Environmental Remediation of Contaminated Sites

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Lecture – 31
Results of Case Study: Natural Attenuation

Hello everyone. So again welcome back to the latest lecture session. Again, we are looking at I believe a case study right with respect to monitor natural attenuation and we had a site that was near the river I believe Mississippi river in Louisiana right and we are looking at let us say spill of DNAPL and some LNAPL and the DNAPL percolated through the both the clay and the relatively more hydraulically conductive alluvium layer right.

And we had the relevant aspects and we had the site characterization looking at complexity of the particular subsurface right or had an idea about the complexity of the subsurface and then we moved on to looking at let us say what are the relevant concentrations at the source and why this particular site might be a good idea or you know good fit for natural attenuation and in that context, we saw that it can be a good fit.

Because you know your relevant reducing agents like ferrous iron and let us say what else now hydrogen you know which are electron donors you know where it relatively high or sufficiently high concentrations. While the relevant competing electron acceptors right competing electron acceptors to your chlorinated solvents which are your contaminants, your contaminants are your chlorinated solvents which is what you want to degrade.

But if you have oxygen and nitrate, nitrite and sulphate let us say they are going to what you say act as competing electron acceptors. Then, your particular contaminant will not be degraded right. So that is something to keep in mind and we saw that those the concentrations of those competing electron acceptors let us say was relatively low right.

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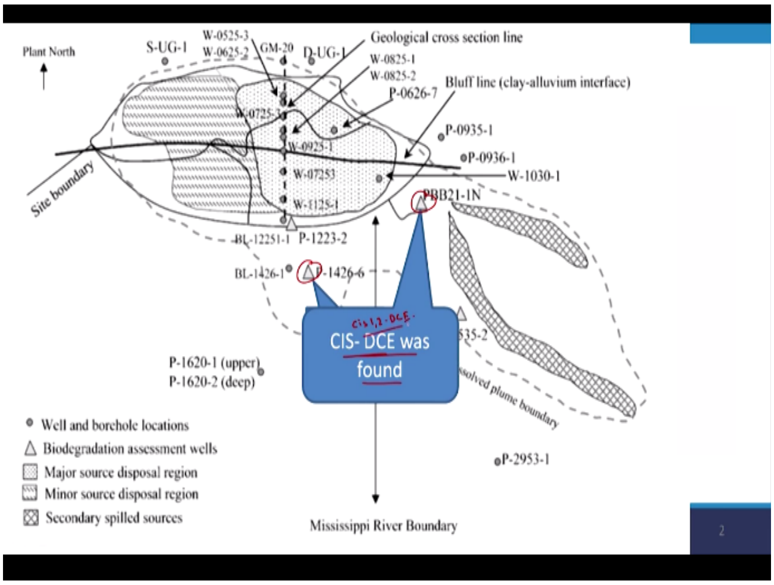

And then we moved on to looking at let us say data at particular sites you know along the flow paths and we saw that daughter product or byproduct of this particular you know degradation let us say was found which was CIS 1, 2 DCE let us say right, it is more or less with respect to the structure let us say right. That was found let us say at relatively high concentrations right.

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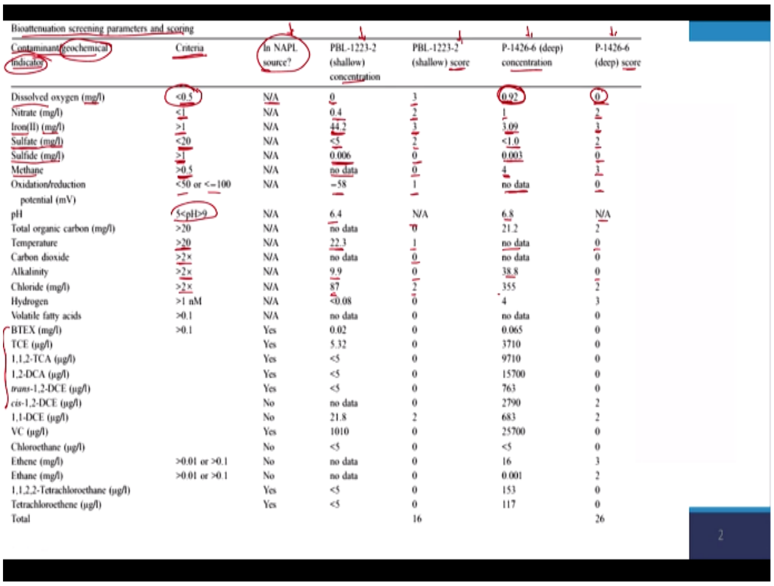

Bioattenuation screening parameters and scoring

Contaminant/geochemical indicator	Criteria	In NAPL source?	PBL-1223-2 (shallow) concentration	PBL-1223-2 (shallow) score	P-1426-6 (deep) concentration	P-1426-6 (deep) score
Dissolved oxygen (mg/l)	<0.5	N/A	0	3	0.92	0
Nitrate (mg/l)	<1	N/A	0.4	2	1	2
Iron(II) (mg/l)	>1	N/A	44.2	3	3.09	3
Sulfate (mg/l)	<20	N/A	<5	2	<1.0	2
Sulfide (mg/l)	>1	N/A	0.006	0	0.003	0
Methane	>0.5	N/A	no data	0	4	3
Oxidation/reduction potential (mV)	<50 or <−100	N/A	−58	1	no data	0
pH	5<pH>9	N/A	6.4	N/A	6.8	N/A
Total organic carbon (mg/l)	>20	N/A	no data	0	21.2	2
Temperature	>20	N/A	22.3	1	no data	0
Carbon dioxide	>2×	N/A	no data	0	no data	0
Alkalinity	>2×	N/A	9.9	0	38.8	0
Chloride (mg/l)	>2×	N/A	87	2	355	2
Hydrogen	>1 nM	N/A	<0.08	0	4	3
Volatile fatty acids	>0.1	N/A	no data	0	no data	0
BTEX (mg/l)	>0.1	Yes	0.02	0	0.065	0
TCE (μg/l)		Yes	5.32	0	3710	0
1,1,2-TCA (μg/l)		Yes	<5	0	9710	0
1,2-DCA (μg/l)		Yes	<5	0	15700	0
trans-1,2-DCE (μg/l)		Yes	<5	0	763	0
cis-1,2-DCE (μg/l)		No	no data	0	2790	2
1,1-DCE (μg/l)		No	21.8	2	683	2
VC (μg/l)		Yes	1010	0	25700	0
Chloroethane (μg/l)		No	<5	0	<5	0
Ethene (mg/l)	>0.01 or >0.1	No	no data	0	16	3
Ethane (mg/l)	>0.01 or >0.1	No	no data	0	0.001	2
1,1,2,2-Tetrachloroethane (μg/l)		Yes	<5	0	153	0
Tetrachloroethene (μg/l)		Yes	<5	0	117	0
Total				16		26

And then this context you were about to look at let us say you know the biattenuation screening parameters and scoring. As we can see here we have different criteria let us say based on upon which you can evaluate your relevant bioremediation feasibility and so on so let us look at those aspects. So first we have contaminant or the geochemical indicator here. We are going to look at that and different criteria out here.

And it is present in the NAPL source, yes or no why is this relevant because let us say some of the byproduct let us say if they are not present in the source but were present downstream which is the case with let us say there is 1, 2 DCE right. You can say that you know biodegradation is taking place let us say or that is one of the indicators of biodegradation. So you have different wells I believe right and also at the deep wells let us say right.

And again you have a score for each of them and the relevant concentrations there right. Based upon these scores, let us look at them. So DO right you wanted to be relatively less right, it is not available I guess, it would not be present in the NAPL source and the shallow it is 0 so they assigned a score of 3 but in the deep well you know it has relatively you know there is 1 milligram per liter right.

I believe these units are in 1 milligram per liter right the milligram per liter pardon me and that is why they assigned a score of 0 for dissolved oxygen and this particular deep source right. So keep that in mind and nitrate again a competing electron acceptor right so here the criteria was that it had to be dissolved oxygen <0.5 but in the deep well it was >0.5 that is why they assigned a score of 0.

For nitrate, it has to be <1 so here it is 0.4 they assigned a score of 2, it was 1 again they assigned a score of 2. Again, there are charts let us say based you know from what you say historical evidence let us say which you can use or which people use to you know come up with these scoring let us say right. So iron which is your electron donor right, reducing agent needs to be present at relatively high concentrations.

So it is present at relatively high concentrations and that is why they assigned a greater score than compared to here I guess, you know above a particular value they are fine with you know any particular concentration but as you see in this shallow well you have greater iron and the deep well you have lesser iron content I guess. So sulphate again another competing electron acceptor, so it should be <20.

But based on the thresholds you can understand the what do we say relative importance of, not importance let us say or relative weightage let us say for I can say so of given two the competing electron acceptors which are dissolved oxygen and nitrates, as in the dissolved oxygen has to be <0.5 milligram per liter, nitrate they are okay if it is <1 milligram per liter and sulphate though can be low you know can be as high as up to 20 milligram per liter.

So in shallow it is <5, they gave 2 so here it is <1. Again, they gave a score of 2 right, so that is one particular case. Sulphide again which is a reducing agent which is an electron donor, you would wanted at higher concentrations so >1 but not present at higher concentrations. This is something we saw as you know consistent with the other data that we looked at earlier so that is why a score of 0.

Again low concentration that is why a score of 0, so methane let us say right depending upon site let us say it can act as you know electron donor and here it should be >0.5 no data so 0, 4 so that is why they gave you know higher score here right for the deep well let us say. So ORP obviously it should be reduced in conditions <50 or -100 so it is -58 so they gave 1 and here they have no data for the deep well so 0 here.

