C-067, in: H.V. Rectanus and S.H. Rosansky (Chairs). *Remediation of Chlorinated and Recalcitrant Compounds—2014.* Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2014). ISBN 978-0-9819730-8-1, ©2014 Battelle Memorial Institute, Columbus, OH, **www.battelle.org/chlorcon**.

Effective, Sustainable In Situ Remediation Approach at Industrial Sites Using a Combination of Zerovalent Iron and Emulsified Vegetable Oil

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Background. Effective in situ remediation starts with sustained contact between the contaminant(s) of concern and the chemical amendment that is emplaced to degrade those contaminants. Success depends on the knowledgeable manipulation of hydrological, biological, geological and chemical interactions. A variety of in situ reductive chemical and biological reactions can be induced in a contaminated aquifer to remove chlorinated volatile organic compounds (cVOCs). These amendments are typically applied at a loading rate between 0.1 and 1% (w/w; amendment/soil mass); and at a cost between $1 and $10/yd. of soil treated. Most of these amendments provide less than 2-years of active remediation. Typical applications of ZVI maintain reductive conditions for 3 to 7 years with some PRB applications that have been in-place for longer than 30-years. As a recycled product with minimal energy needed to process the feedstocks, ZVI is the most sustainable amendment available. Chemical reduction by amendments such as ZVI reactive iron powder have the advantage of being able to treat high concentrations of cVOCs while producing limited amount of intermediates, such as vinyl chloride (VC). Biological reduction by amendments such as emulsified vegetable oil (EVO) have the advantage of being able to treat very low levels (10 ppb) of cVOCs. Combining amendments like ZVI and EVO can work synergistically by creating a reducing environment that thermodynamically promotes biological reductive dechlorination.

Approach. At several active facilities, a strategy to remediate TCE and associated daughter products in a shallow aquifer was need. In general, treated soils consisted of low permeability silty sand with clays. The amount of amendment was limited by the lower effective porosity. Ferox®-Plus, a combination of SRS™ Emulsified Vegetable Oil and a Ferox® ZVI Reactive Iron Powders, was used. At one of the facilities, the treatment depth was from 4 -14 feet and target area which had a baseline of as high as 27,500 ug/L of PCE. The injections were performed in 376 direct push locations utilizing tooling resulting in the injection of 145,000 lbs of solution (Ferox-Plus). Based on the area, the estimated loading around of the ZVI/EVO slurry 0.4 % w/w (soil/slurry). Following the injections, the baseline PCE dropped on average 99% . Several case studies other were combinations of ZVI/EVO has been applied will be presented.

Lessons Learned. Treatability studies were not useful in determining the ratio of ZVI and EVO to be applied to on a site-specific basis. Similarly, pilot study results can be difficult to interpret because varying contact efficiency. The combination of reductive chemistry and biology can be effective, but only if the proper distribution/contact is made in the sub-surface. However, general rule-of-thumb and guidelines were determined from

a series of these applications. Overall cost effectiveness and advantages over other technologies will be summarized.

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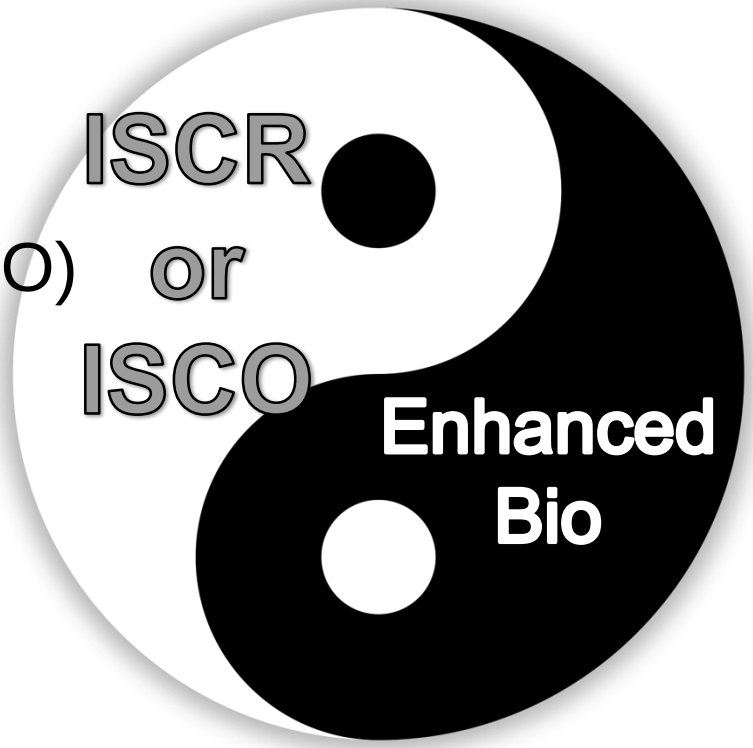
Chemistry & Biology Marriage

- Enhanced Biological
  - Lactate
  - Emulsified Vegetable Oil (EVO)
  - Oxygen
- In-Situ Chemistries
  - ZVI
  - Oxidants



