Biogeochemical Reductive Dechlorination of Chlorinated Solvent Plumes

Status of Practice Shift from Biotic to Abiotic Degradation Pathways

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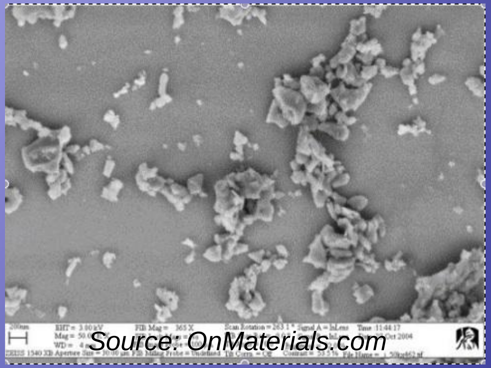
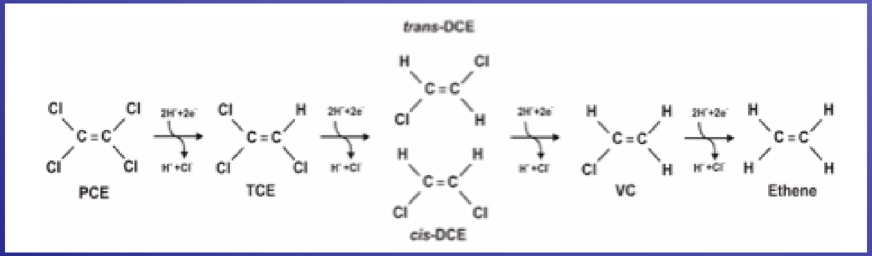
Presentation Objectives

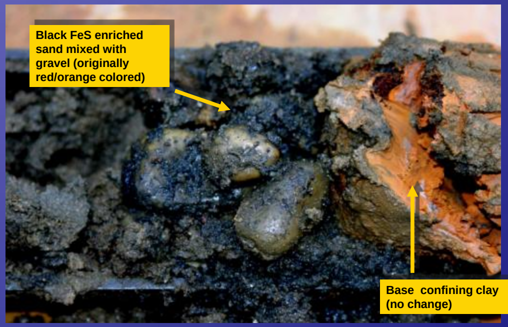
Highlight abiotic, biotic, and biogeochemical reductive dechlorination process discoveries and commercial developments for engineered in-situ reductive dehalogenation of chlorinated aliphatic hydrocarbons such as PCE, TCE, and TCA



Using Dover AFB National Test Site case histories, compare engineered biotic reductive dechlorination to engineered iron sulfide dominated biogeochemical reductive dechlorination (BiRD)



AFCEE



Speculate on where the field practice of engineered in-situ reductive dehalogenation is headed

Milestones In Dehalogenation

WR Grace Daramend™ circa 1996

EHC®, ABC+™, LactOil Nano™, etc.

Sweeney, 1980 Cu^0/Fe^0

Klecka & Gonsior, 1984

Organo-Metallic Complexs

Gillham, 1990 ZVI (Fe^0)

Tratnyek, 1994 ZVI/Fe Oxides

Kriegman-King, 1994 Pyrite

Zhang 1997, Nano-Fe

Batchelor, 1998 ZVI/Clay

Ferrey & Wilson, 2002 Abiotic MNA

Lee & Batchelor, 2002 Pyrite / Magn.

EZVI 2003

Kennedy, 2005 BiRD

1980 A 1990 B C D 2000 E F G 2010

ZVI

DVI

Biogenic

Biotic

A-1981-1983 Initial Discovery (Roberts, et. al., Bouwer & McCarty)

B-1994-1995 Molasses, High Fructose CS used in practice

C-1996 Dehalococcoides (DHC) Maymo-Gatell et. al

D-1999 AMIBA Protocol Paper, Kennedy and Everett

E-2002 AFCEE/ESTCP Technical Protocol for Using Soluble Carbohydrates

F-2007 AFCEE Protocol Insitu Bioremediation of Chlorinated Solvents Using Edible Oil

G-2008 AFCEE Technical Protocol for Enhanced Anaerobic Bioremediation using Pemeable Mulch Biowalls and Bioreactors

Modified from R. Brown, May 2012

BiRD Basics

- ***B**iogeochemical **R**eductive **D**echlorination **(BiRD)** is a patented process for the treatment of chlorinated solvents and certain metals [Kennedy - US Patent Off. #6,884,352 B1]*

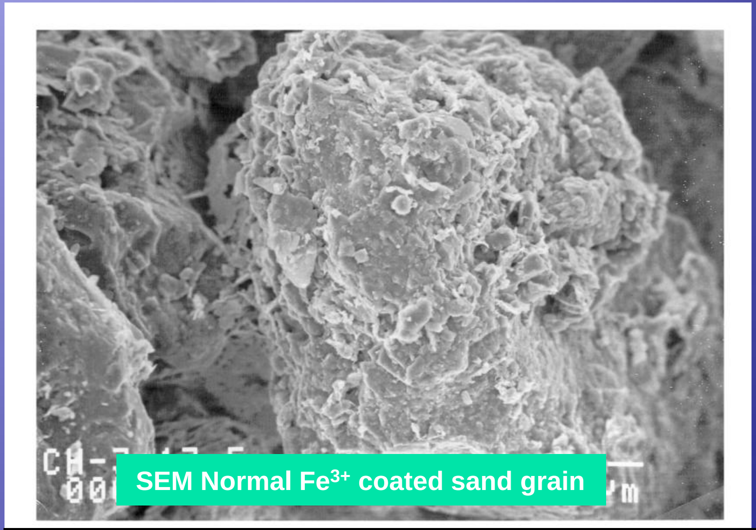
- *Basis for BiRD is:*
  - *Typical clastic aquifers have much native iron and can be supplemented if necessary*
  - *But, this iron is not reactive and can't treat CAH's*
  - *BiRD stimulates natural bacteria to convert native Fe to FeS minerals*
  - *FeS facilitates the complete autoreduction of CAH compounds similar to zero valent iron (ZVI).*

- *BiRD is focused on <u>engineered in-situ iron sulfide</u> reaction zones and the abiotic reactions with contaminants*

