Environmental Soil Chemistry
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Lecture – 54
Modeling the Fate of Pollutants in the Soil, Risks and Remedies Continued

Welcome friends to this fourth lecture of week 11 or module 11 of NPTEL online certification course of environmental soil chemistry and in this week we are talking about the modeling the fate of pollutants in soil and risk and remedies. So in our previous 3 lectures, we have covered the basic description of the models. Then we have discussed the classification of the models.

What are the research type model, what are the management model, what are the screening model, what are the teaching models? Then we have discussed deterministic model, several deterministic types of model. We have discussed CD-based model. Then we have discussed the chemical engineering based model, compartment based model, fugacity based models and also we have discussed the movement to heterogeneous mixture or heterogenous media.

And also we have discussed different types of sink and source phenomena and we have also discussed the stochastic models and also Monte Carlo simulations.

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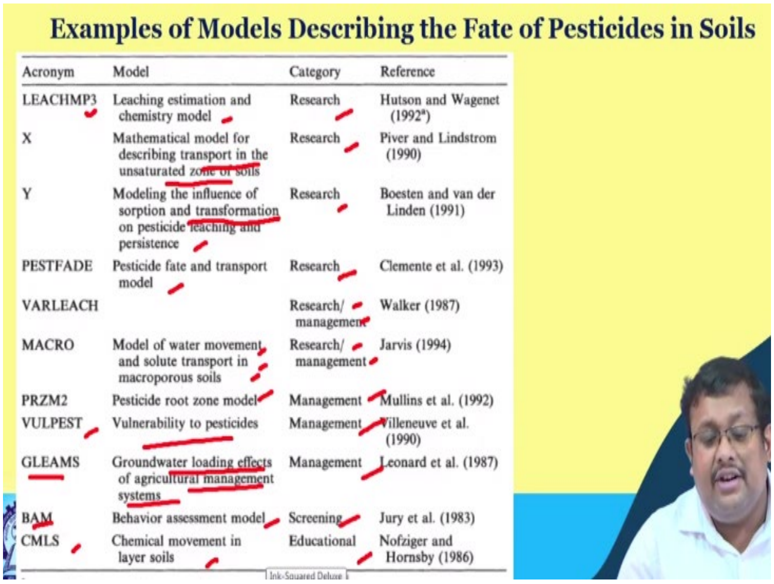

So today, we are going to start with some examples of models describing the fate of pesticides in the soils. So, this slide basically shows the different models and what are their function and in which category they belong and some of the related differences are also there. So here, let us start with the first one that is LEACHMP3 which is basically a model. These are basically the acronyms in the left most column.

So this LEACHMP3 model is basically used for leaching estimation and chemistry model and it is a research category model. Then X is basically mathematical model for describing the transport in the unsaturated zone of soil, which is a research model. Then Y is basically the modeling of the influence of this sorption and transformation on pesticide leaching and persistence that is research model.

PESTFADE is a pesticide fate and transport model that is a research model. VARLEACH is a research management model, we have already discussed VARLEACH. MACRO which is a model for water movement and solid transport in macroporous soils, which is both research and managing model and this PRZM2 is a pesticide root zone model, which is a management model. VULPEST is a vulnerability to pesticide that is a management model.

GLEAMS is a groundwater loading effects of agricultural management system, which is a management model. BAM, which we have already discussed this BAM while discussing the CD equations, so behavior assessment model, which is a screening model, and this CMLS which is a chemical movement in the layered soil that is educational model or teaching models.

So these are some of the examples of model describing the fate of pesticides in the soils and they can be also utilized in other purposes also, modeling other chemical compounds also.

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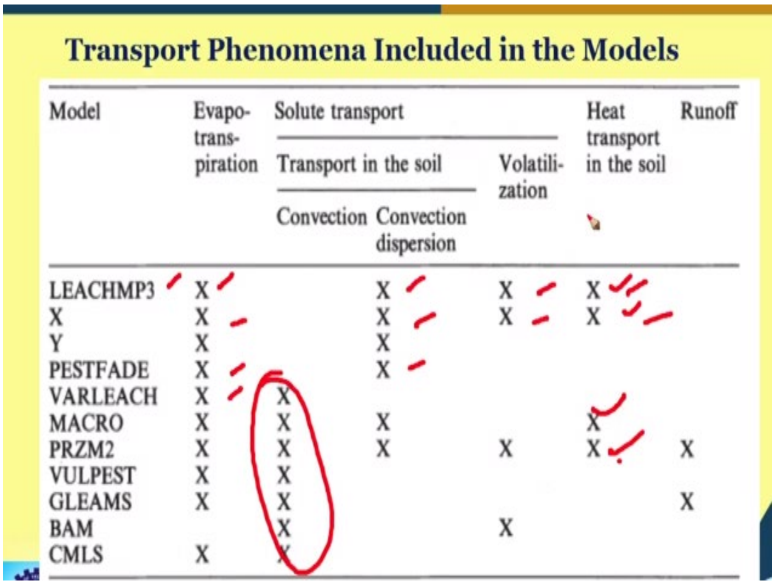

Transport Phenomena Included in the Models

Model	Evapo-trans-piration	Solute transport: Transport in the soil: Convection	Solute transport: Transport in the soil: Convection dispersion	Solute transport: Volatili-zation	Heat transport in the soil	Runoff
LEACHMP3	X		X	X	X	
X	X		X	X	X	
Y	X		X			
PESTFADE	X		X			
VARLEACH	X	X				
MACRO	X	X	X		X	
PRZM2	X	X	X	X	X	X
VULPEST	X	X				
GLEAMS	X	X				X
BAM		X		X		
CMLS	X	X				

Now, what are the different transport phenomena which are included in the model. So let us discuss some of them. So if you consider the LEACHMP3 model, which just discussed in the last slide, it consists of evaporation transportation, then convection-dispersion, volatilization and also heat transport in the soil. Similarly X consider the evaporation transportation, convection-dispersion, then volatilization, and heat transport.

PESTFADE, both evapotranspiration, then solute, then convection-dispersion. VARLEACH consider evapotranspiration. So all the models except for the BAM consider the evapotranspiration model and also these models considering the convection process and convection-dispersion are considered here, volatilizations, heat transport in the models you can consider boats LEACHMP3, X and then MACRO, then PRZM2.

So we can see there are different types of transport phenomena, which had included in different types of models.

