

THE MIN-TRAP™ SAMPLER

A New Monitoring Well-Based Sampling Tool for
Documenting In Situ Mineral Formation

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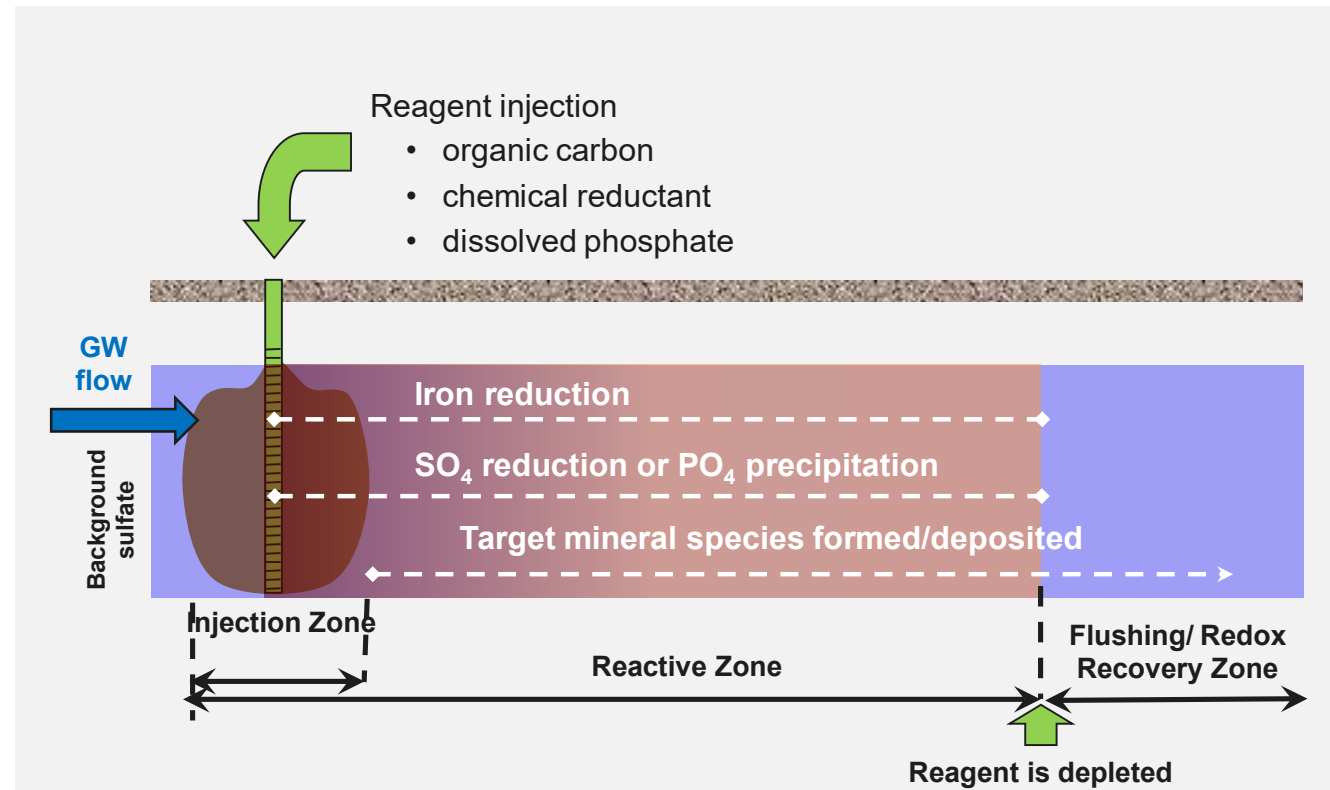
November 13, 2019



In Situ Treatment and Mineral Precipitation

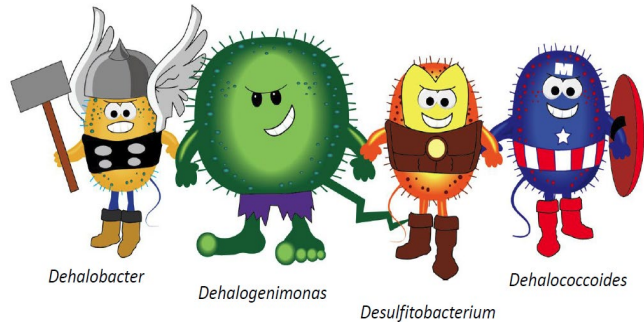
Examples:

- 1 Metal sulfides or phosphates for in situ sequestration (NiS, U-PO₄ compounds, etc.)
- 2 Reactive reduced iron minerals to abiotically degrade chlorinated solvents



Anaerobic Biodegradation

Fermentable organic carbon provides electrons that drive the sequential reduction process

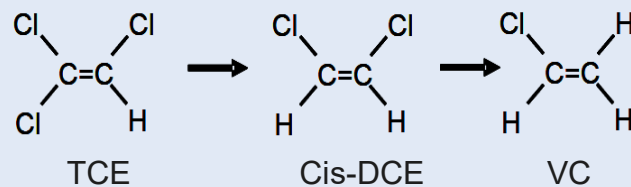


Graphic from Microbial Insights

Biological Reductive Dechlorination

Sequential Reductive Dechlorination

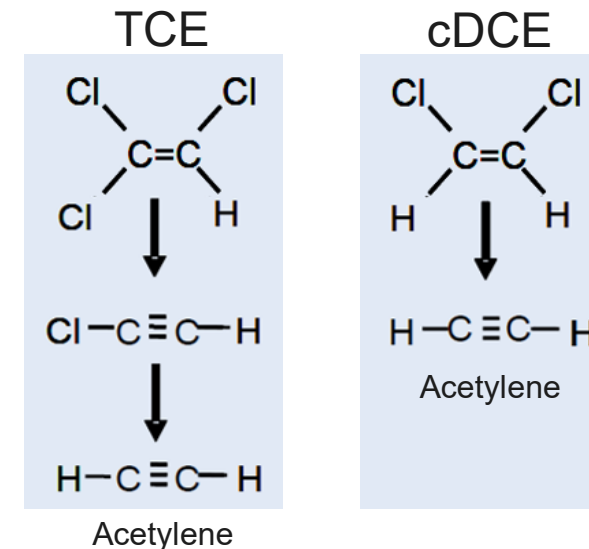
also called Hydrogenolysis



Adapted from Wilson 2014

Abiotic Degradation

- Fermentable organic carbon provides electrons which drive microbial reduction of Fe and SO_4^{2-}
- Fe^{2+} and HS^- are generated and FeS (mackinawite) and FeS_2 (pyrite) can then form
- Reductive elimination results in degradation products not easily measured



How do we know what's really happening under the surface?



