Enhanced Reductive Dechlorination After In-Situ Chemical Oxidation: Moving Past the Myth to Design Effective Combined Treatment Remedies

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ISOTEC REMEDIATION TECHNOLOGIES

Acknowledgements

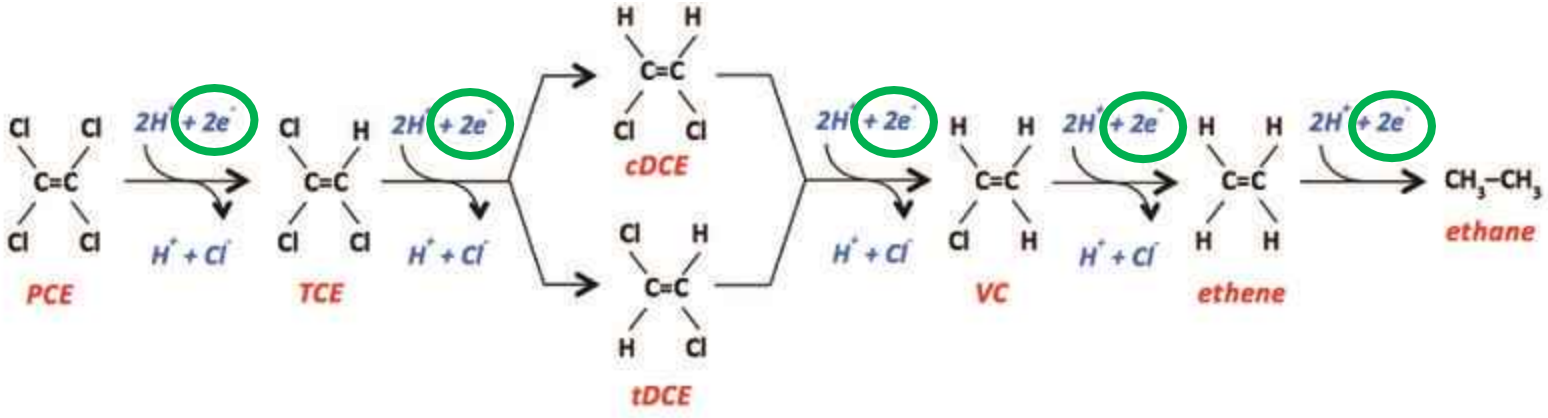
- Scott Pittenger
- Prasad Kakarla, P.E.

- Phil Dennis
- Jeff Roberts

Why Combined Remedies?

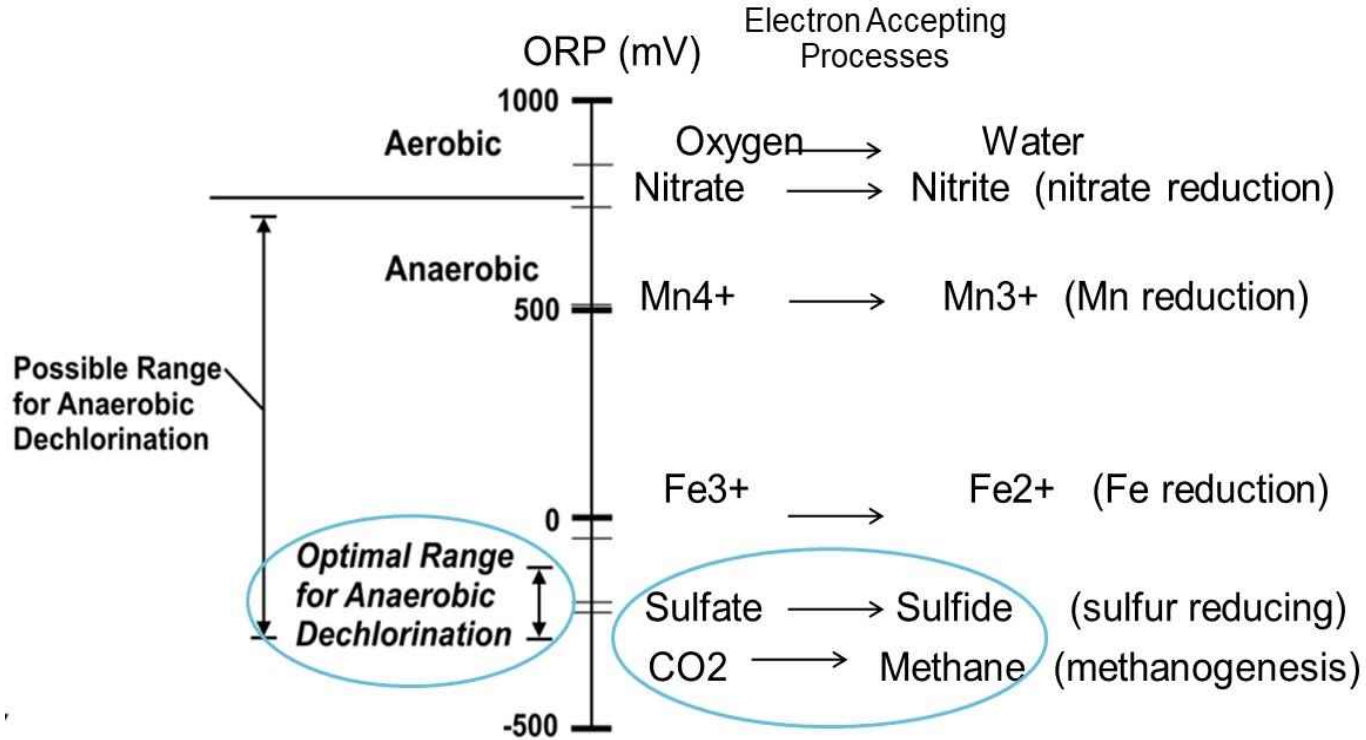
- **One technology cannot be used in all situations**
- **Utilize multiple processes to treat/remove contaminants**
  - Different tools may be most suitable to address different contaminant phases or concentrations and/or different site 'compartments'
  - Overcome limitations of individual technologies
- **Accelerated schedule**
- **Cost savings**

