

## **Lecture 1: Introduction - Importance of soil chemistry and soil fertility in crop production – Concepts of soil fertility and soil productivity. Definitions and differences. Soil as a source of plant nutrients**

As civilization moves to beginning of the twenty first century and as World's population continues to increase, the importance of a continuing increase in food production is obvious. India alone is contributing more than a Billion people. It means that our crop production must be at least doubled by the end of the century. There are two options open to us. One way is to increase the area under the plough and the other to increase production per unit area. The scope is limited for the first option. So greater attention will have to be paid to the increasing of the production per unit area, per unit time. The strategy is to maintain soil fertility and proper nutrient management without impairing soil quality (sustainable agriculture).

**Soil fertility:** Soil fertility is defined as the quality that enables the soil to provide proper nutrient compounds in proper amounts and in proper balance for the growth of specified plants. Soil fertility is also defined as the ability of soil to supply adequately the nutrients normally taken from the soil by plants.

**Soil Chemistry:** It deals with the chemical constitution of the soil - the chemical properties and the chemical reactions in soils. It is the study of chemical composition of soil in relation to crop needs. Traditional soil chemistry focuses on chemical and biochemical reactions in soils that influence nutrient availability for plant growth, and potential environmental consequences associated with inorganic and organic fertilization. Soil chemistry has increasingly focused on the environment over the past few decades, especially as related to ground and surface water quality. Understanding the reactions and biogeochemical processes of potential pollutants and contaminants in soils will enable a more accurate prediction of fate and toxicity of contaminants, and development of remediation strategies.

The overall goal of soil chemistry/fertility research is a more fundamental understanding of chemical and biochemical reactions in soils related to plant growth, sustainability while maintaining soil and environmental quality. Soils are the medium in which crops grow to provide food and cloth to the world. Soil is the major factor that limits the type of vegetation and crops. Under similar climatic conditions, a loose and porous soil that retains little water will support sparse vegetation when compared to deep, fertile loam or clay. The basic need of crop production is to maintain soil fertility and soil productivity

## Soil fertility and Soil productivity

Soil fertility		Soil productivity	
1	It is the inherent capacity of the soil to provide essential chemical elements for plant growth	1.	Soil productivity emphasizes the capacity of soil to produce crops and is expressed in terms of yield.
2	A combination of soil properties and an aspect of soil – plant relationships.	2.	An economic concept and not a property of soil
3	Soil fertility is vital to a productive soil. But a fertile soil is not necessarily be a productive soil. Many factors can limit production, even when fertility is adequate. For eg., soils in arid region may be fertile but not productive.	3.	Soil fertility is one factor among all the external factors that control plant growth like air heat (temp.), light, mechanical support, soil fertility and water. Plant depends on soil for all these factors except for light.
4	Organic matter in the soil improves soil fertility by mineralization of nutrients.	4.	Organic matter also improves soil productivity by improving soil porosity, aggregation and physical condition of soil thus modifying the soil environment for crop growth.

## Concepts of soil fertility and soil productivity

- It is evident from the early writing of Theophrastus (372 – 287 BC) even before the advent of Christian era, Greek and Romans realised the impact of soil on the growth of plants and made a mention about the application of organic wastes and saltpeter for the plants.
- The first experiment aimed at elucidating the increase in the weight of plant during its growth was reported by Nicholas (1401 - 1446).
- Jan Baptiste van Helmont (1577-1644) attributed the increase in weight of willow shoot to water.
- But a German chemist, Glauber (1604-1668), who attributed the growth of plants to the absorption of saltpeter ( $KNO_3$ ) from the soil.
- John Woodward (during the year about 1700) first conducted water culture experiments on spearmint and emphasised that the growth factor is some terrestrial matter but not the water.
- Jean Baptiste Boussingault (1802-1882) carried out field plot experiments.

He was called as 'father of field plot technique'.

- Justus von Liebig (1803-1873) put forth the 'law of minimum' which states that the yield is governed by the limiting nutrient and is directly proportional to the factor which is minimum in the soil.

### **Soil as a source of plant nutrients**

Soils are complex natural formations on the surface of the earth and consist of five main components: mineral matter, organic matter, water, air and living organisms. The rocks and minerals on weathering release nutrients into the soil. The most important part of the soil with respect to plant nutrition is the colloidal fraction which consists of inorganic colloids (clay) and organic colloids (humic substances). Most of soil colloids possess electronegative adsorption sites available for attracting cations including calcium, magnesium, potassium, ammonium etc as well as  $H^+$  arising from the biological activity. Organic matter on decomposition releases nutrients. The cations adsorbed on the surface of the colloids are capable of exchanging rapidly and reversibly with those in soil solution. The principal immediate source of mineral nutrients to plant roots is ions in the soil solution. This nutrient supply is gradually depleted by absorption of nutrient ions by plant roots and continuously replenished by desorption of exchangeable ions on the clay-humus complex and break down of readily decomposable organic debris. The microbes in the soil also help in supplementing nutrients by the way of nutrient transformations. These sources represent the reserves that serve to replace but only at a relatively slow rate. For intensive cultivation of crop plants, however, application of mineral salts to soil is required.

**Lecture 2: Nutrient elements : Arnon's criteria of essentiality – essential, functional and beneficial elements – Scientists responsible for the essentiality of individual nutrient elements – classification of essential nutrients – Ionic forms of plant nutrients in soil.**

### **The criteria of essentiality put forth by Arnon**

In the nature there are nearly one hundred and three elements. Of them nearly ninety elements are taken in by the plants. In order to distinguish the elements which are essential from those which may be taken in by the plants but are not essential, Arnon (1954) has laid down the following criteria.

1. The plant must be unable to grow normally or complete its life cycle in the absence of the element.
2. The element is specific and can not be replaced by another.
3. The element plays a direct role in plant metabolism.

It appears that an element would have to be considered essential even if it has not been possible to demonstrate that it fulfils the second criterion of essentiality. For ex., for many bacteria, diatoms and other algae, vitamin B<sub>12</sub> is known to be essential, but the essentiality of cobalt per se has not been demonstrated. According to this criterion, molybdenum and chlorine can not be considered as essential though they are functional in plant metabolism since they can be replaced by vanadium and halides respectively. D.J. Nicholas gave more exact definition of essential elements and advanced the term “functional or metabolic nutrient” to include any mineral element that functions in plant metabolism, whether or not its action is specific.

Element	Essentiality was established by	Year
H, O	---	Since time immemorial
C	Priestly <i>et al.</i>	1800
N	Theodore de Saussure	1804
P, K, Mg, S	C Sprengel	1839
Fe	E Gris	1843
Mn	JS Mc Hargue	1922
Zn	AL Sommer and CP Lipman	1926
Cu	AL Sommer, CP Lipman and G Mc Kinney	1931
Mo	DI Arnon and PR Stout	1939
Na	Brownell and Wood	1957
Co	Ahmed and Evans	1959

## II. Elements accepted as essential for higher plants only

Ca	C Sprengel	1839
B	K Warington	1923
Cl	Broyer, Carlton, Johnson and Stout	1954

Element	Group or plant sp	Essential requirement	Year
Vanadium	<i>Scenedesmus Obliquus</i>	DI Arnon and G. Vessel	1953
Silicon	Diatoms	J.C. Lewin	1962
Iodine	Polysiphonia	L. Fries	1966
Selenium	Astragalus sp.	SF Trelease and HM Trelease	1938
Gallicum	<i>Aspergillus niger</i>	RA Steinberg	1938
Aluminium	Ferns	K. Taubock	1942

### Terminology

**Plant nutrition:** Plant nutrition is defined as the supply and absorption of chemical compounds required for plant growth and metabolism. It is the process of absorption and utilization of essential elements for plant growth and reproduction.

**Nutrient:** Nutrient may be defined as the chemical compound or ion required by an organism. The mechanism by which the nutrients are converted to cellular material or used for energetic purposes are known as metabolic processes.

**Beneficial elements:** The elements, the essentiality of which for growth and metabolism has not been unequivocally established, but which are shown to exert beneficial effects at very low concentrations are often referred to as beneficial elements, or potential micronutrients. The beneficial effect of these nutrients may be due to the ability of these elements affecting the uptake, translocation and utilization of the essential elements. They may be essential only for certain plant species or under specific conditions. Eg : Silicon, vanadium, cobalt and aluminium.

**Functional element:** Nicholas D J (1961) advanced the term functional or metabolic nutrient to include any mineral element that functions in plant metabolism whether or not its action is specific.

To describe the level of nutrient element in plants the following terms are proposed.

1. **Deficient** : When an essential element is at low concentration that severely limits yield and produces more or less distinct deficiency symptoms.
2. **Toxic** : when the concentration of either essential or other element is sufficiently high to inhibit the plant growth to a great extent.

## Forms of nutrient elements absorbed by plants

### i) Absorbed as single nutrient ion

<u>Nutrient element</u>	<u>Forms absorbed by plants</u>
Potassium	$K^+$
Calcium	$Ca^{2+}$
Magnesium	$Mg^{2+}$
Iron	$Fe^{2+}$
Manganese	$Mn^{2+}$
Copper	$Cu^{2+}$
Zinc	$Zn^{2+}$
Chlorine	$Cl^-$
Silicon	$Si^{4+}$
Cobalt	$Co^{2+}$
Sodium	$Na^+$

### ii) Absorbed in a combined form

Nitrogen	Ammonium ( $NH_4^+$ ) and Nitrate ( $NO_3^-$ )
Phosphorus	$H_2PO_4^-$ , $HPO_4^{2-}$
Sulphur	$SO_4^{2-}$
Boron	$H_3BO_3$ , $H_2BO_3^-$ , $HBO_3^{2-}$ , $BO_3^{3-}$
Molybdenum	$MoO_4^{2-}$ (Molybdate)
Carbon	$CO_2$
Hydrogen	$H_2O$

**Classification of essential nutrients:** Nutrients are chemical compounds needed for growth and metabolic activities of an organism. The essential plant nutrients may be divided into macronutrients (primary and secondary nutrients) and micronutrients.

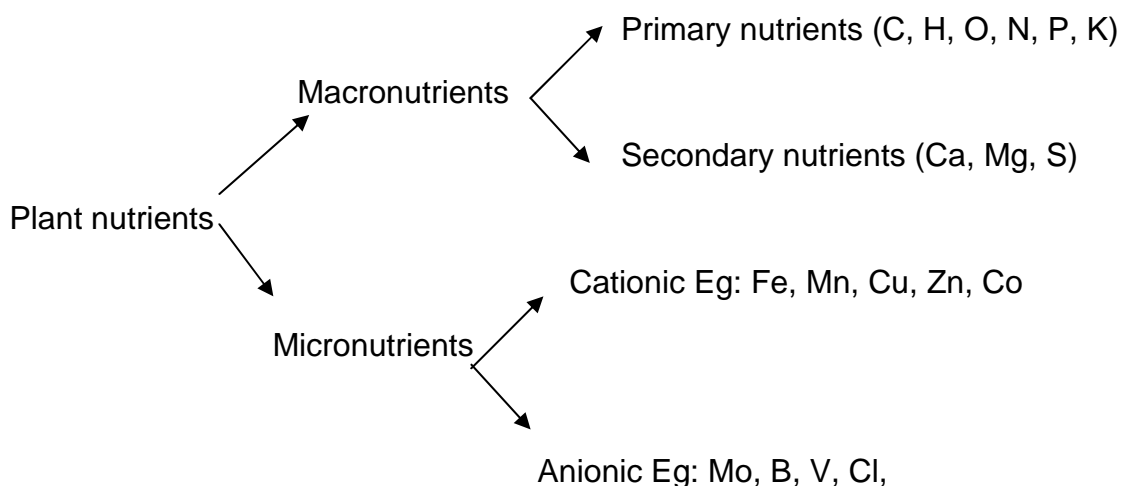
#### A. Macronutrients.

Macronutrients or major nutrients are so called because they are required by plants in larger amounts. These are found and needed in plants in relatively higher amounts than micronutrients. They include C, H, O, N, P, K, Ca, Mg and S. C, H and O constitute 90 – 95 per cent of the plant drymatter weight and supplied through  $CO_2$  and water. Remaining six macronutrients are further sub divided into primary and secondary nutrients.

- i) **Primary nutrients:** Nitrogen, phosphorus and potassium are termed as primary nutrients because the correction of their wide spread deficiencies is often necessary through the application of commercial fertilisers of which these are the major constituents.

- ii) **Secondary nutrients:** Calcium, magnesium and sulphur are termed as secondary nutrients because of their moderate requirement by plants, localised deficiencies and their inadvertent accretions through carriers of the primary nutrients. For example, the phosphatic fertiliser, single super phosphate (SSP) contains both Ca and S. Similarly, ammonium sulphate, a nitrogenous fertiliser also supplements S.

**B. Micronutrients:** Micronutrient is an element that is required in relatively small quantities but is as essential as macronutrients. These elements have often been called trace elements. They are again classified into micronutrient cations (eg. Fe, Mn, Zn and Cu) and micronutrient anions (eg., B, Mo and Cl) depending upon the form in which they are available.



This above division of plant nutrients into macro and micro nutrients is somewhat arbitrary and in many cases, the differences between the contents of macronutrients and micronutrients are considerably less well defined. Therefore, classification of plant nutrients according to biochemical behaviour and physiological functions seems more appropriate. The classification of plant nutrients is as below:

**Essential plant nutrient**

**Biochemical functions**

**nutrient**

1<sup>st</sup> group

C, H, O, N, S

Major constituent of organic material, essential elements of atomic groups which are involved in enzymatic processes and assimilation by oxidation – reduction reactions.

2<sup>nd</sup> group

P, B, Si

Esterification with native alcohol groups in plants. Involved in energy transfer reactions.

3<sup>rd</sup> group

K, Na, Mg, Ca, Mn, Cl

Non specific functions establishing osmotic potentials; enzyme activation, balance of ions, controlling membrane permeability and electro potentials.

4<sup>th</sup> group

Fe, Cu, Zn, Mo

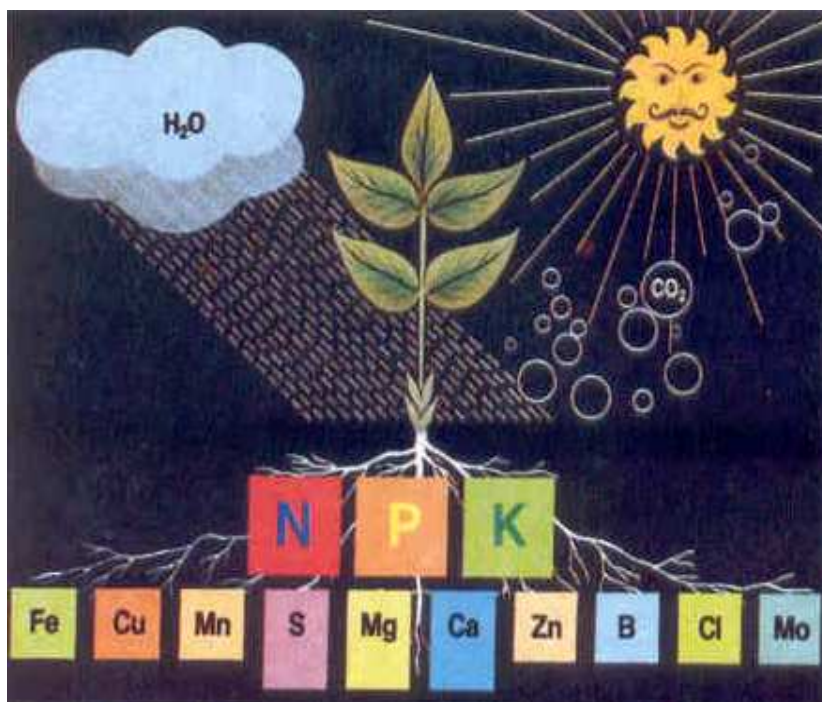
Present predominantly in a chelated form incorporated in prosthetic groups.

**Based on mobility in plant**

<b>Mobile</b>	<b>Partly mobile</b>	<b>Immobile</b>
1. Nitrogen	1. Iron	1. Calcium
2. Phosphorus	2. Zinc	2. Sulphur
3. Potassium	3. Copper	3. Boron
4. Magnesium	4. Molybdenum	

**Mobile nutrient:** Mobile nutrients are those when deficient in the plant, move from the matured tissue (older leaves) to the young meristem thus the deficiency symptoms are manifested on the older tissue.

**Immobile nutrient :** Immobile nutrients are those which under the situation of deficiency in the soil cannot move from older to younger tissue and hence the deficiency symptoms appear first on the younger leaves.



## Essential Nutrients



## **Lecture 3: Movement of ions soils to roots - Mass flow, diffusion, root interception and contact exchange**

### **Movement of ions from soils to roots**

For the ions to be absorbed by plants roots, they must come in contact with the root surface. This generally takes place by three ways in which the nutrient ions in soil may reach the root surface

- I. Movement of ions by mass movement in the soil solution – Mass flow.
- II. Diffusion of ions in the soil solution – Diffusion.
- III. Root interception and contact exchange.

#### **I. Mass flow:**

Movement of ions from the soil solution to the surface of roots is accomplished largely by mass flow and diffusion. Mass flow, a convective process occurs when plant nutrient ions and other dissolved substances are transported in the flow of water to the root in enmass that results from transpirational water uptake by the root. This depends on the rate of water flow or the water consumption of plants. Mass flow supplies an over abundance of calcium, magnesium in many soils and the most mobile nutrients such as N and S.

**Factors affecting mass flow** As mass flow involves nutrient movement with water, both the amount of water and volume of soil it comes from, affect the mass flow.

- 1) Soil moisture content:** In dry soil, no mass flow of nutrients occurs because there is no water to carry them to the plant roots. .
- 2) Soil temperature:** Low temperature reduces transpiration and evaporation; resultantly reduced water flux occurs across the roots.
- 3) Size of the root system:** affects the water uptake and consequential mass flow. Root density, however is much less critical for nutrient supply by mass flow than for root interception and diffusion.

#### **II. Diffusion :**

Most of the phosphorus, potassium (relatively immobile) and micronutrients (present in small quantities), move to root by diffusion. Diffusion occurs when an ion moves from an area of high concentration to one of low concentration by random thermal motion. As plant roots absorb nutrients from the surrounding soil solution, a diffusion gradient is set up. A high root absorbing power results in a high diffusion gradient favouring ion transport. The three principal factors influencing the movement of nutrients into the roots are the diffusion coefficient, concentration of the nutrient in soil solution and the buffering capacity of the solid phase to release nutrients into the soil solutions.

Soil moisture is a major factor that affects the relative significance of the mass flow and diffusion. Diffusion becomes progressively less important as the moisture content decreases.

The amount of nutrient ion diffusing across a unit area in unit time (F) with a concentration gradient,  $dc/dx$  is given for steady state diffusion by

Fick's first law of diffusion

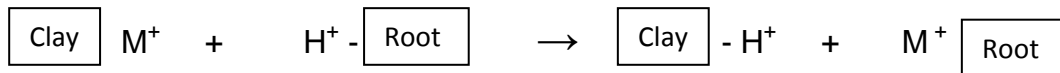
$$F = -D (dc/dx)$$

D is the diffusion coefficient in the soil with units  $cm^2/s$

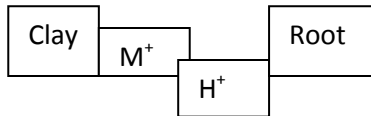
The minus sign indicates movement from higher to lower concentration.

### Factors affecting diffusion

1. **Soil water:** The higher the moisture content, higher will be the diffusion coefficient, until the moisture content reaches saturation.
  2. **Soil compaction:** Incremental increase in the soil compaction at the same moisture content leads to the exclusion of air; soil particles come closer, the continuity of moisture flows increases, path to be traversed by the ion by diffusion becomes less tortuous and resultantly, the diffusion coefficient exhibits an increase.
  3. **Temperature:** The rate of chemical reaction doubles for every  $10^\circ C$  rise in temperature. The increase in temperature increases the effective diffusion coefficient of a nutrient ion.
  4. **Chemical amendments:** Chemical treatments modify the concentration of the nutrient ions in soil solution as given below
    - Amelioration of soil acidity through liming raises the pH of the soil. Thus, diffusion coefficient of cations decreases and anion increases as a result of liming.
    - Application of gypsum to a sodic soil reduces the soil pH, as a result of which diffusion coefficient raises.
    - Organic manures act as the store house of nutrients. In addition, they release low molecular weight organic substances which have the ability to form complexes with cations. This increases the diffusion coefficient of nutrients.
- III. **Root interception and ion exchange:** Jenny and Overstreet (1939) propounded the 'theory of contact exchange'. Theory of contact exchange rests on the concept of overlapping oscillation spaces of adsorbed ions, or redistribution within intermingling electric double layers. Contact exchange as a mechanism for nutrient movement could be pictured as



and modelled as



Cation exchange theory on further refining gave rise to the concept of 'root interception' a term coined by Stanely A Barber, which is used to describe the soil nutrients at the root surface that do not have to move to the interface to be positionally available for absorption, but are approached by the root itself in the soil.

As the root system develops and exploits the soil more completely, soil solution and soil surfaces retaining the adsorbed ions are exposed to the root mass and absorption of these ions by the contact exchange mechanism is accomplished. The quantity of nutrients that can come in direct contact with the plant roots is the amount in volume of soil equal to the volume of roots. It can be assumed that roots usually occupy 1 % or less of the soil. It is estimated that roots would contact a maximum of 3 % of the available nutrients in the soil.

It has been observed that plant roots also possess the cation exchange property, ranging from 10 to 100 cmol/ kg roots. This property could be due to the  $-\text{COOH}$  groups of pectic substances of cell wall. Legumes have high root CEC and absorb more divalent cations, monocots have low root CEC and absorb more of monovalent cations like  $\text{K}^+$ . Ions attached to the surface of roots may exchange with those held on the surface of clays and organic colloids because of the contact between roots and soil particles. The mucilaginous gel around root surface could serve as contact complex. The presence of mycorrhiza, a symbiotic association between fungi and the roots of plants, enhances the uptake of nutrients particularly phosphorus.

**Lecture 4: Nitrogen : Occurrence, content and distribution. Factors influencing the content of nitrogen in soil. Forms of soil nitrogen. Nitrogen cycle – transformations in soil – mineralisation (amination and ammonification) – Fate of released ammonia – Factors affecting ammonium fixation.**

The ultimate source of nitrogen used by the plants is the inert gas nitrogen, which constitutes about 78 % (by volume) of the earth's atmosphere. Among all the essential nutrients, nitrogen is the extensively studied one and still receiving much attention.

The ploughed layer of majority of cultivated soils contains about 0.02 – 0.04 % nitrogen. Indian soils have very low content because of low organic matter accumulation due to tropical climate. Soils developed under cool humid climate have higher N content than those formed under dry climate. On an average, black soils have more nitrogen content (0.08%) than red soils (0.03%).

**Factors influencing the content of N in soils**

**a) Climate**

i) Temperature: Lower the temperature higher is the N content due to more organic matter addition and slow rate of decomposition.

ii) Water supply: Soil N content increases with water supply up to field capacity.

**b) Effect of cultivation:** N content decreases with cultivation due to organic matter loss through decomposition.

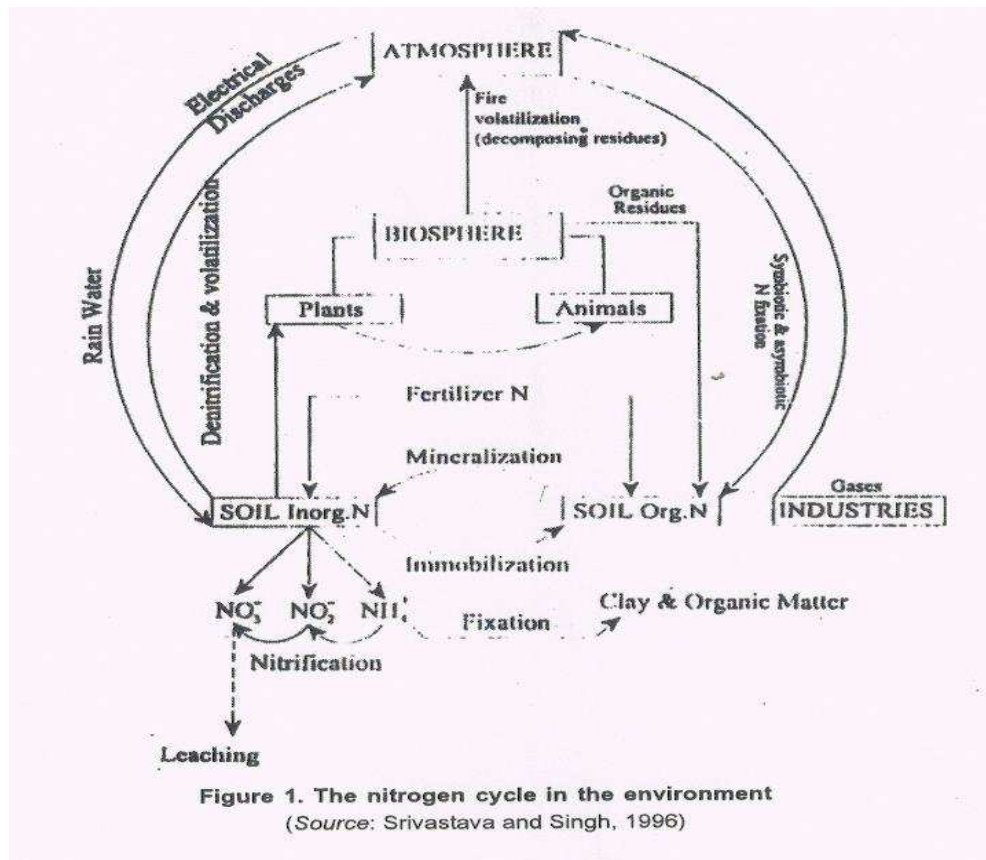
**c) Soil texture:** Finer the texture, higher is the N content.

**d) Depth in the profile:** Surface soil has more N content than deeper soils.

**Forms of soil nitrogen:** The total nitrogen content of soils ranges from less than 0.02 % in sub soils to more than 2.5 % in peat soils. The N present in soil can generally be classed as inorganic (around 2 %) and organic (around 98 %).

1. **Inorganic nitrogen compounds:** The inorganic forms of soil nitrogen include ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), nitric oxide (NO) nitrous oxide ( $\text{N}_2\text{O}$ ) and elemental nitrogen.  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are important in soil fertility and represent 2 to 5 % of total nitrogen.

2. **Organic nitrogen compounds :** occur as consolidated amino acids or proteins, free amino acids, amino sugars and other unidentified compounds like materials that result from the reaction of  $\text{NH}_4^+$  with lignin, polymerisation of quinones and nitrogen compounds, the condensation of sugars and amines. Bound amino acids are to the extent of 20-40 %, amino sugars (hexosamines) 5 to 10 %, purine and pyrimidine derivatives 1 % or less.



**N transformations in soil :** Plants absorb most of the N in the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  forms. Nitrate is the dominant source as its concentration is higher than  $\text{NH}_4^+$  and it is free to move to the roots. Potatoes, sugarbeet, pine apple, prefer both the forms; tomatoes, celery, bush beans, prefer  $\text{NO}_3^-$ , rice and blue berries prefer  $\text{NH}_4^+$ .

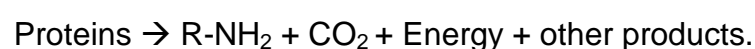
$\text{NO}_3^-$ -N uptake is usually high and is favoured by low pH conditions.

$\text{NH}_4^+$ -N is less subjected to losses by leaching and denitrification.  $\text{NH}_4^+$  uptake is best at neutral pH values. When the plants are supplied with  $\text{NH}_4^+$ -N, it leads to acidity in the soil.

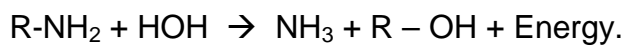
**Mineralization of N compounds:** N mineralization is simply the conversion of organic nitrogen to mineral form ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$ ). When organic residues having a C: N ratio wider than 30 are added to the soil, immobilisation of nitrogen takes place. If C:N ratio is narrow i.e., less than 20 (for legume residues), mineralisation is the result. It takes place essentially by three steps.

1. Aminisation
2. Ammonification
3. Nitrification.

**1. Aminisation:** Heterotrophic soil microbes, mostly, bacteria like *Pseudomonas* and *Bacillus* are believed to dominate in the break down of proteins in neutral and alkaline soils. Under acidic conditions fungi prevail. In this step hydrolytic decomposition of proteins and release of amines and amino acids takes place.



**2. Ammonification** : The amines and amino acids so released are further utilized by still other groups of heterotrophs with the release of ammoniacal compounds. The step is termed as ammonification.



The ammonium thus formed may be nitrified to nitrite and nitrate which are used by plants.

#### **Fate of released ammonium in the soil**

1. It may be converted to nitrites and nitrates by the process of nitrification.
2. It may be absorbed directly by higher plants.
3. It may be utilized by heterotrophic organisms in further decomposing organic carbon residues.
4. It may be fixed in biologically unavailable form in the lattice of certain expanding type clay minerals.
5. It could be released back to the atmosphere through volatilization

#### **Ammonium fixation**

In agricultural soils, 5 – 20 % of the total nitrogen is found as fixed ammonium ion, with an average of 10 %. When ammonium containing or ammonium forming fertilizers are added to the soil, most of ammonium gets adsorbed on the cation exchange sites, but a part of it is susceptible to strong adsorption in the interlayer spaces of some 2:1 layer silicate clay minerals with an expanding lattice. The order of fixation is as follows: vermiculite > fine grained mica > smectites. The ammonium ion has an ionic diameter 2.96 Å, which is close to the 2.8 Å diameter of inter lattice spaces in 2:1 type clay minerals. Fixed ammonium is not easily available for plants and microbes. It comes out by a replacement of  $NH_4^+$  for inter layer cations in the expanded lattices of clay minerals. The fixed ammonium can be replaced by cations that expand the lattice like  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ .

The presence of  $K^+$  (ionic diameter of 2.68 Å) will often restrict  $NH_4^+$  fixation since this ion can also fill fixation sites. Consequently it has been suggested that K fertilization prior to  $NH_4^+$  application is a practical way of reducing  $NH_4^+$  fixation.

Ammonium can also be chemically fixed or bound by the organic matter. The reactions take place most readily in the presence of oxygen and at high soil pH. In organic soils with high fixing capacity, the reaction could result in a serious loss of available nitrogen and would dictate the use of fertilizers other than those that supply  $NH_4^+$ ; however, the fixed  $NH_4^+$  will be slowly released by mineralization.

#### **Factors affecting ammonium fixation**

1. **Type and amount of clay:**  $NH_4^+$  fixation increases with increase in

the content particularly 2:1 type of clay minerals like vermiculite, fine grained mica and smectite.

2. **Moisture content of the soil:** The moisture content and temperature of the soil will affect the fixation of  $\text{NH}_4^+$ . Freezing and drying increases the fixation. Alternate cycles of wetting and drying; freezing and thawing are believed to contribute to the stability of recently fixed  $\text{NH}_4^+$

3. **Amount of  $\text{K}^+$**  : The presence of  $\text{K}^+$  will restrict  $\text{NH}_4^+$  fixation since  $\text{K}^+$  also fills the fixation sites.

4. **Depth of the soil:** Fixation of  $\text{NH}_4^+$  is generally higher in sub soil than surface soil due to higher clay content and lower rate of nitrification.

5. **Organic matter content** : Higher the organic matter content more is the  $\text{NH}_4^+$  fixation.

