

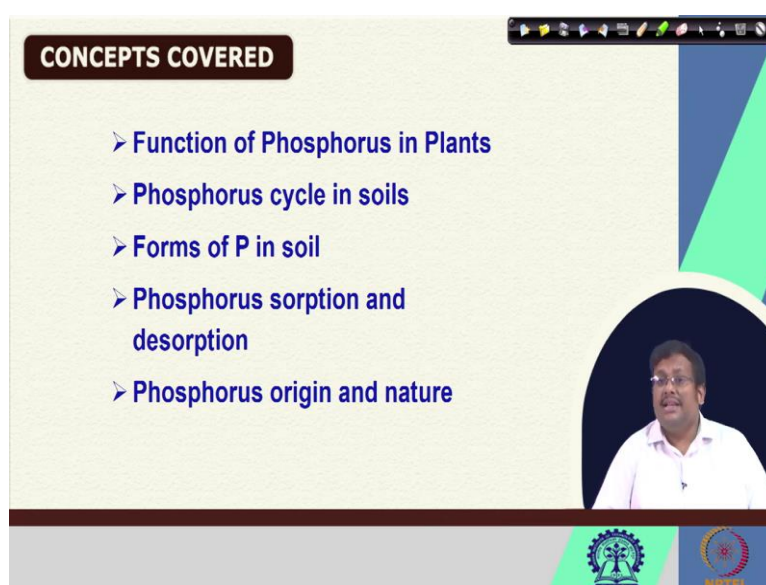
Soil Fertility and Fertilizers
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Week 3
Lecture 11
Soil P and K Plant Nutrition

Welcome friends to this NPTEL online certification course of soil fertility and fertilizers. And we are going to start our week 3. And in our previous week, we have discussed about the soil nitrogen, and how it is important for plant nutrition.

And in this week, we are going to discuss the soil phosphorus, and potassium for plant nutrition. So, this is our week 3, and we are going to start the lecture number 11. So, we already know that among different macronutrients, nitrogen, phosphorus and potassium are considered as the primary nutrients. Because they are required in relatively larger amount than other nutrients, or other essential nutrients.

Although, nitrogen is required in relatively higher quantity, but also this phosphorus and potassium are also very indispensable for the growth of the plant. Both phosphorus and potassium are very important for the growth of the plant in that, in the sense that they provide the energy and also, they regulate all the enzymes which are required for the plant different metabolism, activities of the plant.

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The slide is titled "CONCEPTS COVERED" in a dark blue box at the top left. Below the title, there is a list of five topics, each preceded by a blue right-pointing arrowhead:

- Function of Phosphorus in Plants
- Phosphorus cycle in soils
- Forms of P in soil
- Phosphorus sorption and desorption
- Phosphorus origin and nature

In the bottom right corner of the slide, there is a circular video inset showing a man with glasses and a white shirt, presumably the professor, speaking. At the bottom of the slide, there are two logos: the Indian Institute of Technology (IIT) Kharagpur logo on the left and the NPTEL logo on the right.

So, today, we are going to start our discussion with phosphorus, and these are some of the topics which we are going to discuss. First of all, we are going to discuss what is the function

of phosphorus in plants? Then phosphorus cycle in soils. What are the forms of phosphorus in soil? Then phosphorus sorption and desorption. And then the phosphorus origin and nature which we are going to discuss. So, these are some of the concepts which we are going to discuss in this lecture.

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KEYWORDS

- Phosphorous cycle
- Herbivores
- Carnivores
- Adsorption
- Sorption
- Desorption

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Apart from that, we are also, these are the keywords for this lecture, like phosphorus cycle herbivores, carnivores, adsorption, sorption, desorption. So, these are some of the keywords which we are going to see in this lecture.

