

coastal regions, you will see a lot of coastal industries in India and all over the place all over the world.

So there are a lot of contaminated sediments and sediments are if it is contaminated, it has to be managed because these are also commercial locations as there is a lot of traffic, shipping traffic is there and then you cannot let it be there because if shipping happens, then it is going to re-suspend. Resuspension happens, chemical contamination will move from place to place and all that, so it is a big mess. So people look for options for remediation. So the 3 options that people have looked at.

One is called as monitored natural recovery. I have spoken about this before. What it means is that this is simply based on the idea of you figuring out using a transport model, how much emission is going to occur from the sediment naturally without doing anything. So, essentially we are applying the model which we saw in the last few classes, we predict what is going to be the concentration gradient in the sediment based on the data of measured sediment loading, then we will predict what is the flux that will come out and based on that we will predict what will be the downstream water quality impairment, yeah.

Now, if you determine that the downstream water quality is not bad, you do not do anything, you leave it and the hope is this term here is called natural attenuation because what this assumes is that there is going to be biodegradation naturally, slow biodegradation. So now biodegradation for a lot of organic compound biodegradation may happen eventually because if you introduce microbial culture, microbial populations will adapt themselves to this and will take time for them and eventually it may happen, but there are some chemicals which have been designed to be nonbiodegradable, yeah.

There are human made chemicals which are specifically designed to be nonbiodegradable, they are called as refractory chemicals, and in this case, biodegradation will be very slow, it will not degrade very easily, they are designed like that, but you can also imagine that this is the most attractive component for industries who has been asked to clean up. How do you know which industry is responsible for it, for that we use a mix of analytical chemistry, we use what is called as markers, we use markers. Markers are chemical signatures.

If we find some chemical from chemical analysis which is present in this group and it is coming only from one particular industry, so you know that they are responsible for it. So, it is an investigative kind of back calculation where you know that this is coming through this, where you ask, the regulatory agency will ask that particular entity or group of corporations or individuals to clean it up okay. So, then the cost of cleaning up comes into question. So, this is least expensive because there is nothing needs to be done.

It is monitored natural record, you have to monitor it from time to time, find out that there nothing has changed. What can change? Why do you need to monitor it? We discussed in last class. What can change this? It can re-suspend and go somewhere else. If it is disturbed, it can go and in the first picture we saw in the slideshow is that sediment surface is very flimsy, it will just move very easily and this can happen and people are not very sure that it will move and it can move for 100 different reasons, okay.

Somebody will just go take a boat and ride through it and everything will be destroyed, okay. So, people are not very comfortable with this. We people means general public and the regulatory agencies. So, then the other option that they have is what is called in-situ capping.  
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## Monitored Natural Recovery

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- Leave it Alone!! Let Nature take it's course.
  - Biodegradation
    - Based on native microbial population
    - Modified microbial populations introduced
  - Definition of a Sediment Quality Criteria

So the monitored natural recovery, the philosophy is leave it alone and nature will take its course, but the nature will take its course if it is below a certain level, that is a rule. If you overload it, it will take more time and it may not happen and that will interfere and that is the general this thing.

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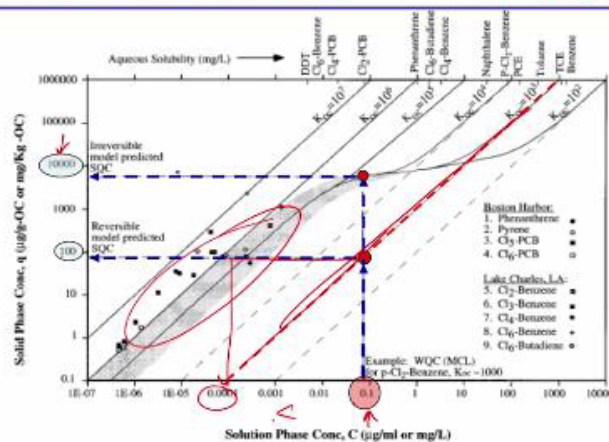
## Sediment Quality Criteria

- Acceptable Sediment Contamination Levels (mass-chemical/mass-sediment).
- Based on “Bio-availability” of the chemical in the pore water for processing by biological receptors.
  - Toxicity of bio-available chemical concentration in water.
- Traditionally, Bioavailability has been estimated by assuming Linear Reversible Equilibrium Partitioning.

