In-Situ Flushing for DNAPL Source Mass Extraction

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Opening Comment

- In making DNAPL site remediation decisions, we have the option of defaulting to:
  - the certainty & comfort of mandated, prescriptive, conservative endpoints (e.g., MCL) that, in most cases, may not be technically achievable at a reasonable cost and within meaningful timelines,

  instead of considering as alternatives,

  - risk-based, technically achievable, cost-effective endpoints that allow some contamination to be left at the site, but with the obligation for long-term site stewardship, and might have significant public perception concerns, in spite of institutional and other controls.

In-situ Flushing: Technical Basis:

Legacy of Enhanced Oil Recovery Technologies

Addition of "modifiers" to injected fluids for enhanced solubilization, mobilization & desorption:

- Reduction in IFT (Total Trapping Number)
- Density modification for mobility control
  - modify DNAPL (e.g., Pennell et al., 2000, US Patent: 6,099,206)
  - modify groundwater (e.g., Miller, 2001; US Patents: 6,190,092: 6,261,029)
- Reduction in Viscosity (temp??)
- Reduction in wettability (of solid matrix or NAPL)
- Significantly increase desorption & mass transfer rate constants

Types of Source Zones

- LNAPLs & DNAPLs
  - Fuel hydrocarbons (gasoline, diesel, kerosene, aviation fuels)
  - Transformer oils
  - Chlorinated & brominated solvents
  - Coal/oil tars
  - Creosotes
- Also used for sources with metals

Complexity of Field Settings

– **Size of Source Zone**
  - Small (e.g., dry cleaner & gasoline station): tens of m^3
  - Intermediate (e.g., manufacturing sites): 100's m^3
  - Large (e.g., disposal sites): 1000's m^3

– **Hydrogeology**
  - Unconfined, mildly heterogeneous ($\sigma^2_{ln\ \tau} \sim 0.2$)
  - Unconfined, moderately heterogeneous ($\sigma^2_{ln\ \tau} \sim 1$)
  - Unconfined, highly heterogeneous ($\sigma^2_{ln\ \tau} \sim 2$)
  - Fractured media & karst
  - Sediments (streams, rivers, estuaries)???

τ is the "reactive travel time"

“Modifiers” Used

- Cosolvents (e.g., alcohols, ethyl lactate, ketones, ??)
- Surfactants (including food-grade)
- “Sugars” (e.g., cyclodextrins)
- “DOC” (e.g., “humics”)
- Organic acids & other “ligands” (for metals)
- Polymers (e.g., viscosity modifiers)
- Salts (injected fluid density modifiers)
- Foam-control additives & air (??)
- “Heat”??

Technology Status

- Extensive lab testing; scientific basis is well established
- Successful field testing for remediation of LNAPL & DNAPL sources in unconfined aquifers with mild to moderate heterogeneity (70-100?% mass depletion reported)
- Simple & sophisticated numerical and "analytical" models available for scientific uses and site remediation design uses
- Several commercial applications, but not *yet* widely adopted at DNAPL sites

Examples of Recent Papers on In-Situ Flushing

- McGuire TM, McDade JM, Newell CJ 2006 Performance of DNAPL source depletion technologies at 59 chlorinated solvent-impacted sites GROUND WATER MONITORING AND REMEDIATION 26 (1): 73-84
- Oostrom M, Dane JH, Wietsma TW. 2006. A review of multi-dimensional, multi-fluid intermediate-scale experiments: Nonaqueous phase liquid dissolution and enhanced remediation VADOSE ZONE JOURNAL 5 (2): 570-598 MAY 2006
- Christ JA, Ramsburg CA, Abriola LM, Pennell KD, Loffler FE 2005 Coupling aggressive mass removal with microbial reductive dechlorination for remediation of DNAPL source zones: A review and assessment ENVIRONMENTAL HEALTH PERSPECTIVES 113 (4): 465-477
- Lee M, Kang H, Do W 2005 Application of nonionic surfactant-enhanced in situ flushing to a diesel contaminated site WATER RESEARCH 39 (1): 139-146
- Martel R, Foy S, Saumure L, et al. 2005.Polychlorinated biphenyl (PCB) recovery under a building with an in situ technology using micellar solutions, CANADIAN GEOTECHNICAL JOURNAL 42 (3): 932-948
- Saichek RE, Reddy KR. 2005. Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: A review CRITICAL REVIEWS IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY 35 (2): 115-192
- Tick GR, Lourenso F, Wood AL, et al. 2005. Pilot-scale demonstration of cyclodextrin as a solubility-enhancement agent for remediation of a tetrachloroethene-contaminated aquifer ENVIRONMENTAL SCIENCE & TECHNOLOGY 37 (24): 5829-5834
- Schaerlaekens J, Feyen J 2004 Effect of scale and dimensionality on the surfactant-enhanced solubilization of a residual DNAPL contamination JOURNAL OF CONTAMINANT HYDROLOGY 71 (1-4): 283-306

