Environmental Quality: Monitoring and Analysis
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Lecture – 57
Unsteady State Release From Sediments

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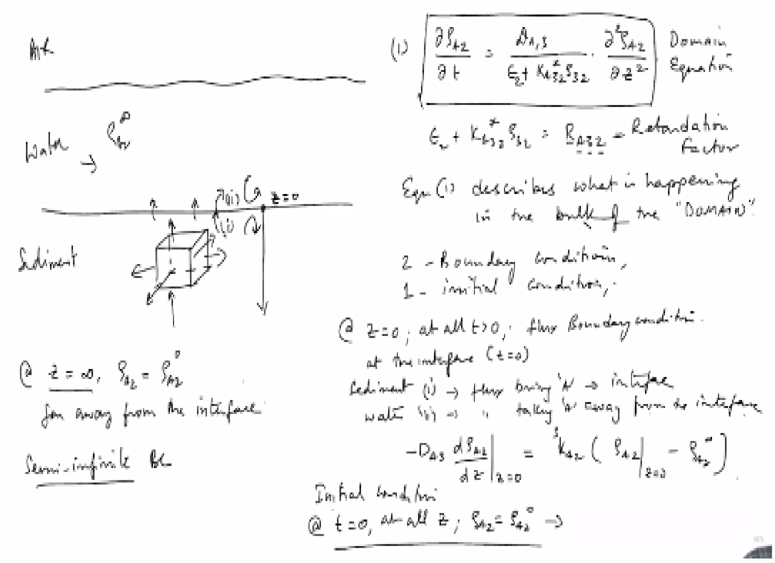

@ $\underline{z = \infty}$, $\rho_{A2} = \rho_{A2}^0$
far away from the interface

Semi-infinite BC

(1) $\boxed{\frac{\partial \rho_{A2}}{\partial t} = \frac{D_{A,3}}{\varepsilon_2 + K^*_{A32}\rho_{32}} \cdot \frac{\partial^2 \rho_{A2}}{\partial z^2}}$ Domain Equation

$\varepsilon_2 + K^*_{A32}\rho_{32} = R_{A32}$ = Retardation Factor

Eqn (1) describes what is happening in the bulk of the "DOMAIN".

2 - boundary conditions,
1 - initial conditions,

@ z=0; at all t>0; flux boundary condition.
at the interface (z=0)
sediment (i) → flux bringing 'A' → interface
water (ii) → " taking 'A' away from the interface

$$-D_{A3} \frac{d\rho_{A2}}{dz}\Big|_{z=0} = {}^3k_{A2}\left(\rho_{A2}\Big|_{z=0} - \rho_{A2}^{*}\right)$$

Initial condition
@ t=0, at all z; $\rho_{A2} = \rho_{A2}^0$ →

Okay, so yesterday we were discussing the contaminate transport. So, we were looking at the development of the transport model within a system here, so we are looking at transport in this z direction. So, the equation we derived yesterday is

$$\frac{\partial \rho_{A2}}{\partial t} = \frac{D_{A_3}}{(\varepsilon_2 + \rho_{32}.K^*_{A32})} \frac{\partial^2 \rho_A}{\partial z^2} \xrightarrow{\hspace{3cm}} (1)$$

So, this is called as general domain equation or the process that is happening in the domain. The sediment is the domain, the process is happening. This describes the processes happening here.

So, this term here, $(\varepsilon_2 + \rho_{32}.K^*_{A32})$ is called as the Retardation Factor, so we have defined it as R_{A32}. So, this retardation of A between 3 and 2 okay, which means that this equation 1 describes what is happening in the bulk of the sediment of the domain that is why we call it as a domain equation. You can of course have transport happening in the y direction and in x direction as well. You can write the main equation for that also. So this will extend into that, that is possible.

As a domain equation we will have all that okay, but for the purposes of this, we will not do that because we will have some simple mathematical solutions for whatever we are doing here. So, you cannot have simple analytical solutions for 3 dimension and 2 dimensions. So that needs separate tools for that. I will talk about that also. Now here, we need the 2 boundary conditions and one initial condition to solve this . So, our domain starts here. This is z = 0 and it goes down, this is how we have defined our system.

So, first let's talk about the boundary condition at z = 0. What could be the boundary condition at z = 0? So, one has to look at what is happening and usually boundary conditions are written at a particular location at all time greater than 0. This is how it is written. This is a full definition of boundary condition, which means it must be applicable at all time okay. So, what is applicable at all times in this particular boundary?

