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Environmental Soil Chemistry
Prof. Somsubhra Chakraborty
Department of Agricultural and Food Engineering

Indian Institute of Technology - Kharagpur
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ION Exchange Processes (Contd.,)

Welcome friends to this third lecture of week 5 of this NPTEL online certification course of environmental soil chemistry and in this week we are discussing about the ion exchange processes in soil. So, before starting the new topic for this lecture, I will just like to review whatever we have covered in past 2 lectures in very briefly.

So, we have started with the definition of the ion exchange process and then we have talked about the what are the sources of cation exchange in soils as well as what are the sources of anion exchange in soils.

And from there we have defined the term ion exchange and we know that it is a basically, broad term which encompasses both cation exchange capacity and anion exchange capacity.

Then, we have seen these 2 pictures of 2 different soil; soil A and soil B differing in their cation exchange capacity based on the magnitude of negative charge generated on their surface; in the clay surface.

Then, we have start, we have focused on the cation exchange capacity and we have discussed about the, what are the units of the cation exchange capacity and how this cation exchange capacity can be an indicator of soil quality.

So, also we have discussed about the methods of determining the cation exchange capacity.

We have talked about the buffered method as well as the unbuffered method and remembered the buffer method always gives the exaggerated or potential cation exchange capacity whereas the effective cation exchange capacity can be measured using the unbuffered method.

Now, then we have talked about the distillation method of you know, of measuring the determining cation exchange capacity and then sodium saturation method.

We have talked about the briefly the principle of steps for determining the CEC in the laboratory and how we can calculate soil CEC from the lab data, there are 2 ways we can calculate based on the individual ion concentration or based on the displaced ammonium ion by using another you know, potassium containing solution.

And I have showed you how to calculate the cation exchange capacity based on the individual cations and how to convert the values into centimole charge per kg of soil.
And so these 2 methods we have discussed in our last lectures.

And I have also showed you the distillation method in the laboratory how we can do that and what are the reactions which are involved, remember in the distillation method basically, this is an using a you know buffer, it is kind of a buffer method where we are adding the neutral normal ammonium acetate solution into the soil which basically, replace, which dissociates to produce the ammonium ion.

These ammonium ion replaces the you know the adsorbed ion in the surface, in the soil surface and these ammonia get converted to; these ammonium ion get converted to the ammonia in the presence of magnesium oxides, so and these ammonia basically is absorbed in excess amount of acids and unreacted acid is basically measured by back titrated with the standard alkali.

Then, we have talked about the relationship between the pH and CEC, remember that CEC increases with the soil pH and the permanent charge of 2 is to 1 type of soil basically, and pH dependent charge of humus and allophane and some you know, 1 is to 1 type of clay whole exchangeable ions.

Then, we have talked about what are the major exchangeable cations in the field soils, we remember that calcium, magnesium, sodium dominate in the low rainfall areas or whereas the iron, aluminium and complex aluminium hydroxyl ions and H+ are more prominent in humid regions.

Then, I have showed you the table how this concentration of different pattern varies depending on different climatic regions.

And what is the implication of cation exchange and nutrient exchange, nutrient content of the soil, we have also discussed.

We have also discussed about the anion adsorption mechanisms, I showed you how anion, one anion can replace another anion reversibly in a soil collide.

Then we have talked about the characteristics of ion exchange you know, what are the selectivity, you know order of the selectivity of different cations for getting adsorbed on to the clay surface based on the hydrated radius and how you know, valency can be an important factor for selecting the particular cation and determining their affinity for adsorption onto the clay surface, we have also discussed, remember aluminium always shows the higher affinity than sodium.

Then, we have talked about the how you know, polarisation can also affect the cation exchange, we have discussed.

Now we have started with a cation exchange capacity based on the mineral structure, so we started with that and I showed you that kaolinite basically, you know external exchange sites are; in case of kaolinite, external exchange sites are present and rate of ion exchange is rapid and in case of 2 is to 1 type of clay minerals, we have also discussed.

So, I also showed you the how the CEC can vary from one soil to another soil, remember always soil humus has the highest cation exchange capacity followed by vermiculite, smectite and then you know kaolinite and iron aluminium oxides, whatever cation exchange capacity, you can see in iron aluminium oxides and 1 is to 1 type of clay like kaolinite is basically pH dependent charge, due to the pH dependent charge.

And then I showed you how addition of organic matter at different pH can increase the cation exchange capacity obviously, as you know we are adding that cation, you know organic matter increasing the pH, the ionization of the different you know, aromatic hydroxyl group as well as aromatic carboxylic groups are more as well and as a result there is more cation exchange capacity due to the more generation of negative charges.

