Environmental Quality: Monitoring and Analysis

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Lecture – 59
Other Mechanisms of Chemical Release From Sediments – Part 2

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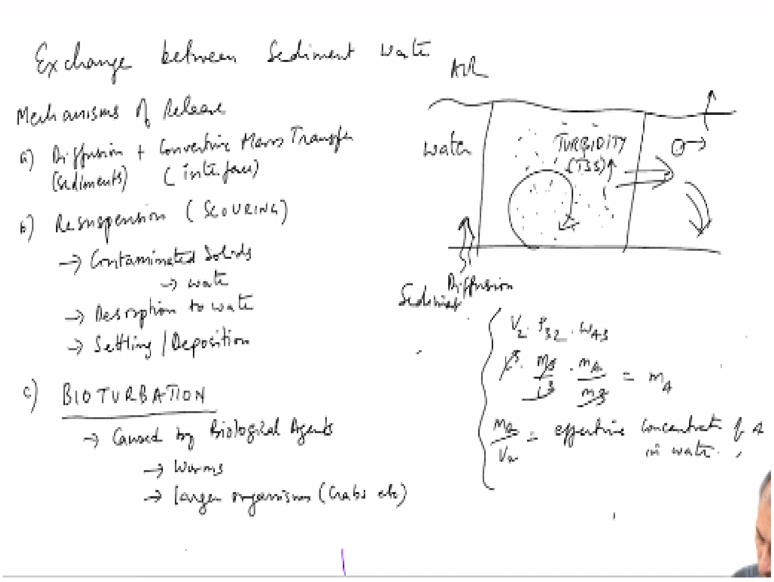

We were looking at the exchange between the sediment-water. So, the mechanisms of release what we had talked about one is by diffusion. So, it is diffusion inside the sediment plus conductive mass transfer at the interface. The second thing that we talked about is resuspension. This is where material can get re-suspended, so solid particles will get into the water and this entire cloud of suspended particles will go downstream. When this cloud of particles goes downstream several things happen.

The contaminated solids are suspended into water and while they are there, the desorption of chemical from the water occurs. Then this particle also settles back. So, when there is a sudden gust of energy, it picks up material and goes into bulk. So, you will see this turbidity or the TSS all increases in the water and then it goes downstream and then it will also deposit back into the sediment. If it is in a lake, it will just sit like that, the system is different. Water quality is modeled differently as we have discussed before.

So, in order to estimate the effect of this, one needs to estimate what is the resuspension that is happening? How much of resuspension happens? That is not in the core purview of this course.

What that means that is more of sediment transport, sediment hydrology, so that depends on the energy, that process is called a scouring. The resuspension is also called as scouring. So it is an energy intensive processor, so it naturally occurs during storms and high flow, high velocities okay.

So, during resuspension, one can estimate, it is complicated process, but very simply one can estimate it based on the loading of the sediment and the TSS. So if you want say in a given volume of water, this is the volume of water multiplied by the suspended solids concentration multiplied by w_{A3}, this will give you m_A.

$$V_2.\rho_{32}.w_{A3}$$

$$L^3.\frac{m_3}{L^3}.\frac{m_A}{m_3} = m_A$$

This will give you the amount of chemical that has now entered the water, but it is now bound to the solid, yeah. So, I can say that the effective concentration of this water, if I take this m_A and divide it by the volume of water, this becomes effective concentration of A in the water. So, we know that it is a combination of both the aqueous phase and the solid phase, but still it is water itself, if you take a sample and extract it, you say this concentration is very high okay. It is something that we looked at during partitioning study where you have a small amount of organic carbon suspended, but the free aqueous phase concentration is smaller.

But if I take this entire water sample and extract, I will get the combination of chemical that is attached to the water as well as on the solid. So, this is what will happen. So, this is the impairment of water quality due to resuspension okay. So, yesterday we also mentioned that the composition, the fraction of solids that have organic contaminant is a lower fraction which tends to stay in the water for a longer period of time. So, it also tends to spoil the water quality over a period of time.

The other consequence to this is once a particle is suspended, it can desorb, it can transfer from the solid phase to a liquid phase, when it comes to liquid phase, it can also go to the atmosphere. So, this is what we considered during our partitioning example. So, this is how it can happen in the real scenario. There is a third mechanism by which chemical can get into the water which is not a very well known process, what is called as bioturbation okay.