So, there are several possibilities, but in this case material is going out at that boundary. So, we can use what is called as a flux boundary condition. Boundary condition can be anything, so, we can have flux boundary condition as one. We are assuming they are at a steady state is that there is no accumulation at the interface. This is something an assumption that we make all the time. So, whatever is coming from here is going here okay at the interface which is z = 0. Material is what is being brought from one side of the interface is leaving to the other side at the same rate, the rate at which it is brought in is going away.

What is the rate at which this is? So, let us call this as (i) and call this as (ii). What is the rate at which material is brought to the interface or the flux in other words, normalized rate is flux, area normalized rate is flux. So, what is the flux of chemical brought in to the interface? You understand what I am saying, one is the process bringing is a flux, bringing A to the interface, and 2 is the process is the flux taking A away from the interface. So, something is happening on this side and something is happening on this side.

That is some transport processes bringing material to the interface and other transport process is taking it away from the interface. So, what is it on the side 1, which is on the sediment side? How would you describe, what is a flux? How do you describe the flux for bringing material to the interface from below? What is the process? What is the mechanism? Diffusion. So, what is the diffusion flux? It is

$$-D_{A_3}\frac{d\rho_{A2}}{dz}\bigg|_{z=0}$$

You notice that the R term is gone now because we are just before the interface.

See there is some material here and there is some material, yesterday we talked about it. We are talking about this particular region, which is no longer interacting with this, it is just about to get out, but this is diffusion here. So, it is just the transport process, it is no longer, it has already finished this interaction with the solid, so this thing retardation is not accounted for at this point. What is on the other side? What is on the water side? How would you define flux on the water side? So we have been seeing last few classes.

It is

$$^{3}K_{A2}(\rho_{A2}|_{z=0}-\rho_{A2}^{\infty})$$

this ρ_{A2}^{∞}, it is the boundary condition that we apply, this is at z = 0. So, what is the other boundary condition that we can write in this system here, which is far away from the interface. So, we have several possibilities, we have at z equals to some finite distance. Now, this finite distance again it is at all time greater than 0, it should be valid for all time greater than 0. How can I say all time greater than 0 is at, some particular location it has to be true every time.

But in this scenario, I do not think there is a particular location away from the interface where it is going to be a known fixed value, a fixed condition, a fixed concentration for example. So, there are a lot of different conditions, so we can go through a set of these conditions for example in this case, one thing that you know for sure is that people use this condition called as semi-infinite boundary conditions where z equals to infinity. Infinity, what is there at z equals to infinity?

What do you mean by z is equal to infinity? z equals to infinity means it is very far away from the interface. So to write down what is there here, $\rho_{A2}|_{z=\infty}$, it will be ρ_{A2}^{0}, the ρ_{A2}^{0} is the initial condition. Initial condition is at time t = 0 at all z. This is the condition for that, which means that everywhere throughout the system at time t = 0, this is the initial condition okay, while this need not be true, at all z is not necessarily true for initial condition at a given z, what we are meaning at some z.

So, it could be that at all z we can have $\rho_{A2} = \rho_{A2}^0$, this is some initial conditions which means. So, when we are writing this statement, we are assuming that it is uniform, everywhere throughout the system $\rho_{A2} = \rho_{A2}^0$, this is one particular case where you can look at it, yeah. So, what we are saying at z equals to infinity $\rho_{A2} = \rho_{A2}^0$ is that somewhere very far away from the interface, the interface is where all the action is happening, transport is happening, very far away nothing is happening.

No movement is happening because the depletion occurs from the interface. So the moment material from near interface gets out first and then there is diffusion gradients set up inside and so on. So, by the time that gradient reaches significantly far into this, it is such a long time. So, you may not want to solve the problem till that time. Your region of interest of time is much below that so we will see that. So, this is called as a semi-infinite boundary condition.

This is used a lot in this kind of transport problems, boundary condition, which assumes this, there is nothing called as infinity. Infinity is some large number and it essentially means that at infinity nothing is happening. No change is happening and that is your infinity, whatever it is. We do not really know what it is. We are assuming that it is there. So, semi-infinite boundary condition is this. The other alternative is, let me just write the solution for this first.