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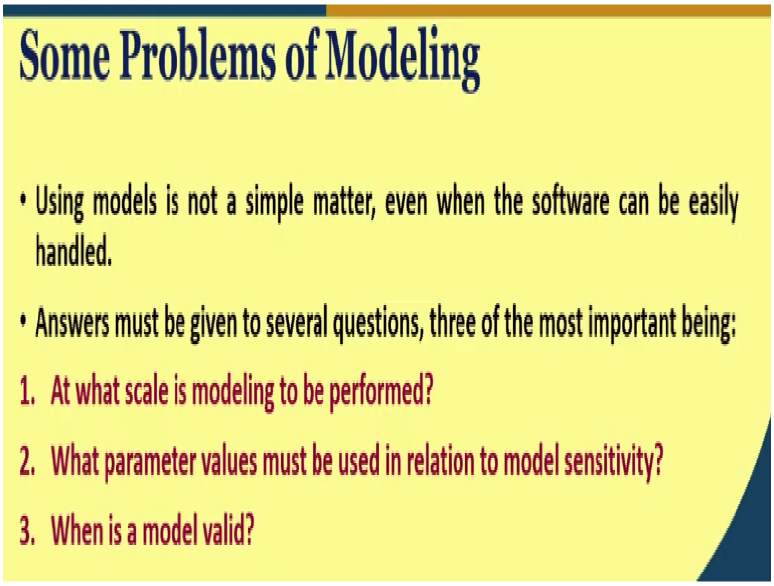

So what are the some problems of modeling. Now remember modeling is basically a simplified representation of complex phenomena and every model has their own limitation. No model is perfect, but some of them are useful. There is a saying that no model is perfect, but some of them are useful. So each of the model has their own limitations. So these limitations come from different sources.

Remember that using a model is not a simple matter, even when the software can be easily handled. Now before we run the model, we have to be sure about these three aspects. So we need to know the answers for different questions. Three of the most important questions are at what scale the modeling to be performed? So in which scale we want to perform this model, this is the modeling, this is very important, otherwise the model will not be valid.

Second, what parameter values must be used in relation to the model sensitivity. Now, in terms of scale, you do not want to use any model which causes the extrapolation because when there is an extrapolation, that creates problem. And secondly what parameter values must be used in relation to the model sensitivity, this is another important question. And third, when is a model valid?

So for this, we are going to discuss in details and we are going to discuss also what is model sensitivity and what is called a validation of a model?

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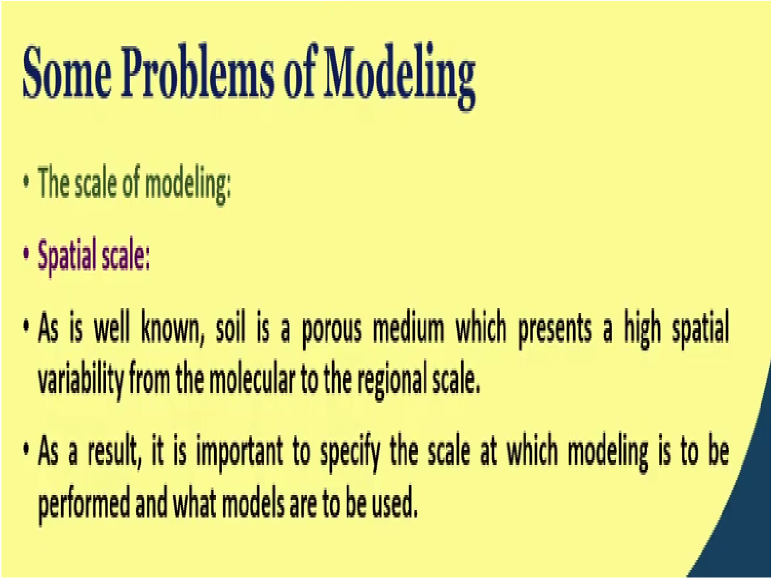

Now, the scale of the model is basically denoted in terms of spatial scale. Now, as it is well known soil is a very porous medium, which presents the highest spatial variability. We just discuss the spatial variability of the soil when we were discussing the preferential flow in our last lecture. So, soil shows high spatial variability from the molecule to the regional scale as it is.

And it is important to specify the scale at which the modeling is to be performed and what models are to be used because for each of the scale, the models are different and you cannot use one model which is meant for one particular scale to other scale. Otherwise there will be problem.

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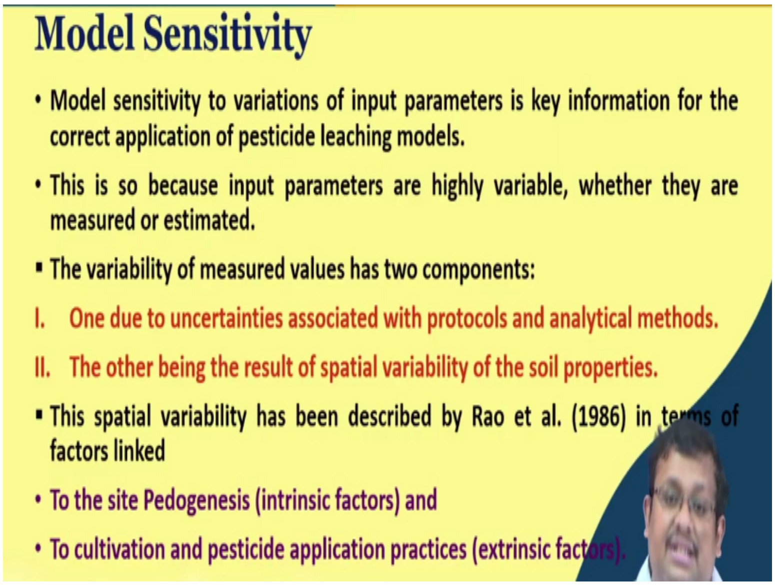

The second important thing is the model sensitivity. Now model sensitivity is to variation of input parameters is key information for the correct application of pesticide leading model. Now, what is model sensitivity? In general terms, the model sensitivity means when we make these input parameters variable, that means in terms of variable input parameters, what will be variation in the output of model simulation.

So that is called sensitivity. A procedure through which we generally test the changes in model behavior when we change the input parameters or vary the input parameter values that is called a model sensitivity. Now, remember that model sensitivity to variation of input parameters is the key information for the correct application of the pesticide leaching model because input parameters are highly variable, whether they are measured or estimated.

If we are considering the input parameter, for example pesticide leaching model for a particular type of soil. Now the soil characteristics also widely variable. So if the soil characteristics is widely variable, for example porosity, for example structure, these are highly variable parameters. So if the structure of the soil variable from one soil, this model also will show different outputs or different types of simulations or different variation in their outputs.

So that is called the sensitivity. So it is very important to identify the input parameters, which are highly variable, whether they are measured or estimated. Now the variability of the measured values has 2 components. One due to the uncertainties associated with the protocol and analytical methods. So you measure the parameters, during the measurement there is some mistakes.

So that is uncertainties which is associated with the protocol of analytical methods. Second is the other being the results of spatial variability of the soil properties. So due to the spatial variability of the soil properties, there is also a wide variation. So this is also source of variability. Now, the spatial variability has been described by Rao et al in terms of factors linked, so what are those?

So to the site pedogenesis which are intrinsic factors and the cultivation and pesticide application practice, which are extrinsic factor. Now the site pedogenesis is an inherent property, so it is an intrinsic factor and the cultivation and pesticide application practices are extrinsic factors okay.

