Remediation of DNAPL Sites

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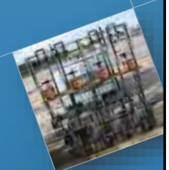

Premise

- Complex sites (such as those containing dense nonaqueous phase liquids (DNAPLs) are some of the most difficult to clean up.
- Multiple-technology remedies often needed to achieve objectives.
- How do you efficiently construct a remedy and set goals at these Sites?

Outline

- Establishing Realistic Remedial Goals
- DNAPL Remedial Technologies
- Evaluating Performance
- Case Studies
- Discussion

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Acknowledgements (and apologies)

- Jennifer Griffin – NEWMOA
- Interstate Technology Regulatory Counsel (ITRC)
- Dr. Tamzen Macbeth, CDM Smith

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Two Key ITRC Guidance Documents

Remediation of DNAPL Sites

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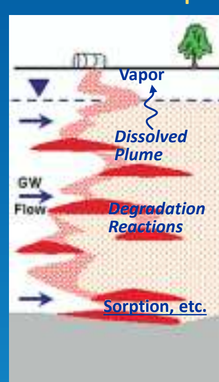
Setting Realistic Goals Requires Understanding of Chemical Phases and Transport of DNAPL Releases

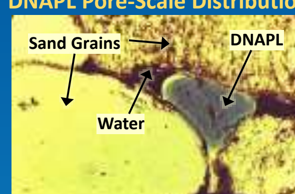
- DNAPL movement and capillary forces
- Chemical phase distribution
- Interphase chemical mass transfer
- Dissolved plume formation & transport
- Vapor migration

Generalize DNAPL Release and Transport

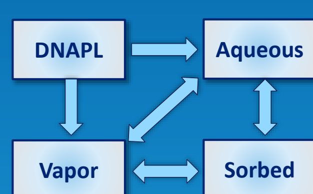


(Modified from Parker et al, 2002)

DNAPL Pore-Scale Distribution



Interphase Chemical Mass Transfer



ITRC IDSS-1, Figures 2-1, 2-3

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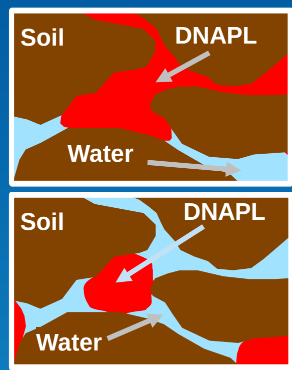
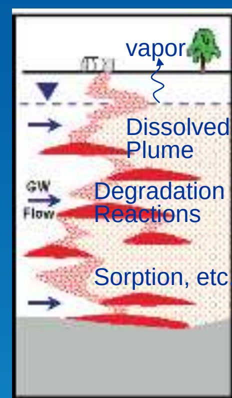
Mobile DNAPL vs. Residual DNAPL vs. Sorbed Contaminant

- Mobile DNAPL
  - Interconnected separate phase that is capable of migrating
- Residual DNAPL
  - Disconnected blobs and ganglia that are not capable of migrating
- Sorbed Contaminant
  - No longer a NAPL
  - Still a residual source





(Modified from Parker et al, 2002)

ITRC IDSS-1, Figure 2-2

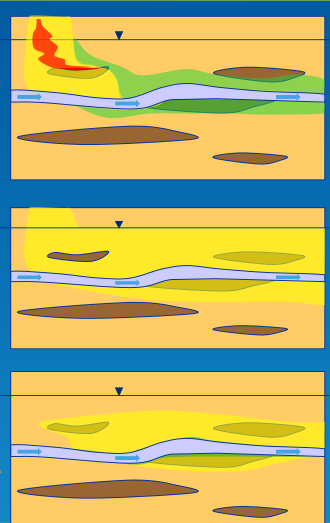
Age of Release's Effect on Plume Response

- Response is dependent on stage of plume evolution
- Is contaminant mass accessible to treatment?
- *In situ* treatment often preferentially treats high permeability zones
- "Back-diffusion" controls plume response

Early Stage

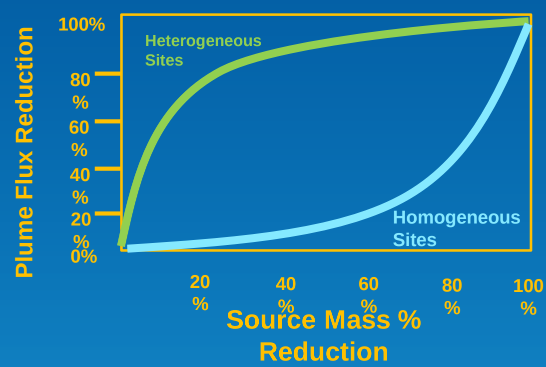
Middle Stage

Late Stage\



Plume Response to Source Treatment

- Mass flux vs. concentration basis
- Heterogeneous sites – greater plume response
- Homogeneous sites – lesser plume response
- Tools – EPA REMChlor (Falta et al, 2007)