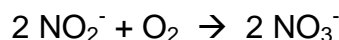
6. **Population of nitrifying bacteria** : Nitrifying bacteria oxidize  $\text{NH}_4^+$  to nitrite and nitrates thus reducing the chances for  $\text{NH}_4^+$  fixation.

**Lecture 5: Nitrification – Factors affecting nitrification – Fate of nitrate nitrogen – Leaching losses of nitrate nitrogen – Denitrification – Nitrification inhibitors – Immobilisation.**

**Nitrification** : The biological oxidation of  $\text{NH}_4^+$  released by the process of ammonification to nitrate is known as nitrification. This process is carried out by nitrifying bacteria referred to as nitrifiers. It is a two step process in which  $\text{NH}_4^+$  is first converted to nitrite ( $\text{NO}_2^-$ ) and then to nitrate ( $\text{NO}_3^-$ ). Conversion to nitrite is brought about largely by a group of obligate autotrophic bacteria known as *Nitrosomonas* as



The conversion from nitrite to nitrate is affected by *Nitrobacter* as follows :



**Factors affecting nitrification**

**i) Supply of the ammonium ion** : Because the substrate for the nitrifying bacteria is the ammonium ion, a supply of this ion is the first requirement for nitrification.

**ii) Population of nitrifying organisms** : Under similar conditions of temperature, moisture and added ammonia, the nitrification is greatly influenced by population of nitrifying bacteria.

**iii) Soil reaction** : Nitrification takes place between pH of 5.5 to 10.0, with an optimum around 8.5.

**iv) Soil aeration** : The nitrifying bacteria are anaerobes and hence require sufficient oxygen supply.

**v) Soil moisture** : The rate at which nitrification proceeds in a soil is governed to a marked extent by the water content being retarded by both very low or very high moisture content.

**vi) Temperature** :Very low nearer freezing and increases rapidly up to 35°C.

**vii) C : N ratio** : when organic residues with wide C : N ratio are added, general purpose decay organisms are dominant and nitrifiers become inactive.

**viii) Pesticides** : Nitrifying organisms are quite sensitive to some pesticides.

#### **Fate of nitrate nitrogen**

Nitrate supplied in commercial fertilizers or produced by nitrification of ammonium may be :

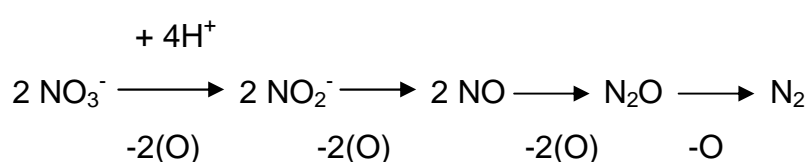
- a) Absorbed by the plants.
- b) Utilised by soil microorganisms.
- c) Lost through excess water by leaching because of its high mobility.
- d) Escapes from soil in volatile condition through nitrate reduction referred to as denitrification.

#### **Leaching losses of nitrate nitrogen :**

Leaching loss of nitrogen from the soil is a loss from the soil-plant system and causes lower efficiency of applied nitrogen. It may vary from 2 to 50 % of applied N. Of the total leaching loss, more than 90 % is in the form of  $\text{NO}_3^-$  as mostly nitrate ions are present in soil solution because of the reason that the anion exchange capacity of the soil is much less than cation exchange capacity. Therefore, its movement is related to the movement of water in the soil. The magnitude of leaching loss of nitrogen depends on soil texture, hydrological condition, water table depth, permeability and hydraulic conductivity of soil. Leaching loss can be reduced by increasing water holding capacity through organic matter addition, split application of fertilizer N, controlled irrigation and by using nitrification inhibitors like N – serve, slow release N fertilizers like neem coated urea, sulphur coated urea.

#### **Denitrification :**

Denitrification is a process limited to anoxic soils in which bacterial reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  takes place leading to the release of NO,  $\text{N}_2\text{O}$  and  $\text{N}_2$  gases. When soils become water logged, oxygen is excluded and anaerobic decomposition takes place. Some anaerobic organisms have the ability to obtain their oxygen from nitrates and nitrites with the accompanying release of nitrous oxide and nitrogen. The most probable biochemical pathway leading to these losses is indicated as





Facultative anaerobic bacteria belonging to the genera *Pseudomonas*, *Bacillus denitrificans* and *Paracoccus* are responsible for this. Autotrophs like *Thiobacillus denitrificans* also brings about denitrification.

**Nitrification inhibitors:** Several products have been developed with the purpose of slowing the release and/or nitrification of applied N to synchronise the supply of N with the crop demand and consequently decrease nitrogen losses via leaching and / or denitrification. These chemicals restrict the growth of *Nitrosomonas* and keep nitrogen in  $\text{NH}_4^+$  form.

**Natural nitrification inhibitors**

Neem cake (*Azadiracta indica*)

Karanj cake (*Pongamia glabra*)

Neem oil and nimin

**Chemical nitrification inhibitors**

N - serve or nitrapyrin (2 chloro – 6 tri chloromethyl pyridine)

DCD (Dicyandiamide)

AM (2 amino, 4 chloromethyl pyrimidine)

ATC (4-amino 1,2, 4 triazole)

Sulphathiozole

Thiourea

Hydroquinone

Calcium carbide ( $\text{CaC}_2$ )

Phenyl phosphorodiamidate (PPD)

However, in India the use of such chemicals to retard nitrification is limited due to the high costs involved.

**Nitrogen immobilization**

Immobilisation of nitrogen is the reverse of mineralisation and it occurs when large quantities of low nitrogen crop residues with wide C:N ratio (>30:1) such as coconut coir or cereal straw begin decomposing in soil, the high amounts of carbohydrates in such residues cause the microbial population to build up quickly. As new cells are formed, nitrogen and other essential elements from soil are used to build protoplasm. This leads to a decrease in the levels of inorganic nitrogen for crops. A shortage of nitrogen can be avoided in such situations by supplying enough fertilizer nitrogen to compensate for immobilization and to meet the crop requirements. This lockup of inorganic N of soil is temporary and slowly will be released after mineralization.

**Lecture 6: Nitrogen fixation – Different types – Biological fixation of nitrogen – Symbiotic and non symbiotic – Nitrogen balance sheet – Gains and losses – Functions – Deficiency Toxicity symptoms – measures.**

Bacteria are capable of reducing nitrogen to ammonia with the help of an enzyme called nitrogenase. The process is known as biological nitrogen fixation (BNF). They contribute 140-170 MT N/yr whereas N input through fertilizer is only 65 MT N/yr.

**Different groups of N<sub>2</sub> fixers :** There are three main groups of N<sub>2</sub> fixers as given below :

**I. Symbiotic :**

Symbiotic nitrogen fixers reduce nitrogen in association with plants by forming some specialized structures in plants.

**a) Legume – rhizobium symbiosis :**

Some plants of leguminosae family form a symbiotic association with bacteria with the genus *Rhizobium* which fix atmospheric nitrogen. *Rhizobia* infect the root moving to the root cortex through an infection thread which results in the formation of a tiny outgrowth called root nodule. *Sesbania rostrata* forms nodules on the stem as well. This association is host specific. The *Rhizobia* turn to bacteroids which have nitrogenase enzyme embedded into leghaemoglobin. The symbiotic association of the host and the bacterium is mutually beneficial to both organisms. Specific species of bacterium infects the roots of a particular group of legumes. This host specificity of different *Rhizobium* species or the group of legume crops nodulated by single *Rhizobium* sp. is referred to as 'cross inoculation group'.

<b><i>Rhizobium</i> sp.</b>	<b>Plants nodulated</b>
<i>R. meliloti</i>	<i>Medicago sativa</i> (alfalfa), <i>Melilotus</i> sp. (sweet clover), <i>Medicago</i> sp., <i>Trigonella foenum graecum</i> (fenugreek)
<i>R. trifolii</i>	<i>Trifolium</i> sp. (red clover, white clover)
<i>R. leguminosarum</i>	<i>Pisum sativum</i> (garden and field peas), <i>Vicia faba</i> (broad bean), <i>Lens esculenta</i> (lentils), <i>Lathyrus</i> sp.
<i>R. phaseoli</i>	<i>Phaseolus vulgaris</i> , <i>P. coccineus</i>
<i>R. lupini</i>	<i>Lupinus</i> sp., <i>Ornithopus sativus</i>
<i>R. japonicum</i>	<i>Glycine max</i> (soybean)
<i>Rhizobium</i> sp.	<i>Vigna unguiculata</i> (cow pea), <i>V. radiata</i> (mung bean), <i>Arachis hypogaea</i> (groundnut), <i>Cajanus cajan</i> (redgram)
<i>Rhizobium</i> sp.	<i>Cicer arietinum</i> (chickpea), <i>Sesbania</i> sp.

## b) Symbiosis with non legumes

### i) Non legume – *Frankia* symbiosis

The member actinomycetes, the *Frankia* forms symbiosis with forest trees belonging to the families *Casuarinaceae* and *Myricaceae*.

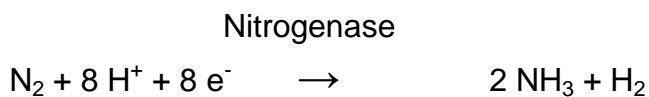
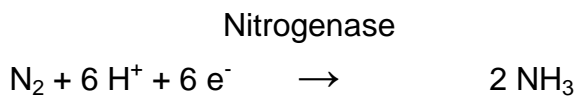
### ii) *Azolla* – *Anabaena* symbiosis :

*Azolla* is a fresh water fern found floating on the surface of water. All the species of *Azolla* have an algal symbiont called *Anabaena azollae* in a specialized cavity in the upper leaf surface. In rice fields the symbiosis can fix N<sub>2</sub> upto 30-40 kg N ha<sup>-1</sup>.

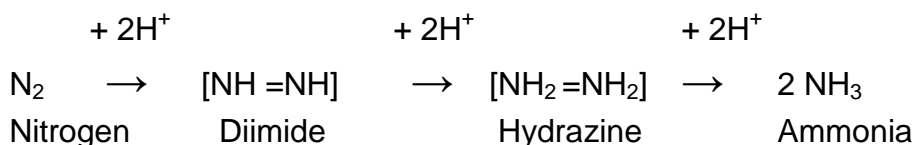
## II. Non specific associative N<sub>2</sub> fixers :

Rhizobacteria like *Azospirillum*, *Acetobacter*, *Azotobacter*, *Flavobacterium*, *Pseudomonas* etc. These bacteria are capable of using exudates of roots as the source of energy.

III. **Free living nitrogen fixers** : Many soil bacteria are capable of reducing molecular N<sub>2</sub> to NH<sub>4</sub><sup>+</sup> without forming any association with plants. They supply about 10-15 kg N ha<sup>-1</sup>. They also function as plant growth promoting rhizobacteria (PGPR).



Ammonia is the end product of the nitrogenase catalysed reaction. The intermediate products are as follows



The requirements of Biological N fixation are

- i) An active nitrogenase enzyme system
- ii) Mg<sup>2+</sup> and a continuous supply of ATP
- iii) A strong reducing agent i.e., suitable e<sup>-</sup> donor
- iv) Low oxygen tension

## Nitrogen balance sheet

**I. Gains of N by soil** : Acquisition of N by soil can happen through four ways.

**1. N fixation by symbiotic bacteria** : The bacteria which live in symbiotic relationship with the host plant (legume) and fix N in the root nodules belong to the genus *Rhizobium*. They derive the energy needed for this purpose from the carbohydrates of the host plant.

**2. Azofication** : Heterotrophic free living bacteria *Azotobacter* and *Clostridium* fix N referred to as Azofication. These organisms derive energy from the decomposing organic matter.

**3. Additions through rain** : on an average it is believed that 5 kg N/ha is added to the soil every year.

**4. Additions through manures and fertilizers** : The greater part of N gain by the soil is acquired through crop residues, organic manures, green manures and N fertilizers.

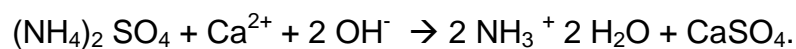
**II. Losses of N from the soil** : The removal of N from the soil may be through

1. Removal by crops and microorganism : This can not be considered as a loss in real sense, but a loss to the soil. Crop removal is the major loss of nitrogen to the soil

2. Leaching : Nitrogen can be lost due to leaching either as  $\text{NO}_3^-$  or  $\text{NH}_4^+$ . More than 90 % in the form of  $\text{NO}_3^-$  because AEC of soil is much lesser than CEC. The magnitude of leaching loss depends on soil texture, soil moisture status, water table depth, permeability and hydraulic conductivity of soil.

3. **Gaseous loss of nitrogen** : as  $\text{NH}_3$  by volatilization or as  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  through denitrification.

a) **Ammonia volatilization** : Losses of N through  $\text{NH}_3$  ranges from 5 to 35 %. The Loss is less in flooded soil. Increase in pH to alkaline side results in volatilization



b) **Denitrification** : When the redox potential of the soil falls below + 250 mV in soil due to submergence, the microbes like *Thiobacillus denitrificans* utilize the oxygen from N compounds. These losses range from 10-40 %.

c) **Chemodenitrification** : Non microbial processes by which nitrogen may be reduced in soil to gaseous form is known as chemodenitrification.

4. **Immobilisation** : Conversion of inorganic nitrogen to organic forms by soil microorganisms is called immobilization.

5. **Ammonium fixation by clay mineral** :  $\text{NH}_4^+$  is adsorbed strongly in the inter layer spaces of 2 : 1 clay minerals.

6. **Soil erosion and runoff**. Runoff may be as high as 70 %.

Balance sheet of Nitrogen can be worked out by taking into consideration of additions and losses of N.

Nitrogen balance = (Amount of fertilizer N added to soil + N added through crop residues, irrigation and rain water, manure) – (crop uptake of N + N loss through various processes + N remaining in the soil).

**Functions of nitrogen in plants:** In N sufficient plants, its concentration varies from 1 to 5 %. Cell cytoplasm and organelles contain N in combination with C, H, O, P and S.

- It's an essential component of amino acids, proteins, nucleic acids, porphyrins, flavins, purines and pyrimidine nucleotides, flavin nucleotides, enzymes, coenzymes and alkaloids.
- N containing chlorophyll fixes atmospheric CO<sub>2</sub> through photosynthesis.
- Being a constituent of RNA and DNA, N is responsible for transfer of genetic code.
- Improves the quality of leafy vegetables and fodders.
- Improves the quality by increasing protein content.

**Deficiency symptoms:** Plants having less than 1 % nitrogen are usually regarded as deficient in N.

- Due to high mobility of N in plants, its deficiency symptoms first appear on the older leaves in the form of light green to pale yellow coloration due to proteolysis).
- Stunted growth is the manifestation.
- In grasses, the lower leaves usually fire or turn brown beginning at the leaf tip, and progressing along the midrib in the form of inverted 'V' shape.
- Reduction in flowering and crop yields and lower protein content are associated with N deficiency.

**Corrective measures:** Nitrogen in the form of NO<sub>3</sub><sup>-</sup> is more prone for leaching especially on light textured soils with more permeability. So, split application of nitrogen is recommended.

Foliar application in the form of urea @ 2 percent concentration is advocated in dry land areas.

<b>N Source</b>	<b>% N</b>
Ammonium sulfate	21.0
Ammonium chloride	25 – 26.0
Ammonium nitrate	33 – 34
Ammonium nitrate sulfate	30.0
Monoammonium phosphate	11.0

Diammonium phosphate (DAP)	18 – 21.0
Calcium nitrate	15.0
Urea	45 – 46
Urea ammonium nitrate	28 – 32

**Toxicity symptoms** Under conditions of large nitrogen availability, succulence of the plant increases; taller plants and heavier heads cause lodging. A nitrogen rich, luxuriant crop is more susceptible to insect pest and disease attacks.



Nitrogen deficiency symptom in rice plant



A close-up of nitrogen deficiency symptom in maize leaf



Nitrogen deficiency symptom in wheat plant

## Lecture 7: Phosphorus- P cycle – content in soils –forms of phosphorus in soils – inorganic and organic P compounds – P fixation – mechanisms of phosphate fixation

Phosphorus (P), an essential nutrient for all living organisms, is a vital component of the substances that are building blocks of genes and chromosomes. Its reserves in soil are found mostly as sedimentary formations and unrefined ore known as phosphate rock. Countries like China, Morocco, Jordan, Egypt, Western Sahara, South Africa and USA are the major phosphate rock share holders. In India, Jhamarkotra (Rajasthan) has reserves of 13.5 Mt of high grade phosphate rock (30%  $P_2O_5$ ).

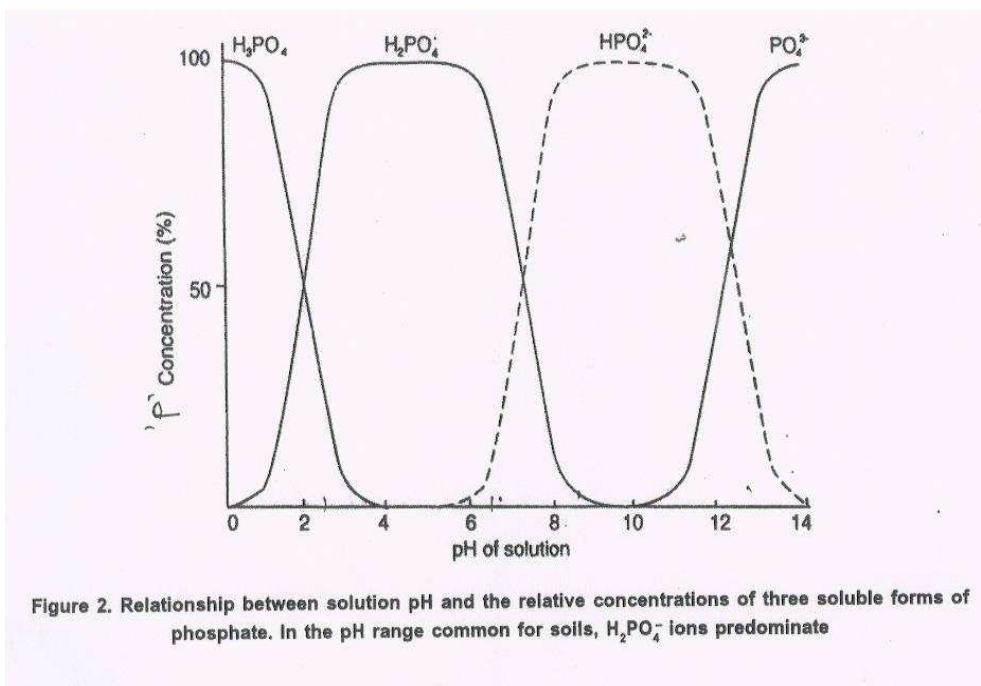
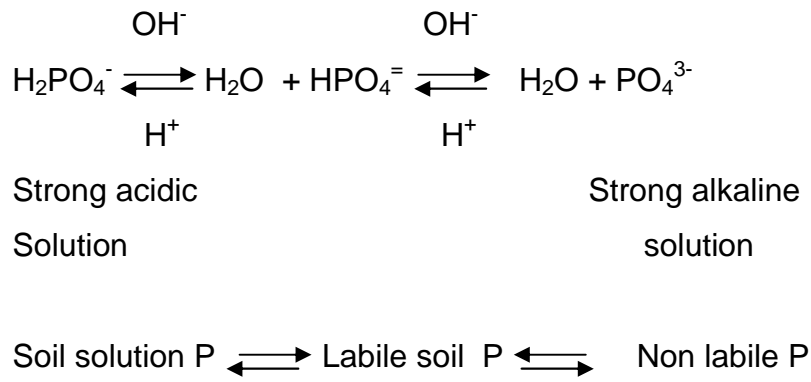
The total P content in Indian soils ranges from 100 to 200 ppm. The total P content is generally highest in soils developed from granite and gneiss followed by shales. The total P consists of inorganic P and organic P.

### Forms of soil P

**I. Inorganic P** : The inorganic phosphorus content of soils is frequently higher than that of organic phosphorus (excepting organic soils) accounting for 54 to 84%. The inorganic P can be further divided into different pools.

**1. Soil solution P** : Phosphorus is absorbed by plants largely as primary and secondary orthophosphate ions ( $H_2PO_4^-$ ,  $HPO_4^{2-}$ ). The amount of each form is dependent on soil pH. Very little P is present in soil solution, concentration being

less than 0.1 ppm.



<p>Readily available P in soil solution <math>\text{H}_2\text{PO}_4^-</math> and <math>\text{HPO}_4^{2-}</math> ions released from other forms of P or added P</p>	$\rightleftarrows$	<p>Slowly available P (labile) Fe, Al and Mn phosphates in acid soils and Ca, Mg phosphates in alkaline soils that are freshly formed</p>	$\rightleftarrows$	<p>Very slowly avail P (non labile) precipitate of Fe, Al, Mn phosphates aged and well crystallized Stable org. P compounds.</p>
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2. **Labile soil phosphorus** is the readily available portion of the quantity factor and it has a high dissociation rate, permitting rapid replenishment of solution phosphorus. Depletion of labile P causes non labile P to be labile again, but at a very slow rate. Phosphorus bound to aluminium (Al-P), iron (Fe-P) and calcium (Ca-P) constitutes the major active labile form of inorganic P. The Fe-P and Al-P constitute 1-25 % of total P in soils. The Ca-P constitutes 40 - 50 % or even more of total P in neutral to alkaline and calcareous soils.



3. **Non labile P:** The relatively less active non labile forms are the occluded and reductant soluble P.

**Calcium compounds found in soil are :**

Flourapatite	$3 \text{ Ca}_3 (\text{PO}_4)_2 \text{ CaF}_2$
Carbonate apatite	$3 \text{ Ca}_3 (\text{PO}_4)_2 \text{ CaCO}_3$
Hydroxy apatite	$3 \text{ Ca}_3 (\text{PO}_4)_2 \text{ Ca}(\text{OH})_2$
Oxy apatite	$3 \text{ Ca}_3 (\text{PO}_4)_2 \text{ CaO}$
Tricalcium phosphate	$3 \text{ Ca}_3 (\text{PO}_4)_2$
Octa calcium phosphate	$\text{Ca}_8 \text{ H}_2 (\text{PO}_4)_5 \cdot 5 \text{ H}_2\text{O}$
Dicalcium phosphate	$\text{CaH PO}_4 \cdot 2 \text{ H}_2\text{O}$
Monocalcium phosphate	$\text{Ca} (\text{H}_2\text{PO}_4)_2$

Of all the above, the readily available forms for plant growth are mono and dicalcium phosphates. The apatite minerals are the most insoluble and unavailable compounds.

**Fe and Al containing P compounds:**

Strengite	$\text{Fe PO}_4 \cdot 2 \text{ H}_2\text{O}$
Vivianite	$\text{Fe}_3 (\text{PO}_4)_2 \cdot 8 \text{ H}_2\text{O}$
Variscite	$\text{Al PO}_4 \cdot 2 \text{ H}_2\text{O}$
Wavellite	$\text{Al}_3 (\text{OH})_3 (\text{PO}_4)_2 \cdot 5 \text{ H}_2\text{O}$

**Organic phosphorus :** In Indian soils, the organic P ranges from 0 to 2160 ppm. It constitutes 20 to 90 % of total soil P.

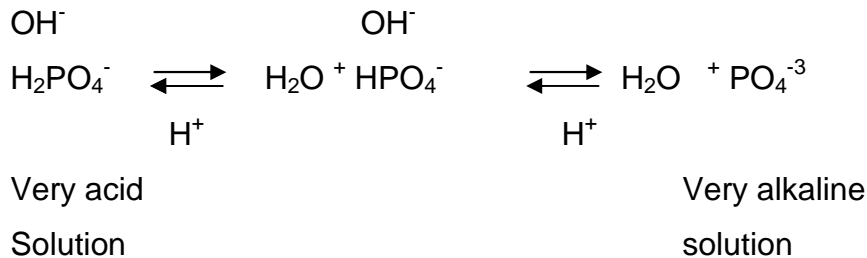
The principal organic P compounds in soil are

- (1) Inositol phosphate (2-9%): Phytin is the calcium magnesium salt of phytic acid (Inositol phosphoric acid) with an empirical formula  $(\text{CH})_6 (\text{H}_2\text{PO}_4)_6$ . It is present in the soil not exceeding 30-40 %
- (2) Phospholipids are P containing fatty acids (1-2 %)
- (3) Nucleic acids to the extent of 1-2 % of soil organic P
- (4) Unidentified esters and phospho proteins.

P present in the above forms is mineralised by microorganisms and the phosphates that are released are available to the plants.

## Factors affecting the availability of inorganic P

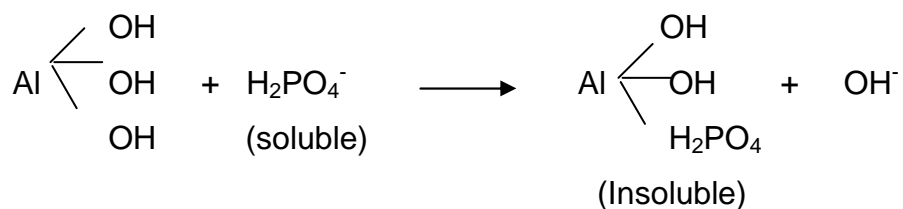
1. **Soil pH** : Soil pH severely influences the reactions of P with different ions



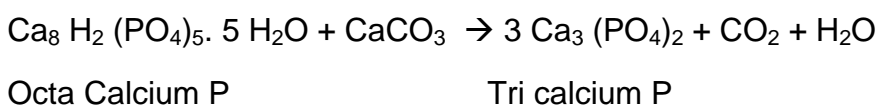
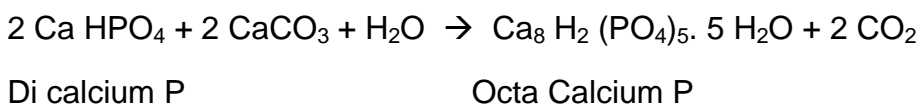
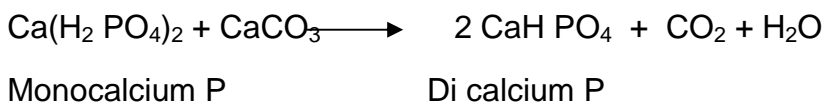
Monovalent forms are preferred by plants than divalent or trivalent. A soil pH of 6.5 – 7.5 is considered to be the best for optimum availability of phosphorus.

In strongly acid soils, the concentration of Fe and Al ions greatly exceeds, forming insoluble compounds with  $\text{H}_2\text{PO}_4^-$  rendering it unavailable.

$\text{H}_2\text{PO}_4^-$  also forms complex insoluble hydrous oxides as follows :



At high pH,  $\text{H}_2\text{PO}_4^-$  may form insoluble tri calcium phosphate by reacting with  $\text{CaCO}_3$ .

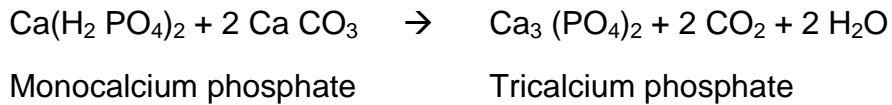


## Phosphorus fixation

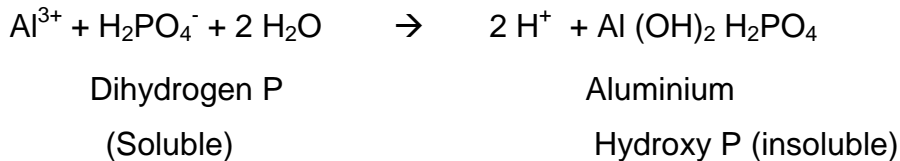
The fixation of P is a chemical reaction that makes it unavailable to crops. Another term often used in this sense is 'P retention'. Phosphate fixation can be the removal of phosphate from solution by soil which reduces the amount that plant roots can absorb. Thomas Way (1850) demonstrated the P fixation. Soil pH has a deep effect upon P fixation. In neutral to alkaline soils (pH 7.0 and above), the presence of lime causes the precipitation of phosphorus. In acid soils (pH < 6.5), iron and aluminium react with phosphorous to form highly insoluble compounds.

These reactions can be represented by the chemical equations. Three mechanisms are involved depending on pH.

### 1. In neutral to alkaline soils



### 2. In acid soils



Since the products of phosphate fixation are practically insoluble, only minute amounts of phosphorus are immediately available for plant growth.

### 3. In neutral soils

P is fixed in the crystal lattices of 1:1 type of clay minerals like the Kaolinite having high AEC by anion exchange phenomenon.

## Lecture 8: Factors affecting phosphate fixation in soil – methods to reduce P fixation – Quantity - Intensity parameters – Functions – deficiency & toxicity symptoms – corrective measures.

### Factors affecting P fixation in soils

- Clay minerals** : The main seat of P fixation in soils rests on the clay fraction. The more the surface area exposed with a given type of clay, the greater is the tendency to retain phosphorus.
- Type of clay** : Phosphorus is retained to a greater extent by 1:1 than by 2:1 clays. Soils high in kaolinitic clay will fix larger quantities of added P due to more AEC.
- Hydrous metal oxides of iron and aluminium** : In soils with significant amounts of iron and aluminium oxides, the P fixing capacity is larger.
- Amorphous colloids** : In Andisols, due to the presence of large quantities of amorphous colloids like allophanes with large negative charges which are balanced by aluminium cations, the phosphate becomes fixed to these aluminium ions.
- Calcium carbonate** : Calcium carbonate precipitates phosphates to form insoluble apatites. The activity of P will be lower in those soils that have a high  $\text{Ca}^{2+}$  activity.

6. **Soil pH** : adsorption of P by iron and aluminium oxides declines with increasing pH.
7. **Organic matter** : High organic matter content decreases P fixation.
8. **Temperature** : The rise in temperature generally enhances P fixation.
9. **Over liming** : Over liming increases P fixation by forming more insoluble Ca-P compounds.

#### **Methods to reduce P fixation**

1. **Organic matter addition** : Incorporation of organic residues into soil influences the reactions of phosphates and its availability to plants. Organic matter counteracts the effect of  $\text{CaCO}_3$ . It also reduces P sorption by soil. Addition of organic matter also increases P concentration in soil solution through mineralization of organic P and solubilisation of native soil P compounds. This effect is more pronounced at higher moisture level. During decomposition of organic matter various organic acids are produced which solubilize the phosphates and other P bearing minerals and thereby lower the P – fixation. The reason is
  - a) By formation of phospho - humic complexes that are easily assimilated by plants.
  - b) Through the mobilisation of the phosphate by humate ion by anion exchange
  - c) By forming a coating on sesqui oxide particles by humus as a protective cover which otherwise fix P.
2. **Placement of fertilizers** : The finer the soil texture, the greater is the retention of added P due to increased speed of reaction with surface area of contact. If finely divided fertilizer P is added to a soil by applying through broadcast the phosphate is exposed to a greater amount of surface, hence more fixation takes place. While band placement reduces the surface of contact between the soil and fertilizer with consequent reduction in the amount of fixation.
3. **Role of mycorrhiza** : Certain mycorrhizal fungi known as VAM colonize plant roots and through this association help the plant to absorb more P.
4. **Role of P solubilising microorganisms**: P solubilising bacteria like *Bacillus megatherium* and *Pseudomonas striatus*; or fungal species namely *Aspergillus awamori* are reported to enhance the availability of fixed P and reported to add  $30 - 35 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  under ideal conditions.
5. **Liming of acid soils**: About one- third of Indian soils are acidic in reaction. The beneficial effect of liming of these acid soils is due to the release of fixed P that was held with iron, aluminium oxides & hydroxides.

**Quantity– Intensity relationships** Schofield (1955) divided the measurements

- i) **Intensity of supply** : which indicates the soil solution phosphate and is measured by phosphate potential.
- ii) **Quantity factor** : which indicates the total quantity of P in the soil. This pool supplies P to the soil solution pool (intensity) when P is taken up by plants.

