gradually comes at steady state we have:

$$EC_{FC} \approx EC_{dw} = \frac{Diw}{Ddw} EC_{iw} \tag{4.5}$$

When we assume ΔEC = 0 (at equilibrium), i.e. salt accumulation kept null. If we assume also that:

$$EC_e = EC_{FC}\frac{FC}{SP} \approx \frac{D_{iw}}{D_{dw}} EC_{iw}\frac{FC}{SP} \tag{4.6}$$

Where EC_e (mS/cm) is the electrical conductivity of the saturation extract and FC (cm^3/100g) the moisture content at field capacity, finally we obtain:

$$LR = \frac{FC}{SP}\frac{EC_{iw}}{EC_e} = \frac{D_{dw}}{D_{iw}} \tag{4.7}$$

In this case LR refers to values of extracting water at field capacity as the relationship of equation (4.6) shows. Here FC is the fraction of soil moisture at field capacity, while SP is the soil moisture of extracting water at saturated paste (cm^3/100g). Values of electrical conductivity of irrigation water considered reasonable were obtained from Kaledhonkar *et al.* (2001) and Pescod ("Wastewater treatment and use in agriculture - FAO - irrigation and drainage paper 47", 1992). These respectively refer to poor alkali water and domestic wastewater of two Egyptian cities, Alexandria and Giza. There is, in fact, a reasonable relationship with the classification of irrigation water proposed by the U.S. Salinity laboratory Staff (1954) and found in Bolt and Bruggenwert (1976):

	EC (mS/cm)
Low salinization hazard (Bolt, 1976)	**< 0.25**
Medium salinization hazard (Bolt, 1976)	**0.25 < X < 0.75**
High salinization hazard (Bolt, 1976)	**0.75 < X < 2.25**
Very high salinization hazard (Bolt, 1976)	**> 2.25**
Kaledhonkar 2001 1st	**1.07 Alkali water**
Kaledhonkar 2001 2nd	**1.11 Alkali water**
FAO 1992 Alexandria	**3.10 Domestic wastewater**
FAO 1992 Giza	**1.70 Domestic wastewater**

Table 4.2: Comparison of different kinds of water.

Values of EC of extracting water (EC_e) are referred to Bolt and Bruggenwert (1976), in which concentration in the saturation extract is related with salinity effects for different crops. Yields of many crops are restricted for EC_e more than 4 mS/cm, with major value of 16 mS/cm in which only a few very tolerant crops yield satisfactorily.

Saline water is generally linked with problems of sodicity, and so it is important to consider also the relationship that exists between them. In fact the process of salinization is accompanied with a gradual adjustment of the composition of the adsorption complex (Bolt and Bruggenwert, 1976).

To enable a direct comparison of salinity and sodicity hazards, we have to harmonize the variable that represents the salinity. For that reason, we will disregard the proxy EC, electrical conductivity, in favour of concentrations. In Bolt and Bruggenwert (1976) is proposed a simple way to change from EC to the total concentration: 1 mS/cm corresponds to 0.01 normal concentration. Moreover, we will not consider concentrations in the saturated paste, but base our analysis on drainage water (C_{dw}, at field capacity). This implies that the equation for LR changes. So that from equation (4.7) now we can delete the FC/SP factor, thus we will obtain:

$$\frac{D_{dw}}{D_{iw}} = LR = \frac{EC_{iw}}{EC_{dw}} = \frac{C_{iw}}{C_{dw}} \tag{4.8}$$

With respect to equation 4.1 here LR is expressed in terms of salt concentration and not in terms of electrical conductivity.

In the second step we will consider the ESP index, but there is not a direct relationship between LR and ESP, in fact we need a ratio that links sodium concentration both in irrigation and drainage water. Thus, at first we re-introduce the SAR index (1.1):

$$SAR = \frac{Na^{+}}{\sqrt{(Ca^{2+}+Mg^{2+})/2}}$$

Where SAR, expressed in $(\text{mmol/L})^{1/2}$, represents the ratio between concentrations of Na^+ and the square root of the sum of the principals divalent cations (Ca^{2+} and Mg^{2+}). Considering now that:

$$ESP = \frac{Na^{+}}{CEC}100 \tag{4.9}$$

We can link SAR and ESP with a satisfactory equation discussed before (1.2):

$$\frac{ESP}{1-ESP} = 0.015\,SAR$$

Where the 0.015 value, expressed in $(\text{mmol/L})^{-1/2}$ is considered relatively constant and depends on composition of soil (with $K_G = 0.5\ (\text{mol/L})^{-1/2}$). Hence it is possible to find an expression for LR needed to limit ESP to a certain value. To find the expression that links LR with ESP we need to use SAR equation because it allows to find the SAR level which is in drainage water. In fact if $SAR = \frac{Na^{+}}{\sqrt{Ca^{2+}/2}}$ and if we consider that at equilibrium sodium ($C_{tot}(1\text{-}f)$) and calcium $C_{tot}f$ (where C_{tot} is the salt content, (1-f) the sodium fraction and f the calcium fraction, both in solution) reach a standstill:

$$(1-f_{iw})C_{tot}D_{iw} = (1-f_{dw})C_{tot}D_{dw}$$

$$\rightarrow (1-f_{iw})C_{tot}\frac{D_{iw}}{D_{dw}} = (1-f_{dw})C_{tot} \tag{4.10}$$

$$f_{iw}C_{tot}D_{iw} = f_{dw}C_{tot}D_{dw} \qquad \rightarrow f_{iw}C_{tot}\frac{D_{iw}}{D_{dw}} = f_{dw}C_{tot} \tag{4.11}$$

Where *iw* and *dw* refer to irrigation and drainage water respectively. Introducing these two equations in the SAR expression we have that:

$$SAR = \frac{(1-f_{iw})\, C_{tot} \frac{D_{iw}}{D_{dw}}}{\sqrt{\left(f_{iw} C_{tot} \frac{D_{iw}}{D_{dw}}\right)/2}} \tag{4.12}$$

which is SAR of drainage water.

$\frac{Diw}{Ddw} = \frac{1}{LR}$ so we can find the equation that links leaching requirement to ESP:

$$LR = \frac{2}{C_{tot}\, f_{iw}} \left(\frac{1.5\, C_{tot}\, (1-f_{iw})}{ESP} - 0.015\, C_{tot}(1-f_{iw})\right)^2 \tag{4.13}$$

The relationship above (4.13) links LR, i.e. water characteristic, and ESP, which is a typical soil parameter. This equation is thus obtained assuming sufficiently true the equation 1.2. Also in this case we can assume that is sufficiently valid the suggested Gapon constant value $K_G = 0.5$ (mol/L)$^{-1/2}$ (Bolt and Bruggenwert, 1976).

In Halliwell *at al.* (2001) is assumed ESP in the range of 1-30%, that the most common range in agricultural soils, even if the critical ESP value may differ for every soils. Also comparing ESP range with results obtained from Bolt and Bruggenwert (1976) values of SAR we have comparable values. Table 4.3 shows this relationship and the comparison between LR and ESP that have been made with the same values.

		SAR (mmol/L)$^{1/2}$
Low sodification hazard	**(Bolt, 1976)**	**< 7 → ESP = 9.5%**
Medium sodification hazard	**(Bolt, 1976)**	**7< X < 13 → 9.5% < ESP < 16%**
High sodification hazard	**(Bolt, 1976)**	**13 < X <20 → 16% < ESP < 23%**
Very High sodification hazard	**(Bolt, 1976)**	**> 20 → ESP > 23%**

Table 4.3: Classification of irrigation waters and values of ESP found.
Source USDA Handbook No. 60, 1954.

Finally table 4.4 summarizes the data set used for the simulations of leaching requirement. Different values of electrical conductivity, soil moisture and sodium concentration were taken to obtain different leaching for sodium and for total salts.

Simulation	Line	FC	SP	EC_{iw} (mS/cm)	EC_e (mS/cm)	ESP (%)	C_{Na} (mmol$_c$/L)	C_{Ca} (mmol$_c$/L)	C_{Mg} (mmol$_c$/L)	C_{tot} irrigation	C_{tot} FC	1-f
LR with respect to salinity	I	0.3	0.5	1.07	0 - 10							
	II	0.3	0.5	1.11	0 - 10							
	III	0.3	0.5	0.20	0 - 10							
	IV	0.3	0.5	3.10	0 - 10							
	V	0.3	0.5	1.70	0 - 10							
LR & ESP, assuming conc. of Na, Mg, Ca	I					0-30	9.90	0.90	0.60			
	II					0-30	11.2	0.70	0.70			
	III					0-30	0.40	1.50	0.80			
	IV					0-30	24.6	1.50	3.20			
	V					0-30	8.90	6.40	8.00			
LR & ESP, assuming different C_{tot}	I					0-20				10.7		0.2
	II					0-20				11.1		0.2
	III					0-20				2.00		0.2
	IV					0-20				31.0		0.2
	V					0-20				17.0		0.2
LR & ESP, assuming different Na^+	I					0-20				10.7		0.8
	II					0-20				11.1		0.8
	III					0-20				2.00		0.8
	IV					0-20				31.0		0.8
	V					0-20				17.0		0.8
LR & C_{tot} at different salinity & sodicity	I					-				0-30	20	0.2
	II					-				0-30	40	0.2
	III					-				0-30	160	0.2
	IV					5				0-30	-	0.2
	V					10				0-30	-	0.2
	VI					15				0-30	-	0.2
LR & C_{tot} at different salinity & sodicity	I					-				0-30	20	0.8
	II					-				0-30	40	0.8
	III					-				0-30	160	0.8
	IV					5				0-30	-	0.8
	V					10				0-30	-	0.8
	VI					15				0-30	-	0.8
ESP & Na fraction keeping ΔLR = 0	I										20	0-1
	II										40	0-1
	III										80	0-1
	IV										120	0-1
	V										160	0-1
ESP & C keeping ΔLR = 0	I										20-160	0.2
	II										20-160	0.4
	III										20-160	0.5
	IV										20-160	0.7
	V										20-160	0.8

Table 4.4: Data set used for the simulations of leaching requirement with respect to salinity and sodicity.