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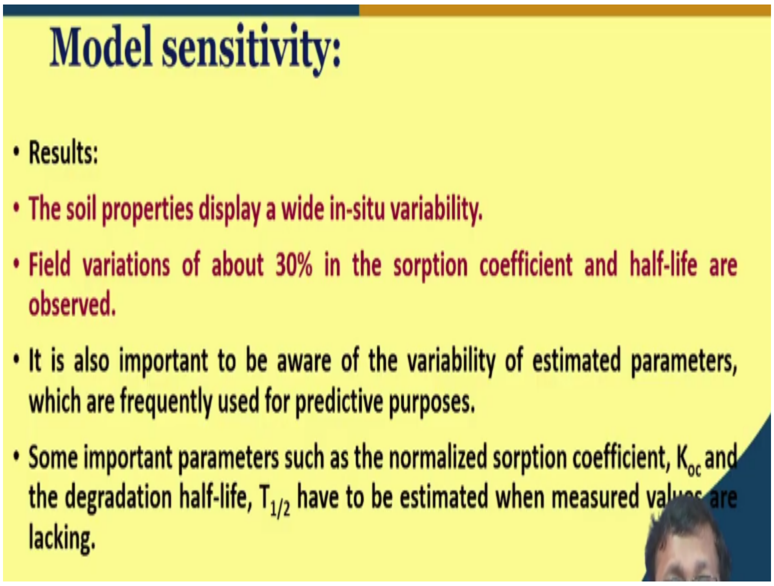

So the results, in terms of result the soil properties display wide in-situ variability, obviously we have already told you that soil structure, soil porosity showing a wide range of variability and also field variation of about 30% in this sorption coefficients and half-life are also observed. So it is also important to be aware of the variability of estimated parameters, which are frequently used to predictive purposes.

Some important parameters such as normalized sorption coefficient that is Koc and the degradation half-life that his T half had to be estimated when measured value are lacking. So basically, these are some of the important aspects you have to very, very carefully handle when you try to simulate the fate of the pollutant because these are very important. If you change this thing, input parameters, obviously the model output will also vary.

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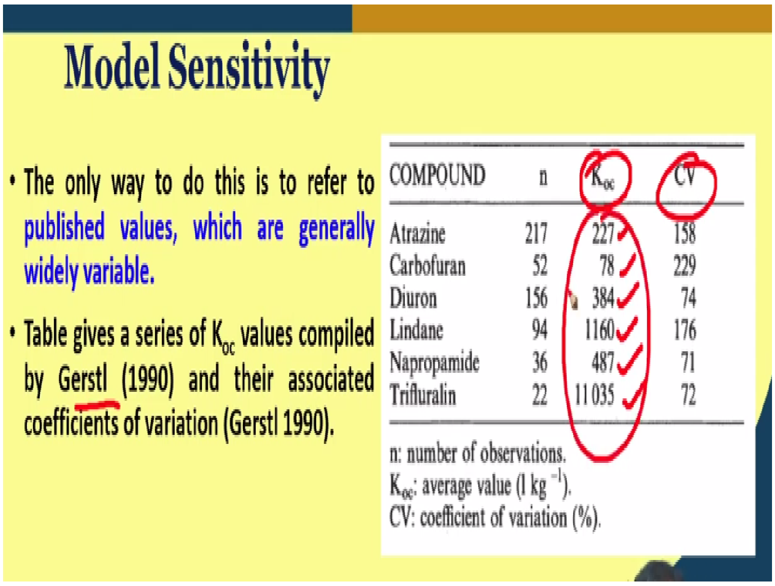

Now the only way, what is the way to deal with this kind of problem because it is highly variable and sometime it is not useful or feasible to measure those parameters. So how to cope up with this model sensitivity issue? Now the only way to do this is to refer to published values, which are generally widely variable. If you see this table, this table shows a series of Koc values, right? Koc values compiled by this scientist and their associated coefficients of variation.

So you can see their associated coefficients of variations. So you can see here the value 227, 78, 384, 1160, 847, 11035. So basically, this is showing a wide variation. So you have to take these values and input to see the sensitivity of the model. Instead of measuring those parameters by yourself, you can just input those values into the model to see the sensitivity of the model. So the best way, only way is to refer to the published values, which are already published and well accepted values.

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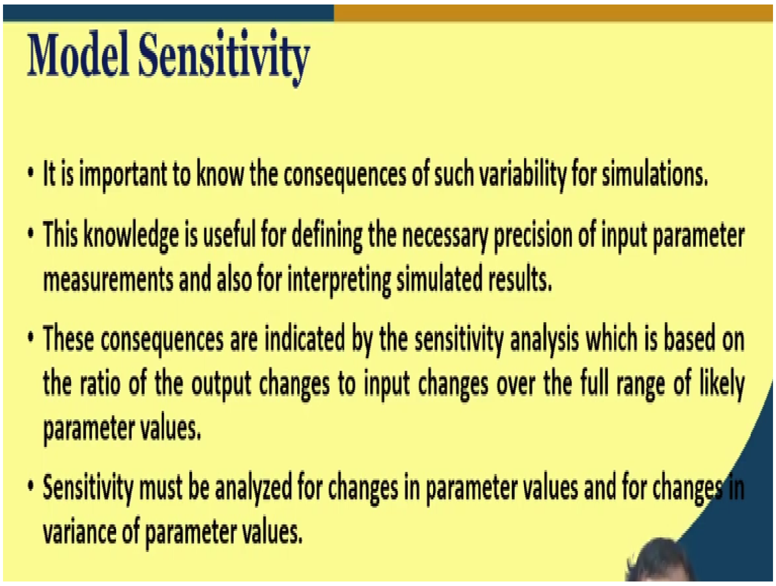

So, it is important to know the consequences of such variability of simulations. Now, this knowledge is useful for defining the necessary precision of input parameters, measurement, and also for interpreting the simulated results. Now, these consequences are indicated by the sensitivity analysis, which is based on the ratio of the output and I have already told you this is basically the ration of output change to input changes over the full range of likely parameter values.

So in the full range of the likely parameter value, for example the values which are seen in case of Koc if you take the whole range of values and we see what is the change, what is the ratio of the output changes to input changes, then it is a measure of the model sensitivity. Remember sensitivity must be analyzed for changes in parameter values and for changes in variance of parameter values.

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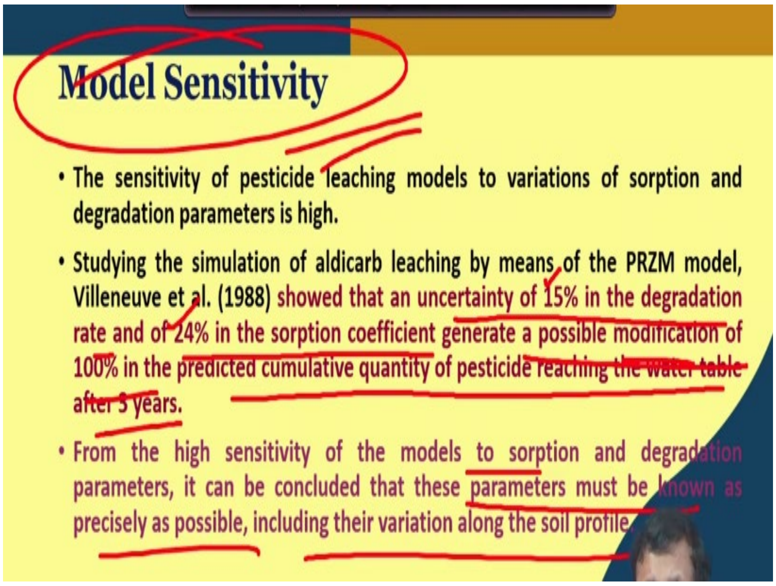

Now, the sensitivity of pesticide leaching model to variation of sorption and degradation parameters is generally very high. Just for some examples studying the simulation of aldicarb which is an important pesticide, leaching by means of PRZM model which we have already discussed. So this scientist this Villeneuve et al in 1988, they have seen that they are studying the simulation of aldicarb leaching by use of PRZM model.

