Environmental Remediation of Contaminated Sites
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Lecture – 46
Case Study: In-situ Chemical Oxidation: Part - III

Hello everyone, so again welcome back to the latest lecture session, right, so a quick recap of what we have been up to, so in the context of remediating contaminate soil or sediment let us say we were looking at in situ chemical oxidation methods, right and in that context, we were looking at a particular case let us say or particular site rather which was contaminated with tetra chloro or you know per chloroethylene let us say, right tetra chloroethylene.

And in that context we saw that let us say there were 2 what do we say sources as in one source was that let us say you know there was one particular spill event where relatively larger volume of the relevant solvent spilt over and you know soil was contaminated and this particular contaminant was transported through the storm water drains too that was one way aspect but that was the one time spill.

And the second one was due to let us say miscellaneous spills or small spills occurring daily and these spills typically were washed into the sanitary sewers and there was a leakage at you know one particular junction of this particular sanitary sewer network let us say and we saw that there was considerable contamination you know of the relevant ground water let us say.

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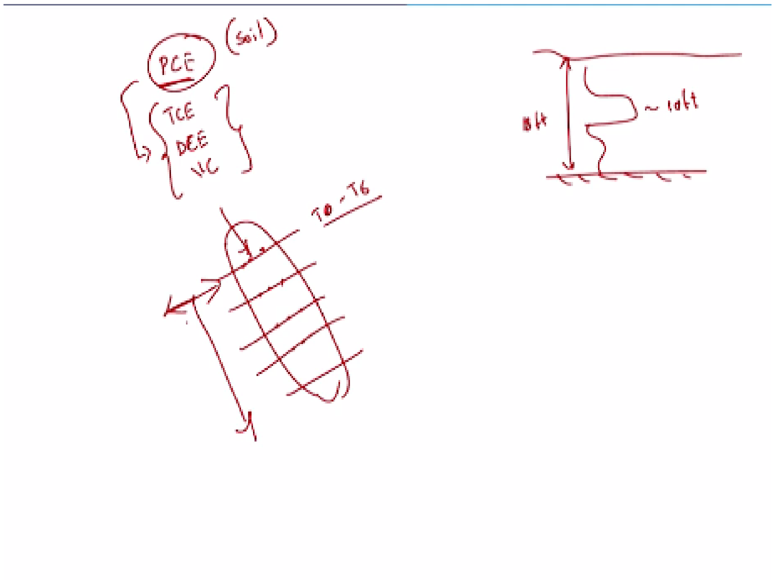

So, obviously this ground water is contaminated with PCE, you will also know or obviously know that typically, soil will also be contaminated because this is hydrophobic compound right, so that is something to keep in mind, also we looked at the different profiles I think we saw that you know there is an impermeable layer, 18 feet from the surface, right, relatively impermeable layer.

And I believe we also saw that the hydraulic conductivity was typically high around let us say 10 feet from the surface, right and this was some such profile I guess, right, we are going to look at these aspects again, right and the other aspect was that PCE let us say would also naturally be degraded let us say in the what do we say soil let us say or the environment but obviously, at much lower rates.

And I believe people also would detected trichloroethylene, 1, 2 DCE, let us say and also vinyl chloride, right, these are all the by-products of PCE let us say, right, so this is what they were using initially but they detected all these compounds, right, so and then we saw that you know for this particular plume, the ground water was moving in this direction and thus the shape let us say, right.

So, this was the shape and they looked at different soil, groundwater and so on sampling locations or you know samples, pardon me, right for transects and so on, we looked at these in general, so let us move on to the next particular aspect let us say, right and again keep in mind that took I believe soil samples along with 6 transects, T0 to T6, right, T0 to T6 and so they were trying to capture the what do we say profile along the axis.

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Retrieving soil cores using the GeoProbe equipment along transects extending across (perpendicular) the ground water plume

And also perpendicular to the axis 2, right, so that is what they are trying to do and I believe here we have a picture of the relevant you know the soil core sampling let us say, right, you know this is the equipment they used and I guess these are the transects that we looked at let us say, right and let us move on, right, retrieving soil cores, again this is a geo probe that is something we also looked at let us say even for you know pumping the relevant oxidant into the relevant soil, right.

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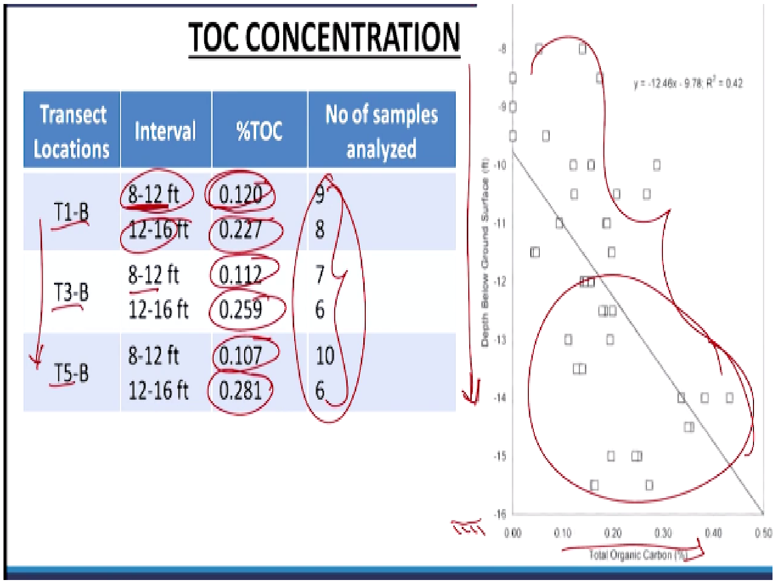

TOC CONCENTRATION

Transect Locations	Interval	%TOC	No of samples analyzed
T1-B	8-12 ft	0.120	9
	12-16 ft	0.227	8
T3-B	8-12 ft	0.112	7
	12-16 ft	0.259	6
T5-B	8-12 ft	0.107	10
	12-16 ft	0.281	6

So, again TOC concentration, so why is this important now, so soil let us say will have some fraction of organic compounds let us say, right, so these organic compounds obviously will be able to adsorb hydrophobic compounds, right and all these 4 compounds that we have looked at let us say are remarkably hydrophobic, some of them are also pretty volatile let us say and this particular contaminates will be adsorbed onto the organic fraction of the relevant soil now, right.

So, you are going to have contamination of the groundwater and also contamination of the soil so, obviously we need to look at those 2 aspects but to be able to get an estimate about the amount of contaminants that is going to be adsorbed onto the soil, you obviously need the total organic carbon concentration typically you have the TOC test that you can do, so let us look at what we have out here.

So, this is the depths below the ground surface let us say from -7 to -16, around 16 or so as we know we have a clay layer or relatively impermeable layer let us say and as you see the general trend I guess they are trying to approximate by linear relationship but it does not, there is no particular relationship here but certainly you can see that there is an increasing trend as in as we go deeper or further away from the surface let us say what do you see; we see that the organic; what do we say, TOC concentration or the fraction of organic carbon in your soil let us say is increasing now, right.

So, what is that mean let us say or what is that you know, how does affect this particular remediation let us say or remediation of this particular site, pardon me that now let us say if the relevant contaminated; contaminant pardon me has permitted through to the lower reaches let us say this reaches let us say, right, what does that mean you know, most of it or considerable fractions of the relevant contaminant would be adsorbed on to the soil.

And it would typically be considerably difficult to relatively degrade that particular or remediate that particular soil let us say, right. So, let us look at it you know here we looked at the generic values, so different transects, right, this is along the direction of the flow of ground water, right, so between 8 to 12 feet, this is the fraction of TOC let us say or percentage of TOC and as you can see they analyse many samples, it is not only from 1 or 2 samples as in as we discuss multiple times during the you know course ideas, right.

