

Cleanup of Small Dry Cleaner Using Multiple Technologies: Sages Dry Cleaner Site

NATO/CCMS Pilot Study Meeting, June 2006

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Site Size Issues

	<u>Large</u>	<u>Small</u>
Waste Type	Mixed	PH/CH
Access Issues	flexible	less
Boundary Issues	some	many
NA-applicable	yes	less likely
Ownership	Gov./Corp.	Private
Time Issues	Varies	Limited by economics

Small Urban Sites are more likely to require source zone treatment to meet remedial time limitations and coordinated remedial approaches to address both source zone and dissolved phase contaminants.

Field Evaluation of the Solvent Extraction Residual Biotreatment (SERB) Technology

Project Team

USEPA-NRMRL-SPRD-Ada

- Guy W. Sewell, PI, Biological Processes
- Lynn Wood, Physical Processes
- Susan Mravik, Site Coordinator**
- Ann Keeley, Norma Duran (Lab Studies)

Site Contractor

- Levine-Fricke Recon

UF

- Mike Annable, PI Solvent Extraction

MSU

- James M. Tiedje, PI Microbial Ecology
- Shannon Flynn, Rebekah Helton, Frank Loeffler (Lab Studies)

Project Funding- SERDP(FIBRC-WES), EPA-TIO, State of Florida

OBJECTIVE

- Integrate Remediation Technologies into a Treatment Train for Comprehensive Site Restoration
- Target DNAPL Source Zone
- Decrease Remediation Costs

LIMITATIONS

- Geology
- Source Zone Delineation
- Time (?)

CONTAMINANT OF INTEREST:

Tetrachloroethene (PCE)

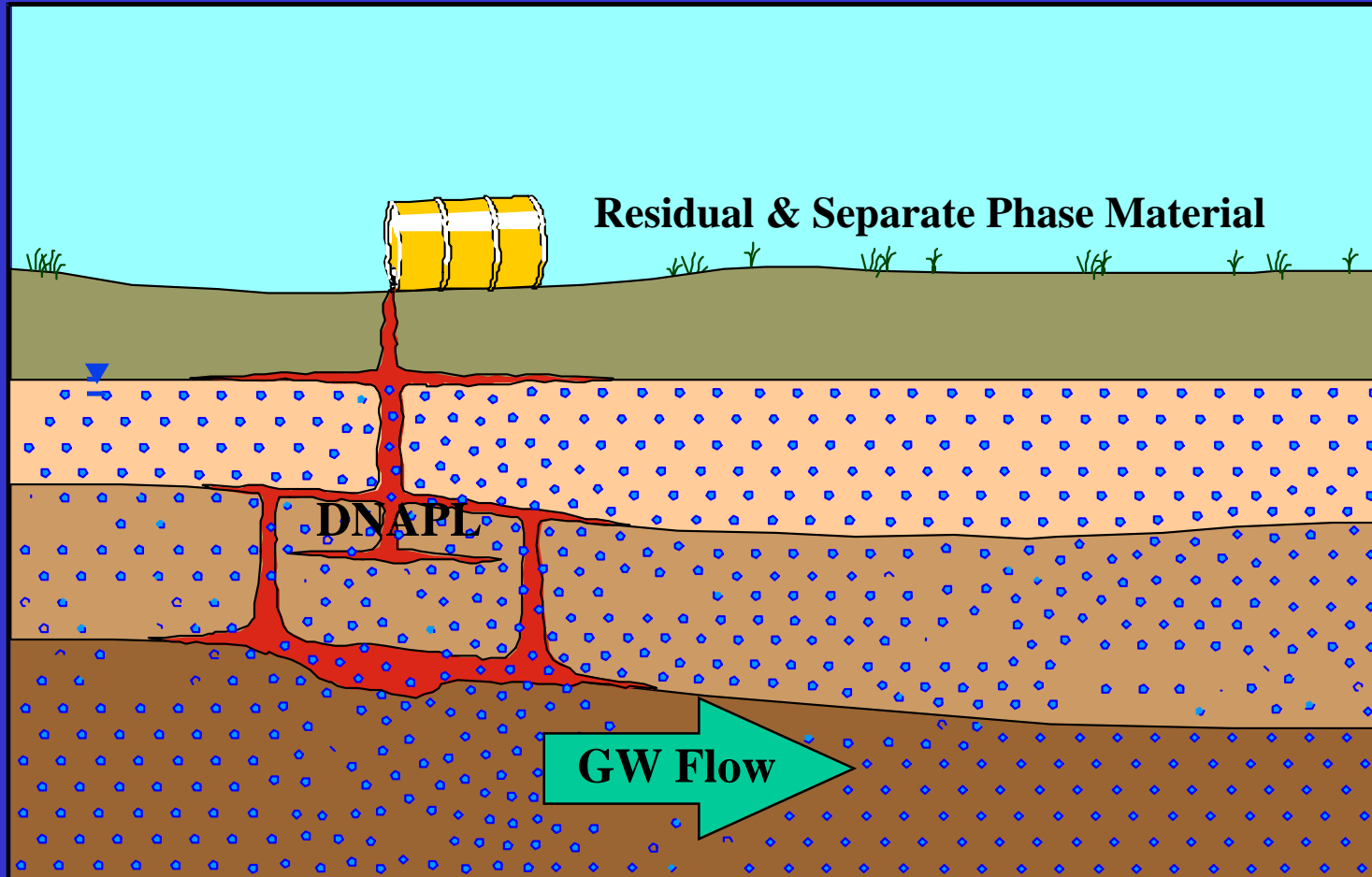
TECHNOLOGICAL BASIS:

Cosolvent Extraction (Ethanol)

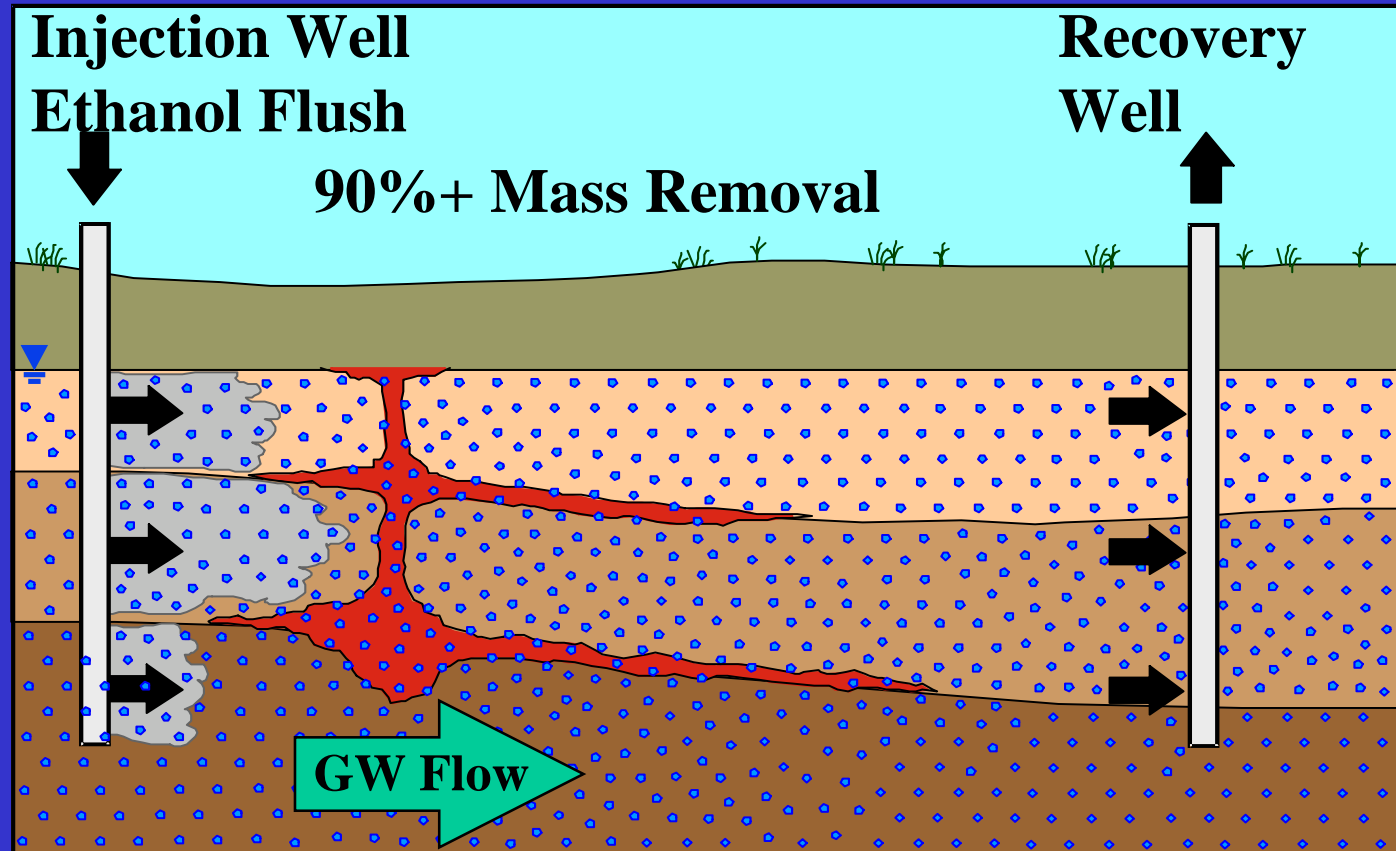
Biodegradation

(Reductive Dechlorination)

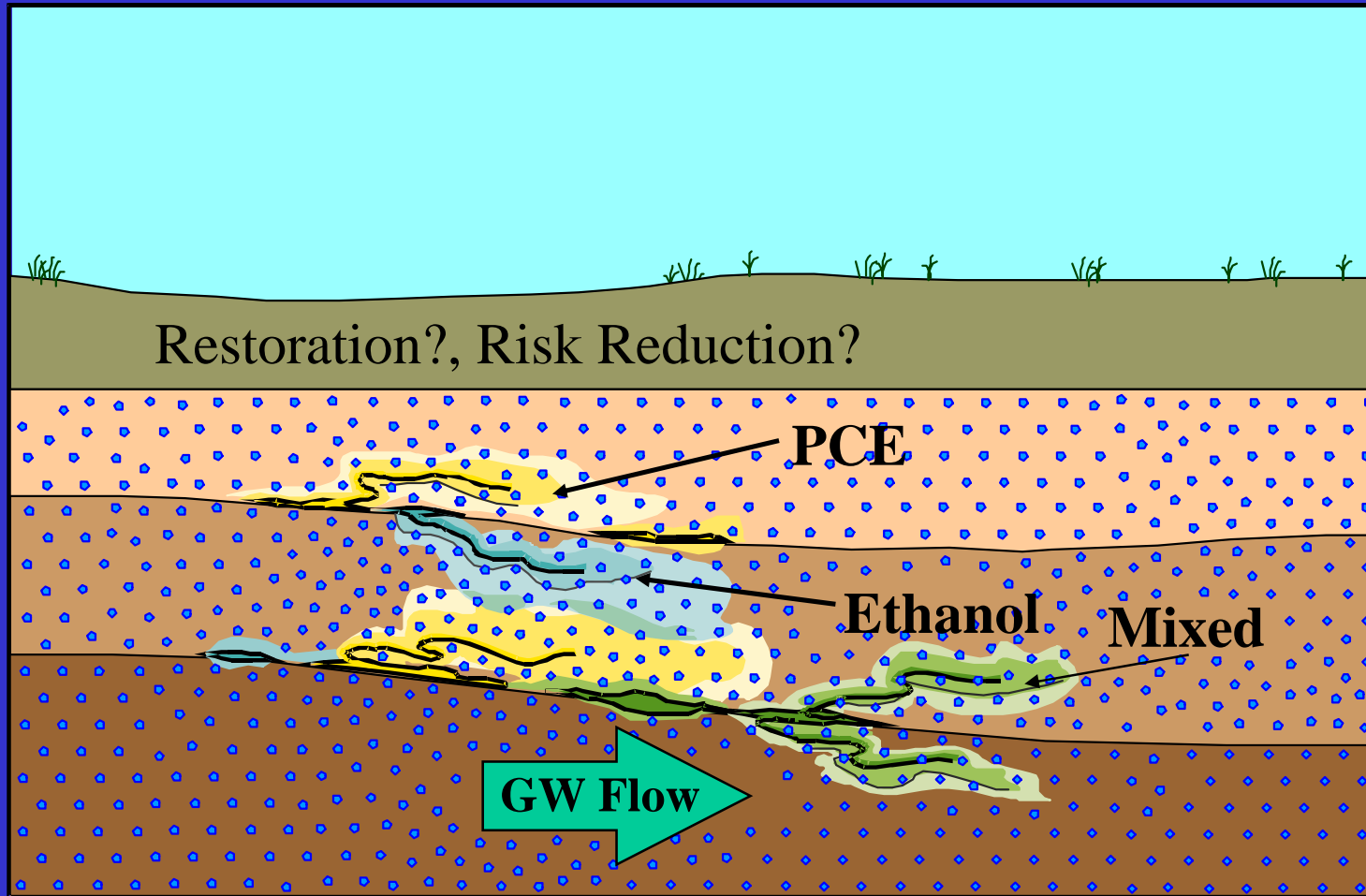
PCE Spill



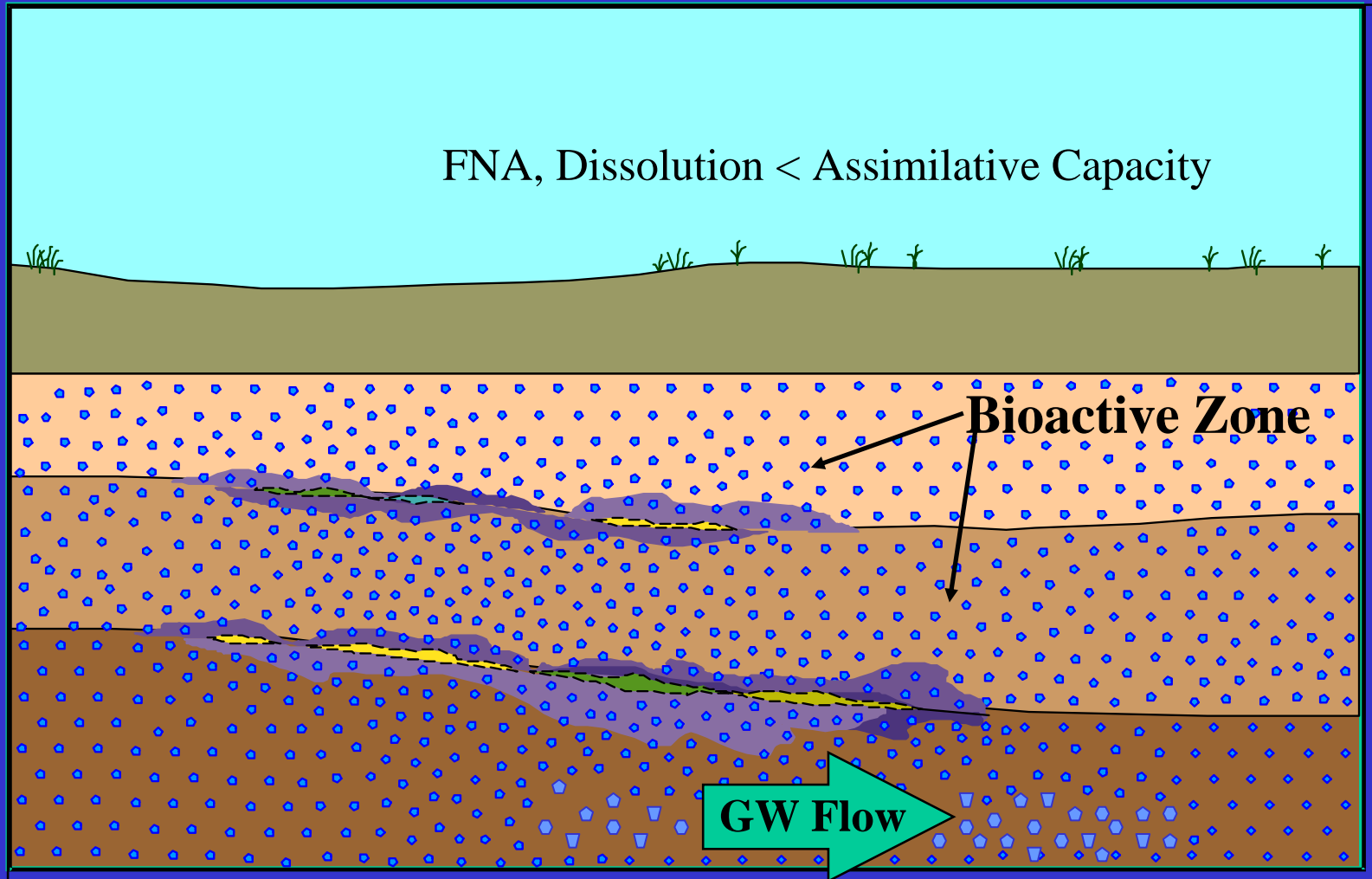
Cosolvent Extraction



Residual Contaminants



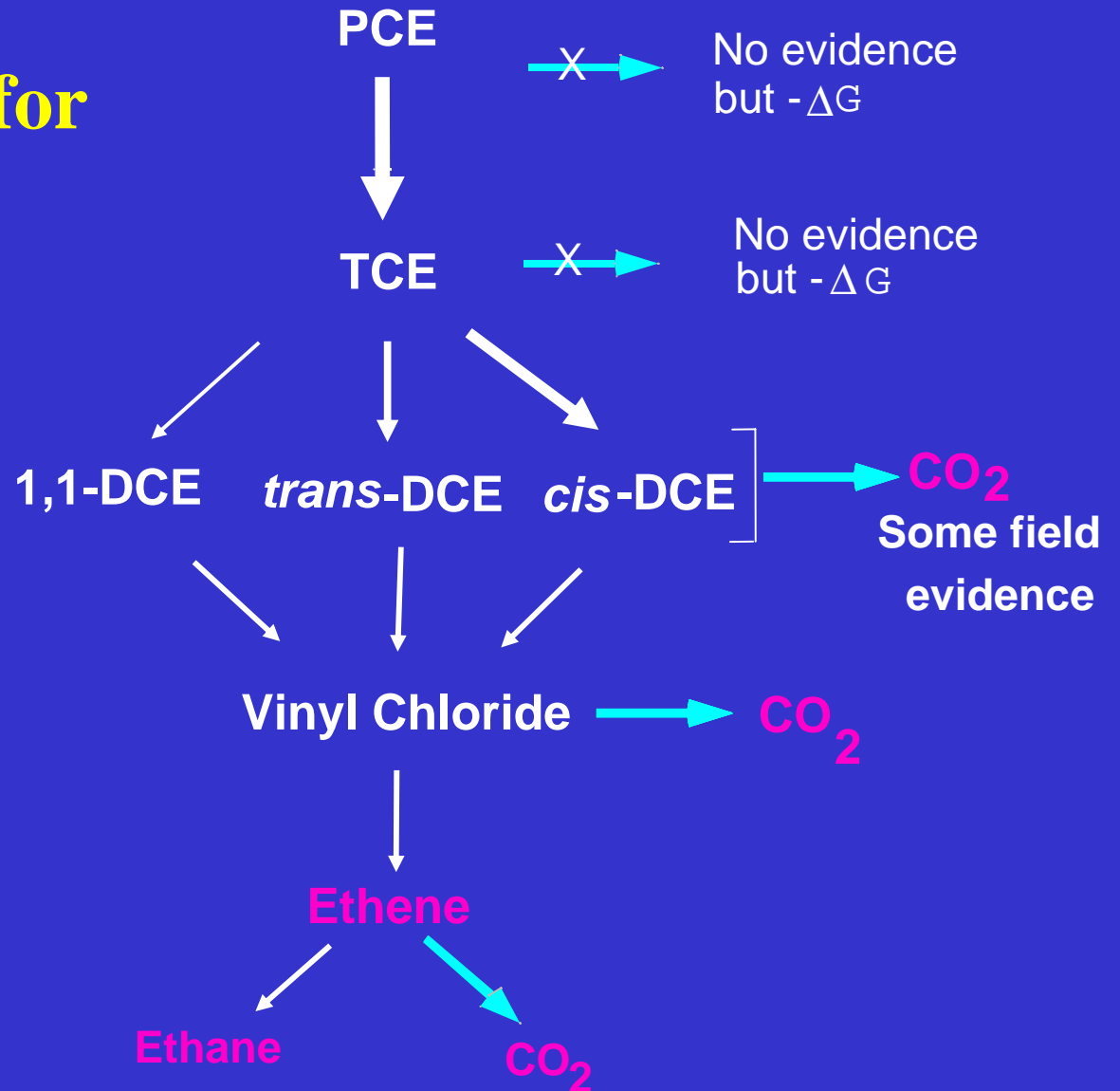
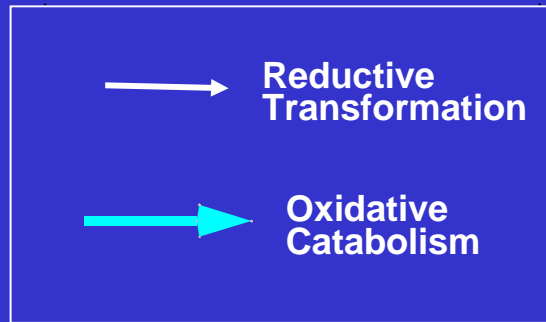
Bioremediation