Then, I showed you how the CEC of secondary soil mineral varies from one clay mineral to another clay mineral, in case of kaolinite, it is lowest, it is a talc, it is also very less and in case of trioctahedral vermiculite, highest current you know 100 to 200 centimole per kg.

Then, we have talked about why in case of kaolinite, the CEC is low now, in case of kaolinite, remember the negative charge generation is only pH dependent and only if the some few impunity are present, then only you can see some amount of negative charge generated in the clay mineral in kaolinite, which is around less than 2 centimole charge per kg, as pure kaolinite has very less isomorphic substitution and interlayer space is also very inaccessible due to the presence of strong hydrogen bonding between the adjacent layers.

And then I showed you the figure of kaolinite structure and you can see that there is a strong hydrogen bonding occurs in between these hydroxyl layer as well as the adjacent you know, oxygen atomic layer of these hydroxyl layer basically, comes from the aluminium octahedral sheet, whereas these oxygen plane basically represents the basal oxygen of silica tetrahedral layer. So, in between these, there is generation of the strong hydrogen bonding and as a result the d-axis spacing or interlayer space is very low.

So, as a result there is no space for adsorption of cations whatever cations can absorb in case of kaolinite, in the ages, they are basically you know adsorbed in the ages because of the negative charge generated due to the pH dependent charge.

Then, we talked about the vermiculite, remember vermiculite; dioctahedral vermiculite however, you know has more layer charge than smectite but it has less CEC due to the presence of K plus in the interlayer and the K plus is very, the potassium ion is very small ion which is snugly fitted in the interlayers and as compared to the dioctahedral vermiculite, the trioctahedral vermiculite has calcium and magnesium in the interlayers. So, more CEC than dioctahedral, as these ions have no restriction for the cation exchange.

So, dioctahedral vermiculite always shows higher CEC in the range of 100 to 200 you know, centimole charge per kg. So, in case of vermiculite, it has the highest cation exchange capacity of all clays, a less swelling capacity than smectite but more than that of kaolinite, obviously due to the high cation exchange capacity, it is nutrient rich and it is stable under low pH condition.

Now, in case of montmorillonite which has the higher CEC due to substantial isomorphic substitution and fully expanded neutral interlayers, there is more space for adsorption of cations. In case of mica, which is a potassium bearing minerals, they has, they have more layer charge than vermiculite but lower CEC due to the presence of potassium ions in the interlayer space.

This potassium ion in the interlayer space is basically snugly fitted, you can see here these 2 pictures; the first picture shows the dioctahedral mica which is Muscovite and the second one, the second picture is showing the trioctahedral mica which is basically dominate;

trioctahedral mica like phlogopite and in the both, in both cases the interlayer space is basically occupied by very small potassium ion.

And as a result of that, there is you can see here these purple colour balls are basically, these potassium ions which are very small and as a result the interlayer space is also very, very limited in both these 2 conditions and this is the result and as a result, the interlayer space which is available for cation exchange is almost negligible, so that is why in case of mica, the CEC is low due to the presence of these interlayer potassium.

So, if we go ahead and see the structure of illite, we know that it is a fine grained of mica, it is basically weathering product of mica, so in case of illite, the isomorphous substitution occurs in the tectahedral sheet and as a result of that, the negative ion; negative charge which is generated in this structure basically satisfied by these small potassium ion in the interlayer space, so again it is producing very cooler structure and so that is why, illite is a non-expanding type of mineral, non-expanding type 2 is to 1 type of mineral.

And as a result of that, the CEC also very limited in case of illite, so the potassium is tightly bound in between the 2 layers giving only d-axis spacing of 1 namometer or 10 angstrom, as a result of that you know there is very less space available for cation exchange.

So, if we move ahead and see the structure of the chlorite, you know that in the interlayer space, there is a presence of hydroxide, so due to the presence of this hydroxide sheet, now it could be either magnesium hydroxide, when it is magnesium hydroxide then we call it you know, brucite layer and when it is aluminium hydroxide we call it gibbsite layer. So, depending on whether brucite or gibbsite is present irrespective of the presence of these brucite and gibbsite, remember the interlayer space is totally collapsed.

Because the interlayer space is totally occupied by these hydroxy sheet and producing a locked structure, it is not a collapsed structure per se but it is the locked structure. As a result of the locked structure, there is no space available for external cations to occupy or getting adsorbed into the clay the surface. So, as a result of that the chlorite also, although in the chlorite there is isomorphous substitution as you can see in both tetrahedral sheet as well as you know, octahedral sheet. However, due to the locked structure because of these magnesium aluminium hydroxide sheet, they do not show any substantial cation exchange capacity.

