

Soil Fertility and Fertilizers
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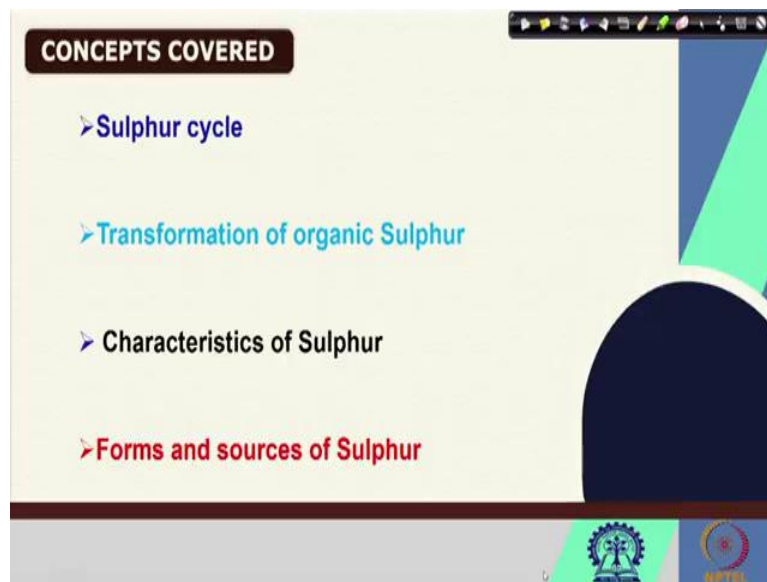
Lecture 17

Soil Secondary Nutrients and Their Role in Plant Nutrition (Cont.)

Welcome friends to this 17th lecture of NPTEL Online Certification Course of Soil Fertility and Fertilizers. And we are at week 4 where we are discussing the Soil Secondary Nutrients and Their Role in Plant Nutrition.

So we have already discussed in our previous lecture regarding the calcium and in this lecture we are going to discuss about sulphur. And sulphur is another important nutrient, which is a component for different important biomolecules. So we are going to discuss them in details.

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So these are the concepts which we are going to cover in this lecture. First of all, we are going to see what is sulphur cycle. And then we are going to discuss what is the transformation of organic sulphur. And then we are going to see the characteristics of sulphur and forms and sources of sulphur. So these are the four major concepts which we are going to discuss in this lecture.

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A slide titled "KEYWORDS" with a list of terms: Pyrite, S cycle, Thiobacillus, Galena, and Elemental S. The slide includes a video inset of a speaker and logos for IITM and NPTEL.

KEYWORDS

- Pyrite
- S cycle
- Thiobacillus
- Galena
- Elemental S

And these are some of the keywords of this lecture; pyrite, sulphur cycle, thiobacillus, galena and elemental sulphur. So these are some of the keywords which we will see in this lecture.

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A slide titled "Sulphur (S)" with a list of facts: More than 95% of the total Sulphur in soil is present in the organic matter. The oxidation of Sulphur is mediated by Thiobacillus bacteria. The soil rich in organic matter will have high Sulphur. In most of cultivated land Sulphur ranges from 30 to 50 mg/kg. Coarse-textured sandy soil have low S content than fine-textured soil. S content more in surface soil than sub-soils. Bulk of inorganic S in rocks is present as pyrites (FeS₂).

Sulphur (S)

