Salt-Affected Soil: Problems and Solutions

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Introduction

A substantial percentage of agricultural land around the world is affected by high salt content. In many cases, salt-affected soils are the result of using high salt-containing water for irrigation purposes. However, the adverse role of salt in soil is frequently misunderstood. Salt, being more precise common salt, is an electrolyte that is composed of Na⁺ and Cl⁻. As in an aqueous environment, salt readily dissociates into Na⁺ and Cl⁻ ions in the presence of moisture in soil. It is always present in the form of Na⁺ and Cl⁻ ions.

The behavior of these dissociated ions in soil must be examined in terms of their affinity to the soil particles. Soil, in general, is composed of sand, silt, humus and clays. In an agricultural environment, these soil components are negatively charged. Of these, clay and humus also have high cationic exchange capacity (CEC). In such an environment, invariably, it is the Na⁺ ions that tend to adsorb into the soil structure. Cl⁻ ions, being like-charged to the surface of the soil-forming components, remain free, and move with the movement of moisture in the soil structure. This means, with adequate irrigation, they can be flushed out of the soil cross section to lower levels.

In terms of the role of Na⁺ and Cl⁻ in the crop physiology, while Na⁺ is toxic to crops, Cl⁻ is a micronutrient. In fact, plants may take up as much chloride as they do secondary elements such as sulfur. However, the salt problem in soil is mistakingly labeled as the chloride problem and not a sodium problem, which is the real culprit. This misrepresentation could possibly be attributed to the chemical analytical practices. Until recently, the analysis of sodium in a substrate or liquid phase has been a tedious task. In fact, for an accurate measurement, one needs a more expensive and sophisticated analytical instrument to measure sodium content. Other elements present in chloride form, such as calcium and magnesium, are much easier to measure. Measurement of chloride, on the other hand, is simple and relatively cheap. Portable analytical tools have also been available for some time. To estimate the extent of salt damage to the soil, it has been customary to measure the chloride content. This may be the reason that chloride is frequently misunderstood as being the problem in the soil.

In this article, the problems associated with salt-affected soil are discussed. Treatment of such soil is recommended for bringing it back to the state that will allow the healthy growth of crops.

Ionic Adsorption in Soil

The mode of adsorption of the ionic species that are present in the soil, or that are introduced to it, could be attributed primarily to the ion exchange phenomenon or to the physical or chemical adsorption of the ions to the soil structure. While cation exchange in soil is considered to be the major factor influencing the adsorption of the available ions in the system, adsorption of cations at the predominantly negatively charged surface of the soil-forming particles is also possible.

The major exchangeable or adsorbing cations in soil are Al^{3+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and H^+ . Other exchangeable cations, which are minor components of soil, but have nutrient values, are Cu^{2+} , Fe^{3+} , Zn^{2+} , Mn^{2+} , and NH_4^+ . Among these, Ca^{2+} , Mg^{2+} , K^+ , and Na^+ are the dominant cations in most soils, and they are frequently measured for the evaluation of soil condition.

Valance is the major factor affecting the likelihood that a cation can be adsorbed. A trivalent Al³⁺ is more likely to adsorb than a divalent Ca²⁺, which is more strongly adsorbed than a monovalent Na⁺. However, for cations of similar valence, smaller cations with greater charge density per unit volume adsorb more strongly. The diameter of these ions includes the water molecules that are adsorbed onto them, forming a hydrated layer. It is the hydrated diameter of the cations that are involved in the adsorption at the particle surfaces. For this reason, Ca²⁺ with hydrated ionic radius of 6A adsorbs with much stronger energy than Mg²⁺ with hydrated radius of 8A. Similarly, NH₄⁺ or K⁺, with their respective radii of 2.6A and 3A, adsorbs with much stronger energy than Na⁺ with hydrated radius of 4A. The general order of selectivity or replaceability, of some important exchangeable hydrated cations (hydrated radius of each ion is given in parenthis) is as follows:

$$Al^{3+}\left(9A\right) > Ca^{2+}\left(6A\right) > Mg^{2+}\left(8A\right) > NH_{4}^{+}\left(2.6A\right) > K^{+}\left(3A\right) > Na^{+}\left(4A\right)$$

Among the above hydrated cations, Al³⁺ has the largest hydrated radius but, due to its higher valence, can adsorb strongest. However, at pH values higher than 4.0, as aluminum starts precipitating as aluminum hydroxide, there is a drastic reduction in the concentration of Al³⁺ ions in the soil environment. As most plants, or vegetation, sustain only at pH values higher than 5.0, use of an aluminum electrolyte is not an option for soil amendment. Consequently, calcium is the most effective element that could be used for soil amendment. Furthermore, aluminum is considered toxic to most of the crops.

