DoD EPA DOE SERDP
Strategic Environmental Research and Development Program

ESTCP
Environmental Security Technology Certification Program

Recent Advances in the Management and Remediation of DNAPL Source Zones

Presented by

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Chuck Newell
Tom Sale
Hans Stroo

Westfield, MA
9 April 2008

DoD's Environmental Technology Programs

Demonstration/Validation

Basic and Applied Research

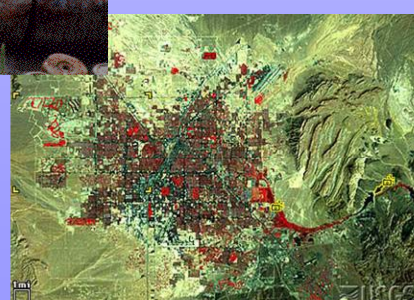
Environmental Drivers:
Sustainability of Ranges and Range Operations


Maritime Sustainability
Threatened and Endangered Species


Toxic Air Emissions and Dust

Unexploded Ordnance

Noise NOX and PM



Urban Growth & Encroachment

Environmental Drivers:
Reduction of Current and Future Liability

Current Liabilities

Contamination from Past Practices

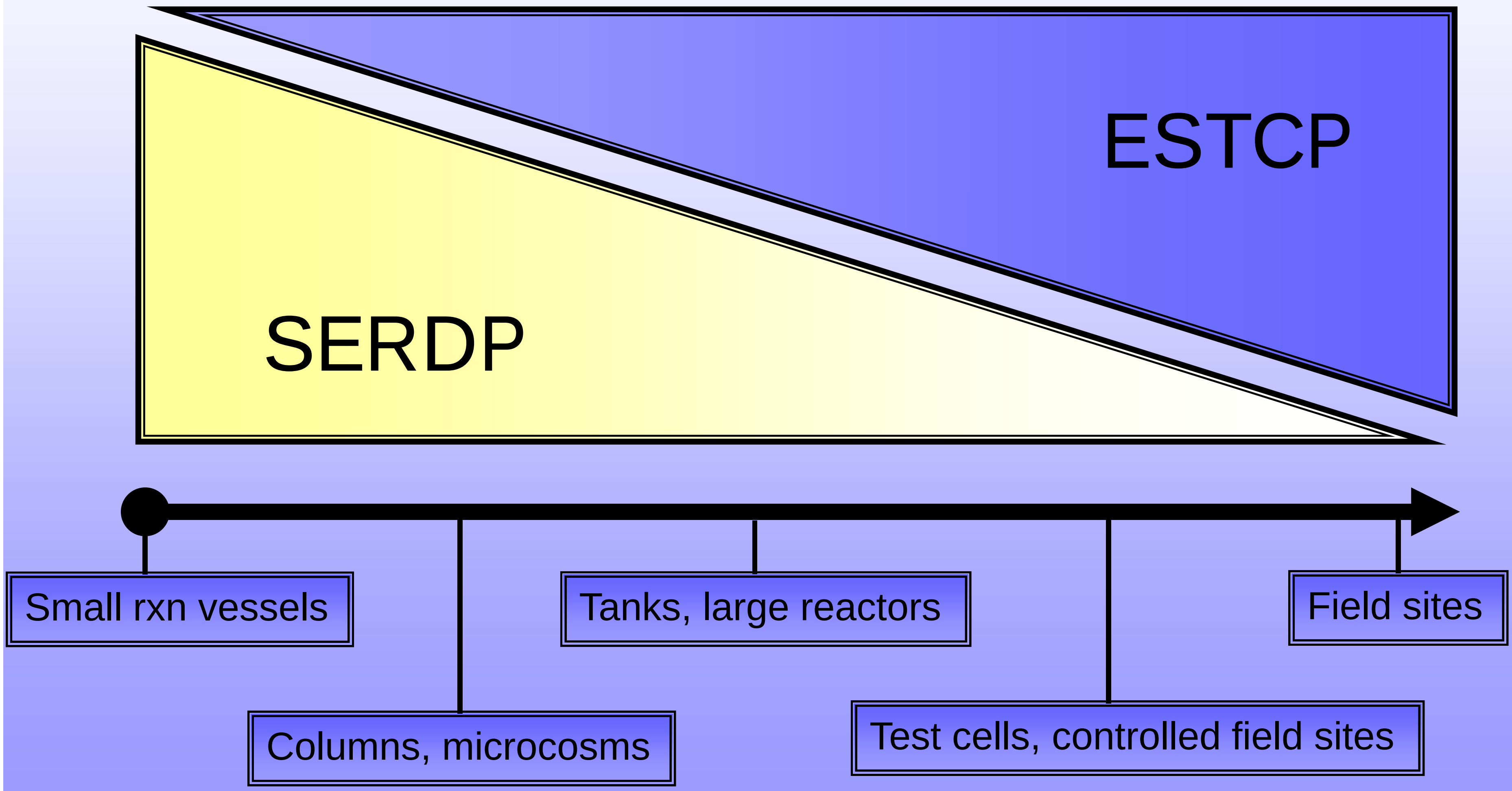
- **Chlorinated Solvents**
- **UXO**
- **Emerging Contaminants (Perchlorate)**

Future Liabilities

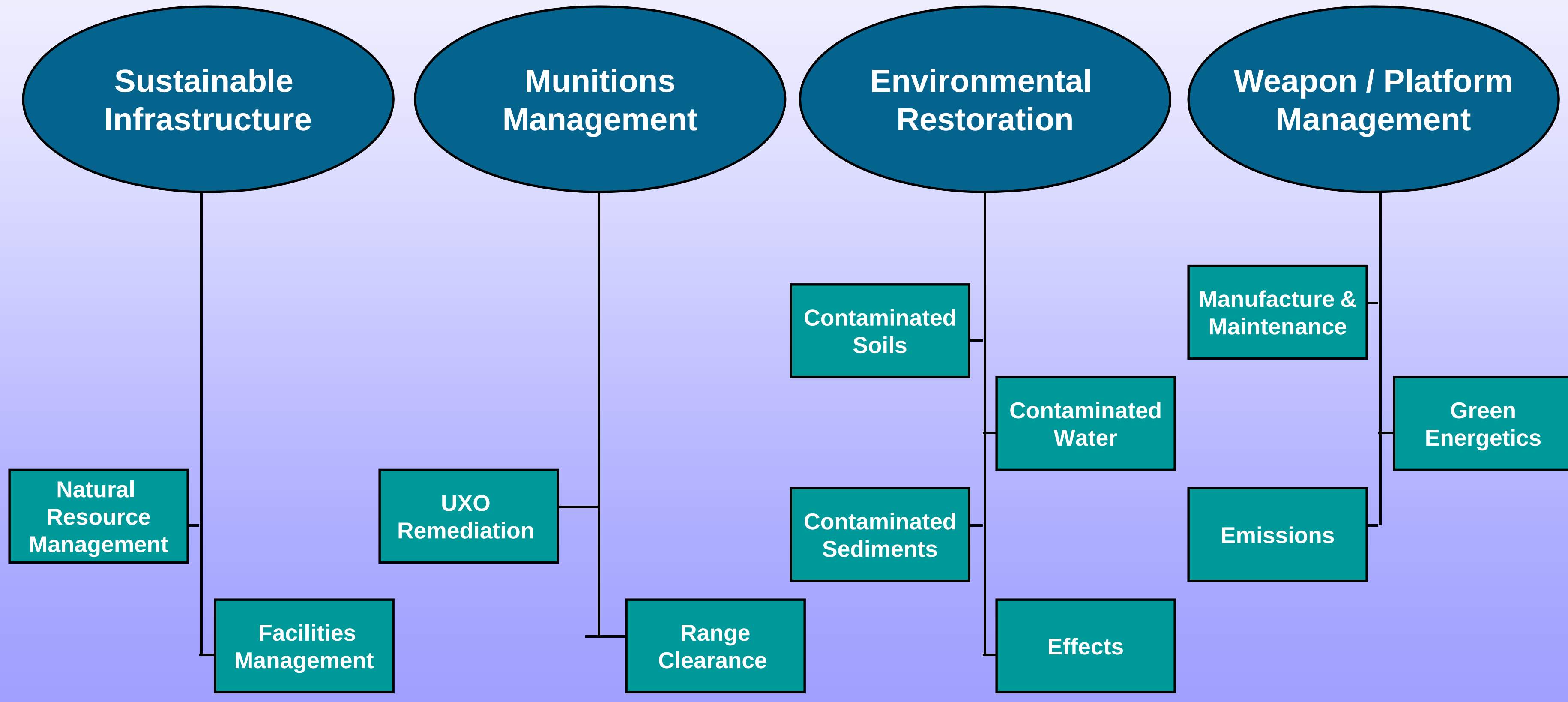
Control Life Cycle Costs

- **Elimination of Hazardous Materials**
- **Achieve Compliance Through Pollution Prevention**

Scales of Research



SERDP and ESTCP Pillars



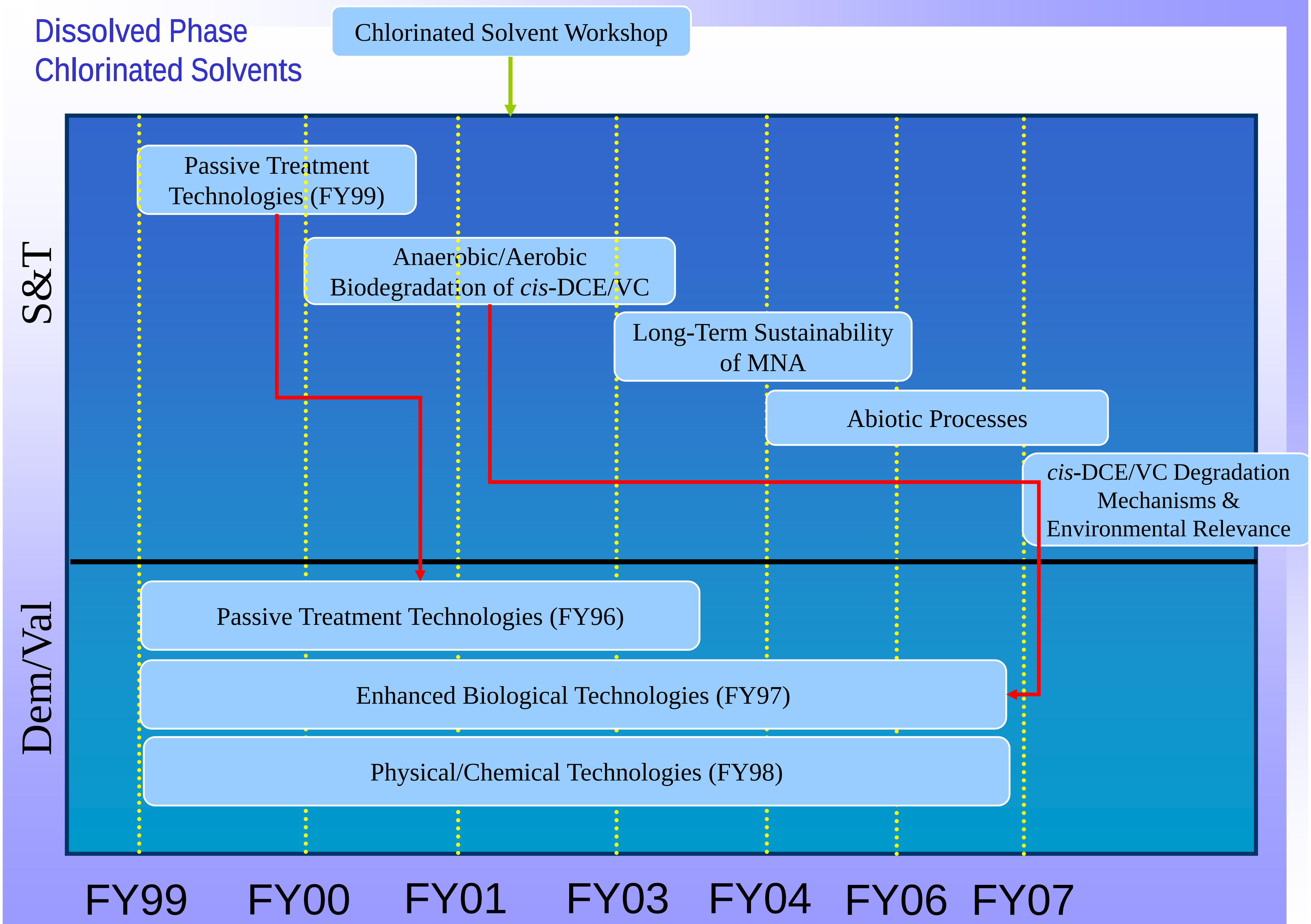
Environmental Restoration Program Characteristics

- ~200 active projects
- Projects range from $85K to 2.5M/year, average size is $400K/year
- 95% of projects are partnered
- Project length runs 1 to 5 years
- Turn over roughly 25% of the program each year

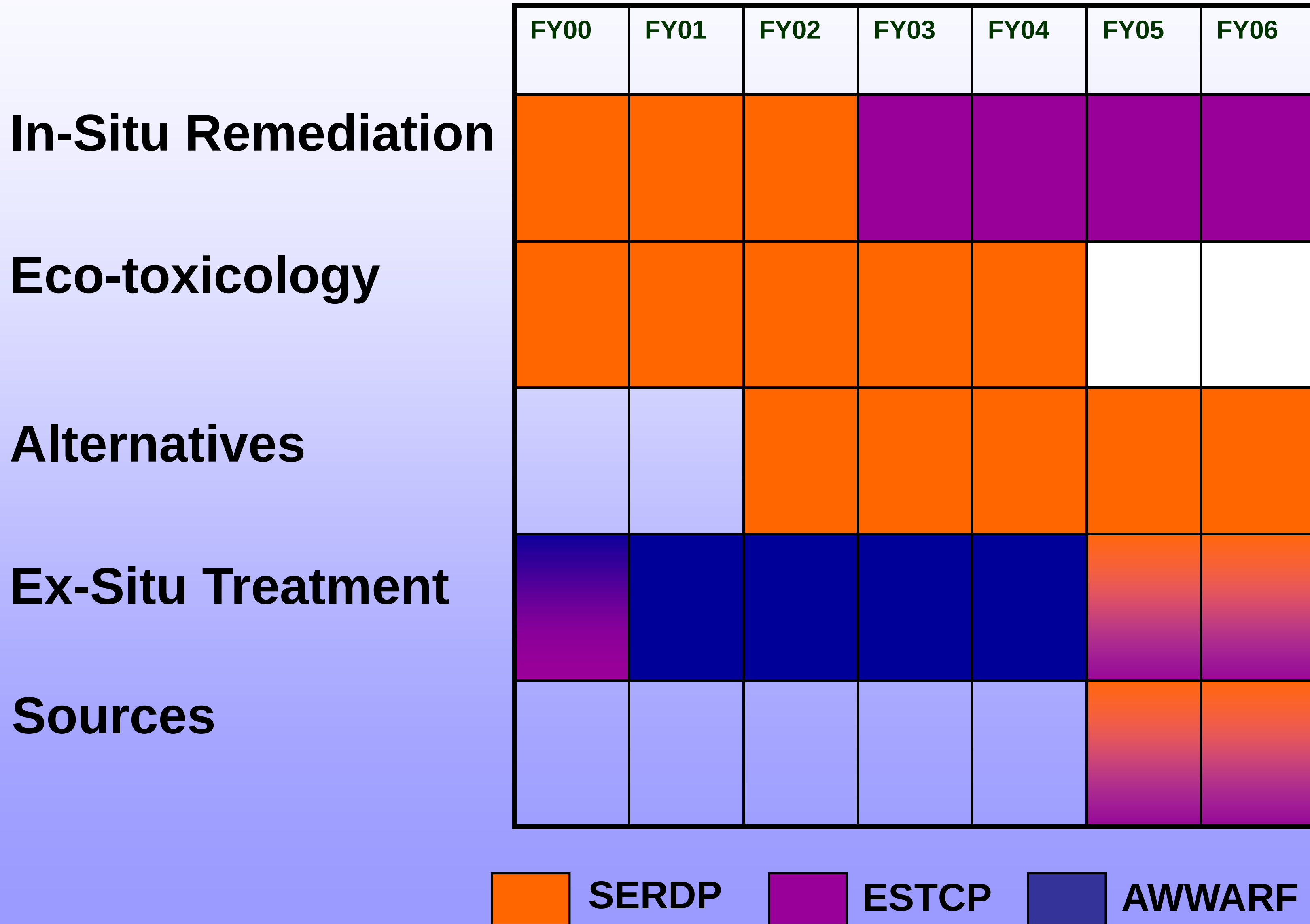
Environmental Restoration Research Focus Areas

- Chlorinated Solvents
  - Dissolved Phase
  - DNAPL Source Zones
    - ISCO
    - Thermal
    - Bioremediation
    - Fractured rock
- Munitions Constituents
  - Perchlorate
  - Energetics
  - Heavy Metals
- Sediments
- Risk Assessment
- Range Sustainability
- Site Characterization and Monitoring
- Performance Assessment & Optimization

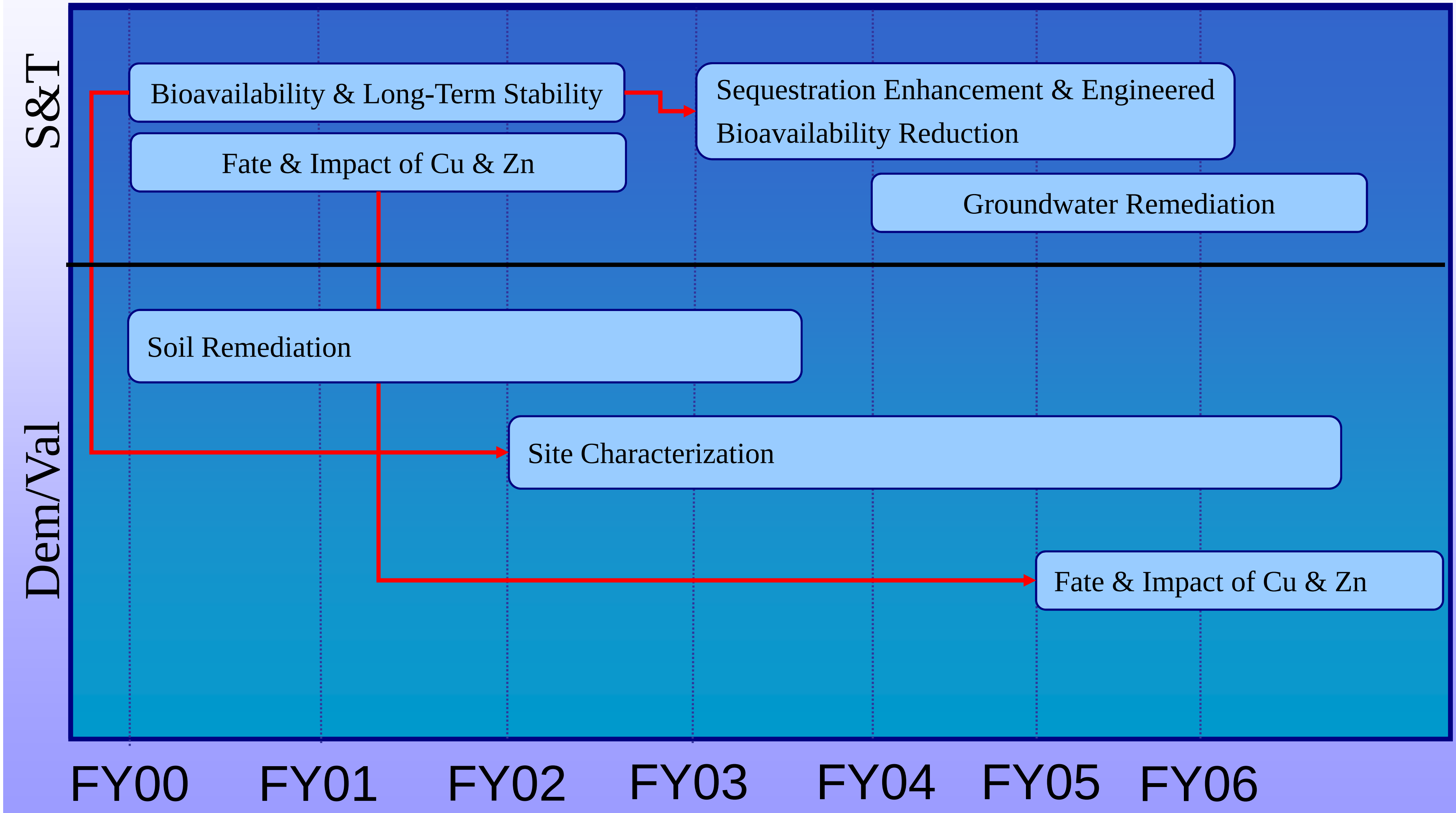
Dissolved Phase Chlorinated Solvents



Perchlorate RDT&E

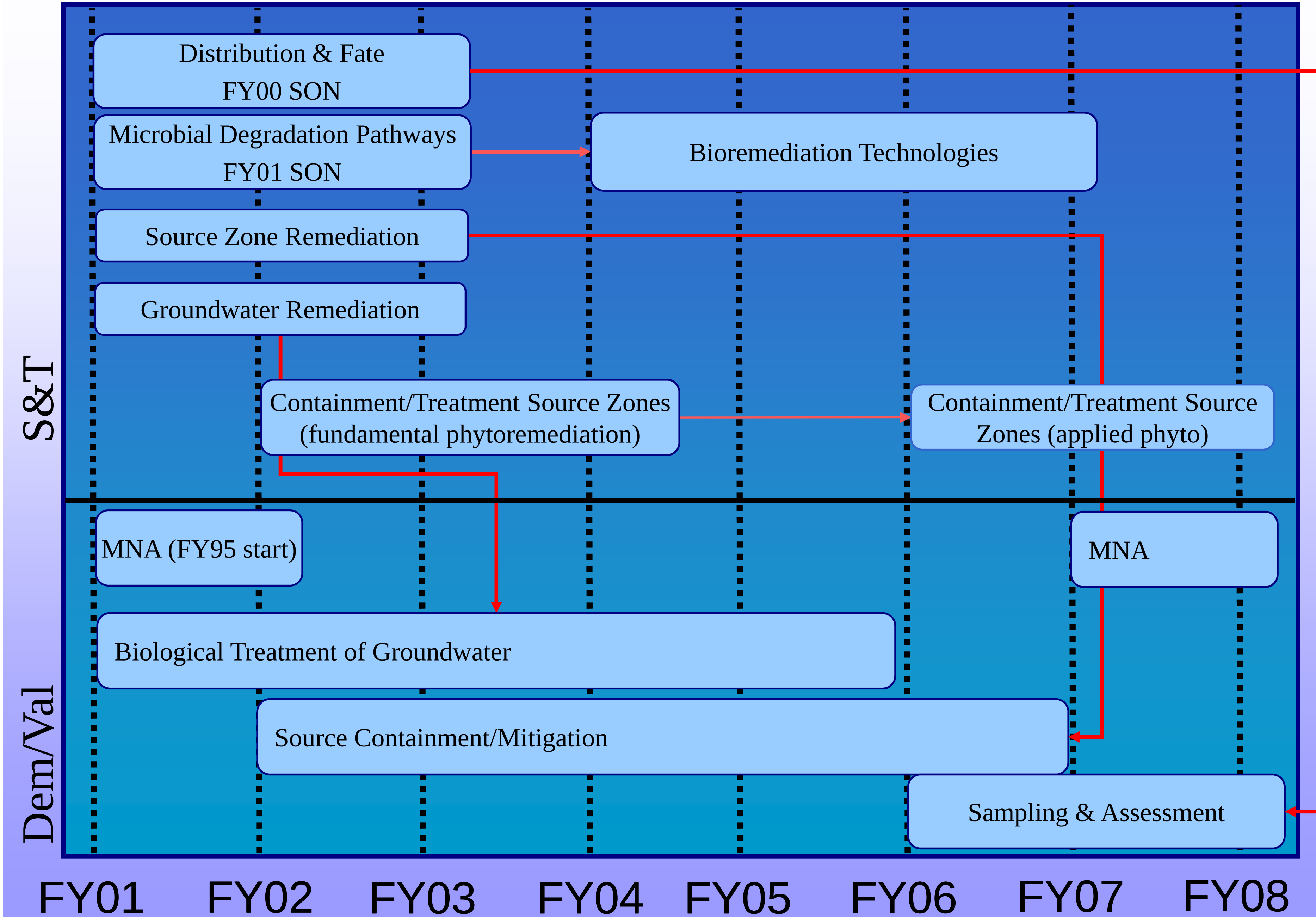


Metals

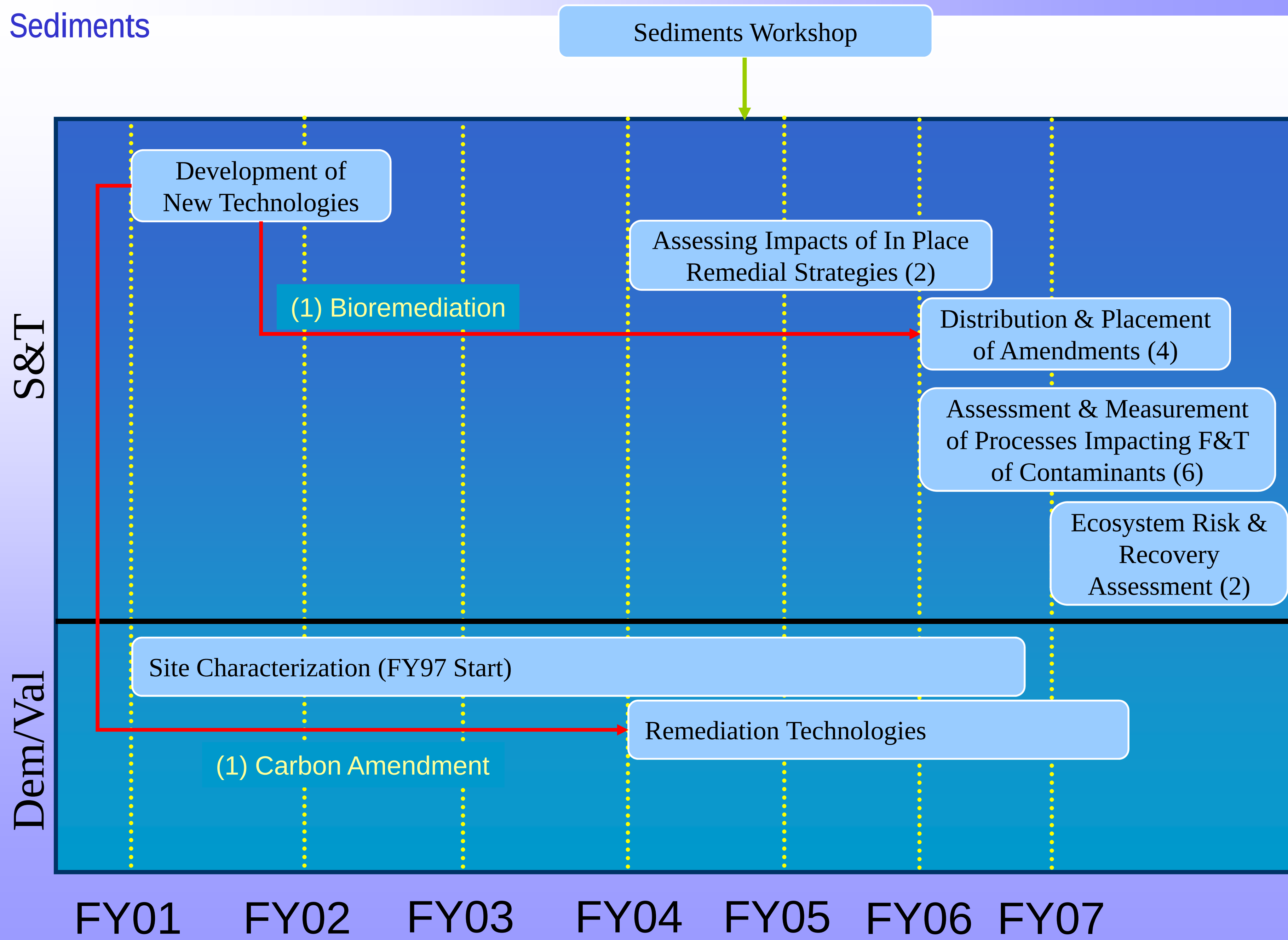


S&T
Dem/Val
Bioavailability & Long-Term Stability
Fate & Impact of Cu & Zn
Sequestration Enhancement & Engineered Bioavailability Reduction
Groundwater Remediation
Soil Remediation
Site Characterization
Fate & Impact of Cu & Zn
FY00
FY01
FY02
FY03
FY04
FY05
FY06

Energetic Compounds



Sediments



Sediments Workshop
S&T
Development of New Technologies
(1) Bioremediation
Assessing Impacts of In Place Remedial Strategies (2)
Distribution & Placement of Amendments (4)
Assessment & Measurement of Processes Impacting F&T of Contaminants (6)
Ecosystem Risk & Recovery Assessment (2)
Dem/Val
Site Characterization (FY97 Start)
Remediation Technologies
(1) Carbon Amendment
FY01
FY02
FY03
FY04
FY05
FY06
FY07

Home Pages

http://www.serdp.org

http://www.estcp.org

Home page contains fact sheets for every project funded, as well as all published documents.

Sponsored by
SERDP and ESTCP

Partners in Environmental Technology
Technical Symposium and Workshop

December 2-4, 2008

Marriott Wardman Park Hotel, Washington, D.C.

Short Courses
- Decision Guide for Management of Chlorinated Solvents
- In Situ Chemical Oxidation
- Introduction to Discrimination of Military Munitions
- In Situ Bioremediation of Perchlorate
- Monitored Natural Recovery of Contaminated Sediments
- State of the Art in Capping and Amendments for Contaminated Sediments

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DNAPL Short Course

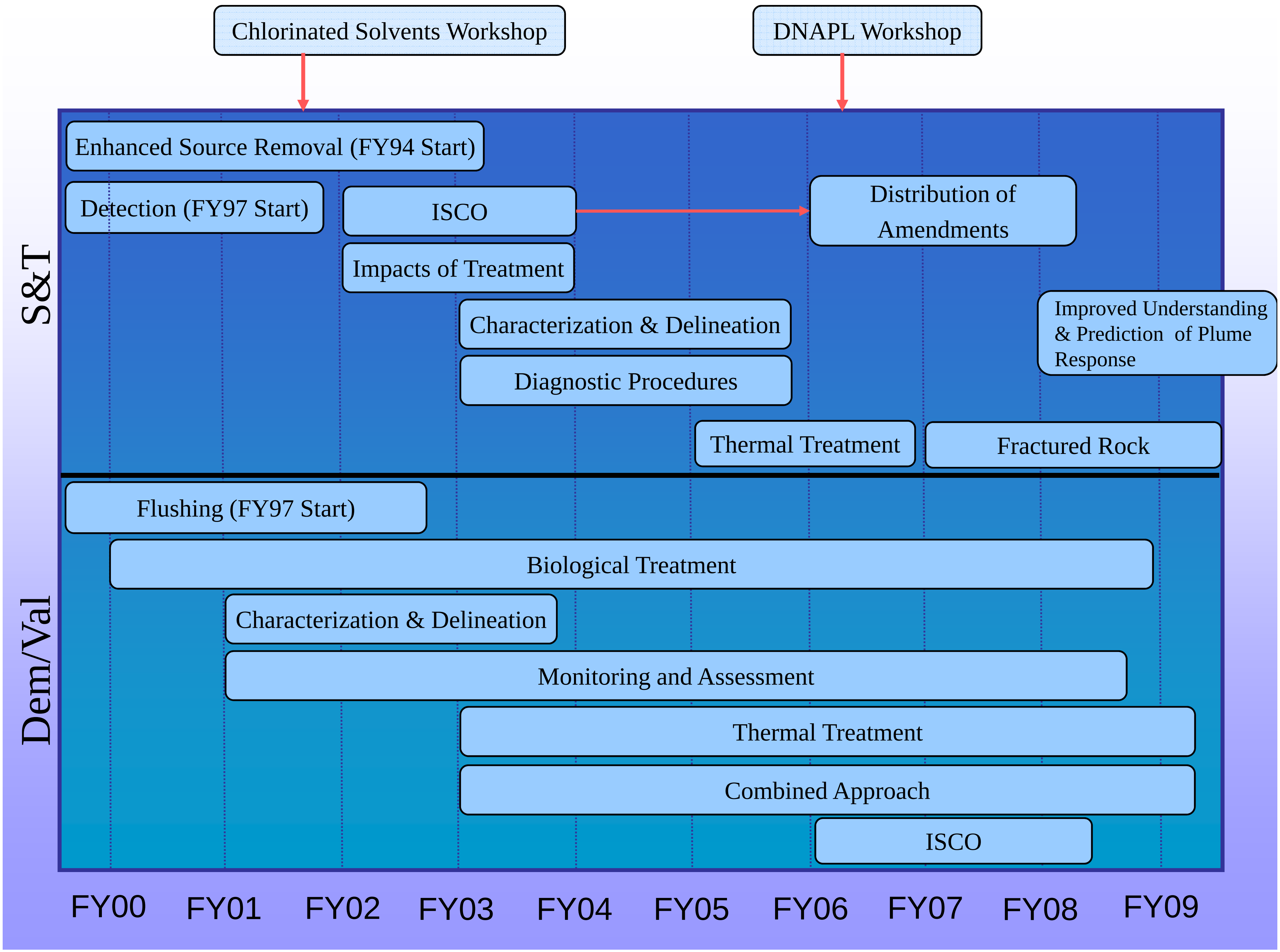
Chlorinated Solvents: A Major DoD Liability

- Chlorinated solvents at approx. 80% of Superfund sites w/ groundwater contamination
- More than 3,000 DoD sites in the United States
- DoD may spend > $100 million annually for hydraulic containment at these sites
- Estimates of DoD life-cycle costs > $2 billion.