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Phosphorus

- ☐ Phosphorus has generally three forms:
 - Phosphorus pentoxide (P_2O_5) - burning form of P
 - Meta phosphoric acid (HPO_3) –when dissolved in water
 - Ortho phosphoric acid (H_3PO_4) – when dissolved in warm water
- ☐ Plants absorb P in $H_2PO_4^-$ and HPO_4^{2-} forms.
- ☐ Three replaceable H^+ of H_3PO_4 combine with Ca^{++} to form three different combined salts of calcium and phosphorus resulting in different classes of phosphatic fertilizers.

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Now, let us start with the phosphorus, basic overview of phosphorus. Phosphorus has generally three forms, phosphorus pentoxide which is P_2O_5 , burning form of phosphorus,

and then meta phosphoric acid that is HPO_3 when dissolved in water, and orthophosphoric acid that is when dissolved in warm water. Plant generally absorb phosphorus in two major forms, one is primary orthophosphate, or H_2PO_4^- minus, and other one is called the secondary orthophosphate ions or HPO_4^{2-} minus. Just like in case of nitrogen, plant can absorb, plant can uptake the nitrate form, and ammonium form. Similarly in case of phosphorus, plant can uptake only these two forms, H_2PO_4^- minus and HPO_4^{2-} minus.

Three replaceable H plus, of proton of this phosphoric acid combine with calcium ion to form three different combined salts of calcium and phosphorus resulting in different classes of phosphatic fertilizers, we are going to discuss this. But at the same time, at this time we should remember that this is the most important information that plant can absorb phosphorus in these two forms, H_2PO_4^- minus and HPO_4^{2-} minus. And the dominance of these two forms depends on the soil pH, which we are going to discuss.

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Functions of Phosphorus

- Phosphorus is found in plants as constituent of:
 - Nucleic acids
 - Phospholipids
 - Co-enzymes NAD and NADP
 - ATP
 - Other compounds
- Heavy concentration of P is found in the meristematic regions of actively growing plants where it is involved in the synthesis of nucleoproteins

Now, phosphorus. What are the functions of phosphorus in plant? Now, phosphorus is found in plant as constituent of nucleic acid, then phospholipids, coenzyme NAD and NADP, ATP, and other components. So, you can see that nucleic acid which is one of the major component of any biological system that is consist of phosphorus. ATP, which is known as the energy source also be made of phosphorus. So, whatever energy is required for their plant growth and metabolism is basically generated from the phosphorus. Because, that the energy plants get from ADP and ATP contents phosphorus.

Now, heavy concentration of phosphorus is found in meristematic region of actively growing plants, where it is involved in the synthesis of nucleoproteins. So, you can see that there is a

wide importance of phosphorus as far as the plant metabolism, plant and plant growth is concerned. Without phosphorus plant cannot grow, and plant growth is stunted when there is a phosphorus deficiency.

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Functions of Phosphorus

- Important for cell division and development of new tissue.
- Phosphorus is also associated with complex energy transformations in the plant.
- Adding phosphorus to soil low in available phosphorus promotes root growth and winter hardiness, stimulates tillering, and often hastens maturity.

Now, if we see how phosphorus influenced the plant growth. Now, it is very much important for cell division, and development of new tissue. Without phosphorus, the cell division cannot occur, and also development of new tissue cannot also occur. And phosphorus is also associated with complex energy transformation in the plant. Adding phosphorus to soil low in available phosphorus promotes root growth and winter hardiness, and stimulates tillering, and often hastens the maturity.

So, you can see that if there is a deficiency of phosphorus, all these important plant growth processes will be hampered, which will ultimately manifest in the stunted growth of the plant. So, that is why phosphorus is a very important macronutrient as far as the plant growth, and metabolism is concerned.

