Flux-Based DNAPL Site Remediation: Field Case Studies

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Flux-Based Characterization at ~30 Field Sites

• Federal Sites
  – Hill AFB; Patrick AFB; Dover AFB; Vandenberg AFB; Ft Lewis; Ft Devin; Indian Head; Port Hueneme; Paris Island; Cape Canaveral; Charleston; SRS; NASA

• Other Sites
  – Manufacturing Facilities in Indiana & Illinois
  – Dry Cleaner sites in Florida & Indiana

• International Sites
  – Borden CFB, Canada
  – Wales, UK
  – Australia (4 sites)
Four DNAPL Case Studies

• Three large sites, one small site
• Two source zones treated, one under consideration
• All sites had considerable archived data
• At all sites new flux measurements made, PFM deployments & Integral Pump Tests conducted
• We will examine:
  – Source & plume characterization
  – Source remediation performance assessment
  – Source & plume treatment options
  – Implications to long-term stewardship
Source Control Plane Fluxes

Unpublished Data: Do Not Cite or Distribute
Cross Section of Source Transect

Contaminant Fluxes are in mg/m²/day

Mass Discharge: ~ 38 kg/year

q = 1-2 cm/day

q = 3-6 cm/day

Unpublished Data: Do Not Cite or Distribute
DNAPL Plume Mass

- Plume mass ($M_p$) was estimated from integration of plume data (monitoring over 2002-2007 period)
- Most of the TriBE mass is found in the Intermediate aquifer
- Total mass of TriBE has stabilized at ~100-200 kg (additional mass in sorbed phase; $R=??$)
- Might be approaching “steady-state” conditions; stable plume??
- Need to consider mass of DBE, VB, Br.

Unpublished Data: Do Not Cite or Distribute

Patterson et al., EST 2006
Lessons Learned: DNAPL Site 1

• Source mass: ~1.5-3 mT? (500-1,000L?)
• Contaminant mass discharge from a small area of control plane
• Archived data integrated with flux data for an improved Conceptual Site Model
• Partitioning Inter-well Tracer Tests & Integral Pump Tests recently completed
• Aggressive source remediation & plume management planned
• Post-remediation monitoring to establish effectiveness & design long-term stewardship
**History**

TCE plume created due to activities associated with the production of detonators from the Second World to the 1970s

**Hydrogeology**

- Multiple interconnected aquifers
- 4 quaternary aquifers and three tertiary aquifers
- $v = 20 – 40$ m/yr
- Water table ~ 10 to 15 m bgs

**Plume Characterization**

- Plume monitored since 1996
- 1,500 m long, 300 m wide and 16 m deep

**Remedial activities to date**

Shallow excavation in source area

**Proposed Site Remediation**

- Chemical oxidation of source??
- Permeable Reactive Barrier??

**Remediation driven by:**

- Industrial redevelopment
- Flexible regulatory environment
- Cost constraints (passive vs aggressive)
TCE & Groundwater Flux Profiles: PFM Deployments

Source Transect Well
- Source Strength = 3 g/day (other sites: 100 – 400 g/day)
- Negative Correlation

Plume Transect Well
- Plume Strength = 6 g/day
- Positive Correlation
- No degradation

Basu et al., JCH 2008 (in review)
• Several small areas with conc >1500 ug/L
• Plume disconnecting from a depleted source zone
• Some shifts in plume shape
• Decrease in source mass discharge
Source Mass Estimation

Method A:

\[ M_{2006} = M_{1996} \exp(-10k) = \left( V_d A C_{t=1996} / k \right) \exp(-10k) \]

\[ M_{2006} = \text{present source mass} < 10 \text{ kg} \]

Method B:

\[ M_P = \int_0^t M_{D,0} \exp\left(-\frac{M_{D,0}}{M_0} t\right) dt = 2250 \text{kg} \]

\[ M_{D,t} = M_{D,0} \exp\left(-\frac{M_{D,0}}{M_0} t\right) = 1 \text{kg/year} \]

\[ M_0 = 2,260 \text{ kg} \]

\[ M_{D,0} = 170–365 \text{ kg/yr} \]

\[ M_{2006} \sim 10 \text{ kg} \]
Integration of Historic Data with Mass Flux Measurements

Proposed Remediation at Site: Chemical Oxidation of Source

Observations

1. Source strength small compared to other sites (3 g/day)
2. Flux data indicate negatively correlated source distribution – high concentrations in low flow regions
3. Mass discharge at source and plume control planes of similar magnitude: plume degradation rates ~ 0
4. Source concentrations are decaying and will attain irrigation standards in <10 years
5. Source mass <10 kg, Plume mass ~ 3800 kg

