Environmental Soil Chemistry
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Lecture – 53
Modeling the Fate of Pollutants in the Soil, Risks and Remedies Continued

Welcome friends to this third lecture of week 11 of this online NPTEL online certification course of environmental soil chemistry and in this week or in this module we are talking about modelling the fate of pollutants in the soil and their risks and remediations.

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So in our previous two lectures we have covered these following concepts. So we have covered the overview of the models, we have discussed the models. Then we have discussed the classification of the models and then we have discussed different types of models and deterministic and stochastic model, we gave you the basic overview of the deterministic and stochastic model. Then we started discussing deterministic models.

So today, we are going to finish the deterministic models. We have already covered the models which are following the CD equation and the models which are following the compartment theory as well as we have completed those models which are following the chemical engineering principles. So today we are going to finish the deterministic model and then we will be talking about the transport in heterogeneous media, sink or source phenomena.

And also we are going to talk about the stochastic model, and if time permits we will be covering also the problems connected with the modeling and then model sensitivity and model validation. So, let us start today’s topic.

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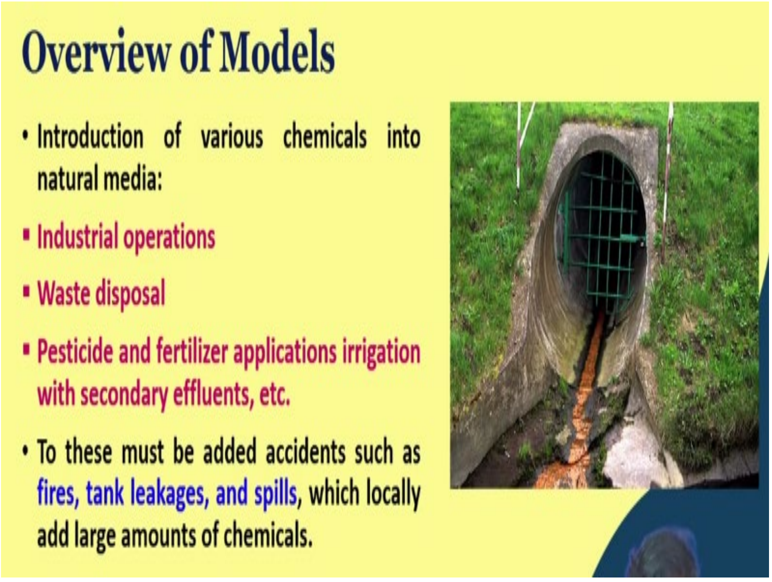

But before going to the today's topic I just want to give you a quick recap of whatever we have covered in the last lecture.

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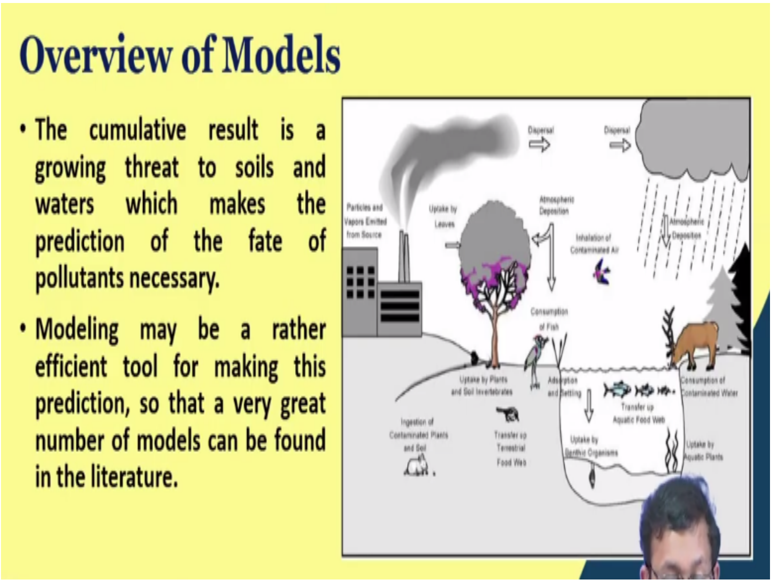

So, overview of the models we have covered that.

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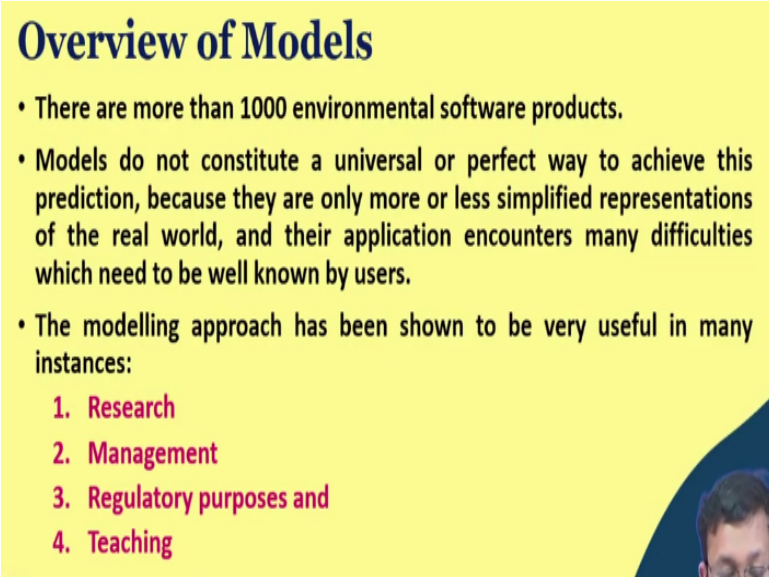

What different types of modeling approach we generally follow either it is a research model or management model or regulatory purpose or teaching purpose we have also discussed.

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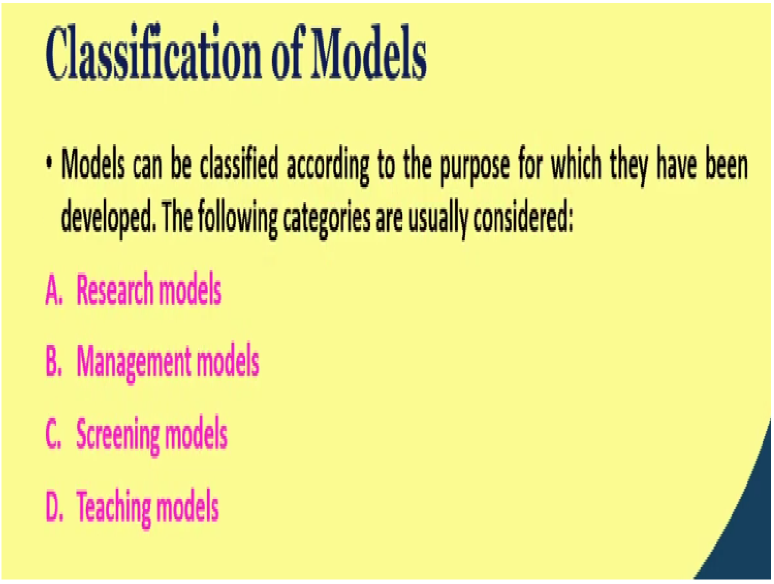

And then the classification of model. Remember there are 4 types of models. One is research model, one is management model, screening models and teaching models and each of them have their own function. Remember the research model is the most complex followed by management models than screening model and teaching model. Teaching model are generally used for teaching the students.

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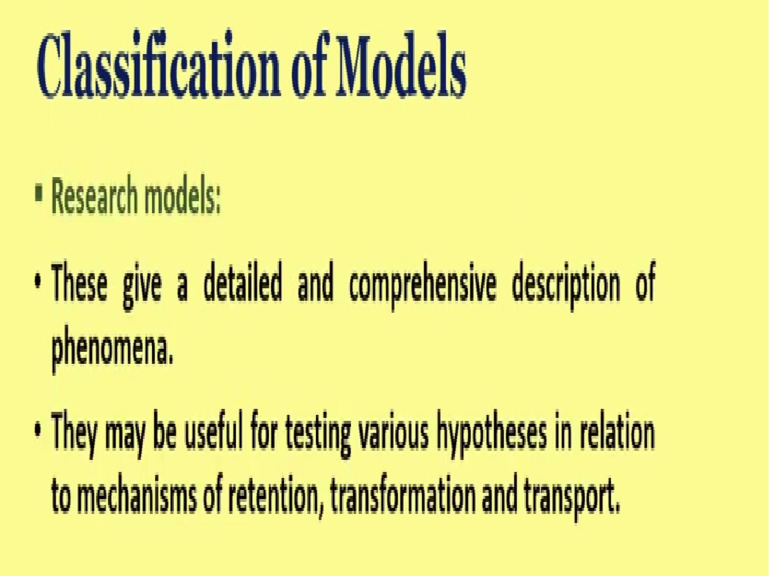

Whereas the research models are used with strict assumptions with accurate measurement of different parameters and inputs.