So pH right you know different criteria so 6.4 they gave no score, 6.8 no score let us say I guess right. So temperature >20 so 22.3 and 1 so no data 0. Obviously, what role does temperature play, the greater the temperature or you now until a threshold anyway the greater the microbial activity or the greater the rate of your reactions and thus the faster the degradation right.

So thus typically temperature they would want to be relatively higher. Carbon dioxide it seems they wanted to be two times and they have no data so thus a score of 0, alkalinity again right and here 9.9, 0, 38.2 so on. Chloride again right so 87 they gave some scores, volatile fatty acids, we can you know skip some of these aspects and now let us move on to the relevant contaminants here.

Until now we have looked at the geochemical indicators right. All these aspects that we have looked at until now are indicators.

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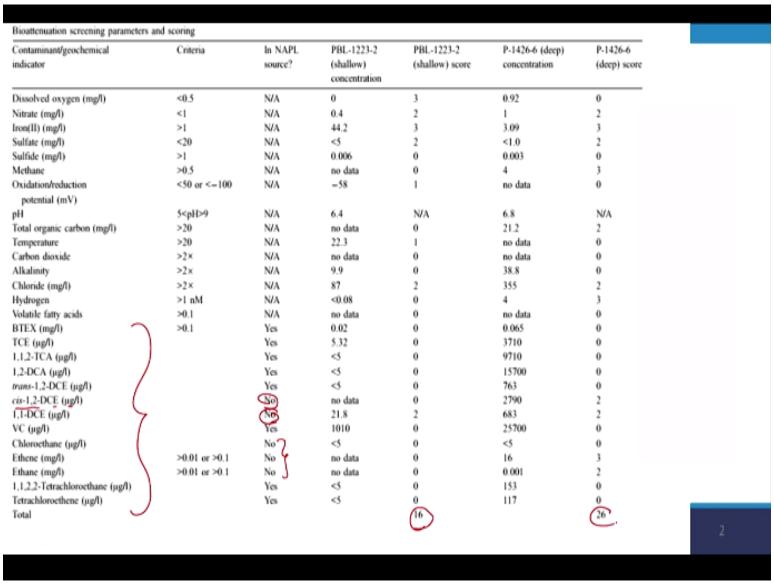

Bioattenuation screening parameters and scoring

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Nitrate (mg/l)	<1	N/A	0.4	2	1	2
Iron(II) (mg/l)	>1	N/A	44.2	3	3.09	3
Sulfate (mg/l)	<20	N/A	<5	2	<1.0	2
Sulfide (mg/l)	>1	N/A	0.006	0	0.003	0
Methane	>0.5	N/A	no data	0	4	3
Oxidation/reduction potential (mV)	<50 or <−100	N/A	−58	1	no data	0
pH	5<pH>9	N/A	6.4	N/A	6.8	N/A
Total organic carbon (mg/l)	>20	N/A	no data	0	21.2	2
Temperature	>20	N/A	22.3	1	no data	0
Carbon dioxide	>2×	N/A	no data	0	no data	0
Alkalinity	>2×	N/A	9.9	0	38.8	0
Chloride (mg/l)	>2×	N/A	87	2	355	2
Hydrogen	>1 nM	N/A	<0.08	0	4	3
Volatile fatty acids	>0.1	N/A	no data	0	no data	0
BTEX (mg/l)	>0.1	Yes	0.02	0	0.065	0
TCE (μg/l)		Yes	5.32	0	3710	0
1,1,2-TCA (μg/l)		Yes	<5	0	9710	0
1,2-DCA (μg/l)		Yes	<5	0	15700	0
trans-1,2-DCE (μg/l)		Yes	<5	0	763	0
cis-1,2-DCE (μg/l)		No	no data	0	2790	2
1,1-DCE (μg/l)		No	21.8	2	683	2
VC (μg/l)		Yes	1010	0	25700	0
Chloroethane (μg/l)		No	<5	0	<5	0
Ethene (mg/l)	>0.01 or >0.1	No	no data	0	16	3
Ethane (mg/l)	>0.01 or >0.1	No	no data	0	0.001	2
1,1,2,2-Tetrachloroethane (μg/l)		Yes	<5	0	153	0
Tetrachloroethene (μg/l)		Yes	<5	0	117	0
Total				16		26

Now let us look at the actual contaminants here let us say right. So these are my contaminants from out here right. So let us look at them. I will just pay attention to those that were not present in the NAPL source let us say which are let us say CIS 1, 2 DCE and 1, 1 DCE right and also chloroethane, ethene and ethane right and so on and so forth. Again, based on them you know they were given different what do we say scores here I guess right.

Here it is at relatively low concentration that is why they are 0 but in this deep well they have at relatively higher concentrations and that is why they gave some scores. So based on this we can total it up and see that you know different scores were given both for the shallow and for the deep wells right.

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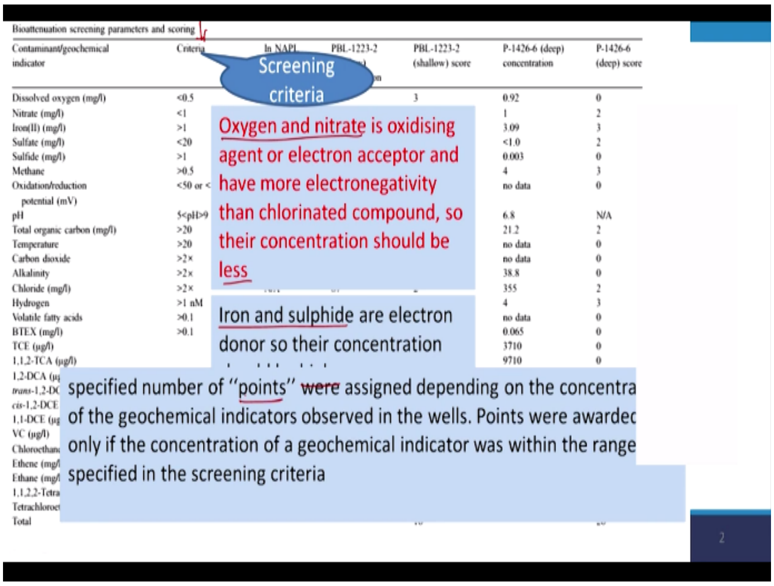

Bioattenuation screening parameters and scoring

Contaminant/geochemical indicator	Criteria	In NAPL	PBL-1223-2	PBL-1223-2 (shallow) score	P-1426-6 (deep) concentration	P-1426-6 (deep) score
Dissolved oxygen (mg/l)	<0.5			3	0.92	0
Nitrate (mg/l)	<1				1	2
Iron(II) (mg/l)	>1				3.09	3
Sulfate (mg/l)	<20				<1.0	2
Sulfide (mg/l)	>1				0.003	0
Methane	>0.5				4	3
Oxidation/reduction potential (mV)	<50 or <				no data	0
pH	5<pH>9				6.8	N/A
Total organic carbon (mg/l)	>20				21.2	2
Temperature	>20				no data	0
Carbon dioxide	>2×				no data	0
Alkalinity	>2×				38.8	0
Chloride (mg/l)	>2×				355	2
Hydrogen	>1 nM				4	3
Volatile fatty acids	>0.1				no data	0
BTEX (mg/l)	>0.1				0.065	0
TCE (μg/l)					3710	0
1,1,2-TCA (μg/l)					9710	0
1,2-DCA (μ						
trans-1,2-DC						
cis-1,2-DCE						
1,1-DCE (μ						
VC (μg/l)						
Chloroethan						
Ethene (mg/						
Ethane (mg/						
1,1,2,2-Tetra						
Tetrachloroet						
Total						

Screening criteria

Oxygen and nitrate is oxidising agent or electron acceptor and have more electronegativity than chlorinated compound, so their concentration should be less

Iron and sulphide are electron donor so their concentration

specified number of "points" ~~were~~ assigned depending on the concentra of the geochemical indicators observed in the wells. Points were awardec only if the concentration of a geochemical indicator was within the range specified in the screening criteria

So let us move on. Obviously, this is just a summary of what I have been speaking until now. So I will skip this. You want your competing electron acceptors to be at relatively low concentrations and you want your reducing agents or electron donors to be at relatively high concentrations right and the criteria that were looked at right.

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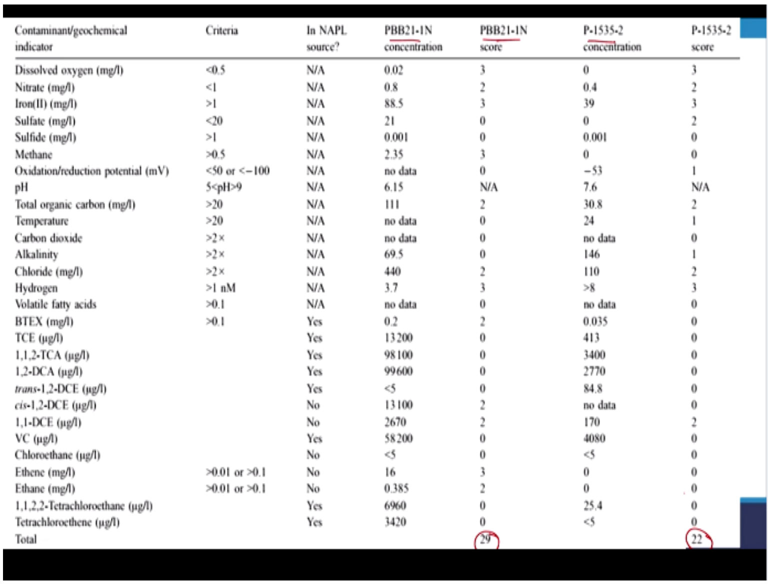

