Environmental Quality: Monitoring and Analysis

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Lecture – 56
Release from Sediments

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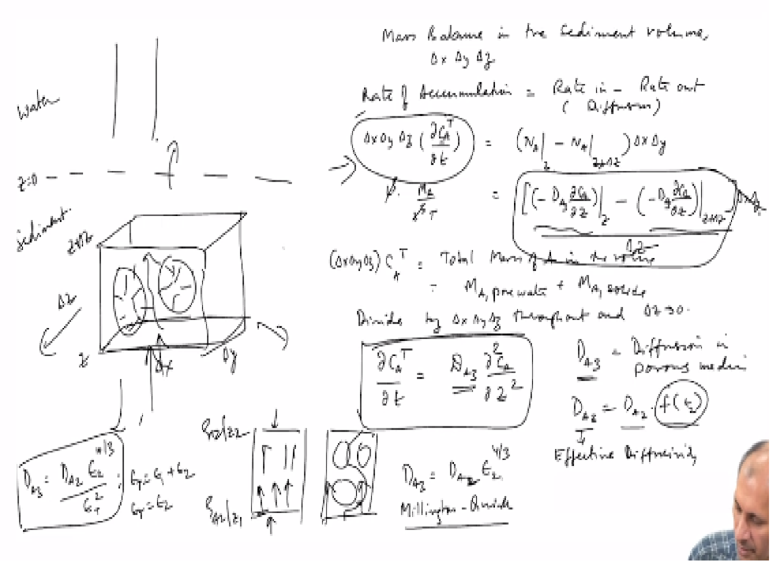


So what we are doing? We do this normally in all box models kind of scenarios. We write again the mass balance in the sediment volume. This is delta x, delta y, delta z is the differential volume of the system. We write

$$rate\ of\ accumulation = Rate_{in} - Rate_{out}$$

Now, here I can write other terms if I want to, yeah, I can write many things. Same as box model, I can write whatever is happening inside the system. This is exactly what we did in box model except for two key differences. One is rate of accumulation is now, it is nonzero, it is not steady state, something is not going out in the same manner. Second is that this rate of accumulation term, what is it? So we have to write this in terms of $\frac{mass}{volume}$, So it is

$$\Delta x \Delta y \Delta z \left(\frac{\partial C_A}{\partial t}\right) =$$

$$L^3 \left(\frac{M_A}{L^3 t}\right) =$$

but is this correct, this term, rate of accumulation as $\Delta x \Delta y \Delta z \left(\frac{\partial C_A}{\partial t}\right)$, is there anything wrong with the way I have written like this.

What will you write in the rate in and rate out. So rate in and rate out is only by diffusion. This is only by diffusion, so which means it is a

$$\Delta x \Delta y \Delta z\left(\frac{\partial C_A}{\partial t}\right) = \left(N_A|_z - N_A|_{z+\Delta z}\right)\Delta x \Delta y$$

So, the diffusion area is this, this is going into the system here, yeah, nothing wrong, so here this term here is diffusion

$$= \left[\left(-D_{A_3}\frac{\partial C_A}{\partial z}\,\Big|_z\right) - \left(-D_{A_3}\frac{\partial C_A}{\partial z}\,\Big|_{z+\Delta z}\right)\right]\Delta x \Delta y$$

There is a problem in this on the left hand side, the right hand side shows what is going through in the fluid. The fluid is moving as diffusion, material A is moving in and out of the system in the form of the diffusion which is occurring only in the fluid phase. The overall accumulation is happening on the entire system, it is happening both in the fluid as well as the solid phase, that is not solid phase, C_A is only the fluid phase. So, therefore, we have to add this is a term called C_A^T, in this case we have

$$(\Delta x \Delta y \Delta z)C_A^T = total\ mass\ of\ A\ in\ the\ volume$$

which includes mass of A in the pore water + mass of A on the solids.

