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Lecture-14  
Chemistry of Soil Organic Matter

Welcome friends to this NPTEL course of environmental soil chemistry and today is the fourth lecture of third week. And in this week we are actually discussing about the chemistry of soil organic matter. And today we are going to talk about the molecular structure of soil organic matter. Then we will be talking about metal and soil organic matter complexes, complex of soil organic matter and clay and how soil organic matter can bind different other pesticides and so on so forth.

So, today we will be starting with the molecular structure of soil organic matter, remember the basic backbone structure of soil organic matter is still an enigma. There are couple of reasons that there has been so many confusion that there is no clear definition of the structure of soil organic matter. And the structure of the soil organic matter comprises of similar functional groups and presence of aliphatic and aromatic compounds. So, you can see the presence of both aliphatic compounds as well as aromatic compounds.

Now using the  $^{13}\text{C}$  NMR study soil was found to have paraffinic carbon and then methoxy carbon, amino acid carbon and carbon in carbohydrates and aliphatic structures containing you know aliphatic structure containing the hydroxyl groups then aromatic carbon, then phenolic carbon and carbon in other groups. So, the carbohydrates then proteinaceous materials like amino acids, peptides and proteins and lipids like you know alkanes, alkenes, saturated and unsaturated fatty acids, alkyl mono, di and tri esters. In soil organic matter are tightly bound by the aromatic soil organic matter compound.

So, this is the you know the molecular structure of soil organic matter proposed by the scientists and Schulten and Schnitzer in 1993. And it is basically a 2D structure as you can see here different types of aromatic rings as you can see these are different types of aromatic rings. These are different aromatic rings which are basically linked covalently by aliphatic chains as you can see different aliphatic chains are there which are you know joined basically through covalent bonds.

So, this is a very complex structure as you can see and so in this structure one thing is clear that oxygen is present as carboxyl. As you can see the oxygen here is present sets carboxyl and then phenolic as you can see the phenolic groups are also present and then alcoholic hydroxyls are there then esters are there, ethers are there and ketones. So, all these different groups are present and nitrogen is present as heterocyclic structures and nitrile.

As you can see these are different heterocyclic structures and the nitriles you can see here. So, the nitrile group and heterocyclic

structures are also present. And the elemental composition is basically the C 308 8 then H 328 O 19 and N 5. And molecular weight basically they have calculated it is 5.540 Dalton. So, the carbon skeleton which we are seeing has you know micro porosity with voids which can bind various like carbo various molecules like carbohydrates and proteinaceous materials.

And you know not only the car organic molecules but also different inorganic components like clay minerals and metal oxides so and water also. So, this is the you know kind of a structure complex structure you know and using different types of covalently bond aliphatic and aromatic ring. And then they are having some micro pores where they can fix different types of inorganic organic as well as water compounds.

So, let us see other structures, so Schulten and Schnitzer in 1993 they have proposed this structure, they have proposed another structure of humic acid. Now in this humic acid structure one molecule weight of humic acid was assume to interact with a 10% carbohydrate carbohydrates and 10% proteinaceous materials. And they proposed the elementals composition as C 342 then H 388 O 124 and N 12.

And they have calculated the molecular weight of 6651 Dalton and elementary analysis they of that humic acid they have found that it contains 61.8% of carbon, then 5.9% of hydrogen, 29.8% of oxygen on only 2.5% of nitrogen. So, these are some you know molecular structure given by different scientists group.

And also Schnitzer in 2000 they have she has proposed a 3D structure of a soil particle assuming that the soil has 3% soil organic matter and you know and 3% water and 94% of inorganic components. So, as you can see this is basically 3D structure and you know we can see the soil organic matter and then trio silica sheets and hexa peptides also there.

So, the basic elements they have seen you know he has proposed that it is carbon which is basically denoted by blue you know blue circles then hydrogens are basically denoted by these white circles, then nitrogens are they you know are nitrogens are shown by these dark cycles dark blue. As you can see these are the dark blue circles, oxygen basically these are red then silicon are purple as you can see purple are there, iron is green and aluminium is basically light yellow. So, they have shown in this 3D structure different elements and how they are bound together to form this 3D structure of soil organic matter.