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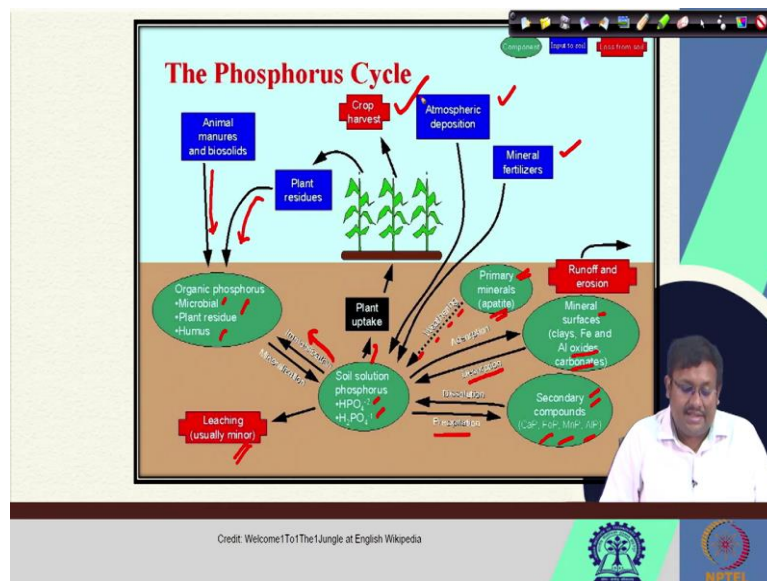
Phosphorous Cycle

- The phosphorus cycle is the biogeochemical cycle (how phosphorus is in between life and earth) that describes the movement of phosphorus through the lithosphere, hydrosphere, and biosphere.
- It differs from other biogeochemical cycles because it does not include a gas phase.
- Because of phosphorus' high reactivity, it exists in combined forms of other elements.

Now, phosphorus cycle just like in case of nitrogen cycle, we have seen the dynamics of different forms of nitrogen in the soil, and how different processes are controlling the conversion of one form of nitrogen into another form. In case of soil also, we can see the soil phosphorus cycle. Now, this phosphorus cycle is the biogeochemical cycle, that describes the movement of phosphorus to the lithosphere, hydrosphere, and biosphere. So, this phosphorus cycle will tell you how phosphorus can move between lithosphere, hydrosphere, and biosphere. In other terms, it shows the dynamics of phosphorus between the lithosphere, hydrosphere, and biosphere, and governed by different processes.

It differs from other biogeochemical cycles, because it does not include a gas phase. In case of nitrogen cycle, we have seen there are different gaseous phases specifically in case of volatilization, denitrification, different gaseous phases are involved. However, in case of phosphorus cycle, there is no gas phase, because of phosphorus high reactivity, it exists in combined form of other elements. So, phosphorus easily combined with other elements like calcium, aluminium, and iron, and they exist in these forms in the earth, or in the soil.

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Now, if you see this is a phosphorus cycle. In the phosphorus cycle, we can see that there are different types of sources of phosphorus, like animal manure and biosolids. This is one of the important source of organic phosphorus, and also plant residues, when they decompose, they can also add to the pool of organic phosphorus. Organic phosphorus can consist of microbial forms, plant residue forms, and humus forms. So, once this organic phosphorus pool is created, that can mineralize to produce these primary orthophosphate as well as secondary orthophosphate ions, which are present in the soil solution. And plant can uptake these two forms from the soil solution.

So, just like the mineralization of nitrogen, conversion of organic form of nitrogen to inorganic form here also you can clearly see, the conversion of organic form of phosphorus to inorganic form of phosphorus is known as phosphorus mineralization, and the opposite process, just like nitrogen immobilization is also known as phosphorus immobilization, which you can see in going in this direction. Some of these phosphate for primary orthophosphate, and secondary orthophosphate ion, are leached away through the leaching process. Of course, this is, this accounts for very minor fraction.

And, these HPO_4^{2-} , and H_2PO_4^- are subjected to different types of other sorption, desorption process, or weathering process. For example, you can see that apart from this organic source of phosphorus, these phosphorus ions like primary orthophosphate ion, and secondary orthophosphate ion, in the soil solution can come also from weathering of primary minerals. Now, primary phosphorus minerals are known as apatites, we are going to

discuss them these appetites. So, due to the weathering process, these appetites enrich the soil solution by producing these HPO_4^- , and H_2PO_4^- ions.