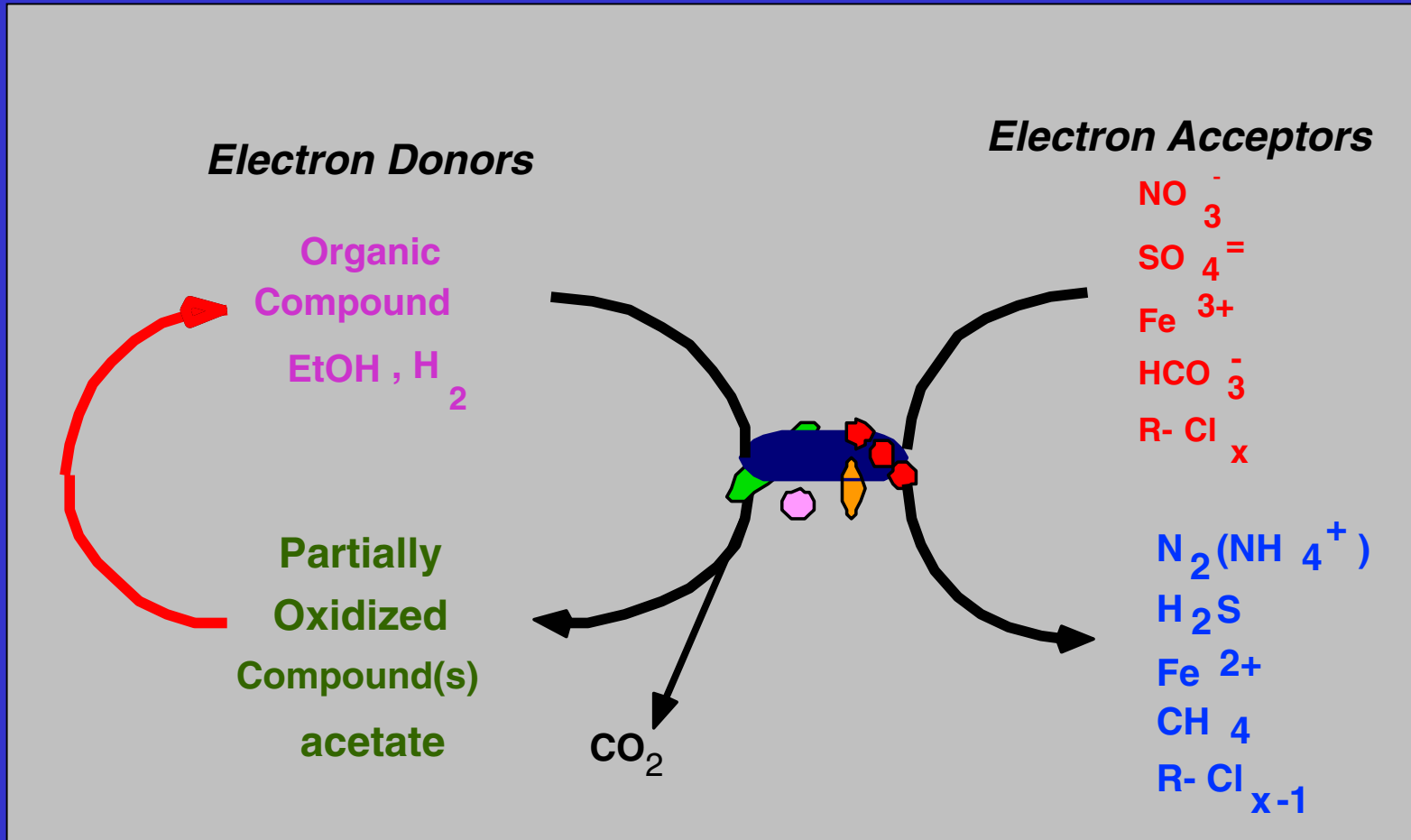
Why SERB (Source Control)

- Remove more mobile fraction of DNAPL, lower dissolved concentrations. Reduce time/distance needed to meet GW quality objectives.
- Activate reductive bio-transformations in high redox environments.
- Insure supply of e- donor, accelerate process and reduce uncertainty.
- Regulatory requirement.

Biotransformations for Chloroethenes



ANAEROBIC OXIDATION-REDUCTION



Reduced Electron Acceptors

SEWELL, '95

Chloroethene Sites

Plume Type

Bio-attenuation

Stable

- Parent Dominant
(PCE or TCE)

No

Yes

- VC/cis DCE
Dominant

Yes

No

- Ethene Forming

Yes

?

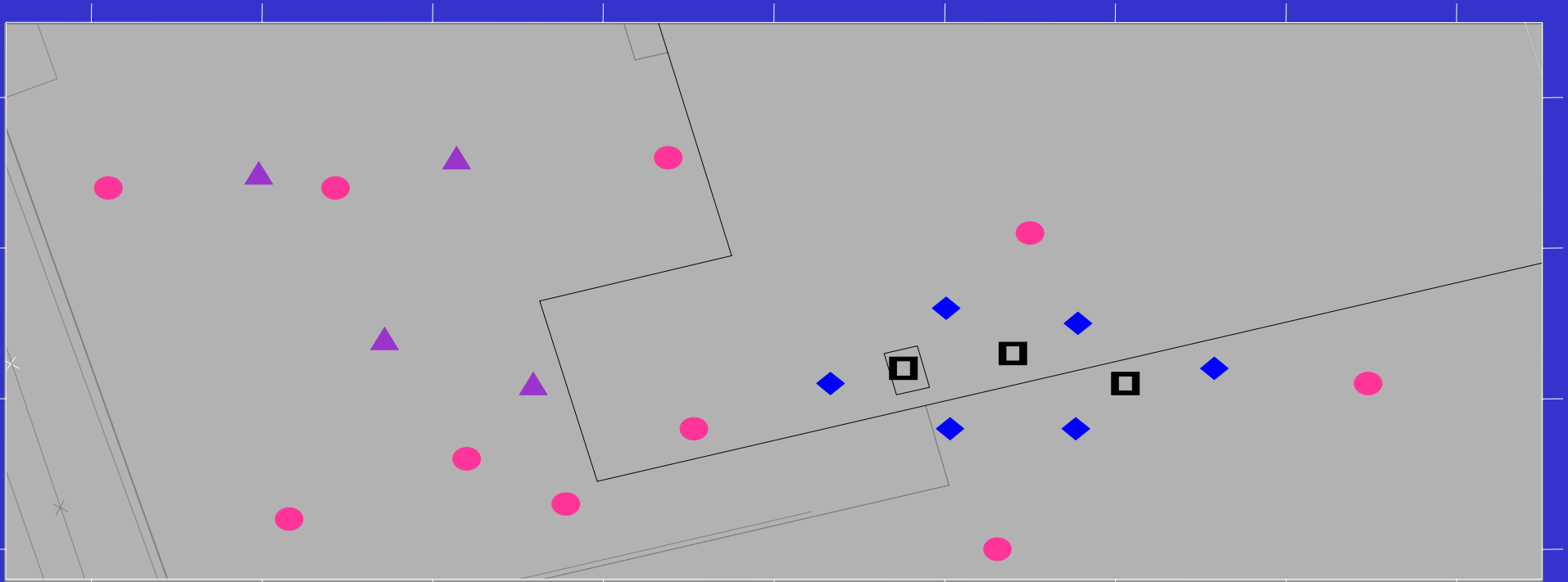
Field Test of the SERB
Technology
Sages Dry Cleaner Site

Results and Discussion

Field Test Table of Events

- July, 1998 Site Characterization, Ground Water Monitoring, & Partitioning Tracer Test
- Aug. 9-15, 1998 Ethanol Flush (9000 gallons)
- Aug. 15, 1998 Partitioning Tracer Test
Start Hydraulic Containment
- Aug. 25, 1998 End Hydraulic Containment
Ethanol < 10,000 mg/L

Sage's Dry Cleaner Site Jacksonville, Florida



0 ft. 20 ft. 40 ft. 60 ft. 80 ft.

Pre-Cosolvent Flush Site Characterization

- Aerobic Conditions
- Low levels of daughter products (TCE)
- DNAPL contamination identified at 26 to 31 ft. bgs

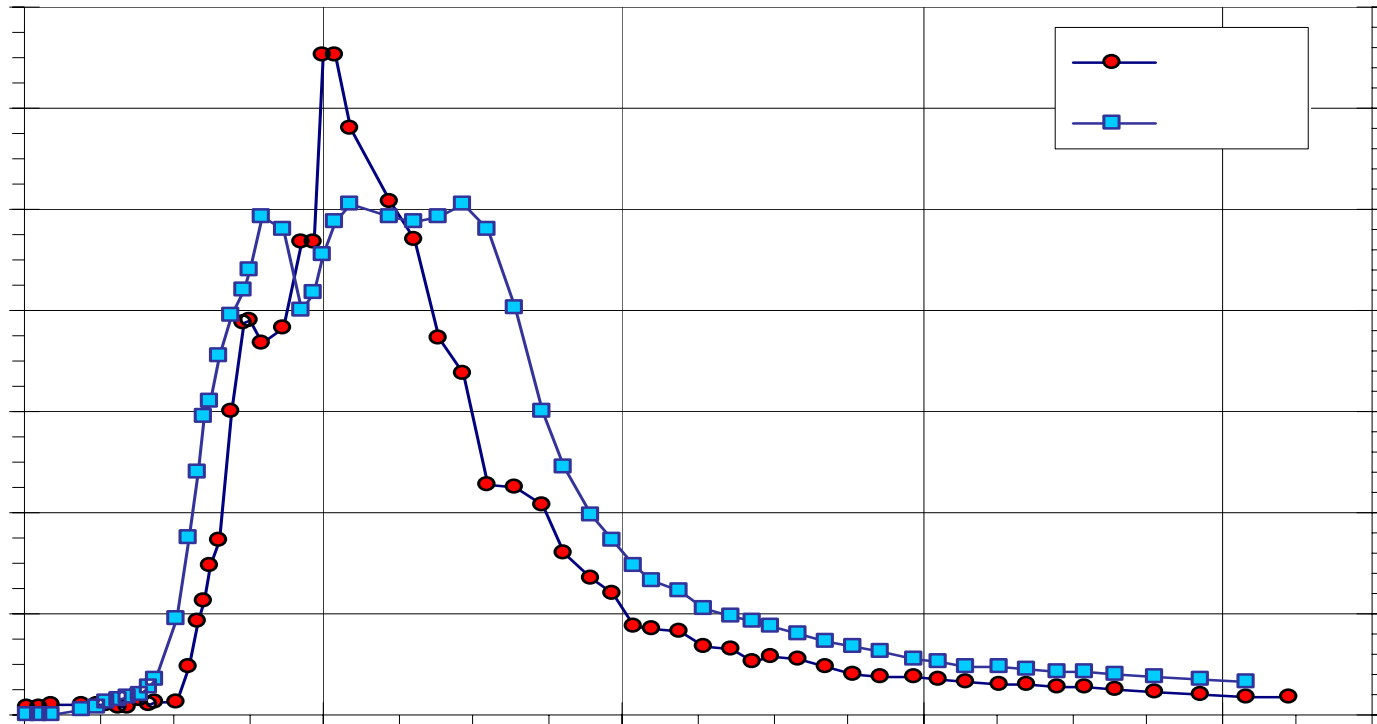
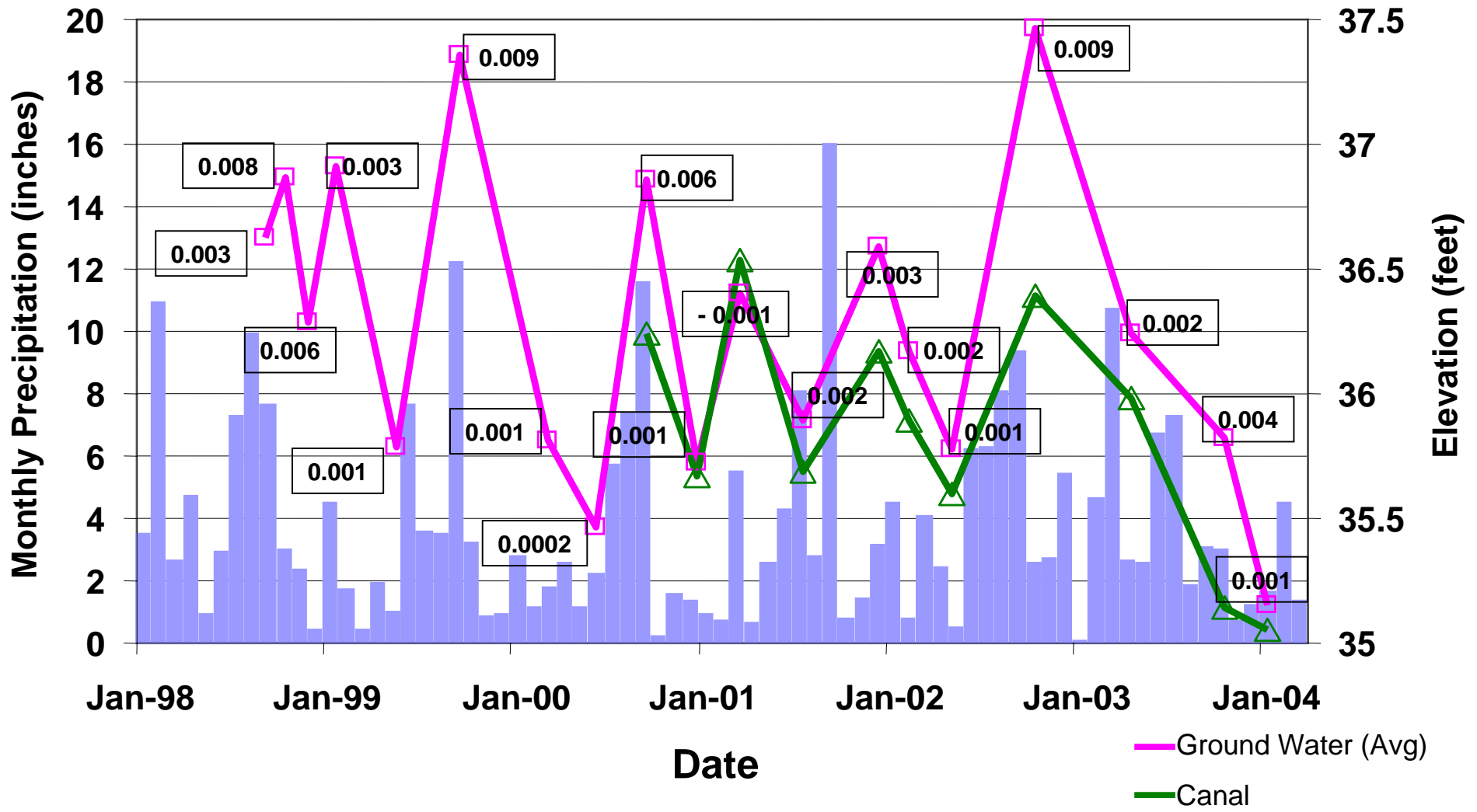


Figure 1. PCE and ethanol concentrations during co-solvent flood at Sages Site in recovery well RW-001.

Cosolvent Flush Performance

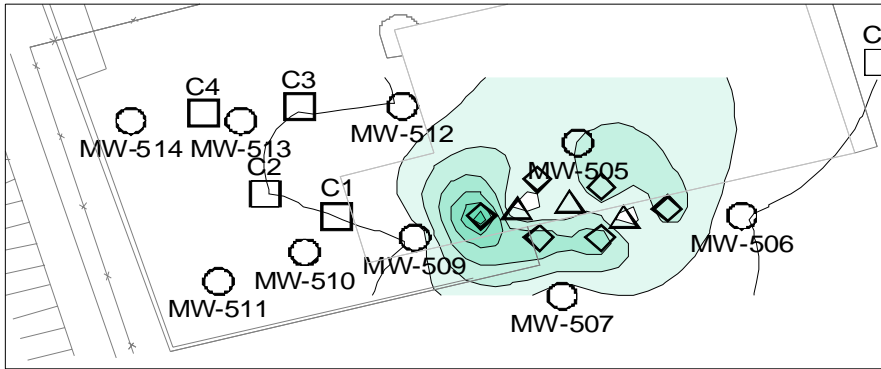
Pre-Cosolvent Flush Partitioning Tracer	44.3 L (PCE)
Post-Cosolvent Flush Partitioning Tracer	13.9 L (PCE)
Estimated Recovery Based on Partitioning Tracer Tests	30.4 L (PCE) (70%)
Mass Recovery Based on PCE Concentrations in Recovery Wells	41.5 L (PCE)



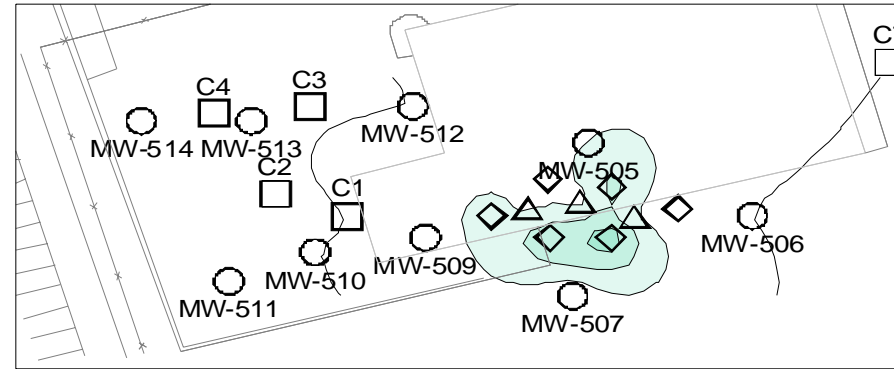
Ethanol

350 mM = 16 g/L = 1.6 %

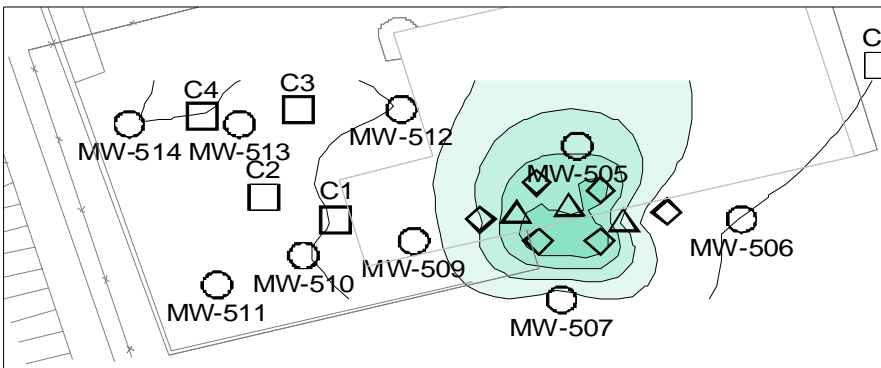
~1 Month Post-Flush



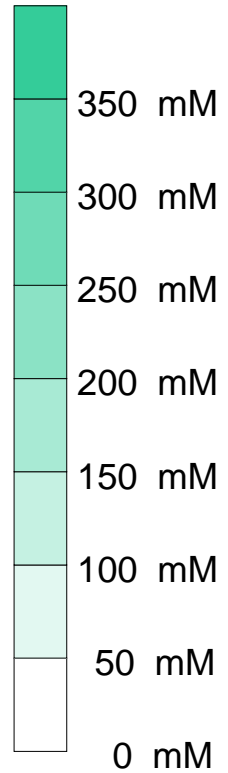
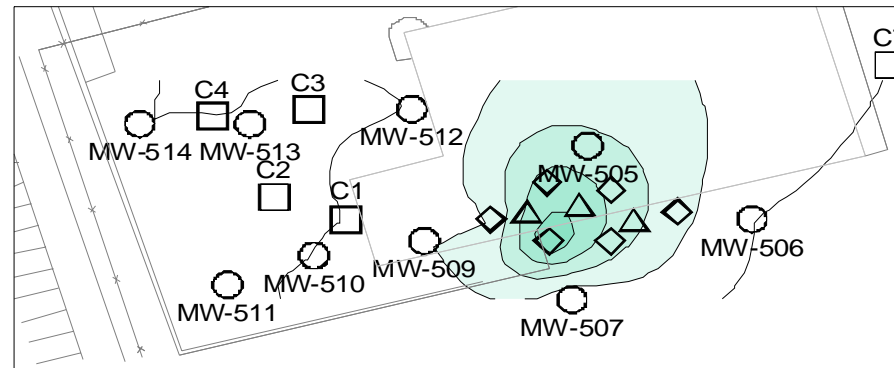
~2 Months Post-Flush



