

Environmental Quality: Monitoring and Analysis
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Lecture – 61
Remediation of Contaminated Sediments – Application of Transport Models

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So this PPT I have here is just to recap some of the things and then we will finish up the discussion that we started last week. So, this is an image of the sediment and water interface. So, a lot of things that we discussed, you can see it here. You can see the interface between water and sediment and see the layers of sediment how it is. This is an image from what is called a sediment profiling camera. You can see there is very light material at the surface which is a kind of re-suspending a little bit from the natural this thing okay.

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Sediments



This is what sediment looks like when you take it out and people take it out for remediation purposes often.

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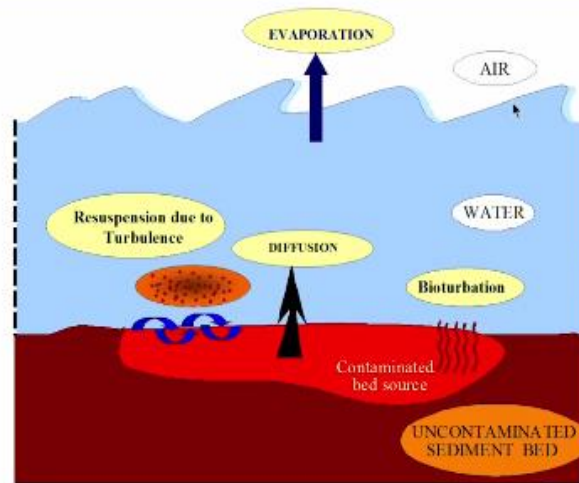
Sediments



This is a picture, these are images of bioturbation. You can see on the left side, you can see worms that are way inside the thing, they are burrowing inside and they are coming out and you can also see that top layer is a bit fluffier compared to the bottom layers, and the second image you can also see is very large animal sitting on the top and this also does that. The third image, the idea of this is to show that the color between the top layer and the bottom layers are very different, bottom layer is dark which indicates it is anaerobic, the slightly lighter color on the top which is also there in the first image.

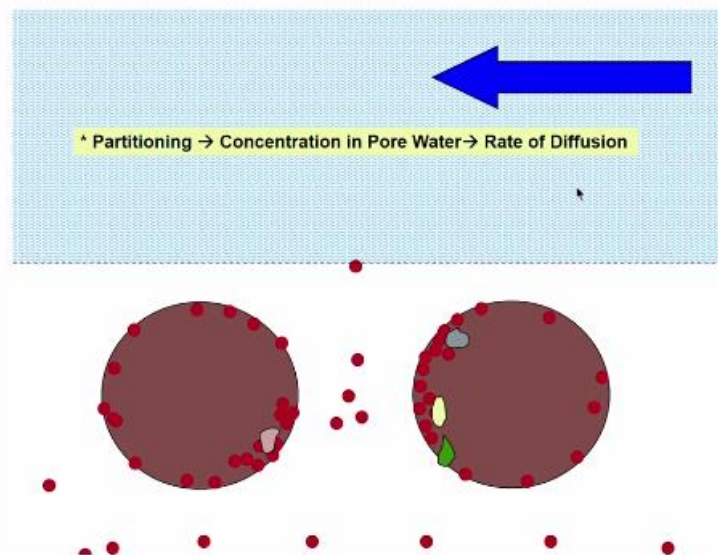
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Chemical Release From Sediments



So this is just a recap of all the things what we have already done.

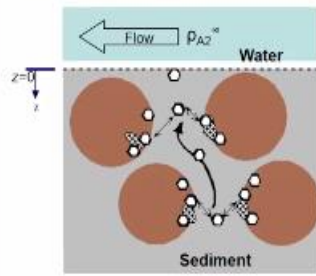
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This is an animation to show the diffusion process. You have water flow there and as diffusion occurs from the surface, material comes from below and then it tries to re-equilibrate and so on. So, again, re-equilibrates here and that is the animation. So at any point in time, there is a snapshot of material.

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Diffusion + Reaction – Analytical Solution



$$\frac{\partial \rho_{A2}}{\partial t} = \frac{D_{A32}}{R_{A32}} \frac{\partial^2 \rho_{A2}}{\partial z^2} - k_r \cdot \rho_{A2}$$

- Uniform/Constant Properties
 - Porosity
 - Partition Constant
 - Concentration
 - **First Order Kinetics**
- Local Equilibrium
- Interface Mass Transfer
- Uniform initial conditions

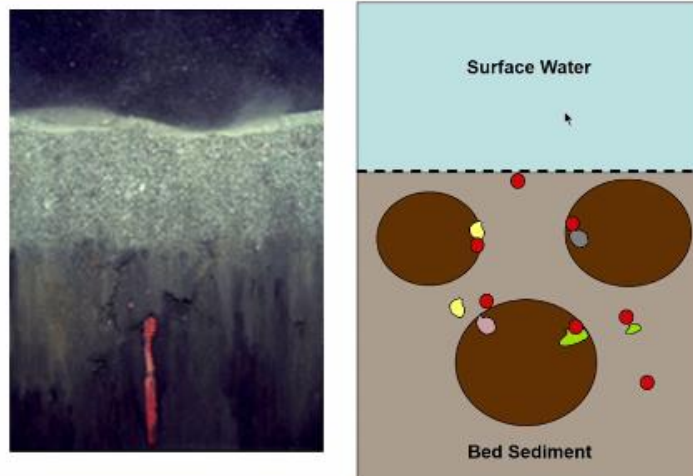
$$\rho_{A2}(z,t) = \rho_{A2}^0 \cdot e^{-k_r t} \cdot \left\{ \operatorname{erf} \left[\frac{R_{A32} z}{\sqrt{4D_{A32} R_{A32} t}} \right] + \exp \left[\frac{{}^3 k_{A2} z}{D_{A32}} + \frac{({}^3 k_{A2})^2 t}{D_{A32} R_{A32}} \right] \cdot \operatorname{erfc} \left[\frac{R_{A32} z}{\sqrt{4D_{A32} R_{A32} t}} + {}^3 k_{A2} \sqrt{\frac{t}{D_{A32} R_{A32}}} \right] \right\}$$

$$N_A(t) = {}^3 k_{A2} \cdot \rho_{A2}^0 \cdot \exp \left(\frac{({}^3 k_{A2})^2 t}{D_{A32} R_{A32}} - k_r t \right) \cdot \operatorname{erfc} \left({}^3 k_{A2} \cdot \sqrt{\frac{t}{D_{A32} R_{A32}}} \right)$$

(Video Starts: 02:19) So the derivation that I did in class, it is all given here, you can go and look at it again. The solutions and the various complications that we discussed. (Video Ends: 02:33)

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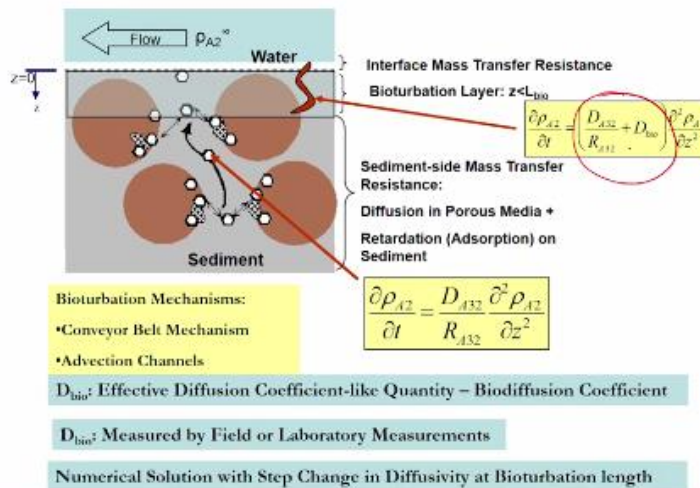
Diffusion + Bioturbation



Divisions of bioturbation. What we are again looking at there is a worm inside the sediment there. So the bioturbation material is taken and transported directly.