So, these HPO_4^- , and H_2PO_4^- can subject to adsorption by different mineral surface like clays, iron, aluminium oxides, and carbonates. So, they can be these clays, iron, and aluminium oxides, or carbonates can adsorb these HPO_4^- , and H_2PO_4^- present in the soil solution, or sometime they are also coming back to the soil solution by the desorption process. So, adsorption and desorption these are two opposite process. Through adsorption, these primary orthophosphate ions, secondary orthophosphate ions gets adsorbed onto the mineral surface. However, desorption process can converse that moves them back to again to soil solution.

Also, these HPO_4^- , or primary orthophosphate ion, and secondary ortho phosphate ion can precipitate in the form of secondary compounds, or secondary minerals. What are the secondary minerals? Like, calcium phosphate, iron phosphate, manganese phosphate, and so on. So, these phosphate ion gets precipitated in calcium phosphate, iron phosphate, and then aluminium phosphate, and then manganese phosphate, and so depending on the soil pH and they became unavailable to the plant. Sometime when they dissolve after dissolving this phosphorus can again come back to the soil solution.

So, these are some of the processes which governs the movement of phosphorus in the solid phase. Of course, phosphorus is also susceptible to runoff and erosion losses, and another pool, other pools of these primary orthophosphate, and secondary orthophosphate ions are mineral fertilizer, and also atmospheric deposition So, when there is a crop harvest that creates the loss of phosphorus from the whole system. So, this is called that phosphorus cycle.

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- ❑ Rocks start out the Phosphorus Cycle.
- ❑ When it rains, phosphates are removed from the rocks and are spread out through both soils and water.
- ❑ Plants use up phosphate ions from the soil.
- ❑ Phosphate moves from the plants to animals when herbivores eat plants and carnivores eat plants or herbivores.

Now, rock starts out the phosphorus cycle, and when it rains, phosphates are removed from the rocks, and are spread out through both soils, and water. And, plants use a phosphate ions from the soil, and phosphate moves from plants to animals when herbivores eat plants and carnivores eat plants, or herbivores.

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- ❑ Animals release the phosphate into the ground.
- ❑ It is then decomposed by bacteria and fungi.
- ❑ It then goes through the soil or releases into the water.
- ❑ As the rocks are forming, they will either join with phosphate or the phosphate will go into the roots of plants and start the cycle over again.

Now, when animal dies, they release this organically bind phosphate in the ground, and they are decomposed by bacteria and fungi, and after this decomposition, this phosphorus goes to the soil or release into the water. As the rocks are forming, they will either join with phosphate, or the phosphate will go into the roots of the plant and start the cycle over again, and this is how this phosphorus moves from lithosphere to the soil, and also to the base, to the

plant body, and so on so forth. So, this is how this phosphorus moves from one part of the ecosystem to another part.

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Phosphorus Sorption and Desorption

- **P-sorption** occurs when the orthophosphates, H_2PO_4^- and HPO_4^{2-} , bind tightly to soil particles.

Factors affecting P-sorption-

Soil Mineral Type-

- Volcanic soils have the greatest P-sorption
- Less weathered soils and organic soils have low P-sorption capacities.

Amount of clay-

- As the amount of clay increases in the soil, the P-sorption capacity increases.

