Laboratory Treatability Study on an Innovative Approach to Remediation of Groundwater Impacted with DNAPL Using Stabilized ClO_2/UV Radiation

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Presentation Overview

- Problem Statement / Opportunity
- Beiseker Compressor Station – Soaking Pit
- Understanding DNAPL?
- Behavior of DNAPL in the Subsurface
- Objectives
- Treatability Lab Work Program
  - Physical Models….
- What is Next?
  - * Field Pilot Remedial Design
- Questions?

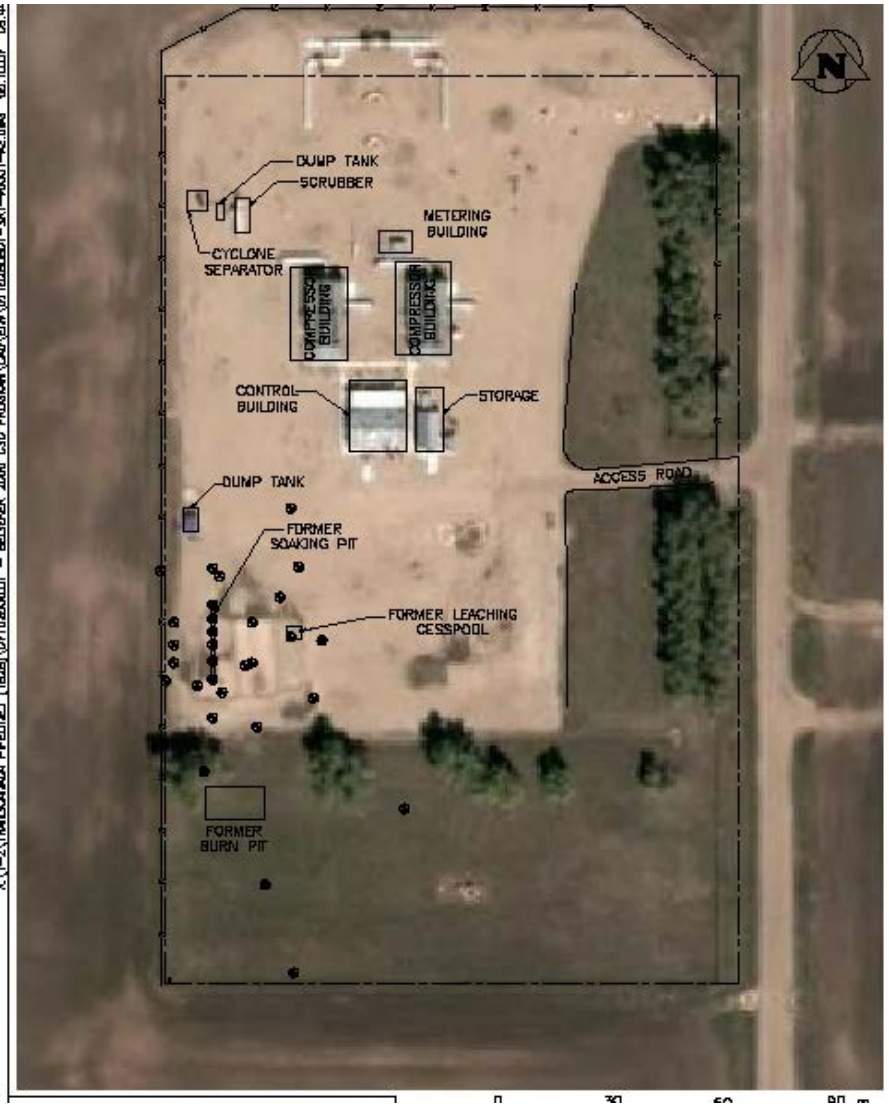
Problem Statement / Opportunity

Remediation of groundwater impacted by DNAPL is a significant challenge facing TransCanada and many industrial sectors in Alberta.

Why?

* Expensive
* Intrinsically Toxic
* Mutagenic / Carcinogenic
* Toxic Metabolites Formation
* Public / Regulatory Pressure
* Environmental / Financial Liabilities

Beiseker Compressor Station – Former Soaking Pit

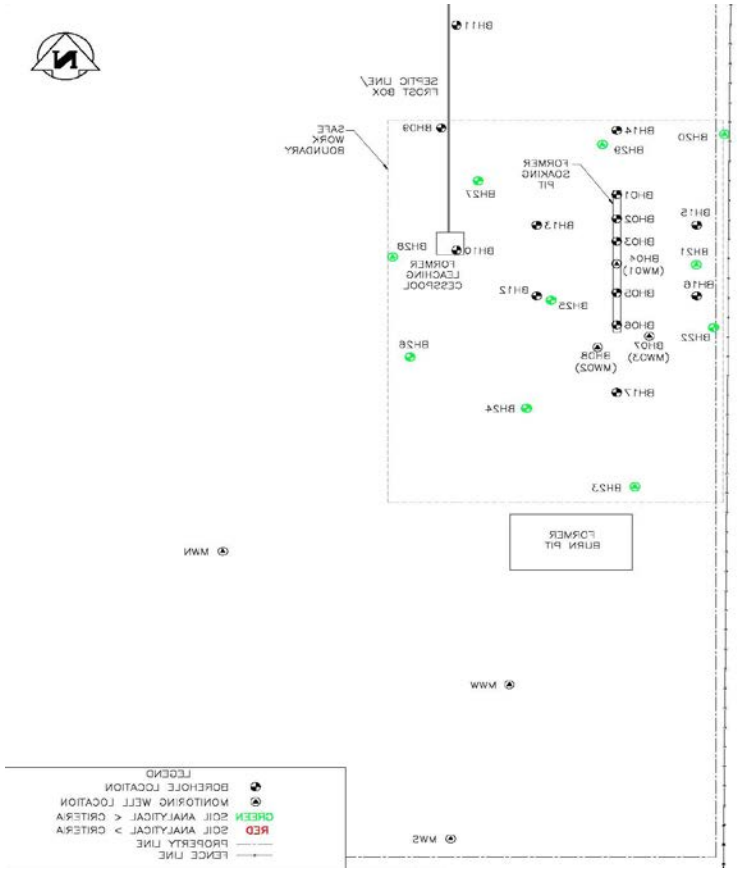


- On-stream Date: 1970-10-26
- Two compressor buildings, a control building and a storage building.
- Original design had subsurface and building floor drains move fluids to a sump.
- These liquids were then pumped to a subsurface absorption pit or soaking pit.
- The former soaking pit measured approximately 21.0 m by 1.0 m, and consisted of a perforated pipe at a depth of 3.7 m to 4.3 m below grade, lined with crushed rock and covered with fill.

