Environmental Remediation of Contaminated Sites
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Lecture - 26
Pathways of Contaminant Transport and Rate of Degradation of Contaminant

Hello everyone. Again welcome back to the latest lecture session. We have been discussing natural attenuation let us say right and in that context, we were looking at the relevant mechanism so again a quick review of the relevant mechanisms right.

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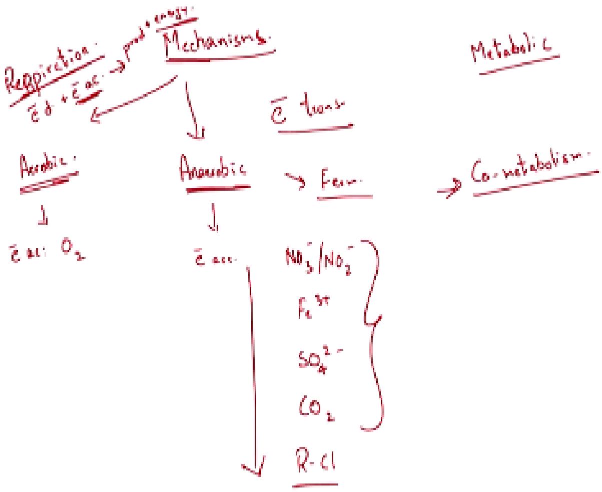

We have different mechanisms and in that context we looked at you know aerobics process. Again they are part of the respiration based process let us say for the microbes respiration and what is this about you know we have electron donor + electron acceptor not + let us say electron acceptor then going to relevant products and energy being released for the utilization by the microbes site.

Anaerobic process obviously the role of electron acceptor electronic acceptor is played by oxygen and then we move on to looked at Anaerobic process and in this context you know you have we do not have oxygen anymore, but the other electron acceptors are available and what are these other electron acceptor available. So you have I believe is the nitrites and nitrates let us say.

And you have what else the ferric I guess Fe3+ so we have No3- No2 Fe3+ and I think we had sulphates carbon dioxide and at the end of the chain right you have the chlorinate organics. So obviously decreasing energy let us say that release or decreasing amount or levels of energy that released when you choose the relevant electron acceptor in these in this order right.

So obviously the key is that if you have nitrite and what do we say chlorinated organics let us say which one will be the microbes choose for the electron to play the role of electron acceptor typically the nitrite basically right. So for your chlorinated organic to be reduced you should not have any of the other competing electron acceptors right that is something we looked at.

And again in the context of what do we say Anaerobic process we looked at fermentation too right and particular organic compound is transformed into a more oxidized form and also more reduced form right we looked at that particular example. And also again what are all these process about they are with respect to the metabolic process let us say or metabolism of the particular microbes or the our body too.

But obviously we are not involved in this context. So the relevant microbes or any living organism have their own metabolic process which are involved in deriving their relevant energy for their particular system let us say right. The reason we bring this (()) (03:03) we also have something called co-metabolism and what are this about now. So it is that your microbes have enzymes let us say they act as catalyst right how do they acts as catalysts.

Again the different aspects obviously, but typically it is a lock and key we call a lock and key mechanism and what do we say it identifies a particular molecular by its shape let us say. So if the enzyme let us say wants to you know prefer to act upon a particular compound. How does it look at it, it tries to identify by its shape now, but if there is another compound with the same shape let us say or size too may be right?

This particular enzyme will mistake this particular competing or similarly shaped compound for the compound that it actually wants to act upon right. So in that context you have co-metabolism taking place, but in this process the energy released if any will not be utilized by the microbes.

So by error or in error let us say are erroneously this particular catalyst acts upon another particular compound which is your particular compound of concern rather than acting on something else that it actually prefer to why is that the shapes let us say were relatively similar right again co-metabolism that is just one aspect right. So these are the different mechanisms right.

And again as you see typically most of them are concerned with the role of electron being transferred and then gathering energy I guess right. So and the energy that is derived from these redox process and obviously what are these equations or reactions or processes we have looked at their redox process. You have reduction and oxidation of the relevant compound occurring redox process and typically what we are looking at electron acceptor right.

