ARCADIS Design & Consultancy for natural and built assets

VERIFIED CARBON TETRACHLORIDE AND CHLOROFORM TRANSFORMATION VIA BIOTIC, ABIOTIC, AND REACTIVE IRON SULFIDE MECHANISMS

Shandra D. Justicia-León, Jennifer Martin Tilton, Matthew Schnobrich, Craig Divine, Shannon M. Ulrich, David Liles, and Dora Taggart

Battelle Fifth International Symposium on Bioremediation and Sustainable Technologies

April 2019 – Baltimore, Maryland

Agenda

Background: Degradation of Chlorinated Methanes

- Biotransformation
- Abiotic Transformation
- Coupled Microbial-Abiotic Transformation

Approach: *In Situ* EHC™ Injections

- Field Site Description
- Reagent (EHC™) Selection & Delivery
- Performance Monitoring

Results: Post-Injection Performance

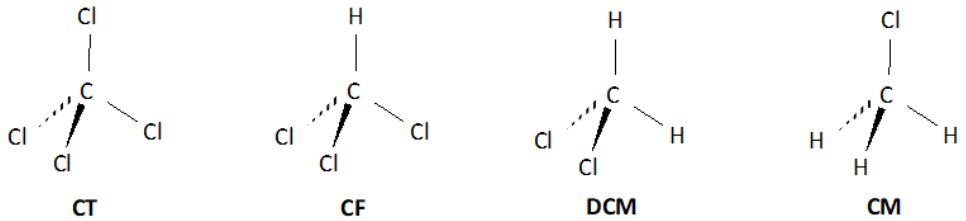
- Geochemical Conditions
- Characterization of Reactive Minerals
- Microbial Community Analysis
- Concentration Trends

Degradation of chlorinated methanes

- Biotransformation
  - ✓ Cometabolic biotransformation
  - ✓ Catabolic biotransformation: sources of carbon/energy or respiratory electron acceptors

organohalide respiration

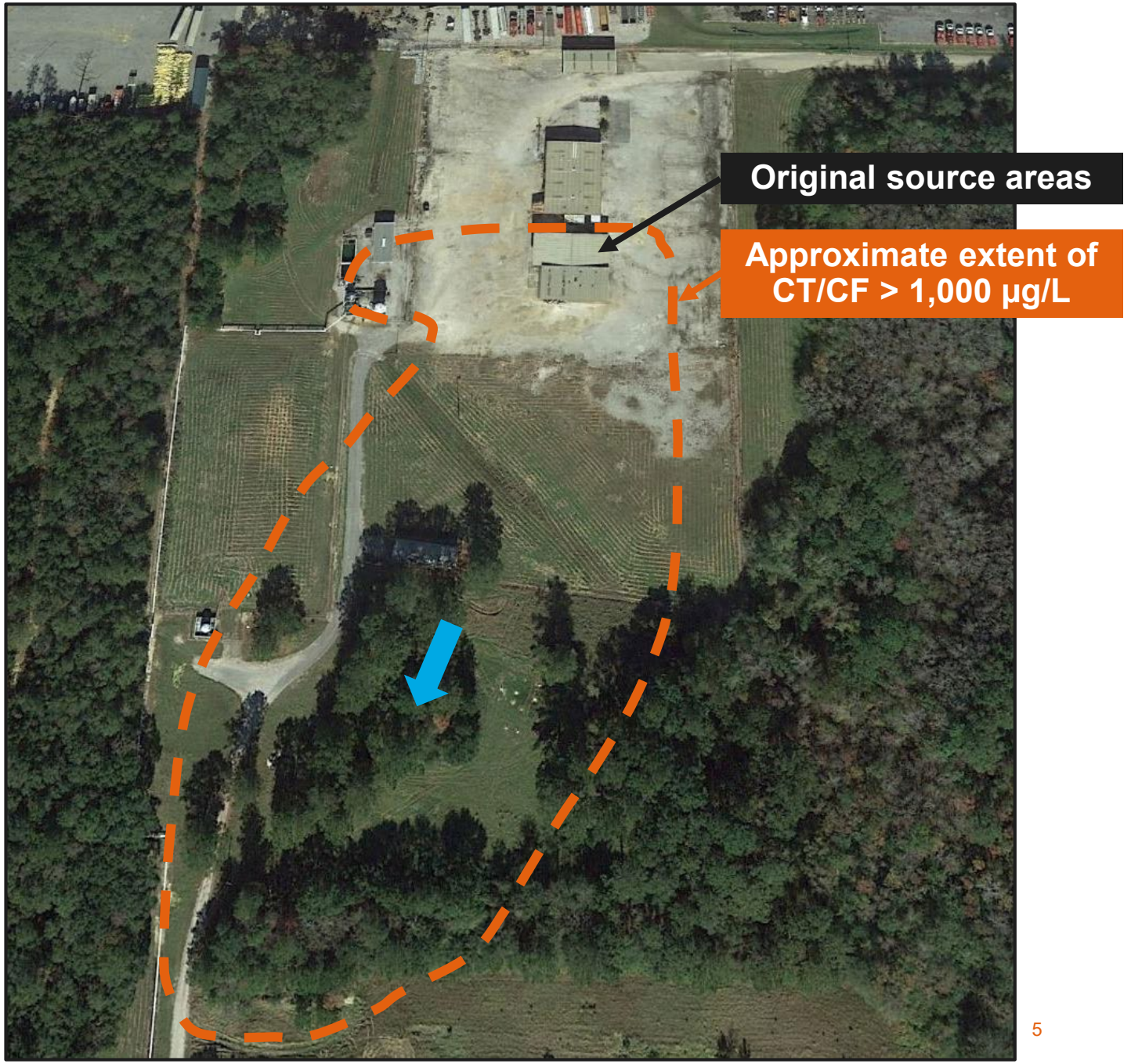
- Abiotic transformation
  - ✓ Degradation by hydrolysis (e.g., via contact with zero-valent metals)
  - ✓ CT more amenable to abiotic transformation
- Coupled microbial-abiotic transformation of chlorinated methanes
  - ✓ Abiotic reactions catalyzed by reactive mineral species (e.g., iron sulfur minerals) typically depend on microbial activity, which generates the reactive species/surfaces



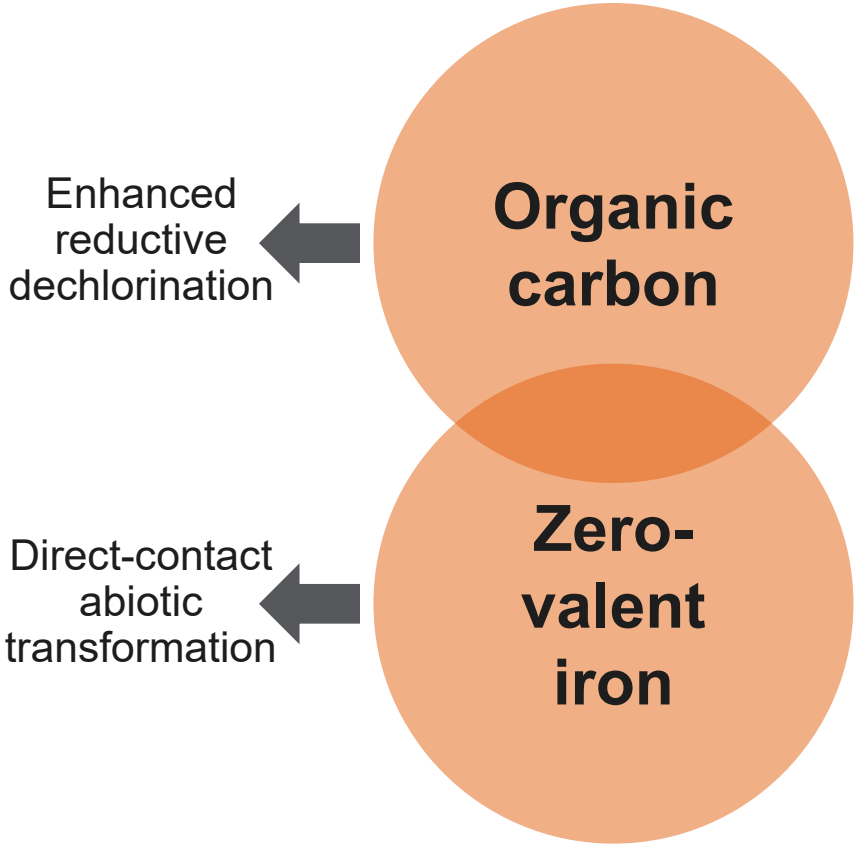
Approach: *In Situ* EHC™ Injections

Field Site Description

- Primary contaminants of concern: CT and CF
- Max chlorinated methane concentration ~ 20 mg/L
- Co-disposed sulfur-containing compounds
- Naturally high iron
- Remedial approach: *in situ* EHC™ injections



