Groundwater Remediation by Biogeochemical Reductive Dehalogenation and Metals Stabilization (BiRDS)

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Presentation Objectives

Introduce the innovative in-situ groundwater treatment technology referred to as BiRD or BiRDS – *Biogeochemical Reductive Dehalogenation and Metals Stabilization*

Present evidence of efficacy of removing Halogenated Compounds, Metals, and Metalloids from groundwater using the BiRDS technology

Summarize features and benefits for brownfields application
Challenges in Brownfields Remediation

Soil, Sediment, Bedrock, Groundwater Impacts by Organic and Inorganic Contaminants

Low Cost Treatment/Closure Approaches

Rapid Deployment of Solutions or at least Compatible with Redevelopment

Sustainable (green) and generally of low impact
Challenges in Brownfields Remediation

Remedial Technology Options:

• Excavation and Off-Site Disposal
• Groundwater Pump & Treat
• Air Sparging & Vapor Extraction
• In Situ Bioremediation
• Abiotic Reduction – Zero Valent Iron
BiRDS Basics

- **Biogeochemical Reductive Dehalogenation and Metals Stabilization (BiRDS)** 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 BiRDS 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
  - BiRDS stimulates naturally occurring bacteria to convert native Fe to FeS minerals
  - FeS facilitates the complete autoreduction of target organic compounds similar to zero valent iron (ZVI)
  - Incorporation of metals and oxy-anions into mineral assemblages is promoted during FeS reactive zone development
  - Newly created reactive mineral surfaces serve to enhanced metal adsorption as well.
**BiRDS Basics**

- *BiRDS* is an engineered process focused on *in-situ generation of iron sulfide* reaction zones that support *abiotic* (and *biotic*) reactions with contaminants

*Effective Characterization and Conceptualization is Necessary*
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/m³.
- This iron is well dispersed and often as poorly crystalline grain coating and/or incorporated into clay structures.
- 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.
InfraSUR BiRDS\textsuperscript{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 within the broken up siltstone
BiRDS Functional Steps:

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

\[
\text{CH}_2\text{O} + \frac{1}{2} \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \frac{1}{2} \text{HS}^- \text{(ag)} + \text{H}_2\text{O} + \text{H}^+
\]

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

\[
3\text{HS}^- + 2\text{FeOOH} \text{(s)} \rightarrow 2\text{FeS} \text{(s)} + \text{S}^0 + \text{H}_2\text{O} + 3\text{OH}^-
\]

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

\[
\frac{4}{9}\text{FeS} + \text{C}_2\text{HCl}_3 + \frac{28}{9} \text{H}_2\text{O} \rightarrow \frac{4}{9}\text{Fe(OH)}_3 + \frac{4}{9}\text{SO}_4^{2-} + \text{C}_2\text{H}_2 + 3\text{Cl}^- + \frac{35}{9}\text{H}^+
\]

- 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 $\text{SO}_4^{2-}$, 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

TCE
1.6 mMol/L = 210 mg/L

0.2 mMol/L = 26.3 mg/L

2500 hours = 104 days

Field Implementation – Construction
BiRDS Permeable Reactive Barriers

Direct Injection PRB
• Direct Push Rods
• Temporary Wells
• Permanent Wells – Vertical or Horizontal

Excavation / Trench PRB
Field Implementation – Construction
BiRDS Permeable Reactive Barriers
Ground water flows through the Permeable Reactive Barrier (PRB) and target contaminants are removed from the mobile phase.
FeS forms a permeable reactive zone into which aqueous organics and/or metals may flow. Dehalogenation is complete and transformation products are mineralized. Heavy metals and oxy-anions such as lead, chromium, arsenic are fixed via mineral incorporation (e.g., arsenopyrite) or strong surface adsorption.
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BiRDS Deployment Status

Technology Development and Demonstration for CAH Plumes

Technology Demonstration Metals/Metalloids
2005 – on-going

Commercialization CAH Plumes 2011 – on-going

Commercialization Metals/Metalloids Plumes
2013 -
Case History

Halogenated Compounds

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
Bioremediation Test Site (Emulsified VegOil)

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
BiRDS 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 PRB BiRD can use municipal yard waste and bulk sand/gypsum ranging in cost from free to about $50/yd$^3$
Main BiRDS 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 $\Rightarrow$ oxidized Fe + S can cycle back into FeS again
Main BiRDS Advantages:

- Halogenated compound treatment (e.g., PCE, TCA, EDB) is complete with virtually no daughter products remaining
- Treatment similar to ZVI with half life of 30 days ±15
- Many metals/metalloids can be treated separately or simultaneous with halogenated organics
- BiRD is low cost so even large plumes could be treated economically
Thank You

Contact Information about InfraSUR BiRDS™ technical services and licensing program:

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