Recent Advances in the Management and Remediation of DNAPL Source Zones

Presented by

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Chuck Newell
Tom Sale
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Westfield, MA
9 April 2008
DoD’s Environmental Technology Programs

Demonstration/Validation  Basic and Applied Research
Environmental Drivers: Sustainability of Ranges and Range Operations

Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

Unexploded Ordnance

Urban Growth & Encroachment

Noise NOX and PM
Environmental Drivers:
Reduction of Current and Future Liability

Current Liabilities
Contamination from Past Practices
- Chlorinated Solvents
- UXO
- Emerging Contaminants (Perchlorate)

Future Liabilities
Control Life Cycle Costs
- Elimination of Hazardous Materials
- Achieve Compliance Through Pollution Prevention
Scales of Research

ESTCP

SERDP

- Small rxn vessels
- Columns, microcosms
- Tanks, large reactors
- Test cells, controlled field sites
- Field sites
SERDP and ESTCP Pillars

- Sustainable Infrastructure
- Munitions Management
- Environmental Restoration
- Weapon / Platform Management

- Natural Resource Management
- UXO Remediation
- Facilities Management
- Range Clearance
- Contaminated Soils
- Contaminated Sediments
- Contaminated Water
- Manufacture & Maintenance
- Green Energetics
- Emissions
- Effects
Environmental Restoration Program Characteristics

- ~200 active projects
- Projects range from $85K to 2.5M/year, average size is $400K/year
- 95% of projects are partnered
- Project length runs 1 to 5 years
- Turn over roughly 25% of the program each year
Environmental Restoration Research Focus Areas

- Chlorinated Solvents
  - Dissolved Phase
  - DNAPL Source Zones
    - ISCO
    - Thermal
    - Bioremediation
    - Fractured rock
- Munitions Constituents
  - Perchlorate
  - Energetics
  - Heavy Metals
- Sediments
- Risk Assessment
- Range Sustainability
- Site Characterization and Monitoring
- Performance Assessment & Optimization
Chlorinated Solvent Workshop

Dissolved Phase

Chlorinated Solvents

Passive Treatment Technologies (FY99)

Anaerobic/Aerobic Biodegradation of cis-DCE/VC

Long-Term Sustainability of MNA

Abiotic Processes

cis-DCE/VC Degradation Mechanisms & Environmental Relevance

Passive Treatment Technologies (FY96)

Enhanced Biological Technologies (FY97)

Physical/Chemical Technologies (FY98)

FY99 FY00 FY01 FY03 FY04 FY06 FY07
Perchlorate RDT&E

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- **SERDP**: Orange
- **ESTCP**: Purple
- **AWWARF**: Dark Blue

10
Metals

S&T

Bioavailability & Long-Term Stability

Fate & Impact of Cu & Zn

Sequestration Enhancement & Engineered Bioavailability Reduction

Groundwater Remediation

Dem/Val

Site Characterization

Soil Remediation

Fate & Impact of Cu & Zn

FY00 FY01 FY02 FY03 FY04 FY05 FY06
Energetic Compounds

- Distribution & Fate
  - FY00 SON
- Microbial Degradation Pathways
  - FY01 SON
- Source Zone Remediation
- Groundwater Remediation
- Containment/Treatment Source Zones (fundamental phytoremediation)
- Bioremediation Technologies
- Containment/Treatment Source Zones (applied phyto)
- MNA (FY95 start)
- Biological Treatment of Groundwater
- Source Containment/Mitigation
- Sampling & Assessment

S&T

Dem/Val

FY01 FY02 FY03 FY04 FY05 FY06 FY07 FY08
Home page contains fact sheets for every project funded, as well as all published documents.
Sponsored by SERDP and ESTCP

Partners in Environmental Technology
Technical Symposium and Workshop

December 2-4, 2008

Marriott Wardman Park Hotel, Washington, D.C.

Short Courses
- Decision Guide for Management of Chlorinated Solvents
- In Situ Chemical Oxidation
- Introduction to Discrimination of Military Munitions
- In Situ Bioremediation of Perchlorate
- Monitored Natural Recovery of Contaminated Sediments
- State of the Art in Capping and Amendments for Contaminated Sediments
Home page contains fact sheets for every project funded, as well as all published documents.

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DNAPL Short Course
Chlorinated Solvents: A Major DoD Liability

- Chlorinated solvents at approx. 80% of Superfund sites w/ groundwater contamination
- More than 3,000 DoD sites in the United States
- DoD may spend > $100 million annually for hydraulic containment at these sites
- Estimates of DoD life-cycle costs > $2 billion.
• **Major Focus Area**
  – Ca. 15% of Cumulative Funding: ’97 - ’07

• **R&D Priorities from ’01 Workshop**
  – Focus more on DNAPL, Less on Dissolved
  – Evaluate Thermal, ISB, and ISCO/ISCR
  – Improve Delivery Methods
  – Quantify Benefits of Source Depletion
  – Improve Decision Support / Diagnostic Tools
Ongoing Initiatives Related to DNAPL Source Zones

- Understanding Sources & Plume Response
- Fractured Rock Site Remediation
- In Situ Thermal Treatment
- In Situ Chemical Oxidation
- Nanoscale Iron
- In Situ Bioremediation
- Site Characterization and Monitoring
- Technology Performance Evaluation & Prediction
R&D Needs: 2006 Workshop

Better Understanding of Plume Response

How To Treat the “Advectively Challenged”

Vapor Transport From Sources

How to Remediate Karst & Complex Sites
SERDP DNAPL Initiative Goals

• Help managers make *best-informed* decisions possible
• Improve predictive capabilities, decision support, and fundamental understanding
• Help develop and validate innovative technologies to improve DNAPL treatment
• Primary drivers:
  – Reduce life-cycle costs
  – Meet schedules for remedies-in-place
• **NOT to promote any technology or any agenda to treat or not treat sources**
• **RIP-tide of source treatment is coming – need to be prepared**
1. Assess Source Zone Treatment Technologies
   - Large-tank tests of ISCO, bio, and thermal
   - Field-scale tests of ISCO, bio, and thermal
   - Models of performance and uncertainty
   - Data mining to document costs and performance
   - Up-scaling mass transfer coefficients
2. Quantify Benefits of Source Depletion
   – Laboratory and field assessments of flux before and after treatments
   – Flux measurements after full-scale treatment
   – Experimental and modeling assessments of source depletion benefits
3. Improve Delivery
   – Nanoscale iron delivery
   – Partitioning electron donors
   – Mobility control methods to enhance sweep efficiency
4. Improve Decision Support
   – Remedy Selection Guidance
   – Optimizing DNAPL source and plume remediation
   – Estimating cleanup times
   – DNAPL Remediation Screening Tool
   – Diagnostic tools
Key Concepts

• **Mass Flux Can Improve Decision-Making**
  – To select, design & assess remediation

• **Understand Mass Storage Compartments**
  – Varying responses to remediation approaches
  – Plume storage and degradation affect source decisions

• **Set Realistic Goals**
  – 90-99.99% source removal, 90-99% plume decrease
  – 1st order rate of restoration – long “tail”

• **Uncertainty is Inevitable**
  – Apply the observational approach

• **“Remedy Packages” Are Needed**
  – Functional objectives for each element
Half Full or Half Empty?
The hydraulic balance
Half Full or Half Empty?
The hydraulic balance

1. Technology has made impressive advances
   - A suite of demonstrated technologies and combinations
   - MCLs are achievable in some cases
   - We can significantly decrease plume extent, longevity, and liability

2. There are serious “practicable” limits
   - Given unlimited resources, we could clean up all DNAPL sites
   - Resources are limited
   - Uncertainty is high

When do benefits justify costs?
You Gotta Know Your Limits
“Trust your passions less, your reasons more, and your limits most”

Daniel Robinson, Oxford University
From NPR Interview: "The Philosophy of Choosing Between Bad Options"
FAQs and Decision Guide for Chlorinated Solvents Releases

Tom Sale, Chuck Newell, Hans Stroo, Rob Hinchee, and Paul Johnson
Highlight current knowledge in support of sound decision for releases of chlorinated solvents

Better use of resources

Better environment
• Parties participating in the process of selecting remedies for chlorinated solvent releases
  – DoD staff,
  – Consultants,
  – Industry
  – Regulators, and
  – Community Representatives
  – ...............
Two-Part Format

• FAQs - Frequently Asked Questions Regarding the Management of Chlorinated Solvents in Soils and Groundwater

• Decision Guide - Guide for Selecting Remedies for Chlorinated Solvents in Soils and Groundwater
Format

- **Entry Level** - The FAQ and Decision Guide Executive Summary provide quick access to key concepts and references.

