

LECTURE 1 Soil Chemistry

Until the late 1960s, soil chemistry focused primarily on chemical reactions in the soil that contribute to pedogenesis or that affect plant growth. Since then concerns have grown about environmental pollution, organic and inorganic soil contamination and potential ecological health and environmental health risks. Consequently, the emphasis in soil chemistry has shifted from pedology and agricultural soil science to an emphasis on environmental soil science.

A knowledge of environmental soil chemistry is paramount to predicting the fate, mobility and potential toxicity of contaminants in the environment. The vast majority of environmental contaminants are initially released to the soil. Once a chemical is exposed to the soil environment a myriad of chemical reactions can occur that may increase/decrease contaminant toxicity. These reactions include adsorption/desorption, precipitation, polymerization, dissolution, complexation, and oxidation/reduction. These reactions are often disregarded by scientists and engineers involved with environmental remediation. Understanding these processes enable us to better predict the fate and toxicity of contaminants and provide the knowledge to develop scientifically correct, and cost-effective remediation strategies.

Reduction potential (also known as **redox potential**) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced.

A reduction potential is measured in volts (V). Because the true or absolute potentials are difficult to accurately measure, reduction potentials are defined relative to the standard hydrogen electrode (SHE) which is arbitrarily given a potential of 0.00 volts. **Standard reduction potential** (E^0), is measured under standard conditions: 25°C, a 1M concentration for each ion participating in the

reaction, a partial pressure of 1 atm for each gas that is part of the reaction, and metals in their pure state. Historically, many countries, including the United States, used **standard oxidation potentials** rather than reduction potentials in their calculations. These are simply the negative of standard reduction potentials, so it is not a major problem in practice. However, because these can also be referred to as "redox potentials", the terms "reduction potentials" and "oxidation potentials" are preferred by the IUPAC. The two may be explicitly distinguished in symbols as E_r^0 and E_o^0 .

The relative reactivities of different half-cells can be compared to predict the direction of electron flow. A higher E^0 means there is a greater tendency for reduction to occur, while a lower one means there is a greater tendency for oxidation to occur.

Any system or environment that accepts electrons from a normal hydrogen electrode is a half cell that is defined as having a positive redox potential; any system donating electrons to the hydrogen electrode is defined as having a negative redox potential. E_h is measured in millivolts (mV). A high positive E_h indicates an environment that favors oxidation reaction such as free oxygen. A low negative E_h indicates a strong reducing environment, such as free metals.

Sometimes when electrolysis is carried out in an aqueous solution, water, rather than the solute, is oxidized or reduced. For example, if an aqueous solution of NaCl is electrolyzed, water may be reduced at the cathode to produce $H_{2(g)}$ and OH^- ions, instead of Na^+ being reduced to $Na_{(s)}$, as occurs in the absence of water. It is the reduction potential of each species present that will determine which species will be oxidized or reduced.

Absolute reduction potentials can be determined if we find the actual potential between electrode and electrolyte for any one reaction. Surface polarization interferes with measurements, but various sources give an estimated potential for the standard hydrogen electrode of 4.4V to 4.6V (the electrolyte being positive.).

LECTURE 2 Soil pH and Buffer pH

Soil pH This is a measure of the soil acidity or alkalinity and is sometimes called the soil "water" pH. This is because it is a measure of the pH of the soil solution, which is considered the active pH that affects plant growth. Soil pH is the foundation of essentially all soil chemistry and nutrient reaction and should be the first consideration when evaluating a soil test. The total range of the pH scale is from 0 to 14. Values below the mid-point (pH 7.0) are acidic and those above pH 7.0 are alkaline. A soil pH of 7.0 is considered to be neutral. Most plants perform best in a soil that is slightly acid to neutral (pH 6.0 to 7.0). Some plants like blueberries require the soil to be more acid (pH 4.5 to 5.5), and others, like alfalfa will tolerate a slightly alkaline soil (pH 7.0-7.5).

The soil pH scale is logarithmic, meaning that each whole number is a factor of 10 larger or smaller than the ones next to it. For example if a soil has a pH of 6.5 and this pH is lowered to pH 5.5, the acid content of that soil is increased 10-fold. If the pH is lowered further to pH 4.5, the acid content becomes 100 times greater than at pH 6.5. The logarithmic nature of the pH scale means that small changes in a soil pH can have large effects on nutrient availability and plant growth.

Buffer pH (BpH) This is a value that is generated in the laboratory, it is not an existing feature of the soil. Laboratories perform this test in order to develop lime recommendations, and it actually has no other practical value.

In basic terms, the BpH is the resulting sample pH after the laboratory has added a liming material. In this test, the laboratory adds a chemical mixture called a buffering solution. This solution functions like extremely fast-acting lime. Each soil sample receives the same amount of buffering solution; therefore the resulting pH is different for each sample. To determine a lime recommendation,

the laboratory looks at the difference between the original soil pH and the ending pH after the buffering solution has reacted with the soil. If the difference between the two pH measurements is large, it means that the soil pH is easily changed, and a low rate of lime will suffice. If the soil pH changes only a little after the buffering solution has reacted, it means that the soil pH is difficult to change and a larger lime addition is needed to reach the desired pH for the crop.

The reasons that a soil may require differing amounts of lime to change the soil pH relates to the soil CEC and the "reserve" acidity that is contained by the soil. Soil acidity is controlled by the amount of hydrogen (H^+) and aluminum (Al^{+++}) that is either contained in, or generated by the soil and soil components. Soils with a high CEC have a greater capacity to contain or generate these sources of acidity. Therefore, at a given soil pH, a soil with a higher CEC (thus a lower buffer pH) will normally require more lime to reach a given target pH than a soil with a lower CEC.

Soil Colloids

During physical and chemical weathering processes in which rocks, minerals, and organic matter decompose to form soil, some extremely small particles are formed. Colloidal-sized particles are so minuscule that they do not settle out when in suspension. These particles generally possess a negative charge, which allows them to attract positively charged ions known as cations. Much like a magnet, in which opposite poles attract one another, soil colloids attract and retain many plant nutrients in an exchangeable form. This ability, known as cation exchange capacity, enables a soil to attract and retain positively charged nutrients (cations) such as potassium (K^+), ammonium (NH_4^+), hydrogen (H^+), calcium (Ca^{++}), and magnesium (Mg^{++}). Also, because similar charges repel one another, some of the soluble negatively charged ions (anions), such as nitrate (NO_3^-) and sulfate ($SO_4^{=}$), are not bonded to soil colloids and are more easily leached than their positively charged counterparts.

Organic colloids contribute a relatively large number of negative charges per unit weight compared with the various types of clay colloids. The magnitude of the soil's electrical charge contributed by colloids is an important component of a soil's ability to retain cationic nutrients in a form available to plants.

Cation Exchange Capacity

The ability of a soil to retain cations (positively charged ions) in a form that is available to plants is known as cation exchange capacity (CEC). A soil's CEC depends on the amount and kind(s) of colloid(s) present. Although type of clay is important, in general, the more clay or organic matter present, the higher the CEC.

The CEC of a soil might be compared to the size of a fuel tank on a gasoline engine. The larger the fuel tank, the longer the engine can operate and the more work it can do before a refill is necessary. For soils, the larger the CEC, the more nutrients the soil can supply. Although CEC is only one component of soil fertility, all other factors being equal, the higher the CEC, the higher the potential yield of that soil before nutrients must be replenished with fertilizers or manures.

When a soil is tested for CEC, the results are expressed in milliequivalents per 100 grams (meq/100 g) of air-dried soil. For practical purposes, the relative numerical size of the CEC is more important than trying to understand the technical meaning of the units. In general, soils in the southern United States, where physical and chemical weathering have been more intense, have lower CEC's (1-3 meq/100 g) than soils in the northern United States, where higher CEC's are common (15-25 meq/100 g) because weathering has not been as intense. Soils in warmer climates also tend to have lower organic matter levels, and thus lower CEC's than their northern counterparts.

Soils high in clay content, and especially those high in organic matter, tend to have higher CEC's than those low in clay and organic matter. The CEC of soils in Maryland generally ranges from 1-2 meq/100 g for coarse-textured Coastal Plain

soils to as high as 12-15 meq/100 g for certain Piedmont and Mountain soils. The CEC of most medium-textured soils of the Piedmont region ranges about 8-12 meq/100 g.

There are many practical differences between soils having widely different CEC's. It has already been mentioned that the inherent fertility (exchangeable nutrient content) of soils varies in direct relationship to the magnitude of the CEC. Another important CEC-related property is soil buffering capacity, that is, the resistance of a soil to changes in pH. The higher the CEC, the more resistance soil has to changes in pH. The CEC and buffering capacity are directly related to the amount of liming material required to produce a desired change in pH. Higher CEC soils require more lime than those with low CEC's to achieve the same pH change.

If CEC is analogous to the fuel tank on an engine, soil pH is analogous to the fuel gauge. The gauges on both a large and a small tank might read three fourths full; but, obviously, the larger tank will contain more fuel than the smaller tank. If a soil test indicates that two soils, one with a low CEC and the other with a high CEC, have the same low pH, indicating that they both need lime, the one with the higher CEC will require more liming material to bring about the desired pH change than will the one with the lower CEC. The reason for this difference is that there will be more exchangeable acidity (hydrogen and aluminum) to neutralize in the high CEC soil than in the lower CEC soil. Thus, a soil high in clay or organic matter will require more liming material to reduce soil acidity (and raise the pH) than a low organic matter sandy soil will.

3 Soil pH and Percent Base Saturation

Soil pH is one of the most important characteristics of soil fertility because it has a direct impact on nutrient availability and plant growth.

The pH scale is a logarithmic expression of hydrogen ion $[H^+]$ concentration in the soil solution. Mathematically, pH equals $-\log [H^+]$ (the negative logarithm of the hydrogen ion concentration). The pH scale ranges from 0 to 14. A soil pH value of 7.0 is neutral. At pH 7.0, the hydroxyl ion $[OH^-]$ and the hydrogen ion $[H^+]$ concentrations exactly balance one another. At pH values below 7.0, soils are acidic because the $[H^+]$ ion concentration is greater than the $[OH^-]$ ion concentration. At pH values above 7.0, soils are basic because there are more $[OH^-]$ than $[H^+]$ ions. Most agricultural soils in Maryland have a pH range between 4.5 and 7.5. Although there are some exceptions, the preferred pH range for most plants is between 5.5 and 7.0. Legumes prefer higher pH's (pH values of 6.2-7.0) than do grasses (pH values of 5.8-6.5).

Because the pH scale is logarithmic rather than linear, the difference in acidity between each pH value varies by a factor of 10, not 1. Therefore, a soil with a pH of 5.0 is 10 times more acid than a soil with a pH of 6.0. A soil with a pH of 4.0 will be 100 times more acid than a soil with a pH of 6.0 and 1,000 times more acid than a soil at pH 7.0. This is an extremely important factor to consider when developing liming recommendations to correct acid soils.

Soil pH also reflects percent base saturation (% BS) of the CEC. This term refers to the relative number (percentage) of the CEC sites on the soil colloids that are occupied by bases such as calcium (Ca^{++}), magnesium (Mg^{++}), and potassium (K^+). In general, at pH 7.0 the base saturation is 100 percent. By rule of thumb, for every one-half unit drop in soil pH, the % BS declines by about 15 percent (pH 6.5 = 85 percent BS, pH 6.0 = 70 percent BS, pH 5.5 = 55 percent BS, and so forth). This information can be useful to calculate the approximate amounts of available nutrients present in a soil at a given pH. Ag-Lime Recommendations

To predict how much liming material (calcium and/or magnesium carbonate) will be necessary to change the pH of a soil from one level to another, other information is needed in addition to the soil's pH. It is also necessary to estimate the soil's buffering capacity, that is, the soil's ability to resist a change in pH.

There are several ways to estimate a soil's buffering capacity so that a liming recommendation can be developed. One of the simplest techniques for Maryland soils is to determine soil texture. Research has shown that, with just a few exceptions, for soils within a particular physiographic region, a positive direct relationship exists between soil texture and the CEC. Thus, as soil texture varies from coarse to fine on the Coastal Plain (for example, from sand to silt loam to loam to clay loam), CEC and buffering capacity increase. Simplified tables and equations have been developed to estimate the amount of liming material needed to achieve a desired pH goal when the current soil pH and texture are known.

Another technique that some soil-testing laboratories use to develop an ag-lime recommendation is known as the lime requirement test. With this procedure, in addition to determining the normal water pH, a second pH measurement, known as the buffer pH, is required. For a normal water pH reading, the soil is allowed to equilibrate in distilled water. A pH meter is used to measure how much the soil changed the pH of the unbuffered distilled water. The buffer pH differs in that the soil is allowed to equilibrate in a specially prepared solution that has previously been buffered to a known pH. The buffer solution, as well as the soil, resists changes in pH. A pH meter is used to determine how much the soil was able to overcome the resistance of the buffer solution to a change in pH.

The buffer pH technique directly reflects the soil's buffering capacity and the result can be used in a formula to calculate the amount of ag-lime required to achieve the desired change in pH.

Nutrient Availability and Soil pH

Nutrient availability is influenced strongly by soil pH. This is especially true for phosphorus, which is most available between pH 6.0 and 7.5. Elements such as iron, aluminum, and manganese are especially soluble in acid soils. Above pH 7.0, calcium, magnesium, and sodium are increasingly soluble.

Phosphorus is particularly reactive with aluminum, iron, and calcium. Thus, in acid soils, insoluble phosphorus compounds are formed with iron, aluminum, and manganese. At pH levels above 7.0, the reactivity of iron, aluminum, and manganese is reduced, but insoluble phosphorus compounds containing calcium and magnesium can become a problem. To maximize phosphorus solubility and hence availability to plants, it is best to maintain soil pH within the range of 6.0 to 7.5. Over liming can result in reduced phosphorus availability just as quickly as under liming.

In general, the availability of nitrogen, potassium, calcium, and magnesium decreases rapidly below pH 6.0 and above pH 8.0. Aluminum is only slightly available between pH 5.5 and pH 8.0. This is fortunate because, although plants require relatively large quantities of nitrogen, phosphorus, and potassium, aluminum in appreciable quantities can become toxic to plants. If managed properly, soil pH is a powerful regulator of nutrient availability. Manganese, zinc, and iron are most available when soil pH is in the acid range. As the pH of acid soil approaches 7.0, manganese, zinc, and iron availability decreases and deficiencies can become a problem, especially on those soils that do not contain appreciable amounts of these elements. These micronutrients frequently must be supplemented with fertilizers when soil levels are low, when over liming has occurred, or when soil tests indicate a deficiency. There is a delicate balance between soil pH and nutrient availability. It is important that soils be tested regularly and that the pH be maintained in the recommended range to achieve maximum efficiency of soil and fertilizer nutrients.

Learning objective :

To understand the importance of soil fertility

To study the essential nutrients in plant growth

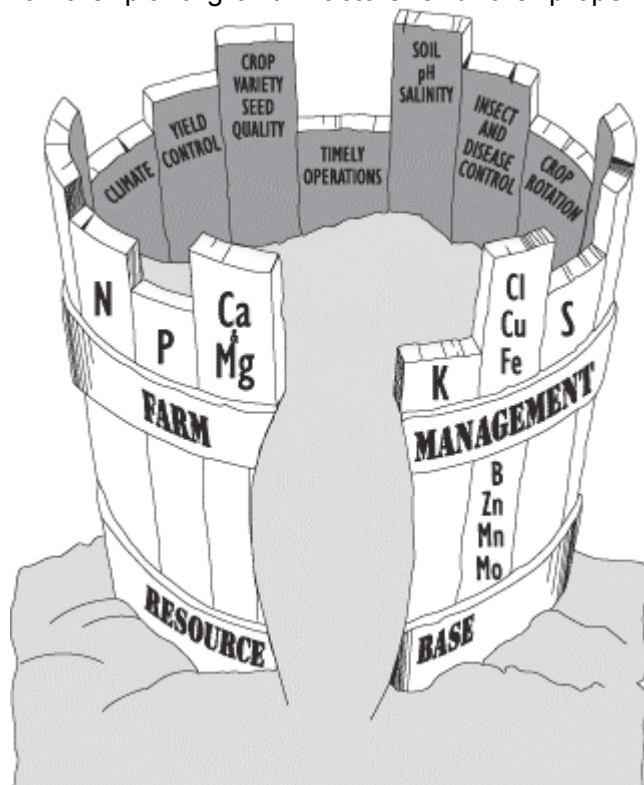
Crops depend on extrinsic and intrinsic factors for their growth and environment to provide them with basic necessities for photosynthesis. These essential plant growth factors include:

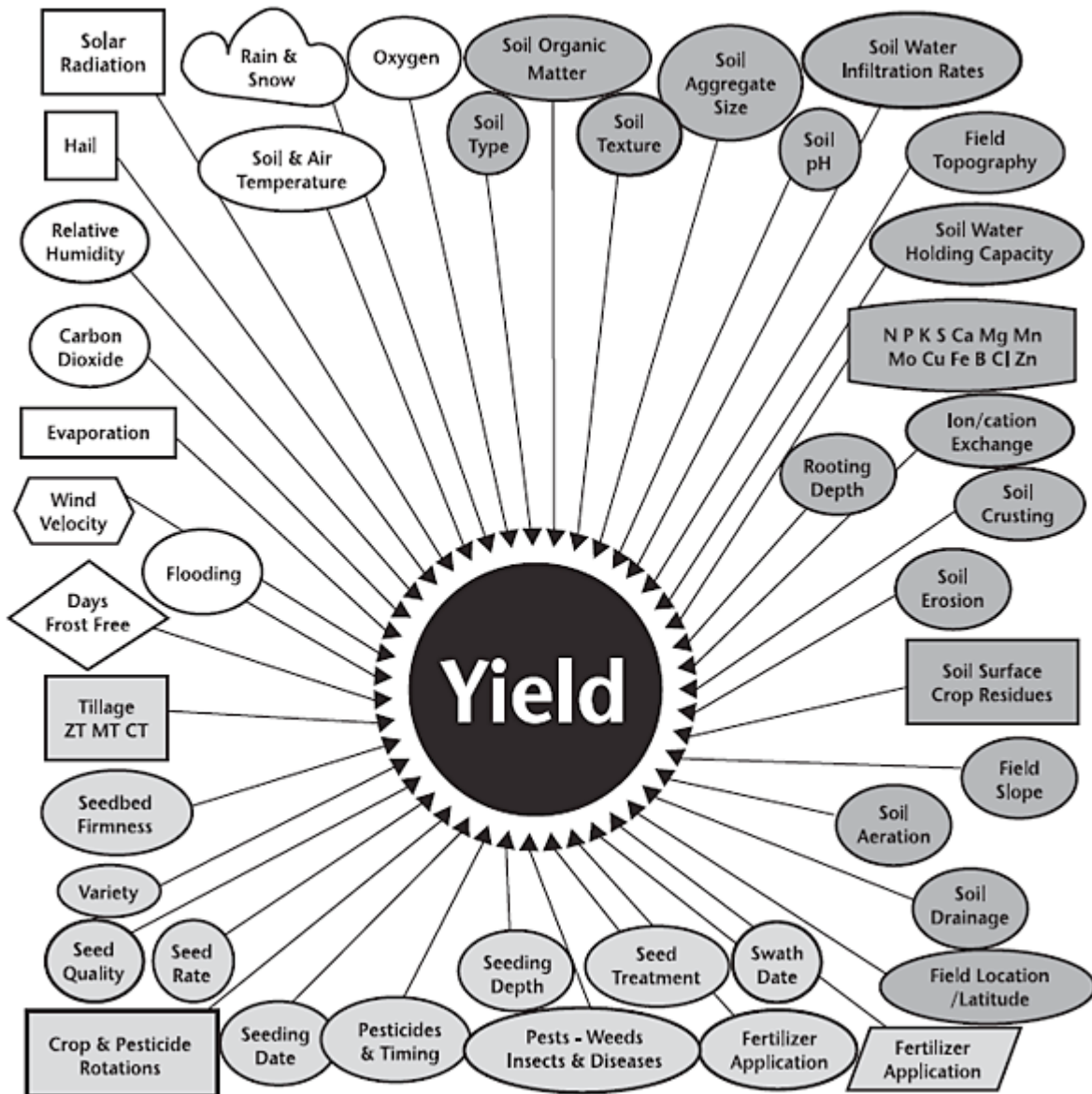
- light
- heat
- air
- water
- nutrients
- physical support

If any one factor, or combination of factors, is in limited supply, plant growth will be adversely affected. The importance of each of the plant growth factors and the proper combination of these factors for normal plant growth is best described by the principle of limiting factors. This principle states: "The level of crop production can be no greater than that allowed by the most limiting of the essential plant growth factors." The principle of limiting factors can be compared to that of a barrel having staves of different lengths with each stave representing a plant growth factor.

Crop yield and quality depends upon the essential growth factors and the many interrelated soil, plant, environmental and agronomic factors or variables. Within this system, some of these factors cannot be controlled; others can be controlled and are manageable.

Soil is one of the key factors affecting plant growth as observed in the figure. The major functions of the soil are to provide plants with nutrients, water and oxygen.





Crop Production Factors

FAO has listed seven important soil qualities which affect crop growth as given below.

Soil Qualities	Soil Characteristics
SQ1 Nutrient availability	Soil texture, soil organic carbon, soil pH, total exchangeable bases
SQ2 Nutrient retention capacity	Soil Organic carbon, Soil texture, base saturation, cation exchange capacity of soil and of clay fraction
SQ3 Rooting conditions	Soil textures, bulk density, coarse fragments, vertic soil properties and soil phases affecting root penetration and soil

		depth and soil volume
SQ4	Oxygen availability to roots	Soil drainage and soil phases affecting soil drainage
SQ5	Excess salts.	Soil salinity, soil sodicity and soil phases influencing salt conditions
SQ6	Toxicity	Calcium carbonate and gypsum
SQ7	Workability (constraining field management)	Soil texture, effective soil depth/volume, and soil phases constraining soil management (soil depth, rock outcrop, stoniness, gravel/concretions and hardpans)

Soil fertility is the key to sustainable agriculture. Soil fertility is defined in several ways.

Soil fertility

“Soil fertility is the ability of the soil to supply essential plant nutrients during growth period of the plants, without toxic concentration of any nutrients”. i.e **“the capacity of soil to supply nutrient in available to crop”**.

Soil productivity

“Soil productivity is ability of soil to produce a particular crop or sequence of crops under a specified mgt system” i.e **the crop producing capacity of soil”**.

All the productive soils are fertile but all the fertile soils may not be productive

Sometimes even if the soil is fertile, they are subjected to drought or other unsatisfactory growth factors or management practices.

History of development of soil fertility

Francis Bacon (1591- 1624) suggested that the principle nourishment of plants was water and the main purpose of the soil was to keep plants erect and to protect from heat and cold.

Jan Baptiste **Van Helmont** (1577 – 1644) was reported that water was sole nutrient of plants.

Robert Boyle (1627 – 1691) an England scientist confirmed the findings of Van Helmont and proved that plant synthesis salts, spirits and oil etc from H₂O.

Anthur Young (1741 – 1820) an English agriculturist conducted pot experiment using Barley as a test crop under sand culture condition. He added charcoal, train oil, poultry dung, spirits of wine, oster shells and numerous other materials and he conducted that some of the materials were produced higher plant growth.

Priestly (1800) established the essentiality of O₂ for the plant growth.

J.B. Boussingault (1802-1882) French chemist conducted field experiment and maintained balance sheet. He was first scientist to conduct field experiment. He is considered as **father of field experiments**.

Justus Von Liebig (1835) suggested that

- a. Most of the carbon in plants comes from the CO_2 of the atmosphere.
- b. Hydrogen and O_2 comes from H_2O .
- c. Alkaline metals are needed for neutralization of acids formed by plants as a result of their metabolic activities.
- d. Phosphorus is necessary for seed formation.
- e. Plant absorb every thing from the soil but excrete from their roots those materials that are not essential.

The field may contain some nutrient in excess, some in optimum and some in least, but the limiting factor for growth is the least available nutrient. **The law of Mn**, stated by **Liebig in 1862**, is a simple but logical guide for predicting crop response to fertilization. This law states that, "the level of plant production cannot be greater than that allowed by the most limiting of the essential plant growth factors". The contributions made by Liebig to the advancement of agriculture were monumental and he is recognized as the **father of Agricultural chemistry**.

J.B. Lawes and J. H. Gilbert (1843) established **permanent manurial experiment** at Rothamsted Agricultural experiment station at England. They conducted field experiments for twelve years and their findings were

- a. Crop requires both P and K, but the composition of the plant ash is no measure of the amounts of these constituents required by the plant.
- b. No legume crop require N. without this element, no growth will be obtained regardless of the quantities of P and K present. The amount of ammonium contributed by the atmosphere is insufficient for the needs of the crop.
- c. Soil fertility can be maintained for some years by chemical fertilizers.
- d. The beneficial effect of fallow lies in the increases in the available N compounds in the soil.

Robert Warrington England showed that the nitrification could be supported by carbon disulphide and chloroform and that it would be stopped by adding a small amount of unsterilized soil. He demonstrated that the reaction was two step phenomenon. First NH_3 being converted to nitrites and the nitrites to nitrates.

Essential and Beneficial elements

"A mineral element is considered to be essential for plant growth and development if the element is involved in plant metabolic functions and the plant cannot complete its life cycle without the element".

There are seventeen essential elements required for plant growth viz., **C, H, O, N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Mo, Cl, Ni**,

The following is the essentiality criteria described by Arnon and Stout (1939)

1. A plant must be unable to complete its life cycle in the absence of the mineral element.
2. The function of the element must not be replaceable by another mineral element.
3. The element must be directly involved in plant metabolism.

Beneficial Nutrients/Elements: Beneficial elements are the mineral elements that stimulate the growth and exhibit beneficial effects at very low concentration or which are essential only for certain plant species or under specific conditions are called as “beneficial elements”. Eg. Na, Va, Co, Si

D.J.Nicholas coined the term “functional or metabolic nutrient”

Any mineral element that functions in plant metabolism, whether or not its action is specific. (Cl, Si, Na, Va, Co, Se)

The following table gives the essentiality of elements established by different scientists

Essentiality of the elements established by

Carbon	: Priestly (1800)
Nitrogen	: Theodore De saussure (1804)
Ca, Mg, K, S	: Carl sprengel (1839)
Phosphorus	: Von Liebig (1844)
Iron (Fe)	: E. Greiss (1844)
Manganese (Mn)	: J.S. Hargue (1922)
Zinc(Zn)	: Sommer and Lipman (1926)
Copper (Cu)	: Sommer, Lipman and Mc Kenny (1931)
Molybdenum (Mo)	: Arnon and Stout (1939)
Sodium (Na)	: Brownell and wood (1957)
Cobalt(Co)	: Ahamed and Evans (1959)
Boron(B)	: Warring ton (1923)
Chlorine (Cl)	: Broyer (1954)
Nickel	: Brown et.al.(1987)

Classification of Essential Elements

- 1) Based on the amount required by the plant
 - i) Major nutrients – required in large quantities eg. N,P,K
 - ii) Secondary nutrients – required in lesser quantities compared to Major nutrients eg. Ca,Mg,S
 - iii) Micronutrients- required in trace quantities eg. Fe, Mn, Zn, Cu, B, Mo

Classification based on the role of element in plant system

(According to TRUOG, 1954)

- | | |
|------------------------------------|-----------------------------|
| Structural Elements | : C, H, O |
| ii). Accessory structural elements | : N. P. S |
| iii). Regulator & Carriers | : K, Ca, Mg |
| iv). Catalyst & Activators | : Fe, Mn, Zn, Cu, Mo, Cl, B |

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Questions to ponder

- 1) How are the essential elements essential to crops?
- 2) Which elements are considered to be essential for crop growth?
- 3) Why is some nutrient deficiencies exhibited in older leaves, while other nutrient deficiencies show up first on newer leaves?
- 4) What are beneficial elements?
- 5) What is the difference between major and micronutrient?

05.

Forms of nutrients in soil and their functions in plants

Learning objective :

To know the functions of each nutrient in plant

Primary or major nutrients: are those nutrients required relatively in large quantities by the plants for its growth and development. Ex: N, P and K.

Secondary nutrients: are those nutrients which are required by plants in moderate amounts and given secondary importance in its supply and management.

Ex: Ca, Mg and S.

Micronutrients: The nutrients which are utilized by plants in relatively smaller quantities for their growth and development, but these are equally important & essential to plants as macronutrients.

Ex: Fe, Mn, Zn, Cu, B, Mo, Cl and Ni.

Plant Nutrients

Sixteen elements are considered essential for plants. They are grouped based on their relative abundance in plants.

