Reducing Time of Remediation at Clay and Fractured Rock Sites:

Marrying Permeability Enhancement with Remediation Chemistry

Presented by: Lowell Kessel, MS, PG
Email: lowell@CERESCorporation.com

C.E.R.E.S.
Remediation Products

ENVIRONMENTAL BUSINESS INTERNATIONAL INC.

C.E.R.E.S. Received the 2021 EBJ Remediation Products Technology Merit Award

C.E.R.E.S. Remediation Products

MTS® Metals Treatment Solution

EVO Emulsified Vegetable Oil

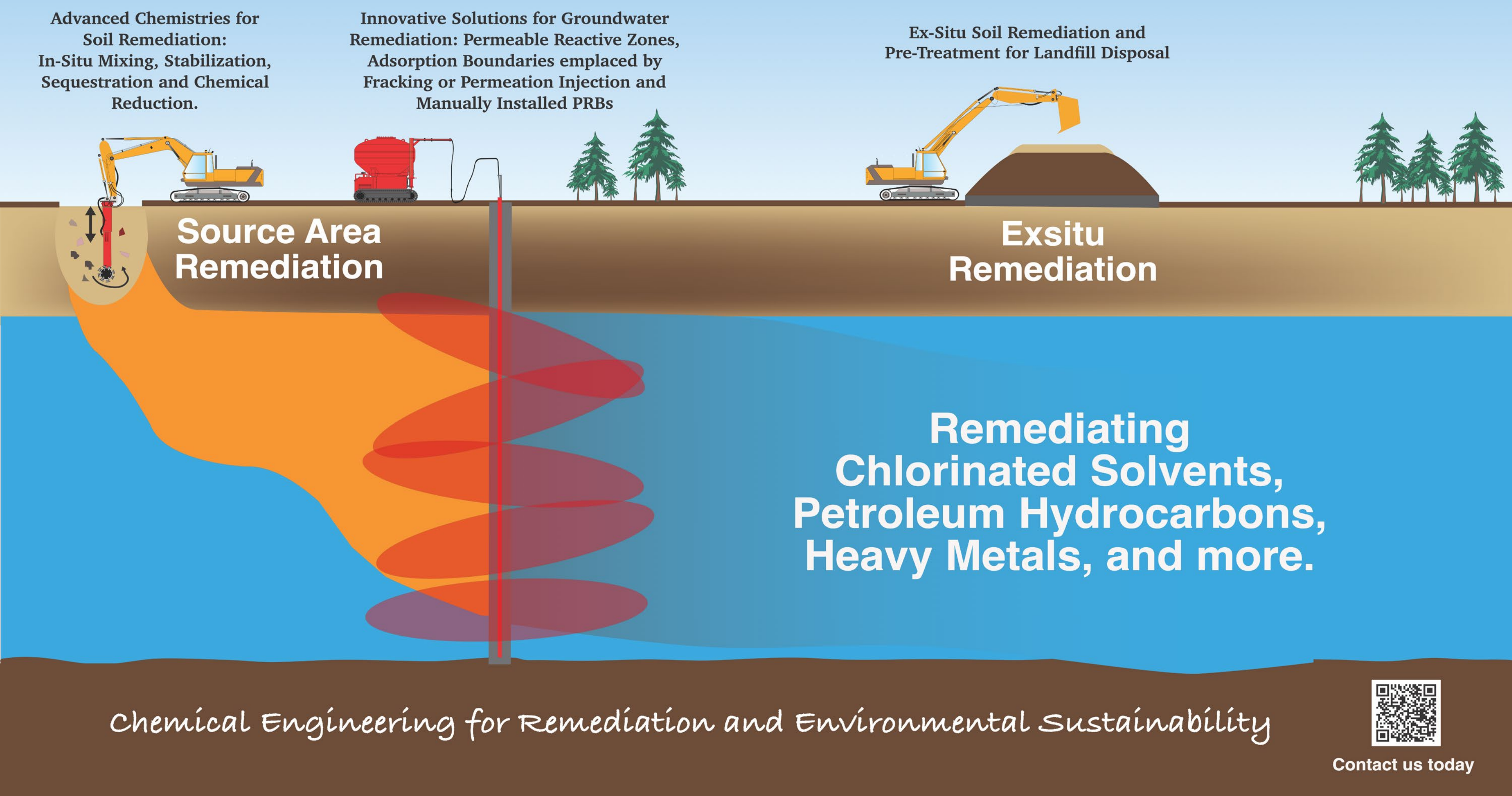
ZVI Zero Valent Iron

PTS™ Petroleum Treatment solution

PTS Advanced™ Surfactant Enhanced Remediation

PTBAC Petroleum Treatment Bacteria

iPAC Injectable Powder Activated Carbon



Delivered to Clients Globally

Approved at US EPA and State Agency site cleanups

C.E.R.E.S. Products = Solutions

Chemical Reduction and Sequestration (Heavy Metals and Organics)

- **Metals Treatment Solution (MTS®)-** the most robust, economical solution compared to current commercially viable chemistries
- **Zero Valent Iron (ZVI) –** Abiotic reduction of chlorinated compounds and others. From 1 micron to mm size available.
- **iPAC- injectable powder activated carbon –** less than 44 micron scale high adsorption carbon for in-situ remediation applications.

Bioremediation (Chlorinated Solvents, Petroleum & select Metals)

- **Petroleum Treatment Solution (PTS)-** Low cost and very effective biostimulant for petroleum hydrocarbon bacteria
  - **PTS Advanced -** Low cost and very effective biodegradable surfactant
  - **Petroleum Bacteria (PTSBac)-** Bacteria consortium specifically designed for long chain petroleum hydrocarbons
- **Emulsified Vegetable Oil (EVO)-** Effective for chlorinated solvents, nitrate and some metals reduction.

C.E.R.E.S. Services

TURN KEY services available to perform all aspects of remediation scope of work

Technical Support (free)

Site Evaluations for remediation feasibility assessment

Data gap evaluations and guidance on design parameters

Preliminary estimates of product demand

Remediation design approach guidance

Bench scale study guidance on reagent dosage and preparation

Product Samples

Bench Scale Treat-ability Study Services

Batch or Column studies

Heavy metals stabilization and sequestration dosage studies

Zero Valent Iron (ZVI) site specific kinetic rates studies

Bioremediation and bioaugmentation performance studies

Ex-situ and In-situ applications for soil and groundwater remediation

Feasibility assessment support

Subcontracted Field Services

Pilot Scale Execution

Ex-situ or In-situ remediation including soil mixing, injection, trenching,

Pilot scale design in accordance with local agency oversight guidance and requirements

Support preparation of workplans for submittal to local agencies including supporting materials

Permit applications like WDR or similar

Field services available to perform all aspects of pilot test

Full Scale Execution

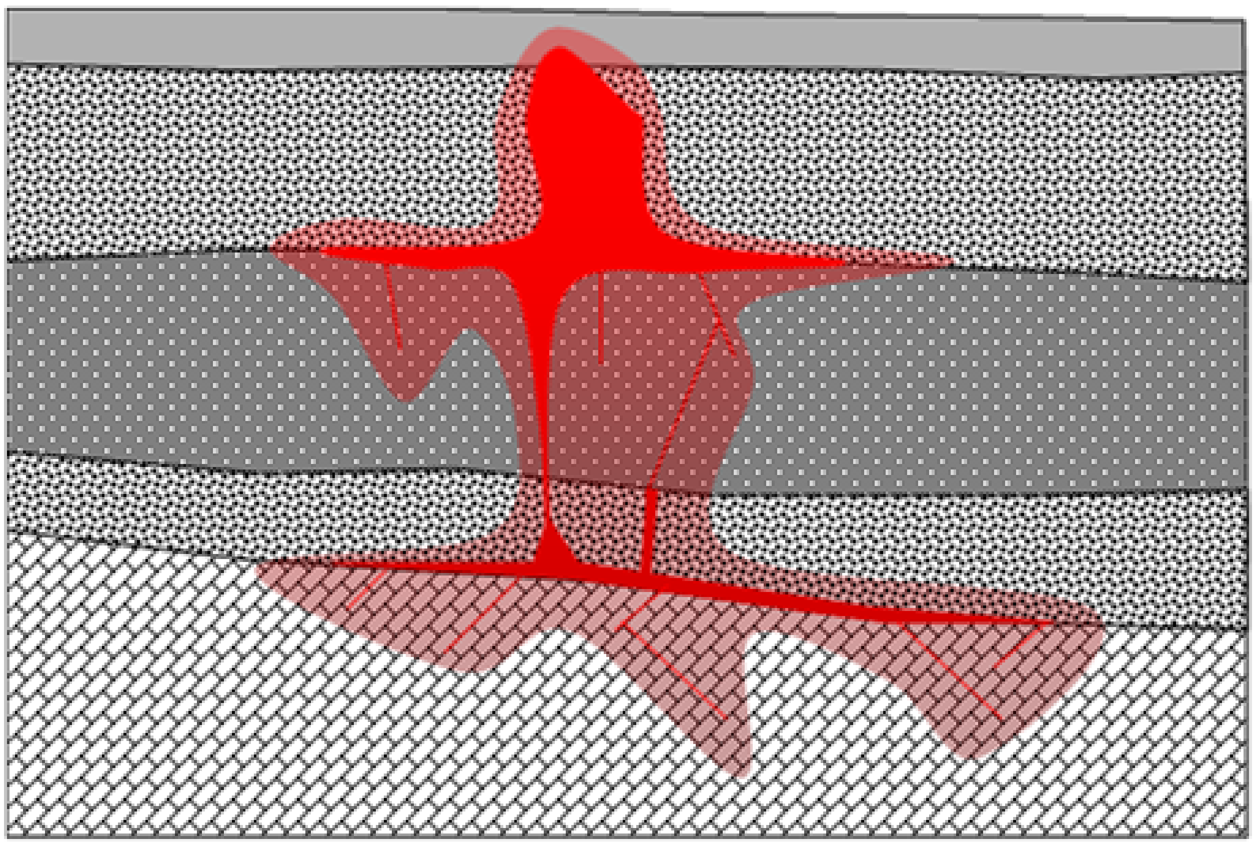
Ex-situ or in-situ remediation including soil mixing, injection, trenching,

Full scale design in accordance with local agency oversight guidance and requirements

