Environmental Soil Chemistry
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Lecture – 52
Modeling the Fate of Pollutants in the Soil, Risks and Remedies Continued

Welcome friends to this second lecture of week 11 or module 11 of online certification course of environmental soil chemistry and in this week we are talking about modeling the fate of pollutants in soil, risk and remedies.

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So, in our first lecture, we basically covered some aspects. So, we basically covered overview of the models and we covered the classification of the models, and we also covered the description of the models. We started the deterministic models. So, in this lecture, we are going to talk about the deterministic models and also we will be talking about the transport in heterogeneous media and if time permits, then we will be also touching the sink and source phenomenona.

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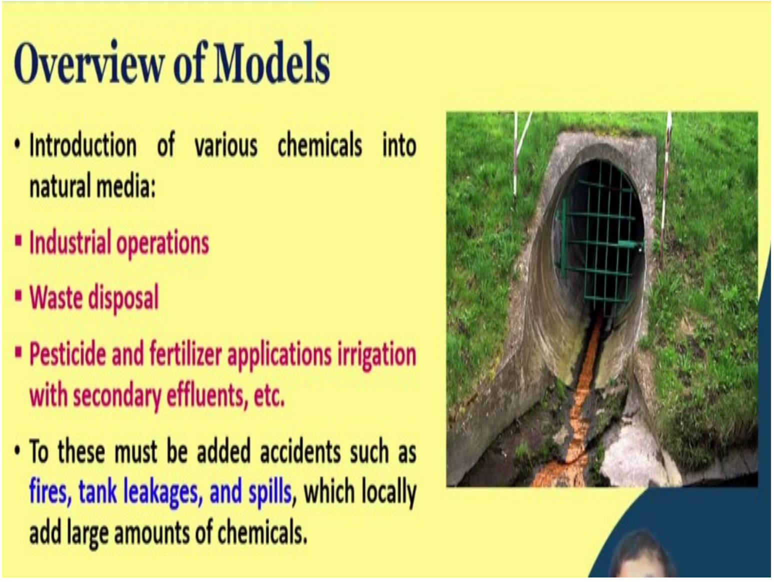

So, let me go very quickly whatever we have covered in our last lecture. So, we started with the overview of the models. We discussed about the different sources of contamination.

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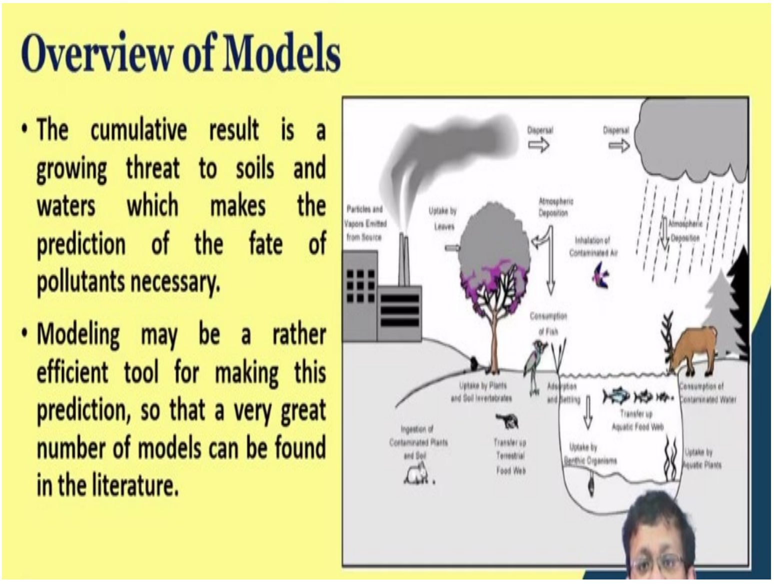

Then we discussed about the cumulative effects and then I showed you this picture, how the pollutant can move from one place to another place and how they interact with different components of the ecosystem.

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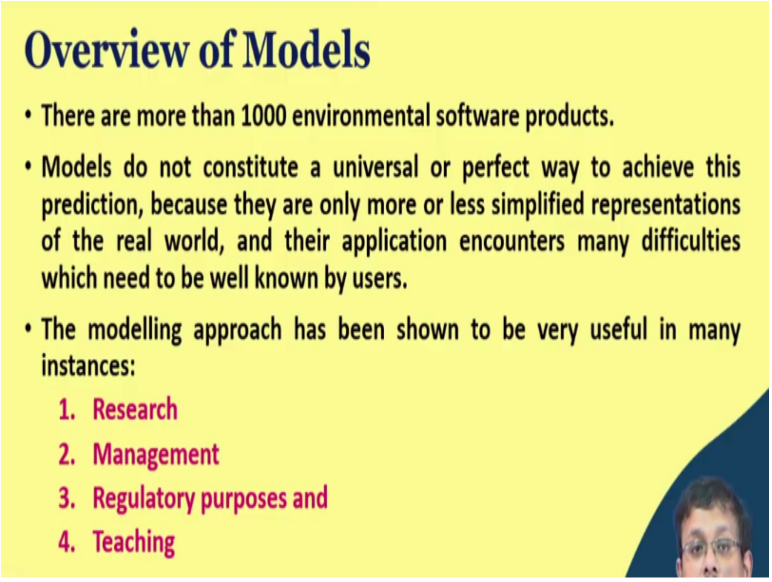

Then we talked about what are the different instances in which they are useful.

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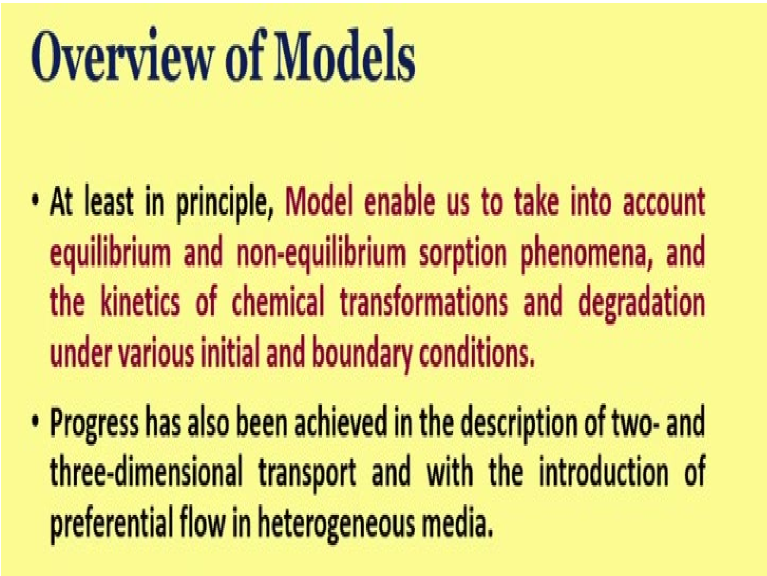

And once he covered this and then we have talked about the classification of the model.

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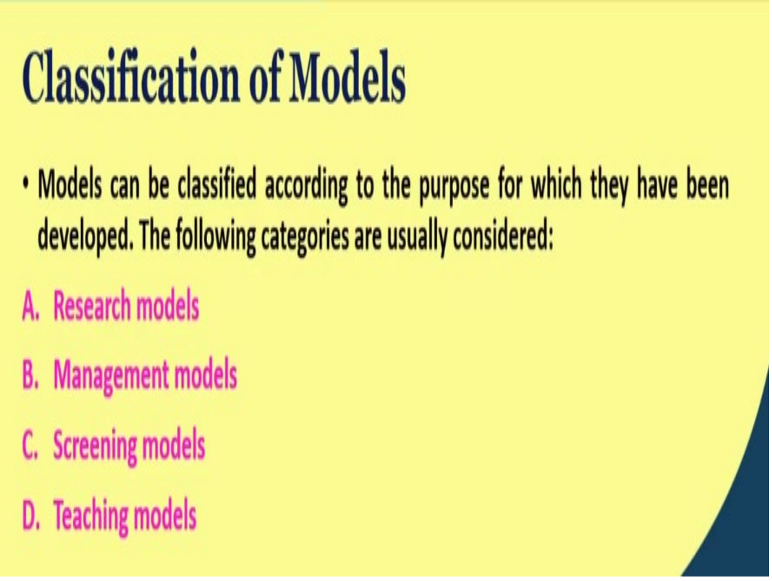

In the classification of the model, we started with the research models, then we have discussed the management models. Then we have talked about the screening models and teaching model.