So, if we see the molecular structure of soil organic matter then voids in this model structure may contain different as I have already told you. That it can contain both organics inorganics and water. Now the functional groups would react with metal and inorganic material, we will see how they are made, how they are interacting with the metals and inorganic materials when we will discuss the chelates.

Now they also provide nutrients to the plants and microbes by the process of chelation which we are going to discuss. You will see that how they are providing the nutrients to the plants as well as microbes. The soil organic matter is bound to silicates by iron aluminium ions as you know that the silicates we have already discuss in our week 2 lectures that

soil contains you know iron aluminium oxides not only that iron aluminium is also present in the clay mineral structure.

So, soil organic matter can be bound in this clay mineral structure and you know that is why the soil organic matter can coexist with clay minerals and it is surrounded by a model of matrix of silica sheets. So, we will see in details of how they are joining together by a model you know by a model of matrix of silica sheets while we discuss the structure in details.

Now the main reason I told you at the beginning of this lecture that the main reason that the basic structure of humic humus is still not fully understand because thereof 3 reasons. First of all the humus structures are very heterogeneous and complex, second there are no regularly repeating structure unit or set of units just like in case of clay minerals we know that in case of crystalline clay minerals like kaolinite, like montmorillonite, they have some repeating you know well defined structure.

However in case of humus there is no repeating well defined structure and that is why there is no 2 humic substance or humic molecules have the similar structure. As a result of that their molecular structure is still not well described. So, if you see that macromolecular structure of soil organic matter, so what is the macromolecular structure of soil organic matter. Macromolecular structure of soil organic matter basically shows its size and shape. So, the macromolecular structure is important as it affects the chemistry of soil organic matter and mineral complexes and stability of organic mineral aggregates and their fate transporter pollutants and carbon cycle in the soil.

So, the macromolecular structure which we have going to discuss are basically affected by several parameters. First of all is pH, second is electrolyte concentration, third is ionic strength and fourth one is humic acid and fulvic acid concentration. We will just see that how by changing these 4 different factors we can see different types of macromolecular structure. Sometime we will see some fibrous structures, sometime we will see some you know some round and you know some round and some round structures and the cluster structures.

So, let us see how they will look like, so basically in 1976 these 2 scientists called Chen and Schnitzer they used electron microscopy to study the macromolecular structure of fulvic acid as a function of pH. So, these are different pictures they have taken at different pH level, so let us see how pH can differentiate or how how pH can produce different macromolecular structure of soil organic matter.

Now at pH 2 as we can see at pH 2 the elongated fibers and bundles are present as we can see this is showing elongated structures and bundles and fibres were curved or linear. Now at pH 4 the fibers were thinner and fibre bundles are more prevalent as you can see the fibres are thinner as and you know their bundles are more prevalent at pH 6 as we increase the pH further there was less and thinner fibers and more bundles and closely knit fibres as you can see.

They are more you know more bundles and closely knit as you can see the fibres are closely knit together. At pH 7 when we have further increasing the pH a fine network of tightly meshed fibers were present. As you can see a fine network of tightly meshed fibres as you can see. At pH 8 further you are increasing the pH the fine network has change into sheet like structure as you can see we are getting a kind of sheet like structure.

So, we started with the thin fibres and then we are getting into the sheet like structure at pH 9 that means the highly alkaline condition you can see the sheets are getting thicker. And finally at pH 10 which is shown by this picture at pH 10 homogeneous grain like particles were present. As you can see this is a homogeneous grain like particles you can see in this electron microscopic view of the soil organic matter. So, this is how the changes of pH basically determines the macromolecular structure of soil organic matter.

Now Gosh and Schnitzer in 1980 used viscosity surface pressure measurement to study the macromolecular structures of humic acid and fulvic acid. And we have seen that these are some of the primary condition based on which the macromolecular structures of different humic acid and fulvic acid molecules basically change. As you can see in case of condition 1 let us consider let us let us consider condition 1.

So, in the condition 1 when the sample concentration is high which is greater than 3.5 to 5 gram per litre and the pH is low the and simultaneously electrolyte concentration is high which is 0.05 and molar and higher. So, if these 3 conditions are made you can see that rigid and unchanged steroids are present in the macromolecular structure. However, when the sample concentration is low and pH is quite high which is greater than 6.5 and electrolyte concentration is low then we will get a kind of flexible linear poly electrolyte structure.