Many non-essential elements are also found in plants that account for over 60 elements. Al is absorbed when soil solution is rich in Al ions. When plant materials is burned, the remaining plant ash contains all the essential and non-essential elements except C, H, O, N, S. Macro nutrients are absorbed in 30-100 times in proportion to that of micronutrients.

1 (3/4)

Essential Nutrients

Non-mineral Nutrients	Macronutrients		Micronutrients	
	Primary	Secondary	By all plants	Some

C	N	Ca	Fe	B	Na
H	P	Mg	Mn	Cl	Co
O	K	S	Zn	Mo	Va
			Cu		Ni
					Si

Chemical nature

Metals	K, Ca, Mg, Fe, Mn, Zn, Cu,
Non-metals	C, H, O, N, P, S, Cl

The plant content of mineral elements is affected by many factors and their concentration in crops varies considerably.

Nutrient		Relative concentration (Times)	Concentration (%)
Primary	N, K	400-1000	1-1.5
	P	30	0.1-0.3
Secondary	Ca, Mg	100-200	0.2-0.5
	S	30	0.1
Micro	Fe, Mn, B	1-2	0.002-0.01
	Others	<1	<0.002

Plant Nutrients

Concentration, Mobility, forms, functions

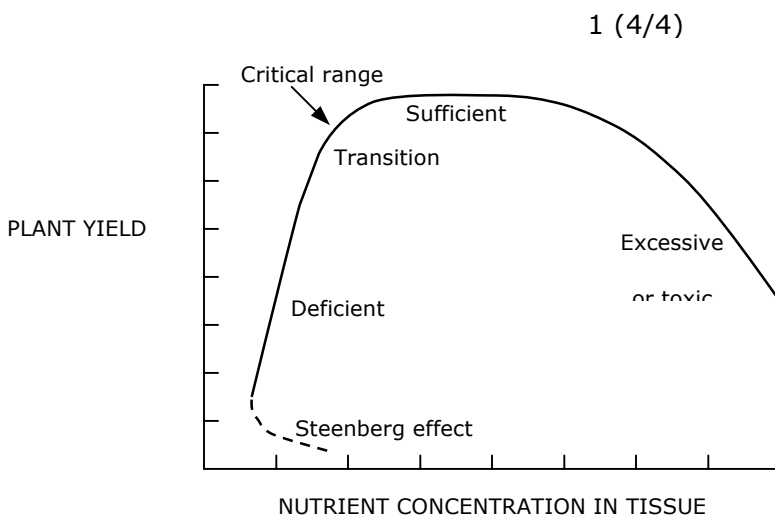
A mineral element is considered essential to plant growth and development if the element is involved in plant metabolic functions and the plant cannot complete its life cycle without the element. Terms commonly used to describe level of nutrients in plants are

Deficient

When the concentration of an essential element is low enough to limit yield severely and distinct deficiency symptoms are visible then that element is said to be deficient. Extreme deficiencies can result in plant death. With moderate or slight deficiencies, symptoms may not be visible, but yields will still be reduced.

Critical range

The nutrient concentration in the plant below which a yield response to added nutrient occurs. Critical level or ranges vary among plants and nutrients but occur somewhere in the transition between nutrient deficiency and sufficiency.



Sufficient

Concentration range in which added nutrients will not increase yield but can increase nutrient concentration. The term luxury consumption is used to describe nutrient absorption by the plant that does not influence yield.

Excessive or toxic

When the concentration of essential or other elements is high enough to reduce plant growth and yield then it is said to be toxic. Excessive nutrient concentration can cause an imbalance in other essential nutrients, which also can reduce yield

Forms of nutrients for Plant absorption	
N	NH_4^+ , NO_3^- , organic N
P	H_2PO_4^- (Primary) and HPO_4^{2-} (Secondary) Orthophosphates
K	K^+
Ca	Ca^{++}
Mg	Mg^{++}
S	SO_3^- (Sulphite) and SO_4^-
Fe	Fe^{++} (Ferrous), Fe^{+++} (Ferric)
Mn	Mn^{++} (Manganous) and Mn^{+++} (Manganic)
Zn	Zn^{++}
Cu	Cu^+ (Cuprous) and Cu^{++} (Cupric)
B	BO_3^- and other forms
Mo	MoO_4^{--} (Molybdate)
Cl	Cl^-

Concentration and plants yield

Yield is severely affected when a nutrient is deficient. When deficiency is corrected, growth increases more rapidly. Under severe deficiency, rapid increase in growth with added nutrient can cause a small decrease in nutrient concentration due to dilution effect. This is called the **Steenberg effect**

Luxury consumption

Nutrient sufficiency occurs over a wide concentration range, wherein yield is unaffected. Increase in nutrient concentration above the critical range indicates that the plant is absorbing nutrient above that needed for maximum yield.

This **luxury consumption** is common in most plants. Elements absorbed in excessive quantities

can reduce plant yield directly through toxicity or indirectly by reducing concentration of other nutrient below critical ranges.

Functions of nutrients in plants:

Nutrient		Functions
Major nutrients		
Nitrogen		Basic component of proteins and chlorophyll (the pigment that gives plants their green colour). Plays an essential role in plant growth. Also feeds microorganisms in the soil
Phosphorus		Plays an important role in root growth and promotes the establishment of young plants, flowering, fruiting and ripening, photosynthesis, respiration and overall plant growth.
Potassium		Moves through the plant. Promotes the movement of sugars, turgor and stem rigidity. Also increases the plant's overall resistance to cold, diseases, insect pests, etc. Promotes the formation of flower buds, the hardening-off of woody plants and fruiting.
Secondary nutrients		
Calcium		Plays a vital role in plant structure, because it is part of cell walls and holds them together. Promotes the development of the root system and the ripening of fruit and seeds. Found in the growing parts of plants (apex and buds).
Magnesium		An important part of chlorophyll. Helps fruit ripen and seeds germinate. Reinforces cell walls and promotes the absorption of phosphorous, nitrogen and sulphur by plants
Sulphur		A component of several proteins, enzymes and vitamins. Contributes to chlorophyll production. Helps plants absorb potassium, calcium and magnesium.
Micronutrients		

Iron		Essential to chlorophyll production. Also contributes to the formation of some enzymes and amino acids.
Boron		Essential to overall plant health and tissue growth. Promotes the formation of fruit and the absorption of water.
Manganese		Promotes seed germination and speeds plant maturity. Plays an important role in photosynthesis by contributing to chlorophyll production. Essential for nitrogen assimilation and protein formation.
Molybdenum		Essential for nitrogen assimilation by plants and nitrogen fixation by bacteria. This means that it is needed for the production of nitrogen-based proteins.
Chlorine		Stimulates photosynthesis.
Copper		Activates various enzymes. Also plays a role in chlorophyll production
Zinc		Plays an important role in the synthesis of proteins, enzymes and growth hormones.
Nickel		Key component of selected enzymes involved in N metabolism and biological N fixation.
Beneficial elements		
Silicon		Strengthens cell walls, energy transfer & drought resistance Reduces water loss & prevents fungal infection.
Cobalt		Essential in N fixation
Sodium		Na replaces K in certain functions in halophytes plants For C4 plants having dicarboxylic photosynthetic pathway
Vanadium		Essential for green algae

Forms of elements in Mineral soil

Macro elements are available in (1) Solid (2) Cations (3) Cations in soil solution

Nutrients	Mineral / solid	Cations	Soil solution as ions
N	Organic compounds and Amino acids	NH_4^+	NH_4^+ , NO_2^- , NO_3^-
P	Organic compounds, nucleic acid and inorganic compounds. Ca, Fe, Al, PO_4 's	-	H_2PO_4^- , HPO_4^-
K	Feldspar, mica, silicate clays	K^+	K^+
Ca	Feldspar, hornblende, lime stone	Ca^{2+}	Ca^{2+}
Mg	Mica, Hornblende, lime stone	Mg^{2+}	Mg^{2+}
S	Organic sources – protein, amino acids inorganic sources – Gypsum, pyrites .	- -	HSO_4^- , SO_3^{2-} SO_4^{2-}

Forms of nutrient element absorbed by plants

Nutrient element	Forms absorbed
C	Mainly through leaves - CO_2
H	HOH (Hydrogen from H_2O) – H^+
O	CO_2 mainly through leaves – O_4^{2-} , OH^- , CO_3^{2-}
N	NH_4^+ , NO_3
K	K^+
Ca	Ca^{2+}
Mg	Mg^{2+}
S	SO_4^{2-}
Fe	Fe^{2+} (Ferrous), Fe^{3+} (ferric)
Mn	Mn^{2+} (Manganous), Mn^{4+} (Manganic)

Zn	Zn^{2+}
Cu	Cu^+ (cuprous), Cu^{2+} (Cupric)
Co	CO^{2+}
Na	Na^+
Si	$\text{Si}(\text{OH})_4$
Cl	Cl^-
B	H_3BO_3 (Boric acid) H_2BO_3^- (Borate)
Mo	MoO_4^{2-}

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<http://edis.ifas.ufl.edu/hs1191>

Questions to ponder

- 1) How will you differentiate between N and K deficiencies of corn visually?
- 2) What is luxury consumption?
- 3) Which element is absorbed both in anionic and cationic forms?
- 4) Which element is specifically involved in nitrate reduction in plants?
- 5) Name the nutrients whose deficiencies are first exhibited in the apical region of the growing plant?

06.

Mechanism of nutrient transport in plants

Learning objectives

- a. Understand ways in which nutrients in the soil reach plant roots
- b. To know how plant roots absorb nutrients and move inside plants

Nutrients must reach the surface of a root for plant uptake of essential elements to occur. There are three major mechanism of movement of ions from soil to roots. They are

Root interception

Root interception occurs when a nutrient comes into physical contact with the root surface. As a general rule, the occurrence of root interception increases as the root surface area and mass increases, thus enabling the plant to explore a greater amount of soil. Root interception may be enhanced by mycorrhizal fungi, which colonize roots and increase root exploration into the soil. Root interception is responsible for an appreciable amount of **calcium** uptake, and some amounts of **magnesium**, **zinc** and **manganese**. The CEC of roots for monocots is 10 - 30 meq/100 g and takes up monovalent cations more readily and that of Dicots is 40 - 100 meq/100 g and takes up divalent cations more readily. The quantity of nutrients intercepted by roots depends on the soil concentration of nutrients and volume of soil displaced by root system.

Factors affecting root interception

- a. Anything that restricts root growth
 - i. Dry soil
 - ii. Compaction
 - iii. Low soil pH
 - iv. Poor aeration
 - v. Root disease, insects, nematodes
 - vi. High or low soil temperature
- b. Root growth is necessary for all three mechanisms of nutrient supply, but absolutely essential for root interception to occur

Mass flow:

Mass flow occurs when nutrients are transported to the surface of roots by the movement of water in the soil (i.e. percolation, transpiration, or evaporation). The rate of water flow governs the amount of nutrients that are transported to the root surface. Therefore, mass flow decreases as soil water decreases. Most of the **nitrogen**, **calcium**, **magnesium**, **sulfur**, **copper**, **boron**, **manganese** and **molybdenum** move to the root by mass flow. Quantity of nutrients transported is proportional to:

- i. Rate of flow (volume of water transpired)
- ii. Solution concentration of nutrient

Nutrients supplied primarily by mass flow are considered mobile nutrients. e.g. N, S, B

Factors affecting mass flow

- a. Soil water content
 - i. Dry soil where there is no nutrient movement
- b. Temperature
 - i. Low temperature reduces transpiration and evaporation
- c. Size of root system
 - i. Affects water uptake and therefore movement
 - ii. Root density much less critical for nutrient supply by mass flow than for root interception and diffusion

Diffusion:

Diffusion is the movement of a particular nutrient along a concentration gradient. When there is a difference in concentration of a particular nutrient within the soil solution, the nutrient will move from an area of higher concentration to an area of lower concentration. This phenomenon is observed when adding sugar to water. As the sugar dissolves, it moves through parts of the water with lower sugar concentration until it is evenly distributed, or uniformly concentrated. Diffusion delivers appreciable amounts of **phosphorus, potassium, zinc, and iron** to the root surface. Diffusion is a relatively slow process compared to the mass flow of nutrients with water movement toward the root. Nutrients supplied primarily by diffusion are considered immobile nutrients e.g. P, K

Factors affecting diffusion

- a. Fick's law is given as $dC/dt = D_e * A * dC/dX$

dC/dt = diffusion rate (change in concentration over time)

D_e = effective diffusion coefficient

A = cross sectional area for diffusion

dC/dX = concentration gradient (change in concentration over distance)

Diffusion rate is directly proportional to concentration gradient, diffusion coefficient, and the area available for diffusion to occur

b. Effective diffusion coefficient

Effective diffusion coefficient $D_e = D_w * q * (1/T) * (1/b)$ where

D_w = diffusion coefficient in water

q = volumetric soil water content

T = tortuosity factor

b = soil buffering capacity

- a. Diffusion coefficient in water (D_w)
 - i. Includes a temperature factor

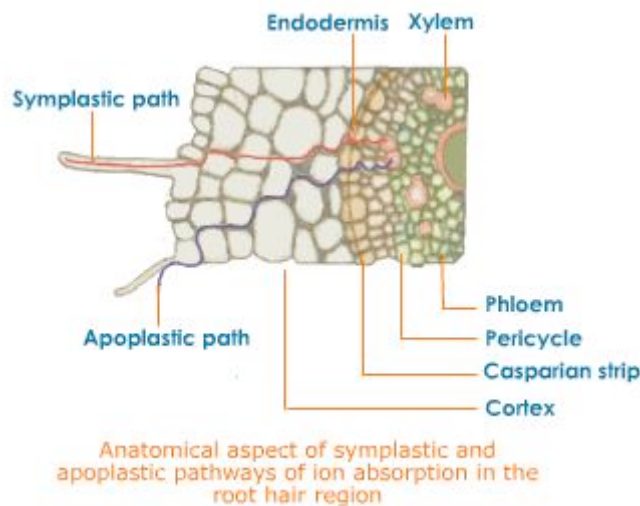
- ii. Colder = slower diffusion
- b. Soil water content
 - i. Drier soil = slower diffusion
 - ii. Less water = less area to diffuse through
- c. Tortuosity
 - i. Pathways through soil are not direct
 - ii. Around soil particles, through thin water films
 - iii. Affected by texture and water content
 - 1. More clay = longer diffusion pathway
 - 2. Thinner water films = longer path
- d. Buffering capacity
 - i. Nutrients can be removed by adsorption as they move through soil, reducing diffusion rate
- c. How far can nutrients diffuse in a growing season?**
 - a. Diffusion distances are very short
 - i. K ~ 0.2 cm
 - ii. P ~ 0.02 cm
 - b. Size and density of plant root systems is very important for nutrients supplied by diffusion
 - c. Has implications for fertilizer placement

Ion traffic into the root

Mineral nutrients absorbed from the root has to be carried to the xylem. This transport follows two pathways namely apoplastic pathway and symplastic pathway.

In apoplastic pathway, mineral nutrients along with water moves from cell to cell through spaces between cell wall by diffusion. The ions, which enter the cell wall of the epidermis move across cell wall of cortex, cytoplasm of endodermis, cell walls of pericycle and finally reach the xylem.

In symplastic pathway, mineral nutrients entering the cytoplasm of the epidermis move across the cytoplasm of the cortex, endodermis of pericycle through plasmodesmata and finally reach the xylem.



Translocation of solutes

P.R. Stout and Dr. Hoagland have proved that mineral nutrients absorbed by the roots are translocated through the xylem vessel. Mineral salts dissolved in water moves up along the xylem vessel to be transported to all the parts of the plant body. Translocation is aided, by transpiration. As water is continuously lost by transpiration on the upper surfaces of the plant, it creates a transpirational pull, by which water along with mineral salts is pulled up along the xylem vessel.

Active absorption of energy can be achieved only by an input of energy. Following evidences show the involvement of metabolic energy in the absorption of mineral salts.

- Higher rate of respiration increases the salt accumulation inside the cell.
- Respiratory inhibitors check the process of salt uptake.
- By decreasing oxygen content in the medium, the salt absorption is also decreased.

These evidences indicate that salt absorption is directly connected with respiratory rate and energy level in the plant body, as active absorption requires utilization of energy.

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http://www.ctahr.hawaii.edu/mauisoil/c_relationship.aspx

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Questions to ponder

- 1) What is contact exchange?
- 2) What soil factors influence diffusion of nutrients to roots?
- 3) What is diffusion?
- 4) Why is anion adsorption little important in agricultural soils?
- 5) What is the mechanism of active absorption of iron by roots?

Nitrogen – Transformation, factors affecting nitrogen availability ,deficiency and toxicity symptoms

Learning objectives

- a. To understand the transformation of nitrogen
- b. To know the factors affecting the availability of nitrogen
- c. To understand the deficiency symptoms of Nitrogen and corrective measures

Nitrogen

The cheap source of N is the crop residues in temperate region. In tropical soils, the total N content is 0.03 - 0.1 %. Rainfall is also source of N at 4.6 kg of N / ha is received $\text{ha}^{-1} \text{yr}^{-1}$. It is converted to NO_3 during lightning addition of organic matter and fertilizer is other major sources. Nitrogen is an essential constituent of protein and also other non protein compounds of great physiological importance in plant metabolism. It is an integral part of chlorophyll, which is primary observer of light energy needed for photosynthesis. Nitrogen also imparts vigorous vegetative growth and governs the utilization of P,K and other elements

Forms of soil nitrogen

Inorganic forms N

1. Ammonium NH_4^+
2. Nitrite NO_2^-
3. Nitrate NO_3^-
4. Elemental N (No)

Organic forms of soil

- Amide form (NH_2)
- Plant absorbs N as both
- NH_4^+ , NO_3^- .

Losses of Nitrogen

1. Crop removal
2. Leaching (or) drainage (11-18% loss)
3. Gaseous losses as NH_4 or elemental N_2
4. Volatilization.
5. Erosion ($8 - 15 \text{ kg ha}^{-1} \text{yr}^{-1}$).
6. Ammonia fixation by clays
7. Immobilization in organic materials.

N transformations in soils

- a. N - Mineralisation
- b. Aminisation
- c. Conversation of urea

- d. N Immobilization.
- e. N factor
- f. Ammonification.
- g. Nitrification
- h. Denitrification
- i. Organic fixation
- j. Elemental N loss.
- k. Nitrogen cycle.

N transformations in soils

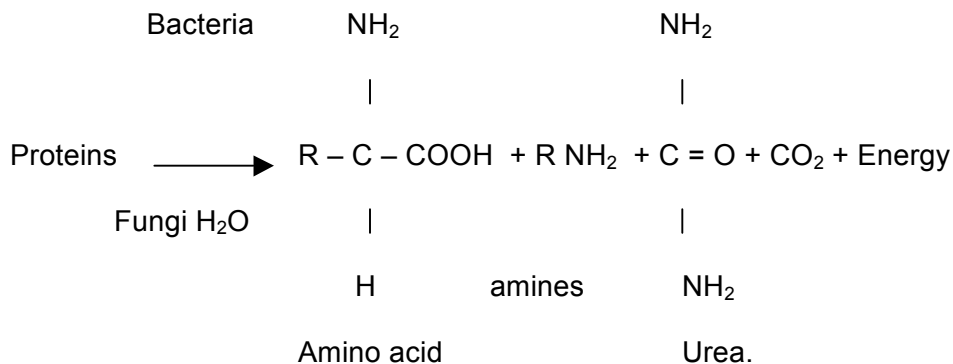
Nitrogen mineralization

Mineralization is the conversion of organic N to NH_4^+ as a result of microbial decomposition. Mineralization increases with a rise in temperature and is enhanced by adequate, although not excessive, soil moisture and a good supply of O_2 . Mineralization of organic N involves in two reactions.

i.e 1) Aminization 2) Ammonification.

Aminisation

Aminisation is the decomposition of proteins and the release of amines, amino acids and urea is called aminisation.



The initial step in the decomposition of organic matter by the enzymatic digestion of proteins into amino acids like, peptones and amino acid. **Under aerobic** protolysis the major end products are CO_2 $(\text{NH}_4)_2\text{SO}_4$ and H_2O . Under anaerobic conditions the end products are ammonia, amides, CO_2 and H_2S .

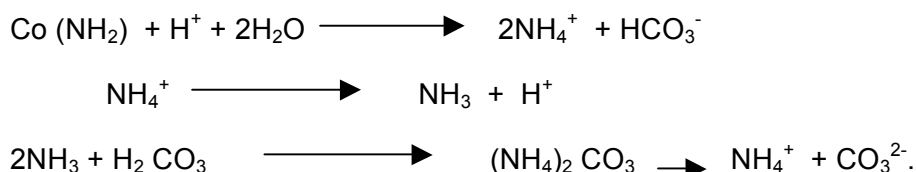
The organic compounds and proteins are mainly decomposed by various species of Pseudomonas,

Bacilli, clostridium, serrotia, Micrococcus

Generally in the neutral and sodic soils, bacteria are active and in acidic soils fungi are active.

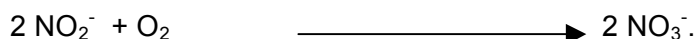
Conversion of urea

Urea is a product of ammonization. The hydrolysis of urea by the action of urease enzyme is effected by Bacilli micrococcus, Pseudomonas, clostridium, Aeromobactor and corynebacter.



The optimum H₂O holding capacity for these reactions is 50 – 75 and optimum temperature is 30 – 50°C.

The NH₄ can be utilized by microorganisms and root of higher plants. Some of the released NH₃ is fixed by clay especially illite. A major portion is oxidized to nitrate form. In the second reaction NO₂⁻ is further oxidized to NO₃⁻ by nitrobacter



Nitrogen immobilization

“Immobilisation is the process of conversion of inorganic N (NH₄⁺ or NO₃⁻) to organic N and it is basically the reverse of N mineralization”.

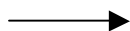
The Microorganisms accumulate NH₄ N and NO₃ – N in the form of protein, nucleic acid and other complexes. If C:N ratio is wider than 30, it favours immobilization and lesser C:N ratio encourage mineralization.

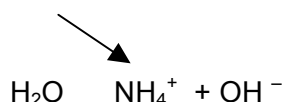
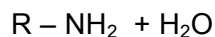
N factor

N factor is the No of units of inorganic nitrogen immobilized for each 100 units of materials under going decomposition”. The average values for the nitrogen factor vary from 0.1 or < to 1.3.

Ammonification

“Amines and Aminoacids produced during amination of organic N are decomposed by other heterotrophs with release of NH₄⁺ is termed Ammonification”





Nitrification

Nitrification is the process of biological oxidation by which the NH_4^+ form of N converts to nitrate form of N. There are two steps. (a) NH_4^+ is converted first to NO_2^- and then to NO_3^- .

Nitrosomonas



Nitrosomonas are obligate autotrophic bacteria that obtain their energy from the oxidations of N and their C from CO_2 .

Others autotrophic bacteria *Nitrosolobus*, *Nitrospira* and *nitroso vibrio* and to some extent heterotrophic bacteria also can oxidize NH_4^+ and other N reduces, compounds to NO_3^- .

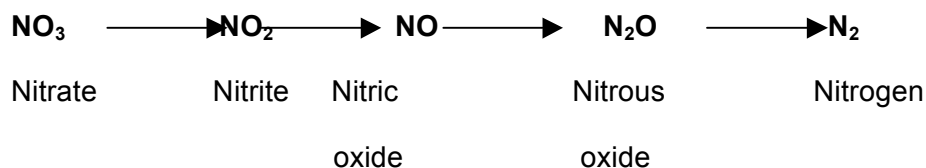
Losses of Nitrogen

The major losses of N from the soil are due to (1) crop removal and leaching, however under certain conditions inorganic N ions can be converted to gases and lost to the atmosphere. The primary pathway of gaseous N losses are

1. Denitrification
2. NH_3 volatilization.

Denitrification

Denitrification is the biochemical reduction of NO_3^- or NO_2^- to gaseous N, either as molecular Nitrogen or an oxide of Nitrogen. The most probable bio chemical pathway is



Nitrogen fixation

The conversion of elemental nitrogen to organic forms readily use able in biological process. Vermiculite and illite are capable of fixing NH_4^+ by a replacement of K^+ or Na^+ for interlayer cations in the expanded lattice of clay minerals. The radius of NH_4^+ ion 0.143° A. K^+ ion 0.133° A.

Because of NH_4 and K have more or less same charge, they easily replace each other in the exchange sites.

Organic fixation

If the soil has more organic matter the NH_4 will lockup as a complex. These complexes are called **Chelates**. It releases the nutrients only after its molecular breakdown. The facultative aerobic bacteria like *Pseudomonas*, *Bacillus*, *Paracoccus* are responsible for denitrification. It also depends upon the texture of soil. In heavy clay soils loss is up to 50% of added fertilizer.

Elemental N loss

It is due to chemical reduction. If chemical fertilizer containing amide (or) NH_4 form of N, it may be oxidized to elemental N and lost.

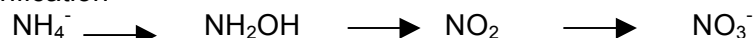


Sources of N leading to N and NO_2 gaseous loss

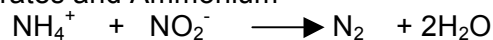
1. Denitrification



2. Nitrification



3. Nitrates and Ammonium



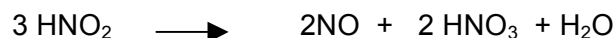
4. Nitrites and amino acids.



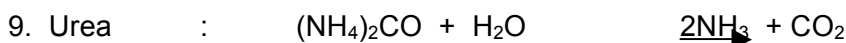
5. Lignin : HNO_2 + lignin $\xrightarrow{\text{N}_2 + \text{N}_2\text{O} + \text{CH}_3\text{ONO}}$

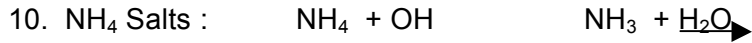
6. Phenols : Phenol $\longrightarrow \text{N}_2 + \text{N}_2\text{O} + \text{Organic residue}$

7. Decomposition of nitrous acid / reaction with metal cations.



8. NH_3 Gas





11. Decomposition of residues and manures

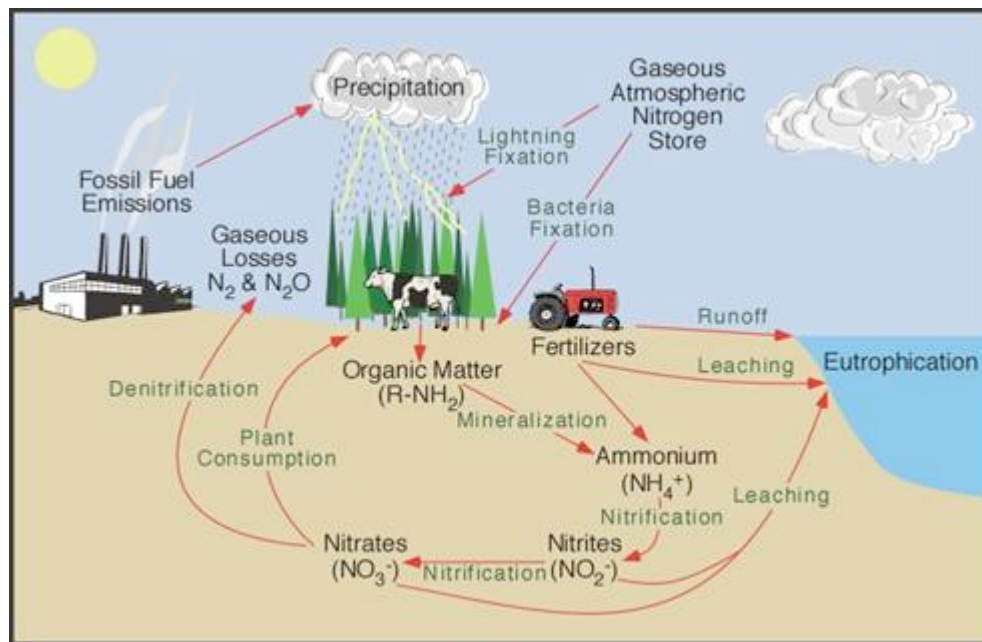
Release and volatilization of NH_3

Nitrogen cycle

The cycling of N in the soil – plant – atmosphere system involves many transformations of N between inorganic and organic forms.

The N cycle can be divided into

1. N inputs or gains.
2. N outputs or losses
3. N cycling with in the soil.
1. N in plant and animal residues and N derived from the atmosphere through electrical, combustion, biological and industrial process is added to the soil.
2. N in the residues is mobilized as NH_4 by soil organisms as an end product of residue decomposition, plant roots absorb a portion of the NH_4 .
3. Much of the NH_4 is converted to NO_3^- by nitrifying bacteria in a process called nitrifications.
4. NO_3 is taken up by the plant roots and is used to produce the protein in crops that are eaten by humans or fed to live stocks.
5. Some NO_3 is lost to ground H_2O or drainage systems as a results of downward movement through the soil in perculating H_2O .
6. Some NO_3 is consorted by denitrifying bacteria in to N_2 and N_2O that escape into the atmosphere, completely the cycle.