Interpretations

1. Source removal is not important at this site??
2. Source treatment maybe inefficient due to accessibility of isolated ‘hotspots’
3. Plume remediation or containment is vital
4. Source removal is not important?
5. Plume remediation more important than source

Recommendations:

1. No source removal is necessary
2. Plume treatment or containment maybe required
Ft Lewis, WA

- TCE source zone delineated (three major zones: NA1, NA2, NA3)
- Electrical Resistive Heating (TRS) of source zones
- Measured mass flux using Passive Flux Meters (PFMs) and Integral Pump Tests (IPTs) -- before and after source treatment at NA1 & NA3
NA1 Source Area

Flux Transect Wells
Hill AFB OU2

History
Created due to disposal of chlorinated solvents from degreasing operations during 1967 to 1975

Hydrogeology
- Shallow unconfined aquifer
- K ~ 2 m/day

Plume Characterization
- DNAPL pooled in the paleo-channel forming a source
- 900 m long, 150 m wide, and 10 m deep plume
Source Remediation Activities

- 40,600 gallons DNAPL recovered
- In 1996 containment wall constructed around the source area
- In 1997, additional DNAPL discovered in a depression in the clay surface, just north of the containment wall in Panel 5.
- Study initiated to investigate effects of mass removal on mass discharge
- SEAR resulted in TCE mass depletion 1,300-2,200 kg; >70% reduction??
Field studies indicate significant decrease in mass discharge from source zones after DNAPL mass removal.

**Ft Lewis Thermal Remediation**

- Flux reduction >98%

**Hill AFB Surfactant Remediation**

- Flux reduction >90%

*Brooks et al. JCH In review*
## DNAPL Mass Depletion: Ft Lewis EGDY Thermal

### Area 1

<table>
<thead>
<tr>
<th>TCE (Kg)</th>
<th>c-DCE (Kg)</th>
<th>TPH (Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Mass Removed</td>
<td>2,580</td>
<td>410</td>
</tr>
</tbody>
</table>

### Area 2

<table>
<thead>
<tr>
<th>TCE (Kg)</th>
<th>c-DCE (Kg)</th>
<th>TPH (Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Mass Removed</td>
<td>1,090</td>
<td>250</td>
</tr>
</tbody>
</table>

### Area 3

<table>
<thead>
<tr>
<th>TCE (Kg)</th>
<th>c-DCE (Kg)</th>
<th>TPH (Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Mass Removed</td>
<td>840</td>
<td>280</td>
</tr>
</tbody>
</table>

**Notes:**
- Numbers provided in table are rounded.
- NA2 configuration changed; all estimates based on revised configuration.
- Total mass removal estimates based on stoichiometric means.
- Thermal treatment objective to maximize CVOC (TCE, cis-DCE) removal, not TPH removal.

*USACE, 2007 Draft Report*
Fort Lewis EGDY NA1

TCE Flux

(mg/cm²/hr)

13 23 33
(Feet bgs)

LC-213 •
LC-212 •
LC-211 •
LC-207 •
LC-206 •
LC-205 •
LC-204 •
LC-203 •
LC-202 •
LC-201 •

USACE, 2007 Draft Report

Pre-Remediation
(Baseline GW Data)
Fort Lewis EGDY NA1

TCE Flux

Thermal Treatment Cost ≈ $6M; Flux cost ≈ 2%

USACE, 2007 Draft Report
Lessons Learned: Ft Lewis EGDY

- Detailed site characterizations required to locate and delineate sources (cost & level of effort?)
- Initial NAPL mass estimates; later revised with additional analysis & interpretation.
- Thermal treatment of NA1, NA2, NA3
- ~2,600 kg TCE recovered during thermal treatment (~70% reduction)
- GW fluxes are large (q ~ 25 cm/day)
- **Thermal treatment reduced (>95%) TCE & DCE mass discharge**
- Flux distributions across NA1 source control plane show small area contributed most of mass discharge
- **How would the source remediation decisions have changed if the flux distribution data were used?**
Lesson Learned: Hill AFB OU2

- TCE Mass discharge estimates using three methods are in agreement.
- TCE mass discharge is across a fraction of the source control plane.
- Source treatment (SEAR) resulted in TCE mass depletion (1,300-2,200 kg removed; ~70% reduction) and an associated decrease (>90%) in TCE mass discharge.
- Increase in DCE mass discharge suggests increased biodegradation after SEAR.
- How does the source treatment influence plume evolution?
# DNAPL Site Attributes

## SITE PARAMETERS

<table>
<thead>
<tr>
<th>Site Hydrogeology</th>
<th>Northwest US</th>
<th>Midwest US</th>
<th>Oz-1</th>
<th>Oz-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater Flux, $q$ (cm/day)</td>
<td>30</td>
<td>10 (6 &amp; 40)</td>
<td>2.5 (1 &amp; 13)</td>
<td>5 (3 &amp; 20)</td>
</tr>
</tbody>
</table>

