Environmental Soil Chemistry
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Lecture - 45
Pollutant-Soil Solution Interaction (Contd.,)

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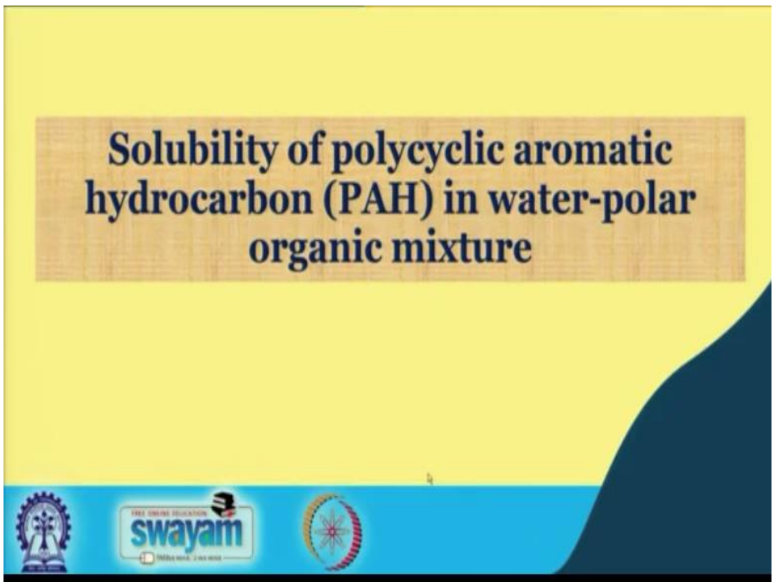

Welcome friends to this fifth lecture of week 9 or module 9 and in this week, we are actually talking about the soil pollutants and pollutant as well as soil solution interaction and today, we are going to talk about the solubility of polycyclic aromatic hydrocarbons, in short, we know this compound as PAH, polycyclic aromatic hydrocarbon in water-polar organic mixture. So we will be basically talking in details about the PAH, their structure, their properties, and their solubility in water-polar organic mixture.

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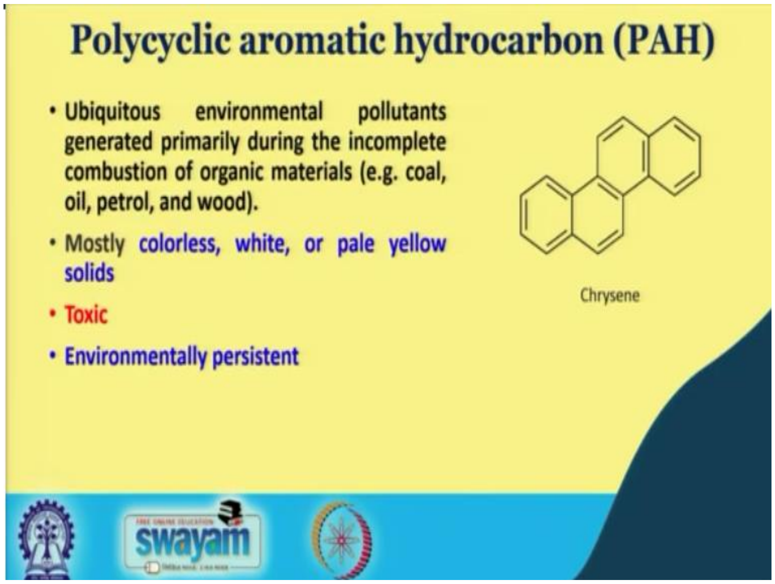

Let us start with the polycyclic aromatic hydrocarbon or PAH. This is basically a ubiquitous environmental pollutants generated during the incomplete combustion of organic materials. We will see the sources of this PAH in the coming slides. So basically, these environmental pollutants generate due to the incomplete combustion of organic materials like coal, oil, then petrol and wood and basically they are mostly colorless, sometime they are white or pale yellow solids.

They are very toxic in nature and they are also environmentally persistent; so that is why it is a problematic compound for environment, because there is both toxic as well as environmentally persistence, so it can remain in the environment for longer duration of time. Here, I just presented one example of this PAH, so the chrysene is one of the examples of this polycyclic aromatic hydrocarbon and you can see here, there are multiple benzene rings attached to each other. So that is why it is called polycyclic aromatic hydrocarbons.

So let us move ahead and see what the toxicity is of PAH. Well, the mechanism of toxicity is considered to be interference with the function of cellular membrane as well as with enzyme system, which are associated with the membrane. So basically, it disrupts the function of the cellular membranes as well as the enzymatic activity, which are associated with the cellular membrane. Remember that these compound or PAH is basically a group of compounds.

These PAH compounds are both carcinogenic and also it can produce mutagenic effects, and also they are basically potent immune-suppressants. So these are the major drawbacks or major ill effects of this PAH, as far as the human health hazards are concerned. So that is why they are considered as important environmental pollutant.

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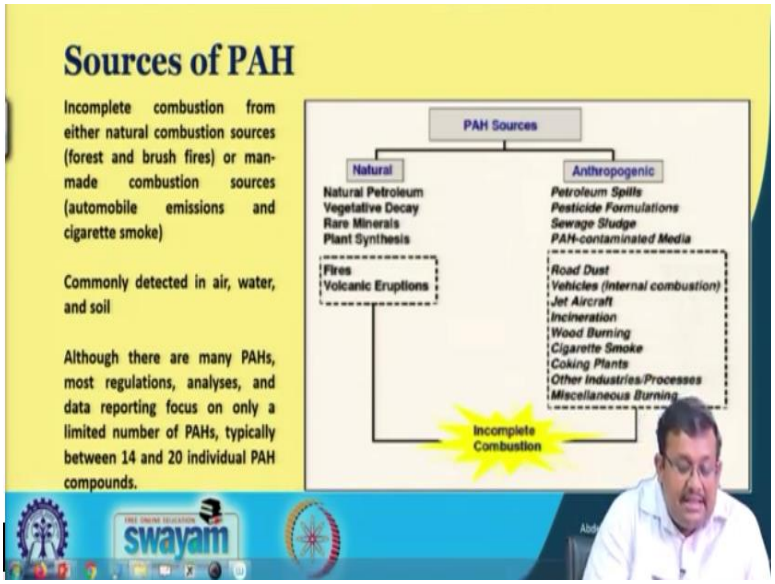

So let us talk about the sources of PAH. I have already told you that it is a product of incomplete combustion from different compounds like petroleum, coal, wood. So let us see in details what are the other sources. So obviously, I have written here, it is basically the major source is incomplete combustion from either natural combustion sources like forest or brush fires. So forest fire, as you know, it is a natural combustion source or brush fire is a natural combustion source.