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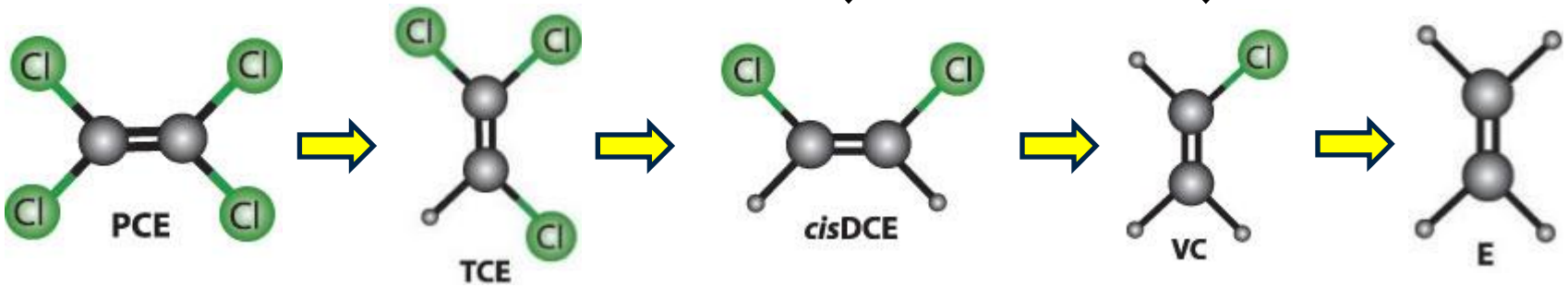
Biological Reductive Dechlorination

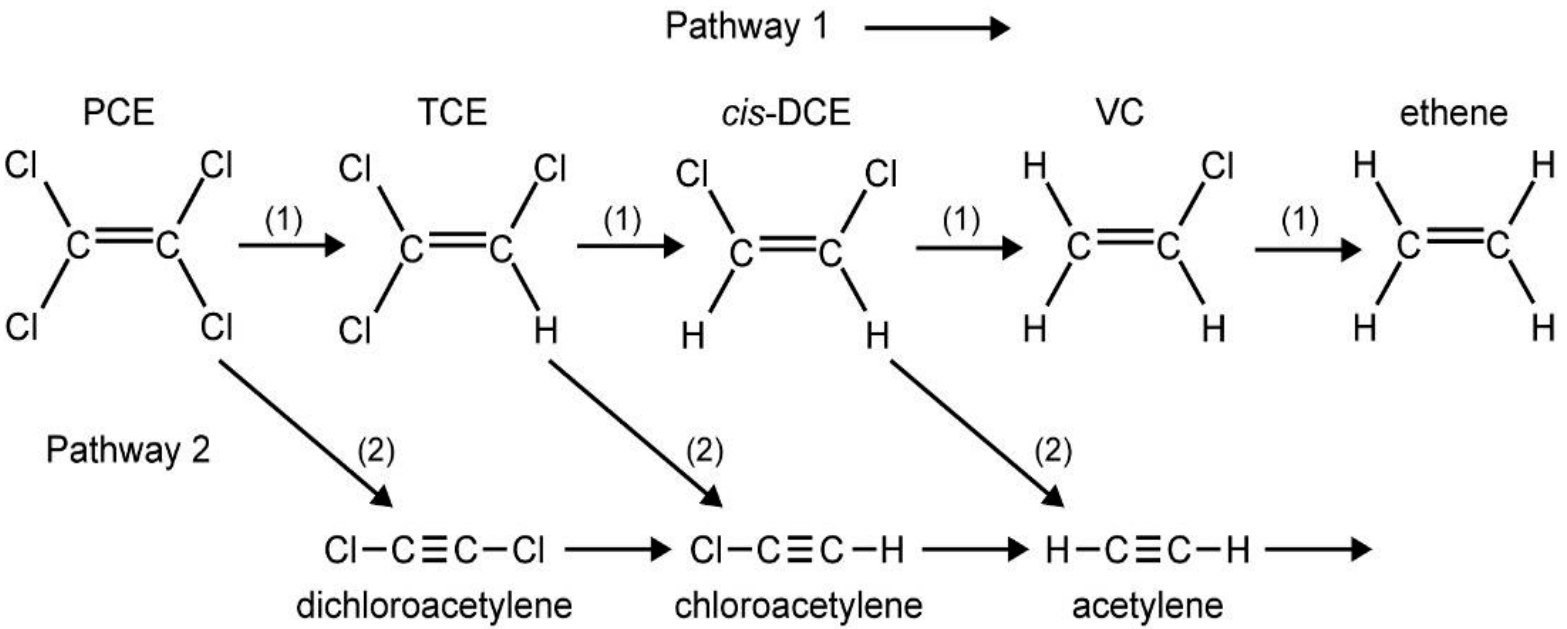
cDCE and VC can stall if *Dehalococcoides* is not present



Common Microbes

Dehalococcoides

Chemical Reduction With ZVI



Marriage of Chemistry & Biology

- Kinetics
  - Bio: PCE>>TCE>>DCE>>VC
  - ZVI: VC>>DCE>>TCE>>PCE
- pH
  - Bio: Decrease pH
  - ZVI: Increase pH
- Mass Action
  - Bio: Typical operates at lower (ppb) concentrations
  - Chem: Higher concentration (ppm) more favorable

