DOCUMENTING IN SITU REACTIVE IRON MINERAL FORMATION WITHOUT DRILLING: A NEW MONITORING WELL BASED APPROACH

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

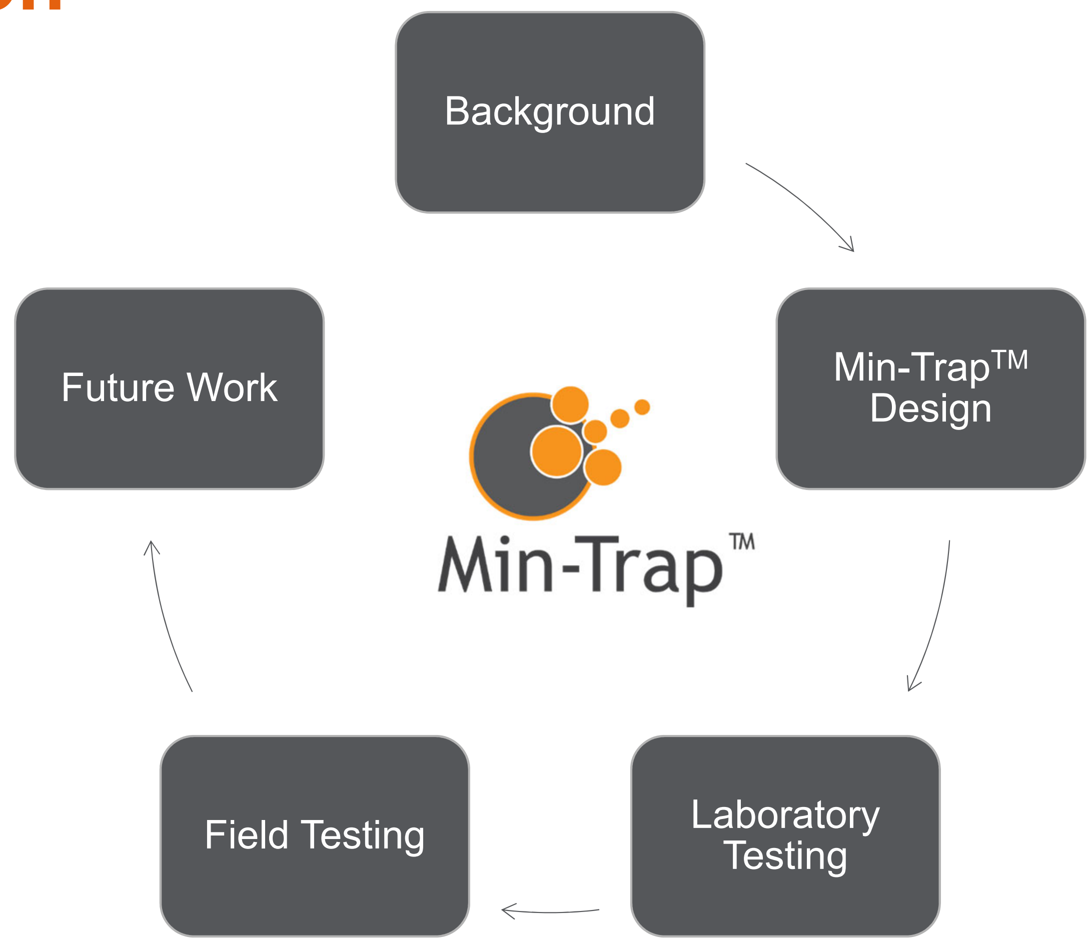
April 17, 2019

Today’s Presentation

Describe results of lab and field testing of a new monitoring well based sampling tool to cost effectively provide site specific data to evaluate the formation of reactive iron minerals

Implications for abiotic degradation processes, longevity of passive treatment potential stored in reactive minerals, and

Ultimately, remedial strategy development and interactions with regulatory agencies and stakeholders



Agenda

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

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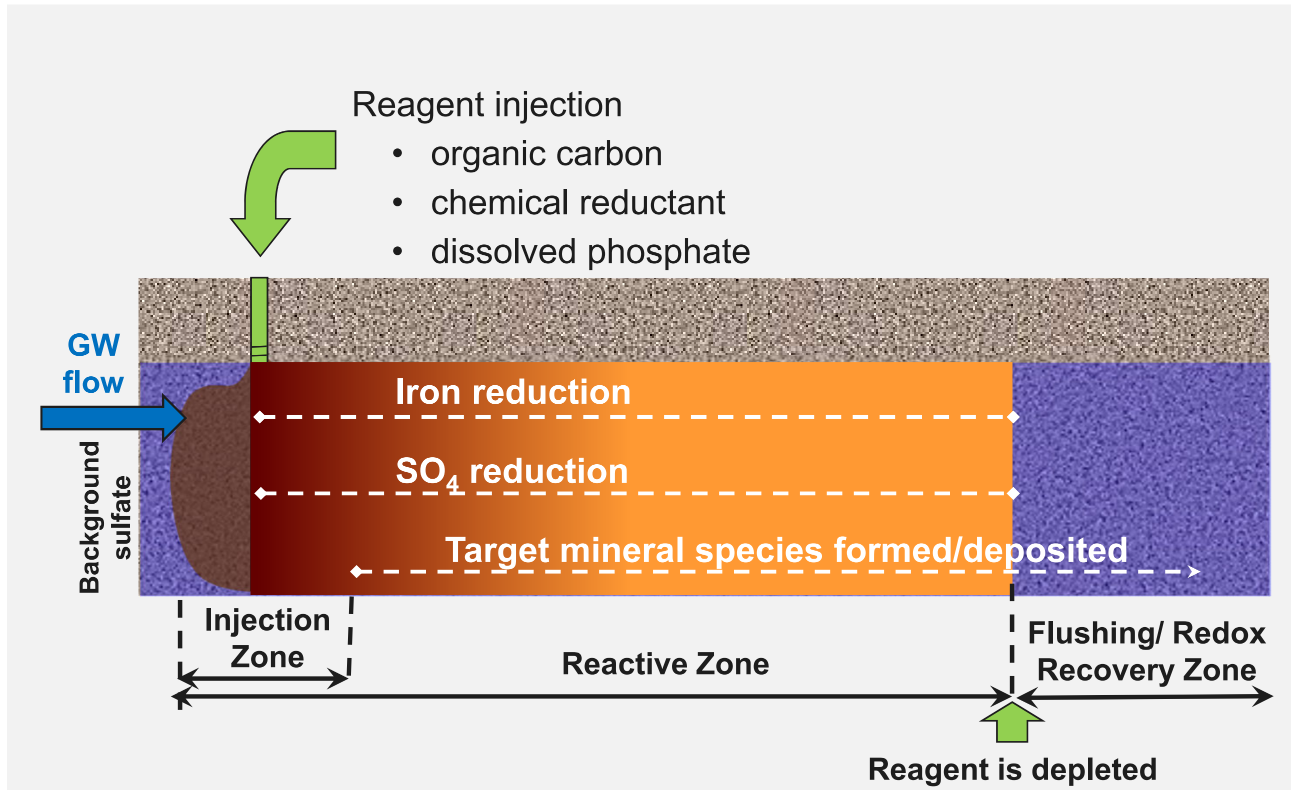
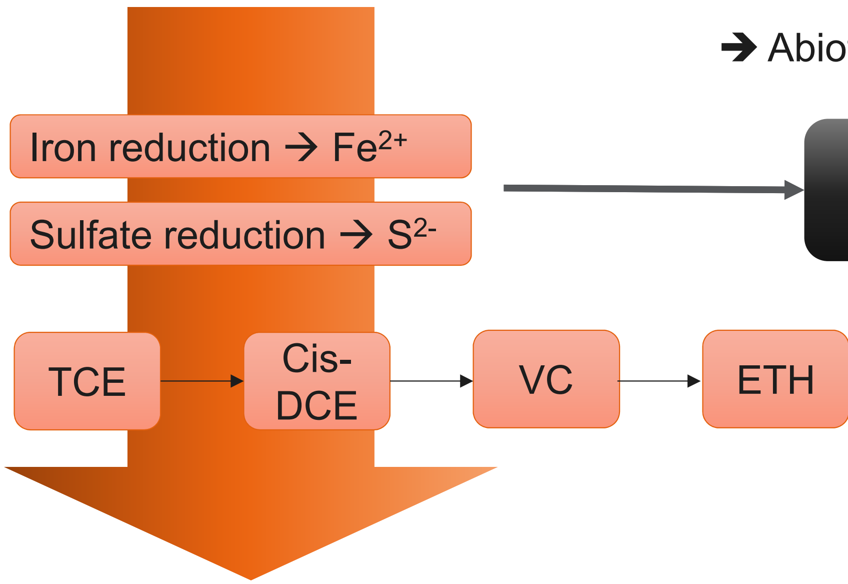
Enhanced Mineral Precipitation