So, basically incomplete combustion happens in the forest and brush fire. It generates the PAH or manmade combustion sources, like automobile emissions and cigarette smoke. So you can see both natural as well as anthropogenic combustion sources or manmade combustion sources, when they result in incomplete combustion, they basically generate this polycyclic aromatic hydrocarbons.

Now basically, this polycyclic aromatic hydrocarbons, since I have also mentioned that they are ubiquitous in nature, so you can find them in air, water as well as in soil. So they are ubiquitous in nature. Now although there are many PAH, most regulations by analysis and data reporting focus only a limited number of PAH. PAH is basically a group of compound. However, as far as the regulations, analysis, and data are concerned, we are focused on a limited number of PAH.

Typically, between 14 to 20 individual PAH compounds. So we will see those PAH compounds in our coming slides, but let us discuss in details what are the natural and anthropogenic sources for this PAH. So you can see the natural sources are natural petroleum, vegetative decay, then rare minerals, plant synthesis, so obviously when there is fire as well as volcanic eruptions and ultimately produces some incomplete combustion, then they generate the PAH compounds.

As far as the anthropogenic impacts are concerned, some sources are petroleum spills, pesticide formulations, then sewage sludge, we have already discussed sewage sludge in our previous lectures and also PAH contaminated media. So all these are important anthropogenic sources and when they produce this incomplete combustion, they also produce the PAH. Now what are those anthropogenic compounds, like road dust, then internal combustion from vehicles, then jet aircraft, incineration, wood burning, cigarette smoke, then coking plants, and also other industries and process and miscellaneous burnings.

So all these basically when they generate the PAH when they undergo the incomplete combustion. As you can see, both the natural sources as well as anthropogenic sources are responsible for the generation of PAH and this PAH can be found both in air, water and soil, so that is where they are ubiquitous in nature.

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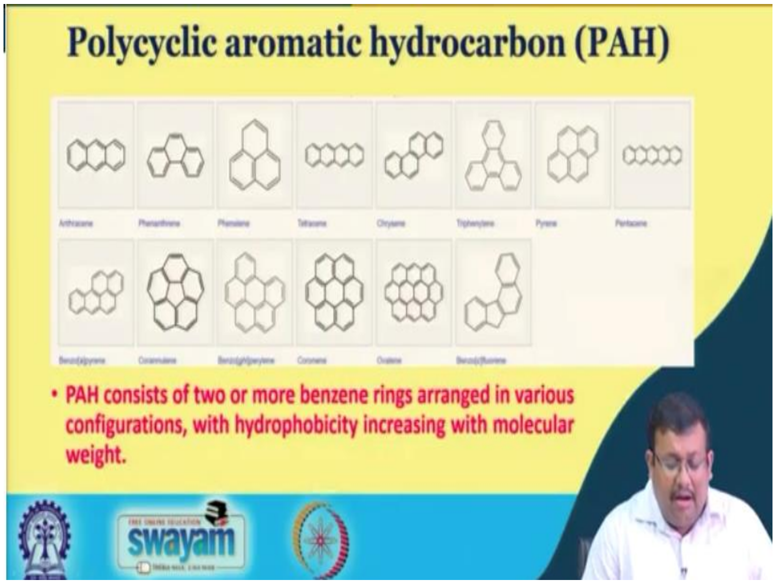

Here a couple of examples of PAH compounds. I told you that it is a group of compounds. We can see here, it is anthracene, then phenanthrene you can see, then phenalene, then tetracene, then chrysene, we have already seen the structure of chrysene in our previous slide, then triphenylene, then pyrene, then pentacene, then benzopyrene, then corannulene, then benzoperylene, then coronene, then ovalene, and benzoflurene.

These are all PAH compounds. Now PAH, the name itself suggests that it is basically polycyclic aromatic hydrocarbons. So there must be more than one cycle of aromatic ring. So basically, the PAH consists of two or more benzene rings. So obviously, the characteristic features of PAH structure is it has two or more benzene rings arranged in various configuration with hydrophobicity increasing with molecular weight.

They are hydrophobic in nature and their hydrophobicity increases with the increase in molecular weight. So basically, we can say that when the number of rings increases obviously their hydrophobicity also increases.

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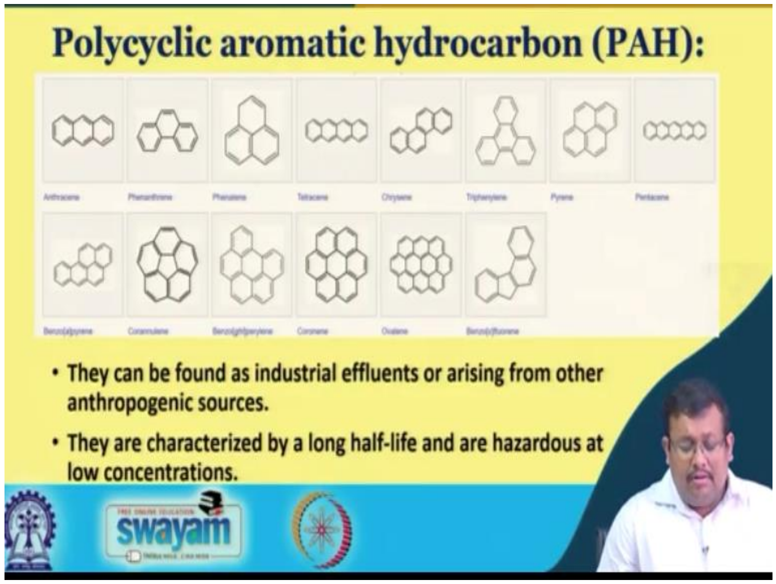

So they also can be found as industrial effluents or arising from other anthropogenic sources. We have seen already the sources of PAH in different industrial sources, industrial effluents, and also different anthropogenic sources in our previous slides. So they are characterized by a long life hazardous at low concentration. In the previous slide, we have seen that they are environmentally persistent.

