Environmental Remediation of Contaminated Sites
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Lecture – 27
Rate of Degradation of Contaminant when Advection is Considered.

Hello everyone. Again welcome back to the latest lecture session right. Again a quick recap of what we have been up to. So I believe you are discussing natural attenuation right in that context we were discussing let us say how if a contaminant is released into the subsurface right. You are going to have different process either destructive or non-destructive that will lead to decrease in or the attenuation of this particular you know affects of this particular contaminants.

So in that context we try to look at how do we go about understanding let us say the rate at which attenuation is taking place if it is taking place and so on and so forth right. In that context one of the ways obviously is to take the samples from the fields and we label them as microcosm studies right. So we take different aquifer samples from the fields. So again keep in mind that we want to replicate the conditions in the field in the lab right and we take the different such samples spike them with the relevant containment concentration.

Typically, in the range that you would expect in the contaminated site right and then you would like to let us say observe the relevant change in concentration if any with time let us say and then model that. Model that in the sense what do we try to do so we need to be able to apply relevant what do we say model or equation let us say to that you know trend we see let us say are the relationship between the concentration and the time or such right.

So in that context obviously the model needs to be based on relevant scientific principles yes so in that context obviously we looked at mass balance right and mass balance we looked at a particular way where we conducted the mass balance on only the volume of water. For example, whenever we conduct or look at material balance or mass balance we need to look at 2 aspects obviously.

First identify the relevant compounds upon which you are conducting the mass balance right so that we are done with and then we need to identify the control volume typically that is the key aspect here. So in this particular case of the microcosm study what do we have here.

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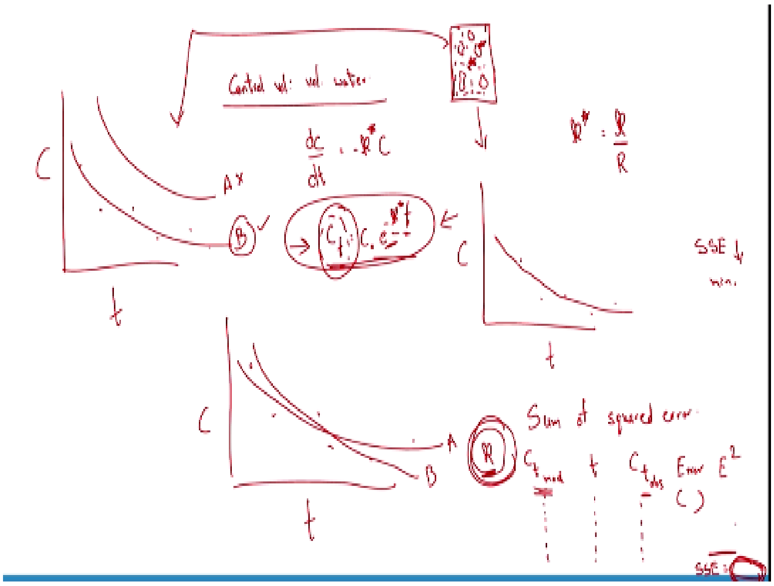

We have let us say if this is consist of the aquifer media let us say. This particular container consist of the aquifer media what does it have. It has let us say the soil particles and the relevant groundwater let us say all this is my groundwater here and obviously some of the contaminants are present either in the ground water dissolved in the groundwater or absorbed on to the soil right. So here let us say there are 2 approaches.

So we looked at one approach to be able to better understand the applications of mass balance and to familiarize ourselves with apply mass balance to various system we looked at another approach too, but the first approach that I believe we looked at was considering that the control volume the control volume was just the volume of water or the water let us say right and in that case we applied the relevant material balance again this is a batch reactor no flow coming in, no flow going out so batch reactor and we apply the relevant mass balance.

And I think we end up with something like dc/dt see the concentration of the contaminant in the water right or in the groundwater in this case let us say. Again it is aquifer media that sampled and put up in the lab right with time=k*c and k* was nothing but= the actual rate constant by the retardation factor and I think that is what we end up with and once we get this equation obviously we can integrate that to ct=c0 and e power –k*t.

