New Approach to Fuel Additive Ethylene Dibromide Removal from Groundwater: BiRD

Biogeochemical Reductive Dehalogenation

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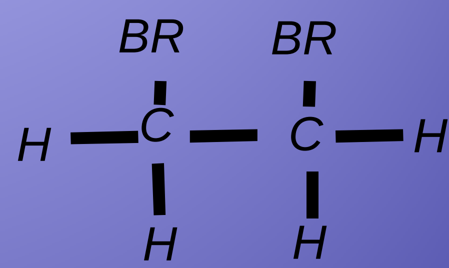
Presentation Objectives

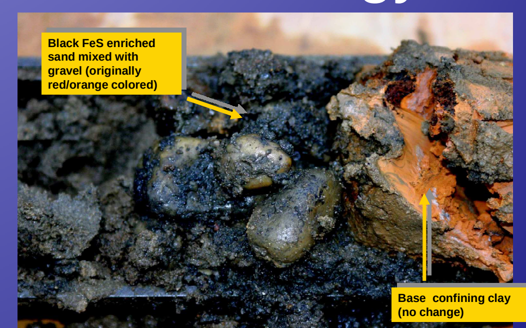
Present the environmental challenge of 1,2-Dibromoethane (Ethylene Dibromide or EDB*)*

Used as a lead scavenger



Introduce the innovative groundwater treatment technology referred to as BiRDS –

Biogeochemical Reductive Dehalogenation and Metals Stabilization



Present evidence of efficacy of removing EDB from groundwater using the BiRDS technology

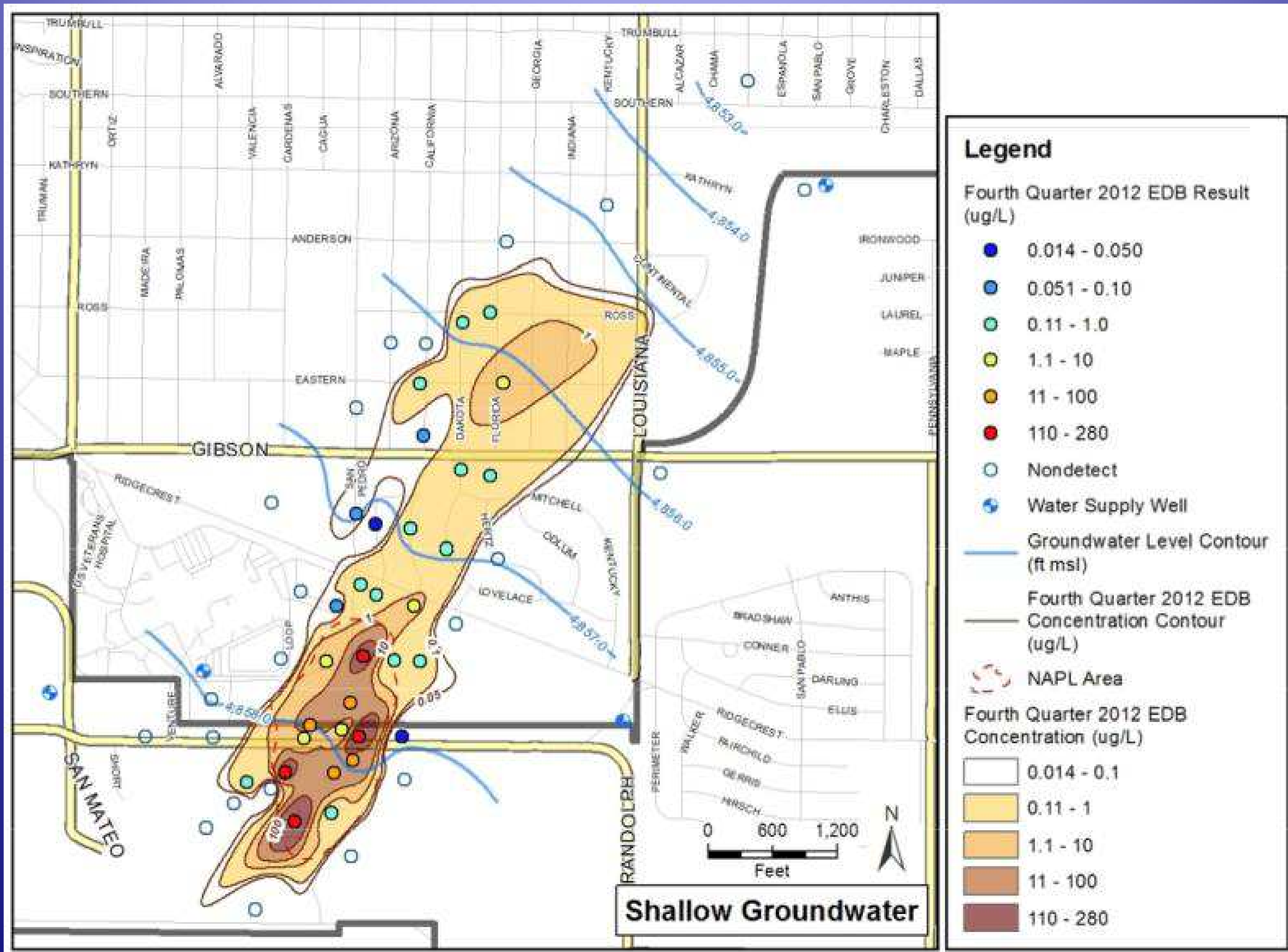
Address practical implementation aspects of BiRDS for EDB including expected project costs

The EDB Challenge

- *Lead Scavenger used in leaded gasoline and continues to be used in off-road fuels*
- *Present at ~290 mg/L in gasoline (BTEX 130,000 mg/L)*
- *Equilibrium. Aq. Concentration 1.9 mg/L (BTEX ~99 mg/L)*
- *Potent Mutagen with serious acute and systemic effects*
- *MCL 0.05 ug/L (benzene 5 ug/L)*
- *Highly mobile in GW, low sorption, low intrinsic biodegradation*
- *In 2005 EPA reported on EDB in production wells across the US - generally between – 1 and 1000 ug/L*

- *Detection in Soil and Groundwater using EPA 8011, 8021B, 5030B, 5021 – EDB not common analyte of concern*

