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Injection and Distribution Monitoring Techniques for Successful Field Application of EHC® Reagent

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PeroxyChem
Webinar
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Presentation Objective / Outline

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- To empirically summarize our experience from a range of EHC injection projects and provide an overview of various methods applied to verify subsurface EHC distribution.

- Outline:
  - EHC composition and mechanisms
  - Typical injection methods and equipment
  - Methods to validate distribution
  - Case Studies

EHC Technology Background

EHC composition:

- *ca.* 40% micro-scale zero valent iron (50 - 150 µm)
- *ca.* 60% fine-grained processed plant fiber particles

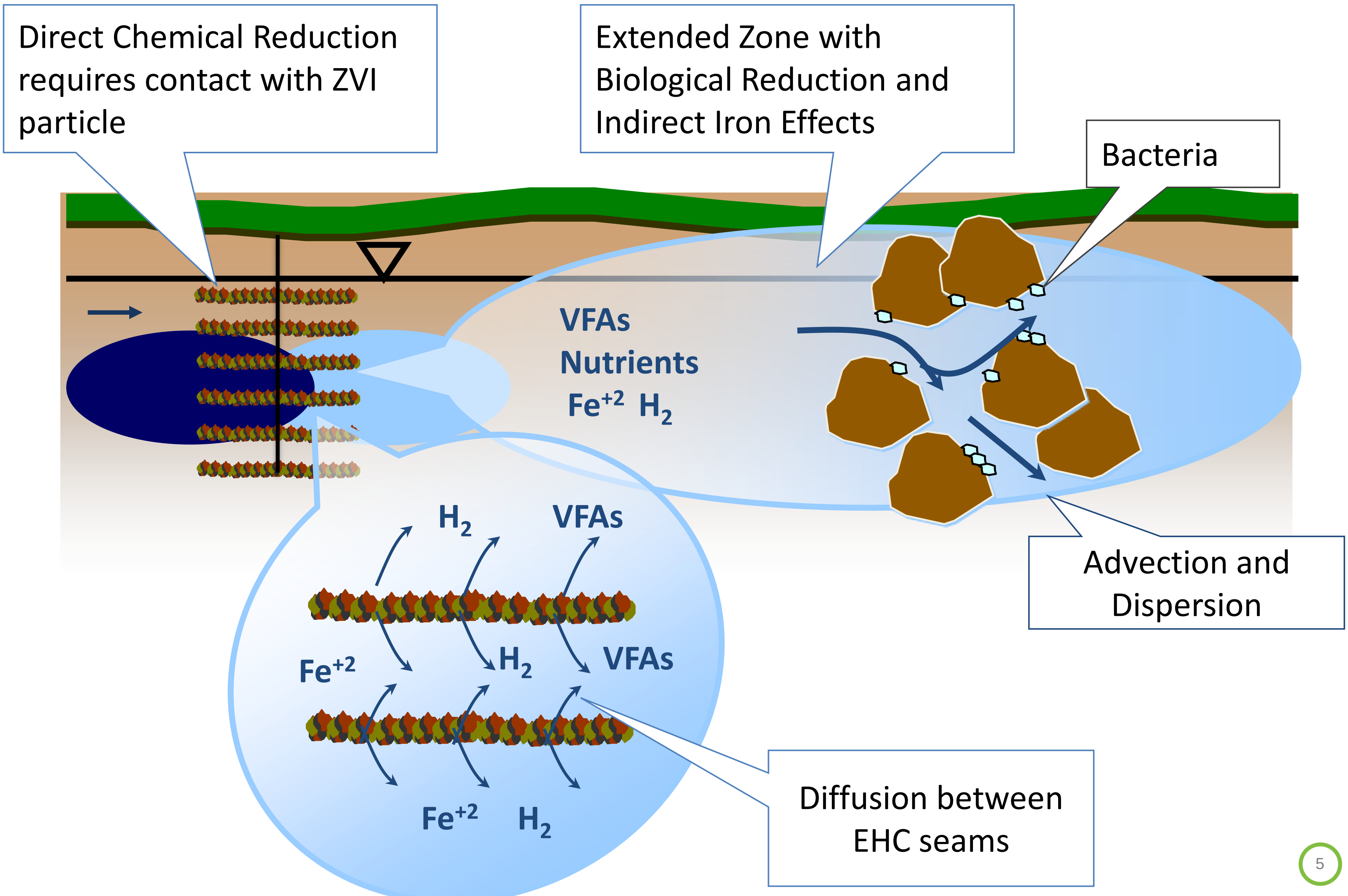
Contaminants treated, including:

- Chlorinated solvents including chlorinated ethenes, ethanes and methanes
- Energetic compounds such as TNT, DNT, HMX, RDX and perchlorate
- Most pesticides including DDT, DDE, dieldrin, 2,4-D and 2,4,5-T

EHC Treatment Mechanisms

Mechanism	Component	Description
Direct Chemical Reduction	ZVI	• Redox reaction at iron surface where solvent gains electrons and iron donates electrons • Abiotic reaction via beta-elimination
Indirect Chemical Reduction	ZVI or Fe(II)	• Surface dechlorination by magnetite and green rust precipitates from iron corrosion
Stimulated Biological Reduction	Organic Carbon Substrate / H2	• Anaerobic reductive dechlorination involving fastidious microorganisms • Strongly influenced by nutritional status and pH of aqueous phase

Mechanisms Zone of Influence



Determining Injection Spacing

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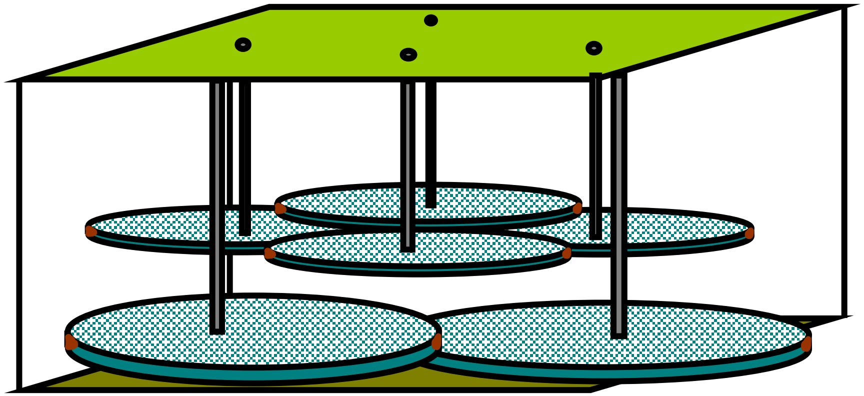
- Radius of Influence:
  - Product placement during injection
  - Extended zone of influence with elevated conc of VFAs and Fe(II) minerals (will depend on groundwater flow)



- Soil acceptance vs. loading requirements:
  - Adjust spacing to not exceed maximum loading per point
  - Depends on lithology, slurry concentration and injection method

EHC Installation Methods

<u>Injection Methods</u>

- Direct injection
- Hydraulic fracturing
- Pneumatic fracturing
- Well injections (EHC-L)

<u>Direct Placement</u>

- Trenching
- Excavations
- Deep soil mixing

Typical Direct Injection Set-Up

ChemGrout's
CG-550 mixing and
injection unit

Injection probe with check valve

Typical injection flow rate: 3 to 10 gpm
Typical injection pressure: <50 to 250 psi

We recommend using a grout / piston pump that can generate a flow rate of at least 5 gpm at 500 psi to allow for flexibility in the field

EHC Slurry

- Water content could be varied depending on lithology, equipment and desired injection properties

EHC Conceptual Designs

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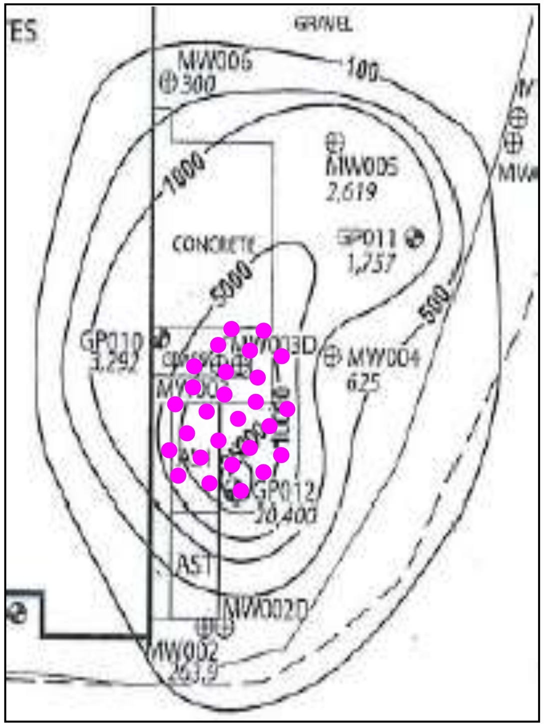
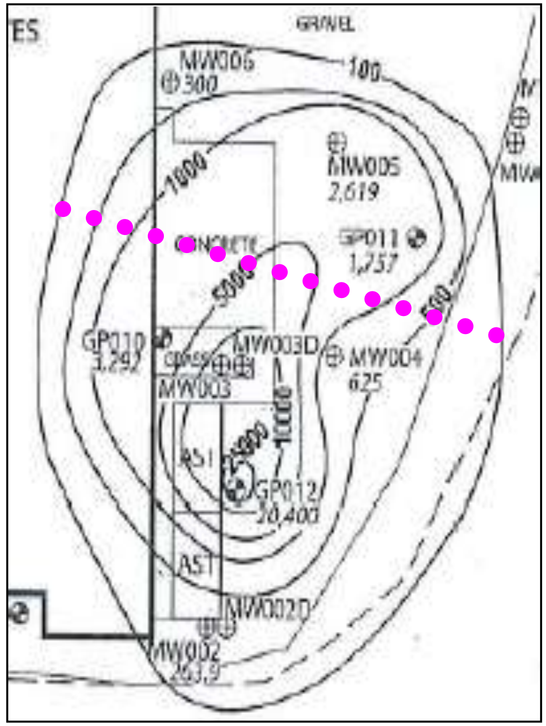
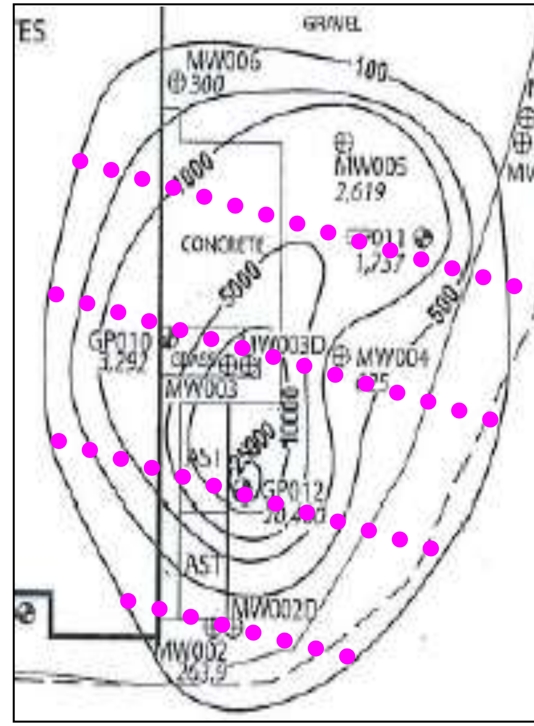
Source Area/ Hotspot Treatment

Injection PRB for Plume Control

Plume Treatment







- Dosing: 0.15 to 1% wt/wt
- Spacing: 6 to 15 ft (DPT)

- Dosing: 0.4 to 1% wt/wt
- Spacing: 6 to 10 ft (DPT)

-Line Spacing: depends on linear gw velocity

Methods to Validate ROI

Verification of direct product placement:

- Visual observation of fractures in soil cores.
- Magnetic separation of the ZVI portion of EHC from soil cores.
- Monitoring of ground deformation using uplift stakes or tilt meters (usually used during fracturing).

Extended zone of influence:

- Groundwater Indicator Parameters (TOC, Fe, geochemical parameters)

Soil Coring

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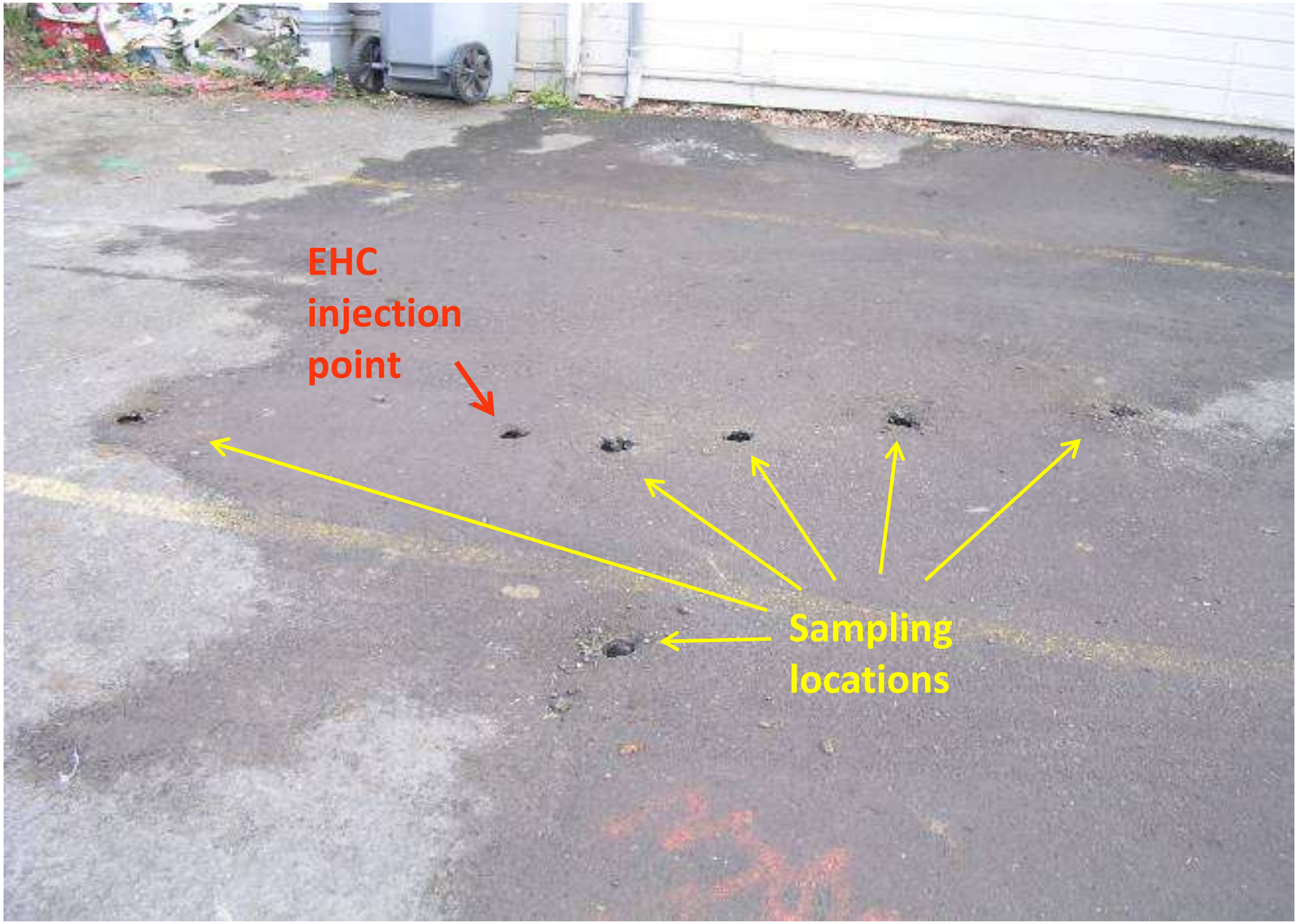
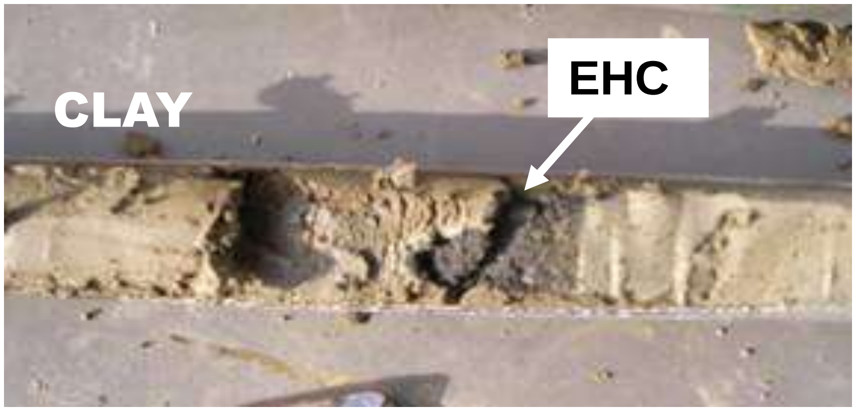
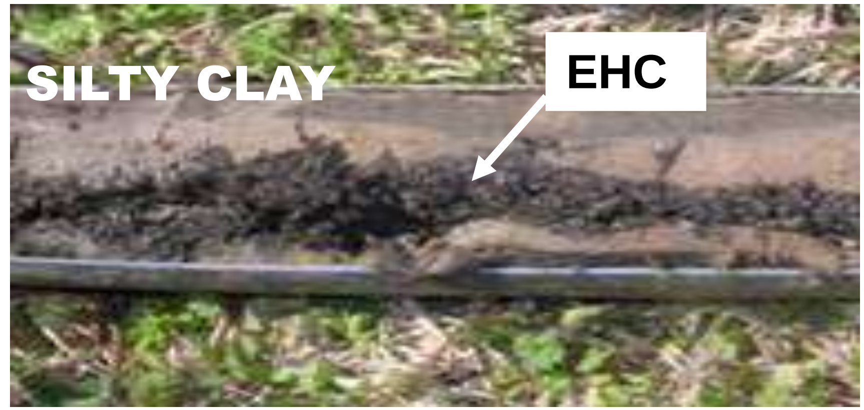
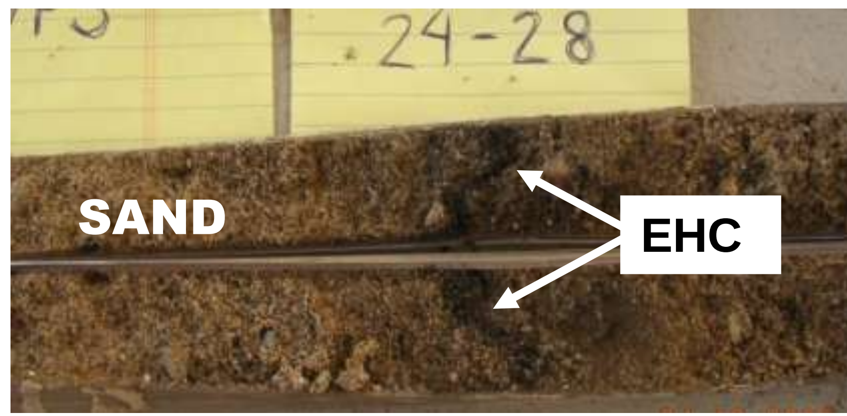


