

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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Overview of Models

- Introduction of various chemicals into natural media:
 - Industrial operations
 - Waste disposal
 - Pesticide and fertilizer applications irrigation with secondary effluents, etc.
- To these must be added accidents such as fires, tank leakages, and spills, which locally add large amounts of chemicals.

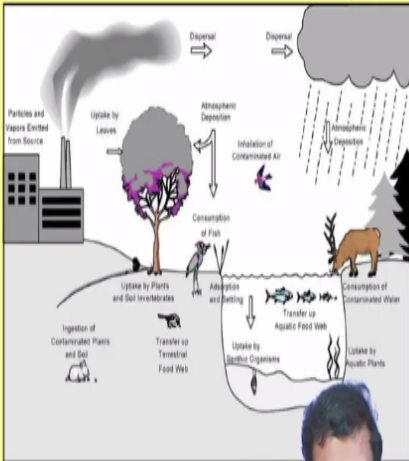


But before going to the today's topic I just want to give you a quick recap of whatever we have covered in the last lecture.

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Overview of Models

- The cumulative result is a growing threat to soils and waters which makes the prediction of the fate of pollutants necessary.
- Modeling may be a rather efficient tool for making this prediction, so that a very great number of models can be found in the literature.



So, overview of the models we have covered that.

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Overview of Models

- There are more than 1000 environmental software products.
- Models do not constitute a universal or perfect way to achieve this prediction, because they are only more or less simplified representations of the real world, and their application encounters many difficulties which need to be well known by users.
- The modelling approach has been shown to be very useful in many instances:
 1. Research
 2. Management
 3. Regulatory purposes and
 4. Teaching

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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Classification of Models

- Models can be classified according to the purpose for which they have been developed. The following categories are usually considered:
 - A. Research models
 - B. Management models
 - C. Screening models
 - D. Teaching models

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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Classification of Models

▪ Research models:

- These give a detailed and comprehensive description of phenomena.
- They may be useful for testing various hypotheses in relation to mechanisms of retention, transformation and transport.

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

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Classification of Models

▪ Management models:

- These generally differ from research models in using less precise descriptions.
- They are able to estimate the integrated effects of various processes that determine, for example, the fate of a pesticide under a given set of practices.
- They may be used in management decision procedures.
- Example: in agriculture for defining the characteristics of plant protection treatments, in industry for designing a waste disposal system.

So we have covered these 4 different types of models.

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Classification of Models

▪ Screening models:

- These are simpler than the preceding ones in both the number of phenomena accounted for and their description.
- They essentially allow the classification of molecules for given pedo-climatic situations.
- They must be simple enough to give a rough basis for regulatory decisions.

▪ Teaching models:

- These are also simpler than research models but they must emphasize the main aspects of chemical behavior, while being easily handled for the training of students.
- The complexity of the models, the number of input data, and the processing time increase as we progress from teaching models to research models.

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

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Deterministic vs. Stochastic Models

- In **deterministic models**, the output of the model is fully determined by the parameter values and the initial conditions.
- **Stochastic models** possess some inherent randomness. The same set of parameter values and initial conditions will lead to an ensemble of different outputs.

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

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Overviews of Models

- In dealing with the fate of a chemical in the soil, all models have the same general structure, which can be described from three points of view:

- **Phenomena:**

- The central part of the model is constituted by the water and solute transport equations.
- These equations are coupled with other equations which represent sink and source processes.
- The number of equations and their mathematical expressions depend on the model category and vary accordingly.

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

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Phenomena Implied in the Fate of Various Pollutants

Inorganic pollutants					Organic pollutants	
Unionized molecules	Ions				Small molecules	Polymers
	Anions		Cations			
N, S molecules	Br ⁻ , Cl ⁻	NO ₃ ⁻	PO ₄ H ²⁻ , PO ₄ H ₂ ⁻	NH ₄ ⁺ Heavy metals	Pesticides, organochlorines, solvents	Hydrocarbons
Transport in solution			Transport in solution and sorbed on solid particles			
Miscible displacement					Immiscible displ.	
Possible gas transport	No gas transport				Possible gas transport	
Transformations	No	Transformations		No	Transformations	
Sorption						

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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Overviews of Models

▪ Compartmentalization of the soil profile:

- The soil profile is divided into several layers in order to take into account the characteristics of the different horizons.
- The layers are frequently divided into segments for calculation purposes.
- The numbers of layers and segments vary among models, depending on their complexity.

