Environmental Quality: Monitoring and Analysis
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Lecture – 58
Other Mechanisms of Chemical Release From Sediments – Part 1

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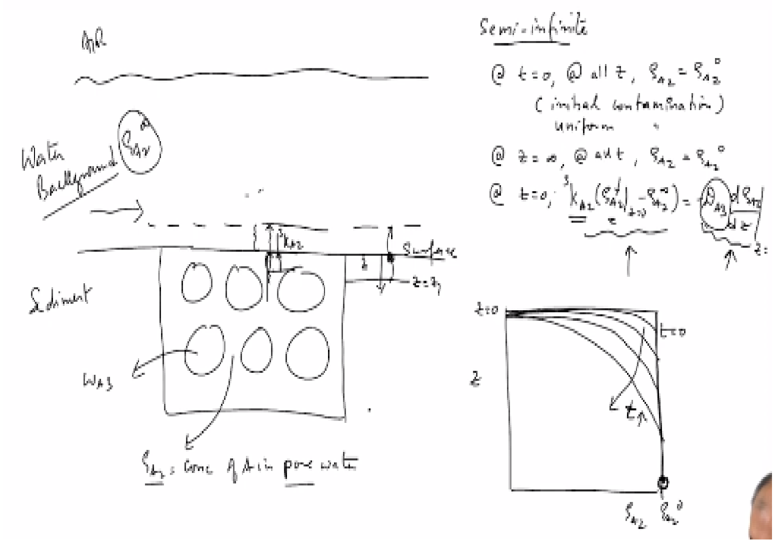

Okay, so we will continue from where we had stopped last time. We will just recap a little bit. We were talking about contaminant transport in sediments. So, last time we looked at a very simple case where the contaminant is uniform, we have a solution for that. In the sediment side we have z = 0 which starts from here. We did the semi-infinite system where we say at time t = 0 and all z, $\rho_{A2} = \rho_{A2}^0$, where $\rho_{A2}$is the concentration of A in pore water.

So, our system is a sediment, this is pore water here. There is ρ_{A2} also in the water, that is also ρ_{A2}, but that is not what we are modeling right now. Our model here is the pore water and this is w_{A3} in the sediment. So, is an initial condition, what this means is that, initial contamination in the sediment $\rho_{A2} = \rho_{A2}^0$ is uniform, it is usually not true, but for this purpose of getting an analytical solution, this is okay.

Then we also have $@\ z = \infty,\ @\ all\ time\ \rho_{A2} = \rho_{A2}^0$, what this means is that very far away from the surface, see the surface is where all the activities, mass transfer, main bulk of the mass transfer is happening. So very far away from here, say somewhere here, nothing is happening.

So, we looked at when we draw the solution to this thing, if you are drawing the concentration ρ_{A2} as a function of height, this is z = 0, this is ρ_{A2}^{0} and this is time t = 0.

Initially the entire thing is at ρ_{A2}^{0}, but as time progresses you will see depletion at the surface and this depletion will then slowly come down. So, you notice that at some z far away from the surface, it is still at initial condition. So, as long as there is some time in the future where this condition does not hold true, but if your analysis is within that time, then it is okay, you can use the semi-infinite boundary condition as long as this part, whichever z you are analyzing and the time that you are analyzing as time progresses you can use the semi-infinite boundary condition to do the analysis. The other boundary condition that we talked about is at z = 0, we said we have ${}^{3}K_{A2}(\rho_{A2}|_{z=0} - \rho_{A2}^{\infty}) = -D_{A_3}\frac{d\rho_{A2}}{dz}\Big|_{z=0}$, where ρ_{A2}^{∞} is the background concentration. This is the steady state boundary condition at the surface.

So this material is coming to the interface by diffusion and it is getting carried away in this region where ${}^{3}K_{A2}$, the convective mass transfer coefficient is in this region, this is all diffusion here okay. So, we are looking at this one small layer across interface little bit on that side, little bit on this side. So, we are seeing that right across interface the material brought into the interface is being carried away at the interface from the other side.