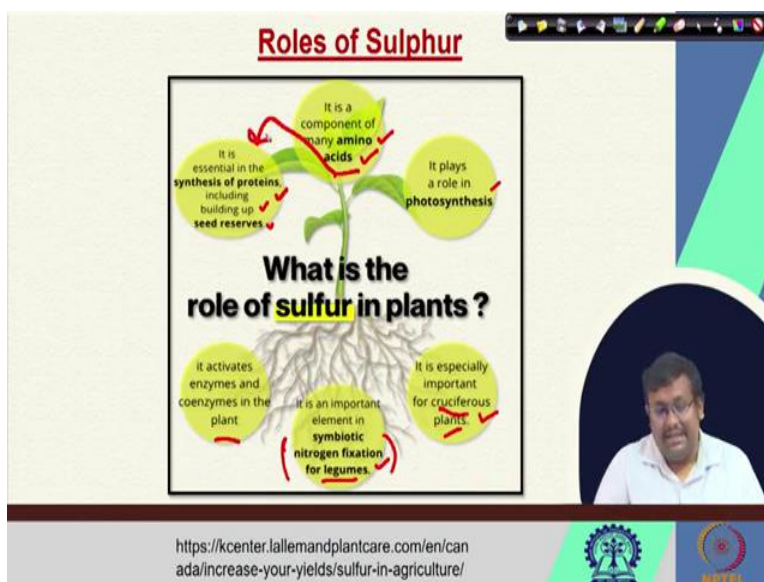
- ❑ More than **95%** of the total Sulphur in soil is present in the organic matter.
- ❑ The oxidation of Sulphur is mediated by **Thiobacillus bacteria**.
- ❑ The soil rich in organic matter will have high Sulphur.
- ❑ In most of cultivated land Sulphur ranges from **30 to 50 mg/kg**
- ❑ Coarse-textured sandy soil have low S content than fine-textured soil.
- ❑ S content more in surface soil than sub-soils.
- ❑ Bulk of inorganic S in rocks is present as **pyrites (FeS₂)**

Now we know that more than 95 percent of the total sulphur in soil is present in the organic matter. So most of the sulphur you will see in organic compound and around 95 percent and the oxidation of sulphur is mediated by a group of bacteria known as thiobacillus bacteria. So the soil rich in organic matter will obviously will have high sulphur content.

Now in most of cultivated land sulphur ranges between 30 to 50 mg per kg or ppm and coarse texture sandy soil have low sulphur content than fine textured soil. Now it is also important to remember that the sulphur content is more in surface soil than subsurface soil. And also bulk of inorganic sulphur in rock is present as pyrites or FeS_2 .

So what we understand? We understand that 95 percent of the total sulphur is present in organic matter, whereas bulk of the inorganic sulphur in rocks is present as a mineral called pyrite or FeS_2 or ferrous sulphide. So this is how sulphur is important, essential element.

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And if you see the roles of sulphur it is a component of many amino acids or essential amino acids like cysteine, cysteine, methionine, all these contain sulphur. So sulphur is an integral part of these amino acids or essential amino acids. And it plays a role in photosynthesis. So this is another important role of Sulphur. It is especially important for cruciferous plant.

So these cruciferous plants are a very much dependent, they dependent on the sulphur for their characteristics and it is an important element in symbiotic nitrogen fixation for legumes. So again this is an important component of amino acids like cysteine, cysteine, methionine, and it plays a role in photosynthesis.

It is also important for different types of cruciferous plants we are going to discuss and also it is very important for symbiotic nitrogen fixation in legumes. We have already discussed about the

symbiotic nitrogen fixation in our previous weeks and it activates enzymes and coenzymes in the plants, so this is another important role.

And it is essential in the synthesis of proteins. Since it is a component of many amino acids, of course, it is essential for synthesis of protein including building of seed reserves. So due to their involvement or since they are structural component of different amino acids they are also required for synthesis of proteins.

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Characteristics of Sulphur

- ✓ 13th most abundant element in earth crust.
- S content in soils: calcareous > peat > marsh > grey brown podzolic > podzolic
- S content in crop families: Gramineae < Leguminosae < Cruciferae
- Concentration of Sulphur in plant ranges from 0.1 to 0.5 %
- Ionic forms absorbed by plants - SO_4^{2-}
- SO_4^{2-} is abundant in arid zones
- % proportion of earth crust - 0.10%