So as the name suggests bioturbation is the transport caused by biological agent. This transport of chemicals in the sediment is due to biological agents, but what do you mean by biological agents? Biological agents can be anything that is living on the surface of sediments okay. So, if you look at the different systems, say in coastal, in ocean sea systems, say salt water systems, freshwater systems, and or lake system, fresh water, surface water, it is both freshwater, salt water and this kind of different systems.

You have a large amount of biological life that resides on the surface of the water. So, what are these biological agents? These can be worms, predominantly a lot of worms, lot of worms. Like if you go and look in soil also you can see a lot of worms, earthworms or other kinds of worms okay and there are larger creatures in this thing, in river water there are larger creatures also, which are things like crabs and other things which crawl on the surface of the water, right, and if you look at the sediment structure, the top layer of the sediment is fairy fluffy.

It is not consolidated, it is loose. If you go deeper, it is more consolidated. Soil is very consolidated, because soil has no moisture, moisture content is very small. So it consolidates, it shrinks and it becomes like a hard mass, you cannot put a spoon in soil, but you can take a stick and spoon in sediment you can take out material, it is like a jelly okay. So, other larger organisms like crabs, etc. So, what do they do?

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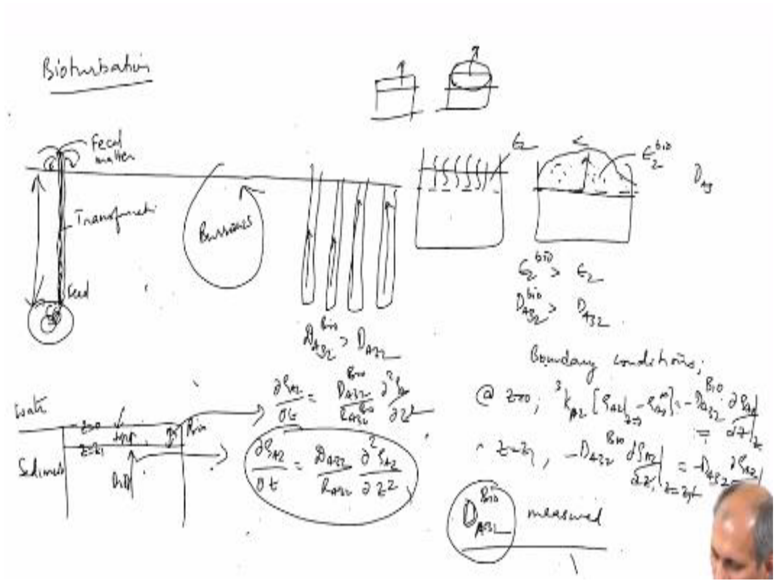

The action of bioturbation itself is different things, so people have observed this action about, how does it affect chemical transport in the top layer? Why are we talking about this because in the absence of resuspension, diffusion is the only way in which chemical can go up. So, if anything that can increase, enhance this transport, okay. How does the bioturbation seen as enhancing? So one of the bioturbators is worms, this worms are creatures that are say from a few millimeters to a few centimeters in thickness, there exist different types of worms.

If you look at sediment and water literature, biological life in sediments, then you will see a lot of variety of worms. So, these worms, they feed in the sediment, head down okay, and they feed and they process the material and they egest it out through the back. What they do is they are feeding at the sediment, the sediment is sent in and the chemical goes in. There could be transformation that is happening in the process, but if this transformation does not happen, what it is doing is it is essentially taking it and conveying it through the body and coming out, egesting here.

So, a lot of times you will notice this is fecal matter of the worms, it contains organic matter and it also contains a lot of whatever is the chemical that is sitting here, so it is a chemical that is picked up from this region. So, this can be a few centimeters depending on the height of the worm. What it is doing is it is serving as a mechanism, it circumvents the diffusion process and directly goes out. So, the processing time of the worm is much faster than the rate of diffusion that happens, that is one mechanism okay.