So, this here what we are asking is this is question of bioavailability is where this essentially uses the partition constant.

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## Irreversible Fraction $m_2 \propto \frac{S_{OC}}{K_{OC}} + (K_{OC} - 1)$



\* Kan et al., *Environmental Science and Technology*, **32**, 892-902, 1998.

So we saw in the last class, in the model that the initial condition the flux is a function of, flux is proportional to  $\rho_A^0$ , yeah,  $\rho_A^0$  is a function of  $K_{A32}^*$ , the partition constant. If the partition constant is very high, the  $\rho_A^*$  will be very small, yeah, and there is an argument that people have made is that the partition constant changes after adsorption. Contamination has happened 20 years back, it has gone into a sediment and nobody has disturbed it.

It has now bound irreversibly to the sediment, which means that while adsorbing, it is behaving like one chemical one partition constant, but the desorption is the partition constant has increased a lot. So, essentially this is what it means. For example, benzene has a KOC of 1000.

So, this is the KOC line, the partition constant, which means that the 100 milligrams per kilogram of sediment contamination of benzene will result in a concentration of 0.1 milligrams per liter in the pore water okay, but if you see that if it follows this line, yeah.

But there is evidence to show that this is now after 10 years or 15 years of contamination all of this is sitting here, the desorption data is there, which means that the partition constant is now gone there. What it means is that it is now following some other lines. So, which means it takes a higher concentration about 100 times higher to give the same concentration, which means in other words, it means that this is the concentration that you are likely to find for this particular contamination.

So this concentration is much lower than this concentration. So, the argument was made that it is not dangerous, it is much safer. So, this is one, this is irreversible fraction.

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### **Irreversible Sorption on Organic Carbon – Proposed Mechanisms**

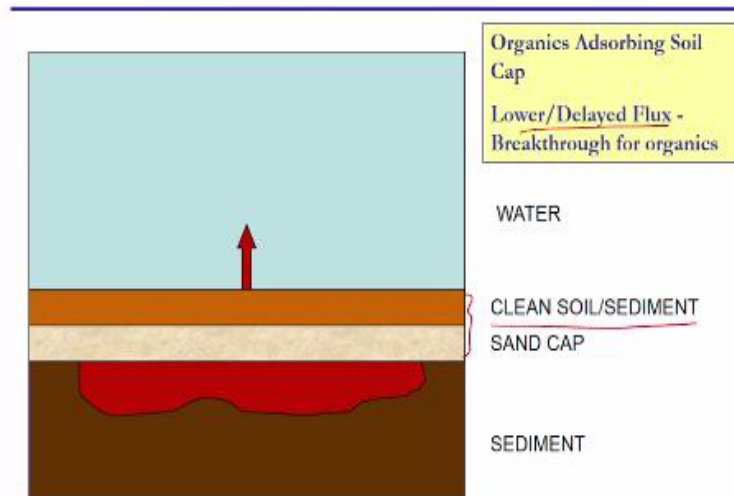
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- Based on Form and Distribution of Organic Carbon in Sediments
  - Slow Diffusion from coal-derived particles
  - ‘Soft’ and ‘Hard’ Carbon – Ageing Effects
  - Glassy and Rubbery Phases
  - Condensed (black carbon, soot etc) and Amorphous Carbon (humic acid based)
  - Conformational Changes and Binding
- Some forms offer greater sorption capacity and slower desorption rates
- Ageing and slow diffusion

So, there are a lot of arguments in this it is not proven, it is very size specific and these are the theories that are offered okay, a lot of theories and there is very little, it is still inconclusive.

