

# Remediation of Chlorinated Solvent Source Zones Using ZVI-Clay in Conjunction with Soil Mixing (ZVI-Clay)



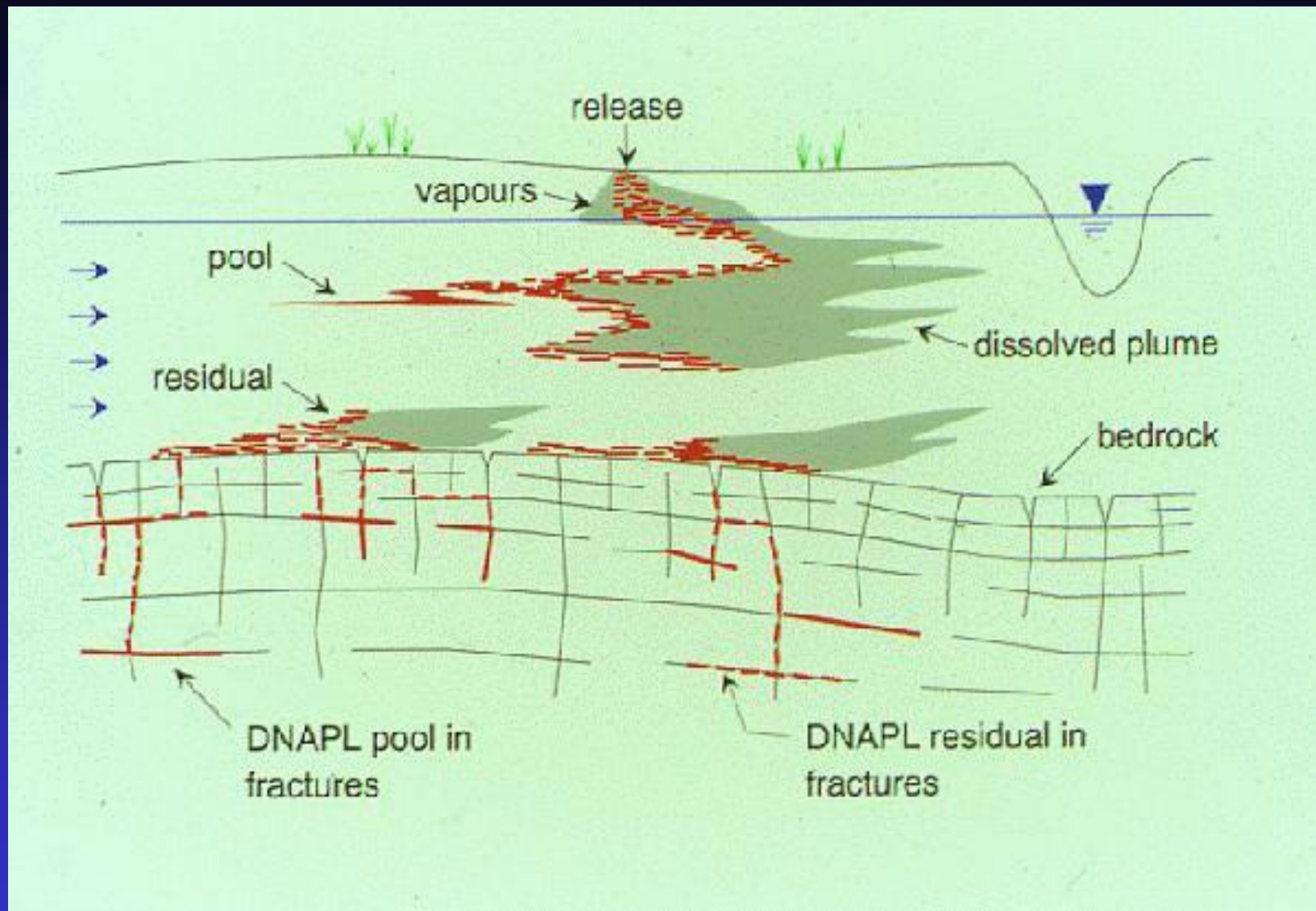
Presented at the RTDF Permeable Reactive Barrier Action Team Meeting  
Albuquerque New Mexico, October 26, 2004

By

Tom Sale, Mitch Olson, Dave Gilbert and Chuck Shackelford

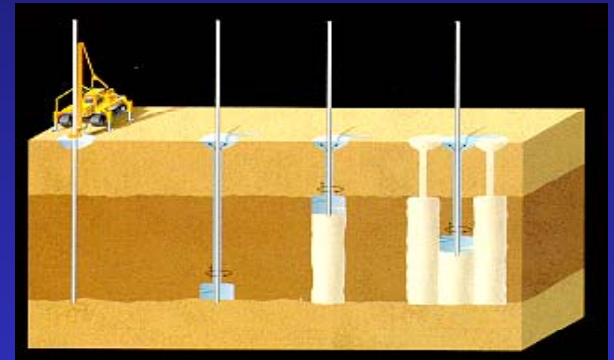
# Presentation

- Process
- Laboratory Results
- Field Results
- Future Plans
- Questions



Conceptual chlorinated solvent source zone  
(Kueper et al., 1993).

# ZVI-Clay



November 2003 DuPont Technology Donation to Colorado State University  
Batchelor et al., 1998 and 2002. United States Patent nos. 5,789,649 and 6,492,572 B2.

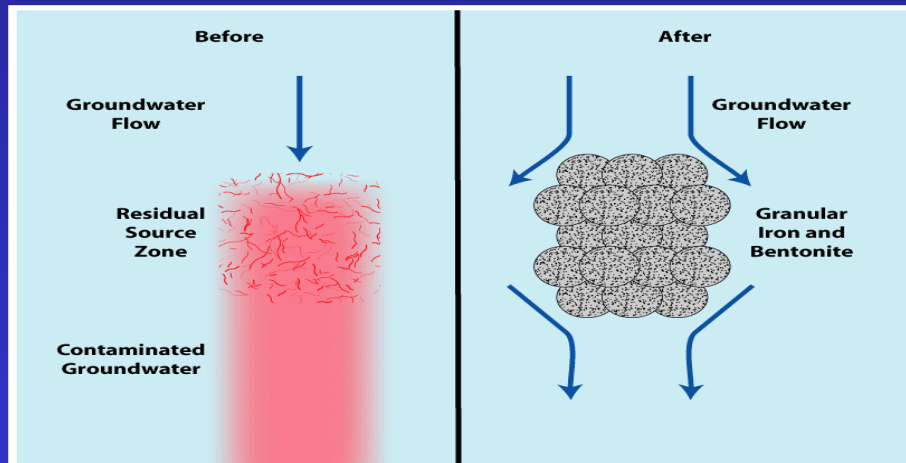
# ZVI



Reactive Media (Zero-Valent Iron) -Drives reductive dechlorination (Gillham and O'Hannesin, 1994).



# Clay



Effect of stabilization of a source zone  
(ETI 2004)