In a limited range of P concentration where Q/I relationship is linear, the slope of the curve is given by  $\frac{\Delta Q}{\Delta I}$  which is referred to as phosphate buffering capacity or simply capacity, which indicates the resistance of soil to a depletion in quantity of P. For a given value of intensity, the quantity values are higher for fine textured soils than coarse textured soils. Availability of P to plants is controlled by the mutual interplay of the three factors viz., quantity, intensity and PBC. Hence, in clay soils depletion is less than sands, hence can supply P to the crops for longer period.

#### **Functions of phosphorus in plants:**

Phosphorus is the second most abundant mineral in human body making up for more than 20 % of body minerals. It is largely absorbed by the plant roots as dihydrogen orthophosphate ion ( $\text{H}_2\text{PO}_4^-$ ). In normal P sufficient plants, P content varies from 0.1 to 0.4 per cent by weight.

The following are the functions of phosphorus in plant system

1. Constituent of nucleoproteins, phytins and phospholipids.
2. Essential constituent of number of enzymes -important in energy transfer.
3. Essential for cell division and development.
4. Stimulates root development and growth.
5. Responsible for early establishment of seedlings.
6. Strengthens the straw and decreases lodging.
7. Brings about early maturity.
8. Counteracts the effect of excessive nitrogen.
9. Increases grain to straw ratio.
10. Improves the quality of food grain.
11. Increases rhizobial activity, increases the formation of root nodules thus helping in more N - fixation.

**Deficiency symptoms** : In general, plants having less than 0.1 % phosphorus are designated as P-deficient. Because of its faster mobility in plants, P gets translocated from older tissues to the meristematic tissue. Therefore, deficiency symptoms of P first appear on the older leaves.

P deficiency results in

- the production of dark green color leaves.
- Severe restriction of root growth.
- thin, erect and spindly plants with sparse and restricted foliage.
- suppressed lateral bud production.
- bluish green foliage, and under continued deficiency the older leaves become bronzed or develop reddish purple tip or leaf margins.

### **Toxicity symptoms**

Excess of P causes trace element deficiency particularly Fe and Zn.

**Correction of deficiency** Generally, P is applied as a basal application by band placement. The following are the phosphatic fertilizers.

1. Single Super Phosphate (SSP) contains 16 to 22%  $P_2O_5$
2. Rock phosphate contains 30-38 %  $P_2O_5$
3. Triple Super Phosphate contains 46 %  $P_2O_5$
4. Diammonium phosphate contains 46 %  $P_2O_5$
5. Monoammonium phosphate contains 52 %  $P_2O_5$
6. Basic slag contains 10-20 %  $P_2O_5$



Phosphorus deficiency in sorghum plants



A close-up of phosphorus deficiency in *gobhi sarson* plant



A close-up of phosphorus deficiency symptom in maize leaf



Phosphorus deficiency symptom in sugarcane

## Lecture 9:

### Potassium:- content in soil – Source – forms of soil potassium – Potassium fixation.

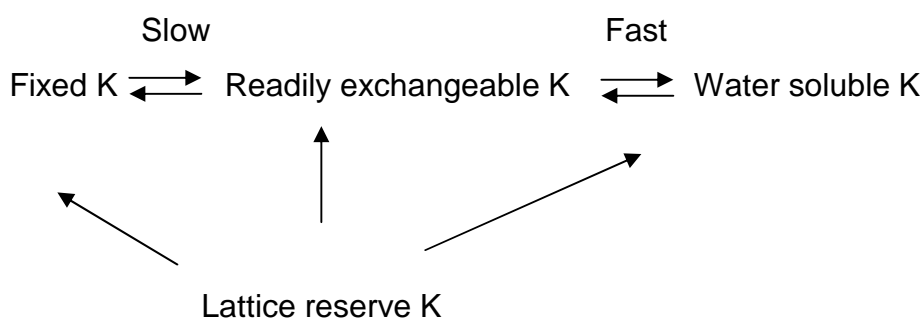
Potassium is one of the three major plant nutrient elements. The consumption of potassic fertilizers in India is 1.33 Mt. The gap between removal of K and its application to crops is widening.

Potassium content in the earth's crust averages about 1.9 % with the range of 0.5 – 2.5 %. In tropical soils the total content of K is quite low because of their origin, high rainfall and high temperature.

**Sources of potassium :** The K in soil originates from the disintegration and decomposition of rocks containing potassium bearing minerals. The minerals considered original source of K are potassium feldspars, orthoclase and microcline ( $KAlSi_3O_8$ ), muscovite  $KAl_3Si_3O_{10}(OH)_2$ , biotite  $K(MgFe)_3AlSi_3O_{10}(OH)_2$ . Potassium is also found in the soil as secondary silicate clays like illite, vermiculite and chlorite.

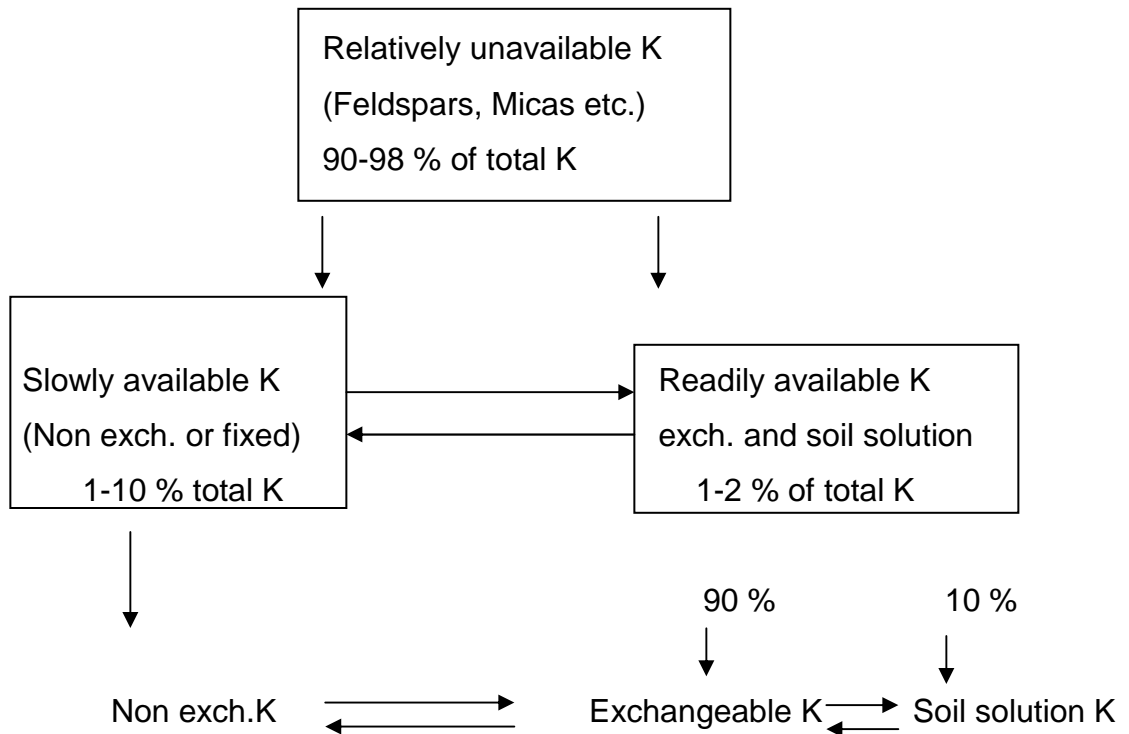
**Forms of soil potassium :** Soil potassium is believed to exist in four categories based on their availability to crops.

1. Water soluble K
2. Readily exchangeable K
3. Fixed K
4. Lattice or inert reserve K



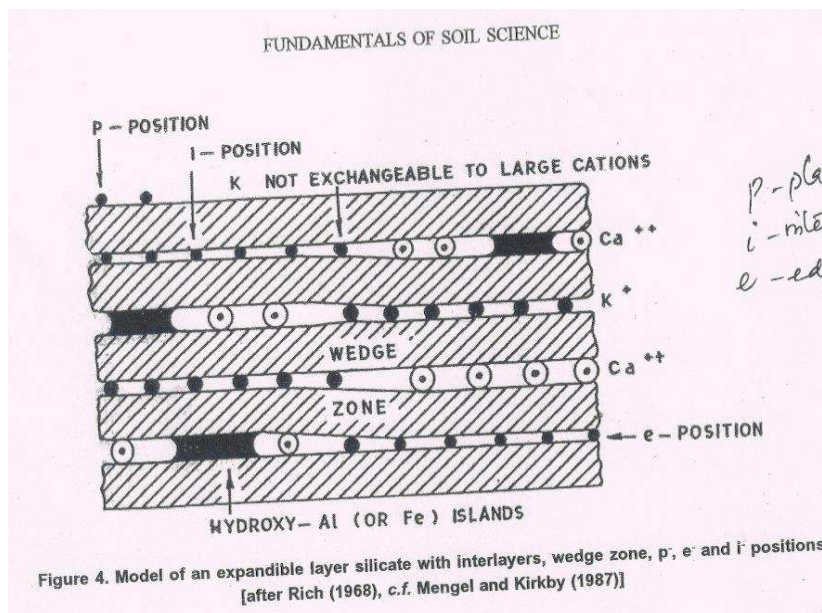
1. **Water soluble K :** Potassium is present as soluble cation in soil solution. It is in equilibrium with exchangeable K.
2. **Exchangeable K :** This fraction constitutes the K adsorbed on soil clay complex and replaceable with neutral salts. In mineral soils, it is less than 1% of the total K.
3. **Fixed potassium :** The part of the added K which is firmly bound by the soil and not immediately replaceable with neutral salts is said to be fixed K. The fixed K is bound between the basal planes of micaceous minerals.
4. **Lattice potassium :** This form constitutes the major part of the total K in mineral soils and present in primary minerals such as muscovite, biotite and potash feldspars. It accounts for 92 – 98 % total K.

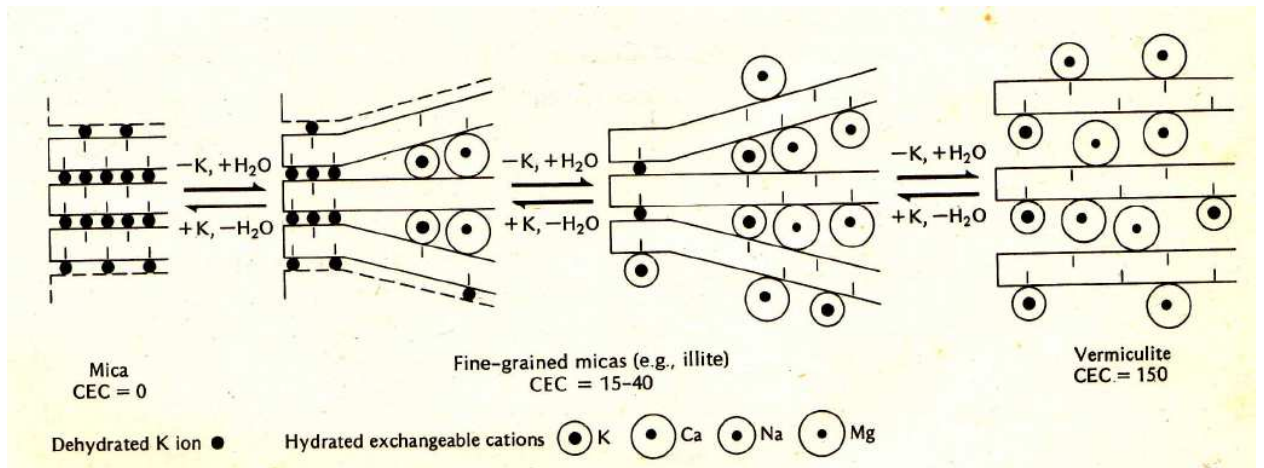




**Potassium fixation :**

Conversion of freshly applied potassium and / or soil solution potassium to fixed or non exchangeable forms that can not be extracted with neutral salts is referred to as K fixation. It is maximum in 2 : 1 clays particularly with high amounts of illite. The fixation is nearly absent in soils dominated by kaolinite, chlorite and unweathered micas; slight in montmorillonite and substantial in illite and high in vermiculite dominated soils. For the clay minerals like illite, vermiculite and weathered mica three different adsorption sites can be distinguished. These sites are at the planar surfaces (planar position), at the edges of layers (e positions) and in interlayer spaces (i positions). The binding of  $K^+$  with organic colloids and kaolinite is at 'p' position which is weak and hence easily replaced by other cations. In smectite rich soils,  $K^+$  is held at i position which has the maximum specificity for  $K^+$ . When dehydration occurs, the lattice sheets come closer and the adsorbed cations lose their water molecules.





According to 'Lattice Hole' theory (Page and Baver, 1940), the exposed surface and surfaces between sheets of minerals consists of oxygen ions arranged hexagonally. The opening within the hexagon is equal to the diameter of an oxygen ion (approximately  $2.8 \text{ \AA}$ ). Ions having a diameter in this magnitude (eg. For  $\text{K}^+$  it is  $2.66 \text{ \AA}$ ) will fit snugly into the lattice holes and such ions will be held very tightly as they come in contact with the negative electrical charges within the crystal. However, ions like  $\text{NH}_4^+$  (dia.  $2.86 \text{ \AA}$ ) has nearly the same ionic radius as the  $\text{K}^+$  and is subject to similar fixation by 2 : 1 clays.

## Lecture 10: Factors affecting potassium fixation – Quantity and intensity parameters – Luxury consumption – Functions and deficiency symptoms – corrective measures

### Factors affecting K-fixation

- Clay minerals** : K fixation is controlled mainly by clay minerals, with both their quantity and nature being important. Illite, weathered mica, vermiculite take part in K fixation but 1:1 type of clays such as kaolinite do not fix potassium.
- Soil reaction** : K fixation capacity can be reduced by the presence of  $\text{Al}^{3+}$  and Al-hydroxide cations.
- Cation Exchange Capacity (CEC)**: Fine textured soils have a higher CEC and hold more exchangeable K.
- Concentrations of added K** : Increasing the concentration of  $\text{K}^+$  in soils with high fixing capacity encourages greater fixation.
- Wetting and drying** : Soils with high exchangeable  $\text{K}^+$  on drying will result in fixation due to air drying.
- Freezing and thawing** : of moist soils may release fixed K.
- Sub soil K and rooting depth** : Exchangeable K varies with depth.
- Soil temperature** : Higher temperature favors dehydration and

contraction of the crystal lattice resulting in higher K fixation.

9. **Ca and Mg (exchangeable cations):** The size of  $K^+$  and other ions that would replace K is important in K fixation. The cations of smaller size of the hydrated ions can easily enter into clay lattices and replace some of the fixed potassium.

### Quantity and intensity parameters

The concept of intensity, quantity and buffering power proposed by Beckett (1964) are useful in measuring the potassium supplying power of soils.

Intensity factor is a measure of K in soil solution that is immediately available for absorption by plants. Since this absorption is influenced by the activity of other cations like  $Ca^{2+}$  and  $Mg^{2+}$  in the soil solution, the potassium activity ratio ( $AR^k$ ) is used in place of K concentration alone to indicate the intensity factor.

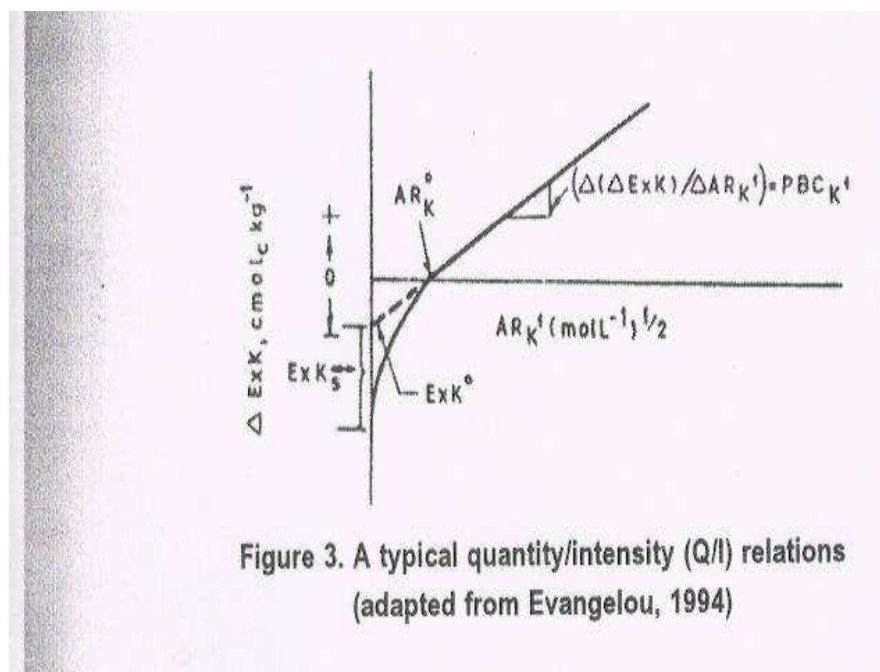
$$AR^k = \frac{[K^+]}{\sqrt{[Ca^{2+} + Mg^{2+}]}}$$

Quantity factor is a measure of the capacity of the soil to maintain the level of K in soil solution over a long period or over the duration of crop growth. The capacity is mainly due to the exchangeable K.

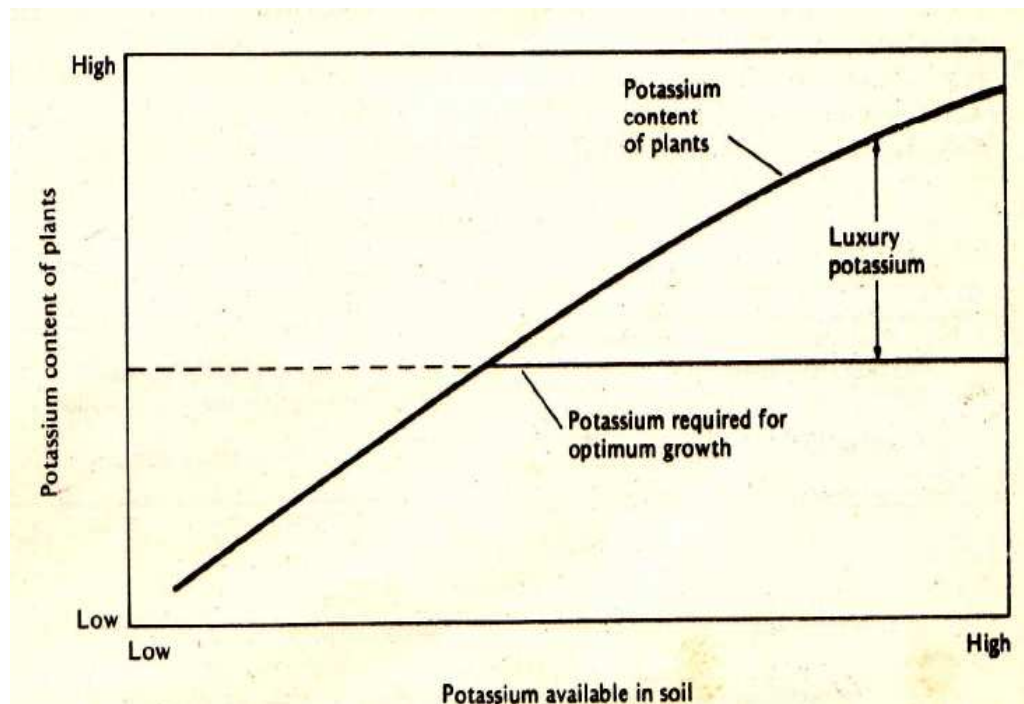
The slope of the curve indicates the potential buffering capacity, which indicates how the K level in the soil solution (intensity) varies with the amount of labile form (quantity)

$$PBC = \frac{\Delta Q}{\Delta I}$$

The wider the ratio, the more buffered is the soil. Soil having smectitic clay have more PBC, than having kaolinite.



**Luxury consumption** : Some crops tend to absorb and accumulate potassium for in excess of their needs if it is present in sufficiently large quantities in the soil. This tendency is termed luxury consumption because the excess K absorbed does not increase crop yields to any appreciable extent. Wasteful luxury consumption occurs especially with forage crops.



**Functions** : K is absorbed by the plant as  $K^+$ . Its concentration in healthy tissue varies from 1-5 %. Potassium is a unique element that plants can accumulate it in abundant amounts without exhibiting any toxicity symptoms. This behaviour is referred to as luxury consumption. Potassium plays a regulatory role in plant metabolism. Potassium is not a component of any organic compound in plants.

- It regulates the opening and closing of stomata.
- Plays a major role in transport of water and nutrients throughout the plant in xylem.
- It improves drought tolerance.
- Neutralizes organic anions and other compounds and maintains the pH of cytoplasm in the range of 7-8.
- Activates > 60 enzymes, including starch synthetase, K is responsible for the activation of nitrate reductase enzyme.
- Enhances crop quality, shelf life of fruits and vegetables.
- Reduces lodging of crops, enhances winter hardiness.
- Imparts disease resistance.

#### **Deficiency symptoms**

- Potassium deficiency does not manifest immediately in the form of visible symptoms. First growth rate decreases and later deficiency symptoms appear. Deficiency symptoms first develop on the older leaves.

- Chlorosis along the margins followed by scorching and browning of tips of older leaves which gradually progresses inwards giving burning appearance. Slow and stunted growth of the plant and crop lodging.
- Shrivelled fruits and seeds.
- Reduced crop yields without the appearance of definite symptoms; the phenomenon is called hidden hunger.
- Decrease in resistance to certain plant diseases
- Decrease in the quality of fruits and vegetables.
- Potassium deficiency disturbs the overall physiological activity within the plant system by altering the activities of enzymes like invertase, catalase in crops like sugarcane.

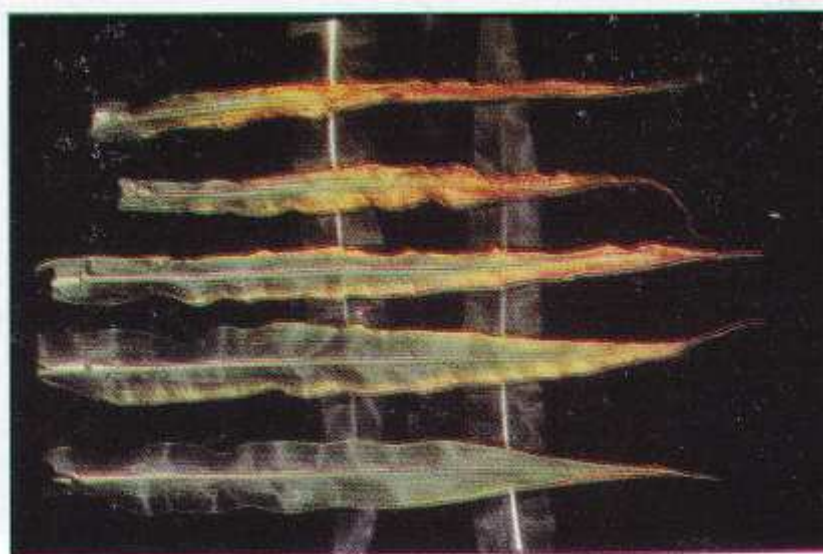
### Correction measures

Potassium chloride or muriate of potash constitutes 99% of usage of K fertilizer and potassium sulphate accounts for 1%. Muriate of potash contains 60%  $K_2O$  or 50% K and sulphate of potash contains 50 %  $K_2O$  or 41.5% K.

Some crops are sensitive to high amounts of potassium chloride. These include tobacco, grapes, cotton, fruit trees, sugarcane, potatoes, tomatoes, strawberries, onion and cucumber. Oil palm and coconut on the contrary appear to be chloride loving crops.

Generally, potassic fertilizers are applied as basal dose, but for light textured soils, split application is advocated. In Andhra Pradesh split application of N and K are recommended for light soils.

Potassium nitrate containing 44%  $K_2O$  (37% K) and 13% N is preferred for spraying on fruit trees and horticultural crops. Spraying of  $KNO_3$  during winters (*rabi* season) to impart cold hardiness is also in practice by the farmers in Andhra Pradesh.



Potassium deficiency in maize



Potassium deficiency in cashew



Potassium deficiency in grapes



Potassium deficiency in potato

**Lecture 11: Secondary nutrients- Calcium- sources and content – forms of calcium in soils – Functions – Deficiency symptoms – corrective measures**

**SECONDARY NUTRIENTS**

Secondary nutrients include calcium, magnesium and sulphur. These nutrients received little attention due to their inadvertent application through fertilizers and irrigation water. Ammonium sulphate (100 kg) supplies 20 kg N and 24 kg S; While single super phosphate supplies 16 kg of P<sub>2</sub>O<sub>5</sub>, 21 kg of Ca and 12 kg of S. Potassium sulphate supplies 52 kg K<sub>2</sub>O and 18 kg of S.

These secondary nutrients though required in equal amounts as primary nutrients, but are added inadvertently along with primary nutrients.

Lime which contains Ca and Mg is applied to raise the pH and sulphur compounds are used to lower the pH of soil.

Irrigation water may contain on an average 25 ppm of SO<sub>4</sub><sup>=</sup>, 50 ppm of Ca and 5 ppm of Mg.

**Calcium**

**Content and sources of soil calcium :** The calcium concentration of the earth's crust is about 3.20 %, it may be as low as 0.015 % in humid region to as high as 5 % in arid region. High calcium content in arid regions could be due to low rainfall and hence little leaching. The major sources of calcium are the weathered products of rocks and minerals containing calcium like the following sources

<b>Mineral</b>	<b>Chemical formula</b>	<b>Total CaO (%)</b>
1. Calcite	CaCO <sub>3</sub>	56.0
2. Apatite	Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub>	50.0 – 53.2
3. Dolomite	CaCO <sub>3</sub> .MgCO <sub>3</sub>	33.2
4. Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	32.2

Besides these secondary minerals, primary minerals like Augite (18.7%), Hornblende (4.6%), Anorthite (10.0 – 20.0 %) Epidote (22.0-25.0%) etc., are the sources of calcium in the soil.

**Forms of calcium in soils :** Calcium is generally the dominant cation in normal cultivated soils. It is present in different forms. The calcareous soils have higher amount of Ca than acid soils.

**a) Mineral particles :** Calcium is mostly present as primary minerals such as

basic plagioclase like anorthite, and basic rocks like basalt, gabbro. They all release Ca on weathering.

- b) **Calcium carbonate** : Calcite mineral is very common. The nodular form of calcium carbonate and amorphous calcium carbonate exist.
- c) **Simple salt** : calcium is present in many simple salts such as calcium chloride, calcium sulphate, calcium nitrate and calcium bicarbonate.
- d) **Exchangeable calcium** : Of all the cations on the exchange complex of soils  $\text{Ca}^{2+}$  is the most dominant cation.

### **The fate of released calcium**

1. **Absorbed by organisms** : Legumes use much more calcium than grasses. Prolonged cropping with crops like alfalfa on sandy soils low in Ca depletes Ca resource.
2. **Losses due to leaching** : The loss of calcium in drainage water due to leaching by rain or irrigation is very large. The loss of  $\text{Ca}^{2+}$  increases with increase in rainfall or with increase in permeability of the soil. Light textured soil suffers greater loss of calcium than heavy soils. Leaching losses range between 84 to 224 kg ha<sup>-1</sup>.
3. **Adsorbed by clay colloids** : If the activity of calcium in soil solution suddenly increases, there will be a shift in equilibrium with subsequent adsorption of some  $\text{Ca}^{2+}$  by exchange complex. Conversely, if the activity of calcium in the soil solution phase decreases due to either leaching or crop removal, the adsorbed calcium releases into soil solution.
4. **Reprecipitated calcium** : Calcium is reprecipitated as secondary calcium compounds in arid climate. In arid region, due to low rainfall, Ca in soil solution will be precipitated as least soluble calcium compounds.

### **Factors affecting the availability of Ca in soils**

1. **Total calcium supply** : Total supply of calcium in very sandy acid soils with low cation exchange capacity can be too low to provide sufficient available calcium to crops.
2. **Soil pH** : High  $\text{H}^+$  activity occurring at low soil pH will impede calcium uptake due to high base unsaturation.
3. **Cation exchange capacity and degree of saturation of exchange complex** : The absolute amount of calcium present is not that important but the relative amount of other cations or degree of calcium saturation is



important. Montmorillonite requires a 70 % base saturation to release Ca, while kaolinite requires only 40 % base saturation.

4. **Type of soil colloid.** The type of clay influences the degree of calcium availability. A much higher degree of saturation is required for 2 : 1 clay minerals than 1:1 clay.
5. **Ratio of calcium to other cations in soil solution :** Calcium availability is influenced by the ratio between calcium and other cations. Calcium / total cation ratio of 0.10 to 0.15 is desirable. Blossom end rot, a calcium deficiency disorder in tomatoes can be prevented by maintaining a Ca / soil solution salt ratio in the range of 0.16 and 0.2.

### **Functions of calcium in plants**

Calcium is absorbed by the plant as calcium ions ( $\text{Ca}^{2+}$ ), the sufficiency range is between 0.2 – 1.0 %.

1. Essential for the formation of cell wall and calcium pectate in the middle lamella of the cell wall which regulates the entry of only those nutrients which are not toxic to plants. In seeds, calcium is present as calcium phytate.
2. In root tip, calcium is very essential for the meristematic activity.
3. Provides a base for neutralisation of organic acids and other toxins (like Al) produced in plants.
4. It plays a role in mitosis (cell division) and helps to maintain the chromosome structure.
5. Essential co-factor or an activator of a number of enzymes like hydrolases.
6. It activates phospholipase, arginine kinase, amylase and Adenosine triphosphatase (ATPase) enzymes.
7. Favours the assimilation of nitrogen into organic constituents especially proteins.

### **Deficiency symptoms**

Soils seldom become calcium deficient, as long as soil pH is maintained towards neutral range. Deficiency of calcium is characterised by a reduction in meristematic tissue

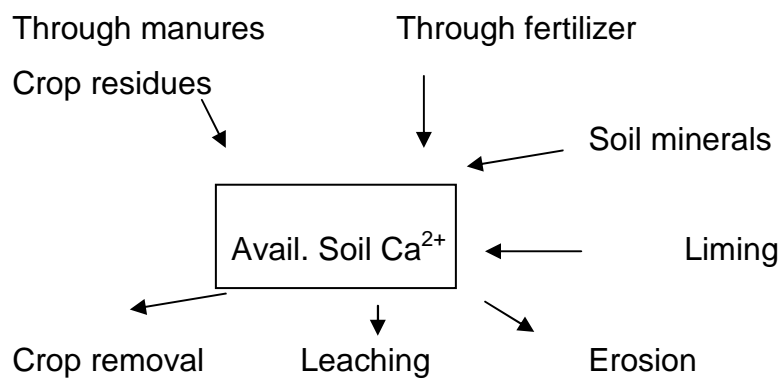
1. Though calcium is highly mobile in soil, in the plant system it is the immobile nutrient and hence the deficiency symptoms manifest at the growing tips of shoots and youngest leaves.
2. Failure or desiccation of terminal bud development.
3. No unfolding of new leaves in corn, whose tips are colorless and are covered with sticky gelatinous material which makes them adhere to one another.