Reagent Selection: EHC™



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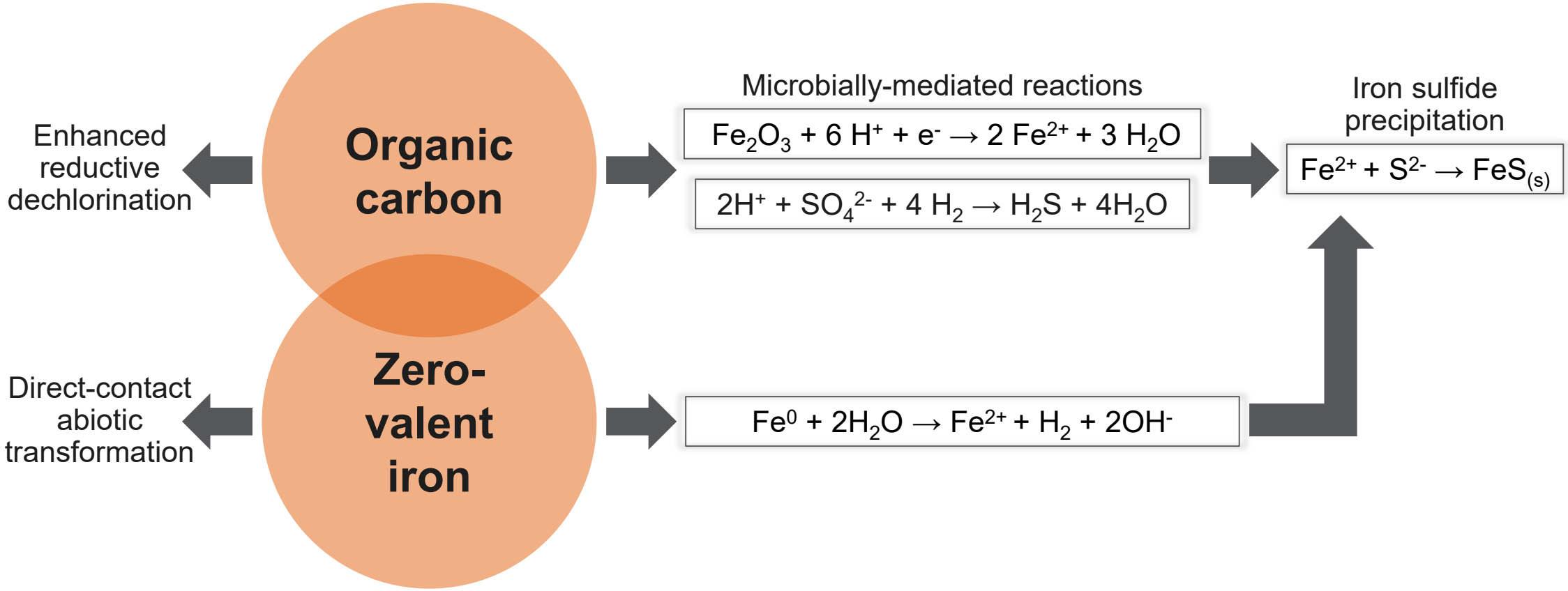

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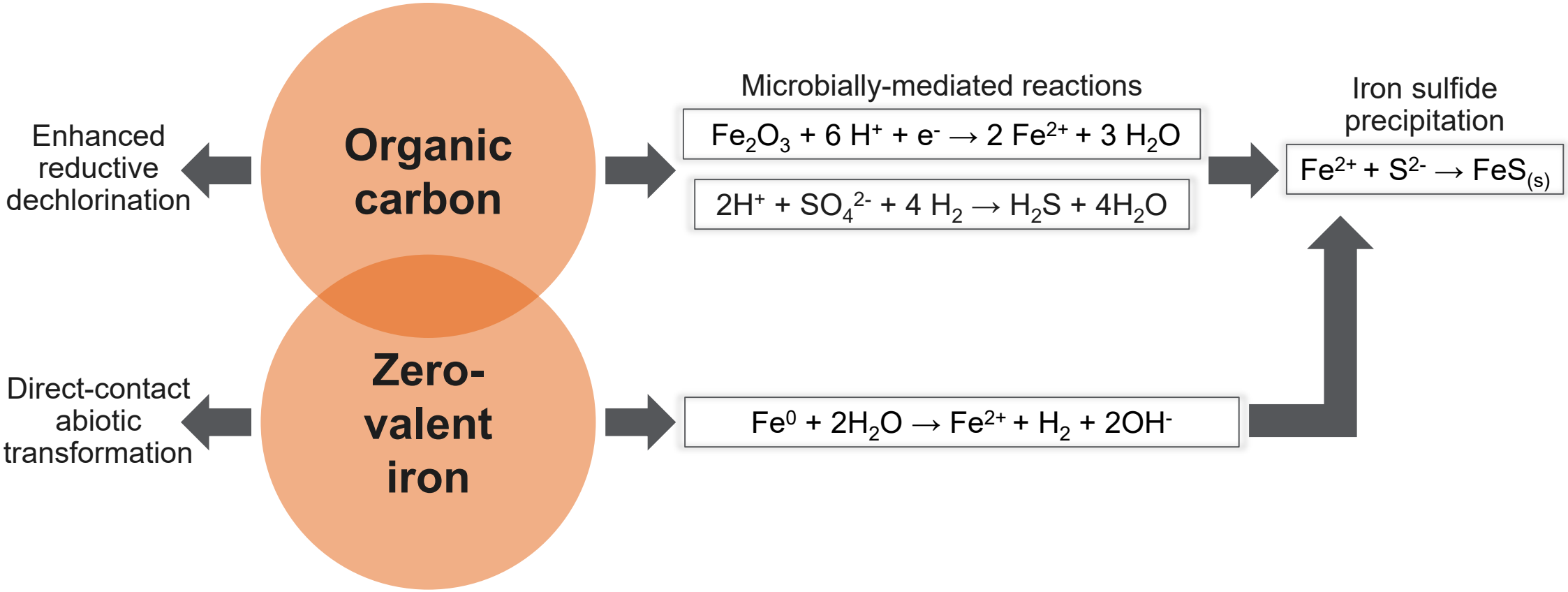
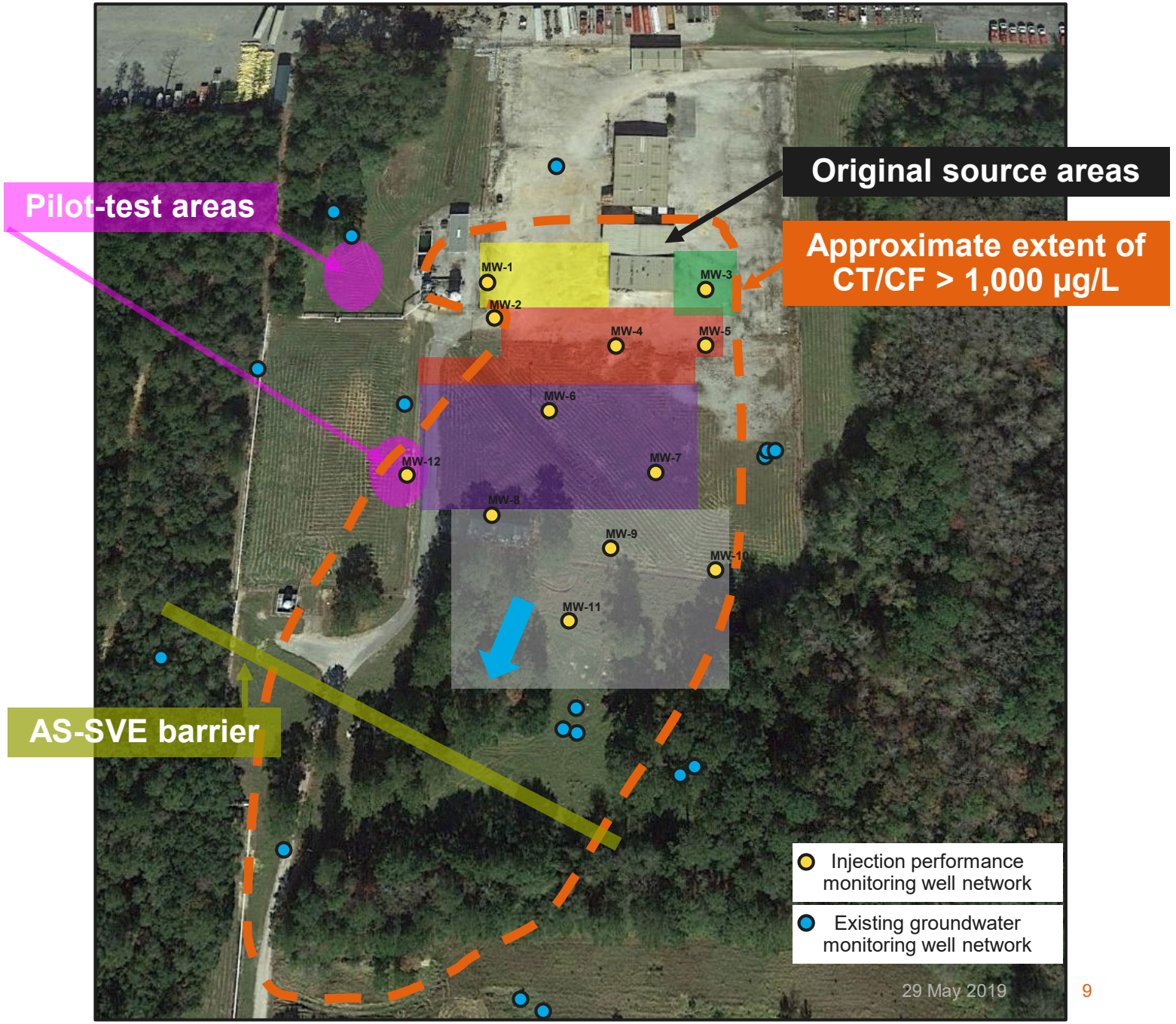