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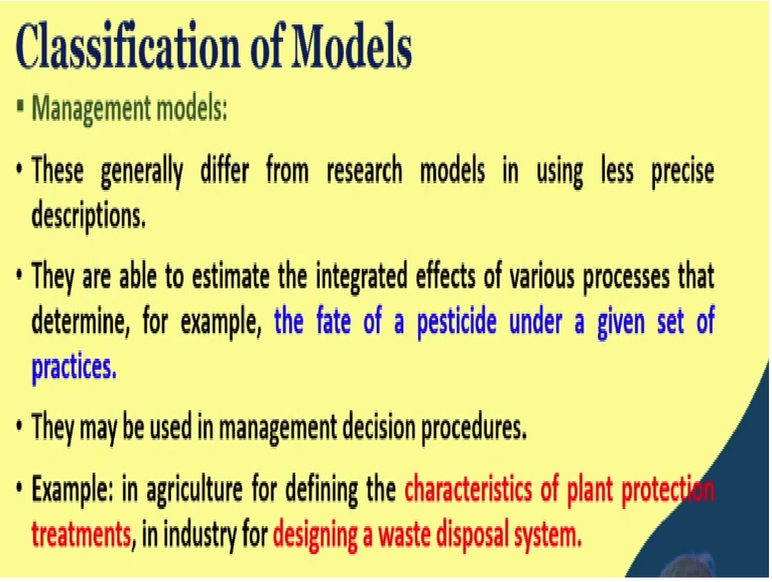

So we have covered these 4 different types of models.

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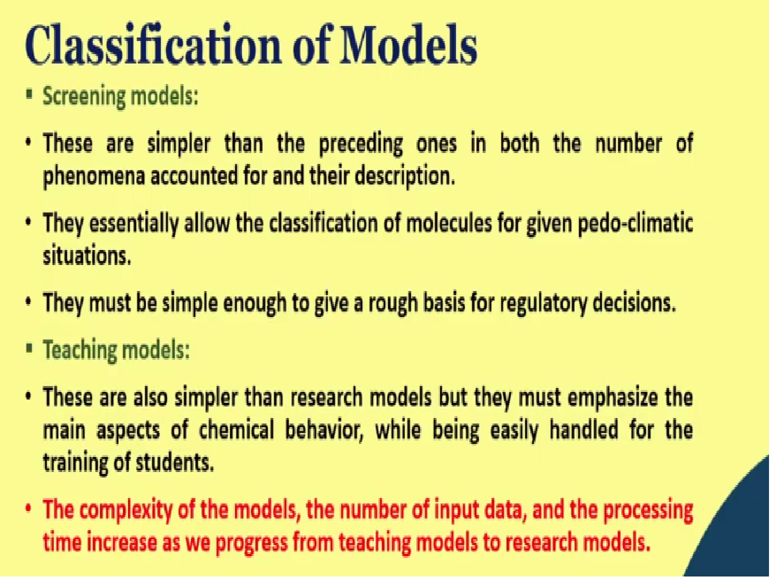

Remember that for management models it is generally used for management decision procedures.

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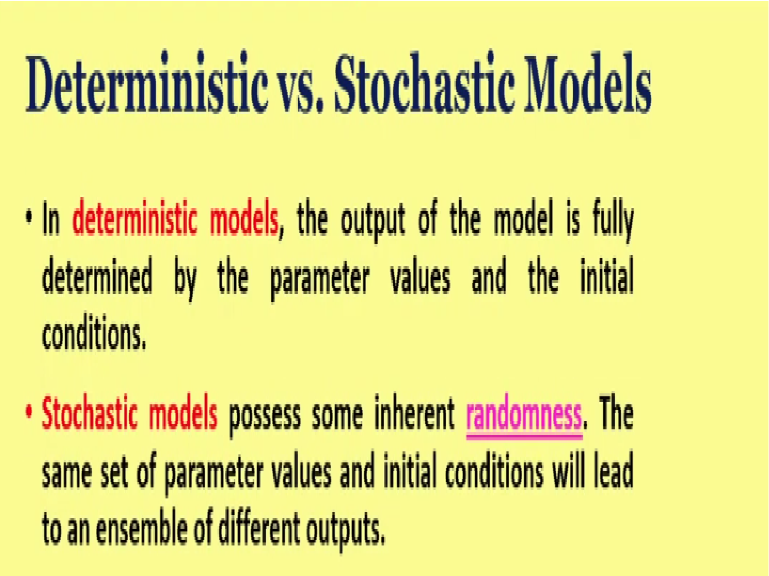

Also we have covered this deterministic and stochastic model. Remember the major characteristics of the stochastic model is the randomness.

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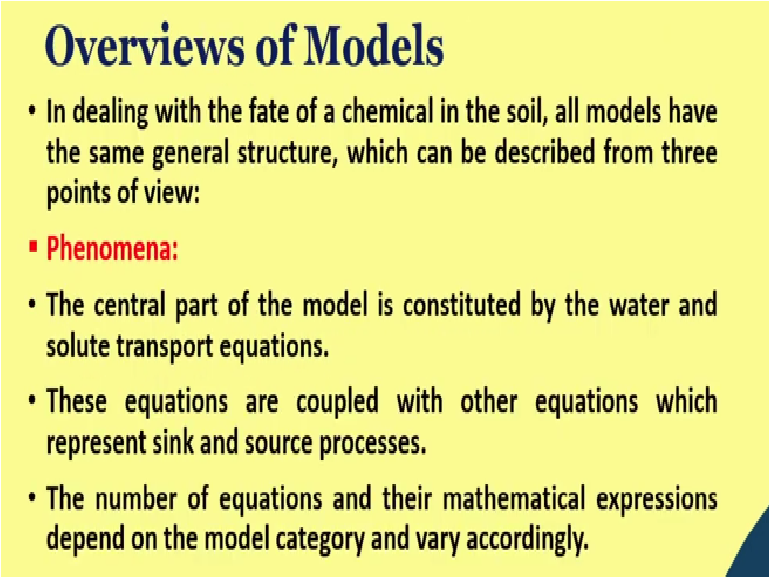

Then we covered the phenomena which is one of the major aspects of this pollutant phase fate models.

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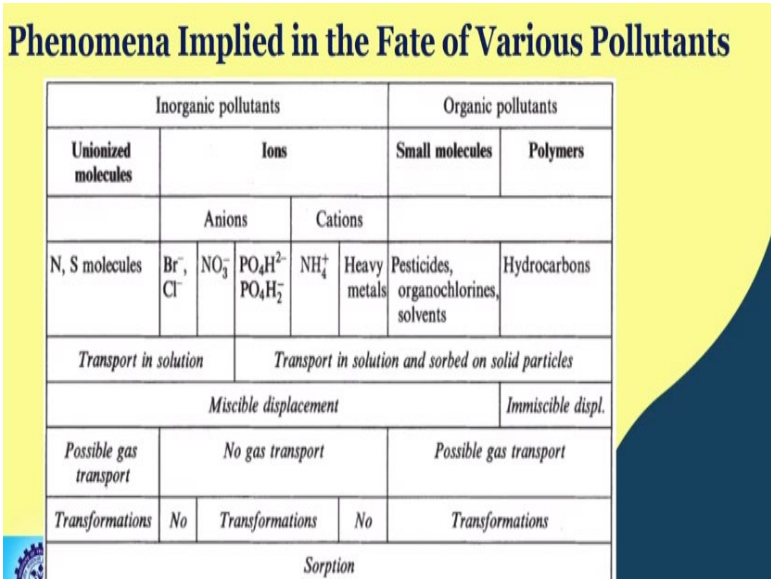

And then we discussed this phenomena implied in the fate of various pollutants. We have divided the pollutants the inorganic pollutants and organic pollutants. Then we have discussed different phenomena.

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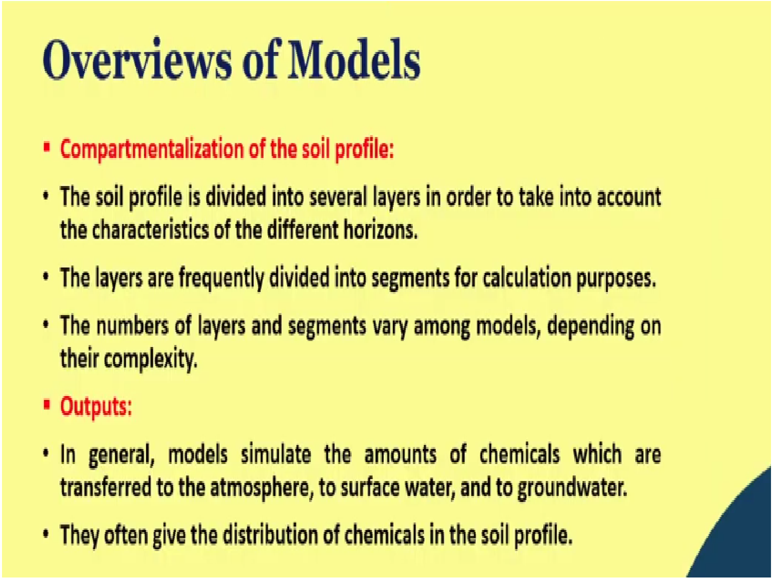

Then we have also discussed this compartmentalization of the soil profile and also the outputs.

