



Lessons Learned from DNAPL Site Remediation

RITS 2013



Give Away the “Ending”: What have we learned from DNAPL Treatments?

- Remediation success is less about “*which technology*” and more about the strategy, planning, design, and implementation
- Biggest limitations are inherent to subsurface complexities
- Characterization and conceptual site model are key – new tools can help
- Complete treatment is not achievable; we have to manage residual
- Most *in situ* technologies have similar performance, except thermal is a higher performer
- Poor treatment performance usually = poor design/implementation
- Robust remedial design and application matters!

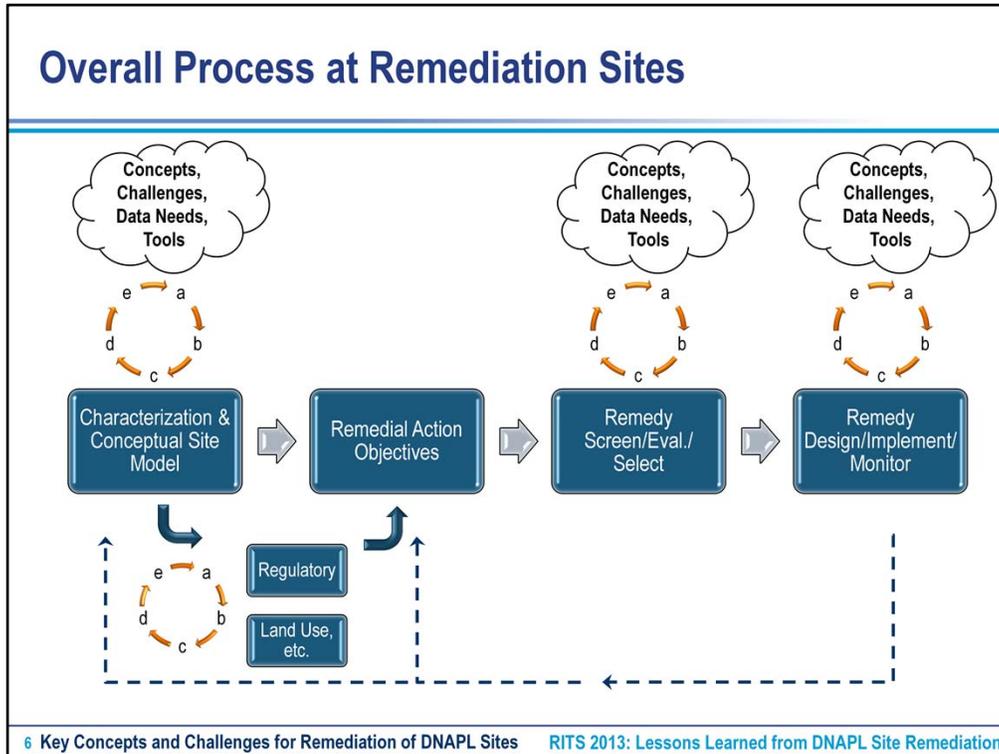
Prior RITS Training Topics Relevant to Today's Topic

- 2012: Integrated DNAPL Site Strategy (IDSS)
- 2012: Optimization...
- 2011: Mass Flux and Mass Discharge
- 2010: *In Situ* Chemical Oxidation (ISCO)
- 2010: Alternative Endpoints and Other Approaches...
- 2010: Green and Sustainable Remediation (GSR)
- 2010: Using SiteWise™
- 2009: Getting the Most Out of Your Conceptual Site Model
- 2009: Environmental Restoration Resources
- And Others...

Presentation Overview

► Key Concepts and Challenges for Remediation of DNAPL Sites

- Objectives, Data Needs, and Tools
- Focused NAVFAC Site Case Studies
- Synthesis – Best Practices and Future Directions
- Summary



Reference: ITRC Integrated DNAPL Site Strategy (IDSS) document.

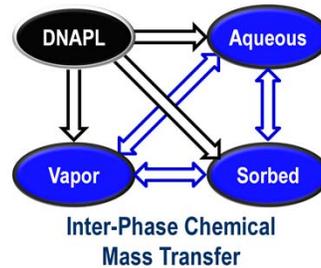
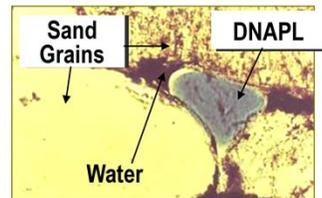
We want to focus on “lessons learned from DNAPL treatment”, but to do so we have to focus on various elements throughout the process.

The CSM, objectives, screening, selection, design, implementation, and monitoring of the remedy all come into play.

Brief Review of DNAPL Science (DNAPL = dense non-aqueous phase liquid)

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

DNAPL Pore-Scale Distribution



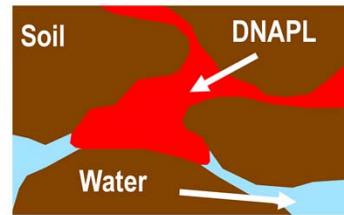
7 Key Concepts and Challenges for Remediation of DNAPL Sites [RITS 2013: Lessons Learned from DNAPL Site Remediation](#)

Only a very brief review of DNAPL science is provided in this presentation.

Mobile vs. Residual DNAPL

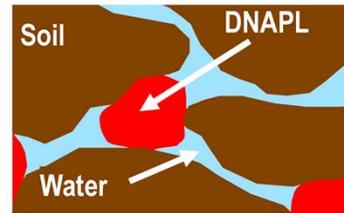
- **Mobile DNAPL**

- Interconnected separate phase that is capable of migrating



- **Residual DNAPL**

- Disconnected blobs and ganglia that are not capable of migrating



Key Points

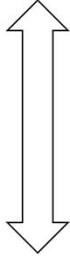
- 1) DNAPL “pools” are extremely rare
- 2) Even if present, DNAPL is hard to detect/locate

Later we will talk briefly about new tools for DNAPL characterization.

However, identifying DNAPL “itself” is perhaps less critical at many sites than we used to think.

What is a DNAPL Source Zone? (Historic evolution of definitions)

**Early:
NAPL-Focus**

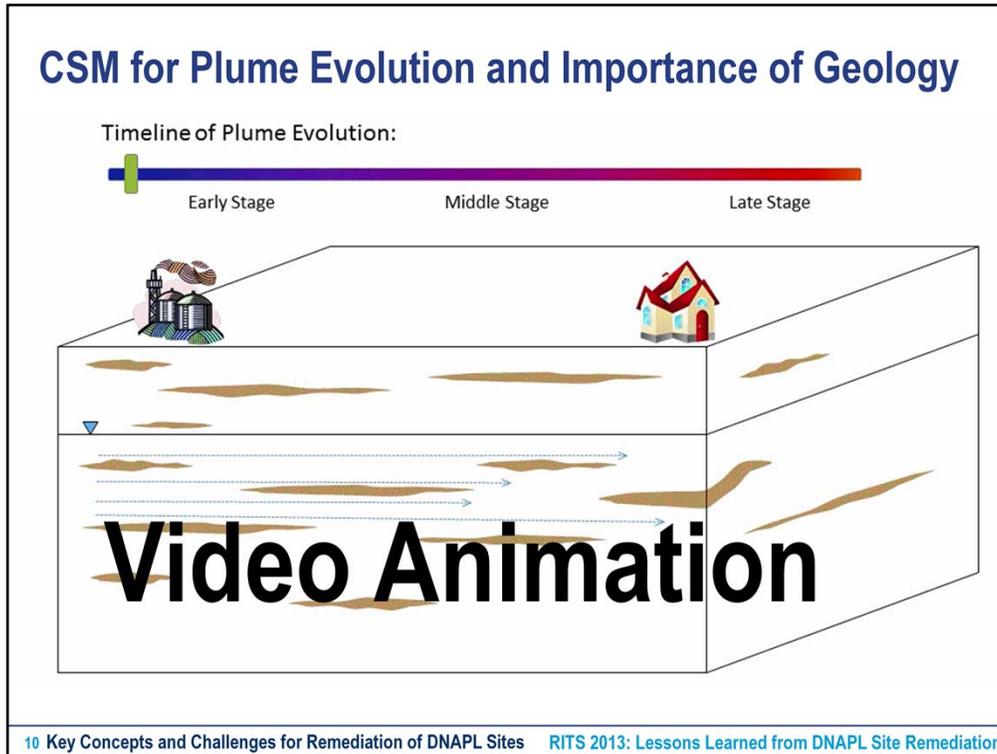


**Recent:
Focus on
Contaminant
Mass Reservoir**

- EPA (1996) “free phase or residual NAPL”
- ITRC (2004): “...ganglia and pools that... act as a long term source for dissolution of contaminants into water.”
- ITRC (2011): “There is no bright line of demarcation between the source zone and the plume... mass may migrate into the aquifer matrix, and act as a reservoir of contaminants that sustains the plume.”

9 Key Concepts and Challenges for Remediation of DNAPL Sites [RITS 2013: Lessons Learned from DNAPL Site Remediation](#)

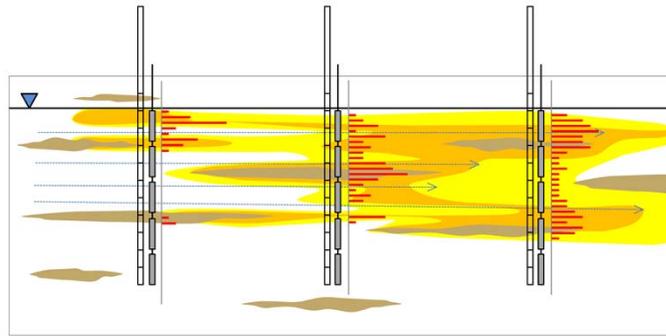
Bottom line – a source zone is now considered to be less defined by the presence of DNAPL and more defined by other factors that lead to plume persistence. Primary in these considerations is the presence of contaminant mass reservoirs held in lower permeability media which provide a long term source of back-diffusion of contaminant mass into the plume.



