Environmental Remediation of Contaminated Sites
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Lecture – 29
Example of Rate of Degradation in Natural Attenuation

Hello everyone. Again welcome back to the latest lecture session. Again as is the norm, let us say, let us have a quick recap of what we have been up to, right in the context of natural attenuation, right. We were trying to understand the system, let us say, and also predict some of the relevant constants and so on. So in that context, we were looking at a particular example, right. In that particular example, what do we have. I think we had a site contaminated with, I think, TCE, right. And then we looked at different cases.

As in one case, we tried to understand the system in terms of, let us say, laboratory experiments which we referred to as the microcosm studies, right. As in we took the sample from the aquifer, let us say, brought it to the lab, spiked it with different concentrations, let us say, of the TCE and then measured the loss with time, right or the change in concentration with time. And then tried to fit the relevant model from our mass balance to that particular data and then get the relevant rate constant and so on and so forth. And part b, let us look at what we have for part b.

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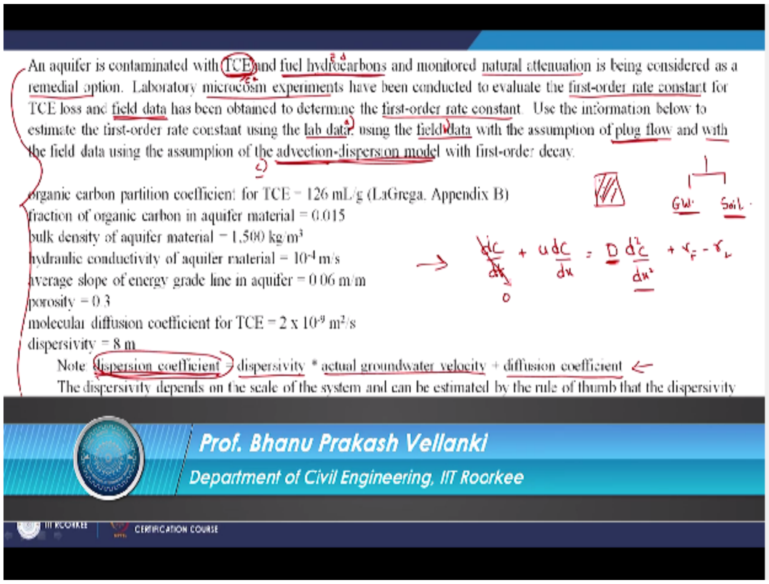

An aquifer is contaminated with TCE and fuel hydrocarbons and monitored natural attenuation is being considered as a remedial option. Laboratory microcosm experiments have been conducted to evaluate the first-order rate constant for TCE loss and field data has been obtained to determine the first-order rate constant. Use the information below to estimate the first-order rate constant using the lab data, using the field data with the assumption of plug flow and with the field data using the assumption of the advection-dispersion model with first-order decay.

organic carbon partition coefficient for TCE = 126 mL/g (LaGrega, Appendix B)
fraction of organic carbon in aquifer material = 0.015
bulk density of aquifer material = 1,500 kg/m^3
hydraulic conductivity of aquifer material = 10^{-4} m/s
average slope of energy grade line in aquifer = 0.06 m/m
porosity = 0.3
molecular diffusion coefficient for TCE = 2 x 10^{-9} m^2/s
dispersivity = 8 m

Note: dispersion coefficient = dispersivity * actual groundwater velocity + diffusion coefficient

The dispersivity depends on the scale of the system and can be estimated by the rule of thumb that the dispersivity

$$\rightarrow \underset{0}{\cancel{\frac{dc}{dt}}} + u\frac{dc}{dx} = D\frac{d^2c}{dx^2} + r_f - r_L$$

So again as quick recap, we have site contaminated with TCE and fuel hydrocarbons, right. So this will be the electron donor, fuel hydrocarbon because it is the carbon here is, what can I say, relatively more reduced, right, when compared to the carbon and TCE, let us say, right. And this is the compound that we are trying to look at. Obviously we need both the electron donor and the electron acceptor here, right, for the redox process to go through.

That is something to keep in mind and for remedial option, we are looking at natural attenuation and microcosm studies, we looked at that. We will again have a brief look at that to evaluate the first order observed rate constant for TCE loss. And then we also have the field data, the actual field data, right. Keep in mind that is the actual field data. For the first and we are asked to calculate the first order rate constant from that field data too.

But obviously we are asked to look at lab data as part a. And then for part b, we considered the field data with assumption of only plug flow as in. When we talk about plug flow, what is it that we are referring to? That we are considering obviously microbial activity and thus degradation. And any adsorption or desorption from the ground water into the soil or desorption form the soil into the ground water that is 1 aspect.

But obviously when we say plug flow, we are also assuming that or not assuming, pardon me, we are also going to look at the effects of advection, let us say, right. So that is something we considered or we are going to consider, pardon me. And then finally though field data with the assumption of advection-dispersion model, right. So in the case that in the, what we say, plug flow model, we have not considered dispersion and diffusion, right.

