



*Overcoming the
Challenges of
Chlorinated Solvent Sites
by Using Design and
Implementation Best
Practices*

Eliot Cooper
Director Combined
Remedies



The Chlorinated Solvent Challenge – Thousands of Sites

- 126,000 sites have residual contamination preventing them from achieving closure
- 10% complex which means complete restoration not likely to be achieved in next 50 to 100 years.
- Estimated cost to complete \$110 to \$127 billion
- Doesn't include sites that likely exist but haven't been identified e.g. dry cleaners, chemical intensive manufacturing facilities.

Complex Sites - 3's & 4's

Contaminant Mass

Lithology	Hydrogeology	Mobile Dissolved (Degrades/Volatilizes)	Mobile Dissolved	Strongly Sorbed, Dissolved	Strongly Sorbed, Dissolved (Degrades/Volatilizes)	Separate Phase LNAPL	Separate Phase DNAPL
	Homogeneous, Single Layer	1	1-2	2	2-3	2-3	3
	Homogeneous, Multiple Layers	1	1-2	2	2-3	2-3	3
	Heterogeneous, Single Layer	2	2	3	3	3	4
	Heterogeneous, Multiple Layers	2	2	3	3	3	4
	Fractured Bedrock	3	3	3	3	4	4

Nobel Prize





Why Have We Not Been More Successful?

- Poorly design and misapplied technologies.
- Poor understanding of what technologies can and will do.
- Misunderstanding the extent and/or distribution of chlorinated solvents in source zones and the technical limits regarding how accurately or completely a source zone can be characterized.
- Poor uncertainties inherent in remedial system design and failure to learn from system performance monitoring data to optimize the cleanup approach.
- Further more, poor design, poor application and poor post-application monitoring at typical sites makes determination of best practicably achievable performance impossible.

Can it Get Any Worse?



Short-Term TCE Exposure



- Reopening Closed Sites
- Closing Schools
- Evacuating Homes

US EPA Action Levels & Response Recommendations

Region 9 Interim TCE Indoor Air Response Action Levels		
<i>Exposure Scenario</i>	<i>Accelerated Response (HQ=1)</i>	<i>Urgent Response (HQ=3)</i>
Residential	2 µg/m ³	6 µg/m ³
Commercial / Industrial (8 hour workday)	8 µg/m ³	24 µg/m ³
Commercial / Industrial (10 hour workday)	7 µg/m ³	21 µg/m ³
<p>Indoor air exposures corresponding to the Accelerated response action levels would pose long-term residential and commercial/industrial exposure cancer risks near the lower end of the Superfund target cancer risk range. HI=1 level truncates Superfund protective exposure range to close to the lower end of the traditional target cancer risk range.</p>		

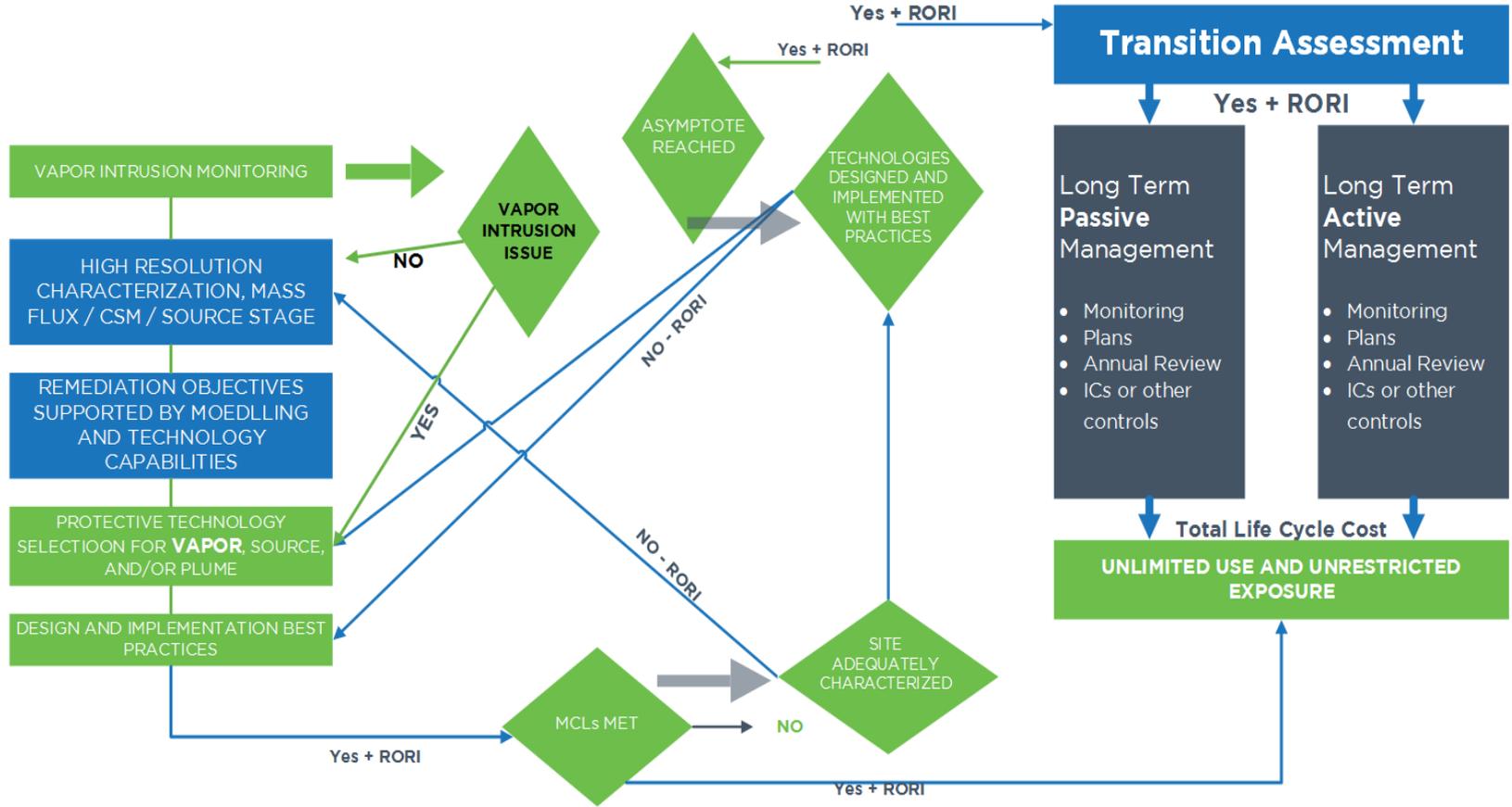
EPA Region 9

Recommended Tiered Response Actions

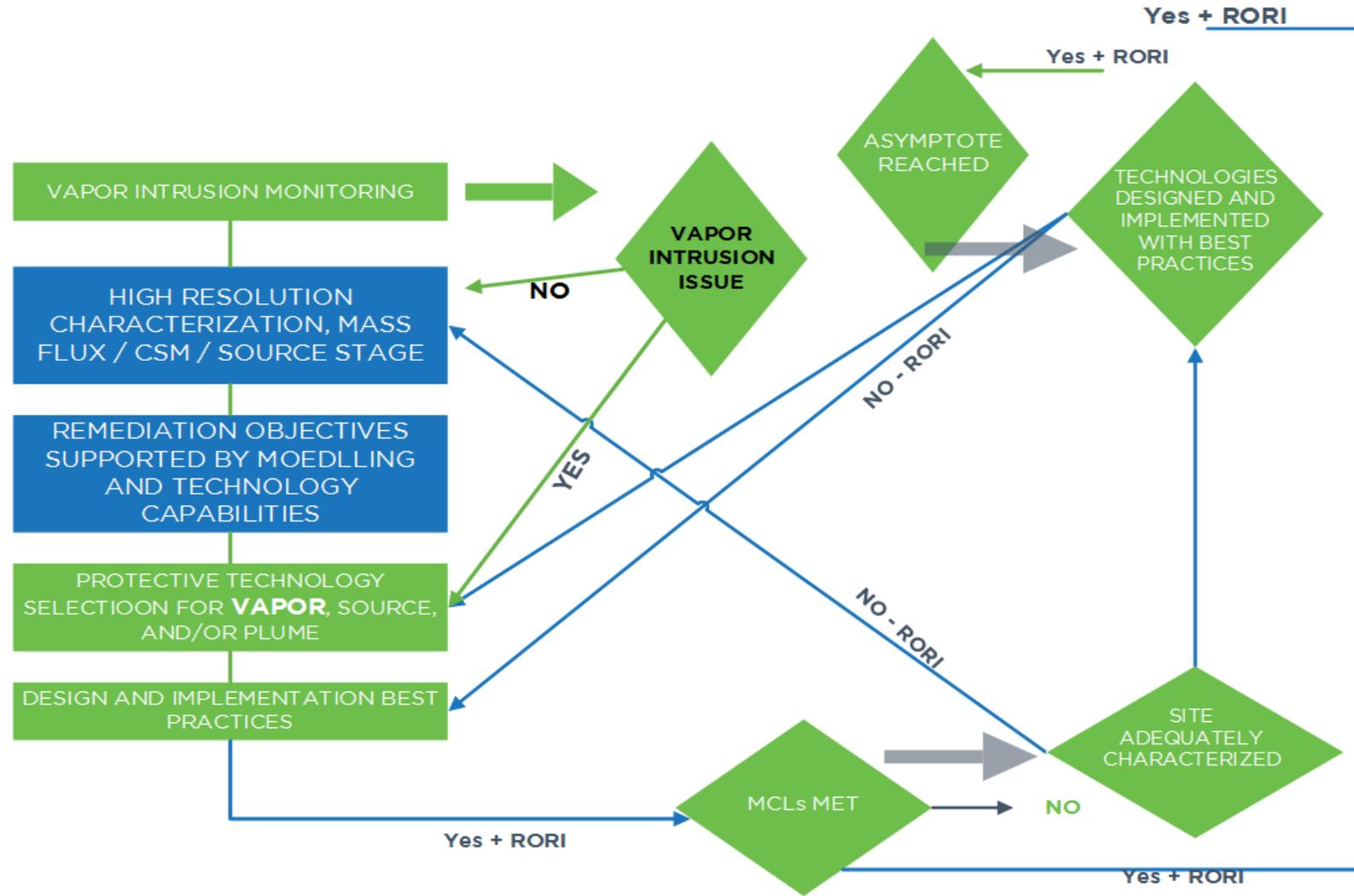
Tiered Response Actions:

- **TCE Indoor Air Concentration \leq Accelerated Response Action Level (HQ=1):** If indoor air TCE concentrations are observed to be equal to or less than the accelerated response action level, then we recommend routine periodic confirmatory sampling and/or monitoring be conducted as appropriate for conditions at the site, including evaluation of the potential for subsurface vapor intrusion into indoor air exceeding health-based screening levels for long-term exposure.
- **TCE Indoor Air Concentration $>$ Accelerated Response Action Level (HQ=1):** In the event indoor air TCE concentrations are observed to be greater than the accelerated response action level, we recommend **early or interim mitigation measures** be evaluated and **implemented quickly**, and their effectiveness (defined as a reduction of the TCE indoor air concentration to below HQ=1 level) confirmed promptly (e.g., **all actions completed and confirmed within a few weeks**).
- **TCE Indoor Air Concentration $>$ the Urgent Response Action Level (HQ=3):** In the event indoor air TCE concentrations are observed to be greater than the urgent response action level, we recommend **mitigation measures** be **initiated immediately** and their effectiveness (defined as a reduction of the indoor air TCE concentration to below HQ=1 level) confirmed before any additional exposure is allowed to occur (e.g., **all actions completed and confirmed within a few days**). Note that temporary relocation may be indicated under these circumstances because of the need to prevent additional exposure.

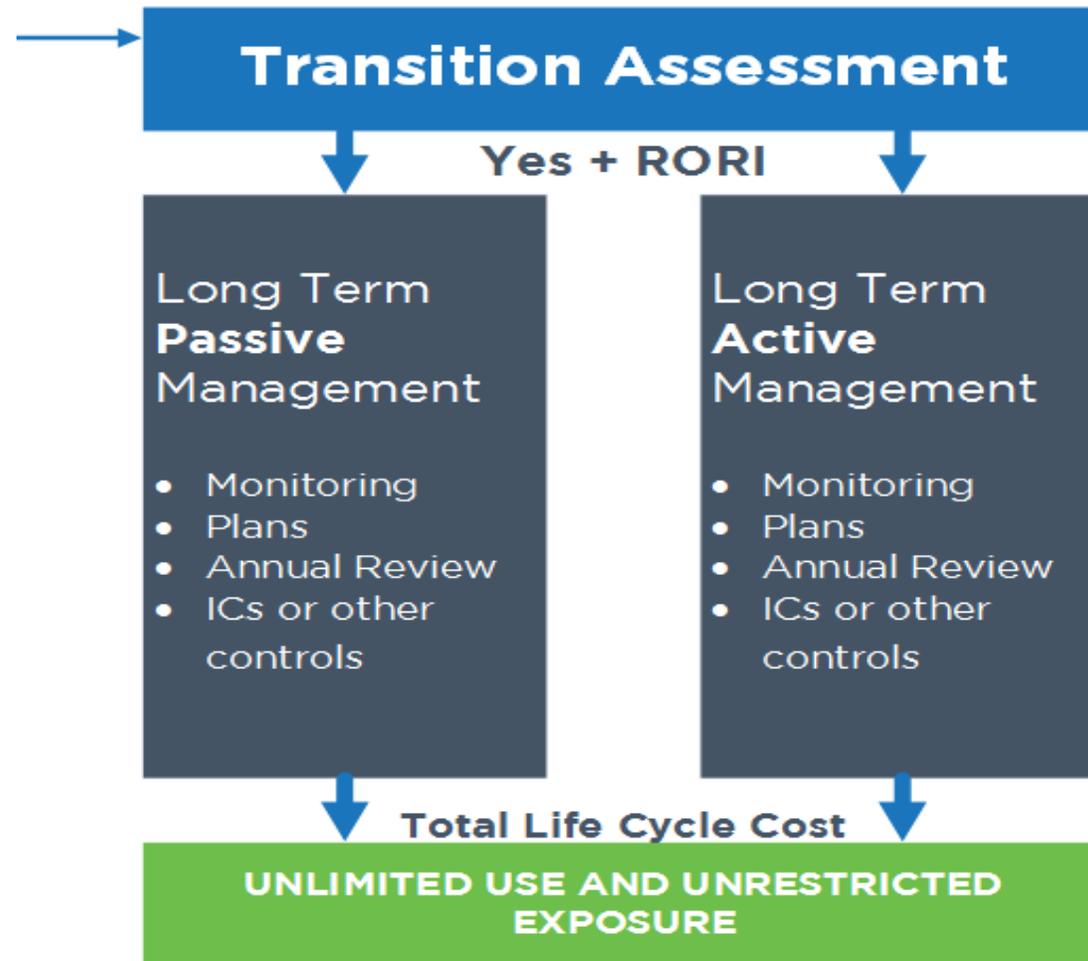
So Where Do We Go From Here



So Where Do We Go From Here



So Where Do We Go From Here



Best Practices

- **Site Characterization**
- Remedial Technology Selection to Meet Remedial Action Goals
- Design and Field Implementation

“A method or technique that has consistently shown results superior to those achieved with other means, and that is used as a benchmark”

Moving On From Monitoring Wells

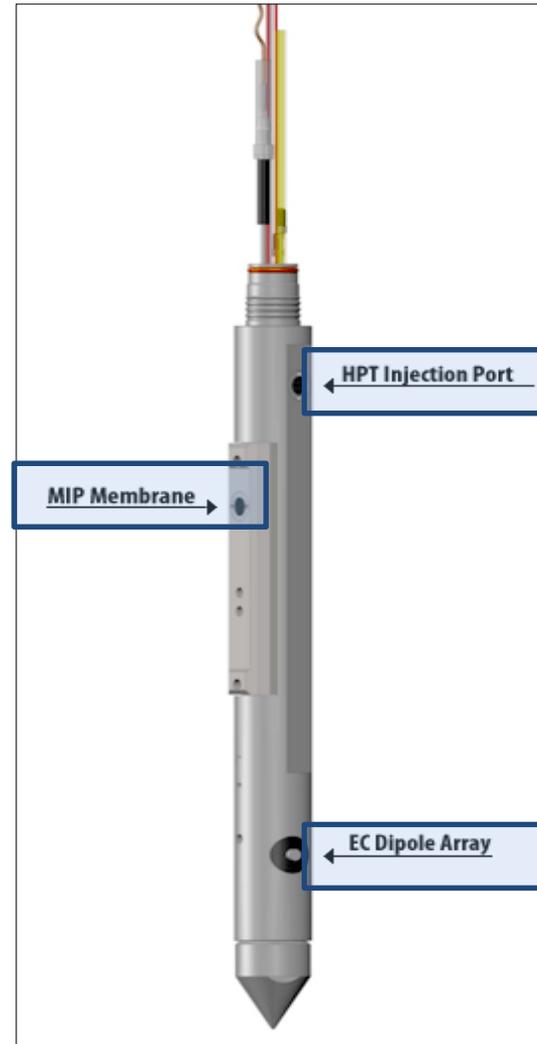


Monitoring Wells (MWs) yield depth-integrated, flow-weighted averaged data, with no vertical distribution of contaminants in the screened interval and do not define the small scale heterogeneities controlling contaminant transport.

