Large and Dilute Plumes of Chlorinated Solvents – Challenges and Opportunities

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Informal Definition…

Large and Dilute (L&D) Plume:

A plume of relatively low concentration that extends over a large area – many L&D plume lengths measured in “km” or “miles”
What conditions create L&D plumes?

Permeable aquifers, generally with low organic carbon contents and low biomass

Aerobic systems where influx of electron acceptors makes it difficult to establish and maintain reducing conditions

Attenuation processes are generally slow (e.g., degradation half-lives more than 1 to 2 years)

Often deep

Often affected by mass transfer in/out of less-transmissive compartments (clay/silt layers)
So What’s the Problem?

There is a desire to actively remediate

High costs and technical difficulties involved in treating large volumes of water and large areal footprint

Sometimes plumes are too deep for cost-effective interdiction or containment (hard to implement PRBs…)

Concentrations will exceed standards for a long time with or without treatment

Significant contaminant mass often present relatively inaccessible (“immobile”) zones, resulting in “secondary sources” and persistent concentrations after primary source mass is removed

Large scale manipulation of the geochemical environment over an entire plume can be very difficult, expensive and undesirable
DOE Examples

M-Area – DOE Savannah River Site

TCE, approximately 2 square miles and extending to 200 feet deep, initial source concentration → DNAPL

200 Area – DOE Hanford Site

Carbon tetrachloride, approximately 3 square miles and extending to 350 feet deep, initial source concentration → DNAPL

Northwest Plume – DOE Paducah Gaseous Diffusion Plant

TCE, approximately 1 square mile extending 75 feet deep, initial source concentration → DNAPL

Test Area North – DOE Idaho National Laboratory

TCE, approximately 1 square mile and extending to 350 feet deep, initial source concentration → DNAPL

Many DOD examples (Hill AFB, Tinker AFB, MMR, Tooele, etc.) and industrial facilities
A few example plume maps from DOE sites

- Paducah Gaseous Diffusion Plant (KY)
- Idaho National Lab Test Area North

bold bar = 1.60934 km
Lifecycle of a Contaminant Plume

Contaminants released into the soil and groundwater will form a “plume”.

As contaminants are attenuated by natural processes the plume will stabilize and then shrink.

time evolution of a plume if it undergoes attenuation
Anatomy of a Contaminated Site

**Waste site**

**Source Zone**
Characteristics: DNAPL and high Concentrations

Need: Aggressive technologies to limit long term damage

Examples: destruction or stabilization in place; heat/steam; chemical oxidation or reduction; immobilization.

**Primary Groundwater / Vadose Zone Plume**
Characteristics: Moderate to high aqueous/vapor phase concentrations

Need: Baseline methods or moderately aggressive alternatives

Examples: pump (gas or water) and treat; recirculation wells; enhanced bioremediation

**Dilute Plume / Fringe**
Characteristics: Low aqueous/vapor phase concentrations; Large water volume.

Need: innovative technologies - sustainable low energy concepts

Examples: MNA, Passive pumping (siphon, barometric, etc.); enhanced attenuation
Continuum of Treatment Technologies for DNAPL sources and resulting plumes

<table>
<thead>
<tr>
<th>Technology Class</th>
<th>Source Removal and/or Treatment</th>
<th>Interdiction and Active Remediation</th>
<th>?</th>
<th>Monitored Natural Attenuation</th>
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<tbody>
<tr>
<td>Technology Examples</td>
<td>excavation</td>
<td>thermally enhanced removal</td>
<td>pump and treat recirculation wells</td>
<td>in situ bioremediation</td>
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</table>

Continuum of Treatment Technologies for DNAPL sources and resulting plumes
Treating a Contaminated Site

Source Zone

Costs:
$/lb contaminant or $/cu yd. Removal examples:
< $50-$100/cu yd or
< $100/lb for chlorinated solvents

hot spot characterization reduces cleanup volume

Primary Groundwater/Vadose Zone Plume

Costs:
$/treatment volume (gallon/cu ft) example:
<$0.5-$10 / 1000 gallons
zone of capture characterization needed, optimize extraction to reduce treatment volume

