Environmental Soil Chemistry
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Lecture – 50
Retention of Pollutants on and within the Soil Solid Phases (Contd.,)

Welcome friends to this fifth and last lecture of week 10 or module 10 that is retention of pollutants on or within the soil solid phase. So in our previous four lectures we have discussed several aspects of adsorption and in our last lecture we started with the non-adsorptive retention and while talking about the non-adsorptive retention we talk about the precipitation.

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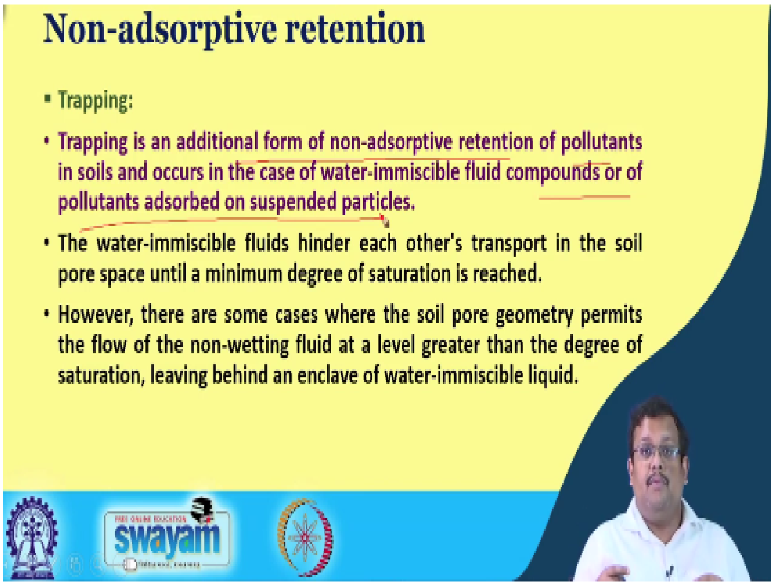

Non-adsorptive retention

- Trapping:
- Trapping is an additional form of non-adsorptive retention of pollutants in soils and occurs in the case of water-immiscible fluid compounds or of pollutants adsorbed on suspended particles.
- The water-immiscible fluids hinder each other's transport in the soil pore space until a minimum degree of saturation is reached.
- However, there are some cases where the soil pore geometry permits the flow of the non-wetting fluid at a level greater than the degree of saturation, leaving behind an enclave of water-immiscible liquid.

And today we are going to talk about the trapping and also we are going to talk about some of the examples of adsorption of pollutants on to the soil solid phase. So if we consider the trapping, trapping is an additional form of non-adsorptive. So trapping is basically an additional form of non-adsorptive retention of pollutants in soil and occurs in the case of water immiscible fluid compounds or of pollutants adsorbed on to suspended particles.

So obviously this trapping occurs it is basically non-adsorptive retention of pollutants in soils and it basically occurs in case of water immiscible fluid and when the pollutants are adsorbed on to the suspended particles. Now the water immiscible fluid hinder each other transport in the soil pore space until a minimum degree of saturation is reached. So, it requires a minimum degree of saturation to reach the water immiscible fluid inside the soil pore space.

So, however there are some cases where the soil pore geometry permits the flow of non wetting fluid at a level greater than the degree of saturation leaving behind an enclave or zone of water immiscible liquid. So as a result of this flow of this non wetting fluid at a level which is quite high, then you will see that there is a zone of water immiscible liquid which is trapped inside the soil pore space. So that is one example of trapping of organic pollutants within the soil.

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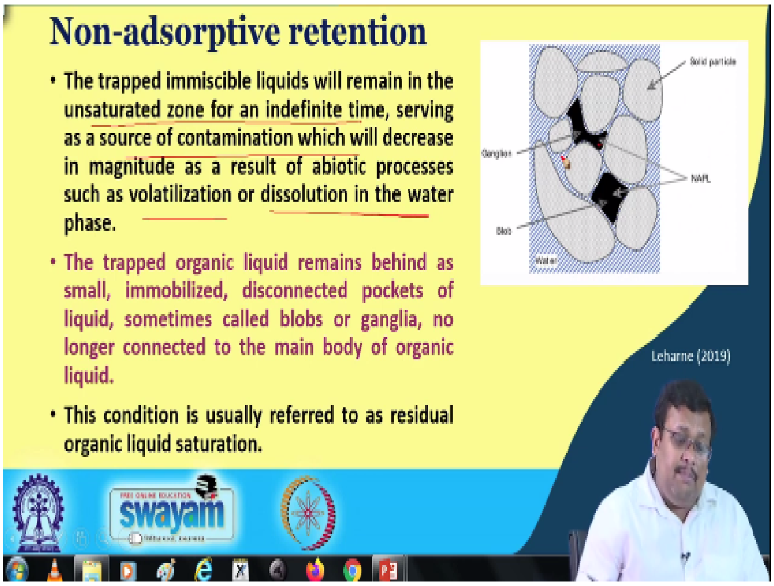

Non-adsorptive retention

- The trapped immiscible liquids will remain in the unsaturated zone for an indefinite time, serving as a source of contamination which will decrease in magnitude as a result of abiotic processes such as volatilization or dissolution in the water phase.
- The trapped organic liquid remains behind as small, immobilized, disconnected pockets of liquid, sometimes called blobs or ganglia, no longer connected to the main body of organic liquid.
- This condition is usually referred to as residual organic liquid saturation.

Leharne (2019)

Now this trapped immiscible liquid will remain in the unsaturated zone for an indefinite time and serving as a source of contamination which will decrease in magnitude as a result of abiotic process such as volatilization or dissolution in the water phase. So you can see that this trapped, for example, in this picture it is quite visible that these organic pollutants are trapped in between the, in the pore space.

And they will basically remain in this unsaturated zone for an indefinite time and serving as a source of contamination which will decrease in magnitude. So by residing in this pore space they will serve as a source of contamination which will decrease in magnitude as a result of abiotic processes. What are those abiotic processes, like volatilization then dissolution in the water phase, we all know that.

Now the trapped organic liquid remain behind which we are seeing here they have different names they are sometimes known as blobs, sometimes they are called as ganglia, okay. So they are basically remain there as a small immobilized, disconnected pockets of liquid, okay and no longer connected to the main body of the organic liquid. So you can see here they are disconnected, they are not connected to the main body of organic liquid.

And they remain there as a small immobilized and connected pocket. So the condition is usually referred to as a residual organic liquid saturation. So this is an example of trapping of organic liquid within the soil solid particle specifically inside the pores of the solid.

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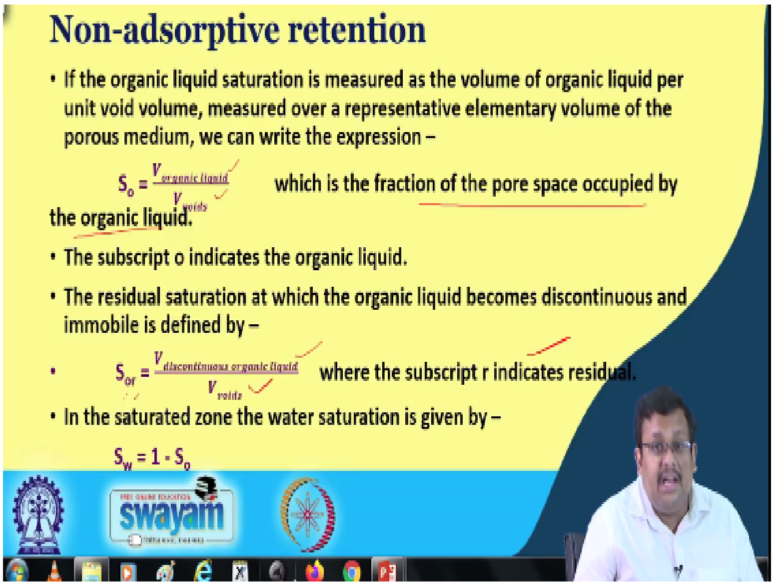

Non-adsorptive retention

- If the organic liquid saturation is measured as the volume of organic liquid per unit void volume, measured over a representative elementary volume of the porous medium, we can write the expression –

$S_o = \frac{V_{organic\ liquid}}{V_{voids}}$ which is the fraction of the pore space occupied by the organic liquid.

- The subscript o indicates the organic liquid.
- The residual saturation at which the organic liquid becomes discontinuous and immobile is defined by –
- $S_{or} = \frac{V_{discontinuous\ organic\ liquid}}{V_{voids}}$ where the subscript r indicates residual.
- In the saturated zone the water saturation is given by –

$S_w = 1 - S_o$

So, if the organic liquid saturation is measured as the volume of organic liquid per unit void volume, measured over a representative elementary volume of the porous medium then we get the following equation where S0 is basically the volume of organic liquid by volume of the voids which is the fraction. So basically this S0 is the fraction of the pore space occupied by the organic liquid where o stands for the, o indicates the organic liquid.