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Diffusion+Bioturbation - Model



The model again, these are the bioturbation layer seen as a separate model and with that the diffusion is enhanced by the bioturbation diffusion as well or you could for this layer bioturbation layer alone, you could have just some effective bio diffusion coefficient it is a combination of both. It is very difficult to justify the equation as it is written because diffusion is occurring in porous media and bioturbation is not occurring in porous media on the same process, so they are not essentially the same.

So, you can club all of this and make it one number, however that is. So conveyor belt mechanism is when the worm feeds inside and ejects it out and that is one and this also causes advection channels and solution method.

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Diffusion+Advection - Model

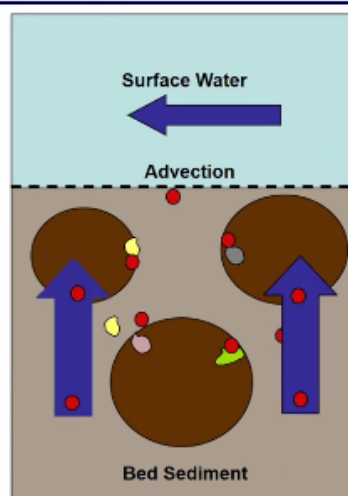
• Advection

- Groundwater flow
- Tidal Fluctuation
- Ebullition
- Bioturbation Channels

$$\frac{\partial \rho_{A2}}{\partial t} = \frac{D_{A32}}{R_{A32}} \frac{\partial^2 \rho_{A2}}{\partial z^2} - v \cdot \frac{\partial \rho_{A2}}{\partial z}$$

v – advection velocity

Analytical Solutions exist for simple cases of boundary conditions



The advection plus diffusion model, we also talked about this and these are the different cases where advection can occur, groundwater flow, tidal fluctuation, ebullition. Ebullition is where gas formed inside we discuss that and then bioturbation channels. All of this can cause advection, this is a bulk flow that is happening.

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Resuspension



- Due to shear at sediment-water interface
 - River flow (turbulence)
 - Navigation
- Particle concentration – Balance between resuspension and Deposition
- River Silting occurs by this process

Talked about the resuspension. This is a very big thing visible thing you can see sometimes in shallow waters and there resuspension, you can see the muddy, different scales, you can see the muddy water.

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Resuspension

- Steady state Sediment Concentration (C_S) downstream from a point of release is a balance of deposition and erosion fluxes

$$\rho_s(x) = \rho_s^0 \cdot \exp\left(-\frac{k_{dep}x}{h_w v_x}\right) + \left[1 - \exp\left(-\frac{k_{dep}x}{h_w v_x}\right)\right] \cdot \frac{k_{erod} \rho_s (1 - \epsilon)}{k_{dep}}$$

- k_{dep} and k_{erod} are depositional and erosional mass transfer coefficients
- Direct ingestion into biological aqueous receptor – small size particles
- Disolution – Steady state aqueous phase concentration
- Evaporation from solution

Then we tried some concentration can be obtained. We did not discuss this in detail, so do not worry too much about it, so which is simple first order mechanism of erosion and deposition, so we have not discussed that in detail. So, these numbers k deposition and k erosion are

similar to the mass transfer coefficients, but they are not governed by a thermodynamic gradient. They are more energy balance kind of substance, sufficient amount of energy and it results in certain rate of release.

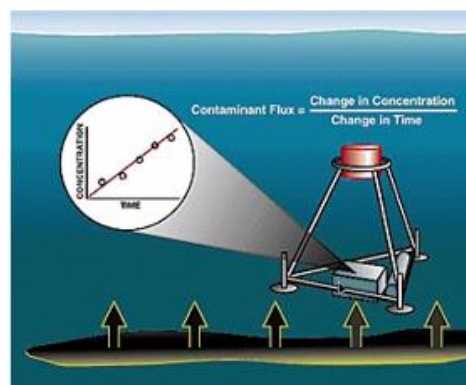
So, it is derived from an energy balance, in this case it is mostly experimental. So, people look at and the k deposition is a function of velocity of the water, the cohesiveness of the sediment which means it depends on the property of the sediment itself. So, the cohesiveness of sediment can be measured by different parameters which are solid mechanics based, which means it relates to the amount of energy required to pull it out from one particle to the other particle and then overcome gravity and get out.

So there are couple of things, it is not a straightforward expression. So, people do not worry too much about it also. It is a measured thing usually.

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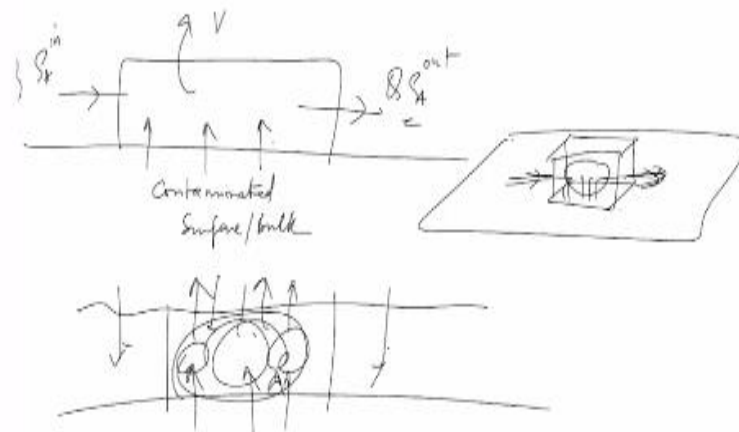
Flux Measurement – Enclosed Samplers

- Measurement near sediment-water interface
– Benthic Flux Sampling Device



So, we were stopped here. Last class we essentially said about measurement of fluxes okay. So, the measurement of flux is you can have different things.

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One is we can have a surface. You are measuring flux at the surface, so you want to measure this. So, you calculate what is the amount coming in. So, this is what is coming in Q and this is what is leaving, the difference between in and out should be the flux okay. A lot of times you can get instantaneous flux if you can get instantaneous concentration values okay very quickly and one very important thing is this boundary, this volume is enclosed. Now, this is important because this now is a closed volume system okay.

Whatever is coming into this close volume and this is what we are doing, we are defining a box here and physically we are defining a box. We are placing a box on a surface and this surface says has contaminated soil or sediment or water surface and from this surface, we are enclosing a volume over a surface So it is like saying we have a large piece of land here which is contaminated we would like to measure flux. I will take a box, I will place it on top of it, and I will send air water through it and whatever the emission is coming from here, it collects into this and it is coming out.

