State of the Art in Developing Conceptual Site Models for DNAPL Groundwater Plumes

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Building a DNAPL Conceptual Site Model

- DNAPL Sites are some of the most difficult sites to understand.

- **Goal**: Build a CSM with sufficient depth and clarity so that risks can be accurately assessed and appropriate remediation strategies developed.
DNAPL—Chemical Phases and Transport

- DNAPL movement and capillary forces
- Chemical phase distribution
- Interphase chemical mass transfer
- Dissolved plume formation & transport
- Vapor migration

Generalized DNAPL Release and Transport

Dissolved Plume

Degradation Reactions

Sorption, etc.

Vapor

DNAPL Pore-Scale Distribution

Sand Grains

Water

Interphase Chemical Mass Transfer

DNAPL

Aqueous

Vapor

Sorbed

(Modified from Parker et al., 2002)
DNAPL Plume Mapping

Understanding your DNAPL plume
**DNAPL Plume Life Cycle**

- **Expanding Phase**
  - Early Stage

- **Stable Phase**
  - Middle Stage

- **Shrinking Phase**
  - Late Stage
“Toolbox Approach”

- High Resolution
- Multiple lines of evidence
- Screening tools contaminant mass
- High Resolution Hydraulic Conductivity Profiling
- Soil coring and sampling in high resolution
- On site groundwater and soil analyses by Mobile Lab (GC/MS)
- Modeling tools
DNAPL Characterization Tools

- Intrastate Technology Regulatory Council
- DNAPL Site Characterization Tools Table
  - Guidance document:
    Integrated DNAPL Site Characterization and Tools Selection (ISC-1, 2015)
  - May 5, 2016 (Thursday) 1:00 PM - 3:15 PM EASTERN TIME
  - Contains over 100 tools
  - Sorted by:
    - Characterization objective
      - Geology
      - Hydrogeology
      - Chemistry
    - Effectiveness in media
      - Unconsolidated/Bedrock
      - Unsaturated/Saturated
  - Ranked by data quality
    - Quantitative
    - Semi-quantitative
    - Qualitative

<table>
<thead>
<tr>
<th>Tool</th>
<th>Data Quality</th>
<th>Subsurface</th>
<th>Zone</th>
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<td>Q - GL</td>
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Case Study: Define Treatment Zones

- PCE DNAPL Dump in Creek Bed.
- Thermal Treatment for DNAPL Removal
- Bioremediation for High Concentration Plume
- Need to Define Treatment Zones
DNAPL Delineation

- 38 MiHPT Borings
  - 7 angled borings
- 14 Confirmation Soil Borings
- Groundwater transect with 5 borings for temporary grab groundwater samples.
Real-Time Data

- ECD/XSD - PCE
- PID/FID - gross detectors for volatiles
- EC - lithology
- HPT - conductivity estimate
- Soil logging and sampling
Geologic Framework

Low Permeability Unit Prevented Vertical DNAPL Migration
Distribution of Soil Mass

Notes:
Visualization of PCE extent was kriged in Ctech’s MVS. The outline of PCE above 10 mg/kg is a 2D maximum extent for each geologic unit created from the 3D volume. Vertical exaggeration for 3D view is 5X.

Legend
Krige d 2D Maximum - PCE
- 10 - 100 mg/kg
- 100 - 500 mg/kg
- 500 - 1,000 mg/kg
- 1,000 - 5,000 mg/kg
- > 5,000 mg/kg

Geologic Interpretation
- Qal - Quaternary Alluvium
- Qapo[h] - Outwash 1
- Qapo[h] - Till
- Qapo[h] - Advance Outwash Sand
- Qapo[h] - Outwash 2
- 3D Display Extent
Refined Treatment Zones

Expanded thermal treatment zone laterally but reduced the vertical treatment interval from 15 m to 8 m - reduced volume by 30%.
DNAPL Attenuation Framework
Understanding Degradation of DNAPL Plumes
Biodegradation: Basics

Basic Metabolism

Electron Acceptor + Electron Donor → Electron Acceptor + Electron Donor + Energy

Aerobic/Anaerobic Oxidation

Electron Acceptor

O₂, NO₃⁻, etc.

