Remediation of DNAPL Sites

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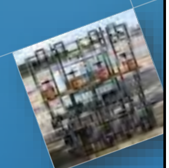
February 10, 2015



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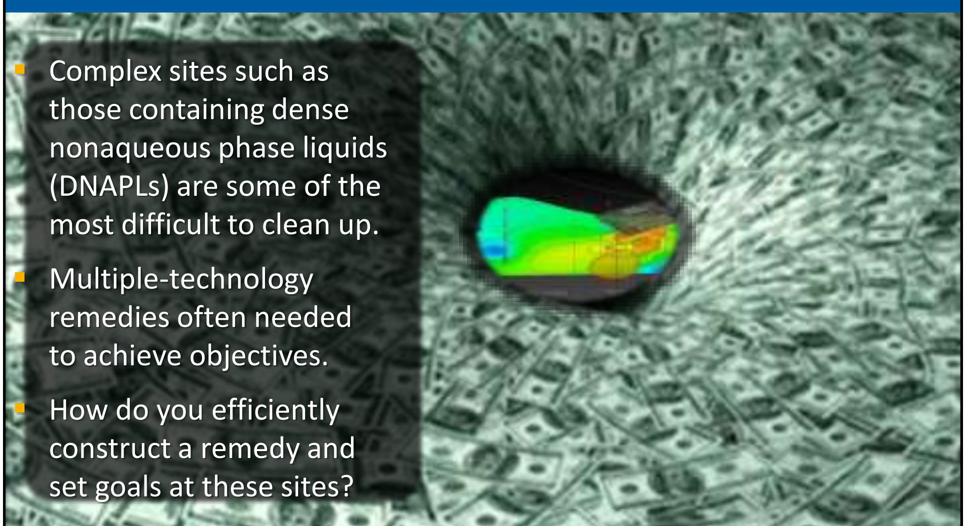
Premise



- 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

- **DNAPL Remediation Technologies**
- Establishing Realistic Remedial Goals
- Case Studies
- Discussion

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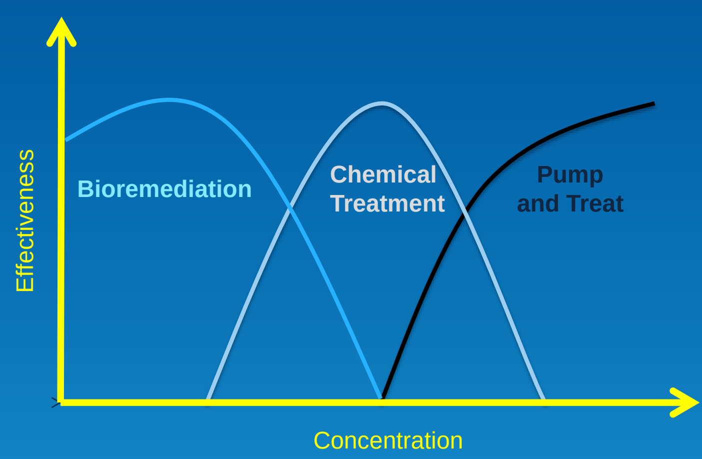
Technologies have sweet spots as well as limitations



Jeremy Birnstingl, Regenesis UK

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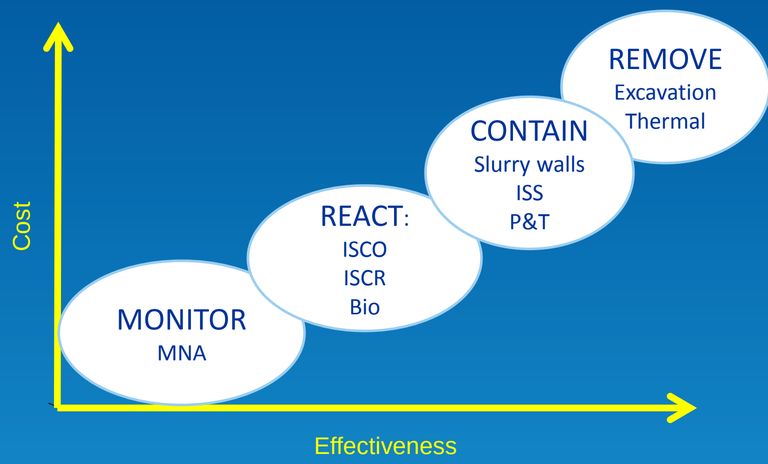
Relative costs of remediation technologies



Consider "OoMs" when setting Remediation Goals

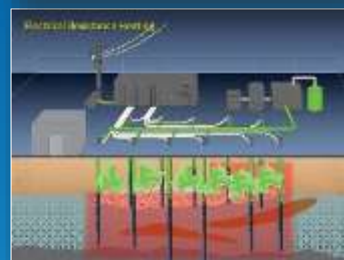
- Orders of magnitude are powers of 10
- Hydraulic conductivity is based on OoMs
- Contaminant distribution is often log-normal (=OoMs)
- VOC concentration reduction can be described with OoMs
- Remediation performance can be also evaluated using OoMs….

