Biogeochemical Processes Enhance In Situ Treatment of Chlorinated Organics and Metals

October 27, 2021 | Daniel Leigh

EVONIK
Leading Beyond Chemistry

Webinar Agenda

- Sulfate and Iron in Groundwater
- Biological, Abiotic and Biogeochemical Degradation/Treatment Pathways of CVOCs and Metals
- Sulfidation of ZVI
- Innovative Sampling and Analytical Methods for Biogeochemical Processes
- Geoform® Biogeochemical Reagents
- Case Studies
  - High Sulfate / Low Iron Aquifer Joint Base Pearl Harbor/Hickam
  - Geoform ER / EHC Barrier for Chlorinated Ethenes
  - Geoform ER Mixed Chlorinated -ethenes, -ethanes, -methanes
  - Geoform ER Arsenic Treatment
- Summary and Questions

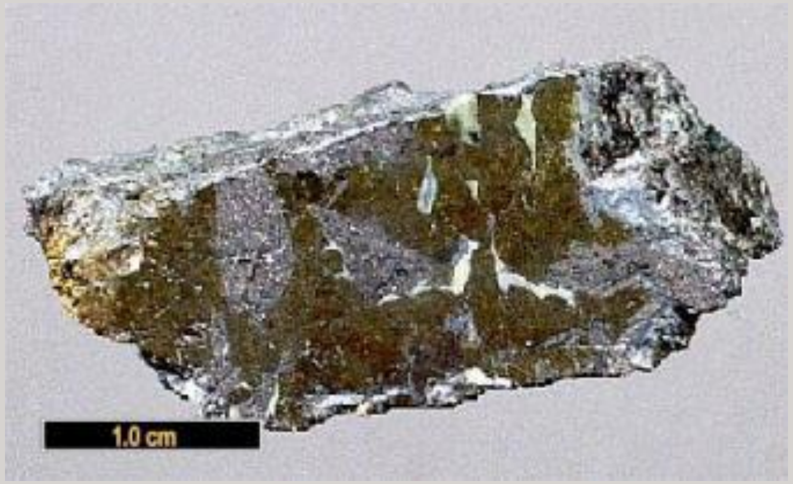
Biogeochemical Transformation

EPA Definition: Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.

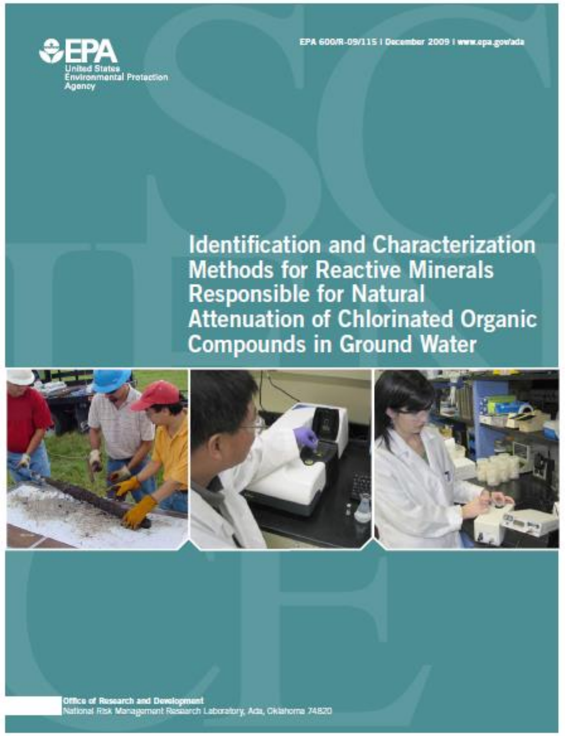
Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)

Focus on Iron-Sulfide Minerals

Pyrite (FeS_2)



Mackinawite ($Fe_{(1+x)}S$



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

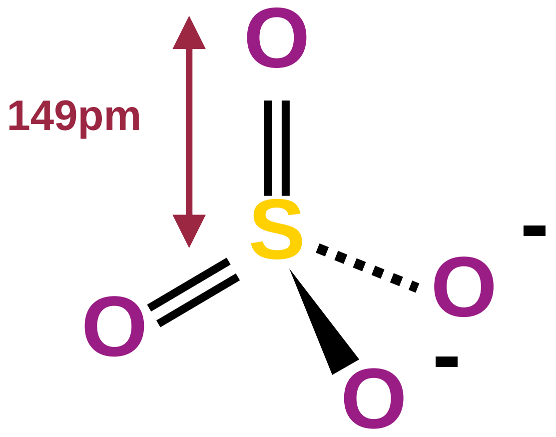
Office of Research and Development
National Risk Management Research Laboratory, Ada, Oklahoma 74820

EPA 600R-09/115 www.epa.gov/ada

Sources of Sulfate/Sulfide in Groundwater

Sulfate is naturally occurring in most aquifers

Many aquifers exhibit high sulfate concentration (up to several thousand PPM)



Primary sources of sulfate in groundwater include:

- Seawater adjacent to coastal aquifers,
  - *Seawater sulfate concentration 2,700 mg/L*
- Dissolution of sulfate containing minerals
  - *e.g., Gypsum* ($CaSO_4 – 2H_2O$)*, Anhydrite* ($CaSO_4$)*, Barite* ($BaSO_4$)
- Dissolution and oxidation of sulfide containing minerals
  - *e.g., Pyrite* (FeS_2)*, Sphalerite (ZnS), Galena (PbS)*
- Evaporation and transpiration of surface water and shallow ground water
  - *Concentrates sulfate which migrates into aquifer*

Concerns with Degradation of Chlorinated Organics (CVOC) in High Sulfate Groundwater

- **Sulfate - competing electron acceptor to biological reductive dechlorination (ERD)**
  - – Each mole of sulfate requires 9 H^+ equivalents to reduce to sulfide, about the same as PCE

Sulfate Reduction $SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O$ $(Eh^0 = -220)$

- Sulfate concentration often several orders of magnitude higher than CVOC concentration
- Usually, most of electron donor (substrate) demand is for sulfate reduction

Hydrogen sulfide (HS^-) – toxic to microorganisms

Inhibits complete biological dechlorination (VC stall and accumulation)

Sulfate has secondary standard (250 mg/L)

Based on aesthetics, not toxicity

Not typically enforced

Benefits to Reductive Dechlorination from High Sulfate Aquifers

Most aquifers contain some solid iron in/on the aquifer matrix.

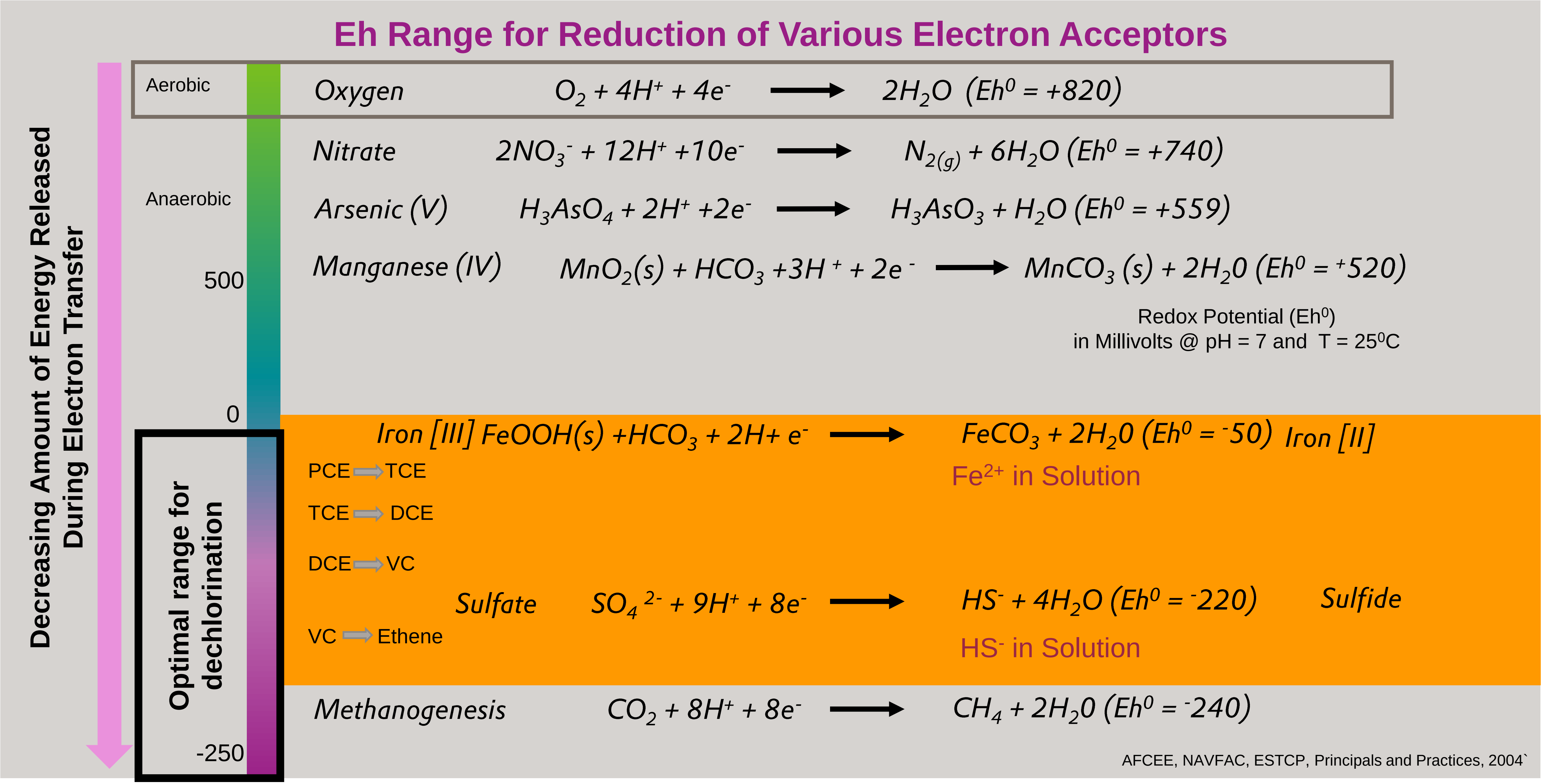
- Under moderately reducing conditions solid ferric is reduced to soluble ferrous.
- Ferrous iron readily combines with sulfide to precipitate iron-sulfide minerals.
- Precipitation of S^{2-} with Fe^{2+} removes potential sulfide toxicity issues
- Electrons are stored in aquifer as reactive iron-sulfide.
- Iron-sulfide minerals abiotically degrade chlorinated organics.

Sulfate is a preferential electron acceptor to CO_2; inhibits methane generation.

Sulfidation enhances ZVI reactivity and longevity.

Iron-sulfide minerals can sequester toxic metals (e.g., As).

Eh Range for Reduction of Various Electron Acceptors



Oxygen $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $(Eh^0 = +820)$

Nitrate $2NO_3^- + 12H^+ + 10e^- \longrightarrow N_{2(g)} + 6H_2O$ $(Eh^0 = +740)$

Arsenic (V) $H_3AsO_4 + 2H^+ + 2e^- \longrightarrow H_3AsO_3 + H_2O$ $(Eh^0 = +559)$

Manganese (IV) $MnO_2(s) + HCO_3 + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_20$ $(Eh^0 = {}^+520)$

Redox Potential (Eh^0)
in Millivolts @ pH = 7 and T = 25^{0}C

Iron [III] $FeOOH(s) + HCO_3 + 2H + e^- \longrightarrow FeCO_3 + 2H_20$ $(Eh^0 = {}^-50)$ Iron [II]

Fe^{2+} in Solution

PCE ⟹ TCE

TCE ⟹ DCE

DCE ⟹ VC

VC ⟹ Ethene

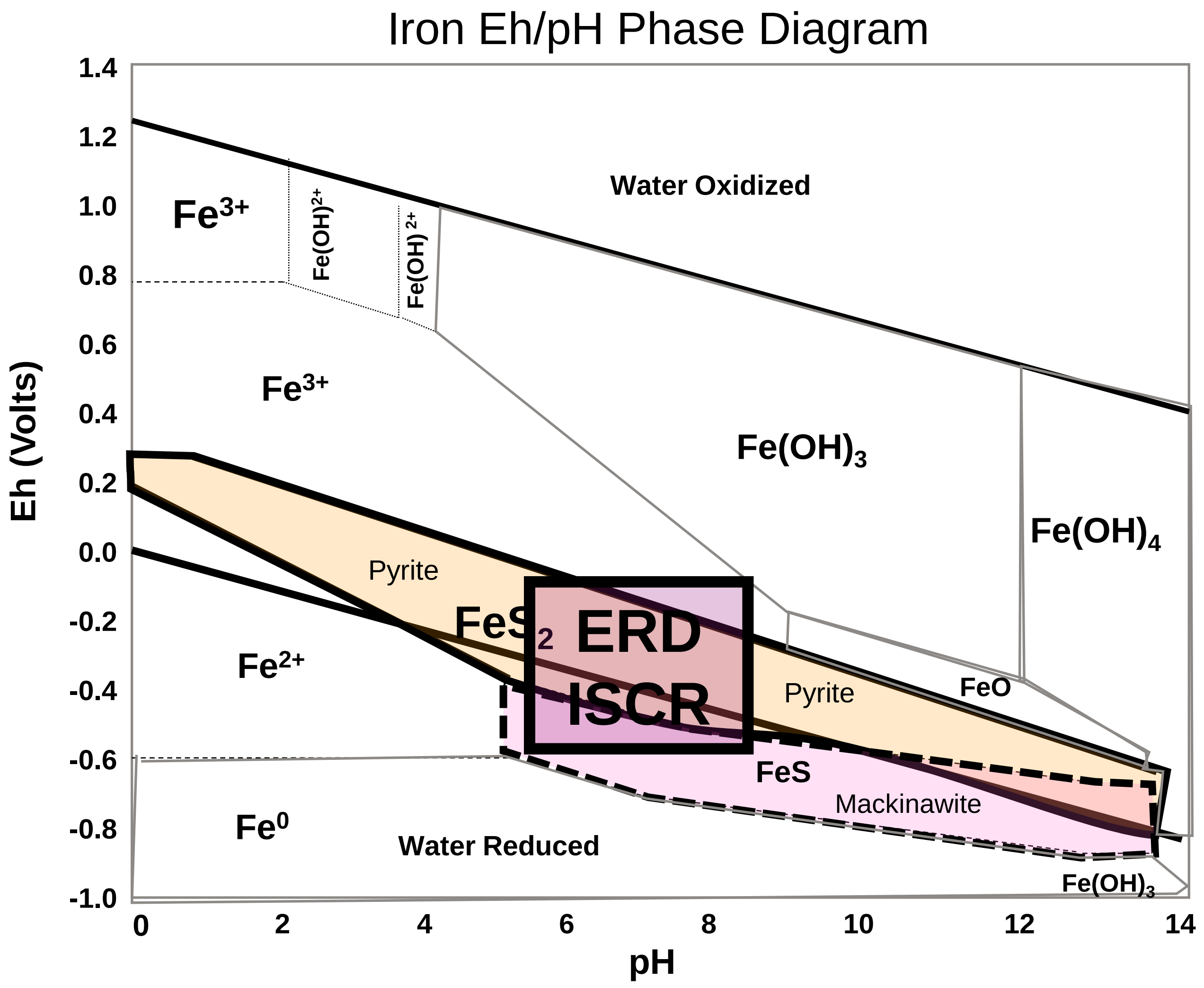
Sulfate $SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O$ $(Eh^0 = {}^-220)$ Sulfide

HS^- in Solution

Methanogenesis $CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_20$ $(Eh^0 = {}^-240)$

AFCEE, NAVFAC, ESTCP, Principals and Practices, 2004`

Iron-sulfide minerals form, and are stable under ERD/ISCR conditions


Iron Eh/pH Phase Diagram

FeS minerals conveniently form, and are stable in the same Eh, pH range as biological reductive dechlorination (ERD) and In Situ Chemical Reduction (ISCR)


Pyrite (FeS_2)

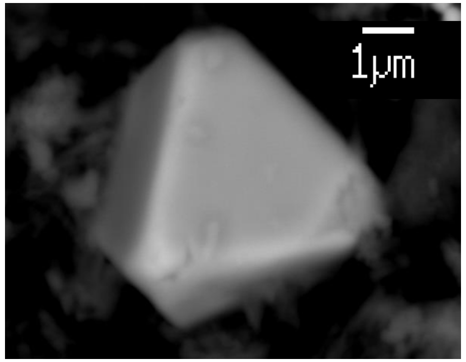
Mackinawite ($Fe_{(1+x)}S$

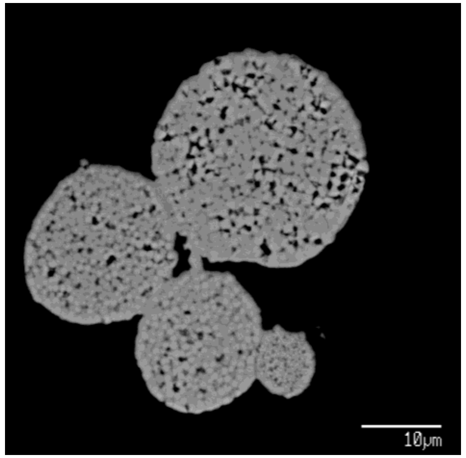
From USGS Water Supply Paper 2254
Fields of stability for solid and dissolved forms of pressure. Activity of sulfur species 96mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 µg/L