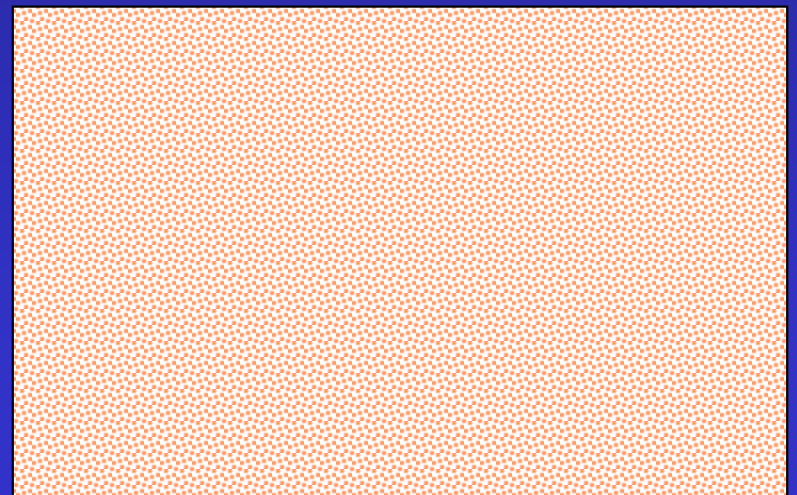
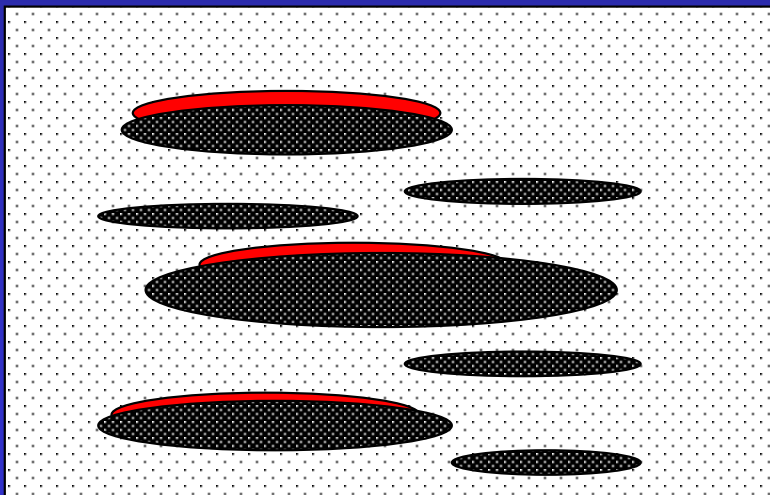
- Reduces discharge of water through source
  - Reduced downstream contaminant discharge
  - Increased time for reactions to proceed
  - Reduced inflow of oxygen and other electron acceptors
- Facilitates mixing
  - High viscosity suspension for uniform iron delivery
  - Reduced energy for soil mixing

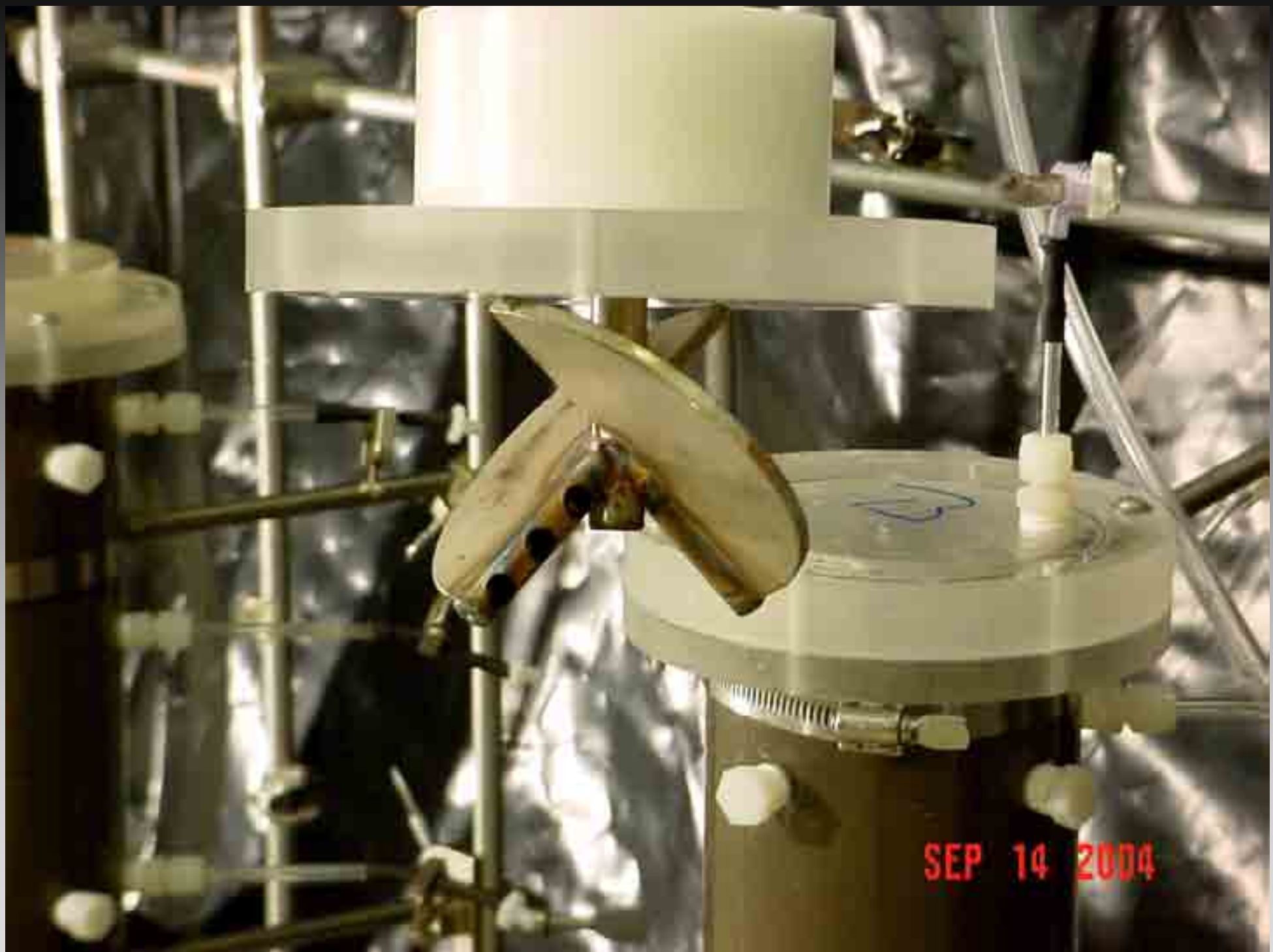
# Mixing



Homogenates source zone:

- Reagent distribution
- Contaminant distribution
- Sediments
- Dispersal of DNAPL pools