So, mass balance is very easy for me. I do not have to worry about it. Imagine a case where you do not have a box. I do not have a box, the problem there is I cannot, in rivers and all it is very easy. Let us say that I am measuring concentration here and I am measuring concentration here, I assume that this is the box and then I can estimate that whatever the difference between this and this is and this is well mixed, this is my assumption.

But when you do that, there is always a question that how do you know this is coming from here this surface and it is not coming from the air because I am neglecting this part or this

part. So, when people want to exactly measure flux from a particular surface, they would like to isolate that surface alone and verify whether it is coming from that surface. So then you have to enclose it, okay. When you enclose it, there is a problem, in that you are destroying the original boundary layer of the system.

You are disturbing it and your mass transfer coefficients and everything are based on the boundary layer theory and all that. So you are disturbing that, even though you are getting some estimate of the flux, you are still disturbing the original flux, but that is the best. It is a very robust method. It is a very dependable method because what it does essentially is it is giving you evidence that something is coming out. So, for example if you take the case of contaminated sediment, if you make a statement saying that chemical x is coming from a particular location in the sediment and that means something.

It means that somebody who was responsible for that pollution now has to take care of it. So, you are generating evidence of chemical release because of sediment contamination, which means that I actually go, isolate that region and give data that there is some flux, some release happening. Whether I can model it accurately using the flow and all that is a different story, but this flux data is very useful okay. So, similar cases happening, right in you see that now this big smug thing has come over North India and it is spreading, prediction is it is coming towards the south.

Now, the conjecture, the hypothesis that somebody is burning something and that is all coming here. How do you know that that burning is causing this? People will want evidence that because that will affect those people's livelihood. So, they will say you please first show evidence that it is being measured and that is what is coming out. So, you have to go to the field and measure, somebody is burning agricultural field, you go and measure the flux there because we are using box model in an atmosphere system, right.

So, how much of particulate matter is being released from burning? Simple question and measurement of this is very complicated because in air you cannot put a box. If you put a box, how big a box will you put. If you put a box, the boundary layer in air is destroyed, but if you do not put a box, what is the boundary layer that you will consider, there is a box height that we consider, this is the problem we had in the beginning also, right? So this is a

problem and so people will do, at least say I will at least put a box and measure what is coming and then we will figure out the rest later.

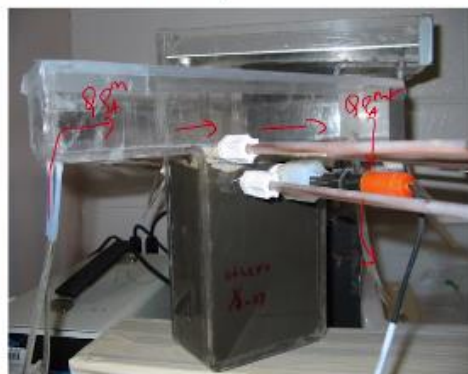
Minimum evidence that it is coming from your agricultural field I will take a box put it there, I will send air through it, we will see if anything is evaporating, simple okay. Further arguments can come later, whether this is, amount of your evaporation will increase or decrease when you expose it to natural air and all that, you can figure it out from the physics of the system, but minimum evidence is this okay. So, normally the enclosed flux method works because there is mass balanced closure.

You can exactly tell that this surface is responsible for this and then try to understand if how different it is from a theoretical system. In any case, the mass transfer coefficient is an empirical quantity, you are not really worried about whether it follows boundary layer theory or not and all that, so you can still get something out of it okay.

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Flux Measurement – Enclosed Samplers

- Laboratory Microcosm with Sediment and Surface Water Samples



$$\bar{n}_A = \frac{m_A(\delta t)}{A \cdot \delta t}$$

This is in the laboratory scale, this is something similar to what you would do. You have sediment in here and you have a chamber where water is flowing out. Water is coming in here and it is flowing across the surface and water is getting out. Here, I will collect this water and measure what is coming out. So, this is $Q \rho A$ in and this is $Q \rho A$ out, but in many cases, if you do not have probes to measure what is coming out, in this case we are measuring polyaromatic hydrocarbons, it is a very small concentrations of 1 ppm below that, you cannot, there are no probes to measure that.

So, which means you have to collect 1 liter of water over how much ever time it takes and then extract the water and find out what is the amount of polyaromatic hydrocarbons which are there in this, over a period of time that is collected. So, here the flux is a measure of mass that is collected in a particular time interval okay divided by the area and the time interval. So this will be an average flux for the entire time period, okay, you cannot, it is not an instantaneous flux, it is an average flux, but that is fine, it is still the best data you can get.

So in this kind of system, we work with the best data that is available and extrapolate backwards and models are useful for us to predict based on this data what will happen.

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Flux Measurement – Time Series Concentration Gradient

- In-situ porewater samplers
 - Membranes
 - Probes
- In-situ Spectroscopic methods
 - Laser Induced Fluorescence
- Sediment Cores
 - Sectioning of thin layers
 - Chemical Analysis



There are a large number of other methods in which people try to measure concentration gradients. Concentration gradients are also, see in the model when we saw, before we measure the flux, we measure concentration gradient, we actually get ρ as a function of z and time. So at any point in time, you should be able to get a concentration gradient. So, that is another way of checking if flux is happening in which direction. So, you can get a concentration gradient.

I can take sediment surface, I can take a gradient, I can take a core and I can measure the concentration as a function of height, and if I see a profile which looks like this, which means that there is a gradient upwards and you can calculate what would have been the flux at the surface based on this, but that still is not, only people who understand diffusion model will understand that, you still need to show evidence that something is coming out. They can also

argue that there is something at the surface which will block everything or mysteriously degrade.

So, all arguments that you pose as scientists have to be shown with evidence to because it is now going into the public domain and into legal domain, so you cannot say the equation like this and therefore this should happen and all that. So evidence is experimental measurement and that is also test for the model. You have a model, you are guessing, you are saying this is the probable theory this is happening and the experimental data is proof of that. So, if the model works with the theory, then you can use the model to predict things which you would not know yet.

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Options for Remediation

- **Monitored Natural Recovery** *Man Key*
 - Natural attenuation ← *Biodegradation*
 - Least Expensive ←
- **In-situ Capping**
 - Clean material cover over contaminated zone
 - Motive is to allow undisturbed natural recovery
- **Dredging**
 - Physical removal of contaminated material
 - Relocation for storage/disposal/treatment

So this quick word on contaminated sediments remediation, this is in sync with the things that we have discussed in the class for risk assessment. The reason we do risk assessment is whether we want to make a decision on a type of remediation option we want to use and so this is an example of that. So there are if for contaminated sediment there are 3 options people have looked at very large visible cases in the world, okay, you can read about it if you want.