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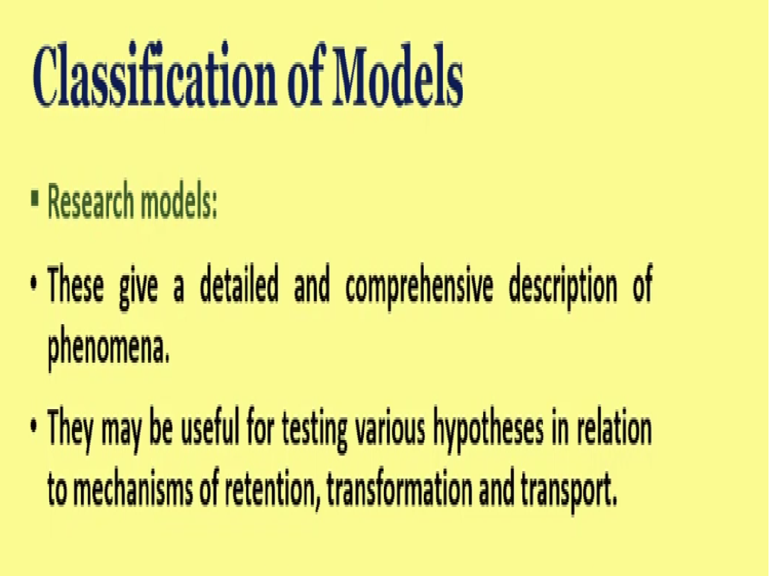

Remember the research model is basically a detailed and comprehensive description of phenomena and may be useful for testing different hypotheses in relation to the mechanism of retention, transformation and transport of the chemicals from one place to another place.

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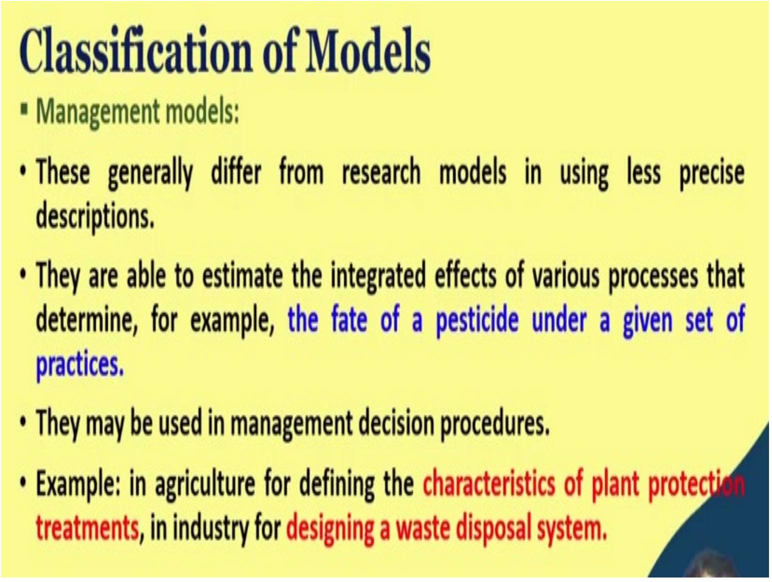

Then management models, management models are basically useful for taking management decisions. For example, in case of agriculture if we take the management decision of you know what are the major management practices to control the movement of pesticide in the soil as well as within plants, so that is a management decision. So, management models are responsible for that. Also in case of industry, there designing a waste disposal system is under the management models.

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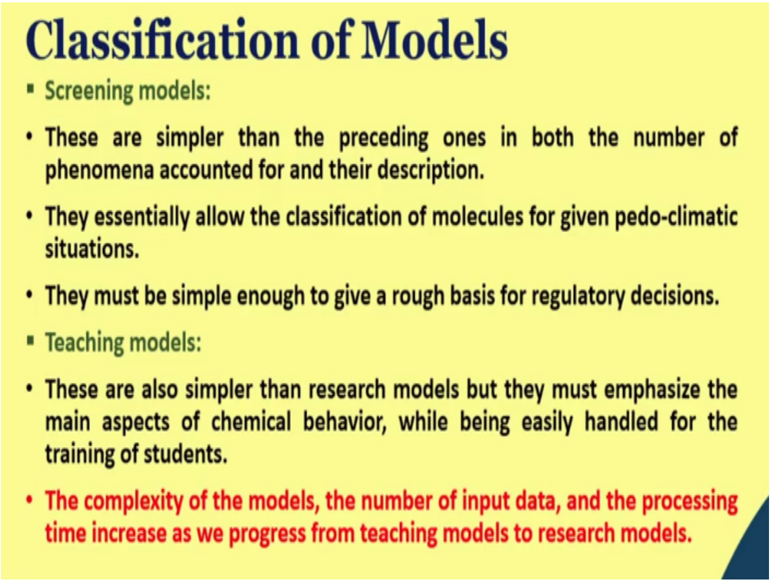

Then the screening models. Screening models are basically also used for regulatory decisions. And finally the teaching models and teaching models are basically used for teaching the students and they are simplest in all the 4 models. Remember the complexity of the modeling increases as you go from the teaching models to screening model to management model to research models.

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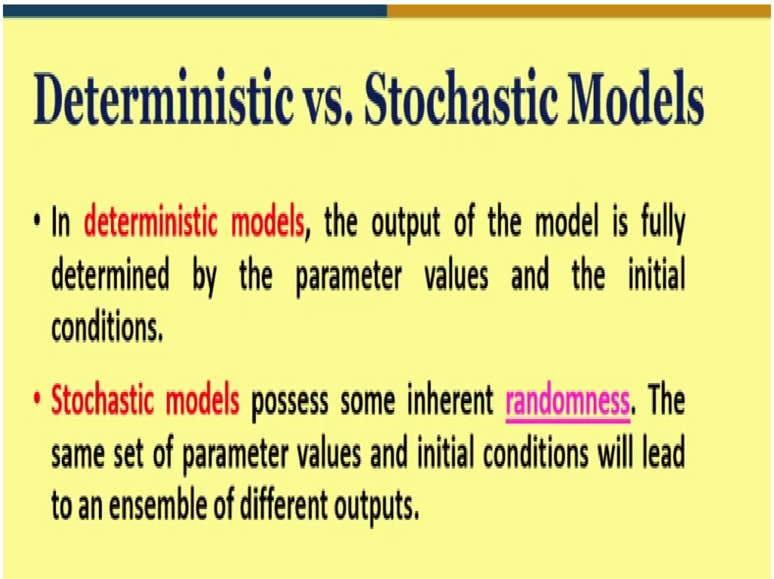

Then, we have discussed the concept of deterministic model and stochastic model. Remember the major difference between the deterministic model and stochastic model is the randomness. Stochastic model possesses the inherent randomness. So, for of same set of parameters, it can produce different types of outputs.

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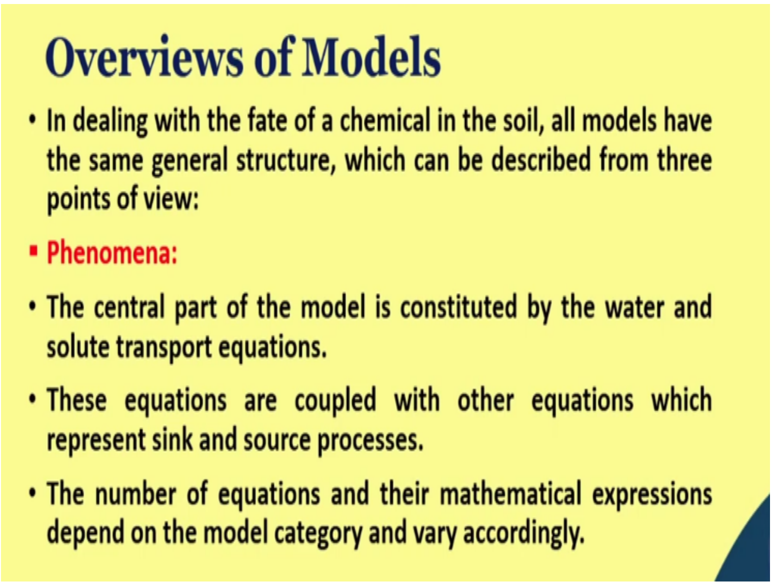

So, when we talk about the overview of the models, you know 3 major points or 3 major aspects of a model we have discussed. First of all is phenomena which is the central part of the model and constituted by water and solute transport equations.