If the diffusion is very slow, however fast the mass transfer it will only carry it at the rate at which diffusion is bringing it okay. So, consequently, this value will change because K_A is not changing, K_A is the function of the convection that side, K_A will not change. If diffusion is very slow and as a result of which let us say there is a concentration at some point, z = to z1, from here to here, to bring it to this point if it takes a lot of time, as a consequence of that, this concentration will be very small.

So, therefore, this flux will also drop down as the result of that. So, the overall transfer rate at which across the interface is controlled by one of these two things, whichever is slower rate, that is usually the rule, it has to happen that way. This boundary condition also is our interface mass transfer that at the interface we said overall mass transfer coefficient and all that. So, we have two resistances here. $D_{A_3}\frac{d\rho_{A2}}{dz}\Big|_{z=0}$ represents the resistance on the sediment side and ${}^{3}K_{A2}(\rho_{A2}|_{z=0} - \rho_{A2}^{\infty})$ represents the resistance on the water side convection.

So typically we will see that the convection is much faster than the diffusion, we expect that, therefore most of the cases irrespective of what the system is, it is diffusion controlled. The rate at which material is going out is controlled by the rate at which diffusion is happening in the system, okay.

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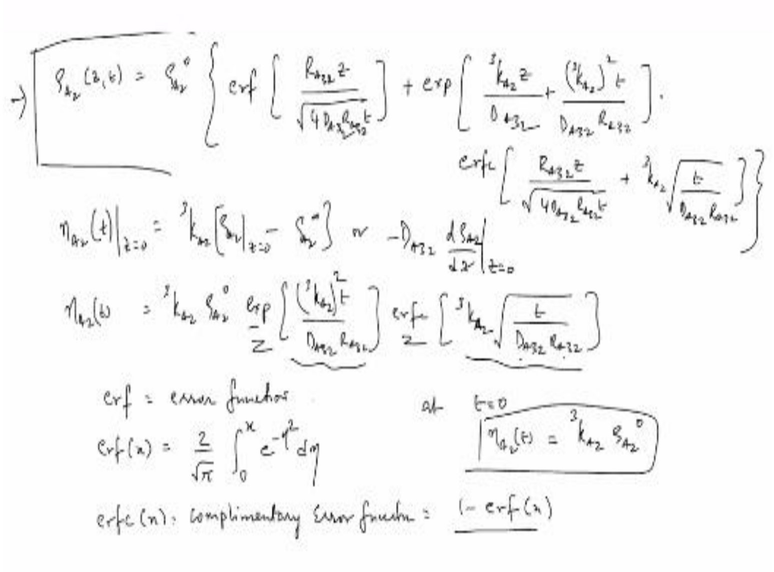

$$\rightarrow \boxed{\rho_{A_2}(z,t) = \rho^0_{A_2}} \left\{ erf\left[\frac{R_{A_{32}} z}{\sqrt{4 D_{A_{32}} R_{A_{32}} t}}\right] + exp\left[\frac{{}^3k_{A_2} z}{D_{A_{32}}} + \frac{({}^3k_{A_2})^2 t}{D_{A_{32}} R_{A_{32}}}\right] \cdot erfc\left[\frac{R_{A_{32}} t}{\sqrt{4 D_{A_{32}} R_{A_{32}} t}} + {}^3k_{A_2}\sqrt{\frac{t}{D_{A_{32}} R_{A_{32}}}}\right]\right\}$$

$$n_{A_2}(t)\big|_{z=0} = {}^3k_{A_2}\left[\rho_{A_2}\big|_{z=0} - \rho^\infty_{A_2}\right] \text{ or } -D_{A_{32}} \frac{d\rho_{A_2}}{dz}\Big|_{z=0}$$

$$n_{A_2}(t) = {}^3k_{A_2} \rho^0_{A_2} \underbrace{exp\left[\frac{({}^3k_{A_2})^2 t}{D_{A_{32}} R_{A_{32}}}\right]} \underbrace{erfc\left[{}^3k_{A_2}\sqrt{\frac{t}{D_{A_{32}} R_{A_{32}}}}\right]}$$

