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Remediation Technology Symposium (RemTech) 2012

Comparison of Approaches to Engineered *In Situ* Biogeochemical Transformation of Chlorinated Solvents

19 October 2012

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Acknowledgements

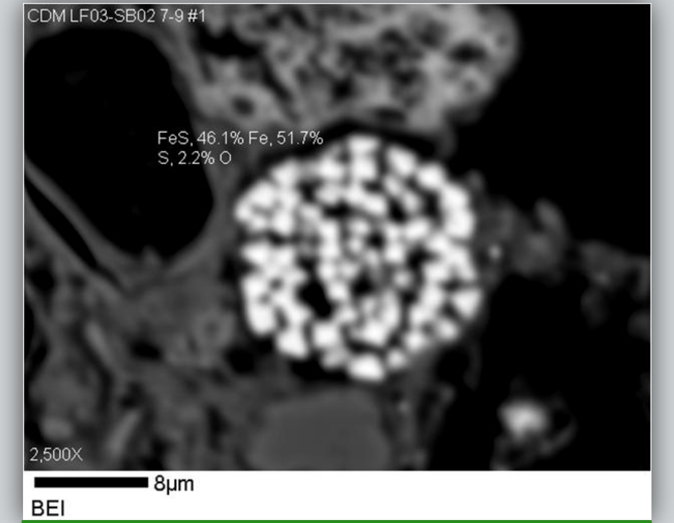
- AFCEE Tech Transfer – Dr. Seb Gillette
- Air Force Demonstration Hosts
    - Joint Base Pearl Harbor-Hickam (JBPHH), Hawaii – Bill Grannis
    - Altus Air Force Base (AFB), Oklahoma – Dan Stanton
    - Joint Base Elmendorf-Richardson (JBER), Alaska – Donna Baumler
    - Little Mountain Test Annex (LMTA), Hill AFB, Utah – Kyle Gorder
- Parsons – John Hicks, John Hall, Mitch Jensen

Presentation Topics

- Technical Approaches
- Engineered Systems – Case Studies
  - Materials
  - Bioreactors
  - Direct Injection
- Factors Impacting Performance
  - Amendment Properties and Distribution
  - Utilization of Iron, Sulfate, and Organics
  - Design Considerations – Special Considerations

Engineered In Situ Biogeochemical Transformation

- Chlorinated compounds degraded by abiotic reactions with naturally occurring or biogenically-formed reactive minerals
- Abiotic processes typically do not produce intermediate dechlorination products
- Alternative or complement to biostimulation using selective *Dehalococcoides* species



Framboidal Pyrite

AFCEE Objective

Demonstrate an in situ technology capable of sustained degradation of chlorinated solvents without accumulation of cis-DCE or VC

Three General Approaches

- Production of reactive iron monosulfide (FeS) minerals while limiting biological activity – “one and done” approach (Dover AFB injection; Kennedy *et al*., 2006)
- Continual production of FeS with high sulfate consumption rate (Altus AFB biowalls and bioreactors; Lebron *et al*., 2010)
- Synergistic approach stimulating both production of reactive FeS minerals and biotic dechlorination with bioaugmentation (JBPHH bioreactor study; Leigh *et al*., 2011)

Engineered Systems – Case Studies

- Materials
  - Iron Amendments
  - Sulfate Amendments
- Bioreactors
  - LF05 Bioreactor, JBPHH, HI
  - LF03 Bioreactor, Altus AFB, OK
- Direct Injection
  - DP98, JBER, AK
  - North Disposal Area, LMTA, Hill AFB, UT

Potential Sulfate Amendments

Material (most common form)	**Percent Sulfate**	**Percent Iron**	**Notes**
Ferrous Sulfate (heptahydrate) - $FeSO_4 \cdot 7H_2O$	35%	20%	Soluble
Magnesium Sulfate (heptahydrate) - $MgSO_4 \cdot 7H_20$	39%	0%	Soluble - Epsom Salt
Calcium Sulfate (dihydrate) - $CaSO_4 \cdot 2H_20$	56%	0%	Moderate Solubility - Gypsum
Sodium Sulfate (decahydrate) - $Na_2SO_4 \cdot 10H_20$	30%	0%	Highly Soluble

Percent by weight in hydrated form

Sulfate amendments are soluble (up to 26,000 mg/L) and migrate with groundwater flow, but dissolution rate may vary (anhydrous versus hydrated forms)

Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$)

Potential Iron Amendments

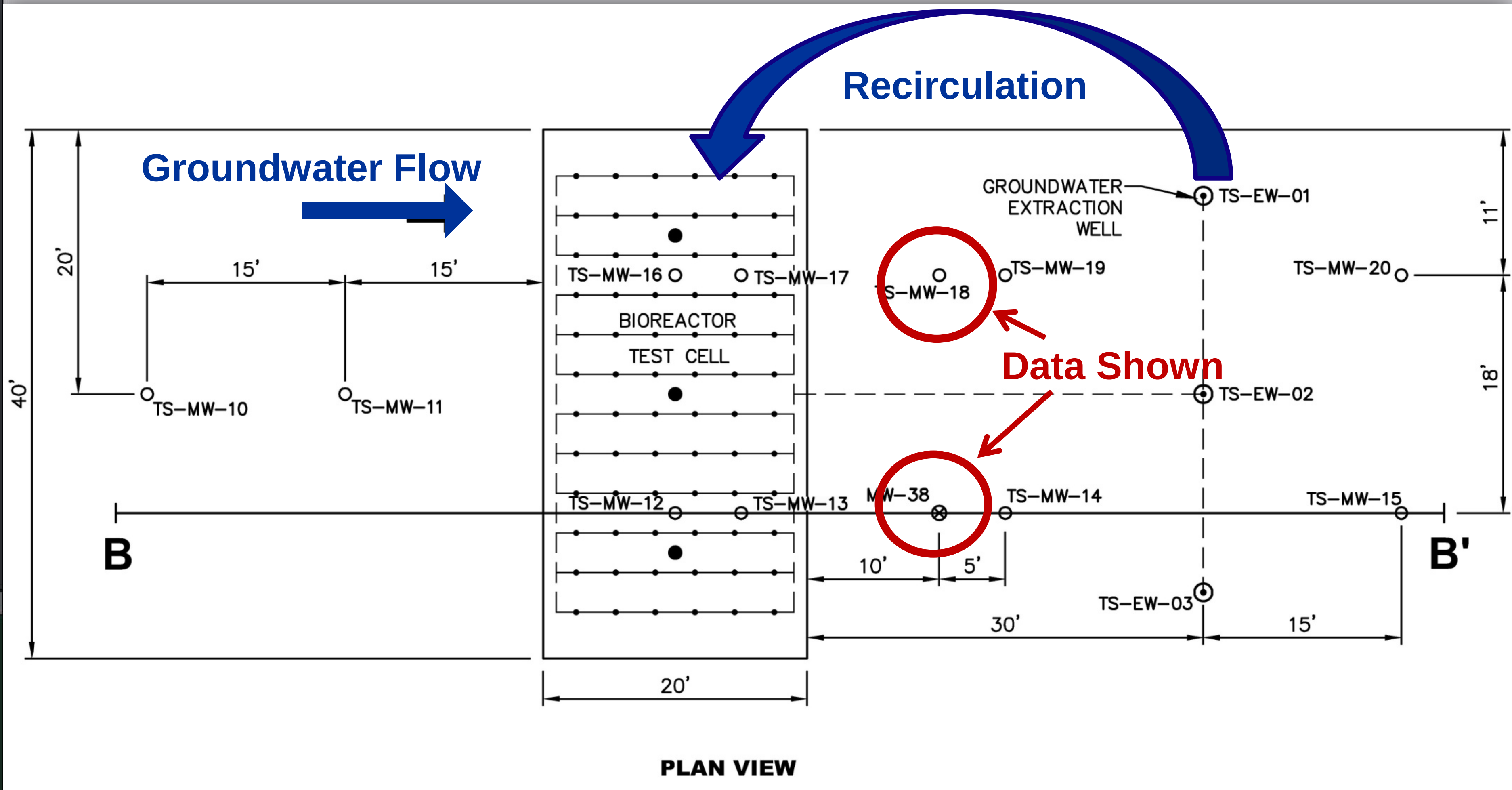
Material (most common form)	**Percent Sulfate**	**Percent Iron**	**Notes**
Crushed or Powdered Hematite - Fe_2O_3	0%	68%	Natural or Synthetic (pigment)
Crushed or Powdered Magnetite – Fe_3O_4	0%	67%	Natural or Synthetic (pigment)
Ferrous Chloride (anhydrous) - $FeCl_2$	0%	34%	Soluble (corrosive - low pH)
Ferrous Lactate - $Fe(C_3H_5O_3)_2$	0%	28%	Soluble – Food Additive
Ferrous Sulfate (heptahydrate) - $FeSO_4 \cdot 7H_2O$	35%	20%	Soluble

Solid iron amendments have a broad range of bioavailability – ranging from 250 to 25,000 mg/kg