Iron-Sulfide Minerals Occur in Several Forms

Scanning Electron Microscopy (SEM) Images

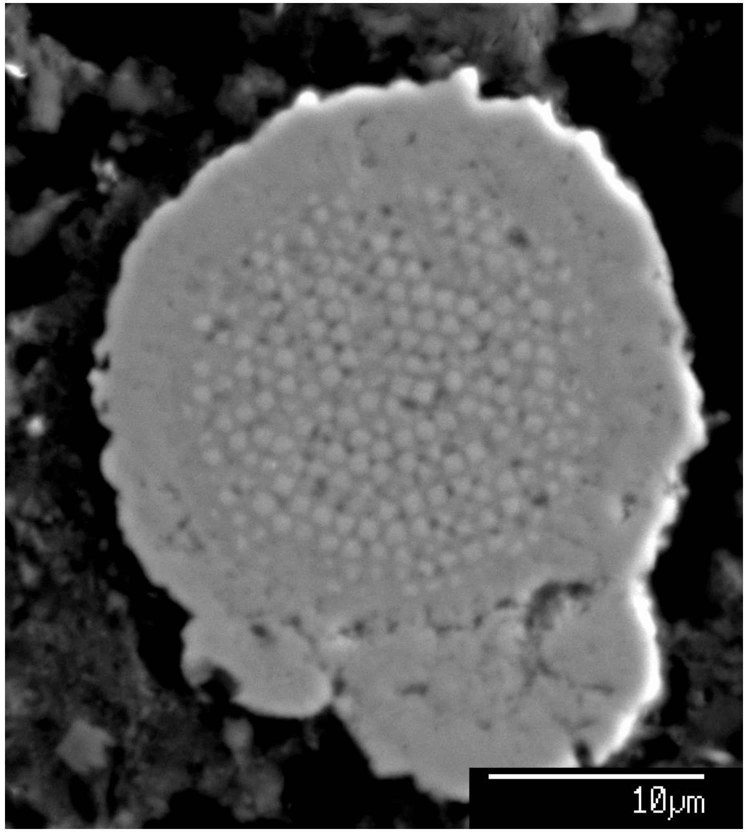
Euhedral Pyrite (FeS_2)



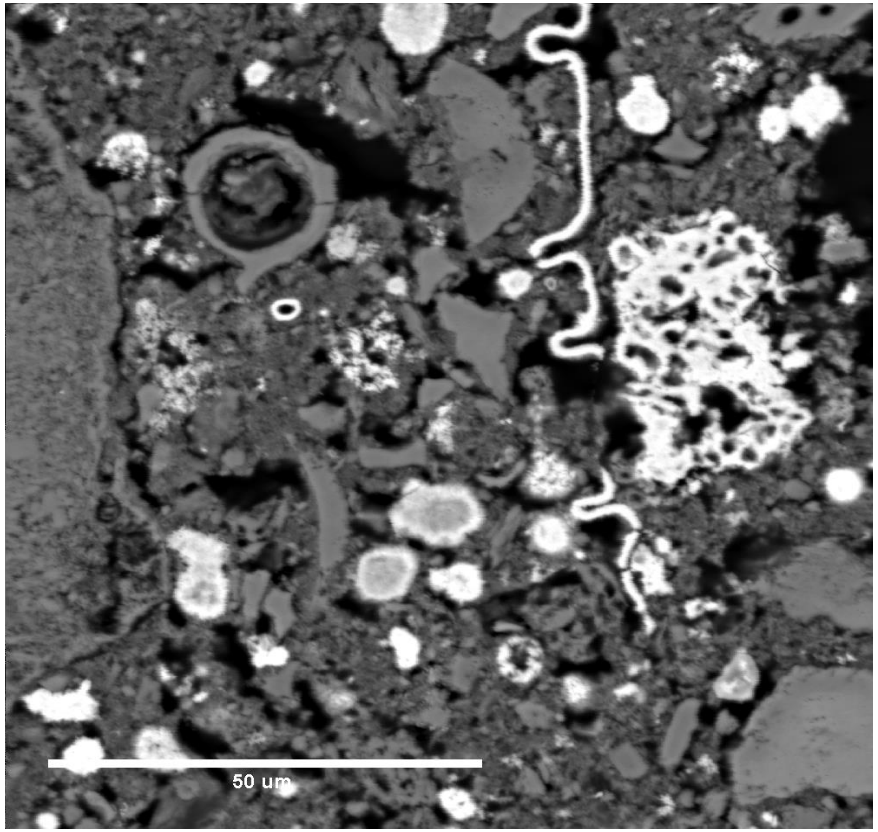


Framboidal Pyrite (FeS_2)

Framboidal FeS_2 and FeS Coating



Fe replacement + FeS coating and nano scale FeS_2



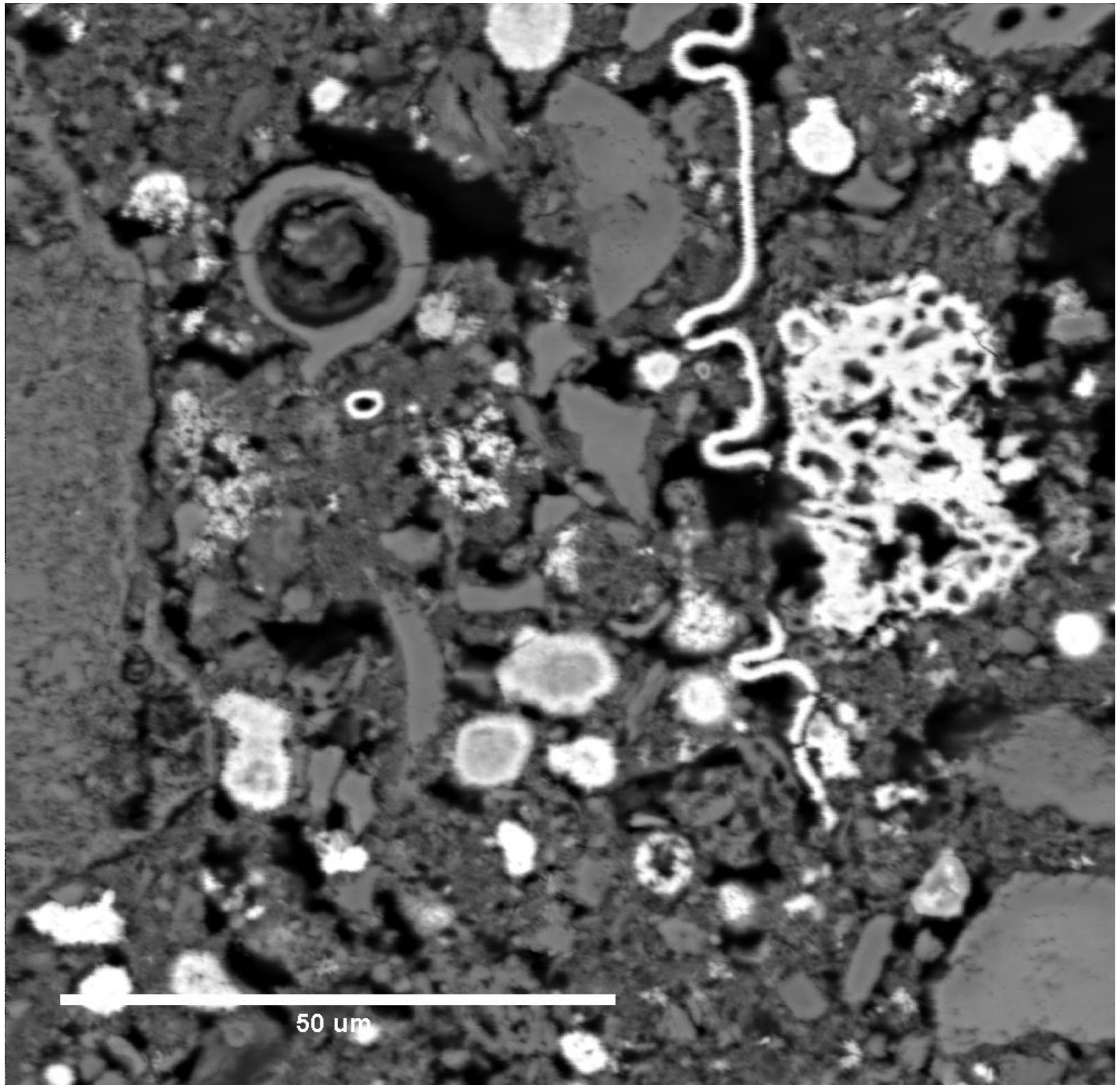
Key Advantage

Expanded Surface Area for Abiotic Pathway Without Aquifer Occlusion

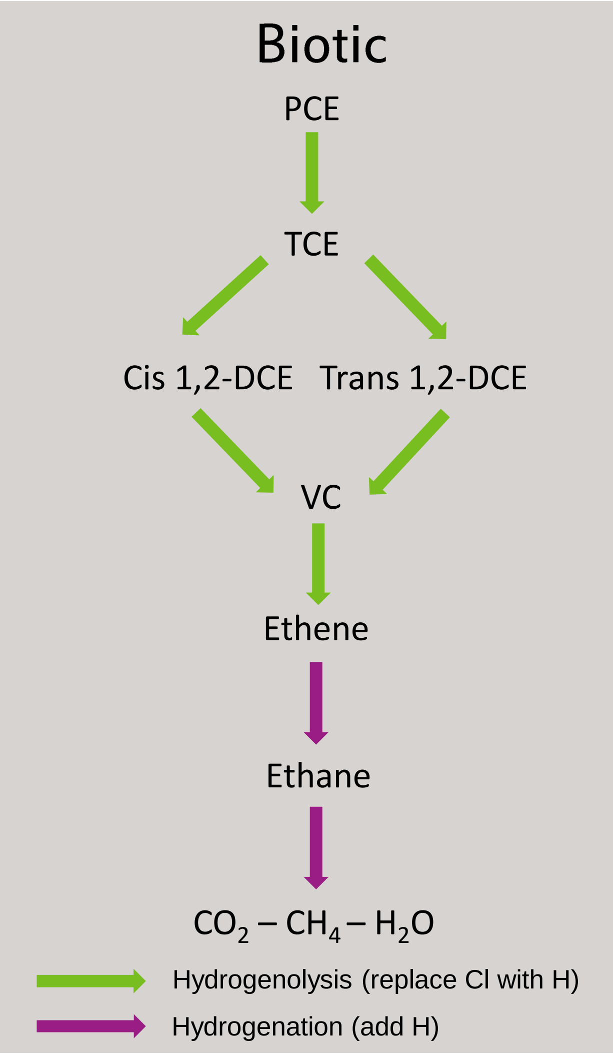
- **Produces a very large surface area:**
  3,000 mg/L SO_4 + Fe generates:
    3 µM coating ~ 2.3 ft^2 (0.21 M^2) per Liter
    ~ 23 ft^2 per ft^3 of aquifer (@35% porosity)
- **Produce a very small volume:**
  ~2.7 g FeS per Liter (@SO_4 = 3,000 mg/L)
  ~2.7 g FeS per Liter (@SO_4 = 3,000 mg/L)

Volume FeS_2~ 0.74 cm^3 per Liter
Volume FeS ~0.65 cm^3 per Liter

~ 0.1% of aquifer pore space



Biotic and Abiotic Chlorinated Ethene Degradation Pathways



Biotic

PCE

TCE

Cis 1,2-DCE Trans 1,2-DCE

VC

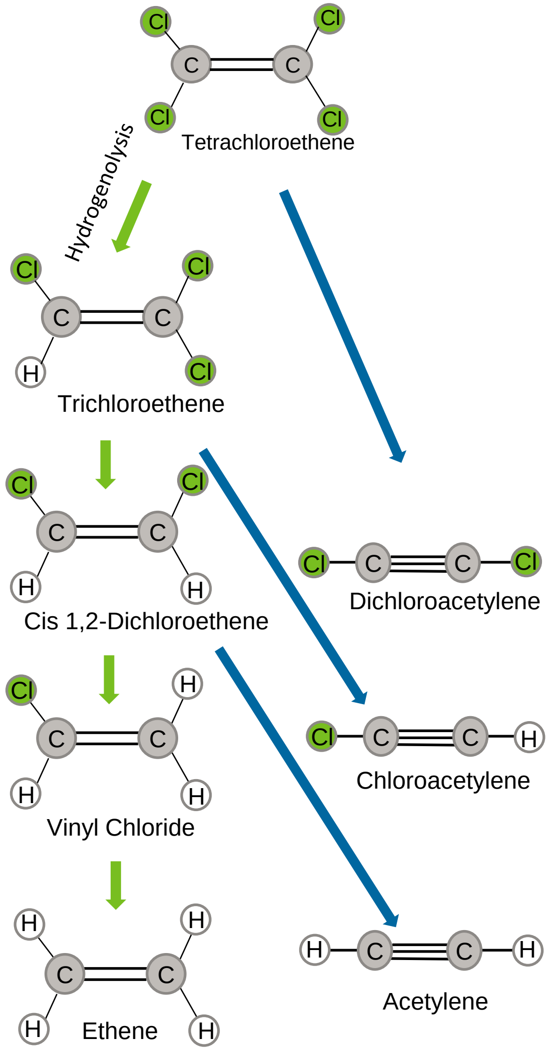
Ethene

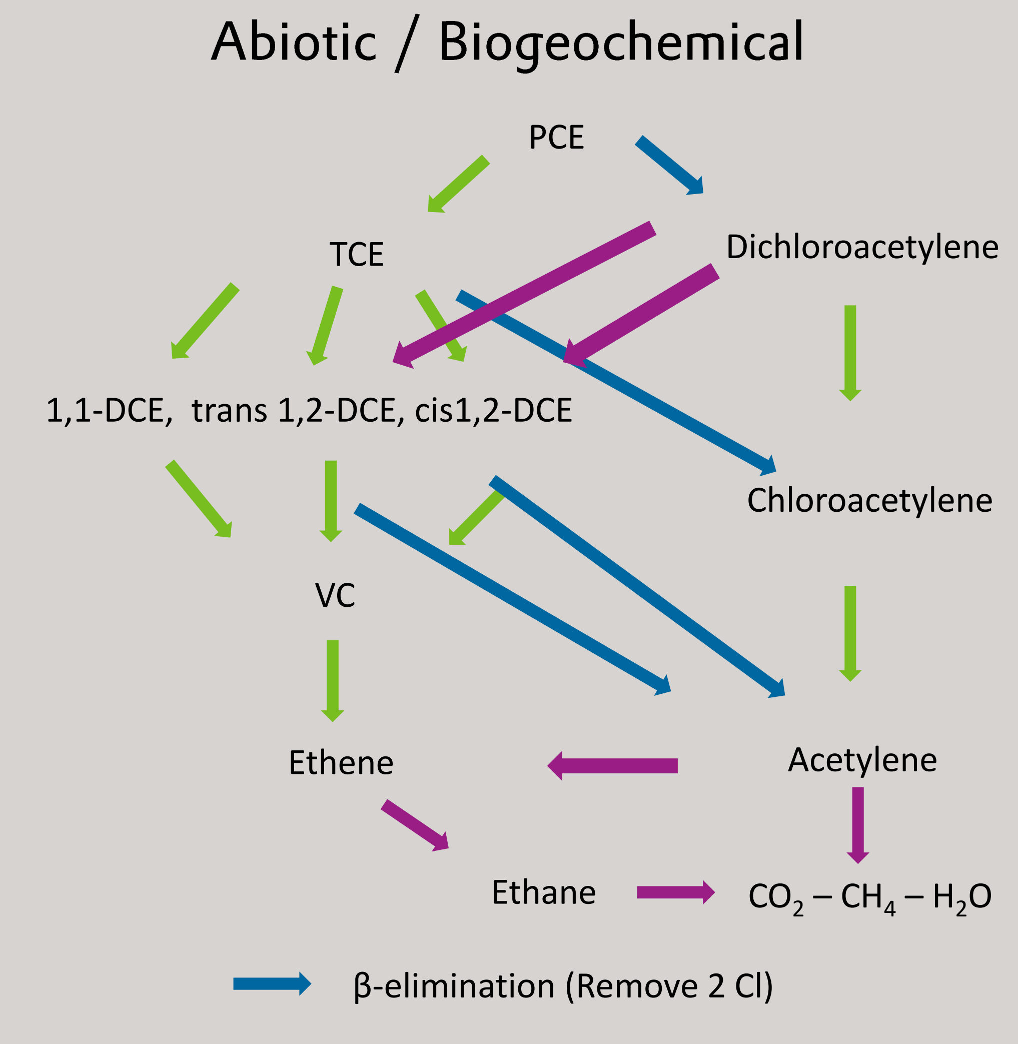
Ethane

$CO_2 - CH_4 - H_2O$

→ Hydrogenolysis (replace Cl with H)

→ Hydrogenation (add H)