So, we know about the 12 soil orders and based on the minerals which are dominate in different soil orders obviously, this different soil orders also show the variation in the cation exchange capacity because you know individual soil order is dominated by a specific type of mineral for example, vertisols; in case of vertisols, it is dominated by basically, smectite or montmorillonite. In case of oxisols, it is mainly dominated by the iron aluminium oxides.

So, so on in for different types of soil, the clay mineralogy varies and accordingly their CEC also varies, so as you can see here in this table I have given, I have shown here the common range of CEC in centimole charge per kg, in case of histosols varies from 110 to 170, in case of vertisol, it is 33 to 67, in case of andisol, volcanic origin you can see it is 13 to 49, spodosol 2 to 57, in case of mollisol high inorganic matter it is 12 to 36 and centimole charge per kg.

In case of inceptisols and entisols, it is 5 to 37 centimole charge per kg, in case of aridisols, occurring in the arid region, it varies from 7 to 29 centimole charge per kg, alfisols shows 4 to 26 centimole charge per kg, ultisols shows 3 to 15 centimole charge per kg and oxisols which are dominated by iron and aluminium shows 2 to 13 centimole charge per kg. So, you can see the variation of cation exchange capacity in different types of soil based on their composition.

In case of oxisol, it is lowest because presence of iron aluminium oxides which only show limited cation exchange capacity due to pH dependent charge that too in acidic soil condition, I am sorry, that too in alkaline soil condition because in alkaline soil condition, they developed negative charges in the edges and as a result of that, they produce the cation exchange capacity in the alkaline range.

However, in case of histosol, you see it is producing the highest, it is quite obvious because histosols are known to contain basically the (()) (16:38), which is basically organic matter, decomposed, undecomposed organic matter, so this histosols which contain huge amount of organic matter obviously, we will have highest CEC among all the soil orders okay.

So, based on that also, we can estimate the cation exchange capacity from mineralogy, let us see one example, so the dominant clay in mollisols are likely to be 2 is to 1 type of clay such as vermiculite and smectite, okay, so thus the average cation exchange capacity of the clays of these type you know basically to be about 100 centimole charge per kg per clay, so at pH 7, the CEC of organic matter is about 200 centimole charge per kg.

So, since 1 kg of this mollisol basically contains 0.20 kg that is 20% of clay and only 4% of organic matter, we can calculate the CEC associated with each of these sources. So, from the clays, you know in the mollisol, we know it is you know, if we have you know only 20% of clay, so from the clays in the mollisol, we should have 100 multiply by 0.2 that is 20 centimole charge.

In case of organic matter in this mollisol, we will have 0.04 multiplied by 200 centimole charge per kg, 8 mole centimole, 8 centimole charge. So, basically the total CEC of the mollisol will be 20 + 8 that is 28 centimole charge per kg of soil that is quite obvious, basically we had just multiplied it with the content, individual content and then we are basically summing their centimole of charge.

Now another problem could be assume that you know a soil contains 60% clay and 4% organic matter and the pH at the; pH of the soil is 4.2, so the acidic soil, so you also know that the CEC is around 5.8 centimole charge per kg, now you want to estimate the types of clay present in the soil, so obviously at pH 4.2, the CEC of the organic matter would be comparatively low about 100 centimole per kg because you know, in the acidic condition, the pH dependent charge basically generate positive; basically generate positive charge.

So, when there is a positive charge obviously, the cation exchange capacity will be less, so in the positive, in the pH of 4.2 that means in acidic condition, CEC generated by organic matter would be comparatively low, in generalities from 200 centimole charge per kg, however in case of acidic condition, you can see here it is only 100 centimole charge per kg of soil. So, therefore we estimate the CEC from organic matter in 1 kg of soil, so we can get 0.04 kg of organic matter.

Because 4% organic matter we know, and and from the 4% organic matter or 0.04 kg of organic matter, we will have a total 4 centimole charge which is; centimole of charge generated from this only 4% organic matter. Now, the remaining we know the total, you know, total CEC is 5.8, among this 5.8, 4 centimole charge is basically contributed by organic matter, so the remaining portion of the CEC will be contributed by the clay.

So, obviously what is the remaining portion, if we subtract 4 from 5.8 centimole charge, we will get 1.8 centimole charge, so this 1.8 centimole charge will be contributed by the soil, by the clay minerals which are present in that soil, okay. Now, since this 1.8 centimole charge per kg of soil is provided by 6; 0.60 kg of clay that is 60% of 1 kg of soil, we have already assume that, that it contain 60% clay.