~3.5 Months Post-Flush



~5.5 Months Post-Flush

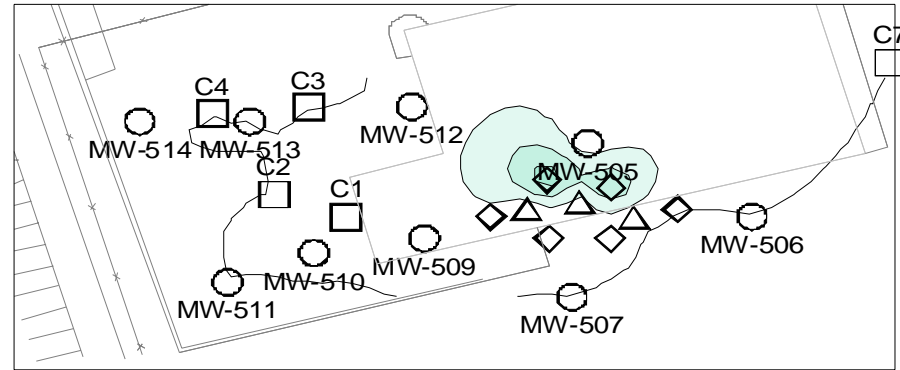
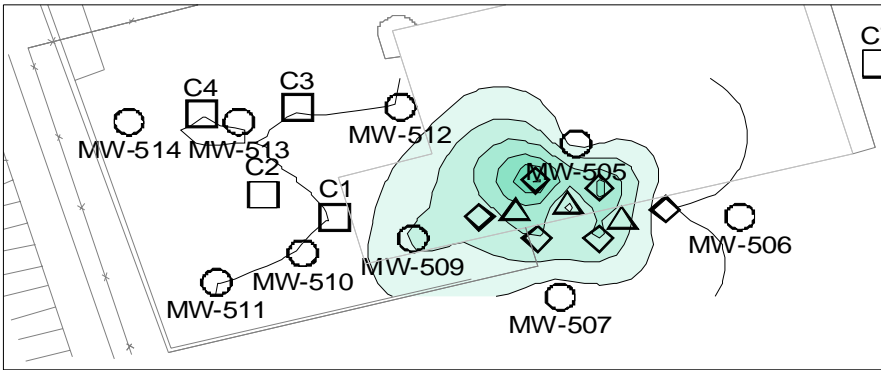


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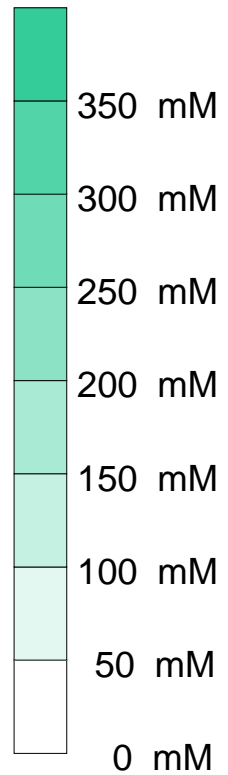
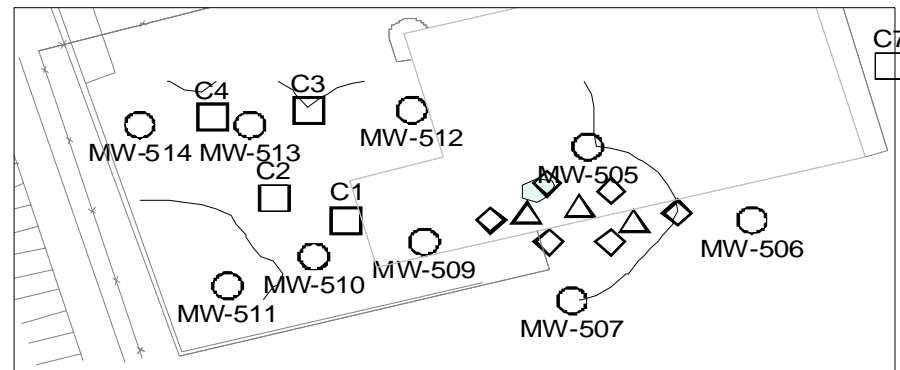
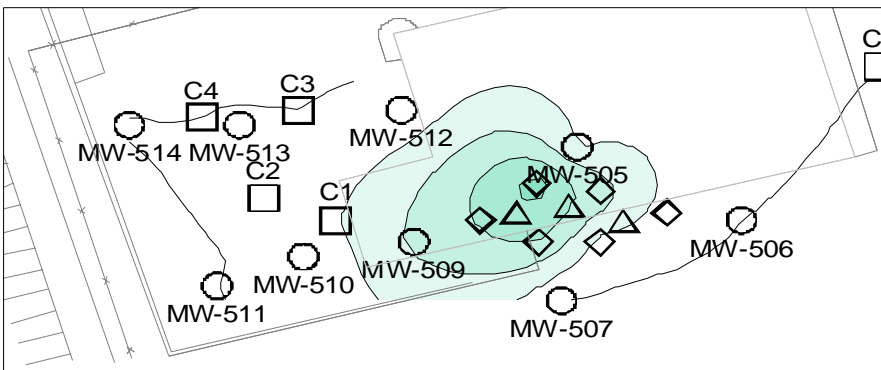
~9.5 Months Post-Flush

~13.5 Months Post-Flush



~19 Months Post-Flush

~22 Months Post-Flush

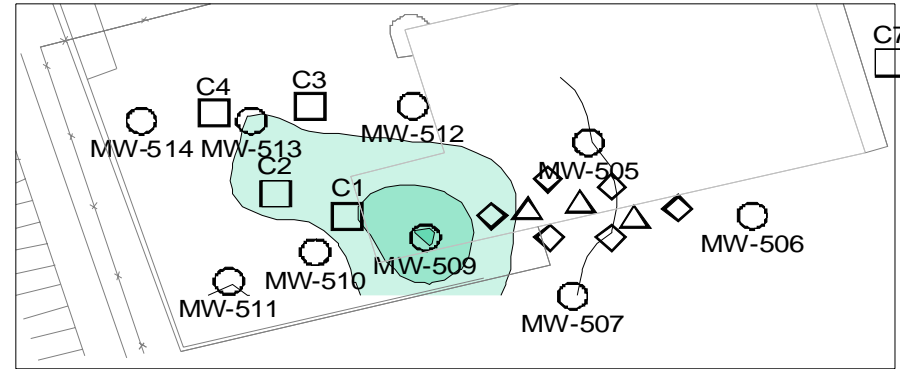
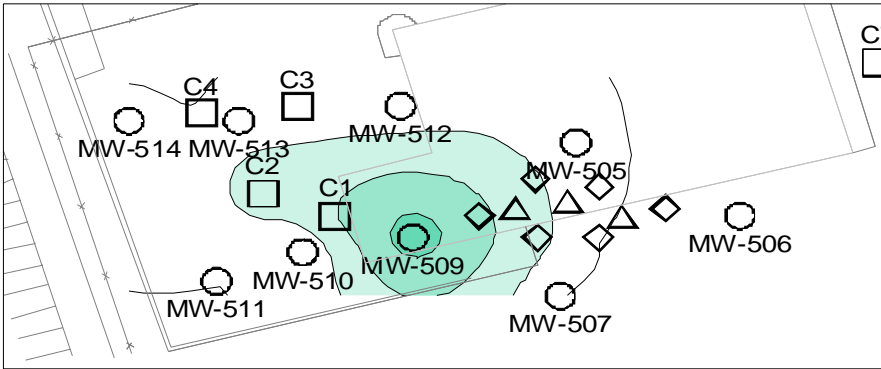


Ethanol

1000 mM = 4.6 g/L = 0.46 %

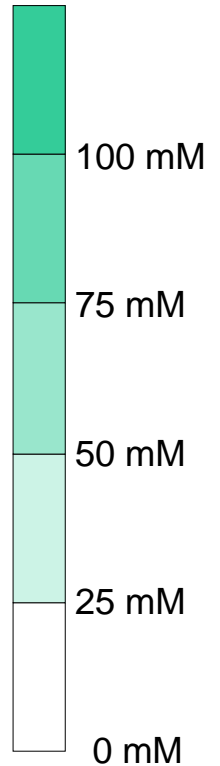
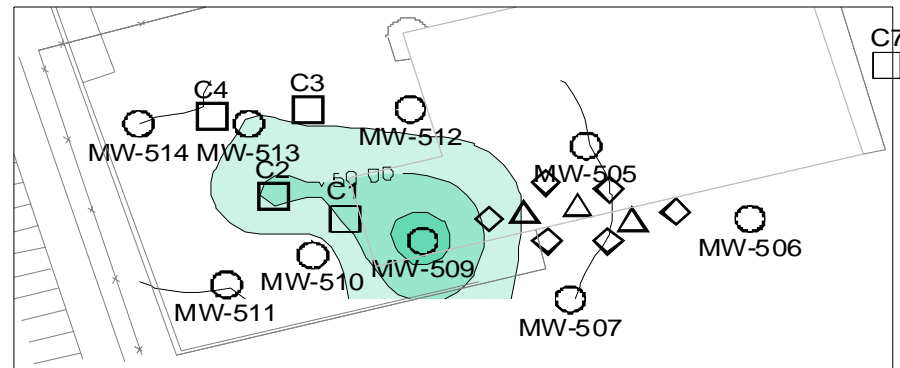
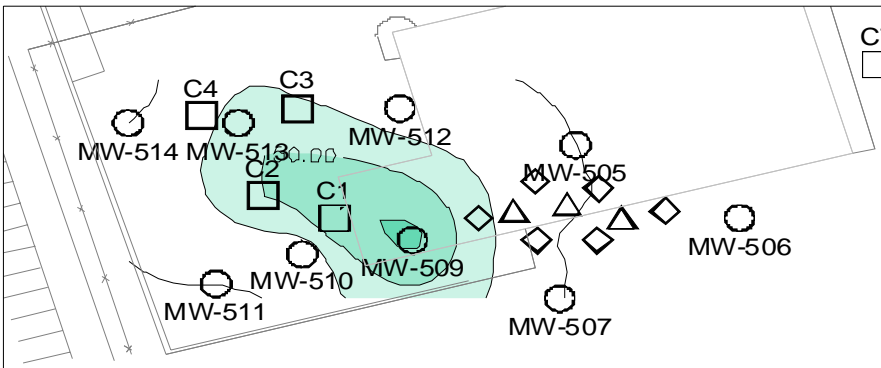
~28 Months Post-Flush

~31 Months Post-Flush



~35 Months Post-Flush

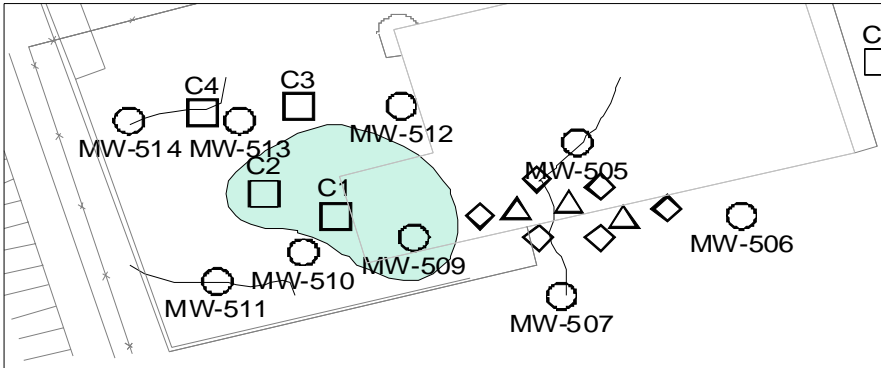
~40 Months Post-Flush



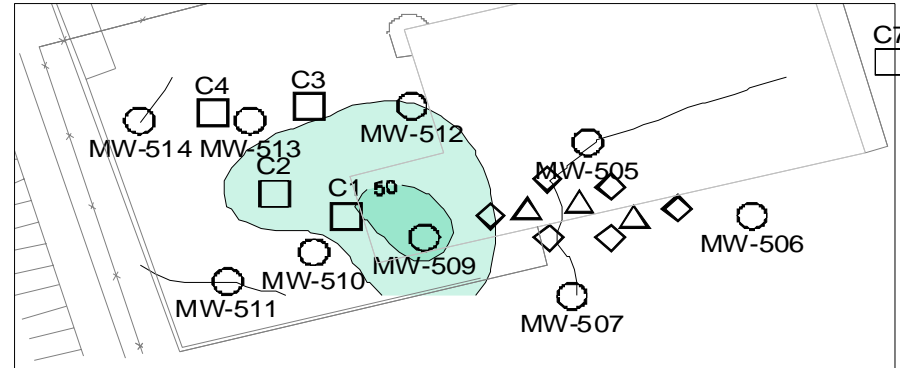
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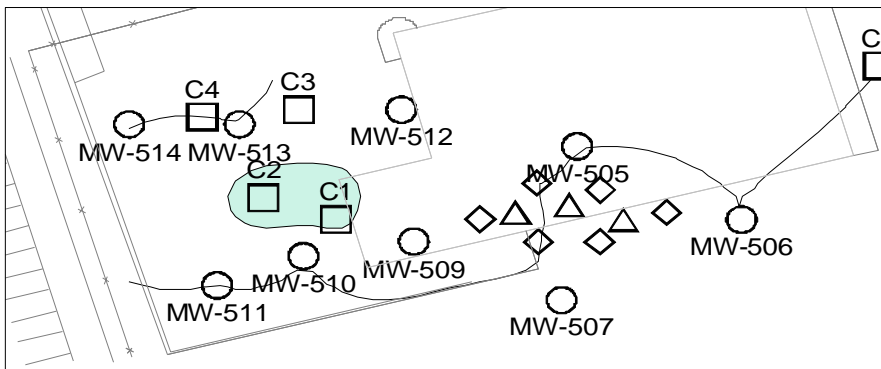
~45 Months Post-Flush



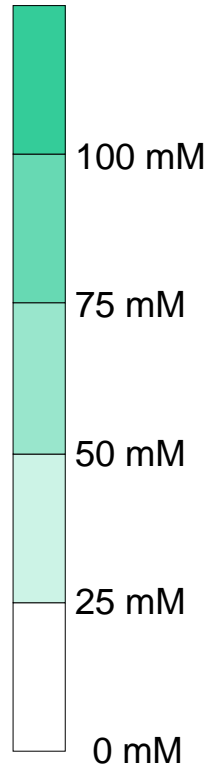
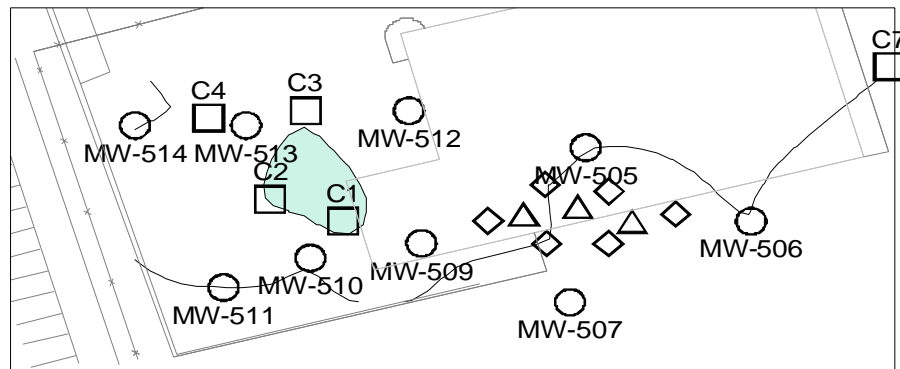
~50 Months Post-Flush



~56 Months Post-Flush



~62 Months Post-Flush



PCE

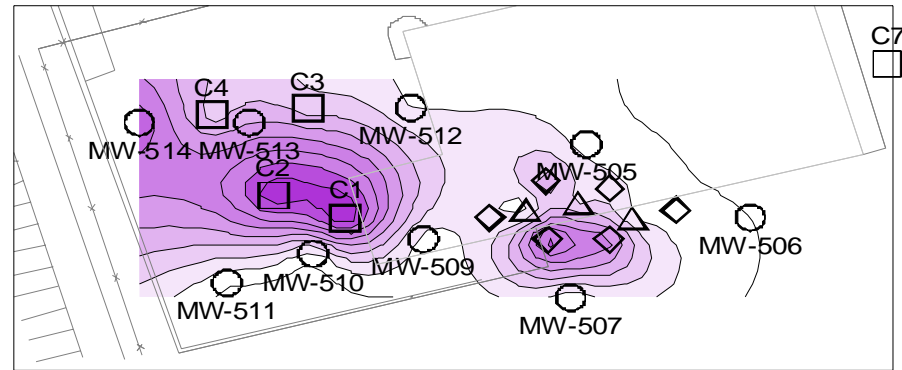
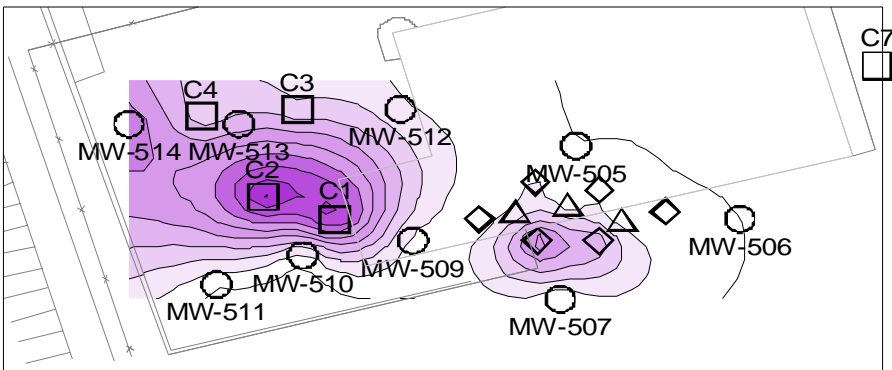
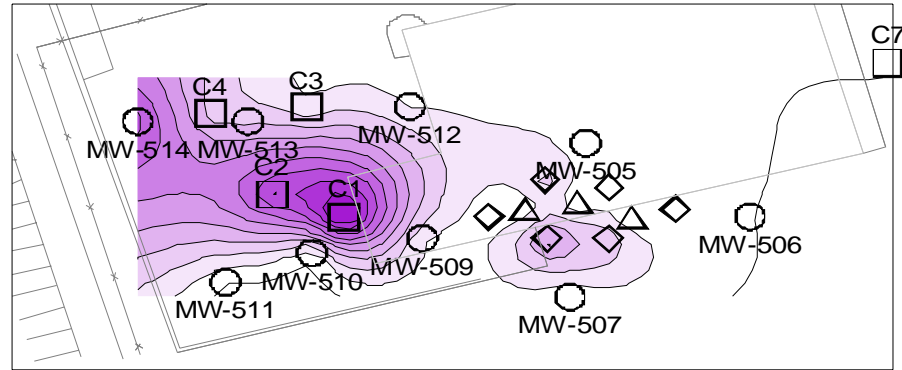
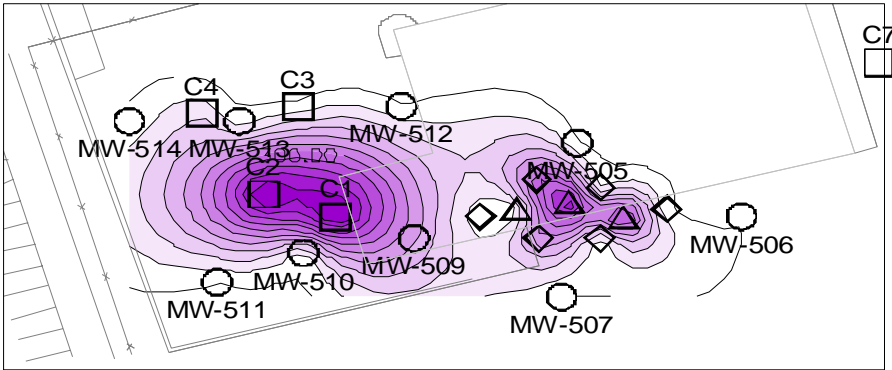
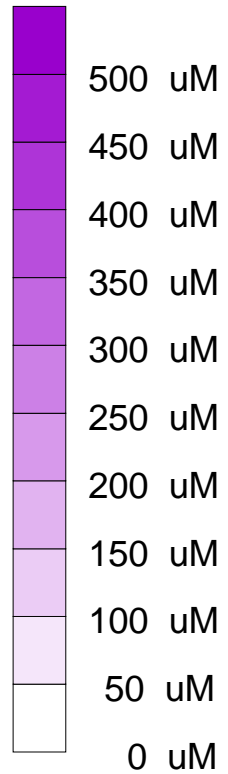
500 uM = 83 mg/L