The major factor affecting the absorption of cations in the soil structure is attributed to its Cationic Exchange Capacity (CEC), which represents the total quantity of negative charge available to attract positively charged ions present in the solution. It is expressed in terms of milliequivalent of negative charge per 100 g of oven-dried soil (meq/100g). The CEC also represents the total meq/100 g of cations that can be held on the negative charge sites of the soil particles.

The CEC of a soil is strongly influenced by the nature and amount of mineral and organic compounds present. Soil containing high clay and organic matters have higher cationic exchange capacity than sandy soils that are low in organic matter content. The CEC of soil with different textures are given in Table 1.

Table 1
CEC Values of Different Soil Textures

<u>CEC (meq/100 g)</u>
3 – 5
10 - 20
10 - 15
15 - 25
20 - 50
50 - 100

It is evident that soils with high clay content or organic matters have high CEC value, and will tend to adsorb larger amounts of cationic species. However, the capacity for the adsorption of cations will also depend on the base saturation of the soil, which is defined as the percentage of total CEC occupied by base cations, e.g., Ca^{2+} , Mg^{2+} , K^+ , and Na^+ . The percentage base saturation is expressed as follows:

% Base Saturation =
$$[\text{total bases (meq/100g) / CEC (meq/100g)}] * 100$$
 (1)

As the presence of Na⁺ in the soil structure is critical to its fertility, it is important that they are replaced by more desirable cations. There is a direct relationship between the *Exchangeable Sodium Percentage (ESP)* of the soil and its CEC value. This can be expressed as follows:

$$ESP = [Exchangeable Na (meq/100g) / CEC (meq/100g)] * 100$$
 (2)

In soils, ESP is the most prevalent criteria to assess the sodium hazard. However, ESP does not apply to irrigation water, since water does not have CEC sites. Instead of ESP, criteria used for irrigation water to quantify sodium induced hazard is *Sodium Adsorption Ratio (SAR)*. Traditional means of assessing Na status is to determine the quantity of Na, Ca, and Mg in irrigation water, and report it as the SAR as follows:

SAR = Na /
$$[(Ca + Mg) / 2]^{0.5}$$
 (3)
Where the concentrations of Na, Ca and Mg are expressed in meg/L.

On empirical basis, for soil, a relationship between soil ESP and its SAR (saturated paste extract) has been determined as follows:

$$ESP = (1.475 * SAR) / (1 + 0.0147 * SAR)$$
(4)

When using the 1:5 extract for SAR determination (practiced in Australia), the relationship is:

$$ESP = 1.95 * SAR + 1.8$$
 (5)

The ESP value that may possibly cause the damage to the soil fertility depends on the mineralogical composition of the soil. For example, soil that may contain kaolinite clay with its relatively low CEC value may require as high as 40% Na saturation in its cationic exchangeable structure before damage can be noted. On the other hand, soil containing montmorillonite clay with its high CEC value may require only 15% Na saturation before the soil is damaged. However, in general, soil with low clay content is subjected to fewer problems, as it has a low cationic exchange capacity and is also waterand air-permeable. It is, therefore, important that when a soil is evaluated along with ESP value, its CEC is also determined.

Effect of Salt Contamination

Salt-contaminated soil can be classified into three groups: *saline*, *sodic* and *saline*/*sodic*.

