Environmental Quality: Monitoring and Analysis

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Lecture – 55
Contamination of Sediments

So, today we will continue from what we were discussing yesterday. The application of mass transfer in the environment, one of the yesterday’s and the last 2 classes we were looking at interfaces where there is a fluid. So, now we look at a case where there is a solid.

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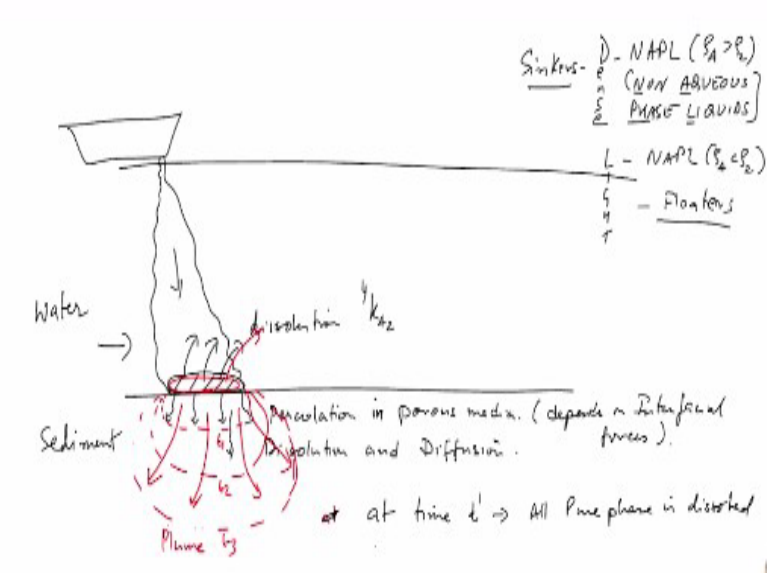

So, specifically what we are interested in is this system where there is a sediment. One is a solid phase, the other one is a fluid phase. So, it is sediment, water or soil, air systems. So, both of them are somewhat similar, but we will start with sediment water, it is the simplest system in terms of what happens. So, in yesterday's class we looked at one example where there was a spillage of material. A chemical which sink down and lands on the surface of the sediment. So, these are what is called as dense NAPL or dense non-aqueous phase liquids.

So, these are abbreviations that are commonly used in the environmental jargon, NAPL is a non-aqueous phase liquid, it can be anything, oils to insoluble chemicals. These are all things that will form a separate phase in water. Things like many other chemicals are under this kind. So, D-NAPL are those chemicals which are dense and then there are L-NAPL which are light. So, again as we discussed earlier, in D-NAPL the density is greater than density of water, for L NAPL, here the density is less than density of water.

So, D NAPL are also called as sinkers and L NAPL are also called as floaters. As the name suggests, if there is a spill, the light NAPLs will float on water and therefore their fate and transport is different from that point of view of the sinkers. D NAPL will sink and they will land on the sediment and from there, their fate and transport is from that point of view and is further calculated. So, what happens to this sinker because this is at the interface of water and sediment?

So when it enters here, one of the things that does happen to the sinkers, is that the dissolution starts taking place straightaway. Water is flowing, away, but it is also traveling inside, because there is a gradient. So, how does it go inside, is based on two mechanisms. One of the problems in this thing is that it will sink, but there is a sediment here which means that if it wants to displace the water it has to now go to this pores and there is a lot of surface tension when it comes to the small pores hence the water will not allow the material to just sink in nicely. It takes a lot of resistance effort to do that and therefore, many of these chemicals do not. They find it difficult to get into, depending on the surface tension between these 3 systems, between the water surface, solid and the other chemical. It may not percolate into the sediment; it may just sit on top of the sediment. So, when that happens, then there is dissolution occurring based on the mass transfer rate that we looked at yesterday using $^4K_{A2}$ equation, and it spreads downwards, mainly again by dissolution, not by percolation.

So it may happen, percolation may happen, but not necessarily okay. It may just spread by dissolution. So two possibilities are there inside here. If percolation is possible, it will do percolation in porous medium. It is very hard especially in the presence of water in a pore provides lot of resistance for displacement. There is no place for buoyancy driven or density driven displacement, difficult for this to happen inside porous media, so it requires a little bit of external energy for this to happen.

