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

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Exchange from sediment-soil

Image Source : Sediment Profiling Camera (http://www.vims.edu/bio/benthic/)

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 fluffy 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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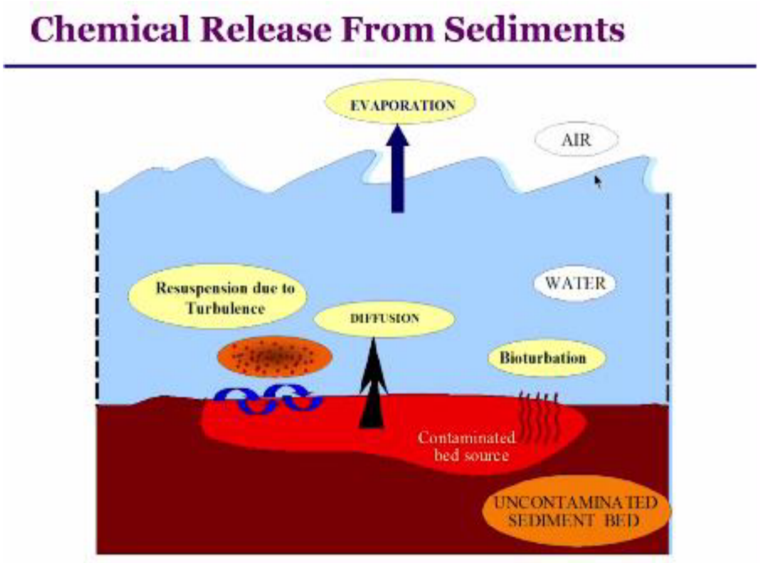

Chemical Release From Sediments

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

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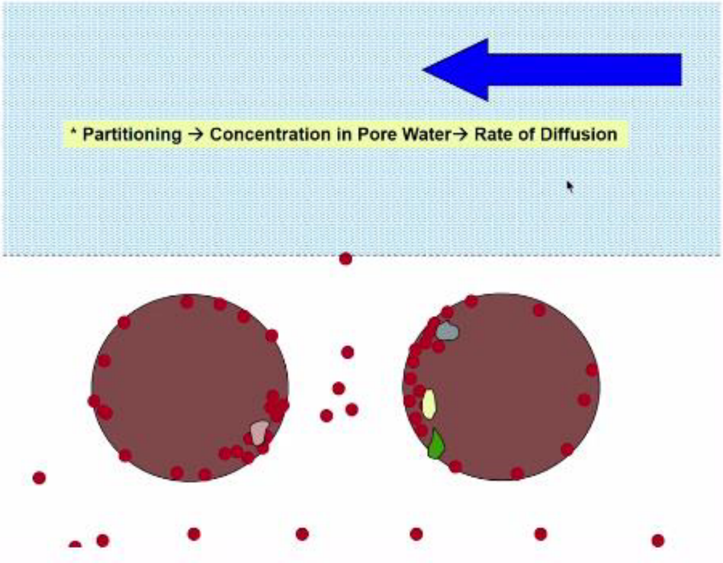

* Partitioning → Concentration in Pore Water→ Rate of Diffusion

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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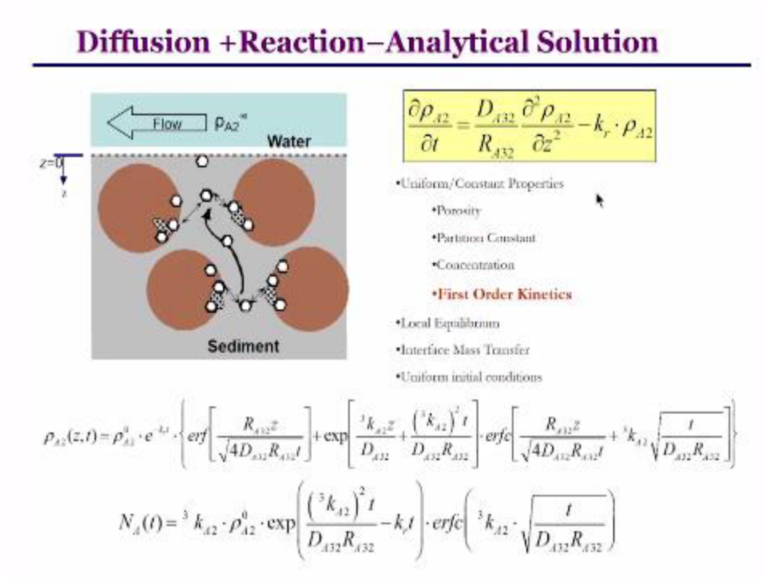