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Groundwater samples

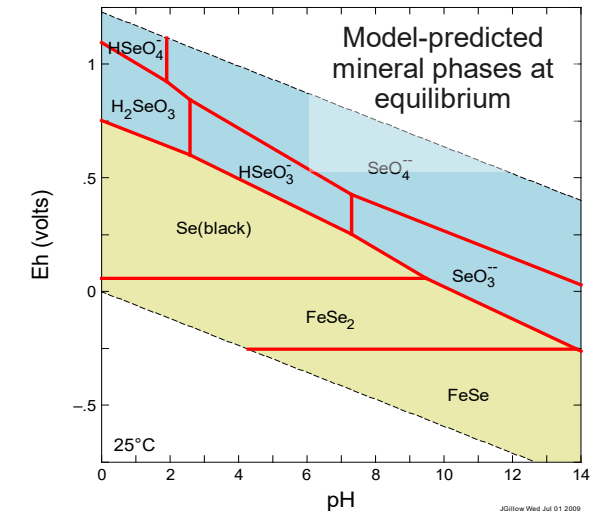
- Must extrapolate data to solid-phase processes
- Loss of reactive species such as HS^- or Fe^{2+}
- Snapshots in time

Geochemical modeling

- All models have simplifying assumptions
- Predicts equilibrium conditions (kinetics not considered)

Soil samples from drill cores

- Costly, often a one-shot opportunity
- Obtaining representative samples can be difficult
- Samples may have significant background “noise”



Soil sample with heterogeneous mineral distribution

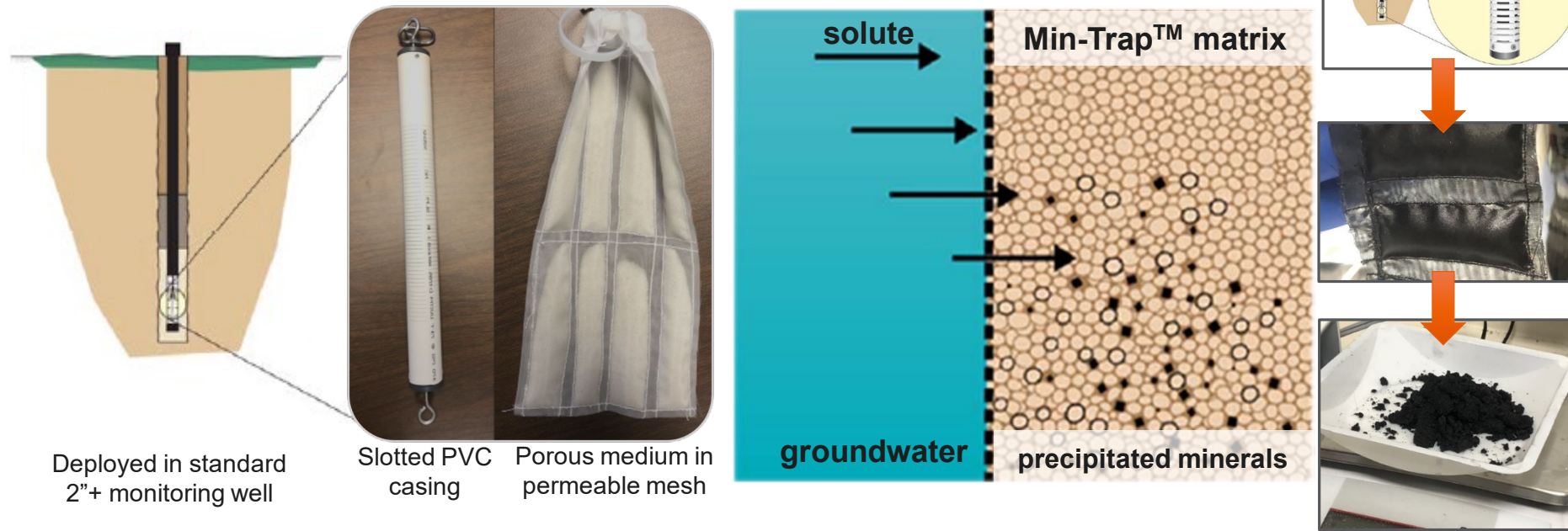
Soil core with heterogeneous mineral distribution



There is a clear need to improve our ability to assess mineralogical changes at remediation sites






Something New: The Min-Trap

- A 15-inch long PVC slot-screen housing containing multiple porous media pillows that collect minerals forming at site using existing monitoring well network
- Customizable porous medium inside mesh pillows acts as a matrix for precipitating minerals
- Analytical packages are tailored based on technical objectives
- Representative of conditions in higher-flux zones
- Inexpensive, easily repeated
- No significant background “noise” in samples
- Patent pending, manufactured and sold by Microbial Insights



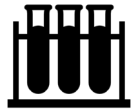
Min-Traps can conclusively document the formation of specific minerals; therefore, they can be used to verify important geochemical and remedial processes that usually are only inferred