Expanded injection radius of influence & increased degradation capacity beyond direct utilization of EHC™

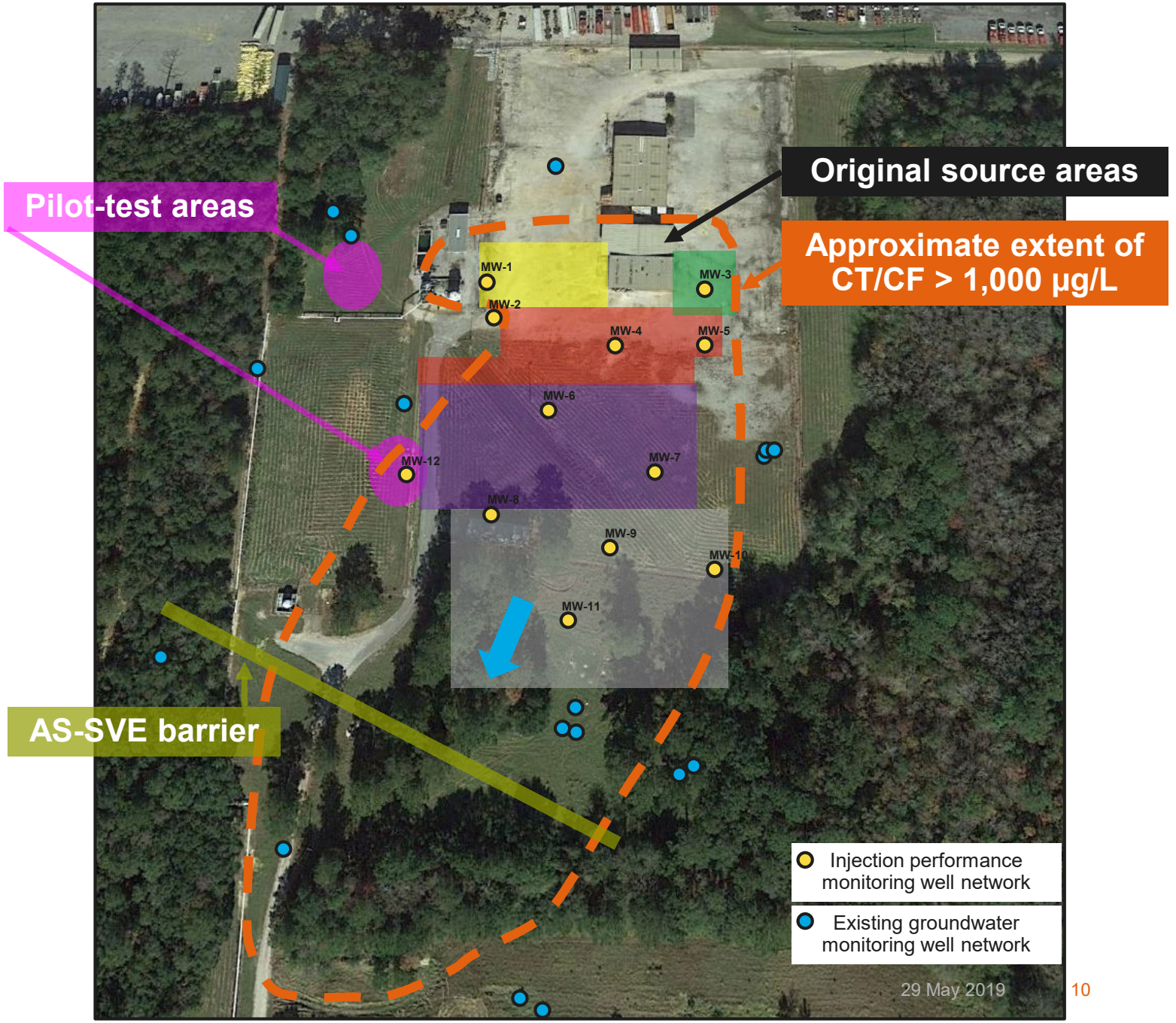
EHC™ Delivery

- Pilot-scale delivery May 2017
- Full-scale delivery June-August 2018
- Direct-push injection of ~ 274,000 lbs EHC™
- ~ 300 injection points
- Performance monitoring August-December 2018



Performance Monitoring

- Assessment of geochemical parameters
- Characterization of iron sulfide minerals
- Characterization of microbial community
- Evaluation of concentration trends for CT, CF and degradation products



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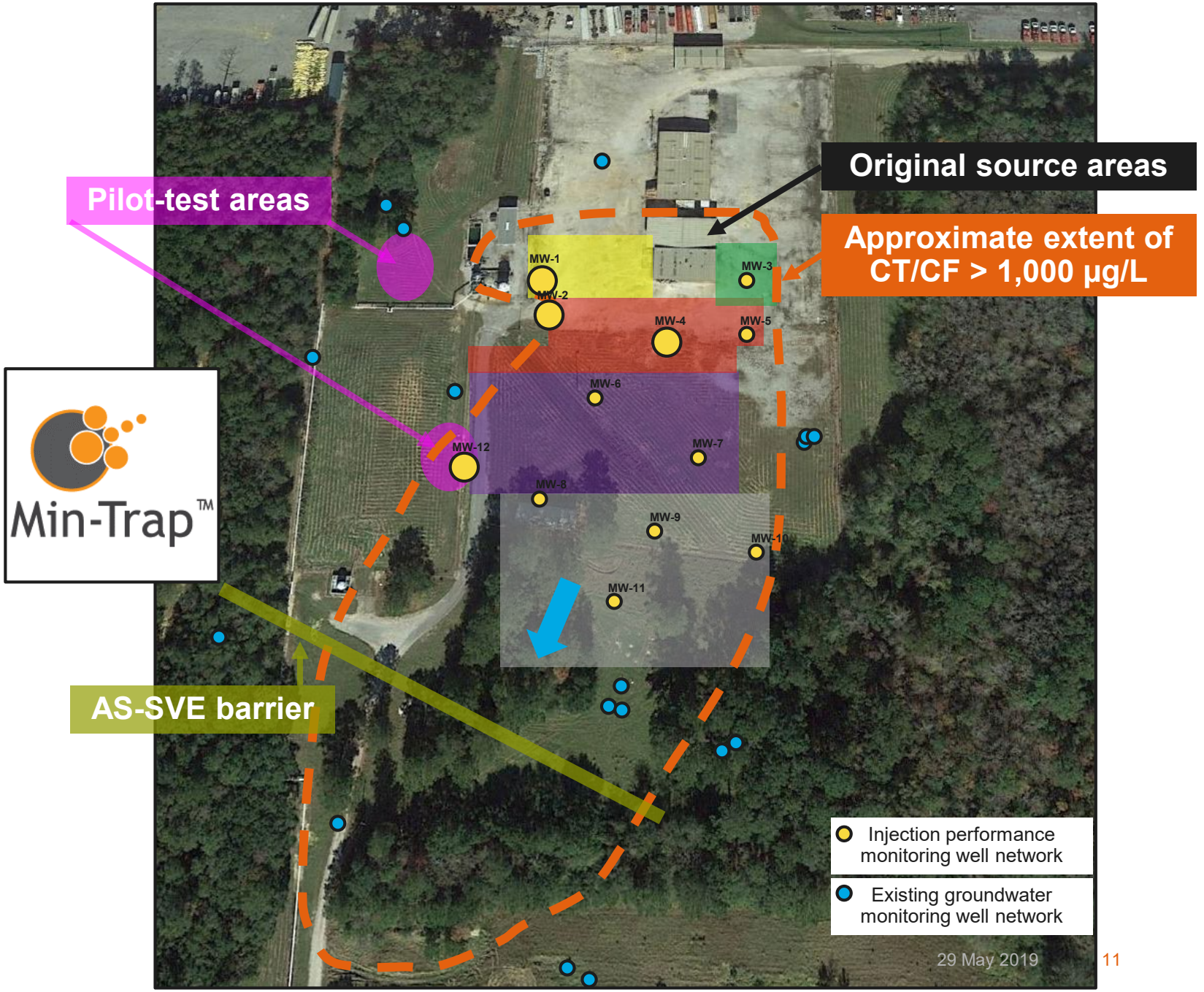
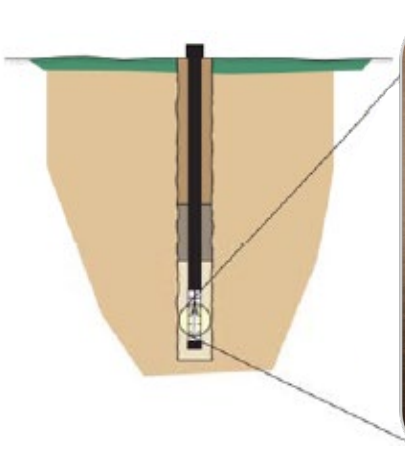


