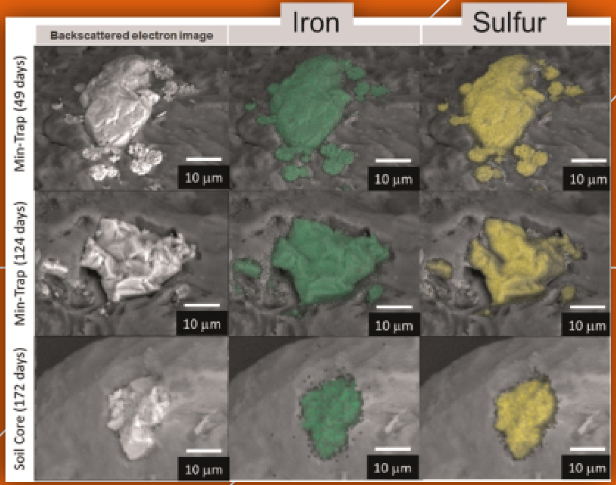
Min-Traps® for Collection and Analysis of Reactive Iron Sulfide Minerals for Abiotic CVOC Degradation

Craig Divine, Shandra Justicia-León, Jennifer Martin Tilton, David Liles (Arcadis)
Dora Taggart and Kate Clark (Microbial Insights)

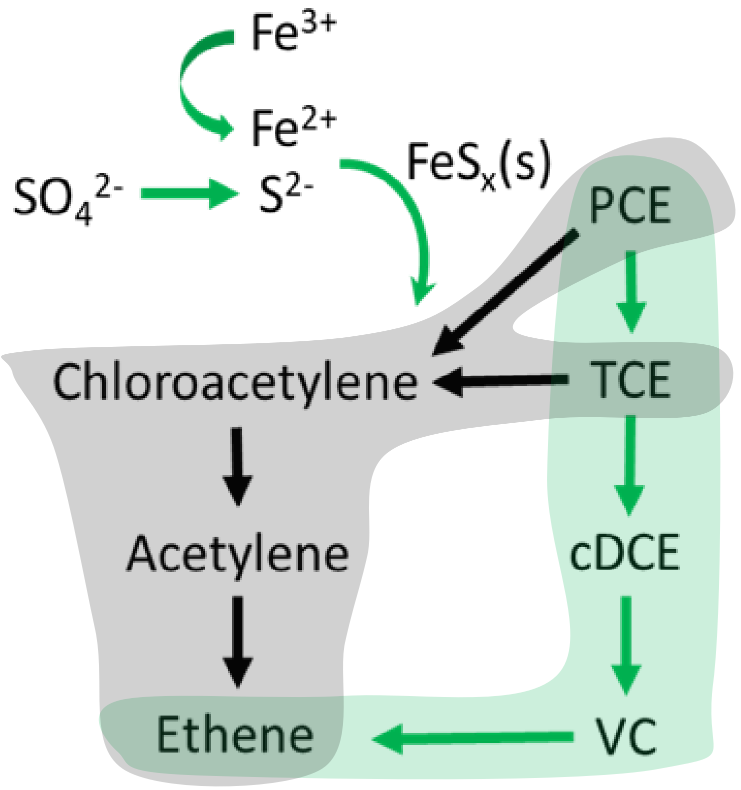


April 9, 2023

In Situ Enhanced Reduction

Abiotic Degradation

- Fermentable organic carbon provides electrons which drive microbial Fe^{3+} and SO_4^{2-} reduction
- Fe^{2+} and HS^- are generated and FeS (mackinawite) and FeS_2 (pyrite) can then form (jointly referred to as FeSx)
- Reductive elimination results in degradation acetylene products not easily measured

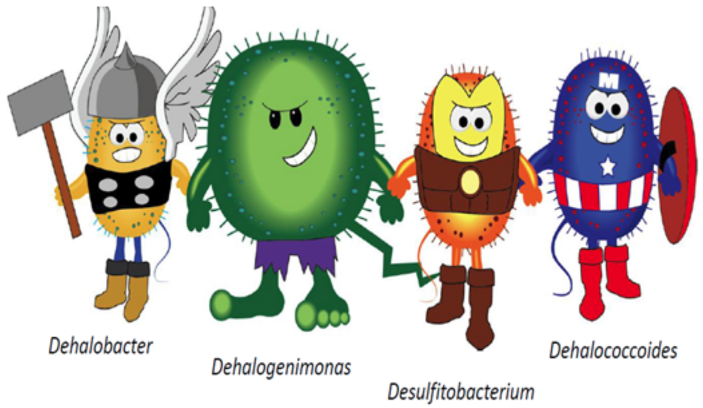


Adapted from Yu et al. (2018) and Horst et al. (2019)

Green arrows indicate biologically mediated processes, **black** arrows indicate abiotic reactions

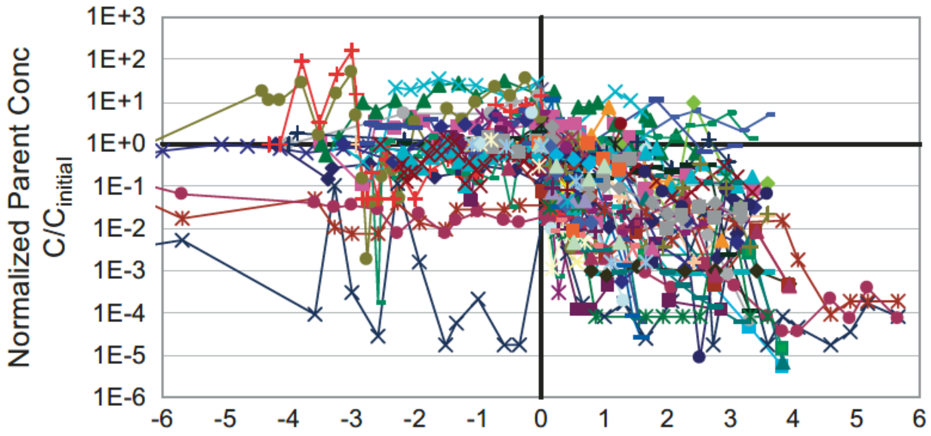
Biotic Degradation

- Fermentable organic carbon provides the electrons that drive the biologically mediated sequential reduction process