You know, we need to get your site characterisation done pretty well, right or you need to characterise your site pretty will otherwise obviously, if you try to what do we say limit your resources when trying to characterise the site let us say, you are more or less a blind man walking out there, right, so as we can see this plant considerable time and resources here and as you see typically let us say in relatively shallow or mid-level regions, the TOC concentration is more or less around 0.1 or 0.11%, right.

And in the lower reaches, it is almost double, right so that is a remarkably high or considerable increase out there, right, so that is something to keep in mind now, right.

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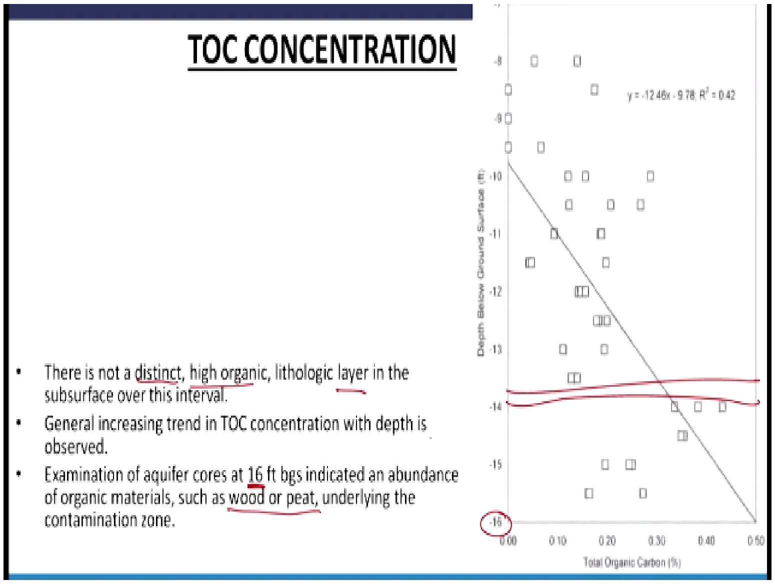

TOC CONCENTRATION

- There is not a distinct, high organic, lithologic layer in the subsurface over this interval.
- General increasing trend in TOC concentration with depth is observed.
- Examination of aquifer cores at 16 ft bgs indicated an abundance of organic materials, such as wood or peat, underlying the contamination zone.

So, let us move on, so again but one aspect looks like is that you know there is no distinct what do we day high organic layer out there as in there is no one distinct organic layer let us say, you know high what do we say layer of soil that has high organic content, let us say that is something to keep in mind let us say, general trend, right that is something that we looked at and they mentioned that let us say after or about 16 feet below the ground surface in abundance of organic materials such as wood and peat was below this contaminated zone, right.

Again, if this particular contaminant has been allowed to let us say, permit further down let us say it would have been adsorbed by you know this particular high organic content soil let us say, right that is again something to keep in mind let us say, right.

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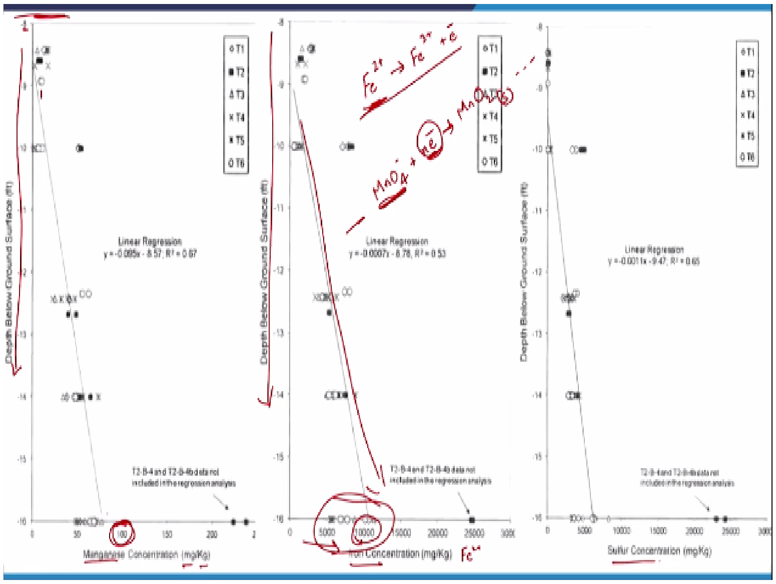

So, concentration of metals and sulphur, why is this important now, so let us look at some of the relevant agents here I guess, here we have manganese and as we see her as we go down or away from the relevant surface let us say, the surface is somewhere out here, so this is 8 feet below the surface, 9 and so on, you typically see that the manganese concentration is increasing here, right and it is maybe maximum of around 100 milligram per kg now, right.

So, let us look at the other more important case, so here as you can see here we are looking at iron and here it is Fe 2+ or the ferrous iron typically let us say, right and as we can see again the same trend as in as you go down let us say or away from the surface of the soil, you see that the iron concentration is typically increasing now, right, so that is what you see here but keep in mind that here the scale is different as in the maximum iron concentration let us say is around 10,000 milligrams of ferrous iron per kg of soil.

And here it is around here as in for manganese it is around 100 milligram of manganese per kg of soil, right, so why is this relevant let us say as in why is the concentration of ferrous iron relevant now, right because ferrous iron is a reducing agent let us say right, it is an electron donor now, right, so as in it can give out an electron let us say and let us say, what do we say release or electron and produce Fe 3+ let us say, right.

Or be oxidised to F2 3+ that is what we have here Fe 2+ going to Fe 3+ + 1 electron let us say, right, so that is what can happen or occur out there, right, this is one particular half reaction but as you know let us say I think for permanganate, I mean obviously, I am going to write the relevant, what is it now; relevant balanced half reaction but we looked at that earlier and some relevant other variables here, right.

I am just writing the generic case, we saw that permanganate let us say is an electron acceptor, right as we can see here it can accept electrons and be reduced to MnO2, this is solid phase, let us say and obviously, you had either H+ or OH- and so on and so forth here, right, so again the key aspect is that MnO4 – accepts electrons, it is as an oxidant, right or it is an oxidising agent but here you have ferrous at very high concentrations let us say or considerably high concentration let us say.

And that is an electron donor, so thus you will have a redox reaction out there, right and this Fe 2+ will reduce MnO4 – or you can even say MnO4- well oxidised Fe2+, so more or less the net effect is that some of the MnO4- or permanganate that you are going to put into the soil is not going to target the relevant contaminants but is going to be consumed by the ferrous iron which is at considerable concentration in the relevant soil, right.

So that obviously needs it to; needs to be taken into account, right so that is what we have out here, so let us move on and then again sulphur concentration typically, only in reducing condition let us say but again similar trend as in with decreasing or you know as we move away from the relevant surface, you see increasing concentrations let us say, right, so that just adds to the complexity of your relevant problem here, right .

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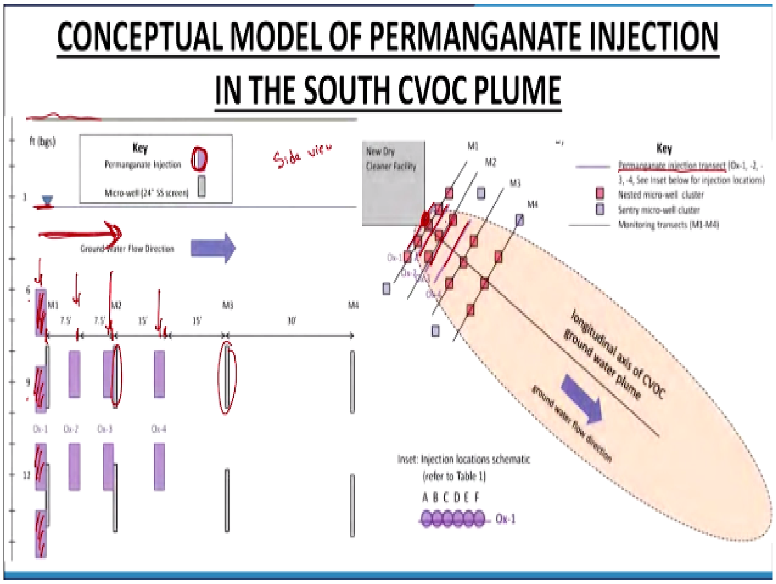

CONCEPTUAL MODEL OF PERMANGANATE INJECTION IN THE SOUTH CVOC PLUME

So, let us move on, so conceptual model of permanganate injection though, right so, here this is the side view obviously, this is the side view, so here is the ground water table, this is the surface, right and ground water flow direction, yes, so here we have the this particular region tells us that you know this purple coloured slots are the permanganate injection points let us say as you see they injected it at multiple depths, right at they are 6, 9, 12 and may be 14 feet below the ground surface.