Potentially Applicable Analyses

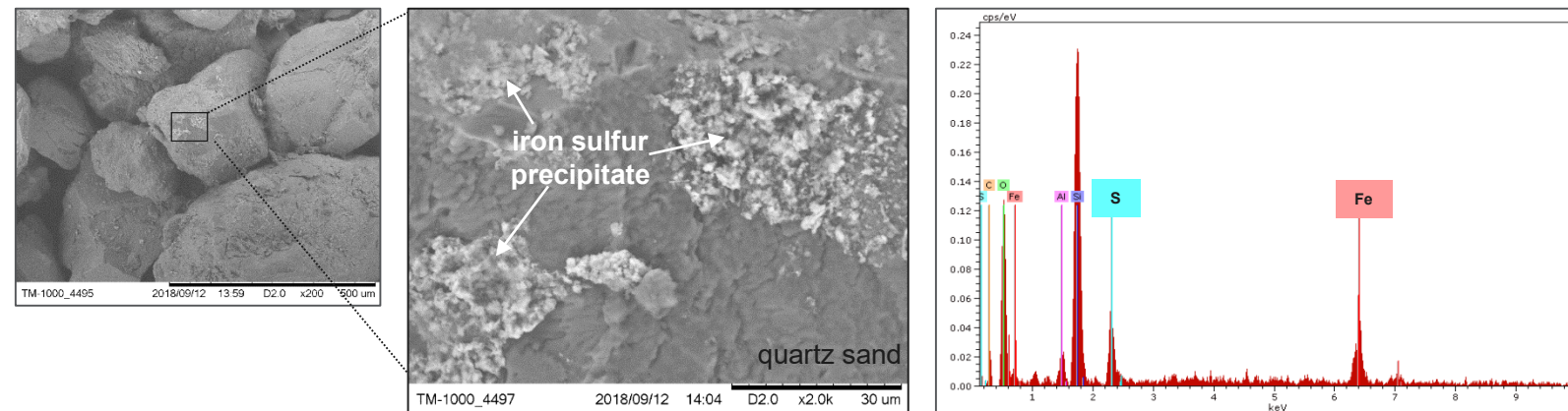
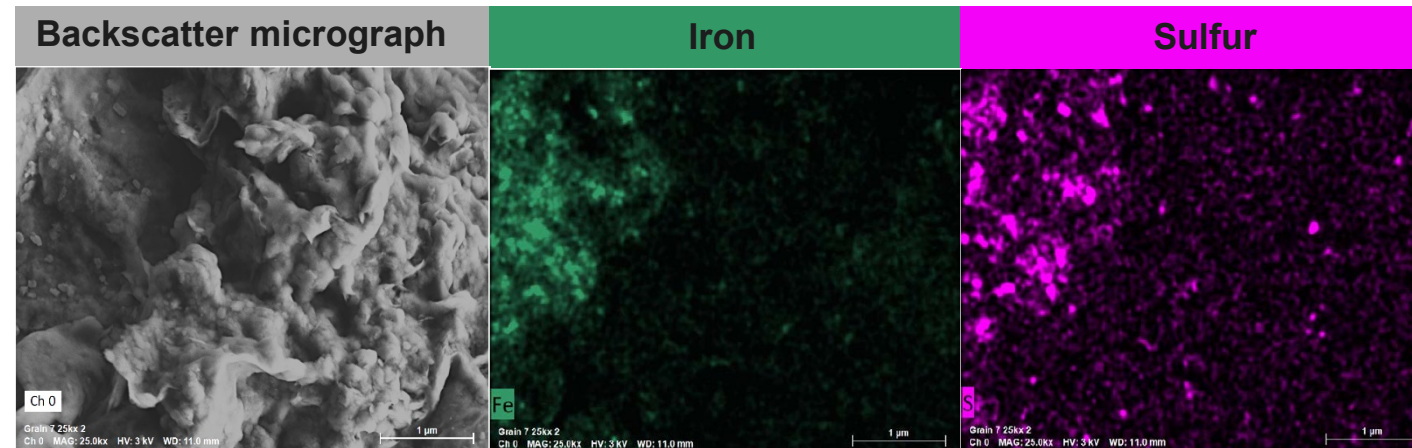
 <p>Chemical</p>	<ul style="list-style-type: none"> • Metals and inorganics • Weak and strong acid soluble iron (WAS, SAS) • Acid-volatile sulfide (AVS), Chromium-extractable sulfide (CrES) 	<ul style="list-style-type: none"> • Precipitated metals & element ratios • Biogenic (pseudocrystalline) vs. crystalline minerals • Sulfur forms: FeS vs. FeS₂ and S⁰
 <p>Microscopy</p>	<ul style="list-style-type: none"> • Light/petrographic • Scanning Electron Microscopy (SEM) • Transmission Electron Microscopy (TEM) 	<ul style="list-style-type: none"> • Mineral grain size, shape, distribution
 <p>Spectroscopy</p>	<ul style="list-style-type: none"> • Energy Dispersive X-ray Spectroscopy (EDS) • X-ray Absorption Spectroscopy (XAS) 	<ul style="list-style-type: none"> • Elemental composition • Elemental coordination
 <p>General</p>	<ul style="list-style-type: none"> • Magnetic susceptibility (magnetite) 	<ul style="list-style-type: none"> • Mineralogy • Magnetic mineral content
 <p>Molecular biology</p>	<ul style="list-style-type: none"> • QuantArray 	<ul style="list-style-type: none"> • Microbial community