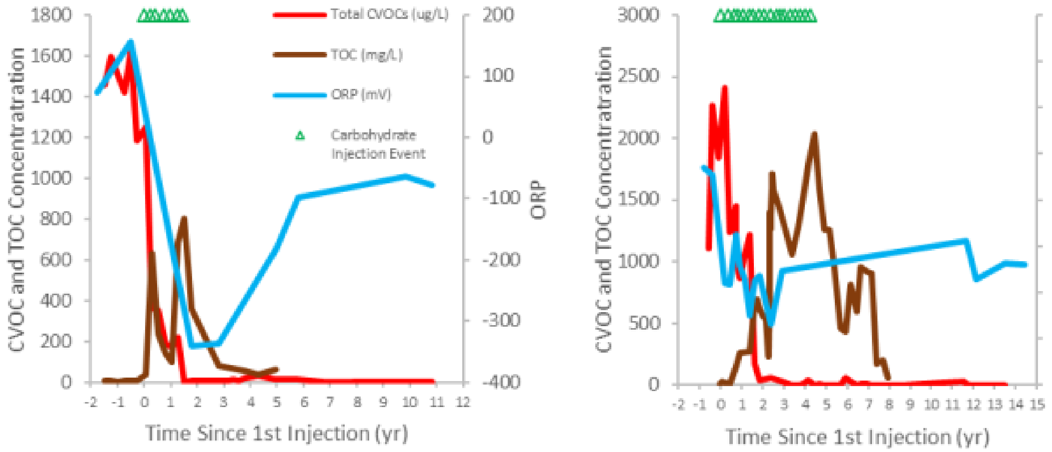


Graphic from Microbial Insights

Evidence for Persistent Synergistic Biotic and Abiotic Treatment

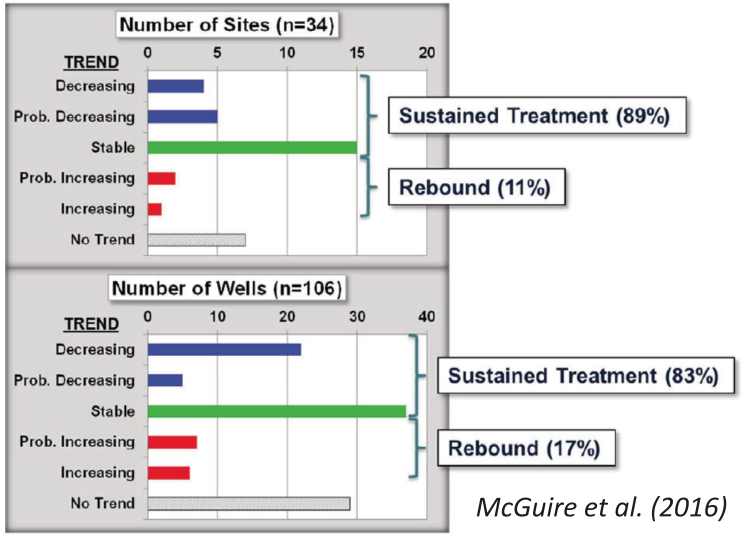


McGuire et al. (2006)



Horst et al. (2022)

- *Biological recycling results in persistent TOC*
- *Long-term redox and treatment likely controlled by newly-formed FeSx*
- *Both processes result in enhanced degradation rates and control "rebound"*



McGuire et al. (2016)

Chlorinated ethene compound	No DVI (days)	DVI added (days)	Difference (days)
PCE	150	85	65
TCE	168	107	61
cis-DCE	236	112	124
VC	193	158	35

Davis et al. (2018)

- *Anaerobic reduction results in **sustained** long-term treatment*
- *Addition of iron can result in faster treatment (and likely increased formation of FeSx)*

There is an opportunity to better optimize the design and operation of these systems, especially the abiotc components

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

Groundwater samples

- Must extrapolate data to solid-phase processes
- Loss of reactive species (e.g., HS^- or Fe^{2+})
- Snapshots in time

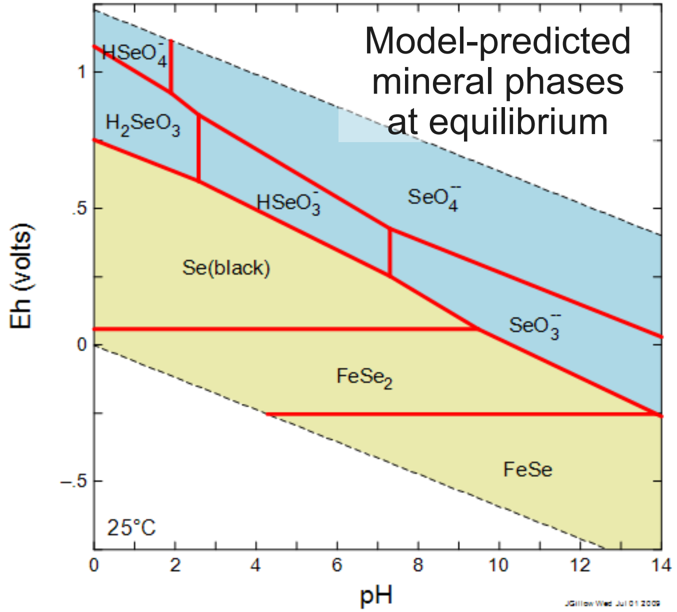
Geochemical modeling

- 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

➔ Collects minerals actively forming at site using existing monitoring well network

➔ Representative of conditions in higher-flux zones

➔ Inexpensive, easily repeated

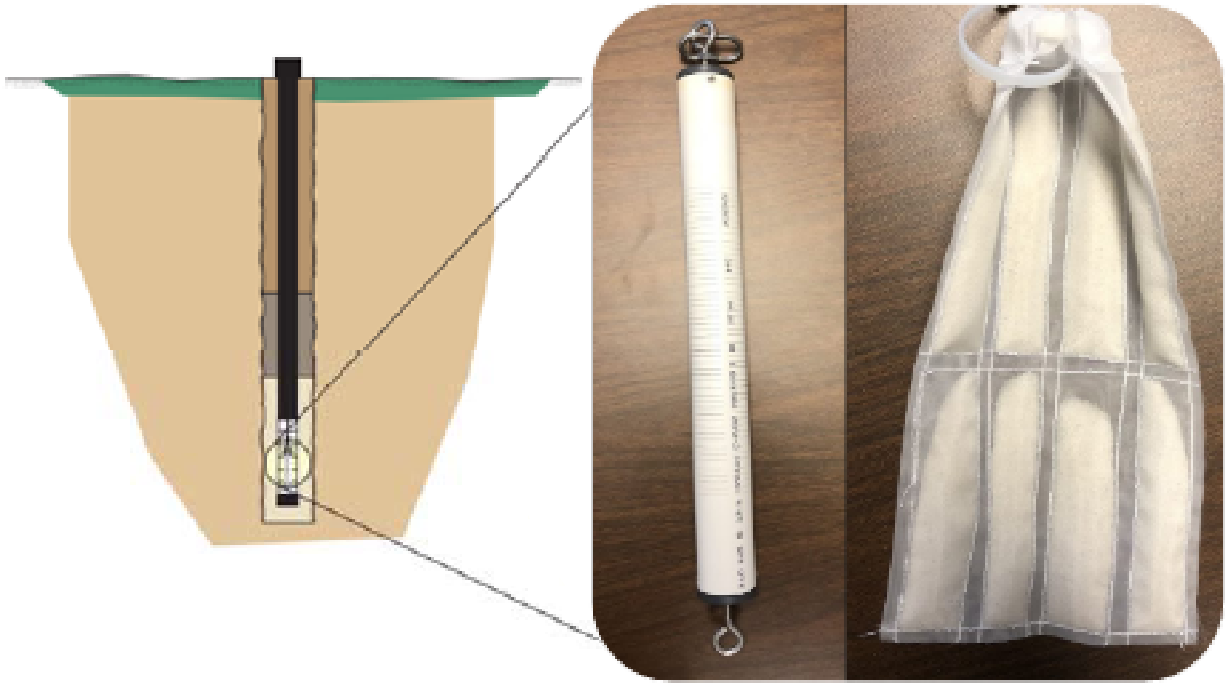
➔ No significant background “noise” in samples

- *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.*

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
- ➔ Patented; manufactured/sold by Microbial Insights