Electron Donor

DCE, DCA, DCM, VC, CA, CM

Cometabolism

Electron Acceptor + Electron Donor → Electron Acceptor + Electron Donor + Energy

Halorespiration

Electron Acceptor

Chlorinated Solvents

Electron Donor

Food (Organic Compound)
### Biotic Attenuation Mechanisms Over Plume Extent

#### Key Processes
- **Aerobic Oxidation**
- **Aerobic Cometabolism**
- **Anaerobic Oxidation**
- **Anaerobic Reductive Dechlorination**
- **Anaerobic Cometabolism**

#### Chlorinated Ethenes
- **DCE, VC**
- **TCE, DCE, VC**
- **DCE, VC**
- **PCE, TCE, DCE, VC**
- **PCE, TCE, DCE, VC**

#### Chlorinated Ethanes
- **DCA, CA**
- **TCA, DCA, CA**
- **HCA, PCA, TeCA, TCA, DCA, CA**
- **HCA, PCA, TeCA, TCA, DCA, CA**
- **HCA, PCA, TeCA, TCA, DCA, CA**

#### Chlorinated Methanes
- **DCM, CM**
- **CF, DCM, CM**
- **DCM, CM**
- **CT, CF, DCM, CM**
- **CT, CF, DCM, CM**

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Abiotic Degradation Processes

Four ways to look for Abiotic Degradation potential:

1. Abiotic dechlorination daughter products in groundwater
2. Ferrous Iron content of rock/soils
3. Magnetic Susceptibility (indicator of magnetite)
4. Laboratory dechlorination studies
Summary

- Many degradation mechanisms may concurrently aid remediation of chlorinated solvents at a site.

- Some “unconventional” processes may be significant contributors to remediation progress but are not yet widely recognized.

Next we’ll talk about the expanded suite of tools to evaluate this expanded set of biotic pathways.
Introduction to Molecular Biological Tools

- Measure sub-cellular molecules such as DNA, RNA, enzymes, lipids
- Variety of matrices
- Becoming standard component of biotic-process monitoring
Case Study: Verifying Degradation and DNAPL Plume Control

Plume (3 µg/L) - defined by wells of multiple strata

Former Underground Storage Tank Area Stored Dichloromethane (DCM) DNAPL

Day Care Center

Property line
## Advanced Characterization Tools to Develop CSM

<table>
<thead>
<tr>
<th>Informational Need</th>
<th>Characterization Tool</th>
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<tbody>
<tr>
<td>Evaluate Secondary Source-Contaminant Diffusion in Rock Matrix</td>
<td>Rock core analysis and diffusion modeling</td>
</tr>
<tr>
<td>Evaluate Contaminant Flux and Groundwater Flux in Transmissive Fracture Zones</td>
<td>Passive Flux Meter (PFM) and Hydraulic and Contaminant Transport Modeling</td>
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<tr>
<td>Evaluate Contaminant Biodegradation in the Source and Plume</td>
<td>Compound Specific Isotope Analysis (CSIA)</td>
</tr>
<tr>
<td>Evaluate Contaminant Biodegradation in the Source and Plume</td>
<td>Microbial Metagenomics</td>
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</table>
Compound Specific Isotopic Analysis (CSIA)

1. Carbon (C$^{13}$/C$^{12}$) Isotopes-8 wells
2. Chlorine (Cl$^{37}$/Cl$^{35}$) Isotopes-4 wells
3. Used Rayleigh model to evaluate:
   • \( \delta^{13}C = \ln(C/C_0) \times \varepsilon + \delta^{13}C_0 \)
4. Rayleigh type fractionation
   • DCM decreases, C$^{13}$ and Cl$^{37}$ ratios increased
   • Biotic and abiotic degradation
5. Degradation mechanisms in literature:
   • \( S_N^2 \) –type reaction (Methylothroph)
   • Cometabolic oxidation
   • Reductive dehalogenation
6. Data most consistent with \( S_N^2 \)
DCM-Degrading Bacteria

1. Molecular tools documented high degradation of DCM DNAPL source and plume.

2. Populations degrading DCM at the source were different than in the plume.

3. Key lines of evidence to getting acceptance of a remedy that includes TI waiver for the source and MNA for the plume.
So What Should We Be Doing?

- Consider biotic and abiotic attenuation processes in high & low transmissivity zones
- Consider the complex biotic degradation mechanisms that might occur over the range of site biogeochemical conditions
- Use a combination of MBTs, laboratory testing, and CSIA to verify and quantify degradation mechanisms and rates
- Remember – even “slow” rates of degradation can be important
- Assess these potential degradation mechanisms early in the process
Summary

- Source-Plume response is complex and evaluation of primary and secondary sources is essential for predicting treatment response.
- Engineering designs need to account for both geologic heterogeneity and chemical mass storage.
- New tools can provide important resolution to CSM.
- New diagnostic tools can now elucidate degradation of contaminants in complex geochemical environments.
Questions?