Pre-Ethanol Flush

~1 Month Post-Flush

~2 Months Post-Flush

~3.5 Months Post-Flush

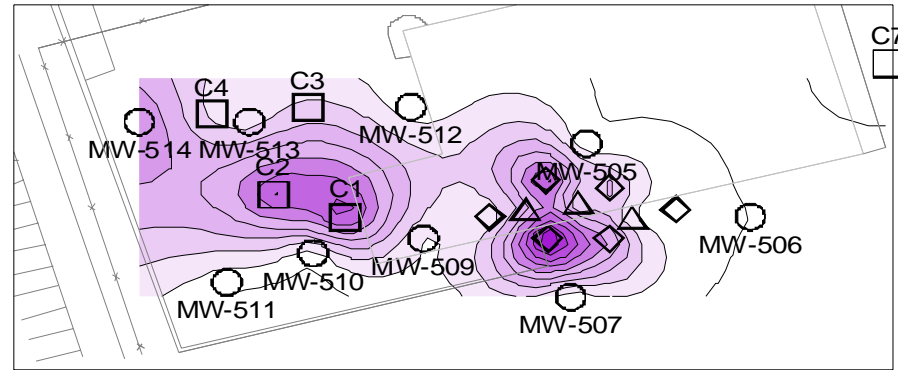
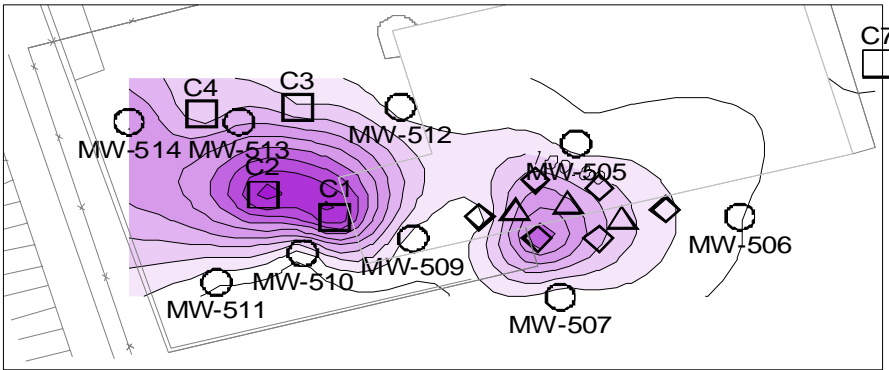


PCE

500 uM = 83 mg/L

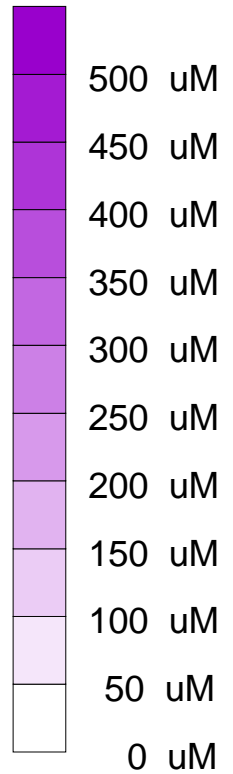
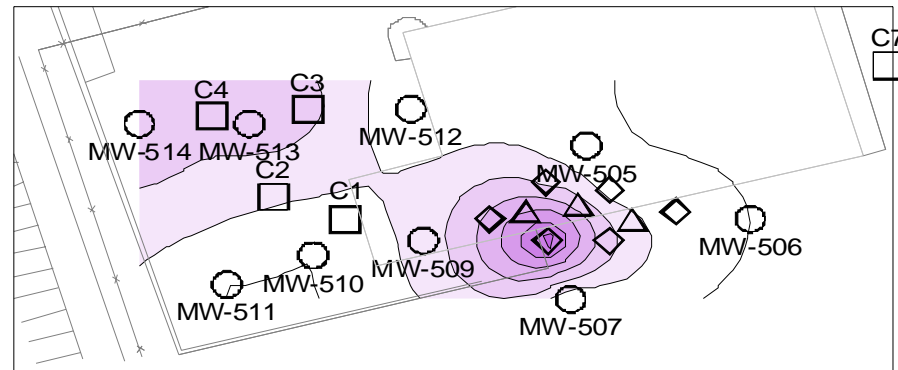
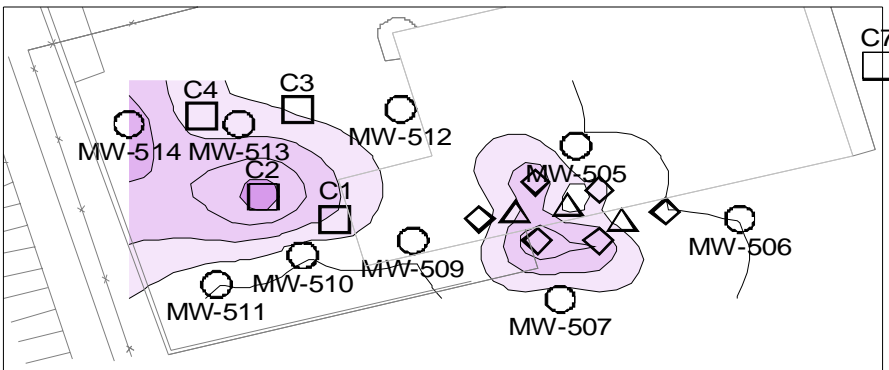
~5.5 Months Post-Flush

~9.5 Months Post-Flush



~13.5 Months Post-Flush

~19 Months Post-Flush

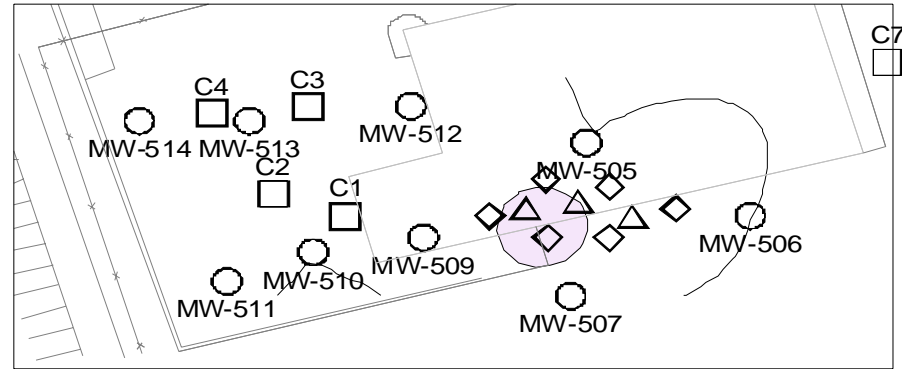
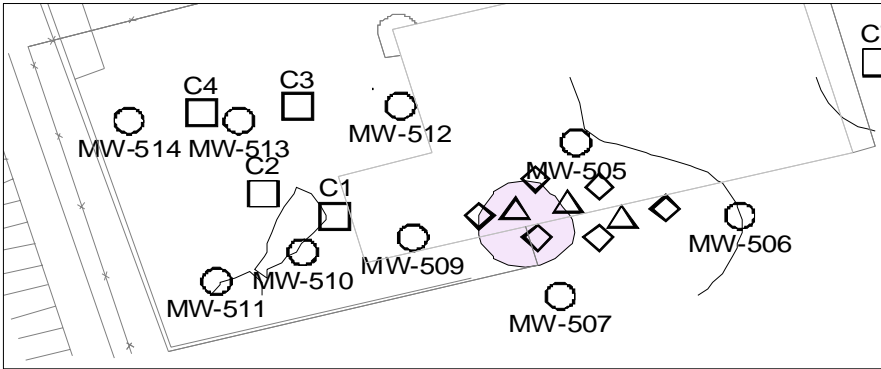


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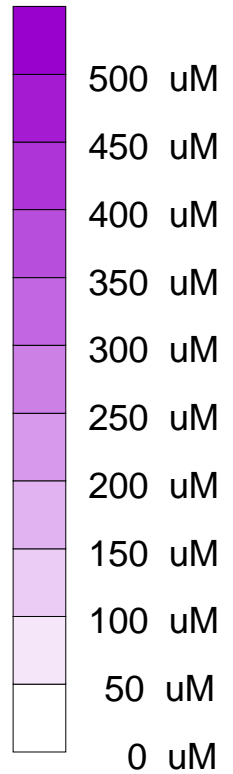
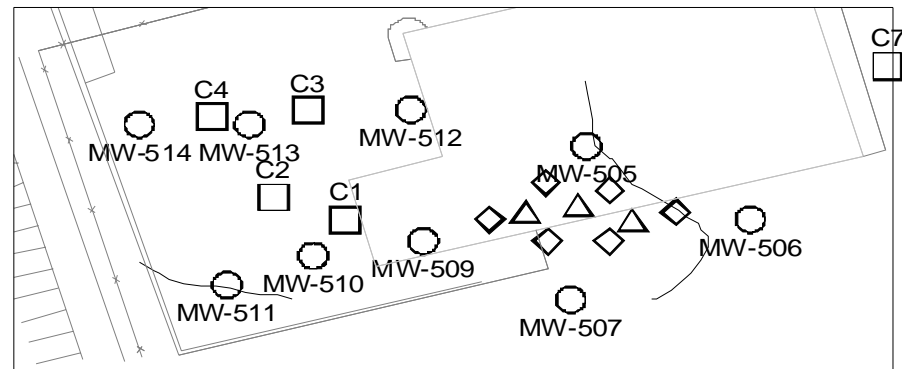
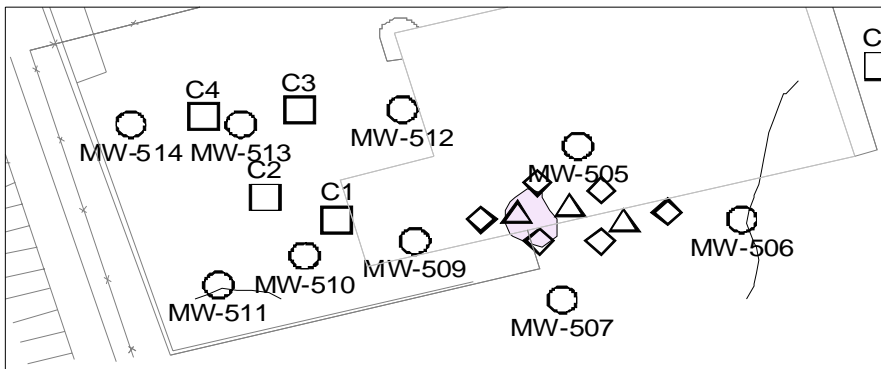
~22 Months Post-Flush

~25 Months Post-Flush



~28 Months Post-Flush

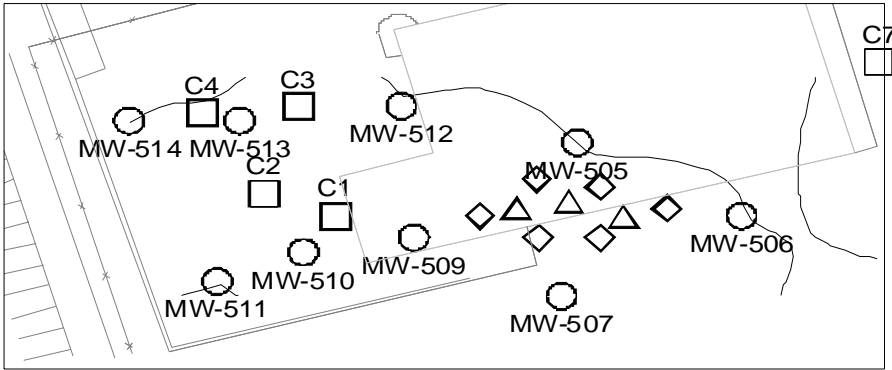
~31 Months Post-Flush



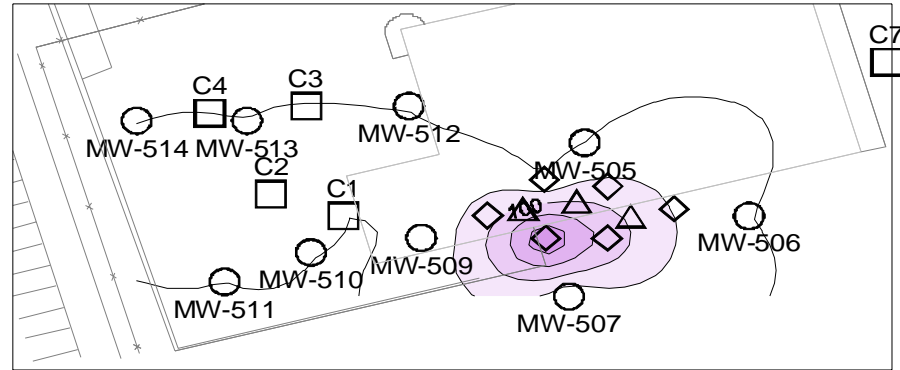
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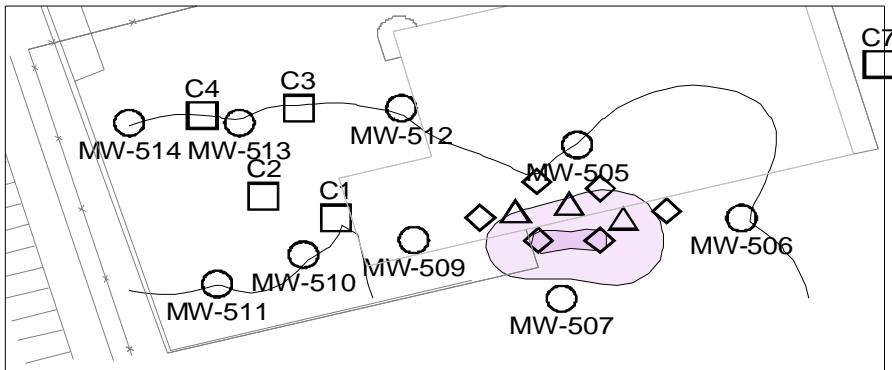
~50 Months Post-Flush



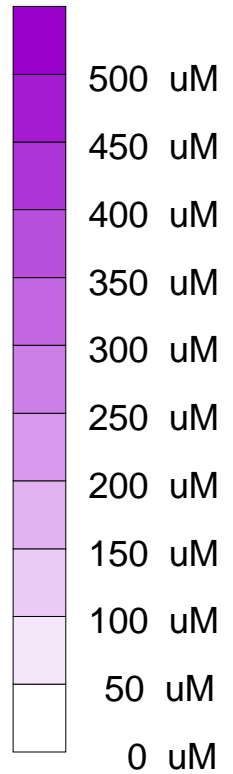
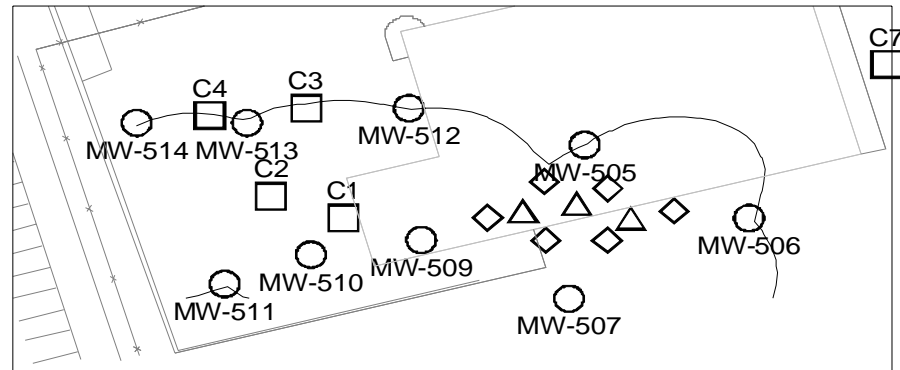
~56 Months Post-Flush



~62 Months Post-Flush



~65 Months Post-Flush

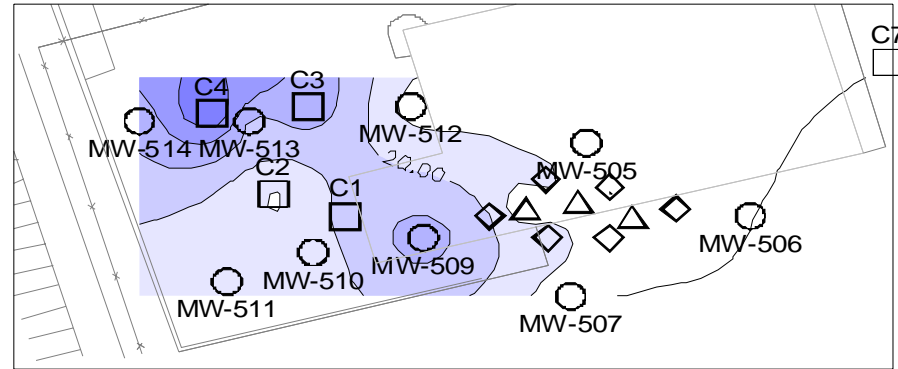
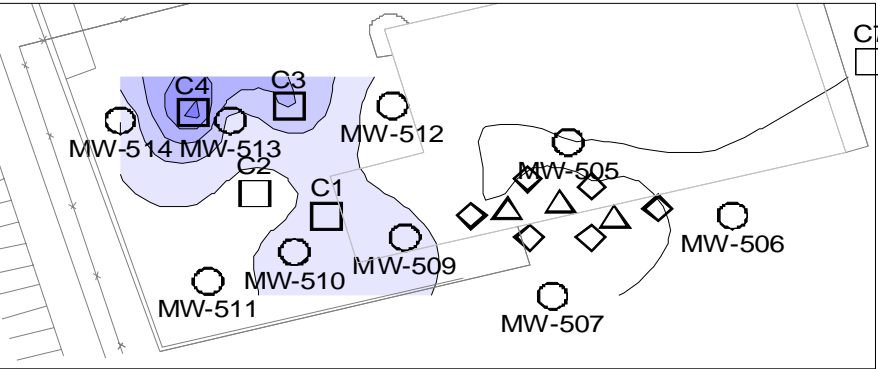