It showed that an uncertainty of 15% of the degradation rate and 24% of the sorption coefficient generate a possible modification of 100% in the predicted cumulative quantity of pesticide reaching in the water table after 3 years. So they showed that an uncertainty of 15% in the degradation rate and 25% in the sorption coefficient, so there are two uncertainties, two input parameters, 15% in the degradation rate and 24% in the sorption coefficient.

Generate a possible modification of 100%, you can imagine a possible modification of a 100% of the predicted cumulative quantity of pesticide reaching to the water table after 3 years. So this shows the importance of model sensitivity and why we should analyze it. It is very, very important. Now from the high sensitivity of the models to sorption and degradation parameters, it can be concluded that these parameters must be known as precisely as possible including their variation along the soil profile.

If possible measure, if it is not possible to measure use some values which are as precise as possible to get the better simulation or fate of transport of the pollutant in the soil.

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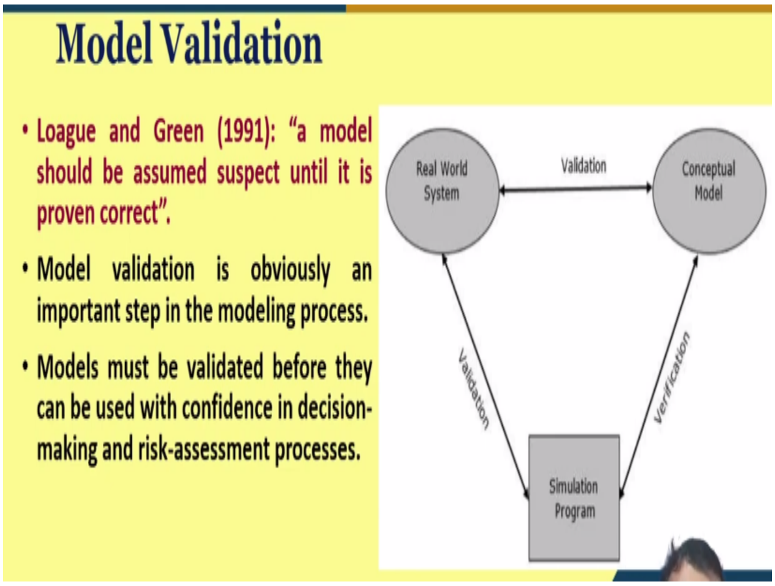

Okay. Now the next important aspect is model validation. Now, you know that a model should be assumed suspect until it is proven correct. So this diagram shows the model validation practice. So model validation an obviously an important step for modeling process, model must be validated before they can be used with confidence in decision making and risk assessment process okay.

So you can see, we do have to develop the conceptual model, then we have to validate it and then we can go for the further simulations okay. So this is how the model validation generally goes.

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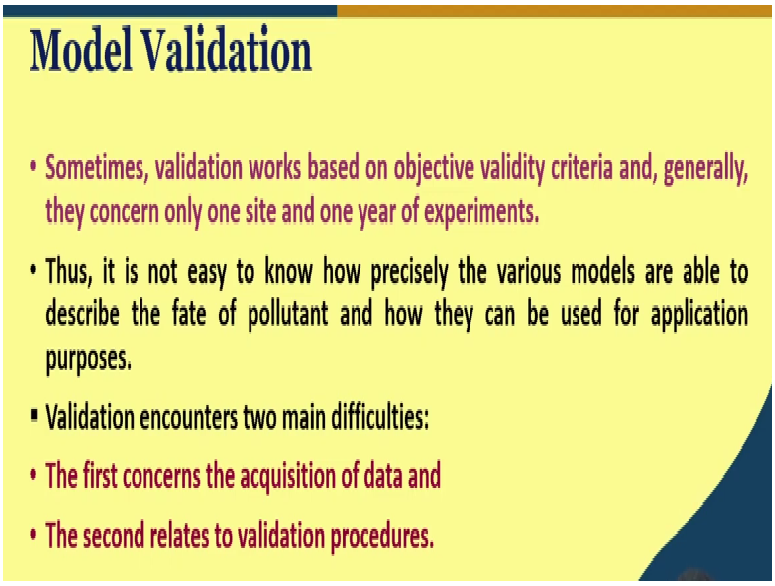

Sometimes, validation works based on objective validity criteria and generally they concern only one site and one year of experiment. Thus it is not easy to know how precisely the various models are able to describe the fate of the pollutant and how they can be used in other application process. So validation encounters 2 major difficulties, the first concerns the acquisition of the data and second relates to the validation procedure.

Remember in the validation process, the most difficult thing is acquisition of the data and validation procedure. Validation has some limitations also because sometimes the validation data is limited and generally we do the validation based on only one year of experiments, which is insufficient. So, these are some of the inherent problems with the model validation.

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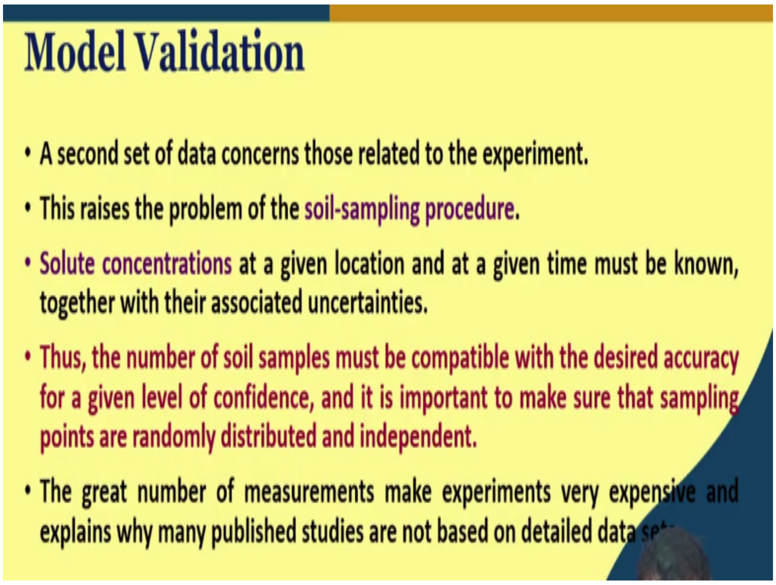

Now, second data set, remember for the model validation, a second set of data concern those to related to the experiment has to be gathered and this raises the problem of the soil sampling procedure and then solute concentration at a given location and at a given time must be known together with that associated uncertainties. Thus the number of soil samples must be compatible with the desired accuracy.