Beiseker Compressor Station – Former Soaking Pit

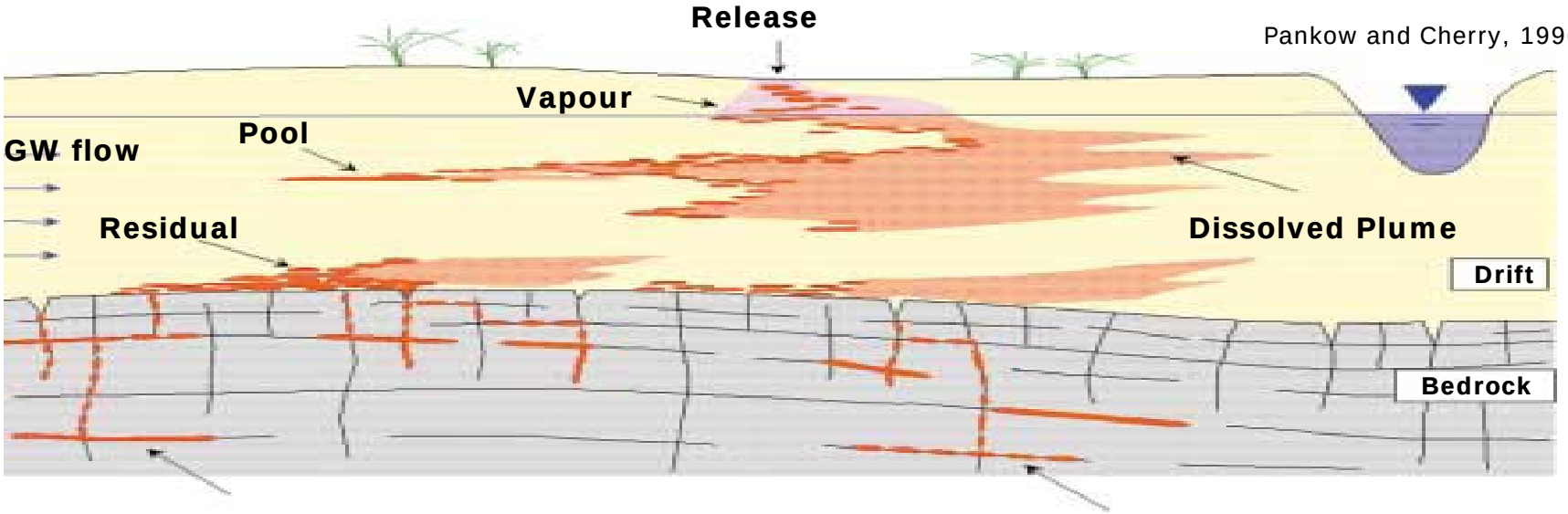
- Former Soaking Pit was removed in 1996.
- Soil and groundwater investigations have been ongoing since 2000.
- Analytical results from the collected DNAPL:
  - BTEX and PHC F1to F4 concentrations are significant with a PHC F3 890,000 mg/l
  - PAHs, PCBs and Phenols are present at significant concentrations
  - The density analyses indicate that the product is about 15% denser than water and it has a kinematic viscosity of 69.57 cSt, which is greater than most lubricating oils
  - DNAPL is comprised of mainly phosphorus and sulphur, these results indicate the product is potentially a triaryl phosphate (TAP), Fyrquel fluid

Phase II Investigation



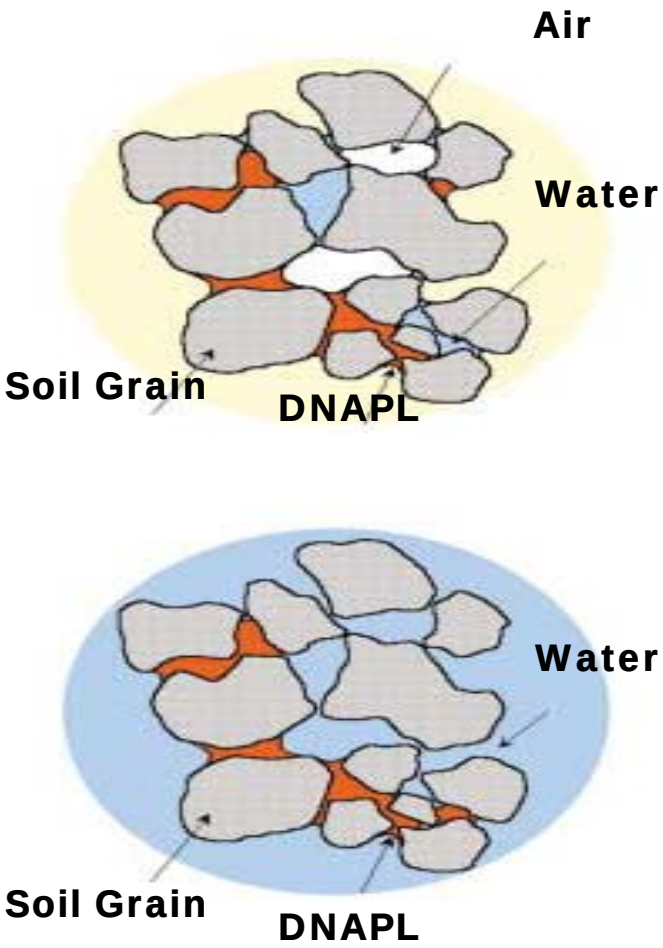
Conceptual Model of DNAPL Pools

- DNAPLs are denser than water allows them to migrate to substantial depths below the water table in both unconsolidated deposits and fractured bedrock.
- The subsurface region containing residual and pooled DNAPL is referred to as the source zone.
- As DNAPLs are only slightly soluble in water, DNAPL source zones can persist for many decades and, in some cases, even hundreds of years.

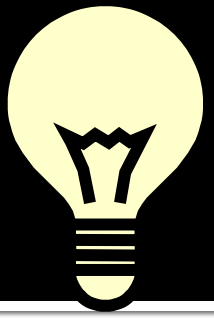


DNAPL in the Subsurface: Residual

- Residual DNAPL formation Saturated : Unsaturated media
- Held in place by capillary and hydrophobic forces
- Adopt the shape of the aquitard
- Residual DNAPL retained is site-specific a typical porous medium such as silt, sand and gravel is typically between 5 and 20 per cent of the pore space in the particular lenses and laminations invaded by the DNAPL.

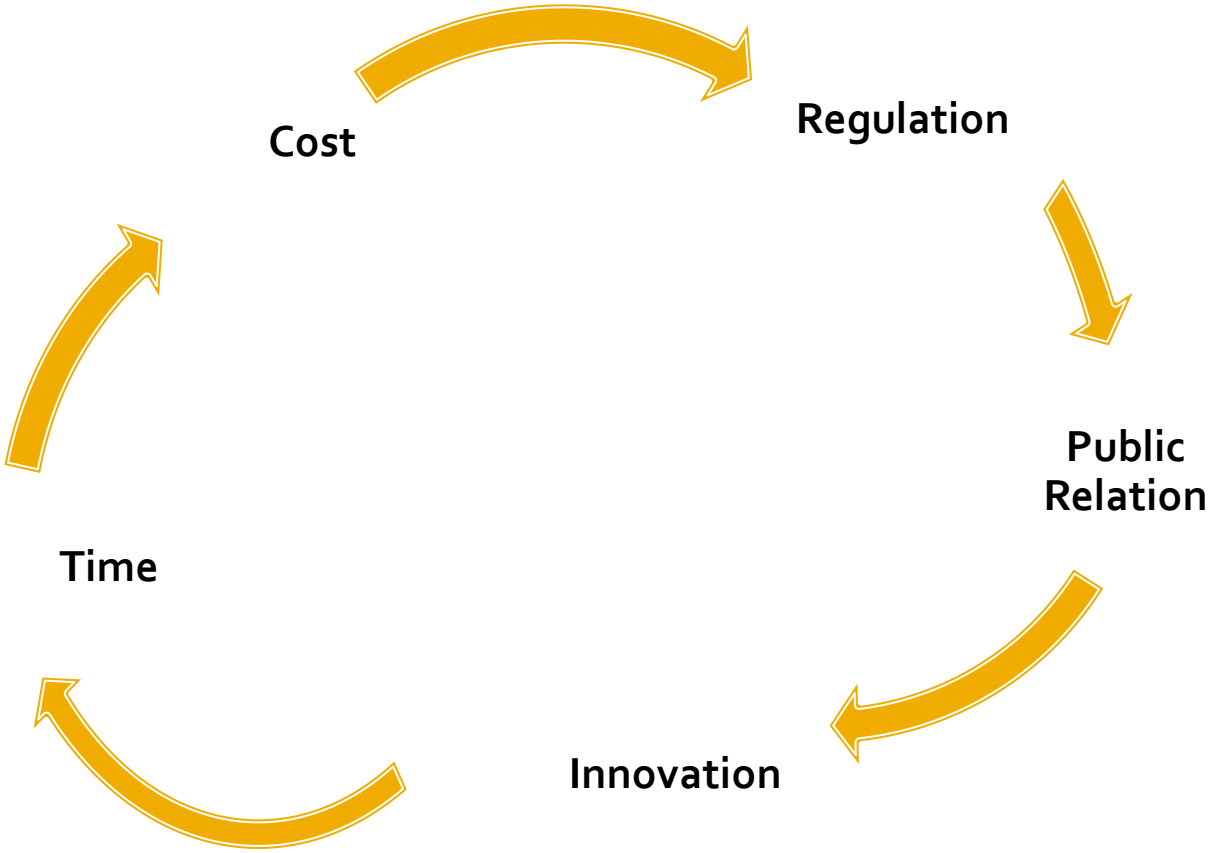


The Opportunity -----



To develop innovative and cost-effective approach to risk manage groundwater contaminated with DNAPL

Components



PRIMARY OBJECTIVES

To ascertain:

* DNAPL constituents chemical degradation
*Dioxins and Furans formation
* DNAPL sorption / travel time….off site
* Physical model for more insights on tracer in the remediation design
* Reactions of fluorescein with ClO_2 at Room/GrH_2O temp, respectively
* Lab simulation for an infiltration gallery design

The above will inform the field pilot implementation!