▪ Outputs:

- In general, models simulate the amounts of chemicals which are transferred to the atmosphere, to surface water, and to groundwater.
- They often give the distribution of chemicals in the soil profile.

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

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Description of Models

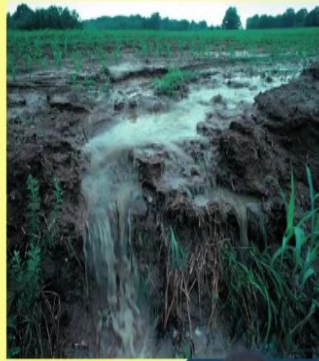
- Modeling the fate of soil pollutants is based on the description of solute transport coupled with sink/source phenomena.
- Three scales are usually distinguished:
 - I. The microscopic scale (at the pore level), where elementary laws of fluid mechanics apply
 - II. The macroscopic scale (classically, the laboratory column), for which an equivalence between the real dispersed medium and a fictitious continuous medium is assumed
 - III. The megascopic scale (the field), where spatial variability of soil properties must be taken into account through a stochastic approach.
- Models for the first two scales are deterministic.
- They may be used locally in the field, but generally they cannot be extrapolated.

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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Description of Models

- It is worth noting that water movements may lead to pollutant transport through the transfer either of dissolved molecules or of molecules sorbed on solid particles.
- In the latter case, the transport takes place essentially on the soil surface during runoff/erosion processes.
- It may also take place to a lesser degree within the soil profile in association with colloidal materials and hydrosoluble humic substances, which can bind pesticide molecules and make them mobile and readily transportable by water movements.



Then, we have described the models.

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Deterministic Models

- Numerous examples can be found in the literature. Most of them are based on the well-known convection-dispersion (CD) equation.
- Others rely on quite different approaches, based on, for example, the residence time distribution, the chemical fugacity, transfer functions, or the reservoir analogy.
- Models Based on the CD Equation:
 - From a general point of view, solute transport is the result of three processes:
 - Diffusion in the aqueous phase
 - Diffusion in the gas phase and
 - Convection combined with hydrodynamic dispersion



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

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Convection-dispersion

- Whenever we consider mass transport of a dissolved species (solute species) or a component in a gas mixture, concentration gradients will cause diffusion.
- If there is bulk fluid motion, convection will also contribute to the flux of chemical species.
- Therefore, we are often interested in solving for the combined effect of both convection and diffusion.

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

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Deterministic Models

- Although transport in the gas and the liquid phases is simultaneously introduced in some models (the **BAM model**, for example), they are often modeled separately.
- The CD equation has been used for a long time to describe solute transport in porous media.
- Various initial and boundary conditions have been applied, which lead to several solution methods, either analytical or numerical.
- There are several analytical solutions for the one-dimensional CD equation.

$$\frac{\partial}{\partial t} (\rho_b S_i) + \frac{\partial}{\partial t} (\Theta C_i) = \frac{\partial}{\partial z} \left[\Theta D(\Theta, q) \frac{\partial C_i}{\partial z} \right] - \frac{\partial}{\partial z} (q C_i) \pm \Sigma \Theta$$

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

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Deterministic Models

$$\frac{\partial}{\partial t} (\rho_b S_i) + \frac{\partial}{\partial t} (\Theta C_i) = \frac{\partial}{\partial z} [\Theta D(\Theta, q) \frac{\partial C_i}{\partial z}] - \frac{\partial}{\partial z} (q C_i) \pm \Sigma \Theta \quad (1)$$

- where i denotes a solute, S_i is the concentration of sorbed solute (expressed on a mass basis ($M M^{-1}$),
- C_i is the concentration of the solute in the liquid phase ($M L^{-3}$),
- Θ is the volumetric water content ($L^3 L^{-3}$),
- ρ_b is the bulk density ($M L^{-3}$),
- q is the soil macroscopic water flux ($L T^{-1}$),
- $D(\Theta, q)$ is the hydrodynamic dispersion coefficient ($L T^{-2}$), which incorporates the effect of mechanical (induced flow) dispersion.