Temperature-

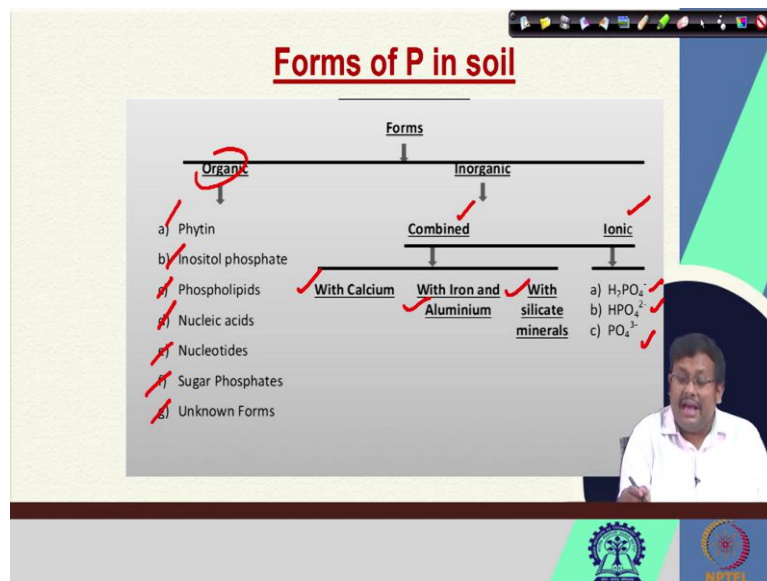
- P-sorption increases as temperature increases.
- Flooding the soil reduces P-sorption

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Now, what about the phosphorus sorption and desorption? Now, phosphorus sorption occurs when the orthophosphates like primary orthophosphate, and secondary orthophosphate bind tightly to soil particles. And, there are several factors which affects this phosphorus sorption. Like soil mineral type, like volcanic soils have the greatest phosphorus sorption capacity, and less weathered soils and organic soils have low phosphorus sorption capacities.

Amount of clay also governs the phosphorus sorption. For example, as the amount of clay increases in the soil, the phosphorus sorption capacity increases. Temperature is another important factor of phosphorus sorption, the phosphorus sorption increases as temperature increases, and when there is a flooding that reduces the phosphorus sorption. Because there is a change of pH when there is a flooding, change of soil pH.

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Now, how these force phosphorus dynamics govern by change, govern this, the whole dynamics of phosphorus availability is governed by the soil pH, we are going to discuss in our upcoming slides. Now, if we see the forms of phosphorus, we can broadly classify them into organic forms, and inorganic forms. Now, in the organic forms, you can see phytin, inositol phosphate, phospholipids, nucleic acid, nucleotides, sugar phosphates, and unknown forms out there.

And all of these are very important for the growth, and metabolism of the plant. Inorganic forms can be further divided into combined forms, and ionic forms. In case of ionic forms, primary orthophosphate ion, secondary orthophosphate ion, and the phosphate ion. And in case of combined forms, you can see they can be combined with calcium, they can combine with iron and aluminium, or they can combine with silicate minerals. So, these are the broad classification of phosphorus forms in soil.

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Organic Phosphates

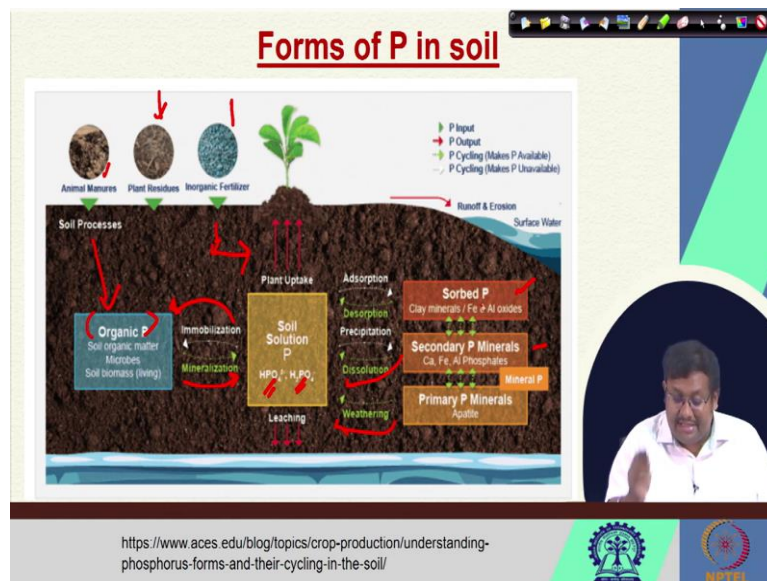
- The organic phosphates in soils are derived secondarily by addition of organic matter to soil through the growth of plants and deposition of plant residues.
- The micro-organisms synthesize organic phosphate compounds and eventually accumulate in the soil mixed with compounds derived from plant tissue.
- The organic phosphates constitute from 20 to 90% of the total soil P, mineral soils containing less and peaty soils or soils under pasture containing more.
- The nature of about 62% of soil organic P is still unknown.