There is Rhine Valley, I have mentioned it before in Germany, this is a very contaminated river valley because a lot of pharmaceutical companies are there and they cleaned it up. The sediment was cleaned up and also in the US many freshwater large lakes, Great Lakes in between Canada and United States, very large freshwater system, that a lot of industries around it, big cities around it Detroit, Chicago and all that, they are all around that big thing

and there are also 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. Somehow 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 in the chemical analysis, we find some chemical 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

- 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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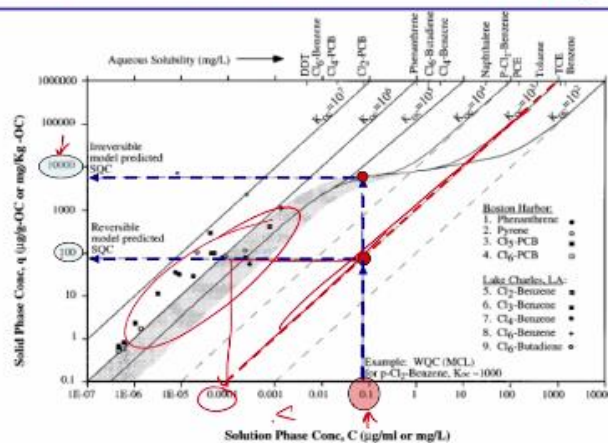
Sediment Quality Criteria

- 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 $m_2 \propto \frac{S_{OC}}{f(K_{OC})}$



* 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 ρA_{20} , yeah, ρA_{20} is a function of kA_{32} star, the partition constant. If the partition constant is very high, the ρA_{20} star will be very small, yeah, and there is an argument that people have made in 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 disruption 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 disruption 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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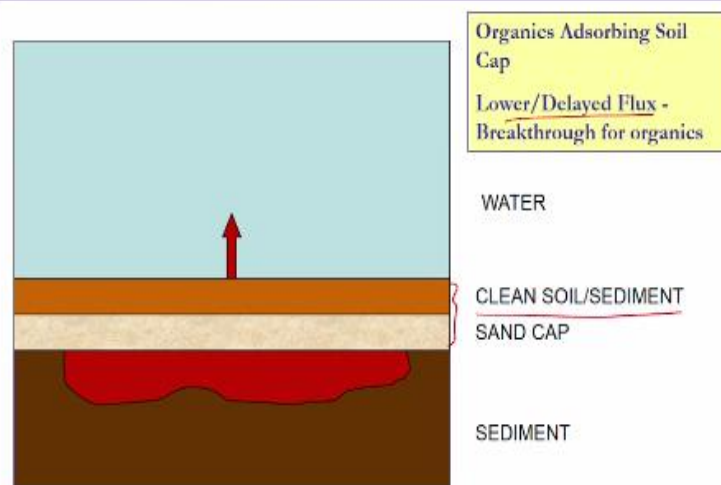
Irreversible Sorption on Organic Carbon – Proposed Mechanisms

- **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

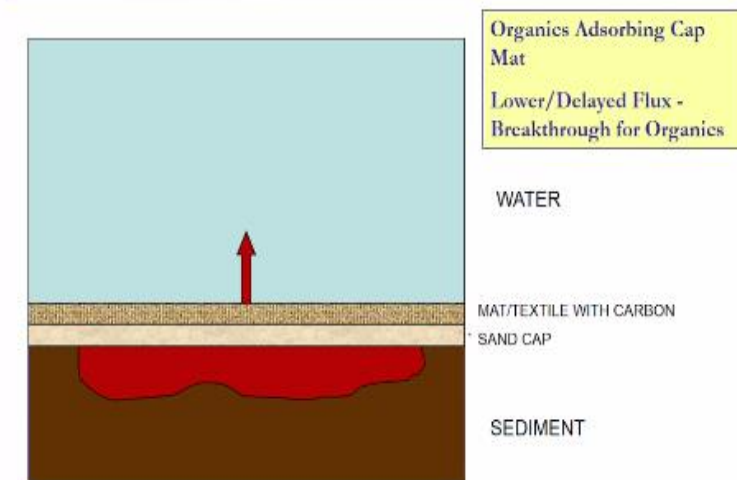


The second option what is called as capping, in situ capping, this is you put a clean material on top of existing. So what you do is there is regular release. On top of it, if I now put a layer of something, what it does is it will add to the mass transfer resistance, it will add layer one layer of mass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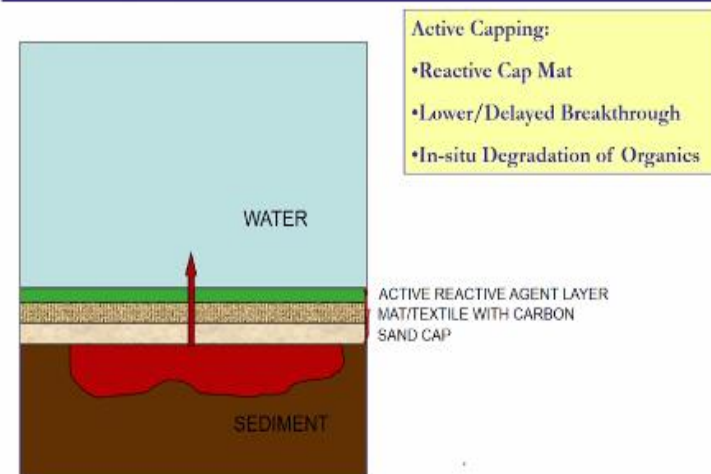
In-situ Sediment Capping



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

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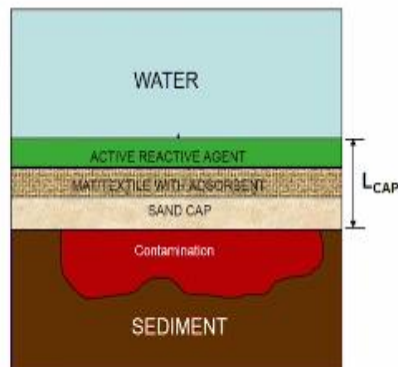
In-situ Sediment Capping



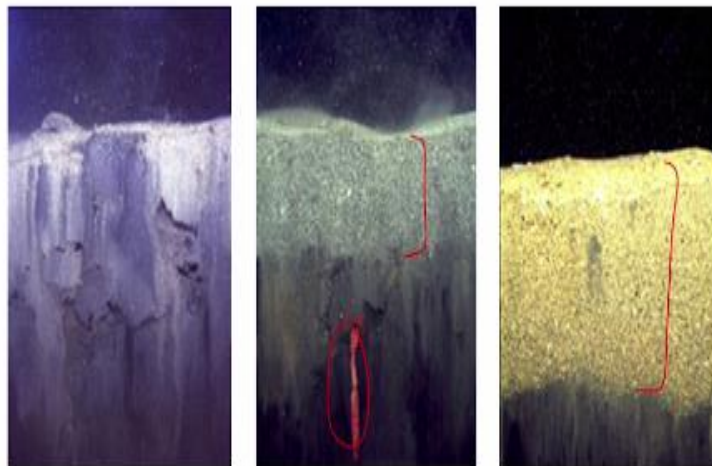
Again, all of this and we have in terms of this different improvements in the type of sand cap and people have invented textile based carpet kind of thing. We will just take it and dump it, put it on the contaminated surface and it has carbon embedded in it. It also has some active ingredients and all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