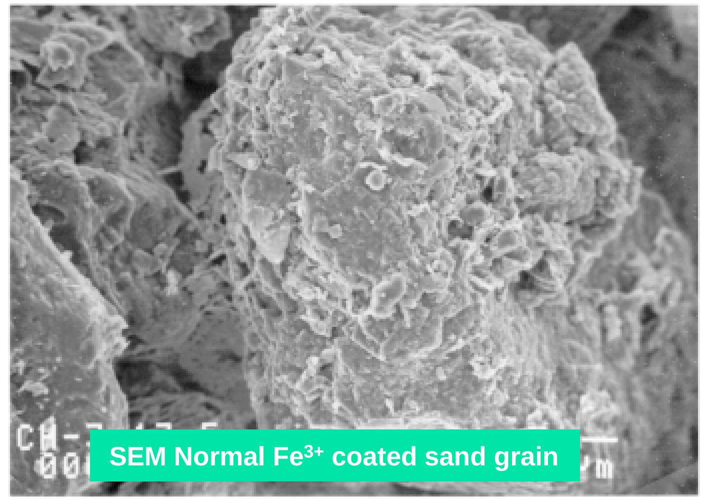
KAFB Bulk Fuel Facility Plume – EDB



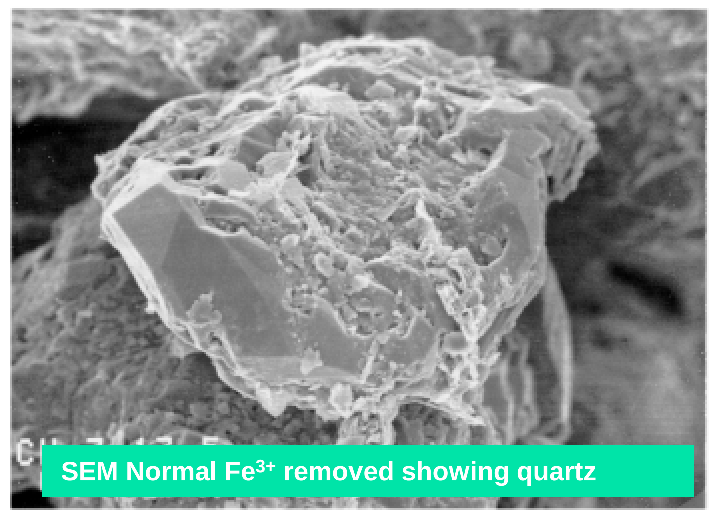
Source: KAFB CAB Meeting, May 21, 2013, Albuquerque, NM

Subsurface 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 CoCs*
- *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

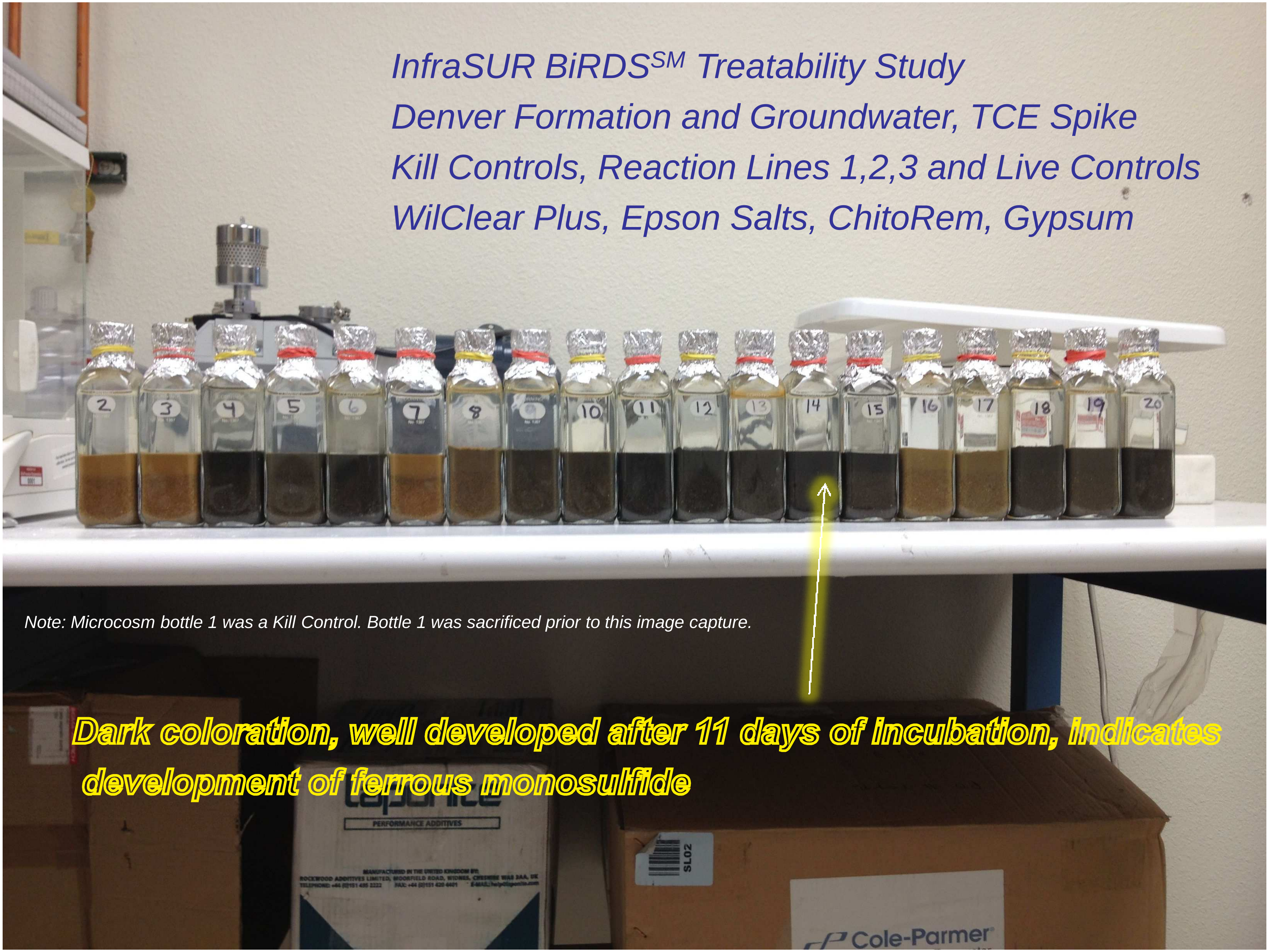
BiRD Basics

- ***B**iogeochemical **R**eductive **D**ehalogenation **(BiRD)** is a patented process for the treatment of halogenated compounds and certain metals [Kennedy - US Patent Off. #6,884,352 B1]. Also referred to as In Situ Biogeochemical Transformation.*