4. Chlorosis of young leaves followed by distortion of the growing points of the stem.
5. In fruit trees, the death of growing points followed by die back.
6. In guava, the old leaves are chlorotic with red brown spots.
7. In apple, the discoloration of the fruit meat, the condition generally referred to as "bitter pit".
8. In Brassica, severe loss of color in young leaves, terminal bud leaves are hooked, leaves below become cup shaped. Old leaves collapse due to terminal bud disintegration.
9. Blossom end rot in tomato is due to Ca deficiency

**Correction measures**

Calcium as a plant nutrient is more important in calcium deficient acid soils. The application of carbonate or sulphate salts of calcium @ 2 – 4 q ha<sup>-1</sup> in furrows could increase the yield by 48 %.

**Balance sheet of calcium**



**Ca deficiency**



Groundnut



Cucurbits



Tobacco

**Lecture 12: Magnesium - Sources – Content – Forms of magnesium in soils.**  
**Factors affecting availability of magnesium. Functions – Deficiency symptoms – Corrective measures**

Magnesium is absorbed by plants from the soil solution as  $Mg^{+2}$ . It constitutes 1.93 % of the earth's crust ranging from 0.1 % in coarse sandy soils of humid region to 4 % in fine textured soils of arid and semi arid regions.

Mg in soil originates from weathering of biotite, dolomite, hornblende, olivine, epsomite ( $MgSO_4 \cdot 7 H_2O$ ) and serpentine. Also found in secondary clay minerals like chlorite, illite, montmorillonite and vermiculite; excess Mg may be seen in soils developed from serpentine bed rock. Magnesium forms 12-80 % of exchangeable bases which is second to calcium (80-85%).

If large quantities of magnesium are added to montmorillonite, it may convert to vermiculite.

**Fate of released Mg :** On decomposition of primary minerals, Mg is released into soil which may then be

- 1) Lost in the percolating water.
- 2) Absorbed by living organisms.
- 3) Adsorbed by surrounding clay colloids.
- 4) Reprecipitated as secondary mineral in arid regions.

The soil Mg available to plants is in the exchangeable plus water soluble forms. The availability of Mg is influenced by

- a) Amount of exchangeable  $Mg^{+2}$  :** Soils are deficient in Mg when they contain less than 25 to 50 ppm of exchangeable  $Mg^{+2}$ .
- b) Soil pH :** Nutritional problems of  $Mg^{+2}$  will arise in strongly acid soils with  $Al^{+3}$  saturation of 65 to 70 %. The availability of  $Mg^{+2}$  can also be adversely affected by high  $H^+$  activity in strongly acid soils.
- c) Degree of Mg saturation :** The more the degree of saturation the greater is its availability. When exchangeable magnesium is more than 45 %, it is toxic to plants. Magnesium availability is high when its saturation is 10 – 20 % on the exchange complex. Normally, the exchangeable magnesium accounts for 4 to 20 % of CEC. Magnesium saturation should not be less than 10 %.
- d) Nature of other exchangeable ions :** Plant deficiencies of Mg can occur in soils with wide Ca / Mg ratio. Ideally it should not be greater than 7:1. High levels of exchangeable  $K^+$  can interfere with Mg uptake. K / Mg ratio should be less than 5:1 for field crops, 3:1 for vegetables and sugarbeet, 2 : 1 for fruit and green house crops.  $NH_4^+$  also interferes with Mg nutrition.

e) **Removal by crop** : Legumes exhaust more Mg than non legumes.

f) **Additions through fertilizers, manures and rains**: FYM and oil cakes are rich source of Mg. Basic slag contains 3 – 4% of magnesium. Serpentine contains 26 %.

### Functions

The usual concentration of  $Mg^{+2}$  in crops varies between 0.1 and 0.4 per cent. A large part of Mg is associated with organic anions like malate. Magnesium

- Mg is the only mineral constituent of chlorophyll located at its centre.
- Chlorophyll formation usually accounts for about 15 to 20 % of total Mg content of plants as Mg - porphyrin.
- Serves as a structural component of ribosomes. Mg activates the formation of polypeptide chains to form amino acids. About 70 % of Mg is associated with anions such as malate and citrate.
- Seeds contain Mg as salt of phytic acids. Mg is required for phosphate transfer from ATP (Phosphorylation) in carbohydrate metabolism.
- Several enzymes (eg : *Ribulose carboxylase*) require  $Mg^{+2}$  as Cofactor.
- It promotes uptake and translocation of phosphorus and movement of sugars within the plants.

**Deficiency symptoms** :  $Mg^{+2}$  is a mobile element and is readily translocated from older to younger plant parts in the event of deficiency and hence deficiency symptoms are manifested in the older leaves. The magnesium deficient plants usually have less than 0.1% Mg. Magnesium deficiency is common in the plants grown on coarse textured acidic soils.

- As a consequence of  $Mg^{+2}$  deficiency, the proportion of protein nitrogen decreases and that of non protein nitrogen increases in plants.
- Shortage of  $Mg^{+2}$  results in an interveinal chlorosis of the leaf in which only the veins remain green and the interveinal areas turn yellow with streaky or patchy appearance. In more advanced stages the leaf tissue becomes uniformly pale yellow, then brown and necrotic.
- Affected leaves turn small in final stage and curve upwards at the margins.
- In some vegetables, interveinal chlorosis with tints of red, orange and purple colors is observed.
- Grass tetany : Cattle consuming forages with low Mg may suffer from “Hypomagnesemia” (low level of blood Mg) commonly known as Grass tetany. This happens due to high levels of  $NH_4^+$  - N and K application.

### Correction measures :

Use of dolomitic lime stone  $\text{Ca Mg} (\text{CO}_3)_2$

Magnesia  $\rightarrow \text{MgO}$  55 % (Mg)

Basic slag  $\rightarrow$  3-4 % Mg

At a dose of 30 – 50  $\text{kg ha}^{-1}$



Lettuce

Mg deficiency



Tobacco



Cotton



Tomato

### Lecture 13: Sulphur – cycle – occurrence – forms of sulphur in soil – sulphur transformations in soil – Mineralisation and immobilisation

The earth's crust contains about 0.06 % sulphur. It is mostly present as sulphides, sulfates and in organic combinations with C and N. More than 95% of total sulphur in soil is present in organic matter under temperate conditions. Under tropical and sub tropical conditions, the organic matter content in the soil is generally less than the temperate soils. The initial source of all sulphur is the sulphide contained in plutonic rocks. Through weathering the sulfides are released. In humid region organic sulphur, while in arid zone, the sulfates of calcium, Mg, Na and K predominate. Another source of sulphur is the atmosphere. Owing to industrial activity or through combustion of fuel, sulphur dioxide is produced which is brought down by rain.

The continuous use of high analysis fertilizers, particularly those which are devoid of sulphur such as urea, triple super phosphate, ammonium nitrate and ammonium chloride may lead to sulphur deficiency in soils.

**Forms of sulphur in soils :** Sulphur is present in the soil in many different forms, both organic and inorganic.

The inorganic forms are readily soluble sulphate, adsorbed sulphate, insoluble sulphate co-precipitated with calcium carbonate and reduced inorganic sulphur compounds.

**1. Easily soluble sulphate** : Sulphur is normally taken up by plants as the  $\text{SO}_4^-$  ion. In sulphur deficient soils the amount of readily soluble  $\text{SO}_4^-$  is frequently between 5 and 10 ppm. Sandy S deficient soils often contain less than 5 ppm.  $\text{SO}_4^-$  when associated with monovalents like  $\text{Na}^+$  are more prone for leaching. Medium losses when bound to divalent like  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  and minimum losses when bound to  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ .

**2. Adsorbed sulphate** : Adsorbed sulphate is an important fraction in soils containing large amounts of hydrous oxides of iron and aluminium like in Oxisols and Ultisols. Adsorbed sulphate can account for upto  $1/3^{\text{rd}}$  of total sulphur.

**3. Sulfate coprecipitated with calcium carbonate** : It is an important fraction in calcareous soils.

**4. Sulfides** : Under anaerobic conditions in water logged soils, there may be accumulation of  $\text{H}_2\text{S}$  formed by the decay of organic matter. Also,  $\text{SO}_4^-$  present in the soil serves as an electron acceptor for sulphate reducing bacteria and it is reduced to  $\text{H}_2\text{S}$ . This reduction takes place at a redox potential of less than -150 mV and at a pH range of 6.5 to 8.5.

**5. Elemental sulphur** : It is an intermediate product formed during oxidation of sulfides by chemical processes.

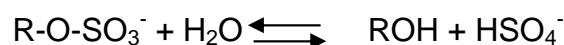
**6. Organic form** : Most of the sulphur in surface horizons of well drained agricultural soils of humid, temperate, semi arid and sub tropical regions is present in the organic form. It accounts for more than 90 %.

Average C : N:S ratio for calcareous soil 113 : 10 : 1.3 and for non calcareous soils it is 147 : 10 : 1.4. The N:S ratio of most soils is in the range of 6 to 8 in the form of amino acid like cystein, cystine and methionine.

**Sulphur Transformations** : The transformations of sulphur in soil are many and varied with changes often being cyclic. Also, the element converts back and forth from inorganic and organic forms due to the presence of living organisms.

When plant and animal residues are returned to the soil they are attacked by microorganisms thus releasing some of the sulphur as sulphate. Most of the sulphur, however, remains in organic form and eventually becomes part of the soil humus.

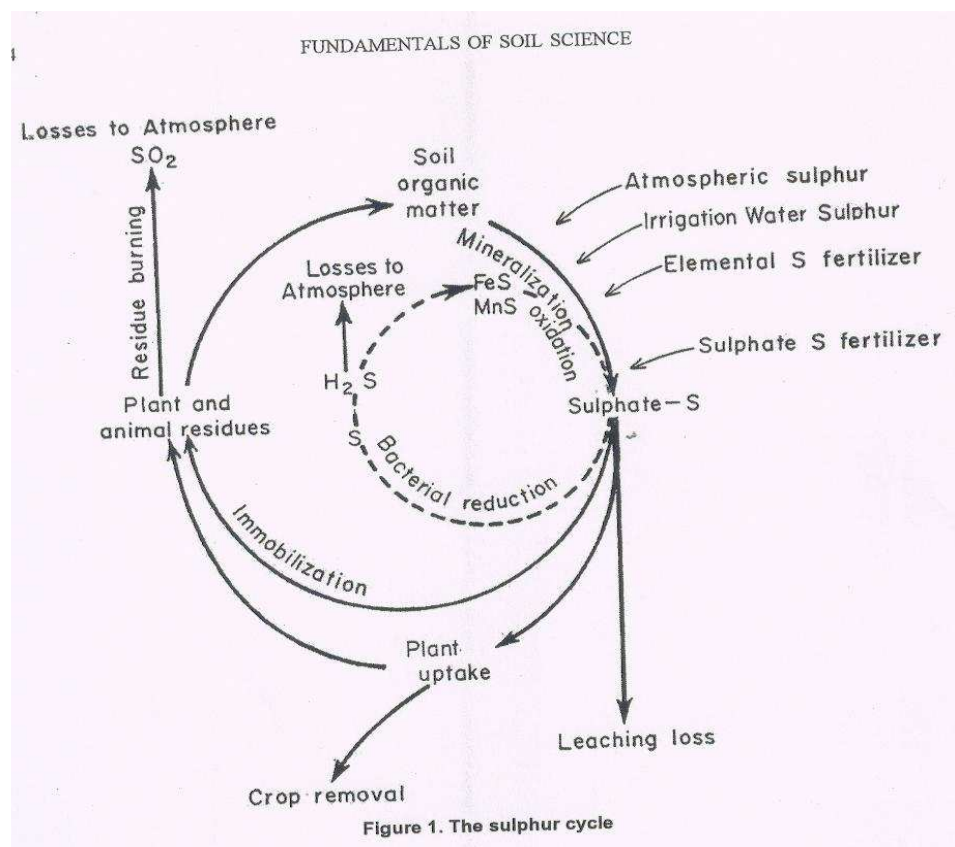
**1. Mineralisation** : Mineralisation of sulphur is the conversion of organic sulphur to inorganic  $\text{SO}_4^-$  by microbes. It depends on the sulphur content of the decomposing material. Mineralisation of sulphur takes place at or below C/S weight ratio of approximately 200 : 1. Heterotrophic microorganisms bring about mineralization. Sulfatase enzyme plays an important role in mineralization.



Mineralisation is more in cultivated soils than fallow due to rhizosphere effect.

**2. Immobilisation** : Sulfur is immobilized in soils in which the ratio of either C : N: S is too wide. At a C : S ratio of above 200 : 1, immobilisation or tie-up of  $\text{SO}_4^-$  with various organic forms is favored. Particularly, if the ratio is greater than 400: 1 i.e., when low sulfur containing organic materials are added to soils not plentifully supplied with inorganic sulphur immobilization of inorganic sulphur takes place. The energy rich material stimulates microbial growth and the inorganic sulphur ( $\text{SO}_4^-$ ) in the soil is locked in the microbial tissues. Only when the microbial activity subsides inorganic  $\text{SO}_4^-$  again appear in the soil solution.

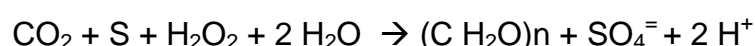
### Sulphur cycle



**Lecture 14: Sulphur oxidation – factors affecting oxidation in soils – sulphide injury- causes – symptoms – and remedial measures – functions – deficiency symptoms – corrective measures**

**A) Sulphur oxidation** : Elemental sulfur, sulfides and several other inorganic sulfur compounds can be oxidized in the soil by microbial oxidation, though chemical non biological oxidation also takes place to a lesser extent. The rate of biological oxidation depends on three factors like

- i) the microbial population
- ii) Characteristics of sulfur source,
- iii) Environmental conditions in the soil



Two classes of bacteria are specially adapted for sulfur oxidation. These are chemolithotrophic sulfur bacteria which utilize the energy released from the oxidation.

eg : *Thiobacillus thiooxidans*.

*Thiobacillus thioparus*

### Factors affecting sulphur oxidation in soils

1. **Soil microflora** : The more the number of sulphur oxidizing bacteria like *Thiobacillus thiooxidans* the more is sulphur oxidation.
2. **Temperature** : Temperature between 25° and 40°C will be close to ideal, the process is slow below 10°C.
3. **Soil pH** : Optimum pH range is 6.5 to 7.2.
4. **Soil type and properties** : S oxidation is not very dependent on soil texture, organic matter content etc. Rapid sulphur oxidation is observed in well fertilized soil than one low in P and K. *Thiobacilli* require NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> is injurious. Organic matter is not essential as *Thiobacilli* are autotrophic but not heterotrophic.
5. **Fertilizer interactions** : Sulphur when applied in combination with N and P increases the rate of sulphur oxidation.

### B) Sulphur reduction or Sulphide Injury or H<sub>2</sub>S injury

Under anaerobic conditions in water logged soils there may be accumulation of H<sub>2</sub>S formed by the decay of organic matter. Also, SO<sub>4</sub><sup>=</sup> present in the soil serves as an e<sup>-</sup> acceptor for sulphate reducing bacteria viz., *Desulfovibrio*, *Desulfatomaculum* and SO<sub>4</sub><sup>=</sup> gets reduced to H<sub>2</sub>S. This reduction of SO<sub>4</sub><sup>=</sup> is both redox potential and pH dependent. Sulphide injury occurs at a redox potential of less than -150 mV and in the pH range of 6.5 to 8.5



In some rice paddies, high in organic matter and low in active metallic elements such as iron, the free H<sub>2</sub>S may be released which is harmful to rice roots. This H<sub>2</sub>S injury to rice in paddies is referred to as "Akiuchi".

#### Symptoms of Akiuchi

- The upper leaves become progressively shorter.
- Lower leaves drying to a dirty yellow color with brown spots on the surface.
- Roots are pale white, mingled with black or rotten ones giving rotten egg smell and when roots are exposed to sun after washing they turn to reddish colour.
- Soil pH is around 6.0.
- Bubbles will be coming out from the affected areas.

In normal submerged soils well supplied with Fe, the H<sub>2</sub>S liberated is almost removed from solution by reaction with Fe<sup>2+</sup> forming FeS<sub>2</sub> which forms protective coating on roots and prevent rotting.





### **Remedial measures**

- Use of Ammonium sulphate or any S containing materials should be avoided.
- Application of material containing iron such as laterites or lake mud.
- Providing aeration to soil by draining the field.

### **Functions of sulphur in plants**

1. It is required for the synthesis of the S containing amino acids cysteine, cystine and methionine and for protein synthesis.
2. It activates certain proteolytic enzymes such as papainase and synthesis of papain.
3. It is a constituent of certain vitamins viz., Thiamine and biotin, coenzymes and glutathione, Acetyl coenz A (precursor for fatty acid synthesis), ferredoxin.
4. It is present in the crops like onion, mustard, cabbage and cauliflower as polysulfides.
5. It increases oil content of crops like flax, soybean, groundnut etc.
6. Disulfide linkages (-S-S - ) have been associated with the structure of proteins.
7. Sulfhydryl (-SH) groups in plants are related to increased cold resistance.
8. It is required for N fixation in legumes and is a part of nitrogenase enzyme system.

### **Deficiency symptoms**

Sulphur content in plants ranges between 0.1 to 0.4 %. In view of the large field scale occurrences of sulphur deficiencies in India, it has been described as the fourth major nutrient after N, P and K. Plants suffering sulphur deficiency accumulate non protein nitrogen in the form of nitrate and amide. N:S ratio of plants is between 9 to 12 : 1. As sulphur is immobile in the plant, its deficiency is manifested on young leaves.

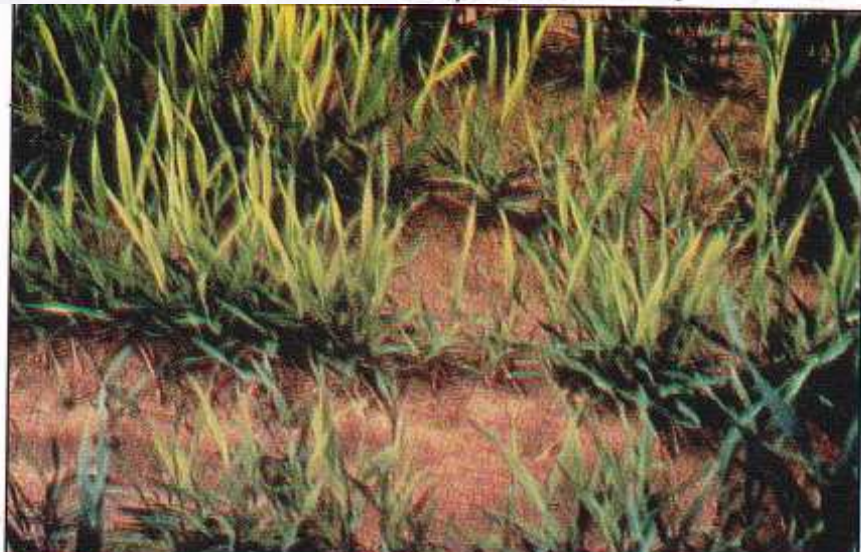
1. The fading of normal green colour of the young meristem followed by chlorosis.
2. Shoot growth is restricted.
3. In *Brassica*, the lamina is restricted and the leaves show cupping owing to the curling of leaves.
4. The older leaves become puckered inwardly with raised areas between veins.
5. The older leaves may develop orange or reddish tints and may be shed prematurely.
6. The stem and leaf petiole may become brittle and may collapse.
7. Reduced synthesis of proteins and oil.

**Management of sulphur or correction measures for S deficiency:**

1. Application of elemental sulphur or gypsum particularly on alkaline soils.
2. Application of sulphur containing fertilizers like single super phosphate (12-14% S), Magnesium sulphate (30 % S), Ammonium sulphate (24.2% S).
3. For correcting deficiencies of sulphur on the standing crop, foliar application of sulphate containing salts like Ferrous sulphate (32.8% S) and ferrous ammonium sulphate (16% S) etc.



Sulphur deficiency in maize



Sulphur deficiency in cotton

**Lecture 15: Micronutrients – sources – forms in soil solution – pools of micronutrients – predisposing factors for occurrence of micronutrient deficiencies in soil and plants**

The term micronutrient or trace element is quite often used interchangeably though most of the scientists prefer to use the term micronutrients to denote the elements which are essential for the plant but are required in small amounts. They are constituents of enzymes and co-enzymes. The micronutrients essential for green plants are iron, copper, manganese, boron, zinc, molybdenum and chlorine.

**Sources** : The main source of micronutrients in soil is the parent material . The micronutrient content of the soil entirely depends on the rocks from which the parent material is derived; soil forming processes, additions and removals.

Cobalt, Nickel and copper are preferentially attached to more basic rocks. Zinc has a greater tendency to be associated with sulphides.

Shales contain boron (20 – 200 ppm), cobalt (10 – 50 ppm), zinc (20 – 100 ppm), copper (20 – 200 ppm) and molybdenum (1 – 5ppm).

**Inorganic forms of micronutrients in soil**

Element	Major forms
Iron	Oxides, sulphides and silicates.
Manganese	Oxides, silicates and carbonates.
Zinc	Sulphides, carbonates and silicates
Copper	Sulphides, hydroxy carbonates and Oxides.
Boron	Sulphides, oxides and molybdates.
Chlorine	Chlorides
Cobalt	Silicates

**Sources of micronutrients and the forms of micronutrients in soil solution**

Major sources	Total content (ppm)	Forms in soil solutions
<b>Zinc</b> Sphalerite (ZnS) Smithsonite ZnCO <sub>3</sub>	7 to 1000	Zn <sup>2+</sup> , Zn (OH) <sup>+</sup>
<b>Copper</b> Chalcocite Cu <sub>2</sub> S Covellite CuS Malachite Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub> Azurite Cu <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>	1.8 to 960	Cu <sup>2+</sup> , Cu (OH) <sup>+</sup>

<b>Iron</b> Haematite $\text{Fe}_2\text{O}_3$ Goethite $\text{FeOOH}$ Magnetite $\text{Fe}_3\text{O}_4$ Pyrite $\text{FeS}_2$ Olivine $(\text{Mg Fe})_2 \text{SiO}_4$	4000 to 27300	$\text{Fe}^{2+}$ , $\text{F(OH)}^+$ , $\text{Fe(OH)}_2$
<b>Manganese</b> Pyrolusite $\text{MnO}_2$ Manganite $\text{MnO OH}$	37 to 115000	$\text{Mn}^{2+}$
<b>Boron</b> Borax $\text{Na}_2 \text{B}_4 \text{O}_7 \cdot 10 \text{H}_2\text{O}$ Tourmaline Na $(\text{Mg Fe})_3$ $\text{Al}_6(\text{BO}_3)_3 \text{Si}_6 \text{O}_{18} (\text{OH})_4$	2.8 – 630	$\text{H}_2\text{BO}_3^-$ , $\text{HBO}_3^-$ , $\text{BO}_3^{3-}$
<b>Molybdenum</b> Molybdenite $\text{MoS}_2$ Wulfenite $\text{PbMoO}_4$ Powellite $\text{CaMoO}_4$	Traces to 12	$\text{MO O}_4^-$ , $\text{HMO O}_4^-$
<b>Chlorine</b> Muriate of potash (KCl) Sodium chloride (NaCl)	20 to 1000	$\text{Cl}^-$

**Forms of micronutrients in soils :** Viets (1962) postulated five distinct pools of micronutrients in soils.

**Pool A:** It is the soil solution pool and contains water soluble ions. It is usually small or almost nonexistent for copper and zinc and very small for iron and manganese in well aerated and natural soils. Poor aeration, low redox potential and low pH can markedly increase manganese and iron but not copper and zinc.

**Pool B :** This comprises of the micronutrient cations exchangeable by weak electrolytes like  $\text{NH}_4^+$ . It is small for Cu and Zn.

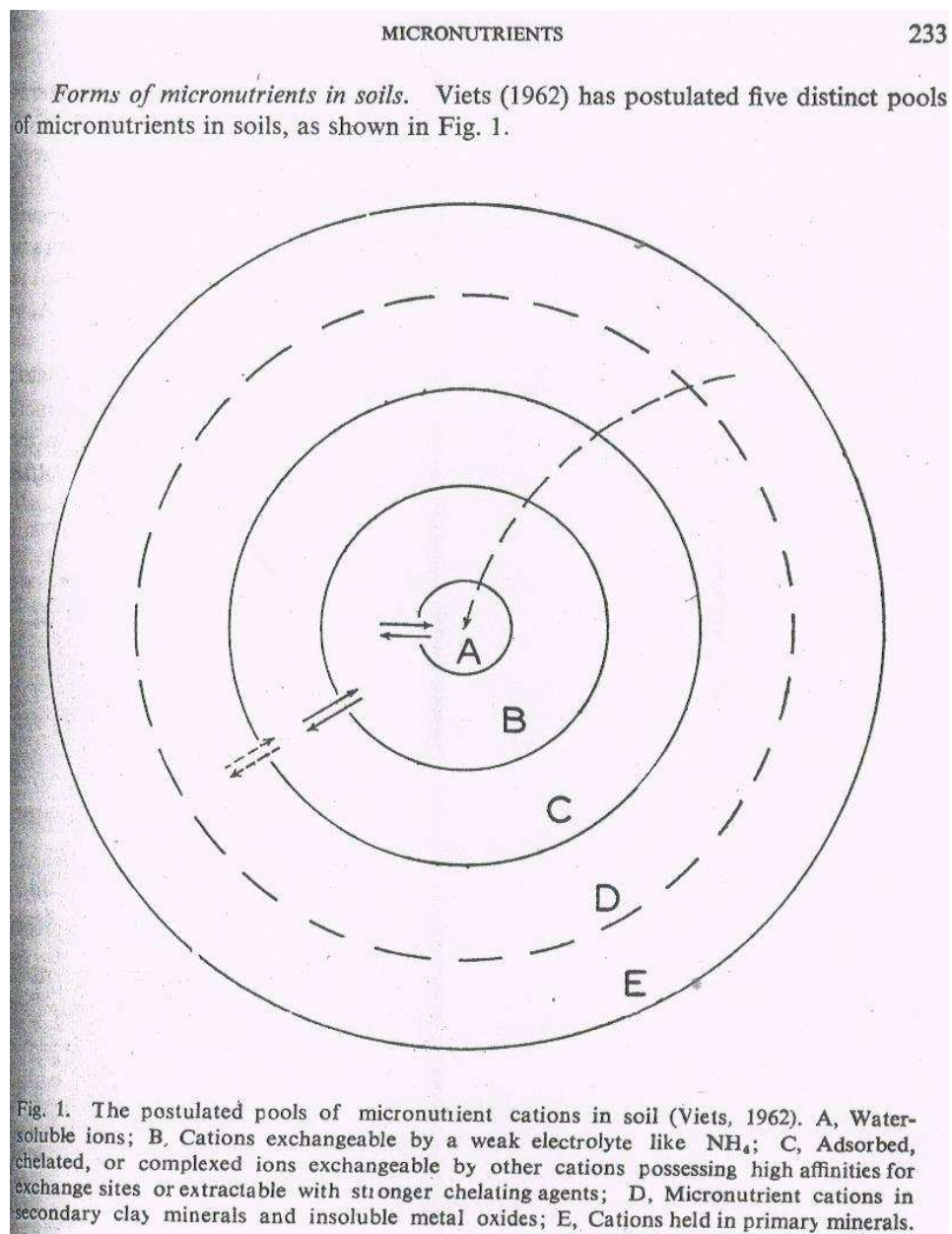
**Pool C :** Includes the adsorbed, chelated or complexed ions exchangeable by other cations possessing high affinities for exchange sites or extractable with strong chelating agents, like EDTA, pyrophosphates, ammonium acetate and carbon tetra chloride and dithizone and other chelating compound which can extract such complexes.

**Pool D:** Micronutrient cations in secondary clay minerals and insoluble metal oxide. It depends upon the content of clay and on the amount of its saturation with micronutrients.

**Pool E:** Comprises cations held in primary minerals. It is determined by the parent material and other geochemical considerations.

The micronutrient anions also occur in pools. For example chloride because of its negative adsorption, occurs mostly in pool A, but it also occur in pool E. Borates occur in pool E, as primary mineral tourmaline and in pool C probably as chelates with humus, but mostly it occurs in pool A in solution. Molybdates occur in all the pools, they can be replaced by oxalates, phosphates and hydroxyl ions. Availability of molybdenum is more in the alkaline pH.

**Organic form** : organic matter is an important secondary source of some trace element. They are held in complex combination with colloid complex.



### Predisposing factors for occurrence of micronutrient deficiencies in soil and plants

- i) **Parent material** : The soils whose parent material originally contain low amounts of micronutrients are most likely to show micronutrient deficiency under leaching and intensive cropping.
- ii) **Soil pH** : Acid soil conditions are most conducive for Mo deficiency. Similarly, high pH soils such as sodic soils show Zn, Fe, Mn and Cu deficiency. Over

liming of acid soils also causes deficiency of micronutrient cations. In acid sulfate soils micronutrient toxicity limits crop growth.

- iii) **Land leveling and shaping** : Land leveling and shaping removes the fertile top soil in which micronutrients are concentrated.
- iv) **High yielding varieties** : HYV require more nutrients depleting the nutrients from soil causing their deficiencies.
- v) **Imbalanced nutrient application** : High doses of macronutrient application induces micronutrient deficiencies.
- vi) **Soil conditions** : Water logged condition reduce the availability of Zn and Cu and increase availability of Fe and Mn.
- vii) **Organic matter**: Organic compounds like humic and fulvic acid form organo - metallic complexes held as insoluble complexes. But some organic ligands can keep micro nutrient cations as soluble chelates and those are plant available.
- viii) **CaCO<sub>3</sub>**: More CaCO<sub>3</sub> leads to less availability of Fe, Mn, Zn, and Cu; and increases Mo availability.
- ix) **Soil texture** : Boron is available in more amounts in coarse fraction, but fixed in fine textured soils.
- x) **Clay content** : Montmorillonite adsorbs more Zn and Cu.
- xi) **Fertilizers** : Fertilizers containing macronutrients when applied to soil induce the deficiency of micronutrients. Basic nitrate salts reduce iron availability.
- xii) **Interactions with macronutrients** : Interaction is defined as the influence of an element upon another in relation to crop growth. Negative interaction is observed between P and Zn leading to P induced Zn deficiency.

### **Lecture 16 : Zinc – content –forms in soils – critical limits in soils and plants – factors affecting availability of zinc – functions – deficiency symptoms and corrective measures**

Essentiality of zinc was established by Sommers and Lipmann.

**Content** : Average zinc content of mineral soils varies between 10 and 330 ppm. Depending upon the type of extractant used, the available zinc in Indian soils varies from less than 1 ppm to few ppm.

#### **Forms of zinc in soils**

1. Water soluble zinc
2. Exchangeable zinc
3. Adsorbed zinc on surface of clay, organic matter, carbonates

and oxide minerals

4. Organically complexed Zn
5. Zinc substituted for  $Mg^{2+}$  in the crystal lattices of clay minerals

#### Critical levels of zinc in soil

Type of extractant	Critical level of deficiency (ppm)
0.005M DTPA + 0.1 M TEA + 0.01 M $CaCl_2$ (pH 7.3)	0.5 – 1.0
0.1 N HCl	1 – 5
1 N $NH_4OAc$ (pH 4.6)	0.2 – 0.5
0.005 N HCl	1.0

In the soil 0.5 ppm of dithizone extractable zinc is considered lower critical limit, but for black soil 0.8 ppm may be considered as critical limit.

#### Critical Limits in plants

Zn content in plant	Rating
Below 20 ppm	Deficiency
20 - 150 ppm	Adequacy level
Above 400 ppm	Toxic

#### For rice plant

If Zn content is less than 5 ppm (is the critical limit) - very high response is obtained to the application of zinc

5 - 10 ppm – High response

10 - 15 ppm – Possible response

15 - 20 ppm – No response

#### Factors affecting availability of zinc in soils

**1. Soil pH :** Zinc is generally more available in acid soils than in alkali ones. Mostly pH induced deficiencies of zinc occur in pH range of 6 to 8. The critical pH for

availability of Zn is 5.5 to 6.5. In the alkaline range particularly above pH 7.85, zinc forms negatively charged ions called zincate ions, thus reducing the availability due to the formation of calcium zincate.