So sometimes it may not happen, it will just sit there, on a surface based on interfacial forces. The other possibilities, which will definitely happen is, dissolution and diffusion into the sediment. So over a period of time, what can happen is you start with this big spill on the surface and over a period of time, this spill can spread. Over a period of time it can spread, there is no chemical, there is no NAPL here, this is just a spread, this is like a plume again.

We are calling this a plume because it marks the boundary of the chemical concentration, as it is similar to the plume we have in the atmospheric dispersion. Now, here the boundary is a plume of dissolved concentrations. Because the chemical is dissolving in the water and it is diffusing slowly and it is spreading. So, over a period of time at T1 you will find little, T2 you will find more spread, T3 you will find even more spread, and therby it is spreading out. So, it will spread out in the manner such that a pure chemical here is spreading out and pure chemicals are also dissolving.

So there may be a point of time in the future, say at some time let us call it t'. Hence all the pure phase is dissolved and there is no more pure phase. So, when percolation is happening, it is also accumulating on this solid surface. It is adsorbing on the solid surface.

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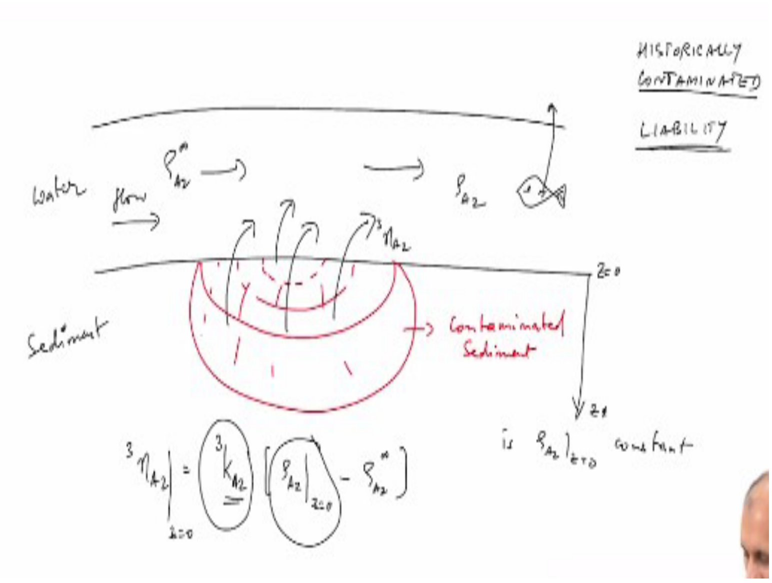

So, at that point in time, the system now will now look like such that, this is water and there is a large section of contaminated sediment that is sitting inside here. There is no pure chemical, all the pure chemical is gone, either pure chemical is gone into the water or gone into the sediment as in this case. So, this is the boundary of contaminated sediment, that is a different concentration. You will find different concentrations as a function of depth inside the system and this is a contaminated sediment volume. Hence it takes a long time for this to happen.

So at this time, there is clean water flowing. Now what happens? This contamination has happened over a period of time, water has been a contaminated, all the pure chemical that was here has gone away. Now, this chemical start going out. To reach this point, it takes a long time because it is diffusion driven and the dissolution is a very slow process. So, this is the reason why we call it as historically contaminated sediment and these things have a contaminated site.

When we invoke the word history, it means that very long back, we are saying 2 decades, 3 decades and all that. So the consequence is that sometimes when something may have been contaminated 30-40 years back and it is still there and it is causing an effect now, there is an aspect of liability. The liability is who is responsible for this, somebody is responsible for this, whoever it may be may not even exist right now.

So they have gone past, some corporation has done this 40 years back when there were no regulations, and now we have to deal with it. So, this liability is a problem and therefore what we should do about it in terms of cleaning up the site and all that then becomes a big issue. So, there are a large number of scenarios in the world where this contaminated sediment is a big problem because usually this contamination takes so long to spread, and it is very difficult for people to see that it is being dumped somewhere. So, under water, you cannot see. You think everything is fine. When will you see it? You will see it when there is a concentration in the water downstream and there are fish are something which are accumulating. Concentration in these any of the receptors is high and if people do fishing and they have problem and then they will realize what is going on. So, if there is a contaminated sediment site, how do you model this flux? We are interested in the flux at the surface.

