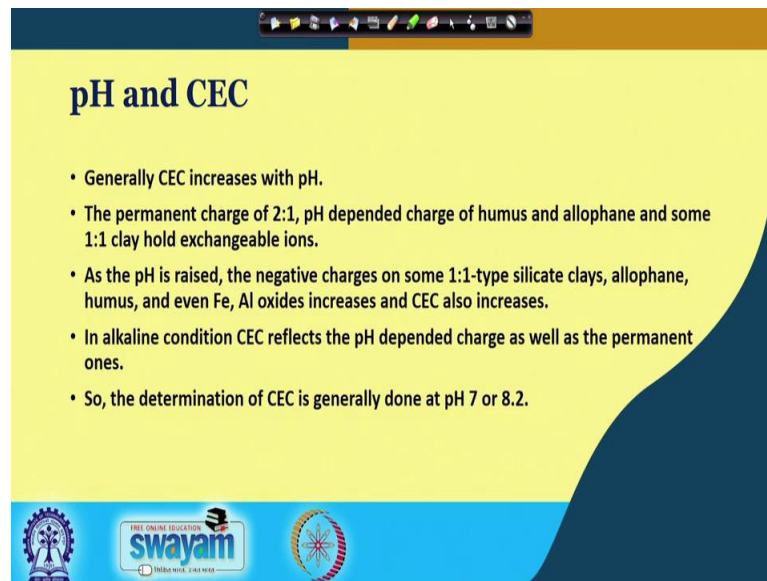


Soil Science and Technology
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Lecture – 25
Sorption of Pesticides

Welcome friends to this new lecture of Soil Science and Technology.

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pH and CEC

- Generally CEC increases with pH.
- The permanent charge of 2:1, pH depended charge of humus and allophane and some 1:1 clay hold exchangeable ions.
- As the pH is raised, the negative charges on some 1:1-type silicate clays, allophane, humus, and even Fe, Al oxides increases and CEC also increases.
- In alkaline condition CEC reflects the pH depended charge as well as the permanent ones.
- So, the determination of CEC is generally done at pH 7 or 8.2.

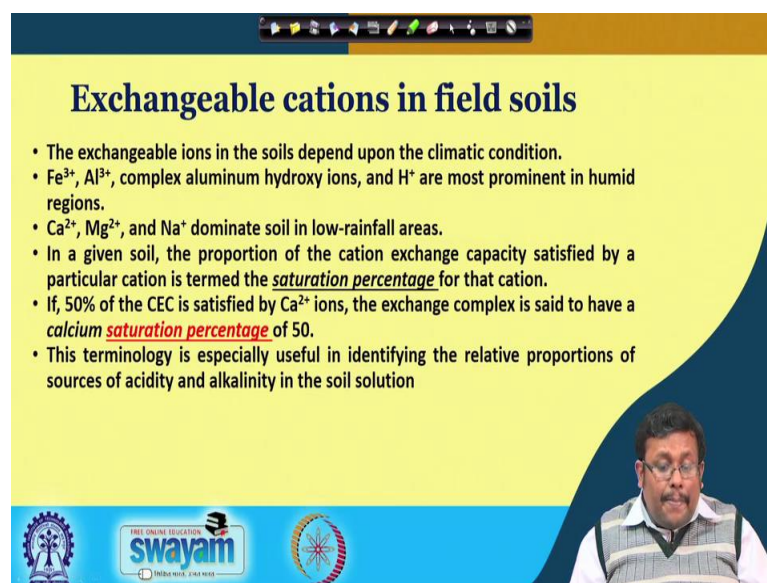
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And in this lecture, we will be trying to finish the cation exchange capacity and anion exchange capacity, where we left in the last lecture and then will be trying will be discussing about a new topic that the adsorption of pesticides. So, what is the relationship between pH and CEC? Obviously, generally CEC increases with the pH and the permanent charge of 2 is to 1 type of clay that is pH depended charge of humus and allophane and some 1 is to 1 type of clay hold exchangeable ions, you already know that.

So, as the pH is raised obviously, the negative charge on some 1 is to 1 type of silicate clays, allophane, humus or even iron aluminium oxide increases and CEC also increases. Because, if you remember the pH dependent charge, when we are increasing the pH that will basically create the negative charge. So, creation of the negative charge is basically, they increasing the CEC because, it is attracting the cations in the soil surface or clay surface. So, as the pH is raised obviously for 1 is to 1 type of clay allophane and even in iron aluminium oxide, there will be increase in CEC. And in alkaline condition CEC

reflects the pH dependent charge as well as the permanent charge because, you know that permanent charge is permanent. However in case alkaline condition just I told you, it will develop their negative charge that is pH dependent negative charge. So, ultimately it will be a total of both permanent charge as well as pH dependant charge. So, the determination of CEC is generally done at pH 7 and or 8.2.

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Exchangeable cations in field soils

- The exchangeable ions in the soils depend upon the climatic condition.
- Fe^{3+} , Al^{3+} , complex aluminum hydroxy ions, and H^+ are most prominent in humid regions.
- Ca^{2+} , Mg^{2+} , and Na^+ dominate soil in low-rainfall areas.
- In a given soil, the proportion of the cation exchange capacity satisfied by a particular cation is termed the saturation percentage for that cation.
- If, 50% of the CEC is satisfied by Ca^{2+} ions, the exchange complex is said to have a calcium saturation percentage of 50.
- This terminology is especially useful in identifying the relative proportions of sources of acidity and alkalinity in the soil solution

The slide features a video inset of a man with glasses and a striped shirt in the bottom right corner. At the bottom, there are logos for 'swayam' and 'Uthirakottai Engineering College'.

So, exchangeable cations in field soils, you know the exchangeable ions in the field soil depend upon the climatic condition. Obviously, the iron and aluminium and complex aluminium hydroxy ions and H plus are most prominent in humid region and calcium, magnesium, sodium dominate you know soil in low rainfall areas because, you know in case of highly leached areas. Obviously, in case of highly leached, warm and humid condition obviously, there will be formation of oxisols. Now why there will be formation of oxisol? Because there will be iron aluminium oxides dominance. So, you will see that in humid region specifically in the warm and humid region, there will be a predominance of iron aluminium ions.

However, in the low rainfall areas; obviously, in arid region, there will be predominance of different types of soils, because of high evaporative demand. And as a result of high evaporative demand, these soils will be much more, I would say dominated by calcium, magnesium and sodium ions. So, in a given soil the proportion of the cation exchange capacity satisfy by a particular cation is termed as a saturation percentage of the cation.

So, for example, if 50 percent of the CEC satisfy by calcium ions the exchange complex is said to have a calcium saturation percentage of 50. So, this terminology is especially useful in identifying the relative proportion of sources of acidity and alkalinity in the soil solution.