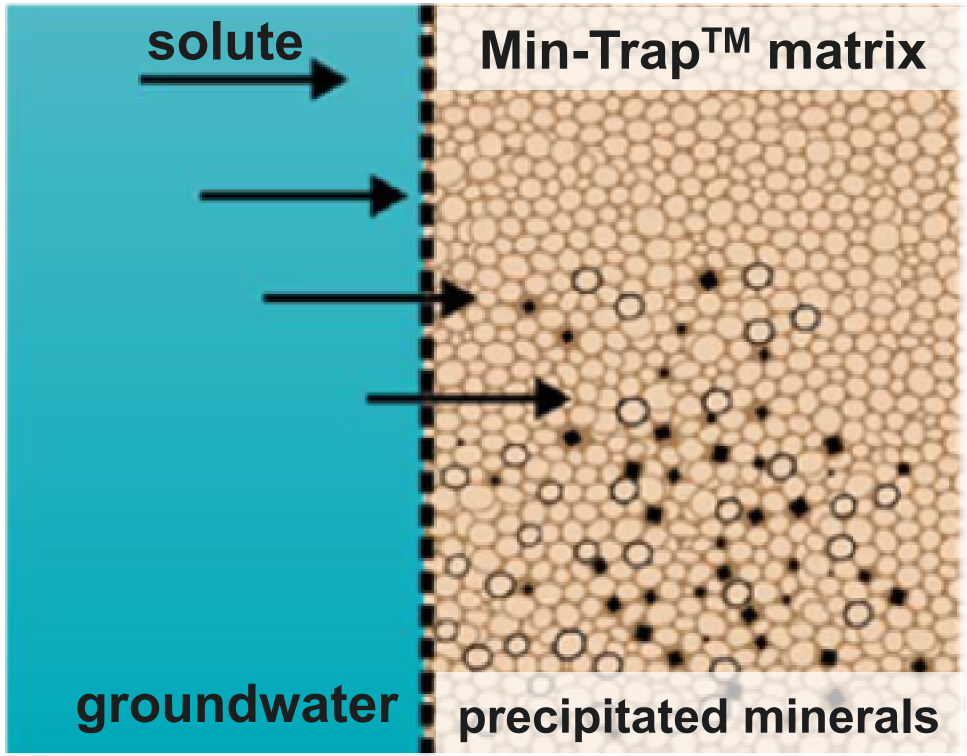
www.microbe.com



Deployed in standard 2"+ monitoring well

Slotted PVC casing

Porous medium in permeable mesh

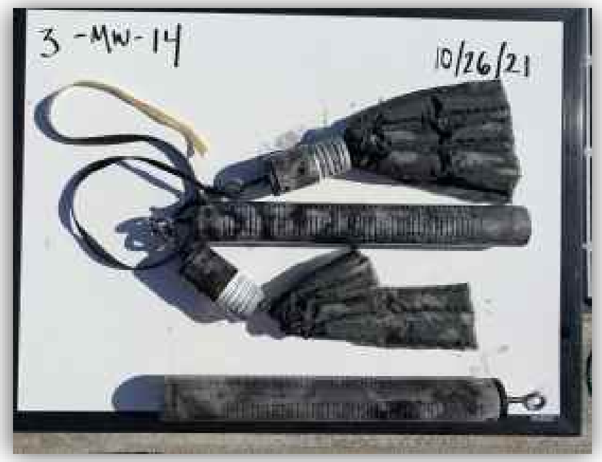


Potentially Applicable Analyses

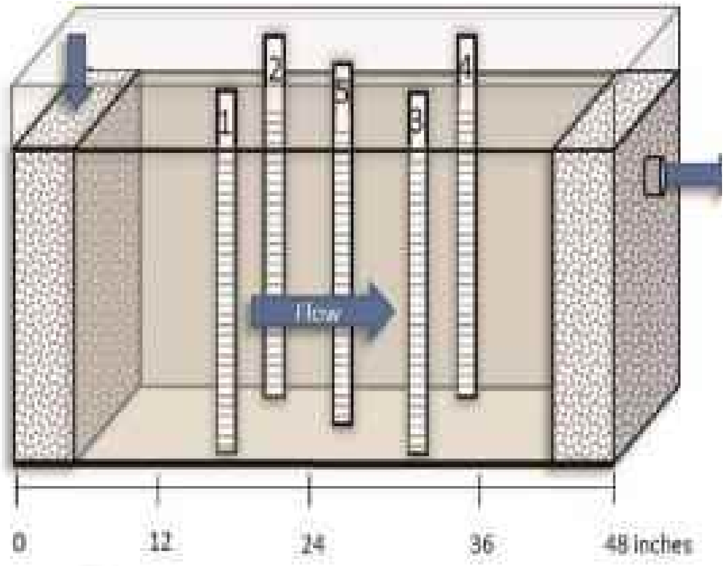
Chemical	• Total Fe • Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) ❖Weak and strong acid soluble iron (WAS, SAS) ❖Acid-volatile sulfide (AVS), chromium-extractable sulfide (CrES)	Fe minerals Biogenic (pseudocrystalline) vs. crystalline minerals Sulfur forms: FeS vs. FeS_2 and S^0
Microscopy	• 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

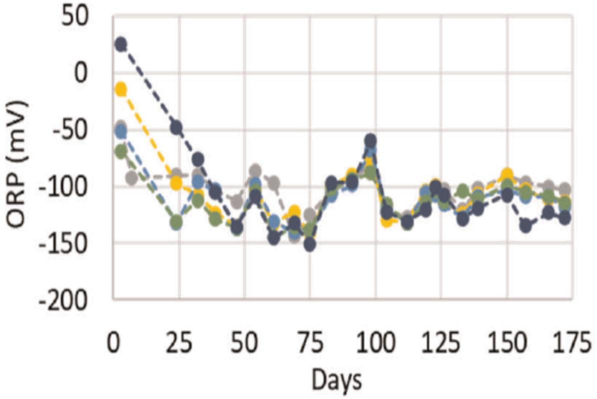
Deployment, Retrieval, and Preservation

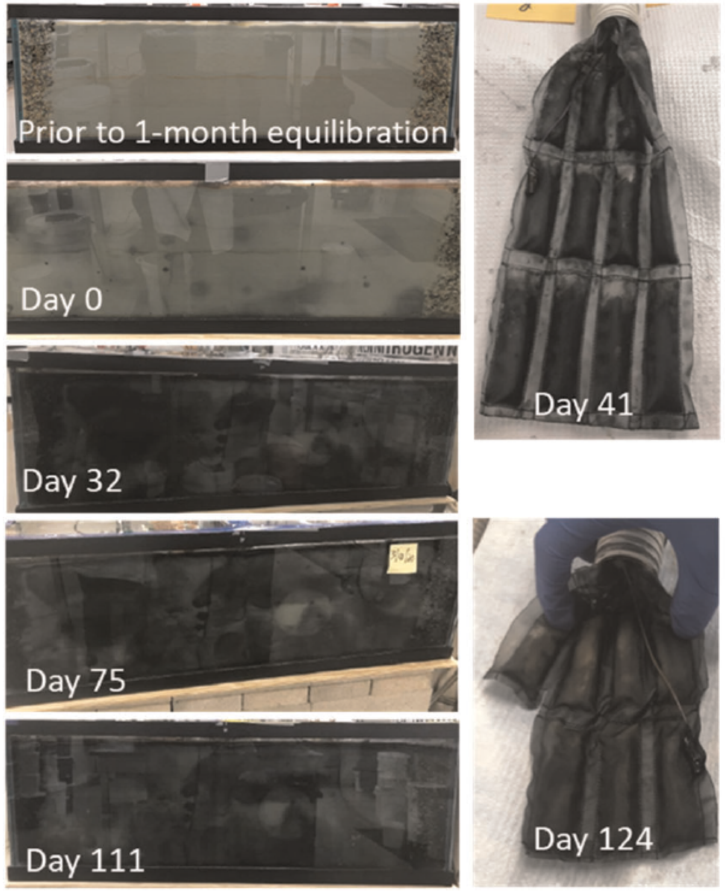
1. Lowering of sampler into monitoring well
2. Minimum incubation time ~4 weeks
3. At retrieval, sample pillows are separated and double-sealed (using a vacuum sealer and O_2 absorbent packets)
4. Can likely hold for a month or more
   - Chill (but don't freeze) - pyrite formation may be induced by freezing (e.g., Hua et al. 2021)



Tank Testing







Begin influent injection
Initial influent concentrations:
558 mg/L Fe^{2+}, 961 mg/L SO_4^{2-},
100 mg/L lactate

