

Soil Science and Technology
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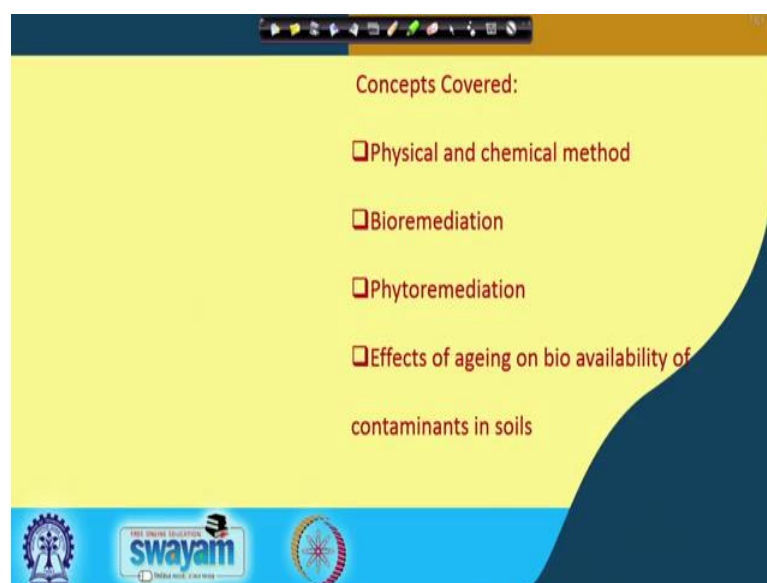
Lecture – 46
Remediation of Organic Pollutant

Welcome students to this week 10 lectures of Soil Science and Technology and in this lecture, we will be starting the first topic that is remediation of soil organic pollution. And in the last week of lectures in that means in week 9 of lectures we have learnt about different types of organic pollutants specifically we talked about different pesticides, herbicides as well as different xenobiotics which are responsible for different environmental pollutions.

And then, we talked about how they you know contaminate you know environment specifically soil. And in this lecture you know in this lecture we will be talking about this remediation of soil organic pollution; that means, what are the different ways of remediating these organic pollutants?

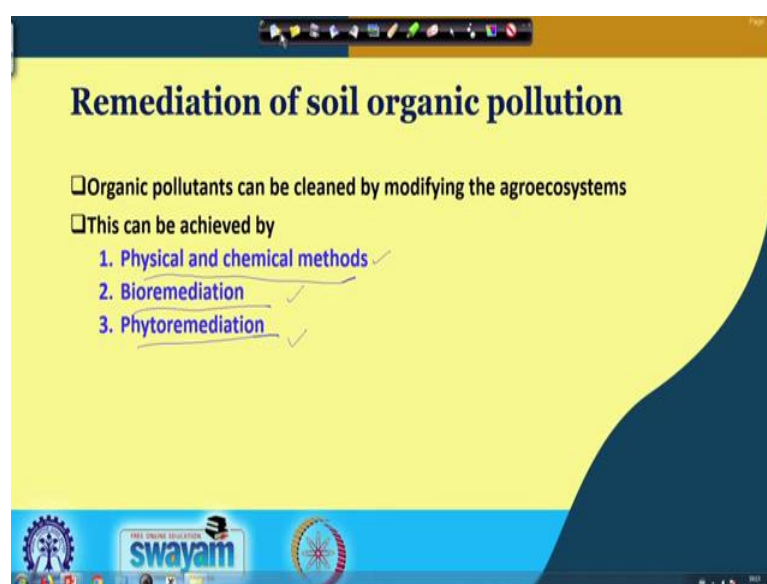
Obviously, remember that the available mechanisms are you know there a numerous available mechanisms and; obviously, it will not be possible to cover each of them. But I will try to give you a basic overview as well as I will try to touch the important mechanisms which we can employ to remediate this soil organic pollutions coming from different pesticides and other organic chemicals like xenobiotics. So, let us start; so, in this topic or in this lecture we will be basically covering the following concepts.

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These concepts are physical and chemical methods of remediation and then we will talk about bioremediation, we will talk about phytoremediation and then we will be talking about effect of ageing on bio availability of contaminants in the soil.

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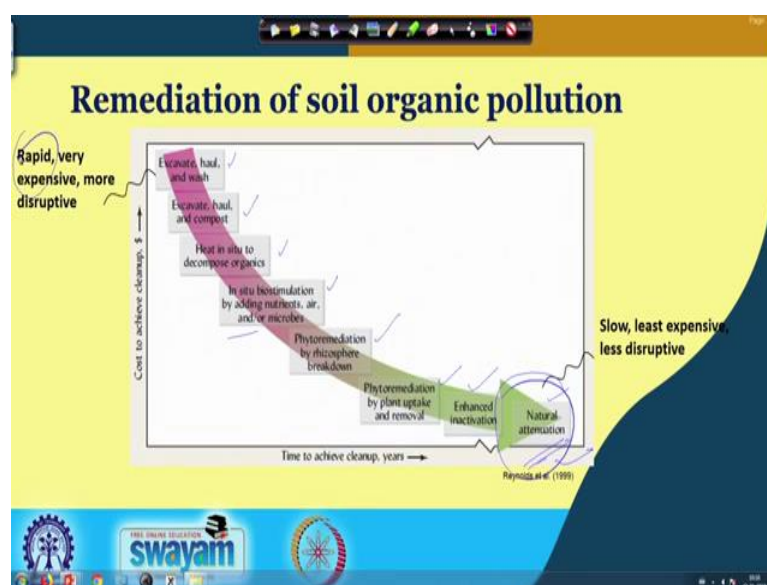