4.4. Results and discussion

The two graphics below (figures 4.1 and 4.2) underlines the same trend, thus to maintain or improve the soil structure and characteristics (low salinity and low sodicity) we need a rising quantity of water leached. Regarding the same kind of water, for example domestic wastewater of Alexandria, we note that the leaching requirement is different in the two cases: for the same good conditions required, we need different ratios of leaching requirement. If we consider the medium value of EC_e equals 4, we need a certain LR less than 1. On the other hand, level of ESP $\geq$ 15 means sodic soil (USDA, 1954); so that considering a medium value of ESP for the soil equals 10 means that LR is near to 5. This can be discussed also for all other kind of waters that we consider here.

Even if we find the same trend, we have different values of LR in the two cases. These should be also bigger because of the different kind of soil that we consider. In fact the LR-ESP relationship (figure 4.2) has been found assuming a certain experimental value of K_G (here equals 0.5). But the same relationship could be found with different K_G, though the USDA (1954) demonstrated that it is constant for a certain number of soils. Besides the problem of sodication also appears earlier at low salt concentrations. This implies that if we have high EC values we can have serious problems of salinization but less of sodication. In fact with high salt concentration a certain quantity of divalent cations (especially calcium and magnesium) tends to buffer the accumulation sodium threat. So that the unbalance between monovalent and divalent cations in the soil is lower than with low salt concentration (Bolt and Bruggenwert, 1976). On the other hand we usually have high sodicity with high value of salinity water, and this increase of the Na^+ fraction adsorbed by the exchange sites is more than with low concentrations. As explained before in paragraph 4.3, for the major part of soils we can consider that SAR and ESP have more or less the same values and even more when we consider high EC value. If we assume this aspect sufficiently true we can assume that the quality of water can be considered in function of SAR and EC, as mentioned before in chapter 1 (table number 1.8). It suggests that the recognizable effects are two, and differ from the ratio between total salts and sodium in the water.

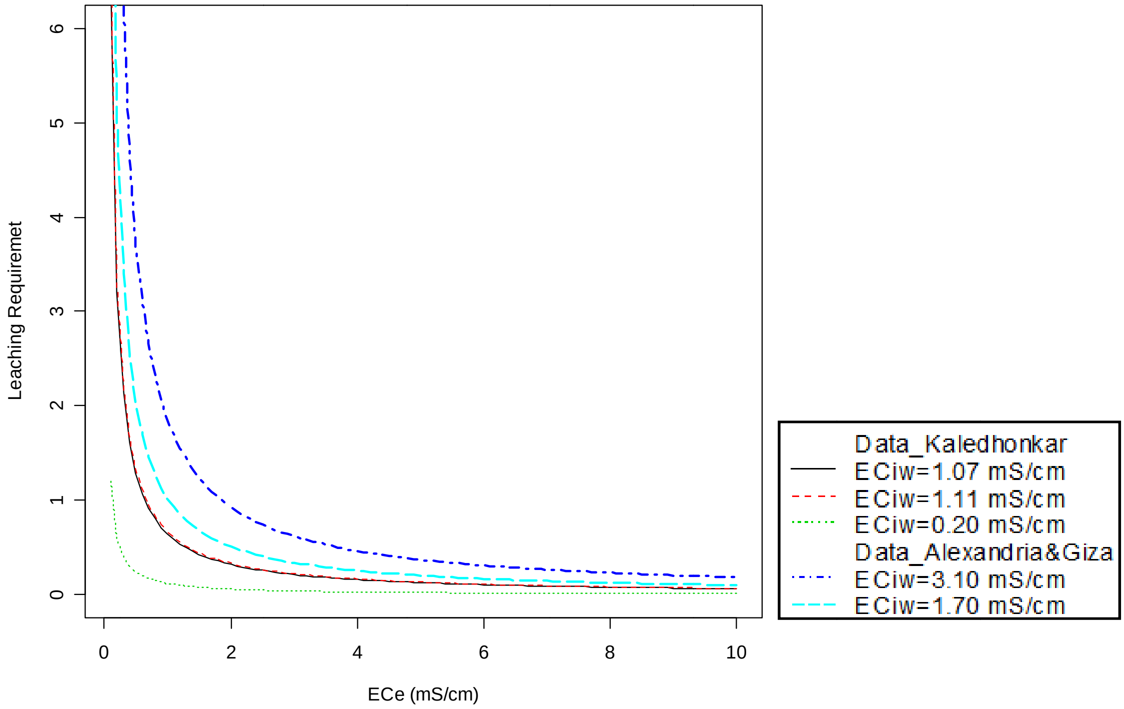


Figure 4.1: Relationship between LR and EC$_e$.
FC = 0.3 and SP = 0.5.

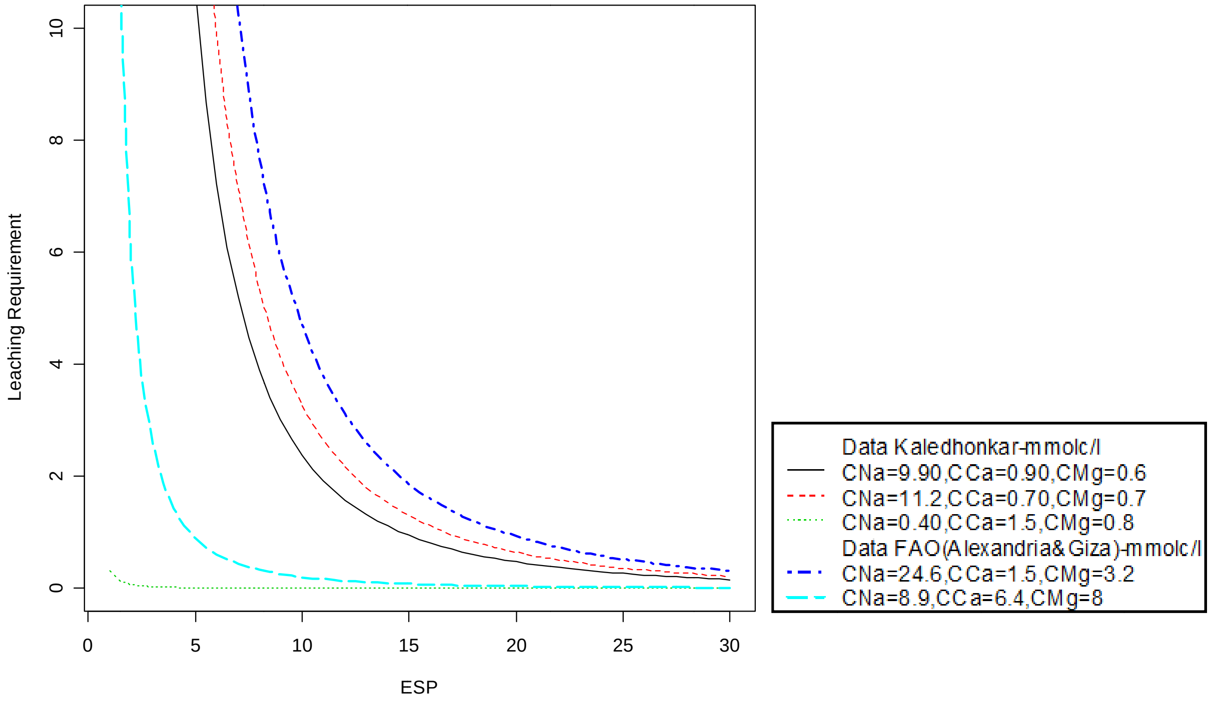


Figure 4.2: Relationship between LR and ESP.

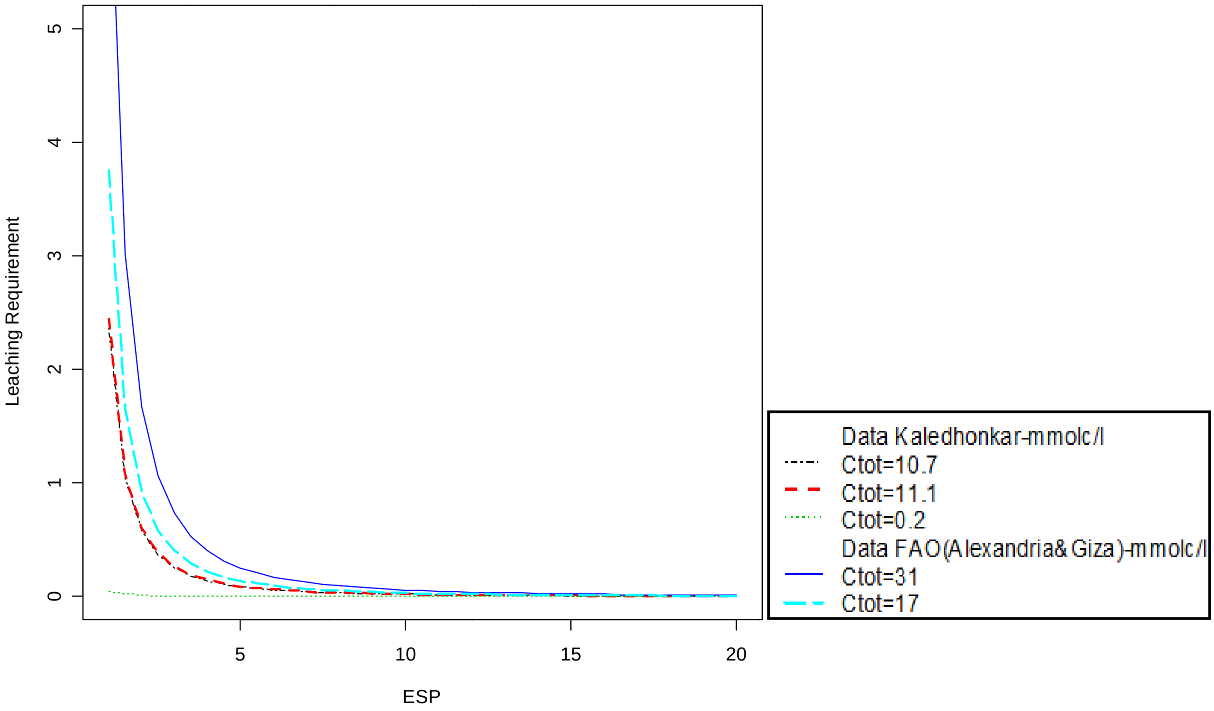


Figure 4.3: Leaching requirement with respect to ESP, with sodium fraction (1-f) = 0.2.