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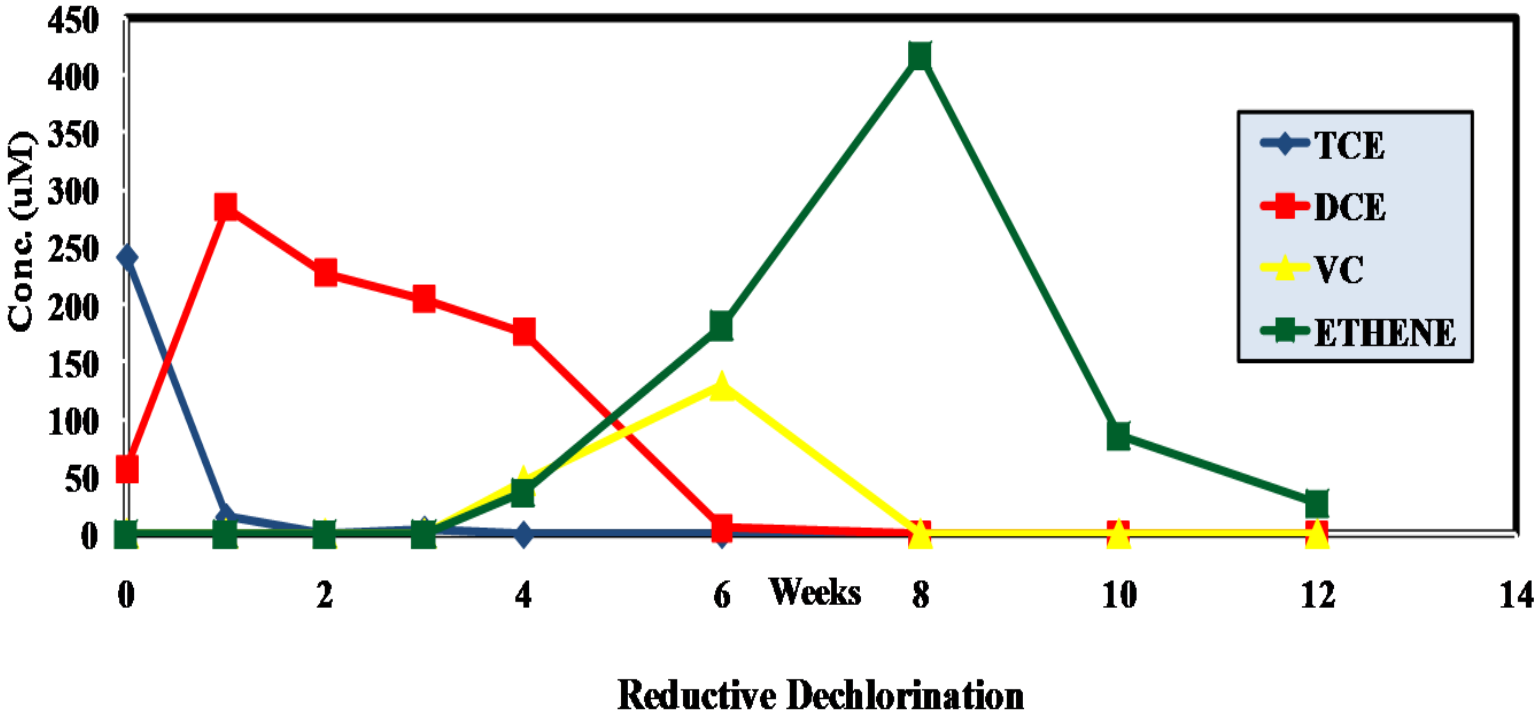
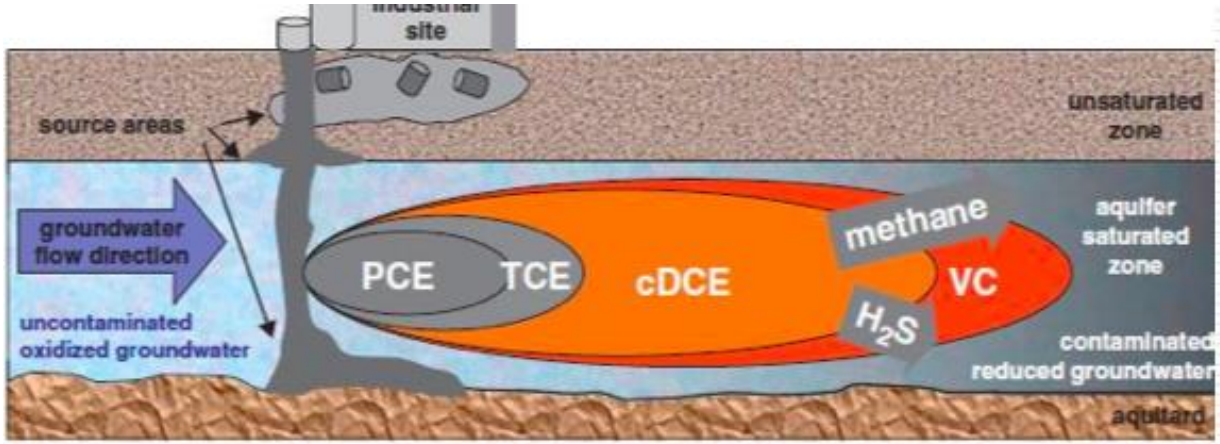
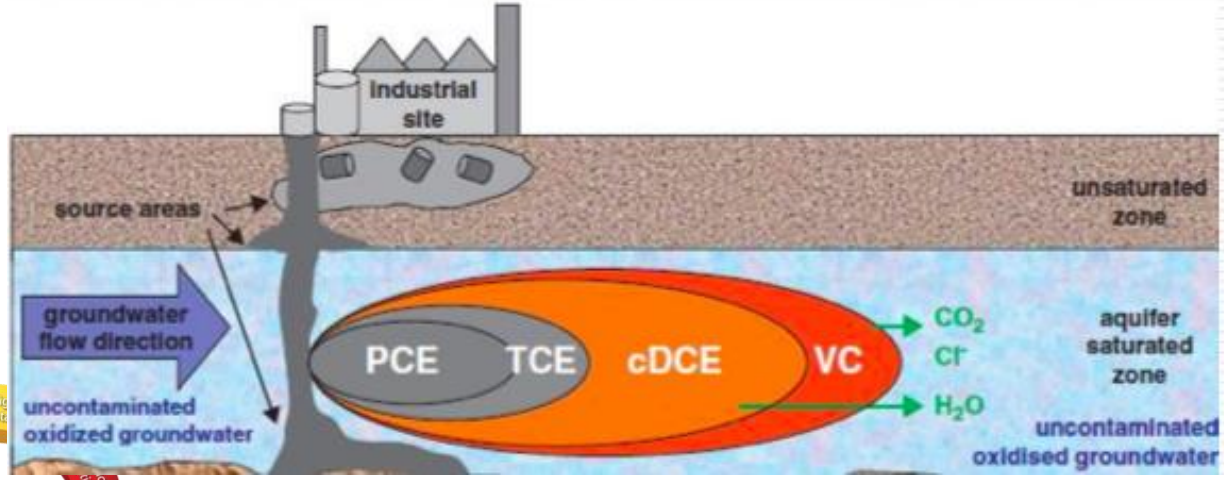
Biological Reductive Dechlorination