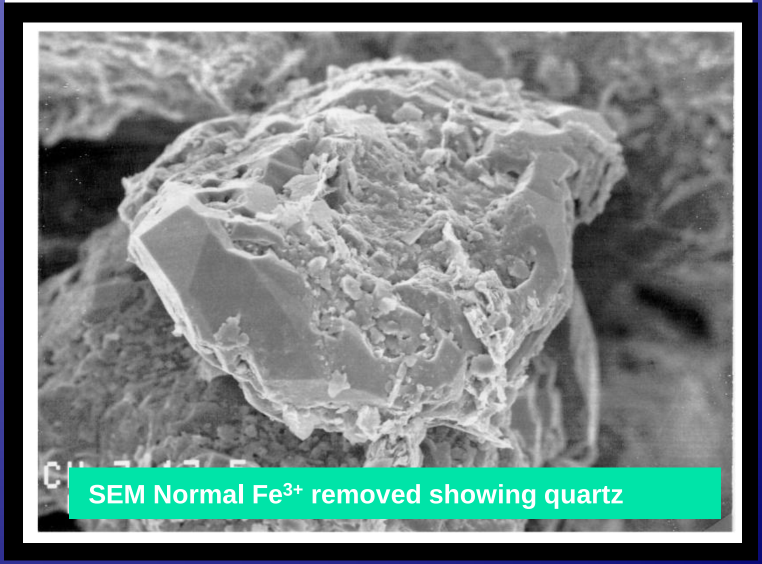
- *No desired role for enhanced <u>biological reductive dehalogenation</u>*

Aquifer Environment

- *Natural mineral Fe is one of the most common earth elements found in all clastic sediments*
- *Typical aquifer matrix has 0.1 to 10% Fe or 4 to 400 lbs/m^3*
- *This iron is well dispersed and often as poorly crystalline grain coating*
- *Most native Fe minerals are Fe(III), stable, and not effective against CAH ‘s*
- *Native Fe can be converted to a reactive mineral form via biochemical reactions*



SEM Normal Fe^{3+} coated sand grain



SEM Normal Fe^{3+} removed showing quartz

BiRD Functional Steps:

- Phase 1 - Biological Step:
  - Supplied organic + sulfate stimulate common sulfate reducing soil bacteria:

$$CH_2O + \tfrac{1}{2}\,SO_4^{2-} \rightarrow HCO_3 + \tfrac{1}{2}\,HS^- (ag) + H_2O + H^+$$

Begins in days

- Phase 2: Geochemical Step:
  - HS- from SRB respiration reacts with native or supplied mineral Fe II or III to produce FeS:

$$3HS^- + 2FeOOH_{(s)} \rightarrow 2FeS_{(s)} + S^o + H_2O + 3OH^-$$

Instantly

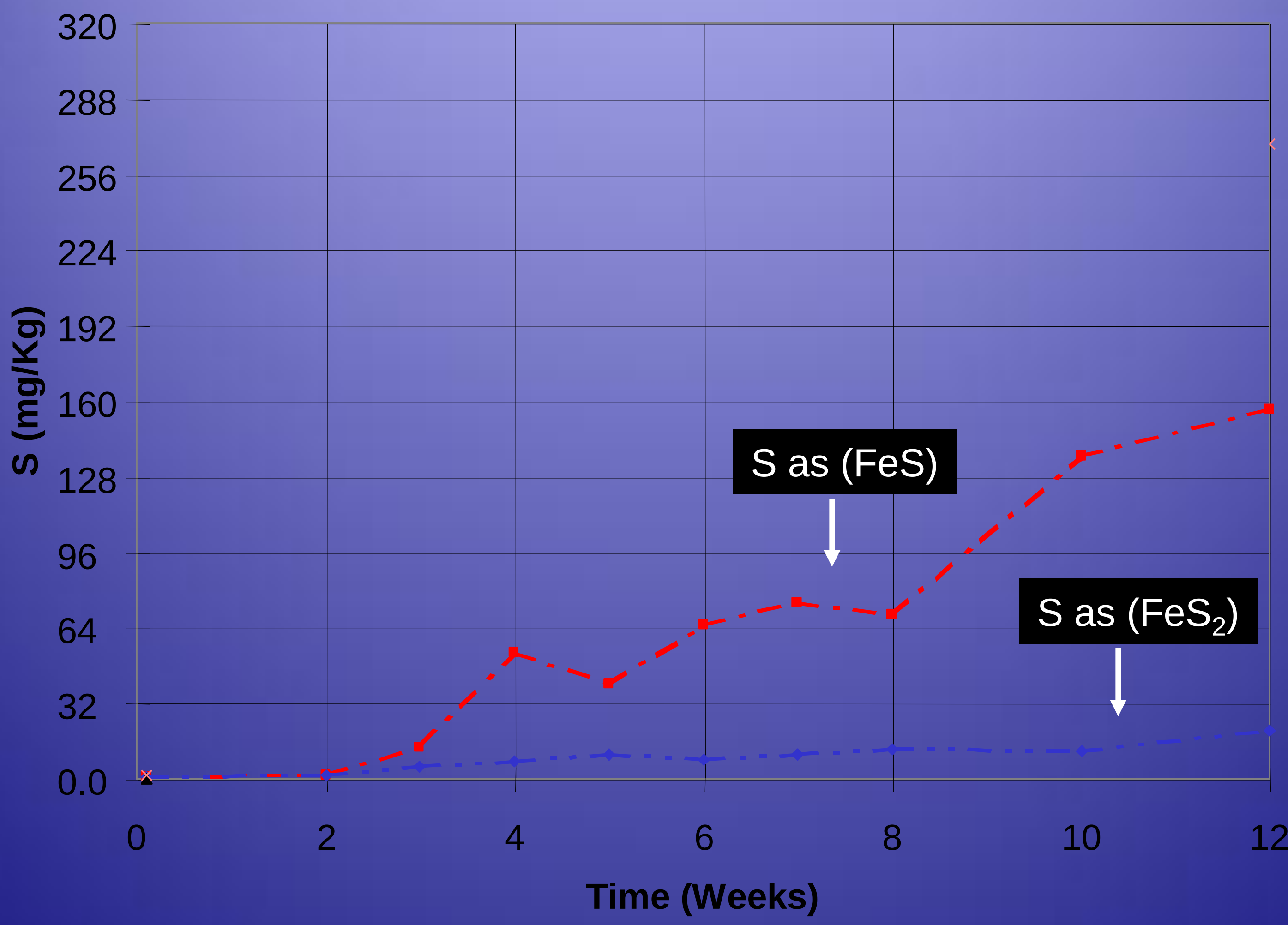
- Phase 3: Dechlorination Step:
  - Reactive FeS reductively dechlorinates CAH abiotically:

$$4/9FeS + C_2HCl_3 + 28/9\,H_2O \rightarrow 4/9\,Fe(OH)_3 + 4/9SO_4^{2-} + C_2H_2 + 3Cl^- + 35/9H^+$$

- With FeS surface area, CAH treatment usually begins within 2 – 3 weeks or sooner.

