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**NPTEL ONLINE CERTIFICATION COURSE**

**Health, Safety & Environmental Management in  
Offshore and Petroleum engineering (HSE)**

**Module 3:**

**Environmental issues and Management**

**Lecture 2: Oil spills**

Welcome to the second lecture on module 3 where we are focusing on environmental issues and management under the course on HSE in offshore and petroleum engineering under the braces of NPTEL IIT Madras in the 2<sup>nd</sup> lecture in module 3 we will talk about the consequences and significance happening in the marine environment which essentially occurs from 1 important outcome of drilling which is oil spills.

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**Oil hydrocarbons - facts**

- Abundant evidence demonstrates global distribution of oil contamination
- Concerns about scale and consequences of oil pollution is increasing over last decades
- Oil spill/content is one of the leading contributors of impact on marine environment
- Crude oil contains some hydrocarbons with hybrid composition
  - Paraffin-naphthenic, naphthene-aromatic etc
- Behavior and biological impact of oil in ecosystems are governed by their physical and physiochemical properties
  - Specific gravity, volatility and water solubility

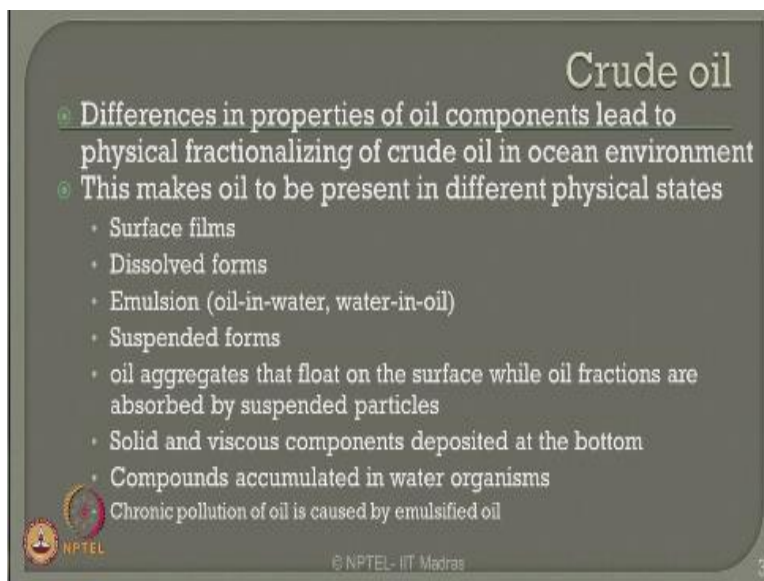
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Let us look at some important facts related to hydrocarbons abundant evidence demonstrates global distribution of oil contamination when tests have been conducted to estimate the content of hydrocarbons in marine pollution. Therefore it is important friends to know that concerns about scale and consequences of oil pollution is increasing day by day over to the last leakages.

Oil spill therefore are oil content in the marine environment is one of the leading contributors of impact cost to the marine environment crude oil contains some hydrocarbons with hybrid composition.

For example paraffin- naphthenic, paraffin aromatic composition which are highbred in nature their behavior and biological impact in the ecosystems are essentially governed by the physical and physiochemical properties for example some of the properties which govern there impact on the ecosystem is essentially based on the specific gravity the volatility and water solubility we can see each one of them separately in detail and see what are the consequences occurring from water solubility and volatility of these physical and chemical properties of this system which cause serious effects on marine pollution.

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**Crude oil**

- Differences in properties of oil components lead to physical fractionalizing of crude oil in ocean environment
- This makes oil to be present in different physical states
  - Surface films
  - Dissolved forms
  - Emulsion (oil-in-water, water-in-oil)
  - Suspended forms
  - oil aggregates that float on the surface while oil fractions are absorbed by suspended particles
  - Solid and viscous components deposited at the bottom
  - Compounds accumulated in water organisms

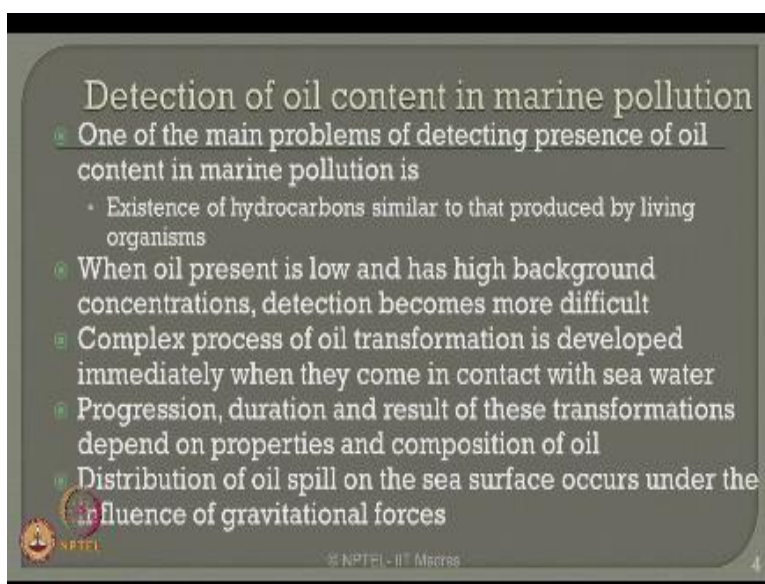
Chronic pollution of oil is caused by emulsified oil

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Let us quickly ask the composition of what a crude oil consists of differences in properties of oil components actually lead to physical fractionalizing of crude oil in ocean environment. This makes oil to be present in different physical states in the marine pollution they can occurs in the form of surface films, they can be also seen in dissolved forms can also see in some emulsions, oil in water, water in oil composition etc..

Can also see crude oil as suspended forms oil aggregates that float on the surface while oil fractions are observed by the suspended particles in the marine environment solid and viscous components are deposited usually at the sea bottom, compounds accumulated in the water organisms as well and chronic pollution of oil is essentially caused by the emulsifying oil content present in crude oil.

