Environmental Soil Chemistry
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Lecture – 40
Soil Pollutants (Contd.,)

Welcome friends to this last lecture of week 8 and we are talking about the soil pollutants, so in the last 4 lectures, we have complete different inorganic pollutants of the soil and we started the organic pollutants of the soil. Among the organic pollutants we have discussed about the cationic organic pollutants and we started with the basic organic molecules.

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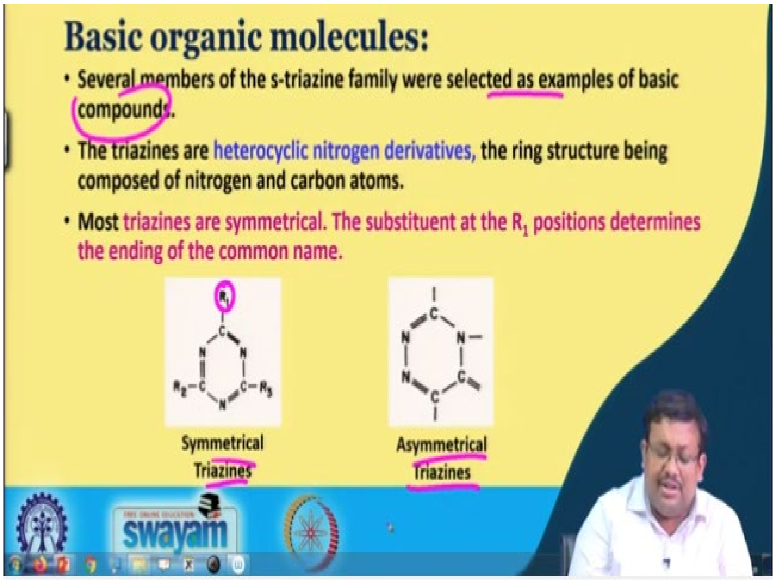

Basic organic molecules:

- Several members of the s-triazine family were selected as examples of basic compounds.
- The triazines are heterocyclic nitrogen derivatives, the ring structure being composed of nitrogen and carbon atoms.
- Most triazines are symmetrical. The substituent at the R_1 positions determines the ending of the common name.

Symmetrical Triazines

Asymmetrical Triazines

So, we start with the basic organic molecules from today's lecture, for today's lecture, so several members of these as I have told in my last lecture that several members of s-triazine family were selected as examples of this basic compounds, okay and the triazines are basically, heterogeneous or heterocyclic nitrogenous; nitrogen derivatives, you can see basically the heterocyclic nitrogen derivatives.

And the ring structure being composed of nitrogen as well as carbon atoms, most triazines are basically symmetrical and the substituent is at the R1 position determines the ending of the common name. So, this is basically symmetrical triazine and this is example of asymmetrical triazine.

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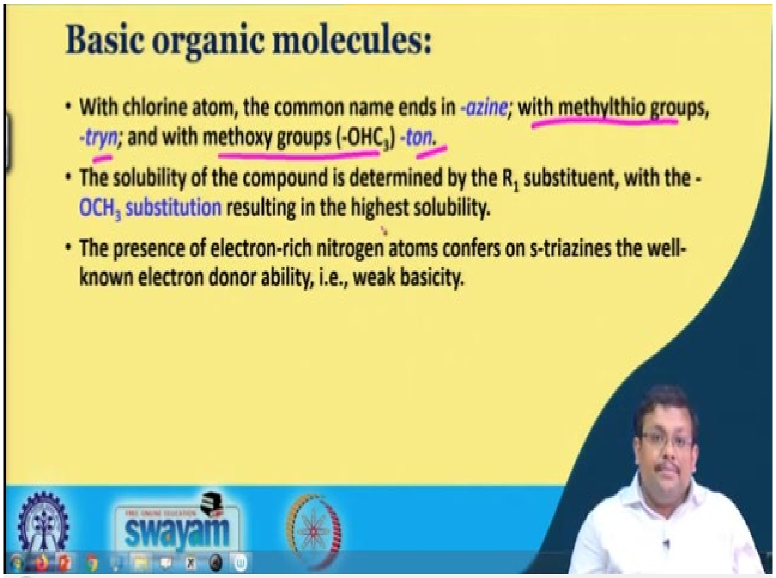

Basic organic molecules:

- With chlorine atom, the common name ends in *-azine*; with methylthio groups, *-tryn*; and with methoxy groups (-OHC_3) *-ton*.
- The solubility of the compound is determined by the R_1 substituent, with the -OCH_3 substitution resulting in the highest solubility.
- The presence of electron-rich nitrogen atoms confers on s-triazines the well-known electron donor ability, i.e., weak basicity.

So, another important point is with chlorine atom, the common name ends is basically tri, azine and when the methylthio groups are present, then the name ends with tryn and when the methoxy groups are present, OHC_3 groups are present, then it is, the name of the compound ends with ton. So, the solubility of the compound is determined by the R1 substituent with the OCH_3 substitution resulting in the highest solubility.

So, when the R1 gets substitute by the OCH_3 that is a methoxy group, then it shows the highest solubility. The presence of electron rich nitrogen atom confers on you know, on s-triazine, the well-known electron donor ability that is weak basicity, so this is about the basic organic molecules.

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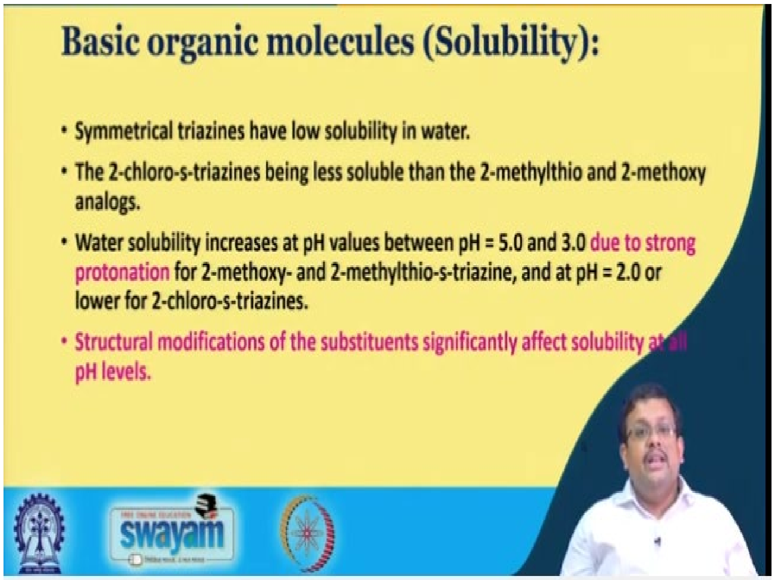

Basic organic molecules (Solubility):

- Symmetrical triazines have low solubility in water.
- The 2-chloro-s-triazines being less soluble than the 2-methylthio and 2-methoxy analogs.
- Water solubility increases at pH values between pH = 5.0 and 3.0 due to strong protonation for 2-methoxy- and 2-methylthio-s-triazine, and at pH = 2.0 or lower for 2-chloro-s-triazines.
- Structural modifications of the substituents significantly affect solubility at all pH levels.

If we consider the solubility of the basic organic molecules, remember the symmetrical triazines have low solubility in water and the 2-chloro-s-triazine being less soluble than the 2-methylthio and 2-methoxy analogs. Water solubility increases at pH values between pH 5 and 3 due to strong protonation for 2-methoxy and 2-methylthio-s-triazine and at pH 2 or lower for 2-chloro-s-triazine.

So, again water solubility increases at pH between 5 to 3 due to strong protonation for these compound that is 2-methoxy and 2-methylthio-s-triazine and at pH 2 or lower for 2-chloro-s-triazine. Structural modifications of the substituents significantly affect solubility at all pH levels, structural modifications of the substituent significantly affect solubility at all pH levels.

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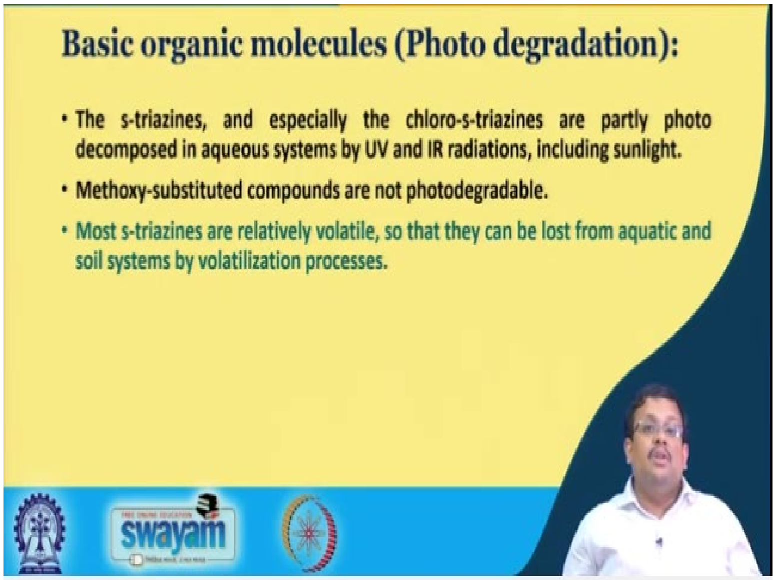

Basic organic molecules (Photo degradation):

- The s-triazines, and especially the chloro-s-triazines are partly photo decomposed in aqueous systems by UV and IR radiations, including sunlight.
- Methoxy-substituted compounds are not photodegradable.
- Most s-triazines are relatively volatile, so that they can be lost from aquatic and soil systems by volatilization processes.

Now, basic organic molecules also show photo degradation, so the s-triazine and especially the chloro-s-triazine are partly photo decomposed in aqueous system by UV and IR radiation including sunlight and methoxy substituted groups and not photo degradable and most s-triazines are relatively volatile, so they can be lost from the aquatic and soil system by volatilisation processes.