- 1) Importance of geology: 90% of flow in 10% of formation
- 2) Evolution: Early vs. middle vs. late stage
 - significant attenuation rate implied by “stable” plume represented here at middle stage
 - NAPL may or may not persist into late stage, although shown here to attenuate at middle stage
 - late stage concepts in source may result from passage of time, or from active source remediation
- 3) Matrix diffusion – early stage diffusion into and late stage back-diffusion out of low-K zones

Characterization and Monitoring Challenges

- Forthcoming ITRC DNAPL Characterization Document (late 2013 or early 2014)
- Multi-level, Hi-Res, and screening-level tools very beneficial
- Fully screened wells have poor representativeness, but are “the” compliance standard



11 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

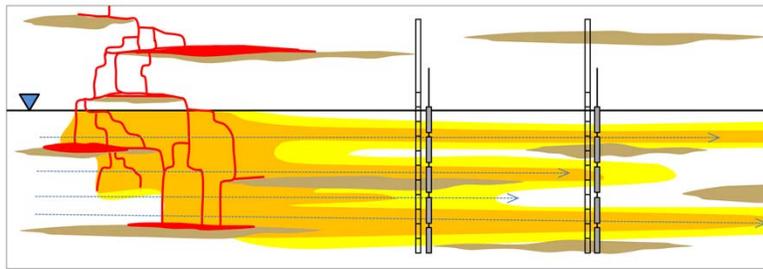
Differences in information gathered through traditional fully screened monitoring wells and multi-level characterization can be visualized on this slide.

3 levels of characterization shown:

- 1) Traditional = fully screened MWs
- 2) Multi-level groundwater sampling (could be 2-3 levels, or more as shown)
- 3) Hi-resolution vertical profile. Could be soil sampling, groundwater sampling, or screening such as MIP

Key Theoretical Challenges for Source Remediation

- Vadose zone impacts
- Geology/diffusion limitations
- DNAPL dissolution
- Contaminant mass tied up in low-K regions!
- Plume response to source treatment!



12 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

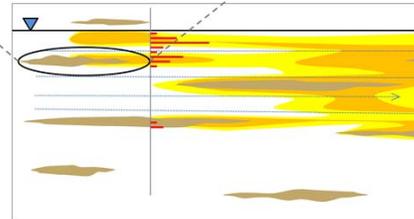
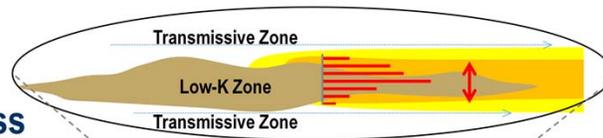
Contaminant mass is very heterogeneously distributed due to both:

- 1) Geology, and
- 2) DNAPL physics leading to discontinuous DNAPL distribution

Traditional fully screened monitoring wells don't give us the full picture, so the importance of more highly resolved characterization data comes into play especially for remediation.

“Back-Diffusion” – A Major Remediation Challenge!

- “Late” stage process (or post-treatment)
- Slow release of contaminant mass over time from low-K zones into transmissive zones
- Diffusion driven by concentration gradients



**Key
Point**

Recognition of back-diffusion has transformed the industry paradigm

13 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

The late-stage contaminant distribution in this figure can result from long-term source attenuation, or from active source remediation that did not fully treat low-K zones.

Larger scale graphic is from video animation, and shows vertical profile of contaminant concentrations.

Zoom-in graphic shows finer-scale vertical delineation of contaminant concentration, which may not be measurable in reality depending on scale.

Transport by chemical diffusion always moves from high to low concentration.

Theory of Source (Mass) - Plume (Conc.) Relationship

Power function model

[Rao et al., 2001; Parker and Park, 2004; Zhu and Sykes, 2004]

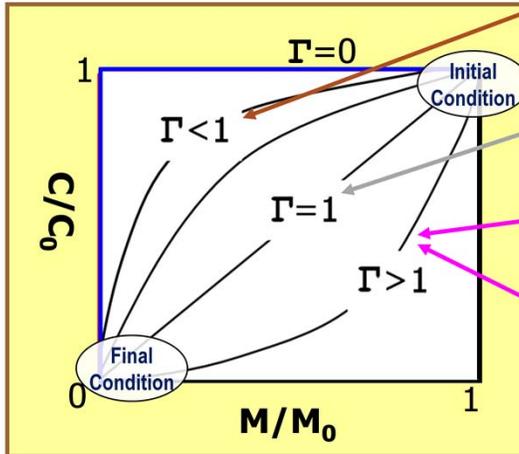
$$\frac{C}{C_0} = \left(\frac{M}{M_0} \right)^\Gamma$$

NAPL is mostly in high conductivity zones, or is present as pools in homogeneous media

Gamma = 1 implies homogeneous geology and dispersed NAPL distr.

NAPL is mostly in low permeability zones in a heterogeneous system

Gamma > 1 implies gradual back-diffusion and greater post-remediation longevity of plume concentrations



14 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

Graphics adapted from Ron Falta presentation via EPA Clu-in.

Multiple possible paths from “initial condition” to “final condition”

Final condition is zero contaminant mass and zero concentration... may be decades or centuries away for highly impacted sites.

Movement along the path occurs over time through attenuation processes, or by active source mass remediation.

As source mass is reduced, can either have a proportional (1:1) reduction in concentration (gamma = 1), or...

Can have a greater or lesser effect of source mass reduction on concentration loading into the plume.

A trade-off exists for a given amount of mass reduction between:

- (a) Greater concentration reduction but more long term plume longevity (gamma >1), and
- (b) Lesser plume concentration reduction but shorter duration longevity (gamma <1).

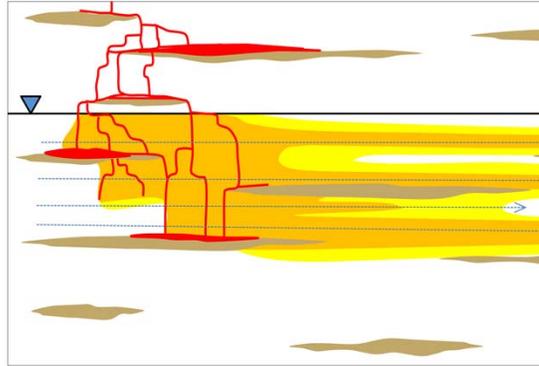
Gamma >1 leads to common observation of (a) significant early-time decrease in groundwater concentration followed by (b) long-term asymptotically low levels. In that scenario, it may require substantial additional mass depletion to achieve lower groundwater concentrations.

Key Practical Challenges for Source Remediation

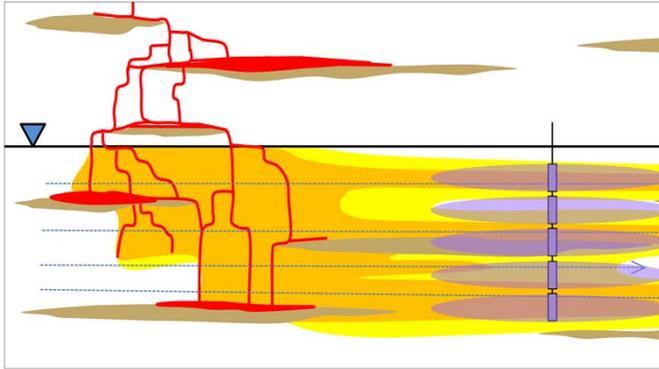
- Subsurface delivery of amendments, *i.e.*, contacting target zone
- Permeability limitations on injection volume
- Having adequate characterization data pre- and post-treatment

Key Point

Remediation design needs to target the contaminant mass distribution



Delivery Systems for *In Situ* Amendment Injection



- **Multiple variations:**

- Permanent wells
- Packers
- Horizontal wells
- Direct push points
- Special injection tools
- Injection only
- Recirculation

- **Commonalities:**

- Lithologic targeting
- Process monitoring for amendment distribution

Key Point Innovation in delivery can be a critical success factor

Delivery systems have to be selected considering site-specific conditions.

Specific Delivery Challenges

- **Stratigraphic/Lithologic Preferential Flow**
- **Density-Driven Flow**
 - Primarily relevant at percent-level amendment concentrations
 - Counteracted by: low vertical/horizontal permeability ratio and horizontal gradients
- **Reactive Transport Limitations**
 - Fast reacting amendments have limited radius of influence

**Key
Point**

Fast-Reacting Amendments (oxidants) will not “drift”
Slow-Reacting Amendments (bio) transport more easily

Key NAVFAC References for Site Restoration

- Department of the Navy Environmental Restoration (NERP) Program Manual (2006)
- Naval Facilities Engineering Command (NAVFAC). 2010. *Guidance for Optimizing Remedy Evaluation, Selection and Design. Prepared by NAVFAC Optimization Workgroup.*
- NAVFAC Environmental Restoration (ER) Technology Transfer Tools & Fact Sheets

18 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

NAVFAC (2010) also discusses many of the broad issues being discussed today such as back-diffusion, and how these issues pertain to remedy selection and design.

General Strategies: DNAPL Site Source Remedies

- **Source containment (physical or reactive barrier)**
- **Source removal (excavation)**
- **Source treatment**
- **Downgradient plume treatment**
- **Monitor and manage receptors/risk**
- **No action**

19 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

Notwithstanding our focus today on in-situ treatment of DNAPL source areas – excavation/ex-situ or other approaches can be the most favorable alternative and have to be considered.