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

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Deterministic Models

- And those of molecular diffusion according to the following expression:

$$D(\Theta, q) = \frac{D_p(\Theta)}{\Theta} + D_m(q) \quad (2)$$

- D_m may be estimated from :

$$D_m(q) = \lambda v \quad (3)$$

- $v = q/\Theta$ is the pore water velocity and λ (L) is the dispersivity, which depends on the nature of the medium and on the scale of observation.
- A first acceptable approximation for λ may be given by (1/10) th the scale of observation.
- $D_p(\Theta)$ is the effective diffusion coefficient, which may be evaluated from:

$$D_p(\Theta) = D_o \exp(b\Theta) \quad (4)$$

- D_o being the molecular or ionic diffusion in solution, a and b are two empirical constants.

We have defined each of the terms.

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Deterministic Models

$$\frac{\partial}{\partial t}(\rho_b S_i) + \frac{\partial}{\partial t}(\Theta C_i) = \frac{\partial}{\partial z} \left[\Theta D(\Theta, q) \frac{\partial C_i}{\partial z} \right] - \frac{\partial}{\partial z}(q C_i) \pm \Sigma \Phi$$

(a) (b) (c) (d) (e)

- Term (a) : time variation of the sorbed solute concentration
- Term (b) : time variation of the solute concentration in the liquid phase
- Term (c) : transfer due to hydrodynamic dispersion
- Term (d) : convective transfer
- Term (e) : sink/source phenomena

So please go through this in very carefully.

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Deterministic Models

- Two situations must be considered when solving Eq. (1):
 - Steady-state water flow and
 - Transient water flow.
- For steady state, Θ and q are constant, and Eq. (1) becomes:

$$\rho_b \frac{\partial S_i}{\partial t} + \Theta \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial z^2} - q \frac{\partial C_i}{\partial z} \pm \Phi \quad (5)$$

- This situation is simpler and allows the relative weights of the various phenomena to be determined quite easily.
- It may correspond to either saturated or unsaturated media.
- An example of a model based on this formulation is the BAM model.

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

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Deterministic Models

- For transient water flow, Θ and q must be known as functions of time and depth.
- When the movement of water is assumed to take place predominantly in the soil matrix and not in macropores or in any kind of bypass, this may be achieved through a mechanistic description of water flow based on an equation derived by combining Darcy's law and the equation of continuity.
- For one dimensional transient vertical flow this equation is:

$$\frac{\partial \Theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\Theta) \frac{\partial H(\Theta, z)}{\partial z} \right] - A(z, t) \quad (6)$$

we have defined all these things.

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Deterministic Models

$$\frac{\partial \Theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\Theta) \frac{\partial H(\Theta, z)}{\partial z} \right] - A(z, t)$$

- Where $H(\Theta, z)$ (L) is the hydraulic head which is the sum of matric $h(\Theta)$ and gravitational $g(z)$ potential energy, neglecting other potential components.
- $K(\Theta)$ ($L T^{-1}$) is the hydraulic conductivity, a function of the soil water content Θ .
- $A(z, t)$ (T^{-1}) represents the uptake of water by the plant.
- Equation (6) may be solved for given initial boundary conditions and soil properties, to give the function $H(z, t)$.
- This allows us to obtain $h(z, t)$, which in turn gives $\Theta(z, t)$, provided $\Theta(h)$ is known.
- Then, the water flux, q , may be calculated from:

$$q(z, t) = \int_{Z_1}^{Z_2} \frac{\partial \Theta}{\partial t} \cdot \delta z \quad (7)$$

- where Z_1 and Z_2 refer to two given depths of the soil profile.