Modified from Basu, et al. (2008)

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Establishing Realistic Remedial Goals

- First and foremost – Address/Prevent Exposure
- Source Removal, Source Reduction, Containment or Control?
- Regulatory Requirements
- MCLs vs. Mass Discharge
- Regulatory Approaches
- Communication

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CERCLA and the National Contingency Plan

- Under CERCLA 121(d)(2)(A), groundwater response actions are governed in part by the following mandate established by Congress
  - Such remedial action shall require a level or standard of control which at least attains Maximum Contaminant Level Goals
- Furthermore, the NCP (40 CFR §300.430(a)(1)(iii)(F)) includes general expectations for purposes of groundwater restoration as follows:
  - EPA expects to return usable ground waters to their beneficial uses wherever practicable, within a timeframe that is reasonable given the particular circumstances of the site. When restoration of ground water to beneficial uses is not practicable, EPA expects to prevent further migration of the plume, prevent exposure to the contaminated ground water, and evaluate further risk reduction.

USEPA's Recent Groundwater Strategy


EPA United States Environmental Protection Agency

Groundwater Remedy Completion Strategy

Moving Forward with the End in Mind

A Groundwater Remedy Completion Strategy is a recommended site-specific course of actions and decision making processes to achieve groundwater RAOs and associated cleanup levels using an updated conceptual site model performance metrics and data derived from site-specific remedy evaluations.

If the existing remedy will not achieve RAOs and associated cleanup levels, either the remedial technology or the comprehensive remedy should be modified.

- *Evaluate the groundwater's restoration potential*
- *Evaluate other technologies*
- *Select alternative approach/modify RAOs*
- *Conduct Technical Impracticability (TI) evaluation*

Remediation of DNAPL Sites

MCP Source Control Requirements

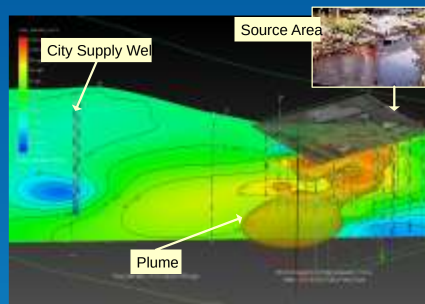
- 310 CMR 40.1003(5), Source Elimination or Control.
  - A Permanent or Temporary Solution shall not be achieved unless and until each source of OHM Contamination is eliminated or controlled:
  - (a) for a Permanent Solution, is eliminated or controlled
  - (b) For a Temporary Solution, is eliminated or controlled, to the extent feasible
  - (c) Parties conducting response actions shall seek to eliminate each Source of OHM Contamination. In cases where such elimination is not feasible, response actions shall control each Source of OHM Contamination.

Connecticut Department of Energy and Environmental Protection (CT DEEP) RSR Amendment Package Wave 2

- **MNA General Pre-Requisites:**
  - Source contaminant must be removed or controlled
  - Soil remediation completed to meet the
    - Direct Exposure Criteria (DEC)
    - Pollutant Mobility Criteria (PMC)
  - No migrating or mobile LNAPL present
  - MNA not applicable to DNAPL
  - MNA not applicable at SW discharge point above 10 times the acute toxicity level (WQS)
  - No one currently exposed to the groundwater that exceeds GW Protection Criteria or Volatilization Criteria

Building the Remedial Action Framework

- Evaluate relationship between source strength, contaminant plume transport and impact to receptors.
- Critical Parameters to Evaluate:
  - Receptors and associated risk pathways
  - Source strength
  - Aquifer assimilation capacity for plume contaminants
  - Contaminant plume dynamics- expanding, stable, shrinking



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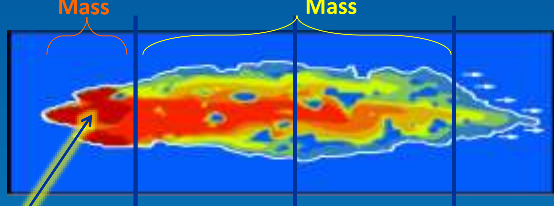
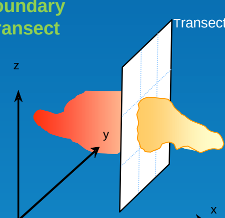
Mass Balance and Flux-Based Site Metrics