So they can remain in the environment, soil, air as well as water for long duration of and at the same time, they are very hazardous and toxic at very low concentration. So these are some of the characteristic features of this PAH compound.

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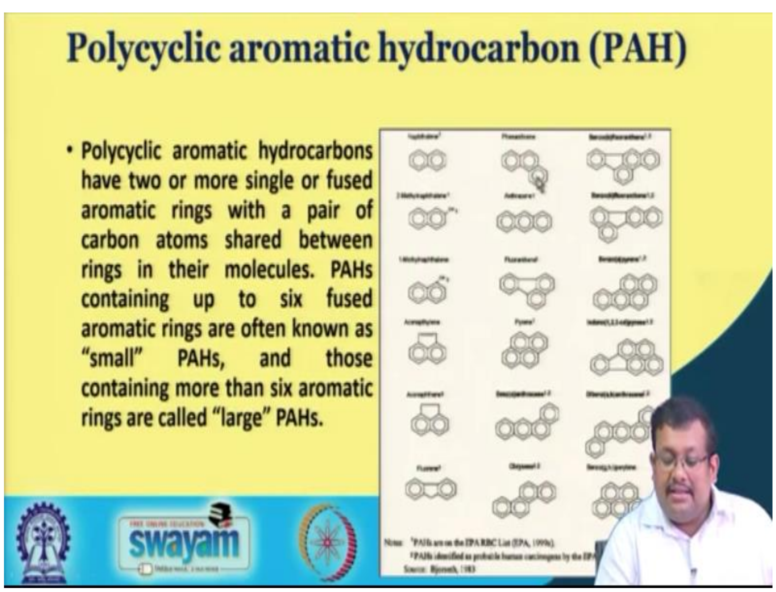

Now polycyclic aromatic hydrocarbons, we have already seen that they have two or more fused aromatic rings with a pair of carbon atom shared between the rings in their molecules. So obviously we can see here in case of naphthalene, phenanthrene, then benzofluoranthene, and so on so forth, then fluorene, then obviously pyrene. So you can see a lot of PAH compounds; they are having the fused benzene rings and with a pair of carbon atoms shared between the ring in their molecules.

Obviously, the pair of carbon atoms, as you can see here, they share between their molecules. PAH contains up to 6 fused aromatic rings, are often known as the small PAH and those containing more than 6 aromatic rings are known as large PAH. So obviously, within the PAH compounds also there is a classification, the small PAH and large PAH. The small PAH are those PAH, which are up to 6 rings and those which are having more than 6 aromatic rings are known as the large PAH compounds.

So the simplest PAH as defined by the international agency for research in cancer are phenanthrene. So phenanthrene as you can see, this is the structure of the phenanthrene, so this is phenanthrene. So as far as this international agency for research and cancer, this phenanthrene and anthracene, so anthracene structure is also given here. So phenanthrene and anthracene, these 2 are the simplest PAH, which both contains 3 fused aromatic rings.

As we can see, this is 1, this is 2 and 3 fused aromatic rings in case of phenanthrene; however, in case of anthracene, this is 1, then 2 and 3. So, 3 fused aromatic rings in case of anthracene. Now on the other hands, smaller molecules such as benzene are not PAH, because in case of benzene, there is only one aromatic ring. Now naphthalene, which consists of 2 coplanar, 6 membrane rings, as you can see here, this is the naphthalene.

So naphthalene, which consists of 2 coplanar 6 membered rings sharing an edge is another aromatic hydrocarbon. Therefore, it is not a true PAH. So this is not a true PAH, though is referred as a bicyclic aromatic hydrocarbon. So these naphthalene, this contains 2 fused aromatic rings. So in the true sense, it is not a PAH, however, it is sometime referred as the bicyclic aromatic hydrocarbons.

So however, as far as the structure of PAH are concerned, obviously we can see phenanthrene and anthracene both of which are showing 3 fused rings, structured aromatic ring structure are known as the simplest PAH among all the PAH compounds.

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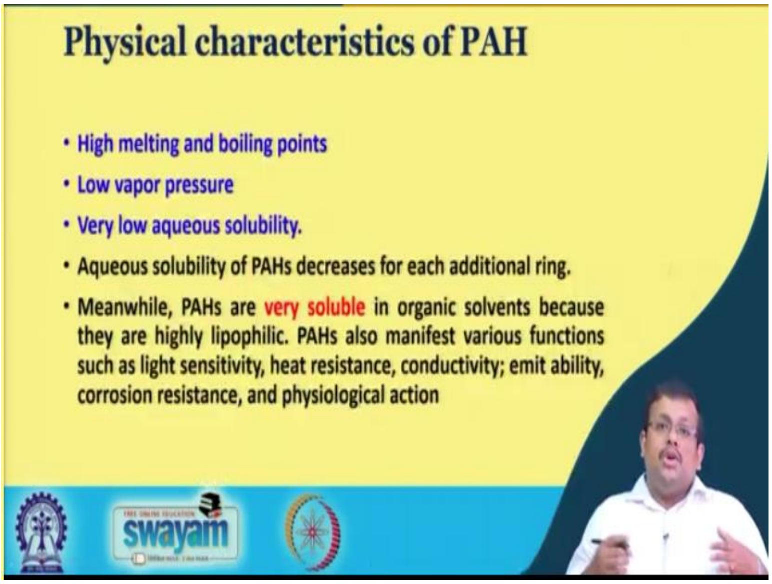

So if you see the physical characteristics of the PAH, we can see there are certain important points. First of all, we can see that PAH compounds have high melting and boiling points and they have low vapour pressure and very low aqueous solubility. So since they are non-polar in nature, they are having very low solubility in polar water. So this aqueous solubility of PAH decreases for each additional ring.

So basically, they are having very low solubility in water and the solubility further decreases with each additional ring. Now remember that PAH are very soluble in organic solvent, because they are highly lipophilic in nature. That means, fat soluble in nature. PAH also manifests various functions such as light sensitivity, heat resistance, conductivity, emitability, corrosion resistance and other physiological actions. So let us see what are the other features of this PAH compounds.