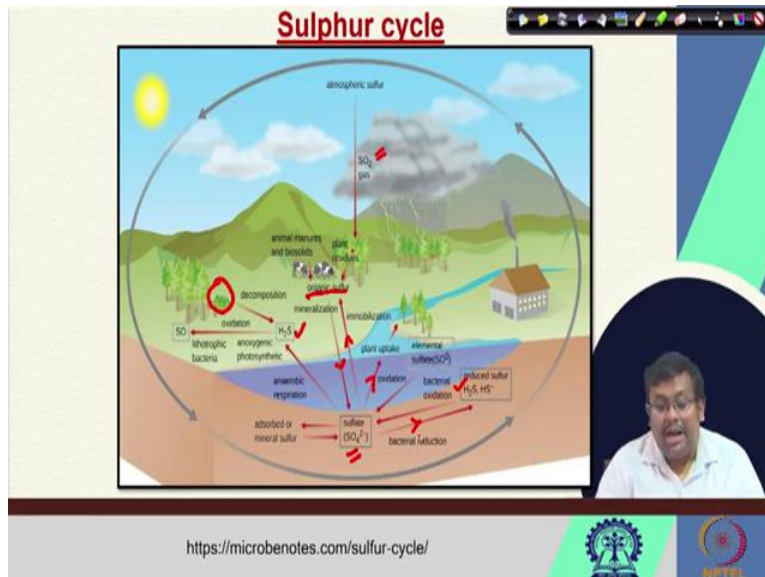
The slide includes a video inset of a man speaking in the bottom right corner. The text on the slide is annotated with red circles and arrows highlighting key terms like 'calcareous', 'peat', 'marsh', 'grey brown podzolic', 'podzolic', 'Gramineae', 'Leguminosae', 'Cruciferae', '0.1 to 0.5 %', and ' SO_4^{2-} '.

So what are the important characteristics of the sulphur? So it is a 13th most abundant element in earth crust. And sulphur content in the soil, if you see what type of soil will contain high amount of Sulphur, so you will see the calcareous soil will high contain high amount of sulphur followed by peat type of soil followed by marshy soil followed by grey brown podzolic soil and pedzolic soil. So among all the soil calcareous soil contain most sulphur.

And sulphur contained in crop families, of course, crucifera, as I have already told you contains highest quantity of sulphur followed by leguminosae and followed by gramineae. So cruciferae crops contain high amount of this sulphur compound. Concentration of sulphur in plant ranges from 0.1 to 0.5 percent. And ionic forms of sulphur absorbed by the plant is sulphate. So this is the only ionic form which plant can absorb through their root.

Remember that sulphate is abundant in arid zones. And the percent proportion or percent content of sulphur in the earth crust is around 0.1 percent. So these are some of the important characteristics of sulphur which you have to remember.

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And this is the sulphur cycle. So if you see the sulphur cycle, like there are some atmospheric, from the atmosphere Sulphur dioxide can come back to the soil in the form of acid rain so, and also when plant residues decompose that can add sulphur into the soil. Animal manure and biosolids can also add Sulphur, so organic sulphur.

So plant residues as well as animal manure and biosolids add organic sulphur. From this organic sulphur due to the mineralization process there will be formation of sulphate and in the opposite process of immobilization this sulphate will again go back to the organic sulphur. So this is mineralization and immobilization.

This sulphate can be further oxidized and then can be uptake by the plant. Elemental sulphur, elemental sulphate where is there can also come into this sulphate pool and bacterial oxidation of the reduced sulphur compounds like hydrogen sulfide can enrich the sulphate in the soil. And also bacterial reduction is the opposite process where sulphate will be reduced to hydrogen sulphide. Now the sulphate which is being produced can be either absorbed or mineral sulphur or they can be further come into this sulphate pool.

So this is how also we can see in the case of anaerobic respiration the sulphate can produce this hydrogen sulfide. Also decomposition of plant residues can create the hydrogen sulphide where hydrogen sulfide can be oxidized also by some lithotrophic bacteria. So this is how the sulphur can moves within water soil and atmosphere. So this is the example of sulphur cycle.

And sulphur, as I have already told you, sulphur is a very, very important component of the plant system because it is a part of essential amino acid structures like cysteine, cysteine, methionine and ultimately they take part, they take an important role in the formation of synthesis of proteins in the plant.