New Monitoring Tool: Min-Traps™

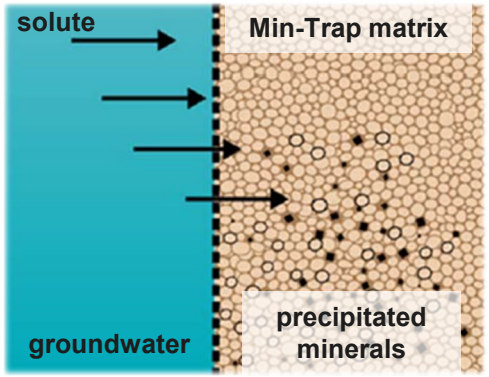
- Collect minerals forming *in situ* using existing monitoring well network
  - ✓ Representative of conditions in higher-flux zones
- Porous medium inside mesh acts as a carrier for target minerals
  - ✓ Medium is customizable
- Inexpensive, easily repeated

Min-Traps can conclusively document in situ formation of specific minerals



Deployed in standard 2”+ monitoring well

Slotted PVC casing & porous medium in permeable mesh



New Monitoring Tool: Min-Traps™

More on Min-Traps!

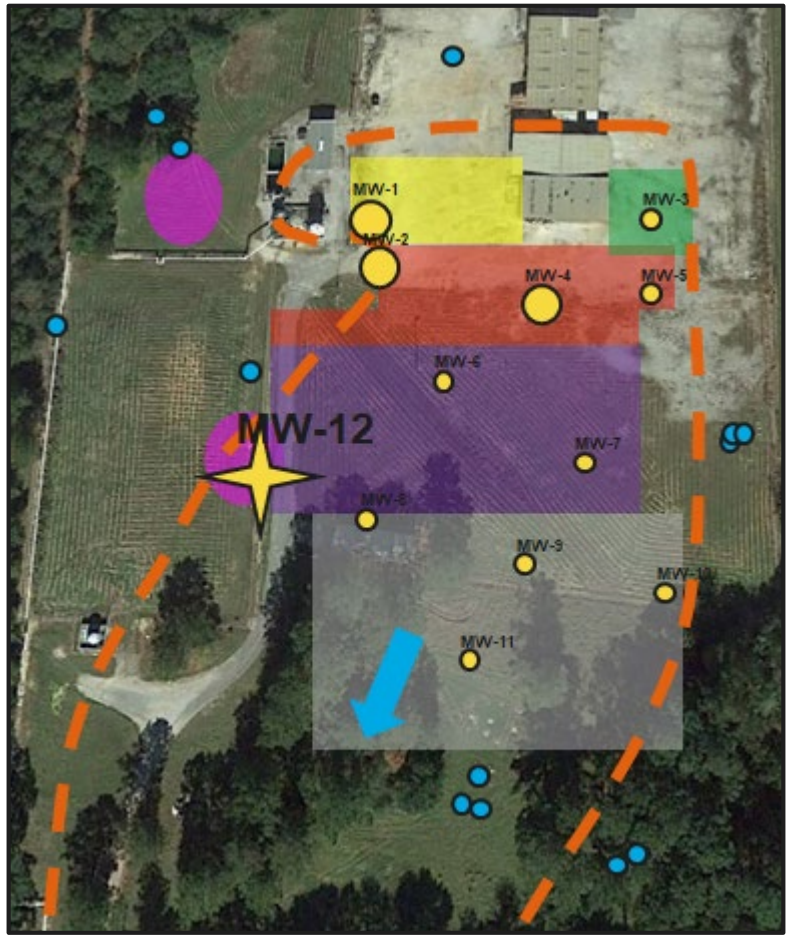
Wednesday, 4:45 pm, D Session (Holiday Ballroom 4)

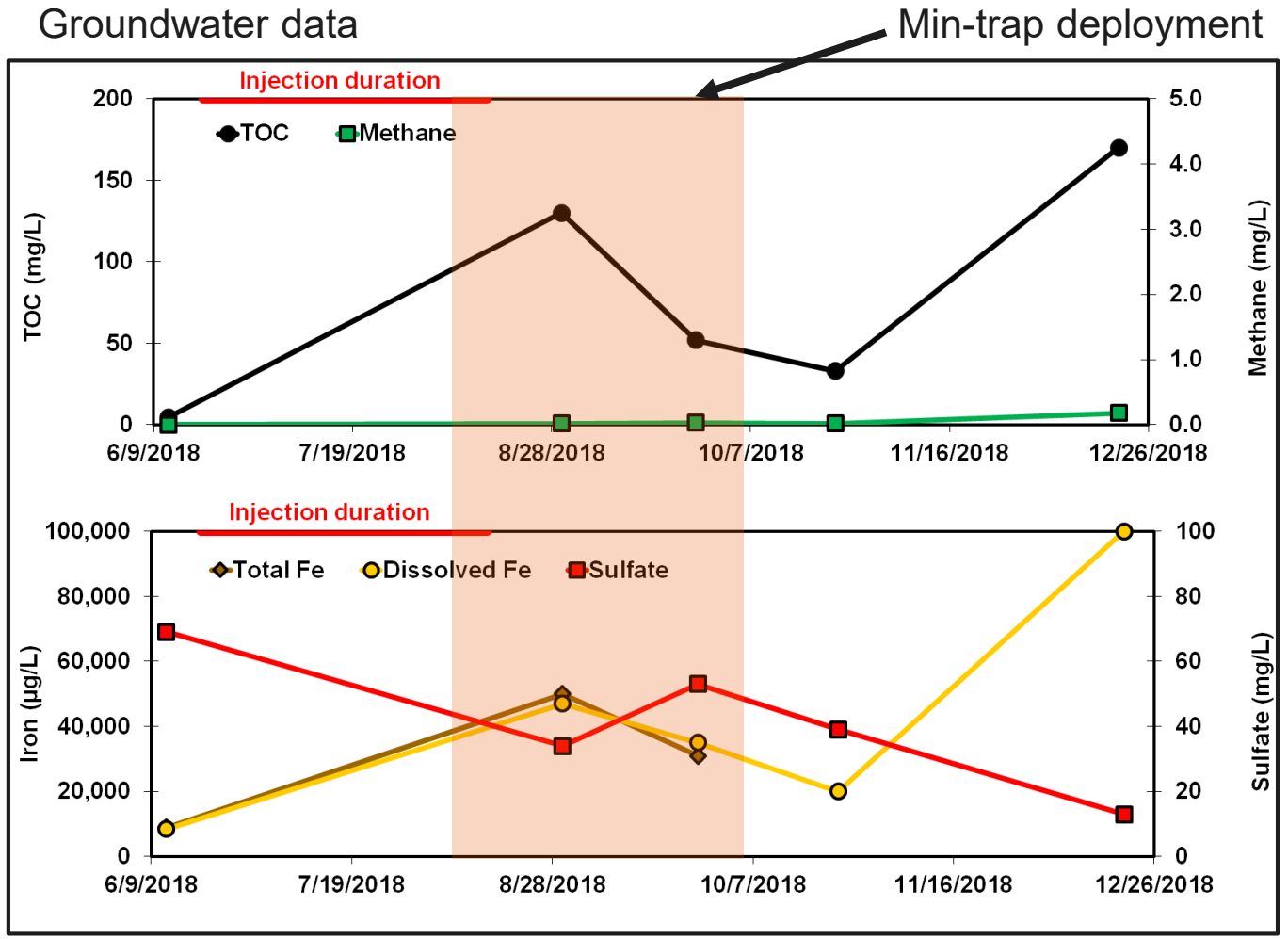
Documenting *In Situ* Reactive Iron Mineral Formation without Drilling: A New Monitoring Well-Based Sampling Approach

Jennifer Martin Tilton (Arcadis)