Before concentration **50,000 ug/L**

After concentration **5 ug/L**

Need **4 OoMs** (99.99% reduction)

Technology Category 1: Remove
Physical and Thermal Removal



- Excavation
  - Early stages of a release
  - Impractical for deep contamination
- Thermal remediation
  - Vendors are confident, give guarantees
  - Treats all types of geology
  - Energy-intensive

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Removal Technologies – What you need to know

- Excavation
  - Extent of source material
  - Degree of contamination
  - Soil types
  - Where you are going to put the stuff
- Thermal Remediation
  - Targeted source material
  - Soil types (density, stratigraphy)
  - Hydrogeology (permeability and GW seepage velocity)

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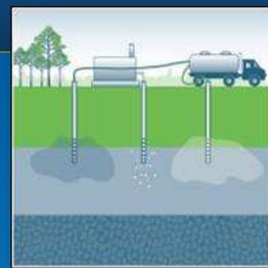
Technology Category 2: Contain

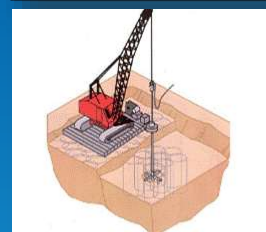
- Not remediation per se, but an important part of our toolkit
- Low-permeability barriers
- Solidification/stabilization
- Permeable reactive walls
  - Zero Valent Iron Walls: Median **0.8 OoMs** TCE from six sites
- Pump and treat

Containment Technologies – What you need to know

- Low Permeability Barriers
  - Limits of targeted material to be contained
  - Unit to key into
  - Soil types and amendments required to reach target low K
- Reactive Barriers
  - Effectiveness of treatment media (bench scale treatability tests)
  - Groundwater seepage velocity
  - Thickness of the reactive barrier to affect sufficient treatment
- Pump and Treat
  - Hydraulic capture areas and volume requirem
  - Treatment and discharge requirements

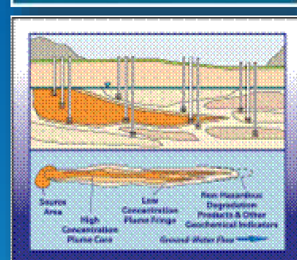
Technology Category 3: React
Chemical / Biological





- *In situ* chemical oxidation
  - Amendments are short-lived
    - Rebound
    - Multiple injection rounds
  - Can be injected to treat mass in transmissive zones
  - Electrokinetics is a new technique to distribute ISCO into low-K zones
- *In situ* chemical reduction
  - Zero valent iron
  - Long-lasting, yet distribution may be difficult

Technology Category 3: React
Chemical / Biological (continued)



- Enhanced bioremediation
  - Bacteria only degrade dissolved contamination
  - Not suitable for direct degradation of DNAPL
  - However, reactive zones surrounding DNAPL can promote dissolution of the DNAPL
  - Products available that combine bio with ISCR for both biotic and abiotic degradation
  - ITRC, 2008 *In Situ Bioremediation of Chlorinated Ethenes: DNAPL Source Zones*

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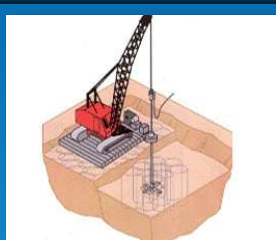
React Technologies – What you need to know

- ISCO, ISCR & Bio
  - Stratigraphy, hydrogeology,
  - Contaminant mass and distribution
- ISCO
  - Chemical Oxygen Demand (COD)
  - Expected duration, repeat events
- ISCR
  - Treatability effectiveness
  - Longevity of
- In Situ Bio
  - Effective substrate(s)
  - Biological makeup