Diffusion +Reaction–Analytical Solution

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

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

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

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

(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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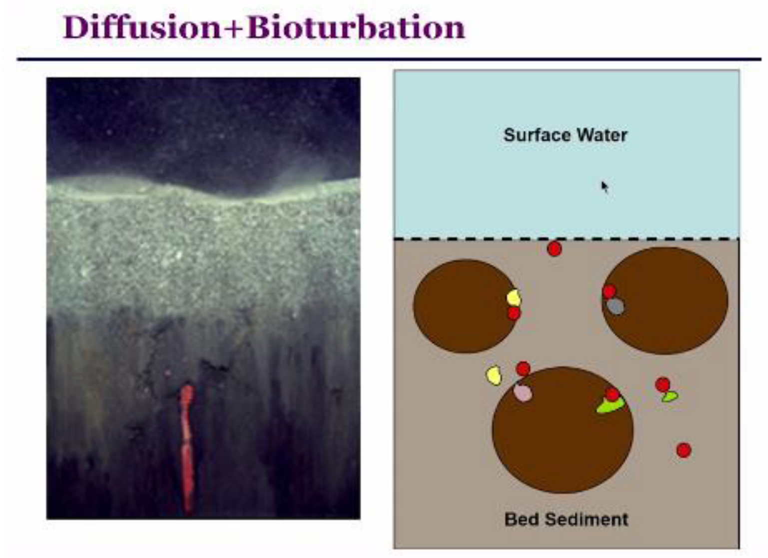

Diffusion+Bioturbation

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

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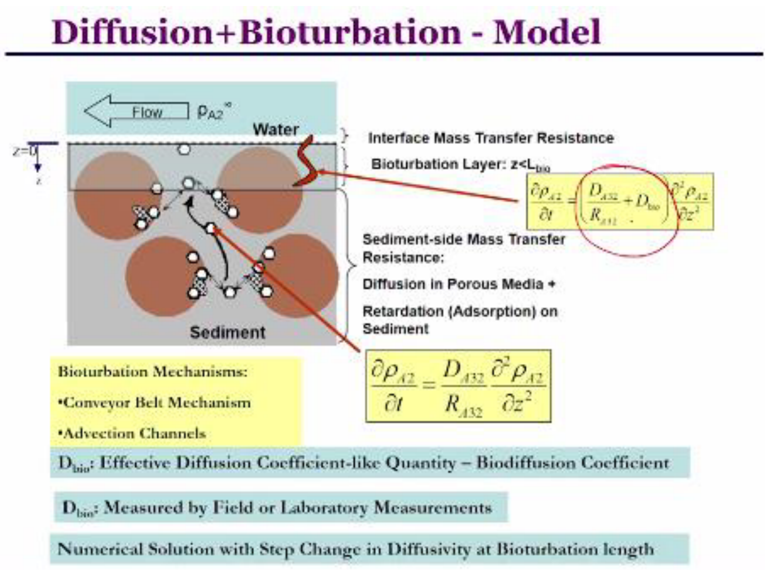

Diffusion+Bioturbation - Model

Interface Mass Transfer Resistance

Bioturbation Layer: $z<L_{bio}$

$$\frac{\partial \rho_{A2}}{\partial t}=\left(\frac{D_{A32}}{R_{A32}}+D_{bio}\right)\frac{\partial^2 \rho_{A2}}{\partial z^2}$$

Sediment-side Mass Transfer Resistance:

Diffusion in Porous Media +

Retardation (Adsorption) on Sediment

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

Bioturbation Mechanisms:

- Conveyor Belt Mechanism
- Advection Channels

D_{bio}: Effective Diffusion Coefficient-like Quantity – Biodiffusion Coefficient

D_{bio}: Measured by Field or Laboratory Measurements

Numerical Solution with Step Change in Diffusivity at Bioturbation length

The model again, these are the bioturbation layer seen as a separate model and within 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 egests it out and that is one and this also causes advection channels and solution method.