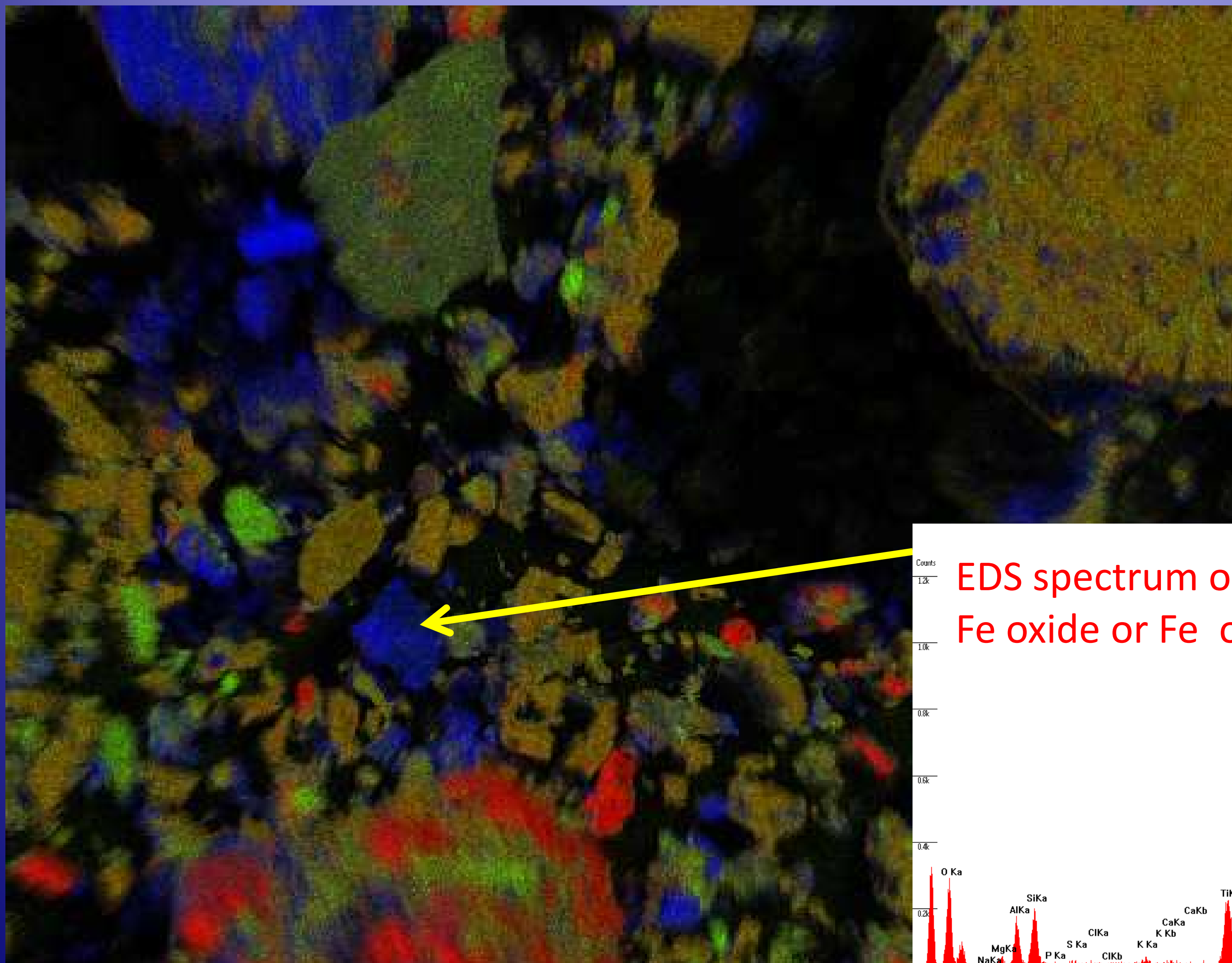
- *Basis for BiRD is:*
  - *Typical clastic aquifers have much native iron and can be supplemented if necessary*
  - *But, this iron is not reactive and can't treat targeted compounds*
  - *BiRD stimulates naturally occurring bacteria to convert native Fe to FeS minerals*
  - *FeS facilitates the complete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

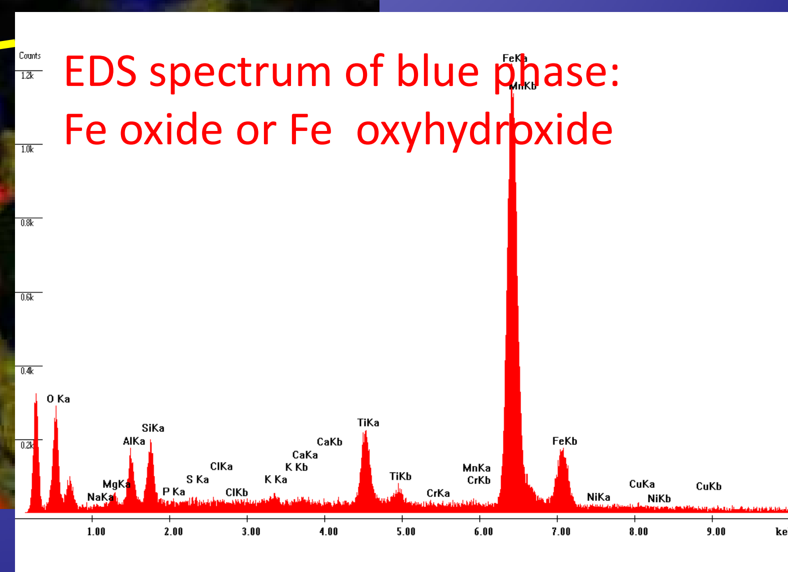
- *BiRD is focused on <u>engineered in-situ iron sulfide</u> reaction zones and the abiotic reactions with contaminants*

- *No particular need or desire to include or enhanced <u>biological reductive dehalogenation</u>*


InfraSUR BiRDS^{SM} Treatability Study
Denver Formation and Groundwater, TCE Spike
Kill Controls, Reaction Lines 1,2,3 and Live Controls
WilClear Plus, Epson Salts, ChitoRem, Gypsum
Note: Microcosm bottle 1 was a Kill Control. Bottle 1 was sacrificed prior to this image capture.
Dark coloration, well developed after 11 days of incubation, indicates development of ferrous monosulfide
Cole-Parmer
PERFORMANCE ADDITIVES
SL02

SEM Image of Denver Formation





BiRD Functional Steps:

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

$CH_2O + ½\ SO_4^{2-} \rightarrow HCO_3 + ½\ HS^- (ag) + H_2O + H^+$

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

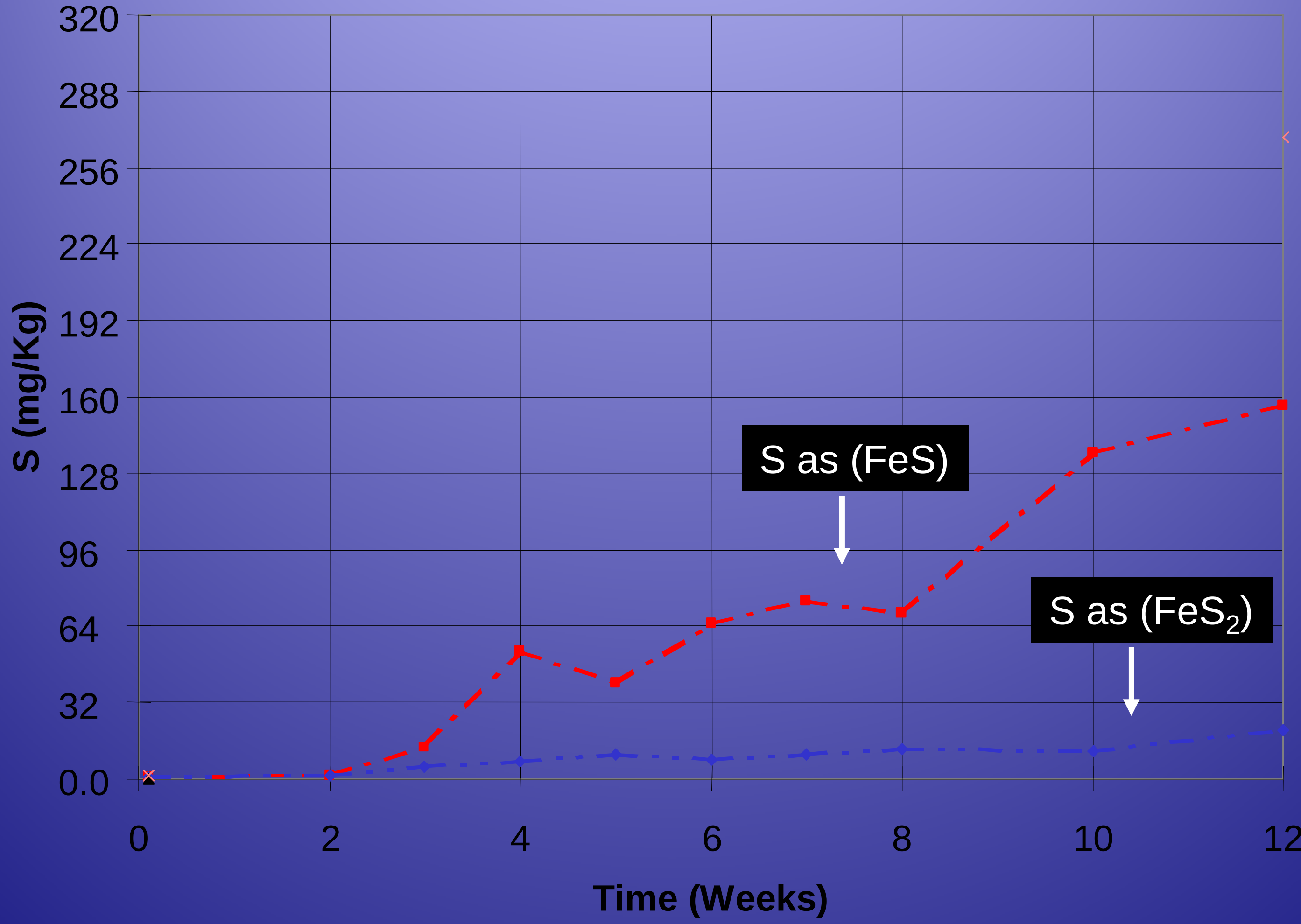
- Phase 3: Dehalogenation Step (using TCE as example):
  - Reactive FeS reductively dehalogenates target abiotically:

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

- With FeS surface area, COC treatment (sorption and transformation) usually begins within 2 weeks or sooner.