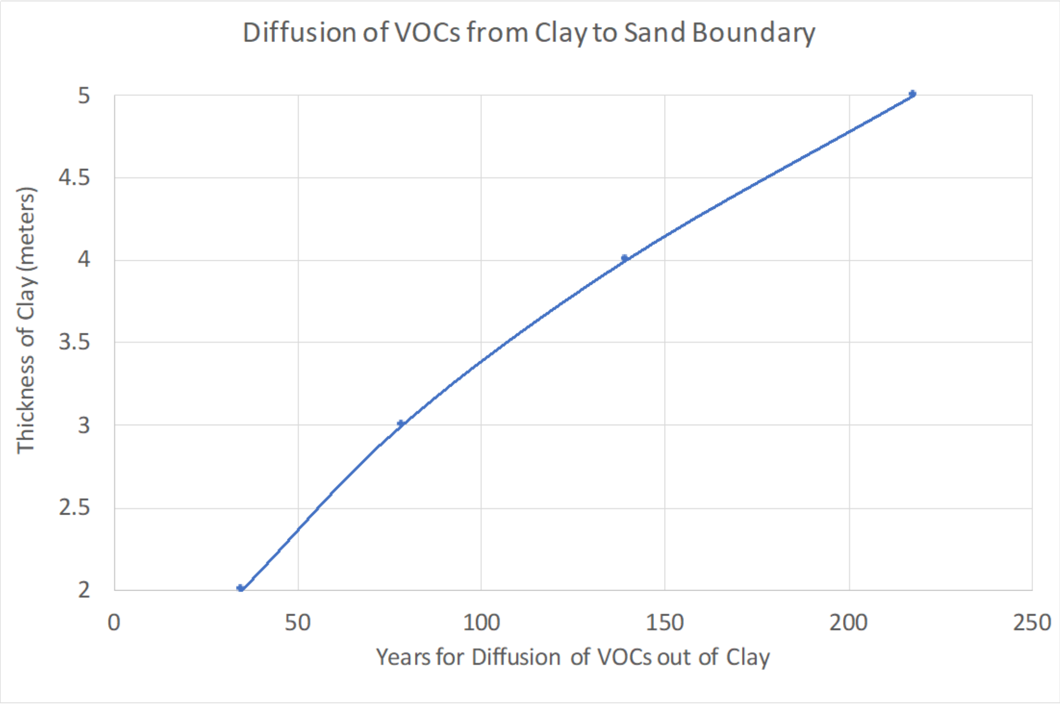
Preparation of full scale design workplans for submittal to local agencies including supporting materials

Permit applications like WDR or similar

Low Permeability Challenges



Typical Approach at Diffusion Limited Sites



Time of Remediation:
10' to 100's of Years to achieve remediation goals if diffusion dominates VOC flux

- Assess feasibility of reagents to target contaminants and select most viable reduction chemistry.
- Inject in the source area and plume by traditional injection methods. Too often it is bottom up injection based on contractor recommendation.
- Observe rebound after 6-18 months and repeat injections. Sometimes 3-4 events over a 10 year period. Everyone is frustrated now…

Time to Change the Rules: Permeability Enhancement

Proppants to the rescue!

- Proppants are sand or similar particulate material suspended in water or other fluid and used in hydraulic fracturing (fracking)

Benefits Include:

- Keeps fissures open after injection
- Provides high-K pathways for groundwater to move through and VOCs to diffuse into.
- Increases flux rate of VOCs (from adsorbed to dissolved)

Key Factors to Successful Use of Reagents with Proppants

Physical properties (size)

- Reagent Size vs fracture aperture
- Reagent density

Longevity or resiliency (how long will it last?)

Application limitations (what equipment?)

Remediation design goals

- Soil remediation
- Source (hot spot) reduction
- Plume reduction
- Plume control (PRB)

Composition (Chemistry)

Stoichiometric demand

biochemical donor / acceptor demand

Secondary Reactions

Precipitation resulting in the reduction in permeability and effective porosity

Back-diffusion from secondary porosity fissures and fractures

pH induced increases in non-target contaminants

In-Situ Injection and Fracturing
How do we inject reagents with proppants?

Injection Design Calculations

- **Permeation Injection** – Injection of soluble reagents into soil. Must move through soil pore throat at low pressure.
- **Fracture Injection** – Injection of suspended solids reagents through created pathways in soil at moderate to high pressures.

Flow Rate Calculations

$$\mathbf{Q = 2 * \pi * K * L * \frac{\Delta H}{\ln(\frac{L}{r_w})}}$$

$K = 9.4*10^{-8}$ m/s
L = 4.6 m (length of well screen)
$r_w = 0.075$ m (borehole radius)
$\Delta H = 11$ m (ΔH is maximum injection pressure based on estimated fracture initiation pressure)
$\boldsymbol{Q = 2 * \pi * 9.4*10^{-8}}$ (m/s)$\boldsymbol{*4.6}$(m)$\boldsymbol{*11}$(m)**/(ln(4.6** (m)**/0.075**(m)**))**
$\boldsymbol{Q = 7.3 * 10^{-6}\ m^3/s \rightarrow\ 0.44\ L/min}$

Predicted: 0.4 L/min
Observed: 0.2 – 0.5 L/min
Example from silty clay till site injecting 100% soluble substrate via injection wells

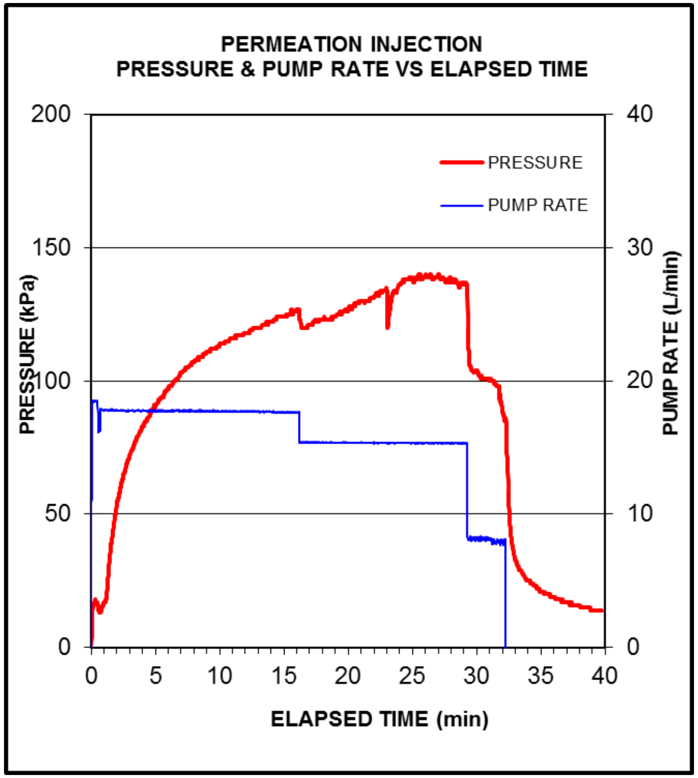
Reagent Particle Sizing

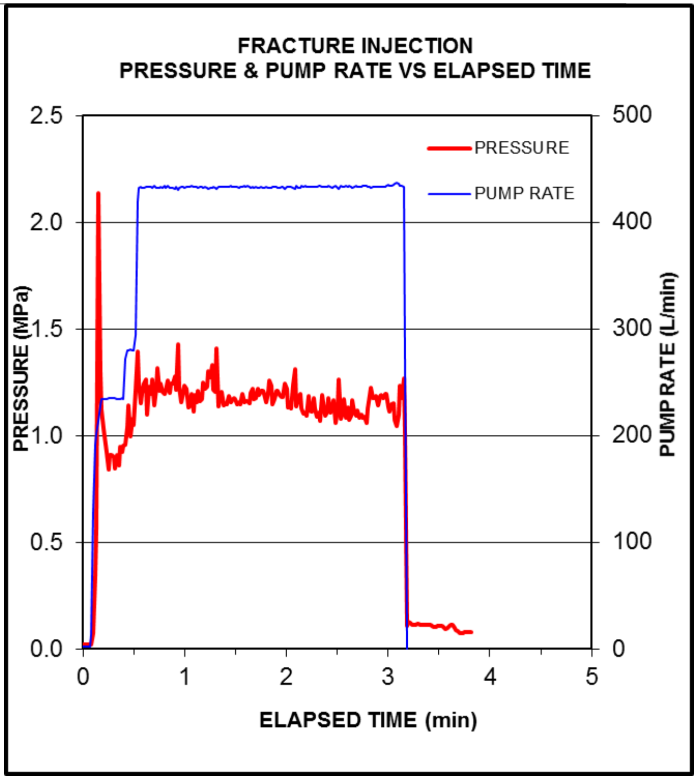
$$Ps < \sqrt{(K * 1.04 * 108)/7}$$

For slurry injections, estimate maximum injectable particle size to determine if permeation injection is possible, if not, then fracture injection for sure!

<u>To avoid screen out during permeation injection, the particles must pass through the pore throats in the aquifer/soils.</u>