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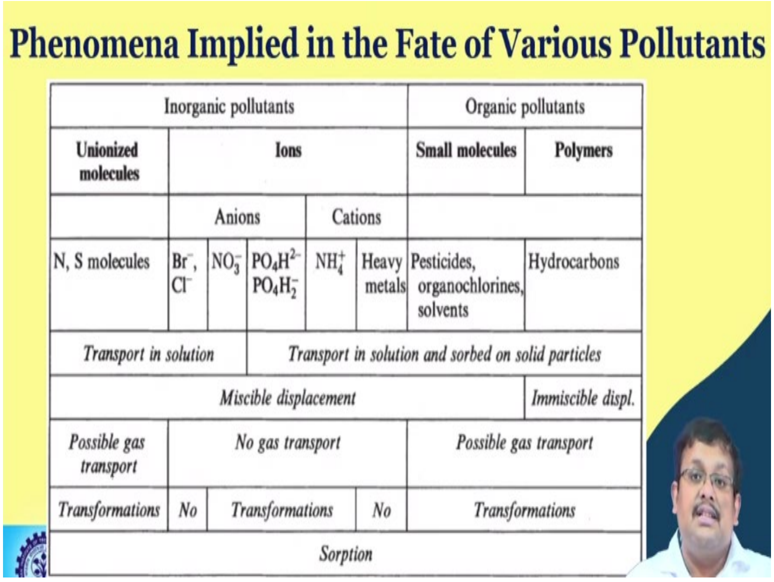

We showed you the in the phenomena which are implied in the fate of various pollutants. We have discussed the inorganic pollutants and organic pollutants and how they can be classified and how they are interrelated. These phenomena are interrelated we have discussed.

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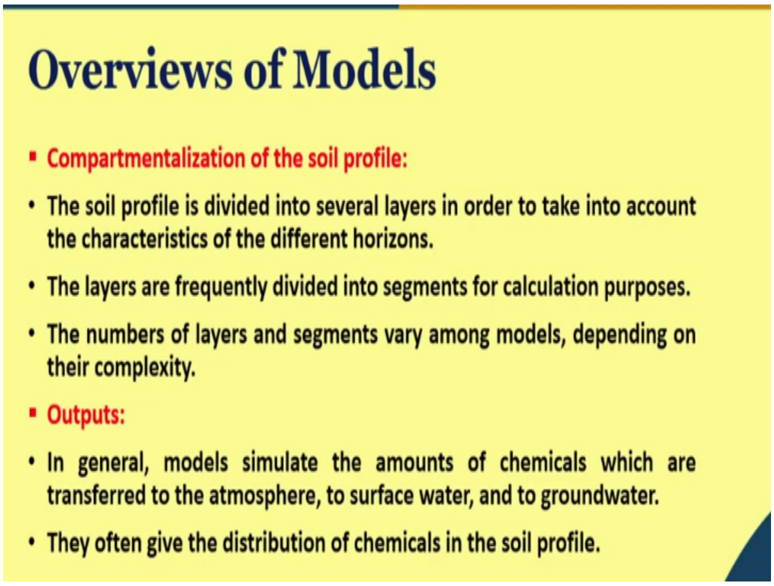

And also the second aspect we have discussed that is compartmentalization of soil profile, where the soil profile is divided into several layers in order to take into account the characteristics of different horizons and how they are interrelated to each other and also finally the third aspect is output which often gives the distribution of the chemicals in the soil profile. So, these are the 3 major aspects which we have talked about.

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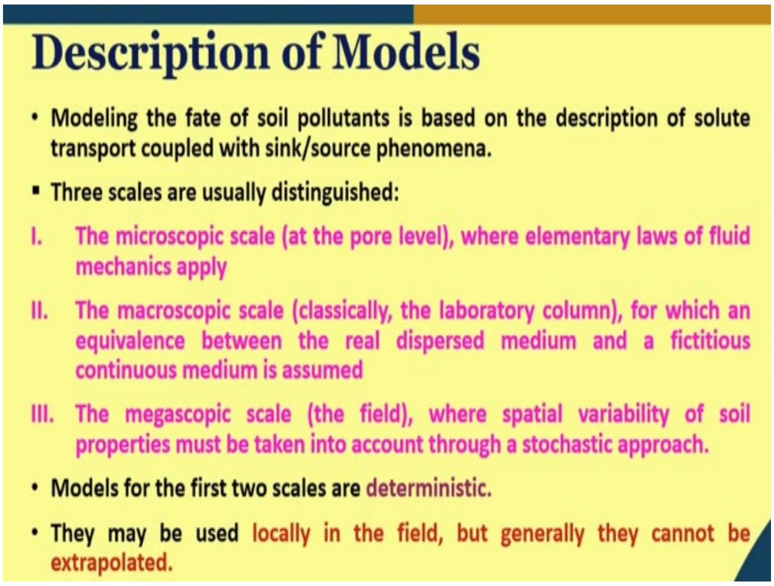

Then we have talked about the 3 major scales of a model. First of all the microscopic scale and then second one the macroscopic scale. These two scales constitute the deterministic model. However, the third one is the megascopic scale. First two that is microscopic scale and macroscopic scale can be applied locally in the field but they cannot be extrapolated, however, the megascopic scale can be extrapolated.

So, this megascopic scale is basically related to the field scale and the microscopic scale is the pore level, whereas the macroscopic scale is classified in the you know for example, laboratory-based soil column leaching studies.

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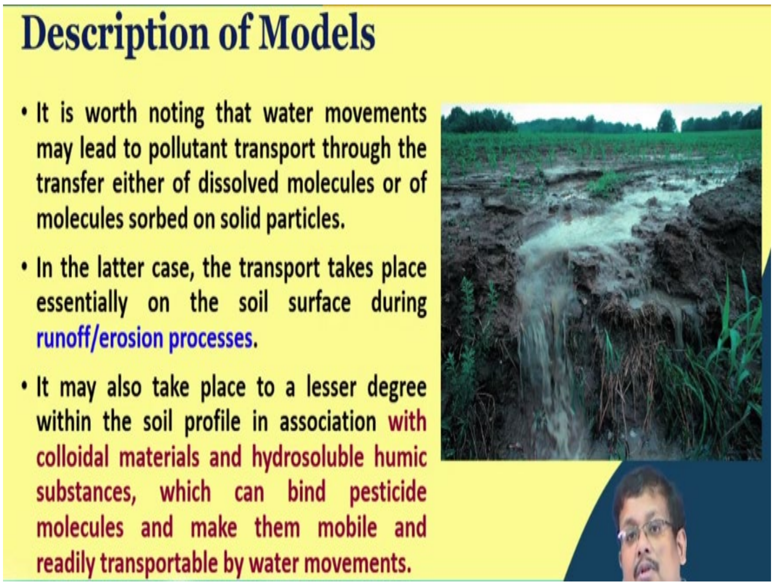

We have talked about how these pollutants move in the water either dissolve in the water or sorbed on to the solid particles. We have shown the runoff and erosion process through which this water move from one place to another place.

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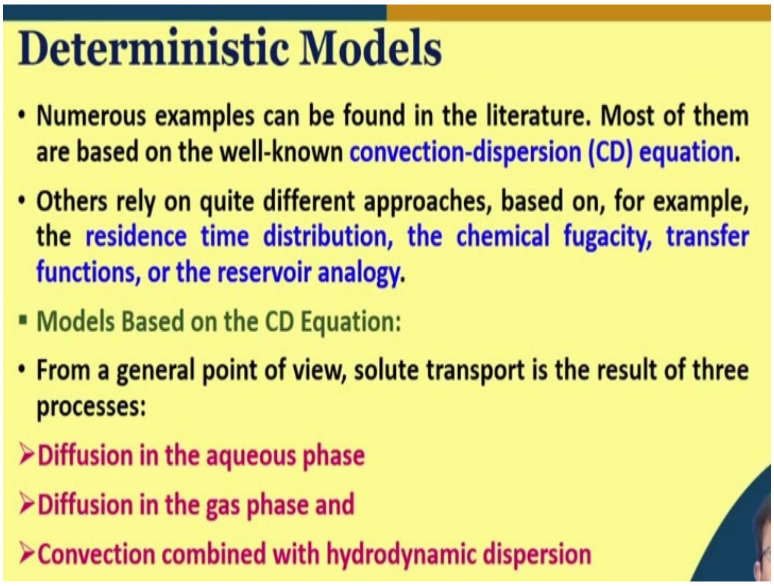

And while discussing the deterministic models, model based on CD equations, we have talked about the model based on the convection-dispersion equation.