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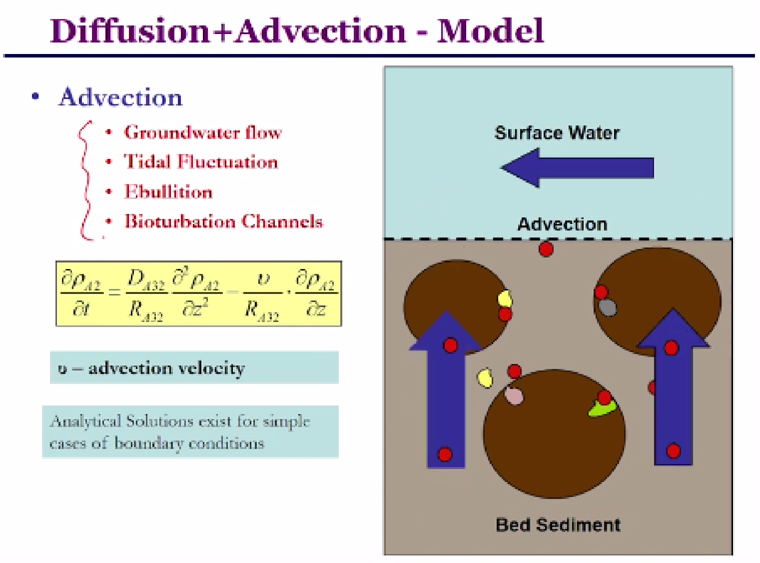

Diffusion+Advection - Model

- Advection
  - Groundwater flow
  - Tidal Fluctuation
  - Ebullition
  - Bioturbation Channels

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

υ – 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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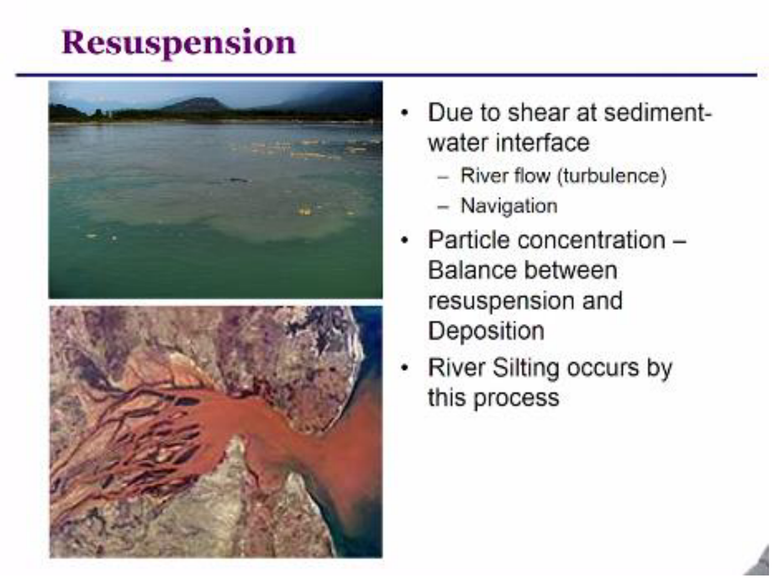