erf = error function

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\eta^2} d\eta$$

at $t=0$ $\boxed{n_{A_2}(t) = {}^3k_{A_2} \rho^0_{A_2}}$

erfc(x): complimentary Error function = $\underline{1 - erf(x)}$

So, we had given a long big solution for this in the last class, I had given you a solution

$$\rho_{A2}(z,t) = \rho^0_{A2} \cdot \left\{ erf\left[\frac{R_{A32} z}{\sqrt{4 D_{A32} R_{A32} t}}\right] + \exp\left[\frac{{}^3k_{A2} z}{D_{A32}} + \frac{({}^3k_{A2})^2 t}{D_{A32} R_{A32}}\right] \cdot erfc\left[\frac{R_{A32} z}{\sqrt{4 D_{A32} R_{A32} t}} + {}^3k_{A2}\sqrt{\frac{t}{D_{A32} R_{A32}}}\right]\right\} \qquad \longrightarrow (1)$$

and the flux is a function of time, we are interested in the surface flux. At z = 0, it is either given as

$$n_A(t)|_{z=0} = {}^3K_{A2}(\rho_{A2}|_{z=0} - \rho^\infty_{A2}) \; or \; -D_{A_{32}} \frac{d\rho_{A2}}{dz}\Big|_{z=0}$$

either of this, but you need to solve equation (1) in order to get the flux okay.

So, the flux is given as

$$n_A(t) = {}^3K_{A2}.\rho^0_{A2}.exp\left[\frac{({}^3K_{A2})^2 t}{D_{A_{32}}.R_{A_{32}}}\right].erf\left[{}^3K_{A2}.\sqrt{\frac{t}{D_{A_{32}}.R_{A_{32}}}}\right]$$

erf is called as the error function, the definition of error function.

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-\eta^2} d\eta$$

And erfc(x) is complimentary error function = 1 – erf(x)

These functions appear in software's, you can use software such as Excel to solve this, the software excels have a toolbox you have to click in add in. If you observe these exponential and the complimentary function terms, they contain the diffusion coefficient R, K everything, all of these things are there. So, the magnitude of these are functions of these coefficients and all. At time t = 0, both of these terms go to 1.

At time t = 0,

$$n_A(t) = {}^3K_{A2}.\rho_{A2}^0$$

the exponential terms and the complementary error function term both go to 1. Error function goes to zero and complementary error function becomes 1.

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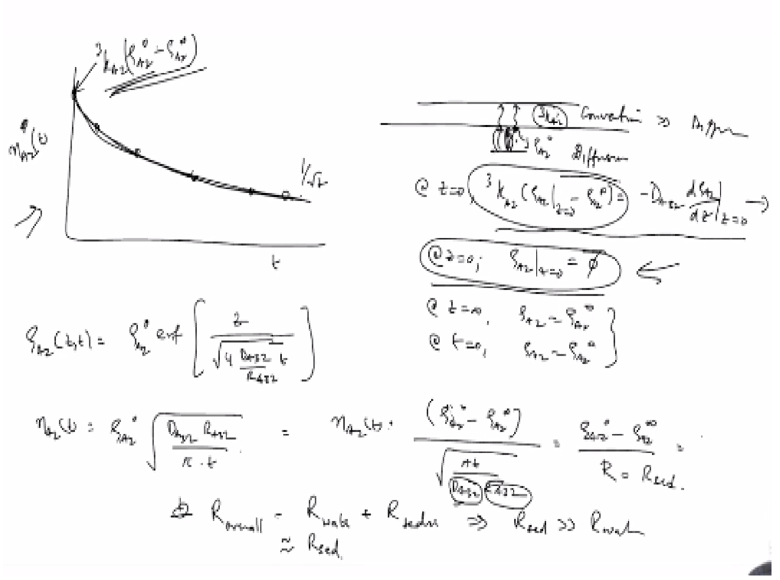

