Environmental Quality: Monitoring and Analysis
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Lecture – 46
Interphase Mass Transfer – Flux and Mass Transfer Resistance

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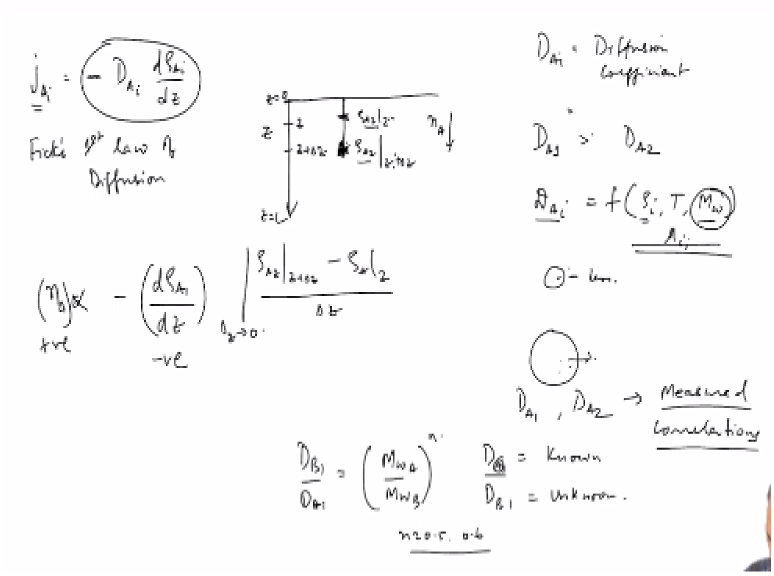

So, the term jA, we had discussed that this is defined by Fick's law of diffusion.

$$j_A = -D_{Ai}\frac{d\rho_{Ai}}{dz}$$

This is very well studied, but it has the same form as what we had discussed last classes, potential difference versus resistance. So, in this, this is a system that we are talking about. This is z, this z is in this direction, So, there is movement that is happening of chemical that is going somewhere okay.

Now, the signage is like this. You see this is negative sign. The negative sign is an indicator of the direction of the flux, so this depends on how you are defining the frame of reference of this thing, okay. So, a lot of times when we do this, so we are assuming, we are defining z in some direction. So, if we are saying that z = 0, and it is increasing, say that equals to L. If I take this point as z and this point is as z + Δz, yeah, but I am looking at flux in the opposite direction. There is a concentration of ρ_{A2} at z and there is a concentration of ρ_{A2} at this z + Δz and z.

So the definition of this is,

$$\frac{d\rho_{Ai}}{dz} = \left.\frac{\rho_{A2}|_{z+\Delta z} - \rho_{A2}|_{z}}{\Delta z}\right|_{\Delta z \to 0}$$

but if you are defining nA in this direction, flux in this direction, this number is smaller than this number, which means that this quantity is negative, yeah. We are going from a higher potential to a lower potential, so, $\rho_{A2}|_z$ is greater than $\rho_{A2}|_{z+\Delta z}$, but the derivative is defined like this, which means $\frac{d\rho_{Ai}}{dz}$ is negative.

But we are saying the flux is, we want to define flux as a positive quantity in the direction of the gradient, we have to put a negative sign here, nA is proportional to negative of $\frac{d\rho_{Ai}}{dz}$, but where nA is positive okay, $\frac{d\rho_{Ai}}{dz}$ is defined in the direction of reducing concentration in increasing z that is the definition that is why this negative sign has to come there. So, whenever we are looking at flux, typically the definition is based on this okay.

So as we discussed D_{Ai} is the diffusion coefficient is the proportionality constant for most part, preliminary things, but now people have figured out what the DA diffusion coefficient, what is it a function of? So, in the last class when we discussed, we looked at DA1 is greater than DA2, which means that diffusion of A in air is greater than diffusion of A in water because there is less resistance in air, where diffusion is seen as a function of drag or resistance.

Less resistance, more diffusion, less resistance happens in the presence of lighter medium, so we are saying that DAi is a function of the density of the medium ρ_i. So, there are other factors in this, it could also be a function of temperature because when temperature increases or decreases, the mean motion velocity of the molecules are all higher, the energy is higher. So, therefore it can influence how it moves, it can overcome it, has more energy therefore can overcome more resistance that is one.