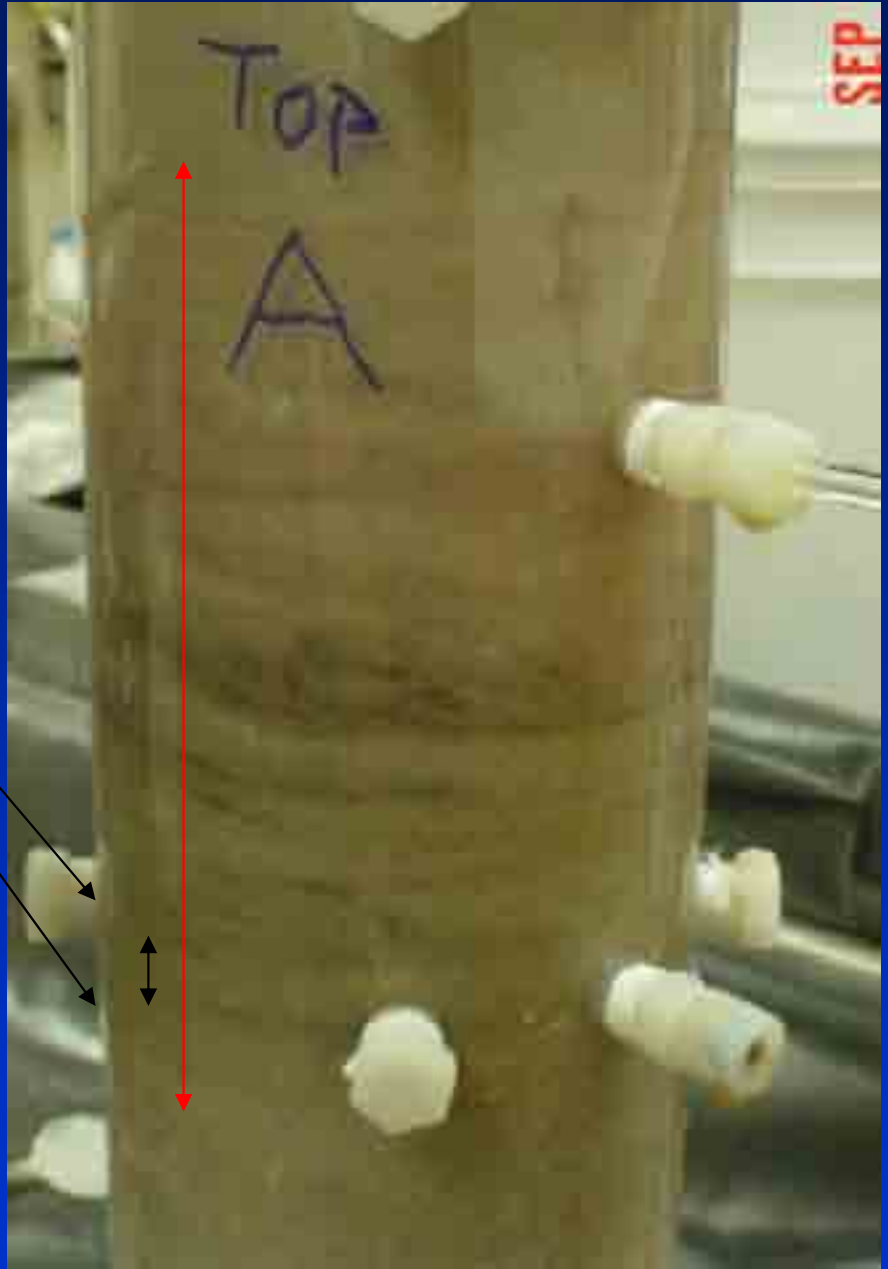
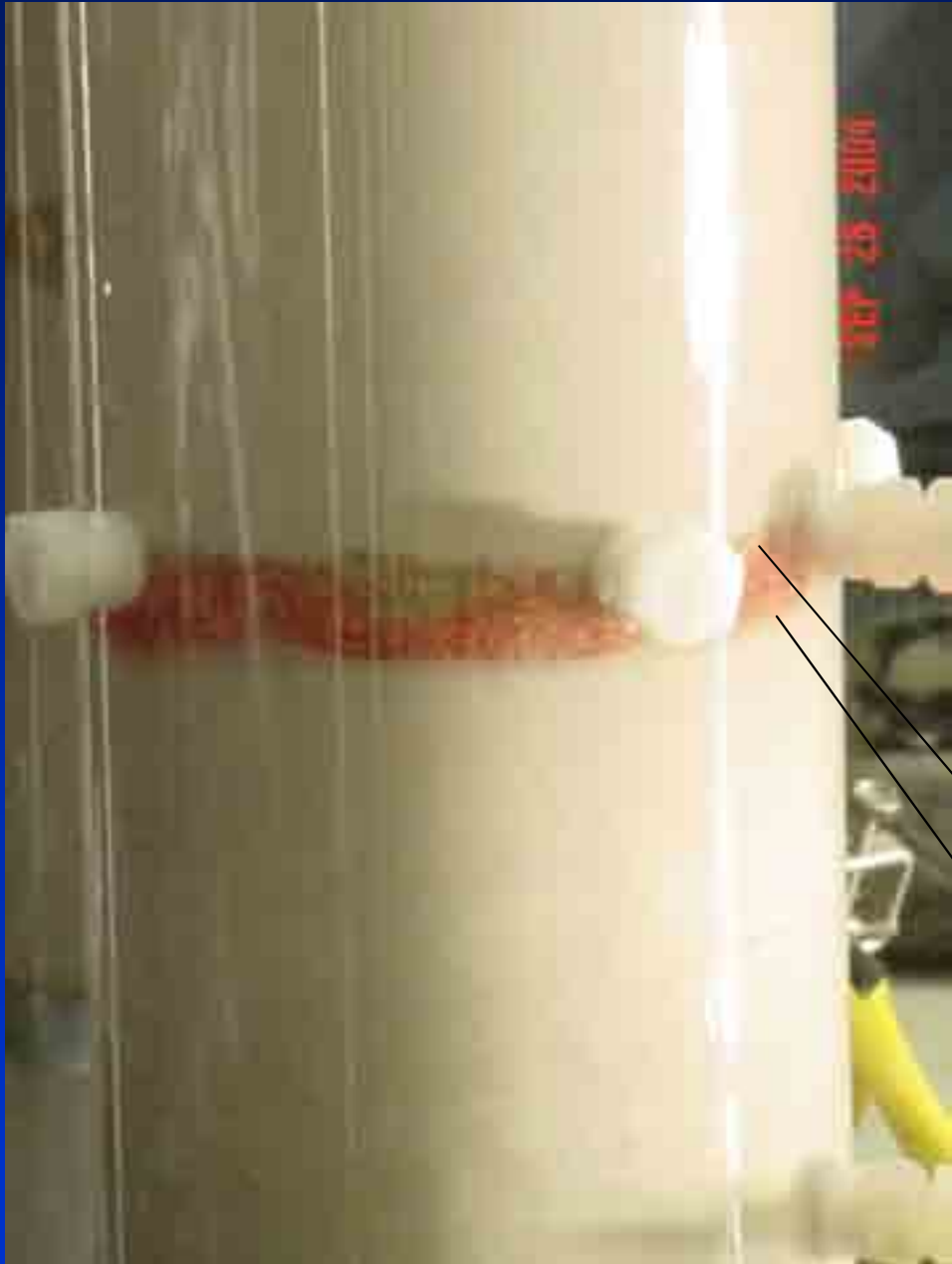
SEP 14 2004













9/28 - Initial



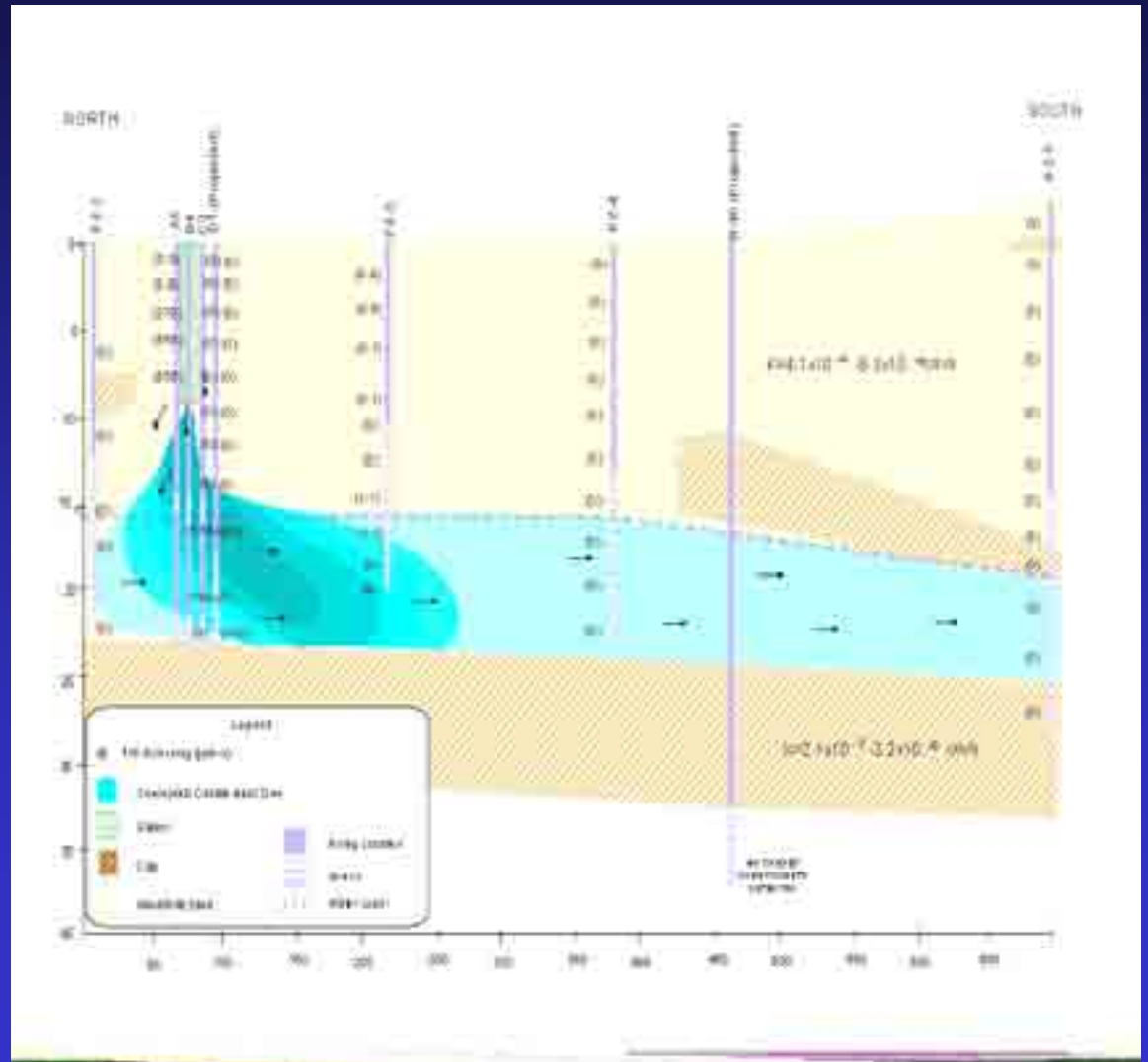
9/28 - Post Mixing



9/30 Two Days

# South Carolina Site

- Small release
- Shallow alluvium
- Active contaminant attenuation
- Located within an industrial property