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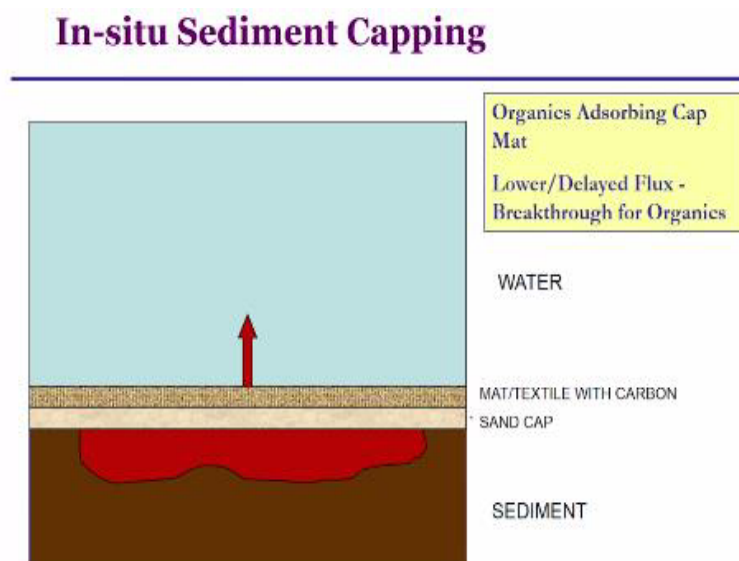
## In-situ Sediment Capping



The second option what is called as in-situ capping, this is you put a clean material on top of existing. So what you do is there is regular release. On top of it, if I now put a layer of something, what it does is it will add to the mass transfer resistance, it will add layer one layer of mass transfer resistance. I can also put a layer, in the case of sand, sand has very little KOC, very little organic carbon, so it will not adsorb anything, it will just offer resistance for pore movement.

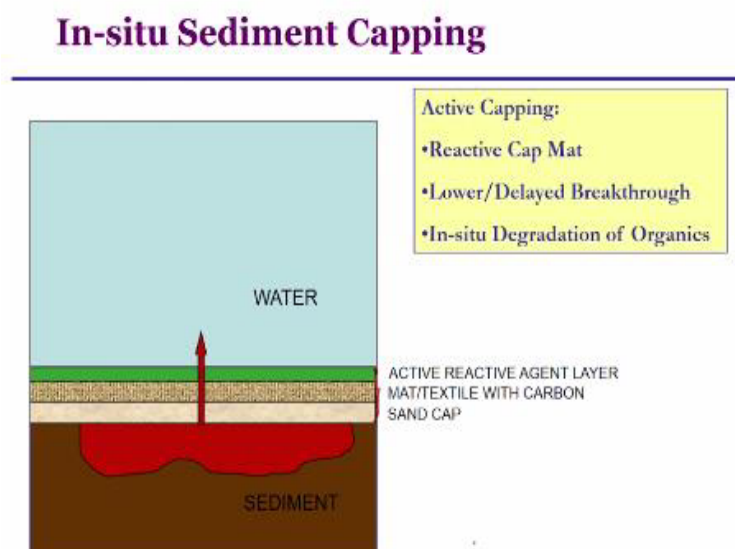
But if I add a layer which has clean soil or sediment which has a lot of organic carbon, it will also adsorb and therefore it will delay the breakthrough of the chemicals through it and one problem with this having the cap is that it decreases depth of the water channel and that is a problem in many places. You cannot have it because there is navigation that is happening there and people are using it for traffic, commercial traffic and all that.

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So people have figured out ways of compressing that layer, engineering small thicknesses of this thing.

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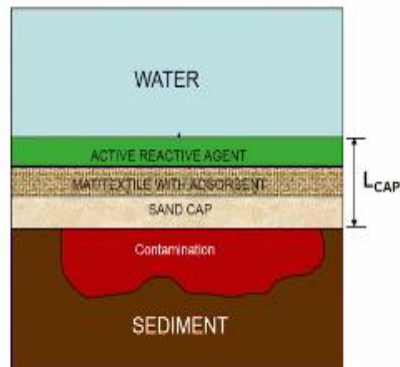


Again, we have these different improvements in the type of sand cap and people have invented textile based carpet kind of thing. We will just take it and dump it, put it on the contaminated surface and it has carbon embedded in it. It also has some active ingredients and all that.