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Cation Exchange Properties Typical for Unamended Clay Loam Surface Soils in Different Climatic Regions

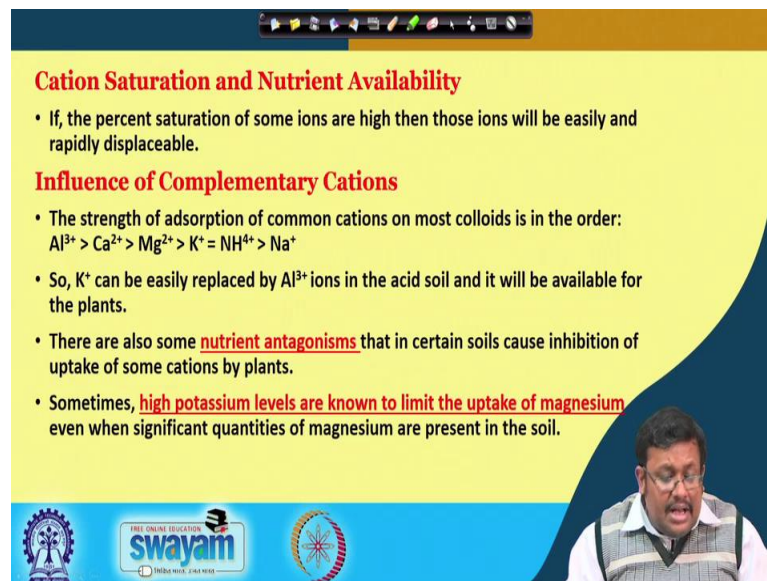
Property	Warm, humid region (Ultisols) ^a	Cool, humid region (Alfisols)	Semiarid region (Ustolls)	Arid region (Natragids) ^b
Exchangeable H ⁺ and Al ³⁺ , cmol _e /kg (% of CEC)	7.5 (75%)	5 (28%)	0 (0%)	0 (0%)
Exchangeable Ca ²⁺ , cmol _e /kg (% of CEC)	2.0 (20%)	9 (50%)	17 (65%)	13 (50%)
Exchangeable Mg ²⁺ , cmol _e /kg (% of CEC)	0.4 (4%)	3 (17%)	6 (23%)	5 (19%)
Exchangeable K ⁺ , cmol _e /kg (% of CEC)	0.1 (1%)	1 (5%)	2 (8%)	3 (12%)
Exchangeable Na ⁺ , cmol _e /kg (% of CEC)	Tr	0.02 (0.1%)	1 (4%)	5 (19%)
CEC, cmol _e /kg	10	18	26	26
Probable pH	4.5-5.0	5.0-5.5	7.0-8.0	8-10
Nonacid cations (% of CEC) ^d	25%	68%	100%	100%

So, cation exchange properties are typical for unamended clay loam surface soil in different climatic region. So, if we can see one interesting trend you can see, we are giving 4 different condition, one is warm and humid region that is represented by Ultisol, which is highly weathered one of the highly weathered soils, and then you know cool and humid region and then represented by Alfisols then semiarid region, you know which is denoted by Ustolls, and then arid region that is Natragids. So, you know if you see a trend the exchangeable H plus and Al³ plus will be continuously reducing from this warm humid region to cool humid to semiarid and arid region.

So, 7.5 percent 75 percent to 28 percent to 0 percent almost; and exchangeable calcium will show the reverse trend, I mean you can get 2 percent in the warm and humid region. However, we are getting 9 percent in cool even humid region, it is increasing to 17 percent in semiarid region and 13 percent in the arid region. And also exchangeable sodium, which is basically present in alkaline soil, which is another type of you know which has the high pH.

So, in these basically this alkaline soil and exchangeable sodium is present in a trace amount in case of warm and humid regions, it is very 0, it is very less 0.1 percent in Alfisol again, 4 percent in Ustolls and arid soil, which is dominated by different sodium salts, you will get almost 90 percent. So, you can see how these, dominance of different cations are changing for a particular type of soil, when it is you know for different climatic conditions. So, that shows the importance of climate for soil development as we have discussed in our earlier lectures of soil.

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Cation Saturation and Nutrient Availability

- If, the percent saturation of some ions are high then those ions will be easily and rapidly displaceable.

Influence of Complementary Cations

- The strength of adsorption of common cations on most colloids is in the order:
 $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$
- So, K^+ can be easily replaced by Al^{3+} ions in the acid soil and it will be available for the plants.
- There are also some **nutrient antagonisms** that in certain soils cause inhibition of uptake of some cations by plants.
- Sometimes, **high potassium levels are known to limit the uptake of magnesium** even when significant quantities of magnesium are present in the soil.

So, cation saturation and nutrient availability obviously if the percent saturation of some ions are high then those ions will be easily and rapidly displaceable; obviously. Now influences of complementary ions. Obviously, the strength of adsorption of common cations on most colloids is generally follow this order, what is the order? That is you know aluminium is strongly adsorbed followed by calcium then magnesium then potassium, which is showing the similar adsorption capacity and which is further you know further more than sodium.

So, potassium can be easily replaced by Al^{3+} ions in the acid soil and it will be available for the plants ok. So, in the acid soil aluminium will replace this potassium and this potassium will be available to the plants. So, there are some nutrient antagonism. So, this is another important aspect, there are some nutrient antagonism that in certain soil cause

inhibition of uptake of some cations by plants. For example, sometime high potassium levels are known to limit the uptake of magnesium.

So, that is means potassium and magnesium has a some nutrient antagonism even when significant quantities of magnesium are present into the soil. So, that shows the different interaction or influence of different complementary cations in the soil system.

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- The half circles are loosely held with soil.
- The root will take cations from the soil in exchange of H^+ .
- In the left figure, the loosely held Na^+ will be easily taken up by the plant.
- In the right figure, the K^+ will be easily taken up by the plant.
- The K^+ will be comparatively more vulnerable to be replaced and sent to the soil solution.
- K^+ will be more available for plant uptake and leaching.

Root exuding H^+ ions to exchange with cations on the colloid

Loosely held complementary ions with large oscillation zones

Tightly held complementary ions with small oscillation zones

Colloid

Colloid

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So, here you can have a better idea in this diagram. So, basically it is a soil colloid; basically in our case, that is clay and this is a root extending H^+ plus and to exchange cations on the colloid and in the cations in the colloid surface, you can see there are several types of cations like sodium and then potassium. And they are basically loosely held complimentary ions with large oscillations zones.

So, if we compare potassium and sodium, sodium has more large oscillation zones. So, this is called the oscillation zone and in this oscillation zone, you know they are loosely held this sodium. So, sodium is easily replaceable than that of potassium. So, root you know and in another condition. Obviously, this aluminium and potassium are present. However, this aluminium are more tightly held complimentary ions with small oscillation zone than that of potassium. So, in these 2 condition, you are seeing basically the difference in oscillation zones and ultimately, difference in their affinity to the clay colloid. So, the half circles are loosely held with the soil.

So, these are the half circles, which are basically loosely held with the soil and the root will take the cations from the soil in exchange with H plus ions. So, in the left figure the loosely held sodium plus will be easily taken up by the plant and in the right figure, the k plus will be easily taken up by the plant. And you know the k plus will be comparatively more vulnerable to be replaced and sent to the soil solution and k plus will be more available to the plant uptake and leaching. So, this is how the interaction or between complementary cations influence their uptake by different plants ok.

