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Environmental Soil Chemistry
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Module - 05
Lecture – 22
ION Exchange Processes (Contd.,)

Welcome friends to this second lecture of Week 5 or Module 5. And in this module we are talking about the Ion Exchange Processes in soil and in the first lecture we have talked about what is ion exchange, capacity of soil and how this ion exchange capacity which is a broad term can be expressed as a summation of cation exchange capacity as well as an ion exchange capacity.

Then we defined what is cation exchange capacity and then what is anion exchange capacity. Remember the cation exchange capacity of a soil is basically the capacity of the soil to exchange the adsorbed cation from his surface to the cations which are present in the surrounding solution and anion exchange capacity is basically the opposite that is within the capability of exchanging the adsorbed anion to the surrounding anions in the soil solution.

So cation exchange capacity basically depends on different types of clay minerals as well as organic matter. The clay minerals which have more permanent charge or producing the negatively charge surface produces negatively charge surface, produces high cation exchange capacity. On the other hand, in 1 is to 1 type of clay mineral it shows variable charge, basically is responsible for the anion exchange capacity.

Amorphous minerals they also shows the variable charge; when they develop the negative charge due to the surrounding solution pH they contribute in cation exchange capacity and when they are positively charged they contribute into the anion exchange capacity.

Organic metal largely contributes into the cation exchange capacity because of the development of negative charge into the surface and this cation exchange capacity and anion exchange capacity are both important. Generally, the cation exchange capacity is higher in case of soil than anion exchange capacity. And cation exchange capacity and anion exchange capacity are both important for soil to maintain the soil fertility and because anion exchange capacity is also important for adsorbing the negatively charged anions which are response like sulfate, phosphate which are responsible for the plant growth.

Now we have also seen that cation exchange capacity in the laboratory can be measured by both buffered method and unbuffered method. In the buffered method it is somehow exaggerate because of; when we are trying this for a variable charge soils and in case of that type of soil where the pH is less than 7 or 8.2 then the CEC which we are getting is basically the maximum CEC or potential CEC which we are getting; we are not getting the effective CEC. For getting the effective CEC we have to go with the unbuffered method.

Now, I have also showed you, how we can measure or calculate the cation exchange capacity using the general step; using the general step, using the general process of ammonium saturation; using two different methods. In first methods, we have considered individual cations and from the individual cation concentration in the leached we have converted them into milligram per kg considering also the amount of soil which we have taken for leaching.

And once you have converted them into the milligram per kg of soil then we converted them into cent; then we have converted into centimol per kg of soil and after that we multiplied with a valency to convert it to centimol charge. So once we get the centimol charge of each and every cation, we basically took some of it and then we got the total CEC. Another method where we leach the adsorbed ammonium with the help of potassium then this ammonium concentration leached is measured.

And therefore they can be further converted into milligram per kg and then subsequently to the cmol charge per kg of soil. So these are the two methods which we generally use and in the laboratory we have also used the distillation method where ammonium acetate solution; neutral normal ammonium acetate is used to leach the; all the cations which are adsorbed and once we saturate the soil with ammonium.

Then we you know, we basically distill that ammonium and in the forms; in the form of ammonia gas in the presence of magnesium oxide or magnesia and these evolved ammonia can be you know, can be adsorbed with an excess acid and ultimately the unreacted acid can be measured by back titration with the standard alkali, from their we can calculate what is the amount of ammonia which has evolved and from there we can get the measure of the CEC.

Now the; in this lecture we will be talking about the relationship between pH and CEC and what is the you know; what are the characteristics ion exchange as far as the soil chemistry is concerned. Now pH and CEC generally we know that CEC increases with pH, obviously. That permanent charge of 2 is to 1 you know, the permanent charge of 2 is to 1, pH dependence charge of humus and allophone and some 1 is to 1 type of clay hold the exchangeable ions.

Now although the permanent charge does not depend upon the pH, the pH dependent charge depend upon the surrounding pH. So if you increase the pH of the surrounding solution the pH dependent charge develop negative charge and this negative charge attract more and more cations and this negative charge develop both in 1 is to 1 type of clay, amorphous clay minerals like allophone or it can be produced by humus because of the negative charge which is produced by humus are variable charge so ultimately these all are responsible for cation exchange capacity.