SERDP/ESTCP DNAPL R&D

- Major Focus Area
  - Ca. 15% of Cumulative Funding: ’97 - ’07

- R&D Priorities from ’01 Workshop
  - Focus more on DNAPL, Less on Dissolved
  - Evaluate Thermal, ISB, and ISCO/ISCR
  - Improve Delivery Methods
  - Quantify Benefits of Source Depletion
  - Improve Decision Support / Diagnostic Tools



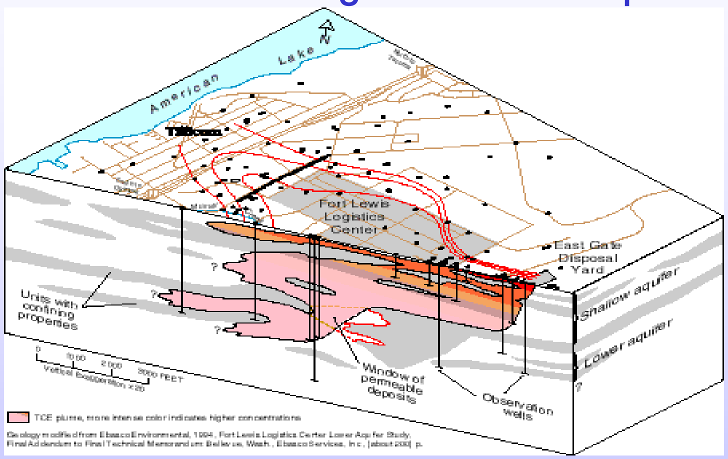
Chlorinated Solvents Workshop
DNAPL Workshop
S&T
Enhanced Source Removal (FY94 Start)
Detection (FY97 Start)
ISCO
Distribution of Amendments
Impacts of Treatment
Characterization & Delineation
Improved Understanding & Prediction of Plume Response
Diagnostic Procedures
Thermal Treatment
Fractured Rock
Dem/Val
Flushing (FY97 Start)
Biological Treatment
Characterization & Delineation
Monitoring and Assessment
Thermal Treatment
Combined Approach
ISCO
FY00
FY01
FY02
FY03
FY04
FY05
FY06
FY07
FY08
FY09

Ongoing Initiatives Related to DNAPL Source Zones

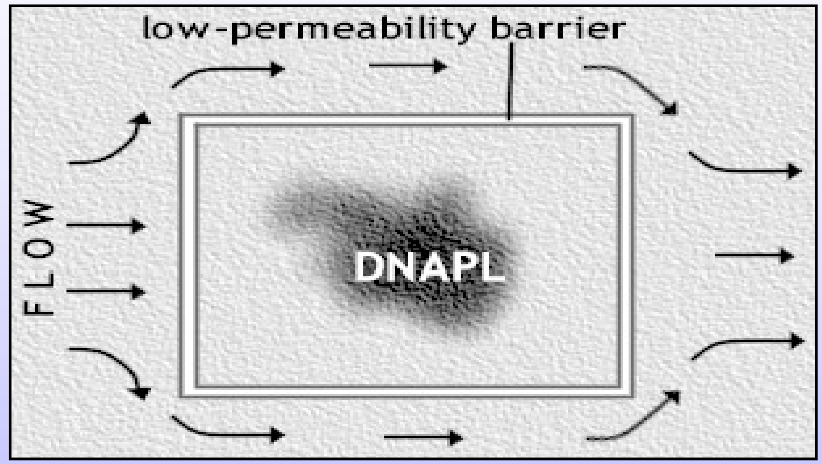
- Understanding Sources & Plume Response
- Fractured Rock Site Remediation
- In Situ Thermal Treatment
- In Situ Chemical Oxidation
- Nanoscale Iron
- In Situ Bioremediation
- Site Characterization and Monitoring
- Technology Performance Evaluation & Prediction

R&D Needs: 2006 Workshop

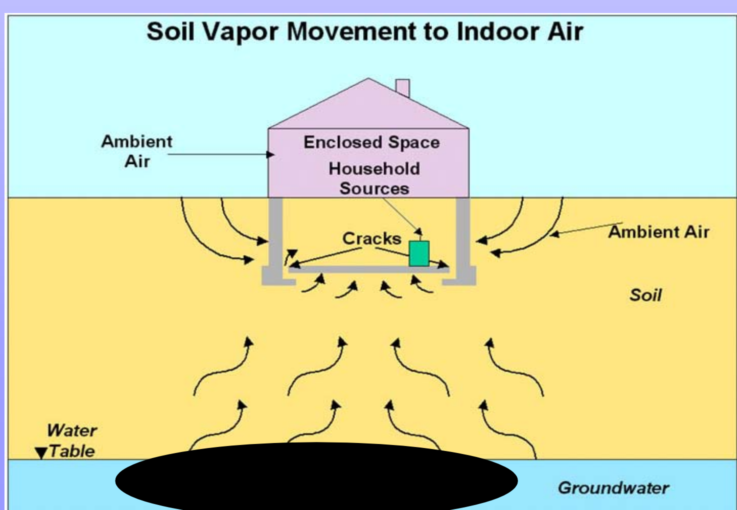
Better Understanding of Plume Response



How To Treat the “Advectively Challenged”



Vapor Transport From Sources



How to Remediate Karst & Complex Sites

SERDP DNAPL Initiative Goals

- Help managers make *best-informed* decisions possible
- Improve predictive capabilities, decision support, and fundamental understanding
- Help develop and validate innovative technologies to improve DNAPL treatment
- Primary drivers:
  - Reduce life-cycle costs
  - Meet schedules for remedies-in-place
- **NOT to promote any technology or any agenda to treat or not treat sources**
- **RIP-tide of source treatment is coming – need to be prepared**

Progress

1. Assess Source Zone Treatment Technologies
   - Large-tank tests of ISCO, bio, and thermal
   - Field-scale tests of ISCO, bio, and thermal
   - Models of performance and uncertainty
   - Data mining to document costs and performance
   - Up-scaling mass transfer coefficients

Progress

2. Quantify Benefits of Source Depletion
   - Laboratory and field assessments of flux before and after treatments
   - Flux measurements after full-scale treatment
   - Experimental and modeling assessments of source depletion benefits

Progress

3. Improve Delivery
   – Nanoscale iron delivery
   – Partitioning electron donors
   – Mobility control methods to enhance sweep efficiency

Progress

4. Improve Decision Support
   - Remedy Selection Guidance
   - Optimizing DNAPL source and plume remediation
   - Estimating cleanup times
   - DNAPL Remediation Screening Tool
   - Diagnostic tools

Key Concepts

- **Mass Flux Can Improve Decision-Making**
  – To select, design & assess remediation
- **Understand Mass Storage Compartments**
  – Varying responses to remediation approaches
  – Plume storage and degradation affect source decisions
- **Set Realistic Goals**
  – 90-99.99% source removal, 90-99% plume decrease
  – 1st order rate of restoration – long "tail"
- **Uncertainty is Inevitable**
  – Apply the observational approach
- **"Remedy Packages" Are Needed**
  – Functional objectives for each element

Half Full or Half Empty?
The hydraulic balance

Half Full or Half Empty?
The hydraulic balance

1. Technology has made impressive advances
   - A suite of demonstrated technologies and combinations
   - MCLs are achievable in some cases
   - We can significantly decrease plume extent, longevity, and liability
2. There are serious “practicable” limits
   - Given unlimited resources, we could clean up all DNAPL sites
   - Resources are limited
   - Uncertainty is high

When do benefits justify costs?

You Gotta Know Your Limits

“Trust your passions less,

your reasons more,

and your limits most”

Daniel Robinson, Oxford University
From NPR Interview:
*"The Philosophy of Choosing
Between Bad Options"*

FAQs and Decision Guide for Chlorinated Solvents Releases

Tom Sale, Chuck Newell,

Hans Stroo, Rob Hinchee, and Paul Johnson

Opportunity

Highlight current knowledge in support of sound decision for releases of chlorinated solvents

Better use of resources

Better environment

WRECK AT DISASTER FALLS.

Audience

- Parties participating in the process of selecting remedies for chlorinated solvent releases
  - DoD staff,
  - Consultants,
  - Industry
  - Regulators, and
  - Community Representatives
  - ……………

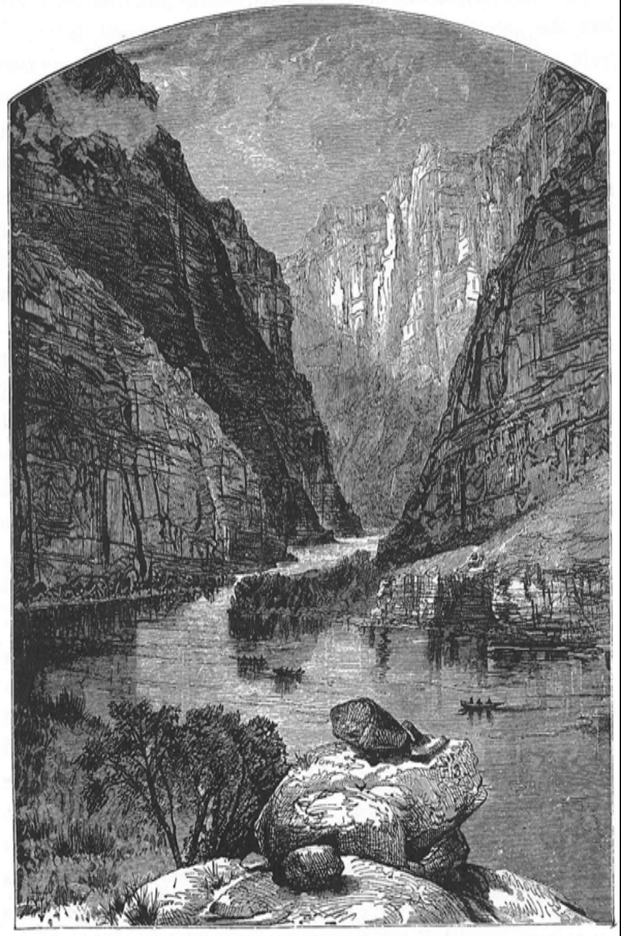
Two-Part Format

- FAQs - Frequently Asked Questions Regarding the Management of Chlorinated Solvents in Soils and Groundwater
- Decision Guide - Guide for Selecting Remedies for Chlorinated Solvents in Soils and Groundwater

Format

- **Entry Level -** The **FAQ** and **Decision Guide Executive Summary** provide quick access to key concepts and references.
- **Middle Level** - The **Decision Guide** highlights new developments re site specific conditions, developing attainable and beneficial goals, selecting technologies, and packaging site remedies.
- **Top Level** - The **documents** refer users to more comprehensive knowledge by highlighting knowledge available through ESTCP, SERDP, and other relevant programs.

FAQs – a one hour read



GATE OF LODORE.

1. What is the Problem?

…chlorinated solvents are central to modern life

…flawed practice was largely a reflection of not clearly understanding

…managing the legacy of our past practices

…direct exposure pathways largely addressed …

…technical challenges make it very difficult or impossible to completely clean up these…

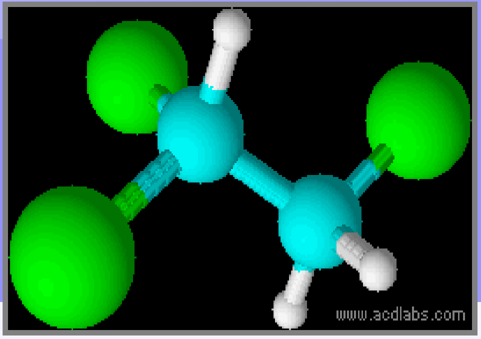
…stakeholders face difficult decisions…

... the science and engineering on which remediation practice is based has improved dramatically…

…we can be more successful in the future than we have been in the past

1950s chlorinated solvent disposal area

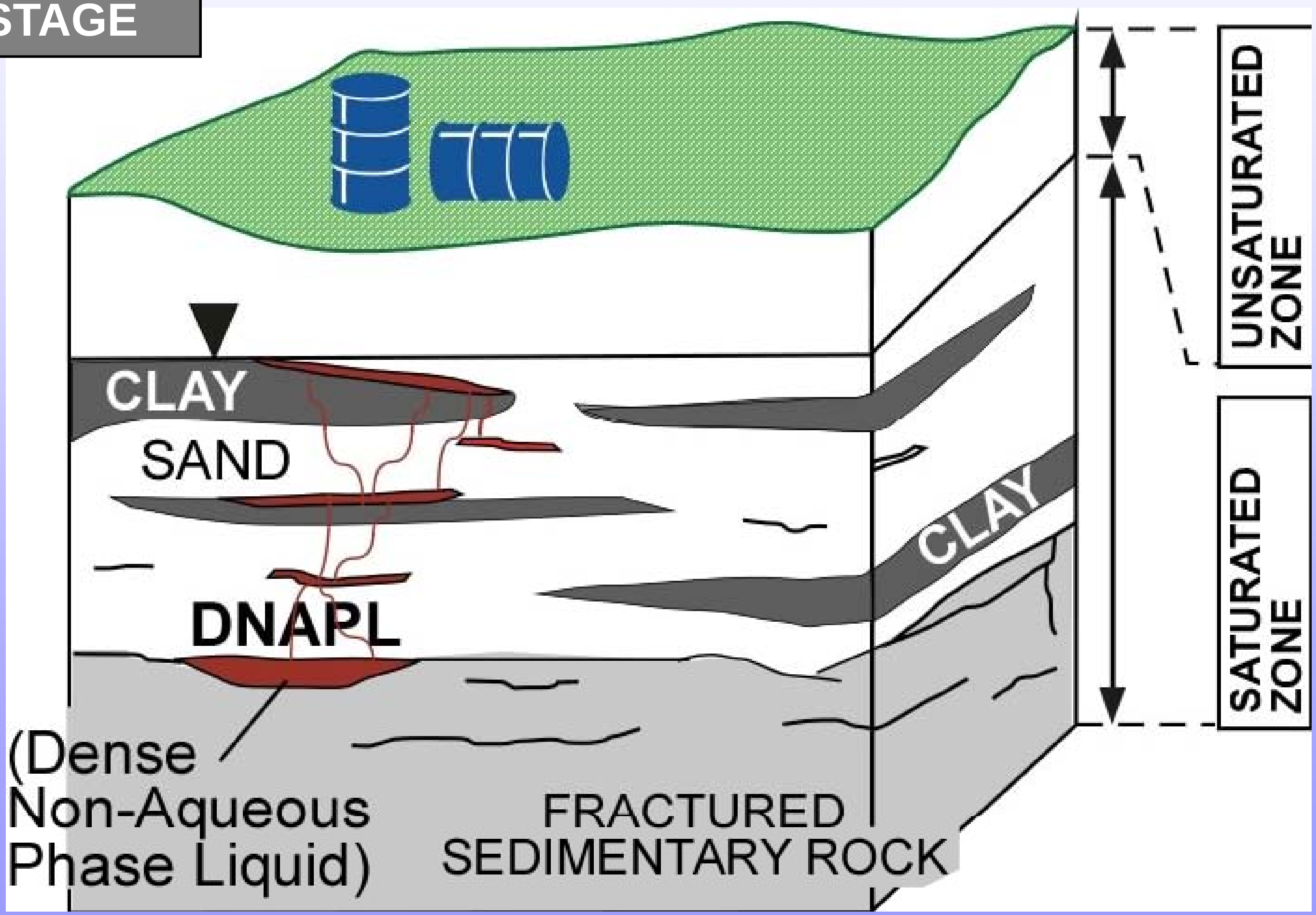
2. What are chlorinated solvents and why are they of concern?



Attributes	Industrial Values	Environmental Challenges
Volatile	Good for cleaning	Readily form vapor plumes in soils
Chemically stable under typical aerobic conditions	Easy to store	Often slow to degrade in aerobic soils and groundwater systems
Non-flammable	Safe from a fire and explosion hazard perspective	Stable under natural aerobic conditions
Slightly soluble in water	Remains in a separate liquid phase when mixed with water (immiscible)	Small releases can contaminate large amounts of water and persist as sources for long periods of time
Densities much greater than water	Easy to separate from water	Can sink through water-saturated media (e.g., aquifers and aquitards), contaminating water deep underground
Low viscosity	Easy to apply to surfaces	Can move quickly through porous media

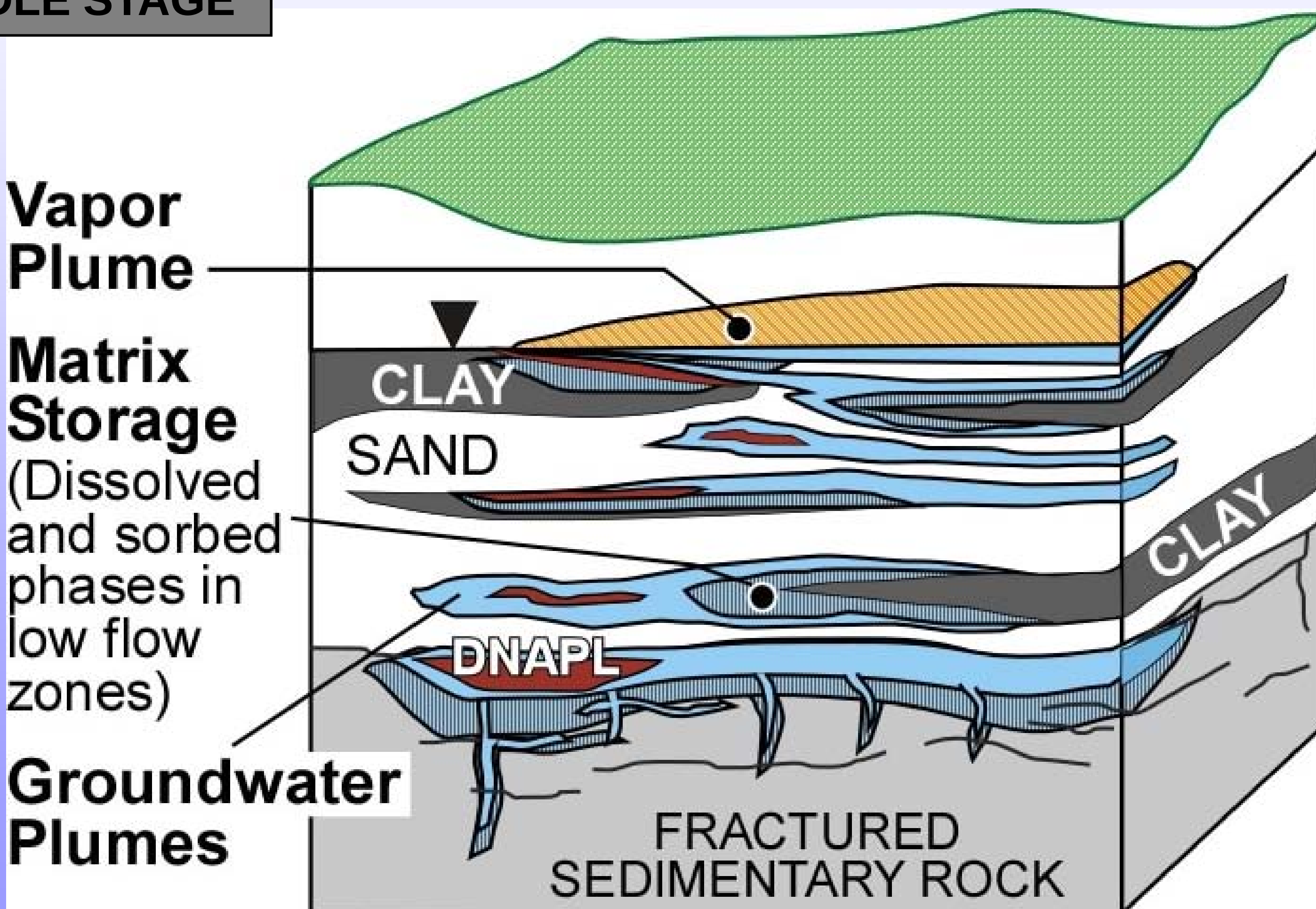
3. What happens when chlorinated solvents are released into the subsurface?

EARLY STAGE

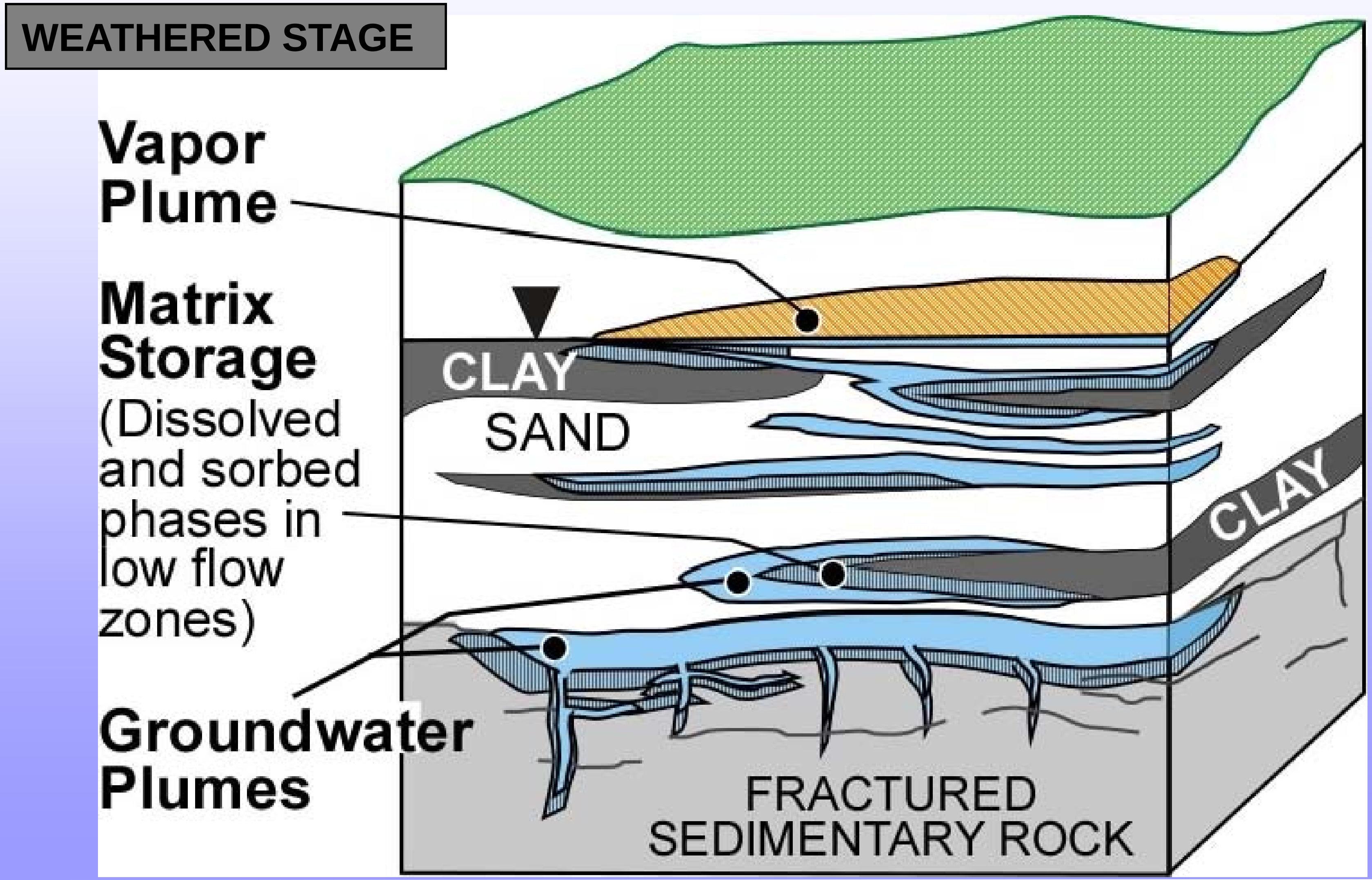


3. What happens when chlorinated solvents are released into the subsurface? (cont'd)

MIDDLE STAGE



3. What happens when chlorinated solvents are released into the subsurface? (cont'd)



3. What happens when chlorinated solvents are released into the subsurface? (cont'd)

14 subsurface compartments potentially containing chlorinated solvents

	Source		Plume	
	Transmissive	Low Permeability	Transmissive	Low Permeability
DNAPL	√	√		
Aqueous	√	√	√	√
Sorbed	√	√	√	√
Vapor	√	√	√	√

DNAPL is absent in plumes by per NRC 2005

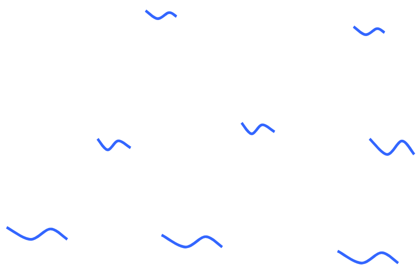
4. What is a chlorinated solvent "source zone"?

National Research Council report (NRC, 2005) defines a chlorinated solvent source zone as:

- … a subsurface reservoir that sustains a plume (primarily dissolved groundwater plumes…
- … the DNAPL-containing region is initially the primary reservoir… also includes high concentration dissolved- and sorbed-phase halos about the DNAPL-containing region…
- … acknowledges that some chlorinated source zones are depleted of DNAPL, and that the high-concentration halo can be a reservoir that sustains plumes.

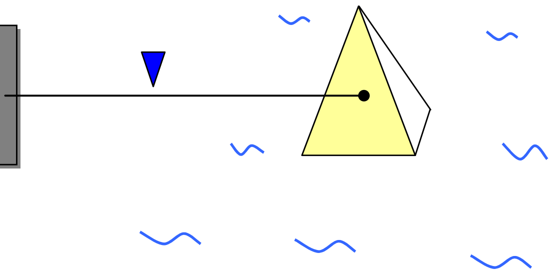
5. Why do we keep finding new challenges?

1960 Problem - Submerged?



5. Why do we keep finding new challenges?

Dissolved solvent plumes in transmissive zones (1970 - 1980s)



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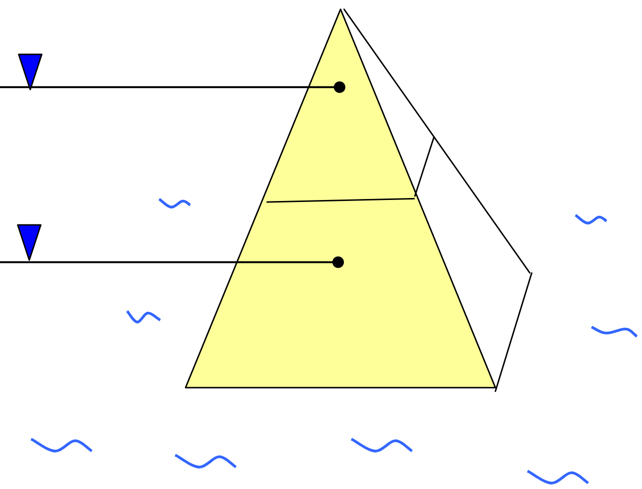
Dissolved solvent plumes in transmissive zones (1970 - 1980s)

Plus DNAPL in transmissive and low permeability zones (1990s)

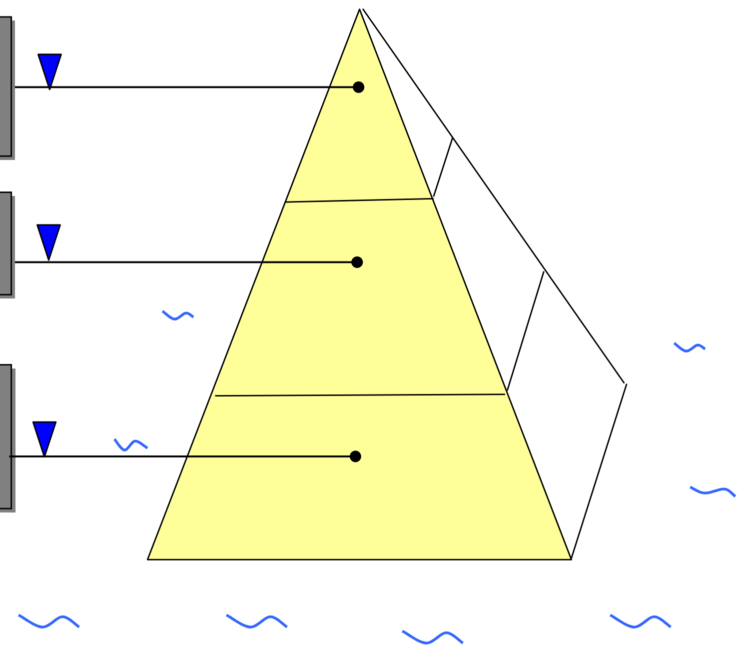


5. Why do we keep finding new challenges?

Dissolved solvent plumes in transmissive zones (1970 - 1980s)

Plus DNAPL in transmissive and low permeability zones (1990s)

Plus dissolved and sorbed phases in low permeability zones in source zones (mid 2000s)



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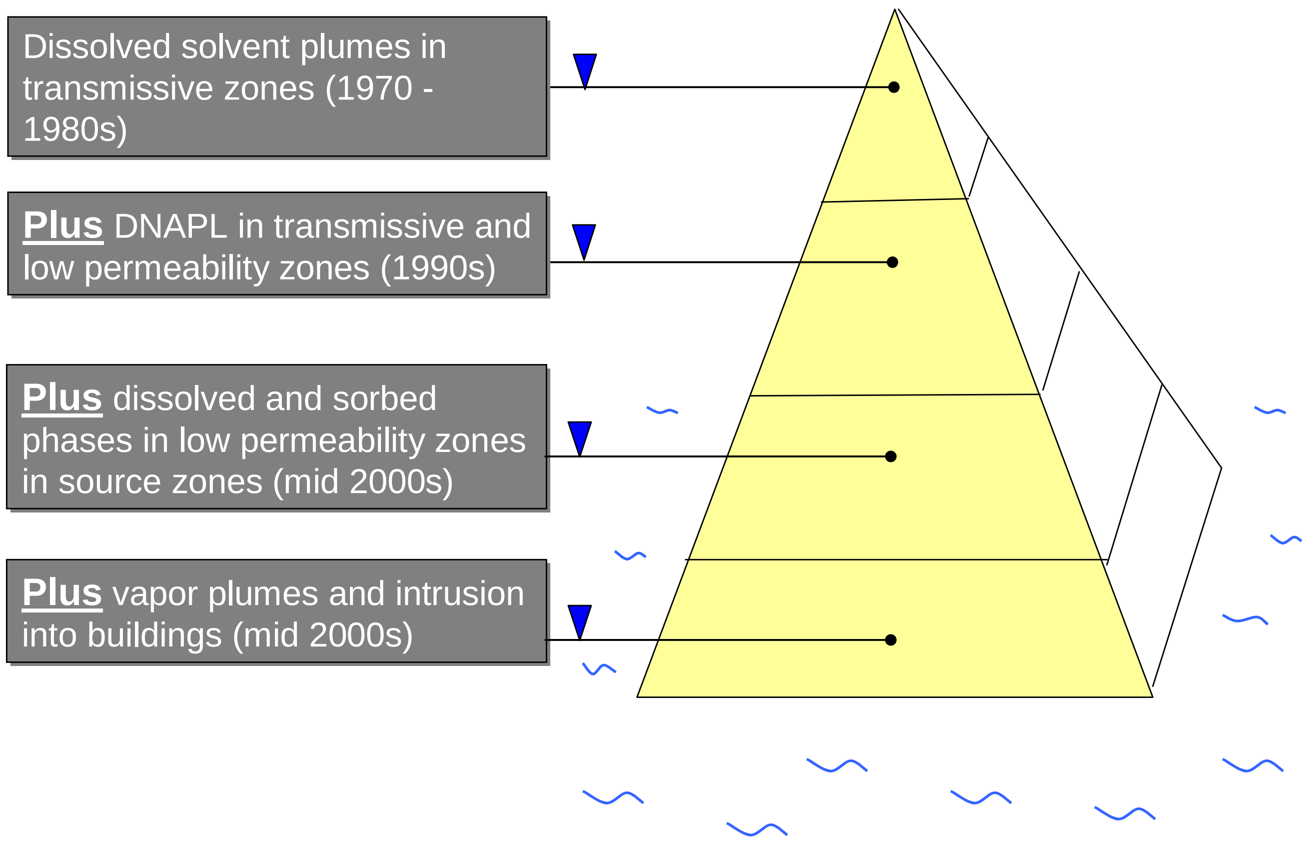

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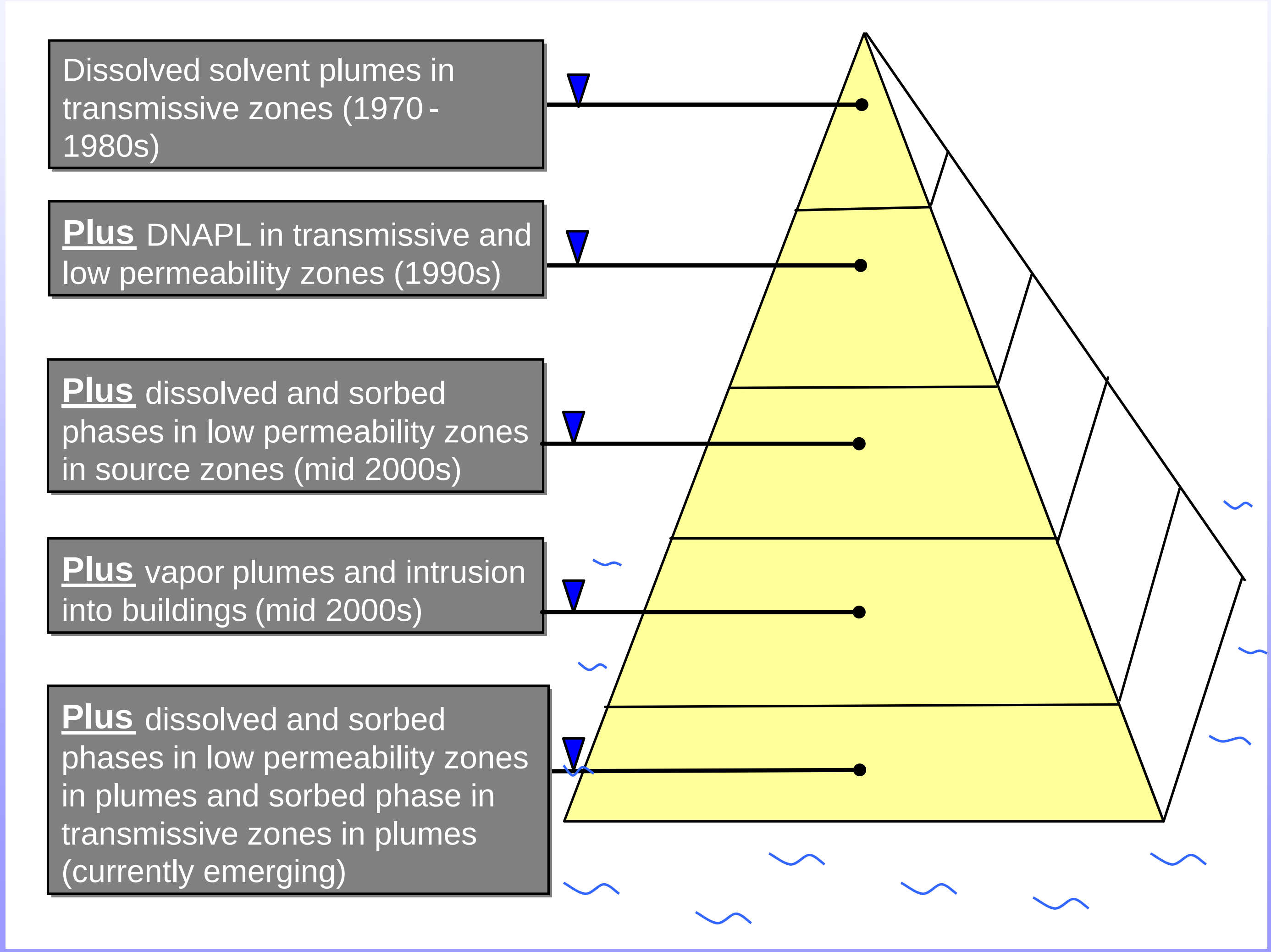


6. Why is it common for source delineation efforts to miss a portion of a source?

… heterogeneous distributions of DNAPL and other contaminant phases

… common reliance on groundwater data collected from large screen intervals in transmissive zones

… at older release sites, DNAPL may have dissolved away (we are not looking for the right thing)

… difficult to resolve where the source ends and the plume begins

… decisions are often made using a limited dataset

… characterization can be de-emphasized in the rush to…

Source Delineation is Difficult

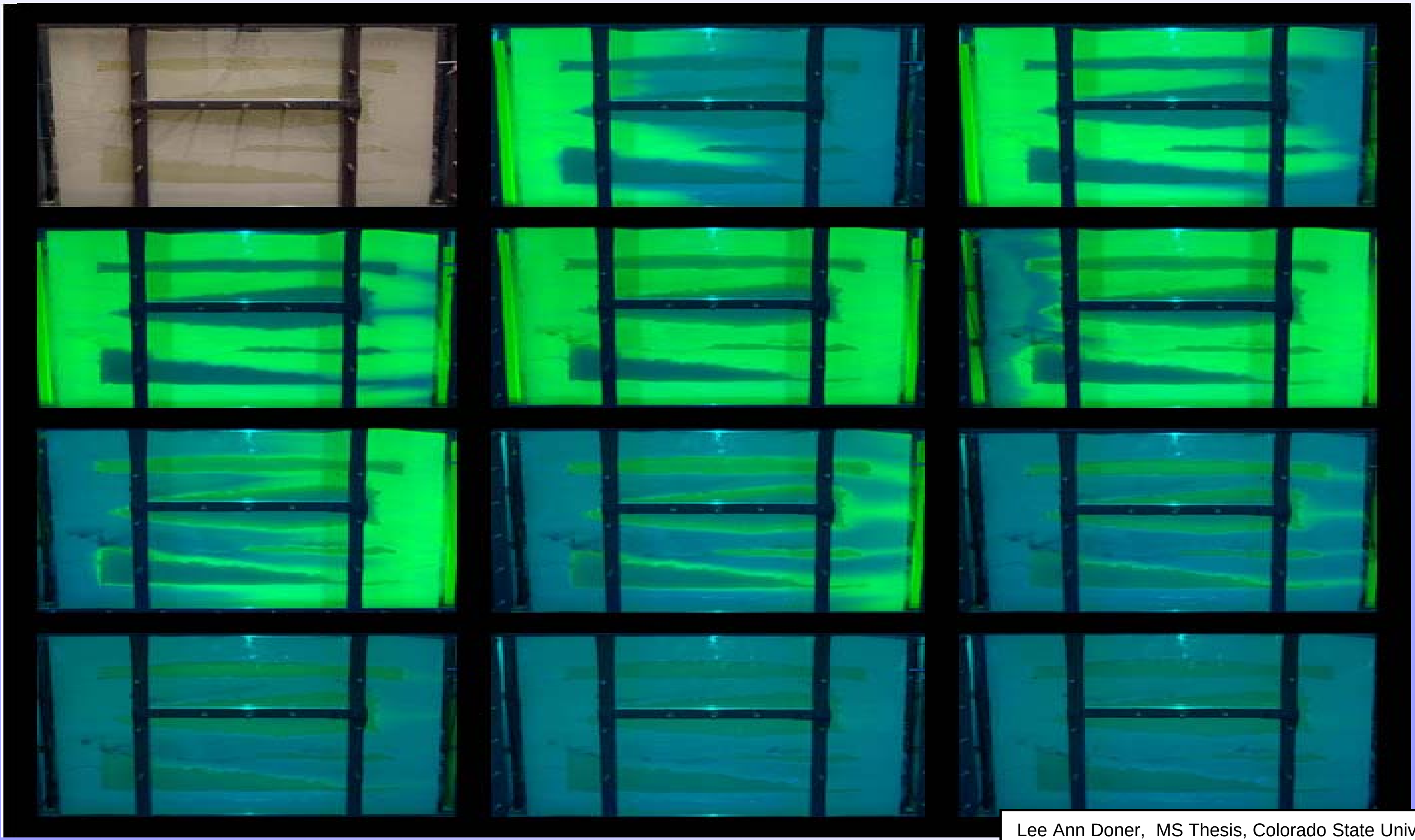
7. Why is it difficult to clean up aquifers by pumping out the contaminated groundwater?