So, as time increases what we expect to see is the flux of nA2 as function of time decreases which means the value is ${}^3K_{A2}.\rho_{A2}^0$, does it make sense? So, you have seen in other cases where we have already done transfer from an oil spill into water or into air where we calculated the flux as this much (${}^3K_{A2}.\rho_{A2}^0$), so does this make sense? So, in the general case, what we will do in the general case is that here we will put ${}^3K_{A2}(\rho_{A2}|_{z=0} - \rho_{A2}^\infty)$, this is what will happen here. So the highest flux is this value ${}^3K_{A2}(\rho_{A2}|_{z=0} - \rho_{A2}^\infty)$, does it makes sense physically? And it is decreasing after that. What does this mean? This means that at time t = 0, there is already chemical available at the surface, so it does not need to diffuse from below to come to the surface. There is already chemical sitting here at the surface at a concentration of ρ_{A2}^{0}. So, if it needs to get out, all it needs to do is cross this resistance which is the film resistance at the surface okay. But as time progresses, ρ_{A2} is now smaller, this is not ρ_{A2}^{0} and material now has to diffuse from below. There is a driving force that is set in. For material to come to the surface, it takes time and therefore this ρ_{A2} starts dropping at z = 0 very rapidly and therefore the flux starts dropping, okay.

To understand this better, we use a different boundary condition at the surface. So, because of this, we have diffusion here and convection here. So, let us say that very small amount of material is being brought to the surface and the convection is very fast, okay. So whatever is appearing here, it gets carried away very quickly okay. If that happens, one of the things that you can do is at the surface instead of using this boundary condition, which is ${}^{3}K_{A2}(\rho_{A2}|_{z=0} - \rho_{A2}^{\infty})$. Instead of this, what we are saying is at z = 0, we are saying that ρ_{A2} at z = 0 is 0. There is nothing there. The moment it comes, it is gone. It is taken away by the convection. However slowly it is coming, it is taken away immediately. So what we are arguing is that this convection is much larger than diffusion and therefore this term dominates in comparison to this, which means that it is a mathematical argument okay, it is not, physically having a zero concentration does not.

We have already discussed that there is nothing like zero, you will never get there, but mathematically it makes reasonable sense in terms of relative rates of how it is. So, this boundary condition is used a lot in different systems. It makes mathematics much simpler. What this will do is then if you do this, the other things remain the same, semi-infinite boundary condition still applies. We are still having that, only the z = 0 boundary condition is different.

Other two, the initial condition and the other semi-infinite boundary conditions are the same, which means at z equals to infinity, we are still saying $\rho_{A2} = \rho_{A2}^{0}$and time t = 0, we are saying $\rho_{A2} = \rho_{A2}^{0}$, these two are same. So this for semi-infinite systems, the initial condition and the far boundary conditions are the same. You can use a similarity transform to solve this equation. We will not get into it here. The solutions are available in almost all textbooks which deal with diffusion, which deal with differential equations, you can go and check it out.

If you are interested in it, I can give you the solution separately. So, if you use this ($\rho_{A2}|_{z=0} = 0$) boundary equation instead of this $\left({}^{3}K_{A2}(\rho_{A2}|_{z=0} - \rho_{A2}^{\infty}) \; or \; -D_{A_{32}} \frac{d\rho_{A2}}{dz}\Big|_{z=0}\right)$ boundary condition, it becomes much simpler using Laplace transform and solve this. What you will get is

$$\rho_{A2}(z,t) = \rho_{A2}^{0}.erf\left[\frac{z}{\sqrt{4.\frac{D_{A32}}{R_{A32}}t}}\right]$$

that is all. So this huge expression becomes very small and then the $n_A(t)$ becomes

$$\rho_{A2}^{0}\sqrt{\frac{D_{A32}.R_{A32}}{\pi.t}}$$

What we are arguing here is this flux equals

$$n_A(t) = \frac{(\rho_{A2}^{0} - \rho_{A2}^{\infty})}{\sqrt{\frac{\pi.t}{D_{A32}.R_{A32}}}}$$

we rewrite this expression in the form of the above.