Both of them because here adsorption is happening or the adsorption and desorption both of them are happening. There is exchange between the liquid and the solid. So, the entire mass of what the change here depends on whatever is totally happening in this phase here, okay. So, now if you divide by $\Delta x \Delta y \Delta z$ throughout and take Δz to 0 limit, we will

$$\frac{\partial {\rho_A}^T}{\partial t} = D_{A_3}\frac{\partial^2 \rho_A}{\partial z^2}$$

$${\rho_A}^T = C_A^T$$

You can work out these things, we have done this before. So this minus this, essentially this term will become delta z and that delta z goes to 0, this is the definition of a derivative. This minus this is the DA by.

Student: Sir, we are considering only in z direction.

Professor: Yeah.

Student: Won’t there be,

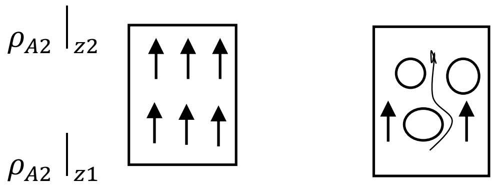
Professor: no, you can do all the 3 directions. Here in this model, we are doing z because that is the primary driving force there. It is always going in every direction, so that is already there. So, this is to just look at our description of the interface at the sediment water interface that is at z = 0 in z direction.

Now, there is also transport going on all the time during this here. So you can write the general 3-dimensional mass balance for the system, as always there, which means you have to define boundary conditions and all that, yeah. So this, as I mentioned this is a synthetic problem. Because we have to start somewhere, we are starting like this. If you want to track the entire history of this contamination, it is still going out, still spreading, it can continue to spread outwards, but we will see why, we are not interested at that for the time being because of some of the things we will do here now.

Now, this term here $\frac{\partial {C_A}^T}{\partial t}$, this is the definition of the derivative, this term here, you will get this, you can check it out D_{A_3} which is diffusion in porous medium, this is different from D_{A_2} because there is water here, diffusion is actually happening in the pore water. So, but D_{A_3} is the term that we have written here. So, D_{A_3} is usually defined as $D_{A_3} = D_{A_2}.f(\varepsilon_2)$ multiplied by a function of the porosity of the system.

This is because normally when you compare, when you look at diffusion in a fluid, you have pore, so if you have same driving force between two systems of diffusion. Look at the case of D_{A_3}. So, the term D_{A_2} the diffusion is reduced because now for two reasons. One is let us say there is diffusion is happening like this, from here to here in an empty channel, yeah.

Now, there is another case where this channel is now filled with some solid. If the same concentration gradient exists, so let us say we have CA1 and so rho A1 and rho A2. So, we call it rho A1 and rho A2 superscript, we are not using the subscript at this point and at this point. So let me more simple, clearer. This we have rho A2 at z1 and rho A2 at z2 two things. So there is a concentration gradient between these two and the same concentration gradient exists here also, but here, material can move diffuse nicely throughout through this.



Here it cannot move, it can only move in this gap, so already it is reduced that is one. Second if it goes here, it will turn, it has to diffuse in this direction, it has to go like this, it takes longer for it to go, less of it can go first that is the problem. Second thing is it takes longer for even that less because it is not a straight path. It is a torturous path. So, this function here therefore reduces the effective diffusion of a material across a porous medium okay. This is the simple explanation, this is called as effective diffusivity in a porous media and it is a function of the porosity.

So, there are different equations for that, DA3 very commonly used expression is

$$D_{A_3} = D_{A_2}.{\varepsilon_2}^{4/3}$$

which is called as Millington Quirk's expression, very old equation, but there are other equations, people dispute this equation and they do not like this equation because it makes some assumptions and it looks too simple. Processes inside porous material is very complicated, especially if the solid has internal porosity and all that. So, here we are not assuming all that, nothing.

The internal porosity means there is pores inside the solid here and the diffusion is not a straightforward process. It can go in, it will take a long time for equilibrium to achieve, all those things are there. So, this is all adsorption desorption is very complicated in these systems. So, we simplify it, so that we can model it reasonably easily in that we use that as a starting point okay. So, general expression for DA3 in the Millington Quirk expression is

$$D_{A_{32}} = \frac{D_{A_2}.{\varepsilon_2}^{10/3}}{{\varepsilon_T}^2}$$

which means that there is another phase in the pore space.