Results: Post-Injection Performance

Post-Injection Performance





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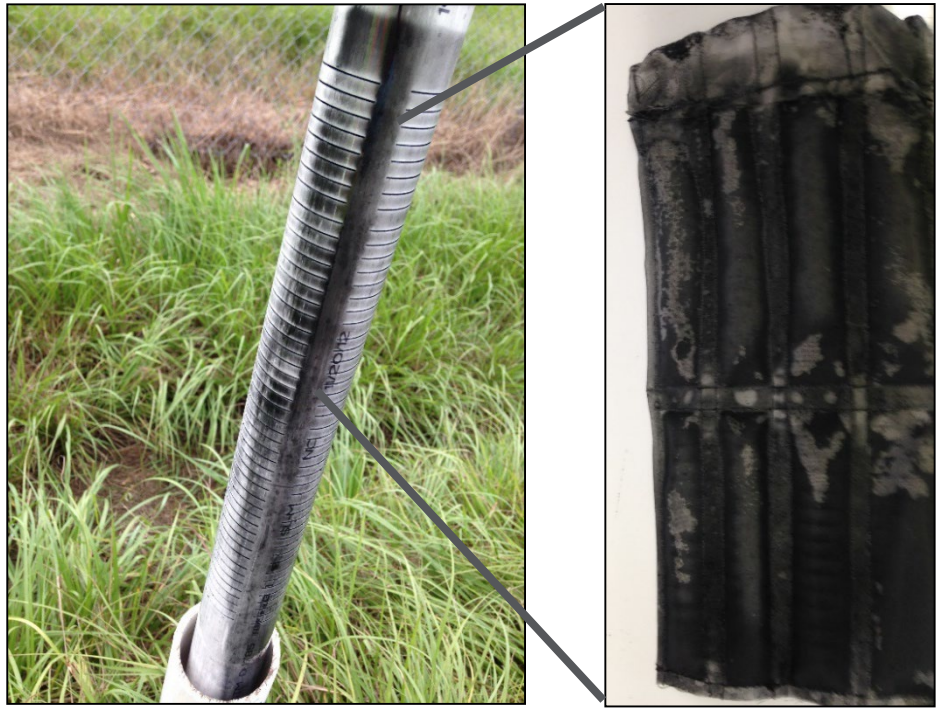
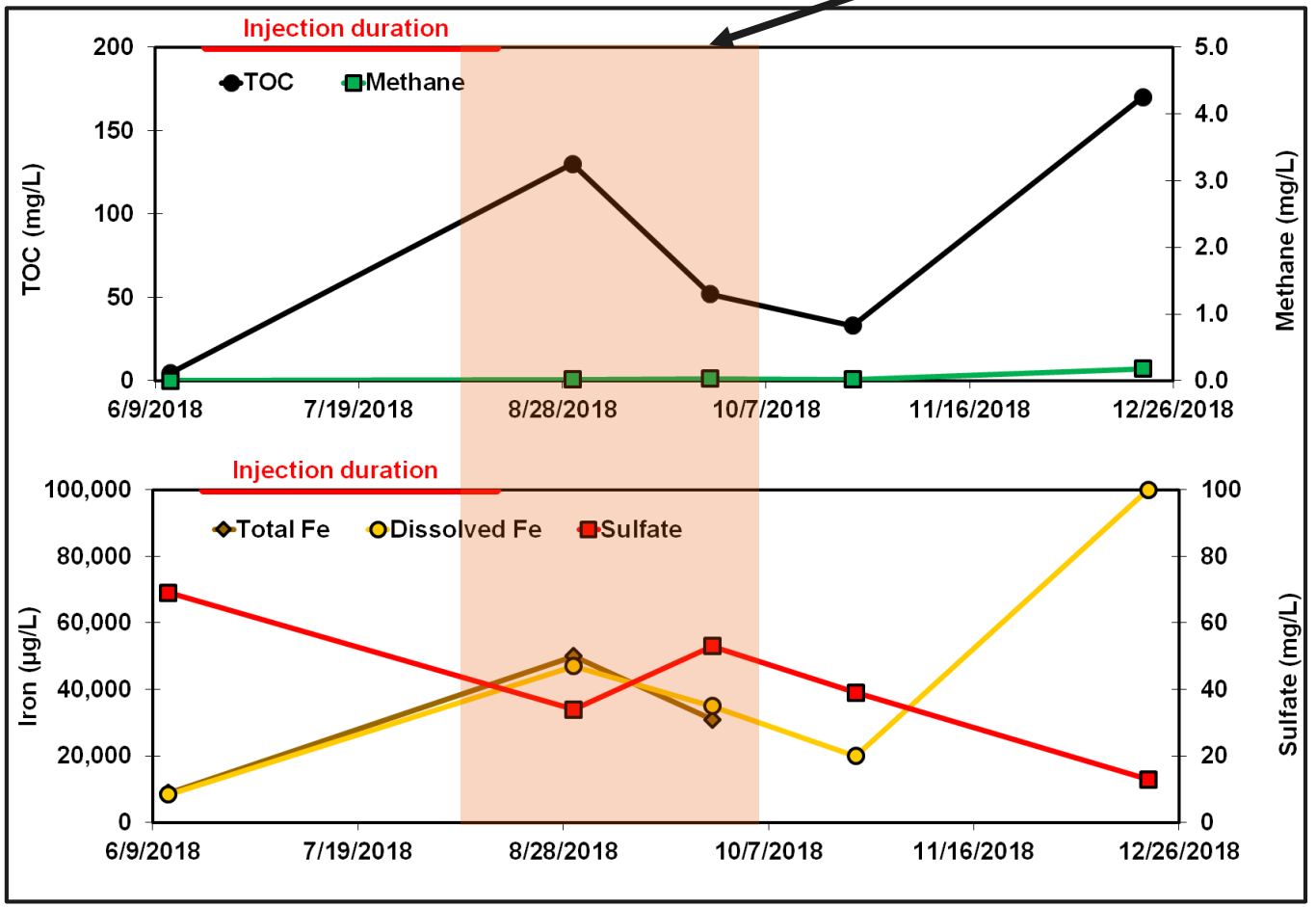


Groundwater data

Min-trap deployment



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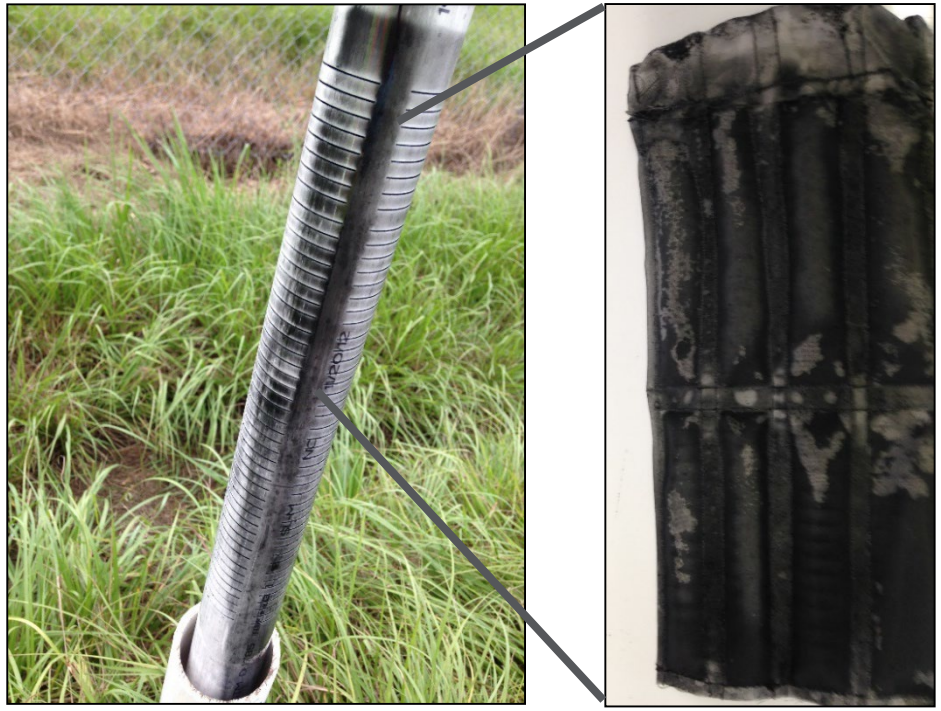