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

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Other Modeling Approaches

- Other approaches are not based on the CD equation.
- Three selected approaches are discussed here as they are being used successfully –
 - Models based on chemical engineering theories
 - Models using a compartment description for calculating water flow
 - Fugacity-based models

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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Other Modeling Approaches

- Fugacity-based models:
 - **Fugacity** is a measure of the chemical potential. When the fugacities of a chemical in two different compartments that are in contact are unequal, the chemical will be redistributed between the compartments, with net transfer of the chemical from the higher fugacity compartment to the lower fugacity compartment. When the fugacities are equal, the net transfer is zero and equilibrium exists.

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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Other Modeling Approaches

- Fugacity-based models:
- The relationship between fugacity, f , and concentration in the i^{th} compartment, C_i , is:
$$C_i = Z_i \cdot f$$
- Z_i is known as the fugacity capacity and can be a function of f and C_i . It follows that the partition coefficient between compartments i and j is:
$$\frac{C_i}{C_j} = \frac{Z_i}{Z_j}$$

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

So basically, this fugacity capacity of Z_i is basically function of fugacity as well as the concentration in the i^{th} 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 C_i by $C_j = Z_i$ by Z_j . 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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Other Modeling Approaches

- Fugacity-based models:

- Fugacity models were developed for describing pollutant distribution in aquatic systems.

- Instead of concentration C (mol m^{-3}) in a compartment, as controlling variable, the models use the fugacity f (Pa).

$$C = fZ \quad (8)$$

- where Z is the fugacity capacity, which is characteristic of the chemical, the medium and the temperature.

- For example, if a compound is distributed among the solid, liquid, and gas phases, the following relation holds at equilibrium:

$$f = \frac{C_g}{Z_g} = \frac{C_l}{Z_l} = \frac{C_s}{Z_s} \quad (9)$$

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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Other Modeling Approaches

- Fugacity-based models:

- Where C_g and Z_g , C_l and Z_l , C_s and Z_s are the concentration and the fugacity capacity of the gas, liquid, and solid phases, respectively.
- It can be shown that fugacity capacity factors are simply related to partition coefficients, so that Eq. (9) can be written:

$$f = C_g (RT) = C_l \frac{P_0}{C_0} = C_s \frac{P_0}{\rho K_d C_0}$$

- Where R is the gas constant, T the thermodynamic temperature, P_0 the saturated vapor pressure at T , C_0 the water solubility at T , ρ the solid phase density, and K_d , the solid/liquid distribution coefficient for the chemical under consideration.

Now where in this case we have already discussed that C_g and then Z_g , C_l and Z_l , C_s and Z_s 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 = C_g multiplied by RT

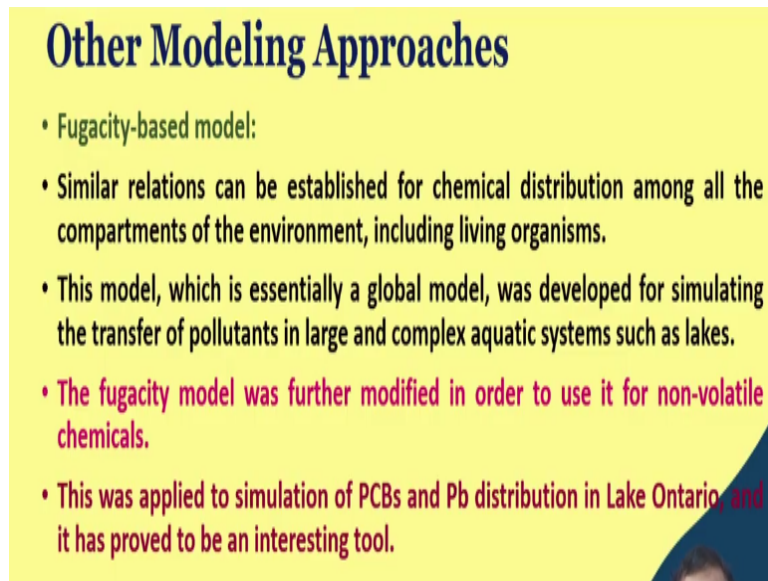
Which is also equivalent to C_l multiplied by P_0 by C_0 which is also equivalent to the C_s multiplied by P_0 by $\rho K_d C_0$, where now remember that these 3 conditions are for 3 different medium, one is here it is for gaseous medium, this is for liquid medium and this for solid medium. Now in this gaseous medium we can represent the fugacity as the C_g that is concentration at compartment and RT .