High Resolution Site Characterization

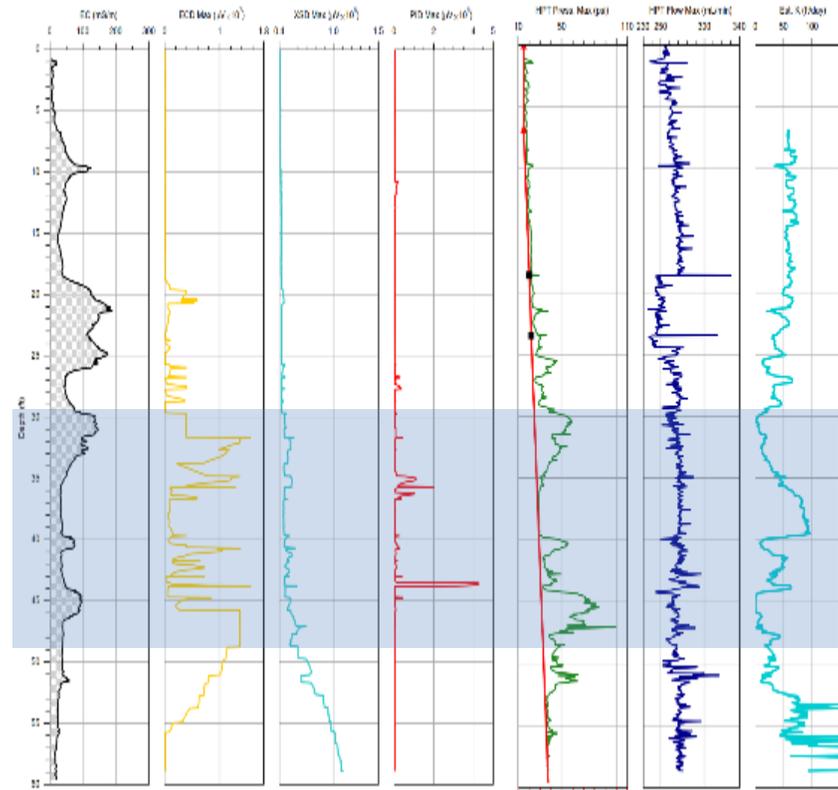
Providing the Whole Picture

- **Lithology**: Electrical Conductivity (EC)
- **VOC Mass**: Membrane Interface Probe (MIP)
- **Hydraulic Conductivity**: Hydraulic Profiling Tool (HPT)



High Res Characterization Technologies - MiHPT

Can reduce remediation footprint and cost but more importantly increases probability of success with a more targeted remediation design.



Red = PID and HPT Dissipation Testing

Yellow = ECD

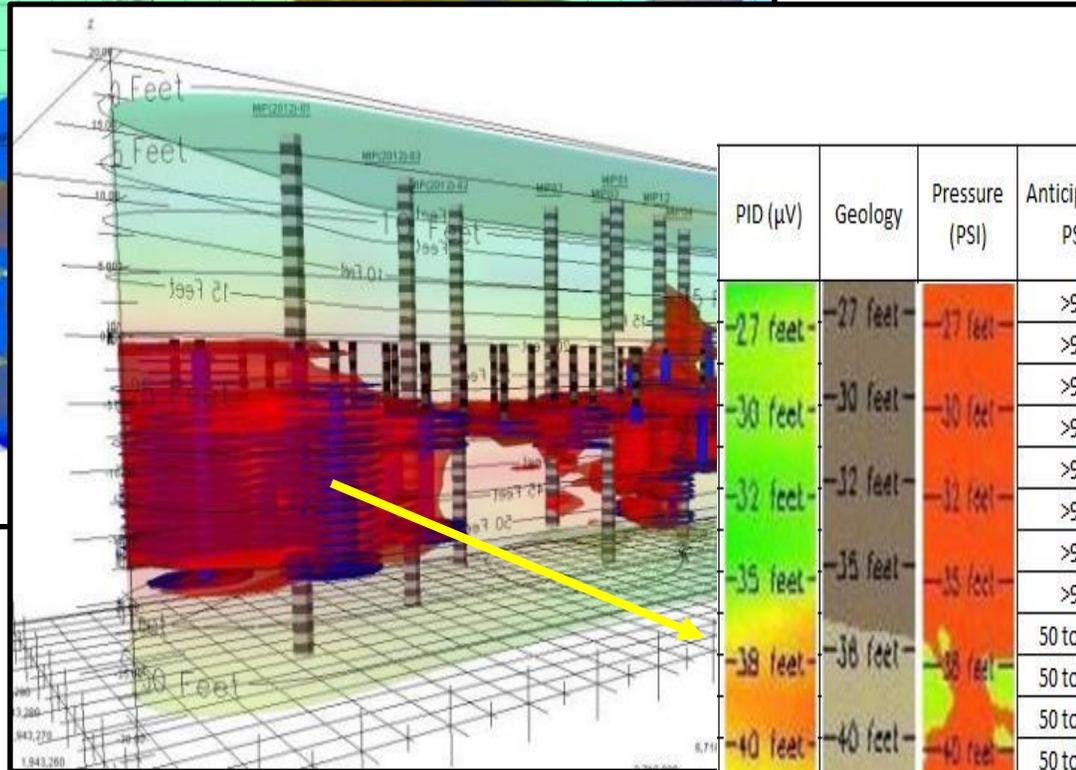
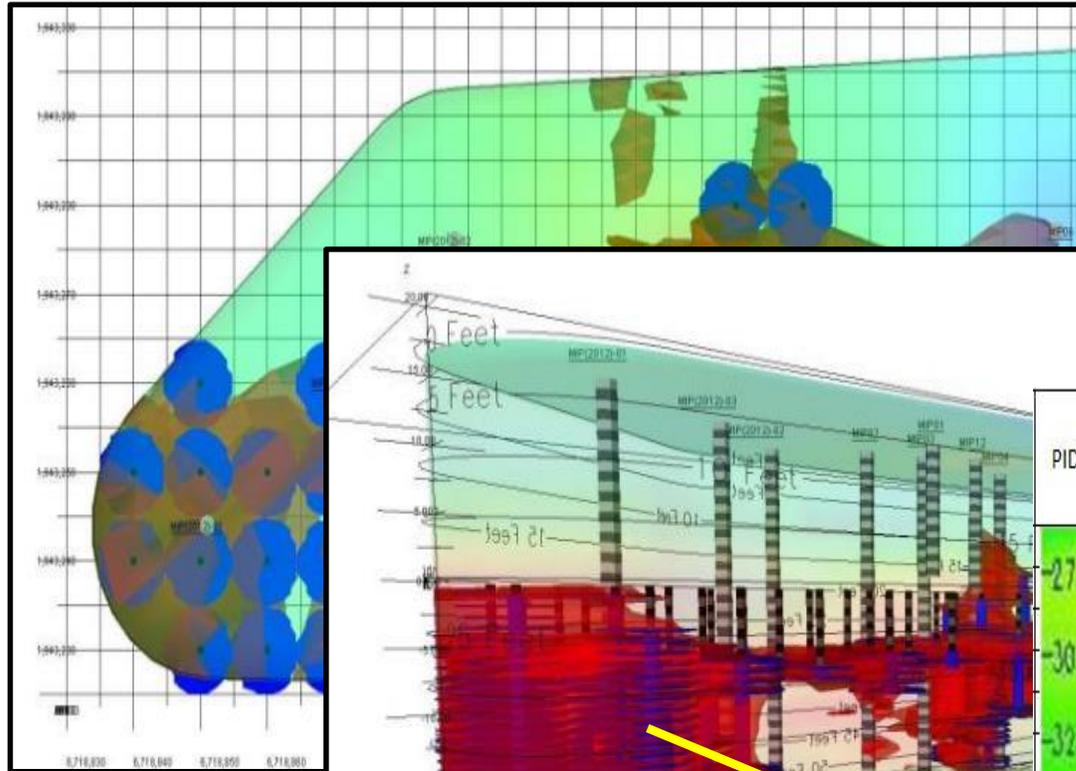
Light Blue = XSD and K

Black = Electrical conductivity

Green = Down Hole Pressure

Blue = Down Hole Flow

3D Imaged Remediation



PID (μ V)	Geology	Pressure (PSI)	Anticipated PSI	Anticipated Reagent Volume (gal)	Anticipated Reagent Pounds
-27 feet	-27 feet	-27 feet	>90	0	0
-27 feet	-27 feet	-27 feet	>90	0	0
-27 feet	-27 feet	-27 feet	>90	0	0
-30 feet	-30 feet	-30 feet	>90	0	0
-30 feet	-30 feet	-30 feet	>90	0	0
-32 feet	-32 feet	-32 feet	>90	0	0
-32 feet	-32 feet	-32 feet	>90	0	0
-35 feet	-35 feet	-35 feet	>90	0	0
-35 feet	-35 feet	-35 feet	>90	0	0
-38 feet	-38 feet	-38 feet	50 to 100	150	200
-38 feet	-38 feet	-38 feet	50 to 100	150	600
-40 feet	-40 feet	-40 feet	50 to 100	150	600
-40 feet	-40 feet	-40 feet	50 to 100	150	600
-40 feet	-40 feet	-40 feet	50 to 100	150	400

High Resolution Transects

- Typically mass discharge occurs over a small fraction of the total cross sectional area of the plume, suggesting that remediation can be targeted more effectively if high resolution sampling is conducted along one or more transects.
- Transects downgradient from the source can reveal locations within the source contributing the most to overall discharge or identify sources not found by soil borings or conventional monitoring wells.