Understanding site mass balance can lead to consideration of alternative site remedial objectives possibly based on mass discharge or mass flux

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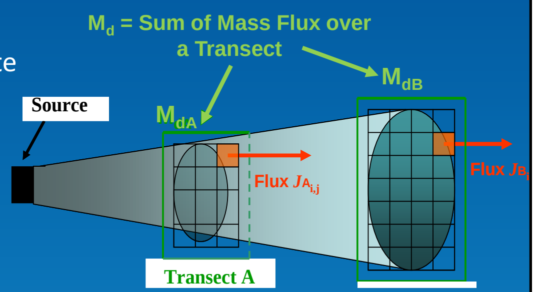
Mass Discharge for a Contaminant Plume

- Mass discharge (M_d)
  - The total mass of any solute conveyed by a plume at a given location per time
  - M_d is a scalar quantity, expressed as mass/time
- Mass per time [M/T]
- Source or plume strength
- Analogous to Total Maximum Daily Loads (TMDLs)



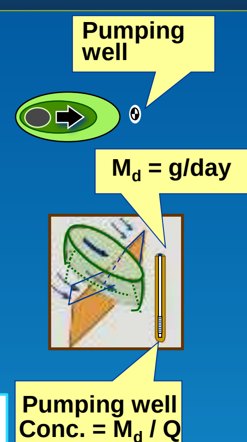
J_{Aij}= Individual mass flux measurement at Transect A

M_{dA}= Mass discharge at transect A

$$M_{dA}=\Sigma[J_{aij} \times A]$$

Concentration vs. Mass Discharge

- ***Traditional Concentration Approach:*** Measure existing plume to assess
  - Impact on receptor (MCLs)
  - Natural attenuation rates
  - Remedial options
- ***Mass Discharge Approach:*** Define rate across specified cross-sectional areas of plume to assess
  - Impact on receptor (TMDLs)
  - Natural attenuation rates
  - Remedial options

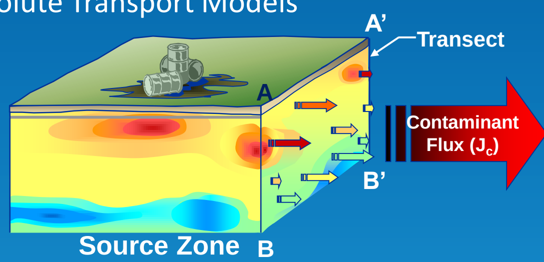


KEY BENEFITS: **Mass discharge approach potentially offers a better understanding of potential risks and attenuation rates, and can lead to sounder remediation strategies.**

Mass discharge approach based on Einarson and Mackay (2001) ES&T, 35(3): 67A-73A

Mass Flux Mass Discharge Measurement Methods

- Method 1: Transects (wells or multilevel samplers)
- Method 2: Well Capture/Integral Pump Tests
- Method 3: Passive Flux Meters
- Method 4: Existing Historical Data
- Method 5: Solute Transport Models



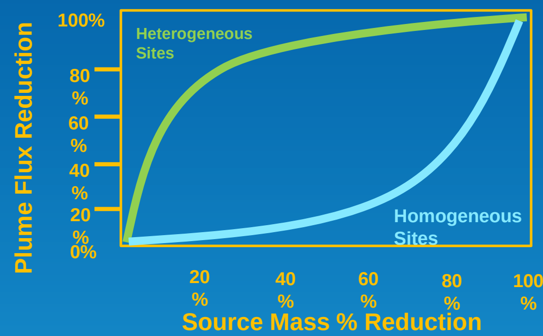
Alternative Remedial Goals

- Mass Discharge at a control plane such source zone, property boundary or surface water discharge (e.g., TMDLs)
- Alternative concentration-based metric with a treatment or buffer zone.
- Natural attenuation-based flux or mass discharge to transition site to MNA.

What degree of source remediation → combined with natural attenuation in the plume → will be protective of the Receptor?

Interim and Transitional Remedial Goals

- Goals applied to different portions of the source and plume
- When to transition from one technology to another
- When to transition from active to passive remediation (MNA)

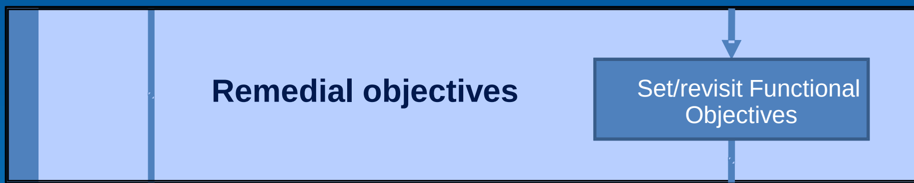


Consider "OoMs" when setting Remediation Goals

Why use Orders of magnitude (OoMs) for remediation?