Contaminant/geochemical indicator	Criteria	In NAPL source?	PBB21-1N concentration	PBB21-1N score	P-1535-2 concentration	P-1535-2 score
Dissolved oxygen (mg/l)	<0.5	N/A	0.02	3	0	3
Nitrate (mg/l)	<1	N/A	0.8	2	0.4	2
Iron(II) (mg/l)	>1	N/A	88.5	3	39	3
Sulfate (mg/l)	<20	N/A	21	0	0	2
Sulfide (mg/l)	>1	N/A	0.001	0	0.001	0
Methane	>0.5	N/A	2.35	3	0	0
Oxidation/reduction potential (mV)	<50 or <−100	N/A	no data	0	−53	1
pH	5<pH>9	N/A	6.15	N/A	7.6	N/A
Total organic carbon (mg/l)	>20	N/A	111	2	30.8	2
Temperature	>20	N/A	no data	0	24	1
Carbon dioxide	>2×	N/A	no data	0	no data	0
Alkalinity	>2×	N/A	69.5	0	146	1
Chloride (mg/l)	>2×	N/A	440	2	110	2
Hydrogen	>1 nM	N/A	3.7	3	>8	3
Volatile fatty acids	>0.1	N/A	no data	0	no data	0
BTEX (mg/l)	>0.1	Yes	0.2	2	0.035	0
TCE (μg/l)		Yes	13 200	0	413	0
1,1,2-TCA (μg/l)		Yes	98 100	0	3400	0
1,2-DCA (μg/l)		Yes	99 600	0	2770	0
trans-1,2-DCE (μg/l)		Yes	<5	0	84.8	0
cis-1,2-DCE (μg/l)		No	13 100	2	no data	0
1,1-DCE (μg/l)		No	2670	2	170	2
VC (μg/l)		Yes	58 200	0	4080	0
Chloroethane (μg/l)		No	<5	0	<5	0
Ethene (mg/l)	>0.01 or >0.1	No	16	3	0	0
Ethane (mg/l)	>0.01 or >0.1	No	0.385	2	0	0
1,1,2,2-Tetrachloroethane (μg/l)		Yes	6960	0	25.4	0
Tetrachloroethene (μg/l)		Yes	3420	0	<5	0
Total				29		22

And then we had score or points that were given and these are other sets of wells you know will just you know skip through this, will just skip through this. Again, you know different sets of wells again here at different wells say here again right and again different scores here. We now have different scores. So in this manner they evaluated all the different monitoring wells that they looked at.

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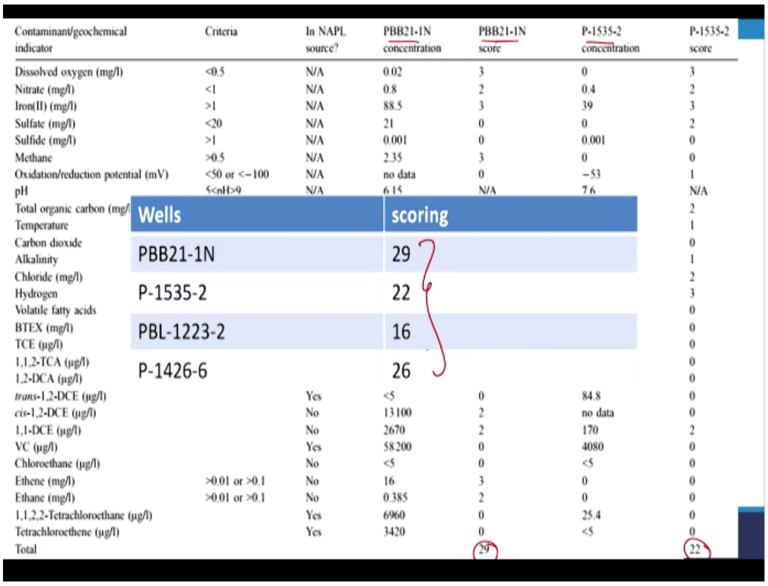

Contaminant/geochemical indicator	Criteria	In NAPL source?	PBB21-1N concentration	PBB21-1N score	P-1535-2 concentration	P-1535-2 score
Dissolved oxygen (mg/l)	<0.5	N/A	0.02	3	0	3
Nitrate (mg/l)	<1	N/A	0.8	2	0.4	2
Iron(II) (mg/l)	>1	N/A	88.5	3	39	3
Sulfate (mg/l)	<20	N/A	21	0	0	2
Sulfide (mg/l)	>1	N/A	0.001	0	0.001	0
Methane	>0.5	N/A	2.35	3	0	0
Oxidation/reduction potential (mV)	<50 or <−100	N/A	no data	0	−53	1
pH	5<pH>9	N/A	6.15	N/A	7.6	N/A
Total organic carbon (mg/						2
Temperature						1
Carbon dioxide						0
Alkalinity						1
Chloride (mg/l)						2
Hydrogen						3
Volatile fatty acids						0
BTEX (mg/l)						0
TCE (μg/l)						0
1,1,2-TCA (μg/l)						0
1,2-DCA (μg/l)						0
trans-1,2-DCE (μg/l)		Yes	<5	0	84.8	0
cis-1,2-DCE (μg/l)		No	13 100	2	no data	0
1,1-DCE (μg/l)		No	2670	2	170	2
VC (μg/l)		Yes	58 200	0	4080	0
Chloroethane (μg/l)		No	<5	0	<5	0
Ethene (mg/l)	>0.01 or >0.1	No	16	3	0	0
Ethane (mg/l)	>0.01 or >0.1	No	0.385	2	0	0
1,1,2,2-Tetrachloroethane (μg/l)		Yes	6960	0	25.4	0
Tetrachloroethene (μg/l)		Yes	3420	0	<5	0
Total				29		22

Wells	scoring
PBB21-1N	29
P-1535-2	22
PBL-1223-2	16
P-1426-6	26

Just for summary they had you know different obviously you know levels of you know bioremediation let us say that would be feasible here let us say right. Different feasibility levels were bioremediation right.

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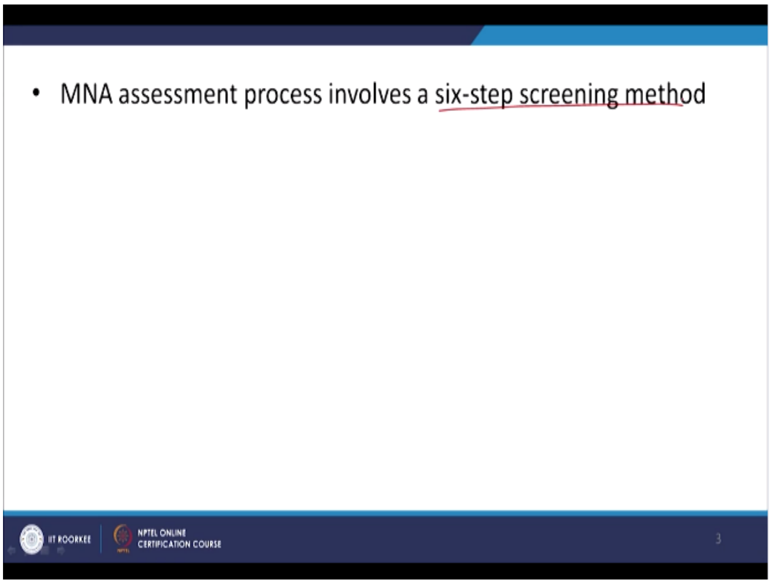

- MNA assessment process involves a six-step screening method

So let us move further so it seems they typically look at six-step method so it is typically logical as we will see.

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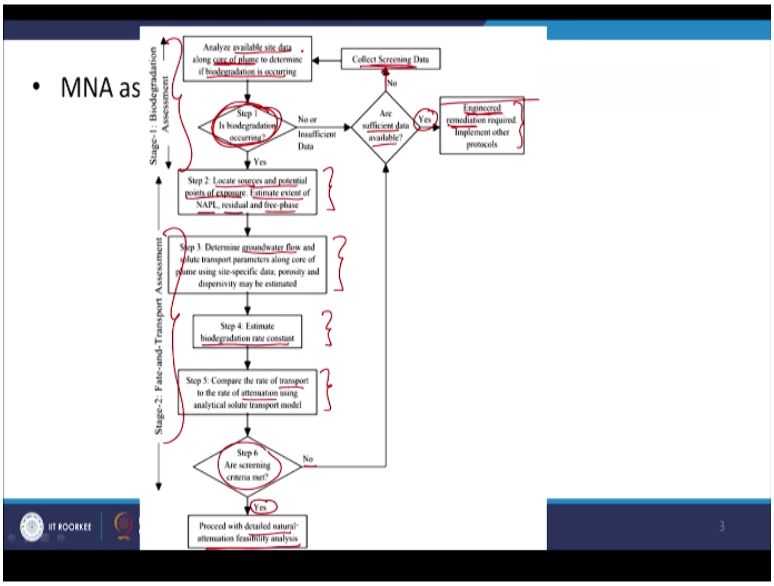

- MNA as

Obviously, what are we going to look at, we are going to look at analyzing the relevant data right. So available data along core of the plume obviously core of the plume initially right we do not want to put in lot of resources to determine if biodegradation is occurring right. Then, we look at is biodegradation occurring, if it is not occurring we look at is it because there is no data available or data is available.

We say that data is available but you know biodegradation is not occurring. Then, what will we do as we talked about engineered remediation might be required as in engineered species might to be introduced right or you know there are other aspects that you can you know use let us say to promote biodegradation, so those aspects need to be looked at let us say engineered remediation.

If it is because of lack of data, then I need to go back to collect screening data and then come back out here. So again if biodegradation is occurring though if the data suggest that as we have seen until now that biodegradation is occurring what do we do, we look at the sources or you know put in more resources and locate the sources and potential points of exposure, estimate the extent of just the NAPL, residual NAPL and the one dissolved let us say or in the free phase let us say right.