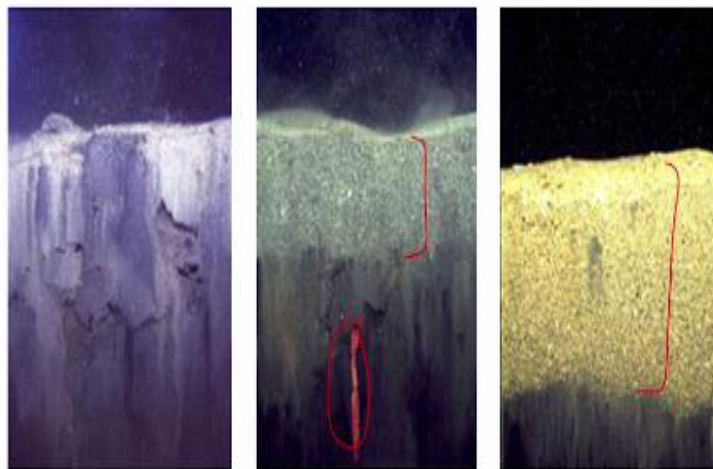
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## In-situ Sediment Capping

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So, essentially, you would put a layer on top of the existing sediment. So it provides  
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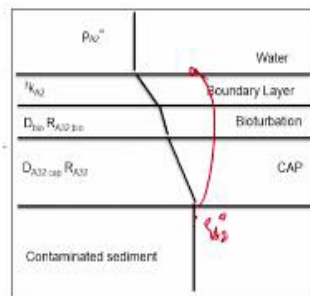


This is like a cap. This is a cap, it looks like that okay the sand cap. One of the arguments against capping is either it destroys the essential biological life there. So this worm is sitting underneath here and then it would have been on the surface, now it is underneath somewhere, it is become more anaerobic and that will change the biogeochemistry of the entire region and you will have other consequences. So this is always the argument for intervention in nature.

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## In-situ Sediment Capping



Simplified Steady State Equation - Approximation

$$\bar{n}_{A,S} = K_{OL} \cdot \rho_{A2}^0$$

$$\frac{1}{K_{OL}} = \frac{1}{K_{cap}} + \frac{1}{K_{bio}} + \frac{1}{K_{A12}}$$

$$K_{CAP} = \frac{D_{A32,CAP}}{R_{A32,CAP} L_{eff}} \quad K_{bio} = \frac{D_{bio}}{R_{A32,bio} L_{bio}}$$

$$I_h = \frac{0.54 L_{eff}^2 R_{A12}}{D_{A12} \pi^2}$$

Numerical Solution Recommended since layers have different properties

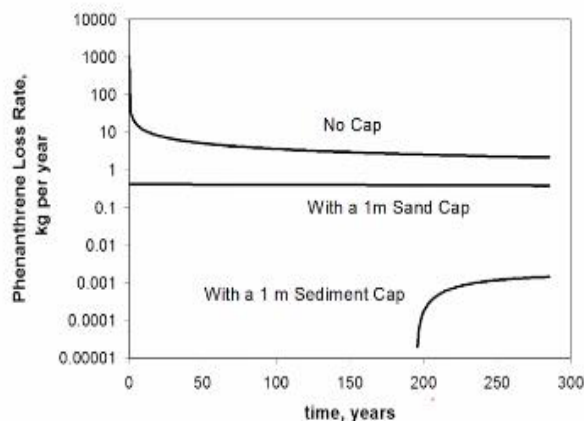
So what this does is in terms of our model, it does this. So, it has now added. So, normally in our original model, we had these 2 layers, bioturbation and we did not have this, now we have this additional layer. So, we have to know model in each of these 2 layers. This is of course the boundary layer, the surface boundary layer. So, each of these layers have to be done separately. So, what we do is a simplified steady state approximation, we say the flux is now some function, some overall mass transfer coefficient multiplied by the sediment concentration here.

This is  $\rho_A^0$  and it jumps from here to here across these 3 resistances and these 3 resistances are indicated by the cap, the biological and the usual  $k_{A23}$  that is the surface mass transfer coefficient and we get estimates of the resistances by these terms here. This is diffusion coefficient divided by, this is the mass transfer coefficient  $DA$  by  $L$  divided by the retardation factor, the adsorption okay. So, this is used in the design. The model is used in the design of the cap.