So, if we talk about the Remediation of soil organic pollutions organic pollutants can be cleared by modifying the agroecosystems; specifically when we talk about the organic pollution agroecosystem; you can you know you can either remediate or clean this organic pollutant by modifying the agroecosystems. And there are three major processes

which you can employ to achieve this goal of cleaning the pollutant organic pollutants from the agroecosystems.

These are mainly physical and these are mainly physical and chemical methods and then bioremediation and phytoremediation. And we will be discussing this physical and chemical methods first, then we will be discussing bioremediation and then we will be discussing the bio you know phytoremediation.

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So, let us go ahead and see you know what is the trends of you know what is the trends or what is the relation between time to achieve cleanup in years as well as cost to achieve the cleanup. So; obviously, this graph shows that and it is clearly visible that as far as the cost is concerned; the high cost is involved in excavating any contaminated soil and then hauling them and then washing them.

So, this is the most expensive method which is available for cleaning the; you know organic pollutants following by excavating haul and then composting this organic compound. You know that due to the composting process all the; you know majority of the pollutant gets remediate or cleaned up; so this is another way and another way of dealing with it is to heat in situ to decompose or organics to decompose organic.

So; basically so, these are the methods which are arrange in the order of their expensiveness. So, you can see excavating, hauling and washing; obviously, it is an most

expensive method following guide excavating hauling and composting. And then heat in situ to decompose the organics; that means, the organic chemicals and organic pollutants followed by there in situ bioremediation or in situ biostimulation by adding nutrients air and or microbes. We will be talking about this later on and then phytoremediation by rhizosphere breakdown and then, you know phytoremediation by plant uptake and removal and then, enhance inactivation and finally, natural attenuation which is the totally natural process of remediating the organic chemicals.

So, you can see that these basically shows the you know the order of you know in the decreasing order of cost involved for clean up and, but; obviously, although it is very expensive to excavate haul and wash, it is very you know it is very rapid as compared to this natural attenuation.

So; obviously, as we go down from this excavating hauling and washing to excavating hauling and composting to all the way to natural attenuation process, it is slowing down the process. So; obviously, the natural as attenuation, although it is the least expensive method and it is less disruptive than that of the excavating hauling and washing; obviously, these natural attenuation is a very very slow process where as these excavating hauling and washing is a rapid process.

So, whenever you need a rapid you know rapid clean up of organic pollutants from your agro ecosystem and you do not have any you know you do not have any limitation resource wise; obviously, the excavating, hauling and washing is the best process.

So, now you will have an idea about you know what is the tradeoff between time to achieve the clean up and then the cost achieve the clean up. So, you can take the best decision which one to practice based on your particular condition of organic pollution. So, guys I hope that, this graph gives some insight on how to select the best remediation practice for remediating soil organic pollution.

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Physical and chemical methods

Ex-situ and in-situ treatment

- ❑ Soil is excavated and transported in ex-situ treatment
- ❑ Incineration, leaching, vacuum pumping etc is done to address the pollutant
- ❑ Ex-situ is highly expensive and disrupts the soil but it is the only option when the soil is extremely polluted
- ❑ In-situ treatment uses same process as ex-situ
- ❑ However, it reduces the excavation and transportation costs
- ❑ Contaminants may be eliminated or immobilized in soil

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So, let us go ahead and see what are the important physical and chemical methods well, in the physical and chemical methods we generally discuss you know divide them into ex-situ and in-situ treatment as you can see. Ex-situ means, you know you know off the side and in-situ means on the side.

So, you can see here you know ex-situ in the you know soil is excavated and transported in ex-situ treatment, because we are excavating the soil from his own original proportion origin original position and then transporting to some other places. And then, you know that incineration leaching and vacuum pumping etcetera is done to address the pollutant. So, these are ex-situ treatments, and remember that ex-situ is a highly expensive and disrupt the soil, but it is the only option when the soil is extremely polluted.