Now the residual saturation at which the organic liquid becomes discontinuous and immobile is defined by this equation where o stands for organic and r stands for residual which is basically again a ratio of volume of discontinuous organic fluid over the volume of the voids where the subscript r indicates the residual. So in the saturated zone the water saturation is given by this equation that is Sw = 1 minus So.

So this is how we can calculate the volume of the fraction of the pores which is occupied by the organic liquid and also residual saturation at which the organic liquid becomes discontinuous, okay. So these are some of the useful relationship.

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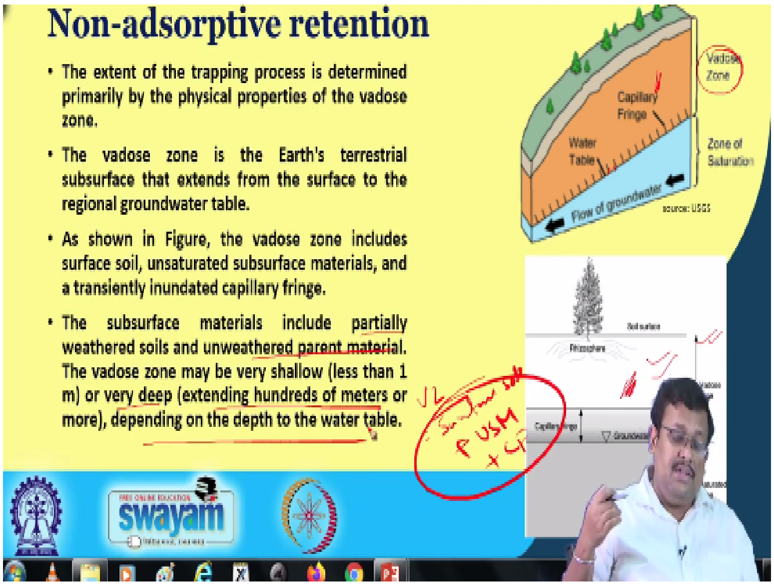

Non-adsorptive retention

- The extent of the trapping process is determined primarily by the physical properties of the vadose zone.
- The vadose zone is the Earth's terrestrial subsurface that extends from the surface to the regional groundwater table.
- As shown in Figure, the vadose zone includes surface soil, unsaturated subsurface materials, and a transiently inundated capillary fringe.
- The subsurface materials include partially weathered soils and unweathered parent material. The vadose zone may be very shallow (less than 1 m) or very deep (extending hundreds of meters or more), depending on the depth to the water table.

Now the extent of this trapping process is determined primarily by the physical properties of the vadose zone. So what is vadose zone? So you might ask me what is vadose zone? So vadose zone is basically the Earth's terrestrial subsurface that extends from the surface to the regional groundwater table. So let us consider this picture. So if this is a surface, soil surface and if this is a zone of saturation that means the regional groundwater level.

So the zone between the surface of the soil to the groundwater is known as the vadose zone, okay. So, so the vadose zone in the Earth terrestrial subsurface that extends from the surface to the regional groundwater table. So as shown in this another figure, the vadose zone includes the surface soil. So we can see it is the surface soil and then unsaturated subsurface material. So unsaturated subsurface material and also transiently inundated capillary fringe.

So here you can see a transiently inundated capillary fringe where there is a movement of water through capillarity. So this transient capillary fringe also included in the vadose zone. So, if we consider the vadose zone, it is basically the surface soil plus the unsaturated subsurface material plus the capillary fringe. So all these three constitutes the vadose zone so this is the vadose zone.

So the subsurface materials which are present here are basically consists of partially weathered soil and unweathered parent material and the vadose zone maybe very shallow which is sometime less than 1 meter or sometime which is very deep which is extending hundred of meters or more depending on the depth of the water table. So, if the depth of the water table is quite high then if the water table is extremely below the soil surface then the depth of the vadose zone is quite high if it is less, then the vadose zone is quite narrow or quite shallow.

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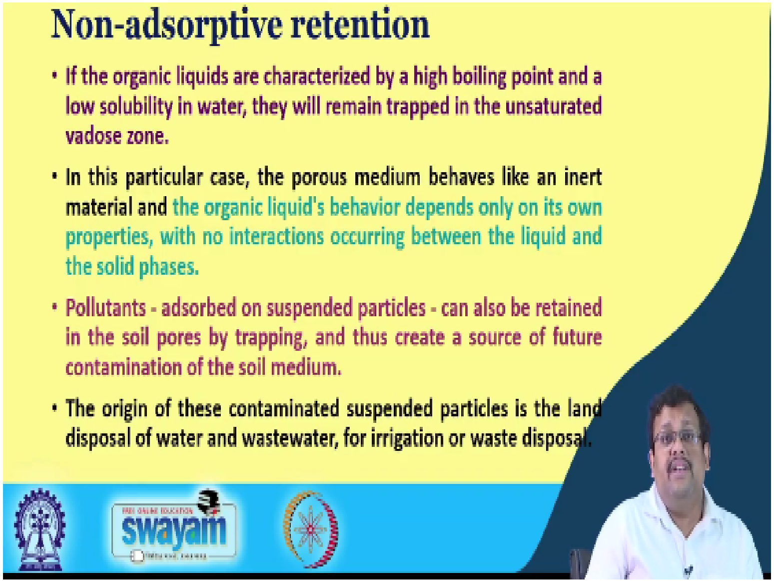

Non-adsorptive retention

- If the organic liquids are characterized by a high boiling point and a low solubility in water, they will remain trapped in the unsaturated vadose zone.
- In this particular case, the porous medium behaves like an inert material and the organic liquid's behavior depends only on its own properties, with no interactions occurring between the liquid and the solid phases.
- Pollutants - adsorbed on suspended particles - can also be retained in the soil pores by trapping, and thus create a source of future contamination of the soil medium.
- The origin of these contaminated suspended particles is the land disposal of water and wastewater, for irrigation or waste disposal.

So, if the organic liquid are characterized by the high boiling point and a low solubility in water they will remain trapped in the unsaturated vadose zone. Now in this particular case the porous medium behaves like an inert material and the organic liquids behavior depends only on its own properties with no interaction occurring between the liquid and the solid phase. So pollutants adsorbed on to the suspended particles.

So when the pollutants has adsorbed on to the suspended particles can also be retained in the soil pores by trapping and thus create a source of future contamination of the soil material. Now the origin of these contaminated suspended particles in the land disposal or water and wastewater for irrigation or waste disposal purposes. So this is how this vadose zone influence the non adsorptive retention of organic liquid.

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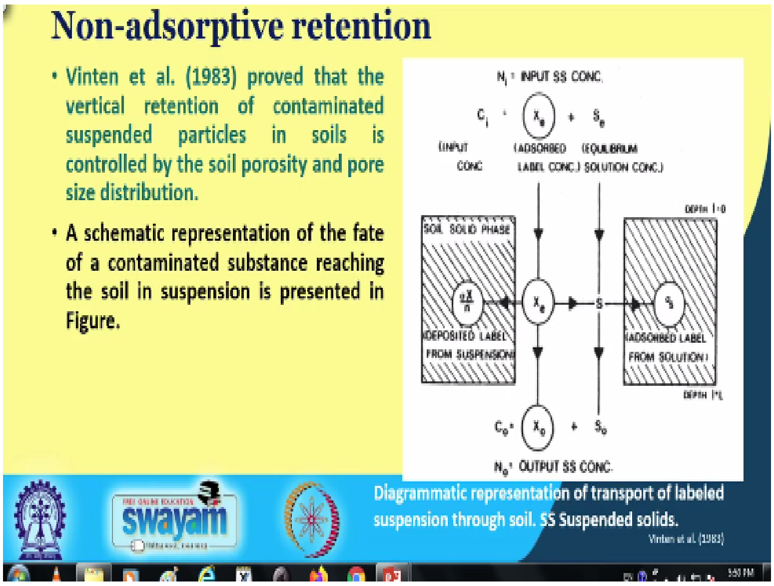

Non-adsorptive retention

- Vinten et al. (1983) proved that the vertical retention of contaminated suspended particles in soils is controlled by the soil porosity and pore size distribution.
- A schematic representation of the fate of a contaminated substance reaching the soil in suspension is presented in Figure.

Diagrammatic representation of transport of labeled suspension through soil. SS Suspended solids.