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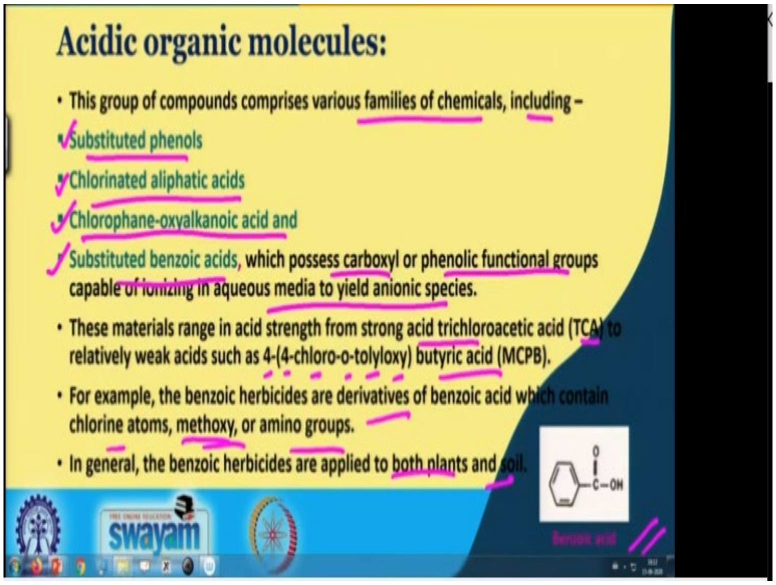

Acidic organic molecules:

- This group of compounds comprises various families of chemicals, including –
- Substituted phenols
- Chlorinated aliphatic acids
- Chlorophane-oxyalkanoic acid and
- Substituted benzoic acids, which possess carboxyl or phenolic functional groups capable of ionizing in aqueous media to yield anionic species.
- These materials range in acid strength from strong acid trichloroacetic acid (TCA) to relatively weak acids such as 4-(4-chloro-o-tolyloxy) butyric acid (MCPB).
- For example, the benzoic herbicides are derivatives of benzoic acid which contain chlorine atoms, methoxy, or amino groups.
- In general, the benzoic herbicides are applied to both plants and soil.

So, third one is the acidic organic molecules; so the acidic organic molecule, these group of compound comprises various family of chemicals including substituted phenols, then chlorinated aliphatic acids, then chlorophane-oxyalkanoic acids and substituted benzoic acids, again 4;

substituted phenols, then chlorinated aliphatic acids, then chlorophane-oxyalkanoic acids and substituted benzoic acids.

Now, substituted benzoic acid possess carboxyl or phenolic functional groups capable of ionising in aqueous media to yield anionic species. So, substituted benzoic acids produces anionic acids in aqueous medium. Now, these materials range in acidic strength from strong acid; the strong acid example is trichloroacetic acid, in small we known as TCA to relatively weak acids such as this 4-4-chloro-o-tolyloxy butyric acids, in short we call it MCPB.

So, for example the benzoic herbicides are derivatives of benzoic acid which contain chlorine atoms, methoxy or amino groups, okay. So, this is an example of benzoic acid molecule, so we can see benzoic herbicides are derivatives of benzoic acids, so benzoic herbicides are basically derivative of these benzoic acid which contains the chlorine atoms, methoxy and amino groups. In general, the benzoic herbicides are applied to both plants and soil. So, these are some of the examples of acidic organic molecules.

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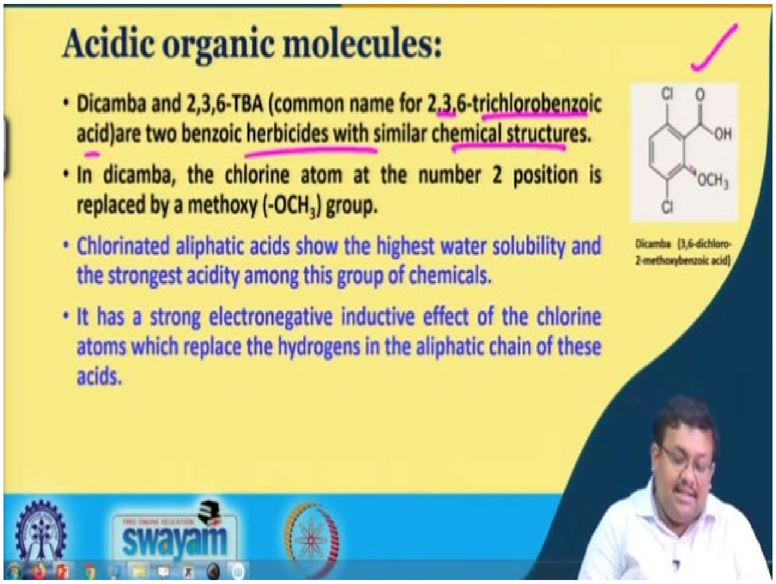

Acidic organic molecules:

- Dicamba and 2,3,6-TBA (common name for 2,3,6-trichlorobenzoic acid)are two benzoic herbicides with similar chemical structures.
- In dicamba, the chlorine atom at the number 2 position is replaced by a methoxy (-OCH_3) group.
- Chlorinated aliphatic acids show the highest water solubility and the strongest acidity among this group of chemicals.
- It has a strong electronegative inductive effect of the chlorine atoms which replace the hydrogens in the aliphatic chain of these acids.

Dicamba (3,6-dichloro-2-methoxybenzoic acid)

So, another important example of this acidic organic molecule is dicamba and 2,3,6-TBA or common name is basically, 2,3,6-trichlorobenzoic acid, these 2 or 2 benzoic herbicides with similar chemical structures. So, you can see this is an example; this is a chemical structure of dicamba which is basically 3, 6-dichloro-2-methoxybenzoic acid. So, basically this is an important acidic organic molecule.

Similarly, this 2, 3, 6-TBA or this 2, 3, 6-trichlorobensoic acid is another important acidic molecule with a similar chemical structure. Now, in dicamba the chlorine atom and at the number 2 position is replaced by a methoxy group, so here you can see that number 2 position, the chlorine atom has been replaced by this methoxy group. Now, chlorinated aliphatic acids show the highest water solubility and the strongest acidity among the group of chemicals.

So, it has a strong electronegative inductive effect of the chlorine atom which replace the hydrogen in the aliphatic chain of these acids. So, these are some examples of acidic organic molecules.

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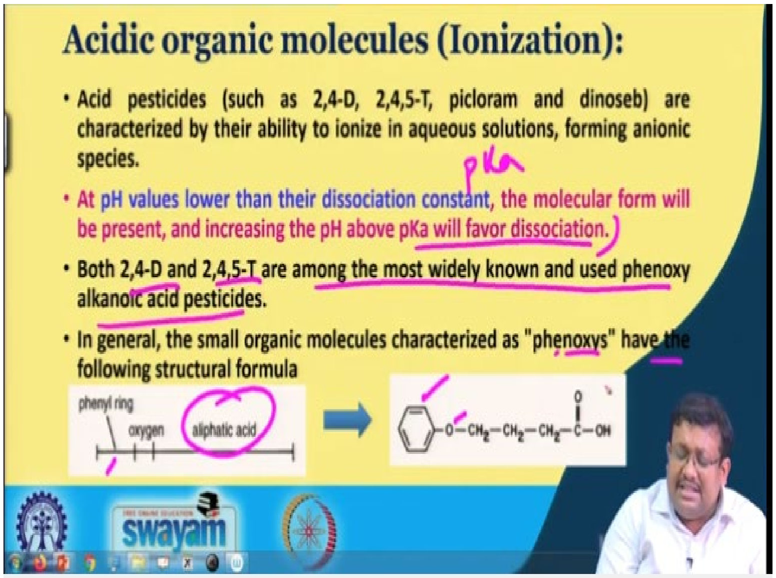

Acidic organic molecules (Ionization):

- Acid pesticides (such as 2,4-D, 2,4,5-T, picloram and dinoseb) are characterized by their ability to ionize in aqueous solutions, forming anionic species.
- At pH values lower than their dissociation constant, the molecular form will be present, and increasing the pH above pKa will favor dissociation.
- Both 2,4-D and 2,4,5-T are among the most widely known and used phenoxy alkanoic acid pesticides.
- In general, the small organic molecules characterized as "phenoxys" have the following structural formula

Now, acid pesticide; now, what is the importance in acid pesticide herbicide like 2, 4-D, 2, 4, 5-T; 2, 4-D is basically short form of 2, 4 dichlorophenoxyacetic acid, okay and 2, 4, 5-T is 2, 4, 5-trichlorophenoxy acetic acid, then picloram and dinoseb. So, these are acid pesticides and they basically are characterised by their ability to ionise in aqueous solution forming anionic species. Now, at pH values lower than that their dissociation constant which is denoted by pKa, so at pH values which is lower than that their dissociation constant, the molecular form will be present and increasing the pH above pKa will favour the dissociation.

So, again pH value; when their pH value is less than their dissociation constant which is denoted by pKa, then the molecular form will prevail, however when the increase in the pH above, pKa will favour the dissociation. Now, both 2, 4-D and 2, 4, 5-T are among the most widely known and used phenoxy alkanoic acid pesticides, okay. So, in general the small organic molecules are characterised by this phenoxy basically have the following structural formula.

So, basically they have a phenyl ring, followed by an oxygen and then an aliphatic acid, so as we can see here this is the phenyl ring followed by an oxygen and then oxygen basically, acts as the link and then there is an aliphatic acid chain. So, this is the basically, structure of this phenoxy you know, this phenoxy's structure.

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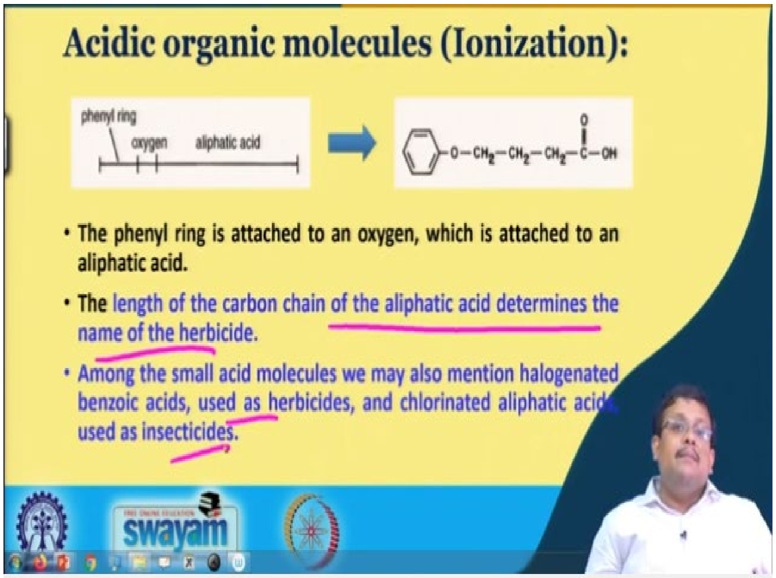

Acidic organic molecules (Ionization):

- The phenyl ring is attached to an oxygen, which is attached to an aliphatic acid.
- The length of the carbon chain of the aliphatic acid determines the name of the herbicide.
- Among the small acid molecules we may also mention halogenated benzoic acids, used as herbicides, and chlorinated aliphatic acids, used as insecticides.

So, the phenyl ring is attached to an oxygen, you can see which is attached to an aliphatic acid, we know that, so the length of the carbon chain of the aliphatic acid determines the name of the herbicides obviously, among the small acid molecules, we may also mention different halogenated benzoic acid, used as herbicides and chlorinated aliphatic acid used as basically insecticides, okay. So, this is basically some of the important examples of acidic organic molecules.