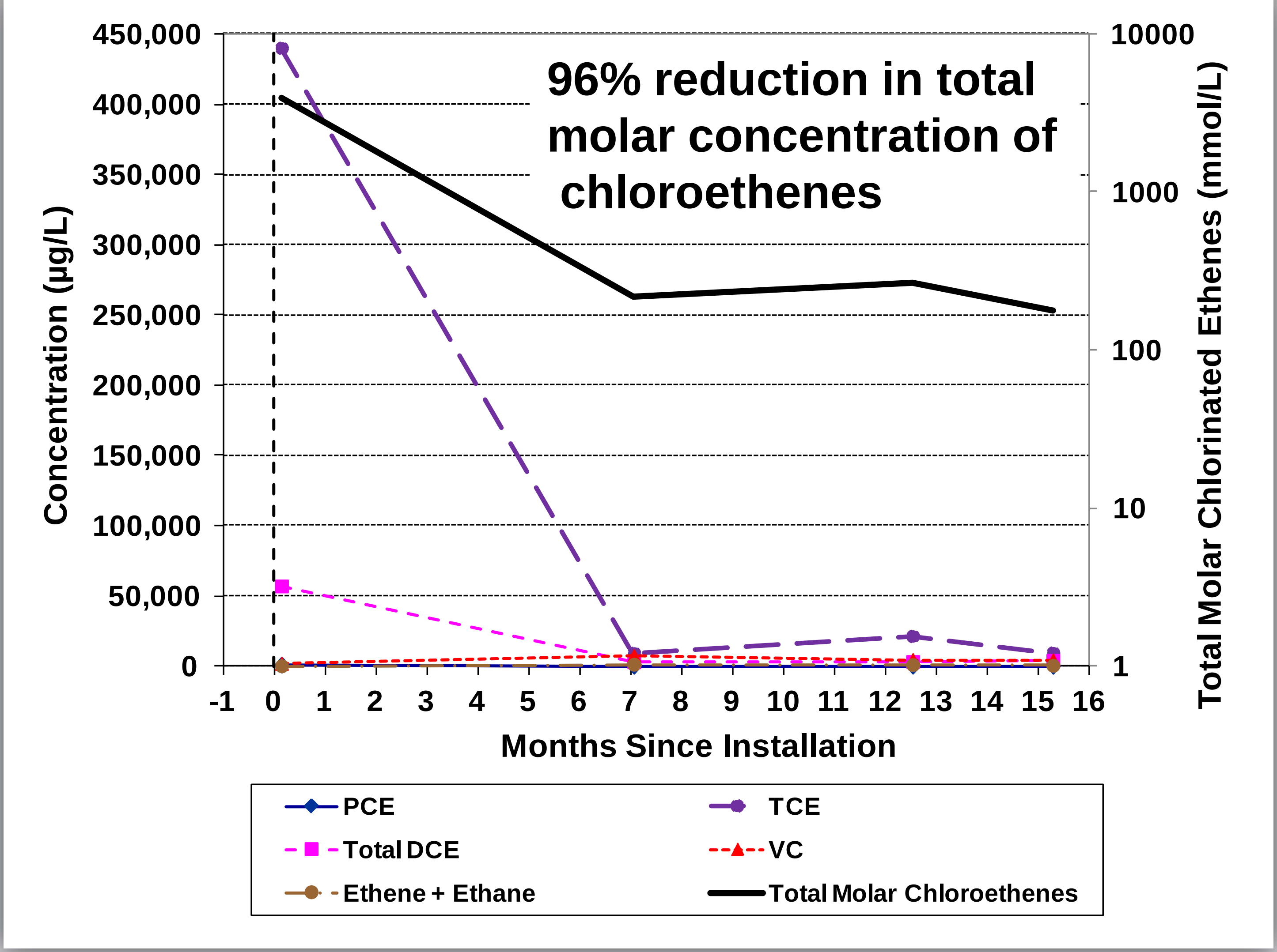
Powdered Hematite (Fe_2O_3)