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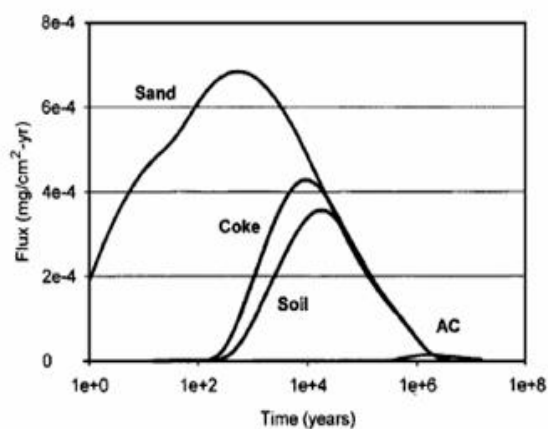
### Simulation of Phenanthrene Flux from Capped Sediments



So you would like to know what is the thickness of the cap that I need to use, so that you can make simulations like this. If I have no cap, this is going to be the emission. If I use a 1 meter sand cap, this is going to be the emission. If I use 1 meter sediment cap, this is going to be the emission, so you design. So for 100 years, look at this x-axis timescale we are modeling for 150 years, 200 years. You really do not know what is the time for which you should design to, but this is shown

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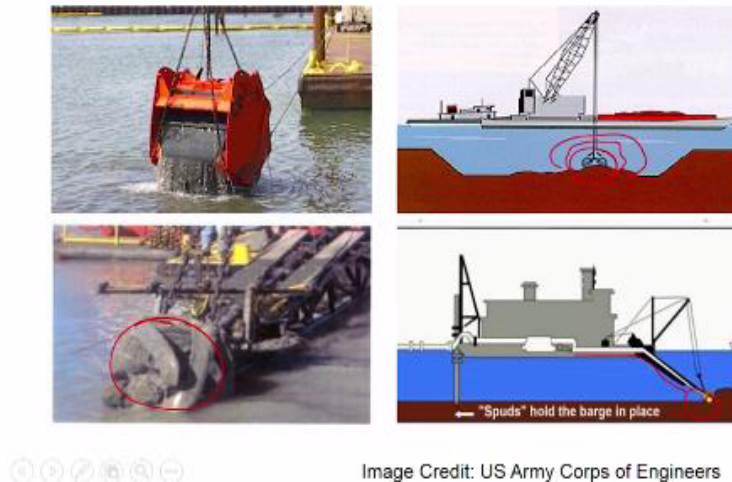
### Simulation of PCB Flux from Capped Sediments



You can also compare different types of capping material. You can compare soil versus activated carbon versus coke versus sand. You can also find out what is the thickness, how much do you need and all that, right.

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## Dredging, Relocation & Treatment



The last method is called dredging. This is dredging, you have seen this a lot here. Dredging is used for land reclamation, a lot of dredging, this is non-remedial dredging. Environmental remediation dredging is different because you can see one of the problems in dredging is following. The mechanical regime uses what is called as, this is called the bucket head dredge this one. It is what you have seen commonly here, it is like a thing it goes in, hooks up, and comes out, it is all mechanical. It retains the solids very effectively.

So, all the water is gone out, only solids retain, it is like a scoop. Problem is you can imagine while it is doing this, it will generate a lot of cloud, resuspension in this region. You can see it here the water is coming out and water is muddy, solid dirty. The other option is what is called as a hydraulic dredging, this one. In this, they use some kind of what we call as a screwdriver kind of thing, it is like a drill. So it is gently drilling it, but at the same time when it drills, you create a small slurry there locally, and a slurry is pumped into this white line, you can see this white line here, that is the pump.

It is pumping the slurry out of the region. So it generates much less resuspension. What is the consequence of that? It generates much less resuspension at the site, but as a result of which it is generating a slurry, which you have to deal with it later because that slurry is contaminated now and that has to be dealt with later, okay. Here, you are not generating much slurry for you to process, it is only solids that are placed in a barge and taken away, but it generates lot of resuspension and this plume can travel from place to place.

