Low Cost Bioremediation Using Dextrose and Recirculation to Treat PCE-Contaminated Groundwater at Drycleaners

Don Hanson
Oregon Department of Environmental Quality
SCRD Fall 2006 Meeting
Austin, Texas
Oregon Program Budget Implications

• More sites than we can work on with given DC Program revenue
• Limits on staff availability and time to work on DC Program sites – Recent “downsizing” of Cleanup Program in Oregon
• Requires prioritization based on Risk
  – Yearly prioritization
• Focus on highest priority (Risk) and most bang for the buck (often based on access and timed with redevelopment)
Department of Environmental Quality

Two Oregon Sites

• **NuWay II Cleaners**
  – Lebanon, Oregon
  – Dextrose pilot test

• **Plaza Cleaners**
  – Sweet Home, Oregon
  – Dextrose full Scale Implementation
A WORD ABOUT UNDERGROUND INJECTION CONTROL (UIC)

• Recirculation process assumes underground injection can be used
• Varies state to state
• Oregon is UIC friendly
• RCRA regulations may be a concern
  – On-site “treatment” – CAMU?
  – In Oregon, Cleanup Law allows exemption of RCRA rules (on-site)
Biostimulation Using Dextrose

Why Consider Dextrose?

– Cheap ($1.60 - $2.00/lb)
– Moves with groundwater
  • Can flush/desorb VOCs rapidly
– Quickly stimulates reducing conditions and reductive dechlorination of VOCs
– Not currently proprietary
Ethene is rapidly utilized, no more problem!

Ethene
Dechlorination Process

Competing electron acceptors:

- $O_2$
- Nitrate $NO_3^-$
- Manganese $Mn^{4+}$
- Ferric $Fe^{3+}$
- Sulfate $SO_4^{2-}$

Chlorinated hydrocarbons:

- PCE
- TCE
- DCE
- VC

Nutrients:

- N
- P
- K
- Trace Metals

Dissolved
- Nitrite $N_2$
- Manganese $Mn^{2+}$
- Ferrous $Fe^{2+}$
- $H_2S$

Food

Dextrose

Ethene / Ethane
- Effective substrate delivery via 24/7 GW recirculation
- Substrate added in **pulsed** or continuous injection mode (pulsed is best)
- Highly soluble substrate, plus nutrients, to grow active biomass in porespace
- Max. microbial activity, ↓ ORP, methanogenic cond., ↑ dissolution
NuWay II Cleaners
Lebanon, Oregon
NuWay II Cleaners Pilot Project
Lebanon, Oregon

- Former Cleaners – Now Retail
- Operated from 1953 to 1976
- Stoddard and PCE Used and spilled
- Beneficial Use Aquifer
- P&T From 1998 to 2003
  - Treated groundwater VOCs w/ Air stripping
  - POTW Discharge
  - Mass removal and hydraulic containment
- Increasing O&M (Aging System)
- Decreasing mass removal
- Failed attempt at aerobic cometabolism pilot in 2004
NuWay Pilot Study Objectives

- Use existing “pump and treat” infrastructure for anaerobic recirculation system
- Two injection wells (direct push – prepack screens)
- Transfer O&M costs (P&T/Air Stripping) to destruction of contaminants in GW and soil matrix
- Evaluate effectiveness of low (<1 gpm) recirculation rate for approach using dextrose
- This was a continuous dextrose delivery system
Pilot Study Plan View – NuWay II Cleaners
NuWay II – Existing Remediation Enclosure
Recirculation System

1.0 GPM

Dextrose and Nutrients added (continuous)

P-1 → MW-3 → MW-2 → MW-15 → IN-1&2

SILT

silty-sandy GRAVEL

silty CLAY (aquitard)
NuWay Pre-Pilot VOC Concentrations
### Theoretical Calculate Carbohydrate Demand – NuWay II Cleaners