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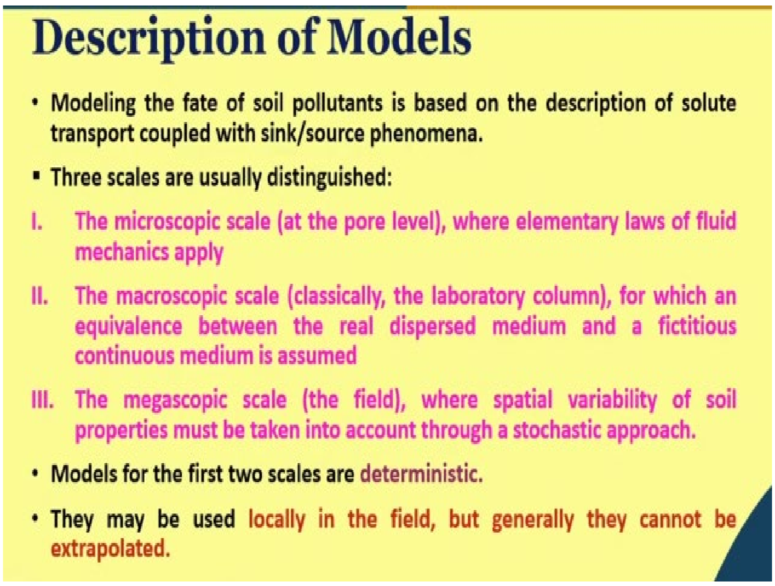

Then we have also discussed the description of the models. Remember we have described the models in terms of 3 different scales. One is microscopic scale which is at the pore level. Then macroscopic scale which is at the laboratory level and then megascopic scale in the field. Remember this microscopic scale and macroscopic scales are basically deterministic in nature.

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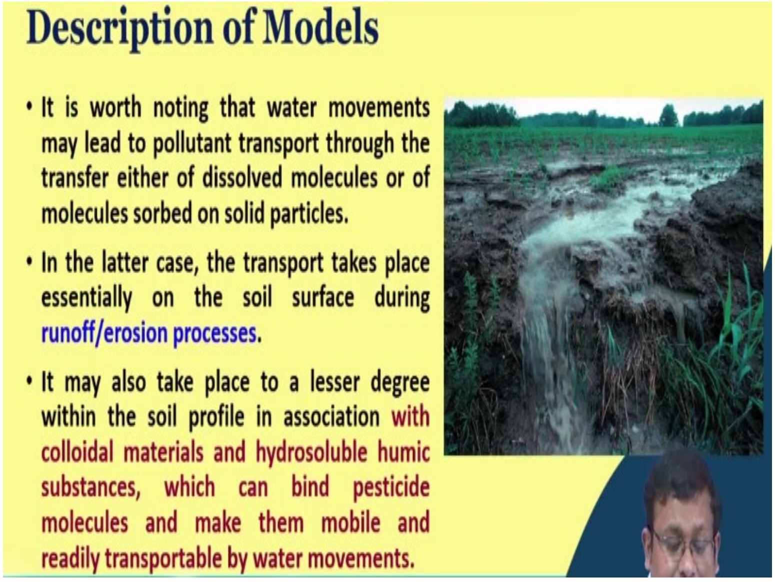

Then, we have described the models.

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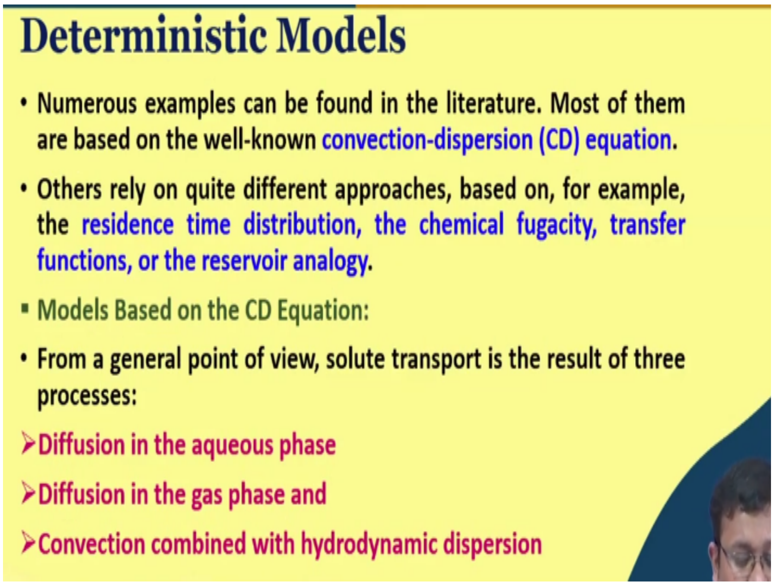

Different types of transport processes we have described for deterministic models.

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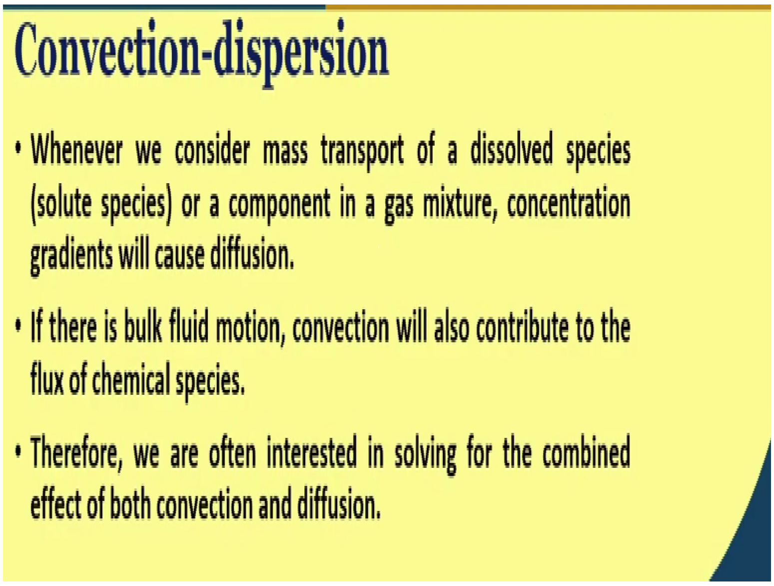

Then we have discussed this convection-dispersion process, how they are coupled together.

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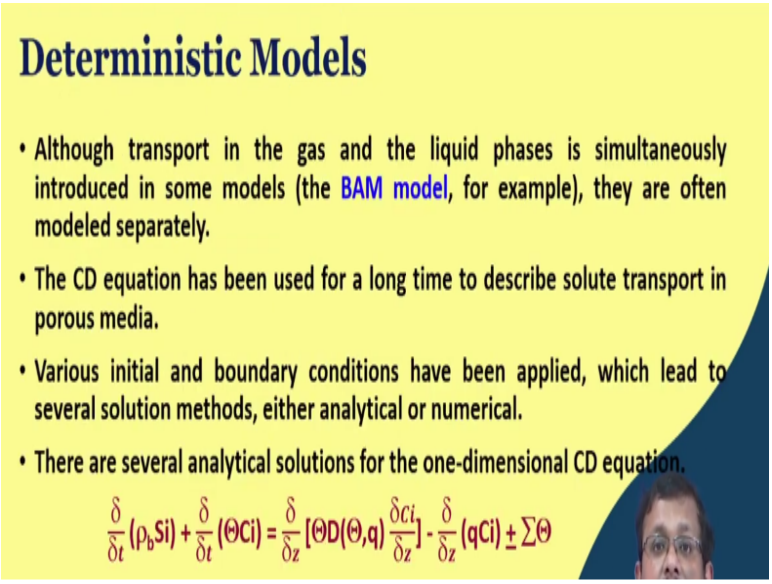

And based on this convection-dispersion phenomena, how we can represent a model one-dimensional CD equation.

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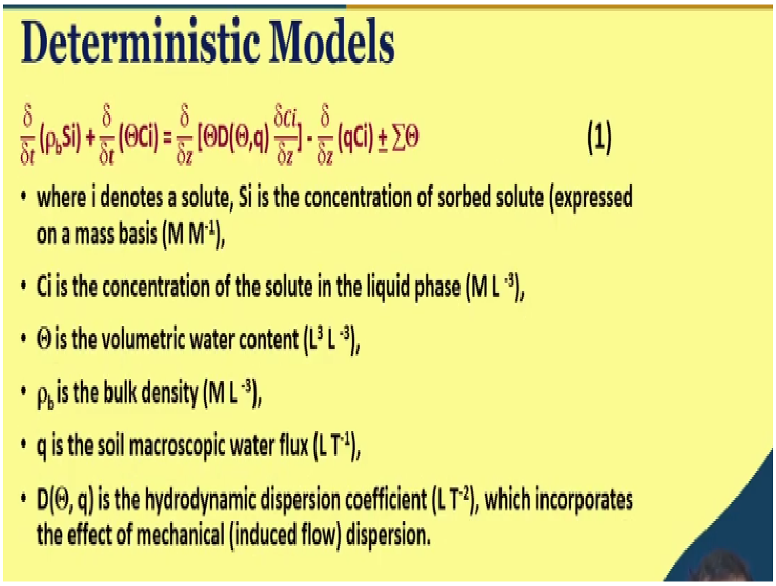

Then we have discussed the CD equation, convection-dispersion equation.