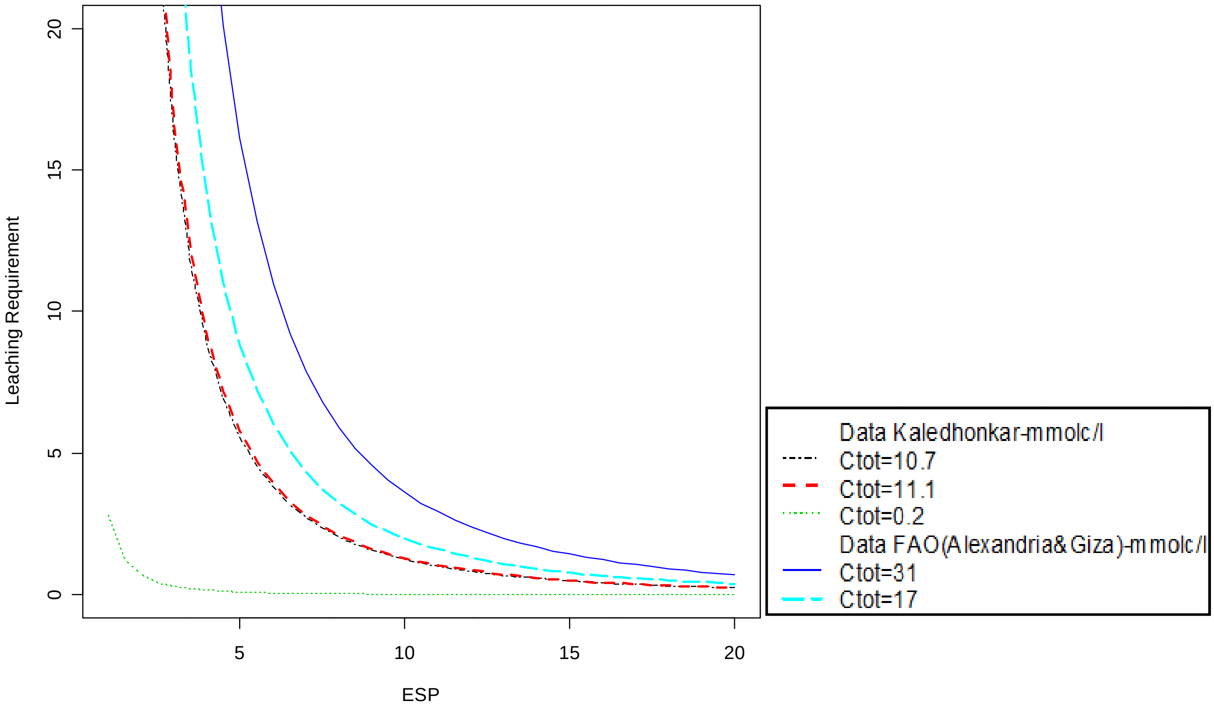


Figure 4.4: Relationship between Leaching Requirement and ESP, with the same total concentration as in figure 4.3, but different fraction of sodium (1-f) = 0.8.

On the contrary, when we consider the same total salts concentration but different fraction of sodium (see figure 4.3 and 4.4) we note that there is an increase of leaching requirement, in fact it goes from 1-f = 0.2 to 1-f = 0.8. Especially in figure 4.4, the comparison between high and low salts concentration shows an increasing request of leaching in the high C_{tot} case. In fact the total sodium incoming in the soil system increases in proportion with the total amount of cations, so that the risk of sodication increases too. But the problem in which we have to focus, instead, and that is different from the simple concentration of sodium in the system, is that swelling and dispersion would not normally occur during wastewater irrigation so long as the concentration of the wastewater remains above critical coagulation value (Halliwell *et al.*, 2001). Unfortunately, the problems that all regions of the earth in which there is crop productions is that rainfall inevitably occurs, which is characterized by low EC value (compare with table 1.8).

At last, we consider LR and C_{tot} (total salt concentration of irrigation water) for both conditions of salinity and sodicity (figures 4.5 and 4.6). In this case the values of C_{dw} of extracting water are in the range proposed in Bolt, according to USDA handbook (1954). Here crop yields are considered as a function of total concentration in the saturation extract. More salinity means difficult growth for plants and inhibition of water uptake because of the osmotic pressure. On the contrary ESP (5% and 15%) is correlated with general range for which sodic soils are considered.

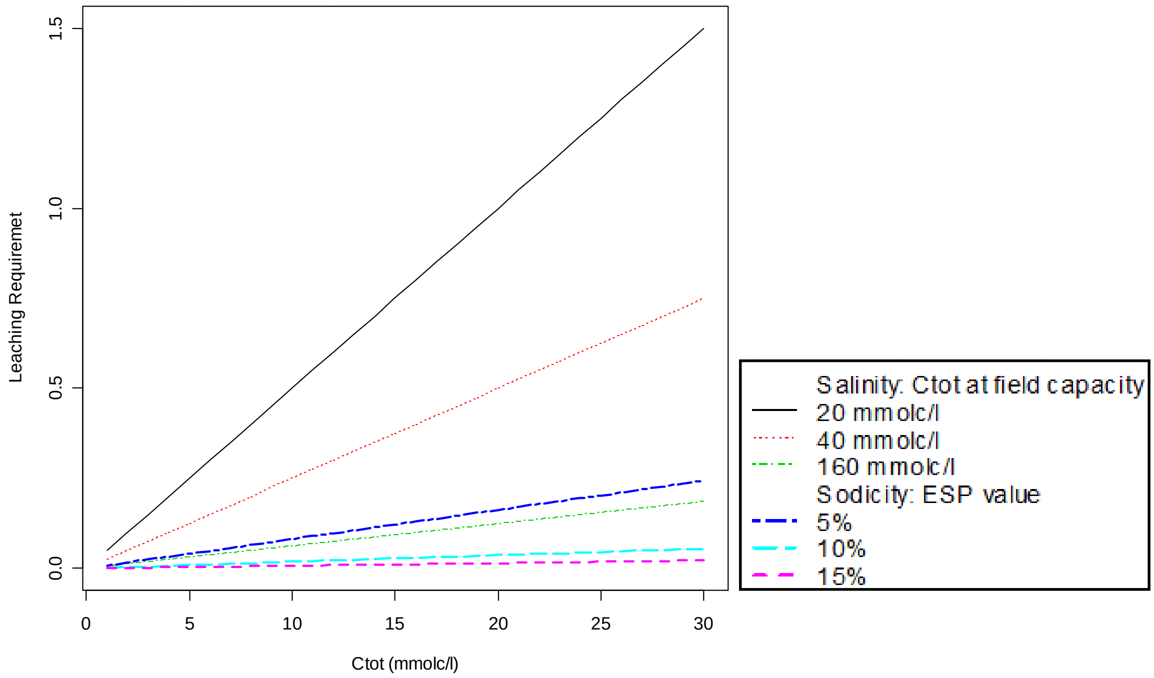


Figure 4.5: LR and C_{tot} of irrigation water at sodium fraction 1-f = 0.2.

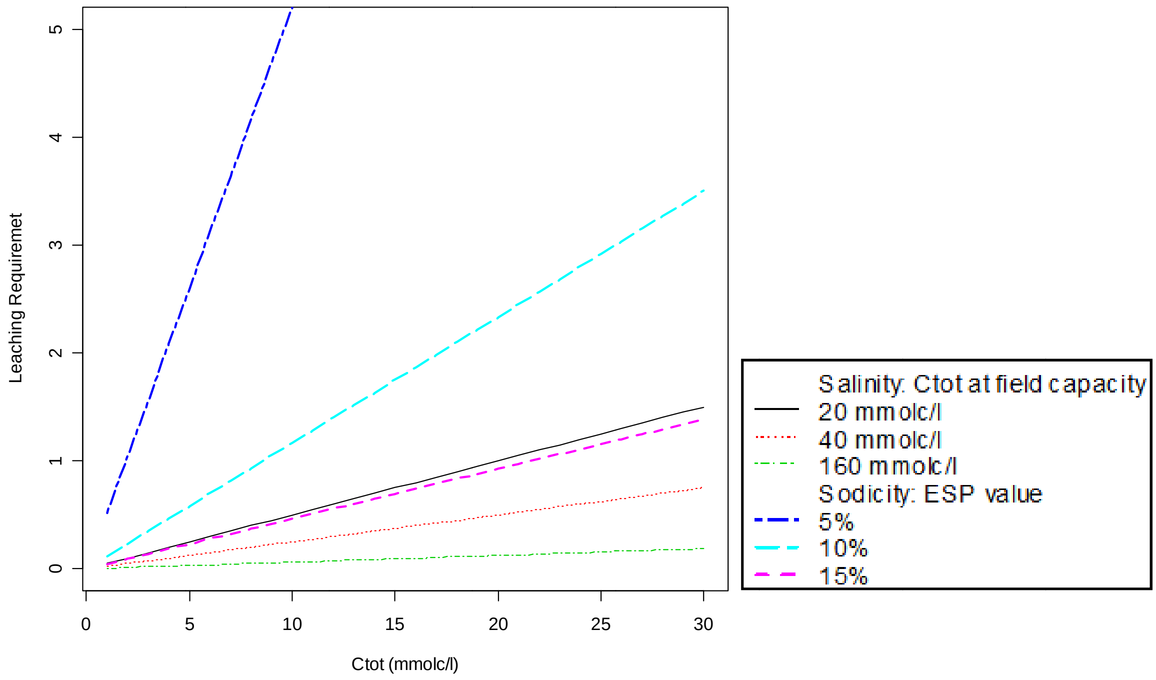


Figure 4.6: LR and C_{tot} of irrigation water at sodium fraction 1-f = 0.8.