<table>
<thead>
<tr>
<th>Compound (Electron Acceptor)</th>
<th>Chemical Formula</th>
<th>Stoichiometry</th>
<th>Compound Concentration (mg/L)</th>
<th>Carbohydrate Demand (mg/L)</th>
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<tbody>
<tr>
<td><strong>Chlorinated Ethenes</strong></td>
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<tr>
<td>Tetrachloroethene</td>
<td>$\text{C}_2\text{Cl}_4$</td>
<td>$\text{C}_2\text{Cl}_4 + 8\text{e}^- + 4\text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 4\text{Cl}^-$</td>
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<td>Trichloroethene</td>
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<td>0.03</td>
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<td>Dichloroethene</td>
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<td>0.1</td>
<td>0.03</td>
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<td>Vinyl Chloride</td>
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<td><strong>Competing Electron Acceptors</strong></td>
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<tr>
<td>Oxygen</td>
<td>$\text{O}_2$</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$</td>
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<td>Nitrate</td>
<td>$\text{NO}_3^-$</td>
<td>$2\text{NO}_3^-$ + $12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$</td>
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<td>0.48</td>
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<td>Sulfate</td>
<td>$\text{SO}_4^{2-}$</td>
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<td>12.51</td>
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<td><strong>Inorganic Solids</strong></td>
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<tr>
<td>Iron</td>
<td>$\text{Fe}^{3+}$</td>
<td>$\text{FeOOH} + \text{e}^- + 3\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$</td>
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<td>0.85</td>
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<td>Manganese</td>
<td>$\text{Mn}^{4+}$</td>
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<td>1.73</td>
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<td><strong>Total Stoichiometric Carbohydrate Demand</strong></td>
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<td>19.53</td>
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Actual Carbohydrate (dextrose) Added

- Theoretical calculations indicated only 30 lbs. dextrose would be needed (did not pass the laugh test)
- Increased dextrose concentration until TOC values were over 100 mg/L
- 2 Pore volumes, 800 lbs dextrose, equals about 480 mg/L dextrose
- Highest TOC value we saw was 200 mg/L (about 10x theoretical needed)
- Dextrose metered in mostly continuously
Monitoring and Troubleshooting – NuWay Cleaners

- Complete dechlorination: PCE, TCE, DCE, VC and ethene
- Adequate food source: TOC analysis, increased feed rate
- Field parameters within range: pH, ORP, DO
- Competing electron receptors: DO, NO$^3-$, Mn$^{4+}$, Fe$^{3+}$ and SO$_4^{2-}$
- Excessive hydrogen production: Methane
- Healthy microbial population: Total heterotrophic bacteria
- Limiting nutrient for microbes: NH$_3$ and P

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>5 Months</th>
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<tr>
<td><strong>Chlorinated Solvents</strong></td>
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<tr>
<td>PCE and TCE</td>
<td>&gt;100 ug/L</td>
<td>&lt;10 ug/L</td>
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<tr>
<td>DCE and VC</td>
<td>&lt;10 ug/L</td>
<td>&gt;10 ug/L</td>
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<tr>
<td>Ethene/Ethane</td>
<td>&lt;1 ug/L</td>
<td>&lt;10 ug/L</td>
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<tr>
<td><strong>Substrate</strong></td>
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<tr>
<td>Total Organic Carbon</td>
<td>&lt;2 mg/L</td>
<td>60 mg/L</td>
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<td><strong>Field Parameters</strong></td>
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<tr>
<td>pH</td>
<td>6.6</td>
<td>6.5</td>
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<tr>
<td>ORP</td>
<td>90</td>
<td>-130</td>
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<tr>
<td><strong>Competing Electron Acceptors</strong></td>
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<tr>
<td>Dissolved Oxygen</td>
<td>2.0 mg/L</td>
<td>0.4 mg/L</td>
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<tr>
<td>Nitrate</td>
<td>0.7 mg/L</td>
<td>&lt;0.1 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>1.0 mg/L</td>
<td>3.7 mg/L</td>
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<tr>
<td>Manganese</td>
<td>2.5 mg/L</td>
<td>8.2 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>9.0 mg/L</td>
<td>&lt;1.0 mg/L</td>
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<td><strong>Hydrogen Sink</strong></td>
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<tr>
<td>Methane</td>
<td>&lt;10 ug/L</td>
<td>1.8 mg/L</td>
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<td><strong>Microbiology</strong></td>
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<tr>
<td>Total Heterotrophic Bacteria</td>
<td>1400 CFU/mL</td>
<td>130,000 CFU/mL</td>
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<td><strong>Limiting Nutrients</strong></td>
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<tr>
<td>Ammonia- Nitrogen</td>
<td>0.5 mg/L</td>
<td>7.9 mg/L</td>
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<tr>
<td>Orthophosphate</td>
<td>0.2 mg/L</td>
<td>8.3 mg/L</td>
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<tr>
<td>Poor Anaerobic Conditions</td>
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<tr>
<td>Marginal Anaerobic Conditions</td>
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<td></td>
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<tr>
<td>Optimum Anaerobic Conditions</td>
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</tbody>
</table>
MW-15s – NuWay II Cleaners

OBSERVATIONS:

- Day 150 system shut down
- PCE/TCE reduced within 30 days
- Cis-DCE stable up to Day 60, then decreased
- VC increased from Day 30 to 120, then rapidly decreased
- Ethene/ethane production correlates with VC generation and transformation
- No PCE/TCE rebound observed
OBSERVATIONS:

- PCE/TCE reduced within 65 days
- Cis-DCE stable up to Day 90, then decreased
- VC increased from Day 30 to 120, then decreased
- Ethene/ethane production correlates with VC
- No PCE/TCE rebound observed, but cis-DCE showing rebound possibly due to LNAPL (Stoddard) at this location
OBSERVATIONS:

- PCE/TCE reduced below detection limits
- Cis-DCE, VC, Ethene/ethane concentrations correlate
- No PCE/TCE rebound observed
- Continuing Activity 10 months after shutdown, likely due to biomass degradation
- Need additional injection point to better contact this location (not in primary flow path)
Pilot-scale Comments
NuWay II Cleaners

- Approach was effective with 1 gpm flow rate, and with using 1 extraction well and 2 pre-packed Geoprobe points spaced 15 ft apart
- Pilot test affected saturated zone far beyond the demonstration area
- Has continued to treat chlorinated solvents 11 months after recirculation ceased
- LNAPL recovery needs to be conducted at MW-2S to remove Stoddard solvent
- Need at least one additional extraction well, and two more injection points for full scale treatment
- Do not expect a rebound in the MW-15S or MW-2S area, but rebound around MW-3 likely since it wasn’t directly in the recirculation flow path
- Continuous electron donor delivery tended to cause fouling at injection points – pulsed delivery preferred to clear injection points
Plaza Cleaners
Sweet Home, Oregon
Plaza Cleaners - Background

- Active Cleaners 1971 to 2001
- Small “strip” shopping center
- PCE was primary solvent used
- No “known” releases
- Buildings demolished in 2001
- 2001 initial investigation found PCE in soil and groundwater
- Site currently level and planned for redevelopment
- Beneficial groundwater use in the area – no private wells currently impacted
Plaza Cleaners – Sweet Home
DEQ Objectives at Plaza Cleaners

- Take advantage of vacant “flat lot” site
- Room and time for focused soil and groundwater assessment and treatment
- Avoid indoor air problems in planned new building!
Plaza Cleaners Removal Assessment
October 2005 - SOIL

- Mobile Lab
- Geoprobe
- 2 days
- Soil and groundwater collected
- No Monitoring wells

Estimated Extent of PCE in Excess of Vapor Intrusion
RBC at 1.5 mg/kg
Plaza Cleaners Removal Assessment
October 2005 – GROUNDWATER
Plaza Cleaners Removal July 2006

- Source soil excavation to water table
- Install infrastructure for recirculation groundwater treatment
Plaza Cleaners Removal – July 2006

- Soil treated on-site w/ SVE Ex-Situ
- Currently in-progress
- Est. 6 months max
- Samples in October showed treatment nearly complete
- Delist soil using Contained In Rule
- Plan to re-use soil on-site
Full Scale Groundwater Remediation
Plaza Cleaners – Sweet Home, Oregon
Begun August 2006

- Full-scale ongoing (Started August 2006) to remediate source area using 6”-dia. Injection well, and 6”-dia. Extraction well
- Inject in piping installed in excavation
- High DO, high groundwater velocity
- All PCE, no co-mingled hydrocarbons
- Recirculating ISD system using dextrose and nutrients
- 6 month estimated timeframe to reduce CAHs by 80%
Groundwater Treatment Regime
Plaza Cleaners

- **Treatment Area** (200’ x 100’ x 25’ sat. thickness)
- **Operated at** 2 gpm
- **Est. 4,000 lbs dextrose to be added**
  - 50 lbs diammonium phosphate/100 lbs dextrose
  - 3 lbs yeast extract/100 lbs dextrose
- **Dextrose/nutrients added in batches weekly**
- **Groundwater pumping and recirculation is continuous**
  - Flushes well screen between batches and avoids fouling
Estimating Dextrose/Nutrient Demand
Plaza Cleaners – Sweet Home

- Estimate pore volume based on treatment zone dimensions (200’x100’x25’)
- Calculate demand by electron acceptors (PCE [5 mg/L], DO 7 mg/L, Nitrate 3mg/L, etc.)
- Calculate electron donor needed to overcome electron acceptors and multiply by factor of 10
- At Plaza, this equated to 4,800 lbs. Backed off to 4,000 initial estimate
- Past experience at NuWay of using straight stoichometric ratio 1:1 was not enough
- Adjust dextrose loading based on TOC analysis (empirical rather than theoretical approach)
## MW-1 (Midpoint)