So as the pH is raised the negative charge and some 1 is to 1 type of silicate and allophones, humus and even iron aluminum oxide increases and CEC also increases. In alkaline condition CEC reflects the pH depended charge as well as the permanent ones. So in the alkaline condition when we are increasing the pH this CEC basically reflects the pH dependent charge as well as the permanent charge.

So that is why when you are using the buffered method in the alkaline condition it shows the potential or maximum CEC not the effective CEC because it measure the CEC which is responsible for the; which is responsible for permanent charge as well as the CEC which is generating from the variable charge surface.

Now exchangeable cations in the field soils: What are the exchangeable cations in the field soils? The exchangeable ions in soils depends upon the climatic condition. For example, if you consider iron aluminum, complex aluminum hydroxyl ions, and ion H + n, they are the most prominent cations in humid region where we see extensive leaching of the soil or weathering of the soil. So in the highly weathered soil and warm and humid climate you see the dominance of iron, aluminum, complex iron aluminum, complex aluminum hydroxyl ions and protons.

And in case of low rainfall areas or arid and semiarid region we will see the dominance of calcium, magnesium and sodium. So in a given soil the proportion of the cation exchange capacity, so in a given soil the proportion of the cation exchange capacity satisfy by a particular cation is termed as a saturation percentage for that cation. This is very important. Saturation, in other words, you know the saturation percentage of a cation is represented by the fraction of the cation exchange capacity which is explained by the particular cation.

So if 50% of the CEC satisfied by the calcium ions, the exchange complex is said to have a calcium saturation percentage of 50 and this terminology especially useful in identifying the relative proportion of sources of acidity and alkalinity in the soil solution. So this saturation percentage is very important and we will see another important term best saturation percentage in the coming lecture.

So before move ahead we can see this table and this table shows a very important trend. The cation exchange capacity properties typical for unamendment clay loam surface soils in difference climatic regions. So we can see here, here there are four different climatic condition Warm, humid climate region, Cool and humid region, Semiarid region and Arid region. So you can see exchangeable H+, Al $^{3+}$.

Percentage of CEC which is occupied by this exchangeable H+ and Al $^{3+}$ is highest in case of warm and humid climate and as you go from this warm and humid climate to acid; arid region we are getting further decrease. And in case of exchangeable calcium and magnesium, you know as we are going from the warm and humid climate to arid region we are getting a constant increase.

Exchangeable sodium, in case of warm, humid climate it is stress concentration; in case of cool, humid region it is only that is only 0.1%; in case of semiarid region we can get 4% and in case of acid region; in case of arid region we are getting 19%. So that basically again shows that how these you know, saturation percentage of different ions changes depending on the surrounding climatic condition.

So cation saturation and nutrient availability, you know that if the percent saturation of some ions are high than those ions will be easily and rapidly displaceable. So the; you know, obviously the percent saturation of some ions are high means they have higher cation exchange capacity so they will be readily, easily and readily displaceable. So influence of complementary cation, so the strength of adsorption of common cations are most soil colloids follows this particular order where Al 3+ which is greater than Ca^{2+} which is further greater than magnesium, potassium ammonium has similar acidity to the surface which is further greater than sodium.

So K+ can be easily replaced by aluminum ions in the acid soil and it will be available for the plants. So there is some nutrient antagonism. So there is some nutrient antagonism which is generally originating from this selective, you know affinity for; or you know, selective strength of absorption. So there are some nutrient antagonism, that in certain soil cause envision of uptake of certain nutrient by the plant.

For example, when there is a high potassium level it can limit the uptake of magnesium, okay. So that says even when the significant quantities of magnesium are present in the soil, so that shows the nutrient, you know antagonism. Because what is the reason behind that, you can see, magnesium have more affinity than that have potassium. So if the soil is saturated in his exchange compresses saturated by potassium ions.

If we add magnesium ions then the magnesium will replace the potassium and this potassium will although the potassium coming to the soil solution the magnesium will get adsorb into the surface slightly and as a result there will be you know, there will be nutrient antagonism. So high potassium levels in the soil solution limit the uptake of magnesium, because magnesium get adsorbed by replacing the potassium in the exchange complex.