CAH treatment half life 30 ± 15 days

Microbial Production of FeS in Microcosm



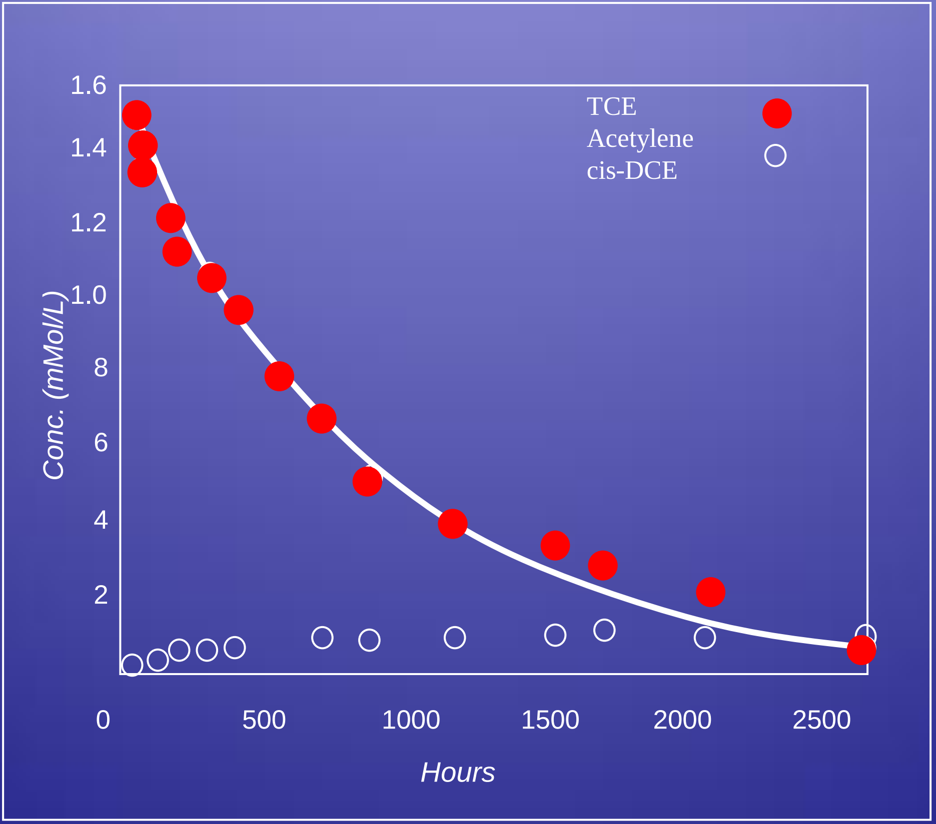
Microcosm consists of native sediment, added SO_4^{2-}, and low carbon organic acids. *These results were reported in Kennedy and Everett, 2001.*

BiRD Response in the Lab

- Dechlorination of TCE by reaction with mineral FeS
- Treatment is rapid and complete – no DCE production