The National Research Council's 1994 report on groundwater clean-up alternatives concluded:
"*Remediation by pump-and-treat processes is a slow process. Simple calculations for a variety of typical situations show that predicted clean-up times range from a few years to tens, hundreds, or even thousands of years.*"

	Source		Plume	
	Transmissive	Low Permeability	Transmissive	Low Permeability
DNAPL	√	√		
Aqueous	√	√	√	√
Sorbed	√	√	√	√
Vapor	√	√	√	√

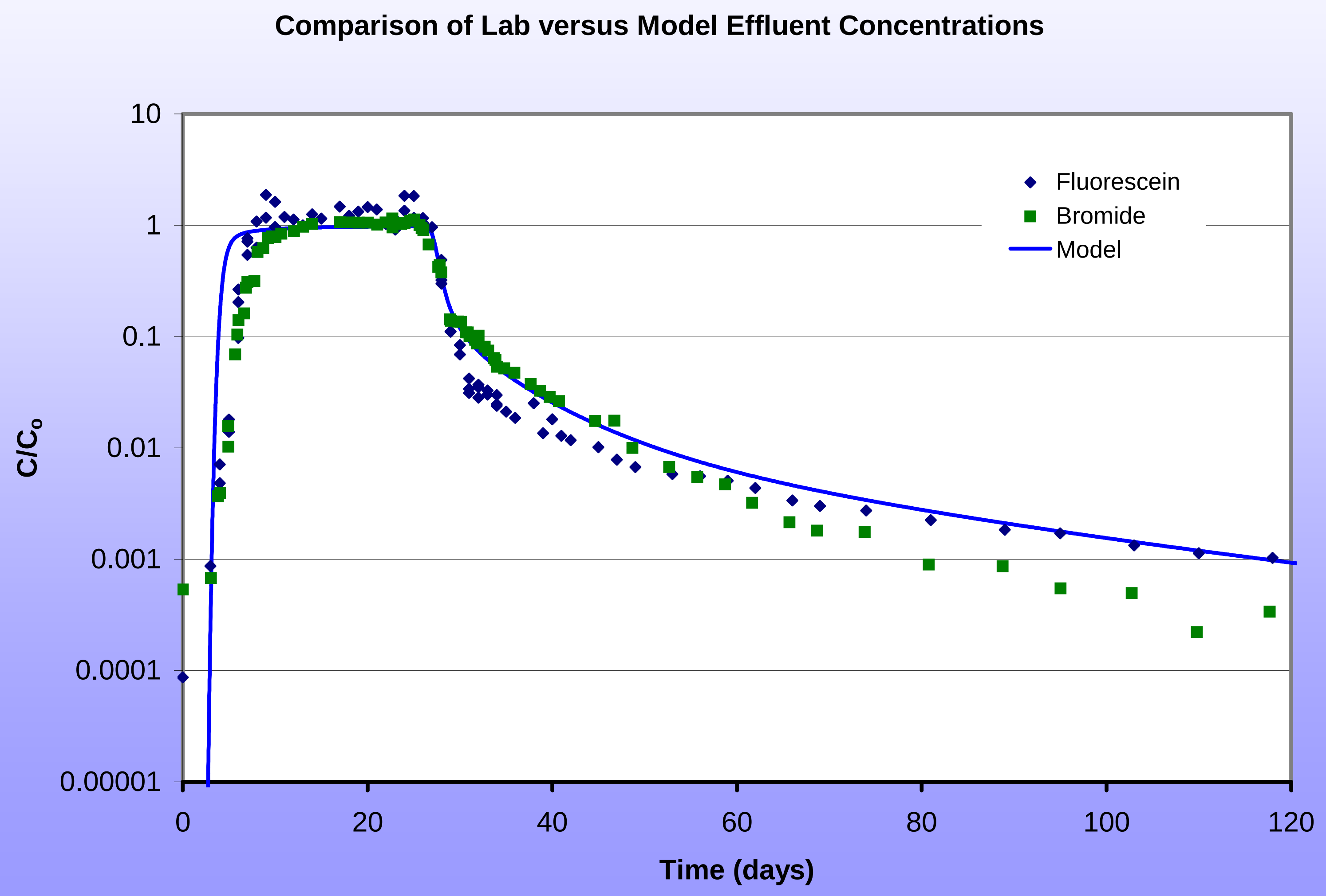
8. Why are contaminants in low permeability zones important?

Abrupt contacts between transmissive zones (e.g., sand) and comparatively stagnant low permeability zones (e.g., clay) are common in geologic media.



Lee Ann Doner, MS Thesis, Colorado State University

3.2 – Parameters Required for Each Model



9. Why are contaminants in the vadose zone important?

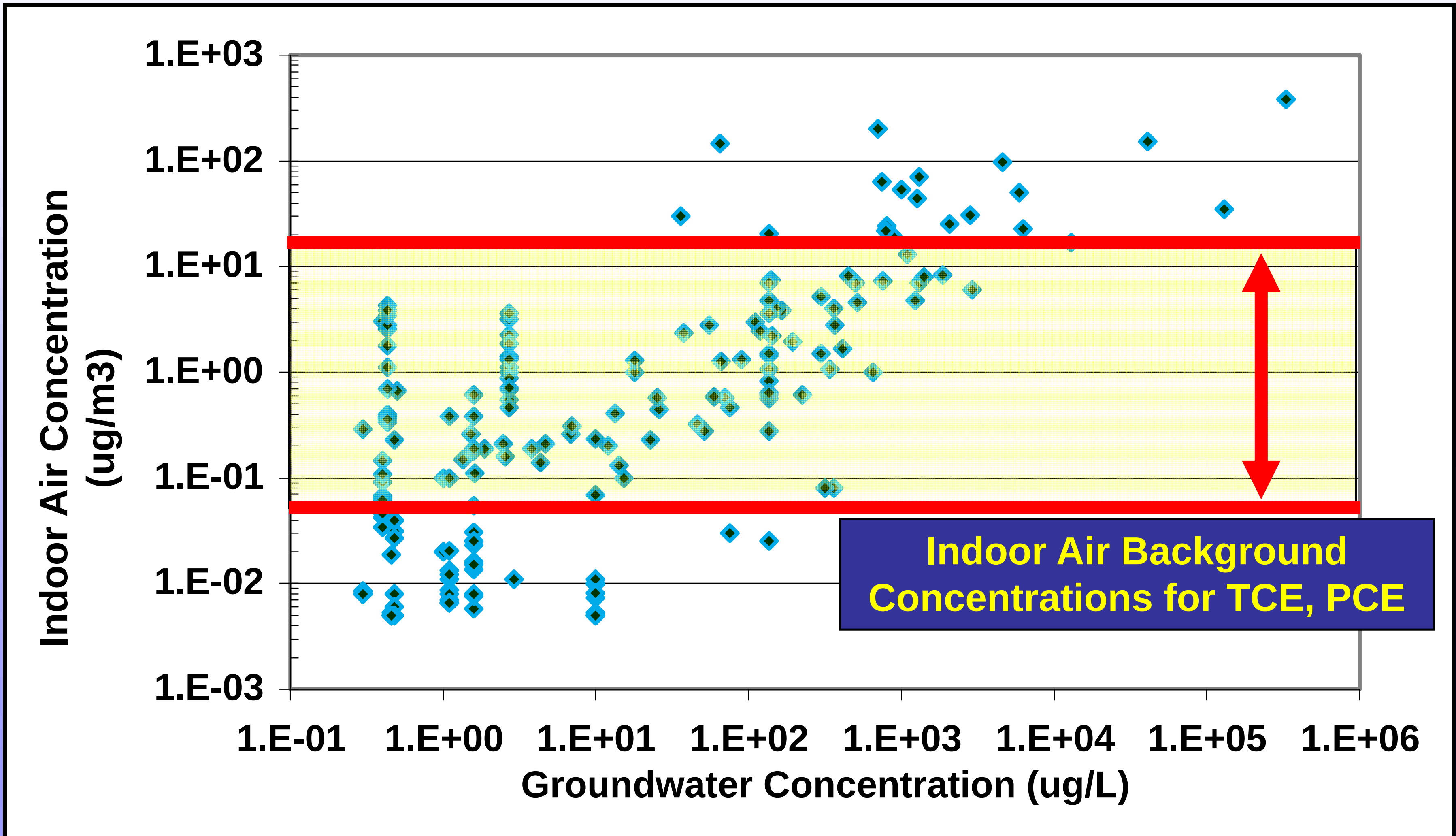
Vadose Zone as *SOURCE*

- **Source compartments from 14 compartment model**
- **Most but not all sites dominated by saturated zone sources**
- **SVE: soil moisture key performance factor**

Vadose Zone as *PATHWAY*

- **Indoor air pathway - empirical studies and model development**
- **Confirming impacts difficult**
- **ESTCP and SERDP projects**

9. Why are contaminants in the vadose zone important? (II)



10. What have we learned in the last half century?

Paradigm shifts of the last half century

Old School Paradigm (Period of prevalence)	New School Paradigm (Time of broad acceptance)
Given the volatility of chlorinated solvents, land disposal is an appropriate practice. *(1940s through 1970s)*	Releases of chlorinated solvents to subsurface environments can create big problems. Few things are more important than limiting future releases. *(Beginning in the 1980s)*
Aquifers may be restored by pumping out the contaminated water (pump-and-treat). *(1970s through 1980s)*	Solvents sorbed to solids, present as DNAPL, and stored in stagnant zones can sustain groundwater concentrations in transmissive zones for long periods. *(1990s through 2000s)*
Chlorinated solvents are recalcitrant. *(1970s through 1990s)*	Chlorinated solvents will degrade under a range of natural and engineered conditions. *(Beginning late 1990s)*
New technologies hold promise of achieving MCLs in source zones. *(early through mid 1990s)*	In many settings (most) available technologies will not achieve MCLs and long-term management will be needed. *(Beginning mid 1990s)*
Primary risks and site care costs can be addressed by removal and/or depletion of source zones. *(1970s through early 2000s)*	Contaminants can remain after source zone treatment in matrix storage or in dissolved plumes, and these can sustain exceedances of MCLs and may necessitate site care for long periods of time. *(mid 2000s)*
Source zone remediation is a necessary component of corrective action. *(1970s through ???)*	Source zone remediation should be considered, but is not always a necessary component of corrective action. Long-term management, containment, and MNA may be more effective strategies at some sites. *(2000s)*
Groundwater represents the primary pathway and media of concern. *(1970s through late 1990s)*	Vapor intrusion is recognized as a pathway of concern of the same order as groundwater. *(2000s)*
Regulators focus on site cleanups. *(1980s and 1990s)*	Some regulators begin to bring natural resource damage (NRD) issues into the site management process, such as filing NRD lawsuits. *(2000s)*

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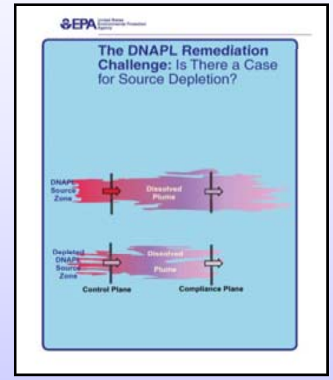
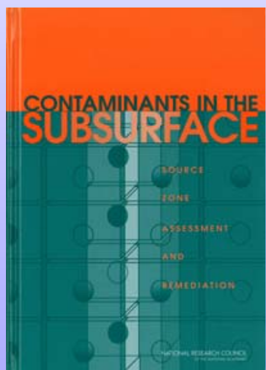
11. What types of goals can we set for chlorinated solvent releases?

The U.S. EPA Source Depletion document (2003):

- Reduce potential for DNAPL migration
- Reduce long-term management requirements
- Reduce mass flux
- Stabilize the extent of plumes
- “Stewardship”





The NRC’s (2005) *Contaminants in the Subsurface*:

- Deplete the source zones
- Reduce concentrations in source zones
- Reduce contaminant flux from source zones
- Reduce DNAPL migration potential
- Reduce plume size
- Reduce contaminant toxicity
- Eliminate barriers to subsequent remedial actions
- Reduce Life-cycle costs

Author’s Experience:

- Meet commitments for expenditure of funds for environmental restoration
- Meet public expectations to make progress
- Comply with regulatory requirements
- Advance new technology

In the end, learning to value that which is:

- *attainable*
- *beneficial*

may be our greatest opportunity for future progress.

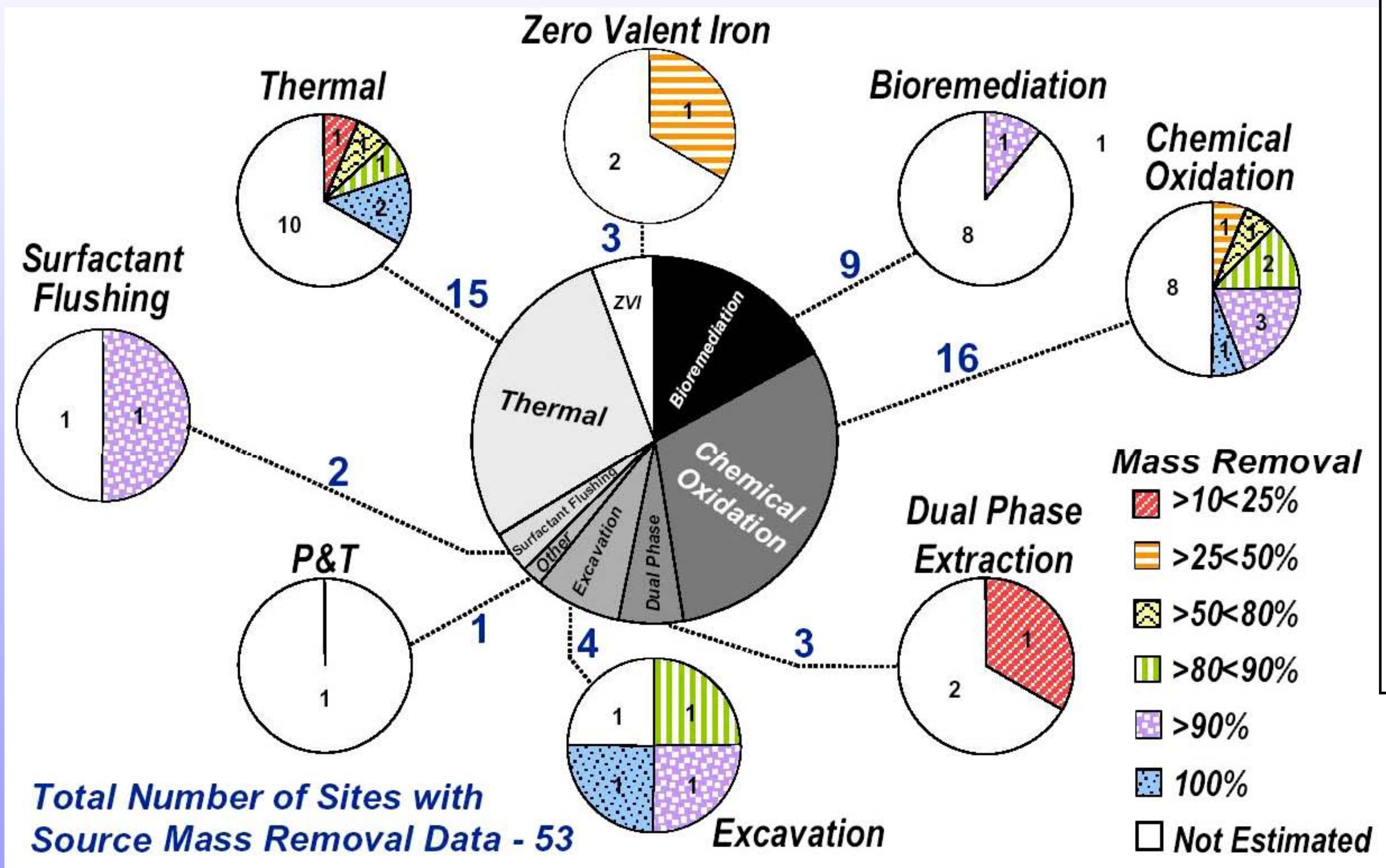
12. Which in situ source treatment technologies are receiving the widest use?

- **Chemical Oxidation**
  - ***Permanganate***
  - ***Peroxide***
  - ***Persulfate***
- **Thermal**
  - ***Conductive***
  - ***Electrical***

12. Which in situ source treatment technologies are receiving the widest use (cont'd)?

- **Bioremediation**
  - ***High Solubility Substrate***
  - ***Low Solubility Substrate***
- **Chemical Reduction**
  - ***ZVI Injection***
  - ***ZVI Soil Mixing***
- **Monitored Natural Attenuation**
- **Soil Vapor Extraction**

13. What can we expect from common source treatment technologies?

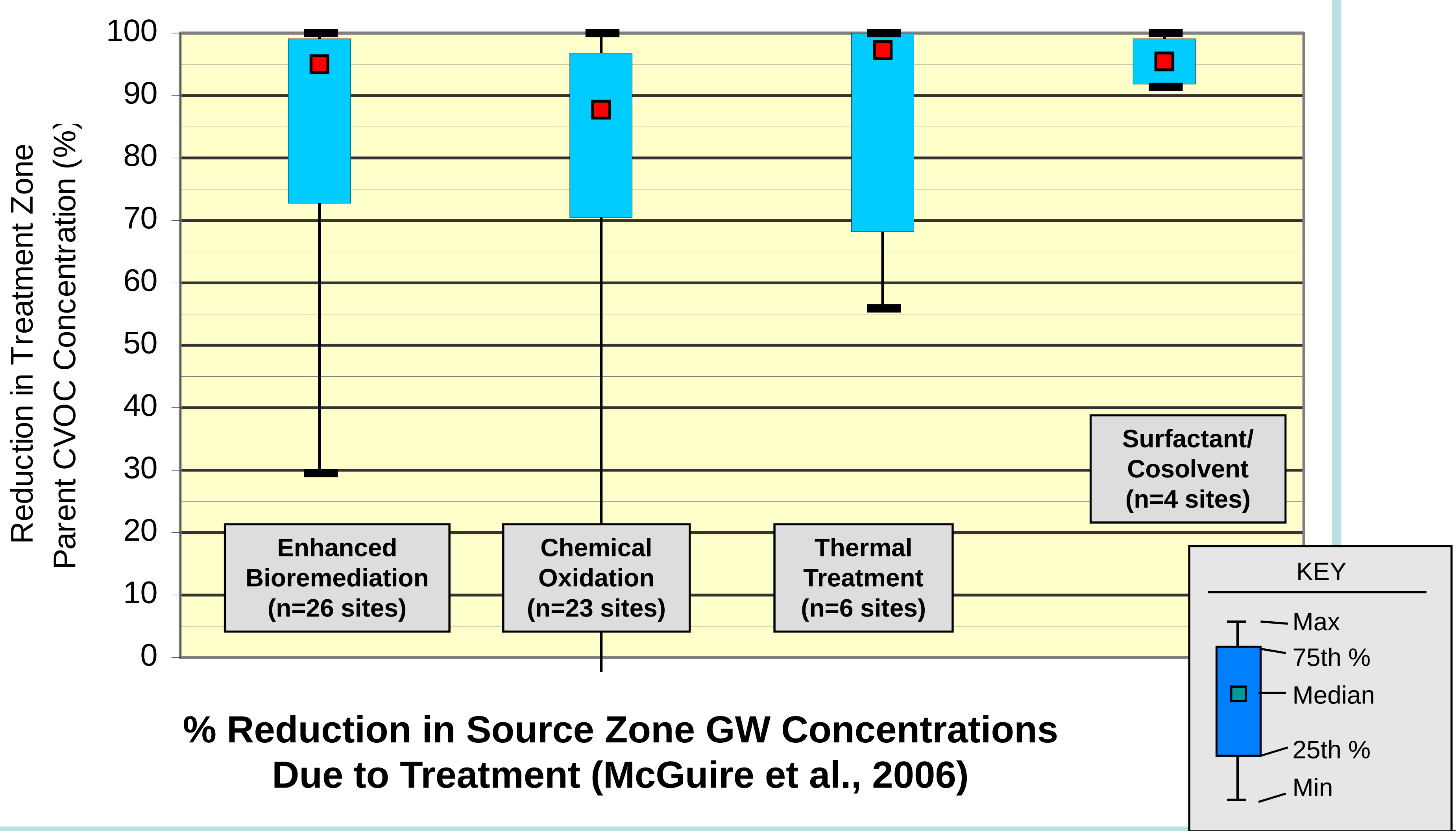


Summary of Source Mass Removal Sorted by Technology (NAVFAC, 2007; based on data from GeoSyntec, 2004)

Key Points:

- Only partial DNAPL mass removal or destruction can be achieved.
- MCLs are extremely unlikely to be met.

13. What can we expect from common source treatment technologies? (cont'd)



% Reduction in Source Zone GW Concentrations Due to Treatment (McGuire et al., 2006)

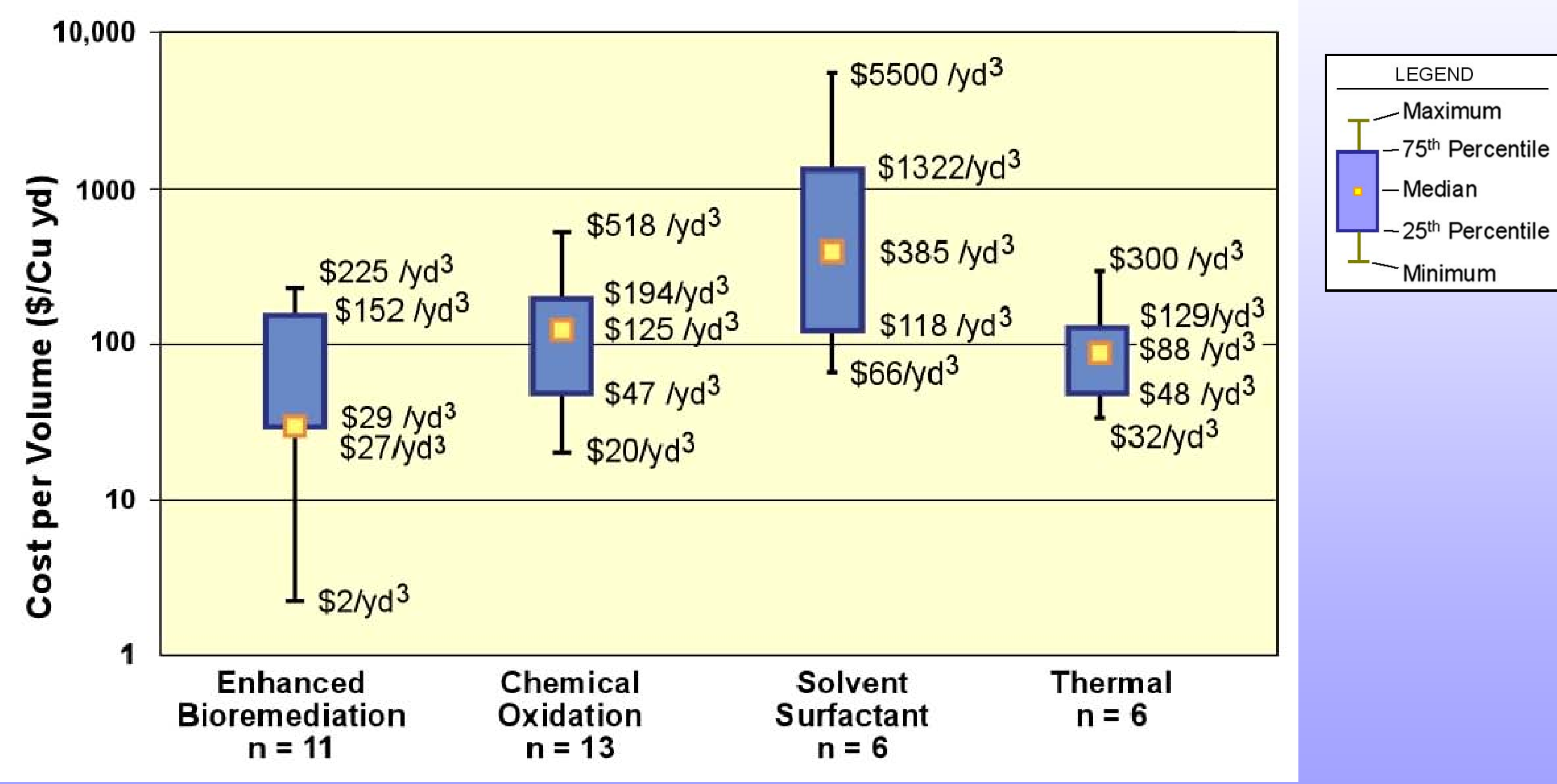
13. What can we expect from common source treatment technologies? (cont'd)

Remediation Rule-of-Thumb:

Well implemented in-situ remediation projects are likely to reduce source zone groundwater concentrations by **about *one order-of-magnitude* (90% reduction)** from pre-treatment levels.

Treatment trains (successive applications of different technologies) may be one approach to reduce concentrations beyond what a single treatment episode can achieve.

14. How much does it cost to treat source zones?



Unit Costs of Source Zone Treatment (McDade et al., 2005)

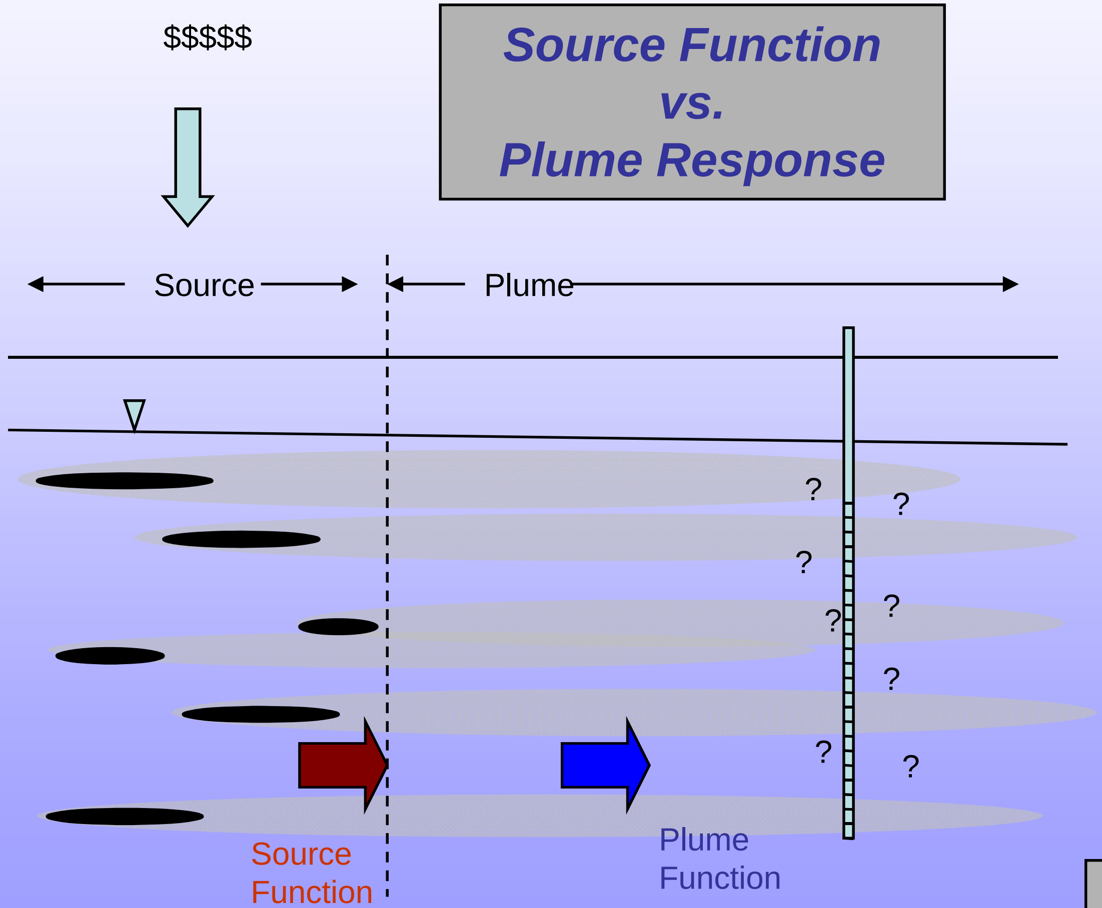
14. How much does it cost to treat source zones? (cont'd)

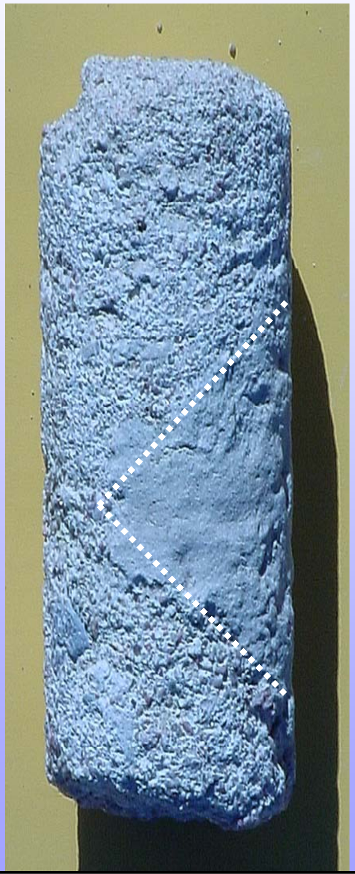
Very General Rule of Thumb

Investments on the order of **millions of dollars per acre appear to have the potential to achieve one order of magnitude** reductions in chlorinated solvent mass and concentration in source zones.

15. How will reduced loading from sources affect plumes?

Source Function vs. Plume Response

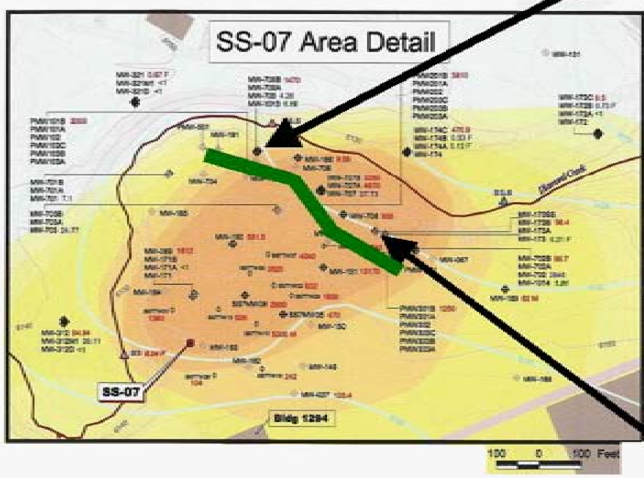




Rock core from the Ogallala Formation at F.E. Warren AFB illustrating a silt bed in sandstone

15. How will reduced loading from sources affect plumes? (cont'd)

F.E. Warren Spill Site 7 PRB



Water quality response in a plume downgradient of an iron permeable reactive barrier, F.E. Warren AFB, Wyoming,

See WRR Chapman and Parker 2005, AFCEE (2007), JCH Sale et al., 2008

15. How will reduced loading from sources affect plumes? (cont'd)

Rule-of-Thumb:

In many instances, complete source removal…

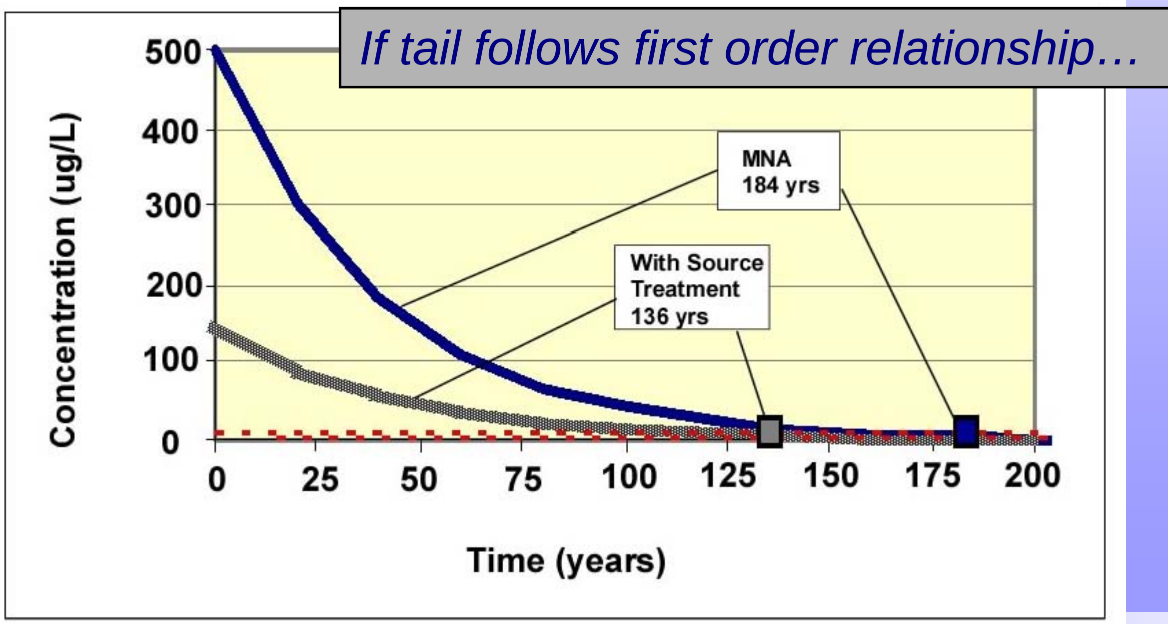
- **gives one order-of-magnitude improvement downgradient.**

But with fast groundwater flow, low mass storage, and/or active attenuation…

- **potentially gives 2-3 orders-of-magnitude improvement downgradient over several years**

16. What are the effects of source treatment on clean-up timeframes?

- **One benefits of source treatment is that time to reach its clean-up goals will be reduced.**
- **Quantifying <u>how much</u> is difficult.**
- **Must account for likely "tails" to source concentration**
- **May not get "equal benefit for equal work"**



LONGEVITY SOFTWARE

- ***SourceDK***
- ***BIOBALANCE***
- ***NAS***
- ***REMCHLOR***

17. Which containment measures are receiving the widest use?

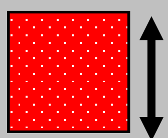
- Hydraulic Containment
- Permeable Reactive Barriers
  - Biodegradation (e.g., mulch)
  - Zero Valent Iron
  - Sparge Walls
- Physical Containment
- Monitored Natural Attenuation

17. What can we expect from containment measures?

- **43 of 52 full scale ZVI barriers are "meeting regulatory expectations"**
- **25 of 29 sites with physical barriers have "acceptable performance" in medium term (10 years or less)**
- **MNA sole remedy (no source treatment) at 30% of 191 MNA sites**

20. How does one compare treatment vs. containment?

- Uncertainty (for both options)
- Plume Response - takes time
- Cost Comparison (Net Present Value)



1 ***SITE A***

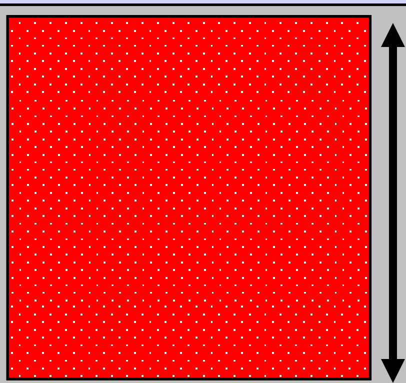
Perimeter = 4

Area = 1

Thickness = 4

Volume = 4

Volume:Perimeter = 1:1



3 ***SITE B***

Perimeter = 12

Area = 9

Thickness = 4

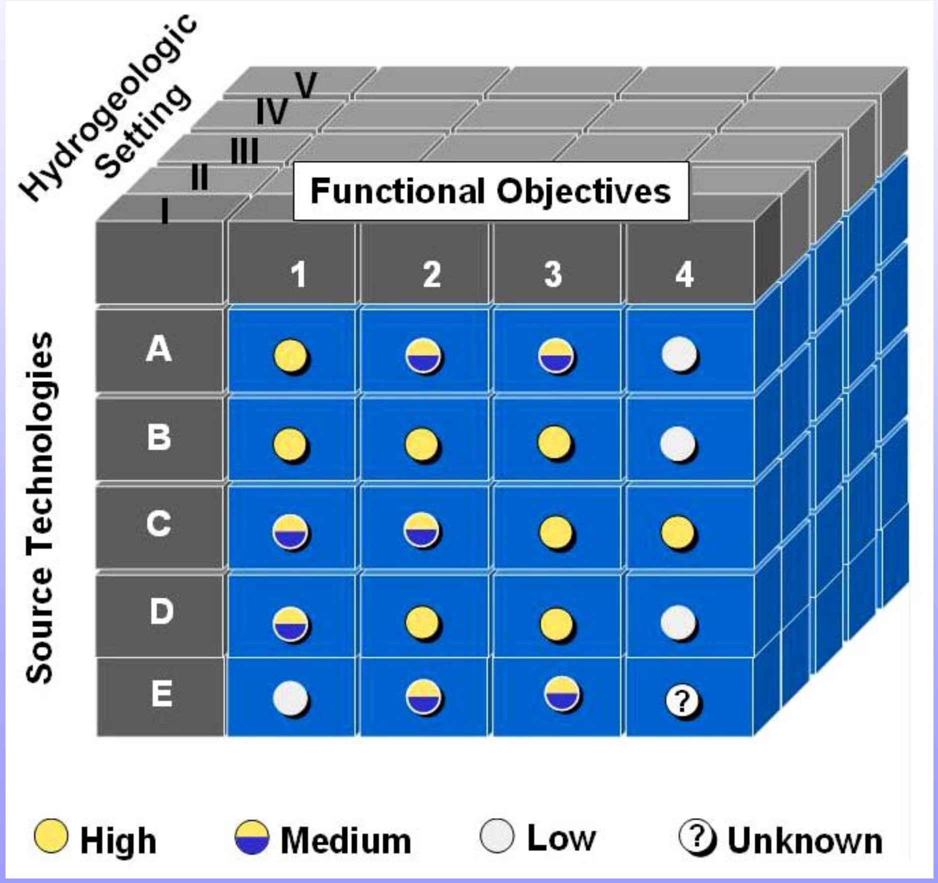
Volume = 36

Volume:Perimeter = 3:1

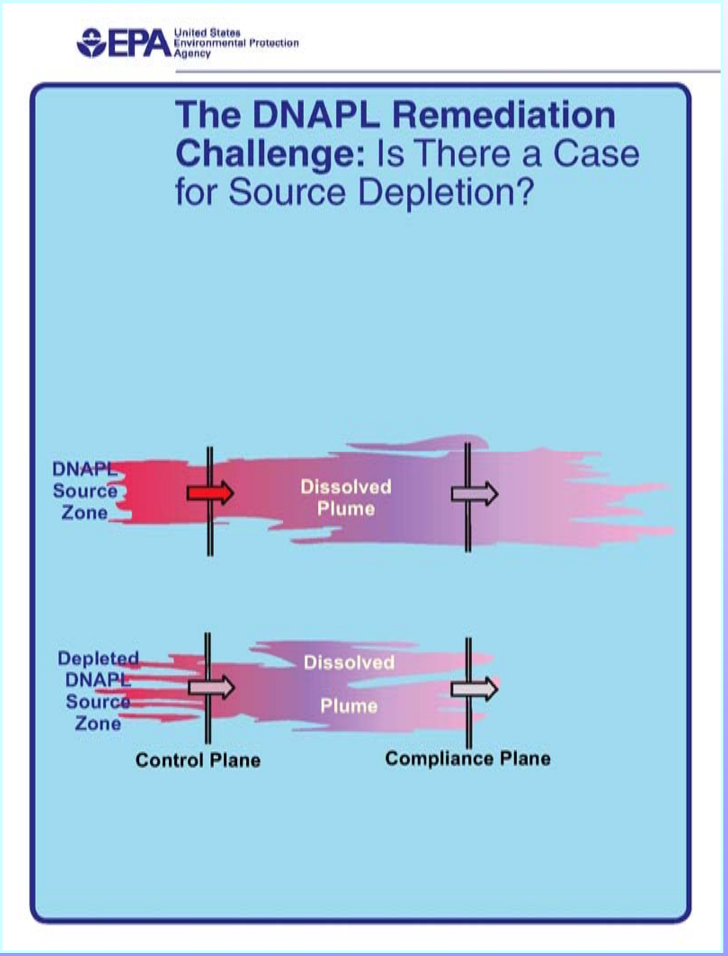
20. How do site characteristics affect clean-up decisions?