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**Detection of oil content in marine pollution**

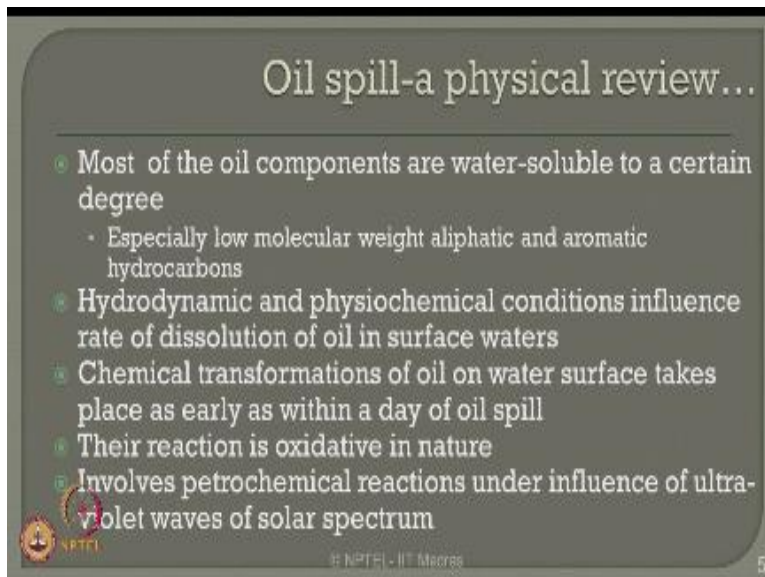
- One of the main problems of detecting presence of oil content in marine pollution is
  - Existence of hydrocarbons similar to that produced by living organisms
- When oil present is low and has high background concentrations, detection becomes more difficult
- Complex process of oil transformation is developed immediately when they come in contact with sea water
- Progression, duration and result of these transformations depend on properties and composition of oil
- Distribution of oil spill on the sea surface occurs under the influence of gravitational forces

NPTPL - III Macro

Now the question comes how do you detect the oil content in marine pollution? Rather it is very difficult and complex because of certain reasons, one of the main problems of detecting presence of oil content in marine pollution is that existent hydrocarbons are similar mostly to that of produced by living organisms and mammals in the sea environment, when oil presence is low and has high background concentration, detection becomes much more difficult.


The complex process of oil transformation is developed immediately when they come in contact with sea water and they disperse very fast. Progression, duration and result of these transformations essentially depend on the properties and composition of the oil, distribution of oil spill therefore on the sea surface occurs under the influence of gravitational forces.

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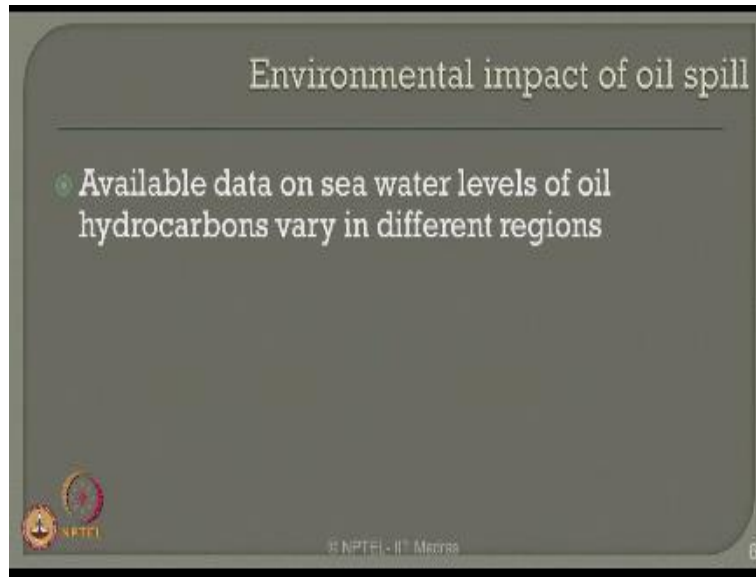
Oil spill-a physical review...

- Most of the oil components are water-soluble to a certain degree
  - Especially low molecular weight aliphatic and aromatic hydrocarbons
- Hydrodynamic and physiochemical conditions influence rate of dissolution of oil in surface waters
- Chemical transformations of oil on water surface takes place as early as within a day of oil spill
- Their reaction is oxidative in nature
- Involves petrochemical reactions under influence of ultra-violet waves of solar spectrum

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If you look at the physical review of how oil spill actually takes place, most of the oil components are essentially water soluble to a certain degree, especially low molecular weight aliphatic and aromatic hydrocarbons are water soluble, hydrodynamic and physical chemical conditions influence the rate of dissolution of oil in surface waters, chemical transformation of oil on water surface takes place as early as within a day of oil spill, the reaction is oxidative in nature, it involves petro chemical reactions under influence of ultra-violet waves of solar spectrum.


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If you look at series of environmental impact cost by oil spill in marine environment the available data on the studies on sea water levels of hydrocarbons vary in different regions, friends it is important for us to know that if really wanted to measure the marine pollution which cost by oil spill you must always look at the contents present in the sea water and try to disintegrate them by some chemical reactions to know what are actually the contents contributed by hydrocarbons from the oil spill.


But unfortunately the available data on thus such test are showing different results of hydrocarbon content in different regions.