1. Metal sulfides (and others) for in situ metals sequestration
2. Reactive reduced iron minerals abiotically degrade chlorinated solvents



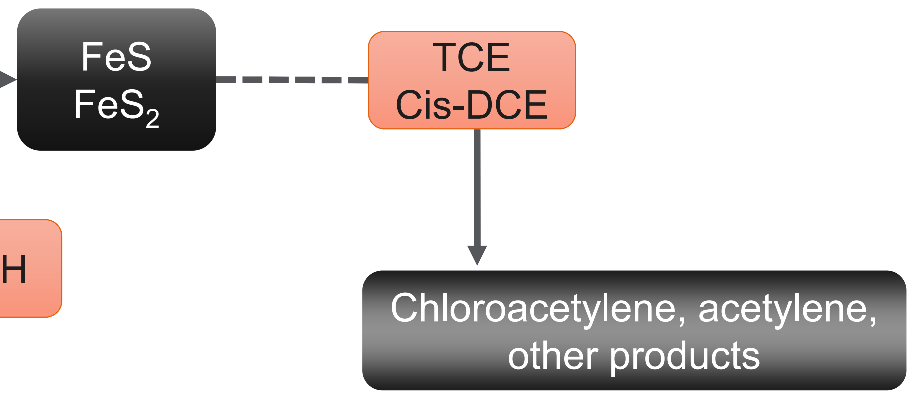
Anaerobic Biodegradation

Fermentable organic carbon provides the electrons that drive the sequential reductive dechlorination process



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
- ➔ Abiotic degradation products not easily measured



How do we know what's really happening in situ?

Groundwater samples

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

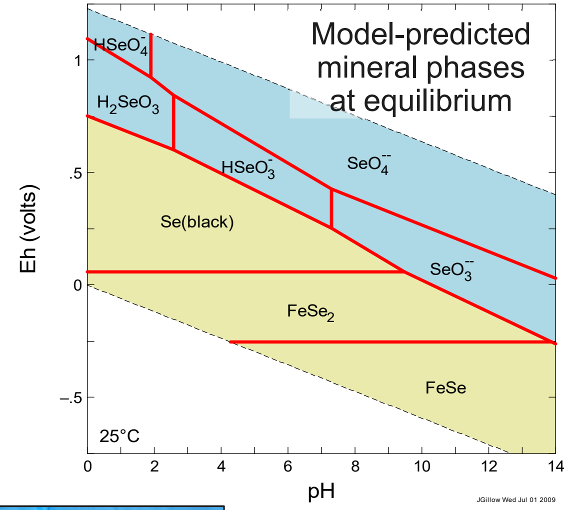
Geochemical modeling

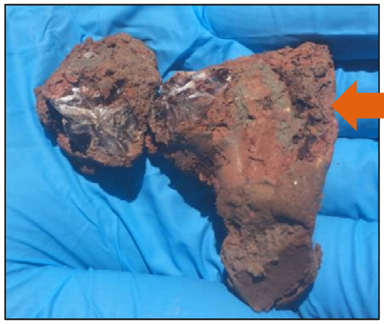
- All models have simplifying assumptions
- Predicts equilibrium conditions (kinetics not considered)

Mineral 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

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Environmental Science & Technology — Article — Cite This: Environ. Sci. Technol. XXXX, XXX, XXX−XXX — pubs.acs.org/est

Mechanisms for Abiotic Dechlorination of Trichloroethene by Ferrous Minerals under Oxic and Anoxic Conditions in Natural Sediments

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ELSEVIER — Geochimica et Cosmochimica Acta 74 (2010) 2025–2039 — Geochimica et Cosmochimica Acta — www.elsevier.com/locate/gca

Impact of iron sulfide transformation on trichloroethylene degradation

Y. Thomas He*, John T. Wilson, Richard T. Wilkin

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 919 Kerr Research Drive, Ada, OK 74820, USA

Groundwater Monitoring & Remediation

Factors Controlling In Situ Biogeochemical Transformation of Trichloroethene: Field Survey

by Kent Whiting, Patrick J. Evans, Carmen Lebrón, Bruce Henry, John T. Wilson, and Erica Becvar

Review of Abiotic Degradation of Chlorinated Solvents by Reactive Iron Minerals in Aquifers

by Y. T. He, J. T. Wilson, C. Su, and R. T. Wilkin

ELSEVIER — Science of the Total Environment — journal homepage: www.elsevier.com/locate/scitotenv

Remediation of chlorinated ethenes in fractured sandstone by natural and enhanced biotic and abiotic processes: A crushed rock microcosm study

Rong Yu[a], Richard G. Andrachek

Groundwater Monitoring & Remediation — Advances in Remediation Solutions

New Tools for Assessing Reactive Mineral-Mediated Abiotic Contaminant Transformation

EPA United States Environmental Protection Agency — EPA 600/R-09/115 | December 2009 | www.epa.gov/ada

Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water

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Tony Lee
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National Risk Management Research Laboratory, Ada, Oklahoma 74820

FINAL REPORT

Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Ethene Sites

ESTCP Project ER-201129

ESTCP

DECEMBER 2015

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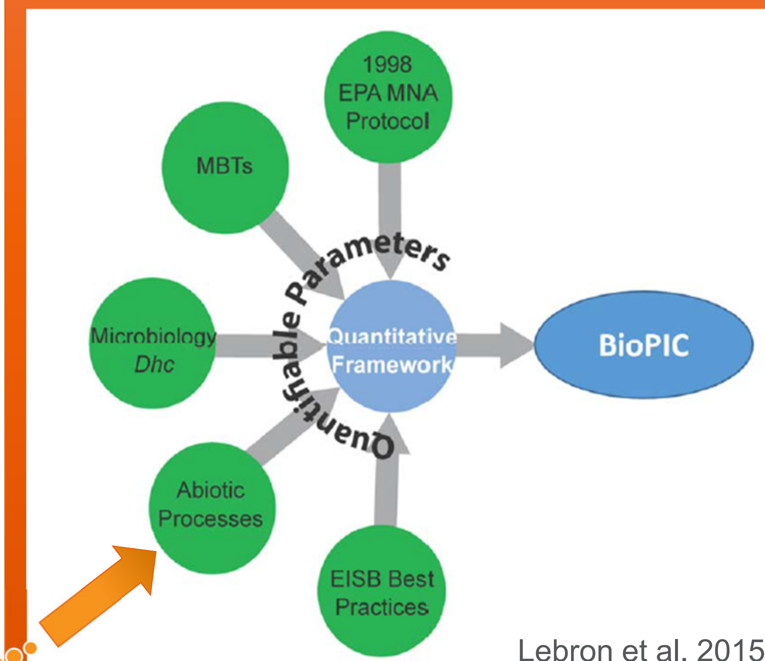
Existing tools infer the potential for abiotic degradation processes based on groundwater data