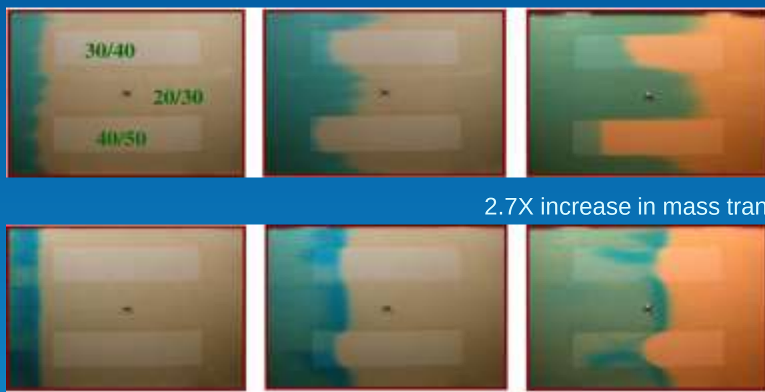
Growing set of technologies to treat mass in low-permeability layers

Soil mixing
Electrokinetics
Shear-thinning fluids
Variable Pressure Injection
- Pneumatic
- Hydraulic



Shear thinning fluids allow greater amendment transport into low permeability regions

Water



2.7X increase in mass transport

Amended with 0.06% Xanthan

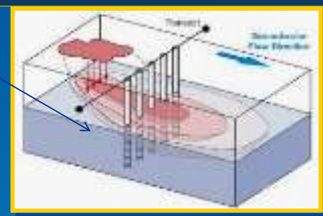
Zhong (2008)

Category 4: Monitoring

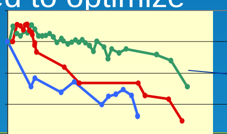
- MNA is NOT a no-action alternative
- Focused on routes of exposure
- Protective of PHATE
  - (public health and the environment)
- Part of every remedy that is still above MCLs

Types of Monitoring

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



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Monitoring – What you need to know

- Receptors
- Plume dimensions
- Hydrogeology
- Key analytes and surrogates
- Expected degradation rates
- CSIA?

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Where will the OoMs removal come from?

Before **50,000 ug/L /** After concentration **5 ug/L**
Need **4 OoMs** (99.99% reduction)

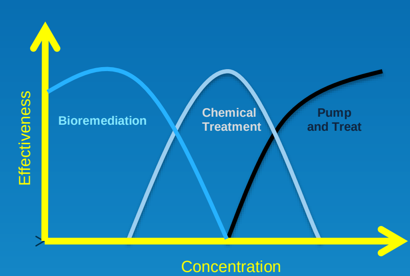
Technology	Median OoMs concentration reduction	Notes
Excavation	Limited to source areas	
Thermal	1.5+	
ISCO	0.3 – 0.8	Depends on rebound.
ISCR	1.7	ZVI deep soil mixing
EAB	1.3	Parent Compound
EAB	0.4	Total VOCs
MNA	0.6	over 9 years
PRBs	0.8	between upgradient and downgradient of PRB

Source: Surveys listed in ITRC IDSS document

Technology Coupling

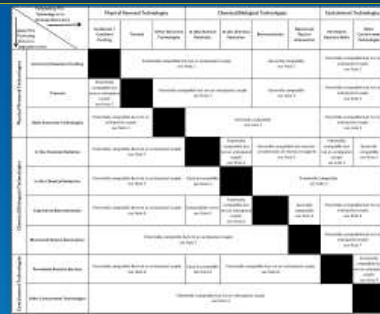
- Three types of coupling: *temporal, spatial, simultaneous*
- Potential approaches:
  - Intensive technology followed by passive
  - Different technology for Source versus Plume
  - Any technology followed by MNA

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



Constructing a Combined Remedy Alternative

- Compatibility matrix of 9 technologies
- Examples:
  - **"Generally Compatible"**
    - Thermal followed by *In Situ* Bio:
      - Potentially synergistic
      - Microbes population may be reduced
      - But then rapid recovery
  - **"Likely Incompatible"**
    - *In Situ* Reduction followed by In-Situ Oxidation
      - Destruction of both reagents
  - **"Potentially Compatible but Not An Anticipated Couple"**
    - Bio followed by Surfactant Flushing
      - Would probably work, but unlikely to be coupled



ITRC IDSS-1, Table 4-2

Constructing a Combined Remedy Alternative

We can construct combined remedies using surveys of OoMs as a guide

Technology	Median OoMs concentration reduction	Notes
Excavation	Complete (given right conditions)	
Thermal	1.5	
ISCO	0.3	Depends on rebound. Other studies show up to 0.8
ISCR	1.7	ZVI deep soil mixing
EAB	1.3	Parent Compound
EAB	0.4	Total VOCs
MNA	0.6	over 9 years
PRBs	0.8	between upgradient and downgradient of PRB