Soil Cores with EHC Fractures







- EHC observed to displace into discrete bands.
- Horizontal and vertical fractures observed during coring.

Verification of ZVI / TOC Content in Soil Cores

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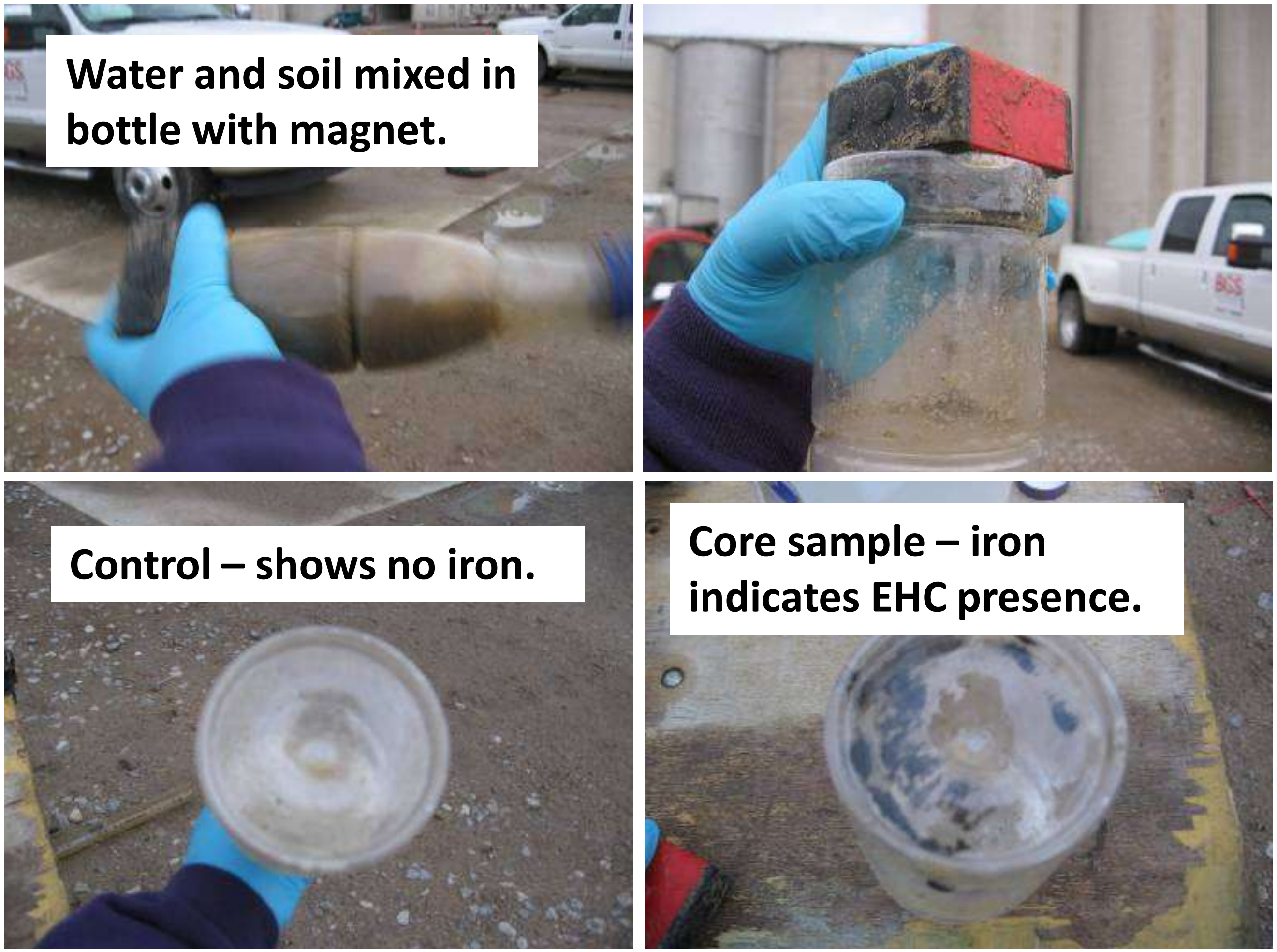
- At sites with more permeable soils such as gravels or more coarse-grained non-cohesive sands, soil coring has often yielded little visual evidence of discrete EHC seams, suggesting that the EHC amendment has been distributed mainly via permeation into the aquifer matrix.
- When EHC seams cannot be visually identified, the EHC presence can be verified by analyzing the soil for iron and/or TOC:
  - Laboratory analyses of TOC and iron
    - Problematic since includes natural iron
  - Wet magnetic separation process

Wet Magnetic Separation Test



Monitoring of Ground Uplift

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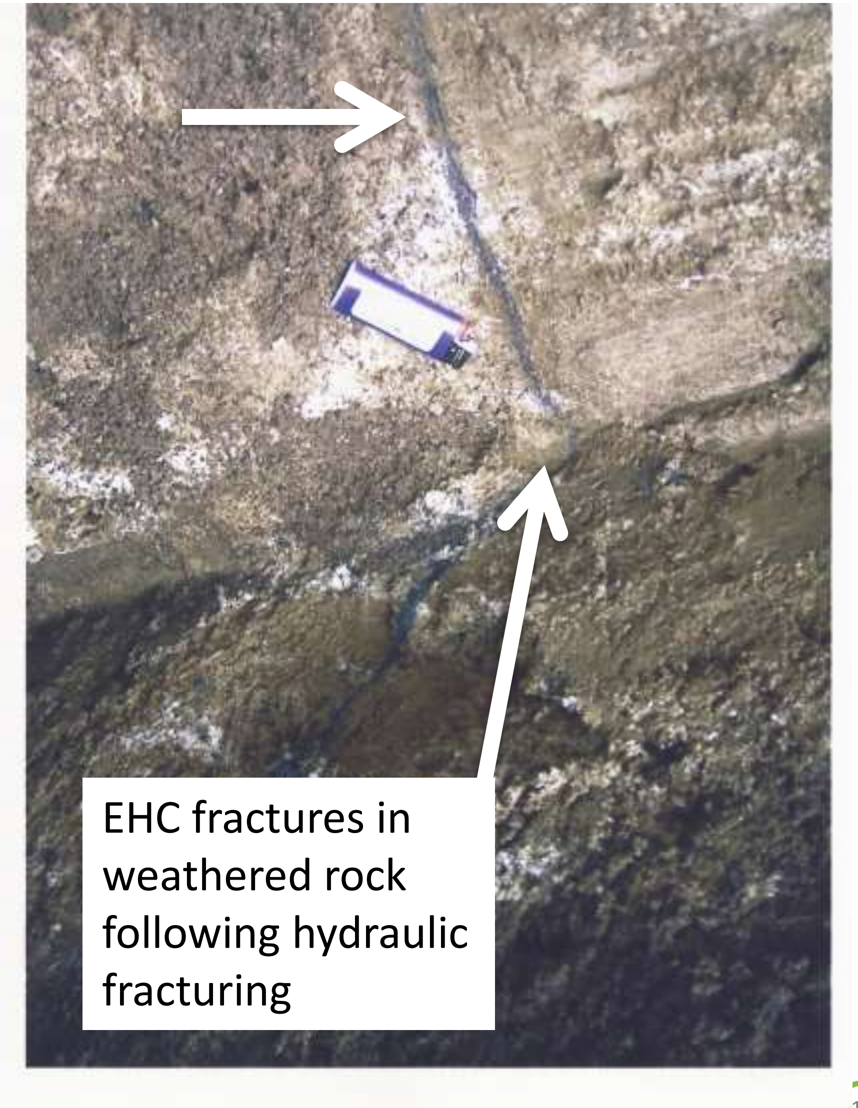
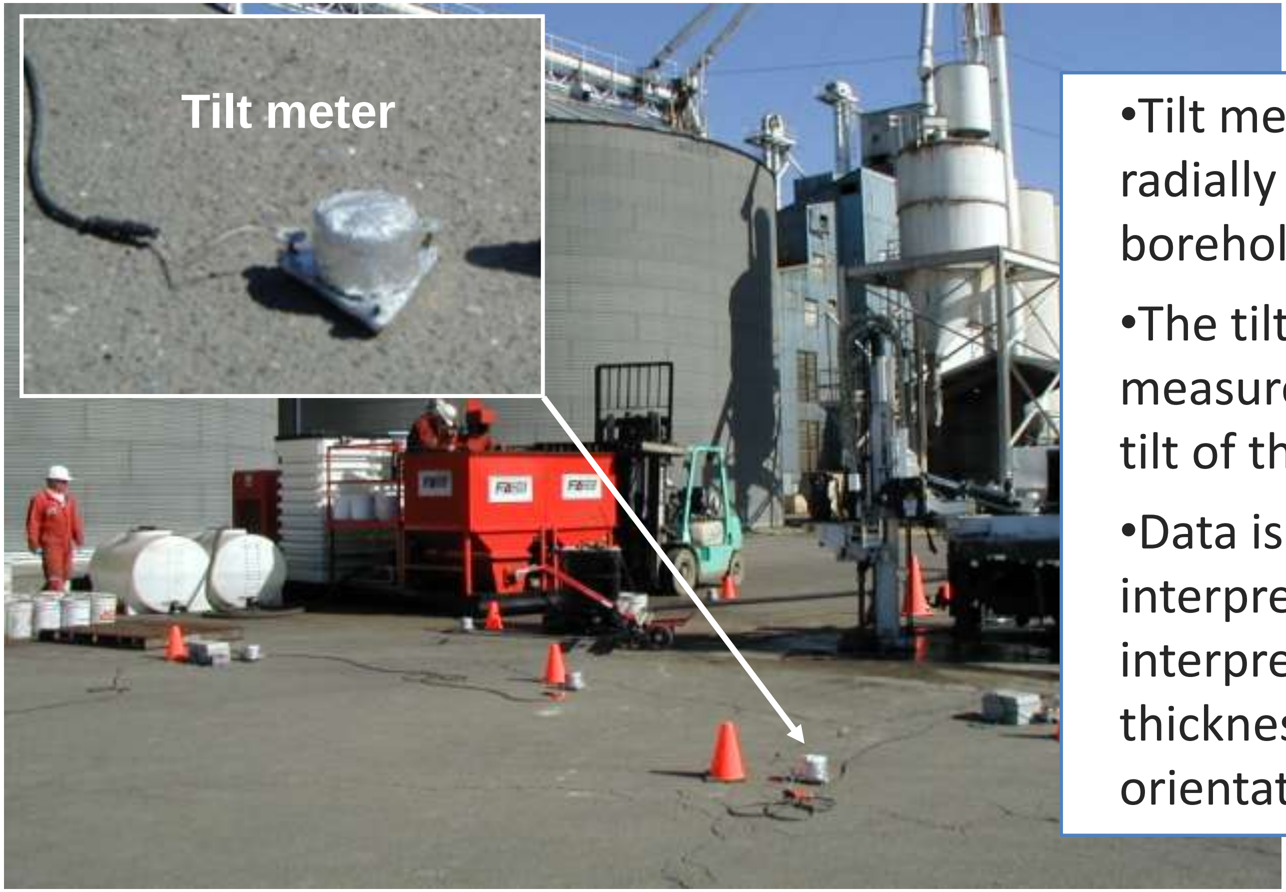
- When amendments are displaced into discrete seams, there is a disturbance in the subsurface as the fractures are propagated.
- It is possible to measure this disturbance by using uplift stakes or tilt meters.
- This evaluation method is commonly applied during hydraulic or pneumatic fracturing to estimate ROI.



Tilt Meters



- Tilt meters positioned radially around the injection borehole.
- The tilt meters continually measure any change in the tilt of the ground surface.
- Data is analyzed using interpretation software to interpret the shape, thickness, extent and orientation of fractures.

- This method was used at Colorado site where EHC was injected into sandstone bedrock via hydraulic fracturing
- Majority of the fractures propagated >30 ft, median fracture thickness ~8 mm (ranging from 1 to 40 mm)

Remediating TCE-Contaminated Groundwater in Low-Permeability Media Using Hydraulic Fracturing to Emplace Zero-Valent Iron/Organic Carbon Amendment

Dana Swift

Joe Rothermel

Lance Peterson

Brennon Orr

Gordon H. Bures

Jennifer Weidhaas

A field pilot test in which hydraulic fracturing was used to emplace granular remediation amendment (a mixture of zero-valent iron [ZVI] and organic carbon) into fine-grained sandstone to remediate dissolved trichloroethene (TCE)-contaminated groundwater was performed at a former intercontinental ballistic missile site in Colorado. Hydraulic fracturing was used to enhance the permeability of the aquifer with concurrent emplacement of amendment that facilitates TCE degradation. Geophysical monitoring and inverse modeling show that the network of amendment-filled fractures extends throughout the aquifer volume targeted in the pilot test zone. Two years of subsequent groundwater monitoring demonstrate that amendment addition resulted in development of geochemical conditions favorable to both abiotic and biological TCE degradation, that TCE concentrations were substantially reduced (i.e., greater than 90 percent reduction in TCE mass), and that the primary degradation processes are likely abiotic. The pilot-test data aided in re-evaluating the conceptual site model and in designing the full-scale remedy to address a larger portion of the TCE-contaminated groundwater plume.