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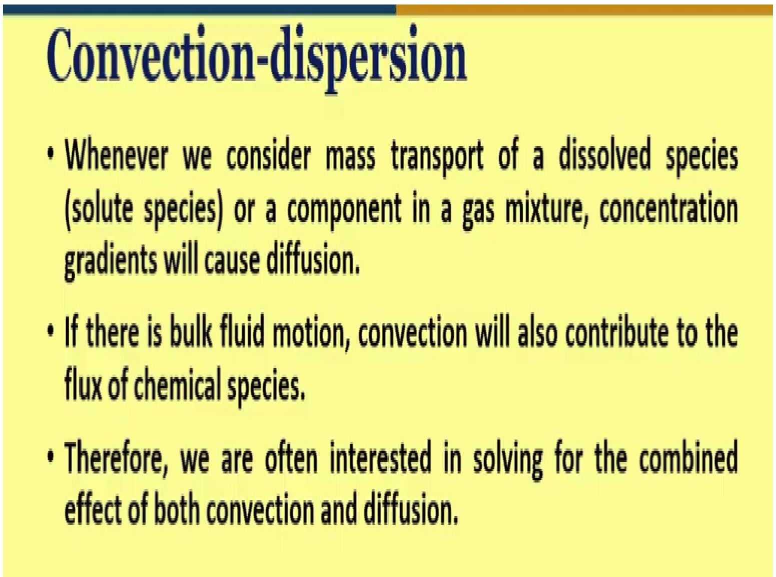

And we have discussed what is the coupling of convection-dispersion, why it is needed to couple convection-dispersion. Remember that when there is a bulk fluid motion, the convective force also you know coupled with the dispersion, so that they can comprehensively characterize the solid transport.

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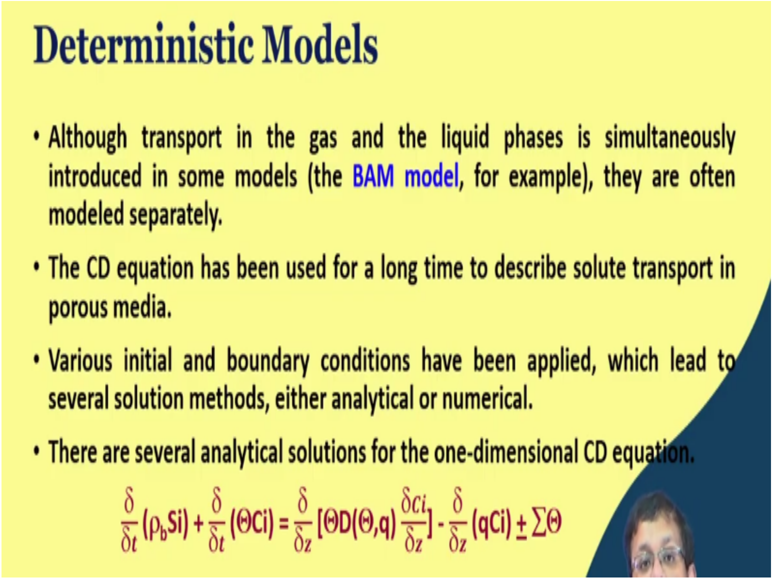

And then we have shown the CD model equation, one-dimensional CD model equation.

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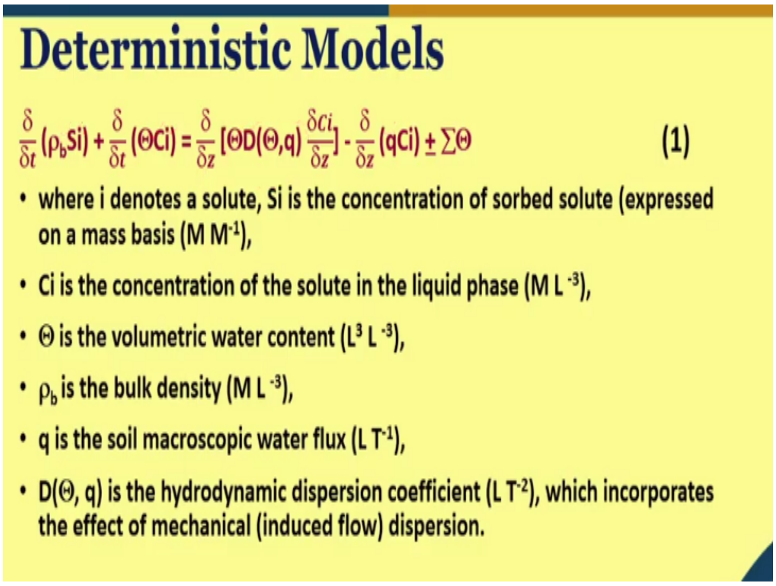

And also we have defined the CD model equation and other parameters or components of the CD model. So, this is where we have stopped in our last class in our last lecture. So, we will start from here today. So, this is the first you know one-dimensional CD model description and we have basically defined all these terms. For example, the i stands for the solute, whereas the Si stands for the concentration of the sorbed solute.

Ci stands for the concentration of the solid in the liquid phase, this rho b stands for the bulk density, theta stands for the volumetric water content, q stands for the soil microscopic water flux and these term stands for the hydrodynamic dispersion coefficient which incorporates the effect of mechanical dispersion or induced flow. So, we have covered up to this.

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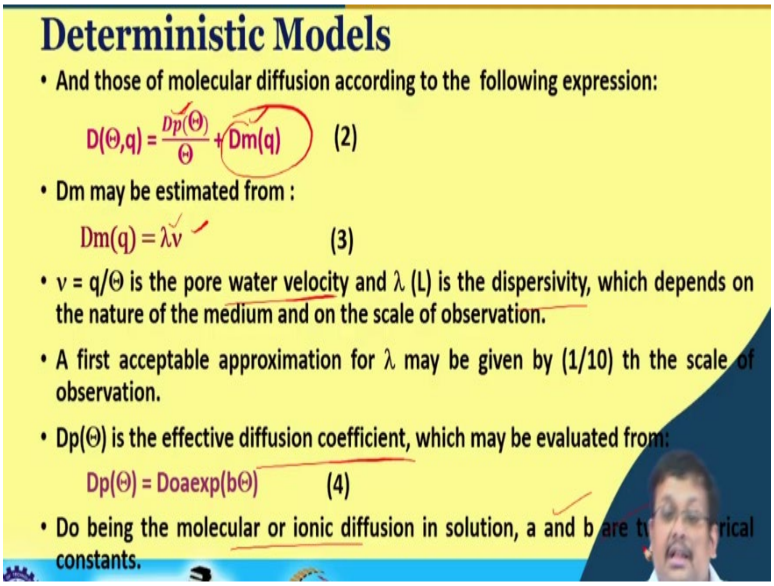

Now, so if we see this term, if we elaborate this term that is D theta, q, this is the hydrodynamic dispersion coefficient. So, if we elaborate this term, so the molecule diffusion according to the following expression can be extended. So, this term that is can be extended using this form where this Dm q can be estimated by multiplying the lambda with v. So, v is basically q by theta, basically this is the poor water velocity and this lambda is that dispersivity.

So, this lambda is the dispersivity and v is the pore water velocity and this v can be you know expressed as q by theta and so this dispersivity which is denoted by this lambda **is** depends on the nature of the medium and the scale of the observation. We have discussed the scale of the observation in our previous lecture and a first acceptable approximation for lambda may be given by one-tenth of the scale observation.

Remember these Dp theta is the, you know this term that is Dp theta is the effective diffusion coefficient which may be evaluated from, so Dp theta can be expressed as D0 aexp b theta. So, basically here D0 a exponential of b theta, So, D0 being here the molecular or ionic diffusion in a solution and a and b are constants. So, this is how we define each of the term of a one-dimensional CD equation.

Again in the CD equation, this dispersion coefficient can be expressed in terms of summation of these 2 components where this component basically can be estimated by lambda multiplied by v, v is basically the pore water velocity, lambda is the dispersivity, and lambda depends on the nature of the medium and the scale of the observation and this Dp theta is effective diffusion coefficient.

Which can be calculated by using this formula D0 exponential b theta whereas D0 is the molecular or ionic any diffusion and a and b are the constant. So, this is how we calculate or define each and every term for a CD, one dimensional CD equation.