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In-situ Sediment Capping



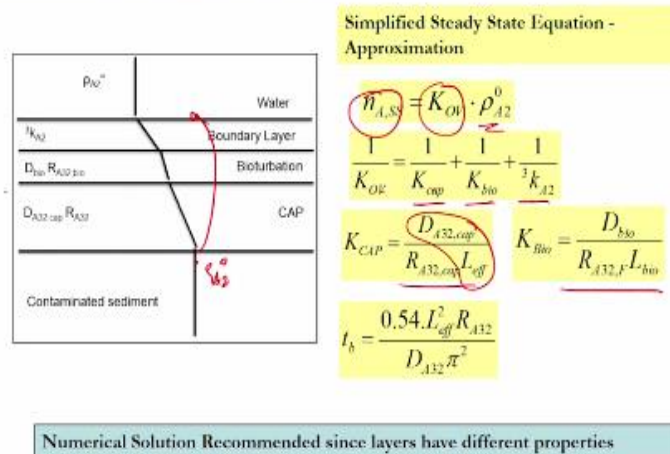
So, essentially, you would put a layer on top of the existing sediment. So it provides
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This is like a cap. This is a cap, it looks like that okay the sand cap. One of the arguments against capping is either it destroys the essential biological life 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

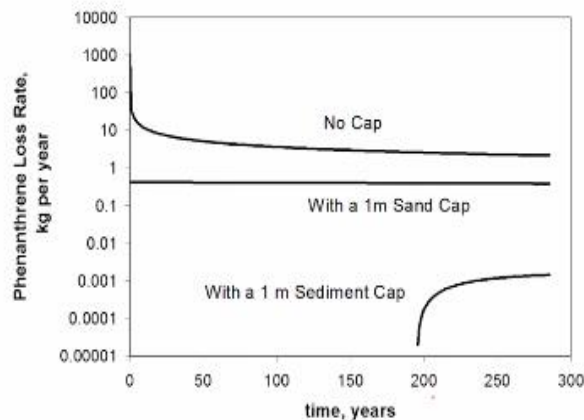


So what this does is in terms of our model, it does this. So, it has now added. So, normally in our original model, we had these 2 layers, bioturbation and we did not have this, now we have this additional layer. So, we have to know model in each of these 2 layers. This is of course the boundary layer, 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 A20 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 kA23 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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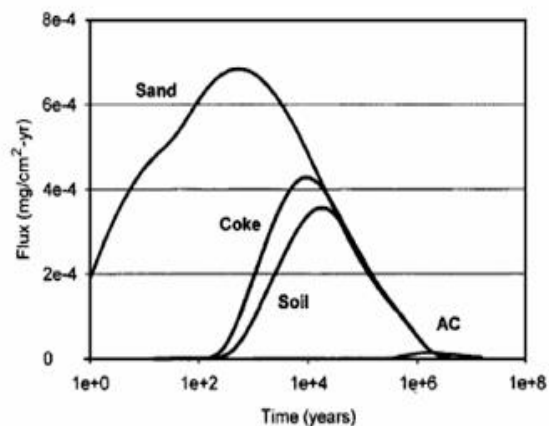
Simulation of Phenanthrene Flux from Capped Sediments



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

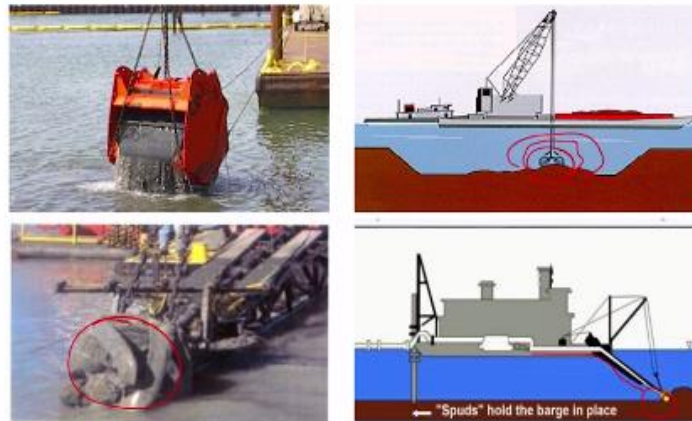


Image Credit: US Army Corps of Engineers

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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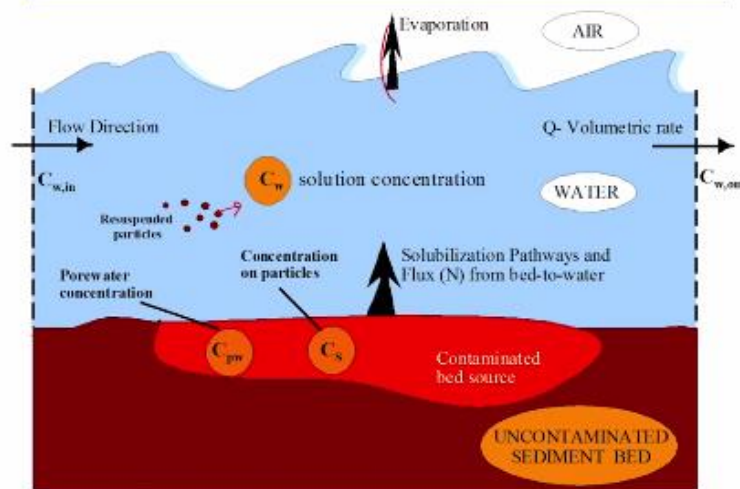
Chemical Release During Dredging



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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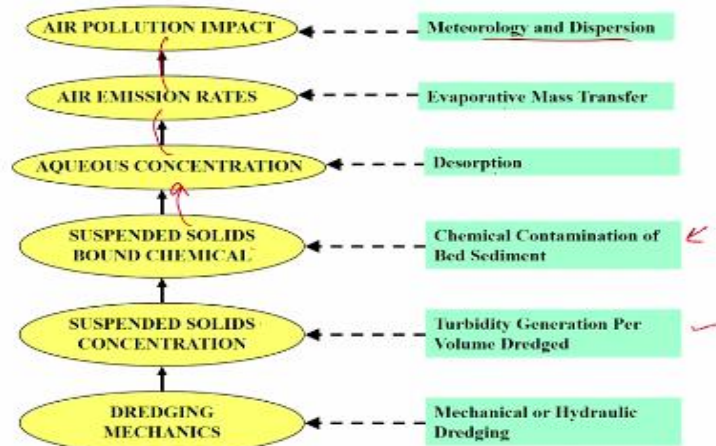
Chemical Release During Dredging



So, this can happen. When you are dredging, chemicals can release into the water okay and we discussed this. Then it can dissolve, 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. Your 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



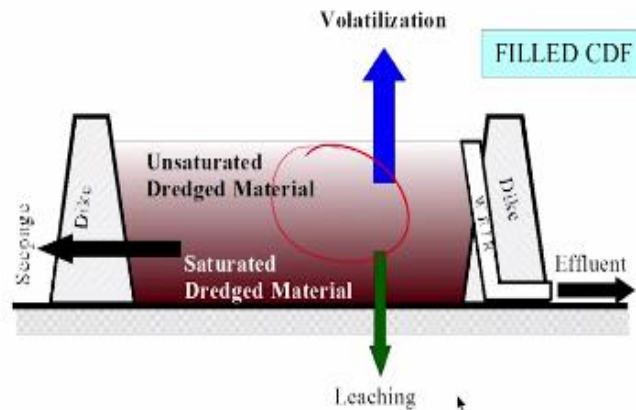
Confined Disposal Facility (CDF)