TCE

100 uM = 13 mg/L

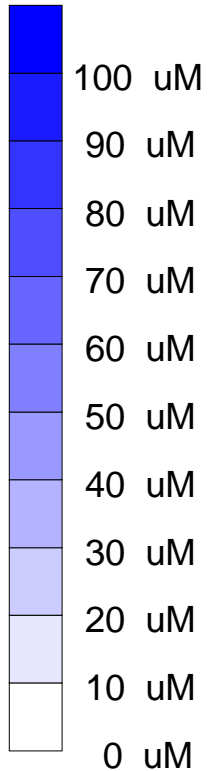
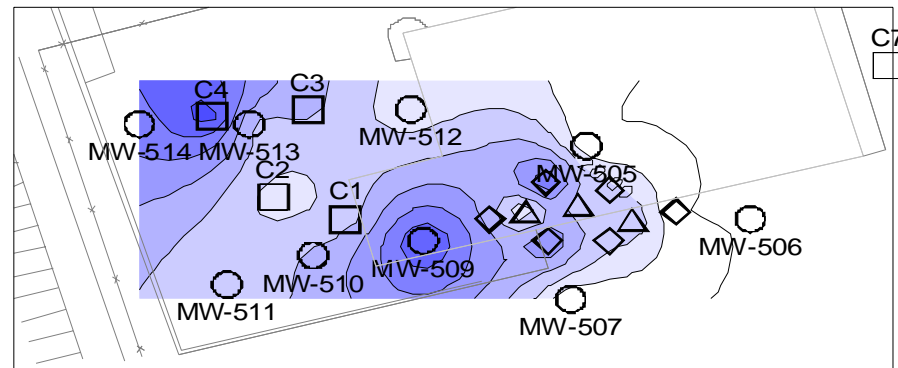
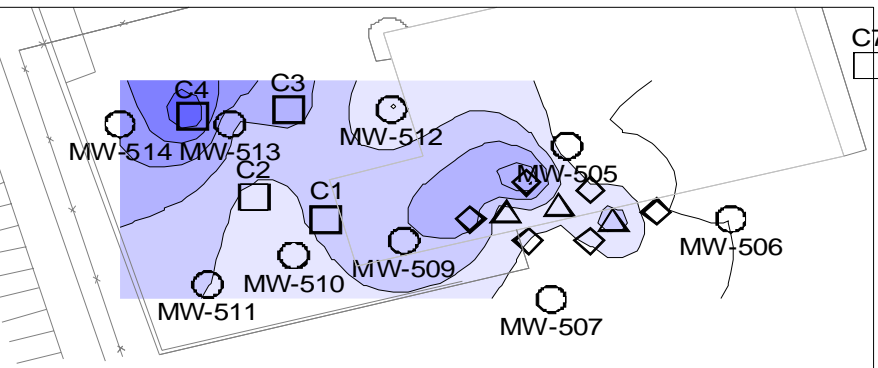
Pre-Ethanol Flush

~1 Month Post-Flush



~2 Months Post-Flush

~3.5 Months Post-Flush

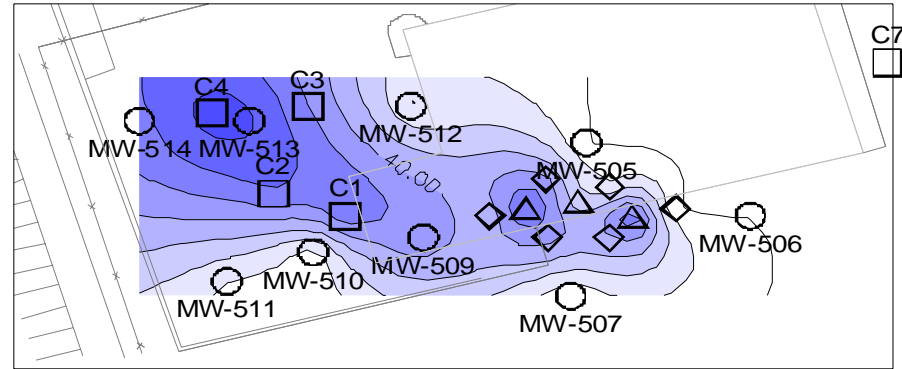
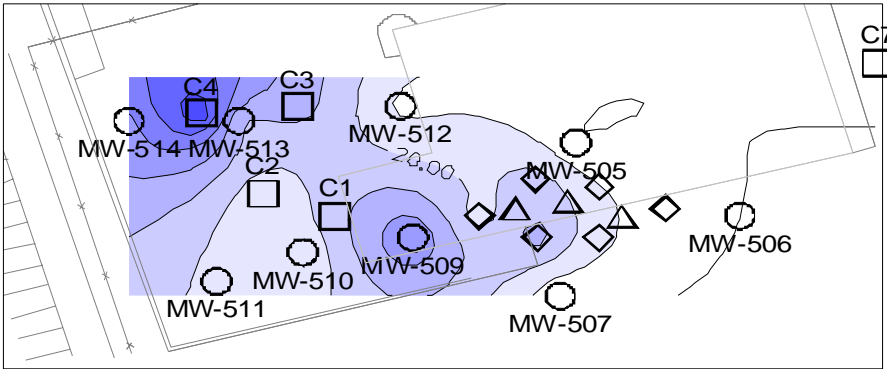


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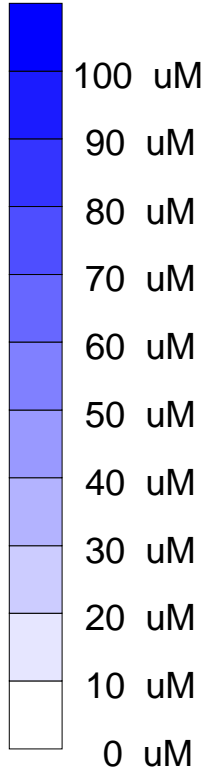
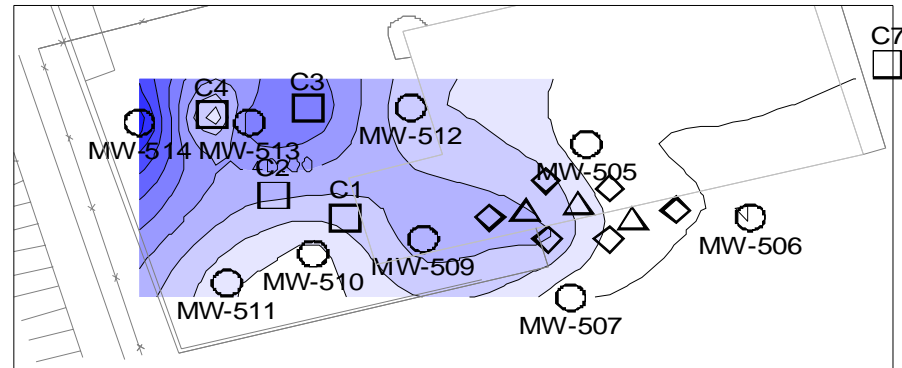
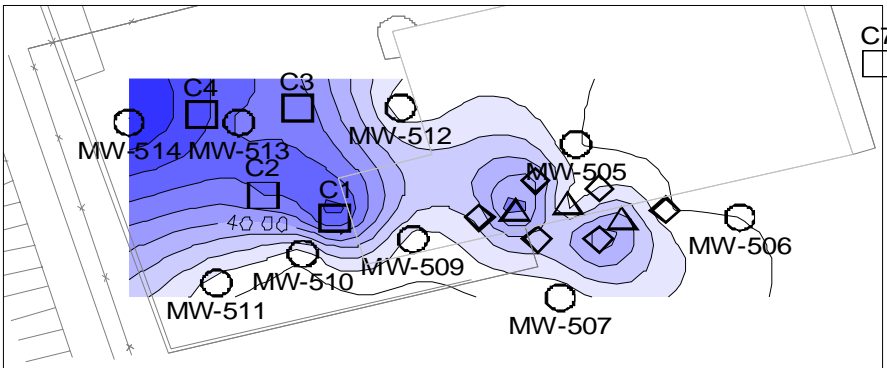
~5.5 Months Post-Flush

~9.5 Months Post-Flush



~13.5 Months Post-Flush

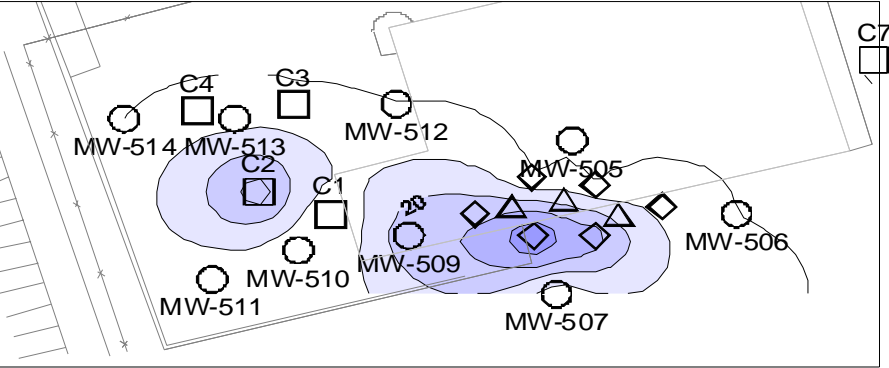
~19 Months Post-Flush



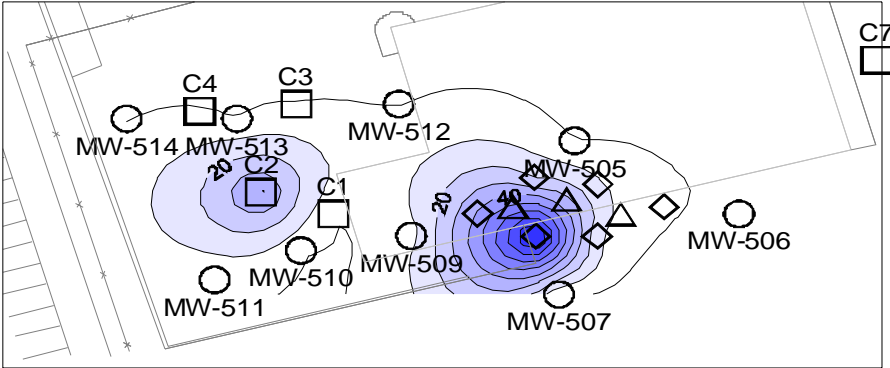
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100 μM = 13 mg/L

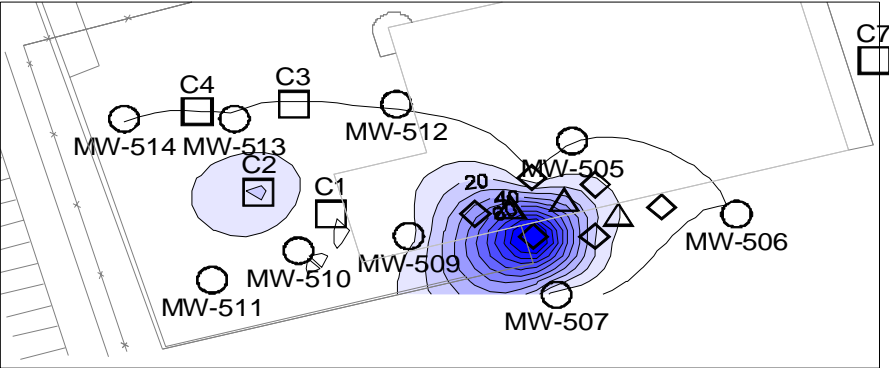
~50 Months Post-Flush



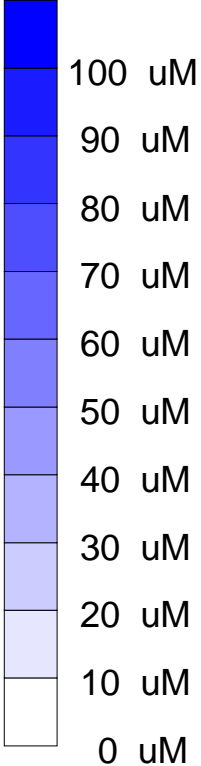
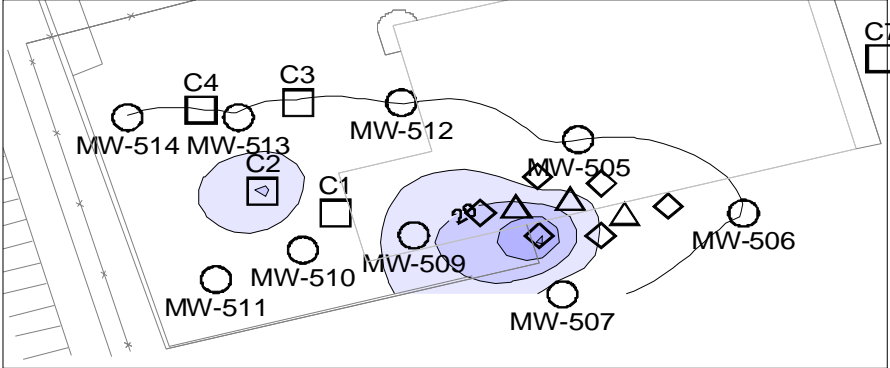
~56 Months Post-Flush



~62 Months Post-Flush



~65 Months Post-Flush



cis-DCE

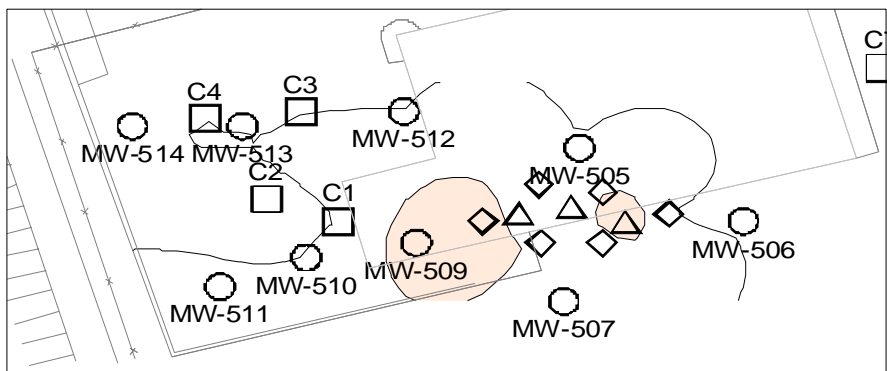
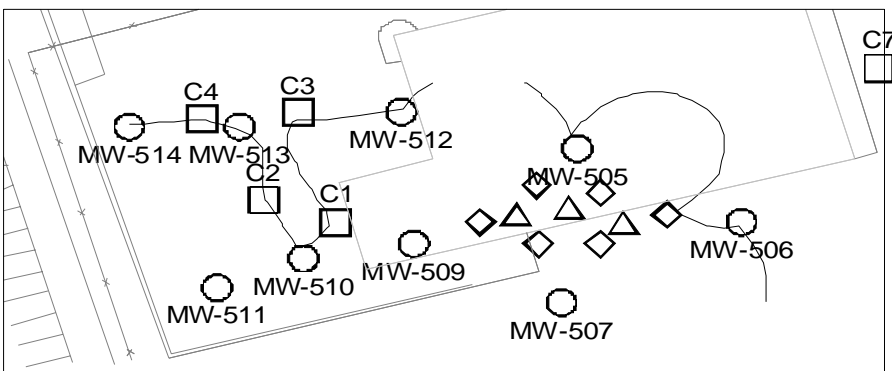
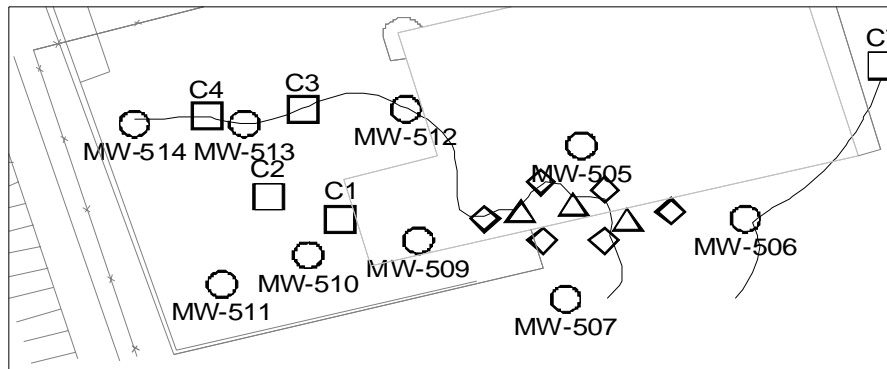
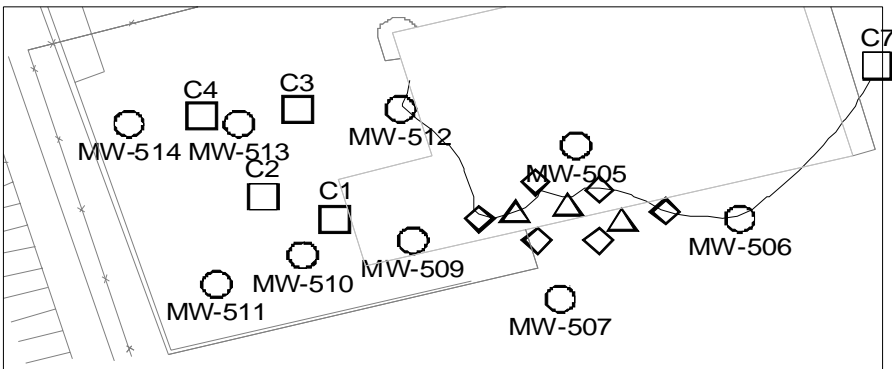
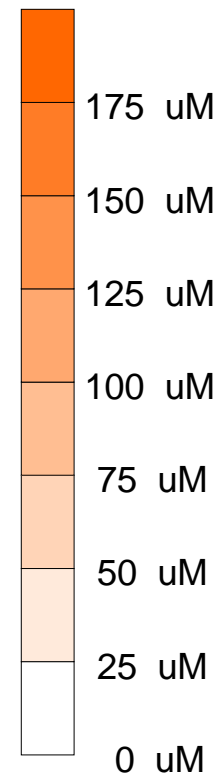
175 uM = 17 mg/L