So now you know that the concentration of the relevant contaminant at different times right is going to have such relationship with time right ct-c0 in the e power –kt. So where did we get this from we got this from the material balance and let us say by observing the data from this particular batch experiment I get c versus t relationship to be something like us say right. So by fitting this model here this model or this equation let us say to this particular set of data such that the sum of square errors are minimum.

I agree we discussed them in some detail again I am going to hopefully have enough time to work out in example in this regard and we will look at the relevant aspect at that particular time too. So we are going to try to or we are going to conduct the regression and try to achieve the best fit right. So here we are going to have to get that particular value of that rate constant which will give me or which will be able to explain the data in the best possible manner. I am just using layman's terms here right.

So how do we do that typically we will be able to try to or you will try to minimize the error right. For example, let us say you know that c versus t and let us say this is your data that you observed from your experiment here right and let us say you have 2 models one is something like this and one is something like this right. So which of these 2 models A or B would you choose now let us say.

Let us say if you had no other tools which model would you presume let us say explains this particular observed data better right. You would obviously say B now right but that is based on visual judgment but what are we trying to do let us say you know we are trying to judge something let us say, we are trying to quantify something may be what are we trying to minimize here if you think of it we arise or let us say the mind was trying to minimize the error let us say right.

So here by visual judgment you can obviously say B explains the model better rather than A right, but if we are presented with a scenario let us say where we have 2 models let us say something like this something like this now. So here let us say how do I know which model is better or which models explains the relevant data in a better manner let us say right and in this context obviously I need to be able to quantify or calculate the errors and minimize them, but if I just look at errors obviously right you are (()) (06:36) have positive error and negative error.

And you know when I try to minimize that obviously because I am going to try to minimize the total error right. I am going to have issues so thus we look at sum of squared errors and also sum of square because we need to also give considerable weightage to the out layers I guess. So thus what are we trying to do we calculate the sum of squares right squared error pardon sum of squared error right.

And obviously how do we get that for example I know that for a particular k value or rate constant here this is ct from the model let us say and t. I will assume some time right not pardon me some rate constant and for different time I can then get the different modeled ct and how do I do that by plugging in the relevant k and t into this equation I can get ct model, but from the lab I know that I have my ct observed value right.

So then first I will calculate the error, error is nothing but ct model- ct observed I will calculate the error and then I will say I will calculate the error square and then calculate sum of all this squared error right and then I will change this rate constant in such a way that this particular sum of squared error is minimum right. So what does that tell you we are trying to get that particular rate constant which will be able to what do we say explain the data in a better manner or we are trying to predict the actual rate constant.

That is what we are trying to do here right. So again this is the approach here obviously right. So now we will move on to the second way or the different way let us say of applying material balance to be able to get to where we want to I guess right.

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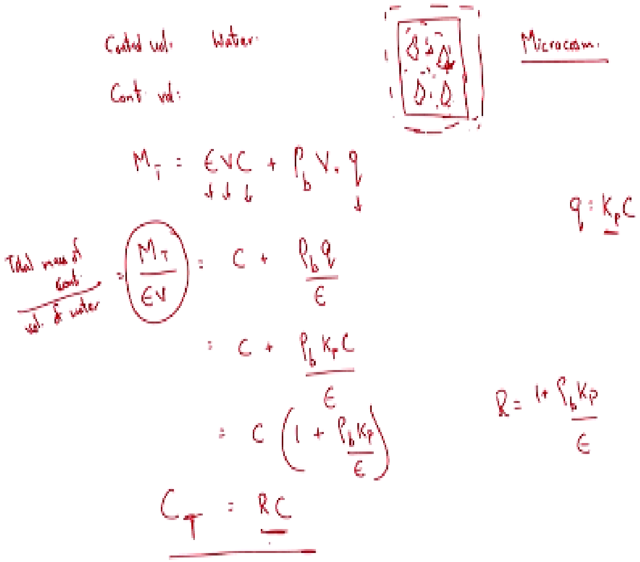

Again what is the same case or what is the case we are looking at. We are still looking at the microcosm studies right and what do we have we have soil here and we have groundwater let us say here or water this is the aquifer media and we also have the contaminant here right. So in earlier case the control volume was only the water right. In this case though the control volume is going to be the entire setup here right so this is the control volume here right.