- **Middle Level** - The Decision Guide highlights new developments re site specific conditions, developing attainable and beneficial goals, selecting technologies, and packaging site remedies.

- **Top Level** - The documents refer users to more comprehensive knowledge by highlighting knowledge available through ESTCP, SERDP, and other relevant programs.
FAQs – a one hour read

DRAFT
Frequently Asked Questions Regarding the Management of Chlorinated Solvents in Soils and Groundwater

November 2007
Tom Sale, Charles Newell, Hans Stroo, Robert Hinchee, and Paul Johnson
1. What is the Problem?

...chlorinated solvents are central to modern life

...flawed practice was largely a reflection of not clearly understanding

...managing the legacy of our past practices

...direct exposure pathways largely addressed ...

...technical challenges make it very difficult or impossible to completely clean up these...

...stakeholders face difficult decisions...

...the science and engineering on which remediation practice is based has improved dramatically...

...we can be more successful in the future than we have been in the past
2. What are chlorinated solvents and why are they of concern?

<table>
<thead>
<tr>
<th>Attributes</th>
<th>Industrial Values</th>
<th>Environmental Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile</td>
<td>Good for cleaning</td>
<td>Readily form vapor plumes in soils</td>
</tr>
<tr>
<td>Chemically stable under typical aerobic conditions</td>
<td>Easy to store</td>
<td>Often slow to degrade in aerobic soils and groundwater systems</td>
</tr>
<tr>
<td>Non-flammable</td>
<td>Safe from a fire and explosion hazard perspective</td>
<td>Stable under natural aerobic conditions</td>
</tr>
<tr>
<td>Slightly soluble in water</td>
<td>Remains in a separate liquid phase when mixed with water (immiscible)</td>
<td>Small releases can contaminate large amounts of water and persist as sources for long periods of time</td>
</tr>
<tr>
<td>Densities much greater than water</td>
<td>Easy to separate from water</td>
<td>Can sink through water-saturated media (e.g., aquifers and aquitards), contaminating water deep underground</td>
</tr>
<tr>
<td>Low viscosity</td>
<td>Easy to apply to surfaces</td>
<td>Can move quickly through porous media</td>
</tr>
</tbody>
</table>
3. What happens when chlorinated solvents are released into the subsurface?
3. What happens when chlorinated solvents are released into the subsurface? (cont’d)

MIDDLE STAGE

Vapor Plume

Matrix Storage
(Dissolved and sorbed phases in low flow zones)

Groundwater Plumes

CLAY

SAND

DNAPL

FRACTURED SEDIMENTARY ROCK
3. What happens when chlorinated solvents are released into the subsurface? (cont’d)
3. What happens when chlorinated solvents are released into the subsurface? (cont’d)

14 subsurface compartments potentially containing chlorinated solvents

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<th>Source</th>
<th>Plume</th>
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<tr>
<td></td>
<td>Transmissive</td>
</tr>
<tr>
<td>DNAPL</td>
<td>✓</td>
</tr>
<tr>
<td>Aqueous</td>
<td>✓</td>
</tr>
<tr>
<td>Sorbed</td>
<td>✓</td>
</tr>
<tr>
<td>Vapor</td>
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*DNAPL is absent in plumes by per NRC 2005*
4. What is a chlorinated solvent “source zone”?

National Research Council report (NRC, 2005) defines a chlorinated solvent source zone as:

- … a subsurface reservoir that sustains a plume (primarily dissolved groundwater plumes…

- … the DNAPL-containing region is initially the primary reservoir… also includes high concentration dissolved- and sorbed-phase halos about the DNAPL-containing region…

- … acknowledges that some chlorinated source zones are depleted of DNAPL, and that the high-concentration halo can be a reservoir that sustains plumes.
5. Why do we keep finding new challenges?
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Dissolved solvent plumes in transmissive zones (1970 - 1980s)
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- Dissolved solvent plumes in transmissive zones (1970 - 1980s)
- Plus DNAPL in transmissive and low permeability zones (1990s)
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- **Plus** DNAPL in transmissive and low permeability zones (1990s)
- **Plus** dissolved and sorbed phases in low permeability zones in source zones (mid 2000s)
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**Plus** DNAPL in transmissive and low permeability zones (1990s)

**Plus** dissolved and sorbed phases in low permeability zones in source zones (mid 2000s)

**Plus** vapor plumes and intrusion into buildings (mid 2000s)
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- **Plus** DNAPL in transmissive and low permeability zones (1990s)
- **Plus** dissolved and sorbed phases in low permeability zones in source zones (mid 2000s)
- **Plus** vapor plumes and intrusion into buildings (mid 2000s)
- **Plus** dissolved and sorbed phases in low permeability zones in plumes and sorbed phase in transmissive zones in plumes (currently emerging)
6. Why is it common for source delineation efforts to miss a portion of a source?

... heterogeneous distributions of DNAPL and other contaminant phases

... common reliance on groundwater data collected from large screen intervals in transmissive zones

... at older release sites, DNAPL may have dissolved away (we are not looking for the right thing)

... difficult to resolve where the source ends and the plume begins

... decisions are often made using a limited dataset

... characterization can be de-emphasized in the rush to...

Source Delineation is Difficult
7. Why is it difficult to clean up aquifers by pumping out the contaminated groundwater?

The National Research Council’s 1994 report on groundwater clean-up alternatives concluded: “Remediation by pump-and-treat processes is a slow process. Simple calculations for a variety of typical situations show that predicted clean-up times range from a few years to tens, hundreds, or even thousands of years.”

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8. Why are contaminants in low permeability zones important?

Abrupt contacts between transmissive zones (e.g., sand) and comparatively stagnant low permeability zones (e.g., clay) are common in geologic media.
3.2 – Parameters Required for Each Model

Comparison of Lab versus Model Effluent Concentrations

- Fluorescein
- Bromide
- Model

Parameters Required for Each Model:
- Fluorescein: 0.1, 0.001, 0.0001
- Bromide: 0.00001
- Model:
  - C/Co: 0, 0.00001, 0.0001, 0.001, 0.01, 1, 10
  - Time (days): 0, 20, 40, 60, 80, 100, 120

Graph showing the comparison of lab versus model effluent concentrations over time.
9. Why are contaminants in the vadose zone important?

**Vadose Zone as SOURCE**
- Source compartments from 14 compartment model
- Most but not all sites dominated by saturated zone sources
- SVE: soil moisture key performance factor

**Vadose Zone as PATHWAY**
- Indoor air pathway - empirical studies and model development
- Confirming impacts difficult
- ESTCP and SERDP projects
9. Why are contaminants in the vadose zone important? (II)
10. What have we learned in the last half century?

Paradigm shifts of the last half century

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<th>New School Paradigm (Time of broad acceptance)</th>
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<td>Regulators focus on site cleanups. (1980s and 1990s)</td>
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11. What types of goals can we set for chlorinated solvent releases?


- Reduce potential for DNAPL migration
- Reduce long-term management requirements
- Reduce mass flux
- Stabilize the extent of plumes
- “Stewardship”

The NRC’s (2005) *Contaminants in the Subsurface*:

- Deplete the source zones
- Reduce concentrations in source zones
- Reduce contaminant flux from source zones
- Reduce DNAPL migration potential
- Reduce plume size
- Reduce contaminant toxicity
- Eliminate barriers to subsequent remedial actions
- Reduce Life-cycle costs

Author’s Experience:

- Meet commitments for expenditure of funds for environmental restoration
- Meet public expectations to make progress
- Comply with regulatory requirements
- Advance new technology
In the end, learning to value that which is:

- attainable
- beneficial

may be our greatest opportunity for future progress.
12. Which in situ source treatment technologies are receiving the widest use?