The nitrogen cycle

Source: <http://www.physicalgeography.net>

Important microorganisms in BNF

Organism s	Properties	Active location
Azotobac ter	Aerobic, free living	Soil, water, rhizosphere, leaf surface
Azospirill um	Micro aerobic rhizobacteri a; free fixers	Free living in Rhizosphere; Colonize roots of cereals and also gives phytotonic effect
Rhizobiu m	Symbiotic	Root nodules of legumes
Actinomy cetes, Frankia, Beijerinck ia	Symbiotic	Non leguminous forest tree roots, leaf surfaces
Cyanoba cteria	Photo autotrophic Anabaena - symbiotic	In wetland flood water; Anabaena associate with Azolla

Symbiotic N fixation

The symbiosis is the mutually beneficial relationship between host plant and bacteria. The location of association is in root or stem nodules, inside cavities, or by colonizing and penetrating plant tissue.

Legume (nodule forming)

Legumes and bacteria of the genera **Rhizobium** and **Bradyrhizobium** provide the major biological source of fixed N (40-60%) in agricultural soils. These organisms infect the root hairs and the cortical cells, ultimately inducing the formation root nodules that serve as the site of N fixation. The host plant supplies the bacteria with carbohydrates for energy and the bacteria reciprocate by supplying the plant with fixed N compound.

Effective nodules cluster on primary roots and have pink to red centers. The red colour of the nodule is attributed to the occurrence of **leghemoglobin**. The quantity of N fixed by properly nodulated legume averages about 75% of the total N used for the plant growth. The amount of BNF varies with Rhizobium strain, host plant, and environment.

Yield of non-legume crops often increase when they are grown following legumes (e.g. maize after soybean). Maximum N fixation occurs only when available soil N is at a minimum. When optimum conditions for N fixation is not prevailing, a legume crop can deplete soil N greatly, more than a cereal, if the legume grown is not incorporated into the same soil.

Fixer	Host plant
Rhizobium	Alfalfa, clover, peas, bean, soybean
	Gliricidia, Leuceana, Sesbania, Mimosa, Acacia 3 (3/4)
Bradyrhizobium	Cowpea, groundnut, red gram

Non-legume (nodule forming)

Roots of many species of angiosperm trees like casuarina in forests and wetlands form distinct nodules when infected with Actinomycetes of the genus **Frankia**.

Non-legume (non-nodule forming)

Azospirillum, **Azotobacter**, and **Azorhizobium**, dominant N fixers in cereals like rice, wheat, corn, sorghum, millets can grow on root surfaces and penetrate root tissues. The organisms use carbohydrates of root exudates as source of energy. They also induce crop growth by hormonal action. The organism **Beijerinckia** fixes N on leaf surfaces of tropical plants.

The **Anabaena** blue green algae (Cyanobacteria) inhabit cavities in the leaves of the floating water fern **Azolla** and fix quantities of N comparable to those of the better Rhizobium-legume complex. It could fix about 30-105 kg N/ season taking care of 75% N requirement of rice.

Nonsymbiotic N fixation

In wetland floodwater photoautotrophic **Cyanobacteria** independently do photosynthesis and fix N up to 20–30 kg N/ ha/ year. The excess ammonia is excreted in floodwater, which is beneficially absorbed by rice plants.

Free-living heterotroph bacteria like **Azotobacter** and **Beijerinckia** in aerobic upland soils and **Clostridium** in anaerobic wetland soils effectively fix N in pockets where O₂ supply is limited. Fixation depends upon the pH, soil N level, and source of organic matter.

Industrial fixation of N

Commercially produced N is the most important source of plant nutrient in agriculture. Industrial N fixation is by Haber-Bosch process, in which H₂ and N₂ gases react to form NH₃ under high temperature (1200^o C) and pressure (500 atm). Anhydrous NH₃ can directly be used as fertilizer or combined to other ions as solid forms.

N additions from atmosphere

Ammonia escapes in to atmosphere from soils, manures, and industries because of volatilization. Organic N compounds remain in fine dust of air lifted from earth surface. Rainfall brings down to soil NH₃, NO₃⁻, NO₂⁻, N₂O, and organic N. About 10 to 20% of the NO₃⁻ in the rainfall is due to fixation of N₂ by energy of lightning.

Deficiency and toxicity symptoms of Nitrogen in plants

Deficiency of N:

1. Plants are stunted and yellow in appearance.
2. The loss of protein N from chloroplasts. In older leaves produces the yellowing or chlorosis. It appears first on the lower leaves, the upper leaves remain green, while under severe N deficiency lower leaves will turn brown and die.
3. The necrosis begins at the leaf tip and progress along the midrib until the leaf is dead.
In cauliflower - young leaves turn pale yellow and old leaves become orange.

In coffee - Veins becomes yellow and new leaves are very small.

Tomato - Stem become purple and hard. Flower buds become yellow and flower dropping rate also increases

Excess of Nitrogen (Toxicity of nitrogen)

- a. Causes excess vegetative growth, dark green leaves, lodging, maturity is delayed with increases susceptibility to pest and disease.
- b. In cotton, weak fibre are resulted. In rice, lodging is common.
- c. Lengthening of crop duration and narrow leaf.
- d. Slender shoot, profuse vegetation, thick peel and skin will be rough and leathery in the case of citrus.
- e. Excess N in coffee plant, interferes the K uptake causing imbalance between N and K.

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Questions to ponder

- 1) How does the soil pH affect the nitrogen availability?
- 2) What climatic factors influence nitrogen availability to crops?
- 3) What is nitrogen fixation?
- 4) What is C: N ratio?
- 5) How does salinity affect nitrogen availability?

Phosphorus – Transformation, factors affecting Phosphorus availability, deficiency and toxicity symptoms

Learning objectives

- a. To understand the transformation of phosphorus
- b. To know the factors affecting the fixation of phosphorus
- c. To understand the deficiency symptoms of Phosphorus

Phosphorus

Phosphorus is taken up by the plant in the form of H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} through **diffusion** and **mass flow** action.

The P availability mainly depends on pH. In acid soils (**Al & Fe**) the presence of Al, Fe, Mn, P gets fixed as AlPO_4 , FePO_4 and not available to the plants. Some times as CaPO_4 . these are insoluble in H_2O .

Under hilly areas (or) high rainfall areas, all the cations will be leached leaving Fe, Al and Mn. The P availability will be reduced.

Ideal pH for available P = 6.5 - 7.5. If pH > 8.5 the fixation will be more. < 6.5 the fixation will be more.

Forms of P

Organic P : Nucleic acid and Phospho lipids

Rock Phosphate - acid soluble. If the organic matter content is high the availability of P is more since it is soluble in acid. It is highly suited to **plantation crops**. Rock Phosphates is black in colour. Roots also exudates acids, which will solublises the P.

Fixation is high so the P_2O_5 deficiency is 15 – 35%.

P is present as Apatities

- | | | |
|--------------|---|---|
| 1. Chlor | - | $\text{Ca}_{10}(\text{PO}_4)_6 \text{Cl}_2$. |
| 2. Fluor | - | $\text{Ca}_{10}(\text{PO}_4)_6 \text{F}_2$. |
| 3. Carbonate | - | $\text{Ca}_{10}(\text{PO}_4)_6 \text{CO}_3$. |
| 4. Hydroxy | - | $\text{Ca}_{10}(\text{PO}_4)_6 (\text{OH})_2$. |

Based on solubility the P fertilizers can be grouped into 4 groups.

1. H₂O soluble : (i) SSP 16% P as H₂O soluble

P : (ii) TSP 45% P as H₂O soluble

2. Citrate soluble : Dicalcium PO₄ 34% P₂O₅.

P : Tricalcium PO₄ 24%

3. Acid soluble P : Anhydrous Rock phosphate 16 - 18 %

4. Both H₂O and citrate soluble P: Kotka PO₄ 25% P₂O₅.

Rock phosphate is obtained in Bihar: Singlahe

Rajaithan: Udaipur

Uttar Pradesh: Mussoorri

Andhra Pradesh: Kasi pattinam

Phosphorus occurs in most plants in concentrations between 0.1 and 0.4%. Plants absorb either H₂PO₄⁻ or H + PO₄²⁻ ortho PO₄ ions Absorption of H₂PO₄⁻ is greatest at low pH values, where as uptake of HPO₄²⁻ is greater at higher values of soil pH, plant uptake of HPO₄⁻ is much slower than H₂PO₄⁻.

Functions of P

1. It has a greater role in energy storage and transfer.
2. It is a constituent of nucleic acid, phytin and phospholipids
3. It is essential for cell division and development
4. P compounds act as energy currency within plants. The most common P energy currency is that found in ADP and ATP. Transfer of the energy rich PO₄ molecules from ATP to energy requiring substances in the plant is known as "**Phosphorylation**"
5. It stimulates early root development and growth and there by helps to establish seedlings quickly.
6. It gives rapid and vigorous start to plants strengthen's straw and decreases lodging tendency.
7. It is essential for seed formation because larger quantities of P is found in seed and fruit-phytic acid is the principle storage form of phosphorus in seeds.
8. It increases the activity of Rhizobia and increases the formation of root nodules.

Soil P its origin and Nature

Soil P exists in many primary and secondary compounds. The **apatite** group of primary mineral is the original source i.e. 55% of soil P.

a) Aluminium and Iron Phosphates

In the initial stages of acid weathering PO_4 becomes increasingly bound to Fe^{3+} and Al^{3+} ions released from silicate minerals by replacing OH^- from **hydroxyl minerals** or oxygen from **oxide minerals**. FePO_4 and ZnPO_4 has been found in H_2O logged or poorly drained soils, sand and silt fraction of some soils.

Calcium phosphates

The group of compounds form an important category in the young soils and the matured soils of **neutral** to **alkaline** pH ranges. The CaPO_4 found either in **stable** or **metastable** state in the soil fertilizer reaction zones.

Eg. Fluorapatite	-	$\text{Ca}_{10}(\text{PO}_4)_3 \text{Fe}$
Carbonate apatite	-	$\text{Ca}_{10}(\text{PO}_4)_3 \text{CO}_3$
Dicalcium PO_4	-	$\text{Ca HPO}_4 \cdot 2\text{H}_2\text{O}$
Monocalcium PO_4	-	$\text{CaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

Organic phosphates

It is derived secondarily by the addition of organic matter to the soil through the growth of plants and the deposition of plant residues. The soil micro organic synthesize organic PO_4 compounds and accumulate in the soil mixed with derived from plant tissues. It constitute 20 – 30% of total soil P. The major classes of organic compounds in soils are

- Phospholipids (0.6 – 0.9%)
- Phospho proteins of nucleic acid (0.6 – 2.4%)
- Phosphorylated sugar
- Phytin and Inositol PO_4

The ideal C : N : P : S ratio in soils are

- | | |
|-------------------|----------------------|
| a. Calcarious | 113 : 10 : 1.3 : 1.3 |
| b. Non calcarious | 147 : 10 : 2.5 : 1.4 |
| c. Indian soils | 144 : 10 : 1.4 : 1.8 |

Chemistry of solid phosphorus compounds and their equilibrium

The PO_4 concentration in soil solution is governed by the heterogenous equilibrium.

P adsorbed in soil $\text{Po}_4 \longrightarrow$ P in soil solution $\longrightarrow$ P' precipitated in soil solution.

The reactions involved in soil Po_4 equilibrium are **dissolution, precipitation, solubility product principle**.

By using radio active p^{32} Larsen (1952) characterized the total soil PO_4 into **Labile** and **Non labile** fractions and found the size of the labile pool primarily depended on soil properties and not a function of the total content of inorganic P. he correlated and equilibrium of

Non labile soil P $\rightleftharpoons$ Labile soil P $\rightleftharpoons$ P in soil solution.

Fixation of phosphorus in soil

“It is the way of removal of PO_4 from solution by soil which reduces the amount that plant roots can absorb”.

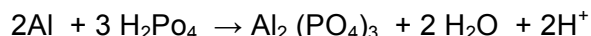
The factors affecting P fixation are.

1. clay minerals

The PO_4 is fixed by clay minerals by reacting with soluble aluminum which originates from the exchanges sites or from lattice dissociation to form a highly **insoluble AlPO_4** .

2. Iron and Aluminum (fixation in acid soils)

The formation of Iron and aluminium PO_4 in the soil results from the combination of P with these metals in solution and their oxides hydroxides in acid soil.



3. Exchange cations and calcium carbonate (Fixation alkaline soils)

In calcareous soils, free Ca CO_3 is a potent sources for 'P' fixation. P fixation in calcareous soil involved a rapid monolayer sorption of P in dilute concentration In CaCO_3 surfaces and form less soluble compounds of di and tricalcium PO_4 .



4. Organic matter

Organic Po_4 can be fixed by soil organic matter also influences in Organic Po_4 fixation. The acids produced during the transformations of Organic matter could decrease the pH and increase fixation by the solubilization of Fe and Al.

P Fixation in soil is affected by

1. Nature and Amount of soil minerals

Soils have high amount of Fe and Al oxides, crystalline hydrous metal oxides are usually capable of retaining more P than amorphous forms. P adsorbed to a greater extent by 1 : 1 than 2 : 1 clays. The greater amount of P fixed by 1 : 1 clays is probably due to the higher amounts of Fe and Al oxides, associated with kaolinite clays that are predominant in highly weathered soils. Soils containing large quantities of clay will fix more P than soils with low clay content.

2. Soil pH

- Fixation of P by Fe and Al oxides decreases with increasing pH.
- P availability is more in soils at a max in the pH range of 5.5 to 6.5
- At low pH values, Fe and Al ions react with to form FePo_4 and FePo_4 oxides.
- As the pH increases, the activity of Fe and Al decreases and the results of higher amount of P liberates into soil solution.

Above pH 7.0, Ca^{2+} can precipitate with P as $\text{Ca}_3(\text{PO}_4)_2$ mineral and P availability again decreases.

3. Cation effects

Divalent cations enhance the P fixation than monovalent cations.

4. Anion effects

Both organic and Inorganic anions can compete with P for adsorption sites, resulting in decrease the fixation of P.

5. Organic matter

Addition of organic matter to soils increased P availability by

- Formation of organo Po_4 complexes that are more easily assimilate by plants.
- Anion replacement of H_2Po_4^- on adsorption sites.
- Coating of Fe and Al particles by humus to form a productive cover and thus reduce the P fixation.

6. Temperature

The rate of most chemical and biological reactions increases with increasing temperature. Mineralization of P from soil organic matter is dependent on soil biological activity and increases in temperature.

7. Flooding

In most soils there is an increase in available P after flooding largely due to conversion of $\text{Fe}^{3+} \text{PO}_4$ to soluble $\text{Fe}^{2+} \text{PO}_4$ and hydrolysis of Al PO_4 and thereby prevent the fixation of P in soils.

8. $\text{R}_2\text{O}_3 : \text{P}_2\text{O}_5$ (Ratio)

" $\text{R}_2\text{O}_3 : \text{P}_2\text{O}_5$ (Ratio) is a measure of amount of P present in the soil". A wide ratio indicates a small P fixation and vice versa. When the ratio is narrow P fixation is more.

9. Addition of ZnSO_4

It may also cause P deficiency since it forms insoluble complex with P. This can be averted by addition of ZnSO_4 more and more.

P Cycle

"Process by which P moves from solid and liquid phase and transformation is called P cycle". P is taken mostly by diffusion in plants.

I. The decrease in soil solution P concentration with absorption by plants roots is buffered by both inorganic and organic fractions in soils.

Primary and secondary P minerals dissolve to re supply $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ in solution.

Inorganic P adsorbed on mineral and clay surfaces as H_2PO_4^- or HPO_4^{2-} (labile inorganic P) also can desorb to buffer decreases in soil solution P. Numerous soil micro organic digest plant residues containing P and produce many organic plant compounds in soil and it can be mineralized through microbial activity to supply solution P.

H_2O soluble fertilizer P applied to soil readily dissolves and increases the concentration of soil solution.

II. In addition to uptake of P by roots, solution P can be adsorbed on minerals surfaces and precipitated as organic P and these organic P compounds are more resistant to microbial degradation.

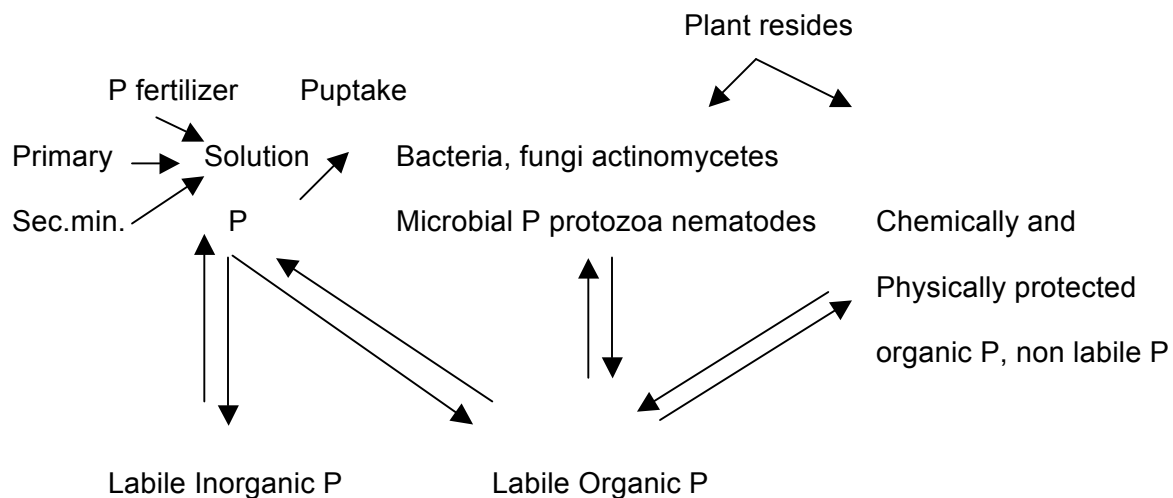
Soil solution P is called **Intensity factor**, while organic and inorganic labile P fractions are collectively **Quantity factor**.

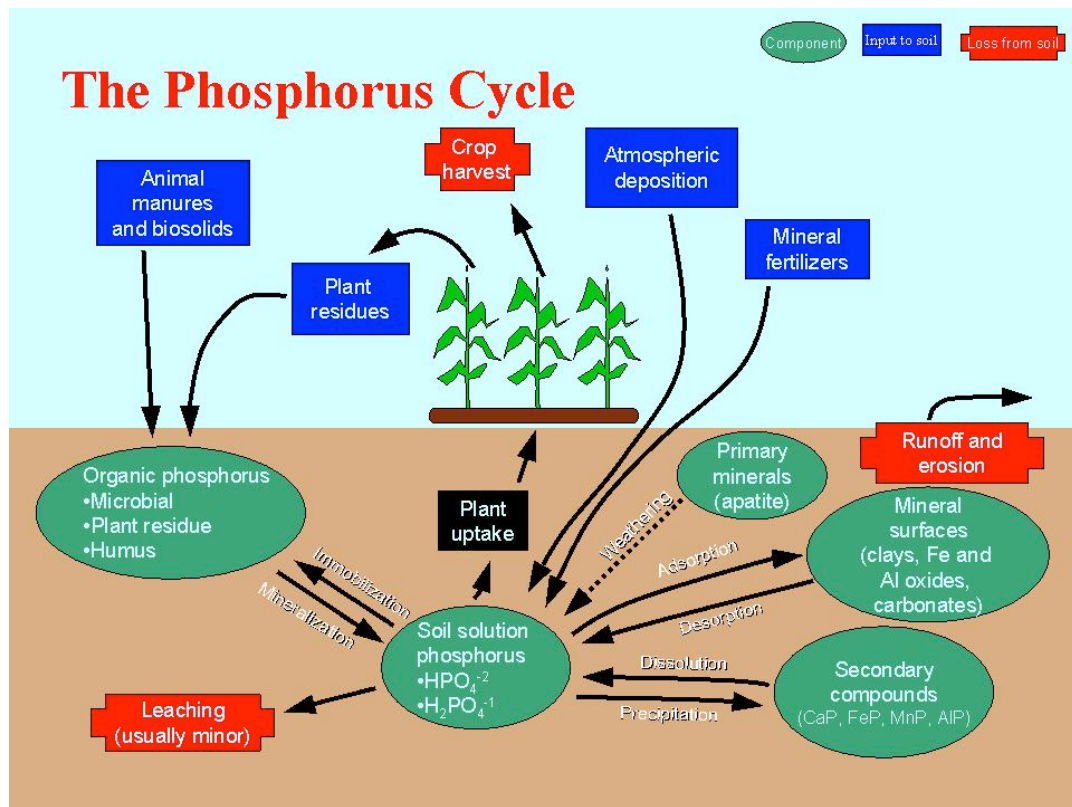
Maintenance of solution P concentration for adequate P nutrition in the plant depends on the ability of labile P to replace soil solution P. “The ratio of quantity to intensity factor is called the **capacity factor**, “which express the relative ability of the soil to buffer changes in soil solution”.

P cycle can be simplified to

```

Soil solution —————> labile P —————> Non labile P
                        (Inorganic)      (Organic)
  
```





Source: <http://phsgirard.org/Biology/Ecology/PhosphorusCycle.jpg>

Y value / L value (Larsens Value)

Larsen measured the quantity of soil P involved in the isotopic dilution of applied radio active P during a growing season. It is used to calculate P supply of the soil.

$$L \text{ (or) } Y = K \times \frac{(C_o - C)}{C}$$

Where, L = Avail P in soil

C_o = K x total P in the Plant

C = K x P taken by the plant

K = Proportionality constant.

Deficiency symptoms

P is mobile in plants and when a deficiency occurs it is translocated from older tissues to the active meristematic regions.

1. It arrests metabolism resulting in reduction of total N of Plants.

2. Reduced sugar content.
3. Premature leaf fall.
4. Develops necrotic area on the leaf petiole and in the fruit
5. Leaves will show characteristic bluish green colour.

Toxicity of phosphorus

- a. Profuse root growth i.e. lateral and fibrous root lets.
- b. It develops normal growth having green leaf colour.
- c. It may cause in some cases trace elements deficiencies i.e. **Zinc and Iron.**

References

Tisdale, S.L., Nelson, W.L., Beaton, J.D., Havlin, J.L. 1997. Soil fertility and Fertilizers. Fifth edition, Prentice hall of India Pvt.Ltd, New Delhi.

Singh, S.S. 1995. Soil fertility and Nutrient Management. Kalyani Publishers, Ludhiana.

<http://phsgirard.org/Biology/Ecology/PhosphorusCycle.jpg>

Questions to ponder

- 1) What is the role of soil pH in P availability?
- 2) P fixation is a blessing in disguise. How?
- 3) What are the natural sources of P?
- 4) What is C: P ratio?
- 5) How does calcareousness affect P availability?

9.

Potassium – Transformation, factors affecting Potassium availability, deficiency and toxicity symptoms

Learning objectives

- a. To understand the transformation of Potassium
- b. To study the forms of K and factors affecting K availability
- c. To understand the deficiency symptoms of Potassium

Potassium

The potassium ion (K^+) is actively taken up soil solution by plant roots. The concentration of K^+ in vegetative tissue ranges from 1 to 4% on dry matter basis.

Functions of potassium

1. Essential for photosynthesis, development of chlorophyll.
2. It improves vigour of the plants to enable to with stand adverse climatic conditions.
3. Reduces lodging in cereal crops.
4. It regulates stomata opening and closing.
5. It regulates the movement of ions with in the plants and hence it is called **traffic policeman** of the plant.
6. Activation of enzymes, enzyme synthesis, peptide bonds synthesis.
7. Regulates H_2O imbalance within the plant.

Sources of K

The micas and feldspars constitute the major K bearing minerals which on weathering slowly release K to the soil.

(Muscovite and biotite)

(Orthoclase and microcline)



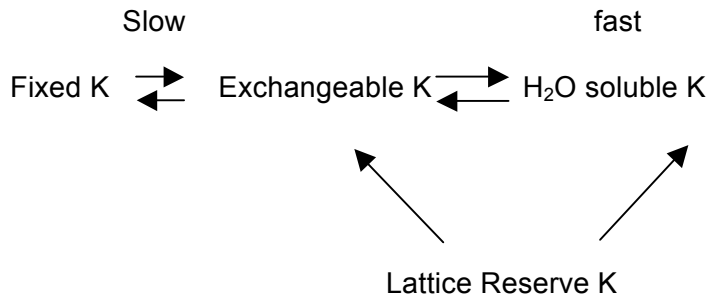
K-Feldspar: $KAlSi_3O_{10}$.

Courtesy: <http://ocw.mit.edu/ans7870/12/12.108/f04/imagegallery/lab3/lab3-32.html>

Forms of potassium in soils

- Water soluble K.
- Exchangeable K.
- Fixed or Non exchangeable K.
- Lattice or Mineral K.

The different forms are in **dynamic equilibrium** with one another and represented as follows.



Water soluble K

The Concentration of H₂O soluble K in soil depends on (a) type of day (b) H₂O content (c) Intensity of leaching (d) Amount of exchange K (e) Kind and concentration of other ions.

The dilution of the soil, increases the concentration of H₂O soluble K and drying decreases it. The uptake of K is influenced by the presence of other cations, ie Ca²⁺ and Mg²⁺, Al³⁺ (acidic soils) and Na⁺ in salt affected soils.

$$\text{The activity ratio } (AR_e^K) = \frac{\text{Activity of } K^+}{\sqrt{\text{activity of } Ca^{2+} \text{ and } Mg^{2+}}}$$

(or)

$$= \frac{a_K}{\sqrt{a_{Ca} a_{Mg}}}$$

2. Exchangeable K

The K adsorbed on soil clay complex and replaceable with neutral salts in relatively short time. The Cl reacts with soil Ca and form Ca Cl₂ which is leached by high rainfall. Hence **K is called as Decalcifier**

3. Non exchangeable or Fixed K

Added K which is firmly bound by the soil and not immediately replaceable with neutral salts.

4. Lattice K or Mineral K

Muscovite, biotite and K feldspar. The capacity of soils to release lattice K by weathering depends on the content of K minerals and soil texture.

Potassium fixation

The important of K fixation is to regulate the supply of the soil a for the plants and protects it against loss through leaching.

In the dynamics of soil Potassium, the phenomenon of fixation of exchange K and the liberation of non-exchange K play an important role. K ions are relatively small to enter the silica sheets where they are held firmly by **electrostatic forces**. The presence of K^+ ions can block the release of fixed NH_4^+ and vice visa.

Factors affecting K fixation.

1. **Soil texture** : Increases the texture grater will be fixation and vice visa.
2. **Wetting and drying**: Fixation is more under dry condition than wet condition.
3. **Type of day min**: Fixation is more in 2:1 type than 1: 1 type
4. **Freezing and thawing** : Enhances the fixation of K depends their clay mineralogy and degree of weathering
5. **Soil pH** : A decreases in pH reduces the K fixation either as result of competition of H_3O^+ for the inter layer exchange position. Liming also favors for the fixation of K.

Factors affecting K availability in plants

a. *Kind of clay minerals*: Soils containing vermiculite or montmorilonite will have more K than kaolinite clay soils.

b. *Cation exchange capacity*: Increases texture soils having higher CEC and can hold more exchange K.

c. *Amount of exchangeable K*: More K in soil solution leads to

Higher fixation.

d. *Subsoil K and rooting depth*: Low soil temperature may exhibit K release and diffusion, thus increasing crop response to K

e. *Soil moisture*: fertilization increasing K levels or moisture contain will accelerate K diffusion.

6. **Soil temperature** : The reduced temperature slow down plant process plant growth and rate of K uptake.
7. **Soil aeration** : Under high moisture levels or incompact soils root growth is restricted, O_2 supply is lowered and absorptions of K is slowed.
8. **Soil pH** : In very acid soils, toxic amount of exchange Al^{3+} and Mn^{2+} create unfavorable root environment for uptake of K and other nutrients.
9. **Ca and Mg** : K uptake would be reduced as Ca^{2+} and Mg^{2+} are increased or uptake of these two cations would be reduced as the available supply of K is increased.
10. **Tillage**: Tillage is increased that K availability is reduced because of increases compaction, less aeration and lower temperature.

Plant factors affecting K availability

1. CEC of Roots :Important for determining the ability of plants to absorb like more slowly available forms of soil K.
2. Root system and crop :Higher root density, higher the removal of exchange K and soil solution K. Fibrous root system absorbs more K than tap root system.
3. Variety or Hybrid :Hybrid absorbs more K than variety.
4. Plant population :Higher plant population and closer spacing increased the K removal.