So, as you can see based on the sample concentration pH and electrolyte concentration as we have discussed the structure of humic acid and fulvic acids are changing. This thing will be more clear when I will show you in the next slide. If you go to the next slide you will see that you know basically what I I have told you in the last last slide that in the sample concentration you can see there are 2 types of sample concentration one is low sample concentration another is high sample concentration. So, in this case we are talking about fulvic acid and this is the chart of humic acid, so low concentration and high concentration.

So, in case of low concentration with the electrolyte concentration in molar electrolyte concentration is basically low, we can see basically linear structures. However as the electrolyte concentration is increasing we are getting by you know different types of spherodic structure. However when the concentration of the sample is increasing we are getting spheroid like structures macromolecular structures.

Similarly in case of pH when it is low we are getting you know spheroid structures however whenever increasing the pH we are getting more thinner fibrous structure . Similarly in case of high concentration also for lower pH values we are getting more cluster you know fiber you know

spheroidal structures. However, the fibrous structures are visible at higher pH. Similarly in case of fulvic in case of humic acid also at low electrolyte concentration and low concentration of sample we are getting the fibrous like structure.

However at higher electrolyte concentration like sodium chloride we are getting spheroidal structures. And in case of pH higher pH we are getting just like in case of fulvic acid in case of humic acid also we are getting fibrous structures. And when the combination of high concentration and low electrolyte concentration we are getting spheroidal structures and also in case of pH at different pH conditions like 6.57 8 and 9.5 we are getting also you know spheroidal and rigid structures.

So, this is how depending on the concentration of the sample as well as the electrolyte concentration and pH the structure of different humic acid and fulvic acid molecule changes. Now in the most moist soil solutions and freshwater when humic acids and salt concentration are low you know humic acid and fulvic acid should occur as flexible linear poly electrolytes. That means what we have seen that moist soils with the fresh water where humic is in salt concentrations are low.

So, humic acids and salt concentration were low that means in this scenario and both humic acid and fulvic acid both of these are showing the flexible linear poly electrolytes. So, this is how the poly electrolyte or macromolecular structures of soil organic matter changes due to the variation of these determinant variables.

So, 1999 another scientist group my headed by my Myneni, so Myneni et al studied the structure of humic you know humus as a function of humus origin pH ionic strength and mineralogy using spectromicroscopy and they have also given different structural patterns. So, in dilute acidic high ionic strength condition like for sodium chloride high ionic strength that means high concentration of the electrolyte, so and dilute acidic solution. So, then humus form the globular aggregates and ring like structures as you can see here.

And as the fulvic acid concentration increase so it was a lower concentration. So, he has the following is it concentration increase large sheet like structure as you can see in this picture appeared and encapsulated smaller structures. And coiling was not prevalent and humus dispersed into the small aggregates less than 0.1 micron in solutions of pH greater than 8. So, as you can see that how this solution, how this structure is changing based on the pH as well as the concentration of humic acid as well as fulvic acid fractions.

So, in concentrated you know in concentrated hyme humus solutions form globular aggregates bound together with thin flims of you know humic substances. Now in picture these 2 pictures you can see in dilute fulvic acid solutions of calcium, copper and iron fulvic acid form thread and knit like structures as you can see thread and net like structures. As fulvic acid cation and cation concentration increases the structures were larger and from rigid sheets.

So, this is the another another group of scientists they have shown different structures of humic acid and fulvic acid. And how they change for different concentration of you know different concentration of humic acid and fulvic acid as well as they are you know. And also due to the presence of certain cations.

Another scientist who call this Namjesnik and Dejanovic and Maurice in 2000 studies soil organic matter structures in hematite and mica. So, they have found that soil organic matter can be bound to hematite and mica and in mica the intermediate pH at intermediate pH and low soil organic matter concentration large spherical aggregates were obtained. And in case of higher soil organic matter concentration reading like structures with considerable porosity was observed.

On the other hand in case of hematite with iron concentration iron present and a pH of 4 globular structure with mean diameter of 0.3 micrometer was observed. So, you can see you know lots of difference you know you know structure structural research have been executed so far. And scientists have produce a lots of information of their macromolecular structures.