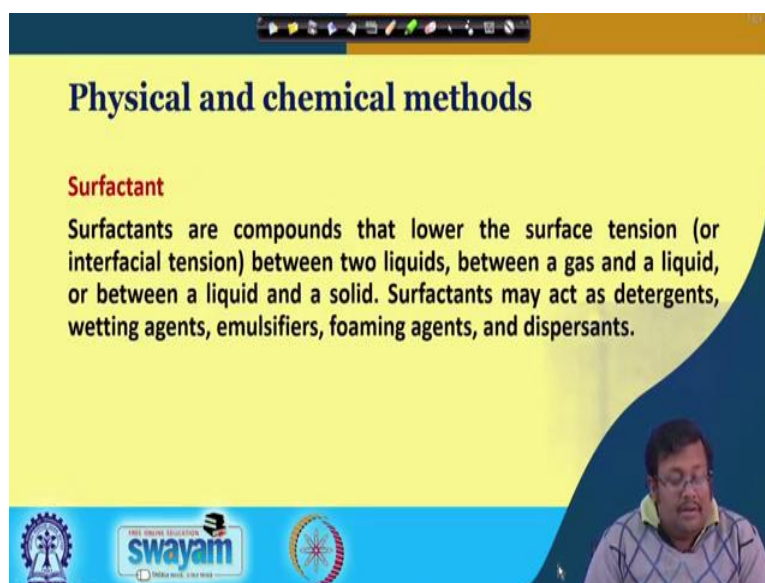
So, whenever the soil is extremely polluted in-situ you know in-situ treatment may not be sufficient and then we need some ex-situ treatment to excavate the soil to disturb the soil and transport the soil to some other places for further treatment. And in comparison to ex-situ treatment, in-situ treatment uses same process as ex-situ ex situ; however, it reduces the excavation and transportation costs.

So, this excavation and transportation costs which you know consist a huge amount of cost involved which involve huge amount of cost for you know for ex-situ treatment is not present in in-situ; however, the contaminates may be eliminated or immobilized in the soil. So, this is the difference between ex-situ treatment and in-situ treatment;

obviously, again in the ex-situ treatment the you know soil is basically excavated and transported for you know for treatment to some other side and it is generally performed when the soil is extremely polluted.

However, in-situ treatment you know does not allow it does not allow for excavation and transportation. So, that is you know that is why it is less expensive and in the in-situ treatment contaminants may be eliminated or immobilized in the soil.

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Physical and chemical methods

Surfactant

Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

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So,,let us see some physical and chemical agents which are responsible for remediating the organic pollutants, one of them is called surfactant. And surfactant are compounds that lower the surface tension or interfacial tension between two liquids between a gas and liquid or between a liquid and solid. We have already discussed about the surface tension in our soil moisture lectures.

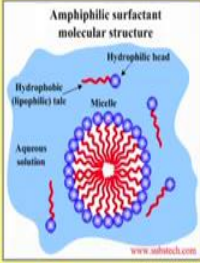
So, I am not going to detail in you know going to further discuss on the surface tension. But remember that this surfactants are basically you know they lower the surface tension between two liquids between a gas and a liquid or between in liquids and solid, and this surfactants may acts as a detergent, wetting agents, emulsifiers, foaming agents and dispersants. So, generally the you know the detergent which we used for cleaning our clothes and other washing purpose can be used as an you know important surfactants. So, let us see how this surfactants works for you know for remediating the organic pollutant.

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Physical and chemical methods

Surfactant

The ability of surfactants to reduce the interfacial energy is related to the polar-nonpolar structure of their molecules. A surfactant molecule consists of two different groups: a hydrophilic head and a hydrophobic tail. Such dual structure of surfactants is essential for reduction of the energy on the interface between a polar and non-polar phases.



Amphiphilic surfactant molecular structure

Hydrophilic head

Hydrophobic (lipophilic) tail

Micelle

Aqueous solution

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So, surfactants are you know as a typical you know structure. So, the ability of surfactant to reduce the interfacial energy is related to the polar-nonpolar structure of their molecule. So, you can see there a you know this is a structure of a surfactant and; obviously, you can see that the structure you know surfactant molecule consists of two different groups a hydrophilic head.

So, this is the hydrophilic head and this is the hydrophobic tail. So, this hydrophilic head you know is responsible for attracting the polar liquid such as water. However, these hydrophobic tail can attract the nonpolar compounds; like, organic like you know any oil or any organic pollutants which are non polar in nature.