Abiotic / Biogeochemical

PCE

TCE

Dichloroacetylene

1,1-DCE, trans 1,2-DCE, cis1,2-DCE

Chloroacetylene

VC

Ethene

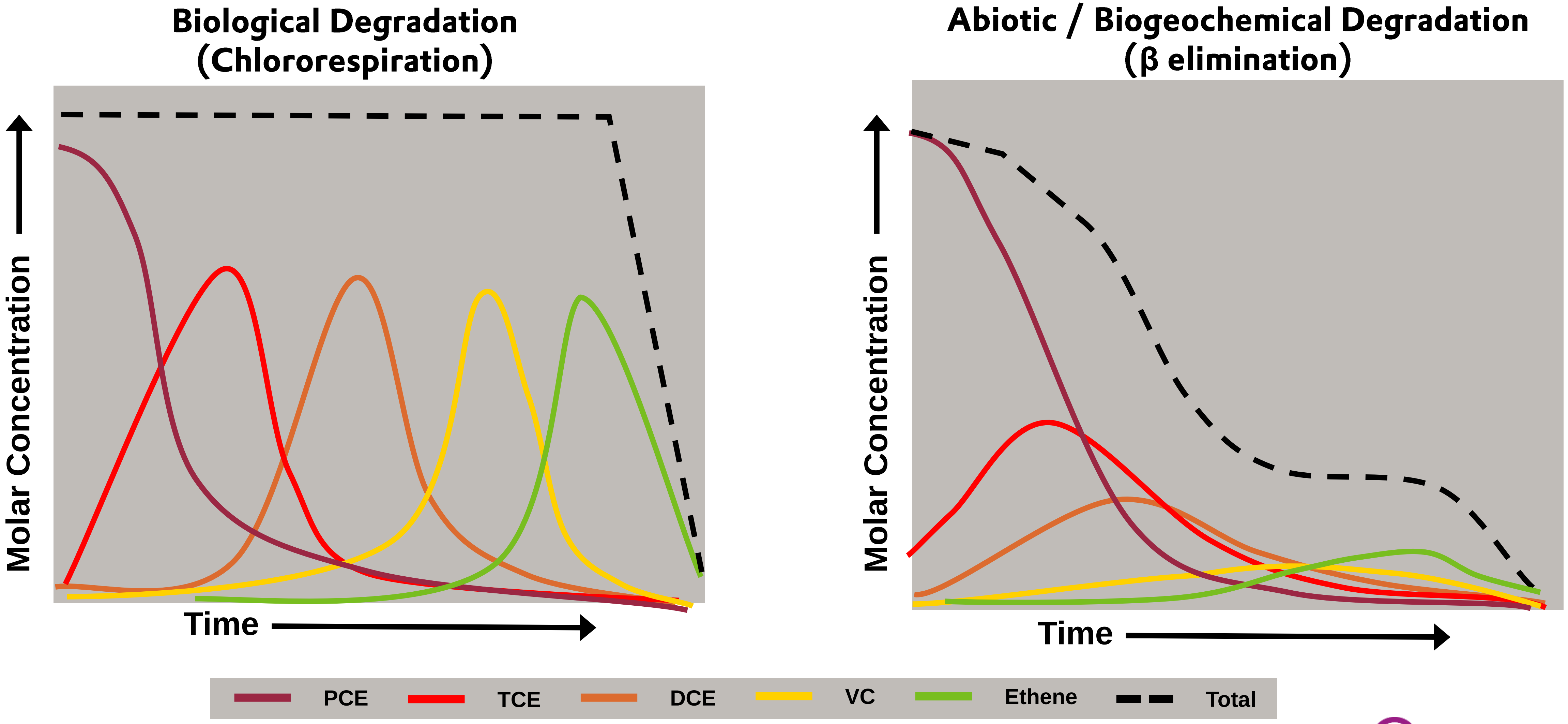
Acetylene

Ethane

$CO_2 - CH_4 - H_2O$

→ β-elimination (Remove 2 Cl)

Anticipated Change in CE Molar Concentration



Biological Degradation
(Chlororespiration)

Abiotic / Biogeochemical Degradation
(β elimination)

Biogeochemical Process Treat Metals

- Heavy metals and metalloids are a common groundwater contaminant
- Heavy metals are often associated with chlorinated organic plumes
- Some naturally occurring metals increase or decrease in groundwater during the establishment of reducing conditions by ERD and ISCR.

Solid Arsenic As[V] → As[III] Soluble

Solid Manganese: Mn [IV] → Mn[II] Soluble

Solid Iron Fe[III] → Fe[II] Soluble

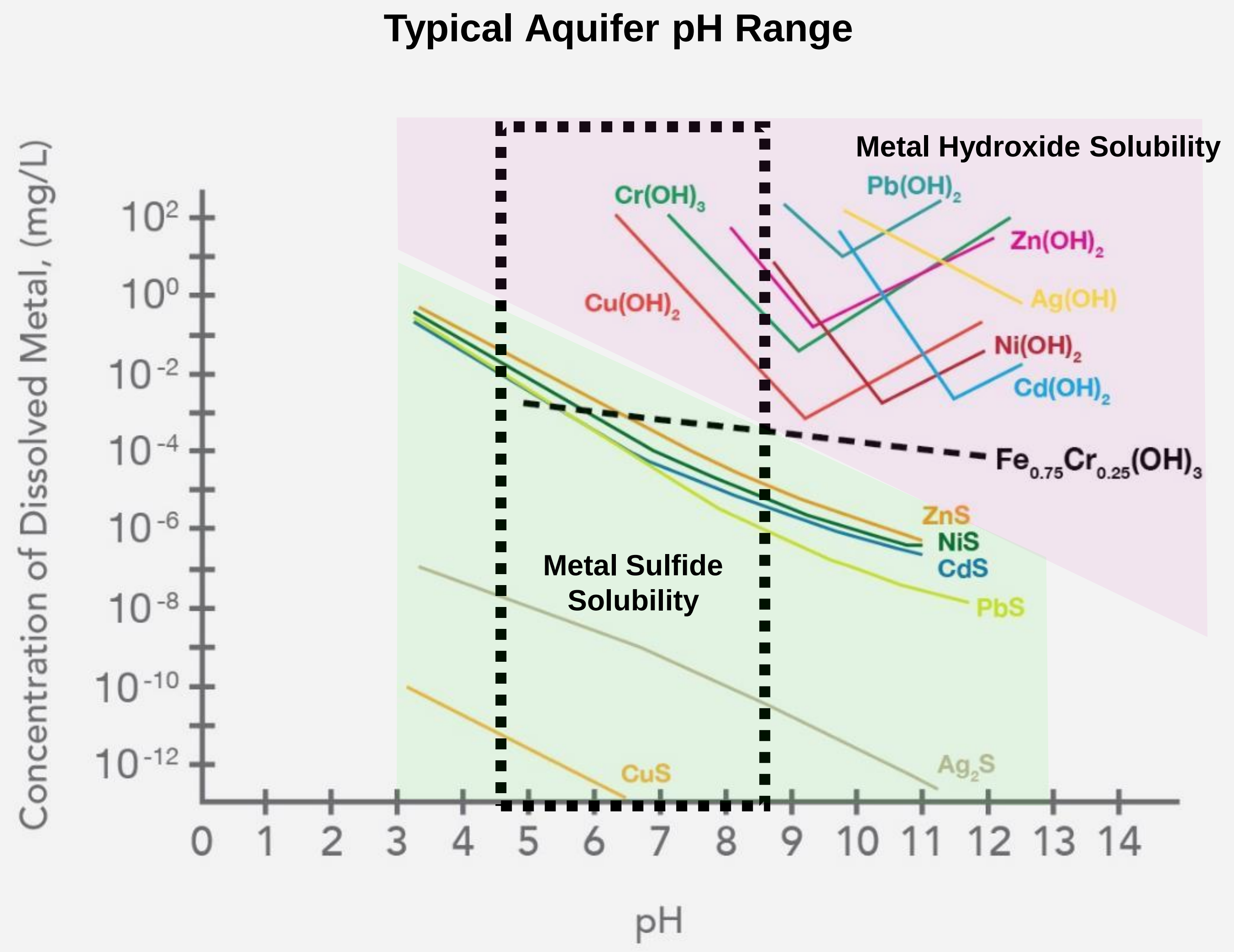
Soluble Chromium Cr[VI] → Cr[III] Solid

Many metals can be precipitated as sulfides / iron sulfides

Arsenic (Arsenopyrite, $FeAsS_2$), Zinc (sphalerite, ZnS), Iron (pyrite (FeS_2), mackinawite (FeS), Cobalt (CoS), Lead (PbS, galena)

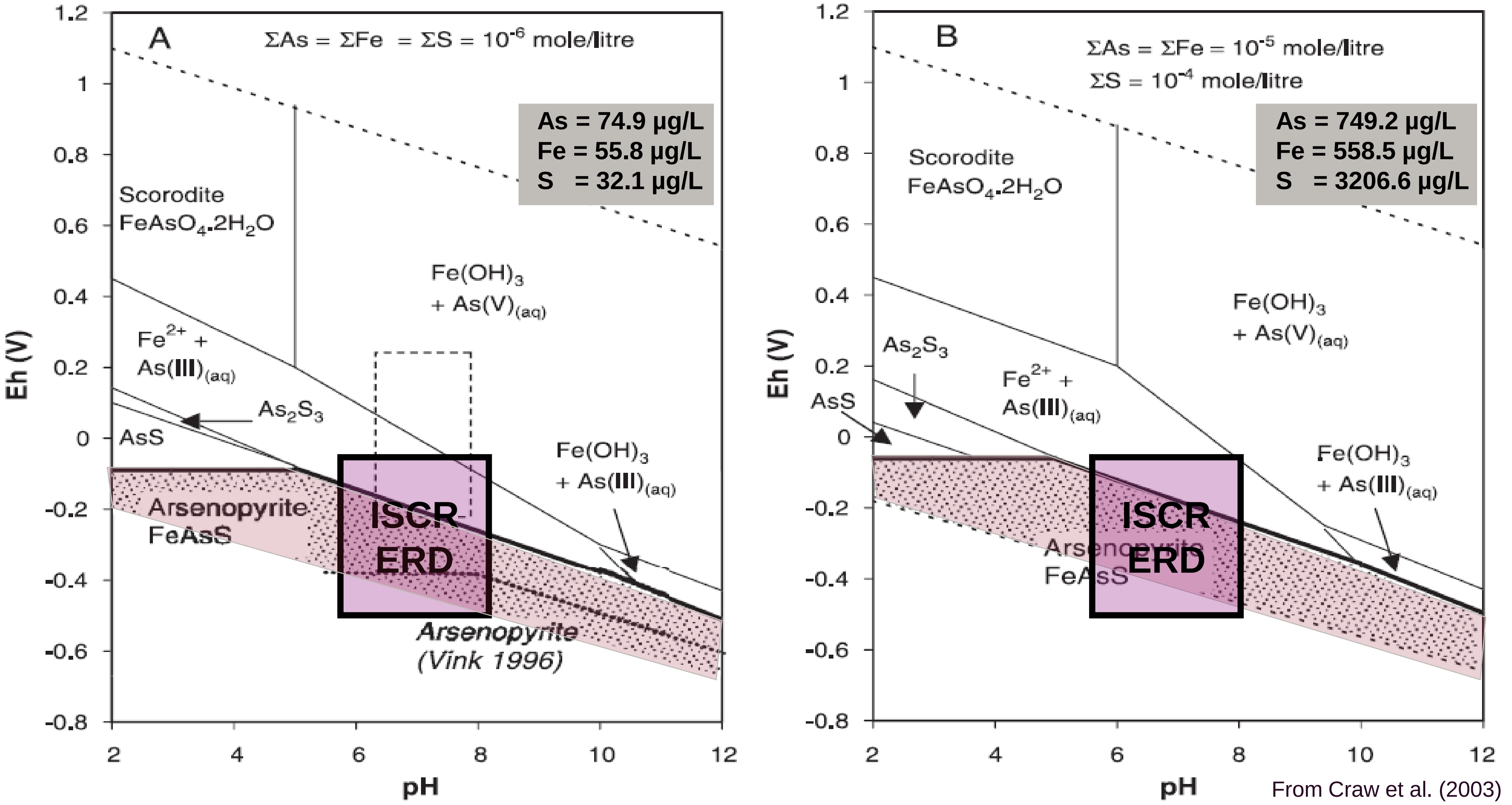
Metal-Sulfides are less soluble than metal hydroxides under typical aquifer pH

Aqueous Solubility & Stability of Heavy Metals as Hydroxides, Iron Oxyhydroxides, and Sulfides



EPA 625/8-80-003, 1980; Banerjee et al., 2013. Veolia Water Inc. Environ. Sci. Technol. 1988, 22, 972-977

Arsenopyrite precipitates, and is stable at typical ERD/ISCR - Eh/pH conditions

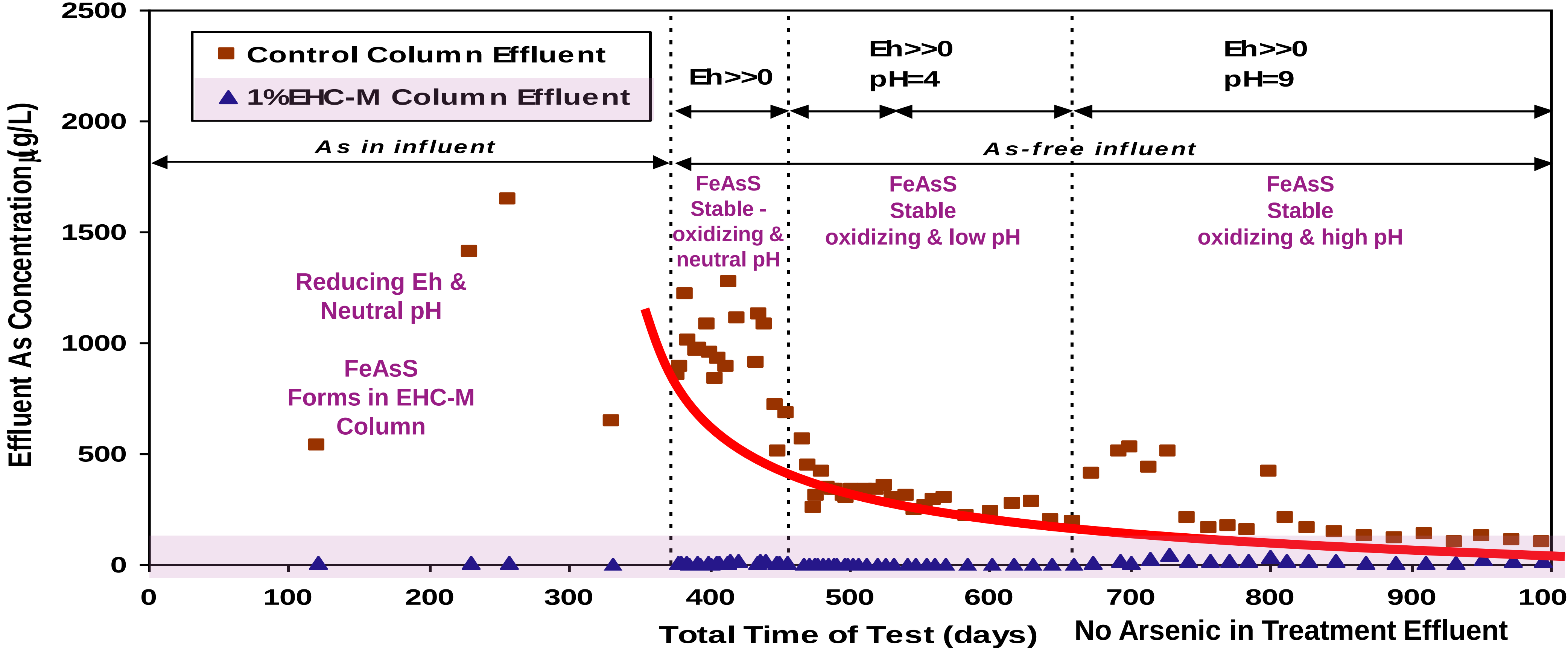


From Craw et al. (2003)

Arsenic Stabilization - Influence of Changing Eh and pH

EHC® Metals = EHC (ZVI + Organic Carbon + Nutrients) + Sulfate

Column: 13 cm long and 5 cm Ø, Flow rate = 50 mL/d, Residence time = 2 days



No Arsenic in Treatment Effluent

Conclusion: Arsenopyrite is Stable Following Precipitation

Study by Andrzej Przepiora

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Sulfidation Increases ZVI reactivity

“Sulfidation” … can refer to any modification or transformation of a metal-based material by exposure to sulfur compounds of various oxidation states…”

- Sulfidation has been demonstrated to increase reactivity and decrease passivation of ZVI

In Situ Sulfidation Process:

ZVI, sulfate (SO_4^{2-}) and organic carbon (**OC**) are distributed in aquifer

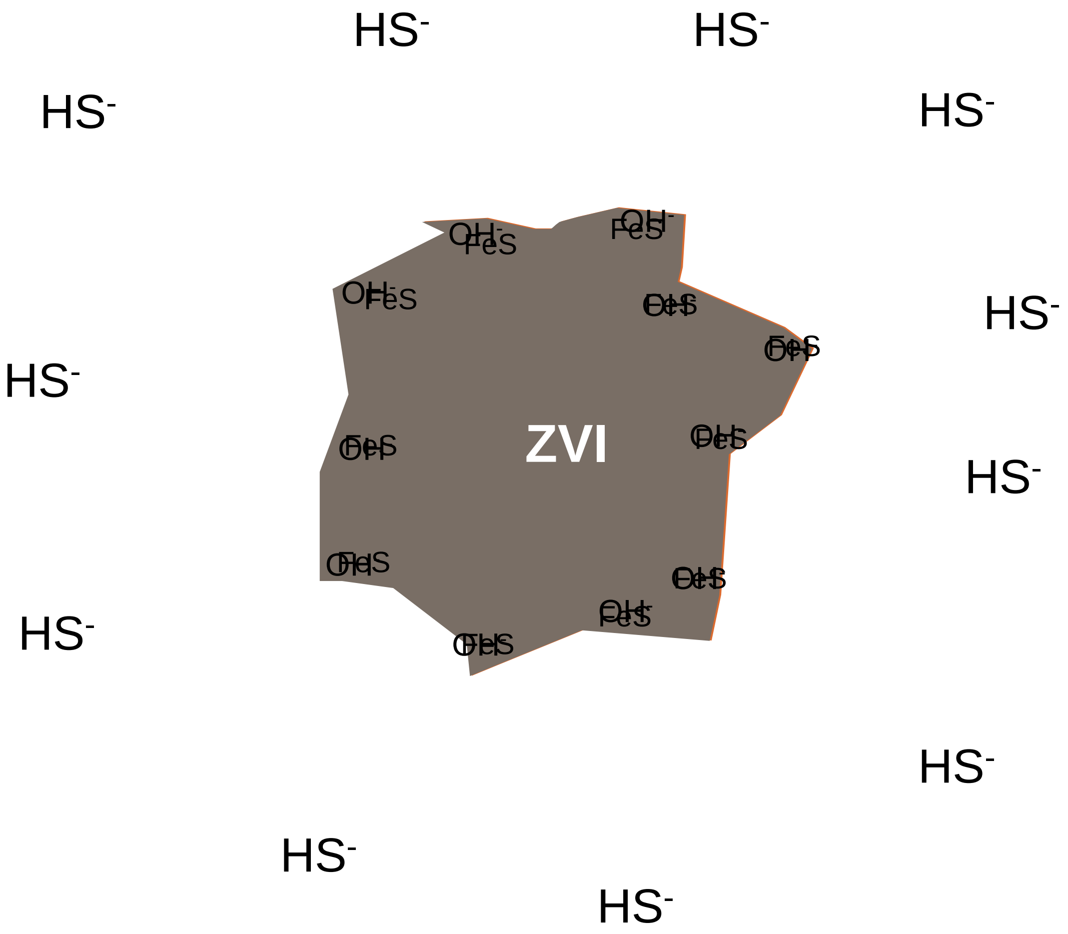
ZVI reacts with water to generate OH^- on surface

Sulfate is biologically reduced to sulfide (HS^-)

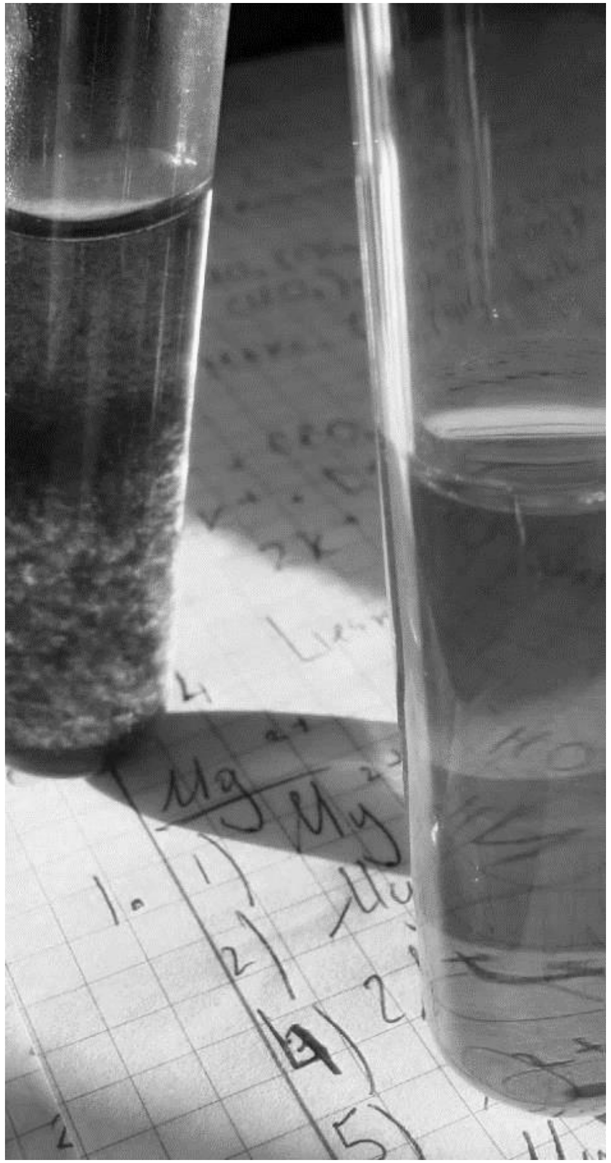
Sulfide replaces OH^- on ZVI

Fe^{2+} (ambient, supplied or from ZVI oxidation,) combines with HS^- to form FeS coating on ZVI

Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation
Dimin Fan, Ying Lan, Paul G.Tratnyek, Richard L. Johnson, Jan Filip, Denis M. O’Carroll, Ariel Nunez Garcia, and Abinash Agrawal, Environmental Science & Technology



Sampling and Analyses for Identification and Quantification of Biogeochemical Processes



Biogeochemical Sampling Methods

- **FeS minerals precipitate in/on the aquifer matrix and in the bottom of wells / Not in GW.**
- **Aquifer matrix sampling / core:**

Advantages
- Well-established technology
- Can collect from multiple intervals/locations

Disadvantages
- Can be expensive
- FeS only small fraction of bulk aquifer matrix
- Reactive minerals not uniformly distributed in aquifer

- **In-well sediment collection:**
  Concentrates reactive minerals:
  e.g., 3,000 mg/L SO_4 in 10 foot well
  2” > 16.8 g FeS, 23 g FeS_2
  4” > 67.3 g FeS, 92 g FeS_2

- **Min-Traps™** – In-well sampling device, by Microbial Insights
  Simulate precipitation in/on aquifer matrix
  Simple installation, collection, preservation & analyses

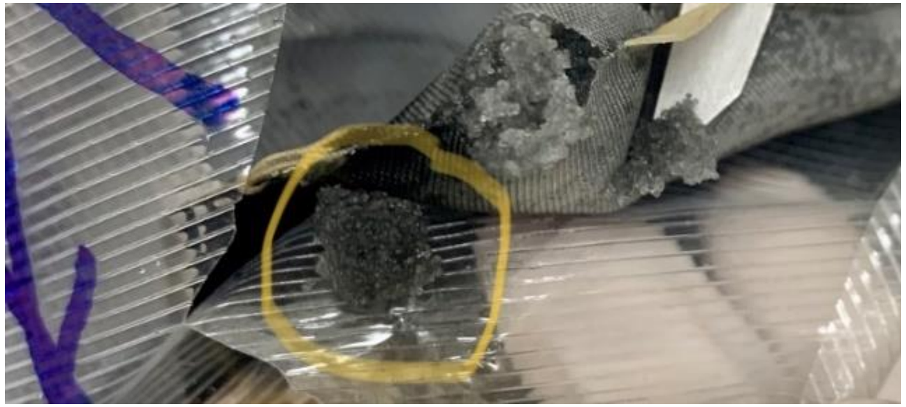
Min-Trap™ Samples
EHC® & GeoForm® ER Application

Upgradient well

EHC® treatment

GeoForm® ER treatment

- Site Conditions:
  - – Aerobic aquifer
  - – Ambient sulfate (SO_4^{2-}) ~ 200 mg/L
  - – EHC® = ZVI + OC (no added SO_4^{2-})
  - – GeoForm® ER = ZVI + OC + SO_4^{2-} + Fe^{2+}
  - – Min-Traps™ recovered after ~3 months



Ulrich, S., Martin Tilton, J., Justicia-Leon, S., Liles, D., Prigge, R., Carter, E., Divine, C., Taggart, D., & Clark, K. (2021). Laboratory and initial field testing of the Min-Trap™ for tracking reactive iron sulfide mineral formation during in situ remediation. Remediation. 1–14. https://doi.org/10.1002/rem.21681

Supplemental Analysis

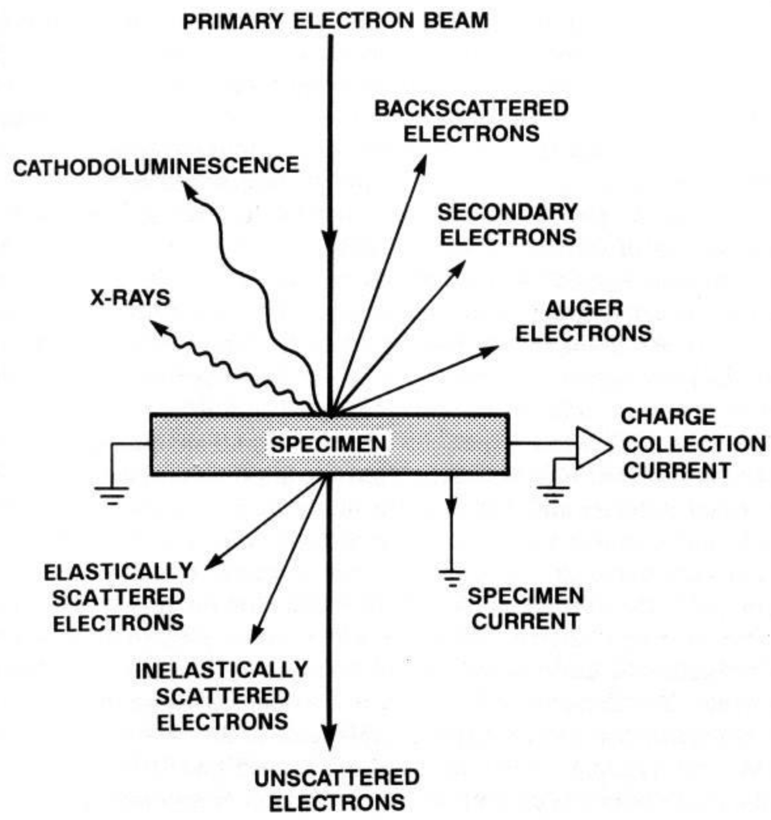
Methods used to identify and quantify reactive mineral species & biogeochemical conditions: (In addition to standard analytical methods)

- X-ray Diffraction

- Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA)

- Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM - EDS)

- Biology e.g., sulfate reducing bacteria, acid producing bacteria, methanogens, iron oxidizers, slime formers, denitrifiers, and sulfur oxidizing bacteria



AMIBA
Aqueous and Mineral Intrinsic Bioremediation Assessment

Before Treatment – Aquifer Matrix

Weak Acid Soluble Iron (WASFe)

The measurement of **surface bound iron** by WASFe. It is useful for assessing if iron reduction has begun and may also be useful for assessing the potential for abiotic degradation.

Strong Acid Soluble Iron (SASFe)

The measurement of the **capacity of material to support iron reduction**. This is a particularly useful measurement when a carbon substrate such as ELS is to be added. It can be determined how much iron must be overcome to get to methanogenesis or sulfate reduction.

After Treatment – Aquifer Matrix, Min-Traps^{TM}, Sediments

Acid Volatile Sulfide (AVS)

The measurement of **FeS (e.g., Mackinawite, Greigite)** produced by the products of iron reduction (Fe^{+2}) and sulfate reduction (S^{-2}). This measurement helps prove that sulfate reduction is an active part of the remediation, even if sulfide is not observed in the ground water. AVS measurement is sometimes referred to as ferrous sulfide measurement.

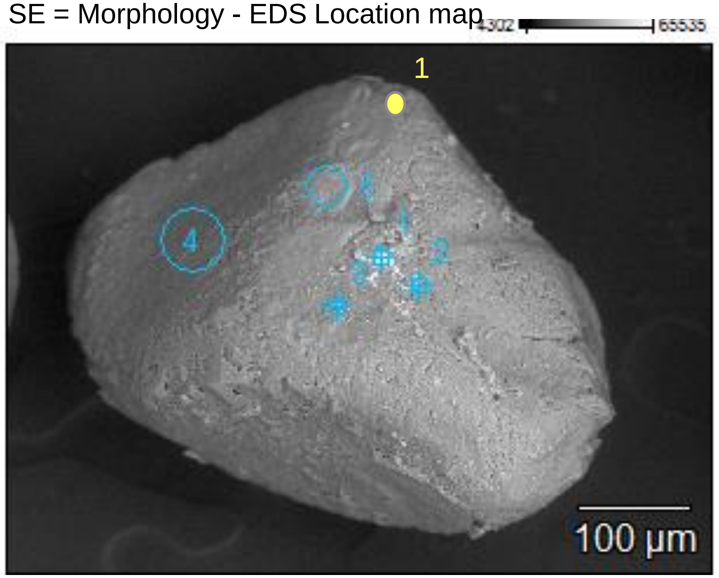
Chromium Extractable Sulfide (CrES)

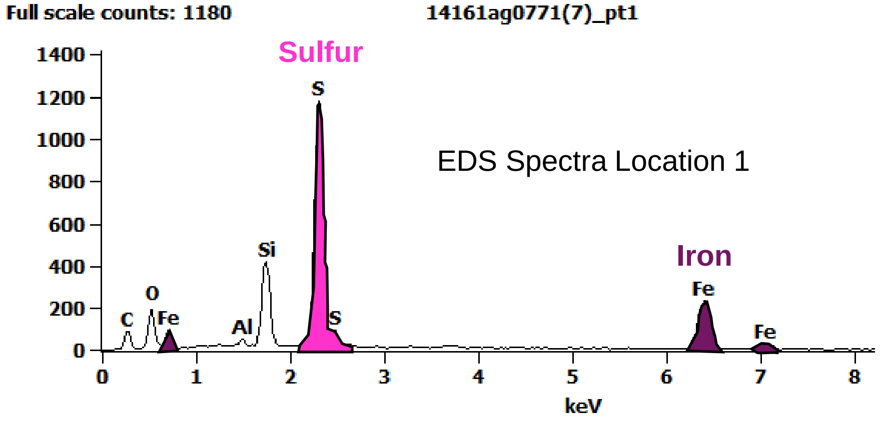
The measurement of slightly aged and oxidized products of sulfate reduction, such **as FeS_2 (pyrite) and elemental sulfur (S)**. This helps assess the historic contributions of sulfate reduction. CrES measurement is sometimes referred to as ferrous disulfide measurement.

SEM-EDS Results Following GeoForm® ER Application

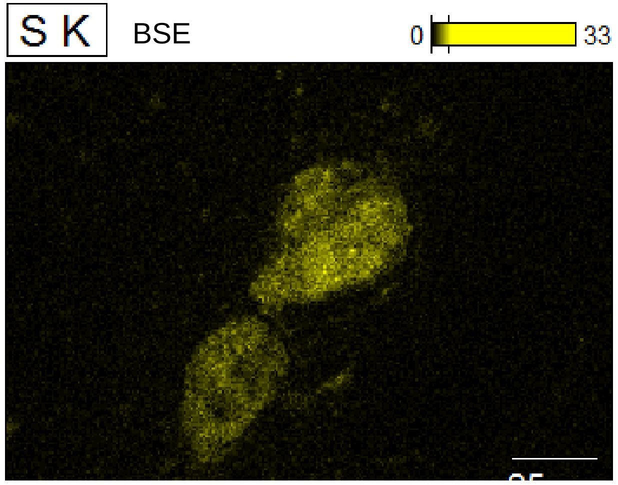
Scanning Electron Microscopy-Energy Dispersive Spectroscopy

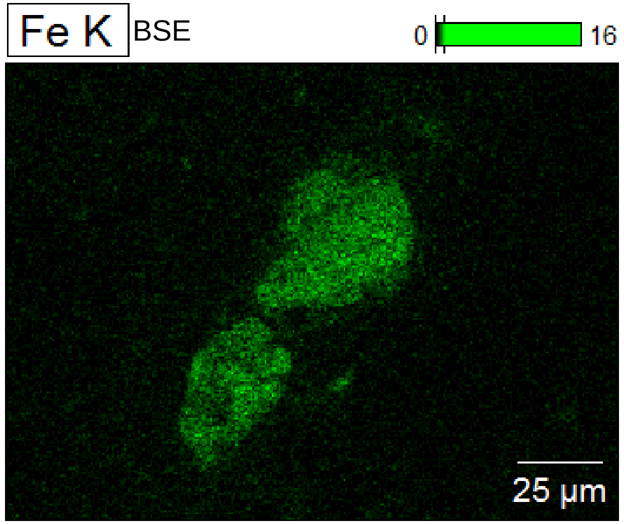
SE = Morphology - EDS Location map

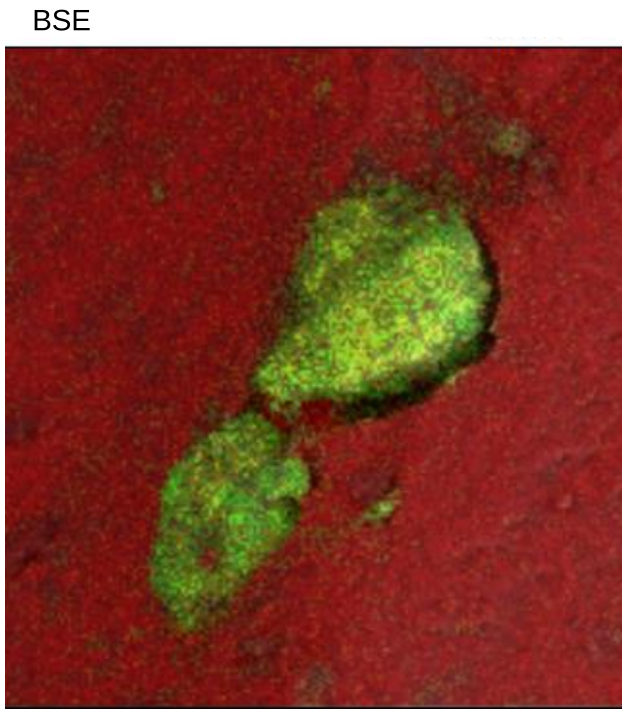




EDS Spectra Location 1







X-ray overlay map
red = Si,
green = Fe,
yellow = S.