# Geochemical Studies

(South Carolina)



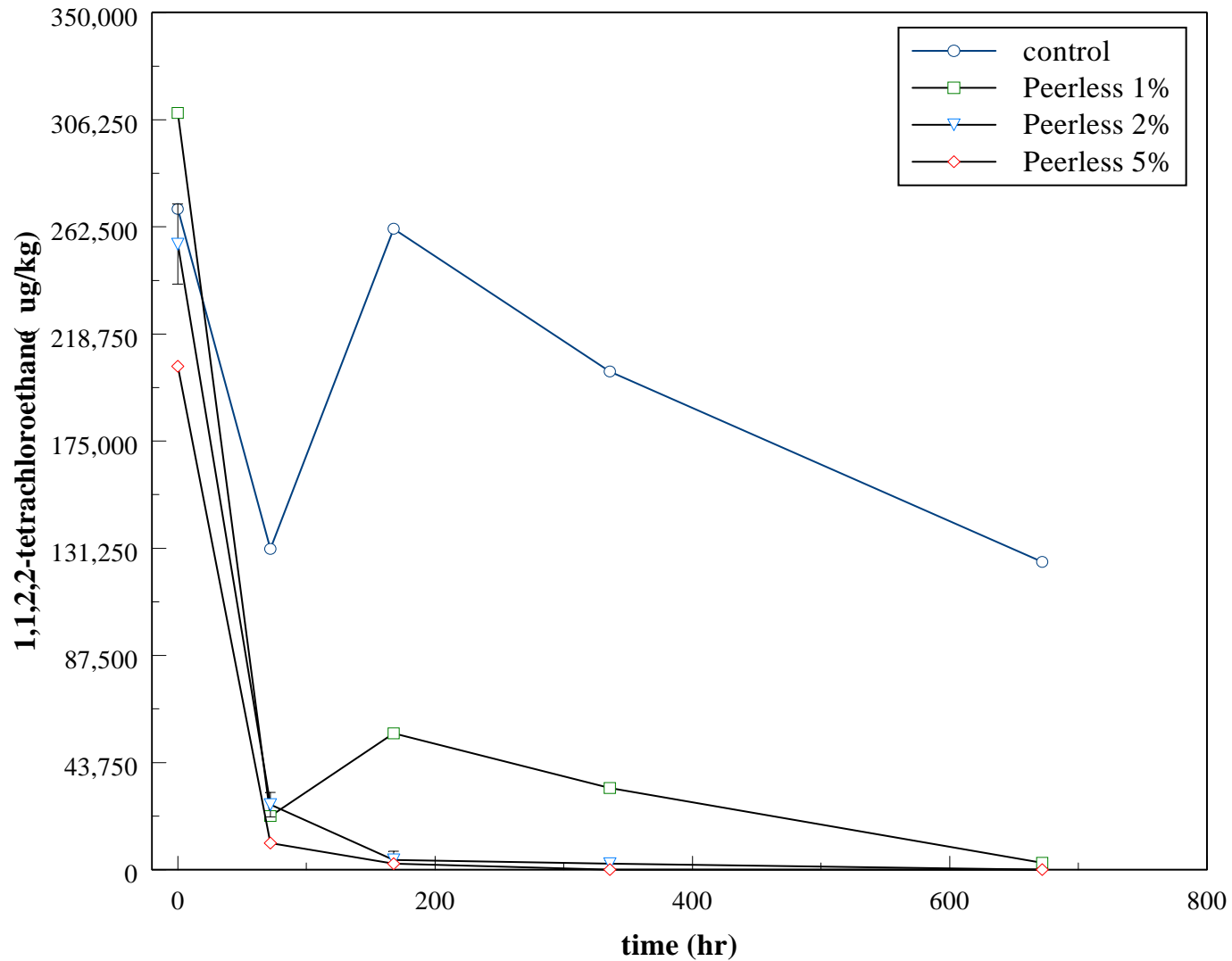
### Spike sample study matrix

			3 days (CSU)	7 days (CSU)	14 days (CSU)	28 days (CSU)	28 days (Outside lab) <sup>A)</sup>
Spiked and Dried Sample s	0% Fe Contro	w/ clay	CC-0-3	CC-0-7	CC-0-14	CC-0-28	CC-0-28L
	1% Fe		S-1-3	S-1-7	S-1-14	S-1-28	S-1-28L
	2% Fe	A	S-2A-3	S-2A-7	S-2A-14	S-2A-28	S-2A-28L
		B	S-2B-3	S-2B-7	S-2B-14	S-2B-28	
		C	S-2C-3	S-2C-7	S-2C-14	S-2C-28	
		D NAPL Spike	CF-0-3	CF-0-7	CF-0-14	CF-0-28	
	5% Fe		S-5-3	S-5-7	S-5-14	S-5-28	
	2% GMA Fe <sup>B</sup>		S-2G-3	S-2G-7	S-2G-14	S-2G-28	S-2G-28L
2% Connelly Fe		S-2C-3	S-2C-7	S-2C-14	S-2C-28		