Enhanced Reductive Dechlorination



- **Sequential reactions performed by bacteria**
  - Replace Cl with H
  - Addition of 2 electrons to each step → more reduced molecules
  - Chlorinated ethenes and ethanes

Enhanced Reductive Dechlorination



- Dissolved Oxygen <1 mg/L
- ORP < -75 mV
- Sulfate reducing conditions
- pH: 6.0 to 8.5 optimal*
- Total Organic Carbon: 10-20+ mg/L

*Can be lowered to 5.5 with specialized bioaugmentation cultures

Chemical Oxidation

- **In-Situ Chemical Oxidation (ISCO):** process of introducing an oxidant into the subsurface in order to degrade toxic organic contaminants "in place" to benign byproducts

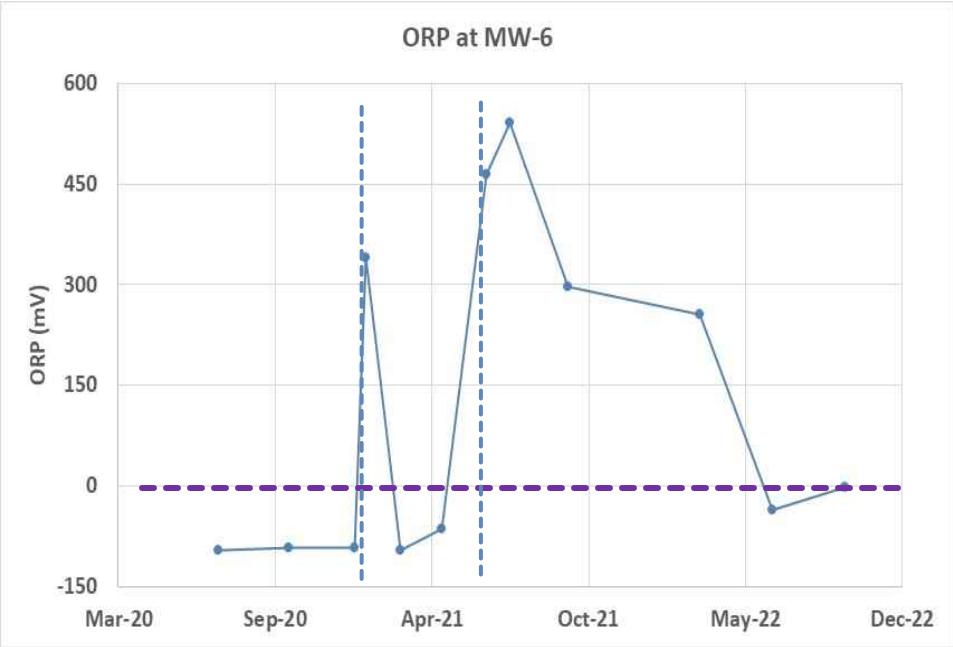
Oxidant	Typical Oxidant Persistence	Reaction Product	Benefit to Combined Remedy	Inhibition to Combined Remedy
H_2O_2	6 – 24 hours	O_2	• Oxygen for aerobic biodegradation	• Oxidizing Conditions • O_2 as e- electron acceptor
MnO_4^-	3 – 12 months	Mn		• Oxidizing Conditions • Mn as e- acceptor
$Na_2S_2O_8$	3 – 12 weeks	SO_4^{2-} / H_2SO_4	• Sulfate for petroleum biodegradation • FeS for abiotic dechlorination	• Oxidizing Conditions • Acidic pH • Sulfate as e- acceptor