Measuring Mass Flux Across Transect

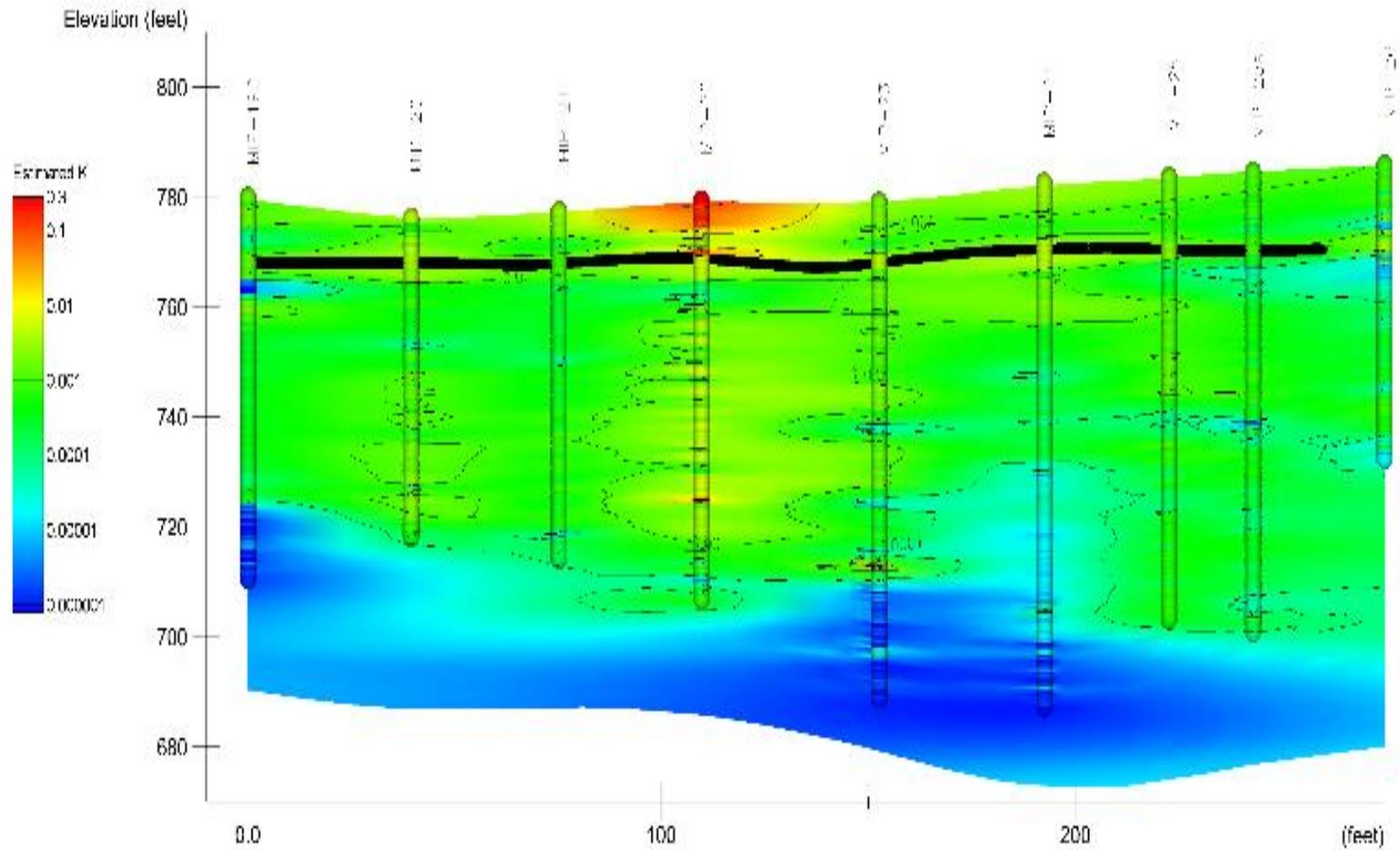
High Resolution
Investigation at a
manufacturing plant

- MIP
- Waterloo^{APS}
- DPT Soil Coring
- On Site
Laboratory

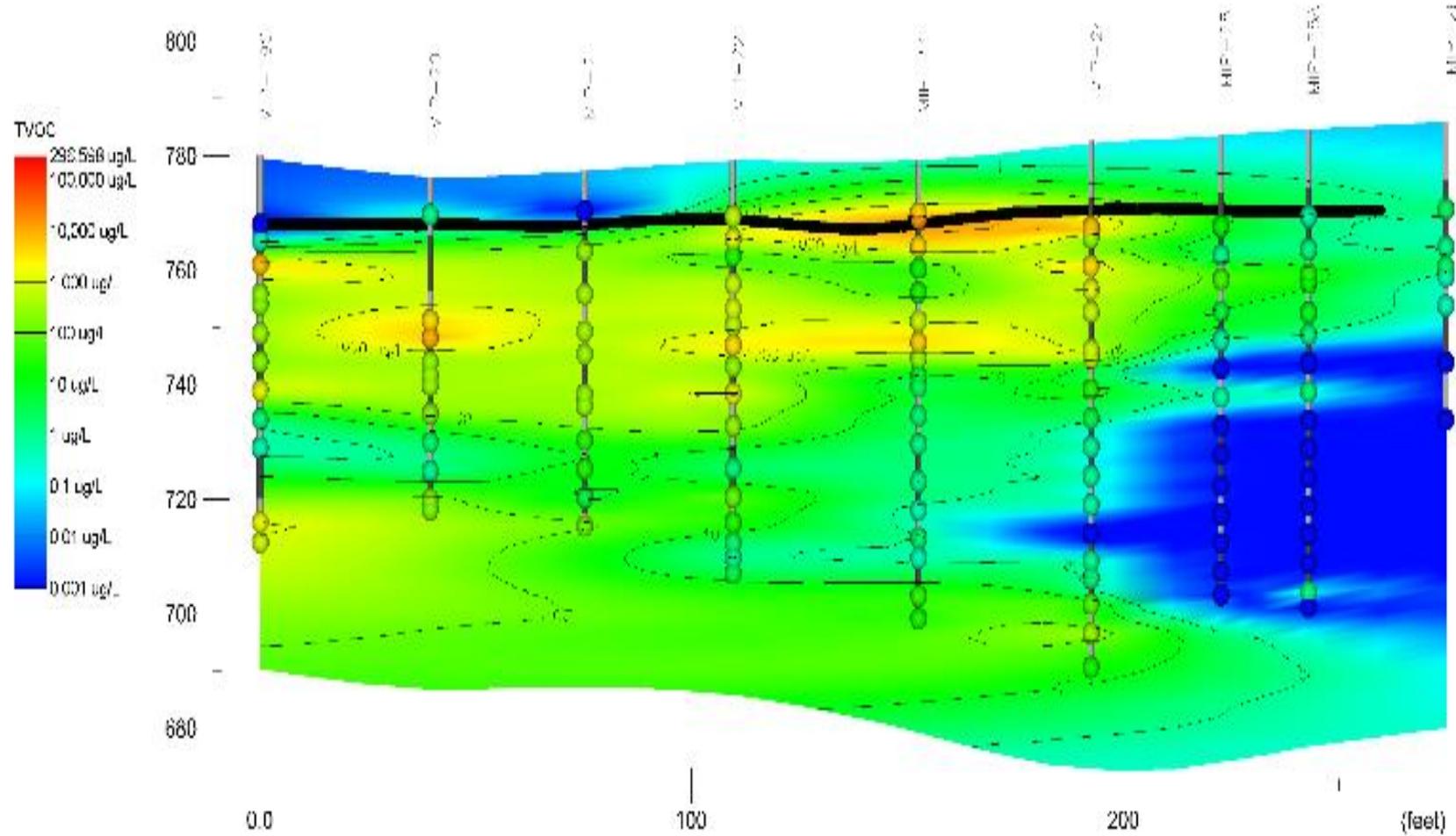


NGWA – “High
Resolution Site
Characterization
Supporting
Focused
Combined
Remedies,” , Seth
Pitkin, 5.23.14