<table>
<thead>
<tr>
<th>Date</th>
<th>PCE (ppb)</th>
<th>TCE (ppb)</th>
<th>cis-DCE (ppb)</th>
<th>VC (ppb)</th>
<th>Ethene/ethane (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/11/06 Baseline</td>
<td>3,000</td>
<td>170</td>
<td>38</td>
<td>&lt;0.2</td>
<td>NA</td>
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<tr>
<td>8/17/06 Day 6</td>
<td>556</td>
<td>1,040</td>
<td>1,540</td>
<td>&lt;0.2</td>
<td>NA</td>
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<tr>
<td>9/13/06 Day 30</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>14,000</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
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<tr>
<td>10/11/06 Day 58</td>
<td>2.0</td>
<td>&lt;1.0</td>
<td>12,000</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
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</tbody>
</table>

- Baseline data shows almost all PCE. Some dechlorination occurred after excavation, likely due to the excavation disturbing the organic layers at the smear zone.
- Over 30 days the PCE/TCE concentrations reduced to ND.
- High DCE concentration indicates significant desorption and microbial activity, beginning to decrease without production of VC (phenomenon has been observed by others) – (Adventus PE).
- If all PCE from baseline was converted to DCE, then it would generate approximately 1,745 ppb DCE. We have observed almost 10 fold this concentration.
MW-1 VOCs
## Extraction well EX-1

<table>
<thead>
<tr>
<th>Date</th>
<th>PCE (ppb)</th>
<th>TCE (ppb)</th>
<th>cis-DCE (ppb)</th>
<th>VC (ppb)</th>
<th>Ethene/ethane (ppb)</th>
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</thead>
<tbody>
<tr>
<td>8/11/06 Baseline</td>
<td>2,700</td>
<td>76</td>
<td>86</td>
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<tr>
<td>8/25/06 Day 14</td>
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<td>760</td>
<td>280</td>
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<td>9/13/06 Day 30</td>
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<td>59</td>
<td>24,000</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
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- Baseline data shows almost all PCE. PCE concentrations increased from Baseline to Day 30, then fell to 170 ppb. No buildup of TCE, rapid conversion to cis-DCE.
- DCE concentration began to breakthrough on Day 30, 10-fold increase by Day 58 showing significant desorption.
- Methane is already above 2 ppm, no VC generation yet.
- Expect next sampling event to show decrease in cis-DCE.
### Plaza Cleaners Groundwater Parameters

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sample Date</th>
<th>Field Parameters</th>
<th>Substrate</th>
<th>Competing Electron Acceptors</th>
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<tbody>
<tr>
<td></td>
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<td>Temp. (°C)</td>
<td>pH</td>
<td>Electrical Conductivity (µMHOs)</td>
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<td>10/11/2006</td>
<td>16.14</td>
<td>6.44</td>
<td>965</td>
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</table>

**Notes:**
1. Total Organic Carbon by EPA Method 415.1/5310C.
2. Nitrate and sulfate by EPA Method 300.0.
3. < = Not detected above the method reporting limit.
4. mg/L = milligram per Liter.
What Next?
Plaza Cleaners

- 4 More months of recirculation treatment planned
- Monitor transformation of CIS-DCE to ethene/ethane
  - Watch for cis “stall”
  - Watch for VC formation (should drop off rapidly)
  - Cis may go directly to ethene/ethane
- Watch for PCE/TCE rebound/desorption
- Bioaugment? Hopefully not. Dechlorination is occurring
Cost Estimate
Plaza Cleaners Groundwater

- Injection and Extraction Wells (sonic)
  - $14,000 (incl. Hart Crowser oversight)
- Infiltration Piping
  - $10,000
- Electron Donor (Dextrose blend) and ETEC O&M for 6 months
  - $18,000
- Hart Crowser Oversight and Monitoring (6 months) and Reporting
  - $34,000

- TOTAL EST. COST $76,000
Dextrose Groundwater Recirculation
Lessons Learned

• Easy to implement;
• Cost effective products;
• Improved success with re-circulation (extraction, amending, re-injection) over gravity feed/slug injections.
• Can mobilize (and treat) sorbed NAPL/source contaminants
• Limited to relatively permeable aquifer materials and shallow aquifers;
• Can destroy a lot of PCE quickly
• Should reduce CIS/VC based on pilot results at NuWay Cleaners
Questions