1.6 mMol/L = 210 mg/L

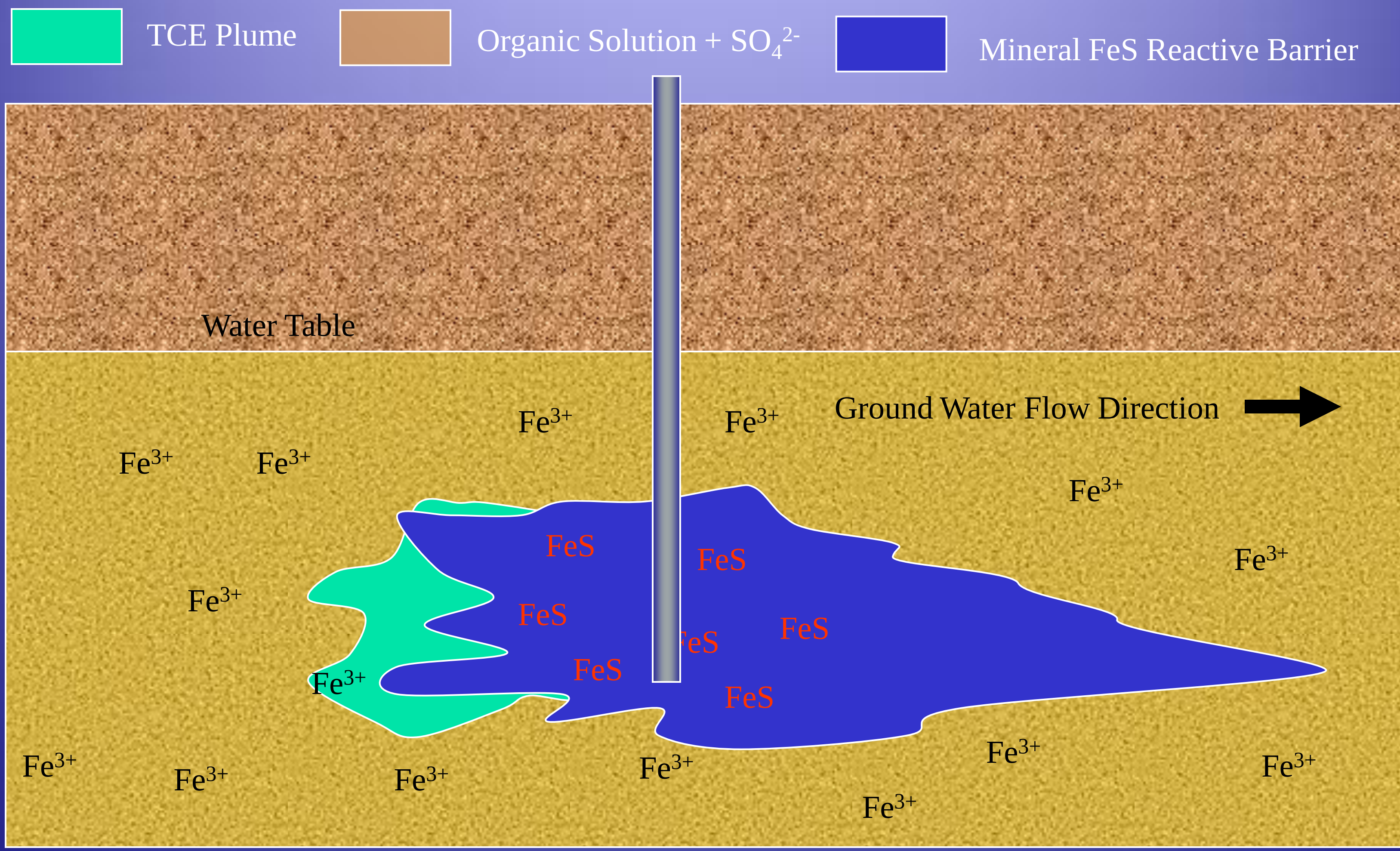
0.2 mMol/L = 26.3 mg/L



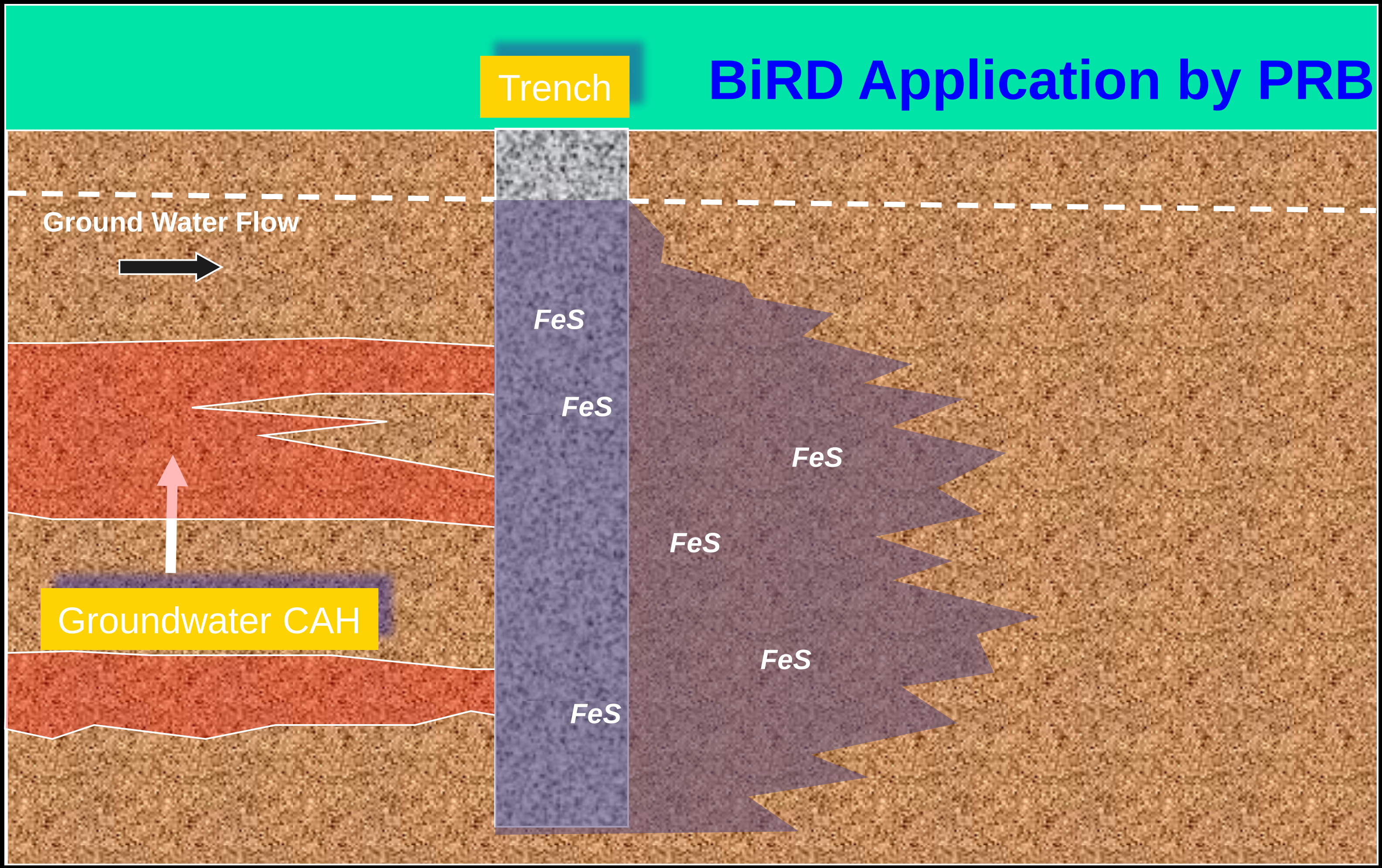
2500 hours = 104 days

Butler and Hayes, Environ. Sci. Technol. 1999, 33, 2021-2027

BiRD Application by Injection



FeS forms a permeable reactive zone into which aqueous CAHs may flow. Dechlorination is complete and dechlorinated products are mineralized to CO2.



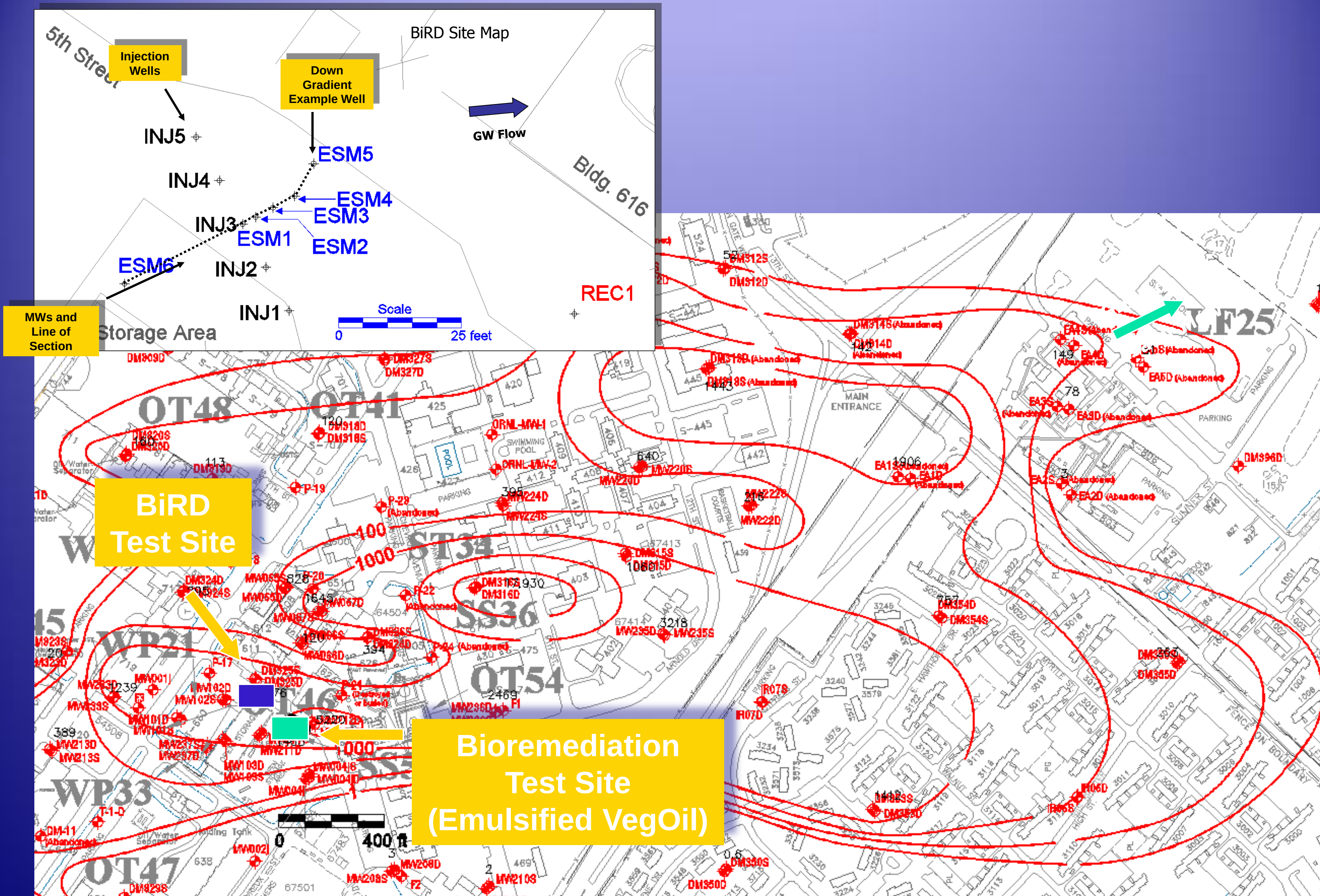
Solid reactants form solid FeS so is mostly “invisible” to aqueous monitoring.
FeS forms in the trench and down-flow gradient