R you know that is gas constant and T is the thermodynamic temperature and C_l you already know that is the concentration of the liquid and p_0 is basically the saturated vapor pressure at T and C_0 is the water solubility at T and here this ρ is basically the solid phase density and K_d 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 K_d 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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Other Modeling Approaches

- Fugacity-based model:
- Similar relations can be established for chemical distribution among all the compartments of the environment, including living organisms.
- This model, which is essentially a global model, was developed for simulating the transfer of pollutants in large and complex aquatic systems such as lakes.
- The fugacity model was further modified in order to use it for non-volatile chemicals.
- This was applied to simulation of PCBs and Pb distribution in Lake Ontario, and it has proved to be an interesting tool.

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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Transport in Heterogeneous Media

- Soils are often non-uniformly textured and are structured so that their pore space is characterized by complex pore shapes and size distributions, which are time- and space-variable.
- This has a profound influence on water and solute transport, because one fraction of the liquid phase is immobile while another is greatly mobile, which leads to preferential flow.
- Immobile water could comprise stagnant water around solid particles and/or water held in intra-aggregate pores.



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

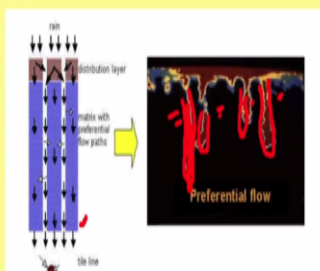
may arise because these distributions are space variable.

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 spaces 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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Transport in Heterogeneous Media

- **Preferential flow** : Preferential flow refers to the uneven and often rapid movement of water and solutes through porous media, typically soil, characterized by regions of enhanced flux such that a small fraction of media (such as wormholes, root holes, cracks) participates in most of the flow, allowing much faster transport of a range of contaminants, including pesticides, nutrients, trace metals, and manural pathogens. This creates significant consequences for ground-water quality.



<http://soilssearch/pin.m> <http://edu/ro/why.ht>

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 manural pathogens.

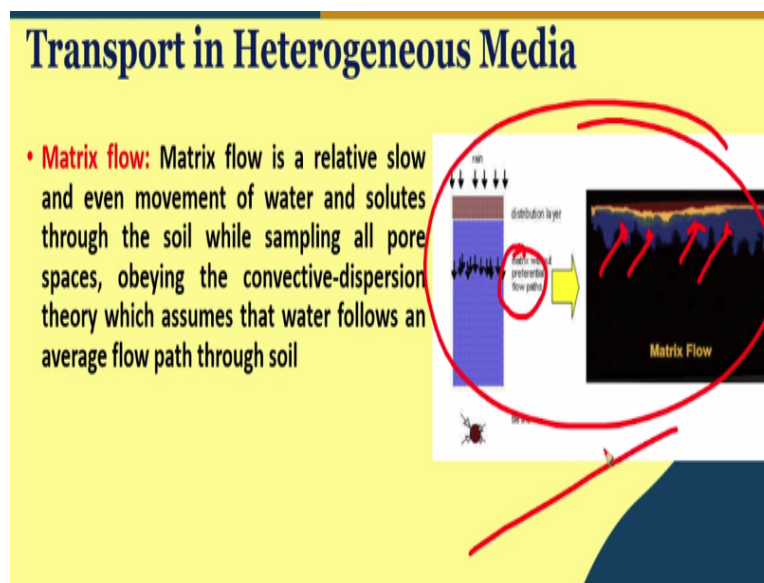
This creates significant consequences for groundwater quality, how let us see. So here you can see that this is showing the preferential flow. So basically, if there is a distributing layer so you can see matrix of preferential flow path when there is a rainfall, so there are some distribution layers.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