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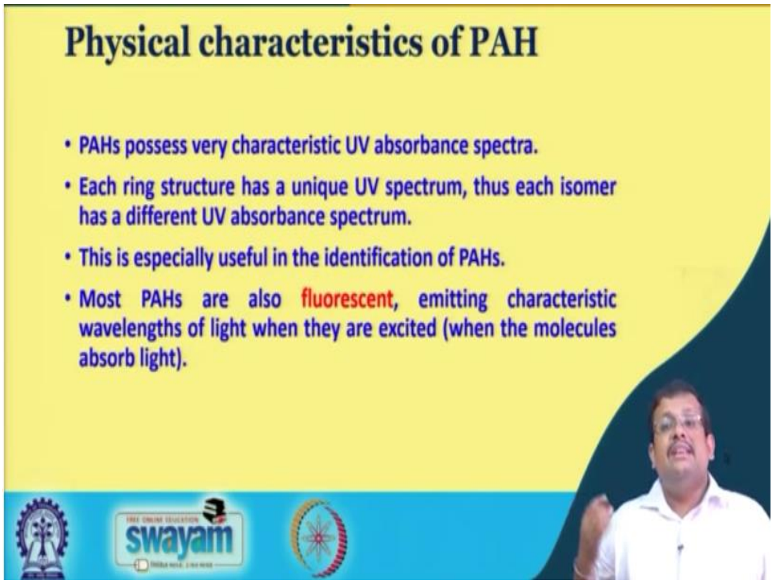

Now PAH also possess very characteristic UV absorbance spectra. Now each ring structure has a unique UV spectrum, thus each isomer has a different UV absorbance spectrum and this absorbance spectrum for these PAH compounds are useful for their identification. So each compound under the PAH group basically has their own unique UV absorbance spectrum. Now most PAH are also fluorescent.

That means, they emit characteristics wavelength of light when they are excited, when the molecules absorb light. So basically, they can emit characteristics wavelength of light or fluorescent when they are excited. So, most PAH compounds are also fluorescent. So, these are the major features of these PAH compounds.

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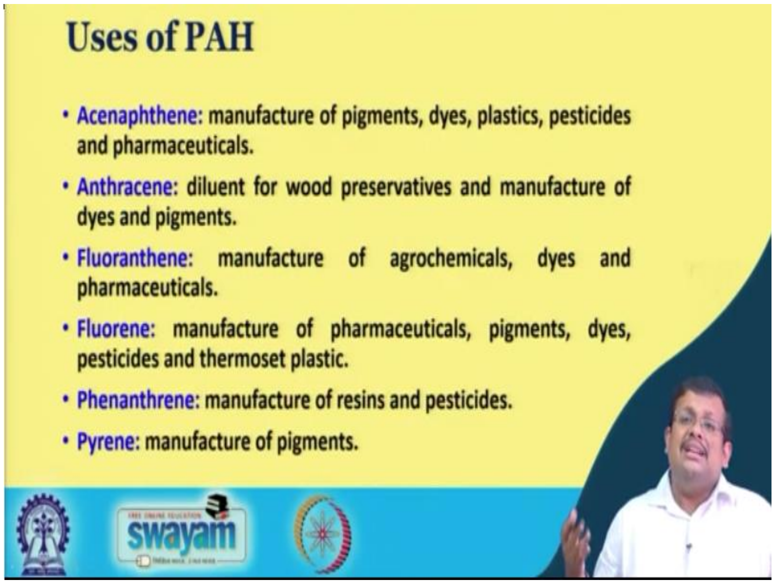

So let us see what are the uses of this PAH compounds. First of all, we can see the acenaphthene. Acenaphthene is basically used for manufacturing of pigments, dyes, plastic, pesticides and pharmaceuticals. If you see the anthracene, anthracene are used as a diluents for wood preservatives and manufacture of dyes and pigments. If you see the fluoranthene, then basically it is used in the manufacture of agrochemicals, dyes, and pharmaceuticals.

Fluorine is basically manufacturer of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic and also phenanthrene, if you see the phenanthrene, phenanthrene is used for the manufacture resins and pesticides and if you consider pyrene, pyrene was also used for the manufacture of pigments. So you can see that these PAH compound has a very good applicability for industrial purpose for the production and manufacturing of different pigments, plastics, polymers, pesticides and pharmaceuticals.

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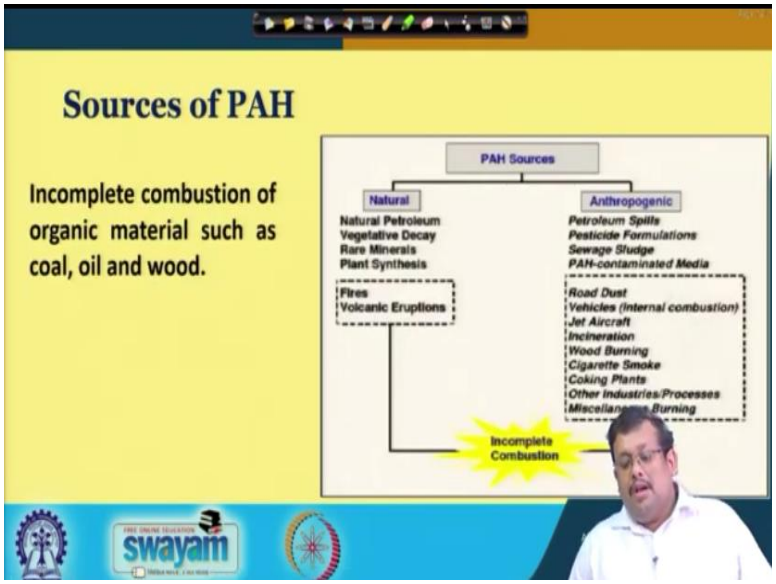

So we have already seen the sources of PAH. It is basically incomplete combustion of organic materials, such as coal, oil and wood base from either natural sources or anthropogenic sources.