- NRC “Cube”
  - Objectives
  - Settings
  - Technologies

- Series of Tables



20. How do site characteristics affect clean-up decisions?



Decision Matrix

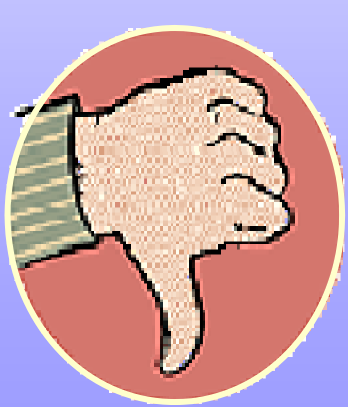
- Evaluation of quantitative and qualitative factors to assess relative need for source treatment.

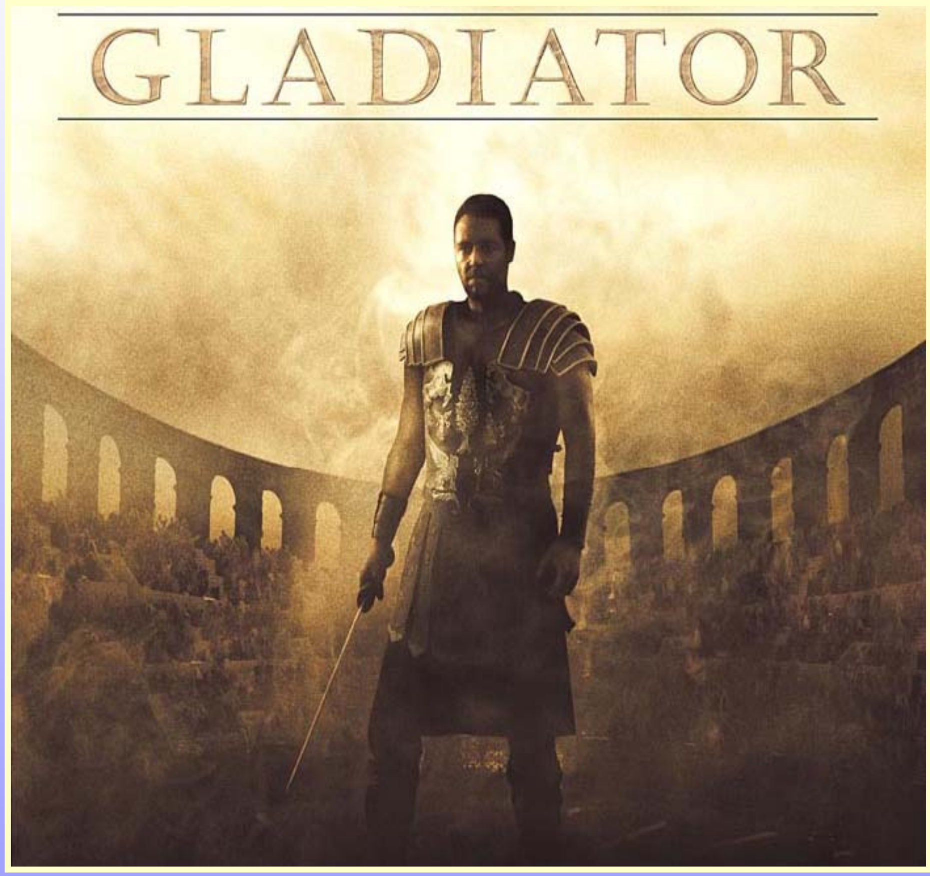
EPA / 600-R-031/143, 2003

Qualitative Decision Chart: RC Approach

Yes, Source Depletion

No, Source Depletion



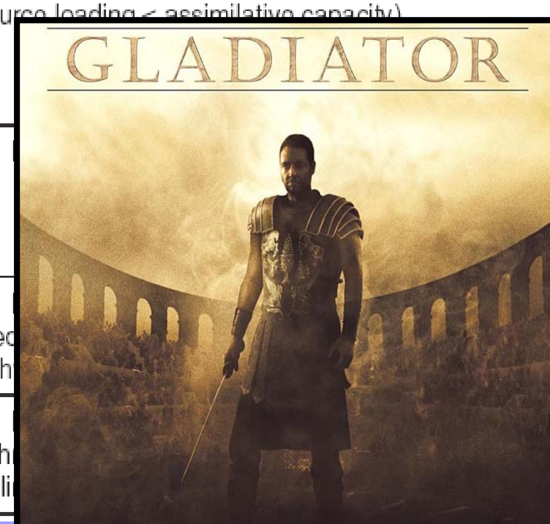


Key Factors for Deciding


	Yes	No
Source Zone:	*Expanding*	*Immobile*
Plume Status:	*Expanding*	*Shrinking*
Resource Value:	*High*	*Low*
Containment Cost:	*High*	*Low*
Will Reduce Remed. Timeframe?	*A Lot*	*A Little*
Need for Rapid Cleanup?	*Yes*	*No*

Weight of Evidence: More Likely to Benefit from Tmt.

DESIRED REMEDIAL BENEFITS[1]	MORE NEED FOR SOURCE DEPLETION		LESS NEED FOR SOURCE DEPLETION
Reduce potential for DNAPL migration as separate phase	1a. Expanding PL Zone (probably are at chlorinated s *(containment ad s problem too)*	1b. Free-Phase DNAPL present but stable in stratigraphic traps	1c. Immobile, residual DNAPL Zone
Reduce source longevity, and reduce long-term management requirements	2a. High life-cycle containment cost (for example, containment Net P Value (NPV) >> cost of remediation) 3a. Low reliabi ment system 4a. High resou t cannot be used due to DNAPL (for exa ole-source aquifer OR Well Yield with TDS < 3000 mg/L)[3] 5a. High proba aningful reduction in time to reach M mple, small sites with low complexity)	2b. Moderate life-cycle containment cost 3b. Moderate reliability of containment system 4b. Moderate resource value 5b. Moderate probability of a meaningful reduction in time to MCLs	2c. Low life-cycle containment cost (for example, containment Net Present Value (NPV) << cost of remediation) 3c. High reliability of containment system 4c. Low resource valu ple, resource not being used AND eithe lved Solids > 10,000 mg/L or Well Yield < 1 5c. Low probability of r reduction in time to reach MCLs (for example, large releases at complex sites)
Near-term enhanced natural attenuation due to reduced dissolved phase loading	6a. Expanding dissolved phase plume (source loading > assimilative capacity) *(containment addresses this problem too)*	6b. Stable dissolved phase plume (source loading ~ assimilative capacity)	6c. Shrinking dissolved phase plume (source loading < assimilative capacity)
Near-term reductions in dissolved phase loading to receptors (e.g., a well or a stream)	7a. Receptor i or impacted sou (for example, < 2 y ne)[5] *(containment ad s problem too)*	7b. Potential longer-term risk to receptor (for example, >2 years travel time)	7c.
Near-term attainment of MCLs	8a. Need for ra (for example, impending prop)	8b. Limited need for rapid cleanup	8c. nee re path
Intangibles	9a. Desire for active remedy; desire to test new technologies; desire to reduce stewardship burden on future generations	9b. Neutral on intangible issues.	9c. n tech for li



22. Taking stock: In the past, why have we not been more successful?

- Poor design
- Poor understanding of what technologies do.
- Misunderstanding the extent and/or distribution
- Poor recognition of the uncertainties inherent in remedial system design
- Stating remedial objectives that can only be achieved over long periods of time

23. How can we set clean-up objectives that are achievable and protective?

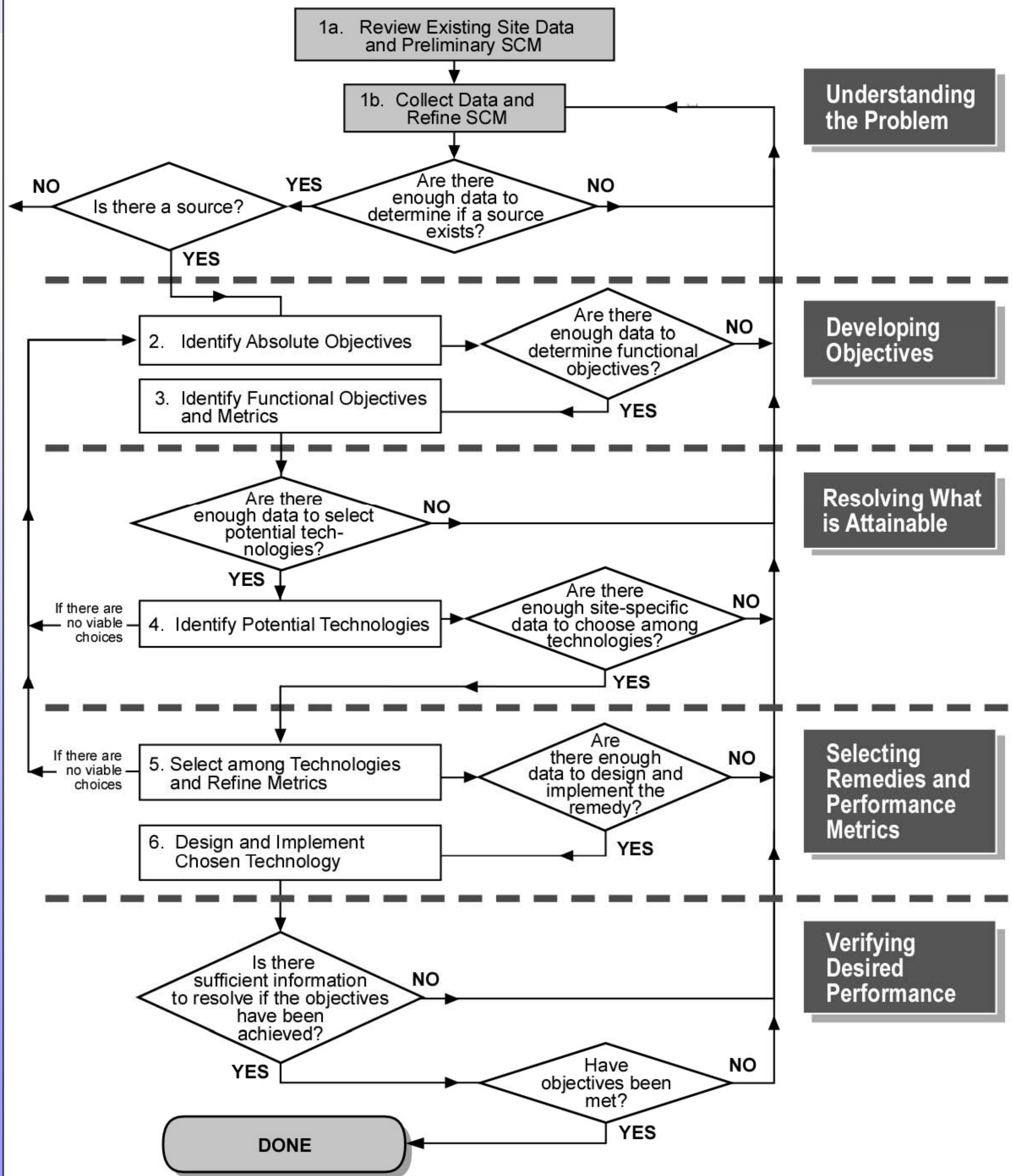
NRC Philosophy:

- Two different categories of objectives:
  - Absolute objectives are objectives that are important in themselves, such as “protect human health and the environment.”
  - Functional objectives are a “means to an end” and include containing plumes, reducing concentrations and mass flux, managing risks, reducing mass, and potentially decreasing plume longevity.

NATIONAL RESEARCH COUNCIL FLOWCHART

(2005)

"Six Step Process for Source Remediation"



24. How can we be more successful at site cleanup?

1. Think about absolute objectives as long-term goals
2. Have an up-to-date understanding of what can be practicably achieved by available technology, and communicate your experiences so that others can gain from your insights
3. Develop shorter-term functional objectives that must be met to confirm progress towards the absolute objectives
4. Recognize uncertainties. Design a remedial strategy that is updated as new observations and data are recorded

24. How can we be more successful at site cleanup (cont'd)?

5. When source containment is the chosen remedial strategy, clearly communicate the long-term nature of this to all stakeholders.
6. When source treatment is chosen as a part of the remedial strategy, clearly communicate the uncertainties associated with the outcome to all stakeholders.
7. Accept that remedial actions will not always lead to achievement of clean-up goals and objectives - and learn from these experiences rather than simply viewing them as failures.

24. How can we be more successful at site cleanup?

The Observational Approach: Originally developed for geotech engineering by Terzaghi & Peck (1948)

- Assess probable conditions and develop contingency plans
  - Example: plan for adverse outcome
- Establish key parameters for observation
  - Example: groundwater concentration, mass flux
- Measure parameters and compare to predicted values
  - Example: compare to model predictions
- Change the design as needed
  - Example: another round of treatment or go to containment

25. Where can I find more information?

Pankow, J.F. and J.A. Cherry, 1996. Dense Chlorinated Solvents & Other DNAPLs in Groundwater, Waterloo Educational Services Inc., Rockwood, Ontario: http://www.amazon.com/gp/product/0964801418/103-1522514-8943817?v=glance&n=283155

Cohen, R.M., and J.W. Mercer, 1993. DNAPL Site Evaluation. CRC Press, Boca Raton, FL, USA.

The Strategic Environmental Research and Development Program (SERDP) and the related Environmental Security Technology Certification Program (ESTCP) are currently funding a number of projects in the area of chlorinated solvent source zone characterization and remediation. The most recent annual report is at: http://www.serdp.org/research/CU/DNAPL%20ANNUAL%20REPORT-2004.pdf.

The ESTCP program convened a workshop to address the research needs in this area. The workshop report is at: http://www.estcp.org/documents/techdocs/chlorsolvcleanup.pdf

Further information on SERDP- and ESTCP-funded research in this area is available at: http://www.serdp-estcp.org/DNAPL.cfm

The EPA sponsored an Expert Panel to assess the benefits of source zone remediation. Their report, "DNAPL Remediation: Is There a Case for Source Depletion?" is at: http://www.epa.gov/ada/download/reports/600R03143/600R03143.pdf

EPA also recently published a document called "Appropriate Goals for DNAPL Source Zone Remediation", available at: http://gwtf.cluin.org/docs/options/dnapl_goals_paper.pdf

The National Research Council recently published a review of the field: NRC, 2004. Contaminants in the Subsurface: Source Zone Assessment and Remediation, at: http://www.nap.edu/openbook/030909447X/html/332.html

The Interstate Technology and Regulatory Consortium has published several documents on DNAPLs, including:

An overview of characterization and remediation technologies:

http://www.itrcweb.org/Documents/DNAPLs-1.pdf

A regulatory review of the challenges of source zone remediation:

http://www.itrcweb.org/Documents/DNAPLs-2.pdf

An overview of bioremediation of DNAPLs:

http://www.itrcweb.org/Documents/BioDNAPL-1.pdf

Air Force Center for Engineering and the Environment has a web page with a number of documents, software, and other tools for chlorinated solvents and other contaminants, at: http://www.afcee.brooks.af.mil/products/techtrans/

Recent Relevant Projects and Useful Tools

DoD EPA DOE SERDP

Strategic Environmental Research and Development Program

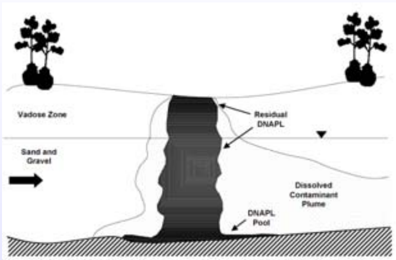
ESTCP

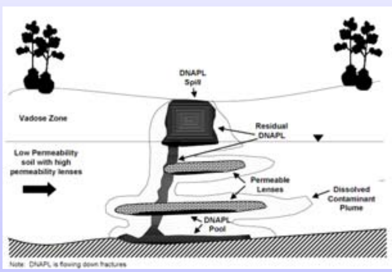
Environmental Security Technology Certification Program

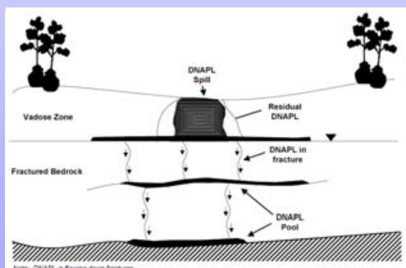
Thermal Treatment Evaluations

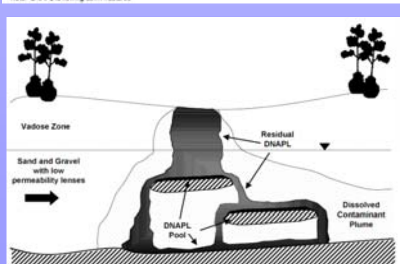
- Develop a tool for use by practitioners, regulators, and site owners to anticipate the likely design and performance of thermal-based DNAPL treatment.
- Link design and performance experience to a small number of generalized site scenarios.
- Evaluate improvements in groundwater quality and reductions in mass discharge (flux).

Final Product Concept









Physical Scenarios ← - - - - → **Experience/ Performance Summary**

Scenario	Technology	# of Sites	# of Pilot Tests	# of Full-Scale Systems	# of Systems Since 2000
Generalized Scenario A: relatively homogeneous and permeable unconsolidated	Steam Heating	7	5	2	2
	Resistance Heating	4	3	0	1
	Other	9	7	1	1
Generalized Scenario C: largely permeable sediments with interbedded lenses of low	Steam Heating	4	0	3	1
	Resistance Heating	12	3	7	3
	Other	7	2	5	3
Generalized Scenario D: largely impermeable sediments with interbedded layers of higher	Steam Heating	17	6	8	7
	Resistance Heating	15	4	8	7
	Other	15	5	9	2
Generalized Scenario E: competent, but fractured bedrock	Steam Heating	3	1	1	1
	Resistance Heating	0	0	1	0
	Other	0	0	0	0
Generalized Scenario F: karst and/or weathered bedrock	Steam Heating	2	2	0	2
	Resistance Heating	0	0	0	0
	Other	0	0	0	0
Generalized Scenario G: unknown	Steam Heating	15	2	5	2
	Resistance Heating	6	0	0	0
	Other	7	3	2	0

This table and others summarize key design and performance attributes, including numbers of energy delivery points, treatment times, temperatures reached, etc.

Conclusions To Date

- Most thermal applications have been poorly documented
- Operating conditions (especially treatment duration) often appear to be arbitrarily selected
- There do not seem to be obvious diagnostic tools for process optimization
- Significant mass removal is possible within the target treatment zone
- Mass flux often is reduced less than anticipated, due to untreated areas and limited treatment durations
- Ongoing evaluations (e.g., Thermal Conduction Heating at fractured bedrock site - NAWC in Trenton, NJ)

Optimal Search Strategy

- George Pinder, Univ. Vermont
- Computer-based search strategy
- Optimizes approach to define the source location and shape of the source zone
- Allows efficient, faster source delineation

DIAGNOSTIC TOOLS FOR DNAPL REMEDIATION

WATERVLIET ARSENAL
FRACTURED BEDROCK SITE

Watervliet NY Demonstration

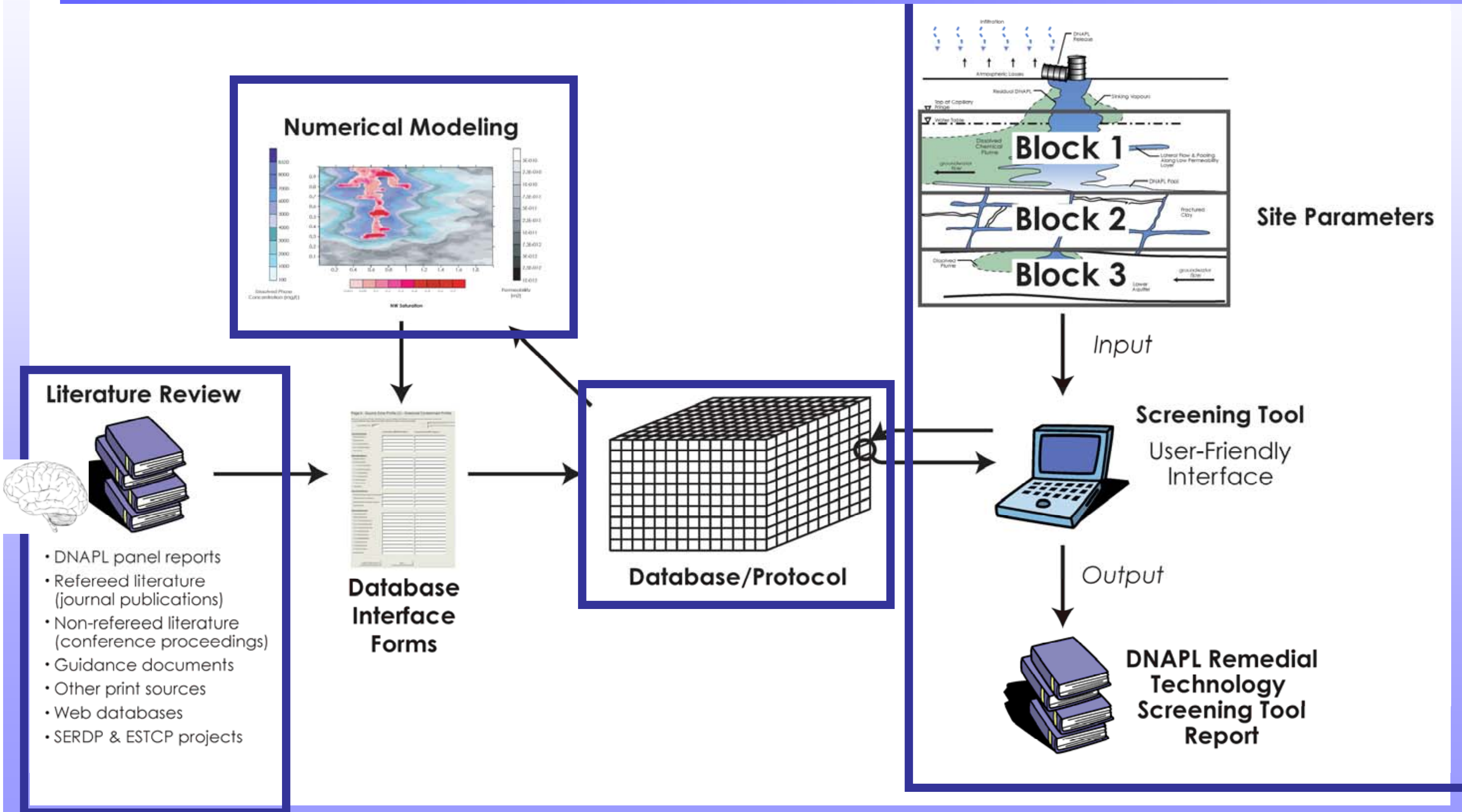
- Permanganate injected into fractured bedrock to treat TCE
- Rock crushing showed TCE has diffused into the rock matrix
- Permanganate reduced before penetrating matrix (high sulfide levels)
- Significant rebound in TCE flux and concentrations to near-pretreatment levels after ISCO

DNAPL-Test: A Screening Tool for Selecting DNAPL Remediation Technologies

Objectives

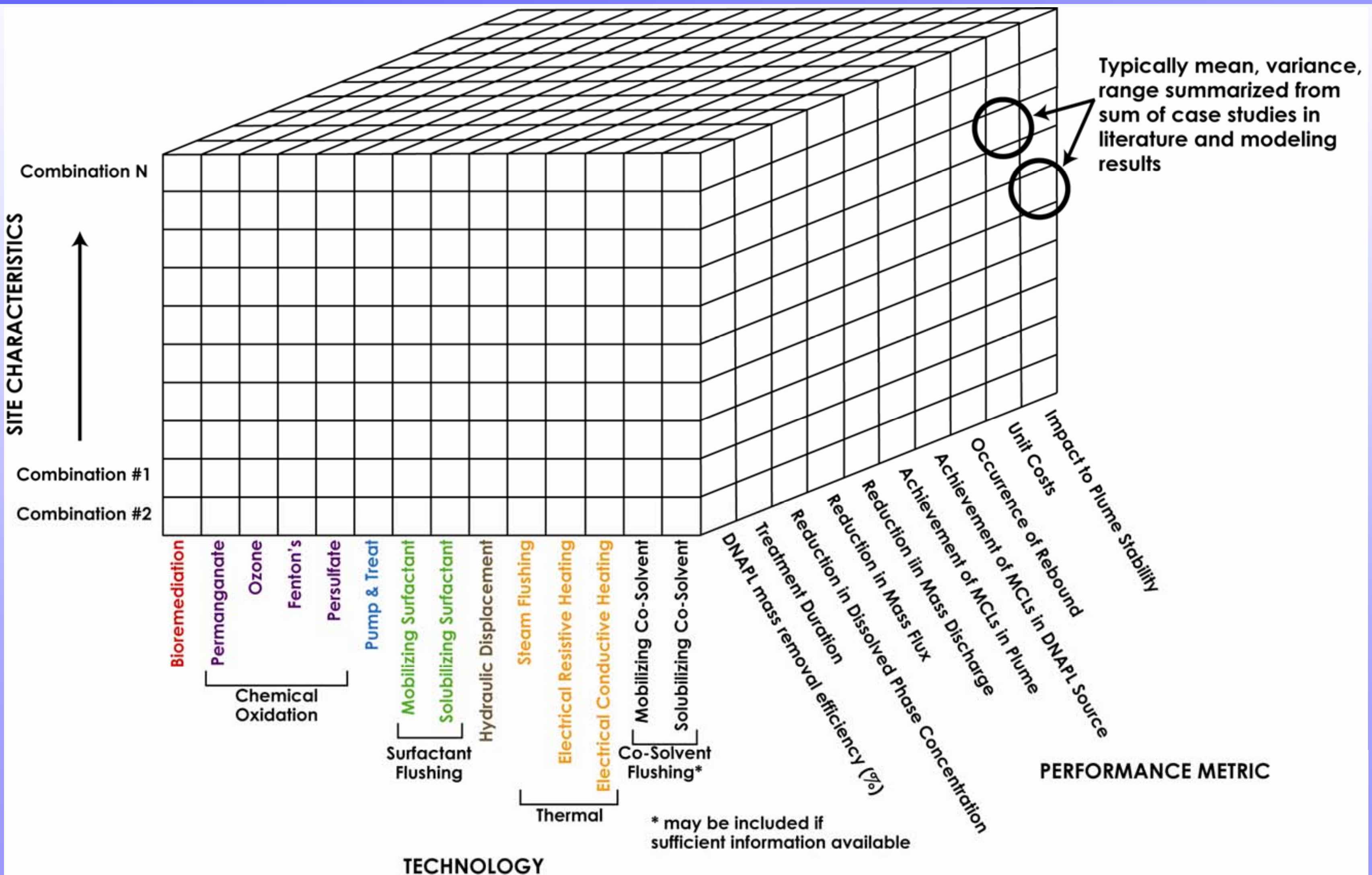
- Reduce uncertainty in estimating remedial outcomes
- Evaluate potential technology performance
- Aid RPMs in technology selection based on desired performance metrics

Technical Approach



3-D Matrix

Beta-test version: DNAPLTEST@geosyntec.com

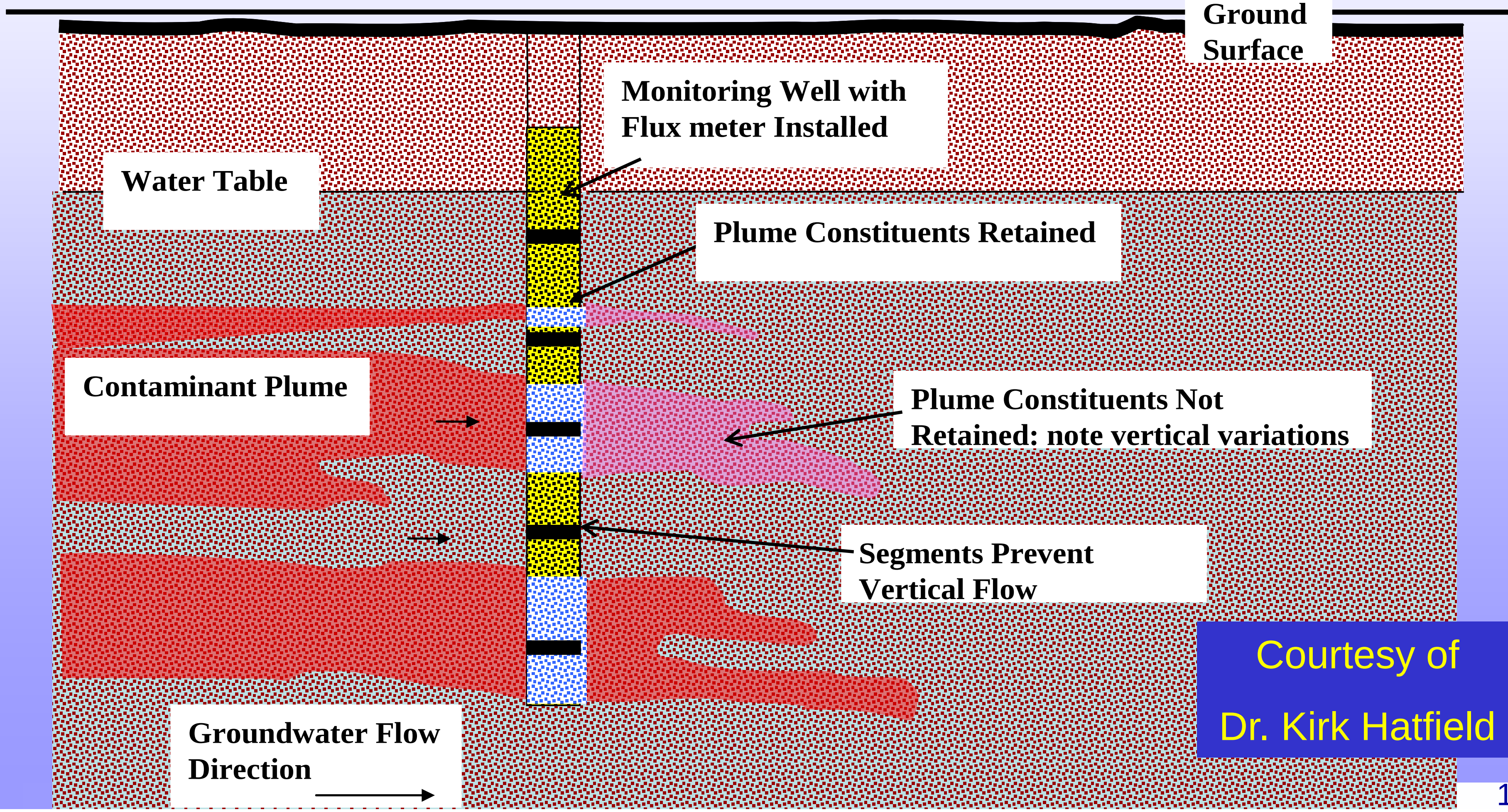


Mass Flux Reductions After Partial Source Treatment

- Method Development and Comparisons:
  - Passive flux meters, integrated pump tests, "traditional methods"
  - Similar results in many cases, given inherent uncertainty
- Pre- and Post-Treatment Measurements:
  - Roughly one order-of-magnitude reductions
  - Often suggest different treatment designs
- Modeling:
  - Valuable insights into likely impacts and controlling factors
  - Useful mass-based design tools (e.g., REMCHLOR, NAS)

Mass Flux Measurements

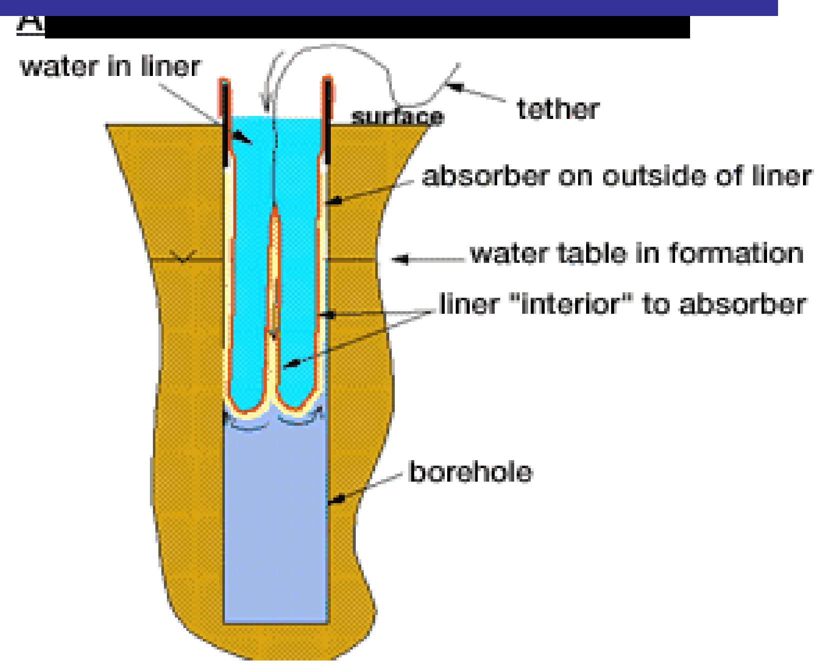
- Passive Flux Meters – Hatfield/Annable, Univ. FL
  - Testing Fractured-Rock PFMs



Courtesy of Dr. Kirk Hatfield

Passive Rock Fluxmeter (PRFM)

- **Inflatable packer or impermeable flexible liner that holds a reactive permeable fabric against the wall of the borehole and to any active fractures.**
- **Reactive fabrics capture target contaminants and release non-toxic resident tracers (e.g., visible dyes and branch alcohols).**
- **Tracer loss is proportional to fracture flow and yields <u>ambient</u> measures of flow.**
- **Leached visible tracers reveal location, orientation, and aperture of flowing fractures and direction of flow.**

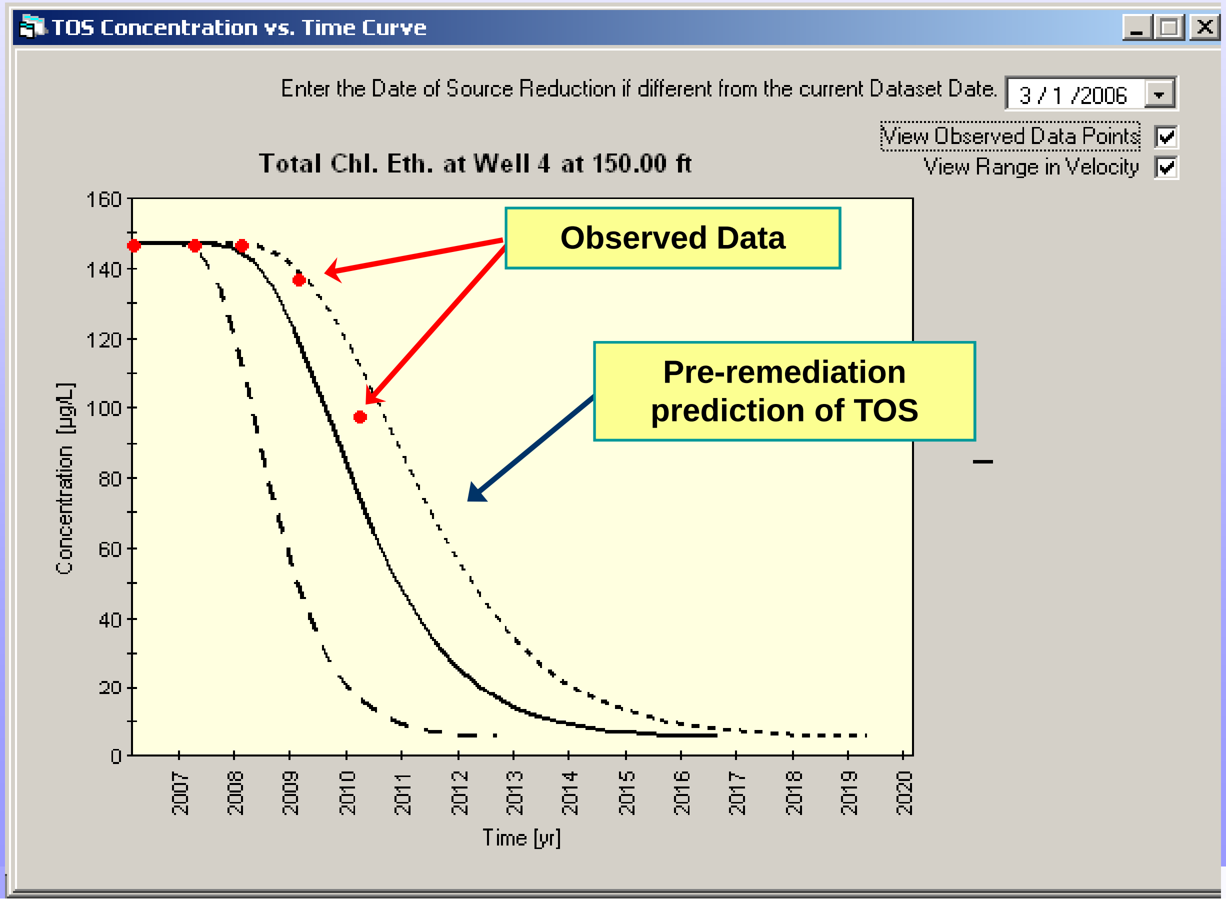


FRPFM FLUTe Design

Contaminant mass captured is proportional to flux and measures the <u>ambient</u> contaminant flux.