Extent of NAPL, residual and free phase and then moving on we will then look at groundwater flow and here as you can see this is biodegradation assessment and this is fate and transport assessment. Initially, we will just try to see okay is it feasible and is it occurring or is there enough evidence to say that it is occurring and then we will look at you know obviously we need to look at monitoring it right or we need to monitor this bloom.

So we need to look at the fate and transport of these particular contaminants so that is the next step. So here we identified the different contaminants, here we look at what are the factors that are going to affect the transport. Here we look at let us say you know the rate at which or the kinetics of your biodegradation right and then we are going to look at both the transport and attenuation models let us say right.

And then we compare or look at all this data to see is screening criteria met, if not go back either to engineering remediation or repeat the process with more data or if it is feasible so then we put in more resources for detailed natural attenuation feasibility analysis right. So again it is pretty logical as in we look at data to see if biodegradation is occurring, if not look at other aspects.

If it is occurring, then look at the fate and transport of the relevant contaminants right. So again this is all at the initial stage itself right. So let us moving on or let us move on.

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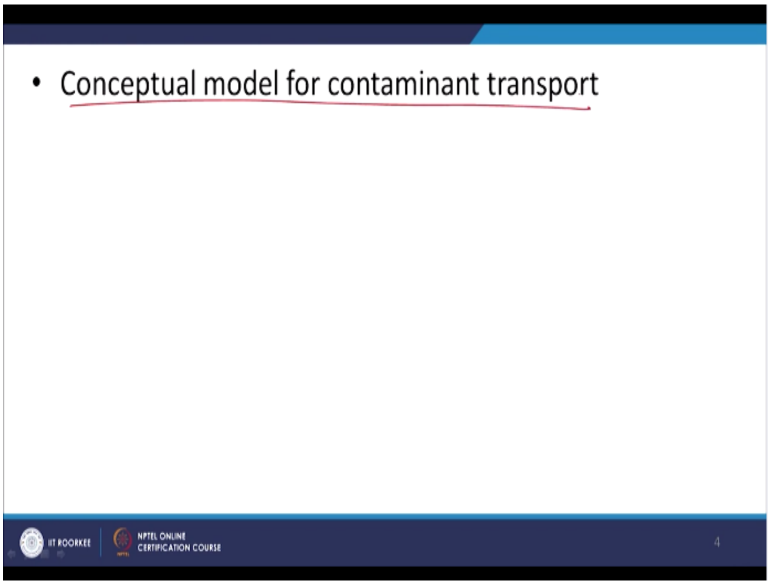

- Conceptual model for contaminant transport

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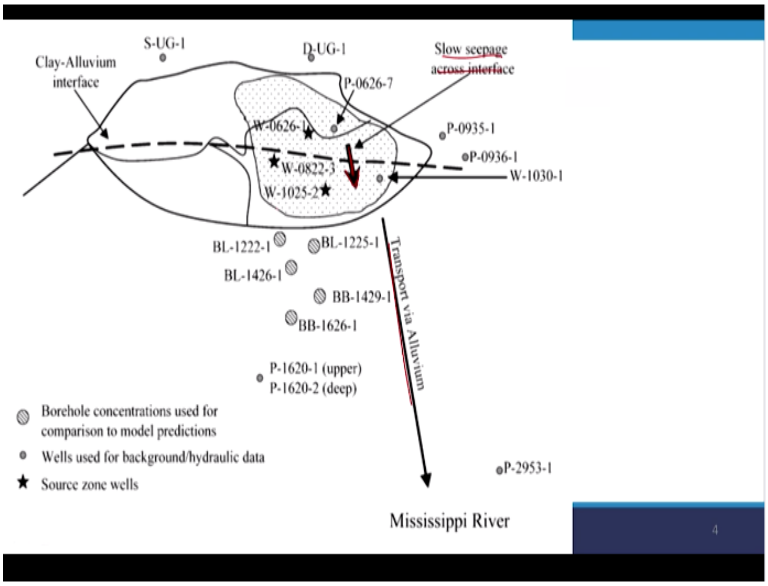

So conceptual model for contaminant transport for this site. Let us look at what they came up with right. So this is what they came up with. So transport via alluvium right, this is something again alluvium as you witness our you know we looked at the data let us say as this particular zone had a remarkably high hydraulic conductivity that is something to keep in mind and also slow seepage it seems across the interface, across the interface here right that is something to keep in mind so that is their model here.

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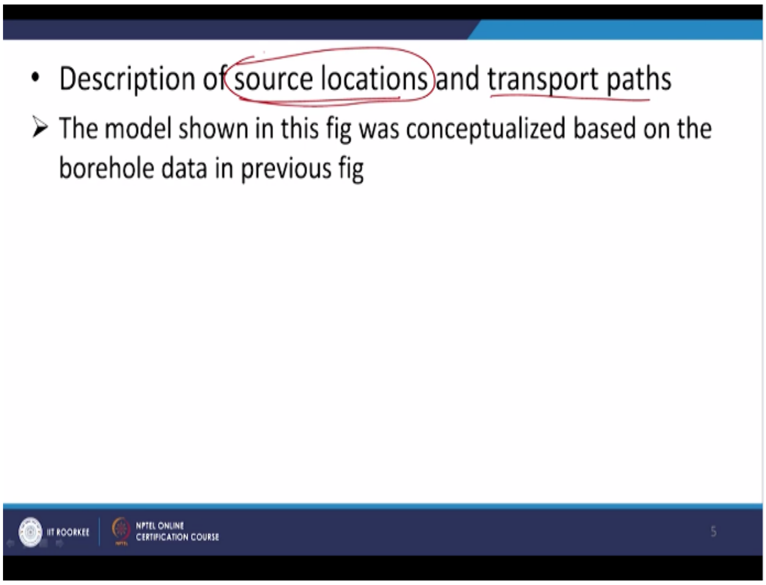

- Description of source locations and transport paths
  - ➢ The model shown in this fig was conceptualized based on the borehole data in previous fig

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And again we are going to look at the source location and transport paths. We already looked at source location in some detail but let us look at some of the transport path let us say.

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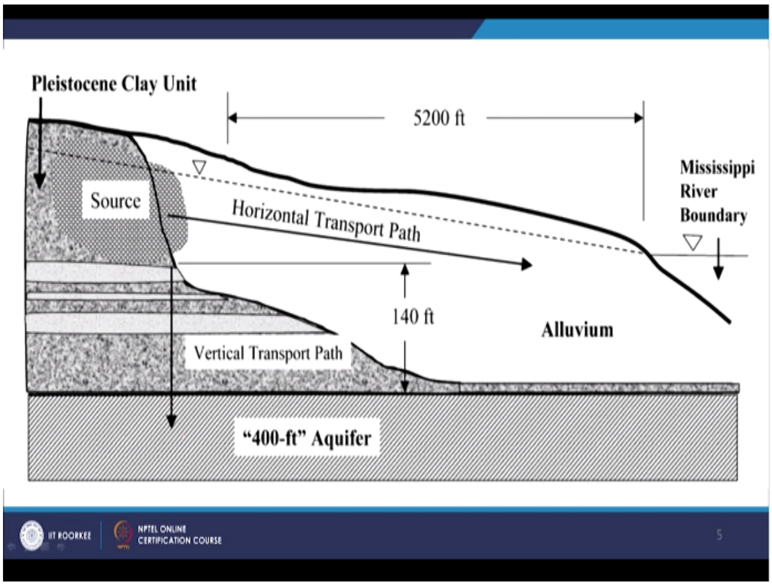

So here they are obviously saying that it is going to flow in this direction, horizontal path obviously as you can see it. Mirror is the path of the flow of the groundwater obviously it is the aquifer or this groundwater is going to move in such a way such that it is going to recharge the relevant river right. Obviously, you know the river is going to be recharged from the groundwater and that is what you see out here.

Again, you think of any river it is going to be a relatively low lying area compared to the relevant what do we say locations around it or the surrounding area right. So obviously horizontal flow path is one and obviously another aspect is the vertical transport path and why is that because we have DNAPL right. So obviously this is the generic what do we say transport what do we say conceptual model right.

So two aspects horizontal path, transport path and vertical transport path. Horizontal transport path can lead to contamination of the river to that something that you see out here right and as you can see the source is somewhere out here and DNAPL it is going to permeate through.

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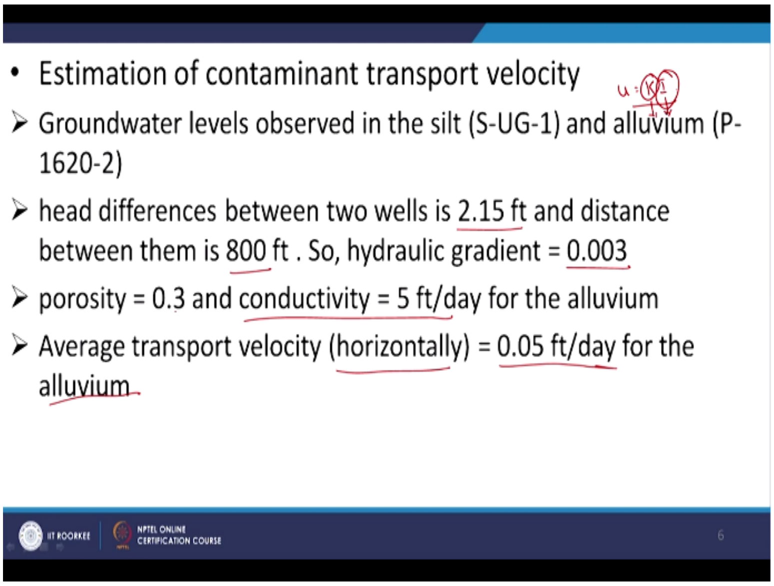

- Estimation of contaminant transport velocity $u = \textcircled{K}\textcircled{I}$
  - Groundwater levels observed in the silt (S-UG-1) and alluvium (P-1620-2)
  - head differences between two wells is 2.15 ft and distance between them is 800 ft . So, hydraulic gradient = 0.003
  - porosity = 0.3 and conductivity = 5 ft/day for the alluvium
  - Average transport velocity (horizontally) = 0.05 ft/day for the alluvium

So let us move on, so contaminant transport velocity so obviously to estimate this contaminant transport velocity what you need right. We typically try to estimate the hydraulic conductivity and the slope of this gradient or the energy gradient is something that we need to estimate. Why is that? Because to get the dark sea's velocity that is equal to KI right. So you need the hydraulic conductivity and the gradient right.