Bench Testing





WAS/SAS iron: >95% ferrous iron
AVS/CrES: 80% FeS , CrES ~20% FeS₂ or S⁰



Field Testing



Chloromethanes up to ~20 mg/L

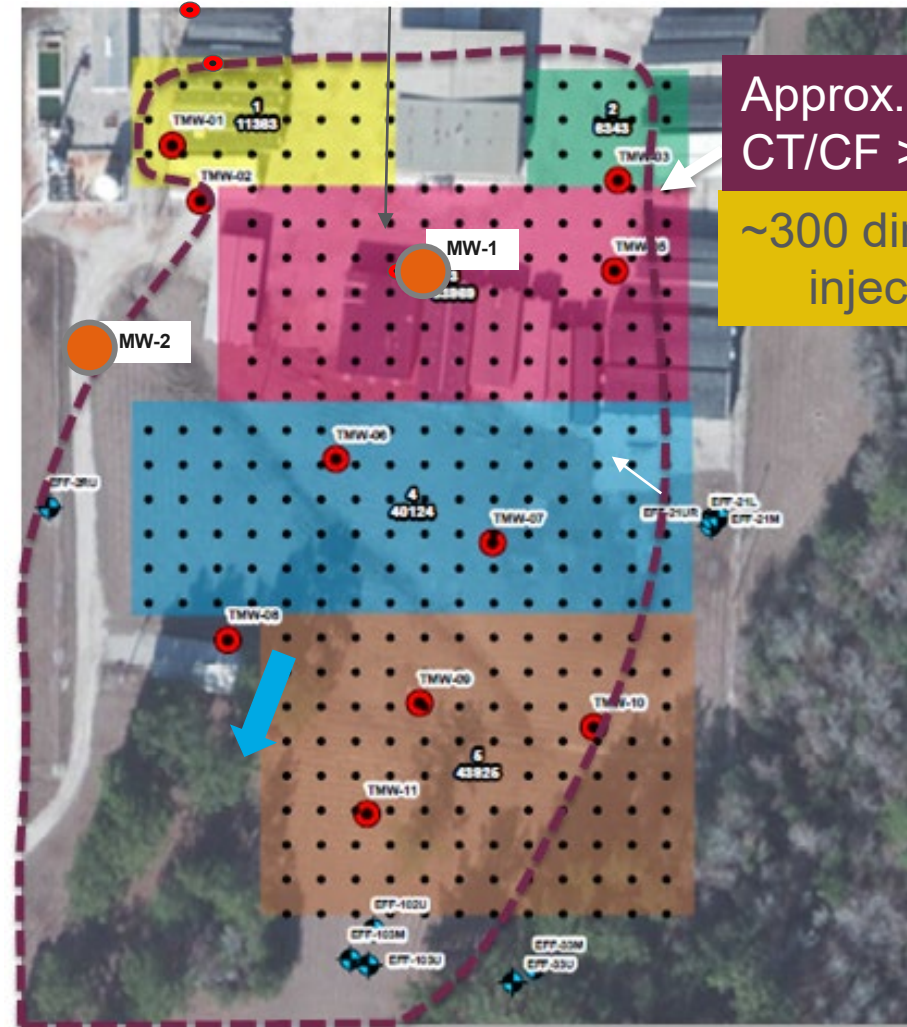
Co-disposed S-containing compounds

Naturally high iron

EHC™ treatment June-August 2018

Min-Traps deployed Aug 2018

Retrieval and analysis October 2018 April 2019, respectively



Approx. extent of
CT/CF > 1,000 ug/L

~300 direct push EHC™
injection locations

Field Testing

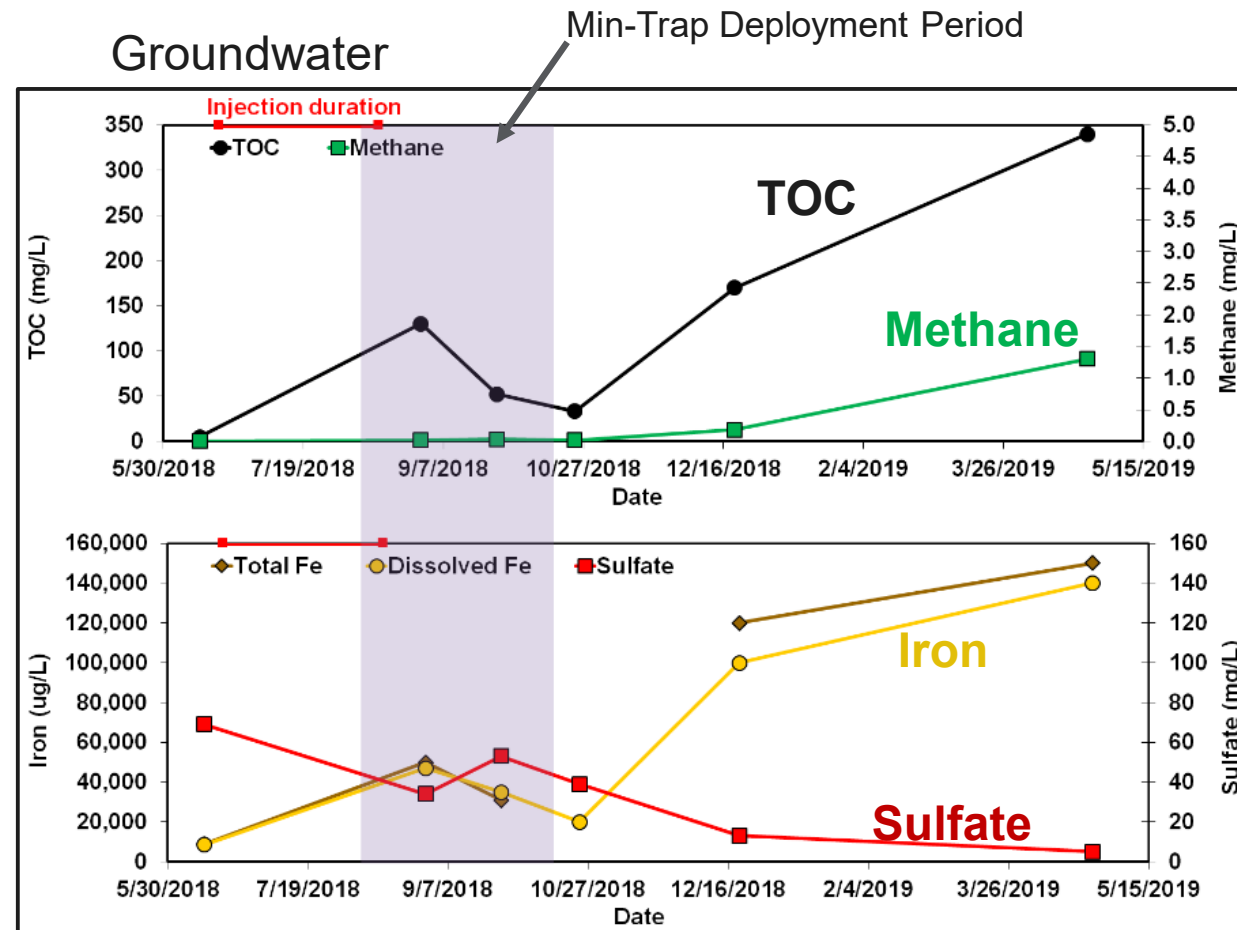
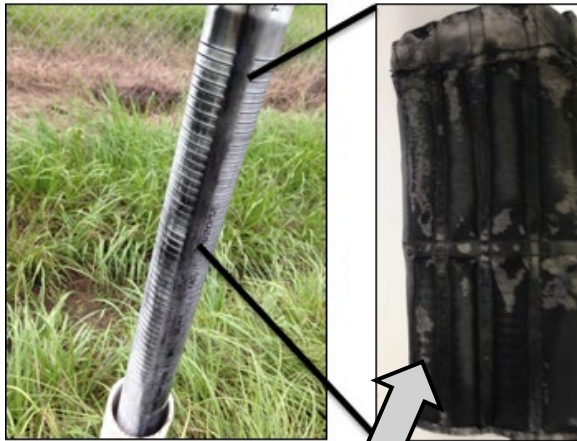
Documentation of FeS, FeS₂ in Min-Traps would confirm:

- ✓ Formation of reactive minerals in the aquifer
- ✓ Presence of multiple CVOC degradation pathways
- ✓ Migration and re-precipitation of dissolved constituents (Fe²⁺) from EHC™ injection site (***increased ROI***)
- ✓ Expanded treatment capacity beyond EHC™'s direct reduction by ZVI/biological ERD by increasing the treatment zone size and longevity

Min-Trap data can help optimize remedial strategies to maximize formation of reactive mineral species.

Field Testing

MW-2: located at downgradient edge of EHC™ injection area



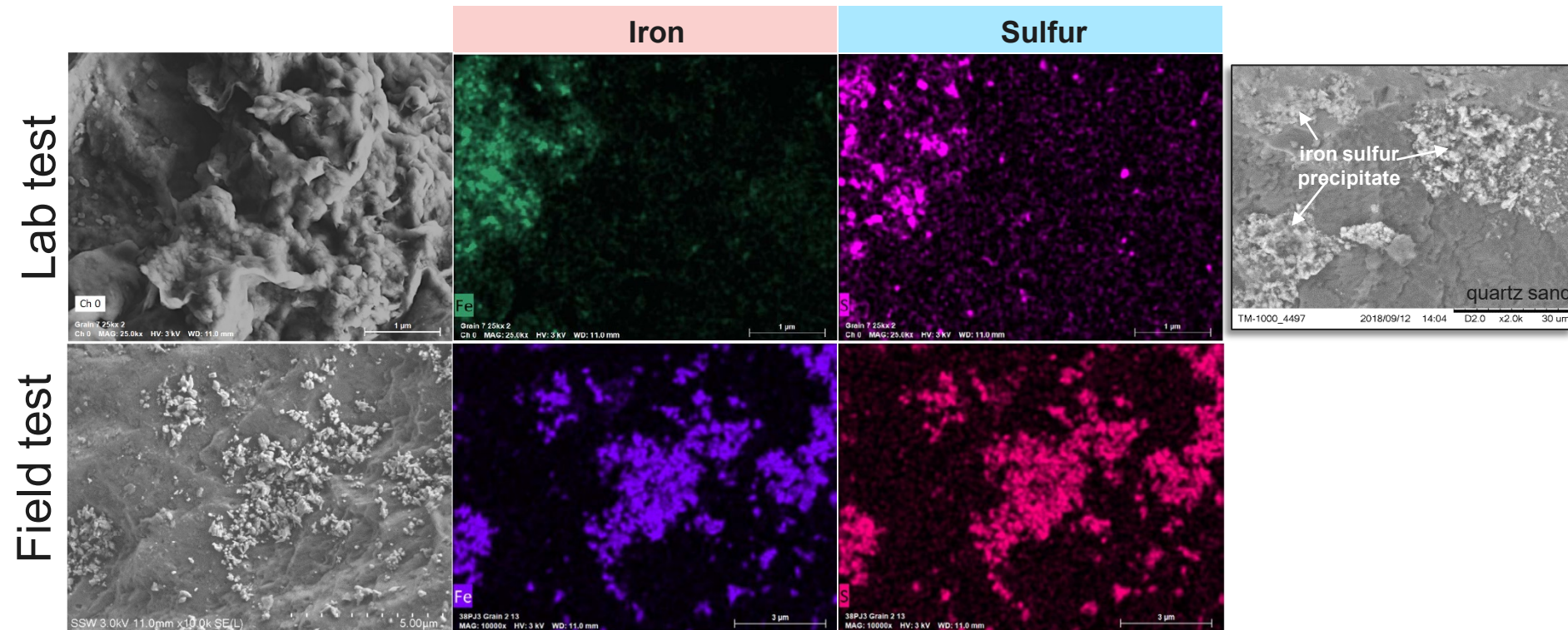
WAS Iron (mg/kg)	SAS Iron (mg/kg)	AVSulfide (mg/kg)	CrESulfide (mg/kg)
Fe2+ = 330	Fe2+ = 300	240	120
Fe3+ = 0	Fe3+ = 30		



WAS/SAS iron: 90% ferrous iron, biogenic
AVS/CrES: Mostly FeS, some FeS₂ and/or co-disposed S

Min-Trap Analysis

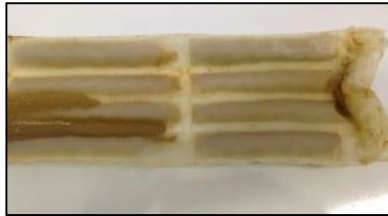
MW-2 Results – SEM with Energy Dispersive X-Ray Spectroscopy (EDS)