LF05 DNAPL Source Bioreactor, JBPHH

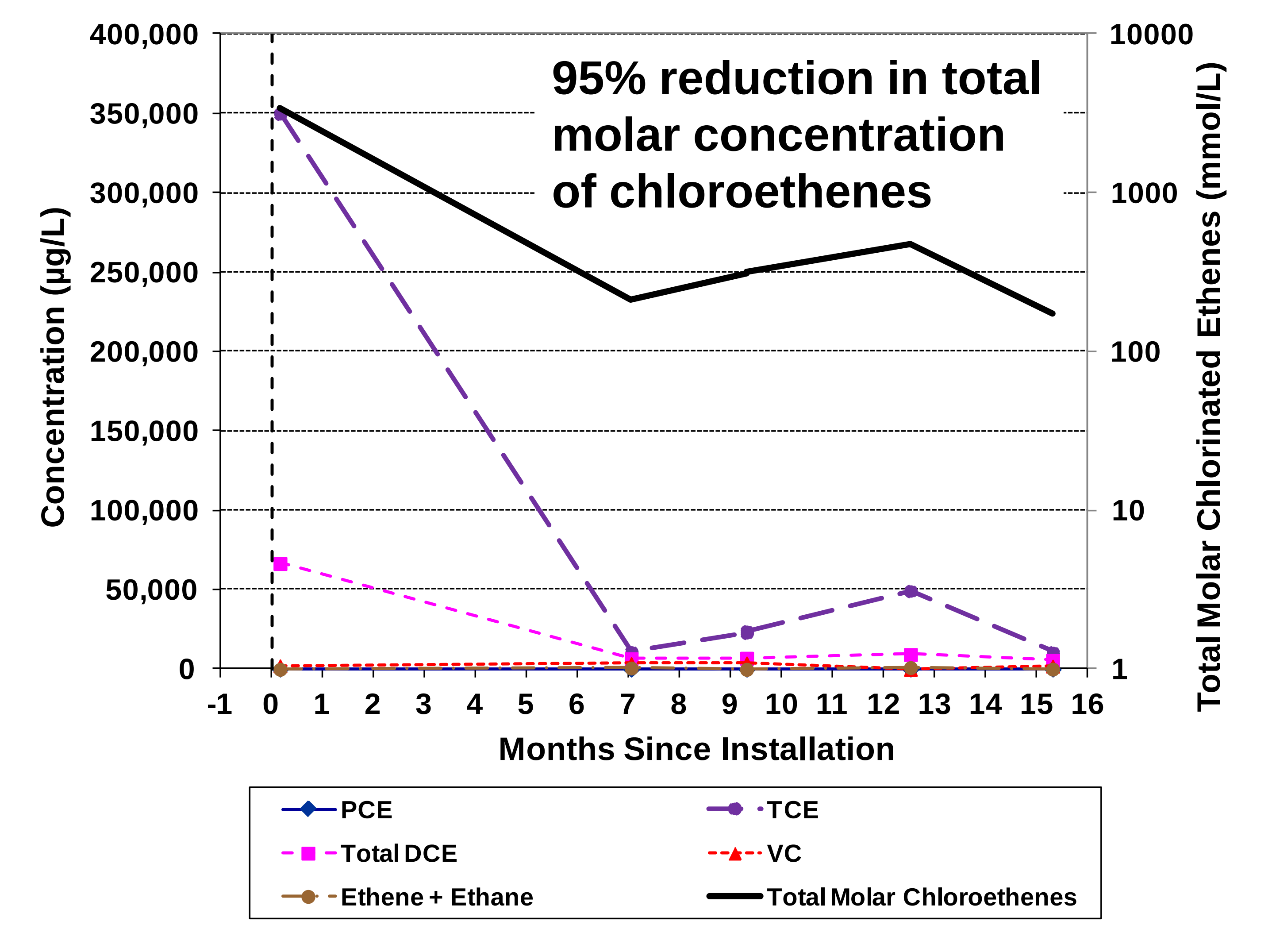
Plan View of Hickam LF05 Bioreactor



Chlorinated Ethenes at Well MW-18



Chlorinated Ethenes at Well MW-38



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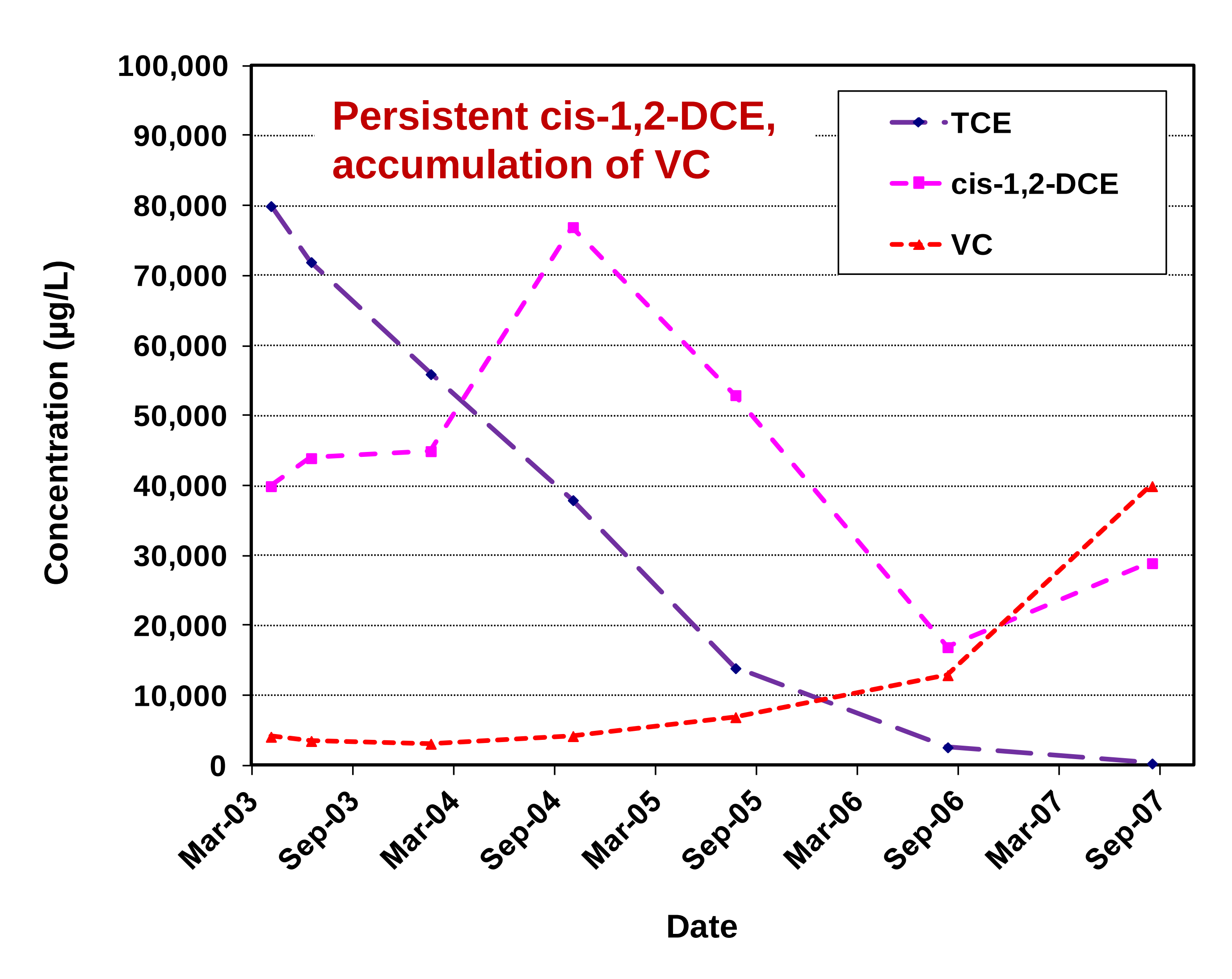
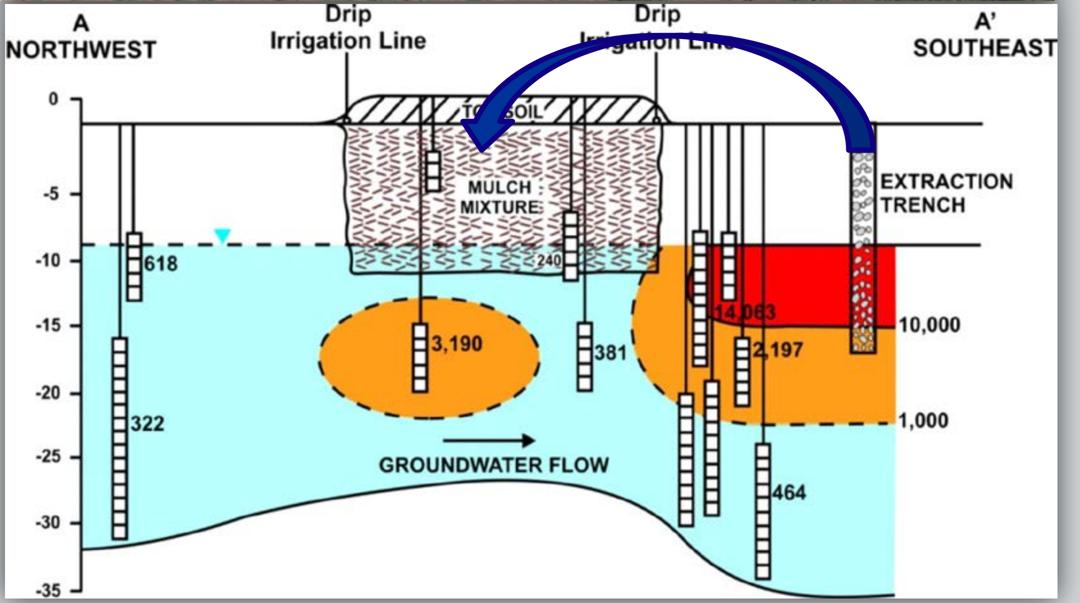
Contrast to MW-04 for a Prior Bioremediation Pilot



LF-03 Recirculating Bioreactor, Altus AFB, OK



- Solar-powered recirculating bioreactor – built in November 2003
- Emulsified vegetable oil (EVO) and ferrous sulfate injected in May-June 2010