Resuspension

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

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

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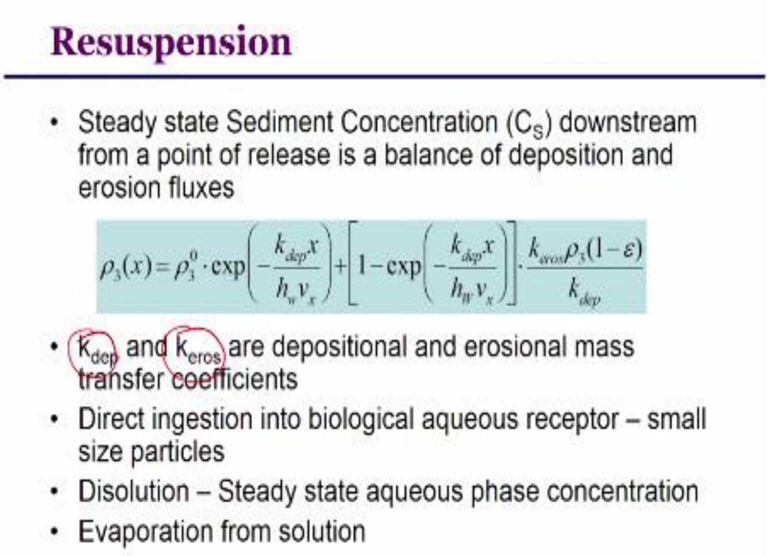

Resuspension

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

$$\rho_3(x) = \rho_3^0 \cdot \exp\left(-\frac{k_{dep}x}{h_w v_x}\right) + \left[1 - \exp\left(-\frac{k_{dep}x}{h_w v_x}\right)\right] \cdot \frac{k_{eros}\rho_3(1-\varepsilon)}{k_{dep}}$$

- k_{dep} and k_{eros} 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 from this concentration. 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 Type equation here.into the air.

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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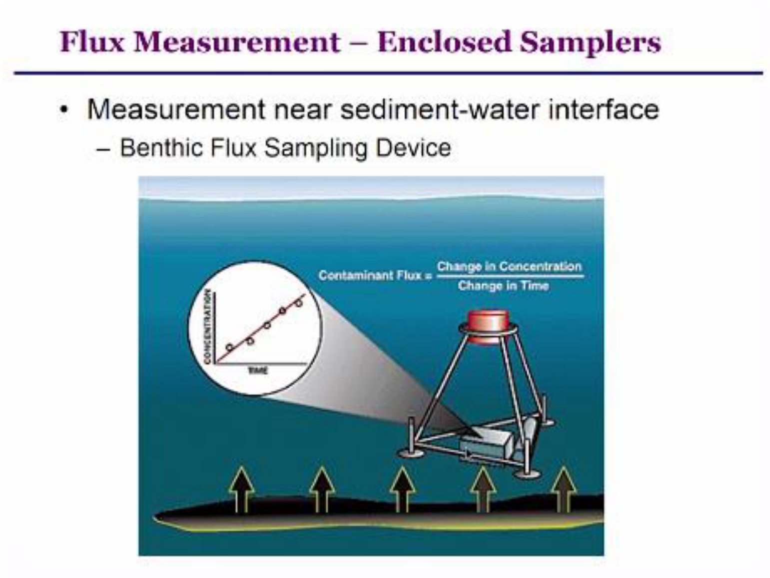

Flux Measurement – Enclosed Samplers

- 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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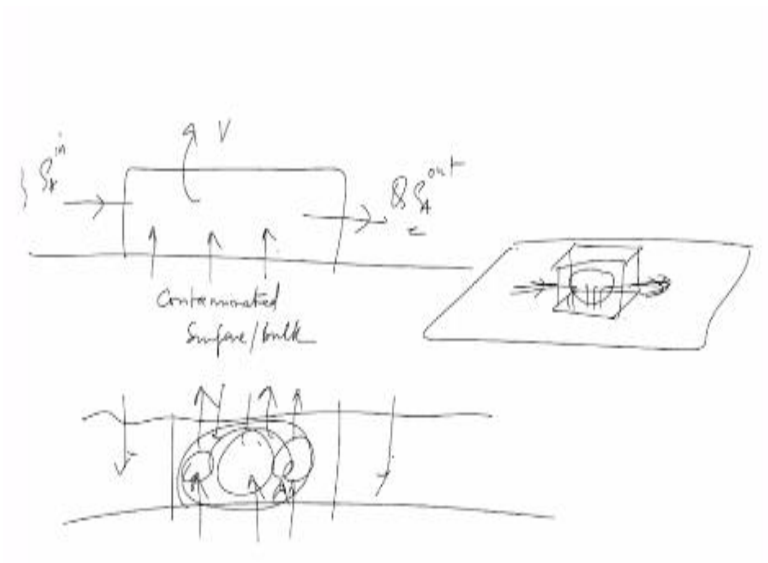

