Comparison of EHC®, EOS®, and Solid Potassium Permanganate Pilot Studies for Reducing Residual TCE Contaminant Mass

Defense Distribution Depot
San Joaquin-Sharpe Site
Lathrop, California

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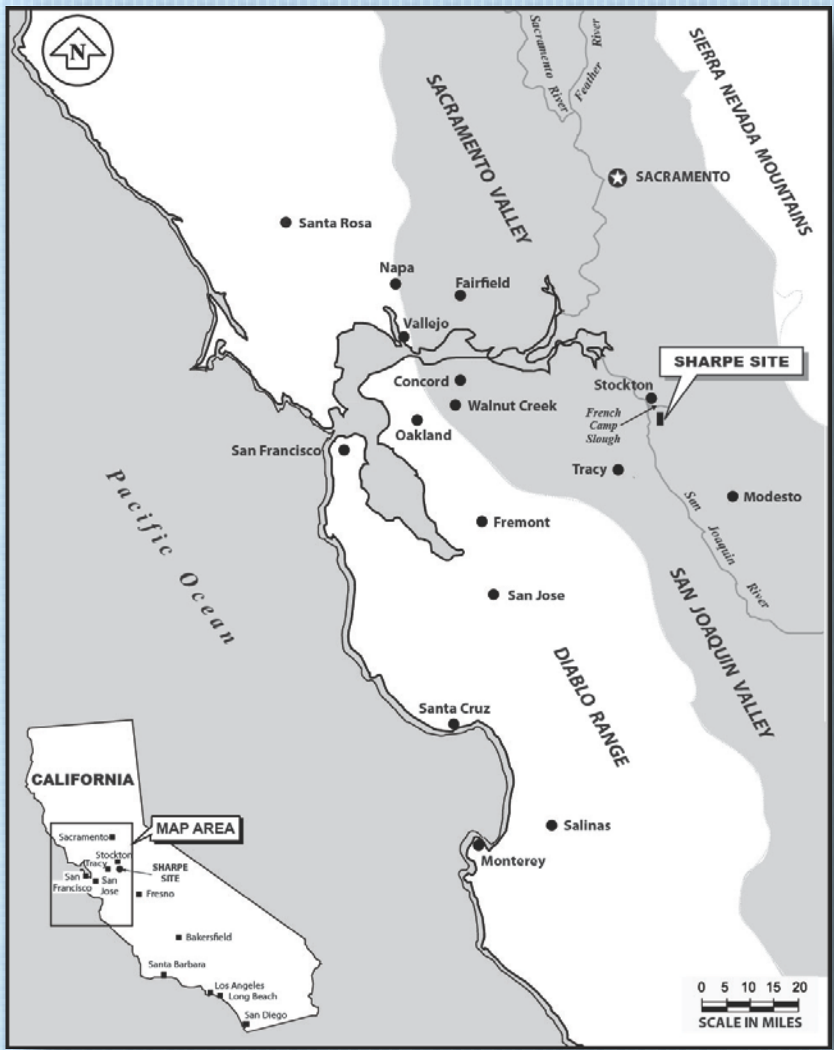
Presentation Outline

- Project Site Overview
- Pilot Study Selection
- EHC® Pilot Study
- EOS® Pilot Study
- Solid $KMnO_4$ Pilot Study
- Pilot Study Comparison
- Benefits of Remedy Enhancement