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Percent base saturation (BS)

- % of the CEC occupied by the basic cations Ca^{2+} , Mg^{2+} and K^+ . Basic cations are distinguished from the acid cations H^+ and Al^{3+} . At an approximate soil pH 5.4 or less, Al^{3+} is present in a significantly high concentration that hinders growth of most plant species, and the lower the soil pH, the greater the amount of toxic Al^{3+} . Therefore, soils with a high percent base saturation are generally more fertile because:
 - They have little or no acid cation Al^{3+} that is toxic to plant growth.
 - Soils with high percent base saturation have a higher pH; therefore, they are more buffered against acid cations from plant roots and soil processes that acidify the soil (nitrification, acid rain, etc.).
 - They contain greater amounts of the essential plant nutrient cations K^+ , Ca^{2+} and Mg^{2+} for use by plants.

So, this is now let us consider another important very very important topic, that is percent base saturation or BS. Now percent base saturation on the CEC occupied by it is basically, the percentage of CEC, which is occupied by the basic cations. So, we have calculated already the CEC. Now if you can calculate what is the percentage of the total CEC, which has been occupy, which is contributing, which we which is being contributed by the basic cations, that is calcium magnesium and potassium then we can calculate the percent base saturation.

So, basic cations are distinguished from the acid cations H plus and Al^{3+} plus. So, if we can distinguish basic cations will be calcium, magnesium and potassium whereas, acid cations will be aluminium and and H plus. So, at an approximately soil pH of 5.4 or less Al^{3+} plus is present in a significantly high concentration then that hinders the growth of

most of the plant species and the lower the soil pH, the greater the amount of toxic Al^3 plus.

So therefore, soil with high percent base saturation are generally more fertile, because when there will be high dominance will of Al^3 plus; obviously, that will create the nutrient toxicity or Al^3 or aluminium toxicity. So, we do not need that condition, we need a fertile soil. That means, that can support the plant growth that can give that can support the plant growth that can supply the required nutrient to the plant. So obviously, the soil with high percent base saturation will have more fertility and they have little or no acid cations Al^3 plus that in the toxic to the plant. So, you know this high you know percent base saturation soil, they have little or no acid cations like Al^3 plus that is toxic to the plant growth.

So, soil with high percent base saturation have a higher pH obviously. Therefore, they are more buffered against the acid cations from plant roots and soil processes that acidify the soil like nitrification, acid rain, etcetera we will discuss nitrification in our coming lectures. And also they can contain greater amounts of essential plant nutrients cation like potassium, calcium, magnesium for they use by the plants.

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Percent base saturation (BS)

- $\%BS = \frac{[(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+)]}{\text{CEC}} \times 100$

Depending on soil pH, the soil's base saturation may be a fraction of CEC or approximately equal to CEC. In general, if the soil pH is below 7, the base saturation is less than CEC. At pH 7 or higher, soil clay mineral and organic matter surfaces are occupied by basic cations, and thus, base saturation is equal to CEC.

http://extension.uga.edu

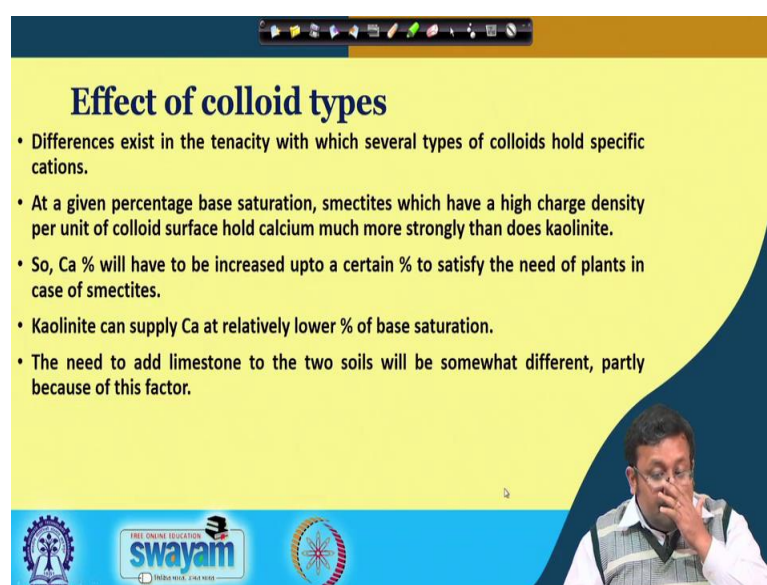
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So, these are very important what is the formula percent base saturation? The percent base saturation is basically, calcium plus magnesium plus potassium over total CEC

multiplied by 100. So, depending on soil pH the soil base saturation maybe a fraction this is very important.

So, depending on the soil pH the soil base saturation or percent base saturation maybe a fraction of CEC or approximately equal to the CEC. So, in general if the soil pH is below 7 the base saturation is less than CEC, because there must be some acidic cations; however, at pH 7 or higher soil clay mineral and organic matter surface are occupied by basic cations and thus base saturation will be equal to the CEC in that condition.

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Effect of colloid types

- Differences exist in the tenacity with which several types of colloids hold specific cations.
- At a given percentage base saturation, smectites which have a high charge density per unit of colloid surface hold calcium much more strongly than does kaolinite.
- So, Ca % will have to be increased upto a certain % to satisfy the need of plants in case of smectites.
- Kaolinite can supply Ca at relatively lower % of base saturation.
- The need to add limestone to the two soils will be somewhat different, partly because of this factor.

So, what are the effect of different colloid types? Difference exists in the tenacity with which several types of colloids will specific cations.

So, at a given percentage base saturation smectites, you know at given percent base saturation smectite, which have a high charge density per unit of colloid surface hold calcium more tightly or more strongly than that of kaolinite. So, calcium percentage will have to be increase up to a certain percentage to satisfy the need of plant in case of smectites and kaolinite can supply calcium at relatively lower percentage of base saturation, and obviously the need to add limestone to the 2 soils will be somewhat differently partly. Because of this factor we will discuss why we add limestone, in why when we will discuss the soil acidity.

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Anion exchange

- Anions are held in two major ways.
- Firstly, they are held by anion adsorption mechanisms similar to those responsible for cation exchange.
- Secondly, they may actually react with surface oxides or hydroxides, forming more definitive inner-sphere complexes.



Now, let us discuss anion exchange, anion exchange is also same anion it is basically, the ability of the soil to exchange anions from it is surrounding medium and anion held in 2 major ways. Firstly, they are held by anion adsorption mechanism similar to the responsible for similar, which are those responsible for cation exchange. Secondly, they may actually reactive surface oxides or hydroxides forming more definitive inner sphere complexes. Now in the last lectures, we have discussed, what are inner sphere, inner sphere complex and outer sphere complex. So, I am not going to discuss them in details.

