Hydraulic Fracturing with ZVI
Emplacement for Treatment of
Chlorinated Solvents in a Low
Permeability Aquifer

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#### Background

- Hunters Point Naval Shipyard (HPNS), Building 134
- Chlorinated benzenes and ethenes in the subsurface as dense non aqueous phase liquid (DNAPL)
- Treatability study evaluated a multi-component treatment strategy including:
  - Hydraulic fracturing
  - EHC® injection
  - Thermal treatment



#### **HPNS Treatability Study Area**

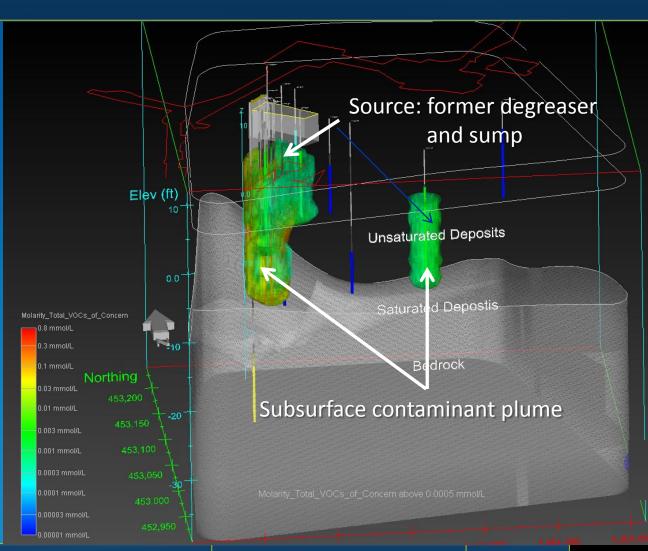




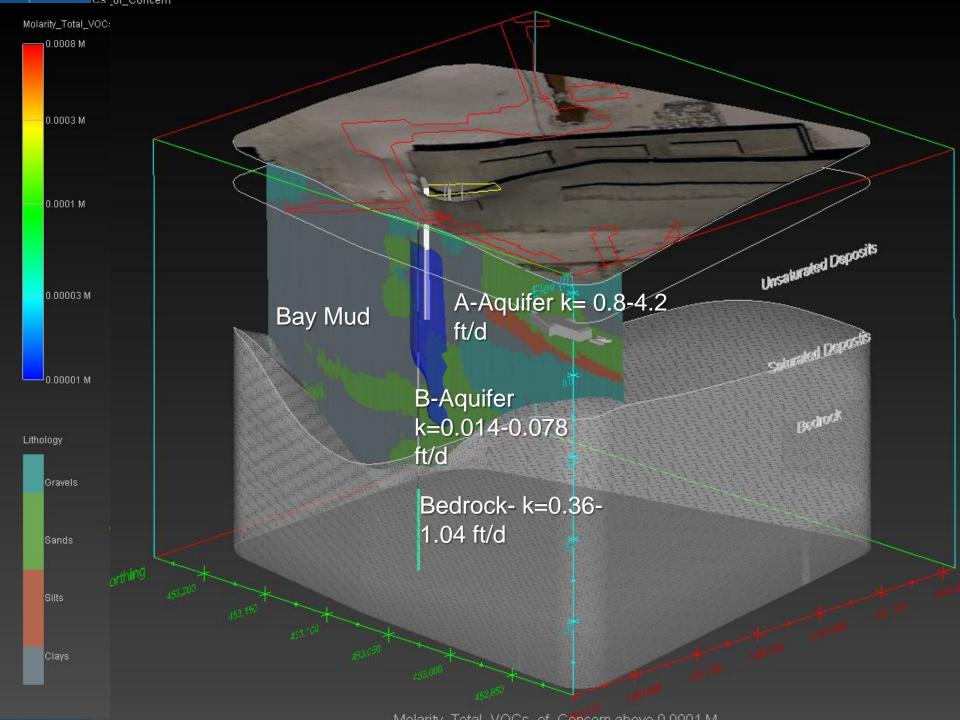
# Problem: Complex Mix of Contaminants in Groundwater and Low-Permeability Soils