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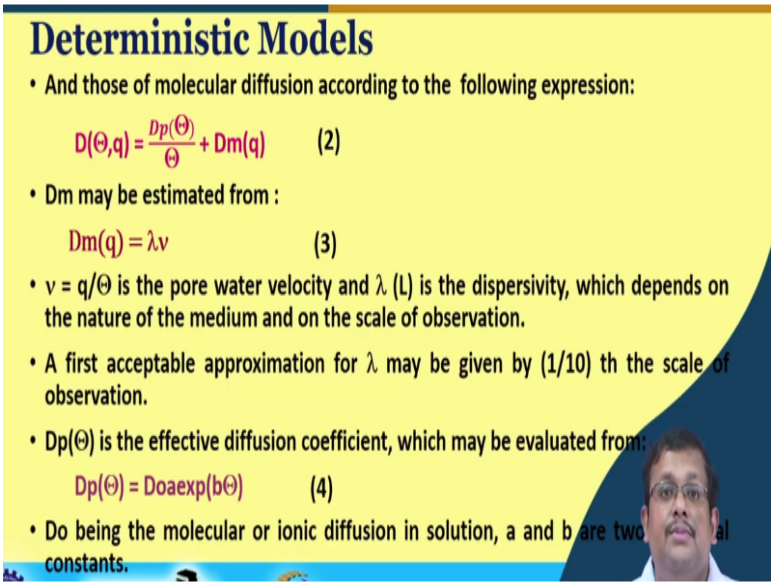

We have defined each of the terms.

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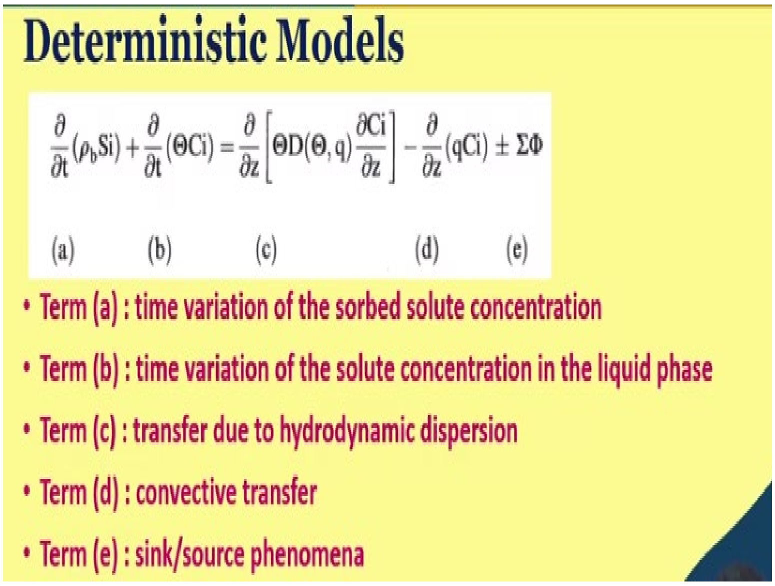

So please go through this in very carefully.

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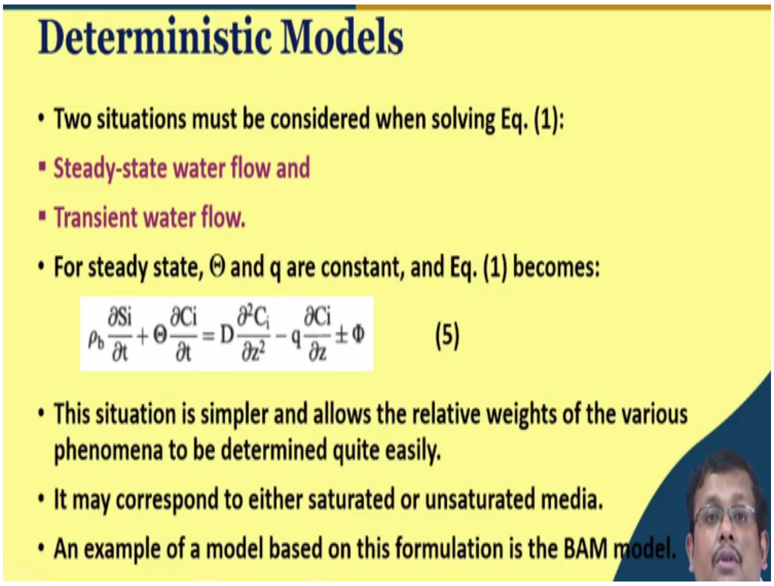

Then we have also defined what is steady state flow and what is the transient state flow/

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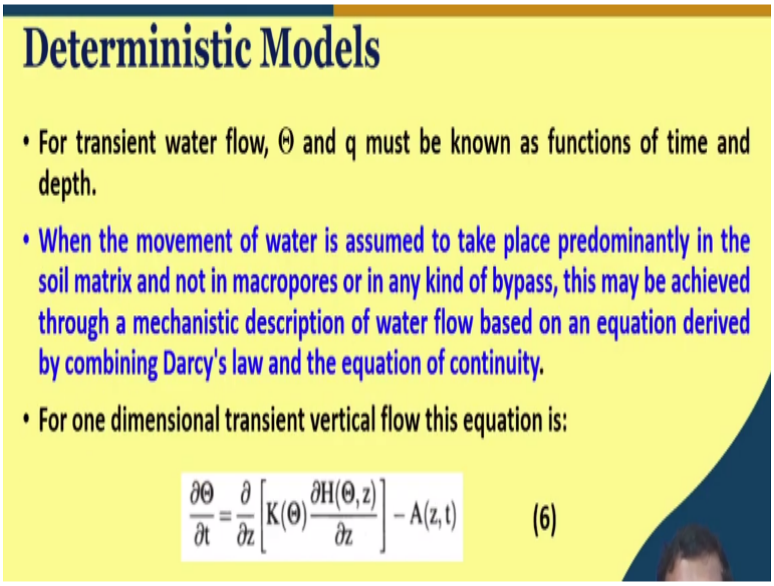

we have defined all these things.

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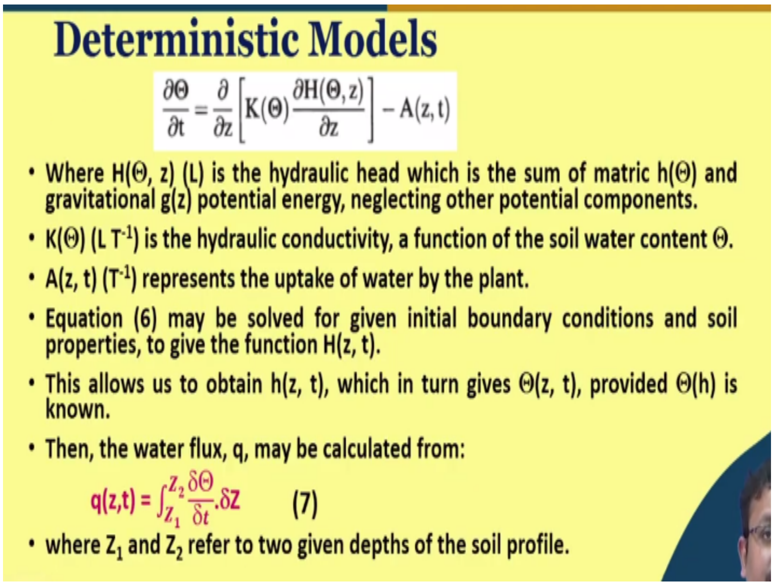

So once we covered the CD based models, then we have also covered the other modeling approaches.

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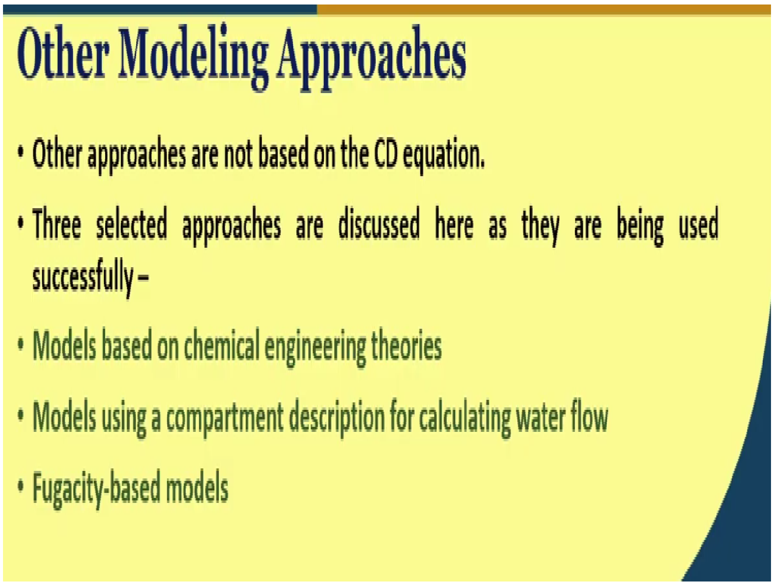

Like model based on chemical engineering theories and model using compartment description for calculating the water flows. We have covered both of these and today we are going to start with the fugacity-bases models. So we have all these covered, compartment based models we have covered in our last two lectures.