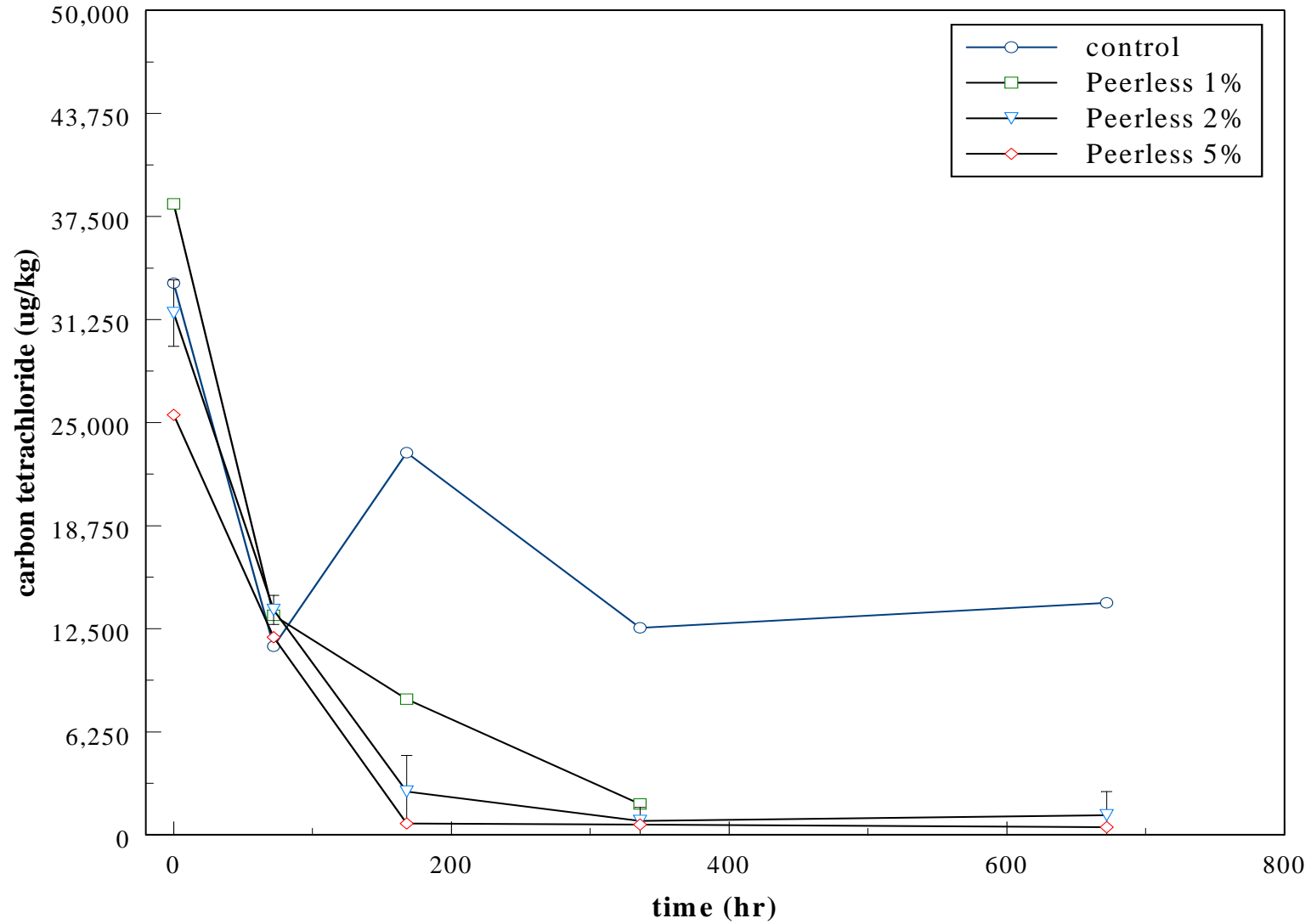




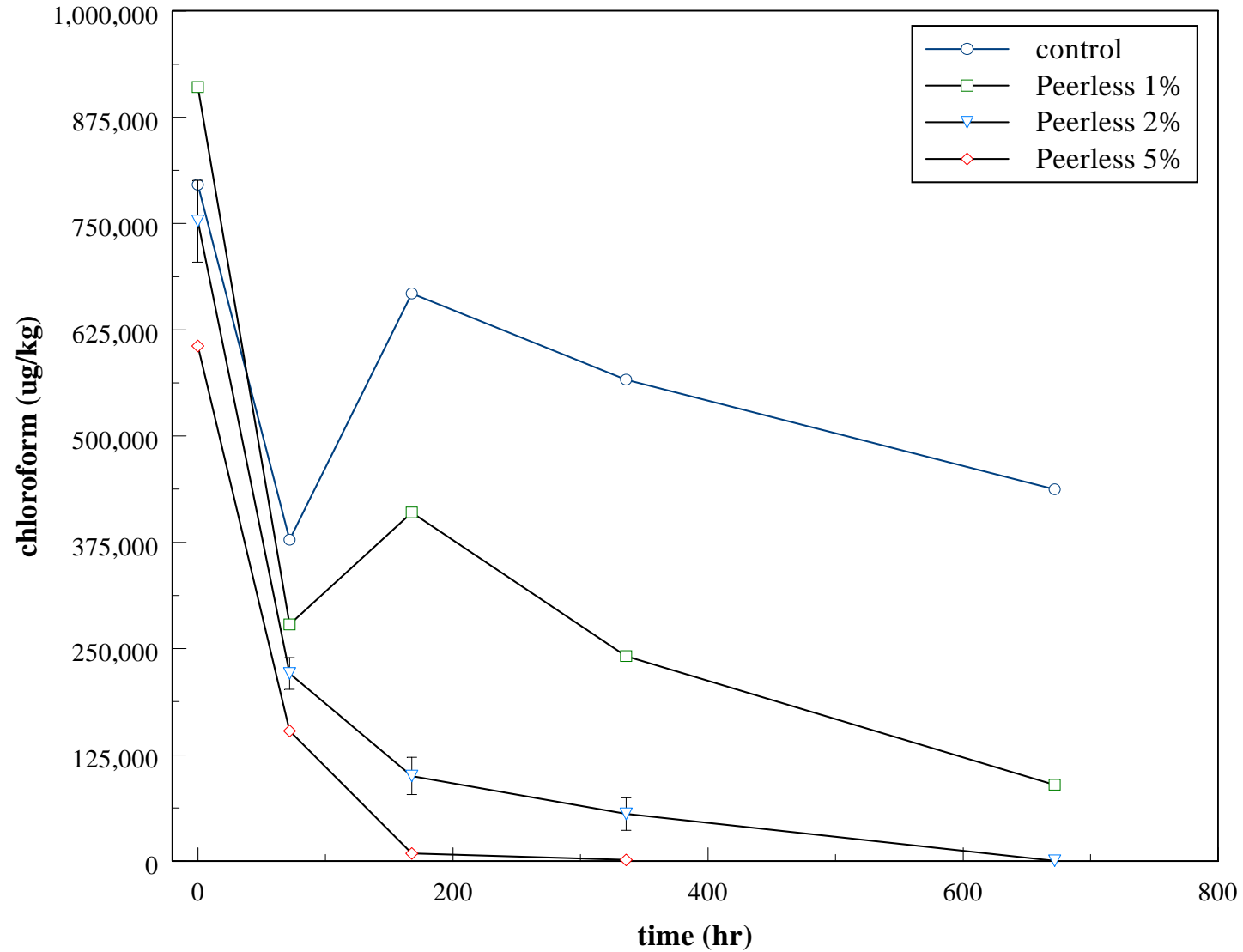
# Rapid degradation of 1,1,2,2-TCA with similar endpoints 680 hours (26 days)



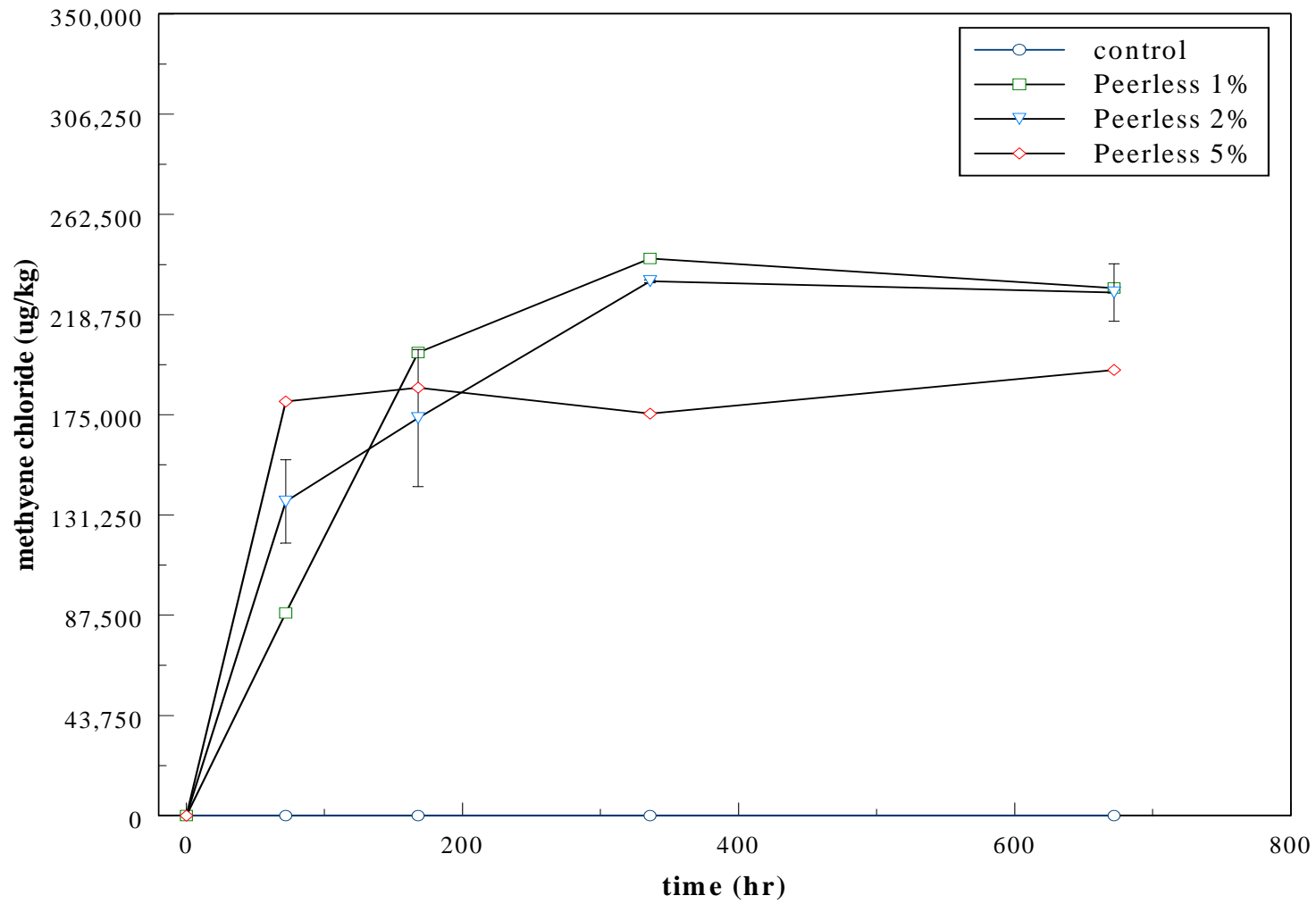
# Rapid degradation of Carbon Tetrachloride with similar endpoints 680 hours (26 days)