Fracture vs Permeation Pressure vs Time Charts

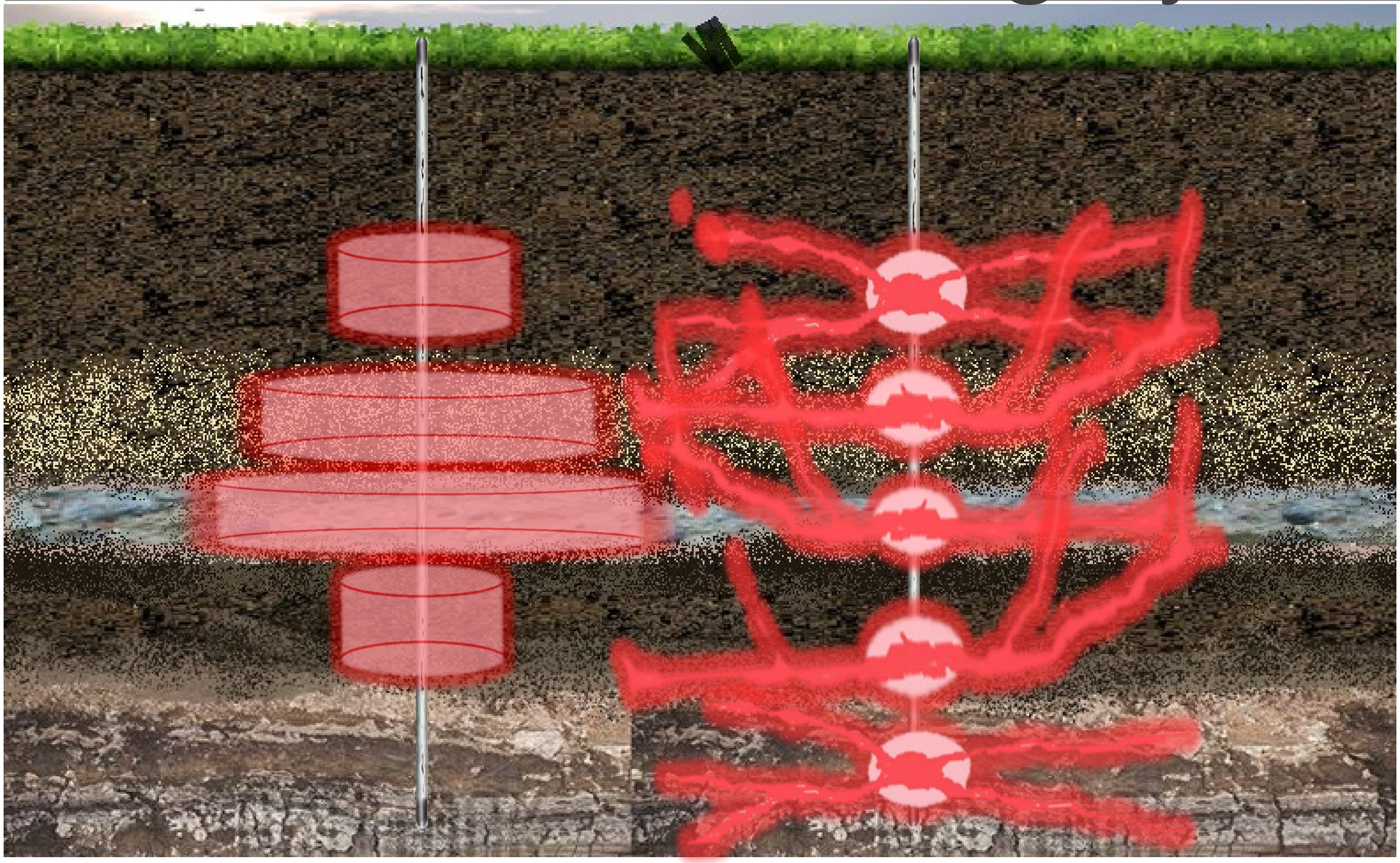




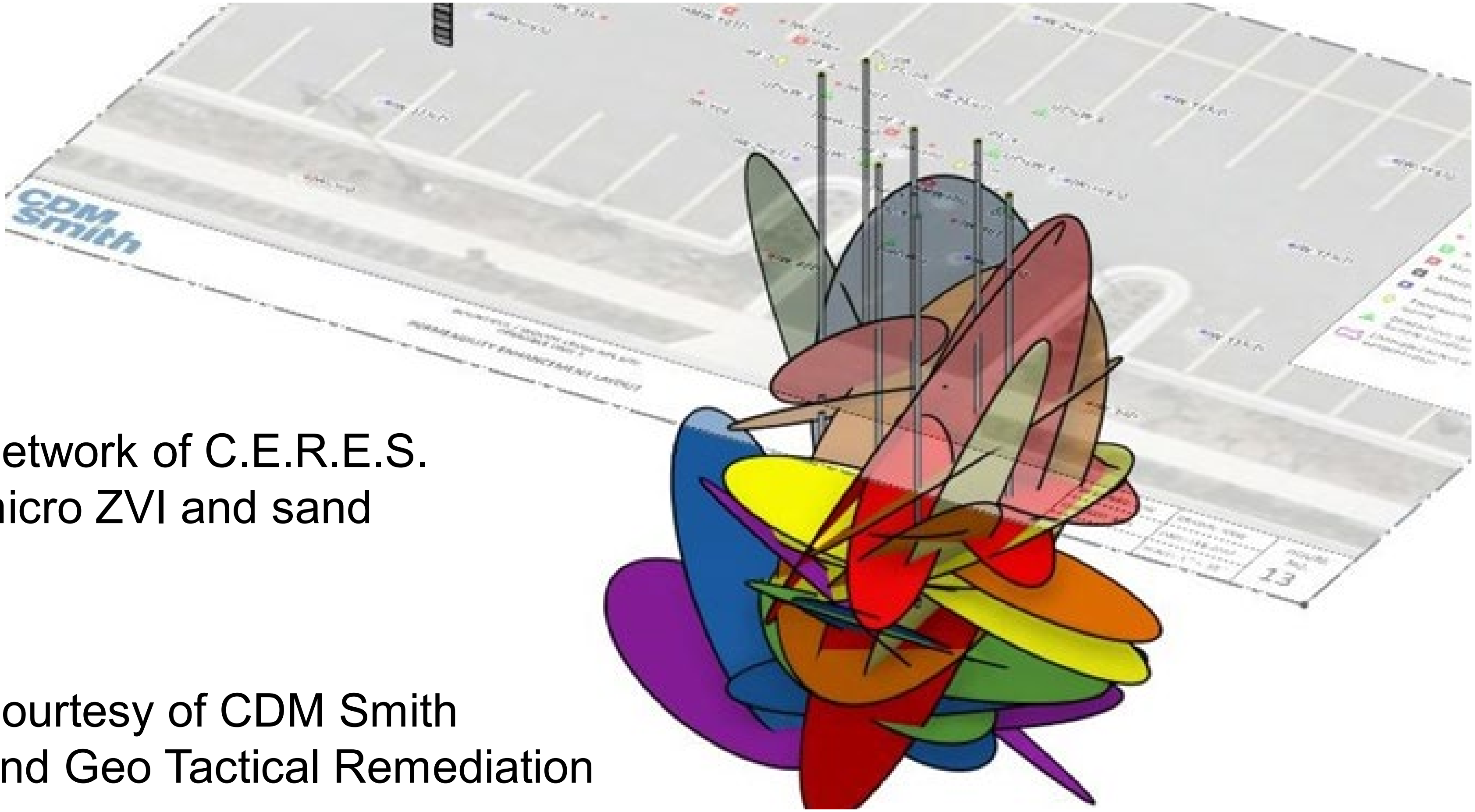
Permeation Injection
Note: Gradual increase in pressure requiring pump rate reductions.

Fracture Injection
Note: Sharp rise and fall of pressure during initial pumping.

Idealized Illustrations Permiation vs. Fracturing injection



True 3D Fracture Imaging with Tilt Meter Technology

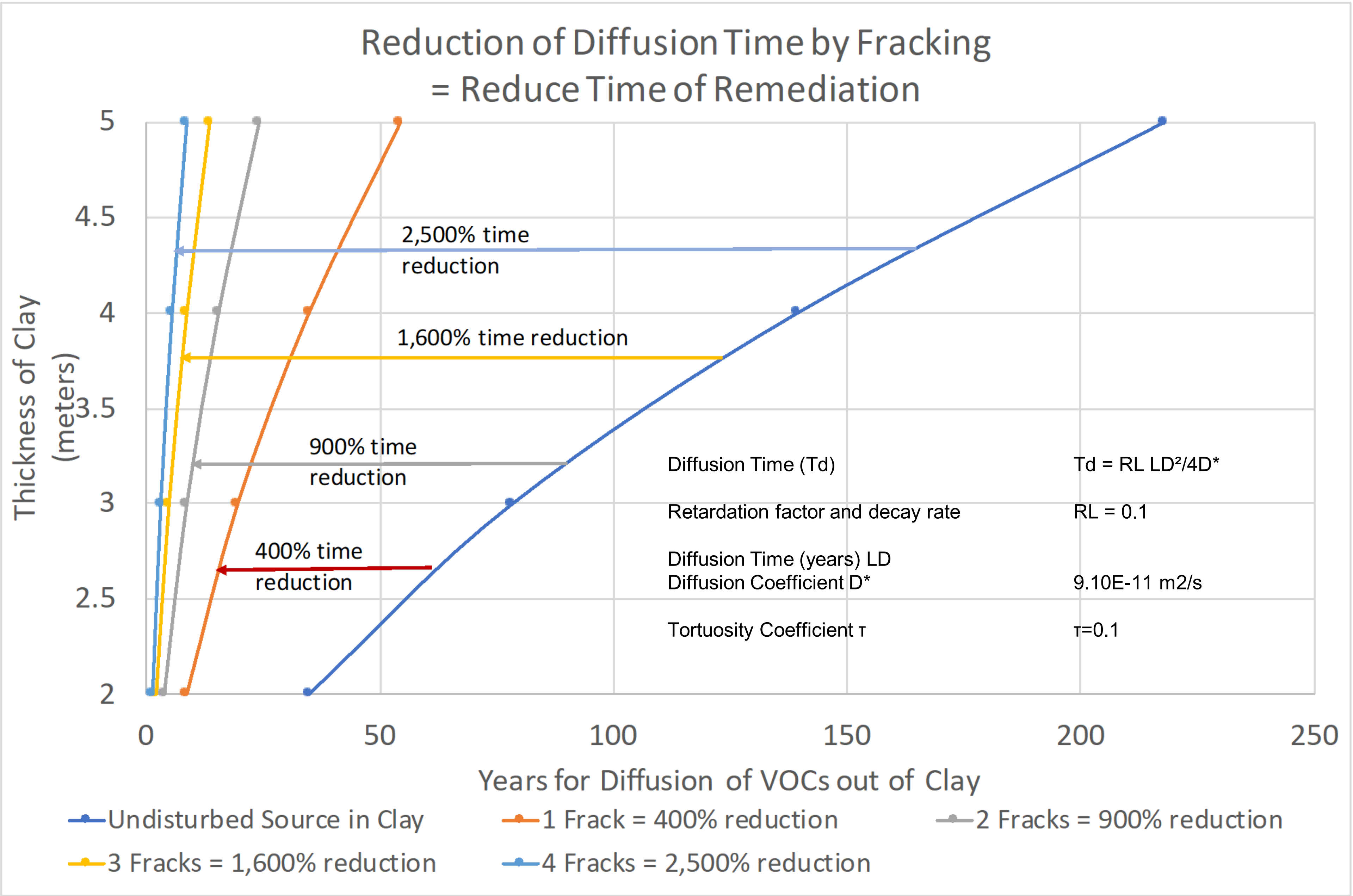


Network of C.E.R.E.S.
micro ZVI and sand

Courtesy of CDM Smith
And Geo Tactical Remediation

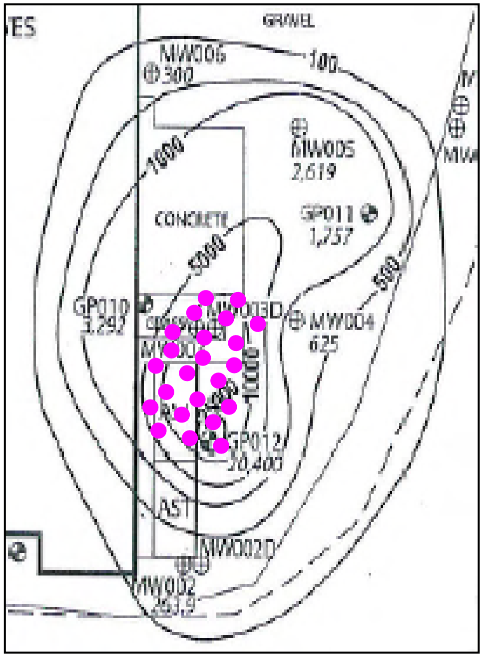
Increased Contact Area

Contact Method	BH Diameter (in)	BH Circumference (ft)	Frac Radius (ft)	Frac Interval (ft)	Frac Area (ft^2)	Unit Contact Area per Injection Interval Length (ft^2/ft)
DP Injection 2.5" OD	2.5	0.7				0.7
DP Injection 3.5" OD	3.5	0.9				0.9
Injection well 6" OD	6	1.6				1.6
Injection well 12" OD	12	3.1				3.1
Injection well 36" OD	36	9.4				9.4
10 ft radius fractures at 5 ft vertical spacing			10	5	315	125
10 ft radius fractures at 2 ft vertical spacing			10	2	315	315
15 ft radius fractures at 5 ft vertical spacing			15	5	705	285
15 ft radius fractures at 2 ft vertical spacing			15	2	705	705
25 ft radius fractures at 5 ft vertical spacing			25	5	1965	785
25 ft radius fractures at 2 ft vertical spacing			25	2	1965	1965

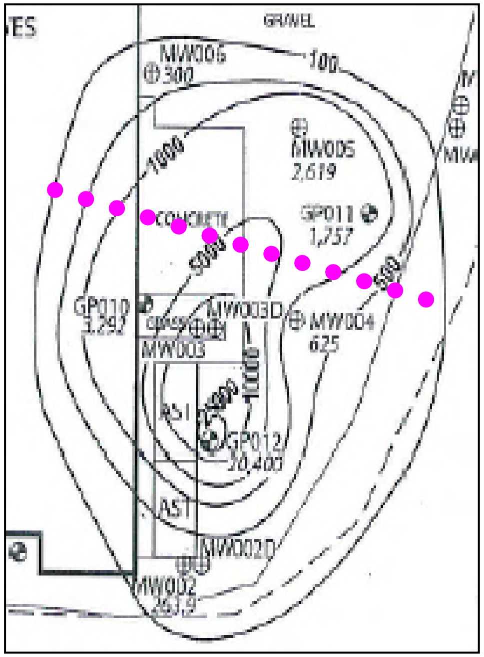

Reduction of Diffusion Time by Fracking
= Reduce Time of Remediation
Thickness of Clay (meters)
5
4.5
4
3.5
3
2.5
2
0
50
100
150
200
250
Years for Diffusion of VOCs out of Clay
2,500% time reduction
1,600% time reduction
900% time reduction
400% time reduction
Diffusion Time (Td)
Td = RL LD²/4D*
Retardation factor and decay rate
RL = 0.1
Diffusion Time (years) LD
Diffusion Coefficient D*
9.10E-11 m2/s
Tortuosity Coefficient τ
τ=0.1
Undisturbed Source in Clay
1 Frack = 400% reduction
2 Fracks = 900% reduction
3 Fracks = 1,600% reduction
4 Fracks = 2,500% reduction

