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Lecture-13
Chemistry of Soil Organic Matter (Contd.)

Welcome friends to this third lecture of week 3 and we are basically discussing the chemistry of soil organic matter. And in the previous 2 lectures we have discuss uhhh the definitions of soil organic matter and humus and other components of soil organic matter, what are the major fractions of soil organic matter. Then we have discuss about different types of soil forming factors and how they influence the formation of soil organic matter.

We have discuss the global carbon cycle and carbon sequestration and also we have discussed different pools of carbon and how the movement of carbon you know can be observed from one pool to the another pool. We have discuss the major difference between the humic substances and non humic substances and then we have discussed about the 4 humus formation theories. (refer time: 01:31)

And also we have seen how water can act as a major carrier for movement of soil organic matter in different water bodies. So, in this lecture we will be talking more about the structure as well as the difference between different types of humic and humic fractions. So, if we see the properties of humic substances, the humic substance has some you know some specific properties which basically differ from any other known compound.

For example their diameter they are very small the diameter ranges from 1 to 0.001 micrometer for humic acid and in case of fulvic acid they are even smaller. So, when we are we are using HA that means it is humic acid and when we are using FA they are basically fulvic acid. In the last lecture we have already discuss that there are 3 major fractions of humic compounds one is humic acid another is fulvic acid and the third one is humin.

So, these humic fractions are hydrophilic and consists of globular particles and humic substances are also considered as coiled long chain molecules or 2D or 3D cross link macromolecules. So, it is complex structure as you can see, as you can see this is a humic acid molecule and this is a kind of a fulvic acid molecule although their structure is not very well defined and their structure can change depending upon different conditions.

So, the negative charge of humic substance derived from ionization of their acidic functional groups. We will see what are the major acidic functional groups which are present in the humic matter or humic substances. So, basically the idea of showing you this slide is to tell you the fact that the you know humic compounds are having very intricate

and complex structure which is different than that of non humic substances.(refer time: 03:52)

So, if you see this structure and the different acidic groups which are present in the humic substance or humic fraction you will see that majority you know the major groups which are present are basically alcoholic hydroxyl groups and phenolic hydroxyl groups as well as carboxyl groups. So, among these carboxyl groups are phenolic hydroxyl groups are more prevalent.

So, you can see that this is basically large complex of organic humus molecule consists of chains and rings of mainly carbon and hydrogen atoms. And these you know this is basically simplified diagram and showing different types of chemical groups you know which are responsible for high amount of negative charge.

I have already discuss during our inorganic component lectures that you know organic matter produces you know couple of you know a couple of folds more cation exchange capacity or negative charges as compared to the clay minerals. So, these negative charges basically developed by the ionization of these different groups which are present. So, the 3 groups highlighted all include these hydroxyl you can see this is one hydroxyl, this is another hydroxyl, this is another hydroxyl.

And that can losses in hydrozine ion by dissociation and does become negatively charged. So, in this side we are showing the whole functional groups however in this right side we are showing you the ionized form of these groups where they are basically donating the protons and getting negatively charged. You note that the alcoholic phenolic and carboxylic groups on the right side of the diagram are showed in the dissociate state.

So, this is basically an alcoholic group which is dissociated, this is phenolic group which is dissociated and this is carboxylic group which is also dissociated. While those in the left side are still have their associated hydrogen ions. Remember whatever charge which is developed in the in the organic humus humus basically this is a pH dependent charge, this is not a permanent charge this is pH dependent charge or variable charge.

And as a result of that you can see either the development of negative charge or there is a presence of positive charge as we have seen in case of clay mineral depending on the surrounding pH conditions. So, you know association of the second hydrogen ions as you can see here can produce also net positive charge. So, this is how this is this is why the charge which is developed in the in the in the soil organic matter is known as the variable charge, it is not a structural charge ok.(refer time: 07:03)

So, let us see the properties of humic substances, if you see the properties of the humic substances the average molecular weight of fulvic acid varies from 500 to 5000 Dalton. Whereas, average molecular weight of humic acid is quite larger than that of fulvic acid and it varies from 3000 to almost 1 million Dalton. And molecular weight of measurement basically depends on pH concentration and ionic strength although.