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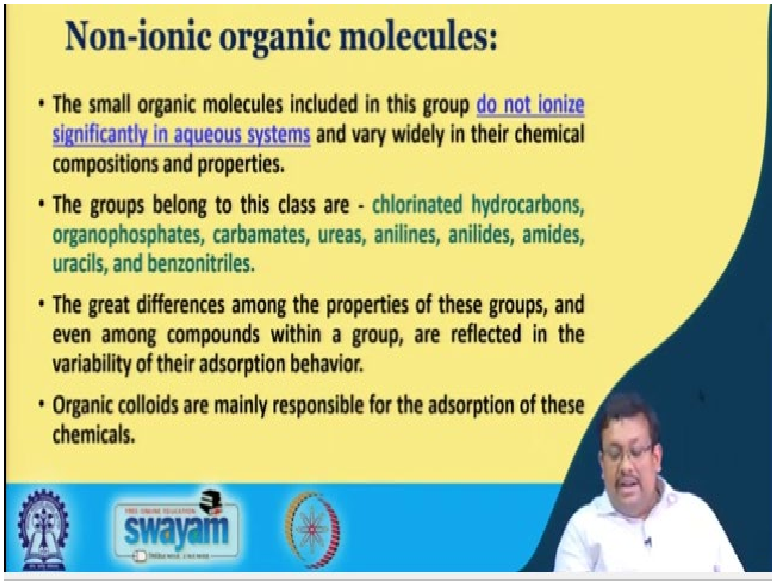

Non-ionic organic molecules:

- The small organic molecules included in this group do not ionize significantly in aqueous systems and vary widely in their chemical compositions and properties.
- The groups belong to this class are - chlorinated hydrocarbons, organophosphates, carbamates, ureas, anilines, anilides, amides, uracils, and benzonitriles.
- The great differences among the properties of these groups, and even among compounds within a group, are reflected in the variability of their adsorption behavior.
- Organic colloids are mainly responsible for the adsorption of these chemicals.

So, the fourth category is non-ionic organic molecules, so the small organic molecules included in this group basically do not ionise significantly in aqueous systems and vary widely in their chemical composition and properties. The groups which belong to this class are chlorinated hydrocarbons, organophosphate, carbamates, urea, anilines, anilides, amides, uracils, and benzonitriles.

So, these are the major groups of compound which are belonged to this class, so the great difference among the properties of these groups and even among compounds within a group are reflected in the variability of their adsorption behaviour. Now, organic colloids are mainly responsible for the adsorption of these colloids, absorption of these chemicals. So, organic matter in the soil takes a major role for adsorption of these chemicals and controlling their mobility in the soils.

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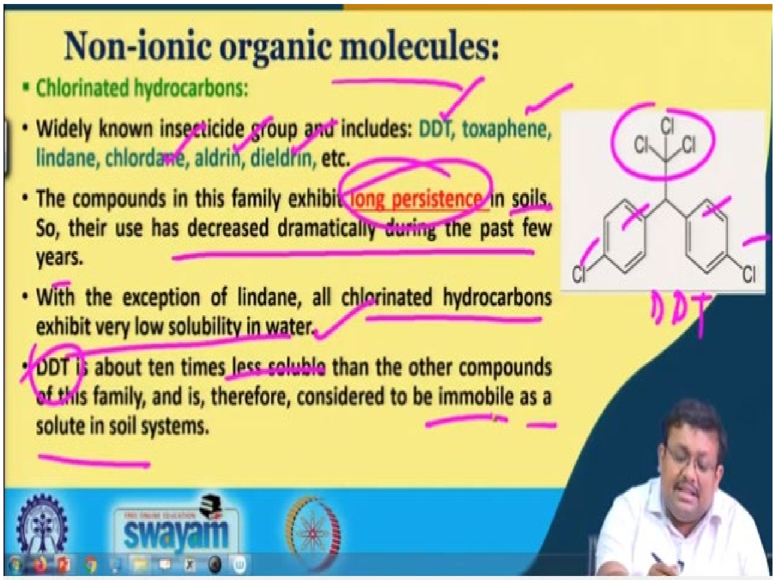

Non-ionic organic molecules:

- Chlorinated hydrocarbons:
- Widely known insecticide group and includes: DDT, toxaphene, lindane, chlordane, aldrin, dieldrin, etc.
- The compounds in this family exhibit long persistence in soils. So, their use has decreased dramatically during the past few years.
- With the exception of lindane, all chlorinated hydrocarbons exhibit very low solubility in water.
- DDT is about ten times less soluble than the other compounds of this family, and is, therefore, considered to be immobile as a solute in soil systems.

Now, let us start with the chlorinated hydrocarbons; widely known as these insecticides, widely known as insecticide group, basically they include DDT, then toxaphene, then lindane, chlordane, aldrin, dieldrin, so the major insecticides are basically, you know, basically denoted by this chlorinated hydrocarbons. Here you can see the you know, the structure of DDT; dichlorodiphenyltricholoroethane.

So, the you know the compounds in this family basically, this chlorinated hydrocarbon exhibit long persistent, this is the major important point, basically all these you know organic molecules or pesticides shows long persistent in the soil, so their use has been decreased dramatically during the past few years. So, since they can reside in the soil for long duration of time due to the high persistence, their degradation is very slow.

As a result, their application in agriculture has been decreased dramatically by regulations and laws for the last couple of years. Now, with the exception of lindane, all chlorinated hydrocarbons exhibit very low solubility in water for example, DDT, toxaphene, then chlordane, aldrin, dieldrin, these are very, very less soluble in water. Now, DDT is about 10 times less soluble than other compounds of this family and is therefore, considered to be immobile as a result, as a solute in the soil system.

So, as a result of that DDT has been banned for agricultural operations, DDT is very, very less soluble and also you know very immobile in the soil, so they can persist in the soil for a very long period of time, as a result of that their application to the soil has been drastically controlled or reduced.

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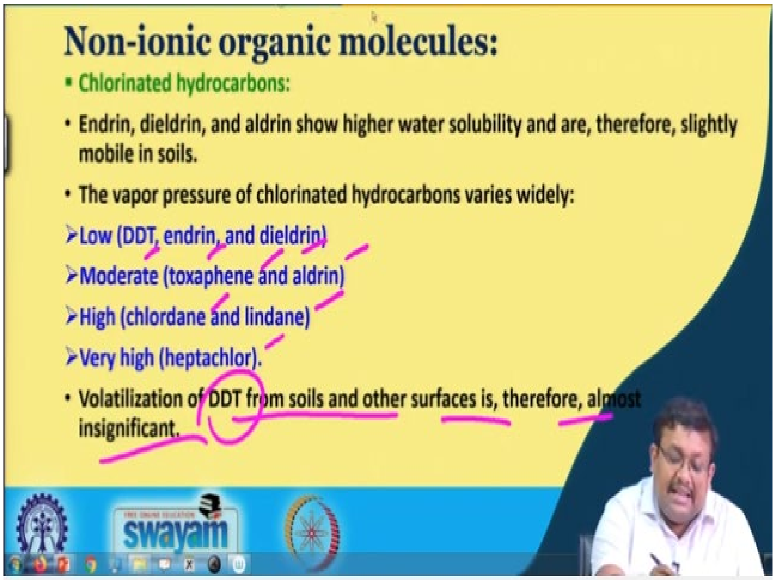

Non-ionic organic molecules:

- Chlorinated hydrocarbons:
- Endrin, dieldrin, and aldrin show higher water solubility and are, therefore, slightly mobile in soils.
- The vapor pressure of chlorinated hydrocarbons varies widely:

➢ Low (DDT, endrin, and dieldrin)
➢ Moderate (toxaphene and aldrin)
➢ High (chlordane and lindane)
➢ Very high (heptachlor).

- Volatilization of DDT from soils and other surfaces is, therefore, almost insignificant.

So, the endrin, then dieldrin and you know and aldrin, all show high water solubility and are therefore, slightly mobile in soils. The vapour pressure of chlorinated hydrocarbons varies basically vary widely. If you consider you know, low vapour pressure, it basically comprised DDT, endrin and dieldrin, moderate vapour pressure you can see toxaphene and aldrin, high vapour pressure you can see chlordane and lindane and very high heptachlor.

So, volatilisation of DDT from soil and other surface is therefore, almost insignificant, so as a result of that DDT can persist in the soil for long period of time. So, DDT has low vapour pressure, as a result of that volatilisation of DDT is low from soil surface and that is why DDT is highly persistent in the soil.

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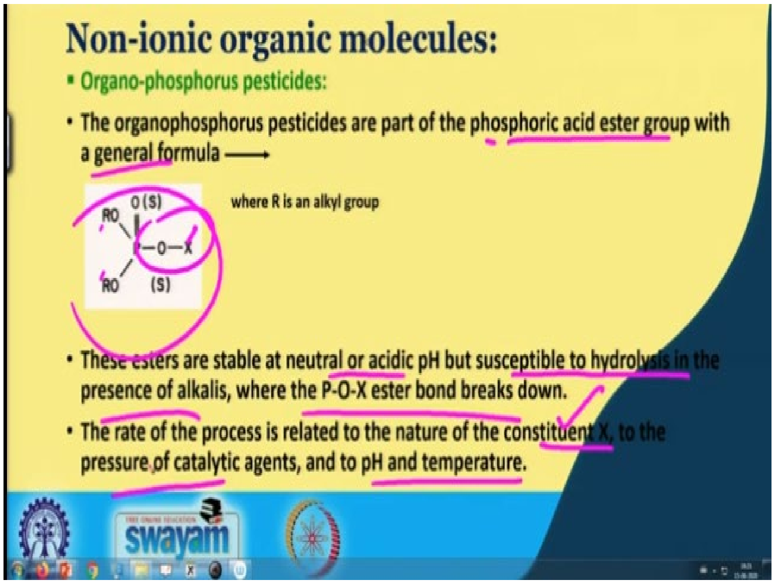

Non-ionic organic molecules:

- Organo-phosphorus pesticides:
- The organophosphorus pesticides are part of the phosphoric acid ester group with a general formula ⟶

where R is an alkyl group

- These esters are stable at neutral or acidic pH but susceptible to hydrolysis in the presence of alkalis, where the P-O-X ester bond breaks down.
- The rate of the process is related to the nature of the constituent X, to the pressure of catalytic agents, and to pH and temperature.

Now, next comes the organophosphate pesticide; now organophosphate pesticides are part of basically, part of the phosphoric acid ester group with the general formula of these. Now, you know the ester, ester basically forms when acid reacts with the alcohol, so basically this is you can see this is a you know phosphoric acid ester group where R, these R basically shows the alkyl group.

Now, these esters are stable at neutral or acidic pH but susceptible to hydrolyse is in the presence of alkalis, where the P-O-X ester bond is broken. So, the P-O-X ester bond is broken due to the presence of alkaline condition. Now, the rate of process; rate of this process is related to the nature of the constituent X to the pressure of this catalytic reagents and then the pH of the and the temperature.