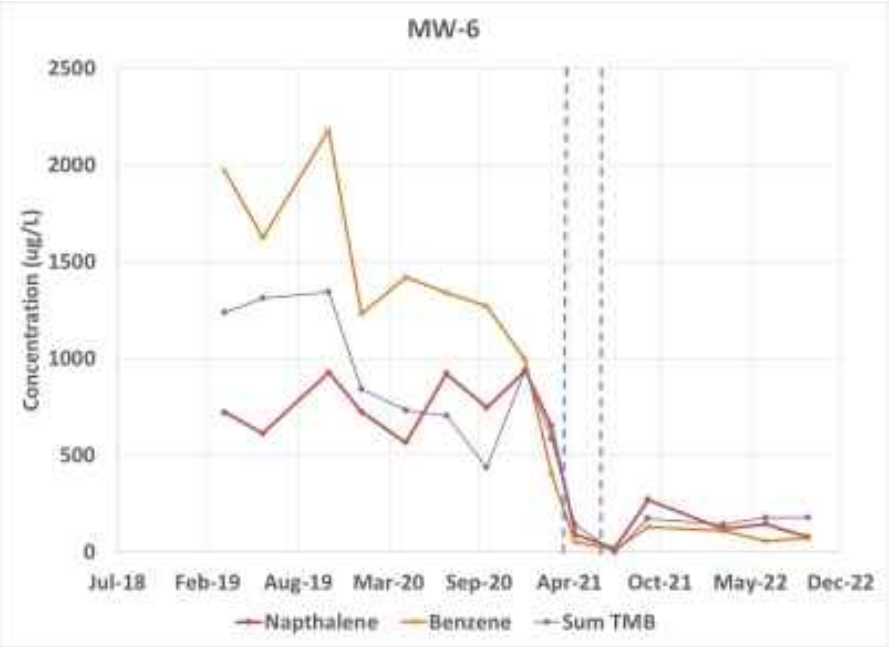
Changing Redox Conditions

https://www.nist.gov/blogs/manufacturing-innovation-blog/challenging-times

Gas Station Case Study

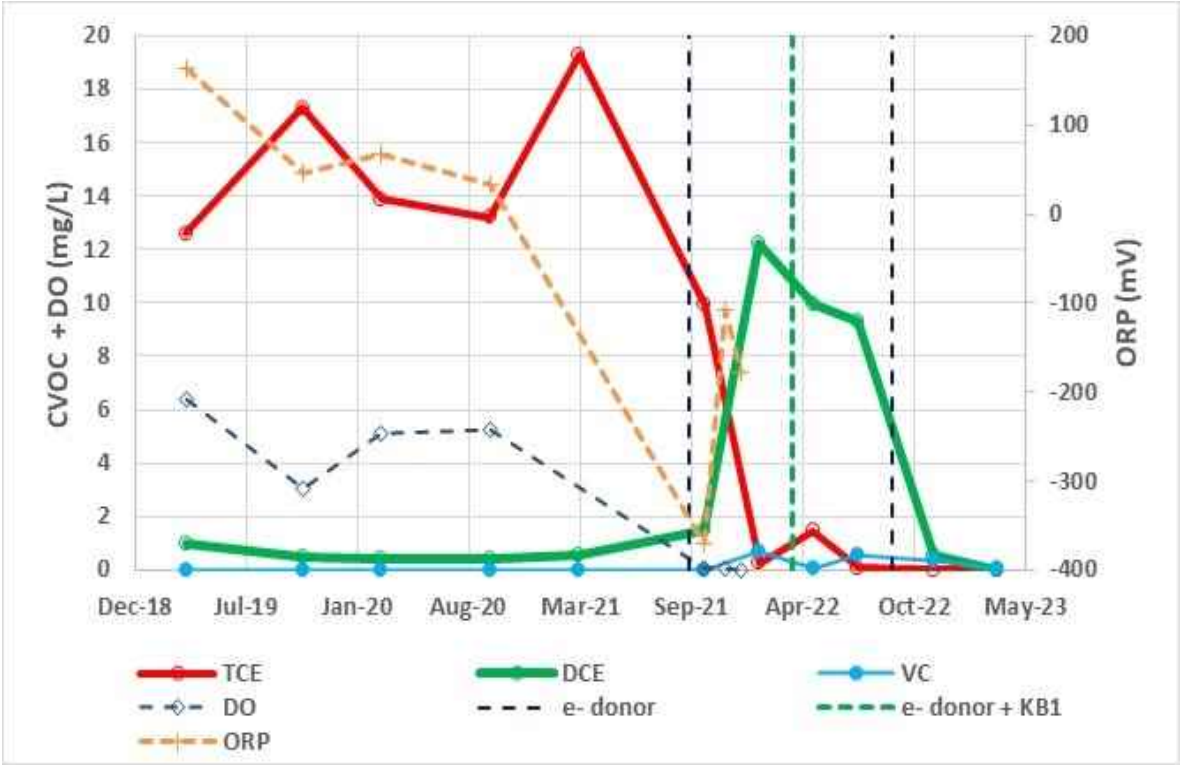
- Baseline Conditions: anaerobic (DO < 1 mg/L, ORP ~ -100 mV)
- Post-ISCO conditions revert to anaerobic





