

**Environmental Quality: Monitoring and Analysis**  
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**Lecture – 53**  
**Evaporation from Different Surfaces**

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Application of Convective Mass Transfer

a) Spill of DNAPL (Dense NAPL)  
 $S_A > S_2$   
 Estimation of flux from Sediment  $\rightarrow$  water.  

$$m_A = \frac{1}{2} K_{A2} (S_{A2}^* - S_{A2})$$
  
 $S_{A2}^*$  = solubility of A in water.  
 $k_{A2}$  = stream MTC

We will continue from where we left last time. We were looking at the application of the different mass transfer. We looked at one or two problems in last class, we will look at more. So last class, we looked at one case where we had a lake system and then we looked at what will happen, how do you apply that, so we will look at now something else. So, we look at a system that such as a river okay. So, in a river, again the problem is stream. So, normally we call this a stream. Stream is a flowing water and we have air and we have sediment there, 3 possibilities here.

So, we are in order to apply it in a box model, I think we have divided this again into segments and we discussed that. So, for the time being we will only look at one particular box that we are not going to be predicting what will be the concentration downstream, 1 kilometer away from the system and all that, so that there is not the scope of things, but we will see how that is also done okay. So, in this kind of system, one very interesting thing is if you take a simple problem, one scenario could be say there is contaminated sediment and we come to this scenario a little later.

So, let us say that there is a case where we start with a sediment. Let us say that there is a spill just as what we saw, in the last class, we saw the case of what happens in land, the spill on the land, this can also be a spill on the sediment. So this is the simplest case. So let us say that there is a barge that is dropping chemical and this chemical is what we call as a dense NAPL, DNAPL or a dense non aqueous phase liquid. The problem itself can be stated as spill of DNAPL. Dense NAPL is the chemical, it says the density of chemical is greater than the density of water.

So there are many chemicals, chlorinated chemicals, and many of them have densities are greater than that of water. So if you drop it into water, it will go down to sink very quickly and it will settle down on the top of the sediment and from there mass transfer will occur over a period of time. So if a river, there is a river that is flowing, so it is very easy for us, convenient for us to consider the section as a box and mass transfer is happening into this section and then going into the next section and so on.

But when it gets to the next section, there is possibility that this will now get transferred back into the soil. So, we will look at that later and that that is a complicated process. So over a period of time what happens that we will see in a minute. So we will look at just this process as an example of extension of what we derived in the last class. So, spill of dense NAPL and now we are interested in estimation of flux from sediment to water okay. This is again like last class what we did, the flux will be  $k$ , this is  $k$  of  $A_2$  from 4 multiplied by  $\rho_{A_2}^* - \rho_{A_2}$ .

This we will call it as  $\rho_{A_2}$ . So this is  $\rho_{A_2}$  which is essentially coming from this previous section  $\rho_{A_2}$ , you can give it any name you want, you can give it  $\rho_{A_2}^{\infty}$ ,  $\rho_{A_2}$  previous one whatever. So, we will call it as  $\rho_{A_2}$ , because this will result in a new  $\rho_{A_2}$  which is representative of this section. So this is  $\rho_{A_2}$  which is this is  $\rho_{A_2}$ . So this  $\rho_{A_2}^*$  is again, because this is pure phase we have written this down because it is mass transfer in the water.

This is in the water, this region in contact with 4 which is pure chemical okay. So therefore, this will be the solubility of A in water, just like what we considered in the last example where we spill something on land and it does not go into soil staying as pure chemical, this  $\rho_{A_1}^*$  in the last class we talked about is the vapor pressure of A, this is the equivalent

of that in the soil, and then this mass transfer coefficient  $k_{A24}$  is now is a stream mass transfer coefficient.

In the sense, this is not the same mass transfer coefficient as what you would see in an air water interface, this is not the same as, see there is a  $k_{A1}$  there is a  $k_{A12}$  here and this is  $k_{A24}$  here, this is what we are talking about. We are talking about a pure chemical sitting here and we are talking about  $k_{A24}$ . This is different from this, it is not the same and the correlations are very different because this system is different. It is a body of water that is moving over sediment.

