Large, Dilute Solvent Plumes

Jim Cummings TAB/TIFSD FRTR Meeting May 13,2010

Large, Dilute Plumes

• Prevalent Problem Set

 Pose characterization and remediation challenges

What conditions create L&D plumes?

Permeable aquifers, generally with low organic carbon contents

Aerobic systems where influx of electron acceptors makes it difficult to establish and maintain reducing conditions

Attenuation processes are generally slow (e.g., degradation half-lives more than 1 to 2 years)

Often deep

Often affected by mass transfer in/out of less-transmissive compartments (clay/silt layers)



Key Insights

- Plumes are heterogeneous
 Not uniform 'blobs'
- 90% of contaminant mass may be sorbed to the matrix in the volume commonly thought of as 'dissolved phase'
 - Manifests as early 'spikes' in contaminant concentration – sometimes >initial concentrations following ISCO as contaminants desorb from matrix (NOT late stage 'rebound')

M-Area – DOE Savannah River Site (TCE, approximately 2 square miles and extending to 200 feet deep, initial source concentration → DNAPL)

200 Area – DOE Hanford Site (Carbon tetrachloride, approximately 3 square miles and extending to 350 feet deep, initial source concentration \rightarrow DNAPL)

Northwest Plume – DOE Paducah Gaseous Diffusion Plant (TCE, approximately 1 square miles extending 75 feet deep, initial source concentration \rightarrow DNAPL)

Test Area North – DOE Idaho National Laboratory (TCE, approximately 1 square mile and extending to 350 feet deep, initial source concentration \rightarrow DNAPL)

Many DOD examples (Hill AFB, Tinker AFB, etc.) and industrial facilities



'Desperately Seeking...'

- Least Cost Amendments
- Least Cost Delivery Mechanisms

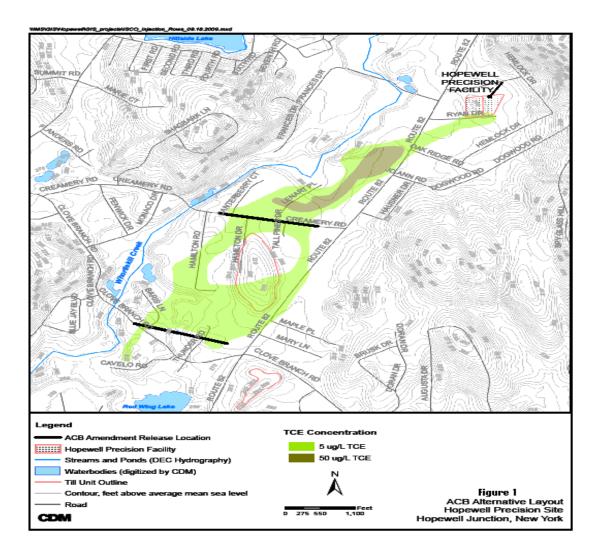
• Exploitable subsurface hydro/ bio/ geological conditions to 'help'...

Hopewell Site, NY

- 7000' solvent plume mainly TCE
- Concentrations generally < 100 ppb

- But...
 - MCL exceedances in private wells
 - <u>Vapor Intrusion</u> above acceptable levels

Heterogeneous Lithologies, Permeabilities and Geometries



Hopewell, NY - Additional Complications

Shallow <u>aerobic</u> plume

- Therefore ERD N/A
- Efforts at other sites to change redox have often been 'ugly'
- Plume depiction accuracy uncertain
 - Based on a variety of monitoring and water supply wells with differing screened intervals

Hopewell, NY - Components of Remedy

• Point of use water systems

• Abate Vapor Intrusion

• Aerobic cometabolic bioremediation to restore plume

Aerobic Co-metabolic Bio

- Much initial research done by Dr John Wilson and his wife at ORD/Ada
- Micro-organisms produce an enzyme which fortuitously destroys contamination
- No toxic daughter by-products (e.g., VC)
- Not widely used heretofore due to slow(er) degradation rates
- "Burn-out" problem

ACB – Necessary Ingredients

• Presence - or addition - of Pseudomonas

 Substrate addition to promote microbial proliferation

 Oxygen to support biodegradation (6-8mg/L)

"Burn-out"