“Spatial” Kinetics



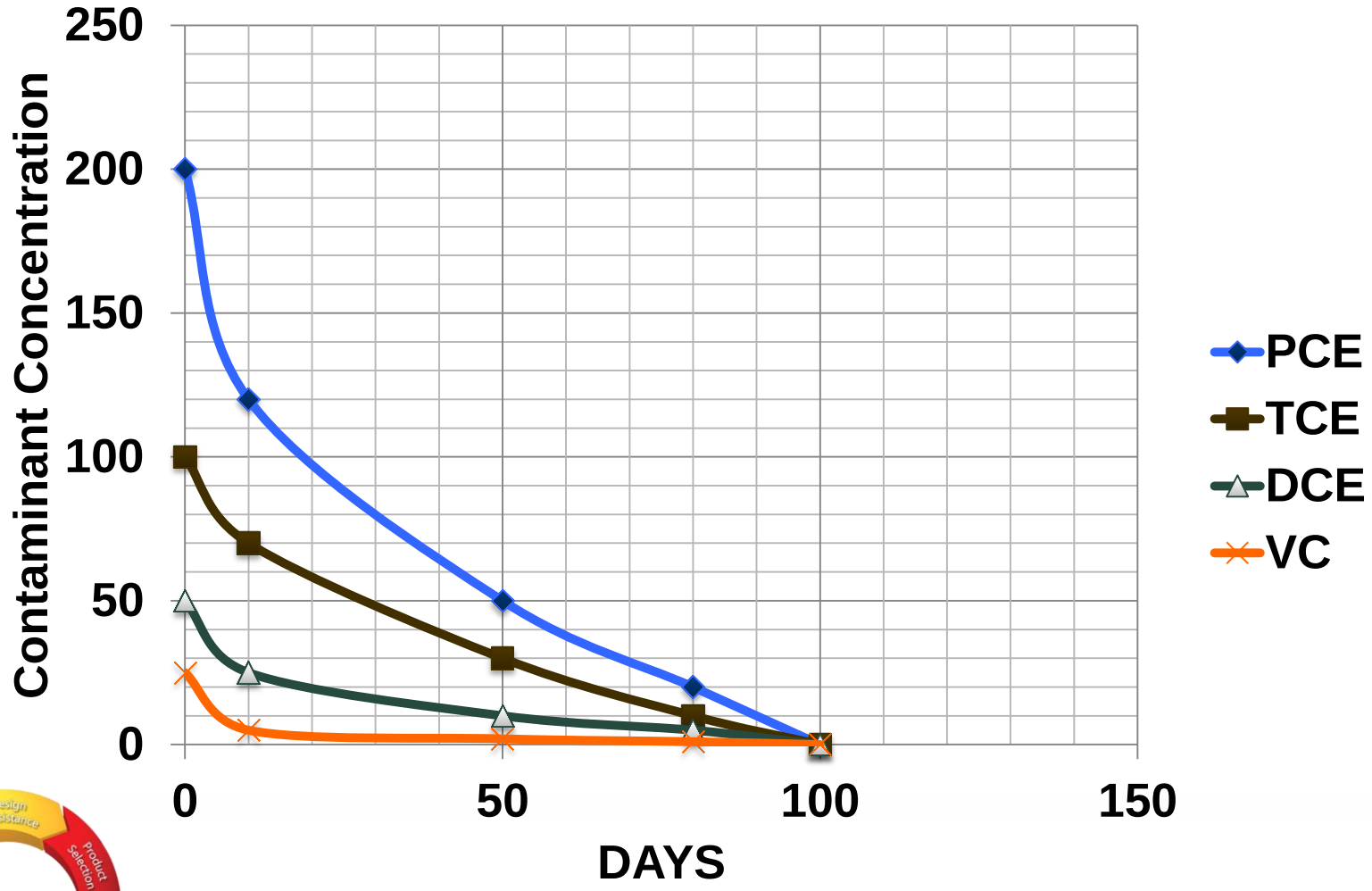
Incomplete reductive dechlorination



Sequential anaerobic/ aerobic degradation

Source: Tiehm and Schmidt 2011

Typical ZVI Kinetics