Remedial Actions – What they include

- **General categories of remedial actions ...**
 - No further action, Land use controls, Containment and other engineering controls
 - *Ex situ* treatment/mass removal
 - Monitored Natural Attenuation (MNA)
 - *In situ* treatment/mass removal
 - *In Situ* Chemical Oxidation (ISCO)
 - *In Situ* Bioremediation (ISB)
 - *In Situ* Thermal (IST)
- **Biggest recent trend – *Coupling Technologies!***

**Our Focus Today –
Mainstays of DNAPL site
Source Remediation**

20 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

These are discussed further in Naval Facilities Engineering Command (NAVFAC) 2010. *Guidance for Optimizing Remedy Evaluation, Selection and Design. Prepared by NAVFAC Optimization Workgroup*

NAVFAC (2010) also discusses many of the broad issues being discussed today such as back-diffusion, and how these issues pertain to remedy selection and design.

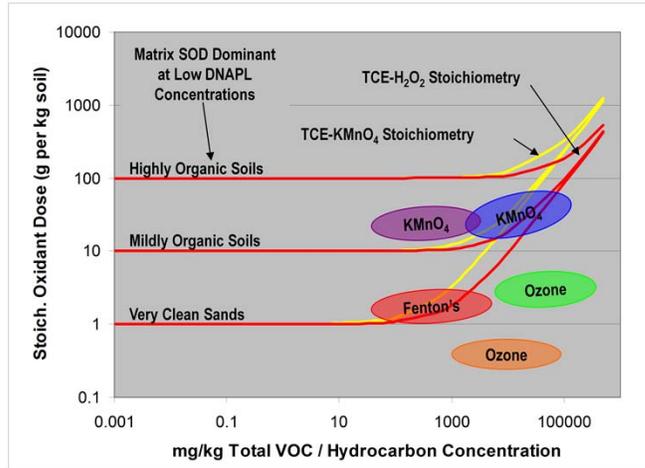
Lessons Learned: Oxidant Dose for Source Treatment

- Example of five successful DNAPL Source Treatments using ISCO

- ISCO requires large oxidant dosing and multiple applications to effectively treat DNAPL sources areas

oxidant

Circles represent full-scale, successful, published DNAPL treatment case studies



***In Situ* Bioremediation (ISB) Source Zone Treatment (ITRC, 2008)**

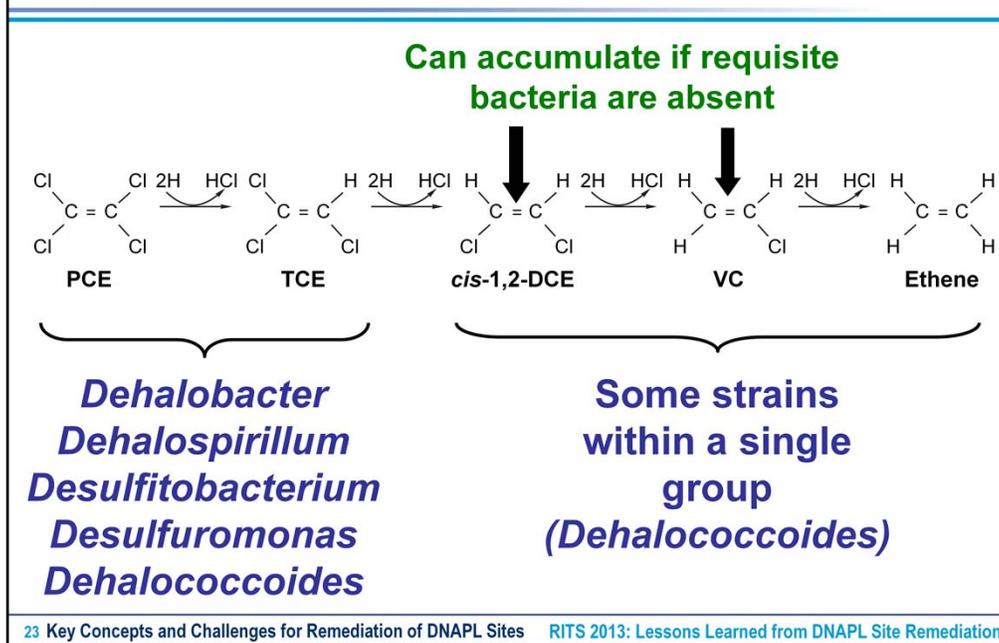
- **Gradual Process: 3-4x increase in DNAPL dissolution rate**
- **Variety of carbon donors available, some very long lasting**
- **Microbial diagnostic tools available**
- **Potentially limited effect for some VOC constituents e.g., chloroform, 1,4-dioxane, sometimes chloro-ethanes**
- **Process involves biostimulation (carbon donors) and potentially bioaugmentation (microbial cultures)**
- **Delivery of microbial cultures can be challenging**

22 Key Concepts and Challenges for Remediation of DNAPL Sites [RITS 2013: Lessons Learned from DNAPL Site Remediation](#)

ISB = in-situ bioremediation

Gradual and persistent process, multiple injections required

ISB – Reductive Dechlorination and Microbial Strains



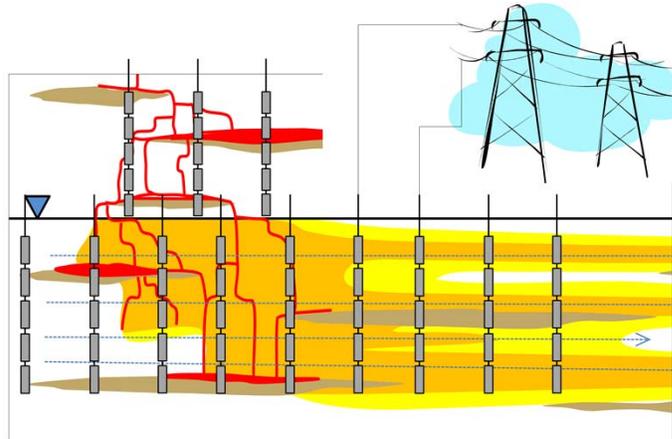
This slide shows the reductive dechlorination pathway for PCE/TCE bioremediation through carbon donor addition.

More on Thermal... ERH and TCH

- **Advantage:** Electrical and thermal conductivities are fairly similar between different lithologies!

- **Still some limitations exist for low-K media**

- Electrode spacing
- Time
- Cost



“Other” Source Zone *In Situ* Treatment Technologies

- ***In Situ* Chemical Reduction**
 - Zero valent iron (ZVI), nano-ZVI, etc.
- **Air sparging/soil vapor extraction**
- **Surfactant/cosolvent flooding**
- **Soil mixing**
- **Other proprietary technologies**

25 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

SVE, thermal and others are able to treat vadose zone sources.

Pump and treat is not listed as a source zone technology because it is not effective for source mass reduction.

Current Thinking re: DNAPL Treatment Efficacy

- Now that we have several decades of experience to draw from, recognition that some level of contaminant concentration and mass will remain after treatment is now considered a reality at most sites.

Big Picture Takeaways – Source Zone Remediation

- Realistic expectations
 - Typically = 80% to 95% removal, not MCLs
- When you drill down... poor performing applications are mostly a result of:
 - Unwise remedy selection
 - Under design and/or substandard implementation (well spacing, dose, etc.)
- ***Robust application matters!***
- Thermal a clear higher-performer
- Bio vs. ISCO debate mostly moot – similar performance
- Multiple applications required for all but thermal
- ***Coupling technologies!***

27 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

ISCO has shown more rebound, but bio has potential for rebound later in time

Bio has more bang for buck in flux reduction, but likely less mass reduction

Impact of Back-Diffusion on Remedy Selection

- **Remedy evaluation/selection and Feasibility Studies (FS) should account for:**
 - **Potential post-remedy groundwater concentration rebound with any technology**
 - ISCO and Thermal (sooner)
 - ISB (later, after reducing conditions no longer present)
 - **Long time frame (decades) for back diffusion of contaminant mass into groundwater**

Remedial Design “Due Diligence”

- **Back to basics!** – performance directly relates to robustness
- **Robust designs have:**
 - Effective amendment delivery method
 - Adequately close well spacing
 - Adequately large amendment volume and dose
 - Account for treatment persistence and re-application
- **Opinion:** Thermal treatment success at least partially reflects design diligence by a small number of well qualified vendors

**Key
Point**

Remediation designs are not “off-the-shelf”,
and robust design matters!

29 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

Note that implementation of a highly robust design will result in increased costs relative to a less robust design.

Role of Pilot Testing

- May or not be required to establish treatability
- Often focused on delivery and design parameters
- Can be scaled approach – “first phase of treatment”:
 - pilot scale > intermediate scale > full scale
- Technology-specific needs
 - ISCO = oxidant delivery and consumption rates
 - ISB = delivery and geochemical/microbial response
 - Thermal = heating rates and soil vapor extraction removal

**Key
Point**

Pilot testing determines actual delivery and distribution/radius of influence!

Elements That May Cause Poor Remedy Outcome

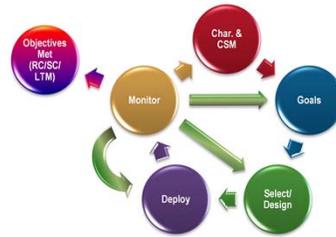
- Fully-screened injection wells in heterogeneous media
- Single treatment application when multiple are required
- Low injection volumes and/or amendment dose
- Performance monitoring in GW only and using...
 - Fully-screened wells and/or amendment injection wells
- Not integrating new information as you go

31 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

These are a few things that have been shown through experience to sometimes result in less than optimal results.

