

## Chemistry of Soil Solution:

Soil solution is defined as the liquid phase in soil, composition of which is influenced by **flows of matter and energy between it and its surroundings** and by the gravitational field of earth. It means that soil solution is an open system that can be isolated from the soil.

1. Composition of soil solution is determined by the type of parent material the soil is derived.
2. intensity & amount of precipitation, density and type of vegetation and drainage conditions.
3. Influence of soil forming factors on weathering of rocks and minerals has a strong effect on the composition and concentration of soil solution. Additions of organic matter, chemical fertilizer and removal of nutrients also have a significant effect on the composition of soil solution.
4. Climatic factors cause a distinct difference between soil solution composition of arid zone soils and that of humid zone soils. Arid zone soils are high in bases and low in acidity, while humid zone soils are leached and therefore, low in bases. Soil buffering capacity, humus content, and type of clay affect the equilibrium between solid and liquid phases, which in turn changes the composition and concentration of soil solution. **Precisely it can be said that it is the soil solution which supplies readily available nutrients to plants.**
5. The management of salt-affected soils is based on the chemistry of soil solution, climate, plants to be grown and skill of the farm manager. **The chemical composition of soil solution is the result of multi phase equilibria which involve the exchange phase, soil minerals and organic phases and various inorganic complex ions.**

## Saline Soil Solution:

Management of saline soils is based mainly on the type and quantity of soluble salts. Various phenomena involved in the saline soils solution are discussed as under:

### Ion Activity (a):

In general, it is defined as the effective concentration of entities taking part in a chemical reaction. The concentration of electrolytes found normally in natural systems precludes the possibility that these system can not be treated as ideal soil solutions, i.e. measured ionic concentration (m) can not be equated to its ionic activity (a).

### Ionic Strength ( $\mu$ ):

It is a fundamental property of electrolyte solutions. Its values reflect the ionic environments resulting from the presence of ions in solution. It is a measure of the intensity of an electrical field due to the ions of an electrolyte. It may be defined as half the sum of terms obtained by multiplying the molality / molarity of each ion by the square of its valence.

$$\mu = \frac{1}{2} \sum (C_1 Z_1^2 + C_2 Z_2^2 + C_3 Z_3^2 + \dots + C_n Z_n^2)$$

where

- $\mu$  = Ionic strength in mol L<sup>-1</sup>
- $C_1$  = Concentration of first ion
- $Z_1$  = Valence of first ion

- d. EC ( $\text{dS m}^{-1}$ )  $10 = \text{TDS or TSS mmol}_e \text{L}^{-1}$  concentration is valid for a solution of NaCl but invalid for systems involving dominantly  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and/or  $\text{SO}_4^{2-}$  ions or  $\text{EC} > 4 \text{ dS m}^{-1}$ .

### Sodium Hazard in Soils:

The presence of sodium in soil solution represents a potential hazard. When ESP or SAR of soil reaches a threshold value, deterioration of physical conditions of soil will occur. Threshold value depends on the soil type with respect to chemical, physical and mineralogical make up. The sodicity hazard is manifested in the dispersion of clay, swelling and subsequent de-flocculation of clays. The result is a general reduction in both air and water entry into soils much earlier than chemical effects of ESP/SAR on plants.

### Sodium Adsorption Ratio (SAR):

The soil sodicity hazard is associated with ESP of soils but now the commonly used diagnostic criterion is SAR which is calculated from the cationic concentration of the saturation extract. The reasons are that ESP are linearly related up to the levels usually encountered in soils where plants can survive, i.e. ESP or SAR just manageable economically for reclamation and growing several sodicity tolerant agricultural plants. It means that SAR calculations are obtained from chemical analysis of saturation extract of soils. The equation for practical SAR calculations as derived by US Salinity Lab. Staff (1954) is:

$$\text{SAR} = \frac{\text{Na}}{[\text{Ca} + \text{Mg}/2]^{1/2}}$$

When concentration of cations in saturation extract is in  $\text{mmol}_e \text{L}^{-1}$  and

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### Root Zone Salinity:

Root zone is defined as the area of the soil from which the roots of a crop extract water and nutrients.

Plants extract water from the soil by exerting an absorptive force greater than that which holds the water to the soil. If the plant cannot make sufficient internal adjustment and exert enough force, it is not able to extract sufficient water and will suffer water stress. This happens when the soil becomes too dry. Similarly, salts in the soil solution increase the force a plant must exert to extract water and this additional force is referred to as the osmotic effect or osmotic potential. e.g., if two identical soils are at the same water content but one is salt free and other is salty. The plants can extract and use more water from the salt free soil than from salty soil. Salts have an affinity for water. If water contains salts, more energy per unit of water must



### Activity Coefficient ( $\gamma$ ):

It is a parameter that measures the extent of ionic interactions in any solution. In simple words, it is a multiplying factor for converting concentration into activity. The activity coefficient for an ideal solution should be 1. All equations used to calculate the activity coefficient are based on the Debye-Huckel (DBH) theory which primarily accounts for long range electrostatic interactions between ions.

### Effect of Salinity on Chemical Equilibria:

There are numerous chemical equilibria in a soil. Although all the interactions of interest may not be in equilibrium under field conditions, yet the predictive models based on thermodynamic equilibrium are being increasingly used in the management of salt-affected soils. **Equilibrium modeling establishes the limits to which the system is approaching**

### Ion Pair Formation:

Ion pairs are defined as pairs of oppositely charged ions that behave as a thermodynamic entity. Strong electrolytes often do not dissociate into their component ions. Because of short range interactions between adjacent cations and anions, these ions remain strongly attached to each other. Therefore, a considerable portion may behave as if they were not illustrated as follows with  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ .



In this case,  $\text{CaCO}_3^0$  is the  $\text{Ca}^{2+}$ - $\text{CO}_3^{2-}$  pair. The equilibrium constant for such a reaction is

$$K_{\text{eq}} = \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{(\text{CaCO}_3^0)}$$

Although  $K_{\text{eq}}$  is formulated in a similar way to that of weak electrolyte, the dissociation of ion pairs is affected by different forces than those in weak electrolytes. **The attraction in ion pairs is caused by coulombic forces, whereas in weak electrolytes, covalent bonds are responsible for a weak dissociation.** In soil solution, cations and anions that pair extensively are  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . Chloride ( $\text{Cl}^-$ ) ions do not form ion pairs with other cations to any measurable amounts.

### Implications of Ion Pair Formation:

- The EC of saturated solution with a high proportion of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions will under estimate the total soluble salts. Similar is the case if some or all of the  $\text{Ca}^{2+}$  is substituted by  $\text{Mg}^{2+}$ .
- Effect of ion pair formation on EC varies with the type of dissolved salts.
- Formation of ion complexes becomes increasingly important as E.C.e increases.

be expended by the plant to absorb relatively salt free water from a relatively salty soil solution

The added energy required to absorb water from a salty soil (osmotic potential) is additive to the energy required to absorb water from a salt free soil (soil water potential)

#### ✓ Determination of average root zone salinity:

The average root zone salinity can be calculated by using the average of five points at the rooting depth. These five points are as under

- 1) The soil surface ( $EC_{s0}$ )
- 2) Bottom of the upper quarter of the root zone ( $EC_{25}$ )
- 3) Bottom of the second quarter depth ( $EC_{50}$ )
- 4) Bottom of the third quarter depth ( $EC_{75}$ )
- 5) Bottom of the fourth quarter or the soil water draining from the root zone ( $EC_{100}$ )

Following assumptions are used to estimate the average root zone salinity to which crop responds

- 1) Salinity of applied irrigation water =  $1 \text{ dS m}^{-2}$
- 2) Crop water demand (ET) = 1000 mm per season
- 3) Crop water use pattern is 40-30-20-10. This means that the crop will get 40 % of its ET demand from the upper quarter of the root zone, 30 % from the next quarter, 20 % from the next and 10 % from the lowest quarter.
- 4) Crop water use will increase the concentration of soil water which drains into the next quarter, i.e.  $EC_{s0} < EC_{25} < EC_{50} < EC_{75} < EC_{100}$
- 5) Desired leaching fraction (LF) = 0.15. The leaching fraction of 0.15 means that 15 % of the applied irrigation water entering the surface percolates below the root zone and 85 % is used by the crop to meet its ET demand and water lost by surface evaporation.

#### ✓ Salinity control in the root zone:

Salinity control in the root zone depends on the adequate leaching which takes place whenever irrigation and rainfall exceed the soil's capacity to store infiltrated water. In humid regions, rainfall results in enough leaching to flush salts from the root zone. The crop's water requirement and salinity control are important in areas where salinity poses hazards, e.g. arid areas. The amount of irrigation water needed to meet the crop's water requirement can be calculated from a water balance of the crop root zone. The major flows of water into the crop's root zone are:

- i. Irrigation (D)
- ii. Rainfall (D)



iii. Upward flow from the ground water ( $D_2$ )

Water flows out of the root zone due to:

- i. Evaporation ( $D_e$ )
- ii. Transpiration ( $D_t$ )
- iii. Drainage ( $D_d$ )

The difference between the water flowing in and water flowing out must be equal to the change in the water storage. Therefore, the water balance equation for change in storage may be written as:

$$D_i = (D_r + D_2) - (D_e + D_t + D_d)$$

If  $D_r + D_2$  in equation are less than  $D_e + D_t$ , the water deficit in soil is met by extraction from soil storage and by reduced drainage. With time, the deficit becomes zero. As  $D_s$  is depleted, soil tends to dry which reduces  $D_t$  and the crop becomes water stressed.

Initially, these processes bring water loss from root zone in balance with water supply at zero drainage. However, without drainage, salts stored in the root zone concentrate in the remaining stored water.

As salinity increases, osmotic stress of the plant increases which further reduces transpiration. If salts continue to increase in concentration, the plant dies.

When a shallow water table exists, the deficiencies in  $D_r + D_2$  may be offset by  $D_2$ . If flow is upward from the ground water, drainage is zero. This situation cannot continue indefinitely. Under the field conditions, upward flow and drainage may take place alternately during the year, particularly in cultivated areas. If upward flow continues and sufficient leaching does not take place, soil salinity ultimately reduces the crop's water consumption to the point that the crop dies. That is why, where salinity is a hazard, a net downward flow of water through the root zone is needed to sustain crop productivity.

The conditions that control the water flow into and out of the root zone rarely last long enough for a true steady state to exist. As a result, the amount of salts in soil solution of the root zone fluctuates continually. The goal of water management is to maintain this fluctuation within limits that neither allow excess drainage nor reduces the growth of crops.

### Salt precipitation:

Salt balance of the root zone is affected by the precipitation of soluble salts. Theoretically, an ideal salt balance means that salt input = salt output. Consequently, the amount of salts leached below the root zone may be less than the applied. At low leaching fractions (LF = 0.1), about 20 % or more of the salt in irrigation water precipitates and is not contained in the drainage water. Consequently, salt precipitation is a significant part of calculating the salt balance when the leaching fraction is low.