• Chemical Oxidation
  – Permanganate
  – Peroxide
  – Persulfate

• Thermal
  – Conductive
  – Electrical
12. Which in situ source treatment technologies are receiving the widest use (cont’d)?

- **Bioremediation**
  - *High Solubility Substrate*
  - *Low Solubility Substrate*
- **Chemical Reduction**
  - *ZVI Injection*
  - *ZVI Soil Mixing*
- **Monitored Natural Attenuation**
- **Soil Vapor Extraction**
13. What can we expect from common source treatment technologies?

Key Points:

- Only partial DNAPL mass removal or destruction can be achieved.

- MCLs are extremely unlikely to be met.

Summary of Source Mass Removal Sorted by Technology (NAVFAC, 2007; based on data from GeoSyntec, 2004)
13. What can we expect from common source treatment technologies? (cont’d)

% Reduction in Source Zone GW Concentrations Due to Treatment (McGuire et al., 2006)

- Enhanced Bioremediation (n=26 sites)
- Chemical Oxidation (n=23 sites)
- Thermal Treatment (n=6 sites)
- Surfactant/Cosolvent (n=4 sites)

KEY:
- Max
- 75th %
- Median
- 25th %
- Min
13. What can we expect from common source treatment technologies? (cont’d)

**Remediation Rule-of-Thumb:**
Well implemented in-situ remediation projects are likely to reduce source zone groundwater concentrations by **about one order-of-magnitude (90% reduction)** from pre-treatment levels.

*Treatment trains* (successive applications of different technologies) may be one approach to reduce concentrations beyond what a single treatment episode can achieve.
14. How much does it cost to treat source zones?

Unit Costs of Source Zone Treatment (McDade et al., 2005)
14. How much does it cost to treat source zones? (cont’d)

**Very General Rule of Thumb**

Investments on the order of millions of dollars per acre appear to have the potential to achieve one order of magnitude reductions in chlorinated solvent mass and concentration in source zones.
15. How will reduced loading from sources affect plumes?

Source Function vs. Plume Response

Rock core from the Ogallala Formation at F.E. Warren AFB illustrating a silt bed in sandstone
15. How will reduced loading from sources affect plumes? (cont’d)

F.E. Warren Spill Site 7 PRB

Water quality response in a plume downgradient of an iron permeable reactive barrier, F.E. Warren AFB, Wyoming,

15. How will reduced loading from sources affect plumes? (cont’d)

**Rule-of-Thumb:**

In many instances, complete source removal…
- gives one order-of-magnitude improvement downgradient.

But with fast groundwater flow, low mass storage, and/or active attenuation…
- potentially gives 2-3 orders-of-magnitude improvement downgradient over several years
16. What are the effects of source treatment on clean-up timeframes?

- One benefit of source treatment is that time to reach its clean-up goals will be reduced.
- Quantifying how much is difficult.
- Must account for likely “tails” to source concentration.
- May not get “equal benefit for equal work”.

If tail follows first order relationship…

**LONGEVITY SOFTWARE**
- SourceDK
- BIOBALANCE
- NAS
- REMCHLOR
17. Which containment measures are receiving the widest use?

- Hydraulic Containment
- Permeable Reactive Barriers
  - Biodegradation (e.g., mulch)
  - Zero Valent Iron
  - Sparge Walls
- Physical Containment
- Monitored Natural Attenuation
17. What can we expect from containment measures?

- **43 of 52** full scale ZVI barriers are “meeting regulatory expectations”

- **25 of 29** sites with physical barriers have “acceptable performance” in medium term (10 years or less)

- **MNA sole remedy** (no source treatment) at **30%** of 191 MNA sites
20. How does one compare treatment vs. containment?

- Uncertainty (for both options)
- Plume Response - takes time
- Cost Comparison (Net Present Value)

<table>
<thead>
<tr>
<th>SITE A</th>
<th>SITE B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perimeter = 4</td>
<td>Perimeter = 12</td>
</tr>
<tr>
<td>Area = 1</td>
<td>Area = 9</td>
</tr>
<tr>
<td>Thickness = 4</td>
<td>Thickness = 4</td>
</tr>
<tr>
<td>Volume = 4</td>
<td>Volume = 36</td>
</tr>
<tr>
<td>Volume:Perimeter = 1:1</td>
<td>Volume:Perimeter = 3:1</td>
</tr>
</tbody>
</table>
20. How do site characteristics affect clean-up decisions?

- NRC “Cube”
  - Objectives
  - Settings
  - Technologies

- Series of Tables
20. How do site characteristics affect clean-up decisions?

**Decision Matrix**

- Evaluation of **quantitative** and **qualitative** factors to assess relative need for source treatment.
Qualitative Decision Chart: RC Approach

Yes, Source Depletion

No, Source Depletion
### Key Factors for Deciding

<table>
<thead>
<tr>
<th>Factor</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source Zone:</td>
<td>Expanding</td>
<td>Immobile</td>
</tr>
<tr>
<td>Plume Status:</td>
<td>Expanding</td>
<td>Shrinking</td>
</tr>
<tr>
<td>Resource Value:</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Containment Cost:</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Will Reduce Remed. Timeframe?</td>
<td>A Lot</td>
<td>A Little</td>
</tr>
<tr>
<td>Need for Rapid Cleanup?</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>
### Weight of Evidence: More Likely to Benefit from Tmt.

<table>
<thead>
<tr>
<th>Desired Remedial Benefits</th>
<th>More Need for Source Depletion</th>
<th>Less Need for Source Depletion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce potential for DNAPL migration as separate phase</td>
<td>1a. Expanding DNAPL Zone (possibly at chlorinated sites, containment addresses this problem too)</td>
<td>1b. Free-Phase DNAPL present but stable in stratigraphic traps</td>
</tr>
<tr>
<td>Reduce source longevity, and reduce long-term management requirements</td>
<td>2a. High life-cycle containment cost (for example, containment Net Present Value (NPV) &gt;&gt; cost of remediation)</td>
<td>2b. Moderate life-cycle containment cost</td>
</tr>
<tr>
<td>Near-term enhanced natural attenuation due to reduced dissolved phase loading</td>
<td>3a. Low reliability of containment system</td>
<td>3b. Moderate reliability of containment system</td>
</tr>
<tr>
<td>Near-term reduction in dissolved phase loading to receptors (e.g., a well or a stream)</td>
<td>4a. High potential for increased DNAPL due to DNAPL (for example, degradable source aquifer OR Well Yield &gt; 800 mg/L)</td>
<td>4b. Moderate potential for increased DNAPL due to DNAPL (for example, degradable source aquifer OR Well Yield &gt; 800 mg/L)</td>
</tr>
<tr>
<td>Near-term attainment of MCLs</td>
<td>5a. High probability of meaningful reduction in time to reach MCL (e.g., small sites with low complexity)</td>
<td>5b. Moderate probability of meaningful reduction in time to reach MCL</td>
</tr>
<tr>
<td>Intangibles</td>
<td>6a. Expanding dissolved phase plume (source loading ~ assimilative capacity) (containment addresses this problem too)</td>
<td>6b. Stable dissolved phase plume (source loading ~ assimilative capacity)</td>
</tr>
<tr>
<td>7a. Receptor is impacted or impacted soon (for example, &lt; 2 years travel time) (containment addresses this problem too)</td>
<td>7b. Potential longer-term risk to receptor (for example, &gt; 2 years travel time)</td>
<td>7c. No potential longer-term risk to receptor</td>
</tr>
<tr>
<td>Near-term attainment of MCLs</td>
<td>8a. Need for rapid cleanup (for example, impending properties)</td>
<td>8b. Limited need for rapid cleanup</td>
</tr>
<tr>
<td>Intangibles</td>
<td>9a. Desire for active remedy; desire to test new technologies; desire to reduce stewardship burden on future generations</td>
<td>9b. Neutral on intangible issues</td>
</tr>
</tbody>
</table>
22. Taking stock: In the past, why have we not been more successful?