Vinten et al. (1983)

So another important relationship can be, process can be seen in this figure which this diagram given by the scientists Vinten et al and they prove that the vertical retention of contaminated suspended particles in soil is controlled by the soil porosity and pore size distribution how let us see. Now this is basically schematic representation of the fate of the contaminated substance reaching the soil in suspension.

So basically this is the soil solid phase and so there are two soil solid phase we can see here and this Se stands for the suspended solid. So here the input concentration is basically the adsorbed contaminant on to the suspended solid and also those which are in the solution phase, okay. So let us see how, what are the different types of processes occurs when the, you know, when the contaminated suspended particles are moved through the soil particle.

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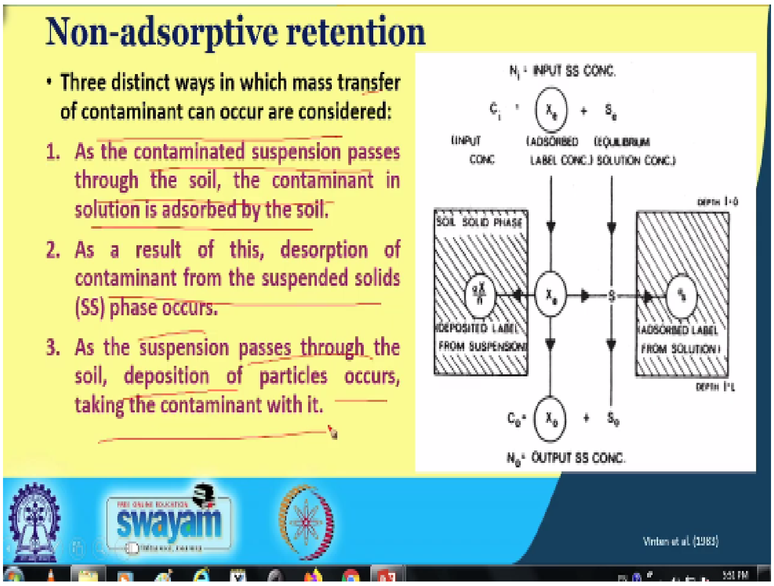

Non-adsorptive retention

- Three distinct ways in which mass transfer of contaminant can occur are considered:

1. As the contaminated suspension passes through the soil, the contaminant in solution is adsorbed by the soil.
2. As a result of this, desorption of contaminant from the suspended solids (SS) phase occurs.
3. As the suspension passes through the soil, deposition of particles occurs, taking the contaminant with it.

Vinten et al. (1983)

So three distinct ways in which mass transfer of contaminant can occur are basically considered in this diagram. One is, as the contaminated suspension passes through the soil the contaminant in the solution is adsorbed by the soil. We can see here this is adsorbed into the soil. As a result of this, desorption of contaminants from the suspended solid phase occurs, obviously.

When there is an adsorption of the contaminant from the suspended particles to the soil solid phase, obviously, that also show simultaneous desorption from the suspended solids. As the suspension passes through the soil, deposition of the particle occurs taking the contaminant within. So obviously, as the suspension passes through the soil also deposition of particles occur which takes the contaminants with it. So basically these three are the distinct ways through which the mass transfer of contaminants can occur within the soil solid phase.

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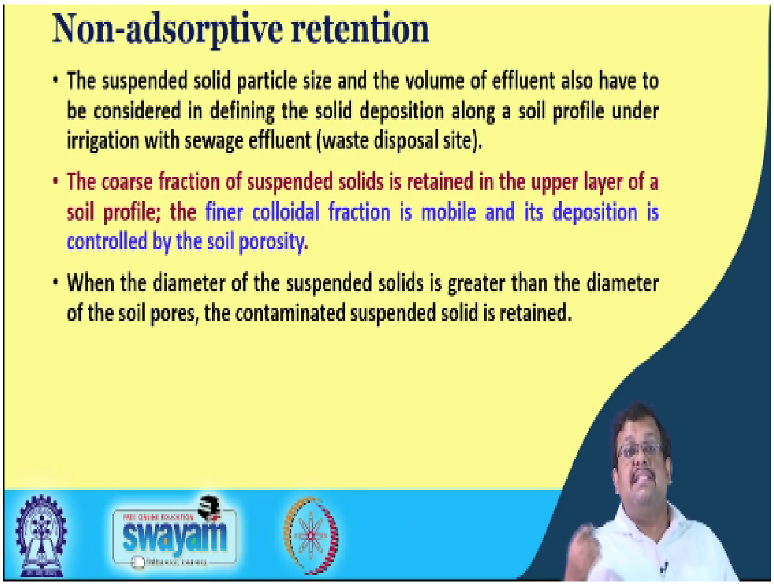

Non-adsorptive retention

- The suspended solid particle size and the volume of effluent also have to be considered in defining the solid deposition along a soil profile under irrigation with sewage effluent (waste disposal site).
- The coarse fraction of suspended solids is retained in the upper layer of a soil profile; the finer colloidal fraction is mobile and its deposition is controlled by the soil porosity.
- When the diameter of the suspended solids is greater than the diameter of the soil pores, the contaminated suspended solid is retained.

So, the suspended solid particle size and the volume of the effluent also have to be considered in defining the solid deposition along a soil profile under irrigation with sewage effluent especially in case of waste disposal site. Now the coarse fraction of the suspended solid is retained in the upper layer of the soil profile while the finer colloidal particles are more mobile and thus the deposition occur controlled by the soil porosity.

Now when the diameter of the suspended solids is greater than the diameter of the soil pores, the contaminated suspended solid is basically retained. Again when the diameter of the suspended solids is greater than the diameter of the soil pores, the contaminated suspended solids is retained within the soil it cannot move freely then.

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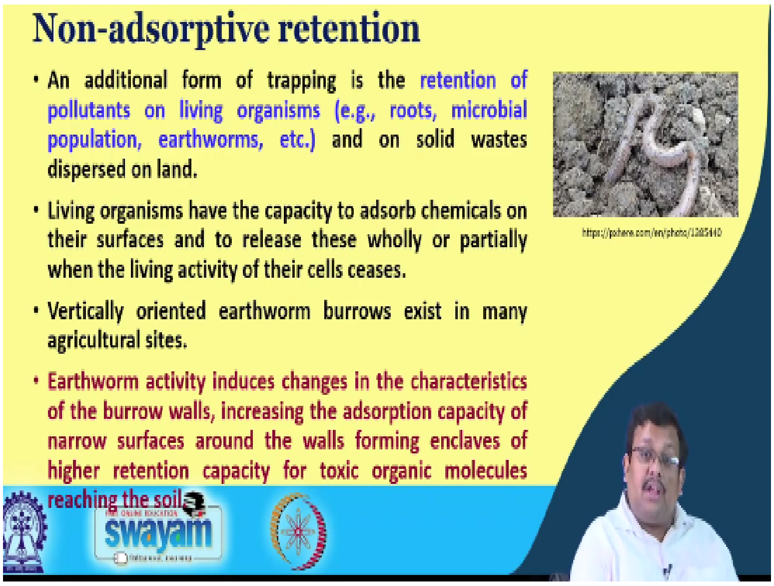

Non-adsorptive retention

- An additional form of trapping is the retention of pollutants on living organisms (e.g., roots, microbial population, earthworms, etc.) and on solid wastes dispersed on land.
- Living organisms have the capacity to adsorb chemicals on their surfaces and to release these wholly or partially when the living activity of their cells ceases.
- Vertically oriented earthworm burrows exist in many agricultural sites.
- Earthworm activity induces changes in the characteristics of the burrow walls, increasing the adsorption capacity of narrow surfaces around the walls forming enclaves of higher retention capacity for toxic organic molecules reaching the soil.

Also an additional form of trapping can be found in case of the retention of the pollutants on living organism. For example, roots, microbial pollutants, earthworm etcetera. As you can see here in this picture earthworm burrowing the soil and also on the solid waste dispersed on the land. So living organisms have the capacity to adsorb chemicals on their surface and to release this wholly or partially when the living activity of their cells ceases.

Now basically vertically oriented earthworm burrows exist in many agricultural sites, so we have seen that the earthworm burrows in the soil. Now earthworm activity induces changes in the characteristics of the burrow walls increasing the adsorption capacity of the narrow surface around the walls forming enclave of higher retention capacity of toxic organic molecules.

So when the earthworm activity digs the soil and basically burrows this wall increasing the adsorption capacity of the narrow surface wall which basically access as site for higher retention of this toxic organic pollutant. So this is how the non adsorptive retention occurs due to the action of different organism which are present in the soil.