So in this context obviously you know the relevant internal transfer of mass from the soil to the water and from the water to the soil which we had to account for in that particular the initial case or the previous case of this particular material balance. It does not need to be looked at, but obviously we need to tweak that equation further. Again here we are not applying the mass balance on only the water.

We are applying the mass balance on both the soil and the water right or the entire set up here for that obviously I need to look at few aspects what is the total mass right I think it is epsilon vc porosity total volume. This is porosity, this is total volume c is the concentration of the containment in the water + you know now mass absorbed onto the soil right. So this is the bulk density of that particular soil volume times mass of containment per mass of soil right.

This is more or less mass of containment per mass of soil this is what we have this is the total mass. So I am just going to look at total mass per volume of water. What is the volume of water porosity times volume right that is now going to give me C+ and I am going to have rho b q/ and epsilon right? So what is this now total mass of contaminant per volume of water. This is how I am this is what I am calculating here right.

Total mass/per volume of water and I end up with this. I know that q or the mass of the particular or the concentration of the containment adsorbed on to the particular soil will be in equilibrium with the concentration of the contaminant in the water right it is always an equilibrium yes and we know q= sum partitioning coefficient times c. We are assuming that it is linear relationship here depending upon the actual material.

You might need to have a different relation. This is (()) (11:02) but c+ rho b q is kp*c/epsilon and so that as you see I take the concentration out 1+ rho b kp/epsilon right and nothing but this is nothing but R times C. The retardation factors if you thus rings a bells again from the previous classes rho b kp times epsilon right. So this is RC and if I can call this particular set of terms the total mass/ volume of water I will represent that by C total.

So what do I have I know that C total=RC right. Again just some background before we look at the second approach. Again what is the second approach again why are we doing this we just want to familiarize ourselves with applying material balance let us say. So instead of previous or unlike the previous where we applied the material balance on only the volume of water or the water pardon me.

And then we had to consider the mass coming into water from the soil. We are just trying to simplify the system by taking the control volume to be the entire volume right. So that is what we have here and in that context I know ct=RC.

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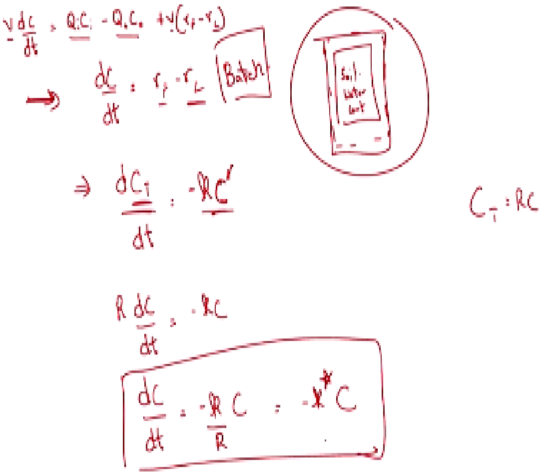

$$V\frac{dC}{dt} = Q_iC_i - Q_oC_o + V(r_f - r_L)$$

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

$$\Rightarrow \frac{dC_T}{dt} = -kC'$$

$$C_T = RC$$

$$R\frac{dC}{dt} = -kC$$

$$\boxed{\frac{dC}{dt} = -\frac{k}{R}C = -k^*C}$$

So let us say now if this is my container with both the soil, water and obviously the contaminant and I am only concerned with the mass balance or the entire system how does my system turn out to be. So I know that I have typically for a batch reactor dc/dt= rate of formation-rate of loss. So now I am talking about the entire system here right. So here for this system what is it going to be dc total/dt= let us say does that being formed in any manner, no and how is it being lost.

It is being lost by the relevant what do we say reaction occurring and where is the reaction occurring is it occurring on to the soil or the compound adsorbed on to the soil it is occurring in the water right. So –kc and why C not C total because the relevant reaction that is leading to loss of this particular what do we say contaminant. Loss is due to typically due to microbial activity that is what we are assuming here right.