You cannot validate the model with a very limited number of samples. You need to have a sufficient number of samples to achieve the desired accuracy for the given level of confidence and it is important to make sure the sampling process points are randomly distributed and independent because if there is a dependence between the points, dependence between the samples, then obviously your validation will not be foolproof.

You cannot apply your model for a new set of samples. So the great number of measurement make experiments very expensive. Now, on the other hand, when you increase the number of samples that also makes the experiment very expensive and explains why many published studies are not based on detailed data. So these are the some of the inherent problems for model validation.

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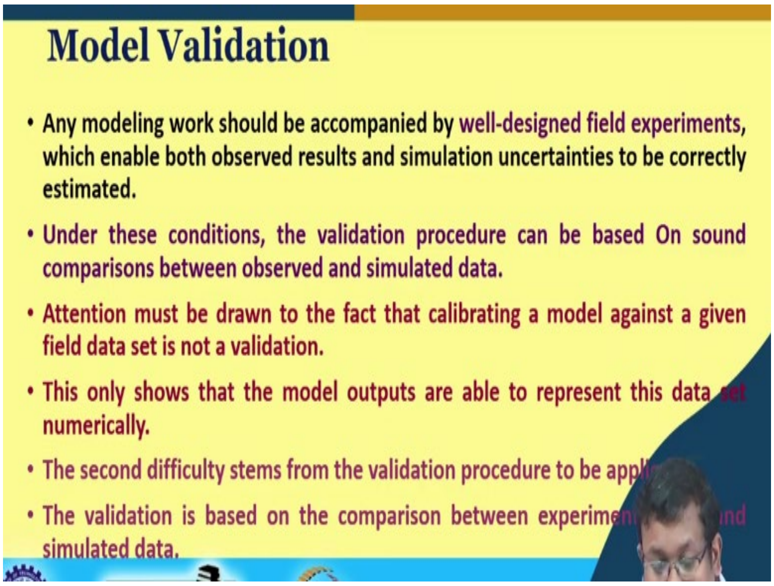

Any modeling work should be accompanied by well-designed field experiments, which enable both observed results and simulated uncertainties to be correctly estimated. Now under this condition, the validation procedure can be based on sound comparison between the observed and simulated data. So you get the observed data, you have the simulated data, you coordinate them and see how perfect your model validation is.

Now remember the attention must be drawn to the fact that calibrating a model against a given field data set is not a validation. This only shows that the model outputs are able to represent the data only numerically. So basically, it is able to explain the variation in the observed data. Now, the second difficulty stems from the validation procedure to be applied. Now, the validation is based on the companies in between experimental data and the simulated data.

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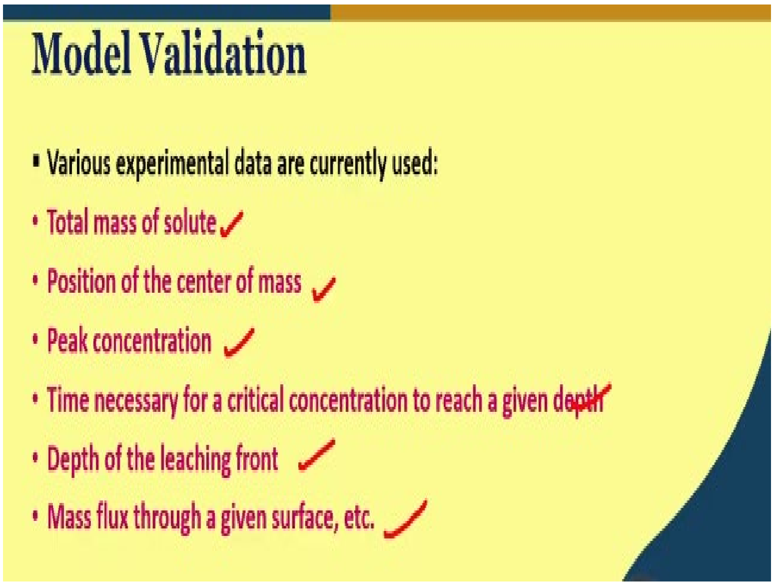

Now various experimental data are currently generally used. For example we know total mass of the solute is important, position of the center of the mass is important. Then peak concentration, time necessary for a critical concentration to reach a given depth, then depth of the leaching front, then mass flux through a given surface, etc. all these are important data for model validation of a pollutant fate transport.

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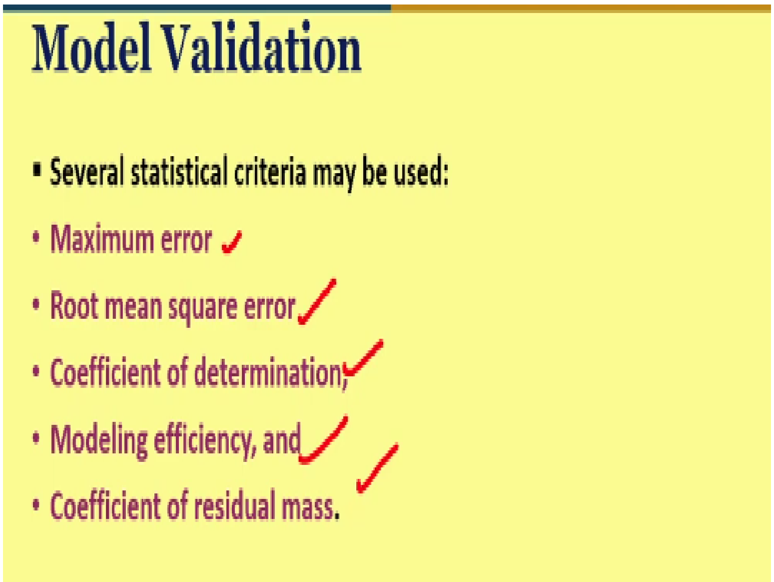

Now, what are the different types of statistical criteria, which are used, these are some statistical objective criteria which you generally use for the model validation or accuracy. One is the maximum error, then root mean square error, then coefficient of determination, modeling efficiency and coefficient of the residual mass. So these are some of the important parameter measuring those we can tell whether this model is good or bad in terms of validation.

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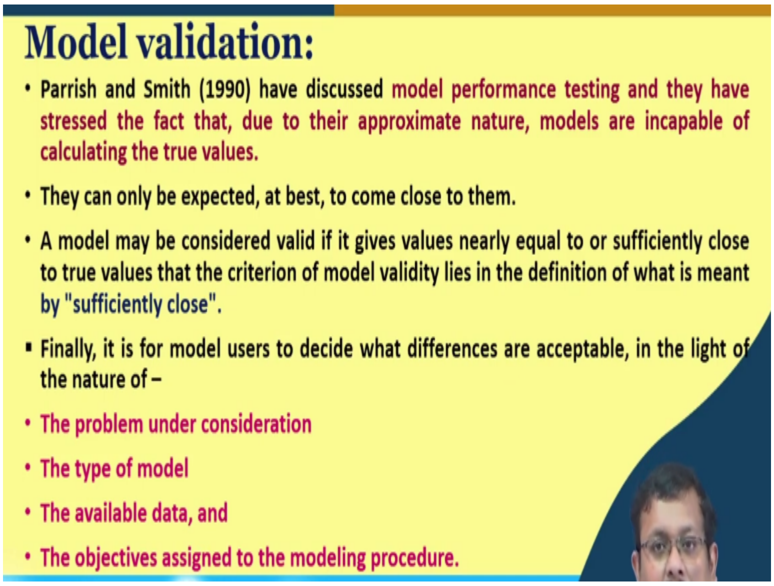

So Parrish and Smith, these two scientists have discussed the model performance testing and they have assessed the fact that due to that approximate nature, models are incapable of calculating the true values. Now they can be only expected, at best, to come close to them. So it is for model users to decide whether differences are acceptable in light of the nature of the problem under the consideration, the type of the model, the available data and objectives assigned to the modeling procedure.