So, all these factor, nature of the constituent X, then pH, temperature, pressure of catalytic agents, all these influence the degradation of or the hydrolysis of different organophosphate pesticides.

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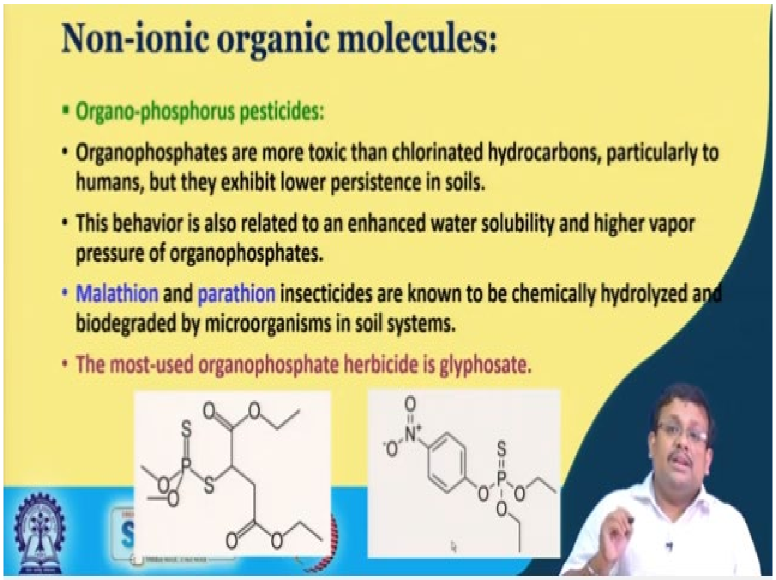

Non-ionic organic molecules:

- Organo-phosphorus pesticides:
- Organophosphates are more toxic than chlorinated hydrocarbons, particularly to humans, but they exhibit lower persistence in soils.
- This behavior is also related to an enhanced water solubility and higher vapor pressure of organophosphates.
- Malathion and parathion insecticides are known to be chemically hydrolyzed and biodegraded by microorganisms in soil systems.
- The most-used organophosphate herbicide is glyphosate.

Now, organophosphates are more toxic than chlorinated hydrocarbons particularly to human but they exhibit lower persistent in soils. Now, this behaviour is also related to an enhanced water solubility and higher vapour pressure of organophosphates, so basically, these organophosphates are more toxic than chlorinated hydrocarbons, specifically as far as the human toxic is concern but they are less persistent in the soil as compared to the organo you know, chlorinated hydrocarbons.

So, malathion and parathion as you can see here is put the structure of malathion and parathion, so malathion and parathion insecticides are known as you know, known to be chemically hydrolysed and biodegraded by microorganisms in soil systems, so these are 2 important organophosphate pesticide. The most used organophosphate herbicide is basically glyphosate.

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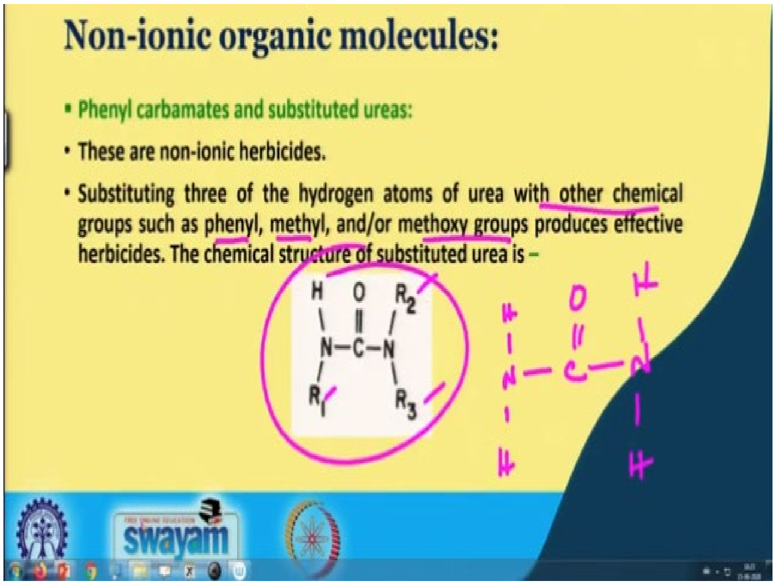

Non-ionic organic molecules:

- Phenyl carbamates and substituted ureas:
- These are non-ionic herbicides.
- Substituting three of the hydrogen atoms of urea with other chemical groups such as phenyl, methyl, and/or methoxy groups produces effective herbicides. The chemical structure of substituted urea is –

Another group is phenyl carbamate and substitute ureas, so you know basically these are non-ionic herbicides, you can see here, substituting 3 of the hydrogen atoms of an urea and other chemical groups such as phenyl, methyl and methoxy group. So, what is the formula of urea; urea formula is, this is the formula of urea, okay. So, this is the formula of the urea, so you can see substituting 3 of the hydrogen atom of the urea.

So, here 3 of the hydrogen atom, the urea have been substituted with other chemical groups such as it can be either phenyl or methyl and or methoxy group produce the effective herbicides. So, the chemical structure of the substituted urea is like this one, so this is you know this is known as either phenyl carbamates or substituted urea, if the substituting group is phenyl group.

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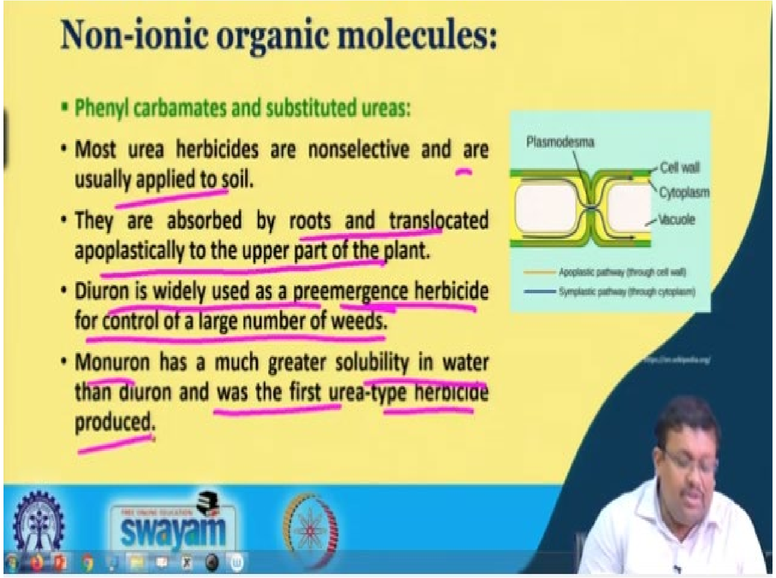

Non-ionic organic molecules:

- **Phenyl carbamates and substituted ureas:**
- Most urea herbicides are nonselective and are usually applied to soil.
- They are absorbed by roots and translocated apoplastically to the upper part of the plant.
- Diuron is widely used as a preemergence herbicide for control of a large number of weeds.
- Monuron has a much greater solubility in water than diuron and was the first urea-type herbicide produced.

Now, most urea herbicides are non-selective and are usually applied to the soil, so they are non-selective so they can kill any you know, any herb or any weed that come in contact with that herbicide, so they are absorbed by roots and translocated apoplastically to the upper part of the plant. Now, you know what is apoplastic movement; so when the movement of compound occurs through the cell wall, then it is called apoplastic movement.

As you can see the movement of the compound is happening to the diffusion through the apoplastic pathway or through the cell wall, as opposed to the symplastic pathway where the movement occurs through the cytoplasm. So, they are absorbed by the roots, so these phenyl carbamates or substituted ureas are basically absorbed by the roots and translocated apoplastically to the upper part of the plant.

Diuron is widely used as the you know, as a pre-emergence herbicide for control of a large number of weeds however, monuron has a much greater solubility in water than diuron and was the first urea type herbicide you know, which is produced. So, these are some of the examples of substituted ureas.

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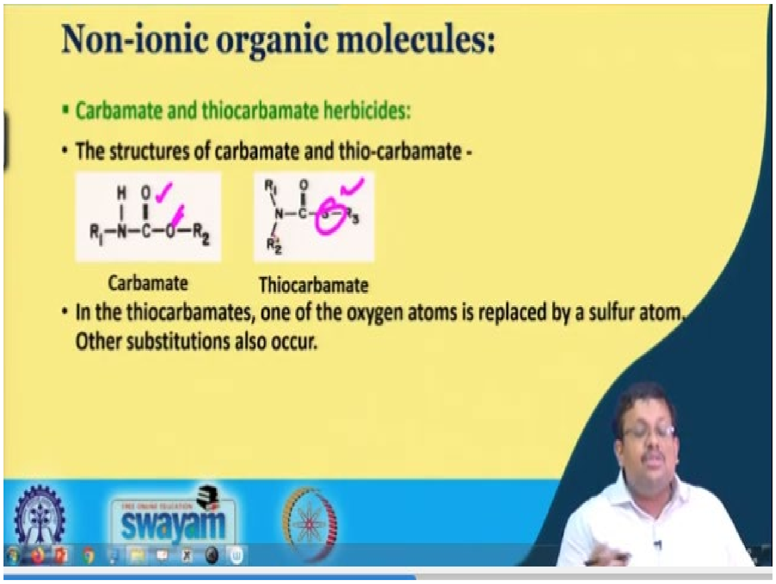

Non-ionic organic molecules:

- **Carbamate and thiocarbamate herbicides:**
- The structures of carbamate and thio-carbamate -

- In the thiocarbamates, one of the oxygen atoms is replaced by a sulfur atom. Other substitutions also occur.

Now, carbamate and thiocarbamate herbicide, if you consider the structure of carbamates and thiocarbamates is given here, so this is carbamate and thiocarbamate. Now, in the thiocarbamate one of the oxygen atom is replaced by a sulphur atom since the word thio is there, so obviously there will be presence of sulphur. So, in the thiocarbamates, one of the oxygen atom is you can see here, this oxygen atom is replaced by sulphur in the thiocarbamate and other substitution also can occur in the; so these are one of the important organic you know, non-ionic organic molecules.