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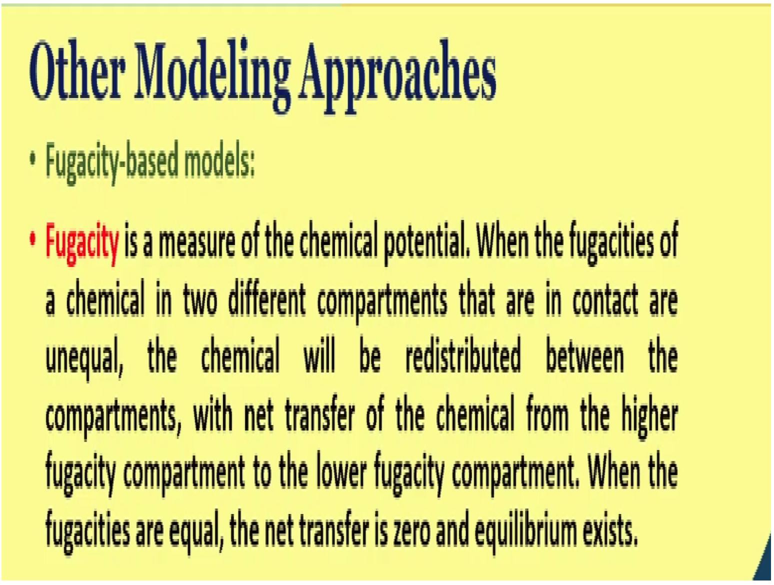

Today, we are going to start the fugacity-based model. Now remember that fugacity is a chemical term. It is basically measure of the chemical potential. Now when the fugacities of a chemical in 2 different compartments that are in contact, so consider there are 2 compartments which are in contact.

So if the fugacities of the chemical which are divided into 2 different compartments which are in contact are unequal, then chemical will be redistributed between the compartments with net transfer of the chemical from higher fugacity compartment to the lower fugacity compartment. Now when the fugacities are equal, the net transfer at zero and equilibrium exists.

So basically, there is a gradient of fugacity from one compartment to another compartment and that basically helps the flow of chemical from one compartment to another compartment.

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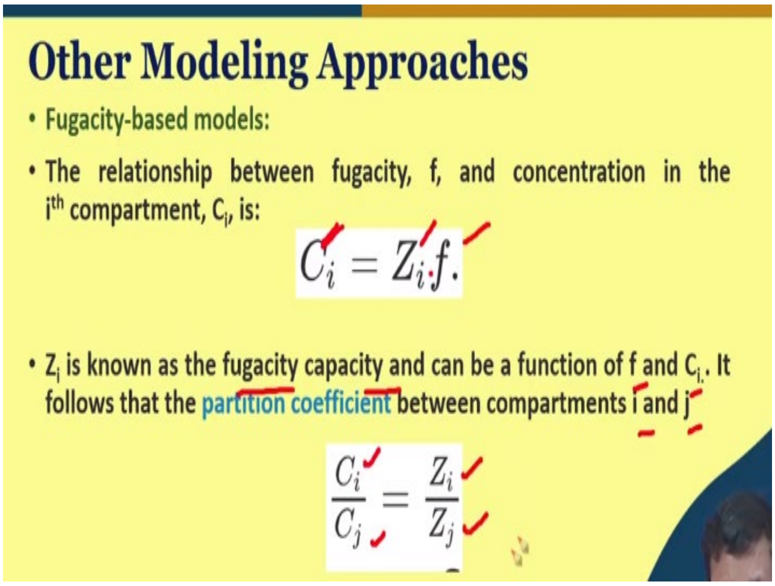

Now if we want to represent the fugacity-based model in terms of mathematics, then we have to discuss is formula. Now remember that the relationship between the fugacity which is basically denoted by small f and concentration in the ith compartment, let us consider there is an ith compartment concentration in the ith compartment if I consider that at Ci, then Ci can be expressed in terms of Zi multiplied by f where this Zi is known as the fugacity capacity and can be a function of both f and Ci.

So basically, this fugacity capacity of Zi is basically function of fugacity as well as the concentration in the ith compartment. Now it follows the partition coefficient between the compartment i and j. So if there are 2 compartments, compartment i and compartment j, then we can deduce this relationship that is Ci by Cj = Zi by Zj. So, this is basically following the partition coefficient between the 2 compartments.

So this is basically the general mathematical representation of the fugacity when 2 compartments with different fugacity of chemicals are attached or in contact.

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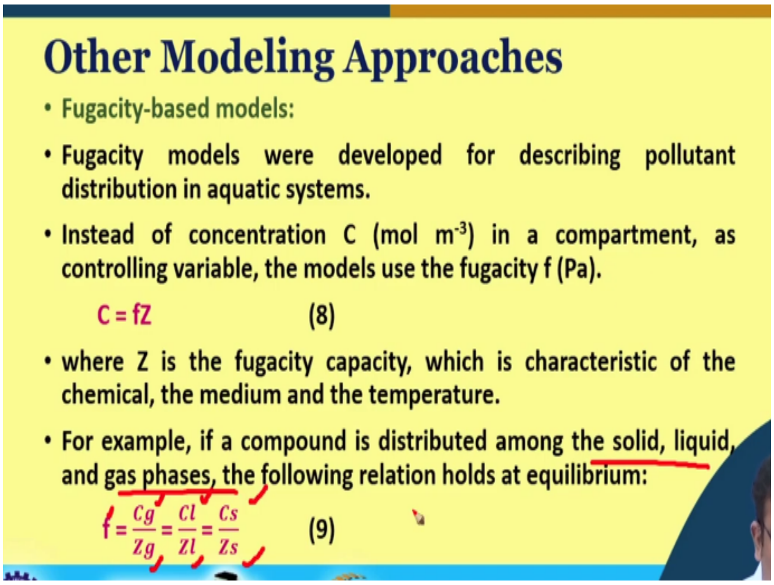

Now what are the fugacity-based models. Now fugacity-based models were developed for describing the pollutant distribution in aquatic system generally. Now instead of concentration C in a compartment as controlling variable, the model use basically fugacity in terms of pascal. So generally, we have already seen this equation that is C = fZ where Z is the fugacity capacity which is the characteristics of the chemical, the medium and the temperature.

Now for example if a compound is distributed among the solid, liquid and gas phases. So let us consider that a compound is distributed among the solid, liquid and gas phases, then the following relation holds at equilibrium, what is this relationship? That is f that is fugacity equal to concentration in gaseous phase by fugacity capacity in the gaseous space which is also equal to the concentration the liquid phase by liquid fugacity capacity in the liquid phase and then concentration in the solid by fugacity capacity in the solid.

So this relationship holds when a compound is distributed among the solid, liquid and gaseous phases, then we can represent this fugacity in terms of this relationship for these 3 medium.

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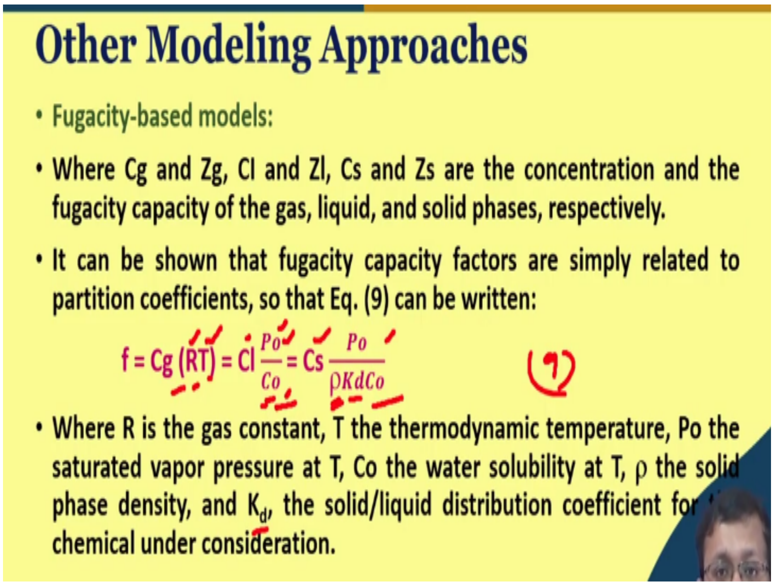

Now where in this case we have already discussed that Cg and then Zg, Cl and Zl, Cs and Zs are the concentration and the fugacity capacity of gas liquid and solid phases respectively. Now it can be shown that fugacity capacity factor or Z are simply related to the partitioning coefficient. So that a new equation, equation 9, let us consider this equation 9. So this equation 9 shows this fugacity = Cg multiplied by RT

Which is also equivalent to Cl multiplied by Po by Co which is also equivalent to the Cs multiplied by Po by rho KdC0, where now remember that these 3 conditions are for 3 different medium, one is here it is for gaseous medium, this is for liquid medium and this for solid medium. Now in this gaseous medium we can represent the fugacity as the Cg that is concentration at compartment and RT.

R you know that is gas constant and T is the thermodynamic temperature and Cl you already know that is the concentration of the liquid and p0 is basically the saturated vapor pressure at T and C0 is the water solubility at T and here this rho is basically the solid phase density and Kd is basically the solid-liquid distribution coefficient. We have already discussed distribution coefficient in our previous lecture, so distribution coefficient for the chemical under consideration.