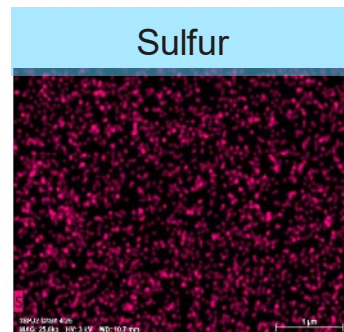
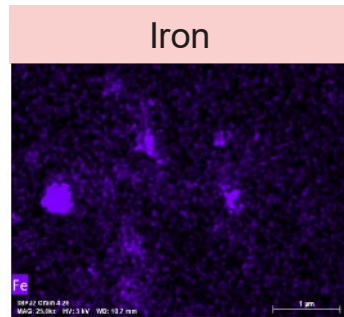
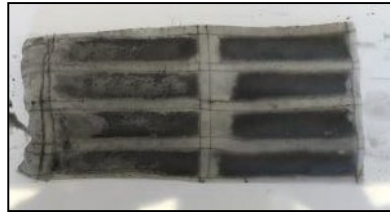
Field Testing

MW-1: Original source area, within injection area

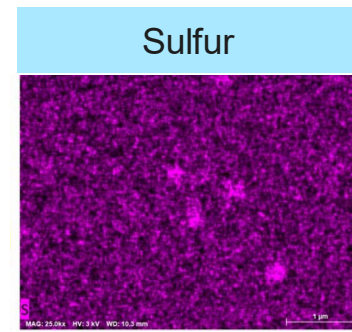
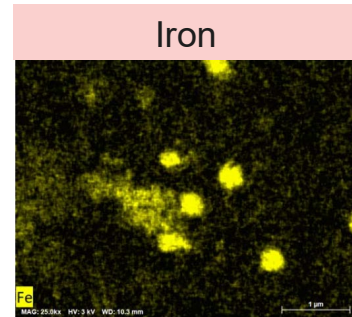
Collected on 10/9/18 (~2 months after deployment)



Collected 4/26/19 (~6 months after deployment)

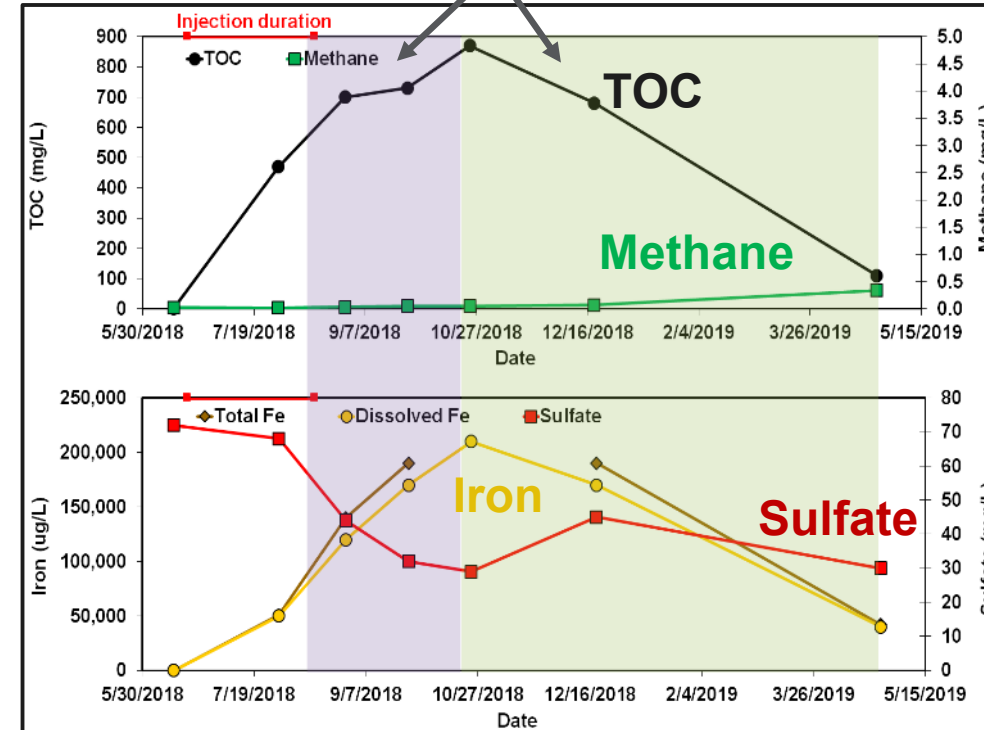


No apparent co-location of Fe and S



Some apparent co-location of Fe and S

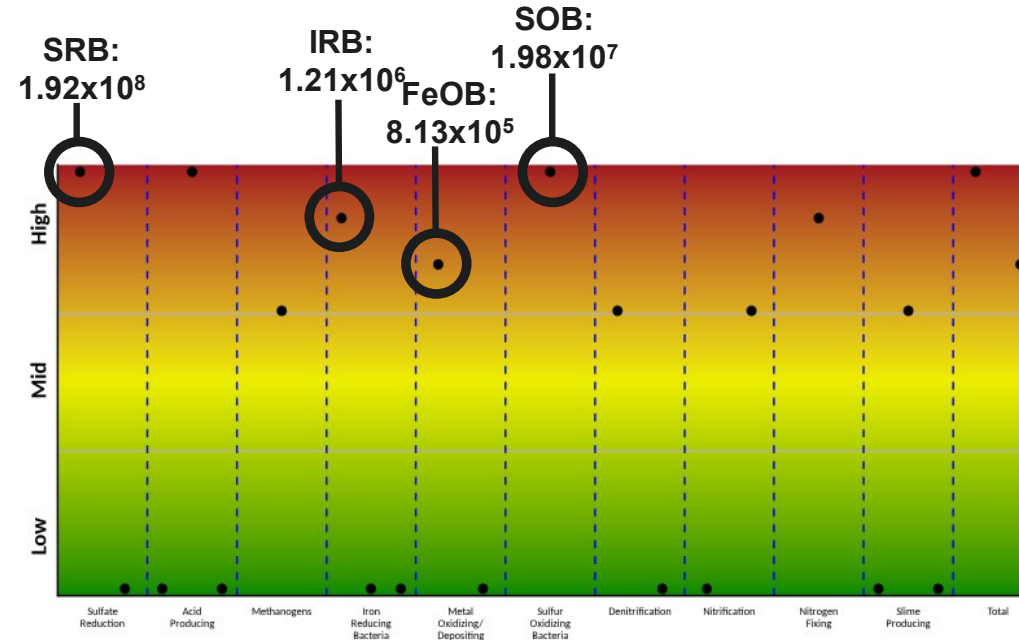
Groundwater Min-Trap Deployment Periods



WAS/SAS iron: Low iron, both Fe^{2+} and Fe^{3+} present, biogenic
AVS/CrES: Some FeS forming in later sample; likely co-disposed S