Enhanced Dechlorination Case Study

- **Baseline: groundwater naturally aerobic**
  - DO 4-6+ mg/L
  - TCE > 97% of total CVOCs
- Injection of quick-release electron donor + bioaugmentation



Reductive Dechlorination after ISCO

- **Oxidants can kill microorganisms (oxidizing conditions, pH)**
  - Klens et al. (2001) Shaw AFB, permanganate addition
    - reduced aerobic and anaerobic plate counts 47-99.95% 6 months after treatment
    - aerobic population rebounded / anaerobic population minimal recovery
  - Battelle (2001)
    - 1 month after ISCO the anaerobic populations were virtually eliminated
    - **9 & 13 months after ISCO plate counts indicated significant anaerobic population**
  - Dennis et al. (2004) – SiREM microcosm study of soil collected ~3 years after permanganate injection
    - Native DHC populations dead or inactive and had not recovered
    - Permanganate may affect ability of microbial community to remediation post-ISCO
    - **Biostimulation and Bioaugmentation can help anaerobic bacteria recover**

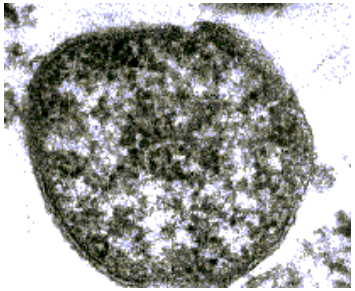
Bioremediation after ISCO

- **Oxidants can kill microorganisms (oxidizing conditions, pH), BUT**

  "the nonideal mechanisms and long-term time frames associated with ISCO under field conditions that strongly influence microbial survival and activity under harsh oxidative conditions. Differences between laboratory and field conditions help explain discrepancies between microbial inhibition results from laboratory studies and the seemingly low impact of ISCO on microbial activity at field-scale."

  -EPA Engineering Issue on ISCO (Huling and Pivetz, 2006) (Section III.F.5)

  - Preferential pathways
  - Heterogenous conditions
  - Microniches in subsurface



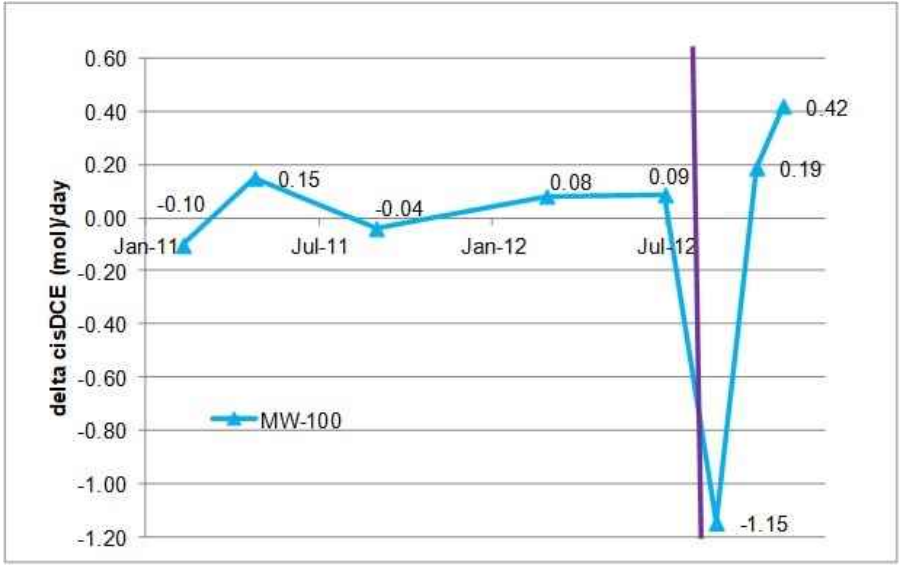
Dehalococcoides mccartyi Strain 195 (SiREM)

- **Many examples of higher biological activity after ISCO**
  - No cases found where an aquifer was sterilized or activity permanently inhibited (including reductive dechlorinating bacteria)

Permanganate Injection

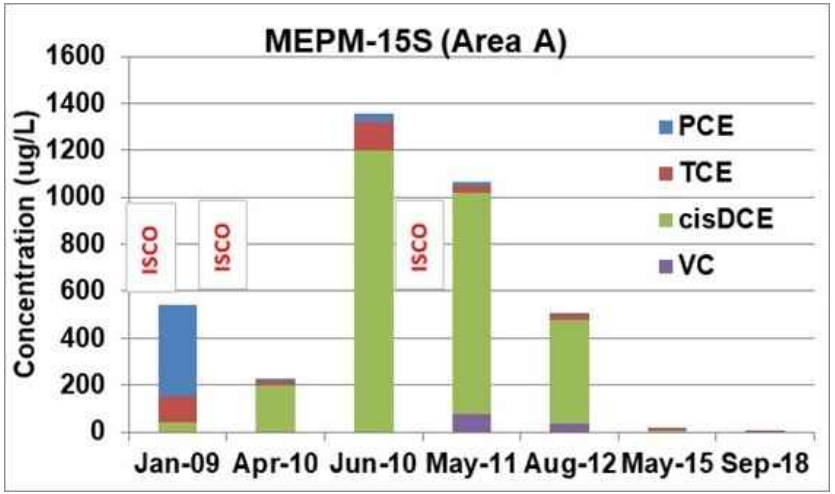
- **Reductive dechlorination lines of evidence post-ISCO**
  - cis-DCE increases
  - VC detection
  - DHC and VC R-tase
- **ORP at MW100**
  - Pre-ISCO -20 to -10 mV
  - Post-ISCO -130 to -90 mV
- **cis-DCE production rate**