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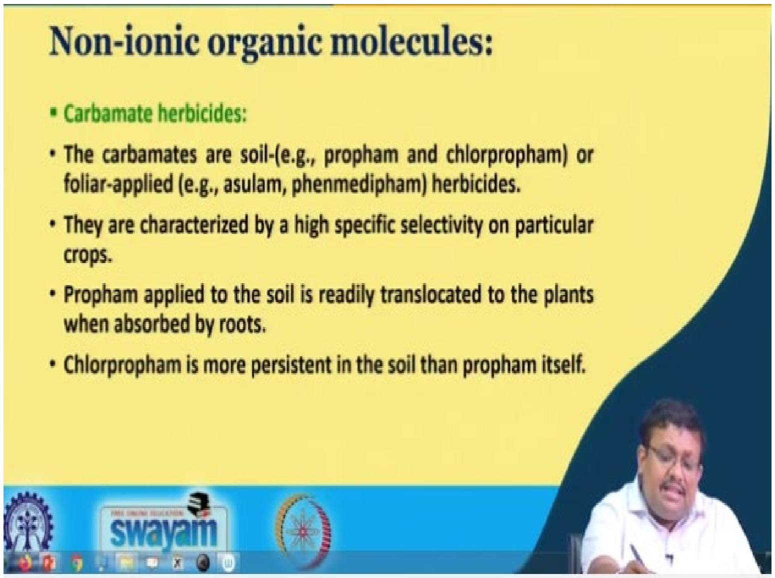

Non-ionic organic molecules:

- **Carbamate herbicides:**
- The carbamates are soil-(e.g., propham and chlorpropham) or foliar-applied (e.g., asulam, phenmedipham) herbicides.
- They are characterized by a high specific selectivity on particular crops.
- Propham applied to the soil is readily translocated to the plants when absorbed by roots.
- Chlorpropham is more persistent in the soil than propham itself.

So, carbamate herbicides; if you consider carbamate herbicides, the carbamates are you know basically soil or foliar applied, so among the soil applied carbamates example are propham and then chlorpropham and then if we consider the foliar applied carbamates, examples are asulam, then phenmedipham, so these are the also herbicides. So, they are basically characterised by high specific selectivity on particular crops.

Now, propham applied to the soil is readily translocated to the plants when absorbed by the roots, whereas chlorpropham is more persistent in the soil than propham itself, so these are some of the example of carbamate herbicides.

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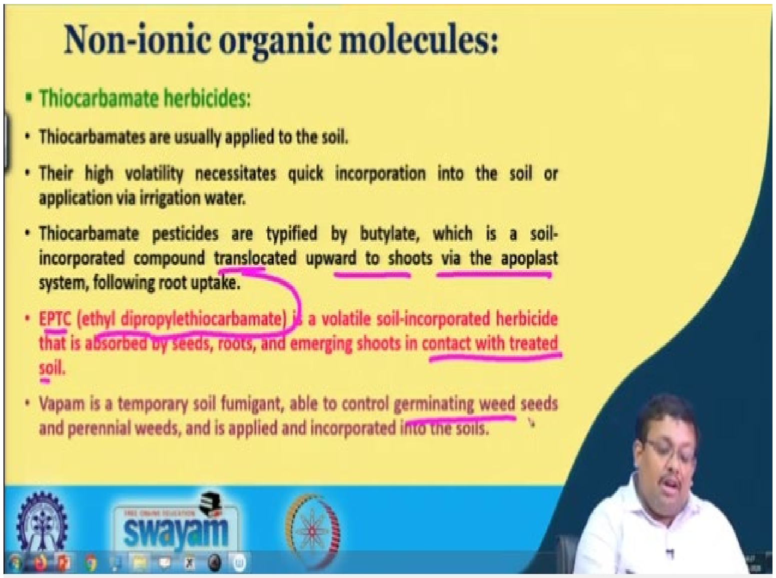

Non-ionic organic molecules:

- **Thiocarbamate herbicides:**
- Thiocarbamates are usually applied to the soil.
- Their high volatility necessitates quick incorporation into the soil or application via irrigation water.
- Thiocarbamate pesticides are typified by butylate, which is a soil-incorporated compound translocated upward to shoots via the apoplast system, following root uptake.
- EPTC (ethyl dipropylethiocarbamate) is a volatile soil-incorporated herbicide that is absorbed by seeds, roots, and emerging shoots in contact with treated soil.
- Vapam is a temporary soil fumigant, able to control germinating weed seeds and perennial weeds, and is applied and incorporated into the soils.

So, if we move ahead and see thiocarbamate herbicides, thiocarbamate are usually applied to the soils, their high volatility necessitates the quick incorporation into the soil or application via irrigation water and thiocarbamate pesticide are you know typified by you know, butylate which is basically a soil incorporated compound translocated upward to shoots via apoplastic movement following the root uptake, we have discuss apoplastic movement.

One example of this thiocarbamate herbicide is EPTC which is the short form of ethyl dipropylthiocarbamate, so ethyl dipropylthiocarbamate or in the short form that is EPTC is a volatile soil incorporated herbicide that is absorbed by seeds, roots and emergence, emerging shoots in contact with treated soils. So, again vapam is a temporary soil fumigant able to control you know, control this germinating weed seeds and perennial weeds and is applied and incorporate into the soils. So, these are some of the examples of thiocarbamate herbicides.

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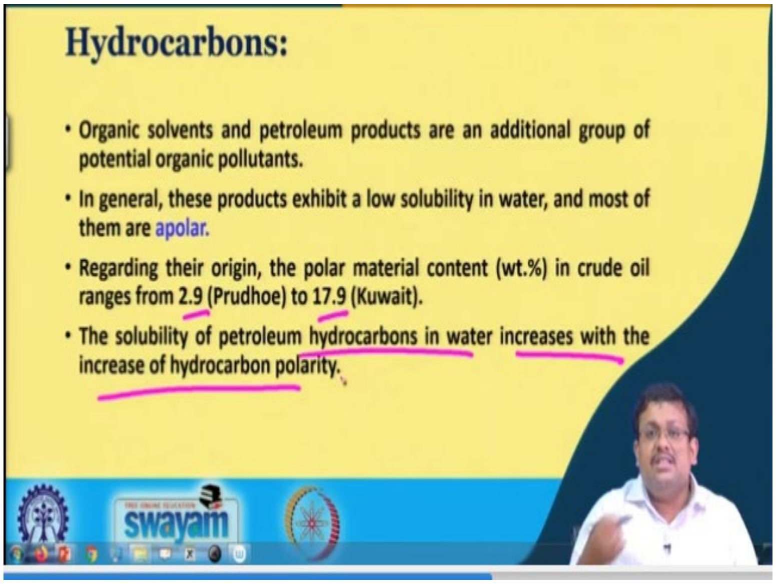

Hydrocarbons:

- Organic solvents and petroleum products are an additional group of potential organic pollutants.
- In general, these products exhibit a low solubility in water, and most of them are apolar.
- Regarding their origin, the polar material content (wt.%) in crude oil ranges from 2.9 (Prudhoe) to 17.9 (Kuwait).
- The solubility of petroleum hydrocarbons in water increases with the increase of hydrocarbon polarity.

So, if we move ahead and see, so the next major group is hydrocarbons, so the next major group is hydrocarbons. Now, hydrocarbons; in the hydrocarbons, organic solvents and petroleum products are an additional group of potential organic pollutants. Now, you know that in general, these product exhibit a low solubility in water and most of them are apolar in nature or non-polar in nature.

So that is why they are not soluble in water and regarding their origin, the polar material content weight percentage, this is in crude oil varies from 2.9 to 17.9% and the solubility of petroleum hydrocarbon in water increases with the increase of hydrocarbon polarity. So, basically if the hydrocarbon polarity increases, their solubility increases, okay but most of them are by nature are nonpolar or apolar.

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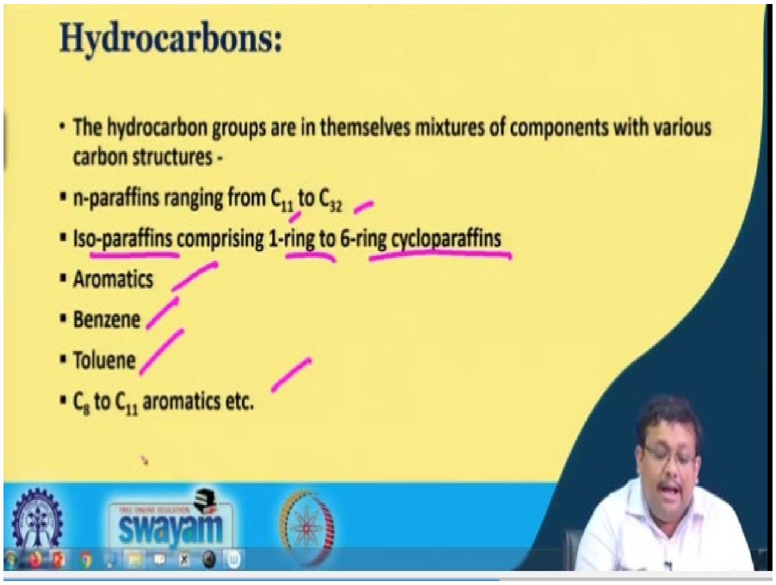

Hydrocarbons:

- The hydrocarbon groups are in themselves mixtures of components with various carbon structures -
- n-paraffins ranging from C_{11} to C_{32}
- Iso-paraffins comprising 1-ring to 6-ring cycloparaffins
- Aromatics
- Benzene
- Toluene
- C_8 to C_{11} aromatics etc.

So, the hydrocarbon groups are themselves mixture of components of various carbon structures. What are those carbon structures; you can see here; n-paraffins ranging from C11 to C32, then iso paraffins comprising 1 ring to 6 ring cycloparaffins, aromatics, benzene, toluene, C8 to C11 aromatics etc. So, you can see these are the different you know, different components which basically mixed together to produce the hydrocarbon.

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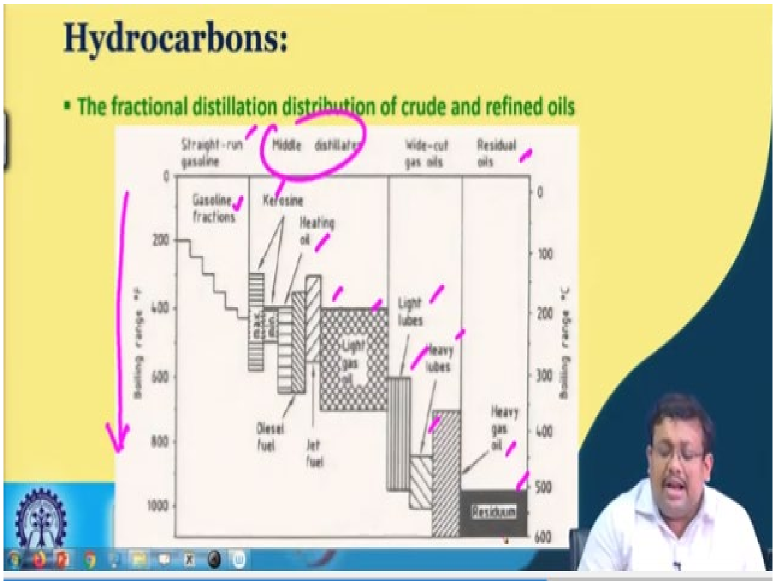

Hydrocarbons:

- The fractional distillation distribution of crude and refined oils

Now, if we see the fractional distillation of distribution of crude oil refined oil, we see that as the boiling point range you know increases the fractional distillation process can produce different fractions of hydrocarbons. So, gasoline fractions this, they can be, we can get them at the lowest boiling point followed by these kerosene and then heating oil followed by these diesel fuels, light gas oil, then light lubes, heavy lubes and heavy gasoil and finally residuum which is basically separated at the highest boiling range.