You cannot blindly use any model for any type of situation. You have to consider these important aspects before applying a model and for proper validation of this model is very important. Sensitivity assessment of this model is very important to justify its use for actual unknown samples and to test their validity.

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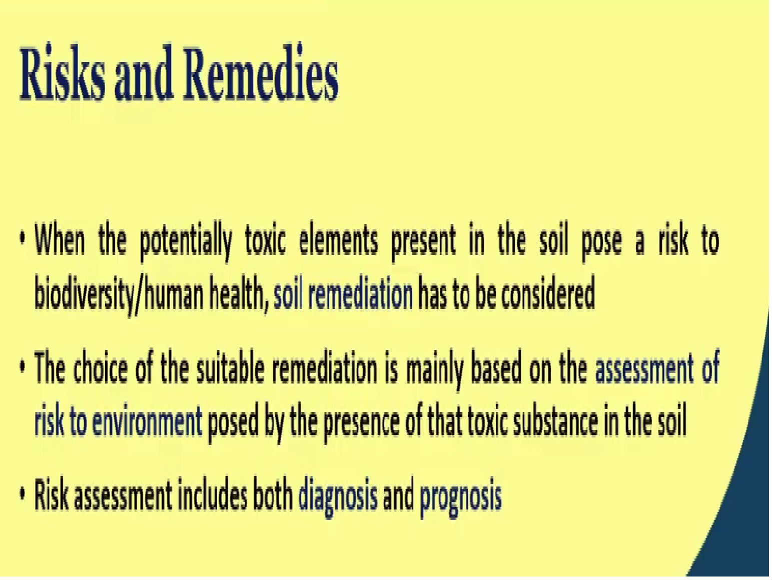

Now, once we complete this model validation, model sensitivity analysis, the next important task, the important aspect which you need to discuss is risk and remedies. So when the potential toxic elements present in the soil pose a risk to the biodiversity or human health, soil remediation has to be considered.

Now, the choice of the suitable remediation is mainly based on the assessment of risk to environment posed by the presence of that toxic substance in the soil and remember that risk assessment includes both diagnosis and prognosis and these are 2 different terms which we are going to discuss in our coming slides.

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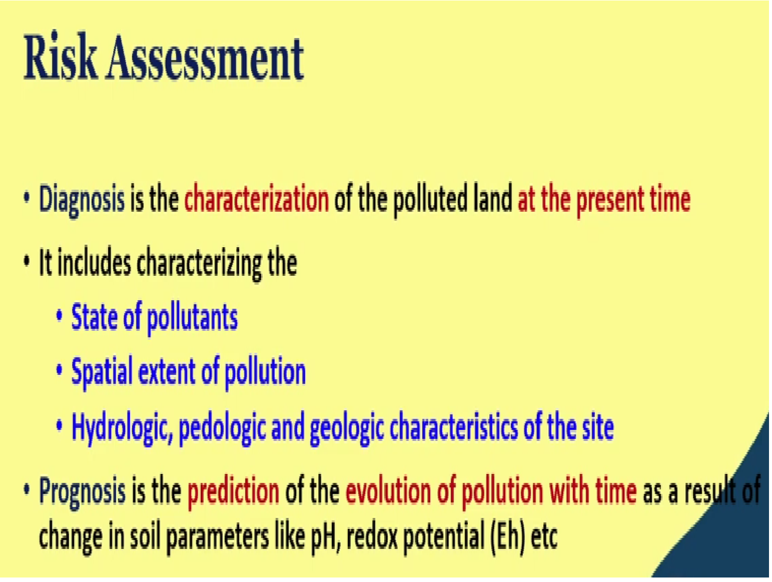

Now, risk assessment is basically the diagnosis is the characterization of the polluted land at the present time and it basically includes characterizing the state of the pollutants and the spatial extent of the pollution, hydrologic, pedologic, geologic characteristics of the site. Whereas prognosis is the prediction of the evolution of the pollution with time as a result of change in soil parameters like pH, redox potential, etc.

So basically, prognosis predict the evolution of the pollution with time when there is a change in soil pH, redox potential, etc. One is current measurement of the characterization of the pollution that is diagnosis and the prognosis is the prediction of the evolution of pollution.

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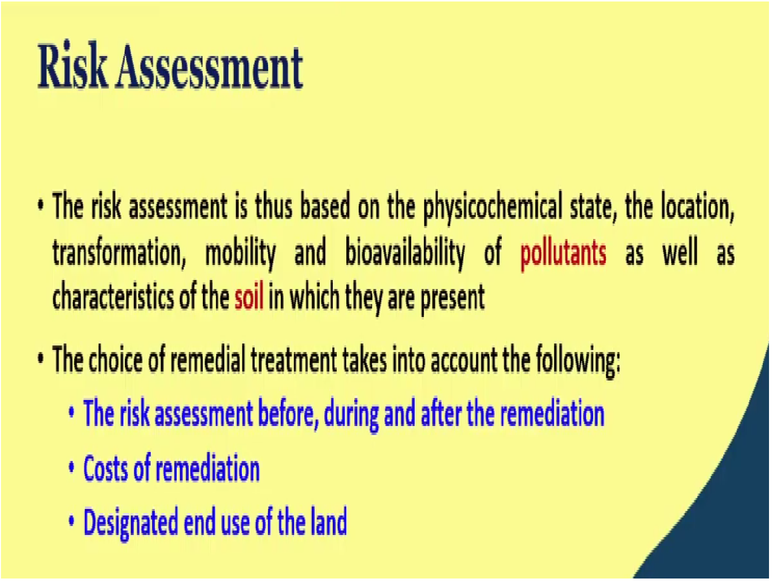

So the risk assessment is thus based on the physiochemical state, the location, transformation, mobility and bioavailability of the pollutants as well as the characteristics of the soil in which they are present. And the choice of remedial treatment takes into account the following. First of all the risk assessment before, during and after the remediation, cost of remediation and designated and use of the land.

So these remedial treatments, when you design a remedial treatment, it is very important that you have considered that risk assessment before, during and after the remediation, you have to consider the cost of remediation, if it is too high, you have to reconsider it and the designated end use of the land.