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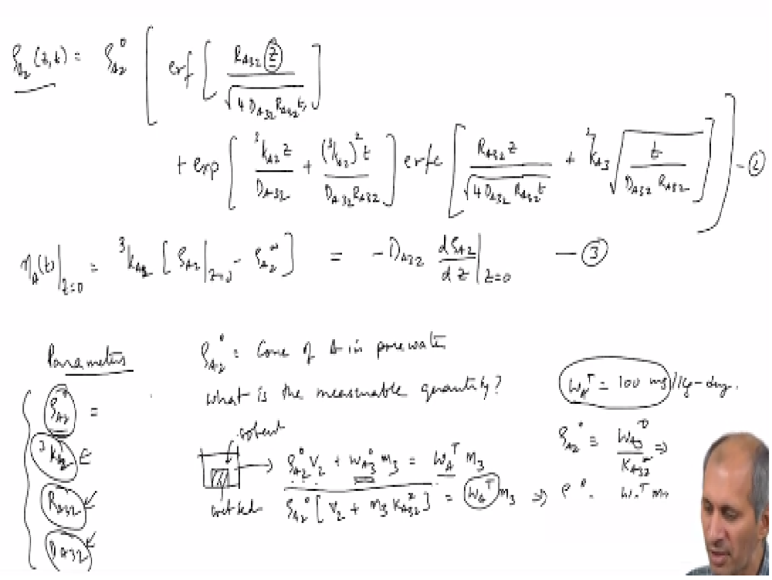

$$\rho_{A2}(z,t) = \rho_{A2}^0 \left[\text{erf}\left[\frac{R_{A32}\, z}{\sqrt{4 D_{A32} R_{A32} t}}\right] + \exp\left[\frac{{}^3k_{A2}\, z}{D_{A32}} + \frac{({}^3k_{A2})^2 t}{D_{A32} R_{A32}}\right] \text{erfc}\left[\frac{R_{A32}\, z}{\sqrt{4 D_{A32} R_{A32} t}} + {}^3k_{A3}\sqrt{\frac{t}{D_{A32} R_{A32}}}\right]\right] \quad -②$$

$$n_A(t)\Big|_{z=0} = {}^3k_{A2}\left[\rho_{A2}\Big|_{z=0} - \rho_{A2}^\infty\right] = -D_{A32}\frac{d\rho_{A2}}{dz}\Big|_{z=0} \quad -③$$

Parameters

ρ_{A2}^0 =

${}^3k_{A2}$

R_{A32}

D_{A32}

ρ_{A2}^0 : Conc of A in porewater

What is the measurable quantity? $w_A^T = 100$ mg/kg-dry.

solvent

wetted

$\rho_{A2}^0 V_2 + w_{A3}^0 m_3 = w_A^T m_3$

$\rho_{A2}^0 [V_2 + m_3 K_{A32}] = w_A^T m_3 \Rightarrow \rho^0 \cdot \; w_A^T m_3$

$\rho_{A2}^0 = \frac{w_{A3}^0}{K_{A32}} \Rightarrow$

So, now we have the solution for this equation. You solve it using Laplace transforms and you will get, the equation that you get

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

$$\longrightarrow \quad (2)$$

it is a pretty big equation yeah. The solution for this is you can use Laplace transform and similarity transform to do it, several possibilities okay, so it will give up this big solution, okay. Now the flux at this is now a function of time at z = 0. This you can use either of the two terms.

Flux you can calculate, once you calculate this, this expression you have. This expression if you notice is a function of z and t, t is here z is here, z and t appear in this equation. The other parameters in this equation are, we will write down that. This is ρ_{A2}^{0}, ${}^{3}K_{A2}$ and diffusion coefficients, these are the 4 parameters that we need. So the flux itself, you can use either of these 2 equations at the interface. You can use either ${}^{3}K_{A2}(\rho_{A2}|_{z=0}-\rho_{A2}^{\infty})$ which means that I have to take this equation and put z = 0 in this equation. In equation 2, I have put z = 0 and whatever I get multiply that by the KA3 - z or I can do $-D_{A_{32}}\frac{d\rho_{A2}}{dz}\Big|_{z=0}$. So, I get the integral, first derivative of this equation 2 and put z = 0 there multiplied by the diffusion coefficient. Either of this is possible, you should get the same expression in doing this.

$$n_{A}(t)|_{z=0}={}^{3}K_{A2}(\rho_{A2}|_{z=0}-\rho_{A2}^{\infty})=-D_{A_{32}}\frac{d\rho_{A2}}{dz}\Big|_{z=0} \qquad \longrightarrow \quad (3)$$