* Ultimately, a field pilot!

CHEMICAL DEGRADATION
Ma. & Me.

Stock Concentrations: Phenol 20 µg/L; PCB 10 µg/L; PAH 20 µg/L; Gasoline 500 mg/L

	Chemical Spikes						
Treatment #	Phenol Addition (µL)	PCB Addition (µL)	PAH Addition (mL)	Gasoline Addition (µL)	UV Exposure	ClO_2 Addition	H_2SO_4 Addition*
1	90	24	1.2	48	No	No	No
2	90	24	1.2	48	Yes	No	No
3	90	24	1.2	48	Yes	Yes	No
4	90	24	1.2	48	Yes	Yes	Yes
Blank	0	0	0	0	No	No	No

** 0.01 mL of 6M H_2SO_4 was added to treatment 4 in order to reduce the pH to 3.5*

- Used clean groundwater from the site

- Initial Standard Analytes Concentration in the treatments:

Phenol	20 µg/L
PAH	20 µg/mL
Gasoline	500 mg/mL
PCB	20 µg/mL

- Blank, Control, Trts with or without ClO_2 and UV combination

All chemical analyses performed by Maxxam Analytics.

CHEMICAL/PHOTOLYSIS DEGRADATION

Batch Degradation Systems

ClO_2/UV

UV Lamp :

254 nm

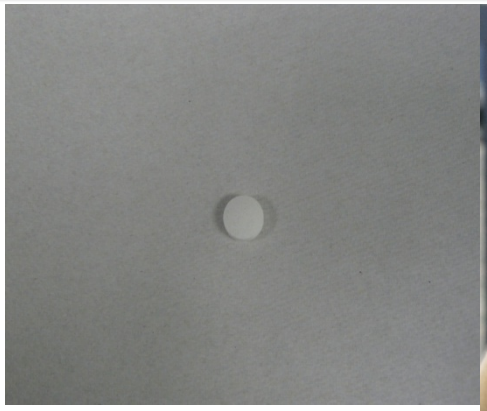
0.4 mW cm-2

6 W / 100 V

11 inch

8 min Rxt time.

Stabilized ClO_2 Chemical?



* Strong Oxidant
* Water Soluble
* Oxidize over broad pH range
* Does not hydrolyze in H_2O
* No potential for toxic byproducts formation

$$\{2\,ClO_{2\,(solid)} + H_2O \leftrightarrow H_2O + ClO_3^- + ClO_2^-\} + UV$$

Chlorate Chlorite

Free radicals solution!
A very high oxidation capacity!

UV enhances quantum vibration in molecules & degradation by ClO2!

Degradation Results

TRT 1: No degradation

TRT 2: ↓ 50-75 % PCBs;60-75% PAH;BETEX 50-80%; Phenol 74%

TRT 3: ↓ 97-100 % PCBs;76-93% PAH;BETEX 82-86%; Phenol 98%

TRT 4: ↓ 97-100 % PCBs;76-93% PAH;BETEX 82-86%; Phenol 98%

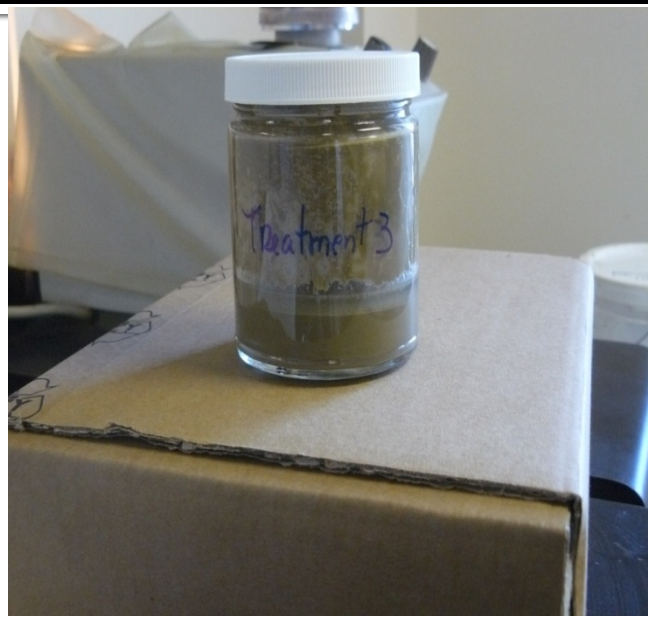
{ClO_2 /UV + Soluble-DNAPL --------> Simple-non toxic by-products + CO_2 + R-OH + Salts

No formation of dioxins or furans as by-products was detected!

BATCH ISOTHERMS @ 6 °C

Contaminants Sorption

- Used clean subsoil substrate from the site 4.5-5 m
-Subsoil characterized for physical / chemical properties
- Spiked substrate with chemical standards / Equilibrated overnight
-Supernatant removed with glass syringe → Vial → Refrigerated



Textural Class = Clay

Sand =34%; Silt = 22%; Clay = 44%; pH = 8.1;
CEC = 19 cmole/kg; Ø = 60% ; SAR = 0.66
BD= 1.23 gmL^{-}; D_{10} = 0.058; Cμ = 1.47;
CG = 0.0058

* Relative mobility / bioavailability / sorbing capacity evaluation

* Can model transport.....

ISOTHERM EXPERIMENTAL DESIGN @ 6 ºC

	Concentration of spiking solution (µg/mL)	Blank	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Jar Weight (g)		183.3	181.13	185.19	185.19	188.25
Sample weight (g)		79.92	79.65	80.15	80.09	79.95
Water Added (mL)		30	30	30	30	30
PAH (µL)	20	0	250	500	1000	2000
PCB-S (µL)	10	0	50	100	200	400
SVPHEN-S (µL)	20	0	100	200	400	800
F24FIDE-S (µL)	70000	0	500	1000	2000	4000
BTEXHSAB-S (µL)	500000	0	10	20	40	80
Total Volume Spiked (mL)			910	1820	3640	7280
Total volume added to soil samples and total volume of water reference samples (mL)			30.91	31.82	33.64	37.28