It is occurring only in the groundwater so that is why the concentration in that particular groundwater so C total though what is C total here. We know that from the previous case C total=RC so I plug that in. So that is R dc/dt=-kc nothing but dc/d total=-k/RC which is-k* or k absorbed let us say time C right. So again I end up with the same equation as we derived in the earlier case let us say when we apply the material balance on just the volume of the water right.

So again different approaches just try to understand you know how to look at the relevant variables and plug in the relevant aspects again how did we do this. So this is the generic mass balance equation right again where does this come from we know that for microscopic system it is v dc/dt right= mass coming in or Q in C in-mass going out or Q out C out+ volume into material being formed or loss due to any reactions.

Because it is a batch reactor these 2 terms are 0 I cancel out the volume and this is what obviously I am left with for a batch reactor right and obviously now I am applying it for this particular control volume which is a total system here. So again as we know we are looking at the total change or change in the total concentration so that is why I have D dc/dt and how is that being lost. It is only being lost by the relevant microbial activity in the water.

That is why we need to take the concentration of that particular what is it now the concentration of particular contaminant only in the water and again (()) (15:06) flowing that further. We end up with the same equation as we did and we considered the previous case or the previous kind of control volume right. So that is one aspect and how to go about this. The second aspect is what did we consider here.

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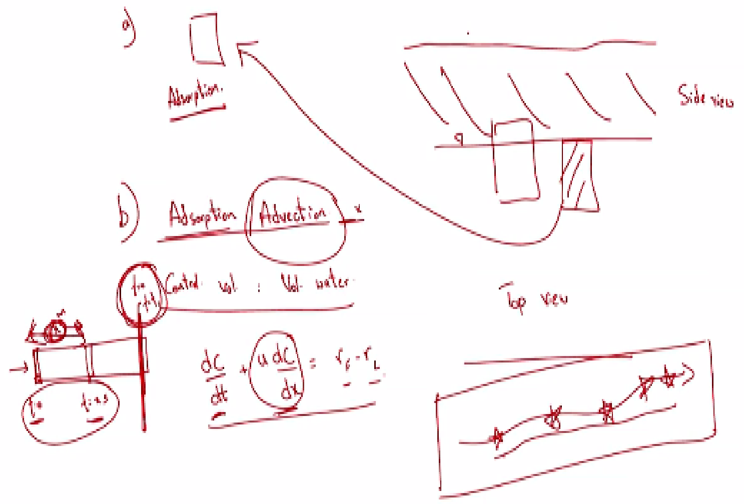

In case a we took the relevant sample let us say this is my field and this is all my soil let us say and groundwater somewhere out here groundwater table and I took the relevant sample let us say right from wherever here okay and I brought that to the lab conduct the relevant experiments and so on and so forth, but here we are only looking at relevant adsorption and any microbial activity right.

But in groundwater or in subsurface what else can happen though you know that the contaminant is what do we say being transported along with the flow of the groundwater or you are also going to have advection. So if you are also going to have advection how do you go about you know trying to understand for the you know (()) (16:13) for the system right. So that is something we need to look at.

So in this case we are not going to look at just adsorption in microbial activity we are also going to additionally look at. We are not just going to look at microbial activity and absorption and desorption like we did in case one we are also going to look at advection right. Again advection how did we understand this or try to understand this anyway in Layman terms.

So if there is net flow fluid in any particular direction and the contaminant is being transported by that particular fluid in that particular direction we call that particular transport of contaminant or refer to that particular transport of contaminant or is or as advection right. So in that context obviously we are trying to understand the affects of this particular advection or the transport of contaminant along with the groundwater in that particular subsurface.

So how do I do that let us say for example if this was the side view let us say I have the top view this is the top view that we are going to look at and let us say this is my flow path let us say right and let us say now I am going to take samples along the flow path I know the relevant distance let us say right. So I have this concentration versus distance let us say right. And then I can find the relevant model from material balance again to this particular data.

And again calculate the rate constant and so on and so forth, but again to be able to fit that particular equation we need to obviously apply material balance. Can we use the particular equation that we derived in the previous case or in case A obviously not why is that because in case A we only looked at adsorption and the desorption in the relevant microbial activity because it was a batch reactor we obviously cannot study the flow of that particular or the effects of flow of the groundwater or the contaminant being transported by the groundwater right?

