Environmental Remediation of Contaminated Sites
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Lecture - 25
Mechanism of Natural Attenuation and the Affecting Factors

Hello everyone. Again welcome back to latest lecture session. So a quick review obviously right. So we were discussing or you know talking about the aspect relevant to groundwater remediation or contaminated groundwater you know remediation of contaminated groundwater right. In that context we are talking about something that we observe out there in the nature and thus we call it obviously natural attenuation right. So let us look at what we have discussed thus far.

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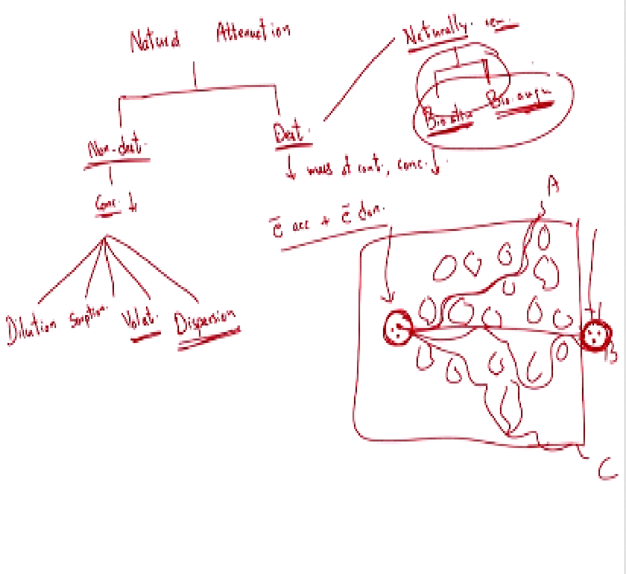

So we have natural attenuation right. See obviously in this context there were 2 aspects that we needed to look at let us say or 2 ways of attenuation. One is the non-destructive as in the concentration decreases, but if you look at the mass of the relevant compound let us say in the entire system that does not decrease though right. So those who were not destructive to mechanisms.

And the other will be or the other one was the destructive mechanism where you had what do we say biological process or such that brought about degradation right. So here we had 2 cases one is the non-destructive and the other is the destructive. So in this case obviously only concentration decreases right, but in this case obviously both the mass of the relevant contaminant and thus obviously the relevant concentration decreases right.

So again what are some of the aspects that bring about or mechanisms that bring about non-destructive that are relevant to this particular case of non-destructive mechanism I guess right. So think of what would happen to the contaminant in the groundwater. So let us say you know at this particular location you have to release of the contaminant and you have groundwater flowing in this particular direction let us say right.

So let us say if there was no groundwater flowing the concentration of the relevant contaminant at this location would always be you know not always more or less be similar to what we have initially right, but if I have groundwater you know flowing along in this direction. So the contaminant or part of the contaminant is going to be transported along with this particular groundwater flow right or advection as we discussed earlier I guess right.

So in this particular case you obviously are going to have dilution right dilution due to the advection let us say right dilution due to advection right. So the concentration here is going to decrease why is that because some of the mass of the compound or contaminant has been transported to somewhere else. So the concentration which is nothing, but mass per volume let us say or moles per volume let us say at this location is going to decrease right.

So you are going to have decrease in concentration of the contaminant, but you are not going to have decrease in the mass the total mass of the contaminant in the system. So and other aspect is obviously in groundwater what else you have you have soil let us say not in groundwater pardon me subsurface you are going to have soil and groundwater. So the contaminant which is in the groundwater let us say depending upon its properties can also be absorbed on to the relevant soil here.

So that particular case is going to be sorption. So let us say if you have the contaminant and the groundwater and part of it changes phase from the aqueous or the groundwater phase on to the soil let us say or is absorbed on to the soil now. So you are going to have less mass and thus less concentration in the groundwater right. So the concentration in the groundwater you can say decreases due to sorption let us say right.

But obviously here we are talking about the contamination changes place from the groundwater to the soil, but not the other way round by depending upon the site conditions or when they release occur of the contaminant you will obviously have those aspects to look at too right. So sorption is one aspect and I think we also looked at Volatilization right. So let us say you have your particular contaminant right either as an NAPL let us say or such.