And also along different you know, locations along the ground water flow, right that is what you see out here and then obviously, you see the different monitoring locations too, right you know keep in mind that we are not going to just pump everything in at one particular location, we will identify the relevant locations and you know pump different oxidant doses depending upon on that particular or local concentration let us say.

And the relevant oxidant demand, we are going to pump the relevant, what do we say oxidant into that particular injection site let us say, right, so that is what we have here and here we have the top view, right and here you see that this is the source more or less, right and these are the different transects I believe, right and here they are; you have the permanganate injection transect let us say that is what you see out here.

Again, nothing but your particular injection points out here, right, this is what you have here, plan view and side view here, right, so again as you can see you have what do we say in series different transects for soil, sampling and obviously for injection of permanganate and again for monitoring wells let us say, right, so just a relatively more complex system.

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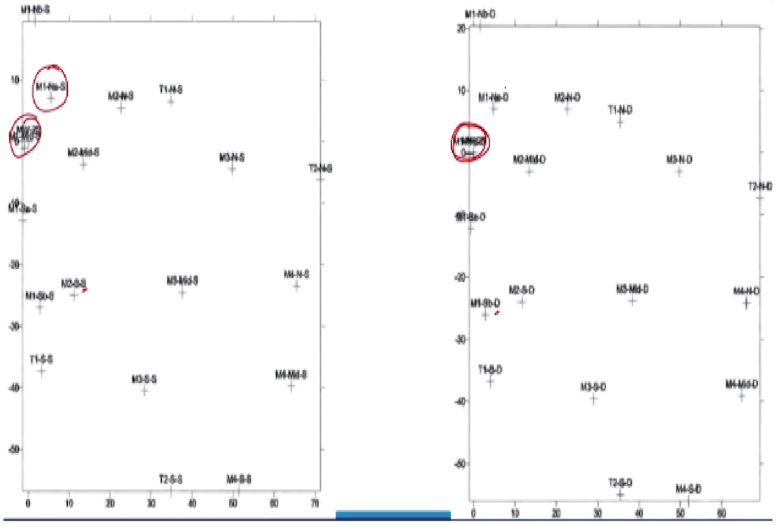
WELL LOCATIONS AND NAMES



So, well locations and names again, just wanted to convey the extent of what do we say monitoring or injection wells located, so here we have deep reflected by D and S reflected by shallow, this is the source of the contamination let us say this particular reference point, just in we have looking or we are looking at this picture, so that I can just convey the complexity of the system let us say, right.

And typically, as we looked at earlier to save on the relevant aspects let us say, they looked at clustered locations as in clustered sampling for both the shallow and the deep wells let us say, right that is what you see more or less similar profiles let us say out here, again let us move on.

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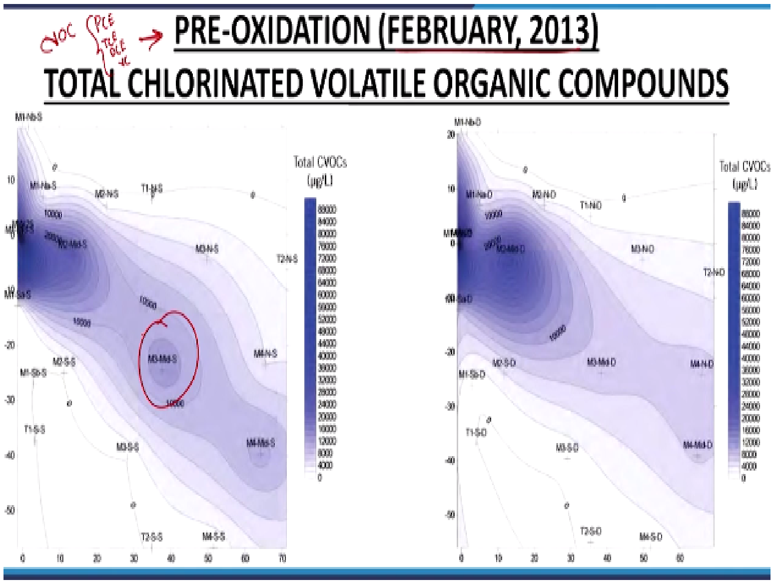

CVOC {PCE TCE DCE VC → **PRE-OXIDATION (FEBRUARY, 2013)**

TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS

So, here we will come to the actual results let us say, so before oxidation which is or before adding the permanganate, you have in February 2013, let us say the CVOC's, right which includes PCE, TCE, DCE and vinyl chloride in this particular case, right, what is the profile here; so in the shallow well, one particular profile and in the deep well, I guess in the deeper locations let us say one particular profile, right.

So, more or less similar profiles, but slightly higher concentrations let us say at some locations in the shallow region let us say, right but as you see still more or less the plumes shapes let us say and the concentrations let us say are relatively similar now, relatively similar right, so that is something to keep in mind.

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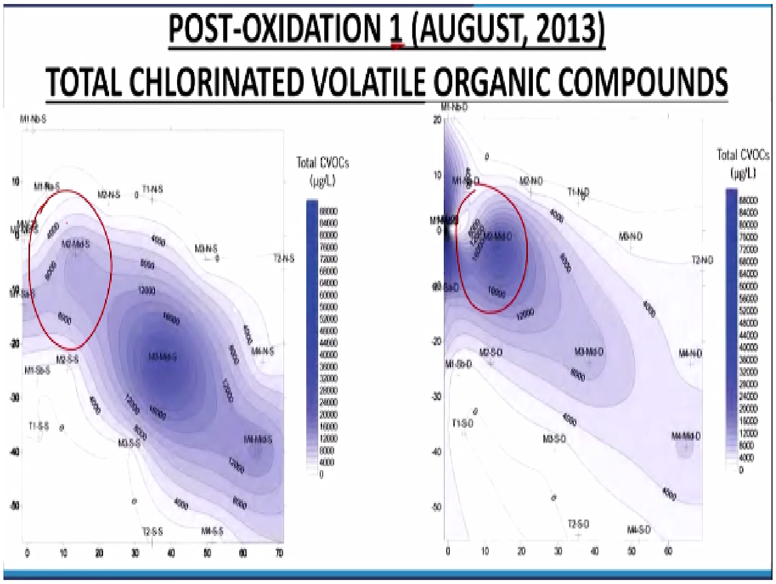

POST-OXIDATION 1 (AUGUST, 2013)

TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS

So, let us see what the scenario is after 1 injection let us say, if you remember the relevant permanganate was injected in or injected 3 times let us say, right and let us look at the scenario after the first injection and as you can see there is considerable improvement, already right, after the first injection itself and keep in mind that initially they only they as in the relevant people who remained at the site, only pumped it in as in the permanganate in the first short anyway at a few locations not all the locations, right.

Typically, in this region that is where they put in the relevant what do we say permanganate, now right, so as you can see this considerable improvement out here, right and also if you remember they waited for around 2 months or so before they monitor the relevant data let us say, right as in if I injected the relevant permanganate into the relevant soil or ground water today only after 11/2 months or 2 month, they did I or you know the relevant people monitor the relevant site.