If you are interested, I can give you the solution for this, but right now for this we do not need it. So, here ρ_{A2}^{0} is the initial boundary condition. So, what we have in initially, so we have some contamination right, we are assuming that this contamination is uniform as a function of depth, okay. So, but we are talking about ρ_{A2}^{0} right, ρ_{A2}^{0} is the concentration of A in pore water. How do you get this? This is predicting a model, so scenarios are like this. So you know there is a contaminated sediment site, you would like to know what is the flux of chemical coming from there into the water. Which means these are the things that you should know in order to be able to calculate equation 2 or equation 3. So, ρ_{A2}^{0} is data that you need, how do you get ρ_{A2}^{0}? You have to get ρ_{A2}^{0} from some measurement and what is the thing that you can measure?

Compared to sediment for sediment quality, what do you measure? What can you measure? You have to go and measure, you need monitoring here. What do you monitor? What do you measure? What is the measurable quantity here? Measurable quantity when you measure

sediment, we did sediment extraction right, what do you measure there? You take a sediment sample, you measure something, what do you measure? So, recall your analysis methods. I take a sediment sample, what do I do with the sediment sample in order to extract?
Student: desorption
Professor: you extract with something. You take some amount of sediment, either with soxhlet extraction or ultrasonication, you take a certain amount of wet sediment and you add some solvent and you extract. What are you extracting here? Which fractions of chemical are you extracting? The chemical that you are extracting is from the solid phase or the pore water?

You are taking wet sediment and dumping it into a container with the soxhlet extraction or adding solvent and extracting it, you are extracting both. So, which means that you are doing both $\rho_{A2}V_2 + w_{A3}m_3$ both of these are happening, but what are you reporting this value as? When you extract everything you are reporting this as w_{A3} only. The reason you are reporting as w_{A3} is this is we are reporting it as a mass of chemical divided by the mass of dry solid. This is a bit tricky because what we measure is not just 'w'.

The theoretical 'w' we say is only the solid phase, but what we are measuring is the total concentration. What we are measuring really is this entire thing, yeah. So, let us call that as ${w_{A3}}^T$. ${w_{A3}}^T$ is the total measurement, let us say I am reporting a value of ${w_{A3}}^T$, I am reporting a value of 100 milligrams per kilogram. What I am reporting is 100 milligrams of kilogram dry okay. So, this 100 milligrams is coming from both solid and liquid phases, but I am reporting it as on the basis of dry, yeah.

So, if I know what the dry mass that is what I am reporting as because that is unchanging, water content is changing so I am reporting as this. So I think this is a bit tricky to get a hold off, but this is what it is. So my mass balance is this, it is

$$\rho_{A2}V_2 + w_{A3}m_3 = {w_{A3}}^T.m_3$$

So, we are talking about this. So, in other words, we are saying the

$$\rho_{A2}^0.V_2 + w_{A3}^0 m_3 = {w_{A3}}^T.m_3$$

and we are also saying if you use the local equilibrium assumption that these two are in equilibrium,

$$\rho_{A2}^0 = \frac{w_{A3}^0}{K_{32}^*}.$$

So, I can write this as

$$\rho_{A2}^{0}.(V_2 + K_{32}^{*}m_3) = {w_{A3}}^{T}.m_3.$$

So, this is a number that we are measuring. This is a measured number, this is what we are measuring. So, in this equation, we will write it as

$$\rho_{A2}^{0} = \frac{{w_{A3}}^{T}.m_3}{(V_2 + K_{32}^{*}m_3)}$$

I am going to write it in the next page.

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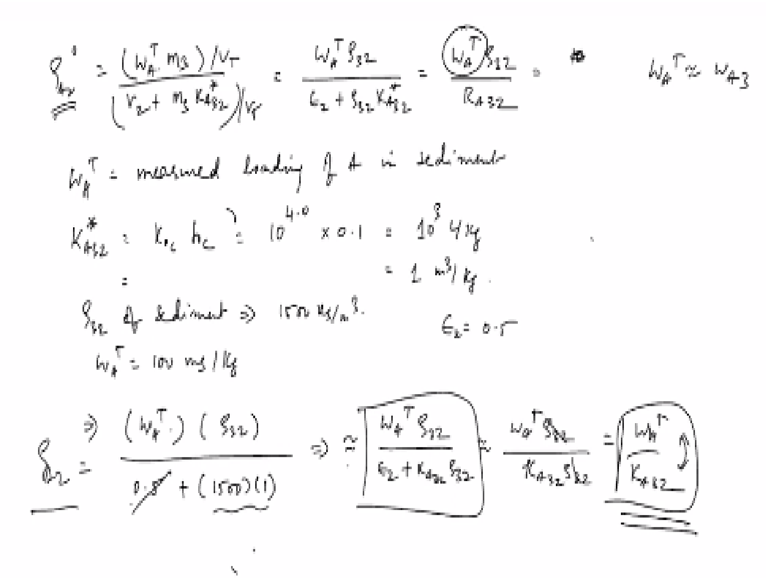