### Volatile Organic Contaminants (VOCs):

- 1,2-Dichlorobenzene (DCB)
- 1,3-DCB
- 1,4-DCB
- Chlorobenzene (CB)
- Trichloroethene (TCE)
- Tetrachloroethene (PCE)
- cis-Dichloroethene (DCE)
- Vinyl chloride (VC)







#### Treatability Study Objectives

## Groundwater Technology: Hydraulic Fracturing/EHC®

- 80% reduction of chlorinated VOCs
- Polish remaining VOCs post-TCH to meet very stringent cleanup criteria (generally less than 5 ppb).

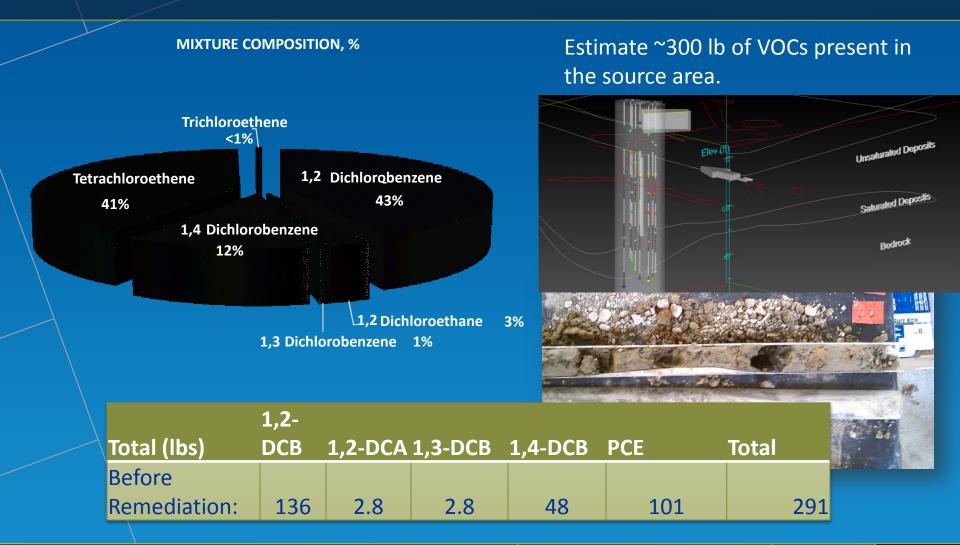
#### Soil/DNAPL Technology: Thermal Conduction Heating (TCH)

- 90% reduction in chlorinated VOCs
- Thermally-Enhanced Extraction of DNAPL

18-month Cleanup Timeframe

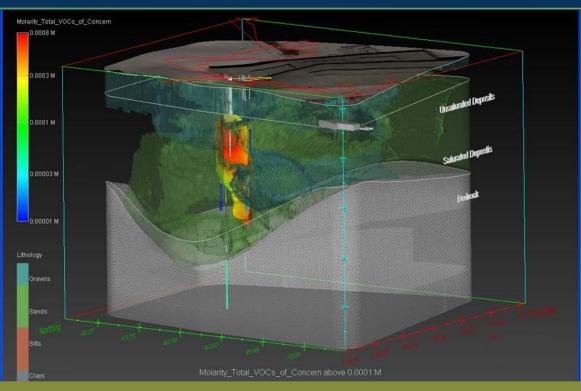


#### Pre-Remediation: DNAPL/Soil Mass Estimate





#### Pre-Remediation: Groundwater Contaminant Plume



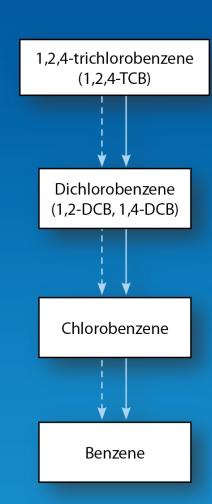
	Parent Compounds					Reductive Daughter Products				
Total (lbs)	1,2-DCB	1,2-DCA	1,3-DCB	1,4-DCB	PCE	benzene	СВ	Cis-DCE	TCE	VC
Before										
Remediation:	4.7	0.7	0.01	1.5	0.6	0.03	0.2	2.1	0.2	0.6
Total Mass in Groundwater: 10.6 lbs										