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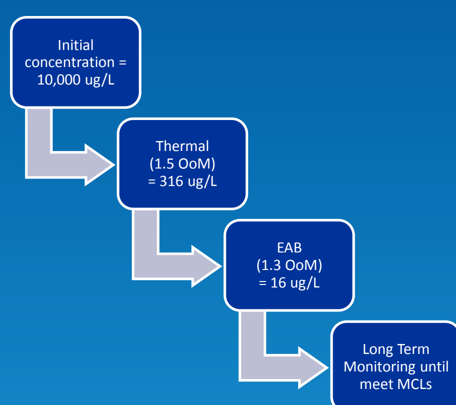

Outline

- DNAPL Remediation Technologies
- **Establishing Realistic Remedial Goals**
- Case Study
- Discussion

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Two Key ITRC Guidance Documents

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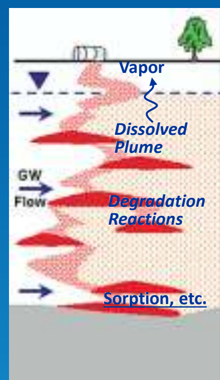
Setting Realistic Goals Requires Understanding of Chemical Phases and Transport of DNAPL Releases

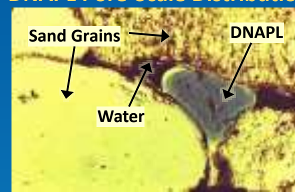
- DNAPL movement and capillary forces
- Chemical phase distribution
- Interphase chemical mass transfer
- Dissolved plume formation & transport
- Vapor migration

Generalize DNAPL Release and Transport

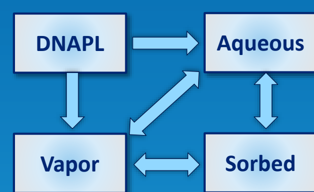


(Modified from Parker et al, 2002)

DNAPL Pore-Scale Distribution



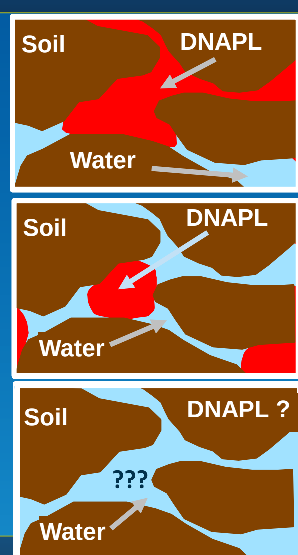
Interphase Chemical Mass Transfer



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

Mobile DNAPL vs. Residual DNAPL vs. Sorbed Contaminant

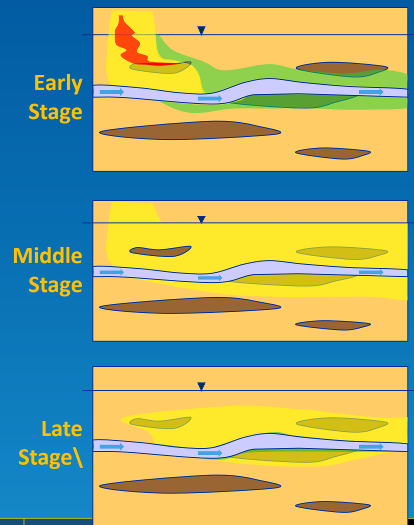
- Mobile DNAPL
  - Interconnected separate phase that is capable of migrating
- Residual DNAPL
  - Disconnected blobs and ganglia that are not capable of migrating
- Sorbed Contaminant
  - No longer a NAPL
  - Still a residual source



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



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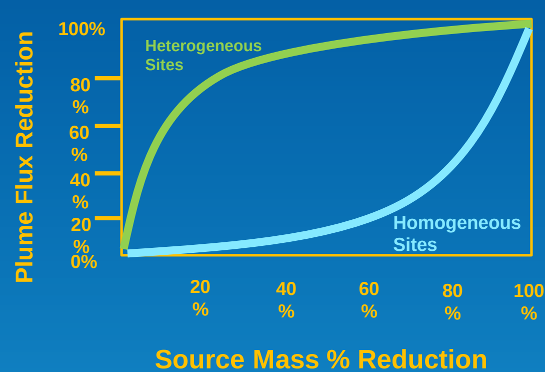
Plume Response to Source Treatment

- 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

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 groundwater, and evaluate further risk reduction.*

USEPA's Recent Groundwater Strategy

A Groundwater Remedy Completion Strategy is a recommended site-specific course of actions and decision making processes to achieve

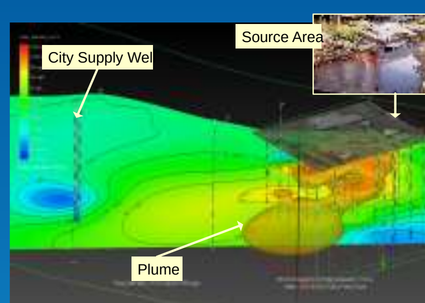
groundwater RAOs and associated cleanup levels using an updated conceptual site model performance metrics and data derived from site-specific remedy evaluations.