But in part c, let us say, we are going to look at obviously the most realistic scenario out there which is the one with microbial activity, adsorption and desorption from or into the soil, right. And then advection as in ground water transporting the contaminant along with its flow, let us say, right. That is one case which is advection. And then dispersion now, right. So that is the case for part c now.

Let us have a quick recap of what we have been up to for part a. So part a microcosm studies, right. I just have the soil and ground water here, contaminated ground water and contaminated soil obviously. And I think we have the relevant data somewhere here, right.

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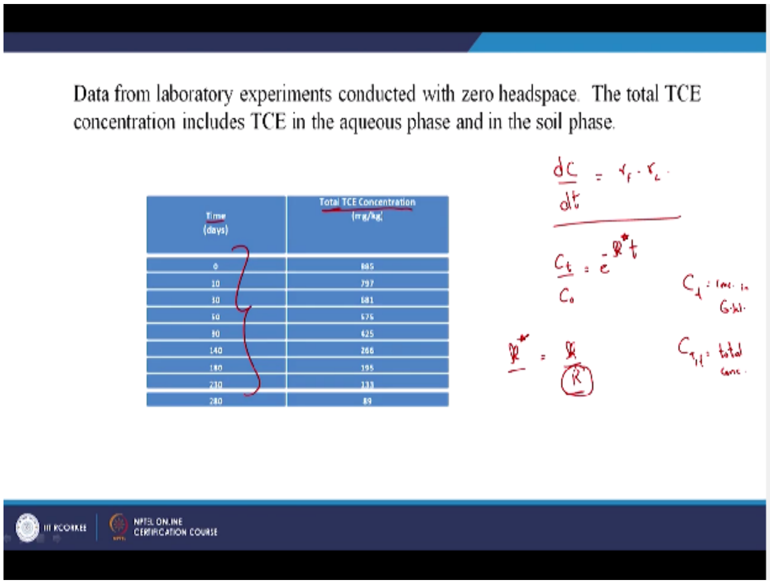

Data from laboratory experiments conducted with zero headspace. The total TCE concentration includes TCE in the aqueous phase and in the soil phase.

Time (days)	Total TCE Concentration (mg/kg)
0	885
10	797
30	681
50	576
90	425
140	266
180	195
230	133
280	89

$$\frac{dC}{dt} = r_f - r_L$$

$$\frac{C_t}{C_0} = e^{-k^* t}$$

C_t : conc. in G.W.

$C_{T,t}$: total conc.

$$k^* = \frac{k}{\boxed{R}}$$

We have the data here for total TCE concentration and time and days, yes. So I have this particular set of information here. And how did we go about that? More or less we know that from mass balance, it is from mass balance it is dc/dt=rate of formation-rate of loss, right. And while either applying it to the entire system as in both the soil or the ground water or applying it to, let us say, just the ground water.

We can come up with different ways and I think we came up with something like Ct/C0=e to the power of -k*t, right. So obviously as you can see we can even replace Ct by C total here or this Ct is the concentration in ground water, right. But we have the total TCE concentration, right. So we have C total, let us say, at time t, that is the total concentration, yes. There is a considerable difference here.

But as you see if you look at the model though, let us say, and even the way that we derived that, let us say, we can even stick with the total concentration too. And that is why I believe we fitted this model and we calculated particular value of k*, the observed rate constant, right. And k*, it is affected by the retardation factor, right. So that is something we looked at in the mass balance in some detail. So now we are going to move on to part b, let us say, right. And what are we going to or how are we going to go about it? First let us look at the data.

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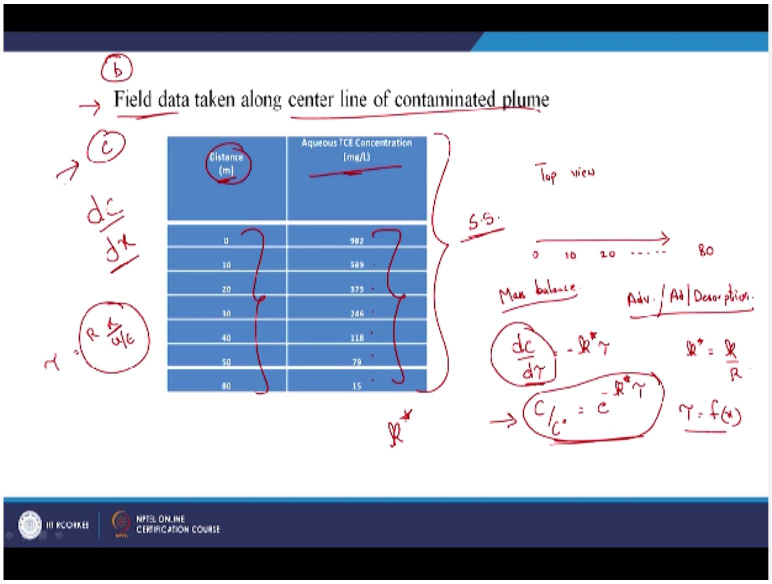

Field data taken along center line of contaminated plume

Distance (m)	Aqueous TCE Concentration (mg/L)
0	982
10	589
20	373
30	246
40	118
50	79
80	15

So what do I have? I have distance, right. And then the concentration. This is from the field obviously and along the central line of the contaminated plume. So if this is the top view, let us say, and let us say, this is the central line of the plume assuming that. So I have a 0 10 20 so on and so forth until 80 m. And we have the relevant, what do we say, readings at that particular case or at those particular sampling sites.