So obviously we need to thus we are going to have take samples here and also modify our equations to be able to take into account advection here right. So again there can be 2 approaches where we look at let us say just the volume of water or the total volume right and in this case just to simplify the relevant aspects I am going to look at or consider the control volume to be the volume of water let us say you can try to out the other approach too.

So let us see how we go about this so first we need to understand what kind of reactor is it that we are trying to model what are the 3 kinds of reactors we have typically looked at we have looked at batch reactor which is the case that we analyzed earlier right earlier in the particular session. Batch reactor no flow coming in no flow going out typically we assume that the concentration of the particular compound is the same throughout the reactor that is one case.

The second case is this continuously stirred-tank reactor or the completely mixed flow reactor right. So again what is the key there though you have flow coming in you have flow going out and completely mix and we assume that the system is completely mix let us say right and again typically what are the applications sometimes (()) (19:15), but typically to the unit process either in your water treatment or waste water treatment plan.

And third kind of ideal reactor that we looked at was or is the plug reactor right and what is that plug flow reactor. So again you have let us say pipe let us say and you have flow in that particular pipe again just layman terms. So in that context obviously what is the key here that the concentration changes with distance now right. So for example if this is my pipe and water comes in here and if consider particular plug or section of that particular water.

So let us say at time=0 it is here and time= (()) (19:56) x second let us say it is out here or what is it though we are trying to see after it travelled distance of x meters let us say so it is out here and so on and so forth. So as you can see the concentration of that particular contaminant in this particular section changes with distance right. So that is the relevant aspect here.

And again we are looking at plug flow reactor here and obviously as you can understand in this system the one that we are going to look at case b where we look at adsorption, desorption advection and the microbial activity it is obviously a case of plug flow reactor right. So let us just try to apply that particular equation. So typically again what do we say modify the microscopic equation right and I think we did that earlier already.

So we are not going to do that or we can apply the basic or the fundamental mass balance equation too and typically what have we looked at we know dc/dt+ u dc/dx right= diffusion relevant aspect, but here we are not considering diffusion or advection. So I am not going to include the diffusion or dispersion terms here=rate of formation-rate of loss here right. So that is the basic mass balance equation we typically apply to the particular plug flow reactor.

What do we have here how is concentration changing with time when we say changing with them we mean to keep the space constant. We only need to look at let us say this particular point in space and only time=0 time=t1 and so on. Why am I explaining this further because time=0 here and time=x second that is an erroneously way to look at it because here we are changing the space right.

So when I say a compound concentration is being monitored with change in time. I need to keep the space constant and typically again as we discussed earlier we looked at the example of the waste being dumped in Haridwar and it is flowing downstream to Roorkee let us say. If

I want to look at the change in concentration with time it does not mean let us say I take this sample at Haridwar travel for let us say half an hour downstream.

And then take the sample and again further half an hour reach Roorkee and take the sample there. You are not taking the sample with respect to time let us say or monitoring the sample with respect to time you are actually monitoring the concentration with distance so if you want to monitor the concentration with time you need to stay in Haridwar and measure the relevant change in concentration with time at that particular point in space or just stay at Roorkee.

And just check how the concentration changes with time and again that is something to keep in mind. So this is obviously concentration change with time right and this will give you an idea about flow coming out and flow going in let us say and that is rate of formation-rate of loss right. Let us move on to the next section here so let us work it out here and what is the basic mass balance equation that we have for plug flow reactor.

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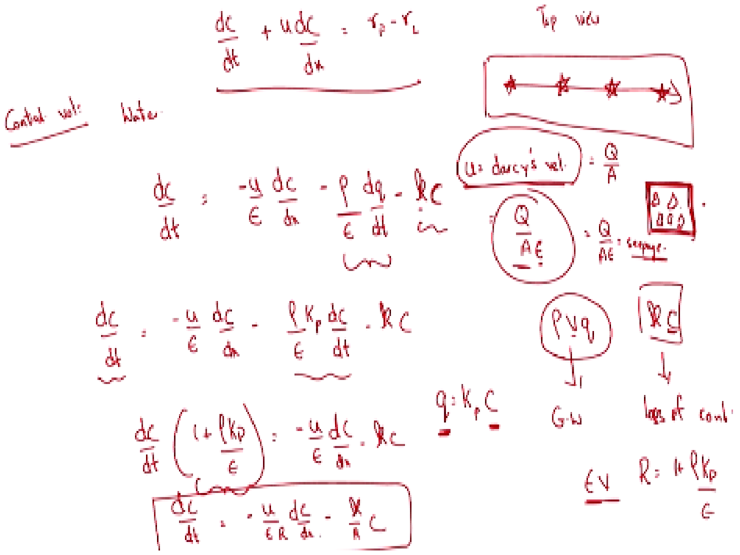