And let us say you have free pore space in your particular between your soil let us say right either in the vadose zone or in the unsaturated zone let us say right and what is going to happen now. Let us say depending upon the type of contaminant let us say if it is a volatile compound let us say hydrocarbon, chlorinated solvents you know these kinds of compounds are typically what do we say that relatively volatile let us say right.

So they would typically want to what do we say be in the gaseous phase. So if a compound let us say is in the aqueous phase and then it comes in contact with what do we say gas or pore space let us say. The contaminant which is relatively volatile you know that is one that I am assuming here obviously is going to try to change phase from the aqueous phase to the gasses phase.

Thus leading to decrease in the relevant concentration in the aqueous phase so Volatilization. And the other aspect we looked at briefly looked at was dispersion I guess right so dispersion. What is that about? So I think we have the relevant schematic let us say I think let me try to draw that out here again that is better. So if this is the soil let us say (()) (05:36) okay and particle A enters here you know it can move in various directions right or various paths pardon me or you can take various paths.

So compound starting at the same location and sub that A, B, C locations why is that because of the tortuous path you know that it takes as it travels at this particular soil let us say or the subsurface media here right. So due to the tortuosity that inherent in this particular system the particles that starts at the same location can end up at multiple locations. So what does that mean.

You have what do we say dilution of the relevant or dispersion of the relevant contaminant here. Thus leading to decrease in the concentration as in for example instead of taking various paths if all the 3 compounds that are present here ended up here let us say right then is the concentration changing. No because all the 3 moles if I can say for now are which were here are still here let us say may be the concentration here is decreasing, but if I look at it with respect to distance it is not changing though.

But that is not how it occurs you know that because of the tortuosity let us say the relevant contaminants will take different paths and thus you are going to see relevant attenuation of the concentration and that is what we have with respect to or that is what we call dispersion. So typically let us say underground water we also look at we also have diffusion depending upon what do we say the molecular diffusion coefficient, but typically we also consider that to be a part of or can considered that anyway to be part of dispersion okay.

So again moving on to the destructive mechanisms so obviously destructive mechanism as in the compound itself is actually degraded as in the mass of the relevant compound is degraded. It is not that you know let us say 3 molecules here in this volume and I remove 2 and put them somewhere else and thus concentration decreases that is typically what we have in the non destructive mechanism right.

But in the destructive mechanism you know out of the 3 let us say 2 of these particular moles this moles of this particular compound are actually degraded let us say right. It is not that they are changing their location or point in space, but they are actually degrading. So how does come about you know that similar to us let us say the microbes want to thrive right. So what do they want they need sources of energy let us say and also energy that is used for their growth and cell synthesis let us say right so they want to grow too.

So what do they need for that they obviously need an electron acceptor and electron donor right again different aspects. So we are going to talk about this in a bit more detail later so I will skip this one now. So in this context of the destructive mechanisms we talked about I think natural remediation, naturally occurring remediation I guess right and in that context we also talked about some aspects like if this is not fast enough let us say.

So I believe we slightly digress from this particular topic of naturally occurring degradation as in we talked about bio-stimulation and bio-augmentation I believe in that context. So obviously you or the human has a role to play here with respect to bio-stimulating the relevant biological activity or augmenting it right, but I wanted to briefly discuss that in the context of this natural attenuation.

But obviously once you start playing a role and trying to fast enough the kinetics typically though it is not naturally occurring remediation anymore, but again as I mentioned I wanted to discuss that in detail. So let us have a quick recap of what we have been up to. So again as I just mentioned naturally occurring by a remediation but what is the issue though kinetics can be an issue and thus leading to incomplete degradation right.

So let us say again compound instead of going towards end product can form byproducts and I think we did look at some examples earlier in the context of PRB. I think when we had PCE or TCE and one of the byproducts was Vinyl chloride which was more toxic than the parent compound. So you can have such issues that depending upon the extent to which you have the relevant remediation right.