The second mechanism is this worm goes in and comes out. So, it burrows and then comes out. So, there is a possibility that, what will happen is if I take sediment and I put a large number of worms in the surface, soon you will see that if I take a sediment that looks like this and I put a lot of worms into it, very soon what you will see is this, now this would become a big mound okay. This top region becomes a big mound. What it does is it goes in and reworks the sediment.

When it reworks the sediment, the property of this ε_2^{bio} changes. This ε_2^{bio} is much larger than ε_2, really it worked it up. Basically, it is the equivalent to somebody going and stamping the entire place and disturbing it okay, but they are working through it. So the bioturbators are un-consolidating the sediment, so making it fluffy, so that from a transport point of view if you apply your diffusion equation through this.

This layer contains a much higher porosity, therefore the resistance, the effective diffusivity (D_{A32}^{bio}) of this region is larger than the effective diffusivity D_{A32}, this is another mechanism.

The third mechanism is the worm will come in, burrow down, and leave, so which leaves a tube. You will see this very commonly in sediments, I do not know how many of you had the opportunity to see it. In sediments, you will see that sometimes you see holes in sediments, these holes can be as deep, very deep okay, because the sediment is consolidated.

You can take a mud and then put a stick through it and take it out. Sometimes, it will stay as it is intact, it will not collapse, fall in, if you take sand and do that, the sand will collapse in, but sediment is very cohesive. There is a lot of clay in it, so it will stick there. If you make hole in it, it will stay there, it is like, for example, if you take clay and poke a hole in it, it stays the hole space, it does not collapse back, it is very cohesive sediment. What does this do? This is again equivalent to increasing the porosity in a given region, that is one.

Second is this one is filled with water, there is no solid in this. So, it offers a nice pathway for material to transport. So, again here, the diffusion coefficient of this bio here is again larger than the diffusion coefficient of the non non-bio-turbated system. So, all these mechanisms are responsible for enhanced transport of chemical in a system that has biological life living in it, right. So, now what has happened is if you want to model, you apply our previous model to this, our previous model was very simple system.

We have, this is our domain, this is contamination, this is sediment here and there is water. We are now simply looking at all of this entire region has same property, so we are looking at

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

we are applying this model throughout for z = 0 onwards to z equal to infinity wherever they are going. Now what has happened is there is a layer that is sitting here, there is a bio layer which does not have the same properties as your rest of the sediment okay.

So, this layer again follows the same equation, but this layer does not have the same properties which means that here

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

It has different properties, it has different retardation factor, it has different this diffusion coefficients because of this layer and there is a certain length. So, now the boundary condition will be different, you cannot write this boundary condition like what we wrote earlier.

Now, the boundary conditions have to be written at the interface between the bio layer and the water, this is the interface z = 0 is here and this is z = some z1, yeah. So, the boundary condition here is the bio term that enters here, not the regular one. At z = z1, this is another boundary condition, there is one intermediate boundary condition now because of 2 layers, one layer here and one layer here, both side diffusion is occurring.

There is diffusion occurring here and there is diffusion occurring here also across these two, bio layer and it will be simply

$$-\frac{D_{A32}^{bio}}{R_{A32}}.\frac{\partial^2 \rho_{A2}}{\partial z^2}\bigg|_{z=z1} = -\frac{D_{A32}}{R_{A32}}.\frac{\partial^2 \rho_{A2}}{\partial z^2}\bigg|_{z=z1}$$

Student: In sediment diffusion is slowed in the bio layer no sir.
Professor: Yeah.
Student: Then it should be controlled by that diffusion only no.
Professor: yeah, it is controlled by that, that is a different issue. When you are modeling it, so eventually when you solve the equation, it will turn out to be like that because it will take time for material to come into the top layer.

So, eventually the overall rate will be controlled by how it is coming from below or whatever comes here will go faster. So, if you take two thicknesses of sediments okay, but there is contaminant already present in the top layer, in a system which is undisturbed by bio or system is disturbed by bio, this top layer, this is much fluffier, which means transport from that layer is faster than transport from this layer. That is why the bioturbation maybe larger, may contribute to higher transport.

Once the contamination is gone from that bio layer, below layer now is controlled by the diffusion. So, there is a reason when we use both these boundary conditions, the boundary condition we used last time and this one, but the two boundary conditions are surface, where we say surface concentration is 0 and the surface concentration is flux boundary conditions.