Deficiency symptoms

1. Plant becomes stunted in growth with shortening of internodes and bushy in appearance.
2. K deficiency in plants show reduced rate of photosynthesis.
3. Chlorosis, yellowing of leaves and leaf scorch in case of fruit trees.

Rice : The leaf tips will turn dark brown in colour and blades will be blueish green, chlorotic and necrotic are seen.

Banana : Deficiency is seen in the margin and bottom of leaves.

Grapes : Leaves are yellow with brown spots which are necrotic, brittle with uneven ripening.

References

Tisdale, S.L., Nelson, W.L., Beaton, J.D., Havlin, J.L. 1997. Soil fertility and Fertilizers. Fifth edition, Prentice hall of India Pvt. Ltd, New Delhi.

Singh, S.S. 1995. Soil fertility and Nutrient Management. Kalyani Publishers, Ludhiana.

<http://ocw.mit.edu>

Questions to ponder

- 1) What is luxury consumption?
- 2) What is activity ratio and what does it measure?
- 3) How does CEC affect the amount of K in solution?
- 4) What is the effect of K: Ca ratio in K availability?
- 5) Does fixed K tend to become available to plants?

10.

Secondary nutrients – Transformation, factors affecting nutrient availability, deficiency and toxicity symptoms

Learning objectives

- a. To understand the transformation of secondary elements
- b. To study the forms of secondary nutrients and factors affecting the availability
- c. To understand the deficiency symptoms of secondary nutrients

Calcium

Calcium is absorbed by plants as Ca^{2+} and its concentration ranges from 0.2 to 1.0% and it is supplied through mass flow method.

Functions of calcium

1. It is immobile in plants and hence the deficiency is observed in younger leaves.
2. It is a constituent of cell wall and increases in stiffness of plants.
3. Promotes root development and growth of plants, root elongation and cell division.
4. Helps to translocate the sugar in the plants.
5. It involves chromosome stability and that it is a constituent of chromosome structure.
6. Affects translocation of CHO in plants.
7. Encourages seed production.
8. Activates enzyme phosphate and kinase.
9. Accumulated protein during respiration by mitochondria and it increases their protein content.
10. It binds DNA to protein molecules.

Deficiency of calcium

- a. Young leaves of terminal buds dieback at the tip and margins.
- b. Normal growth is affected.
- c. Root may become short, stubby and brown.
- d. Causes acidity of soil.
- e. Cell may become rigid and brittle.
- f. Young leaves of cereals remain folded.

Sources of soil calcium

Earth crust contains about 3.64%. The important source of calcium is **anorthite** ($\text{Ca Al}_2\text{Si}_2\text{O}_8$). Generally arid region soils contain high amount of Ca regard less of texture, low rainfall and little leaching.

In arid and semiarid regions Calcite (CaCO_3)

Dolomite ($\text{Ca, Mg, (CO}_3)_2$)

Gypsum ($\text{CaSO}_4, 2\text{H}_2\text{O}$)

In humid regions, even the soils formed from limestone are frequently acid in the surface layers because of the removal of Ca and other cations by leaching.

Calcium transformations in soils

In acid and humid region soils Ca occurs largely in exchange form and as primary minerals. In most of these soils Ca^{2+} , Al^{3+} and H^+ dominates the exchange complex.

The forms of Ca are

1)Solution Ca^{2+} / Mg^{2+}

2)Exchangeable Ca/Mg

3)Mineral Ca/Mg.

The activity of solution Ca is decreased by leaching or plant removal. If solution Ca is increased, the equilibrium shifts in the opposite direction with subsequent desorption of some of the Ca^{2+} by the exchange complex. The rate of solution Ca is less complex than of K^+ . It may be (a) Lost in drainage H_2O 's. (b) absorbed by organisms (c) adsorbed on the CEC (d) Reprecipitated as secondary calcium compound.

Factors affecting Ca^{2+} availability

1. Total Ca supply :Sandy acidic soils with low CEC having less Ca.
2. Soil pH:In acid soils Ca is not readily available to plants at low concentration.
3. CEC:Soils having low CEC might will supply more Ca^{2+} .
4. % Ca saturation:High Ca^{2+} saturation indicates favourable pH for plant growth and microbial activity.
5. Type of soil colloid: 2 : 1 type require higher Ca saturation than 1: 1 type.
6. Ratio of Ca^{2+} to other cations : Increasing the Al^{3+} conc. in soil solution reduces Ca uptake in plant.

Magnesium

Magnesium is absorbed as Mg^{2+} and the concentration in crop varies between 0.1 and 0.6%. It was taken by plant by *Mass flow and diffusion*.

Functions of Mg in plants

1. Primary constituent of chlorophyll
2. Imports dark green Colour in leaves.
3. Serves as a structural components in ribosomes and stabilizing the ribosome configuration for protein synthesis.
4. Involves numbers of physiological and biochemical function.
5. Activates phosphorylating enzymes in CHO metabolism.
6. Act as a cofactor for certain enzymes other than PO_4 transfer enzyme.
7. Increases in the oil content of oil seed crops.
8. Regulates the uptake of other nutrients.

Deficiency of Magnesium

1. Interveinal chlorosis of the leaf in which only the leave veins remain green.
2. Stiff brittle, twisted leaves, wrinkled and distortion of leaves.
3. cotton –lower leaves may develop a reddish purple finally necrotic (Redding of leaves)
4. In brassica, Chlorosis with interveinal mottling uniformly distributed in older leaves while the other vascular tissues remain green. This condition is called “**Puckering**”.

Sources of soil Magnesium

It constitutes 1.93% of earth crust

Primarily minerals (a) Biotite (b) Dolomite (c) Hornblende (d) olivine (e) serpentine.

Secondary minerals (a) Chlorite (b) Illite (c) Montmorillonite.

In arid region substantial amount of Mg present as **Epsomite** ($Mg\ SO_4\ 7H_2O$)

Forms of Mg in the soil

1. It occurs predominately as exchange and solution mg.
2. Coarse text soil exhibits the greatest potential for Mg deficiencies.
3. Competition bet NH_4^+ and Mg^{2+} also lower the Mg^{2+} availability to crops.

Losses of Mg

It is leached by soils and it depends on the Mg content, rate of weathering, intensity of weathering and uptake of plants.

Sulphur

Sulphur is absorbed by plant roots as SO_4^{2-} ions. Concentration of S in plants range between 0.1 and 0.4%.

Functions of sulphur

1. Essential for synthesis of sulphur containing amino acids cystine, cysteine and methionine.

2. Essential for synthesis of other metabolites including Co-enzyme A., Biotin, Thiamin of vitamin B and Glutathione.
3. Synthesis of chlorophyll.
4. It is a vital part of ferredoxins i.e Fe – S – protein occurring in the chloroplasts.
5. Responsible for the characteristic smell or odor and taste of mustard, onion and Garlic. (Puncy smell)
6. Enhances the oil formation in crops (Soya bean)
7. Increasing root growth.
8. Stimulate seed formation.
9. Promote nodule formation – Leguminous species.

Deficiency of sulphur

- a. Stunted growth pale green to yellow colour.
- b. Immobile in plants and plants symptoms start first at younger leaves.
- c. Poor seed set in rapeseed.
- d. Tea –Tea yellows.

Sources of sulphur

1. Amount has <0.05 ppm in the form of SO_2 .
2. Earth crust contains 0.06 to 0.10%.
3. Sulphur bearing minerals

Gypsum	- $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.
Epsomite	- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Mirabilite	- $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$.
Pyrite	- FeS_2 .
4. Silicate min contains <0.01 % S.
5. Igneous rocks 0.02 to 0.07%
Sedimentary rocks 0.02 to 0.22%

Forms of sulphur in soil

Present both organic (90%) and Inorganic forms.

The inorganic forms are

1. Solution SO_4^{2-} .
2. Adsorbed $\text{SO}_4^{=}$ Readily available fraction.
3. Insoluble $\text{SO}_4^{=}$
4. Reduced inorganic compounds.

Factors affecting S oxidation in soils

- a. Microbial population in soil.
- b. Characteristics of the 'S' source
- c. Soil environmental condition.
- d. **Soil micro flora** Chemolithotropic S bacteria Thiobacilli utilized energy from oxide of Inorganic S for the fixation of CO_2 in Organic matter.

e. Soil temperature

An increase in temperature increases the S oxidation rate in soil. Ideal temperature 25 – 40°C.

f. Soil moisture and aeration

S oxidizing bacteria are mostly aerobic and their activity will decline if O_2 is lacking due to H_2O logging. Favourable moisture is field capacity moisture.

g. **Soil pH:** Optimum pH 4.0 or lower.

S transformation in soils

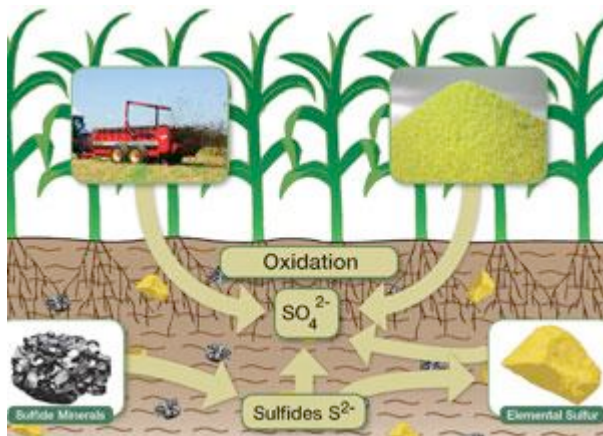
Numerous transformations of S in soil occur from inorganic to organic forms due to the presence of heterotrophic microorganisms viz., Thiobacillus, chlorobium, Desulfotomaculum and Desulfovibrio.

When plant and animal residues are returned to the soil they are digested by microorganisms releasing S as SO_4^{2-} . Most of the S remains in organic form and becomes part of soil humus. The S supply to plants largely depends on the SO_4^{2-} released from the organic soil fractions and from the plant and animal residues.

S Mineralization and immobilization

Mineralization of "S" is the conversion of organic S to inorganic SO_4^{2-} .

Immobilisation is the conversion of SO_4^{2-} to organic S.



Sulphur cycle

http://www.agweb.com/assets/1/9/NewsMainImage/sulfur_cycle2.jpg

Factors affecting S mineralization and Immobilization.

1. S content of organic matter

Mineralization of S depends on the S content of the decomposing material, smaller amounts of SO_4^{2-} are liberated from low S containing residue.

2. Source of mineralizable sulphur :

Most of the available S removed by plants from the SO_4^{2-} fraction of labile S in soil Organic matter.

3. Soil Temperature

Mineralization of S is impeded @ 10°C increases with increasing temperature from 20°C to 40°C and decreases of temperature >40°C.

4. Soil moisture

Mineralization occurs in optimum moisture conditions.

5. Soil pH

S released is directly proportional to pH up to pH 7.5. Above 7.5 mineralization increases more rapidly.

6. Absence or presence of plants.

Soils mineralization more S in the presence of growing plants than in their absence.

7. Time and cultivation

8. S Volatilization

Volatile S compounds are produced through microbial transformations under both aerobic and anaerobic conditions. The volatile compounds are **dimethyl sulfide ($\text{CH}_3 \text{SCH}_3$) (CS_2) Carbamdi sulphide and mercaptans (CH_3SH).**

In low organic matter soils, S volatilization is negligible and increases with increasing organic matter content.

Practical aspects of S transformations.

1. Crops grown on coarse texture soils are generally more susceptible to S deficiency because these soils having low organic matter content and $\text{SO}_4^{=}$ leaching.
2. Leaching losses of $\text{SO}_4^{=}$ can occur highly on coarse texture soils under high rainfall. Under such conditions, $\text{SO}_4^{=}$ containing fertilizers maybe applied more frequently
3. **Immobilization** of added S can occur in soils having a high. **C/S or N/S ratio**. S mineralisation is favored in soils with a low C/S or N/S ratio. S availability generally increases with organic matter content.
4. Actual amount of S needed will depend on the balance between all soil additions of S by precipitation, air, irrigation H_2O , crop residues fertilizers, Agriculture Chemicals and all losses through crop removal. Leaching and erosion.

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Questions to ponder

- 1) What is the importance of C:N:P:S ratio to the availability of soil sulphur?
- 2) Is Magnesium fixed in soils?
- 3) How is a low calcium soil condition usually corrected?
- 4) Which crops have high calcium requirement?
- 5) Can climate influence the availability and uptake of Calcium and Magnesium?

11.

Micro nutrients – Transformation, factors affecting nutrient availability, deficiency and toxicity symptoms

Learning objectives

- a. To understand the transformation of micronutrients
- b. To study the forms of micronutrients and factors affecting the availability
- c. To understand the deficiency symptoms of micro nutrients

Iron

Fe is absorbed by plants roots as Fe^{2+} , Fe^{3+} and chelated forms. Sufficiency range of Fe in plant tissue is 50-250 ppm.

Functions of Iron

1. It helps in the synthesis of chlorophyll.
2. Structural component of porphyrin molecules like cytochromes, hematin, hemes, ferrichrome and hemoglobin. These substances are involved in oxidation-reduction reactions in respiration and photosynthesis.
3. Structural component of non heme compounds like ferredoxins.
4. Constituent of enzyme systems E.g. cytochrome oxidase, catalase, nitrogenase reaction in plants.
5. Component of flavoprotein like

FMN = Flavin mononucleotides

FAD = Flavin Adenosine Dinucleotide.

Deficiency symptoms

1. Deficiency symptoms occur in younger leaves since Fe is immobile element within plant.
2. It occurs in soils of calcareous or alkaline soils and poorly drained H_2O logged soils.
3. Younger leaves develop interveinal chlorosis which progresses rapidly over the entire leaf. Severe cases entire leaf turns yellow colour.

Sources of iron

Earth crust contains about 5%

Primary and secondary minerals such as

1. Olivine, 2. Pyrite, 3. Hematite, 4. Goethite, 5. Magnetite, 6. limestone

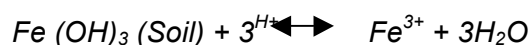
Forms of iron

Fe occurs in Four major forms in soil.

1. Primary and secondary minerals Fe
2. Adsorbed Fe
3. Organic Fe and
4. Solution Fe.

Soil solution Fe

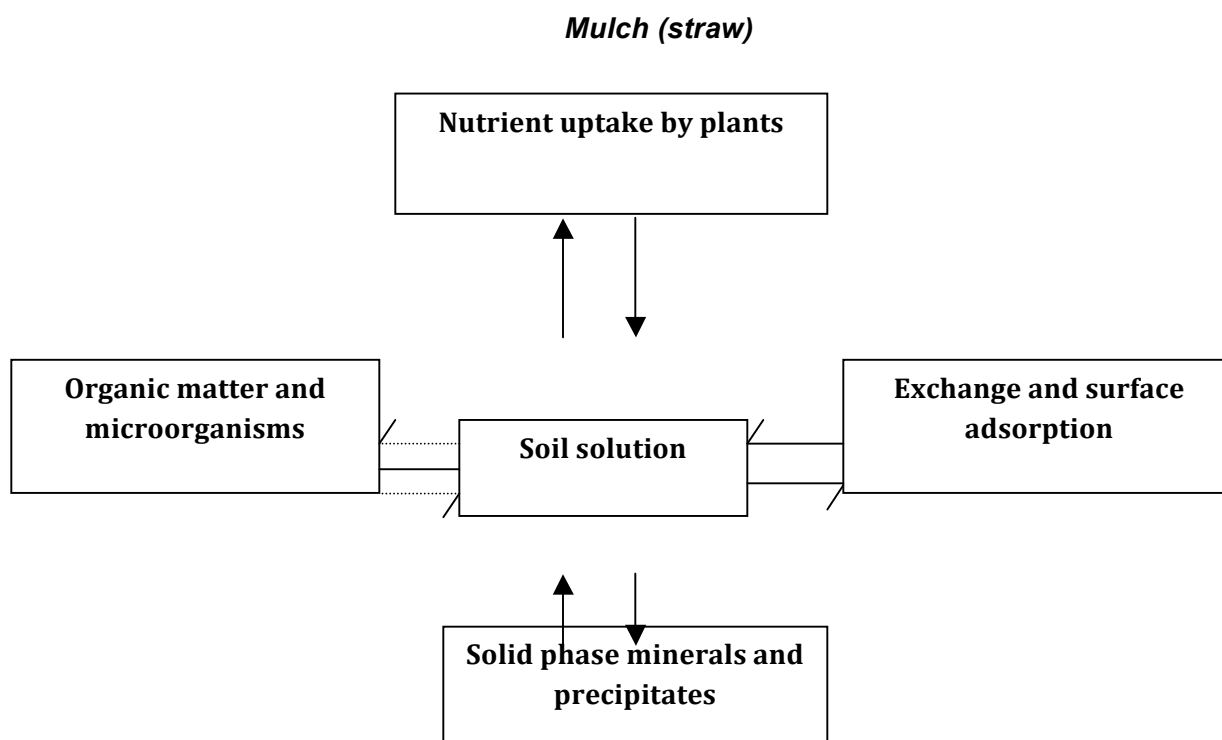
It occurs primarily as $\text{Fe}(\text{OH})_2^+$, Fe^{3+} concentration in solution is very low. In well-drained, oxidized soils, the solution Fe^{2+} concentration is less than that of the dominant Fe^{3+} in solution. The pH dependent relationship for Fe^{3+} is described as



For every increase in pH, Fe^{3+} concentration decreases 1000 fold. Oxidation - reduction reactions, the result of change in O_2 partial pressure, exert considerable influence on the amount of soluble Fe in the soil solution. The insoluble Fe^{3+} form predominates in well drained soils, while levels of soluble Fe^{2+} increase significantly when soils become H_2O logged. In general, lowering Redox increases Fe^{2+} solubility, 10 fold for each unit decrease in pH.

Over the normal pH range in soils, total solution Fe is not sufficient to meet plant requirements for Fe even in acid soils, where Fe deficiency occurs less frequently than in high pH and calcareous soils.

Schematic representation of Fe, Zn, Cu and Mn cycle



Chelates

“Is a term derived from a Greek and meaning “Claw”.

Chelates are soluble organic compounds that bond with metals such as Fe, Zn, Cu and Mn increasing their solubility and their supply to plant roots.

“Natural organic chelates in soils are products of microbial activity and degradation of soil organic matter and plant residues. Root exudates are capable complexing nutrients substantial quantities of organic completed. Fe can be cycled through crop residue and compounds of citric acid and oxalic acids have chelating properties.

Dynamics of chelation

“The dynamics of chelation increasing solubility and transport of micronutrients”.

During active plant uptake, the concentration of chelated Fe or other micronutrient is greater in the bulk solution than at root surface the chelated Fe diffuses to the root surface in response to concentration gradient. After Fe^{3+} dissociates from the chelates and diffused due to concentration gradient. As the unchelated Fe^{3+} concentration decreases in solution because of chelation, additional Fe is desorbed from mineral surfaces or Fe minerals dissolved to resupply solution Fe.

Synthetic chelates

In soils synthetic chelates behave similarly to natural organic chelates. The choice of a chelate to use as chelate depends 1. specific micronutrient ii. Solubility of chelate in the soil. When synthetic or natural chelates are added to soils and they are readily complex with cations in soil solution.

Eg: Citric acid and Oxalic acids, two natural chelates complex Al^{3+} at low pH, but when pH increases above 5 or 6, Ca^{2+} and Mg^{2+} are more readily complexed.

Diethylene triamine penta acetic acid (DTPA) and EDTA (Ethylene diamine tetra acetic acid) readily chelate Fe at pH < 7 and pH < 6.5 respectively. The chelate EDDHA (Ethylene Diamine dihydroxy phenyl acetic acid) will strongly complex Fe and is stable over the entire pH range. As a result Fe EDDHA is commonly used as an Fe fertilizer because it provides more plant available Fe than other chelates.

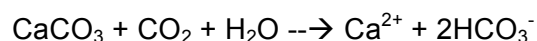
Factors affecting Fe availability

1. Soil pH, Bicarbonate and Carbonates

Fe deficiency is most often observed in high pH and calcareous soils in arid regions, but it may occur in acid soils that are very low in total Fe.

Irrigation waters and soil high in HCO_3^- may aggravate Fe deficiency. Because of high pH levels associated with HCO_3^- accumulation.

In calcareous soils having pH range of 7.3 to 8.5 have Fe deficiency due to the lowest solubility of soil Fe and the formation of bicarbonate ion.



2. Excessive H₂O and poor aeration

Flooding and submergence of soils can improve Fe availability by increasing Fe²⁺ conc. They actually build up of toxic conc. of Fe²⁺ organic matter removed from the eroded portions of semi arid region calcareous net soils lime induced Fe deficiency will occur.

3. Organic matter

Additions of organic matter to well drained soils can improve Fe avail. Due to increases the Fe²⁺ solubility.

4. Interactions with other nutrients

Fe deficiency occur due to the accumulation of Cu, Mn, Zn, Mo and P. Fe availability decreases when the soils are having more NO₃⁻ than NH₄⁺ deficiency of K or Zn can reduce Fe translocation with in plants.

MANGANESE

Mn concentration in plant ranges from 20 to 500 ppm

Functions of Mn

1. Helps in chlorophyll formation
2. Involves in photosynthesis, particularly in evolution of O₂.
3. Involves in oxidation - reduction - process in decarboxylation and hydrolysis reactions.
4. Involves in enzyme systems and various enzyme reactions in the citric acid cycle.
5. It is a substitute for Mg²⁺ in many of the phosphorylating and group transfer reactions.

Deficiency of Mn

1. Immobile in plant and def. starts in the younger leaves.
2. Interveinal chlorosis occur

Oats - Gray specks / streaks

Peas - Marsh spot

Sugarbeet - speckled yellow

Sugar cane - Pahala blight - midrib pale green and white.

3. Deficiency increases aspartic acid and decreases glutamine
4. Increases respiration
5. Accumulation N compounds mainly as amines.

Sources of Mn

Earth crust contains 1000 ppm. Various oxides and hydroxides.

Manganite $\text{MnO}(\text{OH})$

Braunite Mn_2O_3

Factors affecting Mn availability

1. Soil pH and carbonates

Liming to acid soils decreases solution and exch. Mn^{2+} due to precipitation Mn^{2+} as MnO_2 .

2. Excessive H_2O and poor aeration

H_2O logging will reduce O_2 and lower redox potential will increase soluble Mn^{2+} . Poor aeration increases Mn availability.

3. Organic matter

Increases solution and exchangeable Mn.

4. Climatic factor

Increases soil temp during the growing season improves Mn uptake, because of greater plant growth and root activity.

5. Soil micro org

Deficiency caused by soil organisms oxidizing Mn^{2+} to Mn^{4+} .

Forms of Mn

- i. Solution Mn^{2+}
- ii. Exchange Mn^{2+}
- iii. Organic bound Mn
- iv. Mn Mineral

ZINC

Normal concentration in plant 25 to 150 ppm

Deficiency level is < 20 ppm

Toxic level is > 400 ppm

Zn is present in all parts of the plants. In general root contain more zinc than fruits.

Cereals : 27.8 ppm

Pulses : 34.8 ppm

Vegetables : 28.2 ppm

Fruits : 36.6 ppm

Functions of Zn

1. Essential to formation of growth hormones
2. Helps in reproduction of certain plants.
3. Stabilise ribosomal fractions
4. Influence the activity of dehydrogenase enzymes
5. Involves in auxin metabolism like tryptophan synthetase.

Deficiency of Zn

1. Light yellow or white areas bet the veins of leaves particularly older leaves.
2. Death of tissue, discolored
3. Mal formation of fruits
4. Reduced growth hormone production.

Cotton : White bud (or) little leaf

Citrus : Mottle leaf

Potato : Fern leaf

Fruit trees : Rosette (Upnormal growth)

Paddy : Khaira

Foliar spray : 0.2 to 0.5% ZnSO₄.

Sources of zinc

Soil : 10-300 ppm

Igneous rock : >10 ppm

Sedimentary : > 95 ppm

Forms of soil Zn

1. Solution Zn^{2+}
2. Adsorbed Zn^{2+}
3. Organically completed Zn^{2+}

Factors affecting Zn availability

1. Soil pH : Avail of Zn decrease with increase soil pH Zn def occur in neutral and calcareous soil. At soil pH, Zn precipitates as insoluble amorphous soil Zn, which reduces Zn^{2+} in soil.

Al and Fe oxides, OM and CaCO_3 increase with increasing pH.

2. Organic matter
3. Interaction with other nutrients

SO_4 and N can increase the Zn uptake in plants.

Higher the soil pH, poor aeration greater the Zn deficiency

COPPER

Copper is absorbed by plants as cupric ion Cu^{2+}

Normal concentration in plants 5-20 ppm.

Functions of copper

1. Essential for the synthesis of vitamin A
2. Act as a catalyst in respiration
3. Act as a “electron carrier” in enzyme which bring about oxidation reduction reactions in plants.
4. Constituent of chlorophyll.

Deficiency of copper

1. Chlorosis, withering and distortion of terminal buds.
2. Dead tissue appears along the tips and edges of leaves.
3. Multiple bud formation in the leaf axil and mal formation of leaves.
4. Guava - cracking of fruits and terminal bud die back
1. Heavy liming, excessive application of N and P - induces Cu deficiency.

Sources of copper

1. Igneous rock 10-100 ppm of Cu.
2. Sedimentary rock 4-45 ppm
3. Primary minerals contains
 1. Chalcopyrite
 2. Chalcocite
 3. Bornite
4. Sedimentary minerals
 - Oxides, Carbonates, Silicates, Sulphates and Chlorides.

Forms of soil copper

1. Soil solution - ionic and completed
2. Cation exchange sites of clay and organic matter
3. Occluded and co-precipitated in soil oxide material.
4. Specific adsorption sites
5. Inorganic matter and living organisms

Factors affecting Cu availability

1. Soil texture
2. pH
3. CEE
4. Org matter content
5. Hydrous oxides

Soil texture

Sandy soils contain lower amounts of Cu than silt and clay soils.

pH

The concentration of Cu in soil solution decreases with increase in pH.

Interaction with other nutrients

Application of NPK fertilizer induce Cu deficiency

Increase N supply to crops reduce mobility of Cu in plants

High concentration of Zn, Fe and P in soil solution also can depress Cu absorption by plant roots.

BORON

B concentration in mono cotyledons and dicotyledons (20-60 ppm) varies between 6 and 18 ppm.

It is absorbed by plants as undissociated boric acid (H_3BO_3).

Functions of boron

1. New cell development in meristematic tissue.
2. Pollination, fruit / seed set.
3. Translocation of sugars, starches, N and P
4. Synthesis of proteins and amino acids.
5. Nodule formation in legumes
6. Regulation of CHO metabolism.

Deficiencies of Boron

1. Since it is immobile, deficiency Symptoms occurs in terminal bud growth.
2. Flowering and fruit development are restricted.
3. Sterility and mal formation of reproductive organs.
4. Thickened and curled leaves.
5. Discoloration, cracking or rotting of fruit, tubers or roots

Apple - Internal cracking.

Break down of internal tissue in root crops given rise to darkened areas referred to Brown heart / black heart : cotton - weeping disease.

Sources of boron

1. Non metal among the micronutrient
2. Low concentration in earth crust igneous rocks (<10 ppm)
3. Tourmaline and borosilicate contains B.

Forms of boron (Boron cycle)

B exists in 4 forms in soil.

1. Rocks and minerals.
2. Adsorbed on clay surface, Fe and Al oxides combined with O.M.
3. Boric acid (H_3BO_3) and 4 B (OH)_4^- in soil solution.

Boron cycling between the solid and solution phase is very important because of the narrow range in solution concentration the separates deficiency and toxicity in crops.

Soil solution B

H_3BO_3 is the predominant species in soil solution at pH values ranging from 5-9. At $\text{pH} > 9.2$ H_3BO_3^- can hydrolyse to H_4BO_4^- . It was taken by Massflow and Diffusion methods in plants.

Absorbed B

B adsorption and desorption can help to reduce B leaching losses. Main B adsorption sites are

1. Broken Si - O and Al-O- bonds at the edge of clay min.
2. Amorphous hydroxide structure
3. Al and Fe oxides and hydroxides.

Factors affecting B availability

1. Soil texture : Fine text soils added B for longer period than coarse text soil.

Plants can take up larger quantity of B from sandy soils than fine text soil at equal concentration of H_2O soluble B.

2. Type of clay : Mica > mont > kaolinite

3. Soil pH and liming : Less avail to plants with increase pH heavy liming lead to greater adsorption and reduced B uptake.