Pre-Ethanol Flush

~1 Month Post-Flush

~2 Months Post-Flush

~3.5 Months Post-Flush

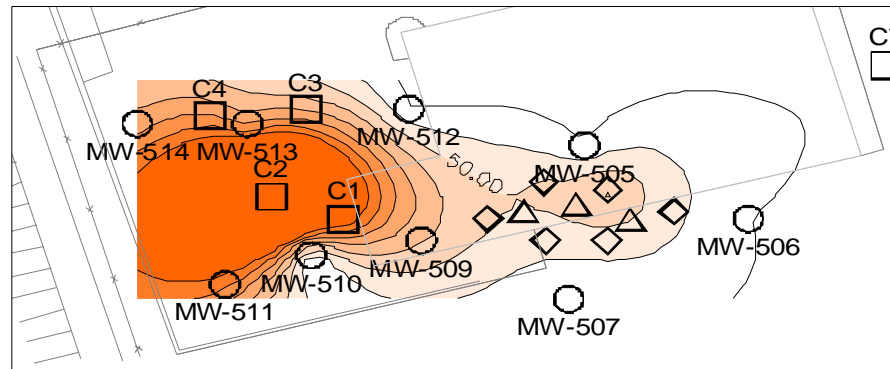
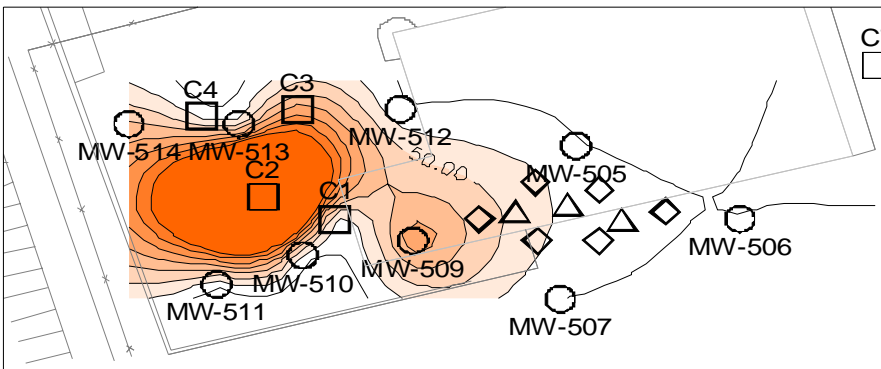


cis-DCE

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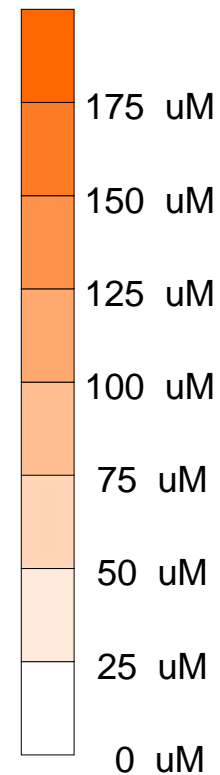
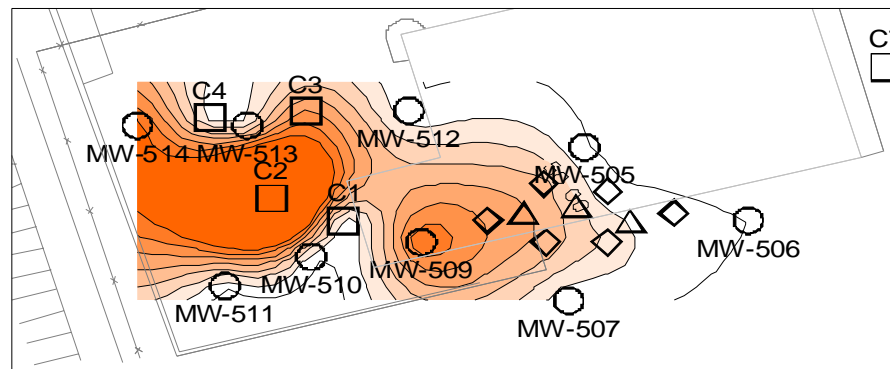
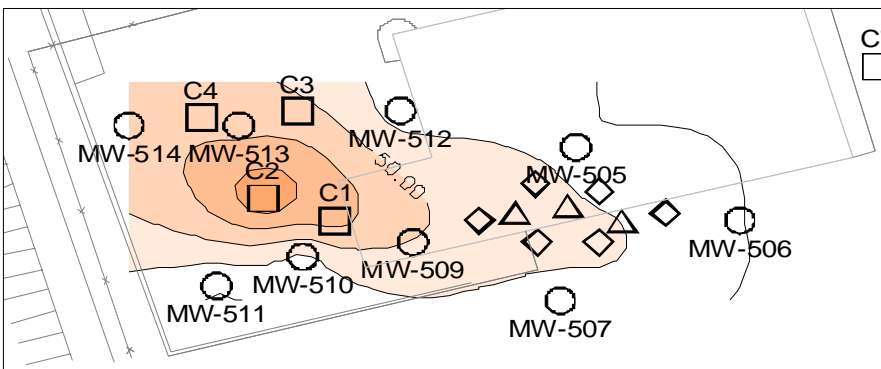
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cis-DCE

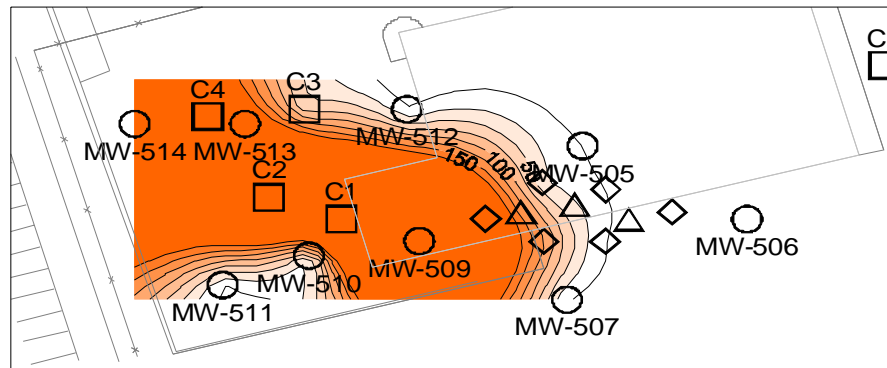
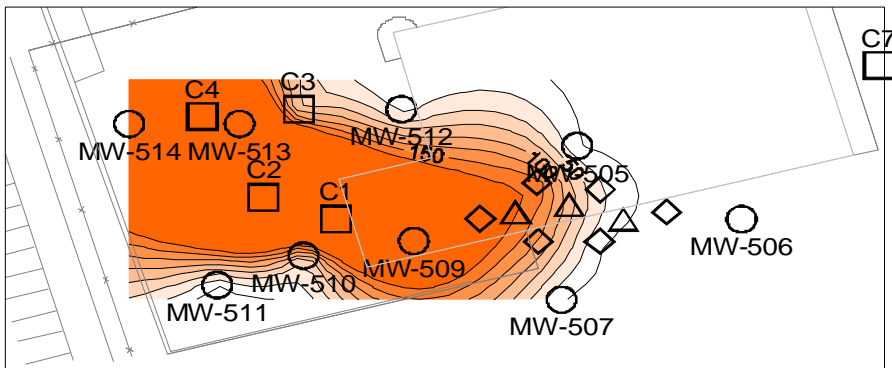
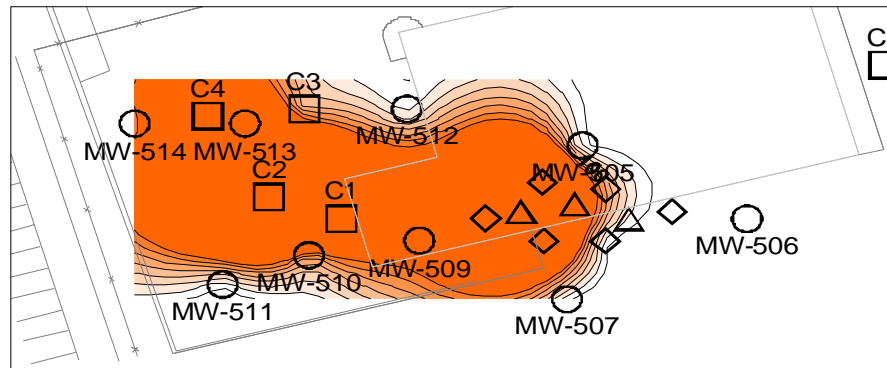
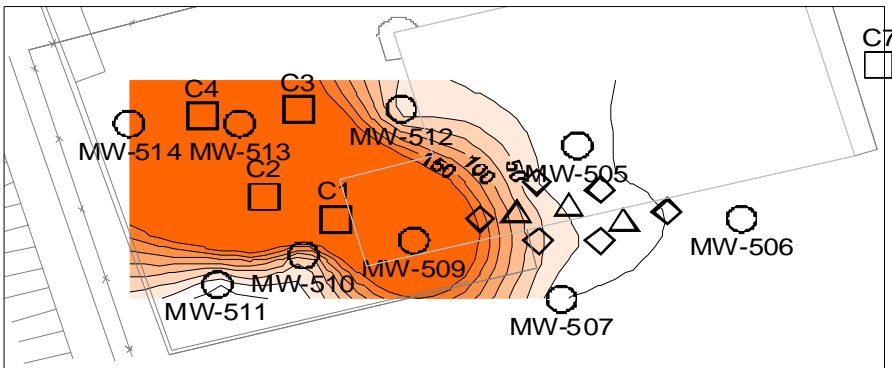
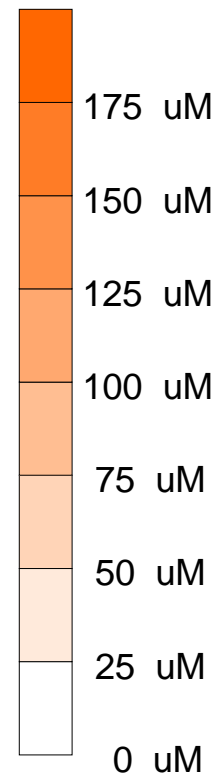
175 uM = 17 mg/L

~50 Months Post-Flush

~56 Months Post-Flush

~62 Months Post-Flush

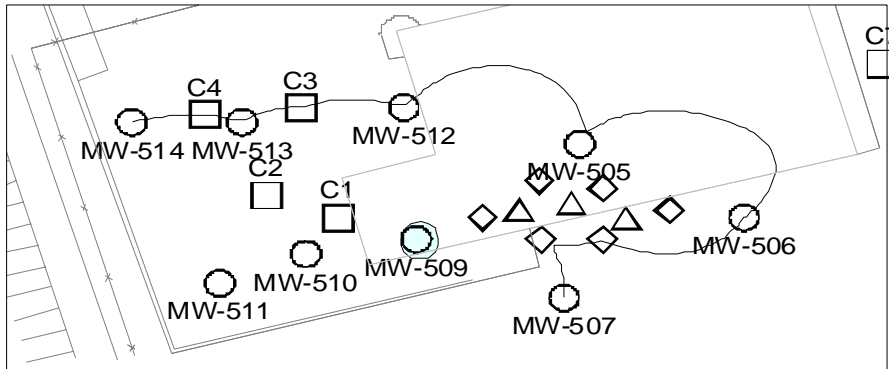
~65 Months Post-Flush



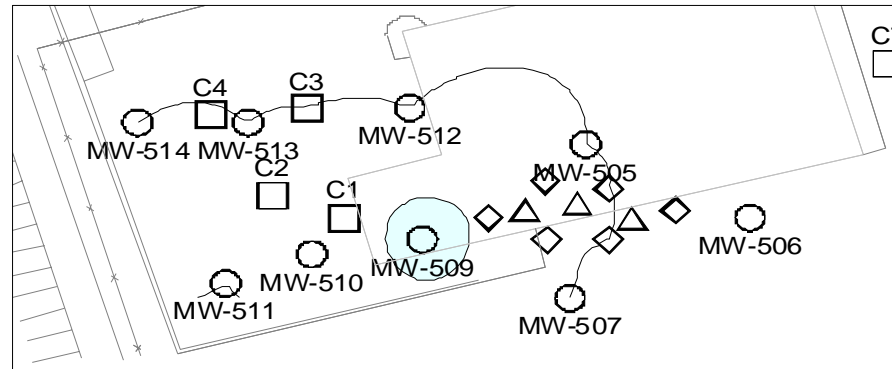
Vinyl Chloride

2.0 uM = 125 ug/L

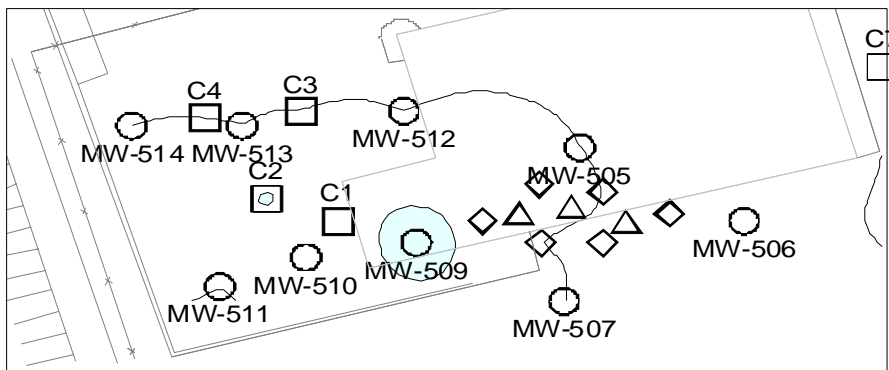
~28 Months Post-Flush



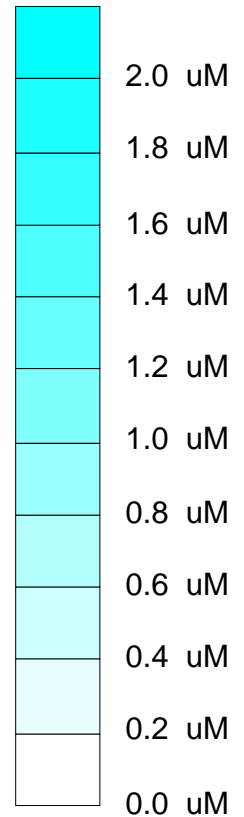
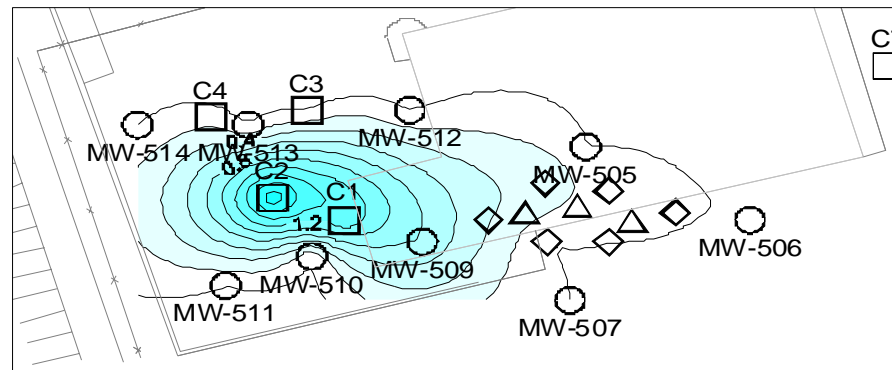
~31 Months Post-Flush



~35 Months Post-Flush



~40 Months Post-Flush

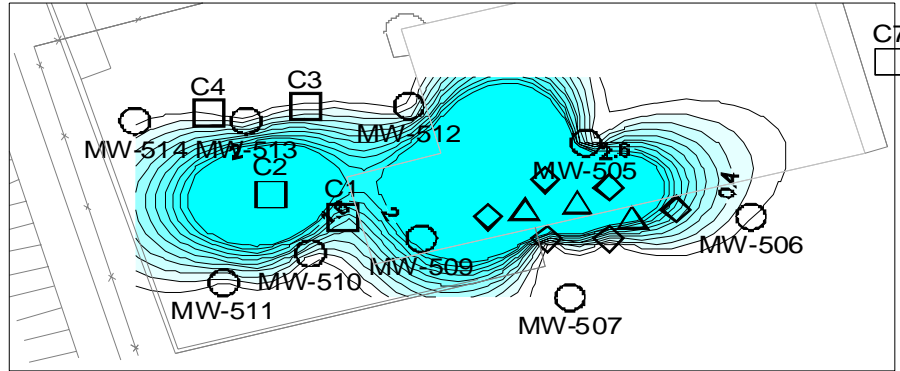
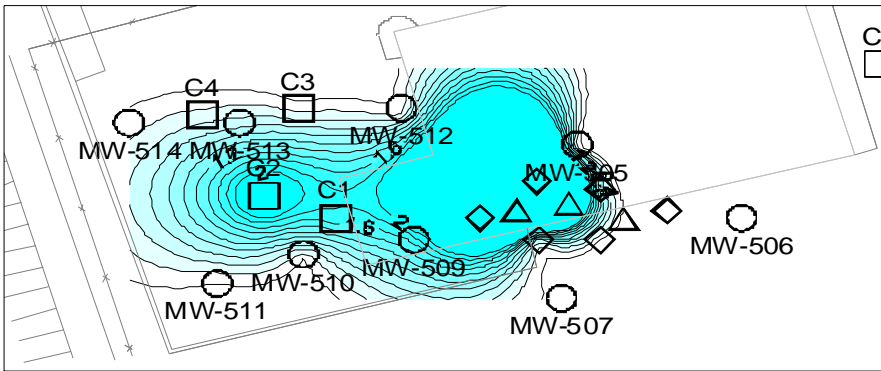


Vinyl Chloride

2.0 uM = 125 ug/L

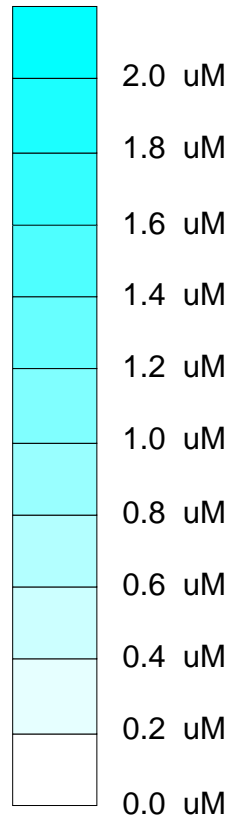
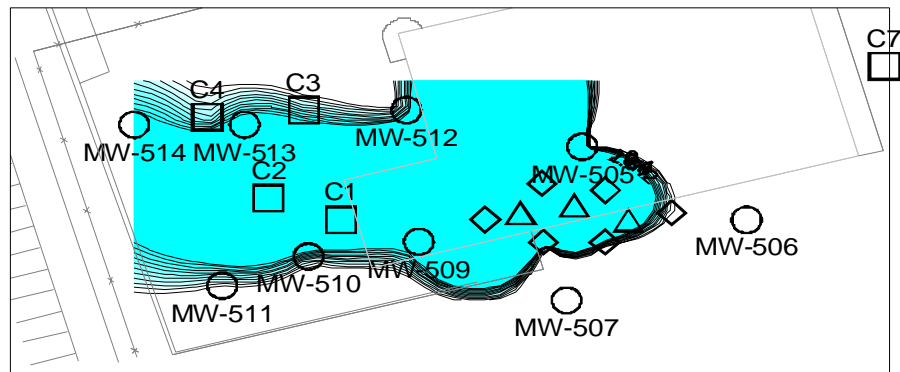
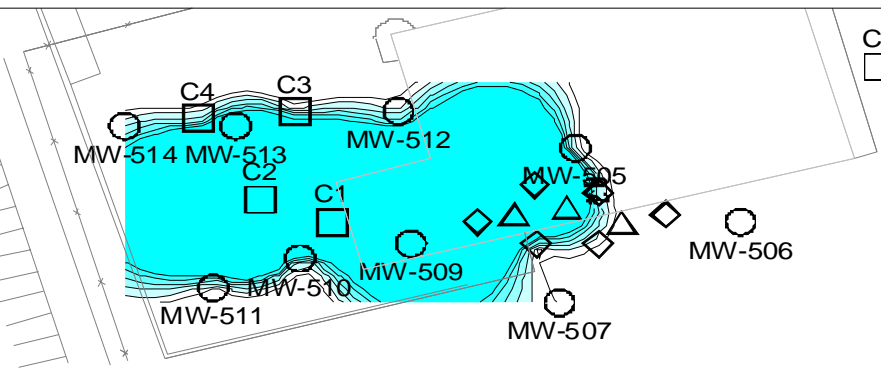
~42 Months Post-Flush

~45 Months Post-Flush



~50 Months Post-Flush

~56 Months Post-Flush

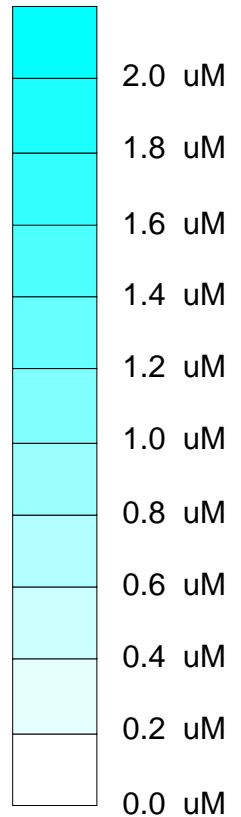
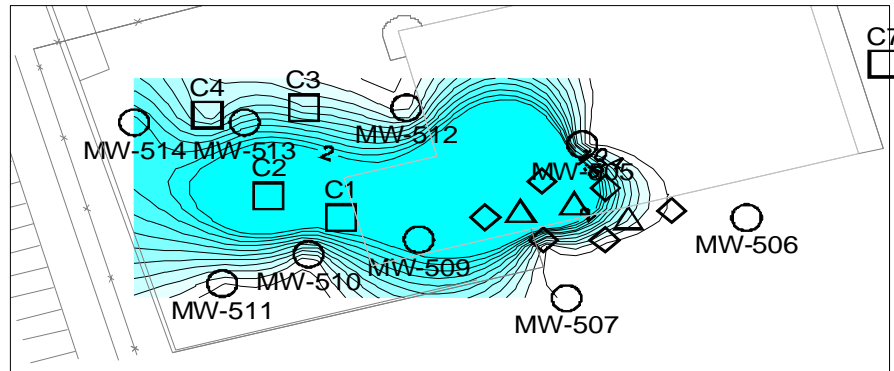
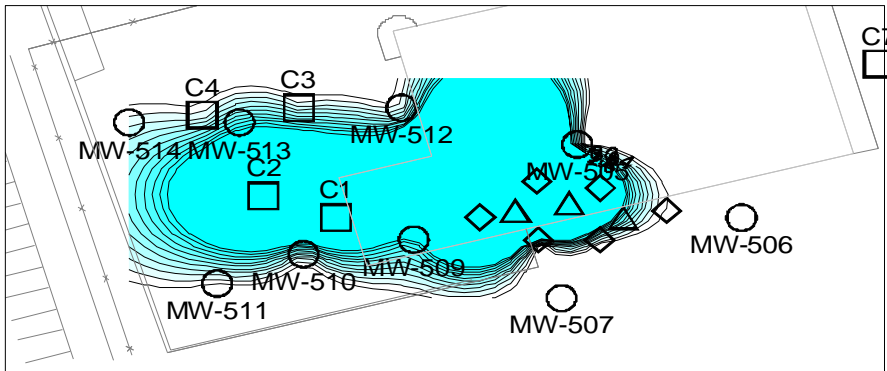