LF-03 Injection – EVO + Ferrous Sulfate

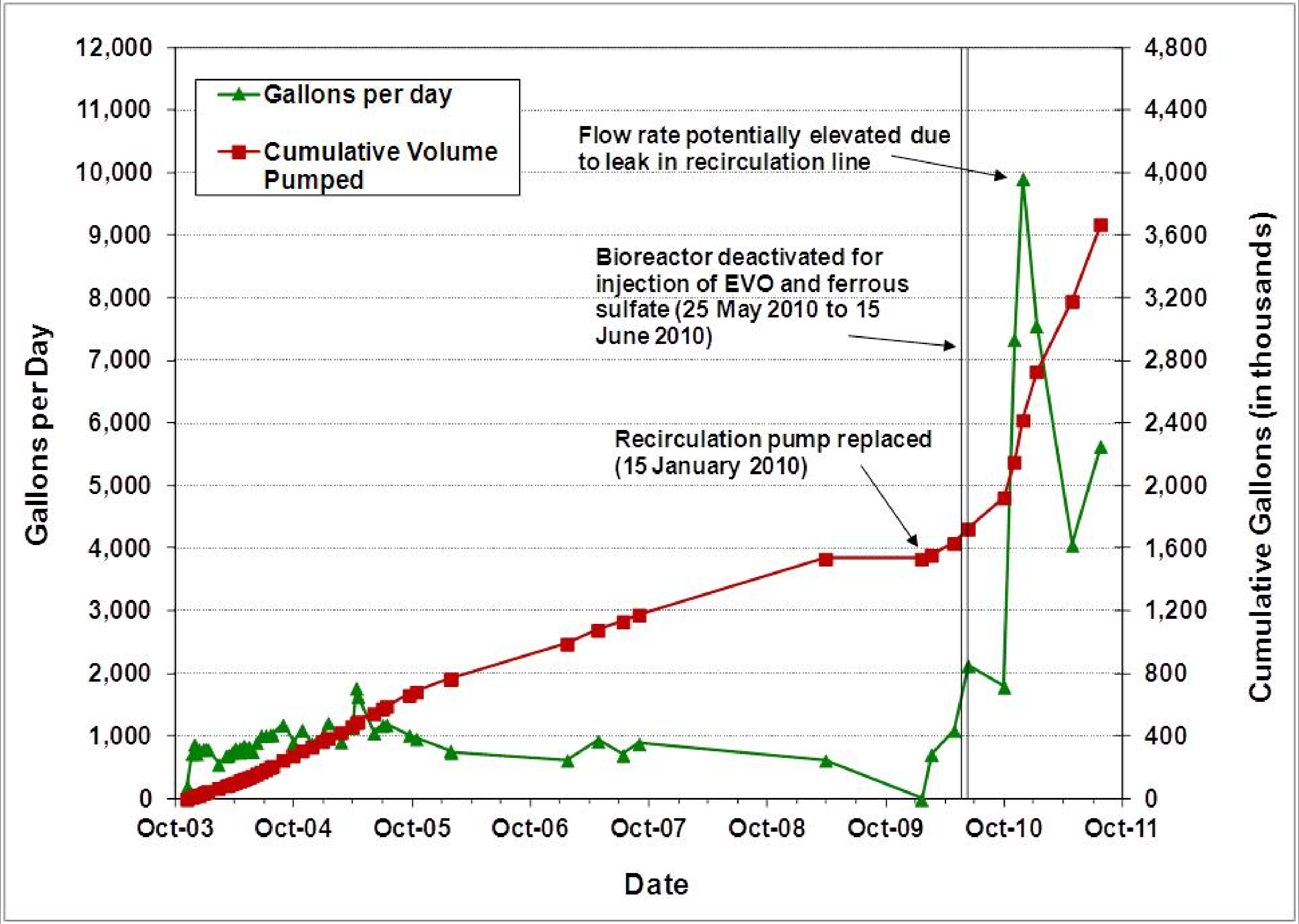
Ferrous Sulfate Product

Mixed w/ GW + AquaBufpH™

Direct Injection into Bioreactor


Frozen Mulch Sample

Cumulative and Average Daily Flow



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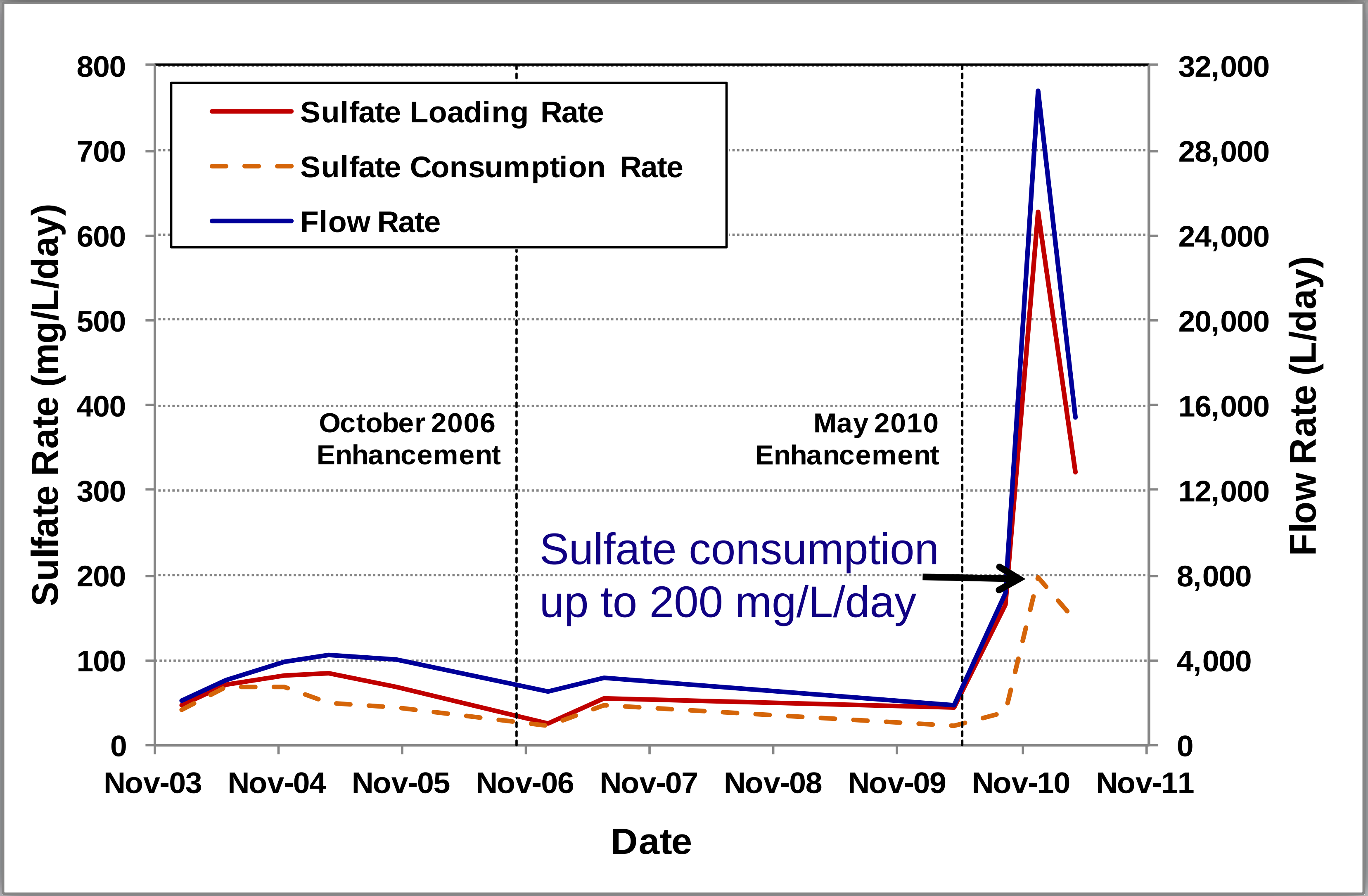
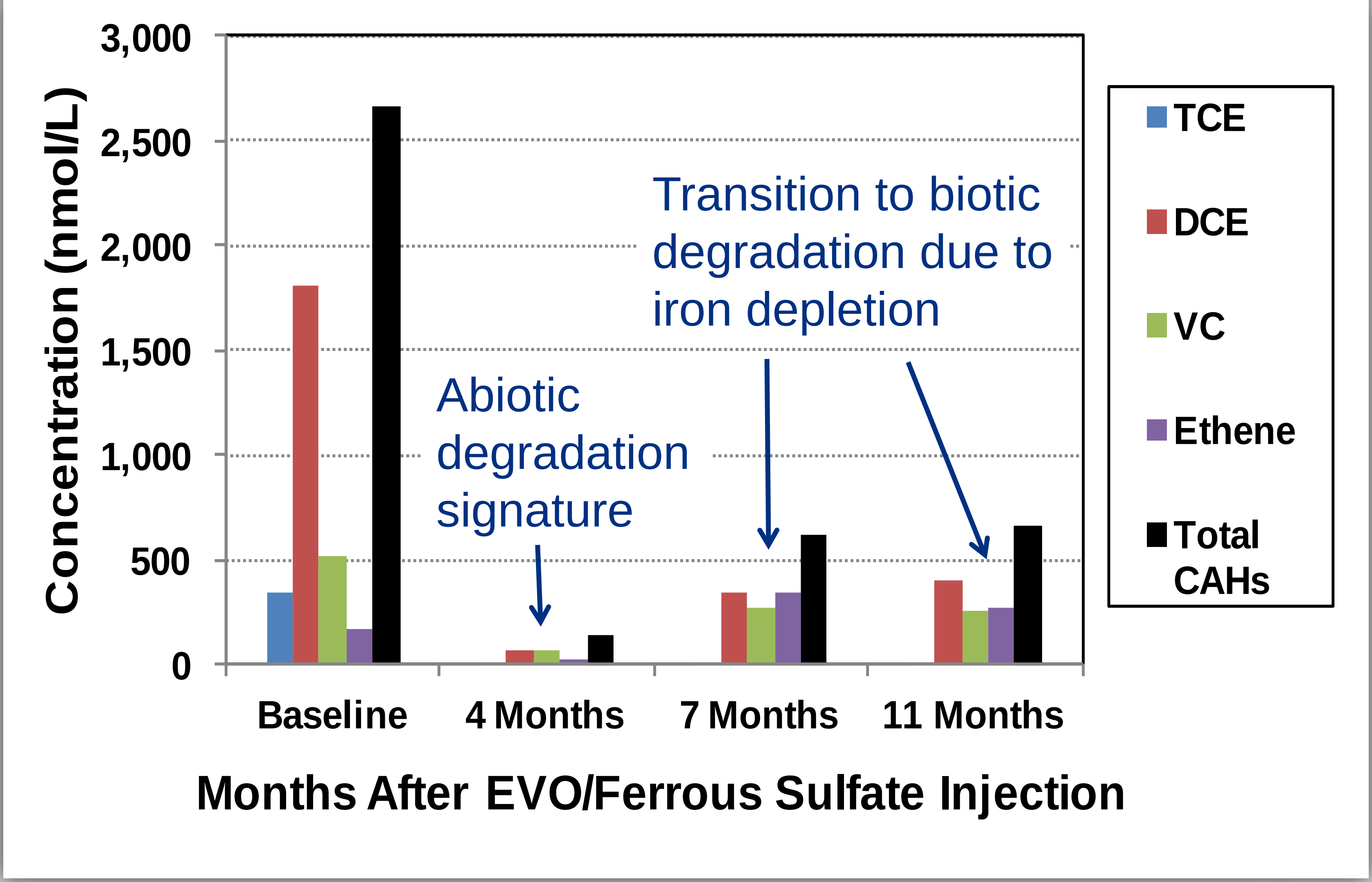
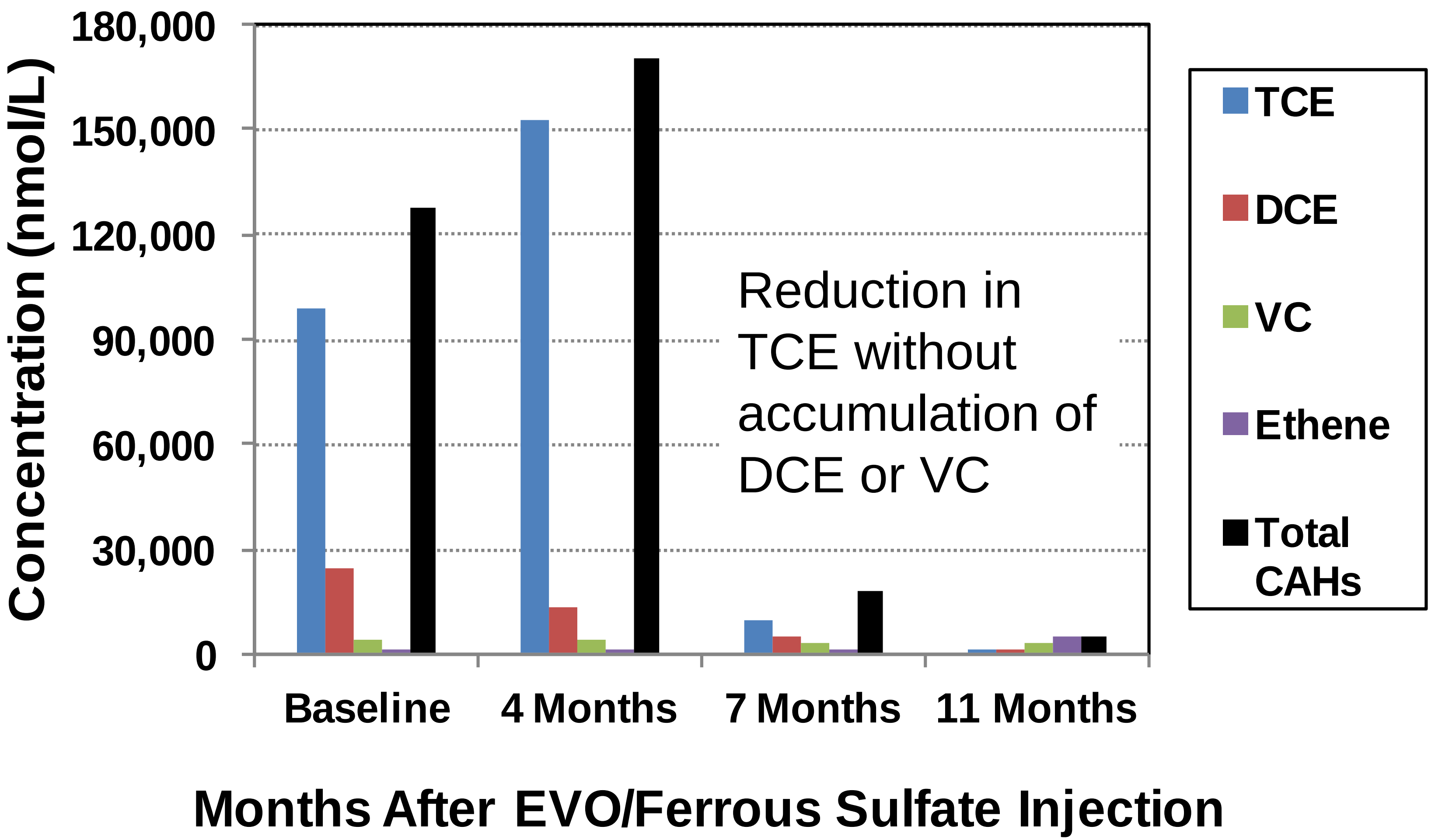
Sulfate Loading/Consumption Rate Over Time