So these are the aspects obviously or the mechanisms. The next aspects obviously is how do I let us say prove or estimate or predict let us say if degradation is actually going to occur or not. So what are the aspects that I need to look at.

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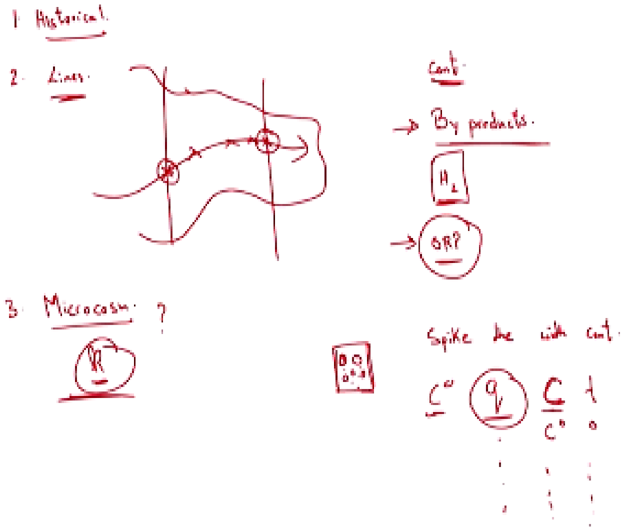

Let us historical data if it is available so for that particular type of contaminant let us say you have if you have data let us see there is considerable data now or considerable body of knowledge are lot of knowledge let us say in this regard. So typically for most of the usual compounds you can find some historical data let us say right or obviously you are also going to have lines of evidence let us say you are going to look at.

If this is my plume let us say right and this is my flow path let us say right and I am concerned with this 2 locations. So I take the samples along the flow path right and then I look at what is the change in concentrations or pardon me the mass let us say in the system or change in relevant concentrations between the relevant locations and so on. So I look at those lines of evidence let us say right.

So in this context what can I analyze for obviously I can analyze for the contaminant itself right. So the contaminant itself can be analyzed for, but for example you know that you also have the non destructive mechanism as sorption can take place, Volatilization can take place you have other non destructive mechanisms. So how do you figure out let us say whether or not your compound is actually being degraded or the destructive mechanism which are brought about by the biological process are taking place.

How do you look at that? So obviously to understand that you can look at the byproduct that you would expect let us say. For example, if a particular degradation is taking place obviously you will have the relevant byproducts so you can try to look for and analyze the concentration of those byproduct along these are in this system let us say and then understand that it is not just what do we say non destructive mechanism that are playing a relevant role.

But obviously the destructive mechanism too. So you can look at byproducts and typically depending upon the type of contaminate obviously people look at hydrogen formation or generation too right for different type of compounds you have the relevant data hydrogen is used at one particular matrix. Some people use ORP measurement let us say to look at let us say to look at whether reducing conditions or oxidizing condition prevail.

And if so then will the relevant process go through or not, but typically it is not a great way to analyze the system especially in the subsurface because you know some of the relevant compounds are not very or the ORP probe it is probe you are putting in a probe it is not very sensitive to some of these compounds that we are looking at again that is a very generic way though.

So typically byproducts, hydrogen or may be sometimes ORP, but again as we mentioned that is not a great way. So these are generic cases so obviously lines of evidence. So what else can I do though obviously I can conduct let us say try to get that particular soil sample, water sample let us say the contaminated one from the lab not from the lab pardon me from the field take it to the lab and you know understand let us say is the degradation going to occur or not.

So what are we looking at we are looking at microcosm study let us say right. So what are we trying to do here from the field I get a sample of the aquifer you know let us say or the media. I get the sample to the lab right and then let us say I am trying to predict let us say the degradation rates or the rates constant let us say of the relevant process that would need to degradation of this particular compound right.