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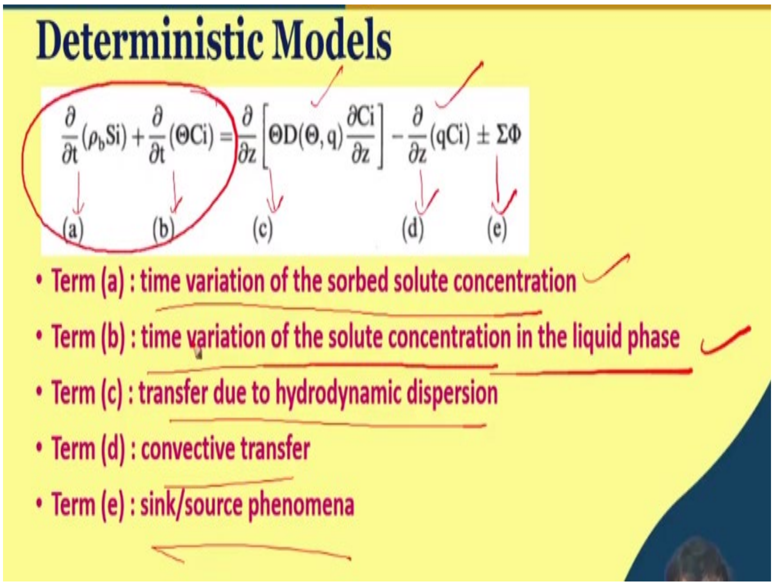

Now, if we see this one-dimensional CD equation, you know there are certain parts, how we can basically generalize this CD equation. So, if you see the CD equation, you see that different components are tagged with different names. So, basically this is a, this is b, this expression is c, this expression is d, and this expression is e. So, these a term shows the time variation of the sorbed solute concentration.

So, it is a time variation of the sorbed solute concentration and this b expression basically shows the time variation of the solid concentration in the liquid phase. So, a + b basically shows the changes or variation of the pollutant concentration, either it is in sorbed solute condition or it is dissolved into the liquid phase, if there is a change it can be calculated by the summation of these two components.

Now, the term c basically shows transfer due to hydrodynamic dispersion and this term d is basically convective transfer and term e is basically seeing sink source phenomena. So, you can see that the move changes in the concentration of a particular chemical or particular pollutant can be estimated by coupling the convection and dispersion process or convective or dispersion process, just we have seen here okay. So, this is the justification of using this term CD while defining this solute transport process.

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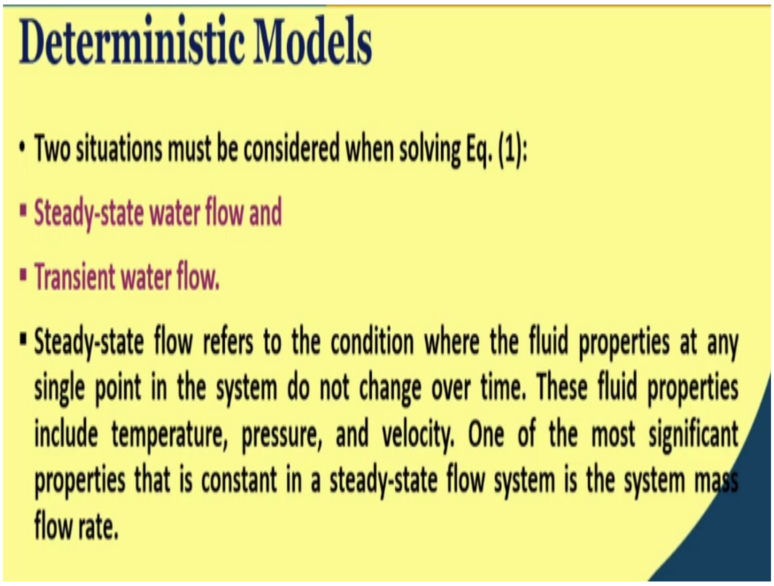

So, two situations must be considered when solving this equation 1 or the CD equation. First of all is the steady state water flow and the second one is the transient water flow. So, what is the steady state water flow and what is transient water flow. So, steady state flow refers to the condition where the fluid properties at any single point in the system do not change over time, it is steady nature.

So again, steady state flow refers to the condition where the fluid properties at any single point in the system do not change over time and these fluid properties include temperature, pressure and velocity. One of the most significant properties that is constant in a steady state flow system is the system you know mass flow rate. So, the system mass flow rate is one of the important properties and which is constant in a steady state flow. So, this is called the steady state flow.

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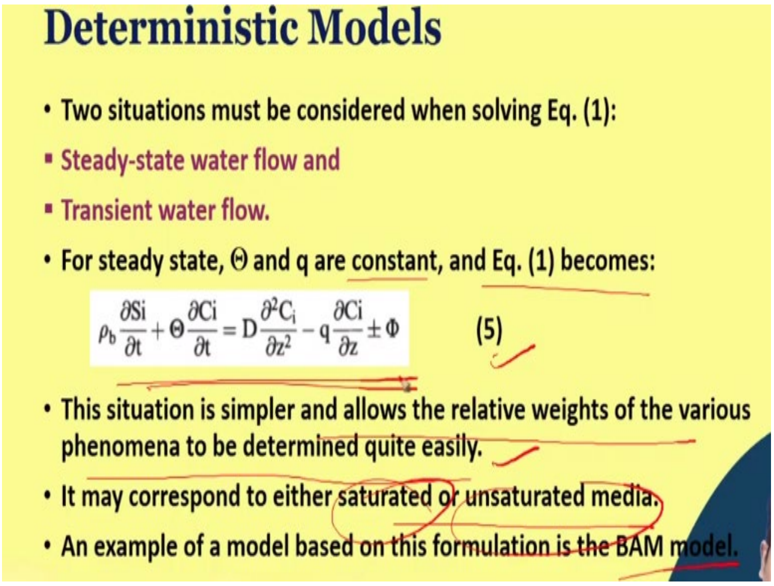

Now, what is steady state, this theta which is the volumetric water content and q which is basically the flux are constant because it is steady state and thus the equation 1 or the CD equation or one-dimensional CD equation will be converted to this equation 5. So, remember that this situation when we are considering a steady state this situation is simpler and allows the relative weights of the various phenomena to be determined quite easily okay.

So, this situation is simpler and allows the relative weights of the various phenomena to be determined quite easily. Obviously here we are considering the steady state condition okay. Now, it may correspond to either saturated or unsaturated media. Now, in this condition this can be present in either saturated or unsaturated media. Now, an example of a model based on this formulation is basically the BAM model and so this is how in the steady state condition, the CD model takes this form which is comparatively simpler.

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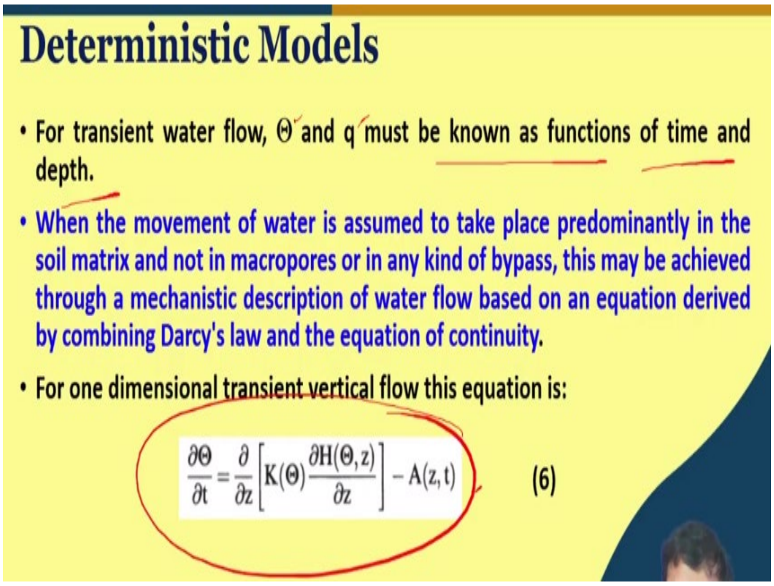

Now, the second one the transient flow. So, in the transient flow, the theta and q must be known as function of time and depth because they are varying, they are not steady state, in the transient state this theta and q are function of time and depth. So, when the movement of water is assumed to take place predominantly in the soil matrix and not in macropores or any kind of bypass, this may be achieved through a mechanistic description of water flow based on equation derived by combining Darcy’s law and equation of continuity.

Now, again let me explain this thing. When the movement of water is assumed to take place predominantly in the soil matrix, so in the soil matrix the movement occurs and not in macropores or any kind of bypass. This may be achieved through a mechanistic description of water flow based on Darcy's law and also combining the continuity equation. Now, for one-dimensional transient vertical flow, this equation basically takes this form okay. So, this is the one-dimensional transient vertical flow okay.

