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Lecture-15
Chemistry of Soil Organic Matter(Contd.)

Welcome friends to this last lecture of module 3 that is of chemistry of soil organic matter. And in this lecture we are going to talk about the in details about the humic substance and metal interactions. And what you know what are the conditions for forming that chelates and some basic concepts and then how the pesticide and organic matter interaction and soil organic matter soil and soil clay as well as organic matter interaction occurs and what are their implications.

So, in the last lecture we have already discuss that the when 2 or more organic functional groups coordinate the metal lines to form a ring like structure, a form of complexation occurs that is called the chelation process and the product is known as the chelate. And here you can see different organic molecules are producing the chelates using the coordinating different metal ions.

So, another important term while we are talking about the chelates is the ligand. So ligand is basically an atom or function groups of molecules attached to the central atom of an coordination compound. And the type of complexation between the metal ion and the complexant like inorganic and organic ligands like carboxyl and phenolic groups of soil organic matter can be predicted based on 2 types of factors.

One is hydrolysis properties of the elements and the second is concept of hardened hardness and softness of the metals. Now again chelate is the coordinated compound where 2 or more functional groups of organic molecules basically coordinate a metal ion and these processes known as the chelation. And ligand is basically the atom or functional groups or molecules which are attached to the central atom of the chelate.

So, basically in case of organic compound these ligands are carboxyl groups and phenolic groups of soil organic matter, now these ligands could be inorganic also. Now what type of ligand is there in case of soil organic matter particular type of chelate. That can be determined by hydrolysis properties of the elements as well as the concept of hardness and softness of the metals which are going to discuss.

Now let us see the hydrolysis properties of the metal, now hydrolysis is basically as you know is the chemical process in which a molecule of water is added to a substance. Now inorganic elements can be divided into 3 groups based on their reaction with hydroxyl and oxygen at oxygen ion. So, you can see there are 3 rules one is called group 1 element another is group 2 elements and third one is group 3 elements.

So, group 1 elements are basically the elements which basically form the non dissociated complexes like sulfate, phosphate and oxy acids as you can see these the sulphate, phosphates and oxy acids. These are basically the group or elements they form the non dissociated complex like this. Group 2 elements are highly hydrolyzed and can also occur as hydrated cations like ferric, you know ferric is a hydrated cation is oxidized an hydrated cations.

Group 3 elements do not have very stable hydro complexes even at high pH like calcium and zinc ions. At the major ligand in water is hydroxyl groups, so ligands other than water will only combine with group 3 elements and to some extent with group 2 but not at all with group 1 elements, so this is one of the major criteria. Ligands except from the water they will basically from the ligands using the group 3 element.

Some time they form the chelates using the group 2 elements however they do not from the chelate using the group 1 element. So this is the difference between the 3 groups as per as the chelation is concerned. So, if we see uhhh here you know white square basically denote the group 1 and these are dark shaded squares are basically these dark shaded squares these are basically the group 2 and the light shaded squares what you are seeing here are basically belong to group 3.

So, based on the hydrolysis property this is how we can differentiate different elements into group 1, group 2 and group 3. Remember again group 3 produces group 3 produce the chelates you know most of most of the ligands except from the water from the ligands with the group 3 elements, sometime with the group 2 elements and not at all with group 1 elements ok.

So, let us move ahead and see the hardness and soft characteristics for determining the chelating determinant for the determination of chelation process. Now before we discuss about the hardness and soft softness characteristics of the metals we have to brush up our knowledge of Lewis acid and base. So, as you can see here this A basically a Lewis acid and B basically is the Lewis base and ultimately AB is the basically acid base complex.

So, Lewis acid as you know an atom molecule or ion which at least 1 atom where you know in which at least 1 atom has a vacant orbital in which a pair of electrons can be accommodated. And they are an electron pair acceptor obviously this is another feature of Lewis acid all metal ions are basically Lewis acid. So we can consider all metal ions are Lewis acid because they can accept an electron pair where A is the metal ion in this reaction, B is known as the ligand.

So, here B is the ligand which can donate a pair of electrons, so Lewis acid are coordinated to Lewis bases or ligands ok, so, this is the definition and features of Lewis acids and ligands. Now what are the Lewis bases, Lewis base is an atom molecule or ion which has which has at least 1 pair of valence electron not being shared with in a covalent band covalent bond. So, it is an electron pair donor as just opposite to the Lewis acid, Lewis base is basically electron pair donor because they have as an extra pair of valence electrons not being shared in a covalent bond.