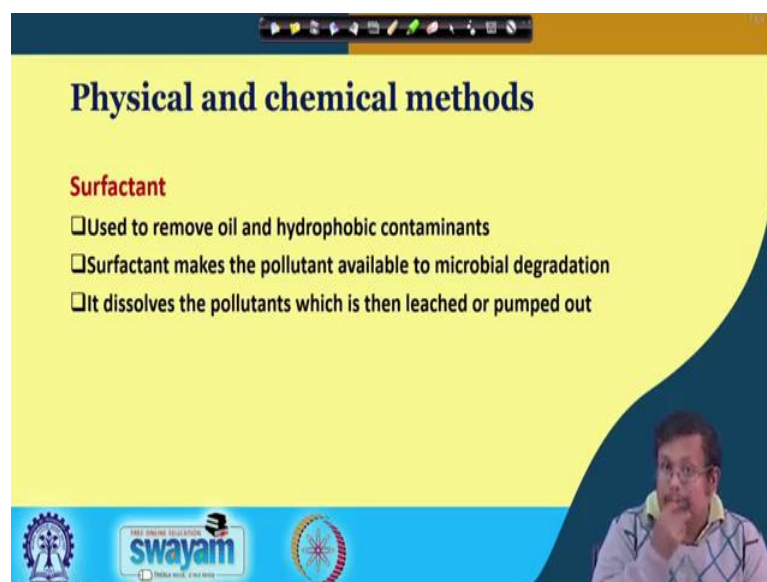
So, when we add these detergent of surfactants in an interface between you know interface between a polar and nonpolar phases. For example, when some non polar organic compound or organic pollutants are mixed with polar solvent like, water. Then if we add this surfactants or detergents, it will you know it will reduce the energy on the interface between polar and nonpolar phases and it does it by a specialized kind of arrangement.

As you can see here, whenever we add this type of detergents or chemical or surfactants in this interface between polar and nonpolar phases, they arrange in such a way that this you know this hydrophilic head or water loving head is arranged you know in the vicinity of water molecule and you know this is an aqueous solution; obviously.

So, these all these hydrophilic heads will be arrange towards this aqueous solution; whereas, this hydrophobic tail is arrange inside, so it should not get you know in touch with this aqueous solution. And this hydrophobic tail basically attracts this organic molecules or organic pollutants which are present in this solvent in this aqueous solution and basically it attracts it binds with those organic pollutants, and then it removes all these organic chemicals.

So, you know a surfactant molecule you know by its hydrophilic head and hydrophobic tail, these dual structure of surfactant is essential for removing any particular you know non polar organic compound which is present within a polar solvent like water or so this is how the surfactant works for removing the pollutant

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Physical and chemical methods

Surfactant

- ☐ Used to remove oil and hydrophobic contaminants
- ☐ Surfactant makes the pollutant available to microbial degradation
- ☐ It dissolves the pollutants which is then leached or pumped out

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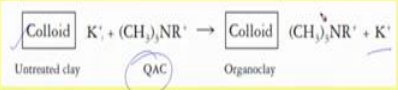
So, surfactants can be used to remove oil and hydrophobic compounds and surfactant makes the pollutant available for further microbial degradation and it dissolves the pollution which is the leached or pumped out. So, this is the three ways through which surfactants can remove all or remediate the organic chemicals from any contaminated agroecosystem.

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Physical and chemical methods

Organoclays

- Certain surfactants replace the metal cations in clays
- Example: Quaternary Ammonium Compounds (QACs) replace K^+ in clay



The diagram illustrates the chemical process of organoclay formation. It shows a reaction where a 'Colloid' of 'Untreated clay' containing K^+ reacts with a 'QAC' (Quaternary Ammonium Compound), represented as $(CH_3)_3NR^+$. The products are a 'Colloid' of 'Organoclay' where the K^+ has been replaced by the $(CH_3)_3NR^+$ group, and a free K^+ ion is released.

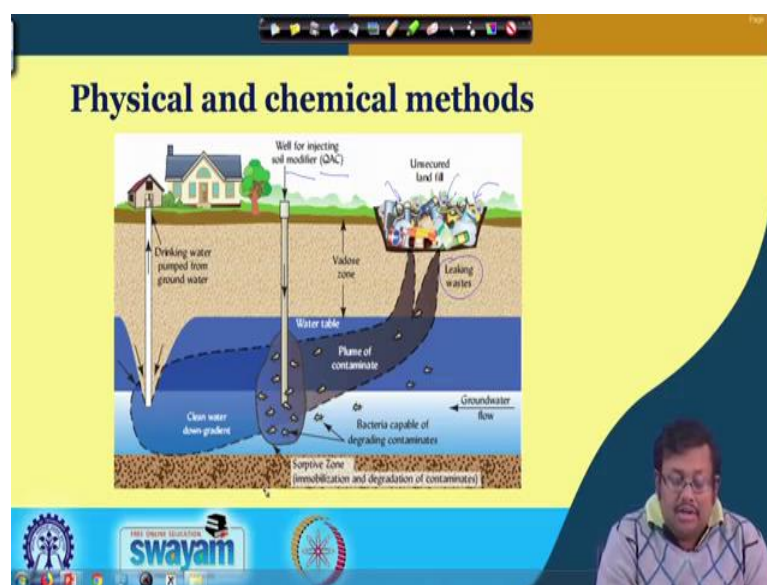
- The modified clay known as 'organoclay' attracts non-polar compounds and immobilizes them until natural degradation takes place

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The second important thing we should talk about these organoclays. Now, you know that certain surfactants replace the metal cations in the clays. An example are Quaternary Ammonium Compounds or QACs, these surfactants can replace the potassium in the clay. You can see here these the soil colloids of untreated clay and which contains potassium which is attached which is absorbed at the clay surface, and this is a quaternary ammonium compounds and this quaternary ammonium compound basically replaces the K and ultimately it produces this modified clay we call it organoclay.