For example, if you take the case of soil, if you have unsaturated soil, some part of the pore space is filled with water and some of it is filled with air. So, this assumes that

$$\varepsilon_T = \varepsilon_1 + \varepsilon_2$$

this is when some part of it is filled with air some powder is filled with water. If this happens, then you have to use this expression, but this expression reduces to this expression when $\varepsilon_T = \varepsilon_2 \; or \; \varepsilon_1$, it becomes

$$D_{A_3} = D_{A_2}.\varepsilon_2{}^{4/3}$$

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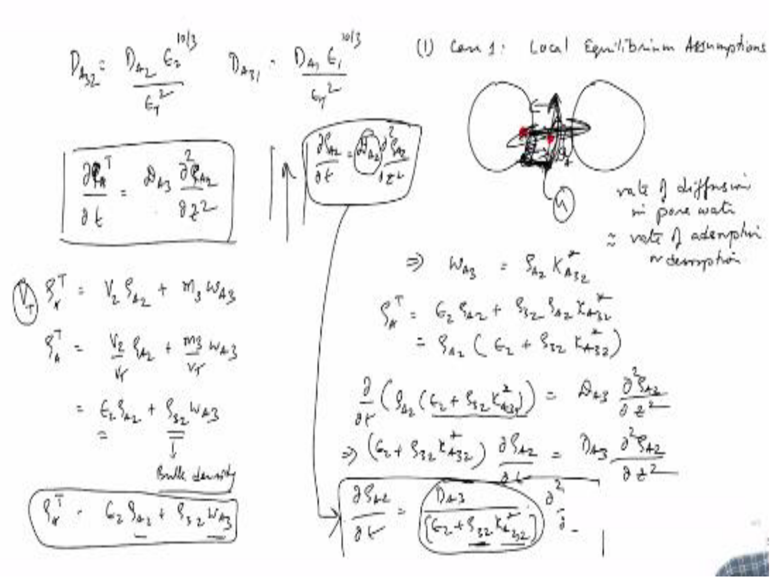

So, the general expression in the Millington Quirk

$$D_{A_{32}} = \frac{D_{A_2}.\varepsilon_2{}^{10/3}}{\varepsilon_T{}^2}$$

$$D_{A_{31}} = \frac{D_1.\varepsilon_1{}^{10/3}}{\varepsilon_T{}^2}$$

There are other equations. So, if you go and look in the literature, search for diffusion coefficients as a function of porosity, there are other equations as well, so the people have devised other, this is a very old.

If you do not have any other equation for your system, you can use this as a starting point. So we now go back to our equation, we now have

$$\frac{\partial C_A{}^T}{\partial t} = D_{A_3}\frac{\partial^2 C_A}{\partial z^2}$$

This is the equation we have, okay. Now, this is a partial differential equation with 2 dependent variables, C_A^T and ρ_{A2}. So, now we need some relationship from here. So, 3 possibilities. There are several possibilities, one of them is the following.

So, rho AT into the total volume, we have said that is mass of chemical in the liquid, so what is that mass of chemical liquid is

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

this is

$$\rho_A{}^T = \varepsilon_2.\rho_{A2} + \rho_{32}.w_{A3}$$

what is this term

ε_2 is the porosity, this term ρ_{32} is what we call as bulk density, we have seen this in our first section.

This is a representation of the porosity of the solid, bulk density, if the bulk density is very high, which means that the porosity of liquid is low, solid fraction is higher. The bulk density is a representation of a solid fraction. It is mass by total volume okay. Now, we have this equation. Now we have

$\rho_A{}^T = \varepsilon_2.\rho_{A2} + \rho_{32}.w_{A3}$

Now we have somewhat split it up, but now still have two numbers here, this one ($\varepsilon_2.\rho_{A2}$) and this one ($\rho_{32}.w_{A3}$) and we cannot put it into the differential equation and solve it, unless we have one more equation that connects $\rho_A{}^T$ to w_{A3}, so there are various options for this, okay.