In-Situ Application Options

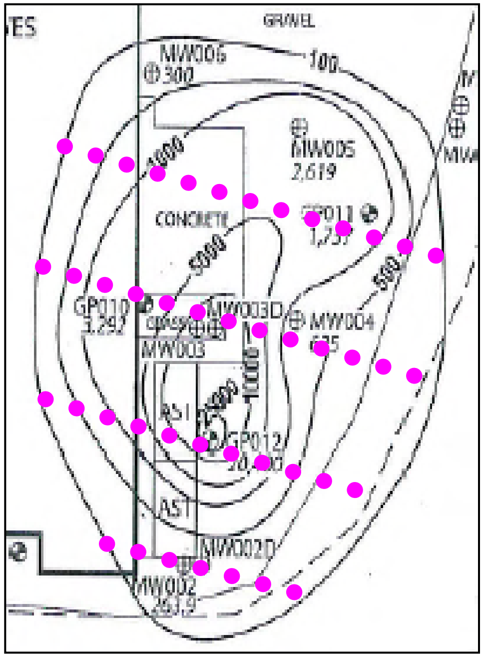
Source Area/ Hotspot Treatment

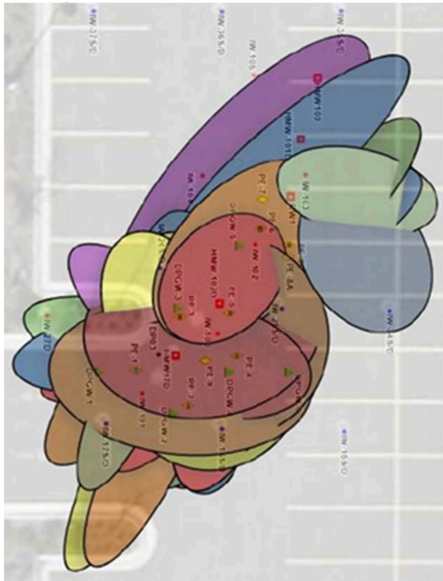


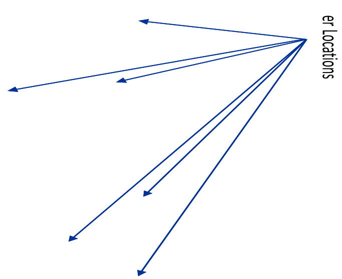
Injection PRB for Plume Control

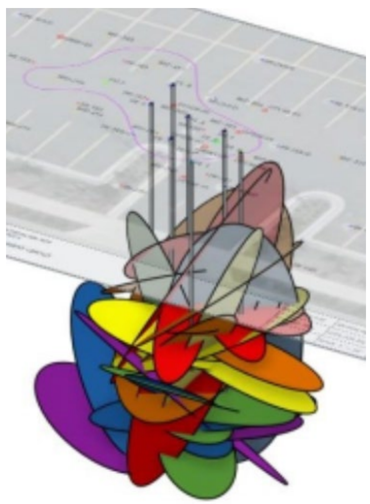


Plume Treatment









Key Planning and Application Considerations

1. One injection event or multiple events?
   - Available pore volume vs. injected volume

2. Application method
   - DPT
   - Permanent Injection Wells
   - High Pressure Fracturing
     - Pneumatic or hydraulic fracturing: The creation of cracks
     - Pressure pulse technology (PPT): high-frequency pressure pulses
   - Soil Blending Ex-Situ and In-Situ

3. ROI and number of injection points?
   - **Tiltmeter Mapping of Amendment Fractures**
   - ROI increases with depth…fewer injection points
   - ROI increases with PV displacement
   - * Spreadsheet Modeling may help in this evaluation

Radius Of Influence Verification

Verification of direct product placement:

Visual observation of fractures in soil cores.

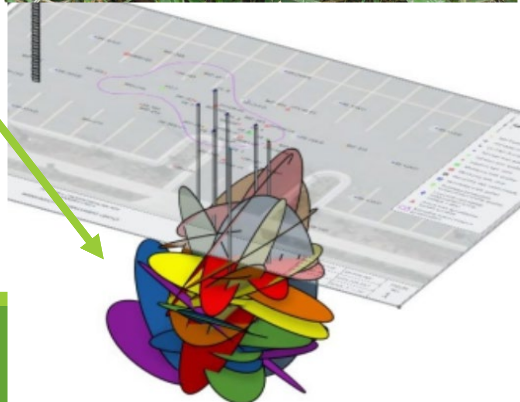
Magnetic separation of ZVI from soil cores.

Monitoring of ground deformation using uplift stakes

Tiltmeter Mapping of Amendment Fractures

Extended zone of groundwater influence:

Groundwater Indicator Parameters (TOC, inorganic, geochemical and redox parameters)



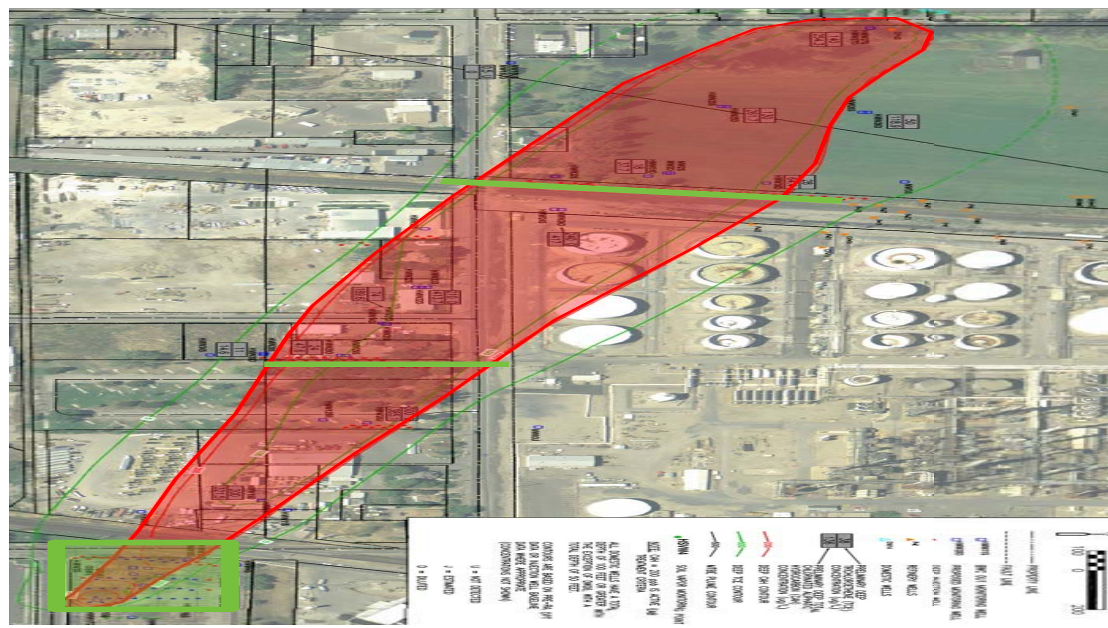
Case Studies

ORGANIC AND HEAVY METAL IMPACTED SITES

Superfund Case Study–Bountiful/Woods Cross Operable Unit

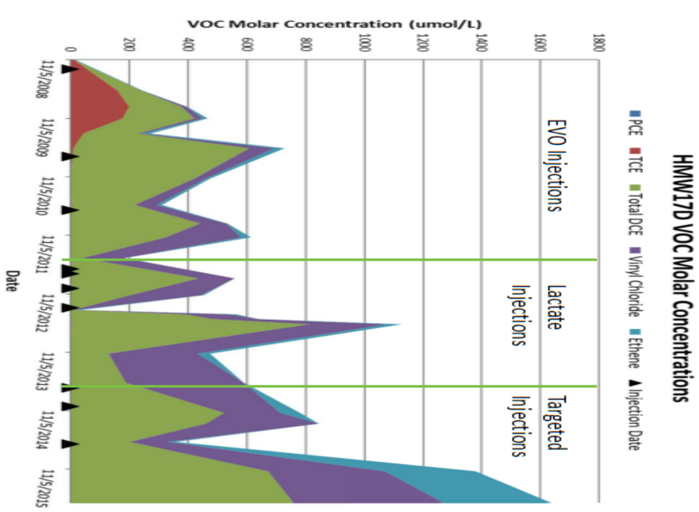
- Dissolved plume > 1 mile
- Interbedded Sands/silts/clays
- Residual DNAPL In source area
- Bioremediation

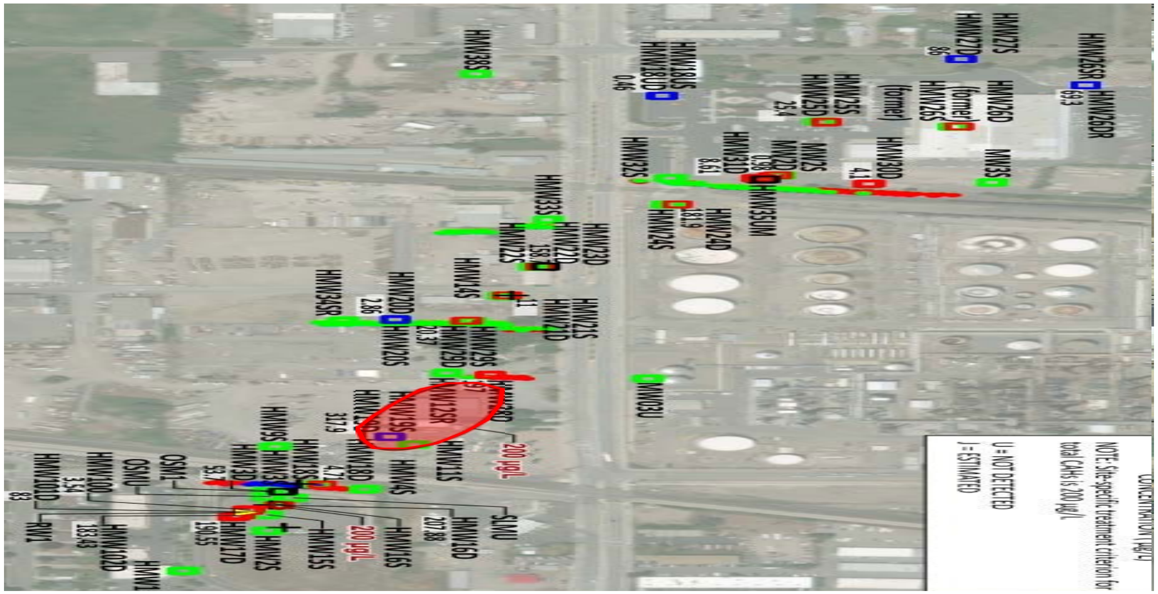
- 2009 Biobarrier 1 and source
- 2011 Biobarriers 2 and 4
- 2013 Targeted Bio Injections