Vinyl Chloride

2.0 uM = 125 ug/L

~62 Months Post-Flush

~65 Months Post-Flush

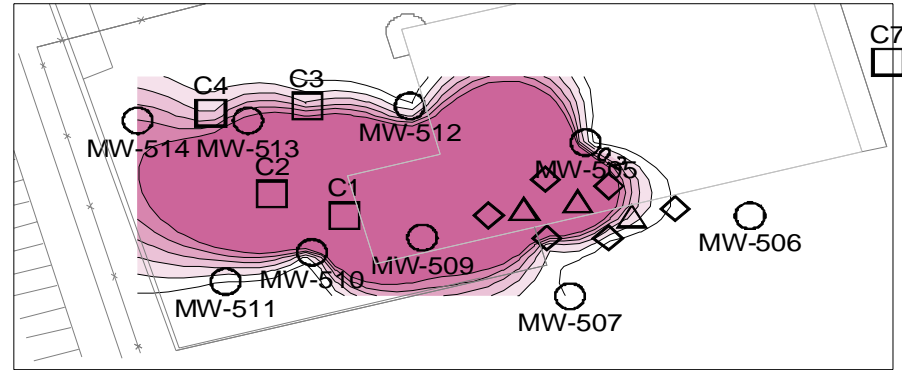
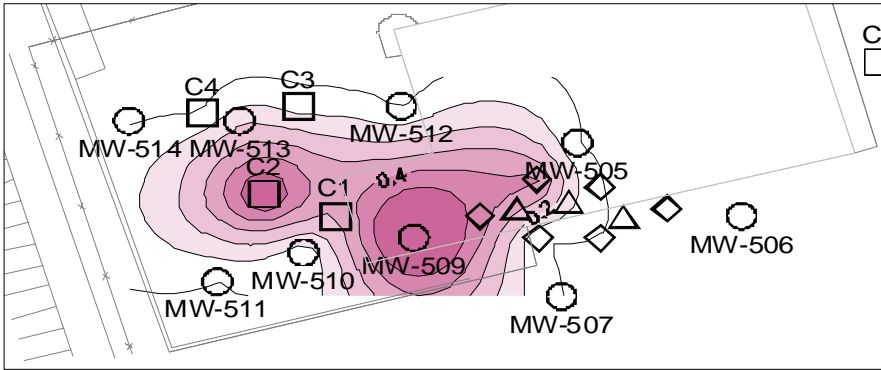


Ethene

0.5 uM = 14 ug/L

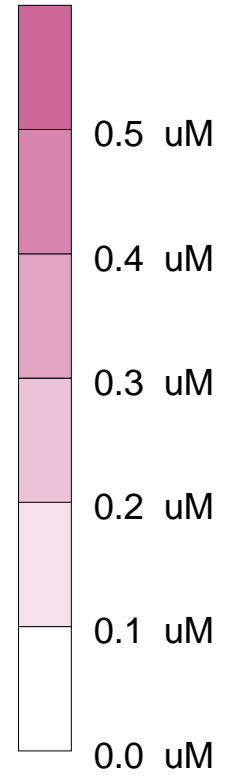
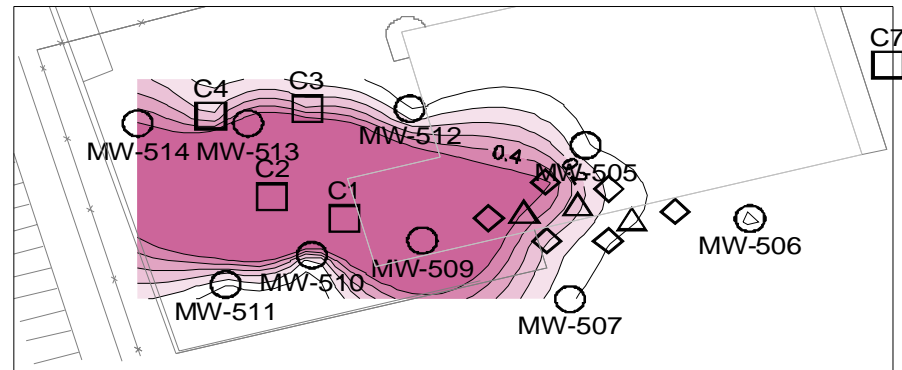
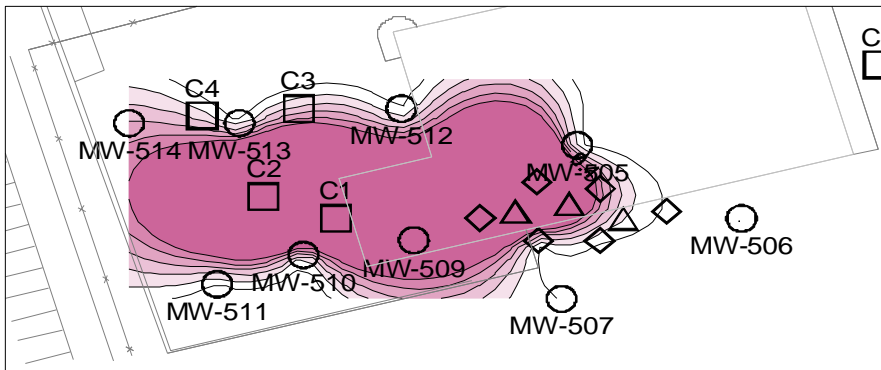
~50 Months Post-Flush

~56 Months Post-Flush



~62 Months Post-Flush

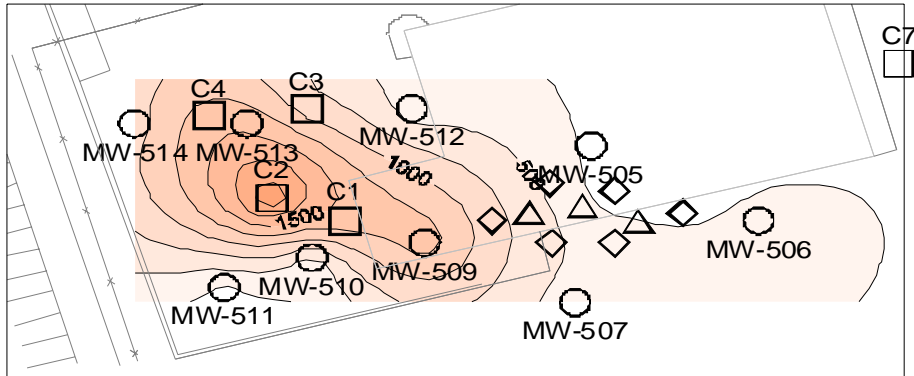
~65 Months Post-Flush



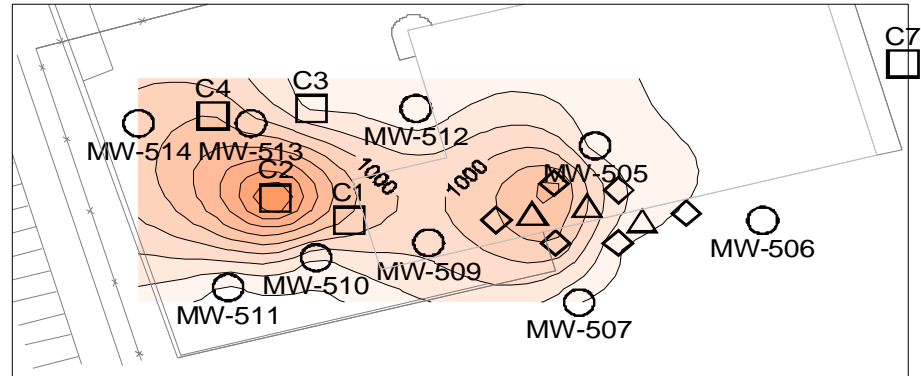
Chloride

2250 μM = 80 mg/L

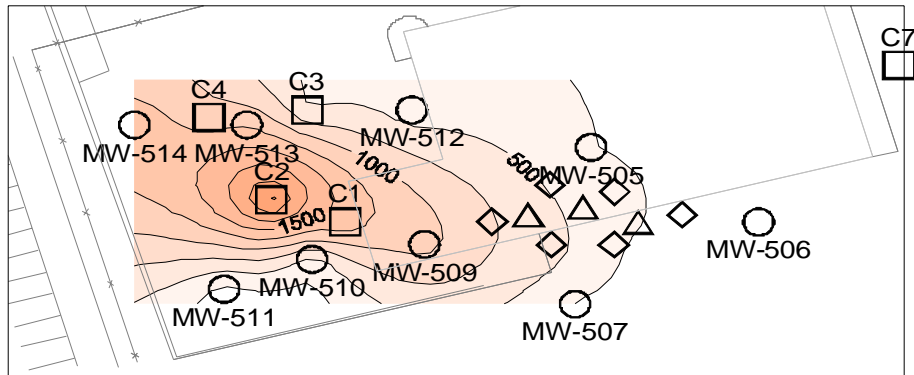
~50 Months Post-Flush



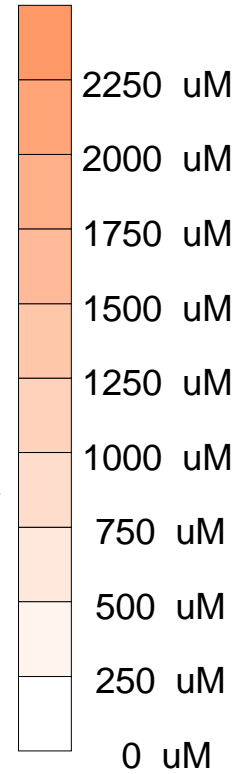
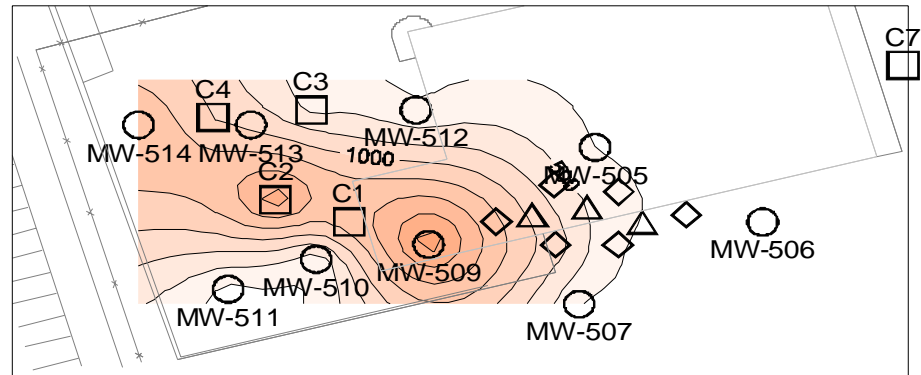
~56 Months Post-Flush



~62 Months Post-Flush



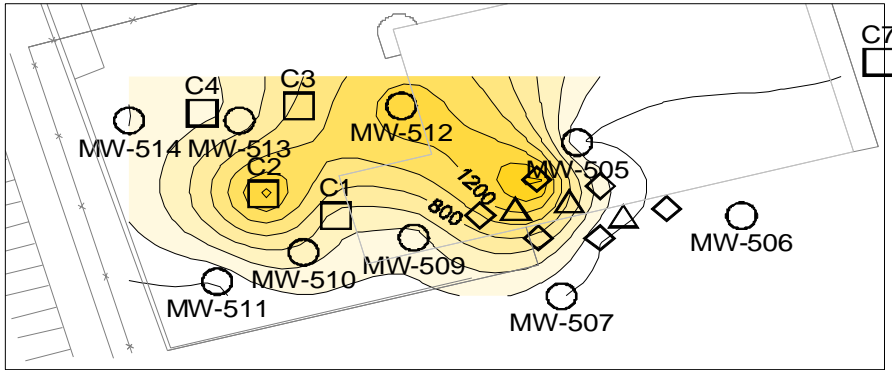
~65 Months Post-Flush



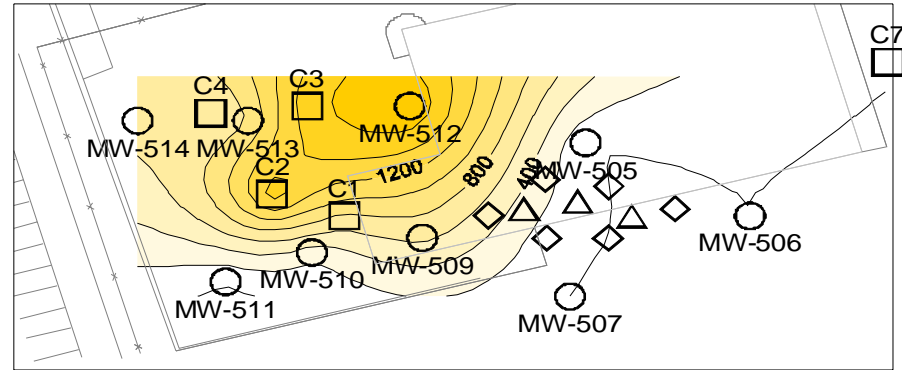
Acetic Acid

1600 uM = 96 mg/L

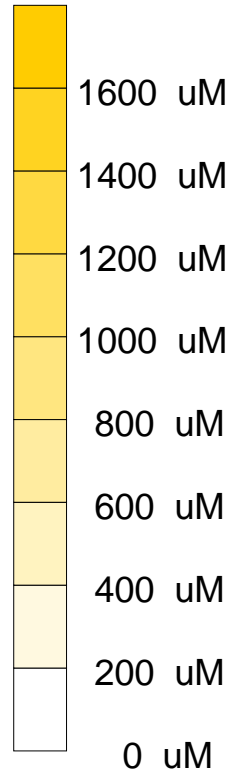
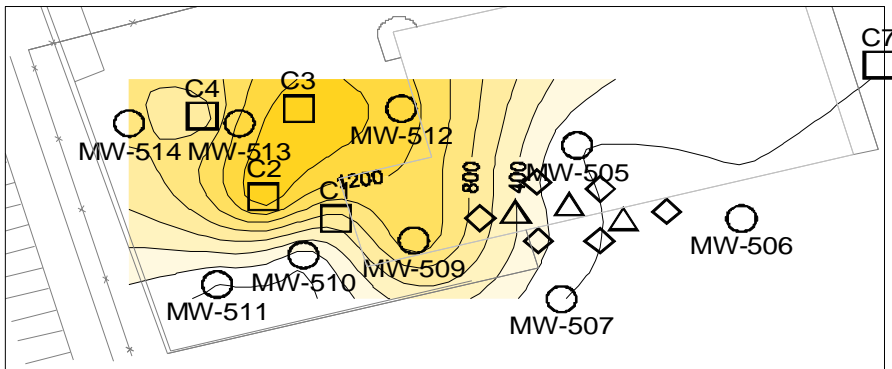
~56 Months Post-Flush



~62 Months Post-Flush



~65 Months Post-Flush

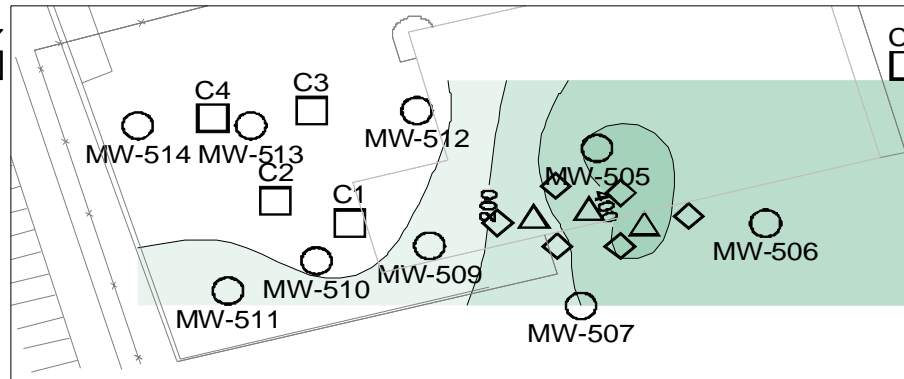
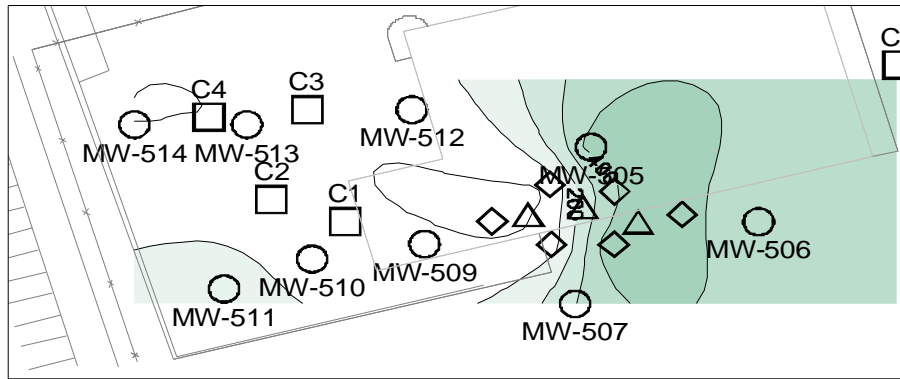


Sulfate

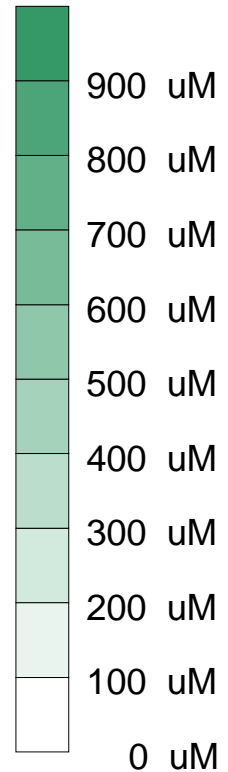
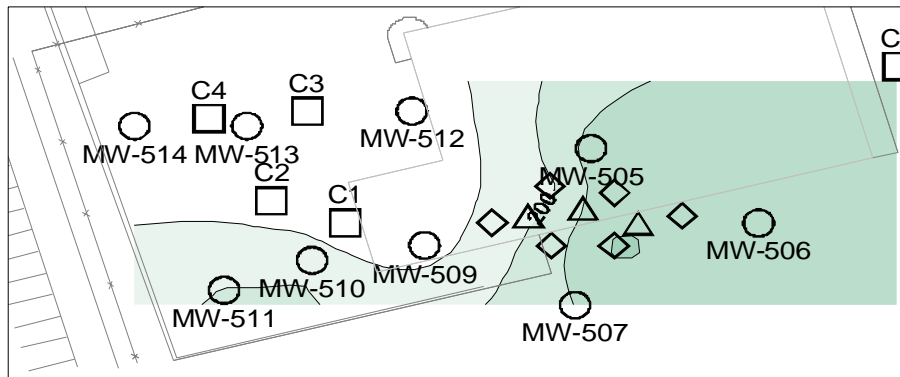
900 μM = 86 $\mu\text{g/L}$

