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USO DE FONTES ALTERNATIVAS DE ÁGUA: IMPACTO NA QUALIDADE DO SOLO E MEDIDAS DE MITIGAÇÃO

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Use of brackish sources of water: impact on soil quality and mitigation measurements

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Resumo

A salinização do solo é um problema a nível mundial, com mais de mil milhões de hectares de área afetada, sendo particularmente relevante em áreas agrícolas com irrigação onde 20-50% são consideradas afetadas por salinidade, resultado da combinação do uso de água de má qualidade, técnicas de irrigação e climas áridos. A prevenção da salinização do solo é fundamental, especialmente as derivadas de fontes antropogénicas.

No entanto, com a crescente escassez de água doce, água de má qualidade (salina) começa a ser aplicada no solo como suplemento criando um equilíbrio delicado: a produtividade das culturas pode sofrer por falta de água ou por excesso de salinidade. Portanto, o uso adequado de água de baixa qualidade pode fazer uma diferença significativa no aumento da sustentabilidade agrícola a longo prazo.

Para o efeito, esta tese tem como objetivo explorar os efeitos da aplicação de água de irrigação de moderada a alta salinidade na química do solo e discutir as medidas de mitigação que podem ser aplicadas.

Após a caracterização inicial dos solos, foram realizados testes com irrigação com água de salinidade semelhante à do mar seguida de lixiviação, e irrigação com água salobra com diferentes riscos de sodificação.

Os dois solos testados demonstraram comportamentos diferentes: o solo mineral testado, devido à sua acidez nos locais de troca catiónica, foi menos afetado pela água de irrigação com elevada quantidade de carbonato de sódio residual, enquanto o solo orgânico, com uma maior quantidade inicial de cálcio e magnésio, foi menos afetado pela irrigação com água do mar.

Irrigação com água do mar resultou em danos na estrutura do solo com a dispersão de microagregados, limitando a sua aplicação de longo prazo mesmo com a lixiviação apropriado.

A aplicação de água salobra é viável mesmo com lixiviação com água de má qualidade, se aplicada a uma frequência relativamente alta.

Palavras chave:

Água salobra, irrigação com água salina, sodificação, salinização, catiões

Abstract

Soil salinization is a worldwide problem with over 1 billion hectares of affected area and it is particularly relevant on irrigated lands, which 20-50% are considered salt affected as a result of a combination of poor quality water, irrigation techniques and arid climates. Prevention of soil salinization is paramount, particularly due to anthropogenic sources.

However, with the increasing scarcity of freshwater resources, poor quality (saline) water is starting to be applied to soil. A delicate balance ensues: crop yield may suffer either from water shortage or salinity. Therefore, adequate use of low quality water can make a significant difference in enhancing long term agricultural sustainability.

To that effect, this thesis aims to explore the effects of moderate and high salinity irrigation waters on soil chemistry and discuss mitigation measurements that can be applied.

Following soil characterization, tests were performed with seawater irrigation followed by leaching, and irrigation with brackish water with varying sodification risks.

The two tested soils demonstrated different behavior: the mineral soil tested, due to high exchangeable acidity, was less affected by irrigation water with high residual sodium carbonate while the organic soil, having a larger pool of native calcium and magnesium, was less affected by irrigation with seawater.

Seawater irrigation resulted in soil structure damage with dispersion of microaggregates limiting its long term applications even with appropriate leaching.

Brackish water application is feasible even with poor water quality leaching if applied at a relatively high frequency.

Keywords:

Brackish, saline irrigation, sodicity, soil salinization, cations

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Abbreviations

% RSD - percentual relative standard deviation

CEC - cation exchange capacity

EC - electrical conductivity

EC 1:5 - electrical conductivity of 1 to 5 soil to water extraction

EC25 - electrical conductivity value for the temperature of 25° C

ECe - electrical conductivity of saturated soil paste

ECt - electrical conductivity measured at temperature t

EDTA - Diaminoethanetetraacetic acid

ESP - exchangeable sodium percentage

FAO - Food and Agriculture Organization

ft - temperature-coefficient

IC - Inorganic carbon

ISA - Ionic strength adjuster

LF - Leaching fraction

LOI - Loss on ignition procedure

LR - leaching requirement

M - Mineral soil

O - Organic soil

OC - organic carbon

OM - organic matter

RSC - residual sodium carbonate

SAR - sodium adsorption ratio

SARadj - Sodium adsorption ratio adjusted

T - Temperature

TDS - total dissolved solids

TOC - total organic carbon

TPH – Total Petroleum Hydrocarbons

W105 - soil weight at 105°C

W60 - soil weight at 60°C

W650 - soil weight at 650°C

W900 - soil weight at 900°C

1. Introduction

The work presented on this dissertation has been developed within the laboratory F402 of the Department of Mining Engineering of the Faculty of Engineering of the University of Porto (FEUP).

The purpose of this study, as the title suggests, is to evaluate the possibility of using other sources of water for soil irrigation different than the commonly used freshwater, which is becoming a scarce resource over the time.

About 15% of the of the world's total land area is considered degraded by physical and chemical degradation processes, which include soil salinization. Salt-affected soils are present in more than 100 countries of the world, a lot of which is irrigation induced salinization. Finding a balance between the quality of water for irrigation and the associated possible effects in the soil is extremely important.

Therefore, the main objectives of this study are is simply to evaluate irrigation with seawater and brackish water of varying qualities and its impact on soil chemistry, followed by the exploration of traditional management options (namely leaching) and the feasibility for long term irrigation.

The structure of the paper start with a first theoretical chapter, *Literature Revision*, where the key concepts involved in the applied techniques are emphasized, which is a summary of the available structured knowledge on this subject. In *Materials and Methods* the various developed tests are described step by step, and in the *Results* section a detailed identification and analysis of the results and trends are presented. Furthermore, in the *Discussion*, a more detailed comparison with previous works from other authors as well as a more holistic approach to the obtained results and their significance is explored.

Lastly, there is a chapter dedicated to *Conclusions and future work*, in which the objective conclusions are described as well as suggestions for future research.

2. Literature revision

2.1 Soil salinization extent and distribution

The world's global water reserves are mainly saline, implicating that only a small portion is freshwater. This corresponds to approximately 2.5% of the total volume of water in the world, and only one third is liquid (Pitman and Läuchli 2002).

With global food production constantly increasing due to the growth of the world's population, the use of water, especially freshwater, is a subject of particular interest and new measures must be found to ensure and satisfy the need for this resource worldwide (Rengasamy 2006). The scarcity of this resource will likely increase due to the impact of climate change (Szabolcs 1990b). Not only will increasing temperatures increase evaporation of superficial freshwater but it will also exacerbate the need to use irrigation for food production with the resulting over usage of freshwater groundwater (Qadir and Oster 2004).

Presently, most of the suitable land is already under cultivation and expansion into new areas is rarely feasible. Therefore, in order to increase agricultural production, the focus will be on increasing yield rather than cultivated area. Alternatively, recovery of degraded lands can help expand cultivated areas or increase yield in existing ones (Rengasamy 2006). However, increasing yield might lead some countries to increase irrigation schemes (often with poor quality water) and nutrient loads leading to increased groundwater and soil salinity.

A relevant fraction of the world's total land area (about 15%) is considered degraded by physical and chemical degradation processes, which include soil salinization (Rengasamy 2006).

Salt-affected soils are characterized as having dissolved salts in the solution phase and/or sodium ions on the cation exchange sites exceeding defined limits (Qadir, Ghafoor et al. 2000). Although a worldwide problem, the occurrence of salt-affected soils is more frequent in arid and semiarid areas, as well as in lowlands and river valleys (Szabolcs 1990b).

Nowadays, salt-affected soils are present in more than 100 countries of the world (Figure 1), where many regions are also affected by salinization induced by irrigation. In the following figure, it is possible to observe the global distribution of salt-affected areas, separated by the three categories of soils affected by salinization. A detailed explanation of these three categories is described in the next section.

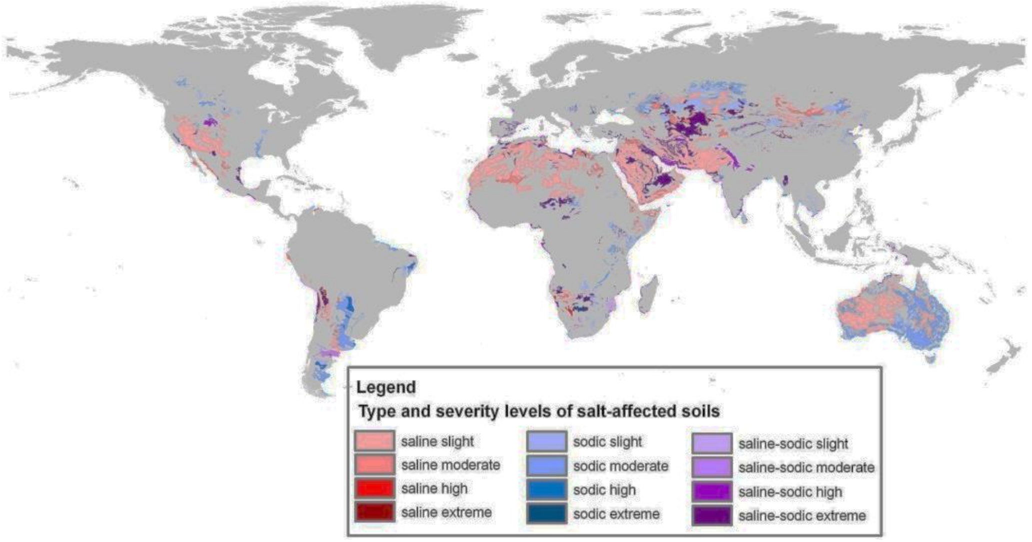

Figure 1- Global distribution of salt-affected soils, including type and severity levels.
(source: http://www.clubgreen.nl/vraag/Biosaline-agroforestry-and-forestry.html)

The table below shows a detailed analysis of the area of saline and sodic soils at global level, representing the affected areas, in million hectares, in various continents and regions.

Table 1- Salt-affected soils on the continents and subcontinents. *(Szabolcs 1989)*

Continent	Area (million hectares)		
	Saline	Sodic	Total
North America	6.2	9.6	15.8
Central America	2.0	-	2.0
South America	69.4	59.6	129.0
Africa	53.5	27.0	80.5
South Asia	83.3	1.8	85.1
North and Central Asia	91.6	120.1	211.7
Southeast Asia	20.0	-	20.0
Europe	7.8	22.9	30.7
Australasia	17.4	340.0	357.4
Total	351.5	581.0	932.2

Table 1 shows a predominance of these soils in Australasia and North and Central Asia as these areas are characterized as dry climates. Soil salinization rarely occurs in well-drained humid regions. However, in the Netherlands, for example, there are also salt-affected soils, mainly as a result of sea water intrusion (Szabolcs 1990a).

All soils contain some soluble salts. Salinization, however, represents the excessive accumulation of water-soluble salts in the soil upper layers. It is responsible for developing unfavorable soil conditions for agricultural production (Szabolcs 1990a). Therefore, soil salinity becomes an issue of land degradation when the concentration of salts in the soil raises to levels that negatively impact agricultural production, environmental health and economic welfare (Rengasamy 2006).

The primordial source of all salts results mainly from geologic erosion. However, the current main sources vary from wind-transported materials, poor quality irrigation water and seawater intrusion into coastal areas (Rengasamy 2006). Poor quality irrigation water combined with saline wastewater discharge are the main direct sources of anthropogenic causes. Changes in land use, most notably removing vegetation, will create water unbalances with concomitant salt accumulation due to increased evaporation (also referred as dryland salinity) (Tanji 2002).

As the main source of anthropogenic salts, irrigation water quality is key to sustainable irrigation schemes. On one hand, use of high quality irrigation water must be controlled to avoid wastes. On the other hand, while potentially affecting soils, poor quality irrigation water can, if properly managed and applied, be an alternative that might allow saving great quantities of quality freshwater for uses other than agricultural.

A more detailed analysis of soil salinity and sodicity, as a main negative consequence of poor irrigation schemes, is therefore necessary to establish potential management options for the future.

2.2 Soil salinity and sodicity – concepts and impacts

Soil salinity is normally measured based on electrical conductivity of soil water extracts. Soil sodicity, on the other hand, is characterized by indexes such as SAR (sodium adsorption ratio) and ESP (exchangeable sodium percentage) and, as the name suggests, focuses on the negative effects of sodium ions on soil and plants.

SAR is the ratio of soluble sodium in relation to calcium and magnesium in soil solution or irrigation water. This hints at the possible adsorption of sodium by soils and therefore the soil sodicity. ESP represents the extent to which the exchange complex (negatively charged sites) of a soil is occupied by sodium (Rengasamy, North et al. 2010).

While SAR and ESP are similar, SAR relates concentrations of soluble sodium with calcium and magnesium while ESP relates the adsorbed sodium with the cation exchange capacity (CEC), which refers not only to calcium and magnesium but also to all other adsorbed cations (Tanji 2002; Chi, Zhao et al. 2011). Exchangeable sodium percentage is a more accurate estimation of sodicity hazard, since the adsorbed sodium is the fraction which will impact the soil structure and is hardly leached away from the soil. However, sodium adsorption ratio is a more easily and reproducible measuring parameter used as a proxy for ESP.