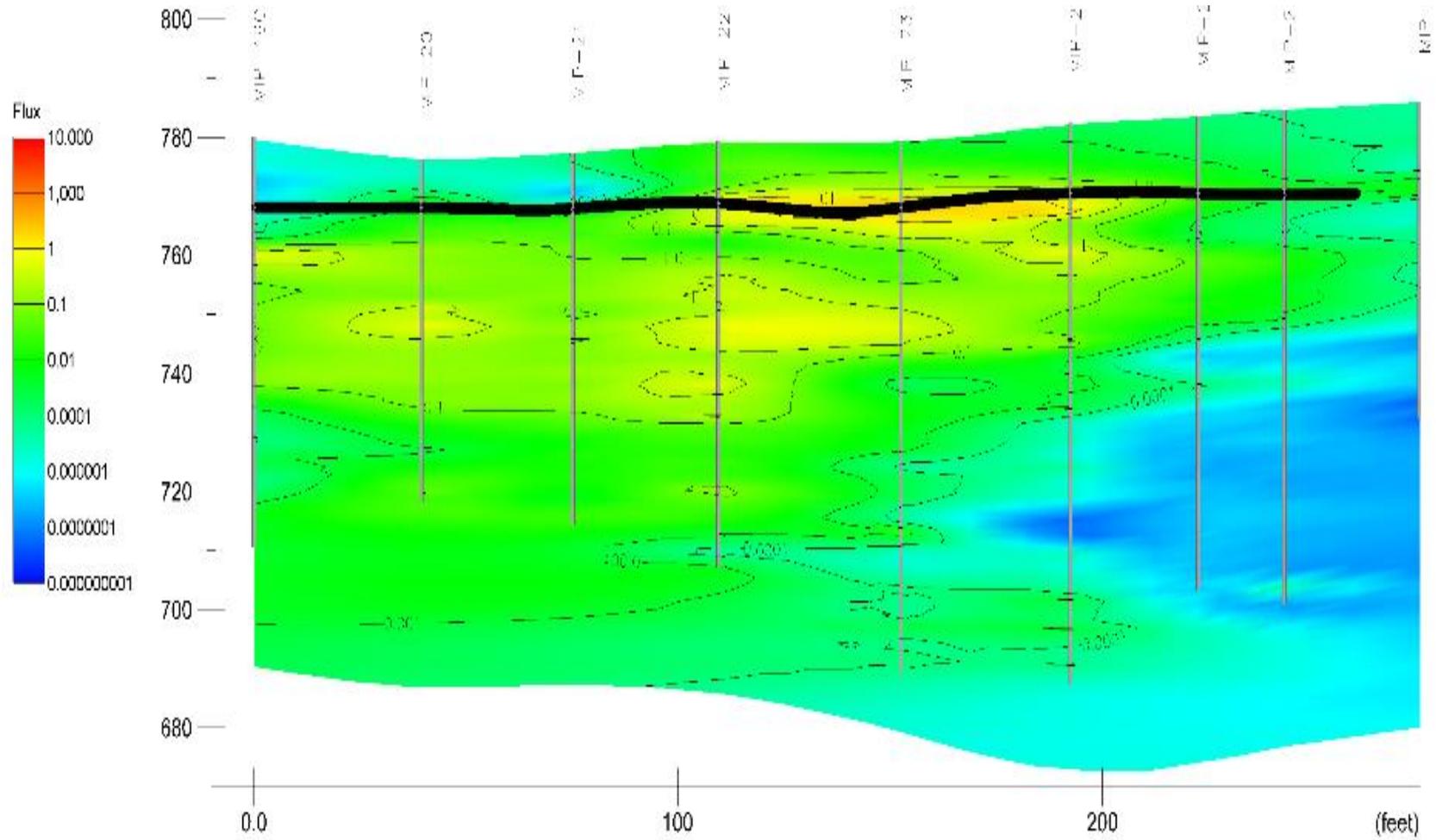
Hydraulic Conductivity (cm/sec)



TVOC Concentration ug/l



Mass Flux (ug/sec/cm²)





Best Practices

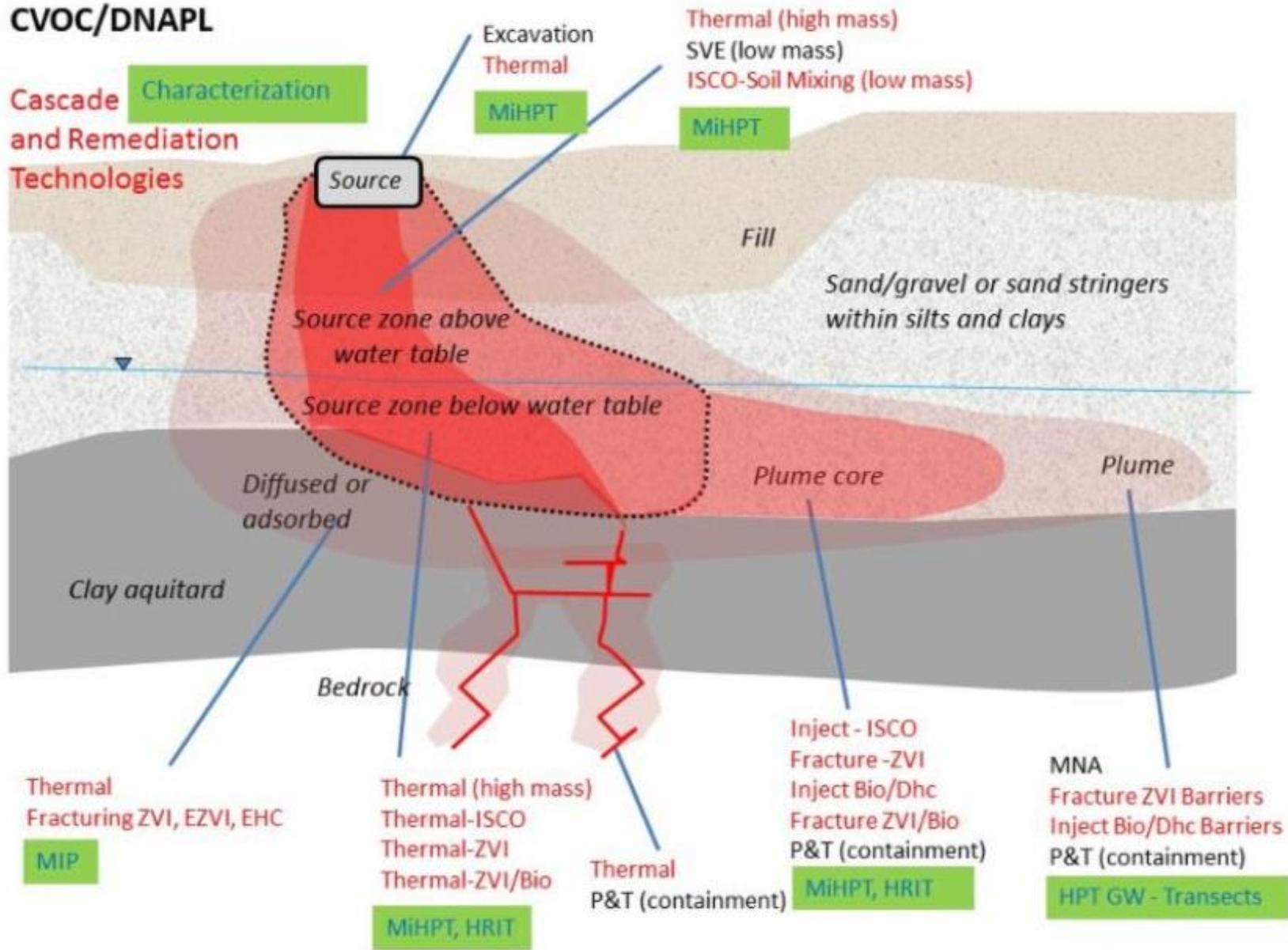
- Site Characterization
- **Remedial Technology Selection to Meet Remedial Action Goals**
- Design and Field Implementation

“A method or technique that has consistently shown results superior to those achieved with other means, and that is used as a benchmark”



