Insights into optimizing *In Situ* chemical oxidation and reduction of contaminants using advanced delivery and mapping techniques

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Outline

- Critical factors in achieving remedial success using ISCO and ISCR
- Mode of Emplacement of treatment amendments (i.e. oxidants/reductants)
- Emplacement techniques for optimum and targeted delivery of amendments
- Mapping techniques to verify the final subsurface distribution of amendments
- Case studies: Oxidation of PHCs and Reduction of CHCs

Critical Factors in consideration of *in situ* chemical oxidation/reduction

- Subsurface Environment: Lithology, Geotechnical, Geochemical, and Hydrogeologic characteristics
- Reaction Kinetics between treatment amendment and contaminants with respect to soil geochemistry
- Mode of Emplacement: ie. what is the predominant delivery mechanism and configuration of amendments in the subsurface?
- Verification of subsurface distribution of amendments with respect to contaminant distribution

Critical Elements for successful In Situ Remediation

DELIVERY + TREATMENT

DRILLING METHOD / TOOLING

EMPLACMENT TECHNIQUE

GEOLOGY

TREATMENT KINETICS / CHEMISTRY

CONTAMINANT TYPE and DISTRIBUTION

Mode of Amendment Emplacement

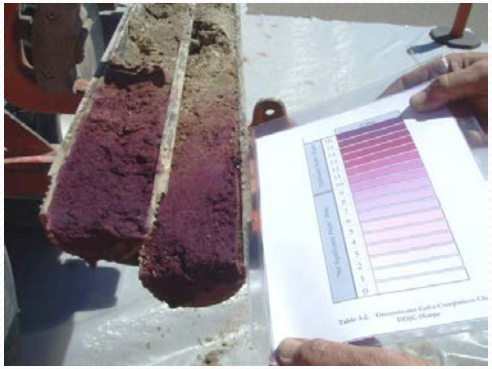
The way an oxidant or reductant amendment travels through the subsurface environment is dependent on the physical state of the amendment (gas, liquid, or solid) relative to the geotechnical properties of the receiving soil or bedrock environment.

Generally, the mode of emplacement fall into these categories:

- PERMEATION also known as *"Permeation Injection"*
- FRACTURING also known as *"Fracture Emplacement"*
- HYBRID (i.e. a combination of both) aka, *"Fracture with leak-off"*
- ADVECTION & DIFFUSION – are secondary transport mechanisms

How to Predict the Mode of Emplacement

- PERMEATION occurs if the amendment particle size can pass through the mean pore throat diameter of a soil or bedrock, i.e. when:



Amendment Particle size,

$$Ps < \bullet \; K/7$$

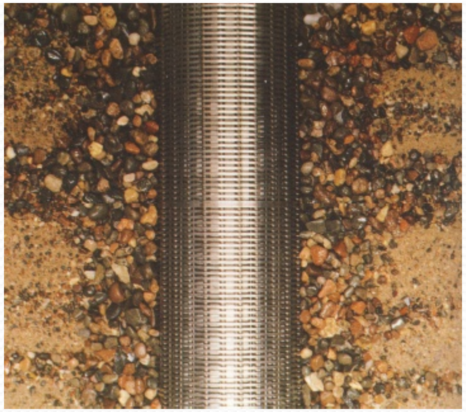
Ps in microns and K in md (Harris and Odom, 1982)

Otherwise, the amendment is being emplaced by FRACTURING

Fracturing vs. Permeation

In general:

- Gases and liquid amendments in highly permeable receiving environments favour PERMEATION →



- Slurries and solid based amendments favour FRACTURING →

- Low permeability receiving environments will result in FRACTURE EMPLACEMENT of amendments

Amendment Emplacement Guide

COMMON AMENDMENTS EMPLACED	MODE OF AMENDMENT EMPLACEMENT INTO SUBSOILS AND BEDROCK									
	$<10^{-2}$ m/s	10^{-3}	to	10^{-5}	$<10^{-5}$	$<10^{-6}$	$<10^{-7}$	$<10^{-8}$	$<10^{-10}$	$<10^{-6}$ m/s
	GRAVEL	SAND coarse	SAND medium	SAND fine	SILTY SAND	SILT	SILTY CLAY	CLAY	COMPETENT BEDROCK	FRAC/POROUS BEDROCK
FRAC SAND (20-40)	INJ	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC
COARSE ZVI	INJ	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC
MICRO IRON	INJ	INJ	INJ/FRAC	FRAC/INJ	FRAC	FRAC	FRAC	FRAC	FRAC	INJ/FRAC
PEROXYGEN / PERMANGANATE SLURRIES	INJ	INJ	INJ	FRAC/INJ	FRAC	FRAC	FRAC	FRAC	FRAC	INJ/FRAC
SOLUTION OXIDANTS	INJ	INJ	INJ	INJ	INJ	INJ/FRAC	FRAC	FRAC	FRAC	INJ
SOLUTION BIO-AMENDMENTS	INJ	INJ	INJ	INJ	INJ	INJ/FRAC	FRAC	FRAC	FRAC	INJ
LACTATES, MOLASSES, VEGETABLE OIL EMULSION	INJ	INJ	INJ	INJ	INJ/FRAC	FRAC	FRAC	FRAC	FRAC	INJ
CELLULOSE, CHITIN	INJ	INJ/FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	FRAC	INJ/FRAC

Note:

INJ: Injection is the primary mode of amendment emplacement

FRAC: Fracturing is the primary mode of amendment emplacement

Case Study: Fracture – Enhanced Chemical Oxidant Injection to remediate Petroleum Hydrocarbons in Clay Soils

- Site was operated as a wood products manufacturing facility since the early 1980's
- Historical gasoline tank release resulted in 1,725 m^2 large contaminant plume of BTEX, F1 & F2 Petroleum Hydrocarbons both onsite and off-site

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Background

- Site was purchased by new owners in 2010
- May 2010 soil excavation was recommended (11,000 t)
- August 2010 application & approval for Tier 2 criteria to reduce area of excavation, but excavation approach was rejected by owner due to cost, site disruption and impracticality for treating off site impacts on City cul de sac