• Poor design

• Poor understanding of what technologies do.

• Misunderstanding the extent and/or distribution

• Poor recognition of the uncertainties inherent in remedial system design

• Stating remedial objectives that can only be achieved over long periods of time
23. How can we set clean-up objectives that are achievable and protective?

NRC Philosophy:

- Two different categories of objectives:
  - Absolute objectives are objectives that are important in themselves, such as “protect human health and the environment.”
  - Functional objectives are a “means to an end” and include containing plumes, reducing concentrations and mass flux, managing risks, reducing mass, and potentially decreasing plume longevity.
“Six Step Process for Source Remediation”
24. How can we be more successful at site cleanup?

1. Think about absolute objectives as long-term goals
2. Have an up-to-date understanding of what can be practicably achieved by available technology, and communicate your experiences so that others can gain from your insights
3. Develop shorter-term functional objectives that must be met to confirm progress towards the absolute objectives
4. Recognize uncertainties. Design a remedial strategy that is updated as new observations and data are recorded
24. How can we be more successful at site cleanup (cont’d)?

5. When source containment is the chosen remedial strategy, clearly communicate the long-term nature of this to all stakeholders.

6. When source treatment is chosen as a part of the remedial strategy, clearly communicate the uncertainties associated with the outcome to all stakeholders.

7. Accept that remedial actions will not always lead to achievement of clean-up goals and objectives - and learn from these experiences rather than simply viewing them as failures.
24. How can we be more successful at site cleanup?

The Observational Approach: Originally developed for geotech engineering by Terzaghi & Peck (1948)

- Assess probable conditions and develop contingency plans
  - Example: plan for adverse outcome
- Establish key parameters for observation
  - Example: groundwater concentration, mass flux
- Measure parameters and compare to predicted values
  - Example: compare to model predictions
- Change the design as needed
  - Example: another round of treatment or go to containment
25. Where can I find more information?


The Strategic Environmental Research and Development Program (SERDP) and the related Environmental Security Technology Certification Program (ESTCP) are currently funding a number of projects in the area of chlorinated solvent source zone characterization and remediation. The most recent annual report is at: http://www.serdp.org/research/CU/DNAPL%20ANNUAL%20REPORT-2004.pdf.

The ESTCP program convened a workshop to address the research needs in this area. The workshop report is at: http://www.estcp.org/documents/techdocs/chlorsolvcleanup.pdf

Further information on SERDP- and ESTCP-funded research in this area is available at: http://www.serdp-estcp.org/DNAPL.cfm


The Interstate Technology and Regulatory Consortium has published several documents on DNAPLs, including:

An overview of characterization and remediation technologies:

A regulatory review of the challenges of source zone remediation:

An overview of bioremediation of DNAPLs:

Air Force Center for Engineering and the Environment has a web page with a number of documents, software, and other tools for chlorinated solvents and other contaminants, at: http://www.afcee.brooks.af.mil/products/techtrans/
Recent Relevant Projects and Useful Tools

DoD  EPA  DOE

SERDP
Strategic Environmental Research and Development Program

ESTCP
Environmental Security Technology Certification Program
Thermal Treatment Evaluations

- Develop a tool for use by practitioners, regulators, and site owners to anticipate the likely design and performance of thermal-based DNAPL treatment.

- Link design and performance experience to a small number of generalized site scenarios.

- Evaluate improvements in groundwater quality and reductions in mass discharge (flux).
### Physical Scenarios vs. Experience/Performance Summary

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Technology</th>
<th># of Sites</th>
<th># of Pilot Tests</th>
<th># of Full-Scale Systems</th>
<th># of Systems Since 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Generalized Scenario A:</strong> relatively homogeneous and permeable unconsolidated</td>
<td>Steam Heating</td>
<td>7</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>9</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Generalized Scenario C:</strong> largely permeable sediments with interbedded lenses of low permeability and with high potential for thermal response</td>
<td>Steam Heating</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>12</td>
<td>3</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>7</td>
<td>2</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td><strong>Generalized Scenario D:</strong> largely impermeable sediments with interbedded layers of higher permeability</td>
<td>Steam Heating</td>
<td>17</td>
<td>6</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>15</td>
<td>4</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>15</td>
<td>5</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td><strong>Generalized Scenario E:</strong> competent, but fractured bedrock</td>
<td>Steam Heating</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Generalized Scenario F:</strong> karst and/or weathered bedrock</td>
<td>Steam Heating</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Generalized Scenario G:</strong> unknown</td>
<td>Steam Heating</td>
<td>15</td>
<td>2</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>7</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

This table and others summarize key design and performance attributes, including numbers of energy delivery points, treatment times, temperatures reached, etc.
Conclusions To Date

- Most thermal applications have been poorly documented
- Operating conditions (especially treatment duration) often appear to be arbitrarily selected
- There do not seem to be obvious diagnostic tools for process optimization
- Significant mass removal is possible within the target treatment zone
- Mass flux often is reduced less than anticipated, due to untreated areas and limited treatment durations
- Ongoing evaluations (e.g., Thermal Conduction Heating at fractured bedrock site - NAWC in Trenton, NJ)
Optimal Search Strategy

• George Pinder, Univ. Vermont
• Computer-based search strategy
• Optimizes approach to define the source location and shape of the source zone
• Allows efficient, faster source delineation
DIAGNOSTIC TOOLS FOR DNAPL REMEDIATION

WATERVLIET ARSENAL
FRACTURED BEDROCK SITE
Watervliet NY Demonstration

- Permanganate injected into fractured bedrock to treat TCE
- Rock crushing showed TCE has diffused into the rock matrix
- Permanganate reduced before penetrating matrix (high sulfide levels)
- Significant rebound in TCE flux and concentrations to near-pretreatment levels after ISCO
Objectives

– Reduce uncertainty in estimating remedial outcomes

– Evaluate potential technology performance

– Aid RPMs in technology selection based on desired performance metrics
Technical Approach

Numerical Modeling

Database/Protocol

Input

Screening Tool
User-Friendly Interface

Output

DNAPL Remedial Technology Screening Tool Report

Literature Review

- DNAPL panel reports
- Refereed literature (journal publications)
- Non-refereed literature (conference proceedings)
- Guidance documents
- Other print sources
- Web databases
- SERDP & ESTCP projects
Beta-test version: DNAPLTEST@geosyntec.com
Mass Flux Reductions After Partial Source Treatment

- Method Development and Comparisons:
  - Passive flux meters, integrated pump tests, “traditional methods”
  - Similar results in many cases, given inherent uncertainty

- Pre- and Post-Treatment Measurements:
  - Roughly one order-of-magnitude reductions
  - Often suggest different treatment designs

- Modeling:
  - Valuable insights into likely impacts and controlling factors
  - Useful mass-based design tools (e.g., REMCHLOR, NAS)
Mass Flux Measurements

- Passive Flux Meters – Hatfield/Annable, Univ. FL
  – Testing Fractured-Rock PFM s
Passive Rock Fluxmeter (PRFM)

- Inflatable packer or impermeable flexible liner that holds a reactive permeable fabric against the wall of the borehole and to any active fractures.

- Reactive fabrics capture target contaminants and release non-toxic resident tracers (e.g., visible dyes and branch alcohols).

- Tracer loss is proportional to fracture flow and yields ambient measures of flow.