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Now, what are the organic phosphates? The organic phosphates in soils are derived secondarily by addition of organic matter to the soil through the growth of plants and deposition of plant residues. The microorganisms synthesize organic phosphate compounds, and eventually accumulate in the soil mixed with compounds derived from plant tissue. So, what happens? The microorganism basically synthesizes the organic phosphate compounds, and accumulate in the soil mixed with compounds derived from the plant tissue. These organic phosphate, or organic forms of phosphorus constitute 20 to 90 percent of the total soil phosphorus.

Remember, this is the major form. Just like in case of nitrogen, the major nitrogen forms are organic in nature, only very small fraction is inorganic in nature. However, in case of phosphorus similarly, 20 to 90 percent of the total soil phosphorus remains in organic forms. Mineral soil containing less and peaty soils, or soils under pasture content more. The nature of about 62 percent of soil organic phosphorus is still unknown. So, remember this is very important thing that, like for nitrogen majority of the most of the phosphorus which are present in the soil remains in organic form.

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Now, if we see this picture, or this photo, we can clearly see what are the dynamics of phosphorus in the soil more clearly. So, you can see there is an animal manure, and different types of soil process that goes into the organic phosphorus. So, where microbes and, soil biomass there is living biomass, they are all containing these organic forms of phosphorus, and from this organic form of phosphorus, mineralization occurs to produce the soil solution phosphorus in primary orthophosphate ion, and secondary orthophosphate. This is the primary orthophosphate, this is secondary orthophosphate ions.

Sometime immobilization occurs, when these orthophosphate ion again converts back into organic forms. Plant generally uptake from the soil solution, also there are inputs from plant residues and inorganic fertilizers. So, they all come to the soil solution, there will be leaching of these phosphatic ions that is primary and secondary orthophosphate ions, these ions get adsorbed by clay minerals, or iron aluminium oxides, and desorbed again to the soil solution. They can precipitate in the form of secondary phosphatic minerals like calcium, iron, and aluminium phosphates, and also they can also these secondary phosphorus minerals can also dissolve to form, to enrich the soil solution with this primary, and secondary orthophosphate.

And also, these apatite minerals they are also, they can also weather to form these primary and secondary orthophosphate. One thing is important that there is a clear linkage or dynamics between these three different forms of, these three different solid fractions were phosphorus, which governs this phosphorus dynamic.

So, you can see primary P mineral, secondary P minerals, and sorbed phosphorus by clay minerals iron and aluminium oxides, they have their no close relationship. So, phosphorus is

generally cycle between these sorbed, between these sorbed phosphorus to secondary phosphorus minerals to primary phosphorus minerals. So, this is how this phosphorus moves between these three solid forms.

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Calcium Phosphates

- These groups of compounds form an important category in the young soils and in mature soils of neutral to alkaline pH ranges
- The calcium phosphates found or expected either in the stable state or in a metastable state in the soil-fertiliser reaction zone are:
 - Fluorapatite $[\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2]$
 - Carbonate apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)(\text{H}_2\text{O})]$
 - Hydroxy apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$
 - Octacalcium phosphate $[\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}]$
 - Dicalcium phosphate $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$
 - Monocalcium phosphate monohydrate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$

So, if we consider the compound of phosphates with calcium, we can see that these groups of compounds form an important category, these calcium phosphates form an important category in the young soil, and in mature soils of neutral to alkaline pH range. Because in case of neutral to alkaline pH range, calcium ion predominate.