Dilute Plume/Fringe

Costs:
Operation and maintenance costs $/time
mass transfer and flux characterization needed
Updated Lifecycle of a Contaminant Plume

a) simplified representations of a groundwater plume in space and time

- Expanding plume
- Stable/shrinking plume due to attenuation and/or remediation

b) potential remedial technologies

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<tbody>
<tr>
<td>Technology Examples</td>
<td>Affixed to chemical destruction</td>
<td>Pumps and/or recirculation wells</td>
<td>Permeable reactive barrier</td>
<td>Permaseal injection system</td>
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<td></td>
<td>Naturally elevated removal</td>
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If mass transfer is the final challenge

Interface targeted reagents

- For sites where mass transfer limited flux/release is maintaining concentrations above final RAOs, focus on the problem (interfaces)
- Consider deployment strategies, density viscosity, etc. for in situ design to limit flux

Work from what is known

- Make sure characterization data are actionable
- Select and build remediation systems that are robust to site conditions
- Do not be paralyzed by the many things you do not know
Attenuation Processes in Large Dilute (Aerobic) Plumes

Degradation?
Dispersion?
Sorption?

We performed a parametric analysis to demonstrate the relative importance of the different processes.
A parametric study is a mathematical exercise. We start simple and then add on additional factors to figure out what is important under different conditions.

\[ x = \frac{v_s}{R} t = v_e t \quad \& \quad (C/C_0) = e^{-\lambda t} \]

plug flow w/ sorption

degradation

\[ x = \frac{v_s}{R\lambda} \ln\left(\frac{C}{C_0}\right) = -L\ln\left(\frac{C}{C_0}\right) \]

steady state plume

Plume Structure - Steady State Predicted Concentration
(no dispersion)

For a range of \( L_\lambda \)

Size of steady state plume where concentration reduction is met
Add dispersion and source degradation...

\[ C_{(x,y,z,t)} = C_0 e^{-k t} \frac{f_x f_y f_z}{2^2 2^2} \]

- Source decay
- Flow and longitudinal dispersion
- Transverse dispersion

\[ f_x = \exp\left[ \frac{x}{2} \sqrt{\frac{y^2 + z^2}{u_x}} \right] \exp\left[ \frac{x}{2} \sqrt{\frac{y^2 + z^2}{u_x}} \right] \]

\[ f_y = \exp\left[ \frac{x^2}{2} \sqrt{\frac{y^2 + z^2}{u_y}} \right] \exp\left[ \frac{x^2}{2} \sqrt{\frac{y^2 + z^2}{u_y}} \right] \]

\[ f_z = \exp\left[ \frac{x^2}{2} \sqrt{\frac{y^2 + z^2}{u_z}} \right] \exp\left[ \frac{x^2}{2} \sqrt{\frac{y^2 + z^2}{u_z}} \right] \]

Impact of Logitudinal Dispersion on 1D Steady State Plume Structure

\[ C / C_0 \]

Distance traveled, x (m)
The rate of attenuation in the plume strongly impacts the ultimate size of the plume.

Confirmed EPA preference for degradation processes. Degradation was a dominant natural attenuation mechanism, but any degradation (anaerobic, aerobic or abiotic) can contribute.

Source decay and source remediation can reduce plume size (but not as much as you might expect).

Sorption is not a dominant mechanism unless the source is very short lived (and is less important if the sorbed material is not degrading).

Longitudinal dispersion is not an important attenuation mechanism and can increase plume length in some cases.

Transverse dispersion can contribute to attenuation – but only for large plumes > about 1000 m.
For Large and Dilute Plumes the size and scale of the steady state plumes will be larger than anaerobic sites. Best case aerobic plumes (weak sources and half lives of about 10 years) will stabilize within 1,000m (less than 1 mile) and worst case aerobic plumes (strong sources and half lives of 30 years) will stabilize within about 5,000 to 10,000m (about 3 to 6 miles)

This is what we see in real-world plumes!
Natural Attenuation of hydrocarbons and chlorinated solvents


- Draft AFCEE protocol for fuel hydrocarbons
- Final AFCEE protocol for fuel hydrocarbons
- Draft AFCEE protocol for chlorinated solvents
- Interim U.S. EPA MNA directive
- Final U.S. EPA MNA directive
- NRC Evaluation of MNA Protocols
- DOE & ITRC Enhanced Attenuation Project
- EPA Monitoring Guidelines
- ASTM task group formed
- Draft ASTM standard released
- ASTM standard finalized
- NRC committee formed
- NOBIS protocol for chlorinated solvents (Europe)
- U.S. EPA protocol for chlorinated solvents

MNA experience, papers, proceedings, and creative ideas?