And we see that obviously as expected concentration decreases, yes. And here obviously we are assuming that the system is at steady state or has reached steady state, right. If it has not, though then we obviously need more data at the same particular location, let us say, when the distance is at 10 m from your reference. You will need, what do we say, data with different times and so on if the system is not at steady state, right.

Even then we can plug it in into our relevant differential equation, let us say, not differential equation, solution to our differential equation and get it done, right. So again this is the data that we have but I think we came up or used the mass balance, right or applied the mass balance pardon me, in the context of advection and adsorption and desorption, right. Obviously microbial activity, right.

And in that context, I think we came up with something like dc/d tau, right, = -k*tau, I believe if

I am not wrong. Or I think we ended up with C/C0=e to the power of -k*tau, right. Again the observed rate constant, let us say, and that is equal to k/R and I think tau obviously is the function of x, right. Obviously because dc/d tau, right as we know here as you can see concentration changes with distance.

So we got the or the initial equation was dc/dx or the concentration was changing with distance or is changing with distance. In a plug flow reactor, obviously that is what you would observe, right. And obviously when we plugged in the relevant, what do we say, aspects, when we try to simplify it, we had a different term and what was that? I think we have tau here and how was that equal to, how is that related to x?

I think we had it by the seepage velocity, u/epsilon and R here, right. I think this is what we had with respect to tau here, right. And that is what you see here, right. So now we are going to fit this model, right, we are going to fit this model to this data, all this data and then calculate the rate constant, right. So let us look at that for now.

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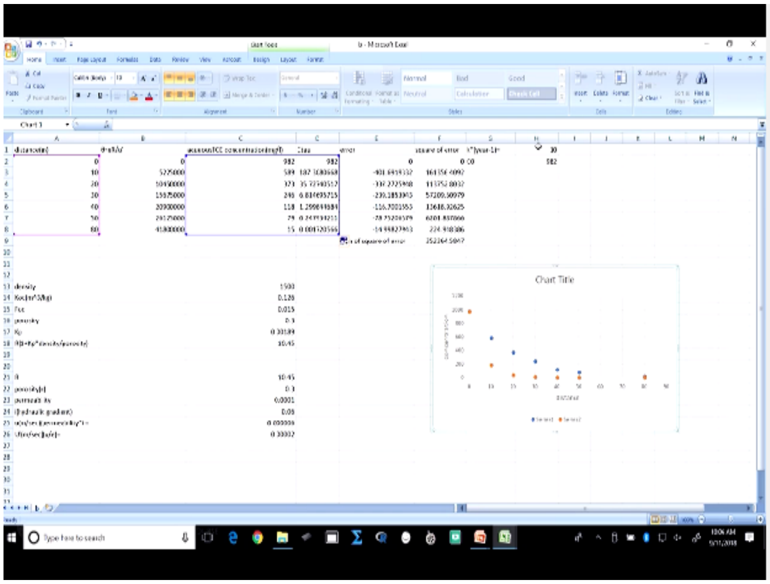

So here I have the relevant data and the relevant constants written down so that we can go ahead without a greater delay, let us say. So here I have the data for distance, right. And here I have the concentration that is the observed concentration from the field data, right. And here obviously I wrote it down as theta because I could not find tau here. But obviously this is tau, tau=x*R or the retardation factor/the seepage velocity, right.

The seepage velocity is nothing but Darcy's velocity as you can see here. This is the Darcy's velocity here, right, ki, yes. How do you get the Darcy's velocity? It was not given in the relevant question but you had the hydraulic conductivity and the gradient, let us say, right and g gradient or such. And you know that this Darcy's velocity=ki, right. And that is what we see out here, right.

And here we have the porosity and from that I am able to calculate the relevant seepage velocity. Again to refresh your memory, what is the seepage velocity and how is this different from Darcy's velocity? So for example, let us say, if the ground water is flowing towards you, let us say, from my direction, let us say, right. So for obviously you are going to have soil and then the pore space occupied by the ground water, yes.

So obviously the ground water has the limited or only a fraction of the area available to it. It does not have the entire area, right. By the Darcy's velocity, let us say, for layman's terms, you can understand that it is more or less consider the normalized area, let us say, right. So in that context obviously though, what is the seepage velocity? Seepage velocity is the actual velocity of this ground water through the pores.