- Leached visible tracers reveal location, orientation, and aperture of flowing fractures and direction of flow.
Estimating Cleanup Times For Combining Source-Area Remediation with MNA

- Kram, Widdowson, Chapelle
  http://www.nas.cee.vt.edu/index.php
NAS Source Depletion Model

- Based on estimates of source zone mass, composition, geometry, and mass flux, NAS/SEAM3D tracks each constituent over time in both the NAPL and aqueous phases.
Natural Attenuation Software

• NAS provides a framework for comparing various remediation strategies and defining remediation goals based on a selection criteria:
  – Site-specific RAOs and hydrogeology/biogeochemical data

• NAS also provides a tool for calculating life-cycle cost estimates by combining
  – Source zone remediation cost estimates and annual monitoring costs based on TOR estimates and reduction in plume size and source strength

• NAS is widely available and easy to use
Robert Siegrist and Michelle Crimi

Develop a design protocol and decision tools

ISCO cost and performance database

Customized searches for specific site conditions

FAQ Guide

Testing design protocol at DoD sites
Four Tools.....

1. Source Depletion Decision Support System (SERDP)
   - Performance & Cost Database
   - Untreated Site Database

2. BIOBALANCE Software

3. Mass Flux Tool Kit

4. REMCHLOR
Temporal Concentration Data From 59 Chlorinated Solvent Sites

FOUR SOURCE DEPLETION TECHNOLOGIES:

- Enhanced Biodeg.
- Chem. Oxidation
- Surfactants/Cosolv.
- Thermal Treatment

- Median Treatment Volume = 3,800 yd³
- ~70% Full-Scale Projects

Source: McGuire et al., 2006, Ground Water Monitoring and Remediation
Data Analysis Methods

PERFORMANCE:

- Compiled conc. vs. time data (before and after treatment) for up to 4 wells within treatment zone

- Calculated geometric mean conc. of before treatment data and after treatment data;

- Then calculated percent reduction for each well

- Median percent reduction of all treatment zone wells as final performance metric

<table>
<thead>
<tr>
<th>Well</th>
<th>% Red’n</th>
<th>Site % Red’n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well # 1</td>
<td>99.9</td>
<td>90.0</td>
</tr>
<tr>
<td>Well # 2</td>
<td>91.0</td>
<td></td>
</tr>
<tr>
<td>Well # 3</td>
<td>89.0</td>
<td></td>
</tr>
<tr>
<td>Well # 4</td>
<td>+10.0</td>
<td></td>
</tr>
</tbody>
</table>
Temporal Records for Thermal Treatment Wells
(6 Sites, 13 Wells)

Thermal Treatment

Normalized Parent Conc. $C/C_{\text{initial}}$

Years From Start-Up

Any site achieve MCLs everywhere? No
Temporal Records for Enhanced Biodegradation
(26 Sites, 68 Wells)

Enhanced Bioremediation

Normalized Parent Conc. vs Years From Start-Up

Any site achieve MCLs everywhere? No

Years From Start-Up

C/C_{initial}

-6  -5  -4  -3  -2  -1  0  1  2  3  4  5  6
Temporal Records for Chemical Oxidation
(23 Sites, 58 Wells)

Any site achieve MCLs everywhere? No
% Reduction in **PARENT** Due to Source Depletion

### Key
- Enhanced Bioremediation (n=26 sites)
- Chemical Oxidation (n=23 sites)
- Thermal Treatment (n=6 sites)
- Surfactant/Cosolvent (n=4 sites)

#### Reduction in Treatment Zone Parent CVOC Concentration (%)

- **GOOD**
- **BAD**
What About Rebound? (Parent Compounds)

(a) ENHANCED BIODEG.
(b) CHEM OXID.
(c) SURFACTANT/COSOLV.
(d) THERMAL

Post-Treatment Concentration at Time / Initial Post-Treatment Concentration

Post-Treatment Monitoring Time (Years)
Summary

1. Source depletion projects routinely achieve >70% reduction in source zone groundwater parent concentration, but no sites met MCLs everywhere.

2. Parent compound rebound not big problem at most sites, but more prevalent for chemox (2 of 7 chemox sites had complete rebound).
What about untreated sites?

For this project:

What about untreated sites?
Untreated Sites: TCE

Normalized Concentration

Time Since Beginning of Temporal Record (years)

Conc. Higher

Conc. Lower
**Change in TCE Over Time**

- **Number:** 13 sites, 21 wells
- **Median Duration:** 10 years
- **Median % Change:** - 81%

**Concentration Trend (MAROS Software)**

- Increasing: 3 sites
- Stable: 3 sites
- Decreasing: 7 sites

Source: Newell et al., 2006, ASCE Environmental Engineering
Temporal Trends In Untreated Source Zones

**PCE: 9 sites, 17 wells**

- Normalized Concentration vs Time Since Beginning of Temporal Record (years)
- % Change: -71%

**TCE: 13 sites, 21 wells**

- Normalized Concentration vs Time Since Beginning of Temporal Record (years)
- % Change: -81%

**DCE: 2 sites, 4 wells**

- Normalized Concentration vs Time Since Beginning of Temporal Record (years)
- % Change: -86%

**TCA: 6 sites, 10 wells**

- Normalized Concentration vs Time Since Beginning of Temporal Record (years)
- % Change: -99%

% Change = median % change for all wells
Example Real-World Source Decay Rates

Ground Water Issue

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell, Hanadi S. Rifai, John T. Wilson, John A. Connor, Julia A. Aziz, and Monica P. Suarez

Introduction
This issue paper explains when and how to apply first-order attenuation rate constant calculations in monitored natural attenuation (MNA) studies. First-order attenuation rate constant calculations can be an important tool for evaluating natural attenuation processes at groundwater contamination sites, or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants (U.S. EPA, 1999). The overall impact of natural attenuation processes at a given
Observed Source Decay Rate for CVOCs: 13 Sites

Max
75th Percentile
Median
25th Percentile
Min

Median Half-Life
PCE: 3.0 years
TCE: 6.1 years
DCE: 4.3 years
TCA: 2.0 years

Decreasing Concentrations Over Time

Increasing Concentrations Over Time

POINT DECAY RATE ($k_{point}$) (per year)

ALL (n=30)
PCE (n=9)
TCE (n=12)
c-DCE (n=2)
TCA (n=6)
Implication

Benefits of partial source depletion is reduced if source is decaying naturally.  

For example:

If source depletion gives 88% reduction in concentration….

That is equal to 3 source decay half-lives…..

These untreated source zones need < 20 years to achieve same result (?)

(median decay values from 23 site database)
Source Depletion Decision Support System

Free download at: www.gsi-net.com
Four Tools...

1. Source Depletion Decision Support System
   - Performance & Cost Database
   - Untreated Site Database

2. BIOBALANCE Software

3. Mass Flux Tool Kit

4. REMCHLOR
Closing the Mass Balance on Sources, Donors, Competing Reactions, and Attenuation Processes at Chlorinated Solvent Sites

Roopa Kamath
Charles Newell
David Adamson
Paul Newberry

GSI Environmental, Inc.
Houston TX

Brian Looney
Karen Vangelas

Savannah River National Laboratory
Aiken SC
Biobalance Software: Four Modules

- Remediation timeframe and to evaluate performance of source remediation technologies

- Long-term sustainability of natural processes

- Stability of the contaminant plume and its potential for migration
Impact of Source Treatment

Life of a Source Zone

Mass Flux from Source (C vs. time)

<table>
<thead>
<tr>
<th>GW In</th>
<th>Mass Flux Out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NAPL Dissolution</th>
<th>Fast Desorption</th>
<th>Slow Desorption &amp; Matrix Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SAND

CLAY

SAND

CLAY

SAND

CLAY
FIRST ORDER DECAY MODEL – With and Without Source Depletion

Assume $C_t$ proportional to $M_t$

$RF$: Remaining Fraction
Impact of Source Treatment

Effect of Source Treatment on Remediation Timeframe (RTF)

FIRST ORDER EQUATION:

\[
\frac{\text{RTF}_{\text{SD}}}{\text{RTF}_{\text{MNA}}} = \ln \left( \frac{C_g}{C_{0\text{ RF}}} \right) / \ln \left( \frac{C_g}{C_{0}} \right)
\]

- \(C_g\) = GW Concentration Goal (such as MCL)
- \(C_o\) = Original Source Concentration
- \(\text{RTF}_{\text{SD}}\) = Remed. timeframe with source tmt
- \(\text{RTF}_{\text{MNA}}\) = Remed. timeframe w/ only natural attenuation