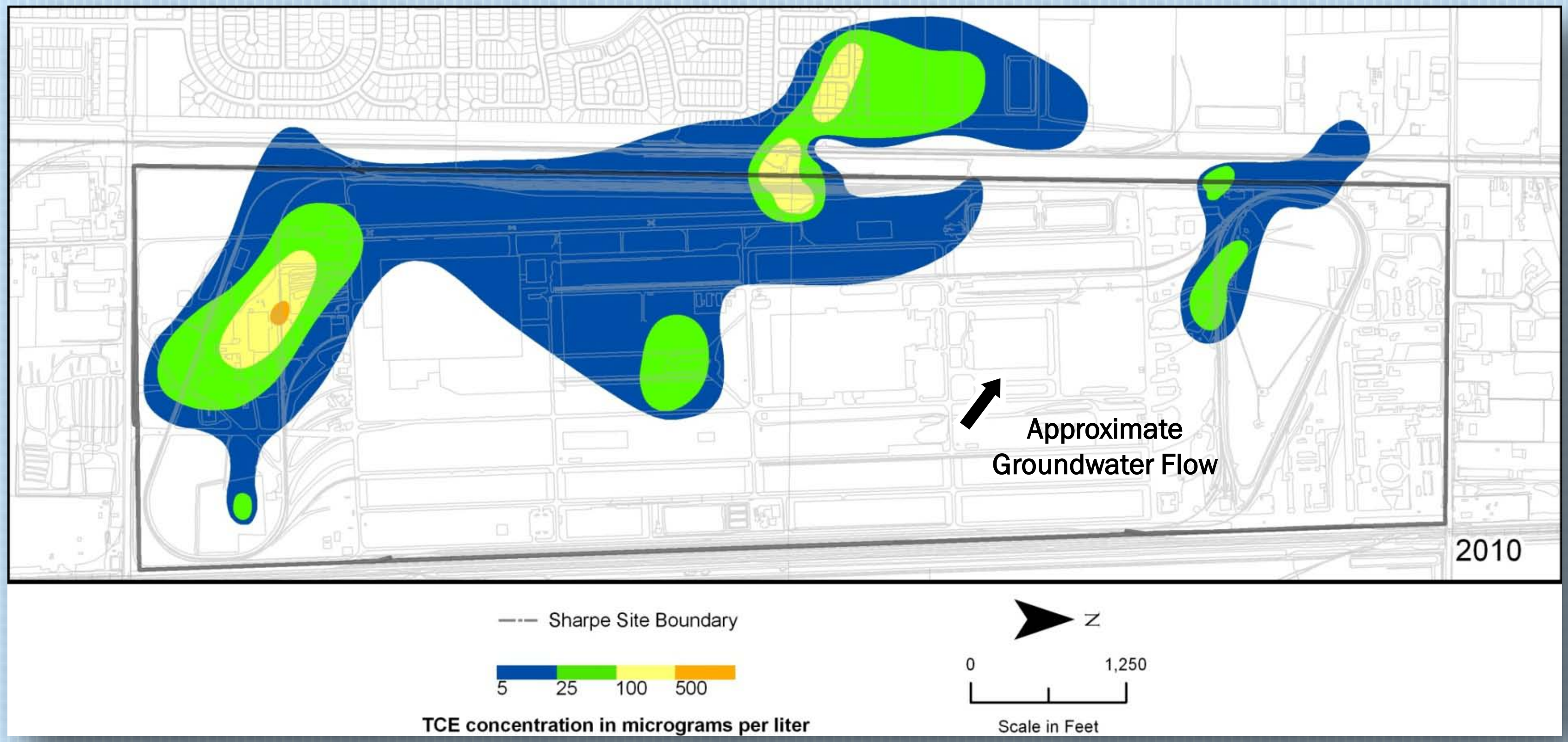
Project Site Overview

- Defense Distribution Depot San Joaquin – Sharpe Site, Lathrop, CA
- Principal mission since 1940s:
  - Storage
  - Shipment
  - Packaging of general supplies
  - Maintenance of equipment
- Groundwater contaminated primarily with TCE
- Added to National Priorities List in 1987
- ROD established TCE cleanup level at 5 µg/L