Well	Date	DHC	VC R-tase	tceA R-tase
		Counts/L	Counts/L	counts/L
MW100	Pre-ISCO (1 month)	6.18E+04	<300	400
MW100	3 months Post-ISCO	1.79E+07	7.33E+06	7.42E+06



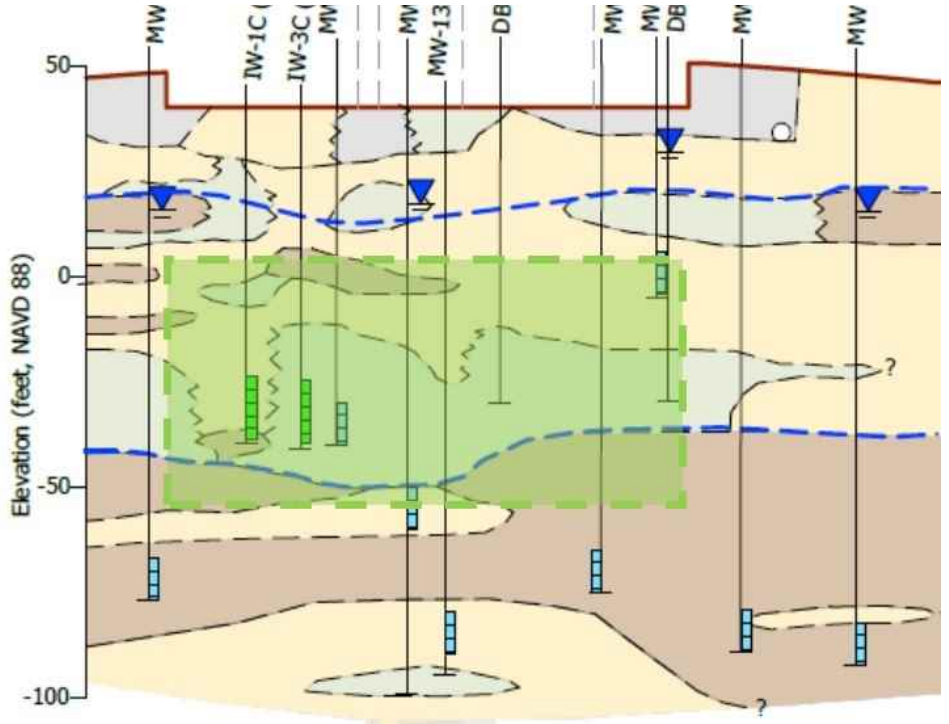
Reductive Dechlorination after ISCO

- **Full-scale ISCO with activated sodium persulfate**
  - CVOCs, BTEX, 1,4-dioxane
  - Objective: significantly decrease groundwater concentrations to transition to MNA
- **Baseline Conditions: reducing groundwater and pH 8 - 11 s.u.**
- **Reductive dechlorination observed post-ISCO**
  - daughter products
  - DHC
  - VC reductase
- **<u>No enhanced bioremediation actions taken</u>**