And let us see what we have so they looked at two wells right and head difference was looked at right so hydraulic gradient was calculated. The gradient was calculated and also conductivity was measured and then they came up with the horizontal transport velocity to be 0.05 feet per day for alluvium mainly for this particular alluvium right. So let us move on. Again, what is the key aspect? You know K hydraulic conductivity and the gradient right.

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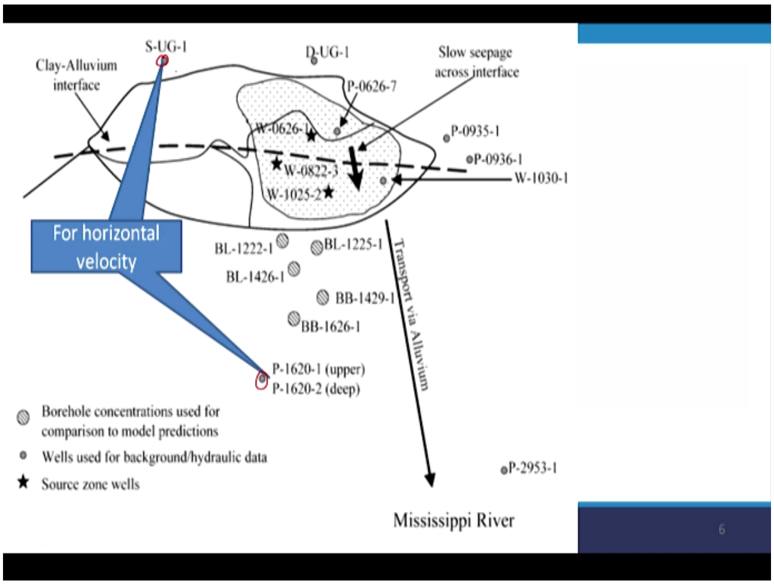

And let us look at the wells that were looked at in this context so they looked at this particular well and this particular well and look like it is they are 800 feet apart and these were the wells that they looked at to look at this or estimate this dark sea's velocity right.

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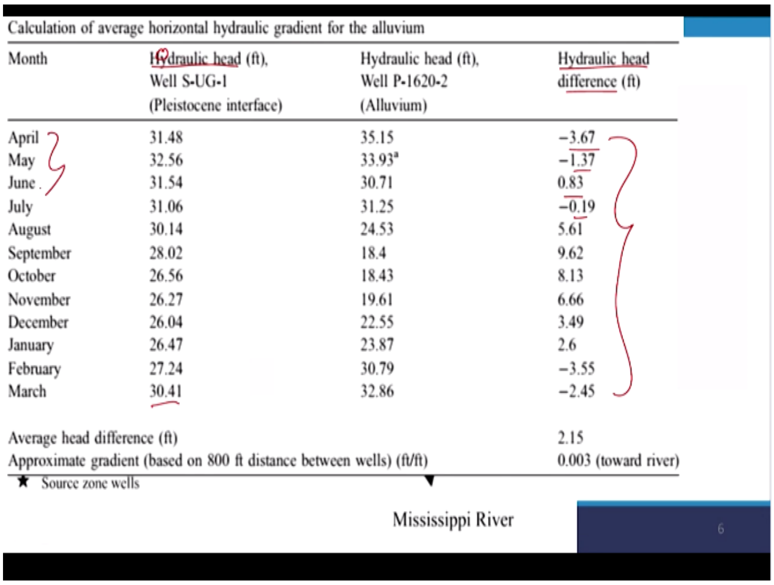

Calculation of average horizontal hydraulic gradient for the alluvium

Month	Hydraulic head (ft), Well S-UG-1 (Pleistocene interface)	Hydraulic head (ft), Well P-1620-2 (Alluvium)	Hydraulic head difference (ft)
April	31.48	35.15	−3.67
May	32.56	33.93^a	−1.37
June	31.54	30.71	0.83
July	31.06	31.25	−0.19
August	30.14	24.53	5.61
September	28.02	18.4	9.62
October	26.56	18.43	8.13
November	26.27	19.61	6.66
December	26.04	22.55	3.49
January	26.47	23.87	2.6
February	27.24	30.79	−3.55
March	30.41	32.86	−2.45
Average head difference (ft)			2.15
Approximate gradient (based on 800 ft distance between wells) (ft/ft)			0.003 (toward river)

★ Source zone wells

Mississippi River

So moving on, let us look at the head difference here so hydraulic head at this you know during different months right we have these values. Hydraulic head at the different well at different months again we have these values but these are just numbers, they do not make obviously much sense so but if I look at the hydraulic head difference as you see it varies right, it is not constant now.

So what is the key aspect here? The key aspect is that we are near the river now right so during monsoon let us say the river is going to act as a you know source of water let us say and the groundwater is going to be recharged right or the flow is going to be from the river towards this particular what do we say aquifer right and during non-monsoon period the flow is going to be from this aquifer into the river right.

So thus you see the difference in heads especially during let us say the different months let us say right.

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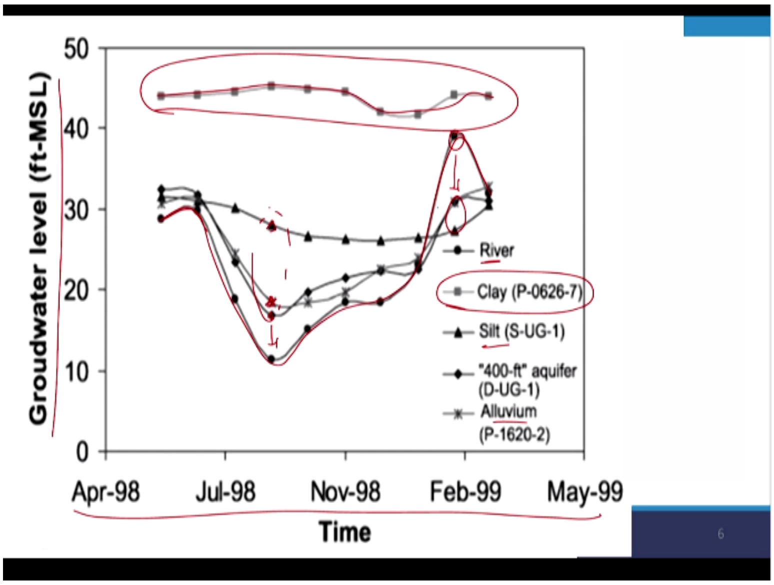

So let us try to look at the next figure where it should be more apparent, so here we have let us say the groundwater level on the y-axis and you know with one-year monitoring. So in the deep clay layer or in the clay layer typically the relevant variation in the relevant what do we say now if not deep clay layer in the clay layer obviously which is relatively far away from the river you see that, you know the groundwater level is relatively constant now right.

But in the layers which are near the relevant river you know this is the profile for the river, let us just try to highlight that. This is the profile for the river now right, so in those layers near the river let us say which your silt and alluvium right let us say silt triangular let us say and most importantly alluvium right and even this 400 feet aquifer let us say right.

What do you see? You see that their profiles let us say or the groundwater levels in these what do we say aquifers or soils that are present near the river let us say are obviously greatly influenced by the profile of the groundwater profile of this particular river now right. So during non-monsoon regions, the flow will be from these particular what do we say from this particular aquifer into the river and during the monsoon period it will be from the river into the relevant locations let us say right.

So that is something to keep in mind, yes and why is that because you know with different heads, the groundwater flow direction is changing and thus the contaminant will in a flow or you know be transport in the other direction so that is something to keep in mind, the seasonal variations anyway.

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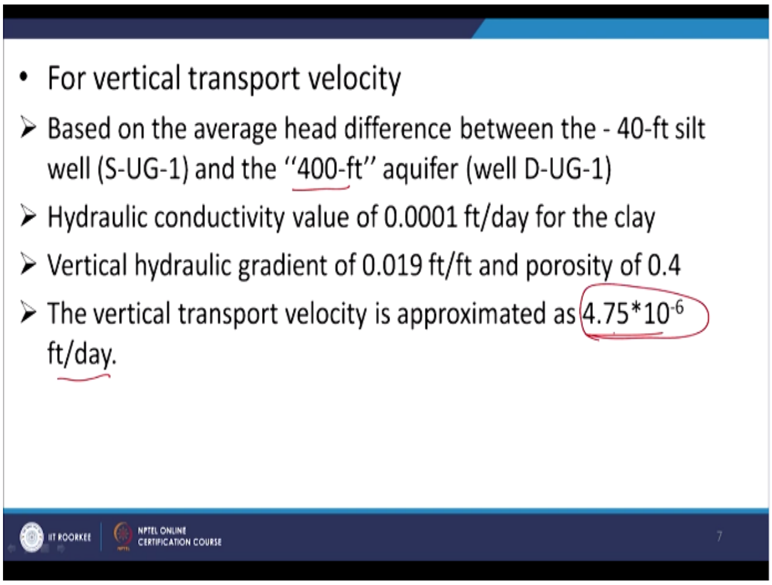

- For vertical transport velocity
- ➢ Based on the average head difference between the - 40-ft silt well (S-UG-1) and the "400-ft" aquifer (well D-UG-1)
- ➢ Hydraulic conductivity value of 0.0001 ft/day for the clay
- ➢ Vertical hydraulic gradient of 0.019 ft/ft and porosity of 0.4
- ➢ The vertical transport velocity is approximated as $4.75*10^{-6}$ ft/day.