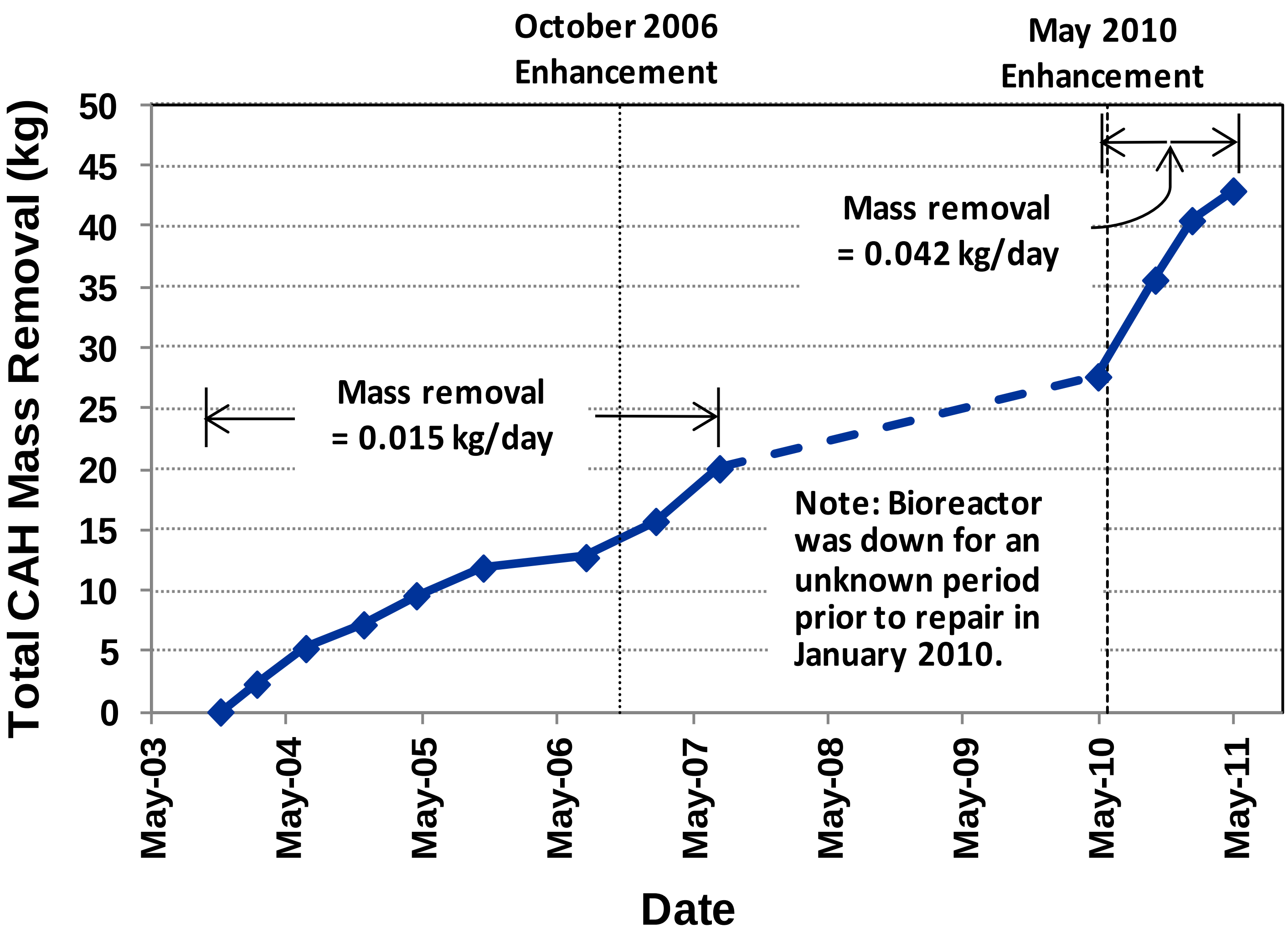
Molar Concentrations of CAHs Over Time at SW3



Molar Concentrations of Chloroethenes and Ethene in Deeper Zone Beneath Bioreactor



Cumulative Mass Removal



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Influent versus Bioreactor Concentrations

May 2010 and May 2011 (1 mo. pre- and 11 mo. post-injection)

Compound	Influent (May 2010)	Within Bioreactor (May 2010)	Within Bioreactor (May 2011)	Percent Reduction (May 2010)	Percent Reduction (May 2011)
TCE (µg/L)	3,600	183	2.6	95% →	99.7%
cis-DCE (µg/L)	2,300	725	169	69% →	91%
VC (µg/L)	80	50	174	38%	+2.3%
Ethene (µg/L)	9	3.3	29	Decrease	Increase
Total Molar Chloroethenes (nmol/L)	52,900	9,890	4,800	81% →	85%

Dechlorination efficiency for TCE, DCE, and
Total Molar Chloroethenes improved after injection

Case Study: DP98, JBER, Alaska

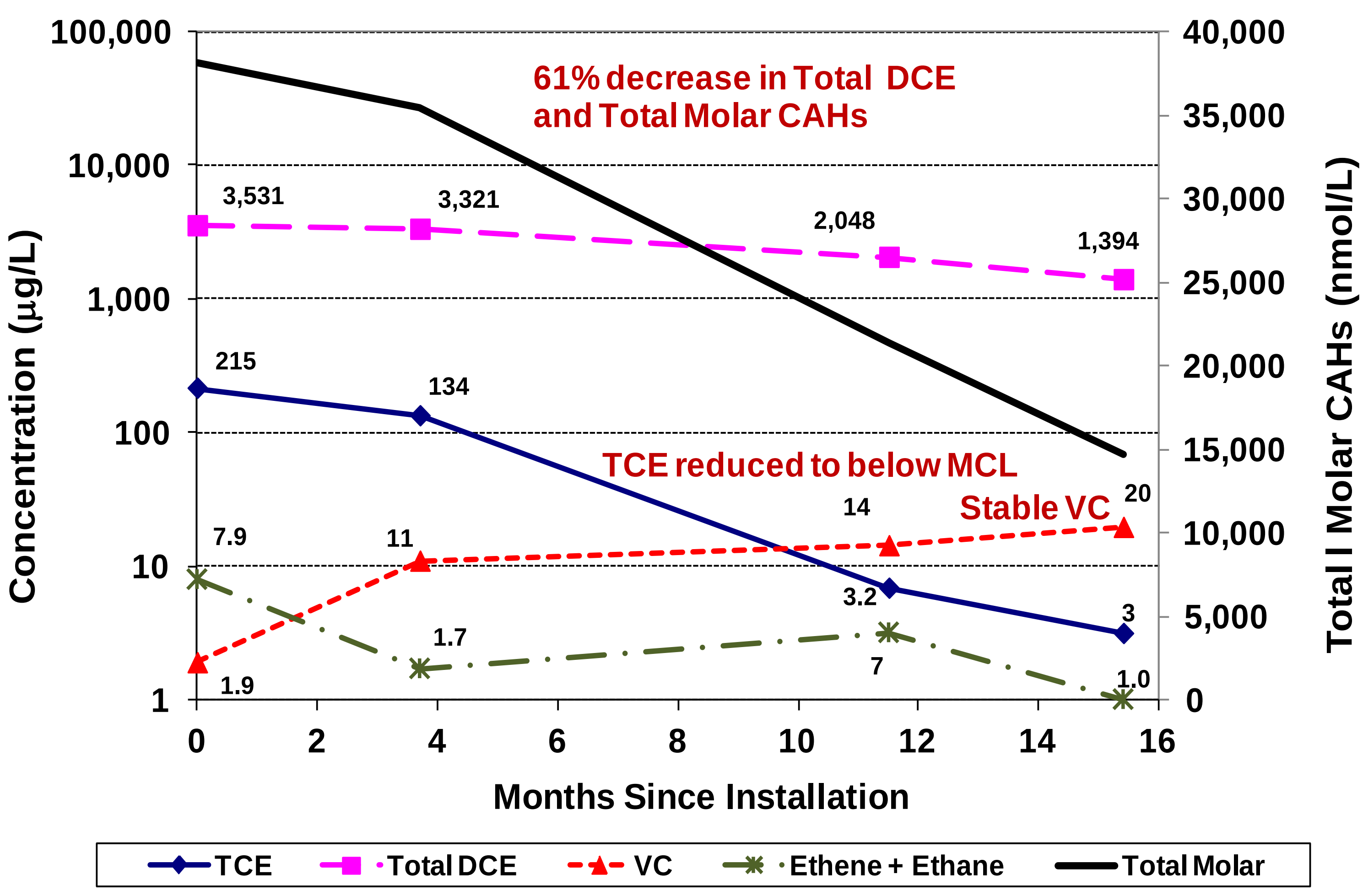
Direct-Push Injection Test Cell No. 1
(May 2010)