- Orders of magnitude are powers of 10
- Hydraulic conductivity is based on OoMs
- VOC concentration is based on OoMs
- Remediation performance (concentration, mass, mass discharge) can be also evaluated using OoMs….
  - 90% reduction: **1** OoM reduction
  - 99.9% reduction: **3** OoM reduction
  - 70% reduction: **0.5** OoM reduction
    Example:
  - Before concentration 50,000 ug/L
  - After concentration 5 ug/L
  - Need **4 OoMs** (99.99% reduction)

Remedial Objectives



- How do you define objectives in a clear and concise manner?
- What is the process to make your objectives SMART?
  - (specific, measureable, attainable, relevant, and time bound)

Types of Objectives

- Absolute objectives
  - Based on broad social values
    - Example: protection of public health and the environment
- Functional objectives
  - Steps taken to achieve absolute objectives
    - Example: reduce loading to the aquifer by treating, containing, or reducing source

Functional Objectives Should be SMART

SMART means:

- **Specific**
  - Objectives should be detailed and well defined
- **Measureable**
  - Parameters should be specified and quantifiable
- **Attainable**
  - Realistic within the proposed timeframe and availability of resources
- **Relevant**
  - Has value and represents realistic expectations
- **Time-bound**
  - Clearly defined and short enough to ensure accountability

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Functional Objectives Time Frame

- Time frame should accommodate
  - Accountability
  - Natural variation of contaminant concentration and aquifer conditions
  - Reliable predictions
  - Scientific understanding and technical ability
- ITRC suggests 20 years or less for Functional Objectives

Site management and active remediation timeframe may continue much longer

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Communication – The Key to Acceptance

- Stakeholders
  - Regulators, Responsible Parties, Affected Parties, General Public
- Conceptual Site Model
  - Key to understanding what is possible
- Absolute Objective
  - Protection of Human Health and the Environment
  - First and foremost – Address/Prevent Exposure
  - Restoring Aquifers / beneficial use.
- Functional Objectives
  - SMART
  - Interim goals and metrics
  - Planned transitions

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DNAPL Treatment Technologies

- Technologies have limitations, especially in heterogeneous DNAPL source zones
- How do you to avoid the trap of relying on a single remedial technology that won't get the OoMs reduction you need, in the timeframe you need it?

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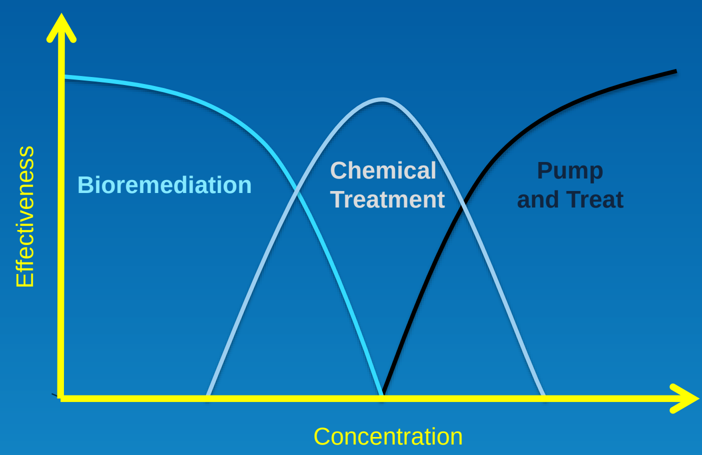
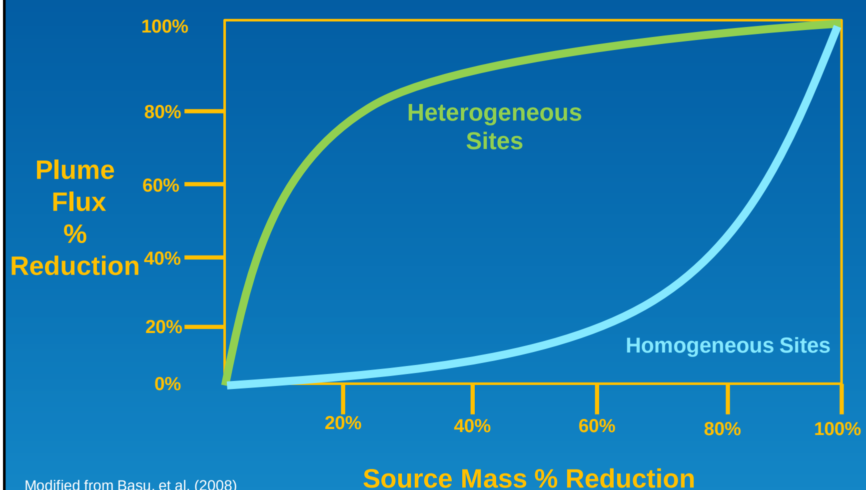
Technologies have Limitations



