THE MIN-TRAP™ SAMPLER

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

March 26, 2019

Today’s Presenters

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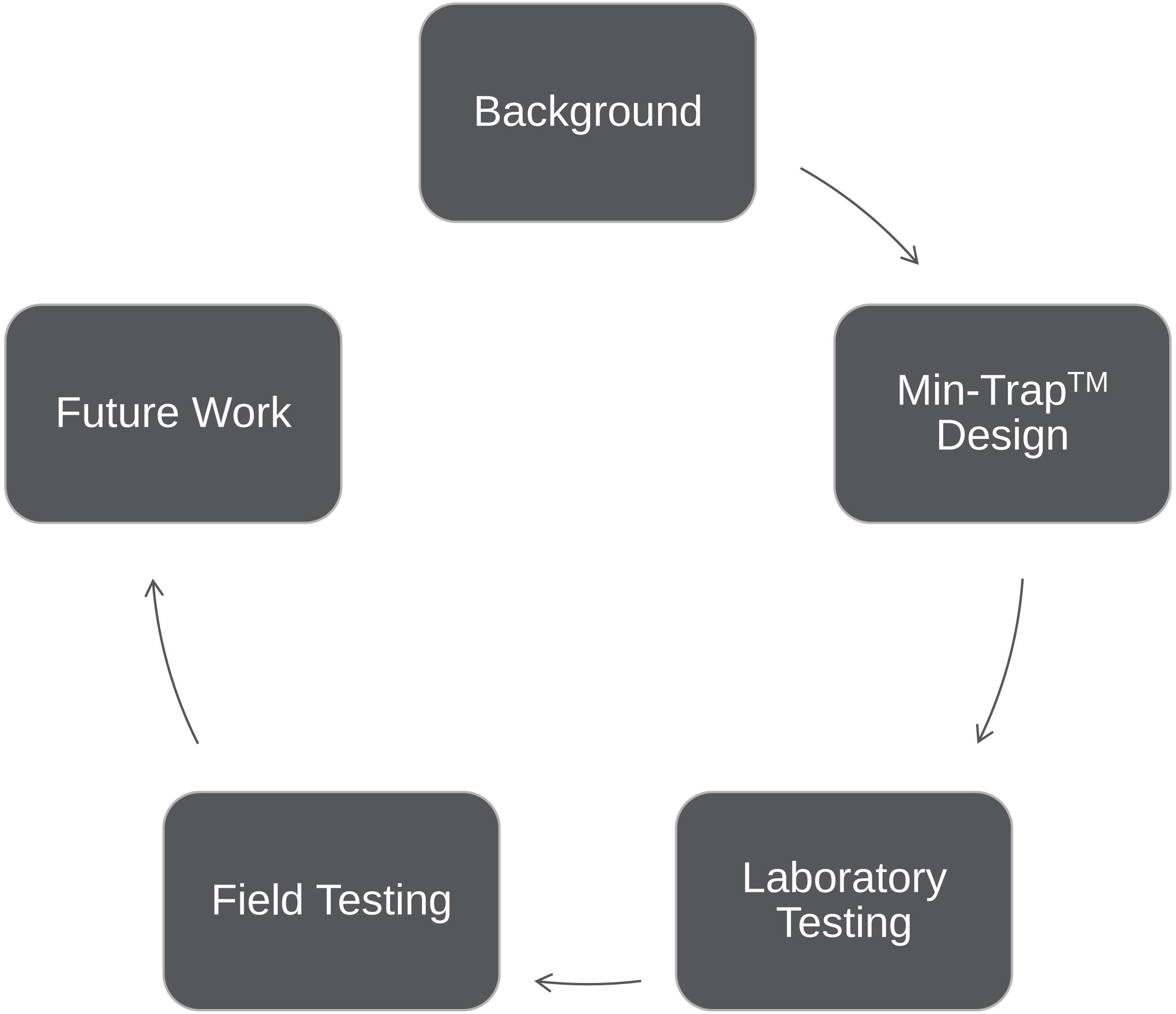
Agenda


Background
Min-Trap™ Design
Laboratory Testing
Field Testing
Future Work

Learning Objectives

After attending this presentation, you should be able to:

- Conceptually describe how a Min-Trap^{TM} is designed and deployed
- Understand the role of reduced iron minerals in abiotic degradation of chlorinated solvents
- Give a hypothetical example where Min-Traps could be used
- List at least two analytical methods that could be applied to Min-Trap samples to assess the presence of reduced iron minerals

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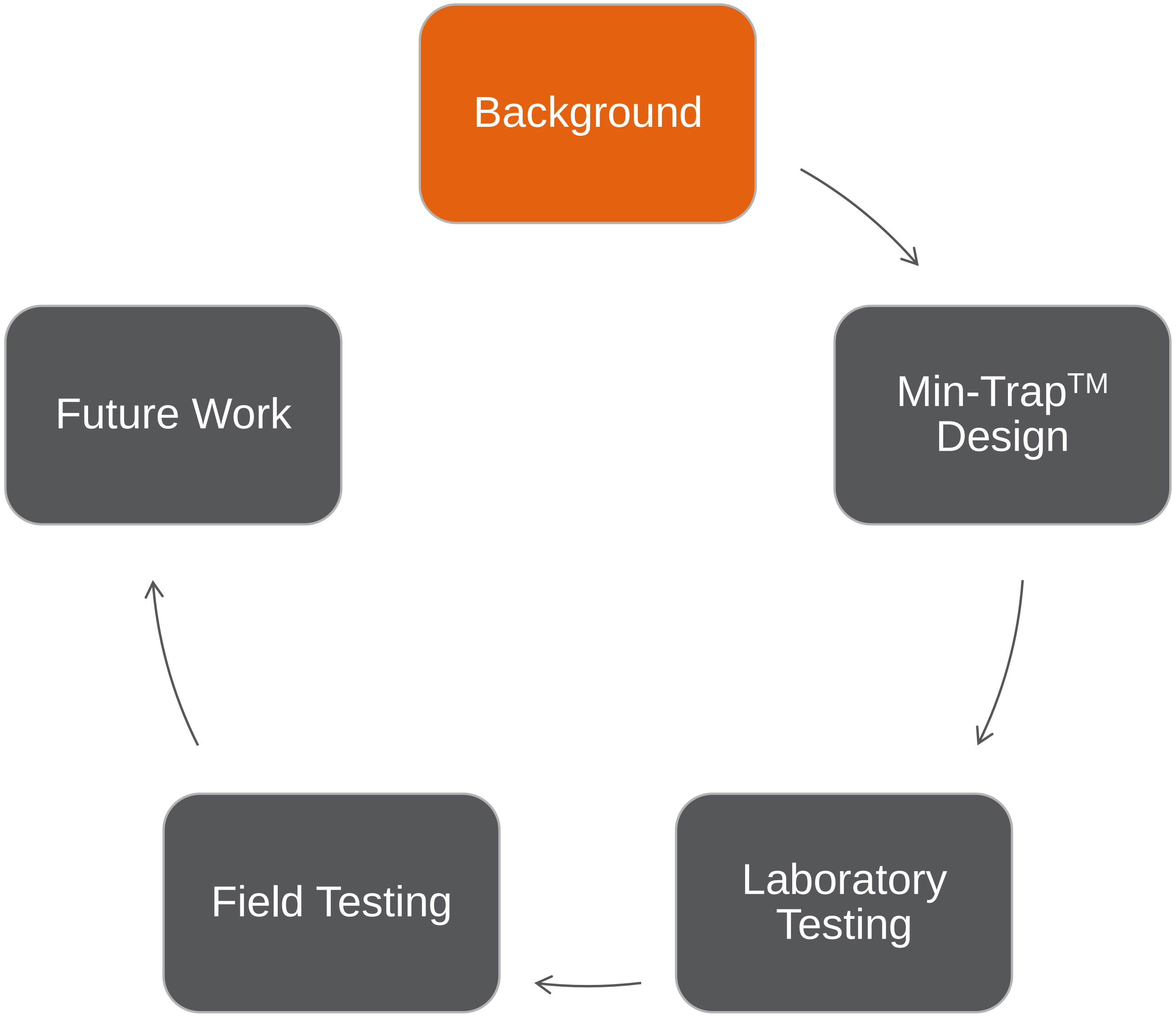
Agenda

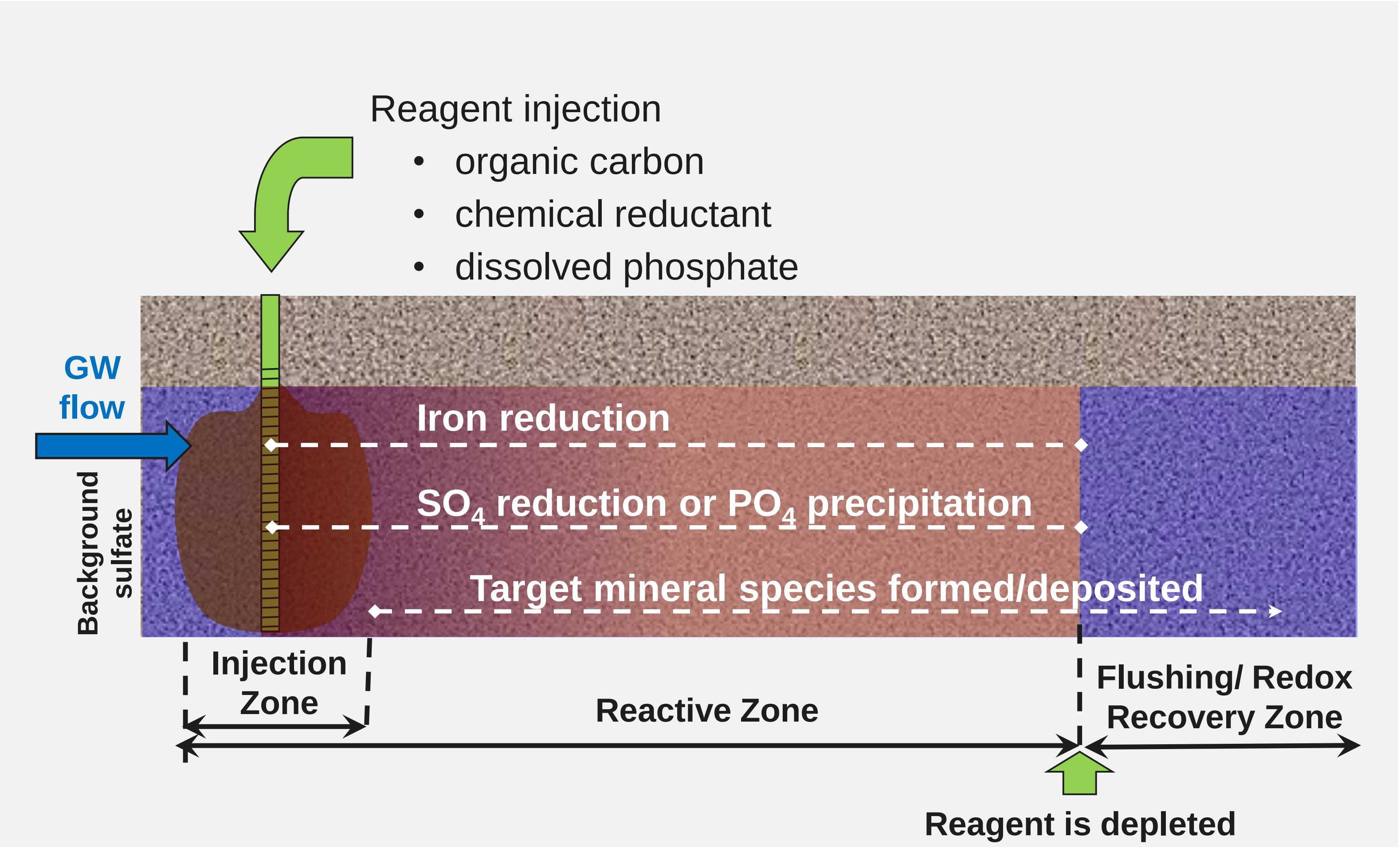


In Situ Treatment and Mineral Precipitation

Examples:

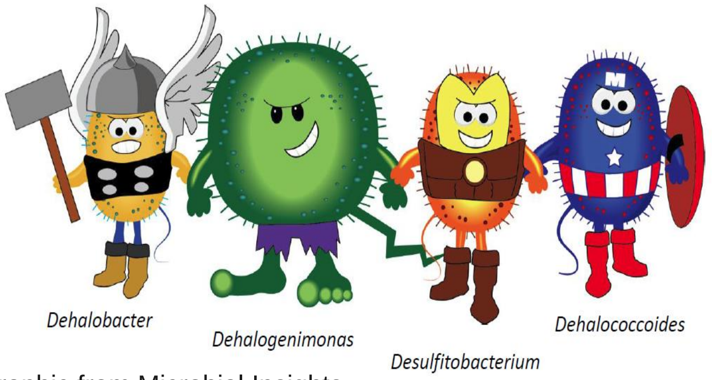
1 Metal sulfides or phosphates for in situ sequestration (NiS, U-PO_4 compounds, etc.)

2 Reactive reduced iron minerals to abiotically degrade chlorinated solvents



Anaerobic Biodegradation

Fermentable organic carbon provides the electrons that drive the sequential reduction process

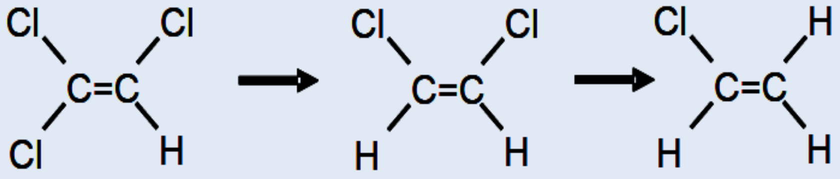


Graphic from Microbial Insights

Biological Reductive Dechlorination

Sequential Reductive Dechlorination

also called Hydrogenolysis



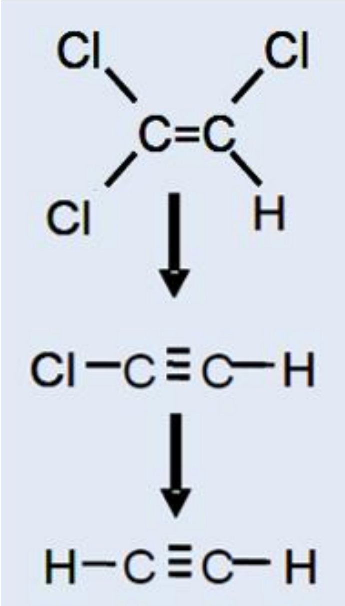
TCE Cis-DCE VC

Adapted from Wilson 2014

Abiotic Degradation

- ➔ Fermentable organic carbon provides electrons which drive microbial Fe and SO_4^{2-} reduction
- ➔ 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

TCE



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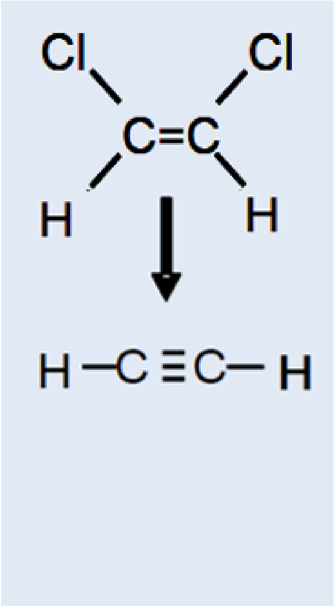


How do we know what's really happening under the surface?

Groundwater samples

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

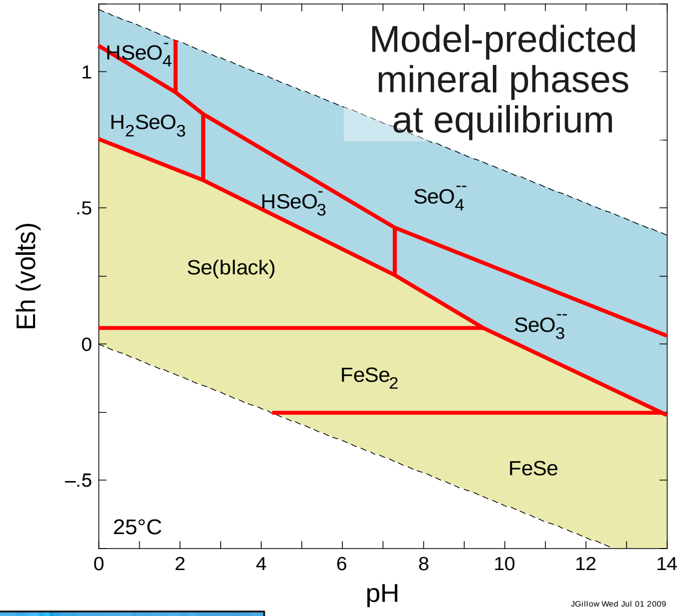
Geochemical modeling

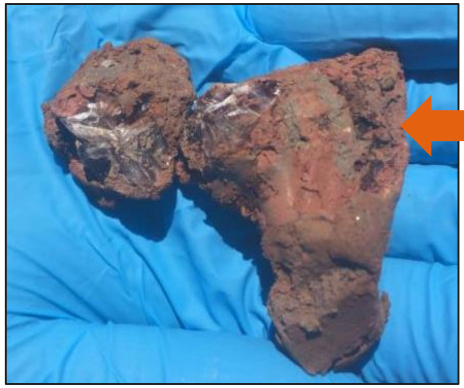
- All models have simplifying assumptions
- Predicts equilibrium conditions (kinetics not considered)

Soil samples from drill cores

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

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





Soil sample with heterogenous mineral distribution

Soil core with heterogenous mineral distribution

Min-Traps: Something New

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- ➔ Collects minerals actually forming at site using existing monitoring well network
- ➔ Representative of conditions in higher-flux zones
- ➔ Inexpensive, easily repeated
- ➔ No significant background “noise” in samples

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.

Process	Contaminants	Target Observation within the Min-Trap™
Enhanced Reductive Dechlorination & Combined Biotic/Abiotic Treatment	Chlorinated solvents	Reactive iron mineral formation, such as magnetite, mackinawite, and/or pyrite
In-situ Chemical Oxidation	Metals that co-precipitate or adsorb to iron oxides (e.g., arsenic), metals that form low-solubility oxides	Iron oxides or other metal oxides containing co-precipitated and/or adsorbed metalloids/metals
In-situ Chemical Reduction	Cr(VI), U, metals that form sulfides	Increase in the total to dissolved ratio of a metal over time, or FeS_x or other metal sulfide formation
pH neutralization (increase or decrease)	Metals	Increase in solid-phase metals in the Min-Trap™

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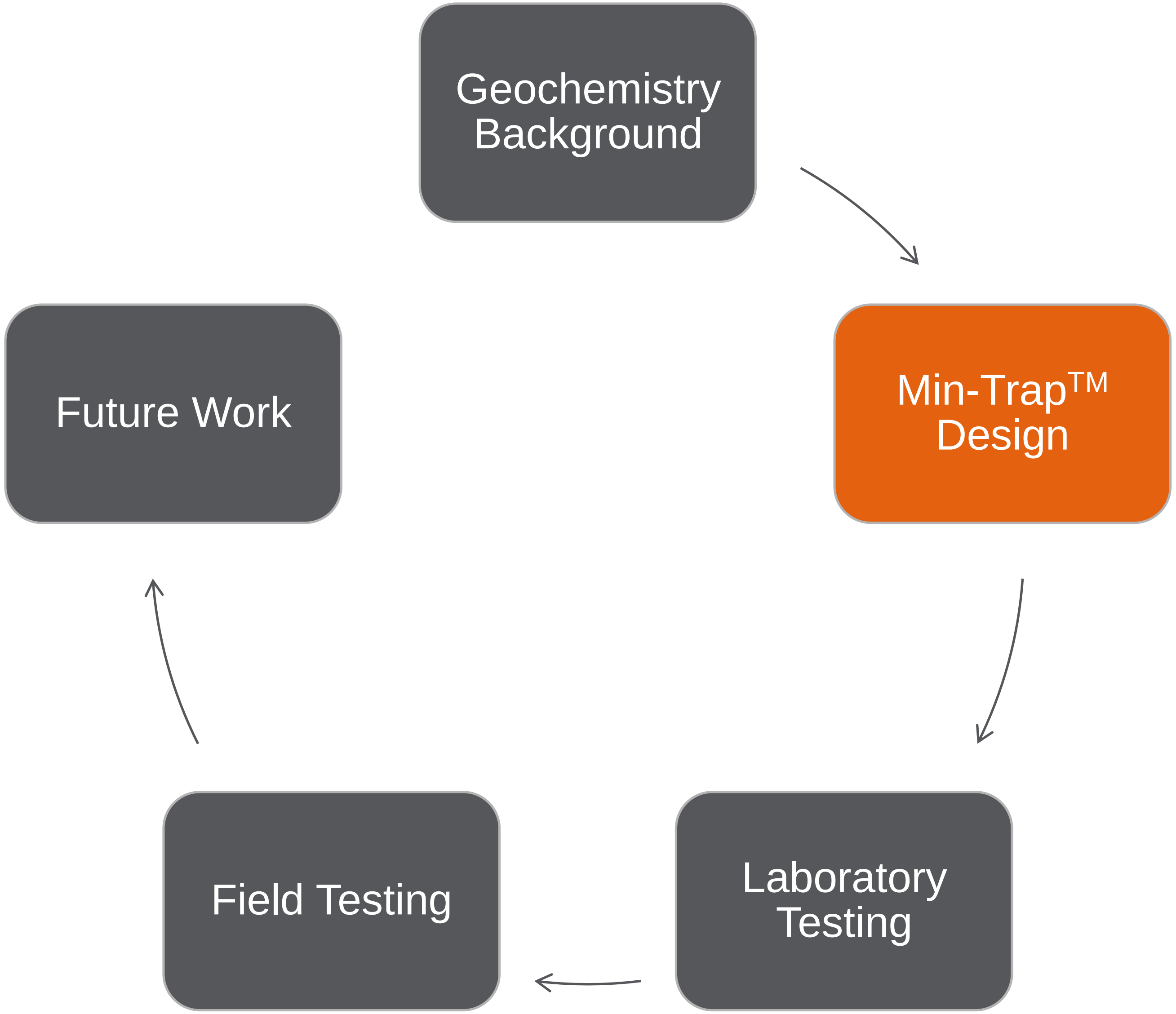
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Min-Trap Design