#### Tetrachloroethene (PCE) reductive dechlorination Reductive Trichloroethene Chloroacetylene Acetylene (TCE) **B-elimination** reductive dechlorination Dichloroethene (trans-1,2-DCE) manganese-reducing conditions ► CO<sub>2</sub> (1,1-DCE)anaerobic oxidation reductive dechlorination acetate -Vinyl Chloride sulfate-reducing/iron reducing co, (VC) conditions'/anaerobic oxidation $CH_{A}$ reductive dechlorination sulfate-reducing conditions Ethene **→** CO<sub>2</sub> biological reaction Ethane

abiotic reaction

#### In Situ Degradation Pathways

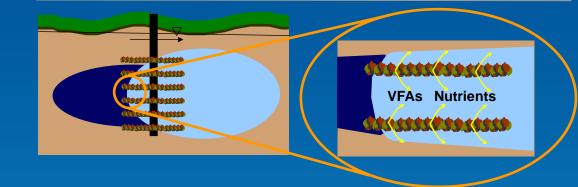


CDM Smith

Chlorobenzene Degradation pathway

#### **Hydraulic Fracturing**

- Oil and gas industry developed in the 1940s
- At HPS: viscous fluid (guar, crosslinkers, breaker, water) carried EHC® and in some cases sand to create fractures containing treatment amendment

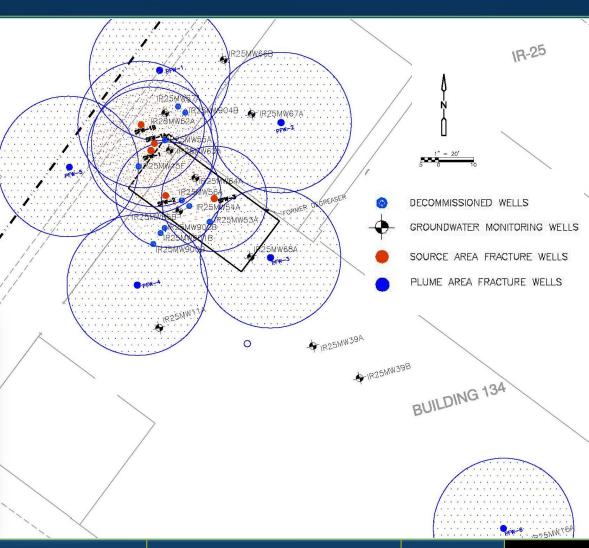




# Technology 1 Implementation: Hydraulic Fracturing/EHC® Emplacement

- 6 source fracture wells and 6 plume fracture wells
- 15- to 20-ft radius of amendment distribution
- Emplaced 13,419 lbs in source and 17,126 lbs of amendment EHC® in plume

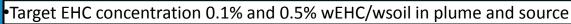






#### Hydraulic Fracturing and EHC™ Emplacement

	Depth interval for fractures, fracs	Mass EHC	Target Loading % EHC	
Frac Boreholes	initiated ~3 ft	(lb)	Met*?	Sand (lb)
PFW1	10-43	3700	1	1100
PFW2	10-33	3150	1	3300
PFW3	10-33	3150	1	3300
PFW4	10-33	3150	1	4400
PFW5	13-43	3540	1	0
PFW6	13-28	2300	1	2200
SFW-1, -1A, and -1B	14-36	5801	1	0
SFW2	13-23	1900	1	0
SFW3	13-40	7450	1	0