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*

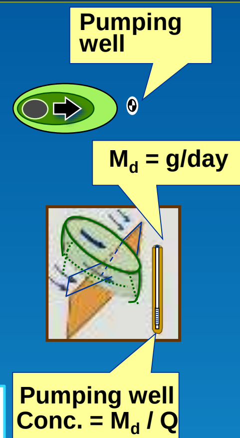
Building the Remedial Action Framework

- 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



Potential Remedial Goals – Concentration vs. Mass Discharge

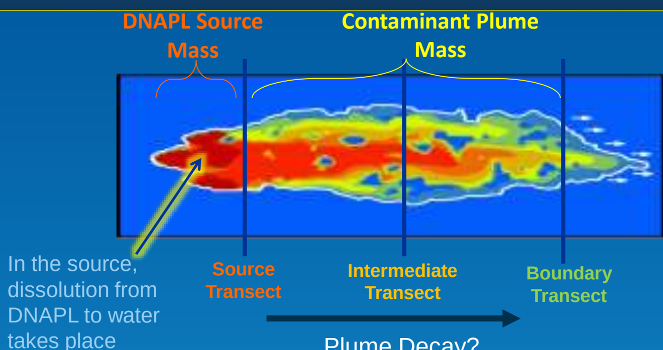
- ***Traditional Concentration Approach:*** Measure existing plume to assess
  - Impact on receptor (MCLs)
  - Natural attenuation rates
  - Remedial options
- ***Mass Discharge Approach:*** Define rate across specified cross-sectional areas of plume to assess
  - Impact on receptor (TMDLs)
  - Natural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

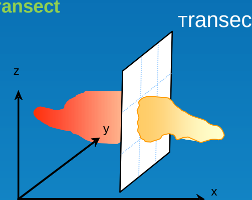


KEY BENEFITS: **Mass discharge approach potentially offers a better understanding of potential risks and attenuation rates, and can lead to sounder remediation strategies.**

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

Mass Balance and Flux-Based Site Metrics

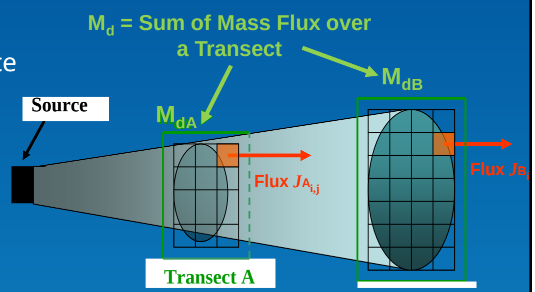




Understanding site mass balance can lead to consideration of alternative site remedial objectives possibly based on mass discharge or mass flux

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)



$J_{A_{ij}}$= Individual mass flux measurement at Transect A

M_{dA}= Mass discharge at transect A

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

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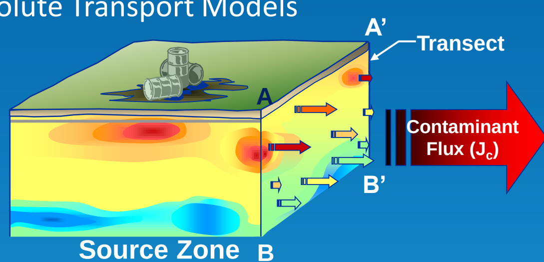
Mass Flux Mass Discharge Measurement Methods

- 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



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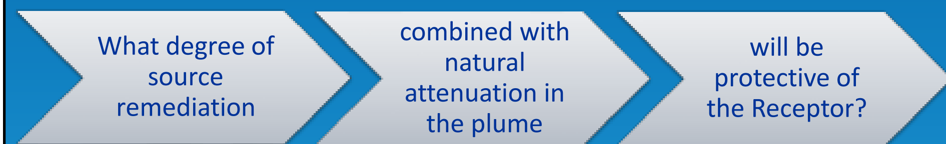
Alternative Remedial Goals

- 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.