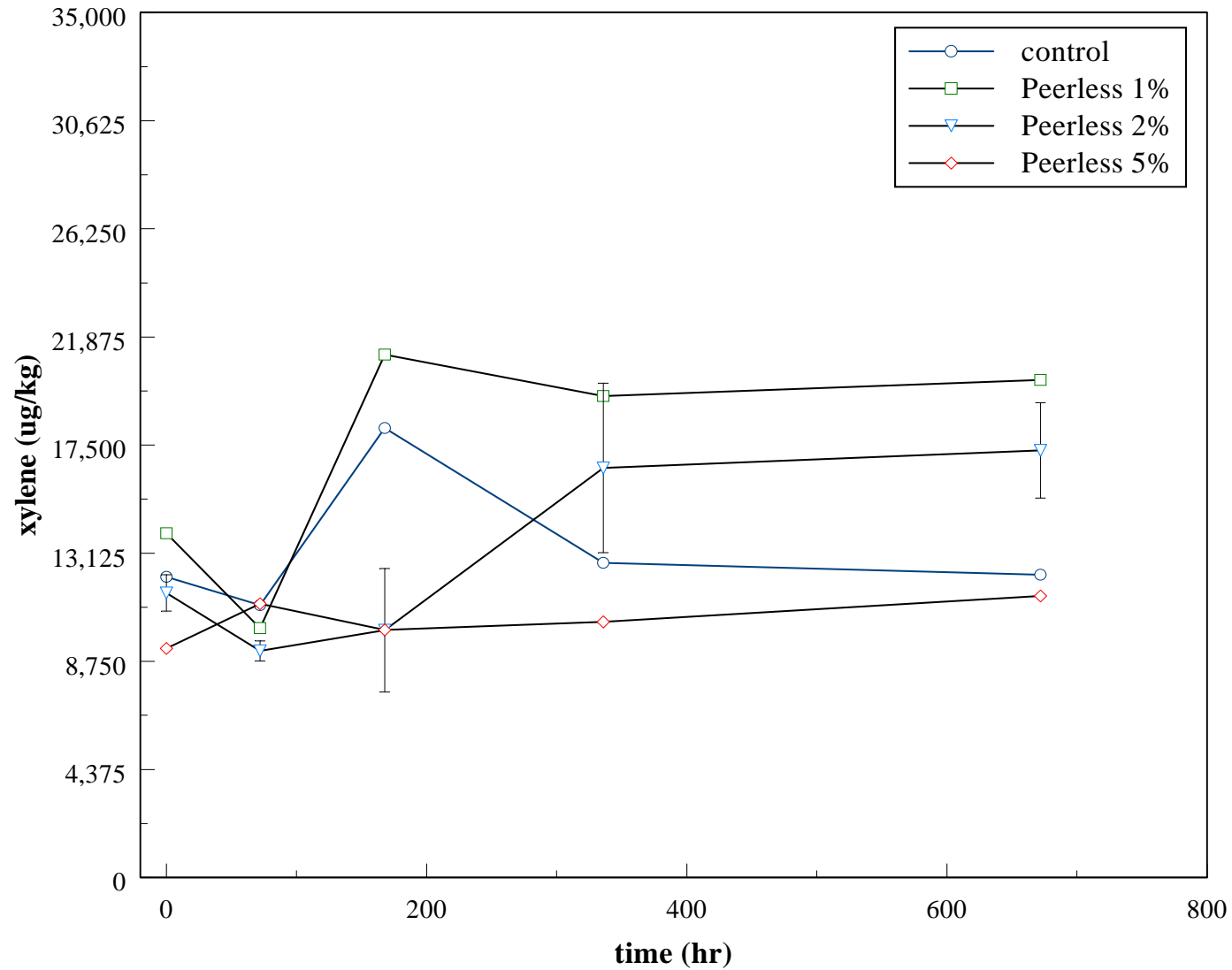
# Rapid degradation of Chloroform



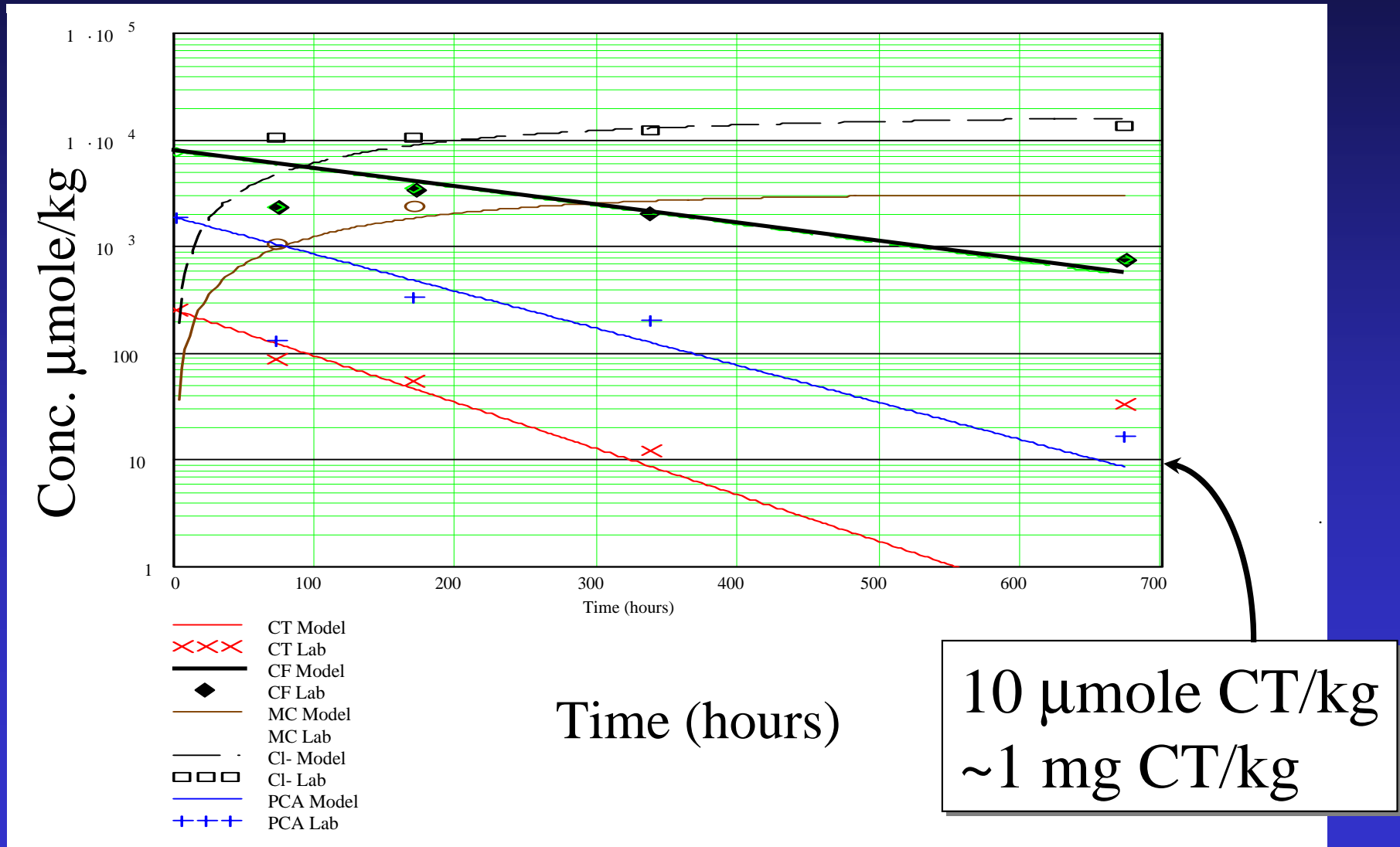
# Apparent slow degradation of MC

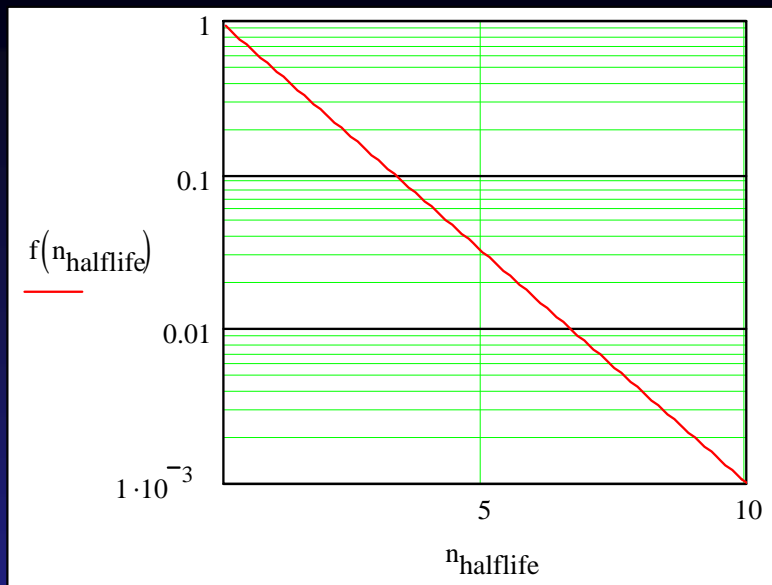


# Xylene – little removal in 28 days



# Modeling – Irreversible first order reactions (Eykoht, 1999)





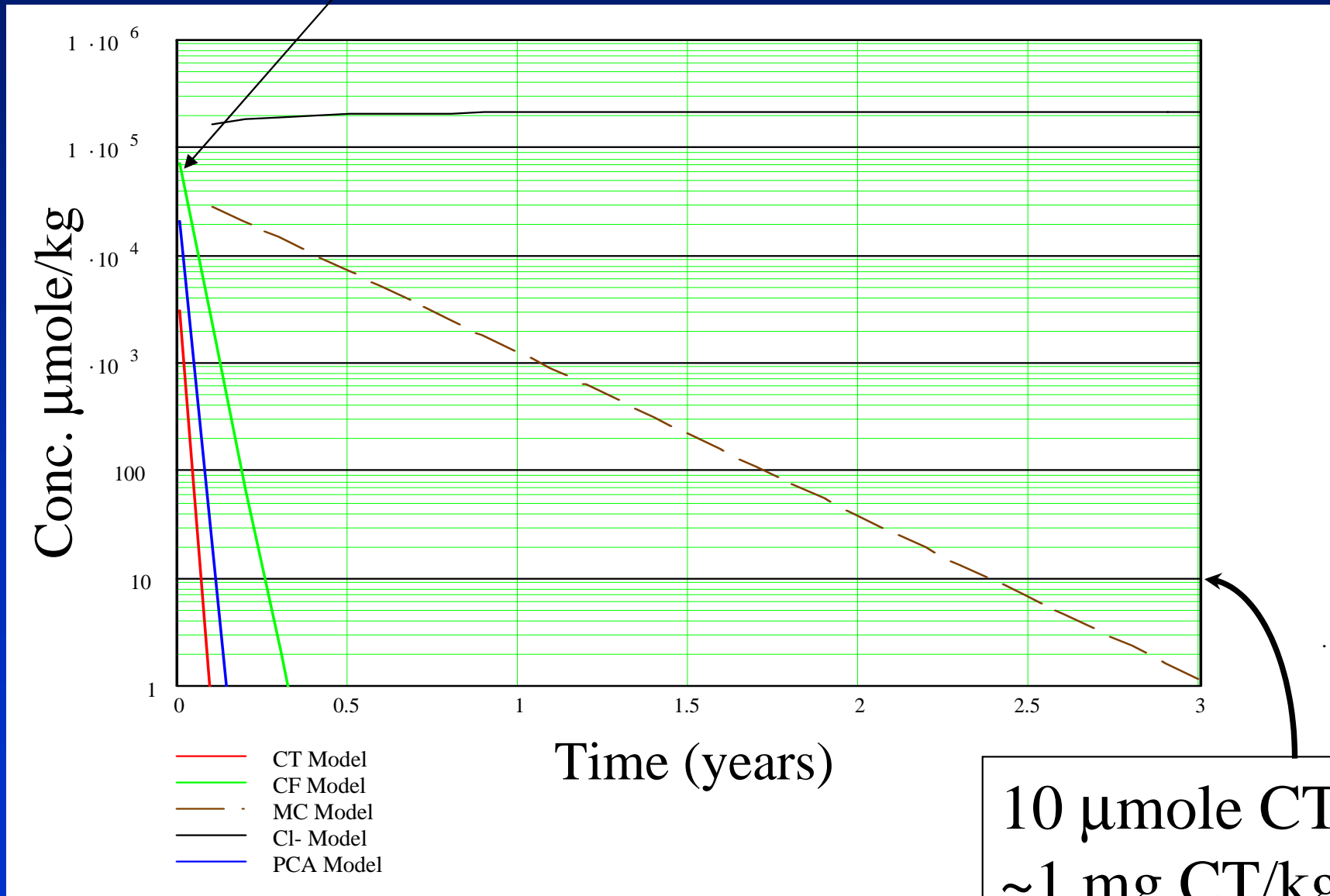
Ten half lives = Three order of magnitude

## Estimated first order reaction rates and contaminant half lives

Treatment	CT		CF		MC		PCA	
	k(1/hr)	$t_{1/2}$ (hr)	k(1/hr)	$t_{1/2}$ (hr)	k(1/hr)	$t_{1/2}$ (hr)	k(1/hr)	$t_{1/2}$ (hr)
1% Peerless	0.005	140	0.002	350	0.0002	3500	0.004	170
2% Peerless	0.006	120	0.005	140	0.0002	3500	0.015	46
5% Peerless	0.008	87	0.01	69	0.0002	3500	0.015	46
2% GMA	0.003	230	0.02	35	0.0002	3500	0.08	9

# Four orders of reduction magnitude reduction after 3-years?

Initial field concentrations



10  $\mu\text{mole CT/kg}$   
~1 mg CT/kg



# Martinsville Virginia



- ~ 20 tons Carbon Tetrachloride
- 8,000 Yards
- Initial ~ 4,000 mg/kg
- 2-6 lbs Fe / ft<sup>3</sup> soil
- 99.99 % removal CT in 1 year
- 99% removal of total chlorinated compounds in 1 year





Shackelford et al (2004)