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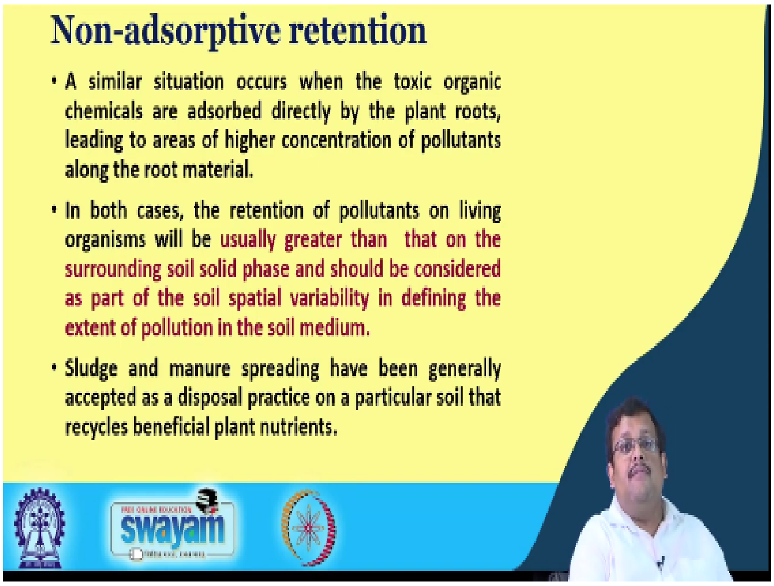

Non-adsorptive retention

- A similar situation occurs when the toxic organic chemicals are adsorbed directly by the plant roots, leading to areas of higher concentration of pollutants along the root material.
- In both cases, the retention of pollutants on living organisms will be usually greater than that on the surrounding soil solid phase and should be considered as part of the soil spatial variability in defining the extent of pollution in the soil medium.
- Sludge and manure spreading have been generally accepted as a disposal practice on a particular soil that recycles beneficial plant nutrients.

Now a similar situation occurs when the toxic organic chemicals are adsorbed directly by the plant roots leading to areas of high concentration of pollutants along the root material. Now in both the cases, the retention of pollutants on living organism will be usually greater than that of the surrounding soil solid phase and should be considered as a part of the soil spatial variability obviously as a result of this spatial variability in both these cases, retention of the pollutants are usually higher than that of surrounding solid phases.

Now also sludge and manure spreading have been greatly accepted as a disposal practice on a particular soil that recycles beneficial plant nutrients. So this is how these different types of organisms can influence the non adsorptive retention of toxic organic pollutants.

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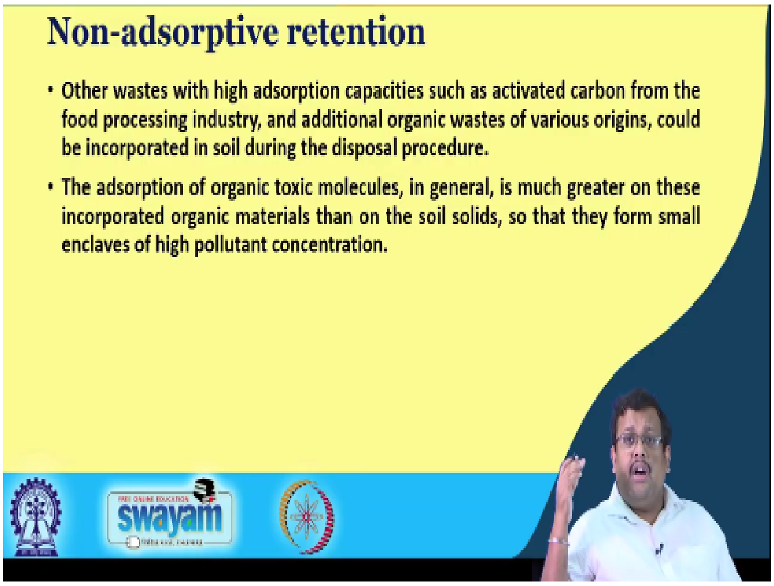

Non-adsorptive retention

- Other wastes with high adsorption capacities such as activated carbon from the food processing industry, and additional organic wastes of various origins, could be incorporated in soil during the disposal procedure.
- The adsorption of organic toxic molecules, in general, is much greater on these incorporated organic materials than on the soil solids, so that they form small enclaves of high pollutant concentration.

Other waste with high adsorption capacity such as activated carbon from the food processing industry and additional organic waste of various origins could be incorporated in soil during the disposal procedure. The adsorption of organic toxic molecules in general, if you say, is much greater on these incorporated organic material than on the soil solid. So they form the small enclaves of high pollutant concentration.

We will see in some examples which we discuss in coming slides organic matter influence organic matter adsorption, one is one of the major factor of adsorption of these pollutants. So adsorption of different pollutants is proportional to the organic matter content of the soil.

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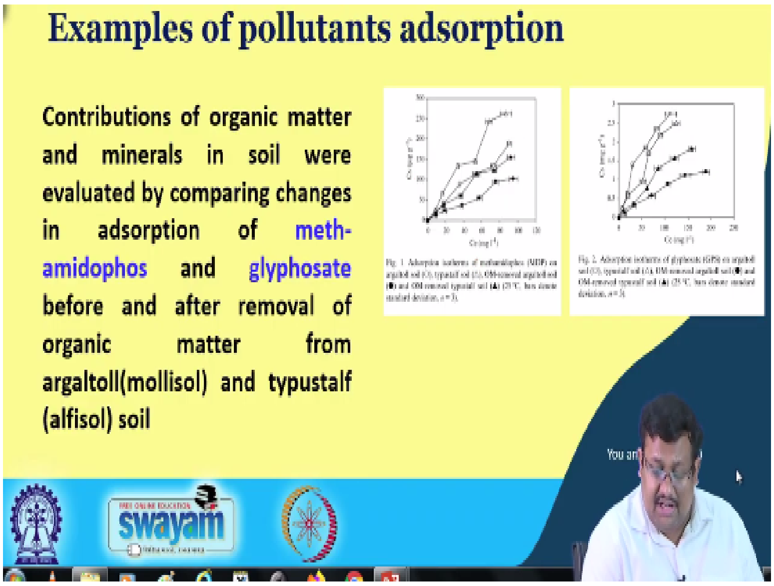

Examples of pollutants adsorption

Contributions of organic matter and minerals in soil were evaluated by comparing changes in adsorption of meth-amidophos and glyphosate before and after removal of organic matter from argaltoll(mollisol) and typustalf (alfisol) soil

So, if you see, now let us see some examples of pollutant adsorption so here in this two graphs we are seeing the contribution of organic matter and minerals in soil for comparing the changes in adsorption of methamidophos and glyphosate both of them are pesticides before and after removal of organic matter. So let us see some influence of organic matter for the adsorption of the pesticide.

Here they have taken two soils, these two scientists You and Zhu in 2005 one soil is mollisol another is alfisol. So here we can see in the first graph this basically shows the adsorption isotherms of methamidophos on this mollisol and this shows the alfisol and both these conditions are having their native organic matter and when the organic matter is removed then we are seeing this is the graph for the organic matter removed mollisol.

And this is the graph for organic matter removed alfisol and here in this graph, we are seeing the adsorption isotherms of glyphosate on the natural mollisols and natural alfisols and organic matter removed mollisols and organic matter removed alfisols. So we can see the trend of adsorption which is given by this term and the concentration of that pollutant in the solution. So what are the important inference from this relationship?

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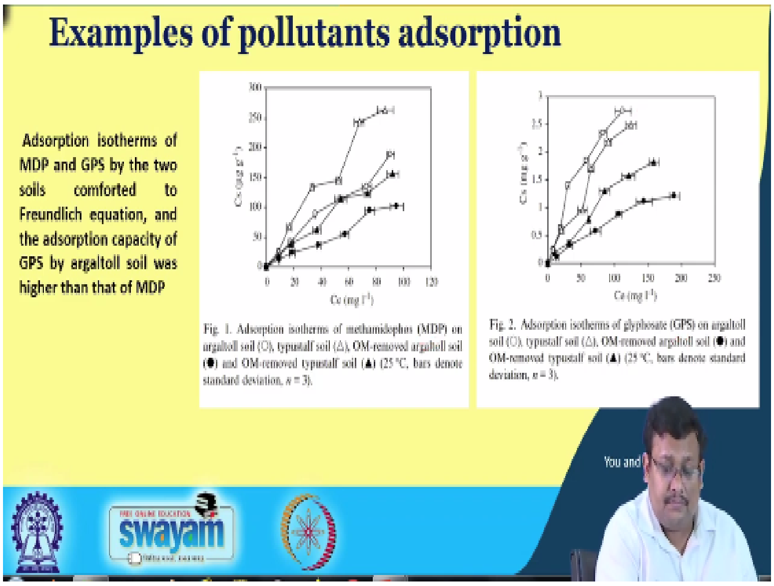

Examples of pollutants adsorption

Adsorption isotherms of MDP and GPS by the two soils comforted to Freundlich equation, and the adsorption capacity of GPS by argaltoll soil was higher than that of MDP

Fig. 1. Adsorption isotherms of methamidophos (MDP) on argaltoll soil (○), typustalf soil (△), OM-removed argaltoll soil (●) and OM-removed typustalf soil (▲) (25 °C, bars denote standard deviation, $n = 3$).