So, what this means is it is $(\rho_{A2}^{0} - \rho_{A2}^{\infty})$ divided by some resistance. This is some resistance. You see that this resistance is now the only resistance that is there, as virtue of this boundary, there is no resistance of mass transfer in the water side. So, only sediment side resistance exists here okay. So, predominantly what we are saying by this model is, this decrease is only because increase of the sediment side resistance.

The resistance on the water side is 0 or constant and very small compared to, what we are essentially saying is that the overall resistance equals resistance on the water side, the resistance on the sediment side and we are saying that resistance on the sediment side is much greater than resistance on the water and therefore this we are equating it to R sediment, the resistance term is this, and if you notice that this resistance increases as a square root function of time. So, this curvature of flux versus time is approximately 1 over square root of time.

So, the flux is approximately decreasing in that order. So, here it is a bit counter intuitive if you look at it, I understand see this resistance, there is a DA32 term here, yeah. This DA32 term is understandable, so as diffusion coefficient increases, resistance decreases, but this R term is appearing here. This R term, if R is high, overall diffusion decreases right, but diffusion is high, overall transport increases. So this R term seems counterintuitive here okay, but the R also appears in the numerator in the ρ_{A2}^{0} you have to remember that.

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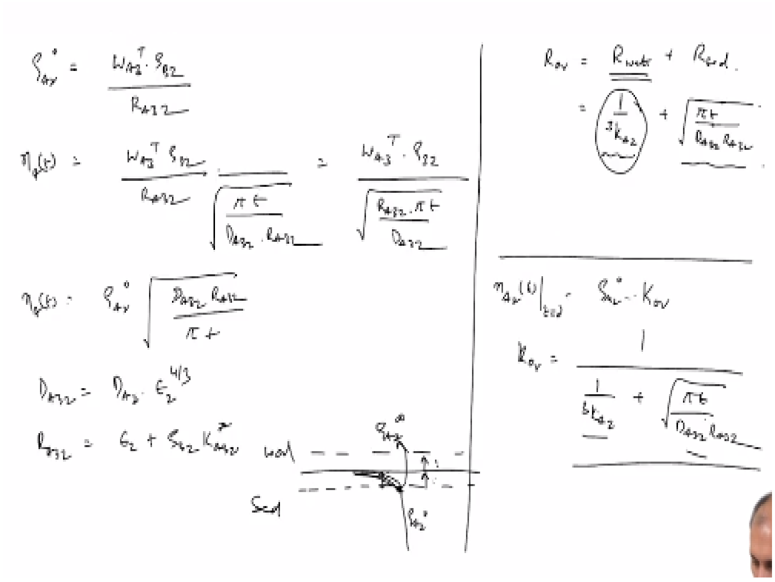

So in the last class we had discussed that the ρ_{A2}^{0} is $\frac{w_{A3}{}^{T}.\rho_{32}}{R_{A32}}$, which means in the flux term if you put this it becomes

$$n(t) = \frac{w_{A3}{}^{T}.\rho_{32}}{R_{A32}} . \frac{1}{\sqrt{\frac{\pi.t}{D_{A32}.R_{A32}}}} = \frac{w_{A3}{}^{T}.\rho_{32}}{\sqrt{\frac{R_{A32}.\pi.t}{D_{A32}}}}$$

now it makes sense. This is now more intuitive. So as the retardation factor increases, resistance increases; diffusion increases, resistance decreases and everything goes away with time. So my suggestion is not to memorize this formula, you keep the other one in mind.