In Situ Remedial Approach

- Environmental fracturing to enhance bulk permeability of fine grained soils (120 fracs)
- Incorporate surfactant into fracture slurry to increase availability of sorbed phase PHCs
- Install 30 dedicated injection wells into Fracture Boreholes
- Repeated chemox injections over 2 years

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Challenges & Objectives

CHALLENGES

- Active facility with significant site traffic
- Off-site impacts
- Remediation timeline relatively short
- Low permeability clays (10^{-9} m/s)

OBJECTIVES

- Remediate on-site plume to Tier 2 guidelines by Summer 2012
- Use several integrated technologies to expedite remediation
- Apply for remediation certificate and achieve site closure

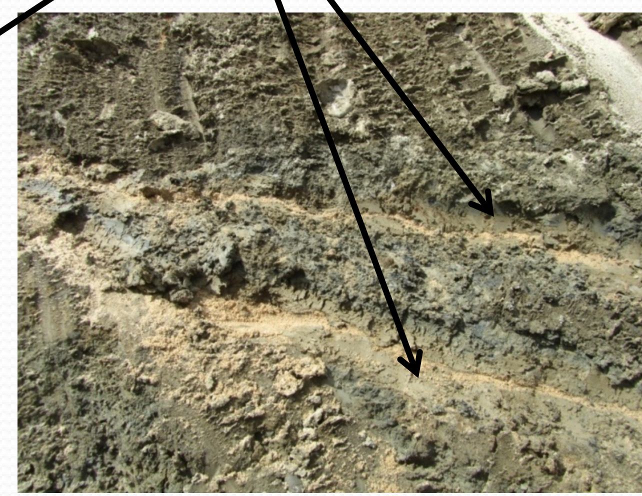
Initial Remedial Treatment

2011 Month	Oxidant / Proppant	Volume
June – July	Sand & Surfactant	106,000 L & 600 L
July	Sodium Persulfate & Hydrogen Peroxide	20,800 L & 7,250 L
September	Sodium Persulfate & Hydrogen Peroxide	9,300 L & 29,500 L
December (Off-site)	Calcium Peroxide & Hydrogen Peroxide	5,000 L & 5,000 L

Fractures as Treatment Pathways

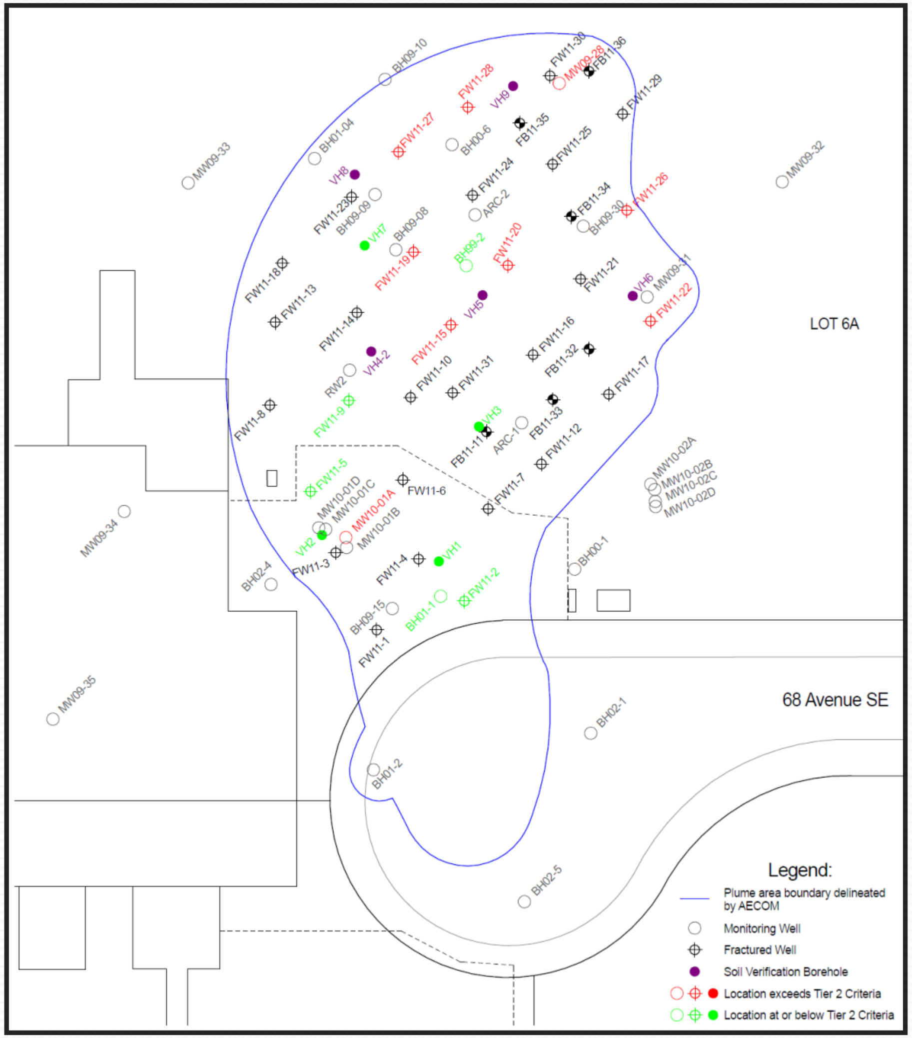
Sand-filled permeable treatment pathway in clay (2 cm thick)

Horizontal permeable treatment pathways in low permeability soils



Brown-coloured oxidation front through contaminated soil

Initial Results (2011)



2011 Year End Results (after 6 months)

- South end of on-site plume below Tier 2 Criteria
  - However, one groundwater well was above criteria
- Overall four of nine soil locations below criteria
- Off-site conditions not yet verified

Optimized Treatment (2012)