Now we have to see the functional groups and charge characteristics of soil organic matter remember that soil organic matter has a higher surface area and CEC than clay minerals. We have already discussed it in details because soil organic matter has a huge number of different functional groups which get you know which dissociate which which form which basically dissociates due to the change of pH and as a result there is a huge amount of negative charge.

Now remember it contributes 80% of the total CEC of the soil is a huge, so that is why soil organic matter is considered one of the major fraction that controls the soil chemical properties. Now organic matter is a variable charge component obviously like you know as like as soil clay mineral there is no crystalline structure defined crystalline structure where isomorphous substitution can occur.

So, due to the absence of isomorphous substitution all the negative charge whatever we see on the surface of the negative on the on the organic matter basically due to the negative charge which which produce due to the variable charge component. So, that is why organic matter is a variable charge component these charge depends on the surrounding pH condition. Now there is a concept called point of zero charge or PZC.

That means the pH at which colloidal particles has no net charge due to the presence of variable charge or pH dependent charge they are may be possibility of producing of either positive charge or negative charge although negative charge is prevalent. However, there will be one pH at which all the positive and negative charge will counterbalance each other and the net charge will be 0 so that point of pH is known as point of zero charge.

So, point of zero charge of soil organic matter is basically comes around pH 3. So, soil organic matter is basically negatively charged as value greater than pH 3. So, if it is if it is pH less than pH 3 then soil

organic matter will produce the positive charge. However at pH greater than 3 it will produce the dissociated hydro you know functional groups. As a result of that they will produce the negative charge, remember that as pH increases the degree of negative charge increases due to the deprotonation or dissociation of  $H^+$  from the functional group.

This we have already seen that as the pH increases the deprotonation occurs from the carboxylic group from the phenolic group which are present in the organic matter. And as a result the negative charge increases and you know as the negative charge increases also the cation exchange capacity increases.

So, functional groups and charge characteristics of soil organic matter if you see major acidic functional groups or carboxyl then quinons, then phenolic hydroxyl groups and Enols. As you can see carboxyl, quinons then phenolic hydroxyl, then in enol these are the major acidic functional groups which are present in soil organic matter.

Now remember that as we have already discuss this structure in our previous lecture. So remember that the carboxyl and phenolic groups are you know this is the carboxyl group as you can see and this is a phenolic group. So, both these groups basically deprotonated at pH common in most soils. So, you can see this is the deprotonated carbo carboxyl group and this is a deprotonated phenolic group.

So, at the normal pH condition they get deprotonated, so, they are major contributors of the negative charge in the soil. So that is why when the organic matter is higher in case of any soil that will have higher cation exchange capacity. And as a result obviously that soil is considered as more nutrient rich because they can attract the positive charge cations. Now carboxyl group remember contributes 55% of the total cation exchange capacity of the soil organic matter.

However, phenolic hydroxyl groups enols and quinonic groups produces around 30% of the CEC of the soil organic matter up to pH 7, so this is very important. So we can see that carboxyl groups and phenolic groups, a carboxyl group is the major producer of the negative charge or CEC and followed by phenol and other groups.

So, so if we consider the contribution of soil organic matter and soil C contribution of soil organic matter in soil CEC. This chart gives us some you know some overview. So with we can see here at pH increases from 2.5 to 8 in this direction clay fraction increases and also organic matter fraction increases. Now one thing you see that the CEC this is the basically the CEC due to the clay fraction and this is basically CEC due to the organic matter fraction.

So, one thing is clear that you know with increase in soil pH as we are going in this direction the CEC of the clay changes much less than that of CEC of soil organic matter. So, soil organic matter is the better contributor of CEC as compared to the clay and this is basically due to the presence of permanent charges in the clay which changes little with pH. So, in case of soil maximum charge except from kaolinite and amorphous iron aluminium oxides.

Most of the charge which is developed in case of crystalline clay minerals are due to permanent charge which changes very little with the pH. However, in case of soil organic matter all the charges are basically pH dependent charge or variable charge. So, you can see with the changes of the pH the magnitude of increase of CEC is higher in case of organic matter as compared to the soil.

So, however CEC of organic matter fraction increases drastically with increase in pH due to the dissolution of H<sup>+</sup> and their functional groups which we have already seen. Now soil organic matter also drastically increase the CEC of the sandy soil. So that is why in case of sandy soil one of the way to increase its fertility is to apply organic matter.