In table 2, the characteristics of the three types of salt-affected soils in terms of Electrical Conductivity (EC), Sodium Adsorption Ratio (SAR) and Exchangeable Sodium Percentage (ESP) are summarized.

Table 2 - Characteristics of the three different salt-affected types of soil (Pitman and Läuchli 2002).

Saline soils	Sodic soils	Saline-sodic soils
EC > 4 dS m^{-1}	EC < 4 dS m^{-1}	EC > 4 dS m^{-1}
SAR < 13	SAR > 13	SAR > 13
ESP < 15	ESP > 15	ESP > 15

The majority of cations in salt-affected soils are Na^+, Ca^{2+} and Mg^{2+}. The cation K^+ might be present as well, only in a lesser extent. In terms of anions, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^- and NO_3^- are usually the most relevant. The referred soils are usually divided in three different categories: saline, sodic and saline-sodic (Table 2) (Qadir, Ghafoor et al. 2000).

Sodic and saline-sodic soils represent about 60 percent of the world's salt-affected area, covering about 10^9 ha. Saline soils complete the remaining 40 percent (Qadir, Schubert et al. 2001)(Malcolm 1989).

The limit above which harmful effects occur can vary depending on factors like the plant type, the soil-water regime or the climatic conditions. Soluble salts inhibit plant growth by osmotic stress, reducing the plant capacity to take up water, while simultaneously suffering from specific ion toxicity. Soil salinization is also conducive to nutritional imbalances in plants, and this instability can range from deficiencies of several nutrients to high levels of Na^+. Salinization may also be caused by inappropriate irrigation, resulting in economic losses when crop yields are reduced by the existence of high water tables and soil salinity (Wichelns 1999).

Structural problems in sodic soils may appear due to some physical processes (slaking, swelling and dispersion of clay minerals) that include specific conditions like surface crusting and hardsetting. These can affect several parameters like the movement of air and water in the soil, the capacity of plants to hold water, root penetration, seedling emergence, runoff, erosion and tillage and sowing operations. The referred physical and chemical changes have an influence on the plant roots activity, soil microbes and on crop growth and yield (Qadir, Schubert et al. 2001) (Vukadinović and Rengel 2007) (Qureshi, McCornick et al. 2008).

Salt-affected soils can become degraded in such a high level that it inhibits them from correctly draining the water. This leads to waterlogging situations and results in the high compression of the affected soil particles (Wichelns 1999).

2.3 Secondary salinization

Secondary salinization is salinization caused by human activities, mainly through irrigation, and it is a threat to sustainable irrigated agricultural production (Szabolcs 1990a). The Food and Agriculture Organization (FAO) stated that more than 77 million hectares of land are salt-affected and approximately 43 million hectares are due to secondary salinization. Estimates show that between 20-33% of global irrigated land is affected by secondary salinization or is expected to suffer from it in the near future (Aragüés, Urdanoz et al. 2011) (Abbas, Khan et al. 2013).

Irrigation water with high levels of Na^+, CO_3^{2-} and HCO_3^- progressively induces sodicity in the soil system. Excessive consumption of fresh water in irrigation and the increased frequency of extreme droughts due to climate changes have forced many farmers to use other sources of water with lower quality, which sometimes causes disastrous consequences for their crops and soils. However, these alternative water sources can, if properly managed, be a vital resource in dry or semi-dry climates for the sustainability of agricultural production and desertification.

Irrigation has a particularly important role on agricultural production in arid and semi-arid areas with low or irregular precipitation. However, the quality of soils and water may be negatively affected by incorrect application.

The natural accumulation of salt in soils is favored by the ecological conditions of the region, as well as influenced by the water balance of the area. Daily human activities such as the previously mentioned irrigation for agricultural production have particular influence in plain arable lands. This is because it is has the ability to affect and modify the water balance in the soil, causing salt accumulation due to the reduced capacity of the soil to naturally drain the excess of water. This means that the salts will be in contact with the soil for a larger period of time, leading to further land degradation (Aragüés, Urdanoz et al. 2011).

Figure 2 represents in a schematic way how the process of salinization arises, particularly secondary salinization in irrigated areas.

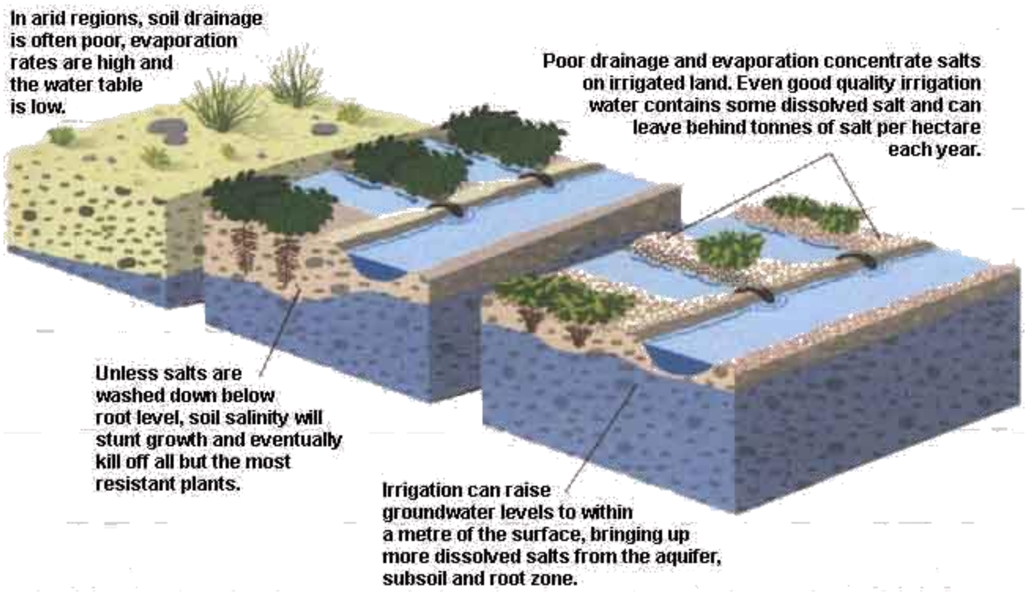

Figure 2- Process of secondary salinization in irrigated areas.
(source:http://12.000.scripts.mit.edu/mission2014/sites/default/files/salinity.jpg)

A combination of poor soil drainage and high evaporation limits the flow of salts and thereby increases its concentration in the soil as well as leading to water accumulation in soil surface (waterlogging). This combination is often visible in arid or semi-arid environments in which waterlogging in combination with salinity will lead to an even greater plant mortality.

Salinization occurrence is difficult to avoid since almost any irrigation water has even trace amounts of dissolved salts and therefore salinization is expected to increase. Approximately 70% of the available superficial water with varying degree of quality used for irrigation worldwide is unceasingly adding considerable amounts of salts to productive lands (Abbas, Khan et al. 2013).

In the future, to manage the rapid population growth and consequent increase of food demand, more land will be used for agricultural production purposes or cropping intensity will have to increase dramatically. Such extensive cropping will be mainly achieved through irrigation and as a result accelerates the salinization risks (Abbas, Khan et al. 2013).

2.4 Monitoring Parameters

In order to characterize salt-affected soils as saline, sodic or saline-sodic, there are some parameters that require previous study. In Table 2 the soils are classified based on electrical conductivity (EC), sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP). These parameters are described in the following sections.

2.4.1 Electrical Conductivity (EC)

Electrical conductivity (EC) is a measure of the ease with which electrical current will pass through water. It is a numerical expression of the inherent ability of a medium to carry an electric current. EC is generally used for indicating the total concentration of the ionized components of solutions. It is closely related to the combination of cations (or anions) as determined chemically and usually correlates with the total dissolved solids (inorganic solids). It is a rapid and reasonably precise determination that does not modify or consume any of the sample (Bui 2013) (Regional Salinity 1954).

Higher salinity implies higher electrical conductivity. However, this relation differs depending on the specific ions present in the solution and their concentrations. The relative water and salt content of the saturation extract is dependent on the soil texture. Therefore, this parameter is necessary to correctly determine salinity hazard. In tests for soil salinity, the saturation point is simulated. When the water level is lower than this saturation point, plants will face a higher salt concentration (Bui 2013).

Conductivity is useful because it can be determined almost immediately and precisely (Regional Salinity 1954). This parameter is not constant with temperature and therefore needs to be expressed at a reference temperature for comparison purposes and accurate salinity expression. The most used reference value is 25°C (Rhoades and Agriculture 1999).

In order to obtain EC_{25}, which represents the electrical conductivity value for the temperature of 25° C, EC is measured at one known temperature different from the reference value and then adjusted to it using a temperature-coefficient (f_t). This is represented in the following equation:

$$\mathrm{f_t} = 1 - 0.20346(\mathrm{T}) + 0.03822(\mathrm{T}^2) - 0.00555(\mathrm{T}^3),$$

where T = [temperature in °C – 25]/10.

After having determined the temperature-coefficient value, it is possible to obtain the electrical conductivity value adjusted for 25° C, by the following equation:

$$\mathrm{EC_{25}} = \mathrm{f_t}.\mathrm{EC_t},$$

where EC_t is the electrical conductivity at the measured temperature t (Rhoades and Agriculture 1999).

2.4.2 Sodium Adsorption Ratio (SAR) and Exchangeable Sodium Percentage (ESP)

Soil sodicity and/or irrigation water sodicity hazard can be assessed by the concentration of the main cations and their ratio.

The sodium adsorption ratio of a soil solution is highly associated with the adsorption of sodium by the soil. Therefore, this ratio is useful as an index of the sodium hazard of the water (Regional Salinity 1954). The following equation defines SAR:

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}{2}}}$$

Water and soil sodicity are expressed in terms of SAR, with high values of this parameter having the capacity for deterioration in soil structure, low infiltration rate, specific-ion toxicity effects, and deficiencies of several nutrients such as K, Cu, Fe, Mn and Zn (Murtaza, Ghafoor et al. 2006). If sodium is predominant, the soil is sodic or there is a high sodicity hazard from using irrigation water with that value. On the other hand, if calcium and magnesium are predominant, the hazard is low (Regional Salinity 1954). The overall concentration, rather than relative ratio between the cations, does not affect soil sodicity but rather the electrical conductivity. In other words, high levels of sodium do not necessary reflect high levels of SAR but rather depend if whether or not calcium and magnesium are also present in high concentrations.

As previously explained, Sodim Adsorption Ratio (SAR) and Exchangeable Sodium Percentage (ESP) are both sodicity measuring parameters. The first is more commonly used, since it is more easily measured (Tanji 2002). ESP, however, can be obtained by the relation between the concentration of adsorbed sodium and the cation exchange capacity of the soil:

$$\mathrm{ESP} = 100 \times \frac{\mathrm{Na}^{+}}{\mathrm{CEC}}$$

As shown in the previous equation, in order to determine ESP, it is necessary to obtain the soil CEC or sum of exchangeable cations. This process is often based on complex laboratory procedures that may take significant amounts of time with a series of technical difficulties limiting the reproducibility of the results. A more simple mean of obtaining ESP can be accomplished by using the sodium adsorption ratio (Chi, Zhao et al. 2011). SAR can be used to approximately estimate soil ESP through the following equation:

$$\mathrm{ESP} = \frac{100(-0{,}0126 + 0{,}01475 \times \mathrm{SAR})}{1 + (-0{,}0126 + 0{,}01475 \times \mathrm{SAR})}$$

This equation allows for a relationship to be established between the ESP scale and the SAR scale (Regional Salinity 1954; Chi, Zhao et al. 2011).

Large SAR values indicates an excess of soluble sodium in relation to calcium and magnesium. The same dominance of sodium will, in time, also translate in a similar ratio of these 3 cations in the soil exchange sites and lead to higher ESP values, which may result in clay dispersion in the presence of low ionic strength water (Sou/Dakouré, Mermoud et al. 2013).

2.4.3 RSC vs SARadj

The sodicity hazard of irrigation water is not exclusively dependent on the concentration of the main soluble cations (Na+, Ca2+ and Mg2+) but also of anions that might reduce the activity of these cations and therefore their ratio. For instance, when the concentration of carbonates and bicarbonates exceed that of calcium and magnesium, it will lead to the precipitation of calcium or magnesium in the soil as calcium or magnesium carbonate, leaving an excess of sodium ions and increasing the SAR of the irrigation water. Consequently, this will increase the SAR level of the soil, which may cause soil structural problems (Rengasamy, North et al. 2010).

That event can be described by the parameter Residual Sodium Carbonate or RSC. This parameter allows for the assessment of whether carbonates and bicarbonates will increase the effects of sodium. Higher values of RSC reflect a more probable occurrence of sodium adsorption by the soil (Rengasamy, North et al. 2010).

$$\mathrm{RSC} = (\mathrm{CO_3^{2-}} + \mathrm{HCO_3^-}) - (\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}})$$

(all ions expressed in meq L^{-1})

As suggested by the equation, RSC reflects a concentration balance between the sum of carbonates and bicarbonates and the sum of calcium and magnesium. A negative RSC has no impact on SAR. In contrast, a positive RSC may increase SAR (Rengasamy, North et al. 2010) (Abrol, Yadav et al. 1988). There are known limits of RSC (Table 3) to assess its impact on sodium adsorption ratio and on water quality.

Table 3 - Water quality and impact on SAR associated to RSC values (Rengasamy, North et al. 2010) (Abrol, Yadav et al. 1988).