$$\rho_{A2}^{0} = \frac{(w_A^T m_3)/V_T}{(V_2 + m_3 K_{A32}^{*})/V_T} = \frac{w_A^T \rho_{32}}{\epsilon_2 + \rho_{32} K_{A32}^{*}} = \frac{\boxed{w_A^T}\rho_{32}}{R_{A32}} \qquad w_A^T \approx w_{A3}$$

w_A^T = measured loading of A in sediment

$K_{A32}^{*} = K_{oc} f_{oc} = 10^{4.0} \times 0.1 = 10^3$ L/kg

$= 1$ m³/kg.

ρ_{32} of sediment ⇒ 1500 kg/m³. $\epsilon_2 = 0.5$

$w_A^T = 100$ mg/kg

$$\underline{\rho_{A2}} = \frac{(w_A^T)(\rho_{32})}{\cancel{0.5} + \underbrace{(1500)(1)}} \Rightarrow \approx \boxed{\frac{w_A^T \rho_{32}}{\epsilon_2 + K_{A32}\rho_{32}}} \approx \frac{w_A^T \rho_{32}}{K_{A32}\rho_{32}} = \boxed{\frac{w_A^T}{K_{A32}}}$$

If I divide both sides by the total volume, I will get

$$\rho_{A2}^{0} = \frac{{w_{A3}}^{T}.m_3 \big/ V_T}{(V_2 + K_{32}^{*}m_3) \big/ V_T} = \frac{{w_A}^{T}\rho_{32}}{(\varepsilon_2 + \rho_{32}.K_{A32}^{*})} = \frac{{w_A}^{T}\rho_{32}}{R_{A32}}$$

you get the pore water concentration at any point is not just 0, right now we are writing 0 because that is what we need, but this value is what is measured. So when this we assume is whatever is the value of the sediment concentration loading at whatever time you are interested in starting the simulation.

So, this bulk density multiplied by the actual measurement ${w_A}^{T}$ is the measured loading of A in the sediment. We remove this subscript T and put a ${w_A}^{T}$ there, so that just to indicate that. So let us take for example, if you are taking some compound which has a log K_{A32}

K_{A32} is K_{OC}. f_{OC}, if you take some compound which has K_{OC} of say 10^4 liters/kilogram and an f_{OC} of 10%,

$$K_{A32} = \mathrm{K_{OC}}.\mathrm{f_{OC}} = 10^4 \times 0.1 = \frac{10^3 L}{kg} = 1\,{}^{m^3}\!/_{kg}$$

The bulk density of sediment it ranges between, the density of water if there is no sediment, so only water, density water is 1000 kilograms per meter cube. So if keep adding solid, the mass goes on because the particle density of solid is around 2000-2500. So the bulk density of sediment is usually higher than 1000. So, let us say this 1500 kilograms per meter cube. If I put these two, so let us say it is 100, let us say the ${w_A}^T$ is 100 milligrams per kilogram dry sediment okay.

This equation here is $\frac{{w_A}^T \rho_{32}}{(\varepsilon_2+\rho_{32}.K^*_{A32})}$, ε, what is the maximum value of epsilon, maximum value is 1, you are not going to have 1, you are going to have somewhere between 0.4-0.5, let us say it is 0.5, the epsilon is 0.5 plus in this denominator we have 1500 multiplied by 1. If you look at this denominator, a lot of times this denominator this value is much greater than this. So you can neglect ε,

$$\frac{{w_A}^T \rho_{32}}{(0.5 + 1500 \times 1)}$$

so then this equation for sediment systems, for very dense systems and with KA32 very large, you can approximate this equation.

We can approximate

$$\frac{{w_A}^T \rho_{32}}{(\varepsilon_2 + \rho_{32}.K^*_{A32})} \approx \frac{{w_A}^T \cancel{\rho_{32}}}{(\cancel{\rho_{32}}.K^*_{A32})} = \frac{{w_A}^T}{(K^*_{A32})}$$

but the accurate representation is this, but you can approximate it to this for certain systems where the product of the bulk density and K_{A32} is very huge, it will not make a big difference if you remove that okay. In essence we are saying that when you are doing ${w_A}^T$ measurement, water is so small that does not matter you can take it at the WA3.