Case History

Dover AFB National Test Site
Biogeochemical Reductive Dechlorination
(BiRD) Pilot
with Comparison to
Biological Reductive Dechlorination Pilot

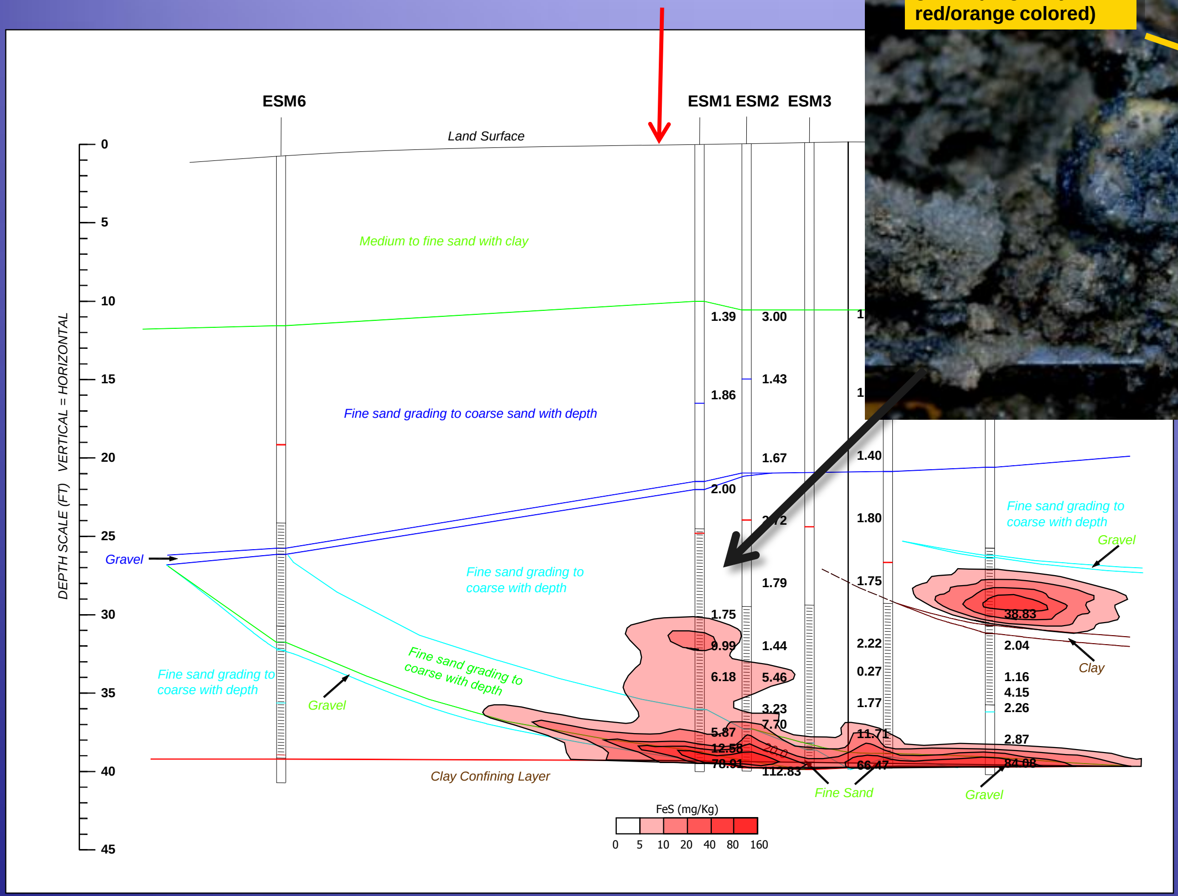
BiRD Reactive Zone Created Using Aqueous Injections

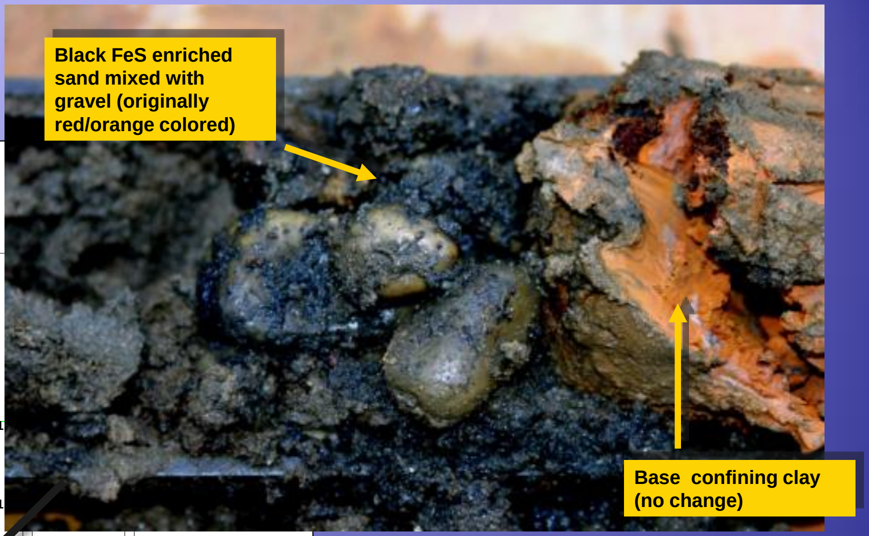
- BiRD was tested next to bioremediation test plot at the Dover AFB National Test site
- Bioremediation was stimulated with emulsified vegetable oil
- BiRD was stimulated by injection of Mg $SO_4 \cdot 7H_2O$ (Epsom salt) and Sodium lactate (Envirolac™)
- For BiRD sediment was sampled pre and post injection to measure FeS development