Why is that, why not let us say tomorrow or just try to look at let us say how much time permanganate will take to reduce these compounds not reduce pardon me, oxidised these compounds and look at immediately because here let us say the reactions are going to occur typically in the aqueous phase, right typically let us say, right and let us say now, the relevant contaminant in the water has been consume let us say or has been oxidised.

What is going to happen now, the contaminant that is on the soil let us say is going to desorp into the relevant water now, right, so you are going to have desorption and thus a rebound or increase in the concentration will be witness let us say, right, so to take that into account typically, you are going to be give some time for the equilibrium to be reached and that is one of the reasons I guess they as in the relevant people monitor the site after a around 11/2 months or even more let us say after injecting the relevant oxidant let us say.

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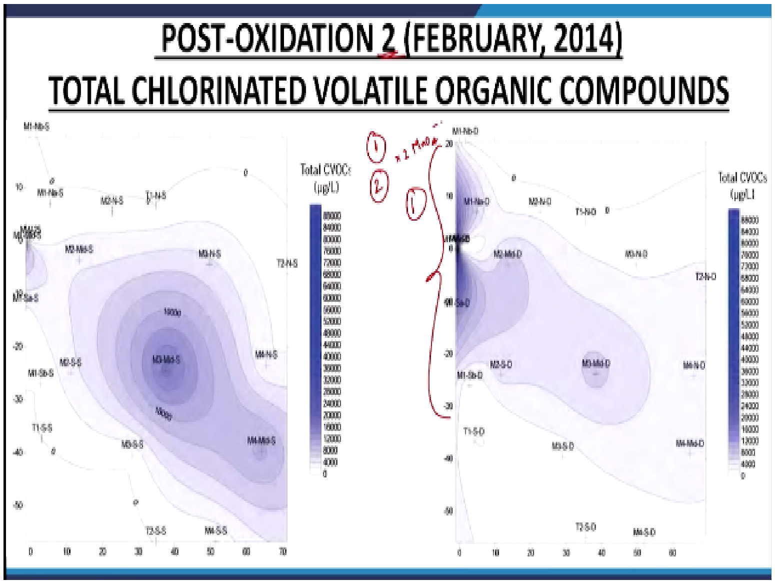

POST-OXIDATION 2 (FEBRUARY, 2014)

TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS

So that is something to keep in mind so, let us look at the case for post oxidation injection t2 let us say, right, so as you see the; you know it is getting better as in especially in the first injection, the deep well it was still considerably contaminated but you see now that not deep well, the deep well locations let us say were relatively contaminated but you see now that it is getting better but one aspect to keep in mind is that completed the first injection, second injection was almost twice the amount of permanganate.

And also they put up or inject the relevant permanganate at more number of locations, right that is something to keep in mind and with that something we covered earlier, right so let's move on.

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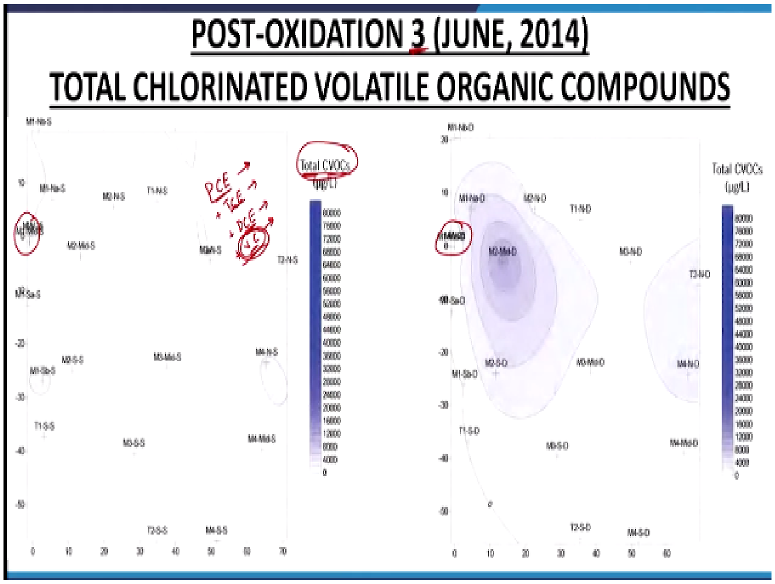

POST-OXIDATION 3 (JUNE, 2014)

TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS

Again this is after the third injection, right, so now as you see more or less within this particular shallow well region anyway or shallow region, most of the relevant sites have been cleaned up; relatively cleaned up, right but one aspect I would like to point out is that we are looking at total COC' CVOC's as in PCE + TCE + DCE + VC let us say, right but typically, the standards let us say based on the toxicity of the relevant compounds or set for individual compounds, now.

But because this was the pilot's case study and they wanted to look at the effects let us say, while also remediating the sites, typically they have looked at total CVOC's but it would have been a much better work let us say or it would have been worthwhile if the resources were available to monitor the concentrations of these particular individual toxic compounds so and not just the total CVOC's.

For example, we do not know let us say, we do not know let us say if most of the total CVOC's after the clean up is just present as vinyl chloride let us say, we did not know that I am just giving out example out here, right, so to prevent those cases let us say, it would be better let us say to also get some idea about the individual concentrations, right . Again, as you see though in the from the point of view of total CVOC's, the situation is much better, right.

And here we see this particular case let us say, again this is the source if you remember, again in the deeper locations, yes it is much better but may be not you know complete cleanup but again let us say you know if required people can inject the relevant permanganate or the oxidant again let us say, right but again this is the case for the pilot scale demonstration let us say but if you see this compared to the initial picture, this is much better though, right.

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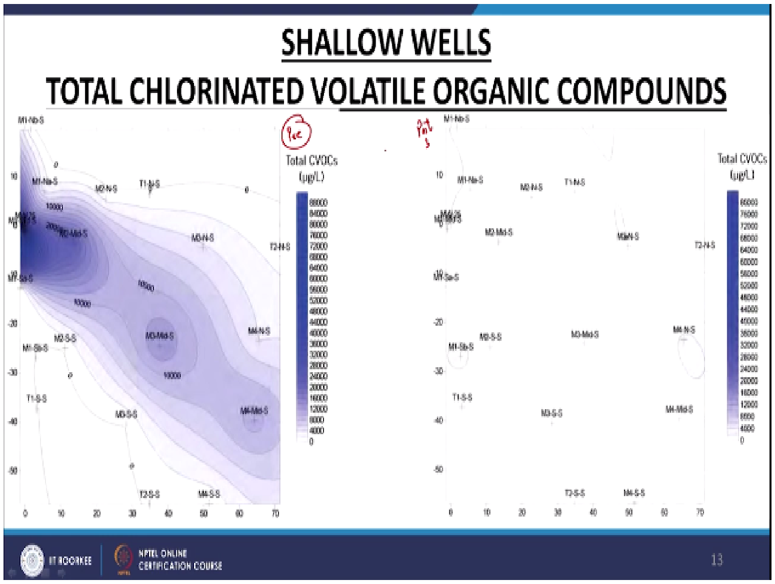

SHALLOW WELLS

TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS

So, this is peroxidation before the cleanup and after post oxidation of third injection let us say, right, pre and post after the third one, as you see now there is a remarkable difference out here, right.