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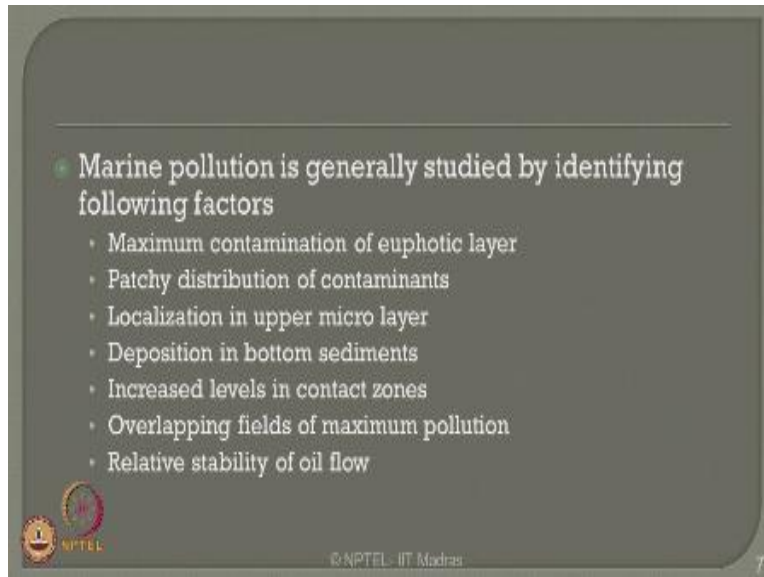
Environmental impact of oil spill

- Available data on sea water levels of oil hydrocarbons vary in different regions
- Factors influence them are complexity of bio-chemical and geo-chemical behavior
- Reports show that tendencies of oil levels tend to increase from ocean pelagic region to the enclosed sea, coastal waters and estuaries

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Now there are many factors this influence them essentially the primary factors or the complexity of bio-chemical and geo-chemical behavior of these hydrocarbons in water, therefore the report show the tendencies of oil level tend to increase from ocean pelagic region to the enclosed sea, coastal waters and estuaries which is very dangerous and very peccary situation which bothers the environmental list in the present state.

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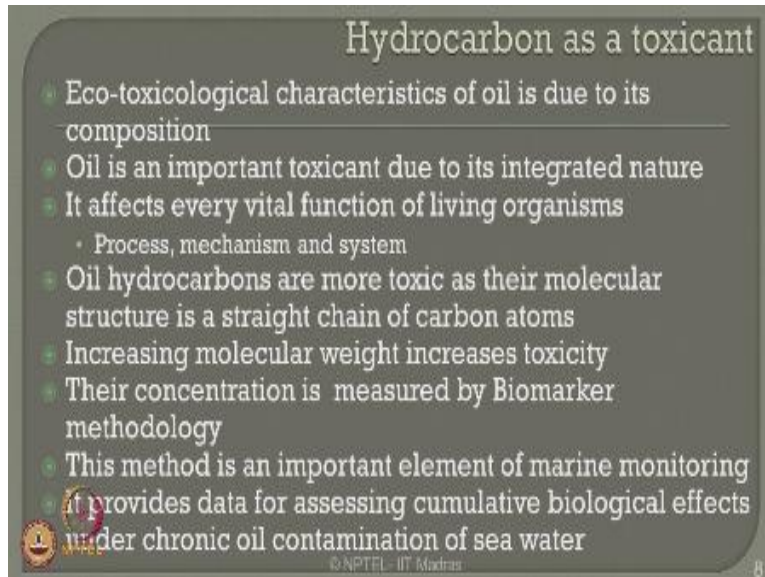
• Marine pollution is generally studied by identifying following factors

- Maximum contamination of euphotic layer
- Patchy distribution of contaminants
- Localization in upper micro layer
- Deposition in bottom sediments
- Increased levels in contact zones
- Overlapping fields of maximum pollution
- Relative stability of oil flow

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Marine pollution is generally studied by identifying the following factors. Maximum contamination of euphotic layer. Patchy distribution of contaminants present term surface water. Localization in upper micro layer, deposition in bottom sediments at sea rate, increased levels in contact zones, overlapping fields of maximum pollution and of course one can also study the relative stability of oil flow in the given situation.

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The slide is titled "Hydrocarbon as a toxicant" and contains a list of eight bullet points. The text is white on a dark grey background. At the bottom left, there is a small circular logo with a lamp and the text "NPTEL". At the bottom center, it says "© NPTEL - IIT Madras". At the bottom right, there is a small number "8".

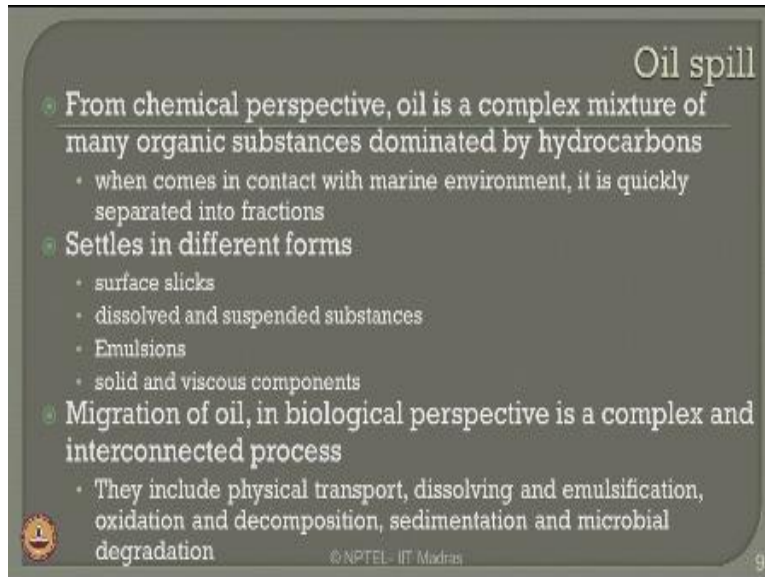
- Eco-toxicological characteristics of oil is due to its composition
- Oil is an important toxicant due to its integrated nature
- It affects every vital function of living organisms
  - Process, mechanism and system
- Oil hydrocarbons are more toxic as their molecular structure is a straight chain of carbon atoms
- Increasing molecular weight increases toxicity
- Their concentration is measured by Biomarker methodology
- This method is an important element of marine monitoring
- It provides data for assessing cumulative biological effects under chronic oil contamination of sea water

If you look at hydrocarbon as one of the important toxicants, let us see what are the contents present in hydrocarbon which classifies or qualifies this as a toxicant. The eco toxicological characteristics of oil is essentially arising from its composition. Oil is an important toxicant due to its integrated nature. It effects every vital function of living organisms for example, it seriously effects the process system, the mechanism and the reproductive system of a given living manners.