Double influent lactate to 200 mg/L

Double influent lactate to 400 mg/L Inoculate with SRB enrichment culture

Add 274 mg/L ascorbate to influent

Stop influent injection
Collect Min-Trap and tank core samples

1-month tank equilibration phase

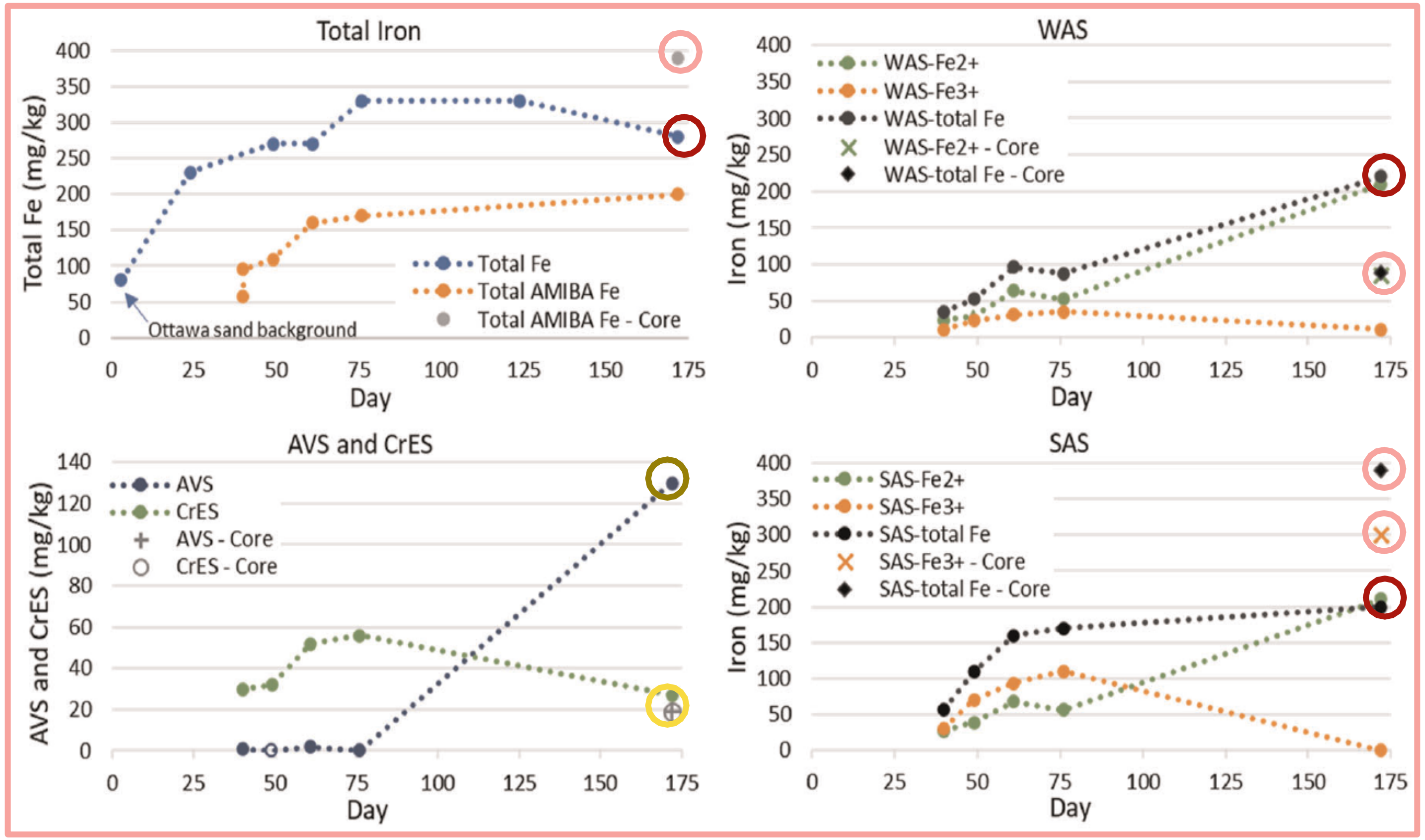
24 40 49 61 76 124 172

Week 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26

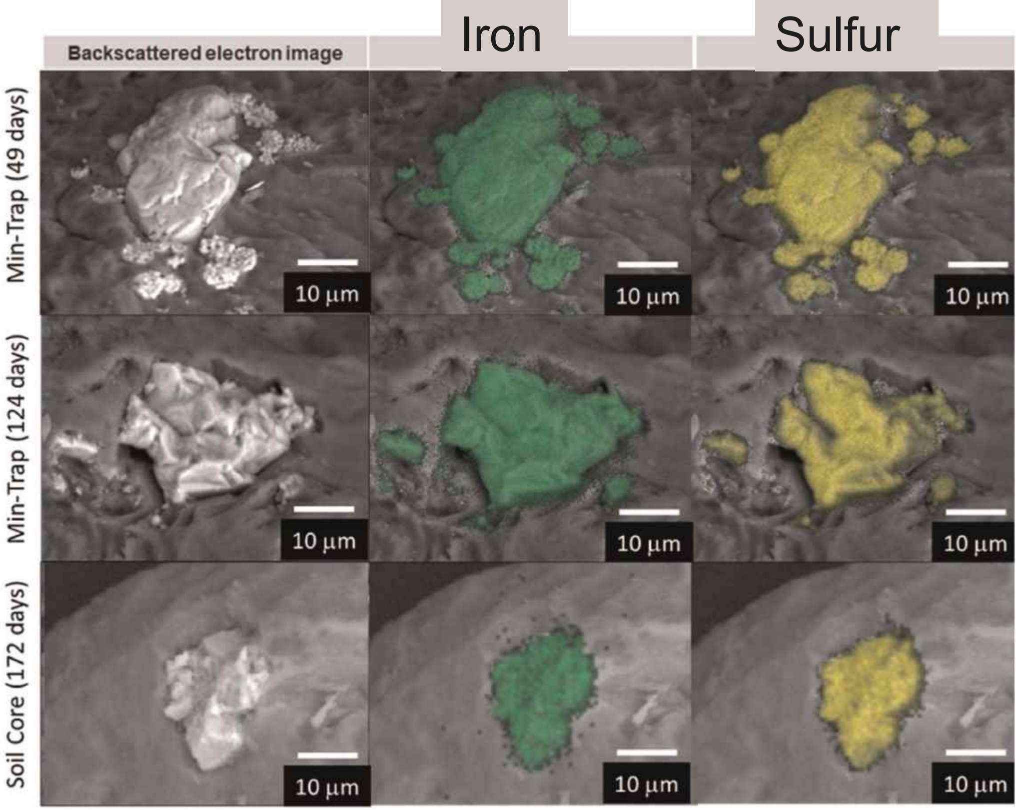
December January February March April May June