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- ➔ A 15-inch long PVC slot-screen housing containing multiple porous media pillows
- ➔ Customizable porous medium inside mesh pillows acts as a matrix for precipitating minerals
- ➔ Analytical packages are tailored based on technical objectives
- ➔ Manufactured and sold by Microbial Insights

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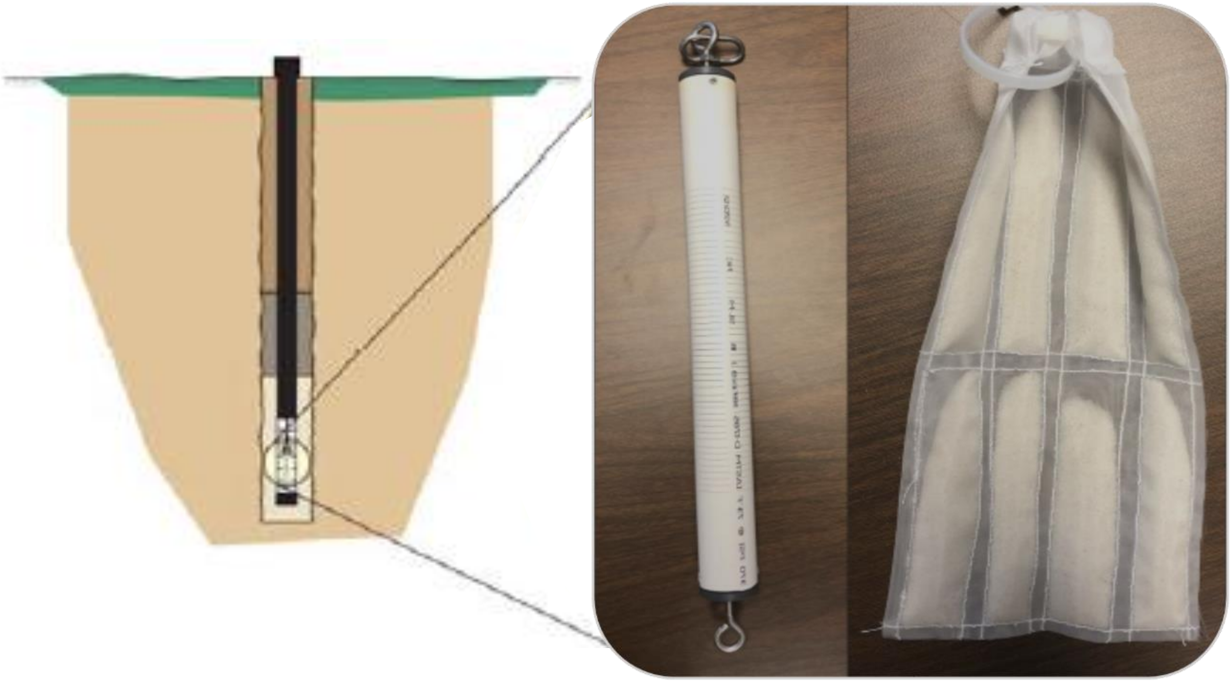
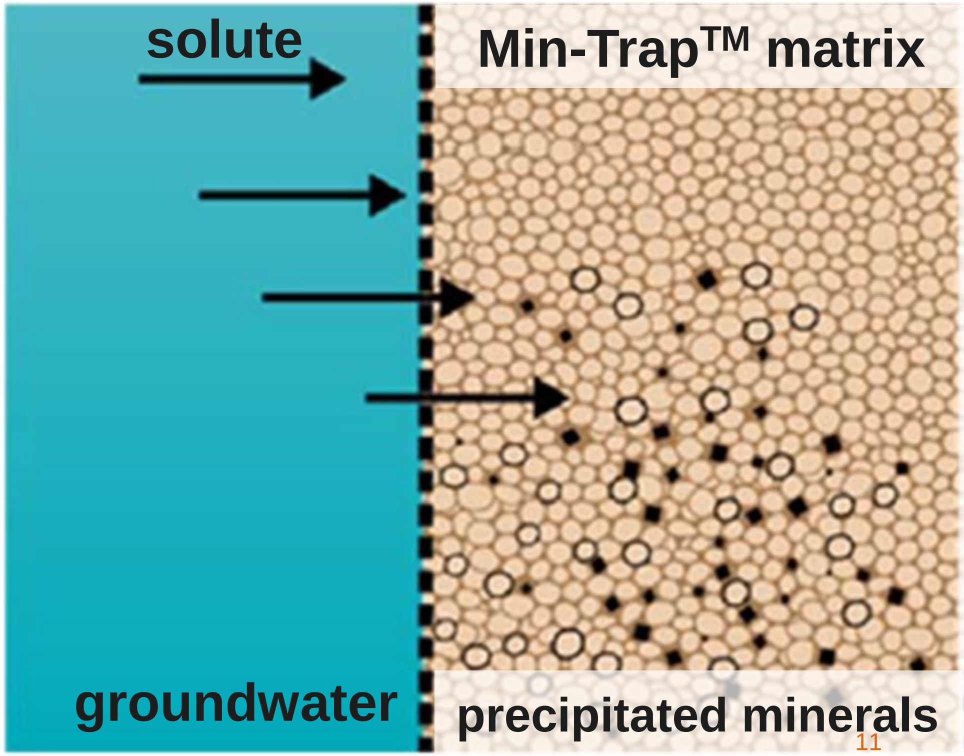


Deployed in standard 2"+ monitoring well

Slotted PVC casing

Porous medium in permeable mesh



Min-Trap Deployment and Retrieval

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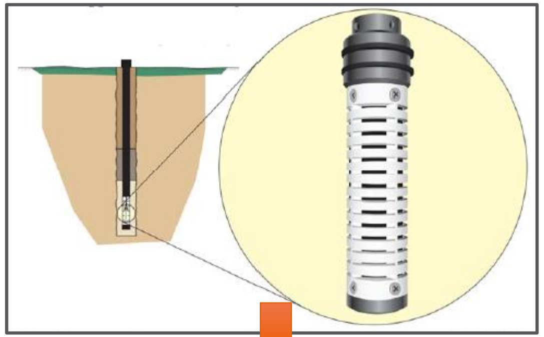
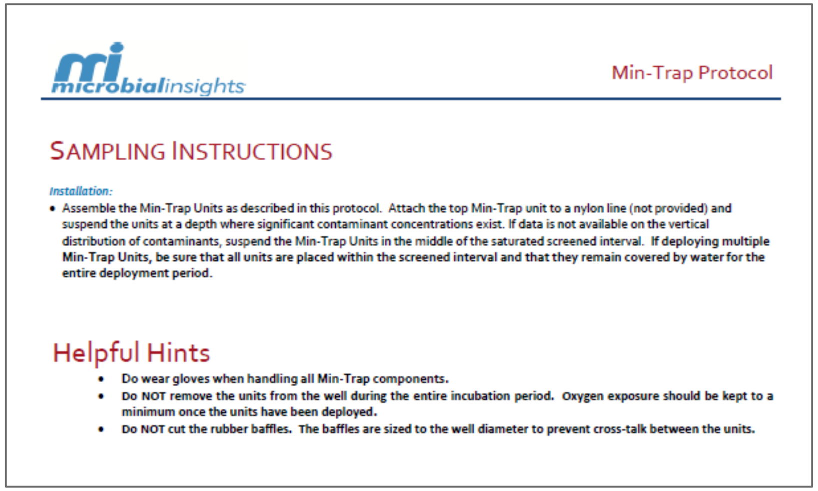


1. Deployment consists of the lowering of sampler in a monitoring well (similar to Bio-Trap or Passive Diffusion Bag deployment)
2. Minimum incubation time is site specific, but plan on at least 4 weeks
3. At retrieval, sample pillows are separated and double-sealed (using a vacuum sealer and O_2 absorbent packets) prior to shipping to lab

Remember to think through hazards:

- Weather conditions
- Biological hazards
- PPE consistent with HASP
- Body positioning
- Knee pads helpful for flush-mount wells
- Traffic control, as needed
- Power needs for vacuum sealer



microbialinsights — Min-Trap Protocol

SAMPLING INSTRUCTIONS

Installation:

- Assemble the Min-Trap Units as described in this protocol. Attach the top Min-Trap unit to a nylon line (not provided) and suspend the units at a depth where significant contaminant concentrations exist. If data is not available on the vertical distribution of contaminants, suspend the Min-Trap Units in the middle of the saturated screened interval. If deploying multiple Min-Trap Units, be sure that all units are placed within the screened interval and that they remain covered by water for the entire deployment period.

Helpful Hints

- Do wear gloves when handling all Min-Trap components.
- Do NOT remove the units from the well during the entire incubation period. Oxygen exposure should be kept to a minimum once the units have been deployed.
- Do NOT cut the rubber baffles. The baffles are sized to the well diameter to prevent cross-talk between the units.