RSC (meq L^{-1})	Water quality	Impact on SAR
< 1,25	Low impact	Moderate
1,25 - 2,5	Moderate impact	High
> 2,5	High impact	Very high

However, this parameter cannot be used alone to assess the sodicity hazard of an irrigation water and should be considered in conjunction with SAR levels. Alternatively, there are several formulations for an adjusted SAR (SARadj) value in which calcium levels are corrected based on the carbonate alkalinity of the water and pH.

2.5 Irrigation water, soil and groundwater relationship

Excessive accumulation of salts in the root zone is one possible consequence of irrigation. In order to prevent that from happening, extra water is applied with irrigation, in particular in cases where rainfall is not occurring in excess of that needed for evapotranspiration. This added water is responsible for moving at least a portion of the salts below the root zone by leaching, a crucial factor for the control of the soluble salts brought into the soil in irrigation processes (Ayers and Westcot 1994).

The fraction of infiltrated water that must pass through the root zone to keep soil salinity in an acceptable level is referred to as the leaching requirement (LR). However, not all excess applied water can pass through the root zone. Leaching fraction (LF) represents the portion of infiltrated irrigation that effectively penetrates through the root zone into deeper levels of the soil, i.e. the water that does not adhere to the soil or is used by plant roots (Qadir, Ghafoor et al. 2000). This is a standard agricultural procedure for dealing with mild irrigation water salinity.

However, in some cases, leaching cannot be applied or it is not an effective method for the removal of soluble salts added through irrigation.

For instance, excessive leaching will cause the migration of irrigation water salts or salts stored deeper in the soil to the groundwater level (Figure 3 left). Depending on the size and utility of the aquifer, chloride levels, for instance, can increase beyond what is recommended for most uses.

On the other hand, leaching may not be physically possible, most notably when the groundwater level is high (Figure 3 right). The groundwater itself might be saline and leaching would only further increase its level and increase soil exposure to soluble salts (Qadir et al 2000). In extreme cases, these effects may lead to waterlogging conditions, which accompanied with salinity is a serious threat to agricultural plants’ yield (McFarlane and Williamson 2002).

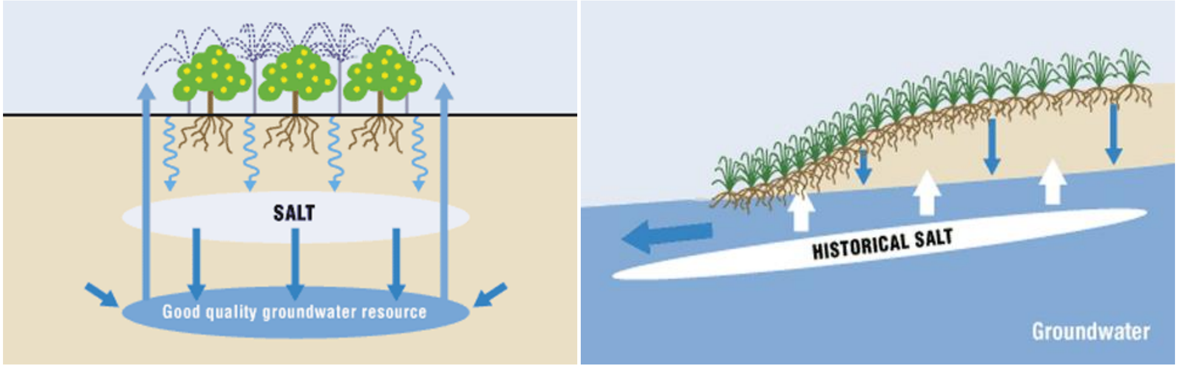

Figure 3- Protecting soil from groundwater (right) or protecting groundwater from soil (left).
(source: http://maxcdn.supergreenme.com/)

Waterlogging can also occur due to the negative effect of sodium added through irrigation on the soil structure. As the soil structure deteriorates, soil porosity and hydraulic conductivity are greatly reduced and irrigation water cannot infiltrate below the root zone.

Yet another potential hazard with leaching is saline seepage at a basin level. Using excessive water for irrigation may exceed the retention capacity of the subsoil and increase the flow to the discharge area. In areas with significant slopes, this may signify that water runoff with low, yet significant concentrations of salts, effectively concentrates excess dissolved salts in valleys (Hughes, Crosbie et al. 2008). These salts can be originated from various surrounding areas, leading to a large salt build up and potentially waterlogging in these low lying areas (Figure 4).

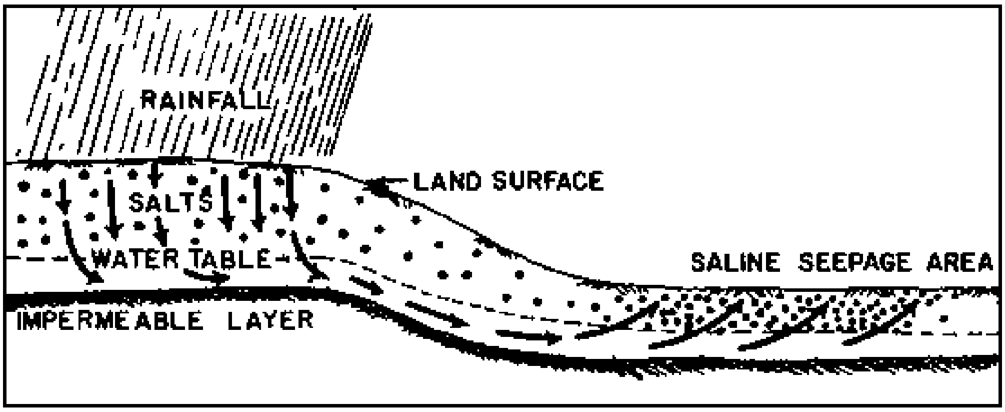

Figure 4 - Representative scheme of a saline seepage area, considering recharge and discharge zone. (source: http://www.fao.org/docrep/x5871e/x5871e06.htm)

2.6 Chemical and physical impacts

Soil structure refers to how the individual sand, silt and clay particles are arranged into stable aggregates. Figure 5 (left) shows several types of soil structure, which are important in terms of evaluating the physical condition of a soil. Structured soils are formed by aggregates while single grain soils may be classified as structureless, since they are constituted by small particles. An ideal soil in terms of structure must have a good balance of micro and macropores that allows for a good equilibrium between water retention and drainage (Raj 2008).

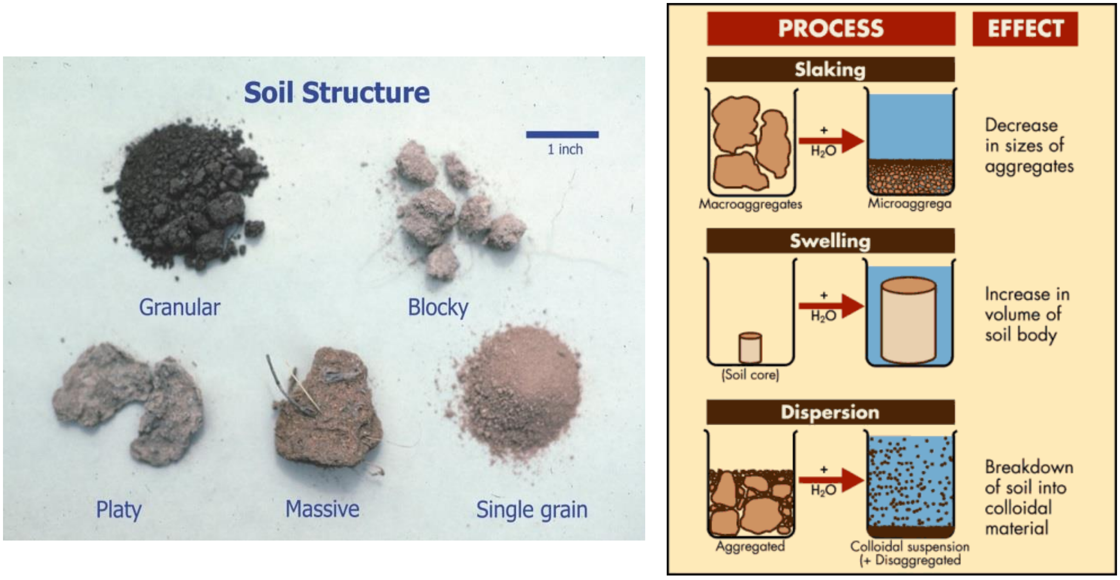

Figure 5- Soil structure: classification of soils (left) and destruction methods due to excess sodium (right).
(source: http://1.bp.blogspot.com/_qudJsVkP_bs/S_rQSvr2dkI/AAAAAAAABCI/M-dsrt2oI24/s1600/soil+structure.jpg)
(source: http://soilwater.com.au/bettersoils/module2/images/14.gif)

The presence of sodium in a soil at considerable levels may lead to soil dispersion and clay platelet and aggregate swelling (Figure 5 right). The forces that contribute for aggregating and binding particles are destroyed when facing significant quantities of sodium ions. This reaction separates particles causing slaking and dispersion as well as swelling of clay particles and this soil dispersion reduces soil permeability by occluding the soil pores. When soil is constantly wetted and dried and clay dispersion occurs, it may turn into cement-like structure, generally presenting no defined structure.

In these conditions, infiltration and hydraulic conductivity are reduced and surface crusting normally takes place. The major consequences related to decreased infiltration due to sodium-induced dispersion include reduced plant available water, increased runoff and soil erosion. The loss of soil structure makes it difficult for the water to circulate and with that the upper layer of the soil can become swollen and waterlogged (Pearson 2003).

It is known that increasing soil solution salinity may have a positive effect on soil aggregation and stabilization, although not necessarily positive for plant growth where high salinity can be considered as negative and potentially lethal. Focusing on the benefits in terms of soil structure, it is common to observe situations where the use of irrigation waters with high levels of calcium and magnesium ions are applied to reduce the amount of sodium-induced dispersion. This leads to increased soil stability due to valence dilution. These ions will compete directly with the sodium in the soil for the same spaces to adsorb to clay particles and have flocculating rather than dispersive properties (Pearson 2003).

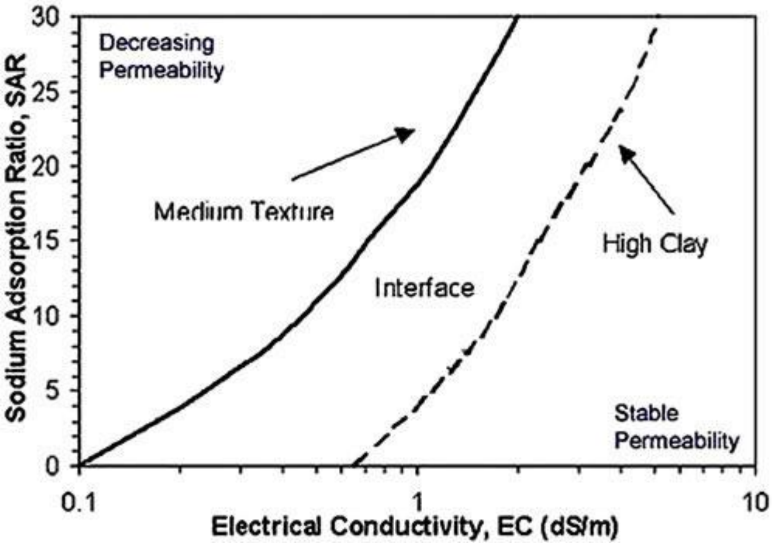

Figure 6 - Soil permeability stability due to valence dilution.

(source: http://www.daff.qld.gov.au/__data/assets/image/0010/65971/piggeries-Sodium-Absorption-500.jpg)

Although the ratio between electrical conductivity and SAR is not precise, some approximations are considered in the literature as to what constitutes safe values to achieve stable permeability (Figure 6). Texture plays an important role in terms of stability as soils with high quantities of clay are more prone to lack of stability due to swelling.

2.7 Exchangeable cations soil dynamics

The total amount of exchangeable cations that a soil can retain is designated as cation exchange capacity (CEC) (Regional Salinity 1954). It is a measure of the quantity of negatively charged sites on the soil surface that have the capacity to retain cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) by electrostatic forces. A soil with a higher CEC has a higher capacity of maintaining acceptable quantities of the referred cations when compared to others with a lower CEC. However, a higher CEC does not necessarily mean that the soil is more fertile, since it is possible that the soil's CEC is occupied by acid cations like hydrogen (H^+) or aluminum (Al^{3+}) (also known as exchangeable acidity) (Ross 1995).

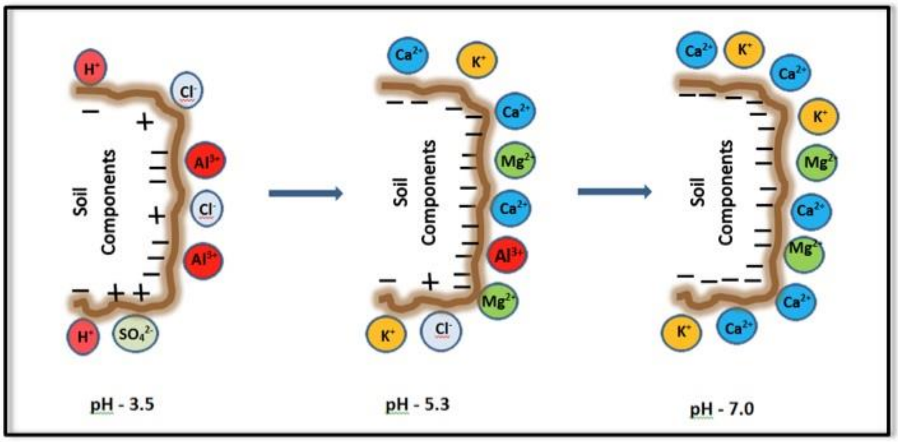

Figure 7 - Variability of exchangeable cations in the cation exchange complex with pH.
(source: http://www.caes.uga.edu/applications/publications/files/html/C1040/images/Figure2.JPG)

Cation exchange capacity is, therefore, extremely important to soil salinity as referred above. While the ESP defines the ratio between sodium and the cation exchange capacity, the actual value of CEC needs to be used to assess quantity, rather than the ratio, of sodium that is adsorbed since it an important parameter for remediation efforts. Soils with high CEC are more susceptible to salinization and therefore should be treated with added care.

