

Viewing the End from the Beginning

Designing for the Transition to Long-Term Passive Phases of In Situ Chlorinated Solvent Treatment

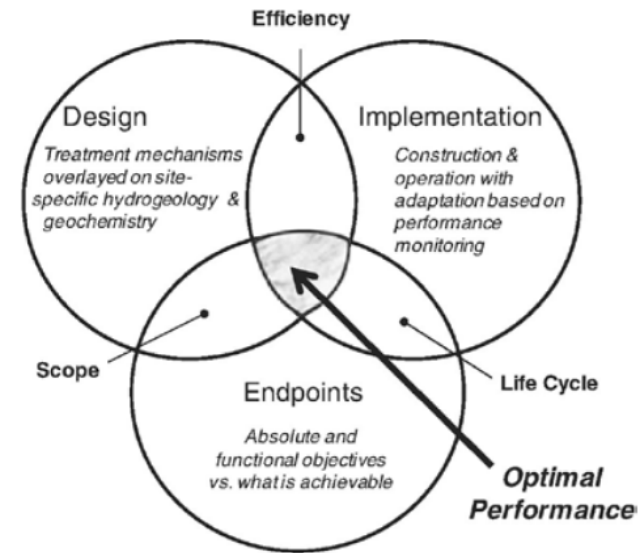
Jason Tillotson, Matt McCaughey, Shandra Justicia-Leon, and Craig Divine

Introduction

“The next wave of advances in the field of in situ remediation will likely include many concepts focused less on technology, and more on aquifer tuning.”

Aquifer Tuning for Optimum Performance of In Situ Remedies (Suthersan et al. 2010)

- In situ groundwater treatment approaches for CVOCs remain critically important
- “Aquifer tuning” refers to alignment of remedial optimization with site-specific constraints within natural environment



Suthersan et al. 2010

- **Application of aquifer tuning concept to integrate in situ enhanced reduction (biotic-abiotic) remedies for CVOCs, considering remedy lifecycle in design and operation**
- Intentional design and operation of the active remedy (i.e., injection) phase to anticipate the persistence of resulting enhanced attenuation rates in the following transition and passive phases

Introduction

These trends reinforce the that we should not lose focus on opportunities to optimize remedial solutions for traditional contaminants

USEPA Superfund Evaluation Report (16th edition, 2020)

- >75% of selected GW remedies include sites with VOC and other COCs
- In situ treatment as a remedy component has steadily increased with time (~50:50 biological:chemical)

Figure 6: COCs at Superfund Sites (FY 1981-2017)