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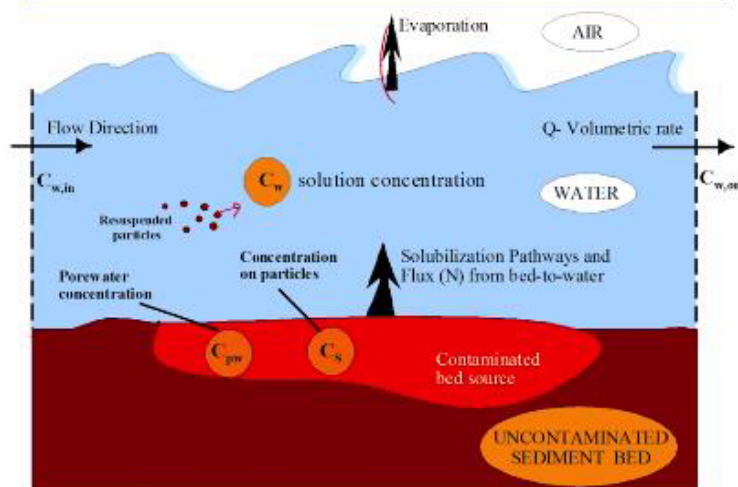
## Chemical Release During Dredging



So this is what it looks like. Dredging site can look like this, very highly turbid. What can happen from this turbid this thing? So, they are isolating it, isolated by blocking flow from that area so that it does not spread. So, this yellow thing is called as a silt curtain.

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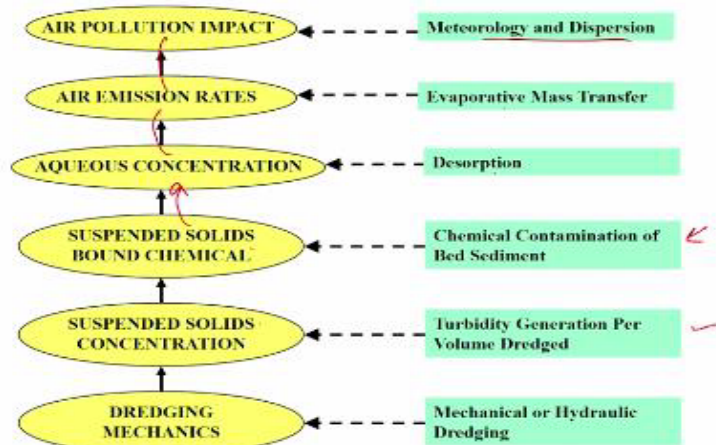
## Chemical Release During Dredging



So, this can happen. When you are dredging, chemicals can release into the water okay and we discussed this. Then it can desorb, it can re-suspend and then during resuspension desorption can happen. If it desorbs, then it can also evaporate and can move okay.

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## Environmental Impact



So the environmental impact is following. You are dredging, based on the dredging mechanics, depending on what dredge do you use, you generate turbidity for unit volume dredge and then this results in a suspended solid concentration in the water. From the suspended solids concentration, there is chemical contamination that is present on the suspended solids will result in the contamination of water and an aqueous concentration through desorption.

From here, it can evaporate and have an evaporation emission of this particular chemical and then it can cause an air pollution impact which you can estimate using dispersion. So you have an entire sequence of operations that you can look at.

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## What happens to the Dredged Material? Post Dredging Relocation - Treatment

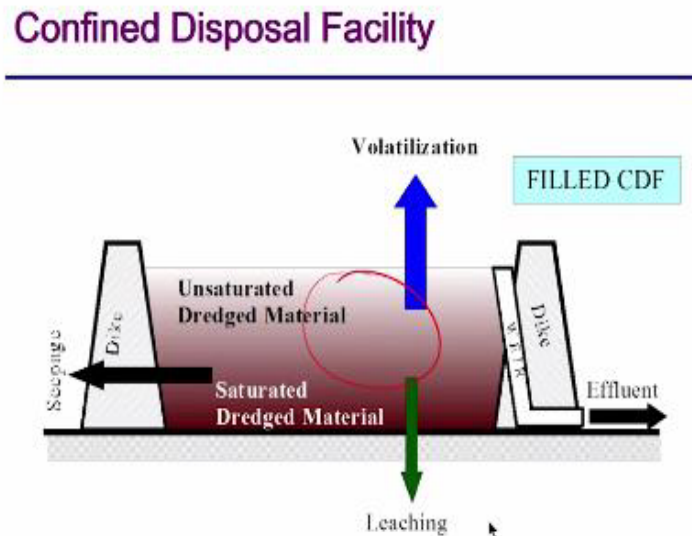


Confined Disposal Facility (CDF)

We are going to skip all of this. So what happens to dredge material when it leaves a dredging site? So it has to go somewhere, it is not finished, you are just removing it from there and you

have to put it somewhere else. So, it is usually placed in something called as a confined disposal facility, it is like a landfill. You can see somewhere, placed somewhere.