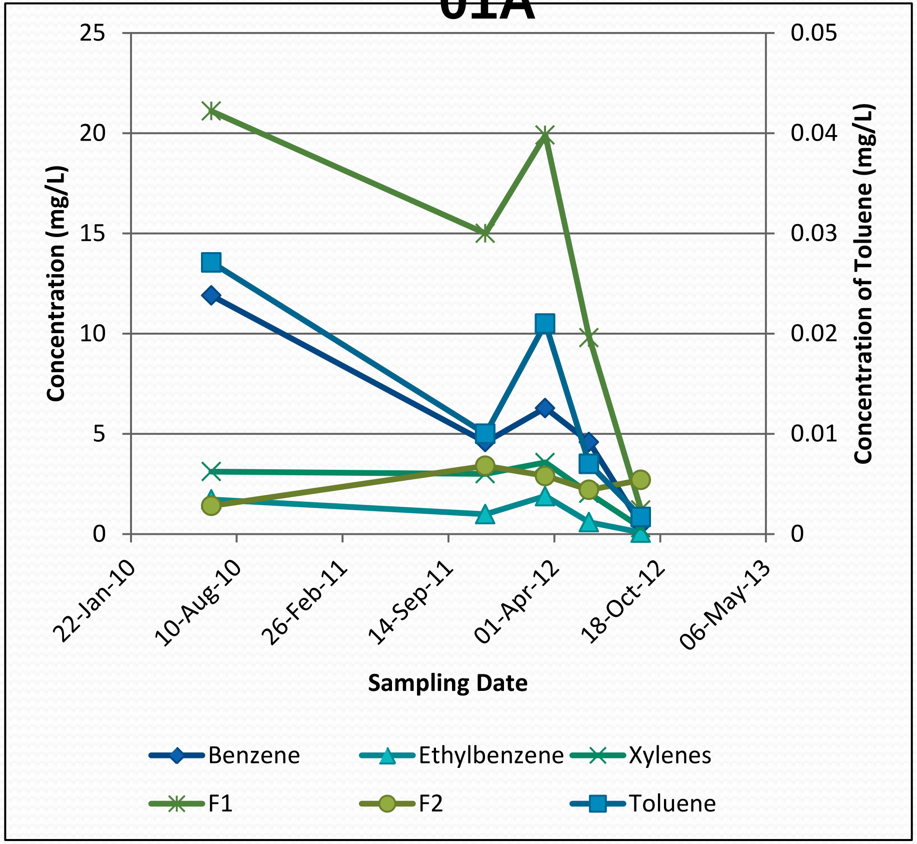
Additional oxidant emplacement:

- January 2012 (18,500L sodium persulfate & 6,000L calcium peroxide)
- March 2012 (10 potassium persulfate treatment canisters)
- April 2012 off site (30,500L hydrogen peroxide & 4,000L calcium peroxide)
- August 2012 (500L sodium persulfate) to treat the groundwater only