Oil hydrocarbons are more toxic as their molecules structure is actually a straight chain of carbon atoms. Increasing molecular weight increases toxicity. Their concentration is usually measures by a method call biomarker method. This method is an important element of marine monitoring system. It provides data for accessing cumulative biological effects under chronic oil contamination of sea water.



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**Oil spill**

- From chemical perspective, oil is a complex mixture of many organic substances dominated by hydrocarbons
  - when comes in contact with marine environment, it is quickly separated into fractions
- Settles in different forms
  - surface slicks
  - dissolved and suspended substances
  - Emulsions
  - solid and viscous components
- Migration of oil, in biological perspective is a complex and interconnected process
  - They include physical transport, dissolving and emulsification, oxidation and decomposition, sedimentation and microbial degradation

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From chemical perspective friends oil is seen as a complex mixture of many organic substances which dominated essentially by hydrocarbons. When they come in contact with marine environment it is quickly separated into fractions. The settle and different forms in sea environment they can also form surface slicks, they can dissolve and also become a part of suspended substances, they also get disintegrated to form emulsions, some of them remain as solid and viscous components in the marine environment.

Therefore, friends migration of oil in a biological perspective is a very complex model because of its interconnection processes they include physical transport, dissolution and emulsification, oxidation, decomposition, sedimentation and of course ultimately the microbial degradation. Because of these interconnectivity between the processes biological perspective adds complexity to estimate oil spill or oil contamination mathematically in modeling sequences.

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• Oil hydrocarbons are continuously released in marine environment due to natural oil seepage from sea floor

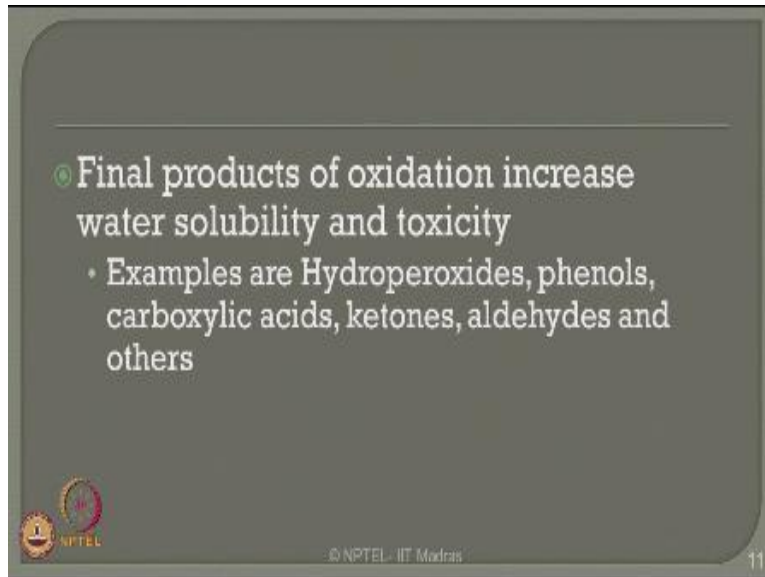
• Global distribution of oil hydrocarbons is characterized by increasing concentration from pelagic areas to coastal waters

• Some traces of vanadium and compounds of sulphur catalyzes the oxidation process

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Oil hydrocarbons are therefore continuously released in marine environment not necessarily only during accidents but they also arise from natural oil seepage from the sea floor. Global distribution of oil hydrocarbons is characterized by increasing concentration from the pelagic areas to coastal waters which is one of the main concern to the environmentalist in the reason past. Some traces are vanadium and compounds of sulphur actually catalyzes even the oxidation process present in the environment which depletes the dissolve oxygen content in the sea water.

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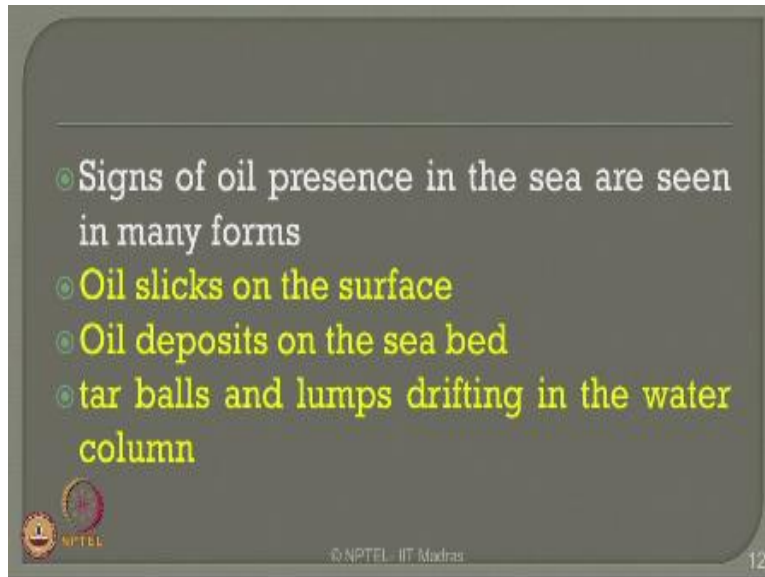
Final products of oxidation increase water solubility and toxicity

- Examples are Hydroperoxides, phenols, carboxylic acids, ketones, aldehydes and others