So you can see that this fugacity term can be expressed in terms of different types of partitioning coefficients okay. So for example this Kd is the solid-liquid distribution coefficient. So this is how we can simplify the fugacity in 3 different medium for solid, liquid and gaseous phases okay and this fugacity relationship is basically followed in this fugacity-based model, which are generally applied for pollutant transport in the aquatic system.

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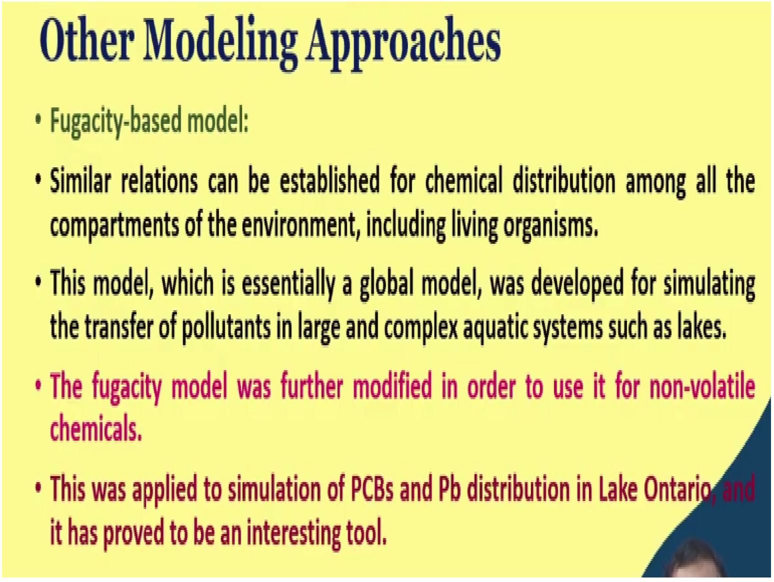

Now similar relationship can be established for chemical distribution among all the compartments of the environment including the living organism. Now this model, this fugacity-based model which is essentially a global model was initially developed for simulating the transfer of pollutants in large and complex aquatic systems such as lakes. Now, the fugacity model was further modified in order to use it in non-volatile chemicals.

So this was applied to simulate the polychlorinated biphenyls and lead distribution in lake Ontario and it has proved to be an interesting tool. So this is how its application was enhanced in subsequent research and subsequent applications. So this fugacity-based model again it is following the law of fugacity and from different compartments which are in contact to each other and there is a fugacity gradient and through which the chemical move from higher fugacity to lower frequency okay.

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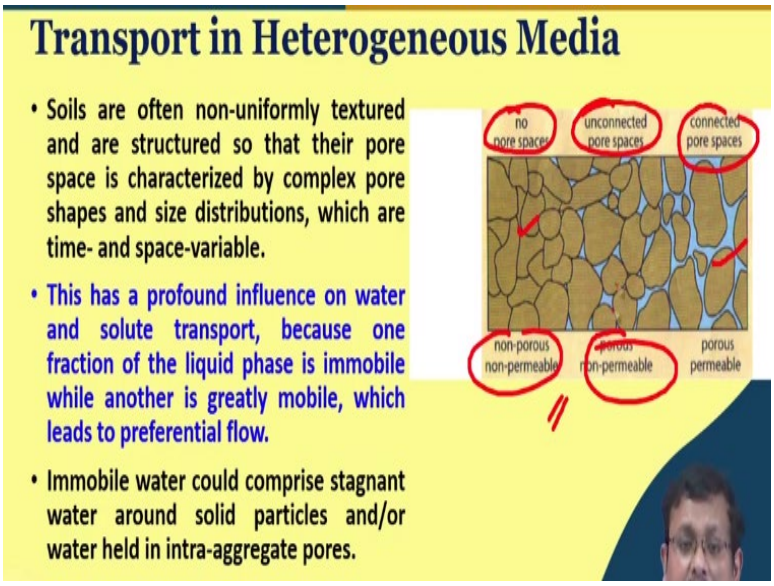

Now, let us talk about the next important topic that is transport in heterogeneous media. Now you know that soil is a very complex heterogeneous mixture. It has got both micropores and macropores and these pores are also interrelated, so it basically a very complex network of pores and also the solid and liquid phases. So soils are often nonuniformly textured and are structured.

So their pore space is characterized by complex pore shape and size and distribution, which are time and space variable obviously. Now this has a profound influence on water and solute transport because one fraction of the liquid phase is immobile while other greatly mobile which leads to preferential flow. So what is preferential flow? We will just see in our coming slides.

But remember that since soil is a heterogeneous mixture and it has a complex network of pores and then structure and different phases, so basically it generally allows the liquid for going for a preferential flow. because sometimes the water is immobile. Now immobile water could comprise stagnant water around the soil particles and or water held in intra-aggregate pores. So let us see, so you can see here there are three, you know this is basically showing the soil pores.

So you can see that connected pore spaces which is a very porous permeable soil and here you can see the unconnected pore spaces. So these are unconnected pore spaces, which is porous but nonpermeable and here in this situation you can see these are no pore spaces, so basically it is nonporous and nonpermeable. So you can see that in one soil this condition may arise because these distributions are space variable.

So you can see in one soil these 3 different conditions depending on different places of the soil profile. So you can see here one is the porous permeable where the connected pores are there, unconnected pore species with porous nonpermeable and the no pore space and nonporous nonpermeable, 3 different conditions. So this is how there is a preferential flow of water and let us see what is preferential flow of water.

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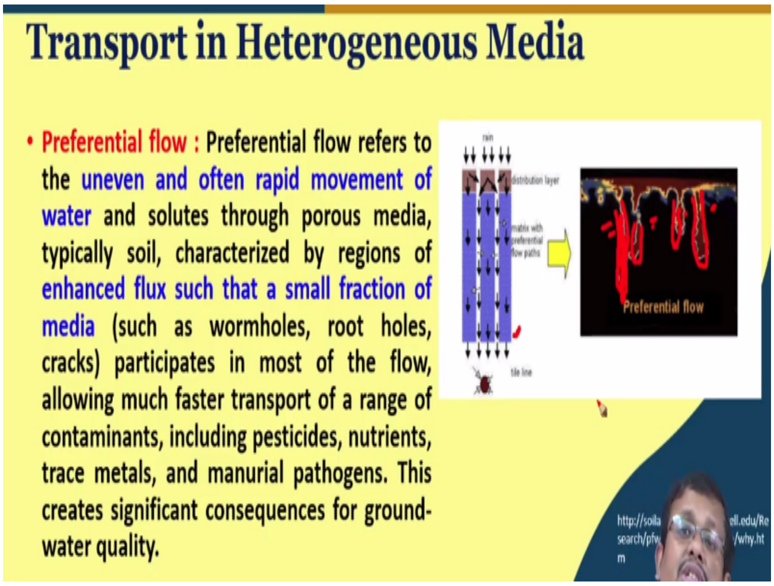

So the preferential flow refers to the uneven and often rapid movement of water and solutes through porous media. Now typically soil which is characterized by region of enhanced flux such that a small fraction of media such as wormholes, root holes or cracks participates in most of the flow allowing much faster transport of a range of contaminants including pesticide, nutrients, trace metals and manurial pathogens.

This creates significant consequences for groundwater quality, how let us see. So here you can see that this is showing the preferential flow. So basically, if there is a distributing layer so you can see matrix of preferential flow path when there is a rainfall, so there are some distribution layers. So obviously the matrix of preferential flow paths are given in this green zone okay.

So similarly, you can see when there is a rainfall the liquid is moving, the soil water is moving in these particular areas more rapidly than the surrounding areas. So you can see there is a preferential flow in these zones, so this is called the preferential movement. So this preferential flow reference we can see this is an uneven and often very rapid movement of water.

And when there is a movement of water, obviously solutes and pesticides also move with them enhancing the flux such that a small fraction of media such as, so this preferential flow may be created by wormholes or root holes because root move into the soil and then provide the holes and cracks. So they participate in most of this preferential flow much faster transport of the contaminants including pesticides, nutrients, trace metals and manurial pathogens and this preferential flow has a significant consequence in the pollutant transfer.

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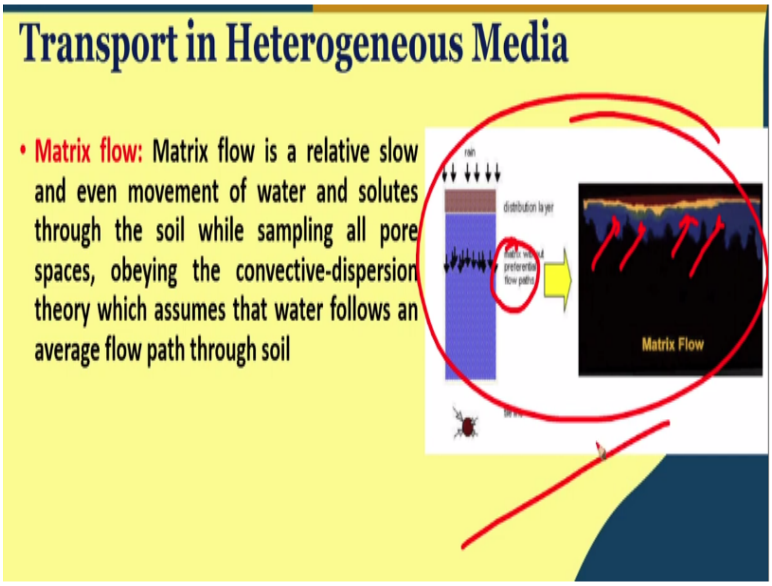

So the opposite to the preferential flow is the matrix flow. Now matrix flow is a relative slow and even movement of water and solutes to the soil while sampling all pore spaces, obeying the convective-dispersion theory which assumed that water flows an average flow path through the soil. So you can see here, clearly you can distinguish this the distribution layer and there is a matrix without preferential flow path.