So, basically when the boiling range or boiling point increases in this direction, then these different you know different fractions of hydrocarbons separate out. So, obviously gasoline fraction shows straight run gasoline, they are highly you know volatile in nature and in the middle distillates you can see, kerosenes, heating oil, light gasoil, a diesel fuels, jet fuels, okay which has separate out.

And in the wide cut gas oils, you can see like light lubes and heavy lubes which are showing higher boiling range and in the highest boiling range, you can see residual soils as well as residuum. So, this is showing the fractional distillation of crude and refined oils.

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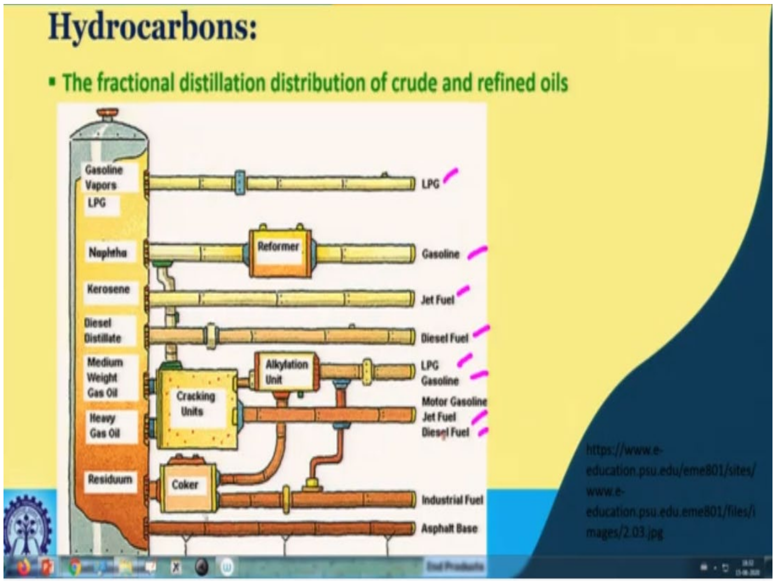

Hydrocarbons:

- The fractional distillation distribution of crude and refined oils

https://www.e-education.psu.edu/eme801/sites/www.e-education.psu.edu.eme801/files/images/2.03.jpg

So, similarly here also you can see how these fractional distillation basically occurs, so vapour gasoline first separate out and then gasoline vapours produces LPG and then naphtha, ultimately produces gasoline, here then kerosene which produces jet fuel. Diesel distillates produces diesel fuel, medium weight gas oils and ultimately heavy gas oil you know, goes to the cracking units and then alkylation units produces LPG gasolines and also produces jet fuels and diesel fuels.

And residuum which is goes to the coker ultimately produces the industrial fuel and finally, you can get the asphalt bases, so this is how the different fractions of hydrocarbons are separate out from each other based on their you know, based on their boiling point and this is called the fractional distillation.

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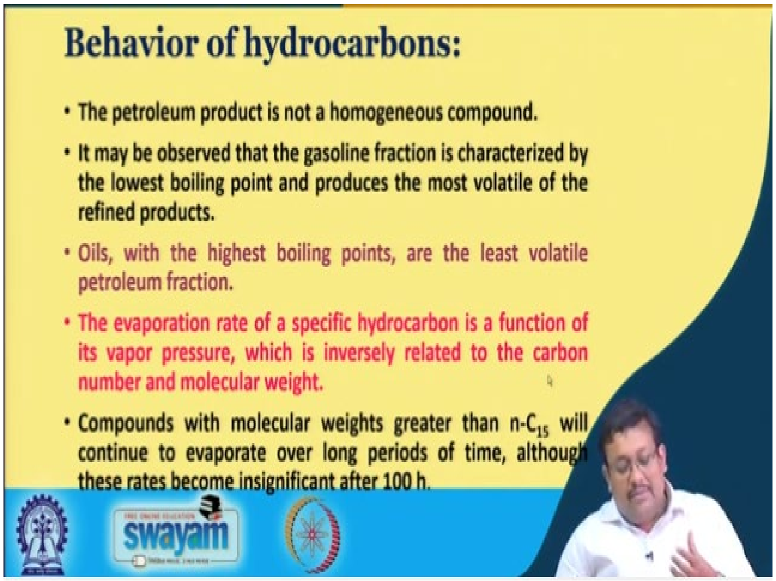

Behavior of hydrocarbons:

- The petroleum product is not a homogeneous compound.
- It may be observed that the gasoline fraction is characterized by the lowest boiling point and produces the most volatile of the refined products.
- Oils, with the highest boiling points, are the least volatile petroleum fraction.
- The evaporation rate of a specific hydrocarbon is a function of its vapor pressure, which is inversely related to the carbon number and molecular weight.
- Compounds with molecular weights greater than n-C_{15} will continue to evaporate over long periods of time, although these rates become insignificant after 100 h.

Now, behaviour of hydrocarbon; we see the behaviour hydrocarbons; the petroleum product is not a homogeneous compound as you have just seen, it may be observed that the gasoline fraction is characterised by the lowest boiling point and produce the most volatile of the refined products. Oils with the highest boiling point are the least volatile petroleum fractions and the evaporation rate of a specific hydrocarbon is a function of its vapour pressure which is inversely related to the carbon number of the molecular weight.

So, obviously compounds you know, compounds with molecular weights greater than 15 will continue to evaporate over long period of time, although these rates become insignificant after 100 hours. So, more complex the structure of the hydrocarbon, more time it will take to evaporate.

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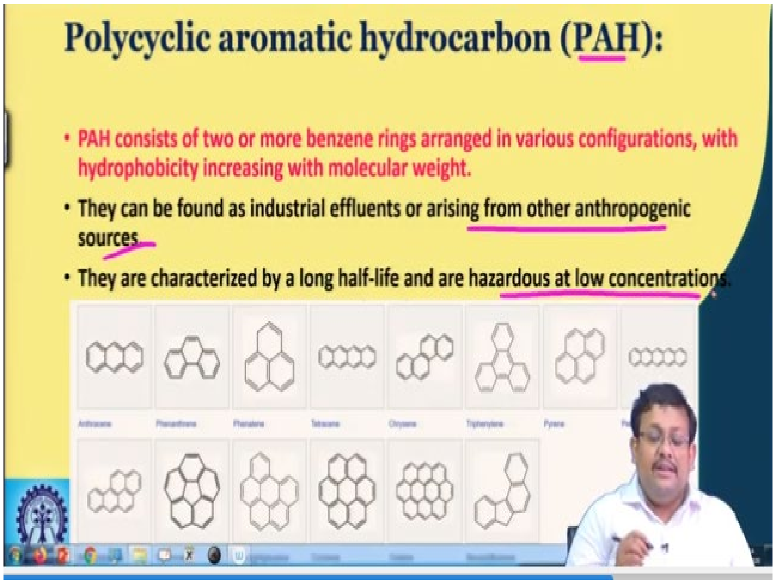

Polycyclic aromatic hydrocarbon (PAH):

- PAH consists of two or more benzene rings arranged in various configurations, with hydrophobicity increasing with molecular weight.
- They can be found as industrial effluents or arising from other anthropogenic sources.
- They are characterized by a long half-life and are hazardous at low concentrations.

Another important compound is polycyclic aromatic hydrocarbon or in short from that is called the PAH. So, PAH consist of 2 or more benzene rings arranged in various configurations with hydrophobicity increasing with molecular weight. So, you can see here I have produce different you know, PAH here staring from anthracene, phenanthrene, you know phenylene, tetrazene and so on so forth. So, these are all the pH compounds they can be found as industrial effluents you know or arising from and you know different anthropogenic sources.

And they are characterised by a long half-life and are basically, hazardous at low concentration, they have got long half-life and they are very hazardous at low concentration okay, so these are very important potential pollutant as far as the soil and environment are concerned.

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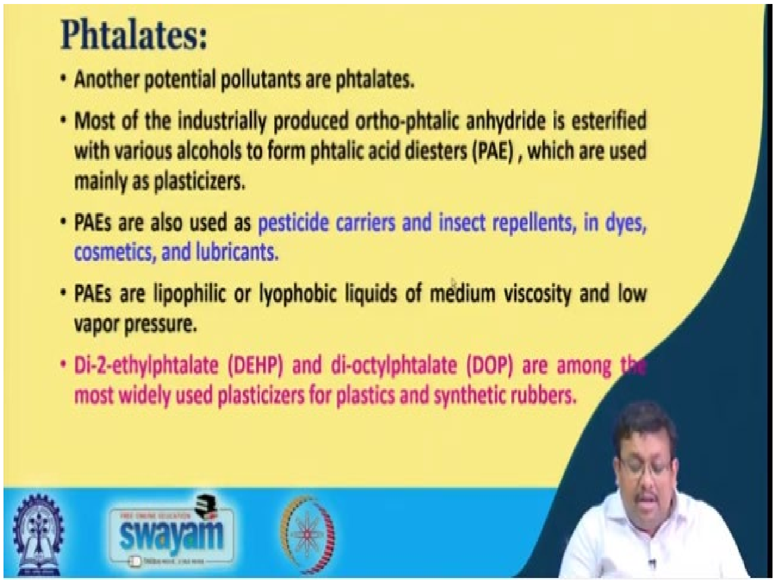

Phtalates:

- Another potential pollutants are phtalates.
- Most of the industrially produced ortho-phtalic anhydride is esterified with various alcohols to form phtalic acid diesters (PAE), which are used mainly as plasticizers.
- PAEs are also used as pesticide carriers and insect repellents, in dyes, cosmetics, and lubricants.
- PAEs are lipophilic or lyophobic liquids of medium viscosity and low vapor pressure.
- Di-2-ethylphtalate (DEHP) and di-octylphtalate (DOP) are among the most widely used plasticizers for plastics and synthetic rubbers.

So, another group of compound is phthalates, so this is phthalates are another potential pollutants, most of the industrially produced ortho-phtalic anhydrides is esterified with various alcohol to produce the phtalic acid diesters, okay. In short form, we know, the phtalic acid diesters is known as PAE, so which are used mainly as plasticisers. So, PAE are also used as you know, pesticide carriers and insect repellents, in dyes, cosmetic, lubricants.