Organic matter is usually added to soils to increase its fertility and improve its structure by causing soil to clump and form aggregates, improving the permeability and the capacity of the soil to take up and hold water. However, the addition of organic matter (OM) to the soil will also lead to increasing cation exchange capacity (Figure 7) (Ross 1995) which may lead to increased sodium adsorption and accumulation in the root zone.

The clay content of a soil, as well as the type of clay minerals, represent an important factor as both greatly influence the soil porosity, hydraulic conductivity and cation exchange capacity. Soils with a high content of clay (> 30%) may have low porosity as well as low hydraulic conductivity, due to lack of macropores (in particular if the soil is lacking in micro and macroaggregates formation). In temperate climates the three mineral types of clay that predominate in the soils are kaolinite, illite and montmorillonite. These types of clay minerals have different surface areas and silicate layers, which result in varying cation exchange capacities (Table 4). The same tendency is shown in terms of swelling and shrinkage, since montmorillonite tends to swell more than kaolinite in water, further reducing the microporosity of the soil (Shevnin, Delgado Rodríguez et al. 2006).

Table 4 - Cation exchange capacity for different materials (Shevnin, Delgado Rodríguez et al. 2006; Schwanke and Pergher 2013).

Material	CEC (meq/100 g)
Organic Matter	130-500
Vermiculite	100-150
Montmorillonite	29-150
Hydro mica	10-40
Kaolin	3-15
Sand	1-4
Clay	4-60
Illite	10-40
Chlorite	10-40
Halloysite	5-50

Not only do soils with higher content of very adsorbing clay types need to be more carefully treated for agricultural purposes to avoid compaction and waterlogging but also particularly in high sodicity hazard. The charge of clays also depends on pH, since a higher pH results in a higher cation exchange capacity (Schwanke and Pergher 2013).

2.8 Adaptive measures

In soils not affected by salt, irrigation water should preferentially be of the highest quality available to help agriculture practice of traditional crops (Qadir, Schubert et al. 2001). Nowadays, low quality irrigation waters (including saline waters, irrigation drainage, treated sewage effluents and wastewaters from food processing plants and confined animals) are continuously being used in agriculture. Brackish or low quality water represents a viable alternative to irrigate soils with some particular characteristics with more tolerant crops (Qadir, Schubert et al. 2001). The long-term use of these low-quality waters needs previous study due to the possible negative effects on soil properties and plant performance (Tanji 2002).

In order to reduce the potential impact of the use of brackish water in irrigation, some alternative techniques may be applied despite the limited efficiency of some. These techniques can vary from sub irrigation to combination with other different sources of water or seasonal use only.

For instance, blending two different waters of different quality can lower salinity to more recommendable levels (Minhas, Dubey et al. 2007a). Although controversial, since inappropriate applications of this technique would result in large volumes of contaminated freshwater, its application is dependent on various chemical properties of the waters to be blended. For instance, in cases in which there is a high level of residual sodium carbonate, blending might increase calcium and magnesium concentration by reducing carbonates either by dilution or a small pH adjustment as well as increasing the competition for cation exchange sites, thereby reducing exchangeable sodium percentage (valence dilution) (Qadir, Schubert et al. 2001; Minhas, Dubey et al. 2007a).

Another option lies in cyclic use of fresh and brackish water (Murtaza, Ghafoor et al. 2006). There are several methods for this technique ranging from different irrigation water at different stages of plants' development (use of freshwater when the plant is more vulnerable to osmotic stress) or alternating use in order to allow the use of freshwater to minimize the negative effects of brackish water previously used.

Brackish water can also be used as supplementary irrigation when there is a seasonal water deficit. The concept of seasonal use can be clarified by the following example: in summer, with scarcer freshwater resources, the use of brackish water could be vital to keep certain levels of irrigation, even though the water quality is not as good as desirable (Qadir, Schubert et al. 2001) (Murtaza, Ghafoor et al. 2006). Although, brackish water induces osmotic salt stress, it is speculated that, in certain cases, water scarcity may be more harmful to crop yield (Chauhan, Singh et al. 2008).

Brackish waters can also be employed if previously amended to improve their quality and lower their negative impact to soil structure. For instance, in waters with high levels of bicarbonate, sulfur applications would result in a pH reduction and therefore a reduction in bicarbonate and residual sodium carbonate (RSC). This would increase the levels of available calcium and magnesium for cation exchange reaction. Alternately, gypsum can be dissolved in irrigated waters to reduce SAR or even a combination of both amendments can be used (Johnston, Vance et al. 2013).

The way the water is fed to the plants and soil also influences the effects of salinity/ sodicity on crop yield. Subsurface drip irrigation allows for a better moisture and salinity distribution, adjusted to the root pattern in the soil and therefore a lesser decrease in crop yield (Oron, deMalach et al. 1999).

In fact, use of brackish waters can improve total suspended solids and maturity index in some fruits, therefore increasing their quality (Botía, Navarro et al. 2005).

Another series of adaptive measurements relate to proper agronomic soil measures. For instance, deep tillage would mix the salts present in the surface zone into a much larger volume of soil and hence reduce its concentration and impact. Many soils have an impervious hard pan which hinders in the salt leaching process. Under such circumstances, chiselling would improve water infiltration and hence downward movement of salts.

Raised beds also allow for a greater control of salts in direct contact with the plants (Figure 8).

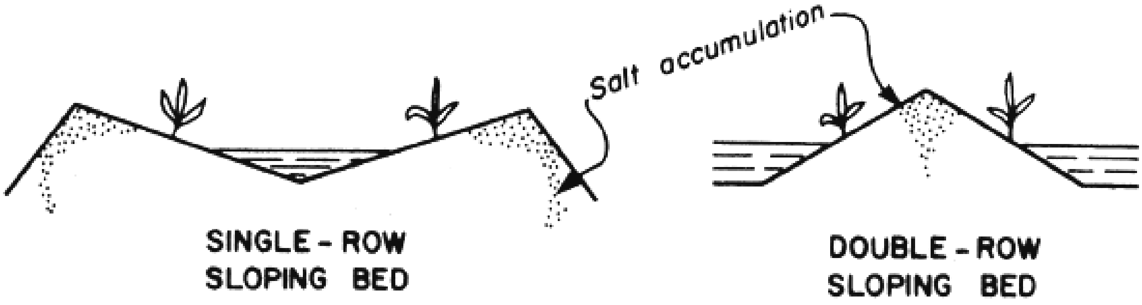

Figure 8 – Raised beds, single or double row, deviate salt accumulation away from plants' roots.
(source: http://www.fao.org/docrep/003/t0234e/t0234e03.htm)

As seen in the figure, raised beds avoid salt accumulation in the root zone. Furthermore, it can also provide a more effective control of drainage, improved nutrient use efficiency, reduce compaction and tillage and improve water saving among other benefits (Singh, Dwivedi et al. 2010).

In extreme cases of waterlogging, either improving existing natural drainage of the soil or creating a sophisticated drainage system (Figure 9) could be an option. This would provide adequate leaching in the wet season to avoid waterlogging while maintaining water in the soil and avoiding capillary rise of salts in the dry season. It also partially compensates for poor soil structure and, with the potential drainage water reuse, it can help compensate for the added costs of the drainage facility (Qadir and Oster 2004).

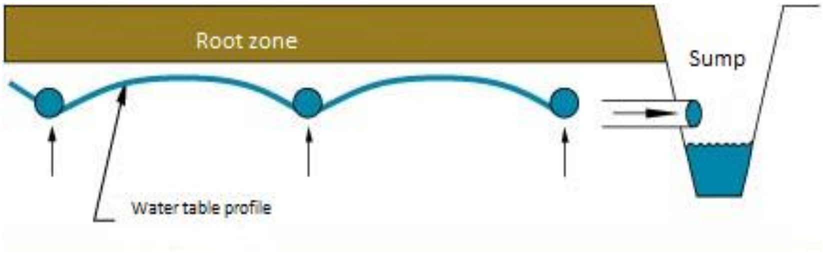

Figure 9- Artificial soil drainage system schematic (source: http://ohioline.osu.edu/b871/images/b871_12.jpg)

Artificial drainage can reduce the water table height by 25% and salinity by up to 50% and in some cases can be cost effective. However, this type of system is usually a major investment that not all farmers are able to make without proper government support (Ritzema, Satyanarayana et al. 2008).

3. Materials and Methods

3.1 Part I: Soil characterization tests

This study involves the use of two different soils: a clear white soil, herein denominated as mineral soil and a dark brown soil, herein denominated as organic soil. These two soils were purposely chosen for their different characteristics upon visual inspection. The soils were air dried before being stored at room temperature and in the dark.

The mineral soil was previously partly characterized in other works, namely Carvalho (2014) and was collected from Leça do Balio (Matosinhos) and it's considered a residual granite soil while the organic soil was collected in Paranhos (Porto) and is a residual artificial urban soil of an unknown lithological source.

Representative samples were collected based on the Portuguese norms NP EN 932-1 and 932-2 2002 for sample collection and reduction techniques. The sampling reduction was made with a multiple slots type sample divider. The soil was poured into the central line of the sample divider and was collected into two recipients. The soil in one recipient was rejected and the remaining was again poured into the sample divider repeatedly until reaching approximately 1 kg of final laboratory sample for analysis.

The soil was sieved according to ASTM norms using the following sieve sizes (25; 20; 12,5; 10; 8; 6,3; 5; 4; 2; 1 mm and 500 and 250 µm). Wet sieving, due to the high organic content of the organic soil, was avoided and instead the fraction under 250 µm was analyzed by a laser diffraction particle size analyzer (Mastersizer 2000). A combination of agitation in water and ultrasound was used to disperse microaggregates, replacing the chemical dispersant use and wet sieving. Texture was then assessed based on the feret diagram (from U.S. System for Texture Designations).

An estimate of heavy metals content in the organic soil was obtained with the use of a Portable Analytical X-Ray Dispersive Energy Fluorescence Spectrometer (Innov-X System) in two different soil samples while TPH (total petroleum hydrocarbons) were obtained using a Remiaid kit.

Soil density was calculated by a pycnometer (for aggregates between 0.063 to 31.5 mm) using the method described in NP EN 1097-6 2003 while bulk density was calculated using a graduated beaker of 100 mL and dropping the soil freely up to 100 mL and weighed. Apparent porosity was calculated from bulk and particle density using the equation:

$$\mathrm{Ap} = 100\left[1 - \frac{\text{bulk density}}{\text{particle density}}\right]$$

Soil saturated percentage was obtained by method 27a of U.S. Lab (1954) derived from a saturated soil paste prepared by method 2 of the same reference.

The qualitative lime content test was prepared based on method 23a effervescence test of U.S. Lab (1954). The procedure involves placing several grams of soil (in this case, exactly 5 g) and adding sufficient water to saturate (in this case approximately 2 mL which is equal to the pore volume of 5 g of this particular soil) in order to displace the air present. Afterwards, a few drops of 3 N HCl are added and the soil was visually inspected for effervescence.

Loss on ignition tests was performed in accordance to Heiri, Lotter et al. (2001). Triplicate soil samples were dried at 105ºC weighed in a crucible and then added to the muffle furnace at 650ºC for 2 hours, allowed to cool and reweighed. The soils were reintroduced into the muffle furnace at 900ºC for 1 hour, allowed to cool and reweighed a final time. The following equations were used for the determination of total organic carbon (TOC), inorganic carbon (IC), organic matter (OM) and carbonate content:

$$\mathrm{TOC} = \mathrm{W}_{650} - \mathrm{W}_{105}$$
$$\mathrm{IC} = \mathrm{W}_{900} - \mathrm{W}_{650}$$
$$\mathrm{OM} = 1.72 * \mathrm{OC}$$
$$\text{Carbonate content} = 1.36 * \mathrm{IC}$$

Cation exchange capacity was tested using the protocol described in Aprile and Lorandi (2012) known as methylene blue adsorption in which the end point is a visual blue halo appearance on a filter paper (that must last more than 5 minutes) after the addition of methylene blue solution in ever increasing amounts to reach this end point (Figure 10).

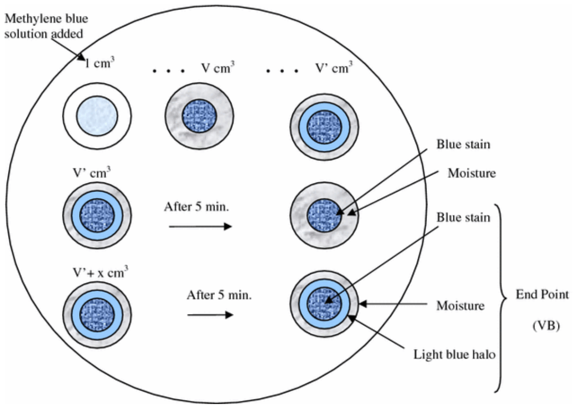

Figure 10- Blue halo end point representation.