COC 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.*

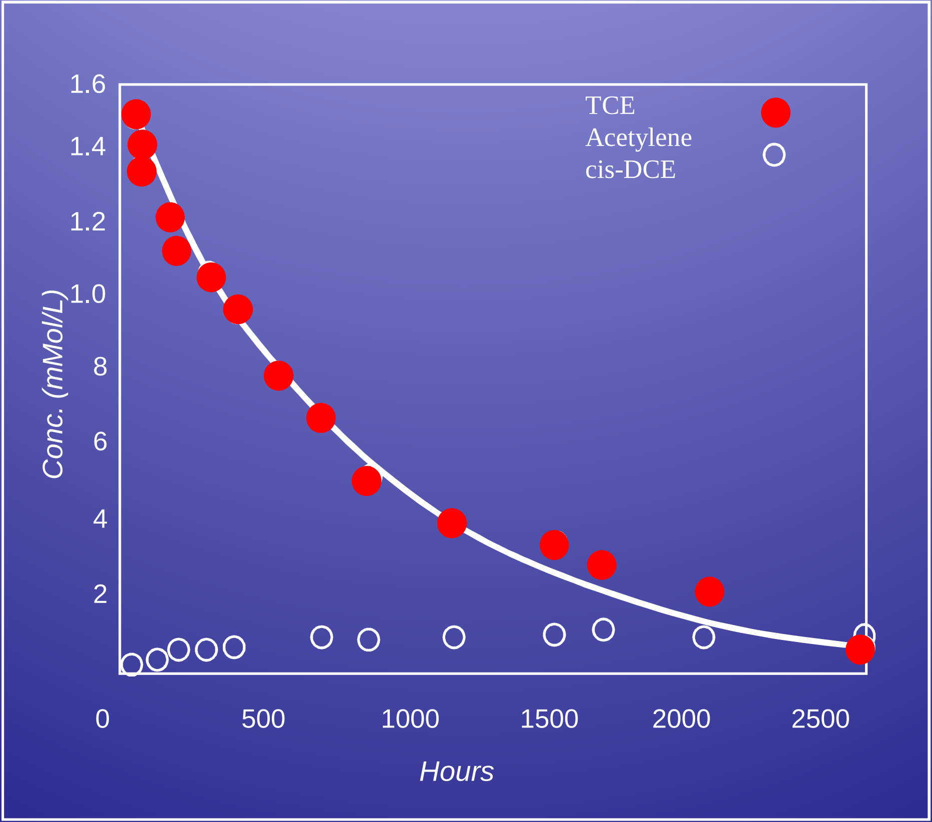
Natural or Engineered FeS Functionality

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

TCE

1.6 mMol/L = 210 mg/L

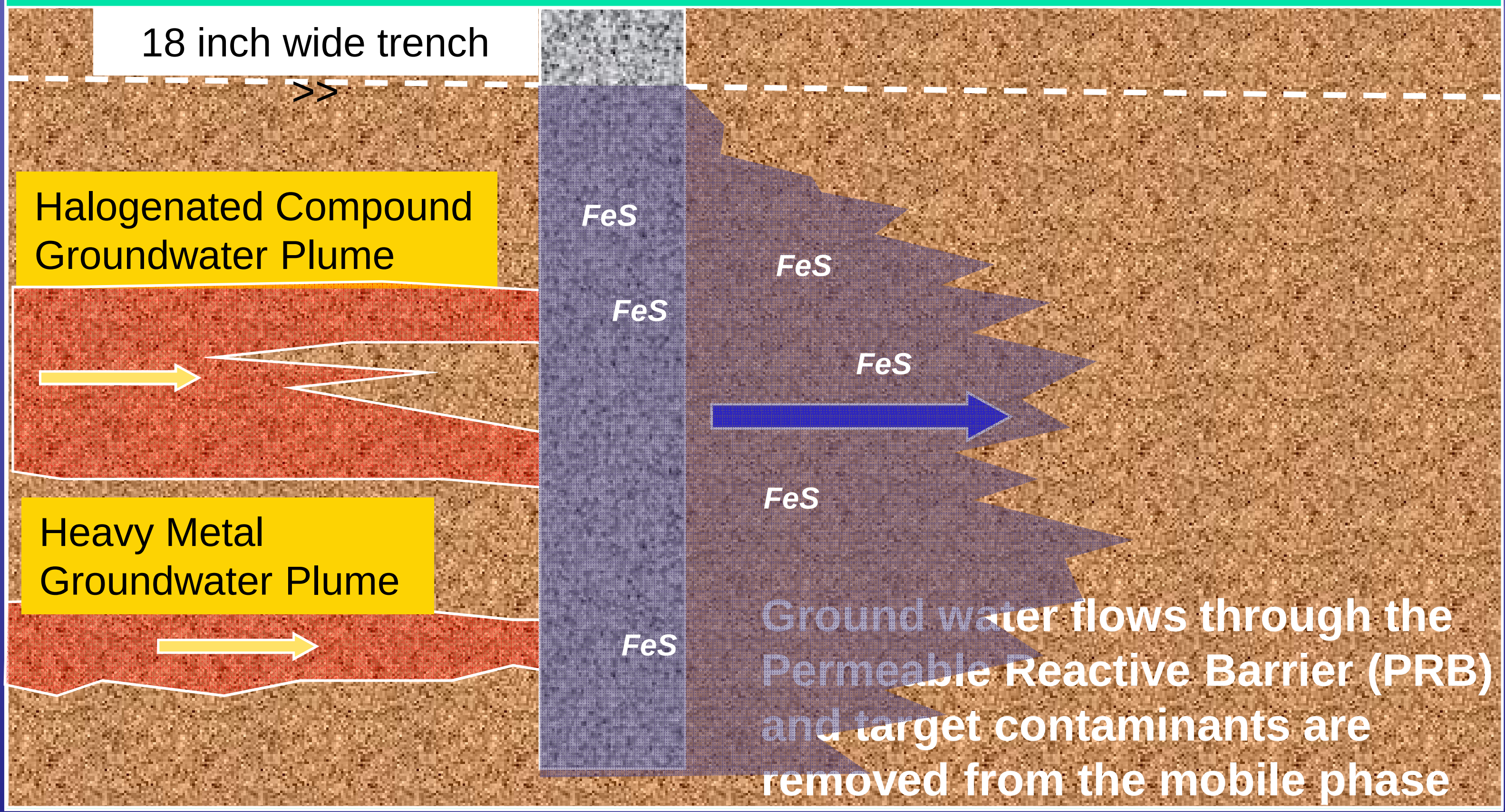
0.2 mMol/L = 26.3 mg/L



2500 hours = 104 days

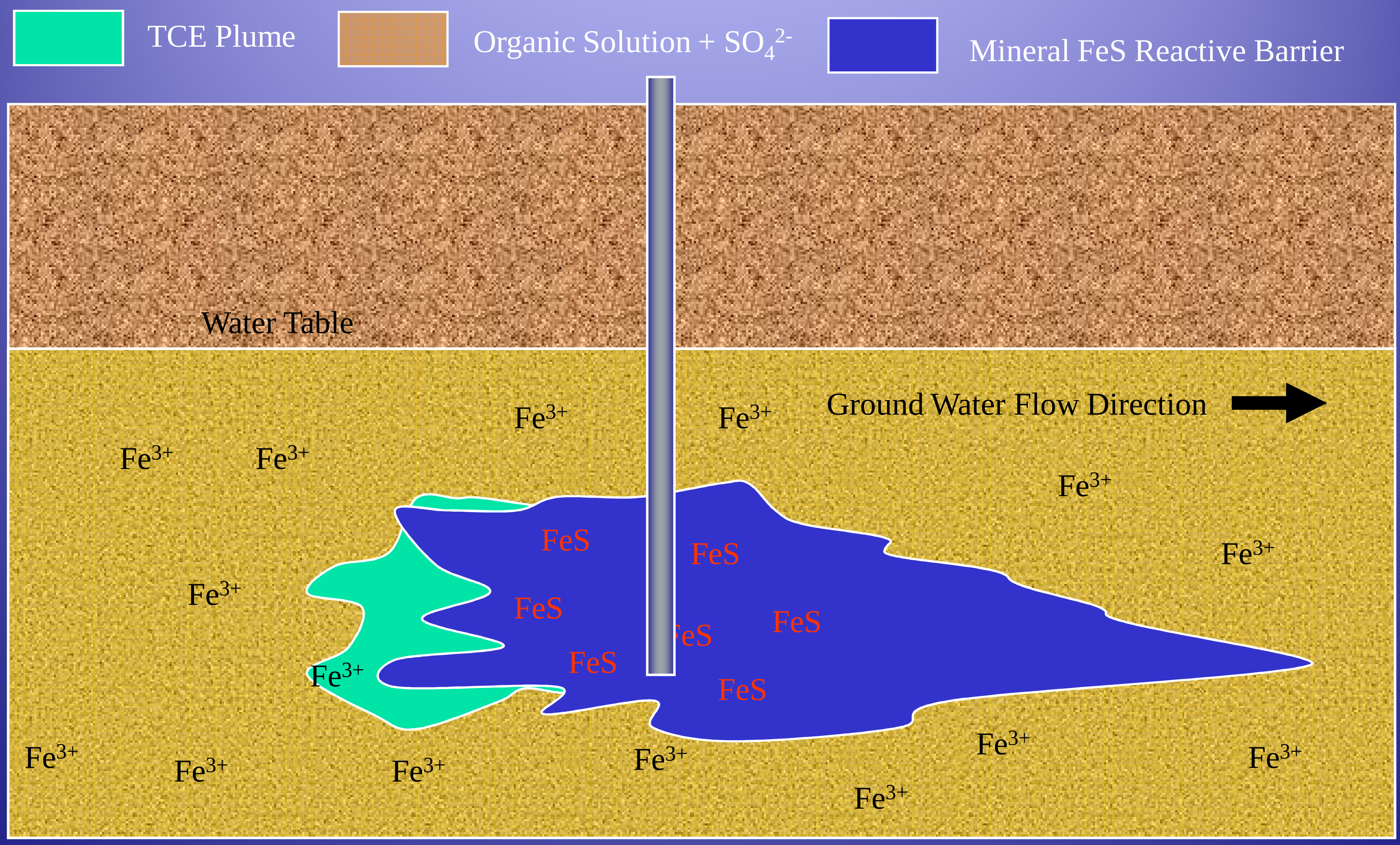
Butler and Hayes, Environ. Sci. Technol. 1999, 33, 2021-2027