We are interested in ${}^{3}n_{A2,}$ flux into the water with an interface with the sediment. Now, how do you define this flux? In the same way as we have defined the other systems so far.

$${}^{3}n_{A2} = {}^{3}k_{A2} \times \left[\rho_{A2}\big|_{z=0} - \rho_{A2}^{\infty} \right]$$

ρ_{A2}^{∞} is the background concentration in the river. So there is some amount of flux that is coming here, this is going here and so this concentration (ρ_{A2}) will be the combination of these two using the box model. This term (${}^{3}k_{A2}$) we looked at a yesterday's class, lot of correlations, you can take one of them and use it. What about this term ($\rho_{A2}\big|_{z=0}$)? What will be this value $\rho_{A2}\big|_{z=0}$ be?. We are defining z = 0 here and z keeps going on, increasing in the downward direction.

So as z = 0 is the interface between sediment and water. The flux is defined there. This is the flux at a z = 0, it is defined as this because we are interested in this flux in the box model. So, what is the nature of the flux at $\rho_{A2}\big|_{z=0}$, how do we estimate it? First question, is it a function of time, is it constant? Can you assume it is constant? No, why? Because it is diffusing into the water, so it is going away, but if this goes away, something is coming from below can replace it.

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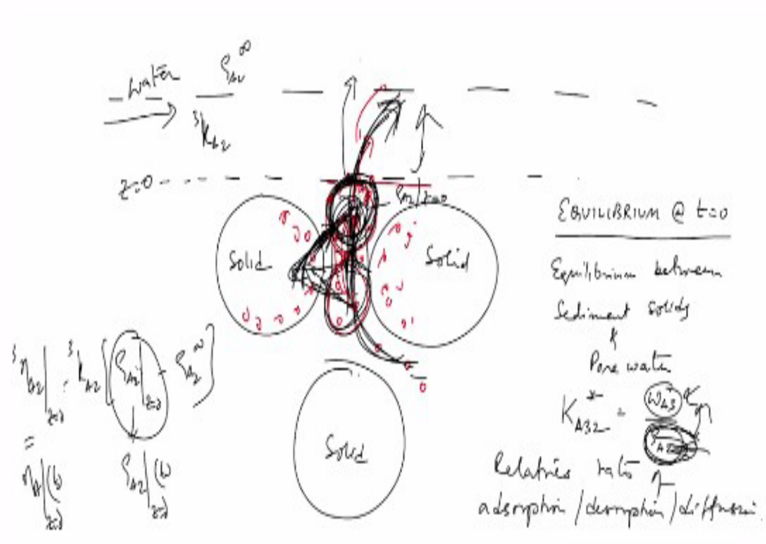

So if you look at the process itself, this is sediment water interface, we are looking at, I have expanded the view of this, this is the water flowing. There are these molecules that are sitting here. This is pore water. This is where the diffusion is occurring in the pore water, this is the solid. So, from this point this is z = 0. So, there are some ρ_{A2}^{∞} here, let us assume that is 0 for the time being. So, there is a big driving force between this and this.

This is a large number here and this is almost nothing here. So, there is the small $^3k_{A2}$ in this zone. So, from here to here, it takes the mass transfer coefficient and jumps into the water okay. What happens here in the zone that is between these two solids, what are the processes that are happening? Because there is a gradient, some of these things go away into the water, then what happens here? There is a reduction. So to begin with, when this happens, when these things move away into the water, what happens then?

Concentration gradient. You are saying diffusion is occurring from here to here. This mass transfer is occurring from here to here, through conductive mass transfer. Then? the amount here reduces which is some of these materials go away, what happens then? That drives. That drives material from here to here, what is the assumption, you are saying that this will go here, which means a at the beginning what was the scenario? Why will this go from here to here now? Concentration gradient.

Which means if you are saying now there is a concentration gradient after some material has moved out, what does it mean the beginning? It was in equilibrium. So you are assuming equilibrium to begin with. This is really not a realistic scenario, okay. There is no equilibrium at the beginning. The beginning is when things started, the chemical was dumped the last time t = 0. So it was never at equilibrium, it is always going in. We are saying it is going in and then it is coming out, all these things are happening. If you are going to model this mathematically, you need to make some assumptions. These assumptions are based on our whatever information we know about transport processes in the system here. So, if we assume equilibrium at t = 0, we are also assuming equilibrium between the solid and the pore space. So, we are assuming that, whatever is there in the pore space is in equilibrium with whatever is there on this solid.