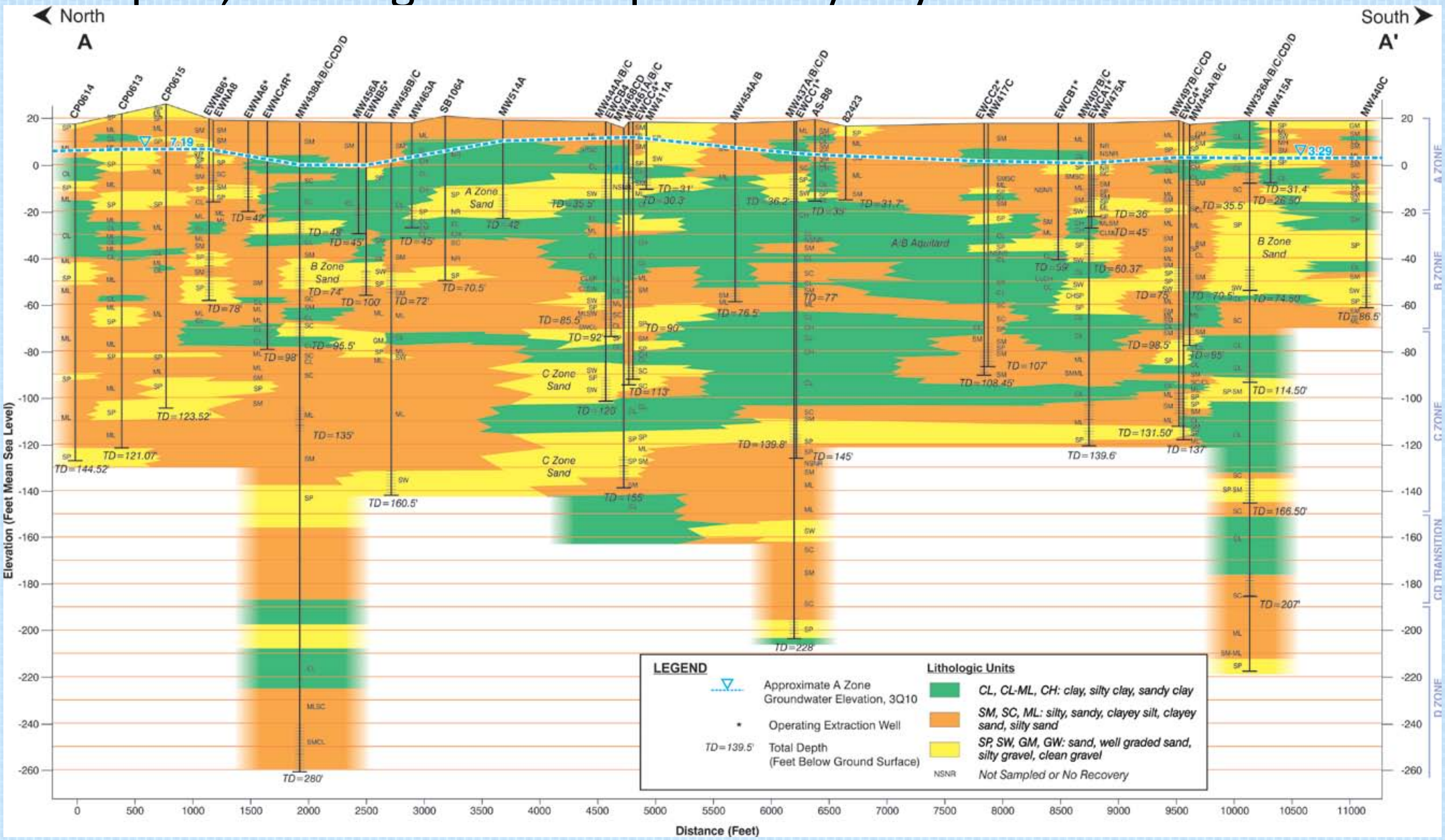
Project Site Overview

- Maximum TCE concentration is 1,020 µg/L (monitoring well data)
- Large plumes



Project Site Overview

- Groundwater depth ~ 20 feet bgs
- Complex, heterogeneous aquifer. Silt/clay & discontinuous sands



Project Site Overview

Remedy Enhancement Evaluation

- Pump and treat operating since 1987
- In 2010, 57 pounds removed at ~$20,000/lb
- **In situ remediation alternatives were evaluated to:**
  - **Improve the effectiveness of the existing groundwater remedy**
  - **Decrease energy consumption**
  - **Reduce lifecycle costs**