So how do I do that. So first I spike the aquifer or the sample were the contaminant. So I have different particular samples obviously not one because obviously I need to look at regression later on right. I am going to have number of such aquifer sample I am going to spike them with the relevant spike as in add the relevant concentration let us say of the contaminant.

So that they are either similar or in the range of the contaminate concentration you would expect in the right scenario right you will do that and then you will check let us say or you will monitor the concentration you know with time in this particular lab and then look at let us say try to model that with respect to your mass balance and try to get your rate constant which will give an idea about the degradation actually occurring let us say.

And also if it is occurring is it relatively fast enough or not. So thus something we are going to spend sometimes upon and it is can seem a bit tricky but it again from the basic or such. So obviously what are the relevant aspects involved here I am trying to get the rate constant here and what data do I have I have the initial concentrations let us say the C0 which is what I am putting in.

And so with time I am measuring the concentration C with time. So at time 0 I have C0 and I have different data here let us say. So here is the key is that we also have soil and groundwater in between and also the contaminate here right. So you can either measure the concentration in the groundwater and also the concentration in the absorbed phase or the one absorbed on to the relevant soil here let us say right.

So q is what I am looking at that or not looking pardon me using to represent the concentration of the compound absorbed on to the soil let us say right. But one aspect again before we need to go further and I think this is something we discussed I believe earlier when we are talking pump and treat right. So we were talking about pump and treat we looked at different scenarios.

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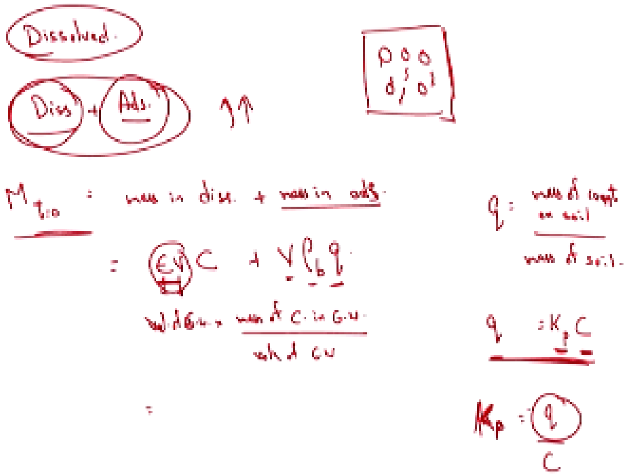

As in we looked at cases when we had the compound only in the aqueous or the dissolved phases and also when it was both dissolved and also absorbed on to the relevant soil let us say right and then also the NAPL phase and so on. Obviously we saw that pump and treat works well if the compound is only in the dissolved phase or most of it is only in the dissolved phase.

But if you have considerable absorption the time taken for pump and treat is too high. In that context how did we analyze the system I believe we looked at the total mass and at time=0= the concentration or the concentration mass in the dissolved phase and mass in the absorbed phase. Why are we looking at that because even in our microcosm study now we get the relevant sample from the field and it has the relevant soil and the groundwater and the contaminate.

So some of the contaminate let us say in the groundwater or the water in the pores and some of the contaminate is absorbed on to the soil here right. So here we obviously need to take into account but these particular aspects let us say right. So in that context we are trying to refresh your memory so what do we have we have the mass in the dissolved phase+ absorbed on to the soil let us say right.

So we already worked this out so it is nothing but epsilon v. What is this epsilon is a porosity v is the total volumes times the concentration of the compound in the aqueous phase right. So this is volumes time volume of water or groundwater let us say* concentration of the compound in the groundwater so that I am going to write as mass of contaminate in groundwater by volume of groundwater.

So obviously these 2 cancel out and I end up with mass of contaminate in groundwater and also mass in absorbed on to the relevant soil. So I believe we looked at so obviously volume bulk density and what else obviously the concentration right. So here I have volume dry bulk density and the concentration. So what is q? Q is nothing but similar to let us say the mass of contaminant on soil or absorbed on to the soil by mass of or per mass of soil let us say right.