We need one more equation that connects WA3 and rho A2 in the porous system. So the first assumption we make is:

- case 1:

  this we will invoke what is called as a local equilibrium assumption. These are all simplifications for what could be the real scenario what is happening in the system. Local equilibrium assumption assumes that when a solid is near a fluid, there are these chemicals that are sitting here we and there is chemical here, the rate at which the diffusion is occurring is almost the same order of magnitude at which this adsorption is happening.

So, what it assumes that every point it is here, it equilibrates very quickly, this is exchanged between the solid and the liquid, the fluid, pore water, it is very quick. So, which means this is diffusion. Here also can be diffusion, the mass transfer coefficient associated with the adsorption is also diffusion, there is no flow anywhere. There is no water flowing anywhere, so everything is diffusion. So, therefore, this scale of this one is equivalent to the rate at which this is happening.

So, it is a fair assumption that this is all at equilibrium quickly, it comes here and, not quickly but it is at the same rate. Material will not go from here to here before it comes, it has a chance to come equilibrium. So, let us say I have a velocity here, flow is happening, definitely a velocity is much higher than the diffusion because adsorption and desorption take place by diffusion only, and therefore, if that is happening, then we cannot have local equilibrium assumption.

We definitely have to have some other equations to describe the concentration on a solid surface with reference to the concentration in the pore water, but right now, I can assume it is local equilibrium assumption, I can assume equilibrium at every point because the process is so slow. The rate of diffusion in pore water is of the same order of magnitude as a rate of adsorption or desorption. What does this mean? This means that

$$w_{A3} = \rho_{A2} K^{*}_{A32}$$

So, if you are using a linear isotherm, we use this, most of the nominal cases this is enough, this will be sufficient. So, we take this equation and put it back into this. So now,

$$\rho_A{}^T = \varepsilon_2 . \rho_{A2} + \rho_{32} . \rho_{A2} . K^{*}_{A32}$$

Now, we take out ρ_{A2} here, it becomes

$$\rho_A{}^T = \rho_{A2} . (\varepsilon_2 + \rho_{32} . K^{*}_{A32})$$

This equation now we put it back into this, we have

$$\frac{\partial\left(\rho_{A2}.\left(\varepsilon_2+\rho_{32}.K_{A32}^{*}\right)\right)}{\partial t}=D_{A_3}\frac{\partial^2\rho_A}{\partial z^2}$$

This now becomes, you pull out all of these, so all of these things is epsilon 2 is porosity, then there is bulk density and partition constant. These are not functions of time, if you believe they are not functions of time in the system. When can it be a function of time? They are not function of time means they are not changing in the process at all, then the only way they can change is if something is happening. The bulk density can only change if I add more solids into the system or if I remove water from the system and these thing shrinks.

It is a very fair assumption that this will not happen at the timescales that you are looking at. Sediments will compress that happens, but that happens over very long timescales much longer than. You look at porosity distribution in sediments that there is a change, very deep below you will find very highly compressed sediment and as you come closer to the surface, porosity is slightly larger, but that is now porosity is a function of space, but not a function of time.

So, if it is a function of space, then we have to worry about something else, but for the time being, we will assume it is not a function of anything, it is constant in space and time, we will pull it out. When it comes out of the derivative, now this term becomes, you can write it now as a

$$\frac{\partial\rho_{A2}}{\partial t}=\frac{D_{A_3}}{\left(\varepsilon_2+\rho_{32}.K_{A32}^{*}\right)}\frac{\partial^2\rho_A}{\partial z^2}$$

This is now the differential equation that we can solve. Now, if you look at this differential equation, this term here if I compare this with this term.