- Due to its rapid movement, preferential flow allows much faster contaminant transport and creates significant consequences for ground-water quality and has direct impacts on drinking water and human health, animal waste management, nutrient and pesticide management, and watershed management.
- In the mining sector, the phenomenon of preferential flow has been used in designing the best configuration for tailings left behind by mining operations. By including clean material at strategic places where preferential flow is directed, the toxicity of leachates can be greatly reduced.
- Preferential flow seems to be observed in various soils, often in structured clay soils, but sometimes also in sandy soils.

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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Transport in Heterogeneous Media

- Three kinds of preferential flow have been suggested:
 - Channeling in pores:
 - In macropores ($\phi > 1$ mm), often comprising biopores,
 - In mesopores ($\phi < 1$ mm) comprising a network of cracks and biological channels,
 - Fingering flow, due to wetting front instability and
 - Funnel flow, caused by redirection of flow by heterogeneities in the profile.

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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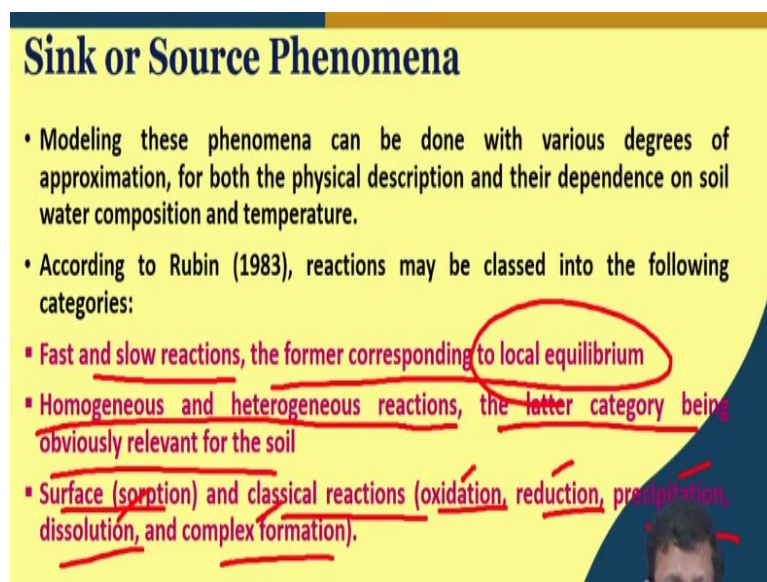
Sink or Source Phenomena

- Soil pollutants are often affected by several phenomena which provide sinks or sources for solutes in the fluid phase.
 - Sink phenomena:
 - Transformation
 - Degradation
 - Retention and
 - Precipitation
 - Source phenomena:
 - Desorption
 - Solubilization and
 - Transformations (e.g., nitrate production)

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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Sink or Source Phenomena

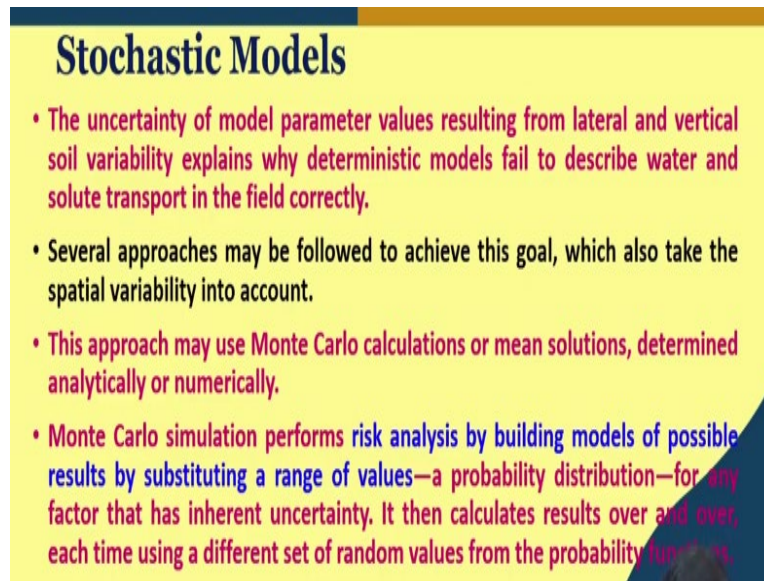
- Modeling these phenomena can be done with various degrees of approximation, for both the physical description and their dependence on soil water composition and temperature.
- According to Rubin (1983), reactions may be classed into the following categories:
 - Fast and slow reactions, the former corresponding to local equilibrium
 - Homogeneous and heterogeneous reactions, the latter category being obviously relevant for the soil
 - Surface (sorption) and classical reactions (oxidation, reduction, precipitation, dissolution, and complex formation).