ISOTHERM MODELS

Freundlich: $X/M = K\,Ceq^{1/n}$

$\Rightarrow \log [X/M] = [1/n] \log [Ceq] + \log [Kd]$

$\Rightarrow K_{oc} = Kd\, f_{oc}$

Langmuir: $X/M = (ab)(Ceq) / (1 + bCeq)$

$\Rightarrow [Ceq] / [X/M] = \{1 / [ab]\} + \{[Ceq] / [a]\}$

Equation

$$V = \frac{K\,(dh/dl)}{(7.48\,\varnothing)\,Rf}$$

Freundlich → $Rf = 1 + \{[Pb/\Phi]\,Kd\}$

Langmuir → $Rf = 1 + [Pb/\Phi]\ \{a\,b\,/\,(1 + a\,C_{eq})^2\}$

Freundlich & Langmuir Linear Regression Model Coefficients

	Freundlich			Langmuir			
	Linear Regression	KD	R2	Linear Regression	R2	a (mg/Kg)	b (mL/g)
Analytes							
BENZENE	y = 38.969x + 9.8344	2.0759	0.9688	y = -0.0057x + 49.433	0.003	-175.4385965	-0.00012
TOLUENE	y = 113.47x - 13.293	2.2267	0.9736	y = -0.005x + 50.378	0.003	-200	-0.00010
ETHYLBENZENE	y = 473.54x - 46.407	2.6529	0.9786	y = -0.0048x + 51	0.002	-208.3333333	-0.00009
m & p- XYLENE	y = 115.86x - 40.364	2.0786	0.9729	y = -0.0047x + 50.095	0.002	-212.7659574	-0.00009
o-XYLENE	y = 312.89x - 34.513	2.471	0.9775	y = -0.0048x + 50.824	0.002	-208.3333333	-0.00009
F1 (C6-C10)	y = 3.2528x + 90.15	2.0252	0.8325	y = -0.0087x + 184.19	0.003	-114.9425287	-0.00005
PAH-ACENAPHTENE	y = 4.3599x - 0.1101	0.892	0.8784	y = 0.0113x + 0.0184	0.043	88.49557522	0.61413
PAH-ACENAPHTYLENE	y = 4.8059x - 0.1076	1.0766	0.8983	y = 0.0098x + 0.0202	0.029	102.0408163	0.48515
PAH-ACRIDINE	y = 4.6739x - 0.104	1.037	0.8949	y = 0.0092x + 0.0204	0.026	108.6956522	0.45980
PAH-ANTHRACENE	y = 4.7797x - 0.1056	1.0172	0.8929	y = 0.0092x + 0.0207	0.024	108.6956522	0.44444
PAH-BENZO(a)ANTHRACENE	y = 4.6154x - 0.1021	0.9978	0.8913	y = 0.0085x + 0.0206	0.019	117.6470588	0.41262
PAH-BENZO(k)FLUORANTHRACENE	y = 4.904x - 0.1025	1.0114	0.9072	y = 0.007x + 0.023	0.013	142.8571429	0.30435
PAH-BENZO(C)PHENANTHRENE	y = 4.6398x - 0.097	0.9588	0.8999	y = 0.0068x + 0.0222	0.010	147.0588235	0.30631
PAH-BENZO(e)PYRENE	y = 4.9427x - 0.1035	1.0245	0.9045	y = 0.0077x + 0.0227	0.016	129.8701299	0.33921
PAH-BENZO(a)PYRENE	y = 5.0572x - 0.1039	0.9917	0.9053	y = 0.006x + 0.0248	0.008	166.6666667	0.24194
PAH-CHRYSENE	y = 4.5006x - 0.1054	1.0607	0.8843	y = 0.0125x + 0.017	0.058	80	0.73529
PAH-FLUORANTHENE	y = 4.6268x - 0.1063	1.0163	0.8853	y = 0.0105x + 0.019	0.034	95.23809524	0.55263
PAH-FLUORENE	y = 4.3412x - 0.1055	1.0659	0.8775	y = 0.0137x + 0.0154	0.078	72.99270073	0.88961
PAH-2-METHYLNAPHTALENE	y = 5.8116x - 0.1004	0.9971	0.9311	y = 0.0006x + 0.0342	7E-05	1666.666667	0.01745
PAH-NAPHTALENE	y = 6.0662x - 0.0985	0.9852	0.9372	y = -0.0015x + 0.0382	0.003	-666.6666667	-0.03927
PAH-PHENANTHRENE	y = 4.2044x - 0.1118	1.2091	0.8633	y = 0.0189x + 0.0111	0.242	52.91005291	1.70270
PAH-PERYLENE	y = 4.482x - 0.1133	1.1139	0.8694	y = 0.0153x + 0.0146	0.112	65.35947712	1.04795
PAH-PYRENE	y = 4.3472x - 0.1091	1.0857	0.8685	y = 0.0152x + 0.0144	0.103	65.78947368	1.05556
PHE-CRESOLS	y = 13.054x - 0.067	3.0488	0.8169	y = 0.0079x + 0.0113	0.021	126.5822785	0.69912
PHE-2,3,5,6-TETRACHLOROPHENOL	y = 9.2898x - 0.0408	2.2951	0.8483	y = -0.0043x + 0.0121	0.002	-232.5581395	-0.35537
PHE-2,3,4,6-TETRACHLOROPHENOL	y = 8.5963x - 0.038	2.5427	0.8781	y = 9E-05x + 0.0097	2E-06	11111.11111	0.00928
PHE-2,4-DICHLOROPHENOL	y = 7.5086x - 0.0395	2.3928	0.7629	y = 0.0031x + 0.0081	0.001	322.5806452	0.38272
PHE-2,6-DICHLOROPHENOL	y = 2.0592x + 0.1705	1.5799	0.0102	y = 0.7926x - 0.0618	0.881	1.261670452	12.82524
PHE-2-CHLOROPHENOL	y=11.131x - 0.0489	2.3212	0.8412	y = -0.005x + 0.0149	0.002	-200	-0.33557
PHE-3 & 4-METHYLPHENOL	y = 13.064x - 0.067	3.0488	0.8169	y = 0.0079x + 0.0113	0.0216	126.5822785	0.69915

Best fit?

Both Freundlich and Langmuir isotherm equations evaluated.
Better represented by Freundlich model:

R^2 ranged from 0.76 t o .98
Kd ranged from 0.89 to 3.05

GLMs will be evaluated also!

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Equation for Predicting Advection Transport