Pilot Study Selection

Site Characteristics		Technology Criteria
❖ Heterogeneous lithology	➡	❖ Readily dispersed
❖ Neither strongly oxidative or reductive	➡	❖ Either a reductive dechlorination or oxidation technology
❖ Contamination extends deeper than 100 feet	➡	❖ Can cost-effectively inject deeper than 100 feet
❖ Residual contamination primarily located in fine-grained soils (silts/clays)	➡	❖ Access fine-grained soils ❖ Long lasting

Pilot Study Selection

- Pilot Study Objective
  - Compare TCE Destruction Effectiveness
    - Reducing amendments
    - Oxidizing amendments
  - Compare Delivery Methods
    - Two delivery methods' amendment distribution into fine-grained soils

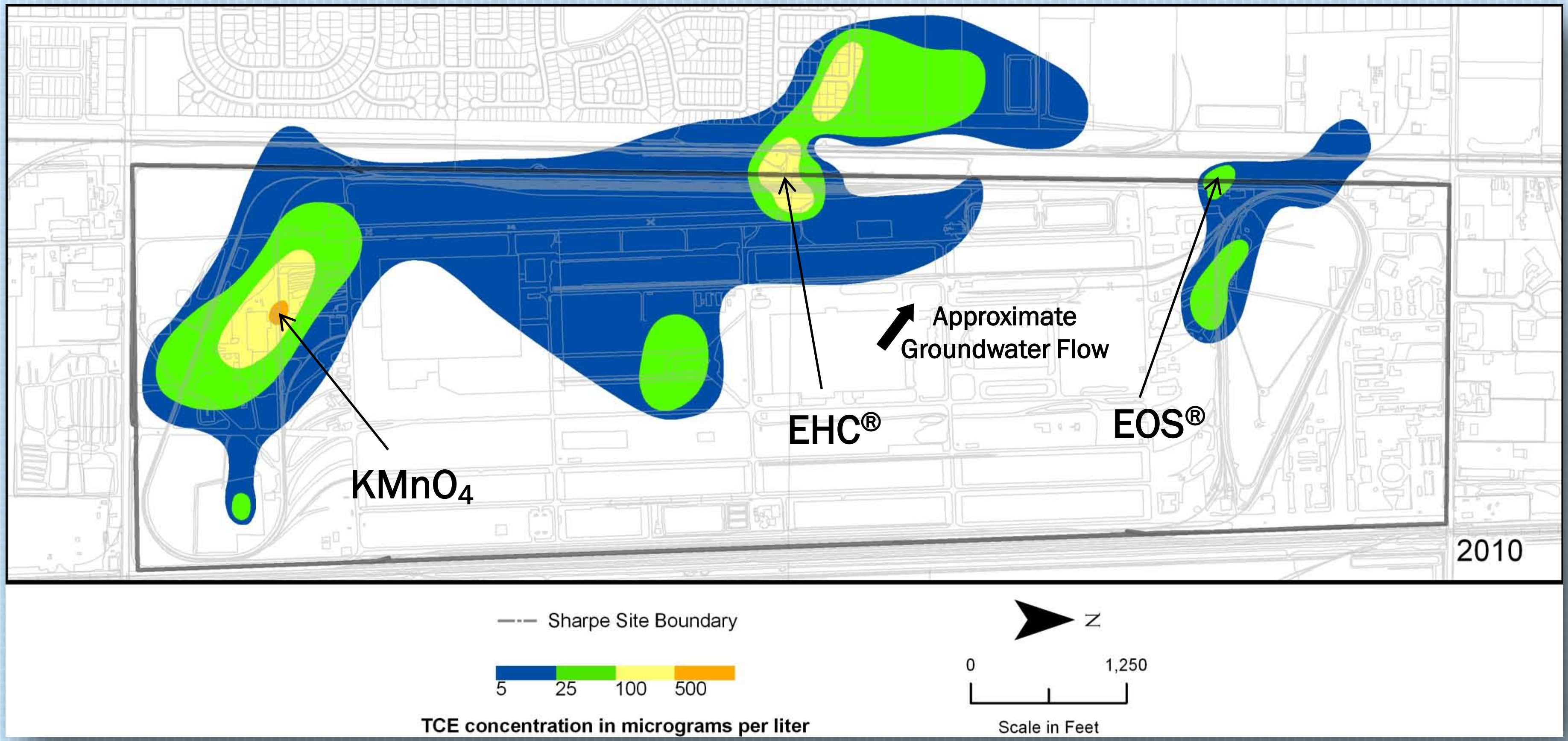
Pilot Study Selection

Amendment and Distribution Selection

- Three amendments and two delivery methods were selected to target residual mass in fine-grained soils
  - EHC® injected by hydraulic fracturing
  - Emulsified vegetable oil (EOS®) injected via gravity fed injection wells
  - Solid potassium permanganate ($KMnO_4$) injected by hydraulic fracturing

Pilot Study Selection

- Pilot Study Locations



EHC® Pilot Study

- EHC® contains fibrous organic material and zero valent iron
- Promotes biotic and abiotic (chemical) reductive dechlorination
- EHC® benefits
  - Long lasting
  - Combines reducing potential of both organics and reduced metals

EHC® Pilot Study

Pilot Study Activities

- Baseline CPT/HydroPunch® sampling
- Inject EHC® at four depths using hydraulic fracturing (rhodamine red dye and bromide added as tracer)
- Monitor performance:
  - Fracture radius determination
  - Groundwater sampling using both CPT/HydroPunch® and monitoring wells