The equation that is convenient for us to use is the following one

$$n(t) = \rho_{A2}^{0}\sqrt{\frac{D_{A32}.R_{A32}}{\pi.t}}$$

Where D_{A32} is calculated by

$$D_{A32} = D_{A2}.\varepsilon_{2}^{4/3}$$

R_{A32} is calculated by

$$R_{A32} = \varepsilon_2 + \rho_{A32}.K_{A32}^*$$

Now if you take this equation, this solution that we have and put it back into the other first one, yeah. For conceptual understanding if I am saying the overall resistance equals resistance on the water side plus resistance on the sediment side and we are assuming in the previous case that the water side resistance is negligible, what if we do not want to do that? Then it becomes as shown in the equation below, this becomes the overall resistance now. To conceptually understand this, $\frac{1}{{}^3K_{A2}}$ is the resistance on the water side, $\sqrt{\frac{\pi.t}{D_{A32}.R_{A32}}}$ is resistance on the sediment side and so this is constant, $\frac{1}{{}^3K_{A2}}$ is not changing. $\sqrt{\frac{\pi.t}{D_{A32}.R_{A32}}}$ is changing with time because of diffusion is an unsteady state process. This is one way of writing this also.

$$R_{overall} = R_{water} + R_{sediment}$$

$$R_{overall} = \frac{1}{{}^3K_{A2}} + \sqrt{\frac{\pi.t}{D_{A32}.R_{A32}}}$$

So, if you do not want to use our error function equation and all that, you can simply use this, but the problem with this is now when we want to use this we are not taking at ρ_A equal to 0 and all that, that does not come in anywhere. You can simply write

$$n_{A2}(t)|_{z=0} = \rho_{A32}.K_{overall}$$

where this mass transfer coefficient overall is

$$\frac{1}{\frac{1}{{}^3K_{A2}} + \sqrt{\frac{\pi.t}{D_{A32}.R_{A32}}}}$$

this is an approximation. Instead of using the error function and exponential solutions, you can also use this.

But the assumption here is there is a region where the concentration is changing, yeah. So, if you take the gradient, there is changing in near interface region, and in the other region concentration is ρ_{A2}^0. What we are saying is from here to a region here, you are taking a mass transfer jump from here to here via through the sediment and through the water film. We are doing a two resistance theory.

What we are saying is it is going from directly from here to here via two resistances and we are simply using the driving force divided by the sum of the resistances, that is all okay. So this is an approximate model. If you have the opportunity, you should use the full model, that is it. You need a calculator to do this, that one needs error function toolbox to do. So, if you do not have that, you want to estimate very quickly, you can simply do this calculation and say flux is going to be this much because it changes with time very slowly, okay.

Because diffusion is a very slow process, you can get quick estimate. So, questions you can answer in this kind of problem is what is going to be the highest flux? What is the highest flux from a contaminated sediment, it is the initial flux, highest flux is the initial flux, all you need is the value of ρ_{A2}^{0} and the mass transfer coefficient on the water side. Then as you go there after 10 days or whatever, what is the flux after 10 days, you can use this equation and calculate what will be the resistance after 10 days okay.

So, what I suggest is you try to plot this, we will give you a problem, in the sense when as a function of time, we will try to see this kind of behavior. Given the problem, we will try to see how the flux changes with time. There is a lot of experimental data for that, flux will change with time, mainly because depletion is occurring at the surface okay. So, now, we will look at a few additional cases.

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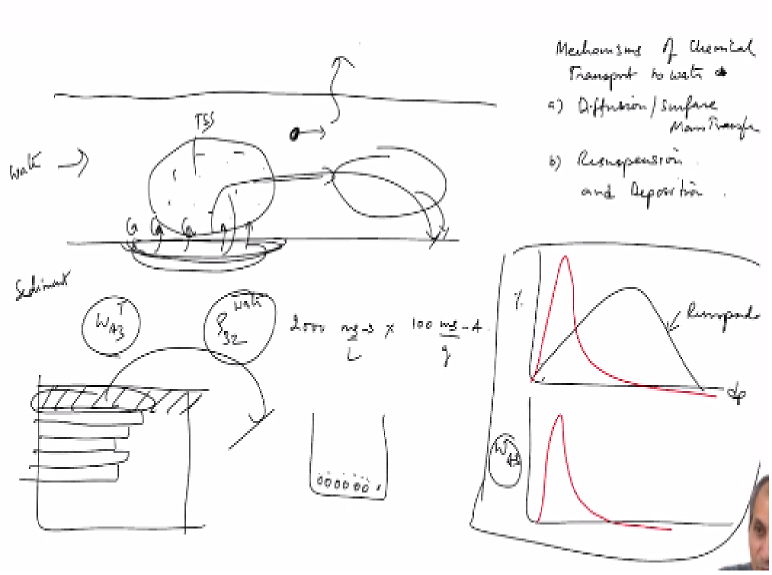