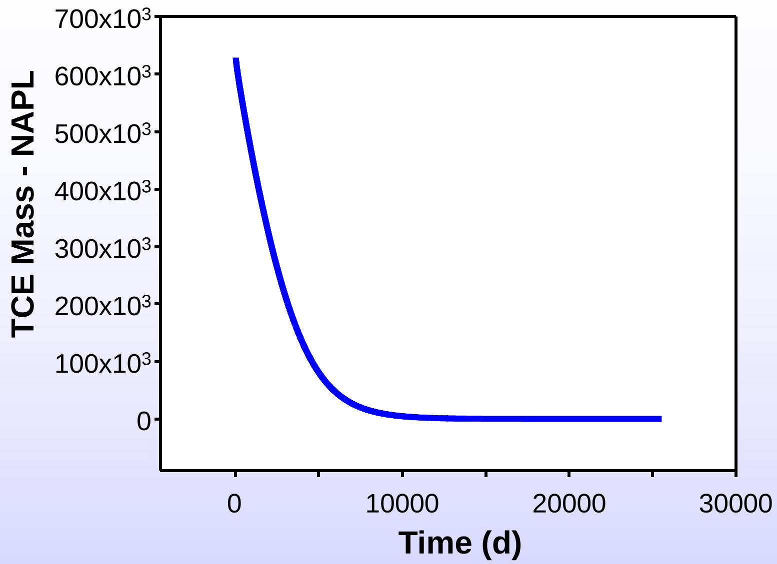
Estimating Cleanup Times For Combining Source-Area Remediation with MNA

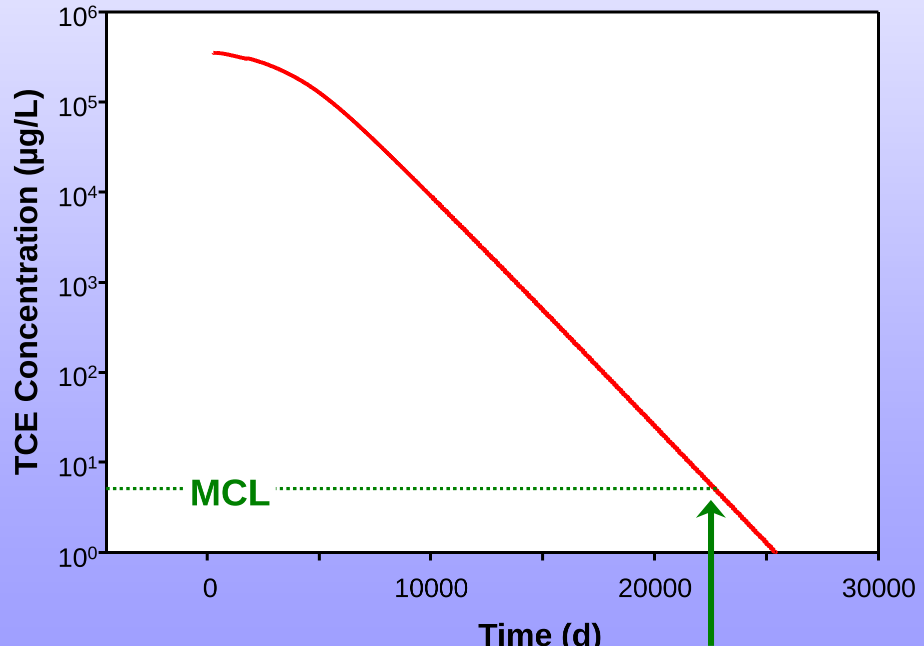
- Kram, Widdowson, Chapelle
  http://www.nas.cee.vt.edu/index.php



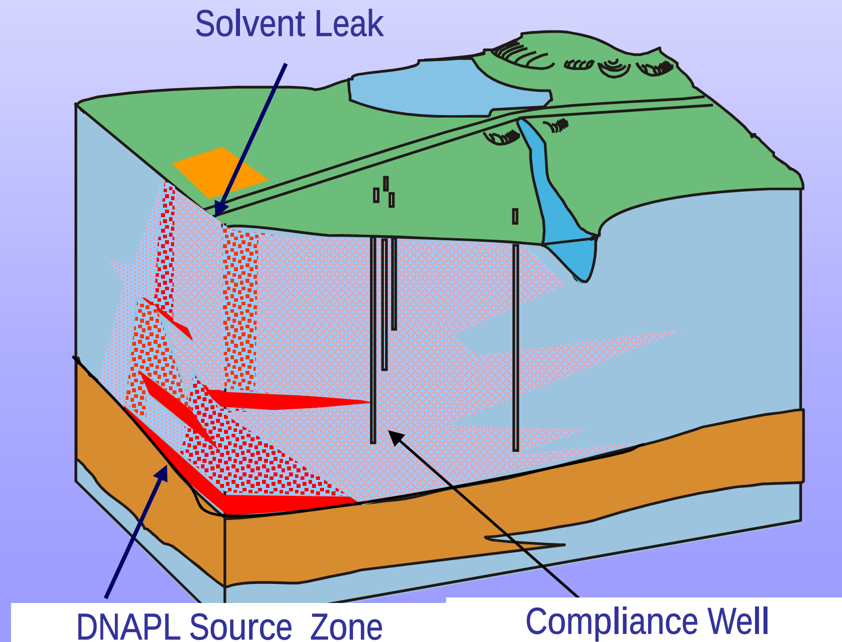
NAS Source Depletion Model

- Based on estimates of source zone mass, composition, geometry, and mass flux, NAS/SEAM3D tracks each constituent over time in both the NAPL and aqueous phases





Time of Remediation
(TOR)



Natural Attenuation Software

- NAS provides a framework for comparing various remediation strategies and defining remediation goals based on a selection criteria:
  - Site-specific RAOs and hydrogeology/biogeochemical data
- NAS also provides a tool for calculating life-cycle cost estimates by combining
  - Source zone remediation cost estimates and annual monitoring costs based on TOR estimates and reduction in plume size and source strength
- NAS is widely available and easy to use

IN SITU CHEMICAL OXIDATION: TECHNOLOGY PRACTICE MANUAL

- Robert Siegrist and Michelle Crimi
- Develop a design protocol and decision tools
- ISCO cost and performance database
- Customized searches for specific site conditions
- FAQ Guide
- Testing design protocol at DoD sites

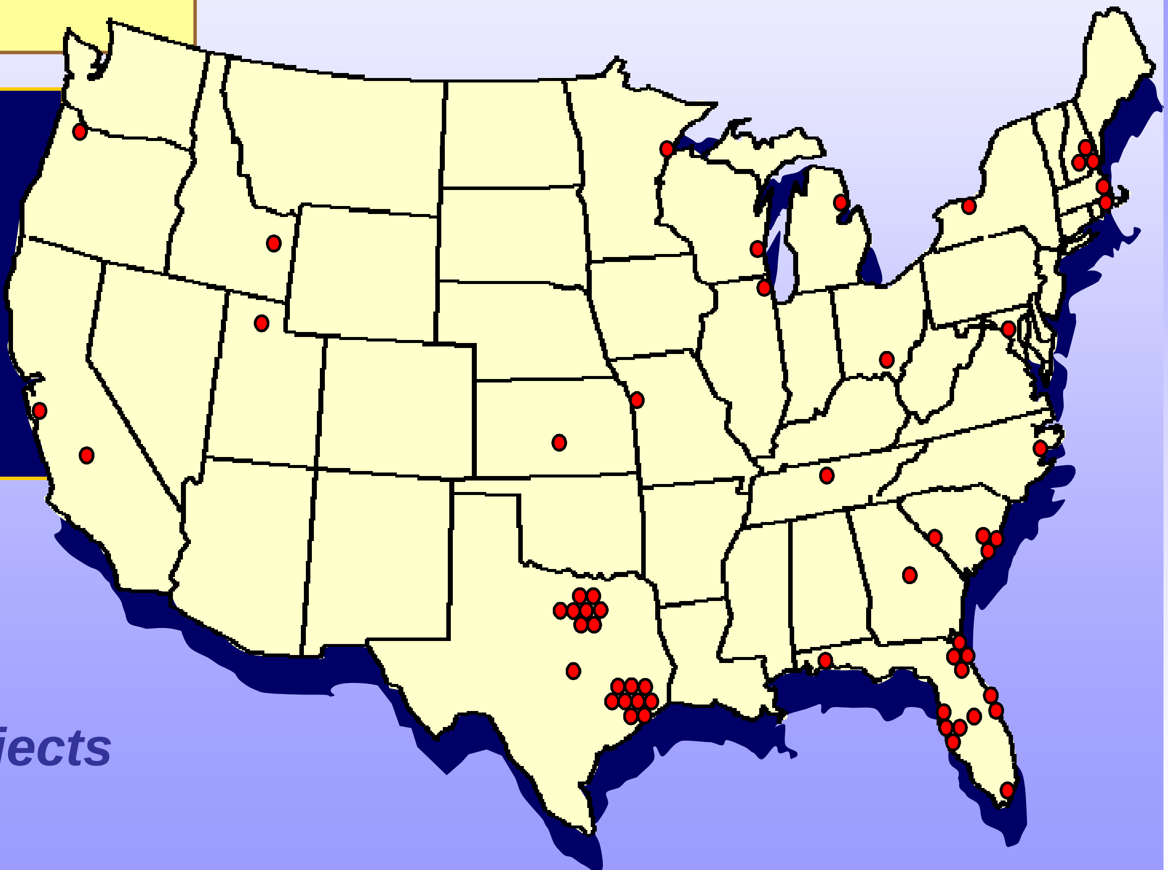
Four Tools…..

1. **Source Depletion Decision Support System (SERDP)**
   - *Performance & Cost Database*
   - *Untreated Site Database*
2. **BIOBALANCE Software**
3. **Mass Flux Tool Kit**
4. **REMCHLOR**

Temporal Concentration Data From 59 Chlorinated Solvent Sites

FOUR SOURCE DEPLETION TECHNOLOGIES:

- ***Enhanced Biodeg.***
- ***Chem. Oxidation***
- ***Surfactants/Cosolv.***
- ***Thermal Treatment***



- ***Median Treatment Volume = 3,800 yd^3***
- ***~ 70% Full-Scale Projects***

Source: McGuire et al., 2006, Ground Water Monitoring and Remediation

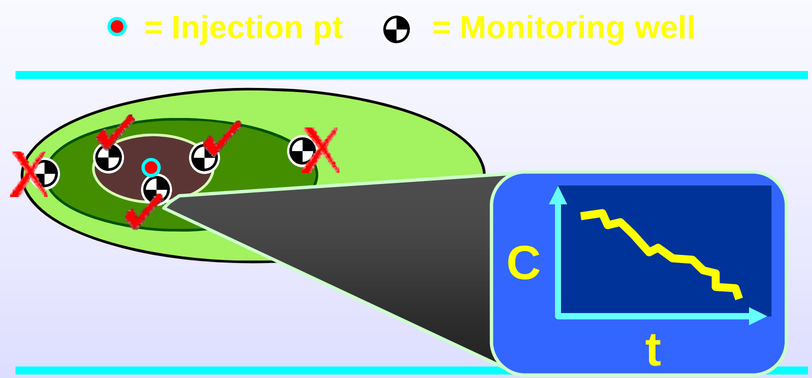
Data Analysis Methods

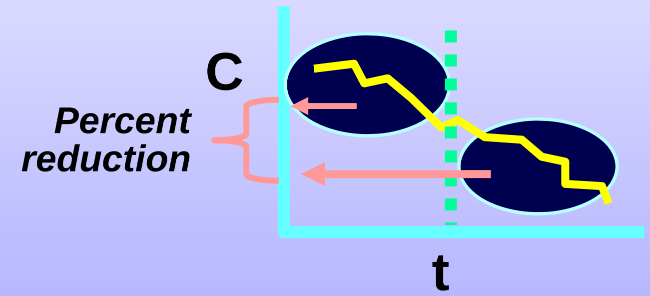
PERFORMANCE:

- Compiled conc. vs. time data (before and after treatment) for up to 4 wells within treatment zone

- Calculated geometric mean conc. of before treatment data and after treatment data;
- Then calculated percent reduction for each well

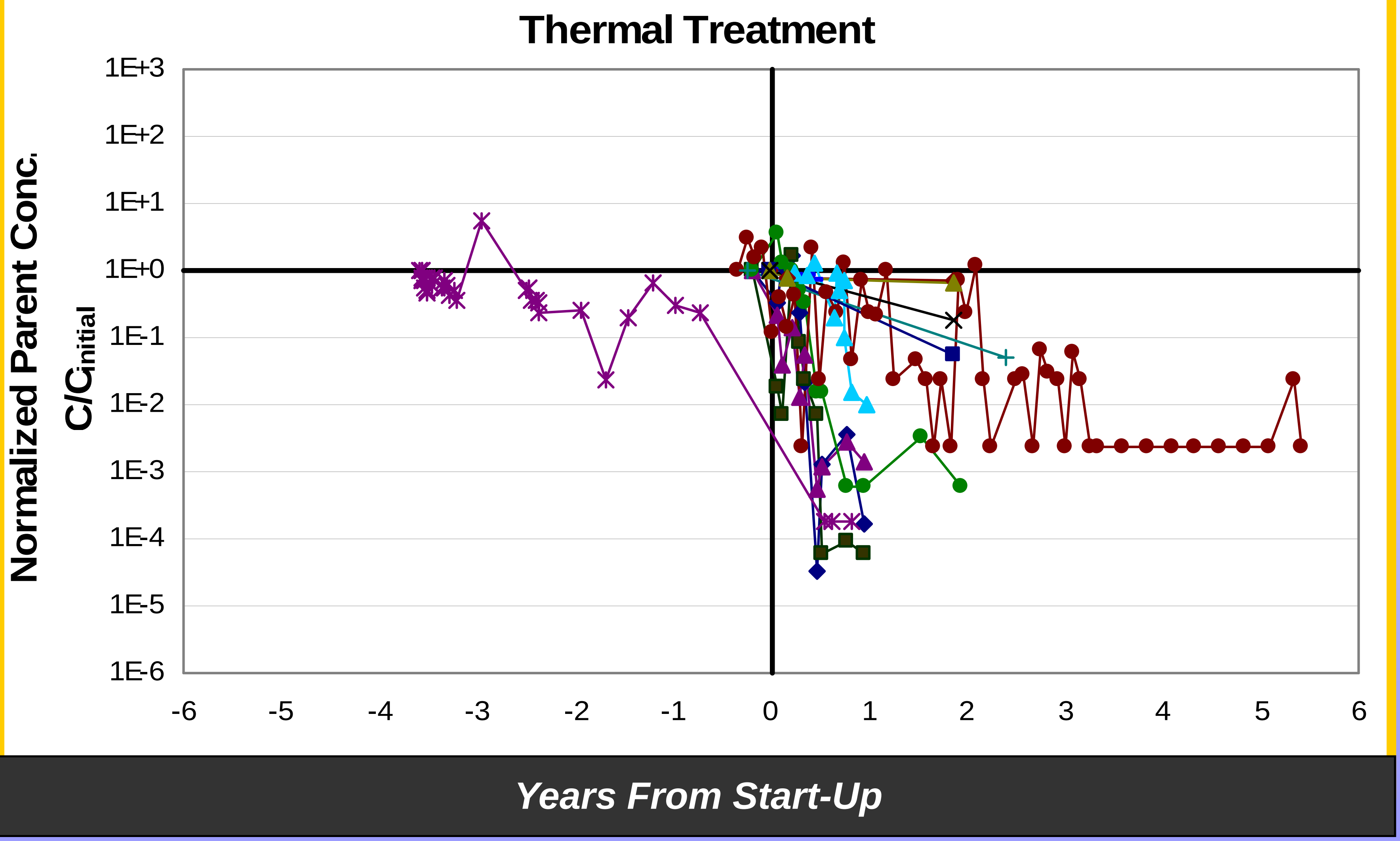
- Median percent reduction of all treatment zone wells as final performance metric





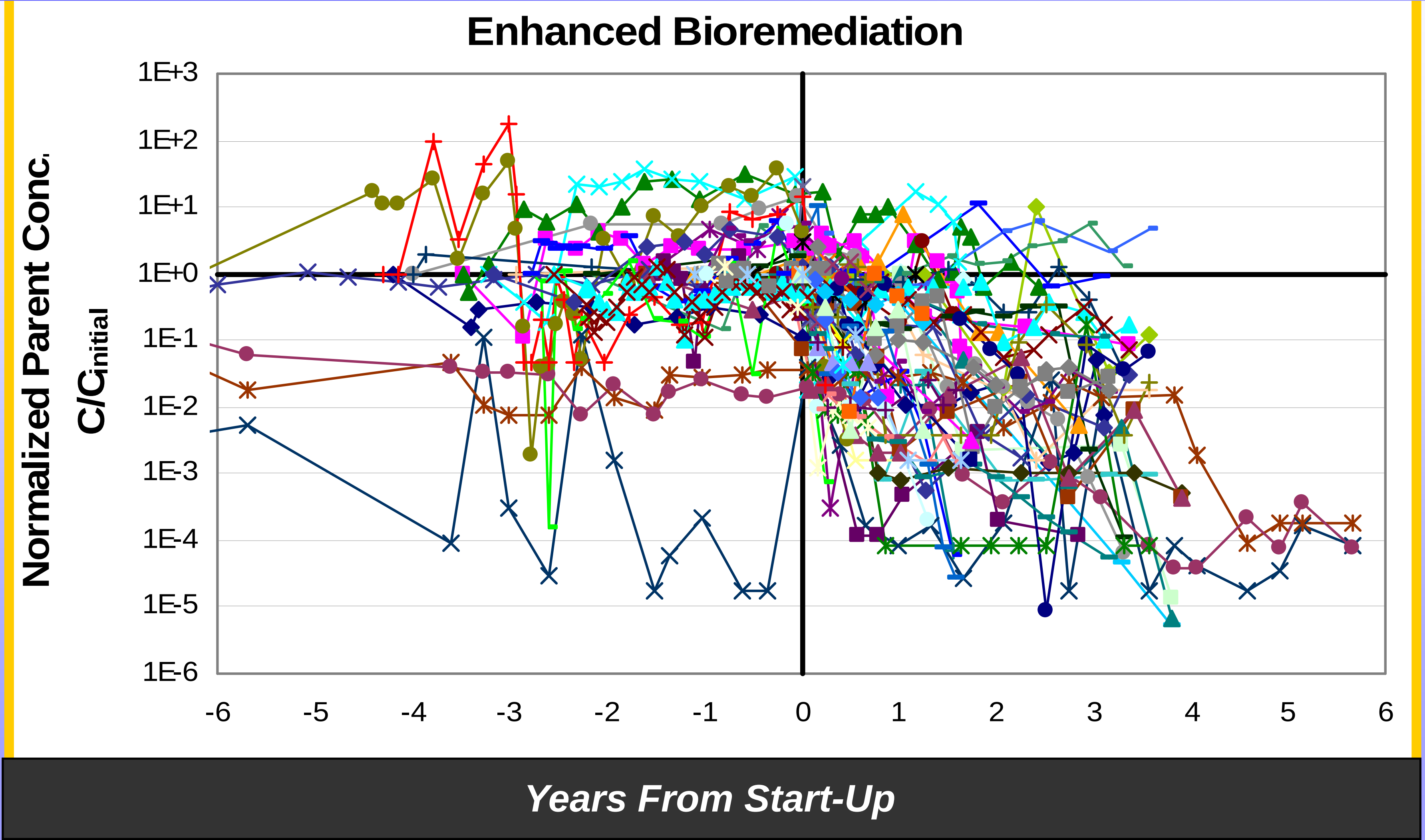
	% Red'n	Site % Red'n
Well # 1	99.9	90.0
Well # 2	91.0	
Well # 3	89.0	
Well # 4	+ 10.0	

Temporal Records for Thermal Treatment Wells (6 Sites, 13 Wells)



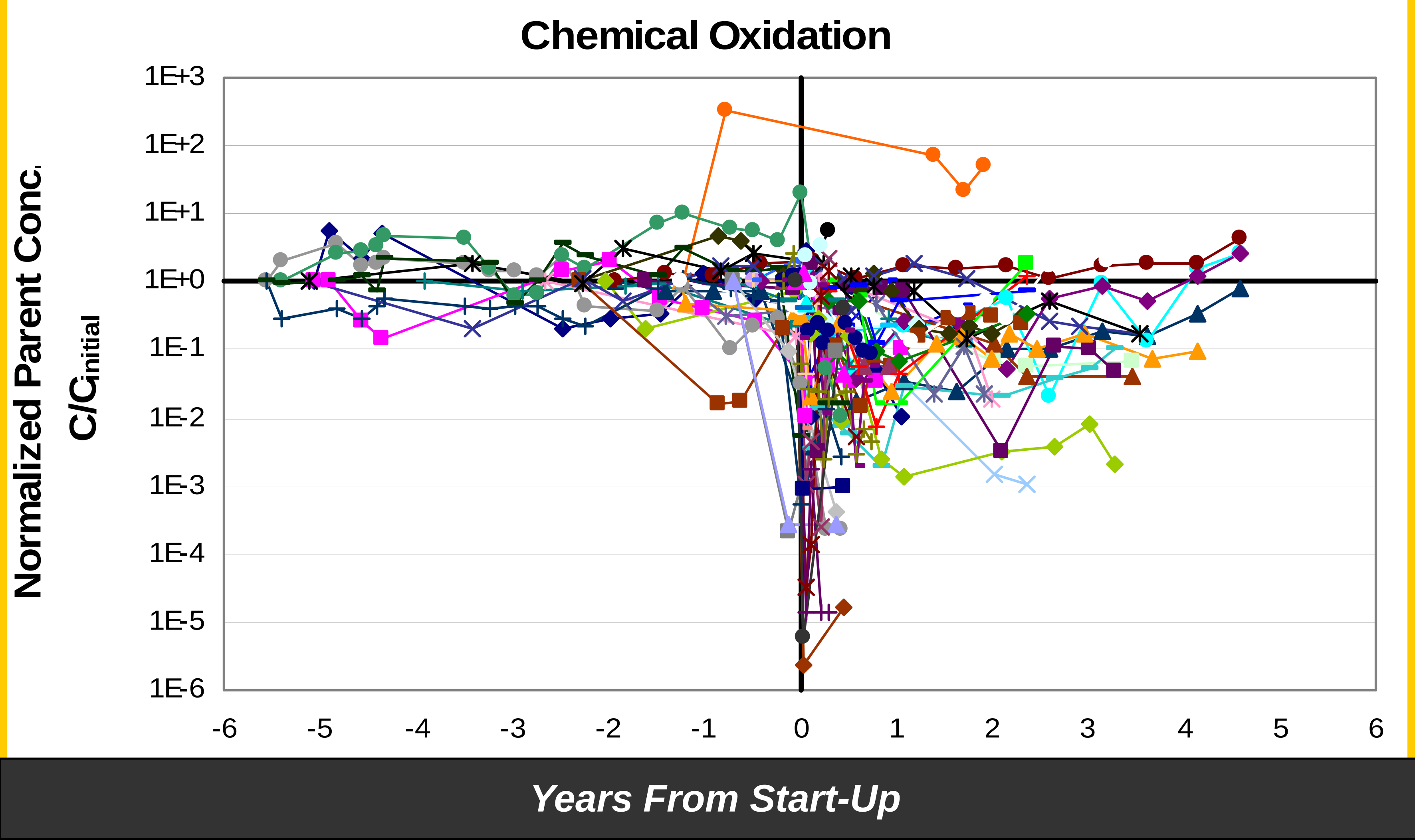
Any site achieve MCLs everywhere? No

Temporal Records for Enhanced Biodegradation (26 Sites, 68 Wells)



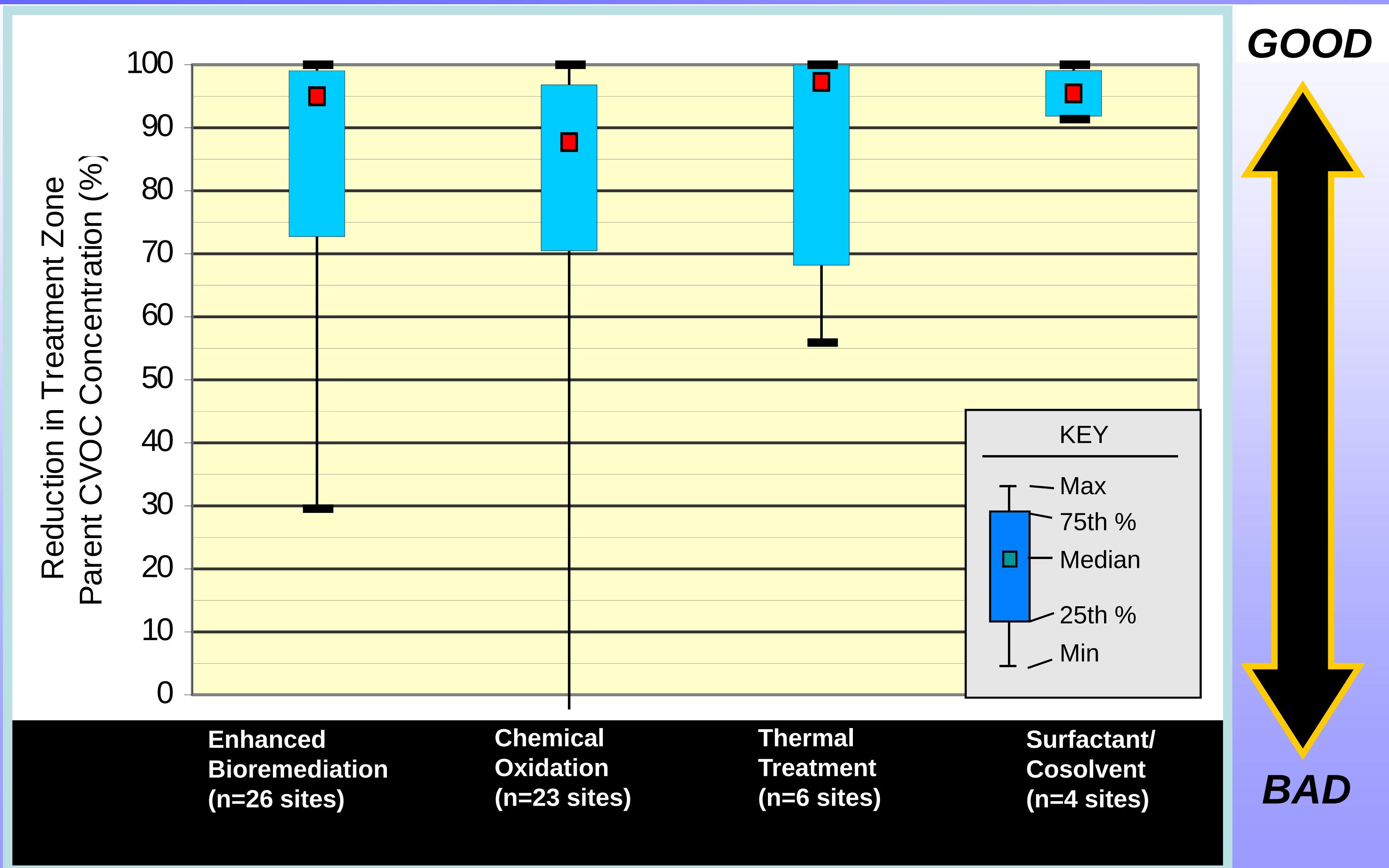
Any site achieve MCLs everywhere? No

Temporal Records for Chemical Oxidation (23 Sites, 58 Wells)

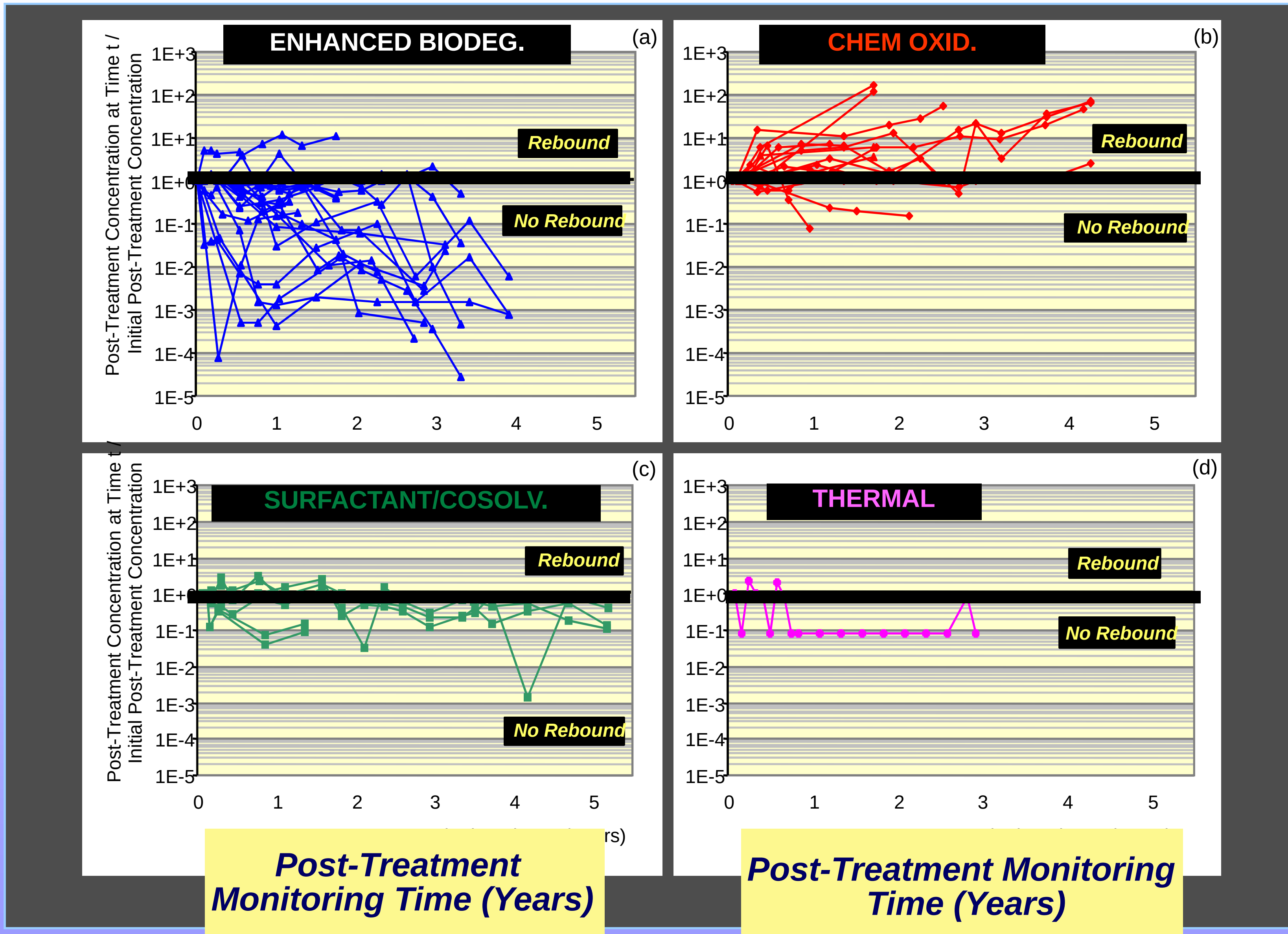


Any site achieve MCLs everywhere? No

% Reduction in <u>*PARENT*</u> *Due to Source Depletion*



What About *Rebound ?* (Parent Compounds)



Summary

1. ***Source depletion projects routinely achieve >70% reduction in source zone groundwater parent concentration, but no sites met MCLs everywhere.***

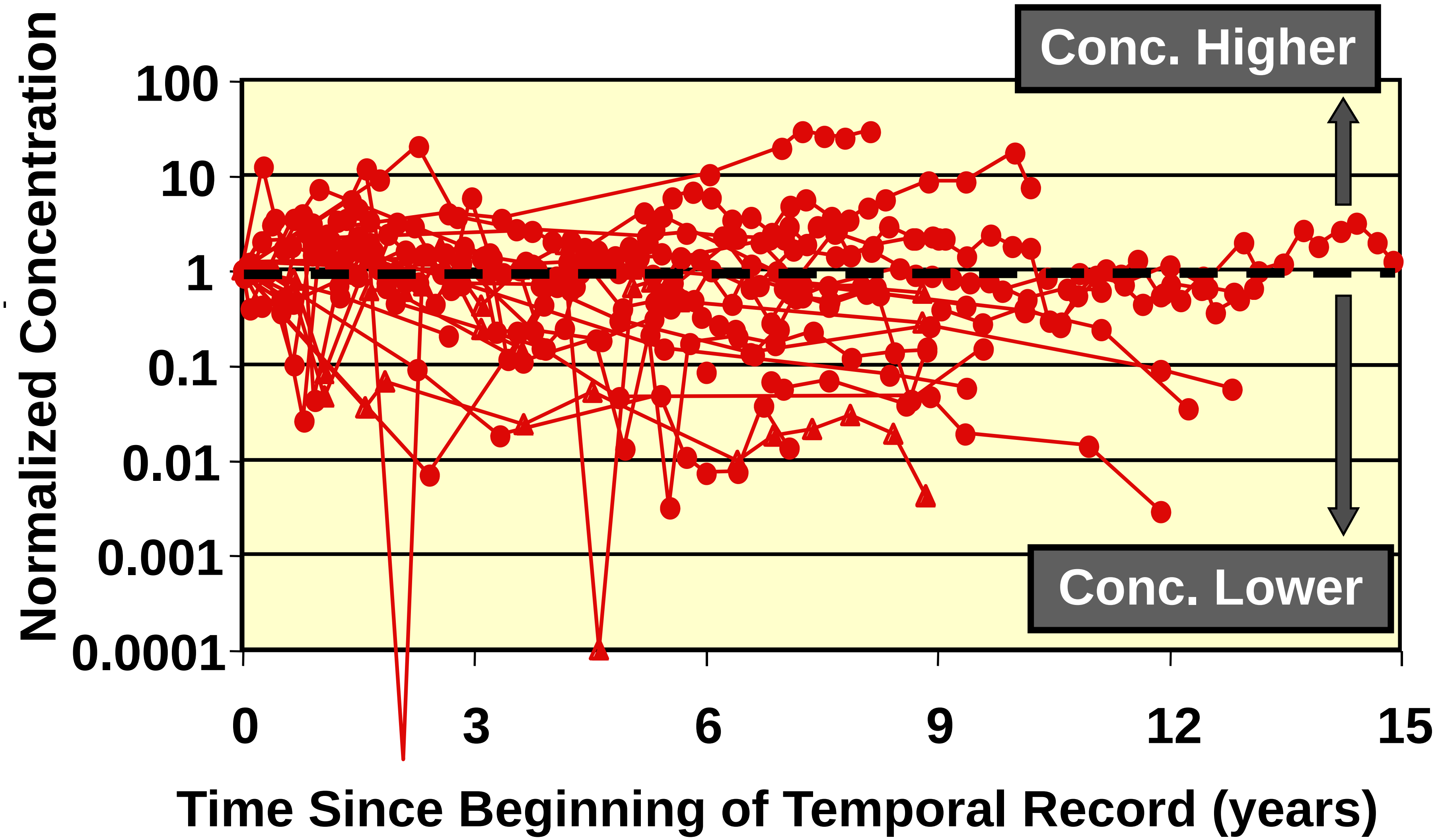
2. ***Parent compound <u>rebound</u> not big problem at most sites, but more prevalent for chemox (2 of 7 chemox sites had complete rebound).***

What About a Control?