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Anion adsorption mechanisms

- The basic principles of anion exchange are similar to those of cation exchange.
- The charges on the colloids are positive and the exchange is among negatively charged anions.
- The positive charges associated with the surfaces of kaolinite, iron and aluminum oxides, and allophane attract anions such as SO_4^{2-} and NO_3^- .

$$\begin{array}{c} \boxed{\text{Colloid}} \text{NO}_3^- + \text{Cl}^- \rightleftharpoons \boxed{\text{Colloid}} \text{Cl}^- + \text{NO}_3^- \\ \text{(positively charged soil solid)} \quad \text{(soil solution)} \quad \text{(positively charged soil solid)} \quad \text{(soil solution)} \end{array}$$

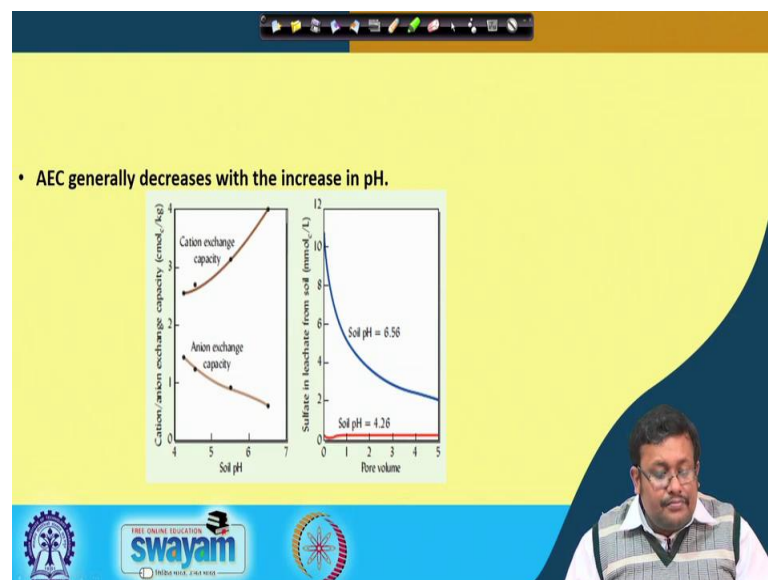
- Just as in cation exchange, *equivalent* quantities of NO_3^- and Cl^- are exchanged.
- The reaction can be reversed, and nutrient anions so released can be absorbed by plants



So, anion adsorption mechanism the basic principles of anion exchange are similar to those of cation exchange and the charge on the colloids are positive. And the exchange is among negatively charged anions, the positive charge develop due to the pH dependent charge you know that, and a positive charge is associated with the surface of kaolinite iron aluminium oxides and allophone, and attract anions such as sulphate and nitrate. You can see here you know the nitrate is first adsorbed to the soil colloid and which is at that getting replaced by another cation that is chlorite.

So, just in case of cation exchange equivalent quantities of ammonia, nitrate and chloride are exchange here. So, the reaction can be reversed and nutrient anions release can be absorbed by the plant.

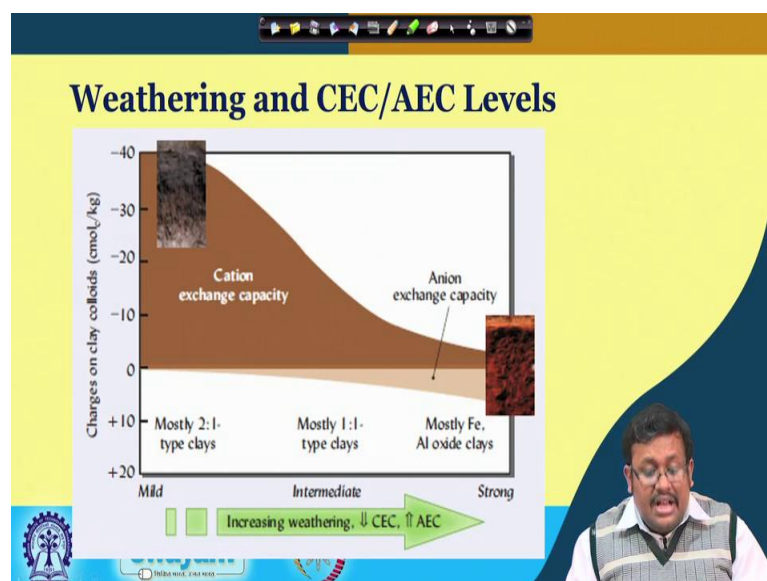
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So, AEC generally decreases with the increase pH. Obviously, when there will be increase pH, there will be negative charge development. So, when there will be negative charge development due to the pH dependant charge; obviously, the AEC or anion exchange capacity will increase. So, this is quiet you know with the increase of the , I am sorry with the increase of soil pH, there will be development of negative charge.

So, when there will be development of negative charge obviously, the anion exchange capacity will decrease and cation exchange capacity will increase because, it will attract more cation and it will repel more, you know anions and attract more cations. So, this graph basically shows that relationship.

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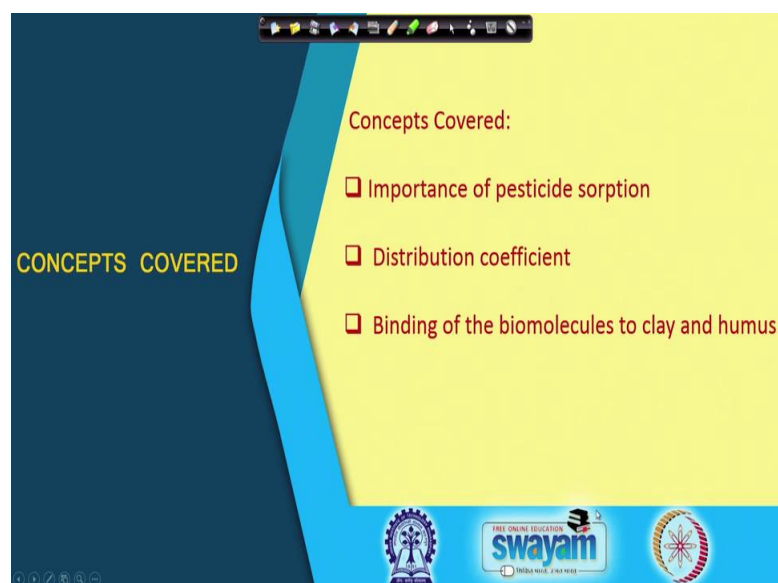


So, what is the relationship between weathering and CEC and AEC level? Obviously, you can see there are three different conditions mostly 2 is to 1 type of clays you know you can see here three different conditions. In the first condition is the mild weathering condition, there is a intermediate weathering condition and strong weathering condition, mild weathering condition obviously, 2 is to 1 type of clays intermediate weathering condition, 1 is to 1 type of clays and strong weathering condition mostly iron aluminium oxide clays, we have already discussed that.

So, increasing weathering is basically in this direction so and which we are an increasing the weathering obviously the cation exchange capacity will decrease. Obviously, you will see most cation exchange capacity in case of 2 is to 1 type of soil, which will further reduced to 1 is to 1 type of soil and it will reduce to almost 0. In case of iron aluminium oxides and in and for anion exchange capacity, we will see the reserve strength. So, as we are increasing from mild to intermediate to strong weathering condition, the anion exchange capacity will further increase ok.