The normal simple diffusion equation is

$$\frac{\partial(\rho_{A2})}{\partial t}=D_{A_2}\frac{\partial^2\rho_A}{\partial z^2}$$

normal diffusion equation. If my diffusion occurring in a simple tube, the equation will be $\frac{\partial(\rho_{A2})}{\partial t}=D_{A_2}\frac{\partial^2\rho_A}{\partial z^2}$ this is simple diffusion equation. You compare this diffusion equation to this equation. Several things are different, one is DA3 is there, it is effective diffusion coefficient. This entire term, if you look at the magnitude of this one is very much smaller than this term here for two reasons.

One is DA3 is there. The second reason is in the denominator if you see there are two terms here, ρ_{32} and K_{A32}^{*} okay. This represent the value of K_{A32} partition constant, what does it mean? If the chemical is highly adsorbing, the K_{A32} number is very big, very large, if the K_{A32} is large, it reduces the magnitude of diffusion, it retards diffusion okay and if you also have a large number of solids, it will retard this further okay. You have a very highly adsorbing solid, but a lot of it is not there.

A very small amount is there, which means bulk density is small and your total magnitude of adsorption, removal is slow, small, but if you have a very highly adsorbing solid and a lot of it, this denominator becomes very big, which means the magnitude of diffusion, the rate of diffusion now is slowed down. So the material is trying to diffuse from here to here is not happening fast, it is happening very slowly, because it has to now interact with the solid. So, this is retardation.

The solid acts as a barrier because it is adsorbing and desorbing, material is coming away from here, but it is also not allowing material to diffuse straight through, it is intercepting it. So, this term in the denominator is known as a retardation factor.

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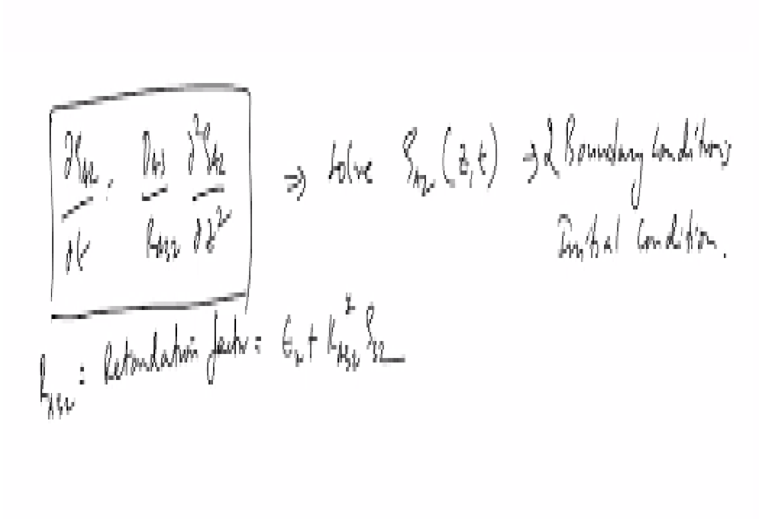

$$\boxed{\frac{\partial \rho_{A2}}{\partial t} = \frac{D_{A3}}{R_{A32}} \frac{\partial^2 \rho_{A2}}{\partial z^2}} \Rightarrow \text{Solve } \rho_{A2}(z,t) \rightarrow 2 \text{ Boundary Conditions}$$

Initial Condition.

R_{A32} : Retardation factor $= \varepsilon_2 + K_{A32}^{*} \rho_{32}$

So, we write this equation as

$$\frac{\partial \rho_{A2}}{\partial t} = \frac{D_{A_3}}{(R_{A32})} \frac{\partial^2 \rho_A}{\partial z^2}$$

R_{A32} called as the retardation factor which is equal to $\varepsilon_2 + \rho_{32}.K_{A32}^*$, so now we have to solve this equation. If you solve, you will get rho A2 as a function of z and time okay. We will see this tomorrow morning, how to solve it different, to solve it, you need boundary conditions and initial conditions, 2 boundary conditions and 1 initial condition. So, you look at what are these and how can we solve this equation, the variations of this equation in different scenarios and then application of this in a soil air system. So, we will see that tomorrow.