## Current Source

| Mass, $m_0$ (kg) | ~5,000 | ?? | <100 | ~2,500 |
| Max. Conc., $C_{max}$ (mg/L) | ~10 | 70 | ~5 | ~150 |
| Mass Discharge, $M_D$ (g/day) | ~800 | ~300 | ~3 | ~100 |
| Depletion Rate Constant, $\alpha$ (yr$^{-1}$), $\alpha = \frac{q A_{cp} C_0}{M_0}$ | 0.2 | 0? | 0.4 | ~0.1 |
| Control Plane, $A_{cp}$ (m$^2$) | 70x12 = 840 | 10x5 = 50 | 25x15 = 375 | 30 x 10 = 300 |

## Current Plume

| Dimensions (m x m x m) | 5,000x500x50 | 500x120x15 | 1500x40x11 | 250x50x15 |
| Mass, $M_p$ (kg) | ~10,000 | ~1,000 | ~3,800 | ~500 |
| Avg. Deg Rate Constant, $k$ (yr$^{-1}$) | ~0?? | ~1 | 0 | ~1 |

## Site Management

<table>
<thead>
<tr>
<th>Source Remediation</th>
<th>ERH (99%+)</th>
<th>ChemOx?</th>
<th>None?</th>
<th>Flushing?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plume Remediation Recommendation</td>
<td>P&amp;T</td>
<td>None?</td>
<td>None?</td>
<td>P&amp;T</td>
</tr>
</tbody>
</table>
REMChlor Simulations of Management Options

SITE 1
- Plume shrinks at both ends
- Both cases 90% mass depletion

SITE 2
- Plume marches on at leading edge
- Total Chlorinated Solvents t=now

Control Plane

SITE 1
- Compliance Boundary
- TCE (ug/L)
- x (m)
- y (m)
- x (m)
- y (m)
- Compliance Boundary

SITE 2
- Compliance Boundary
- Total Chlorinated Solvents t=now
- x (m)
- y (m)
- x (m)
- y (m)

Control Plane

Both cases 90% mass depletion
What Guides Remediation Choices?

1. Remedial Objectives
   - Compliance boundary (“everywhere” or at specified POC?)
   - Performance Metrics:
     - concentration or flux?
     - Mass depletion & residual mass
   - Source and/or plume?

2. Remediation timeframe
   - Short-term responses
   - Long-term site stewardship

3. Site Characteristics
   - Source strength and longevity
   - Degradation rates in the plume
## Source Remediation Options?

<table>
<thead>
<tr>
<th>options</th>
<th>Stable ( M_D(t) = \lambda(t) )</th>
<th>Advancing ( M_D(t) &gt; \lambda(t) )</th>
<th>Shrinking ( M_D(t) &lt; \lambda(t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. No remediation</td>
<td>( M_D(t) ) decreases over time (exponential?); so, if ( \lambda(t) ) is constant (?), eventually all plumes start shrinking--** requires long term stewardship for at least a century</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Reduce source mass through some aggressive source depletion action (e.g., flushing, chem ox, thermal, etc) ( M_D(t) \downarrow )</td>
<td>Plume “pinched off” at the head; tail starts shrinking when reduced ( M_D ) reaches it</td>
<td>Plume “pinched off” at the head but tail continues to move forward – split plumes?</td>
<td>Plume shrinks inwards from both ends</td>
</tr>
<tr>
<td>3. Reduced Source Flux as in the case of n-ZVI or enhanced bio</td>
<td>Plume response similar to 2; but, since the source mass hasn't been reduced, the source treatment has to be maintained for a very long time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Integrated &quot;Treatment Train&quot; Approach: (2) + (3) ( \rightarrow ) Implement &quot;aggressive&quot; short-term action to deplete most of the source mass (say, ~80%?), and then use the &quot;passive&quot; source treatment (nZVI or eZVI) to sustain essentially zero source flux, or a low-grade “chaser” of say chem ox</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary Comments

• Groundwater & contaminant flux characterization at DNAPL source control planes provides critical information needed in source remedy selection and performance assessment.

• “Source Strength” can be used to compare sites, and the required source strength reduction through mass depletion can be determined based on likely plume response.

• Regulatory framework and policy guidance lacking for adoption.
Discussion Items

- How much longer will we debate the benefits/limitations of partial mass removal for DNAPL source zones?
- If “MCL everywhere” can’t really be achieved “at reasonable cost and in reasonable time,” what are the alternatives for site remediation?
- If some DNAPL mass is left behind in the source zone, what are the implications to site stewardship (costs, risks, liabilities, etc)?
- How do short-term discounting procedures influence site remediation decisions at government & corporate sites?
Questions?