So vertical transport too similarly they looked at two particular wells right and it seems 400 feet aquifer well and they looked at hydraulic conductivity let us say and porosity and then calculated the vertical transport velocity to be so on obviously compared to the horizontal transport velocity, the vertical transport velocity is relatively or much lesser though right. So which wells have they looked at?

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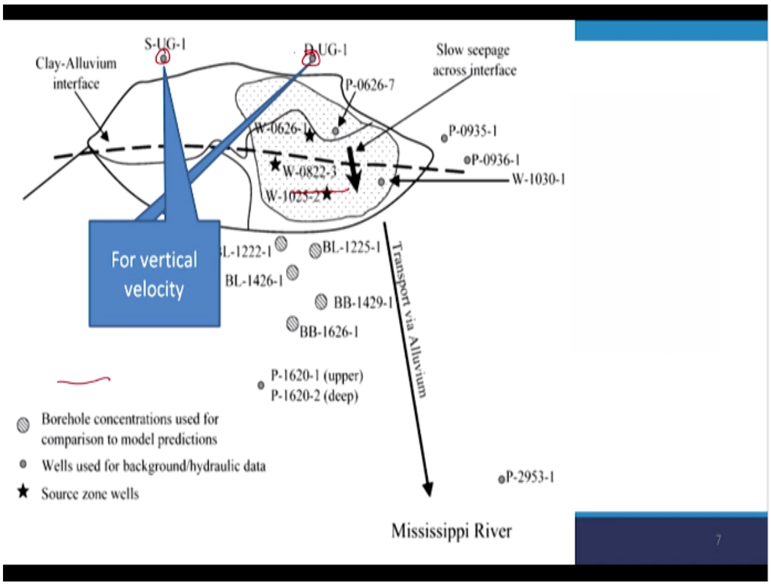

They looked at these two wells to calculate the vertical transport velocity.

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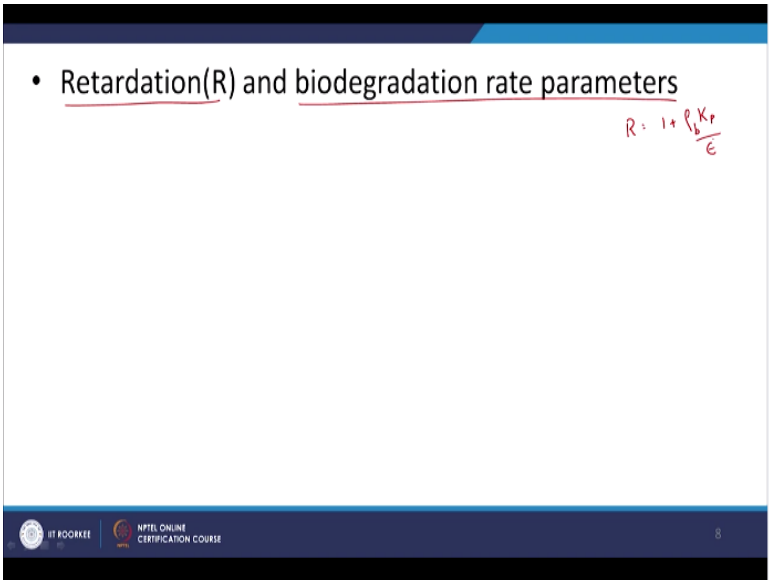

- Retardation(R) and biodegradation rate parameters

$R = 1 + \frac{\rho_b K_p}{\epsilon}$

Let us move on. So we have obviously retardation and biodegradation rate parameters to calculate right. So in our examples how have we done that, we have let us say or we can calculate by I believe 1+rho b or you know dry bulk density of the soil Kp partitioning coefficient by the porosity right. This is how we calculate that, again what does retardation coefficient gives an idea about let us say right.

In this context, we can get an idea about the total mass of the contaminant by mass present in the relevant water let say right. So obviously that gives you an idea about the complexity of the system and such right and rate parameters by fitting the data or the you know fitting the model based on your mass balanced to the relevant data you can get your relevant degradation rate parameters. Let us look at what they are.

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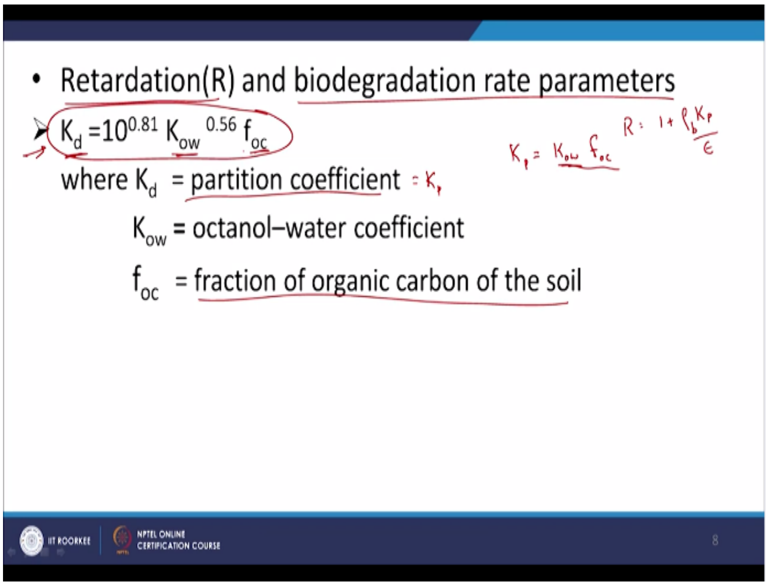

- Retardation(R) and biodegradation rate parameters

➢ $K_d = 10^{0.81} K_{ow}^{0.56} f_{oc}$

where K_d = partition coefficient $= K_p$

K_{ow} = octanol–water coefficient

f_{oc} = fraction of organic carbon of the soil

$K_p = K_{ow} f_{oc}$

$R = 1 + \frac{\rho_b K_p}{\epsilon}$

So before we go there let us say here we are looking at the partition coefficient, you know we looked it as Kp, obviously partitioning coefficient is going to be depend upon the Octanol water partitioning coefficient. So what is this Octanol water partitioning coefficient to refresh your memory right? If you Octanol and water in the same container let us say and I introduce the relevant contaminant or the compound I want to see let us say or I can measure you know in which phase is it you know is it present at what concentrations right.

So as in Octanol if I see that you know after equilibrium has been reached if the contaminant is present mostly in Octanol I would say it is relatively more hydrophobic let us say right. So it gives you an idea about the partitioning let us say. Why is that important? Because in soil you have the organic carbon and let us say if you have this hydrophobic compound rather than staying in the water it will want to be absorbed onto this particular soil now.

So that is why we also need to look at. The fraction of organic carbon in the soil right, so that is what we have here. Looks like for this site they use this empirical formula right which seems to be a better at estimating the partitioning coefficient in terms of the Octanol water partitioning coefficient and fraction of the organic carbon right, so that is something to keep in mind yes.

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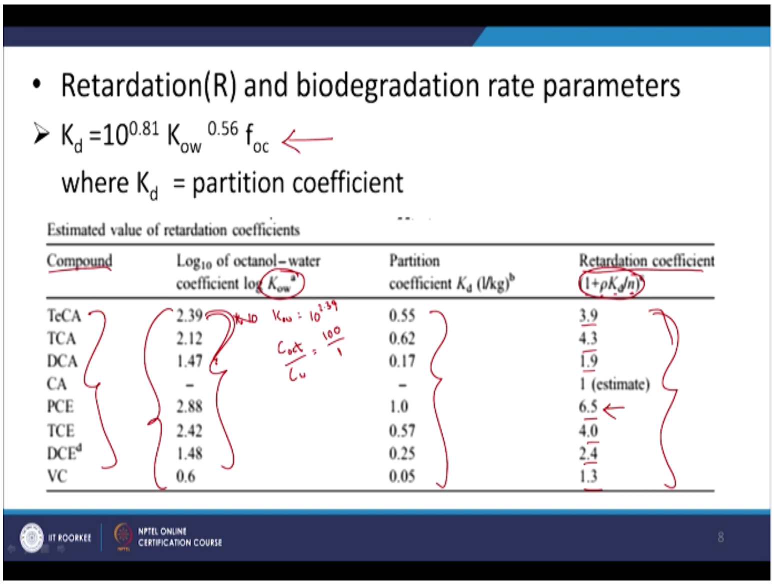

- Retardation(R) and biodegradation rate parameters

➢ $K_d = 10^{0.81} K_{ow}^{0.56} f_{oc}$ ←

where K_d = partition coefficient

Estimated value of retardation coefficients

Compound	$\log_{10}$ of octanol–water coefficient $\log K_{ow}$[a]	Partition coefficient K_d (l/kg)[b]	Retardation coefficient $(1+\rho K_d/n)$[c]
TeCA	2.39	0.55	3.9
TCA	2.12	0.62	4.3
DCA	1.47	0.17	1.9
CA	–	–	1 (estimate)
PCE	2.88	1.0	6.5 ←
TCE	2.42	0.57	4.0
DCE[d]	1.48	0.25	2.4
VC	0.6	0.05	1.3

$K_{ow} = 10^{2.39}$

$\frac{C_{oct}}{C_w} = \frac{100}{1}$

And now let us see what we have for different compound, source compounds right we have different log Kow values. Keep in mind that these are log Kow values. Why is that because that means that this value is or Kow value is 10 to the power of 2.39 right or >100. What does that mean? So concentration of the compound in Octanol/concentration of the compound in water is something like or >100 is to 1 right.