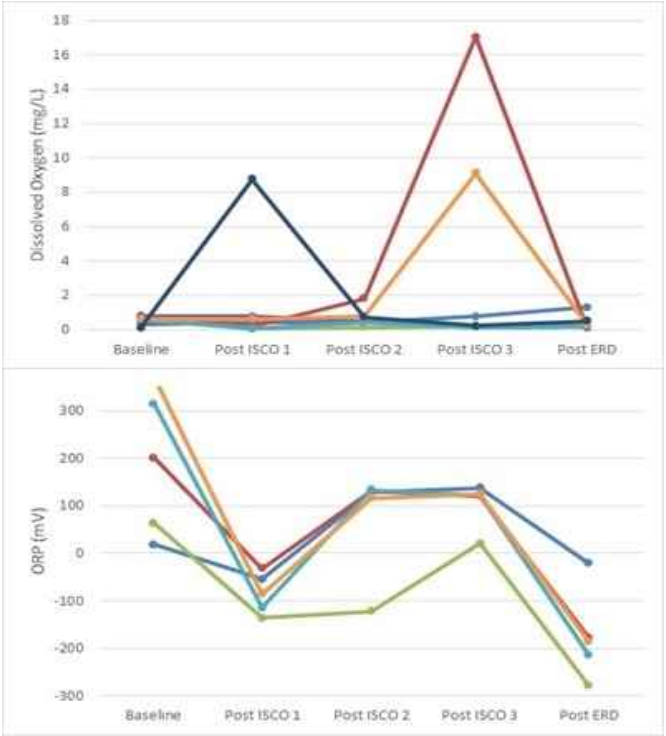
Proactive Combined Remedy

- **Former Industrial Laundry**
  - PCE – up to 237 mg/kg & 97 mg/L
  - Depth to groundwater ~ 25' bgs
  - CVOCs in GW to 110' bgs
  - 1 acre parcel
- **Mixed Use Development**
  - Retail, Office, Lab (500,000 SF)
- **Groundwater Combined Remedy**
  - In-situ Chemical Oxidation
  - Enhanced Reductive Dechlorination
  - 150+ Injection Wells: 4 vertical zones (45-105 feet bgs)



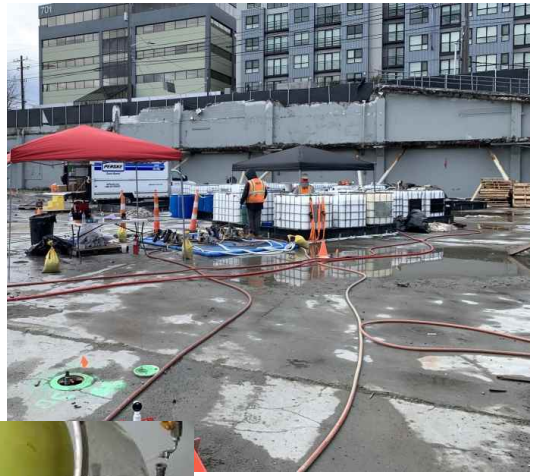
Remedial Design for Combined Remedy

- **In-Situ Chemical Oxidation**
  - Modified Fenton's Reagent
    - Stabilized H_2O_2 catalyzed by chelated iron
    - Enhanced desorption
    - Fast acting oxidant (3 rounds Sept-Jan)
- **Enhanced Reductive Dechlorination**
  - **To be performed 1 month after ISCO**
  - DO monitoring during and after ISCO injections
  - ESTCP Substrate Design Tool Sensitivity (ranges of DO)
  - Emulsified vegetable oil (EVO)
    - Persistent electron donor (2-5 years)
  - Additional sodium lactate as a quick-release substrate to help accelerate the creation of reducing conditions post ISCO
  - Deoxygenating amendment in all EVO batches
  - Bioaugmentation



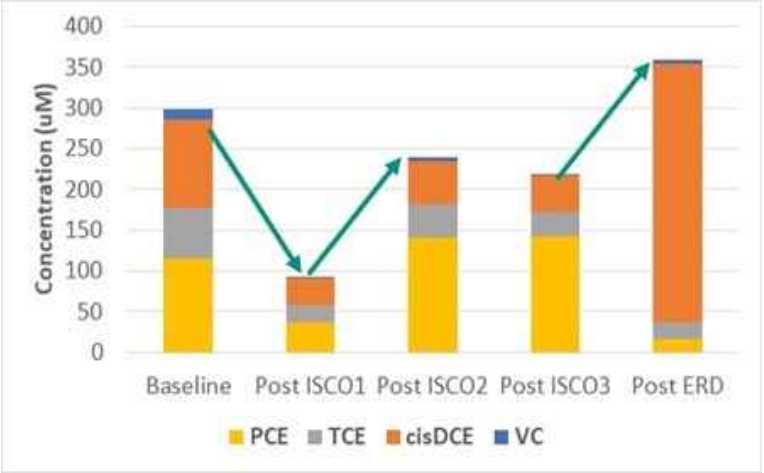
ISCO + ERD Combined Remedy

- **3 rounds ISCO performed in 5 months**
- **ERD Injections performed 1 month after ISCO**
  - 75 totes of emulsified vegetable oil
  - 20 consecutive days in February to meet schedule
    - 7,000 – 10,000 gallons/day
    - Rotating injection staff
  - EVO injection in phases into wells
    - 1/4 of volume
  - Bioaugmentation at end of ERD
    - 2-3 weeks between initial carbon substrate and addition of KB-1