DP98 Test Cell Scenarios

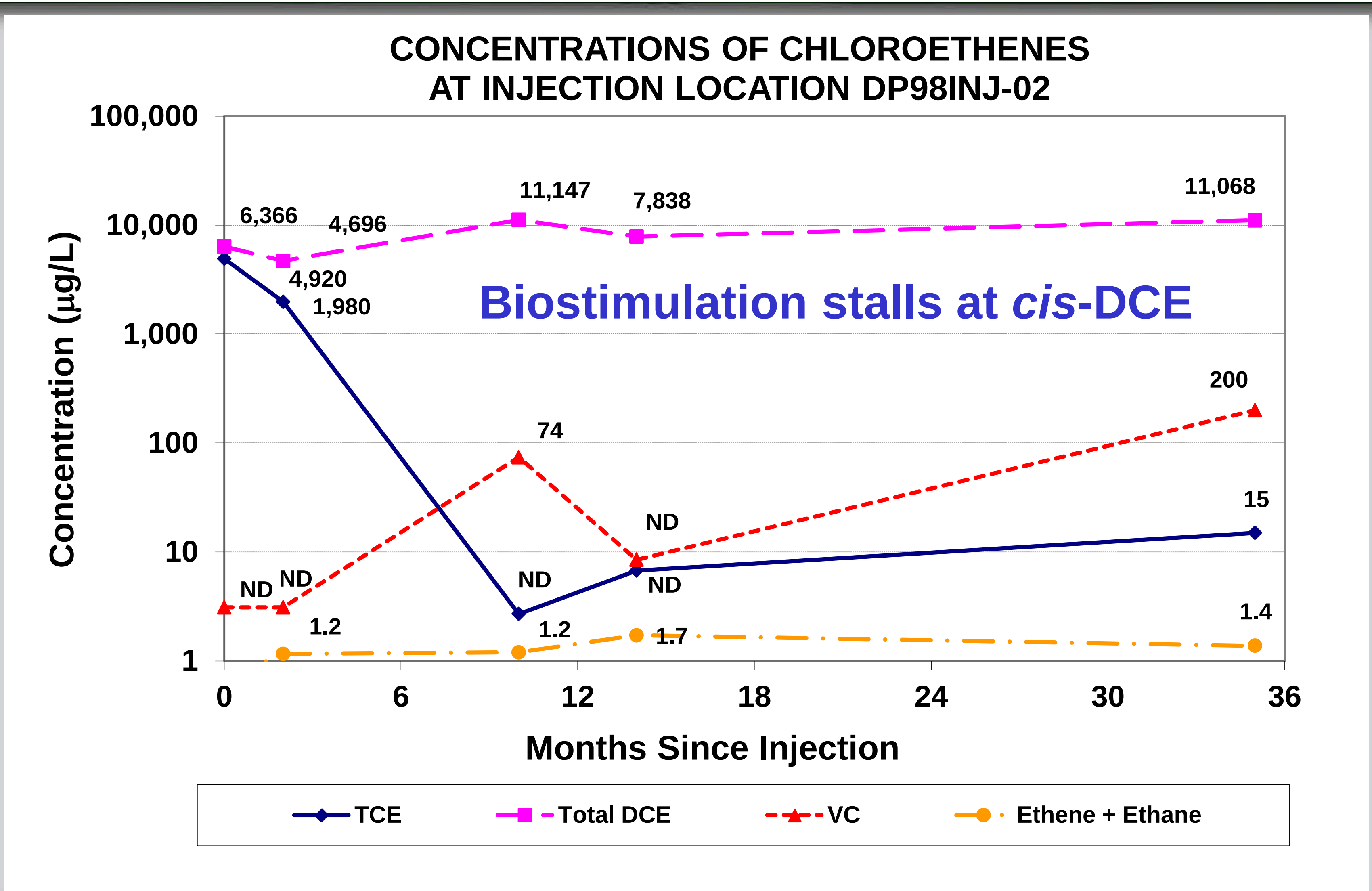
Site/Location	**Amendments**	**Notes**
Test Cell No. 1	EHC® Control	Tight silty clay with silty sand layers, low to moderate GW flow
Test Cell No. 2	Gypsum, Hematite, Emulsified Vegetable Oil (EVO)	Tight silty clay with silty sand layers, low to moderate GW flow
Test Cell No. 3	Ferrous Sulfate with EVO	Injected in former bioremediation pilot test

A buffered EVO product was used to stabilize pH

Chloroethenes at Test Cell No. 2 (EVO + Hematite + Gypsum)



Contrast with 2005 Biostimulation with EVO



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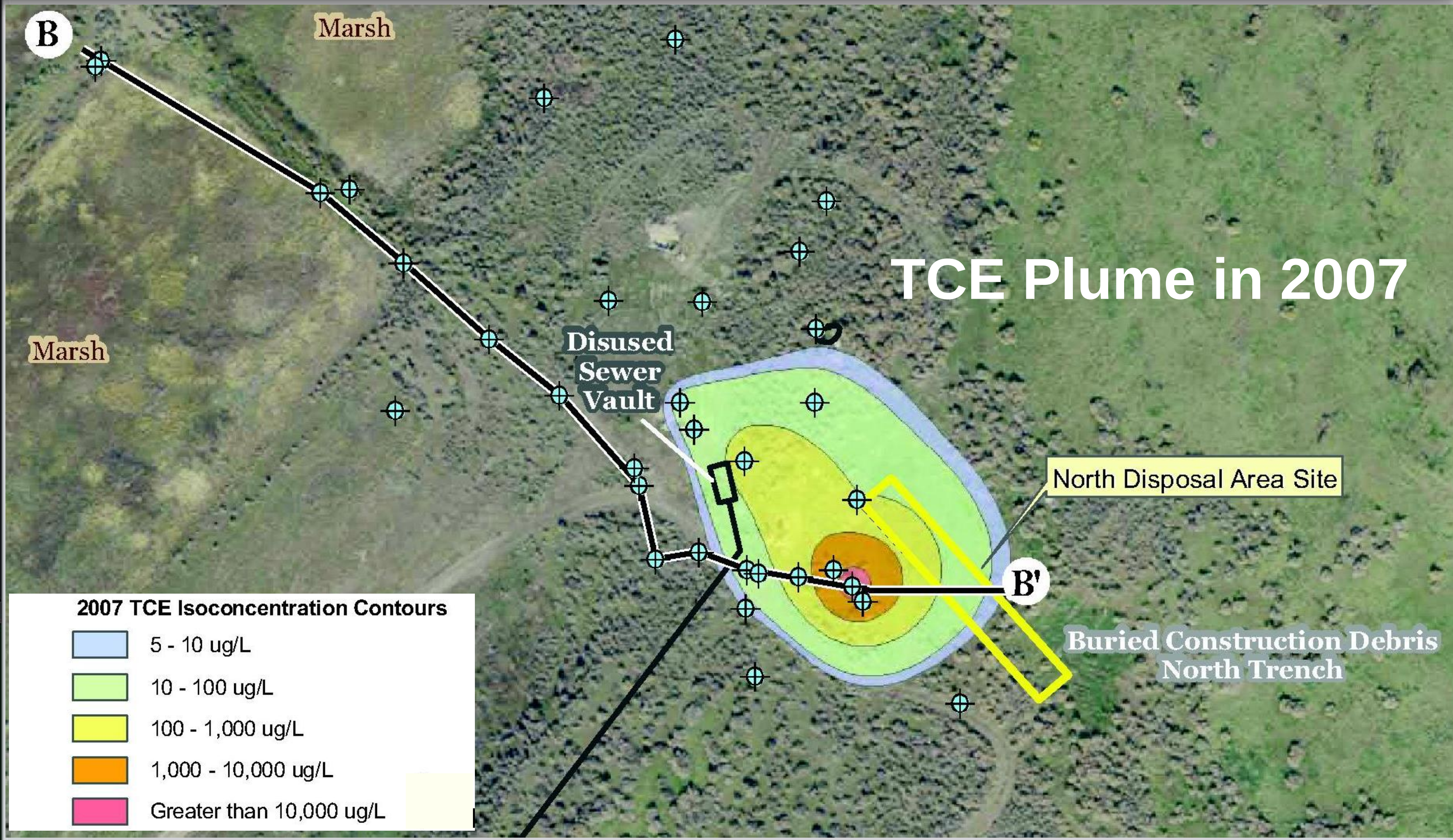
North Disposal Area, LMTA, Utah



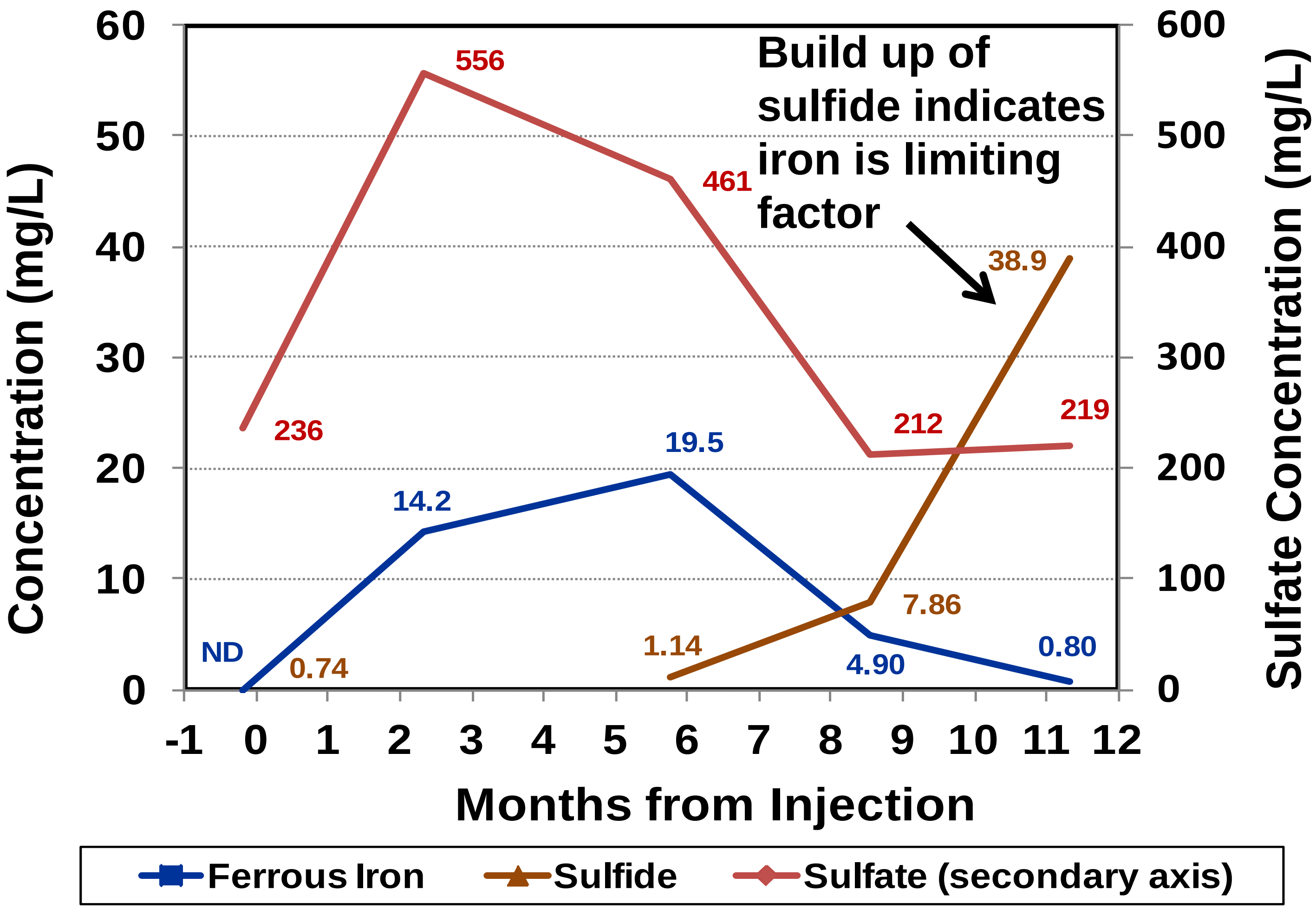
LMTA Performance Objectives

- Generate FeS up to 1,000 to 3,000 mg/kg
- Enhance rates of degradation by an order of magnitude or more over natural rates
- Reduce total molar concentrations by over 90 percent (no increase in cis-1,2-DCE or VC)