Obviously now the seepage velocity is going to be greater than the ground water, not ground water pardon me, the Darcy's velocity, right. So in that context, obviously I need to look at the relevant difference in cross-sectional areas and such. And for that obviously by dividing Darcy's velocity by porosity, I can get my seepage velocity, right. So that is what we have here. And we were somewhere else out here.

So theta, calculating theta, right. x is this distance, R retardation factor I think we can calculate that, right, 1+rho b*Kp/porosity. Based on that, we can calculate this R to be your retardation factor to be 10.45. And now let us move on and calculate Ct though, right, Ct or C tau pardon me or C at x. I should not have written this as Ct, but I could not find the symbol tau though, right. Anyway, this is C tau, maybe I will write that as tau, right, okay.

So I think that is better. C at tau or C at any distance x now, right. Again what is the approach here? We have, what do we say, concentrations at a given or at certain distances along the central line of the plume, that is the observed data. So for some assumed rate constant, let us say, and depending upon your level of confidence in the C0, some assumed value of C0 too, you can end up with different models, let us say, that predict this particular concentration at different distances, right or distance along the central line.

But obviously your particular predicted data, let us say, or model data should obviously be, what do we say, relatively similar to the relevant field data, right. So obviously how do we go about getting this particular job done? By minimizing the error. But obviously the error you will have positive and negative error. So we look at the square of the error. So obviously you have many data points.

So we look at the sum of the squared errors, right. And then we try to minimize the sum of squared errors. And one other aspect that is obviously taken into account when you squared the error is that, we also give considerable importance or greater weightage to the outlier, let us say, right. Again that is something to keep in mind. So again sum of squared errors and then we ask solver or let us say any other, what we say, mathematical tool can be used but in excel, we have this particular tool called solver, right.

And we use that to minimize this sum of squared errors, right. And when we minimize that sum of squared errors, what does that mean? That model is, tell us that, that particular value of rate constant which gives you the minimum sum of squared errors is the best fit, right, for that particular data, right, okay. So let us go on and look at that. Obviously to calculate the error, I need to calculate the C modelled value, right.

I am calculating that. So C modelled value=C0 which is here, right. H2 is 982 and then it is C0*e to the power of -k tau, right. So I think that is what I have here. Where do I have the k here. Okay, that is k here. This is the initial value or I guess this is the answer because I already looked at that. So one minor change I made compared to how I worked it out last time was that. Last time I believe I worked it out in terms of the rate constant when the terms of units of per second or per day though.

But what I should have conveyed at that stage was that, let us say, obviously the rate constant and the natural attenuation, let us say, is going to be relatively less, right. So if I look at units of per day or per second, let us say, any minor change, let us say, and the particular value of the k when I write down the units as per second, let us say, we will have great, what do we say, difference when I write down the unit in terms of per year, let us say, right.

So in such cases, let us say, when I look at per second, let us say, and that can have a greater effect on my relevant results, let us say, because even a minor change can change the system considerably. Excel will sometimes have a difficulty in converging to the solution. So in general, right, try to avoid such situations and to avoid that, I am having the units of rate constant here in terms of per year.

That is why obviously I have 365 days per year, 24 hours per day and 3600 I think seconds per relevant hour and such, right. So that is why I normalized that here. So I have Ct or C tau=C0 which is here 982, *e to the power of -k. This is my trial value, let us say, right. *tau and this is the tau here. Tau obviously is dependent upon x, R and the seepage velocity, right. That is what I have here.

And we set that up. For now, let us choose some other value, let us say, let us choose some trial. Maybe I will go with 10. So 10 is my relevant k*, let us say, okay. 10 per year now, right. So keep in mind it is 10 per year. And let us go ahead and calculate that. So I have this particular value, right. Distance*, I believe, retardation factor/the seepage velocity, that is what we have here, right.

And let me just drag drop that here, okay. So now I have the tau at different particular distances, right. And now same case, I will calculate the C tau at different tau. So again this is tau, right. Okay, I did not get that right. So now I have C tau here, right. And as you see, I think, if I already plotted that here. So series 1, let us look at this data. So the blue data set is the actual data here, right.

And this orange colour data or the data set that is coloured orange, let us say, is the modelled data. As you see, right, you can clearly see it is for the rate constant that the standard, let us say, which is what we say 10 per year. You see that the relevant, what we say, model is not doing a good job in approximating the relevant variable here, right. But how is that or how do I go about it?

Obviously by trying the error such that the sum of squared errors is minimum here. For example, obviously, here as you can see there is considerable error here at each model, at each data point here, right. So obviously we try to minimize that. And so here we calculated that error as you can see. C modelled, this is C modelled, -C observed that is the error here. And here I am going to take the square of that error, right.

That is what I have here, right. And here I have sum of the squares of these errors, right. And now I am going to go to solver and I go to data analysis, right, solver pardon me. And I set the target cell. Which cell am I trying to change, right? I am trying to change or this target cell obviously needs to be the one that I am trying to minimize here, right. So that is going to be my sum of squared errors relevant cell, right.