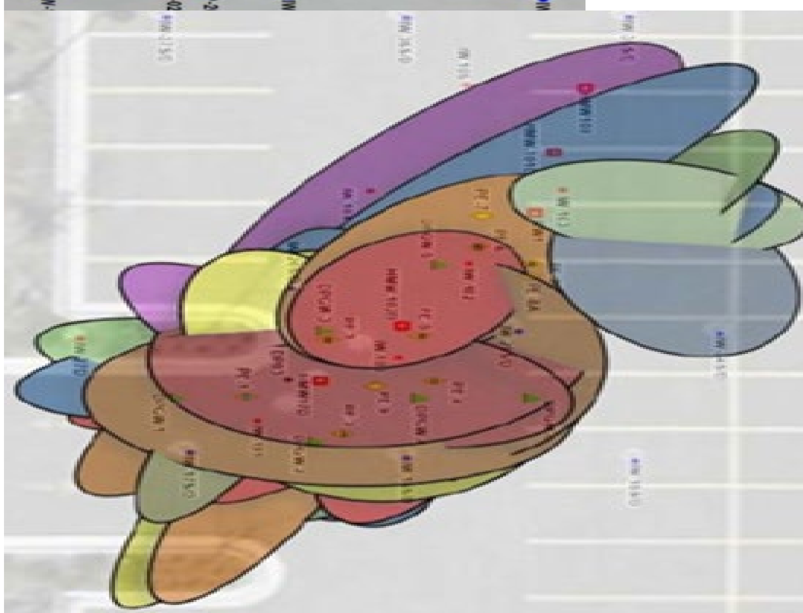
Source Area Challenged with Low Permeability Soils

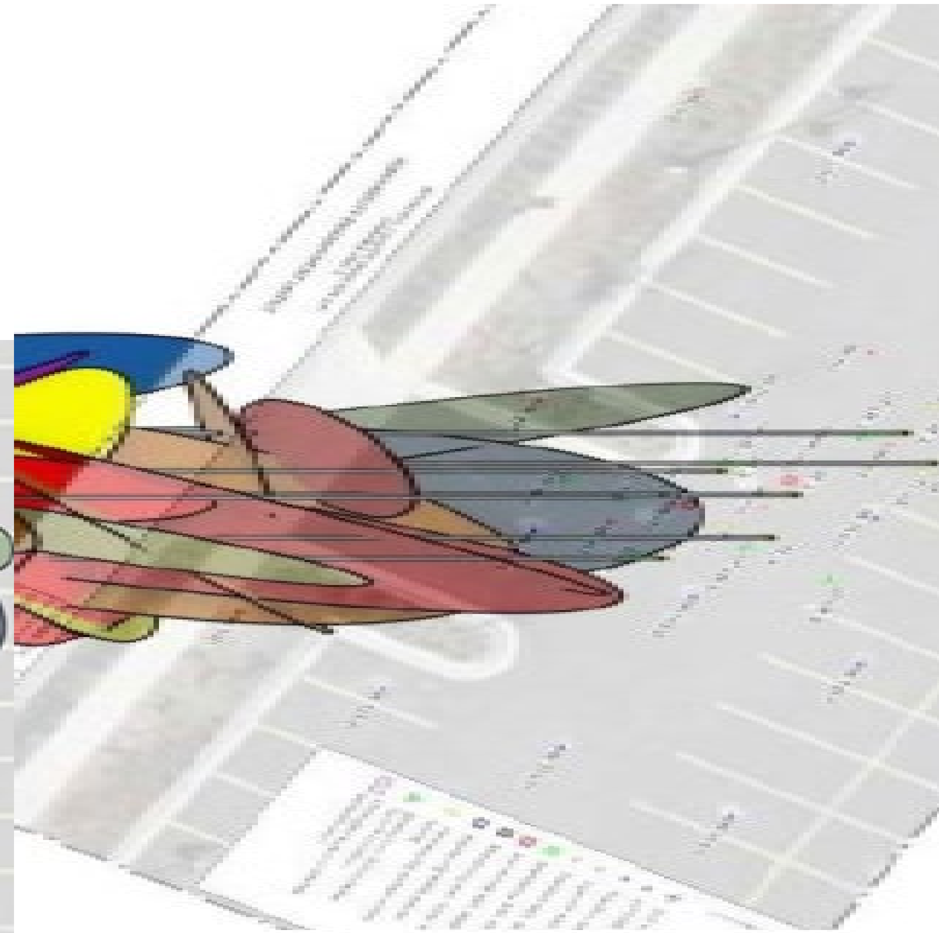
- Plume Treatment mostly achieved with Emulsified Vegetable Oil and bioremediation.
- Source area requires more aggressive options and solution to low permeability soils and residual DNAPL.