For this project:

What about untreated sites?

Untreated Sites: TCE



Change in TCE Over Time

Number: ***13 sites, 21 wells***

Median Duration: ***10 years***

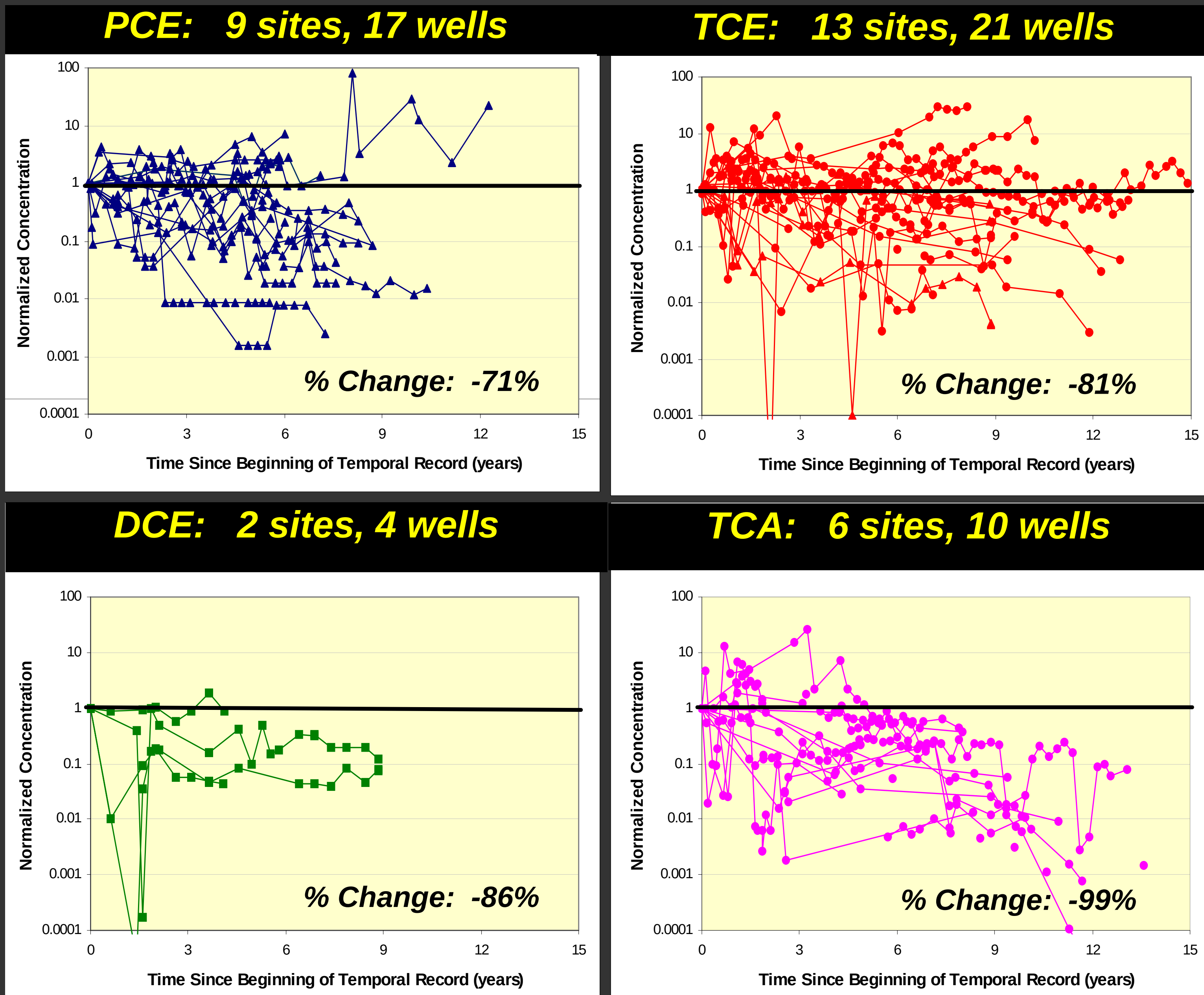
Median % Change: ***- 81%***

Concentration Trend (MAROS Software)

- **Increasing: 3 sites**
- **Stable: 3 sites**
- **Decreasing: 7 sites**

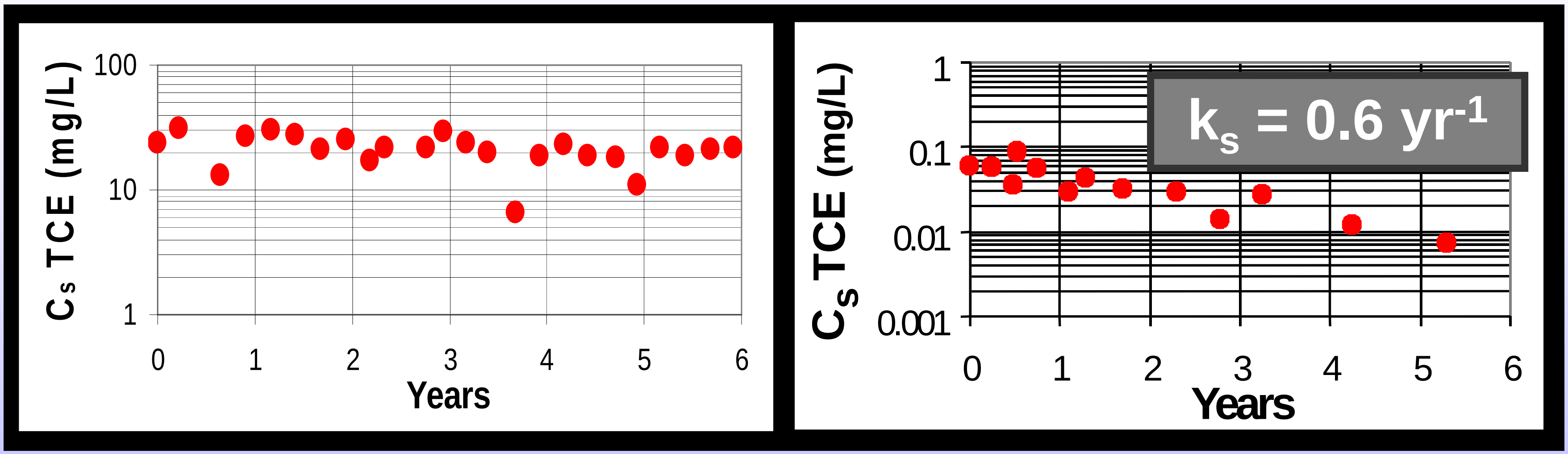
Source: Newell et al., 2006, ASCE Environmental Engineering

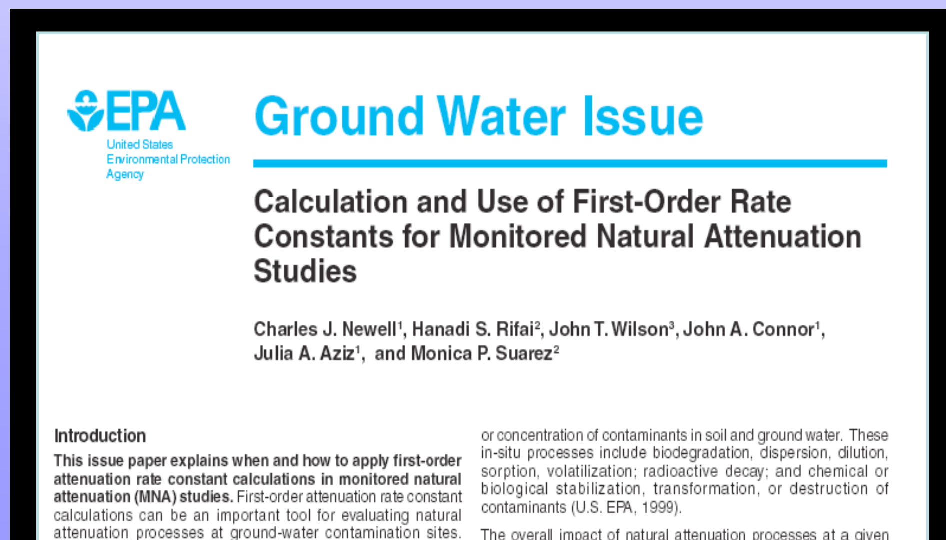
Temporal Trends In Untreated Source Zones



% Change = median % change for all wells

Example Real-World Source Decay Rates





EPA
United States
Environmental Protection
Agency

Ground Water Issue

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell[1], Hanadi S. Rifai[2], John T. Wilson[3], John A. Connor[1], Julia A. Aziz[1], and Monica P. Suarez[2]

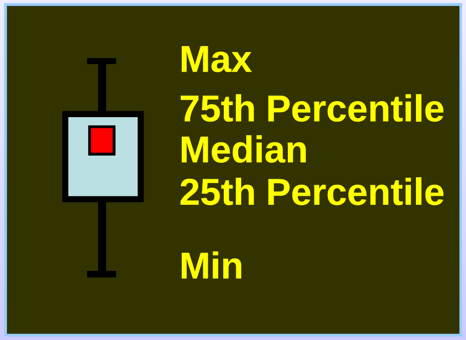
Introduction

This issue paper explains when and how to apply first-order attenuation rate constant calculations in monitored natural attenuation (MNA) studies. First-order attenuation rate constant calculations can be an important tool for evaluating natural attenuation processes at ground-water contamination sites.

or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants (U.S. EPA, 1999).

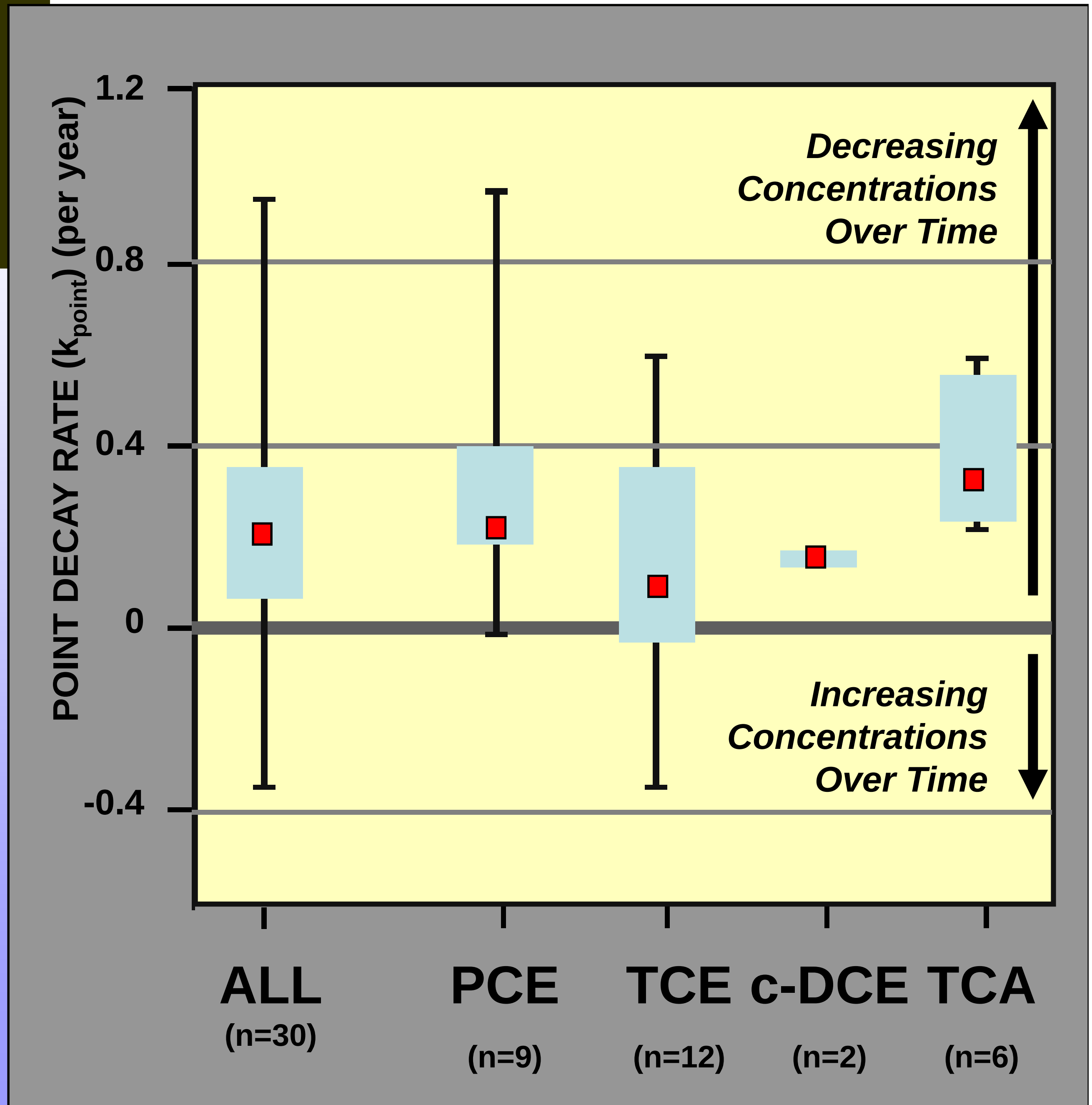
The overall impact of natural attenuation processes at a given

Observed Source Decay Rate for CVOCs: *13 Sites*



Median Half-Life

PCE: 3.0 years
TCE: 6.1 years
DCE: 4.3 years
TCA: 2.0 years



Implication

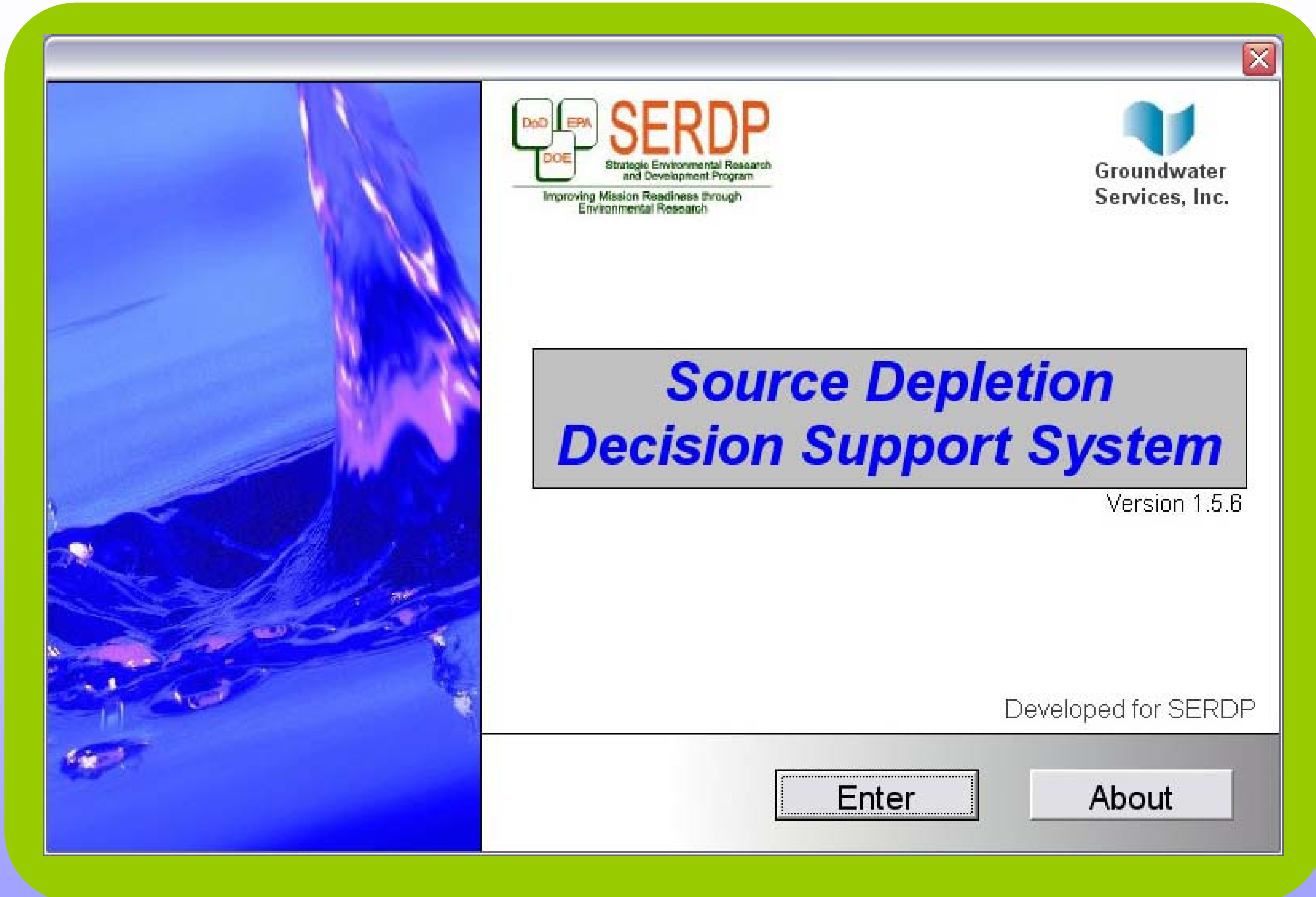
Benefits of partial source depletion is reduced if source is decaying naturally. ***For example:***

If source depletion gives 88% reduction in concentration….

That is equal to 3 source decay half-lives…..

These untreated source zones need < 20 years to achieve same result (?)

(median decay values from 23 site database)



Free download at: www.gsi-net.com

Four Tools.....

1. **Source Depletion Decision Support System**
   - ***Performance & Cost Database***
   - ***Untreated Site Database***
2. **BIOBALANCE Software**
3. **Mass Flux Tool Kit**
4. **REMCHLOR**

BIOBALANCE

A MASS BALANCE TOOLKIT

Closing the Mass Balance on Sources, Donors, Competing Reactions, and Attenuation Processes at Chlorinated Solvent Sites

Roopa Kamath
Charles Newell
David Adamson
Paul Newberry

GSI Environmental, Inc.
Houston TX

Brian Looney
Karen Vangelas

Savannah River National Laboratory
Aiken SC

Biobalance Software: Four Modules

- ***Remediation timeframe*** **and to evaluate *performance of source remediation technologies***

SOURCE

- **Long-term *sustainability* of natural processes**

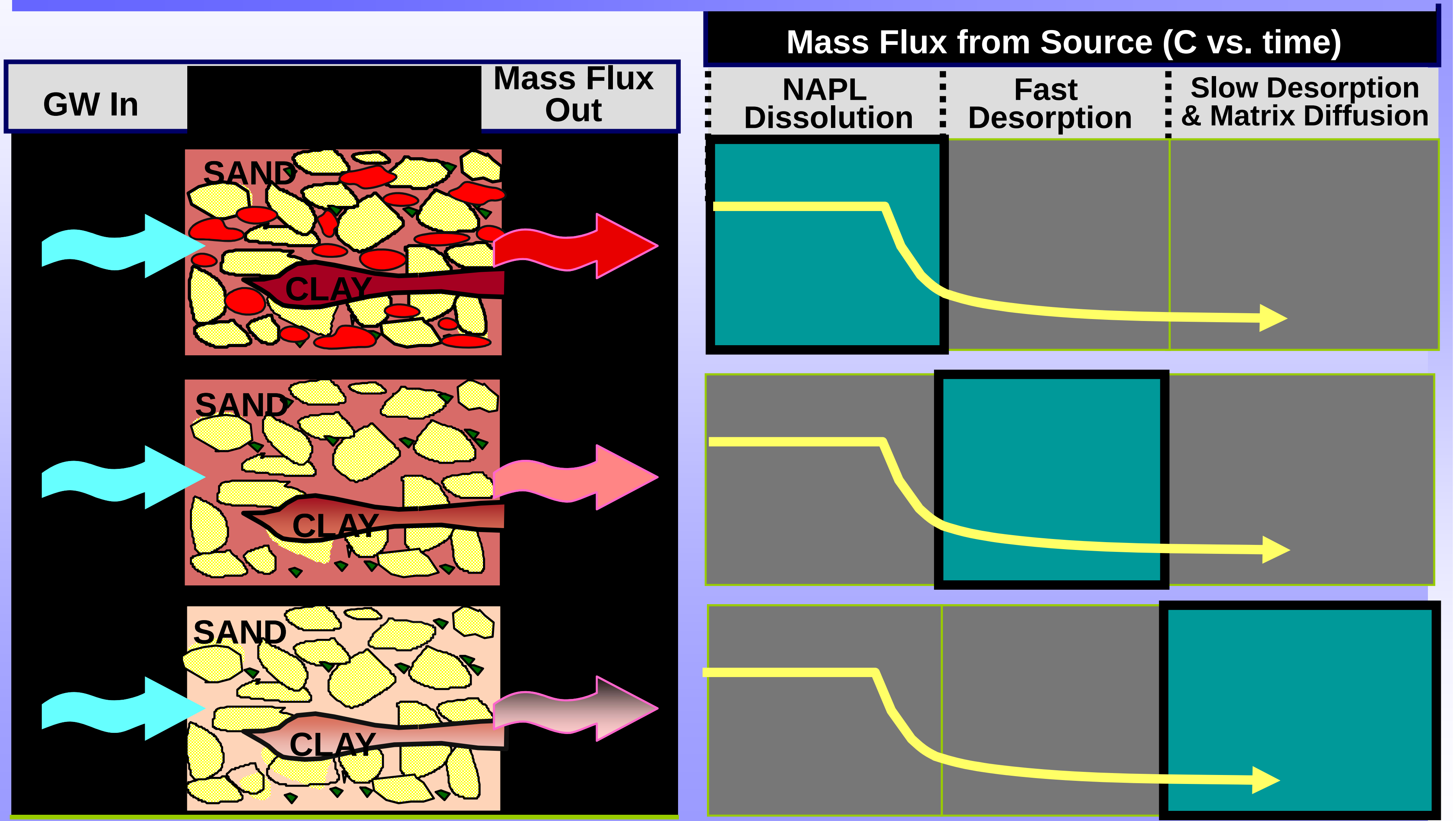
COMPETITION **DONOR**

- ***Stability* of the contaminant plume and its potential for migration**

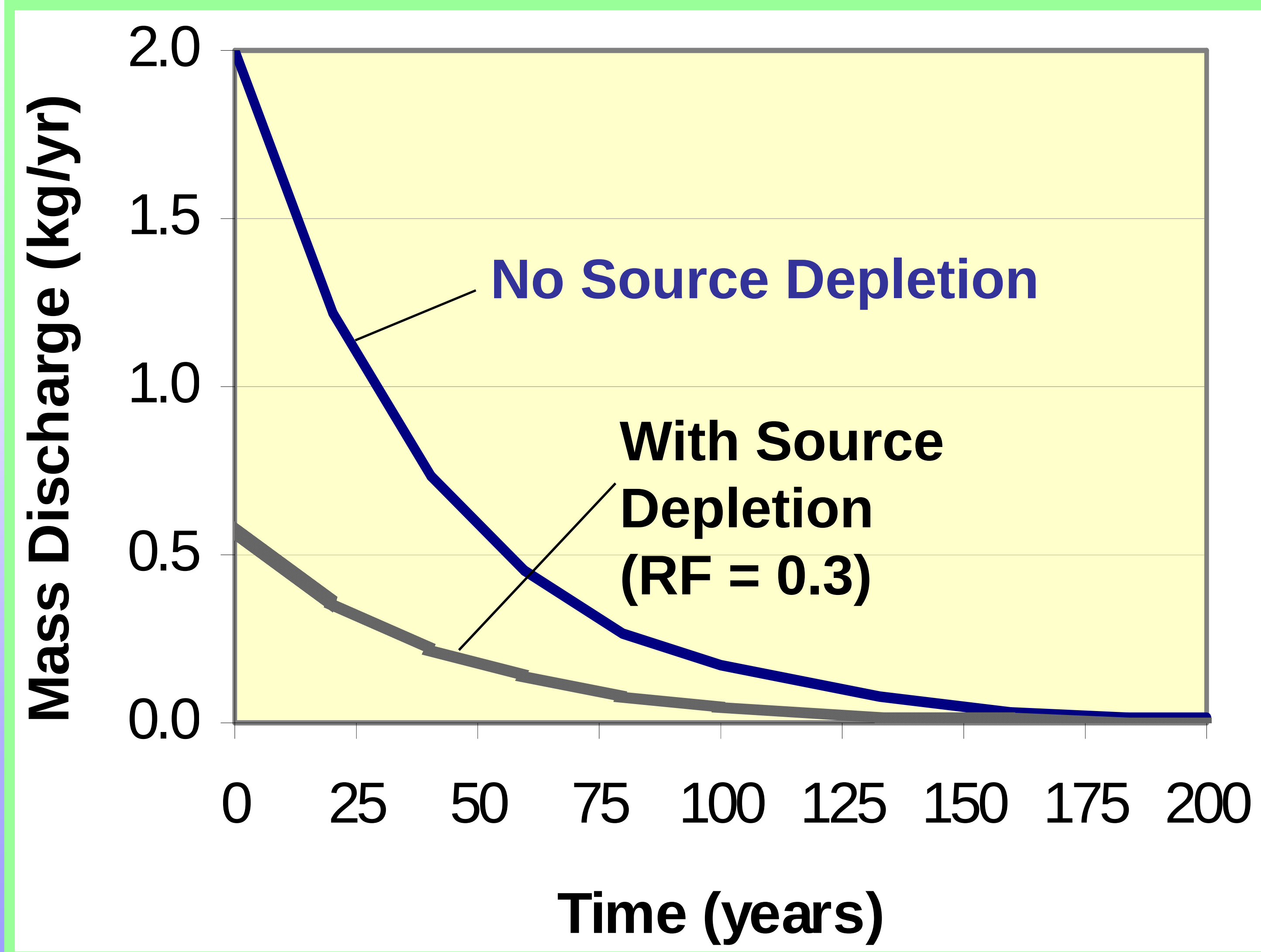
PLUME

Impact of Source Treatment

Life of a Source Zone



FIRST ORDER DECAY MODEL – With and Without *Source Depletion*



Assume C_t proportional to M_t

RF: Remaining Fraction

Effect of Source Treatment on Remediation Timeframe (RTF)

FIRST ORDER EQUATION:

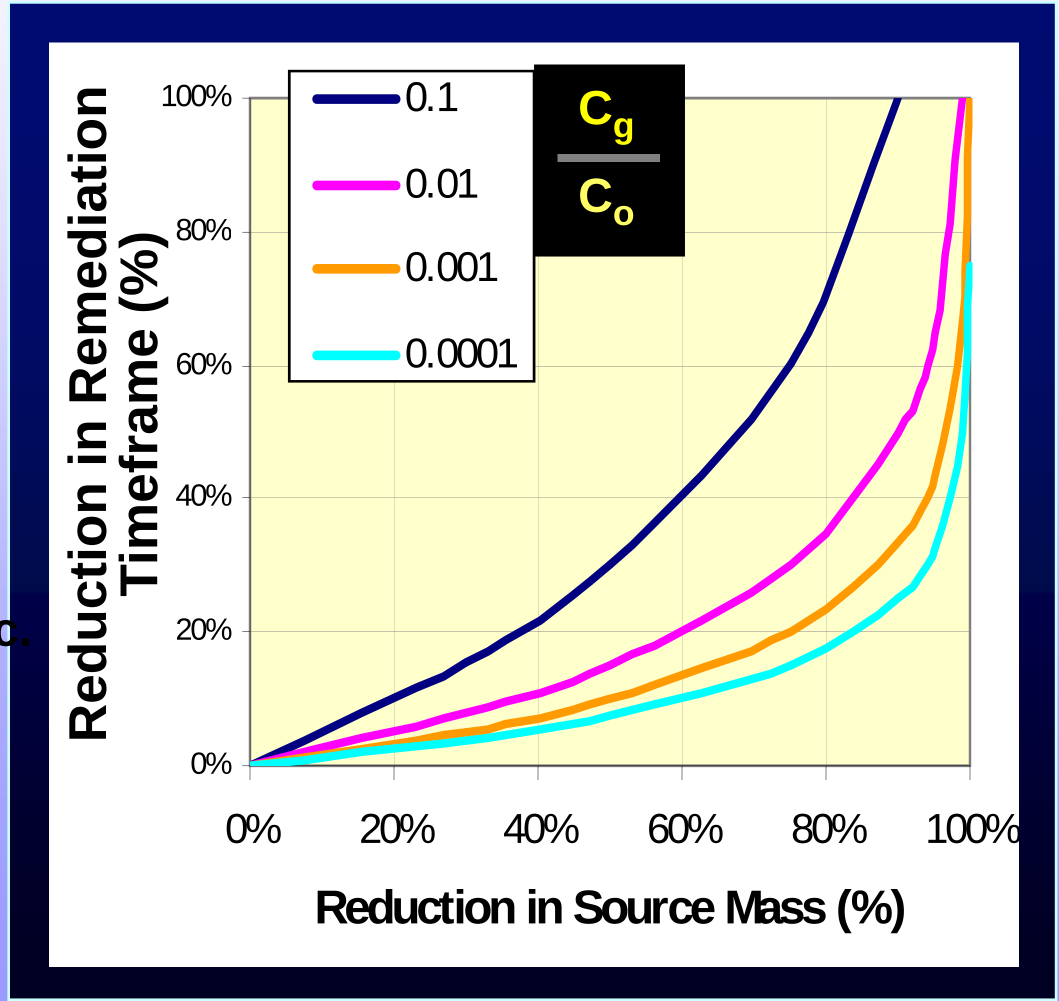
$$\frac{RTF_{SD}}{RTF_{MNA}} = \frac{\ln\left(\frac{C_g}{C_0\,RF}\right)}{\ln\left(\frac{C_g}{C_0}\right)}$$

C_g = GW Concentration Goal (such as MCL)

C_o = Original Source Conc.

RTF_{SD} = Remed. timeframe with *source tmt*

RTF_{MNA} = Remed. timeframe w/ *only natural attenuation*



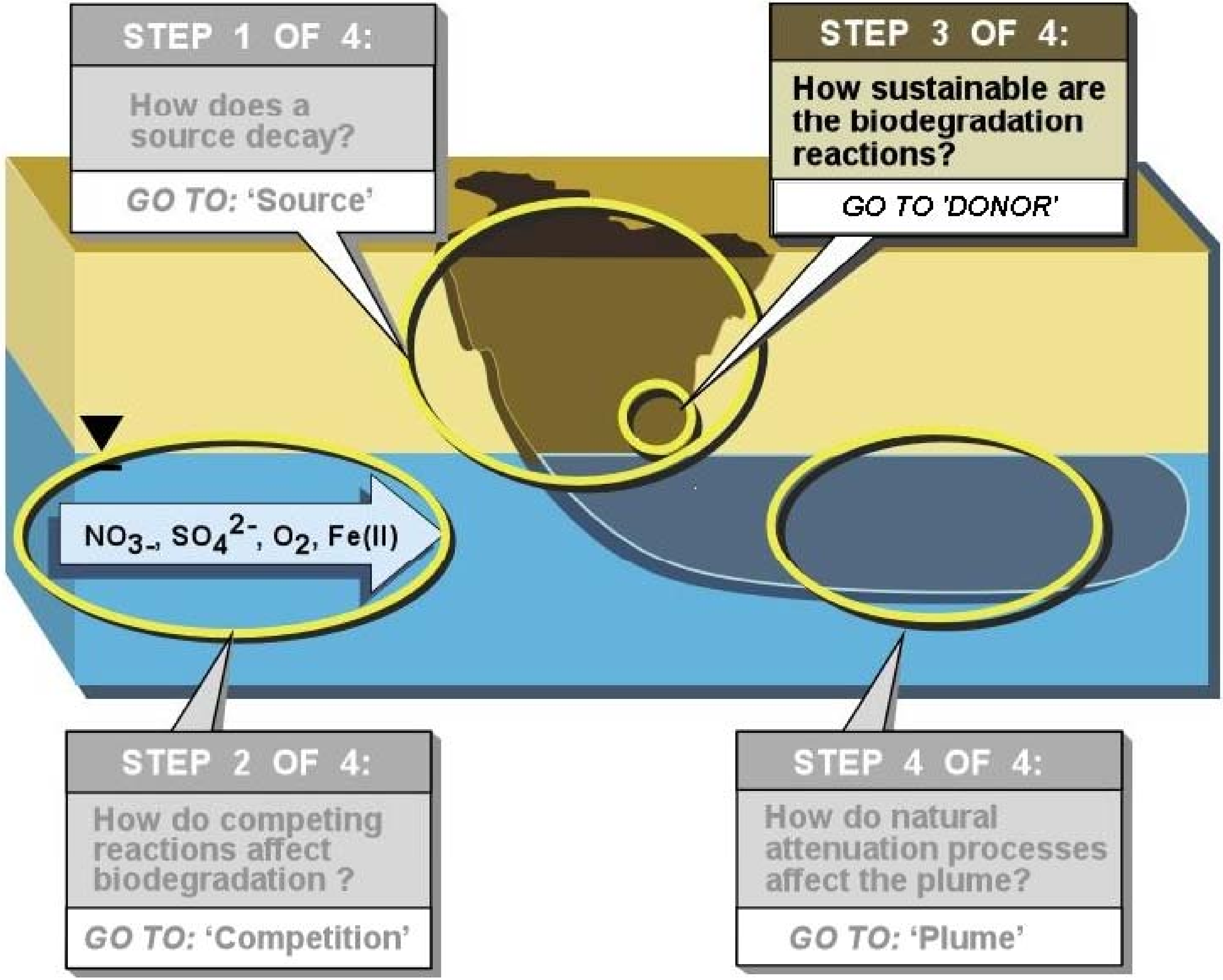
Summary

1. ***Reduction in Remediation Timeframe not likely to be directly proportional to reduction in source mass***

2. ***First Order Source Decay Model:***

80% Reduction in Source Mass = 18% Reduction in Remediation Timeframe

For specific case where $C_g/C_o = 0.0001$



STEP 1 OF 4:
How does a source decay?
GO TO: 'Source'
STEP 3 OF 4:
How sustainable are the biodegradation reactions?
GO TO 'DONOR'
NO_3^-, SO_4^{2-}, O_2, Fe(II)
STEP 2 OF 4:
How do competing reactions affect biodegradation ?
GO TO: 'Competition'
STEP 4 OF 4:
How do natural attenuation processes affect the plume?
GO TO: 'Plume'