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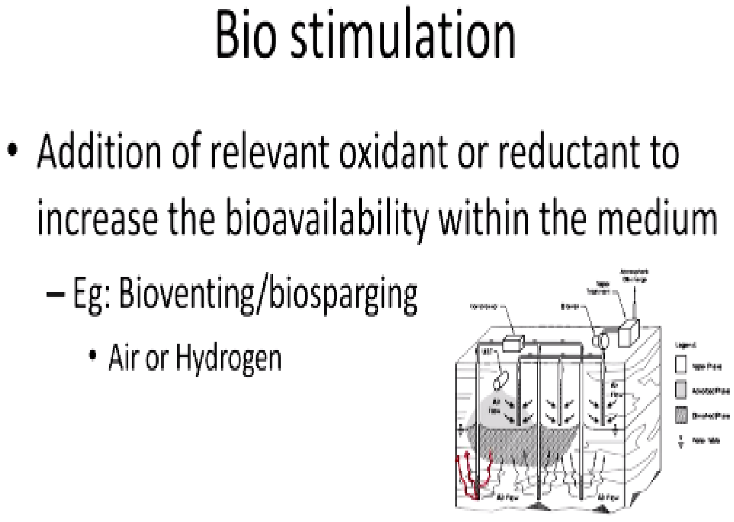

Bio stimulation

- Addition of relevant oxidant or reductant to increase the bioavailability within the medium
  - Eg: Bioventing/biosparging
    - Air or Hydrogen

So bio stimulation we discussed that and in this context we looked at the relevant graph again what do we have here. We have 2 aspects as in they are also putting in the electron acceptor or the oxygen right. So that the biological activity you know increases and they are also removing this particular gaseous compound in the gaseous phase right by pumping the air out and then treating it here right. Again I will skip this because we did looked at that.

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Bio augmentation

Bio augmentation again you isolate microbes from stressful conditions put them here, but again depending upon the type of site conditions obviously they might not thrive right. Again there is a reason why the relative species that are existing right now in that site exist there because they are able to survive in that particular location let us say right.

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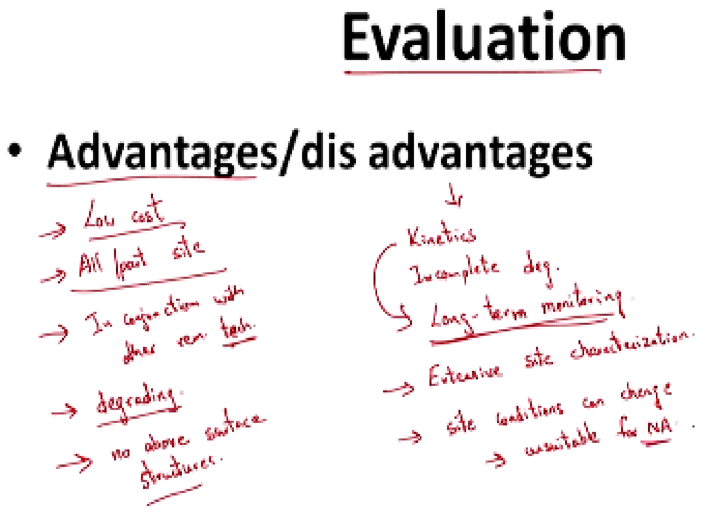

Evaluation

- Advantages/dis advantages

→ Low cost
→ All /part site
→ In conjunction with other rem. tech.
→ degrading.
→ no above surface structures.

Kinetics
Incomplete deg.
Long-term monitoring.
→ Extensive site characterization.
→ site conditions can change
→ unsuitable for NA.

So let us move on the evaluations what are the advantages obviously low cost as in you are not putting any or not any not capital intensive or even monitoring (()) (10:50) but not capital intensive and what else. It can be applied to all or part of the site right. So it can be applicable different ratios of the particular area of the particular site right and then what else do we have here. It can be used in conjunction or together with other remediation techniques.

So that is obviously is something else out here yes so it can be used in conjunction with other remediation techniques and we are actually degrading the compound, we are degrading the compound after looking at and importantly again we have no above surface structures right. So these are some of the advantages and what are the disadvantages obviously as we just discussed kinetics can be slow leading to as I mentioned or we discussed incomplete degradation right.

