Cleanup of Small Dry Cleaner
Using Multiple Technologies:
Sages Dry Cleaner Site

NATO/CCMS Pilot Study Meeting, June 2006

Guy W. Sewell, Ph.D.
Professor of Environmental Health Sciences
Robert S. Kerr Endowed Chair
East Central University
## Site Size Issues

<table>
<thead>
<tr>
<th></th>
<th>Large</th>
<th>Small</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Type</td>
<td>Mixed</td>
<td>PH/CH</td>
</tr>
<tr>
<td>Access Issues</td>
<td>flexible</td>
<td>less</td>
</tr>
<tr>
<td>Boundary Issues</td>
<td>some</td>
<td>many</td>
</tr>
<tr>
<td>NA-applicable</td>
<td>yes</td>
<td>less likely</td>
</tr>
<tr>
<td>Ownership</td>
<td>Gov./Corp.</td>
<td>Private</td>
</tr>
<tr>
<td>Time Issues</td>
<td>Varies</td>
<td>Limited by economics</td>
</tr>
</tbody>
</table>

Small Urban Sites are more likely to require source zone treatment to meet remedial time limitations and coordinated remedial approaches to address both source zone and dissolved phase contaminants.
Field Evaluation of the Solvent Extraction Residual Biotreatment (SERB) Technology

Project Team

USEPA-NRMRL-SPRD-Ada
• Guy W. Sewell, PI, Biological Processes
• Lynn Wood, Physical Processes
• Susan Mravik, Site Coordinator
• Ann Keeley, Norma Duran (Lab Studies)

Site Contractor
• Levine-Fricke Recon

UF
• Mike Annable, PI Solvent Extraction

MSU
• James M. Tiedje, PI Microbial Ecology
• Shannon Flynn, Rebekah Helton, Frank Loeffler (Lab Studies)

Project Funding- SERDP(FIBRC-WES), EPA-TIO, State of Florida
OBJECTIVE

• Integrate Remediation Technologies into a Treatment Train for Comprehensive Site Restoration
• Target DNAPL Source Zone
• Decrease Remediation Costs

LIMITATIONS

• Geology
• Source Zone Delineation
• Time (?)
CONTAMINANT OF INTEREST:

Tetrachloroethene (PCE)

TECHNOLOGICAL BASIS:

Cosolvent Extraction (Ethanol)

Biodegradation
(Reductive Dechlorination)
Cosolvent Extraction

Injection Well
Ethanol Flush

90%+ Mass Removal

Recovery Well

GW Flow
Residual Contaminants

Restoration?, Risk Reduction?

PCE

Ethanol

Mixed

GW Flow
Bioremediation

FNA, Dissolution < Assimilative Capacity

Bioactive Zone

GW Flow
Why SERB (Source Control)

- Remove more mobile fraction of DNAPL, lower dissolved concentrations. Reduce time/distance needed to meet GW quality objectives.
- Activate reductive bio-transformations in high redox environments.
- Insure supply of e- donor, accelerate process and reduce uncertainty.
- Regulatory requirement.
Biotransformations for Chloroethenes

PCE → TCE

1,1-DCE → Vinyl Chloride

trans-DCE → Vinyl Chloride

cis-DCE → Vinyl Chloride

Vinyl Chloride → CO₂

Ethene → CO₂

Ethane → CO₂

Reductive Transformation

Oxidative Catabolism

No evidence but -ΔG

Some field evidence
ANAEROBIC OXIDATION-REDUCTION

**Electron Donors**
- Organic Compound
- EtOH, H$_2$
- Partially Oxidized Compound(s)
- acetate

**Electron Acceptors**
- NO$_3^-$
- SO$_4^{2-}$
- Fe$^{3+}$
- HCO$_3^-$
- R- Cl$_x$
- N$_2$(NH$_4^+$)
- H$_2$S
- Fe$^{2+}$
- CH$_4$
- R- Cl$_x$$_{-1}$