We have dc/dt + u dc/dx right=rate of formation-rate of loss right this is what we have. Again keep in mind that is from this fundamental mass balance equation where we have let us say dc/dt+ the del products of the flux being=sources and sinks and so on, but here in groundwater we have flow only in one direction. So that is why we are assuming that concentration changes along with or along one dimension that is why we have dc/dx and not dc/dy and dc/dz.

And also in this particular case we are not considering dispersion. So that is why we did not have the dispersion or the diffusion term here right so this is the simplified form here. Obviously what are we applying it upon so let say I have my flow path to be this and this is the top view and this is the actual groundwater here let us say and I am taking samples at different points here right.

And this is what I have and I am trying to model this particular case, but here as we mentioned we are going to look at the control volume to be the relevant water only the water here right. So in this case if I am just looking water to be my control volume similar to the case when we looked at the microcosm studies or the batch reactor what do we need to do. We also need to take into account the mass coming in from the desorption of the soil into the groundwater or consider let us say adsorption of the particular contaminant you know by changing phase from the groundwater into the soil right.

So again what are the 2 ways that mass can come in physically and go out of this particular control volume which is groundwater either let us say if the system is not at equilibrium the mass can be desorbed from the soil into the groundwater or can adsorb from the groundwater into the soil right so that also obviously needs to be taken into account and again this is something we have looked at in the earlier case yes.

So let us just try to write that up here and simplify that. So U here is the Darcy's velocity Darcy's groundwater velocity again what is that let us say. For example, if this is the cross section let us say and a groundwater is flowing into the board let us say it is going flowing into that. So what do we understand by that for examples these are soil particles and the groundwater cannot obviously flow through this particular control volume.

It can only flow through this particular (()) (25:28) pores here, but for example when I look at Darcy's velocity let us say what does it look at or how does it calculate that. It takes the q the flow rate of groundwater by the total cross sectional area right. So this is obviously to be able to approximate or understand the velocity because calculating the true groundwater flow through the actual pores will be relatively difficult right.

For example, let us say think of this. You know we are just normalizing this particular flow over the entire cross sectional area, but if the flow occurring through the entire cross sectional area no it is only occurring through those certain pores right. So that something to keep in mind here right so that is something to keep in mind. Again this is the generic equation, but to be able to apply to our particular case and transform it let us say what do I have.

So I have dc/dt=-u/ epsilon right this will be the seepage velocity let us say now dc/dx and also – I need to consider the case when the soil is desorbed right so that was rho b v q right and the derivatives of this. So rho times volume will be cancelled out by porosity times d q/dt- what else do we have here k times c. How is the compound being lost? It is being lost by some microbial activity let us say in the groundwater.

So I have -kc here so we looked at the case when mass of the relevant compound from the soil this is the compound mass adsorbed on to the soil changes phase from here to the groundwater that is this term and this term is nothing but the loss or degradation of contaminant let us say. So that is this particular term obviously this is divided with epsilon v or the volume of water and thus cancelling out terms like volume and so on and so forth.

So again simplifying this further what do I have so I have dc/dt= -u times/ porosity what was u, u was the Darcy's velocity now right, but think of this if I divide this by porosity what am I actually getting here right Q/A times porosity. A times porosity if you think of this in this particular case A times porosity is the actual cross section through which or the actual area through which the groundwater is flowing right.

So that particular q which is the total groundwater flow right by the actual area through which it is flowing through it going to give you the seepage velocity. So Darcy's velocity is nothing but Q/A and Q/A times porosity will give me the seepage or actual groundwater velocity through the pores right. Again just a site factor there dc/dx- rho b/ porosity d q q you know is going to be again kp times c.