Instructions available from MI

Agenda

1. Geochemistry Background
2. Min-Trap™ Design
3. Laboratory Testing
4. Field Testing
5. Future Work

Bench Testing

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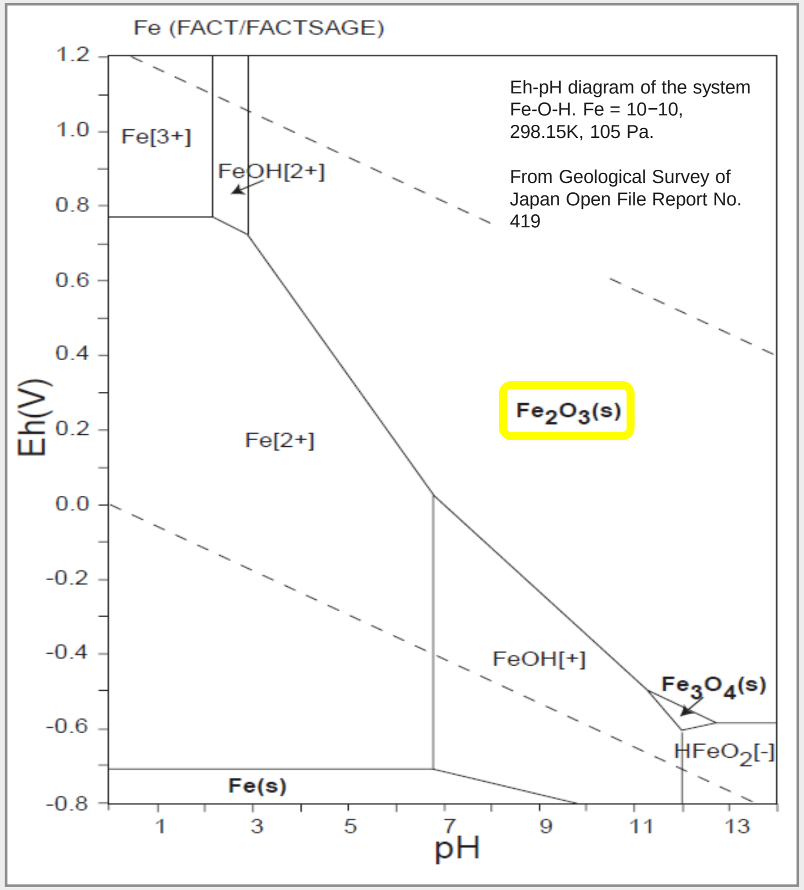
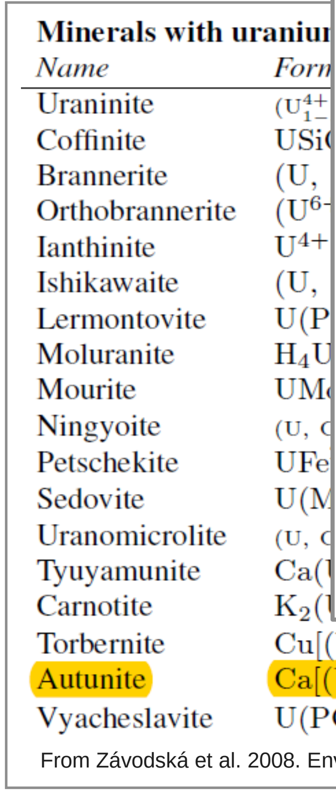
Co-precipitation of arsenic or chromium with iron



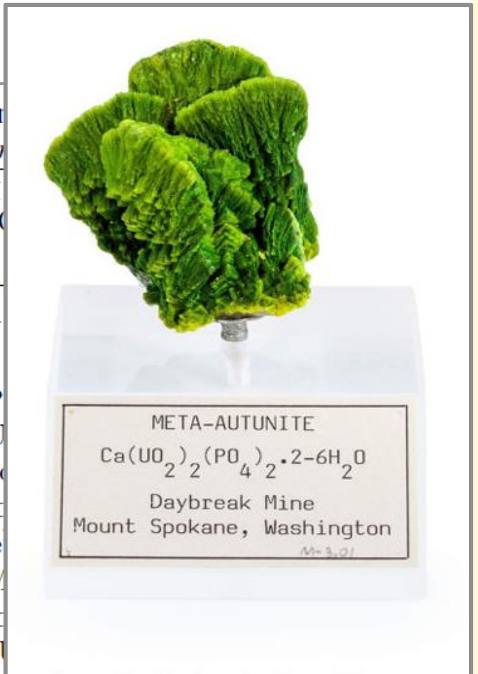
Precipitation of uranium with phosphate



Minerals with uraniu...

Name	*Form...*
Uraninite	$(U^{4+}_{1-}$...
Coffinite	USi...
Brannerite	(U, ...
Orthobrannerite	$(U^{6}$...
Ianthinite	U^{4+}...
Ishikawaite	(U, ...
Lermontovite	U(P...
Moluranite	H_4U...
Mourite	UM...
Ningyoite	(U, C...
Petschekite	UFe...
Sedovite	U(M...
Uranomicrolite	(U, C...
Tyuyamunite	Ca(...
Carnotite	K_2(...
Torbernite	$Cu[(UO_2)(PO_4)]_2(H_2O)_8$
Autunite	$Ca[(UO_2)(PO_4)]_2(H_2O)_{10-12}$
Vyacheslavite	$U(PO_4)(OH)(H_2O)_{2,5}$

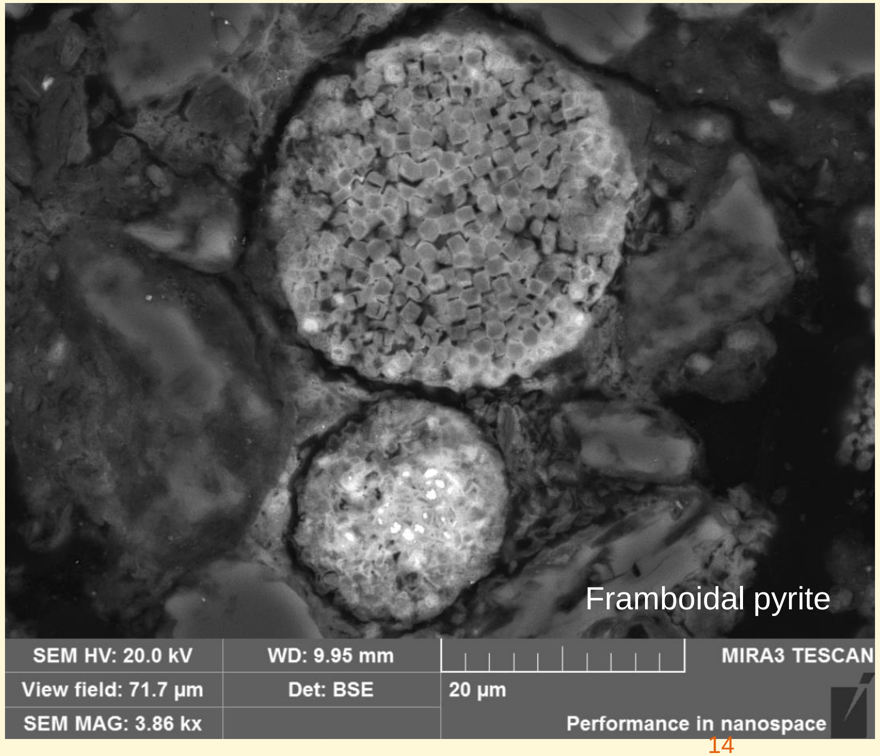
From Závodská et al. 2008. Environmental chemistry of uranium.



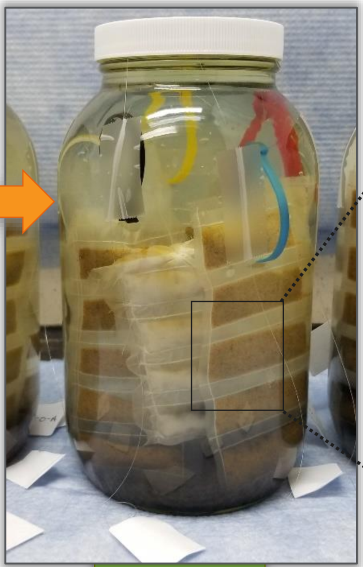
Imaged by Heritage Auctions, HA.com

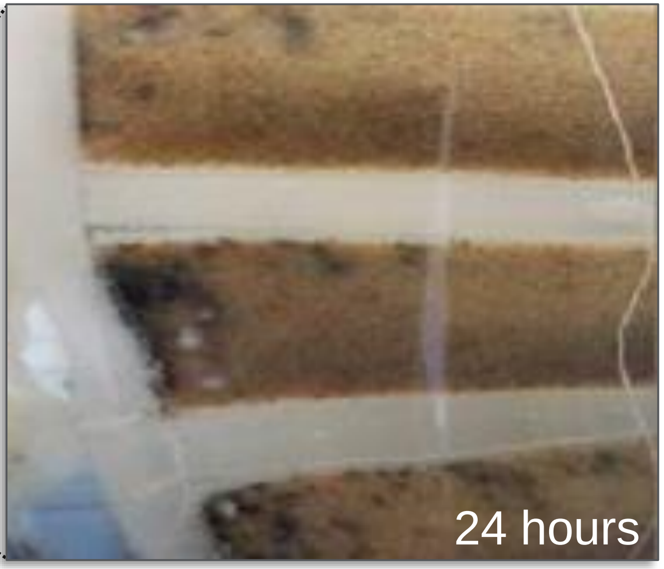
Biological iron and sulfate reduction to form iron sulfides

Simulated enhanced reductive dechlorination (ERD)