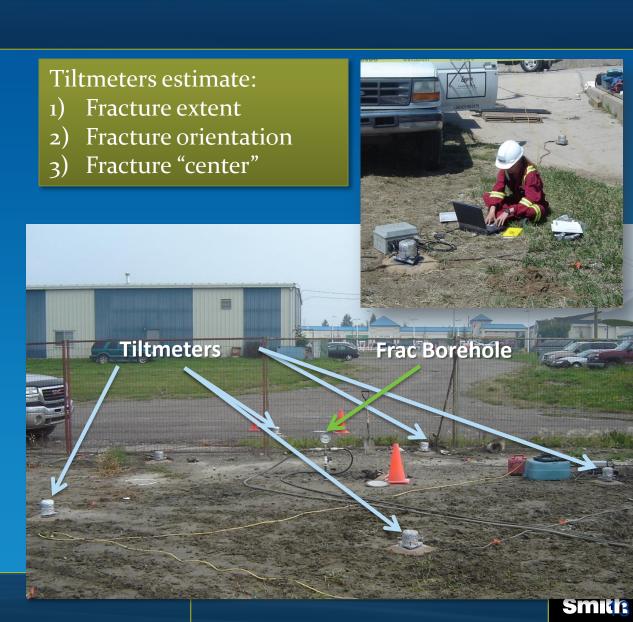
Range EHC dose for PF wells 0.09-0.11% wEHC/wsoil



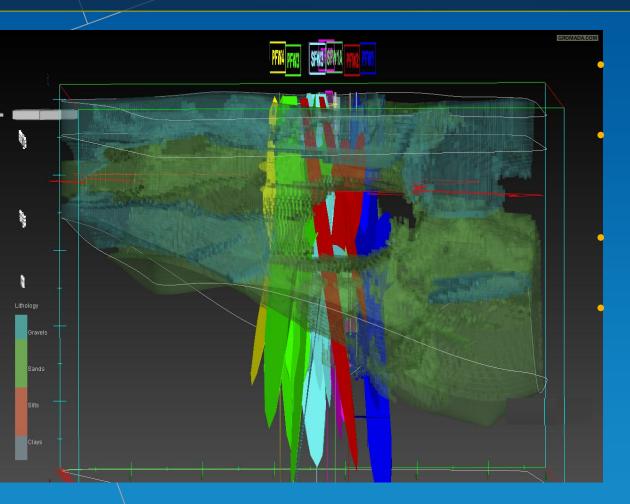
Range EHC dose for SF wells 0.36-0.63 % wEHC/wsoil

#### Evaluate Fracture Propagation: Tiltmeter Geophysics

- Analyzed tiltmeter data for 60 of 87 fracs
- Modeled fracs for every borehole except PFW6 (near IR26MW16A).



#### Results of Fracking: Amendment Distribution



Estimated 18 to 23-ft treatment radius

Geochemical conditions conducive to reductive dechlorination

Heterogeneous distribution of amendments.

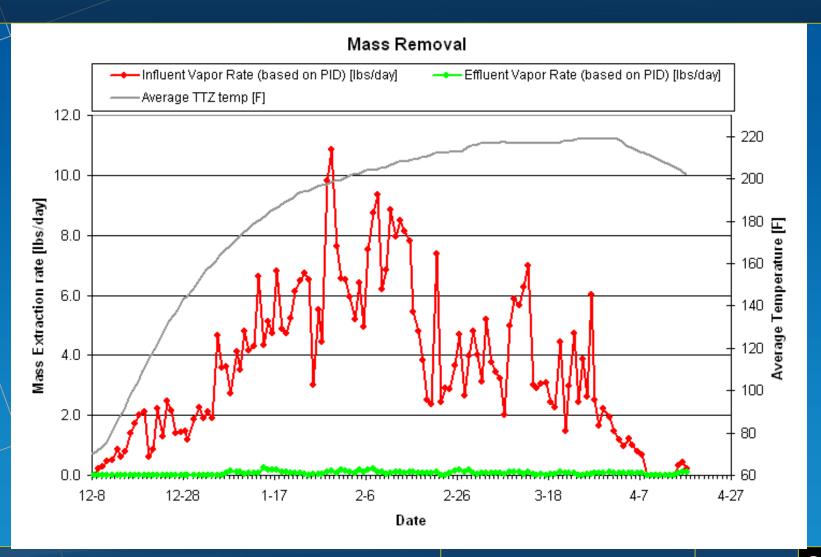
Evaluated technology for 4 months.