So, they are very lipophilic and you know and then lyophobic liquids of medium viscosity and low vapour pressure, so they can produce a huge amount of you know, environmental pollution, if they exist in high concentration in the soil.

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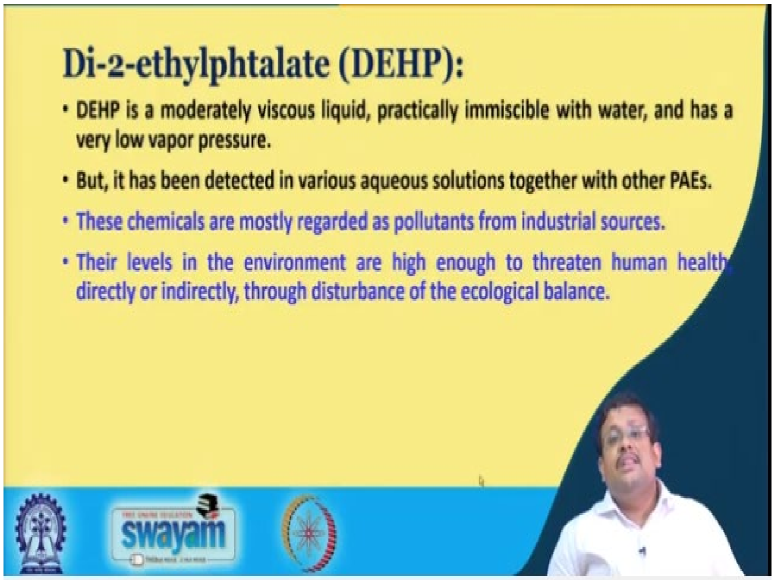

Di-2-ethylphtalate (DEHP):

- DEHP is a moderately viscous liquid, practically immiscible with water, and has a very low vapor pressure.
- But, it has been detected in various aqueous solutions together with other PAEs.
- These chemicals are mostly regarded as pollutants from industrial sources.
- Their levels in the environment are high enough to threaten human health directly or indirectly, through disturbance of the ecological balance.

DEHP or di-2-ethylphtalate is a moderately viscous liquid and practically immiscible with water and has a very low vapour pressure but it has been detected in various aqueous solutions together with other PAE's and these chemicals are mostly regarded as pollutants from industrial sources, their levels in the environment are high enough to threaten human health directly or indirectly through disturbance of the ecological balance.

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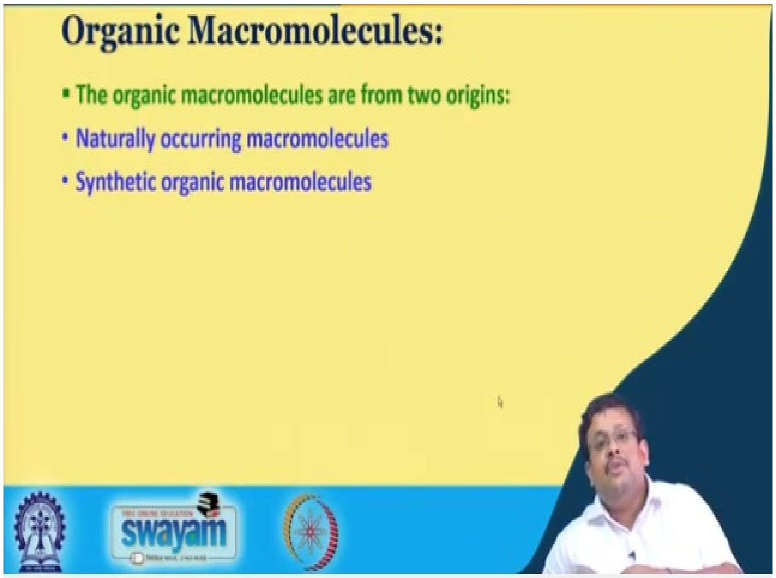

Organic Macromolecules:

- The organic macromolecules are from two origins:
- Naturally occurring macromolecules
- Synthetic organic macromolecules

Now, if we consider the organic macromolecules; in the organic macromolecules there are of 2 origins, one is naturally occurring organic macromolecules and the second one is synthetic organic macromolecules.

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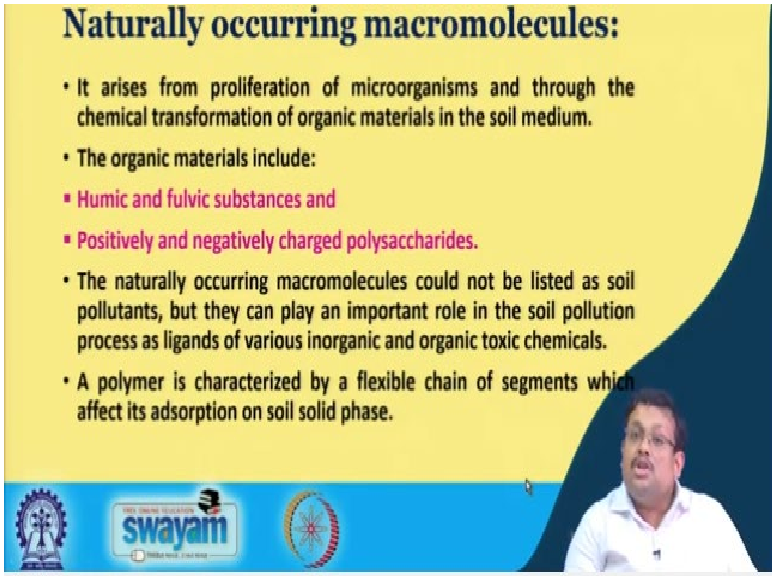

Naturally occurring macromolecules:

- It arises from proliferation of microorganisms and through the chemical transformation of organic materials in the soil medium.
- The organic materials include:
- Humic and fulvic substances and
- Positively and negatively charged polysaccharides.
- The naturally occurring macromolecules could not be listed as soil pollutants, but they can play an important role in the soil pollution process as ligands of various inorganic and organic toxic chemicals.
- A polymer is characterized by a flexible chain of segments which affect its adsorption on soil solid phase.

So, in the naturally organic macromolecules include basically humic acid and fulvic substances and positively and negative charged polysaccharides. So, the naturally occurring macromolecules could not be listed as soil pollutants but they can play an important role in the soil pollution process as ligands of various inorganic and organic toxic chemicals. We have seen that these organic matter which is present in the soil produce ligand, produce chelates through the ligands by complexing these inorganic pollutants or sometimes you know, organic toxic chemicals.

So, that is why these naturally organic macromolecules could you know play an important role in the soil pollution, a polymer is characterised by a flexible chain of segments which affects its adsorption on soil solid phase.

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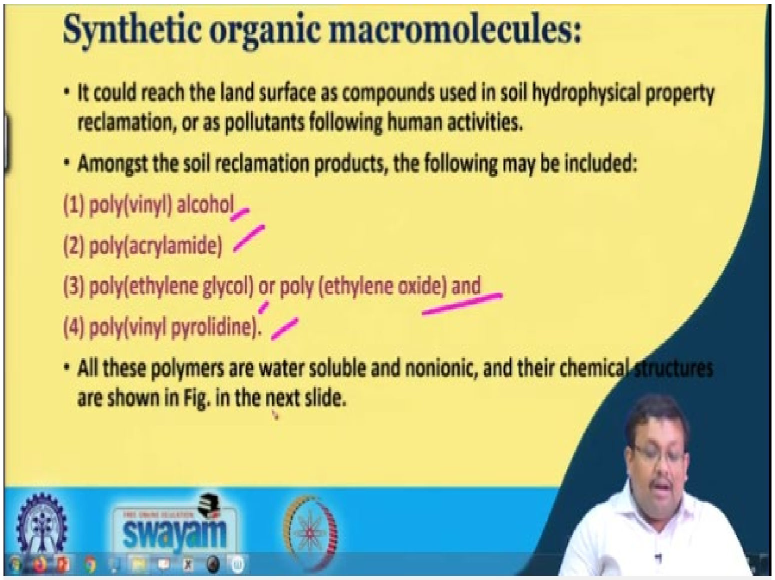

Synthetic organic macromolecules:

- It could reach the land surface as compounds used in soil hydrophysical property reclamation, or as pollutants following human activities.
- Amongst the soil reclamation products, the following may be included:

(1) poly(vinyl) alcohol
(2) poly(acrylamide)
(3) poly(ethylene glycol) or poly (ethylene oxide) and
(4) poly(vinyl pyrolidine).

- All these polymers are water soluble and nonionic, and their chemical structures are shown in Fig. in the next slide.

So, it could reach that is the so; if we discuss; so we have discuss the naturally occurring macromolecules, now if we consider the synthetic occurring organic macromolecules, it could reach a land surface as compounds used in soil hydrophysical property reclamation or as pollutants following the human activities. Among the soil reclamation products, the following may be included.

So, what are these; polyvinyl alcohol, polyacrylamide, then polyethylene glycol or polyethylene oxides and polyvinyl pyrolidine, all these polymers are water soluble and non-ionic and their chemical structures are shown in the next slide.

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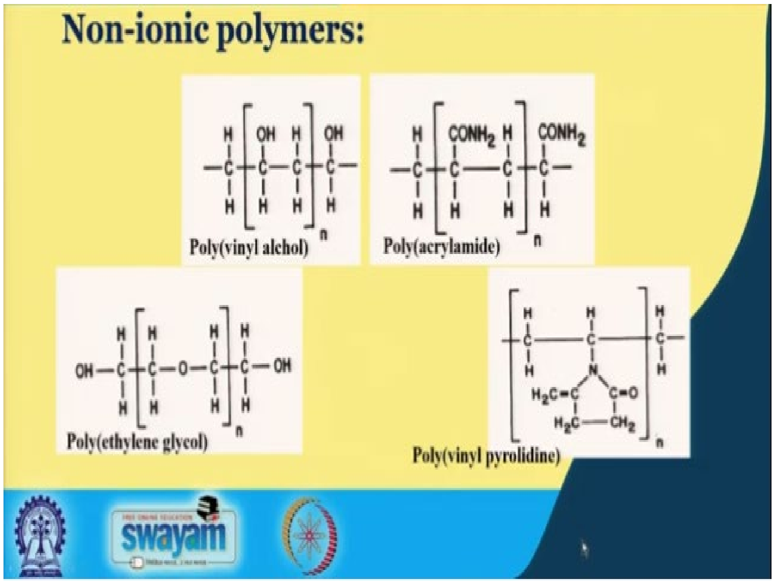

Non-ionic polymers:

Poly(vinyl alchol)

Poly(acrylamide)

Poly(ethylene glycol)

Poly(vinyl pyrolidine)

So, you can see their chemical structures, so this is a polyvinyl alcohol, this is polyacrylamide, this is polyethylene glycol and this is polyvinyl pyrolidine. So, these are different non-ionic polymers.