Incubation solution creates enhanced reductive dechlorination conditions

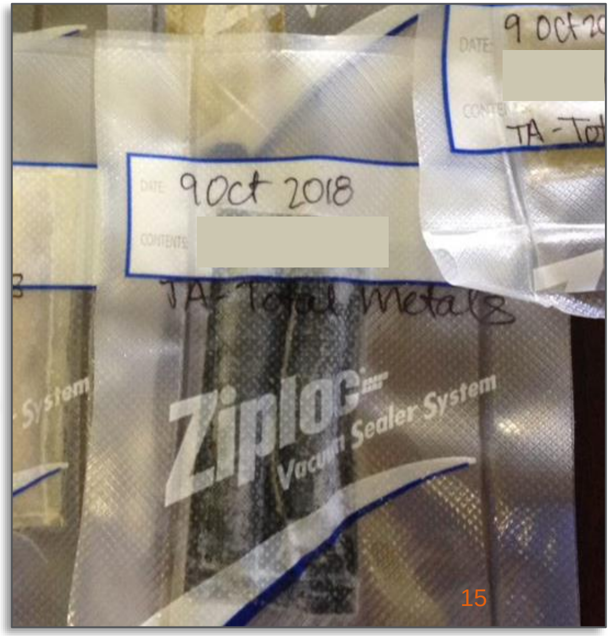




Two weeks

Harvest

Subsample & analyze



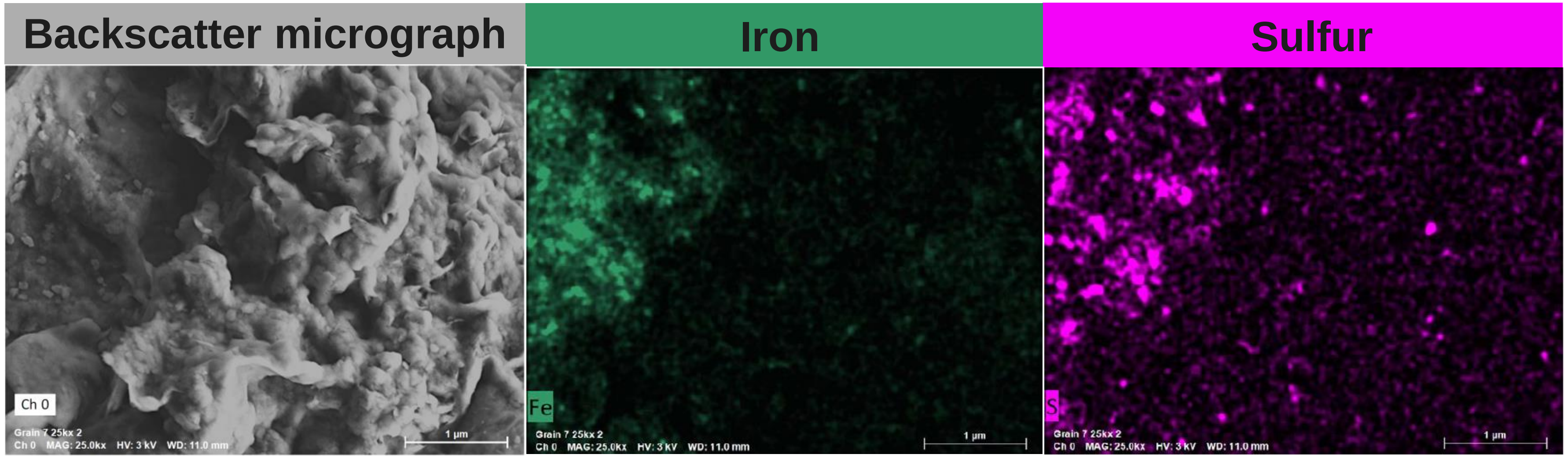
Potentially Applicable Analyses

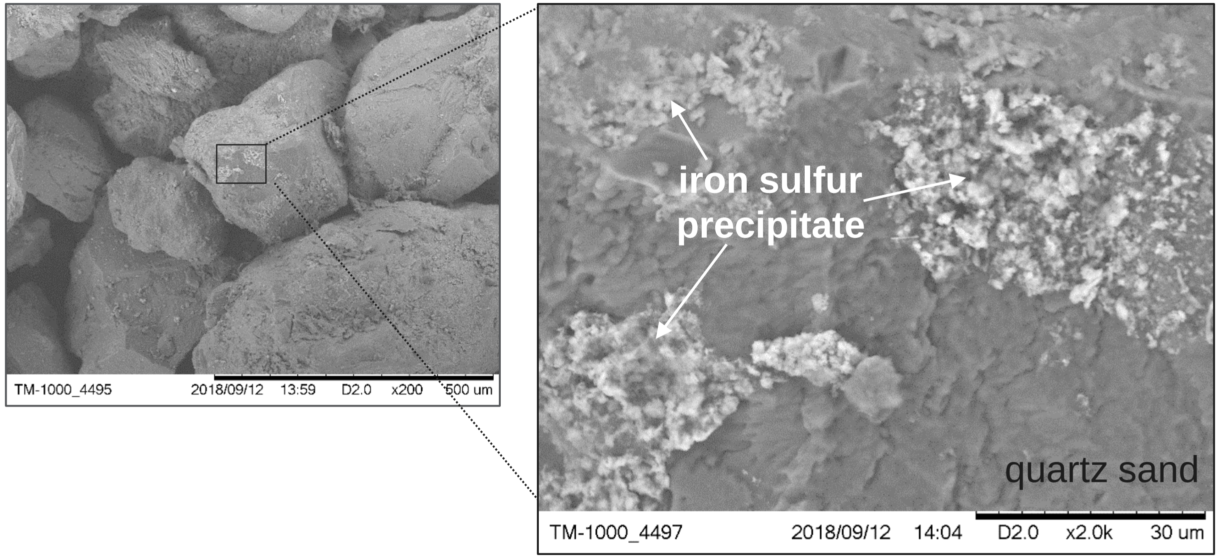
Chemical	• Weak and strong acid soluble iron (WAS, SAS) • Acid-volatile sulfide (AVS) • Chromium-extractable sulfide (CrES)	Biogenic (pseudocrystalline) vs. crystalline minerals Sulfur forms: FeS vs. FeS_2 and S^0
Microscopy	• Light/petrographic • Scanning Electron Microscopy (SEM) • Transmission Electron Microscopy (TEM)	Mineral grain size, shape, distribution
Spectroscopy	• Energy Dispersive X-ray Spectroscopy (EDS) • X-ray Absorption Spectroscopy (XAS)	Elemental composition Elemental coordination
General	• X-Ray Diffraction (XRD) • Magnetic susceptibility (magnetite)	Mineralogy Magnetic mineral content
Molecular biology	QuantArray	Microbial community