  - Assessment of vertical and lateral diffusion of EHC® (HSA core at 12 months)

EHC® Pilot Study

Pilot Study Results

- Distribution
  - The fractures extended 15 feet horizontally in a southwest direction
  - Fracturing was not predictable or uniform
- TCE Destruction
  - TCE concentrations were reduced from 600-760 µg/L to ND-0.8 µg/L (100- 99% reduction) in two wells after 24 months
  - EHC® influence continuing to expand at 24 months

EOS® Pilot Study

- EOS® 598 B42 =
  - Emulsified soybean oil (longer lasting hydrogen source)
  - Lactate (immediate source)
  - Nutrients
- EOS® stimulates biological reduction of chlorinated solvents (TCE, DCE, VC, etc)
- EOS® benefits
  - Long lasting
  - Easily dispersed/distributed

EOS® Pilot Study

Pilot Study Activities

- Install short-screened injection wells in two different soil types
  - Fine-grained soils
  - Sands
- Baseline groundwater well and CPT/HydroPunch® sampling
- Injected EOS®-water-bromide tracer emulsion via gravity feed
- Performance monitoring
  - Groundwater sampling using monitoring wells
  - Slug testing to determine effect on hydraulic conductivity

EOS® Pilot Study

Pilot Study Results

- Distribution
  - Radius of injection was at least 5 feet in fine-grained soils to 8 feet in sands
  - Radius of influence increased by 5 feet due to advection
  - Non-uniform distribution
  - Slug testing – EOS® no effect on permeability
- TCE Destruction
  - TCE concentrations reduced from ~200 µg/L to < 5 µg/L where dissolved organic carbon concentrations remained > 20 mg/L

Solid $KMnO_4$ Pilot Study

Source: http://www.liboxgoa.com

- $KMnO_4$ oxidizes chlorinated solvents
  - $CO_2 + MnO_2 + K^+ + H^+ + Cl^-$
- Solid $KMnO_4$ benefits:
  - Long lasting
  - Diffuses into fine-grained soils