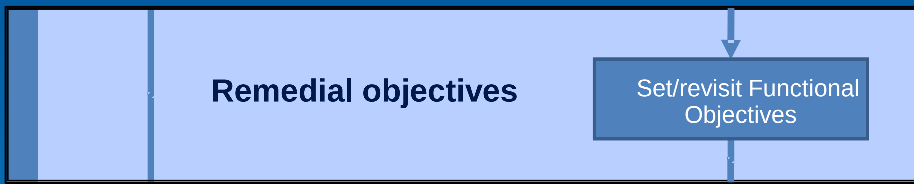


Interim and Transitional Remedial Goals

- 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)

Remediation of DNAPL Sites

Remedial Objectives



- How do you define objectives in a clear and concise manner?
- What is the process to make your objectives realistic?

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

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

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
  - Interim goals and metrics
  - SMART
  - Planned transitions

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Outline

- DNAPL Remediation Technologies
- Establishing Realistic Remedial Goals
- **Case Studies**
- Discussion

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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

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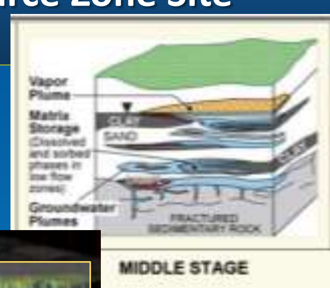
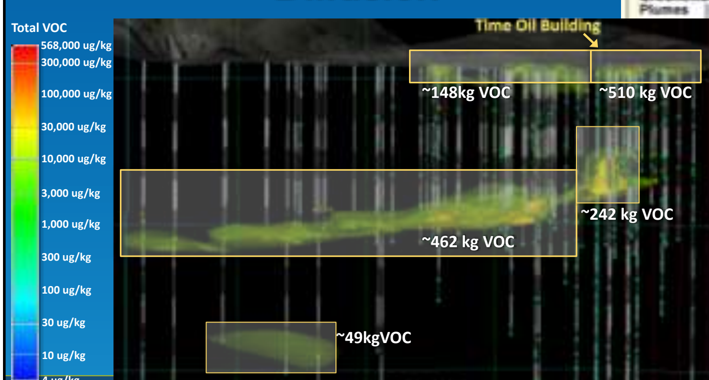
A long ROD history . . .

- 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

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

Both DNAPL and Matrix Diffusion





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

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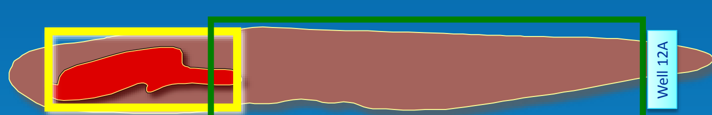
Setting Realistic Goals for a Complex DNAPL Site

- 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?

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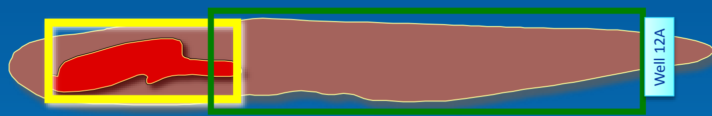
2009 ROD Amendment. First ROD in the US to incorporate mass discharge reduction goals



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

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 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.

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Solvent Finishers

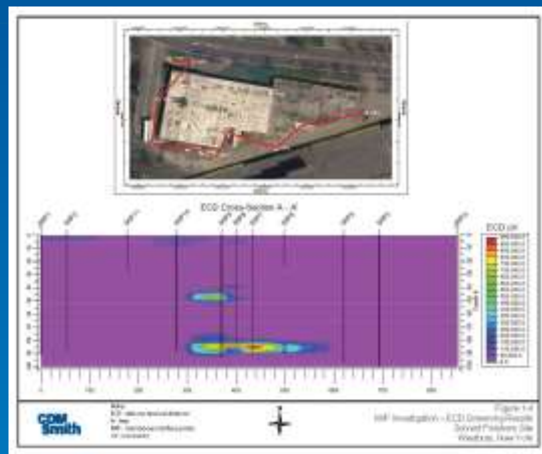
CASE STUDY: APPLYING MULTIPLE TECHNOLOGIES TO ADDRESS CONTAMINATION AT A COMPLICATED DNAPL SITE

Site Background

- Site currently owned by Rubies Costume Company (sales, design, and fabric cutting facility for costumes)
- Previously Industrial Dry Cleaner (Solvent Finishers- late 1970s – early 1980s)
  - used up to 11,000 gallons of PCE annually to clean large rolls of fabric on an automated system
  - Wastewater discharged to the ground surface and into onsite dry wells

High Resolution Site Characterization

- 2008 Membrane Interface Probe (MIP)
- 2011 Vertical Profile Borings & Multi-Level Monitoring Wells (72 Wells at 7 locations)
- 2013 Deep Well Installation (15 Wells at 5 locations)
- Data from nearby sites