Reduction in Remediation Timeframe (%)

Reduction in Source Mass (%)
Summary

1. Reduction in Remediation Timeframe not likely to be directly proportional to reduction in source mass

2. First Order Source Decay Model:

80% Reduction in Source Mass = 18% Reduction in Remediation Timeframe

For specific case where \( C_g/C_o = 0.0001 \)
STEP 1 OF 4:
How does a source decay?
GO TO: ‘Source’

STEP 2 OF 4:
How do competing reactions affect biodegradation?
GO TO: ‘Competition’

STEP 3 OF 4:
How sustainable are the biodegradation reactions?
GO TO: ‘DONOR’

STEP 4 OF 4:
How do natural attenuation processes affect the plume?
GO TO: ‘Plume’

NO₃⁻, SO₄²⁻, O₂, Fe(II)
Scanning Electron Microscope Image of Dechlorinating Bacteria
Calculating Availability of Electron Donor in the Source Zone

Using NAPL Composition Data

NAPL with 15% benzene; 85% TCE

\[
\text{AVAILABLE Hydrogen} = 0.15 \times 0.39 \text{ H}_2\text{-equivalents/g-Donor} \\
= 0.06 \text{ g-}H_2/\text{g-NAPL}
\]

\[
\text{Hydrogen DEMAND by PCE} = 0.85 \times 0.045 \text{ H}_2\text{-equivalents/g-Donor} \\
= 0.04 \text{ g-}H_2/\text{g-NAPL}
\]

Donor Available/Donor Demand = 1.5
Two Ways to Estimate Donor Mass

From Analysis of DNAPL Sample

From Groundwater Samples + Partitioning
STEP 1 OF 4:
How does a source decay?
GO TO: ‘Source’

STEP 2 OF 4:
How do competing reactions affect biodegradation?
GO TO: ‘COMPETITION’

STEP 3 OF 4:
How sustainable are the biodegradation reactions?
GO TO: ‘Donor’

STEP 4 OF 4:
How do natural attenuation processes affect the plume?
GO TO: ‘Plume’

NO₃⁻, SO₄²⁻, O₂, Fe(II)
SCHEMATIC OF TYPE 1 CHLORINATED SOLVENT SITE

RTDF, 1997

Presented in Wiedemeier et al. 1999
• Competing Electron Acceptors (CEA)

\[
\begin{align*}
\delta O_2 &= 2 \text{ mg/L} \\
\delta NO_3^- &= 5.0 \text{ mg/L} \\
\delta SO_4^{2-} &= 10.0 \text{ mg/L}
\end{align*}
\]

Equivalent Hydrogen Demand: 0.03 kg/yr

• Daughter Products (CVOC)

PCE is PARENT COMPOUND
Produces 2 mg/L of TCE
Produces 1 mg/L of cis-DCE

Equivalent Hydrogen Demand: 0.001 kg/yr

30X as much donor going to CEAs vs. Solvent Degradation
• Analytical Solute Transport Model with Decaying Source
  – How long will a plume get before it stabilizes?
  – When will the plume stabilize?
  – What are the dominant attenuation mechanisms?
### Plume Module Output

<table>
<thead>
<tr>
<th>Case</th>
<th>Time (yrs)</th>
<th>Plume Length (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNA</td>
<td>72</td>
<td>1230</td>
</tr>
<tr>
<td>MNA + Source Depletion Technology</td>
<td>64</td>
<td>1030</td>
</tr>
</tbody>
</table>

![Graph showing Plume Length over time](image-url)

The graph illustrates the plume length over time for different cases, with two distinct lines indicating the MNA Scenario and the Source Depletion + MNA technology. The x-axis represents time in years, while the y-axis shows plume length in feet.
BIOBALANCE: A MASS BALANCE TOOLKIT

For evaluating Source depletion, Competition effects, long-term Sustainability, and Plume dynamics.

Free download at: www.gsi-net.com

Companion Product: Solvent “Scenarios”
Four Tools...

1. Source Depletion Decision Support System
   - Performance & Cost Database
   - Untreated Site Database

2. BIOBALANCE Software

3. Mass Flux Tool Kit

4. REMCHLOR
Mass Flux vs. Traditional Approach

**Traditional Approach**
- Measure existing plume concentrations to assess:
  - Impact on receptor wells
  - Natural attenuation rates
  - Remedial options

**Mass Flux Approach**
- Define rate of mass flux across specified cross-sectional areas of plume to assess:
  - Impact on receptor wells
  - Natural attenuation rates
  - Remedial options


**KEY BENEFITS:**
Mass flux approach sometimes offers a better understanding of potential impacts on receptors, natural attenuation rates, and remedial options.
Mass Flux Calculation: Transect Method

**Step-By-Step Approach**

1. Measure groundwater concentrations in transect across plume
2. Calculate average plume concentrations in cross-sectional areas between each well
3. Sum Total Mass Flux as:

   \[ M_f = \sum C_i \times A_i \times q \]

   \[ q = K \times I \]

\[ M_f = \text{Mass flux}; \quad C_i = \text{concentration in segment } i; \quad A_i = \text{Area of segment } i; \]
\[ I = \text{Hydraulic gradient}; \quad k = \text{Hydraulic conductivity}; \quad q = \text{Groundwater Darcy velocity (k x I)} \]

Nichols and Roth, 2004
Mass Flux Toolkit
To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives

Lead author: Shahla Farhat, Ph.D. free at www.gsi-net.com
## Input Data and Grid

### Site Location and ID:
- Location: Texas
- Description: MTBE

### 4. CHOOSE TRANSECT
- Transect 1

### 5. CHOOSE TIME PERIOD
- Time Period: 1

### 6. ENTER TRANSECT DATA
- Distance of Transect 1 from Source: 123 ft
- Hydraulic Conductivity Units: cm/sec
- Uniform Hydraulic Conductivity: Yes
- Uniform Hydraulic Gradient: Yes
- Hydraulic Conductivity: 3.20E-02 cm/sec
- Hydraulic Gradient: 2.00E-03 (cm/sec)

### Monitoring Point

<table>
<thead>
<tr>
<th>Monitoring Point</th>
<th>Distance from Edge of Transect (ft)</th>
<th>Sampling Interval (ft bgs)</th>
<th>Plume Top (ft bgs)</th>
<th>Plume Bottom (ft bgs)</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top</td>
<td>Bottom</td>
<td></td>
<td></td>
<td>Constituent A</td>
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<td>15</td>
<td>2.3</td>
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<td>10</td>
<td>10</td>
<td>5</td>
<td>15</td>
<td>0.47</td>
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<td>37.5</td>
<td>5</td>
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<tr>
<td>15</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

### 7. CHOOSE GRID
- Orig. mean cell width (x-axis): 14 ft
- Orig. cell thickness (y-axis): 1.6 ft
- Refine cell width by: 1
- Refine cell thickness by: 1

### 8. SELECT CONSTITUENT FOR CALCULATIONS
- Constituent A: MTBE
- Constituent B: No selection

**Next Step:** Complete Grid
Key Features

1. Helps you interpolate grid cells
   - Nearest Neighbor
   - Linear or Log-transformed interpolation
   - User Entered Value

2. Uncertainty/Sensitivity Analysis
   - Take out a value
   - Different interpolation schemes
   - Monte Carlo varies K, gradient, conc.

3. Graphing (Flux vs. Time; Flux vs. Distance)

4. Other Methods to Determine Mass Flux
Receptor Impact

**Pumping Well Data**

Calculate mass flux based on capture of plume by pumping system.

\[
C_{\text{well}} = \frac{M_f}{Q}
\]

- \(C_{\text{well}}\) = Concentration in recovery well effluent;
- \(M_f\) = Mass flux;
- \(Q\) = Recovery well pumping rate

**NOTE:** Analysis assumes plume is completely captured by pumping well(s)

Nichols and Roth, 2004
Four Tools...