Jeremy Birnstingl, Regenesis UK

It becomes harder and harder to reduce plume flux at heterogeneous DNAPL sites

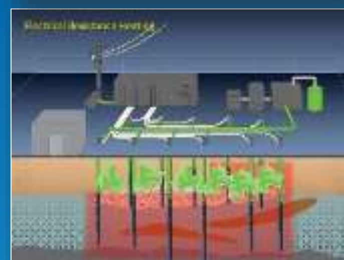


Modified from Basu, et al. (2008)

Technology Category 1: Remove
Physical Removal

- Excavation
- Thermal remediation
  - Reduction in source concentration
    Detailed study of 14 Sites[1]
    ≤ 1 OoMs at 9 sites

    ≥ 2 OoMs at 4 sites



[1]Kingston et al, 2010

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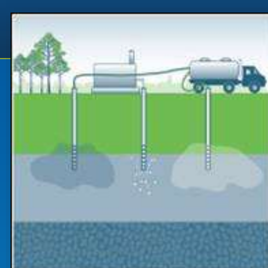
Technology Category 2: React
Chemical / Biological

- *In situ* chemical oxidation
  - Median **0.3 OoMs** for *CVOCs*[1]
  - This and other studies*: rebound more prevalent for ISCO than other technologies*
- *In situ* chemical reduction
  - Deep soil mixing "ZVI Clay" Process: Median **1.7 OoMs**[2]



[1]Krembs et al., 2010
[2]Olsen and Sale, 2009

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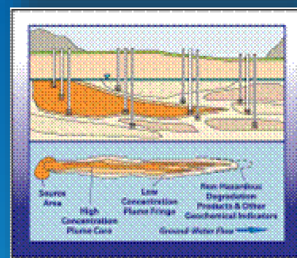
Technology Category 2: React Chemical / Biological (continued)

- Enhanced bioremediation
  - Median **1.3 OoMs** for *Parent*[1]
  - Median **0.4 OoMs** for *Total CVOCs*
- Monitored natural attenuation (MNA)
  - Median **0.6 OoMs** over average of nine years of MNA at 26 "low-risk" CVOC sites[2]
  - Sole remedy at 30% of 45 chlorinated MNA sites[3]



[1]McGuire et al., 2006
[2]Newell et al., 2006
[3]McGuire et al., 2004

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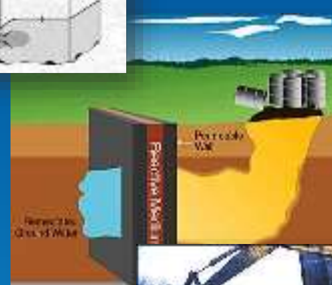
Technology Category 3: Contain

- Pump and treat
- Permeable reactive walls
  - Zero Valent Iron Walls: Median **0.8 OoMs** TCE from six sites[1]
- Low-permeability barriers
  - 83% of sites met design objectives[2]
- Solidification/stabilization



[1]Liang et al., 2010
[2]U.S EPA, 1998

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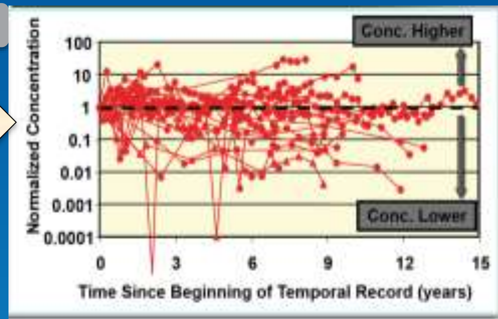
Attenuation of Source Zones

An emerging consensus: YES

1. **Long-term monitoring data showing source attenuation**
2. **Source attenuation modeling tools (BIOChlor, REMChlor, NAS)**



Long-term temporal records from 22 monitoring wells at 13 Untreated TCE Sites (Newell et al., 2006)

2004 survey of 191 sites- MNA was the sole remedy (no active source remediation) at 21% of sites with CVOC concentrations > 10 mg/L (McGuire et al., 2004)