**2. Organic matter** : The presence of organic matter may promote the availability of zinc by complexing with zinc.

**3. CaCO<sub>3</sub>** : Zinc deficiencies are more common in calcareous soils. Zinc was adsorbed on CaCO<sub>3</sub> rendering it unavailable.

**4. Clay minerals** : Zinc adsorption on montmorillonite clays from ZnCl<sub>2</sub> solution occurs as Zn<sup>2+</sup>, Zn Cl<sup>+</sup> and Zn (OH)<sub>2</sub> ions.

**5. Phosphates** : Zn deficiency is very common in soils containing very high amounts of phosphates.

**Functions** : Plants absorb zinc as Zn<sup>2+</sup>. Zinc sufficient plants contain 27 to 150 ppm Zn in mature tissue.

- Zinc is a constituent of three enzymes viz., Alcoholic dehydrogenase, carbonic anhydrase, superoxide dismutase (SOD).
- Zn is involved in the synthesis of indole acetic acid, metabolism of gibberellic acid and synthesis of RNA.
- Because of preferential binding to sulphydryl group, zinc plays an important role in the stabilization and structural orientation of the membrane proteins.
- Zn influences translocation and transport of P in plants. Under Zn deficiency, excessive translocation of P occurs resulting in P toxicity.

### **Deficiency symptoms**

Zn deficiency symptoms show wide variation in different plant species. The common symptoms are chlorosis between the veins, reduction in the size of the young leaves, which are often clustered, bronzing, purple, violet, reddish brown or brown coloration of the foliage.

a) **Khaira disease of rice**: The first symptom of zinc deficiency appear in 3 - 4 week old seedlings when the young leaves develop reddish brown pigmentation. The pigmentation appears first in the middle of the leaves, then intensifies and spreads over the entire lamina. The affected tissue becomes papery and necrotic and under conditions of severe deficiency, the entire mass of leaves collapses and further growth of the plant is arrested.

**2) White bud of maize** : Soon after the emergence of seedlings, areas between the veins of old leaves become light yellow and develop white necrotic spots, which later develop dark brown necrotic areas that enlarge and coalesce, resulting in the necrosis (death of the entire leaf). Leaves that emerge and unroll subsequently appear yellow and white.



### 3) Mottle leaf or Frenching of citrus

4) Reduced leaf size and shortening of internodes in brinjal and mango called as **little leaf**.

#### Varietal susceptibility to Zn deficiency

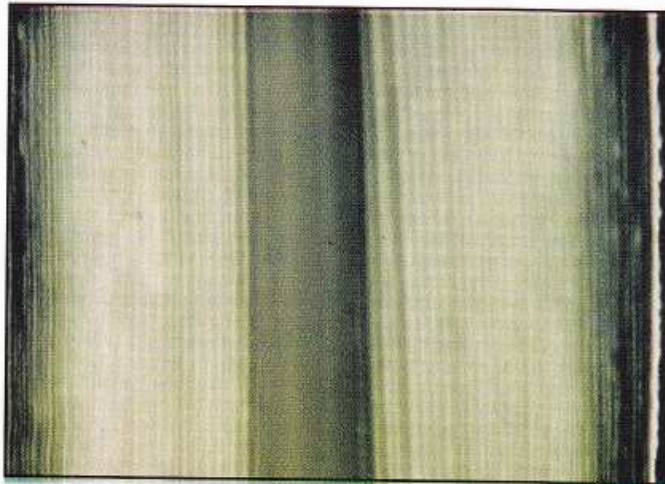
Crop	High susceptibility	Low susceptibility
Rice	Jaya,IR - 8, RP-4,14RP6,17	Cauvery, Tellahamsa, Ratna, Mahsuri
Black gram	T 27, J 9	
Greengram	T1,T2,T3,and Hydrid46	
Groundnut	-----	M 13
Maize	Ganga-5	Ganga -2 Ganga-3 Ganga -101

#### Corrective measures

1. Soil application of zinc sulphate (21% Zn) @ 50 kg ha<sup>-1</sup> once for three crops or years is effective and economic to overcome its deficiency. Zinc sulphate need to be applied on the surface and mixed in the soil through light harrowing.
2. In case of rice, zinc sulphate can be broadcast after final puddling before transplanting.
3. In case of orchards, zinc sulphate can be applied in the basin mixing into the soil.
4. When deficiency appears on standing crop, spraying of 0.2 % ZnSO<sub>4</sub> twice or thrice at weekly intervals or at 0.5 per cent concentration with lime.
5. In case of alkali soils, the dose of zinc sulphate for soil application needs to be doubled to 100 kg ha<sup>-1</sup>.
6. Zinc is also available as zinc chelate (mostly Zn - EDTA form). In case of highly alkaline soils (pH>8.0) zinc chelate is better source than zinc sulphate.
7. In calcareous soils, Zn- HEDTA (Hydroxy Ethylene Diamine Tetra Acetic acid) form is efficient for soil application.



A close-up of zinc deficiency symptom in rice leaf



Zinc deficiency in sugarcane



Zinc deficiency in cotton



Zn deficiency in Maize



**Lecture 17: Copper: and Iron - Content – Forms in soils – Critical limits in soils and plants. Factors affecting its availability –Functions – Deficiency symptoms – Corrective measures- Toxicity symptoms.**

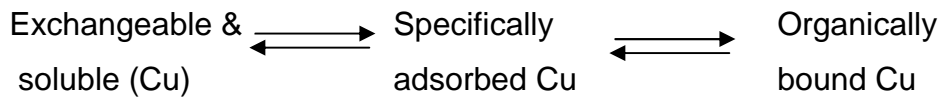
## **COPPER**

Copper concentration in earth's crust ranges from 55 to 70 ppm. Sulfides are the predominant minerals of copper in the earth's crust. Copper deficiency is often the first nutritional disorder to appear in plants grown on newly reclaimed acid

Histosols (organic soils) and this condition is referred to as 'reclamation disease'.

### Forms of copper

**1. In the soil solution :** Ionic and complexed Cu in the soil solution range from  $10^{-8}$  to  $10^{-6}$  (0.6 to 63 ppb). At soil pH below 6.9, it exists as  $\text{Cu}^{2+}$  and above 7.0 as  $\text{Cu}(\text{OH})_2$  and  $\text{Cu}(\text{OH})^+$



**. Occluded and co-precipitated Cu :** Cu is buried in various mineral structures or substituted for other ions or as an impurity in carbonate minerals or trapped in oxides of Fe and Al.

### 3. Adsorbed Cu

$\text{Cu}^{2+}$  is adsorbed to layers silicate clays, organic matter and oxides of either iron or Al.

### 4. Clay minerals and oxides

Cu is held tightly with Cu – O – Al or Cu – O – Fe surface bonds.

### 5. Organic matter

In many soils one fifth to one half of Cu occurs in organically bound form. Organic acid molecules solubilise Cu and make it available to plants. Humic and fulvic acids contain multiple binding sites for Cu, with  $\text{COO}^-$  playing a prominent role.

### Critical limits of copper in soils

Type of extractant	Critical level of deficiency (ppm)
0.005M DTPA + 0.1 M TEA + 0.01 M $\text{CaCl}_2$ (pH 7.3)	0.2 – 0.5
0.1 N HCl	1 – 3
1 N $\text{NH}_4\text{OAC}$ (pH 4.8)	0.2

### Critical limits of copper in plants

Deficiency < 4 ppm

Adequacy 5 – 10 ppm

Toxicity > 720 ppm

## **Factors affecting availability and movement of copper :**

**i) Texture :**  $\text{Cu}^{2+}$  in soil solution is usually lower in excessively leached podzolic sands and calcareous sands

### **ii) Soil pH**

Mobility of  $\text{Cu}^{2+}$  in soil solution increases with increasing pH due to

- a) increased generation of pH dependent sites on colloids
- b) reduced competition with  $\text{H}^+$ ,
- c) conversion of highly soluble  $\text{Cu}^{2+}$  to less soluble  $\text{Cu}(\text{OH})^+$  and  $\text{Cu}(\text{OH})_2$ .

### **iii) Interrelationship with other elements**

Excessive use of NPK fertilizers aggravate Cu deficiency. Acid forming fertilizer increase Cu deficiency due to increased abundance of  $\text{Al}^{3+}$  in soil. High concentration of P, Fe, Zn and Al depress absorption of Cu.

**iv) Incorporation of crop residue:** Incorporation of crop residues reduce Cu mobility due to

- i) Chemical reactions of  $\text{Cu}^{2+}$  and organic compound and other substances originating from decomposing organic residues.
- ii) Competition for available  $\text{Cu}^{2+}$  by microbes
- iii) Inhibition of root development and ability to absorb  $\text{Cu}^{2+}$ .

### **v) Plant factors**

Crops highly responsive to Cu are carrot, lettuce, spinach, table beets, citrus and onions.

Crops tolerant to low Cu are beans, peas, potatoes, lotus species.

## **Functions**

Similar to other micronutrient cations, copper is absorbed by plant roots as  $\text{Cu}^{2+}$ .

- Concentration of  $\text{Cu}^{2+}$  in copper sufficient plants is from 5 to 30 ppm and toxicity occurs between 20 and 100 ppm.
- $\text{Cu}^{2+}$  is a component of large number of proteins and enzymes like plastocyanin, SOD, Diamine oxidase, polyphenol oxidase, Ascorbate oxidase.
- Important in imparting disease resistance.
- Enhances fertility of male flowers.

## **Deficiency symptoms**

- Plants having a copper content of less than 5 ppm are regarded as Cu deficient.
- Male flowers' sterility, delayed flowering and senescence are the most important effects of Cu deficiency.
- Chlorosis of the younger shoot tissue, white tips, reclamation disease,

necrosis, leaf distortion and die back are characteristics of Cu deficiency. Necrosis of apical meristem results in elongation of shoot in cereals and auxiliary shoots in dicots.

- The shoot apex may cease to grow, resulting in the development of several auxiliary buns.
- In cereals symptoms appear as bleaching and withering of young leaves.
- Exanthema and dieback in citrus which manifests as dark brown spots on the leaves, terminal twigs and fruits.
- Yellowish brown blotches on the leaf particularly in legumes.
- Tip drying and bluish green leaf tips are the symptoms in rice.
- Empty glumes in wheat
- Total amino nitrogen accumulates in plants

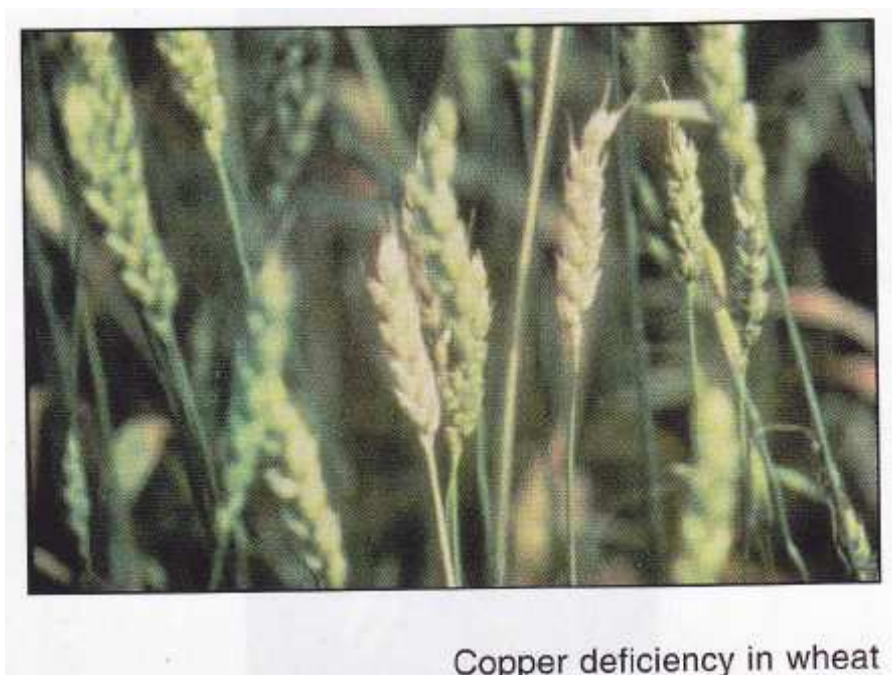
### Correction

Soil and foliar application are both effective. Soil application @ 1.0 – 5 kg /ha of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  (24 % Cu).

Foliar application of  $\text{CuSO}_4$  @ 0.2 % concentration.

Cu-EDTA contains 9-13 % Cu.

**Copper toxicity** occurs in acid soils and also due to the usage of sewage sludge, municipal composts, pig and poultry manures and mine waste and repeated use of copper containing pesticides like Bordeaux mixture,  $\text{CuSO}_4$ . Toxicity symptoms include reduced shoot vigor, poorly developed discolored root system and leaf chlorosis resembling iron deficiency.



## IRON

Iron comprises of about 5 % of the earth's crust and is the fourth most abundant element in the lithosphere. Normal concentration of total iron in soil varies from 0.7 to 5.5 %, average being 3.8 %. Haematite and goethite are the most common iron oxides in earth's crust. Available Fe in Indian soils ranges between 0.09 – 225 ppm.

### Forms in soil :

Iron is taken up by plants as  $\text{Fe}^{2+}$ . In soil solution, iron can be transported to root surface as iron chelates. The low solubility of compounds containing  $\text{Fe}^{3+}$  severely limits availability and uptake of  $\text{Fe}^{3+}$ . Diffusion and mass flow are found to be the two mechanisms responsible for the transfer of iron from soil to root surface. The organic substances capable of complexing or chelating iron originate as root exudates. The insoluble  $\text{Fe}^{3+}$  form predominates in well drained soils, while  $\text{Fe}^{2+}$  increases with a decrease in oxygen content or increase in water content of soil.

### Critical limits of iron in soils

Extractant	range
N $\text{NH}_4\text{OAC}$ (pH4.8)	2
0.005M DTPA + 0.1 M TEA + 0.01 M $\text{CaCl}_2$ (pH 7.3)	2.5 to 5.8 ppm

### Critical limits of iron in plants

50 ppm	Deficiency
50 ppm – 250 ppm	Adequacy level
Not known	toxic

### Factors affecting availability and movement of iron

- Iron imbalance** : Imbalance of ions such as Cu, Fe and Mn reduce the availability of iron.
- Soil pH** : Iron deficiency is most often encountered in high pH and calcareous soils in arid regions. For each unit increase in pH the activities of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  decrease by 1000 fold and 100 fold respectively.
- Excessive water and poor aeration** : Flooding and submergence of soils improve iron availability. Under reduced conditions, sulfides are released which combine with  $\text{Fe}^{2+}$  forming iron sulfide, otherwise if the soils are deficient in iron, the sulfides combine with  $\text{H}^+$  forming  $\text{H}_2\text{S}$  which causes 'akiochi'. The longer the period of submergence the greater is the amount of soluble plus exchangeable iron. Reduction of iron takes place at a redox potential of -130 mV.

4. **Organic matter** : Iron reduction was greatly accelerated by the addition of organic matter.
5. **Interrelationship with other nutrients** : High phosphorus levels usually aggravate iron deficiency.  $\text{NO}_3^-$  application lowers iron solubility. On the contrary,  $\text{NH}_4^+$ -N addition increases iron availability. Other metallic cationic micronutrients compete with iron for adsorption.
6. **Plants factors** : The ability of plants to absorb and translocate iron appears to be genetically controlled. Roots of iron efficient plants alter their environment to improve the availability and uptake of iron.

### Functions

Iron is taken up in  $\text{Fe}^{2+}$  form by plants. Its concentration in the range of 100 – 500 ppm in mature leaf tissue is regarded as sufficient for crop production. Variable valency of iron assigns it a role in biological redox systems.

- Iron is a constituent of two groups of proteins viz., a) Heme proteins containing Fe – porphyrin complex. eg., peroxidase, leghaemoglobin.
- Fe-S proteins in which Fe is coordinated with thiol group Eg : Ferredoxin.
- It activates a number of enzymes including aminolevulinic acid synthetase and Coproporphyrinogen oxidase.
- It plays an essential role in the nucleic acid metabolism.
- It is necessary for synthesis and maintenance of chlorophyll in plants.
- It is structural constituent of pigments in micro-organisms; the black pigment in *Aspergillus niger* contains iron)

### Deficiency :

- The critical limit of iron in plant is 30 ppm, the sufficiency range being 50 and 250 ppm.
- It has been established that  $\text{Fe}^{2+}$  content of the plant rather than total Fe content resolves Fe def.
- Deficiency of Fe results in interveinal chlorosis appearing first on the younger leaves with leaf margins and veins remaining green. Plants having less than 50 ppm of Fe are usually classified as iron deficient.
- In later stage burning of the chlorotic leaves start from the tips and margin, spread inwards.
- The chlorotic leaves may become white and the leaf tissues devoid of chlorophyll die.
- Leaves with large necrotic areas fall off and twigs defoliate.
- In mild cases, mottled pattern may be seen with primary and secondary veins retaining their green color.
- In graminaceous crops, chlorosis consists of alternate strips with green



veins and yellow interveinal tissues.

- In case of barley, maize and jowar, leaves show reddish brown spots on leaves away from the base on margin.
- Under conditions of severe deficiency, growth cessation occurs with the whole plant turning necrotic.

**Correction** : In general soil application of iron salts such as ferrous sulfate is not practiced because of their rapid oxidation to much less soluble ferric iron. Correction of Fe deficiency is generally done by foliar sprays.

### Sources

- ❖  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  : 19 % Fe
- ❖ Iron chelates NaFe EDTA : 5-14 % Fe
- ❖ Fe – EDDHA (Ethylene Diamine Dihydroxy acetic acid salt of Fe) for calcareous soils
- ❖ Fe DTPA (Diethylene Triamine Penta Acetate salt of Fe) for alkaline soils
- ❖ Fe HEDTA (Hydroxy Ethylene Diamine Tetra Acetate salt of Fe) for alkali soils
- ❖ Fe EDTA (Ethylene Diamine Tetra Acetate salt of Fe) for acid soils

### Iron chlorosis in paddy nurseries

Iron chlorosis is common in rice nurseries due to the prevailing irrigated dry condition in the soil which oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  thus reducing its availability. It can be corrected by spraying 1.0% of  $\text{Fe SO}_4$  or FAS (Ferrous Ammonium Sulphate) mixed with 0. 1% citric acid, twice or thrice at 4 to 5 days intervals or till chlorosis disappears.

### Iron Toxicity

Toxic situations occur primarily on acid soils (< pH 5.0) and where excess soluble iron salts have been applied as foliar sprays or soil amendments. Injury due to high soil iron concentration is not common under neutral or high pH soil but under conditions that are saturated, poorly draining, compacted or poorly aerated. Iron toxicity also occurs where zinc levels are low.

### Symptoms

One of the most common symptoms is necrosis or death of the leaves. Necrotic spots will appear on the leaves of plants suffering from iron toxicity. Other symptoms include dark green foliage, stunted top growth and root growth, as well as leaf bronzing—especially on rice—which causes dark brown to purple spots on the foliage. The symptoms developed in rice grown in acid soils are browning of roots and bronzing of leaves.

- Reduced manganese uptake by plants.

## Management

- Management of iron toxicity is mainly through cultural practices. One of the most effective ways to avoid and to treat iron toxicity is by adding lime to the topsoil to raise the soil pH.
- Providing proper aeration to the soil to oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  form.



Iron-deficient bed-planted rice field



Iron deficiency in maize



Iron deficiency in groundnut



**Fe deficiency**  
**in Rice**



Maize

Fe deficiency



Sorghum



Tobacco

Fe deficiency



Cucurbits



Jute

**Lecture 18: Manganese:- Content – Forms in soils – Critical limits in soils and plants. Factors affecting its availability – Functions – Deficiency symptoms – Corrective measures. Toxicity symptoms.**

Manganese concentration in the earth's crust averages 1000 ppm. It is an element that is widely distributed and at least traces of it are found in most rocks. Manganese when released through weathering of primary rocks will combine with  $O_2$ ,  $CO_3^{2-}$  and  $SiO_2$  to form a number of secondary minerals including pyrolusite ( $MnO_2$ ), manganite ( $MnOOH$ ) and hausmannite ( $Mn_3O_4$ )

The total manganese in Indian soils ranges between 92 to 11500 ppm but majority of soils contain 300 to 1600 ppm of Mn. Forms of manganese are usually expressed as water soluble  $Mn^{2+}$ , exchangeable  $Mn^{2+}$ , water soluble and insoluble organically bound manganese, easily reducible manganese and manganese oxides. These forms are in equilibrium with one another.

The principal ion species in solution is  $Mn^{2+}$  and its concentration decreases 100 fold for each unit increase in pH. Concentration of  $Mn^{2+}$  measured in the soil solution of acid and neutral soils have varied from less than 0.01 ppm to almost 13 ppm.

### **Factors affecting availability and movement of manganese**

**1. Effect of pH and carbonates** : Soil pH will also greatly influence  $Mn^{2+}$  availability and uptake. High pH favors the formation of less available complexes of Mn. Activity of the soil microorganisms which oxidise soluble manganese to unavailable forms reaches a maximum near pH 7.0

### **2. Excessive water and poor aeration**

Soil submergence and water logging lower the redox potential and increase the amount of soluble  $Mn^{2+}$  in soils.

**3. Organic matter** : Availability of Mn can be affected in several ways by the presence of organic materials. The low availability of manganese in basic soils high in organic matter is attributed to the formation of unavailable Mn compounds. It may also be held in unavailable organic complexes in peats or muck soils.

**4. Imbalance of metal ions** : High levels of Cu, Zn or Fe in the soil will impede manganese uptake by plants.

**5. Interrelationship with other nutrients** : Acid forming N fertilizers like  $(NH_4)_2SO_4$ ,  $NH_4Cl$ ,  $NH_4NO_3$  will enhance plant uptake of manganese. Neutral chloride containing salts like NaCl, KCl and  $CaCl_2$  have increased the manganese concentration of plants.

**6. Seasonal and climatic effects** : It is believed that wet winter weather favors the presence of  $Mn^{2+}$ , whereas warm dry summer encourages the formation of less available oxidized forms of manganese.

**7. Soil microorganisms** : Deficiencies of Mn is caused by soil micro organism oxidizing  $Mn^{2+}$  to  $Mn^{4+}$ .

**8. Plant factors** : Among cereals, Oats are sensitive to Mn deficiency. Low reductive capacity at the root due to root exudates may be the factor restricting uptake and translocation of manganese.

**Functions :** Healthy Mn sufficient mature plants contain 20 to 300 ppm of Mn. It is a transitional metal, present in plants in  $Mn^{2+}$  form. Because of its variable valence, Mn plays an important role in the photosynthesis and detoxification of superoxide free radicals.

- Mn is an integral component of the water splitting enzyme associated with photosystem II. Because of this role, Mn deficiency is associated with adverse effects on photosynthesis and  $O_2$  evolution.
- It is a constituent of superoxide dismutase (Mn-SOD). Mn SOD, present in mitochondria protects cells against the deleterious effects of superoxide free radicals.
- Mn has a role in TCA cycle in oxidative and non oxidative decarboxylation reactions with Nicotine Adenine Diamide (NAD)
  - Malic dehydrogenase enzyme catalyzing the reaction.  
 $Malate + NADP^+ \rightarrow pyruvate + NADPH + H^+ + CO_2$
  - Isocitrate dehydrogenase catalyzing the reaction.  
 $Isocitrate + NADP^+ \rightarrow Oxalosuccinate + NADPH$

**Deficiency symptoms :** Mn deficient plants contain less than 25 ppm Mn. Deficiency symptoms of Mn are more severe on middle leaves than on the younger ones because Mn is preferentially translocated to the younger tissues. Interveinal chlorosis in dicotyledons is characterized by the appearance of chlorotic and necrotic spots in the interveinal areas. In monocotyledonous plants like cereals, Mn deficiency symptoms appear as greenish grey spots, flecks and stripes more on the basal leaves (Grey speck). Chlorotic leaf areas soon become necrotic and turn red, reddish brown or brown. Symptoms of Mn deficiency are popularly known as

Grey speck of Oats

Speckled yellow of sugar beet

Marsh spot of peas

Pahala blight of sugar cane

Frenching of tung grass

**Critical limit of Mn in soil**

With 0.005 M DTPA + 0.1 M TEA + 0.01 M $CaCl_2$	:	2-4 ppm
1 N $NH_4OAc$	:	3-4 ppm
3 N $NH_4H_2PO_4$ and 0.1 N $H_3PO_4$	:	15-20 ppm

**Corrective measures**

Soil application of  $Mn SO_4 \cdot 3 H_2O$  (26-28 % Mn) @ 10-25 kg/ha and  
 $Mn SO_4 H_2O$  (30-32 % Mn) @ 10-25 kg/ha

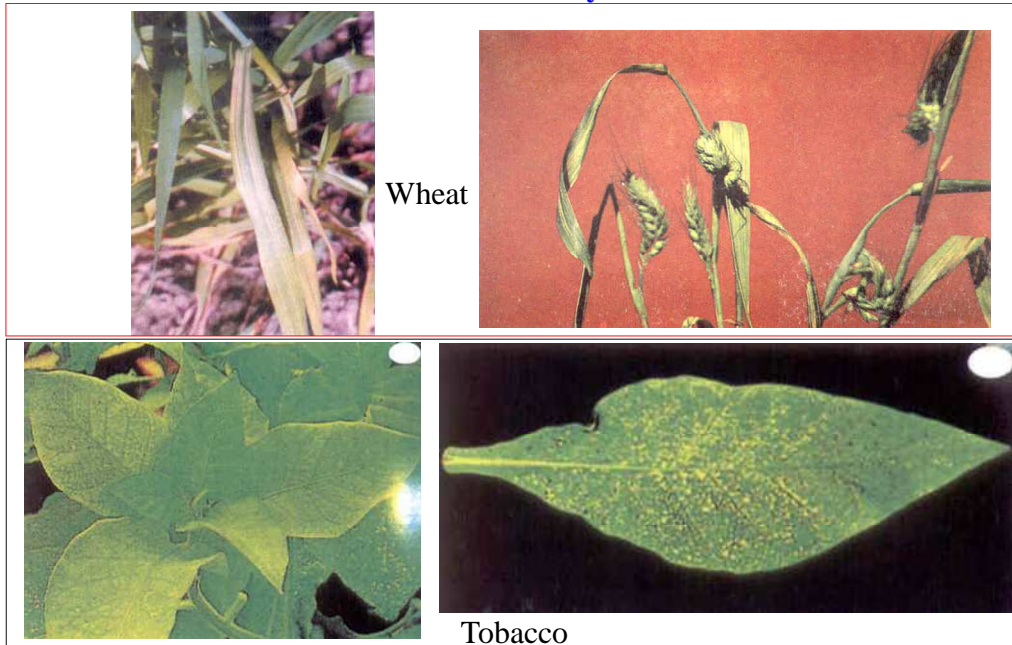
MnO<sub>2</sub> contains 55-65 % of Mn

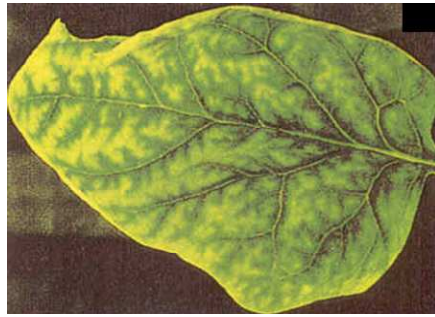
EDTA - Mn supplies 5-12 % of Mn



Manganese deficiency symptom in flag leaf of wheat

**Mn deficiency**





Spinach



Cucurbits



Lettuce



Cashew

Mn deficiency

**Lecture 19: Boron:- Content – forms in soil - Critical limits in soils and plants. Factors affecting its availability – Functions – Deficiency symptoms – Corrective measures.**

The total boron content in Indian soils has been found to vary from 7 to 630 ppm. It is observed that more boron is concentrated in the surface soils than in the sub surface.

**Factors affecting available boron content in Indian soils**

1. **Parent material** : The boron content of granite is 19.3, shales and lime stone 39.2, basalt 42.5 and of alluvium 42.3 ppm.
2. **Texture** : Boron content of the soil depends on the coarse sand fraction than on the clay content. Arid zone soils have higher boron content.
3. **Calcium carbonate** : Calcareous soils are supposed to contain more total boron than non calcareous soils.
4. **Effect of cultivation** : Cultivated soils have more boron than their counter part virgin soils due to its accumulation through irrigation water.
5. **Irrigation water** : Continuous use of irrigation water containing even a small amount of boron would build up the boron content of the soil.
6. **Soil pH** : This element generally becomes less available to plants with increasing pH greater than 6.3 to 6.5. Adsorption of boron by iron and aluminium hydroxides is maximum at pH of 8 to 9 and 7 respectively.
7. **Organic matter** : It is one of the main source of boron in acid soil.
8. **Soil moisture** : Boron deficiency is often associated with dry weather and low soil moisture conditions.
9. **Plant factors** : Crops most sensitive for boron deficiency are sugar beet and celery. High boron requiring crops are apple, asparagus, broccoli, cabbage, cauliflower. Boron needs of gramineae are low.



### **Soils where boron deficiency is common are**

- Soils low in boron such as those derived from acid igneous rocks.
- Highly leached acid soils like laterites and podsols.
- Light textured soils.
- Soils low in organic matter.
- Alkaline soils with high amount of free  $\text{CaCO}_3$ .

**Functions of boron** : Boron is absorbed by plants as boric acid. However, it can also be absorbed in anionic form viz., dihydrogen borate ( $\text{H}_2\text{BO}_3^-$ ), monohydrogen borate ( $\text{HBO}_3^{2-}$ ) under acidic conditions and borate  $\text{BO}_3^{3-}$  under high pH condition. Normal boron sufficiency in plants is between 10 and 200 ppm.

- Boron is neither a constituent of enzymes nor it activates any of the enzymes.
- Most important property of boron ( $\text{H}_3\text{BO}_3$ ) is to form stable complexes with organic compounds with cis - diol configuration.
- It is responsible for cell wall formation and stabilization, lignification and xylem differentiation. As a consequence, B deficiency causes changes in chemical composition and ultra structure of cell wall, accumulation of toxic phenols, inhibition of lignin synthesis and a decrease in the production of indole acetic acid (IAA). Decrease in IAA is responsible for the induction of Ca deficiency.
- It imparts drought tolerance to the crops.
- Plays a role in pollen germination and pollen tube growth.
- It facilitates ion uptake by way of increasing the activities of plasma membrane bound  $\text{H}^+$  - ATPase.
- It facilitates the transport of K in guard cells as well as stomatal opening.

### **Deficiency symptoms**

Plants having B concentration in the order of 5 to 30 ppm are suspected to be boron deficient. Critical deficiency range of B varies from 5 to 10 ppm in gramineae plants and 20 to 70 ppm in dicotyledons.

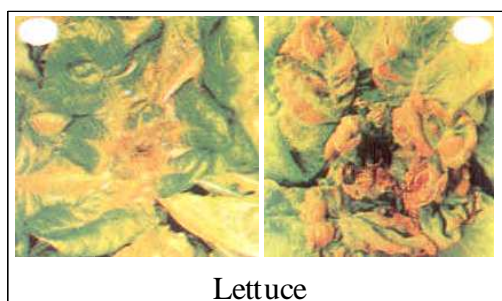
- Boron deficiency symptoms are conspicuous on the terminal buds or the youngest leaves; which become discolored and may die under acute deficiency.
- Internodes become shorter and give appearance of a bush or rosette.
- Increased diameter of stem and petiole gives rise to the typical cracked stem of celery.
- Specific names given to B deficiency in different crops are  
Heart rot of sugar beet.  
Browning or hollow stem of cauliflower.  
Top sickness of tobacco

Internal cork of apple.