Reduced Electron Acceptors
SEWELL, ’95
## Chloroethene Sites

<table>
<thead>
<tr>
<th>Plume Type</th>
<th>Bio-attenuation</th>
<th>Stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent Dominant (PCE or TCE)</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>VC/cis DCE Dominant</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Ethene Forming</td>
<td>Yes</td>
<td>?</td>
</tr>
</tbody>
</table>
Field Test of the SERB Technology
*Sages Dry Cleaner Site*

Results and Discussion
## Field Test Table of Events

<table>
<thead>
<tr>
<th>Date</th>
<th>Event Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>July, 1998</td>
<td>Site Characterization, Ground Water Monitoring, &amp; Partitioning Tracer Test</td>
</tr>
<tr>
<td>Aug. 9-15, 1998</td>
<td>Ethanol Flush (9000 gallons)</td>
</tr>
<tr>
<td>Aug. 15, 1998</td>
<td>Partitioning Tracer Test</td>
</tr>
<tr>
<td></td>
<td>Start Hydraulic Containment</td>
</tr>
<tr>
<td>Aug. 25, 1998</td>
<td>End Hydraulic Containment</td>
</tr>
<tr>
<td></td>
<td>Ethanol &lt; 10,000 mg/L</td>
</tr>
</tbody>
</table>
Sage’s Dry Cleaner Site
Jacksonville, Florida

CONCRETE

SLAB

ASPHALT

DNAPL AREA
Pre-Cosolvent Flush Site Characterization

- Aerobic Conditions
- Low levels of daughter products (TCE)
- DNAPL contamination identified at 26 to 31 ft. bgs
Figure 1. PCE and ethanol concentrations during co-solvent flood at Sages Site in recovery well RW-001.
Cosolvent Flush Performance

Pre-Cosolvent Flush Partitioning Tracer 44.3 L (PCE)

Post-Cosolvent Flush Partitioning Tracer 13.9 L (PCE)

Estimated Recovery Based on Partitioning Tracer Tests 30.4 L (PCE) (70%)

Mass Recovery Based on PCE Concentrations in Recovery Wells 41.5 L (PCE)
Ethanol

350 mM = 16 g/L = 1.6 %

~1 Month Post-Flush

~2 Months Post-Flush

~3.5 Months Post-Flush

~5.5 Months Post-Flush
Ethanol

350 mM = 16 g/L = 1.6 %
Ethanol

1000 mM = 4.6 g/L = 0.46 %
Ethanol

1000 mM = 4.6 g/L = 0.46 %

~45 Months Post-Flush

~50 Months Post-Flush

~56 Months Post-Flush

~62 Months Post-Flush
PCE

500 uM = 83 mg/L
PCE

500 uM = 83 mg/L

~5.5 Months Post-Flush

~9.5 Months Post-Flush

~13.5 Months Post-Flush

~19 Months Post-Flush
PCE

500 uM = 83 mg/L

~22 Months Post-Flush

~25 Months Post-Flush

~28 Months Post-Flush

~31 Months Post-Flush
PCE

500 uM = 83 mg/L
TCE

100 μM = 13 mg/L

Pre-Ethanol Flush

~1 Month Post-Flush

~2 Months Post-Flush

~3.5 Months Post-Flush

100 μM
90 μM
80 μM
70 μM
60 μM
50 μM
40 μM
30 μM
20 μM
10 μM
0 μM
TCE

100 uM = 13 mg/L

~5.5 Months Post-Flush

~9.5 Months Post-Flush

~13.5 Months Post-Flush

~19 Months Post-Flush
TCE

100 uM = 13 mg/L
cis-DCE

175 uM = 17 mg/L

Pre-Ethanol Flush

~1 Month Post-Flush

~2 Months Post-Flush

~3.5 Months Post-Flush
cis-DCE

175 uM = 17 mg/L

~22 Months Post-Flush

~25 Months Post-Flush

~28 Months Post-Flush

~31 Months Post-Flush

Legend:
- 175 uM
- 150 uM
- 125 uM
- 100 uM
- 75 uM
- 50 uM
- 25 uM
- 0 uM
cis-DCE

175 uM = 17 mg/L

~50 Months Post-Flush
~56 Months Post-Flush
~62 Months Post-Flush
~65 Months Post-Flush
Vinyl Chloride