Another important thing you can see here in this picture there are two different conditions, so the half circles, so this is basically colloidal surface and these are adsorbed cations and this is basically root exuding H+ ions to exchange with a cations on the colloids. And you can see the half circles are basically, so this is a half circle, this is a half circle, this is a half circle, this is a half circle, this is a half circle. So these half circles are loosely held with the soil.

And the root will take cation from the soil in exchange with the H+ ions so this H+ ions they replace with this Na and this potassium and so they basically make an exchange with this potassium; you know sodium and potassium. So in the left figure in this figure you can see, they loosely held sodium ion, so the sodium is loosely held will be easily taken up by the plant. So it can be easily taken up by the plant.

In the right figure the K^+ will be easily taken up by the plant and the K^+ will be comparatively more vulnerable to be replaced and send to the soil solution. So K+ will be more available for the plant uptake and leaching. What is the reason behind that? The reason is this sodium and potassium have very low affinity to be adsorbed into the exchange complex of a negatively charge colloid. As a result, they are easily amenable for replacement with H+ ion which is generating from the root exudates. Now as a result this potassium goes to this soil solution and then available for the plant to uptake them and for further leaching, okay.

So what is the anion adsorption mechanism? So the basic principles of anion exchange are similar to those of cation exchange. So the charges on the colloid are positive and the exchange among negatively charge cations. So you know, the positive charge associated with the surface of kaolinite, iron and aluminum oxides and allophone attract anions such as sulfate and nitrate. So here you can see that this is a colloid surface which is positively charge colloid, let us assume this is 1 is to 1 type of kaolinite which is attracts; which is attached with this nitrate anions.

So if we add this chloride then chloride will replace this nitrate, so this is an example of anion exchange reaction, so just as in the case of cation exchange equivalent quantities of nitrate and chloride add exchange in this condition, okay. So the reaction can be reversed and nutrient anions so released can be absorbed by the plants. So this nitrate which is released by this clay colloid can be further adsorbed by the plants.

So we know that cation-exchange capacity increases with the increasing pH, because when you increase the pH you know, the pH dependent charge produces the negative charge into the clay surface as a result it will attract further you know, more cations into the clay surface, so cation-exchange capacity will increase. Opposite trend can be found in case of anion exchange capacity.

Because as we increase the pH there will be generation of negative charge surface and negative charge surface will repeal the anions which are also negatively charged. As a result of that the anion exchange capacity will further go down. So with in case of pH the trend of CEC and AEC are basically just opposite to each other.

Now, let us see what are the characteristics of the ion exchange. So ion exchange involves the electrostatic interaction between a counter-ion in the boundary layer between the solution and a charged particle surface and counter-ions in a diffuse cloud around the charged particles. So obviously this ion exchange is basically the electrostatic interaction between a counter-ion, so let us consider it is a positively charged cations in the boundary layer between the solution and the charged particles obviously of the surface charge, of the particular surface and counter-ions in a diffuse cloud.

So whatever counter-ions which are absorbed into the surface of the negatively charged; colloid will be replaced by the same counter; by the counter-ions which are present in a diffuse layer. So if it is unusually very rapid and basically diffusion-controlled, reversible in nature and stoichiometric, and in most of the cases there is some selectivity of one ion over the another by the exchange surface obviously, just like in case of cation exchange capacity, anion exchange capacity also shows the selectivity among different anions.

So exchange is reversible, you know exchange reversibility is indicated when the exchange isotherm for the forward and backward exchange reaction basically coincide. And exchange irreversibility, exchange irreversibility or hysteresis is sometimes also observed. So these are some you know, these are some aberration, these are some special condition where we can see exchange irreversibility or hysteresis and you know, that has been attributed to the colloidal and these exchange irreversibility or hysteresis can be attributed to the colloid aggregation and the formation of the quasi-crystals in the soil.