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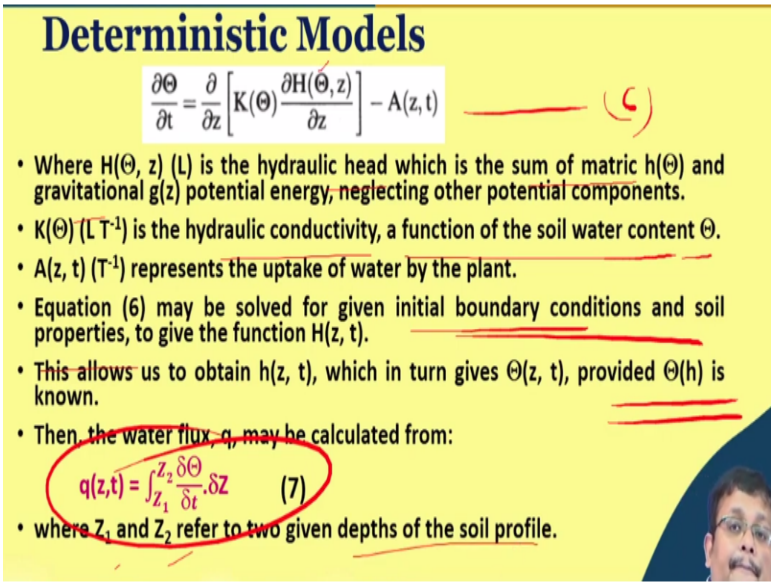

So, let us see what are the different components of this equations, where this is basically the equation which you just saw. Now, in this equation this component that H theta z is the hydraulic head, which is basically the sum of metric head and the gravitational potential energy and neglecting other potential components. So, those who have already gone through the soil water potential you must be aware of this term of hydraulic head.

And this hydraulic head is basically the sum of the metric head and also the gravitational head and basically neglecting other potential components, whereas the K theta is the hydraulic conductivity which is a function of soil water content theta, remember this theta is the volumetric water content. So it is basically equation 6. So, the equation 6 may be solved by given initial boundary condition and soil properties to give a function of H which is you know H z, t.

So, basically this allows us to obtain this small z, t which in turn gives this theta z, t provided this is known. Now, the water flux q may be calculated by this equation where these Z1 and Z2 refers to two given depth of the soil profile. As we have seen this is basically one-dimensional transient vertical flow equation.

Now, this transient vertical flow equation has been described in terms of hydraulic head, in terms of you know volumetric water content, in terms of the in terms of hydraulic conductivity okay and this is how you can obtain those values okay. So, this is one example of deterministic modeling okay.

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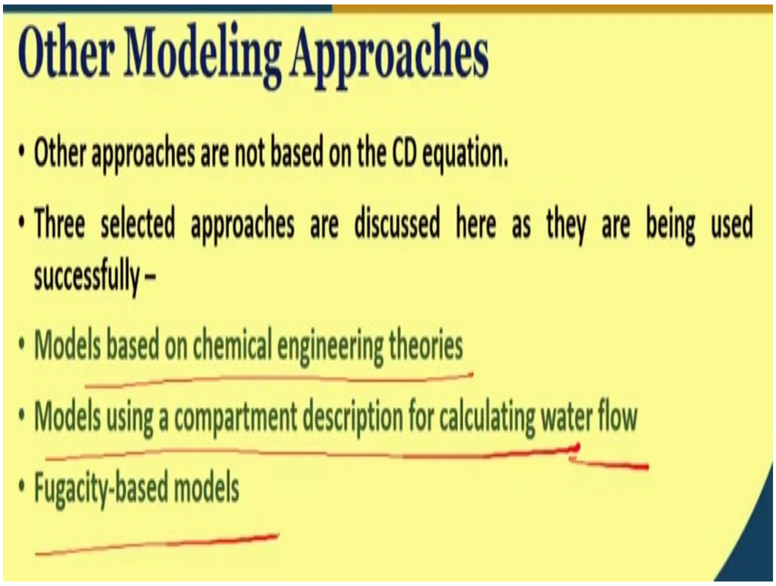

Now, we have discussed the CD equation and what are their forms in case of steady state flow and also transient flow. Let us discuss the other modeling approaches, so the other modeling approaches which are not based on the CD equations. So, basically there are 3 selected approaches which we are going to discuss as they are being used successfully. So, the first one is model based on chemical engineering theories.

Second is models using a compartment decision for calculating water flow and third is fugacity-based models. So, let us discuss first the model based on chemical engineering theories.

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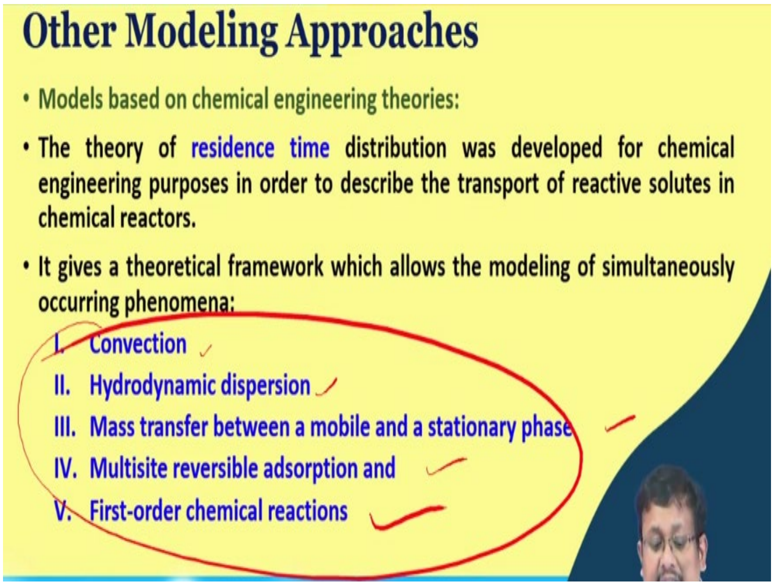

Now, the theory of residence time distribution was developed for chemical engineering purposes in order to describe the transport of reactive solutes in chemical reactors. So, resident time is very important phenomena. So, basically it gives a theoretical framework which allows the modeling of simultaneously occurring phenomena. So those are first of all convection, hydrodynamic dispersion.

Mass transfer between mobile and stationary phase, multisite reversible adsorption and first-order chemical reactions. We have already discussed the first-order chemical reaction and multisite adsorption we have already discussed. So, basically this engineering theories, chemical engineering theories are useful for defining a model based on the residence time and basically it gives a theoretical framework which allows the modeling of simultaneously occurring phenomena.

So, all these phenomena are occurring simultaneously and these chemical engineering based modeling approaches can define all these simultaneously occurring phenomena.

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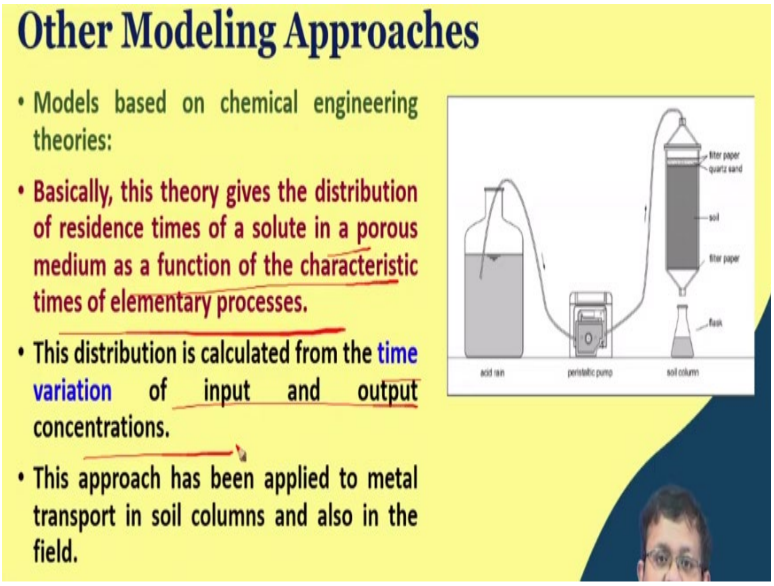

Now, model based on chemical engineering theory. Basically, the theory gives the distribution of resident time of a solute in a porous medium as a function of characteristic time of elementary processes. So, the distribution is basically calculated from the time variation of input and output concentration. Obviously, the time variation of input and output concentration and this approach has been applied to metal transport in soil columns.

So, we can see this is an example of column leaching study where basically different types of solvents are added or different solvents or water basically run through the soil columns to see the movement of different chemical species from one part of the column to other part or in other words how these columns are basically retaining different molecules or species which are present in the solvent.