Fig. 2. Adsorption isotherms of glyphosate (GPS) on argaltoll soil (○), typustalf soil (△), OM-removed argaltoll soil (●) and OM-removed typustalf soil (▲) (25 °C, bars denote standard deviation, $n = 3$).

So adsorption isotherms of this methamidophos and glyphosate by the two soil comforted to the Freundlich equation so they followed the Freundlich equation and the adsorption capacity of glyphosate by this argaltoll that is basically a mollisols soil was higher than that of MDP. So, basically we can see from here that adsorption capacity of glyphosate so let us consider this.

So adsorption capacity of glyphosate by this mollisol is quite high than that of MDP. So here this is the glyphosate and this is the MDP. We can see the concentrations are measured here in microgram per gram whether the concentrations are adsorbed concentration are measured here in milligram per gram. So, obviously the adsorption capacity of GPS by this mollisol was higher than that of MDP, obviously. So if we consider this two, obviously they are higher. Now what are the other inference we are getting.

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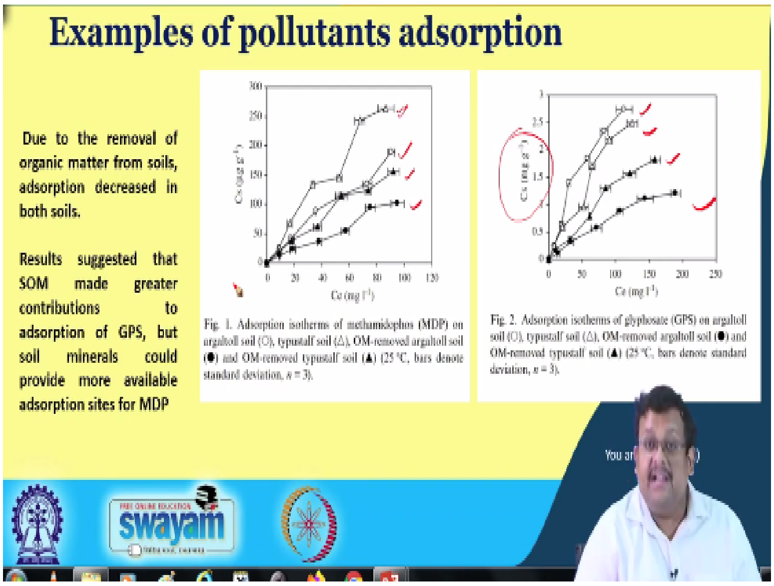

Examples of pollutants adsorption

Due to the removal of organic matter from soils, adsorption decreased in both soils.

Results suggested that SOM made greater contributions to adsorption of GPS, but soil minerals could provide more available adsorption sites for MDP

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Now due to the removal of organic matter from the soils, adsorption decreases in both soil. So obviously you can see from the decrease of organic matter the adsorption decrease for the mollisol from here to here in case of MDP, in case of GPS it is decreasing from here to here and also the slope is also decreasing for alfisol by removal of organic matter in both of these two conditions.

So result suggest that the soil organic matter made greater contribution to the adsorption of GPS, but soil mineral could provide more available adsorption sites for MDP. So here we can see that also that soil organic made greater contribution to the adsorption of GPS obviously we are getting more adsorption of GPS, but soil minerals here could be provide more available adsorption sites of MDP. So, these are some of the important inference which we are getting from these two graphs.

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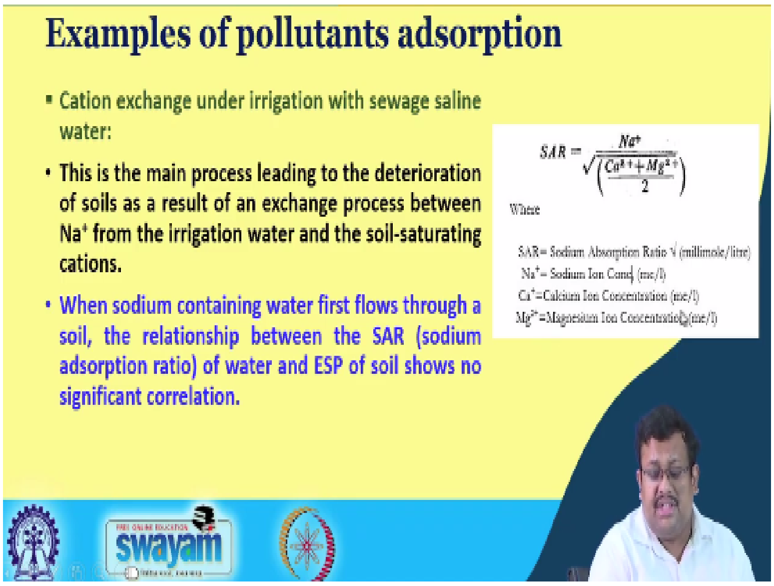

Examples of pollutants adsorption

- Cation exchange under irrigation with sewage saline water:
- This is the main process leading to the deterioration of soils as a result of an exchange process between Na^+ from the irrigation water and the soil-saturating cations.
- When sodium containing water first flows through a soil, the relationship between the SAR (sodium adsorption ratio) of water and ESP of soil shows no significant correlation.

$$SAR = \frac{Na^+}{\sqrt{\left(\frac{Ca^{2+}+Mg^{2+}}{2}\right)}}$$

Where

SAR= Sodium Absorption Ratio √ (millimole/litre)

Na^+= Sodium Ion Conc (me/l)

Ca^+=Calcium Ion Concentration (me/l)

Mg^{2+}=Magnesium Ion Concentration (me/l)

Also let us see an example where cation exchange under irrigation with sewage saline water is concerned and so this is the main process leading to the deterioration of the soils when you are applying the saline irrigation water of soil as a result of exchange process between the sodium from the irrigation water and the soil saturating cations. So basically sodium from the irrigation order basically goes to the exchange complex and then attached to the negatively charge clay soil colloid producing the dispersed soil structure.

So this is the irrigation, through saline irrigation water is a main process of salinization. So when sodium containing water first flows through a soil, the relationship between the sodium adsorption ratio of water and exchangeable sodium percentage of soil shows no significant correlation. Now you already know the formula of sodium adsorption ratio it is basically this where SAR stands for sodium adsorption ratio in millimole per liter. Sodium is sodium ion concentration milliequivalent per liter. Calcium and magnesium also their concentration are also given here milliequivalent per liter.

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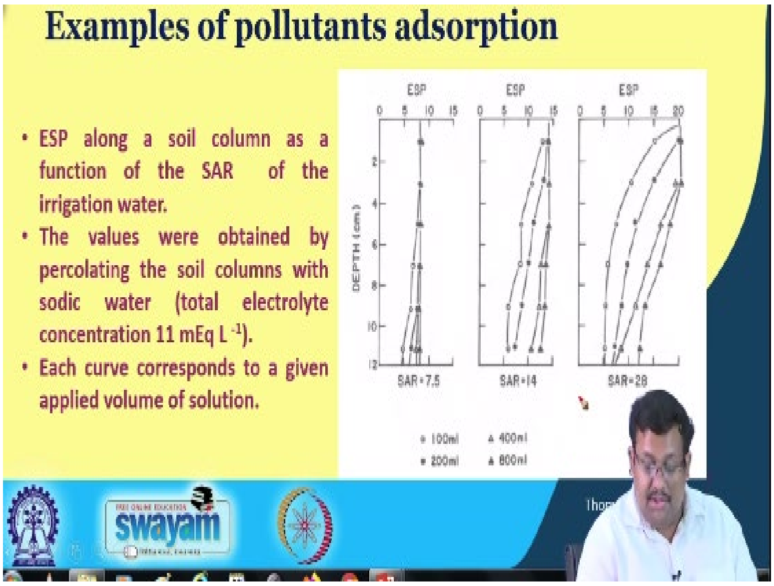

Examples of pollutants adsorption

- ESP along a soil column as a function of the SAR of the irrigation water.
- The values were obtained by percolating the soil columns with sodic water (total electrolyte concentration 11 mEq L^{-1}).
- Each curve corresponds to a given applied volume of solution.