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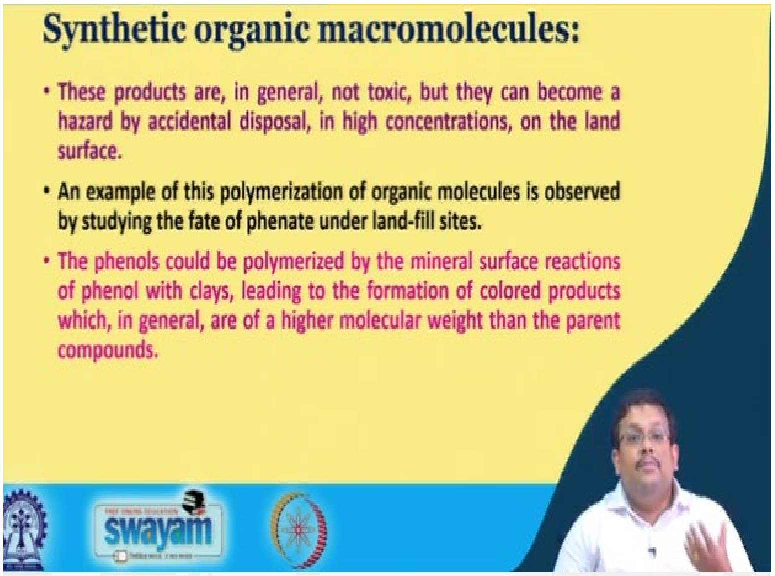

Synthetic organic macromolecules:

- These products are, in general, not toxic, but they can become a hazard by accidental disposal, in high concentrations, on the land surface.
- An example of this polymerization of organic molecules is observed by studying the fate of phenate under land-fill sites.
- The phenols could be polymerized by the mineral surface reactions of phenol with clays, leading to the formation of colored products which, in general, are of a higher molecular weight than the parent compounds.

So, these products are in general, not toxic but they can become a hazard by accidental disposal in high concentration on the land surface. So, the phenols could be polymerised by mineral surface reactions or phenol with clays leading to the formation of coloured products which in general, are of high molecular weight than the parent compounds.

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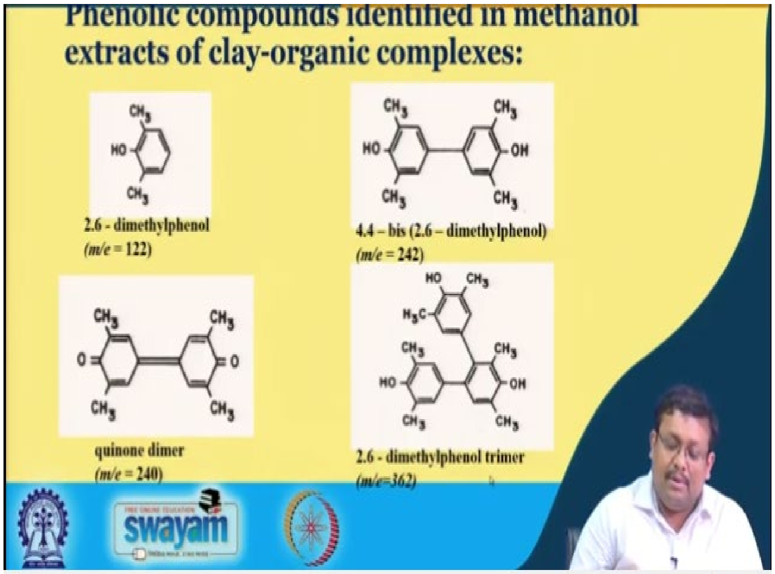

Phenolic compounds identified in methanol extracts of clay-organic complexes:

2.6 - dimethylphenol (*m/e* = 122)

4.4 – bis (2.6 – dimethylphenol) (*m/e* = 242)

quinone dimer (*m/e* = 240)

2.6 - dimethylphenol trimer (*m/e*=362)

So, these are some phenolic compounds identified in you know, identified in methanol extracts of clay organic complexes like this 2, 6 dimethylphenol, then 4, 4 bis 2.6 dimethylphenol, then quinone dimer and also 2, 6 dimethylphenol trimer. So, these are phenolic compounds which are identified in methanol extracts of clay organic complexes.

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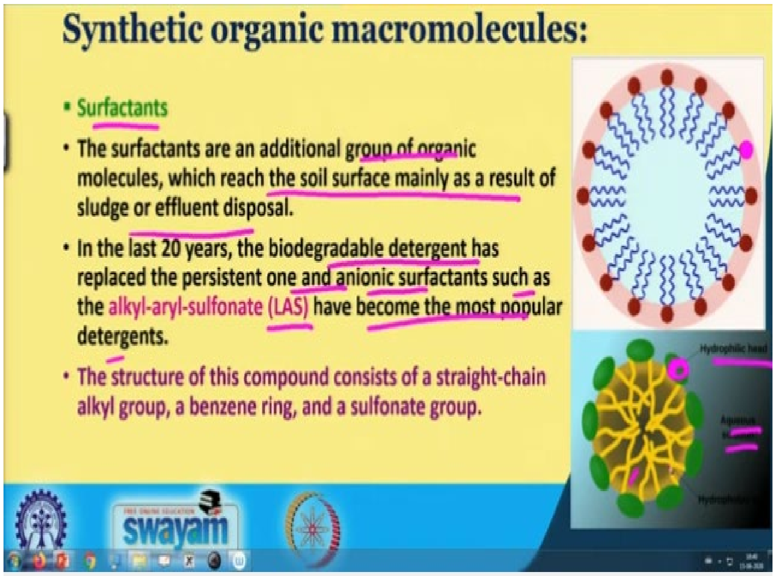

Synthetic organic macromolecules:

- Surfactants
- The surfactants are an additional group of organic molecules, which reach the soil surface mainly as a result of sludge or effluent disposal.
- In the last 20 years, the biodegradable detergent has replaced the persistent one and anionic surfactants such as the alkyl-aryl-sulfonate (LAS) have become the most popular detergents.
- The structure of this compound consists of a straight-chain alkyl group, a benzene ring, and a sulfonate group.

Also, another important, major importance synthetic organic macromolecule is surfactants, so this surfactants are an additional group of organic molecules which reach the soil surface mainly as a result of sludge or effluent disposal. Now, in the last 20 years the biodegradable detergent has replaced the persistent one and anionic surfactants such as these alkyl-aryl-sulfonate, LAS have become the most popular detergents.

Now, this surfactant has a you know, hydrophilic heads, so this is basically hydrophilic head which is remaining in the in contact with the water and it is also hydro you know, it is also a hydrophobic tail. So, these hydrophobic tail basically goes to the oil or organic liquid, so it has hydrophilic head as you can see here, this has hydrophilic head and also this hydrophilic head remains in direct contact with aqueous solution.

Whereas, this hydrophobic end goes directly in contact with the oil or organic solvent, so this is a structure of the surfactant, so the structure of this compound consists of straight chain alkyl group, benzene ring or sulfonate group. Now, these surfactants are known as one of the major you know, source potential source of pollutant in soil.

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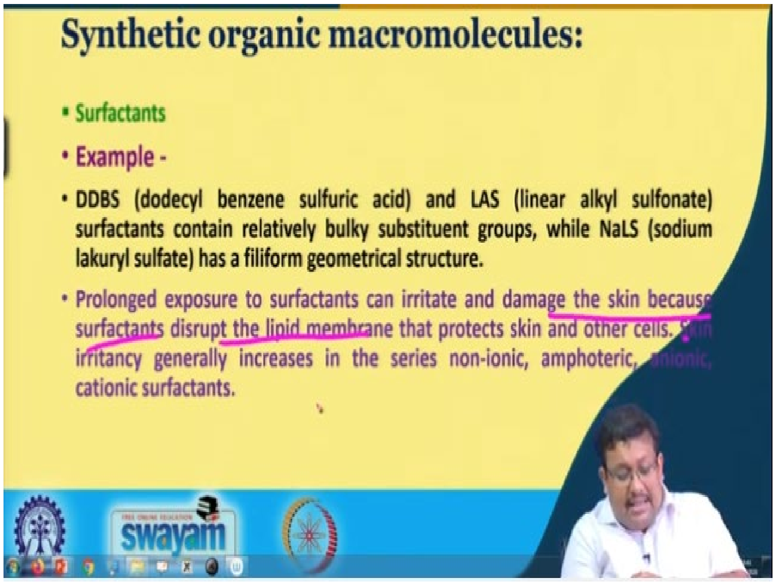

Synthetic organic macromolecules:

- Surfactants
- Example -
- DDBS (dodecyl benzene sulfuric acid) and LAS (linear alkyl sulfonate) surfactants contain relatively bulky substituent groups, while NaLS (sodium lakuryl sulfate) has a filiform geometrical structure.
- Prolonged exposure to surfactants can irritate and damage the skin because surfactants disrupt the lipid membrane that protects skin and other cells. Skin irritancy generally increases in the series non-ionic, amphoteric, anionic, cationic surfactants.

For example is DDBS that is dodecyl benzene sulphuric acid and LAS that is linear alkyl sulfonate, this surfactant contain relatively bulky substituent groups, where NaLS that is sodium lakuryl sulfate has a filiform geometrical structure. Now, what is the problem with this surfactants? Now, prolonged exposure to surfactants can irritate and damage the skin because surfactants disrupt the lipid membrane that protect the skin and other cells.

Now, skin irritancy generally increase in the series of non-ionic and amphoteric, anionic, cationic surfactants, so basically prolonged exposure to the surfactants can irritate and damage our skin and also as since they can disrupt the lipid membrane that protects the skin and other cells and are these irritations, so basically this surfactants are known as one of the major source of pollutants in the soil.

So, guys we have covered a wide range of elements as well as organic compounds which are known as potential soil pollutants, which shows very important you know, influence on soil pollution.

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References

References:

Yaron, B., Calvet, R., Prost, R., 1996. Soil Pollution. SpringerVerlag, Berlin, 313 pp

I hope that you have learned something new in this chapter and obviously, if we go to the last slide, it is the references, this last slide shows the book which I have used for this chapter, this is basically soil pollution process and dynamics. So, you can consult this book to get more information about different soil pollution process and dynamics, so I would request you to go through and read this book in details to enrich yourself among the soil pollution.

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References

References:

Figure in slide 112 was reused from

Yaron, B., Calvet, R., Prost, R., 1996. Soil Pollution. SpringerVerlag, Berlin, 313 pp

Although, the time is limited it is not possible for us to complete all these aspects of soil pollution pollutants however, I have tried to cover the major pollutants which are known for their you know, impacts as far as the soil pollution is concern. I hope you have learned something new in this module and let us wrap up this module and let us discuss other aspects of soil pollution in the next module that is in module 9. Thank you very much.