At this site AVS 51%, CrES 49%

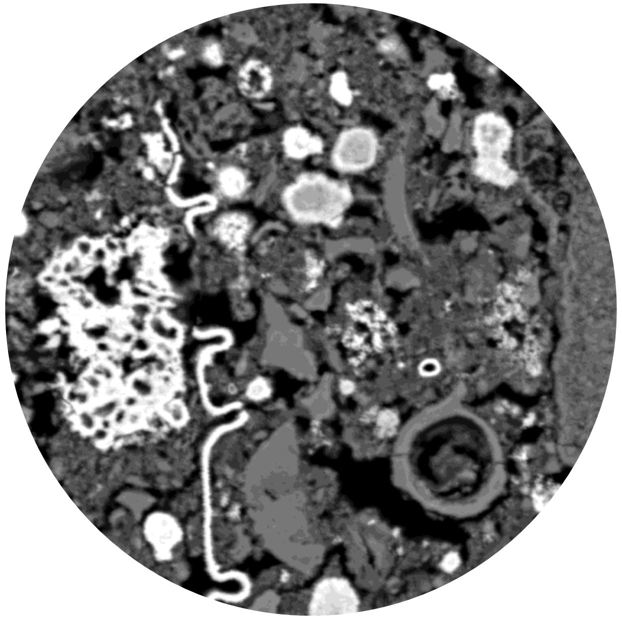
GeoForm® Biogeochemical Reagents

- All-In-One Biogeochemical Reagent

Provides All Building Blocks Needed for Reactive Mineral Formation

Combines Sulfate, Ferrous Iron, Electron Donors, pH Buffer, and Nutrients

Effective for Chlorinated Organics and Many Heavy Metals



GeoForm® Formulations

GeoForm Soluble

- Injects as a solution forming long lasting solids.
- Proprietary blend of Soluble Organic Carbon, Sulfate, Ferrous Iron, pH buffer and nutrients.
- Delivered in 2 parts allowing for custom designs
- Longevity of 2-3 years or more

GeoForm Extended Release

- Provides a longer lasting source of electron donors for continued rejuvenation of reactive minerals.
- Extended Release Organic Carbon, Micro-Scale ZVI, Sulfate, Ferrous Iron, pH buffers and nutrients
- Longevity of 5-10 years

GeoForm™ Formulation	Treatment Mechanisms		
	Biotic Reduction	Abiotic Reduction	
		Reductive Minerals	ZVI
GeoForm® Soluble	•	•	
GeoForm® Extended Release	•	•	•

GeoForm® Applicability Considerations

GeoForm® Soluble custom designed to achieve ~500 to 3,000 mg/L **Sulfate** <u>(You decide).</u>

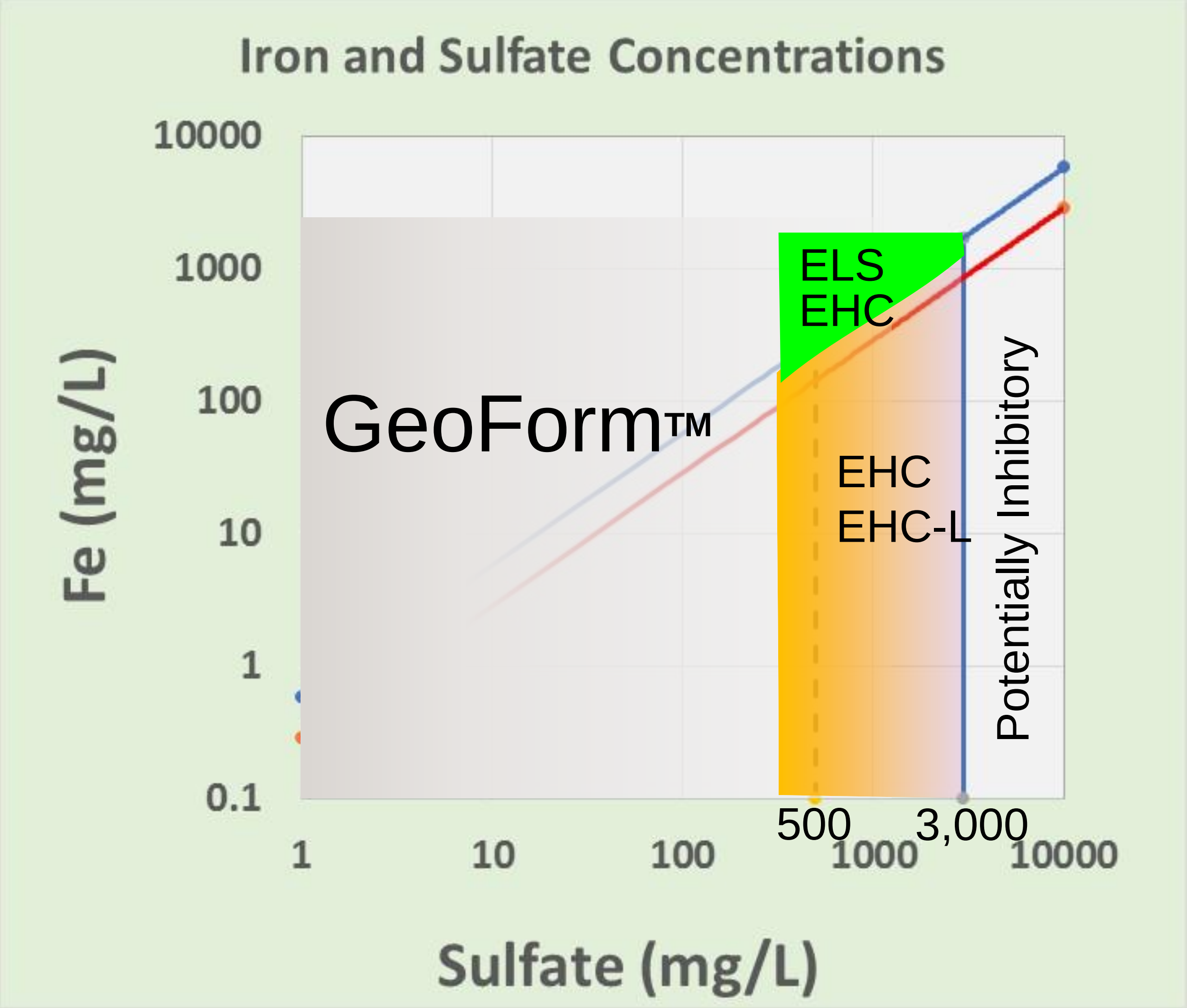
+

ELS (organic component) exceeds demand from sulfate, contaminants and other acceptors

In high sulfate – low iron aquifers consider adding iron in form of EHC, or EHC-L

In high sulfate – high iron aquifers consider ELS or EHC.

Sulfate in excess of 3,000 mg/L may be inhibitory (may try more iron)



Case Studies

1. Biogeochemical treatment in high-sulfate, low-iron aquifer at Joint Base Hickam – Pearl Harbor
2. GeoForm® Extended Release For Treatment of CEs in the San Francisco Bay Area
3. Biogeochemical Treatment of Mixed Chlorinated Organics in the San Francisco Bay Area
4. Bench Study for Biogeochemical Treatment of Arsenic in Florida

Case Study 1: Joint Base Hickam – Pearl Harbor, LF-05
Site Conditions

Unconsolidated calcium carbonate aquifer (little Fe)

Very high sulfate concentrations (up to 3,000 mg/L)

Reducing conditions established in groundwater

Very high concentrations of chlorinated ethenes (PCE, TCE, DCE, VC) (up to 550 mg/L TCE)

Large population of Dhc present at site (Hawaii 05™)

Multiple applications of vegetable oil resulted in incomplete degradation of CEs and accumulation of vinyl chloride

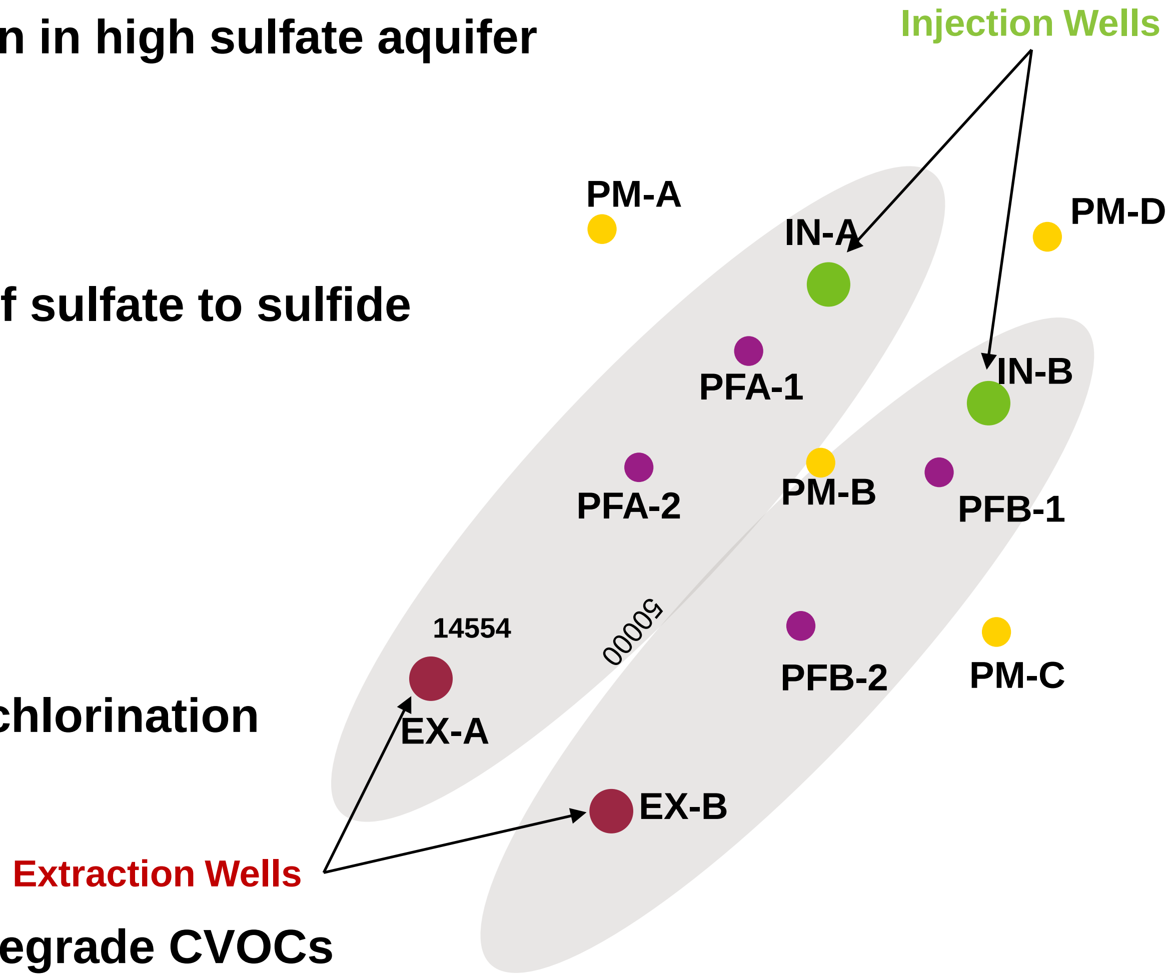
Bench tests confirmed sulfide inhibiting dechlorination

Case Study 1: Joint Base Hickam – Pearl Harbor, LF-05

Field Demonstration Process

Distribute organic substrate and soluble iron solution in high sulfate aquifer

Used groundwater extraction/injection system



Organic substrate promotes biological conversion of sulfate to sulfide

Sulfide is removed from solution with soluble iron removing sulfide toxicity issues

Organic substrate promotes biological reductive dechlorination

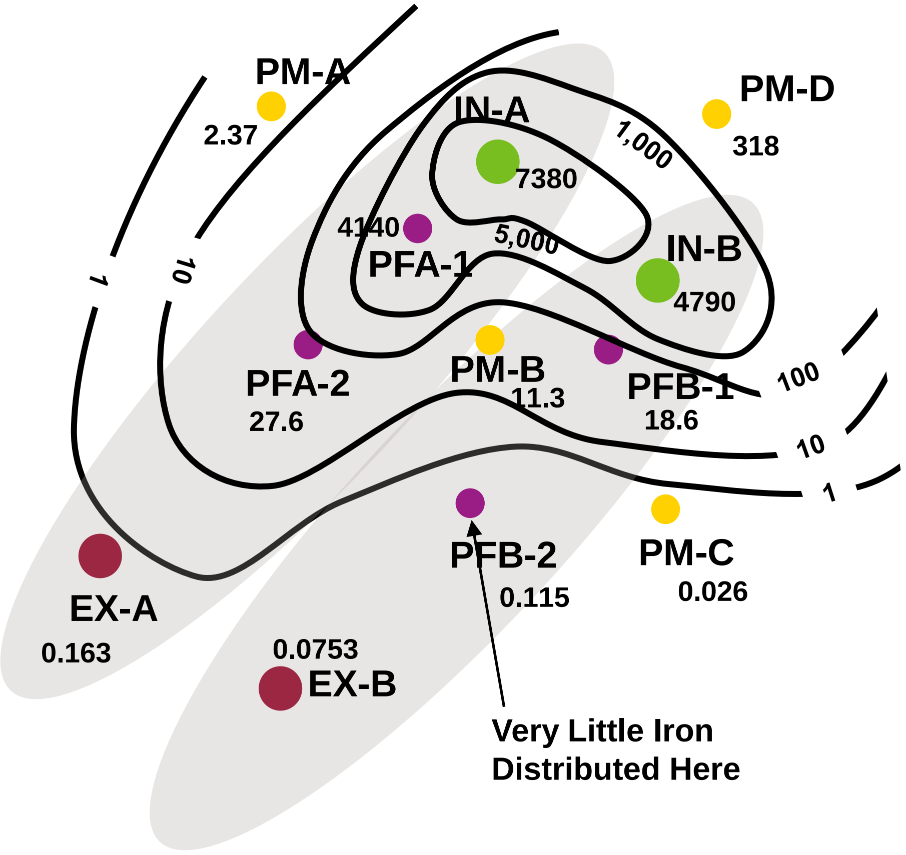
Resulting reactive iron-sulfide minerals abiotically degrade CVOCs