So that is going to be, okay it looks like F9 was already selected. So it is F9 and what do I want that to be? Do I want the sum of squared errors to be the maximum? No. I want it to be the minimum. And how can I get to that particular minimum value? By changing this particular cell, right which is the rate constant here, right.

So if you want to, you can also consider that the initial concentration of 982 mg/l is also, let us say, an unknown, right. Because, not because, let us say, but you typically have greater confidence in the initial sample that you collected. But if you think you have less confidence, obviously you can set that to be a variable too, right.

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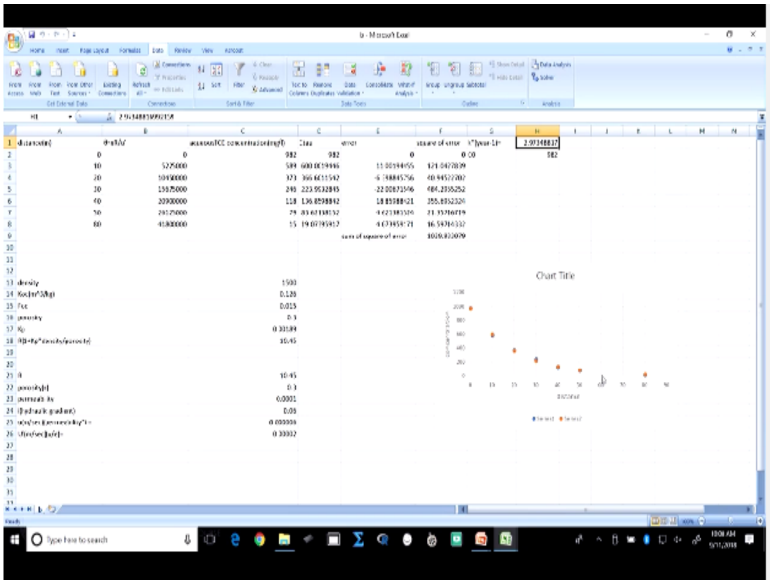

Again so sum of square errors, I want that to be minimized by changing this value of k. Obviously because I tied in this calculation of cell to k here, right. Because we use k here in calculating C modelled. Obviously that is going to affect the sum of squared errors, right. So let us ask for it to solve for it. And okay, I am going to ask for it to keep the solver solution. And now you see that I end up with, what do we say, the relatively accurate estimate of the k* which is 2.9 per year.

And now obviously you see that both the observed and the, pardon me, observed and the modelled values, let us say, are in close concerns with each other, right or the error is relatively less or the minimum that it can be, right. Again as you can see now, the error is considerably less now when compared to what it was earlier, let us say, right. Again, this is the obvious close to go about getting things done in this context, right.

So keep in mind that we are conducting regression and this is something you should or most people out there should be familiar with, right. Again obviously the more the data, the greater the confidence that I will have in my particular regression obviously right, so that I can capture the trends.

So in this regression, let us say, again layman's terms, obviously what are we trying to do? We are trying to capture the trend, right. We are trying to capture the trend here, right. So if I have, let us say, only 2 data points. There are many models or many trends that can be attributed such that they satisfy the conditions for those 2 data points.

But the greater the number of data, let us say, right, obviously the model itself I can understand that either from material bands or from looking at the data, right. But obviously, let us say, any deviations or such will be more accurately captured obviously, let us say, if I have the greater data sets, right? again keep that in mind.

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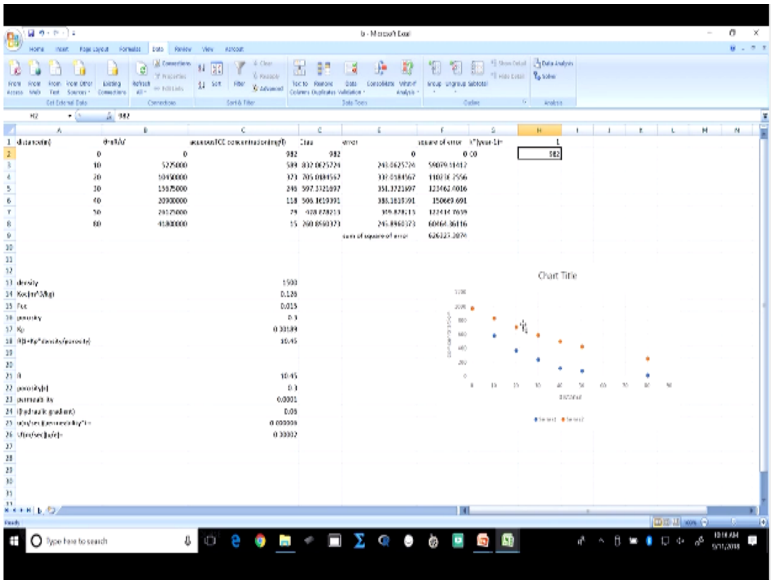

So obviously let me just try out something here with 1, let us say, value that is less than it. And let us hit enter and obviously now you see that it, what do we say, the concentrations are again different from that of the observed values, right. So earlier we looked at the case of 10 and I just plugged in for a case of 1, again you see that it is moving away from the observed data, right.