INTRODUCTION

In situ chemical reduction and bioremediation via anaerobic reductive dechlorination (ARD) are effective and widely applied remediation methods for chlorinated solvent–contaminated groundwater and soils. *In situ* groundwater remediation is often accomplished by injecting liquid or particulate reactive amendments to stimulate biological and/or abiotic degradation mechanisms. This approach is challenging to apply in low- to moderate-permeability media due to the difficulty in distributing amendments in the targeted treatment zone. Amendment delivery methods for *in situ* remediation in low-permeability media include permeation dispersal, soil mixing, electrokinetics (Walden, 1997), direct push, and hydraulic or pneumatic fracturing (Christiansen et al., 2010; Murdoch & Wilson, 1994; Schuring, 2002).

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>90% reduction in TCE mass within sandstone bedrock following emplacement of EHC via hydraulic fracturing

Uplift Stakes

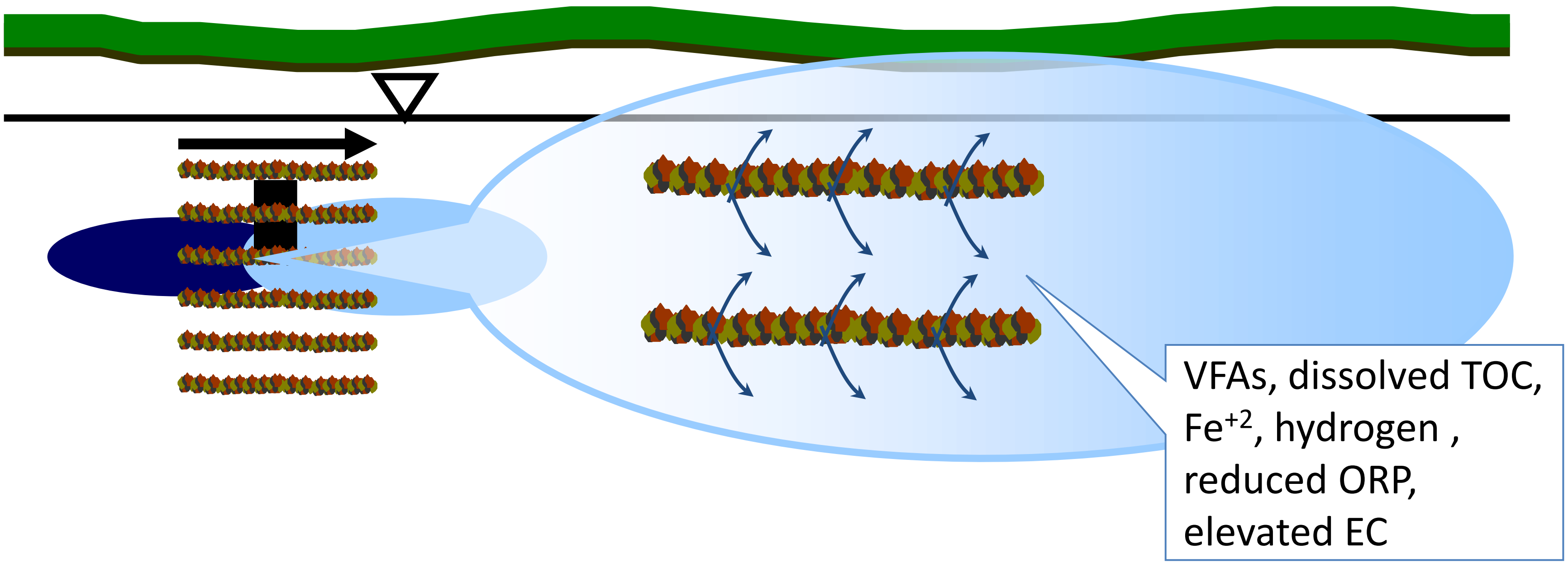
- Uplift stakes are installed at ground surface and are measured before and after the injection using surveying equipment.
- Maximum uplift may range from a few mm to several cm - fracture aperture is always greater than the ground uplift due to compression of overburden soil.
- Uplift stakes usually don’t produce useful results at depths greater than 10 m or so, or in windy conditions.

Trenching following Hydraulic Fracturing

- For research purposes, trenches have been excavated following hydraulic fracturing to directly map fracture local and aperture (Murdoch, Clemson University / FRx Inc.).
- Actual fracture extent has generally been found to exceed the predictions from uplift data (FRx Inc.).
- In general, it has been found that material emplaced via hydraulic fracturing propagate primarily horizontally out to a distance greater than 15 ft with a vertical rise of ca 3 ft (FRx Inc.).

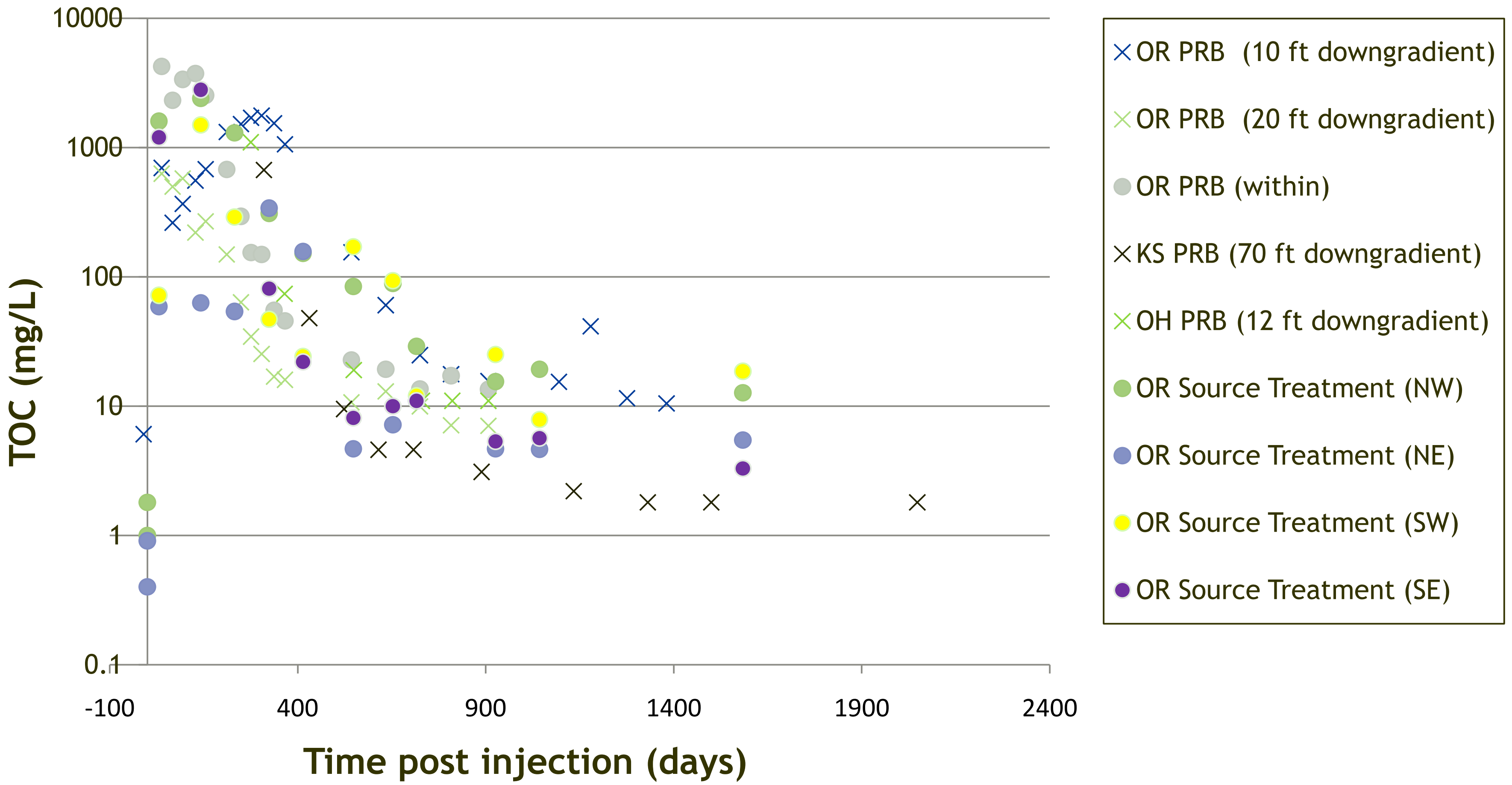
Extended Zone of Influence

Groundwater Indicator Parameters

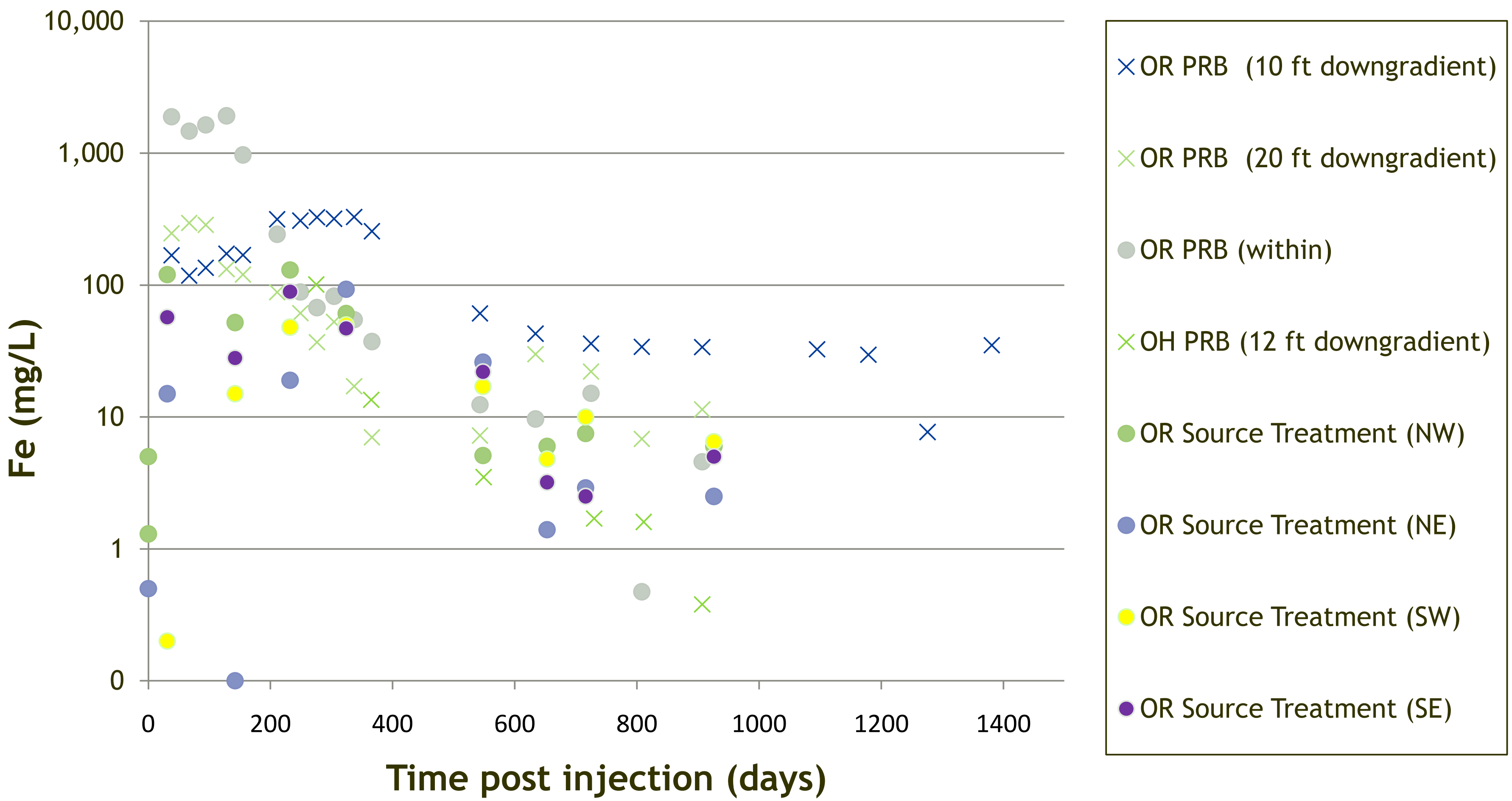


- Elevated levels of TOC and Fe confirms EHC presence
- A sharp drop in ORP and increase in EC is expected within the EHC injection zone → changes to these and other redox indicator parameters confirm EHC zone of influence.
- Response in EC and ORP have been observed in 24 hours within placement zone.

TOC Measured Within and Downgradient from EHC Injection Zones



Dissolved Fe Measured Within and Downgradient from EHC Injection Zones



Summary of Results

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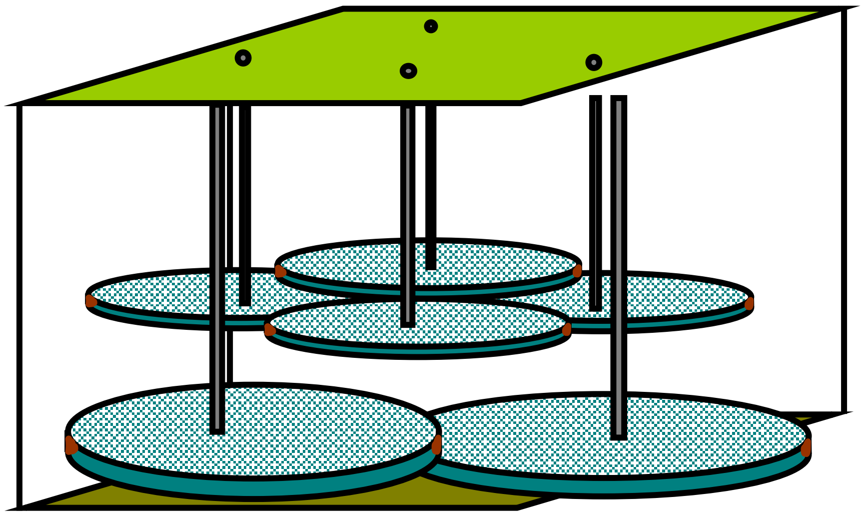
- Most commonly, EHC has been found to distribute into discrete seams during direct injection, as would be expected when a solid material is injected into an aquifer at a pressure exceeding the combined lithostatic pressure and cohesive strength of the soil.

- Observed ROI:
  - Direct push: ~5 to 8 ft
  - Fracturing: 10 to 60 ft
  - Permeation (non-cohesive sands and gravels): ~4 to 5 ft



Soil Acceptance / Surfacing

The EHC seams tend to rise with distance from the injection point and this rise ultimately limits the ROI and the volume that could be injected into each point.

Typical soil acceptance:

- Standard direct injection: 100 lbs of EHC or less per vertical foot.
- Hydraulic fracturing: several tons of EHC per fracture without surfacing.

EHC PRB Case Study – Dallas, TX

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- Managing surfacing at shallow depth

Project location: Dallas TX

Consultant: Burns & McDonnell

COCs: PCE and daughters

Remedial approach: ISCO in the source area combined with an injection PRB along channel

Depth to gw: ~1-2 ft bgs at PRB area

Lithology: Silty clay

Remedial Activities

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- Source Area :
  - Permanganate was injected into source area in June 2004, with supplemental injections in June 2005 and October 2007
- ZVI PRB Installed June 2005:
  - To address the continuing migration of the plume into the channel, a PRB was installed across the plume along the channel.
  - 11,000 lbs of zero-valent iron (ZVI) was emplaced via hydraulic fracturing.
  - Problems with daylighting at eastern portion of PRB resulted in more limited performance in this area.
- Supplemental EHC Injection at Eastern PRB Area - October 2007

EHC Injections

- A total of 2,600 lbs of EHC was injected into 15 injection points spaced 6 ft apart, covering an area measuring 30 ft long x 15 ft wide x 12 ft thick (from 3 to 15 ft bgs).
- Direct injection conducted in a top-down fashion targeting discrete injection intervals spaced 2 ft apart vertically (175 lbs per point, 25 lbs per vertical lift).
- Surfacing limited by increasing the slurry concentration to ~35% solids and limiting flow rate to 3-4 gpm.