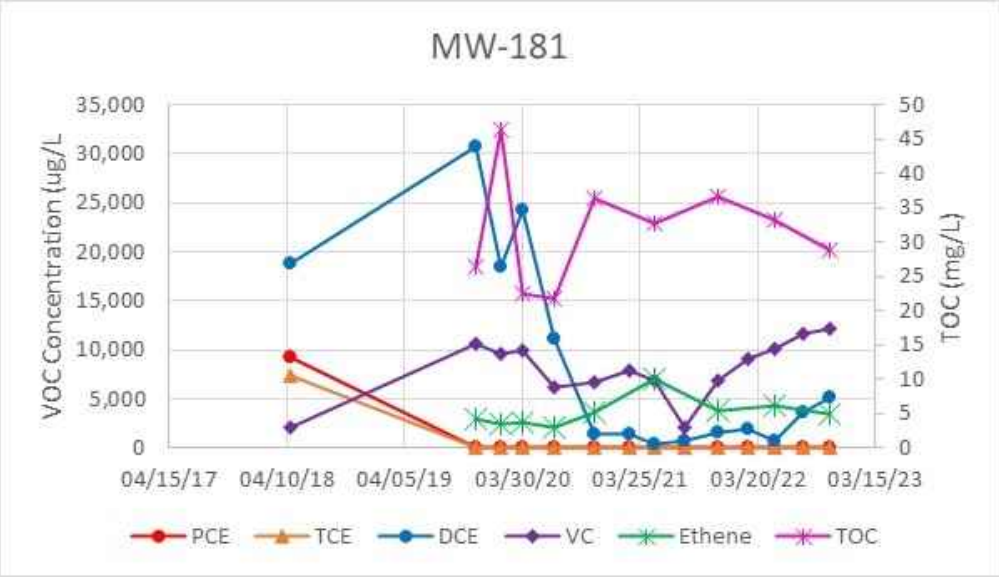
Early Results

1. **ISCO rapidly decreases aqueous VOCs**
2. **Enhanced desorption from MFR**
3. **Reductive dechlorination**
   - 10 days after ERD
     - Negative ORP in all MWs
     - >90% reduction in PCE from baseline
   - Desorbed PCE dechlorinated
   - On-going treatment of CVOCs as construction occurs aboveground



Proactive Combined Remedy

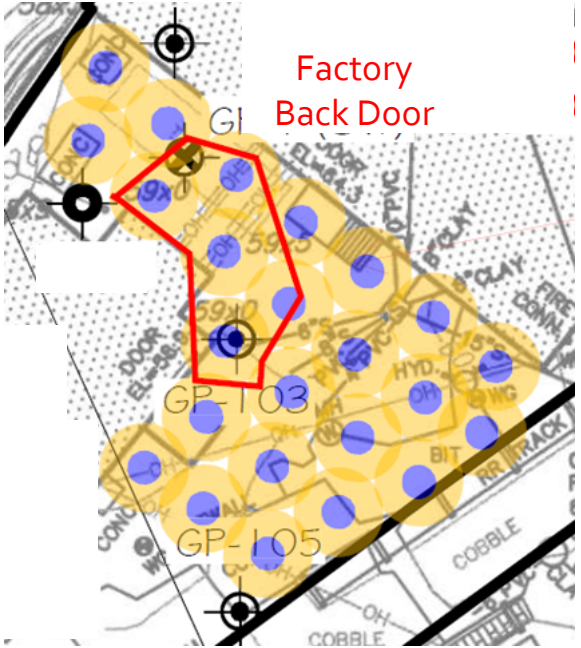
- **Reductive dechlorination ongoing**
- **Significant reduction in CVOC mass (moles)**



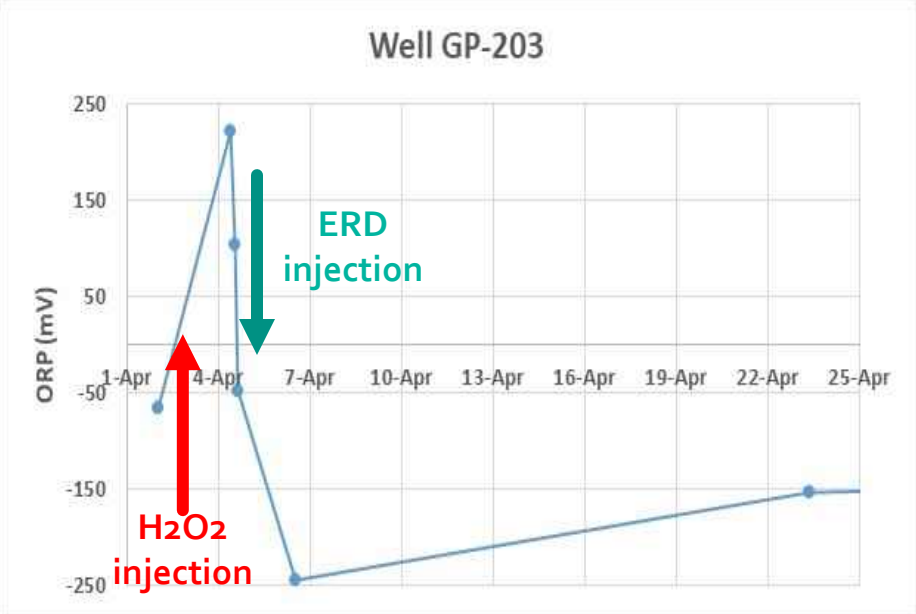
Analyte	Min.	Mean	Max	# of Wells	Time
TOC (mg/L)	2.3	18	84.8	20	27 mo. Post-ERD
Ethene (ug/L)	0.4	347	8,250	20	27 mo. Post-ERD
DHC (Cell/L)	2.00E+06	8.40E+07	9.00E+08	6	30 mo. Post-ERD