 Enzymatic process is uncomfortable to micro-organisms (equiv to a 'hot-foot') so there is natural selection away from the desired organisms

Implementation Challenges*

- <u>Biofouling</u> microbial proliferation around injection point(s) (Solution: H₂O₂ as O₂ source)
- <u>Competitive</u>

Inhibition – substrate competes with contaminants for activation sites

- <u>Deactivation</u> Process stops when substrate consumed (requires continuing addition)
 - Source: Air Force Research Lab Installation Restoration Program AFRL ML-TY-TR-1998-4530

| Table 3-1. Efficiency of Chlorinated Aliphatic Hydrocarbon Removal Obtained at the Moffett Federal Airfield Site with Different Primary Substrates (after Hopkins and McCarty, 1995) | | | | | | | | |
|--|--------------------------------------|----------|---------|-------|-------|-------------------|--|--|
| Primary Substrate | Substrate Concentration (mg/L) | %Removal | | | | | | |
| | | TCE | 1,1-DCE | c-DCE | t-DCE | Vinyl Chloride | | |
| Methane | 6.6 | 19 | NE | 43 | 90 | 95 | | |
| Phenol | 12.5 | 94 | 54 | 92 | 73 | >98 | | |
| Toluene | 9 | 93 | NE | >98 | 75 | NE | | |

| Key: TCE = | Trichloroethylene | 1,1-DCE | = | 1,1-Dichloroethylene |
|------------|----------------------------|---------|---|----------------------|
| t-DCE = | trans-1,2-Dichloroethylene | e NE | = | Not Evaluated |
| c-DCE = | cis-1,2-Dichoroethylene | mg/L | = | Milligrams per liter |

Aerobic Co-metabolic Bio

 Recent work by DOE/SRS on substrates which increase biodegradation rates

- At least one commercial firm CL Solutions has done field scale work (vendor claims >100)
 - Includes bio-augmentation (*Pseudomonas*) w/ dextrose substrate addition
 - But small footprints to date

ACB

 Recent ES&T article reports use of Compound Specific Stable Isotope Ratio (CSIR) analysis to confirm ACB of TCE and DCE in a fractured rock aquifer system Throughout the nation:

80 to 100% of the wells at most sites screen positive for significant numbers of organisms that are expressing the enzymes necessary for cometabolism

- Therefore, cometabolism is occurring in all of the aerobic plumes tested to date
- **Current research focuses on why* and kinetics (rates)**

* how are these organisms living in oligotrophic aquifer systems? What is the carbon source?



Throughout the nation:

Half lives of about 8 to 31 years have been measured

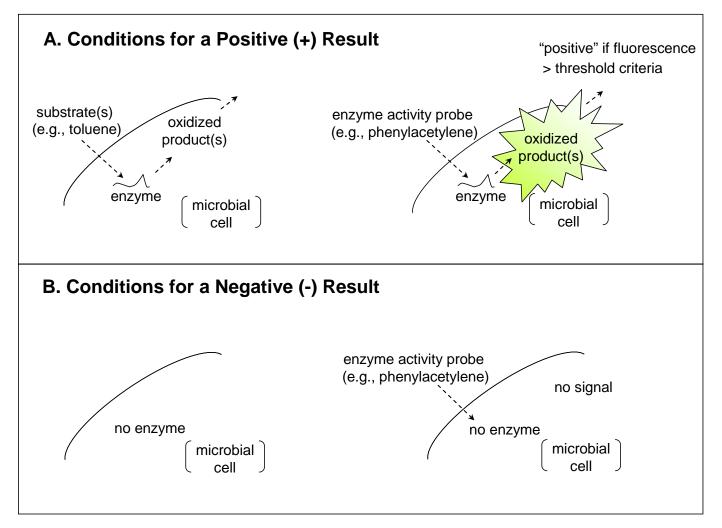
Based on current conceptual model -

process is sustainable

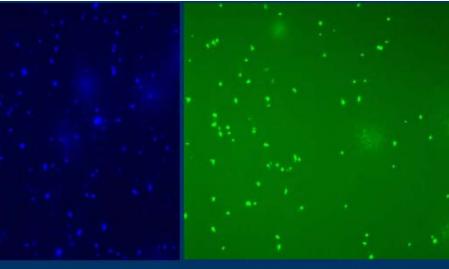
long-lived amendments (natural organic matter) may be deployable on a large scale to enhance rates