In-Situ Flushing Case Studies*
Generation-1 Technology?

* Lauren Strbak, July 2000
http://clu-in.org/download/studentpapers/strbak_flushing.pdf

Why isn't In-Situ Flushing Used More at DNAPL sites?

- No champions in regulatory agencies
- Early concerns about injecting "modifiers" into aquifers for remediation
- Early design/implementation problems
- Misperceptions about "success"
- Misunderstandings about "cost"
- Concerns about "efficiency"
- Lack of large-scale applications @ DNAPL sites w/adequate performance monitoring
- Not enough "committed" technology vendors
- Gen-2 Innovations not yet used at many DNAPL sites?

Second Generation Surfactant Flushing*: Five Key Innovations

- **Well Placement and Screening**
- **Surfactant Formulation**
- **Pore Volumes Injected**
- **Manifolding of Injection & Extraction Wells**
- **Surfactant Disposal**

* Shiau et al., May 2006. Recent advances in surfactant-enhanced aquifer remediation: The Golden, OK case study. Battelle Conf., Monterey, CA.

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DNAPL Source Remediation Goals*

EPA Groundwater Task Force, 2004

- **Site owners:** Cleanup to drinking water standards (e.g., MCLs) not realistic, but are rarely allowed to use alternative goals. Benefits of source mass depletion are outweighed by disadvantages.
- **Technology developers:** Significant mass depletion possible, but stringent cleanup goals inhibit technology use. Alternative performance goals are more relevant.
- **Site managers:** Alternative goals cannot be applied because source zone has not been reliably delineated from plume. No accepted performance measures to determine effectiveness. Concerns about uncertain reliability & long-term costs of alternative goals.