So, what we have now discussed is transport of chemicals from sediment to water by diffusion and surface mass transfer okay, this is the main thing. There are other mechanisms by which chemical can get into water. So, when we do risk assessment if you see that contaminated sediment is there, how do you know that? Because you have gone and you know there is concentration in the water, so you go and check the sediment, you go and take a core and you see that contamination exists in sediment to a certain depth and then you try to estimate what is going to happen if I leave this here for the next 10 years and will that cause damage? So, there is one possibility that you can say that the amount of flux that is coming from diffusion is very small, and if you put this into a box model, it is getting diluted by this water. There is a lot of water flow coming. If you apply the box model, this will get diluted or downstream concentration is going to be very small okay.

Now, the argument will be that leave it alone, do not worry about it, it is not dangerous, let it stay right. Now, we know that it depends on the adsorption coefficient and all that. So if adsorption coefficient is very high, amount of material that is coming, releasing will be very small. So, people do not do it usually and the reasons are the other mechanisms by which chemical can get into the water. What is the other way in which chemicals get into water? Which is actually the most visible way, diffusion nobody is able to see because this a slow process, nothing is happening, is very slow.

So a very visible process, when is it a visible process? When you say that like air pollution, air pollution there may be in this room there may be a lot of vapor phase components which we are not aware of, but we cannot see it. When will you say that this room is polluted, when you can see it, what can you see? What is it that you can see in air or water? Color or turbidity. So, turbidity is a big thing. So, when can turbidity come? What we mean by turbidity here is we call this mechanism called resuspension.

Resuspension is when this surface sediment gets taken away, it gets because of the turbulent action of the water, there is enough energy for it to dislodge this mud from the water and it now becomes a cloud here. The suspended solids, the total suspended solids in water increases and it goes downstream and downstream it can deposit again. So, this layer will go up and it will fall down again. So, resuspension and deposition both occur all the time. When does resuspension occur?

When the normal rivers flow, there is some flow and sediment is static. Resuspension will occur when you increase turbulence. When does turbulence increase? When the velocity of water is increasing. When does velocity of water increases? Flow is increasing. Flow increases during the time of very heavy rainfall, flooding, lot of sediment gets carried, this is what we call as silting. So, sediment gets carried and it floods, it goes over the embankment it drops it, and it loses energy and it drops all the silt. This is what we call a silting floodplain.

A floodplain where all the sediment from the river is getting carried into the floodplain and it deposits there. This is also the reason why we have delta formation and all that. So, when the water loses its ability to carry material, it will drop the sediment. So, this is a problem, resuspension is the problem because when re suspension happens, what is now happening from a way of contaminant transport what happens? You have a large chunk, say we have WA3, WA3 is your total sediment concentration. Now, all of this gets into water, okay.

So, you get TSS total suspended concentration is ρ_{A32} in the water. This is not in sediment anymore, it is water. Suppose you get 2000 milligrams per liter of suspended solids concentrations, how much of this intoWA3, let us say it contains 100 milligrams per gram of A. This is all gone into water now. The water now has an effective chemical concentration of this much okay. But still it has to desorb from the surface. It will desorb then it becomes aqueous concentrations. As a water quality parameter, now it is hazardous enough, so particles can also go into fish and once it gets into fish, it can sit there for a long time. So, this is a very complicated process, this is not as straightforward.