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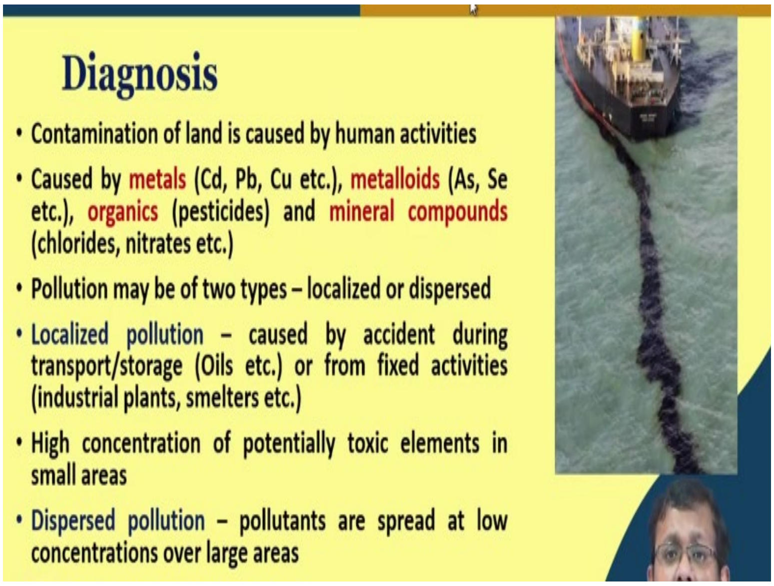

So let us discuss what his diagnosis. Diagnosis for example contamination of land is caused by human activities you know, which can be caused by either metals like cadmium, lead, copper, metalloids like arsenic, selenium, organics like pesticides and mineral compounds, chloride, nitrates, etc. Pollution may be of 2 types, one is localized and disperse. What is localized pollution?

Localized pollutions are caused by accident during the transport or storage oils from the fixed activities like industrial plants, smelters. etc. You can see here, these are localized example, it is an example of localized pollution when there is a leakage of petroleum from a tanker in the sea. So this is an example of localized pollution. And what is the dispersed pollution? Dispersed pollution is pollutants are spread at low concentration over the large areas.

So these are some of the important points of diagnosis. What is whether it is a localized pollution or dispersed pollution.

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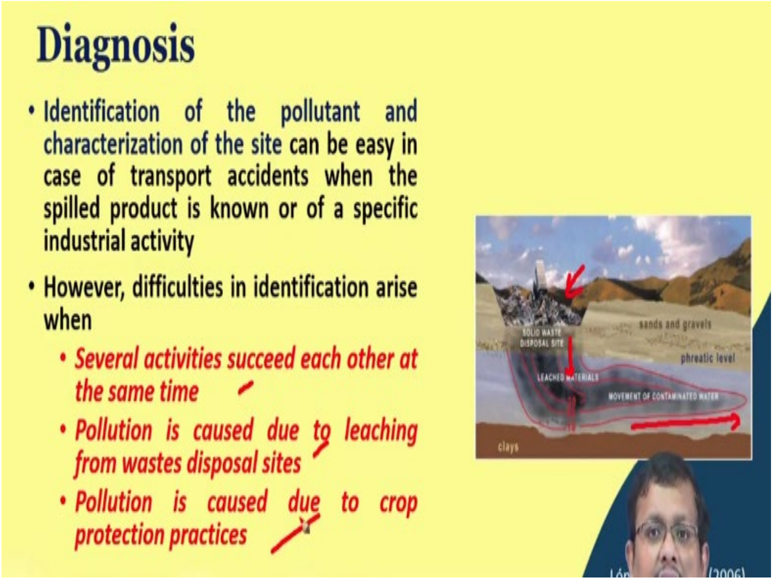

Identification of the pollution and characterization of the site can be easy in case of transport accidents when the spilled product is known or a specific industrial activity. So, you know in the previous slide you have seen that it is very easy to identify the localized pollution because you know the source. However, difficulties in identification arise when several activities succeed each other at the same time.

So if there is several activities are going on, it is very difficult to identify which one is actually responsible for that. Second is pollution is caused due to leaching from waste disposal site. You can see here. I have put here a picture where you can see that materials are leaching from the waste disposal sites. So this is a waste disposal site and when there is a rainfall, the pollutants and organic chemicals are leaching.

And ultimately they go to the different types of water bodies, sometimes it go to the groundwater. So, when this type of pollution is occurred due to the leaching from the waste disposal site is very difficult to identify the localized pollution source. And third is pollution is caused due to the crop protection practices. So, identification of the pollution, pollutant and characterization of the site is very difficult when these conditions generally arise.

Waste disposal site leaching, pollution caused due to the crop protection practice like organic pesticidal chemicals and when there is a multiple process or multiple activities are occurring at the same time, so this is the diagnosis.

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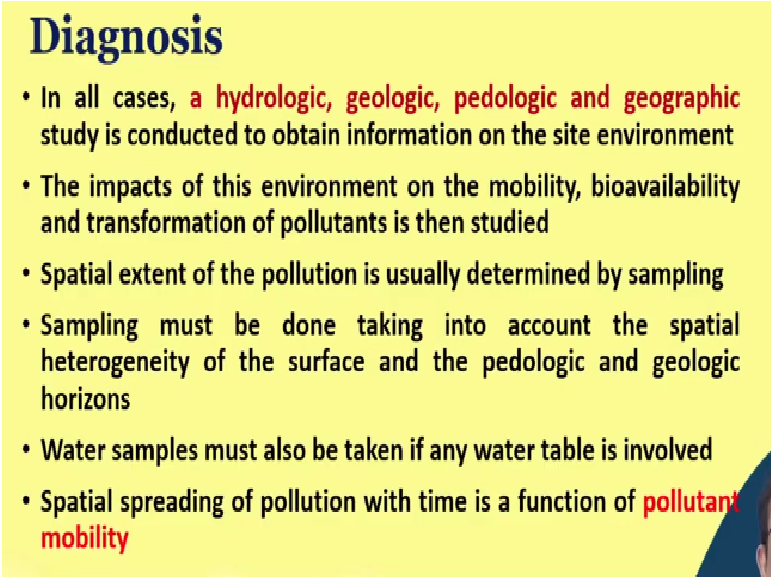

Now in all these cases, hydrologic, geologic and geographic studies conducted to obtain the information on the site environment and remember that the sampling is very important. The impacts of this environment on the mobility, bioavailability and transformation of pollutant is then studied, water samples it is very important. Water sample must also be taken if the water table is involved.

Then spatial spreading of pollution with time, remember that because spatial spreading of pollution with time which is a time function of pollutant mobility. So that is why we have to very, very careful when we collect the water different types of samples for further analysis or diagnosis purposes.