The Observational Approach – Adaptive Remediation

- **Avoids designing to worst case scenario**
 - Assess conditions to reasonable extent
 - Develop design around most probable condition
 - Develop alternatives for possible conditions
 - Measure conditions while implementing
 - Modify design to actual conditions
 - **Must select modifications in advance**



32 Key Concepts and Challenges for Remediation of DNAPL Sites RITS 2013: Lessons Learned from DNAPL Site Remediation

The observational approach was developed to address geologic uncertainty in geotechnical engineering, and has strong applicability to remediation design and implementation.

Presentation Overview

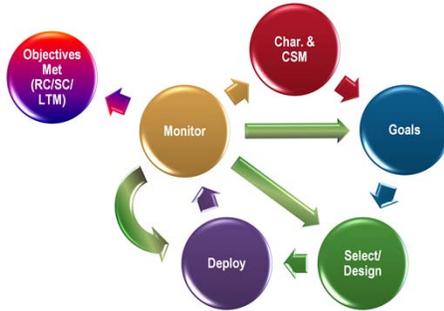
- Key Concepts and Challenges for Remediation of DNAPL Sites

- ▶ Objectives, Data Needs, and Tools

- Focused NAVFAC Site Case Studies
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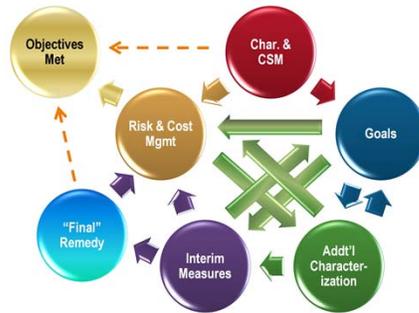
DNAPL Site Strategy Elements

Organized Process



vs.

Sometimes Reality



**Key
Point**

Realign to an organized process to gain value

34 Objectives, Data Needs, and Tools

RITS 2013: Lessons Learned from DNAPL Site Remediation

As described in the ITRC Integrated DNAPL Site Strategy (IDSS) document, following a structured process brings great value to remediation projects.

Critical Pre-Design Characterization Data

- “Source remediation is only as effective as the source delineation”
- “The distribution of contaminants between more and less transmissive zones is critical”
- Improvements:
 - Sampling transects at relatively high resolution
 - Measuring mass flux and discharge

Note – prior RITS topic on mass flux and discharge was presented in 2011 and can be found on the NAVFAC Environmental Restoration and BRAC website under Past RITS

Site Data that, *if Absent*, are Commonly Associated with Remedy Failure

- “Hot-spot” source delineation or undetermined sources
- Vertical delineation of contaminant distribution
- Hydraulic conductivity values in target treatment zone
- Presence, extent, & magnitude of contaminants in low permeability media
- Mass distribution (likely approximate) of contaminants between chemical phases and low- vs. high-K zones

Key Point

If we don't understand the problem, we probably cannot solve the problem

These are a few items that, based on experience, have been found to potentially result in remedy failures.

Remediation Objectives

- **Absolute – High level, *i.e.*, regulatory requirements**
 - Example: protection of public health and the environment
- **Functional – Steps taken to achieve absolute objectives**
 - Example: Remedial Action Objectives (RAOs), *i.e.*, reduce loading to the aquifer by treating, containing, or reducing source

- **SMART**

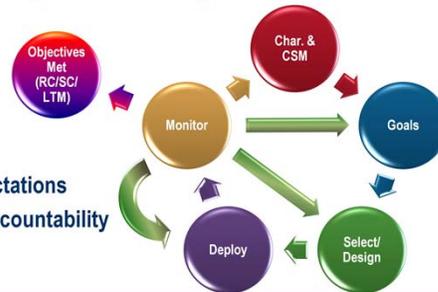
Specific: detailed and well defined

Measurable: specified and quantifiable

Attainable: realistic timeframe and resources

Relevant: has value and represents realistic expectations

Time-bound: well defined and short enough for accountability



See ITRC IDSS document for additional information on absolute and functional objectives applicable to remediation projects.

Traditional Approach to Remediation Objectives

- **Soil concentration target**
- **MCLs in groundwater**
- **ACLs in groundwater**
- **Groundwater concentration at a point of compliance**
- **Technical Impracticability (TI) waivers**

ACLs = alternate concentration limits

Traditional approaches to remediation objectives are driven largely by statutory requirements at the federal or state level, and by the guidelines and policies within the associated regulatory environments.

New Approaches to Remediation Objectives

- **Mass flux/mass discharge**
 - EPA approved PRG for Hamilton Road Interim Actions (OU1)
“Reduce mass discharge of PCE contamination by 90%”
- **GSR analysis using SiteWise™ tool or AFCEE SRT™ tool**
- **Objectives that define “treatment train” transition points**
- **Recognition that Long Term Management (LTMgt) will often be required following *in situ* remedies – because MCLs are not achievable in DNAPL source zones**

New approaches to remediation objectives acknowledge that complexity in DNAPL site conditions leads to multiple parameters considered in setting goals, as well as providing alternative ways to measure remediation end points other than numeric concentration goals.

Characterization: How much is enough to support remedy success?

- *“If we don’t understand the problem, we probably can’t solve the problem”*
- What is a “data gap”?
 - Directly affects decisions being made
 - Considers non-technical factors and tolerance for failure
- **Must ask: How are we going to use this data to support a decision???**

**Key
Point**

It’s not about perfect science, it’s about well informed decisions!

For RPMs, it may be a good idea to ask this question and document the answer.

Advanced Characterization Tools

- **Hi-Resolution**
 - Vertical delineation
 - Plume transects
- **Vertical Profiling Tools – Screening Level Data**
 - Hydraulic Profiling
 - Membrane Interface Probe (MIP)
 - Laser Induced Fluorescence (LIF)
 - FLUTE™
- **Mass flux**

Advanced characterization tools serve to generate more detailed data on both subsurface lithology and contaminant distribution.

NAVFAC ER Technology Transfer Web Site



The screenshot displays the NAVFAC ER Technology Transfer web site. The header includes the NAVFAC logo and navigation links such as 'About Us', 'Organization', 'Document Library', 'Ask NAVFAC', 'Seabees', 'Media Center', and 'Business Opportunities'. A search bar is also present. The main content area is titled 'ER Technology Transfer T2' and features a 'T2 Tools' section with several tool descriptions, including 'Bioremediation of Contaminated Soils Overview', 'Conceptual Site Models', and 'CSIA Web'. A large red watermark 'Example Screen Shot - Illustration Only-' is overlaid on the screenshot.

- Wide variety of ER tools and information

42 Objectives, Data Needs, and Tools

RITS 2013: Lessons Learned from DNAPL Site Remediation

New Tool: DNAPL Test Tool (ESTCP Project)

Analysis Selection

Analysis Selection

Two types of analyses can be performed:

General analysis:

- General comparison of technology performance
- User has option to refine their analysis to include case studies meeting certain criteria such as remedial technology, case study type, data quality ranking, and site characteristics
- Select this option if interested in general performance trends and do not have a particular site in mind

Site-specific analysis:

- More specific analysis tailored to provide performance data on case studies anticipated to have similar performance to a particular site
- User inputs characteristics of site of interest and the tool searches for similar sites (e.g. data quality, case study type, etc.)
- Screening tool will extract performance data from similar sites
- Select this option if you wish to evaluate potential technology performance at a specific site

Output reports include:

- Average technology performance for multiple parameters (e.g. metrics: unit cost, rebound, mass removal, concentration, etc.)
- Data quality information (average rankings, number of sites in analysis, ranges in performance, etc.)

Please select the type of analysis that you are interested in completing:

version 1.0.2011

Example Screen Shot Illustration Only

```

graph TD
    A[Which Site?] --> B[New Analysis: Filter Case Studies]
    A --> C[Existing Analysis: It Fits?]
    B --> D[Which Analysis Should I Choose?]
    B --> E[Output Reports]
    C --> F[New Analysis: Input Data]
    C --> G[Existing Analysis: Edit Site Data]
    F --> H[Selection of Parameters For Analysis]
    F --> I[Output Reports]
    G --> H
    G --> I
    H --> I
    I --> J[Exit Screen]
    
```

DNAPL Test Tool – Database Filters

SSA Step 4 Analysis Name: RITS example

Step 4 Input Non-Statistical Filters

Please fill in the following criteria to refine the analysis for the performance metrics without correlations to site characteristics.

Specify the geological characteristics of sites to include in the analysis:

Select geology: Consolidated Media (Fractured bedrock or clay) Unconsolidated Media (Overburden, Soil)

Degree of heterogeneity: High heterogeneity (variable soil types, orders of magnitude variation in hydraulic conductivity, layering, etc.)

Bioremediation Technologies:

Bioaugmented: Sites without bioaugmentation only

Specify ranges in site characteristic values to include in the analysis:

Characteristic	Minimum	Maximum	Units	Use Filter?
Source Area (m ²)	1	1000000	m ²	<input checked="" type="checkbox"/>
Hydraulic Conductivity	0.00000001	1	cm/s	<input checked="" type="checkbox"/>
Volume of Impacted Soil	1000000	10000000	m ³	<input checked="" type="checkbox"/>
Pre-Remediation DNAPL Mass	0.00000001	1000000	kg	<input checked="" type="checkbox"/>

Trick!
Specify criteria on this page is not required for a site-specific analysis, but can be useful for refining the list of case studies included in the analysis.