So, if we assume that that 1 kg of soil contains 60% of the clay, then we can estimate what will be the CEC of the pure clay, so basically 1.8 centimole charge per kg and then we have to convert into 1 kg, so we will get 3 centimole charge per kg of clay, okay. So, if we get 1.8 centimole charge per 0.6 kg of clay, for 1 kg of clay, we will get 3 centimole charge. So, once we calculate these 3 centimole charge, then we have to tally with the you know, with the table.

And we can see that it could be either oxisols or it could be either ultisols okay, so basically you know in case of oxisol, it is very low, so we can assume that this soil may contain either oxisols or ultisols, so this is how we can calculate the cation exchange capacity and based on the calculation of the cation exchange capacity, we can infer which type of clay mineral or which type of you know soil order is basically present or in other words based on the CEC calculation, we can predict the soil order.

Now, let us discuss another important term, very important term, as far as the soil fertility is concerned, now that is called percent base saturation, in the short call we call it BS. Now, the percent base saturation is basically the percentage of CEC that is occupied by the basic cations, so what are the basic cations? So the basic cations are basically calcium, magnesium, sodium and potassium, so these 4 are the basic main basic cations which are present in the soil.

Now, basic cations are distinguished from the acid cations, H+ and Al^{3+}, now this proton and Al^{3+} are known as base acidic cations. So, why we call it acidic, why we call aluminium as an acidic cation because at an approximate soil pH of 5.4 or less, aluminium is present in a significant high concentration that hinders the growth of most plant species. So, when the soil contains huge amount of aluminium, it basically interferes with the root growth and it basically kills the plant.

So, that is why and this effect is more pronounced in acidic soil, so that is why Al^{3+} ion is considered as an acidic cation, so you know Al^{3+} present in significant high concentration hinders the growth of the most of the plant species and lowers the soil pH, the greater the amount of toxic Al^{3+} that means with the reduction of soil pH, the toxic, aluminium toxicity increases because the aluminium concentration increases.

Now, the soils with a high percent base saturation are generally more fertile because of 3 reasons; the first reason is they have little or no acidic cations, they have very little or no acid cations Al^{3+} that is toxic to the plant growth, so just opposite. When we see that a Al^{3+} is more you know, prevalent or dominant in the exchange complex, we cannot tell that it is high percent base saturated soil, in just opposite in case of aluminium 3+ is not present, then we can say that it has high percent base saturation.

So, obviously due to the absence of Al^{3+} ion, the deleterious effect of aluminium on plant growth is very limited, so that is why the higher the percent base saturation is obviously higher; denotes higher fertility. Now, soils with high percent base saturation have higher pH obviously because base saturation means basic cations are more, when there will be basic cations, the pH will be more.

Therefore, they are more buffered against the acidic cations from plant roots and soil process that acidify the soils, now you know that there are many processes which are growing in the; which are going in the soils and mediated by different microorganism, they are either chemical reaction, either biological reaction, so due to this biogeochemistry and all different types of dynamic reaction, there are some processes which basically produces, which are basically acid producing processes.

For example, nitrification; nitrification is a biological process but you know, the ultimate end product is basically, they are creating some acidic end product, similarly acid rain which is a chemical type of reaction, when all the different types of sulphur dioxide, carbon dioxide and nitrogen di oxide, they basically evolved from different industries or anthropogenic activity and then can go to the atmosphere and then mixed with the water vapour, they produce the acids; sulphuric acid, carbonic acid as well as you know nitric acids.

And they basically, return to the soil in the form of by mixing with the rain and these rain is known as acidic you know, acid rain and these acid rain is very deleterious, this is the one of the major factor of chemical weathering, so these acid rain also interferes with the growth of the plants. So, soils with high percent base saturation, they do not have; they do not produce the you know, in other words sorry, the soils with high percent base saturation, they have high pH, so they are very much buffered against this process which are producing the acidic you know, acidic byproducts in the soil for example, nitrification, acid rain.

And third point is they contain greater amount of the essential plant nutrients like potassium, calcium, magnesium for use by the plants, so this is the reason that is why you know the soils with high percent base saturation are generally more fertile than the soils with low percent base saturation, okay. So, let us wrap up here, in the next lecture we will talk more about the percent base saturation, how to calculate the percent base saturation.

Then, we will also see different numerical problems related to cation exchange capacity and also we will start different types of reactions, different types of selectivity coefficients given for cation exchange capacity or cation exchange reactions, thank you very much, let us meet on in the next lecture that is lecture 4 of week 5, thank you.