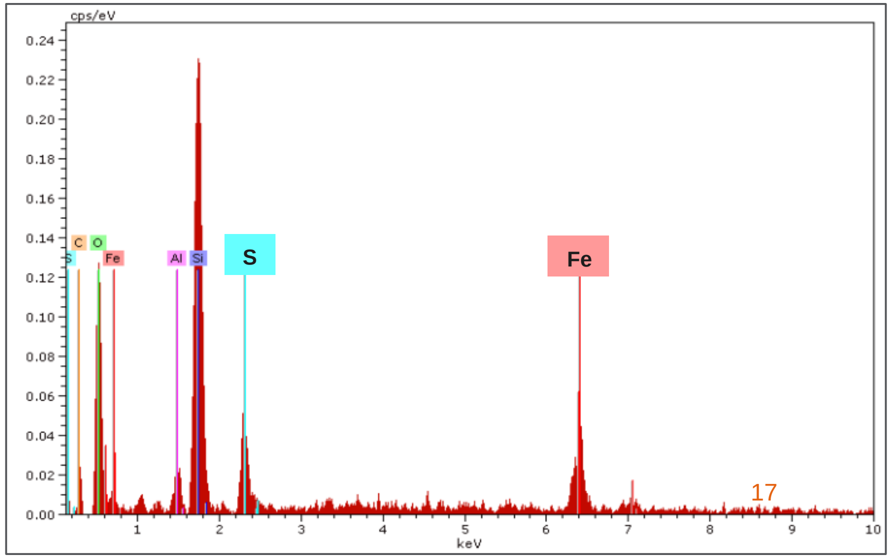
WAS and SAS iron: >95% ferrous iron

AVS: ~80% FeS

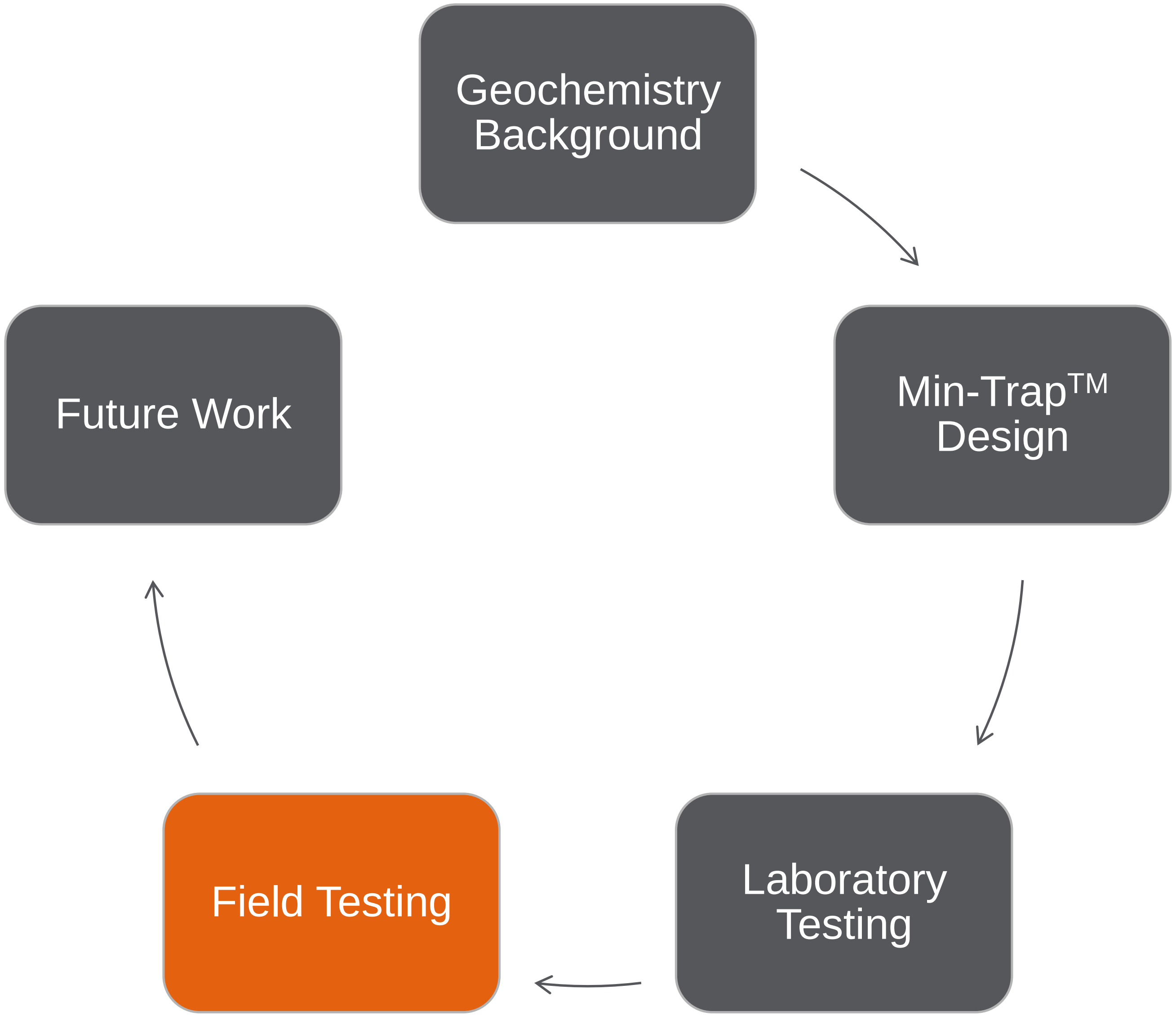
CrES ~20% FeS_2 or S^0







Agenda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Field Testing

Chloromethanes up to ~20 mg/L

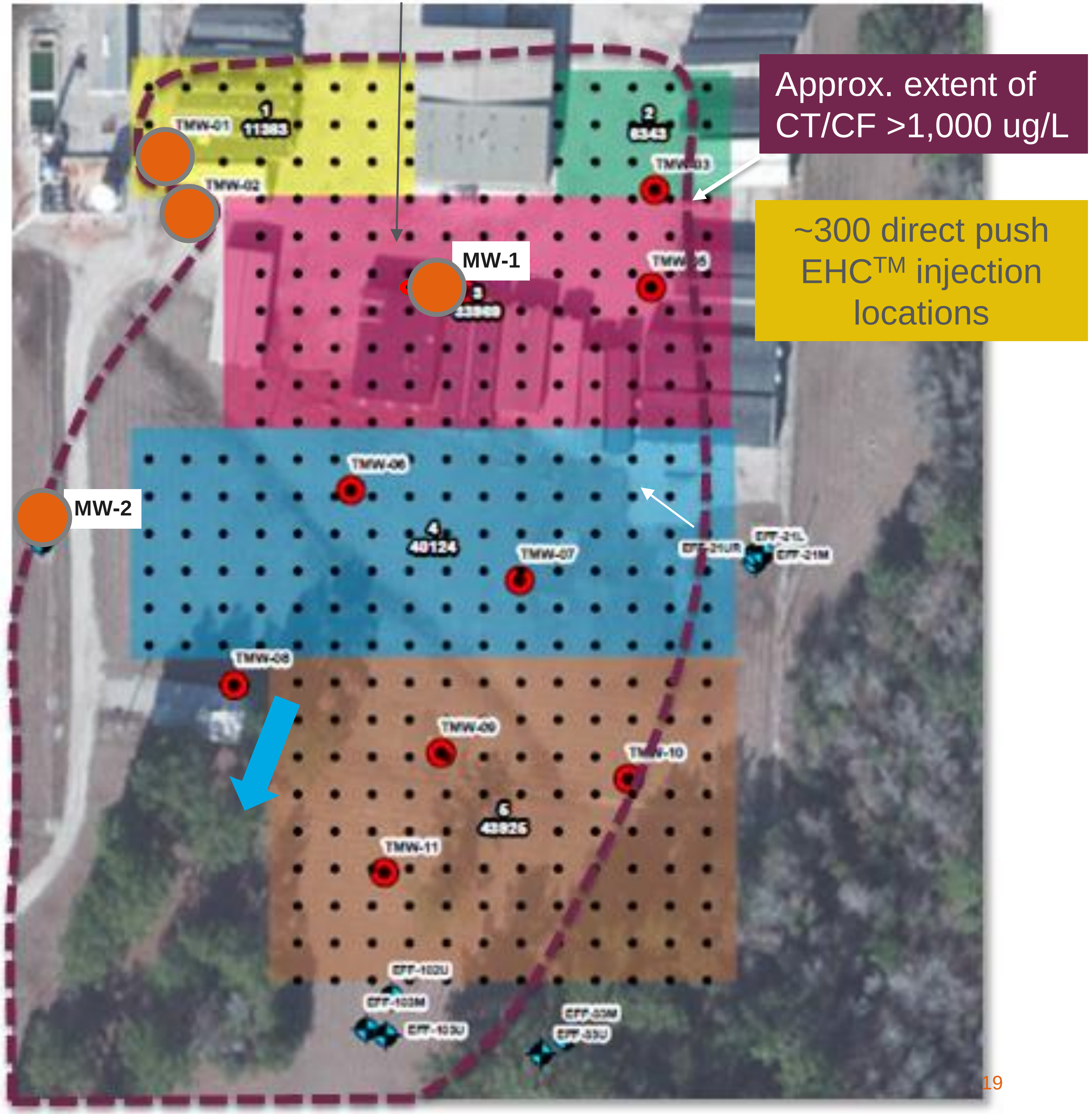
Co-disposed S-containing compounds

Naturally high iron

EHC^{TM} treatment June-August 2018

Min-Traps deployed Aug 2018

Retrieval and analysis October 2018



Field Testing

FeS, FeS_2 precipitation 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 (Fe^{2+}) from EHC™ injection site (***increased ROI***)
- ✓ ***Expanded degradation capacity*** beyond EHC™'s direct reduction by ZVI/biological ERD by expanding the reactive treatment zone and increasing reactive surface area

Organic carbon

Microbially mediated

$Fe_2O_3 + 6\,H^+ + e^- \rightarrow 2\,Fe^{2+} + 3\,H_2O$

$2H^+ + SO_4^{2-} + 4\,H_2 \rightarrow H_2S + 4H_2O$

Fe^0

Abiotic

$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$

Iron sulfide precipitation:

$Fe^{2+} + S^{2-} \rightarrow FeS_{(s)}$

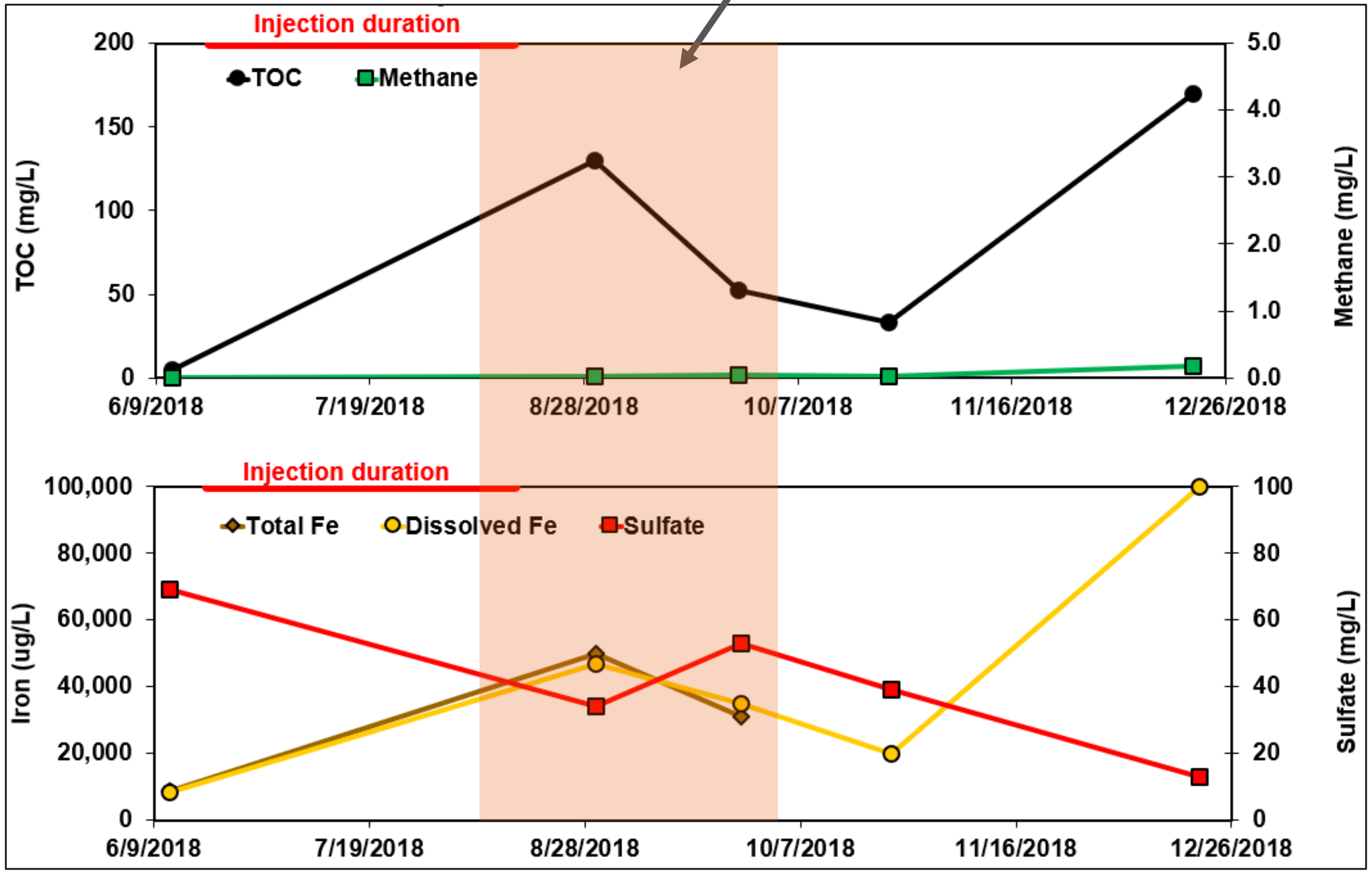
Min-Trap data can help optimize remedial strategies to maximize formation of reactive mineral species.

Field Testing

Min-Trap Deployment

Groundwater

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



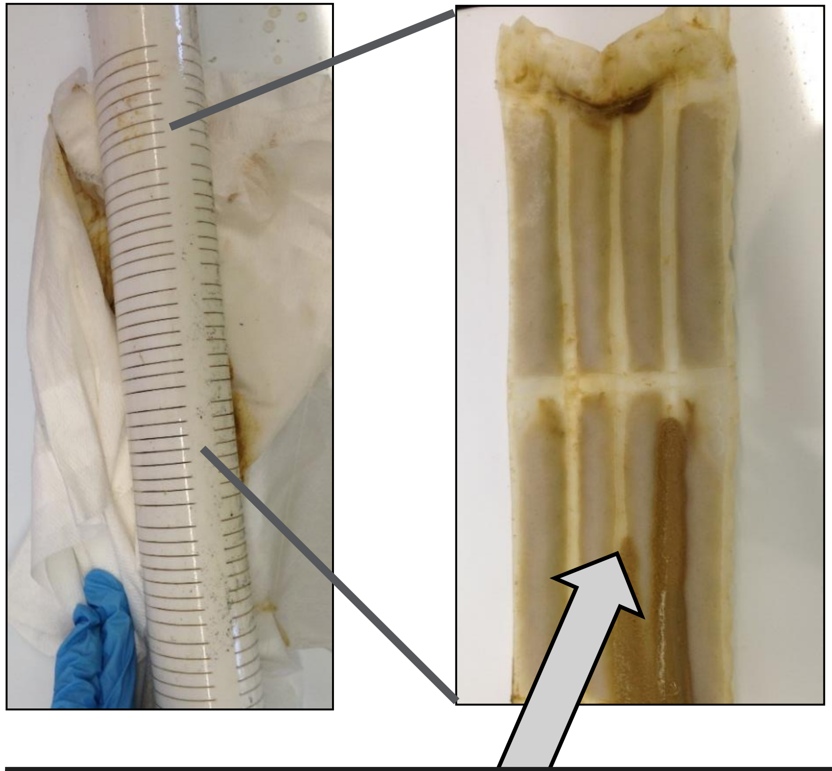
WAS Iron (mg/kg)	SAS Iron (mg/kg)	AVSulfide (mg/kg)	CrESulfide (mg/kg)
Fe^{2+} = 330 Fe^{3+} = 0	Fe^{2+} = 300 Fe^{3+} = 30	240	120