So we have seen that ESP along a soil column as a function of the SAR of the irrigation water. So here is a soil column, three conditions and we are trying to see the ESP which is presented in the x axis. So ESP along a soil column as a function of the SAR or sodium adsorption ratio of the irrigation water. Now the values are obtained by percolating the soil columns with sodic water where the total electrolyte concentration is basically this.

And each curve correspondence to a given applied volume of solution. So here you can see four different curves and these different curves are showing 100 ml, 400 ml, 200 ml and 800 ml so basically 100, 200 ml, 400 ml and 800 ml solution was passed through the soil column and these graph shows the distribution of the ESP across the soil column while they are leached through the irrigation water containing the sodium adsorption ratio of 7.5, sodium adsorption ratio of 14 and sodium adsorption ratio of 28.

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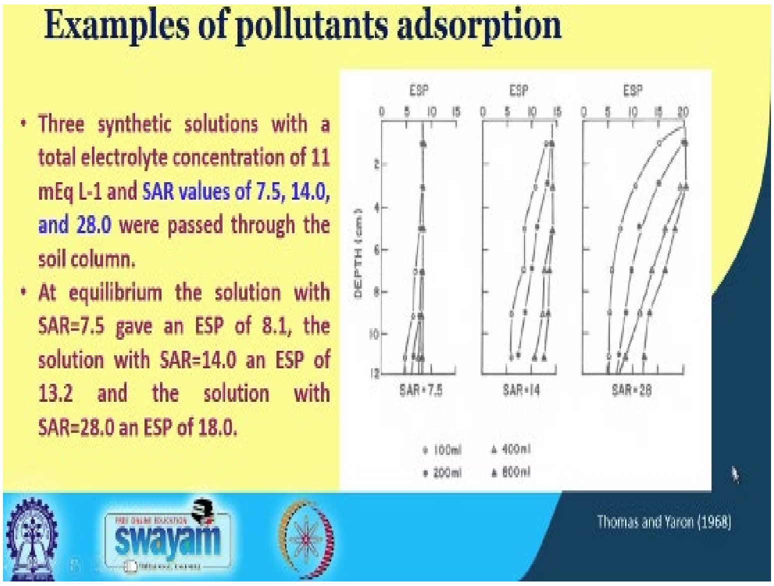

Examples of pollutants adsorption

- Three synthetic solutions with a total electrolyte concentration of 11 mEq L-1 and SAR values of 7.5, 14.0, and 28.0 were passed through the soil column.
- At equilibrium the solution with SAR=7.5 gave an ESP of 8.1, the solution with SAR=14.0 an ESP of 13.2 and the solution with SAR=28.0 an ESP of 18.0.

Thomas and Yaron (1968)

So, three synthetic solution with a total electrolyte concentration we have seen and three SAR values 7.5, 14 as well as SAR values of 28 was passed through the soil column. Now at equilibrium the solution with SAR 7.5 as you can see gave an ESP of 8.1 we can see the solution with SAR 14 gave an ESP of 13.2 and the solution with SAR 28 gave an ESP of 18 so we are seeing that.

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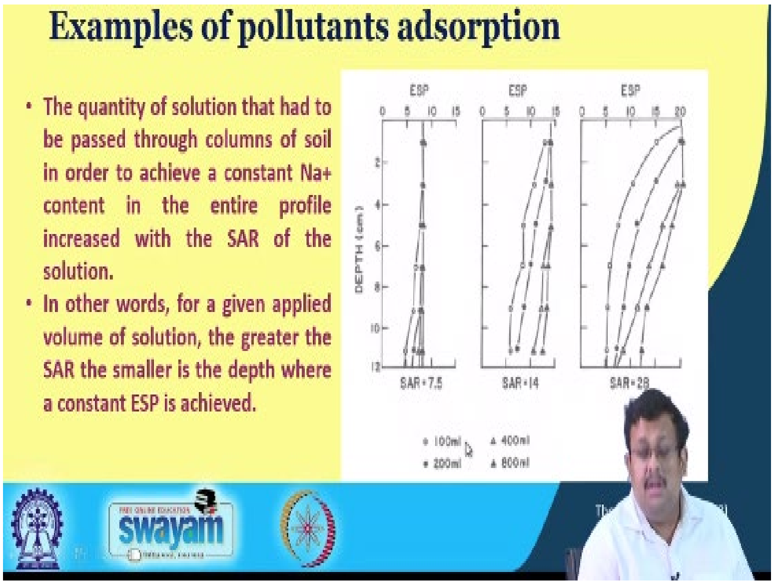

Examples of pollutants adsorption

- The quantity of solution that had to be passed through columns of soil in order to achieve a constant Na+ content in the entire profile increased with the SAR of the solution.
- In other words, for a given applied volume of solution, the greater the SAR the smaller is the depth where a constant ESP is achieved.

Now the quantity, what is the major inference from these graphs? So the quantity of the solution that had to be passed through the column of soil in order to achieve a constant sodium content in the entire profile increase with the SAR of the solution. So basically the quantity of the solution that had to be passed through the column in order to achieve a constant sodium content.

So you can see here constant sodium content here up to this constant sodium content and here you can see constant sodium content. So the volume of quantity of solutions that has be passed through soil column in order to achieve a constant sodium content in the entire profile increase with the SAR of the solution. So we did more and more water as the SAR increase to maintain a constant ESP across the soil column. In other words, for a given applied volume of solution the greater the SAR, the smaller is the depth where a constant ESP is achieved. What is that means?

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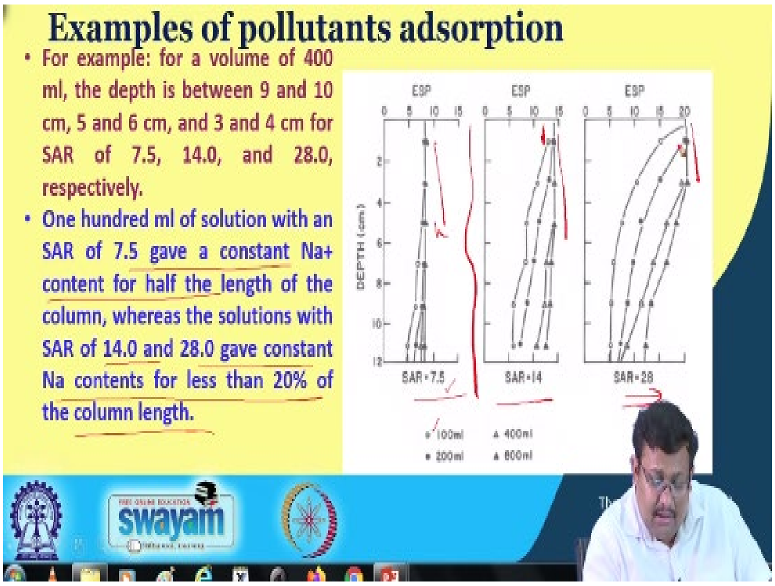

Examples of pollutants adsorption

- For example: for a volume of 400 ml, the depth is between 9 and 10 cm, 5 and 6 cm, and 3 and 4 cm for SAR of 7.5, 14.0, and 28.0, respectively.
- One hundred ml of solution with an SAR of 7.5 gave a constant Na+ content for half the length of the column, whereas the solutions with SAR of 14.0 and 28.0 gave constant Na contents for less than 20% of the column length.

So for example so for a volume of 400 ml so let us consider the volume of 400 ml, the depth is between 9 to 10 centimeter, 5 to 6 centimeter and 3 to 4 centimeter for SAR of 7.5, 14 and 28. So here when the SAR is 7.5, we can see the depth at which the ESP is constant or the sodium is constant is basically in the 9 to 10 centimeter, so here it is higher and in case of SAR 14, we are getting the value between 5 to 6 centimeters.

So 5 to 6 centimeter, we are getting up to this and as we are going for further higher SAR, we are getting only 3 to 4 centimeter. So as we are going from SAR 7.5 to 14 to 28 you can see the constant, the depth of the constant ESP is getting lower and lower and lower. So 100 ml of solution with an SAR of 7.5 gave a constant sodium content for half of the length of the column as you can see here.

Whereas the solution with SAR 14 and 28 gave constant sodium content for less than 20% of the length. So you can see if it is 100 ml so this is a 100 ml so less than 20% of the total column length is giving the constant sodium content in both of this condition. When we are passing 100 ml of both of these solution SAR 14 and SAR 28. So that basically justify the inference which we have discussed.