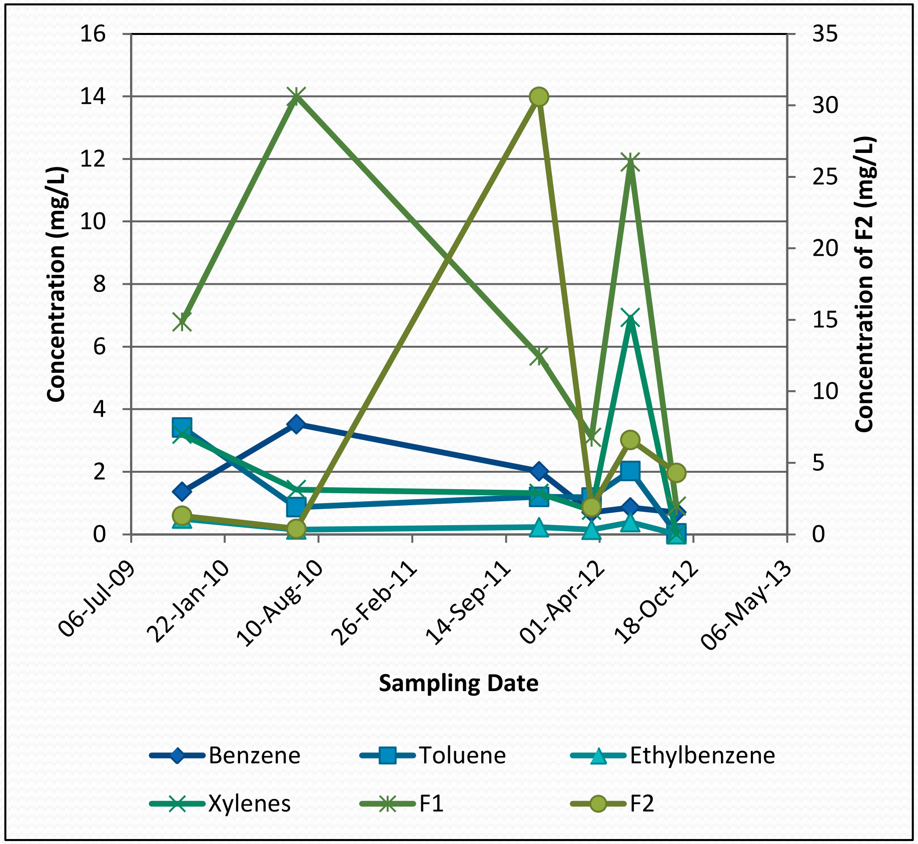
Groundwater Quality Summary

- Groundwater results 15 months after commencing remedial work

Groundwater Analysis MW10-01A



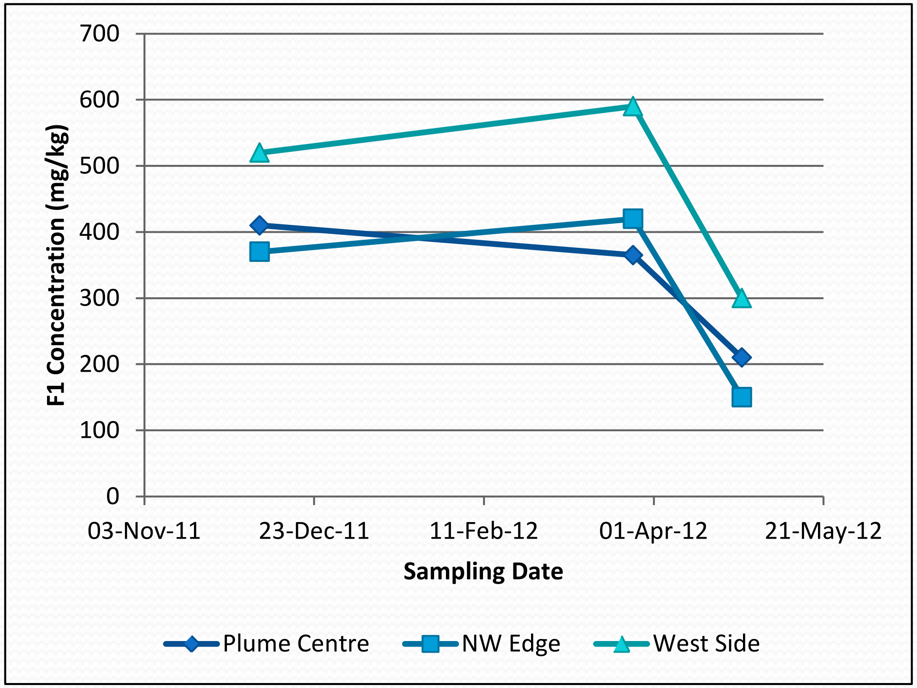
Groundwater Analysis MW09-28



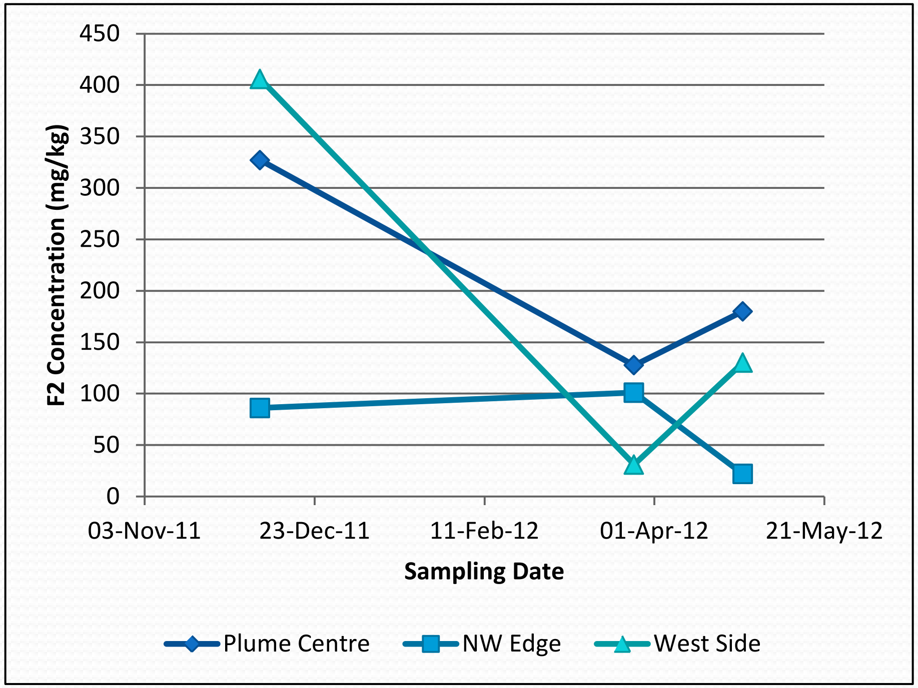
Soil Quality Summary

- All soil samples were below criteria in April 2012
  - 10 months after commencement of remediation
- F1 criteria is 320 mg/kg, and F2 criteria is 260 mg/kg

F1 Hydrocarbon Fractions



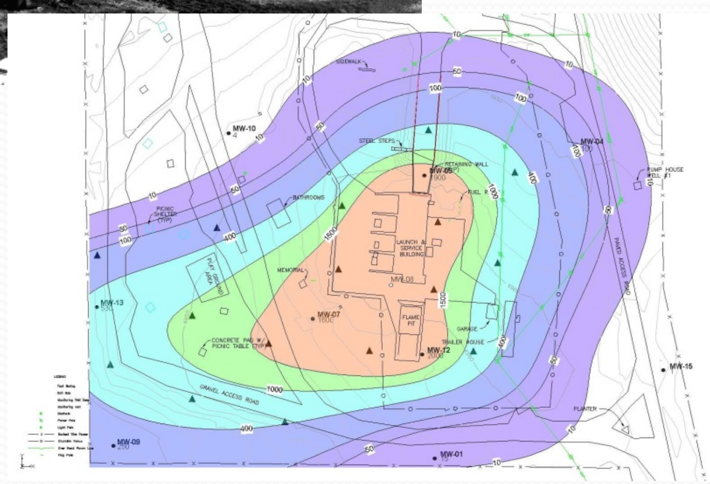
F2 Hydrocarbon Fractions



Summary

- An integrated, in situ remedial approach using environmental fracturing, surfactant treatment, and chemical oxidation (4 oxidants) was implemented
- On-site soil Tier 2 criteria achieved within expected timeframe of 1 year, off site 6 months later
- Minor F2 fraction rebound in groundwater – used multiple treatments to deal with diminishing "rebound" effects – total of over 60,000 kg chemical oxidants injected with very little disruption to business operations
- Total cost to site owner: $725,000 to date vs. $1.5M for excavation and disposal alternative
- Bank refinancing of the property was made possible.

Fracture-emplacement of 140 tons ZVI to remediate TCE contamination in a bedrock aquifer by chemical reduction



- Former USAF “Atlas 12” Missile Site, Colorado
- Operational disposals of TCE (1960-1965) resulted in impacts in underlying sandstone aquifer to 60 ft. depth