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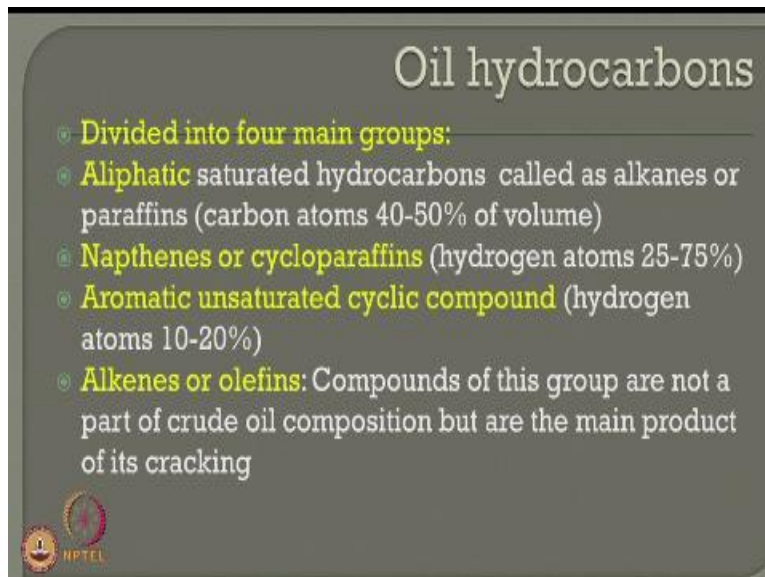
Final products of oxidation increase water solubility and toxicity examples are hydroperoxides, phenols, carboxylic acids, ketones, aldehydes and others.

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Signs of oil presence in the sea are seen in many forms ladies and gentleman oil sleeks or seen on the surface of our marine involvement oil deposited I mean noticed on the sea bed tar balls and lumps drifting the sea water column is also been seen.

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## Oil hydrocarbons

- **Divided into four main groups:**
- **Aliphatic** saturated hydrocarbons called as alkanes or paraffins (carbon atoms 40-50% of volume)
- **Napthenes or cycloparaffins** (hydrogen atoms 25-75%)
- **Aromatic unsaturated cyclic compound** (hydrogen atoms 10-20%)
- **Alkenes or olefins:** Compounds of this group are not a part of crude oil composition but are the main product of its cracking



measures let us look at the contents if hydrocarbons and see what are the factors it influence the toxicity in given marine involvement if you look at oil hydrocarbons there are three divided into four main groups the first group is Aliphatic which is containing saturated hydrocarbons which otherwise called as alkanes or paraffins the carbon atoms present in this contain is about 40 to 50% of volume the second main group is Napthenes or cycloparaffins which contains hydrogen atoms is about 25 to 75% the third group is Aromatic unsaturated cyclic compound.

Which of course contains hydrogen atoms in the range of 20, 20% and the last group of hydrocarbon is alkanes or olefins which are nothing but compounds which are a path of crude oil but the main product of it is cracking in terms of it is dissolution and decomposition.

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Evaporation and dissolution of petroleum hydrocarbons in water environment at 25°C

Hydrocarbon	Partial pressure (Pa)	Solubility (mg/l)	T <sub>e</sub> (hour)	T <sub>d</sub> (hour)
n-pentane	68,400	40	0.012	2,000
n-heptane	6,100	2.5	0.14	3.2E4
n-decane	175	0.03	4.7	1.6E6
n-dodecane	16	0.003	520	2.6E8
Benzene	12,700	1780	0.65	45
n-xylene	1,170	180	0.71	40
Napthalene	11	32	750	2500
Phenanthrene	0.2	1.2	4.2E4	6.7E4
Anthracene	0.001	0.04	8.3E5	2.0E6
Pyrene	0.001	0.14	8.3E5	6.7E5

This table gives a comprehensive layout of understanding in terms of evaporation and dissolution of petroleum hydrocarbons in the water environment as a simple at in temperature over 25°C we can see the content of hydrocarbon varying from pentane to pyrene the partial pressure presents in terms of Pascal their solubility in terms of milligram per liter and the effective time saturation comes of hours and the TD in terms of hours there are different hydrocarbon components which are actually a path.

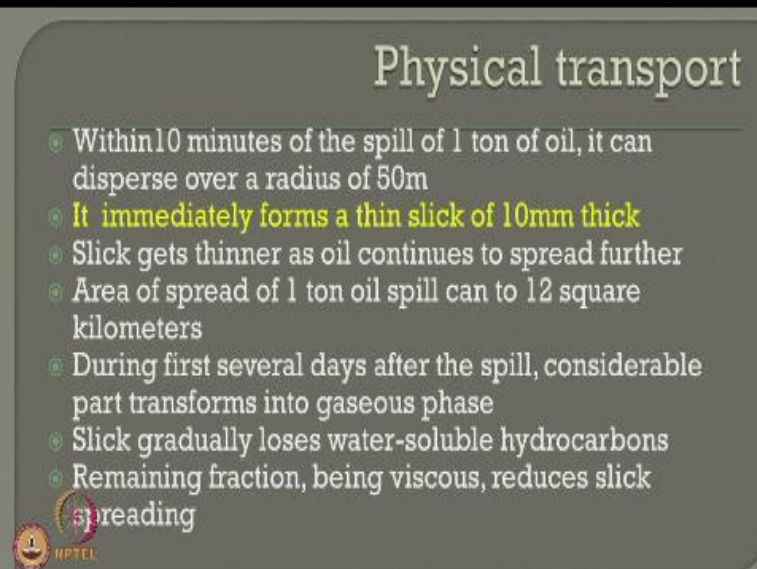
Of evaporation and dissolution process at a specific temperature this shown here now the content in terms of solubility or high as 40mg/l solubility and as minimum has very low value of 0.05 however the retention time varies as high as 200 hours environment very high value of 5.7 10<sup>5</sup> hours so the presents of this hydrocarbons during the process of evaporation and dissolution stays for a longer time and solubility is also very high.

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If you look at the fate and behavior of these hydrocarbon components in the marine environment their different stages at which they can be encounter in the marine pollution in the form of physical transport they can also appeal in the form of dissolution emulsification oxidation and destruction sedimentation microbial degradation and aggregation and lastly self-purification let us look at different forms of this quickly one by one and try to understand the significant contribution of these stages in the marine pollution.