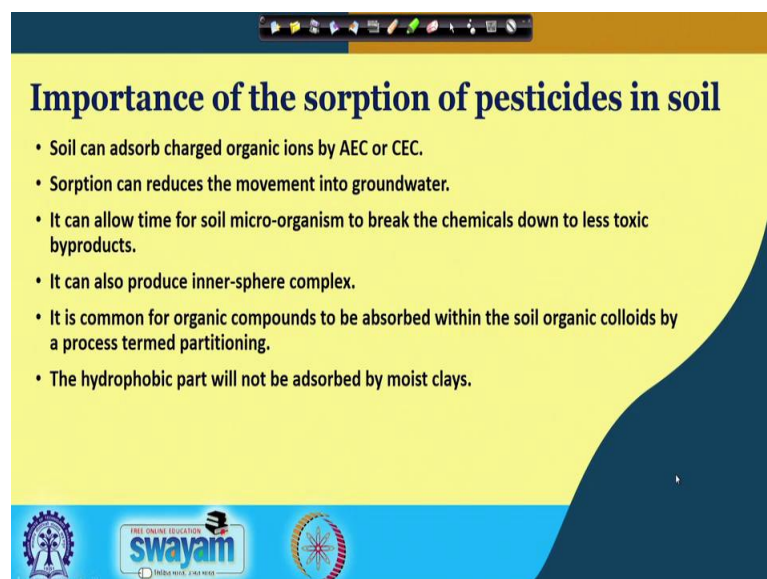
So, we have completed this cation exchange capacity topic, let us start another important topic that is sorption of pesticides in the soil.

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So, we will be covering the importance of pesticides sorption then distribution coefficient then binding of biomolecules and to clay and humus.

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So, importance of sorption of pesticides in soil, you know that soil can adsorb charged organic ions by either AEC or CEC because, either it is positive or negative depending on the positive and negative nature of the charged organic ions, it will be adsorbed and sorption can reduce the movement of the groundwater because, when it will be sorbed.

Obviously, it will not leach down to the ground water and it can allow time for soil microorganism to break the chemical down to less toxic byproducts.

So, when it will be adsorb by the clay colloids, it will be you know the chance of further leaching down to the ground water will be reduced. And there will therefore, it will get more time for the microorganism to degrade this, and also it can also produced inner sphere complexes. So, it is common for organic compounds to be absorbed within the soil organic colloids by a process called partitioning and the hydrophilic part will not be adsorbed by the moist clays.

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What is partitioning?

This method is often called "extraction." Extraction means drawing a compound out of a mixture using a solvent. Solvent partitioning is more specific. It means compounds have a "choice" of two solvents that they can dissolve in. Some compounds dissolve in one solvent. Some compounds dissolve in the other solvent. That way the compounds in the mixture become separated into two groups.

two compounds are dissolved in a solvent

a second solvent is added; it is immiscible in the first solvent

the solvents are mixed together

when the solvents separate again, the compounds go into one solvent or the other based on their polarity

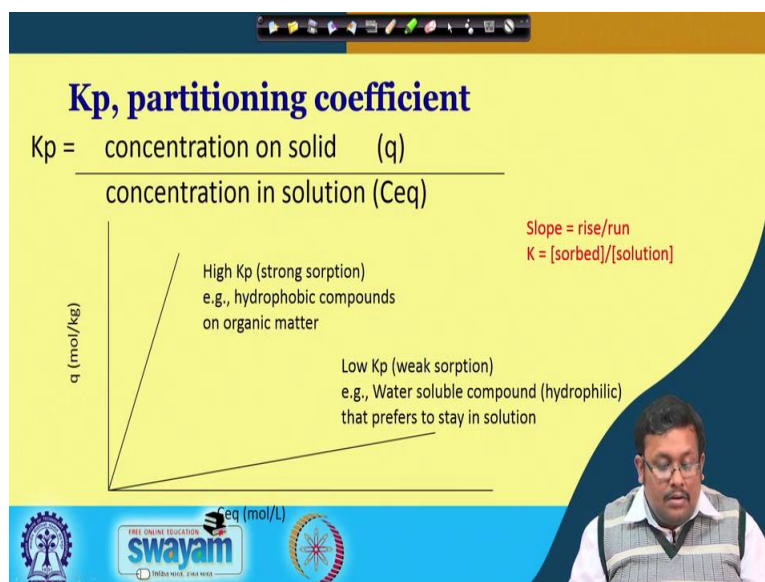
chem.libretexts.org

Now, what is partitioning? Now this is a very good picture of partitioning process. Now this method is also known as the extraction methods an extraction means drawing a compound out of a mixture using a solvent. So, solvent partitioning is you know we can we can call it solvent partitioning is more specific. So, it means compound of a choice of 2 solvents that they can dissolve in some compound, dissolve in one solvent, and some compound dissolve in the other solvent that way the compound in the mixture become separated in 2 groups.

So basically, you can see here in this first condition two compounds the dissolved in a some in a solvent and now we are adding a second solvent, which is denoted by this circles hollow circles. So, we are basically mixing the 2 different solvents as well as 2 compounds together in here. And finally, when the solvent separates again the

compounds go into 1 solvent on the other based on their polarity. So, based on their polarity, they will separate into 2 different solvent. So, this is called partitioning process ok. So, this is very important for pesticides option, how? We will see.

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So, this partitioning can be quantified using a partitioning coefficient or Kp, which is basically concentration on solid over concentration in the solution. So obviously, you can see there are this shows this graph shows the relationship between Ceq, which is equivalent concentration or per and concentration on solid. So, Ceq is basically concentration in solution and here it is q is basically, concentration on solid.

So basically, this line shows the higher Kp and this line shows the lower Kp. So, high Kp means higher sorption; obviously, and low Kp means weak options. So, high Kp means hydrophobic compounds on organic matter when hydrophobic compounds like the organic pollutants like organic pesticides, they are hydrophobic in nature. So, they will not you know they will not mix well with water. So, they will mix more with the you know organic matter into the soil and you know water soluble compounds, which are hydrophilic that prefers to stay in the solution will responsible for this low Kp.

So, let us move ahead and see what are the organoclays?

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Organoclays:

- The hydrated metal cations (e.g., Ca^{2+}) that are adsorbed on the surface of smectites can be replaced with large organic cations, giving rise to what are termed **organoclays** (**Smectites organoclay**).
- Such clay surfaces are more friendly toward applied organic compounds, making it possible for the clay to participate in partitioning.

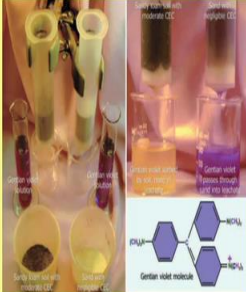


Now, organoclays is very important aspect, the hydrated metal cations like calcium that are adsorbed on the surface of the smectites can be replaced with large organic cations and giving rise to what we are termed as organoclays that is smectite organoclays specifically. Now, such clay surface are more friendly towards the applied organic compounds, making it possible for the clay to participate in partitioning. Obviously, when these clays are more friendly towards the applied organic cordon, you know compounds it will take part more into the portioning processes.