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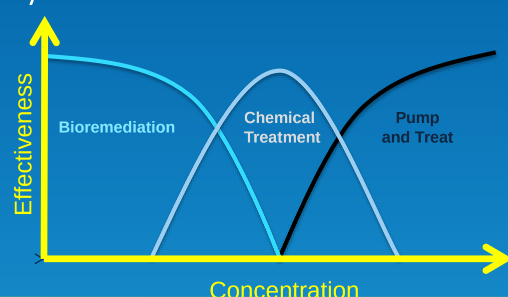
Technology Coupling

- Three types of coupling: *temporal, spatial, simultaneous*
- Potential approaches:
  - Intensive technology followed by passive
  - Different technology for Source versus Plume
  - Any technology followed by MNA

If we know we have a complex DNAPL site, we can plan early to combine technologies during the remedial action



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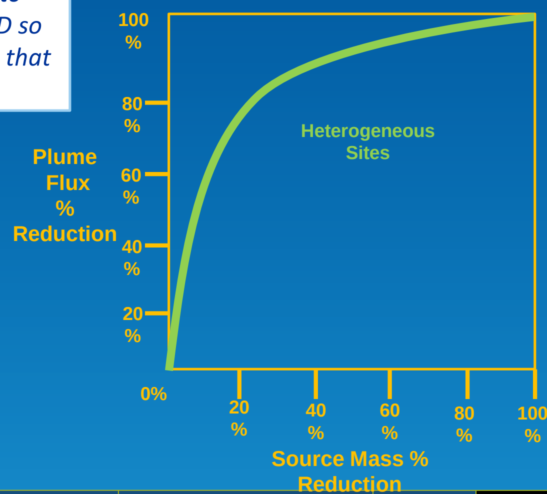
Transitioning Between Technologies

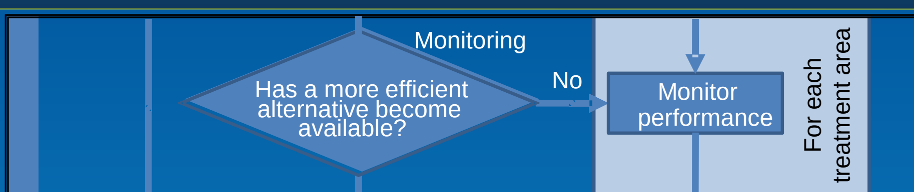
At complex DNAPL sites, one idea is to write transition triggers into the ROD so we don't overspend on technologies that have outlived their effectiveness

Potential Transition Triggers:

- Technology cost-effectiveness meets a certain point ($/cy)
- Contaminant concentrations in source zone decrease to *x* ug/L
- Mass discharge to plume reduces by *x* %



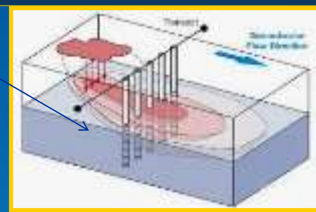
Monitoring and Evaluating Performance



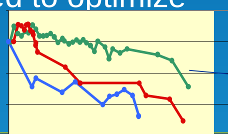
- How do you design a monitoring program that assesses your progress towards reaching your functional objectives?
- What data should you collect to evaluate remedy performance?

Type of Monitoring

- **Performance Monitoring**
  - At end of the day, did it work?
  - Compare to SMART functional objectives



- **Process Monitoring**
  - We turned it on – is it working correctly?
  - Data used to optimize system



- **Compliance Monitoring**
  - How are we compared to regulatory limits?
  - Is everyone safe?

Point of Compliance Well

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Metrics

- Concentration: → mg/L, mg/kg, ppmv
- Mass of contaminants: → Kilograms
- Mass Flux/ Mass Discharge: → Grams per m^2 per day; Grams per day

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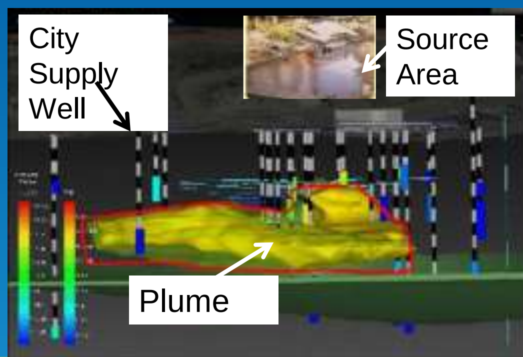
Data Evaluation – Remediation can be the next stage of site characterization

- Key concept: ***Maintaining*** and ***Improving*** the Conceptual Site Model
  - Visualization tools can help
  - Stats help you understand *trends*



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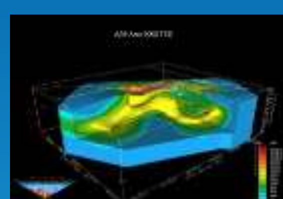
Modeling for Performance Monitoring