Min-Trap Analysis: Microbial

Sample Name	MW-2
Sample Date	10/05/2010
<i>Microbial Induced Corrosion</i>	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 (ACN)	<1.00E+04
Fermenters (FER)	3.11E+08
Iron Reducing Bacteria - Other (IRB)	1.21E+06
IRB <i>Geobacter</i> (IRG)	<1.00E+04
IRB <i>Shewanella</i> (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
<i>Burkholderia cepacia</i> Exopolysaccharide (BCE)	<1.00E+04
<i>Deinococcus</i> spp. (DCS)	5.35E+04
<i>Meiothermus</i> spp. (MTS)	<1.00E+04
<i>Cladosporium</i> spp. CLAD	<1.00E+04

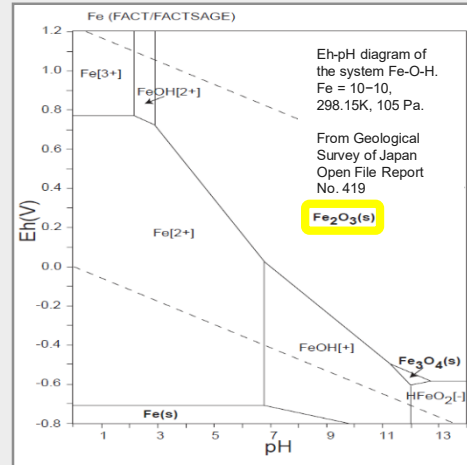


- ➔ Microbial analyses can be performed with Min-Trap samples
- ➔ Data provide insight on geochemical (redox) conditions and abundance of key microbial groups
- ➔ Data from Min-Trap samples are comparable to data from corresponding groundwater samples

Additional Min-Trap Applications

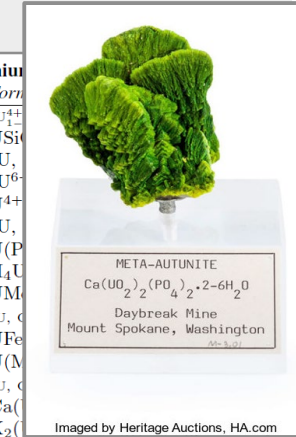
Laboratory
Testing
Completed

Co-precipitation of As with Fe



Precipitation of U with phosphate

Name	Formula
Uraninite	(U ⁴⁺) ₁₋₂
Coffinite	USi ₂
Brannerite	(U, Th) ₃ (PO ₄) ₈
Orthobrannerite	(U, Th) ₃ (PO ₄) ₈
Ianthinite	U ⁴⁺
Ishikawaite	(U, Th) ₃ (PO ₄) ₈
Lermontovite	U ₂ (PO ₄) ₃
Moluranite	H ₄ UO ₇
Mourite	UM ₂ (PO ₄) ₂
Ningyoite	(U, Th) ₃ (PO ₄) ₈
Petschekite	UFe ₂ (PO ₄) ₄
Sedovite	U(Mg, Fe) ₂ (PO ₄) ₂
Uranomicrocline	(U, Th) ₃ (PO ₄) ₈
Tyuyamunite	Ca(UO ₂) ₂ (PO ₄) ₂ ·2H ₂ O
Carnotite	K ₂ (UO ₂) ₂ (PO ₄) ₂ ·6H ₂ O
Torbernite	Cu[(UO ₂)(PO ₄)] ₂ (H ₂ O) ₈
Autunite	Ca[(UO₂)(PO₄)]₂(H₂O)₁₀₋₁₂
Vyacheslavite	U(PO ₄)(OH)(H ₂ O) _{2,5}

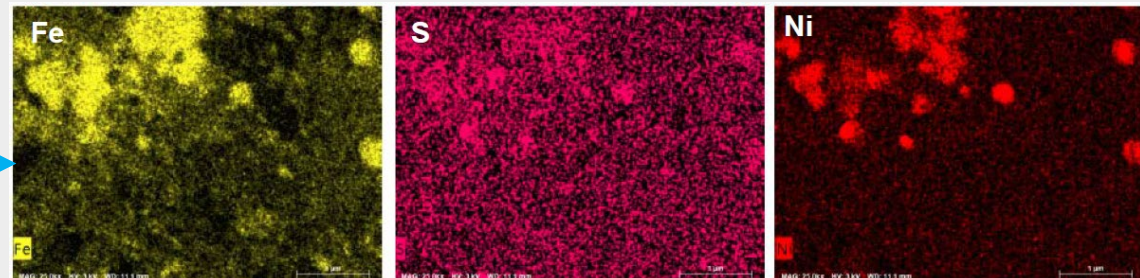


From Závodská et al. 2008. Environmental chemistry of uranium.