And because of this what issues we faced let us say because the kinetics are slow what does it mean the time taken might be relatively 10s of years now right. So what does it mean that long term monitoring is required. So long term monitoring is required in this particular context obviously applicability depends on the site let us say in as in the contaminated site is a densely populated area where the people are taking the water from we would rely on natural attenuation.

Probably not it is not certainly not why is that obviously the kinetics are relatively slower and you know the relevant population might be affected by this particular contaminated soil or the groundwater, but let us say due to let us say some mining activities let us say and I am giving you very generic examples here in a relatively remote location or such or you already have let us say some strata inside in the subsurface that lead to contaminated groundwater generation,

But you know there are no immediate users of what do we say the relevant water or such or expose population in that vicinity what would you do maybe you resource intensive and such, but that is going to disturb the system again right or the cost obviously. So you can look at what do we say attenuation with respect to natural attenuation and then put institutional control about restricting entry to the site or you know trying to (()) (13:28) that this water is not used by the relevant limited population if any in that location and so on right, but again what is the key here.

The key is that long term monitoring is required though and in that context obviously you are trying to rely on what is happening in the nature or the subsurface to you know get your job done let us say. So what is required though you need remarkably extensive site characterization right. I mean different aspects either with respect to understand the groundwater flow paths let us say or even let us say to understand what are the strata out there.

For example, if you have lot of iron let us say in your soil let us say and you have a compound that needs to be oxidized now right. What do you need you need oxygen let us say an electron acceptor, but you have a lot of iron in the relevant soil what is going to happen now that iron can what do we say react with the oxidizing agent or the electron acceptor right? So there are such issues again we look at that later.

So that is something that needs to be looked at. So extensive site characterization, long term monitoring, incomplete degradation so these are typically the major aspects right. Again the other aspect is that site conditions can change though. So the site conditions can change such that it becomes unsuitable for natural attenuation let us say. So that is something obviously you need to be considered as in you are looking let us say 10s of years or maybe 50 years or so let us say in this particularly remote area let us say.

But your particular analysis let us say is based on the current conditions, but let us say the site conditions changed you know obviously that is going to be an issue or it can be faster, but obviously it can also mess up the relevant system out there and decrease the kinetics further here right.

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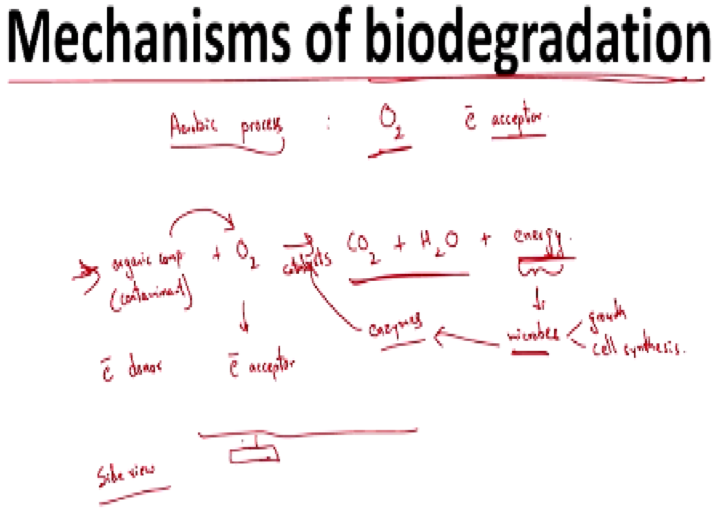

Mechanisms of biodegradation

So let us move on to the mechanisms of biodegradation. So mechanisms of biodegradation how and why let us say do they occur. So obviously one typical aspect is aerobic process right and obviously most people are aware of the term aerobic process (()) (15:45) right. So again typically what are we looking at we are looking at what do we say the presence of oxygen or the degradation of the relevant compound in the presence of oxygen right.

So again I understand they are generic terms but obviously with relevant knowledge of the basics you should be able to do better. So what is the role of this oxygen as we mentioned that it is an electron acceptor right. So again what is the key here let us say we have that oxygen and you have your organic compound which is let say your contaminant right and they can go to if its complete degradation and (()) (16:27) co2 and H2o and energy let us say right.