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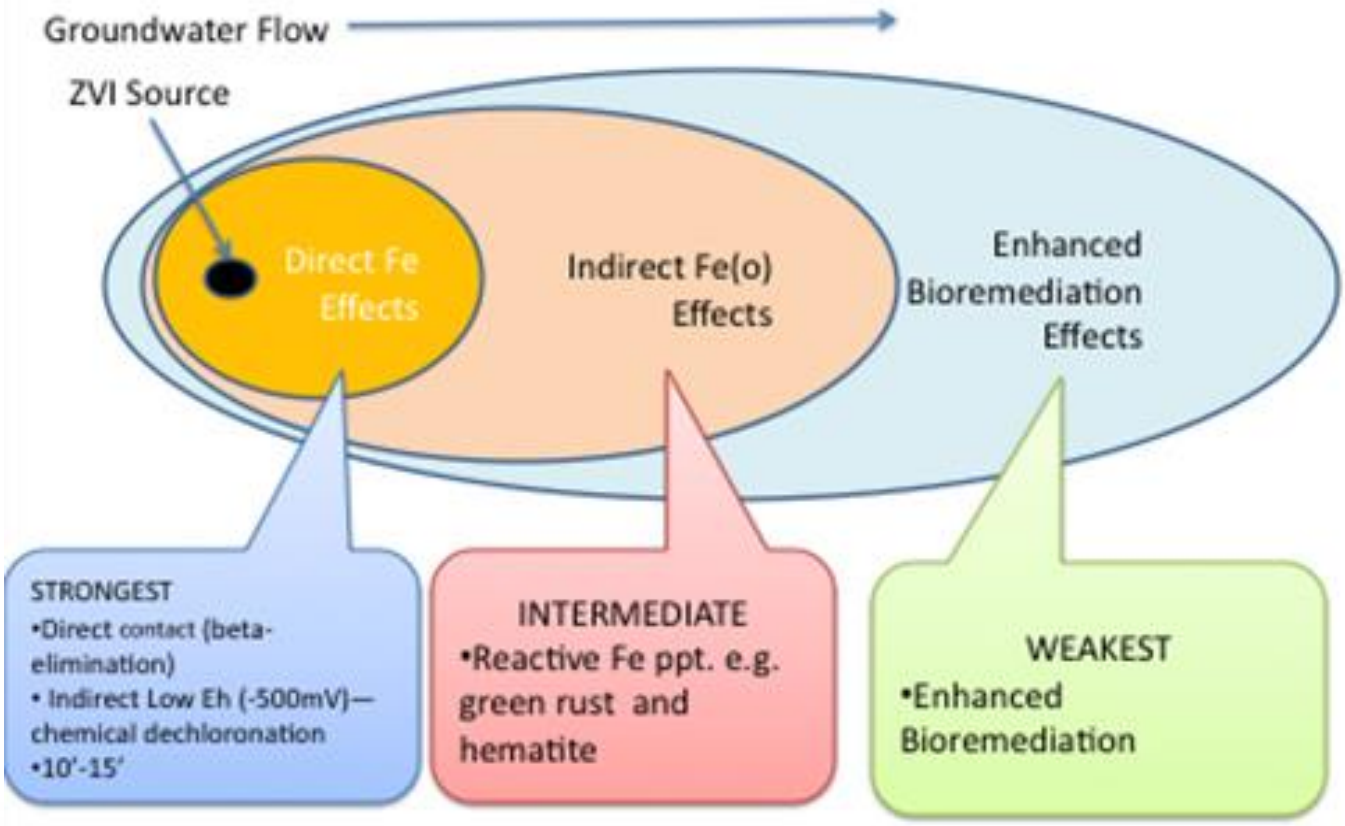
General Effects of In Situ ZVI: "Spatial" Chemistry-Includes Geological and Biological