This is air which is going in whatever manner that is okay. So, the problem now becomes selection of, then this is all it is, this equation is fairly well set. The problem now becomes the selection of the mass transfer coefficient.

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**Natural surface liquid-phase coefficient: (LAKES)**

Lakes  $l/h > 50$  correlation for ethyl ether

$$({}^1k'_{A2})^{(n)} = 0.094 v_x^2$$

$v_x$  velocity (in m/s) measured at 10 m above the surface. The coefficient is in cm/h and is from wind data of  $v_x = 5$  to 16 m/s. Generality of mass transfer equation along with  $n = \frac{1}{2}$  should be used to convert to other volatile substances.

**Natural surface gas-phase coefficient: (LAKES OR STREAMS)**

Evaporation of water from reservoirs

$$({}^2k'_{A1})^{(n)} = 358 v_8 A_r^{-0.05}$$

The coefficient is in cm/h and  $v_8$  is wind velocity at 8 m above the water surface (in miles/hr) and  $A_r$  is the surface area of reservoir (in acres). Generality of mass transfer equation along with  $n = \frac{1}{2}$  should be used from water vapor to other volatiles.

So we will look at a set of mass transfer coefficients that we can look at and there are many mass transfer coefficients. A limited list of this is given here. For example, look at natural surface liquid phase mass transfer coefficients, this list is there in your webpage. So, you look at this correlation, it straightaway says that that lake  $l$  by  $h$  is greater than 50, correlation for ethyl ether. So right here, some information already given, length by  $H$  is this is a lake which is a very shallow lake, which means the length is 50 times the depth and it is made for ethyl ether.

How do you know that it is only applicable for ethyl ether here because in this correlation, this is the correlation KA21, so waterside correlation for evaporation into air. So, from the correlation side we can see there is KA21. So, it is a waterside correlation in contact with air, water in contact with. So it is at the air water interface, but the water side coefficient, n is for natural, do not worry about that, that is not relevant for you. It is taken from one of the books, but it says the correlation is just point, it is  $0.094 v_x$  square, okay.

There is only one factor that is listed in this coefficient, this correlation which it is velocity. So velocity and this is the velocity of air, not velocity of water, the velocity of air okay. It is a water side coefficient, but it is the velocity of air that is given. So it is wind driven turbulence correlation and it is for shallow lakes. It is actually not very accurate because  $l$  by  $h$  can be anything, I can have  $h$  of 50 meters and  $l$  can be 2.5 kilometers. It is still a deep lake. So it is a bit of, it is not a good correlation in my opinion, but that is the best, somebody gives you a correlation like this, this is the only thing you can use.

So, two things directly you can see that there is nothing else in this correlation. There is no length parameter, there is no compound specific parameter which means there is no diffusion coefficient nothing. So, this is only applicable for whatever the conditions they are given, for lakes for this  $l$  by  $h$  greater than 50 and it is for ethyl ether and the data is only valid if the velocity is between 5 to 16 meters per second okay. So, now what if you want to apply for one of our problems.

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$$N_A = k_{A2} [S_{A2} - S_{A1}^0/H]$$

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$$\frac{1}{k_{A2}} = \frac{1}{k_{A2}} + \frac{1}{H k_{A1}}$$

$$N_A = \frac{M_A}{L^2 T} = \frac{L}{T} \left[ \frac{M_A}{L^2} \right]$$

$$k_{A2} = 0.094 v_x^2 \quad \text{Ethyl ether } k_{A2}$$

$$v_x = 10 \text{ m/s}$$

$$k_{B1} = 358 \frac{v_x^{0.5}}{m} \quad \text{Water vapor } k_{B1}$$

$$M_{A1} = 78$$

$$N_A = k_{A2} [S_{A2} - S_{A1}^0/H]$$

So let us say if we want to look at the evaporation. So, we are going back to our old problem. So we have water and air and we have some concentration  $\rho_{A2}$  equals something okay, some value we have, we do not worry what it is right now and we have some  $\rho_{A1}$  infinity here okay. Now, we are worried about we are looking at this concentration. So, we have  $n_A = \text{capital KA}_{21}$  into  $\rho_{A2} - \rho_{A2}^*$ . I will write it as this  $\rho_{A1} H$ ,  $\rho_{A1}$  one infinity okay. Now,  $1/\text{capital KA}_{21} = 1/\text{small kA}_{21} + 1/2$ , that correct?