And thus energy is required by the microbes for their growth and cell synthesis let us say right. Obviously they need carbon again carbon can be you know from this particular organic compound and you know you also need other nucleons, but you know they typically exist out there in the nature in the soil or you can add them obviously, but again what is the driving force here.

The microbes want to grow or thrive obviously and for that they need energy and for that they look at sources of electron acceptors and donors. So what are the electron acceptors and donors in this context do. Here thus obviously oxygen is the electron acceptor right and the organic compound in this and obviously organic compound there are many what do we say kinds so we are talking about the ones that can act as a electron donor right.

So the electron is transferred from here to here let us say right and that process energy is released yes and depending upon the extent to which the degradation goes you end up with co2 and H2o as your end products here. So energy aerobics process here obviously we are talking about the redox process where you are talking about oxidization of the relevant compound let us say in the presence of oxygen or by oxygen let us say.

And again the energy how do the microbes fasten this though how do the microbes precipitate that. So there will be enzyme let us say which acts as catalyst here. So if there are no microbes let us say 100 days’ experiment in the lab and look at or tput in that organic compound and oxygen and look at this the rate of this particular reaction the kinetics might be way too slow.

But let us say if you have the microbes obviously because they want to get the energy they release these enzymes which can what do we day facilitate or fasten the kinetics of this particular process. So this is the what do we say general outline let us say right, but let us look at one particular aspect let us say this is my side view and then l have an underground storage tank let us say and this is something we talked about I think we have a couple of slides here.

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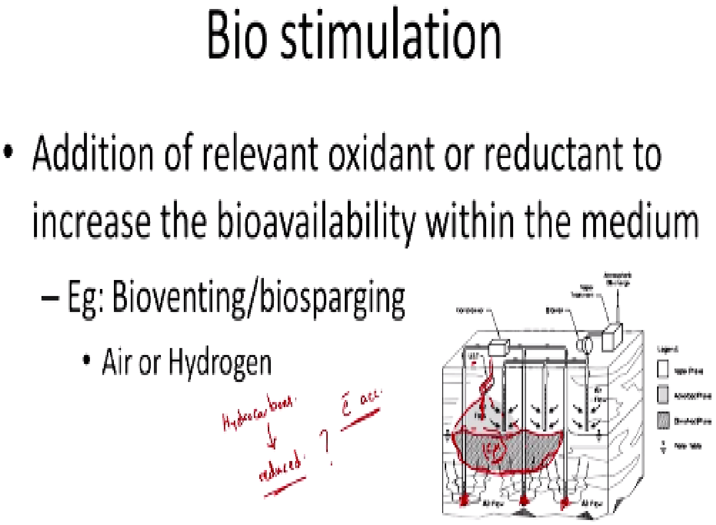

Bio stimulation

- Addition of relevant oxidant or reductant to increase the bioavailability within the medium
  - Eg: Bioventing/biosparging
    - Air or Hydrogen

So here let us say I have you know an underground storage tank and the relevant compound has what do we say you know been released underground storage tank typically used for hydrocarbons or petroleum compound and such or even let us say depending upon the type of industry for safety reasons and such and obviously for economy too, the economy of space I mean.

They are going to have these underground storage tanks let us say right you know but these typically develop leaks and let us say your contaminant not flown pardon me has been released and now you have it some of it in the gaseous phase and obviously you see this particular contaminated plume though right. So assume that we are not having this air being supplied or such right.

So you have this hydrocarbon C and H hydrocarbon, petrochemical and diesel they are hydrocarbon obviously. So C and H as you see what do we say H is relatively more electropositive. It does not want to pull the relevant electrons towards itself. So carbon is relatively more electronegative compared to hydrogen and that is why the electrons let us say are drawn towards the carbon and carbon here in this context of hydrocarbon let us relatively more electronegative or it is reduced right.

So again the key here is that in a hydrocarbons the carbon is typically is in the reduced form right. So obviously what is it that you are trying to do you want to oxidize this reduced compounds and how do you do that you need an electron acceptor right. So the key here is that if you do not provide air what is going to happen to the system. So this is your hydrocarbon contaminated plume let us say okay.