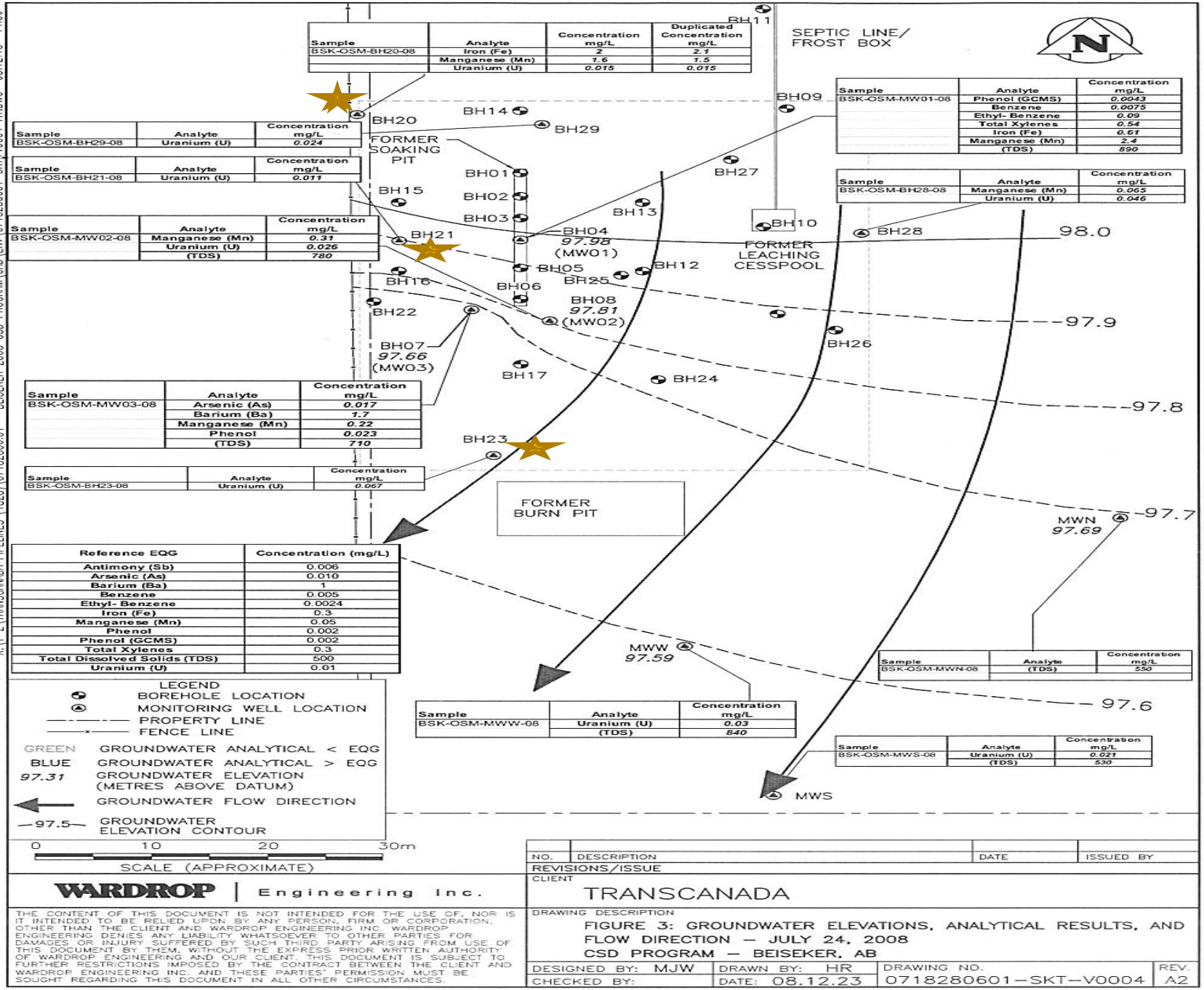
V_s = Q/AØ R ” K (dh/dL)/Ø R

R = Retardation factor

Freundlich, R = 1 +{[pb/Ø] kd}

Langmuir, R = 1 + [pb/Ø] {ab/(1 + a Ceq)²}

Travel Time = L / V_s



Contaminants Transport Calculations

Pertinent Information from Phase II investigation:

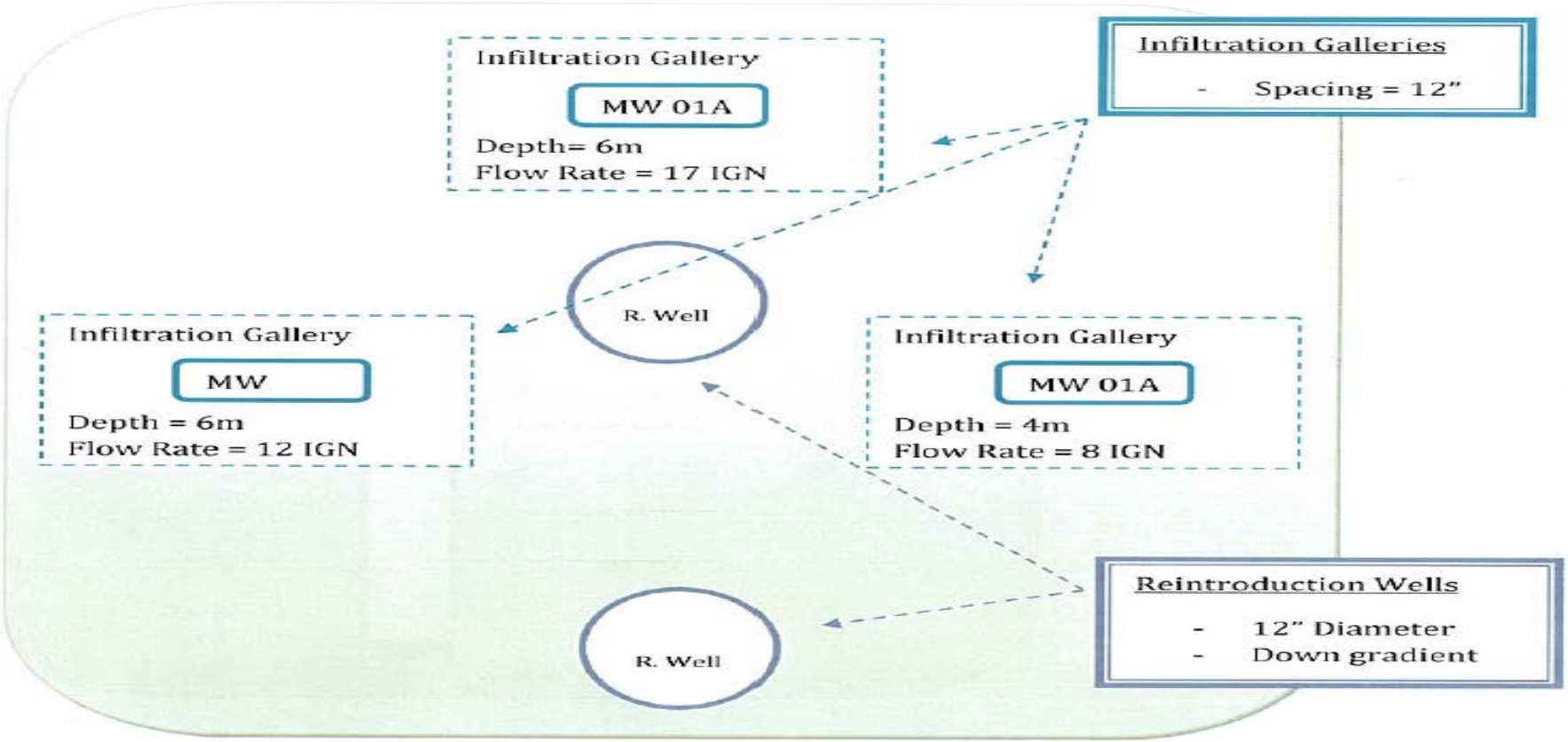
- Ground H_2O elevations
- Flow direction
- Isopleth of equipotential lines
- Slug test method:
  *K values ranged from 1.87×10^{-7} to 1.30×10^{-5} m/s
  * & K as per Falling-Head Method; Ø; BD

Contaminant Isotherm	Freundlich KD	Travel Time (years)					
		July 24 2008			September 23 2008		
		BH-20	BH-21	BH-23	BH-20	BH-21	BH-23
BENZENE	2.0759	17245.33	2328.68	288.56	11487.40	1744.91	288.56
TOLUENE	2.2267	18254.92	2469.42	306.78	12159.91	1850.36	306.78
ETHYLBENZENE	2.6529	21108.28	2867.17	358.27	14060.57	2148.40	358.27
m & p- XYLENE	2.0786	17263.41	2331.20	288.89	11499.44	1746.80	288.89
o-XYLENE	2.471	19890.48	2697.41	336.30	13249.38	2021.20	336.30
F1 (C6-C10)	2.0252	16905.90	2281.37	282.44	11261.30	1709.46	282.44
PAH-ACENAPHTENE	0.892	9319.27	1223.81	145.53	6207.72	917.02	145.53
PAH-ACENAPHTYLENE	1.0766	10555.14	1396.09	167.83	7030.96	1046.11	167.83
PAH-ACRIDINE	1.037	10290.03	1359.14	163.04	6854.36	1018.42	163.04
PAH-ANTHRACENE	1.0172	10157.47	1340.66	160.65	6766.06	1004.57	160.65
PAH-BENZO(a)ANTHRACENE	0.9978	10027.59	1322.55	158.31	6679.54	991.00	158.31
PAH-BENZO(k)FLUORANTHRACENE	1.0114	10118.64	1335.24	159.95	6740.19	1000.51	159.95
PAH-BENZO(C)PHENANTHRENE	0.9588	9766.49	1286.16	153.60	6505.62	963.73	153.60
PAH-BENZO(e)PYRENE	1.0245	10206.34	1347.47	161.53	6798.61	1009.68	161.53
PAH-BENZO(a)PYRENE	0.9917	9986.75	1316.86	157.57	6652.34	986.74	157.57
PAH-CHRYSENE	1.0607	10448.69	1381.25	165.91	6960.05	1034.99	165.91
PAH-FLUORANTHENE	1.0163	10151.44	1339.82	160.54	6762.04	1003.94	160.54
PAH-FLUORENE	1.0659	10483.51	1386.11	166.54	6983.24	1038.63	166.54
PAH-2-METHYLNAPHTALENE	0.9971	10022.90	1321.90	158.22	6676.42	990.51	158.22
PAH-NAPHTALENE	0.9852	9943.23	1310.79	156.79	6623.35	982.19	156.79
PAH-PHENANTHRENE	1.2091	11442.21	1519.75	183.84	7621.85	1138.76	183.84
PAH-PERYLENE	1.1139	10804.86	1430.90	172.34	7197.30	1072.19	172.34
PAH-PYRENE	1.0857	10616.07	1404.58	168.93	7071.54	1052.47	168.93
PHE-CRESOLS	3.0488	23758.78	3236.64	406.11	15826.12	2425.25	406.11
PHE-2,3,5,6-TETRACHLOROPHENOL	2.2951	18712.85	2533.25	315.05	12464.94	1898.19	315.05
PHE-2,3,4,6-TETRACHLOROPHENOL	2.5427	20370.50	2764.32	344.96	13569.13	2071.34	344.96
PHE-2,4-DICHLOROPHENOL	2.3928	19366.94	2624.43	326.85	12900.64	1966.52	326.85
PHE-2,6-DICHLOROPHENOL**	1.5799	13924.67	1865.79	228.64	9275.46	1398.06	228.64
PHE-2-CHLOROPHENOL	2.3212	18887.59	2557.61	318.20	12581.34	1916.45	318.20
PHE-3 & 4-METHYLPHENOL	3.0488	23758.78	3236.64	406.11	15826.12	2425.25	406.11