Third part is it is related to the size of the molecule. So, what we are looking at is molecular weight. So, in general the rule of thumb and also measurement show that the molecular weight, so if there is a smaller molecule versus larger molecule, if molecule is huge, if it has to maneuver and go through a certain medium, the chances of this encounters less resistance than this one, this one encounters larger resistance than this one, this is a general observation.

So, therefore, we expect to see that with increase in density, we see this may go down, with increase in molecular weight or the size also, diffusion will go down. These are intuitive things. Then you also have viscosity, viscosity of the medium. Viscosity of course is a function of temperature and properties and all that, so you can actually reduce viscosity to other properties if you can. Viscosity is a flow property so, we do not really care. So, we define diffusion for static fluids.

You know viscosity is there, but density is what we are more worried about, so predominantly that okay, but in correlations that we see viscosity appears in the correlations, as it is also a function of property of the fluid okay. So, a lot of DAi is measured, people measure, so we have D_{A1}, D_{A2}, these are all measured, people have measured. So, in the case for environmental purposes, D_A we measure it through air and we measure it through water, these are the 2 fluids that we are interested in. We are not worried about other things, though.

These are measured and there are also correlations in order to predict. There is also this thing what we can do is if you know the DA of one molecule, for example if I know DA1 is know, D_{B1} is unknown, D_B is another chemical, I can calculate $\frac{D_{B1}}{D_{A1}}$, by using any of these parameters as a scaling parameter. So, the one which we use, the parameter that will matter the most is the molecular weight. So it is the molecular weight versus molecular weight, so we will scale it.

So, we know that the diffusion coefficient is inversely proportional to the molecular weight. So, we are doing the $\frac{D_{B1}}{D_{A1}}$ by molecular weight, but it is not as simple this thing. So there will be some factor there, depending on whether it is water or air, it changes, this functionality n becomes 0.5, 0.6 depending on where we are.

$$\frac{D_{B1}}{D_{A1}} = \left(\frac{Mw_A}{MW_B}\right)^n$$

So, you can use this kind of scaling. So, if you know the D_A of one compound say for benzene I know and I do not know for trichlorobenzene or something, so I can calculate that based on molecular weight.

This of course neglects other effects, you know there may be electrostatic drag forces and all that, but for to know all that I think you need to know enough about system to calculate that, but this gives you a rough estimate. So, those are additional terms that may add on to when people calculate these kinds of things, okay. So, very simply to estimate this diffusion, one can do this.

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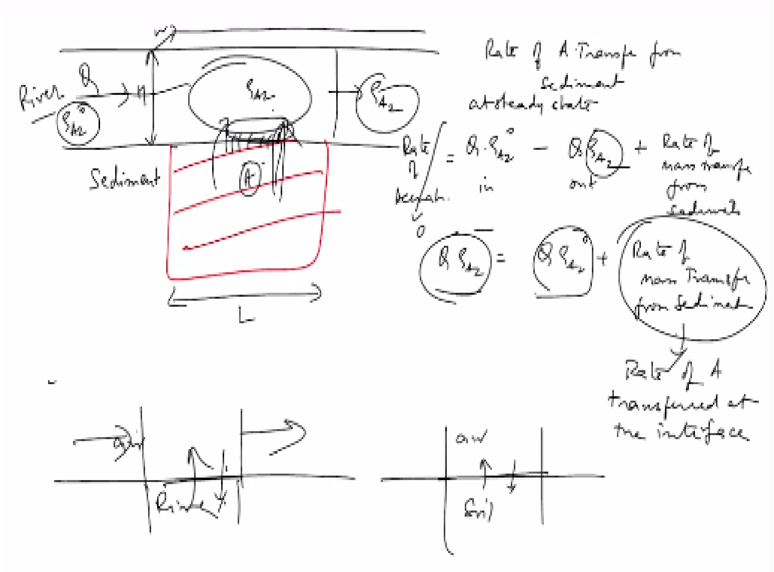

Now, one of our main interest focal points, we will come back diffusion in the soil system later, before that we will do something else which will complete our discussion. So, let us say we are interested in a pollutant, let us say it is sediment, easy system for us to understand, and there is a concentration. There is a region where this is contaminated and now this is in reference to our box model. There is a river and so there is a height of the water and there will be also a width of the water.

There is a certain length where the contamination has happened. Now if I am interested there is A here concentration of water of A. This chemical that is sitting here is a pollutant A that we are interested in. One of the things we are interested in this what is the contribution of this sediment contamination to water quality, is there a change in the concentration of A entering this zone and exiting this zone? Yeah. Typically, if you do a box model, what we are doing is we will assume this entire thing to be one well-mixed volume and then there will be a concentration ρ_{A2}, which is the same as this.