So, when material gets re-suspended, you also have to realize that the adsorption of organic chemical on the solid is in the organic carbon. The size of the organic carbon is colloidal, the submicron. Submicron particles do not settle down fast, so the contamination remains in the water for a long period of time, even if suspended solid concentration goes down these colloids are remaining here. So, let us say if I have a large particle, I have a distribution of particles okay.

What I mean is this, let us say there is a distribution of particles this dp versus percentage, this is particle size distribution in the sediment. The entire thing goes up into water. So, this is the particle size distribution in the suspended water, okay. What I am arguing is the WA3 as a function of particle size distribution is not going to be like this or it is not going to be uniform. Let us say particle size distribution is the same across all particle sizes, which is not true. The particle size distribution is most likely going to be, the particle size distribution the WA3 is most likely going to be like this.

What we mean is that the bulk of the contamination the absorption is happening on the lower particle size because the lower particle size is the organic carbon. All the larger particles are sand, silt and clay and all that which do not adsorb organic chemicals. The lower ones are the ones adsorbing organic chemicals, but they are all lower size. When you re-suspend, the lower size does not come back quickly, yeah. So this is re-suspended yeah, then after deposition, when deposition happens what remains is this (red curve), deposition happens this remains, the size does not deposit very fast.

It takes a long time in the water, especially in rivers, it does not settle down at all, it will take a long time for it to settle down. It will keep going in the water, you can see that. If you take a beaker full of mud, stir it up, it will become very cloudy, you wait for, then stop stirring, it will all settle down, but the water will not go back to its clean color, it will be slightly yellow and the yellow color is because of this colloids, which are there. And if you imagine that lot of contamination sitting in the colloid, the assumption is this collide are not attached to the large particles, that is not, that is again a problem.

So, some part of the collide attached to a large particle will go up and come down with them, but some of them will break free. So in the beginning of the discussion about colloid, organic carbon we had discussed that organic carbon is an amphoteric thing. It is one side is polar, one side is nonpolar, it sticks to the silica and other things on one side, but it is also a function of pH. If the pH changes, it will disengage sometimes. So when the pH is going towards the alkaline, it disengages and comes breaks free.

When it breaks free, a lot of this will remain suspended in the water, it will not remain attached to the solid particles. This is a possibility okay. This is a possibility this impairs water quality quite a bit. So, people are scared of this. You cannot predict when you will have such an event, it is a catastrophe event in the sense it comes and it will destroy the entire ecosystem there and go. It may also do one more thing and in last class I had mentioned that your sediment profiles may look like this.

There is nothing in the top layer and then you will have sediment, you will have layers, you will have contamination which looks like this, nothing in the top layer and then you will have subsequent layers, you may have contamination that looks like this. That is because this top layer maybe clean sediment that is brought from upstream and deposited here, which means that this region must have gone somewhere else, this would have gone and deposited somewhere else.

This is a mechanism of spreading contamination where the contamination was now secluded in say 100 meters square of sediment. Now, it has gone and spread over several kilometers. This is a problem and then so resuspension is a very big mechanism, it is a very complicated process, it is a function of particle size and all that, but there are simple equations to do. So, this is something that we did in our lab, this research because it shows that normally the calculation people do is they assume that the concentration is the same.

The sediment concentration, WA3 is not a function of particle size and they simply make the calculation based on WA3 and the suspended solids concentration. When you do that you underestimate the concentration of chemical part, because if it stays longer in the water, it gets a greater chance to desorb. The particle is now in contact with water, it can desorb. When it desorbs, what can happen next once it desorbs? Once it desorbs, this is solid, it desorbs into water, it can evaporate.

It cannot evaporate until it desorbs, it gets into water, okay. So a lot of times you see that if there is a churning of water in a lake, you can smell some of these things more. You can smell chemicals that have come from the sediment into water, from water they are evaporating now and you can smell. A lot of times contaminated sediments which have a lot of organic waste, on certain days when water is turbid, you can smell it and so this also causes an air pollution risk from this point. So, we will stop here.