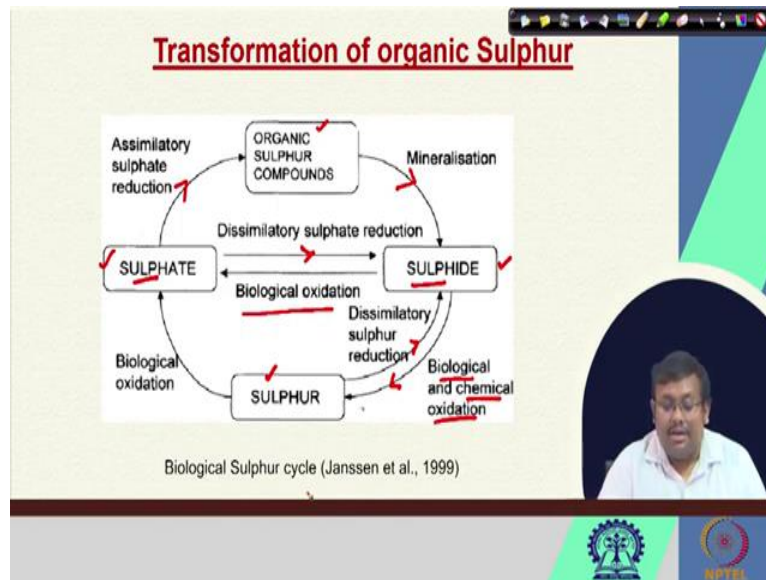
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Steps of Sulphur cycle

- Formation of inorganic Sulphur
 - Biological
 - Geological
- Oxidation of inorganic Sulphur to Sulphate
- Assimilative reduction of Sulphate Sulfide
- Incorporation of Sulfide into organic compounds

Now what are the major steps of the sulphur cycle? Of course, formation of inorganic sulphur can be either biological or geological. And oxidation of inorganic sulphur to sulfate or assimilative reduction of sulphate to sulfide and also incorporation of sulphide into organic compounds. So we can see the oxidation of inorganic sulphur to sulphate is an important step. Another step is assimilative reduction of sulphate to sulfide and incorporation of sulphide into organic compounds. So these are some of the important steps of sulphur cycle.

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Now if you see the transformation of organic sulphur, this is a important pictorial overview, so if we take this sulphur, elemental sulphur in case of biological oxidation due to different types of bacteria, it can produce this sulphate and this sulphate can goes through asymmetry sulphate reduction by some microorganisms to produce organic sulphur compounds.

So this organic sulphur compound can be further mineralized to produce this sulfide and this sulphide can further oxidize both biologically or chemically to produce this sulphur. Now this sulphur can again go through dissimilated sulphur reduction and can produce this sulphide compound. Now remember that there is a direct conversion between sulphate and sulphate by either biological oxidation, where sulphide gets converted into sulphate.

The opposite process is known as dissimilatory sulphate reduction, where sulphate is converted into sulphide. So this is how different forms of sulphur can be seen or we can see the movement of different forms of sulphur or interconnection between the different forms of the sulphur which are mediated by different microbes which are present in the soil.

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Importance of Sulphur cycle

- ❑ Produce fossil fuels such as coal, petroleum and natural gas
- ❑ Contributes to a majority of metal deposits because it act as an oxidizing as well as reducing agent
- ❑ Serving as the source of energy to the sulfur-reducing bacteria present in the hydrothermal vents
- ❑ Reducing global warming caused by the greenhouse gases by absorbing the ultraviolet radiation of the sun
- ❑ Helps in the growth of plants

Now what is the importance of sulphur cycle? Now it produce, the sulphur produce fossil fuels, it is an important component of fossil fuels such as coal, petroleum, and natural gas and it contributes; sulphur contributes to a majority of metal deposit because it acts as a oxidizing as well as reducing agent. And it can serve as the source of energy to the sulphur reducing bacteria present in the hydrothermal vent.

So in the hydrothermal vents you see there are sulphur reducing bacteria and when there is a sulphur gives them energy, so it is a source of energy. Reducing in, sulphur plays an important role in reducing the global warming, which is caused by the greenhouse gases by absorbing the ultraviolet radiation from the sun and also it helps in the growth of the plants. So these are some of the importances of sulphur or sulphur cycle as a whole.