And where is the degradation going to occur let us say is it going to be the edges, center throughout the plume where is it though. So if you look at it or think of it for the redox process to go through what do you need you need the electron donor the donor is available what is that that is the hydrocarbon right. The donor is available, but you need an electron acceptor in this case let us say we are talking about oxygen here right.

So where is the electron acceptor available it is not available throughout this particular plume as initially if you had any oxygen present that would have already been consumed let us say or such. So the degradation is only going to typically occur at the edges of this particular plume. Why is that because that is where you have both the electron acceptor, oxygen and the electron donor the pardon me the electron donor the hydrocarbon and the electron acceptor oxygen in contact.

Where is that obviously typically in the periphery of your particular hydrocarbon contaminated plume right. So again why is that because you need both the electron acceptor and donor in contact let us say or in proximity let us say or they need to be bio available if I can use the term let us say for the relevant degradation to occur right. So obviously you know if it is only occurring at the periphery obviously the relevant degradation is taking place only at the periphery.

For that to fasten that what can you do obviously you know one aspect is to pump or you know provide or stimulate the process by adding oxygen let us say or air that is what this particular graph is about right. Again that is with respect to the relevant aspect out there so we are done with that. So obviously we looked at an aerobic process.

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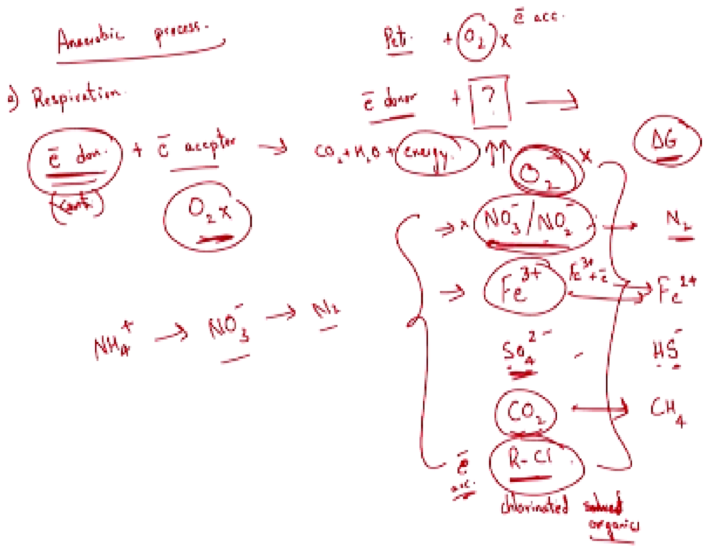

So let us move on to looking at Anaerobic process let us say. So obviously let us say Anaerobic process we are talking about systems that go through or take place let us say in the (()) (22:27) of oxygen. So coming back to our example let us say you had limited oxygen and all that oxygen was consumed actually right. So do you think the degradation can still occur or not occur though right.

It can occur but obviously it as in the hydrocarbon still needs an electron acceptor right. So we continue with the other case so we have petroleum products or the hydrocarbon contaminating the groundwater and earlier you had oxygen, but now you have no more oxygen right. So what do you still need what was the role of oxygen though the role was that it is an electron acceptor.

So now you need an alternative for the electron acceptor for the redox process to go through. As you already still have a lot of electron donor which is your contaminate in this case and you are looking for the electron acceptor. So what are the typical acceptors out there and how does it go about. So again in this context we call this process to be respiration let us say and what is it typically about you have an electron donor which is in this context typically your contaminant let us say typically.

But maybe let me not generalize right now. So you have the microbes trying to look at degradation by using the electron donor and electron acceptor let us say and then that go into the relevant CO2 and H2O and energy let us right. So again transfer of electron you have this particular case and you know the microbes use the energy, but here let us say in this context of the Anaerobic process you do not have oxygen anymore right.

So what are the other electron acceptors that you typically come across or such. So typically let us say you have nitrate or nitrite. Again oxygen is relatively more electronegative again that is why you see that nitrogen is relatively more oxidized right. So again nitrogen here in these forms is relatively more oxidized and then you can look at ferric iron Fe3+ let us say right that also in its oxidized form.