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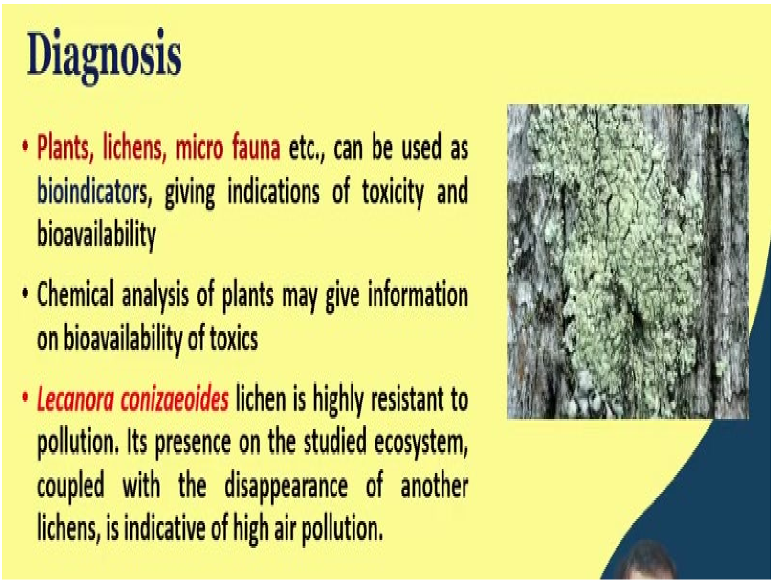

Now plants, lichens, micro fauna, etc. also can be used as bioindicators, giving indication of the toxicity and bioavailability and chemical analysis of plants may give information of the bioavailability of the toxics. For example, I have shown here one lichen that is Lecanora conizaeoides and this lichen is highly resistant to pollution.

And basically its presence in the studied ecosystem, coupled with the disappearance of lichens is generally indicative of high air pollution because they are resistant to pollution. If there is no other test species, we can justify that there is high air pollution. So they act as a bioindicator for diagnosis of pollutions.

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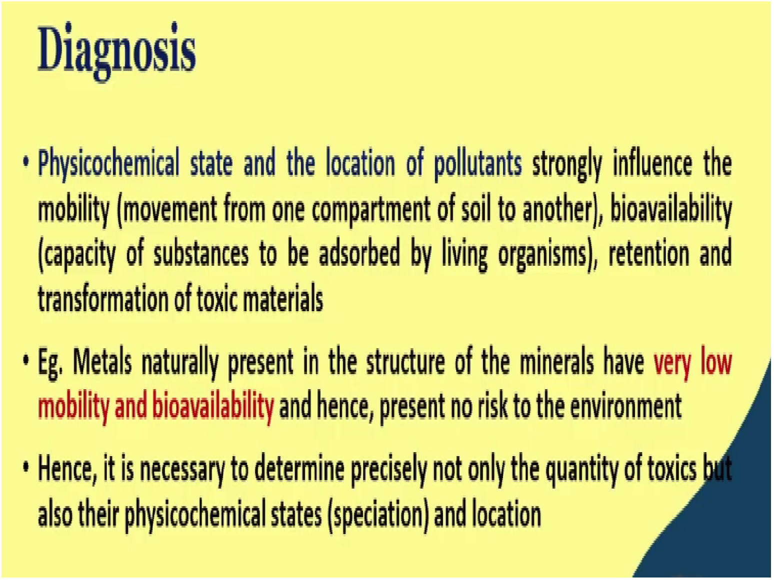

Now physiochemical state and location of the pollutants strongly influences the mobility and retention and transformation of the toxic metals. For example, metal naturally present in the structure of the mineral have very low mobility and bioavailability and hence present no risk to the environment. Hence, it is necessary to determine precisely not only the quantity of the toxic, but also their physiochemical state and location, where they actually belong to identify whether they are basically producing any threat or not.

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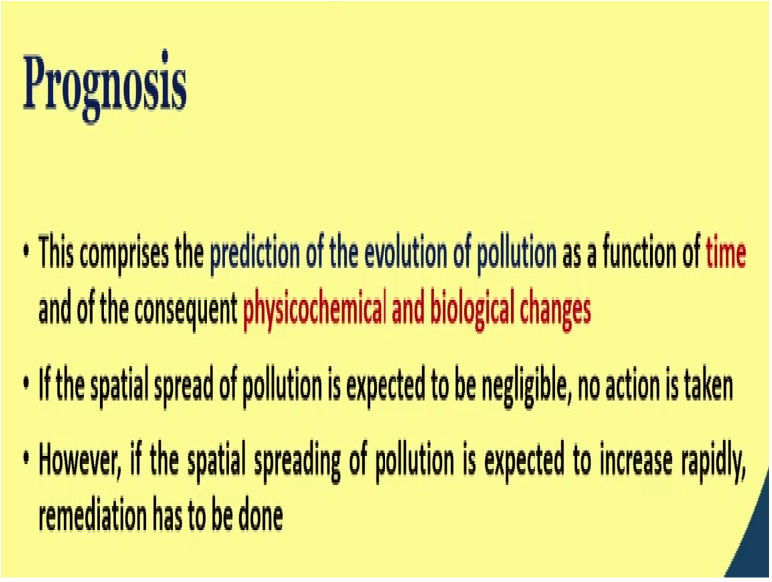

And the second important aspect is prognosis and this comprises the prediction of the evolution of the pollution as a function of time and the consequent physiochemical and biological changes. If the spatial spread of pollution expected to be negligible, no action is taken. However, if the spatial spread of pollution is the expected to increase rapidly, then we have to go for the remediation practice.

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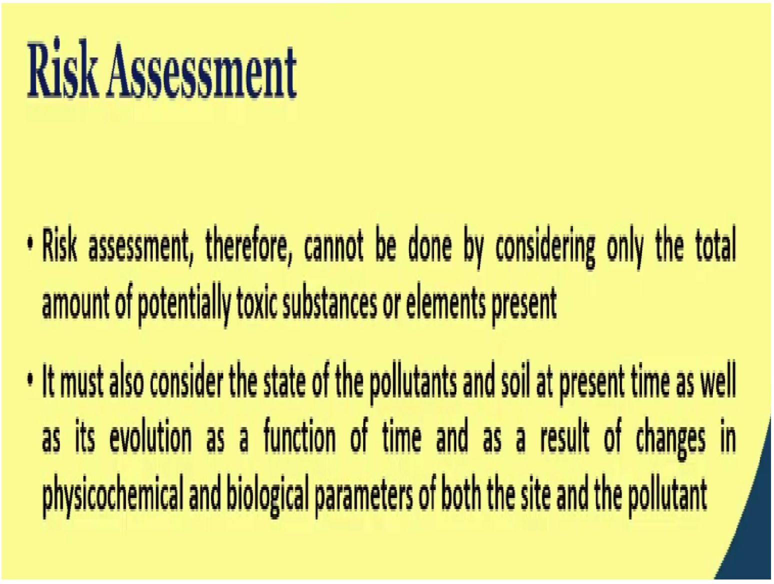

So, risk assessment therefore cannot be done by considering only the total amount of potentially toxic substances or element present. It must also consider the state of the pollutants and soil at present time as well as its evaluation. So both diagnosis and prognosis as a function of time as the result of changes in physiochemical and biological parameters of both the site and pollutants.

So guys let us wrap up our lecture here. We have completed the risk assessment. So in our last lecture of week 11, we are going to discuss some of the remedial measures for this type of pollutants and I hope that you have learned something new in this lecture. If you have any queries, feel free to email me and I will be more than happy to answer your queries. Thank you very much.