We note that for the same kind of irrigation water the need of leaching is different, and it has a great increase in case of sodicity problems if the fraction of sodium is high (1-f= 0.8). We have that leaching for sodicity is a function of sodium and even of total salts, and more attention will be paid in sodicity problem. On the other hand, with low sodium values, the same problem is less important, and salinity becomes the major effect to control. We can observe, as expression of LR-salinity says, that it does not change with different fraction of sodium. In fact we need more leaching to maintain a medium level of salinity (mmol$_c$/L = 40) instead of sodicity of 5% (USDA, 1954; Bolt and Bruggenwert, 1976). Moreover regarding sodicity, an increasing of soil quality needs a very high LR value, which can be seen in high slope line. At last, generally LR$_{\text{SODICITY}}$ is bigger than LR$_{\text{SALINITY}}$. When we deal with poor quality waters we have to pay attention at both aspects, even when we have low salt concentrations, as Halliwell *et al.* (2001) suggests. We can see the same aspects considering the figure 4.7 and 4.8 below: in this case we assume that the difference between LR$_{\text{SODICITY}}$ - LR$_{\text{SALINITY}}$ = 0. In fact equaling the expressions (4.8) and (4.13), and assuming for the (4.13) that the second term in brackets is negligible because very small, we obtain:

$$LR_{SAL} = LR_{SOD} \rightarrow \frac{C_{iw}}{C_{dw}} = 4.5\,\frac{C_{iw}\,(1-f)^2}{f ESP^2} \tag{4.14}$$

The expression (4.14) represents the LR balance between salinity and sodicity.

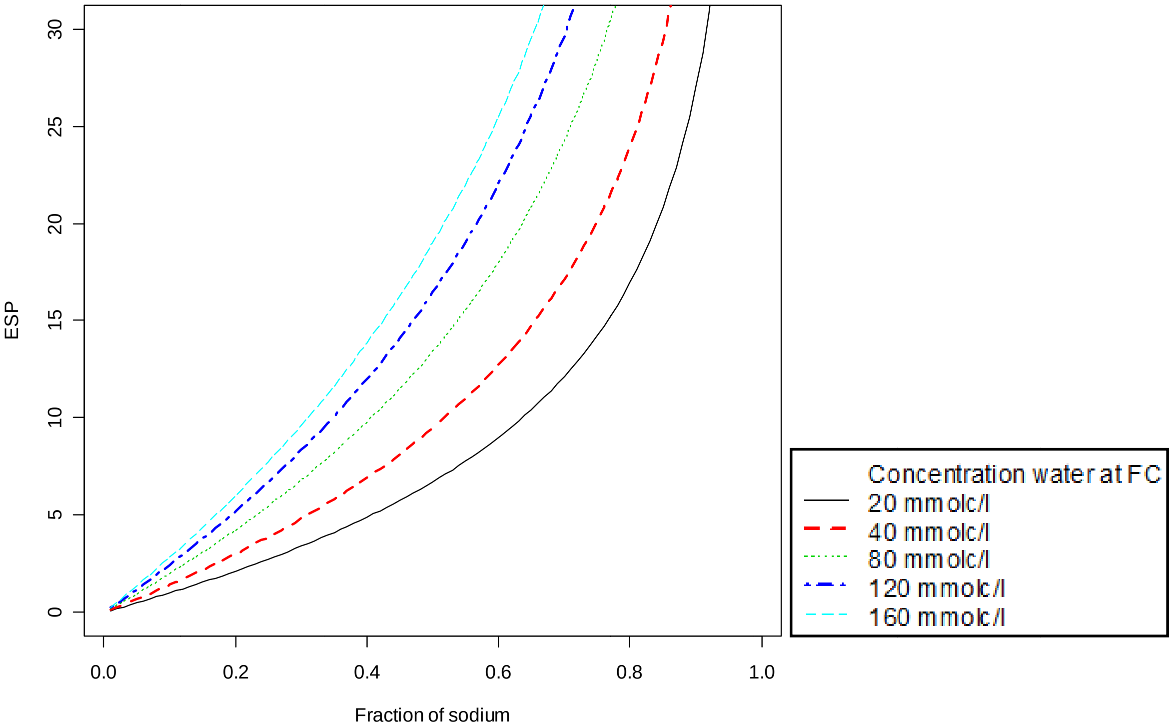


Figure 4.7: Each line represents ΔLR=0 (LR_{SOD}-LR_{SAL} = 0) maintaining C_{dw} constant.

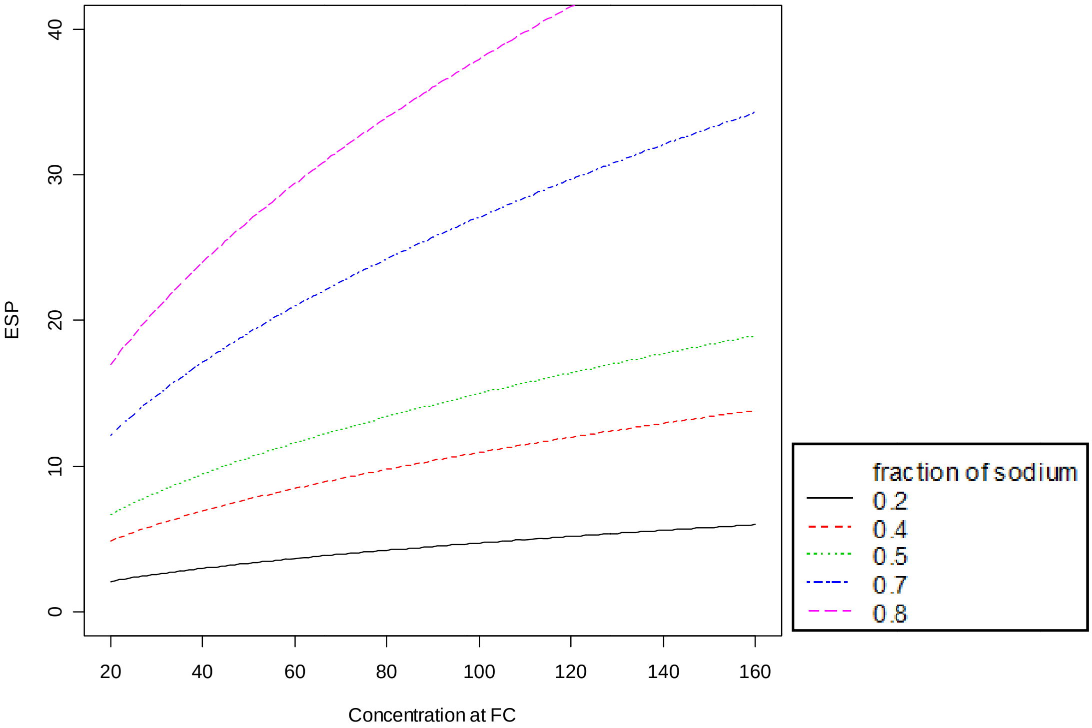


Figure 4.8: Each line represents ΔLR = 0 (LR_{SOD}-LR_{SAL} = 0) maintaining the fraction of sodium (1-f) constant.

The two graphs above (figures 4.7 and 4.8) summarize what is expressed before, but here it arises a new factor; in fact the figures give us an important information regarding the salinity and sodicity leaching. In both figures we know directly which kind of LR to consider. In figure 4.7, for instance, we will have major need of $LR_{SODICITY}$ for conditions that we have in the right side of a certain line, which is referred to a specific water concentration at field capacity, while we need more $LR_{SALINITY}$ on the left side. The trend of the curves demonstrates this aspect: for low fractions of sodium we have to pay more attention to salinity problems instead of sodicity ones. Moreover in figure 4.8 we have the final relationship between salinity and sodicity for different fractions of sodium: the graph gives us an important instrument to evaluate whether the problem concerns one or the other aspect. The result is that we can decide how to operate in the field assuming which is the quality of the soil we want to maintain. The results are even more evident if we consider only some single cases, as underlined in figure 4.9 and 4.10. We have the same conditions as the two figures above, though the meaning is to appreciate the utility of these graphics. In figure 4.10 ESP is plotted in a range of concentration values, while the curves represents two different fractions of sodium. Here the need of leaching requirement with respect to sodicity is bigger under the curves hence, given a certain salt concentration and a constant (1-f) value, more tolerance in ESP conditions may state to pay more attention in salinity problems. Finally we underline how in these two last graphics the curves depend on (1-f) and C_{FC} (concentration of extracting water at field capacity), but not on C_{tot}. Such a relationship means that we do not need this last parameter to evaluate the good management of irrigation and soil system. Finally the last graphic (figure 4.11) shows a 3D representation of ESP with respect to concentration at field capacity and fraction of sodium in solution. Here the graph underlines five different situations with an increase of ESP values for increasing field capacity. Results are comparable with figure 4.7.

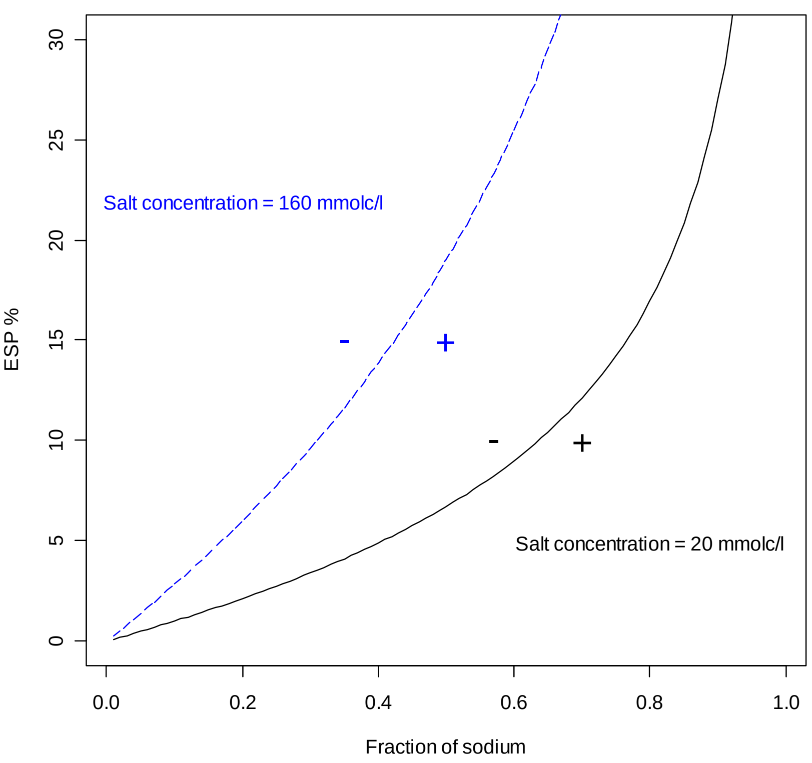


Figure 4.9: The LR_{SOD}-LR_{SAL} = 0 lines show how we need to manage a field to maintain it in certain conditions. LR_{SOD}-LR_{SAL}> 0 means field management with respect to sodicity. Here it is evaluated how ESP changes in the range of sodium fraction. Slat concentration refers to field capacity.