Note: major focus for chlorinated solvents on anaerobic processes
Dominant chlorinated solvent degradation mechanism(s) in aerobic aquifers

Abiotic degradation with reactive mineral phases such as iron sulfides, magnetite (applicable to TCE, CT, etc.)
  John Wilson et al.

Aerobic cometabolism (TCE etc.)
  Hope Lee, et al.

Aerobic direct metabolism (DCE, VC, etc.)
  Paul Bradley, et al.

Hydrolysis (carbon tetrachloride etc.)
  Peter Jeffers, et al.
Abiotic Degradation – reactions with mineral phases

Types of minerals

reactive iron(II) minerals such as pyrite, mackinawite (sulfides), Siderite (carbonate)
mixed iron(II) / Iron(III) minerals such as magnetite, green rusts, and goethite

For several sites, significant attenuation has been documented for magnetite and rates have been correlated to inexpensive magnetic susceptibility measurements -- half lives of 4 to 6 years measured at sites with magnetite present
Aerobic Cometabolism Research Pre-Dates Traditional MNA Timeline

Natural Attenuation of hydrocarbons and chlorinated solvents


McCarty, Semprini, Hazen, Alvarez-Cohen, Fries, …

Lee, Wymore, Looney, …

no toxic daughter products accumulate, maintains high aesthetic water quality…

So why did virtually all natural attenuation and bioremediation research for chlorinated solvents shift to anaerobic? (aerobic slow, indirect process -- active bioremediation difficult to design and not sustainable using hydrocarbon and aromatic reagents…)
**Cometabolism for Chlorinated Solvents**

- **toluene dioxygenase (TDO)**
- **soluble methane monooxygenase (sMMO)**
- **toluene monooxygenases (2-, 3, and 4-TMO)**
- **ammonia monooxygenase (AMO)**
- **toluene dioxygenase (TOD)**
- **Cometabolism for Chlorinated Solvents**

- **trichloroethene (TCE)**

- **chlorella hydrate**
- **TCE epoxide**

- **dichloroacetate halidohydrolase**
- **spontaneous (no enzyme)**

- **formate***
- **glyoxylate***

- **haloacid dehalogenase**
- **trichloroacetate**
- **trichloroethanol***

- **oxalate***

*.... all pathways mineralized to nontoxic terminal products such as CO$_2$, CO, H$_2$O and Cl$^-$
Summary of aerobic cometabolism research

Half lives of about 6 to >40 years have been measured.

Based on current conceptual model the natural attenuation processes appear sustainable and are consistent with the expected microbial ecology of oligotrophic (nutrient limited) systems.

SRNL/INL/PNL team currently working on amendment technology to sustainably enhance aerobic cometabolic rates in L&D settings.
Three Reaction Zones for Mixed Sites

Source: PCE, TCE, DCE, VC, ETH

Zone 1: High Anaerobic Decay Rates (Carbon Present)

Zone 2: Possible Enhanced Aerobic Decay

Zone 3: Low or Background Decay Rates

Putting it all together (REMChlor)
Divide space and time into “reaction zones”, solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone.
Describing a plume’s “space-time story”

REMChlor allows plume to develop for any number of years before remediation (Neat and important).

You can simulate three natural reaction.

You can remediate all or part of the plume by increasing degradation rates for three specific time periods.

The plume will respond to all of these factors:

- natural attenuation processes
  - + plume remediation
    - + source decay
      - + source remediation

EPA currently planning training workshop through C L U-I N c overing R E M C hlor and REMFuel
Some trends in recent modeling results

The concentration reduction required to meet interim or final goals is linked to the amount of source removal needed.

The solubility of the source DNAPL strongly impacts the remediation timeframe (e.g., timeframe for PCE >> TCE). A 90% source reduction does not reduce plume size by 90% -- this type of reduction often has little effect on the ultimate size of the 5ppb contour but a relatively large impact on the 100ppb contour.
The goal of remediation is to protect human health and the environment to the extent practicable.