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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Confined Disposal Facility

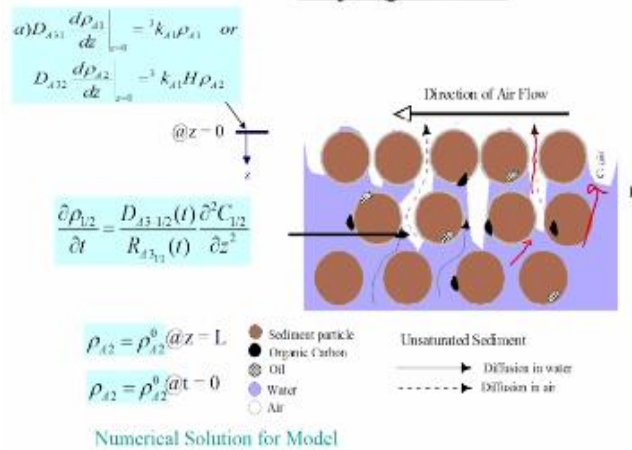


Yeah, but there one of the things is that when it is being filled, it can evaporate, materials can evaporate from it okay and it can evaporate from a solid soil like structure and it can also evaporate from the suspension that is present here. You can model both of these by equations that you have already 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, so you are dredging and 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

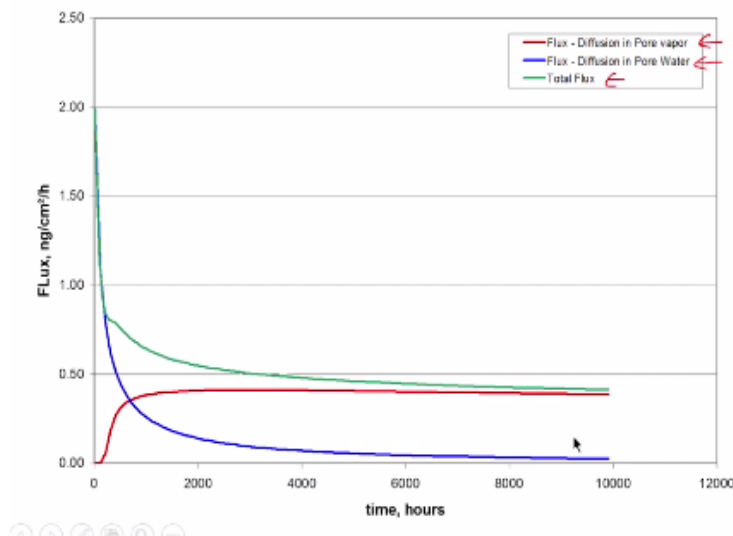


Total Flux = Flux by diffusion in pore water + Flux by diffusion in pore vapor

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

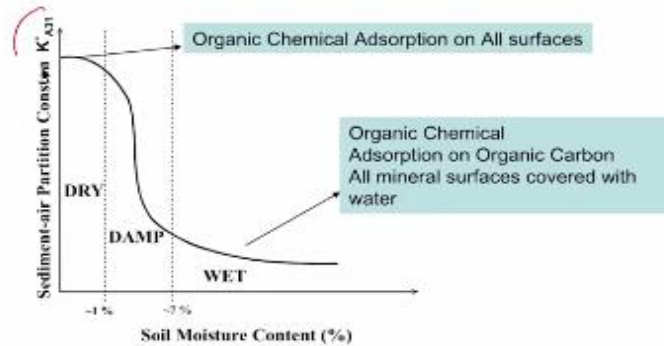


This as you can see another example of a mudflat. Water here and there is no water here. It is receding and then when water comes back.

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Effect of Sediment Moisture and Air Relative Humidity

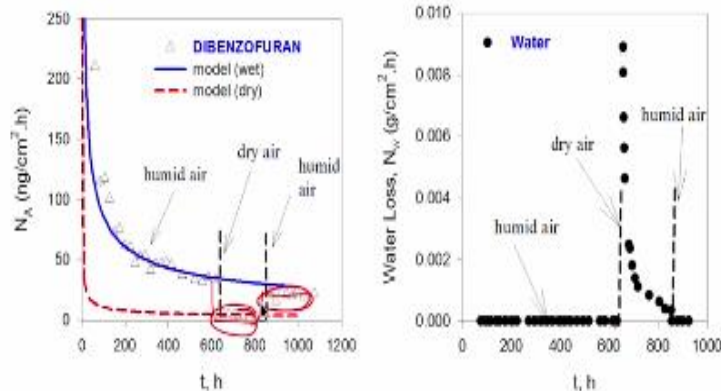
- Sediment-air partition constant is a function of sediment moisture content



So this is again the thing that we discussed in last class. The effect of, when this kind of thing happens, moisture content in the soil is changing as a result emission will change. The partition constant is changing, this is changing.

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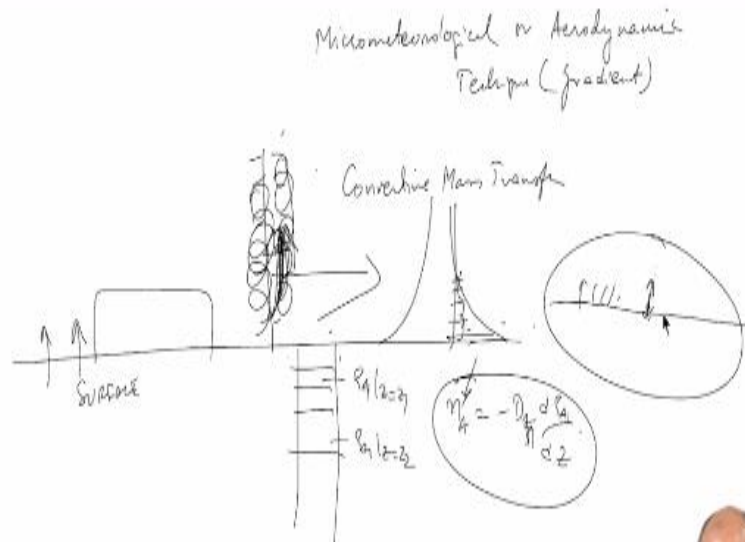
Effect of Sediment Moisture and Air Relative Humidity



This experiment is done in the lab where it shows that there is a chemical called dibenzofuran and this is experimental data. This when the mud is dry and this is the model, the blue line is the model that shows, and then at some point we dry the surface by sending in dry air, okay. So the water content increases. The water flux increases because it is now being dried and then the water increase and then everything is dry. During this period, you see that the flux drops down.

The flux for the dry period is down here, dropped down several macro factors okay. Then again when you hit it with humid air, it goes back up here, okay. So this is illustration of this. When the partition constant changes, the flux changes, okay. Okay, now this is the flux when you are able to measure the flux using a box, putting a box on it. As I mentioned that a lot of times you cannot do that and at the time when you cannot do that, you have to leave it open.