Min-Trap™

Min-Traps

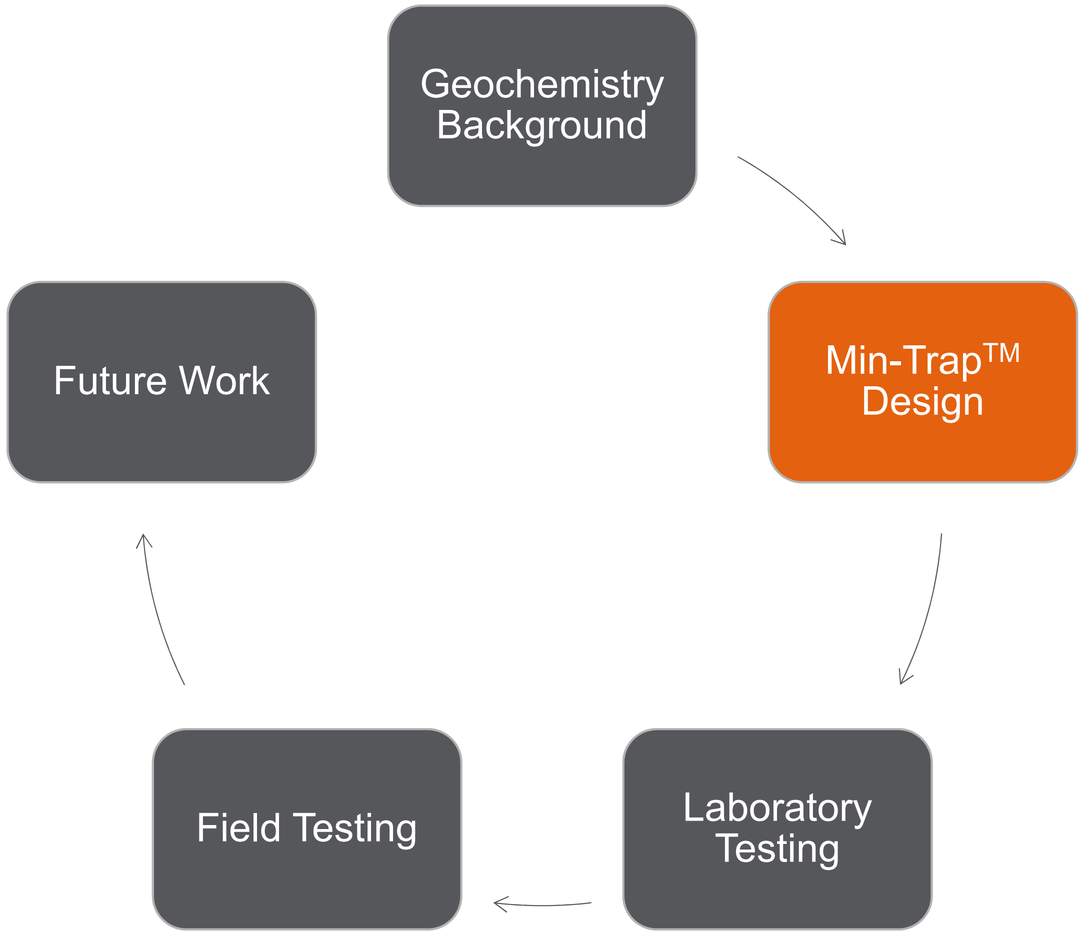
Conclusively document the formation of specific minerals

Therefore verify important geochemical and remedial processes that usually are only inferred.

- ➔ 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

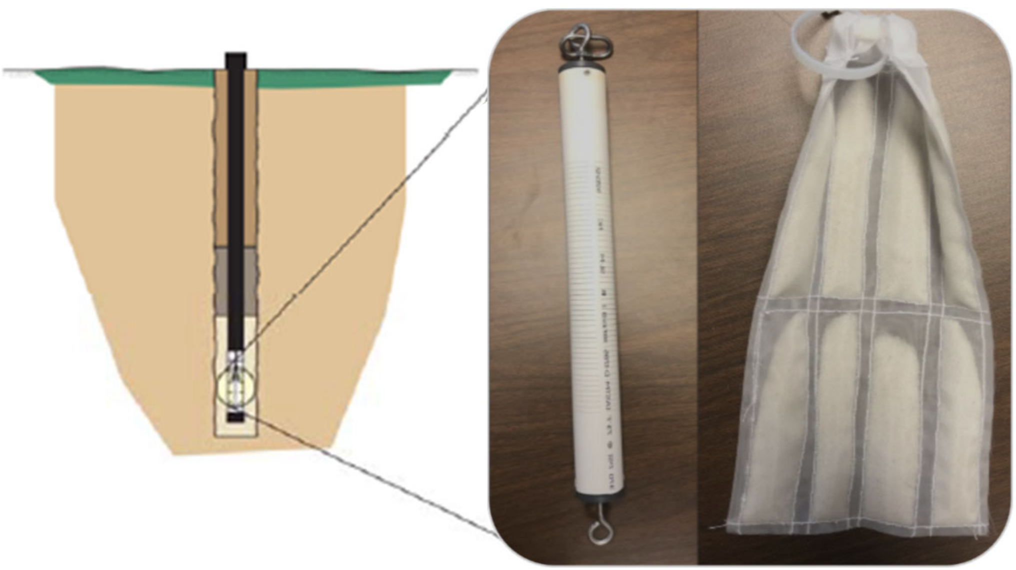
Process	Contaminants	Target Observation within the Min-Trap™
Enhanced Reductive Dechlorination & Combined Biotic/Abiotic Treatment	Chlorinated solvents	Reactive iron mineral formation, such as magnetite, mackinawite, and/or pyrite
In-situ Chemical Oxidation	Metals that co-precipitate or adsorb to iron 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™

Agenda


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

Min-Trap Design

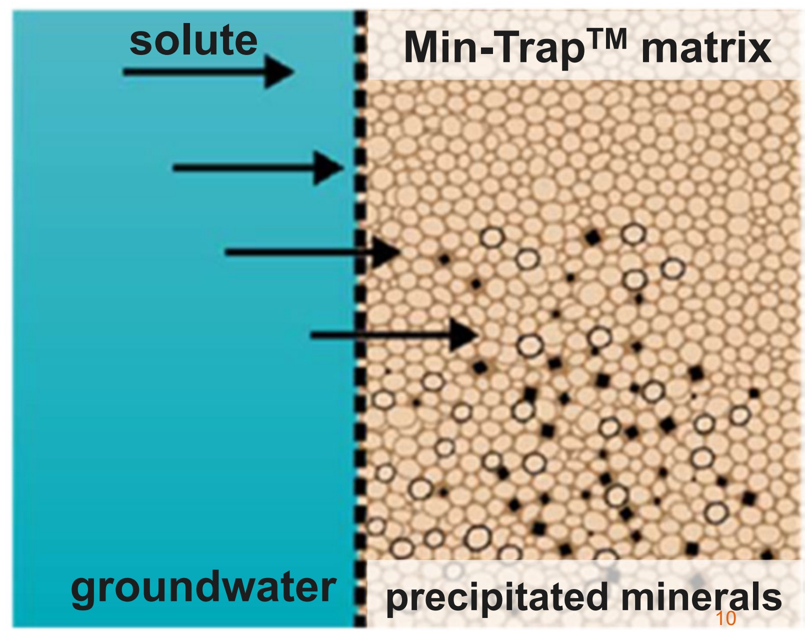
- ➔ A 15-inch long PVC slot-screen housing containing multiple porous media pillows
- ➔ Customizable porous medium inside mesh pillows acts as a matrix for precipitating minerals
- ➔ Analytical packages are tailored based on technical objectives
- ➔ Manufactured and sold by Microbial Insights



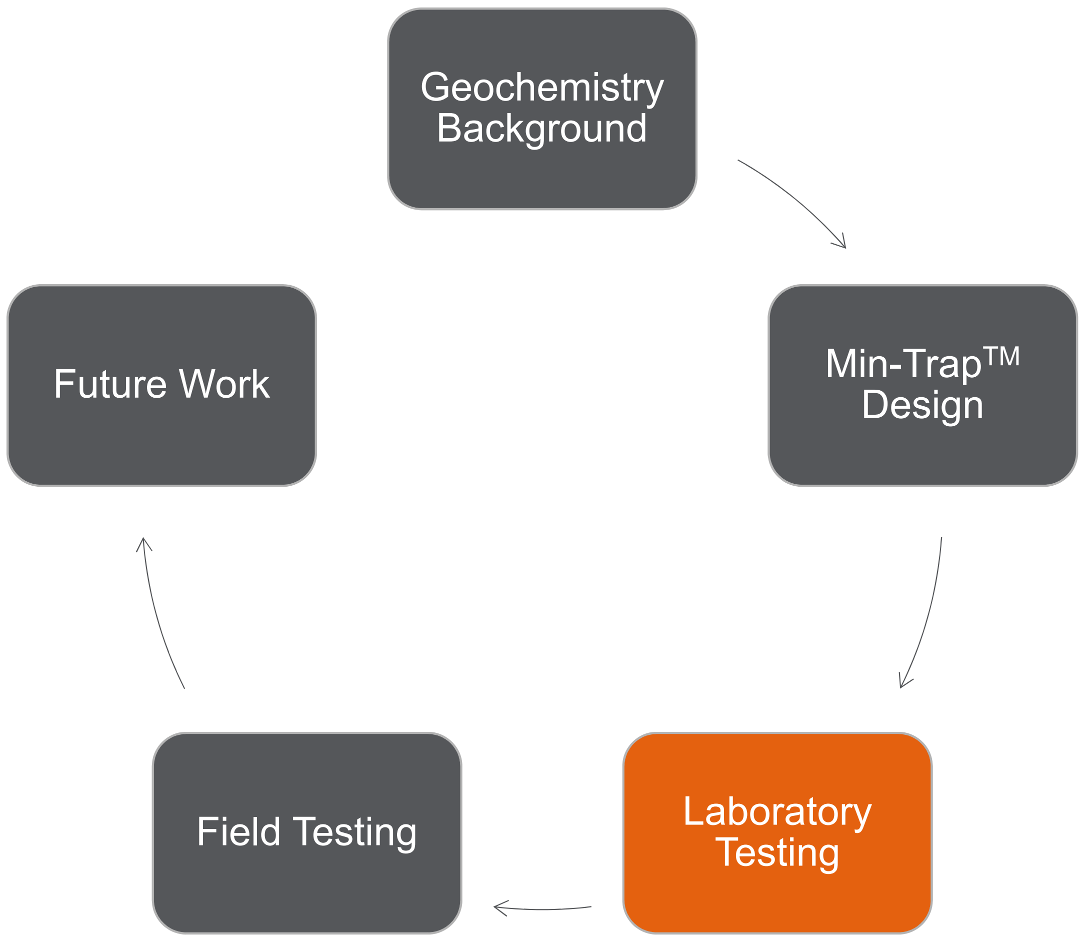
Deployed in standard 2”+ monitoring well