Widespread TCE concentrations in groundwater upwards to 4,000 ug/L

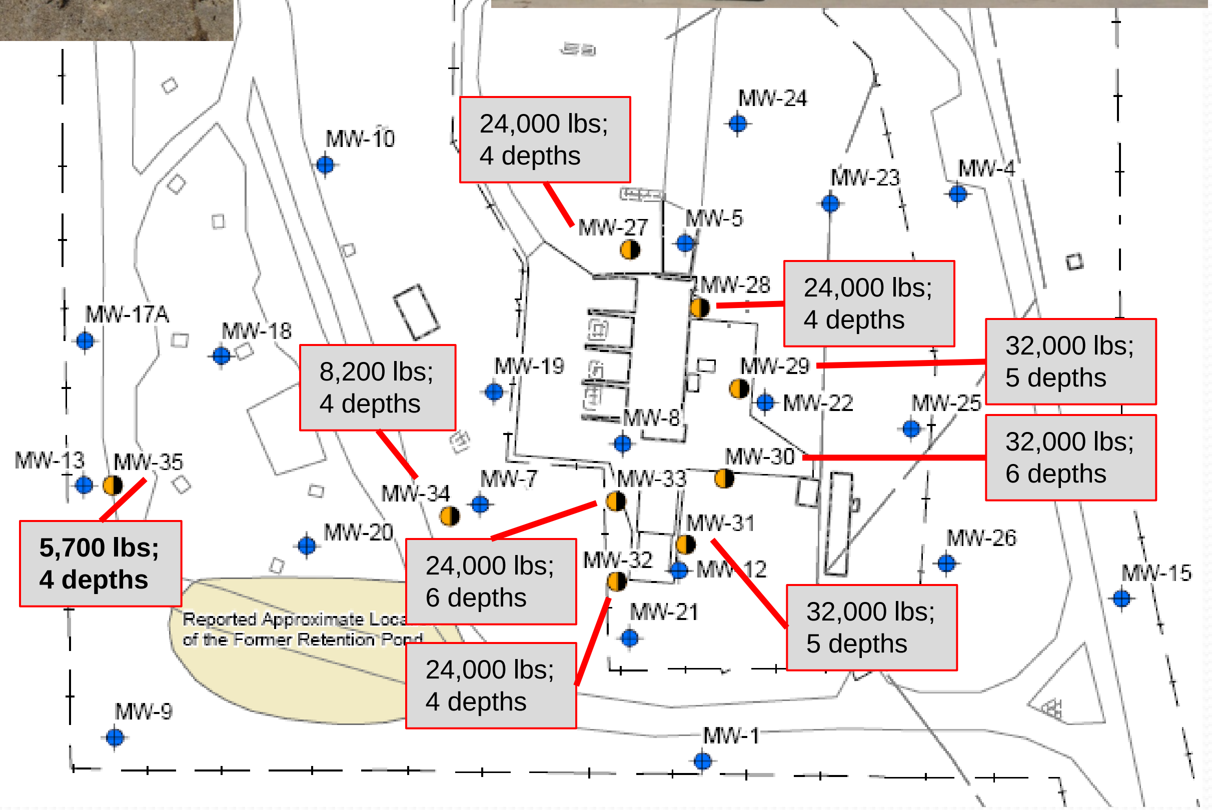
Atlas 12 Pilot Test ZVI Distribution

Source Area:
7 Fracture Boreholes

Dissolved Phase Plume:
2 Fracture Boreholes

EHC-G Injections:
April 20 to May 19, 2009

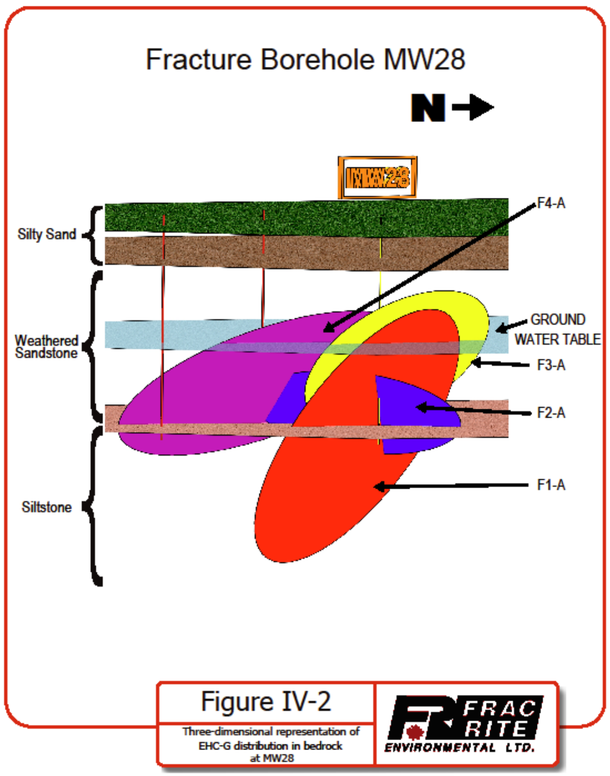
Mass of EHC-G per Borehole; Number of Fracture Depths



Legend

- Monitoring Well Fox Hill Sandstone
- Pilot Test Fracture Borehole/Monitoring Well Fox Hill Sandstone
- Buildings
- Fence
- Former Retention Pond