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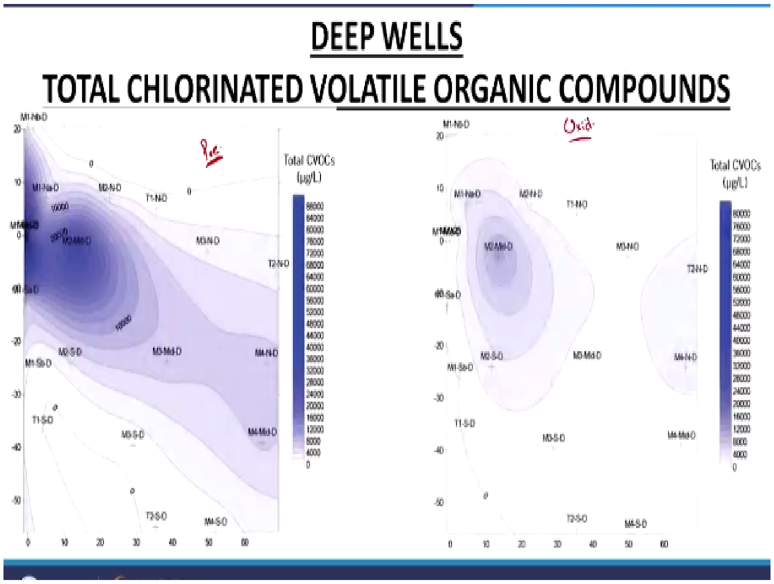

DEEP WELLS

TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS

So, same case with the deep wells, right, so this is the case for the deep wells not the deep wells, pardon me, deep locations let us say, this is pre or before injection of the oxidant and this is after injection of the oxidant out of the third case, this is something we looked at but now, you can compare and you know draw the relevant conclusions I guess, right, so that is something to keep in mind.

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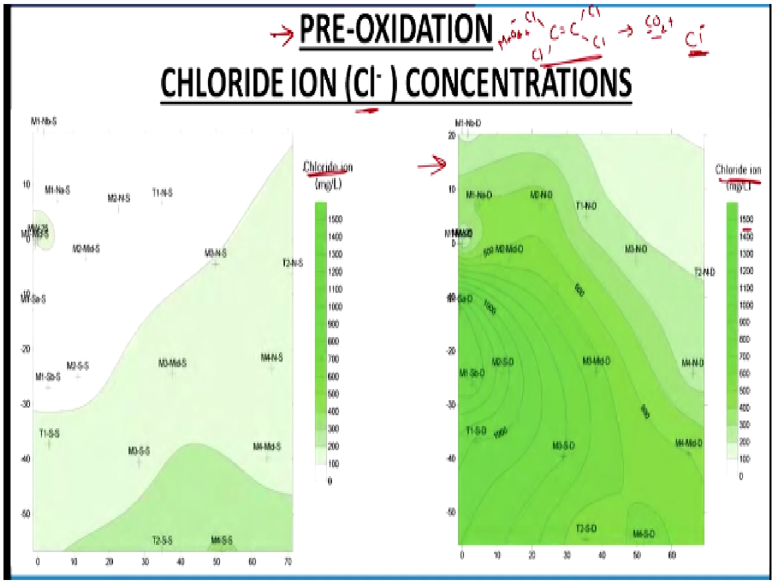

PRE-OXIDATION

CHLORIDE ION (Cl⁻) CONCENTRATIONS

So, let us keep moving, so here we are also going to look at Cl- concentrations, so as we mentioned earlier let us say, one of the other indicators of let us say the degradation taking place is that you know your by products let us say from the relevant half reaction are going to be Cl- let us say, right, because you have C2; Cl4, right; Cl let us say, obviously once you oxidised this and you know, you end up forming carbon dioxide let us say, you are adding MnO4- to this particular matrix let us say, one of which contains this PCE, which has 4 Cl-.

So, C carbon is going to be oxidised to see CO2 and Cl- is going to be release, so what would you typically observe; you typically observed an increase in Cl- concentrations, so let us just try to understand that so, in the shallow region let us say or you know from the samples in the shallow wells let us say, so this is the pre oxidation, concentration but in the deep wells even before oxidation, considerable concentrations of Cl- existed.

But this could be due to 2 reasons as in by the time they started remediating or adding the relevant MnO4- keep in mind that some level of degradation or natural degradation already took place, so some Cl- would have been released or there could also have been sources of Cl- in the relevant ground itself, right but you know looking at the relevant concentrations, you can draw the relevant conclusions as in is the Cl- from the degradation of the compounds.

Or you know, is there a localised source there but again something to keep in my mind is that even before adding the oxidant, you still have considerable levels of Cl- and let us see how it is going to change, typically in the higher what do we say, shallow region, you have relatively less Cl- and in the deeper locations, you have relatively more Cl-, could this be due to the case that typically as you go further away from the relevant surface or you know deeper into the ground let us say, relatively more reducing conditions prevail.

Where, let us say, the degradation of PCE into TCE vinyl chloride or DCE is more favourable, could that be the case we did not know but based on that data maybe that is one particular possibility let us say, while the Cl- concentration is higher in the deeper wells and relatively lower in the shallow regions let us say, right, so let us move on.

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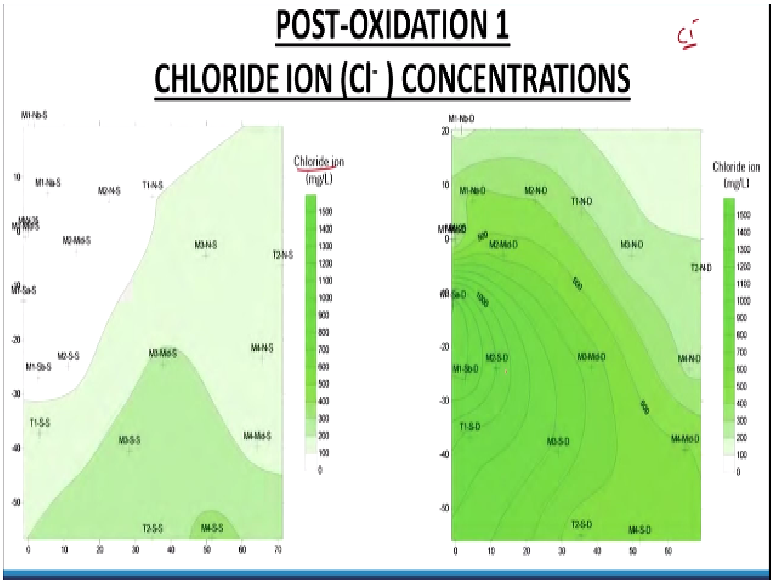

POST-OXIDATION 1

CHLORIDE ION (Cl-) CONCENTRATIONS

So, post oxidation let us say, so you see slight increases in this particular Cl- concentration in the shallow regions, so this is the pre case, right, peroxidation injection and as you can see typically, you know it increased out here, right, it as in Cl- concentration increased, right, again that is something to keep in mind or that is expected, why is that because Cl- is one of your by products, when you add your MnO4- to the relevant compounds, let us say, right.

So, again even in the deeper regions let us say or in the deeper wells that were monitored, you see again in an increase in the Cl- concentration.

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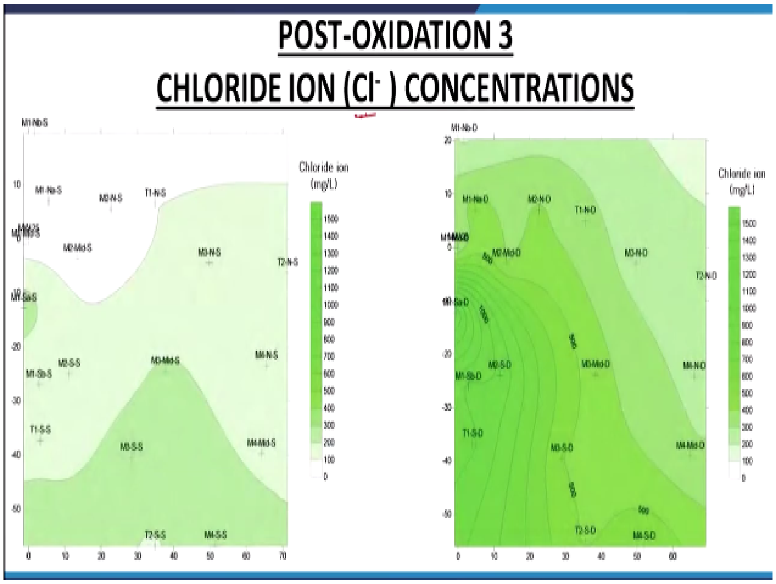

POST-OXIDATION 3

CHLORIDE ION (Cl^-) CONCENTRATIONS

Again, same profile with more oxidant doses further increase in your Cl- concentration, this is dosage number 2, right and again the deep wells, similar case more or less increasing concentrations of Cl- let us say, right, so that is what we observed out here, right, again we never look at only one indicator, typically you know we look at multiple indicators let us say, right because we want to be able to have great confidence in our particular process let us say.