~56 Months Post-Flush

~62 Months Post-Flush



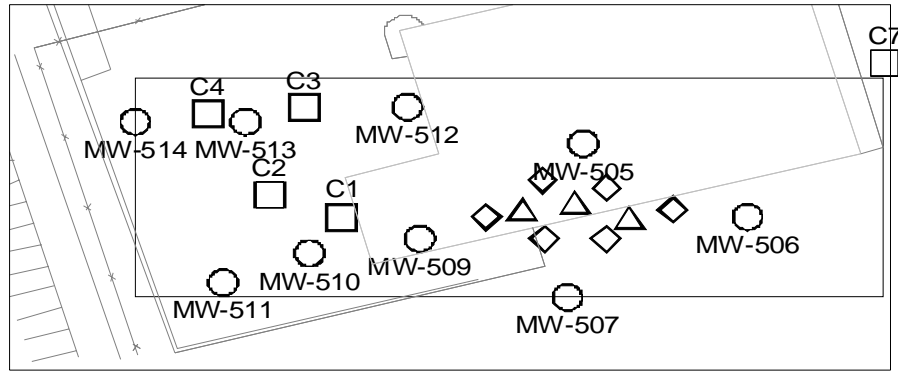
~65 Months Post-Flush



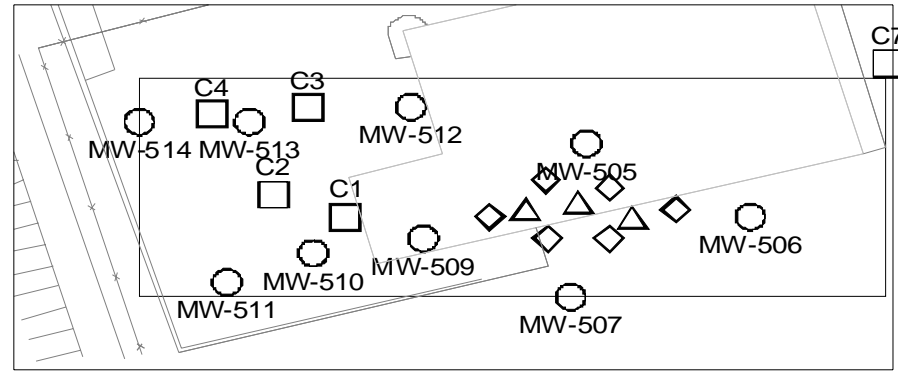
Methane

1100 uM = 18 mg/L

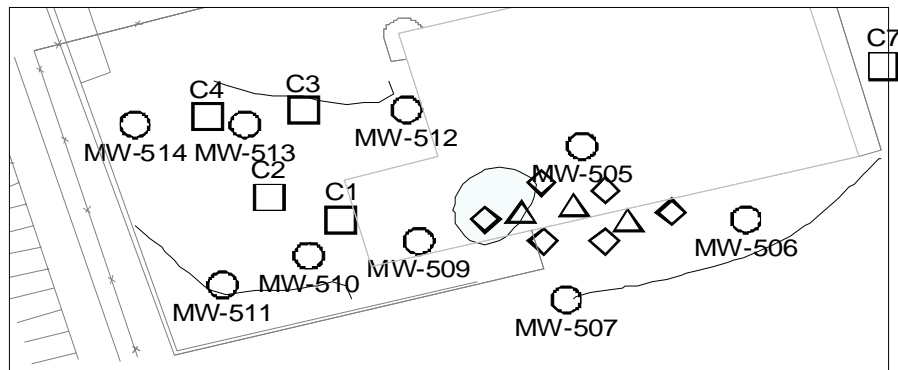
~1 Month Post-Flush



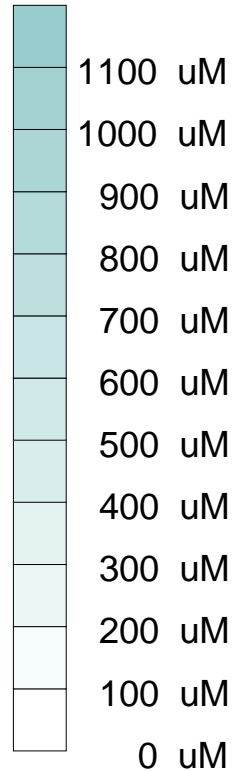
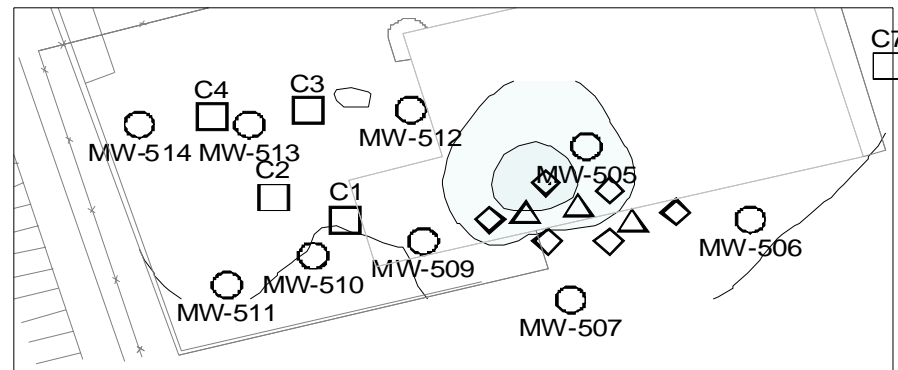
~2 Months Post-Flush



~3.5 Months Post-Flush



~5.5 Months Post-Flush

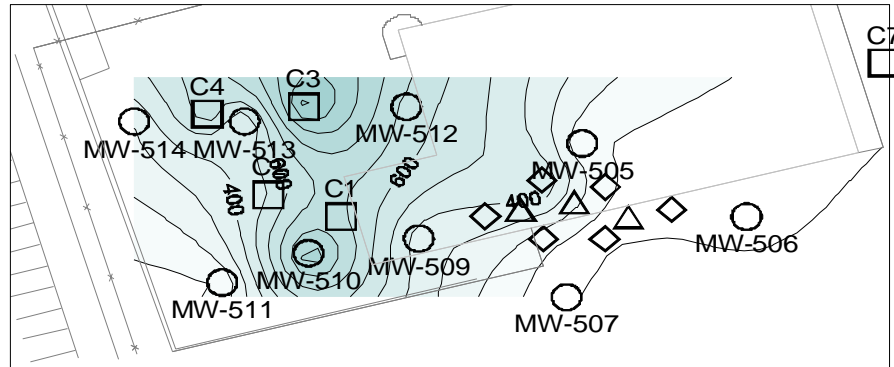
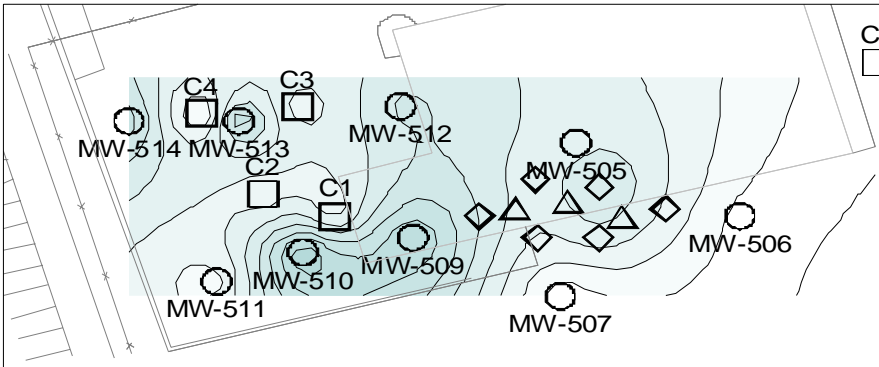


Methane

1100 uM = 18 mg/L

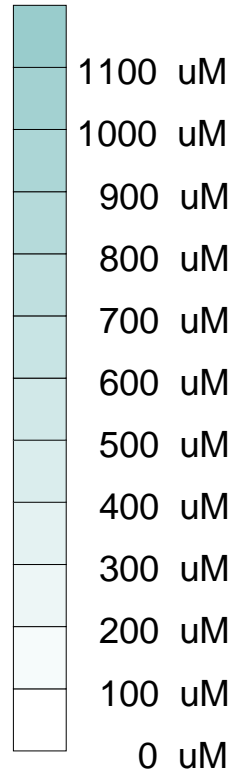
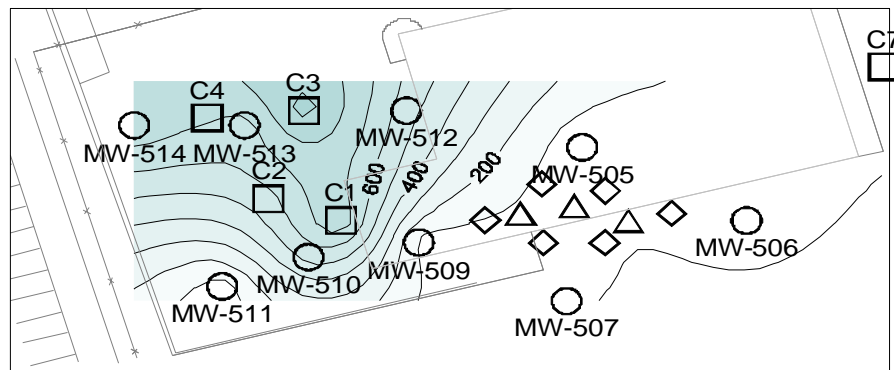
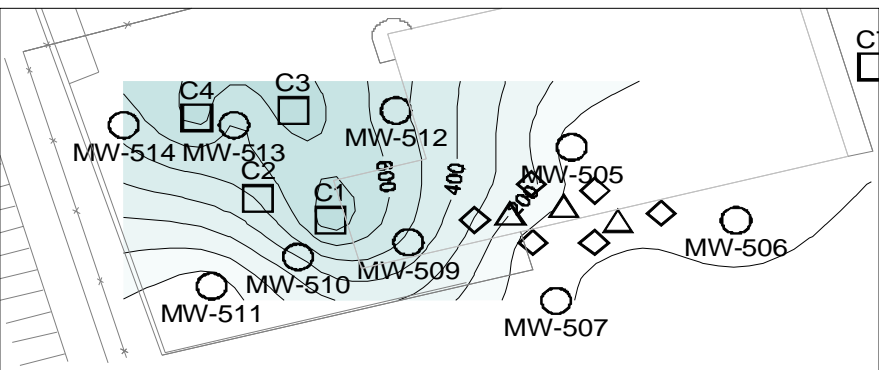
~22 Months Post-Flush

~56 Months Post-Flush



~62 Months Post-Flush

~65 Months Post-Flush



SUMMARY

Solvent Extraction:

41.5 L PCE Removed (Mass Recovery)

~70 % PCE Removed (Partitioning Tracer)

PCE Daughter Product Formation

TCE, *cis*-DCE, VC, ethene, methane (?)

Change in Geochemistry

Dissolved Oxygen, Sulfate, and Redox

Indications of Biological Activity

Methane, Volatile Fatty Acid, and Hydrogen

Partial Oxidation of Ethanol:



Complete Oxidation of Ethanol:



Dechlorination of PCE:



Complete Dechlorination of PCE Requires

1-2 Moles of Ethanol

(excluding competing processes)

Source Area = 40 ft. diameter X 5 ft. depth

Assume Porosity = 0.4

Pore Volume = 70,000 L

Concentrations:

Average Ethanol = 8,000 mg/L

Average PCE = 50,000 ug/L

Total Mass:

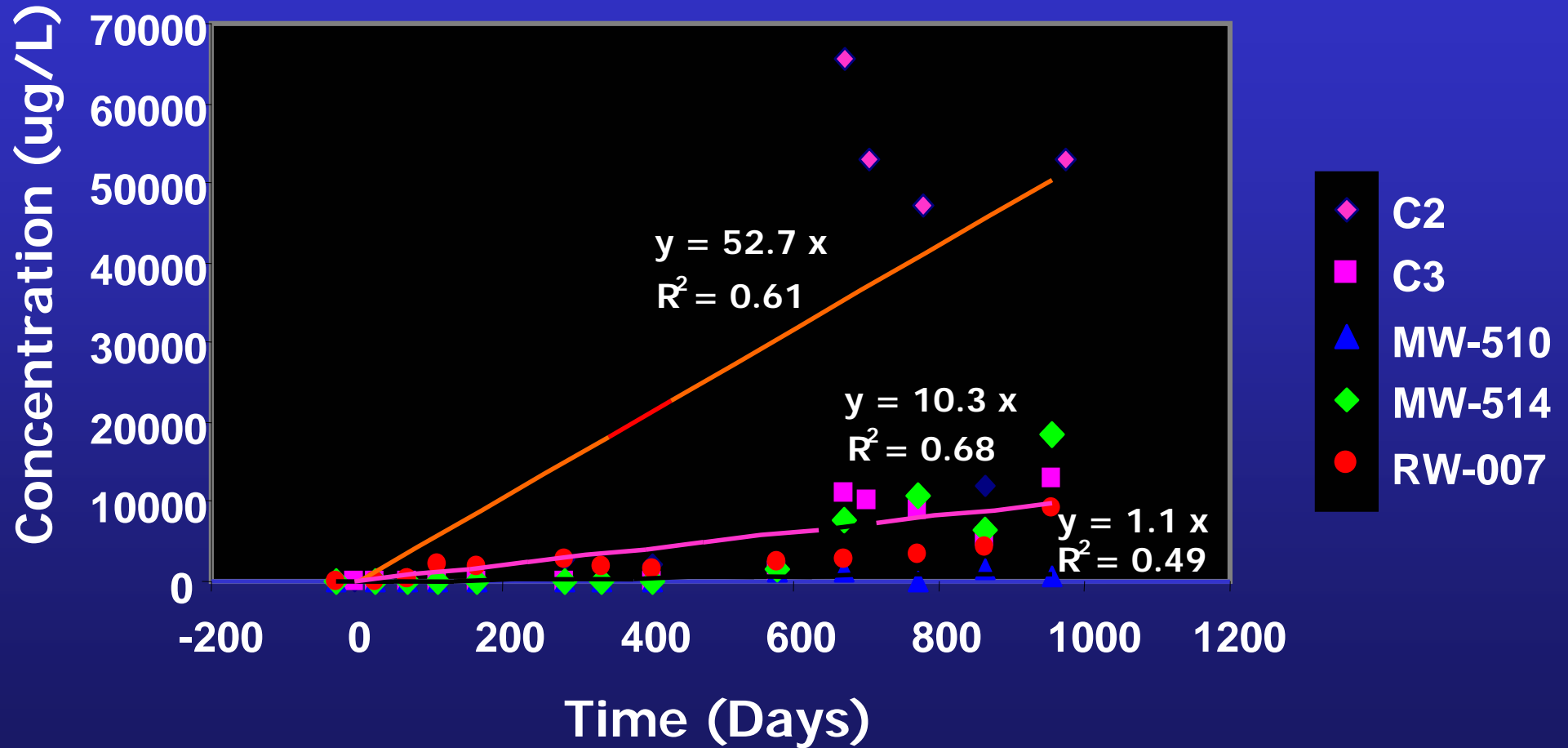
Ethanol - 570 Kg or 12,350 Moles

PCE - 3.6 Kg or 21.5 Moles

Theoretically, we have >250 times the amount of ethanol present for complete dechlorination of the estimated remaining PCE.

38.8 times the amount needed to degrade the 157.1 moles of the (estimated) PCE in the source zone (136 moles residual PCE + 21.1 moles dissolved PCE). While this estimate assumes no competing terminal oxidation processes such as methanogenesis or sulfate reduction, an efficiency greater than 2% would still meet the theoretical demand.

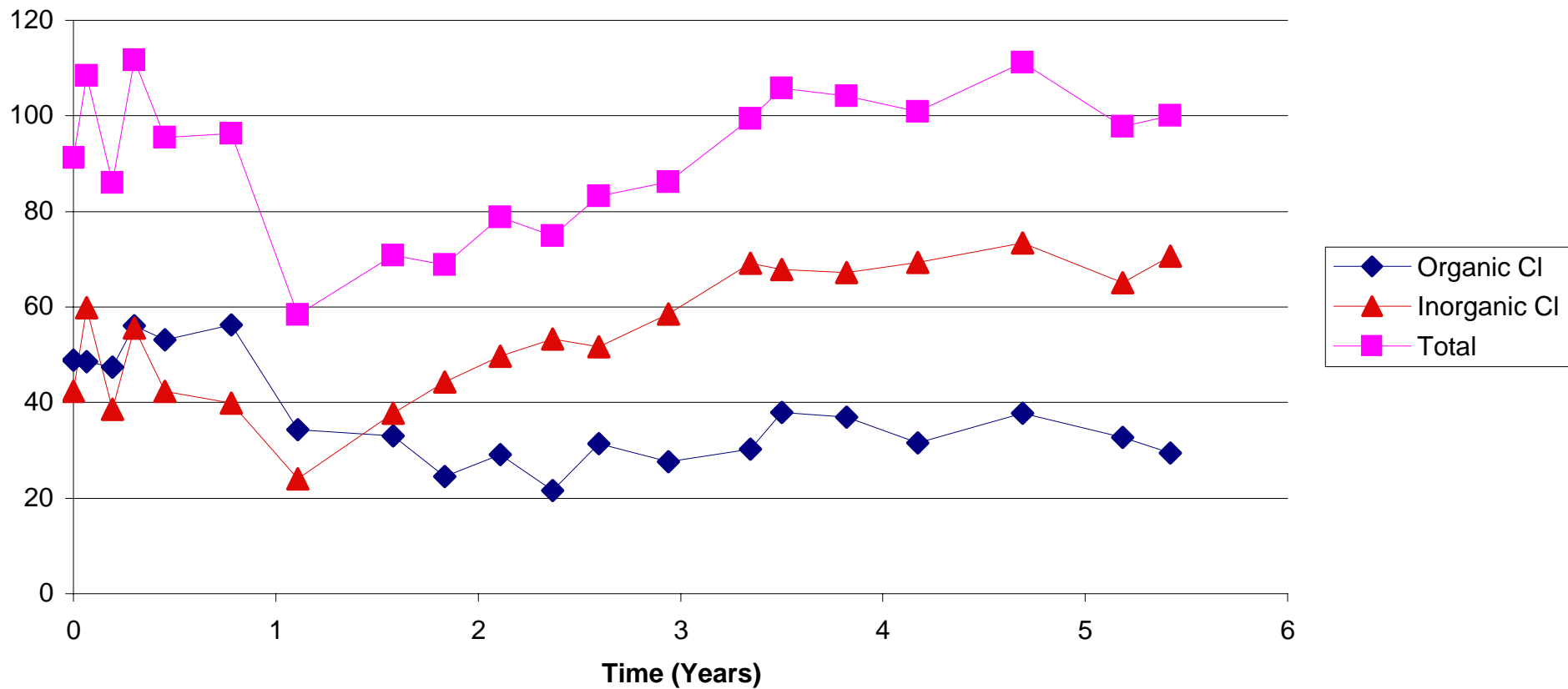
cis-DCE Formation



First Order Degradation Rates (Based on Total Mass)

Ethanol	-0.33 year ⁻¹ (R ² 0.53)	t _{1/2} = 2.1 yrs
PCE	-0.56 year ⁻¹ (R ² 0.82)	t _{1/2} = 1.2 yrs
<i>cis</i> -DCE	0.81 year ⁻¹ (R ² 0.82)	t _{1/2} = 0.9 yrs

Total Chlorides



- Currently the system remains biologically active and the dechlorination products are accumulating.
- High levels of dissolved methane and hydrogen have also been detected in the treatment zone.
- The maximum and minimum observed rate of dechlorination (based on cis-DCE production) are approximately 43.6 and 4.2 ug/liter/day, respectively.
- These rates can be extrapolated to a multi-step, concurrent, dechlorination process to predict that the dissolved phase PCE could be removed in 3 to 30 years, and that the total source zone PCE could be transformed in 24 to 240 years.

Publications

Sewell, G.W. et al. 2005. Chlorinated Solvent Contaminated Soil and Ground Water: Field Application of the Solvent Extraction Residual Biotreatment Technology, Chapter 5. *In* Bioremediation of Recalcitrant Compounds. Taylor & Francis Publishers, Boca Raton. Pp 59-149.

Mravik, S., R.K.Sillan, A.L. Wood, and G.W. Sewell. 2003. Field Evaluation of the Solvent Extraction Residual Biotreatment (SERB) Technology. *Environ. Sci. Technol.* 37: 5040-5049.

Jawitz, J., R.K. Sillan, M.D. Annable, P.S.C. Rao and K. Warner. 2000. In-Situ Alcohol Flushing of a DNAPL Source Zone at a Dry Cleaner Site. *Environ. Sci. Technol.* 34: 3722--3729.

Questions?

Questions