Slotted PVC casing

Porous medium in permeable mesh



Agenda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Bench Testing

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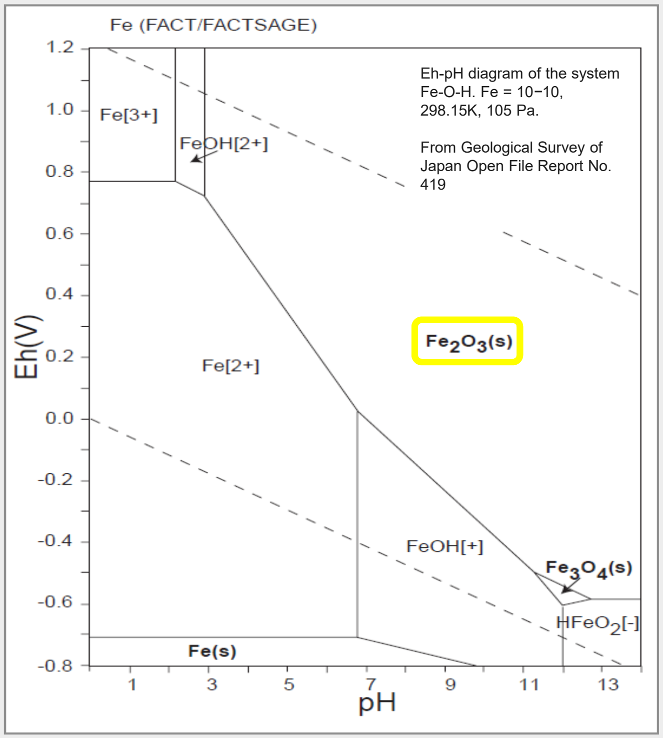
Co-precipitation of arsenic or chromium with iron

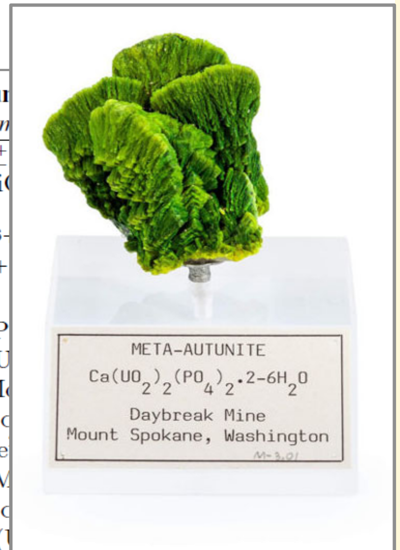


Precipitation of uranium with phosphate

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	$U(PO_4)(OH)(H_2O)_{2,5}$

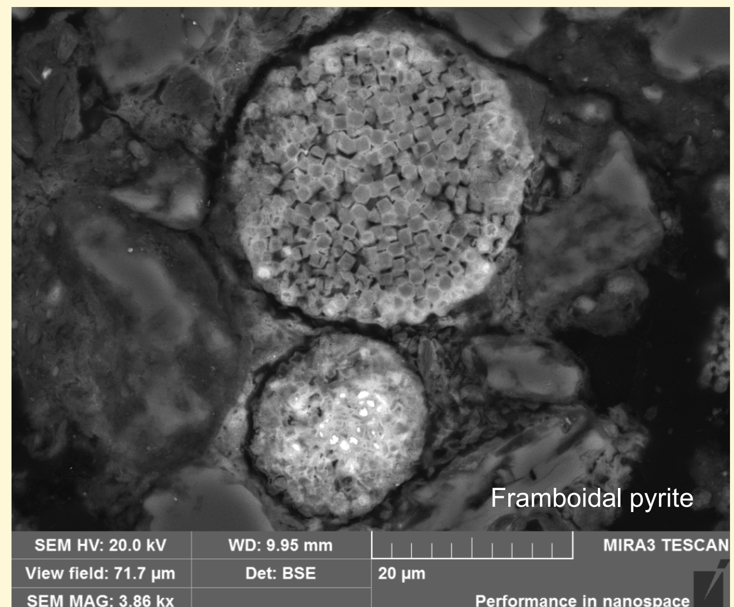
From Závodská et al. 2008. Environmental chemistry of uranium.



Imaged by Heritage Auctions, HA.com

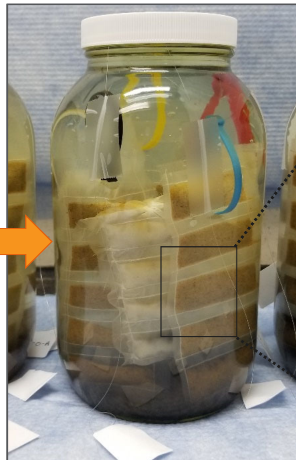
Biological iron and sulfate reduction to form iron sulfides

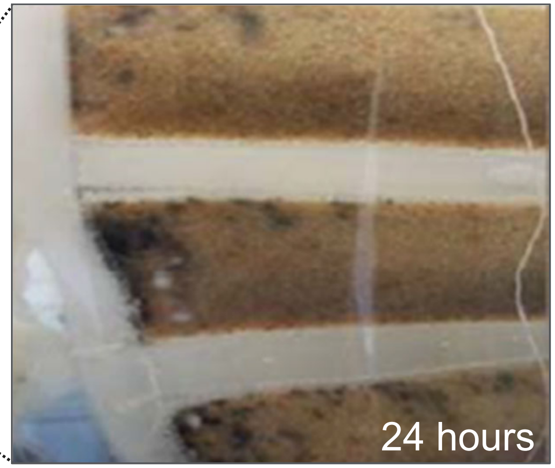
Simulated enhanced reductive dechlorination (ERD)

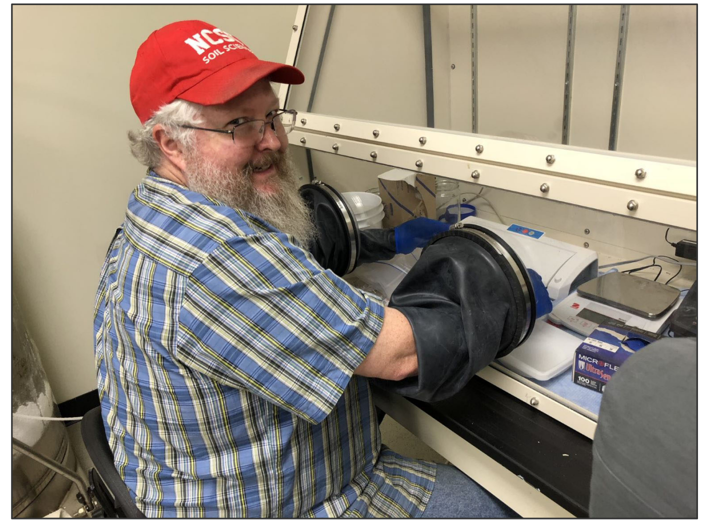


Enhanced reductive dechlorination conditions:

Lactate, ferrous sulfate, and SRB



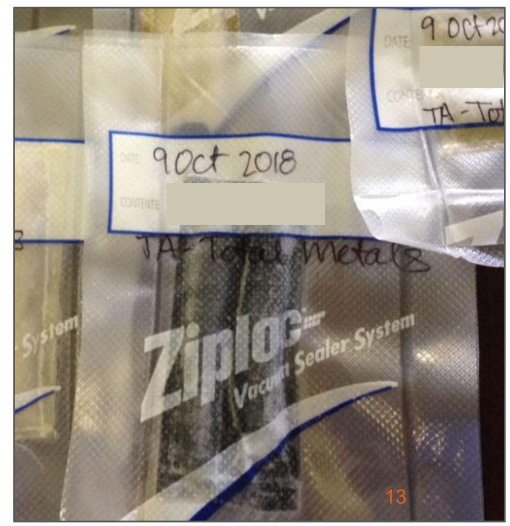




Two weeks

Harvest

Subsample & analyze



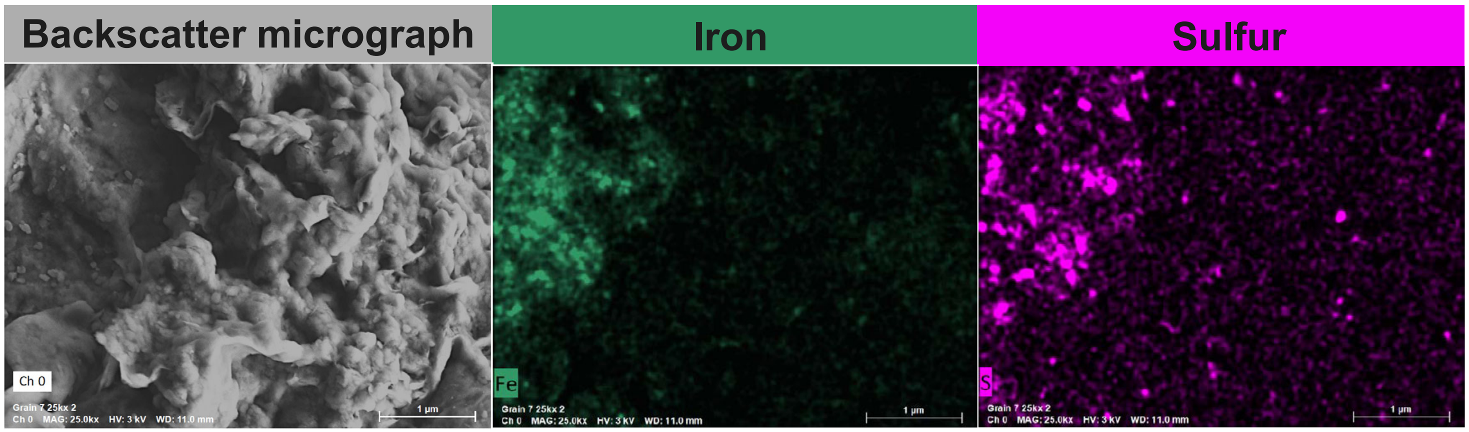
Potentially Applicable Analyses

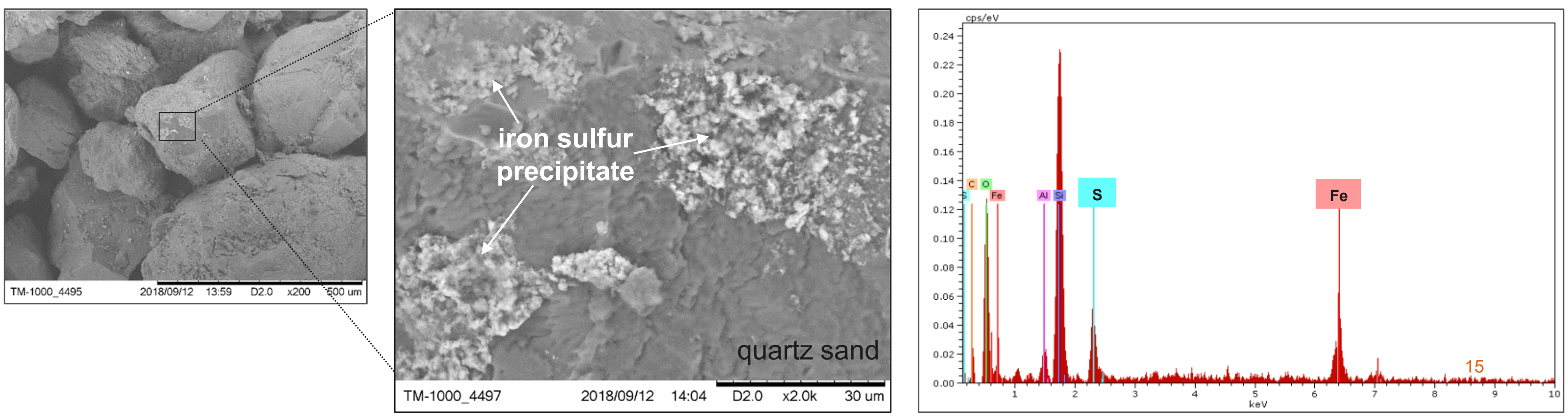
Chemical	• Weak and strong acid soluble iron (WAS, SAS) • Acid-volatile sulfide (AVS) • Chromium-extractable sulfide (CrES)	Biogenic (pseudocrystalline) vs. crystalline minerals Sulfur forms: FeS vs. FeS_2 and S^0
Microscopy	• Light/petrographic • Scanning Electron Microscopy (SEM) • Transmission Electron 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