You cannot see any preferential flow path, the water is moving uniformly through this zone. So for example you can see there is no preferential flow, the water is moving uniformly. So this is an example of matrix flow. So you know you can understand what is the difference between preferential flow and matrix flow. Preferential flow always gives higher movement of different contaminants in particular zones of soil as compared to the matrix flow which is more or less uniform movement.

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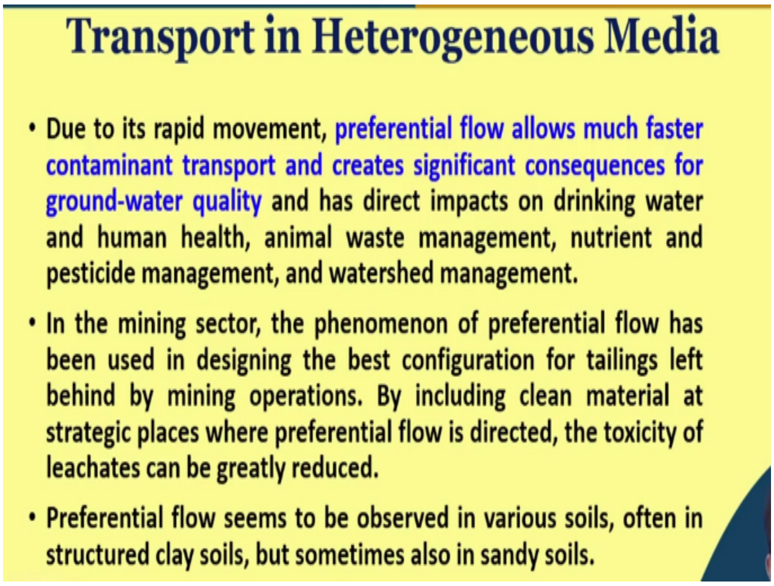

Now due to its rapid movement, this preferential flow allows much faster contaminant transport and creates significant consequences for ground water quality obviously because they have much faster contaminant transport due to this wormholes, due to these root cracks and all these things okay and they have direct impact on drinking water and human health, animal waste management, nutrient and pesticide management and watershed management.

So obviously you know that all these things leach down to the soil and also sometime go to different water bodies or mix into the ground water to create the problem. So this is the problem of which basically problem of pollutant transport which is created by preferential flow. Now in the mining sector, the phenomena of preferential flow has been used in designing the best configuration for tailing left behind by mining operations.

So you know after mining you just leave the tails, mine tails. So you can better management this mine tail if you consider this preferential flow. So if you put this mine tailing in a better way, then by including clean materials at the strategic places where preferential flow is detected, the toxicity of the leachates can be greatly reduced, obviously because when there is a leachate through this mine tailing obviously it carries different types of toxic metals and sometimes some organic chemicals also.

However, better management by considering this preferential flow by putting some clean materials on those places, then you can have a better management of the leachate and consequently better management of pesticide and other you know environmental contaminant transport. Now preferential flow seems to be observed in various soil, often in structured clay soils, but sometimes also in sandy soils.

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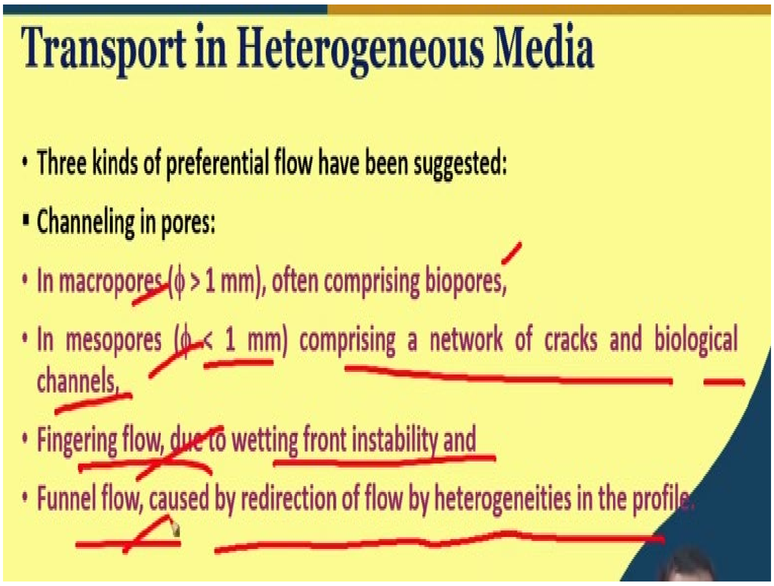

Now, there are 3 kinds of preferential flow have been suggested. One is channeling in pores. So channeling in pores you can see it is greater than 1 millimeter, then which often comprising the biopores. In mesopores which is less than 1 millimeter which is comprising a network of cracks and biological channels and fingering flow, we have already seen the fingering flow due to wetting front instability.

And funnel flow which is caused by redirection of flow by heterogeneities in the profile. So this is how the preferential flow occurs through this 4 different ways. One is macropores, mesopores, fingering flow and funnel flow.

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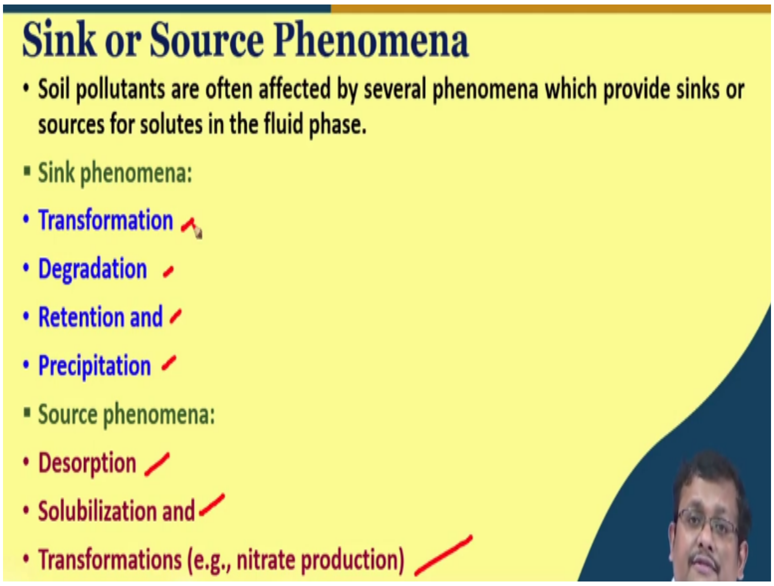

So we have completed the deterministic model, we have completed the movement through heterogeneous media and then let us consider the sink and source phenomena. Now soil pollutants are often affected by several phenomena okay which provides the sink or sources for solute in the fluid phase. So what are the sink phenomena, now by seeing we generally indicate the different final outputs and source means the sources.

So let us see in that pollutant transport and fate models what are the different sink phenomena and source phenomena. Now in the different sink phenomena of transformation, degradation, retention and precipitations are important. However, in different source phenomena this desorption, solubilization and transformation that is for example nitrate production these are very, very important and all these are playing an important part in the description and execution of the pollutant fate and transport models.

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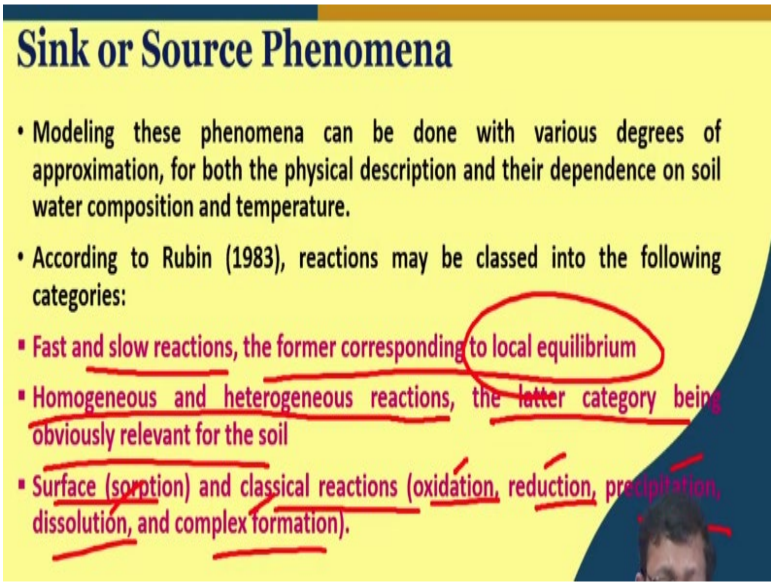

Now modeling the sink and source phenomena can be done with various degrees of approximation or both the physical description and their dependence on soil water composition and temperature. Now according to the scientist Rubin, reactions may be classed into the following categories. We can see there are some fast and slow reactions, the former corresponding to the local equilibrium.