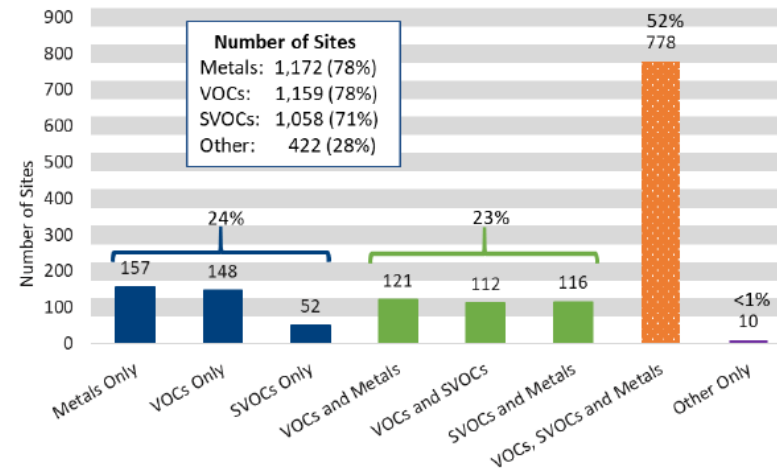
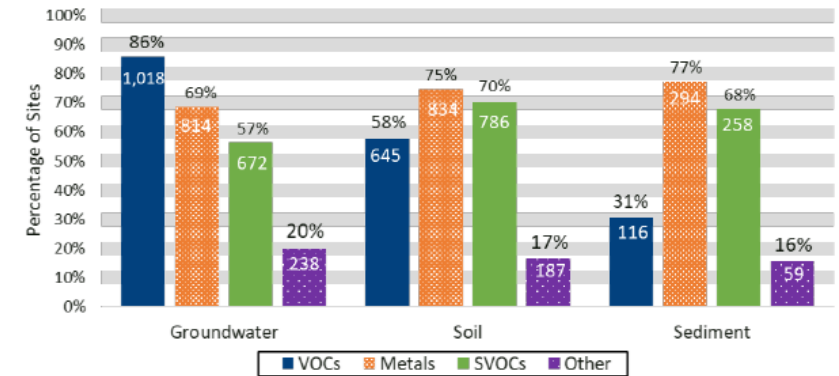
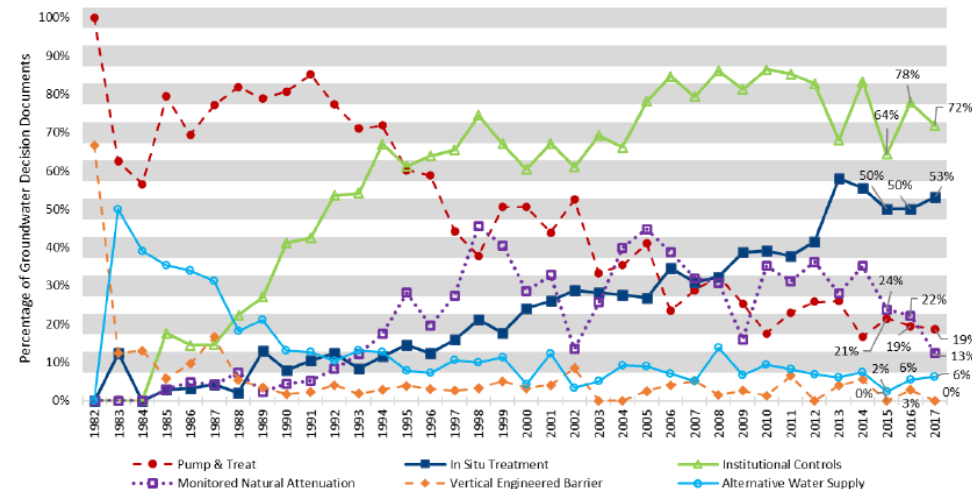


Figure 7: COCs by Media at Superfund Sites (FY 1981-2017)



- Number of groundwater sites with identified COCs and a remedy = 1,187.
- Number of soil sites with identified COCs and a remedy = 1,117.
- Number of sediment sites with identified COCs and a remedy = 380.

Figure 13: Selection Trends for Decision Documents with Groundwater Remedies (FY 1982-2017)