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

Field Testing

Chloromethanes up to ~20 mg/L

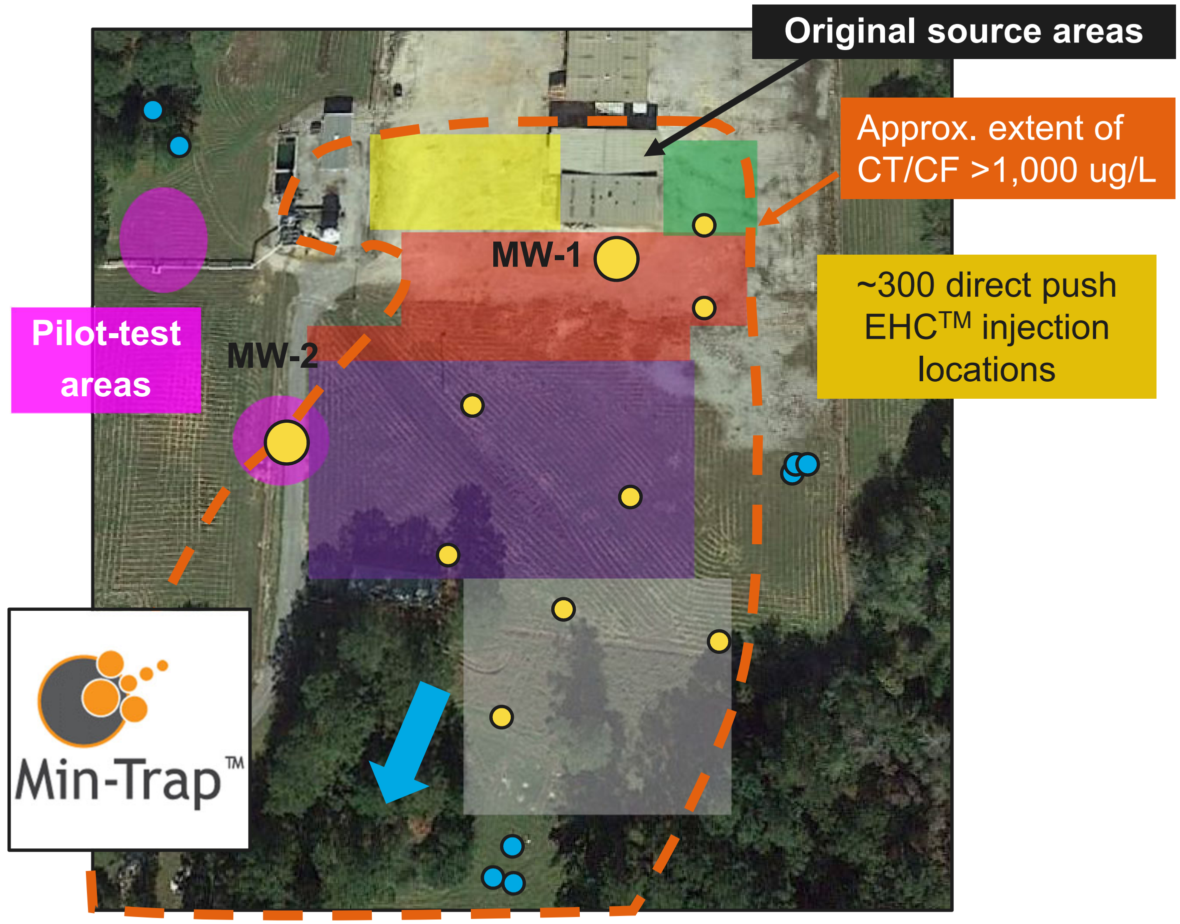
Co-disposed S-containing compounds

Naturally high iron

EHC™ treatment June-August 2018

Min-Traps deployed Aug 2018

Retrieval and analysis October 2018



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

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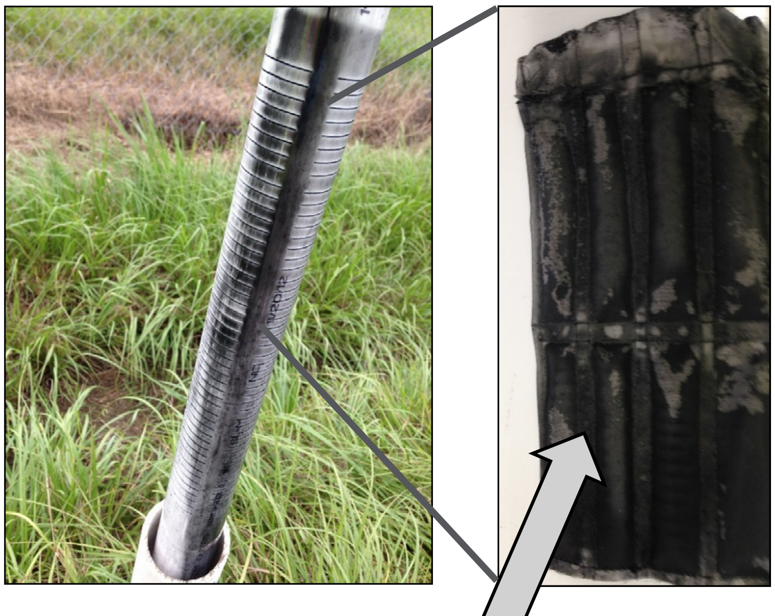
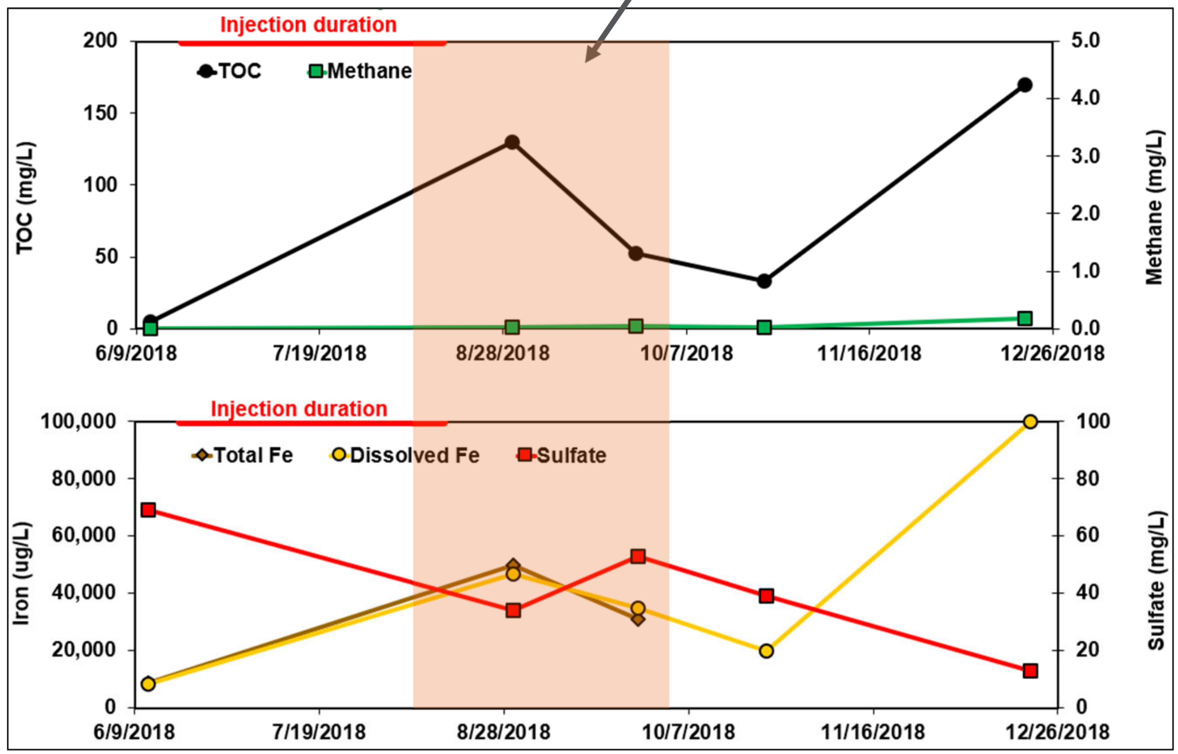
MW-2: located at downgradient edge of EHC™ injection area



Groundwater



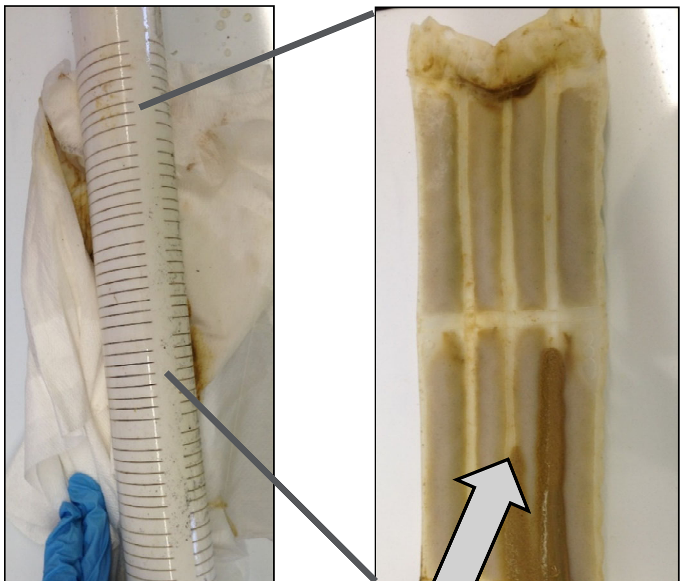
WAS Iron (mg/kg)	SAS Iron (mg/kg)	AVSulfide (mg/kg)	CrESulfide (mg/kg)
Fe^{2+} = 330 Fe^{3+} = 0	Fe^{2+} = 300 Fe^{3+} = 30	240	120