So these are the aspects we looked at. So again what is the case now we have the relevant soil the relevant compound is absorbed on to the soil and also in the groundwater or in the water present in the pore space. So we need to look at these 2 aspects and this is what we have here, but what is one of the aspects we need to look at obviously the concentration in the groundwater is also going to be in equilibrium with let us say the concentration in the soil.

So if it is too let us say if there is an equilibrium right now and then I add more contaminant to the concentration in the groundwater let us say what is going to happen now this is the system earlier it is here and out there. So now the system is again going to try to reach equilibrium right. So the concentration in the relevant groundwater will decrease how is that because some of the compound is now going to change phase into the soil phase.

Again you are always going to have an equilibrium in between q and concentration this is q is the concentration absorbed on to the soil c is the concentration in the groundwater and here if we assume that it is linear there are other what do we say assumptions you can make but for sake of easier analysis I am assuming that I will have a linear what do we say relationship between q and c and p is the portioning coefficient.

Obviously what is kp it is nothing by q/c higher portioning coefficient what would that tell me that more of the compound would want to stay absorbed on to the soil. Again what is kp depend upon if you remember it is the fraction of the organic fraction that is present in the soil, but we are not going to go into that detail, but we just need this to be able to solve for our system right.

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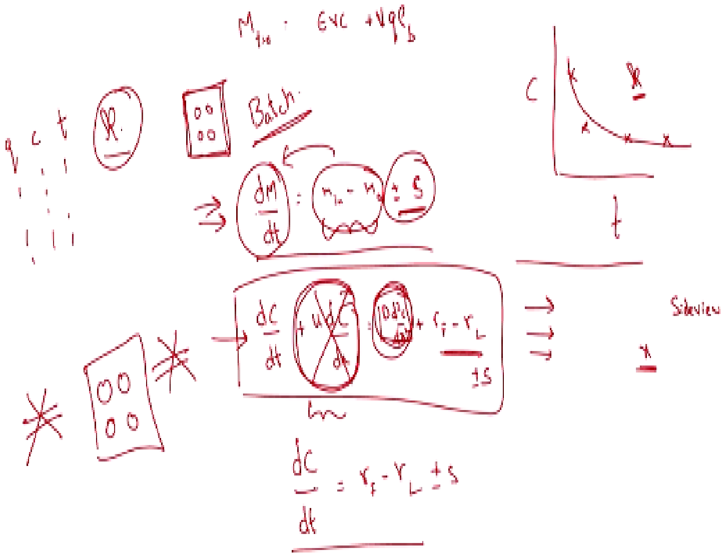

So that is something we have what is it time=0-epsilon epsilon vc+ q volume rho b. This is what we have here, but what are we trying to model or estimate here we are trying to get the rate constant here. We already there the data between q, c, c and t or q and t let us say right. So how do I go about this now let us say. I want to model this system obviously and fit the relevant model to the relevant data that I have.

For example, let us say this is c and t and from absorbed data or the one that I got from the lab you know this is my these are my data points. So from this if I fit the relevant model to this I can get the relevant rate constant right. So for that I need to come up with the relevant model that is applicable in this scenario right. What is the role of this model here? we are obviously trying to estimate something.

But whether this degradation is going to occur if it is going to occur at what rate and so on and so forth. So obviously for that I need the rate constant right so that is the objective here. So I need to obviously look at the mass balance approach here on this particular system and here there are 2 cases. So then we try to apply the mass balance we need to obviously identify what is the compound so there is only one compound so that is not an issue.

Then you need to identify what is the control volume. So here the issue is that is the control volume judge the groundwater or the total volume which includes both the groundwater and the soil. So whichever approach you take if you depending upon the way you work it out if you work it right according to the relevant basics you will end up with the same answer. So that is something we are going to try especially because let us say you need to apply the mass balance which is the key to environment engineering if I may say so to any system out there.

So what is this mass balance about if we discuss that. So it is nothing but we are talking about change in mass with time in that particular control volume will be dependent upon the mass coming in, mass going out right + any sources or things or any reactions occurring or such I will just say + or – sources or thing as in any reaction occurring that lead to either formation or loss of the compound I would include that in here right.