Now we have discussed couple of times about the stoichiometry. However, let me again discuss stoichiometry. Stoichiometry here means that any ions, you know in the context of ion exchange stoichiometry means that any ion that leave the colloidal surface are replaced by an equivalent amount of other ions. Again any ion that leave the colloidal surface are replaced by an equivalent amount of other ions. This is a definition of stoichiometry as well as the ion exchange is concerned.

Now the electrostatic forces are involved in ion exchange. Coulomb’s law can be invoked to explain the selectivity of the preferences of the ion exchanger for one ion over another. Now for a given group of elements with the same valence, the ions with the smallest hydrated radius will be preferred. For the group 1, for example in case of group 1 minerals, elements the general order of selectivity will be caesium will have more affinity than rubidium than potassium than sodium than lithium than H+. Because in case of caesium the ions you know has the smallest hydrated radius.

As a result of that the; the thickness of; the thickness of the diffused layer also very less in case of caesium and there is the attraction is more in case of caesium than rubidium, potassium, sodium, lithium which have more hydrated radius. When there is a more hydrated radius the diffused layer thickness also increases. So if ions of different valences then higher the charge, ion will be preferred.

For example, Al^{3+} will have more affinity than calcium, magnesium and potassium and ammonium which is have further more affinity than the sodium. So here, sodium has the least affinity so that is why in the root example I showed you that sodium and potassium can be easily replaced by the H+ ions. However, this L^{3+} calcium has more affinity to the soil surface.

Now in examining the effect of valence on selectivity polarization is another important aspect. So if you consider, the polarization is basically is the distortion of the electron cloud about an anion by a cation. So here you can see this an idealized ion pair of the both positive ion and the negative ion, cation and anion with the similar size, almost similar size. So progressively you can see as you go in this direction progressively the size of the anions is getting lower.

So the smaller of hydrated radius of the cations, the greater is the polarization obviously you can see, as it is getting smaller there is more and more polarization and due to the distortion of the electron cloud about an anion by cation. So as we go from this idealized ion pair to mutually polarized ion pair to, to this polarized ion pair, so we can see the polarization increases. And the greater is the valence the greater is the polarizing power.

So as we; as we decrease the cation size the polarization increase and with the anions the larger they are the more easily they can be polarized. And also the greater is the valence the greater is the polarizing power. So this polarization has a very important effect on the ion exchange property.

Now selectivity sequence, or lyotropic series, for some of the common cations, follow this order, so we can see barium followed by led and strontium then calcium, nickel, cadmium, copper, cobol, zinc, magnesium, argentums, caesium, rubidium, potassium, ammonium, sodium and lithium. So lithium has the, you know least selectivity however, barium has the highest selectivity. So in case of clay minerals obviously kaolinite has the external exchange sites which are; that are present and rate of ion exchange is rapid. In case of 2:1 type of mineral contain both external and internal exchange sites, for example, vermiculite and in case of micas.

Now, if you consider CEC of different soils. Obviously, sandy soil has lower CEC but clay soil has high CEC values because sandy soil you know, the sands are electrically neutral they do not produce charge, as a result they are electrically neutral, as a result they are very low CEC. Iron aluminum oxides, in case of iron aluminum oxides kaolinite are having low CEC which is less than 10 centimol charge per kg.

In case of Mica and chlorites they have 10 to 40 centimol charge per kg. In case of smectite and vermiculites they are ranges from 80 to 180 centimol charge per kg. And humus is having the highest CEC that is greater than 250 centimol per; centimol charge per kg. So you can see that humus or organic matter shows couple of fold higher cation exchange capacity than the crystalline clay minerals, smectite and vermiculites shows the high cation exchange capacity.

However, iron aluminum oxides shows the low cation because generally they do not produce very high negative charge, there charge is pH dependent, Mica and chlorites produce also very low charge.

So at higher pH, the soil humus basically contributes more CEC to the soil with a constant amount of clay. Obviously, as the pH increases there will be more dissociation of the carboxyl group as well as the phenolic hydrox; the aromatic carbonyl group as well as phenolic group of the organic matter which will attract more cations so obviously that will increase the cation exchange capacity.