Case Study 1: Joint Base Hickam – Pearl Harbor, LF-05

Post Circulation Results

Iron Distribution

Iron distributed through treatment area



Very Little Iron Distributed Here

Legend

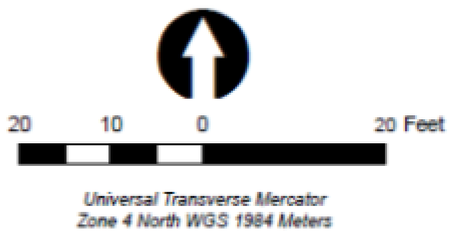
● Injection well

● Extraction well

● Performance Monitoring well

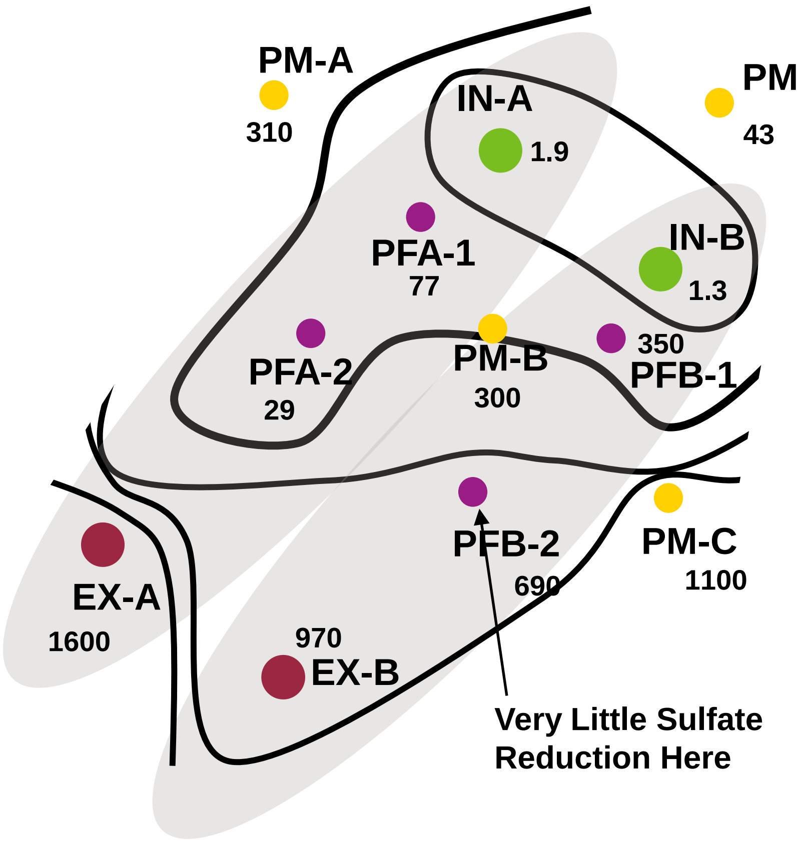
● Perimeter Monitoring well

318 Concentration (mg/L)



Sulfate Reduction

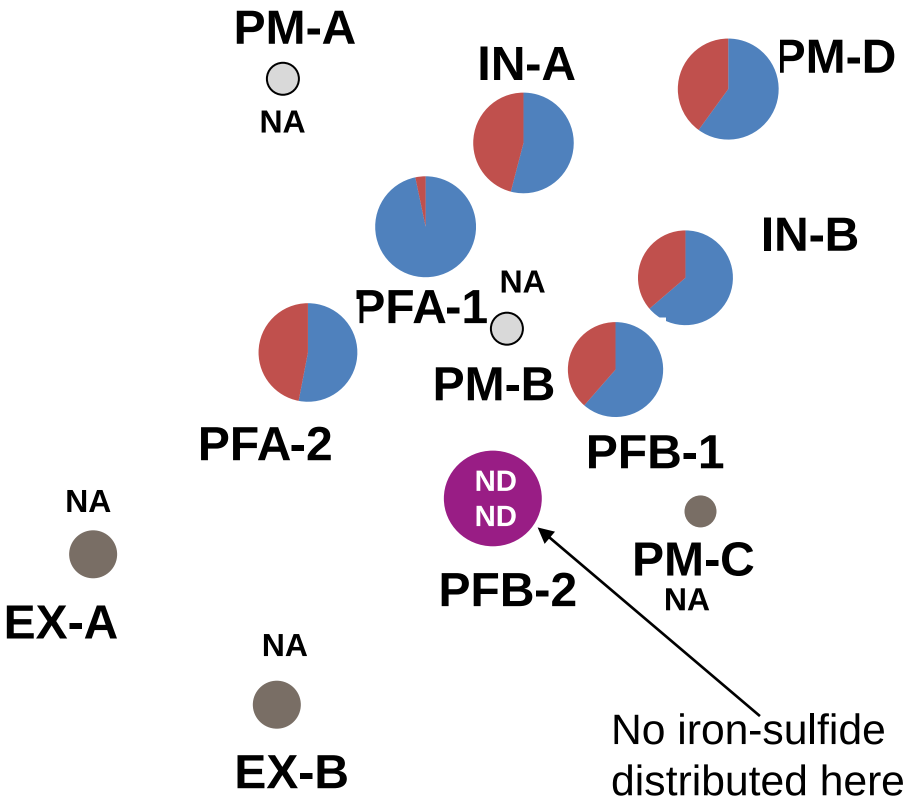
Sulfate Reduced in Treatment Area



Very Little Sulfate Reduction Here

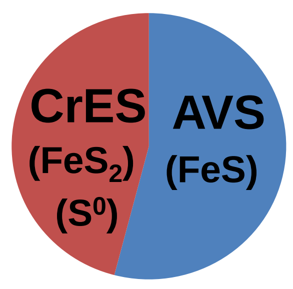
Case Study 1: Joint Base Hickam – Pearl Harbor, LF-05

AMIBA Analysis: Ratio of AVS – CrES in Precipitate Samples



No iron-sulfide distributed here

Legend



AVS - Acid Volatile Sulfide

FeS – Mackinawite, Greigite

CrES - Chromium Extractable Sulfide

FeS_2 & S^0 – Pyrite, Elemental Sulfur

ND ND AVS Not Detected
CrES Not Detected

● **NA – Not Analyzed**

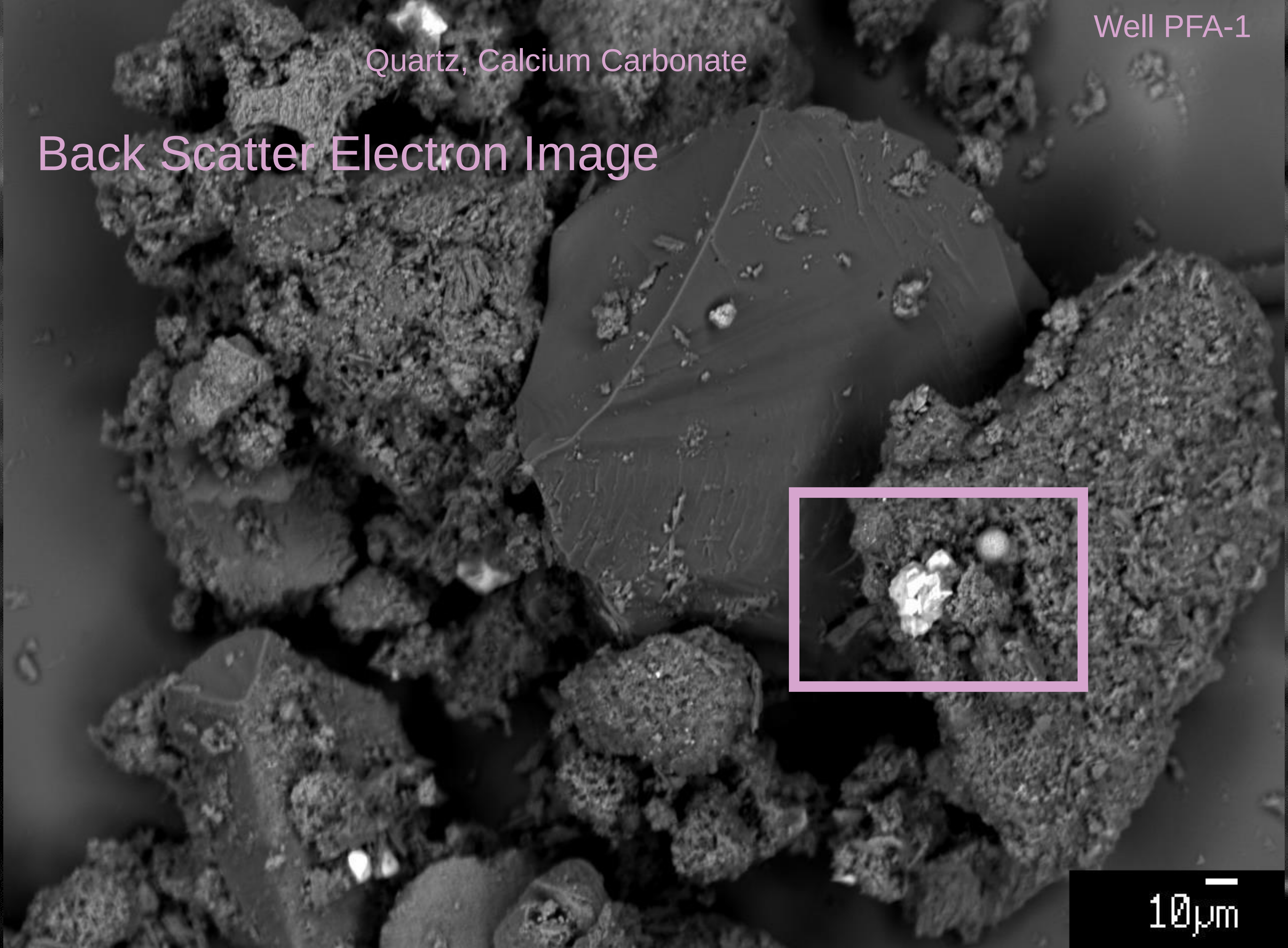
Secondary Electron Image

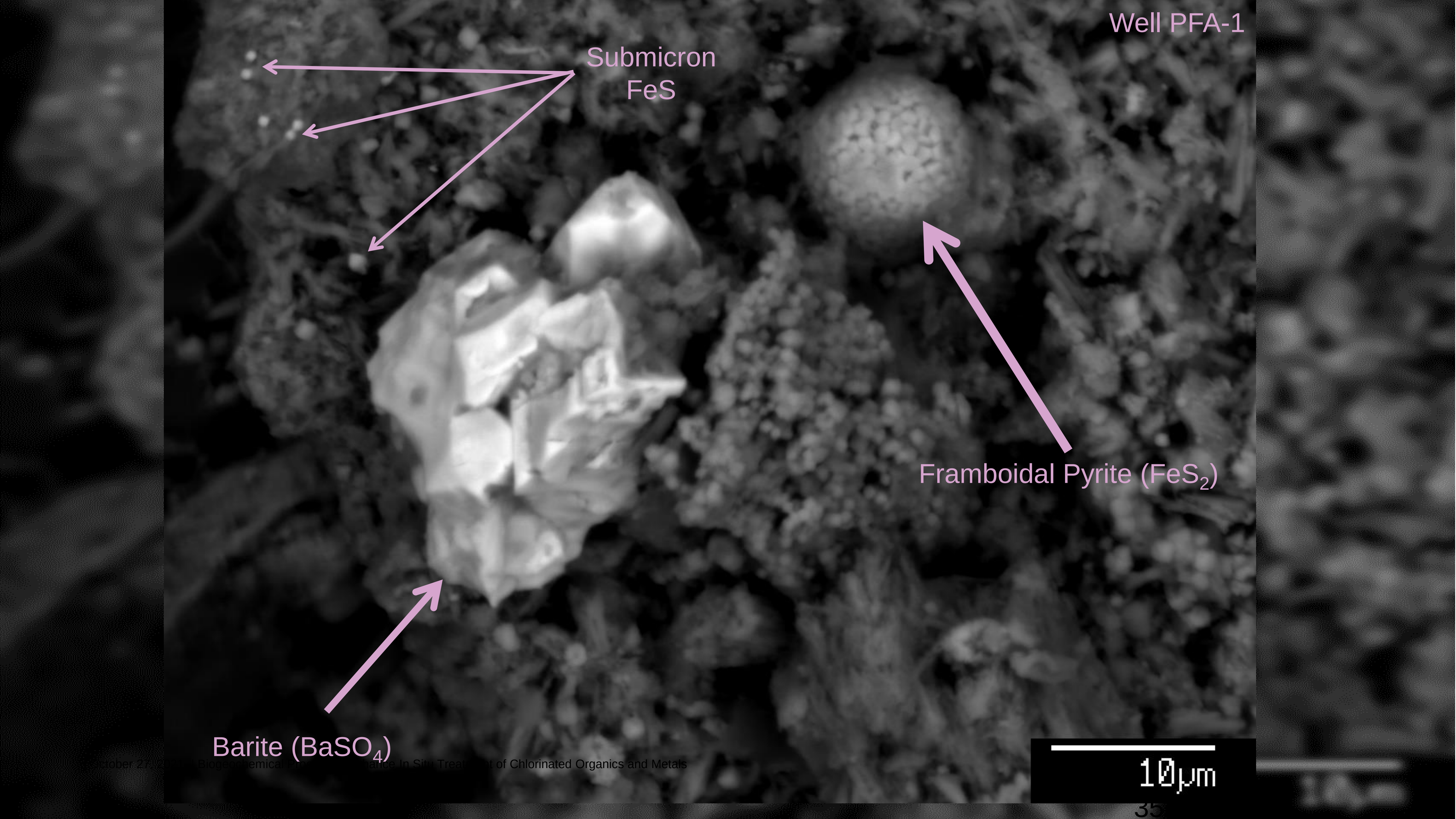
Well PFA-1

Well PFA-1

Quartz, Calcium Carbonate

Back Scatter Electron Image

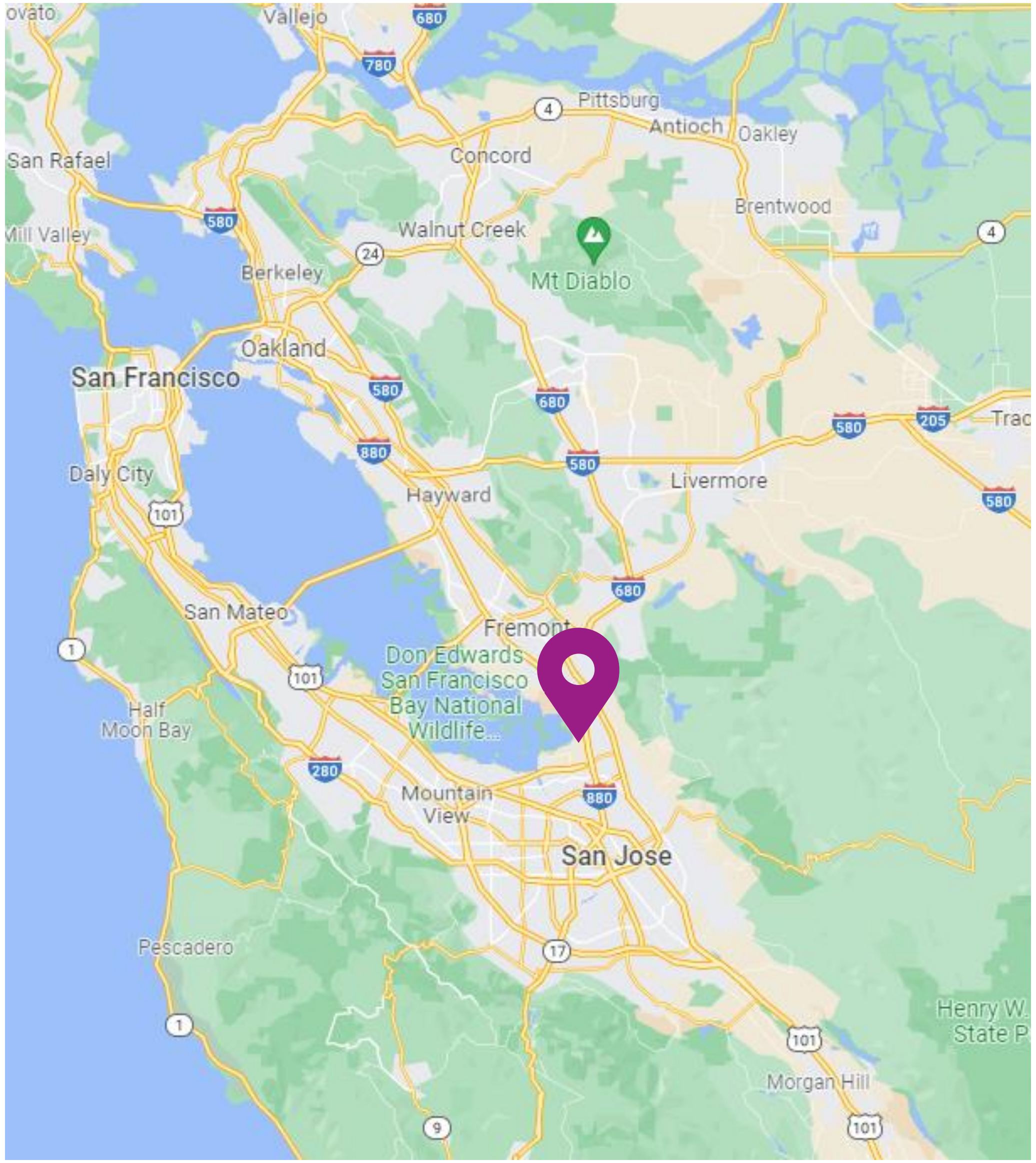



Well PFA-1
Submicron FeS
Framboidal Pyrite (FeS_2)
Barite ($BaSO_4$)
10µm

Case Study 2:

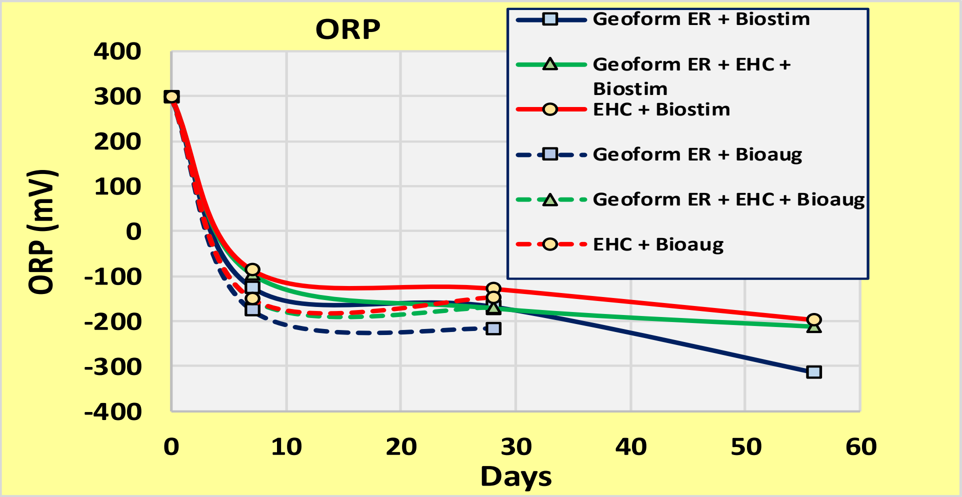
GeoForm® Extended Release For Treatment of CEs in the San Francisco Bay Area