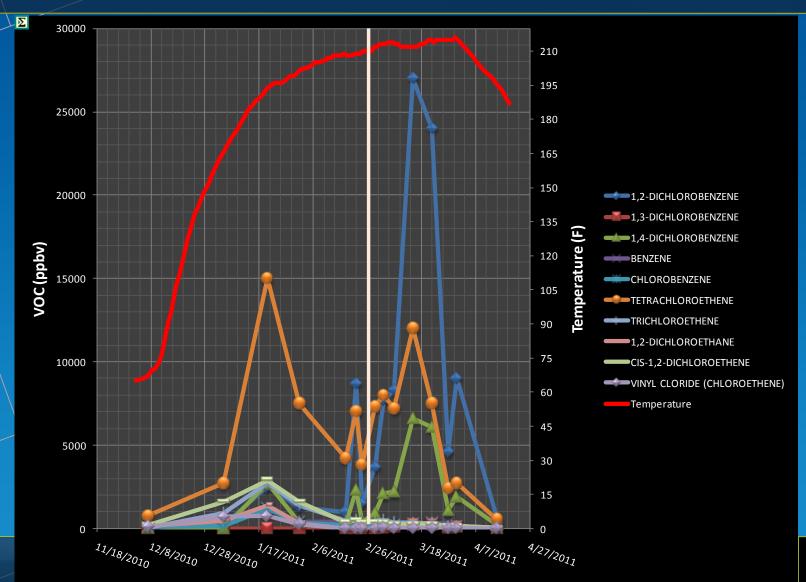
## Technology 2 Implementation: Thermal Conduction Heating