Solid $KMnO_4$ Pilot Study

Pilot Study Activities

- Baseline CPT/HydroPunch® sampling
- Inject <u>*solid*</u> $KMnO_4$ as a $KMnO_4$ solids-gel slurry at four depths using hydraulic fracturing
- Monitor performance
  - Fracture radius determination (HSA cores)
  - Groundwater sampling using both CPT/HydroPunch® and monitoring wells
  - Assessment of vertical and lateral diffusion of $KMnO_4$ (6 & 12 month HSA cores)

Solid $KMnO_4$ Pilot Study

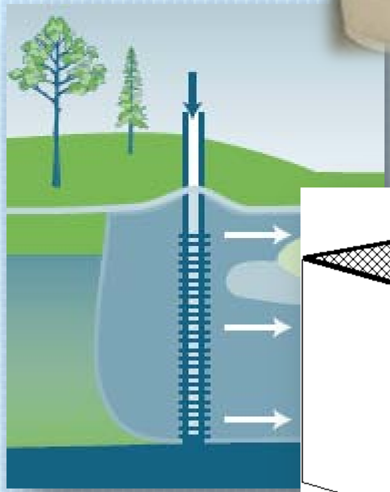
Pilot Study Results

- Distribution
  - The fractures extended 15 feet generally in a southwest direction
  - Fracturing was not predictable or uniform
  - Vertical diffusion rate ~10 inches/month
- TCE Destruction
  - TCE Reduced from > 1,000 µg/L to < 5 µg/L in less than 6 months in all locations

Pilot Study Comparison

- Amendment Comparison
  - EHC®
  - EOS®
  - $KMnO_4$
- Delivery Comparison
  - Injection Wells
  - Hydraulic Fracturing

Source: http://www.liboxgoa.com



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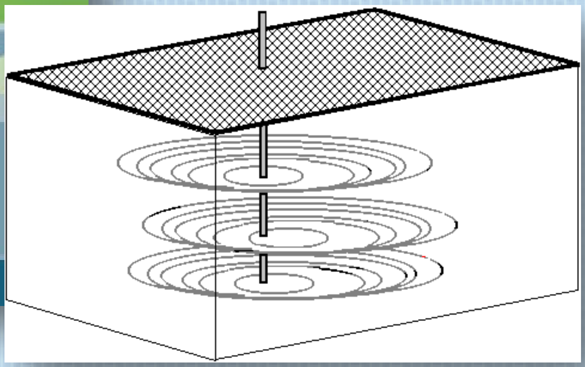
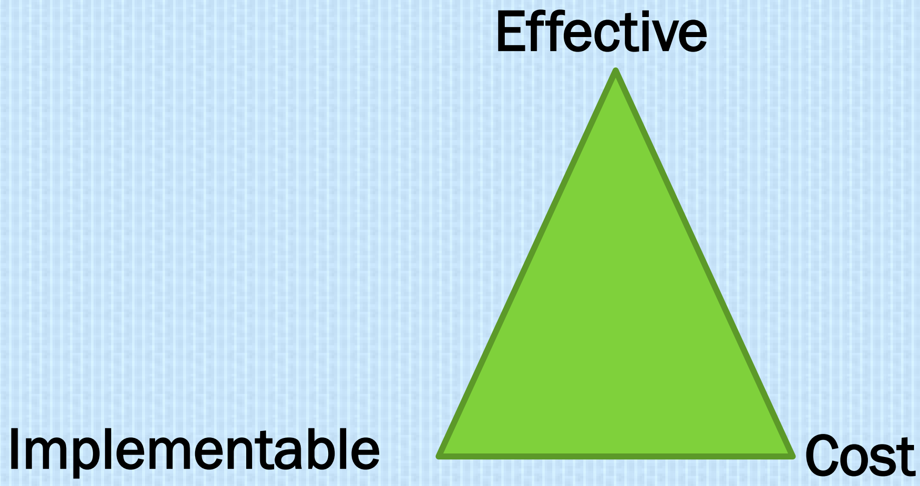


Source: FRx Inc.