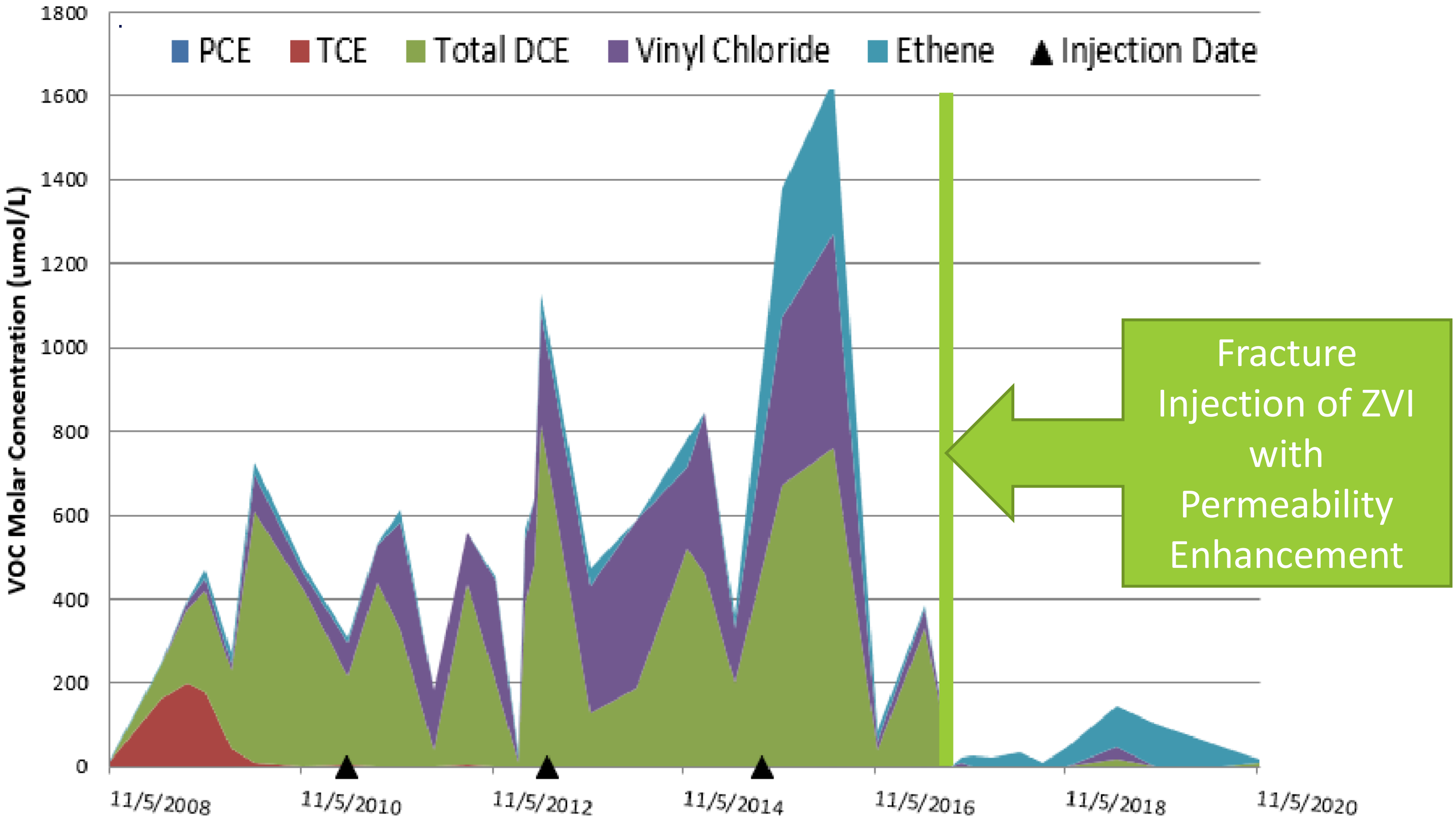


ZVI Injections at Source with Permeability Enhancement

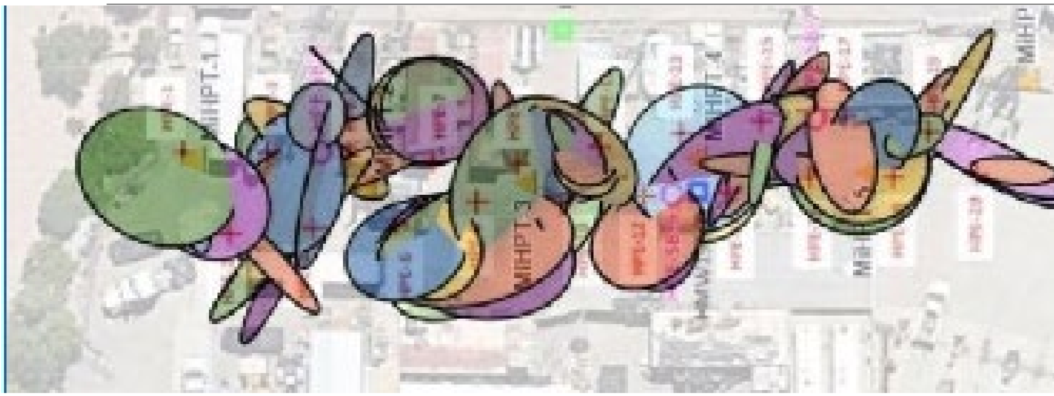


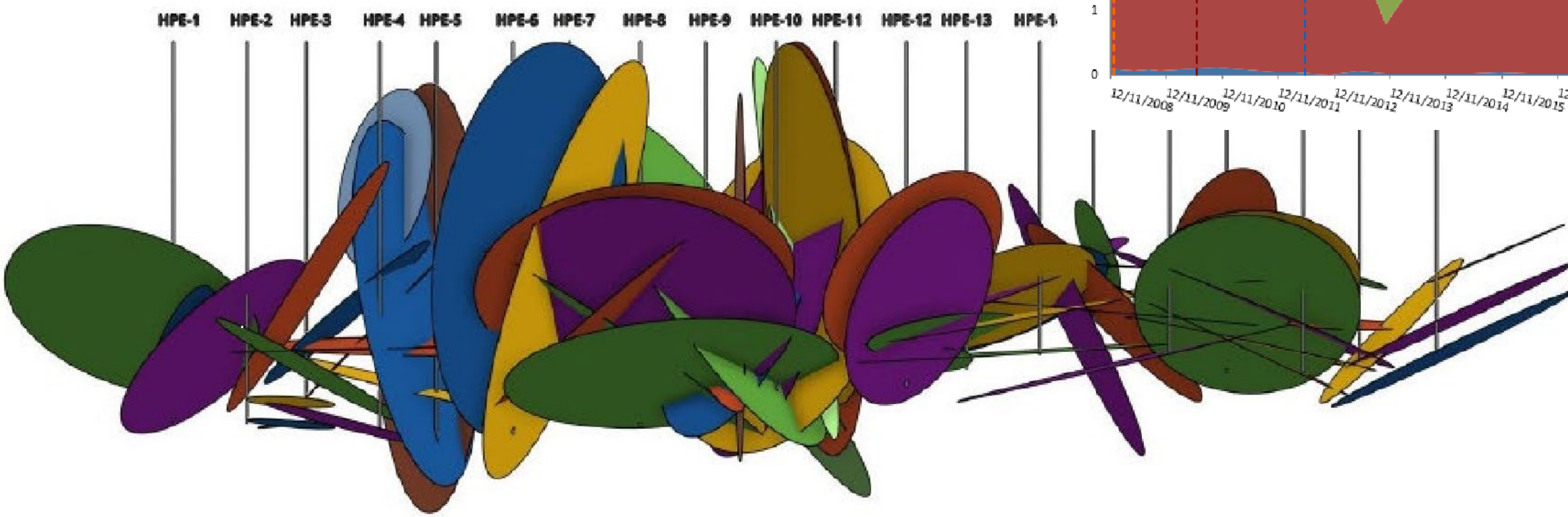


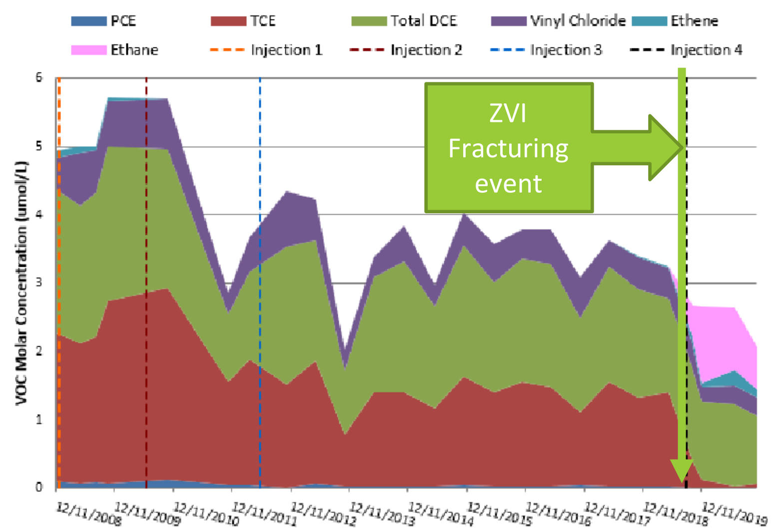
ZVI and Permeability Enhancement
Results = 99.5% reduction in 7 months



Plume Area Injections







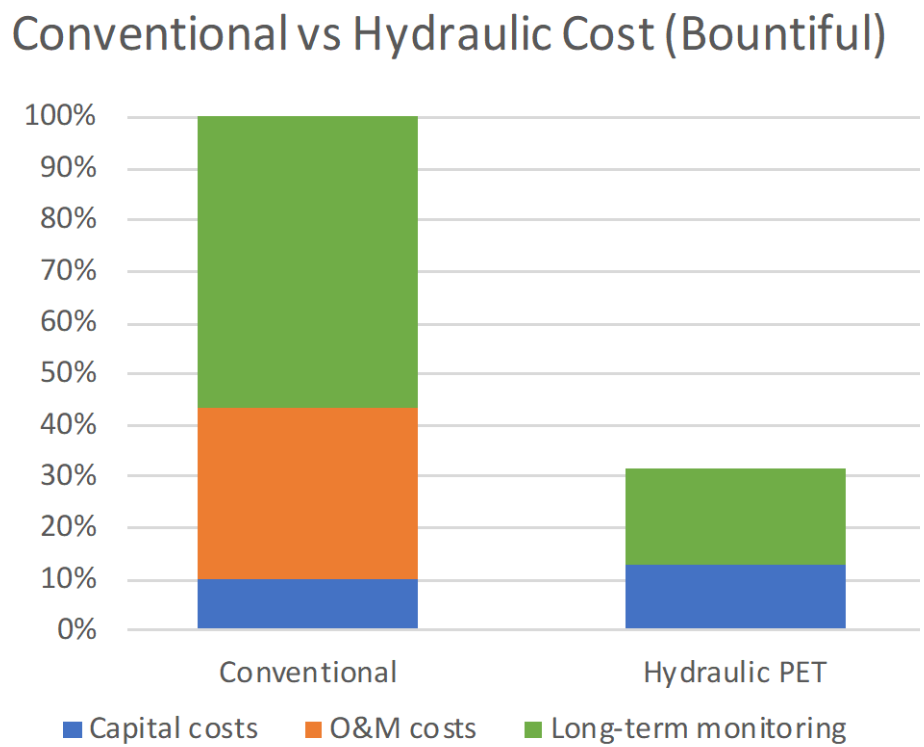
Cost Comparisons- Plume

Approach	Cost	Duration	Years to MCLs
Continue biobarrier injections	~$300k per event	10+ years, 3-4 year intervals	70+
Hydraulic permeability enhancement	~$500k	Single event	<10

Courtesy of CDM Smith

Cost Comparisons- Source Area

	Conventional Injections	HPE
Mass Reduction	44%	99.4%
Time	1 year	4 months
Net Present Value Total Cost	$1.47M	$463K



Courtesty of CDM Smith

Sandstone Aquifer Case Study:

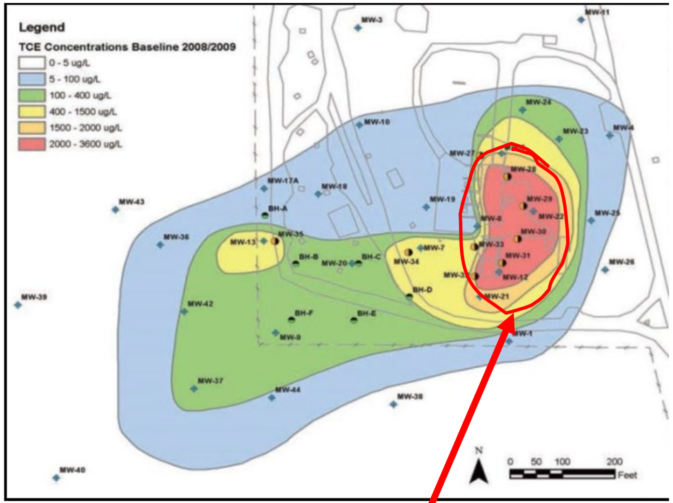
Site: Former US Air Force Missile Site in Colorado, USA

Contaminant: Trichloroethylene (TCE) up to 4,000 ppb

Geology: Fractured sandstone and siltstone bedrock

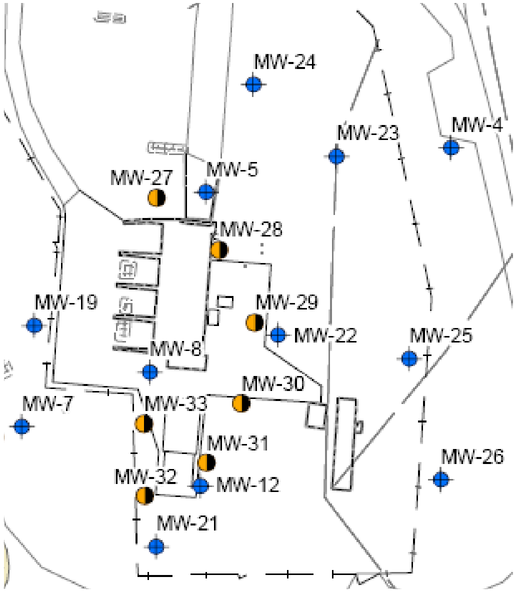
Groundwater Plume in Sandstone aquifer and remediation criteria of 5ug/l

Source Area / Plume



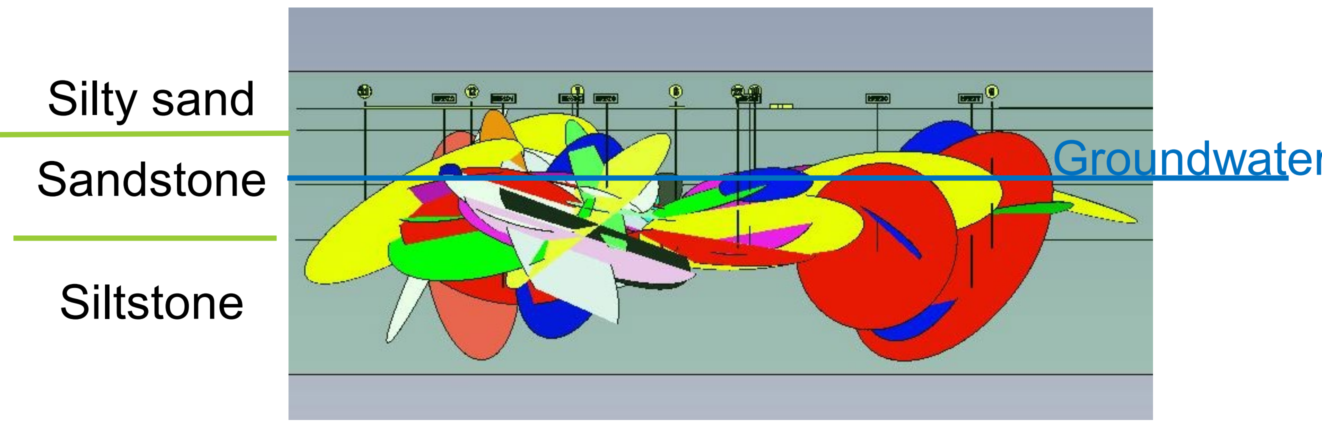
Injection into source area

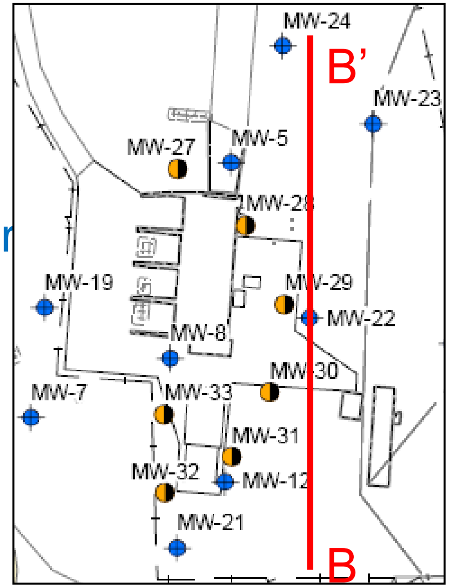
Bedrock Fracture Imaging- Tilt Meters



- Fracture imaging conducted at 7 boreholes locations.