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When you have a surface and you have to measure the flux and it is difficult for you or it is unreliable for you to enclose a surface, you need to still measure the flux and we do it by what is called as a gradient technique or a micrometeorological technique. I am just going to talk a little bit about it, aerodynamic technique. It is also called as a gradient technique. So, for example, you can do this inside the sediment soil, right, I can take a gradient. If I know the concentration of pore vapor at $z = z_1$ rho A1 at $z = z_2$.

If there is a difference, I can use $-DA \frac{dC}{dz}$ rho A1 by dz I can use DA rho A31 by dz. I can use this equation, solution of this equation to calculate what is the flux if I know the diffusion coefficient okay. Basically, I am using a gradient to calculate a flux, yeah. The idea here is can you do the same thing here? You cannot, but the mechanism is not the same. What is happening here is this turbulence that is happening and turbulence is happening in convective eddies that are this kind of structure that is but it moving in this direction, right.

What we are taking advantage of here is that we would like to see if there is a vertical component of the fluid that is going in the upward direction, Yes, this is convective mass transfer right. This is convective mass transfer and therefore we are trying to take advantage

of the convective mass transfer component in the z direction to see what is the concentration difference and we will also see if we can somehow measure the net flux based on that concentration difference at a given location, okay.

Because it is moving in this direction, but there is one component that is moving in this direction also, okay, not clear. This is the essence of the convective mass transfer argument that the transfer is happening, there is a gradient in this direction right. There is a gradient in this direction, when we measure it, we will see that there is a gradient that that appear, concentration gradient that appears like this is very high at the surface and it is decreasing away from the surface, yeah.

Because material is being carried from the surface upwards this way and that this concentration boundary layer that is assumed to be formed is based on, but this is not happening at the same place it is moving down okay, but if you take a large area and you measure the flux here. So, this gradient is already formed. Gradient is already forming right from the beginning of this contaminated zone, mass transfer has started taking place.

So by the time you arrive here, there is a gradient that exists and based on that gradient you can calculate if there is a flux. For that, you need to know what is the vertical structure for the air.

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Thornwaite-Holzman Equation

$$v_x = \frac{v_*}{\kappa_1} \ln \frac{z-d}{z_0} \quad z > h > z_0 + d$$

v_* - friction velocity
 z_0 - roughness height
 d - zero displacement

$$v_* = \sqrt{\tau_0 / \rho_1} \quad \tau_0 = v_*^2 \rho_1 \quad \tau_0 = \text{shear stress at surface}$$

$$\frac{v_*}{\kappa_1} = \frac{(v_{x2} - v_{x1})}{\ln \left[\frac{(z_2 - d)}{(z_1 - d)} \right]} \rightarrow \left(\tau_0 = \frac{\kappa_1^2 (v_{x2} - v_{x1})^2}{\left\{ \ln \left[\frac{(z_2 - d)}{(z_1 - d)} \right] \right\}^2} \right)$$

$$\tau_0 = -\rho_1 \eta_1^{(t)} \frac{dv_x}{dz} \quad n_{A0} = +D_{A1} \frac{d\rho_{A1}}{dz}$$

$\eta_1 = \text{Kinematic Viscosity}$

So, this is the essence of the reason why we do this, the equation called Thornwaite-Holzman equation. This is also the basis for the estimation of dispersion parameters in air mode okay.

because that is also based on same thing, it is vertical structure of air, turbulence in the air, and therefore how does material move in the y direction and z direction as a result of this kind of convective behavior. So the equations, do not worry too much about, the essence of this is this.

In turbulent this things, the idea is that velocity has a gradient, we already know velocity has a gradient with height and the structure of this gradient is this form usually. It is a logarithmic relation v_x , v_x is direction, velocity in the x direction, is a function of z, but in this as a logarithmic function of z and the proportionality constant, this is called as v^* , v^* is called as the friction velocity okay. The friction velocity is defined as this, shear stress at the surface divided by the density and yeah based on this equation, you can derive this.

From here, based on this, I can derive this expression, you can see it for yourself how it is done, essentially the difference in the velocity divided by the log of the height. So, there are 2 quantities here called y_0 and d , do not worry about that, you can assume d to be 0, d is what is called a zero displacement. We are at sea level there is no, if you are a normal ground level there is no zero displacement, what it essentially is zero is some, for example if you are on top of a mountain, the zero displacement will be height of the mountain.

So, that is what it means. The roughness height z_0 . The roughness height is something that is dependent on what structures available on the surface. So, for example, you have grass or you have trees. The boundary layer does not go to 0 nicely at the at ground zero, it will stop somewhere slightly above depending on what is the nature of the surface, okay. So that is called as roughness height. Therefore, at z_0 , the velocity supposed to be 0, we are assuming at the surface, that is the assumption we make in boundary layer at $z = 0$, velocity 0.

That is why you do not see another now v_x minus, so the generalized expression is this one is v_x minus one other v term is there, where we do not assume that the second z is 0. So, what this means is that if you make velocity measurements at two heights z_1 and z_2 , they will likely follow this expression, yeah. If it follows this expression, then the quantities v^* can be calculated from that okay. So v^* is the friction velocity which you can obtain by the velocity gradient in a given location, right.

Now from here, you can calculate tau based on this equation, okay Now, tau 0 is expressed in terms of the Newton's law at the surface by this minus of rho, this one is the kinematic viscosity, usually we use the term, we use a different symbol, but this v and that look very similar, so I changed it, it is kinematic viscosity and then this is the mass flux. Now, you see that the signs are opposite for mass flux and the momentum flux because they are in opposite direction. The momentum flux is traveling upwards, mass flux is down or reverse in this case, the reverse case okay.

Mass is going out. momentum flux is coming down. There is loss of momentum downwards. The velocity is decreasing towards the surface, mass is increasing away from the surface, so this thing change in sign okay. It is all there, you do not have to write it down. So, we are trying to go towards the derivation where so we use these 2 two equations,

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Thornwaite-Holzman Equation

$$\tau_0 = - \frac{D_{A1}^{(0)} (\rho_{A12} - \rho_{A11})}{\eta_1^{(0)} (v_{x2} - v_{x1})}$$

$$n_{A0} = - \frac{D_{A1}^{(0)} (\rho_{A12} - \rho_{A11}) \kappa_i^2 (v_{x2} - v_{x1})^2}{\eta_1^{(0)} (v_{x2} - v_{x1}) \left\{ \ln \left[\frac{z_2 - d}{z_1 - d} \right] \right\}^2}$$

$$n_{A0} = - \frac{\kappa_i^2 D_{A1}^{(0)} (v_{x2} - v_{x1}) (\rho_{A12} - \rho_{A11})}{\eta_1^{(0)} \left\{ \ln \left[\frac{z_2 - d}{z_1 - d} \right] \right\}^2}$$

$D_{A1}^{(0)}$ = turbulent diffusion

Under neutral stability conditions, $D_{A1}^{(0)}$ is approximately equal to $\eta_1^{(0)}$

We take the ratio of these two, we will get this equation and then we substitute tau 0. We substitute tau0 into this expression, now to get this big expression. What we are trying to do now is we are trying to get an expression for flux as a function of the velocity and the concentration gradients, yeah. So, we have measurements of concentration at two heights, velocity at two heights that will give us some idea of the structure v star, the turbulent structure of the thing, and then we are using these terms here.