These two numbers I need now. So based on this correlation, I look at this number. So I have, so it is a lake, this is only for lake. If you are looking at a lake  $\text{KA}_1$  is  $0.094 v_x^2$  and  $\text{KA}_2$ ,  $K_1$  is also given as  $358v_x^2/Ar$ . One of the things you have to also watch here is the units of this thing okay. This is all over the place, if you look at it, this is not normalized to SI units or anything. So you will notice that it is not a dimensionless correlation, the correlation has dimensions which means right hand side the correlation is  $v_x$  and the left hand side the units will be whatever this is.

This is not mass transfer coefficient that we have derived from our this thing, The dimensions are not consistent, which means that some dimensions are hidden in this coefficient 0.094. It includes some dimensional aspects of whatever for usually if  $K_1$ , if you are writing the unit for  $K_1$ , it should be flux is mass. For example, if you are looking at  $n_A$  is  $n_A$  by  $L^2 T = \rho_{A2}$  is  $MA$  by  $L^3$ , which means  $k$  has to be  $L$  by  $T$ , yeah, but in our correlation it says  $\text{kA}_{21} 0.094 v_x^2$ . The unit of this is  $L^2$  by  $T^2$ .

So, for this to be  $L$  by  $T$ , this has to be, this constant has to be  $T$  by  $L$  or weird, okay, you cannot analyze it like this. So, what they are essentially doing is they have measured mass transfer coefficient and plotted it against velocity of air and this is the correlation they are getting and that is all that is it, so that correlation, it is empirical correlation and you have to follow whatever we are seeing very strictly, you cannot make your own assumptions and all that, this is what they have given okay. So, this is the correlation meant for ethyl ether and for the conditions of velocity, wind speed that they have given.

So it says 5 to 16 meters per second and that is all. If your velocity is below that, it may not apply. You have to take it with that bit of suspicion that it may not be accurate at all. So, in most of these cases, we do the best we can, no, we are, that is why it is called an estimate. So, let us say that our  $A$  is benzene, so the molecular weight of 78, yeah. This correlation, this

small  $k_{A21}$  is a correlation for a ethyl ether. This correlation  $k_{A12}$  the next one for the air water, this one,  $k_{A12}$  is for evaporation of water.

This is correlation is for water, again you see that same thing. It has a velocity term and an area term, but it has no reference to any chemical there. So, you have to now, so this is only valid for water evaporation. This is air side evaporation. This is similar to what we have been doing, we had said if you want to measure the individual coefficients, we use pure gas or water for either phases, so they are using that, they are essentially doing that, so water vapor evaporation. So, you have to convert both of these to benzene now.

So, first of what we do is we pick a correlation, we pick those 2 correlations. I am giving you an example. We are not asking you to use that correlation, but if you are looking at a system that is closest to your system, which says gas phase coefficient in lakes and or streams, this is only lakes. So, if your system is a lake and you want to look at this, we use these correlations as an example okay. Now, the first step is to use this, let us say we are using this correlation, we calculate the mass transfer coefficient for ethyl ether.

So, we are using  $k_{A21} = 0.094$  into  $v$  of  $x$  square. So, we know what  $v_x$  is,  $v_x$  is known. This again here if you want, you can use this additional information that is given, it says  $v_x$  is measured 10 meters above the surface. In their experiment, they have measured  $v_x$  is 10 meters of a surface. If your  $v_x$  is measured in a different height, you have to convert that to 10 meters height using one of those correlations we used for dispersion during the boundary layer, those correlations because this is only valid for that okay. This is the problem with correlation.

So you have to understand exactly, sometimes people do not give you full information, they will give you half information if they are not doing it correct. So, if you generate a correlation, you have to give all the information with the correlation, so that people will decide whether they can use it for their system or not, okay. This also assumes that there is no other process in the water that is moving the water. It says only wind induced correlations, essentially assumes that right.