1. Source Depletion Decision Support System
   - Performance & Cost Database
   - Untreated Site Database

2. BIOBALANCE Software

3. Mass Flux Tool Kit

4. REMCHLOR
Performers

- Original Author REMChlor: Dr. Ronald W. Falta, Clemson

- REMChlor ESTCP Project:
  - Dr. Ronald W. Falta, Clemson
  - Hailian Liang, Clemson
  - Dr. P. Suresh Rao, Purdue
  - Nadita Basu, Purdue
  - Dr. Charles J. Newell, GSI
  - Dr. Shahla Farhat, GSI
The Site Managers Dilemma: When MNA alone is not enough

“Should we spend our money and effort on cleaning up the source zone? That’s where most of the contaminant mass is”

“Or should we focus on controlling the plume using pump and treat, a reactive barrier, or enhanced plume degradation?"

“How can any decision be justified given all of the uncertainty?”
Source Reduction Leads To Discharge Reduction

Field and Modeling Data

Power function model

\[
\frac{C}{C_0} = \left( \frac{M}{M_0} \right) \Gamma
\]

Laboratory dissolution experiments

integrated

integrated
Divide space and time into “reaction zones”, solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone.

Example:

- Natural attenuation
- Reductive dechlorination
- Aerobic degradation

Each of these space-time zones can have a different decay rate for each chemical species.
This new source/plume remediation model is called REMChlor, and it will be released by the EPA soon.
Deterministic REMChlor example:
300 kg release of 1,1,1-TCA in 1975

- DNAPL source has $C_0=2 \text{ mg/l}$; water $Q=600 \text{ m}^3 \text{ per year}$
- TCA reductive dechlorination in the $\alpha 0.8/yr$ (very low)
- 1,1-DCA degrades to chloroethane $\alpha 0.2/yr$ (very low)

![Graphs showing contaminant distribution over time](1995, 2005, 2075)
Enhance reductive dechlorination in the plume from 0-200 m, during the period of 2005 to 2010.
REMChlor simulation of source remediation

Remove 70% of source mass between 2005 and 2006
Probabilistic Simulation – treat input variables as uncertain parameters using probability density functions (PDFs)
Vapor transport will be computed using method of Johnson and Ettinger (1991), and with newer vertical mass flux approaches (ESTCP ER-0423).
Four Tools...

1. Source Depletion Decision Support System
   - Performance & Cost Database
   - Untreated Site Database

2. BIOBALANCE Software

3. Mass Flux Tool Kit

4. REMCHLOR
Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents

Tom Sale
Chuck Newell
Rob Hinche
Hans Stroo
Paul Johnson
Decision Guide

• What it is
  – Knowledge bridge to practitioners
  – Things to think about - Rules of thumb, Lessons learned...
  – Small phone book
  – Route for those want more

• What it isn’t
  – Not a prescriptive system
  – Not all inclusive
Content

- Executive Summary
- Introduction
- The Nature of the Problem
- Resolving Objectives
- Screening Technologies
- Packaging Remedies

After NRC (2005)
The Nature of the Problem – How will source depletion or plume interception affect downgradient water quality?
Any mass depletion will decrease subsequent loading to plumes

What remains can cause exceedances of standards for extended periods

The key issues are mass discharge and longevity

- Freeze and McWhorter (1997)
- Sale and McWhorter (2002)
- NRC (2005)
- Suchomel and Pennel (2006)
- Page, Soga, and Illangasekare (2007)
It is not just about Dense Nonaqueous Phase Liquids (DNAPLs)

Per Cohen and Mercer (1991) the total contaminant mass at in a volume of porous media is the sum of the nonaqueous, aqueous, vapor, and sorbed phases. At any point in space each of the phases is trying to equilibrate with the other phases.

\[ \omega_{\text{Total}} = \omega_{\text{DNAPL}} + \omega_{\text{aqueous}} + \omega_{\text{vapor}} + \omega_{\text{sorbed}} \]

Where \( \omega \) is the mass of contaminant (e.g. chlorinated solvent) per unit mass porous media.
AFCEE Source Zone Initiative (2007)

Wilking, Illangasekare, and Sale
Distribution of TCA Mass Recovered vs. Time

Yes DNAPL

Remaining DNAPL by X-ray adsorption

Cumulative Mass Discharged

Mass in low permeability layer

Elapsed Time (Days)

Cumulative TCA (mg)

0 2,000 4,000 6,000 8,000 10,000 12,000 14,000

NO DNAPL

AFCEE 2007
AFCEE (2007) Contaminant storage-release in plumes

Advancing solvent plume

Low permeability silts

Transmissive sand

Expanding diffusion halo in stagnant zone

Simultaneous inward and outward diffusion in stagnant zones
AFCEE (2007)

See also - Chapman and Parker, Water Resources Research, December 2005

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<th>Condition</th>
<th>Concentration</th>
<th>Time (years)</th>
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<td>A)</td>
<td>0.1</td>
</tr>
<tr>
<td>DNAPL Absent</td>
<td>B)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>C)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>D)</td>
<td>0.1</td>
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<tr>
<td></td>
<td>E)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>F)</td>
<td>0.1</td>
</tr>
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<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
<th>Half Life</th>
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<td>$k = k'$</td>
<td>0.023 yr$^{-1}$</td>
<td>30 yr</td>
</tr>
<tr>
<td>$k = k'$</td>
<td>0.23 yr$^{-1}$</td>
<td>3 yr</td>
</tr>
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</table>

Normalized Concentration

- Well at 1m
- Well at 10m
- Well at 100m
Plume Function


  - Given active degradation in the plume
    - Limited storage
    - Rapid downgradient response
Type setting for contaminant storage and release
(following USEPA 2003 & NRC 2005)

(I) Granular Media with Mild Heterogeneity and Moderate to High Permeability
    (e.g. eolian sands)

(II) Granular Media with Mild Heterogeneity and Low Permeability
    (e.g. lacustrine clay)

(III) Granular Media With Moderate to High Heterogeneity
    (e.g. deltaic deposition)

(IV) Fracture Media with Low Matrix Porosity
    (e.g. crystalline rock)

(V) Fracture Media with High Matrix Porosity
    (e.g. limestone, sandstone or fractured clays)
14 subsurface compartments potentially containing chlorinated solvents

<table>
<thead>
<tr>
<th></th>
<th>Source</th>
<th></th>
<th>Plume</th>
<th></th>
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<td>Low Permeability</td>
<td>Transmissive</td>
<td>Low Permeability</td>
</tr>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Aqueous</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Sorbed</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Vapor</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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</table>
The problem we face is dependent on the setting and the age of the release.

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>PLUME</th>
<th>TYPE</th>
</tr>
</thead>
<tbody>
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<td>Transmissive</td>
<td>Stagnant</td>
<td>Transmissive</td>
</tr>
<tr>
<td>DNAPL</td>
<td>HIGH</td>
<td>LOW</td>
</tr>
<tr>
<td>Aquous</td>
<td>LOW</td>
<td>LOW</td>
</tr>
<tr>
<td>Sorbed</td>
<td>LOW</td>
<td>LOW</td>
</tr>
<tr>
<td>Vapor</td>
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<td>LOW</td>
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</tbody>
</table>

**Type 1**

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<tr>
<th>SOURCE</th>
<th>PLUME</th>
<th>TYPE</th>
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<tbody>
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<td>Stagnant</td>
<td>Transmissive</td>
</tr>
<tr>
<td>DNAPL</td>
<td>MODERATE</td>
<td>LOW</td>
</tr>
<tr>
<td>Aquous</td>
<td>LOW</td>
<td>MODERATE</td>
</tr>
<tr>
<td>Sorbed</td>
<td>MODERATE</td>
<td>LOW</td>
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<tr>
<td>Vapor</td>
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**Type 2**

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<td>Transmissive</td>
</tr>
<tr>
<td>DNAPL</td>
<td>MODERATE</td>
<td>LOW</td>
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<td>Aquous</td>
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<td>LOW</td>
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<tr>
<td>Sorbed</td>
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<tr>
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**Type 3**

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<td>DNAPL</td>
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<td>LOW</td>
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<td>MODERATE</td>
<td>MODERATE</td>
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**Type 4**

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<td>MODERATE</td>
<td>MODERATE</td>
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<td>MODERATE</td>
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**Type 5**

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<td>MODERATE</td>
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<tr>
<td>Sorbed</td>
<td>MODERATE</td>
<td>MODERATE</td>
</tr>
<tr>
<td>Vapor</td>
<td>MODERATE</td>
<td>LOW</td>
</tr>
</tbody>
</table>

High, moderate and low relative fractions of CVOC in the 14 compartments.