Biogeochemical Reductive Dehalogenation and Metals Stabilization (BiRDS) by Trench or Direct Injection PRB



$316,000 for 300 ft long 45 ft deep PRB.

BiRD Application by Injection



Lower Capital Cost Than Trenching Based But Operational Cost May Be Higher

BiRDS Deployment Status

Kennedy and Everett at Altus and Dover AFBs (CAHs)

USEPA Ada Labs Bench Studies (TCE and EDB)

Approximately 15 Technology Demonstrations have been conducted by the US Air Force (CAHs)

Over 8 commercial projects underway as of October 2013 (CAHs)

PA, MO, FL, MI, CO, GA, CA, MA

Case History

Dover AFB National Test Site

Biogeochemical Reductive Dehalogenation

(BiRD) Pilot

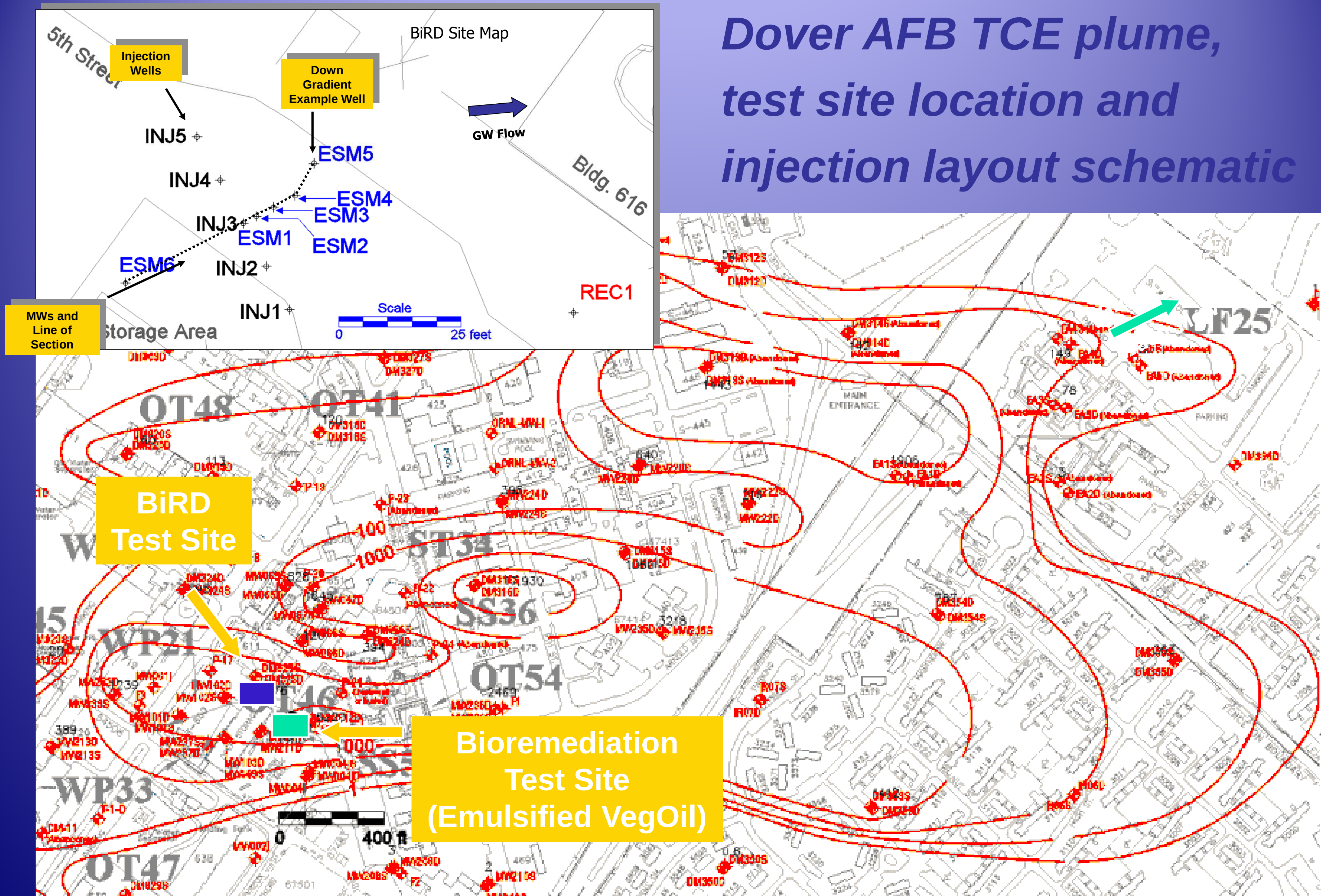
with Comparison to

Biological Reductive Dechlorination Pilot

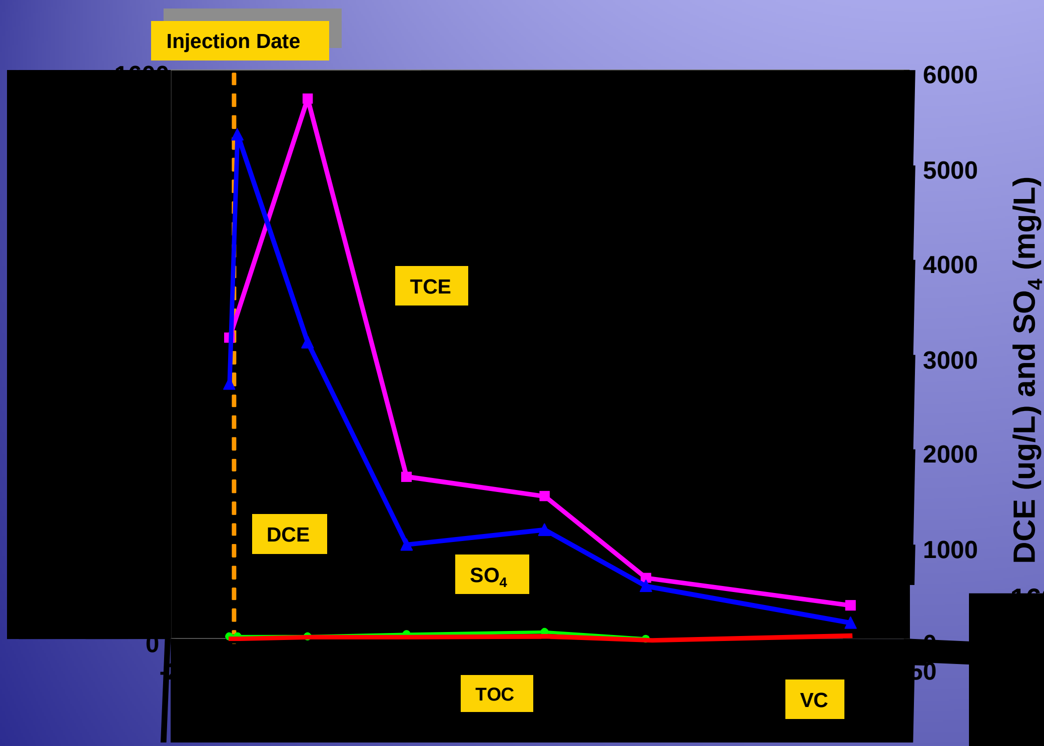
BiRD Reactive Zone Created Using Aqueous Injections

- 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 SO4・7H2O (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

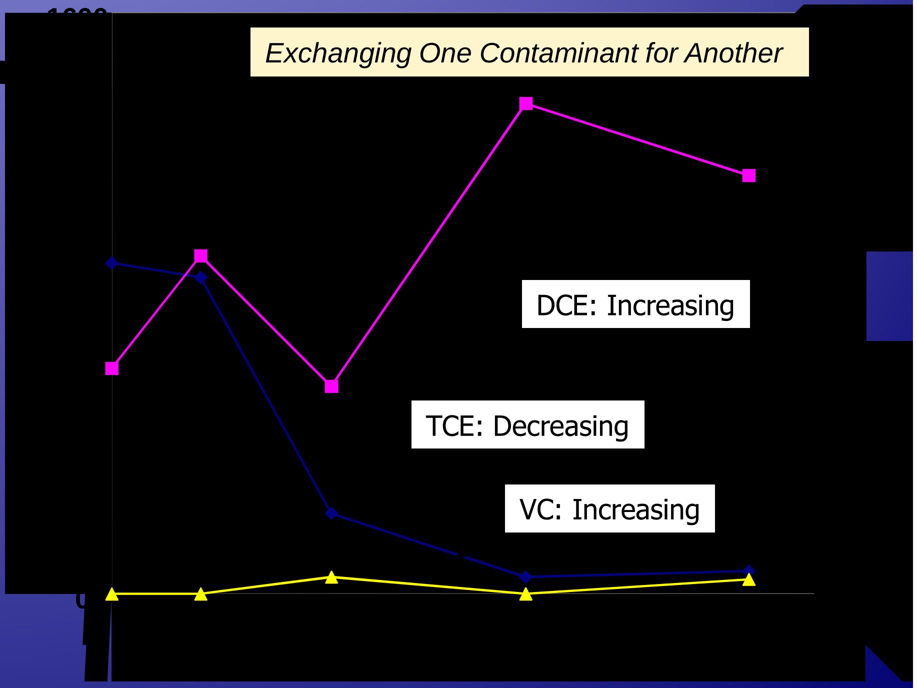


Comparative CAH Treatment Response



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

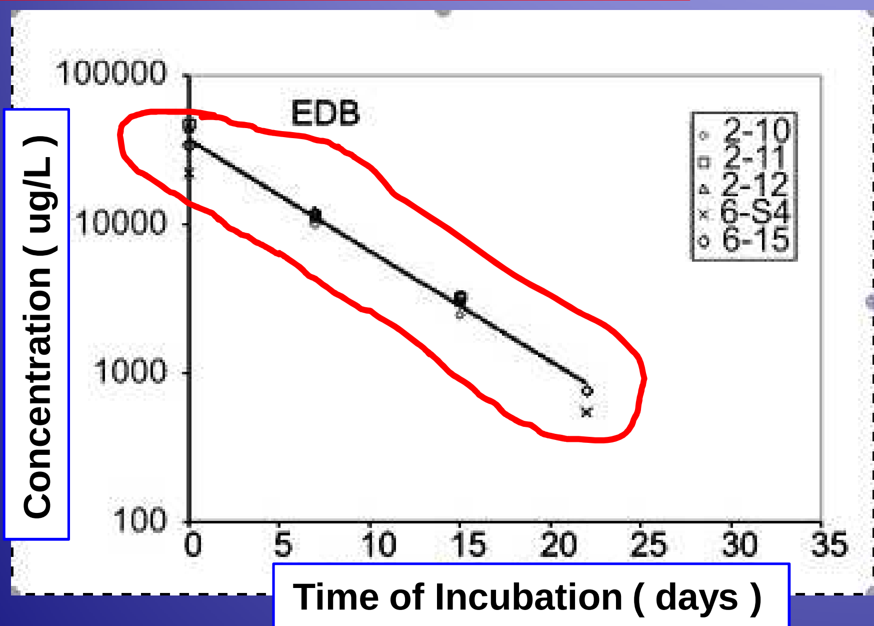
- Bioremediation response (right) showed decreasing TCE but increasing DCE and VC