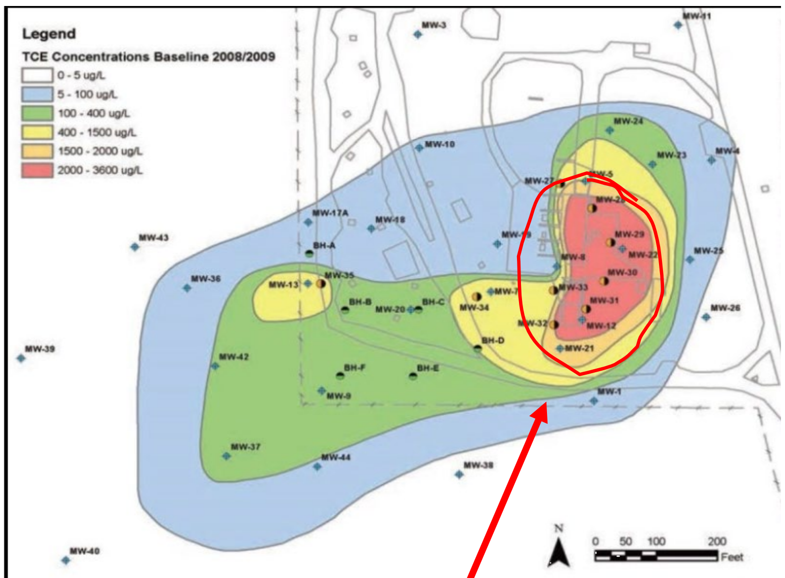
Fracture Imaging of the ZVI and substrates – Tilt Meters





Source Area Treatment Results

Source Area / Plume



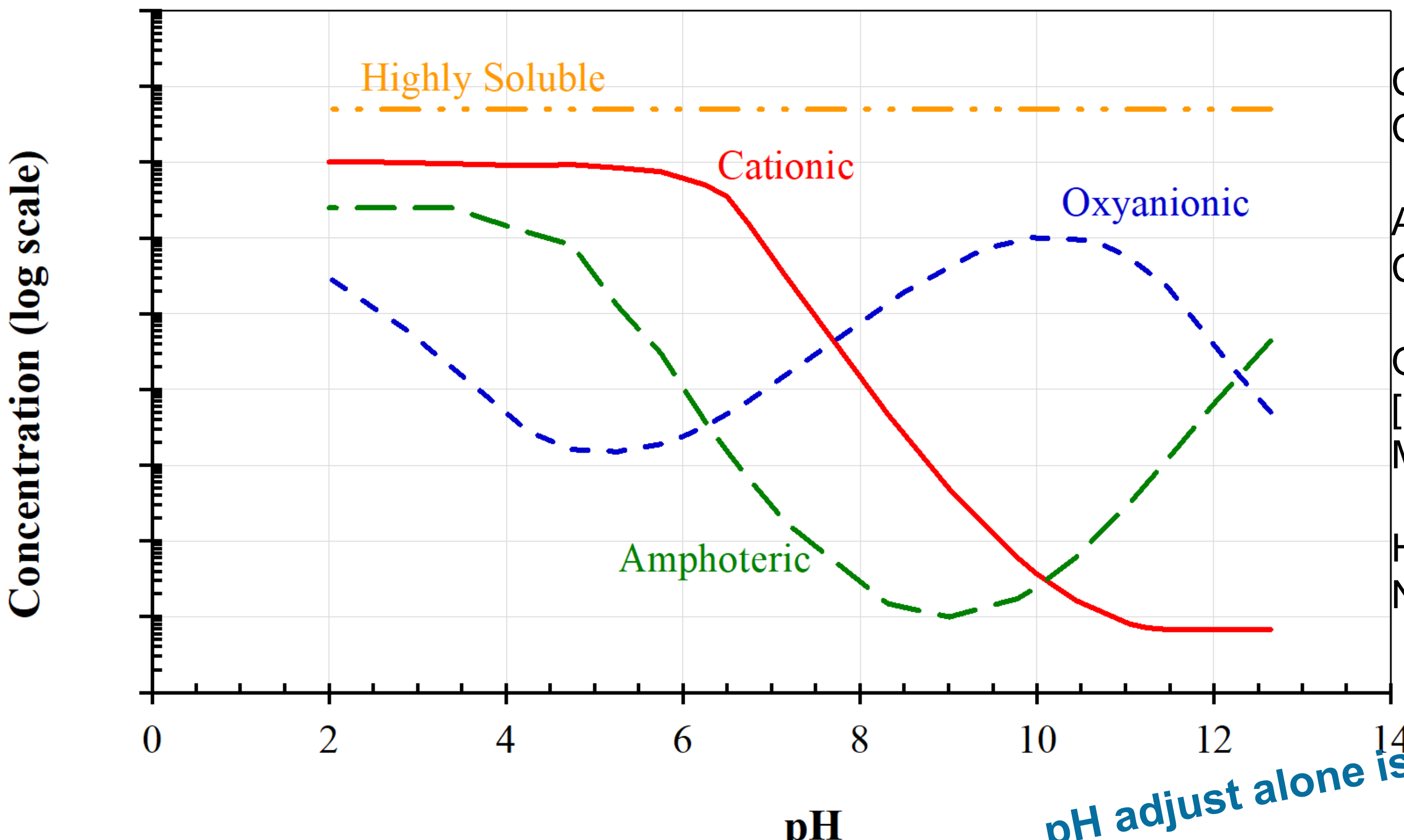
Injection into source area

24 Months after Injection

Heavy Metals Remediation

TECHNOLOGY AND APPLICATION OVERVIEW

Generic behaviors of several inorganic contaminant types showing generalized minima/maxima as a function of pH



Cationic- Cr(III), Cd, Pb

Amphoteric- Cr(III),Pb, Cu

Oxianionic- [CrO4], As, Se, Mo

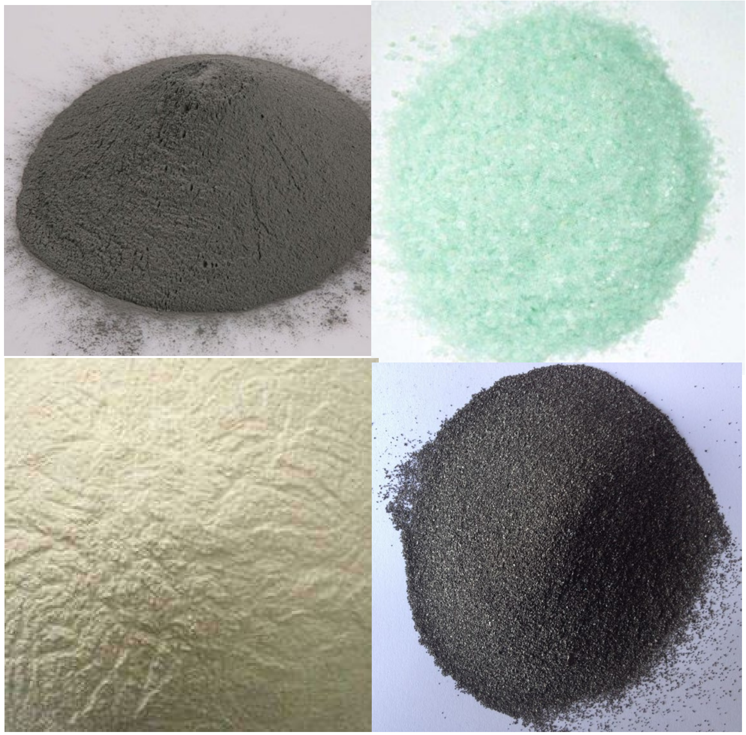
High Solubility- Na , K , Cl

pH adjust alone is not enough!

What is MTS®?

It is a suite of Heavy Metals chemical sequestration or reduction chemistries (12 primary proprietary blended formulations) engineered to reduce the leachability of heavy metals in vadose zone soil and saturated zone soils (groundwater).

Oxides
Hydroxides
Sulfates
Iron
Phosphate
Sulfides
Zeolite
Calcium Carbonate
Activated Carbon
Proprietary reagents and activators



MTS®
METALS TREATMENT SOLUTION

Site	Contaminant(s)	Starting Leachate Concentration	Final Leachate Concentration	Reduction (%)	Target Goal	Test Condition	Matrix	Reagent dose (%) by wt
1	CrVI	41.3 mg/L	<0.03 mg/L	100%	5.0 mg/L	TCLP	Soil	1
2	CrVI	3.7 mg/L	<0.010 mg/L	100%	Not established	SPLP	Soil and Groundwater	1
	Ni	0.49 mg/L	0.11 mg/L	78%	0.30 mg/L	SPLP	Soil and Groundwater	2
3	CrVI	89 ug/L	3.3 ug/L	96%	10 ug/L	SPLP	Soil and Groundwater	2
4	Co	1.2 mg/L	<0.010 mg/L	100%	Not established	SPLP	Soil and Groundwater	2
	Co	>103	<0.385	99.6%	2 ug/L	SPLP	Soil and Groundwater	1.5
5	As	0.57 mg/L	<0.0050 mg/L	100%	0.50 mg/L	TCLP	Industrial waste	5
	CrVI	1.2 mg/L	0.043 mg/L	96%	0.50 mg/L	TCLP	Industrial waste	5
	Pb	0.012 mg/L	<0.0014 mg/L	88%	0.50 mg/L	TCLP	Industrial waste	5
6	Se	22 mg/L	0.011 mg/L	100%	Not established	TCLP	Industrial waste	5.5
7	Cd	16 mg/L	0.05 mg/L	99.7%	0.15 mg/L	TCLP	Industrial waste	18
	Pb	17 mg/L	0.02 mg/L	99.9%	5.0 mg/L	TCLP	Industrial waste	18
	Zn	830 mg/L	0.01 mg/L	99.999%	280 mg/L	TCLP	Industrial waste	18
8	As	0.027 mg/L	0.0090 mg/L	67%	0.010 mg/L	SPLP	Soil and Groundwater	2
9	CrVI	57.2 ug/L	<0.70 ug/L	100%	0.10 mg/L	SPLP	Soil and Groundwater	4
	Cu	119 ug/L	9.5 ug/L	92%	Not established	SPLP	Soil and Groundwater	4
	Ni	24.2 ug/L	<5.0 ug/L	90%	Not established	SPLP	Soil and Groundwater	4
	Zn	60.6 ug/L	<2.2 ug/L	100%	Not established	SPLP	Soil and Groundwater	4
10	As	102 ug/L	20.2 ug/L	80%	36 ug/L	SPLP	Soil and Groundwater	6
	Pb	761 ug/L	3.67 ug/L	99.5%	8.1 ug/L	SPLP	Soil and Groundwater	6
	Zn	849 ug/L	<4.0 ug/L	100%	81 ug/L	SPLP	Soil and Groundwater	6
11	As	36.1 mg/L	0.80 mg/L	98%	3.75 mg/L	TCLP	Soil	2
12	As	0.31 mg/L	<0.03 mg/L	100%	5.0 mg/L	TCLP	Soil and ind waste	13
	Pb	89.0 mg/L	<0.03 mg/L	100%	5.0 mg/L	TCLP	Soil and ind waste	13
13	Pb	56.2 mg/L	<0.03 mg/L	100%	5.0 mg/L	TCLP	Soil	8
14	Cd	8.5 mg/L	0.11 mg/L	98.7%	1.0 mg/L	TCLP	Soil	6
15	Zn	14,700 ug/L	12.3 ug/L	99.9%	2,000 ug/L	GW leach	Soil and Groundwater	2
16	Pb	99 mg/L	1.6 mg/L	98%	5.0 mg/L	TCLP	Soil	7
17	Pb	930 mg/L	0.83 mg/L	99.91%	5.0 mg/L	TCLP	Soil	8
18	Pb	27 mg/L	0.054 mg/L	99.8%	5.0 mg/L	TCLP	Soil	11
19	Cd	131 ug/L	0.20 ug/L	99.8%	5.0 ug/L	GW leach	Soil and Groundwater	3
	Pb	642 ug/L	6.4 ug/L	9900%	15 ug/L	GW leach	Soil and Groundwater	3
	Zn	39,900 ug/L	12.4 ug/L	99.97%	2,000 ug/L	GW leach	Soil and Groundwater	3
20	Pb	20 ug/L	6.7 ug/L	67%	15 ug/L	SPLP	Soil and Groundwater	2
21	Pb	350 ug/L	5.1 ug/L	99%	15 ug/L	SPLP	Soil and Groundwater	3
22	Pb	660 mg/L	<5.0 mg/L	100%	5.0 mg/L	TCLP	Soil	1
23	Pb	51 mg/L	0.65 mg/L	99%	5.0 mg/L	TCLP	Soil	8
24	Pb	60 mg/L	0.78 mg/L	98.7%	1.0 mg/L	TCLP	Soil	5.5
		68.9 mg/L	0.004 mg/L	99.4%	0.02 mg/L	Chinese TCLP	Soil	4
25	CrVI	236	<0.004 mg/L	100%	0.02 mg/L	Chinese TCLP	Soil	5
26	Al	7.83	1.32	83%	4	Chinese TCLP	Soil	7
	As	0.0768	0.0019	98%	0.05	Chinese TCLP	Soil	7
	Pb	0.053	ND	100%	-	Chinese TCLP	Soil	7
	Cd	0.016	ND	100%	-	Chinese TCLP	Soil	7
27	Pb	0.054 mg/L	0.031 mg/L	42%	5.0 mg/L	TCLP	Soil	11
	Cd	8.10 mg/L	0.27 mg/L	97%	1.0 mg/L	TCLP	Soil	11
	CrVI	5.71 mg/L	0.034 mg/L	99%	5.0 mg/L	TCLP	Soil	11
		160 mg/L	1.4 mg/L	99.1%	10 mg/kg	Total		
28	CrVI	2500 mg/kg	5.3 mg/kg	99.8%	2 mg/L	SPLP	Soil and Groundwater	6