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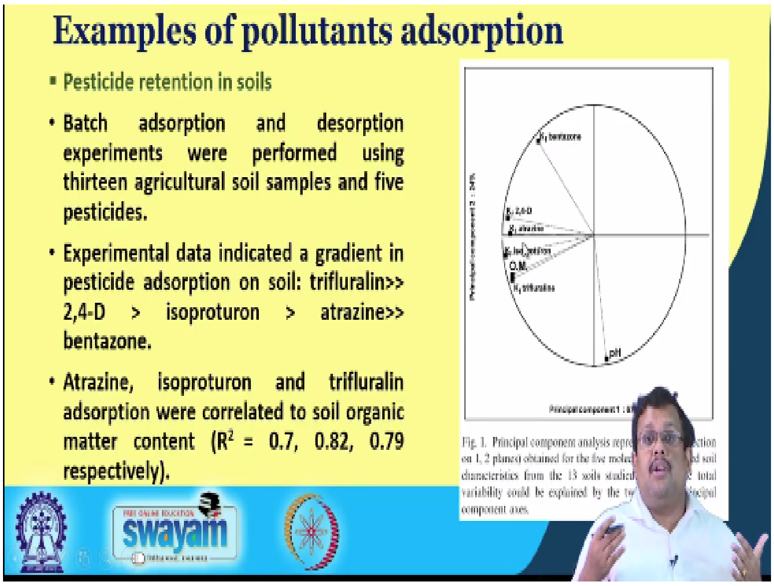

Examples of pollutants adsorption

- Pesticide retention in soils
- Batch adsorption and desorption experiments were performed using thirteen agricultural soil samples and five pesticides.
- Experimental data indicated a gradient in pesticide adsorption on soil: trifluralin>> 2,4-D > isoproturon > atrazine>> bentazone.
- Atrazine, isoproturon and trifluralin adsorption were correlated to soil organic matter content (R^2 = 0.7, 0.82, 0.79 respectively).

Fig. 1. Principal component analysis repre ction
on 1, 2 planes) obtained for the five mole d soil
characteristics from the 13 soils studie total
variability could be explained by the tw ncipal
component axes.

Another example we have seen given by this Boivin et. al in 2008 they have basically studied the pesticide retention in soil. So they did batch adsorption and desorption experiments and using 13 agricultural soil samples and 5 pesticides and experimental data, their experimental data indicated a gradient in pesticide adsorption in soil where trifluralin shows the maximum adsorption followed by 2,4D then isoproturon followed by atrazine and then bentazone.

So atrazine, isoproturon and trifluralin adsorption were correlated to soil organic matter content with an R square values of 0.7, 0.82, 0.79 and they have done a principal component analysis you can see the principal component analysis shows, for the Freundlich adsorption coefficient for 2,4 D atrazine, isoproturon and trifluralin all of these are showing high correlation with organic matter. Because all of them are in the same direction so that shows the high influence of organic matter for their adsorption or pesticide retention in the soil.

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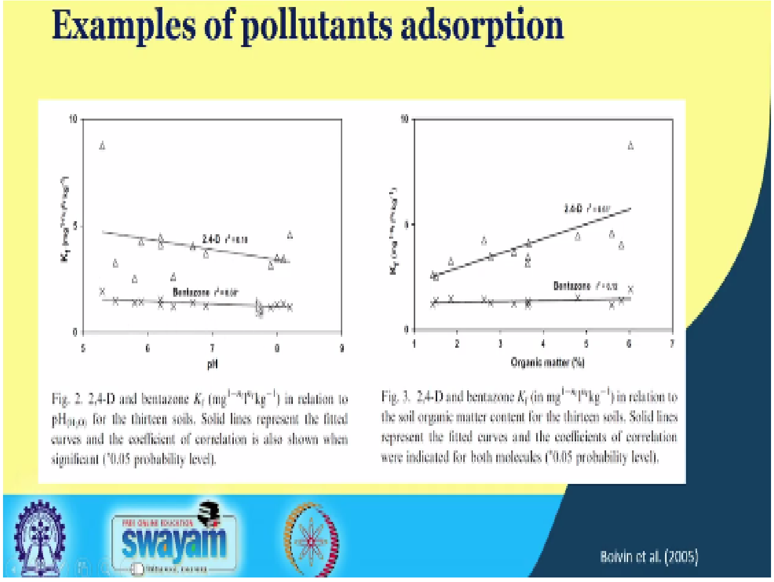

Examples of pollutants adsorption

Fig. 2. 2,4-D and bentazone K_f ($mg^{1-N} l^N kg^{-1}$) in relation to pH_{H_2O} for the thirteen soils. Solid lines represent the fitted curves and the coefficient of correlation is also shown when significant (*0.05 probability level).

Fig. 3. 2,4-D and bentazone K_f (in $mg^{1-N} l^N kg^{-1}$) in relation to the soil organic matter content for the thirteen soils. Solid lines represent the fitted curves and the coefficients of correlation were indicated for both molecules (*0.05 probability level).

Boivin et al. (2005)

Similarly, they have found the relationship between the pH and organic matter with the Freundlich coefficient so they draw the curve between the pH for bentazone this is the curve for 2,4 D they have got this curve and for organic matter, they have got the 2,4 D values with R square values of 0.61 and in case of bentazone, they got an R square values of 0.12. So that shows the positive correlation between organic matter and adsorption of the pesticides.

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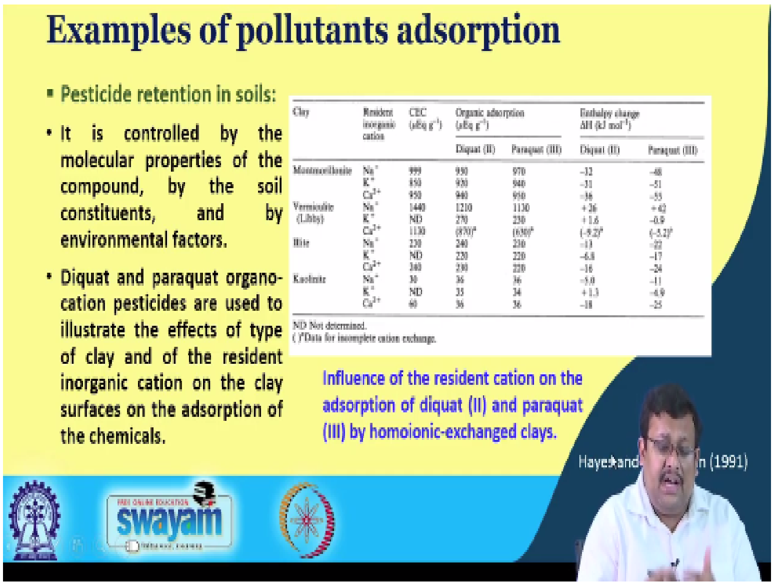

Examples of pollutants adsorption

- Pesticide retention in soils:
  - It is controlled by the molecular properties of the compound, by the soil constituents, and by environmental factors.
  - Diquat and paraquat organo-cation pesticides are used to illustrate the effects of type of clay and of the resident inorganic cation on the clay surfaces on the adsorption of the chemicals.

Clay	Resident inorganic cation	CEC ($\mu Eq\ g^{-1}$)	Organic adsorption ($\mu Eq\ g^{-1}$)		Enthalpy change ΔH ($kJ\ mol^{-1}$)	
			Diquat (II)	Paraquat (III)	Diquat (II)	Paraquat (III)
Montmorillonite	Na^+	999	930	970	−32	−48
	K^+	850	920	940	−31	−51
	Ca^{2+}	950	940	950	−36	−53
Vermiculite (Libby)	Na^+	1440	1210	1130	+26	+42
	K^+	ND	270	230	+1.6	−0.9
	Ca^{2+}	1130	(870)*	(630)*	(−9.2)*	(−3.2)*
Illite	Na^+	230	240	230	−13	−22
	K^+	ND	220	220	−6.8	−17
	Ca^{2+}	340	230	220	−16	−24
Kaolinite	Na^+	30	36	36	−5.0	−11
	K^+	ND	35	34	+1.3	−4.9
	Ca^{2+}	60	36	36	−18	−25

ND Not determined.
( )*Data for incomplete cation exchange.

Influence of the resident cation on the adsorption of diquat (II) and paraquat (III) by homoionic-exchanged clays.

Hayes and n (1991)

And also this table shows the pesticide retention in the soil, so basically this table shows the influence of the resident cation on the adsorption of diquat and paraquat by homoionic exchange clays. So it is controlled by the molecular properties of the compound by the soil constituents and by the environmental factors. Diquat and paraquat organic you know their pesticides are used to illustrate the effects of type of clay and the resident inorganic cations on the clay surface, on the adsorption of the chemical.

So we can see here how the variation of different resident inorganic cation can influence the pesticide adsorption can be found from this table. So we can see the cation can have a significant influence on the extent and the energetics of the adsorption process. Cation exchange capacities on the clay can be seen vary according to the nature of the resident cation.