Scanning Electron Microscope Image of Dechlorinating Bacteria

Calculating Availability of Electron Donor in the Source Zone

Using NAPL Composition Data

NAPL with 15% benzene; 85% TCE

AVAILABLE Hydrogen **= 0.15 * 0.39 H_2-equivalents/g-Donor**

= 0.06 g-H_2/g-NAPL

Hydrogen DEMAND by PCE **= 0.85 * 0.045 H_2-equivalents/g-Donor**

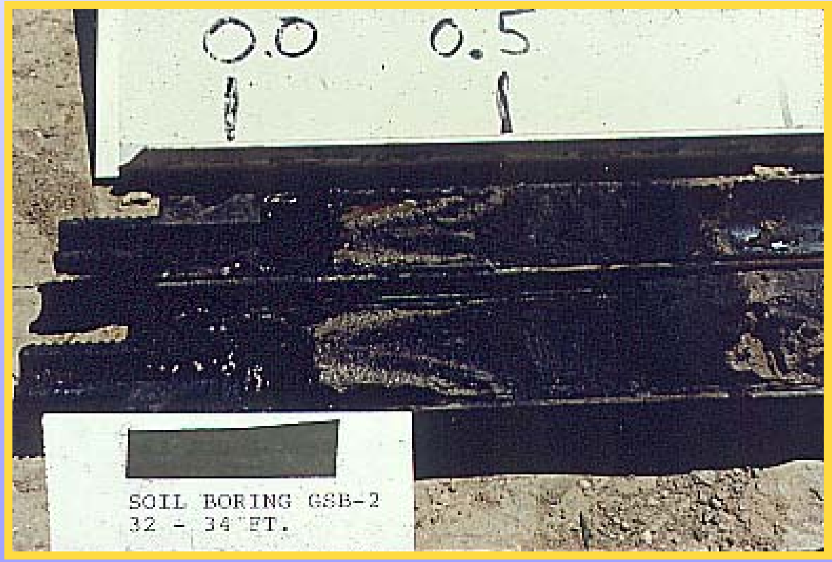
= 0.04 g-H_2/g-NAPL

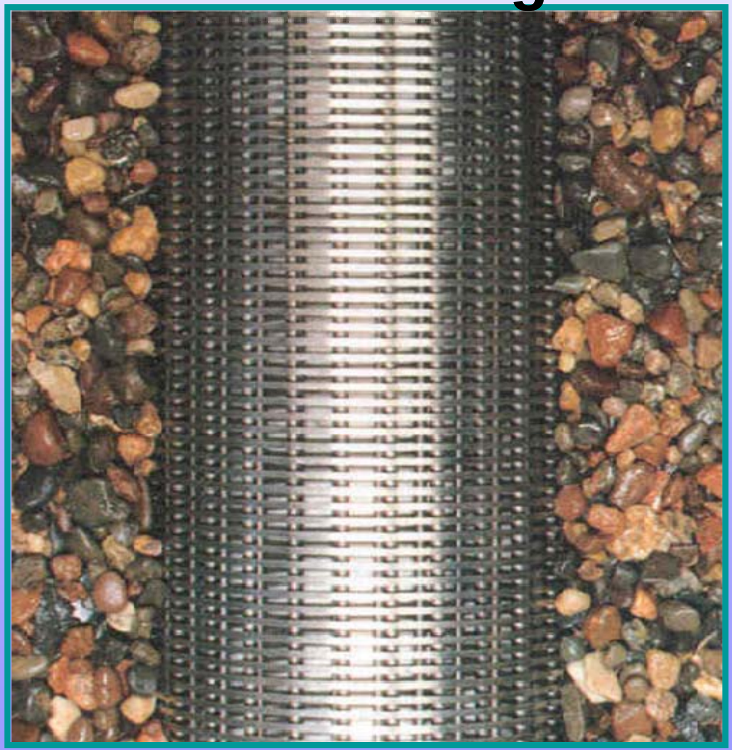
Donor Available/Donor Demand = 1.5

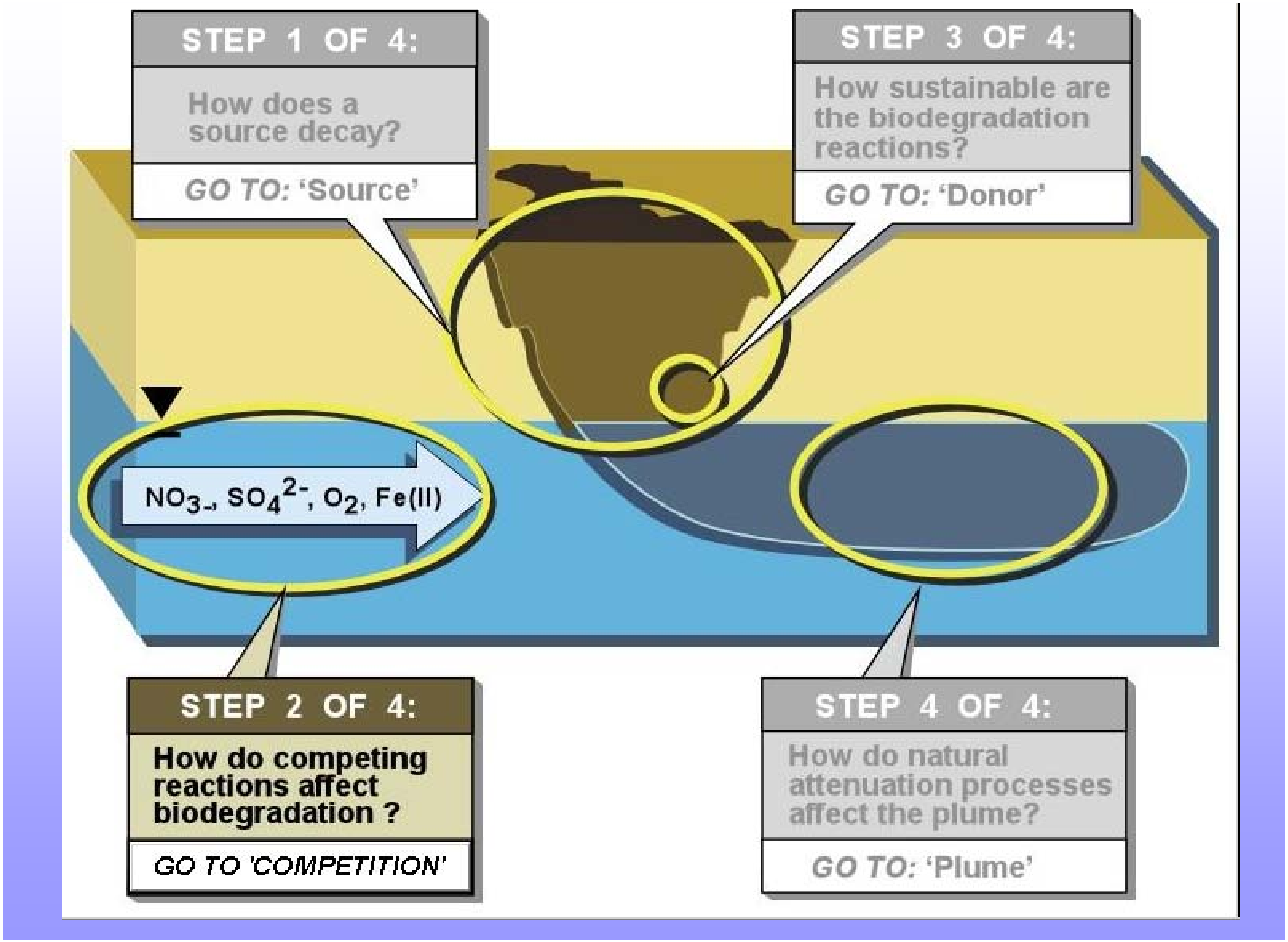
Two Ways to Estimate Donor Mass

From Analysis of DNAPL Sample

From Groundwater Samples + Partitioning







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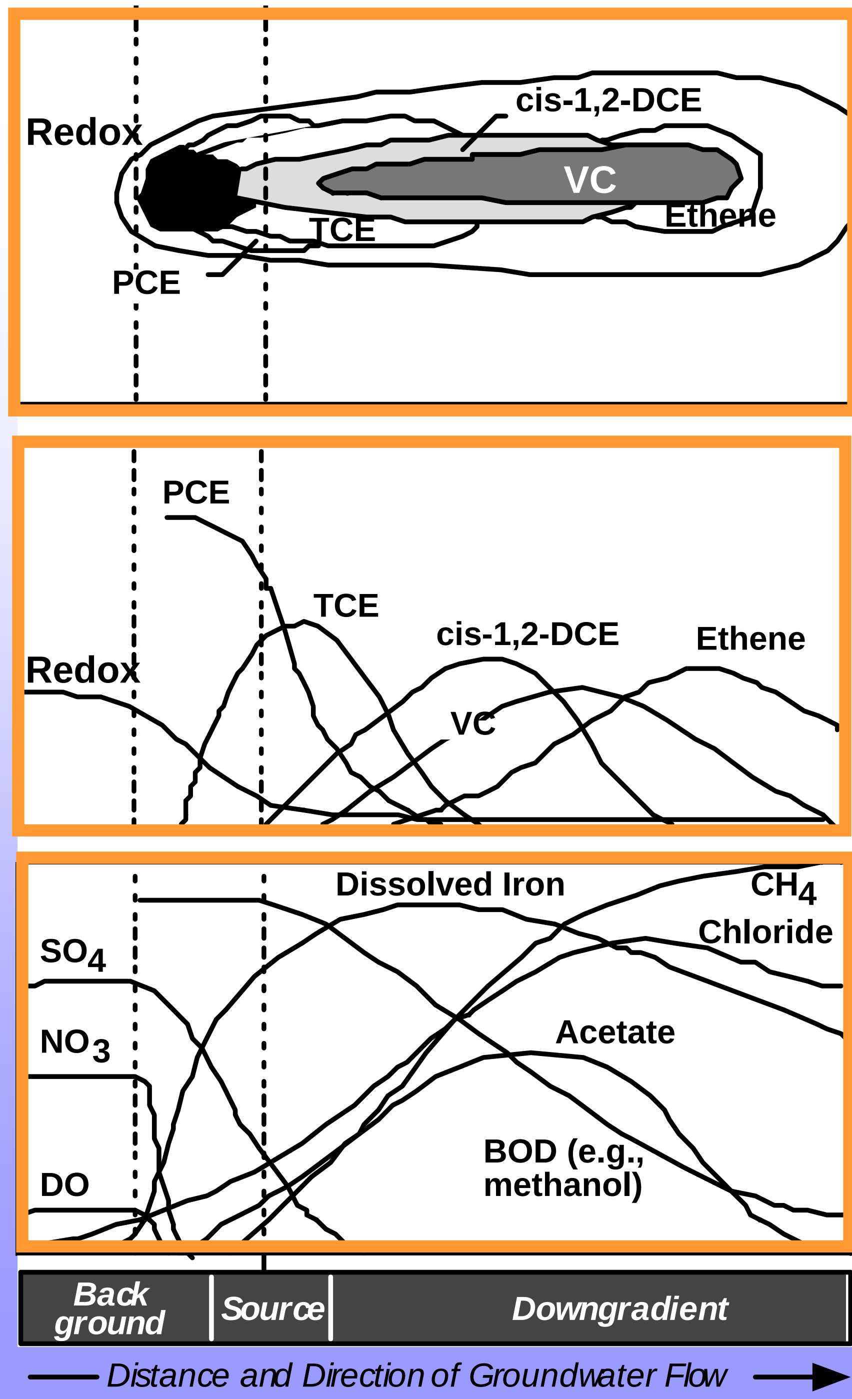
SCHEMATIC OF TYPE 1 CHLORINATED SOLVENT SITE



RTDF, 1997

Presented in Wiedemeier et al. 1999

Example from Competition Module

- **Competing Electron Acceptors (CEA)**

delta O_2 = 2 mg/L
delta NO_3^- = 5.0 mg/L
delta SO_4^{2-} = 10.0 mg/L

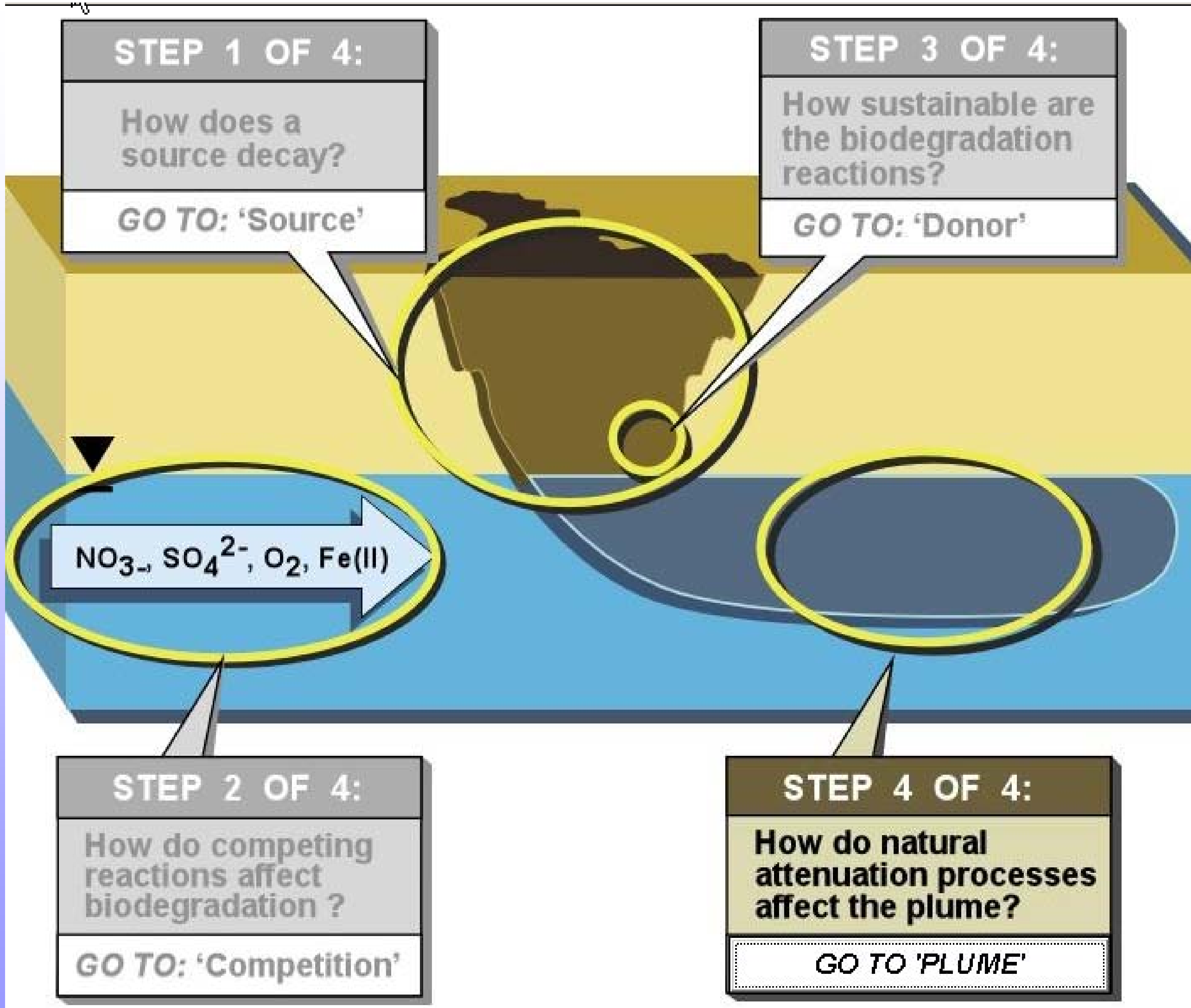
Equivalent Hydrogen Demand: 0.03 kg/yr

•Daughter Products (CVOC)

PCE is PARENT COMPOUND
Produces 2 mg/L of TCE
Produces 1 mg/L of cis-DCE

Equivalent Hydrogen Demand: 0.001 kg/yr

30X as much donor going to CEAs vs. Solvent Degradation



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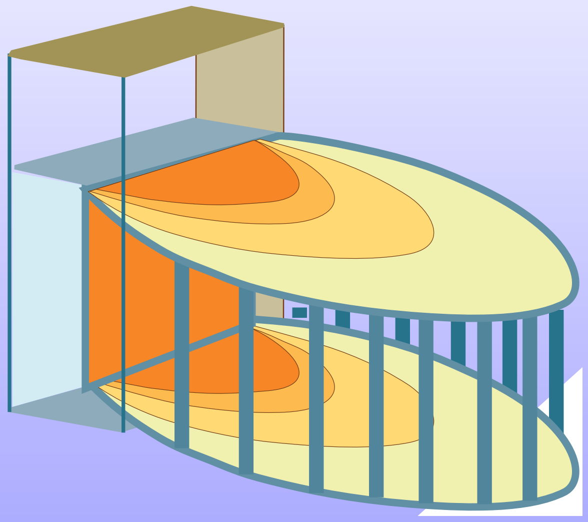
STEP 2 OF 4:
How do competing reactions affect biodegradation ?
GO TO: 'Competition'
STEP 4 OF 4:
How do natural attenuation processes affect the plume?
GO TO 'PLUME'

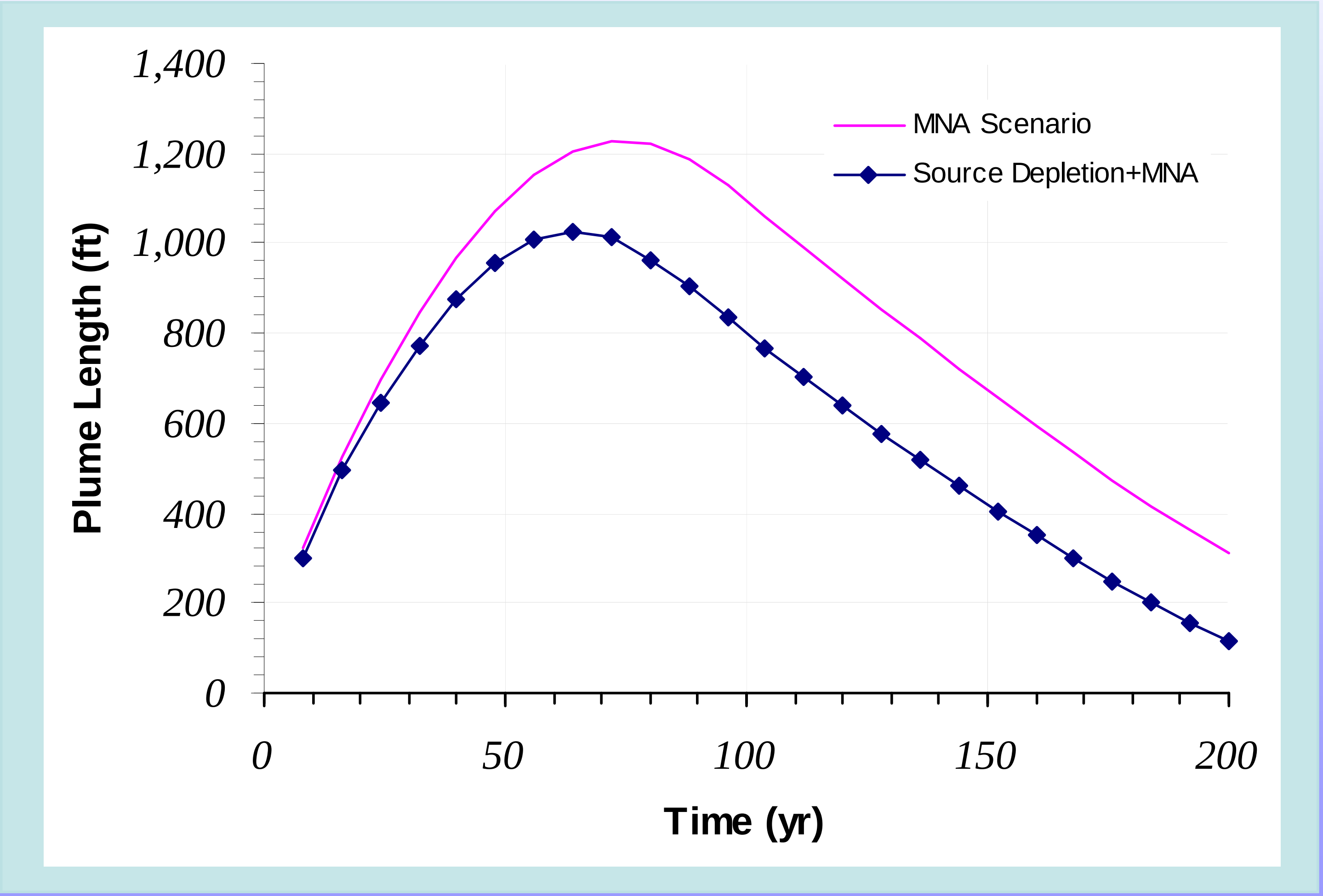
Plume Behavior Over Time

- Analytical Solute Transport Model with Decaying Source
  - How long will a plume get before it stabilizes?
  - When will the plume stabilize?
  - What are the dominant attenuation mechanisms?



Plume Module Output

Case	Time (yrs)	Plume Length (ft)
MNA	72	1230
MNA + Source Depletion Technology	64	1030



Savannah River National Laboratory and
U.S. Department of Energy

BIOBALANCE: A MASS BALANCE
TOOLKIT

For evaluating ***Source depletion***, ***Competition*** effects, long-term ***Sustainability***, and ***Plume dynamics***.

Start   About

Free download at: www.gsi-net.com

Companion Product: Solvent "Scenarios"

Four Tools.....

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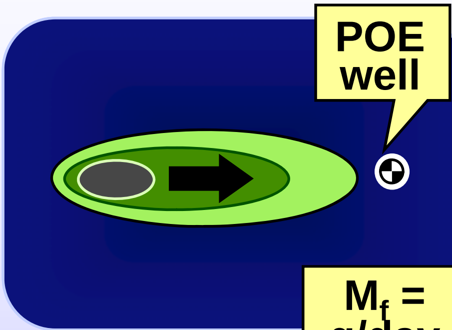
4. REMCHLOR

Mass Flux vs. Traditional Approach

Traditional Approach

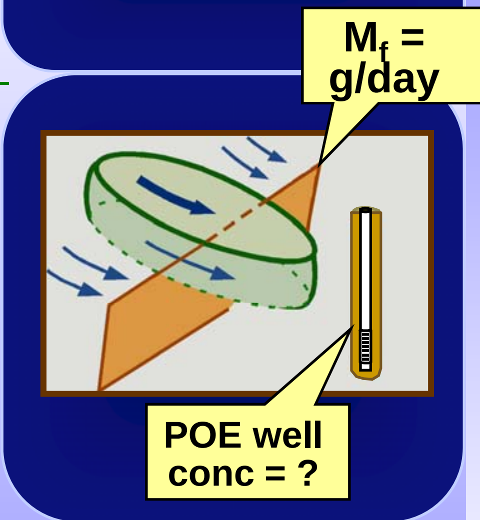
- Measure existing plume ***concentrations*** to assess:
  - Impact on receptor wells
  - Natural attenuation rates
  - Remedial options



Mass Flux Approach

- Define rate of ***mass*** flux across specified cross-sectional areas of plume to assess:
  - Impact on receptor wells
  - Natural attenuation rates
  - Remedial options

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



KEY BENEFITS: **Mass flux approach <u>sometimes</u> offers a better understanding of potential impacts on receptors, natural attenuation rates, and remedial options.**

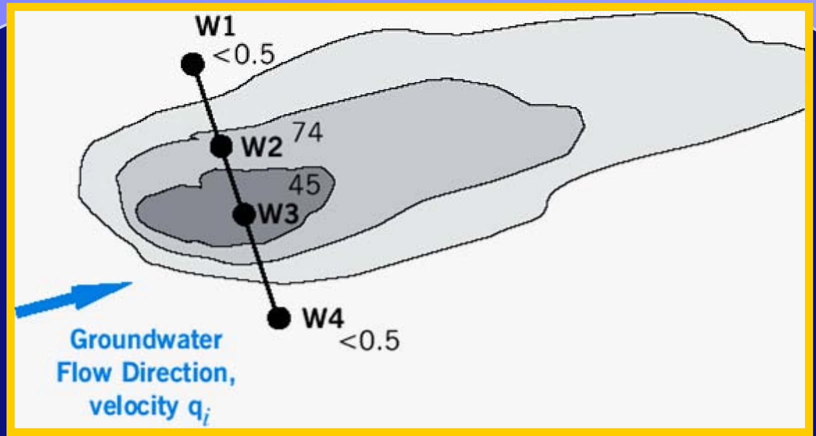
Mass Flux Calculation: Transect Method

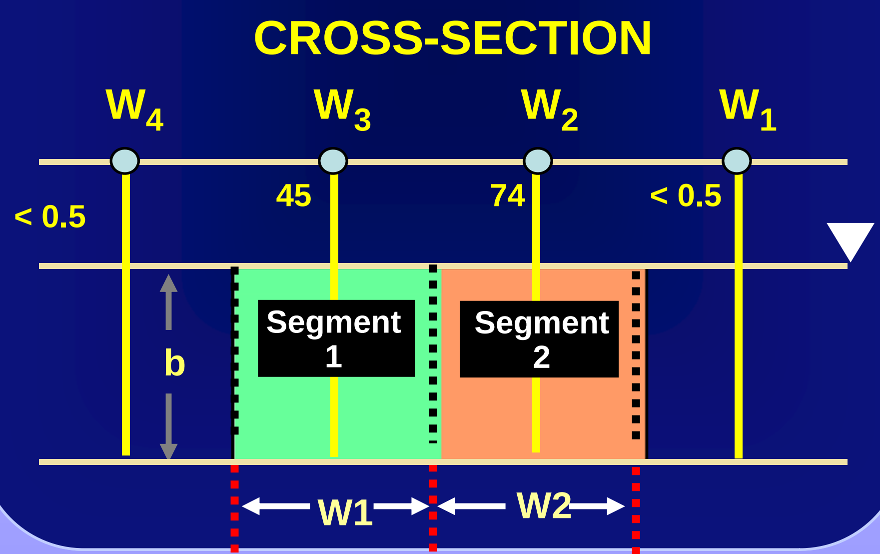
Step-By-Step Approach

1. **Measure groundwater concentrations in transect across plume**
2. **Calculated average plume concentrations in cross-sectional areas between each well**
3. **Sum Total Mass Flux as:**

$$M_f = \sum C_i \times A_i \times q$$

$$q = K \times I$$



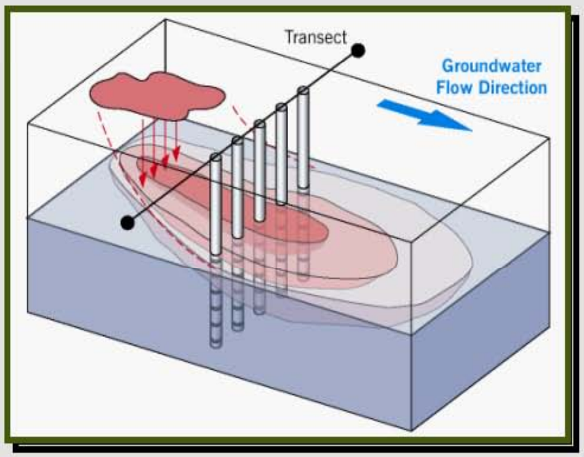


Nichols and Roth, 2004

M_f = Mass flux; C_i = concentration in segment i ; A_i = Area of segment i ;
I = Hydraulic gradient ; k = Hydraulic conductivity; q = Groundwater Darcy velocity (k x I)

Mass Flux Toolkit

To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives



Calculate Flux

Impact of Flux

Learn About Flux

About ***Help***

Version 1.0 Beta

Lead author: Shahla Farhat, Ph.D. free at www.gsi-net.com

Input Data and Grid

Data Input Instructions:

10.80 → Enter value directly.

10.80 → Value calculated by model.

Site Location and I.D.: Texas

Description: MTBE

4. CHOOSE TRANSECT: Transect 1

5. CHOOSE TIME PERIOD: 1

6. ENTER TRANSECT DATA

Distance of Transect 1 from Source → 193 (ft)

○ Darcy Velocity ◉ Hydraulic Conductivity

◉ Sampling Interval ○ Mid Point of Sampling Interval

Hydraulic Conductivity Units: cm/sec

Uniform Hydraulic Conductivity? Yes → Hydraulic Conductivity 3.20E-02 (cm/sec)

Uniform Hydraulic Gradient? Yes → Hydraulic Gradient 2.00E-03 (cm/cm)

	Monitoring Point	Distance from Edge of Transect (ft)	Sampling Interval (ft bgs) Top	Sampling Interval (ft bgs) Bottom	Plume Top (ft bgs)	Plume Bottom (ft bgs)	Concentration (mg/L) Constituent A MTBE	Concentration (mg/L) Constituent B
1	TR1-2	10	5	10	5	15	2.3	
2	TR1-2	10	10	15	5	15	0.47	
3	TR1-4	27.5	5	10	5	20	19.7	
4	TR1-4	27.5	10	15	5	20	7.2	
5	TR1-4	27.5	15	20	5	20	0.34	
6	TR1-6	45	5	10	5	20	87.2	
7	TR1-6	45	10	15	5	20	35.6	
8	TR1-6	45	15	20	5	20	9.5	
9	TR1-8	62.5	5	10	5	20	54.1	
10	TR1-8	62.5	10	15	5	20	15.3	
11	TR1-8	62.5	15	20	5	20	0.67	
12	TR1-12	80	5	10	5	15	4.5	
13	TR1-12	80	10	15	5	15	5.6	
14								
15								

7. CHOOSE GRID

Orig mean cell width (x-axis) (ft) 14.0 → Refine cell width by 1

Orig cell thickness (y-axis) (ft) 1.5 → Refine cell thickness by 1

8. SELECT CONSTITUENT FOR CALCULATIONS

◉ MTBE ○ Constituent B

Next Step: Complete Grid | Go Back | Clear Screen | Paste Example | See Saved Grids | Print | HELP

Key Features

1. **Helps you interpolate grid cells**
   - ***Nearest Neighbor***
   - ***Linear or Log-transformed interpolation***
   - ***User Entered Value***

2. **Uncertainty/Sensitivity Analysis**
   - **Take out a value**
   - **Different interpolation schemes**
   - **Monte Carlo varies K, gradient, conc.**

3. **Graphing (Flux vs. Time; Flux vs. Distance)**

4. **Other Methods to Determine Mass Flux**

Receptor Impact

Pumping Well Data

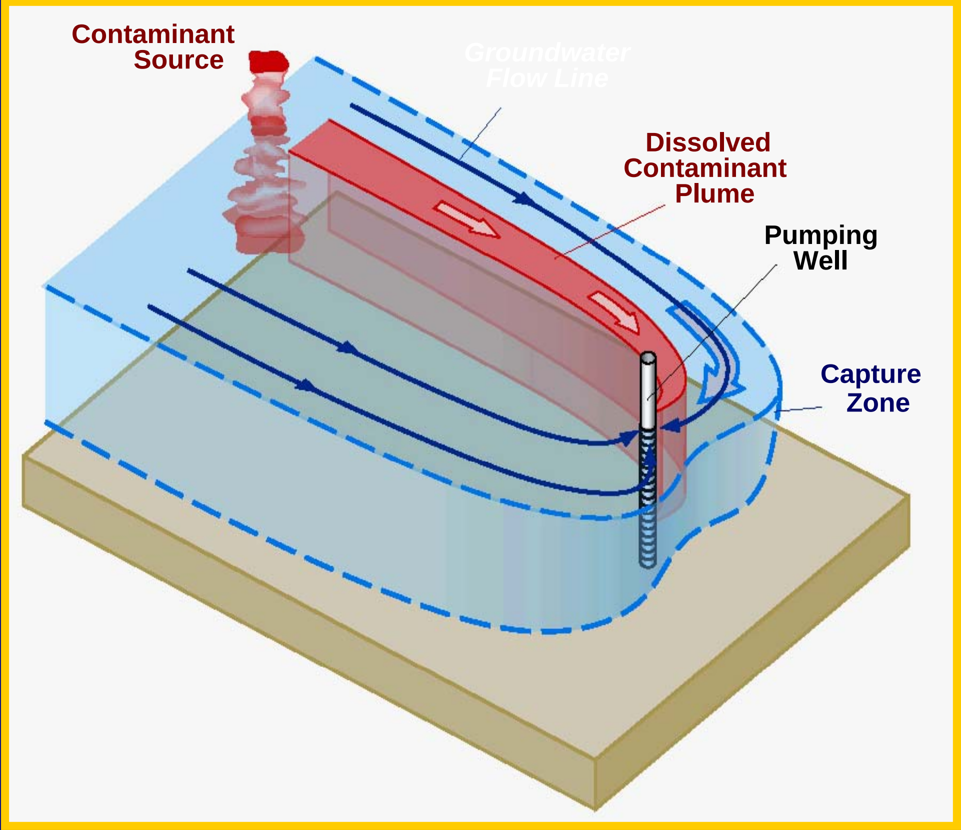
Calculate mass flux based on capture of plume by pumping system.

$$C_{well} = M_f / Q$$

C_{well} = Concentration in recovery well effluent;

M_f = Mass flux;

Q = Recovery well pumping rate



NOTE: Analysis assumes plume is completely captured by pumping well(s)

Nichols and Roth, 2004

Four Tools.....

1. **Source Depletion Decision Support System**
   - Performance & Cost Database
   - Untreated Site Database

2. **BIOBALANCE Software**

3. **Mass Flux Tool Kit**

4. **REMCHLOR**

Performers

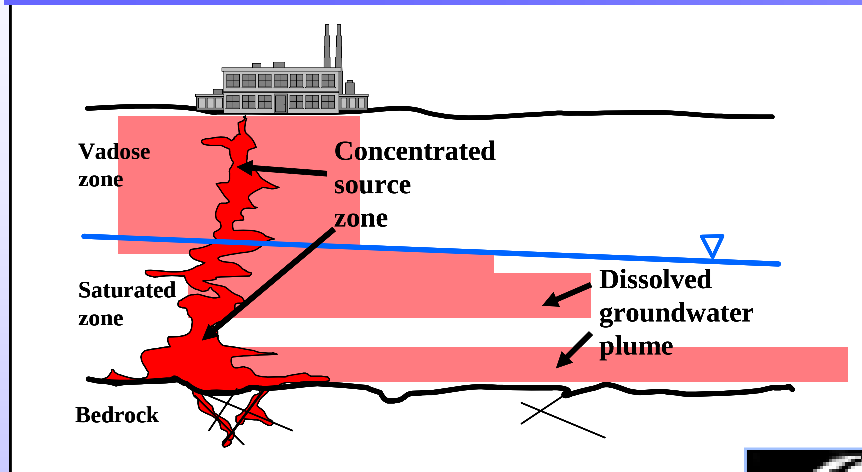
- Original Author REMChlor: Dr. Ronald W. Falta, Clemson

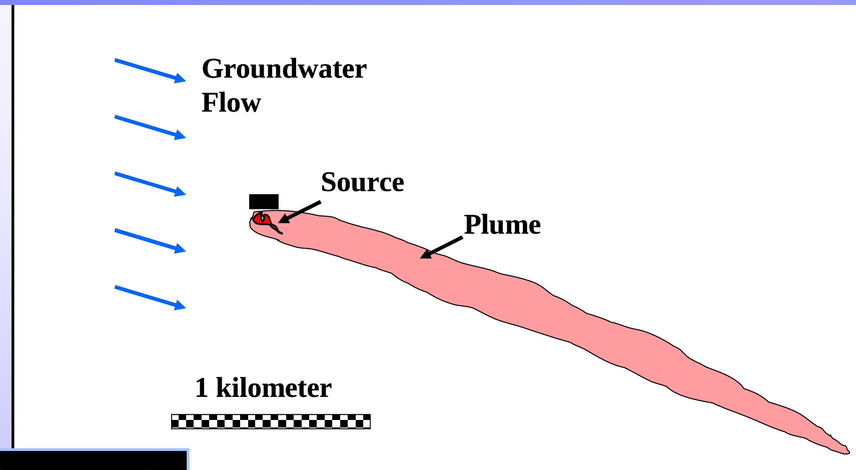
- REMChlor ESTCP Project:
  - Dr. Ronald W. Falta, Clemson
  - Hailian Liang, Clemson

  - Dr. P. Suresh Rao, Purdue
  - Nadita Basu, Purdue

  - Dr. Charles J. Newell, GSI
  - Dr. Shahla Farhat, GSI

The Site Managers Dilemma: When MNA alone is not enough





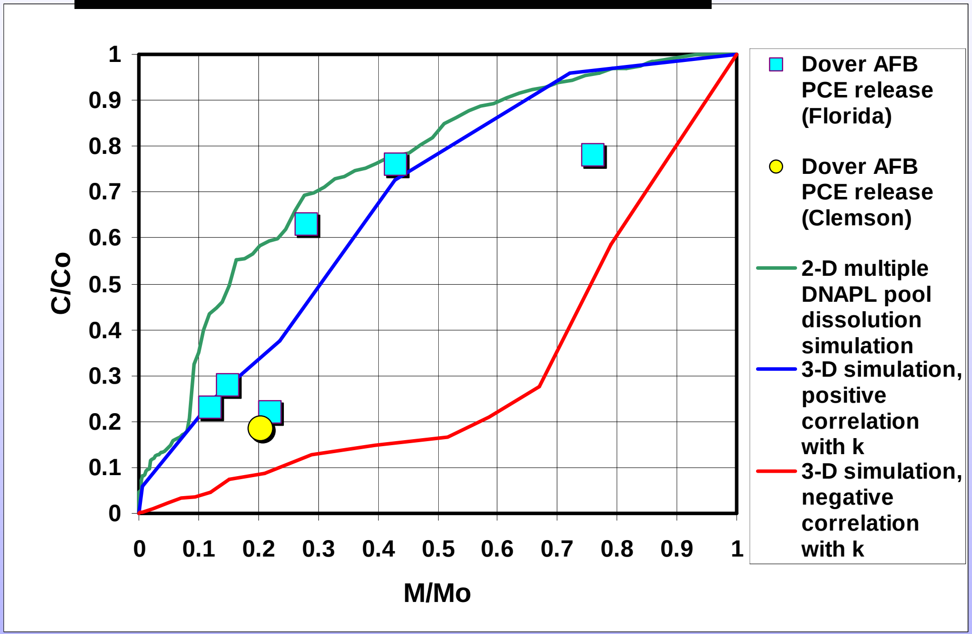
“Should we spend our money and effort on cleaning up the source zone? That’s where most of the contaminant mass is”

“Or should we focus on controlling the plume using pump and treat, a reactive barrier, or enhanced plume degradation?”

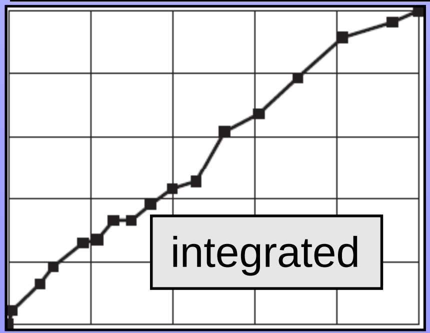
“How can any decision be justified given all of the uncertainty?”