Iron: Solid iron is reduced

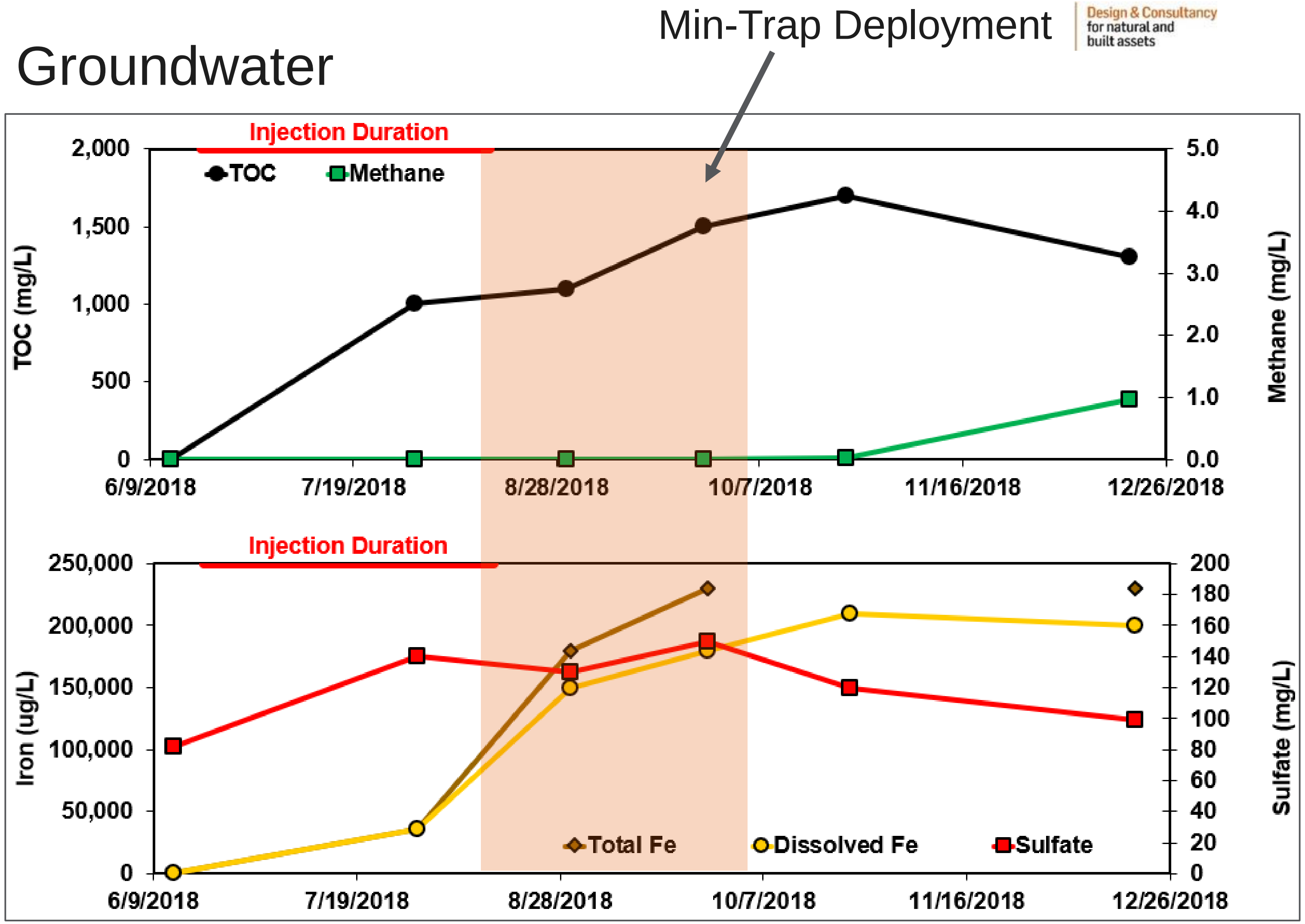
Sulfur: Mostly FeS, some FeS_2

Field Testing

MW-1: Original source area, within injection area



Groundwater



WAS Iron (mg/kg)	SAS Iron (mg/kg)	AVSulfide (mg/kg)	CrESulfide (mg/kg)
Fe^{2+} = 48 Fe^{3+} = 0	Fe^{2+} = 55 Fe^{3+} = 37	0.80	94

Iron: Lower solid iron, some is reduced

Sulfur: Very little FeS; CrES is likely co-disposed S^0

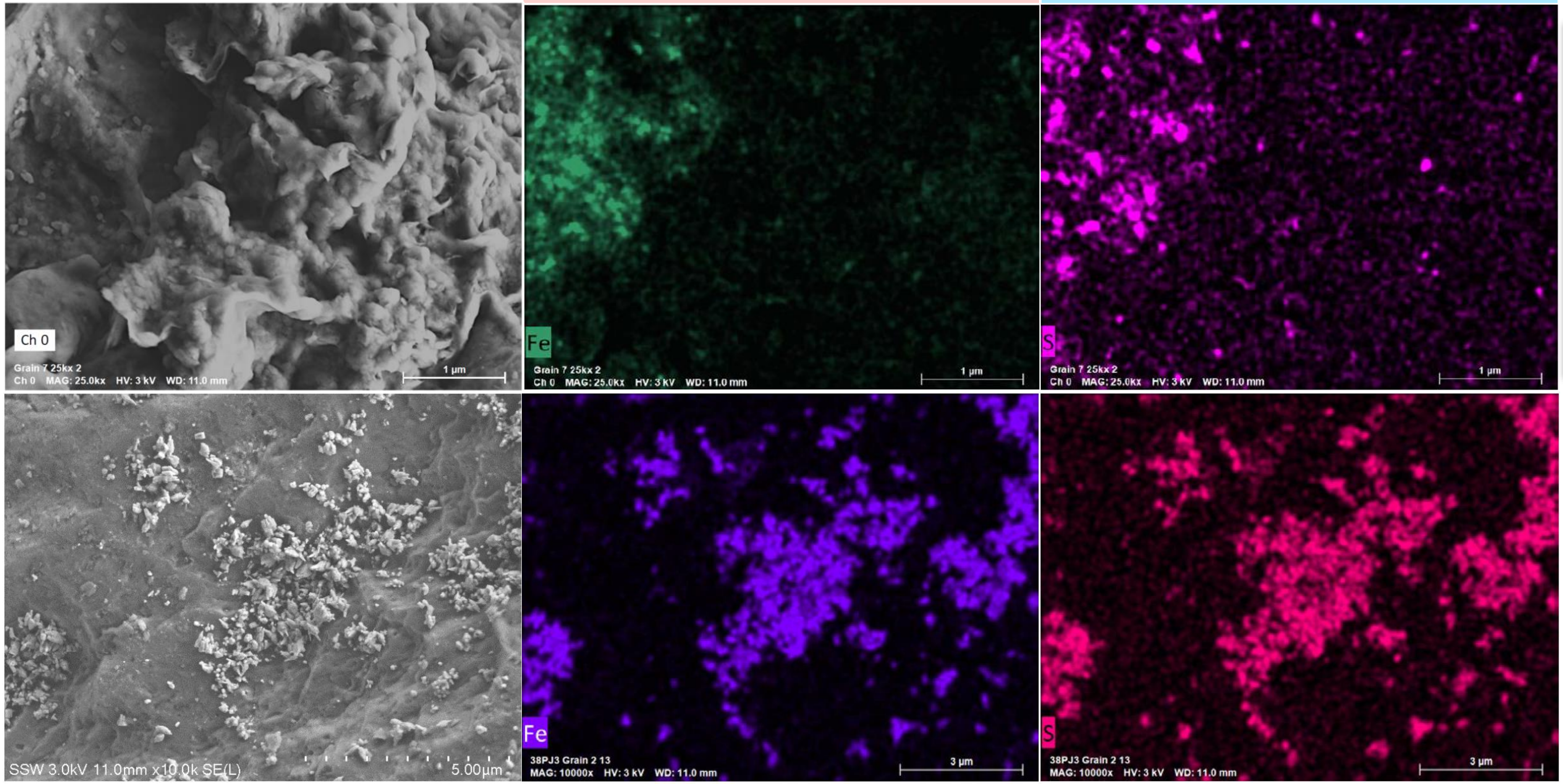
Min-Trap Analysis

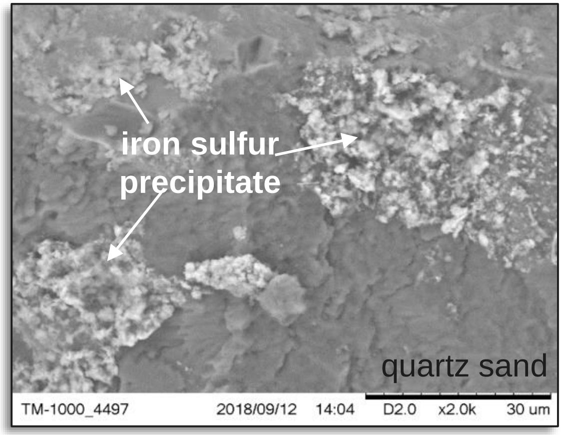
MW-2 Results – SEM with Energy Dispersive X-Ray Spectroscopy (EDS)