FEROX®-PLUS ZVI/Carbon

Ingredient	Weight%
Food grade edible soy bean oil	30-40%
Iron	10-40%
Emulsifiers, thickners, and proprietary nutrient package containing nitrogen, phosphorus and vitamin B_{12}	3 - 6%
Sodium Lactate	2 - 4%
Water	10 - 55%

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Copley Site


United States Environmental Protection Agency
Copley Square Plaza, OU #1 Superfund Site
In-Situ Chemical Reduction
Groundwater and Soil Remediation
This project is the result of a partnership between the
U.S. EPA and Ohio EPA
ST SulTRAC
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Copley Square

- **Description:** Former dry cleaning operation with a seven acre PCE/TCE plume
- **Geology:** Unconsolidated glacial deposits and underlying bedrock. The treatment zone consists of interbedded silt, sand, clay, and gravel.
- **Hydrology:** Hydraulic conductivities for the shallow water-bearing units is 7.37×10^{-3} with an average linear groundwater flow velocity of 2.98 feet per day [ft./day].
- **Soil Contamination:** Concentrations of PCE up to 39 ppm and TCE concentrations up to 3.2 ppm (RI)
- **Groundwater Contamination:** Approximately 2 ppm of PCE and 1 ppm TCE
- **Remediation Goal:** MCLs for Groundwater (5 ppb) and PRGs for soil (480 ppb)

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Installation Method

- Enhanced ZVI Injection
- Installed Using Direct Push Technology
- Top Down Injection Method
- Anticipated Five Foot ROI
- ROI Verified with Infield Screening

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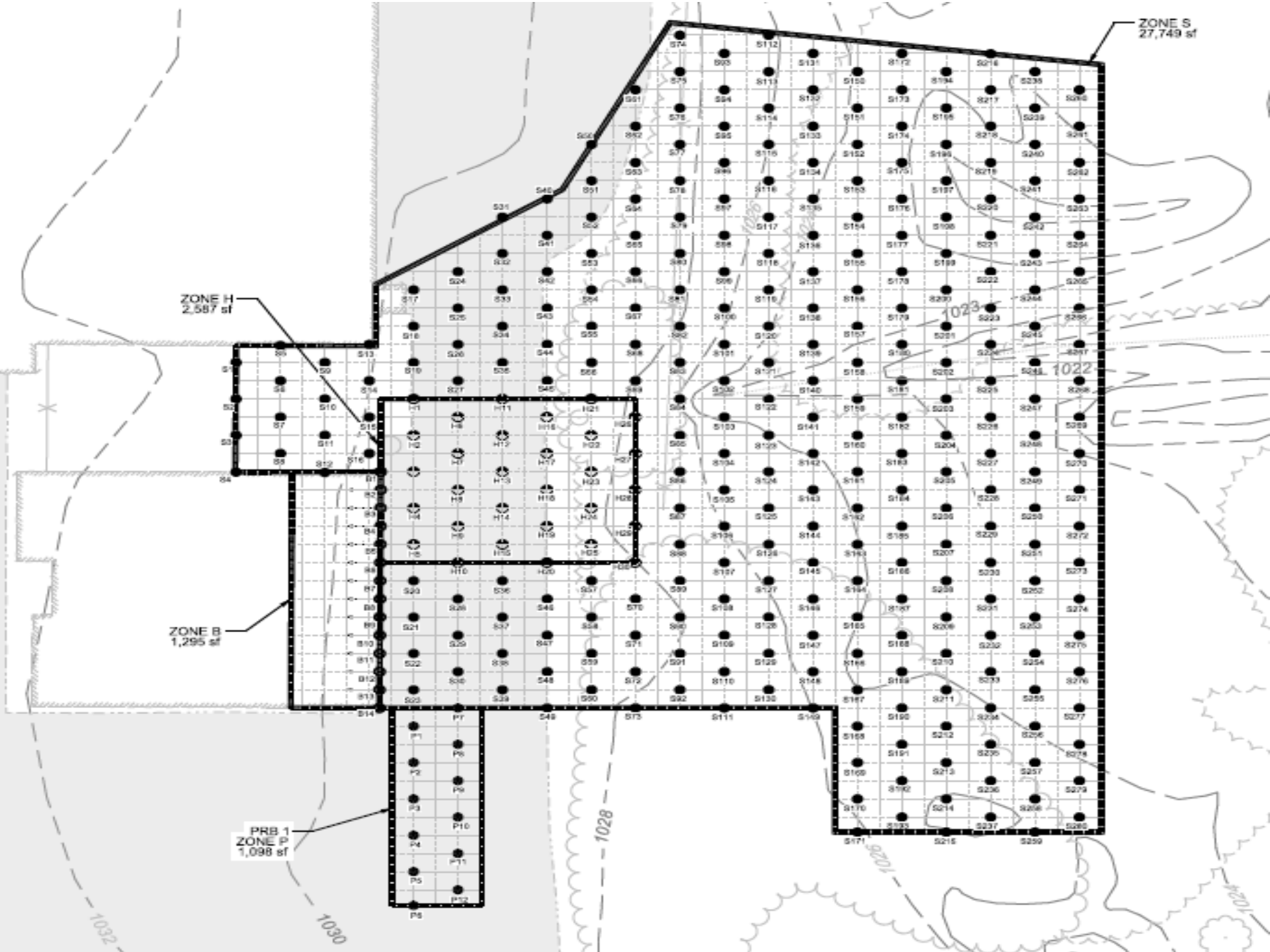
Directional Injection