Dover AFB TCE plume, test site location and injection layout schematic

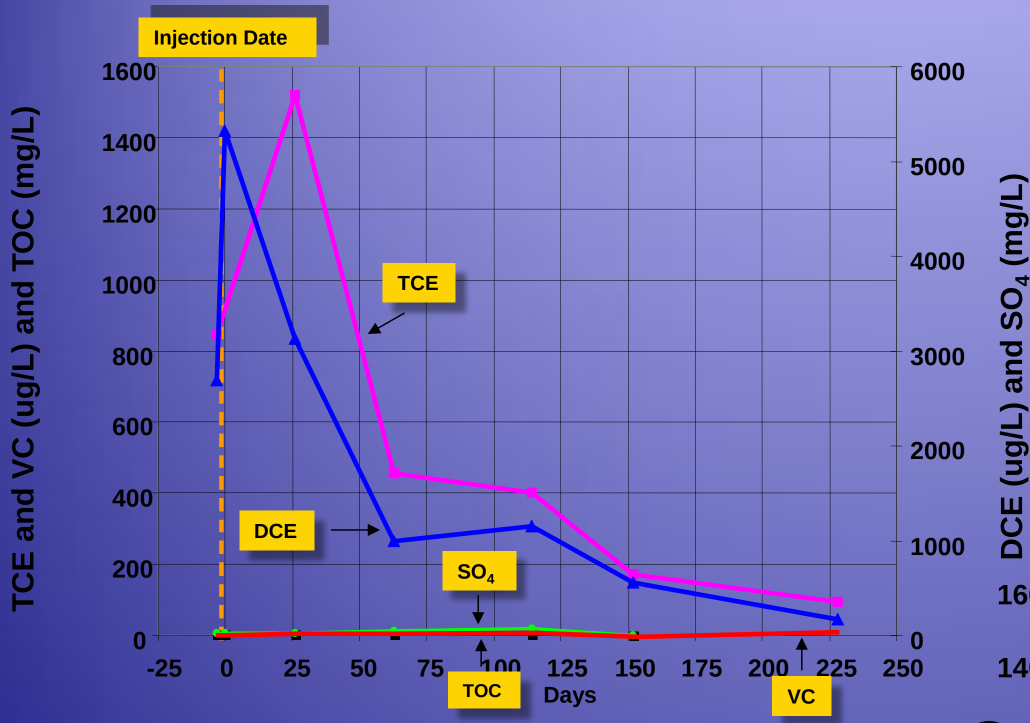
Line of 5 Injectors Perpendicular to Profile





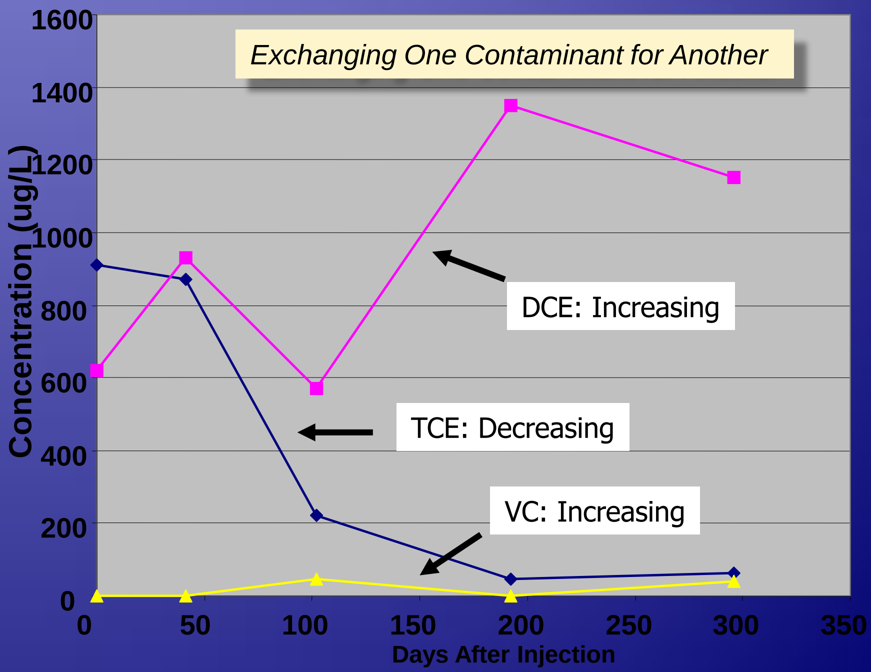
Profile of mineral FeS development (mg/Kg as S) and example photo of sediment core with FeS.

Comparative CAH Treatment Response



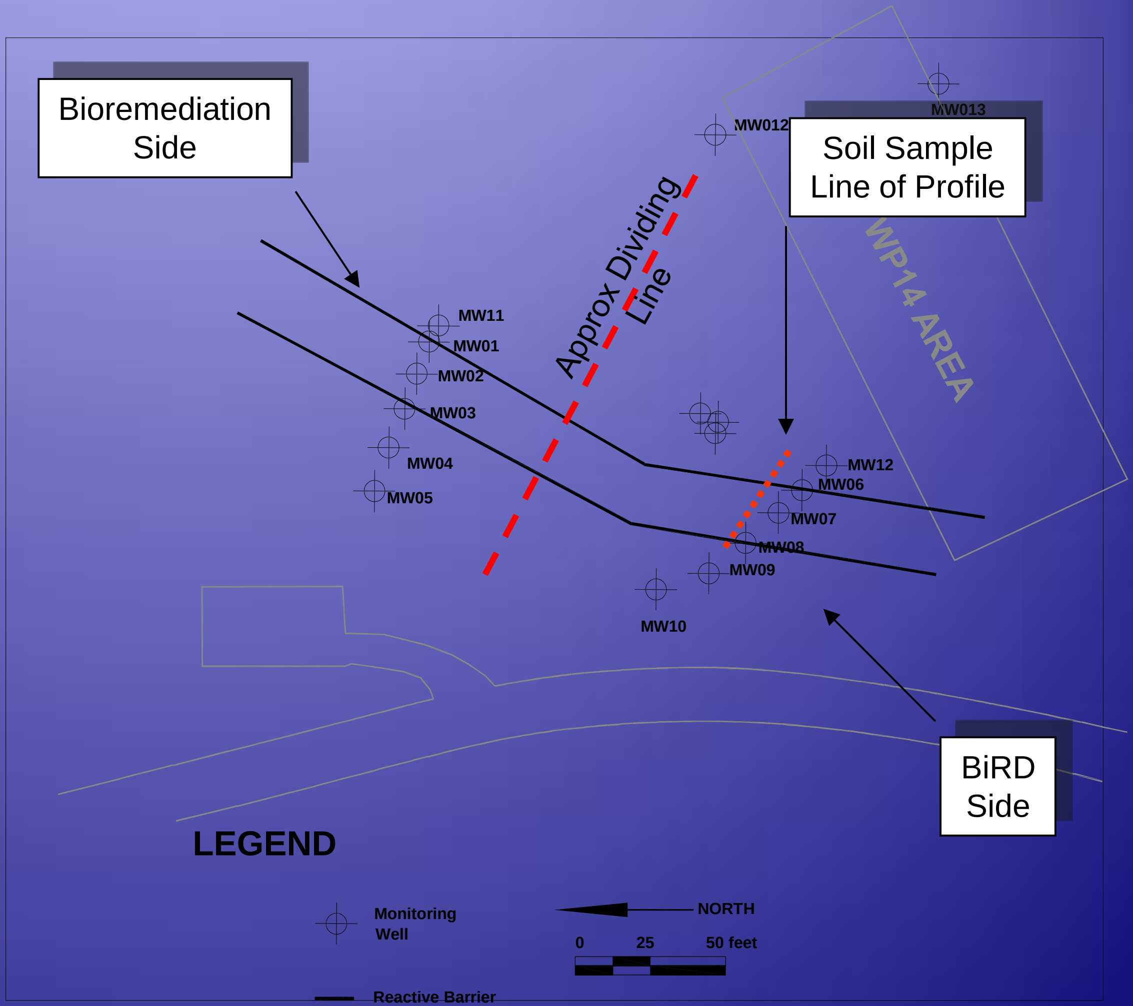
- *BiRD response (left) showed complete treatment of TCE and DCE with no daughter products.*
- *BiRD was rapid and complete*