Iron: Solid iron is reduced

Sulfur: Mostly FeS, some FeS_2

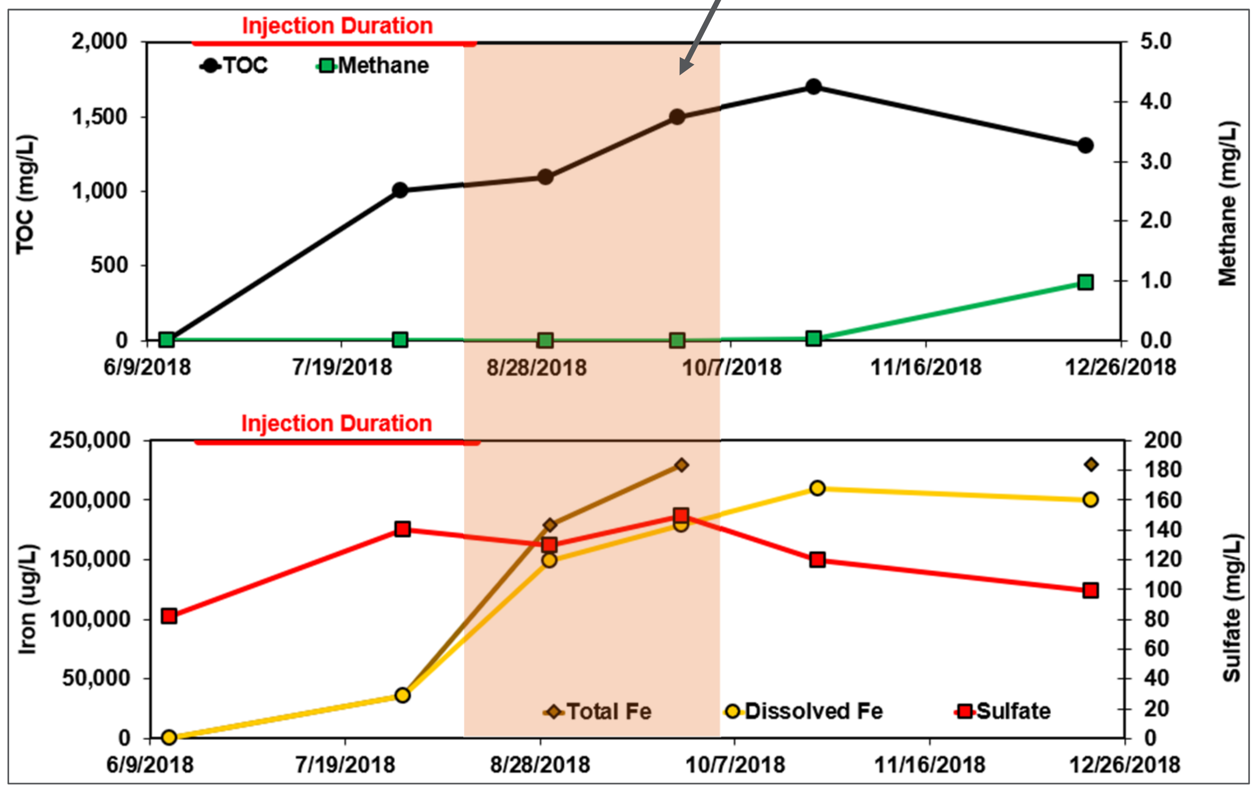
Field Testing

MW-1: Original source area, within injection area



Min-Trap Deployment

Groundwater



WAS Iron (mg/kg)	SAS Iron (mg/kg)	AVSulfide (mg/kg)	CrESulfide (mg/kg)
Fe2+ = 48 Fe3+ = 0	Fe2+ = 55 Fe3+ = 37	0.80	94

<u>Iron:</u> Lower solid iron, some is reduced

<u>Sulfur:</u> Very little FeS; CrES is likely co-disposed S^0

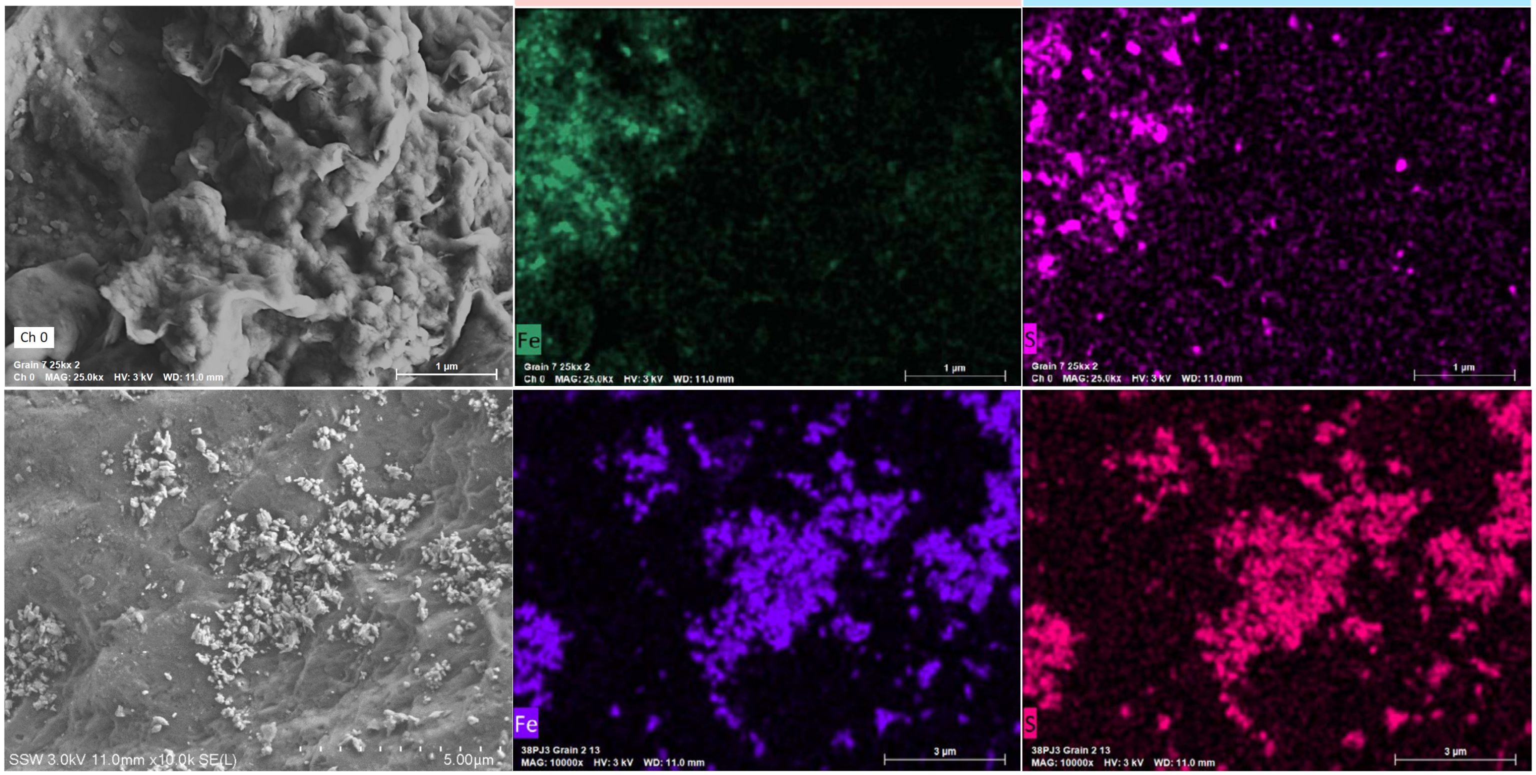
Min-Trap Analysis

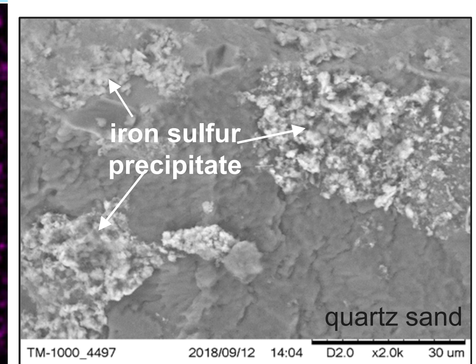
MW-2 Results – SEM with Energy Dispersive X-Ray Spectroscopy (EDS)