Acronyms

Step 1 Case Study Selection Process Overview → Step 2 Select Data Quality and Study Type → Step 3 Select Technologies and DNAPL Constituents → **Step 4 Input Non-Statistical Filters** → Step 5 Input Statistical Filters → Step 6 View Output

Exit Restart FAQs

version 1.0 2011

DNAPL Test Tool – Example Outputs

Performance Metric Summary

Performance Metric	Statistic	Chem. Ox. Fenton's Reagent or H2O2	Chem. Ox. Permanganate	Chem. Ox. Ozone
DNAPL Mass Decrease	Minimum	96%	77%	NA
	Maximum	96%	77%	NA
	Average	96%	77%	NA
	Median	96%	77%	NA
	Studies Achieving Decrease	1	2	NA
Groundwater Concentration Decrease	Minimum	NA	63%	NA
	Maximum	NA	77%	NA
	Average	NA	70%	NA
	Median	NA	70%	NA
	Studies Achieving Decrease	NA	2	NA
Soil Concentration Decrease	Minimum	96%	80%	NA
	Maximum	96%	80%	NA
	Average	96%	80%	NA
	Median	96%	80%	NA
	Studies Achieving Decrease	1	1	NA
Achieve MCLs	Probability	1/1 (100%)	12 (55%)	NA
	Standard Deviation	NA	NA	NA
	Studies Achieving MCLs	1	12	NA
	Studies Reporting Data	1	22	NA
	Total Studies	1	22	NA
Probability of Rebound	Probability	0%	NA	NA
	Standard Deviation	0%	NA	NA
	Studies Achieving Rebound	0	1	NA
	Studies Reporting Data	1	2	NA
	Total Studies	1	2	NA
Treatment Duration	Minimum (weeks)	21	12	NA
	Maximum (weeks)	21	12	NA
	Average (weeks)	21	12	NA
	Median (weeks)	21	12	NA
	Studies Reporting Data	1	2	NA
Unit Cost of Source	Minimum (\$/m ³)	NA	170	NA
	Maximum (\$/m ³)	NA	245	NA
	Average (\$/m ³)	NA	210	NA
	Median (\$/m ³)	NA	210	NA
	Studies Reporting Data	NA	2	NA
Zone Treatment	Minimum	NA	2	NA
	Maximum	NA	2	NA
	Average	NA	2	NA
	Median	NA	2	NA
	Studies Reporting Data	NA	2	NA

Reduction in Groundwater Concentrations



Study	Reporting Concentration (ppm)	Percent Reporting Concentration Decrease	Average Percent Decrease	Median Percent Decrease	Minimum Percent Decrease	Maximum Percent Decrease
CC-01	0	1	0%	17%	17%	17%
CC-02	2	2	100%	70%	70%	77%
CC-03	2	2	100%	94%	94%	96%
CC-04	4	4	100%	74%	63%	95%
CC-05	2	2	100%	90%	90%	90%

Acronyms: FRTS research Thursday, December 20, 2012 Page 1 of 2 GeneratedBy: Statistics.mdb www.rits.org

Example Screen Shot - Illustration Only

Summary of Input Selections - Site Specific Analysis

Fenton's Reagent
 Permanganate
 Ozone
 All
 None

Groundwater
 Soil
 None

DNAPL Mass
 Concentration
 None

Probability of Rebound
 Treatment Duration
 Unit Cost of Source
 Zone Treatment
 None

All
 None

Case Study Details

Notes:
 If a percent concentration reduction was not specified in the data file report, the reduction was calculated as the difference in pre and post-treatment maximum total mass concentrations of all reported volatile organic compounds. Concentration reductions of less than 20%, which is within the background range of analytical uncertainty, were not considered to be significant and were excluded from the analysis.
 * Percentage is based on the number of case studies reporting concentration data.

New Tool: Matrix Diffusion Toolkit (ESTCP Project)

Model Selection Screen
Matrix Diffusion Toolkit Version 1.0

Evaluate Matrix Diffusion

- Use Simple "Square Root Model" (SRM)
- Use More Detailed "Dandy-Sale Model" (DSM)

Groundwater Flow Direction

Source Loading

Transmissive Zone

Low-K Zone

Diffusion from low-k zone causing mass discharge into transmissive zone

Former Source Loading

Transmissive Zone

Low-K Zone

Diffusion from low-k zone causing mass discharge into transmissive zone

Depiction of Square Root Model

Return to Main Screen Apply Related Tools Which Model Should I Choose?

46 Objectives, Data Needs, and Tools RITS 2013: Lessons Learned from DNAPL Site Remediation

Recently released tool that will be introduced herein.

Matrix Diffusion Toolkit – DSM Module Inputs

DSM Data Input Screen
Matrix Diffusion Toolkit Version 1.0
Site Location and ID: RITS Example

1. SYSTEM UNITS
SI Units English Units

2. HYDROGEOLOGY
Transmissive Zone Description: Sand
Transmissive Zone Effective Porosity: 0.35
Low-k Zone Description: Silt
Low-k Zone Total Porosity: 0.43
Transmissive Zone Seepage Velocity: 3.70E-01
Calculate V

3. TRANSPORT
Key Constituent: TCE
Plume Loading Concentration Immediately Above Low-k Zone in Vertical Plane Source During Loading Period: 1100
Molecular Diffusion Coefficient in Free Water: 9.10E-10
Transmissive Zone Apparent Tortuosity Factor Exponent: 0.33
Low-k Zone Apparent Tortuosity Factor Exponent: 0.25
Bulk Density of Transmissive Zone: 2.65
Bulk Density of Low-k Zone: 2.65
Distribution Coefficient: 1.18
Transmissive Zone Fraction of Organic Carbon: 0.0004
Low-k Zone Fraction of Organic Carbon: 0.0004
Dynamic Organic Carbon: 0.0004

4. SOURCE ZONE CHARACTERISTICS
Source Zone Length: 32.1
Source Zone Width: 39.3
Transverse (Vertical) Hydrodynamic Dispersivity: 1.00E-01
Source Loading Starts in Year: 1952
Source Removed in Year: 2012

5. GENERAL
See Release Period Results for:
Year: 2012
Lateral Distance from Source: 50
Depth into Low-k Zone: 3

DATA INPUT INSTRUCTIONS
Enter value directly. Value calculated by Toolkit. Do not enter data.

DNAPL Source
Transmissive Zone
Low-k Zone
"L" is only used to define the vertical concentration for the vertical plane source.

Results Calculated Here

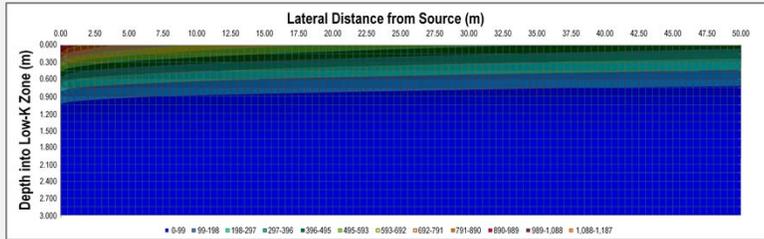
47 Objectives, Data Needs, and Tools RITS 2013: Lessons Learned from DNAPL Site Remediation

Input screen for DSM module.

An example will be used herein – 50 years of source loading from 1952 through 2012.

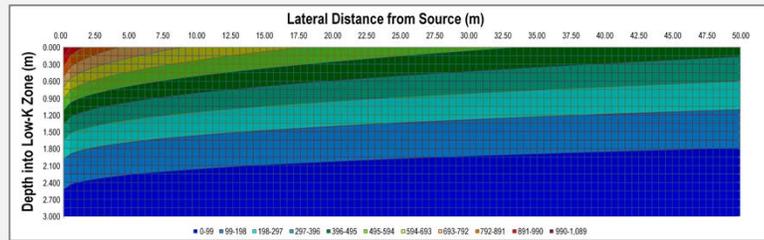
We will then look at source removal in 2012 followed by back-diffusion out of the low-K zone.

Matrix Diffusion Toolkit – (Diffusion into low-K layer)



1962

After 10 years of
source loading

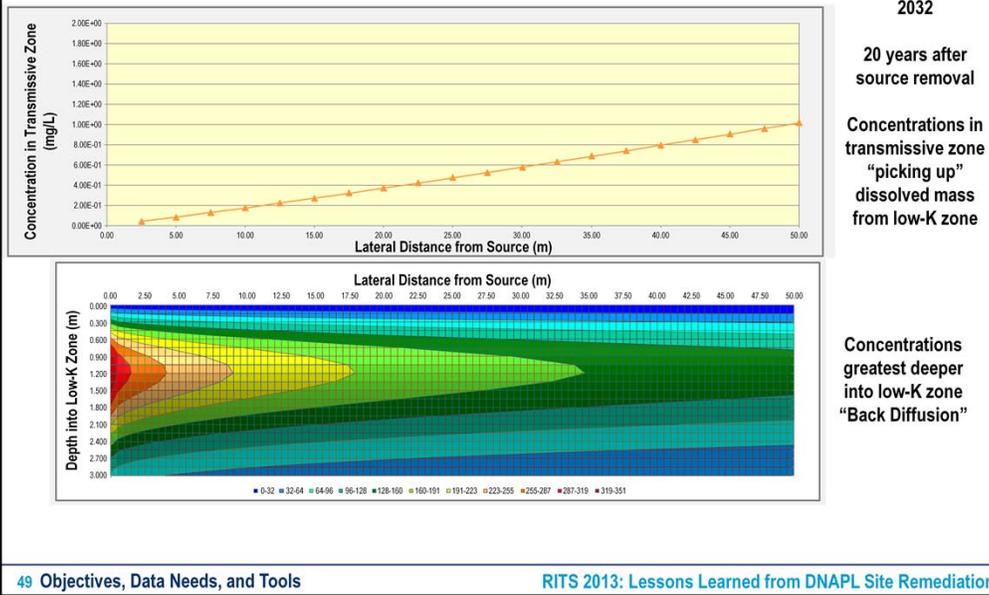


2012

After 60 years of
source loading

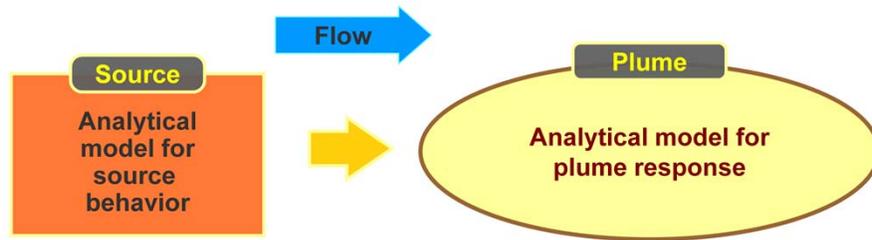
Note increase in concentrations diffused into the clay layer over both time and with closer distance to the source.