Tank Testing

AMIBA

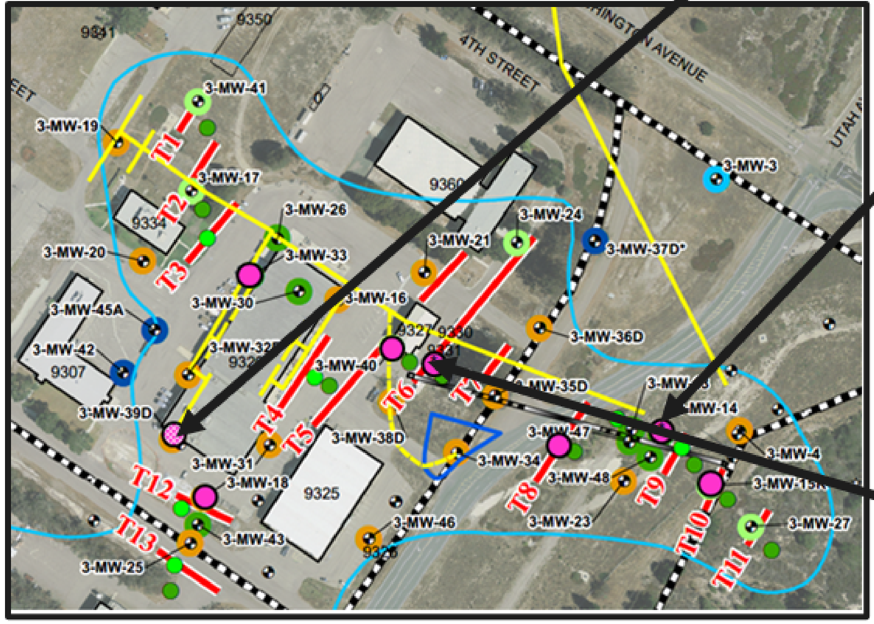


SEM-EDS



AMIBA and SEM-EDS definitively show presence of iron sulfide minerals

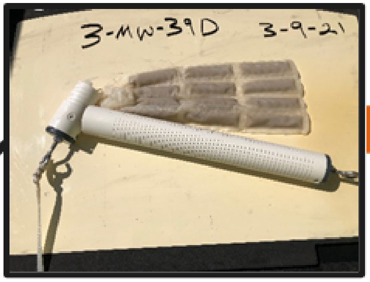
Demonstration Site 1 (“Immature Site”)

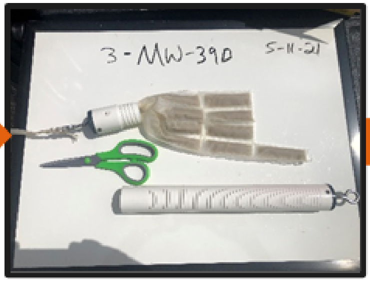


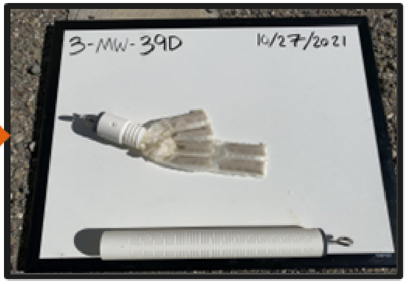
*Min-Traps deployed in 8 wells

2-months	4-months	9-months

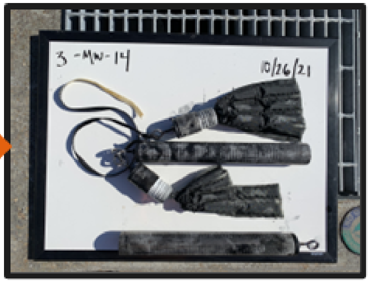
3-MW-39D (background)