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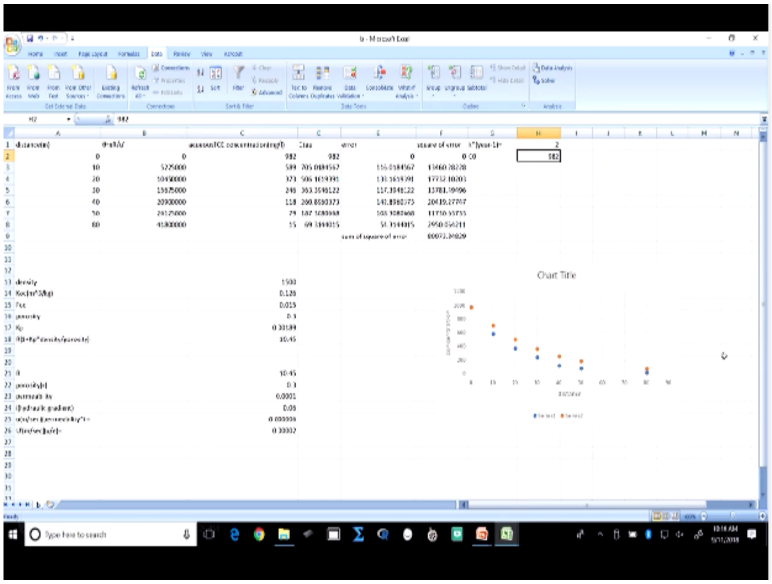

So if I go to 2, right, as we know the true value is 2.97. So now again it is approaching the true data.

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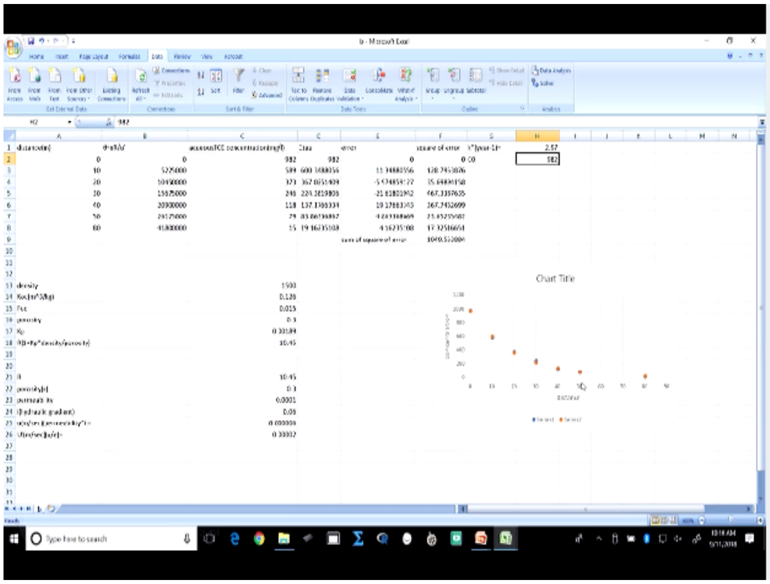

And now, let us say, if I end up with plug-in the true value which was 2.97, if I am not wrong, right. You see that you more or less end up closely approximating your particular observed data, right. So I guess with that, we will wrap up part b and now we will move on to part c, right. So what is here in part c now. So part c, we are asked to look at advection and dispersion model, right.

So dispersion obviously again I think we looked at that, let us say, because of the tortuous path that a particular water molecule and thus the contaminant, let us say, can take in the subsurface as in you have soil particles, let us say, right closely, what do we say, in close proximity, right or in proximity. And thus obviously the water molecule from particular location can take different paths from the same location, let us say, right.

Starting from the same initial point, let us say, right. So obviously you are going to have, what do we say, decrease in concentration. And again you are going to also have molecular diffusion, let us say, right. And thus, let us say, dispersion, let us say, in this context, we are looking at both these aspects and obviously here, let us look at how we are looking at the dispersion coefficient. So obviously we need to calculate dispersion coefficient here.

We are going to consider that to be dispersivity * actual ground water velocity + diffusion coefficient, right. So here we are looking at both diffusion and dispersion when we talk to or refer to as dispersion coefficient, right. Again what was the mass balance or what is the fundamental mass balance?

So it is dc/dt and assuming that is there is flow in only one direction, so c will change in only along x direction, =to the diffusion coefficient*derivative of or second derivative of c with respect to x, + or - any sources (()) (22:23) any rate of formation-rate of loss. This is the fundamental mass balance equation. So if it is at steady state, obviously this will end up being 0. And in part b, we assumed that this was 0 but now we cannot. So here instead of diffusion coefficient, I am now going to have dispersion coefficient, right.