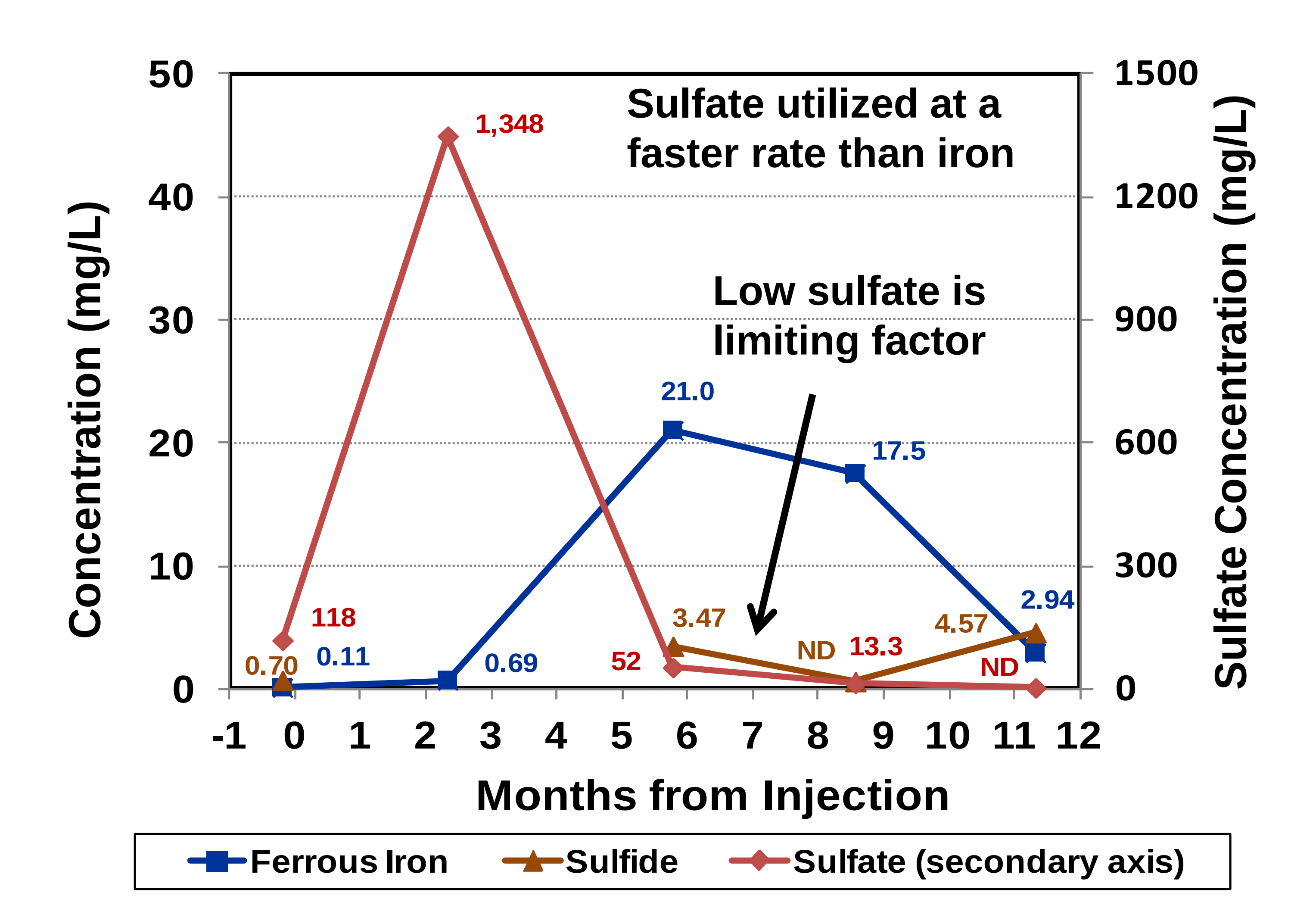
Soil cores before injection, LMTA, Utah

Soil cores 6 months after injection, LMTA, Utah

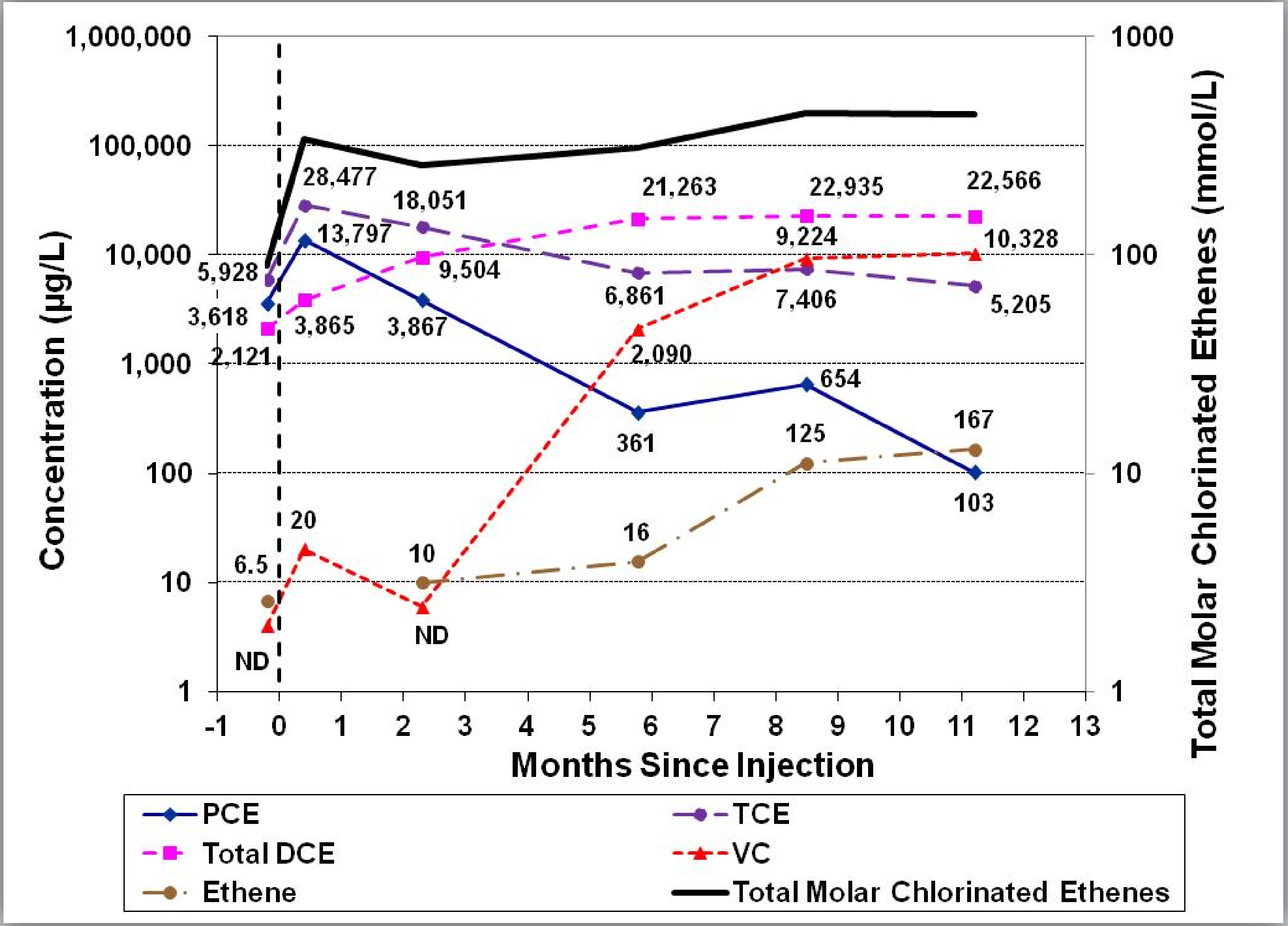
Ferrous Iron, Sulfate, and Sulfide at LM-679 in Test Cell No. 1 (Ferrous Sulfate + EVO)