And this modified clay or organoclay attracts nonpolar compounds and immobilizes them until natural degradation takes place. So, this is how this organoclays helps in you know remediation of organic pollutants from the environment.

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So, this picture gives a snapshot of how this physical and chemical methods acts you know act for you know removing the organic pollutants from the soil as you can see a soil and water. As you can see here, let us consider these is an unsecured landfill where all the municipal solid waste and other solid waste are being dumped. And; obviously, there is some leaking wastes through is this leaches are contaminate you know the important contaminates are basically coming to the ground water.

At this basically, the vadose zone and this is the groundwater flow as you can see. So, this basically shows the plume of contaminate and ultimately it is contaminating the ground water. However, if we are injecting the soil modifier or quaternary ammonium compound, this quaternary ammonium compound will basically goes into this is a groundwater and you can see here this is a sorptive zone which is basically immobilize which is you know which is characterized by this immobilization and degradation of contaminants.

So, in the sorptive zone, in the presence of quaternary ammonium compound these bacteria are basically, you know multiply and ultimately these bacteria you know degrade this contaminants and ultimately clean water goes to down the gradient for drinking water pump and ultimately the drinking water is pumped up from this groundwater. So, again we are introducing the leaking wastes into the groundwater.

However, we are also injecting the soil modifier or QASC which is basically you know modified the soil and ultimately producing the organoclays.

And these organoclays basically all the either you know helps in the degradation of helps in the degradation or attachment of organic pollutants within the organoclays. And also bacteria also degrades these organic chemicals and ultimately this clean water you know goes, and ultimately the drinking water pump from the groundwater. So, this is how this physical and chemical methods work together.

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Distribution coefficient, K_d

□ K_d is the ratio of the pollutant sorbed in soil to the one present in solution

$$K_d = \frac{(\text{mg contaminant/kg soil})}{(\text{mg contaminant/L solution})}$$

□ Higher the K_d , more the contaminant in soil than in solution, the stronger the pollutant is held by soil and the lesser it leaches

□ Organic matter rich soils and organoclays have higher K_d

□ This strongly adsorbed pollutant is then naturally degraded by microbes

Diagram illustrating the distribution of a pollutant in soil. The diagram shows a cross-section of a soil particle with labels: 'Nonpolar (hydrophobic) organic molecules' (green dots), 'Organic matter' (green area), 'Mineral particle' (brown area), and 'Water film' (blue area). A person is visible in the bottom right corner of the slide.

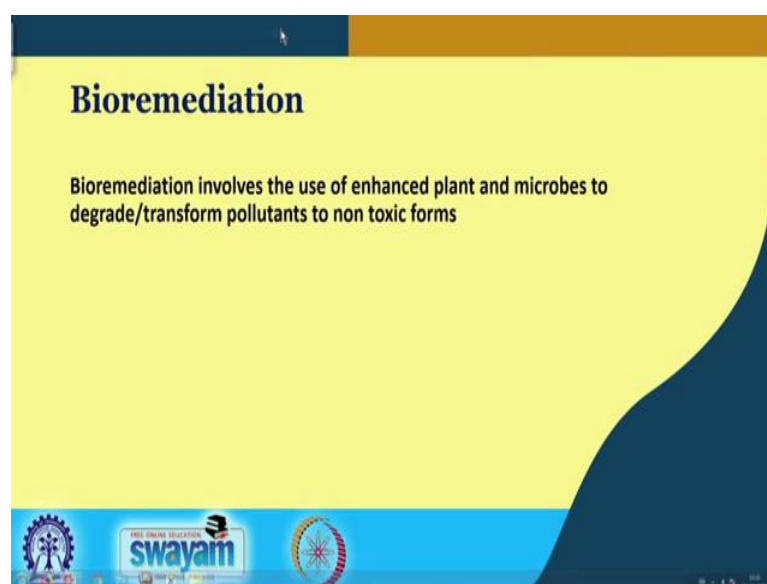
So, let us go ahead and see, what is ok; one more thing we want to talk; obviously, this distribution co-efficient we have already talked about it in our previous lecture. So, a give; so, I am just going through very quickly. So, you know that K_d is the ratio of pollutant sorbed in soil to the one present in solution.

So; basically, takes this format you know this formula of K_d is basically when you have you know mg of contaminate per kg of soil and over mg contaminate per liter of solution. An; obviously, the higher the K_d values is the more the contaminant in soil than in solution. The stronger the pollutant is held by the soil and lesser it leaches, and organic matter rich soils or you know and organoclays have higher K_d ; obviously, that is why they can attract more organic chemicals as compared to other as compared to the soils which are devoid of organic matter and this strongly absorbed pollutant is then naturally degraded by microbes.