But in general humic acid has you know several times higher molecular weight than that of fulvic acid. And the salt you know soil humic acid have you know we have already said that soil humic acid have higher molecular weight than aquatic humic acid. So, that is why I am telling you they although their humic acid their structure varies from one environment to another environment.

And the mean formulas of humic acid is basically C 10 H 12 O 59 however in case of fulvic acid it is C 12 H 12 O 99 for fulvic acid. So, this is the difference in their mean formulas and their weight molecular weight also quite different from each other.(refer time: 08:25) So, if we also see the composition of humic acid and fulvic acid, this table shows the clear difference between composition and composition of humic acid and fulvic acid.

One thing is clear that humic acid contains higher carbon than that of fulvic acid. As you can see in case of humic acid the carbon concentration varies from 53.8 to 58.7% whereas in case of fulvic acid it is 40.7 to 50.6%. The hydrogen content is 3.6 to 6.2% in case of humic however is also 3.8 to 7% in case of fulvic, so we are not seeing very much difference here. Oxygen, on the other hand you see the new humic compound we have only 32.8 to 38.3 and in case of fulvic acid it varies from 39.7 to 49.8. So, fulvic acid contains more oxygen because they contain more oxygen bearing groups than that of humic acid.

And as a result of containing more oxygen bearing groups in fulvic acid are more acidic in nature than that of humic acid. So, nitrogen, nitrogen where you know concentration in humic acid varies from 0.8 to 4.3 whereas in case of fulvic acid it varies from 0.9 to 3.3%. Sulfur, if you consider sulfur the concentration varies from 0.1 to 1.5% however in case of fulvic acid it is 0.1 to 3.6%.

So, this is the difference between the difference of composition between humic acid and fulvic acid. And one thing is pretty you know it is very, very clear that carbon is more in case of humic acid whereas oxygen is more in case of fulvic acid.(refer time: 10:28)

So, as we have seen in the previous slide the major elements of humic acid and fulvic acid are basically carbon and oxygen because they this carbon basically forms the backbone. And fulvic acid have lower carbon but higher oxygen we have seen that from the previous table. And also another important criteria is generally considered for classifying different humic type is the atomic ratio.

And among the atomic ratio O/C ratio or OC ratio is considered as the base to classify different humic types. Now remember in case of humic acid these OC ratio is basically 0.50 however you know around 0.50. However in case of 5 fulvic acid the OC ratio is more 0.7 because the oxygen content is more in case of fulvic acid whereas carbon content is less in fulvic acid as compared to the humic acid. So, depending on this OC ratio we can differentiate humic acid from fulvic acid, so, let us see what are the values in details.(refer time: 11:43)

So, if you see this table, this table shows the atomic ratio of elements inside humic acid and fulvic acid. So, one thing is clear there are 3 different types of ratio atomic ratio you can see hydrogen carbon ratio, oxygen carbon ratio or nitrogen carbon ratio. And we are focusing more on these oxygen carbon ratio. One thing is clear that in case of soil fulvic acid the OC ratio is quite higher that you can see that Schnitzer and Khan they have proposed this value.

They have calculated these values 0.74 in case of Ishiwatari they have calculated these at 0.70 in case of Malcolm they have calculated it is 0.64. However in case of soil humic acid the OC ratio is less than or around 0.50 as you can see in case of the Schnitzer and Khan they have calculated it is 0.48, in case of Ishiwatari they have he has calculated it 0.50, in case of Hatcher they have calculated you know 0.47.

Steelink they have calculated 0.46 and in case of Lenheer they also calculate is 0.5% which is near 0.50. So, one thing is clear that this OC ratio can be an important criteria for separating 2 different types of humic compounds that means humic acid and fulvic acid.(refer time: 13:19)

So, if we see the properties of the humic substances, this is a very you know compact representation of different compact different compact representation of variation of properties between fulvic acid, humic acid and humine. So, one thing is clear that if we consider the humic substances or pigmented polymers they can be different uhhh you know differentiate into fulvic acid, humic acid and humin, humin is basically the non insoluble part.