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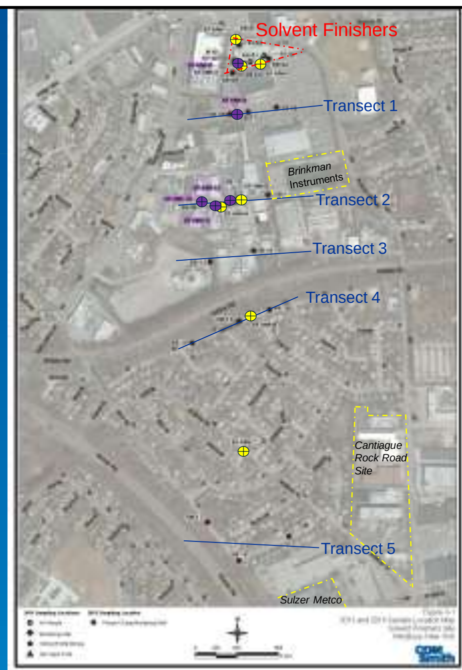

2011 and 2013 RI Investigation Locations

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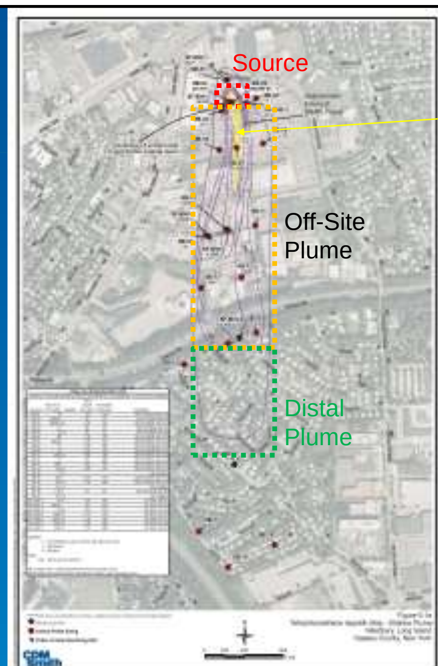
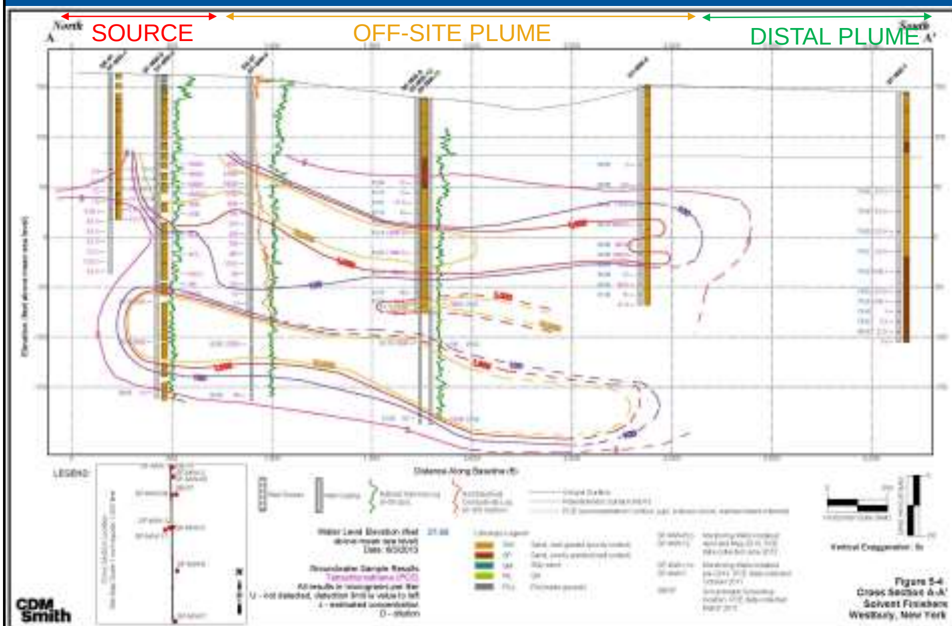
Target Groundwater Remediation Zones

- Given the nature and extent of the Site contamination, a single technology would not be appropriate or sufficient to address the entire plume
- Design objective is to pair the appropriate treatment technology to the various levels of contamination.
- 3 zones:
  - **On-site Source**
  - **Offsite Plume**
  - **Distal Plume**