DRAFT
Primary fields of interest

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
<th>Type 4</th>
<th>Type 5</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Aqueous: LOW</td>
<td>MODERATE: LOW</td>
<td>Aqueous: LOW</td>
<td>MODERATE: LOW</td>
<td>MODERATE: HIGH</td>
</tr>
</tbody>
</table>

| Middle Stage| Transmissive: LOW       | Stagnant: LOW           | Transmissive: MODERATE  | Transmissive: LOW       | Transmissive: LOW       |

Physical Containment

~70,000 kg released

Early Stage

<table>
<thead>
<tr>
<th>SOURCE</th>
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<td>Sorbed</td>
<td>LOW</td>
</tr>
<tr>
<td>Vapor</td>
<td>LOW</td>
</tr>
</tbody>
</table>

5,000-20,000 kg, remaining isolated source zones

~3,000 kg downgradient in low k zones

Middle Stage

~62,000-47,000 kg in transmissive zones in the plume or degraded?
Resolving Objectives

Establishing goals that are attainable and beneficial

After NRC 2005
Making decisions requires balancing priorities
Objectives need to reflect the values of the impacted parties

- Clean water
- Clean air
- Net benefit
  - Beneficial land use
  - Sustainability
- Stewardship of Resources
- Compliance
Screening Technologies

After NRC 2005
Source Zone Technologies

- Excavation
  - Disposal
  - Treatment
- In situ
  - Stabilization
  - Flushing
    - SVE
    - Surfactants
  - Destruction
    - Thermal
    - Chemical Oxidation
    - Biological Reduction
    - Chemical Reduction

14 tons of PCE
ZVI-Clay - Percent removal in soils at 15 ft

<table>
<thead>
<tr>
<th></th>
<th>PCE&gt;99.99%</th>
<th>TCE&gt;99.8%</th>
<th>Initial ~ 1,500 mg/kg</th>
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</thead>
<tbody>
<tr>
<td>0 to 30 months</td>
<td>PCE&gt;99.95%</td>
<td>TCE&gt;99.5%</td>
<td>Initial ~ 1,500 mg/kg</td>
</tr>
<tr>
<td>0 to 12 months</td>
<td>PCE&gt;99.93</td>
<td>TCE&gt;96%</td>
<td>Initial ~ 700 mg/kg</td>
</tr>
<tr>
<td>0 to 7 months</td>
<td>PCE&gt;99.98%</td>
<td>TCE&gt;97%</td>
<td>Initial ~ 2,200 mg/kg</td>
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</table>
Technology Effectiveness – Type III geology, Middle stage system

### Pump and Treat

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<tr>
<td>Aqueous</td>
<td>Addressed?</td>
<td>MODERATE</td>
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<td>MODERATE</td>
</tr>
<tr>
<td>Vapor</td>
<td>MODERATE</td>
<td>LOW</td>
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</table>

### Conductive Heating or ZVI-Clay

<table>
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<td>Addressed</td>
</tr>
<tr>
<td>Aqueous</td>
<td>Addressed</td>
<td>Addressed</td>
</tr>
<tr>
<td>Sorbed</td>
<td>Addressed</td>
<td>Addressed</td>
</tr>
<tr>
<td>Vapor</td>
<td>Addressed</td>
<td>Addressed</td>
</tr>
</tbody>
</table>
• Containment
  – Hydraulic barriers
  – Physical barriers
  – Reactive barriers
    • Sparge
    • Iron
    • Biological

Electrolytic reactive barriers
ER-0112 and ER-0519
Technology Effectiveness – Type III geology, Middle stage system

<table>
<thead>
<tr>
<th>Containment</th>
<th>Zero dissolved flux to plume</th>
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<table>
<thead>
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<th></th>
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<th>PLUME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transmissive</td>
<td>Stagnant</td>
</tr>
<tr>
<td>DNAPL</td>
<td>MODERATE</td>
<td>MODERATE</td>
</tr>
<tr>
<td>Aqueous</td>
<td>MODERATE</td>
<td>MODERATE</td>
</tr>
<tr>
<td>Sorbed</td>
<td>MODERATE</td>
<td>MODERATE</td>
</tr>
<tr>
<td>Vapor</td>
<td>MODERATE</td>
<td>LOW</td>
</tr>
</tbody>
</table>

DRAFT
Potential for success also depends on the objectives.
Remedial Packages

- Technologies
- Plans for subsequent land use
- Focused monitoring
- Contingency Plans
- ...
We set out on a journey into the unknown

**Paradigm shifts of the last half century**

<table>
<thead>
<tr>
<th>Old School Paradigm (Period of prevalence)</th>
<th>New School Paradigm (Time of broad acceptance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Given the volatility of chlorinated solvents, land disposal is an appropriate practice. (1940s through 1970s)</td>
<td>Releases of chlorinated solvents to subsurface environments can create big problems. Few things are more important than limiting future releases. (Beginning in the 1980s)</td>
</tr>
<tr>
<td>Aquifers may be restored by pumping out the contaminated water (pump-and-treat). (1970s through 1980s)</td>
<td>Solvents sorbed to solids, present as DNAPL, and stored in stagnant zones can sustain groundwater concentrations in transmissive zones for long periods. (1990s through 2000s)</td>
</tr>
<tr>
<td>Chlorinated solvents are recalcitrant. (1970s through 1990s)</td>
<td>Chlorinated solvents will degrade under a range of natural and engineered conditions. (Beginning late 1990s)</td>
</tr>
<tr>
<td>New technologies hold promise of achieving MCLs in source zones. (Early through mid 1990s)</td>
<td>In many settings, most available technologies will not achieve MCLs and long-term management will be needed. (Beginning mid 1990s)</td>
</tr>
<tr>
<td>Primary risks and site care costs can be addressed by removal and/or depletion of source zones. (1970s through early 2000s)</td>
<td>Contaminants can remain after source zone treatment in matrix storage or in dissolved plumes, and these can sustain exceedances of MCLs and may necessitate site care for long periods of time. (Mid 2000s)</td>
</tr>
<tr>
<td>Source zone remediation is a necessary component of corrective action. (1970s through 1990s)</td>
<td>Source zone remediation should be considered, but is not always a necessary component of corrective action. Long-term management, containment, and MNA may be more effective strategies at some sites. (2000s)</td>
</tr>
<tr>
<td>Groundwater represents the primary pathway and media of concern. (1970s through late 1990s)</td>
<td>Vapor intrusion is recognized as a pathway of concern of the same order as groundwater. (2000s)</td>
</tr>
<tr>
<td>Regulators focus on site cleanups. (1980s and 1990s)</td>
<td>Some regulators begin to bring natural resource damage (NRD) issues into the site management process, such as filing NRD lawsuits. (2000s)</td>
</tr>
</tbody>
</table>
Closing

We have encountered unanticipated challenges.

In contemplating this problem, a landmark 1994 National Research Council (NRC) study, *Alternatives for Groundwater Cleanup*, observed "the nation may be wasting large amounts of money on ineffective remediation efforts."
Closing

We have come a long way. Today, given new knowledge, we are far better prepared to meet the challenges that lie before us.
Discussion
Key Findings - Characterization

“It isn't that they can't see the solution. It's that they can't see the problem”

G.K. Chesterton

Need To Use The
“Observational Approach”

Trade High Spatial Data Density for Time Data?

Sources, & People, Age & Change Morphology