And what else can I look at let us say. I think I can look at sulphates SO4-2 right I can also look at carbon dioxide let us say and then I can look at R cl let us say carbon dioxide and so on. So these are the other typical electron acceptor let us say that can be looked at in the particular situation now. So we look at each of this because they are important. So let us say if there is no oxygen and all these compounds are present let us say in your particular water.

So which one would your particular system choose now system as in the microbes choose as the electron acceptor to you know degrade the relevant compound let us say which let us say in this case is your electronic donor let us say right which one would you choose. For example, if it is you let us say what would you choose you would choose the option that would give you the greatest benefit for the lesser amount of work if I can say that or I think the (()) (25:24) for your buck.

So in that context you are looking at the microbes getting that energy. So they will look at or choose that particular acceptor which will give them greater energy right. So typically let us say oxygen is somewhere out here if all these compounds or electron acceptors are present microbes will choose oxygen let us say as their electronic acceptor why is that. If you look at the delta G values or such greater energy is released when let us say oxygen is used as the electron acceptor let us say.

Again it obviously relevant to thermodynamics, but I am not going to look at that here though. So if electron acceptor or the oxygen is not present in this context and you are looking for other electron acceptors if you choose the next particular option which will provide greater energy let us say and that typically is the nitrite and nitrate let us say right and people might have heard of Denitrification and such and Facultative bacteria.

I think in relevant biological or (()) (26:24) treatment plans you also need to look at removal of nitrogen let us say what do you typically do. You have ammonia let us say and H4+ they oxidize it to let us nitrite let us say right and then this is nitrification and then Denitrification too and sometimes the oxidized form of this N2 right. Again typically you know this is what can happen.

So here too after your particular degradation this can form nitrogen gas and again what types of microbes I think people might have heard of facultative microbes let us say if there is oxygen present they will use oxygen as electron acceptor. If oxygen is not present you know for the electron acceptor then they will use these nitrates let us say oxidized forms of nitrates let us say.

And typically the end products is N2 and here let us say then if these nitrates and nitrites are not present what will be used or what will be used or what will be the next preferred electron acceptor you are going to move on to iron let us say ferric iron and that can be degraded to or reduced to F2+ here right. Keep in mind that these are acting as the electron acceptor obviously if Fe3+ accepts and electron what it is going to transform into F2+.

And again So2-4 once it oxidized it can go to the hydrogen sulphide which is more reduced form of sulphur obviously sulphur here and oxygen relatively more oxidized form of sulphur and here sulphur and hydrogen so thus relatively reduced form of sulphur and Co2 can be what do we say C02 itself can also act as an electron acceptance and be degraded to CH4 or reduced to CH4.

And then this comes this particular bottom of this particular chain why is it at the bottom obviously because it gives relatively the least energy when compared to the other electron acceptor when the electron acceptor is involved in a redox process. So here we have thus obviously I am using for denoting the chlorinated because they have chlorinated solvents let us say or chlorinated organic pardon me let us chlorinated organic right.

So you have the chlorinated organic let us say that can be further degraded or reduced now. Right here they are relatively oxidized now and they can act as electron acceptor. So if you have let us say PCE or TCE and you have oxygen present in your particular system when the degradation takes place let us say if you provided some organic compound.

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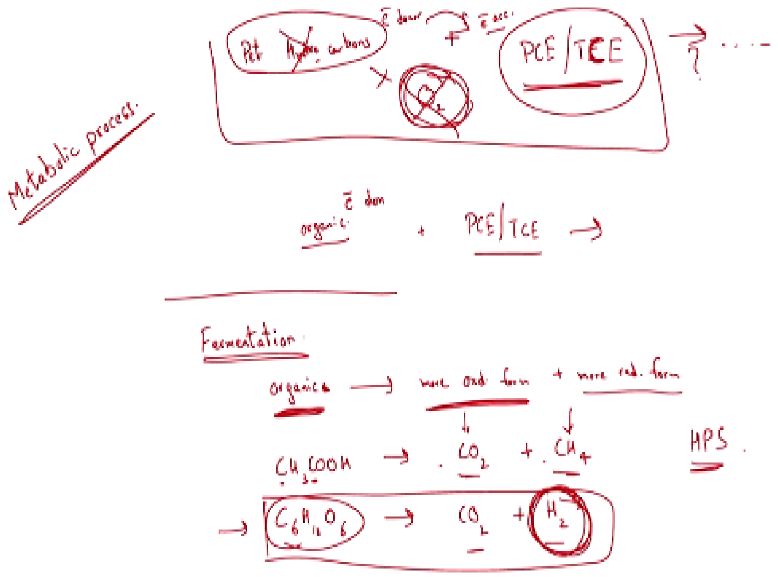