So, the color of the fulvic acid varies from light yellow to you yellowish brown whereas the color of humic acid varies from dark brown to grey black and in case of humin it is pure black. So, as we go from fulvic acid to humic acid to humine obviously as you can see the intensity of the color is continuously increasing. And also increase in degree of polymerization as you can see from fulvic acid to humic acid to humin.

Obviously the structure of humic acid is more complex than that of fulvic acid however the structure of humin is more complex than that of humic acid. And also increase in molecular weight we have already discuss this point that the molecular weight is less in case of fulvic acid and it is in you know more than fulvic acid in case of humic acid, in case of humin it is the highest.

And in case of carbon content, the carbon content is lowest in case of fulvic acid, the carbon content also increases from fulvic acid to humic acid to humin. And decreasing the oxygen content as you know that fulvic acid contains more oxygen than that of humic acid. So, fulvic acid as we go from fulvic acid to humic acid to humine we are seeing that there is a decrease in oxygen content from 45 you know 48% to 30%.

As a result of more oxygen containing groups in case of fulvic acid obviously their exchange acidity is higher than that of humic acid as well as humin. So, exchange acidity if we considered exchange acidity it is highest in case of fulvic acid because it contains more oxygen as well

as you know acidic groups. And as a result there oxygen acidity is higher than that of humic acid and also which is further higher than that of humin.

And also the fulvic acid is the soluble fraction of humic compounds whereas humic acid is you know their degree of solubility decreases from fulvic acid to humic acid to humine. And in this fulvic acid is soluble fraction, the humic acid is insoluble in acid however this humin is typically insoluble fraction. This fulvic acid can be soluble in both acid and alkali however humic acid can be soluble only in alkali and humin is a non soluble fraction.

And these are different you know macromolecular structure of humin, humic acid as you can see this is the humic acid a peaty sandy hydro earth soil. And this is a humic acid of haplic phaeozems, humic acid in podzolic soils and so on and so forth. So, basically we can see the differences of different properties clearly in this slide as we go from fulvic acid to humic acid to humin.

Remember one thumb rule that humic acid is lighter than that of humic is that humin that humic acid. Humic acid is come what intermediate between humine and fulvic acid colored intensifies from fulvic acid to humin humin molecular weight intensive molecular wise increases, oxygen containing group decreases, oxygen acidity decreases and you know degree of solubility also decreases.

And you know degree of polymerization increases as you go from the fulvic acid to humic acid to humin.(refer time: 17:52) So, let us see the functional groups of humic substances, a couple of slides back I showed you the complex structure of organic humic substances and 3 or 4 major groups which are present in the humic compound. Now in this slide we are going to discuss the all different types of functional groups which are present in the humic substances. So, the primary acidic functional groups are carboxyl groups and phenolic OH groups.

I have shown you both these groups in that in that slide that the carboxylic group and phenolic groups are the primary acidic functional groups. So, we can see here in the functional groups we have seen carboxyl and this phenolic hydroxyl groups apart from that phenol groups are there quinone groups are there. So, the other functional groups are basically alcoholic OH groups which you see here and also the quinonic and ketonic group groups, so, these are the major functional groups.

And Humin are high in alcoholic OH groups and humins are basically high in alcoholic OH groups. Fulvic acid mainly consists of this carboxyl group because and as a result they produce more oxygen acidity. And total acidity of fulvic acid is a higher than that of humic acid it is quite we have already discuss. So, we can see that among the acidic groups, carboxylic groups, phenolic OH groups, phenol groups and these quinine groups are major groups.

In the neutral groups alcoholic OH and then ether, ketone, aldehyde, esters they are the major neutral groups and among the basic groups amine and amides are the major basic groups ok. So, these are the you know

different groups which are present in the humic substances. Ok.(refer time: 20:00)

So, what are the different types of amino acids which are present in soil organic matter, one thing we can see that there are different types of amino acids which are present in the soil organic matter and we can classify them also. So, the first classification says it is a neutral amino acids, so, among the neutral amino acids you can see the glycine also alanine and leucine these are the you know neutral amino acids which are present in soil organic matter.