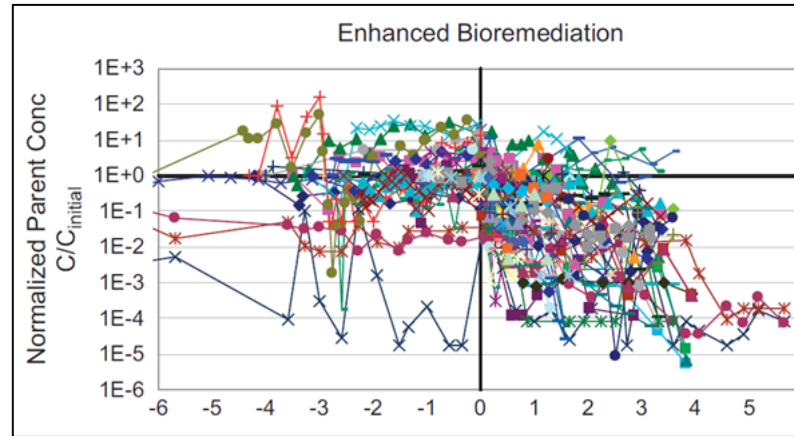


Introduction

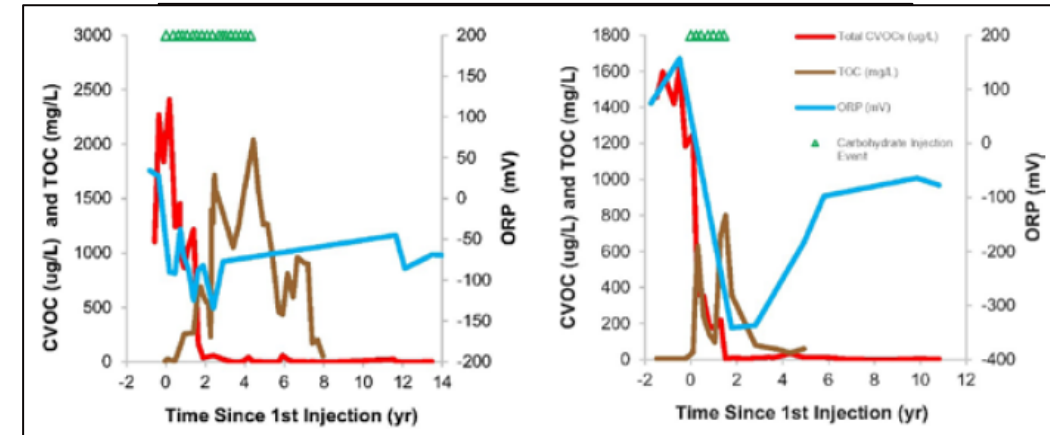
“We have consistently observed enhanced attenuation rates are often sustained more than a decade after the active injection has ceased.”

Viewing the End from the Beginning... (Horst et al. 2022)

- Contaminant “tailing” and post-remediation “rebound” are expected for remedial technologies that only address contaminants in the more permeable zones
- In situ biotic reduction strategies create zones where higher treatment rates are persistent, and can mitigate rebound behavior



McGuire et al. 2006







Horst et al. 2022

Two important components of sustained treatment

- Biomass recycling/endogenous biomass decay
 - EPS and SMP are released into subsurface during biomass growth; added into available electron pool
 - Decaying biomass provide additional hydrogen (20 hydrogen equivalents per mole of substrate) for use by dehalogenating organisms
- Formation of reactive mineral species
 - Organic carbon source stimulates iron- and sulfate-reducing bacteria → formation of iron sulfide mineral precipitates
 - Several iron-bearing minerals (e.g., mackinawite and pyrite) can directly react with CVOCs

Integrated Biotic-Abiotic Conceptual Model

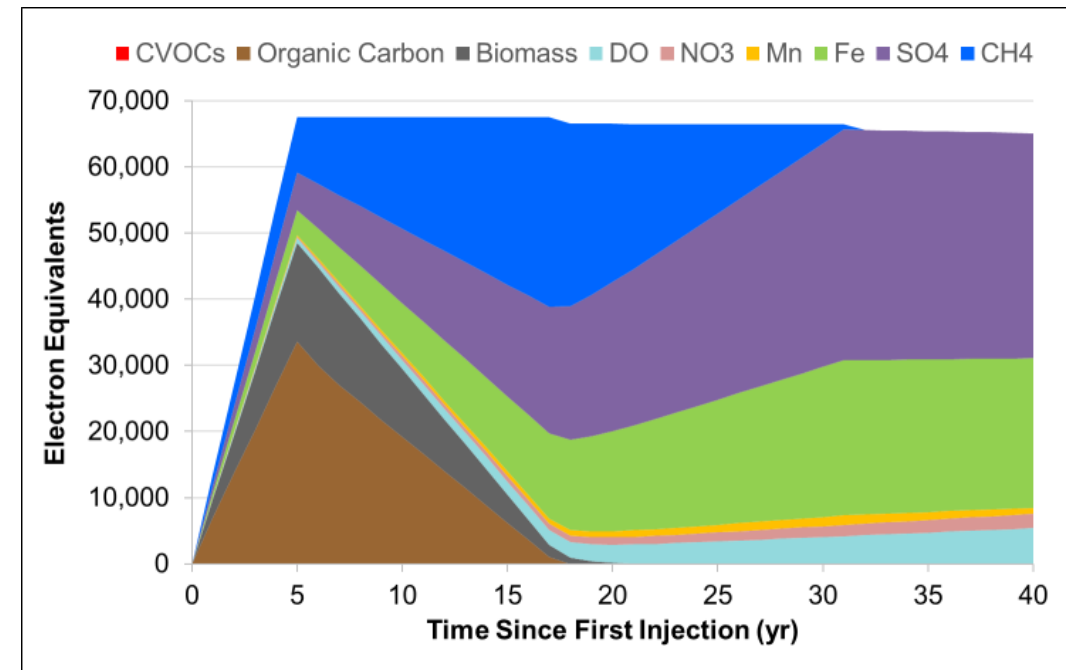
Biotic-Abiotic Conceptual Model for Electron Transfer and Tuning