If this contamination is very long, we will do what is called as a plug flow model, where we will take series of boxes okay, that is a little more complicated in this scenario, we will explain that a little bit, but we will not deal with it in a large sense, this is sufficient for scope of this particular course. So, here we need to know in the box model, we need to know what is the rate of A transfer from sediment. This becomes a term in the mass balance in the balance.

So, the overall mass balance we will write this

$$rate\ of\ accumulation = 0 = \underbrace{Q\rho_{A2}^{0}}_{in} - \underbrace{Q\rho_{A2}}_{out} + rate\ of\ mass\ transfer\ from\ sediment$$

we will say rate in equals rate out, there is no accumulation, let us assume there is no accumulation at this time, steady state. At steady state, the rate of accumulation which we are saying is 0, so in this case, this is the equation that we write, mass balance equations for this box assuming there are three things happening.

Something is coming in, something is going out, and something is being transferred from the sediment. So here ρ_{A2} is expected to be greater than ρ_{A2}^{0}.
So
$\rho_{A2} = \rho_{A2}^{0}$ + mass transfer from sediments.

What is coming out equals what is going in plus what is coming in from sediment. What is the general suggestion is that you write the full equation, cancel out terms that are not applicable, so steady state, unsteady state all that and this comes. Now we know these terms, these terms. What is this term, this term rate of mass transfer from the sediment. You have to now calculate what is the rate at the interface? This is now we are getting into interfacial rates. So this is the interface between sediment and the water, okay. Same kind of thing can happen, the same system I can apply to a river and air.

We can take a small section of air or a small section of river and say what is going out of the river or what is coming into the river and what is going in and going out. So in this case, I am looking at rate of transfer across the air water interface. Here, I am looking at rate of transfer across sediment and water. You have a third system we are looking at the same kind of system we are looking at soil and air. We are looking at a rate of transfer across the soil air interface. All of these three things are there.

So, we look at the interface transfer, so this has to be, we are saying rate of transfer, it has to be some combination of velocity and a concentration.

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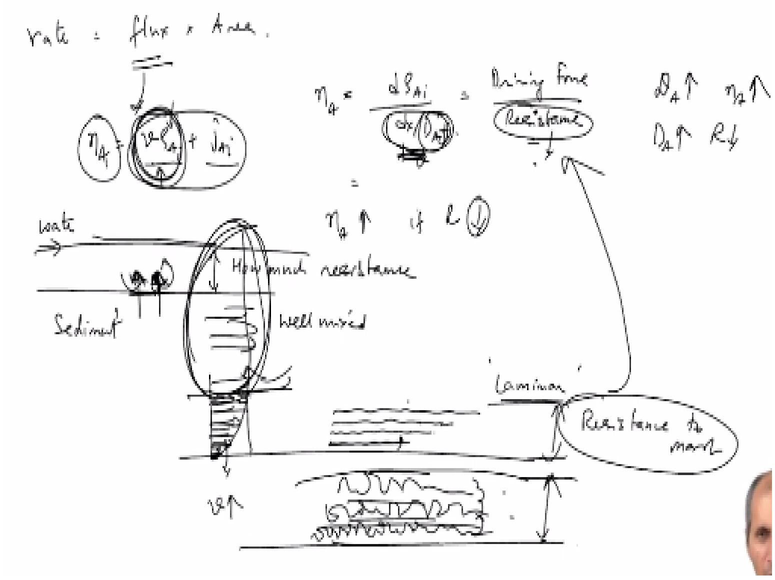

So first before we do that, so the rate usually we will explain as flux into area, yeah. We already defined the flux, $n_{Ai} = v.\rho_{Ai} + J_{Ai}$, we have already defined this, this is the flux, but this direction of the flux we are talking about here is in transverse to the direction of the fluid. So, we have this is the sediment and this is the water, what we discussed in some of the cases there is flow of chemical along the direction of the water flow and all, but we are now interested in this direction.

So, you analyze what is happening to the chemical from this point to this point okay, yeah. So, is there this or this? This is the next question that we ask, can we apply this equation, how do we apply this equation to the system okay. Is there diffusion? Is there some amount of convection, what is there? Okay. So, to help you analyze this, let us say that this water is completely static, is not moving at all, what do you expect will be the mechanism? Diffusion, only diffusion. If there is a little bit of water movement, well this term keeps adding on okay.