Let us look at this particular scenario as in let us say I have the petroleum or the products or the hydrocarbons let us say. And I have let us say PCE or TCE oxidized form chlorinated organics right. These are obviously the more what do we say oxidized form. So if there is oxygen present what is going to happen to the system or which one would the microbes obviously preferred to degrade let us say.

So in this case obviously what would be degraded petroleum hydrocarbon will be degraded because oxygen can act as electron acceptor this can act as electron donor and then the degradation is going to take place right, but PCE or TCE going to be degraded in this case obviously not. Why is that because the microbes want greater energy and obviously by using oxygen as the electron acceptor they get more energy thus.

But if there is no oxygen and none of the other electrons acceptors we have discussed let us say No3, Fe3+ So4 2-CO2 and so on let us say. And what happens now then this is still your electron donor and this is your electron acceptor and then you have the transfer of the electrons here and then degradation let us say. So that is what occurs. So for your particular let us say chlorinated organic to be degraded right.

Here the role is that it plays the role of an electron acceptor. There should be no other competing electron acceptor so that is the key here. So even if you do not have petroleum hydrocarbon what can you do though. You can add some other organic compound let us say right to your system that can act as an electron donor that can then provide the electron to this

PCE or TCE (()) (30:52) tetrachloroethene I guess right and then that goes to degradation.

So these are the aspects that you need to keep in mind at least when you look at the initial analysis as in does it make sense when I say that microbes can degrade the relevant compound in this particular site or these conditions right. So that is one particular aspect to look it. So the other aspect or that I would like to point out is that you know you have fermentation let us say right.

So what takes place here let us say you have an organic compound and from here you are from same organic compound you have what do we say the formation of more oxidized form and the more reduced form right. So here you know your electron acceptor and donor they are not too distinct compounds. So here we are looking at one organic compound and that you know turning into or transforming into 2 parts.

One of which would be more oxidized and the other one would be more reduced form. So let us say I have CH_3 $COOH$ that can go to CO_2. So this is the relatively more oxidized form as you can see here and you can also have CH_4 formation. So obviously I am not balancing the relevant Stoichiometry I guess right or is it already balanced yes it is balanced I guess. So here this is the more oxidized form of carbon if you look at this here.

And this is the more reduced form as you can see from this particular carbon right fermentation I guess right and again the relevant process yes takes place. Again all these process that we have looked at are part of these metabolic process right the aerobics process that the microbes look or the Anaerobic process or the respiration that we look at or the fermentation what are they about or how do I have a term for trying to understand all these term.

They are involved in the metabolism or you know in the metabolic process of the relevant microbes. Even we have our own metabolic process and they are obviously involved in generating the relevant energy for our particular system right. So in this context obviously we have other or we have other examples to I guess C_6 H_{12} O_6 I am not balancing this can go to CO_2+ H_2 if I am not wrong right.

And so the key here is that you have another particular interesting compound that is being formed here that is hydrogen here let us say. And hydrogen let us say is worthwhile in your particular subsurface because that itself can again act as an electron donor let us say right. So that acts as a reducing agent here and some particular microbes are quite a few at least in the subsurface are very particular about what their electron donor needs to be and so typically even though this process is not what you would add value to your system.

People try to promote this because you need to have or they want let us say hydrogen in the system if not from this compound from other compounds they want to have hydrogen producing substances. Some of them are called hydrogen producing substances so you know H2 tries to be promoted in the particular system let us say right. Again these are different aspects but looks like I am running out of time.

So we will move on what do I say the relevant aspects in the next class and they are typically about natural attenuation I am saying all this occurs but how do I prove let us say that it is occurring or what are the aspects that I need to look at right. So with I am done for today and thank you.