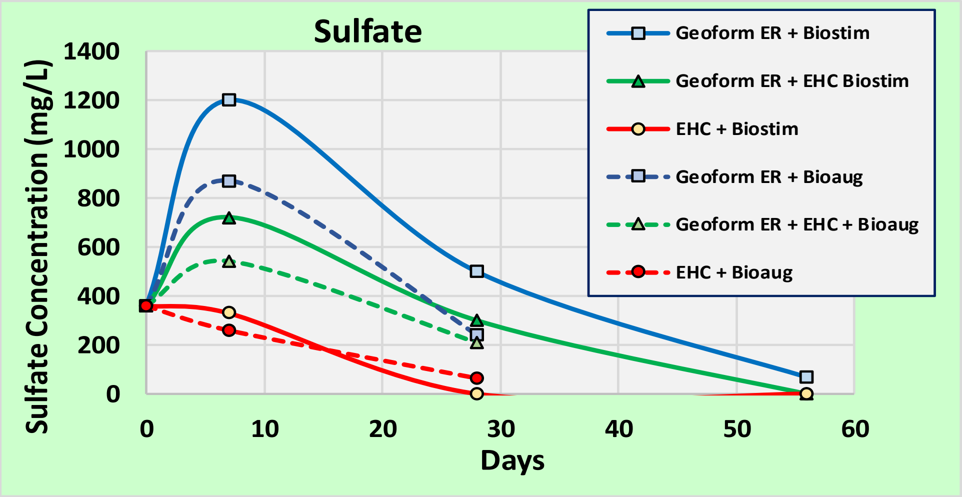
- Site Overview
  - Very high concentration chlorinated ethenes (CEs) (10s mg/L)
  - Moderate sulfate groundwater (~ 400 mg/L)
  - Low DO, slightly reducing
  - GW flow rate ~ 50 feet per year
- Evaluated BGCR enhanced ISCR
- Simultaneous Laboratory Batch, Column Tests and Field Pilot Test
- Subsequent Full-Scale Field Application



Case Study 2: CE Treatment at Bay Area Site

Batch Test Results



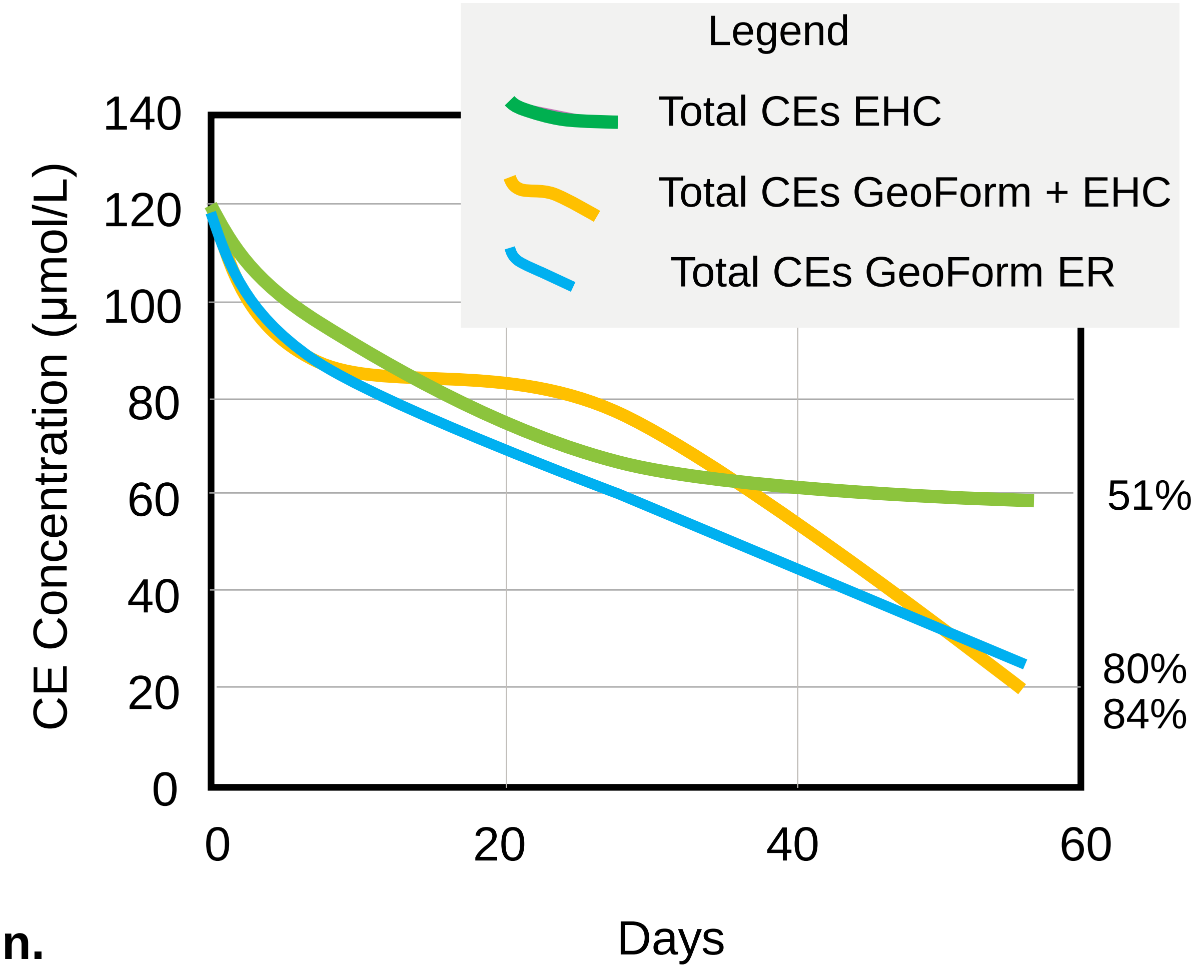


- Bench Test compared:
  - EHC® ISCR Reagent (no added sulfate)
  - GeoForm® Extended Release + EHC®
  - GeoForm® Extended Release
- EHC® similar to GeoForm® ER except EHC® does not contain ferrous iron and sulfate as does GeoForm® ER
- With ambient sulfate (~ 400 mg/L)
- With and without bioaugmentation (SDC-9™)

Case Study 2: CE Treatment at Bay Area Site

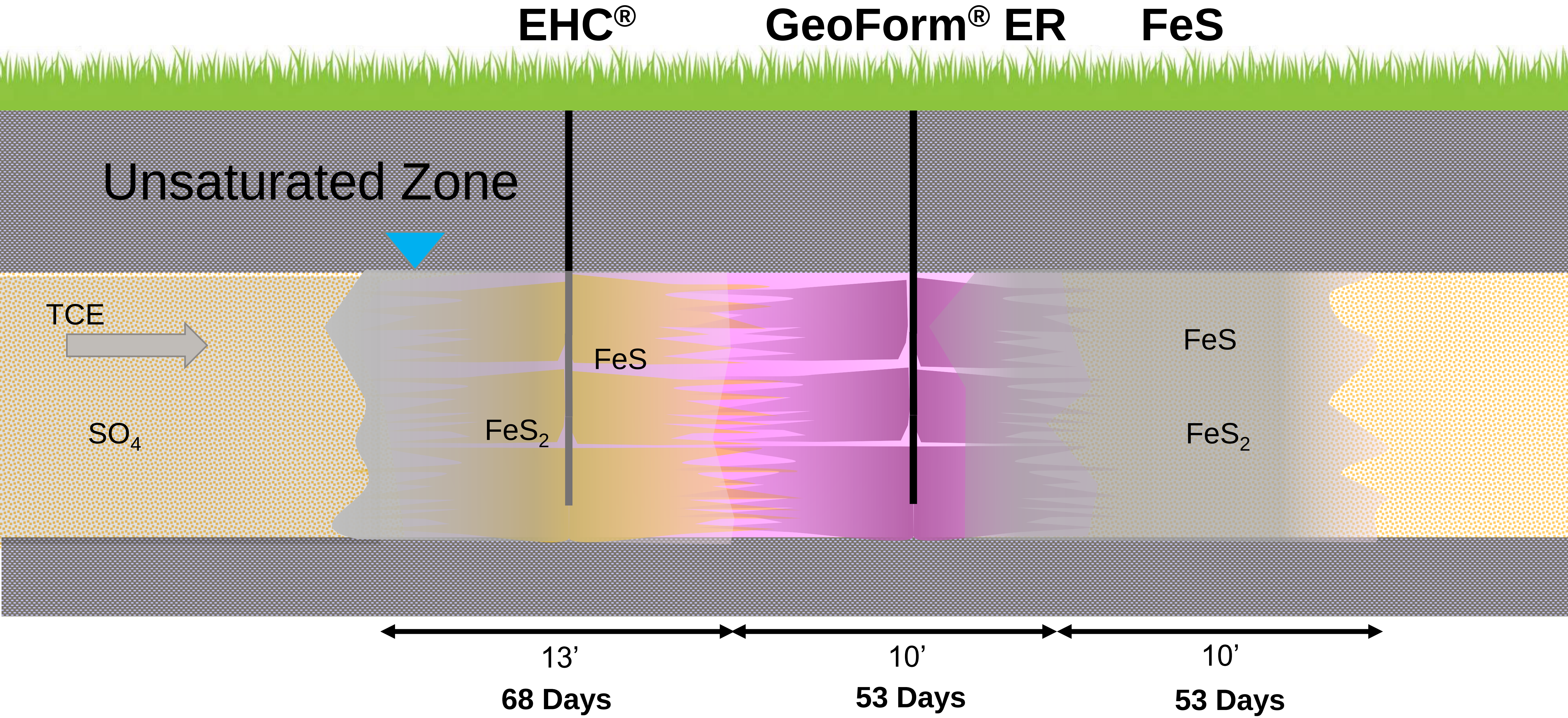
Batch Test Results GeoForm® Extended Release Increases EHC® Degradation Rates

Addition of GeoForm® Extended Release Increased degradation rate ~63% Relative to EHC® (ISCR) (with sulfate).



Results are similar with or without bioaugmentation.

PRB Construction

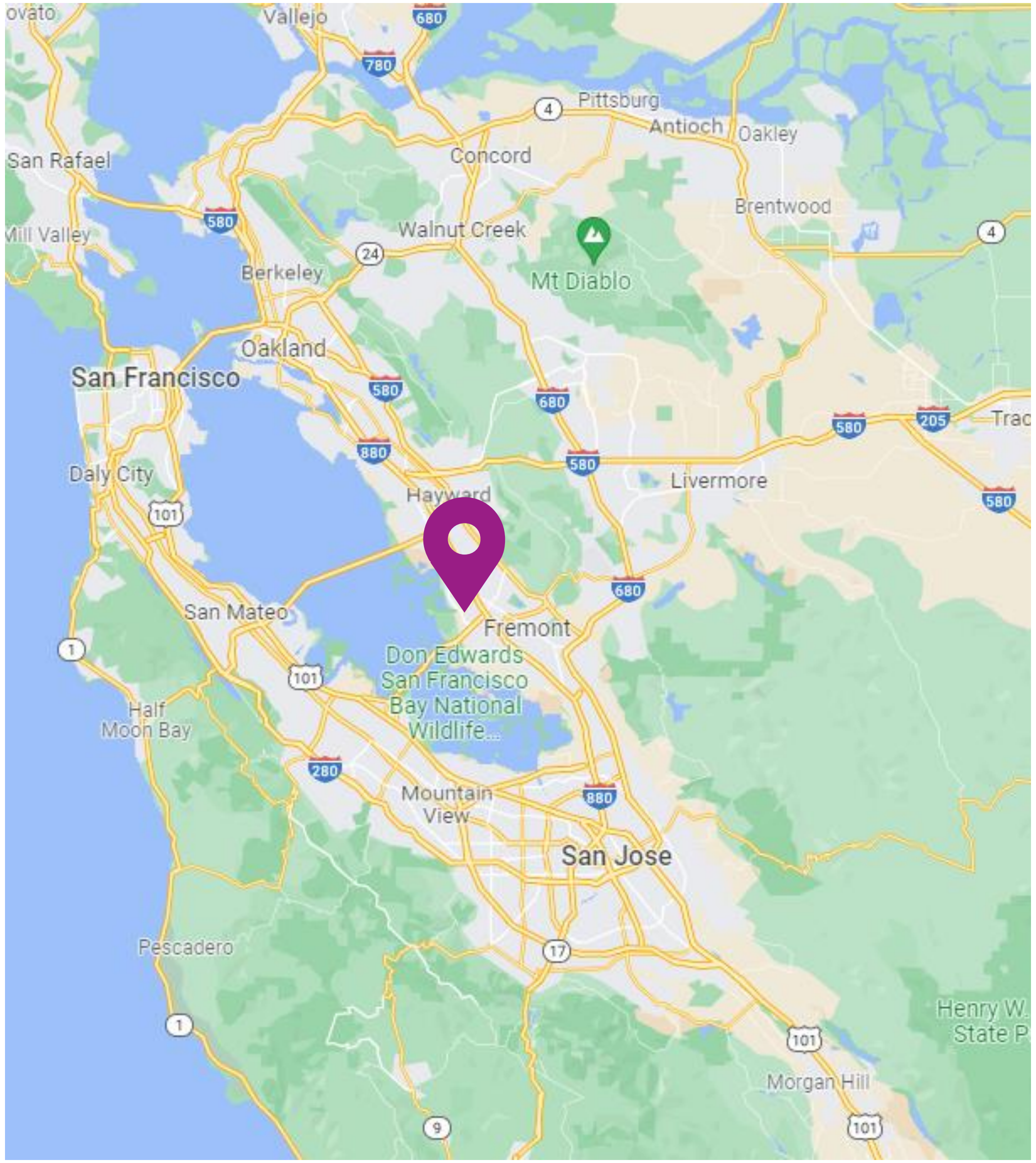


Total Residence Time ~ 6 months

Case Study 3:

Biogeochemical Treatment of Mixed Chlorinated Organics in the San Francisco Bay Area

- Site Overview
  - High sulfate groundwater (~ 700 mg/L)
  - Mixed plume (TCE, 1,2-DCA, CF)
  - One recalcitrant area
- Property being developed
- Client wanted aggressive approach
- Sequentially applied reagents appropriate for contaminants



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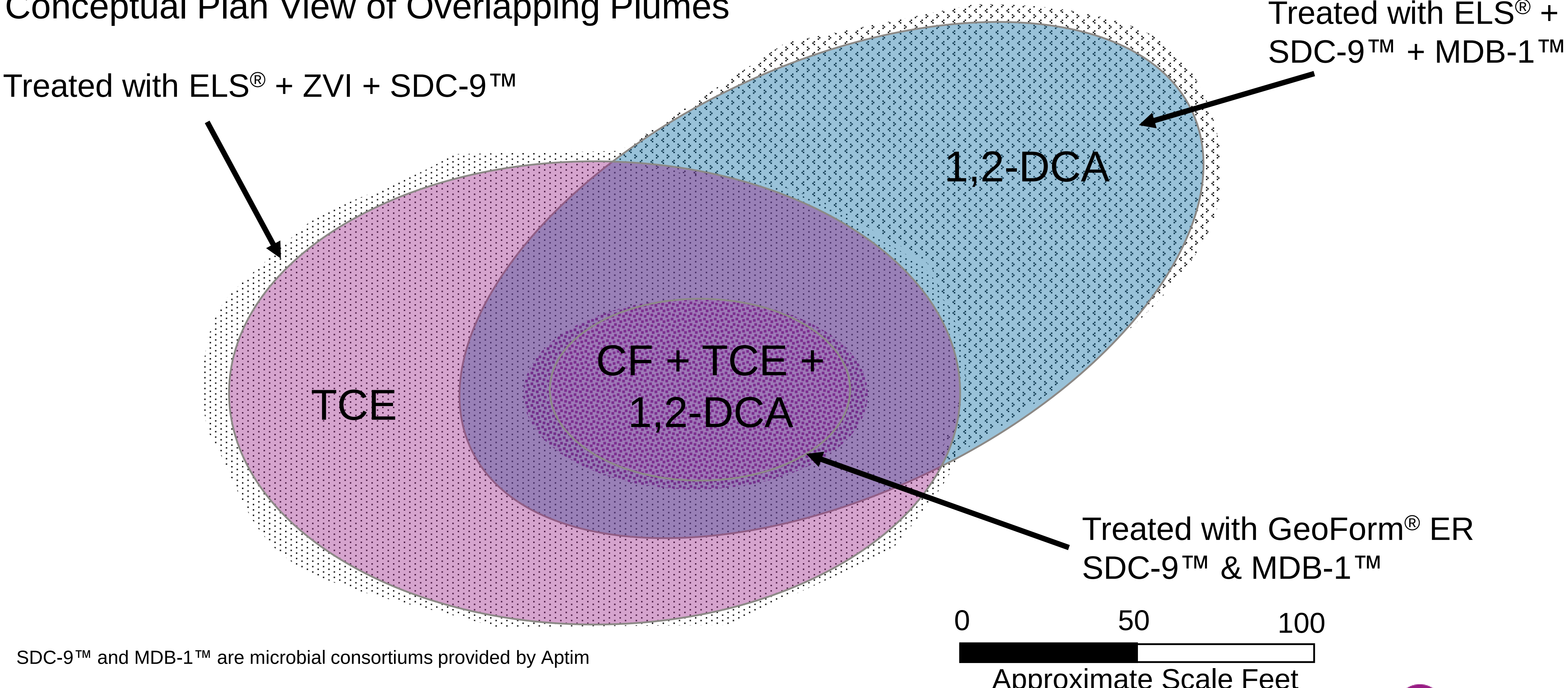
Case Study 3: Mixed Chlorinated Organics at Bay Area Site