So, this is how we can calculate. So, this is an example of the models based on chemical engineering theories where we consider the time variation of inputs and output concentrations.

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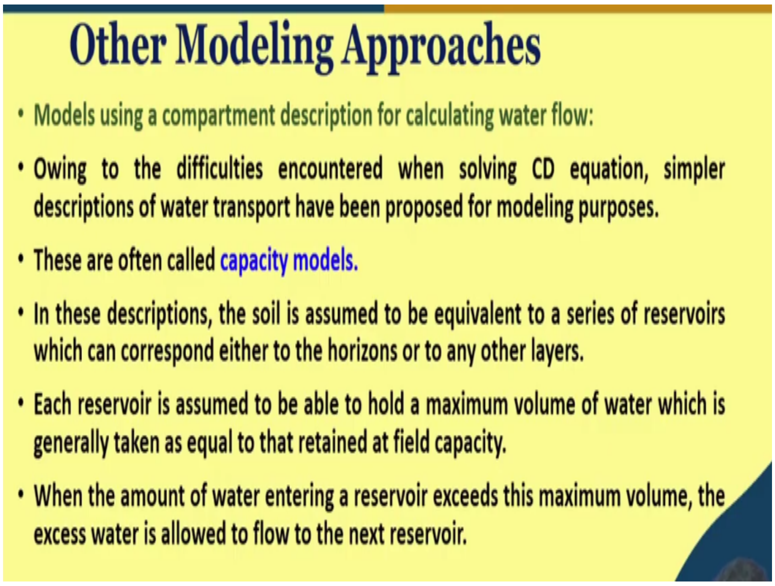

So, the second thing is that models using a compartment description for calculating the water flow now. Now owing to the difficulties encountered when solving a CD equation, simpler description of water transport has been proposed for modeling purposes and they are known as the capacity based models, where we are considering the compartment description. Now, in this description, the soil is assumed to be equivalent to a series of reservoirs.

Which can correspond either to the horizon or to any other layers, so just like if you dig a soil vertically, you will see some horizon. So, these horizons are separated from each other from morphologically and from physiochemically, and similarly we are considering, in this approach we are also considering the soil is assumed to have equivalent a series of reservoirs which can correspond to the horizons or any layers.

Now, each reservoir is assumed to be able to hold a maximum volume of water which is generally taken as equal to that retained at field capacity. Now, when the amount of water entering into the reservoir exceeds this maximum volume, the excess water is allowed to flow to the next reservoir okay. So, this is the basic principle of this compartment models okay.

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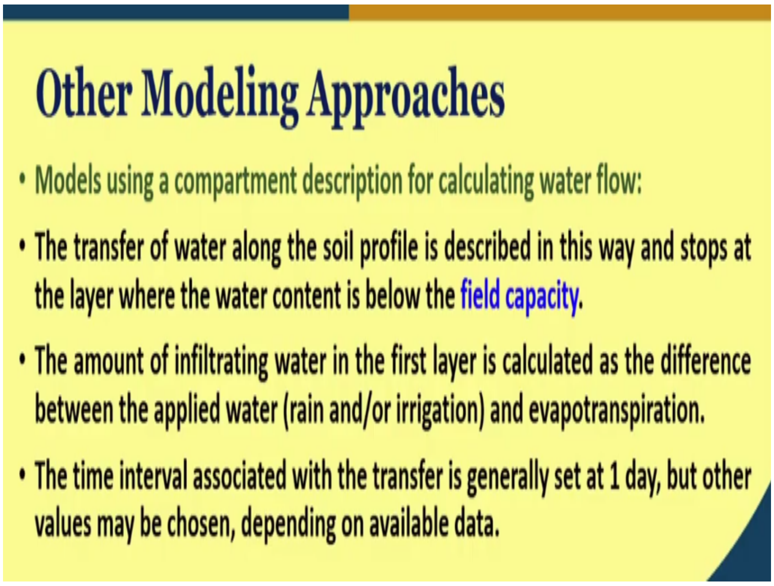

Now, models using compartment description for calculating water flows. Remember the transfer of water along the soil profile is described in this way and stops at the layer where water content is below the field capacity and the amount of infiltrating water in the first layer is calculated as the difference between the applied water in terms of rain or irrigation and the evapotranspiration. So, here the input is rain or irrigation and the output is evapotranspiration.

So, the difference between the supplied water and the evapotranspiration is basically calculated to see the amount of infiltrating water and the time interval associated with the transfer is generally set at 1 day, but other values may be chosen depending on the availability of data. So, generally for simulating this type of model, we generally take a duration of 1 day, however, that duration can be also changed.

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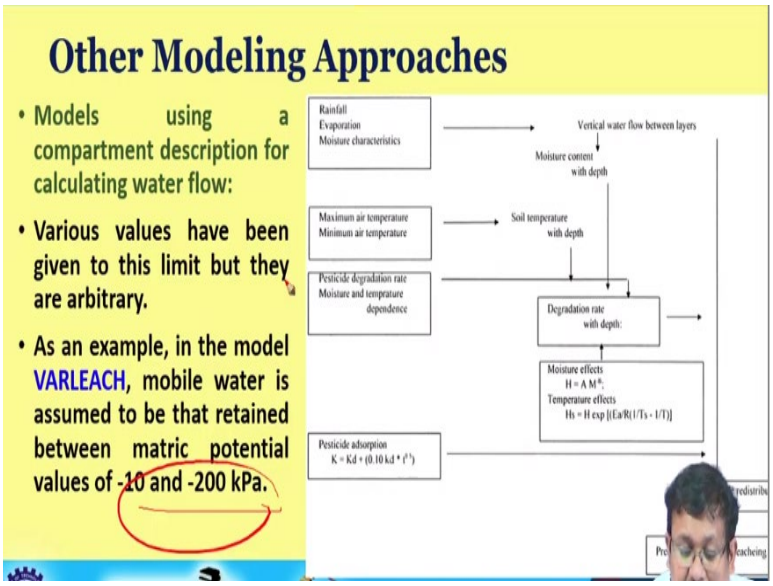

Now, here I am showing a description or flow diagram of a model showing the compartment description for calculating the water flow. Example is this varleach model. This varleach model, this is basically the flow diagram of the operation of the varleach. So, various values have been given to this limit, but they are arbitrary. Now, remember that we are talking about simulating the model output for 1 day. However, this duration can be also changed.

So, this limit can also be you know arbitrary. Now as an example in the model this varleach, mobile water is assumed to be that basically retained between the matric potential of -10 to 200 kilopascal. So, here in this model mobile water is assumed, which is retained between the matric potential of -10 to -200 kilopascal. So, this is the flow diagram of operation of this varleach model you can see here.

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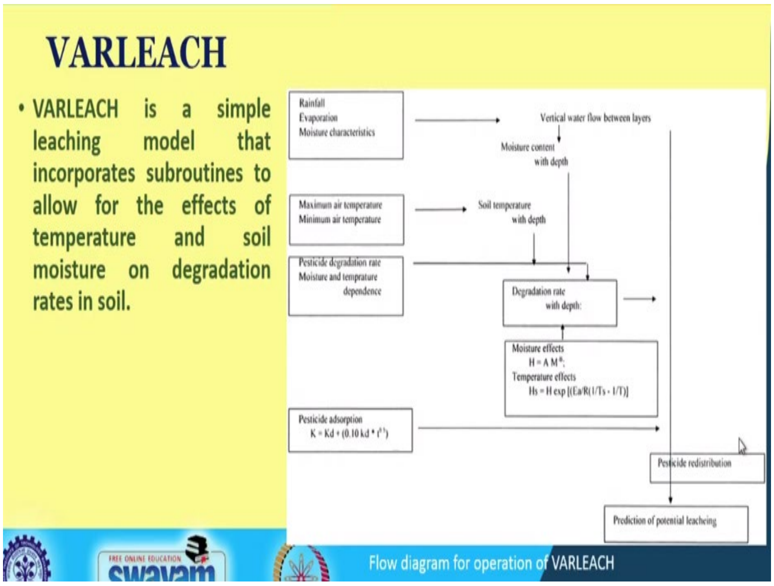

Now, let us see some description of the varleach model. Remember that the varleach model is a simple leaching model that incorporates the subroutine. So, there are different types of subroutines to allow for the effect of temperature and soil moisture on degradation rates in the soil. And what are the benefits of using these varleach model you can see here for example vertical water flow between the earth is affected by this rainfall, evaporation and moisture characteristics.