Role	Process Description	Compounds of Interest	Illustrated Example of Remedial Phases			
			Background/ Baseline	Active Treatment (Early)	Active Treatment (Late)	Transition to Passive Monitoring
Geochemistry			Oxic	Anoxic	Anoxic	Anoxic
Bulk reductant	Serves as electron donor to mediator and/or electron acceptor	Organic carbon (nominal organic matter, organic carbon substrate, biomass recycling) Iron (magnetite, green rust, iron sulfides, ferrous iron species) Sulfur (hydrogen sulfides and polysulfides) Titanium citrate	Limited electron donation	Increasing electron donation	High degree of electron donation	Sustained electron donation (from electron shuttling and/or biomass recycling)
Mediator	Transfers electrons between the electron donor and acceptor; depending on redox state, can serve as an electron donor to chlorinated compounds or as an electron acceptor from bulk reductant(s)	Nominal organic matter (humic substances) Mixed valent state iron minerals (magnetite, green rust, ferrous hydroxide) Metallocoenzymes (vitamin B ₁₂)	Limited electron shuttling	Active electron shuttling	Active electron shuttling	Active electron shuttling
Electron acceptor	Accepts electrons from electron donor (either bulk reductant or mediator)	Oxygen Nitrate Manganese Iron Chlorinated compound Sulfate Carbon dioxide	O ₂ reduction	NO ₃ ⁻ reduction Mn(IV) reduction Fe(III) reduction Chlororespiration SO ₄ ²⁻ reduction Methanogenesis	Mn(IV) reduction Fe(III) reduction Chlororespiration SO ₄ ²⁻ reduction Methanogenesis	Mn(IV) reduction Fe(III) reduction Chlororespiration SO ₄ ²⁻ reduction Methanogenesis
Iron sulfide mineral formation			No	Yes	Yes	Yes
Battery strength	Relative size of available electron pool					

Modeling Reactive Zone Longevity

- Developed empirical aquifer tuning model, based on previous SERDP project (ER-2131)
 - Most terminal electron acceptors (TEAs) reduced sequentially, go to equilibrium
 - CVOC degradation, biomass decay via first-order kinetics
 - Influx of TEAs; TOC remains in system until utilized to reduce electron acceptors
- Injections of organic carbon leads to geochemical changes
 - Background TEAs rapidly reduced
 - Organic carbon remains in system for 17 years (12 years after cessation of injections)
 - 96% of electrons equivalents during this time go to Fe(III), SO₄ reduction and methanogenesis
 - Methane depleted over additional 17 years by incoming TEAs
 - Minimal contribution from CVOCs, DO, NO₃, Mn
 - Re-oxidation will require long time frames, even with relatively elevated incoming TEAs
 - After 50 years, 85% of donated electrons still present as reduced iron and sulfide species