<u>Saline Soils</u> have saturated Extract Conductivity (EC_{se}) > 4 mmhos (or mS)/cm, pH < 8.5, and ESP < 15%. This means that most of the salt in the soil is still in the free-state, and sodium has not adsorbed into the soil structure, as of yet. However, the presence of the soluble salt in soil is sufficient to interfere with vegetation, or plant growth. In such case, depending on the CEC value of the soil, the excessive soluble salts may be removed by leaching through irrigation, and the soil again can become normal. If the CEC value of the soil is low, irrigation with fresh water can alone resolve the problem. However, if the CEC value of the soil is high and attracts the Na⁺ ions from the salt solution, the adsorbed Na⁺ ions would need to be replaced by more preferred ions, such as Ca^{2+} .

Saline soils are often recognized by the presence of white crusts of salts on the surface. The damage to vegetation or plants in saline soil is primarily attributed to its high EC_{se} , which imparts high osmotic pressure of the soil solution that keeps moisture away from the root structure. This, in turn, could produce devastation on vegetation or plants.

<u>Sodic Soils</u> occur when ESP > 15%, EC_{se} < 4 mmohs/cm, and pH > 8.5. This is the state after a certain period of soil being exposed to the salt solution and the CEC value of the soil is adequate to adsorb $\mathrm{Na^+}$ ions into its structure. In such case, the adsorption of sodium disperses the colloidal fraction of the soil structure and makes the soil more impermeable to moisture or air. The presence of sodium in the soil structure in the sodic soil, creates a nutritional disorder in most plants and vegetation. In contrast to saline soil, in the sodic soil, when free salt is leached out of its structure, the

exchangeable sodium hydrolyses, and there is increase of pH. In this case, as the free salt is leached out of the soil structure, the EC_{se} value is lower than the saline soil.

Sodic soils are primarily found at the sites which were exposed to salt in the past. In the soil structure, sodium ions are adsorbed at the colloidal clay particles. Chloride, being like charged to the soil particles, drains out of the soil system, and follows the movement of water. However, due to the dispersion of colloidal clay particles in the soil structure, soil becomes increasingly impermeable. The free chloride ions are also physically entrapped in to the impermeable soil structure. These entrapped chloride ions can be removed from the soil structure, by replacing the sodium ions with preferred calcium ions. Adsorption of calcium ions also destabilizes (flocculate) the soil particles, making the soil structure more permeable.

<u>Saline/Sodic Soils</u> is a combination of the two states, which has high salt concentration with $EC_{se} > 4$ mmohs/cm and high ESP > 15%. However, it has a pH < 8.5. This is a typical case of periodic occurrence of salt spills to the soil that has been exposed to salt for some time. Although, the return of the soluble salt to the soil that has achieved the sodic state may lower the pH, the management of this soil continues to be a problem until the excess salts and exchangeable sodium, are removed from the plant or vegetation root zone, and a favorable physical condition of the soil is restored.

The high EC_{se} value of soil due to high concentration of salt increases the osmotic pressure of the soil solution. The roots of plants and vegetation under this environment are unable to overcome the osmotic pressure of the soil, and they die from the lack of water.

As there is a statistical relationship between EC_{se} and osmotic pressure, on the basis of easily measurable EC_{se} , potential damage for the crops can be estimated. Apart from the lack of water being available to the roots in the high EC_{se} environment, high salt concentration in the soil solution also reduces the availability of essential plant nutrients. This results in a drop in plant yields, and in many cases there is total devastation.

There is no one threshold salinity level for all plants or vegetation. Generally, vegetables are more sensitive to salts than grains and grasses. A general crop tolerance level to salt has been developed by the US Salinity Laboratory (1954), as given in Table 2, which indicates no effect on the plant yields if EC_{se} value of the soil is lower than 2 mmhos/cm.

 $\begin{tabular}{ll} Table 2 \\ General Crop Response as a Function of EC_{se} \\ \end{tabular}$

EC _{se} (mmhos/cm)	Effect on Crop Yield
0 - 2	None
2 - 4	Slight
4 - 8	Many crops affected

At higher than 16 mmhos/cm values of EC_{se}, either there is drastic reduction in plant yield or there is complete devastation. High sodicity, or high ESP, or high sodium content, of the soil also influences the crop yield, as shown in Table 3.