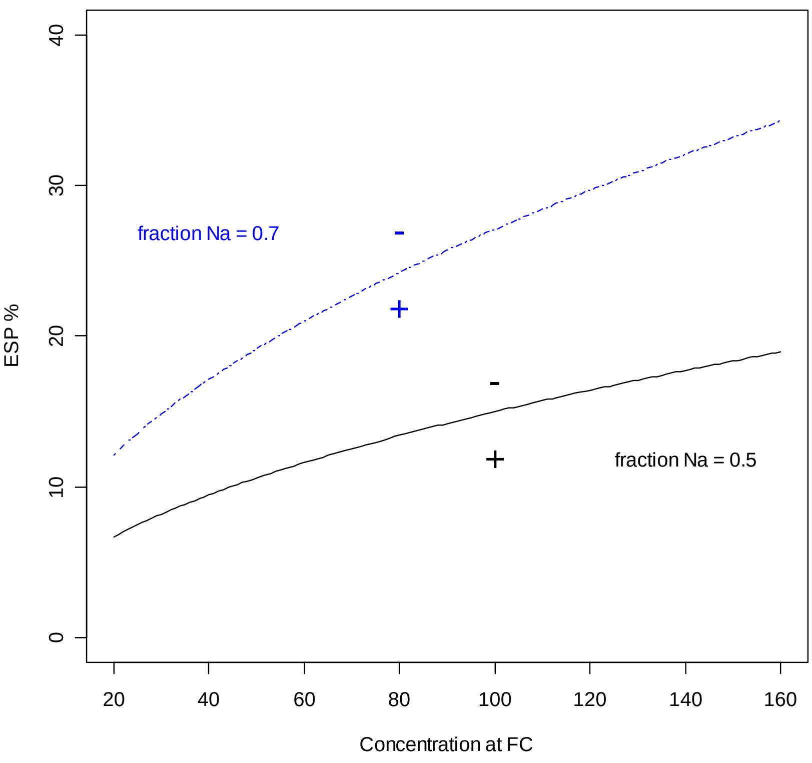


Figure 4.10: Same practical meaning of figure 4.9; LR_{SOD}-LR_{SAL} > 0 means field management with respect to sodicity. Here it is evaluated how ESP changes in the range of salt concentration at field capacity.

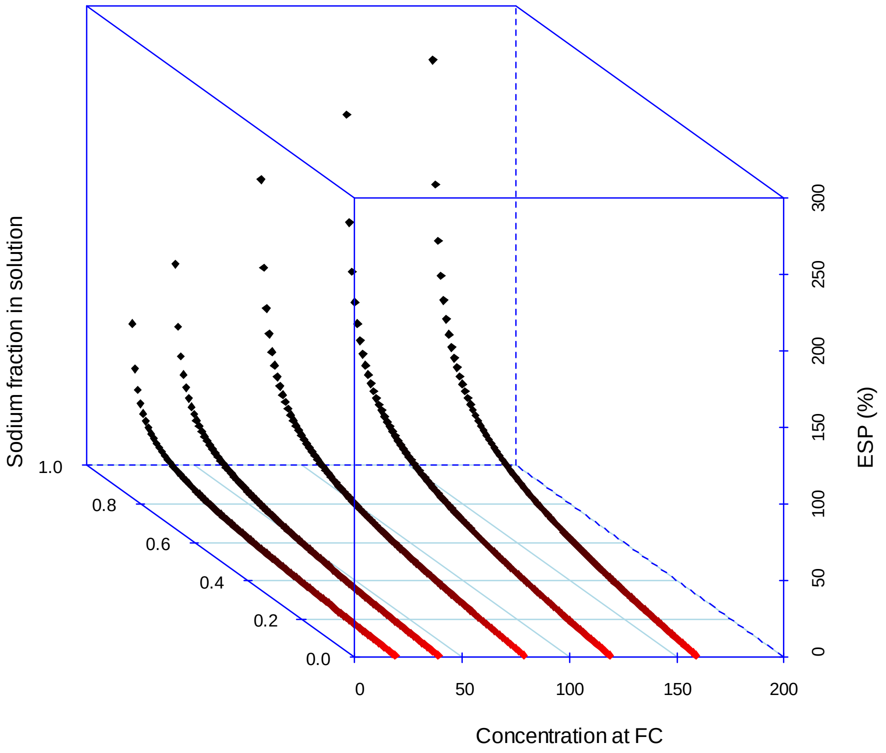


Figure 4.11: 3D representation of ESP with respect to different fraction of sodium of irrigation water and different concentration at field capacity.

4.5. Conclusions

The need of leaching requirement using saline and sodic waters is necessary and to evaluate the real request of leaching involves the good knowledge of water resources. Moreover, it is not possible to estimate how the soil properties behave and change, if salinity or sodicity are considered separately. The two aspects are linked with a relationship that does not allow us to consider them separately. In fact sodicity problems can occur with high or low values of salinity. Additionally salinization and sodication depend upon the initial characteristics of the soil. Thus the problem is really complicated and needs to be seen in all its aspects. We can suggest, considering the discussion above, that for low salt concentrations the LR is similar if we evaluate C_{dw} and ESP, and problems are masked till there is a certain quantity of good water incoming. On the contrary, when we regard in high salt concentration waters, the LR increases more in ESP than in C_{dw} results, and the problem of sodicity, as well as salinity, is immediately present. So the request of leaching is even present for low salt concentrations but high fraction of sodium. Hence we need leaching requirement for different kinds of water that must be evaluated in C_{tot} and the fraction of sodium, keeping in mind the soil properties. Finally we can say that there is the possibility of previsions in the ratio of LR and to realize whether salinity or sodicity is the major problem to follow up.

Finally we can plot together the two aspects studied before in chapter 3 and 4. In fact the graphs 4.12 and 4.13 show the relationship between the risk of soil sodication and the leaching requirement as a possible technique to avoid the accumulation of sodium. The two figures have been obtained using respectively poor quality water and good water parameters referred to accumulation and leaching period in the model of chapter 3. For this reason, especially in figure 4.12, the request of leaching is very high, in fact the sodium concentration reaches very high values, with SAR = 19. As a consequence, maintaining the soil sodicity at ESP = 15% the request of leaching is about 5.

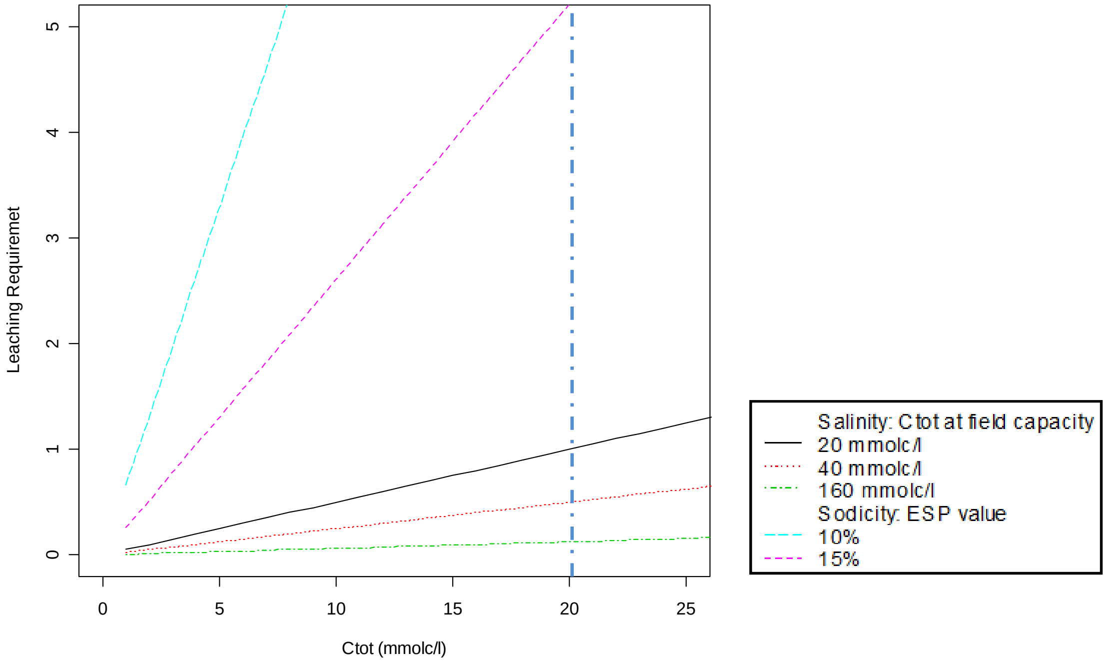


Figure 4.12: Leaching requirement both for sodicity and salinity. Irrigation water is assumed of poor quality. The blue vertical line refers to salt concentration of irrigation water.