Injection of EHC at channel using DPT.

Injection locations.

EHC slurry (35% solids)

EHC Injections

Results – PRB Area

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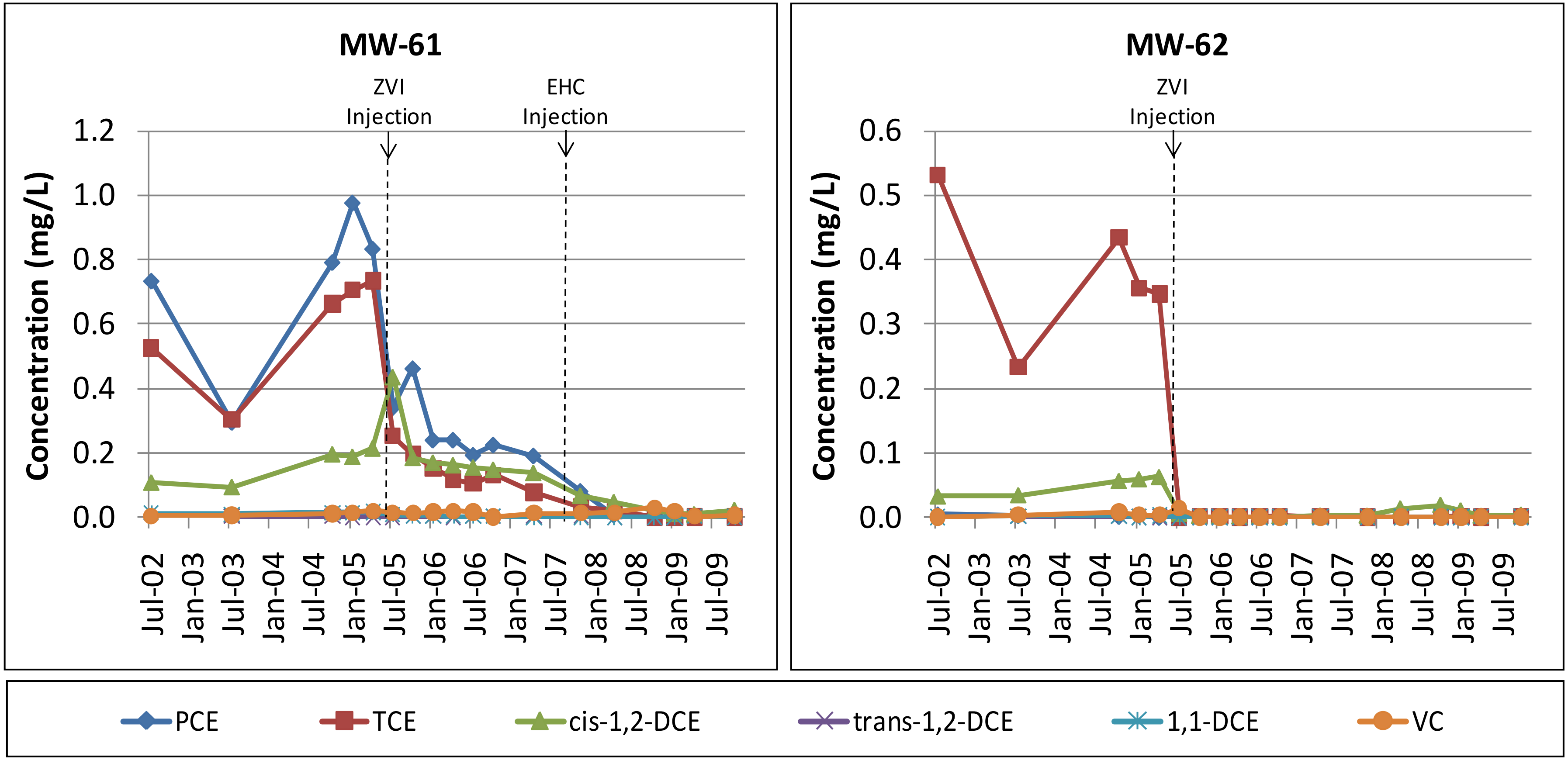

EHC Case Study - Source Area Treatment Former Dry Cleaner, Oregon

Primary CVOCs included chlorinated ethenes at concentrations up to:

- PCE ~ 22,000 ug/L
- TCE ~ 1,700 ug/L
- DCE ~ 3,100 ug/L
- VC ~ 7 ug/L

Site-Specific Challenges:

- Low permeability lithology – high degree of sorbed impacts expected
- Large seasonal variation in groundwater table (range from ca 7 to 13 ft bgs) → 6 ft thick smear zone
- Groundwater flow direction change with season

Test Injection using Direct Push
Displacement of liquid vs. solid amendments

Flow rate: 3-5 gpm, Injection pressure: 150-200 psi for EHC, 50-200 psi for EHC-A

Displacement of liquid vs. solid amendments: Direct push injection test

Full-Scale Application - EHC Injection layout and sampling locations

- A total of 10,000 lbs of EHC was injected into 32 injection points targeting an area measuring 825 ft^2 x 20 ft deep (from 10 to 30 ft bgs).
- Application rate of 0.6% EHC to soil mass.

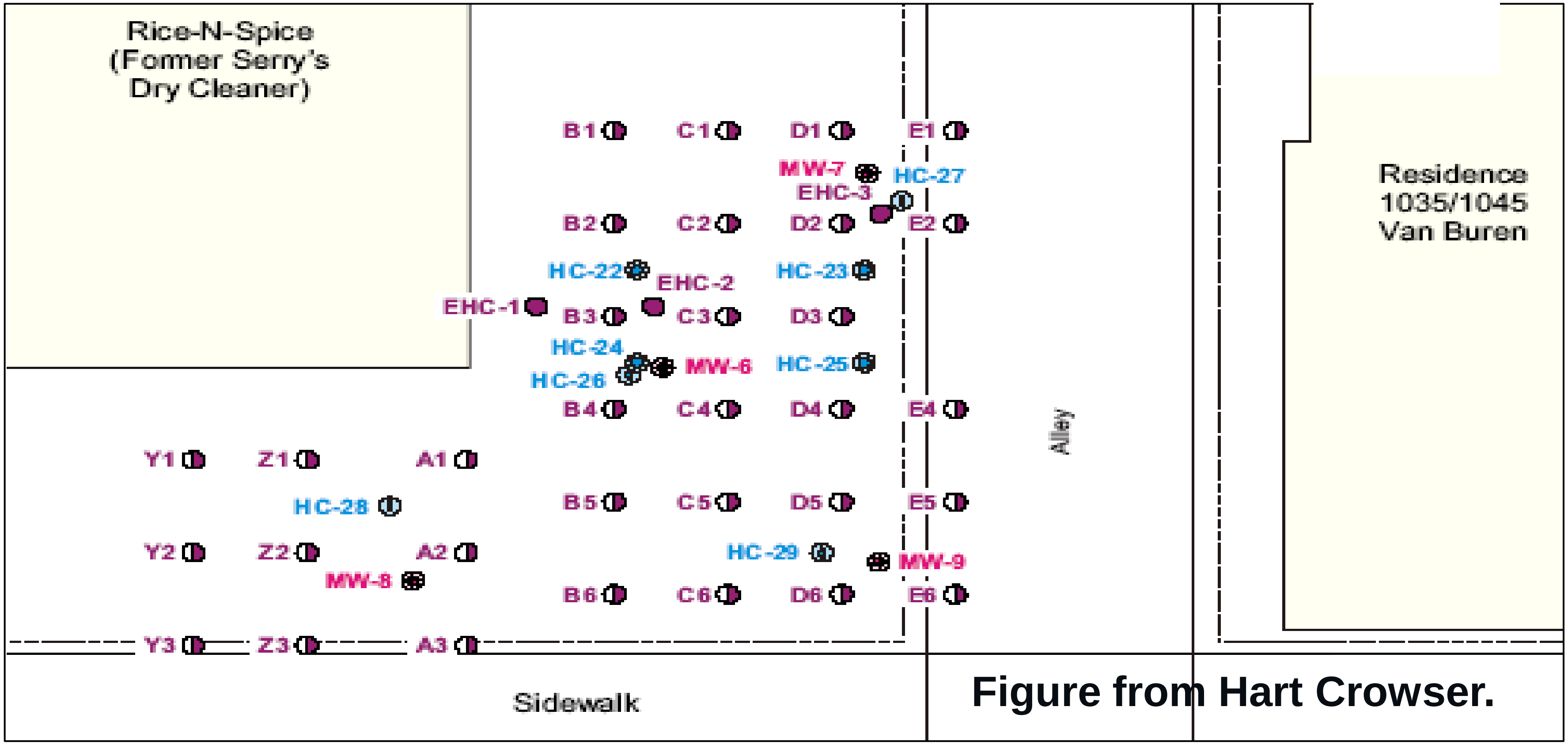

Figure from Hart Crowser.

EHC® Effect on Geochemistry

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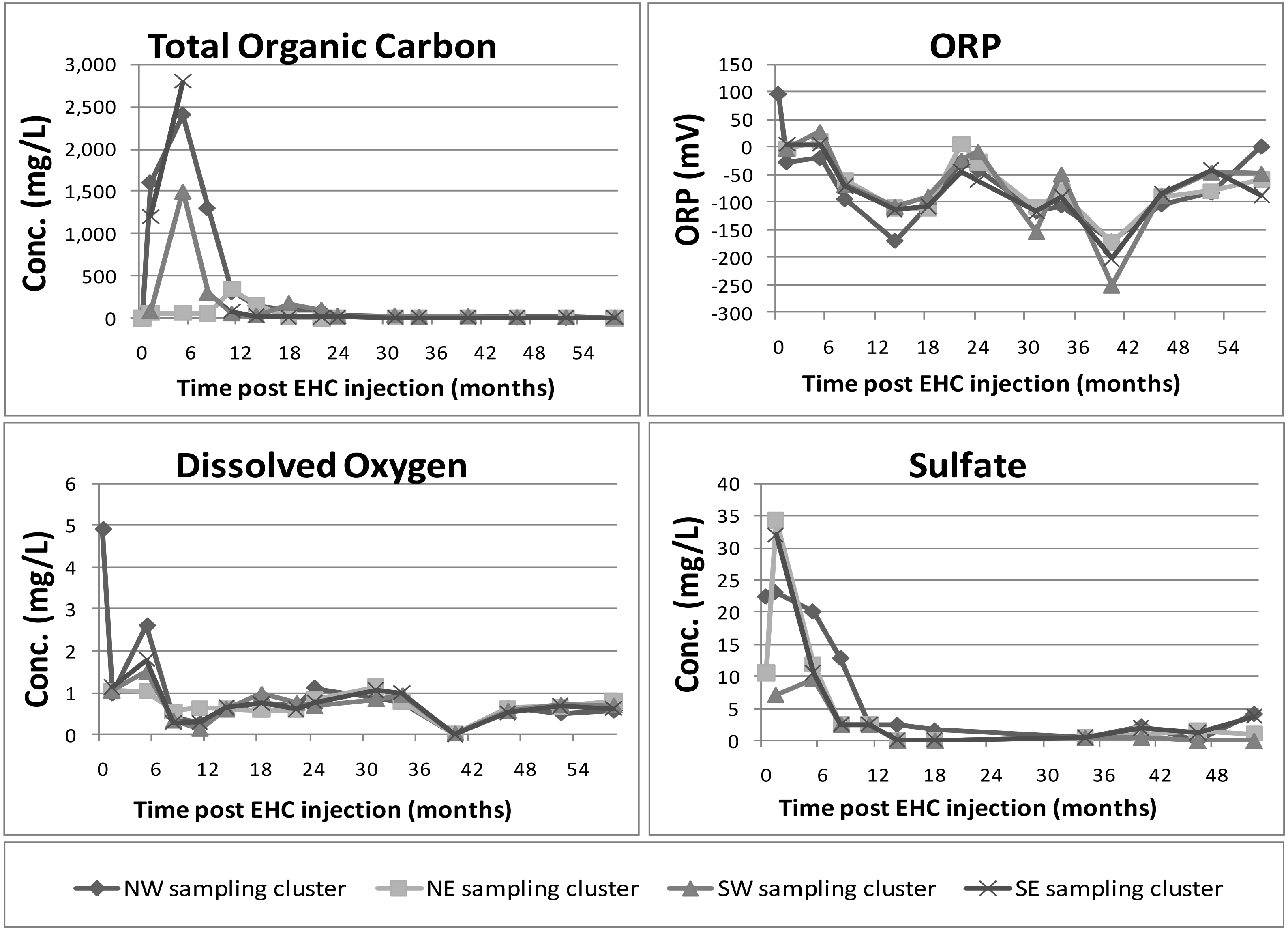
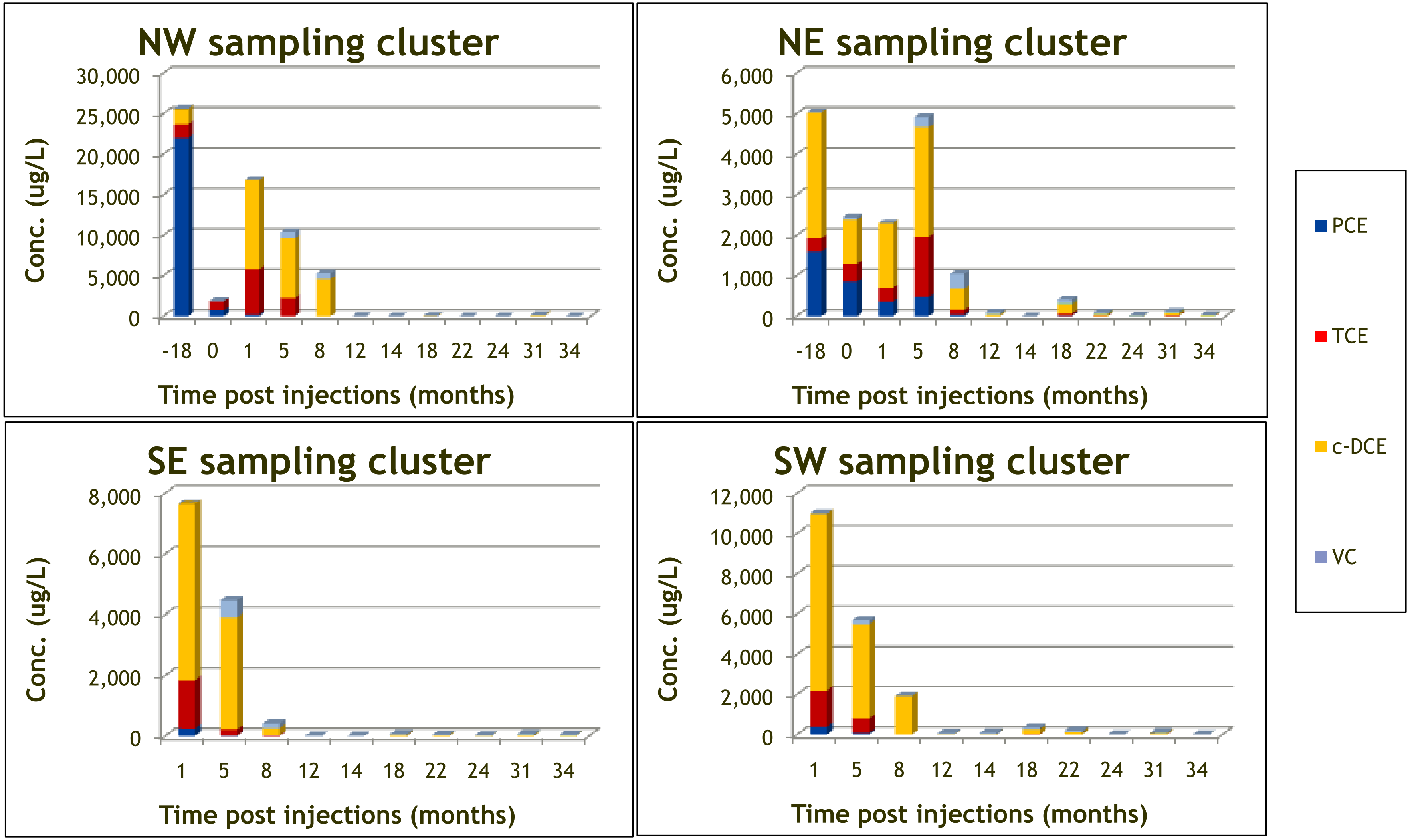
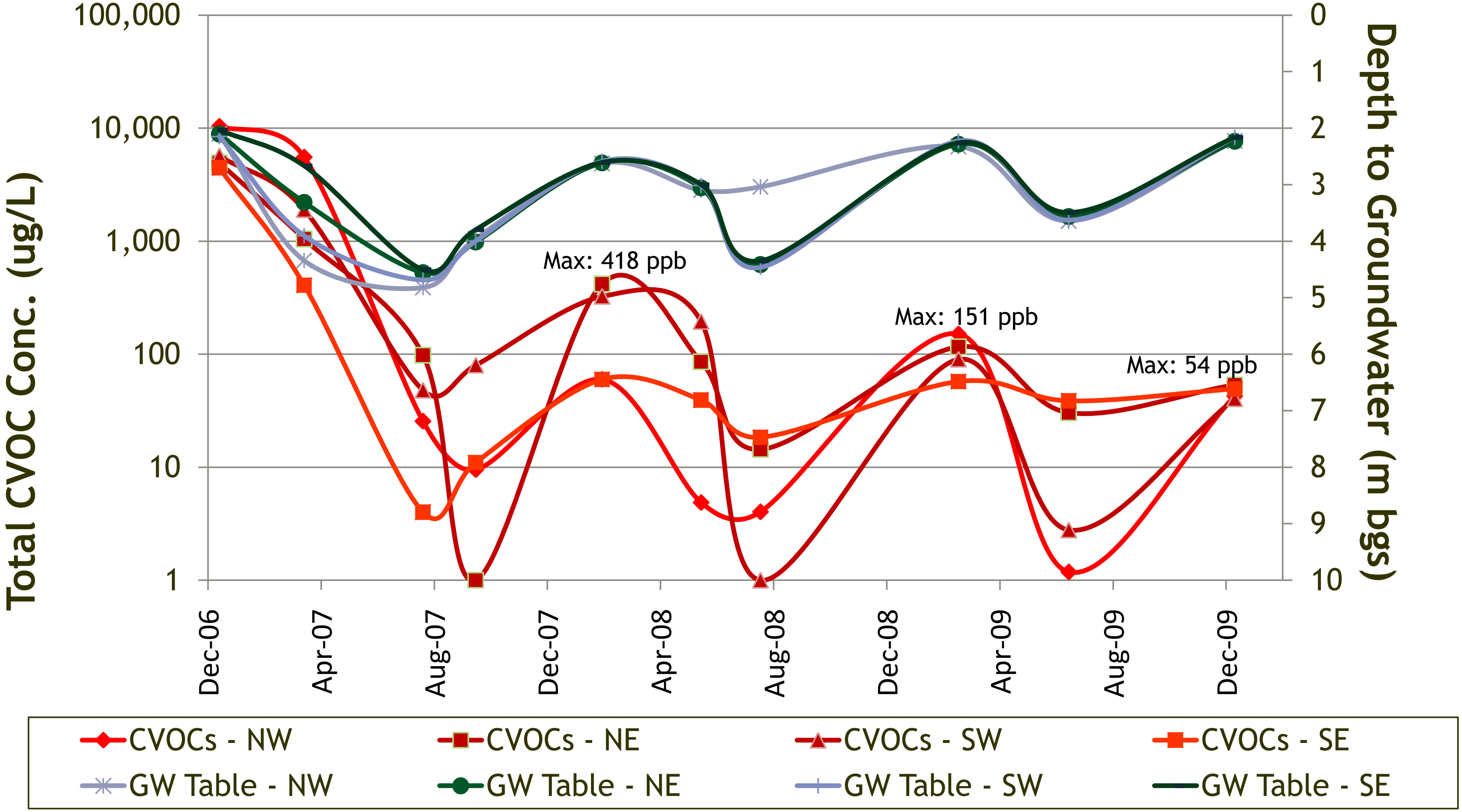