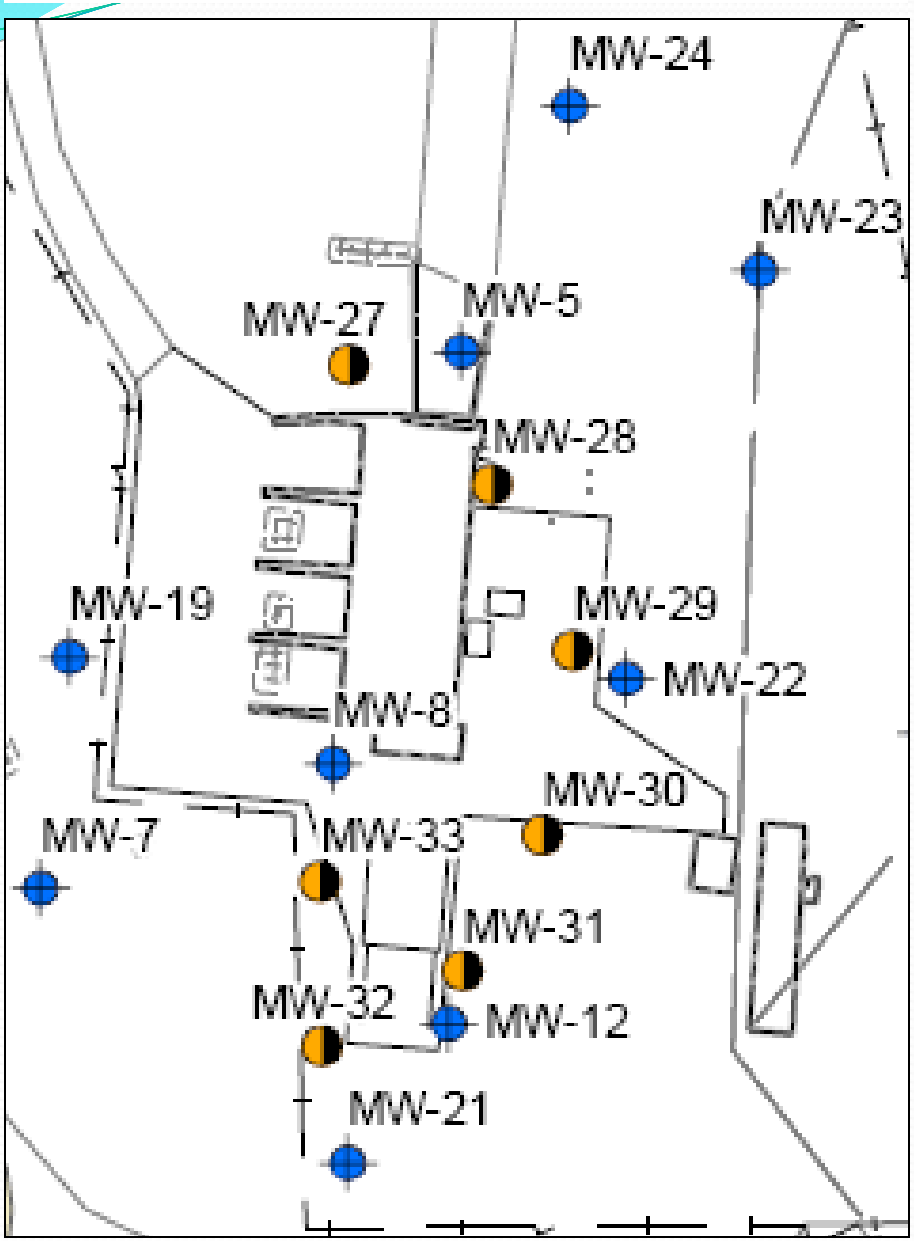
Fracture Mapping of ZVI using Tiltmeter Geophysics

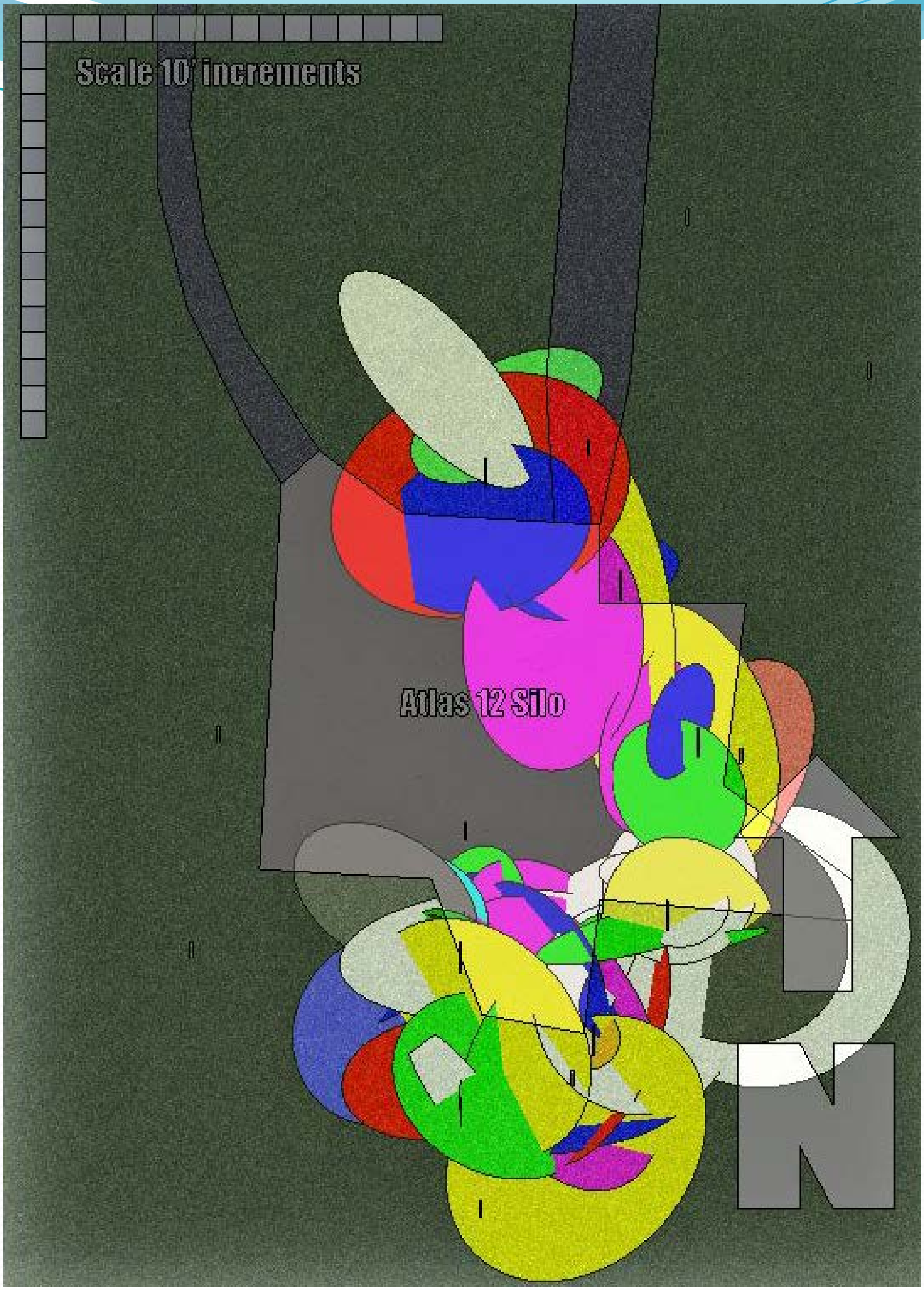


- Tiltmeters are ground surface sensors that detect tilt angle and tilt direction in response to a fracturing or injection event in the subsurface