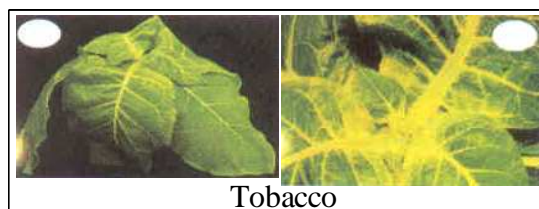
**Boron fertilizers** : Generally crops like alfalfa and other legumes, cruciferous plants such as cabbage, cauliflower and turnip and fruit trees such as apple, need boron fertilization.

- i) Foliar application of Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  which contains 10.6 % B) at 0.1 % concentration.
- ii) Calmonite  $\text{Ca}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  is suitable for sandy soils due to slow solubility.
- iii) Boric acid  $\text{H}_3\text{BO}_3$  contains 17 % B
- iv) Solubor :  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} + \text{Na}_2\text{B}_{10}\text{O}_6 \cdot 10\text{H}_2\text{O}$  contains 20-21 %

### B deficiency



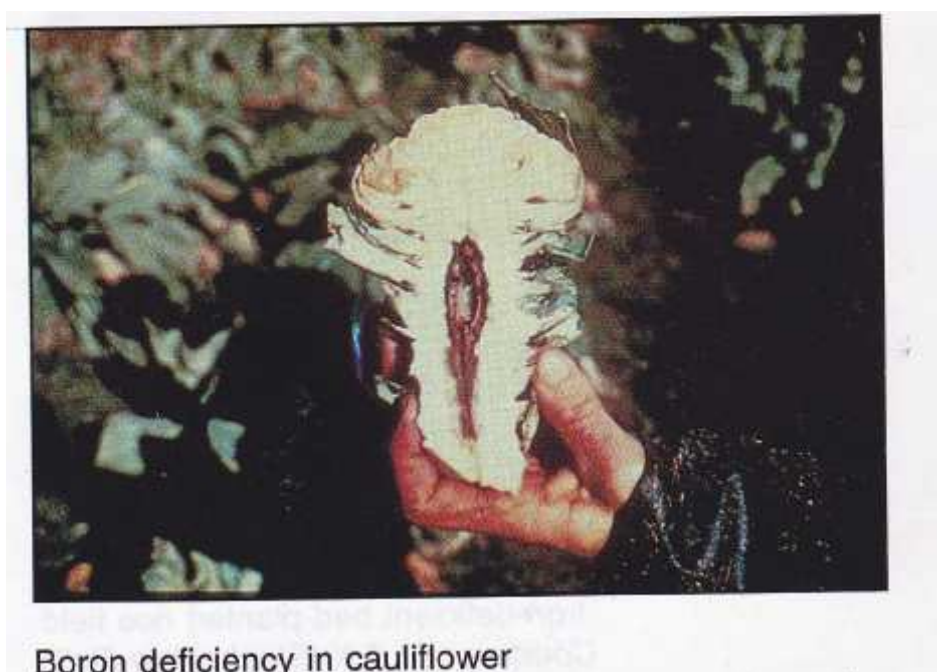
Lettuce



Tobacco



Groundnut



Boron deficiency in cauliflower

**Lecture 20: Molybdenum and Chlorine - Content – Forms in soils – Critical limits in soils and plants. Factors affecting their availability – Functions – Deficiency symptoms – Corrective measures. Toxicity symptoms.**

The essentiality of Mo was established by Arnon and Stout (1939). The total Mo content of most soils varies from 0.2 to 5.0 ppm with a mean of 2 ppm.

**Forms of molybdenum:** Molybdenum is generally present as

- i) Part of the crystal lattice of primary and secondary minerals.
- ii) Adsorbed as molybdate ( $\text{MoO}_4^{=}$ ) on clay or exchange complex.
- iii) Part of the organic matter.
- iv) Water soluble compounds.

The available Mo content of Indian soils extractable with ammonium oxalate at pH 3.3 (Tamm's extractant) varies from traces to 1.65 ppm.

<b>Soil type</b>	<b>Mo content</b>
Alluvial soils	1.0 to 5.5 ppm
Black cotton soils	0.6 to 11.80 ppm
Laterite soils	1.34 to 2.0 ppm.

**Critical limits in soil:**

Ammonium oxalate extractable molybdenum is 0.05 to 0.2 ppm. Soils with less than 0.15 ppm of available Mo respond to the application.

**Critical limits in plants:**

0.1 ppm	deficiency
0.5 ppm	adequacy level
Not known	toxic level.

**Factors affecting the availability of molybdenum**

1. **pH** : Availability of Mo is low in acid soils, with increase in pH the availability increases upto 7.9.
2. **Organic matter** : The role of organic matter in increasing the availability of Mo is due to the protection of molybdenum from anion adsorption.
3. **Calcium carbonate** : Liming of acid soils increases Mo availability. Liming makes the native molybdenum available by increasing its availability.
4. **Texture** : Mo availability increases with increase in clay content.

5. **Phosphate and sulphate fertilizers** : Phosphate and sulfate ions may compete with molybdate ions for exchange sites in the soil and plant.
6. **Manganese** : Mn induces Mo deficiency because of antagonism between them due to changes in pH.
7. **N and K fertilizers** : N fertilizers reduce the response to Mo in case of legumes due to reduced biological N fixation. However, a positive interaction exists between K and Mo.
8. **Oxides of iron and aluminium** : Availability of Mo may depend upon the molybdate adsorbed to free iron oxides.

### Functions

- Mo is a constituent of nitrate reductase.
- Activates several enzymes like catalase, peroxidase and polyphenol oxidase.
- Inhibits acid phosphatase.
- Required by N fixing organisms like Azotobacter, clostridium, Nostoc, Anabaena.
- Being a constituent of the Hydrogenase enzyme, helps in enzymatic transfer of  $e^-$  for reduction of  $N \equiv N$  bonds.
- Deficiency of Mo results in accumulation of nitrates.
- Involved in carbohydrate metabolism and sugar formation.

### Deficiency :

- ❖ In most plants with reticulate venation, the first effect of Mo deficiency appears as chlorotic mottling between the veins.
- ❖ Brassica crops are very susceptible to Mo deficiency, the symptoms developing in 3-4 week old plants.
- ❖ Tomato, lettuce, spinach, beet root and Brassica species especially cauliflower, broccoli and rape seed are very sensitive to restricted Mo supply.
- ❖ Legumes develop symptoms which resemble N deficiency.
- ❖ Grasses seem to have low Mo requirement.
- ❖ Citrus plants develop 'yellow spot'.
- ❖ Cauliflower exhibits whiptail (leaves get twisted elongated)
- ❖ Cabbage shows cupping, veins become purple, leaves become necrotic and malformed along the margins.
- ❖ Tomato – chlorotic mottling – old leaves roll inwards along leaf margin.
- ❖ In rice, slight chlorosis between the vein in the middle of the upper

and middle leaves and extending across the width.

### **Correction measures**

- Application of 400 -500 gm of sodium molybdate ( $\text{Na}_2\text{MoO}_4$ ) along with super phosphate to the soil.
- Mo deficiency can be corrected by spraying 0.1 % sodium molybdate.
- Liming of acid soils helps in correcting Mo deficiency.
- Seed treatment with Mo as sodium molybdate is very effective method of correcting the deficiency.

### **Toxicity**

- ✓ Plants develop brilliant tints of golden yellow or blue due to formation of granular complex between Mo and tannins.
- ✓ In potato, tomato and flax, Mo toxicity manifests as reddish or golden yellow color of the shoots.



Molybdenum deficiency in cauliflower

## **CHLORINE**

Chlorine has recently been established as one of the essential nutrients for plant growth. Wilting is considered the most general symptom of chlorine deficiency. It is present primarily in igneous and metamorphic rocks. In the soil,  $\text{Cl}^-$  occurs as  $\text{NaCl}$ ,  $\text{Ca Cl}_2$  and  $\text{Mg Cl}_2$ . The quantity of  $\text{Cl}^-$  in soil solution may range from 0.5 ppm or less to over 6000 ppm.

### **Behavior of Chlorine in soil**

Chloride is highly mobile in soils. Chloride ion will accumulate in ground water which will move into the root zone by capillarity.

## Functions

- Chlorine has been shown to be involved in the oxygen evolution in photosynthetic reactions.
- Claimed to be involved in photophosphorylation.
- In microorganisms, chlorine containing metabolically active compounds like chlorometabolites were found.
- In higher plants, chlorides largely accumulate in free ionic form in cell vacuoles.

## Deficiency symptoms

- Common symptoms are wilted appearance of the foliage and stumpy roots with laterals showing branching.
- Tomato leaves show chlorotic mottling, bronzing and tissue necrosis.

## Toxicity symptoms

Excess chloride will increase the osmotic pressure of soil water and lower the water availability to crops. Some plants are sensitive to chloride and develop leaf burn symptoms when chloride concentration reaches about 0.5%.leaves of tobacco and tomatoes thicken and begin to roll due to excess chloride.

The other toxicity symptoms include reduction in the number and size of leaves, burning or firing and scorching of the leaf tips or margins, bronzing, premature yellowing and abscission of leaves. Sometimes growth reduction may occur without any leaf symptom.

## High concentration of $\text{Cl}^-$ in soil is due to

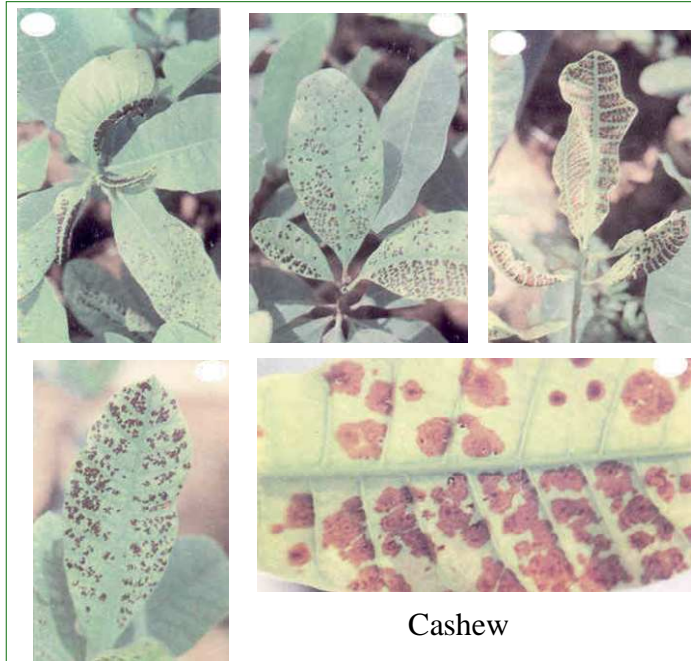
- High amount of chloride in irrigation water.
- Inadequate leaching of salts from the root zone of the plant.
- Inadequate permeability and drainage of the land.
- High water table and capillary movement of  $\text{Cl}^-$  into the root zone.

## The crops have been classified into different grades of tolerance to $\text{Cl}^-$ like

1. Low tolerance to  $\text{Cl}^-$  ( $< 20 \text{ me L}^{-1}$ ) eg : Peach, Avocado, Lemon, Beans, Apple
2. Medium tolerance ( $20\text{-}25 \text{ me L}^{-1}$ ), eg : Orange, Apricot.
3. High tolerance ( $> 25 \text{ me L}^{-1}$ ), eg : Tomato, Beet

Chloride is beneficial for some salt loving plants like beetroot, spinach, cabbage etc. There is a negative interaction between chloride and nitrate ( $\text{NO}_3^-$ ) ions in plants.

### Chloride toxicity



## Lecture 21: Soil pH – pH scale – Active and potential acidity-Factors affecting soil pH – Problems on soil pH.

### SOIL REACTION

The soil reaction describes the degree of acidity or alkalinity of a soil. Water molecule is very stable and dissociates as  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ . The ionization constant of water  $K_w = [\text{H}^+][\text{OH}^-]$  is called ionic product of water. The value of which is  $10^{-14}$  at  $22^\circ\text{C}$ .

$$\text{Log } 1/K_w = \text{log } 1/\text{H}^+ + \text{log } 1/\text{OH}^- = 14$$

Thus when the hydrogen ion concentration of an aqueous solution increases, its hydroxyl ion concentration decreased to maintain the ionic product of water.

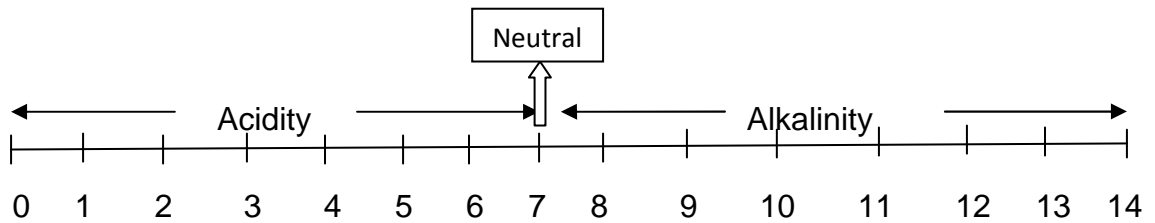
### pH and its method of Expression.

**pH** : Sorenson (1909) suggested the term pH (pH puissance dehydrogen or pouvoir hydrogen ), which means the power of hydrogen. pH is the negative logarithm of hydrogen ion activity.

$$\text{pH} = -\log_{10} (\text{H}^+)$$

pH 6.0 is ten times more acidic than pH 7.0

**pH scale**: The pH value represents the amount of free or active acidity and not the total acidity. That means it represents the intensity of acidity of a soil solution.



In this scale, the pH value ranges from 0 to 14 where pH value of 0 represents the highest limit of active acidity; pH '7' represents neutrality and pH '14' represents the highest degree of alkalinity or basicity.

### **Relationship between H<sup>+</sup> and OH<sup>-</sup>**

The reaction of a solution represents the degree of acidity or basicity caused by the relative concentration of active H<sup>+</sup> or OH<sup>-</sup> present in it. According to the theory of dissociation, the activity is due to dissociation or ionization of compounds into ions. Acidity is due to excess of H<sup>+</sup> ions over OH<sup>-</sup> and alkalinity is due to excess OH<sup>-</sup> over H<sup>+</sup>. A neutral reaction is produced by an equal concentration of H<sup>+</sup> and OH<sup>-</sup>.

### **Classification of soils based on pH:**

Based on the pH value of soil solution, the soils have been classified into the following categories.

<b><u>pH Range</u></b>	<b><u>Category (Rating)</u></b>
< 4.5	Extremely acidic
4.5 – 5.0	Very strongly acidic
5.1 – 5.5	Strongly acidic
5.6 – 6.0	Medium acidic
6.1 – 6.5	Slightly acidic
6.6 – 7.5	Neutral
7.5 – 7.8	Mildly alkaline
7.9 – 8.4	Moderately alkaline
8.5 – 9.0	Strongly alkaline
> 9.1	Very strongly alkaline

### **Classification of soil acidity**

Soil acidity is of three kinds, namely

- a) Active acidity
- b) Exchangeable acidity
- c) Reserve acidity



### **a) Active acidity**

The hydrogen ions in the soil solution contribute to active acidity which is measured in terms of pH of the soil. It may be defined as the acidity developed due to concentration of hydrogen and aluminium ions in the soil solution. This acidity is very small, implying that only a meagre amount of lime would be required to neutralise the active acidity. In spite of smaller concentration, active acidity is important since the plant root and microbes around the rhizosphere are influenced by it and because a dynamic equilibrium exists among active, exchangeable and reserve acidities in the soil.

### **b) Exchangeable acidity:**

In strongly acidic soils, the concentration of exchangeable aluminium and hydrogen ions contribute to exchangeable acidity. It may be defined as the acidity developed due to adsorbed hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) ions on soil colloids. However, this exchangeable hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) ions concentration is meagre in moderately acidic soils.

### **c) Reserve acidity:**

Aluminium hydroxyl ions; hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) present in the non exchangeable form with organic matter and clays account for the reserve acidity. It is measured by titrating a soil suspension up to a certain pH, normally about 8.0, the amount acidity in the soil being equivalent to the amount of NaOH used.

The potential acidity refers to the acidity caused by  $H^+$  held in different chemical combinations and those adsorbed on the surfaces of soil clay particles and organic colloids. The potential acidity is much higher as compared to active or exchangeable acidity requiring much larger dose of lime to neutralise than what is required for neutralising active acidity. Liming is always limited to neutralise the active acidity and part of the exchangeable acidity.

When an active acidity is neutralised progressively, the  $H^+$  from the potential sources are released into soil solution. The total acidity is the summation of active and exchangeable acidity.

**Factor affecting pH of soils:** Soil pH results from the interaction of soil minerals, ions in solution and cation exchange. High pH is caused by the reaction of water and the bases calcium, Magnesium and sodium to form hydroxyl ions. Low pH is due to the acidic constituents like  $Al^{3+}$  released by hydrolysis of primary minerals. The factors affecting soil pH are

1. **Nature of soil colloids:** When the soil colloids have  $H^+$  as adsorbed ion on the exchange complex, the soil reactions becomes acidic.
2. **Percentage base saturation (PBS) and kind of adsorbed base:** Soils having low PBS show acidic reaction. Sodium saturated soils have much higher pH values than Ca and Mg saturated soils.
3. **Soil solution:** Under field conditions, the concentration of salts varies with the moisture content of the soil. More dilute the solution of a base unsaturated soil; more is the number of hydrogen ions that dissociate into the soil solution. The pH lowers with increase in concentration of  $CO_2$  of soil solution due to the formation of carbonic acid.
4. **Climate:** In general, soils formed in the areas of high rainfall are acidic, while those formed in areas of low rainfall are alkaline.
5. **Soil management:** As a result of constant cultivation basic cations are lost from the soil through crop removal and leaching making the soil acidic. Acidic fertilizers like ammonium sulphate make the soil acidic, while basic fertilizers like  $NaNO_3$  make the soil alkaline.
6. **Oxidation – Reduction state of soil** under anaerobic or reduced conditions as in water logged soils the ferric and manganic ions are reduced to ferrous ( $Fe^{2+}$ ) and manganous ( $Mn^{2+}$ ) states, thus increasing pH, under such conditions sulphides are converted to  $SO_4^{=}$  thus lowering the pH upon formation of acid.

### Problems on soil pH

#### Hints

1. When  $H^+ = 10^{-X}$ ,  $pH = X$  and  $pOH = 14 - X$
2. When  $OH^{-1} = 10^{-Y}$ ,  $pOH = Y$  and  $pH = 14 - Y$
3. If pH of a solution is a,  $H^+ = 10^{-a}$  and  $OH^- = 10^{a-14}$

1. pH of a solution is 5. Find out the  $OH^-$  concentration.

⇒ When  $pH = 5$ , the  $pOH$  will be  $10 - 5 = 9$

When  $pOH$  is 9; the hydroxyl ion concentration is  $10^{-pOH}$   
i.e.,  $10^{-9}$  moles  $L^{-1}$

The  $OH^-$  concentration of the solution is  $10^{-9}$  moles  $L^{-1}$

2. What is the pH of a solution having hydrogen ion concentration of

$4.2 \times 10^{-6}$  moles  $L^{-1}$

$$\begin{aligned}
 \Rightarrow \quad \text{pH} &= -\log_{10}[\text{H}^+] \\
 &= -\log_{10}[4.2 \times 10^{-6}] \\
 &= -0.62 - [-6] \\
 &= -0.62 + 6 \\
 &= 5.38
 \end{aligned}$$

3. What is the hydrogen ion concentration of a solution having pH of 4.38?

$$\begin{aligned}
 \Rightarrow \text{Hydrogen ion concentration } [\text{H}^+] &= 10^{-\text{pH}} = 10^{-4.38} \\
 &= 10^{-5} \times 10^{0.62} = 4.2 \times 10^{-5} \text{ moles L}^{-1}
 \end{aligned}$$

The hydrogen ion concentration of the solution is  $4.2 \times 10^{-5} \text{ moles L}^{-1}$

4. Find out the pH of 0.01 M  $\text{H}_2\text{SO}_4$  solution.

$$\begin{aligned}
 \Rightarrow \text{H}^+ \text{ concentration of the solution} &= \text{Normality of acid} = 0.002 \\
 &= 3 - \log 2 = 3 - 0.3010 \\
 &= 2.699 = 2.7
 \end{aligned}$$

The pH of 0.01 M  $\text{H}_2\text{SO}_4$  solution is 2.7.

5. Find the pH of 0.0001 M KOH.

$$\begin{aligned}
 \Rightarrow 0.0001 \text{ M KOH} &= 0.0001 \text{ N KOH} \\
 \text{OH}^- &= \text{Normality of the base} = 0.0001 \text{ N} \\
 \text{pOH} &= -\log_{10}[0.0001] = -\log_{10}[1 \times 10^{-4}] \\
 &= 4 - \log 1 = 4.0 \\
 \text{pH} &= 14 - \text{pOH} = 14 - 4 = 10
 \end{aligned}$$

The pH of 0.0001 M KOH is 4.0.

## **Lecture 22: Importance of soil pH on nutrient availability of plant nutrients – Buffering capacity of soils.**

**Influence of soil reaction on the availability of plant nutrients :** Soil reaction is the important factor which governs the availability of various nutrients by influencing the soil properties like physical, chemical and biological etc.

**Soil reaction and microbial activity:** The activity of microbes is influenced by the variations in soil pH.

- Bacteria and actinomycetes prefer near neutral to slightly alkaline reaction (pH 6.5 – 8.0).
- Fungi work satisfactorily at all pH ranges. They face a large competition at higher pH values with bacteria and actinomycetes. Hence they grow better in acidic reaction of pH between 4.5 to 6.5.

**Nitrogen:** Plants absorb nitrogen in the form of  $\text{NO}^{-3}$  whose formation depends on the ability of nitrifying bacteria. The microbes responsible for nitrification are active when the soil pH is between 6.5 to 7.5. Nitrogen fixing bacteria also fail to function below a soil pH of 6.0.

**Phosphorus :** Phosphorus availability is high when soil pH is between 6.0 to 7.5.

At pH values less than 5.0, soluble phosphates are fixed as complex and insoluble compounds of Fe, Al and Mn.

At pH values of more than 7.5, complex insoluble calcium phosphates like apatites. Excess calcium also hinders the phosphorus absorption and utilisation by the plants.

**Calcium and magnesium and other basic cations** like potassium become deficient due to their leaching.

**Sulphur:** The bacteria responsible for the oxidation of sulphides to sulphates can function satisfactorily at all pH values.

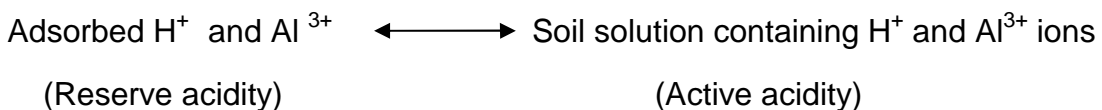
**Micronutrients :** The availability of micronutrients like zinc, iron, copper and manganese are more in the acidic range. Under acidic conditions as in the humid regions because of high rainfall due to leaching of bases, aluminium, iron and micro nutrients become toxic. They are more soluble at low pH. At a soil pH of less than 5.5, aluminium starts to leave the structure of silicate clays. High levels of soluble aluminium are injurious to crops. Aluminium toxicity increases water stress during dry period.

## Buffering capacity of soils

Buffering refers to the resistance to a change in pH. Buffering in soils is their resistance against any change in the concentration of hydrogen or other cations in the soil solution. This power to resist a change in pH is due to the Buffering action. In soils, the clay and humus act as buffer systems. Soil exchange complex has reserve and active acidity and there exists equilibrium between these two. If the active acidity is neutralized by the addition of lime, the reserve acidity will release exchangeable  $H^+$  into the soil solution to maintain the equilibrium and resists any change in soil reaction. The buffering capacity is greater in clay soils than in sandy soils. The colloidal complex behaves in a way similar to a mixture of weak acid and their salts thus acting as a buffer. In soils, the buffering action may be due to one or several of the following buffering agents

- Carbonates, bicarbonates and phosphates present in the soil.
- Colloidal complex with associated cations.
- Organic acids being released continuously in the soil act as weak acids.
- $H^+$  released from the soil exchange complex provides the reserve acidity.

Soils are a mixture of acidoids and basoids and hence act as amphoteric. The basis of buffering capacity lies in the adsorbed cations (both acidic and basic). There is equilibrium between the adsorbed hydrogen and aluminium ions and  $H^+$  in the soil solution. This can be represented as follows



## Factors affecting buffering capacity of soils

Buffering capacity of the soil depends on the factors like amount and kind of clay, organic matter content, cation exchange capacity, carbonates, bicarbonates, phosphate content and organic acids.

1. Amount of soil colloids: Soils containing large amounts of clay and organic matter are said to be highly buffered and require large amounts of lime for affecting a certain change in pH than an acid soil containing smaller amounts of clay and organic matter.
2. Cation exchange capacity: Keeping all the factors constant, buffering capacity of the soil increased with increase in cation exchange capacity.
3. Soils having higher amounts of calcium carbonate, organic acids and phosphates show higher buffering capacity.
4. Soils containing large amounts of 1:1 type clays are generally less strongly buffered than soils in which the predominant clay minerals are 2:1 type.

5. The degree of buffering is highest between the soil pH of 4.5 and 6.0 and drops off below and above this range.

### **Importance of buffering in agriculture**

The importance buffering in soils is mainly two folds

- i) The stabilization of soil pH
- ii) Calculations of amount of amendment necessary to affect a certain change in soil reaction.

An abrupt change in pH causes a radical modification in soil environment and if it fluctuates too widely, the plants and microorganisms would suffer seriously. Changes in soil reaction not only have a direct influence on the plants but also exerts an indirect influence on soil environment by creating sudden changes in the availability of nutrients. Deficiencies of certain plant nutrients and excess of others in toxic amounts would seriously upset the nutritional balance in the soil.

The amounts of amendments necessary to affect a given alteration in soil reaction also relate to the effectiveness of pH stabilization. The greater the buffering capacity of the soil, the larger must be the amounts of amendments to affect a given change in pH.

### **Lecture 23: Problem soils: Definition – Classification - Acid, Saline, Saline Sodic, Sodic and Calcareous soils - characteristics – Formation and Nutrient availability in problem soils**

Problem soils are the soils whose productivity is lowered due to inherent unfavourable soil conditions viz., salt content and soil reaction.

In India, the extent of salt affected soils increased enormously to 10 M ha. Soil salinity is one of the major problems restricting crop production in the arid and semi arid regions of the world.

#### **Units of expression for salinity and alkalinity :**

Salinity is measured in terms of electrical conductivity (EC) which is the ability of salt solution to conduct electricity. It is expressed in terms of deci Siemens per metre (dS m<sup>-1</sup>).

$$1 \text{ dS m}^{-1} = 1 \text{ mmho cm}^{-1} = 1000 \text{ } \mu\text{mho cm}^{-1}$$

Sodium is involved in alkalinity. It is expressed in terms of exchangeable sodium percentage (ESP), which is the degree of saturation of exchangeable complex with sodium; and sodium adsorption ratio (SAR) which is a comparative ratio of Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>.

$$\text{ESP} = \frac{\text{Exchangeable Na [c mol (p}^+) \text{ kg}^{-1}\text{]}}{\text{CEC [c mol (p}^+) \text{ kg}^{-1}\text{]}} \times 100$$

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

Salinity Class	EC (dSm <sup>-1</sup> )
Salinity effect negligible	: 0 – 2
Yield of very sensitive crops restricted	: 2 - 4
Yield of many crops restricted	: 4 - 8
Only tolerant crop yields are satisfactory	: 8 – 16
Yield of a few tolerant crops are satisfactory	: > 16
Critical value for EC	: 4

**Characteristics of saline soils** : Saline soils contain neutral soluble salts of chlorides and sulfates of sodium, calcium and magnesium. The electrical conductivity of saturated extract of the soil is more than 4 dS m<sup>-1</sup>. ESP is less than 15 and pH is less than 8.5. Because of the presence of excess salts and low amount of Na<sup>+</sup>, these soils are in a flocculated state and their permeability is higher than alkali soils. Their physical condition is good and water can pass through them. These soils have a white crust of salts on their surface. Salinisation refers to the accumulation of neutral soluble salts in soils.

**Characteristics of saline - Alkali soils**: These soils have both soluble salts and exchangeable sodium. The soil reaction becomes strongly alkaline because of hydrolysis of exchangeable sodium. The physical condition of the soil is deteriorated. The EC of saturated extract is more than 4 dS m<sup>-1</sup>, ESP is more than 15 and pH is around 8.5. They are transitional soils that they may be converted into saline or into sodic soils.

**Characteristics of alkali or sodic soils**: Most of the Na<sup>+</sup> is in exchangeable form. EC of saturated extract is less than 4 dS m<sup>-1</sup>. ESP is more than 15 and pH more than 8.5. Such soils are not in a good physical condition and the surface of these soils is sometimes black due to dispersion of organic matter and humus. Such soils if ploughed when wet, turn into slick furrow slice referred to as slick spots.

**Comparison of characteristics of salt affected soils**

<b>Characteristic</b>	<b>Saline soil</b>	<b>Alkali soil</b>	<b>Saline – alkali</b>
Content in soil	Excess soluble salts of calcium, magnesium and sodium	Presence of excess exchangeable sodium on the exchange complex	These are transition soils. They contain sodium saturation and excess soluble salts
Exchangeable calcium/sodium	Exchangeable calcium	Exchangeable sodium	---
Colour	White	Black	---
Dominant salts	Sulphates, chlorides and nitrates of calcium, magnesium and sodium	Sodium carbonate and bicarbonate	
SAR	<13	>13	>13
ESP	<15	>15	>15
Soil pH	~ 8.5	>8.5	~ 8.5
Physical condition of the soil	Flocculated, permeable to water and air	Deflocculated, permeability to water and air is poor.	Flocculated or deflocculated
Morphological character	White crust on the surface	High amounts of exchangeable sodium leads to dispersion of the clay, which together with humus may form dark colored soil	---
Organic matter content	Slightly less than normal soil	Very low	Variable
Total soluble salt content	>0.1 %	<0.1%	>0.1%
EC	> 4 dS m <sup>-1</sup>	< 4 dS m <sup>-1</sup>	> 4 dS m <sup>-1</sup>



### Rice in salt affected soils



Sodic soil

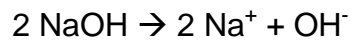
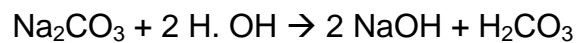


Saline soil



### Formation of saline and alkali soils

1. **Weathering of rocks and minerals** : The soluble salts released during weathering leach down with rain water, but again move upward due to high temperature and accumulate as white crust forming a saline soil.
2. **Hydrolysis of sodium saturated exchange complex in the formation of an alkali soil** : Sodium carbonate undergoes hydrolysis to form sodium hydroxide, which dissociates to increase concentration of hydroxyl ions in soil solution.



Formation of  $\text{OH}^-$  results in an increase in pH.