And most anions are Lewis base as you can see here this is basically a Lewis base which is donating an extra pair of atoms sorry extra pair of electrons to the Lewis acid. So, based on these we have you know there is a classification between Hard acid and Soft acid. So, what is the hard acid and soft acid based on the Lewis acid base complex, hard acid is the acceptor atom of high positive charge whereas soft acid is the acceptor atom is of low positive charge. In case of hard acid they will have small size, in case of soft acid they have large size, in case of hard acid they does not have any easily excited outer electrons.

However in case of soft acid they have several easily excited outer electrons. In case of hard acid they are not polarizable however in the case of soft acid they are polarizable. Hard acid prefers hard basis to ionic bonds and soft acid prefer soft basis through covalent bonds. So, this is how we differentiate hard acids, Lewis acid as well as soft Lewis acid.

Similarly there is some correct there is some characteristics of hard basis as well as the soft basis like the donor atom is low polarizability in case of hard base, in case of soft base the donor atom has the high polarizability. That in case of hard base this has the hard to reduce, in cases of soft base this is easily oxidized. So, these are some differential characteristics between the hard base and soft base.

So, based on this we can differentiate the Lewis acid and base into 3 categories each, in case of Lewis acid as you can see we can differentiate into you know Lewis acids are basically differentiate into hard acid, transition acids and soft acid. As you can see here in case of hard acid we we we turn them group 1 metals. Transition acids are known as group 2 metals and in case of soft acid there are known as group 3 metals.

So, one of the group 1 metals you can see H +, lithium, sodium, potassium, beryllium, magnesium, calcium then strontium then ferrous Al 3+ all these are hard acid. In case of in case of transition acid in case of group 2 metals basically chromium, manganese, Fe 2+, cobalt, nickel, copper. And in case of group 3 materials you can see silver then gold all these are coming under the group 3 metals.

Similarly in case of Lewis bases we can differentiate in their hard base, transition base and soft base. In the hard base you can see water, then hydroxyl, then fluoride all these ions phosphate, sulfate, chloride, carbonate most of the anions which are present in the salts are basically in the Lewis basis. And transition bases like bromide, then nitrite, nitrogen and then soft bases iodide, cyanide these are different categories.

So, you can see classification Lewis acids and Lewis bases, now some thumb rules are there based on these you know hardness and you know different different degrees of hardness and you know of the Lewis acids and Lewis base there are certain rules. For example hard cataions react to form ionic bonds that is hard cataions react to form ionic bonds in this group 1 we know that.

These are the hard acid like sodium, potassium, manganese, then sorry sodium, potassium, magnesium and calcium and soft cataions react to form covalent bonds in group 3, so basically copper, zinc, cadmium. And transition metals form complexes of intermediate state that is group 2 ok. So, these are some rules of based on these are some rules of complexation or based on the hardness characteristics of Lewis acids ok.

So, also the degree of hardness, the degree of hardness is given by a formula which is basically this z square by r where z is the charge of the cation and r is the radius of the cation. And the preference of hard metals for ligand atoms decreases in the order of these the the following order, so hard donor atoms and then the sub donor atoms ok. Then fluorine followed by oxygen, then nitrogen, chlorine followed by bromine, iodine and sulfur.

So, these are the hard donor atoms and these are the soft donor atoms. So the hard donor atom such as floor fluorine and oxygen prefers hard metal ions and the soft donor ions atoms like iodine and sulfur prefers soft metal ions. So, So far we are talking about different types of Lewis acids and Lewis base and their hardness classification and their complexation.

Now since we have discuss all these differentiation between the Lewis acids and Lewis base. Now it is time to apply those rules into the actual soil organic matter and metal chelates metal chelation process. So, we can see that the ligands, the complexants or ligands can be classified into 3 major big categories. One is the simple inorganic ligands which are denoted by capital X, they are the major anions which prefer hard metals obviously.

And hard sides of natural organic matter we call them NOM denotes by L H these are the hard sites and mainly carboxyl. And these are basically carboxyl and phenolic acid because they had the major you know they are the major complexant or ligand present in the soil organic matter, so they are known as a hard site. And also there also some soft sites, soft soil organic matter denoted as L s and they are basically nitrogen, sulfur containing sites. So, this is how the 3 different types of ligands are basically present in nature.

Now let us see how these different types of ligand basically interacts with different metals. So this picture shows or this chart basically shows you know these are the basically the simple ligands. As you can see these are the simple ligands as you know sulfates, carbonates, chlorides then fluoride, phosphate all these. So, group 1 metals like alkali and alkaline earth preferred hard ligands but form weak complexation with them, so this is thumb rule one of them rule.