Fracture Mapping of ZVI fracs

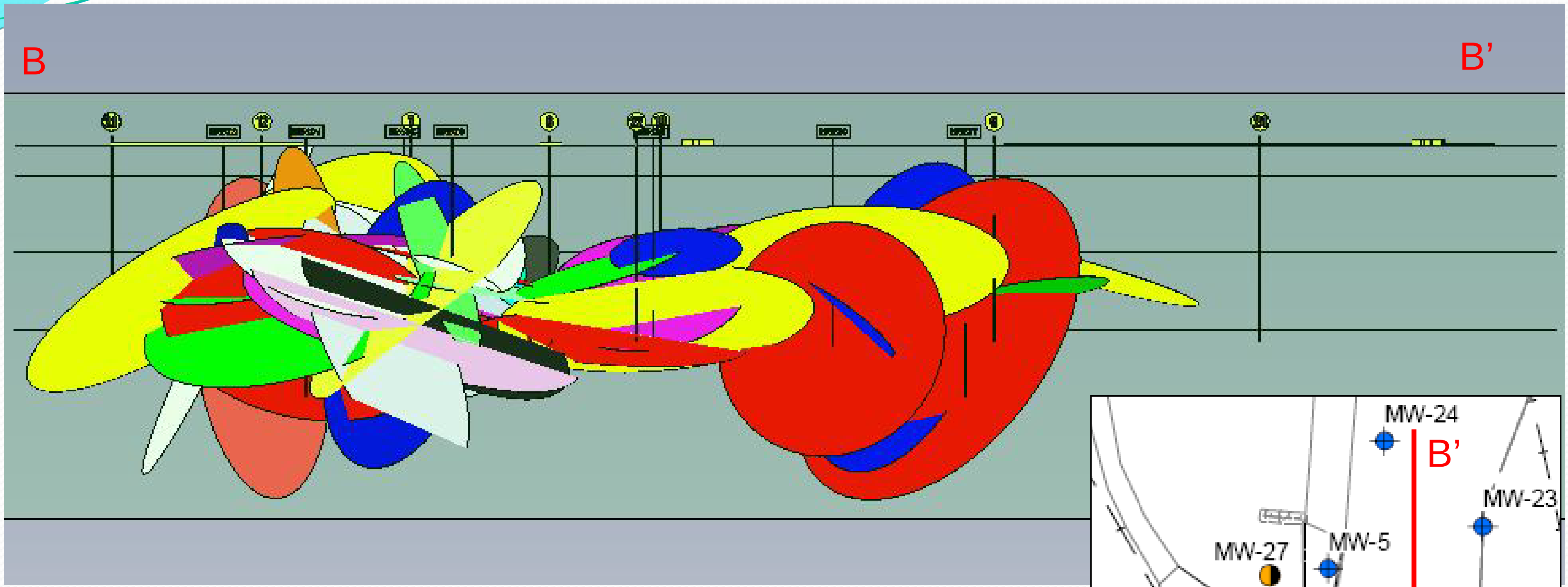
Conducted for 7 boreholes in source area

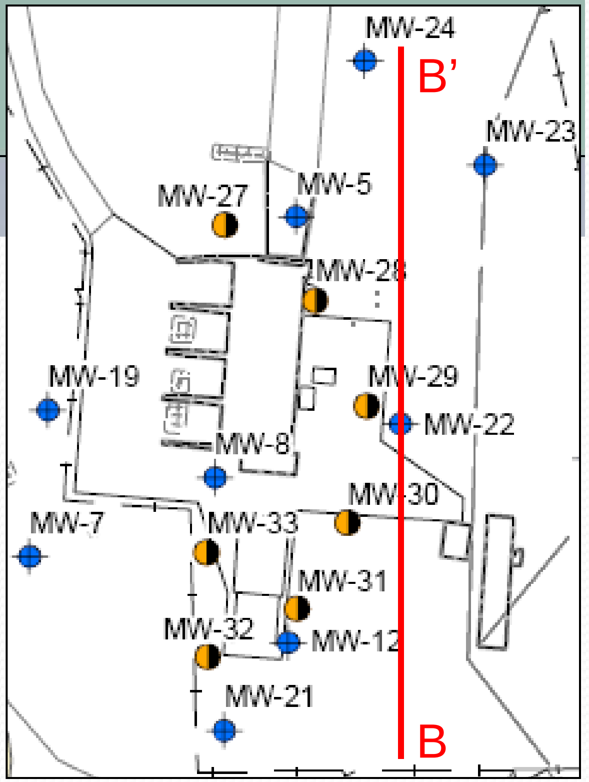




Fracture Mapping of ZVI fracs

From MW-22 looking west





North-South extent of continuous ZVI/C coverage is approximately 450 ft, effectively comprising a treatment barrier

TCE Treatment Perfomance after 21 months

- **<u>Source Area</u>**:

Pre-treatment TCE levels - >2000 to 4,000 ug/L

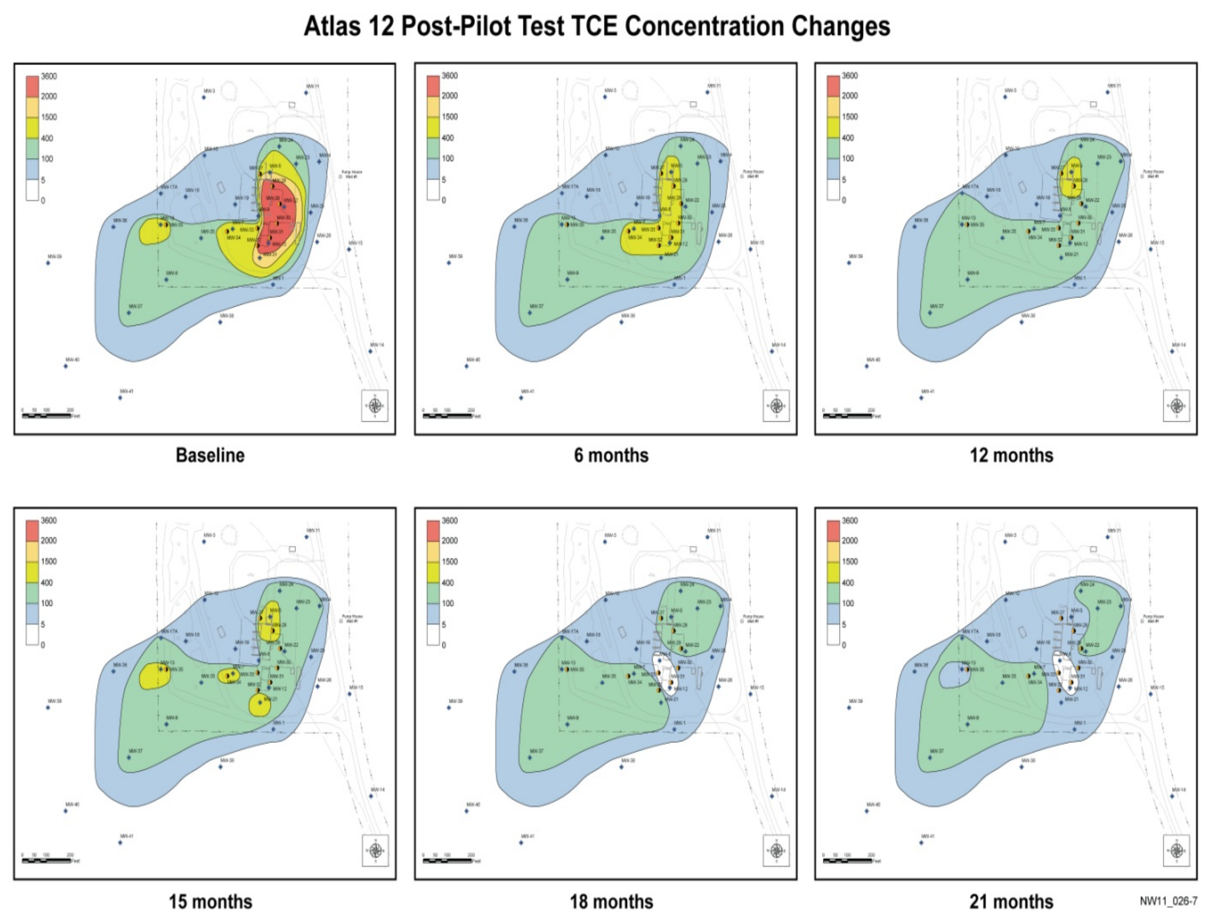
After 12 months – less than 400 ug/L except at 2 wells

After 21 months – less than 100 ug/L generally

- **<u>Dissolved Plume Area</u>**:

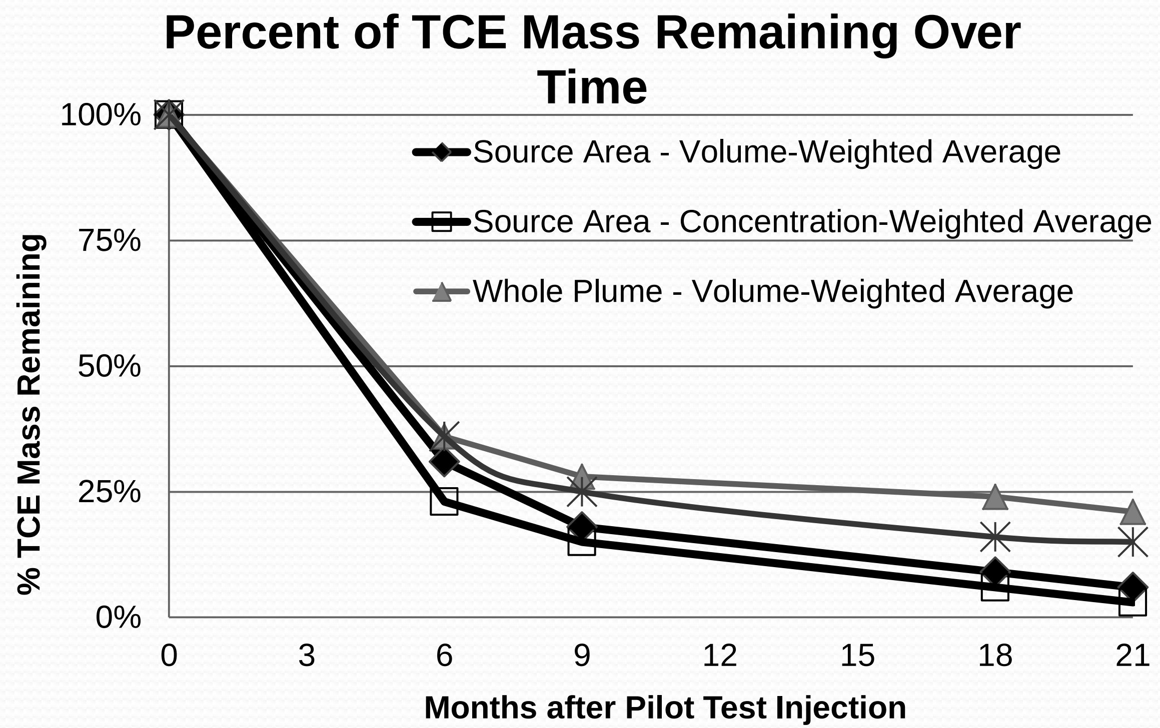
Pre-treatment TCE levels - 500 to 700 ug/L

- After 21 months – 200 to 400 ug/L



21 Month Performance Evaluation

- 94% of Source Area below RMC of 100 ppb TCE
- 82% of Dissolved Plume Area below TCE RMCs
- Phase 2 ZVI Injection of another 40 tons ZVI completed in August 2011, TCE is ND to 100 ug/L
- Treatment cost equivalent: $8 per ton
- Approach in now the model for USACE missile site clean-ups **(Journal of Remediation, Spring, 2012).**
- Phase 3: unrestricted land use – Sept. 2013



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CONCLUSIONS

- In situ remediation using oxidants and reductants can be very problematic in certain soil and bedrock conditions, primarily due to limitations of permeability and contact area achieved between treatment amendments and contaminants by conventional means.

- Any in situ remedial design involving the delivery of treatment amendmemts must consider their reactions with the contaminants in the context of soil or bedrock geochemistry and their physical properties

- The Mode of Distribution of treatment amendments into contaminated subsoils/bedrock is an often overlooked component of remedial design that can lead to failure**

- Advanced techniques such as environmental fracturing and injection techniques coupled with innovative treatment and verification technologies can overcome traditional limitations to *in situ* remediation using oxidants and reductants.

Thank you !!

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