(Refer Slide Time: 12:59)

Mineralization

- The oxidation of organic matter into SO_4^{2-} is done by microorganism is called as mineralization.
- The mineralization process is expressed as;
$$\text{Organmic S} \xrightarrow{\text{Aeration}} \text{SO}_4^{2-} + \text{H}^+$$
- The formation of end product SO_4^{2-} is associated with the formation of H^+ , hence this process lowers the soil pH
- Rate of mineralization is affected by following factors;
 - Moisture
 - Aeration
 - Temperature
 - Soil pH

Now let us see what is sulphur mineralization. Now the oxidation of organic matter into sulphate is basically, it is a sulphur of mineralization and it is done by microorganism and this mineralization process can be expressed using these equations. So the organic sulphur in the aerobic condition they will be converted into sulfate and proton.

So the formation of this end product sulfate is associated with the formation of proton, hence this process lowers the soil pH. So the formation of this end product sulphate is associated with the formation of protons. So here you can see not only sulfate but also the proton is formed, so ultimately due to this, during this mineralization process it will lower the soil pH. And also rate of mineralization is affected by these four factors moisture, aeration, temperature and soil pH. So these four are important process which affects the mineralization.

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Immobilization

- ❑ Microbial conversion of inorganic Sulphur compounds to organic Sulphur compounds is called **Immobilization**
- ❑ Immobilization is temporary phase
- ❑ Sulphur in soil is associated with organic carbon in a fixed C:S ratio of about **140:1**
- ❑ Immobilization of Sulphur takes places in soil when the ratio of either C or N to S is very wide
- ❑ Optimum temperature is **35 to 40 °C**

The opposite process of mineralization is immobilization. Immobilization is a microbial conversion of inorganic sulphur compounds to organic sulphur compounds and immobilization is a temporary phase. Now sulphur in soil is associated with organic carbon in fixed CS ratio of about 140 is to 1. So generally if the CS ratio which you can see in the soil is around 140 is to 1.

Now immobilization of sulphur takes place of the soil when the ratio of the either C or N to sulphur is very wide. And optimum temperature for this immobilization of sulphur is around 35 to 40 degree centigrade. So sulphur generally, in case of soil the CS ratio is around 140 is to 1, but in case of higher CS ratio that will help in the immobilization of sulphur.

(Refer Slide Time: 15:16)

Reduction-Oxidation reaction

- These reactions are biochemical in nature and are mediated by autotrophic bacteria belonging to the genus *Thiobacillus*
- Sulphate can be reduced to hydrogen sulphide by *Desulphovibrio* and *Desulphatamaculum*

By the action of soil
micro-organisms (*Thiobacillus* sp.)

$S^0 \xrightarrow{\text{Oxidation}} SO_4^{2-}$

(Elemental sulphur) (Sulphate sulphur)
available to plants


Chemolithotrophic
bacteria (oxidation)

$CO_2 + S^0 + H_2O \rightarrow (CH_2O) + SO_4^{2-} + 2H^+$...I

In presence of
light (Photo-lithotrophic
bacteria (oxidation))

$CO_2 + 2H_2S \rightarrow (CH_2O) + H_2O + S^0$...II

(Elemental sulphur)



So there is a redox reaction or reduction oxidation reaction which is also involved with the sulphur. So these reactions are biochemical in nature and are mediated by autotrophic bacteria belonging to the genus thiobacillus and sulphate can be reduced by hydrogen sulphide by these two groups of bacteria; one is disulphovibrio another other is desuphatomaculum.

So you can see here this is an elemental sulphur, this elemental sulphur can be oxidized into sulphate sulphur by the action of soil microorganism which are thiobacillus species and, so this chemolithotropic bacteria can oxidize this elemental sulphur into sulphate and also in the presence of light photolithoautotrophy bacteria can also oxidize this hydrogen sulphide into elemental sulphur.

So these are oxidation reaction we can see here. Here first the elemental sulphur is oxidized to sulphate and here these H₂S is oxidized to elemental sulphur. So and these are mediated by different chemolithotropic bacteria as well as photolithoautotrophy.

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Forms of Sulphur

A. Inorganic form:

- ✓ Readily soluble Sulphates
- ✓ Adsorbed Sulphates
- ✓ Insoluble Sulphates
- ✓ Co-precipitated with CaCO_3
- ✓ Reduced inorganic Sulphur compounds (Sulphide and elemental Sulphur)

B. Organic forms:

- ✓ Hydroiodic acid (HI) reducible Sulphur
- ✓ Carbon bonded
- ✓ Residual or unidentified Sulphur

The slide includes a video inset of a man in a white shirt and logos for IIT Bombay and NPTEL at the bottom.