So that is what we have and I believe you also looked at it in some detail earlier. So there are 2 forms obviously I am going to look at the fundamental form and here I am going to look at the case that is going to be applicable to groundwater let us say right. So I am going to look at this system where let us say I have groundwater flowing in this direction this is the side view let us say.

As in there is flow only along one direction x flow or in advection let us say. So how does this transform into if you remember that it is nothing but you know $dc/dt + u\, dc/dx =$ + or – the sources or things. So here we also can have the diffusion related term or the dispersion term. So in the earlier case when we looked at some examples let us say we did not consider the let us say I believe the diffusion term.

But from now on for groundwater we are going to look at that, but that something we are going to let be for now and then this sources or things let us say rate of formation- rate of loss let us say. So now I need to be able to apply this to my batch reactor. So thus as in the case is the one in the lab. So this is a batch reactor so what do we understand from the batch reactor. We understand that there it is a closer system no flows coming in and going out.

So if there is no flow coming in and going out so then this term will be 0 right. What is this term giving an idea about? It is nothing but mass out-mass in I mean we bring this term out to the left and that is what you have here. Again let me try to clarify that further I will again come back to this particular mass balance equation. Here we are trying to look at how the mass or the concentration is changing with time.

What is that depend upon? It will depend upon mass coming into the system, mass going out of the system and any reactions that are leading to formation or loss of the compound in the system right so that is what we have in this particular case. So I apply the relevant what do we say advection and diffusion relevant flux simplify further and this is what I end up with. Again as I said what is this going to give me an idea about.

This is going to give me an idea about mass out-mass in and rate of formation-rate of loss and obviously I will have a diffusion term that is going to be D del square c/dx square let us say. Again we are not considering this for now. So again I am applying it to the case where I have soil and groundwater in the contaminant here. So this is a batch reactor no flow coming in, no flow going out.

So I am going to remove this term so I will just end up with dc/dt= rate of formation-rate of loss right. So the key here is that let us say initially let us think of it as if we are trying to apply that for particular just the groundwater not including the relevant soil in your particular control volume. So again as I mentioned when you choose the control volume right you are have 2 aspects or ways to go about it here choose just the groundwater as your control volume and the second one as the one that includes both the soil and the groundwater.

Here let us say I am choosing what do we say just the groundwater as my control volume let us say only the groundwater. So how do I go about this obviously there are still the sources or things if any so how do I go about this now.

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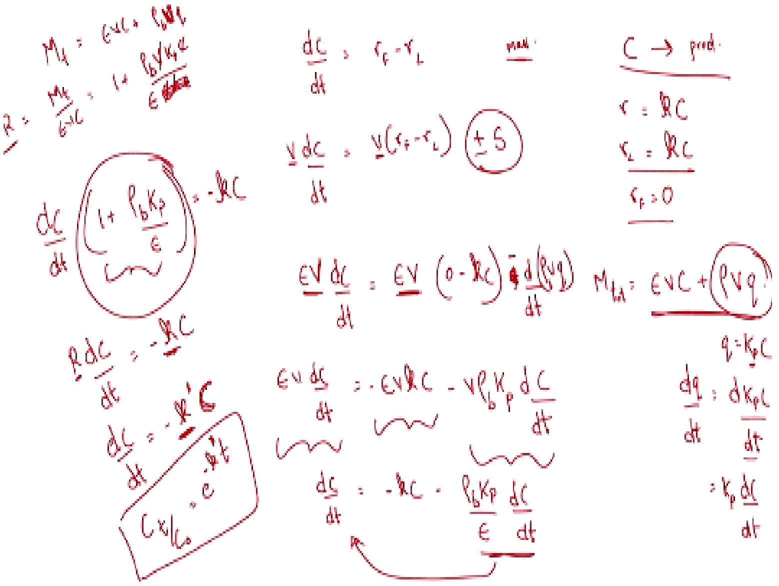

So we have this dc/dt=rate of formation-rate of loss right and how can I transform this or make it simpler if I am trying to look at the mass too. Here is the genuine concentration so if I multiply that by v dc/dt that is= volume* rate of formation-rate of loss this will give me an idea about the mass I guess. So if I have any other additional sources or things obviously I have that term out here right.