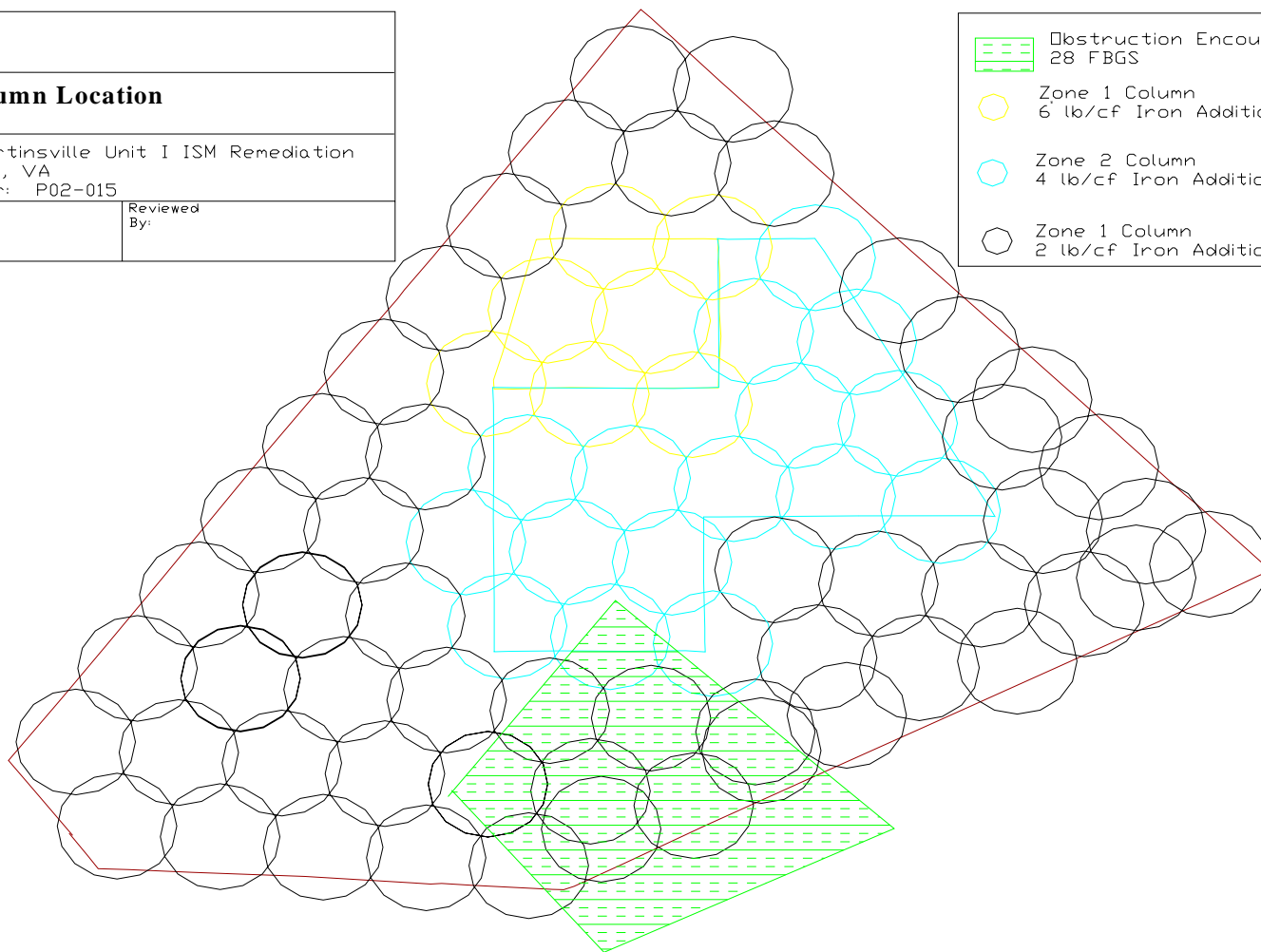
# Implementation



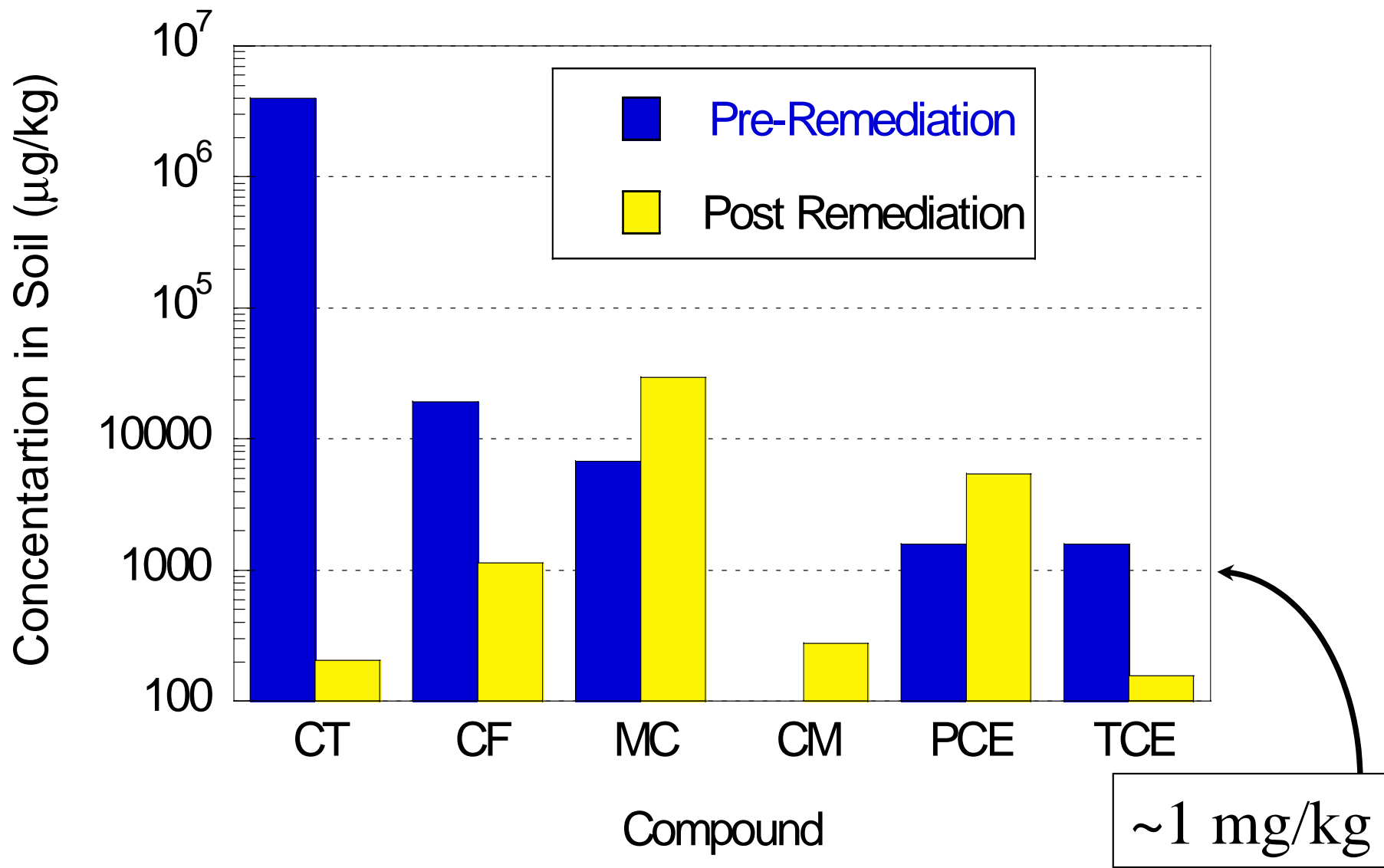
# As built mixing and ZVI content

<b>Final Column Location</b>	
<b>As-Built</b>	
Dupont Martinsville Unit I ISM Remediation Martinsville, VA Job Number: P02-015	
Drawn By:	Reviewed By:

	Obstruction Encountered 28 FBGS
	Zone 1 Column 6 lb/cf Iron Addition
	Zone 2 Column 4 lb/cf Iron Addition
	Zone 1 Column 2 lb/cf Iron Addition



# Martinsville VA - Initial and 1 Year Data



# Year 2 Sampling



# ZVI Clay Niche

- Chlorinated Compounds
- Mixable alluvium
- Best with limited overhead and/or buried obstructions
- Desire for quick results

# Issues

- Longevity of the iron as a function of iron amount and size
- Losses of iron to potentially unproductive reactions
- Process controls (reactions rates, diffusion, biological processes)
- The ability to treat DNAPL
- Field-scale performance monitoring techniques

# Acknowledgements

- DuPont
- Solvents-in-Groundwater Research Consortium



# Questions