Now, you can see here this is a mineral particle, and these are the organic matter. And; obviously, there is a thin layer of water molecule which is basically polar and in the polar water film you can see some non polar hydrophobic organic molecules. And these nonpolar organic molecules are absorbed over the non polar organic matter in a quite high concentration as compared to the mineral particles which is basically you know as compared to the water also.

So, this shows basically, the attraction between the hydrophobic organic matter to other organic you know other non polar organic compounds or in other words other non polar organic pollutants.

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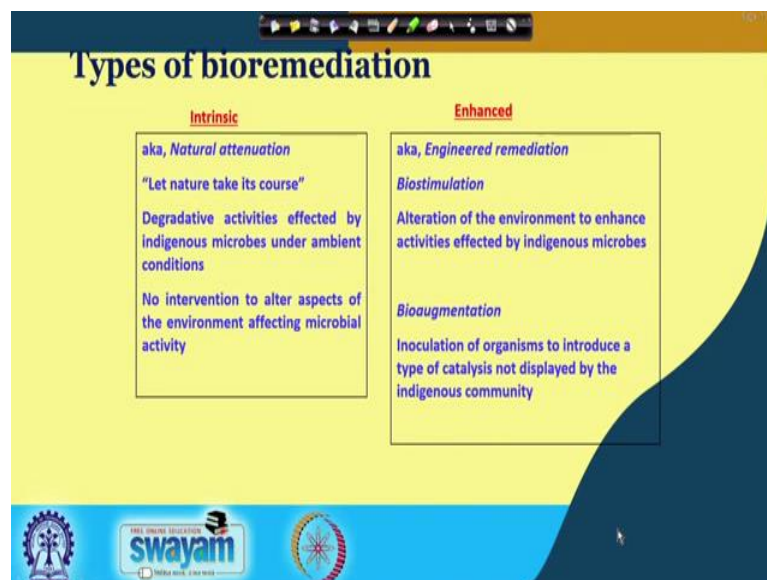


So, another important term is bioremediation; now bioremediation involves the use of enhanced plant and microbes to degrade and transform pollutants to non toxic forms. So, whenever you know remember one thing with the terms bio comes from whenever we are adding, whenever we are remediating the soil pollution or any environmental pollution through the help of any biological organisms.

Now, this biological organisms maybe some microbes, you know some indigenous microbes are some microbes which we can introduce in that particular environment or this bioremediation can be achieved through some plants. And we will be discussing those you know microbial bioremediation and plant and plant bioremediation the other name of plant bioremediation is basically phytoremediation and we will discuss those.

So, basically these microbes and plant transform the pollutants to non toxic form and we will see how they do it.

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So, let us see what are the major types of bioremediation? There are two major types of bioremediation, one is called intrinsic bioremediation other is enhanced bioremediation. Now, intrinsic bioremediation also known as the natural attenuation and, enhanced bioremediation known as the engineered remediation.

So, if you see the intrinsic bioremediation, intrinsic bioremediation basically, works on the principle that let nature take its course. So, it is basically natural process and it is the degradative activities affected by the indigenous microbes under the ambient condition, and no intervention to alter aspects of the environment affective microbial activity is there in case of intrinsic bioremediation.

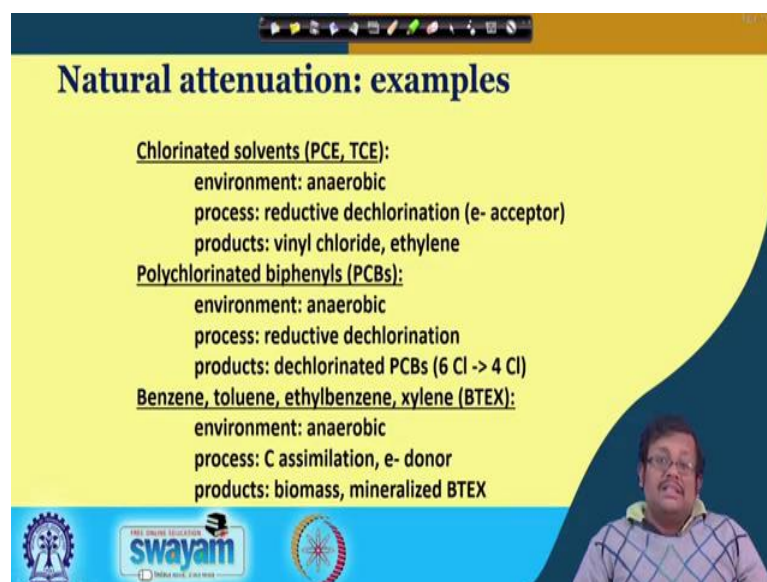
However, in case of enhanced bioremediation; since, we are talking we are terming a as an engineered remediation you know there are couple of ways we can you know engineer this enhanced bioremediation. One of the way is biostimulation, the biostimulation is basically alteration of the environment to enhance the activities effected by indigenous microbes.