So this is obviously for the batch reactor we are looking at how the concentration is changing with time, but keep in mind that the control volume is only the relevant groundwater right so but what else will take place right. You have desorption or possibly the compound from the relevant soil being desorbed into the groundwater. Let us try to understand this. So let us say initially the concentration of the relevant compound in the soil will be an equilibrium with the concentration in the aqueous phase right this is where we are let us say.

And the microbes are doing their job and you have degradation of the concentration in the groundwater or in the water, but is this going to stay as it is or this particular concentration in the soil and the concentration groundwater no because this particular what do we say concentration in the groundwater decreases you no more have equilibrium between the soil and the relevant water right.

So again you are going to have desorption from the soil into the relevant groundwater or the system is going to be something like this. So you are going to have this occurring simultaneously as in desorption occurring simultaneously. So that is something that we are also going to have to take into account let us keep that in mind. So what do we have here. So we are going to consider that its pseudo first order or first order loss C goes to products.

And what is the rate of this particular reaction it is nothing but the rate constant time c and what is the rate of loss of this particular compound it times the Stoichiometry coefficient. Stoichiometry is 1 here so it is kc is the compound being formed. No the compound is not being formed so the rate of formation is zero. So I plug that into here right so what do I end up with.

So v is the volume of water, but if I try to express it in the terms of variables that I have and v is the total volume so it is porosity times total volume is the volume of water* dc/dt = again here too it is volume of water. So instead of writing it as v I am writing it in terms of the total volume porosity times total volume because that is what you typically have. You measure the porosity and the total volume and then estimate the amount of groundwater times rate of formation is 0 rate of loss as you can see from here is kc though right.

And obviously we have to also look at this particular term what is that about. What is the desorption that is occurring from the soil into the groundwater we always have this particular equilibrium maintained right? So assuming that let us say these rate at which this desorption takes place is faster than the rate at which this degradation takes place. So I am going to make that minor assumption and go ahead and work that out.

As we looked at earlier in this case here where do we have that M total we all have the concentration both in the aqueous or in the groundwater and also in the soil right. So let us just try to write that out here total=total= epsilon vc+ rho b v*q right. So this is what we have out here right. So let us try to use this out here so I am going to have a change in this particular term.

So I am going to have to say d/dt of rho v q let us say rho b bulk density, but do I have a positive term or negative term and how do I understand that. So here keep in mind that the term I have here is d dq/dt more or less right. How is the concentration in the relevant soil changing how is that going to help me as in let us say the concentration in the soil is decreasing what does that mean now where is the contaminant going.

It can only go into the water or the groundwater. So the concentration or the change in concentration in the soil is going to be the reverse direction of the change in concentration in water as in if the concentration in the soil decreases the concentration in the water would increase why is that because the desorption takes place from the soil into the groundwater, but let us say of the concentration in the soil is changing or increasing with time pardon me what would you observe.

That means that the concentration in the groundwater is decreasing as in let us say this is the case if the concentration in the soil is increasing what is the driving force obviously the concentration in the groundwater will decrease so it is in the opposite direction. So that is why it should not be positive out here it needs to be negative out here. So let us try to simplify this further. So we still have epsilon v dc/dt= epsilon- epsilon v kc- these 2 are constant volume and rho b and dq/dt what is dq/d t.

As we know earlier it is q depends upon the portioning coefficient times the concentration in water so q kpc/dt this is the concentration obviously kp so I am ending up with kp*dc/dt right. So I plug that in here kp dc/dt right. So obviously we have relevant equation, but we should always try to understand the relevant variables in terms of what we see out there right. So let us try to understand this again.