EHC® Case Study Results



Total CVOCs and Fluctuations in Groundwater Table



Degradation End Products

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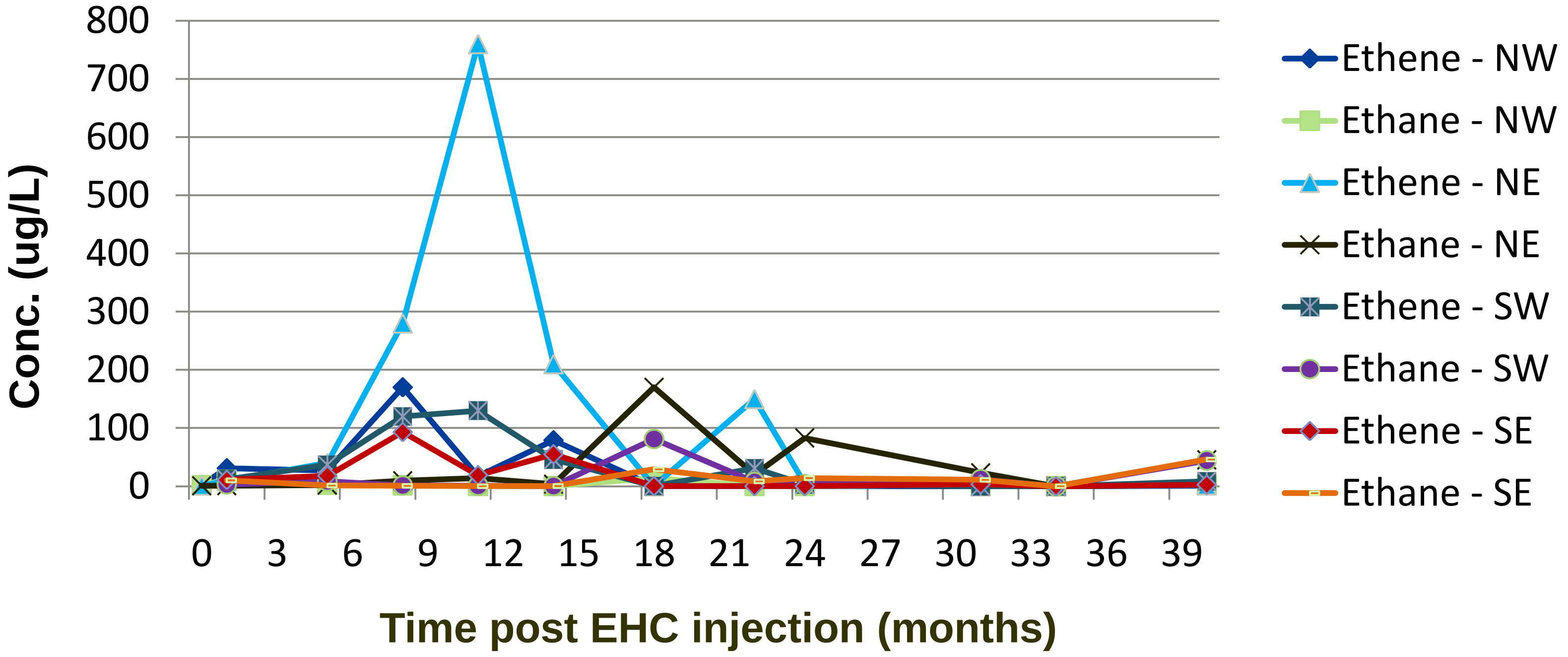

- Increase in ethene & ethane confirms complete dehalogenation
- Ethene levels of up to 760 ug/L measured in July 2007 (11-month data) → 96% increase compared with maximum baseline levels
- Correlation observed between total CVOC concentrations and ethene plus ethane measured in GW following initial acclimatization period of 7 months

Economics

- A total of 10,000 lbs of EHC was applied at a product cost of $20,000.
- The material cost of using EHC was $1.24/ft^3$ ($44/m^3$).
- The injections were completed in 5 days.

EHC PRB Case Study, Kansas

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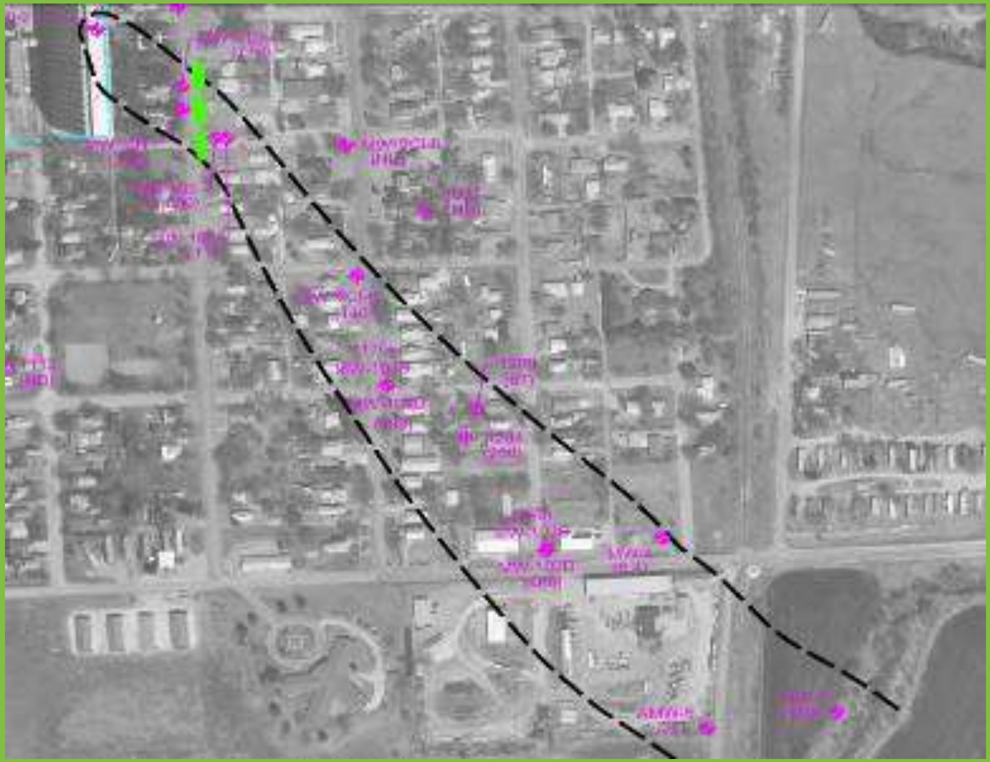


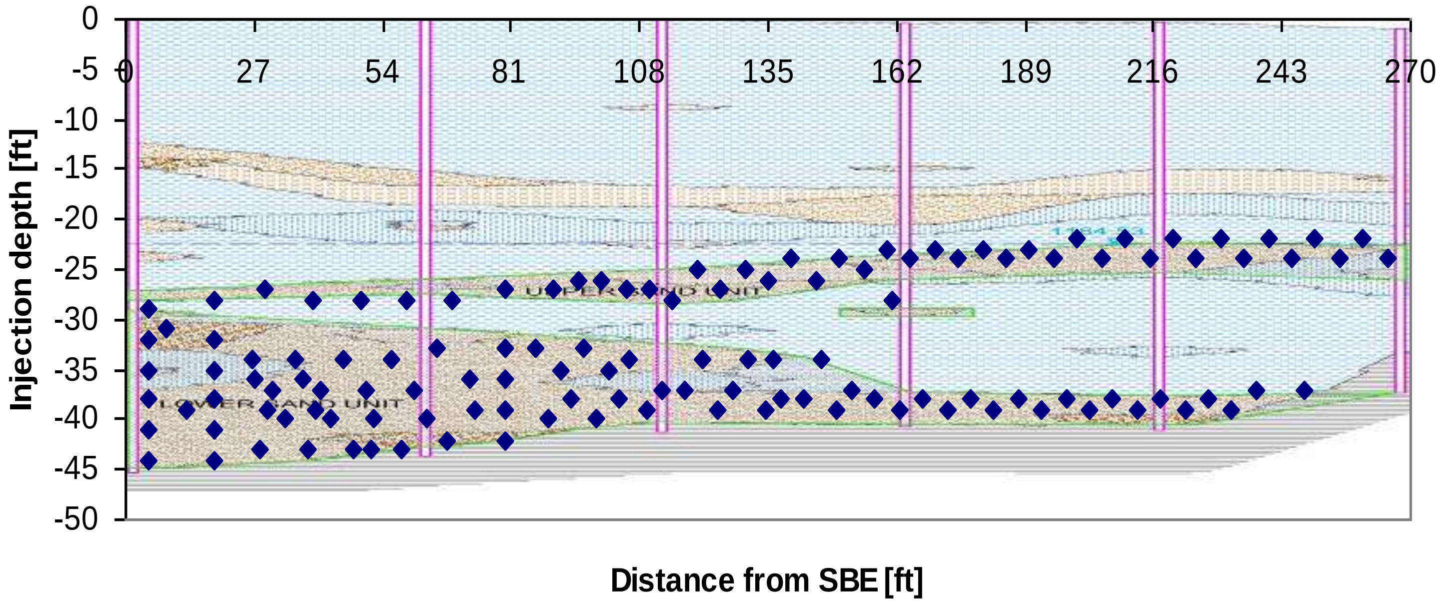
Figure courtesy of Malcolm Pirnie Inc.

- ❖Plume extends 2,600 ft / 800 m from grain elevators.
- ❖Discharges into small creek.
- ❖The bedrock rises to an elevation of ca 9 ft / 3 m above the present day water table at the presumed source area.
- ❖PRB installed down-gradient of suspected source area in April 2005.
- ❖The PRB is installed as a line of injection points spaced approximately 10 ft / 3 m apart.
- ❖The PRB extends across the width of the plume and measures ca 270 ft / 90 m long.

EHC Injection Set-Up

- A total of 48,000 lbs (21,818 kg) of EHC was injected into an area measuring approximately 270 ft (83 m) long x 15 ft (5 m) wide x 9 ft (3 m) thick on average.

Cross Section from PRB Area



Soil Cores

- Discrete EHC seams observed in soil cores collected up to 5 ft away from an injection point
- Seams observed in both clay and sand zones

Horizontal EHC fracture.

Vertical dipping fracture.