4. Organic matter : Avail of B in surface soil is high compared to subsurface soil.

5. Interactions with other cations

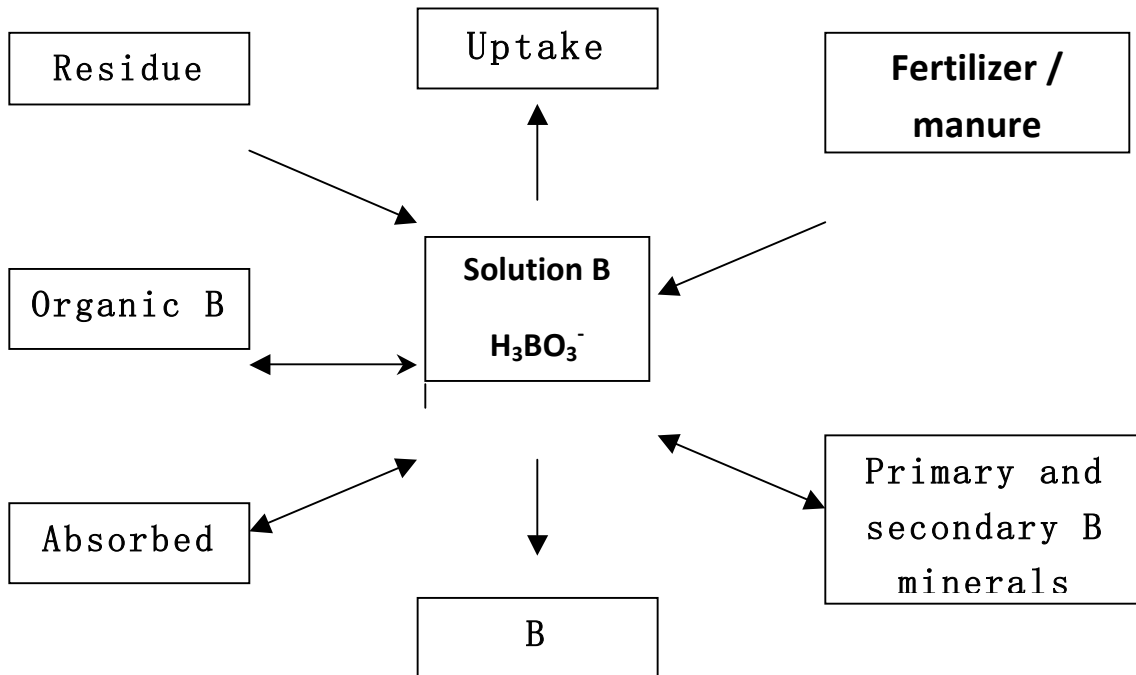
Occurrence of Ca in alkaline soil with restrict B availability. Increased K rates causes B toxicity.

6. Soil moisture

Restricted moist supply reduce the B availability in the root zone.

Boron cycle in soil

Mulch (straw)



MOLYBDENUM

Non metal anion absorbed as molybdate (MoO_4). It is weak acid and form complex poly anions such as phosphomolybdate. Plant contains <1 ppm Mo.

Functions of Mo

1. Essential component of enzyme NO_3 reductase, which catalyses NO_3^- to NO_2^- .
2. Structural component of nitrogenase enzyme - involved in N fixation.
3. Essential for absorption and translocation of Fe in plant.

Deficiency of Mo

1. Inhibits flower formation
2. Imbalances various Amino Acids in plants.

3. Reduce activity of symbiotic and non symbiotic N fixation.

Cauliflower - Whip tail.

Sources of Mo

Earth crust 2 ppm : and range from 0.2 to 5 ppm.

Forms of Mo

1. Non exchangeable Mo in primary and secondary minerals.
2. Exchangeable Mo held by Fe and Al oxides.
3. Mo in soil solution
4. Organically bound Mo.

Mo in solution occurs mainly as $\text{Mo}_4^{=}$, HMoO_4^- , H_2MoO_4^0 .

Factors affecting Mo availability

1. Soil pH and liming

Mo availability increases with increasing pH. Liming to correct acidity will increase Mo avail. Mo avail decrease with application of acid forming fertilizer $(\text{NH}_4)_2\text{SO}_4$.

2. Reaction with Fe and Al

Strongly absorbed by Fe and Al oxides.

3. Interaction with other nutrients

Mg and P enhances Mo absorption by plants.

High level SO_4 decrease Mo absorption by plants.

Cu and Mn decrease Mo uptake by plants.

$\text{NO}_3^- \text{N}$ encourages Mo uptake

$\text{NH}_4^+ \text{N}$ reduces Mo uptake

The beneficial effect of NO_3^- nutrition is related to the release of OH ions.

CHLORINE

Normal concentration in plant is about 0.2-2.0%. Absorbed by plants as Cl^- through roots and aerial parts.

Functions of chloride

1. Essential for biochemical reactions Osmotic cation neutralization reactors.
2. Act as a counter ion during rapid K fluxes.
3. Involves in the evaluation of O_2 in photosynthesis.
4. Creates disease resistant by increase osmotic pressure in cell sap.

Deficiency of Cl

1. Partial wilting and loss of turgidity.
2. Necrosis, leaf bronzing and reduction in growth.

Sources of Cl

- i. Igneous and metamorphic rocks
- ii. Soluble salts such as NaCl, $CaCl_2$ and $MgCl_2$.
- iii. Earth crust 0.02-0.05%.

It is mobile with in the plant it can be rapidly recycled through soil systems.

COBALT

Normal concentration of Co in dry matter - 0.02 - 0.5 ppm.

Functions of cobalt

1. Essential for M.O. fixing atmosphere. N. It forms vit. B12 during growth and development of symbiotic M.O.
2. Improves growth, transpiration and photosynthesis.
3. Take parts in leg hemoglobin metabolism and Ribonucleotide reductase.

Deficiency

1. Acidic, highly leached, sandy soils with total Co low.
2. Calcareous and peaty soils.

Factors affecting : Co availability

1. Soil pH : Avail increase with increase in soil acidity, H_2O logging conditions.
2. Liming and drainage practices - reduce co availability.
3. Application $CoSO_4$ rectify the deficiency.

VANADIUM

Low concentration of Vanadium is beneficial for growth of Microorganisms.

Vanadium substitute for Mo in N fixation by Rhizobia.

Involves in Biological - oxidation-reduction reactions.

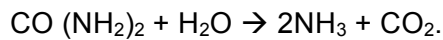
NICKEL

Nickel content in plant is 0.1 - 1.0 ppm dry matter basis.

Taken by plant as Ni^{2+}

High levels of Ni may induce Zn or Fe deficiency

1. Ni - metal component of urease that catalyse reaction.



2. Essential for N metabolism.

3. Stimulates nodule weight and yield of crops.

SODIUM

Functions

1. Essential for maintaining turgor and growth of Plants.

2. Helps oxalic acid accumulation in Plants.

3. Helps in stomatal opening and regulate NO_3^- reductase activity.

Sources of Na

Earth crust 2.8% soils

Minerals.

Forms of Na in soil

Solution, exchangeable Na and in silicate minerals.

In arid and semi arid soils Na exist in silicates, NaCl, Na_2SO_4

Na salts accumulating in poorly drained soils of arid and semi arid regions and causes soil salinity and sodicity.

Effect of Na on soil properties

Dispersing action of Na^+ on clay and organic matter reduces soil aggregation, permeability to air and H_2O , germination and root growth.

Sodium fertilizers

Sodium NO_3 : 25% Na

Rhenania PO_4 12% NA

Abundant element. in lithosphere and absorbed as monosilicic acid.

Cereals and grass contain 0.2 - 2.0%.

Functions of silica

1. Contributes structure of cell wall.
2. Contributes drought tolerance to crops.
3. Regulates photosynthesis.
4. De activates invertase enzyme activity in sugarcane resulting grater sucrose production.

Larger amounts of Si are accumulated in intracellular deposits known as 'PLANT OPALS'.

5. Increased available P.
6. Responsible for plant disease resistance.

Sources of silicon

Earth crust : 27.6% Most abundant element in earth crust.

Soils 23-35%

Primary and secondary mineral and quartz - major source.

Quartz is the most common mineral in soil, comprising 90-95% of all sand and silt fractions.

Factors affecting Si availability

1. High H_2O content encourages Si uptake
2. Heavy application of N decreases Si concentration
3. Liming decreases Si uptake in plants.
4. Acidification increases Si uptake
5. Fe and Al oxides influence Uptake of Si by plants.

Si fertilizers

1. Calcium silicate slag ($\text{CaAl}_2\text{Si}_2\text{O}_4$) - 18.21% Si
2. Calcium silicate (CaSiO_3) - 31% Si.
3. Sodium metasilicate NaSiO_3 - 23% Si.

Chelates

Chelate is a term derived from a Greek word meaning, “claw”. Chelates are soluble organic compounds that bond with **metals ions** such as Fe^{3+} / Fe^{2+} , Zn^{2+} , Cu^{2+} , Mn^{2+} , and other, thereby *increasing their solubility and supply to plant roots*. It is important particularly in micronutrient availability.

Numerous natural organic compounds in soil, or synthetic compounds added to soils, are able to complex or chelate ions of micronutrients.

Natural organic chelates in soils are products of microbial activity and degradation of soil organic matter and plant residues. Root exudates also are capable of complexing micronutrients.

The concentration of metal ions in solution and the quantity transported to the root by mass flow and diffusion can be greatly increased through complexation with natural organic chelating compounds in soil.

Substantial quantities of organic-complexed metal ions can be cycled through crop residue, which remain available for the succeeding crop.

Many of the natural organic chelates have not been identified; however, compounds like citric and oxalic acids have chelating properties.

Common synthetic chelates are:

Ethylene diamine tetra acetic acid (EDTA)

Diethylene triamine pentaacetic acid (DTPA)

Ethylene diamine di-o-hydroxy phenyl acetic acid (EDDHA)

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Questions to ponder

- 1) What is the role of organic matter addition on micronutrient availability to plants?
- 2) How does Fe and Al oxides affect the micronutrient availability?
- 3) Why is copper deficiency often referred to as reclamation disease?
- 4) What are the ways to avert Fe chlorosis?
- 5) What are the common manganese fertilizer materials?

LECTURE 12

NUTRIENT DEFICIENCY AND TOXICITY

Causes and Symptoms

Nitrogen

When N supplies are more than sufficient, carbohydrates are converted to proteins. Hence, vegetative portion is less with carbohydrates and more with protein as protoplasm. As protoplasm are highly hydrated more succulence results.

Excessive succulence may have a harmful effect. With cotton, a weakening of the fiber; with grain crops, lodging particularly with a low K supply; more susceptibility to disease and insect attack occurs.

N deficient plants become stunted and yellow in appearance. The loss of protein N from chloroplasts in older leaves produces **yellowing or chlorosis** - indicative of N deficiency. Chlorosis appears first on lower leaves; upper leaves remain green. Under severe N deficiency, lower leaves turn brown and die. This necrosis begins at the leaf tip and progresses along the midrib until the entire leaf is dead. The tendency of the young upper leaves to remain green as the lower leaves yellow or die is an indication of the mobility of N in the plant.

Phosphorus

The marked effect of P deficiency is **retarding** overall **growth**; the striking foliar symptoms that are evident with N or K deficiency are seldom observed for P, In corn and some other grass species, purple discoloration of the leaves or leaf edges appears.

Potassium

When K is limiting, characteristic deficiency symptoms appear in the plant. Typical K deficiency symptoms in alfalfa are white spots on the leaf edges; in corn and banana **chlorosis** and **necrosis** of the leaf edges.

Since K is mobile in plant, visual deficiency symptoms appear first in the lower old leaves, progressing toward the top with severity. K deficiency also occurs in young leaves of high-yielding, fast maturing crops like cotton and wheat. Another symptom is weakening of straw in grain crops, causing lodging in small grains and stalk breakage in corn and sorghum, reducing crop yields.

In fact, serious yield reductions may occur without deficiency symptoms. This phenomenon is termed *hidden hunger* and is not restricted to K alone.

Calcium

In corn, Ca^{2+} deficiency prevents the emergence and unfolding of new leaves, the tips are almost colorless covered with a sticky gelatinous material that causes them to adhere to one another.

In fruits and vegetables, the most frequent indicator of Ca^{2+} deficiency is disorders in the storage tissues: **rot in tomato, bitter pit of apples**. Often Ca^{2+} is an immobile element in the plant; hence, there is very little translocation of Ca^{2+} to fruits and storage organs.

Magnesium

Deficiency symptoms often appear first on the lower leaves. In many species, shortage of Mg^{2+} results in interveinal chlorosis of the leaf, in which **only**

veins remain green. In more advanced stages the leaf tissue becomes uniformly pale yellow, then brown and necrotic. In cotton, the lower leaves may develop a reddish-purple cast, gradually turning brown and finally necrotic.

Sulphur

S deficiency has a pronounced retarding effect on plant growth, characterized by **uniformly chlorotic** plants - stunted, thin-stemmed, and spindly. In many plants, these symptoms resemble those of N deficiency. Unlike N, deficiency symptoms occur first in younger leaves.

S deficient cruciferous crops such as cabbage and rapeseed will initially develop a reddish color on the underside of the leaves. In rapeseed the leaves are also cupped inward. In **cabbage**, there is a reddening and purpling of both upper and lower leaf surfaces; the **cupped leaves** turn back on themselves, presenting flattened-to-concave surfaces on the upper side.

Boron

B deficiency symptoms appear as thickened, wilted, or curled leaves; a thickened, cracked, or water-soaked condition of petioles and stems; and a discoloration, cracking, or rotting of fruit, tubers, or roots.

22 (2/6)

Internal cork of apple is caused. In **citrus** fruits uneven thickness of the peel, lumpy fruit, and gummy deposits result. The breakdown of internal tissues in root crops appear as darkened areas and referred as ***brown heart or black heart.***

Iron

Fe deficiency is most frequently seen in crops growing on calcareous or alkaline soils. Fe chlorosis is exhibited by citrus and deciduous fruit crops, by sorghum, grown in neutral to alkaline soils. Other crops are soybeans, beans, corn, strawberries, avocado, vegetable crops, and many ornamentals.

Deficiency of Fe shows up first in young leaves, as a result, growth ceases. The young leaves develop an **interveinal chlorosis**, which progresses rapidly over the entire leaf. In severe cases, *the leaves turn entirely white*.

Fe **toxicity** causes nutritional disorders in rice grown on poorly drained, submerged soils. This condition known as **bronzing** is associated with Fe levels > 300 ppm in leaf blade of rice at tillering.

Manganese

In broad-leaved plants, interveinal chlorosis appears. Mn deficiency of several crops is described by terms: **gray speck** of oats, **marsh spot** of peas, **speckled yellows** of sugar beets. Wheat plants low in Mn are often more susceptible to root rot diseases.

Plants are injured by **excess** of Mn. *Crinkle leaf of cotton* is an Mn toxicity observed in highly acid red yellow soils. Mn toxicity in tobacco, soybeans, tree fruits, and rapeseed is noted on extremely acid soils.

Copper

Deficiencies of Cu are reported in numerous plants, *although they are more prevalent among crops growing in peat and muck soils*. Crops most

susceptible to Cu deficiency include alfalfa, wheat, onions, carrots, clover, corn, and fruit trees.

Symptoms vary with crops. In corn, the youngest leaves become yellow and stunted, and if more severe, the young leaves turn pale and older leaves die back. In advanced stages, dead tissue appears along the tips and edges of the leaves *in a pattern similar to that of K deficiency*.

Cu-deficient small-grain plants lose color in young leaves, which break, and die. In many vegetable crops, the leaves lack turgor, developing a bluish-green cast, with chlorotic curl; flower production fails.

Zinc

Crops sensitive to Zn deficiency are corn, beans, citrus, flax, grapes, onions, rice, and soybeans. Mildly sensitive crops are alfalfa, clovers, sorghum, sudan grass, and tomatoes.

Deficiency symptoms appear frequently in leaves; sometimes in fruit or branches or affect in overall development of the plant. Symptoms include light green, yellow, or white areas between the veins of leaves particularly the older lower leaves resulting in: Chlorotic leaf areas. Shortening of the stem **rosette** appearance of the leaves; Malformation of the fruit, often with low or no yield.

White bud in corn and sorghum, **little leaf** in cotton, **mottle leaf or frenching** in citrus crops, **fern leaf** in potato are described terms of Zn deficiency.

Molybdenum

Mo is a structural component of nitrogenase enzyme that actively involves in N_2 fixation. Mo deficiency arrests biological N_2 fixation. Legumes exploit soil N supplies, turning soil to low N fertility, if the legume residues are not incorporated in soil.

Chloride

As Cl^- is the active osmotic agent, its deficiency results in partial wilting and loss of leaf turgor. Chlorosis in younger leaves and an overall wilting of the plants are the two most common symptoms of Cl^- deficiency. Necrosis in some plant parts, leaf bronzing, and reduction in root growth may be seen. Tissue concentrations below 70 to 700 ppm are usually indicative of deficiency.

Symptoms **high level of Cl^-** in wheat plants are increase total leaf water potential and cell sap osmotic potential. Excess of Cl^- can be harmful, and crops vary widely in their tolerance to this condition. Tobacco, legumes are among the most sensitive crops. Leaves of tobacco and potatoes thicken and tend to roll. The storage quality of potato tubers is adversely affected.

Cobalt

The essentiality of Co is for the growth of symbiotic microorganisms such as symbiotic rhizobium, free-living N_2 -fixing bacteria, and blue-green algae and in the formation of vitamin B12. Hence, lack of cobalt affects N_2 fixation in soil.

Silicon

Freckling, a necrotic leaf condition is a symptom of low Si in sugarcane receiving direct sunlight due to Ultraviolet radiation. Adequate Si in sugarcane plant filters out harmful ultraviolet radiation.

The oxidizing power of rice roots and accompanying tolerance to high levels of Fe and Mn were dependent of Si nutrition. Si application is necessary when Si concentration in rice straw falls below 11%. Many of the favorable effects of Si on plant growth, such as disease resistance, stalk strength, and reduction in lodging, have also been attributed to K.

Nickel

High levels of Ni may induce Zn or Fe deficiency because of cation competition. Application of some sewage sludge may result in elevated levels of Ni in crop plants.

LECTURE 13

SOIL FERTILITY EVALUATION

Calibration, Correlation of crop responses, yield prediction, fertilizer recommendation

SOIL TESTING RESEARCH IN INDIA

Farming is a business and, like all businesspersons, the farmer operates farming business for profit. Obviously, to reach a decision before planting a crop, a farmer needs all of the reliable information from the country's soil evaluation programme. In our country, system of fertility evaluation is being modified from time to time in various stages incorporating crop response data.

Some Important landmarks in soil testing research in India:

Year	Landmark
1953	Soil fertility and fertilizer use project
1955	Establishment of Soil Testing Laboratories
1956	All India Coordinated Agronomic Research Project
1960s	Establishment of Agricultural Universities
1967	All India Coordinated Research Project on Soil Test Crop Response (STCR) correlation
1967	All India Coordinated Research Project on Micronutrients in Soils and Plants
22 (6/6)	All India Coordinated Research Project on Long term Fertilizer Experiments
1980s	Emphasis on fertilizer prescription for whole

cropping system based on initial soil tests.

Since Liebig's time around 1840 many methods and approaches have been tried to get a precise or workable basis for predicting the fertilizer requirements of crops. The fertilizer use project initiated in 1953 following a study by Stewart (1947) was the first systematic attempt in the whole of the country to relate the knowledge of soils to the judicious use of fertilizers. The establishment of soil testing laboratories was initiated in 1955-56.

The project on Model Agronomic Experiments on Experimental Farms and Simple fertilizer trials on cultivators' Fields was started in 1957. The Soil Test Crop Response (STCR) correlation work carried out at Indian Agricultural Research Institute, New Delhi had resulted in the selection of soil test methods and categorizing the tests into low, medium, and high soil fertility classes.

Soil fertility evaluation

Soils are very heterogeneous in respect to forms of nutrients they contain, which greatly complicates the interpretation of Soil Test for assessing fertilizer needs. The total amount of a nutrient present in a soil offers little information relative to the amount of that nutrient which is available. Numerous extracting solutions and procedures have been used to remove nutrient elements from the soil, but none remove exactly the amount that plant roots obtain.

This means that, in order to interpret the data, the results from each analytical procedure must be correlated with the plant response obtained in field experiments by applying that fertilizer nutrient.

By this calibration, the requirement of fertilizer is calculated for achieving specific yield target. Soil fertility evaluation preferably employs a particular method of calibration as per the utility of the outcome.

Crop Response Data

In nutrient rating experiments, soil test data is correlated with the response of crop. The response is measured in terms of 'percent yield' or 'percent yield increase'. Both represent the ratio of the yield obtained in unfertilized soil (nutrient limiting deficient soil) to the yield in fertilizer nutrient applied soil (non-limiting or nutrient sufficient soil). The yield in non-limiting soil is otherwise known as maximum attainable yield or yield of standard treatment with all nutrients applied.

While comparing native fertility, in experiments that are conducted at different locations, *percent yield* is used.

$$\text{Percent yield} = \frac{\text{Yield without fertilizer nutrient}}{\text{Yield in standard treatment}} \times 100$$

While conducting multi location trials, or a pot experiment in a single location with soils brought from different locations, *percent yield increase* is worked out for every level of fertilizer application. The highest yield obtained in the experiment with all fertilizer nutrient applied, is taken as Maximum attainable yield

$$\text{Percent yield increase} = \frac{\text{Yield at fertilizer nutrient level} - \text{Yield without fertilizer nutrient}}{\text{Maximum attainable yield}} \times 100$$

The soils analyzed by standard nutrient extraction method are grouped. The soil tests are calibrated into different fertility groups by various procedures.

Present approaches in formulation of fertilizer recommendations extensively used in India:

Soil testing programme was initially started adopting the International soil fertility evaluation and improvement programme (Fitts, 1956). In this approach much stress is laid on laboratory characterization, followed by potted-plant studies ultimately leading to field - verification trials. These two initial steps help in eliminating arbitrariness of field trials. However, this approach had low adoption as it arrived one critical value below which economic responses are possible. Later, many improvements were suggested.

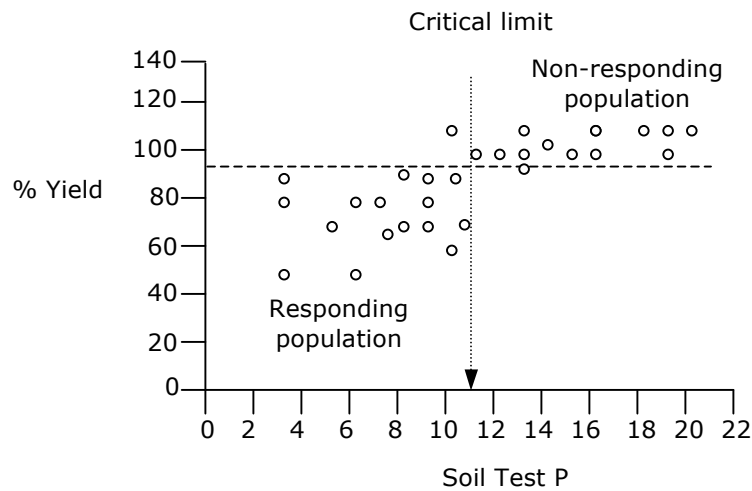
AGRONOMIC APPROACH

This is based on **fertilizer rate experiments** (recording yield at increasing nutrient levels) conducted at many locations. The level at which yields are high are recorded and averaged. From these results, the optimum dose of fertilizer is recommended for a crop at given agro-climatic region. Eg. A blanket dose of 120-50-50 kg/ha of N, P₂O₅, K₂O respectively is recommended for rice.

CRITICAL LIMIT APPROACH

Waugh and Fitts (1965) developed this technique which is largely meant for less mobile nutrients like P, K and micronutrients. Soils vary considerably in fixing capacities. Due to it a part of applied P, which is fixed in soil, is not readily available to plants.

The method includes incubation study. For P, Soil is incubated for 72 hours with graded doses of soluble P in the form of monocalcium phosphate. Then, the amount of phosphates released (extracted) with an extracting reagent (Olsen or Bray) will be determined. The extracted P versus the amount of P applied is plotted. If the relationship is unique, then for high P fixing soils a larger amount of fertilizer P application is needed. This amount of P fixed is estimated as X-value.



Then, in potted experiment fertilizer P is added at 0, 0.5X, X, 2X levels, and the test crop was grown to find out the soil critical value. The percentage yield obtained is plotted against the soil-test value for different soils. By using a plastic overlay, these data are grouped into two populations as described by Cate and Nelson (1965). The soil-test value where the vertical line crosses the x-axis is designated as the soil critical limit.

Critical limit for the soil test value is *the limit below which a positive or economic response to added fertilizer is possible and above which the response diminishes at a faster rate or vanishes.*

The validity of critical value is verified by conducting verification trials in the field locations where from the soil samples have been collected for pot studies.

14. PREDICTING YIELDS USING NUTRIENT FUNCTIONS

Nutrient function Crop yield is a function of 4 major factors:

$$\text{Yield} = f(\text{crop, soil, climate, management}).$$

Nutrient functions are fitted using data obtained in experiments conducted either in *deductive* or *inductive* approach.

Deductive approach

Deductive approach utilizes the natural variation in soil fertility for calibrating soil test values. Multilocation trials are carried out with same set of treatments. The responses are then fitted in the fertilizer prescription models.

Colwell (1967) developed this approach on the basis that some variables, which affect the response of crop to fertilizers, if omitted from the correlation between soil test and yield led to poor correlations. To prevent this difficulty, a calibration model was suggested based on the generalization of coefficients of an *orthogonal polynomial yield-response model*, which can include all the variables affecting the responses to fertilizers.

Inductive approach

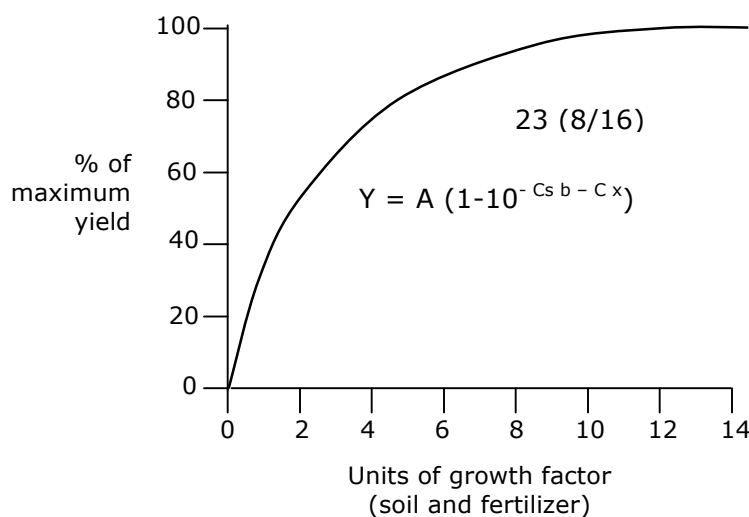
This approach is by creating fertility gradient artificially in a particular experimental location by addition of fertilizers. The approach of inducing fertility gradient (Ramamoorthy, 1970) aims at eliminating influence of the 3 out of 4 factors in the yield function, namely: crop, climate and management in the experimental location.

A large field having wide variation in fertility is chosen in a location. It is divided into 4 strips, which are treated with 4 doses of N, P and K fertilizers, viz., control ($N_0P_0K_0$), $\frac{1}{2}$ normal dose ($N_{\frac{1}{2}}P_{\frac{1}{2}}K_{\frac{1}{2}}$), normal dose ($N_1P_1K_1$) and double dose ($N_2P_2K_2$). The normal doses are fixed based on **nutrient fixing capacity** of the soil. Exhaustive crop like maize is grown. The calibration crop experiment is then laid out. For the purpose of correlation, 21 treatments having one untreated check plot are tested.

Quadratic Model:

Percentage of yield maximum concept (sufficiency concept)

This is commonly known as Mitscherlich and Bray approach. An empirical relationship is developed between percent yield, soil test, and fertilizer maximum yield (Bray, 1944).



Presently, this approach is modified and used by the Department of Agriculture, Tamil Nadu for giving site-specific fertilizer recommendations.

The modified Mitscherlich-Bray equation is:

$$\text{Log } (A-Y) = \text{Log } A - C_s b - C_x$$

Where,

A	=	calculated maximum yield
Y	=	percentage yield
C _s	=	proportionality factor for soil nutrient
b	=	soil test value
x	=	dose of fertilizer added.

The maximum yield (A) is calculated by extrapolation.