When there is neutral conditions, which means that there is no, neutral condition means stability is neutral, there is no thermal forces pushing up and down, no buoyancy effects, the terms DA and this are supposed to be seem similar, they are the same. DAt and kinematic

viscosity and diffusivity are assumed to be same. This DAt is not molecular diffusion, it is turbulent diffusion, some other number okay, turbulent diffusion. We use the Fick's law structure very nicely because we are using gradients.

So, we will use the same Fick's law structure, but it is not molecular diffusivity anymore, it is some diffusivity, it is turbulent diffusivity. So, what this does is here I can calculate the flux from a surface using this equation, yeah, gradient. It is called a gradient method. This only works as long as there are no thermal forces.

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Modified Thornwaite-Holzman Equation

Based on Monin-Obukhov similarity theory

$$\zeta = \frac{z}{L_m}$$

L_m - Monin-Obukhov Length scale

Monin-Obukhov Length scale

$$L_m = - \frac{\rho_1 C_p v_*^3 T_1}{\kappa g q_0}$$

q_0 - positive heat flux into the atmosphere

Physically, L_m is the length scale at which the production of turbulence by buoyancy effects are comparable to that of shear stress.



For that, there is something called as modified Thornwaite-Holzman equation. When you have thermal forces, you bring into this question, so all font is all become very scary font, anyway, can you see it? There is something called as a Monin-Obukhov length scale. This comes up there also, you can read, there is one page set of things I have put in your, if you are interested you can read it, and if you go and read AERMOD derivations, this morning Monin-Obukhov length scale comes there.

So, this is L_m , this is physically the length scale at which the production of turbulence by buoyancy effects are of the same order of the shear stress. The buoyancy becomes that important here and then it is defined as this, L_m is defined as this. So, if you look at this carefully, this is a ratio of this this is the friction velocity which is a turbulent length scale. What is in the denominator is a q_0 , q_0 is the positive heat flux into the atmosphere. How do you get a heat flux? What do you need for heat flux? You need temperature gradient, yeah.

So the temperature gradient comes into question. If you calculate Lm, you need two, at least two measurements of temperature, you need a temperature gradient also, yeah. So Lm is that. So there is a negative sign here. Depending on whether the temperature gradient is this way or this way, the stability is defined, the magnitude of the values of the Lm the stability is defined on basis of that, not just the lapse rate anymore.

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Modified Thornwaite-Holzman Equation

Based on Monin-Obukhov similarity theory

$$\frac{dv_x}{dz} = \frac{v_*}{\kappa_1 z} \phi_m$$

ϕ_m - function of ζ

$$\phi_m^2 = (1 - 15\zeta)^{-1/2} \text{ for } \zeta < 0$$

$$\phi_m^2 = (1 + 5\zeta) \text{ for } \zeta \geq 0$$

Also

$$\zeta = Ri \text{ for } Ri < 0$$

$$\zeta = \frac{Ri}{1 - 5Ri} \text{ for } 0 \leq Ri \leq 0.2$$

Ri - Richardson Number

$$Ri \sim \frac{g (T_{12} - T_{11})(z_2 - z_1)}{T_1 (v_{x2} - v_{x1})^2}$$

So based on this, we define a bunch of other things. So we add a correction factor called as phi m. This is the original equation that we have, to this we add this correction factor phi m which is now dependent on the stability as well and this when we have a bunch of equations where we calculate phi m for different values of, in the equation previous slide, this number is dependent on z by Lm, z is any height, at any height it is the comparison of that height with the Lm. You can get these values of psi and phi m based on this Lm.

The other option to do this, instead of Lm you can also use what is called as Richardson number. This Richardson number is defined like this, you see that the temperature gradient in there. So, when you plug all of this in back into your main equation, you will get one big equation which now has 3 gradients. You have a velocity gradient, you have a concentration gradient and temperature gradient which now takes into account everything and now gives you a value of flux.

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Modified Thornwaite-Holzman Equation

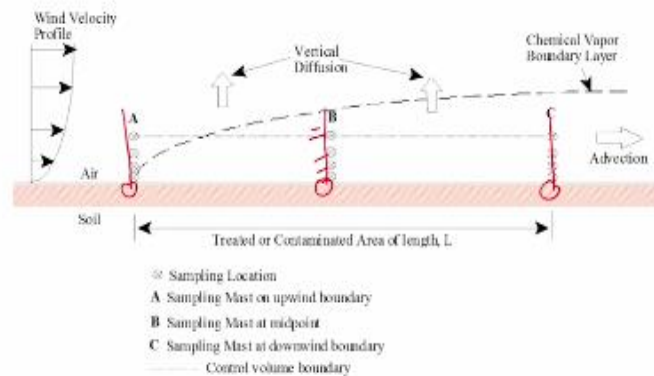
$$n_{A0} = - \frac{k_1^2 D_{A1}^{(t)} (v_{x2} - v_{x1}) (\rho_{A12} - \rho_{A11})}{\phi_m n_1^{(t)} \left\{ \ln \left[\frac{z_2 - d}{z_1 - d} \right] \right\}^2}$$

So, this final expression, the corrected expression for the flux at a surface is given by this where the temperature gradient is implicitly sitting here inside this in this equation okay. Here also you can assume DA_t and this is the problem, if you assume that to be 1, then of course ϕ_m value will take care of the rest of it. So, this is a bit, it is not a very accurate method as you can see because depending on how many measurements you are making, there bounds to be errors in this and the way we do it, but this is the best we have got at this point.

Added to this problem that the concentration measurements sometimes you do not get instantaneous concentration measurement. You can get instantaneous velocity and temperatures, you cannot get instantaneous concentration, which means that all this is velocity may be changing because it's turbulent, but you cannot use that, you have to wait for that timescale at which you are measuring your concentration gradient. So it is inaccurate that way, but it will still give you an estimate of what the flux is. You can add a factor of 10 if you want for conservative measures point of view.

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Direct Emission Flux Measurement – Field Scale – Aerodynamic method



So what people do is they have a mast. This is a gradient measurement. You can have a mast of different measurements at multiple locations in a given area. So this is the flux that you get is only for this location and flux you get for this location is this one. So, then you get an average over an area. You have to do all this because now you are unwilling or it is not correct for you to enclose the given air, amount of air in order to measure flux from a given surface, okay?

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Pilot Field Scale Experiment - Aerodynamic Method



Physically it looks like this. There is a field experiment that was done, there you have contaminated mud or something like that, so this is releasing. So you have this mast here you can see and each of these different locations where we have measurements of the chemical, the wind speed, temperature, everything. As a massive exercise, so you have to put it, people

have done this over different surfaces. They have done it over water. They have done it over agricultural fields. They have done it over this thing.

So this works for vapor phase okay. For particles, it is a different story because particles have aerodynamic behavior and they would not behave nicely, they does not go up nicely. Only particles below a certain size will go up nicely. Particles above 1 micron, 2 microns, they will even deposit on top of your sampling device and all that, so it is a bit difficult to do all that okay.