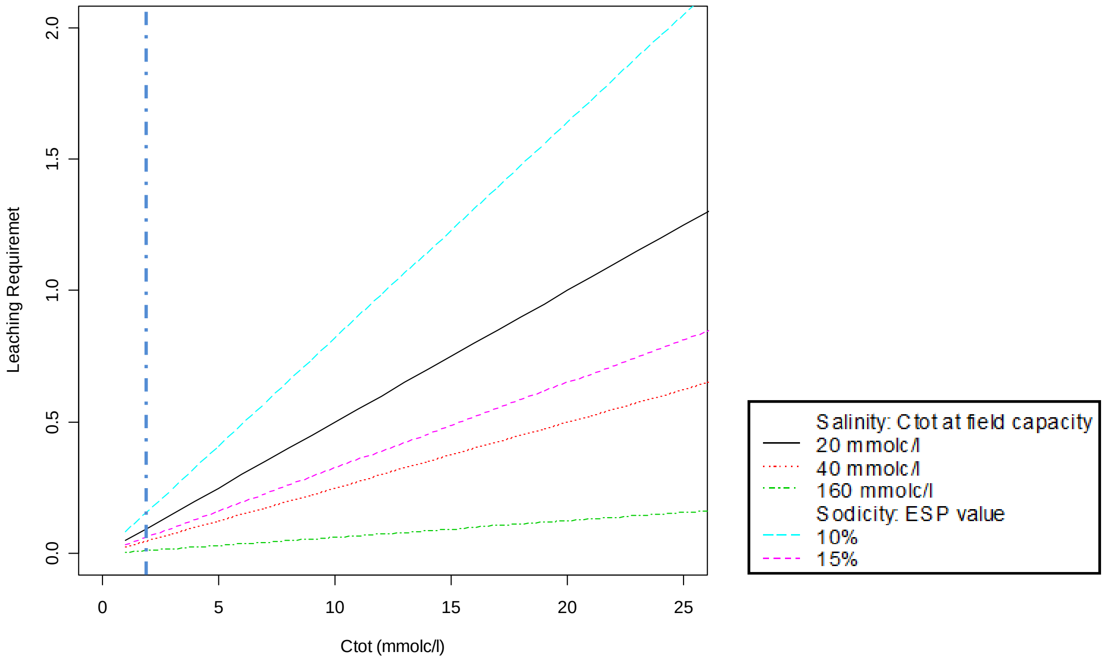


Figure 4.13: Leaching requirement both for salinity and sodicity. Irrigation water is assumed of good quality. The blue vertical line refers to salt concentration of irrigation water.

5. GENERAL CONCLUSIONS

We demonstrate that the risk of increasing soil sodicity is separated from salinity. Maintaining a good soil quality with respect to salinity does not mean that sodicity is under control. At this point one could evaluate whether leaching requirement is a solution to the problem. With respect to the initial values used in the model (table 3.1, reference at figure 3.2) we can state some important things:

1. the formula of leaching requirement with respect to sodicity can be used for the major part of the soils, and variations of CEC values of clay soils are usually not relevant. In fact it has been demonstrated (figures 3.6 and 3.7) that in the long period CEC has low effects until to reach a single ESP steady state. On the contrary, from one year to another, different CEC buffers ESP in a different way, but with negligible effects. In fact the bigger is CEC the smaller is the variations between the maximum and minimum ESP value within the same year. This is quite clear if we consider that the sodication process, expressed in terms of ESP, is a percentage index: assuming different CEC the accumulation of sodium in the soil takes a longer time to reach the same value of ESP with a bigger CEC value;
2. results in leaching requirement using values of the model demonstrate a great need of leaching requirement. For instance, keeping ESP at 15% means that LR = 5.2, which is a very high value. Hence the results highlight that we need a quantity of water 5 times more than the real quantity we would apply into the soil;
3. initial values of poor quality water that have been used in the model evidence the need of leaching requirement with respect to sodicity, if the main purpose it to maintain the sodicity of the soil within ESP = 15% or ESP = 10%;
4. also with good quality water, used in the model, the risk of sodication is quite high, even if the salt balance is already under control. In this case SAR = 2.1 $(\mathrm{mmol/L})^{1/2}$ (instead of the previous case in which SAR = 19 $(\mathrm{mmol/L})^{1/2}$) and usually it is not a value of sodication hazard (reference table 1.6). The problem can arise due to the low electrical conductivity of the water, as expressed in paragraph 1.3. In fact even if ESP, that is related to SAR, has a low value the soil can exhibit loss of structure when EC of irrigation water is low.

5. The leaching requirement needs few parameters to use it as a possible technique to manage salinization and sodication processes. Figures 4.12 and 4.13 demonstrate that salt concentration of irrigation water, fraction of sodium of irrigation water and final soil conditions are the only parameters we need to calculate the request of leaching. As highlighted before CEC has a negligible effect on the soil management.

Even if the leaching requirement seems to be a solution of the problem, both for salinity and sodicity, the assumptions that have been done can give a partial solution. In fact there are some limitations that can change the results:

1. original LR was calculated by considering steady state conditions with associated good management and uniformity of leaching;
2. in LR forms of bad management are not included, such as runoff, water uptake by shallow groundwater, leaching from effective precipitation;
3. steady state conditions do not exist under most field situations, i.e. generally the soil is under transient soil moisture conditions;
4. the traditional method also ignores the chemical processes, such as precipitation/dissolution reactions or exchange equilibrium;
5. the traditional model does not occur for preferential flow which influences water flow and the efficiency of salt leaching.

We can conclude that the leaching requirement may be a solution to the salinization and sodication processes occurring in the soil. On the other hand the need of research in this field is still big and the solution here proposed is not enough to solve completely the problem. Hence the work that have been done could be the beginning of a more deep and flexible study on the sodication process and its solution, that may also include, for example, change in water flow, solute transport and rainfall.

APPENDICES

Appendix A: R environment

The analytical model of chapter 3 and consequent outputs, as the simulations of chapter 2 and 4, are obtained and implemented with R, a freeware software used for many purposes. R is an integrated suite of software facilities for data manipulation, calculation, modeling and graphical display. It is called R environment because it is characterized by the possibility to add tools, as it is frequently the case with other data analysis software. It is almost considered a statistic system, but usually it is used even for other purposes, as to create functions and to obtain graphical outputs.

A.1. Vectors

R operates on named data structures. The simplest one is the numeric vector, which is a single entity consisting of an ordered collection of numbers. Vector is assigned with the function `c()` which can take an arbitrary number of vector arguments and whose value is a vector got by concatenating its arguments end to end.

```
> x <- c(10.4, 5.6, 3.1, 6.4, 21.7)
```

In this simple example we assign to the new vector `x` five vector elements. In this particular case `x` has length five. A number occurring in an expression is taken as a vector of length one. Assignment of a vector can also be made with the function `assign()`.

```
> assign("x", c(10.4, 5.6, 3.1, 6.4, 21.7))
```

Vectors can be used in arithmetic expression in which the operations are performed element by element. Vectors in the same expression can also be of different lengths. If they are not, the final value of the expression is a new vector, that was assigned before, with the same length of the longest vector which occurs in the expression. As well as numerical vectors, R allows to manipulate logical quantities that are characterized by the names `TRUE` and `FALSE` and `NA` (not available).

A.2. Data frame

A data frame is a list that in R is called with the function `data.frame`. For many purposes it may be regarded as a matrix with columns possibly of different modes and attributes. It may be displayed in matrix form, and its rows and columns extracted using matrix indexing conventions. Vectors that can compose the data frame must all have the same length, while matrix structures, that can even be components of the data frame, must all have the same row size. The simplest method to construct a data frame from scratch is to use the function `read.table()`to read an entire data frame from an external file. In addition, a data frame generally has a `names` attribute labeling the variables and a `row.names` attribute for labeling the cases. To create a `data.frame` we need to assign it as here below:

```
> ESPvalue <- data.frame(esp1=soil1, esp2=soil2, esp3=soil3)
```

In this example `ESPvalue` is the name assigned to the `data.frame` which will contain three columns of elements. We point out that each column must be of the same length; `esp1`, `esp2` and `esp3` are the name of the columns that contain the values referred to `soil1`, `soil2` and `soil3`. If the elements of the column are obtained by an equation and after we want to use only one of the column we have in the `data.frame`, it is necessary to call the specific column of the `data.frame`. In fact it is not possible to call directly the elements with the name assigned at the single column, as for instance `esp1`. It is also useful to assign it to a new vector as written below:

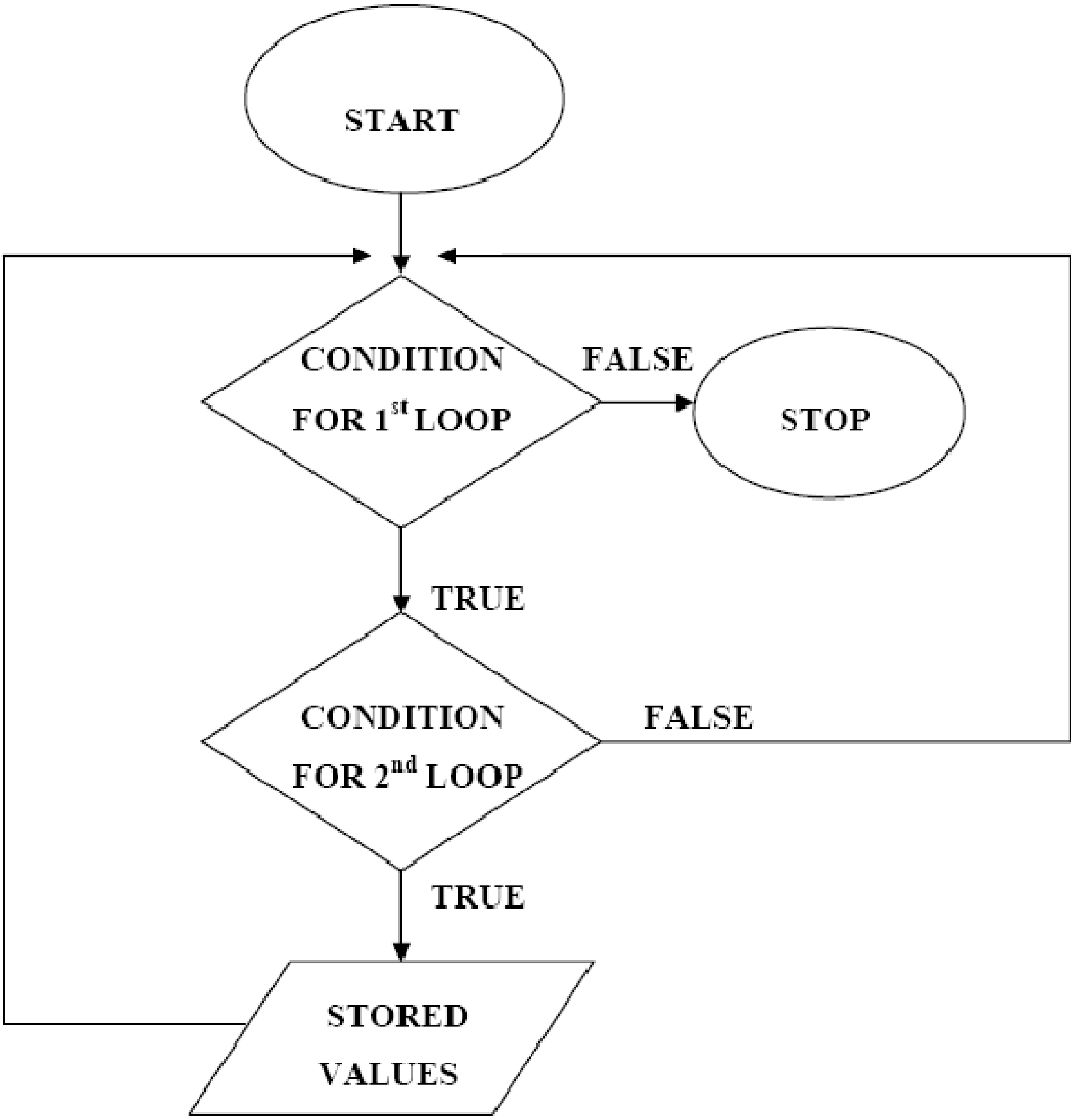
```
> Esp11 <- ESPvalue[,1]
```

A.3. The `for` loop function

R has three statements that provide explicit looping. They are `for`, `while` and `repeat`. Each of the three statements returns the value of the last statement that was evaluated. The for loop has the syntax:

```
for (name in vector)
statement1
```