Hydraulic Profiling Tool

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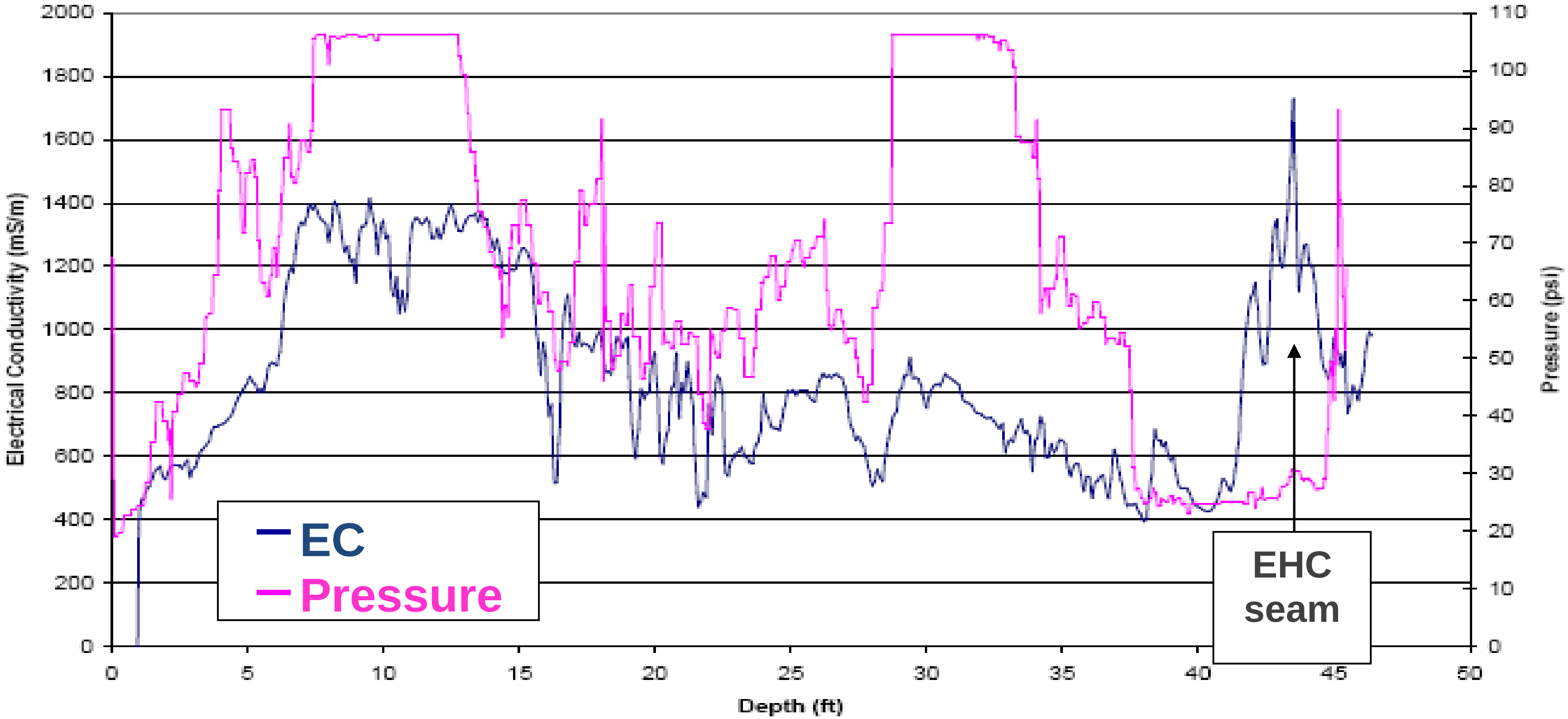
- The HPT uses a downhole transducer to simultaneously measure:
  - The pressure response of the soil to injection of water.
  - The electric conductivity (EC).

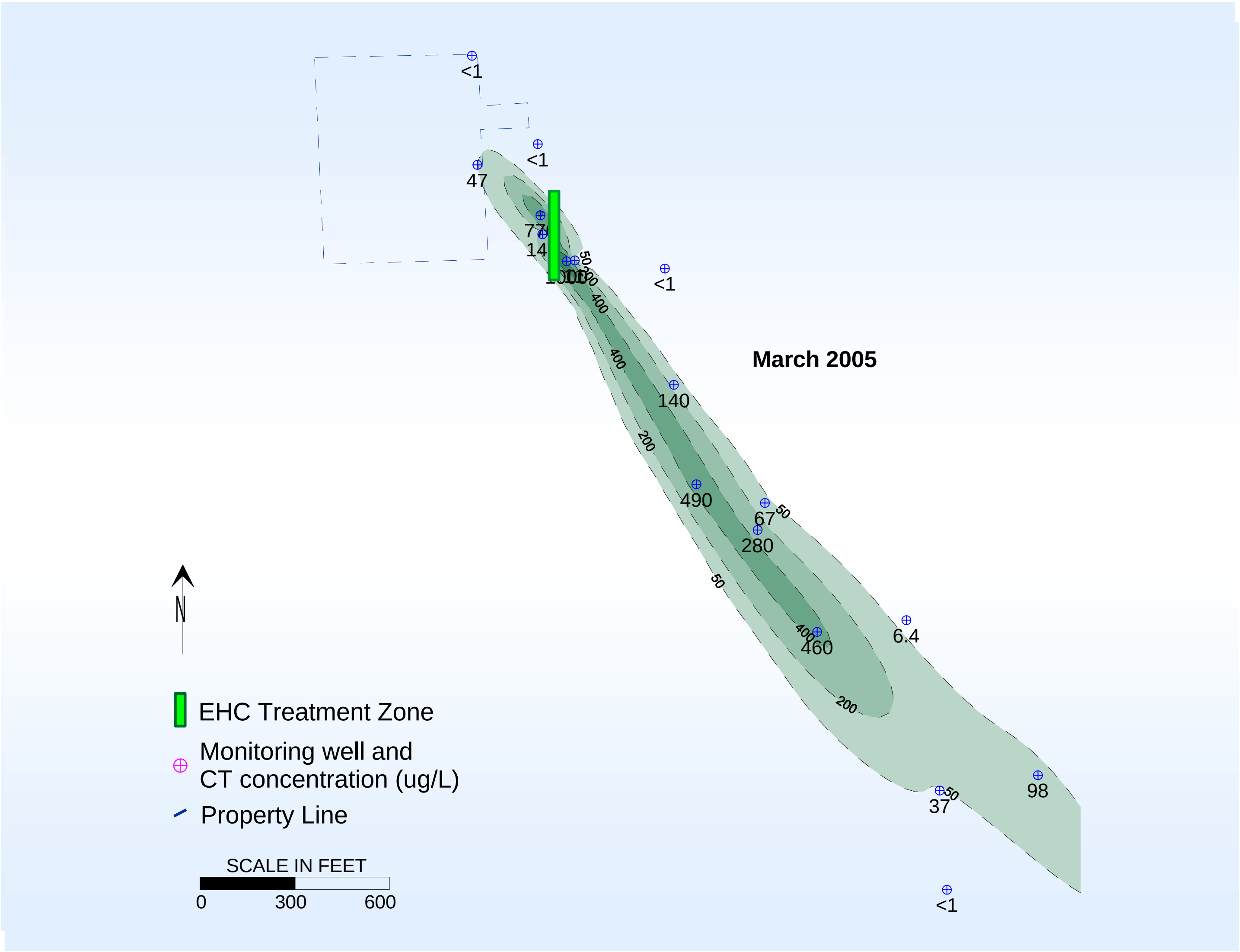
- Used to log soil type:
  - A low injection pressure and EC indicates a more permeable formation.
  - A high injection pressure and EC indicates finer grain sediments.
  - An anomaly in the graph with a simultaneous high EC and low pressure reading would indicate ZVI.

HPT Results – Kansas Site



- Only thicker fractures were detected by HPT (0.5 to 5 cm).
- This method likely more efficient in homogeneous soils.

CT Plume Progression



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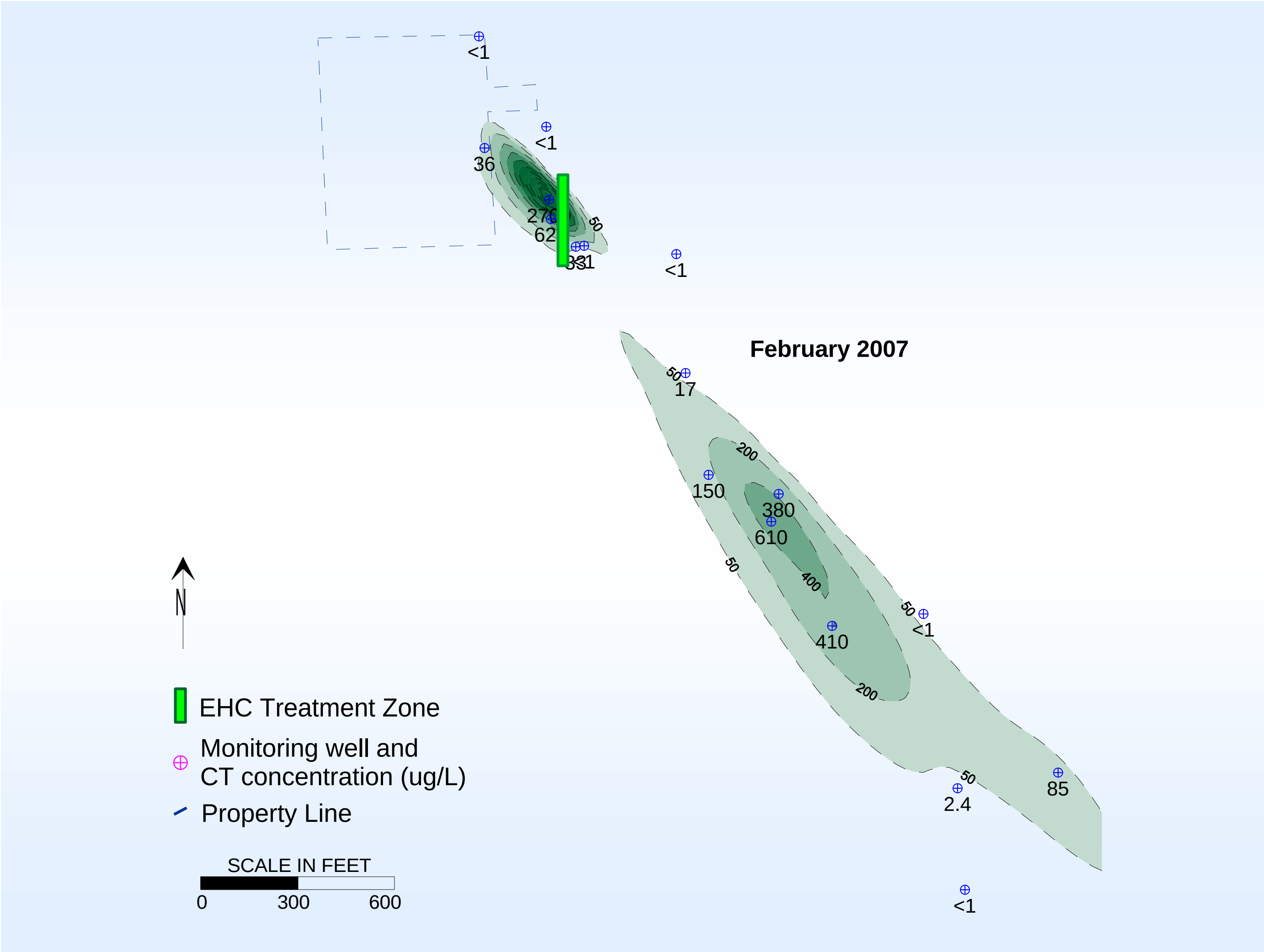

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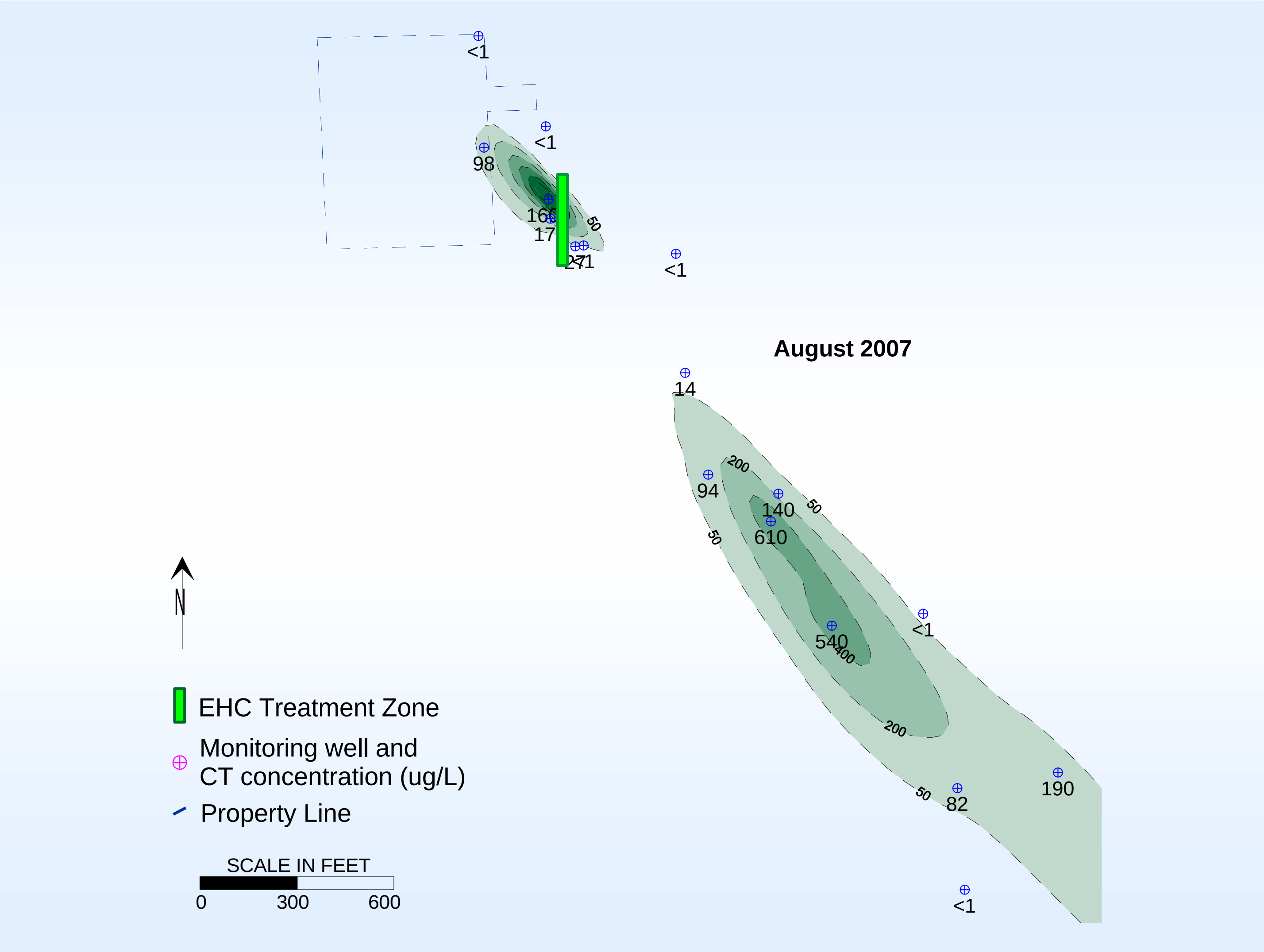
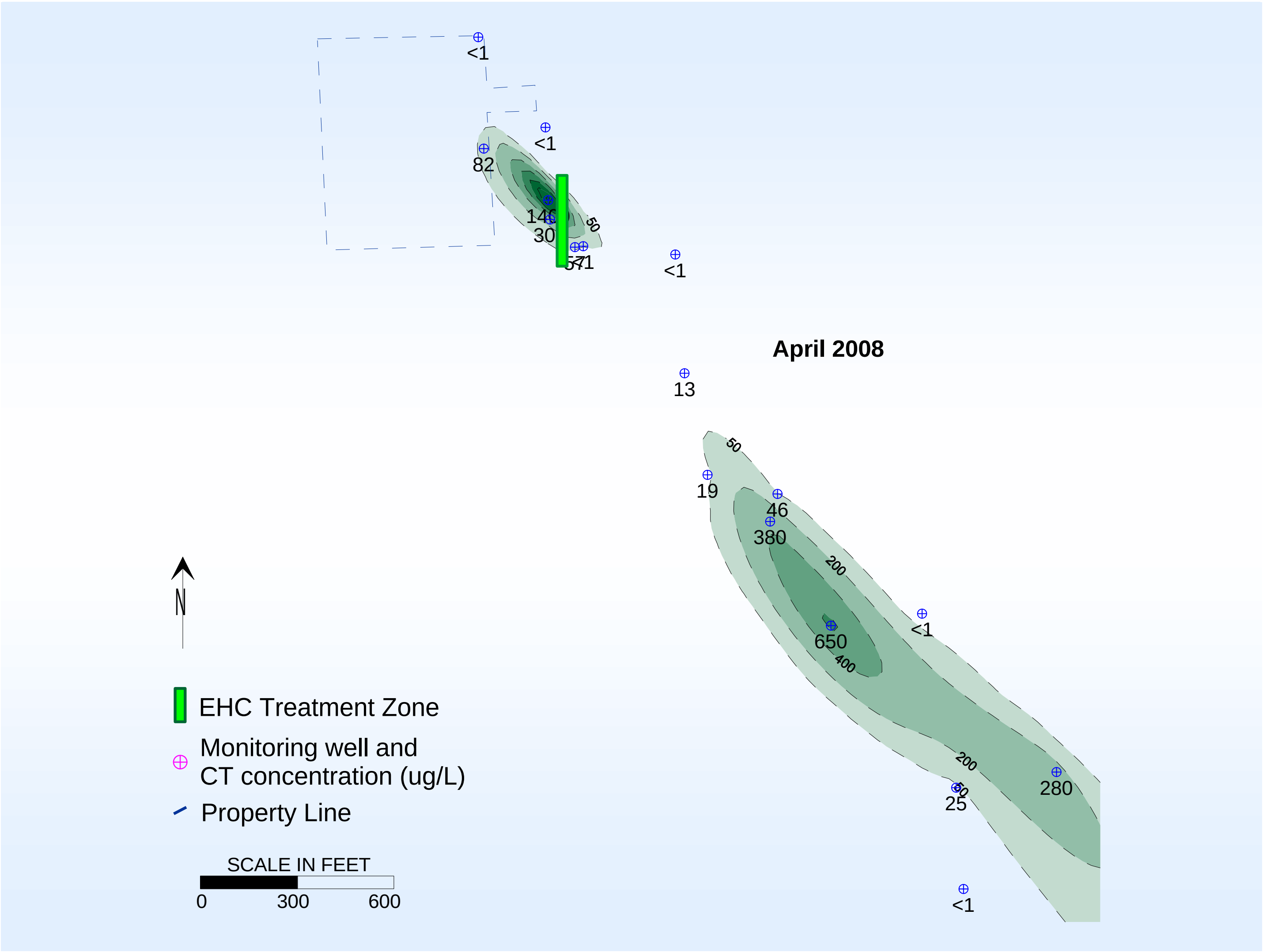