Or to say with greater confidence let us say that what I presume would happen actually occur let us say, right, so I am going to look at multiple indicators here and one of the such indicators is the by-product here which is Cl- let us say, right, so let us move on.

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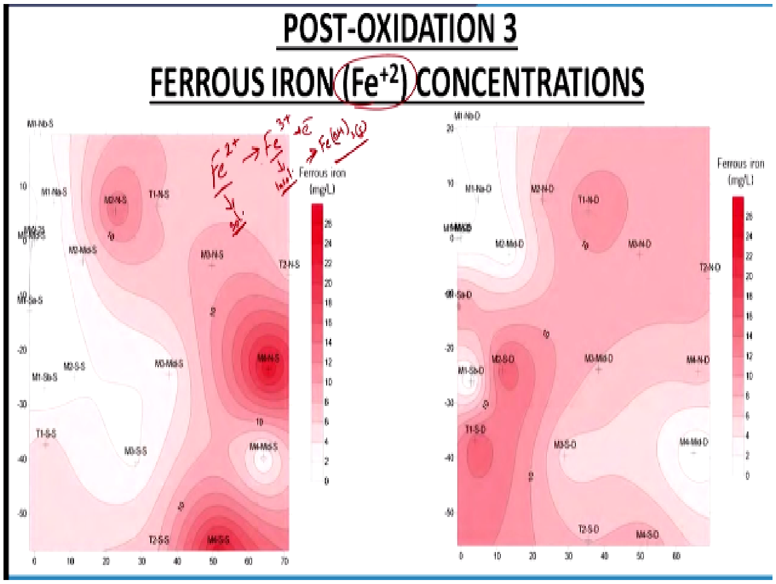

POST-OXIDATION 3

FERROUS IRON (Fe+2) CONCENTRATIONS

So, one another aspect is obviously as we mentioned earlier, Fe 2+ is present in the relevant soil and that will be oxidised by MnO4-, so now let us look at the data, so before injection of MnO4- let us look at what the status was, so in the shallow regions, considerable iron and in the deeper regions again considerable amount of ferrous iron present, right and this is something that we did look at here let us say, so that is something to keep in mind, right.

We have considerable levels of ferrous iron let us say, so after addition, what would be typically presume; we would presume that it would decrease and that is what you see out here in the shallow region and even in the deeper regions, its relatively decrease now, let us say, right, relatively decrease if you can compare the relevant data, this is in the shallow and the deeper wells let us say, right.

So, again there should be further decrease typically, again that is what you observe here, as you now see, right, there is a decrease or further decrease in Fe 2+, right and after the third injection and final injection, right most of the Fe2+ seems to have been converted to Fe3+, let us say, right, here they will looks like they specifically looked at Fe2+ let us say, right and one other aspect to keep in mind that Fe2+ is relatively soluble.

Or will be present in or can be present at higher concentrations in water let us say but Fe3+ is typically insoluble, okay and depending upon the pH let us say, if typically precipitates out, let us say right, typically in this form let us say, right, again different ligands and it can also precipitate out probably in different forms but this is one form that Fe3+ can precipitate out let us say, right.

So, Fe2+, if you add in oxidant let us say or if it is oxidised Fe3+; Fe3+ is typically precipitates out and very little Fe3+ will be present in the relevant ground water let us say, again, so this is again as you can see the concentration of Fe2+ has considerable decrease and this is in line with what we expected based on the MnO4- addition which is the strong oxidant let us say, right.

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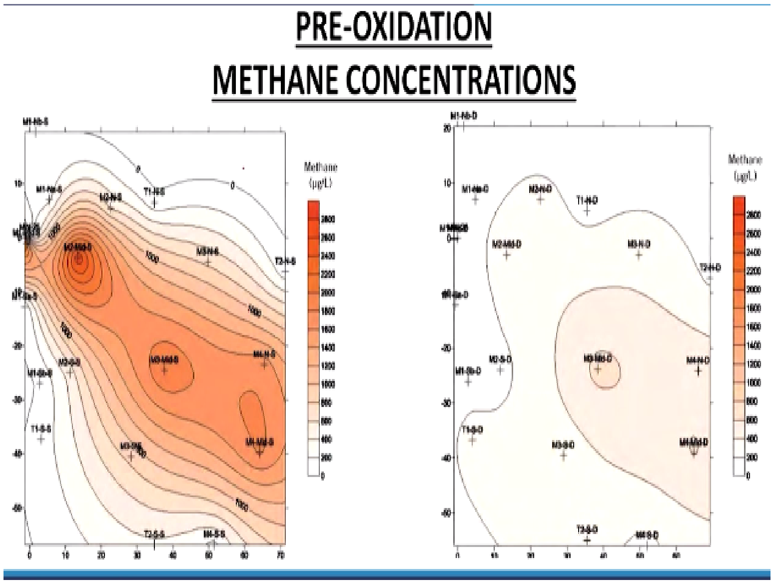

PRE-OXIDATION
METHANE CONCENTRATIONS

So, let us move on, again methane let us say, right typically in reducing conditions, so in pre oxidations, this is what we have in what do we say, the shallows wells and the deep wells here, shallow wells to the left here, right.

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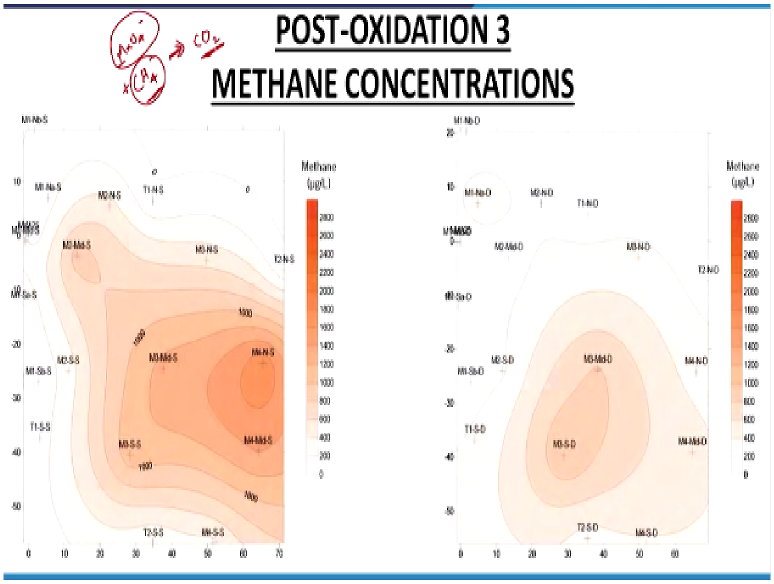

POST-OXIDATION 3

METHANE CONCENTRATIONS

And post oxidation, you see decrease, so CH4 is what we had earlier, so if there was complete oxidation, CH4 could have been transformed into or been oxidised into CO2 by what now; by the oxidant that you are adding let us say, MnO4- + CH4 let us say or MnO4- would oxidised methane into CO2 let us say, if the complete degradation did occur let us say or that is one particular possibility anyway, right.

So, as you see the methane concentrations typically, decreased yes, so let's move on, so now we are also going to look at some other cases but only in the post oxidation after the injection of; the third injection let us say of the oxidant and these are aspects that are important because sometimes while adding your particular oxidant, you can; you know have some or you know come across some scenarios which it did not foresee let us say, right.