So, hence complexation occurs when metal ligand concentration is high and predominantly complexant is inorganic ligand. So basically in case of alkali and alkaline material the you know the ligand is formed when the predominant complexant is inorganic which is denoted by this capital X. Now group 3 metals have greater affinity for soft sites than hard sites for simple ligands ok. So group 3 metals have high affinity for soft sites then for the hard sites we know that.

Now group 2 metals like divalent cations have affinity for both hard sites and soft sites. So these are the basically hard sites and these are the soft sites. In that the hard sites like you can see the carboxylic group, phenolic group and then this is nitrogen and sulfur groups and they react with all 3 types of ligand. So, the group 2 metals like divalent cations have affinity for both soft and hard sites and they react with all 3 different types of ligands all 3 different types of ligands.

And they compete for the hard sites with metals from group 1 and also compete for soft site with group 3 metals. So, this is how they can interact and form the ligands by competing with each other.

So, now we have seen the ligands we have seen the we have seen the basic concept of chelates. Now it is time to discuss the stability constant of metal humus complexes, this is very important this discussing the stability constant. Now the stability constant tells the affinity of a metal for organic ligand. So it determines the fate of the heavy metal in the environment.

If you know the stability is quite high it will persist if the stability is less then it will not persist in the environment. So, the complexation of the reaction between a metal and ith deprotonated ligand or binding site is generally given by this reaction where this m denotes the metal L I denotes the deprotonated ligand and these ML i basically the chelate compound.

So, the stability compound constant for this reaction can be given by this formula where this key i you know it is basically the stability constant which is a ratio between these chelate concentration as well as the concentration of the metal as well as the ligand. So, since it is difficult, now it is very difficult to calculate the concentration of this of this Li that means ligand.

So, basically a more realistic approach would be to calculate based on the concentration of all forms of ligand not bound to M. It is always better to calculate the all forms of ligand not bound to M then to calculate the ligand specific ligand by different empirical process obviously. Now so the the another approach where we are considering all forms of ligand not bound to M is basically in this case we are calculating another stability constant where MLi.

As you know the concentration of the ligand, M is the concentration of the material where H xi Li this term is basically the concentration of all forms of ligands not bound to M. So, we are seeing there are 2 types of you know stability constant ok, so 2 types of stability constant.

Now these 2 tables those 2 types of stability constant are basically referred as conditional stability constants. So, they are valid only for the condition like pH neutral salt concentration, remember that as the pH and you know salt concentration changes they are also variable. So, see and this basically stated for a particular system, so Ki you know this is the modified or the second stability conditional stability constant.

And the first conditional stability constant basically reload by related, so this is basically the second conditional probability conditional stability constant which is MLi by M concentration Li concentration ok and multiplied by Li and by HXi Li. So, we can see that this is basically we can simplify is that by Ki condi this first stability constant followed by multiplication of the concentration of the ligand by the concentration of the ligand not bound to a particular metal M.

So, these fraction these fraction is basically is a constant at constant pH and neutral salt concentration. Again there are 2 conditional stability constant, the first stability constant which we have calculated is this, the second stability conditional stability constant which we calculated is this. Remember for calculating the second conditional stability constant we considered the concentration of the ligand which had all the ligand which are not bound to M.

And then we can basically simplify these their relationship by using this formula, so basically the conditional stability constant the second conditional stability constant basically the multiplication of the first conditional probability constant multiplied by this fraction which is constant at pH and you know which is constant at a constant pH and neutral salt concentration.

Now since it is difficult to determine individual since I mean although we have simplified these but still it is very difficult to determine these individual stability conditional stability constant. So, basically for that we calculate the average by different empirical relationship empirical test, so let us see how we do that.

So, for that we calculate the average conditional stability constant. So, this is the first average conditional stability constant where this is the you know condition you know we have already know this the formulas of this is the conditi average conditional curve stability constant ok. Now if we simplify that it will take this form. So, basically we know that K conditional is if we see the key condition we know that it is basically the MLi by concentration of M and concentration of Li ok.

So, if we multiply it with basically Li in both denominator and numerator. So basically it will give us Ki condition and other ok. So basically we can simplify these as Ki condition and then we can get these 2 terms. So, basically you can see it is been simplified but you know when we are taking the you know taking the average based on getting this summation. So, basically then how this Ki condition came into this equation ok.