What we are essentially doing is we are doing ${w_A}^T$is approximately equal w_{A3}. This is what we are doing. This is what this means. Because this is what we did when we want to calculate pore water concentration, we are just directly doing this right. This is equilibrium. This is ρ_{A2} equals $\frac{{w_A}^T}{(K^*_{A32})}$. This is what we did in our calculation in the beginning when we were doing equilibrium and all that, okay.

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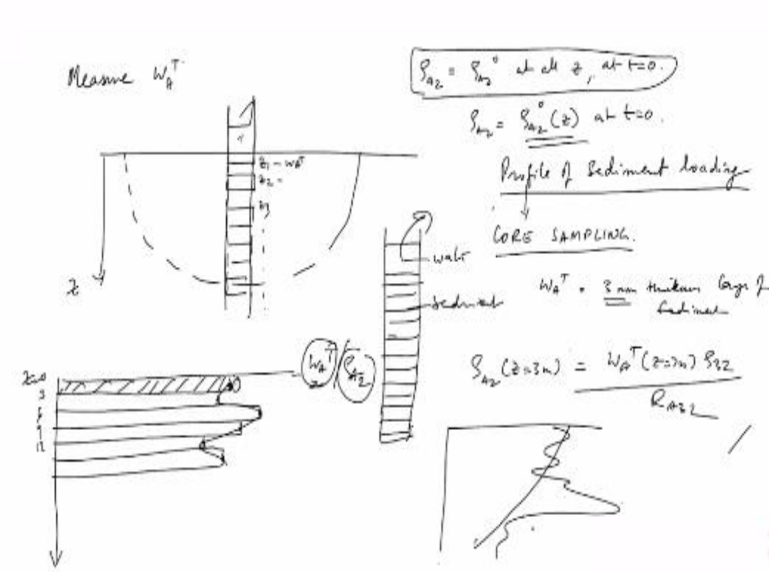

So now the next thing is when you take measurements which we did not discuss this when we were doing the measurement part. When we measure WAT normally, see we have our system of interest is here. So, we have a sediment that is contaminated, this zone right, there is a certain distance to which it is contaminated. How will I take a sediment sample? So, my assumption that $\rho_{A2} = \rho^0_{A2}$ at all z is the initial condition at time t = 0 assumes that this is uniform, but it need not be uniform, yeah. Most likely it will not be uniform.

Why will it not be uniform? Yesterday we discussed that it cannot be uniform because as sediment starts from one end, as the contamination start from one and it is diffusing inside the sediment. So, it will never be uniform. It is going to be decreasing. It is going to be very high at the top and it is going to be decreasing towards the bottom, that is one possibility. So, this assumption is, it is not a good assumption. So, you have to measure $\rho_{A2} = \rho_{A2}(z)$ as a function of z at time t = 0. This is the correct representation of it.

We are now fixing that $\rho^0_{A2}(z)$ is the same for all, but that may not be true okay. How do you get this data? We are getting ρ_{A2} from ${w_A}^T$, which is a measured value. So, how do you get this data? So, if you are getting a profile of sediment loading rather than one location okay. So, when we want a profile, what we are saying is that I would like to have measurements made at every distance z1, z2, z3 and so on. I need to know what is the value of ${w_A}^T$ at each of these locations.

How do you do this? To do this your sampling procedure for the sediment is not, you just go there and pick up one sample of sediment, it needs to be a profile and this profile is obtained from what we call as core sampling. This is true for soils also because continuously in these systems, transport process is going on, happening, transport is happening, diffusion is happening, degradation may be happening, other things also may be happening. So, we will see some of those things. So, we do what is called as core sampling.

So, core sampling usually we put a tube into the sediment and we pull it out. So, it is a very tricky process. The moment when you put a tube inside, it is sometimes difficult for a tube to go inside, but this is for sediments is reasonably wet so it is fine, for soils and all that it will not go, you have to hammer it in. You have to send it in and then loosen this thing and then pull it out. So, here when you push it in, this is water, almost is it cohesive material, so you have to seal the top, so which means that you are almost putting a vacuum.