Quadratic Model:

Regression model for maximum profit

The amount of fertilizer that produces the greatest profit per hectare is called the optimum dressing (Cooke, 1972). Ramamoorthy (1974) established a significant relationship between soil tests, added fertilizers and crop yields by fitting a multiple regression of the quadratic form (*orthogonal polynomial yield-response model*):

$$Y = A + b_1 SN + b_2 SP + b_3 SK + b_4 SN^2 + b_5 SP^2 + b_6 SK^2 + b_7 FN + b_8 FP + b_9 FK + b_{10} FN^2 + b_{11} FP^2 + b_{12} FK^2 + b_{13} SNFN + b_{14} SPFP + b_{15} SKFK$$

Where

Y	=	Crop yield (kg/ ha)
A	=	Intercept
b _i	=	Regression coefficient

SN, SP, SK = Available contents of soil N, soil P and Soil K
 FN, FP, FK = Fertilizer N, Fertilizer P, Fertilizer K

Fertilizer calibrations for varying soil test value for obtaining maximum profit per hectare could be derived where the response to added nutrient follows the law of diminishing returns (Ramamoorthy, 1974)

Fertilizer adjustment equation is derived in the form:

$$\begin{aligned} \text{FN} &= a - b \text{ SN} - c R \\ \text{FP}_2\text{O}_5 &= a - b \text{ SP} - c R \\ \text{FK}_2\text{O} &= a - b \text{ SK} - c R \end{aligned}$$

Where,

$$R = \frac{\text{Cost of fertilizer nutrient (Rs./kg)}}{\text{Value of produce (Rs./kg)}}$$

Linear model:

Targeted Yield approach

Fertilizer recommendation must aim at providing balanced nutrition to crops. Balanced nutrition should have 23 (10/16) nutrients to be present in available forms in adequate quantities and required proportion for the plant in order to produce maximum yield. The requirement of nutrient to produce the expected yield can be worked out based on **nutrient uptake**.

Nutrient requirement of crops

Crop	Nutrient Requirement (kg) to produce 100 kg of economic produce		
	N	P ₂ O ₅	K ₂ O
Rice	2.01	1.12	3.00
Wheat	2.45	0.86	3.28
Maize	2.63	1.39	3.58
Sorghum	2.24	1.33	3.40
Finger millet	2.98	1.13	3.90
Chick pea	4.63	0.84	4.96
Soya bean	6.68	1.77	4.44
Ground nut	5.81	1.96	3.01
Potato	0.39	0.14	0.49
Cotton	4.45	2.83	7.47

Liebig's law of minimum states that the growth of plants is limited by the plant nutrient element in the smallest quantity, when all others being present in adequate amounts. This forms the basis for fertilizer application for targeted yields, first advocated by Troug (1960) by significant **linear relationship** between the yield of grain and uptake of nutrients. Yield target can be projected within the linear region of the response function.

This approach, popularly known as **Soil Test Crop Response Function (STCR)**, implies that for a specific yield (grain or any other economic produce) a definite quantity of the nutrient must be taken up. This value can be determined by the magnitude of the expected yield (T in q/ha) and the nutrient requirement to produce unit quantity of that target (NR in kg/ha).

Once it is known for a target yield, the fertilizer dose (FD kg/ha) can be estimated.

It is done by taking into account the efficiency of soil contribution (CS in percent) from the soil available nutrients (STV in kg/ha), and the efficiency of fertilizer of fertilizer contribution (CF in percent) from the fertilizer nutrients (FD in kg/ha) towards the total uptake.

$$FD = \frac{NR}{CF} \times 100 T - \frac{CS}{CF} \times STV$$

Where F and S stand for fertilizer and soil nutrient in Kg/ha and T is yield target in q/ha.

LECTURE 15

FERTILITY EVALUATION BY PLANT ANALYSIS

Plant analysis is a useful diagnostic tool to ascertain if a nutrient has been or is being assimilated. Plant analysis is also important in ascertaining the nutrient requirements and nutrient status of plants during various stages of growth.

A reasonably simple laboratory test of plant sample provides a measure of nutrient availability in soil or nutrient status of plant at the time the sample was collected. If these tests are to be useful in making fertilizer recommendations, a coordinated laboratory-field research program must be conducted in order to obtain the desired information.

Deficiency symptoms

Careful inspection of growing seedling or plants can help identify specific nutrient stress. If a plant is lacking in a particular nutrient, characteristic symptoms may appear. Nutrient deficiency symptoms must be related to some function of the nutrient in the plant. Visual symptoms may be caused by more than one nutrient. In a set of nutrient omission and addition pot experiments, exact limiting nutrients can be identified.

Tissue tests

The concentration of the nutrients in the cell sap is usually a good indication of how well the plant is supplied at the time of testing. These semi-quantitative tests are intended mainly for verifying or predicting deficiencies of N, P, K, S and several micronutrients.

Method: the plant parts may be chopped up and extracted with reagents. The intensity of color developed is compared with standards and used as a measure of nutrient concentration. Tissue tests are quick, easy to conduct and interpret.

For tissue tests, the time of sampling and plant part to be sampled have already been standardized for many crops. Tissue test can be done 5-6 times in a season and concentration can be monitored in the *farm premises*.

There can be two peak periods of nutrient demand, one during maximum vegetative growth and second during reproductive stage. Fertilization can be done to maintain the peak concentration at critical stages.

Total plant analysis

As in tissue tests, a standardized method for time and method of sampling of plant part are available for total analysis, which is done at *laboratory*. The critical nutrient concentration is commonly used in interpreting plant analysis results and diagnosing nutritional problems.

Diagnosis and Recommendation 23 (12/16) **System (DRIS)**

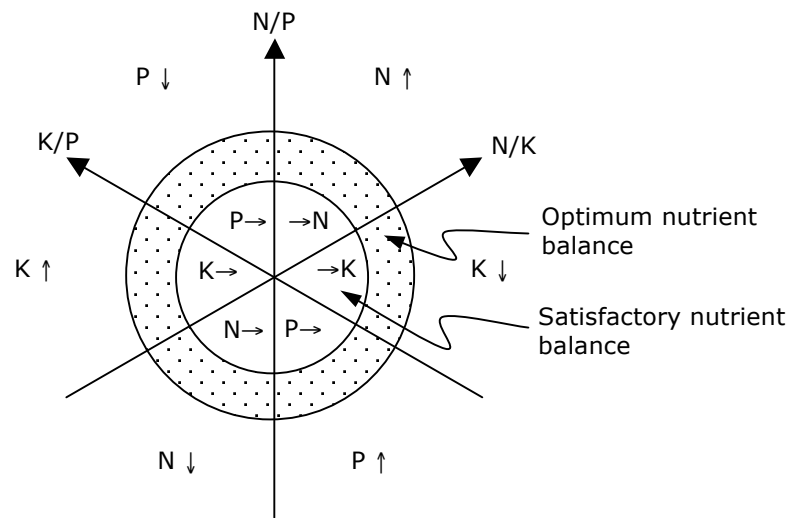
DRIS is a system that identifies all the nutritional factors limiting crop production. Index values measure how far particular nutrients in the leaf or plant are from optimum levels. Index values are used in the calibration to classify yield factors in the order of limiting importance. To develop a DRIS for a given crop, the following criteria are to be well considered.

- All factors having effect on yield
- Relationship among factors
- Calibration norms
- Continually refined recommendations

DRIS was developed based on **nutrient ratios**. When compared to concentration that normally varies with season, nutrient ratio does not vary much. When a nutrient ratio has an optimal value, optimum yield occurs unless some other limiting factor reduces the yield.

$\frac{N \rightarrow}{P \rightarrow}$	$\frac{N \uparrow}{P \uparrow}$	$\frac{N \downarrow}{P \downarrow}$
Both numerator and denominator optimal	Both numerator and denominator excessive	Both numerator and denominator insufficient

When the ratio is too low a response in the numerator will be obtained if it is limiting. If the nutrient in the denominator is excessive, a yield response may or may not occur depending on the level of other yield factors.



General diagram for a DRIS; constructed on nutrient ratios for N-P-K

When the ratio is too high the reverse is true. Usually N/S, K/Mg, K/Ca, Ca + Mg /K, N/P ratios are commonly used. Initially relationship among N-P-K is calibrated.

Thus, DRIS has several advantages to integrate much nutrient concentration at various stages, in different seasons suitable for many cultivars of a crop.

DRIS has been found suitable for several grain crops and perennial fruit trees.

23 (14/16)

CROP LOGGING

An excellent example of the use of plant analysis in crop production is the crop logging carried out for sugarcane in Hawaii. The crop log, which is a graphic record of the progress of the crop, contains a series of chemical

and physical measurements. Critical nutrient concentration approach is used in the crop log system.

In sugarcane, plant is sampled at 35 days and analyzed for N, sugar, moisture and weight of young sheath tissue. Nutrients like P and K are monitored at critical stages. Based on moisture, irrigation is scheduled. Based on nutrient content, fertilizer application is done. By this record keeping, the productivity of crop is increased.

BIOLOGICAL TESTS

Simpler and rapid laboratory/ green house techniques utilize small quantity of soil to quantify nutrient supplying power of a soil.

Tests using higher plants:

Neubauer seedling method: The neubauer technique is based on the uptake of nutrients by a large number of plants grown on a small amount soil. The roots thoroughly penetrate the soil, exhausting available nutrient supply within a short time. Usually 100 seedlings of rye or oats made to feed 100 g soil mixed with 50 g sand. Blair (1956) is also run. Total P_2O_5 and K_2O uptake is calculated and blank value is detected to get root soluble P_2O_5 and K_2O . Values designated as Neubauer Nos. (mg/ 100 g soil) are used to determine the deficiency. These tables give the maximum values of available macro and micronutrients for satisfactory yields of various crops.

Standard and Demont technique: It is a modified neubauer technique. Round cardboard cartons with bottom removed are nested in a container and filled with sand. Seeds are sown. After 2-3 weeks of growth, a carton containing the plants is nested in a second carton holding 200 g soil or soil + fertilizer. When the mat of roots meets soil, it is allowed to feed for 3-4 days. Then nutrient uptake is estimated.

Deficiency test of sunflower for Boron

Sunflower is grown in the test soil supplied with nutrient solution with all essential nutrients excepting boron. From the day of appearance of B deficiency symptoms of leaves, the soil is identified as deficient (<28 days), moderately deficient (28-36 days), and not deficient (>36 days).

Microbiological methods:

In the absence of nutrients, certain microorganisms exhibit behavior similar to that of higher plants. For example, growth of *Azotobacter* or *Aspergillus niger* reflects nutrient deficiency in the soil. The soil is grouped from very deficient to not deficient in the respective elements, depending on the amount of colony growth. In comparison with methods that utilize growing of higher plants, microbiological methods are rapid, simple and require little space.

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Sacket and Stewart technique

For identifying P and K deficiency test soil is divided in to 4 portions. Solution containing soluble P, K, and P+K are added in 3 portions and one portion was allowed as check. They are inoculated with *Azotobacter* and incubated for 72 hrs. Based on colony growth deficiency is identified.

Melich Cunninghamella – plaque test:

Cunninghamella is sensitive for P. Test soil is mixed with nutrient solution and a paste is prepared. The paste is spread on a clay dish. *Cunninghamella* is inoculated at the centre and incubated for 5-6 days. Based on the diameter of mycelial growth, the soil is diagnosed as deficient (<10 cm), moderately deficient (11-21 cm), or not deficient (>22 cm).

Mulder *Aspergillus niger* test for Cu and Mg

Colours of mycelial and spores are used to delineate the deficiency of Cu and Mg. This method is used for Mo, Co, Mn, S, Zn also.

LECTURE 16

SOIL TESTING AND CORRELATION

The composite samples obtained from fields are used in pot-culture plant studies to assess the crop responses (in terms of dry matter) to added fertilizers. Calibration of the responses to soil - test values was obtained by using different methods. Fixation studies are conducted to ascertain the capacity of soil to fix nutrient to be applied, finally, the results are interpreted to confirm nutrient deficiencies, index soil fertility, and establish "critical level" for each nutrient. The results are verified in the next stage, in field experiments.

Fertility group/ Index

The International soil fertility evaluation and improvement programme (Waugh and Fitts, 1965) advocated grouping of soils into low-medium-high categories.

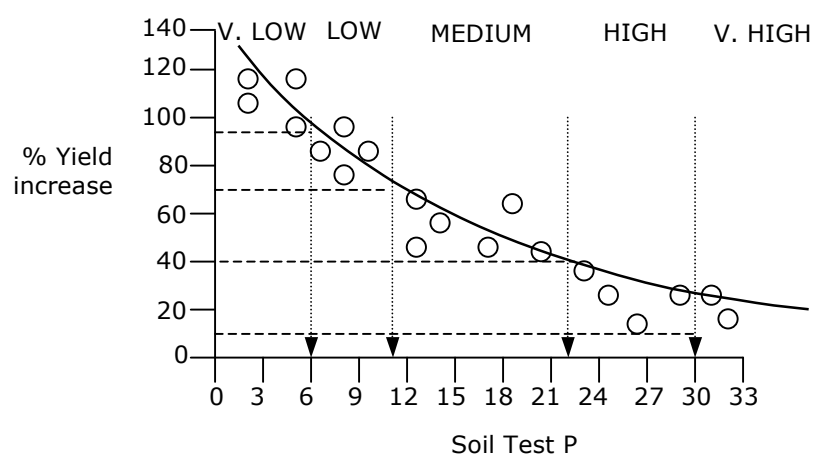
The method:

- Collection of representative soil samples and analysis by using different extractants for the 'available' nutrient
- Conducting of potted-plant studies with graded doses of added nutrient supplying all other nutrients to meet the crop requirement
23 (3/16)
- Computing of the percentage yield responses
- Plotting of the soil-test data obtained with different methods and the percent yield response; and to find the scatter distribution for the best correlating soils test methods. The scatter diagram will be generally curvilinear. The response is less, as the soil test value increases.
- The general groups are low, medium and high

The fertility groups followed in Tamil Nadu

Fertility group	Available nutrients (kg/ ha)		
	KMnO ₄ -N	NaHCO ₃ -P	NH ₄ OAc-K
Low	<280	< 11	< 118
Medium	280-450	11- 22	118-280
High	>450	> 22	>280

This classification indicates that low classes of soils would markedly respond to added fertilizers and high status of soils does not respond to them. In the medium range, nothing could be predicted. In addition, by this grouping, it was not possible to indicate how much fertilizer was to be added to get economic yields. Thus, this grouping is qualitative. Arbitrarily, the recommended dose of fertilizer for a crop is increased by 25% in low status and reduced by 25 % in high status.



Fertility index

Fertility index expresses the **relative sufficiency as a percentage of soil nutrient amount adequate for optimum yields**. The probability of a response to fertilizer application increases with decreasing soil test level.

More than 85% of soils testing very low may give greater response and profit. About 60-85% of soils, having medium soil test value may give little profit. Around 15% soils with very high soil test may have little response.

In general, the very low to very high classification is easily understood by the grower. However, separate group classification need to be done accounting for greater variability associated with crops and soils.

Soil Test Rating	Probability of Crop Response (% Yield increase)	Fertility Index
Very low	95–100	0-10
Low	70-95	10-25
Medium	40-70	25-50
High	10-40	50-100
Very High	0-10	100+

LECTURE 17

SOIL TESTING

Soil Testing, STL Functions

Soil Testing

Soil testing is defined as a 'programme for procedural evaluation of soil fertility by Rapid chemical analysis particularly to assess the *available nutrient status and reaction* of a soil'.

A **soil test** is a chemical method for estimating nutrient supplying power of a soil. Compared to plant analysis, the primary advantage of soil testing is its ability to determine **the** nutrient status of the soil before the crop is planted.

The result of a soil test is known as **soil test value**. A soil test value measures a *part of the total nutrient supply in the soil and* represents only as an index of nutrient ability.

Soil test do not measure the exact quantity of a nutrient potentially taken up by a crop. To predict nutrient needs of crops a **soil test must be calibrated against the response of crops** in nutrient rate experiments in greenhouse and fields. Thereafter, interpretation and evaluation of the soil test values primarily form the basis for fertilizer recommendation.

Soil test programmes have the following objectives:

- To provide an index of nutrient availability
- To predict the probability of profitable response to fertilizer

- To provide a basis for fertilizer recommendation
- To evaluate the soil fertility status and a county soil area or a statewide basis by the use of the soil test summaries.

Phases of Soil Testing programme

1. Collecting the soil samples
2. Extraction and determining the available nutrients
3. Calibrating and interpreting the analytical results
4. Making the fertilizer recommendation and management

Soil sampling

The most critical aspect of soil testing is *obtaining a soil sample* that is **representative of the field**. There is always a considerable opportunity for sampling error. If a sample does not represent a field, it is impossible to provide a reliable fertilizer recommendation.

The soils are normally **heterogeneous**, and wide variability can occur even in a uniform fields. Intensive soil sampling is the most efficient way to evaluate variability. The sampling error in a field is generally greater than the error in the laboratory analysis.

Soil Unit: It is an area of soil tested by a composite sample. After the soil unit is determined, the soil samples are collected throughout the area. The number of samples for combining into each representative composite sample varies from 5-20 samples in an area of an acre. Usually a composite sample of one kg of soil is taken from a field.

The size of the area may be sometimes even less for areas that vary in appearance, slope, drainage, soil types, past treatment These areas are

to be sampled for separately. The purpose of the procedure of making a composite sample is to minimize the influence of any local non-uniformity in the soil.

Normally for all field crops, sampling soil up to 15 cm depth is practiced. For deep-rooted crops and tree crops samples up to 1-2 m may be necessary. While sampling, first a uniform portion is taken from the surface to the depth desired. Second, the same volume is obtained from each area.

Preparation of the composite soil sample in the laboratory

It involves the following steps: Drying, grinding, sieving, mixing, partitioning, weighing, and storing. Uniform mixing and sampling is done by **Quartering Technique**:

The soil sample is coned in the center of the mixing sheet. Cone is flattened and divided through the center with a flat wooden sheet. One half is moved to the side quantitatively. Then each half is further divided into half, the four quarters being separated into separate 'quarters'. Two diagonally 'opposite quarters' are discarded quantitatively. The two other are mixed by rolling. This process is repeated, until 250-500 g composite soil material is obtained.

24 (3/4)

For micronutrient analysis – sampling and processing of samples should alone be done only with stainless steel materials, plastic, or wood to avoid contamination.

The soil test values calibrated nutrient functions are advocated to the farmers as a package of nutrient management that aims at **judicious use of fertilizers**. Ultimately any soil testing and interpretation must involve

‘**economics**’ because it is used to make a fertilizer recommendation to achieve an economic goal that would give ***maximum profit per hectare*** of land.

Extraction and determining the available nutrients

Many chemical extractants have been developed for use in soil testing. The ability of an **extractant** to extract a plant nutrient in quantities related to plant requirements depends on the reactions that control *nutrient supply and availability*. The extractants commonly used in soil testing programmes are given below.

Plant nutrient	Common extractant	Nutrient source extracted
NO_3^-	KCl, CaCl_2	Solution
NH_4^+	KCl	Solution - Exchangeable
Available N	KMnO_4 - NaOH	Mineralizable Organic N
$\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ (Available P)	NH_4F - HCl (Bray-p)	Fe/ Al mineral solubility
	NaHCO_3 - P (Olsen-P)	Ca mineral solubility
K^+ (Available K)	NH_4OAc -K	Exchangeable
Ca^{2+} , Mg^{2+}	EDTA	Exchangeable
SO_4^{2-}	CaCl_2	Solution AEC
Zn^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+}	DTPA	Chelation

H ₃ BO ₃ ⁰	Hot water	Solution
Organic C	Chromic acid	Oxidizable C

SOIL TESTING LABORATORY

Soil Testing Laboratories of the Department of Agriculture funded by State Government are functioning at identified centres in each district. Soil testing services are also extended to the farming community in the Soil Laboratories operated by Central government and Agricultural Universities.

The major functions of State Soil Testing Laboratory are:

- Analysis of soil samples which are collected from the farmers by the Assistant Agricultural Officers for texture (by feel method), lime status, Electrical conductivity, pH and available N, P and K status at lower charges/ sample; and advocating fertilizer recommendation for different crops. Available micronutrients will be analyzed on request.
- Analyzing irrigation water samples for EC, pH, cations, and anions; Assessing their quality based on different parameters; and suggesting suitable ameliorative measures for different soil condition and crops.
- Adopting two villages for a particular period by each soil testing laboratory; collecting and anal 10 (4/8) and irrigation water samples at free of cost and advocating the recommendations.
- Collection of benchmark water samples from the wells marked in a particular block/ water shed/ taluk. After analyzing the water samples for different properties, water quality map will be prepared.

- Based on the soil test value for the soil samples collected during the particular year they are rated as low, medium, and high; and village fertility indices will be prepared.
- Conducting trials related to soil fertility to solve the site-specific problems.

Functions of mobile soil testing laboratory

- The staff of the Mobile STL will visit the villages, collecting and analyzing the soil and irrigation water samples in the village itself and giving recommendations immediately.
- Showing the audio-visual programmes through projectors in the villages educating the importance of soil testing, plant protection measures and other practices related to crop production.
- In addition, Mobile STL is carrying out other regular functions of stationary soil-testing laboratory.

LECTURE 18

FERTILITY SURVEY AND MAPPING

Survey, village indices

Soil Fertility Survey

Soil survey essentially aims at taxonomical classification of soils in well-defined units. The properties studied in the survey are ultimately used to plot the extent of boundaries on a map. The maps are referred for various purposes particularly for predicting yields based on soil fertility.

Fertility surveys are carried out in profile studies. Profiles in representative locations in each soil series are opened and thoroughly examined. From samples collected at different depthwise layer, soil physical, chemical, and biological properties are thoroughly studied. The factors limiting crop growth are identified in field and laboratory estimations.

Parameter on the depth of soil, rooting depth, bulk density, particle density, porosity, water holding capacity, possible profile moisture storage, soil reaction, salinity, total and available nutrients, presence of hard pans. By interpretive analysis the fertility, data are grouped and used for mapping.

The division of Soil Survey and Land Use Planning of State Department of agriculture, which is operating in selected districts of the Tamil Nadu compiles the information and publish them as a Report. The reports are available on cost basis to needy persons and institutions. The results of survey are further classified and mapped by National Bureau of

Soil Survey and Land Use Planning located in Nagpur, Bangalore and in many other locations in India. The Maps are distributed on cost basis for their effective use. Soil Maps of Agro-climatic regions, fertility status, irrigability, soil depth, crop suitability, salinity, etc are available.

Besides, the State Agricultural Universities and other national Institutes conduct soil surveys and prepare maps on nutrient status marking the macro and micronutrient deficient soils for ready recognition. The remote sensing tools are also used in Mapping.

Village Fertility Indices and Mapping

In our country, the soil testing laboratories are functioning in all the states. In Tamil Nadu, the soil testing and mobile soil testing laboratories are functioning in almost all the districts.

One of the major functions of these laboratories is to analyze the soil samples collected from the farmers for available N, P and K status. For every year few taluk will be adopted. After analyzing the soil samples for available NPK, they are grouped as low, medium and high based on the soil test value as follows.

After grouping soils as low, medium and high, **Village Fertility Index** (VFI) will be worked out for every revenue village.

$$VFI = \frac{N_L + 2 N_M + 3 N_H}{N_L + N_M + N_H}$$

Where N_L , N_M , N_H are the number of soil samples falling under the category low, medium and high, which are given weight of 1,2,3

respectively. Arbitrarily an index below 1.5 is low, between 1.5-2.5 is medium, and above 2.5 is high.

Using these fertility indices, the current area wise fertilizer recommendation for each crop can be modified. A soil fertility map may be prepared in any outline map of block / taluk by plotting the index values within the boundary of villages.

LECTURE 19

PERMANENT MANURIAL EXPERIMENTS

OPM, NPM, LTFE, Findings

Permanent Manurial Experiments

Permanent manurial experiments are conducted to study the long term effect of continuous application of plant nutrients either singly or in combination and with or without organic manure on crop yield, nutrient uptake, and physico-chemical and biological properties of soil.

The first one started was the classical field experiment at **Rothamsted** Experimental Station, Harpenden in **England** in 1854 by Lawes and Gilbert.

Most of PME test common treatment combinations like: Fertilizer N or P or K alone, Fertilizer N and K, Fertilizer N and P, Fertilizer NPK, Farmyard Manure (FYM), Residual effect of FYM, Hand weeding, Zn or S addition, Control (no manure), tillage, irrigation, etc.

Similar to Rothamsted experiment, in India PME was started at **Coimbatore** in **1909** and this was the first of its kind in our country. This called as Old Permanent Manurial experiment (**OPM**) is being conducted in red soil (Alfisol) with cereal-cotton crop rotation under **rainfed** conditions.

Subsequently in **1925**, a second experiment was started with the same treatments and called as New Permanent Manurial (**NPM**) experiment to test the effect under **irrigated** conditions.

In **OPM** and **NPM** a uniform fertilizer dose of 25-60-75 kg N, P₂O₅ and K₂O/ha is being applied in all these years. As these are designed with very low dose of fertilizers and manures without any replication and randomization, they do not match to the present day use pattern of fertilizer/manure and statistical analysis.

Therefore, to study the effect of **intensive cropping and manuring** new set of experimental design was implemented all over India by ICAR by a coordinated scheme on Long Term Fertilizer Experiment (**LTFE**). During 1972, LTFEs were started at 11 centres and later further expanded at seven more centres.

Under this scheme, a third experiment was started in 1972 at Coimbatore called as Long Term Fertilizer Experiment (LTFE) in medium black soil (Inceptisol) to test intensive cropping system with Ragi-maize cropping system.

The **major findings** in these experiments are:

- Application of single nutrient (N or P or K) alone resulted in lower crop yield. Combination of NP and NPK gave higher yield.
- Phosphorus became a limiting factor when it was not applied and it reduced the yield to the extent of 50-60 per cent. Application of P along with N, K, and FYM raised the available soil P from low to medium status.
- Potassium was depleted even when it is applied continuously.

- Continuous use of N fertilizer alone reduced the soil productivity. Addition of FYM with NPK significantly increased the crop yield to the tune of 15-20 per cent over NPK alone. Addition of organic manure improved pore space and water holding capacity of soil. Combined application of organic manure and inorganic fertilizer not only increased the yield of crops but also improved the soil productivity.
- Population of bacteria, fungi, *Actinomycetes* and *Azotobacter* were increased due to organic manure incorporation. The activities of enzyme urease, dehydrogenase, cellulase, and amylase were favored by organic manure application.

LECTURE 20

FERTILIZERS - USE AND LEGISLATION

Definition, Classification, Indian Scene, products, consumption, Legislation

Fertilizers

Fertilizers are the materials either natural or manufactured, containing nutrients essential for normal growth and development of plants. It may also be defined that any material or substance intended for use as a nutrient carrier in soil or crops for boosting crop yields.

In India, the use of artificial fertilizers was first initiated in 1896 when imported Chilean nitrate was used as a fertilizer. By about 1905 calcium nitrate, calcium cyanamide, ammonium sulphate, super phosphate and potassium sulphate were also imported and used.

After the World War I, the Imperial Chemical Industries carried out valuable field experiments on different crops particularly on rice with ammonium sulphate during the period 1920-30, which established the general superiority over other nit^{26 (2/2)} fertilizers. The manufacture of ammonium sulphate in India was first started at **Belegolla in Mysore** in 1938 on a small scale.

Share of total fertilizer consumption (%) in India	
Rice	40.5
Wheat	24.2
Sugarcane	8.7

Later in 1947, its manufacture was started at **Alwaye**. In 1951, the Government of India set up fertilizer factory at **Sindri** for the production of ammonium sulphate in the public sector. Gradually several factories were established and use of fertilizers become increasingly popular.

Presently India is the **Third** producer of N and P fertilizers in the world.

Classification of fertilizers

The fertilizer materials may be classified in several ways

Based on fertilizer mixture behavior

- Straight or simple nitrogenous, phosphatic or Potassic fertilizers;
- Complex fertilizers having more than one nutrient in single material and fertilizers having more than one nutrient in single material
- Fertilizer mixtures home mixed or factory mixed materials.

Based on their chemical reaction and nature

- Acidic, neutral, and basic fertilizers

Based on nutrients present

- Simple fertilizers which contain only one nutrient
(Single carrier)
- Compound fertilizers which contain more than one nutrient
(Multinutrient carrier)

Physical properties of fertilizers:

Physical properties of fertilizers have bearing on bagging storage, transportation, handling, and application. They are properties include –

hygroscopic nature, free moisture content, particle size, melting point,
solubility, specific gravity, segregation,
granule hardness, angle of response, drillability etc.,

Chemical properties of fertilizers:

Chemical properties include the nature and amount of **nutrients** present, **associated elements**, their **chemical reaction**, and **salt index**. These make a basis for their selection by the cultivators so that they may achieve highest productivity with least damage to soil fertility and least unit cost of fertilizers.