So, depending on the amount of so if I then say flux, so we are looking at, now it is a bit tricky, please those of you who have not seen this before. So, we are writing this in terms of

$$n_A = \frac{d\rho_{Ai}}{\left(dx/D_{Ai}\right)} = \frac{Driving\ force}{Resistance}$$

we are saying that this resistance, we are only considering diffusion here, the Fick's law, but if I generalize this, I say driving force by resistance need not be just diffusion, it could be anything. If I add the velocity part, if I add this also, what happens to the resistance, resistance is higher or lower?

So very simply nA flux is higher if resistance is low, yeah. In the case of where you have some amount of convection, the flux is higher, this mass transfer is higher, the diffusion is obviously slower and if I add convection, it is going to keep on increasing the flux. So, if my flux is higher as resistance is lower, which means that if I have convection versus diffusion, this resistance decreases, my resistance keeps on decreasing, okay, which means this term, there is another term, instead of Di I can add another term which increases.

The diffusion coefficient term increases, it relates to lower resistance. The DAi is higher, nA is higher, yeah, resistance is lower. So, in this example what we are saying is that if we add convection, the resistance goes down. So, the point is there is the next question that comes up, why we are asking this question is, how much is the resistance here in this zone? Because we have related no resistance to the scale of convection, so if there is no convection, the resistance is very high because it is only diffusion.

So, the amount of resistance that is there in this case depends on how much convection is there in this region and this relates to, the amount of convection in the water relates to how to the hydrodynamics of water itself, the flow of water alone okay. So, we have to now go back to what we did in the atmospheric thing also, so looking at the surface itself okay. At the surface, we know that there is a velocity profile and if you notice this velocity profile, the way it is usually drawn, right here it is very close to 0.

So, the assumption is as we had discussed earlier that there is friction at the surface and theoretically the water is static at that point. The way we are talking about this is energy is lost into, because of the friction energy is pulled into the solid, and somewhere far away from the solid, there is no influence of this solid surface, here there is no change in velocity, they are all the same, the profile is almost the same okay. So, but there is a region below which there is some certain amount of these things.

Why is the velocity same here? Because the general assumption is that it is all mixed, there is no gradient, which means it is all mixed that is the assumption, there may be a gradient which we are not able to measure, but in general we assume that this region is all well mixed. So this region, it could be very low velocity here, slightly increased, slightly higher velocity and so on. So, there are layers of fluid flow and therefore chemical has to move from one to the other to the other.

So, it is very likely that if you have a gradient like this and if you do not have a gradient, if you have full total velocity, where there is higher velocity you are expecting to see higher. So, one nature of fluid motion if you have a velocity here, it will also induce some amount of, as you increase the velocity, you see there is another concept that has to be introduced that is observed is the nature of the fluid itself.

The fluid flow is very slow, it is seemed to be moving in a relatively straight simple fashion, layer fashion, but you have layers, but according to the profile each layer is moving at a different velocity, but they are moving as a separate layer one over the top of the other, this is velocity 1, 2, 3, 4, so say higher velocity, lower velocity, slower velocity, and so on, but it is moving like this, moving in layers. This is called as laminar flow and is observed physically, there are experiments which people have done, they can see the fluid moves like that.

If you put a tracer in it, it will move nicely. It is not a straight line, but it is almost a straight line as compared to if I keep increasing, if I increase the velocity, the velocity goes up, the fluid start behaving like this, it has local fluctuations like this. So, what happens here is from here to this point, there is no convection, it has to diffuse. Fluid has to diffuse from one layer to the other layer to other layer and there maybe a little bit of convection near the interface, so that will increase it.

As you increase velocity, the scale of convection increases and therefore you have a higher chance of transferring from this to this, this to this, so on and when it reaches this layer, it is well mixes with the rest of it. So, what this is translated to is that there is a region small region next to the surface where there is a resistance to mass transfer. This is translated according to this, the resistance is defined based on what we had discussed here and this resistance to mass transfer depends on the structure of fluid here.

So, it is linked to the velocity profile okay and the velocity itself. The velocity profile is a function of velocity, so it is linked to the velocity itself. We will just stop with this. So, the resistance to mass transfer is based on this. So, here we now have to define a quantity that will link the flux to the concentration gradient. We will define what the concentration driving force is and what the resistance is, we will do it tomorrow.