So, here moisture content you know with depth and also which is affected by maximum air temperature, minimum air temperature, which affects soil temperature with depth and also you can see that ultimately impacts the pesticide degradation rate and also ultimately the pesticides adsorption and prediction of potential leaching of the pesticide. So, this is flow diagram of varleach.

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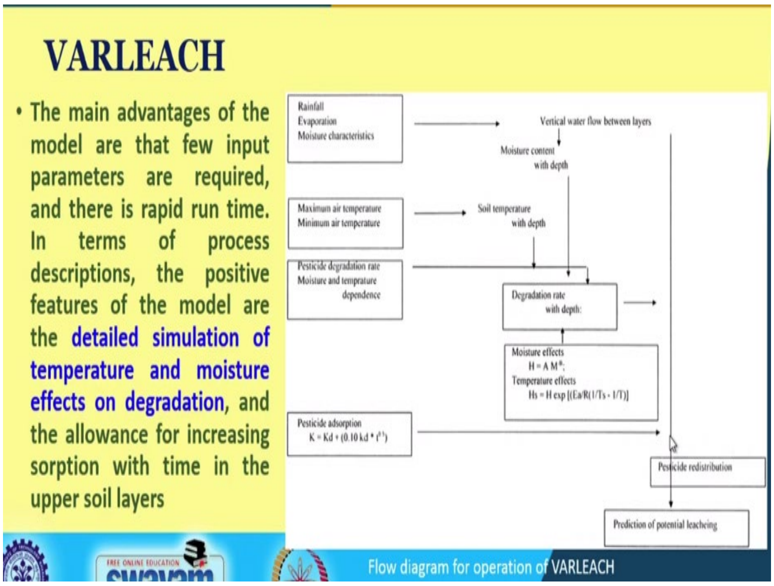

Now, varleach the main advantage of this varleach model is that few input parameters are declared and there is a rapid run time in terms of process description and positive features of these models are the detailed simulation of temperature and moisture effects on degradation and the allowance for increasing sorption with time in the upper soil layers. So, these are some of the advantages of this varleach model.

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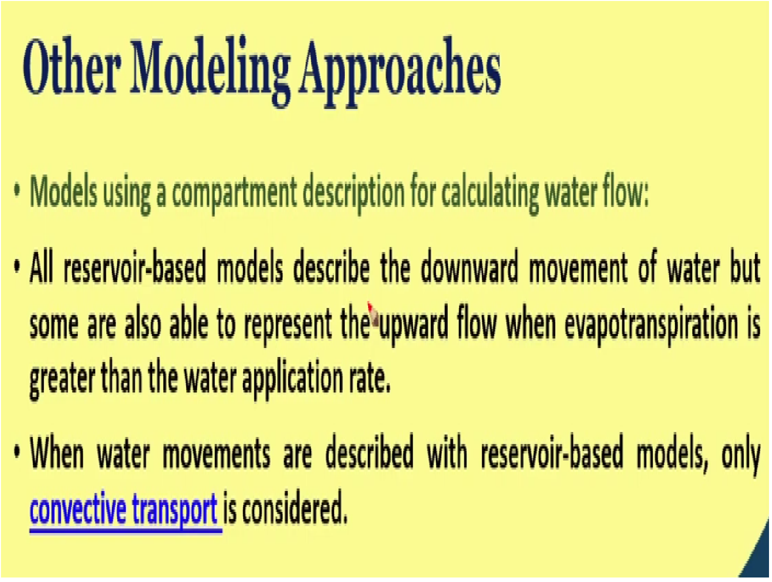

Now, in the other models, for example the models which use the compartment description of calculating water flow, remember that all reservoir-based models describe the downward movement because water always move downwards. So, all reservoir-based models describe the downward movement of water, but some of them are also able to represent the upward movement flow while evaporation, evapotranspiration is greater than the water application rate.

We are applying water either through rain or irrigation water and evapotranspiration is dragging the water upward. So, when the evapotranspiration is greater than that of the application of water, obviously there will be upward movement of water, some reservoir-based models are able to capture that upward movement. Now, when water movements are described with reservoir-based models, only convective transport is considered okay.

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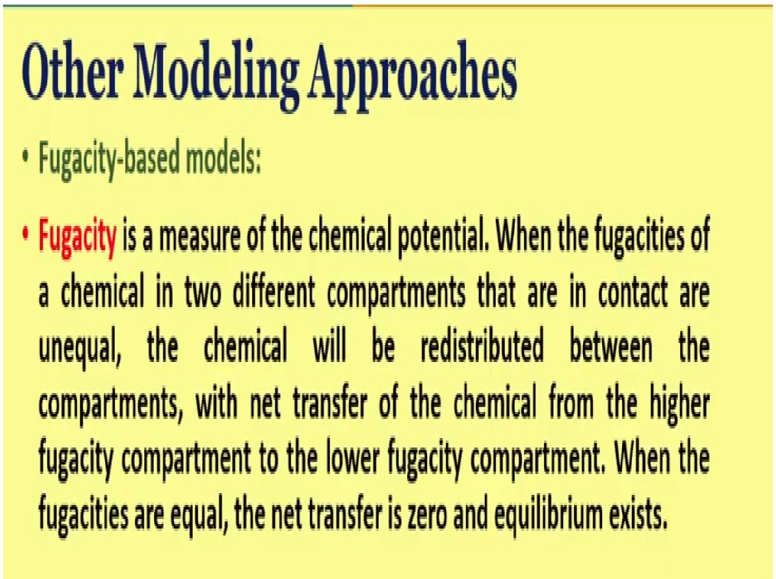

So, the next is fugacity So, fugacity-based models, **is** but before going to the fugacity-based model, let us discuss what do you mean by fugacity. Now, fugacity is the measure of the chemical potential when the fugacities of a chemical into different compartments are in contact are basically unequal to each other, the chemical will be redistributed between the compartment with net transport of chemical from higher fugacity compartment to the lower fugacity compartment.

When the fugacities are equal, the net transfer is zero and equilibrium exists. So, focus fugacity is basically a chemistry term, it is a measure of the chemical potential where fugacities of a chemical in 2 different components are different and they are connected to each other, there will be net transfer of chemicals from higher fugacity to lower fugacity till they attain equilibrium and the transfer will be stopped. So, these are fugacity-based model.

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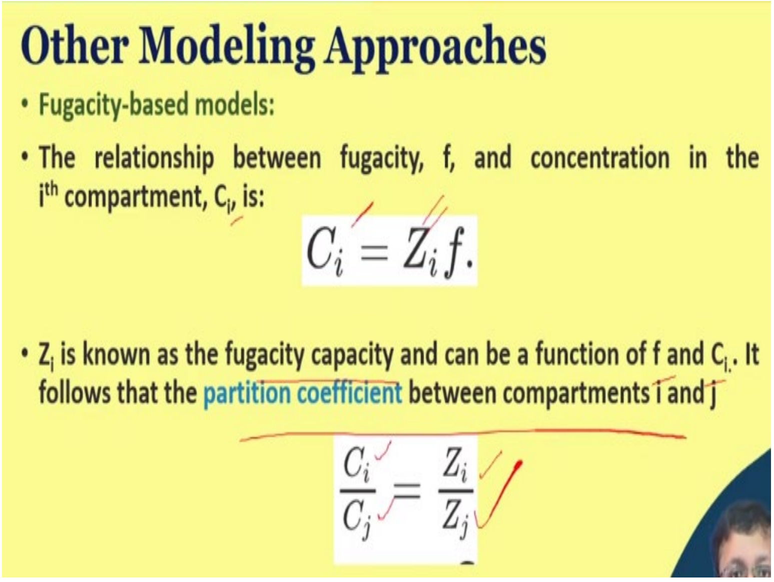

And if you see the mathematical expression of fugacity, so the relationship between the fugacity which is denoted by f and the concentration of ith compartment that Ci, so Ci basically can be calculated as a multiplication of Zi into f. So Zi is basically known as the fugacity capacity and can be a function of both f and Ci. Now it follows the partition coefficient between compartment i and j.

So, if there are 2 compartments, so the ratio of concentration of compartment i and compartment j, it basically the ratio of fugacity capacity in compartment i and compartment j. So, this is a mathematical representation of fugacity-based models. We will see how we can apply that relationship for movement of chemical within the soil. So, let us wrap up our lecture here, and in the next lecture, we will start from here and we will discuss the fugacity-based model.

Then we will discuss the movement through heterogeneous media and also we will be discussing the stochastic model. I hope that you have learned something new in this lecture. If you have any question, feel free to email me, I will be more than happy to answer your queries and let us meet in our third lecture to discuss more on this model of pollutant fate. Thank you very much.