What is this term giving me an idea about how is the mass of the particular contaminant in that particular groundwater changing with time and what is this giving me an idea about? The mass of the compound that the microbes are degrading. What is this giving me an idea about the mass of the contaminant what do we say either coming in or going into the soil let us say and because that is an equilibrium with the groundwater that is why we have this term out here.

So dividing by epsilon v what do I end up with dc/dt=-kc right – rho b kp/epsilon times dc/dt and I take this term out to the left hand side and I am going to work this out here. I am going to write work this out here I am going to take this term out here so I now dc/dt times 1+ rho b kp/porosity= -kc right. So at this point in time we should be able to understand or try to this particular set of variables that I just highlighted here should seem familiar.

Where is that from if you remember we have Mt= epsilon vc+ rho b Vq right and to understand let us say in the context of pump and treat let us say. How much more time I need to pump let us say the contaminant is also on the absorbed on to the relevant soil we looked at the retardation factor right. What was that was the total mass by mass in the aqueous phase right.

So that was nothing but 1+ rho b times v q is kp times c/epsilon vc. So v epsilon this is epsilon so I am left with epsilon here. So as you see the retardation factor is what we end up here right. So we have nothing but Rdc/dt= -kc right k is the actual rate constant let us say, but if I take this R out so dc/dt=-k dash c. This is the apparent one let us say or observed one why is that because it is also takes into account the absorption or desorption from the relevant soil into the groundwater right. So this is the k dash here right.

So let us say I solve this integration I end up with Ct/c0= e to the power of –k dash t right. So this is my model and once I have this model.

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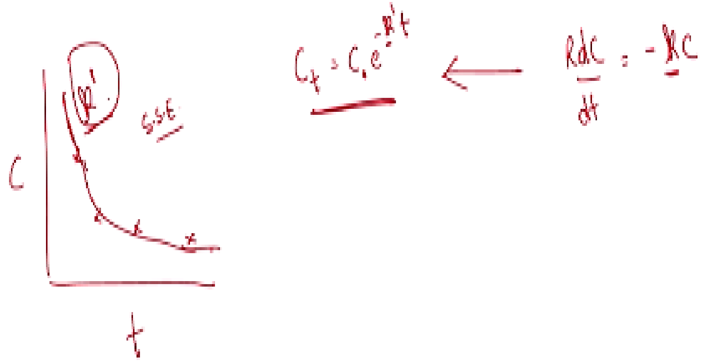

Let me try this out here Ct=c0* e power k dash t. Where did we get this from again we have R dc/dt=-kc what is the true rate constant k dash or k it is k though, but why do we have k dash it is the observed one because let us say you have desorption also taking place between or from the soil into the groundwater or may be the other way too right. You have that particular aspect to take into account.

So if we see that dc/c and-kt and so on. I end up with this here right ct/c0=e power-k dash t. So again now what do I need to I have the initial data c and t here right and now I am going to fit this model to this data and I am going to conduct the regression which ever will give me the least sum of square errors. We are going to look at what this is again right. I am going to get k dash right.

So from this particular aspect let us say I can now estimate k dash let us say and keep in mind that when we are spiking the relevant aquifer in our lab you know we got the aquifer from the site. We have different such what do we say batch reactor and we spike them with either the same concentration or slightly different concentrations and we get multiple such data let us say and then I can fit this model because I know this is the model as we analyze for the system for that particular system I can fit this model and get the relevant data.

So for today we have looked at the case so we looked at the control volume to be just the groundwater, but let us say in the next session let us say we are going to looking at the case when the control volume includes both the ground water and the soil right. So then whatever desorption or absorption takes place you know will be an internal issues or does not come into picture here, but obviously that need to be worked out slightly different.

But whatever way we work out we again come out with this model again what is the need for this model. Obviously when you are fitting a particular model to a data you need to know what the model is. So that is why we developed the model and from this we get the rate constant. Once I know the rate constant I can estimate the kinetics or how fast this particular attenuation is going to takes place.

And also if it is worthwhile or is it too slow or so on and so forth. So I guess again as I mentioned I am out of time and that is it from me for today and thank you.