ZONE S
27,749 sf
ZONE H
2,587 sf
ZONE B
1,295 sf
PRB 1
ZONE P
1,098 sf
1028
1030
1032

Chemicals Used

- Two Carbon Enhanced ZVI Products
  - Ferox Plus™
    - Premixed
    - ZVI and soybean oil
    - Constancy of a thick oil
  - EHC® ISCR Reagent ZVI Carbon by Peroxychem®
    - Requires Mixing
    - ZVI and dry carbon source
    - Consistency of a wet grout

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Injection Set Up

- Direct Push Rig
- Three Inch Positive Displacement Pump
- Three Man Field Team

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EFS Project Team


ChemGrout
49 HP
XAS 185
EFS
TECHNOLOGY
TNT Blue

QA/QC

- Injection ROI Demonstrations
- Samples Collected at Ten Percent of Injections
  - Each two foot interval was tested using magnetic separation
  - Objective of successfully treating the majority of injection intervals
- Background Iron

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Magnetic Separation Field Screening

Background Iron

Confirmed Iron Sample

Non Typical Results

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Large Full Scale Application of Ferox®-Plus ZVI Carbon

- 150,000 lbs of Ferox-Plus
- 34 lbs/ft
- **0.43 lbs/ft^3**
- DPT Application (376 Injection pts.)
- 5’ Emplacement ROI
- Production Rates
  - 4645 lbs./day
  - 130 Linear Feet/Day Injected
  - ~12 points/Day
  - ~942 Ft.^{2}/Day

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Comparison Application of EHC® ISCR Reagent ZVI Carbon

- 74,333 lbs of Slurry
  - 22,299 lbs of EHC® ISCR Reagent
- 47 lbs./ft.
- **2.3 lbs/ft^3 (>5-times loading rate)**
- DPT Application (208 Injection pts.)
- 2.5’ Emplacement ROI
- Production Rates
  - 4551 lbs./day
  - 113 Linear Feet/Day Injected
  - ~13 points/Day
  - ~255 Ft.^{2}/Day

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Ferox Plus™ is a ZVI/Carbon Formulation

- Easier to Inject
- Easier to distribute in subsurface
- Works as well or better than competing products

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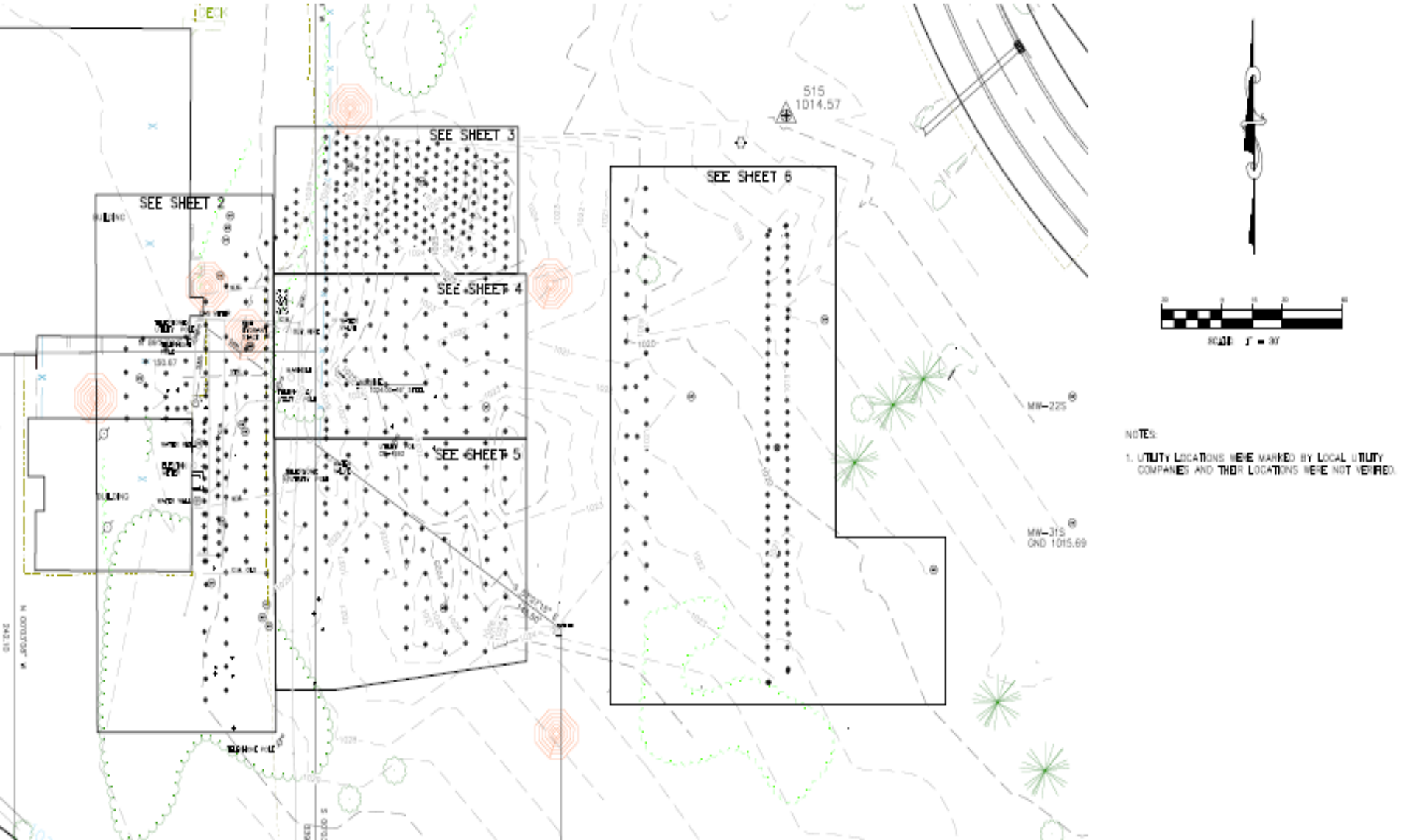
Over 500 DPT Injection Points In the Shallow Plume: As-Built