So, we can restore the CEC that means we are basically applying soil organic matter into the sandy soil which are basically electrically neutral to increase the organic matter concentration. And as a result the negative charge increases in the soil organic as a result the negative charge increases attracting more plant available nutrients or cationic nutrients.

Now if you see the contribution of soil organic matter to soil buffering capacity one thing is clear this graph shows us that pH versus a base. So, here there are 2 graphs and we can see A is basically the peat humic acid and B is basically the soil humic acid, so 2 fractions we can see. So, basically if we add the base if we continue to add base how their pH changes they will basically produce this type of pattern.

And soil organic and this pattern is basically we are getting to the buffering capacity of the soil organic matter. Remember soil organic matter is a major contributor to the buffering capacity of the soil. A typical titration curve we are seeing here by adding the base into the organic matter which is you know inherently somewhat acidic in nature. So we are seeing here 3 zones zone 1, zone 2, and zone 3.

So, in case of zone 1 most acidic region we can see it is called the most acidic region where dissociation of the carboxyl groups are happening. In the zone 2 intermediate range attribute you know basically it is an intermediate range which is attributed to the combination of dissociation of weak carboxyl groups and very weak acid groups. However, in zone 3 we are seeing the dissociation of phenolic hydroxyl and other very weak acid groups.

So, you can see this is the basically titration curve showing a you know showing a you know the and these slope shows the buffering capacity of the soil organic matter and dividing the area into 3 zones by dissociation by you know by dissociation of different groups which are present or functional groups which are present in soil organic matter.

Now soil organic matter generally has weak acid characteristics, that is why you know it has some buffering capacity and this is due to the complex of soil organic matter with metals like aluminum then ferric Cu<sup>2+</sup> etc. and hence the important functional groups like carboxyl and you



know they are mostly occurs at complexes with metals producing the chelates.

So, if we see that the humic substances and metal interactions soil organic matter complexes with various metal ions. And basically we will see that these effects retention and mobility of metal contaminants in soil and water. And the affinities of various functional groups towards metal ions are as follows. Basically the highest affinity can be seen in case of enolate followed by amine then azo compound then ring nitrogen compound followed by carboxylate, then ether then carbonyl.

So, the humic substance also vary in their affinity to produce the metal you know complex and their affinity towards the metal ion also varies from one functional group to another function good as we can see here. Now humic substance metal interaction if you want to see that the interaction of between the soil organic matter and humics humus you know and soil organic metal and metal. In case of water body can be described by this picture, you can see here. Now there are 3 types of interaction you can see, one is the reaction between dissolve oxygen dissolved organic carbon and metal ions as you can see.

This is the dissolve phase where we can see that humic substances are interacting with copper here and reaction between the suspended organic carbon and metal ions. So, this is the suspended organic carbon and you know suspended organic carbon and metal ions, you can see here this is the metal ion and suspended sediments basically which is and this organic matter is basically coated in the sand grain and getting suspended.

And the final is a reaction between the bottom sediments and the metal ions as you can see here. Where basically the dissolve DOC is the organic carbon which passes through the 0.45 micrometer silver filter and SOC is the organic carbon which is retained on the 0.45 micrometer silver filter, so this is the difference. So, in case of water body we can see these different types of humic substance and metal interaction in 3 different phases.

So, total binding capacity of in case of total in total binding capacity of humic acid for metal is varies from 200 to 600 you know micro mole per gram. But at 33% of these due to retention of cation complexing site and carboxyl and phenolic groups are the major complexing sites.

And when two or more organic functional groups coordinate the metal ion to form a ring like structure a form of complexation occurs known as chelation. So we can see here there you know chelation of metal by organic compounds where it is the salicylic acid it is chelating the copper phallic acid it is selecting the copper, picolinic acid it is also chelating the copper, oxalic acid chelating the copper.

So, different organic compounds how they are you know you know coordinating with the metal ion to for me ring like structure. And remember that it is always 2 or more organic functional groups ok, so this is how this chelates occurs. So, friend let us wrap up here this lecture and in the next lecture we will be discussing more about this

chelation process and how this chelates affects the movement and availability of different metals.

So, let us wrap up this lecture here and in the next lecture we will be discussing these in details, thank you very much.