CVOC/DNAPL

Cascade and Remediation Technologies



Understand the Capabilities of Technologies Site Conditions

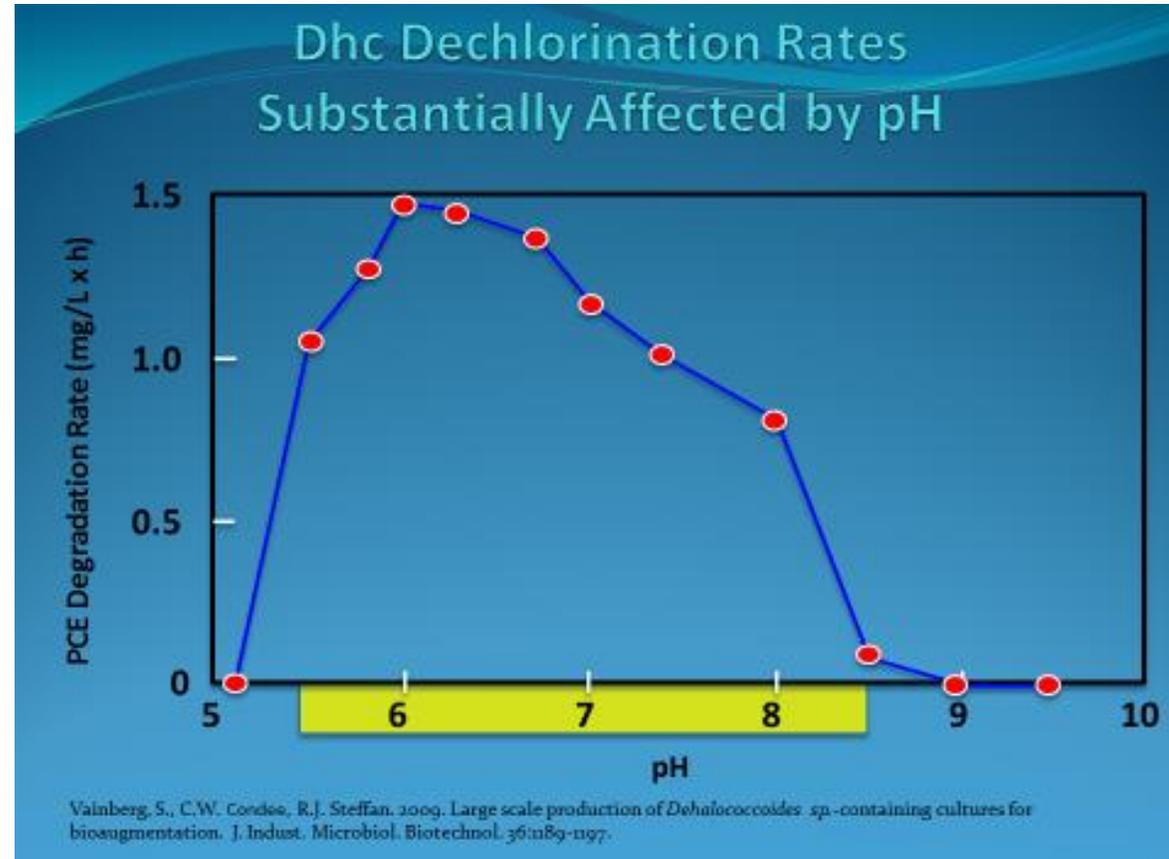
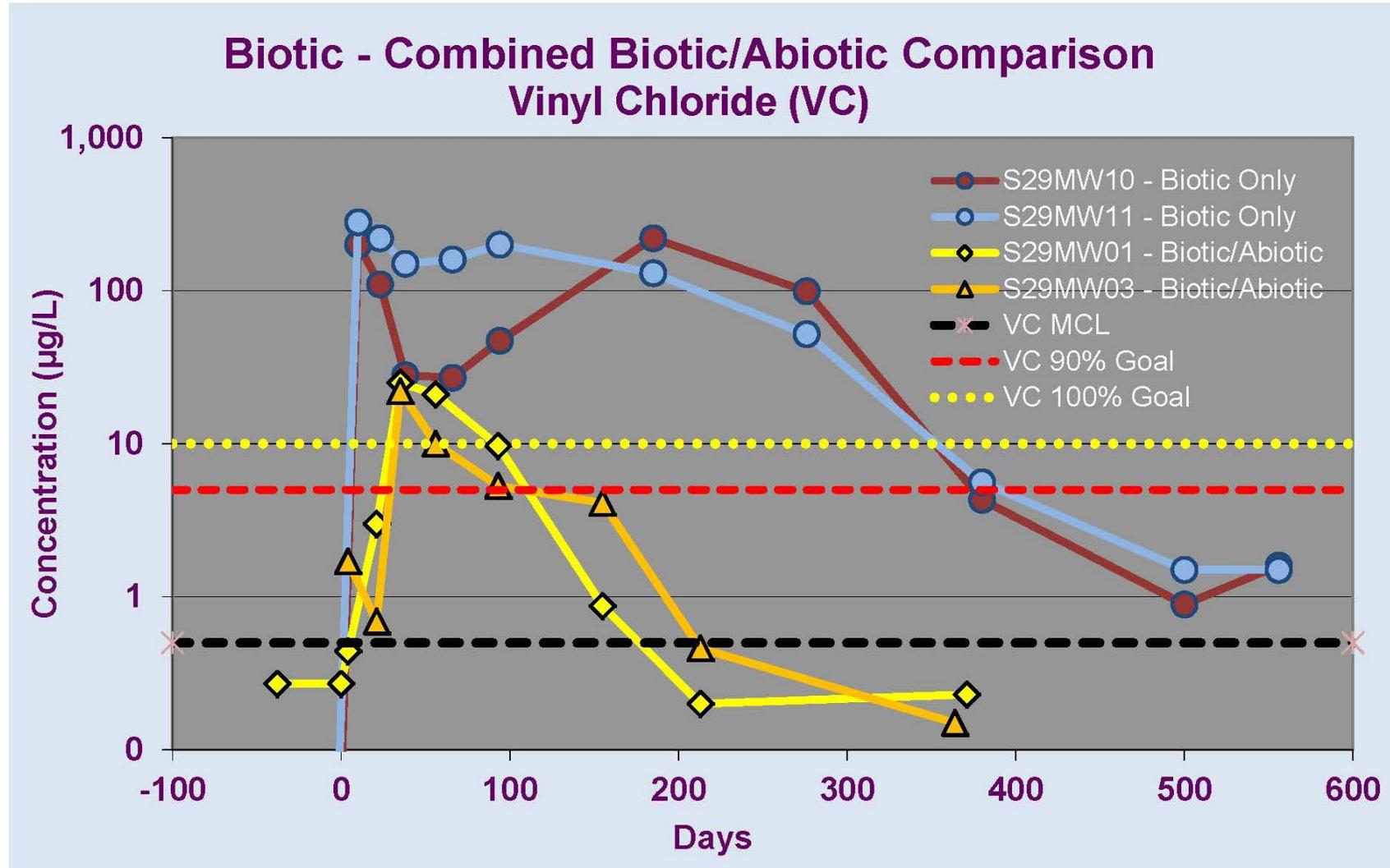
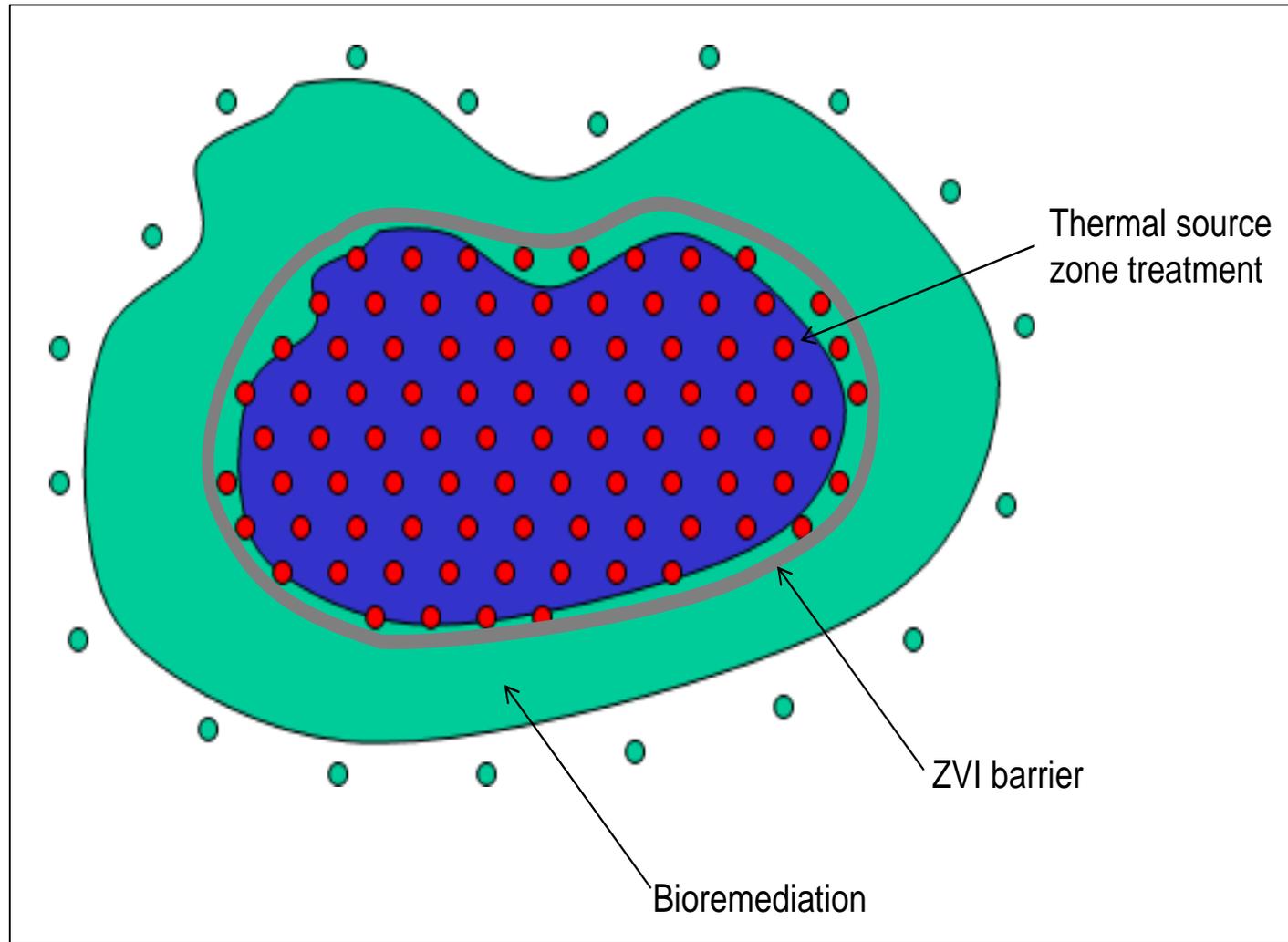