The ultimate objective is to restore the impacted resource and the services that the resource provides (ecological, drinking water, etc.)

A binary metric (pass-fail) for success may discourage clean-up

A variety of metrics for interim goals are currently being explored -- Mass flux an example metric to link source treatment and plume impacts (but only if cost-effective and reliable flux measuring methods are available) – new concepts such as the “Plume Magnitude Scale” are emerging
Summary for Goal Setting

Interim source/mass balance objectives may be useful for DNAPL source treatments and tie into “combined remedy” constructs

“impacts on the 5 ppb contour are a weak metric for success of the treatment”

“mass flux to the plume to a predetermined level may be a good interim metric”

“impacts on plume structure (e.g., the 100 ppb contour) are more diagnostic metrics of the success of source treatment”

Other regulatory and legal constructs may be needed (e.g., natural resource damage assessment) to effectively compensate for lost resources/services.

Technical impracticability 😞
Finishing up -- M Area Example from the DOE Savannah River Site

2013 is the 30th anniversary of p&t
15 years of SVE
Thermal remediation (steam) of solvent storage tank and M Area Basin
Air sparging, cometabolic bioremediation, ERH and RF heating, oxidant, etc.

Finish up with a quick final look at the real remediation site
We will examine an early mass balance model for source and plume remediation and some current totals
M Area – DOE Savannah River Site
Early Mass Balance

\[
M_{s,t} = \sum_{t=0}^{t} (inputs - outputs) = \sum_{t=0}^{t} (M_R - (M_{SVE} + M_{P&T}))
\]

A simple 1\textsuperscript{st} order equation was developed for each activity and calibrated to about 9 years of remediation operation.
TCE Mass Removal (A/M Area Case Study)

- SVE On
- Pump & Treat On

- Mass Released
- Mass in Groundwater
- Mass Removed
- DNAPL Mass Remaining

Year

1950 2000 2050 2100 2150 2200 2250 2300 2350
Groundwater Concentration Responses (A/M Area Case Study)

Year
Dennis Jackson is currently preparing a paper on M Area (in honor of the 30th anniversary)

Here are some preliminary tally numbers…
<table>
<thead>
<tr>
<th>Method</th>
<th>lbs</th>
<th>% removal based on total from active treatments</th>
<th>% removal based on total est. release of 3.5 million lbs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump and Treat</td>
<td>4900000</td>
<td>33%</td>
<td>14%</td>
</tr>
<tr>
<td>Soil Vapor Extraction</td>
<td>4480000</td>
<td>30%</td>
<td>13%</td>
</tr>
<tr>
<td>Field Testing</td>
<td>36000</td>
<td>2%</td>
<td>1%</td>
</tr>
<tr>
<td>Recirculation Wells</td>
<td>5700</td>
<td>0.40%</td>
<td>0.20%</td>
</tr>
<tr>
<td>Steam / Thermal</td>
<td>508163</td>
<td>34%</td>
<td>15%</td>
</tr>
<tr>
<td><strong>Total from all active</strong></td>
<td>1490000</td>
<td>100%</td>
<td>42%</td>
</tr>
<tr>
<td><strong>MNA (40 yr half life)</strong></td>
<td>1230000</td>
<td>na</td>
<td>35%</td>
</tr>
<tr>
<td><strong>Grand Total</strong></td>
<td>2717098</td>
<td>na</td>
<td>78%</td>
</tr>
</tbody>
</table>
Conclusions – Challenges

Large and Dilute!

Aerobic – relatively slow (“weak”) attenuation rates for chlorinated solvents

Deep

Persistent plumes with long tails due to mass transfer processes

Any treatment must provide sustainable (long-lived) performance and be deployable over a large area for a reasonable cost

Treatments should avoid large scale adverse collateral impacts when possible
Conclusions – Opportunities

remediation “successes” will:

- match technology and deployment to site specific conditions
- focus on actionable data for a reasonable cost
- set technically based realistic and achievable goals
- link source treatment to desired impacts in the downgradient plume
- combine technologies as needed

The is lots of emerging science for the plume: Abiotic processes may be “significant” at some/many sites; aerobic cometabolism occurring at most sites and rates appear to be related to microbial measurements

The breadth of work on remediation amendments may lead to attenuation enhancement materials that are viable for L&D conditions