The determination of electrical conductivity (EC), calcium and magnesium, pH and estimated sodium plus potassium required soil water extractions. Soil water extractions were performed in accordance to U.S. Lab (1954) from saturated soil paste or 1:1, 1:2 or 1:5 soil to water ratios followed by filtration with Whatman® 2.5 µm filter paper. To convert from soil to water ratios to saturated values, the following formula was used: denominator value of ratio (for example 5 in a 1:5 extraction) * 100/saturation percentage.

EC was determined with a WTW Tetracon® 325” conductivity meter and a WTW inolab level 1 cond terminal while pH was determined using a WTW pH-electrode SenTix 21 and a WTW inolab level 1 pH terminal.

Calcium and magnesium were determined simultaneously following EPA method (denominated # 130.2 Hardness, Total (mg/L as $CaCO_3$) (Titrimetric, EDTA), a complexing titration using Eriochrome Black T as the color indicator and EDTA as the titrant. Sodium and potassium were estimated considering that EC * 10 = total cations and that calcium, magnesium, sodium and potassium are likely the most representative cations and therefore (EC * 10) – (Ca^{2+} + Mg^{2+}) is a possible estimation of sodium plus potassium concentration in the soil extract.

Sodium was later analyzed in the performed tests using a HANNA FC 300 B Na^+ electrode connected to a HANNA HI 4214 bench top measuring unit after daily calibration before use and required the use of an ionic strength adjuster (ISA) solution of 4 M NH_4Cl / NH_4OH which also adjusted pH above 9 or 10 to limit the concentration of potential interfering substances (namely heavy metals).

Further technical details for the EDTA titration and sodium electrode are described in Annex A.

3.2 Part II: Irrigation with seawater

The objective of this test was to simulate an extreme case scenario as suggested by several authors (Abideen, Ansari et al. 2011): irrigation of soil with seawater or water with seawater levels of salinity (approximately 54 dS m^{-1}). This initial phase of the test is herein referred as Part II a) for clarity.

Acrylic columns with 25.5 cm of total height and 5 cm of internal diameter were used. The bottom of each column was initially packed with glass wool to a height of 5 cm for drainage. Soils were subsequently added to 10 cm height above the glass wool, allowing it fall freely to avoid undue compaction and to retain similar bulk density (although both soils could be considered disturbed samples and therefore not representative of their respective natural setting in terms of physical characteristics).

The columns were perforated in the bottom to allow for drainage and were set vertically in metal stands at a 10 cm height from the lab bench top (Figure 11).

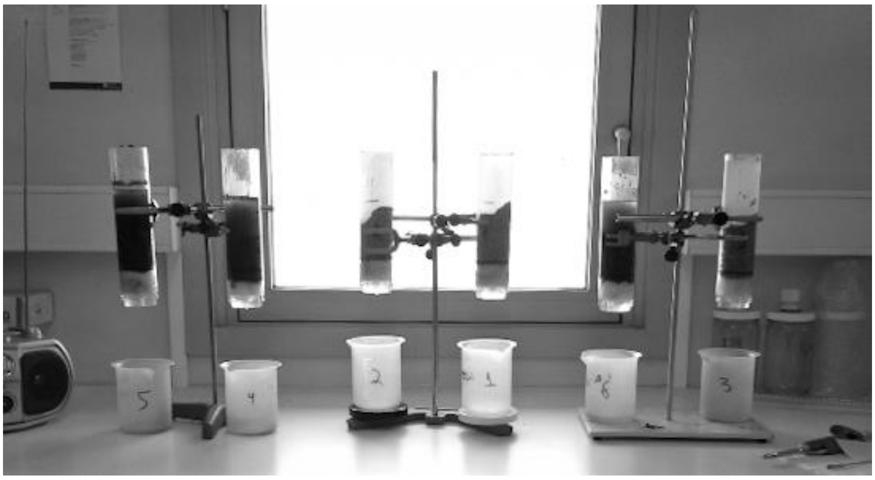

Figure 11 - Experimental set up of the soil columns, randomly set.

Two sets of columns were prepared in triplicate with each soil type. Before testing, the soils were prewetted to saturation and allowed to drain in order to avoid hydrophobicity problems from dry soils and respective drainage problems observed in preliminary tests.

Afterwards, 2 pore volume of a prepared solution with seawater levels of salinity (EC = 54 dS m^{-1}, pH 6.021, sodium levels: 13950 mg L^{-1}) was added. Since porosity of the organic soil was 40.2% and the mineral 60.0%, the pore volume values of 157.58 mL for the organic and 235.2 mL for the mineral were added to the columns resulting in the addition of 95.58 meq and 142.7 meq of sodium added to the organic and mineral soil, respectively. Irrigation was simulated as ponding (Laboratory 1954) in which water is added in large volumes at the same time and allowed to leach through the soil. The leachate was collected and analyzed.

Contact time between soil and saline solution was dependent on the infiltration rate of each replicate and therefore may vary.

The electrical conductivity and pH of the leachate and soil water extracts were assessed along with calcium and magnesium and sodium levels.

At a second phase of the test (Part II b), leaching with distilled water was simulated in order to simulate a cycling use of seawater and high quality water to maintain adequate soil characteristics. Distilled water was added at 2 pore volumes (157.58 mL for the organic soil and 235.2 for the mineral soil). Since soil samples were collected in the previous experiment, the pore volume applied was actually slightly larger than 2. The previously mentioned volume of distilled water was allowed to leach through the soil once and then repeated with a new volume of the same quality.

Both the first and the second washing leachates were collected and analyzed at the end of the experiment. The electrical conductivity and pH of the leachate were assessed along with calcium and magnesium and sodium levels.

3.3 Part III: Irrigation with brackish water

The objective of this series of tests was to simulate a moderately severe case of irrigation with brackish water. Two sets of solutions were used for the contamination of organic soil and mineral soil in a first phase (phase a). The same solutions were subsequently used for leaching at 2 pore volumes (phase b).

In this test, a similar column set up as the previous one was used, except that:

The columns were set in an oven at 60ºC to increase evaporation and accelerate salt accumulation. Evaporation was monitored by weighting in the soil column that was covered with a petri dish to avoid increasing the moisture content after removal from the oven.

Two sets of columns were tested for each soil type: in the first set of 3 columns, the irrigation solution added was composed of NaCl 1g L^{-1}, $CaCl_2.2H_2O$ 1.325 g L^{-1} and $NaHCO_3$ 1.85 g L^{-1} resulting in a theoretical EC of 5.73 dS m^{-1} (actual EC of 5.20 dS m^{-1}, or 8.8% lower), SAR of 13.08 and RSC of 4.00.

The second set of columns were irrigated with NaCl 2.3 g L^{-1} and $CaCl_2.2H_2O$ 1.325 g L^{-1} resulting in a theoretical EC of 5.77 dS m^{-1} (actual EC of 6.10 dS m^{-1} or 5.7% higher), SAR of 13.21 and RSC < 0. Irrigation was added with a few drops at a time, more closely resembling sprinkling than ponding as an irrigation method (U.S. Lab 1954).

Initially, 67 mL of volume (approximately 75% of the saturation percentage of the mineral soil), was added to soil columns. The same volume was added for the organic soil, which represented more of the saturation percentage of that soil.

Subsequent irrigations were made to compensate for evaporation in 3 different irrigations for each soil (evaporation was allowed for the same period of drying at 60 ºC: 2 hours in a first period, 8 h in a second period and 8 h in a third period followed by a weekend at room temperature). Added volume was based on evaporation of each column resulting in the following additions (after the first 67 mL):

- Organic soil: First irrigation: 3.86±26.2%; Second irrigation: 23.77±17.43%; Third irrigation: 40.27±11.00%.
- Mineral soil: First irrigation: 6.53±0.62%; Second irrigation: 23.70±1.67%; Third irrigation: 39.09±1.69%.

Salt build up was monitored by small sample collection (approximately 7 g of soil at 1:5 soil to water extraction) determining EC and pH as well as soil moisture.

After 4 days, larger samples were collected (65 g) to evaluate electrical conductivity, pH, calcium and magnesium and sodium concentration.

During the second phase of the test (Part III Phase b), leaching with the same solutions used for irrigation was performed resulting in the addition of 106 mL of irrigation solution in the organic soil and 145 mL in the mineral soil. This phase of the test was done in order to see if even a brackish solution, when used in excess volume, could perform some leaching of the soil salts. The leaching solution was collected and monitored for pH, EC, calcium and magnesium and sodium.

Final soil samples were collected to assess how leaching might have changed salt concentrations in the leached columns.

4. Results

4.1 Part I: Soil characterization tests

A thorough series of relevant tests were conducted for assessing important characteristics of the two tested soils. The mineral soil was previously tested in other works (Carvalho 2014) and the values were taken from previous researchers and are summarized in Table 5.

Table 5- Soil characterization data for the two studied soils.

	Organic		Mineral	
	Average	%RSD	Average	%RSD
Gravel (%)	6.7	-	5	-
Sand (%)	65.4	-	60*	-
Silt (%)	24.7	-	28*	-
Clay (%)	3.2	-	7*	-
Texture	Loamy sand	-	Sandy loam	-
TPH	53.4	2.1	0.35*	-
Saturation percentage	33.3	5.1	46.3	1.7
Lime content	no effervescence	N.A.	no effervescence	N.A.
CEC (meq per 100 g)	42.3	4.49	179.7	3.24
TOC (%)[1]	4.30	8.0	0.396*	-
OM (%)	7.40	8.0	0.68	-
IC (%)[1]	0.45	26	Below detection*	-
Carbonate	0.6	19	Below detection	-
EC (dS m^{-1})	0.9	N.A.	1.28	-
Ca^{2+} + Mg^{2+} (meq L^{-1})	3.05	22	4.18	7.4
Na^{+} + K^{+} (estimated)	6.4	6.7	8.63	3.6
Soil density (kg L^{-1})	2.14	0.05	2.68*	-
Bulk density (kg L^{-1})	1.101	4.6	1.16	-
Apparent porosity %	48	0.17	60	-
pH (1:2)	6.837	-	7.066	-

* Taken from Carvalho (2014), PhD thesis.

[1] Total organic matter (TOC) and Inorganic Carbon (IC) where tested using different methods between the soils. Organic soil was tested using the loss on ignition procedure (LOI) and the mineral soil was tested using a TOC analyzer from Shimadzu TOC-VCSN with a SSM-5000A module.

The main differences between the two soils are the organic matter content and cation exchange capacity. Although the organic soil has a significantly larger content in organic matter, the larger clay percentage of the mineral soil makes its cation exchange capacity larger than the organic soil.

The higher soil density of the mineral soil translates into a higher apparent porosity. The higher TPH value for the organic soil is unlikely to be of any significance as it is lower than the limit concentration of 100 mg/kg (EPA, 2001).

In summary, both soils can be considered as non-saline, sodic or calcareous with neutral pH and similar soluble calcium and magnesium content.

In addition, a screening test for possible heavy metal contamination was conducted for the organic soil with the results shown in Table 6.

Table 6- Heavy metal content in the organic soil (ppm).

	Average (ppm)	% RSD		Average (ppm)	% RSD
Ti	2185	11.1	Cu	< 101	-
Mn	138	15.9	Co	< 173	-
Fe	12858	1.2	Ni	< 32	-
Cu	25	28	Hg	< 9	-
Zn	116	5.2	Se	< 3	-
As	19	21	Mo	< 8	-
Pb	171	3.5	Ag	< 34	-
Rb	134	2.2	Cd	< 40	-
Zr	199	1.5	Sn	< 66	-
Ba	< 397	-	Sb	< 70	-

From the analyzed heavy metals, iron is the one with a potentially interfering concentration. This method of analysis estimates the total presence in the soil of the metals including in minerals and insoluble precipitates and therefore, the difference between the obtained values and the potentially soluble and therefore available metals is great. The EC value further confirms that solubility is limited.

4.2 Part II: Irrigation with seawater

4.2.1 Phase a)

An initial test was conducted with extremely high salinity (approximately seawater levels) in order to assess the most extreme response observable for the two soils in terms of salt build up and accumulation as well as potential effects on soil structure (Table 7). The applied solution had the following characteristics:

EC	53.45	dS m^{-1}
pH	6.021	
Na^+	13950	mg L
Na^+ added to organic soil	95.58	meq
Na^+ added to mineral soil	142.7	meq

Table 7- Results from addition of simplified seawater simulating solution to the mineral soil (1 to 3) and organic soil (4 to 6).

		pH	EC (dS m^{-1})	Na^+ (meq L^{-1})	% RSD	Na^+ estimated (meq L^{-1})	Ca^{2+} Mg^{2+} (meq L^{-1})	% RSD	SAR	% RSD
initial	O	6.84	0.91	N.D.	N.D.	N.D.	2.70	7.0	N.D.	N.D.
	M	7.07	1.28	N.D.	N.D.	N.D.	4.18	16.0	N.D.	N.D.
Leachate	M1	4.24	21.80	204.9	5.0	199.7	18.3	4.0	67.7	1.3
	M2	4.09	34.30	286.8	11.0	323.7	19.3	4.0	92.3	6.0
	M3	4.00	32.00	299.6	10.0	299.5	20.5	5.0	93.6	0.0
	O4	6.00	24.80	196.7	12.0	220.4	27.6	0.0	52.9	5.7
	O5	6.26	20.10	180.7	12.0	175.1	25.9	0.6	50.2	1.6
	O6	4.93	27.40	263.7	7.0	261.8	12.2	4.0	106.8	0.4
Soil (1:2)	M1	4.80	50.82	452.3	8.0	505.7	2.50	1.0	402.1	5.6
	M2	4.57	65.03	601.5	5.0	648.6	1.80	0.0	641.2	3.8
	M3	4.70	57.02	522.8	6.0	568.0	2.20	0.0	498.5	4.1
	O4	7.14	60.24	481.4	15.0	596.1	6.30	0.6	271.2	10.6
	O5	6.99	66.00	536.1	14.0	652.8	7.20	0.0	282.5	9.8
	O6	6.75	40.32	291.9	20.0	387.0	16.2	0.4	102.6	14.0

Soil 1 and 6 are clear outliers throughout the test based on the measured values of sodicity and EC. However, this effect is likely due to different leaching velocities through the soil profile when compared to the other soils.