So you see when you put a tube into water and seal the top, when you close the top and pull it out, the water column stays intact. So you have to do the same thing here. You have to seal it off and then this core comes out. This core will now contain a little bit of water on top, this is the water here. This water is there in the water, river or lake or wherever you are sampling, and then this is the sediment. So, how do you measure? The sediment now you take out this pore water out and then you slowly push the sediment out and take one layer by layer.

So, you get a value of WAT for say a 3 mm thickness layer of sediment. I am just arbitrarily saying 3 mm, it could be 1 mm, 2 mm. It is to the extent to which you can divide, you can push out and divide. This is not an easy process to do because when you are pushing it out, so extruding it out now, sometimes these layers will mix, at the wall they will stick and the one in the center will get out, so what you are getting maybe a slightly mixed layer. So, these are all errors that will come in this thing.

So, what you will get here is data like this, so z = 0, if you draw and this is the concentration WA3 of T, you will get some value like this. So the data from this will look like this. You will get something like this. This is the first layer, this may be the second layer, this may be the third layer, this may be the fourth layer, this may be the fifth layer and so on, it can be arbitrary. If you are assuming that there will be a nice gradient, this top one closest to the surface will be highest and then it will keep on decreasing, but this can be arbitrary.

The value of WAT, so I am drawing a some kind of a bar chart here because this is now a composite of say 3 mm, 6 mm, 9 mm, 12mm and so on. So, this value corresponds to this layer between 0 to 3 mm and so on, okay. So, when you are doing the modeling when you are representing this as this thing, it is your choice, you can say that I will call this 3 mm, I will say between 0 and 3 mm the concentration is the same or I will draw a point like this and then I will fit a line curve through this and then I will give an equation to that, that is one possibility.

But more often when you get these kinds of gradients, our model that we solve is for uniform concentration, you cannot apply this and go there. This is a discrete distribution of concentration right, corresponding to WA3 you will get. So, for ρ_{A2} at z = 3 mm, you will get

$$\frac{{w_A}^T(z = 3mm).\rho_{32}}{R_{A32}}$$

This is the calculation that we do. So, you can also have ρ_{A2}, from the ${w_A}^T$ when calculate ρ_{A2}, you will get a profile of ρ_{A2} also here. You cannot solve this analytically.

The analytical equation we presented is only valid for concentrations which are uniform, okay. When you get these kinds of systems, automatically you have to do a numerical solution. You have to take this and do a numerical solution using any of the methods available. When you do a numerical solution, automatically you will take a numerical step delta z and delta t that you are looking at. So, when you take delta z, if you have data for some delta z here already, you take that same step, so which means that within that step you are calculating.

Anyway, you do not have values for ρ_{A2} within resolution less than 3 mm or whatever you are measuring. So, you might as well do it this way. So, this is the way it is done. Now, just a small point. Why do we have when we say gradients, initial gradients, we expect that since contamination is highest at the surface and it is going out, we expect a gradient to be in this direction, this kind of system. Why have I drawn this haphazard this kind of system, any guesses?

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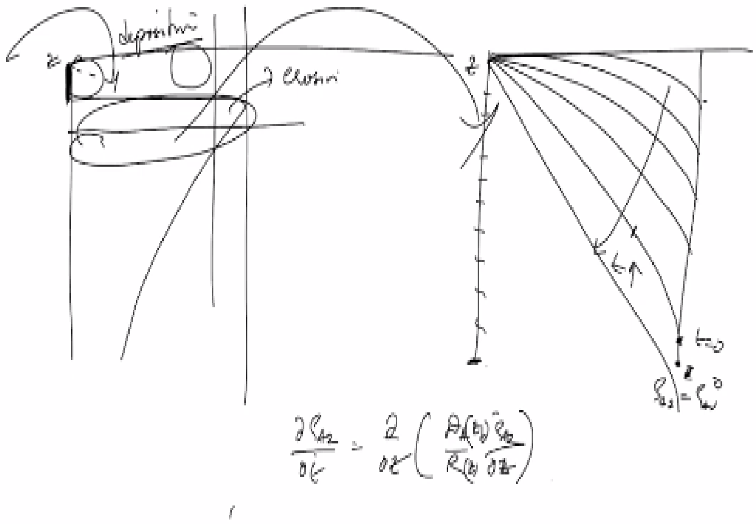

$$\frac{\partial \rho_{A2}}{\partial t} = \frac{\partial}{\partial z}\left(\frac{D_A(\varepsilon)}{R(\varepsilon)}\frac{\partial \rho_{A2}}{\partial z}\right)$$

Very often you will find profiles that look like this. If I am drawing like this, profiles maybe like this, z = 0. There is nothing in the top and then there is a big, it may look like this. Can you guess why it may look like this? In the sediment, this does not happen in soils, it happens in sediment only.