- Source zone models
  - Simulates impact of remediation or MNA on source
- Fate and transport models
  - Evaluates plume stability
- Example:
  - *REMChlor* – Search "REMChlor EPA"
  - *NAS* – Search "Natural Attenuation Software"



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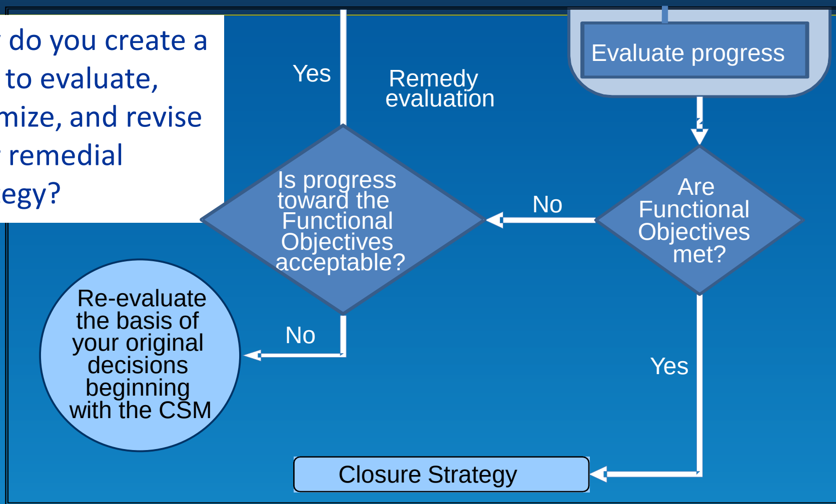
Remedy Evaluation

- How do you create a plan to evaluate, optimize, and revise your remedial strategy?



ITRC IDSS-1, Figure 1-2 excerpt

Outline

- Establishing Realistic Remedial Goals
- DNAPL Remedial Technologies
- Evaluating Performance
- **Case Studies**
- **Discussion**

Well 12A

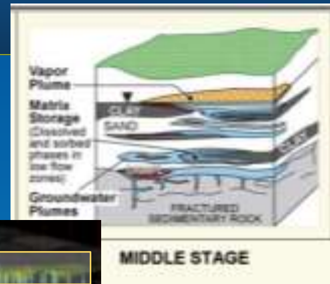
CASE STUDY: SETTING REMEDIAL OBJECTIVES AT A COMPLICATED DNAPL SITE

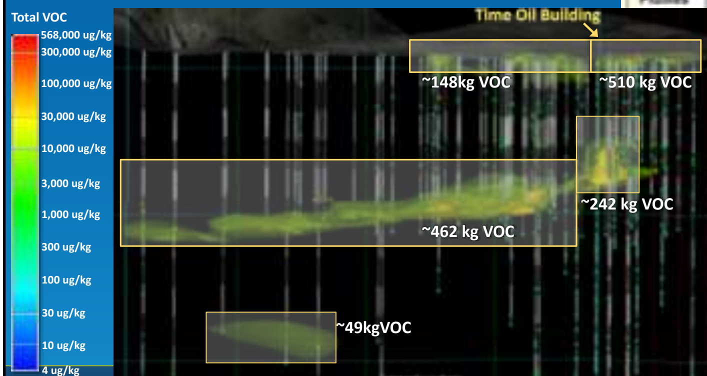
TCE Source Zone and Plume Impacting Water Supply Well 12A in Tacoma, WA

Tacoma supply wells are green symbols

Well 12A is a "Middle Stage" Source Zone Site

Both DNAPL and Matrix Diffusion



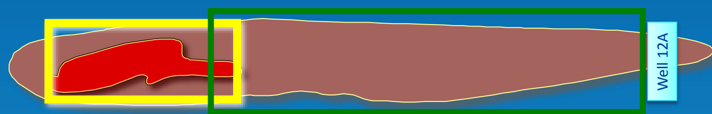


A long ROD history . . .