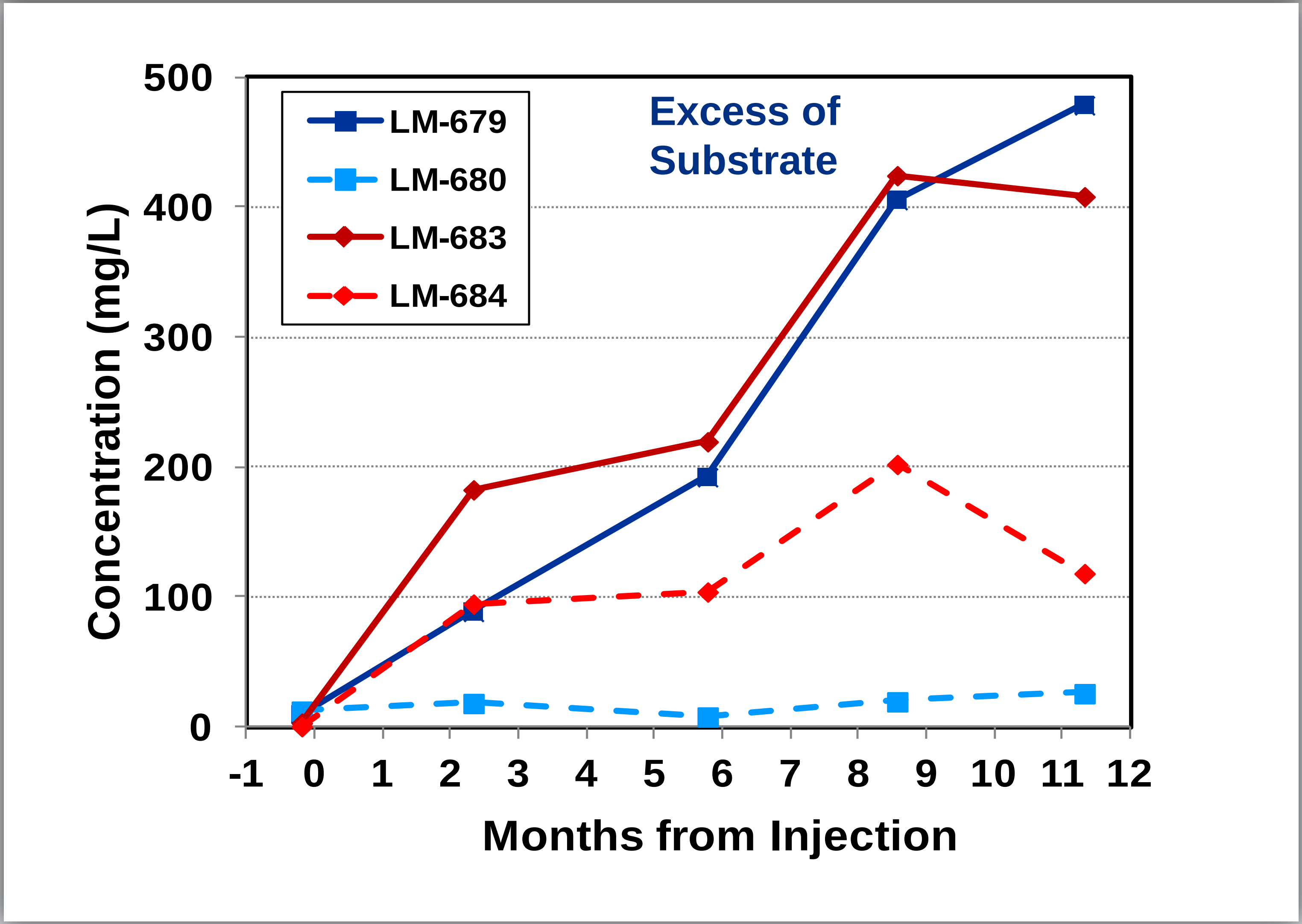
Ferrous Iron, Sulfate, and Sulfide at LM-683 in Test Cell No. 2 (Powder Hematite + Mg Sulfate)



Chloroethenes at Test Cell No. 1 (Ferrous Sulfate w/ EVO)



Dissolved Organic Carbon in NDA Test Cells



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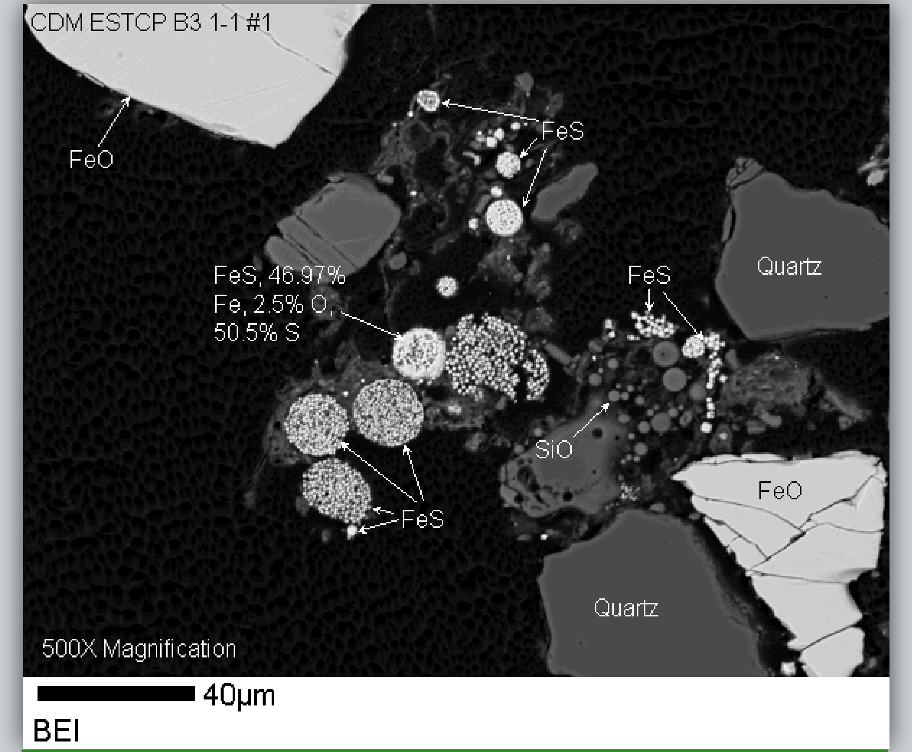
Factors Impacting Performance

- High sulfate consumption rate is desirable
- Substrate type should behave like amendment type (soluble with soluble and solids with solids)
- Utilization rates – in general soluble sulfate reduction will be greater than solid phase iron reduction
- Mineral saturation/super saturation states for iron sulfide minerals (geochemical modeling)

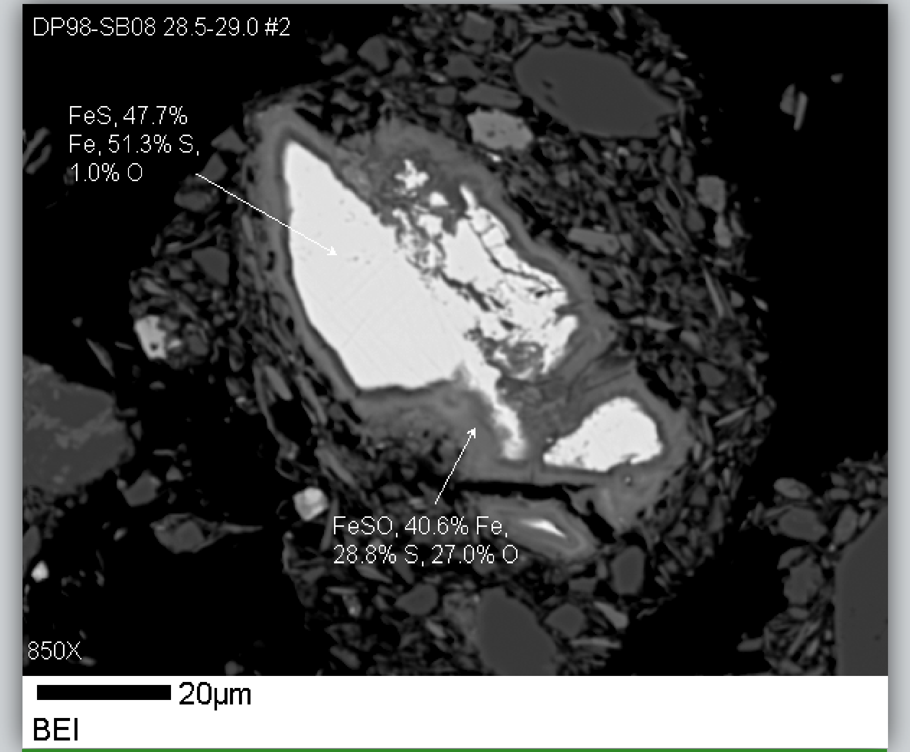
Slow release substrates such as EVO are not
a good fit with soluble amendments

Factors Impacting Performance (continued)

- Adequate groundwater mixing – nucleation versus crystal growth



Pyrite Framboids with high surface area



Large pyrite grain with low surface area

Design Considerations

- Limit substrate to avoid over stimulation of biological processes, yet provide for continual production of fresh FeS minerals
- Use conservative tracers to confirm utilization of soluble sulfate and ferrous iron amendments
- Configurations suitable for multiple injections or recirculation allow the greatest potential for optimizing the ratio of organic substrate to sulfate to iron

Optimal Approach

Given the challenges to enhancing abiotic processes without significant biotic dechlorination, a synergistic approach optimizing biogeochemical processes along with bioaugmentation may be an optimal approach.

Special Considerations

- Co-contaminants such as nitrate and heavy metals
- Low pH, poor buffering capacity
- Very high or very low rates of groundwater flow
- Overstimulation of biotic dechlorination
- Sites with high initial populations of dechlorinators (sites with high concentrations of DCE, VC, or DCA)

Mitigation Measures

- Buffering products for pH control
- Bioaugmentation for sites with DCE, VC, or DCA

References

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- Leigh, D.P., R.J. Steffan, W. Grannis, and E. Becvar. 2011. *Biogeochemical Degradation of Chlorinated Ethenes at Hickam AFB, Hawaii, Using Sustainable Processes.* Presentation C-01, 2011 Battelle Symposium, Reno, NV.

Questions and Discussion

Comparison of Approaches to Engineered
In Situ Biogeochemical Transformation
of Chlorinated Solvents

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