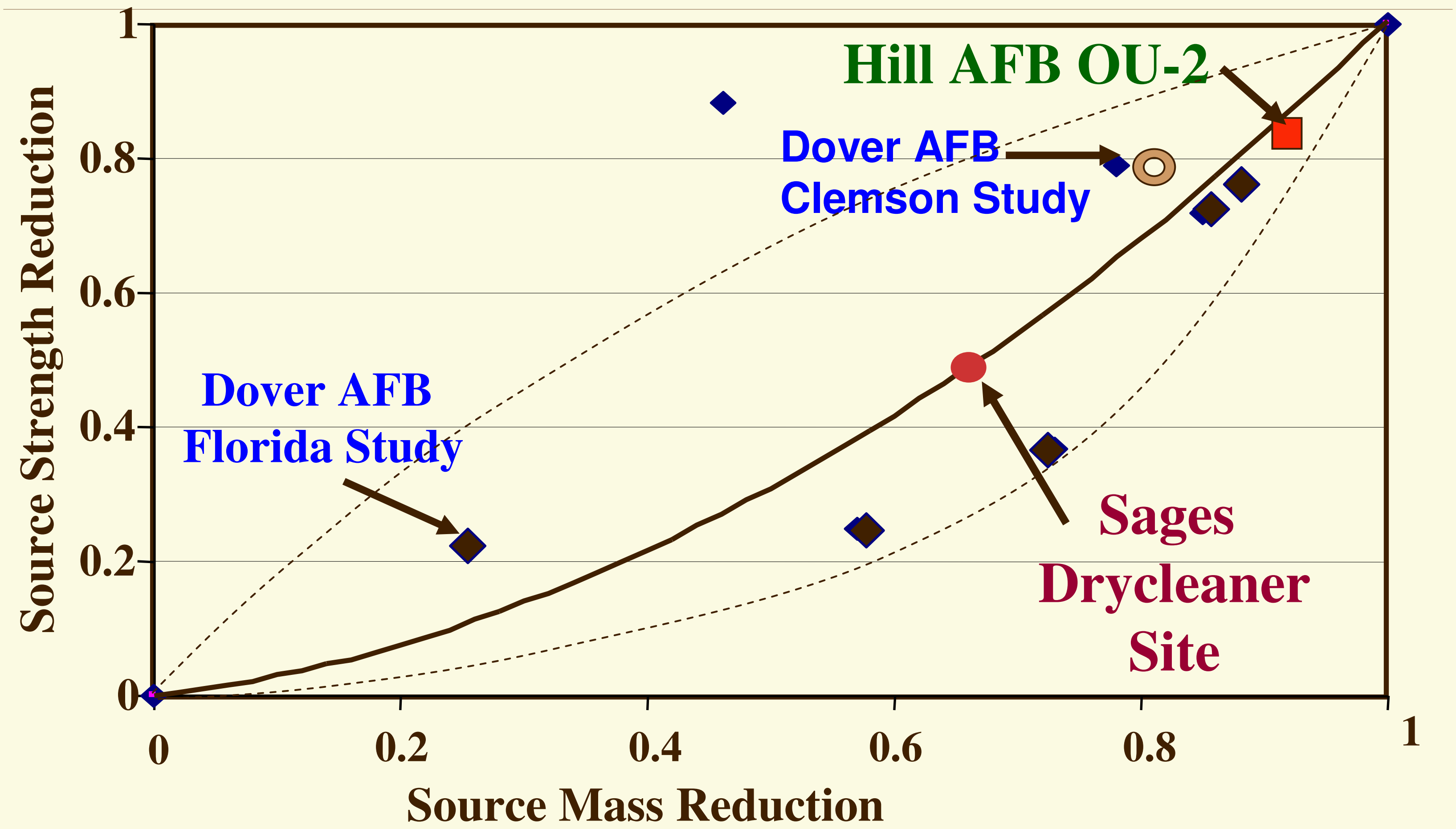
* http://gwtf.cluin.gov

Performance metrics included in evaluation:

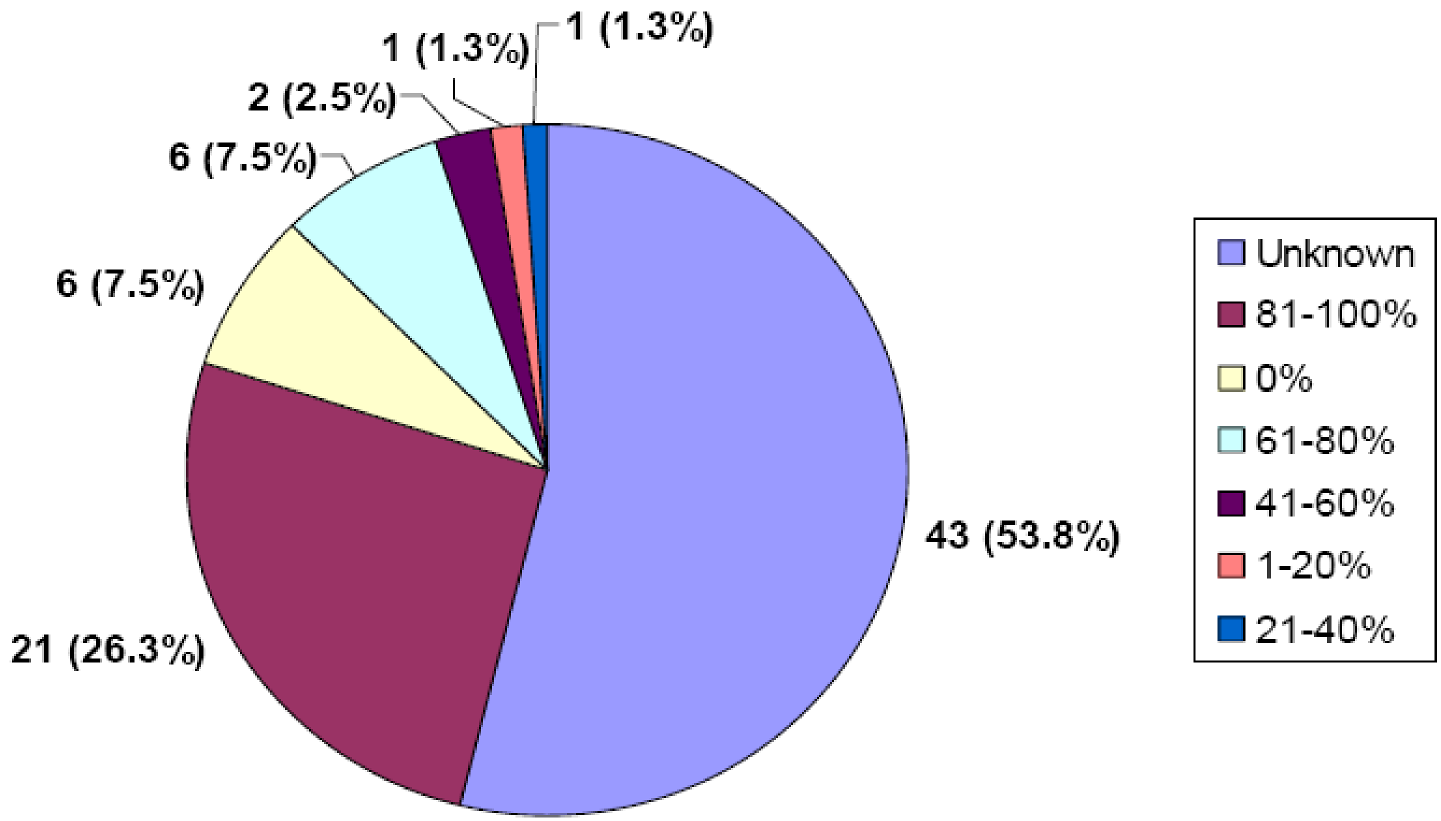
- *Impact to DNAPL source:*
  - Reductions in DNAPL mass
  - Reductions in soil concentrations
  - Reductions in source zone lifespan
- *Impact to plume:*
  - Reductions in concentrations
  - Achievement of MCLs
  - Reduction in mass flux/discharge
  - Changes in plume stability/growth
- *Adverse remedial impacts*
  - DNAPL mobilization
  - Adverse changes in 2ndry gw quality
  - Poor attenuation of toxic byproducts
- *Implementation considerations:*
  - Unit cost (volume/mass)
  - Treatment duration
  - Occurrence of rebound
  - Achievement of site closure

Slide courtesy of Carmen Lebron, NFESC (2006)

DNAPL Source Remediation: In-Situ Flushing Field Studies



Decrease in Mass Flux:



Total number of Sites with Mass Flux Data = 80

*From: Assessing the Feasibility of DNAPL Source Remediation: Review of Case Studies. Naval Facilities Engineering Command, Contract Report (May 2004), CR-04-002-ENV. **Slide Courtesy of: Carmen Lebron, NFESC (2006)**

Performance of DNAPL Source Depletion Technologies*

- Data for 147 wells at 59 DNAPL source depletion sites were examined.
- Technologies included: Chemical Oxidation; Enhanced Bioremediation; Thermal Treatment; Surfactant/Cosolvent Flushing
- Criteria: CVOC conc.; rebound; treatment duration
- At 11 sites for which data were evaluated, "*concentration reduction for a given mass reduction was within 30% of the 1:1 relationship at most sites*."
  [Note: This implies Γ~1, and source longevity large].
- However, MCLs were not achieved & sustained at all wells.

* McGuire, McCade, Newell, 2006. GWMR 26(1):73-84

In-Situ Flushing & Changes in Source & Flux Architecture*

- ***The contaminant flux architecture at the source control plane (CP) is essentially invariant with time.***
- For DNAPL source zones cleaned up through in-situ flushing, areas with high contaminant fluxes remain high throughout the DNAPL mass depletion process.
- The contaminant flux distribution at the source CP gradually *fades away* with time.