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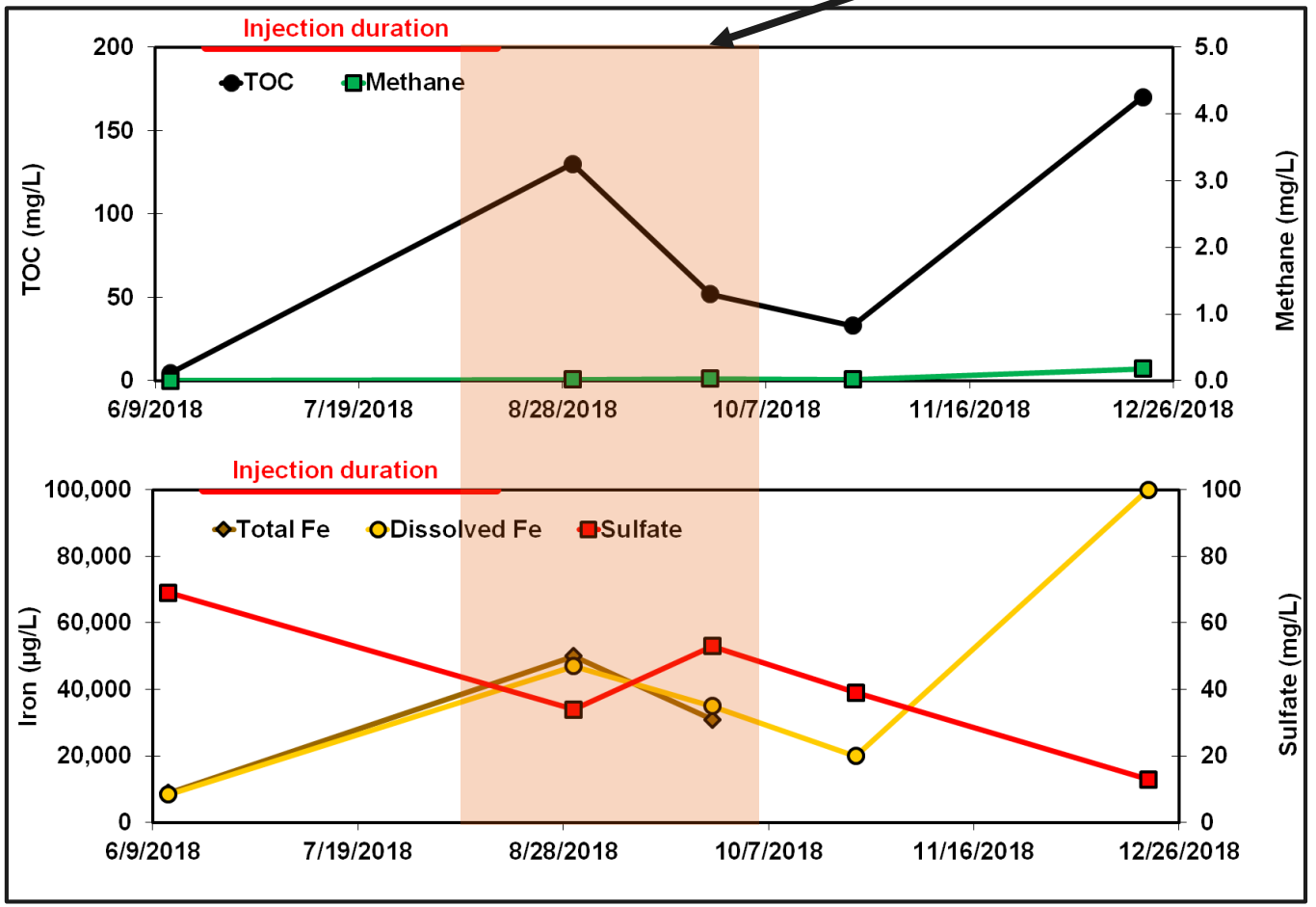


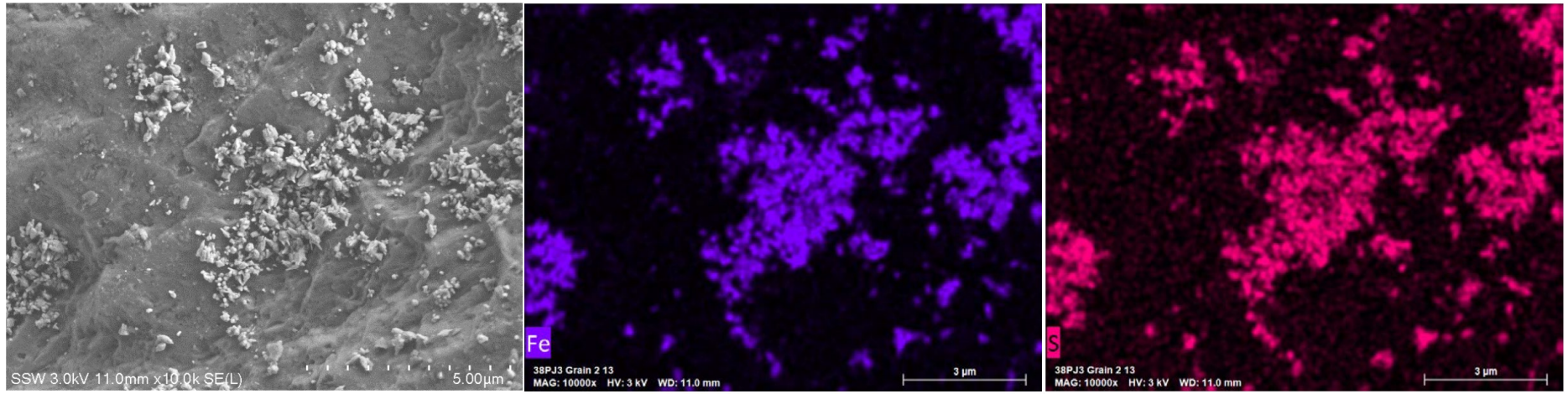
Iron: Solid iron is reduced

Sulfur: Mostly FeS, some FeS_2

WAS Iron (mg/kg)	SAS Iron (mg/kg)	AV Sulfide (mg/kg)	CrE Sulfide (mg/kg)
Fe2+ = 330 Fe3+ = 0	Fe2+ = 300 Fe3+ = 30	240	120

Post-Injection Performance: SEM with Energy Dispersive X-Ray Spectroscopy (EDS)

Backscatter micrograph | Iron | Sulfur

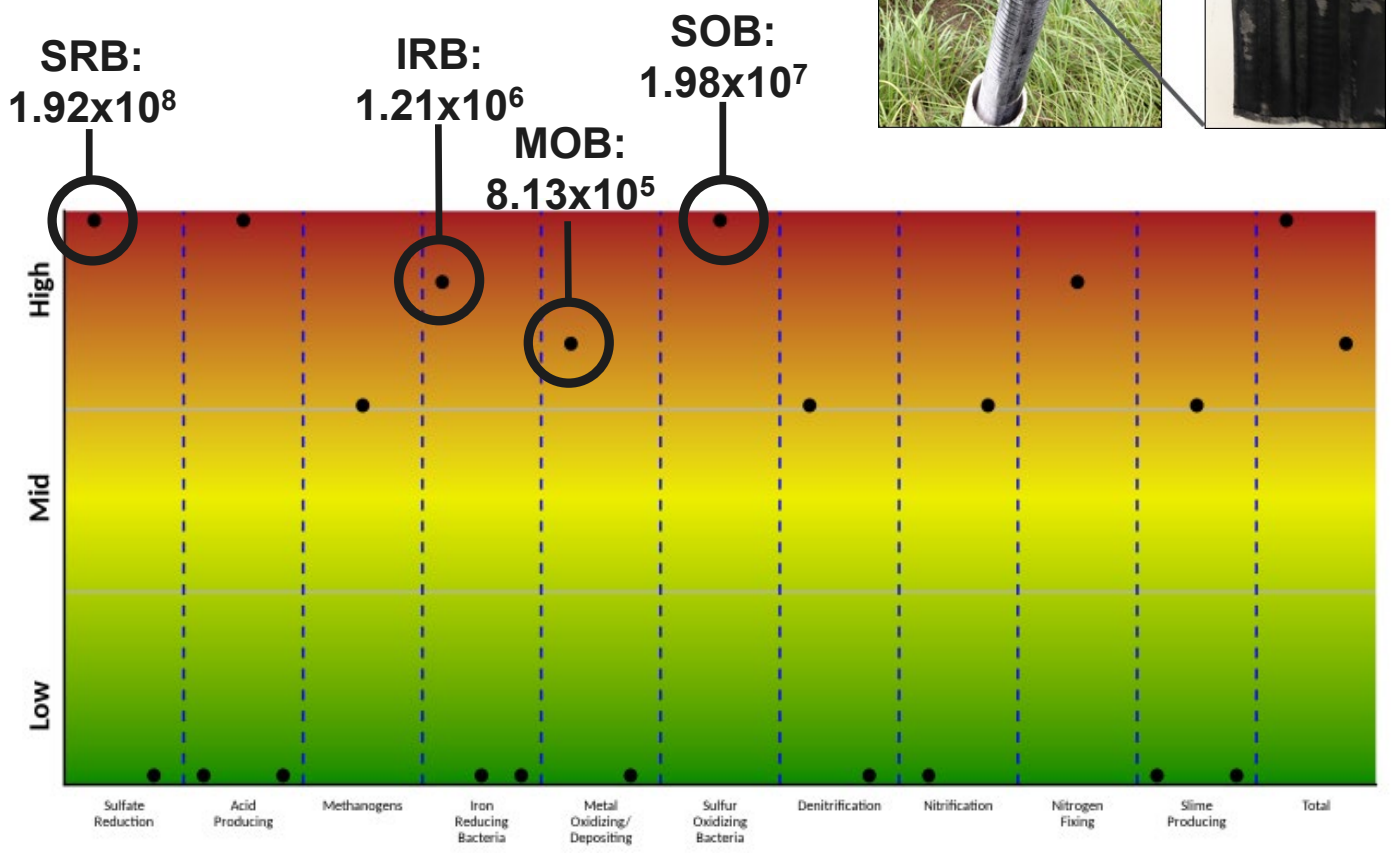


EDS spectra confirmed presence of iron and sulfur particles

Co-located iron and sulfur particles indicate that precipitates are iron-sulfur minerals