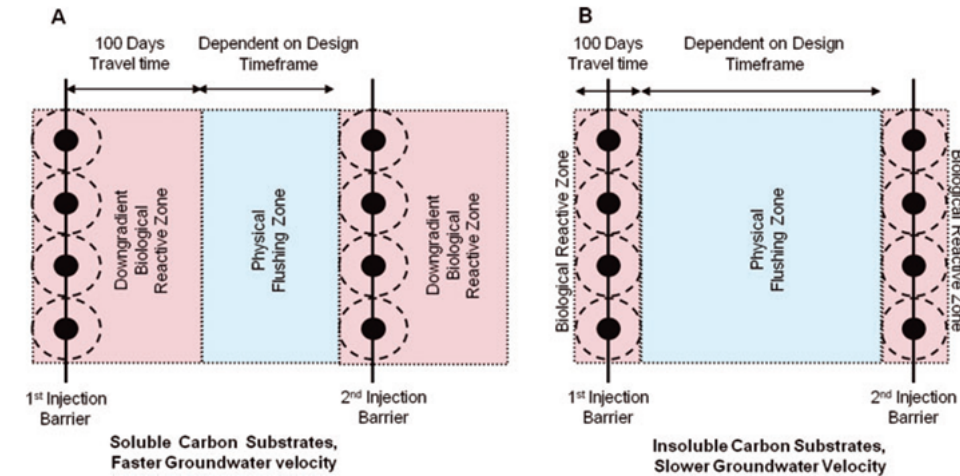
Parameter	Value
Injections	5 annual injections, 2% EVO
DO	8 mg/L
NO ₃	5 mg/L
SO ₄	100 mg/L
Bioavailable Mn _(s)	0.05 g/kg/yr
Bioavailable Fe _(s)	1 g/kg/yr
Maximum CH ₄	25 mg/L
TCE	10 mg/L
GW Flow	50 m/yr
Dissolved H ₂	129 mol H ₂ /kg EVO
Biomass Recycle	0.35 kg/kg EVO
Biomass Decay	0.73 yr ⁻¹
CVOC Decay	1.05 yr ⁻¹



Remedial Design Considerations

Substrate Selection

- GW velocity is important design consideration in reactive zone formation, substrate selection
- Soluble substrates can travel farther, extending downgradient biological (and abiotic) reactive zone
- EVOs provide longer-lasting source of carbon
- Can combine EVOs and soluble substrates to extend treatment zone and organic carbon life



(Suthersan et al. 2011)

Summary of Liquid Amendment Options

Amendment Categories	Solubility	Amendment Options	Typical Injection Frequency (months)
Organic carbon	Soluble	Alcohols, lactates	1–3
	Soluble	Sulfured molasses (TOC: sulfate ratio, 15:1), sulfured whey (30:1)	3–6
	Semi-soluble	Emulsified vegetable oil blends	12–36
Sulfate	Soluble	Magnesium sulfate, sodium sulfate	1–3
Iron	Soluble	Ferrous iron	1–3

Native Geochemistry

- How is aquifer naturally tuned? Is there sufficient iron/sulfate to encourage abiotic reduction pathways?
- May consider addition of sulfate and/or ferrous iron to enhance reactive mineral formation

Type A

- High sulfate, high Fe
- High potential for abiotic reduction
- Primary degradation mechanism is abiotic
- Organic carbon alone sufficient

Type B

- Low sulfate, high Fe
- Primary degradation mechanism is biotic; abiotic reduction depends on substrate additions
- May add sulfate source

Type C

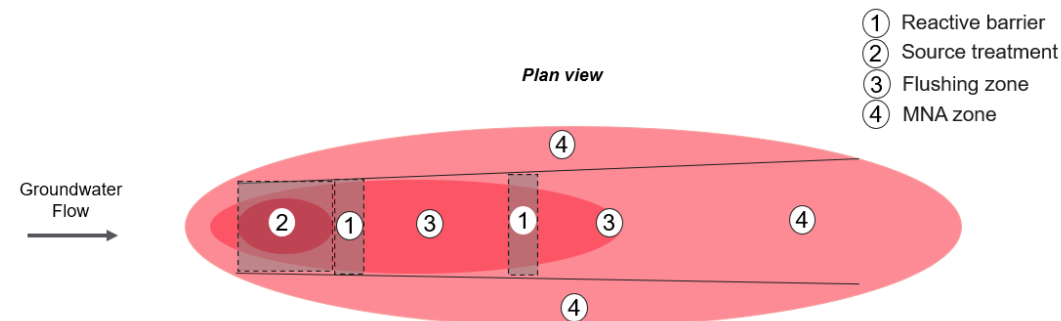
- Low Fe, high sulfate
- Primary degradation mechanism is biotic; abiotic reduction depends on substrate additions
- May add soluble iron source

Type D

- Low sulfate, low Fe
- Primary degradation mechanism is biotic
- May add sulfate and soluble iron source

Performance Monitoring Considerations

- We present a heat map framework for weight-of-evidence type evaluations, which can also be used to guide operational decision-making.
- The middle three columns show a range of conditions reflecting the potential presence of iron sulfide minerals (with green for favorable, yellow for possible, and red for unfavorable conditions)
- The right three columns show an illustrative example of three locations within, on the fringe, and outside a reactive zone.