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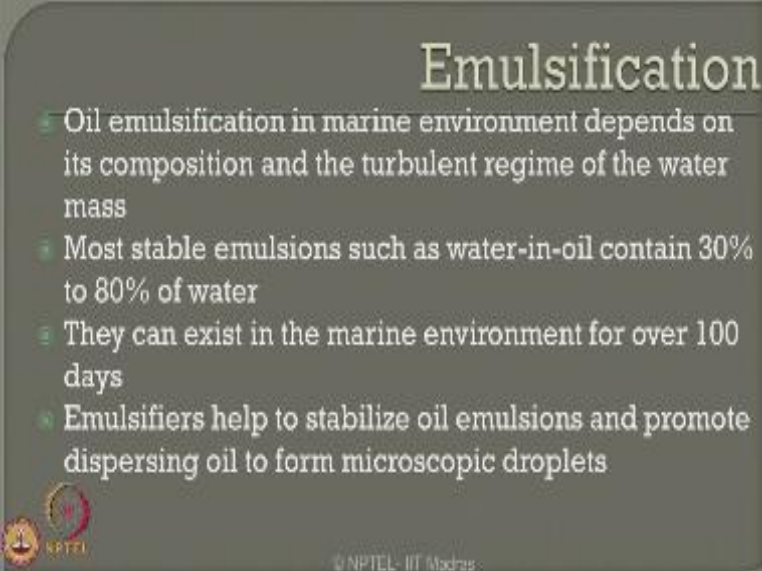
The slide is titled "Physical transport" in a large, white, serif font at the top right. Below the title is a list of seven bullet points, each preceded by a small circular icon. The second bullet point is highlighted in yellow. At the bottom left of the slide, there is a logo for "HPTEL" featuring a stylized globe and the text "HPTEL" below it.

- Within 10 minutes of the spill of 1 ton of oil, it can disperse over a radius of 50m
- **It immediately forms a thin slick of 10mm thick**
- Slick gets thinner as oil continues to spread further
- Area of spread of 1 ton oil spill can be as high as 12 square kilometers
- During first several days after the spill, considerable part transforms into gaseous phase
- Slick gradually loses water-soluble hydrocarbons
- Remaining fraction, being viscous, reduces slick spreading

We look at the physical transport form it is evident from literature that within 10 minutes of the spill of let us say one ton of oil it can disperse over a radius about 50m so dispersion is very fast it immediately forms a thin slick of 10mm thick slick becomes thinner as oil continues to spread for the area spread of 1 ton oil spill can be as high as 12 square kilometers day in the first several days after the spill their considerable amount transforms into gaseous phase slick gradually loses water soluble hydrocarbons as it stays longer the remaining fraction brings discoloration reduces the slick spreading automatically.




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**Emulsification**

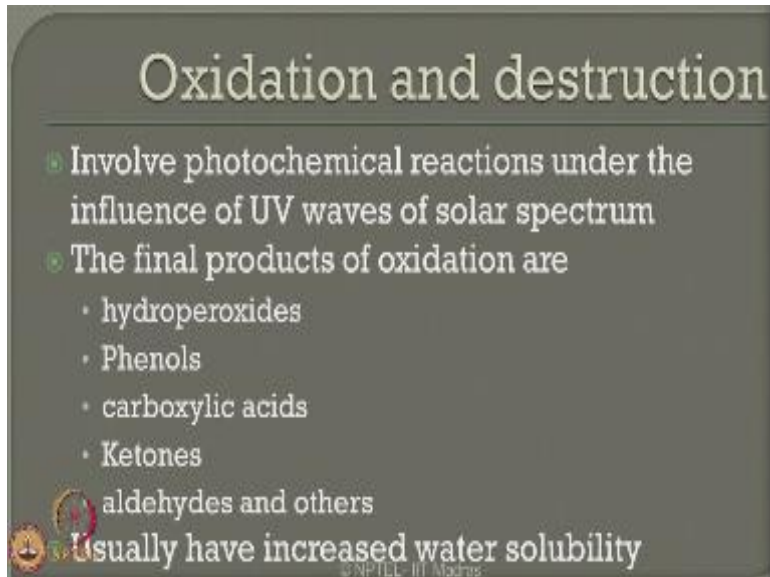
- Oil emulsification in marine environment depends on its composition and the turbulent regime of the water mass
- Most stable emulsions such as water-in-oil contain 30% to 80% of water
- They can exist in the marine environment for over 100 days
- Emulsifiers help to stabilize oil emulsions and promote dispersing oil to form microscopic droplets

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To talk about the next stage which is emulsification oil emulsification in marine environment depends on its composition and the turbulent regime of the water mass most stable emulsions such as water in oil contain about 30% to 80% of water, therefore they can exist unfortunately in the marine environment for more than over 100 days so the retention period in marine environment is very large and the spirit is very fast.

Emulsifiers help to stabilize oil emulsions and also promotes unfortunately the dispersing of oil perform microscopic droplets and they stay for a loner time this sea surface.

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**Oxidation and destruction**

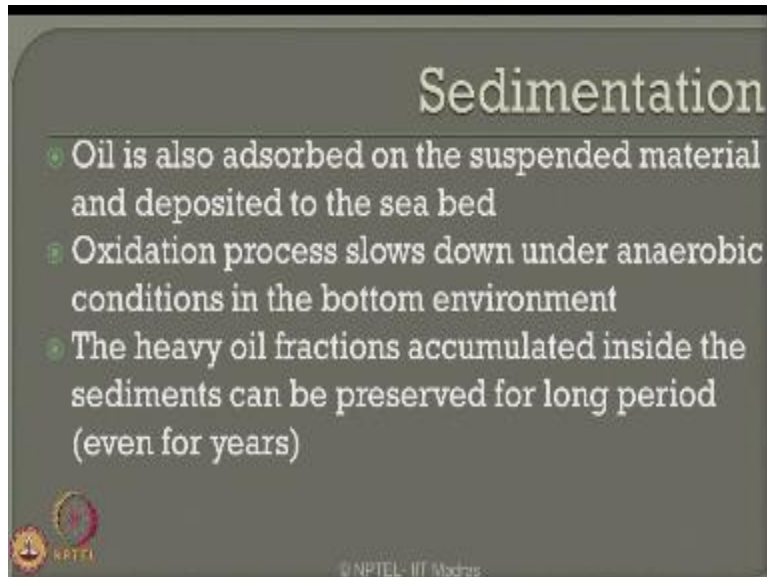
- Involve photochemical reactions under the influence of UV waves of solar spectrum
- The final products of oxidation are
  - hydroperoxides
  - Phenols
  - carboxylic acids
  - Ketones
  - aldehydes and others

Usually have increased water solubility

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Now look this next state of oxidation and destruction it involves photochemical reactions under the influence of ultra violet waves of the solar spectrum the final products of oxidation are the following it can form hydro peroxides can form phenols carboxylic acids ketones aldehydes and others, it usually has increased water solubility.