Shallow PCE Plume

Reduction in PCE

PCE	MW-3S	MW-4S	MW-5S	MW-14S
Start	214	857	1,060	27,500
Oct. 2013	1.1	6	4.6	660
Jan. 2014	3	2	2.8	0.82
% REDUCTION	99%	99%	100%	98%
ORP	-120	-117	-146	-241

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Shallow TCE Plume: Before

TCE	MW-3S	MW-4S	MW-5S	MW-14S
Start	85	123	77	1305
Oct. 2013	3.8	8.4	3.2	90
Jan. 2014	1.8	3	2.7	1.3

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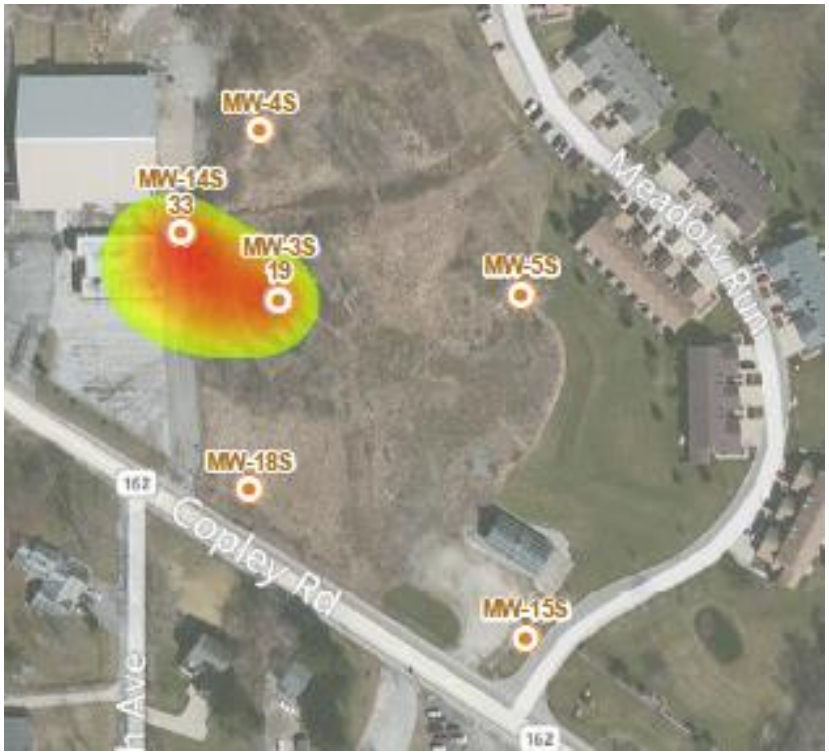
Shallow Daughter Plume

cis-DCE



Vinyl Chloride

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Cis-DCE	MW-3S	MW-4S	MW-5S	MW-14S
Start	367	123	88	1033
Oct. 2013	160	110	410	7600
Jan. 2014	110	11	120	220
Vinyl Chloride	**MW-3S**	**MW-4S**	**MW-5S**	**MW-14S**
Start	31	175	15	43
Oct. 2013	56	24	54	450
Jan. 2014	29	0.5	18	150

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Take Home Messages

- Synergistic & Sustainable Chemistries are Possible
- ZVI & Carbon Can Effectively Remove cVOCs
- Ferox™-Plus is Most Sustainable, Cost-effective Fe/Carbon Product on the Market

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Questions?

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