Enzyme Activity Probes (EAP) look for Key Enzymes



Sample Images



Total bacterial cell count

Positive probe response

Negative probe response



Least Cost Amendments

• Gases would be the cheapest

 But: Amendments suggested by DOE are liquids

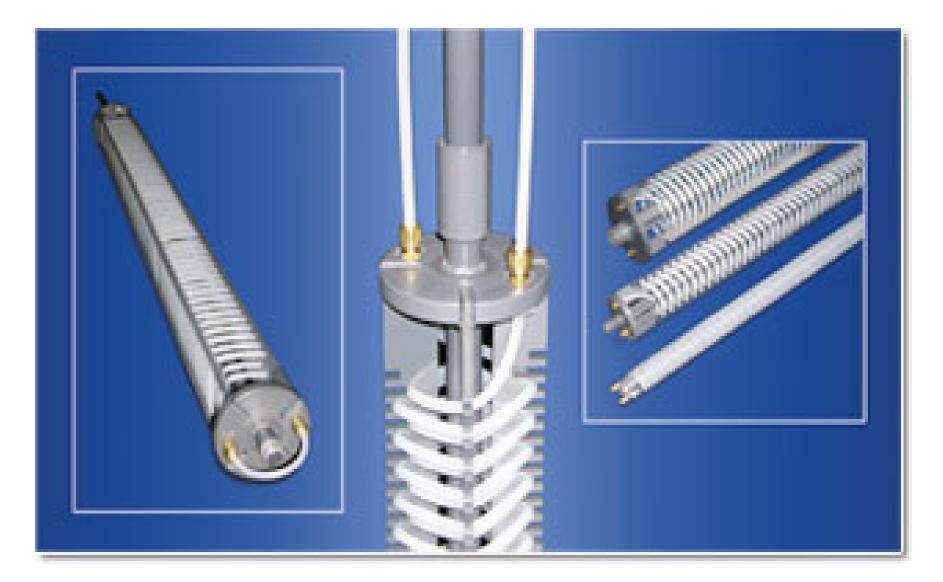
Amendments

• Oxygen for aerobic bioremediation

 Toluene, Methane, Propane – possible gaseous substrates

Least Cost Delivery Mechanisms

Waterloo Emitter



Simple Technology

- PVC frame wrapped with tubing that can be pressurized to obtain the desired diffusive transfer of gas
- <u>No pumps required</u>
- Sized for 2", 4" and 6" wells
- Units can be stacked in a well and joined from one well to another, to allow the controlled continuous diffusion of gas into the plume
- BUT: Limited to gases

Other Possible Delivery Mechanisms

• Horizontal Biosparge Wells

Cost Comparison – 20 acre facility 400'x70'x20'deep plume

| Remedial Alternative | Capital Cost | <u>Annual Cost</u> | Present Worth |
|-----------------------------|-----------------|--------------------|---------------|
| Ozone/Air Sparging | \$ 460 - 680 | 63 - 123 | 630 - 1,120 |
| Fenton's Reagent Injection | \$ 625 - 900 | 22 - 46 | 720 - 1,260 |
| KMnO4 Injection | \$1,100 - 1,600 | 22 - 46 | 1,300 - 1,900 |
| Iron PRB Installation | \$ 760 - 1,110 | 22 - 46 | 1,250 - 2,120 |
| Horizontal Biosparge Well | \$ 350 - 490 | 57 - 91 | 550 - 950 |

Cost Effectiveness of Horizontal Biosparge Well Application for Aerobic Co-Metabolic Groundwater Remediation Mark M. Meiac, Hal W. Taylor, and Jeanne M. Tarvir

Mark M. Mejac, Hal W. Taylor, and Jeanne M. Tarvin, STS Consultants, Ltd.

Ongoing Cogitation

 Hopewell - How, what (and <u>where</u>) to inject...in progress

 Numerous expressions of interest from DOD facilities to DOE ESTCP ACB site selection survey

The ACB 'Brain Trust'

John Wilson – ORD/Ada Ok

Brian Looney- DOE/SRNL

• Hope Lee – DOE/INEL