- Bioremediation response (right) showed decreasing TCE but increasing DCE and VC



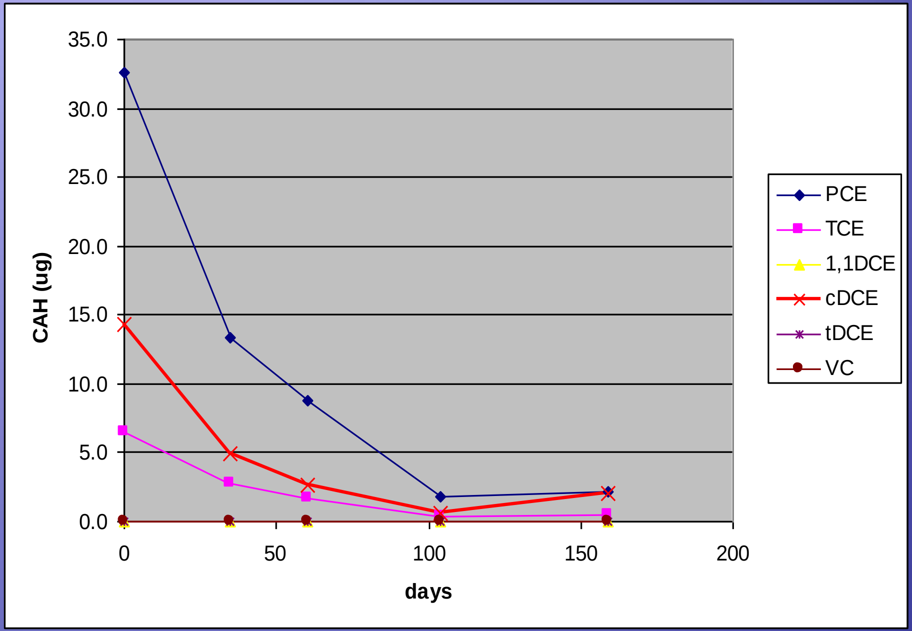
BiRD Tested by Solid Permeable Reactive Barrier (PRB)

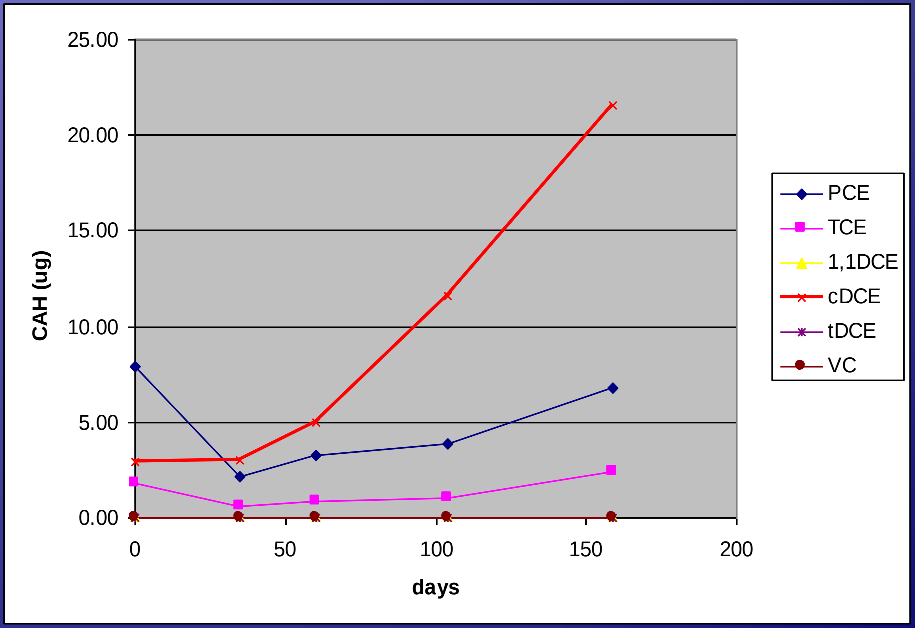
- BiRD was tested in an “apples to apples” with bioremediation using PRB approach
- Bio used municipal mulch as organic & sand for weight
- BiRD also used municipal mulch & sand but added crushed gypsum ($CaSO_4$) for sulfate.



Comparative CAH Treatment Response

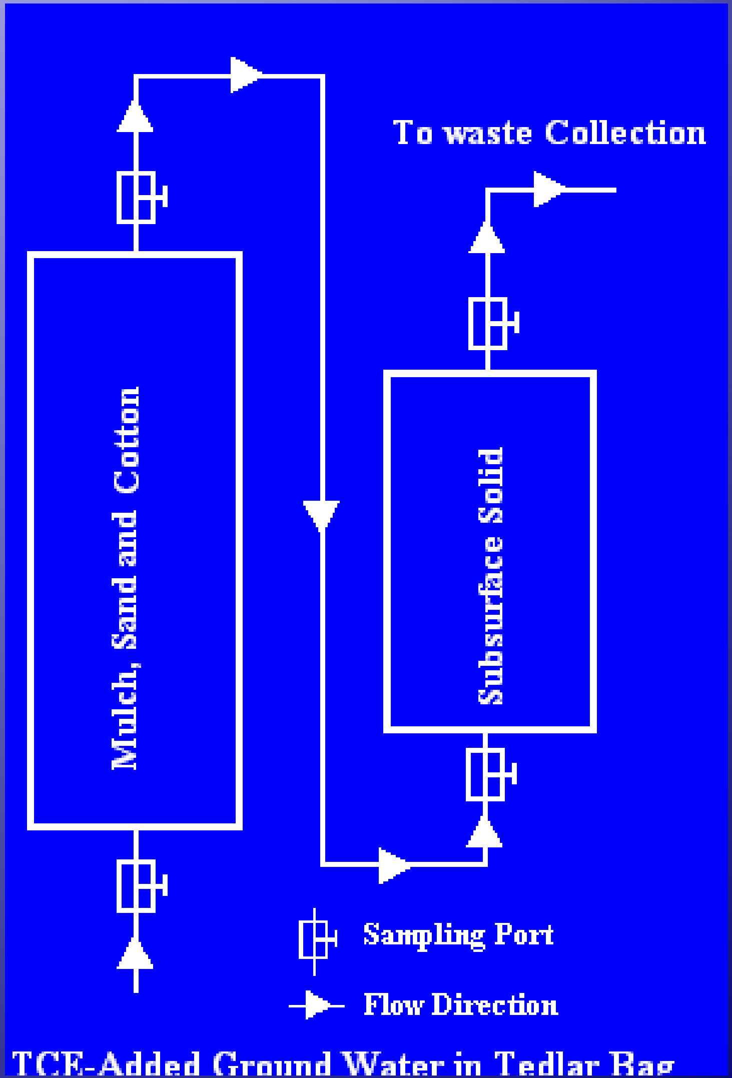
- BiRD (top) showed rapid and complete treatment of PCE, TCE & DCE
- Bioremediation (bottom) showed TCE transformed to DCE with <u>no</u> net treatment