Some homogeneous and heterogeneous reaction, the latter category being obviously relevant for the soil and surface sorption and classical reaction that is oxidation, reduction, precipitation, dissolution and complex formation. So surface and classical reaction obviously includes this oxidation, reduction, precipitation, dissolution and complex formation. So these are different types of sink and source phenomena encountered in the pollution fate transport.

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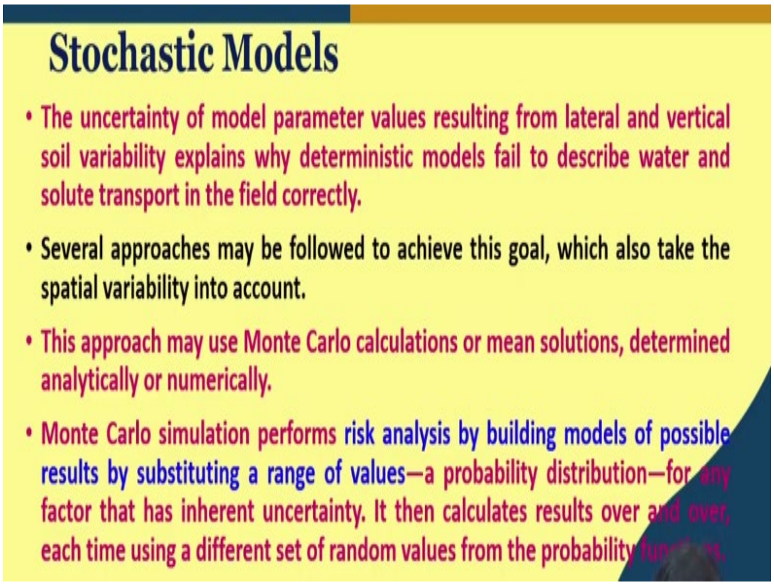

Now let us see what are the stochastic models. Now we have already seen the basic difference between the deterministic model and the stochastic model. Remember the stochastic model is characterized by a sense of randomness. Now the uncertainty is one of the major you know part of the stochastic model.

So uncertainty of model parameter values resulting from lateral and vertical soil variability explains why deterministic models fail to describe water and solute transport in the field correctly. So basically due to the uncertainty of the model parameter values resulting from different lateral and vertical soil variability, we have just seen preferential flow. So obviously there are some variability, there are some pressure variability, so that is why there are some preferential flow.

So due to this variation, due to this heterogeneous nature of the soil, deterministic model often fails to describe the water and solute transport in the field correctly. Now several approaches may be followed to achieve this goal which also takes the special variability into account. So these approach may use the Monte Carlo simulation or mean solution, determined analytically or numerically. Now what is Monte Carlo simulation?

Now Monte Carlo simulation is basically a mathematical procedure which performs the risk analysis by building models of possible results by substituting a range of values. So basically, a probability distribution for any factor that has inherent uncertainty. So, it then basically calculates results over and over each time using a different set of random values for the probability functions.

So again this Monte Carlo simulation performs basically the risk analysis by building models of possible results by substituting a range of values which is basically a probability distribution for any factor that has you know inherent uncertainty, some factors haver inherent uncertainty, so basically they provide the probability distribution and build the models over and over.

So basically it then calculates the results over and over each time using a different set of random values and the probability functions. So this is called Monte Carlo simulation.

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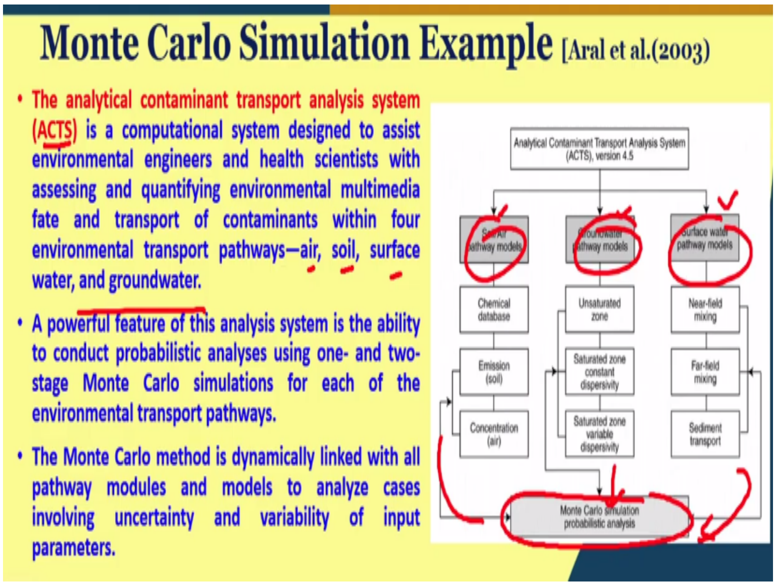

Now let us see one example of the Monte Carlo simulation and this is what actually published by this Aral et al in 2003 and they have actually proposed analytical contaminant transport analysis system. They have named that ACTS which is basically computational system designed to assist the environmental engineers and health scientists with assessing and quantifying environmental multimedia fate and transport of contaminants within 4 environmental transport pathways.

What are those 4 environmental pathways? One is air, soil, surface water and groundwater. So it is basically computational. This ACTS is basically computational system which basically assists environmental engineers and other scientists to quantify and assess the environmental multimedia fate and transport in 4 different transport pathways, air, soil, surface water and ground water.

This basically a flow chart of this ACTS system. So basically, you can see that they have soil, both soil or air pathway models. Then they have ground water pathway models and also surface water pathway models. So 4 different transport pathways they have okay. Now a powerful feature of this analysis system is the ability to conduct probabilistic analysis using one or two stage Monte Carlo simulation for each of the environmental transport pathways.

Now this Monte Carlo method is dynamically linked with all the pathways. You can see here Monte Carlo simulation for probabilistic analysis which is basically dynamically related to both the soil and air pathway models, then it is also related to the groundwater pathway models and also surface pathway models. Basically, it generates a range of, a host of values of the parameters and then basically generates the results.

So the Monte Carlo method is dynamically linked with all the pathway modules and models to analyze the cases involving uncertainty and variability of the input parameters. So you can see there are certain input parameters in all these pathway models right. In the soil air pathway models, in the groundwater pathway models, in the surface water pathway models, these are related to different inputs which have inherent variability.

So if you consider those inherent variability and simulate, so this Monte Carlo simulation is relating all these 4 pathways is basically dynamically linked and calculating the uncertainty and variability of the input parameters it produce the different types of simulations and also show the pathway of the pollutant.

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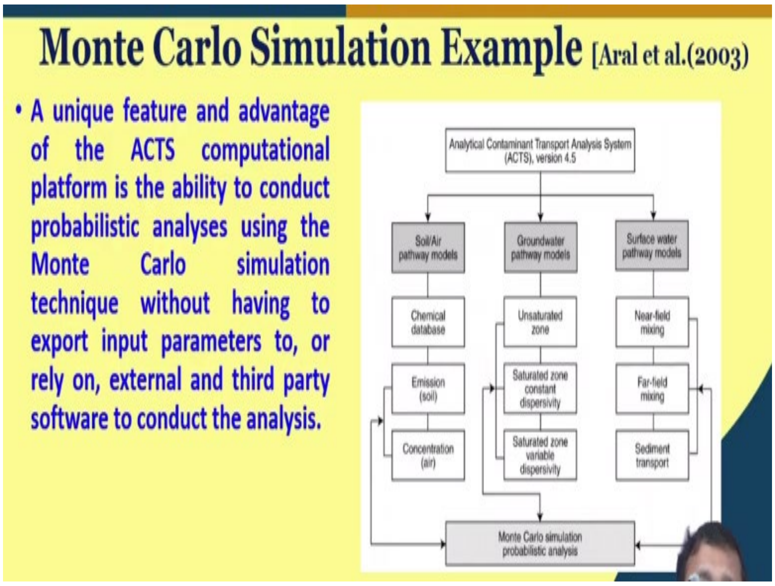

Now a unique feature and advantage of this ACTS computational platform is the ability to conduct the probabilistic analysis using the Monte Carlo simulation technique without having to export input parameters to or rely on external third party software to conduct the analysis. Now generally what happens, different types of inputs when you put into the model, in any type of simulation model when we input different parameters, those parameters are also predicted or generated by third party models.

For this ACTS computational platform, it has the ability to use this Monte Carlo simulation so that we do not need any third party software to conduct this analysis for the inputting parameters. So this is the basically benefit of using this Monte Carlo simulation in different types of fate transport models okay. So friends, we have completed this stochastic model, there is you know some aspects are still need to be discussed which we will discuss in our next class.

So let us wrap up our lecture here and let us meet in our next lecture to discuss some examples of the pollutant fate models and then we will discuss the risk assessments and then diagnosis and prognosis and so on and so forth. So if you have any questions, please feel free to email me and I will be more than happy to answer your queries. So, let us meet in our next lecture of week 11. Thank you very much.