So, there it forms the calcium phosphates. So, the calcium phosphates found, or expected either in the stable state or in a metastable state in the soil fertilizer reaction zone, and these are generally, these like fluorapatite you can see where there is a fluorine presence, carbonate apatite when there is a carbonate, hydroxy apatite when there is a hydroxyl ion, octacalcium phosphate, then dicalcium phosphate, and monocalcium phosphate monohydrate. So, these are the major calcium compounds, calcium-based phosphate compounds, or calcium phosphates which are formed in the neutral to alkaline pH range.

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Combined With Iron and Aluminium

- ❑ Crystals or Colloids
- ❑ Surface Precipitated or Adsorbed

And other, when phosphate combines with iron, aluminium, they produce the iron aluminium phosphates, they are generally, crystals or colloids and surface precipitated or adsorbed.

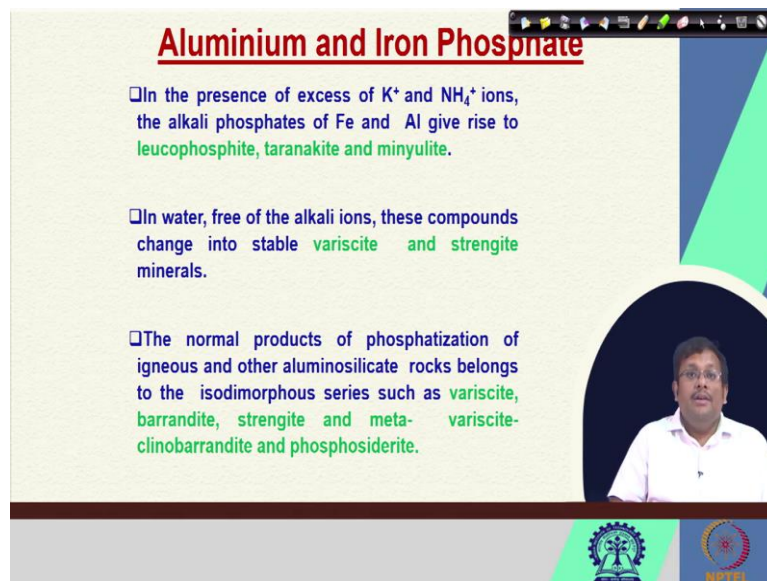
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Aluminium and Iron Phosphate

- ❑ In the initial stages of acid weathering, phosphate 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.
- ❑ Ferrous phosphate, Vivianite [$Fe_3 (PO_4)_2 \cdot 8H_2O$] has been detected in waterlogged or poorly drained soils and in profiles having fluctuating water and air regimes.
- ❑ Aluminium phosphates [$Al_3 (OH)_3 (PO_4)_2 \cdot \%H_2O$] or wavelite has also been detected in the sand and silt fraction of some soils.

So, in the initial stage of acid weathering, phosphate becomes increasingly bound to iron, and aluminium ions released from silicate minerals by replacing the hydroxyl from hydroxyl group from the hydroxyl minerals, or oxygen from the oxide minerals. So, ferrous phosphate also known as Vivianite has been detected in waterlogged, or poorly drained soil, and in profiles having fluctuating water and air regimes. So, in case of acidic soil condition, you can expect the formation of iron phosphate, and also aluminium phosphate, or wavelite has also been detected in the sand and silt fraction of some soils.