3. **Salty underground water** : If the ground water is salty, the salts move upward with water and get deposited when water evaporates.
4. **Arid and semi arid climate** : The low rainfall is not sufficient to leach down the soluble weathered products and hence the salts accumulate in the soil.
5. **Quality of irrigation water** : If water contains excessive amounts of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{BO}_3^{3-}$  their continuous application develops salt affected soils. Besides this, a rise in the groundwater level, poor drainage which prevents leaching of salts and continuous use of bad quality irrigation water lead to the secondary salinisation and alkalisation.
6. **Use of basic fertilizer** : Basic fertilizers like  $\text{NaNO}_3$  and basic slag may develop soil alkalinity.

### Nutrient availability in saline and alkali soils

- ❖ Presence of excessive quantities of salts in saline soils result in an increase in osmotic pressure of soil solution (osmotic effect). This results in the movement of water from plant cell into the more concentrated soil solution.

This inhibits uptake of water and nutrients into the plant cell.

- ❖ Alkali soils adversely affect plant growth in many ways.
  - i. Such soils are in poor physical condition. The presence of high  $\text{Na}^+$  keeps the soil particles suspended.
  - ii. Soils contain excessive amounts of boron, bicarbonates and sodium.
  - iii. Active sodium ions interfere with plant nutrition and metabolism. It adversely affects  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  nutrition of plants.
  - iv. Due to high pH, availability of phosphorus and micronutrients becomes low; the soils encounter Fe, Cu, Zn and Mn deficiencies.
  - v. Plant suffers oxygen deficiency as soil structure is adversely affected due to the dominance of sodium.

**Acid soils** : Soils with  $\text{pH} < 5.5$  have been defined as acid soils by USDA. However, soils with  $\text{pH} < 6.5$  can also be categorized as acidic soils. Out of 157 M ha of cultivable land in India, 49 M ha are acidic, of which 26 M ha land is having a pH of less than 5.6 and the rest 23 M ha of land is having a soil pH in the range of 5.6 to 6.5.

**Formation** : The leaching of bases is the prerequisite for the formation of acid soils which are dominantly found to occur in regions with high rainfall. The major process involved in the formation of acid soils is podzolisation in areas of temperate climate; laterization of varying degrees, marshy conditions with significant amounts of partly decomposed organic matter. Acid soils occur in almost all major soil groups except the black soils (Vertisol). Acid soils occur in Assam, Manipur and Tripura, peaty and marshy soils of West Bengal and Kerala. Very low pH (4 or less) is an indication of the presence of sulfuric acid as in the cat clays in Kerala, the soils are referred to as acid sulfate soils.

### **Characteristics**

#### **Nutrient availability**

Low pH, high exchangeable  $\text{H}^+$  and  $\text{Al}^{3+}$ , low CEC and high base unsaturation are the characteristics of acid soils. Adverse effect is due to toxic concentration of Al, Mn and Fe and deficiency of Ca and Mg. Acid soils are low in available P and have high P fixing capacity. Available micronutrient status is adequate except molybdenum. The population of bacteria and actinomycetes is lower and those of fungi higher.

#### **Calcareous soils**

Calcareous soils are soils in which a high amount of calcium carbonate dominates the problems related to agricultural land use. They are characterized by the presence of calcium carbonate in the parent material and by a calcic horizon, a layer of secondary accumulation of carbonates (usually Ca or Mg) in excess of 15% calcium carbonate equivalent and at least 5% more carbonate than an

underlying layer.

These soils are formed under arid or semi-arid climatic conditions when the carbonate concentration in the soil solution remains high. In some soils the calcium carbonate deposits are concentrated into layers that may be very hard and impermeable to water (also called "Caliche"). These caliche layers are formed by insufficient rainfall (at nearly constant annual rates) leaching the salts to a particular depth in the soil at which the carbonates precipitate. They are also formed by salts moving upward from a water table (caused by irrigation) and precipitating near the top of the capillary fringe.

The total extent of calcisols is estimated at 800 million hectares worldwide mainly concentrated in arid or Mediterranean climates.

The land use of calcareous soils is highly variable: it ranges from non-used wastelands (deserts) to intensively cultivated irrigated areas.

### **Main production constraints**

Calcareous soils develop in regions of low rainfall and must be irrigated to be productive. Therefore one of the main production constraints is the availability of water for irrigation. The quality of the irrigation water is of crucial importance for sustainable agricultural production on calcareous soils. Crusting of the surface may affect not only infiltration and soil aeration but also the emergence of seedlings. Cemented conditions of the subsoil layers may hamper root development and water movement characteristics. Calcareous soils tend to be low in organic matter and available nitrogen. The high pH level results in unavailability of phosphate (formation of unavailable calcium phosphates as apatite) and sometimes reduced micronutrient availability e.g. zinc and iron (lime induced chlorosis). There may be also problems of potassium and magnesium nutrition as a result of the nutritional imbalance between these elements and calcium.

### **Management:**

- Addition of copious amounts of organic matter which release organic acids during decomposition for solubilising  $\text{CaCO}_3$  and to release the fixed P.
- Regular application of  $\text{ZnSO}_4$  @ 25 – 50 kg ha<sup>-1</sup>
- Application of phosphatic fertilisers by placement method to overcome the problem of P fixation.
- Foliar application of micronutrients in their respective sulphate form.

**Lecture 24: Reclamation of problematic soils – Mechanical, Chemical and Biological methods. Lime requirement – Different liming materials - Organic amendments – FYM, compost, press mud, green manures - Green leaf manures, problems associated with over liming. Gypsum requirement – Classification of crops based on their tolerance to salts**

✓ **Reclamation of salt affected soils :**

Before proceeding for reclamation of salt affected soils, the following points should be considered and available information should be collected on

- i) Nature and extent of salinity.
- ii) Quality of irrigation water with respect to sodium, boron and bicarbonate and salt content.
- iii) Drainage conditions.
- iv) Nature and distribution of salts in the root zone.
- v) Calcium carbonate content of the soil.

**I. Mechanical amelioration of salt affected soils**

The commonly followed physical or mechanical method of amelioration of salt affected soils include deep ploughing, sub soiling, sanding, profile inversion and scraping.

- The first two methods break the impermeable layer, hard pan or cemented sub soil layer existing at various depths in soil profile to improve the internal drainage of the soil and to facilitate the transportation of salts dissolved in water to deeper layers.
- Incorporation of sand in salt affected soils is done to bring about
- permanent changes in texture, increase permeability and to improve water relations in the root zone.
- Profile inversion can be adopted only under conditions where surface soil is good but the soil below is sodic or saline.
- Scraping is adopted to remove the few centimeters of salt encrustation.

**II. Chemical amelioration**

**A. Reclamation of a saline soil**

**Leaching** : The main objective in reclamation of these soils is to leach the salts below the root zone (hence, drainage system should be installed if necessary). Leaching requirement (LR) has been defined as that fraction of water that must be leached through the root zone to control soil salinity at a specified level.

This is achieved by flooding and draining. To make it effective, bunds are raised around plots prepared and water is applied depending on their water

requirement to leach salts.

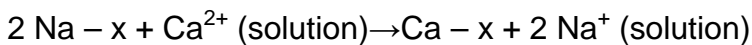
$$\text{Leaching requirement (LR)} = \frac{\text{EC}_{\text{aw}}}{\text{EC}_{\text{dw}}}$$

EC<sub>aw</sub> is the EC of applied water.

EC<sub>dw</sub> is the EC of drainage water.

In saline soils with high water table artificial drainage should be practiced (Drainage is the removal of excess water from the soil).

**B. Reclamation of alkali (Sodic) soil :** Reclamation of sodic soils involve two stages. First, the replacement of sodium by another cation and second, the leaching of the desorbed sodium salts out of the root zone. This may be done with gypsum (CaSO<sub>4</sub>. 2 H<sub>2</sub>O) and leaching with good quality irrigation water.



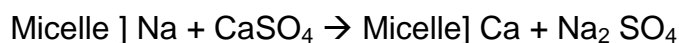
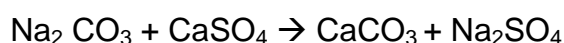
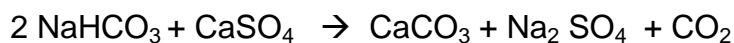
Where x is the soil exchange complex

**Gypsum requirement :** Gypsum requirement is the calculated amount of gypsum necessary to add to reclaim the soil. It is the amount of gypsum required to be added to a sodic soil to lower its ESP (Exchangeable Sodium Percentage) to a desired level.

$$\text{Gypsum requirement} = \frac{\text{ESP (initial)} - \text{ESP (final)} \times \text{CEC}}{\text{me of Ca/ 100 soil} \quad \quad \quad 100}$$

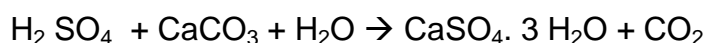
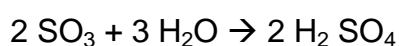
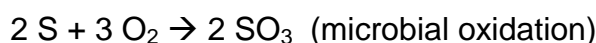
ESP (Initial) is the ESP of soil before application of gypsum

ESP (Final) is the ESP of soil after bringing it to desired level.



This should be followed by application of good quality water to leach salts. Rate of gypsum application depends on soil pH and the amount of exchangeable sodium present on the soil exchangeable complex. Gypsum is suitable for alkali soils upto a pH of 9.0.

Elemental sulphur or pyrites are effective on alkali soils which are calcareous (contain calcium carbonate) in nature



H<sub>2</sub>SO<sub>4</sub> produced also reduces soil pH.

**III. Biological amelioration** Organic materials and the activity of plant roots

improve biological activity in the soil. During the decomposition of organic materials CO<sub>2</sub> is released which forms carbonic acid thus dissolving calcium compounds. This can be accomplished by greenmanuring, incorporation of crop

residues, application of FYM, pressmud and other organic materials.

**Classification of crops based on salt tolerance** plant tolerance to salt concentration is due to

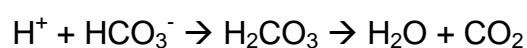
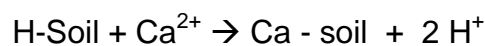
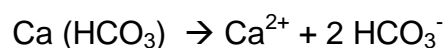
- 1) Accumulation of high level of sodium and chloride in shoots
- 2) Exclusion of salts by root cells,
- 3) Excretion of adsorbed salts from the plant by means of salt glands as in halophytes.

### **Salt tolerance of crops**

1. Highly tolerant      eg : *Sesbania*, rice, sugarcane, oats  
sugarbeet, Turnip, Date palm, ber
2. Moderately tolerant      eg : Castor, cotton, sorghum, maize, wheat,  
spinach, guava, pomegranate.
3. Moderately sensitive      eg : Radish, cabbage, tomato, sweet potato.
4. Highly sensitive      eg : Carrot, onion, lemon, orange, grape, apple,  
pulses, sesamum, pea.

Green manure crop is to be raised and incorporated at flowering stage into the soil immediately after reclamation. Rice crop is preferred to be grown after the green manure crop owing to its high tolerance to soil sodicity.

- ✓ **Management of acid soils:** Acid soils can be managed by either growing crops suitable for particular soil pH or by ameliorating the soils through the application of amendments which will counteract soil acidity. Acid soils are made more suitable for agricultural use by liming which raises the soil pH. Liming increases the exchangeable base status, influences nutrient uptake, reduces toxic concentration of aluminium and manganese by neutralizing effect, improves the soil structure and promotes root distribution.



The higher the soil moisture, the rapid is the rate of reaction.

**Lime requirement of acid soil** is the amount of a liming material that must be added to raise the soil pH to some prescribed value usually in the range of 6.0 to 7.0. The buffer method was proposed by Shoemaker et al. (1961). Liming material is the material which contains Ca and Mg that can neutralize soil acidity.

Lime stone, marketable lime, lime shells, paper mill sludge and basic slag are

some of the liming materials available in the market.

The efficiency of liming materials can be judged on the basis of the following factors

i) Neutralizing value (N.V) or  $\text{CaCO}_3$  equivalent (CCE) is defined as the acid neutralizing capacity of an agricultural liming material expressed as a weight percentage of calcium carbonate.

$$\text{CCE of liming material} = \frac{\text{Molecular weight of CaCO}_3}{\text{Mol. Wt. of a liming material}} \times 100$$

The  $\text{CaCO}_3$  equivalent of burnt lime is calculated as

$$\begin{aligned} & \frac{\text{Molecular weight of CaCO}_3}{\text{Mol. Wt. of Cao}} \times 100 \\ & = 100/56 = 1.786 \end{aligned}$$

Rock phosphate is the suitable P fertilizer than soluble phosphate

ii) Purity of liming material: The more purer the material the higher will be the effectiveness.

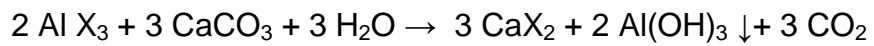
iii) Degree of fineness of liming material: The rate of reaction of liming materials with an acid soil depends upon the fineness of the material.

### **Classification of crops based on acidity tolerance**

1. Slight tolerance (upto pH6.5): eg., Alfalfa and sugar beet
2. Moderate (pH 6.0): eg., Peanut, cabbage, carrot, onions, radish, spinach and cauliflower.
3. Medium (pH 5.5) : eg., Cowpea, soybean, cotton, wheat, oats, peas, tomato, sorghum and millets
4. Strong (pH 5.0): eg., Tobacco, apple, grapes, plum, watermelon
5. Very strong (pH 4.5) : eg., Citrus

**Problems associated with over liming:** When excessively large amounts of lime is applied to an acid soil, the growth of the plant is influenced by one or many of these causes

- ✓ Deficiency of iron, copper and zinc will occur.
- ✓ Phosphorus and potassium availability is reduced.
- ✓ Due to high  $\text{OH}^-$  concentration by over liming, root development will be inhibited in association with tip swelling brought about by hydrations. Due to dehydrating properties of boron, it acts as a protective agent for excess  $\text{OH}^-$  concentration.
- ✓ Due to over liming, boron deficiency occurs.



Where 'X' is the exchange site. The freshly formed  $\text{Al(OH)}_3$  is then available for adsorption of boron thus causing boron deficiency.

- ✓ Due to the application of lime in excess, the incidence of diseases like scab in root crops will be increased.
- ✓ Due to over liming, the soils may become calcareous.
- ✓ All these effects can be reduced by the application of large amounts of organic manures like FYM, incorporation of green manure crops

**Lecture 25 Irrigation water:- Quality of irrigation water – Classification based on EC, SAR, RSC and Boron content. Indian standards for water quality. Use of saline waters in agriculture**

Quality of water is an important consideration in any appraisal of salinity or alkali conditions in an irrigated area. Salinity is one of the most important criterion for assessing quality of irrigation water especially under arid and semi arid region. Ground water contributes to about 40 % of all irrigation. The quality of irrigation water depends on the amount and kind of salt dissolved in it.

**Harmful effects of poor quality irrigation water :** If water containing excessive soluble salts is applied to the field, the soil turns saline to alkali. Harmful effects due to poor quality water through increased osmotic pressure of soil solution, thus inhibiting uptake of water and nutrients from soil to plant roots.

Excessive sodium adsorbed by clay causes deflocculation, destroys soil structure resulting in poor circulation of air and water in the soil.

**A. Classification of irrigation water or criteria for judging the quality of irrigation water given by USSL**

**1. Classification based on EC (Electrical Conductivity)**

C<sub>1</sub> – Low salinity water, EC < 250 μ mho/cm. This water can be used for most crops

C<sub>2</sub> – Medium salinity water, EC ranges between 250 – 750 μ mho/cm. Can be used with moderate leaching.

C<sub>3</sub> – High salinity water, EC between 750 to 2250 μ mho/cm. This water cannot be used on soil with restricted drainage.

C<sub>4</sub> – Very high salinity water, EC > 2250 μ mho /cm. Not suitable for irrigation.



## 2. Classification based on SAR (Sodium Adsorption Ratio)

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

The concentrations of  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  are expressed as  $meq L^{-1}$

S1 – SAR < 10. Low sodium water can be used on all soils with little danger of development of harmful level of exchangeable sodium.

S2 – SAR is 10-18. Medium sodium water, can produce hazards with fine textured soils which have high CEC especially with low leaching conditions.

S3 – SAR is 18-26. High sodium water; may produce harmful level of exchangeable sodium in most soils. It requires special management practices such as good drainage, high leaching and organic matter additions. Exchangeable Na should be replaced by the use of chemical amendments..

S4 – SAR > 26. Very high sodium water, not suitable for irrigation. This water can be used with the addition of gypsum or other amendments.

## 3. Classification based on RSC (Residual Sodium Carbonate)

$$RSC \text{ me L}^{-1} = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

**RSC value (me L<sup>-1</sup>)**

**Water quality**

< 1.25

Water can be used safely

1.25 – 2.5

Water can be used with certain management

> 2.5

Unsuitable for irrigation.

**4) Boron concentration :** It is evident that boron is essential for normal growth of the plant, but the amount required is very small. The permissible levels of boron in irrigation water are :

Boron class	Boron concentration (ppm)			Remarks
	Sensitive crops	Semi tolerant crops	Tolerant crops	
Very low	< 0.33	< 0.67	< 1.0	Can be used safely
Low	0.33 – 0.67	0.67 – 1.33	1.00 – 2.00	Can be used with

				management
Medium	0.67 – 1.0	1.33 – 2.0	2.0 – 3.0	Unsuitable for irrigation
High	1.0 – 1.25	2.0 – 2.5	3.0 – 3.75	
Very high	> 1.25	> 2.5	> 3.75	

### 5. Chloride concentration

**Chloride concentration  
(me L<sup>-1</sup>)**

**Water quality**

< 4

Excellent water

4-7

Moderately good water

7-12

Slightly usable

12-20

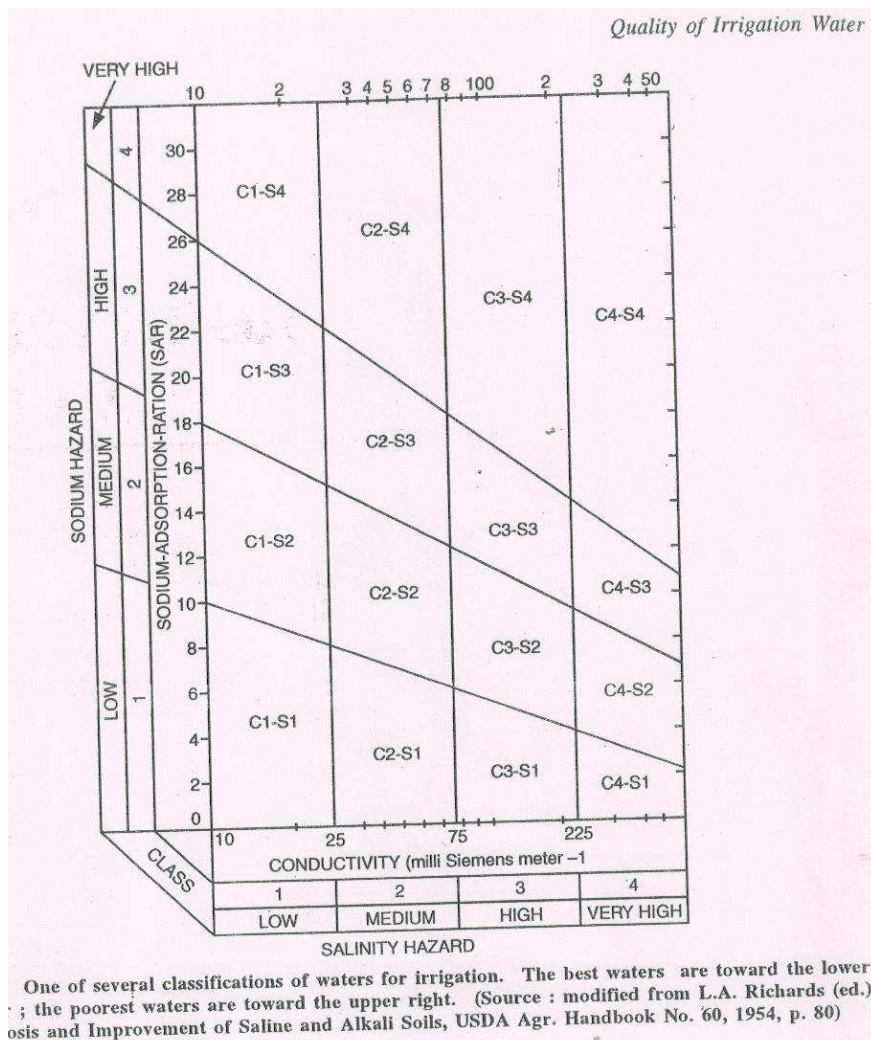
Not suitable for

> 20

irrigation purpose

### B. Grouping of irrigation water (Gupta et al., 2000)

S.No.	Main class	Sub-class	EC <sub>iw</sub> dSm <sup>-1</sup>	SAR <sub>iw</sub>	RSC (me L <sup>-1</sup> )
I.	Good	-	< 2	< 10	< 2.5
II.	Saline	Marginally saline	2- 4	< 10	< 2.5
		Saline	> 4	< 10	< 2.5
		High SAR saline	> 4	> 10	< 2.5
III.	Alkali	Marginally alkali	< 4	< 10	2.5 – 4.0
		Alkali	< 4	< 10	> 4.0
		Highly alkali	Variable	> 10	> 4.0



### Use of saline water in agriculture

The change in quality of irrigation water is technically not feasible and not economically viable. The following measures should be adopted for the use of saline water.

1. Selection of salt tolerant crops and varieties.
2. Deep ploughing to break the hard pan of salts if any.
3. Furrow planting is best for saline conditions because the seed can be safely planted below the zone of high salt accumulation.
4. Poor germination, high mortality of young seedlings and poor tillering are common features when the crop is grown with poor quality water. So, higher seed rate and close spacing is advisable. An additional seed rate of 25% should be adopted.
5. Dhaincha as a green manuring crop improves physical properties of the soil.
6. Addition of organic manures to some extent mitigates the adverse effect of poor quality water.
7. Fertilizers should be applied 1.25 - 1.5 times the normal rate of their application.
8. Application of Zn @ 20 kg ZnSO<sub>4</sub> ha<sup>-1</sup> counteracts the negative effect of higher salinity and sodicity.
9. Split application of nitrogen to prevent N losses through volatilization and denitrification. Correction of nutrient deficiencies by foliar application of nutrients.

10. Dilution and cyclic use of good and saline waters. When good quality water is limited, it can be used as follows :

- Presowing and first irrigation should be with good quality water. Later saline water can be used.
- Poor quality water can be mixed with good water.
- Drip or pitcher irrigation is found suitable.

11. Use of mulches to reduce the requirement of water for evaporation.

- Use of mulches and intercultural operations reduce water requirement of crops, thus with saline water salinity develops at a relatively lesser intensity.

**Salt tolerance of different crops.**

High tolerant : Rice, cotton, sugarbeet, tobacco, date palms, ber.

Moderate tolerance : Spinach, sugarcane, wheat, guava, pomegranate, tomato, sweet potato.

Highly sensitive : Beans, pea, grape, orange, apple, pear, carrot.

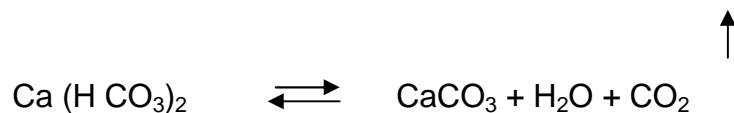
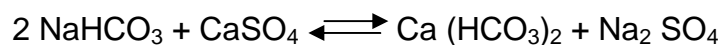
**Treatments with amendments**

Water of high RSC can be used for crops having low water requirement. The rain water should not be allowed to leave the field as runoff but should be allowed to percolate through the soil profile.

**Use of gypsum** : In water containing excess of sodium (when RSC > 4 me L<sup>-1</sup>), gypsum can be successfully used. With the addition of gypsum, the adverse effects of sodium can be mitigated.

Gypsum can be applied by

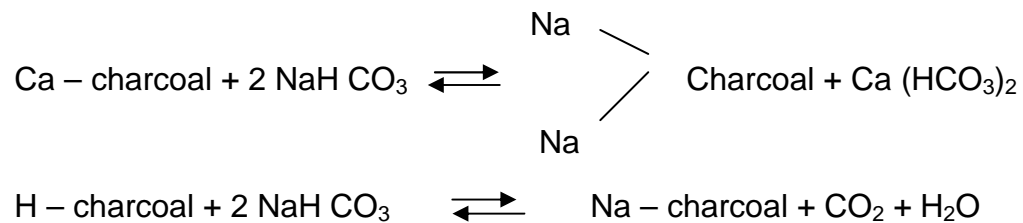
- a) Keeping gypsum lumps or powdered gypsum in bags in small tanks constructed at the mouth of the tube well or water passage.
- b) Application of gypsum @ 75 kg ha<sup>-1</sup> for each irrigation of 5 cm depth for 1 me L<sup>-1</sup> of RSC above 2.5 me L<sup>-1</sup> should be applied to the soil.
- c) A saturated solution of gypsum may be added at a constant rate to the flowing water.



Na<sub>2</sub> SO<sub>4</sub> being soluble can be leached.

- Water containing toxic amounts of boron can be reduced by mixing with gypsum. Sodium borate is converted to calcium borate which being soluble can be leached out of root zone.

**Use of ion exchange resins :** On a limited scale, water containing excess amounts of Na is passed through high CEC calcium and H-charcoal, which adsorbs Na.



- Liberal application of organic manures specially growing of green manures like sunhemp and *dhaincha* and incorporating the same at the time of flowering in the soil also reduce the adverse effects of high RSC water.
- Phosphorus should preferably be applied as SSP.

**Lecture 26 Soil fertility Evaluation: - Approaches – Nutrient deficiency symptoms. Soil testing – Objectives of soil testing – Chemical methods for estimating available nutrients**

Literally the word fertile means ‘bearing abundantly’ and a fertile soil is considered to be one that produces abundant crops under suitable environmental conditions.

**Soil fertility :** is concerned with the inherent capacity of soil to provide nutrients in adequate amounts and in proper balance for the growth of specified plants when other factors such as light, moisture, temperature and the physical condition of the soil are favourable. Soil fertility is an aspect of the soil plant relationship viz., plant growth with reference to plant nutrients available in soil.

Justus Von Liebig 1840 propounded the ‘law of Restitution’ which states that in order to maintain soil fertility nutrients removed from the soil by crops must be restored by the application of manures and fertilizers.

The assessment of nutrient supplying capacity of the soil is soil fertility evaluation. It necessitates understanding of certain major concepts having definite bearing on soil fertility.

The law of minimum was put forward by Von Liebig which envisages that if a soil contains optimum / adequate amounts of all but one nutrient element, crop growth is regulated by that single nutrient.

**Approaches for soil fertility evaluation :** The wide variety of diagnostic techniques used so far can be broadly grouped into

- 1) Soil Analysis
- 2) Plant Analysis
- 3) Biological methods

#### 4) Visual symptoms of nutrient deficiency or toxicity.

Soil testing and plant analysis are useful tools for making recommendations for application of fertilizers to crops. Soil testing gives a measure of the availability of nutrients to crops, plant analysis indicates the actual removal of the nutrients from the soil.

#### **Objectives of soil testing**

1. Grouping soils into classes relative to the levels of nutrients for suggesting fertilizer practices.
2. Predicting the probability of getting profitable responses.
3. Helping to evaluate soil productivity.
4. Determining specific soil conditions like alkali, salinity and acidity which limits crop yields.

**Available nutrients** : Plants draw their nutrients from air, water and soil. The bulk of mineral nutrients come from soil. Soil available form of nutrient is that fraction which is distributed in different discrete chemical forms, which often exist in a state of dynamic equilibrium and constitute the pool from which plants draw it. Soil available form of a nutrient is also that fraction whose variation in amount is responsible for significant changes in yield and responses. The nutrient available to biological organisms is termed as bioavailable nutrient.

#### **Chemical methods for estimating nutrients**

Soil testing includes measurement of available N, P, K, S, micronutrient, lime and gypsum requirement, besides measuring pH, EC and calcium carbonate, texture by Bouyoucos hydrometer method.

#### **The different extractants for the available nutrients**

<b>Nutrient</b>	<b>Extractant</b>
Available P	0.5 M NaH CO <sub>3</sub> , pH 8.5 Olsen's extractant
	0.03 N NH <sub>4</sub> F + 0.025 NHCl Bray's No.1 extractant
Available K	Neutral normal ammonium acetate
Available S	0.15 % CaCl <sub>2</sub>
Available Zn, Fe, Cu, Mn	0.005 M DTPA, pH 7.3 Diethylene Triamine penta Acetate
Gypsum requirement	Schoonover method
Lime requirement	Shoemaker et al.

### Rating limits of soil test values

Nutrient	Low	Medium	High
Organic carbon (%)	Below 0.5	0.5 – 0.75	Above 0.75
Avail. N (kg ha <sup>-1</sup> )	Below 280	280 – 560	Above 560
Avail. P (kg ha <sup>-1</sup> )	Below 10	10 – 24.6	Above 24.6
Avail. K (kg ha <sup>-1</sup> )	Below 108	108 – 280	Above 280

Avail. S (ppm)	Deficient < 10 ppm	Sufficient > 10 ppm
DTPA Zn	Deficient < 0.6 ppm	Sufficient > 0.6 ppm

### Visual symptoms of nutrient deficiency or toxicity

Chemical analysis of plants may indicate the presence of more than 90 elements but 16 of them have been established to be essential for their successful growth and development; as per the criteria of essentiality. A constant balanced supply of these nutrients is essential for normal plant growth. Any imbalance among them leads to the emergence of nutritional disorders owing to their deficiencies or toxicities when an essential nutrient is in extremely short / excess supply, the plant suffers from its deficiency which is manifested in the form of specific sign termed as deficiency / toxicity symptom of the nutrient.

Visual deficiency symptoms are generally characteristic enough to permit easy identification of the deficiency of a nutrient as these appear on particular plant part at specific growth stage. The mobility of nutrients within a plant differs markedly. Nutrients like N, P and K are readily translocated from old to young leaves under stress condition and are termed as mobile nutrients within the plant and they show up their deficiencies initially on the old leaves. The nutrients such as calcium, sulphur, boron and iron which are not retranslocated are called immobile nutrients and their deficiency symptoms first appear on young leaves. Mobility of other nutrients is intermediate.

Eg : Shortening of internodes due to Zn deficiency results primarily from impaired auxin metabolism.

The visual identification of nutrient deficiencies or toxicities is considered as a simple and inexpensive diagnostic tool in plant nutrition as it does not involve the use of any analytical equipment.

## **Limitations**

- Confident diagnosis by this approach requires much experience as the symptoms of some nutrient deficiencies are difficult to differentiate.
- By the time the deficiency / toxicity symptoms appear, the crop has undergone marked set back and the ameliorative measures taken at that time may not produce optimum yields. The appearance of deficiency symptoms is an extreme limit of nutrient deficiency but even if the symptoms are not manifest, reduction in the yield of crop may occur. This condition has been termed as hidden hunger.

## **Lecture 27 Plant analysis – Rapid tissue tests – DRIS – Indicator plants**

### **Plant analysis**

Although plant analysis is an indirect evaluation of soil, it is a valuable supplement to soil testing. Plant analysis is useful in confirming nutrient deficiencies, toxicities or imbalances, identifying hidden hunger, evaluating fertiliser programme and determining the availability of elements. Sometimes adequate nutrients may be present in the soil, but because of other problems like soil moisture and inadequate amounts of some other nutrients, the plant availability of the nutrient in question may be constrained.

Plant analysis is based on the fact that the amount of a given element in plant is an identification of the supply of that particular nutrient and as such is directly related to the quantity in the soil.

For most diagnostic purposes, plant analyses are interpreted on the basis of critical value approach, which uses tissue nutrient concentration calibrated to coincide 90% or 95% of the maximum yield, below which the plants are considered to be deficient and above that value sufficient.