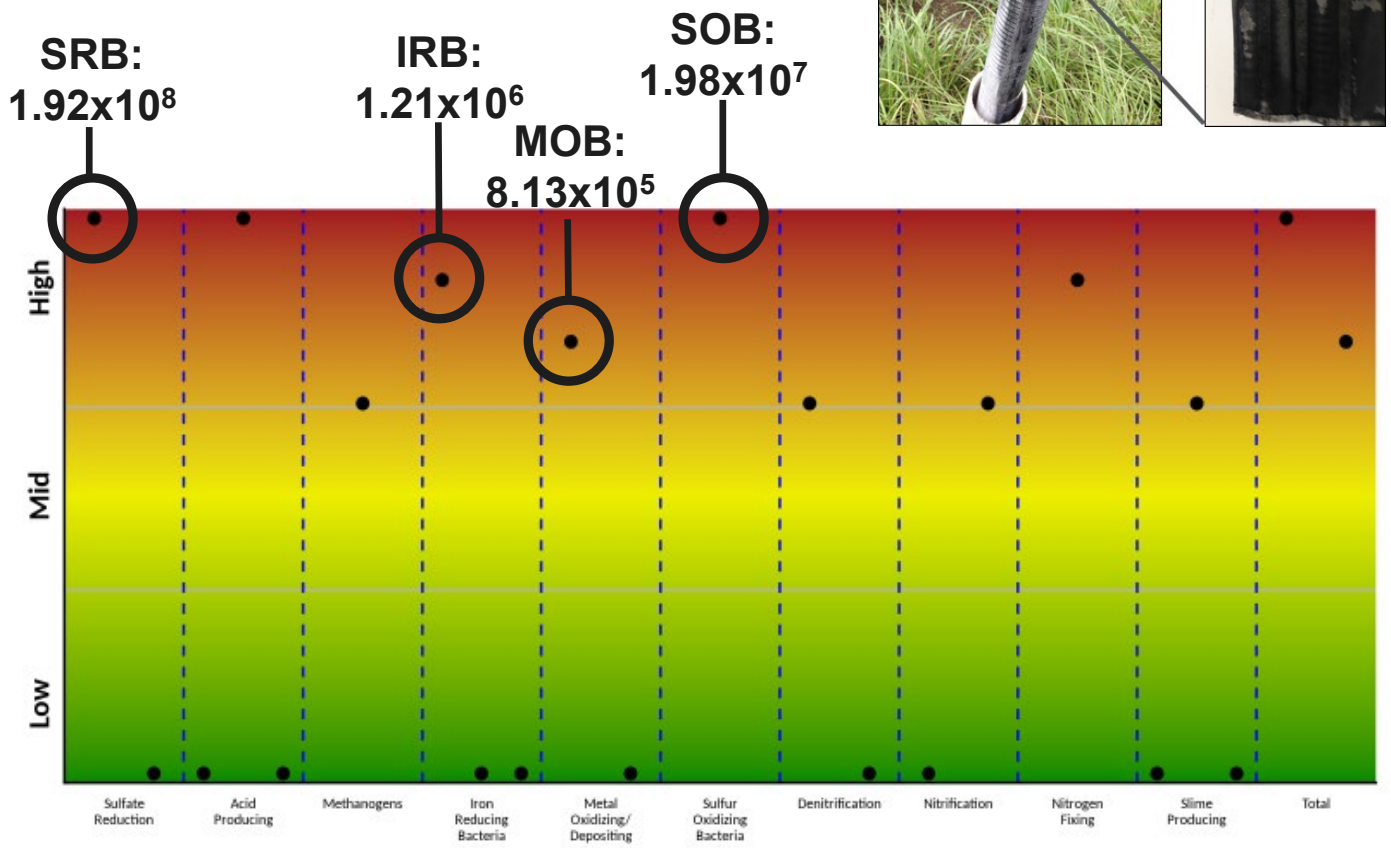
Post-Injection Performance: QuantArray-MIC

Sample Name Sample Date	OBS-5 10/09/2018
Microbial Induced Corrosion	cells/g
Total Bacteria (EBAC)	**7.74E+08**
Total Archaea (ARC)	**3.58E+05**
Sulfate Reducing Bacteria (APS)	**1.92E+08**
Sulfate Reducing Archaea (SRA)	<1.00E+04
Methanogens (MGN)	**1.69E+04**
Acetogens (AGN)	<1.00E+04
Fermenters (FER)	**3.11E+08**
Iron Reducing Bacteria - Other (IRB)	**1.21E+06**
IRB *Geobacter* (IRG)	<1.00E+04
IRB *Shewanella* (IRS)	<1.00E+04
Iron Reducing Archaea (IRA)	<1.00E+04
Iron Oxidizers (FeOB)	**8.13E+05**
Manganese Oxidizing Bacteria (MnOB)	<1.00E+04
Sulfur Oxidizing Bacteria (SOB)	**1.98E+07**
Denitrifying Bacteria (nirK)	**1.02E+04**
Denitrifying Bacteria (nirS)	<1.00E+04
Ammonia Oxidizing Bacteria (AMO)	<1.00E+04
Nitrite Oxidizing Bacteria (NOR)	**8.37E+04**
Nitrogen Fixers (NIF)	**5.57E+06**
Burkholderia cepacian Exopolysaccharide (BCE)	<1.00E+04
Deinococcus spp. (DCS)	**5.35E+04**
Meiothermus spp. (MTS)	<1.00E+04
Cladosporium spp. CLAD	<1.00E+04
CENSUS Targets	
Dehalobacter spp. (DHBt)	**2.42E+07**
Dehalobacter DCM (DCM)	**2.74E+05**
Chloroform Reductase (CFR)	**6.00E+03 (J)**



Post-Injection Performance: QuantArray-MIC

- Data provide insight on:
  - ✓ Geochemical conditions
  - ✓ Abundance of key microbial groups for degradation of CT/CF and formation of reactive minerals species
- Microbial analyses can be performed with Min-Trap samples
  - ✓ Media appropriate for sampling
- Min-Trap data comparable to corresponding groundwater data



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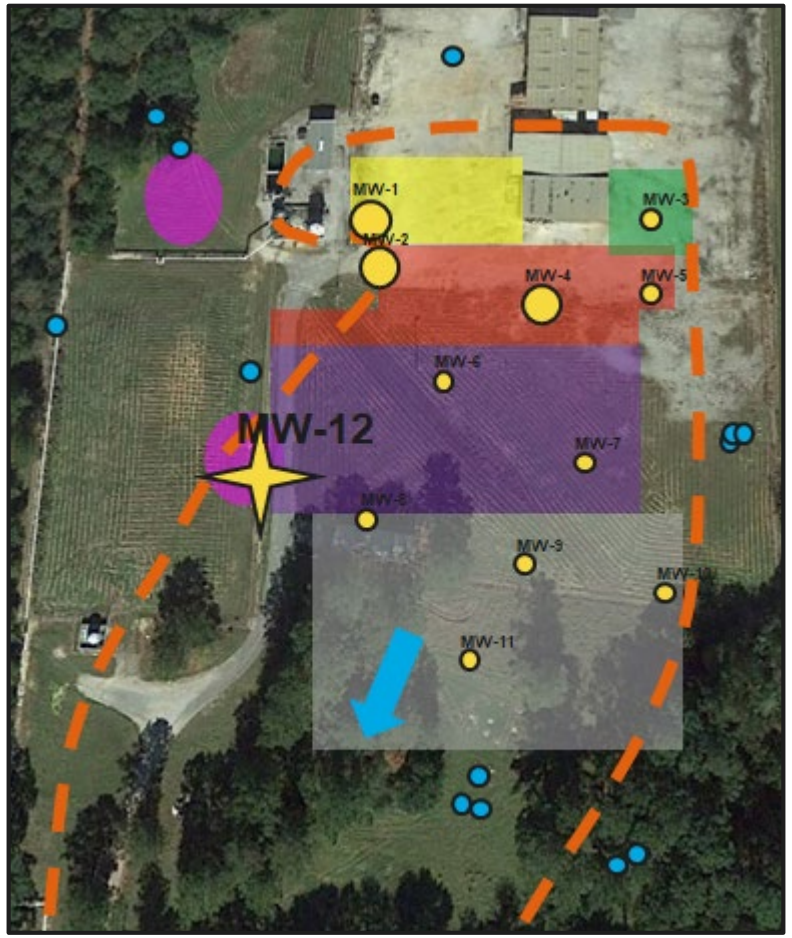