where `vector` can be either a vector or a list. For each element in `vector` the variable name is set to the value of that element and `statement1` is evaluated. A side effect is that the variable name still exists after the loop has concluded and it has the value of the last element of the vector that the loop has evaluated for. If we need to have all the elements that were found with the loop, we would store them before the loop start the new iteration again. The data flow diagram explicates how the loop function works:



In this case we have two loops that are cascaded together. The first loop allows to call the first column of the `data.frame` and to change it with the following one each time the second loop starts to calculate new results again. The results we obtain with the second loop function will be stored in the first column of the `data.frame`. In other words, calculations of the second loop can be stored separately in the columns of the `data.frame` we created before. The scripts of the example above will be written in R in the following way:

```
for(j in 1:length(ECdw))
{
B <- b+1
for(i in 1:length(ECiw))
lr[i] <- ECiw[i]/ECdw[j]
result[,b] <- lr
}
result
```

A.4. Writing functions

The R language allows the user to create objects of mode function. These are true R functions that are stored in a special internal form and may be used in further expressions and so on. Most of the functions are already part of R system and are called "built-in functions", such as `sqrt()`, `mean()`, `var()` etc. and they are stored in the R environment. However there is another kind of functions, which are called customized functions, that do not differ from built-in functions. They are made with their own assignment that is `function()`. Hence the R language gains enormously in power and convenience, and learning how to write useful functions is one of the main ways to make a personal and comfortable use of R. For example we can assign this function:

```
N <- function(frac)
{
N1 <- 1/(1+k*(sqrt(2*c1))*(1/(sqrt(frac))-sqrt(frac)))
return(N1)
}
result <- N(frac=fo)
```

The example above shows that the function N is thus assigned, whereas the `return` script allows to use further the results in other functions. Hence `return` is the command that permits to have outputs from the assigned function. Thus two important meanings of `return` are: at first to obtain results of the function, and second to call further the function, inside another one, and to have results without writing the single values, but calling the same function.

A.5. Variables

R uses two important kinds of variables, called "local" and "global" variables. Local variables can only be called within a function, that could be a customized or a built-in function. Thus local variables are those whose values are determined by the evaluation of expressions in the body of the functions. As a consequence, if we want to use them directly, we need to assign them in a new vector. Variables which are not local are called free variables. These are even called global variables. In this case we can use them directly out of a single function.

A.6. Solve ordinary differential equation

The R environment is furnished by a great number of free packages that can be used in particular cases, such as solving differential equation by numerical methods as the Runge-Kutta 4th order integration. The package "Odesolve" owns a built-in function to solve this kind of expressions, hence we do not need to write it, but calling the right `rk4()` function in the correct way we have the results. In this case we have:

```
rk4(y, times, func, parms, ..)
```

- `y` the initial values for the "ode" (ordinary differential equation) system. If `y` has a name attribute, the names will be used to label the output matrix;
- `times` times at which explicit estimates for `y` are desired. The first value in times must be the initial time;
- `func` a user-supplied function that computes the values of the derivatives in the "ode" system at time `t`. The user supplied function must be called before using it, in terms of `t`, which is the time, `y`, which is the current estimate of the variable in the system, and `parms`, which is a vector of parameters that remains constant. The return value of the function is a list, whose first element is a vector containing the derivatives of `y` with respect to `time`, and whose second element is a vector of global values that are required at each point in `times`;

- `parms` vector or list holding the parameters used in function (`func`) that is modifiable without rewriting the function.

The values that we obtain are organized in a matrix, with a number of rows equals the time steps we use, and with as many columns as elements in `y`, plus the number of global values returned in the second element of the return from `func`. In this case we have global variables that are eventually stored in the matrix, outside the function. If `y` has a name attribute it will be used to label the columns of the output values. Here is an example of using the `rk4` function:

```
 saltmodel <- function(tt,x,parms)
{
cc <- x[1]        #salt concentration (molc/kgw)
with(as.list(parms),{
dcc <- j*cinn/v   #function for salt balance in accumulation
list(dcc)
})
}
times <- seq(0,0.5, length=51)
parms <- c(j=300, cinn=0.02, v=90)
xstart <- c(cc=0.0098)
out1 <- as.data.frame(rk4(xstart,times,saltaccmodel,parms))
saltacc <- out1$cc
```

A.7. Tinn-R

R comes with a simple editor. A file editor can be opened in which you can type R commands. We find useful to work with Tinn-R software, which is a more elaborated program that is used for editing R code under Windows. It is specifically designed for working with R script files. In addition to syntax highlighting of R code, Tinn-R can interact with R using specific menus and tool bars. As a consequence sections of commands can be highlighted and sent to the R console with a single simple command.

Appendix B: examples of R scripts

B.1. Relationship between leaching requirement and ESP

```
#Relationship between LR and ESP

#Values of poor water and good quality water from Kaledhonkar et al., 2001 & FAO

CNa=c(9.9, 11.2,0.40, 24.6, 8.9) # 1st & 2nd referred to poor quality water Kaledhonkar

#4th & 5th referred to domestic wastewater FAO (considered all meq/l as sum of Na&Ca)

CCa=c(0.9, 0.7,1.5, 1.5, 6.4)

CMg=c(0.6, 0.7,0.8, 3.2, 8)

esp=seq(1, 30, by=1)

result=data.frame(CNa9.9=numeric(length(esp)),CNa11.2=numeric(length(esp)),

CNa0.4=numeric(length(esp)),

CNa24.6=numeric(length(esp)),CNa8.9=numeric(length(esp)))

b=0

for(j in 1:length(CNa)){

b=b+1

for(i in 1:length(esp))

lr[i]=(2/(CCa[j]+CMg[j]))*((0.015*CNa[j]/esp[i]*100)-0.015*CNa[j])^2

result[,b]=lr

}

plot(esp, result[,1],type="l", xlim=c(1,30),ylab="Leaching Requirement", xlab="ESP",ylim=c(0,10),col=1

,main=paste("Relationship between LR and ESP for Waste&Good water"))

lines(esp, result[,2], col=2, lty=2)

lines(esp, result[,3], col=3, lty=3)

lines(esp, result[,4], col=4, lty=4)

lines(esp, result[,5], col=5, lty=5)
```

```
lgd.txt<-c("Data Kaledhonkar-
meq/l","CNa=9.90,CCa=0.90,CMg=0.6","CNa=11.2,CCa=0.70,CMg=0.7
",

"CNa=0.40,CCa=1.5,CMg=0.8","Data FAO(Alexandria&Giza)-meq/l",

"CNa=24.6,CCa=1.5,CMg=3.2","CNa=8.9,CCa=6.4,CMg=8")

legend("topright",lgd.txt,
col=c(NA,1,2,3,NA,4,5),lty=c(NA,1,2,3,NA,4,5))

savePlot("LRvsESP Poor&Good Water1_Kal.&FAO", type="jpeg")
```

B.2. Relationship between leaching requirement and EC_e

```
# Relationship between leaching requirement and Electrical

# Conductivity of extracting water

############################################################

#salinity

sp=(0.5) #Moisture at saturated paste

fc=(0.3) #field capacity

eciw =seq(1,30, by=1) #EC of irrigation water  meq/l

ece=c(10,20,40,80,160) #EC of extracting water meq/l (Bolt &
Bruggenwert,1976)

result1=data.frame(frl=numeric(length(eciw)),slr=numeric(leng
th(eciw)),tlr=numeric(length(eciw)),fo=numeric(length(eciw)),
filr=numeric(length(eciw)))

b<-0

lr1<-vector("numeric",30)

for(i in 1:5)

{

b=b+1

for(j in 1:length(eciw))

lr1[j]=eciw[j]/ece[i]

lr1

result1[,b]=lr1

}

############################################################
```

```
#sodicity

fna<-0.8

fca<-0.8

esp<-c(5,10,15)

result2=data.frame(frlr2=numeric(length(eciw)),slr2=numeric(l
ength(eciw)),tlr2=numeric(length(eciw)))

lr2<-vector("numeric",length(eciw))

k=0

for(z in 1:length(esp))

{

k=k+1

for(w in 1:length(eciw))

lr2[w]=(2/((1-fna)*eciw[w]))*((1.5*fna*eciw[w]/esp[z])-
(0.015*fna*eciw[w]))^2

lr2

result2[,k]<-lr2

}

plot(eciw, result1[,2], type="l", xlab="Ctot (mmolc/l)",
ylab="Leaching Requiremet",

ylim=c(0,5),main=paste("Relationship between LR&Ctot, for
salinity and sodicity (fNa=0.8)"))

#lines(eciw, result1[,2], lty=2,col=2)

lines(eciw, result1[,3], lty=3,col=1)

#lines(eciw, result1[,4], lty=4,col=4)

lines(eciw, result1[,5], lty=4,col=1)

lines(eciw, result2[,1], lty=6, col=1)

lines(eciw, result2[,2], lty=11, col=1)

lines(eciw, result2[,3], lty=8, col=1)

lgd.txt<-c("Salinity: Ctot at field capacity","20
mmolc/l","40 mmolc/l","160 mmolc/l","Sodicity: ESP
value","5%","10%","15%")

legend("topright",lgd.txt, col=c(NA,1,1,1,NA,1,1,1),
lty=c(NA,1,3,4,NA,6,11,8))
```

```
savePlot("LR_Ctot_sal_sod_together_highNa",type="jpeg")
```