#### Contaminant Removal During TCH

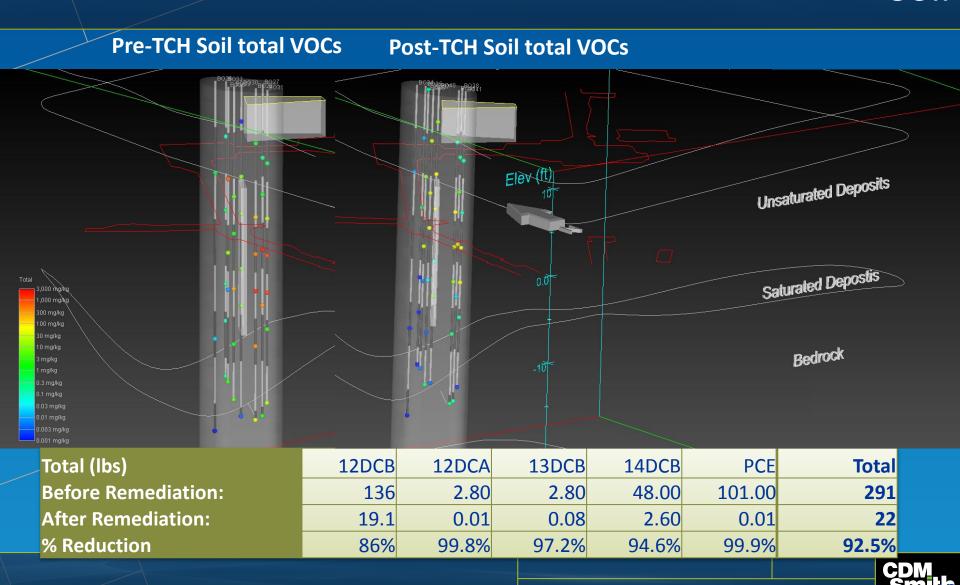


#### Contaminant Removal During TCH





## Contaminant Mass Before and After-Treatment in Soil



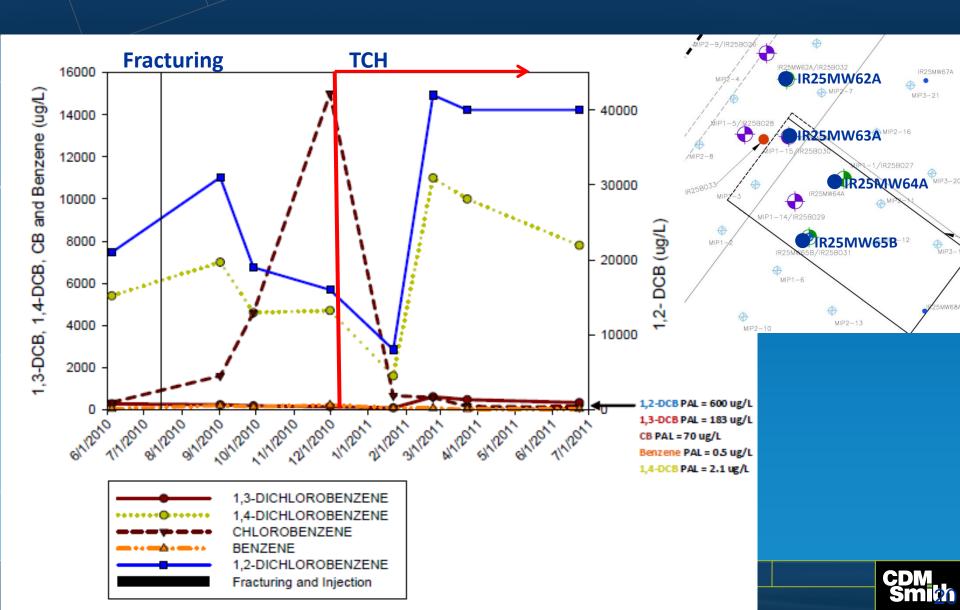
## Contaminant Mass Before and After-Treatment in Groundwater

	Parent Compounds					Reductive Daughter Products				
Total (lbs)	1,2-DCB	1,2-DCA	1,3-DCB	1,4-DCB	PCE	benzene	СВ	Cis-DCE	TCE	VC
Before Remediation:	4.7	0.7	0.01	1.5	0.6	0.03	0.2	2.1	0.2	0.6
After Remediation:	2.7	0.0	0.04	1.2	0.01	0.0	0.0	0.04	0.0	0.0
% Reduction	44%	100%	-300%	21%	99%	95%	96%	98%	78%	100%

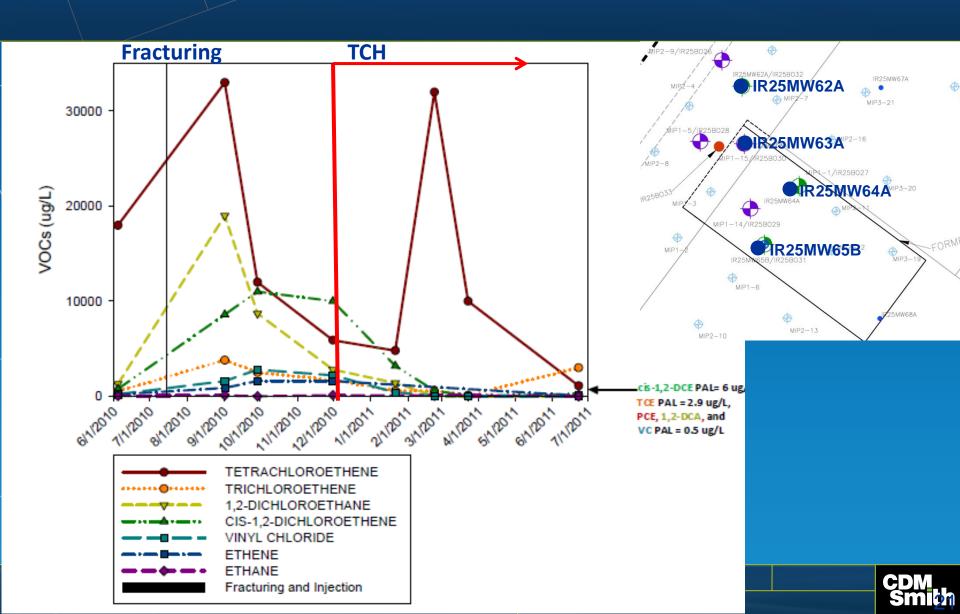
Total CoC Mass In Groundwater Pre-Treatment- 10.6 lbs Total CoC Mass In Groundwater Post-Treatment- 4.1 lbs