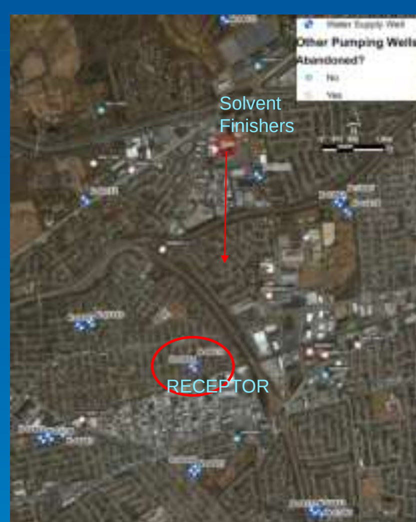


Approximate
Extent of
Residual DNAPL



Remedy Evaluation

- **Remediation Goals**
  - **Long term goal**: Reduce groundwater contamination to meet groundwater quality standards
  - **Near term goal**: Protect Key receptors and stabilize the plume.
    - Reduce contaminant mass discharge to the downgradient contaminant plume to achieve plume retraction



What is "Substantial" Mass Removal?

- Concentration-based data does not address the level which contaminants are being mobilized from the source area
- Measuring mass discharge (Md) or flux of contaminants from a source area combines chemical data, groundwater flow velocity, and discharge area into a single measurement (expressed as mass/time or grams/day).
- Using Md as a performance measure or near term goal is a more direct way to measure contaminant migration from the source zone.
- Using information obtained during the PDI, Md can be calculated to determine the percent of mass removal needed to achieve plume retraction.   Add a timeframe to this and….

It can be a SMART goal

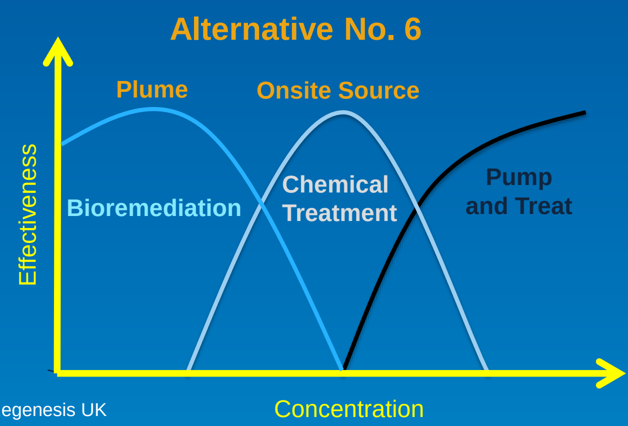
Source Mass Discharge → Source Strength → Discharge to Plume

Multi-Technology Strategy
Solvent Finishers Remedial Alternatives

- **Alternative 1**: No Action
- **Alternative 2**:
  - Onsite Source: Air Sparge/Soil Vapor Extraction (AS/SVE) and Enhanced *In-Situ* Biological and Abiotic Remediation (EIBAR)
  - Offsite Plume: EIBAR
  - Distal Plume: Monitored Natural Attenuation (MNA)/ Institutional Controls (IC)
- **Alternative 3**:
  - Onsite Source: AS/SVE and *In-Situ* Thermal Remediation (ISTR)
  - Offsite Plume: EIBAR
  - Distal Plume: MNA/ IC
- **Alternative 4**:
  - Onsite Source: AS/SVE and Pump and Treat (P&T)
  - Offsite Plume: EIBAR
  - Distal Plume: MNA/IC
- **Alternative 5**:
  - Onsite Source: AS/SVE and ISTR
  - Offsite Plume: *In-Situ* Chemical Oxidation (ISCO)
  - Distal Plume: MNA/IC
- **Alternative 6**:
  - Onsite Source: AS/SVE and ISCO
  - Offsite Plume: Enhanced *In-Situ* Biological and Abiotic Remediation (EIBAR)
  - Distal Plume: MNA/ IC

Why Multiple Technologies?

- A single technology was not appropriate given the complexity of the plume
- Map the technology to the contamination – Find the Sweet Spot!



Jeremy Birnstingl, Regenesis UK

Conclusions

- Remediating a complex DNAPL site is ….Complex
- High resolution characterization was critical to developing an accurate conceptual site model
- A single technology is not appropriate to address the multiple components of the contaminant plume
  - Combining technologies allows specific technologies to be used to address the area of contamination that they are best suited for
- Setting near term goals is SMART
  - Allows for immediate focus on protecting receptors and retracting the plume
  - Provides a way to measure and demonstrate progress
  - Goals are realistic and cost effective

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.

Remediation of DNAPL Sites

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Thank you for your interest and time.

Questions ?

Discussion?

Remediation of DNAPL Sites

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