And again rate of formation or rate of loss for that particular compound. In our case, the compound is being lost due to microbial activity, right. So in that context, obviously I need to, I can plug that in and so on and so forth and solve for this. But obviously this is a second order differential equation, so we did look at a particular model that was developed I think at, and it is available in Metcalf and Eddy, right.

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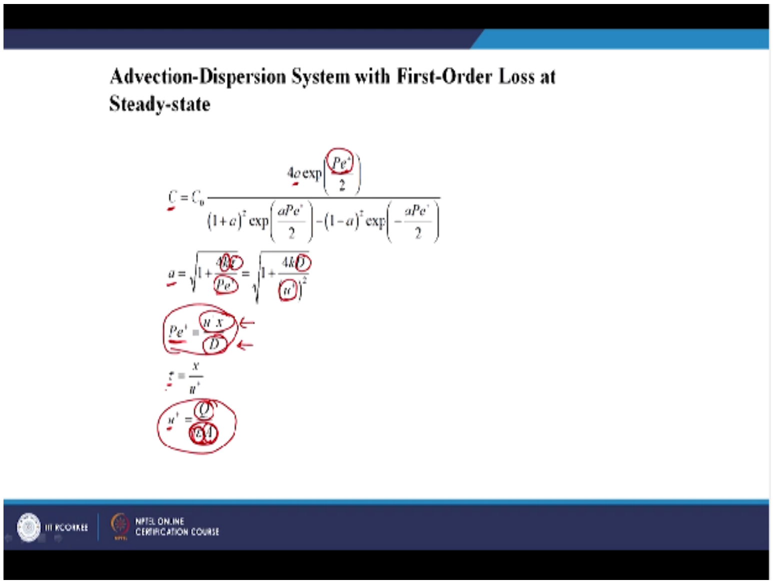

Advection-Dispersion System with First-Order Loss at Steady-state

$$C = C_0 \frac{4a\exp\left(\frac{Pe'}{2}\right)}{(1+a)^2\exp\left(\frac{aPe'}{2}\right)-(1-a)^2\exp\left(-\frac{aPe'}{2}\right)}$$

$$a = \sqrt{1+\frac{4k\tau}{Pe'}} = \sqrt{1+\frac{4kD}{(u')^2}}$$

$$Pe' = \frac{u'x}{D}$$

$$\tau = \frac{x}{u'}$$

$$u' = \frac{Q}{\varepsilon A}$$

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So C as a function of Peclet number, right. And what is this, and also a constant a, right. A constant a and Peclet number here. So a obviously depends upon as you can see k, tau and the Peclet number, right. Or in terms of k and the diffusion coefficient and I believe the seepage velocity. So again interchangeable terms here obviously, right. And but obviously if they are interchangeable, you are going to have relationship between Peclet number.

And what is this particular numerator? And what is this in the denominator? So if you look at that particular Peclet number, it gives you an idea about, if you look at that particular system, the transport, let us say, the relative transport or importance of transport, if I can say that again in layman's terms, of the contaminant by advection in the numerator and by dispersion, let us say, in the denominator, right.

So here we have the terms for advection based transport and here for the dispersion based, let us say. Again a generic layman's term anyway, right. So again Peclet number and so on and so forth. This obviously the seepage velocity, right. Q is the ground water flow. A is the cross-sectional area, divided by porosity because then this will be the area available for the ground water to flow through, right or the cross-sectional area of the relevant pores if you can think of that.

And I can now get the seepage velocity, tau, right. That is something we have looked at but slightly different in this context here though, right. Again I can go ahead and solve for this, right.

I can fit this model and solve. So let us look at that particular case. Again which data am I going to fit it to? I am going to fit it to the field data again. The same field data for that I used in part b, right. But now I am going to use that for part c now, right. So let us look at that. I already have that here somewhere, right.

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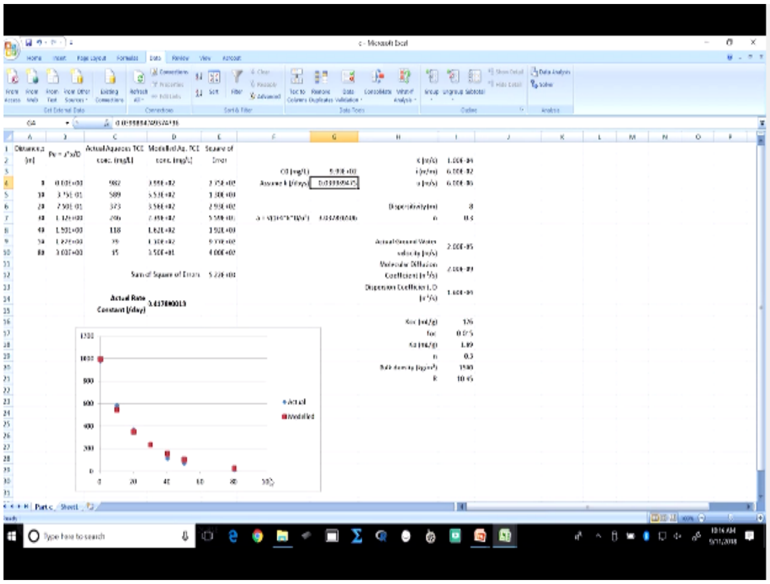

So I have that here. So I have distance again and now Peclet number, we are calculating that out here. And aqueous concentration, this is the observed data. Model concentration based on some particular values of C0 and a, let us say, the constant. So instead of Peclet number, I have it in terms of a and C0, let us say, right. And here, right, we can calculate that. And obviously a is dependent upon k as you can see, right.