Contaminant Mobility Index (CMI)	
Rating	Time (years)
Fast	<100
Medium	100-200
Slow	>200

Infiltration Gallery Design

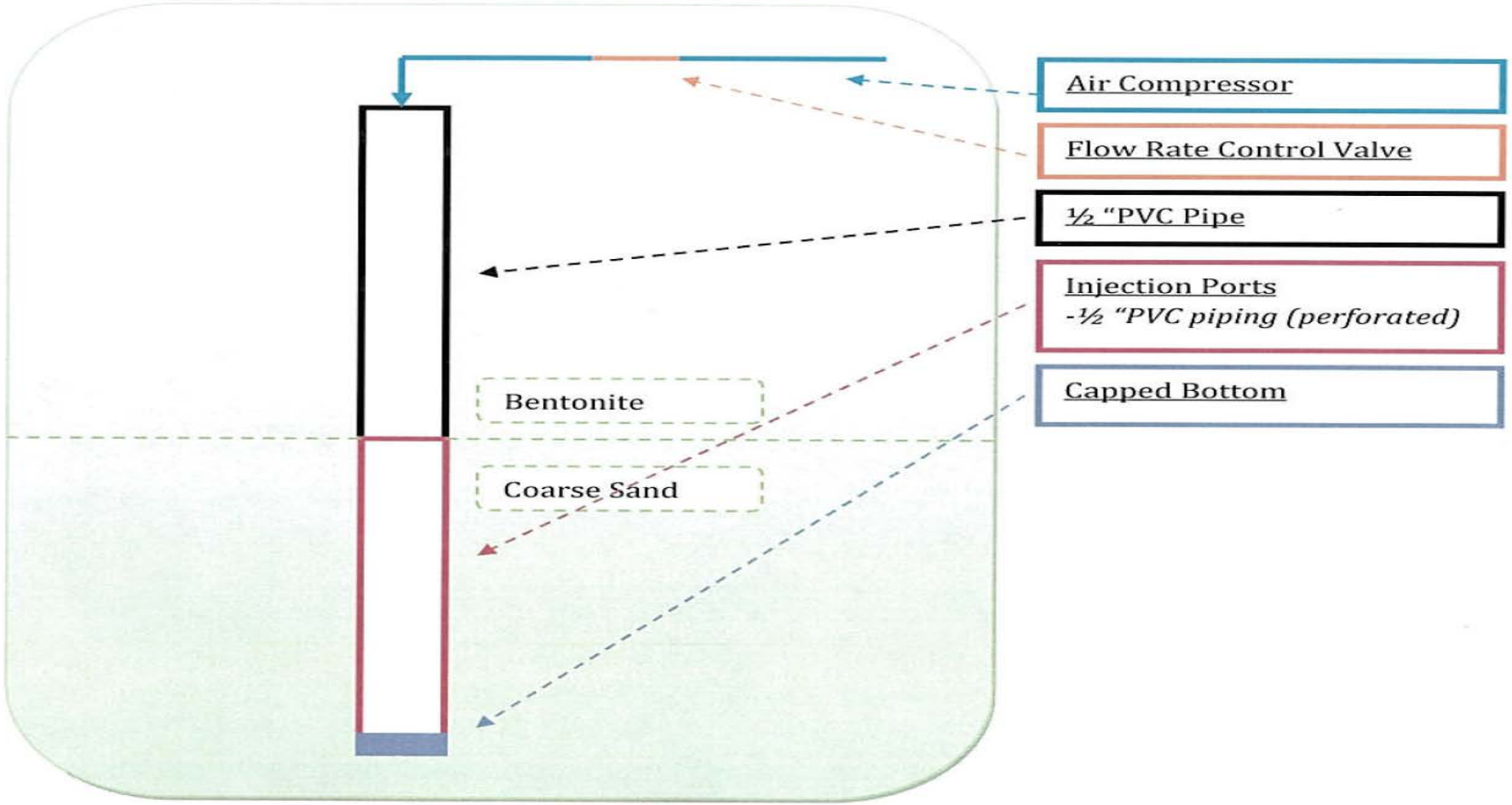
Proposed Infiltration Gallery System (NTS)



ClO_2 Treatment Method

- Aboveground NAPL degradation
  - ClO_2 and UV exposure
- Reinjection of treated Groundwater with 10ppm ClO_2
- Radius of influence overlaps by 4" (shown below)

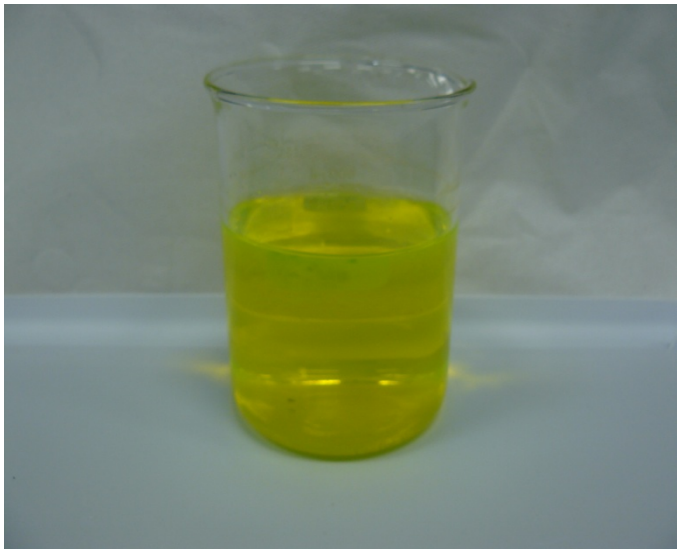
INFILTRATION GALLERY PROFILE (NTS)