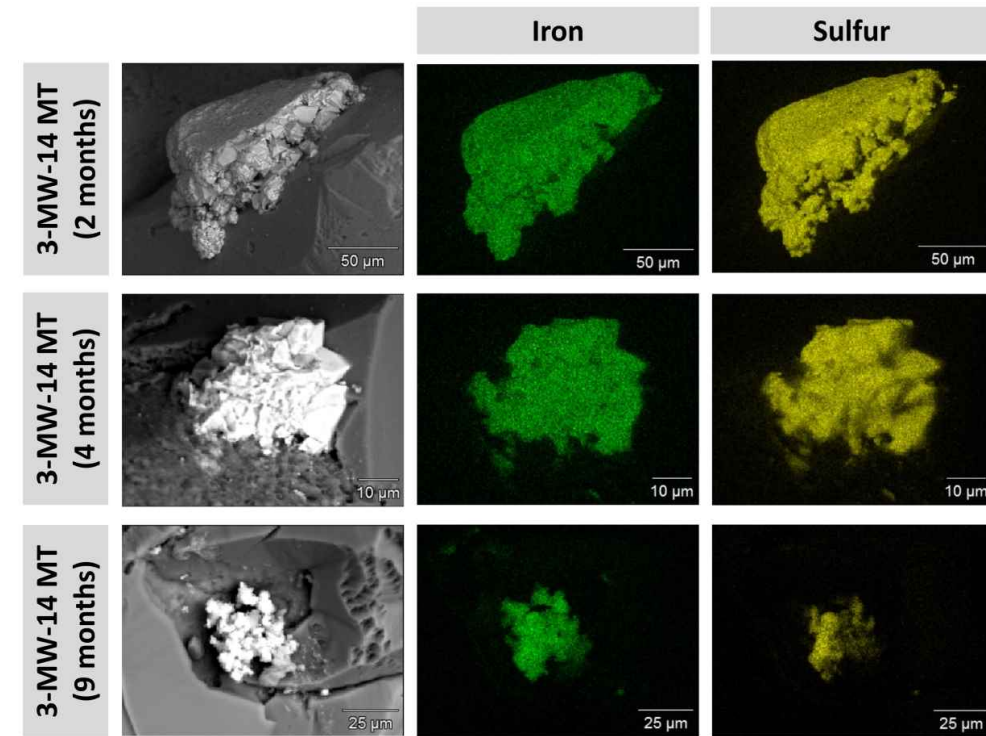


Heat Map for Assessing Likelihood and Optimal Conditions for FeSx Formation Within In Situ Reaction Zones

Parameter Description	Parameter ID	Approximate Costs, Specialty Analyses Vendors	Conditions Indicating Potential Presence of Iron Sulfide Minerals			Example Application		
			Favorable	Possible	Unfavorable	① In Situ (Ideal Conditions)	② Fringe of In Situ Reactive Zone	③ (Non-Ideal Conditions)
Field measurements: low cost, poor accuracy	GW DO (mg/L)	NA	<0.1	<1, >0.1	>1	0.52	0.98	2.62
	GW ORP (mV)	NA	<-50	<150, >-50	>150	-277	-104	86
Geochemical evidence (proxy): easy/fast sampling; low cost; good accuracy and precision	GW-dissolved Fe (mg/L)	\$30	>20	<20, >1	<1	3.7	23.8	0.0559
	GW Δ sulfate (mg/L)	\$25	>200	<200, >25	<25	870	158	227
	GW sulfide (mg/L)	\$30	>1	Detectable		7.15	0.0426	0.0905
	GW methane (mg/L)	\$65	>5	<5, >0.5	<0.5	0.02	0.47	0.0033
	GW acetylene (µg/L)	\$65	Detectable			0.89	<0.28	<0.28
	GW TOC (mg/L)	\$40	>20	<20, >5	<5	35.3	89.7	21.9
Geochemical evidence (conclusive): longer deployment/sampling times; higher costs; good accuracy; low precision	Black-tinted Min-Trap	\$300 per sampler (Microbial Insights)	Significant presence of black precipitates	Limited distribution of gray/black precipitates	Absence of black precipitates	Significant presence of black precipitates	Significant presence of black precipitates	Absence of black precipitates
	Min-Trap total Fe (mg/kg)	\$30	>100	>50	<50	78	97	107
	Min-Trap AMIBA: (WAS-Fe ²⁺ + SAS-Fe ²⁺)/ (WAS-Total Fe + SAS-Total Fe)	\$1000	>0.75	<0.75, >0.25	<0.25	1.02	1.03	0.28
	Min-Trap AMIBA: AVS + CrES (if SAS Fe ²⁺ detected) (mg/kg)		>20	Detectable	Non-detectable	48	26.3	11.23
	Min-Trap SEM-EDS	\$1200-\$1800 per sample	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	Iron-reducing bacteria and sulfate-reducing bacteria	\$300-600 individual targets \$750-\$950 per	<1.00 × 10 ³	<1.00 × 10 ² - 1.00 × 10 ³	Non-detectable	8.83 × 10 ³ - 2.67 × 10 ⁶	6.17 × 10 ⁴ - 1.23 × 10 ⁵	Not analyzed