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**Sedimentation**

- Oil is also adsorbed on the suspended material and deposited to the sea bed
- Oxidation process slows down under anaerobic conditions in the bottom environment
- The heavy oil fractions accumulated inside the sediments can be preserved for long period (even for years)

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The next problem is from sedimentation oil is also adsorbed on the suspended material and deposited on the sea bed oxidation process slows down under anaerobic conditions in the bottom environment in the segment. Therefore the heavy oil fractions accumulated inside the sediments can be preserved for a very long period and that period can be as high as even many number of years.

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The slide features a dark grey background with the title 'Microbial degradation' in a light-colored serif font at the top. Below the title, there are two bullet points, each preceded by a green circular icon. The first bullet point reads 'Many known species and fungi use oil components to sustain their growth and metabolism'. The second bullet point reads 'Paraffin compounds biodegrade faster than aromatic and naphthenic substances'. In the bottom left corner, there is a small circular logo with a globe and the text 'NPTEL'. In the bottom right corner, there is a small copyright notice: '© NPTEL- IIT Madras'.

## Microbial degradation

- Many known species and fungi use oil components to sustain their growth and metabolism
- Paraffin compounds biodegrade faster than aromatic and naphthenic substances

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If we look at the next stage as microbial degradation it is known species and fungi uses oil components to sustain the growth and metabolism for a longer time, paraffin compounds biodegrade faster than aromatic and naphthenic substances.

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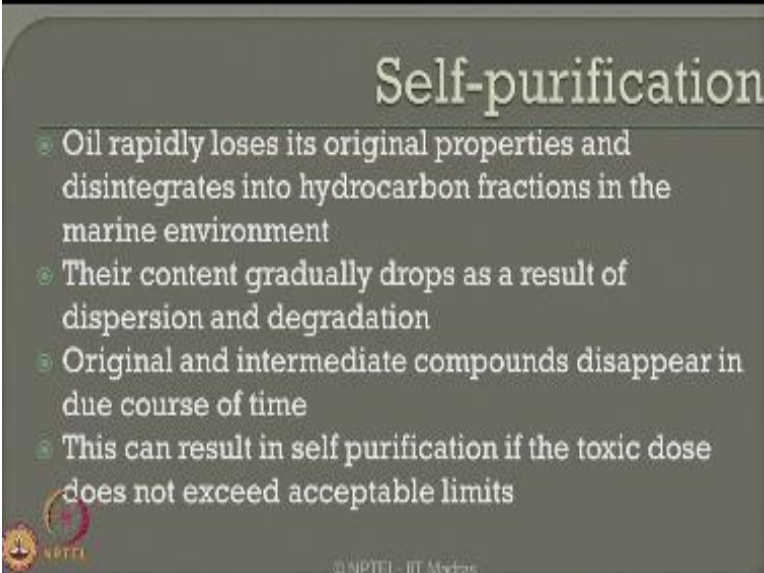
## Aggregation

- Oil aggregates in the form of petroleum lumps and tar balls
- These can be found in the coastal waters and on beach side
- They derive high fractions from crude oil after evaporation
- Subsequently results in dissolution of light fractions, emulsification of oil residuals, chemicals and microbial transformation
- Oil aggregates can exist several years in the open ocean

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The aggregation process results in oil aggregates in the form of petroleum lumps and tar balls they can be found in coastal waters and on beach side they derive high fractions from crude oil after evaporation subsequently they result in dissolution of light a fraction emulsification of oil residuals chemicals and microbial transformation oil aggregates can exist several years in the open ocean.

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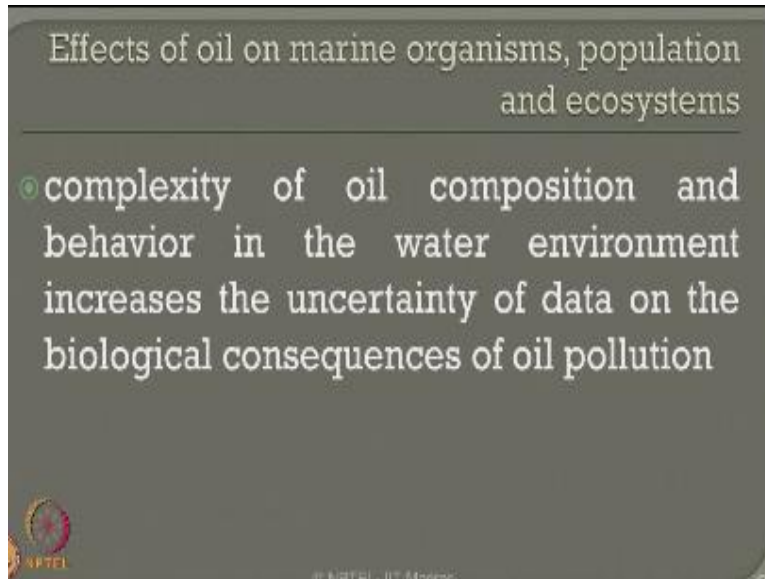
**Self-purification**

- Oil rapidly loses its original properties and disintegrates into hydrocarbon fractions in the marine environment
- Their content gradually drops as a result of dispersion and degradation
- Original and intermediate compounds disappear in due course of time
- This can result in self purification if the toxic dose does not exceed acceptable limits

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If we talk about self purification oil rapidly loses its original property and disintegrates into hydrocarbon fractions in the marine environment their content gradually drops as a result of dispersion and degradation original and intermediate compounds disappear in due course of time, this can result in self purification of course if the toxic dose arrays from the process does not exceed the acceptable limits.