*Details to be included in: Basu et al., 2006 (in preparation)

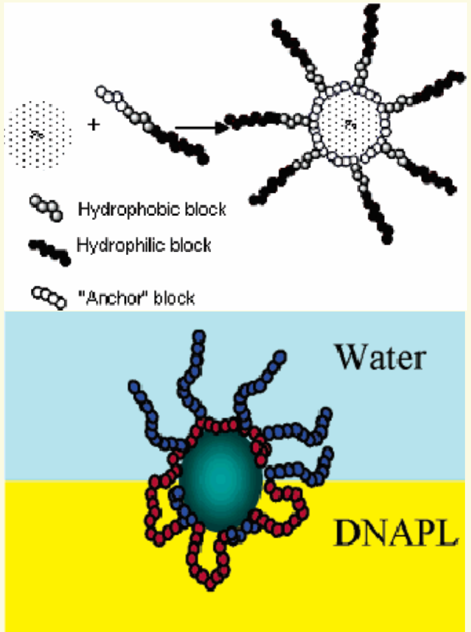
Technology Integration:

Combined Uses as "enhancers" with other technologies

- Enhanced reduction
  - **Surfactants & cosolvents with ZVI (UF)**
  - **Emulsified ZVI (Reinhart et al., 2003, 2006; US Patents: 6,664,298; ?? (NASA)**
- Enhanced oxidation
  - **Permanganate (LFR Levine Fricke, 2005; US Patent 6,869,535; Purdue; Colorado School of Mines**
- Enhanced Air Sparging (& SVE?)
  - **Kim et al.; UF: Purdue**
- Electro-kinetically Enhanced Flushing
  - Reddy & Saichek (UIC)

Surfactant-Assisted Delivery of Nano-Iron Particles

Targeting of the NAPL-water interface



Saleh et al. 2005 *Nano Let.*

Encapsulations

Quinn et al. 2005 *ES&T*

Allaire and Ramsburg, 2006 unpublished

Delivery & Influence on NAPL Architecture?

Ramsburg et al. 2004 *JCH*

- Encapsulation of active ingredients has been demonstrated.
- Design must consider the stability of the NAPL architecture

Courtesy of: Andrew Ramsburg, Tufts Univ.

Technology Integration:

Sequential Uses with other technologies as "chasers" or "finishing" step

- Cosolvents/surfactants followed by reductive dechlorination (UF, Michigan, Hill OU2,?)
- Surfactants followed by low level chem. ox (Fenton) (B. Shiau, 2005, US Patent 6,913,419); Surbec LNAPL sites (e.g., Golden, OK)
- Thermal followed by low-level cosolvent/surfactant (primarily as e-donors)??
- Cosolvent/Surfactant flood followed by n-ZVI??
- ??

Integration of Remedial Technologies: Combinations, Sequencing & Optimization

Pre-Flood Source Management	Source Removal	Post-Flood Plume Management
Free-phase recovery	In-situ Flushing	Natural Attenuation
SVE/sparging		Enhanced Bioremediation
Physical Barriers		Bio-Sparging
Pump and Treat (hydraulic Containment)		Pump and Treat
		Permeable Reactive Walls
		Chemical oxidation

Technology Implementation Challenges

- Concerns about “uncontrolled migration” & expansion of source zone
- “Incomplete” cleanup (Compliance/Closure)
  - Hydrodynamic Access
  - Sweep Efficiency
- Recovery/Reuse of “modifiers”
- Costs & Competitiveness
  - Net Present Value
  - Cost-to-Complete
- Scale – Which “niche” markets?

Research Needs

– Defining DNAPL source treatment goals by linking to benefits derived in the plume zone:

- How much source mass should be depleted to achieve target source strength? (Mass reduction & Flux reduction relationships; what is Γ value? Initial mass?)
- Where should mass depletion be targeted? Is cleanup of "hotspots" sufficient? (Source & flux architecture changes with remediation)
- What is the role of mass *not* depleted (diffusive fluxes from low-permeability zones)?
- What is the required e-donor flux to *enhance & sustain* plume attenuation?
- Importance of increased total VOC flux??

Research Needs

– Secondary effects

- Concerns about eco-toxicology
  - Changes in microbial diversity & functions
  - Increased BOD effects
- Concerns about human-health effects
  - Safety issues (flammable?)
  - Mobilization of metals (e.g., Fe, Mn under reducing conditions induced by e-donor addition)
  - Human-health effects of modifiers