And Bioaugmentation, bioaugmentation is inoculation of organisms to introduce a high you know a type of catalysis not displayed by the indigenous community. So, again what

is the difference between bioaugmentation biostimulation? Biostimulation is basically, alteration of the environment to enhance activities effected by the indigenous microbes we are not inoculating you know foreign organisms. However, in case of bioaugmentation we are introducing or inoculating organisms to introduce a type of catalysis not displayed by the indigenous community.

So, we are introducing some new community in that particular area to enhance the microbial activity or bioremediation potential; so that is called bioaugmentation. Now, I hope that it is clear, what is the difference between intrinsic and enhanced bioremediation.

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Natural attenuation: examples

- Chlorinated solvents (PCE, TCE):
 - environment: anaerobic
 - process: reductive dechlorination (e- acceptor)
 - products: vinyl chloride, ethylene
- Polychlorinated biphenyls (PCBs):
 - environment: anaerobic
 - process: reductive dechlorination
 - products: dechlorinated PCBs (6 Cl -> 4 Cl)
- Benzene, toluene, ethylbenzene, xylene (BTEX):
 - environment: anaerobic
 - process: C assimilation, e- donor
 - products: biomass, mineralized BTEX

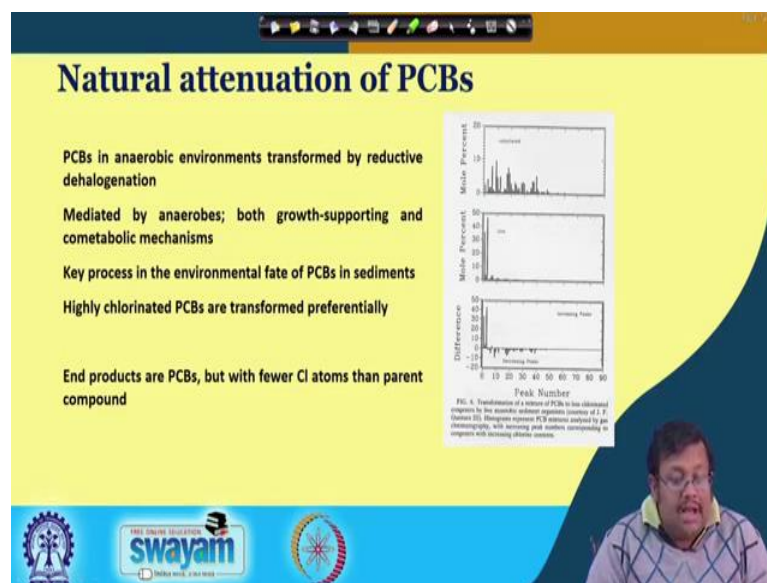
The slide is a presentation slide with a yellow background and a blue header. It lists three categories of contaminants and their bioremediation details. At the bottom, there are logos for 'swayam' and 'INDIA RISE, I WILL RISE' along with a small image of a person in the bottom right corner.

So, what are the some examples of natural bioremediation; obviously, I have given here several example. First of all the bioremediation of chlorinated solvents like, you know like Tetrachloroethylene and then PCE. And; basically, for remediating this chlorinated solvents you know or Perchloroethylene and this Tetrachloroethylene, we require anaerobic environment and in the anaerobic environment in the process of reductive dehalogenation they generally you know they generally the remediation process is governed by this reductive dechlorination process I am sorry. Reductive dechlorination process and this reductive dechlorination process ultimately produces the products of vinyl chlorides and ethylene.

Let us talk about polychlorinated biphenyls PCBs. So, in case of PCBs the environment is; obviously, anaerobic in nature and the process involved is reductive dechlorination. And in the ultimate products we will get that dechlorination and dechlorinated PCBs are having less number of chlorine than, that of the polychlorinated biphenyl which is the starting point of this remediation process.

Then; obviously, this BTEX, BTEX stands for Benzene, Toluene, Ethylbenzene and, Xylene and these 4 compounds are degraded in the anaerobic environment and the process is basically carbon assimilation and ultimate products are biomass as mineralized BTEX. So, you can see that these are some of the examples of natural attenuation process and this natural attenuation is you know again which you know what I am talked in my earlier slides, that it is natural attenuation. Although, it is least expensive, but it takes a long period of time to remediate all these organisms sorry all these organic pollutants.

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So, this shows this graph basically shows transformation of a mixture of PCBs to less chlorinated you know congeners by live anaerobic sediment organisms, and this histograms basically represent the PCB mixtures analyzed by gas chromatography with increasing peak numbers corresponding to the congeners with increasing chlorine contains.

So; obviously, the PCBs in anaerobic environment transferred by deductive dehalogenation and mediated by the anaerobes both growing growth supporting and co-metabolic mechanisms. Now, the co-metabolism is a specific type of metabolism, where two compounds are metabolize simultaneously, whether the metabolism of the second components depends on the presence of the first compound or component.