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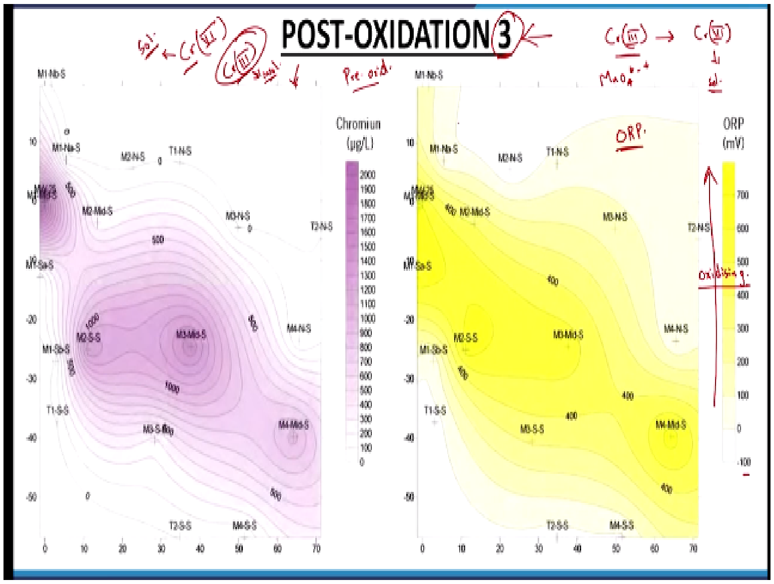

POST-OXIDATION 3

Let us look at this particular case as in chromium concentration, right, so chromium let us say, so here we did not have which oxidation state it is but typically chromium is present in water at relatively higher concentration only when it is in +6, because chromium in oxidation state 3 is typically insoluble and will precipitate out let us say, so this is typically insoluble, chromium in oxidation state 3 is insoluble.

And only in oxidation state 6 is relatively soluble let us say, right, so let us look at this particular case, again in we do not have the data for the pre oxidation case let us say or data for chromium concentration in the ground water let us say or subsurface before addition of MnO4-, anyway that was in presented let us say but let us look at one scenario here, right, so let us say you have chromium 3 let us say in the relevant soil let us say, right.

And then you are adding manganese ore permanganate, pardon me or which is an oxidant, so what can happen; chromium which was in the oxidation state 3 and which was insoluble let us say or relatively present at very low concentrations in the groundwater will now be transformed by MnO4- which is an oxidant to chromium 6, right which is relatively much more soluble and thus relatively higher concentration in the groundwater.

What does that mean now, the chromium concentration or chromium can be transported over a wider area, let us say, so you know that is looks like you know that is one possible case but obviously, we do not have the pre-oxidation data here, this is only from the post oxidation after the third injection, let us say, right, you see considerably higher concentrations of chromium here, right and that typically would have been chromium 6.

And so that is one unintended let us say consequence of addition of your particular oxidant let us say, right, a the compound; a toxic compound which was relatively immobile earlier is now relatively more mobile let us say, right, so that is chromium out here and let us look at the other case, so ORP, so it is a potential here, right again keep in mind this is you know post oxidation after the third injection.

So, earlier it would have been typically reducing conditions and I think we looked at some brief data there, earlier if not the graph but after you add considerable the amount of oxidant doses, what is going to happen now, obviously you are going to have oxidising conditions present, right and so that is what you see here as an minus typically reducing conditions and here what does this mean?

As you go higher up, it means that oxidising conditions prevailed let us say, right, oxidising conditions prevail and that is what you see here after the third injection, the subsurface, how is it now; its such that the potential is you know, typically oxidising conditions let us say, so that is something that you see and again obviously that is expected right, you are adding a lot of what do we say oxidant out here, right, so that is something to keep in mind, right.

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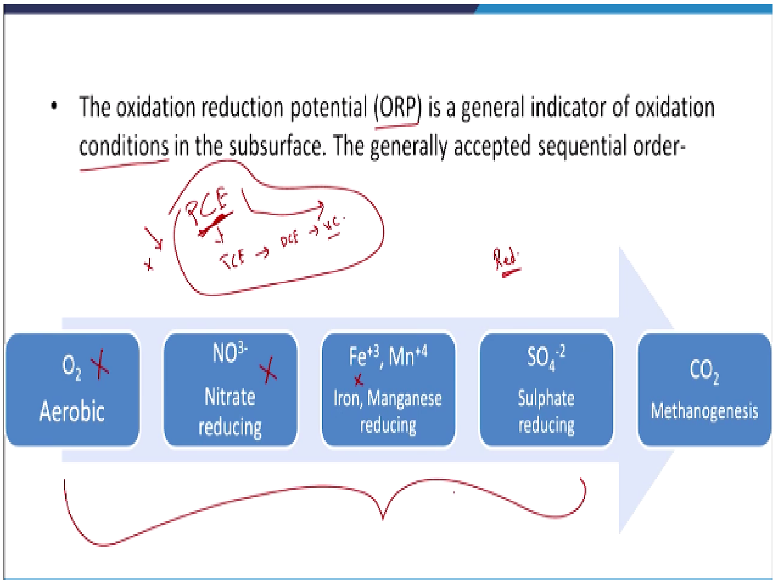

- The oxidation reduction potential (ORP) is a general indicator of oxidation conditions in the subsurface. The generally accepted sequential order-

O_2 Aerobic

NO^{3-} Nitrate reducing

Fe^{+3}, Mn^{+4} Iron, Manganese reducing

SO_4^{-2} Sulphate reducing

CO_2 Methanogenesis

But one particular data again based on the stoichiometry let us say, right as we know is general ORP is a general indicator of oxidising conditions in the subsurface, right one aspect I want to point out here is that earlier, we had PCE and that was degraded to TCE, then DCE and then VC, right, this is one order that can occur let us say, right but when would this have occur; only when reducing conditions prevailed let us say.

But for reducing conditions to prevail what should not be present, certainly not oxygen, typically not even nitrate, not even Fe3+ let us say, what are all these; all these are electron acceptors let us say, right, if all these electron acceptors are present let us say, this particular process would not take place, why is that because this is also an electron acceptor, right and the microbes would have degraded in this way, right as in this order; PCE going to TCE going to DCE and VC.

Only if all these, what do we say compounds, let us say that we have out here are not present why is that because if they are present, the microbes would not have used PCE to as the electron acceptor, they would have used oxygen as the electron acceptor or nitrate as the electron acceptor, right, so if the relevant PCE was degraded into the by-products, what does that mean; typically it would have meant that, earlier reducing conditions were prevailing.

And also that all these competing electron acceptors were not present, right so that is something to keep in mind.

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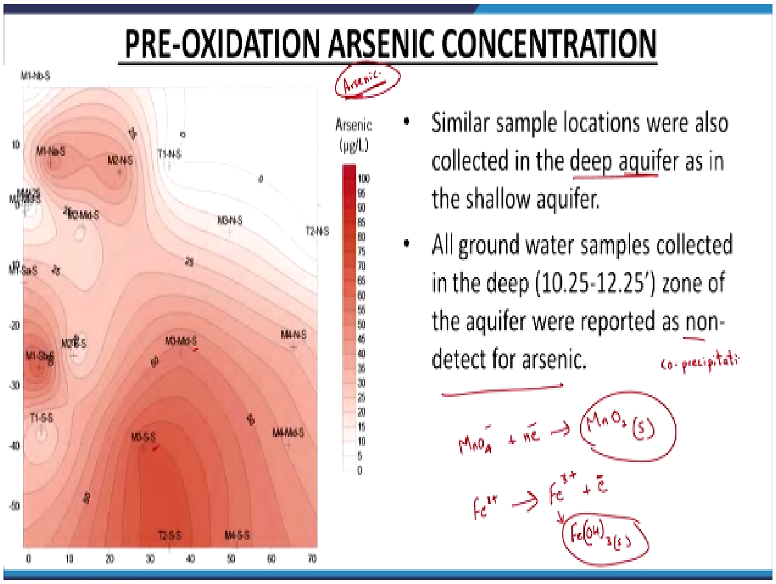

PRE-OXIDATION ARSENIC CONCENTRATION

Arsenic

- Similar sample locations were also collected in the deep aquifer as in the shallow aquifer.
- All ground water samples collected in the deep (10.25-12.25') zone of the aquifer were reported as non-detect for arsenic.

co-precipitati

$MnO_4^- + ne^- \rightarrow \boxed{MnO_2(s)}$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$\boxed{Fe(OH)_3(s)}$

So, pre-oxidation arsenic concentration, so looks like they had arsenic, right remarkably toxic and carcinogenic compound arsenic, right and post oxidation let us say similar were also collected in deep aquifer as in this is I believe from shallow wells but what we say is that even in the type deep aquifer, we have considerable concentrations of arsenic or rather we had considerable concentration of arsenic let us say, right.