So higher pH will soil humus will contributes more CEC to the soil of the constant amount of clay because in case of clay the permanent charge does not vary with the surrounding pH. So at pH 4.5; 4 to 4.5 1 gram soil humus increases the CEC of 0.13 centimol charge per kg, however, at pH 5.5 to 5 it increases almost double that is 0.26 centimol charge per kg. So you can see here this is more clear in this graph where we are increasing the organic carbon in the x-axis and the cation exchange capacity.

So the two condition, when you are increasing the organic carbon concentration the cation exchange capacity increases and this increase is low in case of lower pH intermediate; this is for intermediate pH and this is for higher pH. More pH means more disassociation of the aromatic carbonyl group or phenolic groups and more disassociation of the groups means more negative charge, more negative charge means more attraction of the opposite counter charge or positive charge cation that means more CEC.

So this table basically shows the CEC of different secondary minerals, so you can see kaolinite has only 2 to 15 centimol per kg whereas as Halloysite has 10 to 40, Talc has less than 1, Montmorillonite 80 to 150, Dioctahedral vermiculite 10 to 150, Trioctahedral vermiculite 100 to 200, Muscovite 10 to 40, Biotie 10 to 40, Chlorite 10 to 40 and Allophane from 5 to 350. Now Allophane produce more you know, variable CEC because it does not have any specific crystalline structure.

Now in case of Kaolinite CEC of a secondary clay minerals, now in case of kaolinite, the CEC of a kaolinite varies depending on the imparity present in it. So if the imparity is present its CEC as low as less than; it shows the CEC of as low as less than 2 centimol per kg, as pure kaolinite has very less isomorphic substitution. So kaolinite does not have isomorphic substitution because there is no; as a result there is no negative charge development, only CEC can be shown when there is an imparity, so this, that CEC also varies that is less than 2 centimol per kg.

Negative charge resulting from surface functional edge groups such as aluminum hydroxide which are deprotonated with the neutral pH extracting solutions such as ammonium acidic cause unexpected variation in CEC measurement. Again, negative charge resulting from surface function edge group such as aluminum hydroxide which are deprotonated with the neutral pH extracting solution called unexpected variation in CEC measurement, obviously this variable charge surface when we add different solution the variable charge surface create different types of unexpected variation.

In case of Kaolinite we know that, this is the structure of the kaolinite and in the structure of the kaolinite it is, it can been shows that there is no, you know isomorphic substitution as a result there is no negative charge development. Here you can see this is 1 is to 1 type of layer where one silica octahedral sheet is attached to the one aluminum octahedral sheet by sharing the oxygens and the d-axis spacing is 0.74 nanometer.

And you can see one thing that due to the absents of isomorphic substitution there is no you know, permanent charge development, only the permanent charge develop in case of; I am sorry there is no permanent charge development only the CEC can be seen very low CEC can be seen around 2 centimol charge per kg when there is some imparity, when there is some imparity, when there is some imparity we can see some charge development.

In case of Vermiculite, Diotahedral vermiculite has more layer charge than smectites but less cation exchange capacity due to the presence of potassium ions in his layer. Remember that potassium, it has a smaller hydration radius and it swedes snuggly into the interlayer space, the attraction between the K+ and clay's interlayer surface is more, hence, it is less available to; for exchange.

And presence of aluminum hydroxide in interlayer also reduces the cation exchange capacity by blocking any exchange site such as in case of chloride. And trioctahedral vermiculite has calcium and magnesium in its interlayer. Hence, more CEC; in case of trioctahedral vermiculite we can see more CEC than dicotahedral vermiculite as this calcium and magnesium have no restriction for cation exchange.

So structure of vermiculite you know, the; it has the highest cation exchange capacity of clays. It has the lowest; less swelling capacity than smectites but more than that of kaolinite. It is nutrient rich because of high cation exchange capacity and it is stable under low pH condition. So guys you have seen something important information in this lecture we have discussed a practical implication of cation exchange capacity and its properties and how this cation exchange capacity and you know, cation exchange capacity shows different affinity for different; different ions and what are the reason for this variation in the affinity we have discussed.

And also depending on the structure of different clay minerals, how this cation exchange capacity varies we have seen. So I hope that you have; you have seen some useful information in this lecture. Let us meet in our third lecture of Week 5 to discuss different other aspects of ion exchange phenomena in soils.