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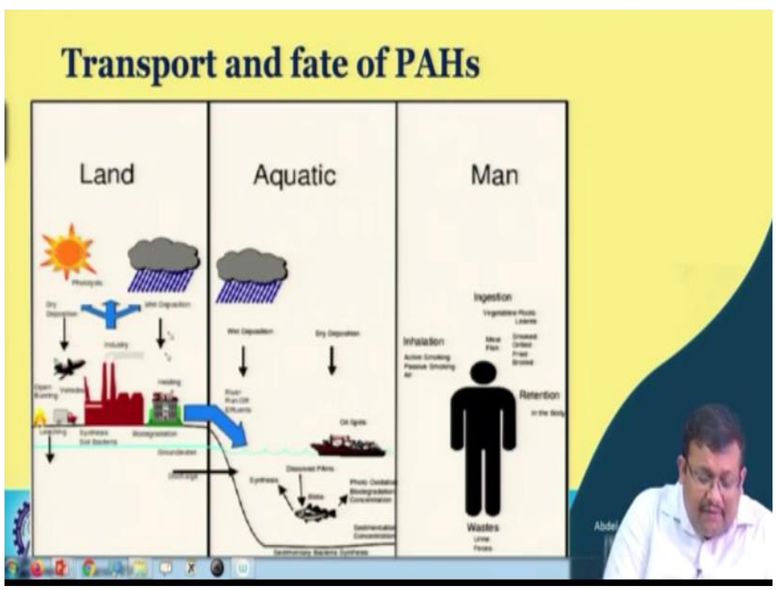

Now if you see the transport and fate of PAH, this is very important. How PAH can move from land to aquatic system and ultimately they produce the human health hazards. This figure shows very good representation of the transport and fate of PAH. So you can see that when there is an open burning and also due to the leaching from the vehicles and in case of land. If you first consider the land, we see the transport of these PAH in the land system can occur through leaching, through dry deposition, as you can see, and also through wet deposition and from industrial emission.

So these are some of the reasons and vehicular emissions, and also when they go to the soil, they produce different types of biodegradation, and ultimately they reach into the ground water and ultimately they discharge into different water bodies. When they discharge into the different water bodies, these PAH they basically dissolve into the water and then they are basically affecting the biota, which is present in the aquatic system, also due to the rainfall there are wet deposition.

Now this discharge, which we are seeing through these blue arrow is basically from river, then ran off on different effluents from the industrial sources, and also in the aquatic system, we can see dry deposition and then oil leaks from different tankers. These are some of the reason through which we can see the PAH compounds in the aquatic environment and also these PAH compounds or petroleum compounds basically go through photo-oxidation and biodegradation.

And these are the important process, as far as the fates of these PAH are concerned. Now if you see the human effect or inhalation, in case of due to inhalation, like active smoking or passive smoking in air. Through this inhalation like active smoking or passive smoking in air, these PAH compounds can enter into the human body. They can be retained into the human body. Ingestion, how, due to the vegetables, roots and leaves, then meat and fish and also smoke, grilled and fried and all these things, when human ingest, they basically uptake these PAH through these compounds.

Again, if we summarize, in the land we can see different sources of PAH. First of all, the wet deposition and then dry deposition, also vehicular emission and also the generation from different types of industries and this petroleum basically goes to the soil and then undergoes biodegradation, and ultimately will be discharged into the water bodies through rivers, effluents and runoffs, and then affecting the biota of the aquatic system and then finally go for biodegradation, photo-oxidation, and also here you can see wet deposition and dry deposition are the other sources.

And also, different types of oil spills from different tankers or petroleum digs can occur. So these are some of the sources. As far as the human consumptions are concerned inhalation, ingestion are the major route through which the PAH are transporting inside our body.

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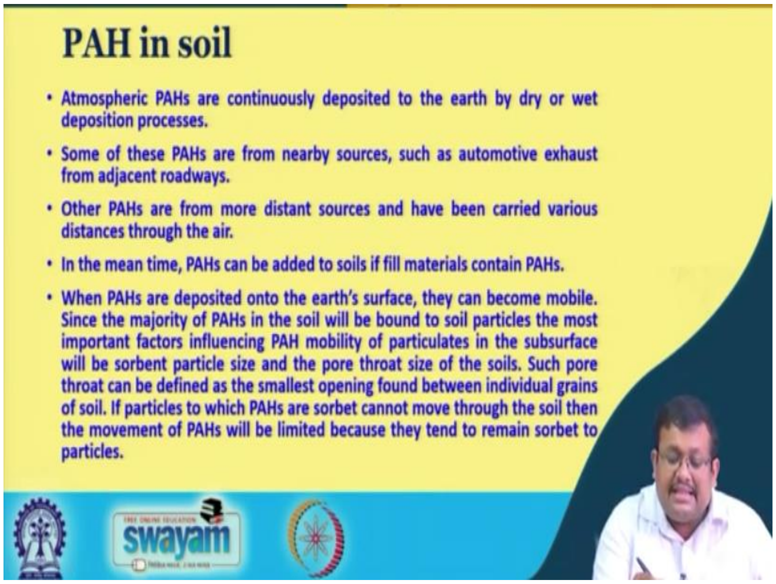

So if you see the PAH compounds in the soil, there are certain important points. Now atmospheric PAH are continuously deposited by dry and wet deposition process. Now some of these PAH are from nearby sources, such as automobile exhaust from adjacent roadways, other PAH are from distant sources and have been carried various distance through the air. In the meantime, PAH can be added to the soil in field materials containing the PAH.

So when PAH are deposited on to that surface, they become basically mobile in nature. Since the majority of the PAH in the soil will be bound to soil particles are most important factors influencing PAH mobility of the particles of the subsurface will be sorbent particle size and the pore throat size of the soil. Such pore throat can be defined as a smallest opening found between the individual grains of soil.

So if particles to which the PAH are sorbent cannot move through the soil, then the movement of PAH will be limited, because they tend to remain sorbent to the particle. So this is how the movement of PAH in the soil is basically controlled.