Pilot Study Comparison

Basis for Evaluation of Pilot Studies

- Evaluate based on:
  - Effectiveness
  - Implementability
  - Cost



Pilot Study Comparison

Amendment Comparison

	EHC®	EOS®	Solid Potassium Permanganate
Destruction Mechanism	Biotic and abiotic (chemical) reductive dechlorination	Biotic reductive dechlorination	Chemical oxidation
TCE Destruction	1,000 µg/L to <5 µg/L (in 2 of 4 wells)	200 µg/L to <5 µg/L (if DOC > 20 mg/L)	>1,000 µg/L to <5 µg/L (in all locations)
Treatment Time	24 months for TCE >24 months for cis-1,2-DCE	3-6 month for TCE 12-28 months for cis-1,2-DCE	< 6 months for all VOCs (based on first post-fracture sampling event)

Pilot Study Comparison

Amendment Comparison (continued)

	EHC®	EOS®	Solid Potassium Permanganate
Formation of TCE daughter products	Yes	Yes	No
Rebound or influx from upgradient	Yes	Yes	None observed after 12 months
Distribution (by diffusion and advection) after injection	5 feet horizontally in 12 months	5 feet horizontally in 12 months	5 feet horizontally in 12 months 5 to 15 inches/month vertically (in first 6 months)

Pilot Study Comparison

Amendment Comparison (continued)

	EHC®	EOS®	Solid Potassium Permanganate
Secondary Water Quality Changes	• Increased calcium, potassium, sodium, magnesium, arsenic, barium, boron, iron, manganese, strontium, TDS	• Increased arsenic, iron, manganese, TDS • Decreased pH	• Increased barium, chromium, manganese, TDS • Decreased arsenic and cadmium • Did not increase chromium VI

Pilot Study Comparison

Amendment Comparison (continued)

	EHC®	EOS®	Solid Potassium Permanganate
Amendment Dosage (Design)	1,635 gallons (0.20% EHC by soil mass)	3,300 gallons • Clays/Silts: 1,000 gallons of 12% EOS®-water emulsion • Sands: 2,300 gallons of 5% EOS®-water emulsion followed by 440 gallons of "chase" water	1,490 gallons (2,000 lbs/ fracture [equiv. to 12,000 gallons 2% solution])
Pilot Study Amendment Cost per Cubic Yard Soil (Design)	$14 (sands or fines)	• $39 (fines) • $13 (sand)	$19 (sands or fines)

Pilot Study Comparison

Amendment Comparison Conclusions

- All three amendments:
  - Reduced TCE concentrations to less than 5 µg/L (cleanup level) where amendment contacted contaminant
  - Continued to distribute/diffuse horizontally after injection
  - Had secondary water quality impacts
- Solid $KMnO_4$ was selected as the preferred amendment
  - $KMnO_4$ distributed/diffused significantly more in fine-grained soils than the other two amendments
  - Destroyed TCE more quickly than other amendments without daughter products
  - Cost effective since multiple injections are not necessary

Pilot Study Comparison

Delivery Method Comparison

	Injection Wells	Hydraulic Fracturing
Extent of Delivery	5 to 8 feet	6.5 to 12.5 feet
Distribution	• Non-uniform • Distributed more in coarse-grained soils	• Non-uniform • Distributed in both fine-grained and coarse-grained soils • Short circuiting potential
Time to Inject	2 days	1 to 4 days
Pilot Study Cost (Injection cost only. No oversight costs included)	$40k	$60k – EHC® $80k – $KMnO_4$

Pilot Study Comparison

Delivery Method Conclusions

- Both delivery methods resulted in non-uniform distribution
- Hydraulic fracturing costs more initially but can be cost effective since multiple injections are not necessary
- Hydraulic fracturing was selected as the preferred delivery method
  - Hydraulic fracturing increased the distribution of the amendment in fine-grained soils when compared to gravity-fed injection wells

Benefits of Remedy Enhancement

- Benefit of effective destruction of residual contaminant mass in fine-grained soils is that it increases the effectiveness of the existing system by:
  - Reducing overall cleanup time
  - Reducing long-term costs
  - Reducing long-term energy demands

Questions?