INDIAN FERTILIZER SCENE

India is the **Third** largest producer and consumer of fertilizers in the world. At present, there are 59 large size fertilizer plants in the country manufacturing range of fertilizers. The current installed capacity is 12.1 m tonnes per annum (tpa).

This fertilizer sector is highly subsidized. It relies heavily on imports to meet domestic demand. Indian Government incurs a total subsidy bill about 14% of fiscal deficit every year.

The major grades of fertilizers are Nitrogenous (N), Phosphatic (P) and Potassic (K). N accounts for 71%, P for 22%, and K for 7% of the total fertilizer consumption. Potassic grade of fertilizer is totally imported and is not manufactured in India.

Urea (85% of N fertilizer consumption) constitutes 58% of the total consumption of fertilizers in India. Di-ammonium phosphate (DAP) accounts for approximately 66% of consumption of phosphatic fertilizers.

The N based fertilizer uses indigenously available feedstock (raw material) to produce ammonia, which is processed further to make urea.

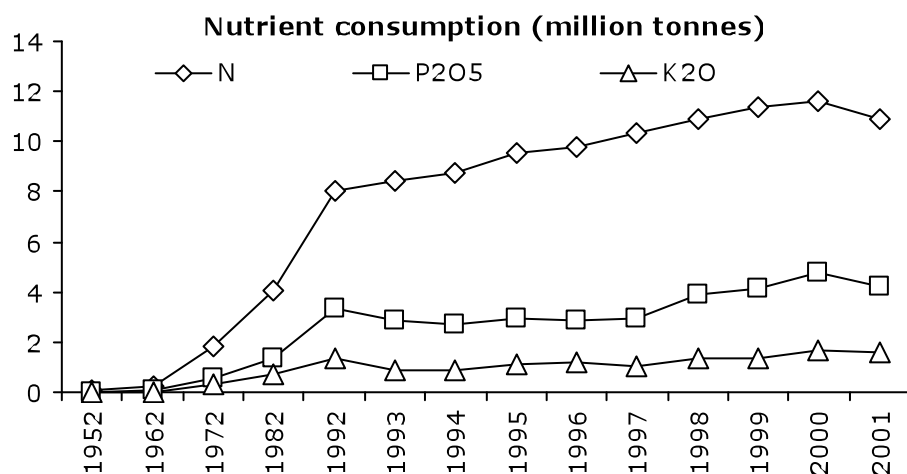
Rock phosphate and potash, the key raw materials for Phosphatic and Potassic fertilizers respectively are **imported** into India, due to lack of domestic availability.

Before April 1, 1997, the State Governments fixed fertilizer prices at non-remunerative levels. In addition, there were procedural delays in fixing prices for each crop season, and delays in reimbursing subsidy to the producers.

The reimbursement price fixation is now done by the Central Government, which may lead to more realistic price levels, and faster disbursements of subsidies.

Consumption of Fertilizer by Nutrients ('000 tonnes)

Year	N	P ₂ O ₅	K ₂ O	Total
1951-52	58.7	6.9	-	65.6
1961-62	249.8	60.5	28.0	338.3
1971-72	1798.0	558.2	300.6	2656.8
1981-82	4068.7	1322.3	676.2	6067.2
1991-92	8046.3	3321.2	1360.6	12728.0
1992-93	8426.8	2843.8	883.9	12154.5
1993-94	8788.3	2669.3	908.7	12366.3
1994-95	9507.1	2931.7	1124.8	13563.6
1995-96	9822.8	2897.5	1155.8	13876.2
1996-97	10301.8	2976.8	1029.6	14308.1
1997-98	10901.8	3913.6	1372.5	16187.8
1998-99	11353.8	4112.2	1331.5	16797.5
1999-00	11592.7	4798.3	1678.7	18069.7
2000-01	10861.9	4212.4	1557.1	16631.4



Important Fertilizer Products in India

	Grade (%)	Consumption (1999-2000) ‘000 tonnes
Produced in India		
Straight Nitrogenous		
Urea	46 N	20277.66
Ammonium sulphate	20.6 N	638.10
Ammonium chloride	25 N	75.19
Calcium ammonium nitrate	25 N	347.25
Straight Phosphatic		
Single super phosphate	16 P ₂ O ₅	3600.99
Diammonium phosphate	18-46-0	6937.68
NP/NPK Complex Fertilizers N: P ₂ O ₅ : K ₂ O		
Ammonium Phosphate Sulphate	16-20-0	220.89
Nitro Phosphate with Potash	15-15-15	341.82
Urea Ammonium Phosphate	27 (4/8) 28-0	173.66
	14-35-14	184.32
Nitro Phosphate	20-20-0	1531.56
	23-23-0	222.19
Others	10-26-26	529.79
	12-32-16	499.45
	17-17-17	681.00
	19-19-19	126.63

	14-28-14	11.47
Imported Fertilizers		
Straight Potassic		
Muriate of potash	60 K ₂ O	2049.24
Sulphate of potash	50 K ₂ O	17.50
Straight Phosphatic		
Rock phosphate	12-18 P ₂ O ₅	102.96

LECTURE 21

PROSPECTS OF FERTILIZER USE

Growth in the future will have to come from an increase in cropping intensity and productivity growth, which implies the higher use of fertilizers. This is because during 1991-2000, food grain production grew at a rate of 1.7% (population growth over the same period: 1.9%), while net sown area stagnated at 1.41 m hectares.

Agriculture constitutes 33% of GDP and farmers constitute over 60% of the vote bank in India. Considering the importance and sensitivity of the sector and the strong lobby of farmers in Indian politics, it is unlikely that the government will frame a clear longterm policy in near future to resolve problems faced by manufacturers. Hence, regulated pricing and subsidies is likely to continue.

Availability of natural gas will be crucial to the fortunes of fertilizer manufacturers as it is the preferred feedstock. Any reduction in availability and changes in its pricing will affect production and profitability of the companies in this sector.

In a much-deregulated environment, market forces will dictate the competition. Distribution network competitiveness and regional imbalances will assume importance. In such a scenario, efficient producers and distributors will do well. Potash fertilizer will continue to be imported, as it cannot be manufactured domestically due to the absence of supplies of critical raw materials.

FERTILIZER LEGISLATION

Chemical fertilizers are becoming increasingly expensive day by day due to hike of prices of petroleum, inflation etc., which tempts dealers to adopt malpractices for earning more profits through adulteration, supplies of underweight materials or blending of degraded fertilizers etc. Thus, the farmers are ditched and often they fail to get good response of applied fertilizers. Therefore, the laws regulating the manufacture and sale of various fertilizers are essential to ensure that the consumer or the farmer is supplied with fertilizers of standard quality.

Keeping these points in mind, the Government of India brought in the fertilizer Control Act.

FERTILIZER CONTROL ACT

The Union Government of India promulgated the fertilizer Control Act (F.C.O) in **1957** under the ***Essential Commodities Act***, 1955 (section 3) with a view to regulate fertilizer business in India.

The F.C.O. keeps a strict watch on quality control of fertilizers, provides for the registration of dealers and statutory control of fertilizer prices by Government. Therefore, everybody involved in fertilizer business as a manufacturer, dealer or a salesperson, must have proper understanding of the F.C.O. in order to avoid infringement of Government regulations.

The provisions given in the Order will also help the consumers/ farmers to know their rights and privileges in respect of fertilizer quality and Authorities to be approached for their grievances regarding supply of sub-standard materials, overcharging or containers of underweight supplies.

The F.C.O. is published by the Fertilizer Association of India (F.A.I.), updated when ever felt necessary. The Order has provisions on quality for

each consumed fertilizer product and F.C.O. should be consulted under infringement of any of them.

Control of Quality of Fertilizers

The F.C.O. has provisions to penalize manufactures, distributors, and dealers for supply of spurious or adulterated fertilizers to consumers or farmers. The F.C.O. has fixed specifications for various fertilizers, which must be present in them failing which the legislation comes in force, and guilty is punished.

Example: The specifications for **urea**

Moisture % by weight (Max.)	...	1.00
Total nitrogen % by weight (Min.)	...	46.00
Biuret % by weight (Max.)	...	1.50

Particle size:

Granules must pass through IS sieve 320 and

Not less than 80% by weight shall be retained on IS sieve 100.

If it is in the form of **prill**, it shall pass IS sieve 200 and

Not less than 80% by weight shall be retained on IS sieve 100.

Example: The specifications for **Rock phosphate**

Particle size:

The material must completely pass through 6.3 mm IS sieve and not less than 20 % material shall pass through 1.50 micron IS sieve.

Total P₂O₅ content is to be guaranteed by the dealer.

Example: The specifications for Potassium **Schoenite**

Moisture per cent by weight	...	1.50
Potassium % (K ₂ O) by weight (Max.)	...	23.00

MgO % by weight (Min. on dry basis)	...	10.0
Total chloride % (Cl) by weight (Max. on dry basis)	...	2.5
Sodium % (as NaCl) (Max. on dry basis)	...	1.60

LECTURE 22

Tolerance limit in Plant Nutrient for various fertilizers

Category	Limit
Straight fertilizers containing <20% plant nutrients	: 0.1 Unit of nutrient
Straight fertilizers containing >20% plant nutrients	: 0.2 Unit of nutrient
Calcium ammonium nitrate	: 0.3 Unit of nutrient
Complex/ Mixed fertilizers	: 0.5 unit for each and maximum of 2.5 % for all nutrients

Fertilizer Movement Control Order

The Fertilizer Movement Order (F.M.O.) was promulgated by Government of India in April 1973 to ensure ***an equitable distribution*** of fertilizers in various States. According to the fertilizer movement order, no person or agency can export chemical fertilizers from any State. However, Food Corporation of India, Warehousing Corporation of India and Indian Potash Limited; materials like Rock phosphate, bone meal (both raw and steamed) and zinc sulphate are exempted from the movement restriction.

Agency responsible for Enforcement of F.C.O

The Controller of Fertilizers for India, usually a **Joint Secretary** to the Government of India (Ministry of Agriculture) is responsible for the enforcement of F.C.O. throughout the country.

Electrical Conductivity of the soil saturation extract

Measurement of EC of the soil saturation extract is essential for the assessment of saline soil for the plant growth.

EC (dS m ⁻¹)	<2	-	Salinity effects mostly negligible
	2-4	-	Yields of very sensitive crops may be restricted
	4-8	-	Yields of many crops restricted
	8-16	-	Only tolerant crops yield satisfactorily
	>16	-	Only a few tolerant crops yield satisfactorily

Concentration of water soluble boron

The determination of water-soluble boron concentration is also another criteria for characterization of saline soils. The critical limits of boron concentration for the plant growth are given below.

Boron	<0.7	-	Crops can grow (safe)
concentration	0.7-1.5	-	10 (19/26)
(ppm)	>1.5	-	Unsafe

Reclamation of Saline Soils

In saline soils, reclamation consists mainly in removing the excess salts. This can be done either

- By scraping the salts from the surface (or)

- Washing them down into lower layers beyond the root zone preferably completely out of the solum (or)
- By growing salt tolerant crops (or) by a combination of two (or) more of these methods

Scraping helps to remove salts that have formed an encrustation on the surface, but it is never very helpful in complete reclamation. Substantial quantities of soluble salts are still present in the soil body and hinder plant growth.

Salt tolerant crops

High salt tolerant crops - Rice, sugarcane, Sesbania, oats

Medium salt tolerant crops - Castor, cotton, sorghum, cumbu

Low salt tolerant crops - Pulses, pea, sunnhemp, sesamum

The growing of salt tolerant plants with a view to remove salts is also not a practical proposition. Although these plants remove substantial quantities of salts from the soil, comparatively larger quantities are still left behind. Salt formation is a continuous process; hence, the reclamation is never complete

LEACHING REQUIREMENT (LR)

It may be defined as

The fraction of the irrigation water that must be leached through the root zone to control the soil salinity at any specified level.

$$LR = \frac{D_{dw} \times 100}{D_{iw}} = \frac{EC_{iw} \times 100}{EC_{dw}}$$

Where

LR - Leaching requirement in percentage

D_{dw} - Depth of drainage water in inches

D_{iw} - Depth of irrigation water in inches

EC_{iw} - EC of irrigation water (dSm^{-1})

EC_{dw} - EC of drainage water (dSm^{-1})

If the soil is not free draining, artificial drains are opened (or) tile drains laid underground to help to wash out the salts.

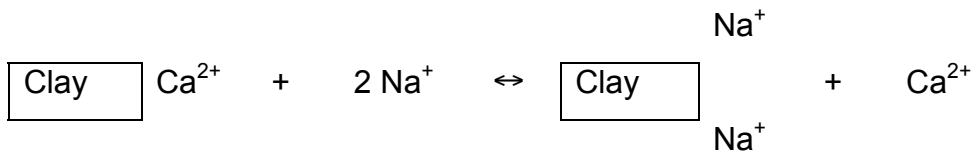
ALKALI SOIL (sodic/ *Solonetz*)

Alkali (or) sodic soil is defined as a soil having a conductivity of the saturation extract less than $4 dS m^{-1}$ and an ESP of > 15 . The pH is usually between 8.5 and 10.0. Formerly these soils were called “**black alkali soils**”

Genesis/ origin

It is evident that soil colloids adsorb and retain cations on their charged surfaces. Cation adsorption occurs due to electrical charges at the surface of the soil colloids. While, adsorbed cations are combined chemically with the soil colloids, they may be replaced by other cations that occur in soil solution. The reaction of cation in solution that replaces an adsorbed cation is called as cation exchange and is expressed as $cmol (p^+) kg^{-1}$.

Calcium and magnesium are the principal cations found in the soil solution and on the exchange ^{10 (20/26)} normal soils in arid regions. When excess soluble salts accumulate in these soils, sodium frequently becomes the dominant cation in the soil solution. In arid regions as the solution becomes concentrated through evaporation or water absorption by plants, the Ca^{2+} and Mg^{2+} are precipitated as $CaSO_4$, $CaCO_3$ and $MgCO_3$ with a corresponding increase in sodium concentration. When the Na^+ concentration is **more than 15% of the total cations** a part of the original exchangeable Ca^{2+} and Mg^{2+} replaced by sodium resulting in alkali soils.



Though the reaction is reversible, Ca^{2+} are removed in drainage water as soon as they formed. Hence, the reaction proceeds in one direction from left to right only. The process whereby a normal soil is converted into an alkali soil is known as “**alkalization**”.

Characteristics various methods are available to characterize

- A direct determination of exchangeable sodium

$$\text{Exchangeable sodium} = \text{Total sodium} - \text{Soluble sodium}$$

- The soil pH also gives an indication of soil alkalinity indirectly. An increase in pH reading of 1.0 or more, with change in moisture content from a low to high value has itself been found useful in some area for detecting alkali conditions.

The higher the ESP, the higher is the soil pH.

- Sodium Adsorption Ratio (SAR)

The US Salinity Laboratory developed the concept of SAR to define the equilibrium between soluble and exchangeable cations

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

10 (21/26)

(Na^+ , Ca^{2+} , Mg^{2+} are concentrations in saturation extract in me L^{-1})

The value of SAR can be used for the determination of exchangeable sodium percentage (ESP)

$$\text{ESP} = \frac{100(-0.0126 + 0.01475 \text{ SAR})}{1 + (-0.0126 + 0.01475 \text{ SAR})}$$

The following regression equation is also used to work out ESP

$$Y = 0.0673 + 0.035 X$$

Where Y - indicates ESP and X - indicates SAR

Soils having SAR value greater than 13 are considered as sodic soils.

Impact of soil sodicity

- Dispersion of soil colloids leads to development of compact soil
- Due to compactness of soil, aeration, hydraulic conductivity, drainage and microbial activity are reduced
- High sodicity caused by Na_2CO_3 increases soil pH
- High hydroxyl (OH^-) ion concentration has direct detrimental effect on plants.
- Excess of Na^+ induces the deficiencies of Ca^{2+} and Mg^{2+}
- High pH in alkali soil decreases the availability of many plant nutrients like P, Ca, N, Mg, Fe, Cu, and Zn.

23.

Genesis, Characteristics, and Reclamation of acid soils

Learning objectives

To study the genesis, characteristics and reclamation of acid soils

Soil acidity refers to presence of higher concentration of H^+ concentration in soil solution and at exchange sites. Soil acidity is a major problem in relation to plant growth and therefore acid soils are called a problem soil. Acid soils are characterized by low soil pH, which varies from strongly acidic (4.5-5.5) to extremely acidic (<4.5) and with low base saturation.

Soil acidity is of three kinds viz., active acidity, exchangeable acidity and residual acidity. The hydrogen ions in the soil solution contribute to active acidity. It may be defined as the acidity developed due to concentration of H^+ and Al^{3+} ions in the soil solution. The concentration of hydrogen ion in soil solution due to active acidity is very small, implying that only a meager amount of lime would be required to neutralize active acidity. In spite of smaller concentration, active acidity is important since the plant root and the microbes around the rhizosphere are influenced by it.

The concentration of exchangeable Al and H ions contribute to exchangeable acidity. It may be defined as the acidity developed due to adsorbed H and Al ions on soil colloids.

Aluminium hydroxyl ions and H and Al ions present in non – exchangeable form with organic matter and clay account for the residual acidity.

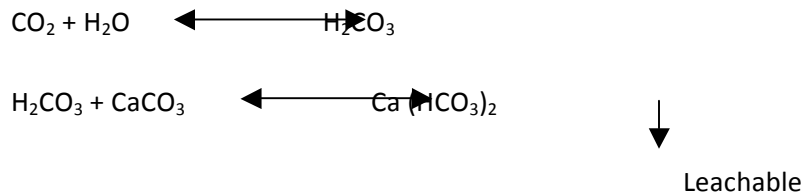
Total acidity = Active acidity + Exchangeable acidity + Residual acidity

Sources of soil acidity

Leaching due to heavy rainfall

Acid soils are common in all regions where rainfall or precipitation is high enough to leach appreciable amounts of exchangeable bases from the surface soils and relatively insoluble compounds of Al and Fe remains in soil. The nature of these compounds is acidic and its oxides and hydroxides react with water and release hydrogen ions in soil solution and become acidic. Besides, when the soluble

bases are lost, the H^+ ions of the carbonic acid and other acids developed in the soil replace the basic cations of the colloidal complex. As the soil gets gradually depletes of its exchangeable bases through constant leaching, it gets desaturated and becomes increasingly acid.

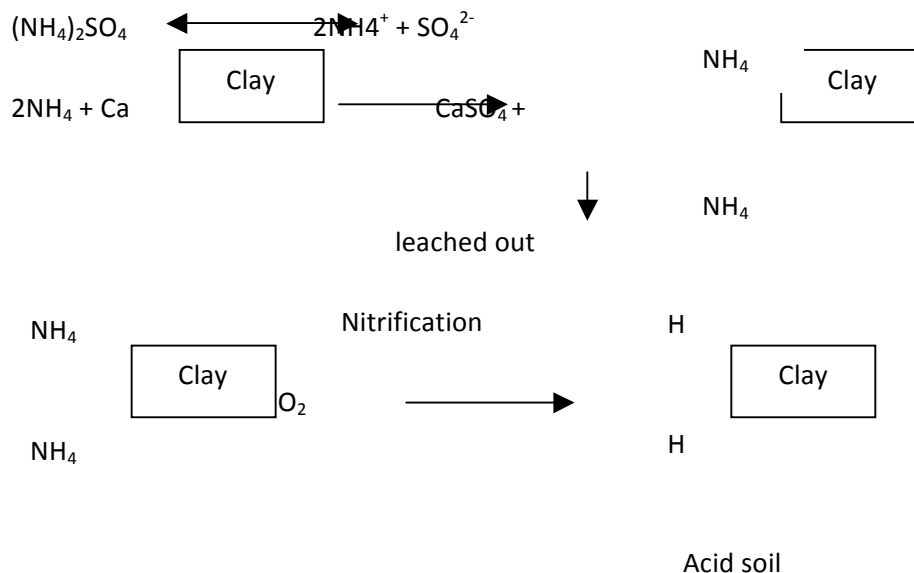


Acidic parent material

Some soils have developed from parent materials which are acid such as granite and that may contribute to some extent soil acidity.

Acid forming fertilizers and soluble salts

The use of ammonium sulphate and ammonium nitrate increases soil acidity. Ammonium ions from ammonium sulphate when applied to the soil replace calcium ions from the exchange complex and the calcium sulphate is formed and finally leached out.



Besides, basic portion of ammonium sulphate is NH_4^+ and it undergoes biological transformation in the soil and form acid forming nitrate ions. Similarly, sulphur also produces acid forming sulphate ions through oxidation. Divalent cations of soluble salts usually have a greater effect on lowering soil pH than monovalent metal cations.

Humus and other organic acids

During organic matter decomposition, humus, organic acids and different acid salts may also be produced and also concentration of CO_2 increased. The increased concentration of CO_2 , hydrolysis of acid salts and various organic acids increased the total acidity of soil.

Aluminosilicate minerals

At low pH values most of the Al is present as the hydrated Aluminium ions, which undergoes hydrolysis and release hydrogen ions in the soil solution.

Carbon dioxide

Soil containing high concentration of CO_2 , the pH value of such soil will be low and the soil becomes acidic. Root activity and metabolism may also serve as sources of CO_2 , which ultimately helps the soil to become acidic.

Hydrous oxides

These are mainly oxides of iron and aluminium. Under favourable conditions they undergo stepwise hydrolysis with the release of hydrogen ions in the soil solution and develop soil acidity.

Production constraints

- ❖ Increased solubility and toxicity of Al, Mn and Fe
- ❖ Deficiency of Ca and Mg,
- ❖ Reduced availability of P and Mo and
- ❖ Reduced microbial activity

Management of acid soils

Management of the acid soils should be directed towards enhanced crop productivity either through addition of amendments to correct the soil abnormalities or by manipulating the agronomic practices depending upon the climatic and edaphic conditions.

Soil amelioration

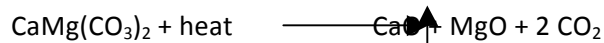
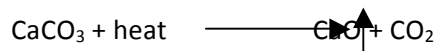
Lime has been recognized as an effective soil ameliorant as it reduces Al, Fe and Mn toxicity and increases base saturation, P and Mo availability of acid soils. Liming also increases atmospheric N fixation as well as N mineralization in acid soils through enhanced microbial activity.

Liming materials

Source of lime material is an important aspect of acid soil management and the economics of application of different sources need to be given due importance. Commercial limestone and dolomite limestone are the most widely used amendments. Carbonates, oxides and hydroxides of calcium and magnesium are referred to as agricultural lime.

Among, the naturally occurring lime sources calcitic, dolomitic and stromatolitic limestones are important carbonates. The other liming sources are marl, oyster shells and several industrial wastes like steel mill slag, blast furnace slag, lime sludge from paper mills, pressmud from sugar mills, cement wastes, precipitated calcium carbonate, etc were found to be equally effective as ground limestone and are also cheaper. Considering the efficiency of limestone as 100%, efficiencies of basic slag and dolomite were found to be 110 and 94 % respectively.

Burnt lime is the oxide of lime or quick lime. Quick lime is produced in large kilns. Its reactions in soil are much faster compared to those of carbonates.

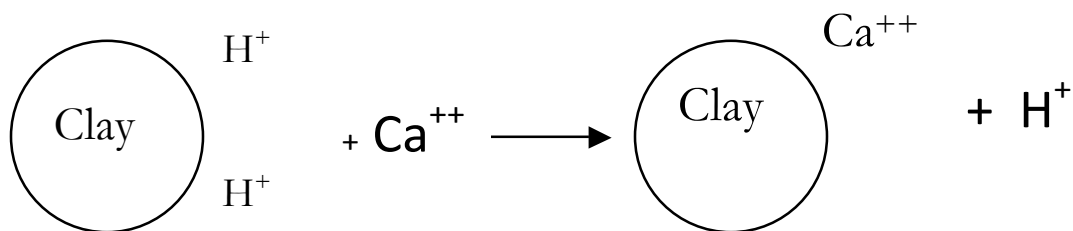


Addition of water to burnt lime makes hydroxide or hydrated lime (slaked lime), which is more caustic than burnt lime.

Lime when applied to acidic soils either in the form of oxide, hydroxide or carbonate reacts with carbon dioxide and water to form bicarbonate.



These liming materials on reaction with soil colloid, replace hydrogen and aluminium ions from the colloidal phase to soil solution.



Lime requirement:

Four important factors govern the lime requirement, viz.,

- The required change in pH
- The buffer capacity of the soil to be limed
- The chemical composition of the liming materials used
- The fineness of the liming materials.

A fine textured acid soil requires much larger quantity of lime than does a sandy soil or a loamy soil with the same pH value. Calcitic or dolomitic limestone reacts slowly with soil colloids, whereas burnt lime and hydrated lime react faster and bring about changes in soil pH within a few days.

Lime requirement of an acid soil may be defined as the amount of liming material that must be added to raise the pH to some prescribed value. Shoemaker *et al.* (1961) buffer method is used for the determination of lime requirement of an acid soil. Lime requirement in terms of pure CaCO_3 can be observed from the following table.

Lime requirement of an acid soil

pH of soil buffer suspension (Field soil sample)	lime required to bring pH down to indicated level (CaCO_3) in tonnes per acre		
	pH 6.0	pH 6.4	pH 6.8
6.7	1.0	1.2	1.4
6.6	1.4	1.7	1.9
6.5	1.8	2.2	2.5
6.4	2.3	2.7	3.1
6.3	2.7	3.2	3.7
6.2	3.1	3.7	4.2
6.1	3.5	4.2	4.8
6.0	3.9	4.7	5.4
5.9	4.4	5.2	6.0
5.8	4.8	5.7	6.5
5.7	5.2	6.2	7.1
5.6	5.6	6.7	7.7
5.5	6.0	7.2	8.3

5.4	6.5	7.7	8.9
5.3	6.9	8.2	9.4
5.2	7.4	8.4	10.0
5.1	7.8	9.1	10.6
5.0	8.2	9.6	11.2
4.9	8.6	10.1	11.8
4.8	9.1	10.6	12.4

Benefits:

The most conspicuous effect of liming was on the exchangeable acidity, which registered a decrease up to 95 %. A decrease of 70-74% in pH dependent and total acidity was recorded by liming. An average yield improvement of 30 % could be obtained.

Crop choice:

Selection of crops tolerant to acidity is an effective tool to counter this soil problem and breeding of such varieties is of specific importance for attaining higher productivity, particularly in areas where liming is not an economic proposition. The crops can be grouped on the basis of their performance in different soil pH range.

Relative tolerance of crops to soil acidity

Crops	Optimum pH range
Cereals	
Maize, sorghum, wheat, barley	6.0-7.5
Millet	5.0-6.5
Rice	4.0-6.0
Oats	5.0-7.7
Legumes	
Field beans, soybean, pea, lentil etc.	5.5-7.0
Groundnut	5.3-6.6
Other crops	

Sugarcane	6.0-7.5
Cotton	5.0-6.5
Potato	5.0-5.5
Tea	4.0-6.0

Occurrence in India:

95% of soils of Assam and 30% of geographical area of Jammu and Kashmir are acidic. In West Bengal, 2.2 Mha, in Himachal Pradesh, 0.33 Mha, in Bihar, 2 Mha and all hill soils of erstwhile U.P. come under acid soils. About 80% of soils in Orissa, 88% in Kerala, 45% in Karnataka and 20% in Maharashtra are acidic. The laterite zone in Tamil Nadu is covered with acid soil and about 40,000 ha are acidic in Andhra Pradesh.

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Questions to Ponder

- 1) What ions are the principal sources of soil acidity?
- 2) Is soil pH altered by fertilizer application?
- 3) What is agricultural lime?
- 4) What are the factors that determine the frequency and rate of liming?
- 5) What is fluid lime?

24.

Genesis, Characteristics, and Reclamation of saline soils

Learning objectives

To study the genesis, characteristics and reclamation of saline soils

Saline soils are defined as soils having a conductivity of the saturation extract greater than 4 dS m^{-1} and an exchangeable sodium percentage less than 15. The pH is usually less than 8.5. Formerly these soils were called white alkali soils because of surface crust of white salts.

Relationship between EC_{SE} and $\text{EC}_{1:2.5}$

EC (dS m^{-1})	
Saturation extract	1: 2.5
4-8	1-3
8-12	3-8
12-16	8-16

Formation

The process by which the saline soil formed is called salinisation. Saline soils occur mostly in arid or semi arid regions. In arid regions saline soils occur not only because there is less rainfall available to leach and transport the salts but also because of high evaporation rates, which tend further to concentrate the salts in soils and in surface waters.