They assume that only air wind velocity is causing water side turbulence, and that is water side is changing, yeah. So we plug in all the values here into this and get the value for this

thing. So we get the value of  $k_{A21}$ , but it is for ethyl ether and similarly we get the value for  $k_{A12}$ , which is  $358v^8$ , so 8 will again, wind is 8 meters above the water surface. It is all arbitrary everywhere all around the place, right, into area and you notice that the mass transfer coefficients are all in centimeters per hour, the velocity is in meters per second in this equation.

The velocity here is in miles per hour. So, I am just giving you an example of this is miles per hour, the area here is in acres. I do not even know what conversion for acres, you all go and check what acres is, okay. So it is all over the place. So you have to worry about these things, this is acre, and then again this is for water vapor only. Once you calculate this one, we have calculate this, we have calculated  $k_{B12}$  and  $k_{B21}$  where B is ethyl ether here and B is water here. Now, you have to convert this to benzene, which is in your problem, if you want to use these correlations.

So, we use the scaling laws that we talked about, okay, and it is also given here, it is a suggestion that is given, generally it is  $n$  equals to half should be used to convert to other volatile substances. So, this  $k_{A1}$  is  $k_{B1}$  multiplied by the molecular weight of A divided by molecular weight of B raised to half, sorry this is 2. So, this number will change, so sometimes people will give you a suggestion whether it is what to use there, 0.5, 0.6, 0.4 and you have to look at that, and in an examination, so I give you other correlations which you can use to do this.

So, which means that now we will take whatever value we get, so ethyl ether, for example ethyl ether has molecular weight is what  $C_2H_5$  over  $C_2H_5$ , whatever the molecular weight, that is it is forty 48, 58 plus 16, 74, yeah. So it is not that big of a difference, benzene is 78, this is 74, it would not be that different, so same, almost the same, but in the case of water, it will be very different. This is molecular weight is  $H_2O$ , molecular weight is 18.

So, there will be a big difference between this and the if you look at the correlation for  $k_{A12} = k_{A21}$  into the molecular weight of A, sorry B molecule, this is the molecular weight of B. No, I think it is the other way around, sorry. You will have a decrease in the mass transfer coefficient. So, A is here and B, yeah it will be decrease, it will be the molecular weight of B by molecular weight of A raise to half. So, the molecular weight for benzene will be smaller than that.

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Water Side MTC (STREAMS)

$$N_{Sh} = 4.4 \times 10^{-3} N_{Sc}^{0.5} N_{Re}^{0.5} (1 + F^{0.5})$$

$$N_{Sh} = \frac{k'_{A2} h}{D_{A2}}$$

$$N_{Re} = \frac{u_s h \rho_2}{\mu_2}$$

$$F = \frac{u}{\sqrt{gh}}$$

$$u_s = \sqrt{ghS}$$

S = water surface slope; h = mean stream depth;  $D_{A2}$  is diffusion coefficient of A in water; u = mean stream velocity;

Next, so we look at other correlations here, we have a few others and we can look at that. There is a correlation for water side mass transfer coefficient in streams. So, to avoid all that problems that we had in the previous two correlations, they are not good correlations, they are bad correlations for various reasons. One, it does not take into account compounds. So, every time I have to worry about what is this for ethyl ether, water and all that.

So, the best correlation and good correlation is something that takes into account all possible factors and it is a generalized correlation for a variety of scenarios for a particular geometry at least. So, for streams if you are looking at water side coefficient for streams, the good correlation's standard is where you have a dimensionless number. So if here dimensionless advantage is that irrespective of what units you are using. So long as you are using one set of units, you do not have to do any conversion business and all that. So, it is all there in one set.

So this is an example of good dimensionless correlation, it is dimensionless to a large extent, but also has things here, one of the things that you can look at it here is it has this term called NSc. The NSc is called as a Sherwood number okay, Schmidt number sorry, and Nsh is here and the definitions are given there. So, this is Sherwood number okay.