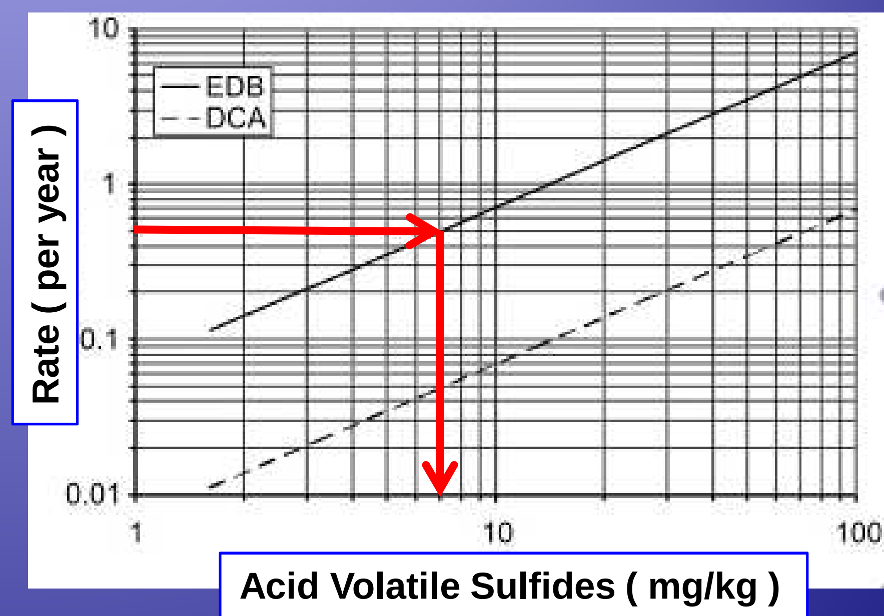


Removal of EDB in Presence of Biogenic FeS (BiRD) and Expected Rates of Abiotic Transformation

First Order Kinetics without a Lag Period

A first order rate constant K exceeding 0.5 per year is desirable





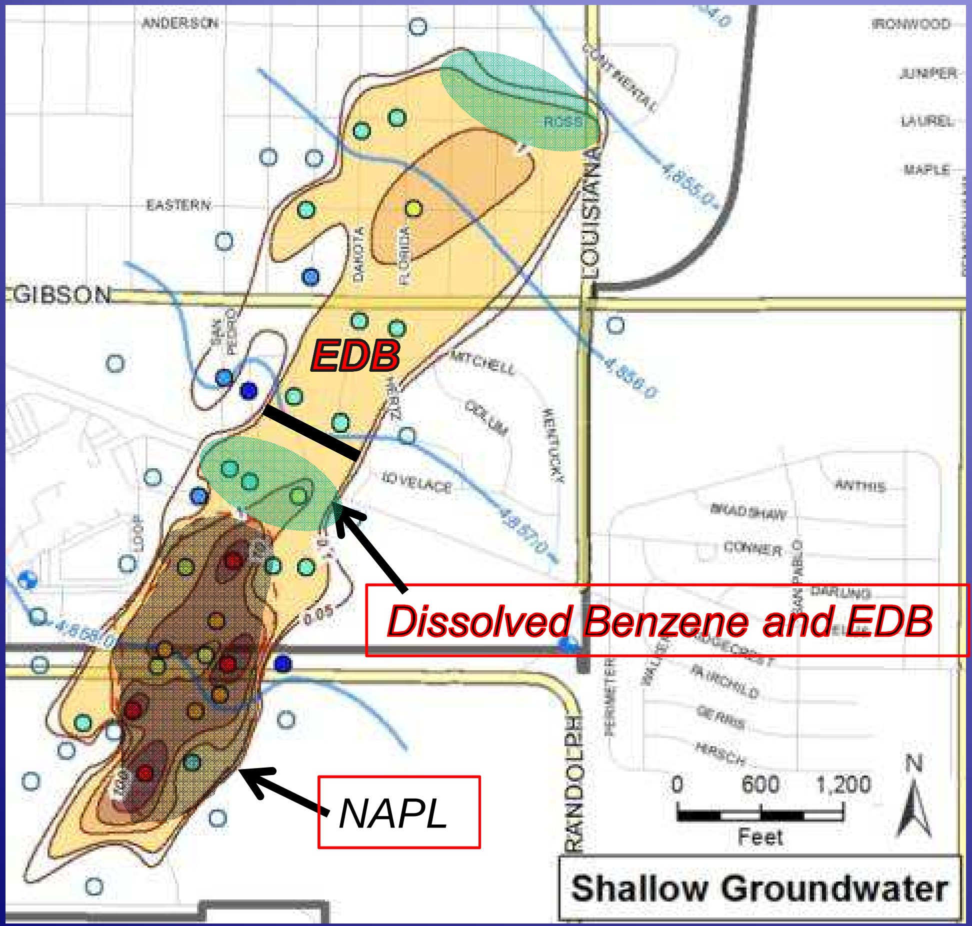
Both Graphs modified from EPA 600/R-08/107 Sept 2008 John T. Wilson USEPA NRMRL, Ada, Oklahoma, lead author

Experimental data based on batch experiments at pH ~7

Predictions based on aquifer sediment with water-filled porosity of 25% and pH ~7

Special Engineering Considerations EDB vs CAHs

Unlike CAHs, EDB is integral to the carbon source (fuel NAPL)



Stay out of NAPL

Redox Zonation – DO and NO3 Depletion, Iron/Mn Reduction, Sulfate Depletion

Iron and Sulfate Reducing Bacteria

Carbon Based Electron Donor – Quality and Mass Flux

Carbon and Mineral Recycling

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 – e.g., bioaugmentation, carbon maintenance, low pH
- Injectable BiRD can use bulk organic and fertilizers for $< \$1.5$/lb ($< \$3.30$/kg)
- Trench 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 and direct injection)
- Amplifies natural processes through engineering
- Reagents need not be continuously applied as solid phase FeS remains
- Reservoir permeability is not adversely affected
- Reacted FeS → oxidized Fe + S can cycle back into FeS again

Main BiRD Advantages:

- Halogenated compound treatment is complete with virtually no daughter products remaining
- Treatment similar to ZVI with half life of 30 days $\pm$15
- Many metals can also be treated simultaneously
- BiRD is low cost so even large plumes could be treated economically

Breaking Dawn
in Albuquerque

Thank You

Contact Information about
InfraSUR BiRDS ^{SM} technical services and licensing program:

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