Q is the mass of the contaminant in the soil. C is the mass of the contaminant not mass pardon me the q is the mass concentration of the contaminate in this soil, C is the concentration of the contaminant in the groundwater. As we know both of these 2 variables are going to be in equilibrium. If the equilibrium is disturbed let us say again it is going to shift such that the new equilibrium is reached right.

So that is what we have here and that time so q this derivative will be kp is a constant dc/dt-kc right. So again I am going to take this term out here to the left and what is that now so that is dc/dt into 1+rho kp/porosity=-u/porosity dc/dx- kc right. Again this is what we have what is this particular term as we know the retardation factor= 1+ rho b kp/porosity and as you see this is the retardation factor.

So I am going to represent this retardation factor and take this down to the right hand side. So dc/dt=-u/porosity retardation factor dc/dx- k/R C right this is what I have and I am going to write this in the next page and also simplify this further.

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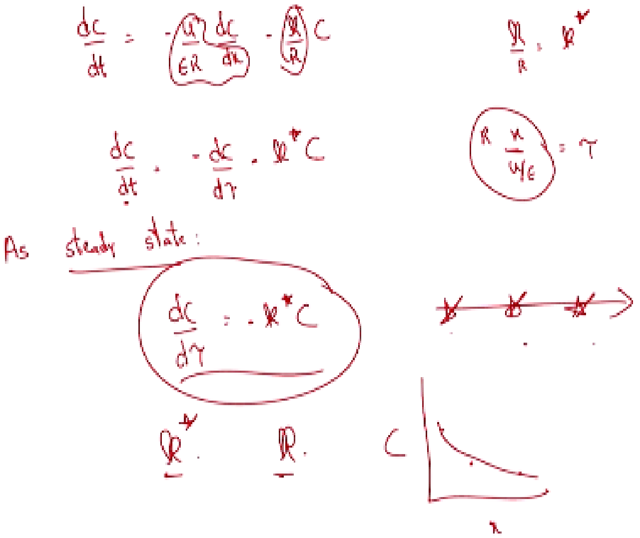

Let me just write that down here dc/dt=- u/porosity times R right and I think I have dc/dx-k/R times C right that is what we have here. So again as we did in the earlier case k/R what is that R is the retardation factor k is the actual rate constant so k/R we represent this that as k dash or apparent first order rate constant so that is what we are going to have and let us look at what we have here right.

So we have here if I can transform that further you know x/u/epsilon right and let us say that is going to be R. So this is what I can write this out as. So this I am going to represent by tau right. So this is nothing but dc/dt=-dc/d tau- k*c right. So at steady state how does this simplify steady state meaning concentration does not change with time so this is 0 so end of with dc/d tau.

Tau is just the variable I am using to represent these sets of variables right dc/d tau=-k*c right and now I can integrate and get this particular c at different tau let us say or different x right with respect to the relevant what do we say distance yes. So again now I have the relevant equation expressing c in terms of x right tau is nothing but you know something in terms of x right or the distance.

So here I have what do I have here the concentration changing with distance you know this is the equation I have and again I can integrate this and what do we say try to fit this particular equation to the relevant data I get from the field what is the data I get from the field. So as we know let us say if groundwater is flowing in this direction and this is the top view I take samples at different distances.

So I have let us say c versus x right I have the data and I can fit the relevant equation after integrate this particular equation to this particular model and what can I get I can calculate k dash and when I calculate k dash I can calculate k right. So that will again obviously give me an idea about how to be able to understand the extent of microbial activity. How much of the particular contaminant is being what do we say transported by groundwater flow and how much is being adsorbed or desorbed and so on and so forth right.

So that is what we have here and I guess I am running out of time so I will end this for today and in the next session let us say I am going to talk about very briefly about the advection. So what did we look at today we looked at only microbial activity and adsorption desorption and second case we looked at microbial activity adsorption desorption and advection, but as you know in groundwater you are also going to have dispersion and diffusion taking place right.

So in the last aspect we are going to briefly look at that and look at the typical equations used and then move on to an example where we are going to solve for cases a and b let us say and I guess with that I end today session and thank you.