Figure 22- Dhc degradation rate (PCE) versus pH

Combined Abiotic/Biotic Results



Combined Remedies





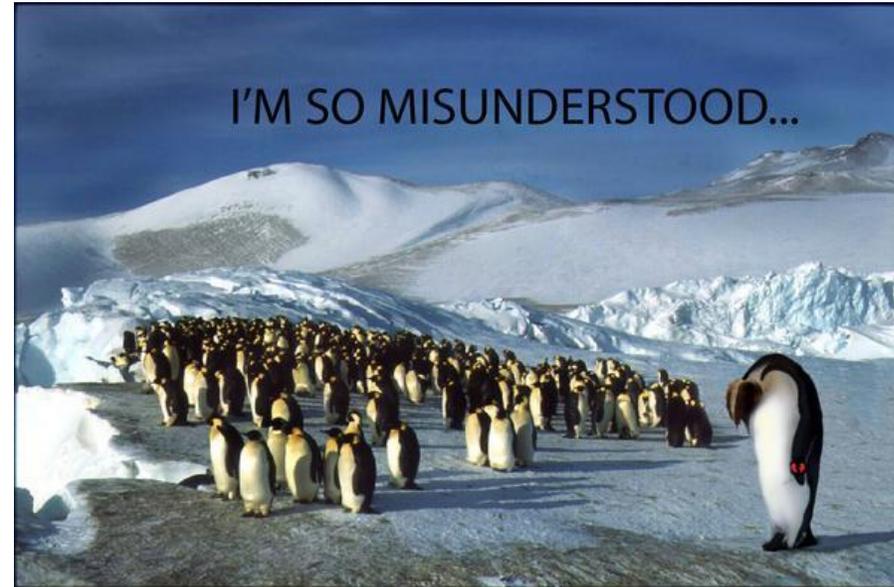
Best Practices

- Site Characterization
- Remedial Technology Selection to Meet Remedial Action Goals
- **Design and Field Implementation**

“A method or technique that has consistently shown results superior to those achieved with other means, and that is used as a benchmark”

Radius Of Influence – So Misunderstood

- Injection point spacing rules of thumb for sands to clays?
- Distance where chemistry or reaction products shows up in MWs?
- Dependent on:
 - Chemistry dilution and volumes? Yes
 - Chemistry persistence? Yes
 - Seepage velocity and residence time? Yes

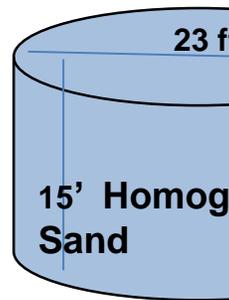
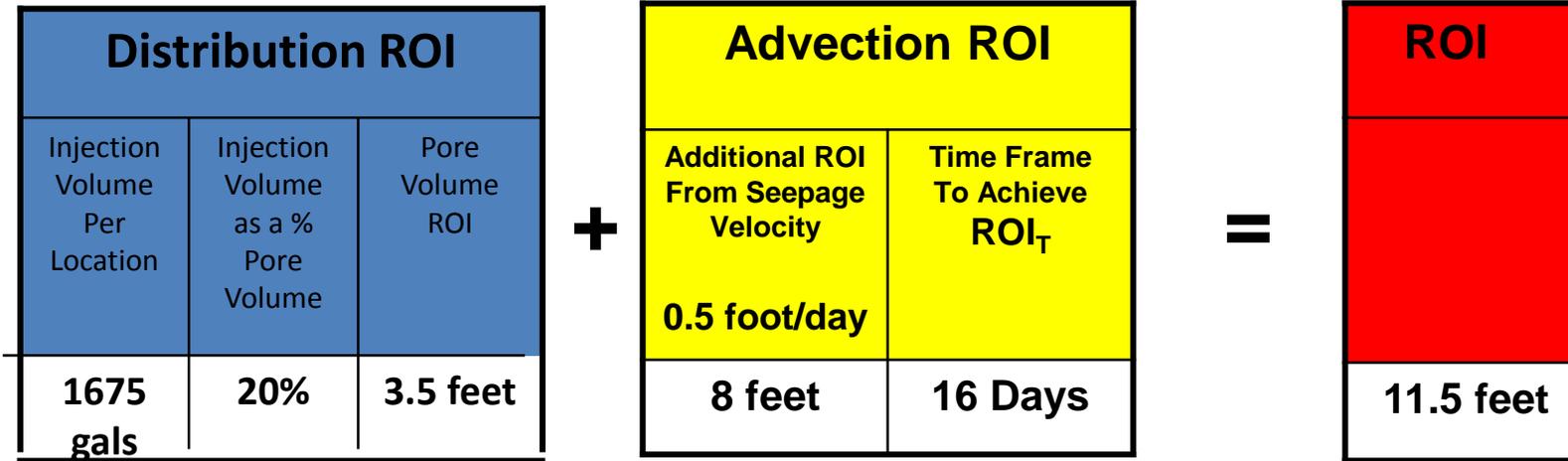


ROI Conundrums

- Low Seepage Velocity versus High Pore Volume For Contact
- High Seepage Velocity Resulting in Low Residence Time



Radius Of Influence Conceptual Model



Reagent Persistence Vs ROI_T
 60 Days (Persulfate) > 16 Days
Increase ROI and/or Lower Volume and Increase Concentration to Increase Residence Time

Reagent Kinetics Vs ROI_T
 30 Days (Persulfate) > 16 Days
Groundwater Recirculation to Increase Residence Time

Design Considerations For DNAPL, Sorbed Mass / Matrix Back Diffusion

- C_S = Contaminant Concentration in soil (mg/kg)
- C_{GW} = Contaminant Concentration in groundwater (ug/l)
- C_{NPL} = Contaminant Concentration in NAPL phase (mg/l) P_E = Effective Porosity
- G = Gallons Water To Be Treated ($X*Y*Z*P_E$)
- Y_S = Yards of Soil To Be Treated ($X*Y*Z*(1-P_E)$)
- **S = Stoichiometric requirements per pound of contaminant**
- S_R = Scavenging Reactions
- C_F = Confidence Factor (*lithology, hydrogeology, characterization*)
- **T_R = Total Pounds of chemistry required**