Now what are the forms of the sulphur? So sulphur can be broadly classified into two major forms, one is inorganic form another is organic forms. So in the inorganic form we can see readily soluble sulphates, adsorb sulphates, insoluble sulphate, co-precipitated with calcium carbonate and also reduce inorganic sulphur compounds like sulphide and elemental sulphur. In the organic form we can see hydroiodic acid reducible sulphur, then carbon bonded sulphur and residual or unidentified sulphur. So these are some of the forms of sulphur.

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Forms of Sulphur

Readily soluble Sulphates:

- ☐ Sulphur is usually taken by plants as the **Sulphate ions**.
- ☐ Concentration of 3 to 5 mg/kg SO_4^{2-} in the soil have been found adequate for most plant growth
- ☐ In Sulphur deficient soil easily soluble sulphate content lies between **5 and 10 mg/kg**
- ☐ However, the coarse textured soils like sandy and sandy loam soils are contains Sulphur less than 5 mg/kg

The slide includes a video inset of a man in a white shirt and logos for IIT Bombay and NPTEL at the bottom.

And readily soluble sulphates also we can see. So sulphur is usually taken up by the plant, we know that is sulfate ions concentration of 3 to 5 ppm of sulphate ion in the soil have been found adequate for most of the plant growth and in sulphur deficient soil easily soluble sulphate content lies between 5 to 10 ppm. However, the coarse texture soils like sandy and sandy loam soils contain sulphur less than 5 ppm.

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Forms of Sulphur

Adsorbed Sulphates

- ❑ Contains higher amounts of hydrous oxides of Fe and Al e.g., ultisols, oxisols and alfisols
- ❑ Contribute Sulphur requirement in **highly weathered soils**.
- ❑ Concentration is found higher at depths ranging from **15 to 75cm** below the surface.
- ❑ Adsorbed sulphate can account for up to one third of total in sub soils, and less than 10 % of the total Sulphur in the surface soil.

So another form of sulphur we can see it is called adsorbed sulphates. So this, it contains higher amount of hydrous oxides of iron and aluminum like in case of ultisol, oxisols and alfisols. We can see these adsorb sulphates and they contribute sulphur requirement in highly weathered soils as you can see they are present in oxisols and ultisols; these are highly weathered soil so they contribute the sulphur requirement in the highly weathered soils.

Concentration of sulphur found higher at depths ranging from 15 to 75 centimeter below the surface and absorb sulphate can account for up to one third of the total in sub soils and less than ten percent of the total surface in the surface soil. So these are some of the important features of adsorbed sulfate.

(Refer Slide Time: 19:00)

Forms of Sulphur

Co-precipitated with CaCO_3

- ☐ Mostly found in calcareous soils particularly when calcium carbonate is present as its coarse particles.
- ☐ This fraction is relatively available to plants.

Reduced inorganic Sulphur

Sulphide form

- ☐ Magnitude of such accumulation may be greater in soils containing higher amount of organic matter.

Elemental Sulphur

- ☐ It is an intermediate product of oxidation process of Sulphide.

Forms of Sulphur

A. Inorganic form:

- Readily soluble Sulphates
- Adsorbed Sulphates
- Insoluble Sulphates
- Co-precipitated with CaCO_3
- Reduced inorganic Sulphur compounds (Sulphide and elemental Sulphur)

B. Organic forms:

- Hydroiodic acid (HI) reducible Sulphur
- Carbon bonded
- Residual or unidentified Sulphur

Also we can see co-precipitated, when it is co-precipitate so we have already discussed about this readily soluble sulphate, adsorbed sulphates we have discussed. Now the co-precipitate with calcium carbonate, so let us see what are the features. So this form that is, this form of sulphur can be or inorganic sulphur can be mostly found in calcareous soil particularly when calcium carbonate is present as its coarse particles.

And this fraction is relatively available to the plants. And another part is reduced inorganic sulphur compounds; so this reduced inorganic sulphur compounds you can see they can be

observed as sulphide form or elemental sulphur form. Now this sulphide form we can see magnitude of such accumulation may be greater in salts containing higher amount of organic matter. And elemental sulphur it is an intermediate product of oxidation process of sulphide.