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Effects of oil on marine organisms, population and ecosystems

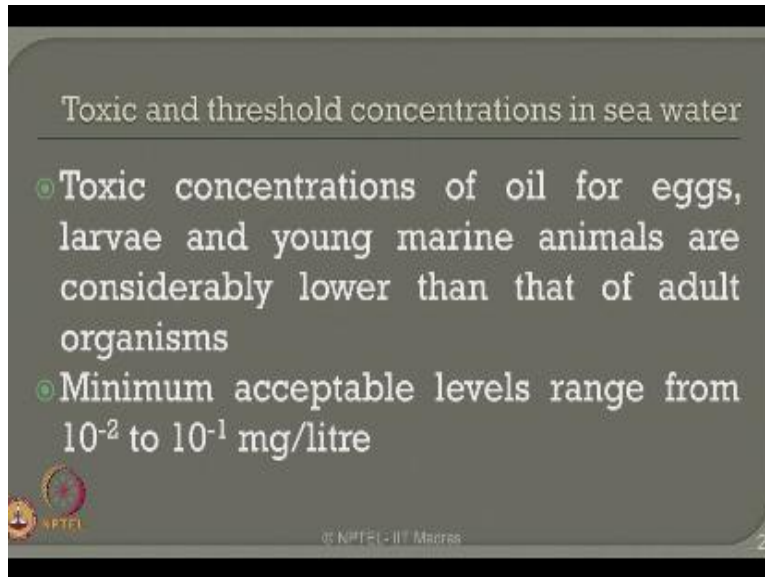
- complexity of oil composition and behavior in the water environment increases the uncertainty of data on the biological consequences of oil pollution

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If you look at the effects of oil on marine organism's population and eco systems complexity oil composition and its behaviour in water environment increases uncertainty of data on the biological consequences of oil pollution.

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Toxic and threshold concentrations in sea water

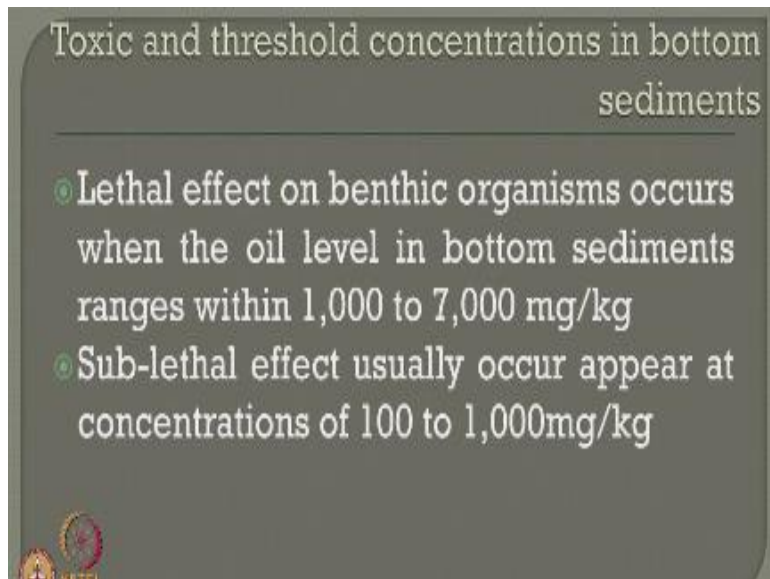
- Toxic concentrations of oil for eggs, larvae and young marine animals are considerably lower than that of adult organisms
- Minimum acceptable levels range from  $10^{-2}$  to  $10^{-1}$  mg/litre

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You look at the toxic and threshold concentration of this in sea water the toxic concentration of oil for eggs lava and young marine animals are consider lower than that of adult organisms the minimum acceptable level ranges from  $10^{-2}$  to  $10^{-1}$  mille gram per litre any toxic level more than this will not allow the lava to mature in to mammal or a egg.



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Toxic and threshold concentrations in bottom sediments

- Lethal effect on benthic organisms occurs when the oil level in bottom sediments ranges within 1,000 to 7,000 mg/kg
- Sub-lethal effect usually occur appear at concentrations of 100 to 1,000mg/kg

The toxic and threshold concentration in bottom sediments at sea bottom or sea bed can be seen like this the lethal effects on benthic organisms occur when the oil level in the bottom sediments are in the range of 1000to 7000 mille gram per kg the sub lethal effects will be caused when they are seen in concentration varying from 100 to 1000mille gram per kg so friends any lethal effect will be resulting from a concentration of sediments seen at sea bottom as minimum as 100 mille gram per kg to as high as 7000 milligram per kg which are generally seen but unfortunately friends the strategic show and the literature study show that the sediment concentration on the sea bed is much higher than these numbers shown in the slide.

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**Toxicity of oil and oil hydrocarbons for developing eggs (96-hour LC<sub>50</sub>)**

Hydrocarbon	LC <sub>50</sub> (mg/litre)
Crude oil	24
Napthalene	1.25
Xylenes	4
Phenol	13

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We look at toxicity of oil and hydro carbons for developing eggs as a result of 96 hour lethal concentration 50 ,we already know how to find out the lethal concentration 50 in the last module we are explained you a logarithmic curve depending upon how one can estimate lethal concentration if we look at the hydrocarbon contents like crude oil, naphthalene, xylenes and phenol the lethal concentration in mille gram per litre is seen in the screen now crude oil is seen to be very high as 24mille gram per litre whereas the naphthalene concentration in hydro carbon are seen as well as 1.25 mille gram per litre.

So friends in this lecture we have tried to understand what are the chemical composition the biological content and the physical separation and different processes involved in hydrocarbon how they can be separated and what are the different constants present in hydrocarbons and what are the individual influences on oil spill as well as marine pollution ,how do they effect physically biologically the organisms present in sea water we I will talk about in detail about this in the next lecture thank you.

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