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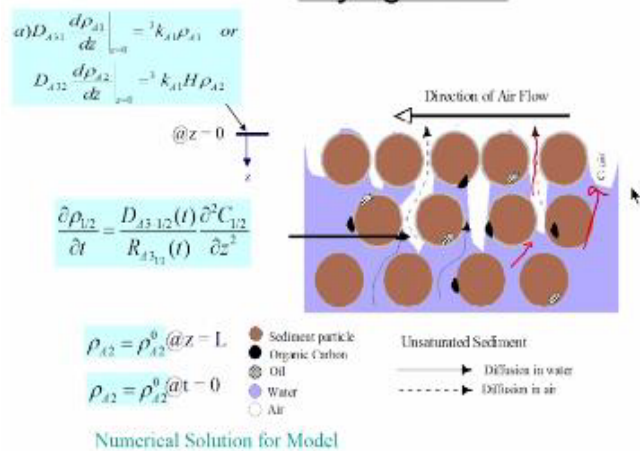


Yeah, but there one of the things is that when it is being filled, it can evaporate, materials can evaporate from it okay and it can evaporate from a soil like structure and it can also evaporate from the suspension that is present here. You can model both of these by equations that you have already seen and when it is completely filled, it looks like soil, some region of it is unsaturated, some of it is saturated, all of it probably is unsaturated at some point in time. So, it now resembles soil.

So, this is a very dynamic system. It keeps filling, as it is filling it starts from a river like, lake like system and then it goes to a soil like system and all that. So, the excess water is removed and that goes to an effluent treatment plant, but this is of interest to do whether how much of it will evaporate which is done over a long period of time. You cannot have small, small region, dredging happens over a long period of time. So, the timescales involved here are of the order of several months, several years sometimes to fill up.

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## Drying Model

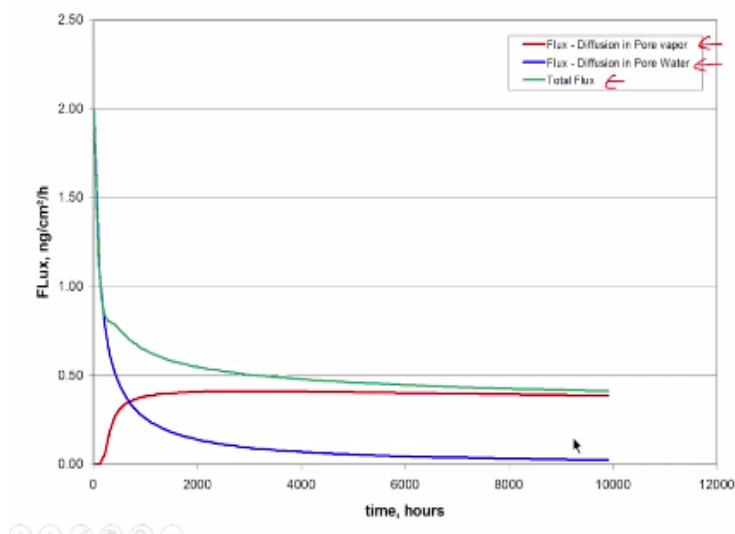


Total Flux = Flux by diffusion in pore water + Flux by diffusion in pore vapor

As a result, what we are interested in again this, while it is sitting in the confined dispose facility, it will dry. When it dries, our model of evaporation contaminant transport now depends on whether it is evaporating diffusion through pore air or through pore water and all these combinations exist and so and so.

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## Flux Model - Drying



So, you can predict whatever is the total diffusion in the system, what is the diffusion in pore water and what is the diffusion in pore air and the total flux based on that, it is possible for us to do this, okay.

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## Mudflats



Image Source: Shunya.net

The other kind of natural systems that you see this happening is in what is called as mudflats, you see a lot of this in India, it is very common. It is a riverbed or a lake bed or this thing. When it has water, very nice. When water goes away, the bottom soil is exposed and then bottom soil is exposed and evaporation can occur directly from this and that is one thing.

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## Mudflats



This as you can see another example of a mudflat. Water here and there is no water here. It is receding and then when water comes back.

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