CT Plume Progression



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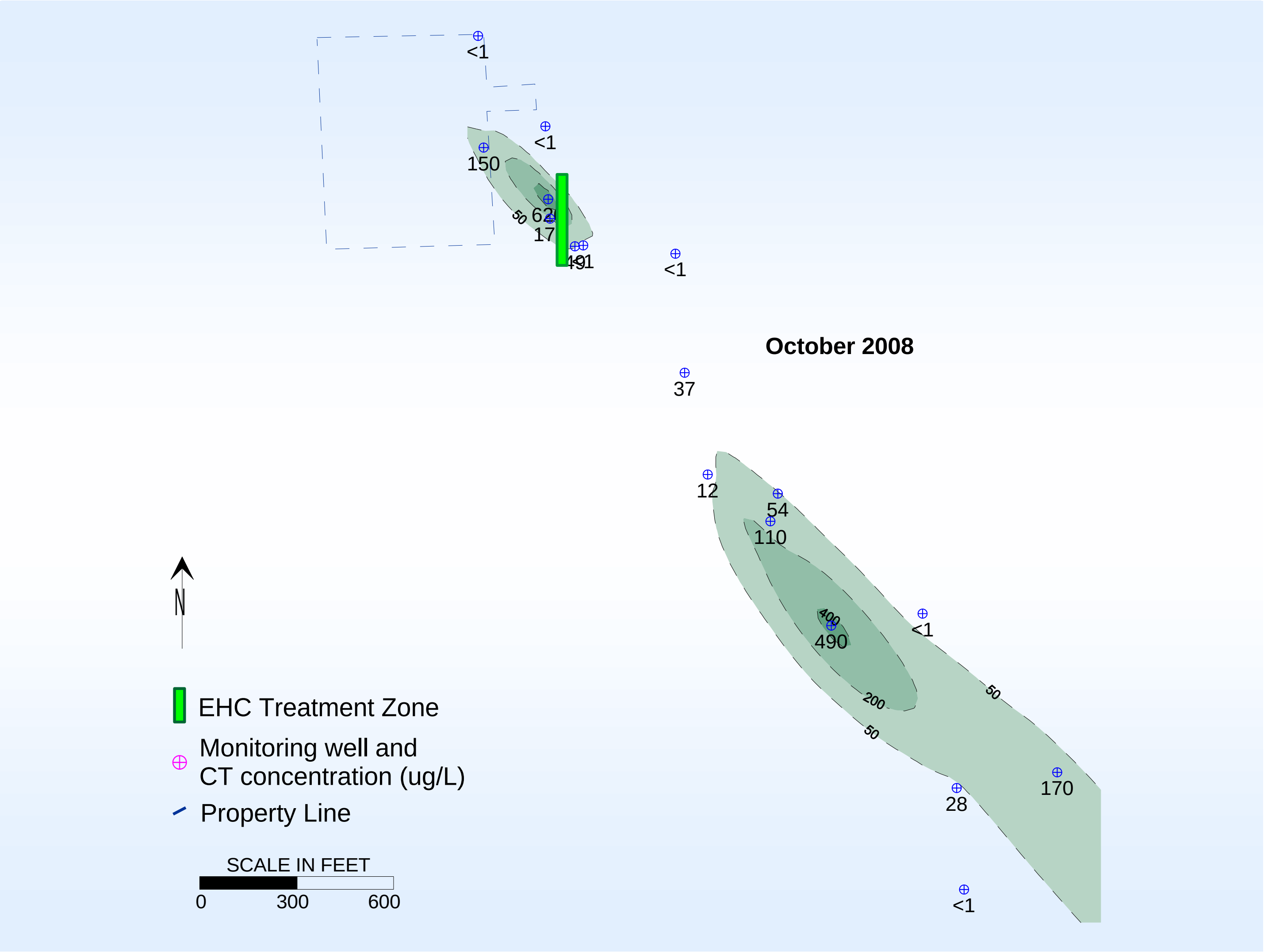

CT Plume Progression

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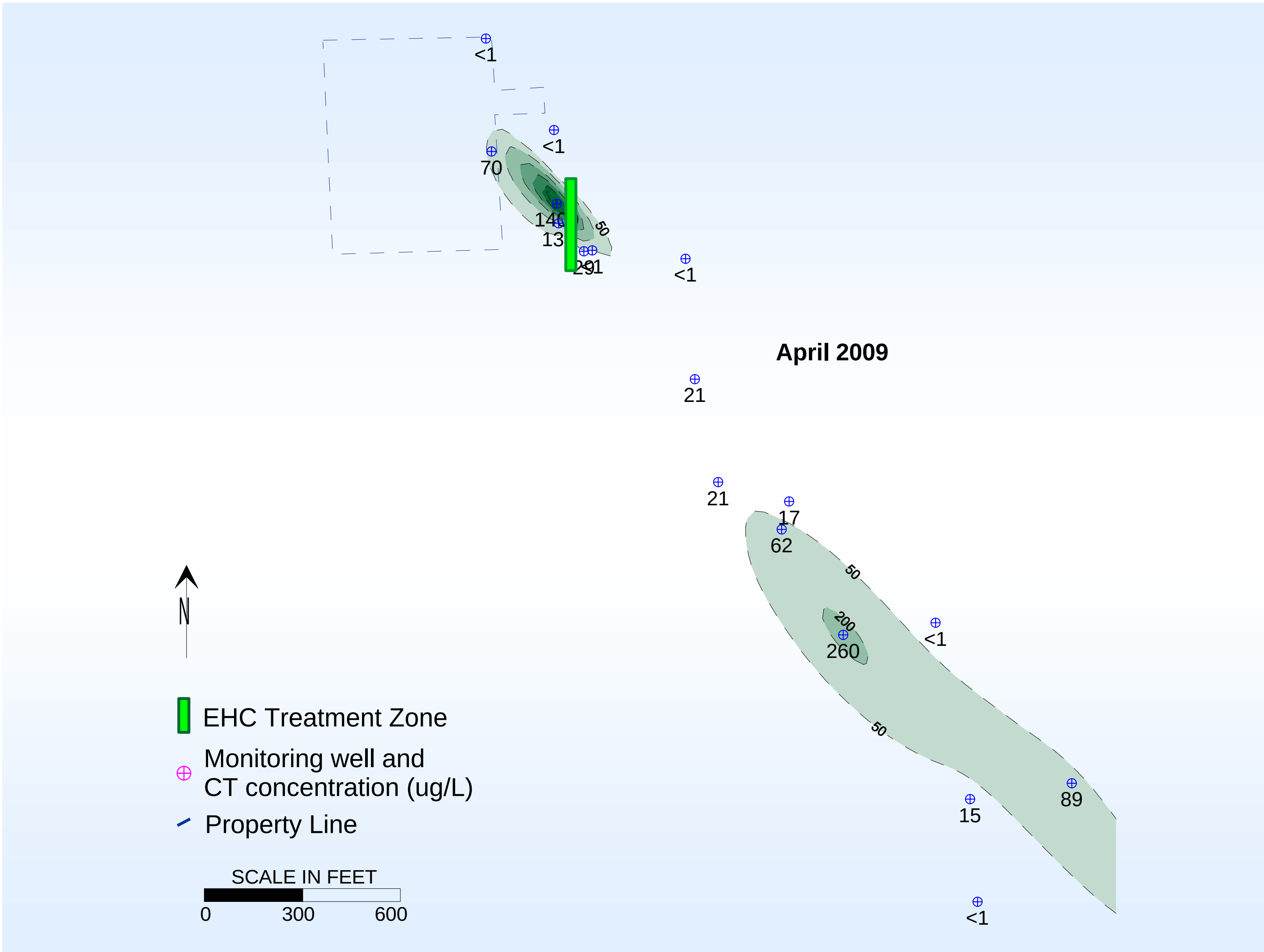

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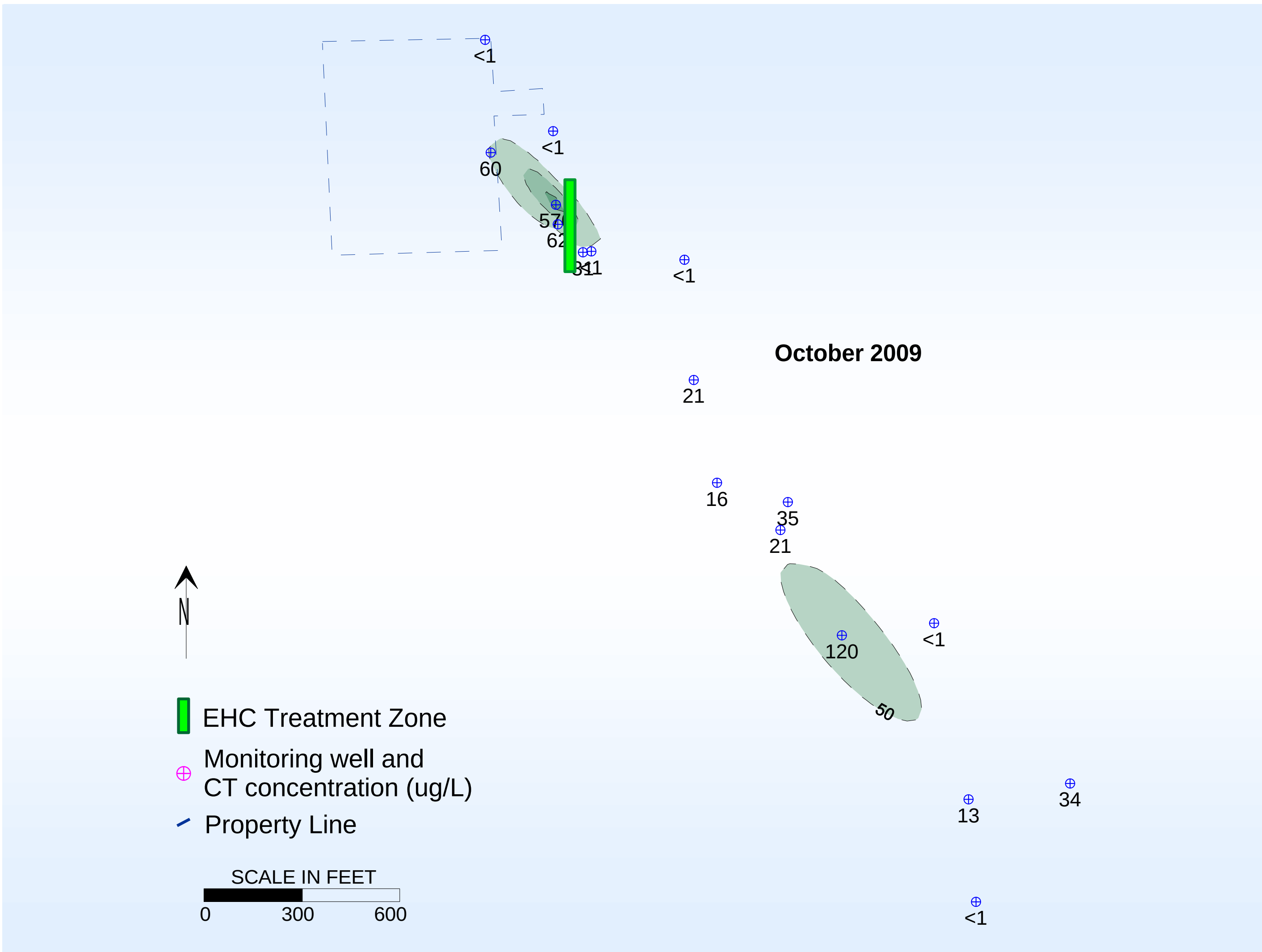

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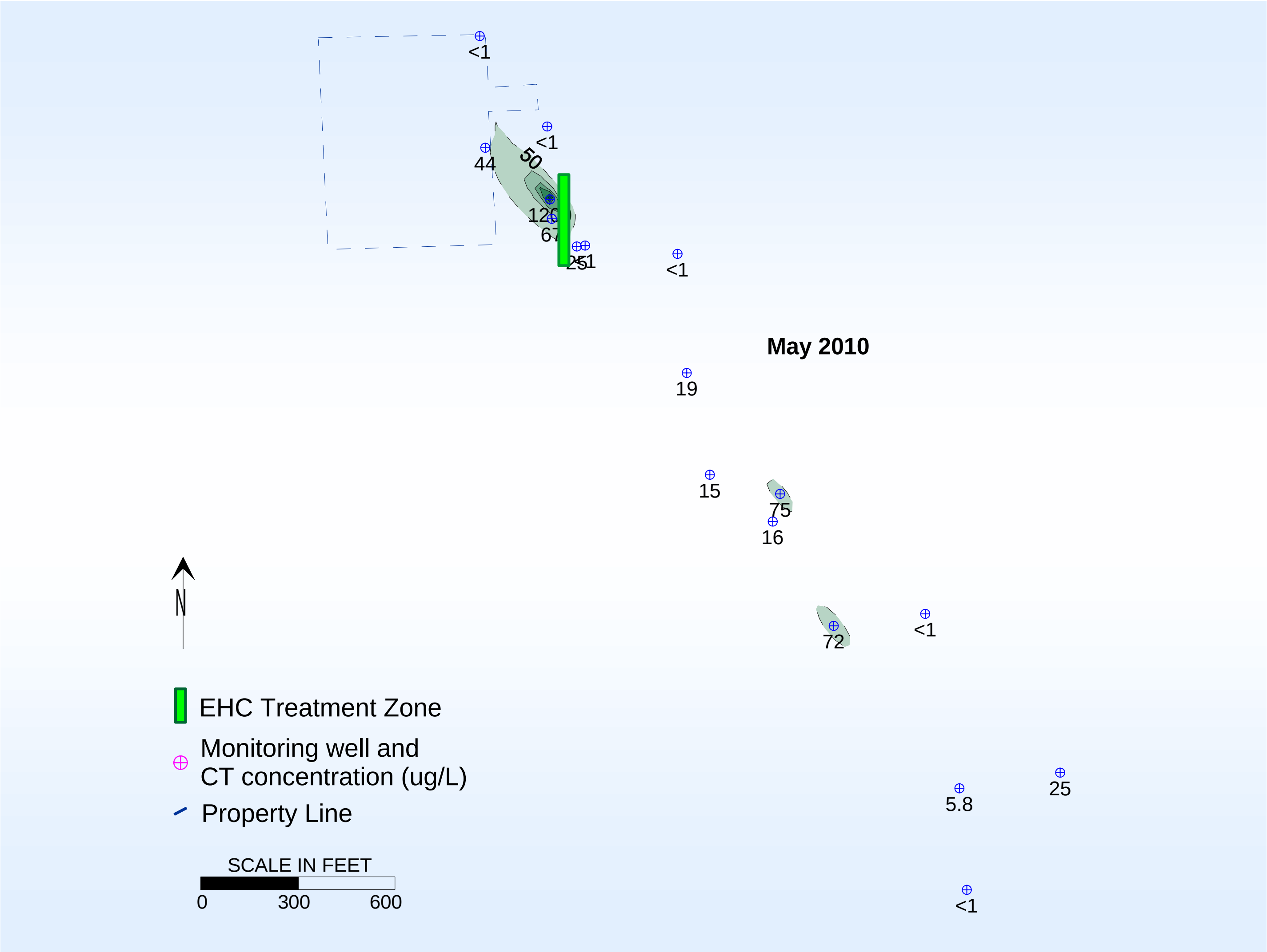