And we can see, in case of montmorillonite for example homoionic montmorillonite clays like sodium, potassium you can see slight preference from paraquat over diquat. So if you see in case of paraquat, it is quite higher than that of diquat in both the cases. However, these affinities were reversed when we are seeing the adsorption by sodium vermiculite and illite clays.

So if we can consider sodium in case of diquat, it is showing higher and in case of also vermiculite sodium vermiculite it is showing higher, in case of diquat adsorption than that of paraquat. So the trends are reversed so depending on the resident inorganic cations, it shows the high influence on the adsorption of the pesticide in the clay mineral.

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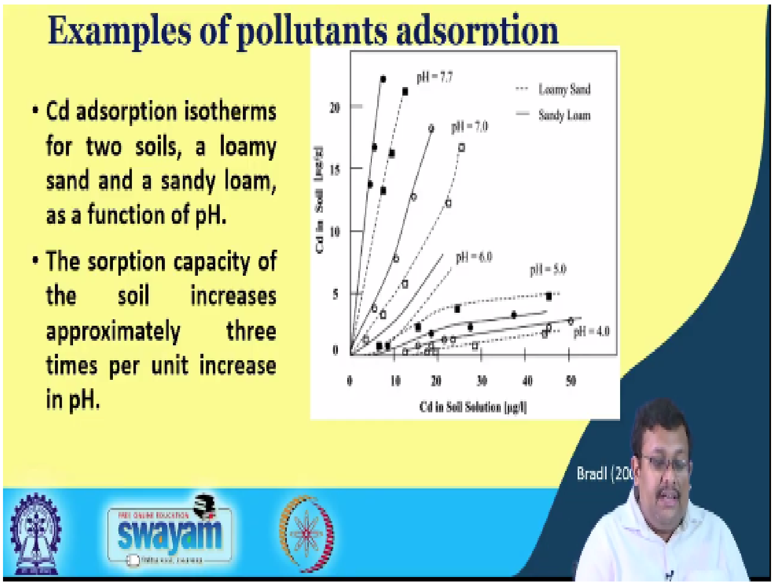

Examples of pollutants adsorption

- Cd adsorption isotherms for two soils, a loamy sand and a sandy loam, as a function of pH.
- The sorption capacity of the soil increases approximately three times per unit increase in pH.

Bradl (20

Cadmium adsorption isotherms we have seen, cadmium isotherms of two soils, a loamy soil and sandy soil as a function of pH and the sorption capacity of the soil increases approximately three times per unit increase in pH. As you can see, with an unit increase in pH in two soil the sorption capacity of the soil also increases.

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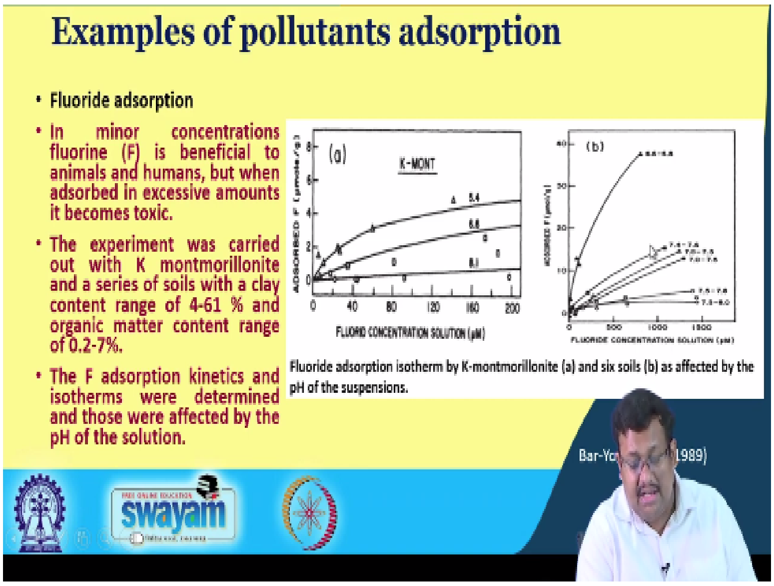

Examples of pollutants adsorption

- Fluoride adsorption
- In minor concentrations fluorine (F) is beneficial to animals and humans, but when adsorbed in excessive amounts it becomes toxic.
- The experiment was carried out with K montmorillonite and a series of soils with a clay content range of 4-61 % and organic matter content range of 0.2-7%.
- The F adsorption kinetics and isotherms were determined and those were affected by the pH of the solution.

Fluoride adsorption isotherm by K-montmorillonite (a) and six soils (b) as affected by the pH of the suspensions.

Bar-Yo 1989)

Fluoride adsorption also we have seen the fluoride adsorption in minor concentration, fluorine is beneficial for the animals and humans, however but when the concentration is excessive, that becomes toxic. These experiments by Bar-Yosef et al in 1989 was carried with potassium montmorillonite as a series of soil with a clay content ranging between 4% to 61% and organic matter ranging between 0.2 to 7%.

And they have seen the fluorine adsorption kinetics and isotherms and they determine these fluorine adsorption kinetics and isotherms and those were affected by the pH of the solution and these are the fluoride adsorption isotherms by potassium montmorillonite and so this is the potassium montmorillonite and these are the fluoride adsorption isotherms by 6 soils as affected by the pH of the suspension so for different pH you can see.

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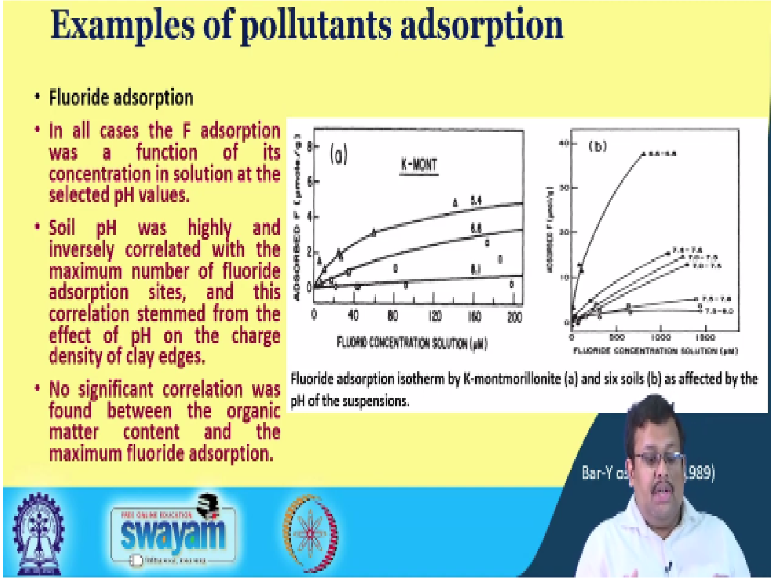

Examples of pollutants adsorption

- Fluoride adsorption
- In all cases the F adsorption was a function of its concentration in solution at the selected pH values.
- Soil pH was highly and inversely correlated with the maximum number of fluoride adsorption sites, and this correlation stemmed from the effect of pH on the charge density of clay edges.
- No significant correlation was found between the organic matter content and the maximum fluoride adsorption.

Fluoride adsorption isotherm by K-montmorillonite (a) and six soils (b) as affected by the pH of the suspensions.

Bar-Y 989)

In all the cases, the fluorine adsorption was a function of its concentration in solution of the selected pH values and soil pH was highly and inversely correlated with the maximum number of fluoride adsorption sites and this correlation stemmed from the effect of pH of the charge density of the clay edges and also they have seen that there is no significant correlation was found between the organic matter content and the maximum fluoride adsorption.

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References:

Soil Pollution Processes and Dynamics-(1996) By Yaron, Calvet, and Prost

P.A. Holden, N. Fierer, in Encyclopedia of Soils in the Environment, 2005

Sparks, D.L. (2003). " Environmental Soil Chemistry" 2nd ed, Academic press.

So friends I hope that you have learned something new in this module. We have discussed in details different processes, adsorption processes, non adsorption processes, trapping processes, precipitation processes and some examples also while discussing the trapping and retention of different organic and inorganic pollutants within the soil solid phase. I hope that things are clear to you.

If you still have any queries, just email me and I will be more than happy to answer your queries. I request you to go through these three books, you know, soil pollutions processes and dynamics by Yaron, Calvet and Prost and also this Encyclopedia in soil in the environment by Holden and Fierer and also environmental soil chemistry by D. L. Sparks to gain more comprehensive knowledge of these type of interactions.

And these type of retention of pollutants and I hope that you have gained some new knowledge from this module and let us meet in our next module to discuss other aspects of soil pollution and their fate and how to model their fate. Thank you very much.