Geochemical Sampling Tools and Indicators

- Geochemical parameters (dissolved iron, sulfate, dissolved gases, TOC)
- End-products (ethene/ethane, acetylene)
- Min-Trap Sampler – tool for assessing reactive mineral formation
 - *Min-Traps for Collection and Analysis of Reactive Iron Sulfide Minerals for Abiotic CVOC Degradation* – Session A2, 10:55



Groundwater 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

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>



HOW TO USE MIN-TRAP™ SAMPLERS:

The Min-Trap™ sampler is applicable to a wide variety of contaminants and treatment approaches.

Use Min-Trap™ samplers to help answer...

- Are reactive iron minerals formed for combined biotic/abiotic degradation of chlorinated solvents?
- Will metals like arsenic co-precipitate or adsorb to iron oxides during in situ chemical oxidation?
- Are metal sulfides formed during in situ chemical reduction at Cr(VI) sites?
- Will pH neutralization increase solid phase minerals?



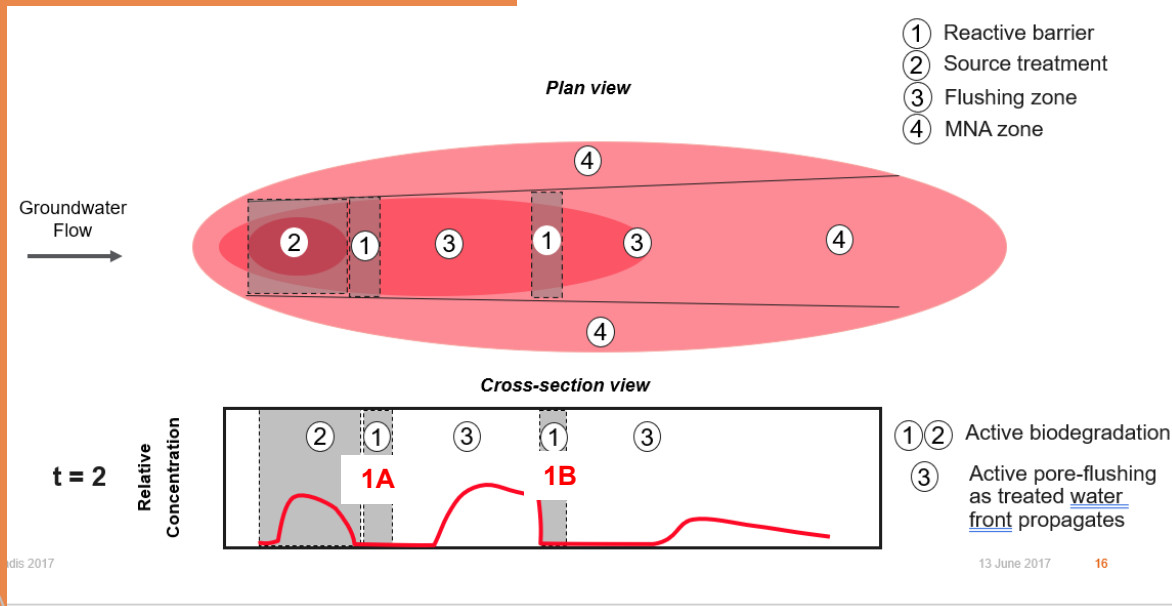
<https://youtu.be/Yhos82jAuY4>

Conceptual Application

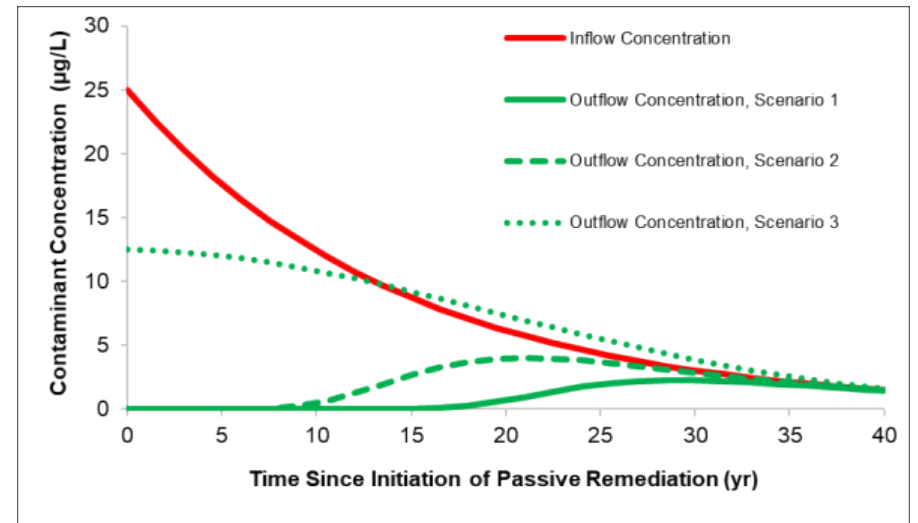
Better forecasting saves money!!!

- We recognize better forecasting tools are needed to improve remedial performance predictions, which can help improve our designs and guide our field program decision making
- We discuss a conceptual application of the benefits of better forecasting
- Consider an in situ treatment application under three scenarios
 - Scenario 1 - Injections continue for a time period after outflow achieves endpoint
 - Scenario 2 - Injections stop when outflow achieves final end point
 - Scenario 3 - Injections decrease concentrations orders of magnitude but stop before outflow achieves final end point
- Based on the predicted outflow concentrations, which scenario would you choose?

Conceptualization of Treatment Effects on Plume Concentrations