The EC values obtained for the leachate are within excepted values if one is to consider the expected dilution of the contaminant solution, expected EC would be 23.4 and

24.5 dS m^{-1} for mineral and organic soil, respectively. Leachates 2 and 3 have a higher EC resulting from a combination of smaller water recovery from the leaching event and over mobilization of native salts.

The pH of the solution decreased significantly in the mineral soil, from an initial value of 6.021 to between 4.24 and 4.00. This reduction is likely also related to the over mobilization of native cations, more specifically the cations responsible for exchangeable acidity: aluminum and hydrogen. In these soil samples, sodium replaced these acid cations in the exchange sites due to its high concentration and despite having lesser affinity.

The same effect is visible in the organic soil, in replicate 6, with a lower pH than the remaining solutions. This also explains the higher electrical conductivity of this replicate when compared with the remaining two. However, the lower initial pH of the mineral soil and higher cation exchange capacity account for the larger pH drop as this soil will undoubtedly have a superior exchangeable acidity than the organic soil.

The SAR value demonstrates, simultaneously, which soil absorbed and adsorbed more sodium and leached more calcium and magnesium and therefore the higher the value, the better.

Without outliers 1 and 6, the mineral soil leachate average SAR is 92.95 ± 1% while the organic soil leachate is 51.55 ± 3.7%. In fact, the mineral soil leachate had a higher sodium concentration (293.2 ± 3.1% > 188.7 ± 6.0%) and lower calcium and magnesium leached (19.9 ± 4.3% < 26.75 ± 4.5%). Therefore, the mineral soil seemingly was less affected by the salt contamination.

However, when analyzing the results obtained from soil extracts after contamination, the mineral soil had a marginally higher concentration of sodium (562.15 ± 9.9% > 508.75 ± 7.6%) but significantly lower calcium and magnesium concentration (2.0 ± 14% < 6.75 ± 9.4%) resulting in a higher SAR value for this soil (569.85 ± 17.7% > 276.85 ± 3%). Higher sodium levels are likely a result of a higher saturation percentage of the mineral soil, resulting in increased saline water absorption.

The counterintuitive conclusion that the mineral soil is in fact more affected by saline irrigation than the organic soil is a direct result of the higher exchangeable calcium and magnesium pool of the organic soil when compared to the mineral soil.

A mass balance of total dissolved solids (TDS) is difficult in these conditions: while EC is a suitable approximation of TDS levels, the solutions being compared are radically different: the initial added solution is a clear and simple NaCl solution while the leachate and soil water extracts are more turbid with organic solutes and a far more complex mineral composition. However, a mass balance of a single cation, i.e., sodium (Table 8) is feasible in particular because initially it was not a significant part of the soil solution (a condition not applicable to calcium and magnesium).

However, this mass analysis approach lacks the necessary precision, in this high range of concentrations, to accurately assess adsorbed quantities of sodium and the noticeable variability's are more likely a result of water absorption and conversion errors than actual concentrations of adsorbed sodium. In the future, extractions with other solvents than deionized water are recommended for a detailed analysis of adsorbed sodium in the soil.

Table 8- Sodium mass balance analysis in the soil.

	Na^+ meq soil solution	Na^+ meq in leachate	Na^+ meq total	Na^+ meq added	% difference from added
M1	81.08	48.20	129.28	142.65	-10.35
M2	107.84	67.45	175.29	142.65	18.62
M3	93.73	70.47	164.20	142.65	13.12
O4	62.84	30.99	93.83	95.58	-1.86
O5	69.97	28.47	98.44	95.58	2.91
O6	38.11	41.56	79.67	95.58	-19.97

Furthermore, although a complete mass balance of Ca^{2+} + Mg^{2+} ions is not possible, a sum of the leached concentration and the concentration remaining in the soil solution reveals that in all the replicates of each soil the total concentration is similar even in the outliers 1 and 6 (mineral soil total concentration = 21.5 ± 4.7% and organic soil 31.8 ± 9.3%).

4.2.2 Phase b)

In order to simulate excessive leaching in an attempt to maintain the soils physically viable for a longer period of time, the previously contaminated soils were washed with 2 pore volume of distilled water, twice, and leachate values as well as final soil values were assessed (Table 9).

The pH of the mineral soil leached first remained low however still indicating the presence of exchangeable acidity. In this case, the results for EC and sodium content are more erratic between replicates. This is particularly true for the mineral soil sample no. 2 being a clear outlier.

However, this is potentially the result of soil structure degradation as this soil, in the previous test, was the one with the highest SAR value and revealed during this experiment a far lower infiltration rate since it took up to twice the amount of time for the leaching to occur when compared to the other soils. Considering that this soil had higher sodium concentration and a more prolonged time of infiltration, is not surprising that the leachate has higher EC, sodium and SAR content. A similar behavior was observed for soil sample no. 5, although less strongly.

Table 9- Results of simplified rainfall simulating on to the mineral soil (1 to 3) and organic soil (4 to 6).

		pH	EC ($dS\ m^{-1}$)	Na^+ meq L	% RSD	Na^+ meq L estimated	Ca^{2+} Mg^{2+} meq L	% RSD	SAR	% RSD
Leachate (1st)	M1	4.13	18.68	165.0	2.0	181.4	5.4	5.0	100.4	4.7
	M2	3.97	26.50	286.0	10.0	259.0	6.0	0.0	165.1	5.0
	M3	4.01	20.50	165.0	3.0	199.5	5.5	8.0	99.5	9.5
	O4	5.44	19.83	152.0	5.0	188.3	10.0	6.0	68.0	10.7
	O5	5.78	28.40	239.0	6.0	268.8	15.2	7.0	86.7	5.9
	O6	6.04	11.03	73.0	7.0	101.0	9.3	5.0	33.9	16.1
Leachate (2nd)	M1	5.58	1.75	9.0	5.0	17.0	0.8	0.0	14.3	30.7
	M2	4.79	3.67	20.7	5.0	36.0	0.45	16.0	43.7	26.9
	M3	4.60	3.45	19.1	3.0	34.0	0.65	11.0	33.5	28.1
	O4	6.97	2.41	13.3	5.0	23.0	1.0	0.0	18.8	26.7
	O5	7.18	3.34	18.1	4.0	32.0	1.7	8.0	19.7	27.7
	O6	6.44	4.72	24.4	3.0	40.0	7.3	2.0	12.7	24.3

With the second leaching event, the same general tendencies are observed: the mineral soil leachate had a higher SAR value than the organic soil, mostly due to low calcium and magnesium. However, it is important to point out that the estimation method of sodium is less reliable in this case, with a higher difference compared to the measured SAR. It is possible that the estimation method, at least for these soils in particular, is mostly valid at high concentrations of sodium and/or EC where the potential interfering cations (like potassium and other cations) exist in a relatively low percentage in comparison with the total quantity of cations present.

In the second leachate, pH values start to increase and EC and sodium are relatively low. However, the water could still be classified as sodic (SAR > 13) in most samples although not saline (EC < 4 $dS\ m^{-1}$).

Still, both soils at this stage had lost a significant portion of soluble and exchangeable calcium and magnesium through leaching (mineral soil lost 6 ± 4% meq of Ca^{2+} + Mg^{2+} and the organic soil 5.8 ± 19% meq). This is also visible by the new equilibrium concentration obtained from the soil solution which is 66% and 56% lower than the initial values for the mineral and organic soil, respectively. Additionally, all soil extractions were much more turbid and difficult to properly filtrate, indicating a soil structural problem similar to the one previously reported for soil sample no. 2.

These facts signify that the leaching disproportionately reduced soil salinity over sodicity, destabilizing the soil aggregates further. Additionally, despite the high volume of pore volume added to both soils, the leaching event did not restore the soils to their initial state despite effectively reducing soil salinity and sodicity: without the leached calcium and magnesium any new increase in sodium will disproportionally increase SAR levels; the reduction of exchangeable acidity limits soil buffer capacity to changes in pH; the destroyed soil structure leads to soil drainage problems and waterlogging and a more challenging (and potentially more costly) agricultural management problem.

The problems with drainage were verified for some replicates, namely no. 6, and help to explain the larger accumulation of salts and sodium. The drainage problem is, therefore, more complex than simply the prevention of water flow downwards but also the time in which the saline solution remains in contact with the soil during leaching. In fact, lack of drainage leads to floods and subsequently to lateral movements of salts to lower areas.

4.3 Part III: Irrigation with brackish water

In this particular test, the two different soils were studied in separate. Both soils were exposed to irrigation with low quality water (brackish water EC approximately 5 dS m^{-1}). The two solutions used for contaminating the soils differ in terms of carbonates, which were only present in the solution used for irrigating columns 1 to 3, whether in organic or mineral soil.

The test was distributed in two phases: in phase a) the soils in each column were irrigated with the corresponding referred solutions, and in phase b) the same solutions were subsequently used for leaching at 2 pore volumes. The leached volume was analyzed, as well as a sample of soil extracted after leaching was completed. Due to predicted varying values of calcium and magnesium due to carbonates, a mass balance was not possible.

4.3.1 Organic soil

4.3.1.1 Phase a)

The organic soil was exposed multiple times to brackish water irrigation either with or without high residual sodium carbonate (RSC). The obtained results are presented in Table 10.

Table 10- Results of irrigation with brackish water applied to the organic soil.

Column	Moisture (%)	EC (dS m^{-1})	pH	Ca^{2+} + Mg^{2+}		Sodium		SAR	
				Average	% RSD	Average	% RSD	Average	% RSD
1	10.9	5.74	7.45	11.20	24.74	32.8	3.2	13.85	3.18
2	8.3	7.83	7.24	9.60	12.50	30.6	3.0	13.97	2.97
3	6.8	4.80	7.60	7.60	9.12	24.4	0.4	12.51	0.35
4	12.0	9.60	7.25	60.40	7.52	38.9	0.7	7.09	0.71
5	9.3	11.14	6.80	65.20	1.06	60.0	10.6	10.52	10.59
6	9.7	11.34	7.33	89.20	3.39	42.7	1.1	6.40	1.06

The pH values did not significantly change, similar to previous results where it was established that the likelihood of a significant pool of exchangeable acidity in this soil was low.

Calcium and magnesium levels, however, are clearly different. The first 3 columns, which are for columns irrigated with brackish water with high RSC, not only have lower levels of calcium and magnesium but also a higher relative standard deviation between measurements. Both these effects reflect the action of the introduced carbonates, which likely induced calcium and/or magnesium carbonate precipitation lowering the activity of either or both of these ions, reflecting in the lower detectable concentrations.

Furthermore, the time it took between soil filtrations and EDTA titrations helps to explain not only why the relative standard deviation is higher in these initial 3 columns but also why it seems to be decreasing from 1 to 3: with more contact time, calcium carbonate dissolution was possible, reducing the results' variability over time.

Considering how both irrigation solutions were prepared, it is not surprising that the sodium levels do not vary significantly (with the exception of the outlier column 5): the added sodium was equal for all columns.

Therefore, the higher SAR levels obtained for columns 1 through 3 is due to lower calcium and magnesium levels. The same effects explain the lower EC levels obtained.

4.3.1.2 Phase b)

In phase b, the organic soil was again irrigated with the same solutions but with a high leaching fraction (2 pore volumes). The obtained leachate and final soil quality was analyzed and shown in Tables 11 and 12.

Table 11- Results of leaching with brackish water in the organic soil.

Column	EC (dS m^{-1})	pH	$Ca^{2+} + Mg^{2+}$		Sodium		SAR	
			Average	% RSD	Average	% RSD	Average	% RSD
1	5.85	6.07	47.33	4.88	34.11	1.06	7.01	1.06
2	6.63	6.10	61.33	1.88	34.54	0.71	6.24	0.71
3	6.00	6.27	68.00	2.94	25.45	1.42	4.37	1.42
4	7.66	5.88	83.33	3.67	33.69	2.12	5.22	2.12
5	7.37	5.93	84.67	7.59	31.48	0.35	4.84	0.35
6	8.05	6.13	78.00	4.44	38.65	0.35	6.19	0.35

The calcium and magnesium values obtained, although following a similar trend as before, are much higher than expected in columns 1 through 3. This is a result of a higher water volume available for dissolution of calcium and/or magnesium carbonates, i.e, a less saturated solution that made calcium more available for EDTA titration.