Zinc – Heavy Metal Case Study PRB Remediation

Permeable reactive barrier installed via Geoprobe injection to mitigate zinc concentrations to surface water discharge

Site: Redevelopment of Industrial Site

Contaminant: Zinc

Soil Volume: 5,300 m^3

Approach: Injection of reactive barrier

Benefits:

- No removal of soil from site
- Existing redevelopment remained in-tact
- Zinc no longer a surface water discharge concern

In Situ Zinc - Pilot Test

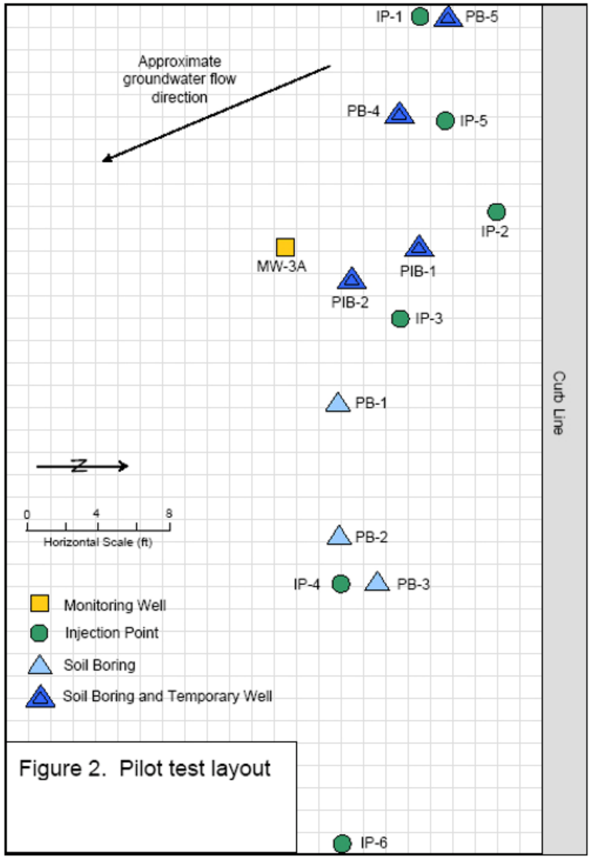
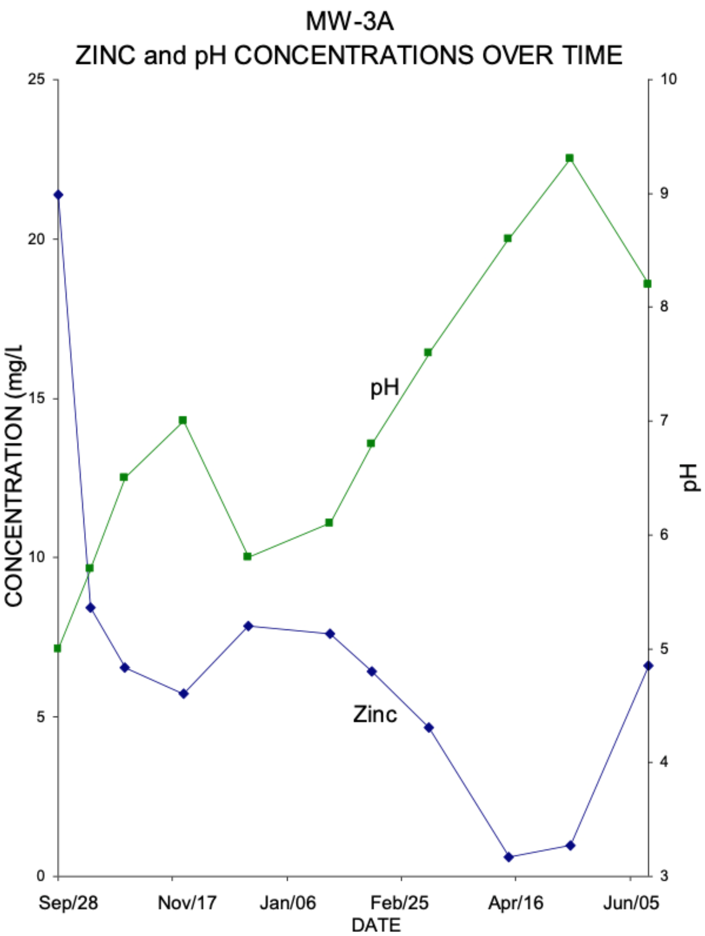


Figure 2. Pilot test layout



Zinc Case Study: PRB Remediation

Pilot Testing (6 injections, 5 borings, 3 monitoring wells)

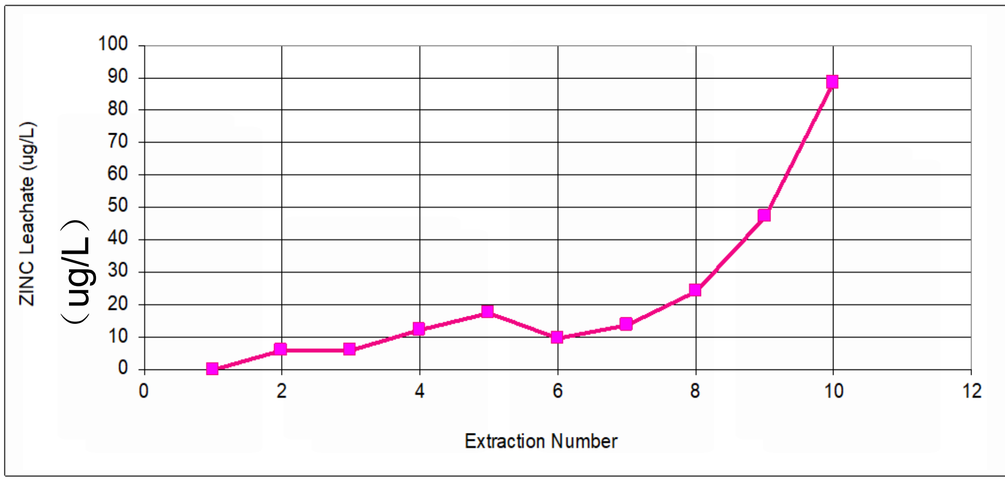
- Visual observations of reagent distribution in soil cores
- Soil pH and SPLP measurements in cores
- Monitoring well groundwater samples to assess “integrated” effect of heterogeneous reagent distribution

Only 2-days allowed for reagent effects to permeate the injection zone

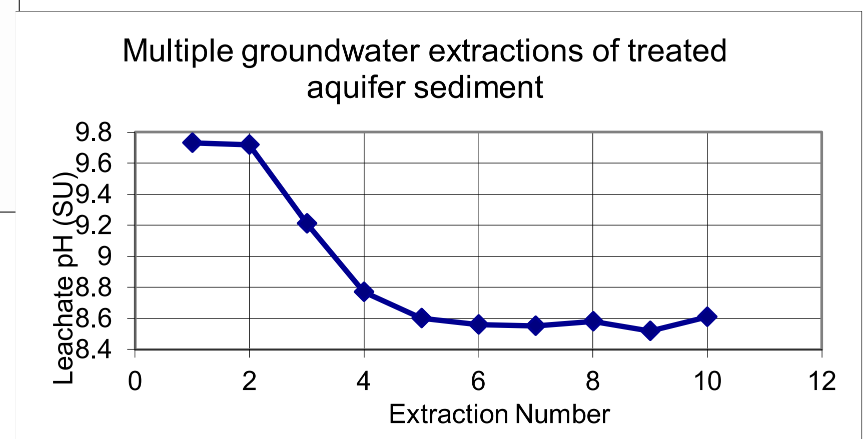
RESULTS - 0.61 mg/L in the pilot study

Simulated Long Term Stability Multiple Extraction Procedure (MEP)

Permeable Reactive Barrier. Goal of 2 mg/L from 20 mg/L.
Represents 480 years of groundwater flow



LEFT: Demonstrates simulated life of reactive barrier stability



RIGHT: Demonstrates long term stability of pH regardless of acid washing

In some cases the encapsulating mineral formed may by be susceptible to dissolution under environmental conditions. Also the regulatory agency wants project-specific demonstration of long-term stability.

Zinc Case Study
Full Scale Implementation

45,000 gallons of diluted reagent injected in 63 locations over a 4-week period

Soil – 97% reduction

83 percent of post-injection soil samples SPLP <0.020 mg/L of zinc

Surfacewater

- Within 1 year surface water zinc concentrations decreased by 50 to 70 percent
- Surface water goal achieved within 3 years

	Zinc (mg/L)		
Date	**MW-1**	**MW-2**	**MW-3**
Aug-yr0	1.64	---	---
Jul-yr1	0.750	0.389	---
Aug-yr1	2.32	0.999	0.701
Aug-yr2	1.53	0.915	0.434
Sep-yr2	1.27	0.749	0.451
Feb-yr3	0.966	0.746	0.543
May-yr3	0.279	0.315	0.221
Aug-yr3	0.382	0.324	0.230

No further action for soil, continued groundwater and surface water monitoring
Former 21-acre industrial site redeveloped into apartments

Thank you

Lowell Kessel, MS, P.G.
General Manager,
Remediation Specialist
Hydrogeologist
CERES Corporation
lowell@cerescorporation.com

www.CEREScorporation.com

Phone: (714) 709-3683

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