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Examples of Sorption

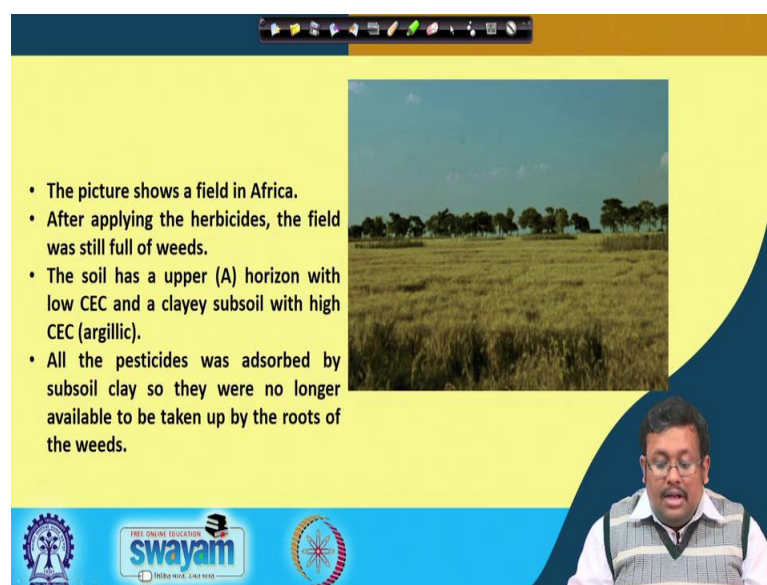
- The experiment was done by a gentian violet colour solution, sandy loam soil with moderate CEC and sandy soil with negligible CEC.
- After leaching, a clear solution was found in case of sandy loam soil.
- In contrast, the water drained from the sandy soil was still purple in colour.



So, let us see an example of sorption. So, this is a very good example of sorption process experiment. Now this experiment was done by a gentian violet colour solution and in a sandy loam soil with moderate CEC and it is sandy soil with negligible CEC. So, these are 2 you know different soil, which is sandy loam soil with moderate CEC and this is sandy soil with negligible CEC. So, after we leach these 2 soil with these gentian violet solution, a clear solution and we collect the leach it at below in a beaker.

So, after leaching we will see a clear solution was found in case of sandy loam soil and in contrast water drained from the sandy soil was still purple in colour in case of you know, in case of sandy soil with the lower CEC so that means, higher CEC or moderate CEC because, in the sandy loam soil there was some amount of silt or organic matter. However, in case of you know sandy soil; there is low amount of organic matter and due to the presence of organic matter. In case of sandy loam soil you know these organic matter will adsorb, all the gentian blue solution. So ultimately, it will you know the clear solution will leach. However, in the second case the total. So, there is no change. So, further the purple colour solution was leach down. So, that shows the import of sorption by different by organic matter which is present into the soil.

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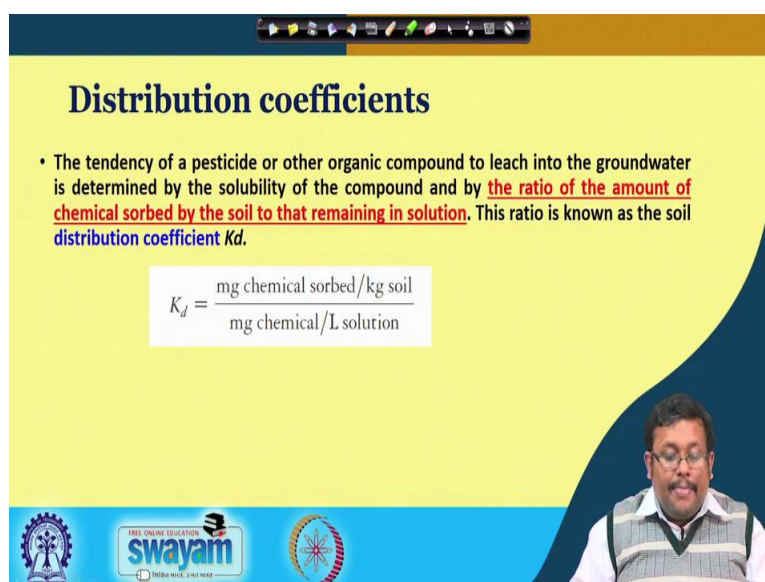
- The picture shows a field in Africa.
- After applying the herbicides, the field was still full of weeds.
- The soil has a upper (A) horizon with low CEC and a clayey subsoil with high CEC (argillic).
- All the pesticides was adsorbed by subsoil clay so they were no longer available to be taken up by the roots of the weeds.

Now, this is a picture of an African field and you can see after applying. So, in this field scientist are applied you know the farmers are applied herbicides and the field is still full of weeds, what is the reason behind this? There is a bizarre condition, where applying the

herbicides to kill the weeds, but we still finding that this is full of weeds. So, what happens the soil has a upper A horizon, you know what is A horizon with a low CEC and a clay subsoil with high CEC, argillic.

Now you know, what is argillic? Argillic is dominated by clay clay mineral. So, this soil have upper A horizon with low CEC and lower argillic horizon with high CEC. So, when they applied all the pesticide, all the pesticides was adsorbed by subsoil clay. So, that there is no longer available to be taken out by the roots of the weeds. So, as a result of that, weeds further grow. So, that also shows the importance of sorption of different organic pesticides by clay and different other component, which are present into the soil.

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Distribution coefficients

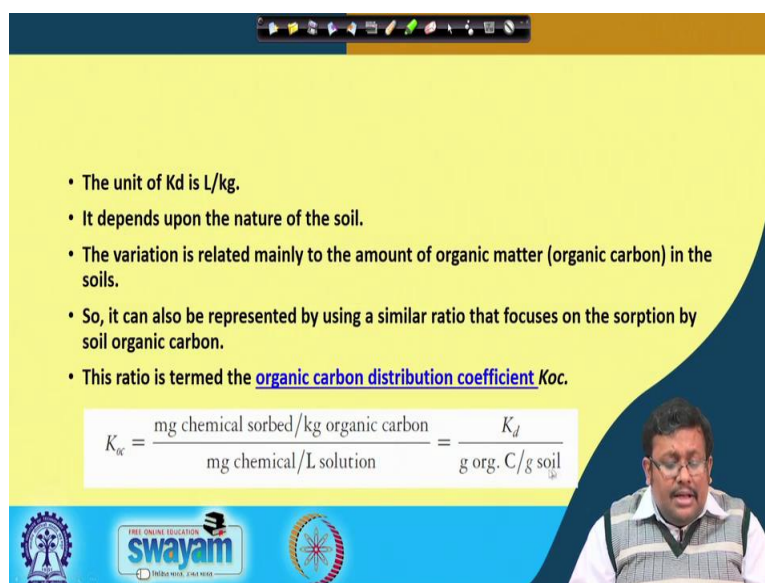
- The tendency of a pesticide or other organic compound to leach into the groundwater is determined by the solubility of the compound and by **the ratio of the amount of chemical sorbed by the soil to that remaining in solution**. This ratio is known as the soil distribution coefficient K_d .

$$K_d = \frac{\text{mg chemical sorbed/kg soil}}{\text{mg chemical/L solution}}$$

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Now, what is distribution coefficient? The tendency of a pesticide or other organic compound to leach into the groundwater is determined by the solubility of the compound. And by the ratio of amount of chemical solved by the soil to remain into the solution and this ratio is basically known as the distribution coefficient or K_d . So, K_d is basically, you know milligram of chemical sorbed per kg of soil over milligram of chemical per litre of soil solution.