	Iron	Sulfur

Lab test

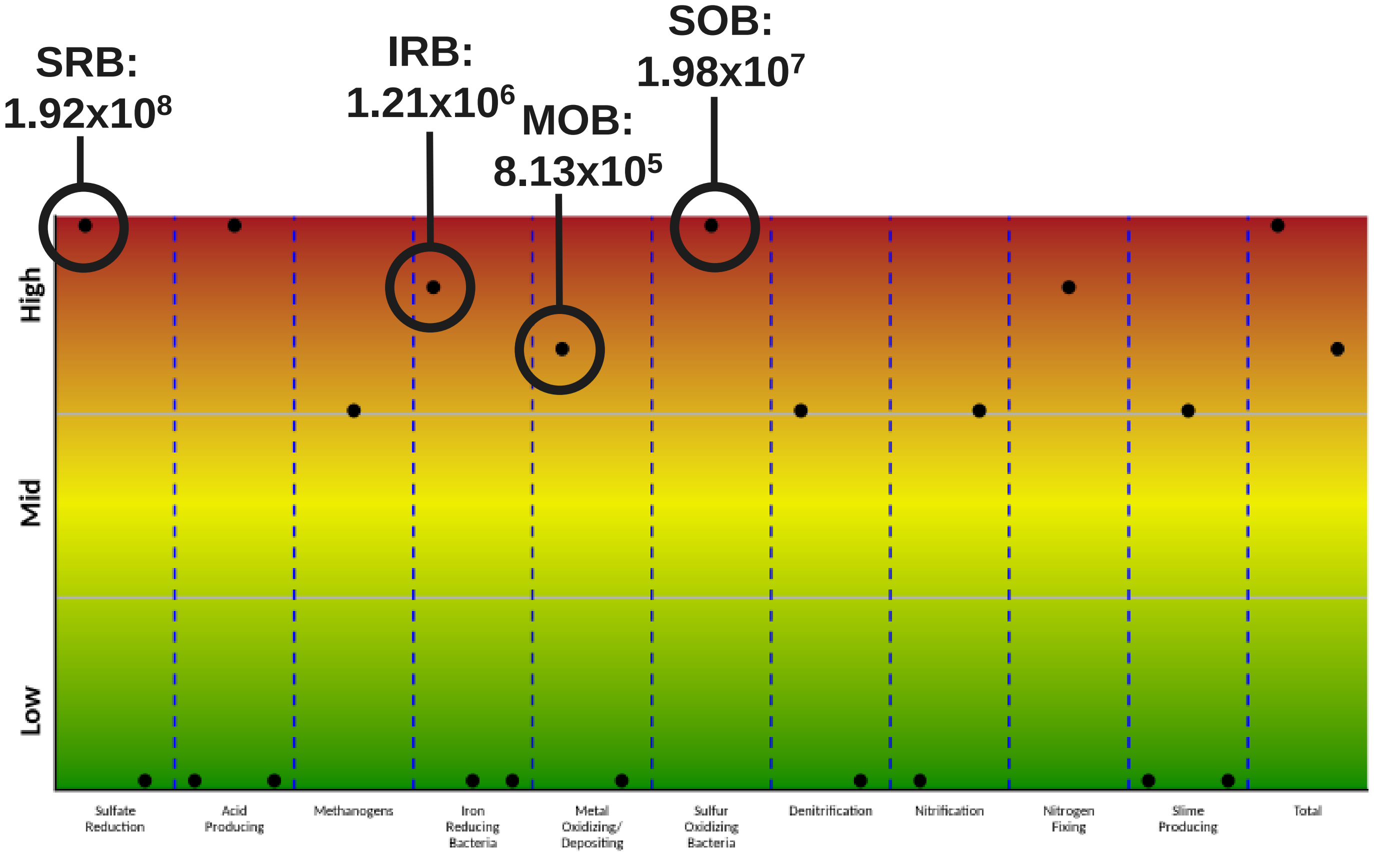
Field test





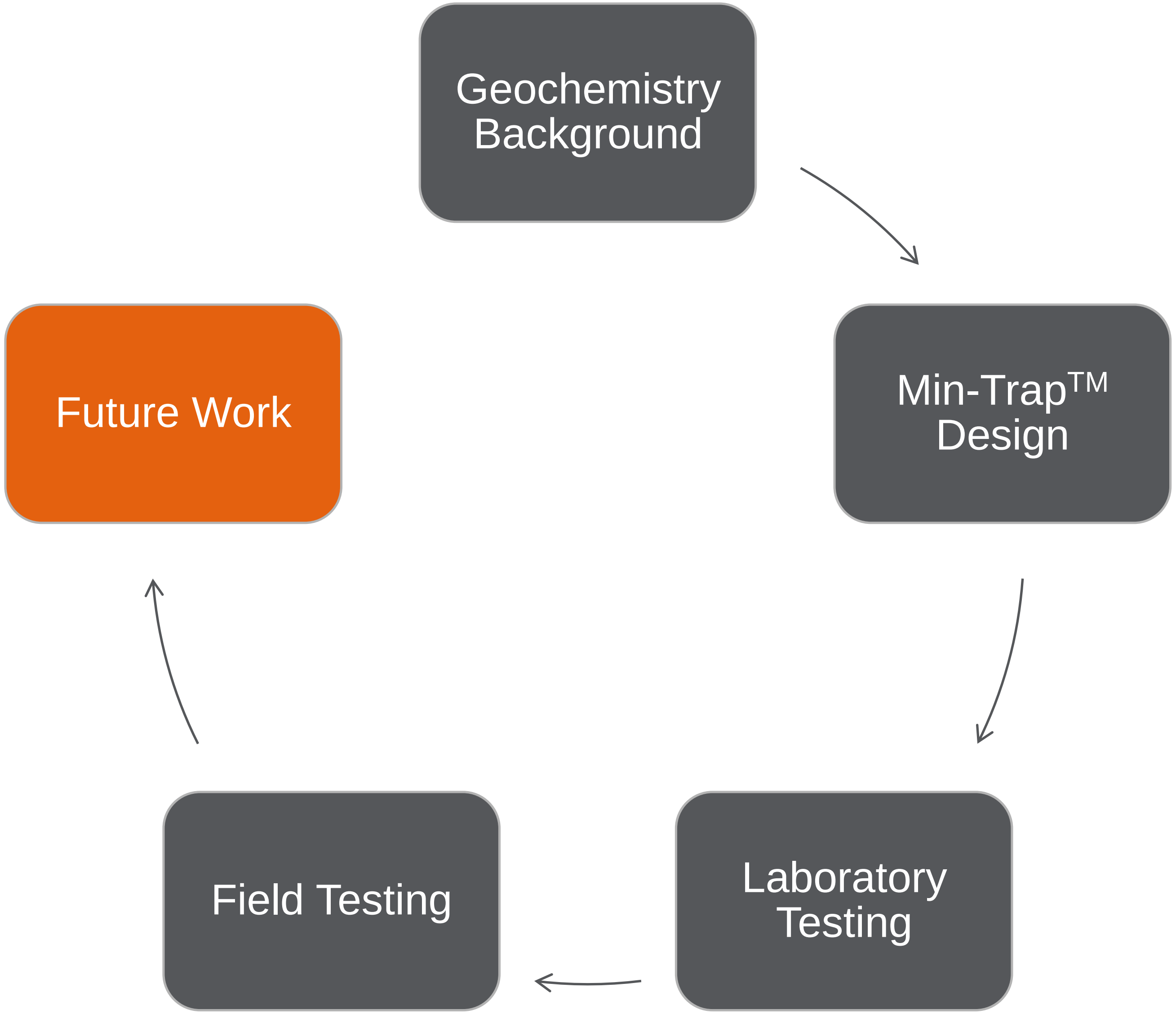
Min-Trap Analysis: Microbial

Sample Name	MW-2
Sample Date	
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



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

Agenda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Development Path

2015-2016

SATELLITE

Powered by Lovinklaan Foundation

2016-2018 Lab Testing

- Arsenic and chromium precipitation
- Metals Immobilization: Uranium phosphate precipitation
- ERD: Iron sulfide mineral formation
- 2017 Satellite Imagine contents Finalist

2018 Initial Field Testing

- Iron sulfide mineral formation confirmed
- Nickel sulfide precipitation testing ongoing
- Patent pending

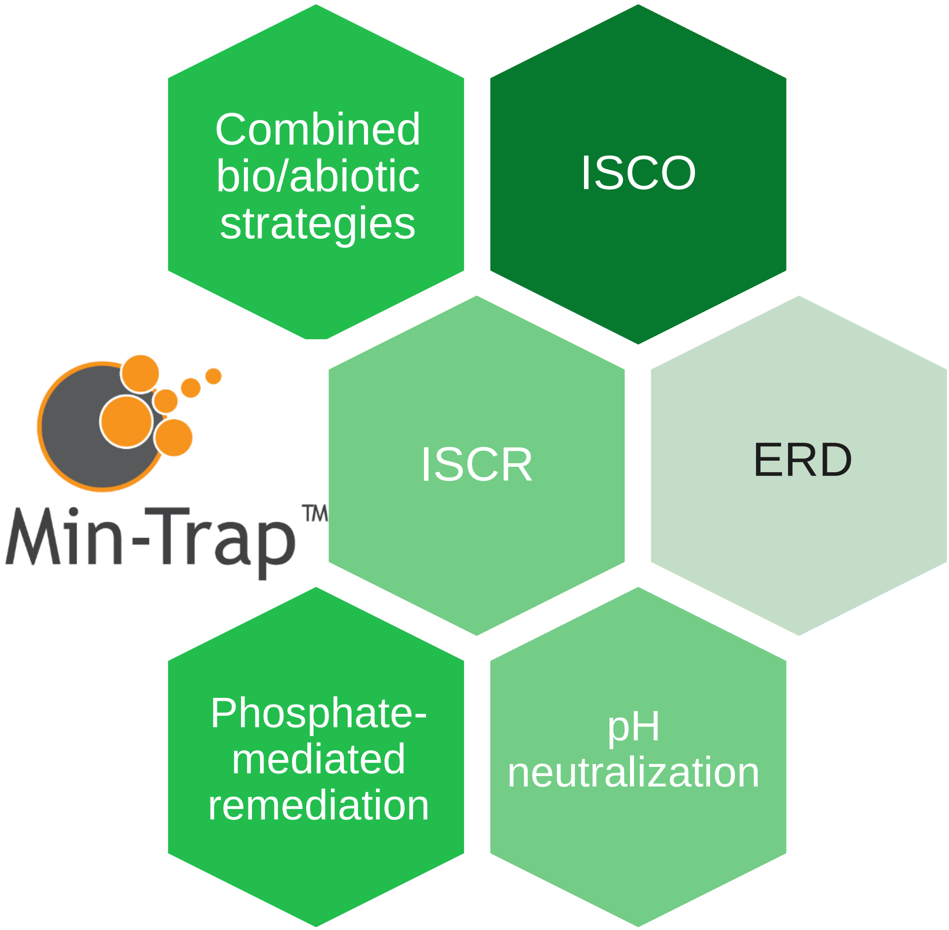
2019- Technology validation and demonstration

- ESTCP funding to validate Min-Trap^{TM} performance and develop standard practices at Dept of Defense sites
- Develop techniques to quantify characteristics of minerals formed in Min-Traps

Expand Applications

- Increased use on new project sites and new applications
- Additional capabilities (mineral reactivity, microbial analyses, flux measurement, isotope analyses, etc.)

- Fills major data gap for metals and CVOC treatment performance evaluations
- Inexpensive and easy to use
- Can advise treatment program and expected treatment behavior, longevity, permanence
- Applicable anywhere you have active precipitation or dissolution of minerals



Questions

Acknowledgements

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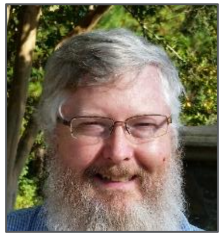

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