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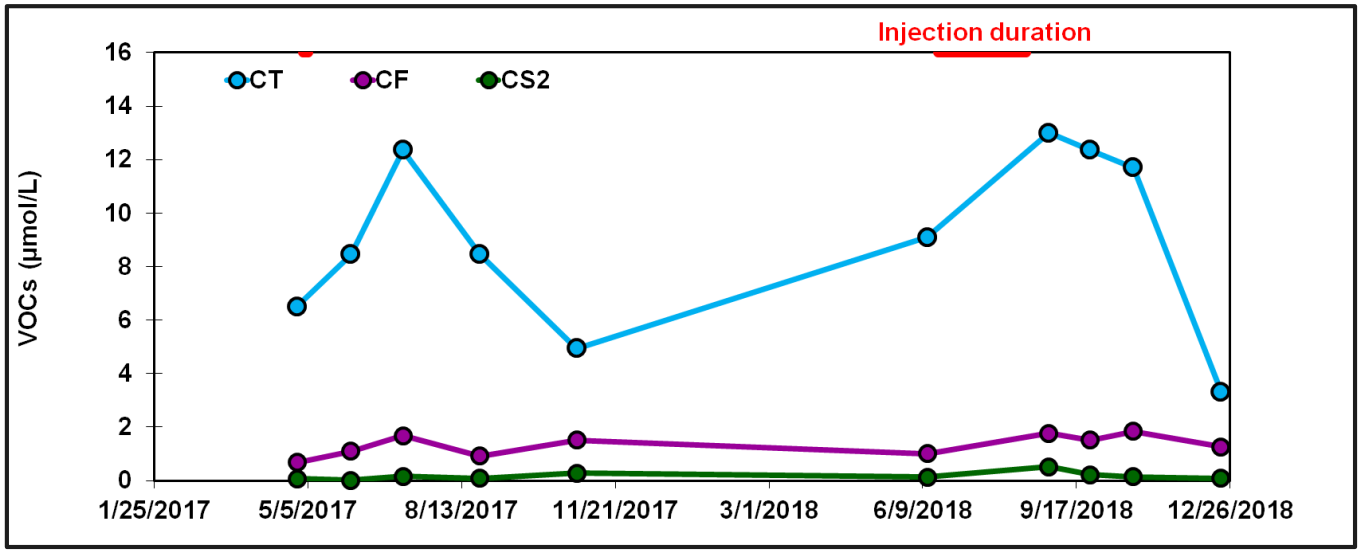
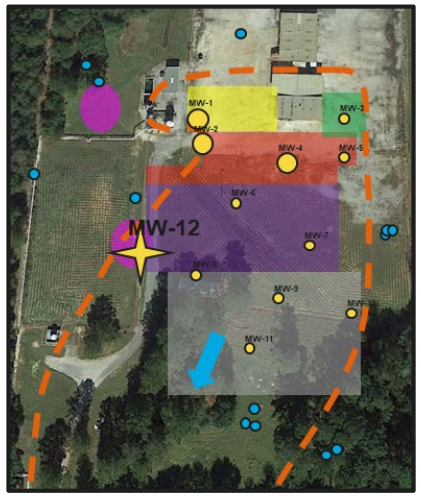
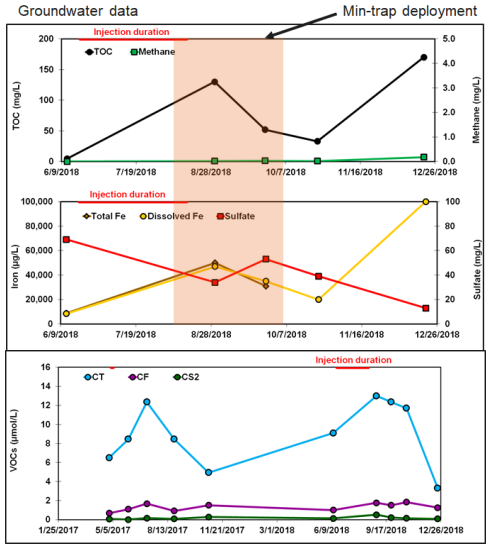
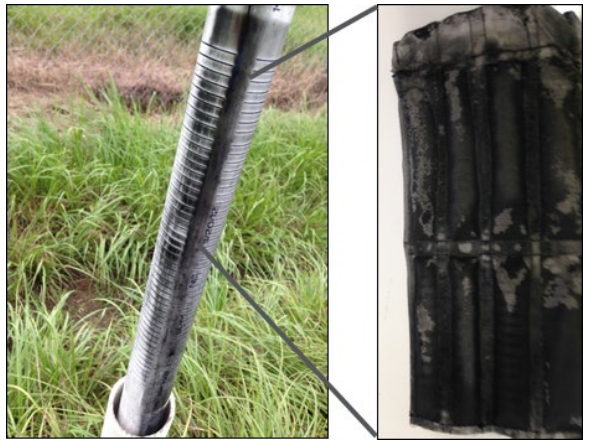


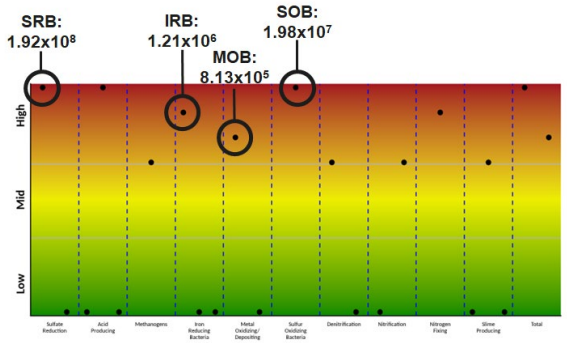
Conclusions

- CT and CF were successfully treated via *in situ* EHC™ injections
- The selected remedial approach enhanced biotransformation, as well as abiotic and coupled microbial-abiotic transformation of CT and CF
- Remedial performance was evidenced through evaluation of geochemical conditions and CT/CF concentration trends, characterization of reactive iron sulfur minerals, and analysis of microbial community









Questions?

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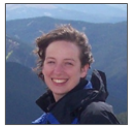


Erika Carter, PhD
Arcadis

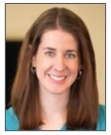
Dave Liles
Arcadis

Shannon Ulrich
Arcadis

Min-Trap™

Jennifer Tilton
Arcadis

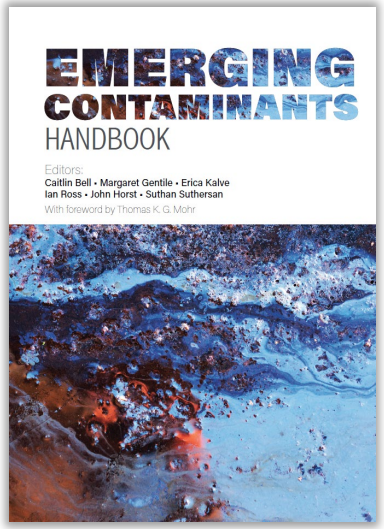
Dora Taggart,
Microbial Insights

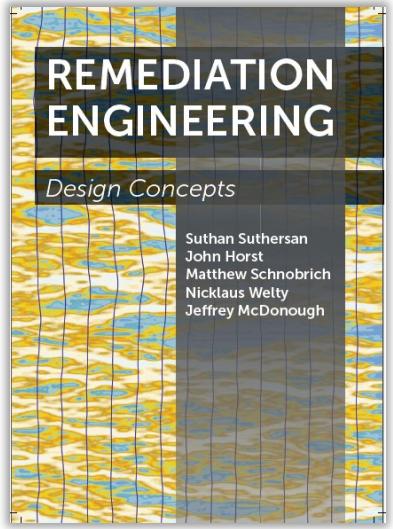


Kate Clark, PhD
Microbial Insights

ARCADIS Design & Consultancy for natural and built assets

Technical Knowledge





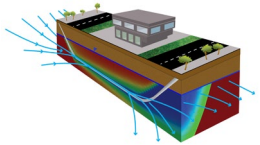
Innovation

Min-Trap™

(Well-Based Mineral Traps)

TISR^{SM}

(Thermal In-Situ Sustainable Remediation)



HRX Well™

(Horizontal Treatment Well)

Oleophilic Bio Barriers (OBBs)

(for Hydrocarbon Sheens)

Zipliner

(Safer DPT Liners)