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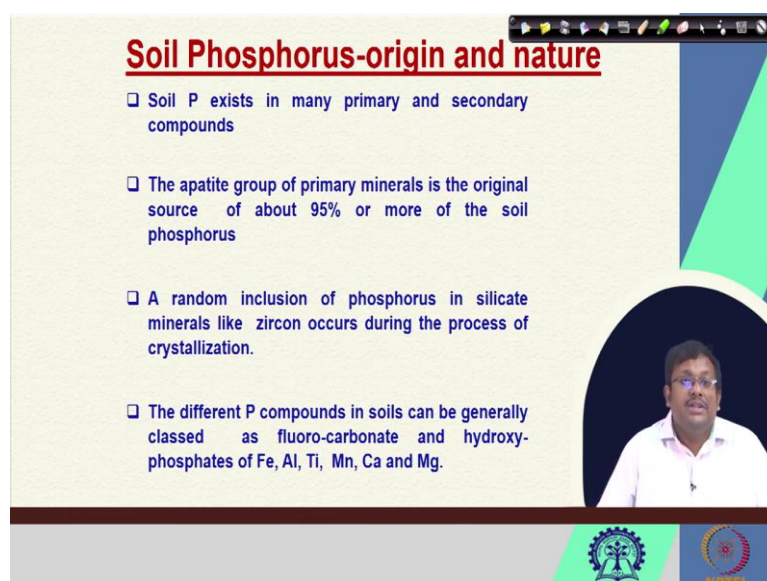
Aluminium and Iron Phosphate

- In the presence of excess of K^+ and NH_4^+ ions, the alkali phosphates of Fe and Al give rise to leucophosphite, taranakite and minyulite.
- In water, free of the alkali ions, these compounds change into stable variscite and strengite minerals.
- The normal products of phosphatization of igneous and other aluminosilicate rocks belongs to the isodimorphous series such as variscite, barrandite, strengite and meta-variscite-clinobarrandite and phosphosiderite.

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And, in the presence of excess of potassium and ammonium ions, the alkali phosphates of iron and aluminium give rise to leucophosphite, taranakite, and minyulite. And in water free of the alkali ions, these compounds free of the alkali ion, these compounds change into stable variscite and other strengite minerals. And, the normal products of fossilization of igneous and other aluminosilicate rocks belongs to these isodiamorphous series such as variscite, that barrandite, strengite, and meta-variscite-clinobarrandite, and phosphosiderite, etcetera. So, these are some of the compounds which these phosphate produce when they combine with aluminium and iron.

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Soil Phosphorus-origin and nature

- Soil P exists in many primary and secondary compounds
- The apatite group of primary minerals is the original source of about 95% or more of the soil phosphorus
- A random inclusion of phosphorus in silicate minerals like zircon occurs during the process of crystallization.
- The different P compounds in soils can be generally classed as fluoro-carbonate and hydroxy-phosphates of Fe, Al, Ti, Mn, Ca and Mg.

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Now, if you see the origin, and nature of soil phosphorus, soil phosphorus exist in many primary, and secondary compounds, and apatite group of primary minerals is the original source of about 95 percent or more of the soil phosphorus. So, we have already discussed what is appetite? This is the primary minerals, and these are the major source of soil phosphorus, a random inclusion of phosphorus in silicate minerals like zircon occurs during the process of crystallization, and the different phosphorus compounds in soil can be generally classed as fluoro-carbonate, and hydroxy phosphates of iron, aluminium, then titanium, manganese, calcium and magnesium.

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REFERENCES

- Filippelli, Gabriel. (2009). Phosphorus Cycle. 10.1007/978-1-4020-4411-3_186
- https://www.ctahr.hawaii.edu/mauisoil/c_nutrients02.aspx.
- Ryan, John & Rashid, Abdul. (2005). Phosphorus.
- Nair, Vimala & Reddy, Konda. (2013). Phosphorus sorption and desorption in wetland soils.

So, these are some of the references which are used for this lecture. You please go ahead and read these references for more comprehensive idea about soil phosphorus. And let us wrap up this lecture. And we will continue from here, and then we will discuss the other important aspects of soil phosphorus dynamics in our next lecture. Thank you.