B.3. Soil sodication: one year simulation

```
require(odesolve)

require(scatterplot3d)

# Salt Balance Accumulation Period (classical Runge-Kutta 4th
order integration)

saltaccmodel<-function(tt,x,parms)

{

cc<-x[1]        #salt concentration (molc/kgw)

with(as.list(parms),{

dcc<-j*cinn/v   #function for salt balance (in accumulation)

list(dcc)

})

}

times<-seq(0,0.5, length=51) #vector of timesteps

# j=l/m2/y | v=l/m2 | cinn=molc/kgw

parms<-c(j=300, cinn=0.02, v=90) #steady states parameters

xstart<-c(cc=0.0098) #start values for steady states
conditions

out1<-as.data.frame(rk4(xstart,times,saltaccmodel,parms))

saltacc<-out1$cc

#############################################################

# Calcium Balance Accumulation Period (classical Runge-Kutta
4th order integration)

calaccmodel<-function(tt,x,parms)

{

ff<-x[1]  # calcium fraction in soil solution

with(as.list(parms),{

dff<-(j*finn*cinn+(-
v*ff+(M*y)/(2*((cc+j*cinn*tt/v)))*(1/(1+k*(sqrt(2*(cc+j*cinn*
tt/v)))*
```

```
(1/sqrt(ff)-sqrt(ff))))*(1-1/(1+k*(sqrt(2*(cc+j*cinn*tt/v)))*

(1/sqrt(ff)-sqrt(ff)))))*(j*cinn/v)) /
(v*(cc+j*cinn*tt/v)+y*M*((1/(1+k*(sqrt(2*(cc+j*cinn*tt/v)))*

(1/sqrt(ff)-
sqrt(ff))))^2)*k*(sqrt((cc+j*cinn*tt/v)/2))*(1/sqrt(ff)+1/ff/
sqrt(ff)))

list(dff)

})

}

times=seq(0,0.5,length=51) #vector of timesteps

# j=l/m2/y | v=l/m2 | cinn=molc/kgw | M=kgs/m2 | y=molc/kgs |
cc=molc/kgw |

# k=(mol/l)-1/2

parms<-c(j=300, cinn=0.02, v=90, finn=0.05, y=0.25, M=390,
cc=0.0098, k=0.5) #steady states parameters

xstart<-c(ff=0.98) #start values for steady states conditions

out2<-as.data.frame(rk4(xstart,times,calaccmodel,parms))

calacc<-out2$ff

############################################################

# Calcium accumulation in exchangeable complex (N)

NN<-vector("numeric",51)

k<-0.5

for(i in 1:51)

{

NN[i]<-1/(1+k*(sqrt(2*saltacc[i]))*(1/sqrt(calacc[i])-
sqrt(calacc[i])))

}

############################################################

# Total Calcium content in accumulation (molc/kgs)

v=90

y<-0.25

M<-390
```

```
totcalacc<-vector("numeric",51)

for(ii in 1:51)

{

totcalacc[ii]<-(calacc[ii]*saltacc[ii]*v+NN[ii]*y*M)/M

}

##############################################################

# Salt Balance Leaching Period (classical Runge-Kutta 4th
order integration)

saltleamodel<-function(ttt,x,parms)

{

lea<-x[1] #salt concentration (molc/kgw)

with(as.list(parms),{

dlea<-j*(cinnn-lea)/v

list(dlea)

})

}

times=seq(0,0.49,length=50) #vector of timesteps

parms<-c(j=300,v=90,cinnn=0.002)

xstart<-c(lea=0.04313333)

out3<-as.data.frame(rk4(xstart,times,saltleamodel,parms))

saltlea<-out3$lea

##############################################################

# Calcium Balance Leaching Period (classical Runge-Kutta 4th
order integration)

calleamodel<-function(tt,x,parms)

{

f<-x[1]  # calcium fraction in soil solution

with(as.list(parms),{

dff<-((j*finnn*cinnn-j*(1-tauu)*f*(z+(co-z)*exp(-a*tt)))+(-
v*f+M*y*

(1/(1+k*sqrt(2*(z+(co-z)*exp(-a*tt)))*(1/sqrt(f)-sqrt(f))))*
```

```
(1-(1/(1+k*sqrt(2*(z+(co-z)*exp(-a*tt)))*

(1/sqrt(f)-sqrt(f)))))/2/(z+(co-z)*exp(-a*tt)))*

(j*(cinnn-(z+(co-z)*exp(-a*tt)))/v)) /

(v*(z+(co-z)*exp(-a*tt))+y*M*(1/(1+k*(sqrt(2*(z+(co-z)*exp(-
a*tt))))*

(1/sqrt(f)-sqrt(f))))^2*k*(sqrt((z+(co-z)*exp(-
a*tt))/2))*(1/sqrt(f)+1/f/sqrt(f)))

list(dff)

})

}

times=seq(0,0.49,length=50) #vector of timesteps

# j=l/m2/y | v=l/m2 | cinn=molc/kgw | M=kgs/m2 | y=molc/kgs |
cc=molc/kgw |

# k=(mol/l)-1/2 ! a=(1-tauu)*j/v ! b=j*cinnn/v ! z=b/a

parms<-c(j=300, cinnn=0.002, v=90, finnn=0.25, y=0.25, M=390,

k=0.5,co=0.04313333,tauu=0,a=3.33,z=0.002) #steady states
parameters

xstart<-c(f=0.8425897) #start values for steady states
conditions

out4<-as.data.frame(rk4(xstart,times,calleamodel,parms))

callea<-out4$f

##############################################################

# Calcium leaching in exchangeable complex (N)

NNN<-vector("numeric",50)

k<-0.5

for(i in 1:50)

{

NNN[i]<-1/(1+k*(sqrt(2*saltlea[i]))*(1/sqrt(callea[i])-
sqrt(callea[i])))

}

##############################################################

# Total Calcium content in leaching (molc/kgs)
```

```
v=90

y<-0.25

M<-390

totcallea<-vector("numeric",50)

for(ii in 1:50)

{

totcallea[ii]<-(callea[ii]*saltlea[ii]*v+NNN[ii]*y*M)/M

}

#+++++++     PLOT   +++++++++++++++++++++++++++++++++++++++#

# Total calcium content during accumulation and leaching

perd1<-seq(0,0.5, length=51)

perd2<-seq(0.51,1, length=50)

perd12<-c(perd1,perd2)

totCAL<-c(totcalacc,totcallea)

plot(perd12,totCAL, type="l",ylim=c(0.24,0.26),xlim=c(0,1))

#lines(perd2,totcallea, lty="dotted", col=2)

#############################################################

# Calcium content in exchangeable complex during accumulation
and leaching

# in molc/kgs

perd1<-seq(0,0.5, length=51)

perd2<-seq(0.51,1, length=50)

perd12<-c(perd1,perd2)

y<-0.25

ex1<-NN*y

ex2<-NNN*y

ex12<-c(ex1,ex2)

plot(perd12,ex12, ylim=c(0.24,0.26), type="l", xlim=c(0,1))

#lines(perd2,ex2, lty="dotted",col=2)

#############################################################
```

```
# Together total calcium and exchangeable

perd1<-seq(0,0.5, length=51)

perd2<-seq(0.51,1, length=50)

perd12<-c(perd1,perd2)

y<-0.25

ex1<-NN*y

ex2<-NNN*y

plot(perd12,totCAL, ylim=c(0.24,0.255),
xlim=c(0,1),type="l",xlab="Time (year)",

ylab="calcium content (molc/kg soil)")

lines(perd12,ex12, lty=2,col="blue")

#lines(perd1,ex1, lty="dotted")

#lines(perd2,totcallea, lty=1, col=2)

#savePlot("calcium balance", type="wmf")

#############################################################

# Total salt content during accumulation and leaching

perd1<-seq(0,0.5, length=51)

perd2<-seq(0.51,1, length=50)

totSALT<-c(saltacc,saltlea)

perd12<-c(perd1,perd2)

plot(perd12,totSALT,ylim=c(0,0.045), xlim=c(0,1),
type="l",xlab="Time (year)",

ylab="salt concentration (molc/l)")

#lines(perd2,saltlea, lty="dotted",col=2)

#savePlot("salt balance", type="wmf")

#############################################################

# Sodium content in exchangeable complex(molc/kgs)

y<-0.25

perd1<-seq(0,0.5, length=51)

perd2<-seq(0.51,1, length=50)
```

```
perd12<-c(perd1,perd2)

ex11<-(1-NN)*y

ex22<-(1-NNN)*y

ex1122<-c(ex11,ex22)

# Total sodium content in accumulation and leaching
(molc/kgs)

v=90

M=390

y=0.25

totsodacc<-vector("numeric",51)

totsodlea<-vector("numeric",50)

for(i in 1:51)

{

totsodacc[i]<-((1-calacc[i])*saltacc[i]*v+(1-NN[i])*y*M)/M

}

for(ii in 1:50)

{

totsodlea[ii]<-((1-callea[ii])*saltlea[ii]*v+(1-
NNN[ii])*y*M)/M

}

totSOD<-c(totsodacc,totsodlea)

plot(perd12,totSOD,xlim=c(0,1),ylim=c(0,0.01),type="l",xlab="
Time (year)",

ylab="sodium content (molc/kg soil)")

lines(perd12,ex1122, lty=2, col="blue")

#savePlot("sodium balance", type="wmf")

###################################################  3D  ###

perd1<-seq(0,0.5, length=51)

perd2<-seq(0.51,1, length=50)

perd12<-c(perd1,perd2)
```

```
scatterplot3d(perd12,totCAL,totSOD,angle=145,pch=18,xlab="Time (year)",highlight.3d=TRUE,

ylab="total Ca (molc/kg soil)",zlab="total Na (molc/kg soil)",

col.grid="lightblue",lty.hide=2,col.axis="blue")

#savePlot("Ca_Na_3D",type="wmf")
```

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