Matrix Diffusion Toolkit – (20 yrs after source removal)



20 years after source removal, still see significant increase in concentration along flow path in transmissive zone due to back diffusion out of clay layer.

New Tool: REMChlor Model (SERDP/ESTCP Project)



- **Newer variations:**

- Probabilistic outcomes (PREMChlor)
- Fuel hydrocarbon sources (REMFuel)

REMChlor model links source behavior and plume behavior.

Applying Advanced Tools to Remedial Design

- **No SOPs... currently as much art as engineering**
 - What-if? scenarios
 - Addressing one specific aspect of remedy design at a time
- **Advanced design tools require advanced data – more than has been the historical norm!**
- **Accurate estimates of treatment rate and extent likely requires a very detailed pilot study**

Presentation Overview

- Key Concepts and Challenges for Remediation of DNAPL Sites
- Objectives, Data Needs, and Tools
- ▶ Focused NAVFAC Site Case Studies
- Synthesis – Best Practices and Future Directions
- Summary

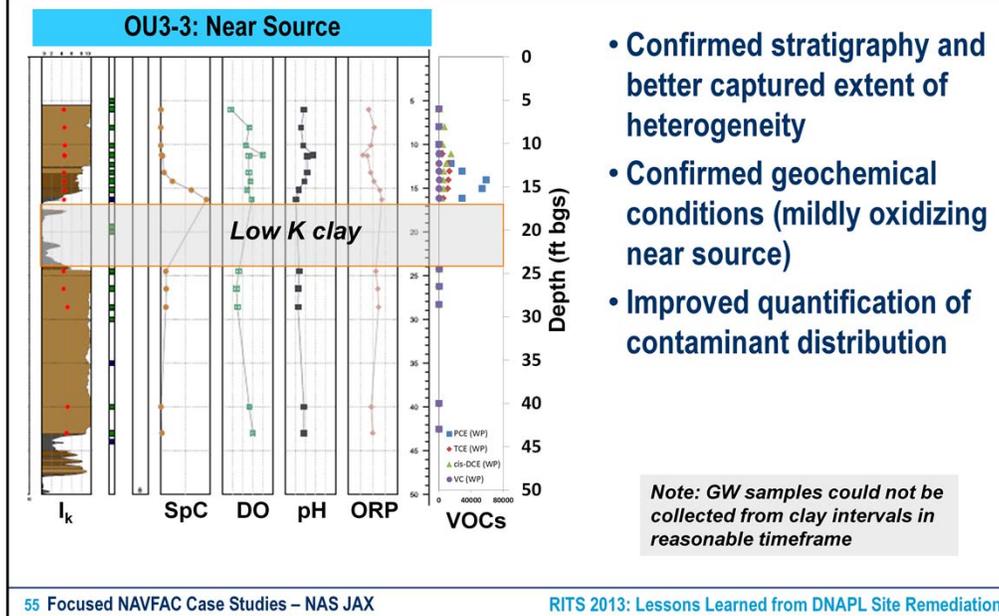
Case Study 1: Advanced Characterization at NAS JAX

- Data from ESTCP Project 201032
- Broader purpose of ESTCP project is to assess “source history” through advanced characterization and application of modeling tools
- Data collected illustrate remediation-related concepts
 - Evaluation of new hi-res characterization tools
 - Mass distribution between low-K and transmissive zones
 - Rich data set that would support advanced design approaches

Test Design Step 1B: Multi Port Sampler

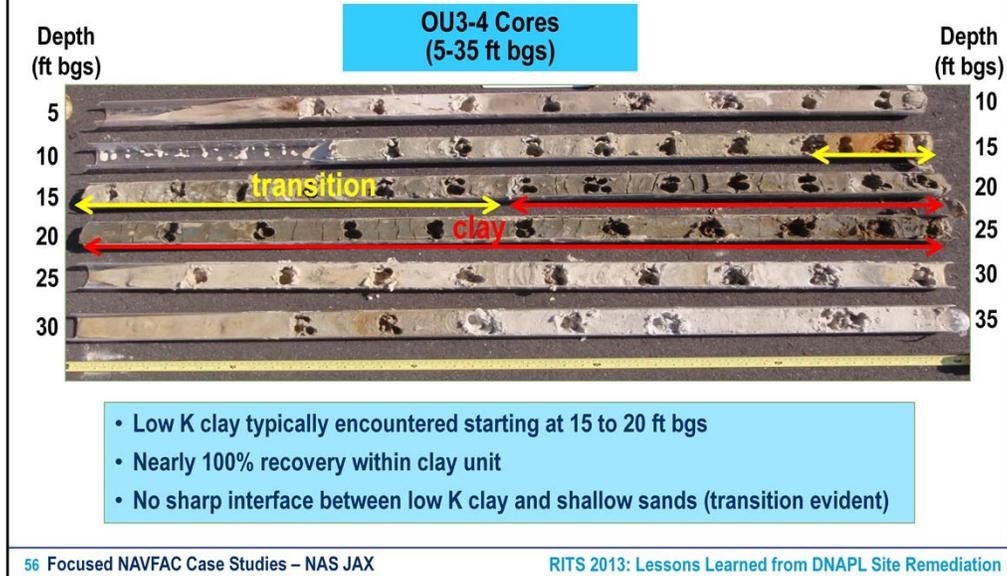
- **Objective: Obtain detailed vertical permeability profile (index of hydraulic conductivity or “ I_k ”)**
- **Collect depth-discrete GW samples for quantifying CVOC concentrations and geochemical parameters**

GW Typical Results: Source Area #1



I_k data (left column) identifies clay layer.

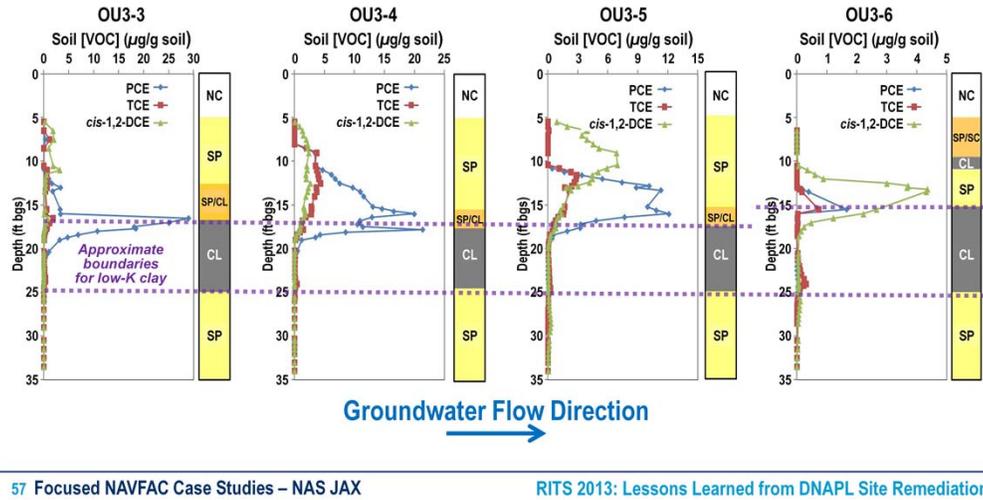
Soil Coring Typical Results: Source Area #1



Hi-resolution characterization using closely spaced soil samples submitted for laboratory analysis.