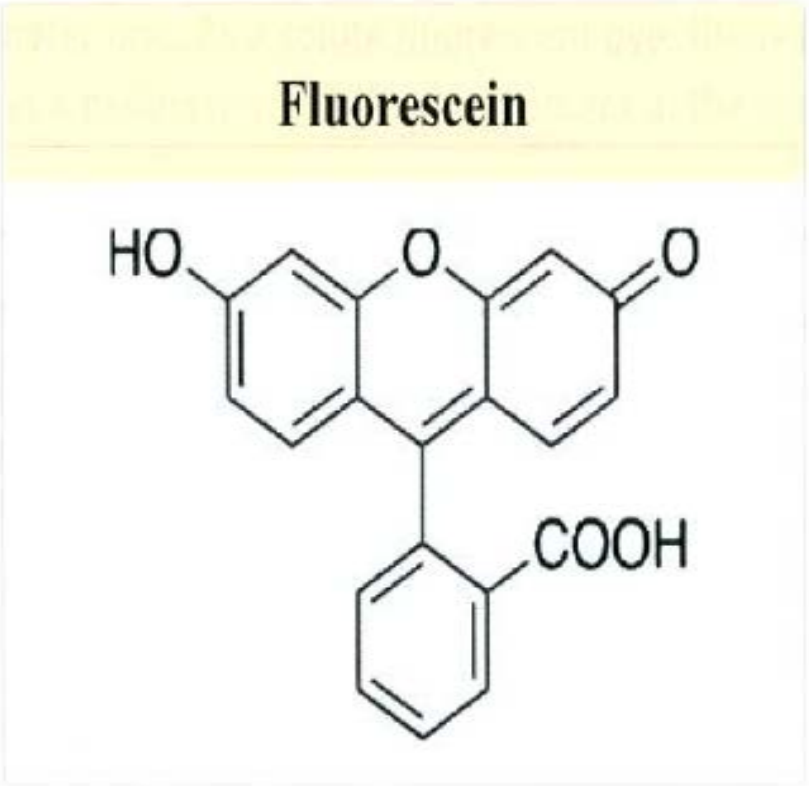


Infiltration Gallery Notes

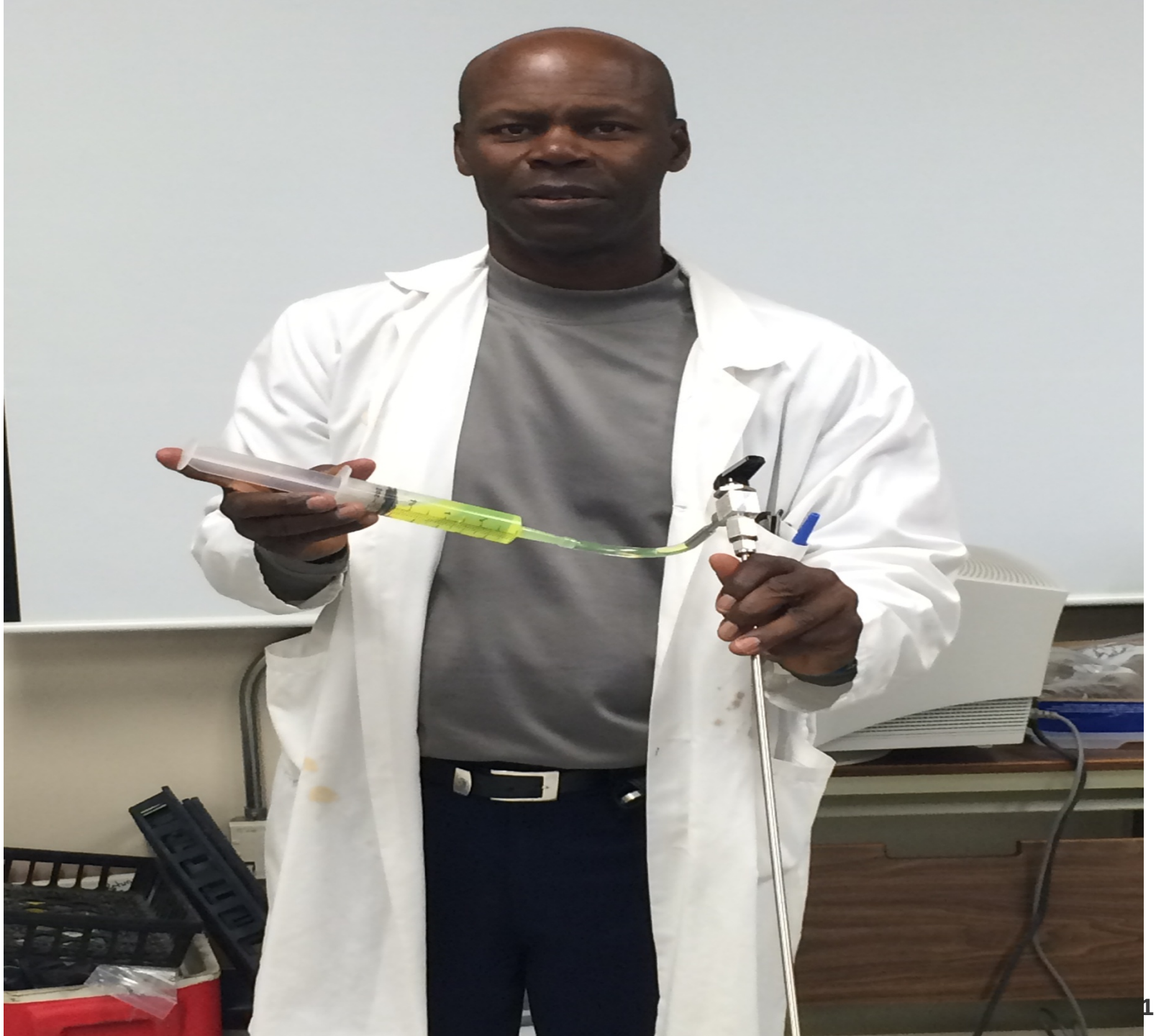
- Dedicated pump and treatment systems will be used for each monitoring well
- Treatment systems will be sheltered
- Reinjection of treated ground water will be up gradient
- Field monitoring of residual ClO_2 in the ground water will be performed

Fluorescein Tracer Applications

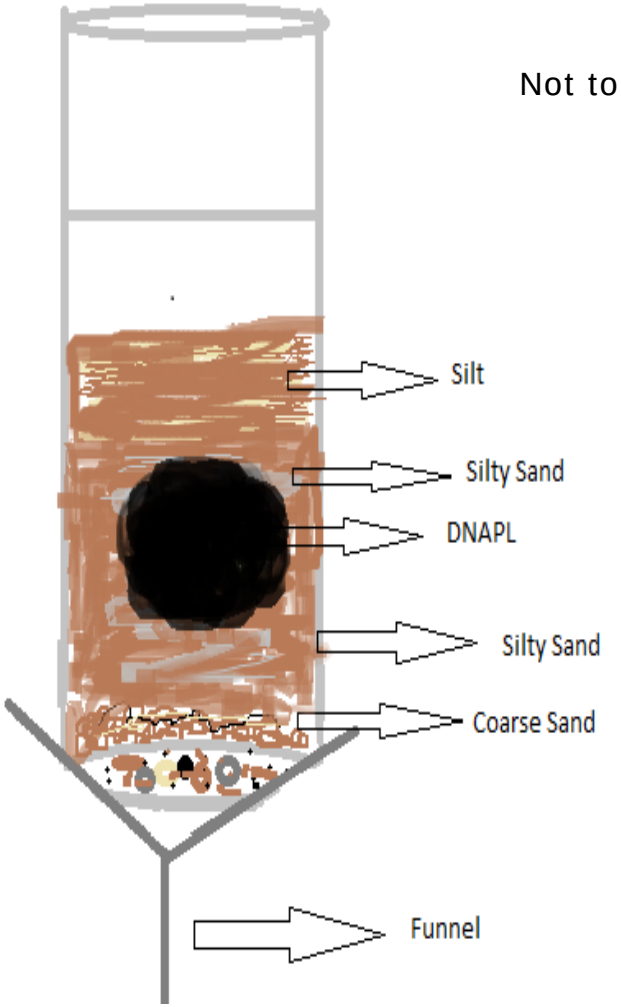




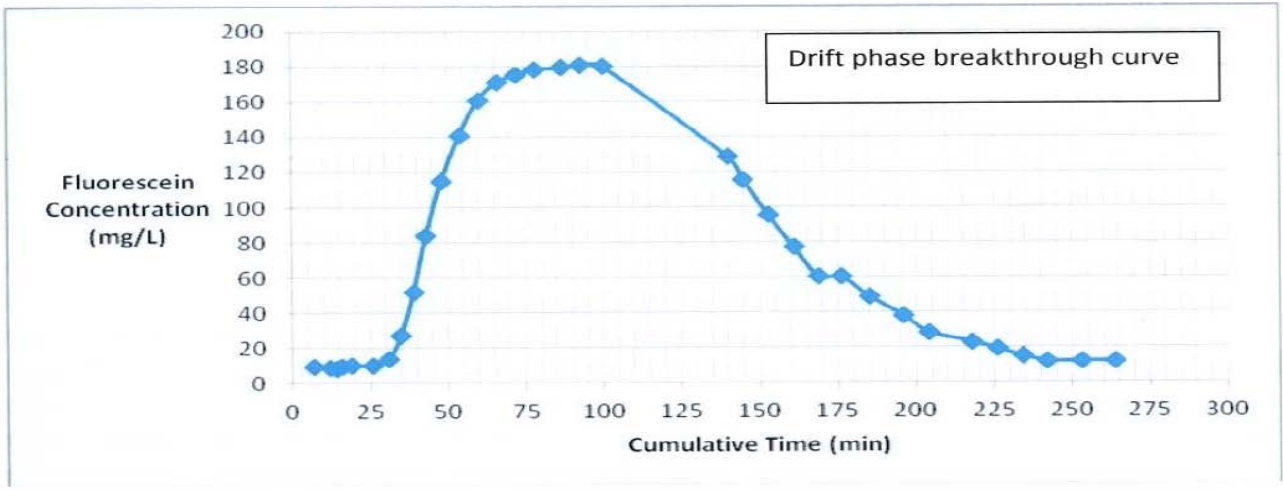
- Slightly soluble in water
- Visually detected
- Fluorophone
- Exhibit a yellow color/can appear red
- Non-toxic
- Inert
- Analysed with a fluorometer / turbidimeter