$$T_R = \{((C_{GW} * G) + C_{NPL} + (C_S * Y_S)) * S + (S_R)\} * C_F$$

← ←
Not Readily Available for Treatment Until They Transition
to Dissolved Phase

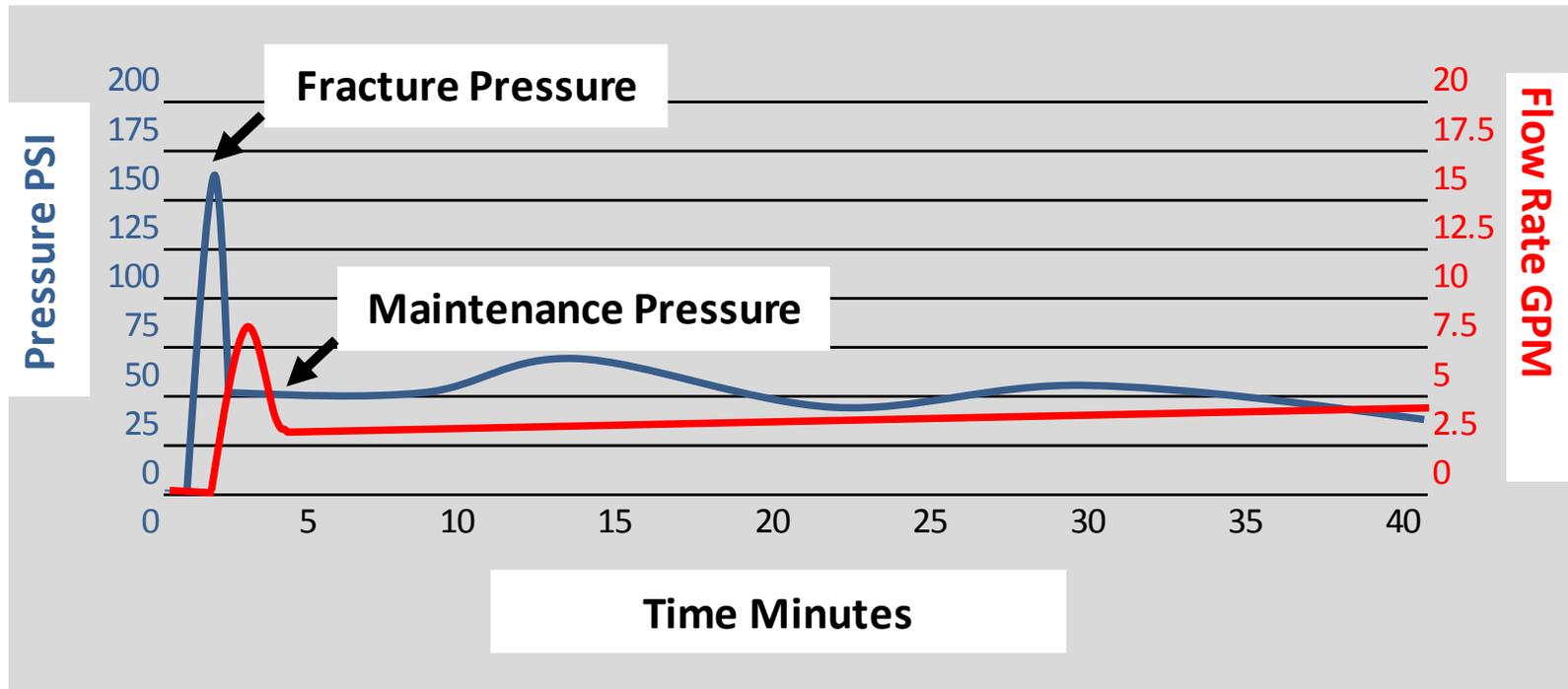
“To Frack or Not to Frack”



“To Frack or Not to Frack”

- Inject liquids into tight zones?
- Inject solids into any zone?
 - Need to open pathways for solids to flow through.
- **Inject liquids into transmissive zones?**

What Does A Fracture Look Like



DPT Best Practices For Maintaining Consistent Pressures

- Injection with inner-hose to maintain pressure on the injection tooling to avoid plugging and inadvertent fracturing as tools are advanced or retracted
- Use pressure relief on pumps to avoid flow rate spikes

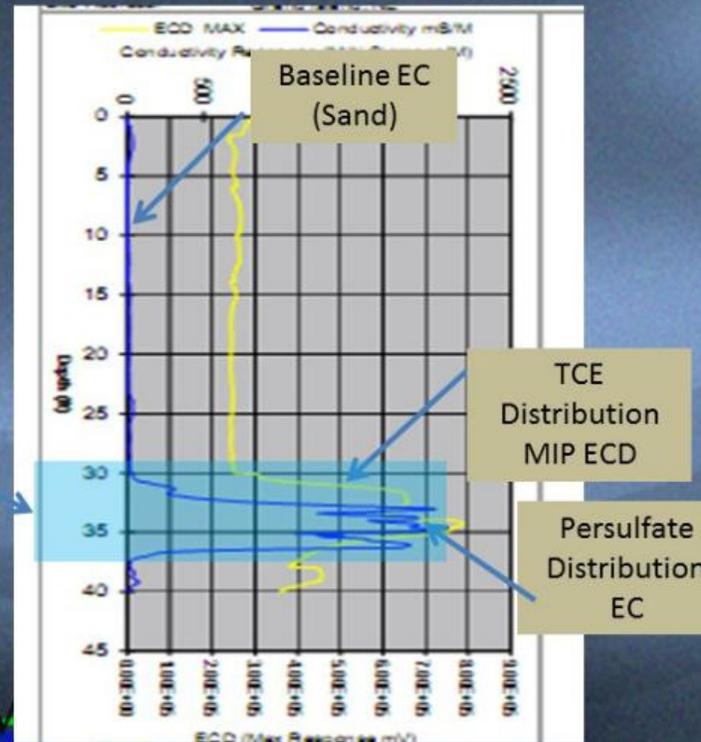


Design Optimization Testing – Distribution of Caustic Persulfate

High Resolution Distribution Verification

- 5 ft downgradient from Injection location
- 30 ft to 40 ft bgs
- 1 day post injection

TCE/Persulfate
Contact



White Paper



Remediation of Complex Chlorinated Solvent Sites While Maximizing Return on Remediation Investment

Elliot Cooper, Director Combined Remedy Strategies, Gorm Heron, Chief Technology Officer, Neil Hey, Program Manager and National Bioremediation Lead, Karen Suchomel, Key Accounts Manager

1. Introduction

As the environmental remediation industry matures, the focus of technological advancement has shifted to addressing the remaining "complex sites". The National Research Council (NRC) (2005) estimated that more than 126,000 sites have residual contamination preventing them from reaching closure and of those, 12,000 sites have residual contamination that will require between 50 to 100 years to achieve restoration, at an estimated cost of between \$110 to \$127 billion dollars. Many complex sites are characterized by persistent chlorinated solvent impacts that for various reasons have not responded to traditional or simplistic technologies. In these cases, achieving a positive return on remediation investment (RORI) should be considered as a factor in evaluating the overall existing and future remediation approaches. RORI at a complex site is not optimized merely through technology selection but rather by designing an overall process to manage restoration from characterization through remedy implementation.

Tools for Management of Chlorinated Solvent-Contaminated Sites

Type: On Demand Video

Chlorinated Solvents On-Demand Video

Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater

July 2008

Tom Sale, Charles Newell, Hans Stroo, Robert Hinchee, and Paul Johnson




Chlorinated Ethene Source Remediation: Lessons Learned

Hans F. Stroo,^{1*} Andrea Lesson,² Jeffrey A. Marquese,³ Pajal C. Johnson,⁴ C. Herb V. Michael,⁵ C. Kavanaugh,⁶ Tom C. Sale,⁷ Charles J. Newell,⁸ Kurt D. Pennell,⁹ Carme and Marvin Unger.

Technical/Regulatory Guidance

In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones



FINAL Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents



August 2004



ADDENDUM TO THE PRINCIPLES AND PRACTICES MANUAL
Loading Rates and Impacts of Substrate Delivery for Enhanced Anaerobic Bioremediation

ESTCP Project ER-200627

JANUARY 2005

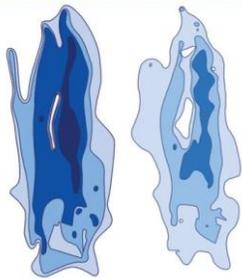
Don Day
Peters International & Technology Corp., Inc.

In Situ Chemical Oxidation for Groundwater Remediation

R. L. Siegrist
M. Crimi
T. J. Simpson
Editors

NATIONAL RESEARCH COUNCIL OF THE NATIONAL ACADEMIES

ALTERNATIVES FOR MANAGING THE NATION'S COMPLEX CONTAMINATED GROUNDWATER SITES



Study and Interpretation of the Chemical Characteristics of Natural Water

Third Edition

United States Geological Survey
Water-Supply Paper 2254

EPA **Engineering Issue**

In-Situ Chemical Oxidation
Scott G. Huling¹ and Bruce E. Peierl²

I. PURPOSE

The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers are a series of technology transfer documents that summarize the latest available information on specific technical issues, including the use and ongoing, specific considerations, related research and the information to develop, and related other items. This Engineering Issue Paper is intended to provide essential background information on some conditions (PCEs), conditions, and other sites, industry, or process remediation strategies with information to guide in the evaluation and possible selection of appropriate in-situ chemical oxidation (ISCO) remedial alternatives.

II. INTRODUCTION

II.A. Background

In-situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of oxidizing ground water or soil contamination into less harmful chemical species. There are several different forms of oxidants that have been used for ISCO, however, the focus of this Engineering Issue Paper will be on the two most commonly used oxidants: permanganate (MnO₄⁻) and hydrogen peroxide (H₂O₂) and on the two most common oxidant delivery systems: permeable reactive barriers (PRBs) and in-situ wells. The type and physical form of the oxidant influence the general oxidant availability and reaction requirements. The placement of the oxidant in the subsurface is important since this allows the oxidant to be delivered and diffuse through and ultimately the delivery of oxidant to targeted areas in the subsurface. For example, permeate flow rates for long periods of time and diffusion rates are generally limited to meters or less, and the diffusion rates are generally limited to centimeters per day. Radial oxidant transport distances will be severely limited. Radial oxidant transport using some oxidants (H₂O₂, MnO₄⁻, O₃) that are highly susceptible to various environmental transformations may occur quickly and pass the very short period of time (10-1000).