Table 3
Reduction in Crop Yield as a Function of Soil ESP

Type of Soil	ESP	Average % Reduction in Crop Yield
Slightly Sodic	7 – 15	20 - 40
Moderately Sodic	15 - 20	40 - 60
Very Sodic	20 - 30	60 - 80
Extremely Sodic	> 30	> 80

Treatment of Salt-Affected Soil

As discussed earlier, the soil that is exposed to salt contamination goes through different phases. The soil freshly exposed to the brine solution is at the saline stage. The majority of salt in this case is still in the free-state. With irrigation, saline soils can be amended by leaching free salt present in its cross section. Leaching salt this way can remove it from the root zone to a lower level. The amount of irrigation water required will depend on the salt level or EC_{se} value of the soil and on the quality of irrigation water being available. However, it should be noted that the introduction of calcium, as a cation source in the irrigation water, will not only improve the drainage of the salt content, but it will also ensure the liberation and removal of any Na⁺ ions that could have adsorbed into the soil structure.

With time, when the saline soil is frequently irrigated naturally through rainfall, or artificially, the free-salt solution drains to the lower level of the soil cross section. However, due to ion exchange phenomenon, the cationic Na⁺ species are adsorbed into the soil structure. The Cl⁻ species of the salt, on the other hand, do not adsorb at the like-charged surface of the soil particles. A substantial portion of Cl⁻ species drains to a lower level. They remain free to be drained to even lower levels of the cross section with further irrigation. Yet, a significant portion of Cl⁻ species can be mechanically entrapped in the soil structure. This mechanical entrapment is further compounded by the fact that, due to the adsorption of Na⁺, soil becomes dispersed. This is the typical state of sodicity. The ESP value of such soil will determine the degree of its sodicity. However, with subsequent exposure to salt, the sodic soil may reach a complex state of sodic/saline type.

It is important that the fates of Na⁺ and Cl⁻ species in the soil structure are clearly understood. The general chemical environment of most natural soils is such that Cl⁻ species do not adsorb at the particles. They remain free. However, Na⁺ species do adsorb at the predominantly negatively charged surface of the soil particles. Once the soil that is dispersed due to the adsorption of Na⁺ species is destabilized through amendment, its permeability and, therefore, its drainage property is improved. This results in the removal of Cl⁻ species that are mechanically entrapped in the soil structure to a lower level. If an adequate amount of soil amendment and irrigation is applied, adsorbed Na⁺ species and free Na⁺ species that are mechanically entrapped in the soil structure, along with Cl⁻ species, can be liberated and removed from the soil cross section to a lower level. Soil at the root zone, thus, can be restored to the state of fertility.

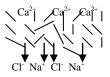
Amendment of salt-affected soil, through cationic exchange, is postulated in Fig. 1. Due to the adsorption of Na⁺ species, the soil particles, particularly the clay fractions, are dispersed. The parallel plate-like arrangement of the dispersed clay particles impedes the movement of moisture in the soil structure. As shown in Fig. 1 (A), while Na⁺ ions are adsorbed into the clay structure, the negatively charged Cl⁻ ions remain free, but entrapped in the dispersed clay system. The excess Na⁺ ions, that are not adsorbed in the clay structure, and are free, could also be mechanically entrapped in this system. When this soil is analyzed, it will show high Na⁺ and Cl⁻ ions. Nature of the presence of Na⁺ can only be determined through the measurement of the ESP of the soil in question.

Once the cationic additives are added to the salt-affected soil for its amendment, the replacement of the adsorbed Na⁺ species in the clay structure with more preferred cations such as Ca²⁺ would liberate Na⁺ from the system. The adsorption of Ca²⁺ ions also aggregates (flocculates) otherwise-dispersed particles. This results in better drainage of moisture in the soil. With adequate irrigation, both mechanically and chemically liberated Na⁺ and Cl⁻ from the system will drain to a lower level, as shown in Fig. 1 (B). Removal of these species from the plant or vegetation root zone restores the fertility of soil. At this stage, if Na⁺ and Cl⁻ were measured at the root zone, significant reduction in their concentration would be noted.