Again a is dependent upon k and the ground water velocity or I think the seepage velocity too and the dispersion coefficient and so on and so forth. So I plugged these in. Again same approach as last time. What was that? I mean we looked at minimizing the sum of squared errors by changing some of these cells. So I can either ask for excel to change this constant, not constant, variable a which is again dependent upon the rate constant or ask the excel to change this particular rate constant directly.

And I end up with the particular model and I can get the relevant rate constant from there. Again here I have it in m/second. I should have had it in per year anyway, right. So again that is the hydraulic conductivity, pardon me, in per days here. This is the value that I ended up with, right. Again as you can see there is a considerably, what do we say, there is a good fit out here after I solve for the relevant solution, right. So let me just try one thing out here.

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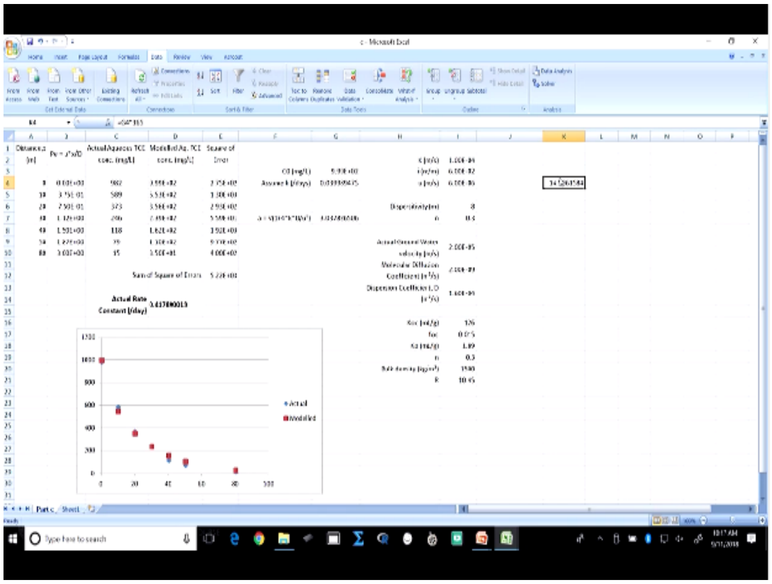

Let us say, I want to say, this is in per days, right. So let me get the key here and I am looking for equal to here, cut please. Just equal to, okay. Go ahead. So rather than having it in per day, let us try to understand it in terms of per year, right. So that is going to be this*365 and enter. So it turns out to be around 14.6 per year, right. Earlier we had around I think 3 or so per year, right.

Again keep in mind that there might have been minor errors, let us say, if even one of these variables was not plugged in right or if I reduce some of the variables, but it should be in this particular ball park and that is expected though, right. So with that I will move on to or go back to the relevant question again, right. So this is the typical scenario that you would see or expect in the field though, right.

Part a, how is that easier, not part a, the microcosm studies where the better or easier for you. Obviously because controlled environment, let us say, right, and I can get that done, yes. And, let us say, resources and such might be easier too, yes. But obviously if I want to approximate the field conditions better, obviously I need to get the data from the field. And in that case, part b is better.

And obviously c is the particular case that most closely reflects the real life scenario, let us say, or the practical scenario. But obviously for this as you see, you need more and more resources and more and more, what do we say, it is more and more data intensive, let us say. Let us say, you are getting the dispersion coefficient or such, that is tricky because it is not going to be typically uniform and such.

So there are aspects involved. So it is a balance between resources and kind of information that you are looking for, right. So I guess with that I am almost up with time. And by now though, we are more or less done with or done with rather all the aspects with respect to natural attenuation, right. And natural attenuation is a last topic or the last aspect we are going to discuss in terms of remediation of contaminated ground water.

So we will look at one, what do we say, case study, let us say, in the next session that is relevant to natural attenuation. And then we will move on to the relevant aspects of dealing with the other set of contamination, let us say, or other aspects within contamination. What is that? Obviously until now what have we looked at?

We have looked at remediating contaminated ground water. Obviously in the subsurface, you are also going to have soil, let us say. So we are going to look at those cases, let us say, when only the soil is contaminated or both the soil and the ground water are contaminated, right. So with that I will end today's session. And thank you.