What does that mean? The compound strongly wants to or is strongly hydrophobic right. That is something that you can see out here for almost all of these compounds right and then they calculated the partitioning coefficient and here we have the relevant formula out here or the empirical formula that they observed for this. So this is the partition coefficient here right liters per kg of soil I believe.

And here retardation coefficient something that we looked at in our examples too. It is R=1+rho b*Kp/porosity here. As you can see here typically retardation coefficient is relatively high and what does that tell you, most of it is adsorbed onto the or you know considerable fraction of it is adsorbed onto the relevant soil rather than being dissolved in water right.

As you can see what does this tells you that you know it is 6.5 or 6 as in the ratio of the total contaminant to the contaminant in the water is 6.5 right. So that tells you, you know that most of it is not present in the water let us say but again keep in mind here the way that they calculated the retardation coefficient, they have not taken into account just the free NAPL. So if you consider the free NAPL or NAPL present as itself then the retardation coefficient will be remarkably high right.

Here they just looked at adsorption and the NAPL present in the water that is something to keep in mind right. So let us move on.

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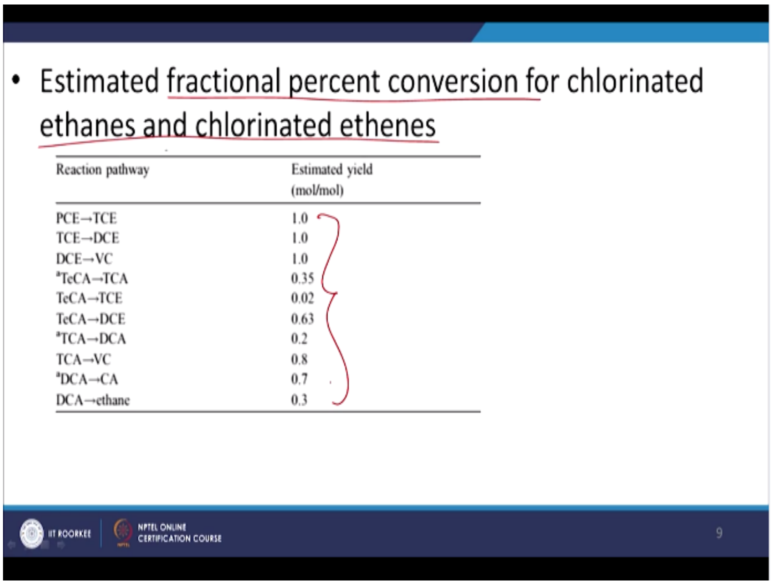

- Estimated fractional percent conversion for chlorinated ethanes and chlorinated ethenes

Reaction pathway	Estimated yield (mol/mol)
PCE→TCE	1.0
TCE→DCE	1.0
DCE→VC	1.0
[a]TeCA→TCA	0.35
TeCA→TCE	0.02
TeCA→DCE	0.63
[a]TCA→DCA	0.2
TCA→VC	0.8
[a]DCA→CA	0.7
DCA→ethane	0.3

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So here they looked at fractional percentage conversion for chlorinated ethanes and chlorinated ethenes right. So this is more or less based on stoichiometry and the relevant estimations. So different yields let us say right. So why is this relevant now or why is this required because later on let us say not later on when we look at the relevant data and try to analyze the system, we need to obviously understand the sources of different compounds.

And how much of the compound is going to be ill you know or you know end up being degraded for one mole of the source compound right. So in that context obviously we need such data right.

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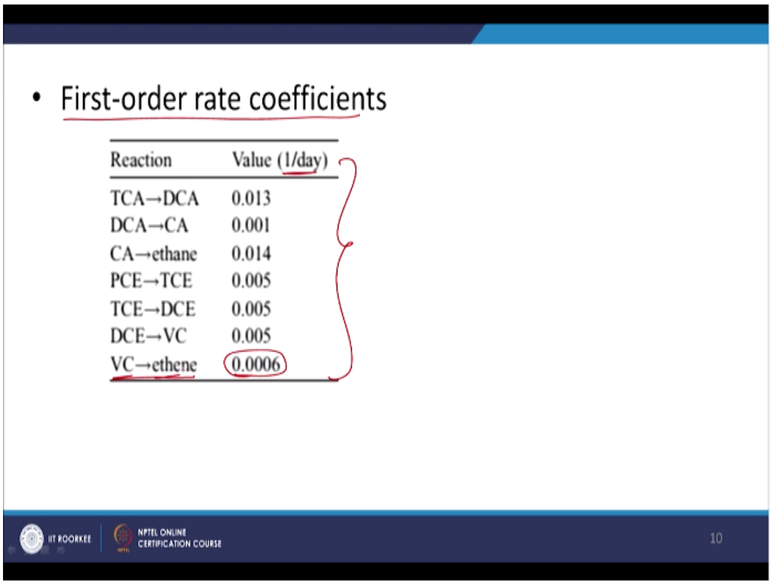

- First-order rate coefficients

Reaction	Value (1/day)
TCA→DCA	0.013
DCA→CA	0.001
CA→ethane	0.014
PCE→TCE	0.005
TCE→DCE	0.005
DCE→VC	0.005
VC→ethene	0.0006

So again we can fit the relevant models and to the data and get the different rate coefficients right and I think they might have fidgeted for the pseudo first-order rate coefficients if I am not wrong here right. They gave or even based on historical evidence let us say you can get these values but typically obviously the best way would be to fit your model to the relevant data and get the relevant constants right.

You got the relevant constants. As you can see, VC to ethane degradation is taking considerable time maybe that is the rate limiting step. What is the rate limiting step now? You know how can you identify that the one where let us say your reactants are building up now. As in if you need to go from A to Z let us say all the other steps are pretty fast enough but let us say P to Q right is not fast enough right.

So you are going to observe or build up there so that is your rate limiting step and looks like here looks like anyway from this generic data that VC to ethane is your rate limiting step let us say right.

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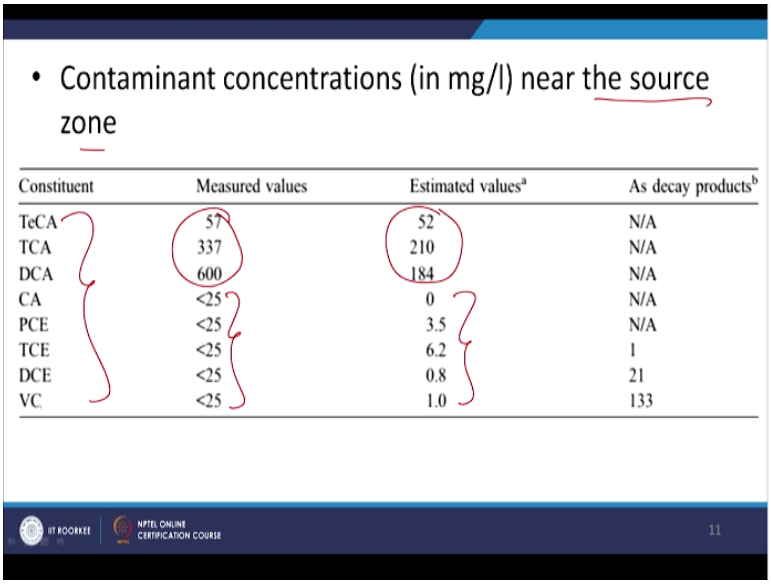

- Contaminant concentrations (in mg/l) near the source zone

Constituent	Measured values	Estimated values^a	As decay products^b
TeCA	57	52	N/A
TCA	337	210	N/A
DCA	600	184	N/A
CA	<25	0	N/A
PCE	<25	3.5	N/A
TCE	<25	6.2	1
DCE	<25	0.8	21
VC	<25	1.0	133

So let us move on, so here contaminant concentrations near the source zone right, near the source zone so measured values and estimated values obviously for most of the byproducts let us say you see that they are relatively low right, at least initially in the source right that is something to keep in mind at the source most of these byproducts DCE and VC are at relatively low concentrations right.

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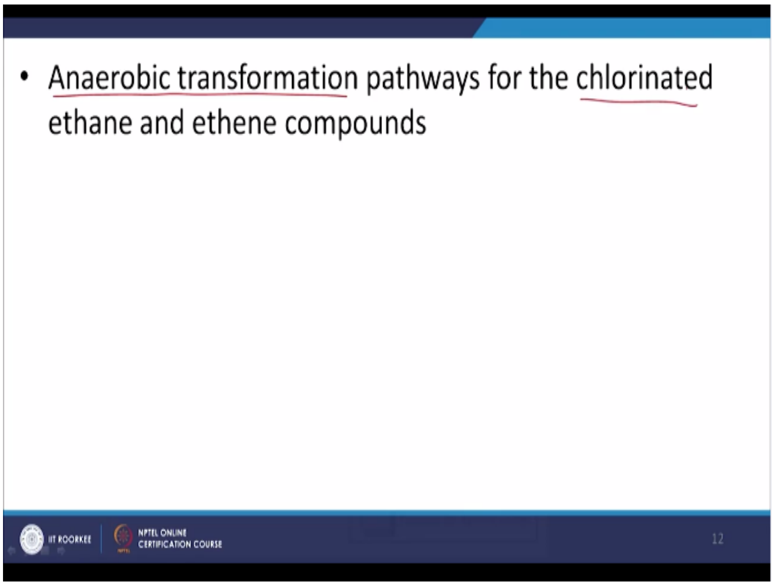

- Anaerobic transformation pathways for the chlorinated ethane and ethene compounds

So let us move on so here again let us look at the pathway which is obviously the anaerobic pathway right based upon your particular degradation for chlorinated ethane and ethenes.