EHC PRB Economics

Remediation Costs

Amendment:	48,000 lbs (21.7 MT) EHC used in PRB Product cost = ~$100,000
Injection:	2 weeks of Geoprobe Injection Cost = ~$50,000
Total Fixed Cost:	$150,000
Operating Cost:	None

PRB treated 2,500,000 ft^3 GW over six years

Treatment Cost = $0.06/ft^3 ($ 2.12/m^3)

This is significantly lower than the pump and treat alternative where just the annual O&M Costs can range from $ 50K to $ 300K

Case Study

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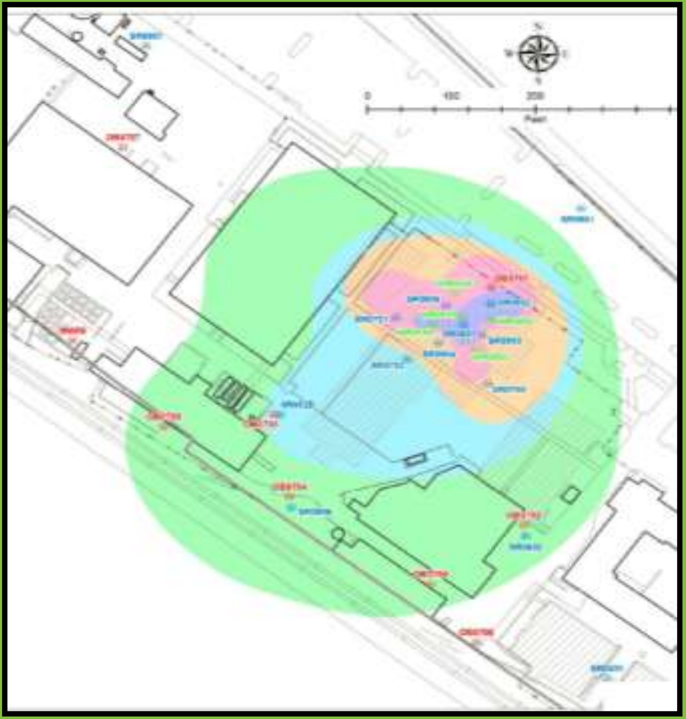
Hydraulic fracturing of EHC to treat 1,2 DCA in a fractured bedrock

Project location:
Former Herbicides Manufacturing Facility, PA

Consultant:
AMO Environmental Decisions

COC:
1,2-DCA (>220,000 ppb in shallow rock)



Lithology: The Stockton Formation beneath the site consists of moderately cemented, red-brown to light-gray, thin to moderately-bedded mudstone, siltstone and sandstone.

Pilot Test Injection

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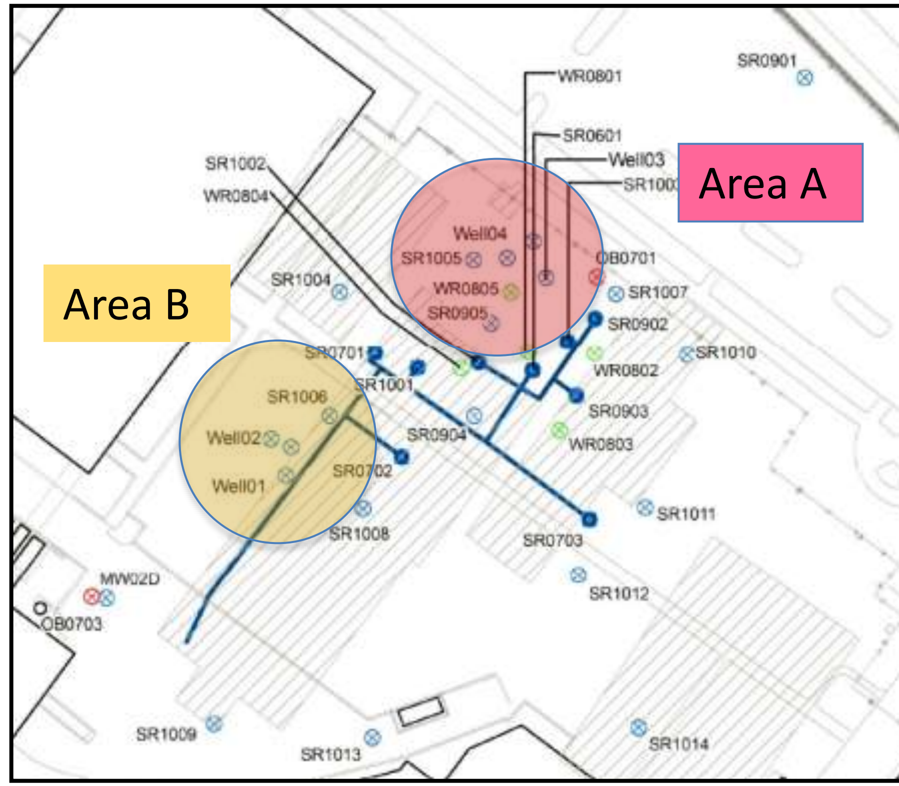
1. One injection point each in **Area A** (> 10 mg/L 1,2-DCA), and **Area B** (1-5 mg/L 1,2-DCA) to a depth of 50 ft bgs.

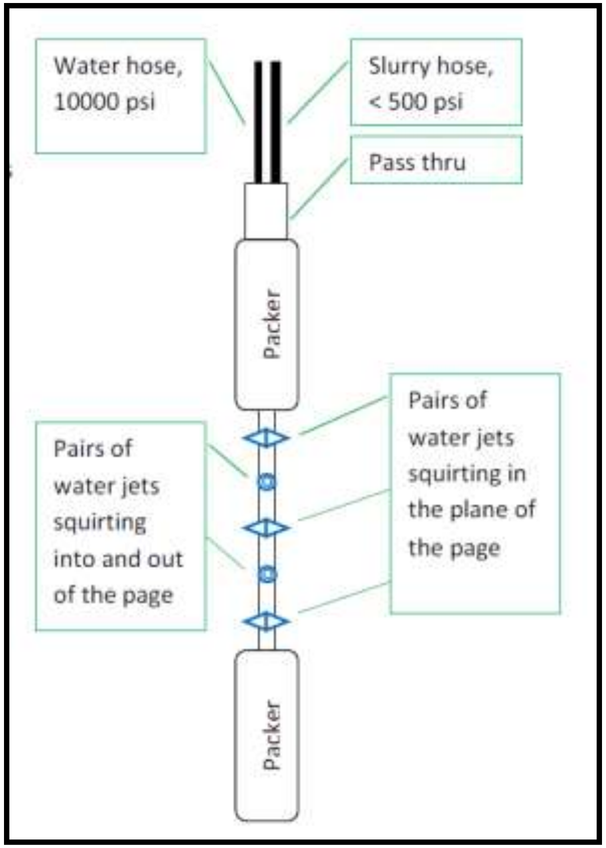
2. The objective was to effectively fracture the formation outward 20 feet radially from the proposed injection points.

3. For **Area B** injection point, a total of 3,600 lb of EHC was injected into 4 fractures (900 lb per fracture).

4. For **Area A** injection point, a total of 7,200 lb of EHC was injected into 8 fractures (900 lb per fracture).



Hydraulic Fracturing Set Up



Source: FRx

Guar

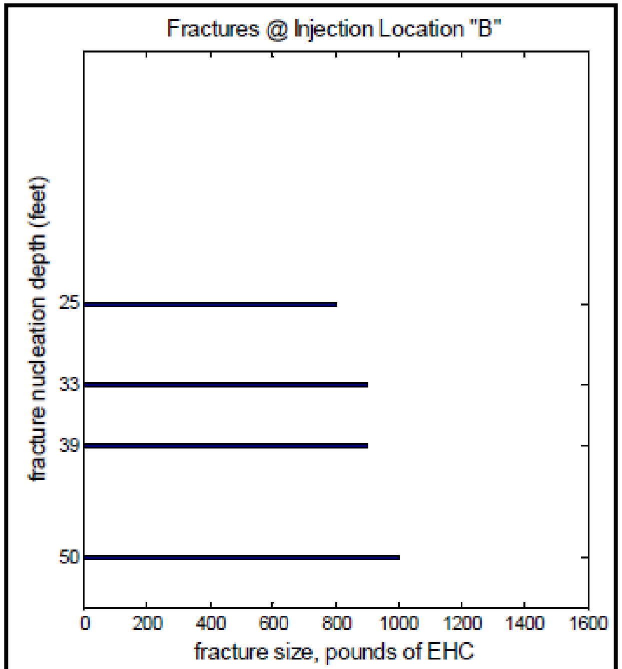
EHC mixed with Guar

Fracturing Results – ROI

ROI of > 75 ft estimated based on various measurements such as :

- ZVI in cores
- Uplift stakes
- Tilt meters
- EHC residue in extraction wells
- Observed changes in geochemistry

Figure 3. Iron collected during coring of 33'-38', 38-43', 43'-48' and 48'-53'. A clean magnet is shown for comparison.



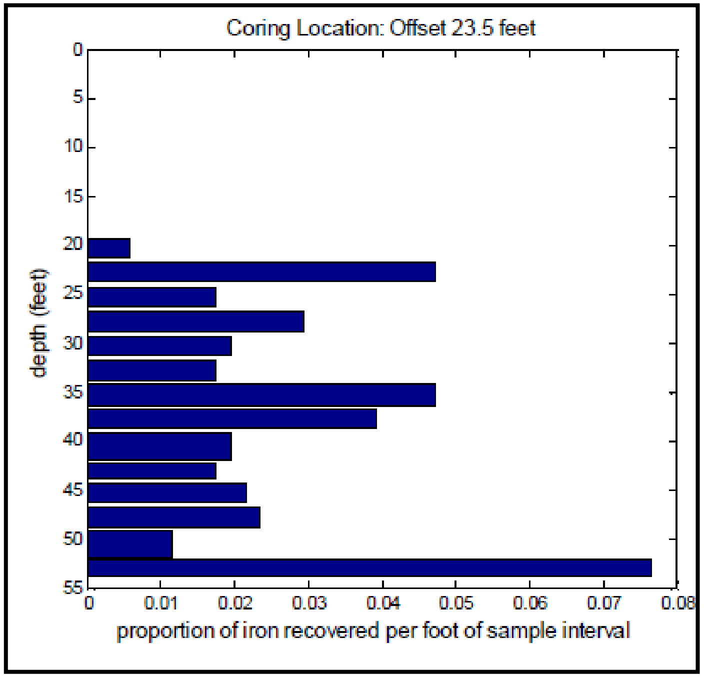


Figure 2. Magnets, within protective latex glove, placed within coring returns on A-6.

1,2 DCA Plume Trend: Pilot 2010/Full Scale 2012

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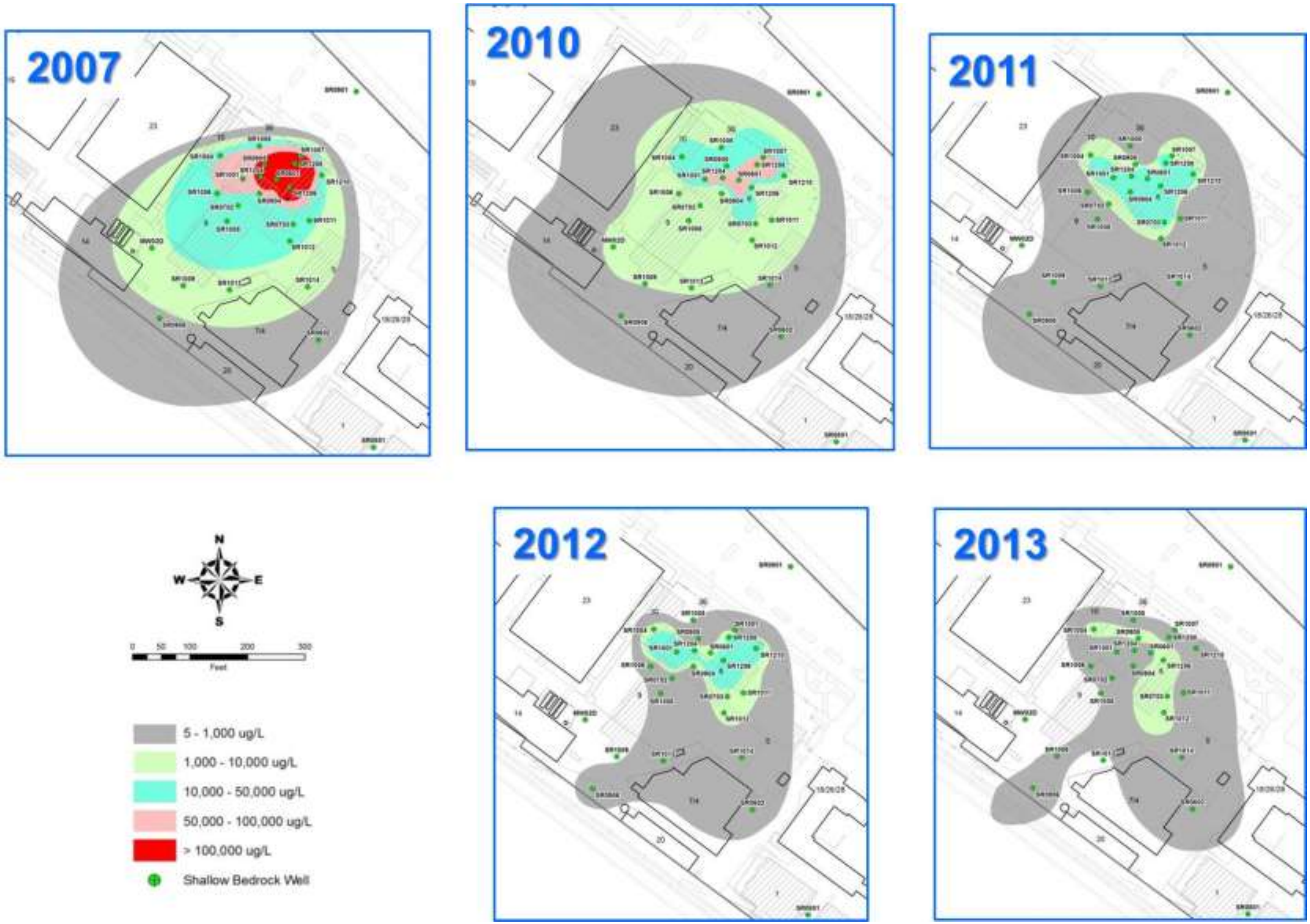

Source:AMOED

So in conclusion..

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Complete degradation of targeted constituents has been achieved at numerous sites where the distribution could be viewed as “non-homogenous”

→ Uniform distribution is NOT required during injection, but rather the creation of a sufficiently uniform network of “reagent seams”.

→ The longevity of EHC is a key attribute in formations where uniform distribution is difficult to achieve.

Thank you!

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