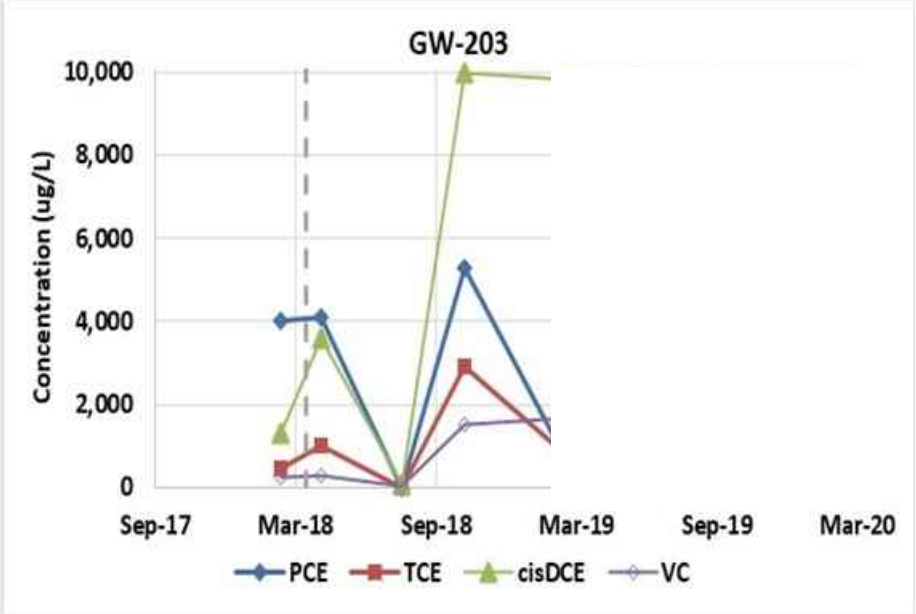
Single Event Case Study

- **Historic Mill Redevelopment**
- **Low CVOCs in soil and groundwater**
  - Except within focused area
- **Catalyzed Hydrogen Peroxide – Day 1**
  - Desorption + Oxidation
- **ZVI-ERD – Inject Outside In – Day 2-4**
  - Small micron ZVI + glycerol (S-Micro ZVI)
  - Bioaugmentation
  - Deoxygenating reagent added to batches



Single Event Case Study





- Temporary oxidizing conditions
- Reductive dechlorination observed <1 month post injection

Summary

- **Many benefits of proactive combined remedies**
  - Chemical Oxidation: rapid mass removal
  - Enhanced Bioremediation: persistence and resistance to rebound
  - Combined Remedies best applied in proactive manner

- **Bioaugmentation can be used where there was no indigenous community or to "augment" communities that may have been stunned by ISCO**

- **Bench-scale testing, pilot-scale tests, and molecular tools can be used to optimize remedial design and implementation**

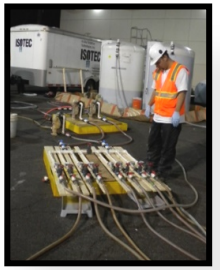
Thank you

Chemical Oxidation

Bioremediation

Activated Carbon Injectates (BOS 100® & BOS 200®)

Soil Mixing (Chemical Reagents & Stabilization)



Metals Remediation

Bedrock Injections

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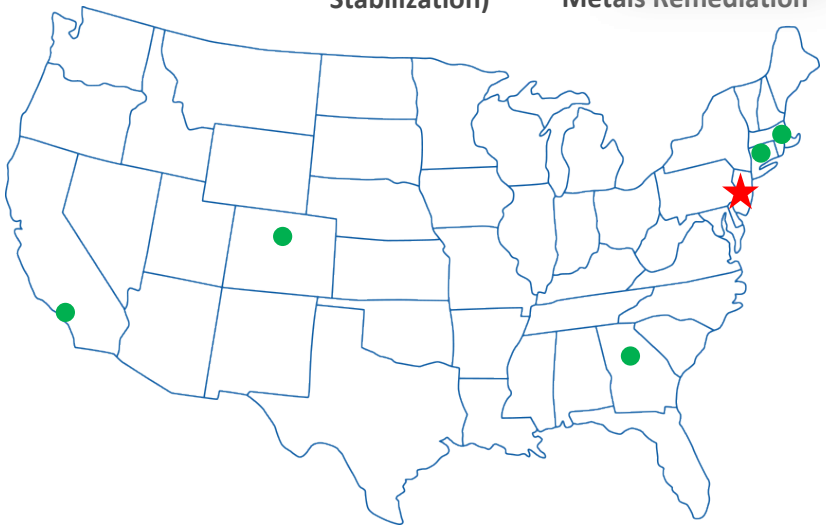

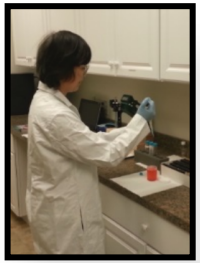

Treatability Laboratory