Student: That has gone into water in the down.

Professor: Yeah, but you would expect that is still a diffusion based process, the gradients are preserved, why like this? I agree what you are saying, but there is a big zero thing here. What you are saying is true. See, normally this is what you would expect. Suppose I start with the constant concentration; this is time t = 0. As time progresses, what do you expect to see is something like this, this will happen and so on. So, the time is increasing. So, in the semi-infinite calculation, one of the things you have to do is here at this point the ρ_{A2} is still ρ_{A2}^0 at this point at your maximum z, whatever you are calculating yeah.

So, in the solution of the model, we saw that there is a z term there, right. This is there is a z term here, that z you have to put it into the model, so that this is the z axis, you are calculating it for different z's. So, as long as the time for which you are calculating computing, it does ensure that you have still not reached that point. So, let us say that your profile looks like this. It is no longer valid, semi-infinite condition is no longer valid, yeah.

You can only solve the semi-infinite conditions for times where the diffusion process has not reached that edge of your system. Anyway, this is what you expect when a diffusion process happening. So there is depletion in the top, so you are seeing that there is loss here and there is decreasing order, but what I am saying is looks very random. There is nothing in the top section. Why can this happen? Why will this happen? Can you guess why this happens? In sediment systems, this is not related anything we have discussed so far.

This is something which is very different from what we have discussed, just think about it. So in rivers, this happens mostly in rivers, does not happen in lakes, happens in rivers, it can happen in oceans, in seacoast.
Student: Bioturbation.
Professor: No, there is no accumulation, is lost, complete, there is no. So, let me give you another hint. What if you see a profile like this, what does it mean? This is what you would expect to see. The contamination is happening, but then you see this one layer on the top, which there is nothing in that, no contamination.

What does this mean? What could this mean?
Student: The top layer is carried away with water,
Professor: but top layer carried away with water you should see something like this. Can you make another guess? The reverse of that, what you just said is the reverse of that. Material top layer will get carried away with water that is erosion, but this part is because erosion is happening somewhere else that can get deposited here. It happens a lot when you have heavy rainfall, erosion happens.

Lot of sediment gets carried away, but it gets deposited elsewhere, which means this layer can get carried somewhere else and it drops somewhere else, which is a reason why you cannot go into a sediment and take a top layer sample. I cannot take a small bucket and pick the top layer and declare that there is no contamination. There is contamination sitting below, which is a reason why you have to take a core sample to a certain depth. See, the modeling helps a lot. The modeling will not give you accurate results, but it gives you a very nice estimate because we are talking about long timescales.

It gives you an estimate of where you are. It can give you some very good reasonable estimate, provided you have all the other numbers estimated accurately. So, we will stop here. The other parameters that we talked about, we will go one by one. So this is the most important one we talked about ρ_{A2}^{0} estimation. The partition constant. This is the diffusion constant. So, all these terms, KA32 we get from correlation, retardation factor we need to know the bulk density and the partition constant okay, which you can get.

If you get a sample of the sediment, you can measure the partition constant. You know which compound you are looking at, if you know the fraction of organic carbon which you know how to measure and you know the KOC of that compound, KA32 you can measure, you can estimate and therefore all this. Bulk density also you can measure. That is the reason of having a core because bulk density will change the moment you take a grab sample because if you take a grab sample, put it onto this thing, it is all gone.

It is all open now, you are not retaining the original structure of it, but you can measure the bulk density, in-situ bulk density by grabbing the core and then carefully measuring what is the amount of water, what is the volume corresponding to that mass and all that. You can do all those calculations based on that. So, one other thing is because it is a sediment, when you are taking a core, it is very likely that the porosity and the retardation factor of this layer is very different from this layer.

Often the sediment is not, composition of sediment changes even within a few feet okay. So, the core will allow you to get that, in that case this model will become entirely, everything will go into the derivative, so it will become if you are assuming everything to be a function of space, all your thing will go in. So, you

$$\frac{\partial \rho_{A2}}{\partial t} = \frac{\partial}{\partial z}\left(\frac{D_A(z)}{R(z)} . \frac{\partial \rho_{A2}}{\partial z}\right)$$

everything goes inside the derivative, which means DA is now a function of z, R is a function of z okay.