So, similarly in case of K dash condition also we can simplify it by this condition. Now we can further simplify it by C M - concentration of M where divided by concentration of M and then C L – C M and + M. So, basically here C M and C L are the stoichiometric concentration of metal and total ligand you know respectively. Now what is stoichiometric concentration. Stoichiometric concentration are basically the ratio of 2 reactants which are reacting together to form a compound, so this is a stoichiometric concentration.

So, ultimately since you know just like we have seen previously the in case of these average stability constant also we get this type of relationship. So 2 type 2 average stability constant also we can relate them each other by using this formula ok.

So, the stability constants of metal HS complex or humus complex are basically affected by 7 factors. First of all source of humus and extraction or isolation procedure employed then concentration of humus, then ionic strength of the solution, then temperature, pH, method of analysis of the complex and method of stability constant calculation. So, all these are different factors which can impact the you know the stability the stability constant of metal humus complexes.

And that order of stability constant for metal humus complex metal fulvic acid complexes was found you know following these order were followed you know iron followed by Al 3+ then copper 2+ then nickel, then cobalt, then lead, then calcium, zinc, manganese, magnesium. So they are following these stability constant ok in case of fulvic acid. So obviously iron fulvic acid complex will be more stable than that of magnesium fulvic acid complex.

So stability constant at higher at higher pH than 3.5 due to higher dissociation of functional groups. So obviously at pH increases we know that in case of organic matter more dissociation occurs, more dissociation occurs mean more step you know more complex formation when more complex formation obviously there will be get a stability. Also H+ ion compete for binding site on ligand at you know and hence less metal is bound to lower pH of 3.5 ok, so less metal is bound at lower p at lower pH of 3.5.

So, what is the practical implication of humus metal complexation and metal transport. So complexation of metal you know humus prove both beneficial as well as deleterious, so these we so the the there are some there are some beneficial implication. First of all humic acid reduces a more toxic form of metal, this humic acid reduces a more toxic form of metal that is chromium 6 to less toxics of chromium 3.

Then further chromium 3 being a Lewis acid forms a stable complex with carboxyl group of humic acid. So as a result it is availability to the plants and animal is limited ok, so as they are falling the forming the stable complexes with the carboxyl groups of humic acid. They are forming the stable complexes and they are available to the plants and elements is limited. However what are the negative effects, so humus serves as a carrier of toxic metals in water by forming stable complexes with them.

And the stable complexes of heavy metals are difficult to remove by precipitation because they are making the stable complexes, so they are not getting precipitated. So, these prove deleterious in water treatment scenarios, so you cannot defend you cannot strain out, you cannot get it precipitated to separate out. However the binding of this heavy metals to humus can enhance the biological treatment of the inorganic contaminants ok. So this is how they have both positive and negative effect.

Now in case of plant growth, in case of exchangeable aluminum, aluminum bound electro statically on soil colors such as soil organic matter and clay and they have very deleterious effects especially in acidic soil. And in acid soil when pH is less than 4 enhancing the surface of organic matter content can help in lowering the activity of exchangeable aluminum.

How if you see in this graph it is quite clear that it is showing the addition of organic matter as the reduction of aluminum concentration. And these increase in organic matter basically we can see in all this condition lowering the exchangeable aluminum concentration ok, lowering the exchangable aluminum concentration here. However this effect is higher at low pH condition, so, in this pH condition you can see there is a steep decrease as compared to the higher pH condition like 4.75.

And this effect and this is basically due to the complexation of soil organic matter with exchangeable aluminum thereby reducing it is activity. So, as we are increasing the as we are increasing the organic matter they are getting complex with aluminum and they are basically they are basically reducing the concentration of aluminum. In case of lower pH condition it is better because in case of lower pH condition the concentration of aluminum is higher than that of higher pH condition.

So, effects of humus on mineral dissolution obviously minerals are naturally occurring inorganic solids with a definite chemical composition and ordered internal structures. So, humic substance called dissolution of the minerals, the presence of microbes which produce organic complexity materials can enhance this and at pH greater than 6.5 humus sub attack and degrade the mineral form of water soluble and water insoluble mineral complexes.

Now also humus can extract mineral from galena, Pyrulosite, malachite different compounds and they also can extract mineral from silicates but a lesser degree. Humus also can solubilize various metals sulfides and carbonates ranging from 2100 microgram for lead sulfide and 95 microgram for zinc sulfide.