- ROD signed 1983
- ROD amendment 1985
- ROD modification 1987
- 1993, 1998, 2003, and 2008.
- The reviews documented:
  - Cleanup goals for the site have not been attained
  - Extraction wells not performing at the expected rate
  - NAPL is present
  - Existing pump and treat is not providing containment and treatment of the entire contaminated groundwater source

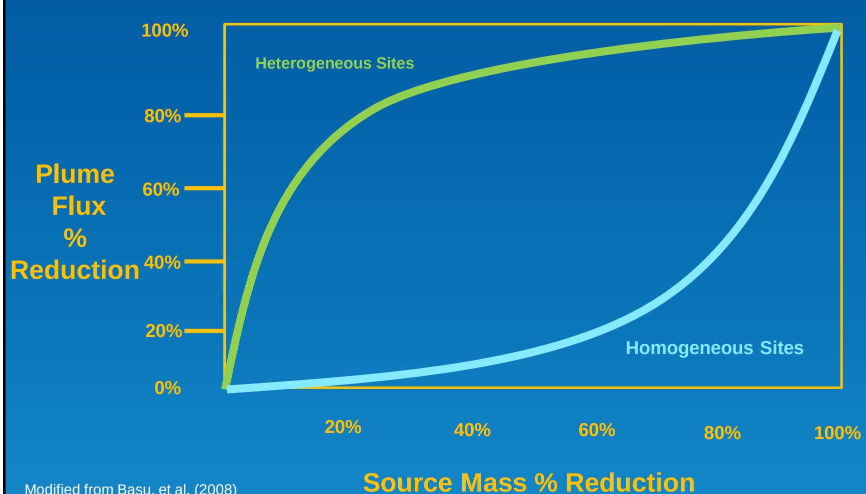
Setting Realistic Goals for a Complex DNAPL Site

- DNAPL in a heterogeneous geology plus matrix diffusion
- Long history of ineffective treatment
- Drinking Water supply wells are impacted
- **What are realistic and cost-effective remedial goals for this site?**



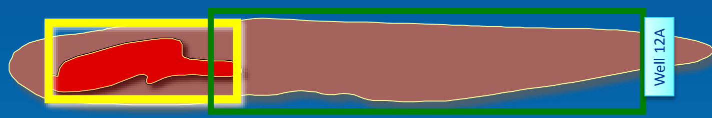
What degree of source remediation → combined with natural attenuation in the plume → will be protective of the Receptor?

Relationship between Source Mass Reduction and Plume Flux Reduction is rarely linear



Modified from Basu, et al. (2008)

2009 ROD Amendment. First ROD in the US to incorporate mass discharge reduction goals



Tier 1: Reduce mass discharge from the source to the plume by 90% in 5 years

Tier 2: GW criteria are being met at interim compliance points between source and receptor

Tier 3: Monitor natural attenuation of residual contamination

Source remedy will be considered "operational and functional" when mass discharge from the source area to the plume has been reduced by 90%

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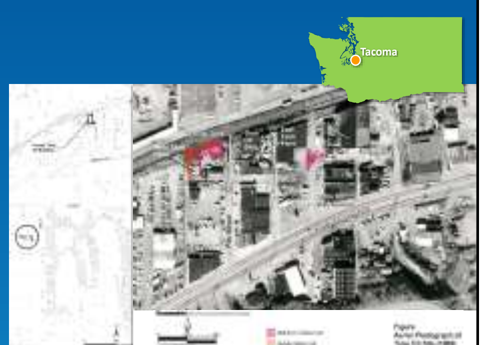
Combined Technologies in Source Zone

- Multi-component remedy
  - Excavation
  - *In situ* thermal remediation (ISTR)-
    - address NAPL
  - Enhanced anaerobic bioremediation
    - (EAB)- address concentrated plume
  - Groundwater extraction and treatment system (GETS) - existing source pump and treat system



Note that Tier 1 goal is *not* "source remedy will be considered operational and functional when groundwater is restored in source zone to drinking water quality."

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Well 12A SMART Functional Objectives

- SMART Functional Objective
  - Reduce mass discharge from the source zone to the plume by 90% in 5 years
- Meets SMART Criteria
  - Specific – Yes, 90% reduction
  - Measureable – Yes, via transects or pumping well
  - Achievable – Yes, excavation and/or thermal
  - Relevant – Yes, protection of drinking water well/resource
  - Time-bound – Yes, 5 years

Remediation of DNAPL Sites

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Well 12A Conclusions

- The long-term objective is still restoration of the aquifer as a drinking water source
- Three-tiered compliance
  - to allow for a multi-component remedy
  - and Transition Triggers from one treatment technology to another.
- Source remedy (thermal, EAB, excavation) will be considered “operational and functional” based on a mass discharge reduction goal and *not* MCLs

Well 12A is an example for setting Realistic Remedial Goals for source zone remediation where there is DNAPL and matrix diffusion in heterogeneous geology.

Remediation of DNAPL Sites

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Remediation of DNAPL Sites

- Complex sites such as those containing dense nonaqueous phase liquids (DNAPLs) are some of the most difficult to clean up.
- Multiple-technology remedies often needed to achieve objectives.
- SMART, functional and interim goals and good communication facilitate remediation progress.