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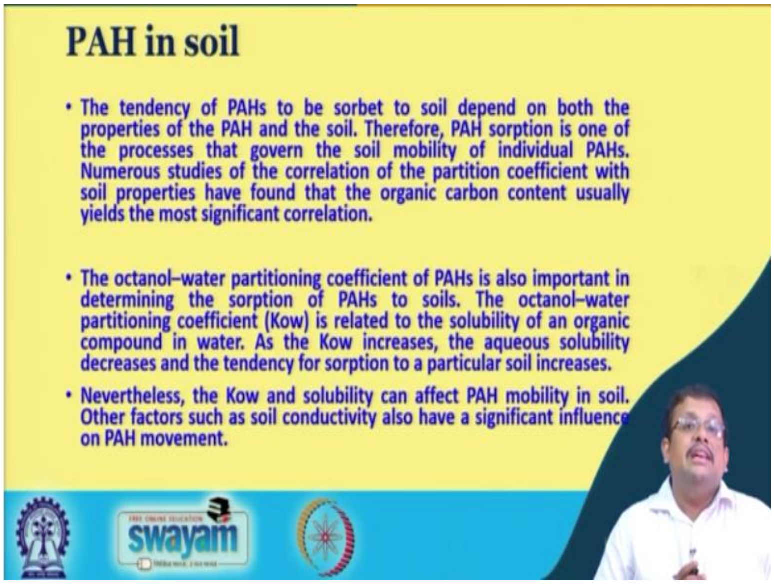

Now if we see other factors for PAH retention in the soil, the tendency of the PAH to be sorbet on the soil depends on both the properties of the PAH and the soil. So therefore, PAH sorption is one of the process that governs the soil mobility of individual PAH. Numerous studies of PAH related studies of the partition coefficient with the soil properties have found that the organic carbon content usually yields the more significant correlation.

Obviously, because organic compounds have their own attractive adsorption capacities. Now this octanol-water partitioning coefficients of PAH is also important in determining the sorption of PAH into the soil. The octanol-water partitioning coefficient, we generally denote this as Kow is related to the solubility of an organic compound in water. So as the Kow increases, the aqueous solubility decreases and the tendency for sorption to a particle soil increases. Now nevertheless, the Kow and the solubility can affect PAH mobility in soil. Other factors such as soil conductivity also have significant influence in the PAH movement.

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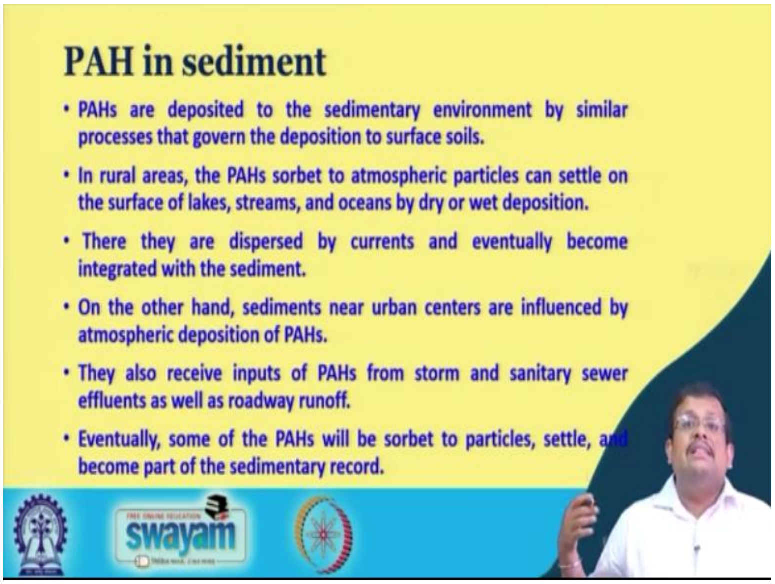

Now if you consider the PAH retention in the sediment, then PAH are deposited to the sedimentary environment by similar process, which we have seen already for the soil. Now in rural areas, the PAH sorbet to atmosphere, atmospheric particles can settle on the surface of the lake, streams and oceans by dry and wet deposition. There, they are dispersed by currents and eventually become integrated with the environment.

On the other hand, sediments near urban centers are influenced by atmospheric deposition of the PAH. Now they also receive inputs of PAH from storm and sanitary sewer effluents as well as roadway runoff. Now eventually, some of the PAH will be sorbet to the particles, settle, and become part of the sedimentary record. So basically, if you see the PAH movement in soil and sediment, they basically resemble to each other. So their interaction to the sediment and soil somewhat matches between each other.

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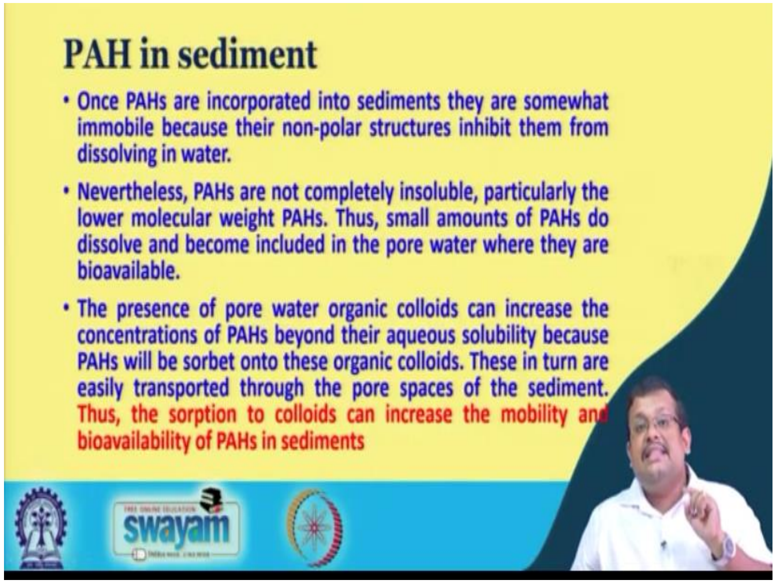

Also we have seen that once PAH are incorporated into the sediment, they are somewhat immobile, because they are non-polar structure inhibit them from dissolving in the water. Now nevertheless, PAH are not completely insoluble, particularly the lower molecular weight PAH. So these lower molecular weight PAH are somewhat soluble in water. Thus, small amounts of PAH do dissolve and become included in the pore water, where they are bioavailable.

So the pore water, which contains small amount of water, they are able to dissolve some amount of PAH and then this is how the PAH become bio-available. Now the presence of pore water organic colloids can increase the concentration of PAH beyond their aqueous solubility because PAH will be sorbet on these organic colloids. So since this pore, water organic colloids then also further increases the concentration of the PAH, because of their inherent solubilizing power.

Because these PAH are basically hydrophobic in nature, so in turn are easily transported through the pore spaces of the sediment. Thus, the sorption of the colloids can increase the mobility and bioavailability of PAH into the sediment. So this is how the PAH can move from one place to another place and making themselves bioavailable.