Both of them after a very long time will become similar, the flux will be very high in the first one, because after a longer time, it is more controlled by diffusion deep inside the sediment.

So, in the beginning this flux likely to be higher, which is also again as we are discussed throughout this topic, it does not happen overnight, even contamination of sediment takes a long time, while it is contaminating itself microbes will start their work and so the process of contamination itself will be influenced by bioturbation. So, it is a process that is of chemical going into the sediment also is controlled by it, okay. So, how do people measure this?

It is difficult for us to estimate the actual process and all that, so people try to measure the D_{A32}^{bio} for a given bioturbation layer either by laboratory experiments or by taking field measurements of fluxes. So, the way we do it, again we will get, we use a model and we measure flux and then we use these numbers, we fit the experimental data of flux to these numbers. The advantage of a model is that we are parameterizing this transport process like this, you can use the model to get the parameters, you have set the diffusion based process.

So, DA32 bio is not purely molecular diffusion anymore. It is some process which could be a bunch of things, okay. I do not even know if we can call the feeding process as diffusion and all that. So it is D bio. It is diffusivity, but it is not molecular diffusivity, it is some other diffusivity okay. So, the magnitude of D bio is measured and then depending on the organism or the location of the site, you can characterize it faster or slower or it is the same order of magnitude as the regular diffusion okay.

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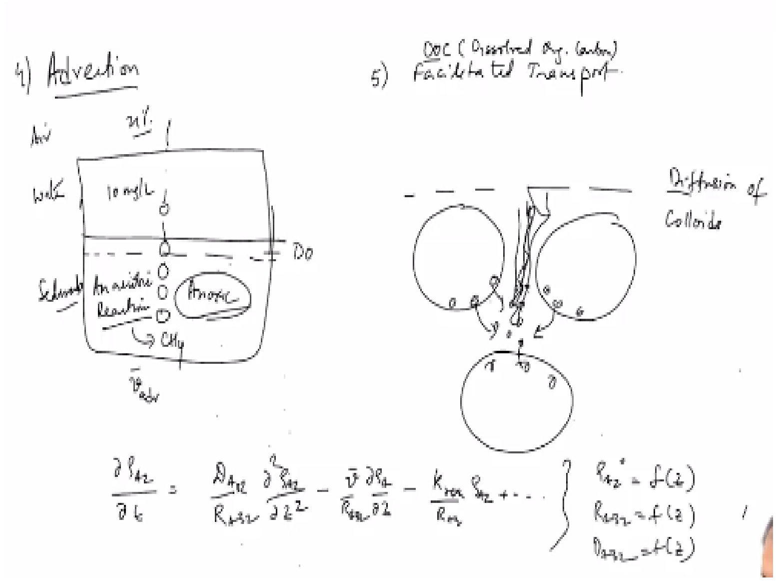

There is a fourth mechanism which can also affect, it is called as advection. Now, advection is bulk flow of material coming out, unlike soil, sediments have very little opportunity of advection. Soils have some possibilities of advection, but sediments are very, because it is already saturated, it has already reached its static equilibrium and all that. There is no way in which material can go up and down. The only reason it will go up and down is if there is something else causing material to go up.

So a lot of times in sediments, I had mentioned this before in one of the earlier classes, there is anaerobic reactions that happen. So if you look at the oxygen profile in the sediments, there is water here. So here, oxygen is 21% in the atmosphere. In the water, oxygen ranges from anywhere up to a maximum of about close to 10 milligrams per liter, the concentration of dissolved oxygen in water. Imagine here oxygen has to diffuse further into sediment okay. So the concentration of oxygen rapidly decreases into the sediment.

So there is a region here where there is some amount of oxygen, some amount of DO is present. Below this it is mostly no oxygen, anoxic. The anaerobic reactions can take place here, bacteria that survive without oxygen can be present here okay and there anaerobic reactions can cause because of organic matter there and then reactions can have happen, there is biological reactions going on. If there is also chemical sitting there that will also undergo biological reactions.