Two general types of plant analysis are in use.

1. The tissue test which is customarily made on fresh tissue in the field.
2. Total analysis performed in the laboratory with precise analytical techniques.

#### **A. Tissue Tests:**

Rapid tests for the determination of nutrient elements in the plant sap of fresh tissue. In these tests, the sap from ruptured cells is tested for unassimilated nitrogen, phosphorus and potassium. They are semi quantitative tests mainly intended for verifying or predicting deficiencies of N, P or K. The results are read as low, medium or high. Through the proper application of tissue testing it is possible to anticipate or forecast certain production problems which still in the field. The concentration of the nutrients in the cell sap is usually a good indication of how



well the plant is supplied with nutrients at the time of testing.

- (1) **Plant Part to be Selected:** In general the conductive tissue of the latest mature leaf is used for testing.
- (2) **Time of Testing:** The most critical stage of growth for tissue testing is at the time of bloom or from bloom to early fruiting stage. Nitrates are usually higher in the morning than in the afternoon if the supply is short.

- Test for nitrates → Diphenylamine
- Phosphates → Molybdate + Stannous oxalate test
- For potassium → Sodium cobalti nitrate

**B. Total Analysis:**

Total analysis is performed on the whole plant / plant parts. Precise analytical techniques are used for measurement of the various elements after the plant material is dried, ground and ashed and used for estimating total nutrient content.

**Relative and Average Plant Nutrient Concentrations**

Plant Nutrient	Average Concentration*
H	6.0%
O	45.0%
C	45.0%
N	1.5%
K	1.0%
Ca	0.5%
Mg	0.2%
P	0.1%
S	0.1%
Cl	100 ppm (0.01%)
Fe	100 ppm
B	20 ppm
Mn	50 ppm
Zn	20 ppm
Cu	6 ppm
Mo	0.1 ppm

\* Concentration expressed by weight on a dry matter basis.

**Critical Nutrient Concentration:**

Critical Nutrient Concentration is the level of a nutrient below which crop

yield, quality or performance is unsatisfactory. However it is difficult to choose a specific concentration.

For crops such as sugarbeet excessive concentration of N seriously affects the quality. So, CNC is maximum rather than a minimum consequently it is more realistic to use the critical nutrient range (CNR) which is defined as the range of nutrient concentration at a specified growth stage above which the crop is amply supplied and below which the crop is deficient.

**Diagnosis and Recommendation Integrated System (DRIS)** proposed by Beaufils (1973) which considers nutrient concentration ratios rather than individual elemental concentration for interpreting plant tissue composition. The DRIS approach measures the relative balance between nutrients by means of index values with negative values indicating insufficiencies and vice versa. DRIS reveals not only the limiting nutrient but also the order in which the nutrients are likely to become limiting. It is a comprehensive system which identifies all the nutritional factors limiting crop production and in doing so increases the chances of obtaining high crop yields by improving the fertilizer recommendations. Index values which measure how far particular nutrients in the leaf or plant is deviating from the optimum are used in the calibration to classify yield factors in the order of limiting importance.

To develop a DRIS for a given crop the following requirements must be met. All factors suspected of having an effect on crop yield must be defined.

1. The relationship between these factors and yield must be defined.
2. Calibrated norms must be established.
3. Recommendations suited to particular set of conditions and based on correct and judicious use of these norms must be continuously refined.

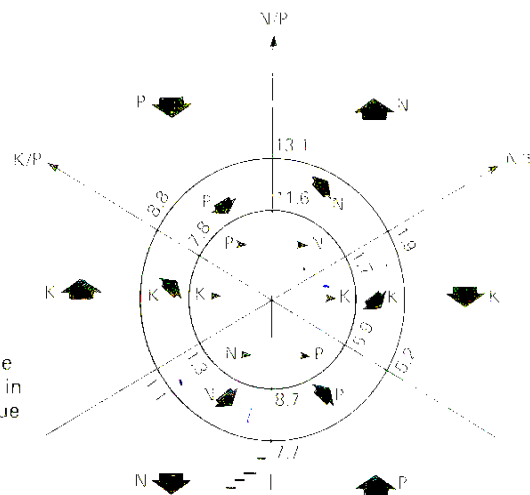
#### **Establishment of DRIS Norms:**

Large number of sites is selected at random in order to represent the whole production area. At each site plants and soil samples are taken for all essential element analyses. The entire population of observation is divided into two sub populations (high and low yielders) on the basis of vigour, quality and yield. Each element in the plant is expressed in as many ways as possible. For eg: Nutrient ratios N/P, N/K or products NxP, NxK etc. Each form of expression which significantly discriminates between high and low yielding sub populations is retained as a useful diagnostic parameter. The mean values of all the sites for each of these forms of expression then constitute the diagnostic norms.

NPK requirement of the crop is diagnosed using DRIS chart. The chart is constructed of three axes for N/P, N/K and K/P represented with mean values of the sub populations of the high yielder. The concentric circle can be considered as



confidence limits. Horizontal arrows ( $\rightarrow$ ) in the inner circle indicate the balance between nutrients. Diagonal arrows indicate ( ) a tendency to imbalance. The inner being set at  $\pm 15\%$  and outer at the mean  $\pm 30\%$  for each expression. Vertical ( $\downarrow\uparrow$ ) arrows representing nutrient imbalance. The arrow notation can be replaced by DRIS indices.



**FIGURE 12-12.** DRIS chart for obtaining the qualitative order of requirements for N-P-K in corn. Means of significant expressions (value at origin in chart) are: N:P = 10.04, N:K = 1.49, and K:P = 6.74. [Sumner, *Solutions*, 22(5):68 (1978).]

1. The importance of nutritional balance is taken into account.
2. The norms for the elemental content can be universally applied.
3. Diagnosis can be made over wide ranges of stages.
4. The nutrients limiting the yield either through excess or insufficiency can be readily identified.

**Indicator plants:** Certain plants are very sensitive to deficiency of a specific plant nutrient and they produce specific symptoms which are different from other deficiency symptoms. Thus the deficiency of that element can easily be detected.

The indicator plants are the following

Element	Deficiency indicator plant
N	Cauliflower, Cabbage
P	Rape seed
K	Potato
Ca	Cauliflower, Cabbage
Mg	Potato
Fe	Cauliflower, Cabbage, Potato
Na	Sugar beet
Mn	Sugarbeet, Oats, Potato
B	Sunflower

**Lecture 28 Biological methods of soil fertility evaluation:- Microbiological methods – Sackett and Stewart Techniques, Mehlich technique – Cunninghamella plaque method and Mulder’s *Aspergillus niger* test**

For calibrating crop response, besides chemical soil test values other procedures are also available. They are

1. Mitscherlich pot culture method
2. The Jenny pot culture test
3. The Neubauer seedling method
4. The Stanford and Dement technique
5. Sunflower pot culture technique for boron
6. Sackett and Stewart technique (*Azotobacter* test for  $P_2O_5$  and  $K_2O$ )
7. Mehlich technique for available  $K_2O$
8. Mehlich *Cunninghamella* plaque method for phosphorus
9. The Mulder’s *Aspergillus niger* test for copper and magnesium
10. A – value (tracer technique)

**Microbiological methods are**

**1. Sackett and Stewart technique :** Used to find out  $P_2O_5$  and  $K_2O$  status in the soil judged by colonization of *Azotobacter* in the culture prepared from soil. Three containers having soil culture are used of which one portion is supplied with  $P_2O_5$  another with  $K_2O$  and rest with both  $P_2O_5$  and  $K_2O$ . The cultures are inoculated with *Azotobacter* and incubated for 72 hrs and growth of colony may be classified as under.

<b>Class</b>	<b>Growth of the colony</b>
Class I	Very deficient – None or few small pin head sized colonies are seen.
Class II	Moderately deficient – few colonies
Class III	Slightly deficient – The colonies on unfertilized cultures are equal in number and development.
Class IV	Not deficient – colonies on both fertilized and unfertilized plaques are equal in number and development.

**2. Mehlich technique for available  $K_2O$  :** A small amount of soil is taken in conical flasks in which appropriate nutrient solution is added and then it is

inoculated with *Aspergillus niger* and incubated for four days. Weight of mycelial pad and its K<sub>2</sub>O content are taken into account.

**Critical limits for available K by using the *Aspergillus niger* method**

Weight of 4 pads (g)	K <sub>2</sub> O absorbed by <i>A niger</i> per 100 g soil (mg)	Degree of potassium deficiency
<1.4	<15	Very deficient
1.4 to 2.0	15 to 20	Moderate to slight deficiency
2.0	>20	Not deficient

**3. Mehlich's *cunninghamella* plaque method for P :** *Cunninghamella* is sensitive for P<sub>2</sub>O<sub>5</sub> status. The soil is mixed with nutrient solution and paste is prepared which is spread in clay dish. Then inoculated with *cunninghamella* and allowed to incubate for 4-5 days. The diameter of the mycelial growth is considered as an index for P status.

**P – deficiency and mycelial growth**

Diameter of colonies (mm)	Degree of P deficiency
<10	Very deficient
11-15	Moderately deficient
16-21	Slightly deficient
>22	Not deficient

**4. Mulder's *aspergillus niger* test for Cu and Mg :** Color of the mycelia and spores give an indication of either deficiency or sufficiency of Cu and Mg. For comparison, known standards are prepared as follows and their colors are compared with those on the unknown soil.

**Ranges for Cu and Mg in Mulder's test**

Cu in µg /g of air –dry soil	Deficiency degree	mg in µg/3 g of air – dry soil
< 0.4	Very deficient	< 50
1 – 1.5	Slightly deficient	50 - 100
>2.0	Not deficient	>100

**Lecture 29: Pot culture test:- Mitscherlich’s pot culture method - Jenny’s pot culture test. Neubauer’s seedling method. Sunflower pot culture technique for Boron. A - Value**

Besides plant analysis there are some biological tests which may be used to evaluate soil fertility.

**1. The Mitscherlich pot culture method :** In this method pots containing 2.72 kg soil are taken for growing oats as test crop. N, P and K are added in different combinations in these pots [N<sub>o</sub> - one pot, P<sub>o</sub> - three pots (NK), K<sub>o</sub>- three pots (NP) and NPK - three pots ]. The crop is grown till maturity and percentage increase in yield is calculated by using Mitscherlich tables from rotation of given quantity of fertilizers over native fertility status (control).

**2. The Jenny’s pot culture test :** Smaller pots consisting of 1.81 kg soil are used for growing lettuce (*Lactuca sativa longifolia*) as test crops for 6 weeks. Following treatments are used in four replications.

Control	NoPoKo
Full fertilizer	N150 P150 K100
No nitrogen	N0 P150 K 100
No phosphorus	N150 P0 K100
No potash	N150 P150 K0

The percentage values are categorized as deficiency, probable deficiency and uncertain deficiency as mentioned below :

Jenny’s values	% yield		
	Definite deficiency	Probable deficiency	Uncertain deficiency
N	20	20-50	51-70
P	20	20-50	51-65
K	70	70-75	76-80
S	66	66-76	77-83

**3. The Neubauer’s seedling method**

In this technique, 100 seedlings of rye or oats are made to feed exhaustively on 100 g of soil mixed with 50 g of sand for 17 days in dishes of 11 cm and 7 cm depth. A blank without any soil also is taken. The total P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O uptake is

calculated and the blank value is deducted to obtain root soluble P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O in 100 g of air dry soil. These values are designated as Neaubauer's numbers and expressed as mg/100 g of dry soil. The following Neaubauer limit values are used to determine the deficiency.

**Neaubauer limit values mg/100 g soil**

Nutrient	Barley	Oats	Rye	Wheat	Turnip	Potato	Sugarbeet
P <sub>2</sub> O <sub>5</sub>	6	6	5	5	7	6	6
K <sub>2</sub> O	24	21	27	20	39	37	25

**4. The Stanford and Dement technique :** Round waxed cardboard cartons of about 100 g capacity with bottom removed which are nested in similar containers having intact bottom filled with 680 g of sand. The seeds of the test crop are sown about 1.25 cm deep. After growing the seedlings for 2 to 3 weeks, a carton containing the plants are nested in second carton holding 200 g of soil or soil mixed with fertilizers. The plant roots enter the second carton where these plants are allowed to feed for 3 to 5 days. Four plants of maize and 30 plants of wheat are maintained for the study. After 5 days the plant samples are taken to determine the nutrient content.

**4. Sunflower pot culture technique for Boron :** In this method 500 g soil is taken in small pot and 5 sunflower seedlings are allowed to grow. The soil is fertilized with a solution containing all the nutrients except B and deficiency of B is noticed and ranked.

<b>Class</b>	<b>Days after which B deficiency is noticed</b>
Marked deficiency	< 28
Moderate deficiency	28 – 36
Little or no deficiency	> 36

**5. A value :** By using radioactive isotopes, it has now become possible to calculate the available nutrients in the soil. Fried and Dean (1952) defined A-value as that amount of nutrients in soil which behave in a similar way as the applied fertilizer nutrient doses. This can be calculated by the formula.

$$A = B \left( \frac{1-y}{y} \right)$$

Where.,

A = Available soil nutrient

B = Amount of fertilizer nutrient applied.

Y = The fraction of the nutrient derived from fertilizer contained in the plant.

**Lecture 30 Soil test based fertilizers recommendation:- Critical nutrient concept (Cate and Nelson) – Critical levels of nutrients in soils. Use of empirical equations for scheduling fertilizers P dosage to crops**

**Soil test based fertilizer recommendations or Fertility gradient approach:**

This was put forth by Ramamoorthy (1971). The underlying principle is to get as a large variation as possible in the soil fertility levels in one and the same field in a given locality where an elaborate field experiment is conducted so that the real relationship between the yield and the level of soil fertility could be evaluated without interference from other factors affecting the yield.

A large field of certain amount of natural variation in fertility is chosen. It is divided into four strips which are treated with four different doses of N, P and K viz., control ( $N_0P_0K_0$ ), half of the normal dose ( $N_{1/2}P_{1/2}K_{1/2}$ ), normal dose ( $N_1P_1K_1$ ) and double normal dose ( $N_2P_2K_2$ ) of N, P and K fertilizers that are usually applied to the high yielding varieties of the crops in the country. Exhaustive crop like sorghum, maize, wheat or rice are grown on this field to deplete the soil fertility level in the strips treated with fertilizers. An experiment is then laid out on this field for the purpose of Soil Test Crop Response (STCR) correlation with 21 treatments having different N, P and K randomly arranged in each strip in such a way that there is an untreated check plot on either side of the treated plot.

The soil test crop response correlation work is then carried out taking the yield of treatments and the average of the two controls (check) plots into consideration.

**Critical soil test level approach**

The critical soil test level, concept advanced by Cate and Nelson (1965) is the level of the nutrient below which a reasonably satisfactory economic response should be expected from the application of that particular nutrient and above which the probability of such response is low. In order to apply this concept, the soil is collected from each field are analysed, field experiments are conducted with application of graded doses of nutrient and response curve is fitted. A scattered diagram of percentage yield on Y-axis and soil test value on X-axis is then plotted. It is divided into four quadrants positioning the lines in such a way that the number of points in the upper right and lower left quadrants is maximum. The point where the vertical line crosses the X-axis is defined as the critical soil test value.

**Critical levels of nutrients in soils** Critical value may be defined as the nutrient concentration below which the plants are expected to respond to the application of that nutrient.



### Critical level of micro nutrients in soils

Micronutrient	Indices	Critical level (ppm)	
		Range	Mean
B	Hot water soluble	0.1 – 2.0	0.7
Cu	Mehlich No.1	0.1 – 10.0	3.0
	DTPA + Ca Cl <sub>2</sub> (pH 7.3)	0.12 – 2.5	0.8
	AB-DTPA (pH 7.6)		1.8
Fe	DTPA + Ca Cl <sub>2</sub> (pH 7.3)	2.4 – 5.0	4.0
	AB-DTPA (pH 7.6)		4.0
Mn	Mehlich No.1	4.0 – 8.0	7.0
	DTPA + Ca Cl <sub>2</sub> (pH 7.3)	1.0 – 2.0	1.4
	0.03 M H <sub>3</sub> PO <sub>4</sub>	0-20.0	10.0
	AB-DTPA (pH 7.6)		1.8
Mo	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (pH 3.3)	0.04 – 0.2	---
Zn	0.1 N HCl	2.0 – 10.0	5.0
	Mehlich No.1	0.5 – 3.0	1.1
	DTPA + Ca Cl <sub>2</sub> (pH 7.3)	0.25 – 2.0	0.8
	AB-DTPA (pH 7.6)		1.5

### Use of empirical equations for scheduling fertiliser P dosage to crops

Krishnamoorthy et al., (1963) worked out empirical relationships between the nature of the soil and the extractable P. They found that the capacity to fix added phosphates is largely a function of the type and amount of clay present in the soil.

- i) In the case of typical black cotton soil consisting of montmorillonite and beidellite type of clay minerals, the extractability of added phosphates is given by the formula

$$\text{Percentage extractable P} = 100 - \text{Clay percentage}$$

- ii) In the case of red and alluvial soils where illite dominates, the relationship appears to be

$$\text{Percentage extractable P} = 100 - 2 (\text{Clay percentage})$$

## Lecture 31 Nutrient use efficiency:- Soil, plant and management factors influencing Nutrient use efficiency in respect of N, P, K, S, Fe and Zn fertilizers

Nutrient use efficiency (NUE) may be defined as yield per unit input. In agriculture, this is usually related to the input of fertiliser, whereas in scientific literature, the NUE is often expressed as fresh weight or yield per content of nutrient. Improvement of NUE is an essential pre-requisite for expansion of crop production in marginal lands with low nutrient availability. NUE not only depends on the ability to efficiently take up the nutrient from the soil, but also on the transport, storage, mobilization, usage within the plant, and even on the environment.

Nutrient use efficiency is defined as the extent to which the nutrients and management practices interact to give a specified yield level.

$$\text{NUE (\%)} = \frac{\text{Yield with applied nutrient} - \text{Yield without applied nutrient}}{\text{Amount of nutrient applied}} \times 100$$

### Factors affecting NUE

**A. Soil factors :** The most important factors are soil physical conditions, soil fertility and soil reaction. On soils with poor physical condition, plant growth will be poor due to impeded drainage, restricted aeration and unfavourable soil temperature due to which the nutrients will not be used efficiently. Coarse textured soils are usually poorer in available nutrients than fine textured soils. On such soils nitrogen and potassic fertilizers should be more frequently applied than in fine textured soils. The higher the fertility status of the soil, the lower is the response. Soil reaction is an important consideration in the selection of right type of P fertilizers. The higher the organic matter status, the more is the nutrient use efficiency.

**B. Climatic factors :** include temperature, rainfall and its distribution, evaporation, length of day and growing season. Rate of nitrification is slower in cooler climate than in warmer climate, hence more amounts of fertilizers should be added in cool climate. Higher amount of fertilizers are required in high rainfall region due to leaching to obtain an expected yield potential. In arid regions, soil moisture is a limiting factor to get higher nutrient use efficiency. The higher the light intensity, the better is the nutrient use efficiency.

**C. Crop factors :** CEC of plant roots influences the fertilizer responsiveness of the crop. A large ramifying root system of the plant absorbs nutrients more efficiently. The time of application of fertilizer should match the pattern of nutrient uptake to increase nutrient use efficiency. For legumes N fertilizer may be reduced as they can fix atmospheric N to increase N use efficiency.

**D. Agronomic factors** : include selection of fertilizer responsive crops and varieties, timely sowing, proper spacing, proper dose, time and method of fertilizer application to increase the yield and thereby increasing NUE.

#### **How to enhance nutrient use efficiency**

Use efficiency of any nutrient can be increased by achieving potential yields of crops by optimizing the factors of crop production.

1. Selection of suitable crops and varieties, which are input responsive recommended for the region.
2. Sowing or planting the crops at optimum time.
3. Maintaining optimum plant population.
4. Use of organic manures and biofertilizers to supplement nutrients and also to bring ideal conditions for crop growth.
5. Inclusion of legumes in the cropping system as intercrop.
6. The crops should be irrigated at least to save life at critical growth stages.
7. Fertilizer scheduling must be based on soil test values to prevent nutrient deficiencies or luxury consumption.
8. P and K fertilizer and part of N fertilizer should be applied as basal and N in splits doses; for light textured soils K also should be applied in splits.
9. Band placement of fertilizers preferable to prevent losses. (Especially P to reduce fixation).
10. Under moisture stress condition, foliar application of urea at 2% concentration is effective.
11. Micronutrient deficiencies should be corrected instantly.
12.  $ZnSO_4$  should be applied as package once in two seasons @ 25-50 kg/ha.
13. Problem soils must be ameliorated by taking reclamation measures.

NUE of individual nutrients also can be increased by following the above management practices along with some specific measures as follows

#### **Nitrogen use efficiency** : can be increased through

- Split application of nitrogenous fertilizers to prevent losses due to leaching.
- The use of slow release nitrogenous fertilizer like urea formaldehyde, sulphur coated urea, Neem coated urea etc.
- Use of nitrification inhibitor (Eg: N-serve) to retard the conversion of  $NH_4^+$ -N to  $NO_3^-$ -N to prevent leaching and make it available to crops for quite longer period.
- By the integration of inorganic N with organic sources the soil physical condition can be optimized besides adding nutrients to the soil.

**P use efficiency** can be increase by decreasing P fixation and balanced application of the nutrients. P fixation can be reduced by judicious application of

organic manures, application of P fertilizer by placement, inoculation (either seed or soil) with phosphorus solubilising bacteria like *Pseudomonas*, *Bacillus megathrium* var. *phosphaticum*.

**K use efficiency** : can be enhanced by preventing leaching loss either by split application on light soils, applying organic manure and balanced application of nutrients.

**S use efficiency** : Sulphur in soil solution is present as  $\text{SO}_4^-$  and more prone for leaching losses. The losses can be prevented by applying organic manures to improve water holding capacity of the soil and it also acts as a source of S. S oxidation can be facilitated by providing oxidized conditions in the soil.

**Fe use efficiency** : Most available form of iron is  $\text{Fe}^{2+}$ . All the measures which govern the soil reaction will influence Fe availability. Fe availability is more in acidic soil pH.

- ❖ Application of organic manures including greenmanuring improve the use efficiency of iron by
  - i. Acidifying the rhizosphere due to the release of organic acids
  - ii. Supplementing with iron after decomposition
  - iii. Act as substrate for heterotrophic bacteria that can reduce ferric to ferrous form (eg., *Bacillus*, *Clostridium* and *Klebsiella* etc.).
  - iv. The microbes also produce chelating ligands called as 'siderophores' that can form complex with  $\text{Fe}^{3+}$ , which can be absorbed into the plant.
- ❖ Reclamation of alkali soils
- ❖ If deficiency appears on standing crop foliar application of Fe.

### **Zn use efficiency**

- Zn fertilizer should not be applied with phosphatic fertilizers.
- Maintaining the soil pH between 5.5 – 6.5 by applying organic manures.

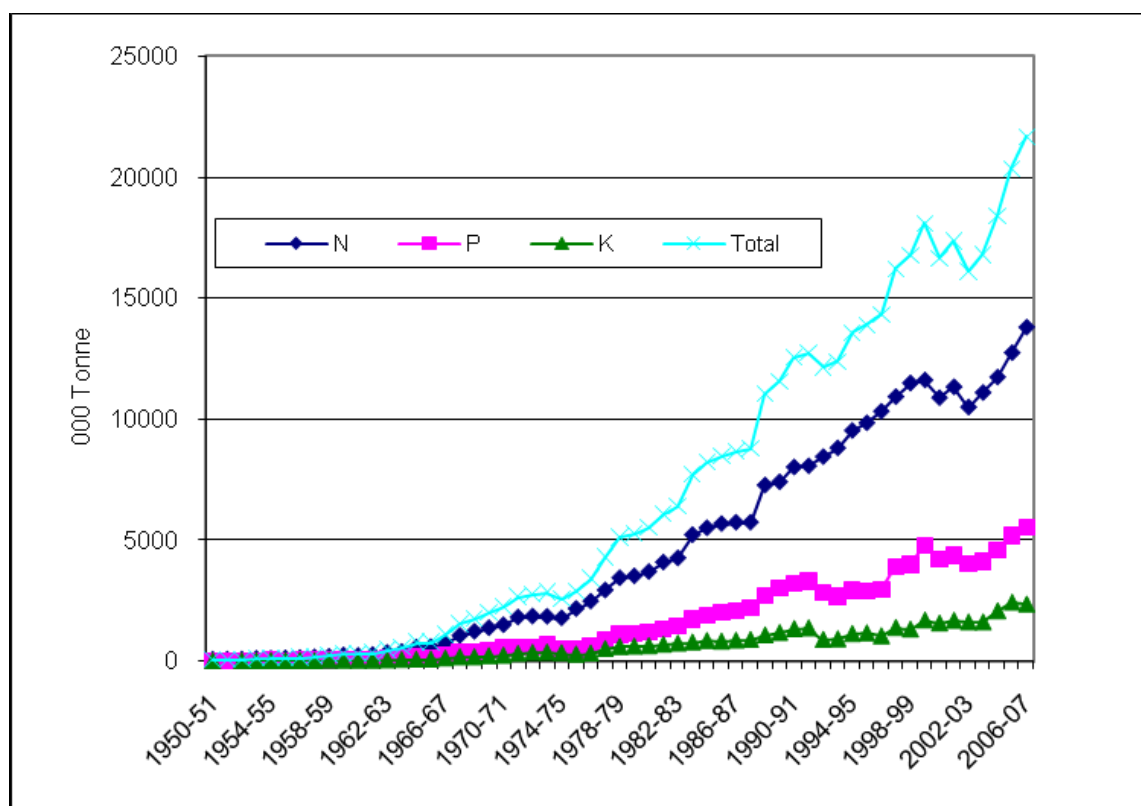
## **Lecture 32 Use of fertilizers and insecticides in Agriculture Trends in their use – effect of excess use on soil and water**

Role of fertiliser in increasing agricultural productivity and production during the last five and half decades has been well documented. A very close association is observed between growth of fertiliser and crop productivity in almost all the states of the country. No input in agriculture has seen as much growth as witnessed in the use of fertiliser in the recent history of agriculture. Fertiliser consumption was around 67 thousand tonnes in early 1950s and it picked up very fast during mid 1950s. By early 1960s consumption of NPK crossed 400 thousand tonne and at the time of onset of green revolution consumption of fertiliser approached 1 million tonne. On per hectare basis, fertiliser consumption in India increased from 0.5 kg in early 1950s to 7 kg at the time of onset of green revolution

in 1966-67. It is worth mentioning that in the pre green revolution post Independence period fertiliser consumption remained quite low but its growth rate was higher than that of crop production. Fertiliser consumption crossed 22000 thousand tonnes by 2006-07.

The common perception about fertiliser use in India is that use of nitrogenous fertiliser has increased at a relatively faster rate compared to the use of potassic and phosphatic fertilisers and this has increased the imbalance in use of plant nutrients, which, in the long run, is considered to cause adverse impact on soil fertility and crop productivity.

Several problems linking excessive use of fertilizer with environment have been identified.



**Fig: Trends in fertilizer use in India**

**Pollution due to excessive nitrate in soil :** The increase of nitrates in the drinking water due to excessive use of nitrogen fertilizers and animal manures is regarded as the most important fertilizer related pollution issue. The nutrient enrichment and deterioration of surface water quality due to transportation of nutrients applied through fertilizers via leaching or runoff or sediment erosion. The excessive nitrate leaching below the root zone constitutes a potential threat for surface and ground water bodies.  $\text{NO}_3^-$  when denitrified forms  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases leading to global warming. Nitrates can also be absorbed in large amounts by plants particularly fodders and vegetables, and may result in nitrate toxicity (particularly the plants belonging to Chenopodiaceae family) to the consumers. Slowly mineralizing organic manures result in less accumulation of nitrate in plants.

**Nitrate pollution of ground water :** High soil nitrate level and sufficient downward movement of water to move nitrate below the rooting depth are often

encountered. The consumption of water containing high levels of nitrate – N leads to ‘methaemoglobinemia’ called as ‘blue baby syndrome’ in infants in the age of < 6 months.

The World Health Organisation standard for drinking water is 10 mg NO<sub>3</sub><sup>-</sup>-N/L. An excessive ingestion of nitrates may also increase the risk of cancer in humans due to the formation of nitrosamines.

### **Eutrophication**

It refers to the process of enrichment of surface water bodies with nutrients. The nutrient enrichment of water bodies results in intense proliferation and accumulation of algae and higher aquatic plants in excessive quantities that can result in detrimental changes in the water quality. Estimates indicated that more than 80% of N entering the surface waters originates from agricultural activities. Both N and P are important in stimulating eutrophication.

### **Nitrous oxide emissions from soil in relation to climate change effects**

Nitrous oxide is a trace gas that is formed during the microbial processes of nitrification and denitrification in soils which contributes around 6% to the anthropogenic greenhouse effect according to the estimates of IPCC (Intergovernmental Panel on Climate Change 2001). Up to 50% of the applied nitrogen can be lost through denitrification.

### **Ammonia emissions from soil and environmental degradation**

Out of all fertilizers, urea application is responsible for more than 90% of total contribution in volatilization due to fertilizers. Deep placement of urea in the soil as such or its application before irrigation results in substantial reduction in ammonia volatilization losses from agricultural fields.

**Heavy metal contaminants in fertilizers as soil pollutants** The contamination of soils by heavy metals through fertilizers such as cadmium from phosphatic fertilizers is also receiving increasing attention; rock phosphate being highly potential source, for lead and cadmium. Leafy vegetables accumulate more heavy metals.

Strategies for minimizing the adverse effects of N use on environment

There are two approaches

1. The optimum use of the ability of the crop plants to compete with processes that lead to losses of N from soil – plant system to the environment.
2. The direct reduction in the rate, duration and extent of loss of N to the environment by loss processes themselves.

**Pollution due to pesticides** : The use of pesticides in India is increasing at the rate of 2 to 5 % per annum. Inappropriate pesticide application can also lead to off – target contamination due to spray drift and run off from plants, causing contamination of the soil.

## **Insecticides**

The chlorinated hydrocarbons like DDT persist for a long period in the soil (half life of three years); while organophosphate insecticides persist only for few days or months. The carbamate insecticides are harmful to earthworms.

When pesticide enters the soil, some of it is adsorbed to soil particles, particularly organic matter and some gets dissolved in soil water. The ratio of pesticide concentration in the adsorbed state and the solution phase is defined as the partition coefficient. Pesticides with smaller partition coefficient values are more likely to be leached compared to those with large partition coefficient values. DDT has very high partition coefficient value of 243000 as against aldicarb with 10.

## **Fungicides**

Toxicity from the accumulation of copper based fungicides may render the soil useless for growing the crops.

Oxidation of sulphur contained in the fungicides can alter the chemistry of organic matter in the surface horizon of soils.

On the contrary, other fungicides like captan, carboxin and benomyl are decomposed very rapidly within a few weeks of their application.

## **Herbicides**

In the intensive and diversified crop rotation systems, a herbicide applied to one crop may persist in the soil at concentrations high enough to damage the subsequent sensitive crops eg., Atrazine.

## **Reducing pesticide levels in soils**

Degradation of even the most resistant pesticides is encouraged by conditions that favour overall microbial proliferation in the soil. The biochemical degradation by soil organisms is the single most important method by which pesticides are removed from the soil. The application of large quantities of organic manures can help in this task.

Excessive use of fertilizers and pesticide not only lead to degradation of soil health but also create human health hazards. In this regard, soil organic matter could be an important attribute to be considered to maintain soil quality for sustainable productivity of crops