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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Stochastic Models

- The 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.
- Several approaches may be followed to achieve this goal, which also take the spatial variability into account.
- This approach may use Monte Carlo calculations or mean solutions, determined analytically or numerically.
- Monte Carlo simulation performs risk analysis by building models of possible results by substituting a range of values—a probability distribution—for any factor that has inherent uncertainty. It then calculates results over and over, each time using a different set of random values from the probability functions.

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?

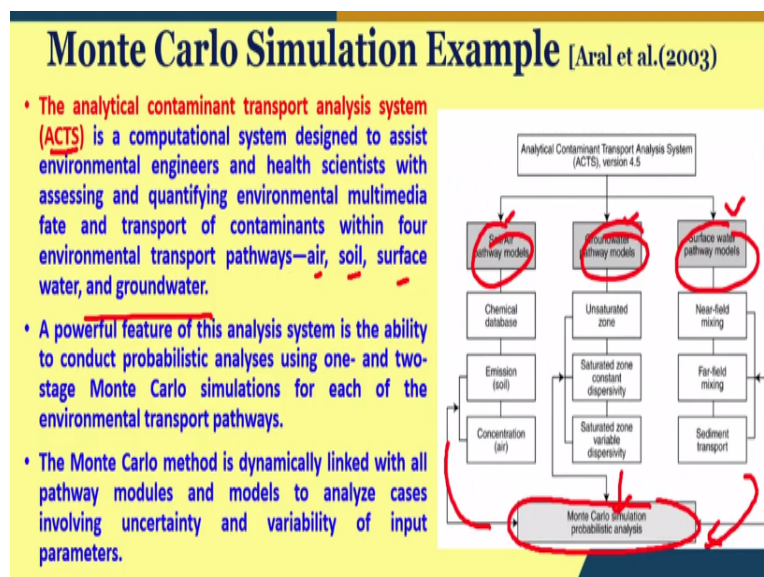
Now Monte Carlo simulation is basically a mathematical procedure which performs the risk analysis by building models of possible results by substituting a range of values. So basically, a probability distribution for any factor that has inherent uncertainty. So, it then basically

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 have 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.

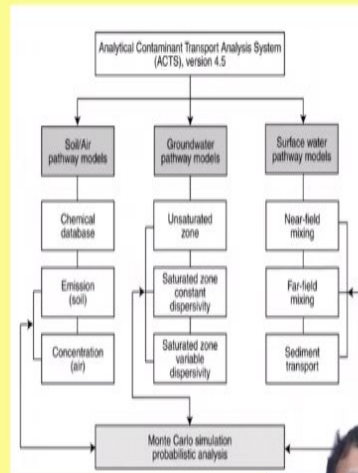
So the Monte Carlo method is dynamically linked with all the pathway modules and models to analyze the cases involving uncertainty and variability of the input parameters. So you can see there are certain input parameters in all these pathway models right. In the soil air pathway models, in the groundwater 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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Monte Carlo Simulation Example [Aral et al.(2003)]

- A unique feature and advantage of the ACTS computational platform is the ability to conduct probabilistic analyses using the Monte Carlo simulation technique without having to export input parameters to, or rely on, external and third party software to conduct the analysis.



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.