As discussed earlier, calcium being divalent with small hydrated ionic radius and having favorable solution chemistry (calcium being predominantly present in Ca²⁺ form at pH up to 11.0), is the preferred cationic species for the amendment of salt-affected soil. There are a number of calcium compounds that are available for use. However, their effectiveness are based on the amount of calcium that could be available for cationic exchange in the soil structure. The availability of calcium in these compounds, for such use, depends on their water solubility. Limestone, lime, gypsum, and dolomite have been used for soil amendment. Yet, their effectiveness is grossly limited by their poor water solubility. Consequently, the amount of these materials that is needed to achieve the required degree of amendment can be very large. This could be restrictive, particularly in the regions where there are low rainfalls and artificial irrigation is expensive. Calcium chloride, due to its high water solubility, is a preferred additive for soil amendment. The

effectiveness of these additives can be compared in terms of their solubility products that determine their water solubility, as shown in Table 4.





A: Sodium Affected Dispersed Soil

B: Ca²⁺ Amended Open Soil Structure

Fig. 1: Soil Amendment Postulate

Table 4
Solubility Products of Some Soil Amendment
Additives with Calcium Source (at 25°C)

Amendment Additives	Ca Content (wt %)	Solubility Product (K_{sp})	Water Solubility (g/100g)	
Limestone, CaCO ₃	40	9.95 x 10 ⁻⁹	0.0007	
Lime, Ca(OH) ₂	54	7.88×10^{-6}	0.147	
Gypsum, CaSO ₄ .2H ₂ O	29.4	1.2×10^{-6}	0.0149	
Dolomite*, CaMg(CO ₃) ₂	21.7	5.26×10^{-6}	0.0423	
Calcium Chloride**, CaCl ₂	36	8,883.66	82.0	

^{*} Calculated based on the K_{sp} of CaCO₃ and MgCO₃

Among the amendment additives in Table 4, though limestone and lime have higher calcium content than calcium chloride, they are very insoluble in water. Lime, having higher solubility than limestone, is limited to its use in acidic soil. Its use, in the alkaline or moderately acidic soil would render the soil undesirably alkaline. Gypsum, though often used in soil amendment, is more forgiving from the soil pH point of view. However, its effectiveness in soil amendment is restricted by its extremely low water solubility. When compared against these additives, calcium chloride, being highly soluble in water, is the preferred additive in soil amendment. Readily available calcium speeds up the rate of remediation.

The rate at which soil restoration can be achieved by calcium chloride is demonstrated by this example. In this case, the salt spillage occurred due to a storage tank into a pasture land. Soil was classified as clayey loam. At this site, tilling was possible at the time of ReNew[™] (a TETRA product, calcium chloride and urea blend composition) application. In this case, following the application of ReNew, the site was immediately irrigated with water. To evaluate the quick action of the additive, from the top 6 inches of

^{**} Calculated using the solubility data on CaCl₂

the surface, a set of samples were taken after only three hours of treatment. They were analyzed for sodium content and for SAR and ESP values. Test results are summarized in Table 5, which indicate that within the short period of three hours there were significant reductions in sodium content, SAR and ESP values of the treated soil. This behavior suggests a rapid rate of interaction between the cations of ReNew and the soil system.

Table 5
Remediation of Salt-Contaminated Site at Kilgore, Texas
(After Mishra et.al., 1999)

Sample	Na (mg/kg)			SAR			ESP		
	Before	<u>After</u>	% Red	Before	<u>After</u>	% Red	Before	<u>After</u>	% Red
1	5626	1950	65	44	14.5	67	75.5	4.6	94
2	3993	1516	62	27.5	2.6	91	41.3	8.7	79

Concluding Remarks

Problems associated with salt-affected soil are primarily attributed to the Na⁺ and not the Cl⁻. Adsorption of Na⁺ in the soil structure, mainly clays, while it disperses and drastically impedes the moisture permeability of the soil, is also toxic to most of the plants and vegetation. The most effective method of amending such soil is through the replacement of undesirable Na⁺ with other cations that function as a nutrient to plants and vegetation. Ca²⁺ is the most effective cations for this role. As water is the workhorse for the cationic exchange process in the soil, solubility of the calcium containing chemical is critical to its effectiveness. Calcium chloride, being highly water soluble, which allows calcium to be readily available, is the most effective chemical additive that is used for the amendment of the salt-affected soil.

References:

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