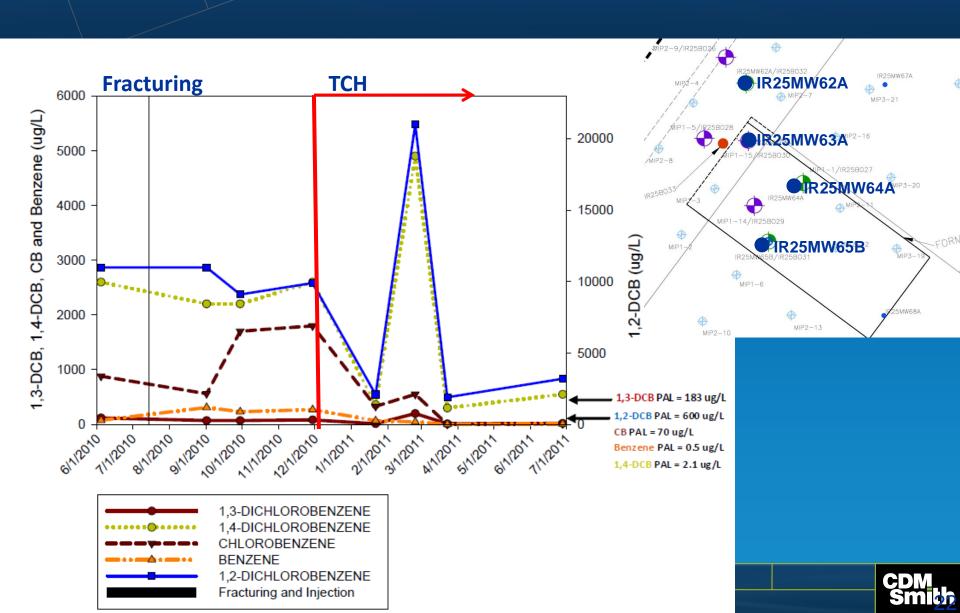
#### Chlorinated Benzenes: IR25MW63A



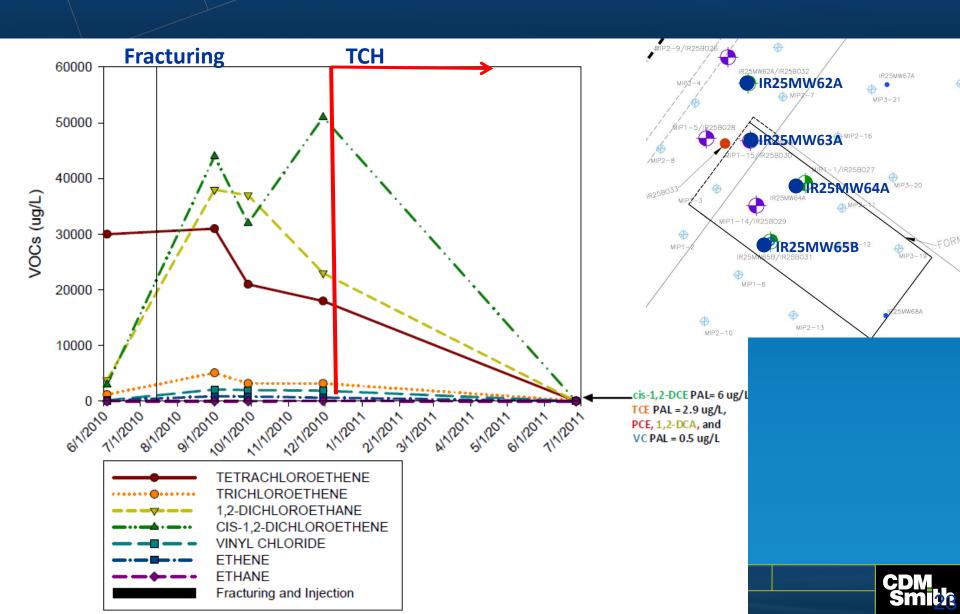
#### Chlorinated Ethenes: IR25MW63A



#### Chlorinated Benzenes: IR25MW65B



#### Chlorinated Ethenes: IR25MW64A



#### Conclusions: HPNS Treatability Study

- Fracture extents: 2.5 to 89 ft
  - Averaged 18-23 feet in the source area
  - Averaged 13-24 feet in the plume
- Treatment radius of influence > 20 ft
  - EHC® emplaced as discrete "sheets"
  - Diffusion of amendments created reducing conditions
- Fracturing/EHC <sup>®</sup>: 24-99.9% reduction in PCE and 1,2-DCA and 5-57% reduction in 1,2-, 1,3- and 1,4-DCB within four months.
- Biological degradation pathways predominated



#### Conclusions: Impact of Thermal Treatment

- Insignificant biological degradation at temperatures >70°C.
- Removed >90% of total VOC mass in soil
  - Lowest removal for 1,2-DCB (86%)
  - Highest removal for PCE (99.9%)
- Parent compound groundwater concentrations reduced :
  - 50-93% for 1,2-DCB, 1,3-DCB, 1,4-DCB, except in IR25MW63A
  - >94-100% for PCE and 1,2-DCA