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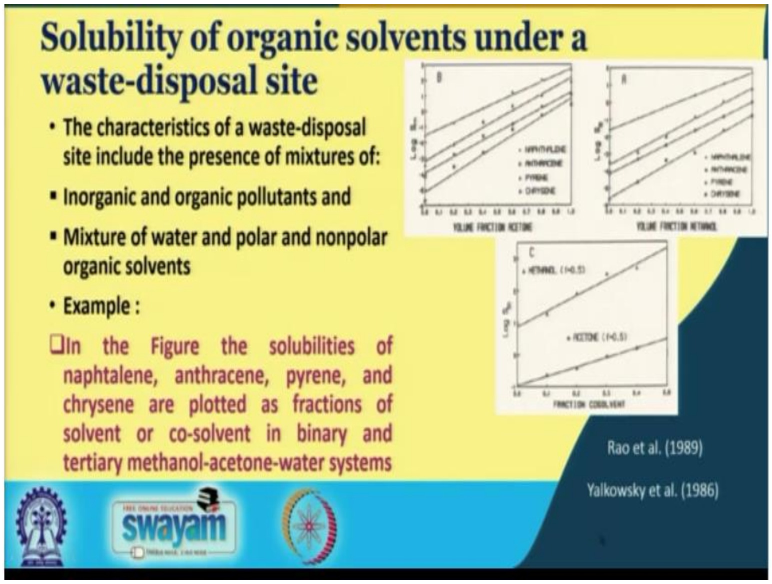

Now if you see the solubility of the organic solvents under a waste disposal site, this graph shows. These are some important graphs. So basically, the characteristics of waste disposal site includes the presence of mixture of inorganic and organic pollutants and mixture of water and polar and nonpolar organic solvents. So if you see the waste disposal site, this is a complex site and different complex biological and biogeochemical processes are going on.

So you can see in those waste disposal site or landfill site, inorganic and organic pollutants as well as mixture of water and polar and nonpolar organic solvents. Now in these 3 figures, you can see the solubilities of naphthalene, then anthracene, then pyrene, and chrysene are plotted as fraction of solvent or co-solvent in binary and tertiary methanol-acetone-water system. So these are tertiary methanol-acetone and water system.

So these are tertiary system and these are the binary system and so here we can see that these are basically, we are plotting the log of solubility and here volumetric fraction of acetone and also here in the second figure in the x axis, we are producing the volumetric fraction of methanol and the y axis we are putting the log of solubility and these graphs are showing for naphthalene, anthracene, pyrene, and chrysene. So let us see what are the inference which we can make from these graphs.

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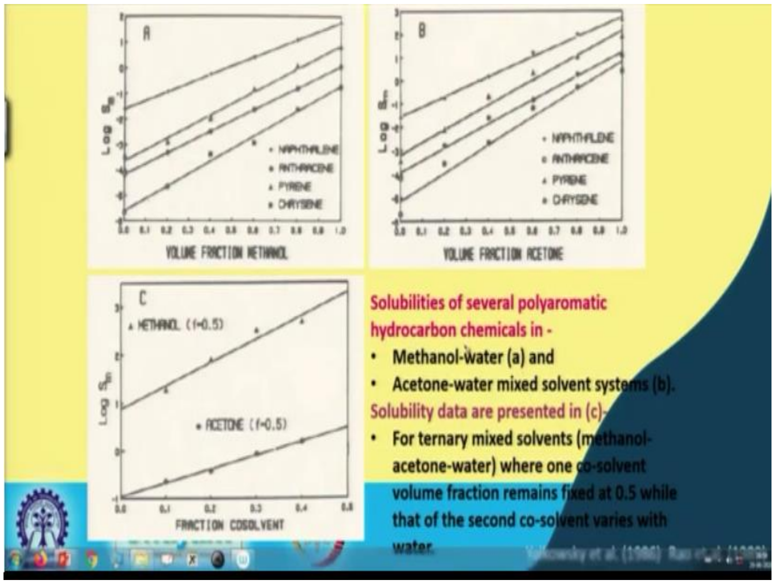

Now the solubility, we can see that the solubility of several poly aromatic hydrocarbons or PAH in basically here methanol water, so this is basically methanol water binary mixture. This is acetone water binary mixture and this third one is the ternary mixed solvent that is methanol, acetone and water. So here it is a binary mixture. This is another binary mixture, this is ternary mixture of solvents like methanol, acetone, and water, where one co-solvent volume fraction remains fixed at 0.5 while that of the second co-solvent varies with water.

Here, in the third figure, you can see that one co-solvent, here there are 3 co-solvents with water, so water and then co-solvents are methanol and acetone. So one co-solvent volume fraction remains fixed at 0.5 while the other second co-solvent varies with water. So what we can see from these graphs.

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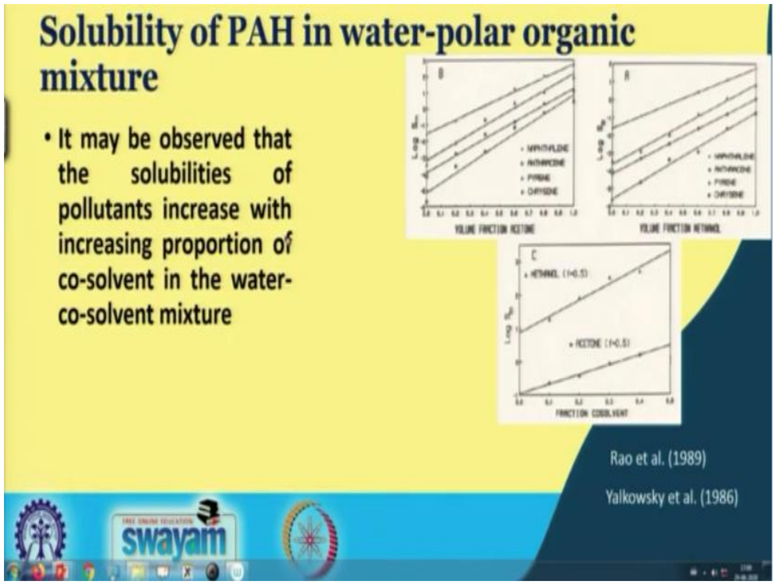

It can be observed that the solubilities of pollutants increase with increasing proportion of co-solvent in the water co-solvent mixture. So you can see here, in this binary mixture of water acetone and in this binary mixture of water methanol, we can see as the co-solvent fraction increases or proportion of this co-solvent increases just in this direction, that is volume fraction of acetone as well as volume fraction of methanol, we can see the solubility of the pollutants also increases as we can see here with the positive slope. So this is the major inference we can see from these plots.