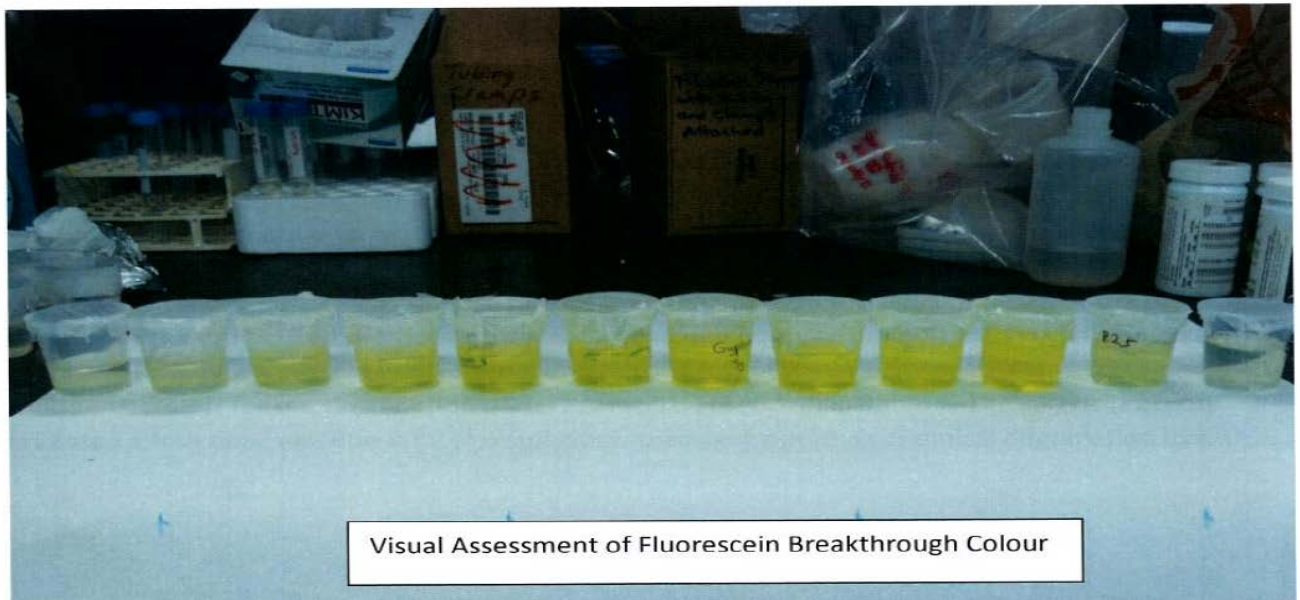


Physical Model

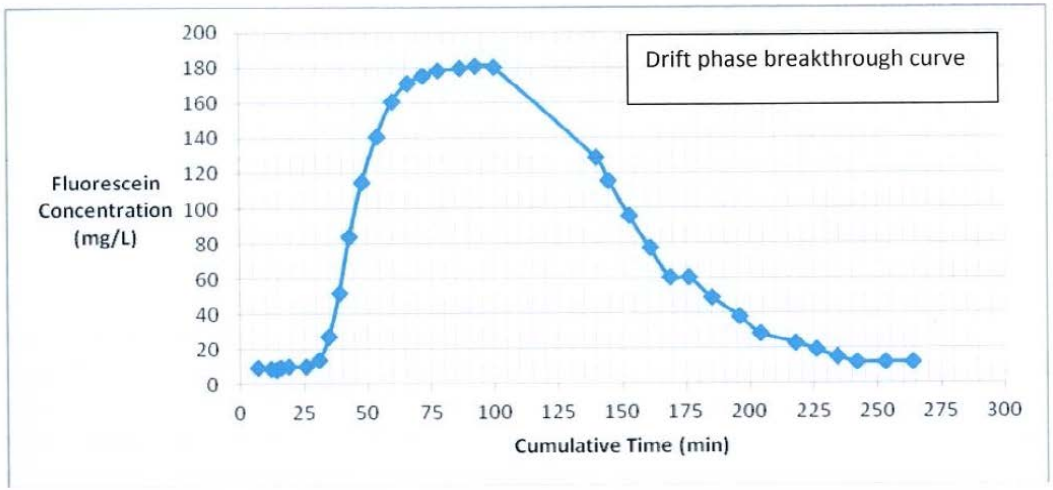


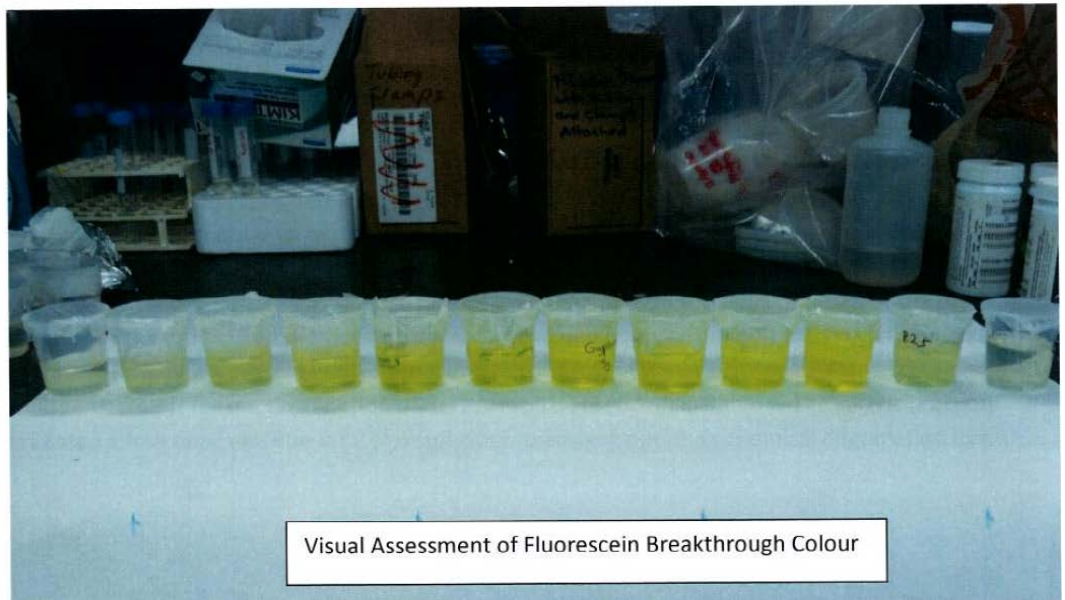
Breakthrough Curve





Breakthrough Curve





Arrival time reflects advective transport through the physical model.

Field Pilot

Batch aboveground treatment System

↓

Reinjection of treated $GrH_2O + ClO_2$

↓

Network Infiltration Gallery

Ongoing Monitoring…….

Conclusions

- ClO_2/UV effective treatment system for dissolved DNAPL plume
- No detectable dioxins or furans as by-products of the chemical reactions
- Travel time ranged from 145 to 80,817 years
- Public health risk & financial liabilities can be cost effectively / confidently managed

Thank You!

Questions?