So we have discussed the major inorganic forms like readily soluble sulphates, adsorb sulphate, co-precipitated with calcium carbonate and reduced inorganic sulphur.

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Forms of Sulphur

- HI reducible (non-carbon bonded) Sulphur**
 - ❑ Sulphur in this pool is extracted using **hydroiodic acid**
 - ❑ Out of the total organic Sulphur about half is present in this fraction.
- Carbon bonded Sulphur**
 - ❑ In this fraction Sulphur is determined by reduction to Sulphide with Raney nickel
 - ❑ This fraction of Sulphur amounting about **20%** of total organic Sulphur.
- Residual or unidentified Sulphur**
 - ❑ This accounts for **30-40%** of total organic Sulphur.
 - ❑ Most stable form of Sulphur

So let us see the forms of, organic forms of sulphur. So the first one is hydroiodic acid reducible sulphur. So the sulphur in this pool is extracted using hydroiodic acid. Out of the total organic sulphur about half is present in this form. And the second fraction we can see is called the carbon bonded sulphur. So in this fraction sulphur is determined by reduction to sulphide with Raney nickel and this fraction of sulphur amount about 20 percent of the total organic sulphur.

And the third type of fraction of organic sulphur is residual or unidentified sulphur. This account for 30 to 40 percent of the total organic sulphur and it is the most stable form of sulphur. So these are some of the important organic forms of sulphur.

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Sources of Sulphur

- ❑ S occurs as sulphide in igneous and sedimentary rocks
- ❑ As the fertilizer products become more concentrated and refined sulfur content becomes very low
- ❑ The S-bearing minerals in rocks and soils are:
 - ✓ Gypsum
 - ✓ Epsomite
 - ✓ Mirabilite
 - ✓ Pyrite (سولفور)
 - ✓ Chalcopyrite
 - ✓ Cobaltite
 - ✓ Galena

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Now if you want to see what are the sources of sulphur, sulphur occurs as a sulfide in igneous and sedimentary rocks, we know that. We have already discussed about pyrite or FeS_2 . Now as the fertilizer product becomes more concentrated and refined sulphur content become very low. And the sulphur bearing minerals in the rocks and soils are these.

First of all, gypsum. Gypsum is calcium sulphate dehydrate, so apart from calcium it also supplies sulphur, then epsomite, mirabilite, pyrite; we have already discussed. FeS_2 , pyrite and then chalcopyrite, cobaltite and also galena. So all these are important source of sulphur. So these are basically sulphur bearing minerals which are present in rocks.

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Sources of Sulphur

- ❑ About 95% of Sulphur in soil is contained in organic matter
- ❑ Sulfur dioxide in the atmosphere is **highest** in industrialized areas
- ❑ Sulfur is present in the irrigation water as sulfate-sulfur.
- ❑ Cow and Pig manure, Compost and Poultry manure
- ❑ **Acid rain** also provide Sulphur

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If we are interested to know what are the major sources of sulphur we already know that 95 percent of the sulphur in the soil occurs as inorganic form and sulphur dioxide which is the gaseous form of sulphur, we can see their enrichment in the industrial areas, because of industrial emission they go to the atmosphere and this sulphur dioxide goes to the atmosphere and ultimately, they react with the with the water vapor to produce the acid drain.

And this acid drain comes back to the soil. So this acid rain basically is sulphuric acid, so when the sulphur dioxide reacts with the water vapor that produce sulphuric acid and comes back to the soil as acid rain. Also sulphur can be present in irrigation water as sulphate sulphur and cow and pig manure also compost and poultry manure contains sulphur. So these are some of the important sources of sulphur.

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<https://thebiologynotes.com/sulfur-cycle/>

So guys let us wrap up this lecture and in the next lecture we will discuss some of the important sulphur containing fertilizers and other aspects of sulphur and their importance for plant nutrition. We are going to discuss their deficiency symptoms. So these are some of the references for this lecture. Please go through these references.

And if you find any difficulty please feel free to post your question in the forum and I will be more than happy to answer your queries. So thank you. Let us meet in our next lecture.