So, there is some amount sitting on solid. This is sediment solid, what is the equilibrium between sediment solids and the pore water? How do you describe the equilibrium between sediment? What is the description of this equilibrium between sediment solids and pore water? How do we define this? How would you describe the equilibrium between sediment and pore water?

$$K_{A32}^{¿}=\frac{w_{A3}^{'}}{\rho_{A2}}$$

where there is this concentration in the sediment and this is the concentration in the pore water in that system, this is equilibrium that we are talking about.

In the beginning, we are saying this is all in equilibrium and then driving force starts going in the reverse direction. so we are saying that over a period of time, so in our equation when we are writing

$$ {}^{3}n_{A2}\big|_{z=0} = {}^{3}k_{A2} \times \left[\rho_{A2}\big|_{z=0} - \rho_{A2}^{\infty} \right] $$

which this equation we have written. The only way that this flux is going to be constant at this $\rho_{A2}\big|_{z=0}$ is if the rate at which it is getting out is equal to the rate at which stuff is being brought in. For that, diffusion has to be of the same order of magnitude as what is going out in this case, right. Usually, it is not true because this is a very slow process, material has to come out. Additionally, what is happening is material is not allowed to go out here. When material is lost from here, it is in non-equilibrium state, where there is only some initial concentration which is in equilibrium with the solid.

The moment it leaves, this equilibrium is disturbed, so this concentration is reduced. This concentration is reduced which means that from the solid this desorption will occur. Desorption will occur to replace whatever is there here and then material from below will then absorb onto this. When this equilibrium is disturbed, all these things are happening and then therefore there is a gradient that is always set up. A material from below here cannot go and replace this, it is going here, then it is going here, all these things are happening.

As a result, it is usually, for us to keep this constant which depends on the relative rates of adsorption, desorption, and diffusion because this process is faster than the rest. Mass transfer at the interface is happening at a much faster rate. The moment it appears that, it can get carried away and then it has to wait for material to come. So, what happens is that these processes are slower. So it is an unsteady state process. This is a function of time, at z = 0 it is really a function of time and because this is a function of time, the flux also becomes a function of time.

It is not a constant flux, it is only constant if material is being supplied to the surface as quickly as it is being taken away that steady state, this is unsteady state because it does not happen. So, depletion occurs, as a result of which, this lag behind. The supply of material to the surface lags behind this one, okay. So, accumulation is slowing down, material is being not being brought in as quickly as it is being taken out, so it is unsteady in state that way.

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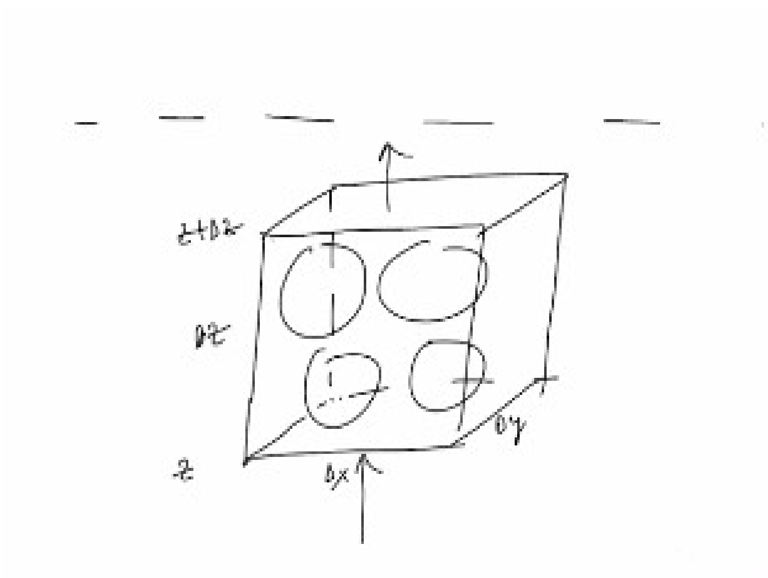

So, in order to model this system, we need to calculate what is the composition, what is the value of $\rho_{A2}\big|_{z=0}$. So, we will look at the system for modeling. So, we take a control volume approach to this. So, we take again like the box model, inside the sediment. So, we take a box inside the sediment. This is the sediment interface. So, we take a box inside in which there are solids and we are saying and this is z and this is z + delta z, this is a delta x and this is delta y.