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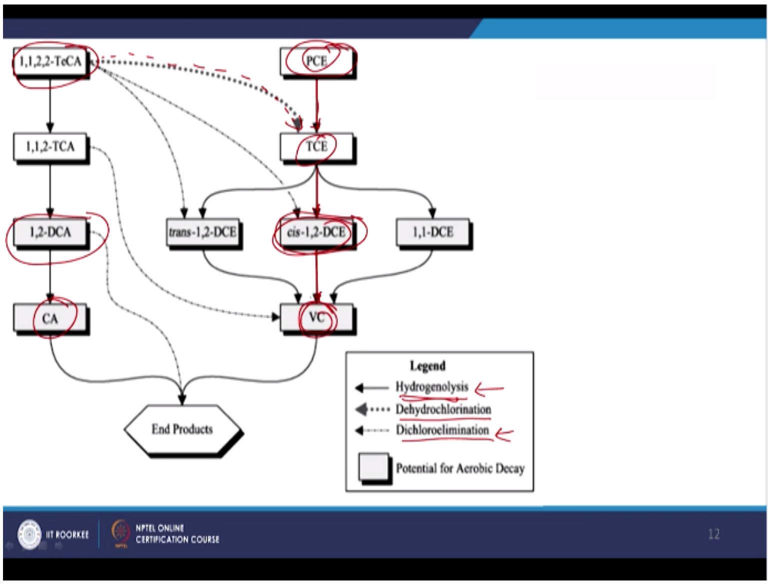

1,1,2,2-TeCA

PCE

1,1,2-TCA

TCE

1,2-DCA

trans-1,2-DCE

cis-1,2-DCE

1,1-DCE

CA

VC

End Products

Legend

- Hydrogenolysis
- Dehydrochlorination
- Dichloroelimination
- Potential for Aerobic Decay

Let us look at what we have and this might seem familiar to you because I believe we looked at one of these pathways as in PCE going to TCE and 1, 2 DCE, vinyl chloride and then further to you know further degradation let us say right. So here let us say the pathway is hydrogenolysis that is something that we observed or you know we looked at earlier too hydrogenolysis.

And you know in other cases we have dehydrochlorination and dichloroelimination we looked at this particular pathway and also hydrogenolysis and we have also looks like a transformation in this case right from 1, 1, 2, 2 TeCA to TCE right trichloroethene right and what else so again what is the take home message here that let us say if I have these source products right and then I observe that my byproducts as I can see here like 1, 2 DCE or 1, 2 DCA or CA or VC or vinyl chloride are at relatively higher concentrations.

Downstream let us say what does that tell you that you know microbial activity is being able to you know is leading to degradation of your relevant contaminants right. So that is something we are going to try to look at.

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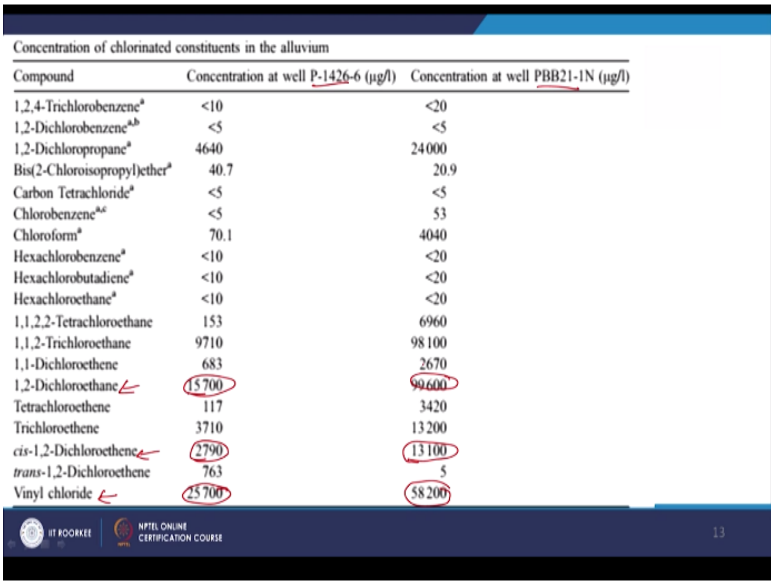

Concentration of chlorinated constituents in the alluvium

Compound	Concentration at well P-1426-6 (μg/l)	Concentration at well PBB21-1N (μg/l)
1,2,4-Trichlorobenzene^{a}	<10	<20
1,2-Dichlorobenzene^{a,b}	<5	<5
1,2-Dichloropropane^{a}	4640	24 000
Bis(2-Chloroisopropyl)ether^{a}	40.7	20.9
Carbon Tetrachloride^{a}	<5	<5
Chlorobenzene^{a,c}	<5	53
Chloroform^{a}	70.1	4040
Hexachlorobenzene^{a}	<10	<20
Hexachlorobutadiene^{a}	<10	<20
Hexachloroethane^{a}	<10	<20
1,1,2,2-Tetrachloroethane	153	6960
1,1,2-Trichloroethane	9710	98 100
1,1-Dichloroethene	683	2670
1,2-Dichloroethane	15 700	99 600
Tetrachloroethene	117	3420
Trichloroethene	3710	13 200
cis-1,2-Dichloroethene	2790	13 100
trans-1,2-Dichloroethene	763	5
Vinyl chloride	25 700	58 200

So let us try to look at that data. So let us say we have at some particular well here and some other well here will look at those again. We are trying to identify 1, 2 DCE CIS 1, 2 DCE that is out here. As you see the concentrations downstream in these wells are remarkably high as we looked at earlier they were not present in the source right and even vinyl chloride as you can see is remarkably at high concentrations right.

That is something that we can observe out here. What were the other compounds we are trying to look at? 1, 2 DCA and CA right 1, 2 DCA I think that is out here right 1, 2 DCA right. So from here you can see that you know your particular there is degradation taking place and the only way it can be is due to natural attenuation let us say right. So that is some particular aspect to keep in mind here right.

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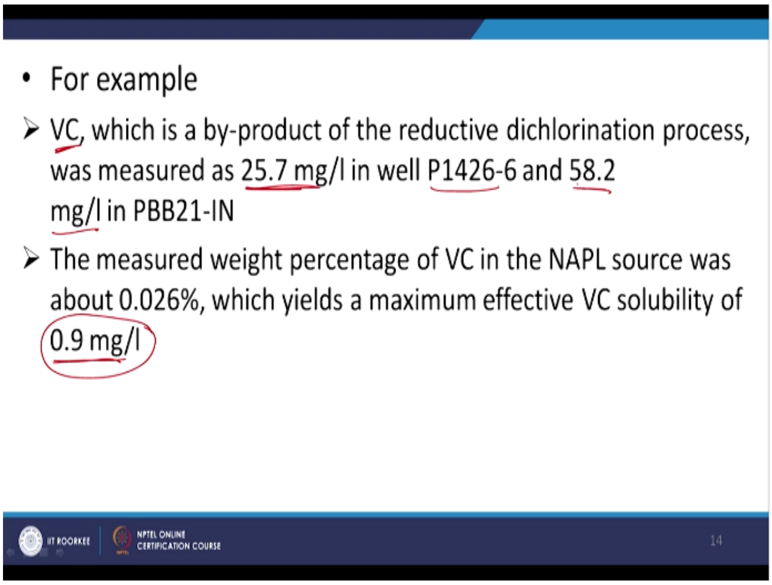

- For example
  - VC, which is a by-product of the reductive dichlorination process, was measured as 25.7 mg/l in well P1426-6 and 58.2 mg/l in PBB21-IN
  - The measured weight percentage of VC in the NAPL source was about 0.026%, which yields a maximum effective VC solubility of 0.9 mg/l

So for example let us say vinyl chloride which as we saw is a byproduct let us say was measured at you know this particular concentration at these two wells let us say remarkably high concentrations, these are milligram per liter but if you look at it in the source it should only be present at 0.9 milligram per liters. So as you see, it increase from 0.9 milligram per liter in the source to either 25 or 60 milligram per liter downstream and that is only because of the biological degradation right or natural attenuation.

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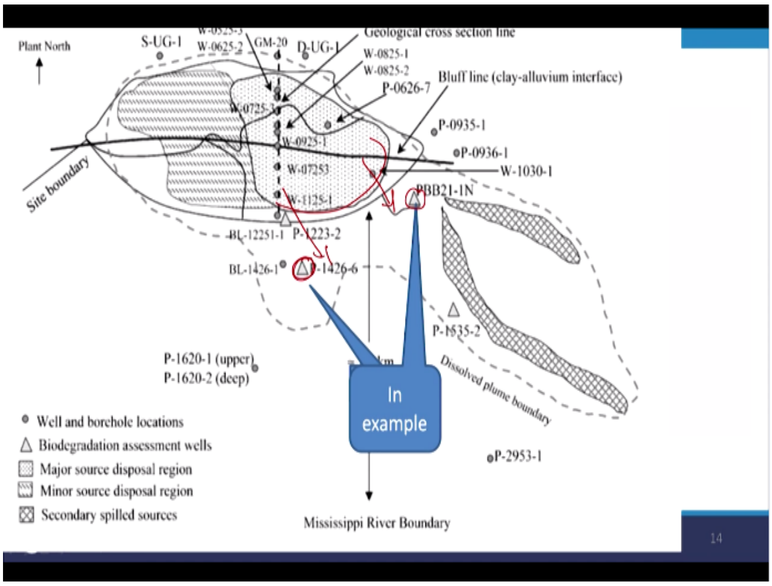

So high VC concentrations were observed and let us look at the wells where we looked at them right, these are the wells where the these are the two wells where we you know for which we looked at the relevant data right and this is the source obviously and as we saw earlier we had horizontal transport in this direction and at this location let us say a few feet downstream we see that there is considerable degradation let us say right.

So I guess with that I am done for today. Again, we have seen or we you know the relevant aspects with respect to this case study and also the complexity of this particular system right. So I guess with that I will end today’s session and thank you.