Major production constraints

Presence of salts leads to alteration of osmotic potential of the soil solution. Consequently water intake by plants restricted and thereby nutrients uptake by plants are also reduced. In this soil due to high salt levels microbial activity is reduced. Specific ion effects on plants are also seen due to toxicity of ions like chloride, sulphate, etc.

Management of saline soils

The reclamation of saline soils involves basically the removal of salts from the saline soil through the processes of leaching with water and drainage. Provision of lateral and main drainage channels of 60 cm deep and 45 cm wide and leaching of salts could reclaim the soils. Therefore, provision of adequate drainage system is a pre-requisite for any reclamation process. Sub-surface drainage is an effective tool for lowering the water table, removal of excess salts and prevention of secondary salinisation.

Irrigation management

Efficient water management leads to increased crop yield under saline soil condition. Proportional mixing of good quality (if available) water with saline water and then using for irrigation reduces the effect of salinity. Alternate furrow irrigation favours growth of plant than flooding. Drip, sprinkler and pitcher irrigation have been found to be more efficient than the conventional flood irrigation method since relatively lesser amount of water is used under these improved methods.

Fertilizer management

Addition of extra dose of nitrogen to the tune of 20-25% of recommended level will compensate the low availability of N in these soils. Addition of organic manures like, FYM, compost, etc helps in reducing the ill effect of salinity due to release of organic acids produced during decomposition. Green manuring (Sunhemp, Daincha, Kalingi) and or green leaf manuring also counteracts the effects of salinity. Application of farm yard manure at 5 t ha⁻¹ at 10-15 days before transplanting in the case of paddy crop and before sowing in the case of garden land crops can alleviate the problems of salinity.

Crop choice / Crop management

Crops are to be chosen based on the soil salinity level. The relative salt tolerance of different crops is as follows:

Relative tolerance of crops to salinity

Plant species	Threshold salinity (dS m ⁻¹)
Field crops	
Cotton	7.7

Sugarbeet	7.0
Sorghum	6.8
Wheat	6.0
Soybean	5.0
Groundnut	3.2
Rice	3.0
Maize	1.7
Sugarcane	1.7
Vegetables	
Tomato	2.5
Cabbage	1.8
Potato	1.7
Onion	1.2
Carrot	1.0
Fruits	
Citrus	1.7

Soil / cultural management

Planting the seed in the centre of the raised bed / ridge may affect the germination as it is the spot of greatest salt accumulation. A better salinity control can be achieved by using sloping beds with seeds planted on the sloping side just above the water line. Alternate furrow irrigation is advantageous as the salts can be displaced beyond the single seed row. Application of straw and polythene mulch had been found to curtail the evaporation from soil surface resulting in the reduced salt concentration in the root zone profile within 30 days.

Management of saline soils becomes essential and unavoidable particularly in areas where both soil as well as irrigation water is saline in nature.

Occurrence in India:

Extent and distribution of salt affected soils in India

Sr. No.	State	Saline soils (ha)	Alkali soils (ha)	Coastal saline soil (ha)	Total (ha)
1	Andhra Pradesh	0	196609	77598	274207
2	A & N islands	0	0	77000	77000
3	Bihar	47301	105852	0	153153
4	Gujarat	1218255	541430	462315	2222000
5	Haryana	49157	183399	0	232556
6	J & K	0	17500	0	17500
7	Karnataka	1307	148136	586	150029
8	Kerala	0	0	20000	20000
9	Maharashtra	177093	422670	6996	606759
10	Madhya Pradesh	0	139720	0	139720
11	Orissa	0	0	147138	147138
12	Punjab	0	151717	0	151717
13	Rajasthan	195571	179371	0	374942
14	Tamil Nadu	0	354784	13231	368015
15	Uttar Pradesh	21989	1346971	0	1368960
16	West Bengal	0	0	441272	441272
	Total	1710673	3788159	1246136	6744968

Source : www.cssri.org

Questions to Ponder

- 1)What is the relationship between salts and electrical conductivity?
- 2)What is the fate of leached out salt during saline soil reclamation?
- 3)What is the nutrient management in saline soil?
- 4)Where is saline soil predominant in India?Why? ?
- 5)What are halophytes?

25.

Genesis, Characteristics, and Reclamation of sodic soils

Learning objectives

To study the genesis, characteristics and reclamation of sodic soils

Sodic soils - Definition

Alkali or sodic soil is defined as a soil having a conductivity of the saturation extract less than 4 dS m^{-1} and an exchangeable sodium percentage greater than 15. The pH is usually between 8.5 – 10.0.

Most alkali soils, particularly in the arid and semi-arid regions, contain CaCO_3 in the profile in some form and constant hydrolysis of CaCO_3 sustains the release of OH^- ions in soil solution. The OH^- ions so released result in the maintenance of higher pH in calcareous alkali soils than that in non – calcareous alkali soils.

Expected loss of soil productivity due to ESP in different soils

ESP	Loss in productivity (%)	
	Alluvium derived soils (Inceptisols / Alfisols)	Black soils (Vertisols)
Up to 5	Nil	Up to 10
5-15	<10	10-25
15-40	10-25	25-50
>40	25-50	>50

Formation

Soil colloids adsorb and retain cations on their surfaces. Cation adsorption occurs as a consequence of the electrical charges at the surface of the soil colloids. While adsorbed cations are combined chemically with the soil colloids, they may be replaced by other cations that occur in the soil solution. Calcium and Magnesium are the principal cations found in the soil solution and on the

exchange complex of normal soils in arid regions. When excess soluble salts accumulate in these soils, sodium frequently becomes the dominant cation in the soil solution resulting alkali or sodic soils.

Major production constraints

Excess exchangeable sodium in alkali soils affects both the physical and chemical properties of soils.

- a) Dispersion of soil colloids
- b) Specific ion effect

Reclamation of alkali / sodic soils

Physical Amelioration

This is not actually removes sodium from exchange complex but improve physical condition of soil through improvement in infiltration and aeration. The commonly followed physical methods include

- Deep ploughing is adopted to break the hard pan developed at subsurface due to sodium and improving free-movement water. This also helps in improvement of aeration.
- Providing drainage is also practiced to improve aeration and to remove further accumulation of salts at root zone.
- Sand filling which reduces heaviness of the soil and increases capillary movements of water.
- Profile inversion – Inverting the soil benefits in improvement of physical condition of soil as that of deep ploughing.

Chemical Amelioration

Reclamation of alkali / sodic soils requires neutralization of alkalinity and replacement of most of the sodium ions from the soil – exchange complex by the more favourable calcium ions. This can be accomplished by the application of chemical amendments (the materials that directly or indirectly furnish or mobilize divalent cations, usually Ca^{2+} for the replacement of sodium from the exchange complex of the soil) followed by leaching to remove soluble salts and other reaction products. The chemical amendments can be broadly grouped as follows:

- ❖ **Direct Ca suppliers:** Gypsum, calcium carbonate, phospho-gypsum, etc.

❖ **Indirect Ca suppliers:** Elemental Sulphur, sulphuric acid, pyrites, FeSO_4 , etc.

Among them gypsum is, by far, the most commonly used chemical amendment. Calcium carbonate is insoluble in nature which of no use in calcareous sodic soils (have already precipitated CaCO_3) but can be used in non calcareous sodic soils (do not have precipitated CaCO_3) since pH of this soils are low at surface and favouring solubilisation of CaCO_3 . Some of indirect suppliers of Ca viz. Elemental sulphur, sulphuric acid, iron sulphate are also used for calcareous sodic soils. These materials on application solubilise the precipitated CaCO_3 in sodic soils and releases Ca for reclamation.

Other sources

Distillery spent wash

Distillery spent wash is acidic (pH 3.8-4.2) with considerable quantity of magnesium. About 2 lakh litres of distillery spent wash can be added to an acre of sodic soil in summer months. Natural oxidation is induced for a period of six weeks with intermittent ploughing once in a month. In the second month (after 45-60 days) fresh water may be irrigated and drained. Such a treatment reduces the pH and exchangeable sodium percentage and increases the productivity of the sodic soil.

Distillery effluent

Distillery effluent contains both macro and micronutrients. Because of its high salt content, it can be used for one time application to fallow lands, About 20 to 40 tonnes per ha of distillery effluent can be sprayed uniformly on the fallow land. It should not be allowed for complete drying over a period of 20 to 30 days. The effluent applied field has to be thoroughly ploughed two times for the oxidation and mineralization of organic matter. Then the crops can be cultivated in the effluent applied fields by conventional methods.

Pulp and paper mill effluents

Pulp and paper effluents contain lot of dissolved solids and stabilized organic matter. The properly treated matter can safely be used for irrigation with appropriate amendments viz. pressmud @ 5 tonnes ha^{-1} , fortified pressmud @ 2.5 tonne ha^{-1} or daincha as in situ green manure.

The following crops and varieties were found to be suitable for cultivation in Tamil Nadu along with recommended doses of amendments viz. pressmud @ 5 tonnes ha⁻¹, fortified pressmud @ 2.5 tonnes ha⁻¹ or daincha as in situ green manure (6.25 tonnes ha⁻¹).

Rice	IR 20, TRY 1, CO 43
Maize	CO 1
Sunflower	CO 2
Groundnut	TMV 2, TMV 7
Soybean	CO 1
Sugarcane	COC 92061, COC 671, COC 6304, COC 91064
Fodder crops	Cumbu-Napier hybrid, Paragrass, Guinea grass

Certain oil seed crops like gingelly and castor, pulses like greengram and blackgram were found to be sensitive for effluent irrigation.

Benefits

- Application of gypsum, pressmud and pyrite increases the grain yield of rice grown in a sodic soil by 79, 81 and 69 % over control respectively. Pyrite was as effective as one third of gypsum, when applied on total S content basis.
- Gypsum alone enhanced the grain yield significantly by > 50 % over control. When the manures (Green manures, FYM) were added with gypsum further improvement in yield (15 %) was observed.
- An average yield improvement of > 50 % could be possible according to severity of the problem.

Crop choice

Rice is preferred as first crop in alkali / sodic soil as it can grow under submergence, can tolerate fair extent of ESP and can influence several microbial processes in the soil. Rice-Wheat / Barley – *Sesbania*, rice-berseem are some of the rice based cropping sequences recommended for sodic soils during reclamation. Some of the lands where aerable cropping after reclamation is not economically feasible can be brought under different agroforestry systems like silviculture,

silvipasture etc. which can improve the physical and chemical properties of the soil along with additional return on long-term basis. Some grasses like *Bracharia mutica* (Para grass) and *Cynodon dactylon* (Bermuda grass) etc. had been reported to produce 50% yield at ESP level above 30.

The sodicity tolerance ratings of different crops is as follows

Relative tolerance of crops to sodicity

ESP (range*)	Crop
2-10	Deciduous fruits, nuts, citrus, avocado
10-15	Safflower, blackgram, peas, lentil, pigeonpea
16-20	Chichpea, soybean
20-25	Clover, groundnut, cowpea, pearl millet
25-30	Linseed, garlic, clusterbean
30-50	Oats, mustard, cotton, wheat, tomatoes
50-60	Beets, barley, sesbania
60-70	Rice

*Relative yields are only 50% of the potential in respective sodicity ranges.

Relative tolerance of fruit trees to sodicity

Tolerance to sodicity	ESP	Trees
High	40-50	Ber, tamarind, sapota, wood apple, date palm
Medium	30-40	Pomegranate
Low	20-30	Guava, lemon, grape
Sensitive	20	Mango, jack fruit, banana

Benefits

Sodic soil reclamation through afforestation is a slow process measuring about 20-30 % during 9 years with a better efficacy of *A. indica* than *Pongamia pinnata*.

Saline-alkali/ sodic soils

Saline-alkali / sodic soil is defined as a soil having a conductivity of the saturation extract greater than 4 dS m^{-1} and an exchangeable sodium percentage greater than 15. The pH is variable and usually above 8.5 depending on the relative amounts of exchangeable sodium and soluble salts. When soils dominated by exchangeable sodium, the pH will be more than 8.5 and when soils dominated by soluble salts, the pH will be less than 8.5.

Formation

These soils form as a result of the combined processes of salinization and alkalization. If the excess soluble salts of these soils are leached downward, the properties of these soils may change markedly and become similar to those of sodic soil.

Management of saline alkali soils

The reclamation / management practices recommended for the reclamation of sodic soil can be followed for the management of saline – sodic soil.

Occurrence in India:

Extent and distribution of sodic soils in India

Sr. No.	State	Alkali soils (ha)
1	Andhra Pradesh	196609
2	Bihar	105852
3	Gujarat	541430
4	Haryana	183399
5	J & K*	17500
6	Karnataka	148136
7	Maharashtra	422670
8	Madhya Pradesh	139720
9	Punjab	151717
10	Rajasthan	179371
11	Tamil Nadu	354784
12	Uttar Pradesh	1346971
	Total	3788159

Source : www.cssri.org

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Questions to Ponder

- 1) What is the relationship between salts and electrical conductivity?
- 2) What is the fate of leached out salt during saline soil reclamation?
- 3) What is the nutrient management in saline soil?
- 4) Where is saline soil predominant in India? Why? ?
- 5) What are halophytes?

26.

Characteristics and Remediation of heavy metal contaminated soils

Learning objective

To study the characteristics of heavy metal contaminated soils and remediation

Soil contamination

Soil contamination is the presence of man-made chemicals or other alteration of the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, percolation of contaminated surface water to subsurface strata, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. This occurrence of this phenomenon is correlated with the degree of industrialization and intensity of chemical usage. The concern over soil contamination stems primarily from health risks, both of direct contact and from secondary contamination of water supplies.

The unscientific disposal of untreated or under-treated effluents has resulted in accumulation of heavy metals in land and water bodies. Heavy metal contamination due to the sewage and sludge application to soils imposes a major limitation on potential land use. Cultivated areas under peri-urban agriculture are worst affected by this problem. The heavy metals accumulating in soil may get entry into the human and animal food chain through the crops grown on it.

Heavy metals prevailing in soils and their regulatory limits

Elements	Conc. range (mg kg ⁻¹)	Regulatory limit (mg kg ⁻¹)
Lead	1-6900	600
Cadmium	0.1-345	100
Arsenic	0.1-102	20
Chromium	0.005-3950	100

Mercury	0.01-1800	270
Copper	0.03-1550	600
Zinc	0.15-5000	1500

Management of soil pollution

Bioremediation

Bioremediation can be defined as any process that uses microorganisms, fungi, green plants or their enzymes to return the environment altered by contaminants to its original condition. Bioremediation may be employed to attack specific soil contaminants, such as degradation of chlorinated hydrocarbons by bacteria. An example of a more general approach is the cleanup of oil spills by the addition of nitrate and / or sulfate fertilizers to facilitate the decomposition of crude oil by indigenous or exogenous bacteria.

Important and widely reported hyper-accumulators used for metal remediation

Elements	Plant species	Max conc. (mg kg ⁻¹)
Cadmium	<i>Thlaspi caerulescens</i>	500
Copper	<i>Ipomoea alpina</i>	12300
Cobalt	<i>Haumaniastrum robertii</i>	10200
Lead	<i>Thlaspi rotundifolium</i> , <i>Brassica juncea</i> , <i>Zea mays</i>	8200
Nickel	<i>Alyssum lesbiacum</i> , <i>Sebertia accuminata</i>	47500
Zinc	<i>Thlaspi caerulescens</i> , <i>Brassica juncea</i> , <i>B. oleracea</i> , <i>B. campestris</i>	51600
Selenium	<i>Brassica juncea</i> , <i>B. napus</i>	900
Chromium	<i>Brassica juncea</i> , <i>Helianthus annus</i>	1400

Microorganisms used for metal remediation

Elements	Microorganisms
Cadmium	<i>Citrobacter spp.</i>
Copper	<i>Bacillus spp.</i>
Cobalt	<i>Zooglea spp.</i>
Nickel	<i>Zooglea spp.</i>
Zinc	<i>Bacillus spp.</i>
Chromium	<i>Pseudomonas ambigua</i> , <i>Chlamydomonas sp.</i> , <i>Oscillatoria sp.</i> , <i>Arthrobacter sp.</i> , <i>Agrobacterium sp.</i>

It is therefore imperative that to solve the soil chemical constraints and make the lands highly productive on a sustainable basis, we need to develop the technologies suitable to specific locations which will be economically feasible and workable at farmer's field. So we have to give

emphasis on increasing the current yield level and at the same time develop suitable technologies to reclaim the problem soils.

Questions to Ponder

- 1)What are heavy metals?
- 2) What are the long term effects of irrigation with distillery spent wash?
- 3)Which effluent contains high amounts of chromium?
- 4)What is the effect of heavy metals in foraging animals?
- 5)What are the critical levels of heavy metals in soils ?

LECTURE 27

ASSESSMENT OF IRRIGATION WATER QUALITY

Water quality parameters, management

Irrigation water quality criteria

Water quality is determined according to the purpose for which it will be used. For irrigation water, the usual criteria include salinity, sodicity, and ion toxicities.

Various criteria are considered in evaluating the quality of irrigation water namely:

1. Salinity hazard
2. Sodium hazard
3. Salt index
4. Alkalinity hazard
5. Permeability hazard
6. Specific ion toxicity hazards

SALINITY HAZARD

The concentration of soluble salts in irrigation water can be classified in terms of Electrical Conductivity (EC) and expressed as dS m^{-1} . There are four classes of salinity viz., C_1 , C_2 , C_3 and C_4 .

The classes C₁ and C₂ of water are considered suitable for irrigation purposes (no problem). C₃ and C₄ classes of water are not suitable for irrigation purpose (severe problems).

Water class	EC (dS m⁻¹)	Remarks
C ₁ - Low salinity	0-0.25	Can be used safely
C ₂ - Medium salinity	0.25-0.75	Can be used with moderate leaching
C ₃ - High salinity	0.75-2.25	Can be used for irrigation purposes with some management practices
C ₄ - Very high	2.25-5.00	Can not be used for irrigation purposes

SODICITY HAZARD

High concentrations of sodium are undesirable in water because sodium adsorbs on to the soil cation exchange sites, causing soil aggregates to break down (deflocculation), sealing the pores of the soil and making it impermeable to water flow. The sodicity hazard of irrigation water is usually evaluated by:

- Sodium Adsorption Ratio ($\frac{[Na^+]}{[Ca^{2+}] + [Mg^{2+}]}$)
- Adjusted SAR
- Sodium to calcium activity ratio (SCAR)
- Sodium ratio
- Figure of merit

Sodium adsorption ratio (SAR)

United States Salinity Laboratory (USSL) staff introduced the concept of sodium adsorption ratio (SAR) to predict sodium hazard. It is calculated as

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

the

Where all the ions expressed as me L⁻¹

The sodium hazard of irrigation water expressed through SAR does not take into account the effect of anionic composition. Sodicity hazard also classified as S₁, S₂, S₃ and S₄.

Water class		SAR	Remarks
S ₁	low sodium hazard	0-10	Little or no hazard
S ₂	medium sodium hazard	10-18	Appreciable hazard but can be used with appropriate management
S ₃	High sodium hazard	18-26	Unsatisfactory for most of the crops
S ₄	Very high sodium hazard	> 26	Unsatisfactory for most of the crops

Adjusted SAR : To predict sodicity hazard more correctly for those water which contain appreciable amounts of HCO_3 but no RSC. Ayers and Wescot pointed out that sodicity hazard of these irrigation waters should be determined by Adjusted SAR to be calculated as follows.

$$\text{Adj. SAR} = \text{SAR} (1 + (8.4 - \text{pH}_c))$$

Where SAR = Sodium Adsorption Ratio

$\text{pH}_c = (\text{pK}_2 - \text{pK}_c) + \text{pCa} + \text{p}(\text{Alk})$

$\text{pK}_2 - \text{pK}_c = \text{conc. of Ca} + \text{Mg} + \text{Na in me L}^{-1}$

$\text{pCa} = \text{Ca in me l}^{-1}$

$\text{pAlk} = \text{from conc. of CO}_3 + \text{HCO}_3 \text{ in me L}^{-1}$.

The adjusted SAR should be evaluated for such water which have EC higher than 1.5 and less than 3.0 dS m^{-1} because only this group of water are more likely to have twin problem of RSC and SAR.

Sodium to Calcium Activity Ratio (SCAR)

The application of SAR to the group of water, which have $\text{EC} > 5 \text{ dS m}^{-1}$ and $\text{Mg/Ca ratio} > 1$ is obviously questionable. For the ground water having $\text{EC} > 5 \text{ dS m}^{-1}$ and dominance of magnesium over calcium, the SAR value should be calculated as $\text{Na}^+ / \sqrt{\text{Ca}^{2+}}$.

The classification of SAR/ SCAR ratio was given by Gupta (1986) by following 6 classes of sodicity.

11 (3/8)

1. Non-sodic water (< 5)
2. Normal water (5-10)
3. Low sodicity water (10-20)
4. Medium sodicity water (20-30)
5. High sodicity water (30-40)
6. Very high sodicity water (>40)

Sodium ratio

$$\text{Sodium ratio} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}}$$

For good water, this ratio should not exceed one.

Figure of merit

This term was proposed by Cassidy to express the relative proportion of divalent to monovalent cation and calculated by

$$\text{Figure of merit} = \frac{(\text{Ca}^{2+} + \text{Mg}^{2+})}{\text{Na}^+ + \text{K}^+}$$

Salt index

It is also used for predicting sodium hazard. It is the relation between Na^+ , Ca^{2+} , and CaCO_3 present in irrigation water.

$$\text{Salt index} = (\text{Total Na}) - (\text{total Ca-Ca in } \text{CaCO}_3) \times 4.85$$

Where all ions are to be expressed in ppm. Salt index is negative for all good water and positive for those unsuitable for irrigation.

Alkalinity hazard

is evaluated by

Residual Sodium Carbonate (RSC)**Residual Sodium Bicarbonate** 11 (4/8)

Bicarbonates (HCO_3^-) occur in low salinity water and its concentration usually decreases with an increase in EC. The proportion of bicarbonate ion is higher than calcium ions are considered undesirable, because after evaporation of irrigation water bicarbonate ions tend to precipitate calcium ions. Hence, the effect of bicarbonate together with carbonates evaluated through RSC.

$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$, all ions expressed as me L⁻¹.

<i>RSC (me l⁻¹)</i>	<i>Water quality</i>
< 1.25	Water can be used safely
1.25 - 2.5	Water can be used with certain management
> 2.5	Unsuitable for irrigation purposes

Since carbonate ions do not occur very frequently in appreciable concentrations, and as bicarbonate ions do not precipitate magnesium ions, Gupta suggested that alkalinity hazard should be determined through the index called Residual Sodium Bicarbonate (RSBC) to be calculated as below.

$RSBC = HCO_3^- - Ca^{2+}$, all ions expressed as me L⁻¹.

Based on RSC/ RSBC ratio there are 6 alkalinity classes proposed

Non-alkaline water	(-ve)
Normal water	(0 me l ⁻¹)
Low alkalinity water	(2.5 me l ⁻¹)
Medium alkalinity water	(2.5-5.0 me l ⁻¹)
High alkalinity water	(5.0-10.0 me l ⁻¹)
Very high alkalinity water	(> 10.0 me l ⁻¹)

Permeability hazard

High sodium in the irrigation water can cause severe soil permeability problem. Permeability is affected not only by high sodium but also by CO₃²⁻ and HCO₃⁻ content in water. A part of CO₃²⁻ and HCO₃⁻ is precipitated as CaCO₃ (or) MgCO₃ removing Ca and Mg from irrigation water and leads to

increased proportion of solution. The effect on permeability has been evaluated by the term permeability index, which is calculated as

$$\text{Permeability index} = \frac{\text{Na}^+ + \sqrt{\text{HCO}_3^-}}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+} \times 100$$

Where ions are expressed as me L⁻¹. If permeability index value exceed 65, water is considered suitable for irrigation.

SPECIFIC ION TOXICITY HAZARD

Sodium: Among the soluble constituents of irrigation water, sodium is considered most hazardous. Excess of sodium ions characterizes the water as saline or alkaline depending upon its occurrence in association with chloride/ sulphate or carbonate/ bicarbonate ions. For some time in the past, the quality of irrigation water used to be evaluated with respect to sodium based on soluble sodium percentage (SSP) calculated as below.

$$\text{SSP} = \frac{\text{Soluble sodium concentration}}{\text{Total cation concentration}} \times 100$$

It has been useful in characterizing water, since a high value indicates **soft water** and low value **hard water**. When water with excess of sodium (SSP=66) is used for irrigation, $\text{pH} = 11 \frac{6}{8}$ is absorbed by the soil. Both, soils and plants are adversely affected by high sodium irrigation water. Sodium soils are relatively impermeable to air and water. They are hard when dry, difficult to till and plastic and sticky when wet. These adverse physical conditions prevent germination and are generally unfavourable for plant growth. Even though, sodium is not as essential as other nutrients, it is taken up freely by many plants and it may be specifically toxic to plants.

Magnesium: It is believed that one of the important qualitative criteria in judging the irrigation water is its Mg content in relation to total divalent cations, since high Mg content in relation to total divalent cations, since high Mg adsorption by soils affects their physical properties. A harmful effect on soils appears when Ca: Mg ratio decline below 50.

$$\text{Mg Adsorption Ratio} = \frac{\text{Mg}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}}$$

Chlorides: The occurrence of chloride ions in irrigation water increases with increase in EC and sodium ions. Therefore, these ions are most dominant in very high salinity water. Unlike sodium ions, the chloride ions neither affect on the physical properties of the soil, nor are adsorbed by the soil. Therefore, it has generally not been included in modern classification system. However, it is used as a factor in some regional water classification.

$$\text{Chloride Concentration (me L}^{-1}\text{)} = \frac{\text{Cl}^{-} + \text{NO}_3^{-}}{\text{CO}_3^{--} + \text{HCO}_3^{-} + \text{SO}_4^{--} + \text{Cl}^{-} + \text{NO}_3^{-}}$$

Chloride concentration (me L⁻¹)	Water quality
4	Excellent water
4-7	11 (7/8) od water
7-12	Slightly usable
12-20	Not suitable
> 20	Not suitable

Sulphate: Sulphate salts are less harmful when compared to chlorides. This is because when both the ions occur in this concentration, only half of the sulphate ions contribute to salinity due to the fact that approximately half

of the sulphates gets precipitated as CaSO_4 while the other half remains in soluble form as Na-MgSO_4 in the soil. That is the reason, the potential salinity of irrigation is calculated as $\text{Cl}^- + \frac{1}{2} \text{SO}_4^{2-}$.

Eaton proposed three classes for sulphate

- < 4 me l^{-1} - Excellent water
- 4-12 me l^{-1} - Good to injurious
- > 12 me l^{-1} - Injurious to unsatisfactory

Potential salinity

It can be worked out by using the formula $\text{Cl} + \frac{1}{2} \text{SO}_4^{2-}$ where ions are expressed in me l^{-1} .

Potential salinity (me L^{-1})	Remarks
3-15	Can be recommended for medium permeability soils
3-7	Recommended for soils of low permeability

Boron: It is evident that boron is essential for the normal growth of the plant, but the amount required is very small. The occurrence of boron in toxic concentration in certain irrigation water makes it necessary to consider this element in assessing the water quality. The permissible limits of boron in irrigation water are:

Boron class	Crops			Remarks
	Sensitive	Semi-tolerant	Tolerant	
Very low	< 0.33	< 0.67	< 1.00	For safely use
Low	0.33-0.67	0.67-1.33	1-2.0	Can be managed
Medium	0.67-1.00	1.33-2.00	2.0-3.0	Unsuitable

High	1.0-1.25	2.00-2.50	3.0-3.75	Unsuitable
Very high	> 1.25	> 2.50	> 3.75	Unsuitable

Fluorine: fluorides are only sparingly soluble and are in only small amounts. The concentration of fluoride ranges from traces to more than 10 mg L⁻¹ in natural water, and surface water do not exceed 0.3 mg L⁻¹ unless they are polluted. Irrigation with fluoride saline water (upto 25 mg L⁻¹) has not been found to affect yield of wheat. Therefore, it is doubtful if fluoride requires any monitoring in India. At present, the average concentration of fluoride has not been observed to be very high (10 mg l⁻¹).

Nitrate: Very frequently ground water contain high amount of nitrate. When such type of irrigation water is applied on soils continuously, various properties of soils are affected.

	< 5	No problem
NO ₃ me l ⁻¹	5-30	Intensity of problem is moderate
	> 30	Intensity of problem is severe

Lithium : Lithium is a trace element may be found in most of saline ground water and irrigated soils. It has been found that 0.05-0.1 ppm of lithium in water produce toxic effects on growth of citrus. It has also been reported that saline soils of varying degrees found in India contain lithium upto 2.5 ppm. Fortunately, the ^{11 (8/8)} of majority of crops is not affected with this level of lithium content.