And the key process of the environmental and this you know this reductive dehalogenation is the key process of environmental fate of PCBs in sediment. And remember that highly chlorinated PCBs are transformed preferentially the less chlorinated PCBs. And end products are also PCBs, but with fewer chlorine atom than the parent compound, as I have told in my previous slide. So, these are some this is an one example of natural attenuation of polychlorinated biphenyls.

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Enhanced ioremediation

Bioaugmentation

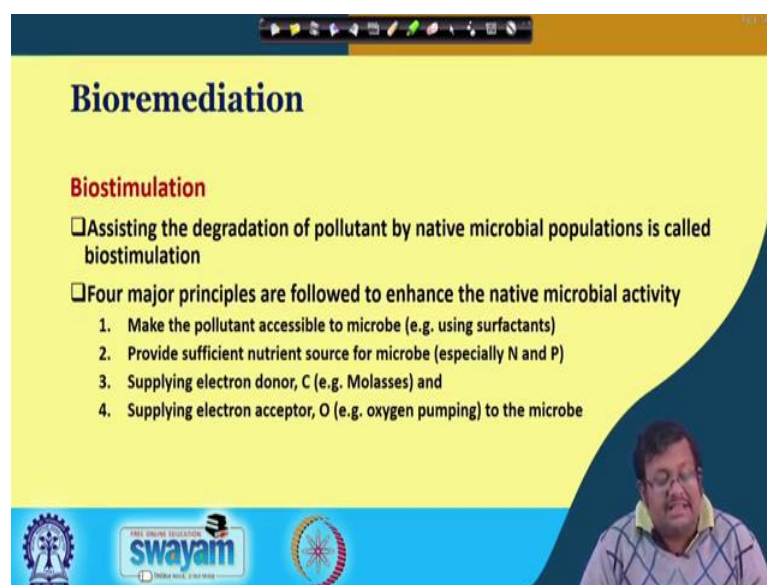
- ☐ Special microbes which degrade the pollutant is introduced into the soil
- ☐ These microorganisms degrade the pollutant more readily than native population

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So, what is; so, we have seen one couple of examples of a natural attenuation. Let us see what is bioaugmentation; let us see ok, bioaugmentation is an example of enhanced remedy I have you know enhanced remediation, enhanced bioremediation.

So, it should read as bio remediation and this special you know this bioaugmentation basically you know special microbes which degrades the pollutants is introduced into the soil. And this microbes or microorganism degrade the pollutants more readily than native population. So, these are two important features of bioaugmentation.

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Bioremediation

Biostimulation

- Assisting the degradation of pollutant by native microbial populations is called biostimulation
- Four major principles are followed to enhance the native microbial activity
 1. Make the pollutant accessible to microbe (e.g. using surfactants)
 2. Provide sufficient nutrient source for microbe (especially N and P)
 3. Supplying electron donor, C (e.g. Molasses) and
 4. Supplying electron acceptor, O (e.g. oxygen pumping) to the microbe

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And then, biostimulation is assisting the degradation of pollutants by native microbial population is called biostimulation. Now 4 major principles are followed to enhance the native microbial activity, you can see here making the pollutant accessible to the microbes that is by using the accessible to the microbes by using surfactants.

You know in the surfactants they have the capability by using their hydrophilic and hydrophobic, hydrophilic head and hydrophobic tail. Using the hydrophobic tell they can attract those non polar organic compounds, and these non polar organic compounds further they can make accessible to the microbes are further by degradation.

And they can provide sufficient nutrient source to the; for microbes especially nitrogen and phosphorus and supplying the electron donor, like carbon in the form of molasses. And supplying the electron acceptor organ you know oxygen through oxygen pumping to the microbes. So, these are the 4 major principal follow you know we generally followed to enhance the native microbial activity you know by biostimulation processes.

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And then; let us show, let us see one example of oil spill cleanup and in the oil spill cleanup we can see that clearing oil spill in cooler and nutrient poor region is very very slower. And this is due to the lack of nitrogen and phosphorus source for oil degrading microbes and also you know slow reaction at low temperatures. And it is special oil soluble nitrogen and phosphorus fertilizers are applied in this case and apart from providing nitrogen and phosphorus they also disperse the oil making them more available to the microbes.

So, you can see here, this is an oil spill treatment in controlled versus fertilized plots. So, you can see in the X axis, it is basically time after treatment in weeks; and in the Y axis, it is basically index of crude oil remaining basically index of crude oil remaining. So, you can see that in the fertilized plot; obviously, there is a steep decrease in index of crude oil remaining as a time goes on. However, so; when we are adding the fertilizers in the form of you know nitrogen phosphate fertilizers. And; obviously, this will enhance the microbial activity to degrade the oil as compared to the control or unfertilized soil.

So, guys you know we have talked some basic ideas about you know remediation of organic chemicals. We started with organic, you know we started with different physical and chemical methods. And then we started talking about different bioremediation techniques. You know let us wrap up here and in the next lecture we will be starting

from here and we will try to finish this, and then will be talking about different inorganic pollutants which are present in the soil environment.

Thank you very much.