2.0 uM = 125 µg/L
Vinyl Chloride

2.0 uM = 125 ug/L

~42 Months Post-Flush

~45 Months Post-Flush

~50 Months Post-Flush

~56 Months Post-Flush
Vinyl Chloride

2.0 uM = 125 ug/L

~62 Months Post-Flush

~65 Months Post-Flush
Ethene

0.5 uM = 14 ug/L
Chloride

2250 μM = 80 mg/L

~50 Months Post-Flush

~56 Months Post-Flush

~62 Months Post-Flush

~65 Months Post-Flush
Acetic Acid

1600 uM = 96 mg/L
Sulfate

900 uM = 86 ug/L
Methane

1100 uM = 18 mg/L
Methane

1100 uM = 18 mg/L
SUMMARY

Solvent Extraction:
  41.5 L PCE Removed (Mass Recovery)
  ~70 % PCE Removed (Partitioning Tracer)

PCE Daughter Product Formation
  TCE, cis-DCE, VC, ethene, methane (?)

Change in Geochemistry
  Dissolved Oxygen, Sulfate, and Redox

Indications of Biological Activity
  Methane, Volatile Fatty Acid, and Hydrogen
Partial Oxidation of Ethanol:

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2 \]

Complete Oxidation of Ethanol:

\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6 \text{H}_2 \]

Dechlorination of PCE:

\[ \text{C}_2\text{Cl}_x + \text{H}_2 \rightarrow \text{C}_2\text{Cl}_{x-1} + \text{H}^+ + \text{Cl}^- \]

Complete Dechlorination of PCE Requires

1-2 Moles of Ethanol
(excluding competing processes)
Source Area = 40 ft. diameter \times 5 \text{ ft. depth}
Assume Porosity = 0.4
Pore Volume = 70,000 \text{ L}

**Concentrations:**
- Average Ethanol = 8,000 \text{ mg/L}
- Average PCE = 50,000 \text{ ug/L}

**Total Mass:**
- Ethanol - 570 \text{ Kg or 12,350 Moles}
- PCE - 3.6 \text{ Kg or 21.5 Moles}

Theoretically, we have >250 times the amount of ethanol present for complete dechlorination of the estimated remaining PCE.

38.8 times the amount needed to degrade the 157.1 moles of the (estimated) PCE in the source zone (136 moles residual PCE + 21.1 moles dissolved PCE). While this estimate assumes no competing terminal oxidation processes such as methanogenesis or sulfate reduction, an efficiency greater that 2% would still meet the theoretical demand.
cis-DCE Formation

\[ y = 52.7 \times \quad R^2 = 0.61 \]

\[ y = 10.3 \times \quad R^2 = 0.68 \]

\[ y = 1.1 \times \quad R^2 = 0.49 \]
### First Order Degradation Rates (Based on Total Mass)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Rate Constant ( \text{year}^{-1} )</th>
<th>( R^2 )</th>
<th>Half-Life ( t_{\frac{1}{2}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>-0.33 ( \text{year}^{-1} ) ( R^2 0.53 )</td>
<td>( t_{\frac{1}{2}} = 2.1 \text{ yrs} )</td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>-0.56 ( \text{year}^{-1} ) ( R^2 0.82 )</td>
<td>( t_{\frac{1}{2}} = 1.2 \text{ yrs} )</td>
<td></td>
</tr>
<tr>
<td>cis-DCE</td>
<td>0.81 ( \text{year}^{-1} ) ( R^2 0.82 )</td>
<td>( t_{\frac{1}{2}} = 0.9 \text{ yrs} )</td>
<td></td>
</tr>
</tbody>
</table>
• Currently the system remains biologically active and the dechlorination products are accumulating.

• High levels of dissolved methane and hydrogen have also been detected in the treatment zone.

• The maximum and minimum observed rate of dechlorination (based on cis-DCE production) are approximately 43.6 and 4.2 ug/liter/day, respectively.

• These rates can be extrapolated to a multi-step, concurrent, dechlorination process to predict that the dissolved phase PCE could be removed in 3 to 30 years, and that the total source zone PCE could be transformed in 24 to 240 years.