Soil Coring Typical Results: Source Area #1 Soil VOC Results Along Plume Flowpath

- Significant transformation along plume flowpath
- Lower % of mass associated with clay



57 Focused NAVFAC Case Studies – NAS JAX

RITS 2013: Lessons Learned from DNAPL Site Remediation

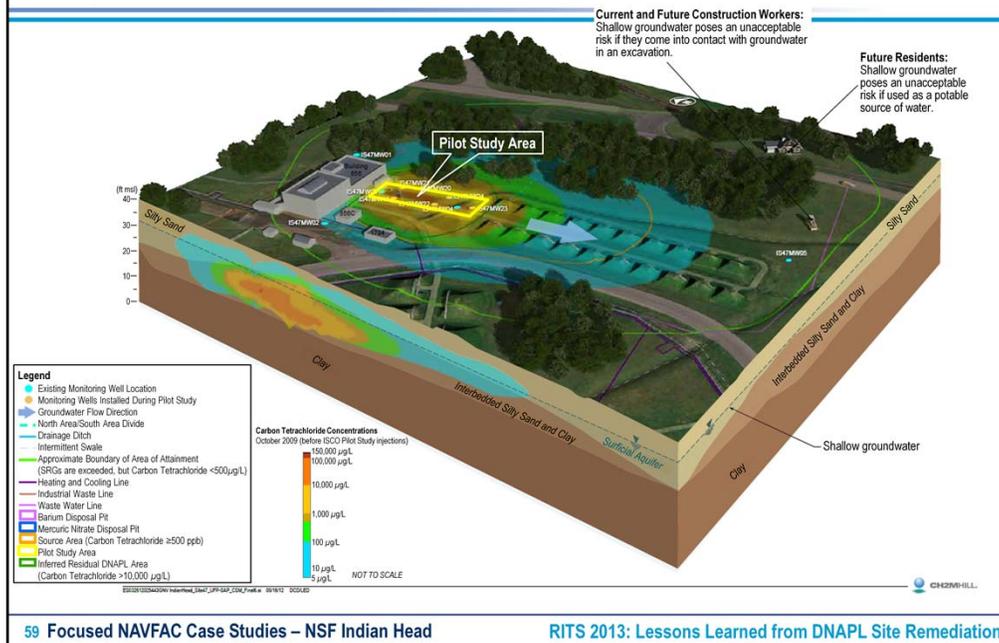
Closely vertically-spaced soil analytical data evaluated in cross section provides a rich understanding of the conceptual site model, showing “early stage” plume. No back diffusion observed, as concentrations are greatest at or above clay interface. Active diffusion into clay near source, limited diffusion into clay at distance. Slow groundwater flow and transformation to cis-1,2-DCE are consistent with active natural attenuation.

Case Study 2 – NSF Indian Head, MD Site 47 ISCO Pilot

- “Deep Dive” into selected data – focused on deriving key lessons learned
- Not a comprehensive review of all pilot study aspects
- Primary COCs and approximate baseline concentration ranges:
 - Carbon Tetrachloride (CT)
 - Chloroform (CF)
 - PCE, TCE

	Soil (ppb)	Groundwater (ppb)	Solubility (ppb)
CT	10,000-260,000	100-150,000	793,000
CF	1,000-8,000	50-44,000	7,920,000
PCE	10-1,000	10-2,200	200,000
TCE	5-50	3-250	1,100,000

NSF Indian Head Site 47 – Conceptual Site Model



Very nice macro-scale CSM figure. Newest thinking about DNAPL site conceptual site models would suggest that a smaller-scale perspective on geologic heterogeneity and contaminant distribution across different permeability zones would also be valuable.

NSF Indian Head Site 47 – Full Scale Remedy Objectives

- **Absolute Objectives (from ROD)**
 - Prevent unacceptable risks to human receptors from exposure to contaminants in shallow groundwater
 - Prevent migration of shallow groundwater above Site Remediation Goals (SRGs) from Site 47 to uncontaminated media
 - Return the shallow groundwater to its beneficial use designation to the extent practicable
- **Functional Objectives (from 100% basis of design)**
 - SRGs: Carbon Tetrachloride 5 ppb, PCE 5 ppb (plus others)
 - Implement ISCO in the source area where the CT and PCE concentrations are greater or equal to 500 $\mu\text{g/L}$
 - Use MNA processes for the remaining dissolved plume and the source area following ISCO
 - Enforce ICs in the form of land and groundwater use restrictions
 - Incorporate sustainable remediation strategies

Both absolute and functional objectives expressed in project documents.

ISCO Pilot Study Design at NSF Indian Head Site 47

- Alkaline activated persulfate
- Two 5-ft injection intervals (7-12 ft. bgs and 13-18 ft. bgs)
- Initially planned as 2 injection events; 46,200 lbs. oxidant followed by 35,200 lbs. oxidant. Second event not performed due to site logistics.
- Actual = 46,692 lbs. persulfate in 91,622 gallons solution
 - Oxidant Dose 8 g/kg (grams oxidant per kg soil)
 - Volume = ~ 75% of pore volume (PV)
- Electrical Conductivity profiling done to confirm persulfate extent, and overall good distribution obtained
- Baseline and Post-treatment sampling in soil and groundwater

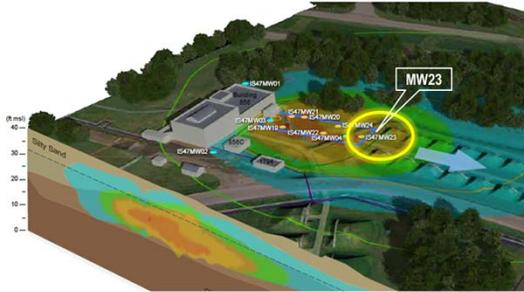
61 Focused NAVFAC Case Studies – NSF Indian Head

RITS 2013: Lessons Learned from DNAPL Site Remediation

A well-planned and highly robust ISCO pilot test was pursued. The second planned injection event was not able to be applied, and results need to be viewed in that context, as some partial/incomplete treatment was observed.

Post-ISCO Reductive Dechlorination??

- 6 Months post-ISCO @ MW23 – downgradient end of treatment zone
 - ORP = -331 mv
 - *cis*-1,2-DCE @480 ppb and increasing (max. at site pre- or post-ISCO)



62 Focused NAVFAC Case Studies – NSF Indian Head

RITS 2013: Lessons Learned from DNAPL Site Remediation

Partial oxidation of soil total organic carbon as well as organic contaminants can result in post-ISCO reductive dechlorination, as apparently occurred at this site.

Geochemical Results of ISCO Pilot – TOC Oxidation

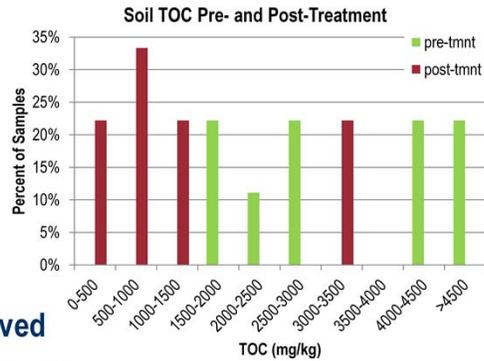
- Soil TOC oxidation by persulfate shifts sorption equilibria and releases sorbed VOCs to groundwater

- Avg. TOC in soil

- Pre-Tmnt: 7,100 mg/kg
- Post-Tmnt: 1,300 mg/kg

- 10 ppm soil equivalent

- Pre-Tmnt: 10,000 ppb dissolved
- Post-Tmnt: 29,000 ppb dissolved



Soil TOC oxidation results in significant desorption of contaminant mass – and release into the dissolved phase. This makes it accessible to treatment, but can also result in anomalously high dissolved concentrations if not taken into account.

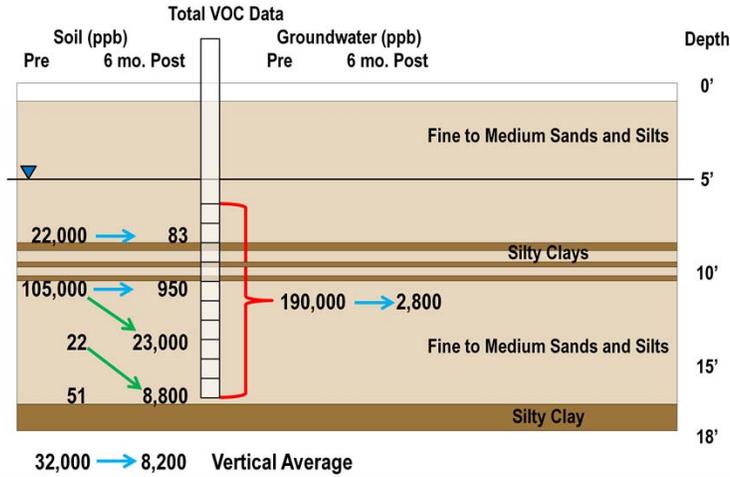
NSF Indian Head Site 47 – MW19 (within treatment zone)

SoilMOD est GW conc from soil & TOC
Pre = 62,000 ppb
Post = 27,000 ppb

TOC
Pre = 2,700 ppm
Post = 1,000 ppm

Reductions:

75% soil
98.5% GW



**NAPL
Displacement??**

**Spatial
Variability in
Soil Sampling??**

64 Focused NAVFAC Case Studies – NSF Indian Head

RITS 2013: Lessons Learned from DNAPL Site Remediation

Note that vertically-spaced soil data provides a richer understanding of post treatment changes than does the fully screened monitoring well data.

NSF Indian Head Site 47 – MW21 (within treatment zone)

SoilMOD est GW conc from soil & TOC

Pre = 9,800 ppb
Post = 3,290 ppb

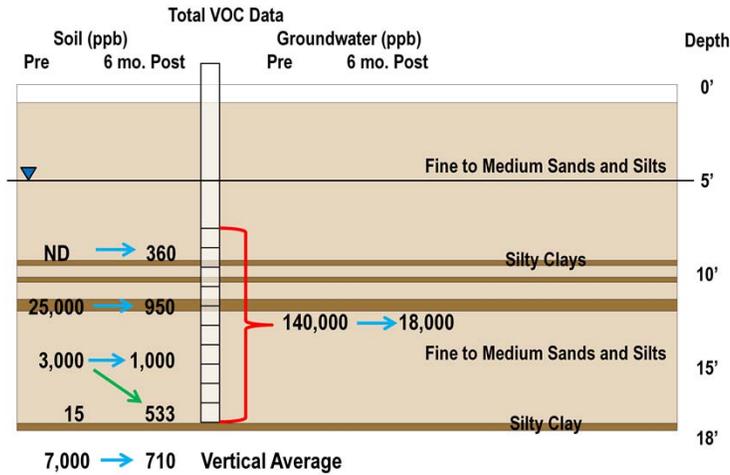
TOC

Pre = 4,300 ppm
Post = 350 ppm

Reductions:

90% soil

87% GW



65 Focused NAVFAC Case Studies – NSF Indian Head

RITS 2013: Lessons Learned from DNAPL Site Remediation

Note that vertically-spaced soil data provides a richer understanding of post treatment changes than does the fully screened monitoring well data.