Due to this more similar value of calcium and magnesium between set #1-3 and set #4-6 columns, SAR values are not clearly higher in one or the other. This is because the SAR calculation involves the square root of the concentration of calcium and magnesium, and any change in these values have to be larger to have a significant impact on the overall value.

However, it should be noted that the values of calcium and magnesium for all leachates are likely over estimated because the concentration was extremely high and a 1:10 dilution was required for EDTA titration further dissolving calcium or magnesium carbonates.

A possible solution for this problem in future tests is the measurement of EC at the same dilution rate in an attempt to confirm the obtained results by the approximation EC * 10 = Sum of all cations (in this case approximately calcium, magnesium and sodium) or at the very least EC * 10 > calcium and magnesium concentration.

EC values are much more similar now as well, due to the same effect: more water available for the dissolution of calcium and magnesium carbonates result in EC values closer to the original irrigation water value.

Table 12- Results of extracted soil sample after leaching with brackish water in the organic soil.

Column	Moisture (%)	EC (dS m^{-1})	pH	$Ca^{2+} + Mg^{2+}$ Average	$Ca^{2+} + Mg^{2+}$ % RSD	Sodium Average	Sodium % RSD	SAR Average	SAR % RSD
1	7.8	3.64	7.71	8.60	10.66	27.47	7.91	13.25	7.91
2	10.3	3.94	7.58	8.00	8.66	30.93	15.44	15.47	15.44
3	5.1	3.74	7.64	9.60	0.00	23.57	2.31	10.76	2.31
4	7.1	6.13	7.05	38.00	3.65	30.18	0.33	6.92	0.33
5	9.3	7.47	6.94	47.53	1.35	36.20	0.33	7.43	0.33
6	6.9	5.92	7.24	41.60	4.41	26.80	1.32	5.88	1.32

After the leaching process, there is a noticeable decrease in EC levels (Table 12). Calcium and magnesium levels, however, only decreased significantly in columns 4 through 6. In the first 3 columns, as calcium and magnesium is leached, the soil solution becomes less saturated in these ions enabling the dissolution of calcium and magnesium carbonates in a direct proportion to partially compensate the losses.

Although, the leaching process allowed for a reduction in the levels of sodium in the soil, there is a concomitant decrease in calcium and magnesium and, therefore, the SAR level is maintained despite the decrease in EC. This EC reduction without SAR reduction further contributes to soil degradation, reducing soil structure stability.

To compare the results in the soil before and after leaching, a graphical analysis is presented in Figure 12.

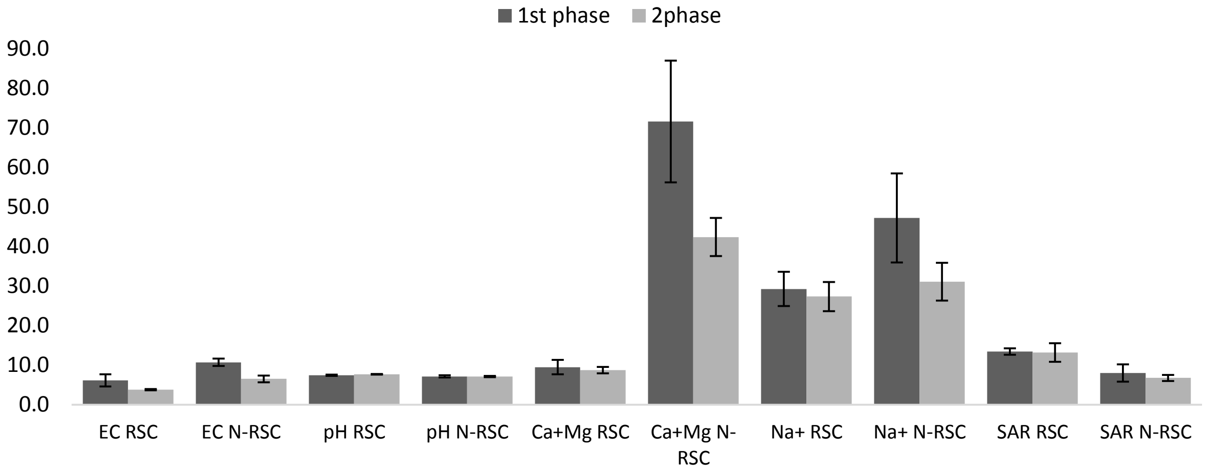

Figure 12- Comparison of results before and after leaching in the organic soil (RSC – signifies results from treatments with high RSC while N-RSC signifies results from treatments with low RSC).

EC, Ca^{2+} and Mg^{2+}, Na^{+} and SAR parameters present a reduction values from 1st to 2nd phase, confirming the effectiveness of the leaching process in terms of reducing the concentration of the measured parameters. The pH of the samples irrigated with high RSC suffered a slight increase between phases, result of the leaching process.

4.3.2 Mineral soil

4.3.2.1 Phase a)

The mineral soil was exposed multiple times to brackish water irrigation either with or without high residual sodium carbonate (RSC). The obtained results are presented in Table 13.

Table 13- Results of irrigation with brackish water applied to the mineral soil.

Column	Moisture (%)	EC (dS m^{-1})	pH	Ca^{2+} + Mg^{2+}		Sodium		SAR	
				Average	% RSD	Average	% RSD	Average	% RSD
1	7.8	4.52	7.53	7.63	13.32	25.12	0.99	12.86	0.99
2	10.2	5.04	7.16	7.48	8.32	26.26	0.66	13.58	0.66
3	9.1	4.75	6.97	7.04	0.00	25.33	7.27	13.50	7.27
4	7.7	7.30	5.19	42.53	1.19	28.72	4.63	6.23	4.63
5	8.0	10.25	5.21	68.35	3.72	41.95	5.29	7.18	5.29
6	9.4	8.27	5.42	45.76	1.92	32.26	-	6.74	-

The first 3 columns have lower calcium and magnesium levels and with higher variability among replicates, reflecting lower EC and higher SAR values when compared to columns 4 through 6. This effect is likely due to calcium and/or magnesium carbonate precipitation. Sodium levels, however, remain relatively constant within all of the columns tested.The pH in columns 4 to 6 decreased considerably (the initial pH of this soil is 7.066). The reduction is related to an over mobilization of native acid cations, especially aluminum and hydrogen, the cations responsible for exchangeable acidity. In these soil samples, sodium replaced these acid cations in the exchange sites due to its high concentration and although having lesser affinity.

This pH reduction is not visible in columns 1 to 3, in which pH actually increases. This is a consequence of the presence of carbonates in the irrigation water, which was responsible for offsetting the released H^+ ions.

4.3.2.2 Phase b)

In phase b, the mineral soil was again irrigated with the same solutions but with a high leaching fraction (2 pore volumes). The obtained leachate and final soil quality was analyzed (Table 14 and 15).

Table 14 - Results of leaching with brackish water in the mineral soil.

Column	EC (dS m^{-1})	pH	Ca^{2+} + Mg^{2+}		Sodium		SAR	
			Average	% RSD	Average	% RSD	Average	% RSD
1	4.62	4.98	40.67	2.84	32.75	1.12	7.26	1.12
2	5.13	4.83	40.67	5.68	37.68	0.00	8.36	0.00
3	4.95	5.21	43.33	2.66	33.46	1.87	7.19	1.87
4	6.42	4.68	67.33	6.86	41.33	0.37	7.12	0.37
5	6.28	4.78	64.00	5.41	40.68	2.62	7.19	2.62
6	6.58	4.87	68.00	2.94	41.66	0.00	7.14	0.00

The obtained values for calcium and magnesium in the leachate are again likely to be an over estimation due to the necessary dilutions for EDTA titration, which lead to increased dissolution of calcium carbonate. The removal of calcium, magnesium and sodium is similar amongst columns despite a slightly higher value for columns 4 to 6.

Table 15 - Results of extracted soil sample after leaching with brackish water in the mineral soil.

Column	Moisture (%)	EC (dS m^{-1})	pH	Ca^{2+} + Mg^{2+}		Sodium		SAR	
				Average	% RSD	Average	% RSD	Average	% RSD
1	14.7	3.46	6.84	8.80	20.83	24.91	0.37	11.88	0.37
2	10.1	3.42	6.72	16.40	15.23	21.89	2.99	7.64	2.99
3	9.0	3.26	6.88	20.80	3.33	19.33	1.12	5.99	1.12
4	11.1	4.84	5.94	39.60	0.00	26.96	0.37	6.06	0.37
5	9.4	5.43	5.33	44.80	4.09	29.27	0.00	6.18	0.00
6	11.4	4.90	5.39	40.00	4.58	27.91	0.00	6.24	0.00

The soil samples obtained after leaching indicate an EC reduction as well as in sodium (Table 15). However, concerning calcium and magnesium, there is a slight increase in columns 1 through 3 leading to a significant decrease in SAR for these columns.

Yet another trend visible is the increase in pH in columns 4 to 6 and the reverse effect in columns 1 to 3. In all columns, pH is stabilized after leaching removed hydrogen ions and carbonate ions. This is indicated by the low pH in the leachate and the decreased in pH in columns 1-3, respectively.

It is possible that the reduction in pH lead to lower carbonate and bicarbonate concentration and/or increased calcium and/or magnesium carbonate solubility. This would limit its negative effects on calcium and magnesium availability.

Following the same procedure than with the organic soil, a comparative graphic is presented to ease the results' analysis in terms of the effect of leaching in the measured parameters in the soil (Table 13).

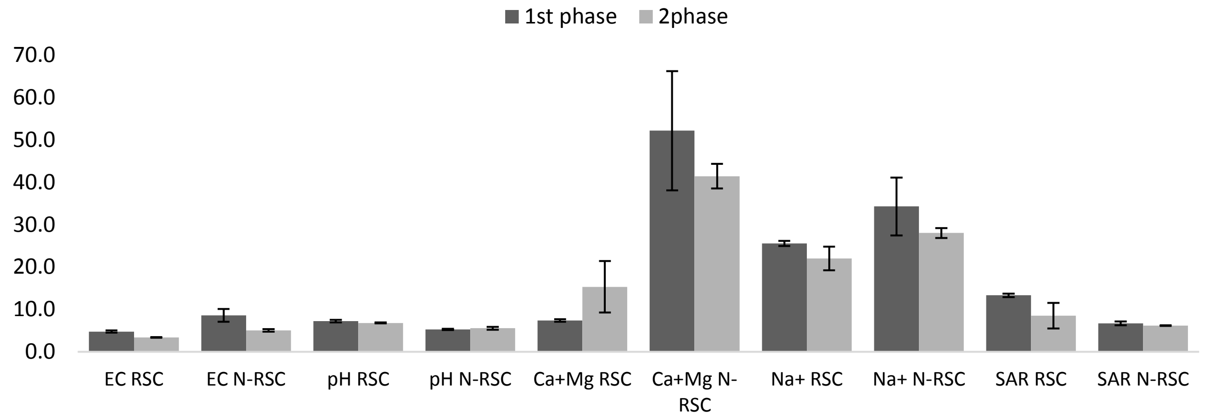

Figure 13 – Comparison of results before and after leaching in the mineral soil (RSC – signifies results from treatments with high RSC while N-RSC signifies results from treatments with low RSC).

EC, Na^+ and SAR parameters present a reduction from 1st to 2nd phase, confirming the effectiveness of the leaching process in terms of reducing the concentration of the measured parameters. Ca^{2+} and Mg^{2+} in the samples irrigated with high RSC is higher after the leaching process, result of the increased capacity of these cations to be dissolved due to the higher volume of added solution and the leaching of dissolved carbonates.

5. Discussion

Comparing the two soils from part II, the organic soil showed a better performance when irrigated with seawater due to a higher content of native calcium and magnesium that were replaced by sodium in cation exchange reactions (organic soil 6.75 ± 9.43% mg L^{-1}, mineral soil 2.00±14.14% mg L^{-1}). This resulted in lower SAR at phase a (organic soil: 276.85 ± 2.89; mineral soil: 569.85 ± 17.7).

However, in phase b, possibly due to difficulties in drainage, leaching removed more SAR in the mineral soil than in the organic soil in both leaching tests (mineral soil 1st and 2nd leaching events respectively: 99.95 ± 0.64 %; 38.6 ± 18.8%; organic soil 1st and 2nd leaching events respectively: 77.35 ± 17.10%; 19.25 ± 3.30%).

A more direct comparison between the soils in part III (Table 16) indicates that the mineral soil tends to have less concentration of all tested parameters before leaching.

Table 16- Difference between average values between mineral and organic soil (in % of mineral soil result over organic soil)

	Before leaching			
	EC	SAR	Sodium	Ca^{2+} + Mg^{2+}
W/RSC	77.9	99.1	87.4	82.0
Without RSC	80.5	84.0	72.6	72.9
	After leaching			
W/RSC	89.6	64.6	80.7	213.0
Without RSC	77.7	91.4	90.3	97.9

However, after leaching, calcium and magnesium in soils irrigated with a solution with high RSC is more than 2x higher in the mineral soil than in the organic soil. To further understand this difference, an analysis of the effect of leaching on both soils is warranted (Table 17).

Table 17- % reduction (expressed as the % difference between final and initial results) of analyzed parameters after leaching in both soils. (Note: a few outliers were removed from this analysis(Mineral soil 1 and organic soil 3 and 5).