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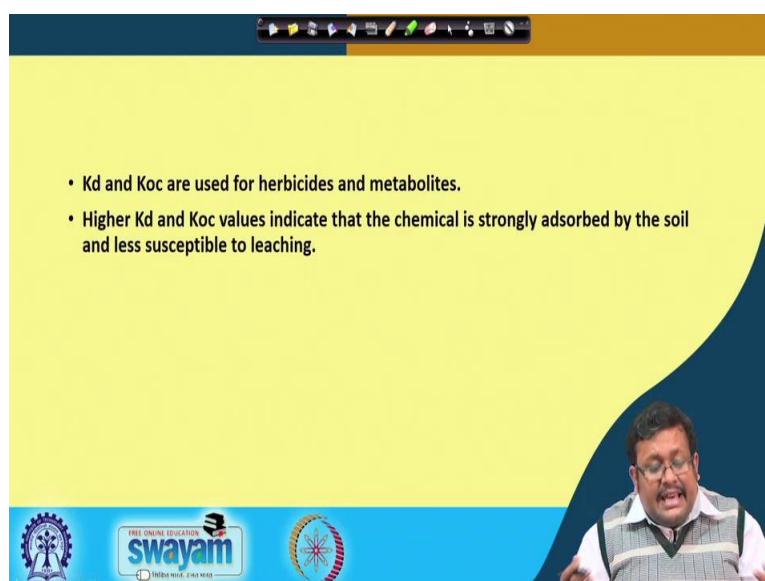
- The unit of K_d is L/kg.
- It depends upon the nature of the soil.
- The variation is related mainly to the amount of organic matter (organic carbon) in the soils.
- So, it can also be represented by using a similar ratio that focuses on the sorption by soil organic carbon.
- This ratio is termed the organic carbon distribution coefficient K_{oc} .

$$K_{oc} = \frac{\text{mg chemical sorbed/kg organic carbon}}{\text{mg chemical/L solution}} = \frac{K_d}{\text{g org. C/g soil}}$$

So, the unit of K_d obviously it is litre per kg and it depends upon the nature of the soil; obviously, the variation is related mainly to the amount of organic matter or organic carbon into the soil. So, it can also be represented by using a similar ratio, we call it K_{oc} or other name is organic carbon distribution coefficient. So, K_{oc} is basically, mg of chemical sorbed per kg of organic carbon and mg of chemical per litre of solution.

So basically, we are you know this is the formula of K_{oc} that is K_d over gram of organic carbon per kg of soil.

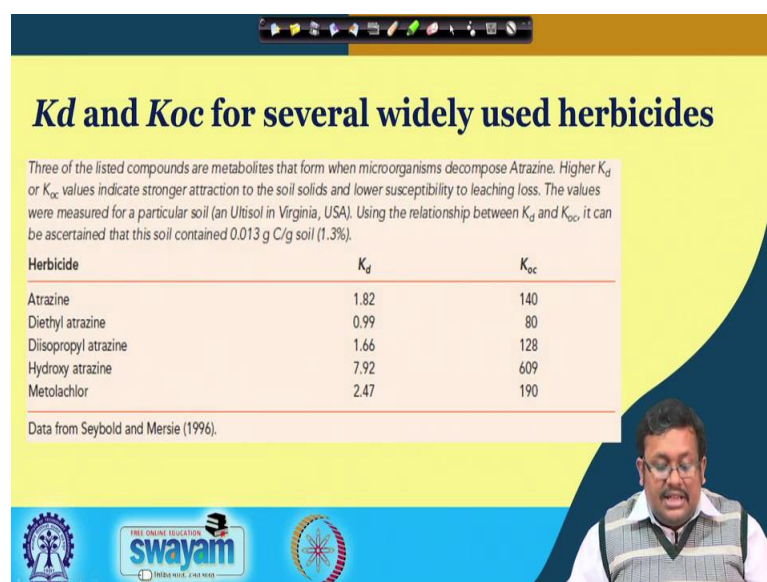
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- K_d and K_{oc} are used for herbicides and metabolites.
- Higher K_d and K_{oc} values indicate that the chemical is strongly adsorbed by the soil and less susceptible to leaching.

So, let us see K_d and K_{oc} are used for herbicides and metabolites, you know one soil which has higher K_d and K_{oc} values will absorb more pesticides obviously. And these high values indicates that chemicals are strongly adsorbed by the soil and less susceptible to leaching.

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K_d and K_{oc} for several widely used herbicides

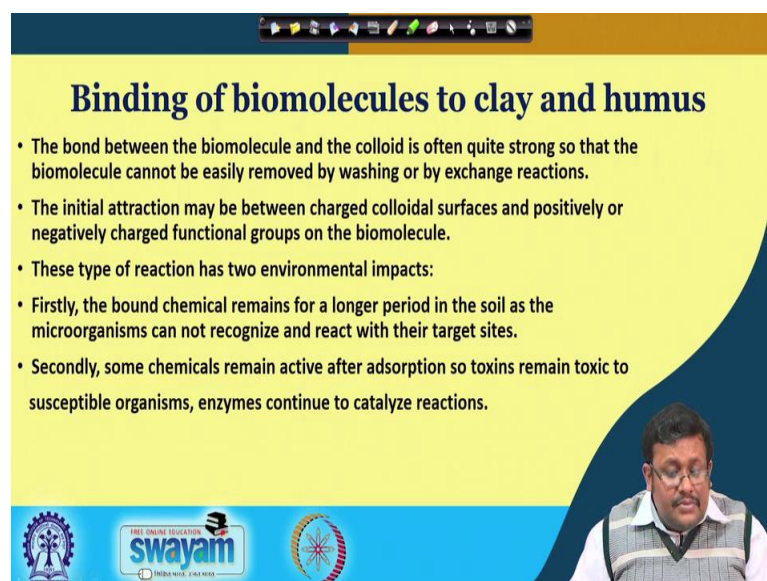
Three of the listed compounds are metabolites that form when microorganisms decompose Atrazine. Higher K_d or K_{oc} values indicate stronger attraction to the soil solids and lower susceptibility to leaching loss. The values were measured for a particular soil (an Ultisol in Virginia, USA). Using the relationship between K_d and K_{oc} , it can be ascertained that this soil contained 0.013 g C/g soil (1.3%).

Herbicide	K_d	K_{oc}
Atrazine	1.82	140
Diethyl atrazine	0.99	80
Diisopropyl atrazine	1.66	128
Hydroxy atrazine	7.92	609
Metolachlor	2.47	190

Data from Seybold and Mersie (1996).

So, these are some K_d and K_{oc} values for several widely used herbicides like atrazine, diethyl atrazine, metachlor, metolachlor. And all this thing, you can see what are the variation of their K_d and K_c values and these are the very important or the adsorption in the soil.