Anaerobic reactions typically result in the formation of things like methane, CH_4 can produce and when CH_4 is produced, where will it go, it is a gaseous phase reaction, it will form a bubble and this bubble will rise up and break through and keep going through this. So, it is a very small process, so you can imagine how much methane is produced by this, quantity is not very large, but what it can do is it can do what bioturbation is doing. It can create a channel, it can create one long channel and you can say the process of methane generation is very slow, but you can calculate an average velocity of advection.

It can be very slow, but it can be faster than diffusion still though. So, when it is going up, it can carry chemicals along with it okay. This is one. Within diffusion, there are very minor things, DOC facilitated transport, DOC is dissolved organic carbon. The hypothesis behind this mechanism is the following. It is a simple diffusion process, but what we are saying is this is a solid, now the organic carbon that is present attached to the solid phase, some of it may disengage.

Why will it disengage? The reason it will disengage is for the same reason why there is anaerobic reaction. So, when there is oxygen depletion in the system, it can result in other reactions that will change the pH, the oxidation reduction potential will change, as a result of this pH can change. When pH changes, this organic carbon, the colloids which are attached to the solid particles can disengage, can come, can release into water. If they release into the pore water, they can travel by diffusion.

Now, this is diffusion of colloids, so this is Brownian motion. Collides, see when you look at the theory of particle diffusion where the diffusion of molecules, they assume molecules are spheres which interact with each other like small particles. These small particles and large molecules, they meet somewhere. So, this theory is coming from there. It is that collides they would not settle down, they have random motion inside and diffusion theory is based on random motion. So, the theory is that this collider will travel up.

What is the danger in this colloids traveling up? These are the ones which are carrying all your chemicals. The entire chemical is sitting, is piggybacking on the colloids. The colloids are themselves moving, you do not have to worry about diffusion anymore, this colloid is itself moving up, so it is facilitated transport, but this occurs only under certain conditions. It does not occur always because collides as we have mentioned organic carbon has both organic and inorganic groups.

It is very likely what may happen is it may come, get released from the lower part and come and adsorb again on the top layer somewhere, okay, so this can happen. So if you want to add this into your transport model, you have to assume that there is certain amount of concentration of colloids, you have to model colloids as a separate phase, as a separate entity, and that is moving through okay, so the concentration of A, the chemical associated with the colloids is different from the concentration of A in the pore water itself.

So, we won't go into the details of modeling that, but that is something that people have worked out. So, this sediment transport is fairly complex because there are a lot of things that are happening in sediment and problem with sediments again is sediments at different locations are very different. If you look at sediments in coastal regions along seacoast, there is very little organic carbon, it is all mostly sandy. If somebody dumps, in India large number of industries are located on the coast.

If somebody dumps a waste, it is going to sit on these sand, it is going to go down. It does not adsorb. There is no adsorption in organic layer, it is sitting as pure chemical. Dissolutions are very different, profiles are very different from if it is in a river or a lake which has a lot of organic carbon and a lot of clay, which affects its fate and transport into the sediment as well as its release from the sediment later on, okay. So these are all very complex issues related to the biogeochemistry of the region, okay.

Addition to this, so if you look at the general process, we have now

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

this is diffusion. I can add advection, I can add reaction, this is a biological reaction or some reaction that is taking place. So, the reaction also will have the RA32 term come here, rho A2, so on, so other things, you can have a few other things, whatever is happening here. In sediments there is no evaporation.

So you can write this entire equation, you can write it in 3 dimensions if you want, you can write in whatever dimension you want. The equation become big and you can then solve it happily using whatever technique you know, I am not going to discuss it here, that is a mathematical problem at that point. You have to find out whatever mathematical tools are available. A lot of times when you get into the systems where in the natural system I mentioned that ρ_{A2}^0 is a function of height.

It is not uniform, that itself will make it impossible for you to do analytical solutions, so you have to do it numerically, numerical solutions are the only way possible. In addition to this, RA32 is also a function of height, DA32 will also be a functional height assuming that there is no function of time, so it is function of height fine, function of time another problem, but typically function of time we do not consider that much because the process is so slow. You are predicting it for a long period of time.

So, we will do some simple examples from the problem sheet. I will give it next week to see what do you get, simple models, what kind of data can you get out of it and how you interpret the data and work on it.