	Iron	Sulfur

Lab test

Field test





Min-Trap Analysis: Microbial

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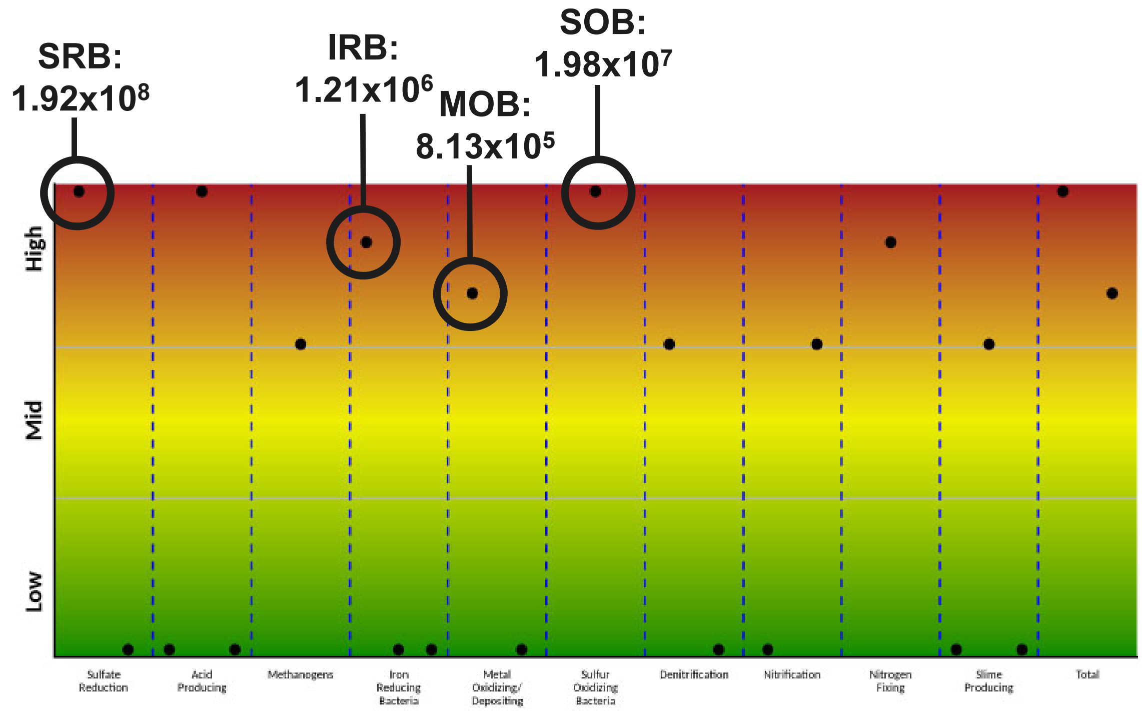
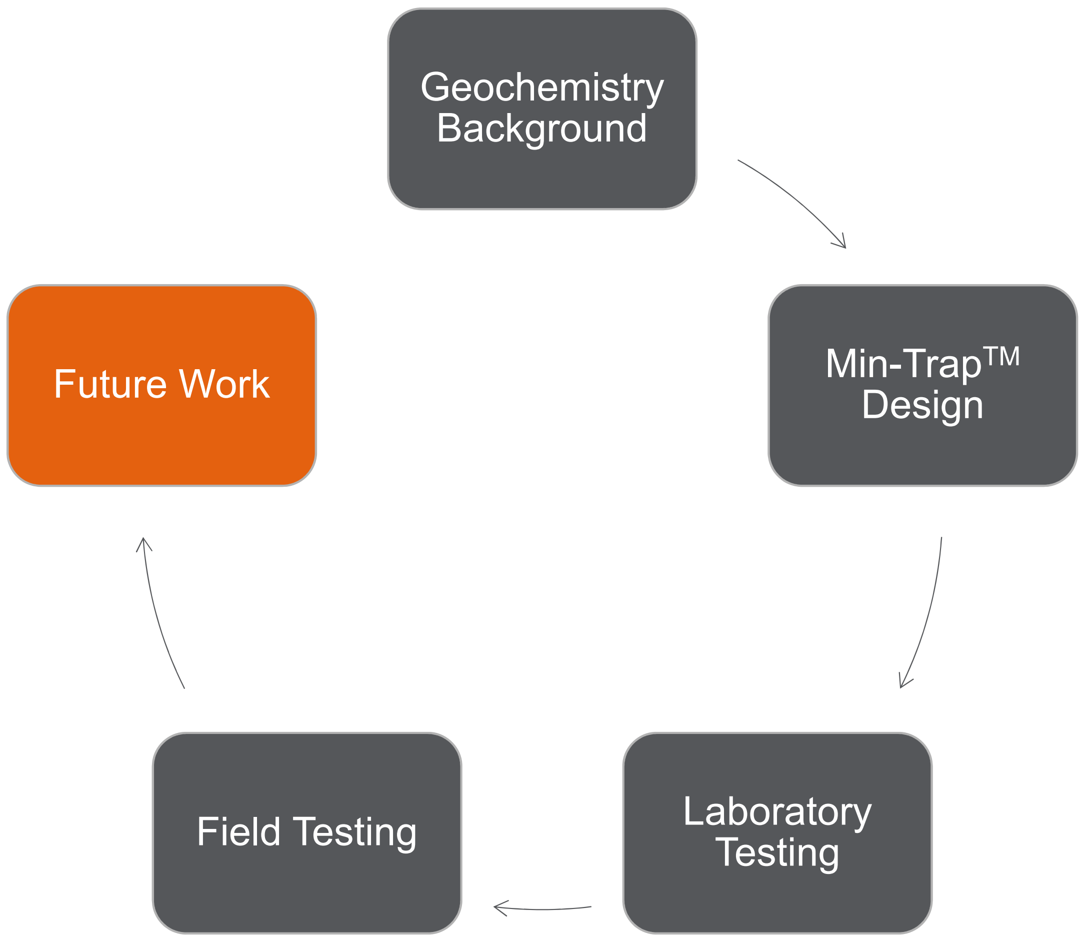
Sample Name Sample Date	MW-2
Microbial Induced Corrosion	cells/g
Total Bacteria (EBAC)	**7.74E+08**
Total Archaea (ARC)	**3.58E+05**
Sulfate Reducing Bacteria (APS)	**1.92E+08**
Sulfate Reducing Archaea (SRA)	<1.00E+04
Methanogens (MGN)	**1.69E+04**
Acetogens (AGN)	<1.00E+04
Fermenters (FER)	**3.11E+08**
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


Geochemistry Background
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Development Path

ESTCP

microbialinsights

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2016-2018 Lab Testing

- Arsenic and chromium precipitation
- Iron sulfide mineral formation

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
- 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.)

ESTCP ER195190

Field validate a monitoring well-based approach to characterize in situ geochemical processes, evaluate abiotic CVOC destruction mechanisms, optimize in situ remedies, and document the potential longevity of passive remedies.

Performance: design and ease of use in field deployment/retrieval, preservation, and analysis

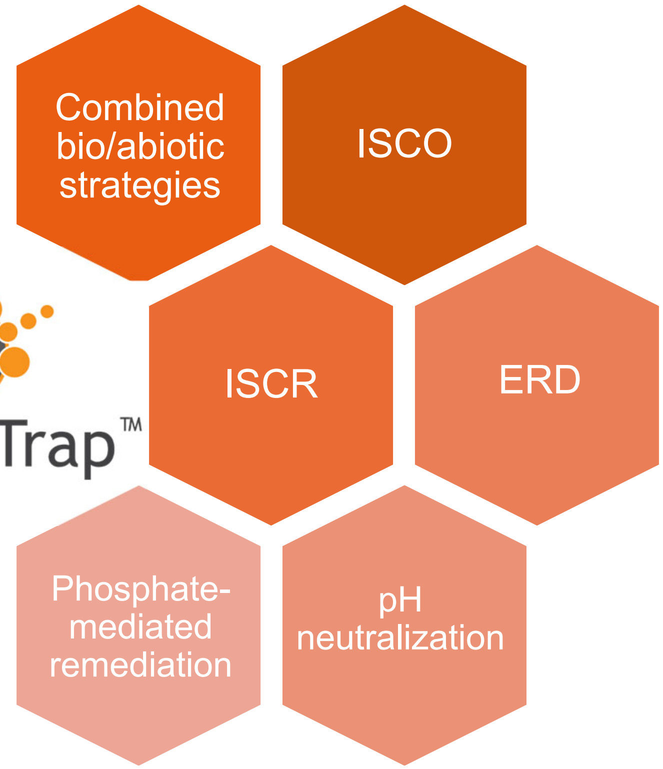
Effectiveness: produce data representative of aquifer conditions and geochemical processes

Influence: impact on remedial decision making and interactions with stakeholders

Primary Quantitative Objectives	Primary Qualitative Objectives
Min-Traps produce expected mineralogical results	Define appropriate conditions for application
Confirm the deployment time	Identify potential challenges and limitations of design
Compare Min-Trap and core sample data	Use results to inform remedial decision making
Evaluate consistency and variability in results	Develop technical guidance for use

- 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

Min-Trap™



Questions?

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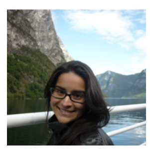
Min-Trap™



Shandra Justicia-Leon, PhD
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Dora Taggart,
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Kate Clark, PhD
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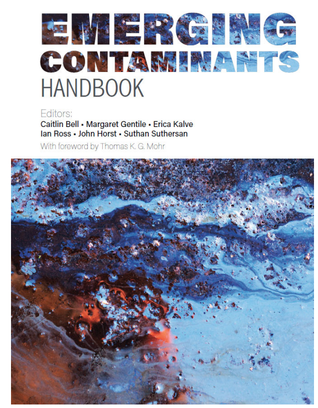
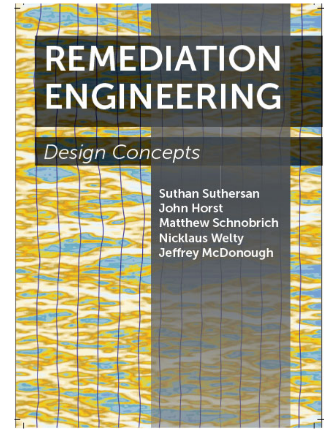
Technical Knowledge

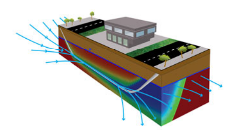




Innovation

Min-Trap™
(Well-Based Mineral Traps)

TISR℠
(Thermal In-Situ Sustainable Remediation)



HRX Well™
(Horizontal Treatment Well)

Oleophilic Bio Barriers (OBBs)
(for Hydrocarbon Sheens)

Zipliner
(Safer DPT Liners)