Precipitation of Ni under reducing conditions as NiS



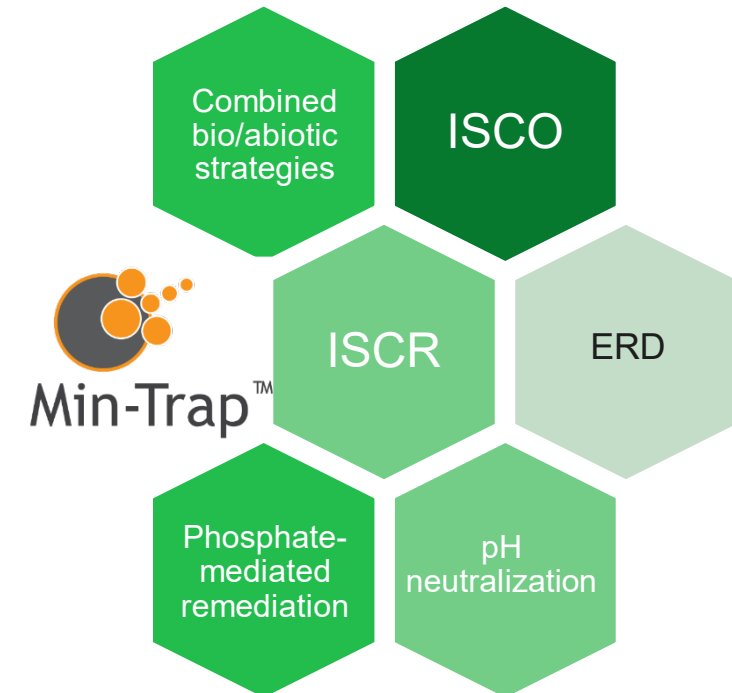
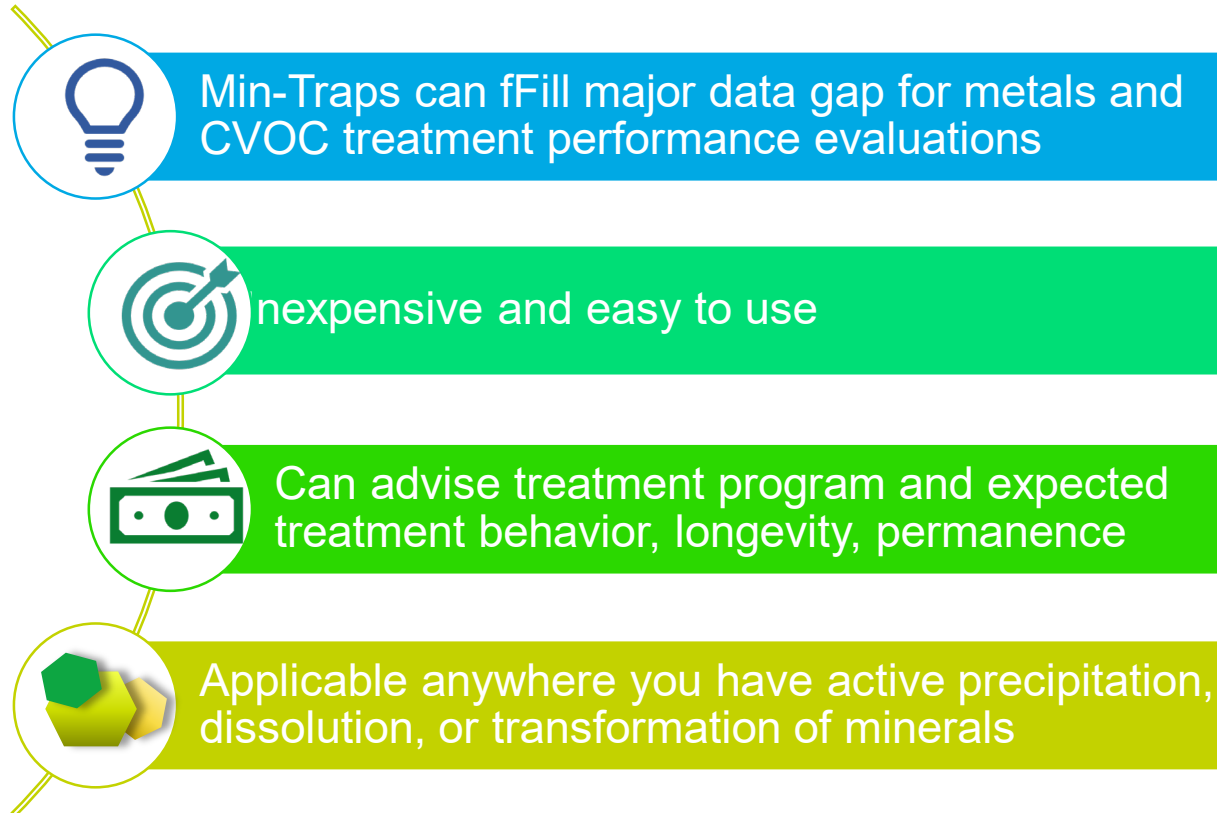
Min-Trap @ ~2 months



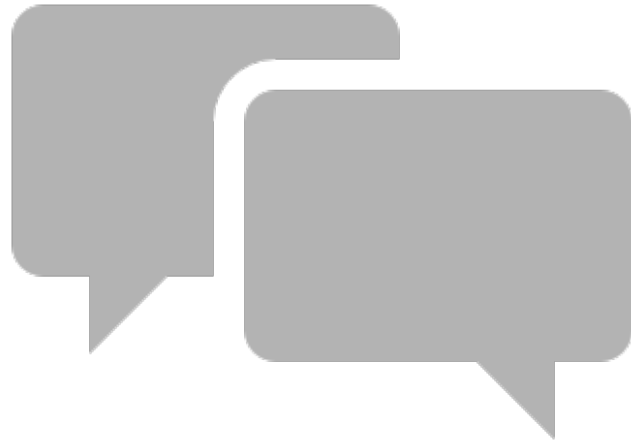
- Apparent co-precipitation of Ni, Fe, and S.
- Leaching tests imply Ni is both sorbed to Fe (temporary) and incorporated into sulfide minerals (stable)
- Verified the process is working but it's more complex and harder to achieve consistent treatment than expected

Testing
Completed

Key Takeaways



Questions



Additional Information



<https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER19-5190>

Demonstration of Mineral Traps to Passively
Evaluate and Monitor In Situ Reactive Minerals
for Chlorinated Solvent Treatment

Dr. Craig Divine | Arcadis U.S., Inc.
ER19-5190

[Objective](#) | [Technology](#) | [Benefits](#)

Objective