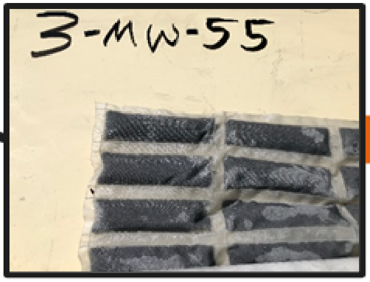


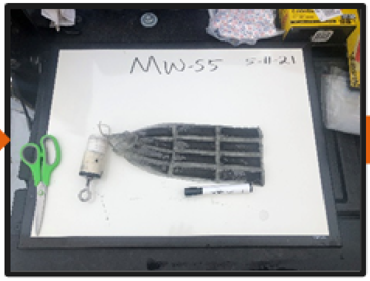


3-MW-14



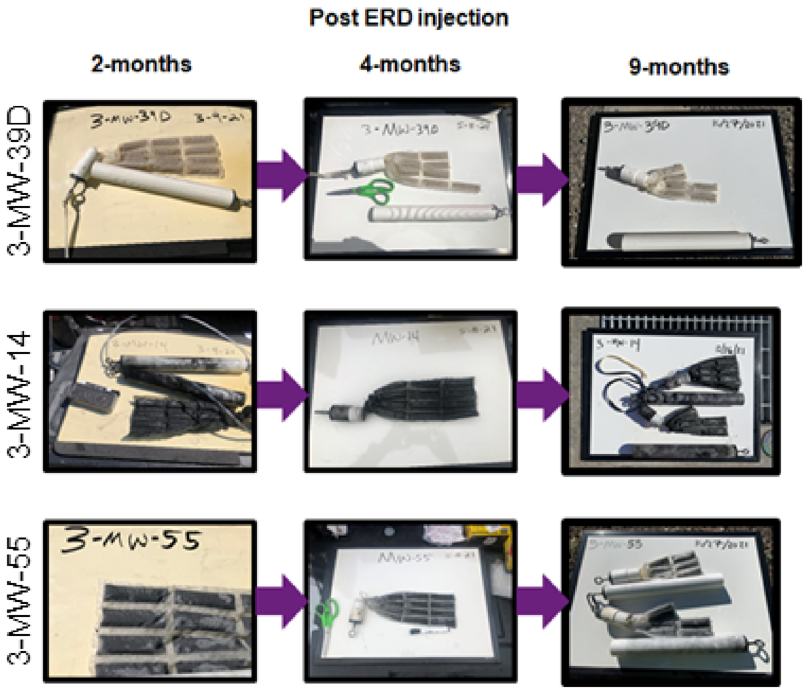
3-MW-55



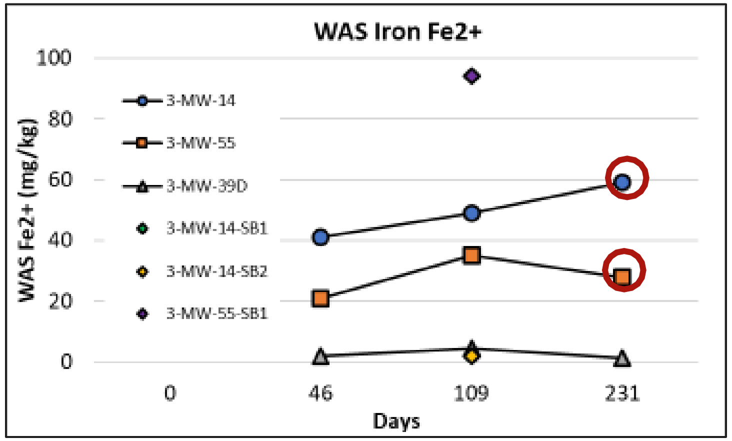


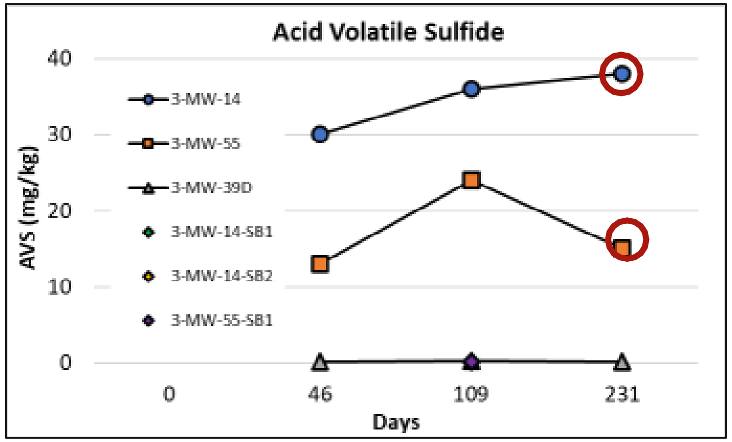
Demonstration Site 1 Results

Visual Observations

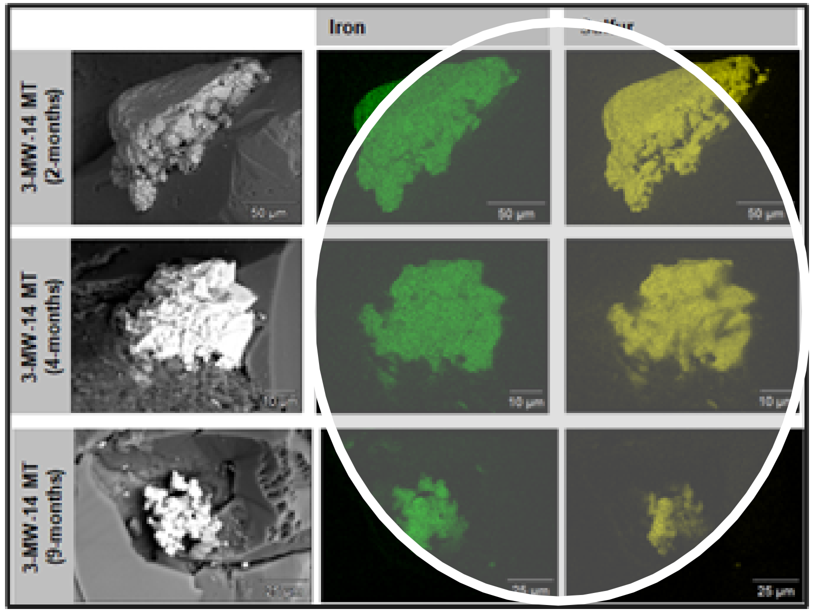


AMIBA



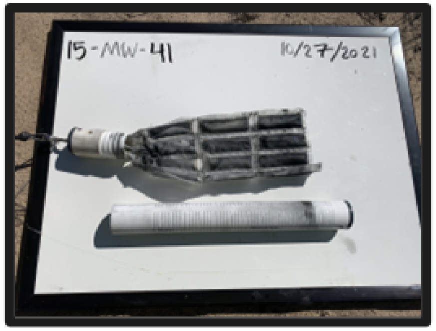


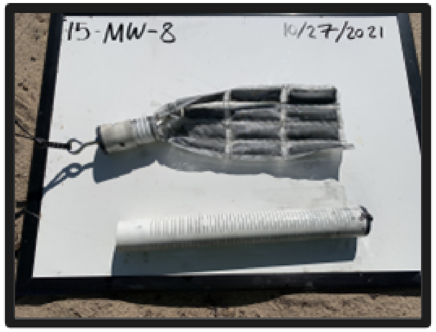
SEM-EDS



Min-Traps indicate presence of FeSx minerals at locations where expected

Demonstration Site 2 ("Mature Site")

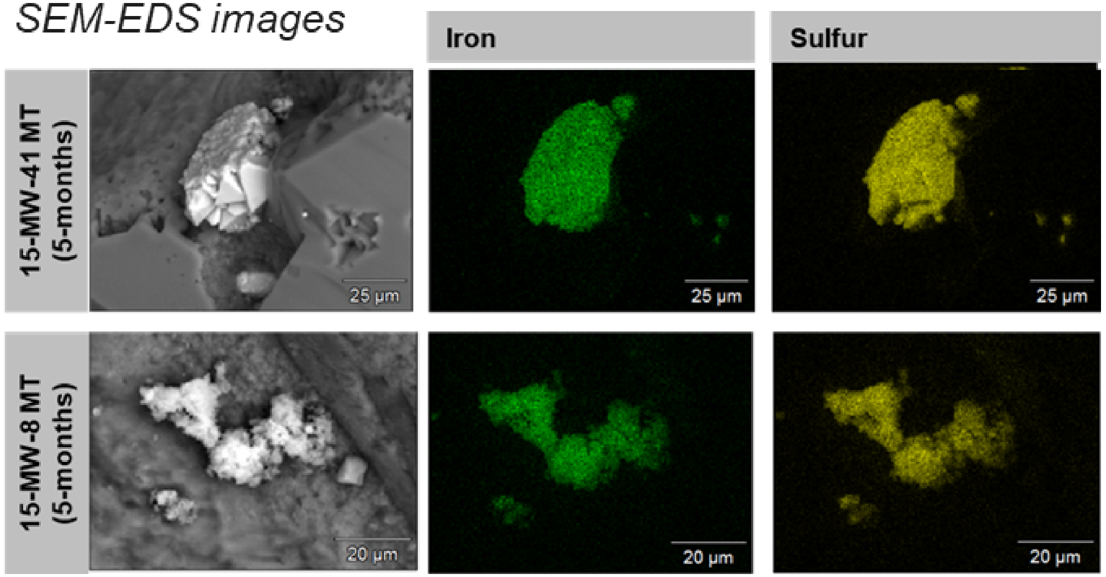




AMIBA results

Sample	Total Fe (mg/kg)	WAS Fe Fe2+ (mg/kg)	WAS Fe Fe3+ (mg/kg)	WAS Fe Total Fe (mg/kg)	SAS Fe Fe2+ (mg/kg)	SAS Fe Fe3+ (mg/kg)	SAS Fe Total Fe (mg/kg)	AVS (mg/kg)	CrES (mg/kg)
MW-41	100	38	0.0	38	44	18	62	13	41
MW-8	114	14	1.8	15	18	23	42	1.2	24

SEM-EDS images



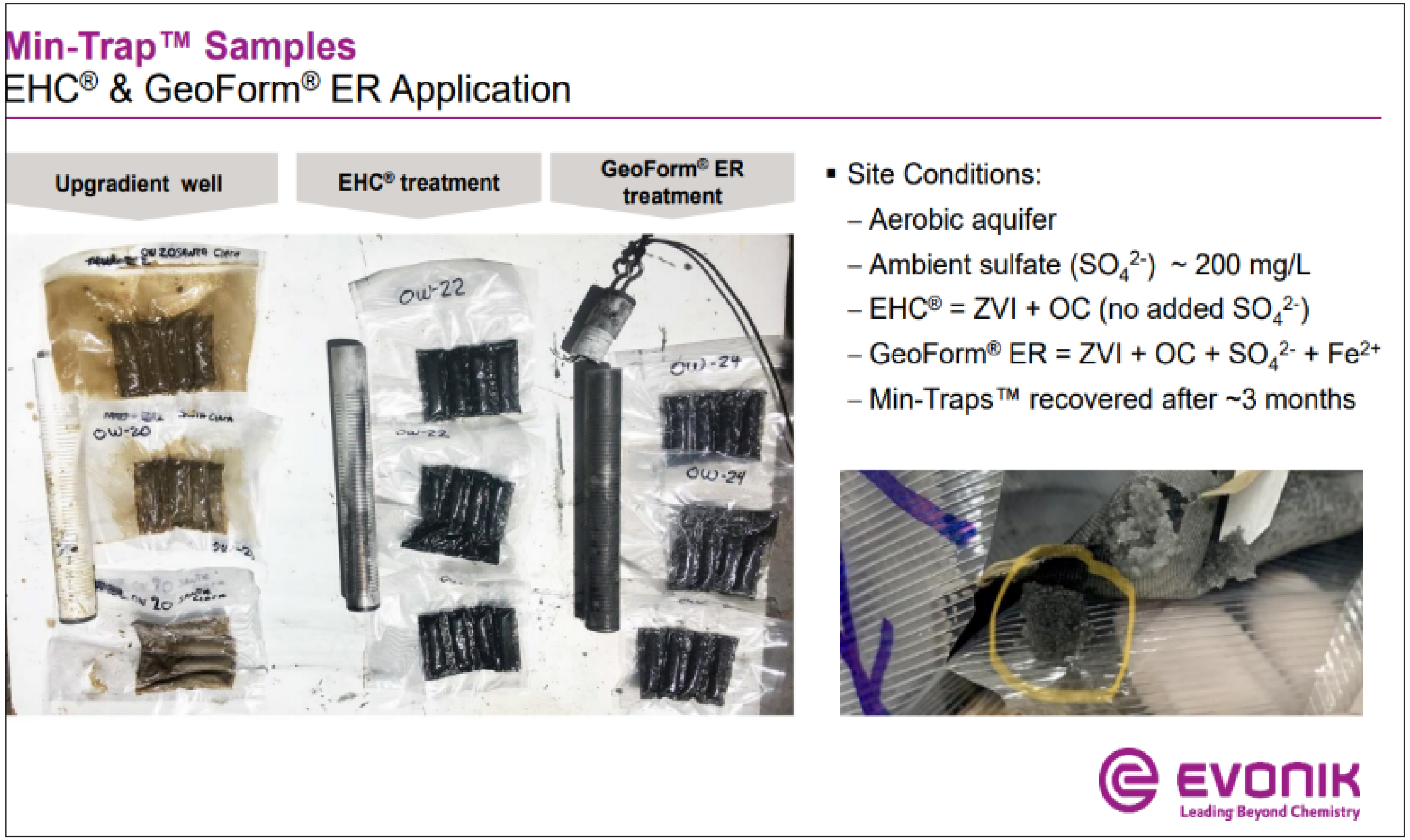
- AMIBA: presence of iron sulfide minerals, as expected
- SEM-EDS: Co-located iron and sulfur identified after 5-months' incubation