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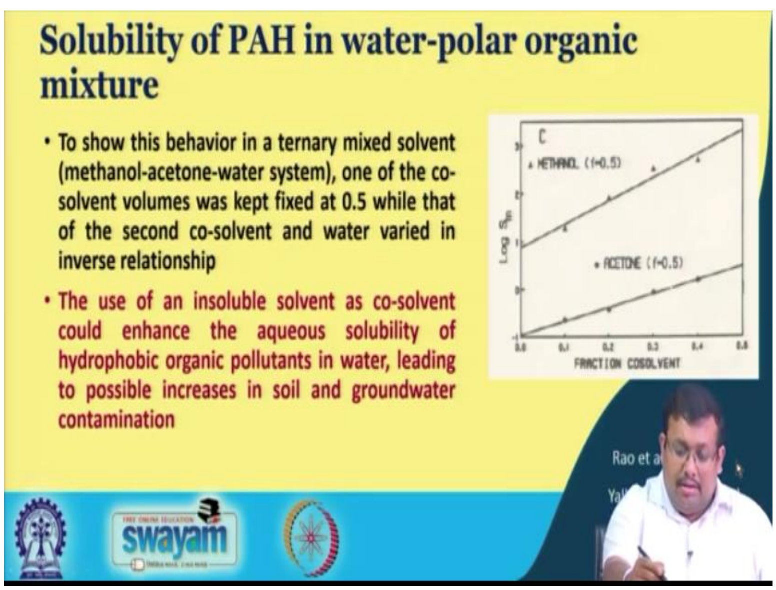

Now the third plot, to show this behavior in ternary solvent, so we have seen the increase in solubility of the pollutants with increasing volume fraction of a co-solvent in a binary mixture;

however for a ternary mixture solvent like methanol-acetone and water system, one of the co-solvent volume was kept as 0.5, while the second co-solvent was varied with inverse relationship.

Now we can see that the use of an insoluble solvent as co-solvent could enhance the acquired solubility of hydrophobic organic pollutants in water leading to possible increase in soil and ground water contamination. So as we can see, as we are basically fraction of co-solvent is increasing, so solubility of organic pollutants are basically increasing. So the use of insoluble solvent as co-solvent could enhance the aqueous solubility of these hydrophobic organic pollutant as you can see in water leading to possible increase in soil and ground water contamination. So these are some of the important inference. So guys, let us wrap up our module 9 and these are the references, which I used for these module 9.

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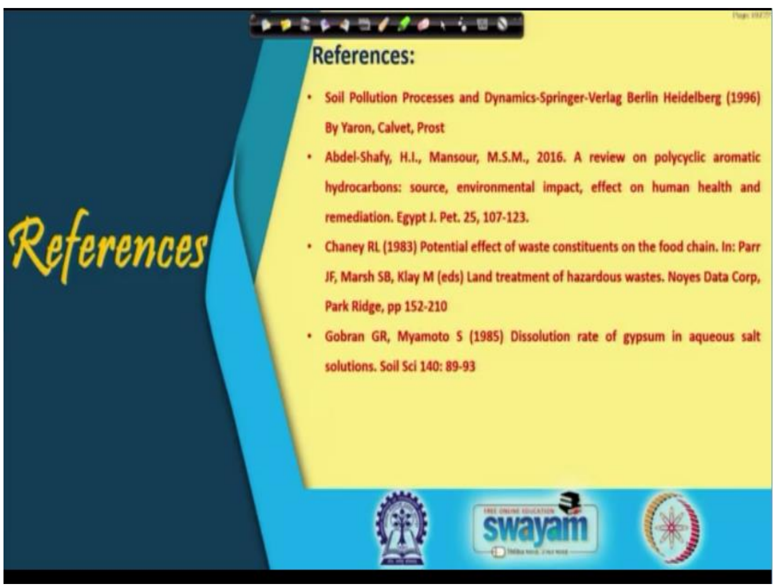

These are very good references. You can follow, for example, soil pollution process and dynamics written by Yaron, Calvet, and Prost as well as these very good review, that is the review on polycyclic aromatic hydrocarbons written by Abdel-Shafy and Mansour in 2016 and also potential effect of waste constituents on the food chain written by Chaney, Gobran, Myamoto dissolution rate of gypsum in aqueous salts.

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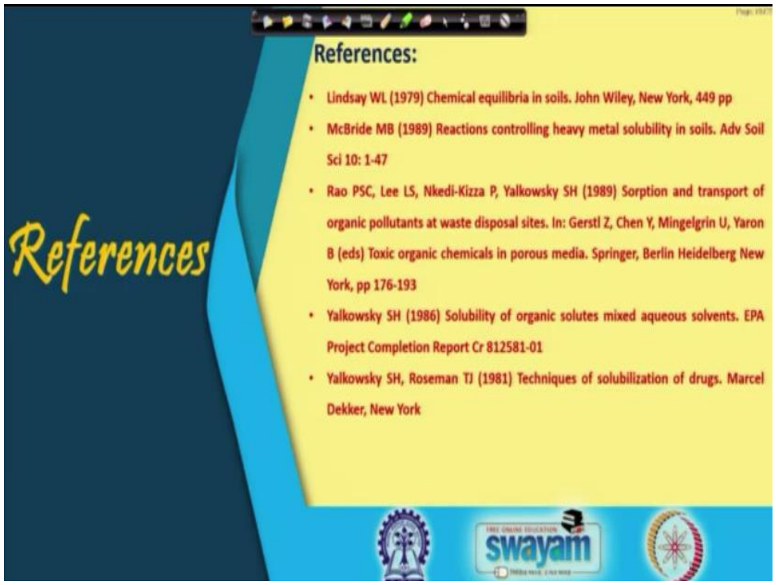

And also these articles by Lindsay, McBride, Rao et al, as well as Yalkowsky and so these are some very good references. You should learn, you should consult in more details to gain more comprehensive knowledge of pollutants and soil solution interaction and if you find any difficulties, just feel free to email me and let me know your queries and I will be more than happy to answer you guys. Thank you very much. Let us meet in our week 10 lectures to discuss some other aspects of environmental pollution. Thank you.