NSF Indian Head Site 47 – MW22 (within treatment zone)

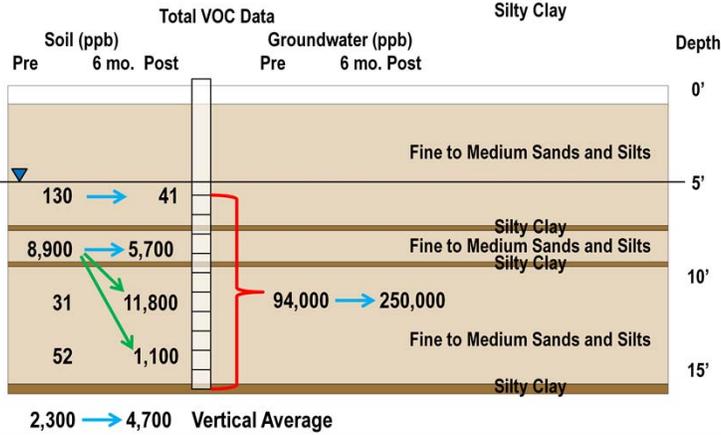
SoilMOD est GW conc from soil & TOC
Pre = 5,000 ppb
Post = 7,600 ppb

TOC
Pre = 2,150 ppm
Post = 3,500 ppm

Increases:

104% soil

166% GW



**NAPL
Displacement??**

**Spatial
Variability in
Soil Sampling??**

Note that vertically-spaced soil data provides a richer understanding of post treatment changes than does the fully screened monitoring well data.

NSF Indian Head Site 47 – MW23 (downgradient end of treatment zone)

SoilMOD est GW conc from soil & TOC
Pre = 26,000 ppb
Post = 1,500 ppb

TOC
Pre = 19,000 ppm
Post = 3,200 ppm

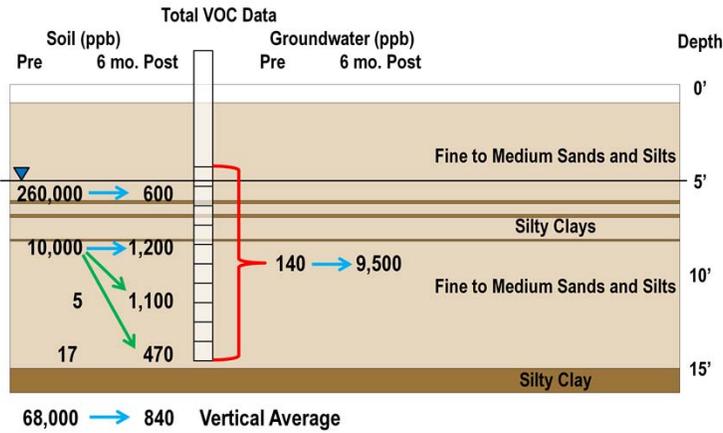
Reductions:

98.7% soil

Increases:

6,700% GW

Downgradient migration??



67 Focused NAVFAC Case Studies – NSF Indian Head

RITS 2013: Lessons Learned from DNAPL Site Remediation

Note that vertically-spaced soil data provides a richer understanding of post treatment changes than does the fully screened monitoring well data.

NSF Indian Head Site 47 ISCO Pilot – Treatment Summary

- **Significant VOC mass reduction (estimated ~ 80%)**
- **Dissolved VOC concentration reduction ~ 47% on average**
- **Some VOC concentrations declined while others increased**
- **Shallow soil VOC decreases accompanied by deeper soil increases (net 83% avg. decrease)**
- **ISCO appeared to promote additional reductive bio-treatment**

NSF Indian Head Site 47 ISCO Pilot – Lessons Learned

- **Fully screened MWs did not reflect subsurface complexity**
- **Potential vertical movement of COCs observed**
- **Vertically spaced multi-level soil sampling very valuable**
- **A single ISCO application resulted in partial treatment, significant residual contamination remained**
- **Multiple applications needed for >90% reductions**
- **Combined technologies – ISCO can promote subsequent biodegradation and further attenuation downgradient**

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Best Practices from the NAS JAX Case Study

- **Hi-resolution site characterization can provide data that elucidates a valid Conceptual Site Model**
 - New field tools can be valuable, *BUT...*
 - Doesn't always have to be "high-tech" new tools, because hi-density vertical interval soil sampling (e.g., NAS JAX) can provide valuable data
- **Dense vertically-delineated data**
 - Elucidates differences in mass distribution both across lithologies and with distance from the source
 - Allows targeting treatment to the zones that matter

Best Practices from the Indian Head Site 47 Case Study

- ISCO Application was fairly robust, above average
- Soil sampling pre- and post-treatment was helpful to assess treatment results on a mass basis – but variability and uncertainty remains
- Results after partial treatment (first injection event) will often be confounding due to displacement, desorption, etc.
- Even with a thorough and robust approach, multiple treatment applications will likely be required for ISCO at this site (same for bio, *i.e.*, all but thermal)

ISCO application:

Oxidant Dose 8 g/kg (grams oxidant per kg soil)

Volume = ~ 75% of pore volume (PV)

Alignment (or Lack Thereof) with Standard Practice

- **Relative to the “Gold Standard” at most sites...**
 - We don’t really understand the contaminant distribution
 - Common characterization/monitoring approaches pre- and post-treatment are not adequate to understand the complexities of treatment results and what remains
- **Mediocre DNAPL source remediation performance likely results from:**
 - Mediocre characterization
 - Mediocre robustness of design and implementation

Future Directions for DNAPL Source Remediation

- Can probably move from 80% to 95% removals to 95% to 99% removals, *IF WE...*
 - Use hi-resolution characterization tools to understand contaminant distribution
 - Very robustly target remedies at high-mass zones, including low-K media
 - Implement the Observational Approach, use hi-res performance monitoring, measure results then apply additional treatment
- But, residual mass will still remain and we have to understand the site specific benefit gained by the additional incremental treatment

Presentation Overview

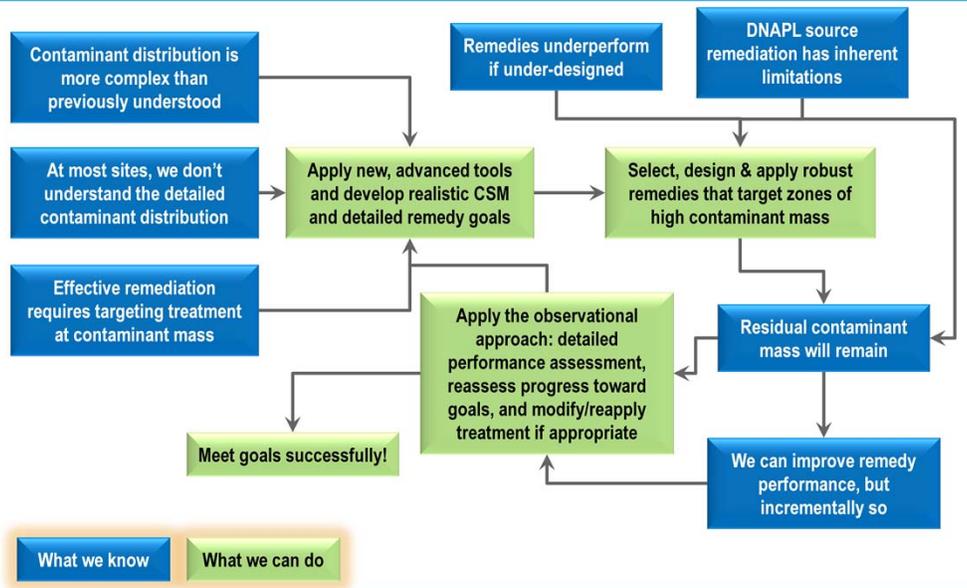
- Key Concepts and Challenges for Remediation of DNAPL Sites
- Objectives, Data Needs, and Tools
- Focused NAVFAC Site Case Studies
- Synthesis – Best Practices and Future Directions

▶ Summary

Key Take-Home Points

- **To succeed we need to:**
 - Accept LTMgt as inevitable at many sites to manage the residual
 - Determine what is an acceptable and achievable residual level
 - Be realistically robust in our short-term source treatment remedy to reach the acceptable and achievable level of residual
 - Focus more on strategy/application and less on “*which technology*”

Final Graphical Summary



References

- ITRC, Technical and Regulatory Guidance for Integrated DNAPL Site Strategies (IDSS), Interstate Technology and Regulatory Council, 2011.
- ITRC, Technical and Regulatory Guidance for *In Situ* Bioremediation of Chlorinated Ethene DNAPL Source Zones, Interstate Technology and Regulatory Council, June 2008.
- ITRC, Technical/Regulatory Guidelines – Strategies for Monitoring the Performance of DNAPL Source Zone Remedies, Interstate Technology and Regulatory Council, August 2004.
- NAVFAC 2010 – Naval Facilities Engineering Command (NAVFAC). 2010. Guidance for Optimizing Remedy Evaluation, Selection and Design.
- EPA 540/R-96/023 October 1996. Presumptive Response Strategy and *Ex-Situ* Treatment Technologies for Contaminated Groundwater at CERCLA Sites.
- Strategic Environmental Research and Development (SERDP) project ER-201126, Decision Support System for Matrix Diffusion Modeling.