Predicted Concentrations at Transect 1B



Final Thoughts

Perception #1: Biotic and abiotic treatment processes occur independently.

Reality: Engineered abiotic processes associated with biological remedies can contribute significantly to treatment, both during the active phase and for years after injections have stopped.

Perception #2: Aquifers do not stay tuned to anoxic engineered geochemical conditions after the active treatment operations.

Reality: Biological-based reductants often tune aquifers toward anoxic conditions for years to decades after active treatment as a result of the battery-like storage of electrons stored in biomass and reduced iron minerals.

Perception #3: Active treatment is required until concentrations approach established end points.

Reality: Persistence of biogeochemical conditions result in enhanced treatment capacity that can last years and, in some settings, may continue to significantly reduce contaminant concentrations and achieve water quality goals within the passive transition phase.

Perception #4: Concentration rebound is a significant risk and commonly observed following active biological treatment.

Reality: Sustained treatment mitigates against concentration rebound. Significant concentration rebound (e.g., 20% or more) is uncommon, and usually associated with the nearby presence of residual phase.

If and when rebound is observed, it's typically limited and occurs within about three years of completion of active treatment, suggesting that extended high-resolution sampling programs to evaluate rebound potential and/or delay formal approval of active to passive remedy may (generally) not be necessary.

Questions?



Jason Tillotson

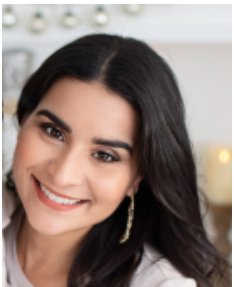
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Groundwater
Monitoring & Remediation

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