- Degradation product concentrations reduced 61-99% for chlorobenzene/benzene except IR25MW62A and IR25MW63A, which increased (due to post-TCH attenuation of DCBs).
- Post-treatment polish from emplaced carbon and EHC ® will be evaluated over the next year.



#### Summary of Technology Performance

	Treatment Component	TC1	TC2	TC3	Total lbs removed
	Cost (\$) per cubic yard	<b>\$50</b>	\$1,950	\$28/\$32	
	Reduction (%) of PCE and 1,2-DCA	45.0%	99.0%	95.2%	
	Reduction (%) of 1,2-DCB, 1,3-DCB and 1,4-DCB	33.9%	1.34%	45.9%	
mpun	Reduction (%) of total PCE, TCE, 1,2-DCA, 1,2-cis-DCE, VC	33.0%	97.6%	93.2%	
	Reduction (%) of total 1,2-DCB, 1,3-DCB, 1,4-DCB, chlorobenzene, benzene	15.9%	25.5%	51.3%	
	Total DCB mass removed (lbs)	1.7	1.1	0.40	3.2
	Total PCE, 1,2-DCA mass removed (lbs)	5.25	6.36	0.09	11.7
Soil	Reduction (%) of PCE and 1,2-DCA mass	NA	99.98%	NA	
	Reduction (%) of 1,2-DCB, 1,4-DCB, 1,3-DCB mass	NA	88.3%	NA	
	Reduction (%) total VOC mass	NA	92.4%	NA	
	Total VOC mass removed (lbs)	NA	269	NA	269
	Total 1,2-DCB, 1,4-DCB, 1,3-DCB mass removed (lbs)	NA	165	NA	165
	Total PCE and 1,2-DCA mass removed (lbs)	NA	104	NA	104

# THANK YOU! Questions?