Sequential Treatment of Mixed Plume

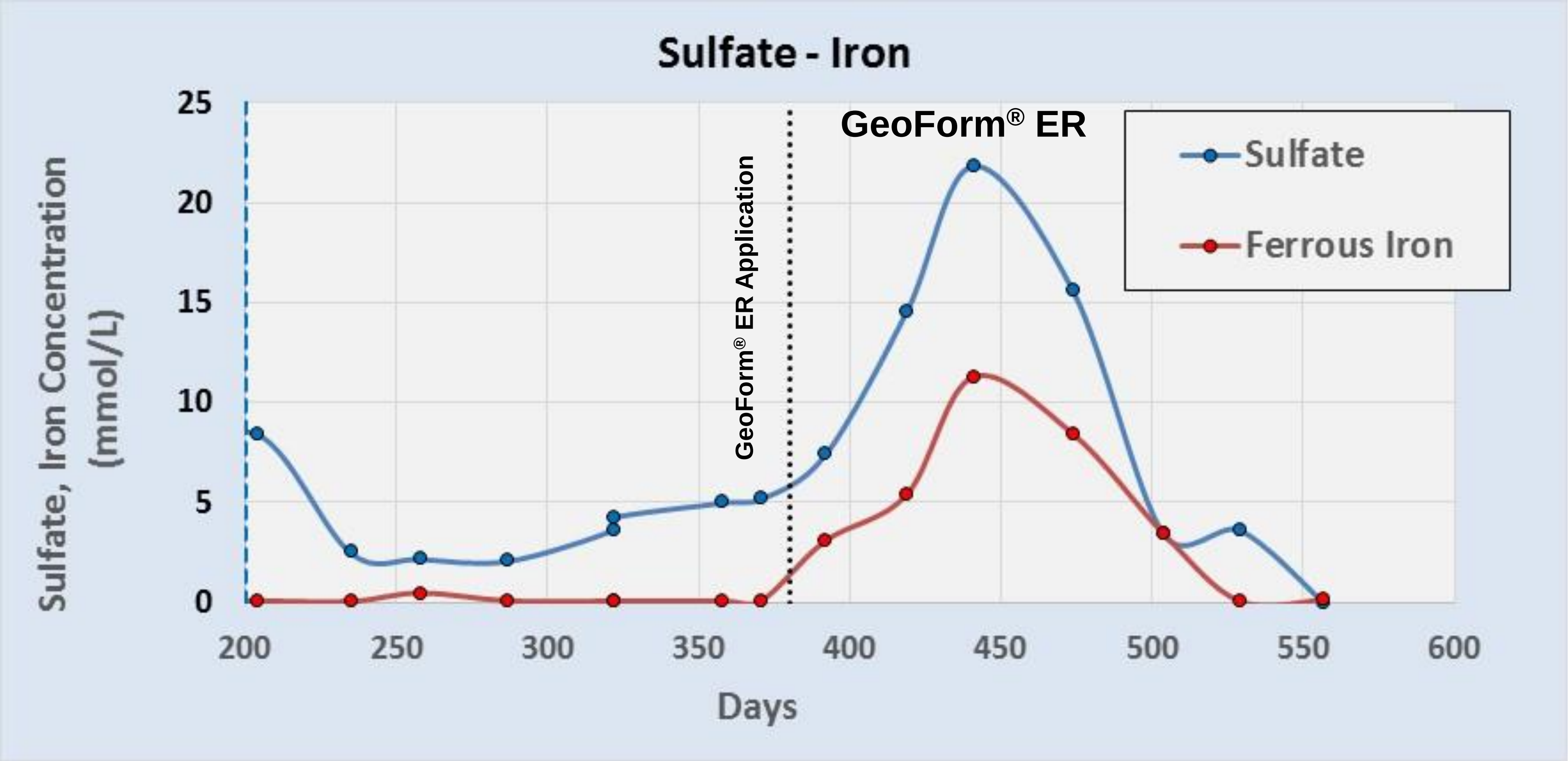
Conceptual Plan View of Overlapping Plumes



SDC-9™ and MDB-1™ are microbial consortiums provided by Aptim

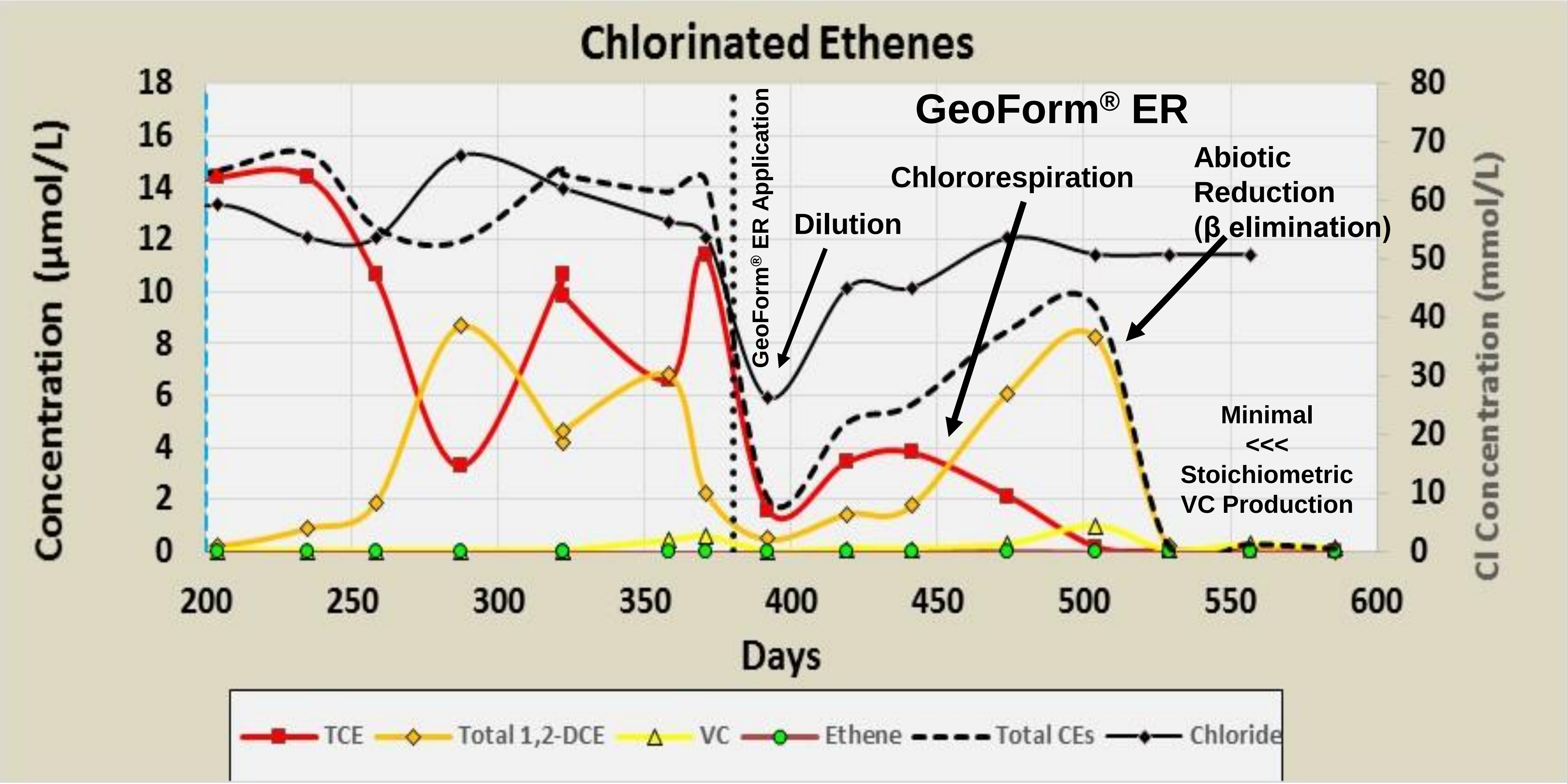
Case Study 3: Mixed Chlorinated Organics at Bay Area Site

Sulfate & Iron Temporarily Increase Following GeoForm® ER application



Case Study 3: Mixed Chlorinated Organics at Bay Area Site

Biogeochemical Treatment of Chlorinated Ethenes (CEs)



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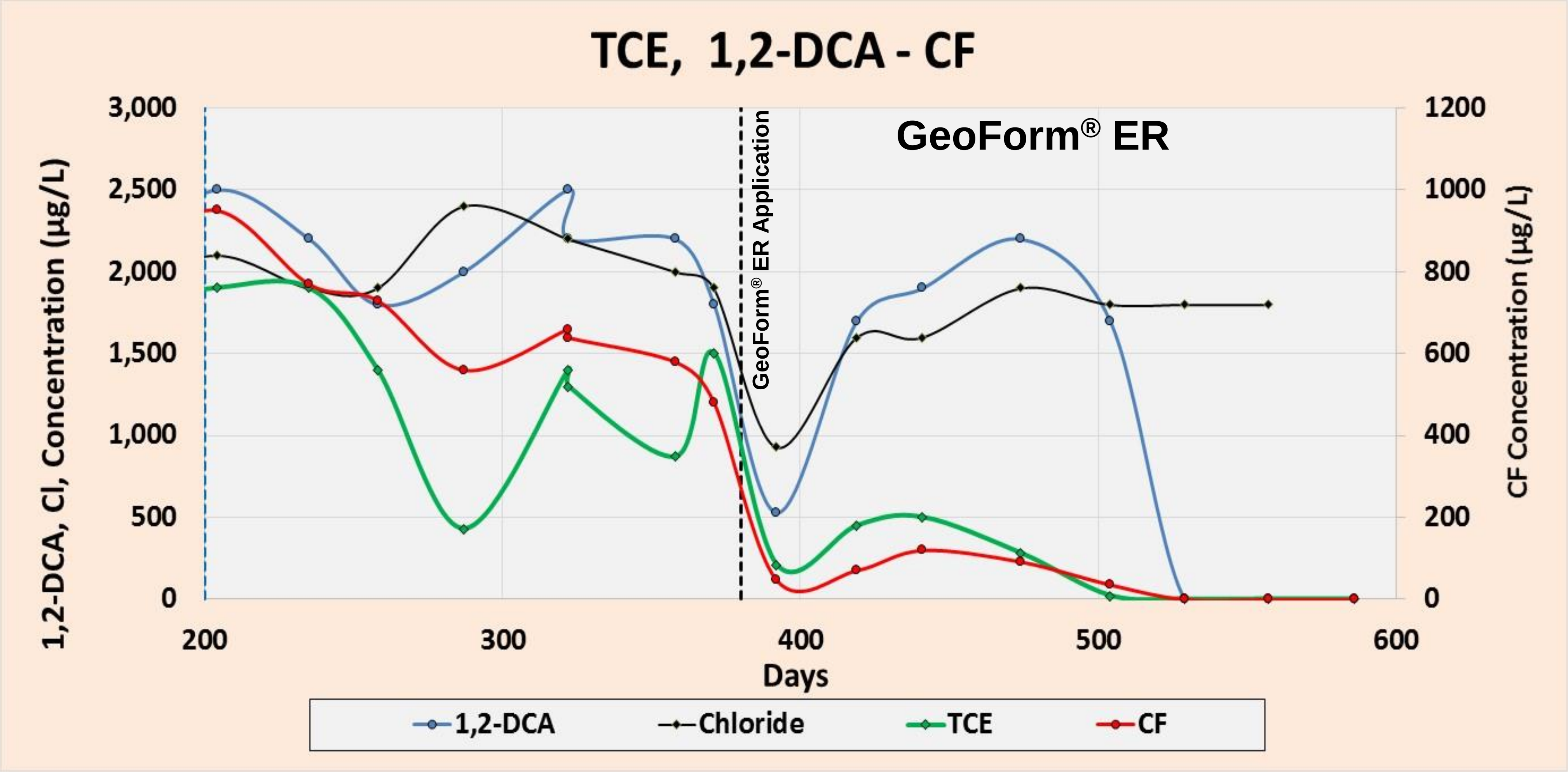
Case Study 3: Mixed Chlorinated Organics at Bay Area Site

GeoForm® ER Treats Mixed CEs, CA and CMs



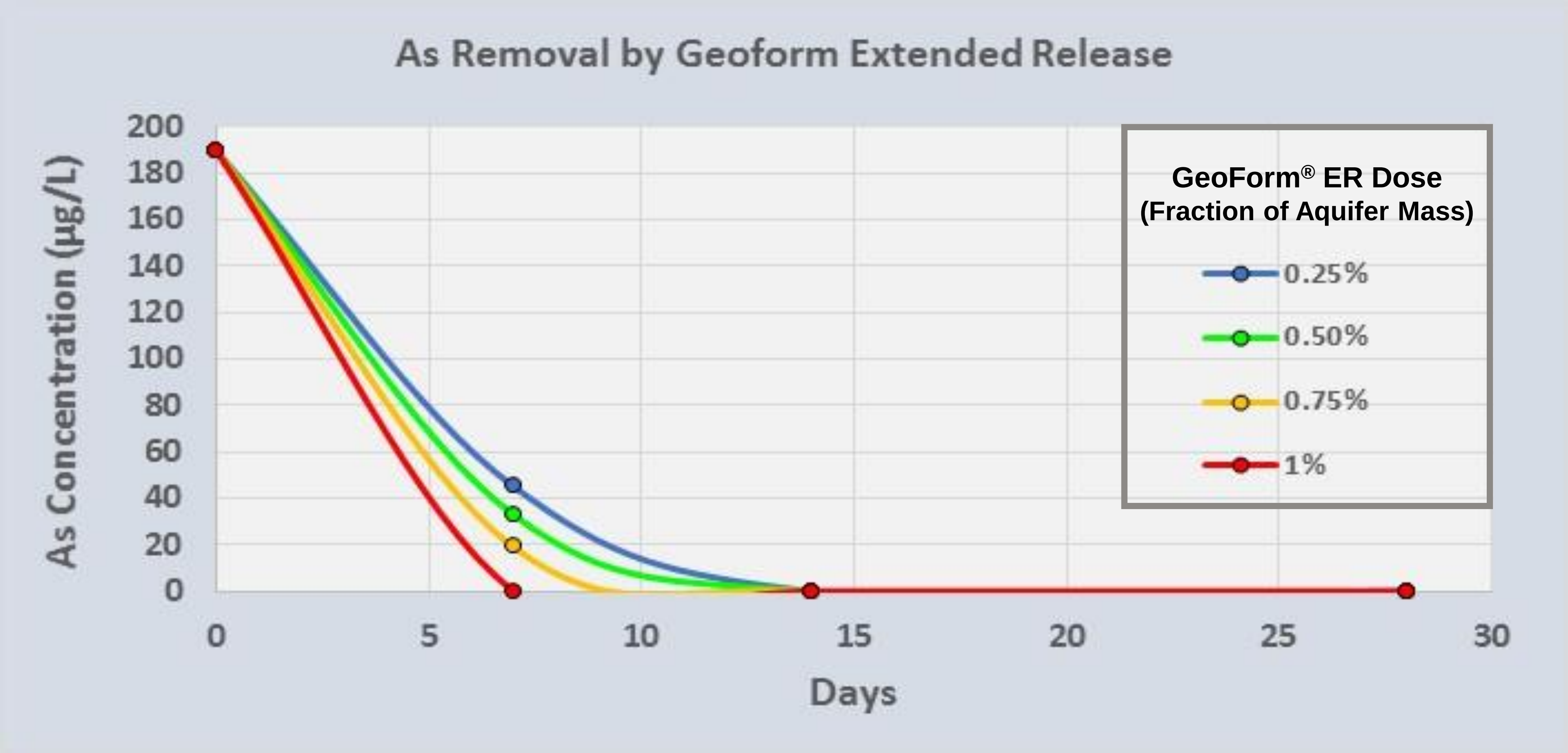
Case Study 4:

Biogeochemical Treatment of Arsenic in Florida

- Carbonate aquifer
- Soil and groundwater impacted with arsenic (As) (possible cattle dip)
- Arsenic Groundwater Concentration - several hundred µg/L
- Bench tests conducted to evaluate GeoForm® ER for treatment of As

Case Study 4: Biogeochemical Treatment of Arsenic in Florida

Bench Test Results: Biogeochemical Treatment of Arsenic



Summary

Biogeochemical Reduction (BGCR) is a naturally occurring process.

BGCR processes occur with and will improve ERD and ISCR processes.

Most site conditions can be modified to optimize BGCR processes

BGCR processes enhance the reactivity and longevity of Zero Valent Iron (ZVI)

BGCR extends the size and longevity of treatment zones.

BGCR sequesters toxic metals from groundwater for extended periods of time.

Questions?

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