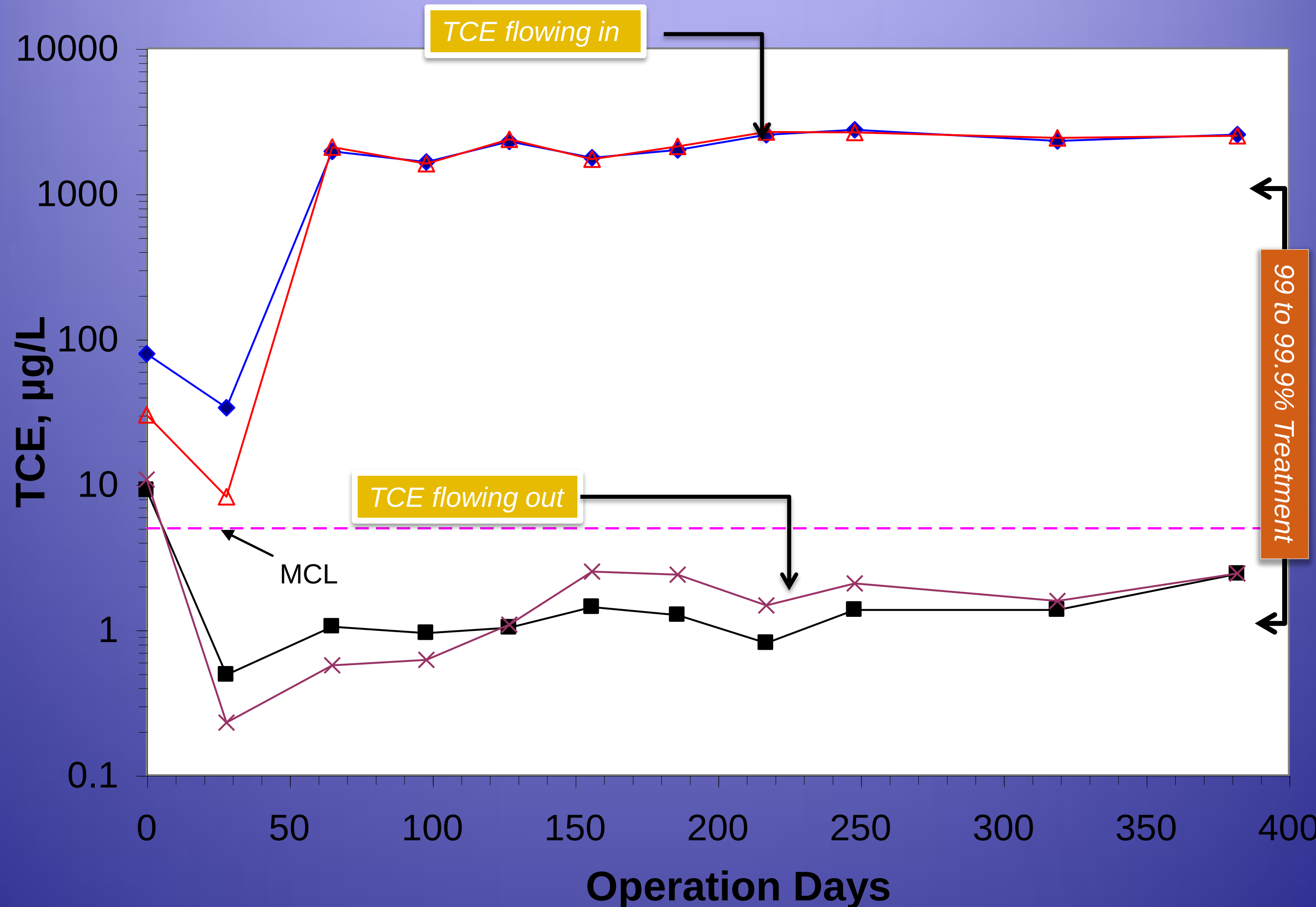




EPA Independent BiRD Testing

- EPA Kerr Lab tested BiRD for over a year (H. Shen and J. Wilson)
- Two column experiments made with cotton seed (organic) mixed with sand & sand with hematite (natural iron)
- Ground water was pumped at normal velocity with:
  - 1500 mg/L sulfate
  - 2000 ug/L TCE
  - 10 ug/L residual DCE
- During the experiment aqueous samples were obtained:
  - Before the mulch mix column
  - After the mulch mix column
  - After the aquifer sediment column





EPA's study showed that:

- *The 2000 ug/L flowing into the BiRD treatment columns was treated to 99.9% in both treatment test cells.*
- *No daughter products were generated.*

BiRD Costs

- BiRD will typically be the least expensive treatment option compared to bioremediation and ZVI
- Similar dependency on quality site characterization and subsurface engineering
- Fewer optimization concerns – bioaugmentation, carbon maintenance, low pH
- Injectable BiRD can use bulk organic and fertilizers for < $1.5/lb (< $3.30/kg)
- Trench-based PRB BiRD can use municipal yard waste and bulk sand/gypsum ranging in cost from free to about $\$50/yd^3$

Main BiRD Advantages:

- Flexibility in application (trench-based and direct injection)
- Is a natural process enhanced by engineering design
- Reagents need not be continuously applied as solid phase FeS remains
- Reservoir permeability is not adversely affected
- Reacted FeS → oxidized Fe + S can be cycled back into FeS again
- CAH treatment is complete with virtually no daughter product generation
- CAH treatment similar to ZVI with half life of 30 days ±15
- BiRD is low cost so even large plumes could be treated economically

Looking Ahead:

- Consistent success in subsurface remediation is challenging and requires competency in several areas:
  - Subsurface Characterization / Conceptual Site Modeling (50%)
  - Treatment Technology Selection (20%)
  - Subsurface Engineering (30%)

- While engineered approaches based on abiotic dechlorination pathways (e.g., ZVI and BiRD) offer intrinsic advantages, the future will favor technology promoted by solution providers that demonstrate “50-20-30” competency.

Thank You

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