So, the next important thing is soil clear clay complexes as you can see this is showing how the soil organic matter helps for increasing the soil aggregation. As you can see these are the soil micro aggregates, these soil micro aggregates, how they you know different plant and fungal debris can improve these micro aggregates which are varying in different sizes and also you can see microbial hyphy mycorrhizal hyphyare there.

Then particulate organic matters colonized by saprophytic fungus are there and different clay you know these these are the clays microstructure. So as you can see based on these factors the soil aggregation is hugely depend on the clay organic matter complexation ok. Now one thing is important that 52 to 98% of the carbon of in soil occurs in soil occurs a soil organic matter K complexes and soil organic matter form complexes with clay coated with iron aluminum oxides.

And humus also coat the clay particles that the surface of such cold clay particles is still reactive. So, we can see that organic acids also get adsorbed in the intellect space of expendable clays like montmorillonite. We have already discussed that in the intellect space is quite high in case of montmorillonite. So, in this huge intellect space soil organic matter can enter and then get absorbed.

So, mechanisms of interaction between soil organic matter K complex is depends on physical adsorption 3 types of absorption is there. One is and this physical absorption can be caused by this van der waal force and this Vam der wall force you know it is the it is the you know when there is a the chance of caused by this physical adsorption caused by these Van der waal force and the chance that an electron in an atom.

So, if it is an atom and these electrons in this certain area the electron cloud, so electrons move, so electron cloud maybe in at a certain point of time here. So, electron charge density at the specific time the electron charge density must be here. And if all electrons at go to the same area at once a momentary electrical dipole as you can see it is the positive pole and there is a negative pole.

So, as a result of that you know momentary electrical dipole is created in both this condition you know dipole is created and these electrically negative fluctuation of 1 atom induces an electrically electrically positive fluctuation as you can see in the neighboring atom. So, this is the neighboring atom resulting in an attractive forces. So, due to the orientation of the electrons the momentary electric dipole which is created can produce the attraction between the adjacent neighboring atoms which is due to the then this is called the Van der Waal attraction.

Now another bonding is there that is called electrostatic bonding and polyvalent cataions like aluminum, iron, calcium present in clay surface acts as a bridge between the clay particles and the humus by these electrostatic bonding. And aluminum and iron cataions are primary bridge between the clay and humus we have already discussed this where a calcium is weakly held and easily can be displaced.

The third type of bonding is called the hydrogen bonding results from the linkage between 2 electronegative atoms through bonding with a single H + ion. Remember that the hydrogen bonding is weaker than ionic and covalent bond but stronger than Van der Waal forces ok. So, the last thing which we want to discuss is the retention of pesticides and other organic substances by humic substances.

Now pesticides always have a strong affinity for the soil organic matter. So soil organic matter is a very important component in pesticide retention and soil organic matter affects the bioactivity, persistent, biodegradability, leachability and volatility of the pesticide by their you know complexes with the pesticide. So, the pesticide quantity must be adjusted according to the soil organic matter content of the soil.

And pesticides are strongly retained in the internal voids of the humus molecule. They are also absorbed via ion exchange, protonation, hydrogen bonding, Van der Waal force, cation and water bridging and ligand exchange. And humic substances can also combine with non polar organic compounds via a partitioning mechanism.

So, fate of if you see the fate of pesticide bound to soil organic matter, soluble humic complexes can enhance the transport of pesticide in soil and into ground waters. And fulvic acid which have low molecular weight and a high you know acidities and are more soluble than humic acid can transport pesticides and other organic materials quick effectively. So, you can see how they are you know affecting the movement of the pesticide by their solubility by their solubility properties. And how they are import and how they are affecting the environment by producing these complexes with organic matter and pesticides.

So, friends this makes the you know these basically ends the whole module of chemistry of soil organic matter, we have discuss a lot from you know structure of organic matter. And then their carbon cycle then carbon sequestration then soil organic matter structure their humic fractions, their properties, their differences and also we have different we have seen you know different types of clay, humic complexes, metal humic complexes and humuses, humus pesticide interactions.

So, I hope that you have gathered some new information and these are the references environmental soil chemistry by Donald sparks. Then Aiken et al in 1985 they have you know humic substances in the soil sediments and water. And Buffle that is metal ions in biological system and also Buffle in 1994 that is general chemistry of aquatic systems which is present in chemicals and biological regulation aquatic systems.

So, these are the some of the references you can you can see also you can you can you can consult the nature and properties of soil by nyle c brady. So which also discussed the details about the different soil organic matter and their and their properties. So, thank you very much for listening this lecture and in the next lecture will be starting a new module and let us meet in our next module in week 4, thank you very much.