So, looks like there were some local sources of arsenic let us say, you know, typically arsenic is also present subsurface typically, or depending up on the relevant site obviously right, it can either be dump let us say or you know due to some conditions or it can also be present naturally in the subsurface, we do not know what the case is but we do know that prior to adding the permanganate, we do have a arsenic in the relevant location let us say, right.

So, all ground waters samples in the deep region were reported as non-detect for arsenic, it is okay I guess did you know, it was only present in shallow regions and not in the deep regions let us say, right.

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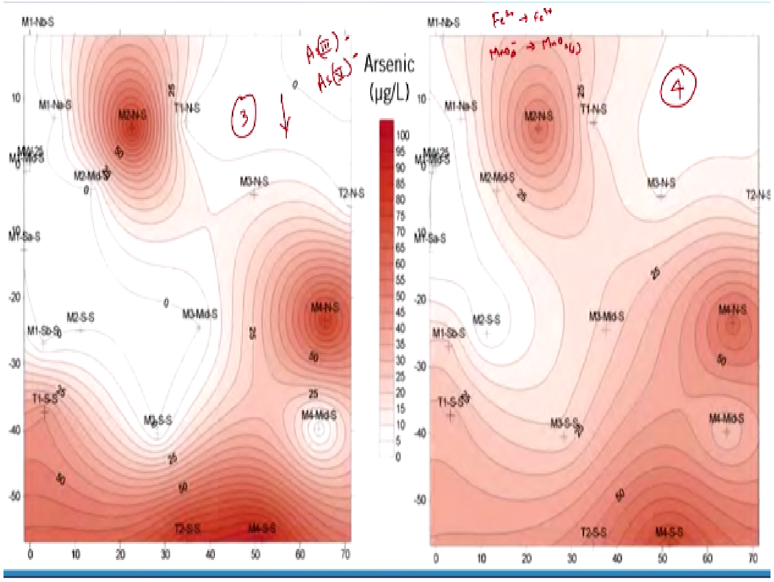

So, let us look at the case here, after addition of your particular oxidation let us say, this is post oxidation 3 and 4 let us say, as you can see what is happening now, typically the arsenic concentration has decreased, now so why is that let us say, right, arsenic can be present in different forms, arsenic I believe in oxidation 3 and if I am not wrong, arsenic in the form of oxidation 5 let us say.

But both these forms are relatively soluble, now right as in no form is relatively more insoluble to my knowledge than the other, but why do we see a decrease let us say in this particular arsenic concentration, right, this is after post injection 3 I guess and after 4 let us say, that is what they say here and what is it earlier ; so you had earlier considerably high concentrations of arsenic and the concentration of arsenic is decreasing now.

So, why is that though, right, so the reason here is that or one probable reason is that if you remember, what is happening to the permanganate we are adding, Mno4-, its taking in some electrons or accepting some electrons and it would have been transformed into MnO2, the solid let us say or we also know that Fe2+ in this condition would have been oxidised to Fe 3+ and while releasing an electron, we know that Fe3+ will not stay as Fe3+.

But would precipitate out let us say, right, so we know that this solid can be formed now, right, so what happens is as these particular solids precipitate out let us say, arsenic will be adsorbed onto this particular solid that are precipitating out and you will have something called co-precipitation let us say, right, so this is one mechanism by which let us say some of the heavy metals are going to be removed.

And in this case I believe that is what happened with arsenic in this case let us say as in ferric iron and also manganese let us say after a relevant reduction let us say, ferric iron from ferrous , right and then so we had Fe2+ going to Fe3+ and then release of the relevant electrons and MnO4- going to MnO2 solid, right and both these solid Fe3+ with the relevant I mean the one that precipitates out.

And I mean O2 let us say, while they are precipitating out, they can acts as sites for adsorption of the relevant arsenic let us say and that is one very probable way and again that is typically used out too there right as in to remove arsenic and this one probable way, how arsenic would concentration would have decreased, so the planners might not have plan for it but that is were one unintended benefits let us say, right,

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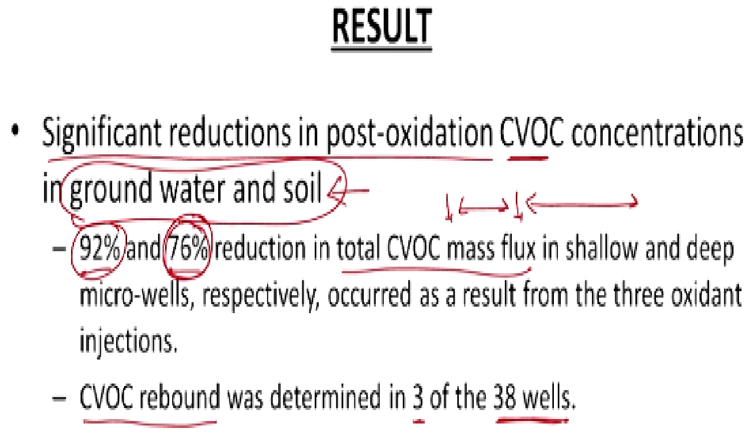

RESULT

- Significant reductions in post-oxidation CVOC concentrations in ground water and soil
  - 92% and 76% reduction in total CVOC mass flux in shallow and deep micro-wells, respectively, occurred as a result from the three oxidant injections.
  - CVOC rebound was determined in 3 of the 38 wells.

So, these are some of the aspects to keep in mind, so what are the conclusions here; significant reduction obviously in CVOC, right both in ground water and soil that is the key here and how can we be sure as you know that let us say if they inject it today, they looked at the monitoring after around 2 months let us say and I think around 6 months and so on let us say, so any partitioning between the relevant soil and water or the equilibrium would have been relatively reach, right.

So, that is something to keep in mind, so both the ground water and soil were remediated, so typically 92% and 76% reduction in total COC; CVOC mass flux right as in a different wells, right you have different well, you will be able to calculate the flux as in mass that is being transported per area per time, so now that has decreased considerably both in shallow to a greater region and also considerably in the deeper region but not to such a great extent though, right.

And also this is what we have talked about earlier but looks like CVOC rebound was determined in 3 out of 38 wells as in it is not as if there is no rebound or increase in the CVOC concentration, again how is this rebound going to occur now, so let us say you have soil and the CVOC on the particular soil and groundwater here, you remove all the contaminate in the groundwater, some of the contaminant is going to change phase from the soil into the ground water, right.

So that is; thus you will absorbed rebound now, so in most of the wells obviously, no rebound was what do we say, we detected but looks like some rebound was detected in 3 of the wells and that could be the reason for let us say the deeper or the efficiency being relatively less in the deeper regions let us say, right, so that is one particular case, so I guess we did look at one comprehensive what do we say comprehensive what do we say case study here.

And now, we looked at the case where both the groundwater and soil were contaminated let us say with relatively more hydrophobic compounds, we went ahead with the chemical process and we had some, not some considerable benefits with respect to the primary contaminants and then some unintended advantages and disadvantages in the sense that chromium was released, while arsenic was removed, right.

So, you understand that there are different aspects at play, right, so I guess again I ran out of time, so I am going to end my session today and that is it for me for today and thank you.