Min-Traps indicate presence of FeSx minerals at locations where expected

Other Field Sites

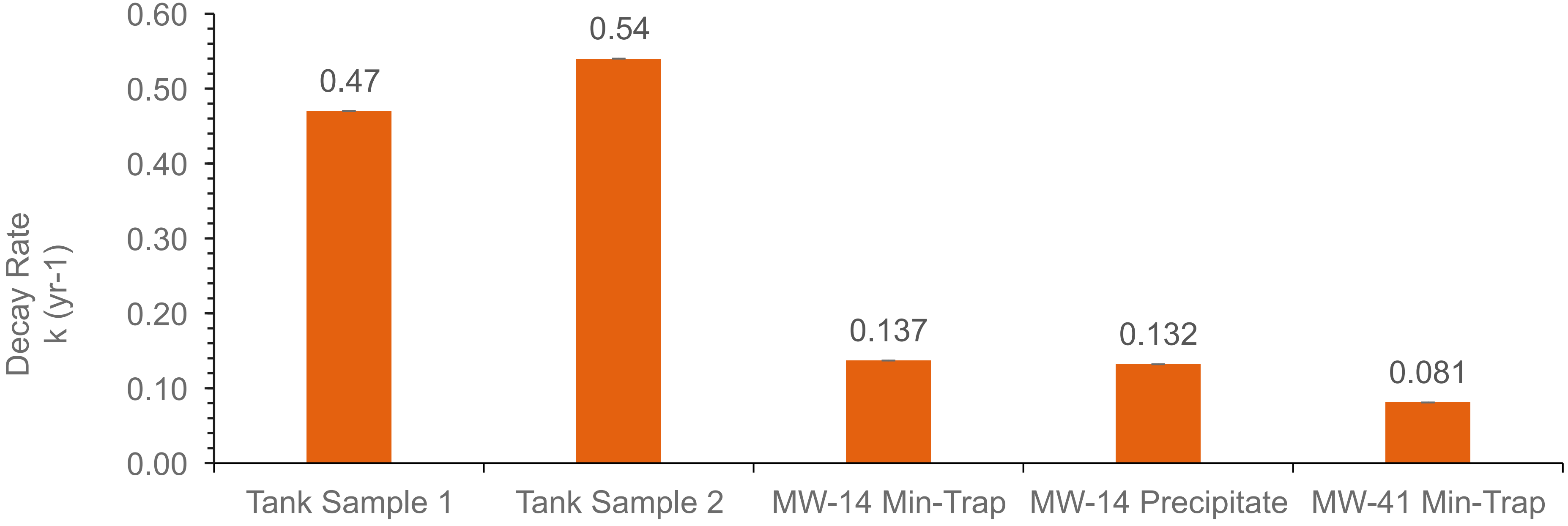
Well located at downgradient edge of EHC™ injection area

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



Leigh 2021; https://www.peroxychem.com/media/351499/evonik-webinar-leigh-biogeochemical-processes-web-2021-10-27.pdf

Measuring Abiotic Reaction Rates

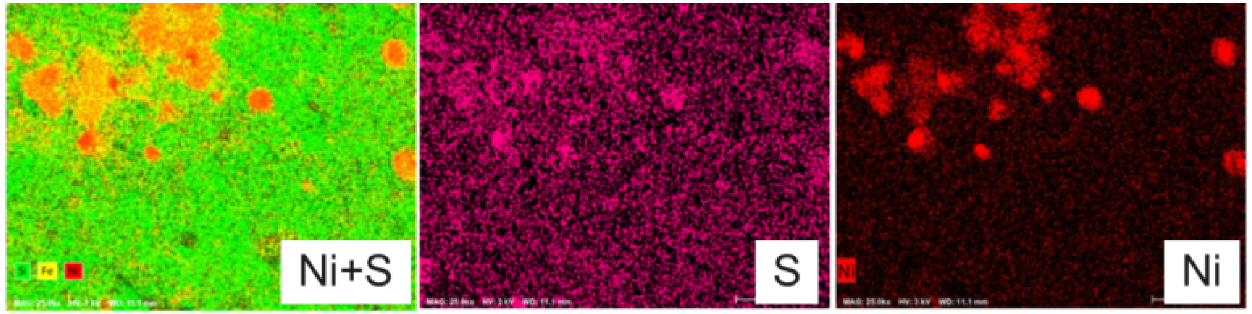


- ^{14}C assay can measure mineral reactivity for TCE on Min-Trap samples
- Standard preservation method is appropriate
- Several pillows are needed to ensure enough sample mass
- Further work is needed to utilize rates in models and decision making

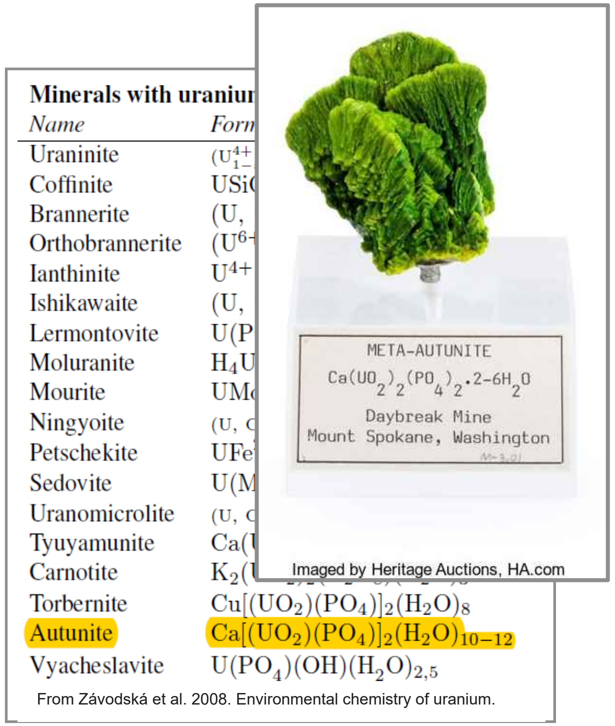
Abiotic reaction rates can be measured from Min-Trap

Other Contaminants

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™



Nickel



Imaged by Heritage Auctions, HA.com

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

Uranium

Min-Trap Resources

ARCADIS Design & Consultancy for natural and built assets

Monitoring&Remediation   Advances in Remediation Solutions

New Tools for Assessing Reactive Mineral-Mediated Abiotic Contaminant Transformation

by John Horst, Craig Divine, Jennifer Martin Tilton, Shandra Justicia-León, Shannon Ulrich, and Robert J. Stuetzle

Introduction

It has long been recognized that both biotic and abiotic contaminant transformation processes may be significant

and techniques for assessing mineral reactivity and abiotic transformation, and offers some recommendations for incorporating abiotic processes in remedy design and natural attenuation evaluations.