One is we can have a surface. You are measuring flux at the surface, so you want to measure this. So, you calculate what is the amount coming in. So, $Q\rho_A^{in}$ is what is coming in and $Q\rho_A^{out}$ is what is leaving, the difference between in and out should be the flux okay. A lot of times you 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 what we are doing is we are defining a box here and physically we are defining a box. We are placing a box on a surface and this surface say is a 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 that 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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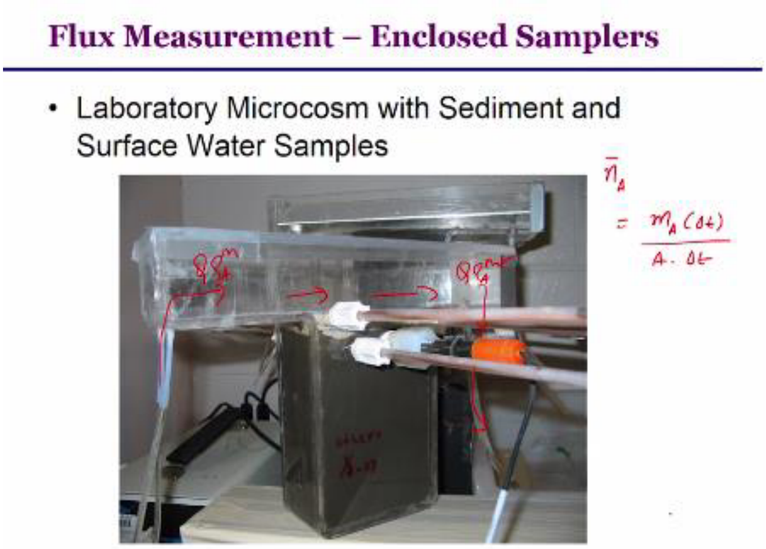

Flux Measurement – Enclosed Samplers

- 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, 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 to know what will happen.

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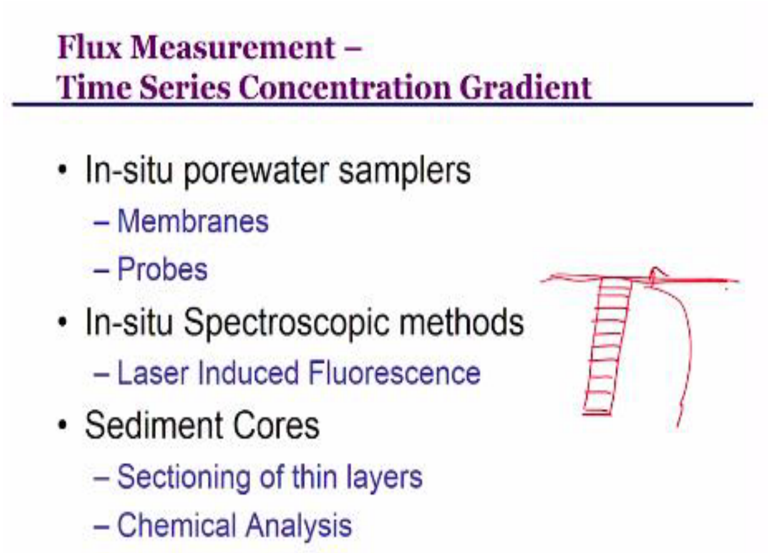

Flux Measurement –
Time Series Concentration Gradient

- 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 rho 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
  - 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

Markers

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 in 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