However in case of aromatic amino acids as you can see the aromatic rings are there. So, in case of aromatic amino acids phenyl alanine, tyrosine and tryptophans are present in the soil organic matter.(refer time: 20:47) And other groups other amino acids which are present, so in the previous slide we have seen. In the previous slide let us go back to the previous slide we have seen neutral amino acids and aromatic amino acids. So, also there are other neutral amino acids like isoleusine, valine, serine and threonine.

And among the acidic amino acids aspatic acid and then glutamic acid, basic amino acids are arginine then lysine, histidine and secondary amino acids you can see proline and hydroxy proline. So, these are different types of amino acids which are present in soil organic matter.(refer time: 21:40)

So, now we are going to start a very important portion of soil organic matter that how we can fraction it, different humic fractions like humic acid fulvic acid and humin. So, the study of soil organic matter you know to study the soil organic matter it must be first separated in you know from the inorganic components. And this is basically activated this is basically you know activated or achieved by different classical fractionation schemes.

Now fractionations involve precipitation of humic substances by 3 ways either by adjustment of pH and salt concentration which is the classical method or addition of organic solvents or additional of metal ions. So, these are the 3 ways through which the fractionation of soil organic matter can be done.(refer time: 22:47)

So, if we see the fractionation of soil organic matter in details in this diagram, alkali extraction using the 0.1 to 0.5 molar sodium hydroxide or sodium bicarbonate are usually generally done for fractionation of soil organic matter and alkali extractions are based on solubility principles. So, if we see the soil organic matter it can be broadly differentiated into non humic substances we already know that recognizable plant debris + polysaccharides, proteins, lignins etc in their neutral and transform state.

Also they can be divided into they can be also uhhh you know classified into humic substances and in this humic substances these are basically fractions on the basis of the solubility. We can see fulvic acid, humic acid and humin. I As I have told you in previous slide the fulvic acid is basically solid it is a soluble fraction so it is soluble in both acids

and alkali. The humic acid is the fraction which is insoluble in acid however it is soluble in alkali.

However, humin is is generally inside it is insoluble in acid and as as well as alkali. So, this is how we can you know this is these diagrams shows the differences in their solubility let us see how we can actually implement this fractionation in this slide.(refer time: 24:16)

So, in this slide we start with the soil organic matter and then we start the fractionation of the soil organic matter as we have told in the last slide. So, once we treat this soil organic matter with alkali obviously humin and non humic matter which are insoluble in nature will separate out. And basically all the humic substances that means humic acid and fulvic acid will come into the solution.

And then this humic substances or soluble humic substances when we you know they are being treated with acids they will be differentiated into a soluble fraction that is fulvic acid and insoluble fraction that is humic acid. Now in the soluble fraction that is fulvic acid when we adjust the pH at 4.8 they can be again further fractionated into fulvic acid which is a soluble fraction and beta humus which is insoluble fraction.

And in case of humic acid which is basically insoluble if we reflects it with alcohol we will get 2 fraction one is the soluble hematomelanic acid another is insoluble humic acids. Now these insoluble humic acid if we further treat it with neutral salt then it will further divided into brown humic acid and grey humic acid. So, this shows the step by step process through which we can fractionate the soil organic matter.

Again the soil organic matter fractionation starts with the alkali either sodium hydroxide or sodium carbonate. And then we it basically differentiate into the humic fraction which is soluble and non humic fraction as well as humin which are which are insoluble, humic substances will be treated with the acid you know that humic acid are insoluble acid.

So, they become insoluble they remain insoluble and fulvic acid again will be solubilized and further we adjust their pH to get either soluble fulvic acid or insoluble beta humus. In case of humic acid if we reflects it with alcohol will get humic acid which is insoluble which will further treat with neutral salt to get soluble brown humic. And also insoluble grey humic fractions and hematomelanic acid is basically the soluble fraction of humic acid which basically get solubilized after reflexing with alcohol.

So, friends we have discuss in details about the composition of the soil organic matter, humic substances and their difference in the properties as well as how we can separate them from each other in this lecture, I hope that you have learned something new in this lecture. In the next lecture we will be seeing in detail structure of soil organic matter. And let us meet in the next lecture to discuss the structure of the soil organic matter in details, thank you.