Horst et al., 2019. New Tools for Assessing Reactive Mineral-Mediated Abiotic Contaminant Transformation. *GWMR*, 39(2): 12-21.

REMEDIATION

THE JOURNAL OF ENVIRONMENTAL CLEANUP COSTS, TECHNOLOGIES, & TECHNIQUES

RESEARCH ARTICLE

Laboratory and initial field testing of the Min-Trap™ for tracking reactive iron sulfide mineral formation during in situ remediation

Shannon Ulrich, Jennifer Martin Tilton, Shandra Justicia-Leon, David Liles, Robert Prigge, Erika Carter, Craig Divine, Dora Taggart, Katherine Clark

First published: 05 May 2021 | https://doi.org/10.1002/rem.21681

Ulrich et al., 2021. Laboratory and Initial Field Testing of the Min-Trap™ for Tracking Reactive Iron Sulfide Mineral Formation During in situ Remediation, *Remediation*, 31(3): 35-48.

ESTCP

DRAFT

MINERAL TRAP USER GUIDANCE

Min-Trap™

ESTCP Final Report

https://www.serdp-estcp.org/projects/details/a5c9108a-49ff-4cf4-a222-95f1b2e8cda8/er19-5190-project-overview

REMEDIATION

THE JOURNAL OF ENVIRONMENTAL CLEANUP COSTS, TECHNOLOGIES, & TECHNIQUES

DOI: 10.1002/rem.21752

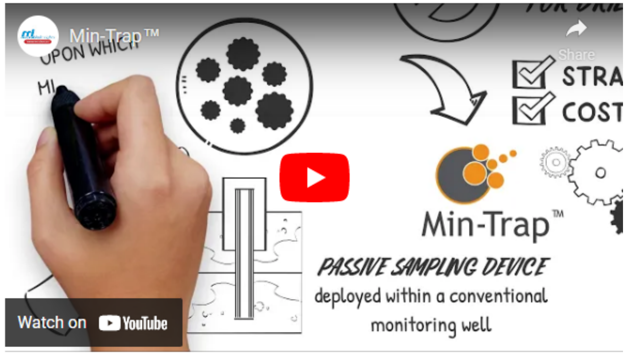
PRACTICE NOTE   WILEY

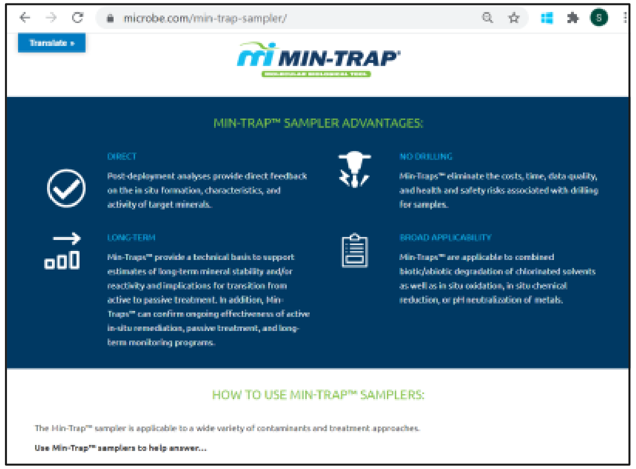
Field methods and example applications for the Min-Trap® mineral sampler

Craig Divine[1] | Shandra Justicia-León[2] | Jennifer M. Tilton[3] | Erika Carter[4] |

Divine et al., 2023. Field Methods and Example Applications for the Min-Trap® Mineral Sampler, *Remediation*, doi.org/10.1002/rem.21752

Explainer Video





https://microbe.com/min-trap-sampler/

Questions

Acknowledgements

ARCADIS


Erika Carter, PhD


Dave Liles


Jennifer Tilton

microbialinsights

CLEMSON UNIVERSITY


Dora Taggart


Kate Clark, PhD


David Freedman, PhD

ESTCP

UNITED STATES SPACE FORCE

VSFB (AFCEC/CZOW)

Francesca Perrell

Scott Laria

Kathy Gerber

Assessment Framework

Parameter		Conditions Indicating Potential Presence of Iron Sulfide Minerals			Sampling Location		
		Favorable	Possible	Unfavorable	In Situ Reactive Zone (Ideal Conditions)	Fringe of In Situ Reactive Zone	Background (Non-Ideal Conditions)
Field measurements: low cost, poor accuracy	GW DO	<0.1 mg/L	<1 mg/L, >0.1 mg/L	>1 mg/L	0.52 mg/L	0.98 mg/L	2.62 mg/L
	GW ORP	<-50 mV	<150 mV, >-50 mV	>150 Mv	-277 mV	-104 mV	86 mV
Geochemical evidence (proxy): easy/fast sampling; low cost; good accuracy and presicion	GW Dissolved Fe	>20 mg/L	<20 mg/L, >1 mg/L	<1 mg/L	3.7 mg/L	23.8 mg/L	0.0559 mg/L
	GW Δ Sulfate	>200 mg/L	<200 mg/L, >25 mg/L	<25 mg/L	870 mg/L	158 mg/L	227 mg/L
	GW Sulfide	>1 mg/L	Detectable		7.15 mg/L	0.0426 mg/L	0.0905 mg/L
	GW Methane	>5 mg/L	<5 mg/L, >0.5 mg/L	<0.5 mg/L	0.02 mg/L	0.47 mg/L	0.0033 mg/L
	GW Acetylene	Detectable			0.89 ug/L	< 0.28 ug/L	< 0.28 ug/L
	GW TOC	>20 mg/L	<20 mg/L, >5 mg/L	<5 mg/L	35.3 mg/L	89.7 mg/L	21.9 mg/L
Geochemical evidence (conclusive): longer deployment/sampling times; higher costs; good accuracy; low precision	Black-tinted MT	Significant presence of black precipitates	Limited distribution of grey/black precipitates	Absence of black precipitates	Significant presence of black precipitates	Significant presence of black precipitates	Absence of black precipitates
	MT Total Fe	>100 mg/kg	>50 mg/kg	<50 mg/kg	78 mg/kg	97 mg/kg	107 mg/kg
	AMIBA: (WAS-Fe2+ + SAS-Fe2+)/(WAS-Total Fe + SAS-Total Fe)	>0.75	<0.75, >0.25	<0.25	1.02	1.03	0.28
	AMIBA: AVS + CrES (if SAS Fe2+ detected)	>20 mg/kg	Detectable	Non-detectable	48 mg/kg	26.3 mg/kg	11.23 mg/kg
	SEM-EDS	Extensive co-location of Fe and S	Limited co-location of Fe and S	No significant S	Extensive co-location of Fe and S	Limited co-location of Fe and S	Not analyzed
Microbiological evidence: fast sampling; high costs; good accuracy and precision	DIRBs and SRBs	$<1.00 \times 10^{3}$	$<1.00 \times 10^{2} – 1.00 \times 10^{3}$	Non-detectable	$8.83 \times 10^{3} – 2.67 \times 10^{6}$	$6.17 \times 10^{4} – 1.23 \times 10^{5}$	Not analyzed

Horst et al. (2022)