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Binding of biomolecules to clay and humus

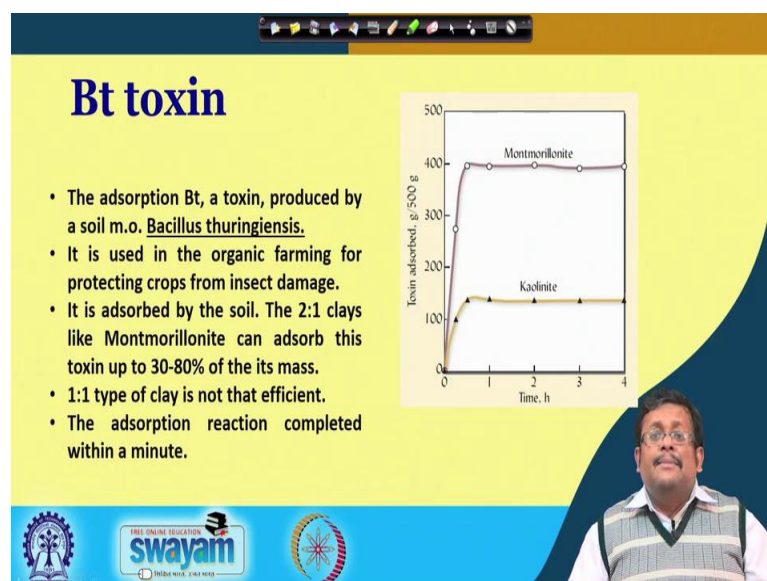
- The bond between the biomolecule and the colloid is often quite strong so that the biomolecule cannot be easily removed by washing or by exchange reactions.
- The initial attraction may be between charged colloidal surfaces and positively or negatively charged functional groups on the biomolecule.
- These type of reaction has two environmental impacts:
 - Firstly, the bound chemical remains for a longer period in the soil as the microorganisms can not recognize and react with their target sites.
 - Secondly, some chemicals remain active after adsorption so toxins remain toxic to susceptible organisms, enzymes continue to catalyze reactions.

The slide features a yellow background with a blue wave-like shape on the right. At the bottom, there is a blue banner with logos for 'swayam' and 'INDIA WISE'.

Now, binding of biomolecules and to clay and humus is very important. Now the bond between the biomolecules and the colloid is often quite strong. So, that the biomolecules cannot be easily removed by washing or exchange reactions and the initial attraction maybe between charge colloidal surface and positively or negatively charged functional groups on biomolecules and these type of reaction has 2 environmental impact, obviously the first the bound.

Firstly, the bound chemical remains for a long period of the long period longer period in the soil as the microorganism cannot recognize and react with their target sites. And secondly, some chemicals remain active after adsorption to so toxins remains toxic to the susceptible organism, enzyme continuous to catalyze the reactions. So, these are 2 types of impacts environmental impacts, you can get from this sorption of biomolecules, you know to the clay and humus.

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Let us see some example Bt toxin, you already know that.

Now, Bt toxin is basically a toxin produced by a soil micro organism called Bacillus thuringiensis, and basically it is used for organic farming for protecting crops from insect damage. So, it is adsorbed by soil. So, the 2 is to type of clay montmorillonite soil, you can see in this graph. Obviously, the 2 is to 1 type of soil like montmorillonite can adsorb the toxin up to 30 to 80 percent of it is mass. So, 1 is to 1 type of obviously it is not that efficient, because of low charge development. And obviously, the adsorption reaction completed within a minute, in case of montmorillonite.

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DNA

- Scanning electron micrographs (SEMs) of DNA from *Bacillus subtilis* bound on kaolinite clay (left) and on montmorillonite clay (right).
- The arrow point to stands of bound DNA.
- DNA bound to clay or humus is protected from decomposition but retains the capability of transferring genetic information to living cells.



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Second let us see DNA, now it this is a scanning electron micrographs or SEM image, SEM image of DNA from *Bacillus subtilis* bound on kaolinite clay, which is represented in the left picture or montmorillonite clay, which is shown in the right picture. So, the arrow point stands for basically, the stands bound to DNA stands of bound DNA. Now, DNA bound to clay or humus is protected from decomposition, but retains the capability of transferring genetic information to living soil.

So, this is implication of DNA sorption in the soil antibiotics.

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Antibiotics

- The antibiotics also adsorbed by soil colloids via the process CEC.
- It also has a very high K_d values.
- After sorption, it develops positively charged sites in the soil.
- Increasingly research shows that even though sorption to soil colloids may reduce their efficacy somewhat, the soil-bound antibiotics still work against bacteria.
- There is evidence that at least some antibiotics can be taken up from soil by food crops and so enter the human food supply.
- It will increase the resistant against the life saving drugs in the body.

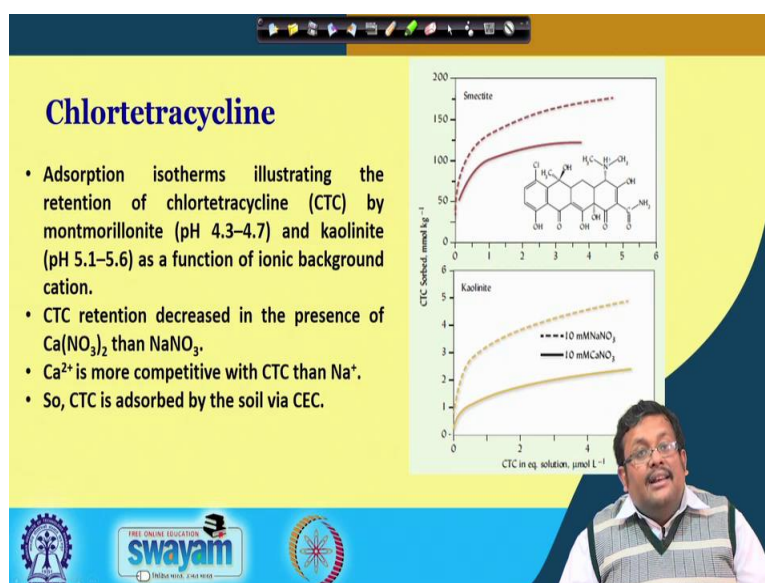


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So, antibiotics also adsorb by soil colloids by the process of CEC, it also has a very high K_d values, after sorption it develops positively charged sites in the soil. And increasingly research shows that even though sorption to soil colloids, may reduce their efficacy somewhat the soil bound antibiotics still works against bacteria and there is evidence that at least some antibiotics can be taken up from soil by food crops.

So, enter into the human food supply. So, it will increase the resistance against the life saving drugs into the body. So, this is the implication.

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And let us see one example of antibiotic, that is chlorotetracycline, it is the first antibiotic which has been you know developed. Now adsorption isotherms illustrates, the retention of chlorotetracycline or CTC by montmorillonite and kaolinite as a function of ionic background cation. So, you can see the montmorillonite or smectite. Obviously, montmorillonite is showing more you know adsorption you know more adsorption than that of kaolinite and calcium CTC retention decrease in the presence of calcium nitrate than that of sodium nitrate; obviously, because calcium is more competitive with CTC than sodium. So, CTC is adsorbed by the soil via CEC.

So, you can see in case of presence of sodium nitrate, the adsorption is higher. However, in case of presence of calcium nitrate the adsorption is somewhat lower because, calcium is more competitive with the CTC than sodium. So, these are some complex interaction between the different molecules, which is present into the soil, which we apply into the

soil and the components, which are already present into the soil and you know you can search some literature. Obviously, consult some literature to gain a in depth knowledge of these sorption characteristics. These are very interesting and I would suggest you to go and discuss and to consult some literature to gain more in depth knowledge of this sorption process, which will be giving you more practical perspective of learning soil science and technology.

Thank you guys we are completing this week 5 of lectures. So, we will be starting the week 6 of lectures from our next lecture. Hope you have understood and learnt something new in this week, we have discussed you know several important topics of soil chemistry, and we will be also discussing some other important topics of soil chemistry related to the soil silicate clays in the week 6.

Thank you, and let us meet and in our next weeks lecture. Bye.