		EC	SAR	Sodium	Ca^{2+} + Mg^{2+}
W/RSC	Mineral	31.7	49.7	20.2	-157.4
	Organic	40.5	8.0	16.6	18.0
Without RSC	Mineral	36.1	9.2	9.8	16.0
	Organic	39.0	5.2	29.9	45.2

The most marked difference is in calcium levels, which defines the observed differences in SAR levels. A combination of the leaching of precipitated calcium or magnesium carbonates and dissolved Ca^{2+} and Mg^{2+} resulted in a less saturated soil solution. This enabled the dissolution of remaining calcium carbonates and explains the lower reduction of calcium and magnesium in the organic soil with RSC irrigation water and the increase in the mineral soil with the same irrigation scheme.

However, the difference between both soils remains significant, particularly when considering that it was previously established that the organic soil had more native exchangeable calcium and magnesium in its cation exchange sites.

The large increase in dissolved calcium and magnesium in the mineral soil irrigated with a solution with high RSC is likely due to a significant pH reduction observed in the mineral soil, a result of a higher exchangeable acidity when compared to the organic soil, which lead to an increased calcium or magnesium carbonate solubility.

Comparing the two soils, the organic soil has a larger pool of calcium and magnesium to compensate excessive amounts of sodium when it is contaminated while the mineral soil, due to its exchangeable acidity, is better equipped to cope with rising RSC, provided that the irrigation water also has calcium. It would also seem that the mineral soil is more structurally stable and leaching is more effective in reducing SAR in this soil, which is possibly due to higher porosity.

One mitigation measurement already extensively applied is the reuse of drainage water (Sharma and Tyagi 2004; Barnes 2012), here represented as the leachate. This drainage water can be collected by a multitude of engineered systems from complex drainage piping to sloped ditches. A comparison between the quality of the original solutions used for irrigation and leachate (Table 17) reveals that, despite an occasional increase in EC, the leachate is always of better quality as both soils tend to enrich the water in calcium and magnesium, therefore lowering SAR.

There is little difference between the leachate with initial high RSC and the one without high RSC. However, the leachate that originated from the organic soil is richer in calcium and magnesium and therefore with a significantly lower SAR than the leachate originated from the mineral soil.

This is a result of a more mobile pool of calcium and magnesium that the organic soil presents and the more quality the leachate is, the less quality the soil that is present.

Table 18- Comparison of initial irrigation water (with RSC and without) with the corresponding leachates from both soils.

	EC (ds m^{-1})	SAR	Sodium (meq L^{-1})	Ca^{2+} Mg^{2+} (meq L^{-1})	RSC
Initial RSC irrigation	5.2	13.0	39.0	18,0	4.0
Mineral RSC leachate	4.9	7.6	34.63	41.56	N.A.
Organic RSC leachate	6.3	2.35	31.37	58.89	N.A.
Initial irrigation	6.1	13.2	39.0	18.0	0.0
Mineral leachate	6.4	7.15	41.22	66.44	N.A.
Organic leachate	6.0	2.17	34.61	82.0	N.A.

Using leaching as a mitigation measure in this case, can be applied only because there is a small window between irrigations and leaching. If the time between continuous long term irrigation and soil leaching would increase, a much lower quality of leachate would be presented. This is also a legitimate way to control soil salts, particularly if treatment and disposal of the leachate is considered and if available water resources are low. The choice between these two techniques depend on economic and on site characteristics.

Further measurements for mitigation could involve acidification of the irrigation water with high residual sodium carbonate that would eliminate or significantly reduce the carbonate system (depending on the final pH obtained) or, for example, dissolution of a calcium source (either gypsum or others) in both irrigation waters or cyclic use of good and poor quality water to sustain adequate soil quality (Choudhary, Ghuman et al. 2006; Barnes 2012).

Comparison with different works in the literature is complex, since there are too few studies that incorporate residual sodium carbonate and field studies can be in a non-comparable scale and are normally with a widely different scope, in which the potential of brackish or seawater use for irrigation is evaluated by plant response (relative short term response, one or two crop cycles) and the impact on soil quality is, at times, slightly neglected. With the use of either high salinity water or extremely high evaporation, the salt accumulation processes were highly accelerated in this thesis.

Although with limitations, this approach enables the estimation of the impact of poor quality water for irrigation in a shorter period of time and is more useful in a qualitative comparison between different options rather than being a precise estimation of any particular one.

Still, a few comparisons are possible. Prasad, Kumar et al. (2001), for instance, performed similar work although at a larger scale. A few of its conclusions, however, are similar to what was observed in the tests conducted throughout this thesis. These include the following:

- An increase in SAR was also attributed to calcite precipitation when the soil was irrigated with increasing RSC levels;
- The pH increase observed for the organic soil after irrigation with water with high RSC was also observed, a result of increased alkalinity (due to carbonate and bicarbonate addition) and reduced CO_2 partial pressure in the soil.
- However, it also mentions that the soil EC increases with RSC and attributed this increase to higher sodium content. In this thesis the reverse was found as sodium content did not change significantly amongst replicates and calcium and magnesium decreased with increasing RSC and therefore reducing EC. This discrepancy between this work and Prasad, Kumar et al 2001, is difficult to explain as the author neglects to quantify the initial concentration of calcium, magnesium and sodium in the soil tested.

Other authors reached similar conclusions, namely pH increase with residual sodium carbonate as well as sodicity (Choudhary, Ghuman et al. 2006; Minhas, Dubey et al. 2007b; Choudhary, Ghuman et al. 2011).

Choudhary, Ghuman et al. (2006) also reported a pH and SAR reduction with application of organic amendments. This suggests that the presence of organic matter in one of the tested soils in this thesis would prove beneficial in SAR accumulation. However, the most likely mechanism by which organic matter reduces pH and SAR is due to its decomposition and so a more readily degradable organic source is needed than the stabilized humus that is likely present in the organic soil tested.

6. Conclusions and future work

A few key conclusions can be drawn from the experimental work developed:

- The high content of calcium and magnesium in the organic soil causes a higher reduction of SAR when irrigated with seawater;

- The mineral soil has higher porosity, therefore presenting a faster drainage, which results in a more effective SAR removal in this soil through leaching in seawater irrigation;

- The organic soil contains more exchangeable bases like calcium and magnesium ions, since it is more adapted to irrigation water with low levels of calcium and RSC. Conversely, the mineral soil has more exchangeable acidity, since it is richer in terms of H^+ ions, aluminum and more adapted to irrigation water high in RSC.

- Salinization processes have a strong effect on pH. The observed variability can be damaging to plant development and potentially be a limiting factor as relevant as salinity and sodicity, particularly for salt tolerant plants.

- Irrigation with brackish water is feasible if combined with semi-constant leaching of the soil. However, economic feasibility of this option should also be considered because it can be an obstacle for field applications.

- Although application of leaching could help control salinity levels in the soil, the leaching of nutrients should also be investigated.

Future work should focus on improving the available monitoring tests at high RSC values, in particular for calcium and magnesium. Furthermore, exchangeable cations should also be monitored in the future, when more precise measuring methods become available.

Future tests should also focus on different mitigation options such as blending different quality waters and gypsum addition. The effects on plant growth should also be examined at the same time as the changes in the soils' geochemistry.

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Appendix A - Detailed methodology

Sodium measurement methodology

Measuring principle

The FC 300 B sodium electrode used in this thesis functions as a sensor or ionic conductor. As a combination electrode it is able to complete its electrolytic circuit without a reference electrode.

The tip of the sensor is a selective glass membrane that exchanges ions (it's more selective to sodium ions) with the samples solution creating a charge imbalance which, in turn, creates a voltage proportional to sodium ion activity following a Nernstian response (provided that the ionic strength is fixed and hydrogen ions are eliminated).

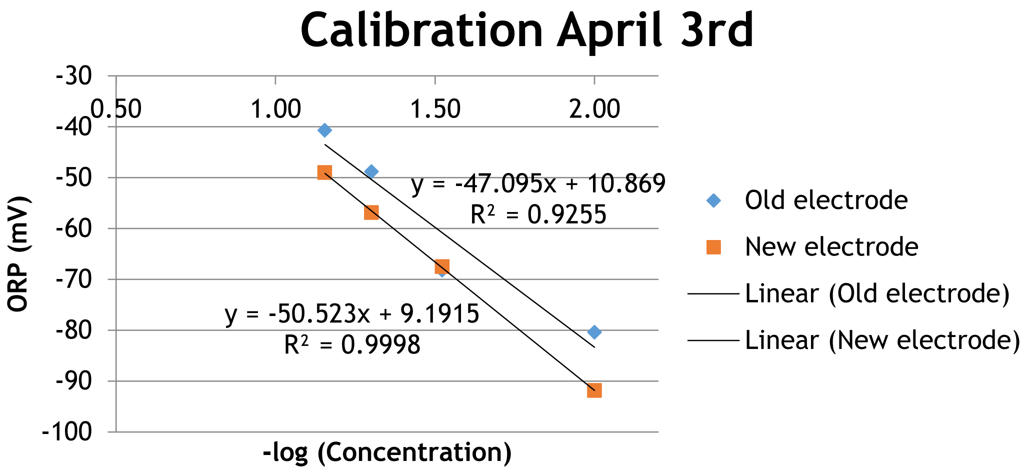
In order to maintain the same ionic strength a ISA (Ionic Strength adjuster) is needed as well as a pH buffer solution to increase and maintain pH at a high enough level to eliminate hydrogen interference.

Procedure

Before starting to use the electrodes for the desired measurements, there was a need for proper calibration. Repeated calibrations are required because the slope might chance over the course of the electrode lifespan and particularly with heavy usage, which may make the electrodes desensitized at low concentration values. As a way to make a distinction of the two used electrodes in some of the measurements, they were labeled as “old” and “new”, referring to the date at which each was acquired.

The preparation of the calibration curves involved an initial dilution of 1M NaCl stock solution in increasing order (for instance, 1, 2, 5 and 10 mL in 100 mL dilutions). Between measures, the electrodes were cleansed with a portion of the following solution and then dried. The response time varies from 5 to 10 minutes, and therefore each dilution results were registered after said interval. It is important not to assume that the electrodes are stable before that, regardless of what the display shows.

Figure 1– Example of prepared calibration curves



The sodium solutions (1M NaCl) was prepared by dissolving 5,854 g of NaCl in 100 mL. Subsequent dilutions were prepared from this solution by pipetting 1, 2, 5 or 10 mL of this concentrated dilution and 10 mL of ISA solution 4M (corrosive), and then diluted to 100 mL flask. The referred ISA solution was prepared by adding 20 g of NH_4Cl to 27 mL of concentrated NH_4OH and diluted to a 100 mL flask.

Calcium + Magnesium measurement methodology

Measuring principle

The determination of calcium and magnesium ions present in a solution was accomplished by EDTA Titrimetric Method (US Lab 1954, Standard Methods).

To perform this test a buffer solution needs to be added to the sample followed by colorimetric indicator. The buffer is intended to provide a metal ion (in this case magnesium) in an EDTA standard solution that binds well with the indicator (Eriochrome Black T in this case) changing its color to red-violet. The buffer solution also contains an ammonium buffer created by NH_4Cl / NH_4OH meant to increase and maintain a high pH to prevent the interference of other metals ($pH > 10$) and avoid hydroxide precipitates of calcium or magnesium.

During the addition of the titrant (EDTA), the complex of the indicator + magnesium will remain unchanged up until the point of equivalence at which time all the calcium and magnesium in the sample have been titrated.

At that point, the magnesium in the complex returns to solution to create a more stable complex with the excess EDTA, therefore leaving the indicator uncomplexed which causes it to change its color to blue, indicating the end point of the titration (near the end point there is a slight change of color from red-violet to violet).

Procedure

The determination of calcium and magnesium involved the previous preparation of some solutions, as described below.

Solution 1:

1) 1,17772 g of disodium EDTA.$2H_2O$ + 0,7820 g of $MgSO_4.7H_2O$ added to 50 mL (assumed that analytical grade disodium EDTA = disodium EDTA.$2H_2O$);

2) 16,9002 g of NH_4Cl + 144 mL NH_4OH in 250 mL

The first was added to the second and made into a solution of 250 mL with expiration time of one month more or less.

Solution 2: 0,10 g methyl red in a 100 mL vessel. This solution is an indicator and has no indication of expiration date.

Solution 3: 3,7231 g of disodium EDTA in 1 L.

Solution 4: 105 mL of concentrated NH_4OH in 500 mL, resulting in NH_4OH 3N

Solution 5: 35 mL of concentrated NH_4OH in 500 mL, resulting in NH_4OH 1N

Solution 6: It was assumed that $CaCO_3$ < 30 µm anhydrous is appropriate. The solution preparation involved the following steps: 1,0005 g of $CaCO_3$ + drops of 6N HCl + boiling for a 10 minutes period + drops of methyl red solution + adjust to orange / weak yellow with 6N HCl and NH_4OH.

Indicator: 99,67 g of NaCl + 0,5023 g of Black T mixed.

The procedure for titration involved the previous addition to an Erlenmeyer flask of 50 mL of distilled water + 10 mL of Ca standard (solution 6) + 1 mL of buffer solution (solution 1) + small scoop of indicator, attributing a pink tone to the solution. After this, the titration with solution 3 was made, until the solution color reached blue.

To test a sample, it was added 1 to 2 mL of buffer solution and a small scoop of indicator and titrated with solution 3.