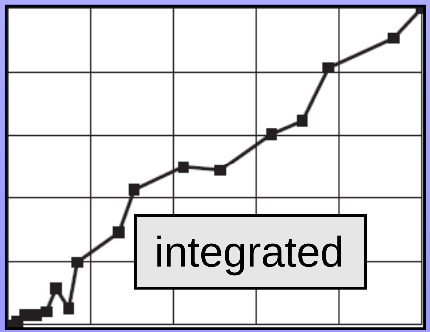
Source Reduction Leads To Discharge Reduction

Field and Modeling Data



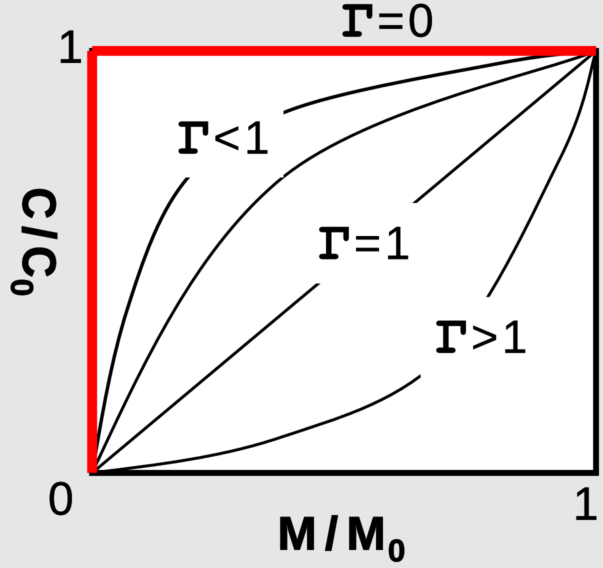
Laboratory dissolution experiments





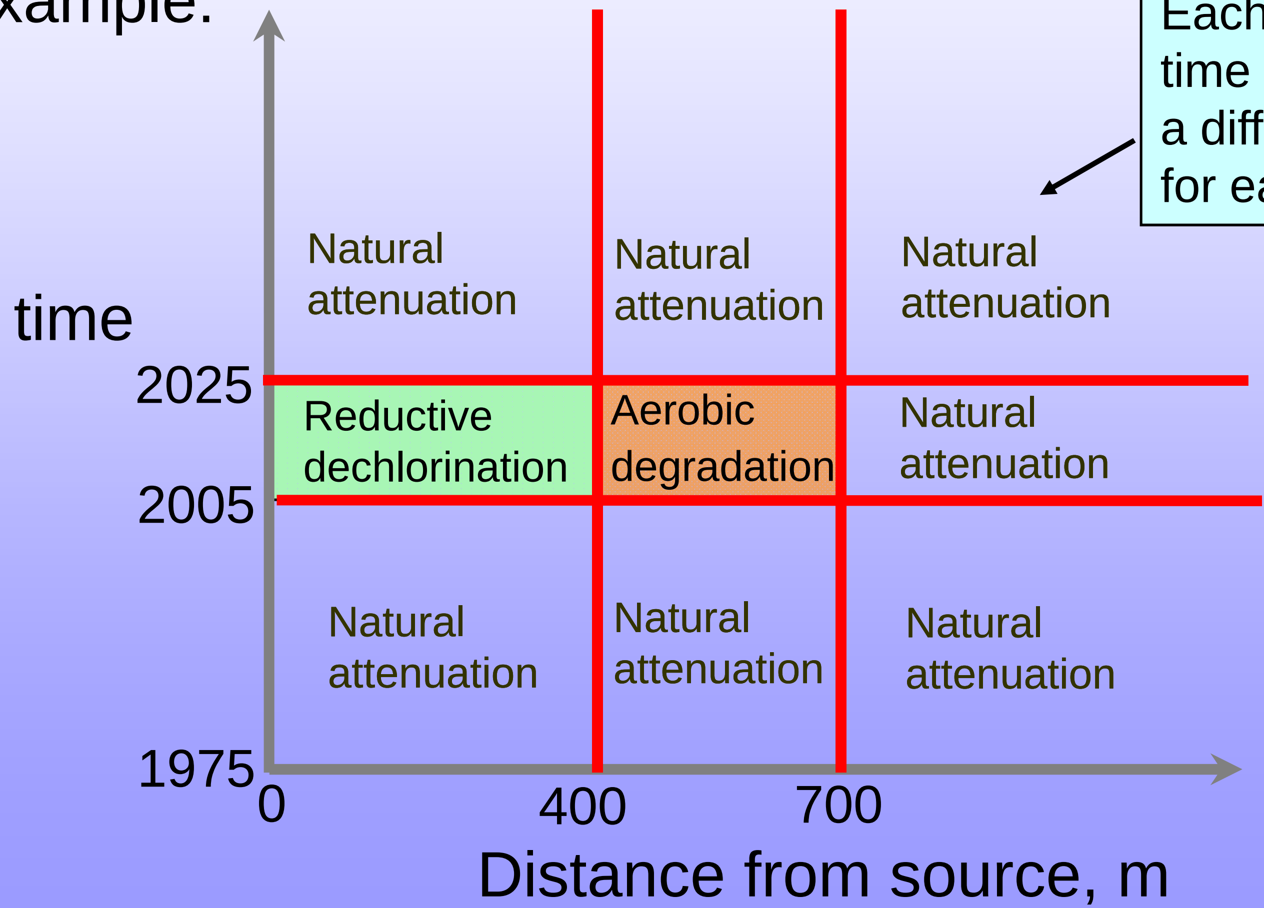
Power function model

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



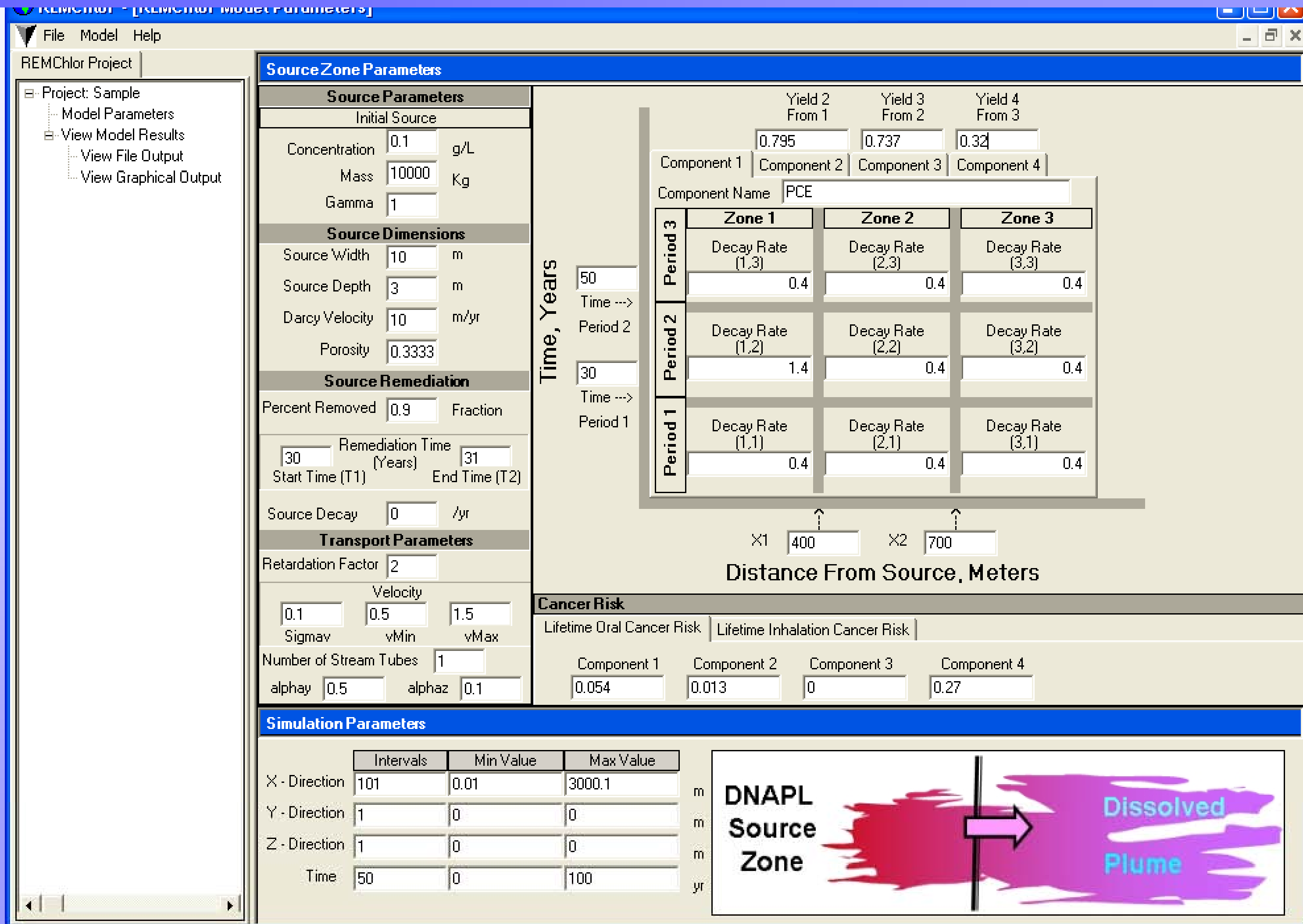
Divide space and time into "reaction zones", solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone

Example:



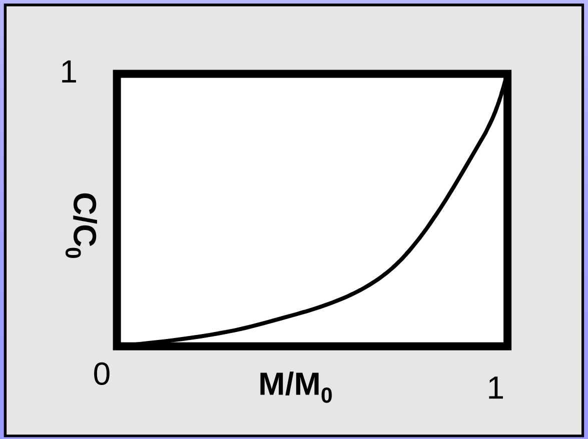
Each of these space-time zones can have a different decay rate for each chemical species

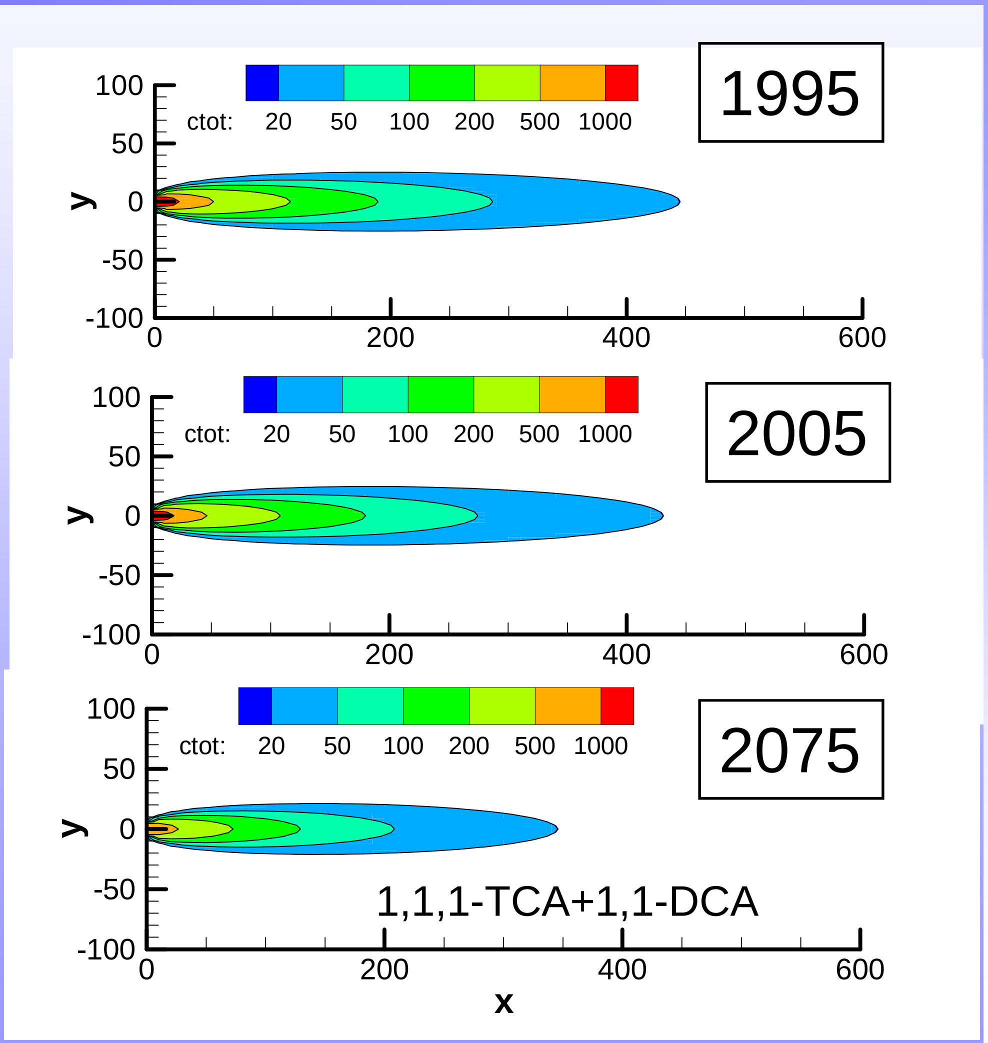
This new source/plume remediation model is called REMChlor, and it will be released by the EPA soon



Deterministic REMChlor example: 300 kg release of 1,1,1-TCA in 1975

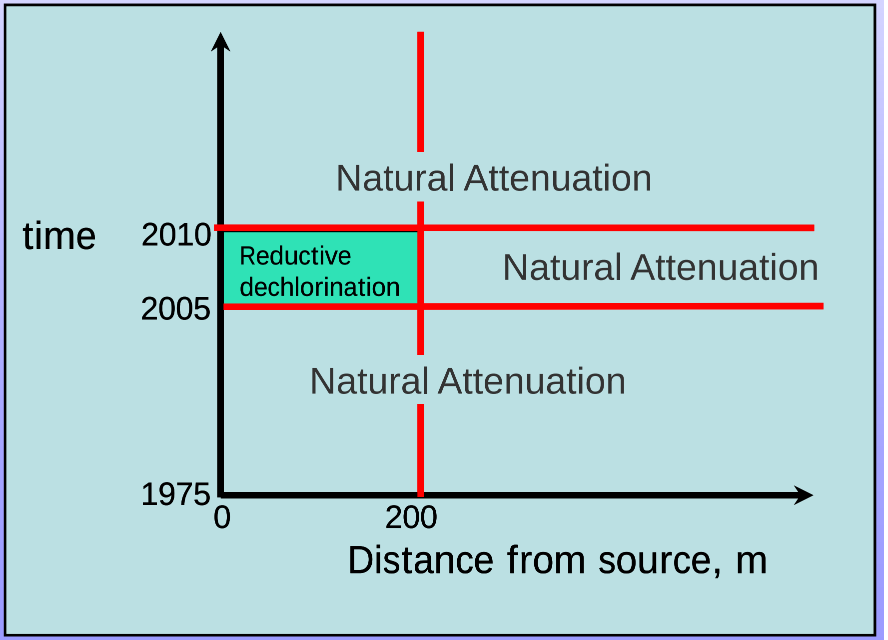
- DNAPL source has C_0=2 mg/l; water Q= 600 m^3 per year
- TCA reductive dechlorination in the @ 0.8/yr (very low)
- 1,1-DCA degrades to chloroethane @ 0.2/yr (very low)

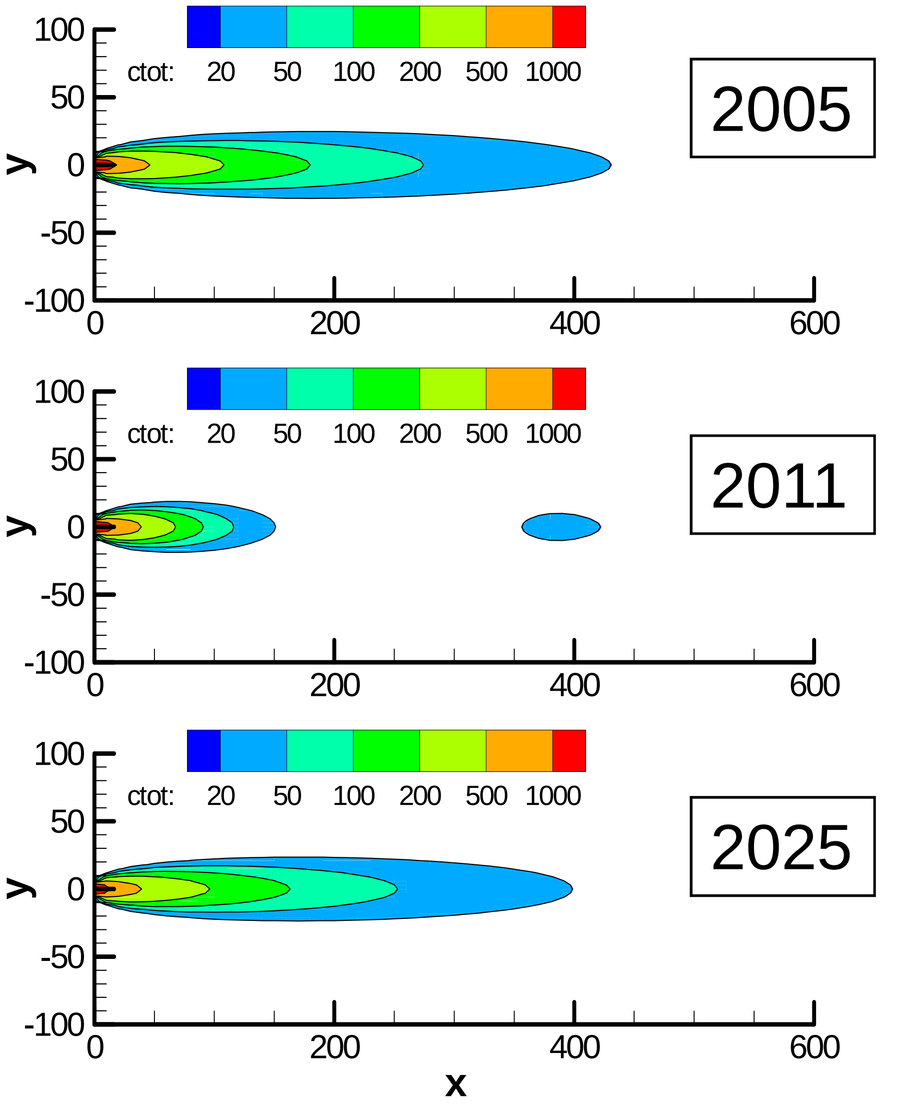




REMChlor simulation of plume remediation

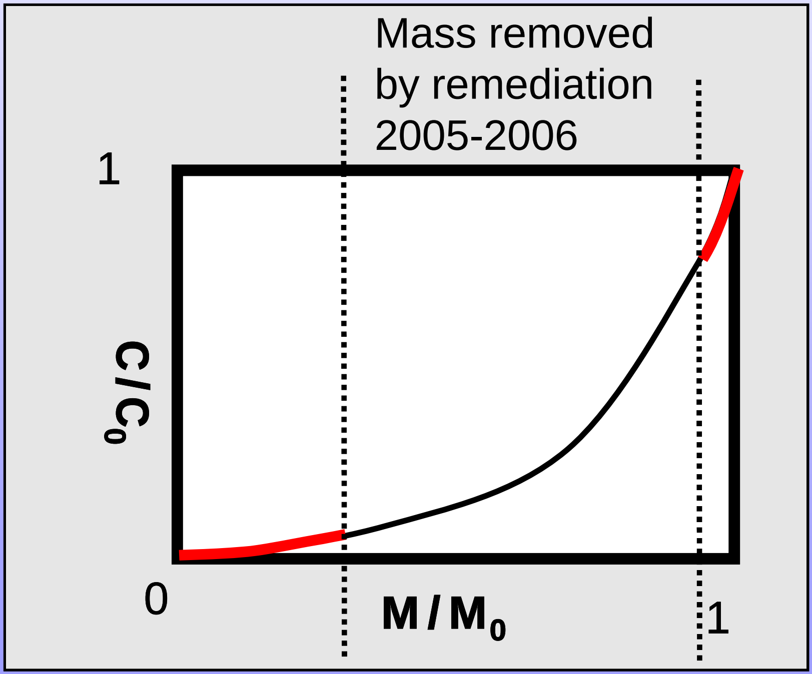
Enhance reductive dechlorination in the plume from 0-200 m, during the period of 2005 to 2010

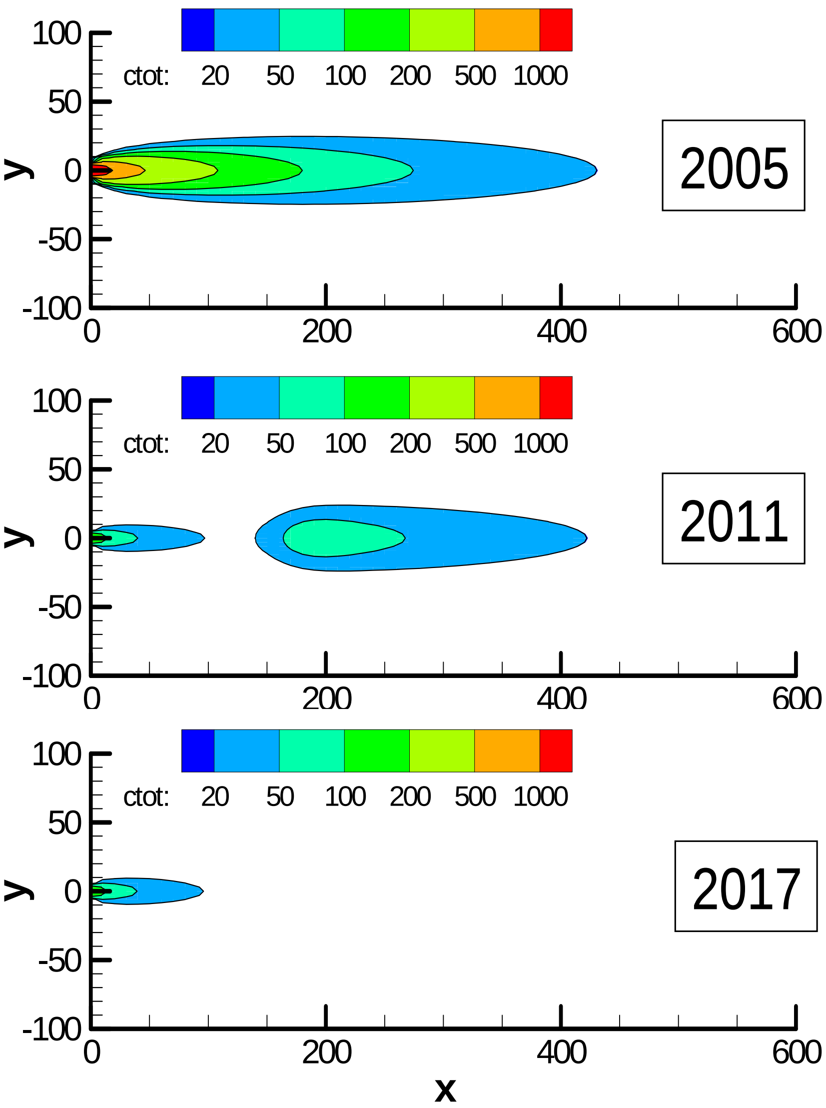




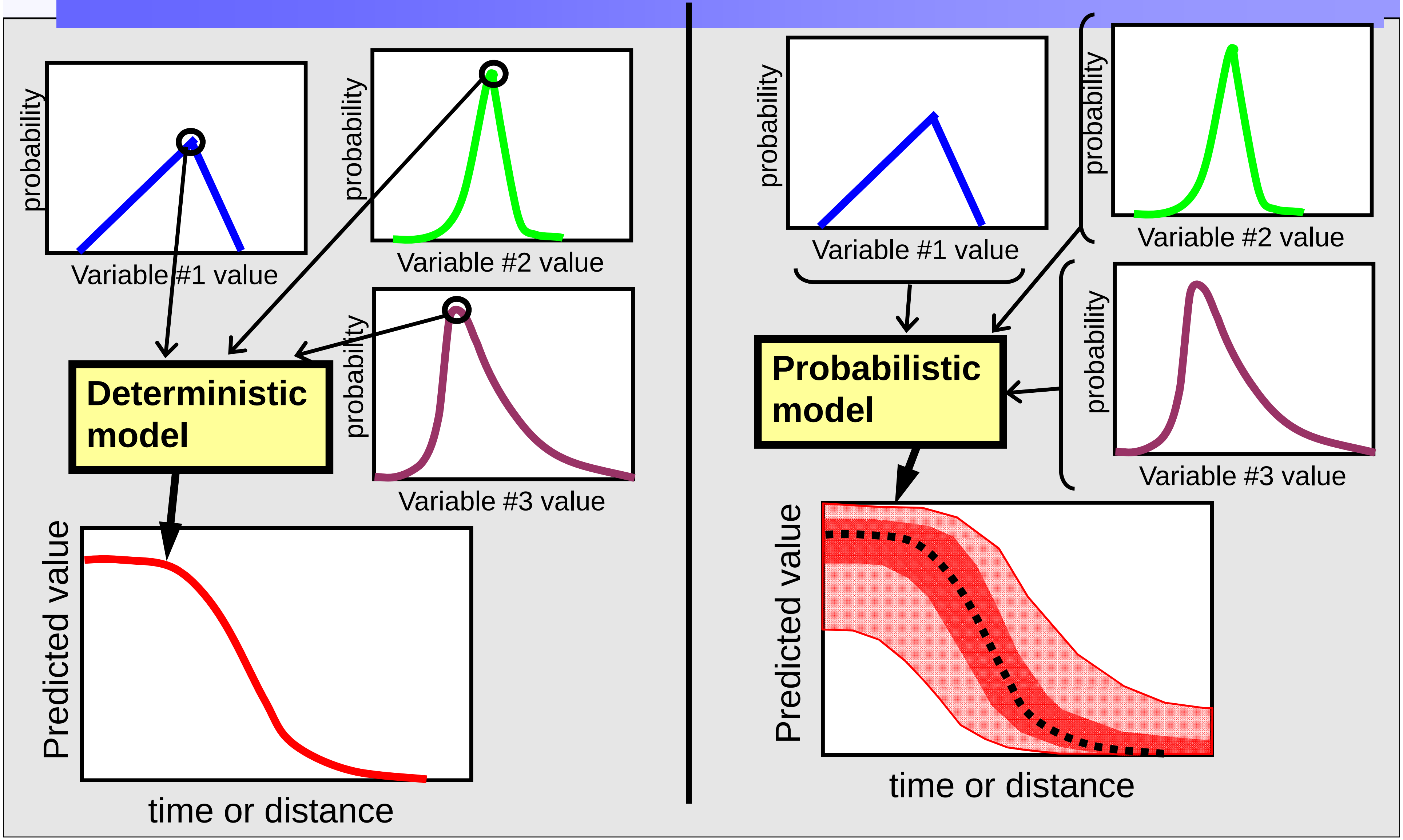
REMChlor simulation of source remediation

Remove 70% of source mass between 2005 and 2006

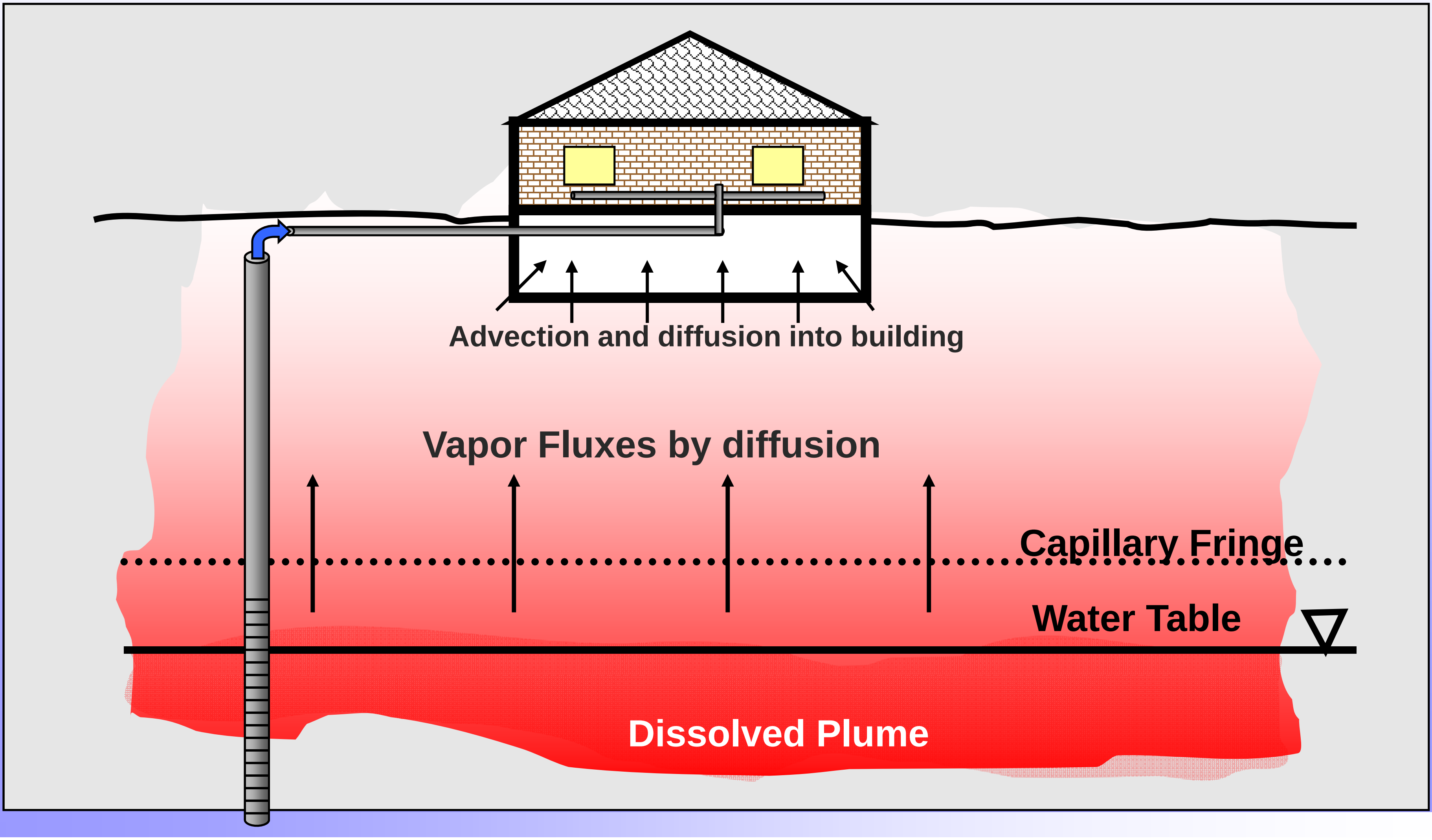




Probabilistic Simulation – treat input variables as uncertain parameters using probability density functions (PDFs)



Vapor transport will be computed using method of Johnson and Ettinger (1991), and with newer vertical mass flux approaches (ESTCP ER-0423)



Four Tools.....

1. **Source Depletion Decision Support System**
   - ***Performance & Cost Database***
   - ***Untreated Site Database***

2. **BIOBALANCE Software**

3. **Mass Flux Tool Kit**

4. **REMCHLOR**

Decision Guide – The Longer Answer

Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents

Tom Sale
Chuck Newell
Rob Hinche
Hans Stroo
Paul Johnson

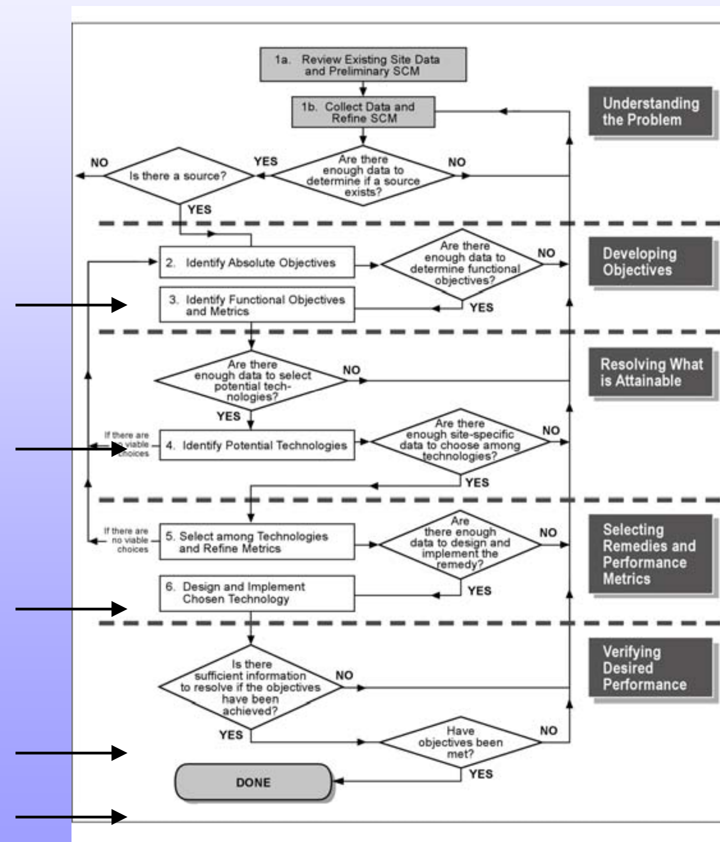
GATE OF LODORE.

Decision Guide

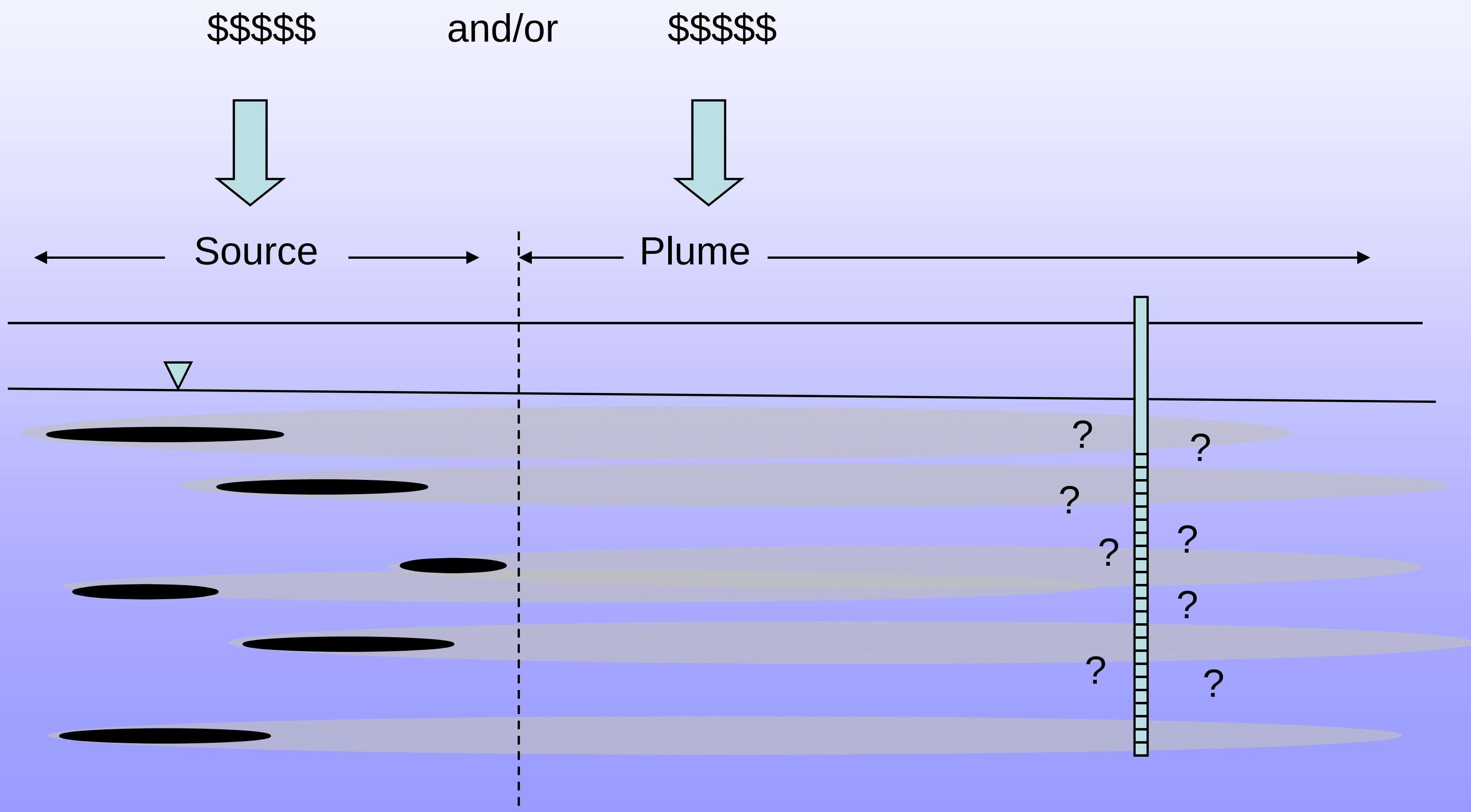
- What it is
  - Knowledge bridge to practitioners
  - Things to think about - Rules of thumb, Lessons learned...
  - Small phone book
  - Route for those want more
- What it isn't
  - Not a prescriptive system
  - Not all inclusive

Content

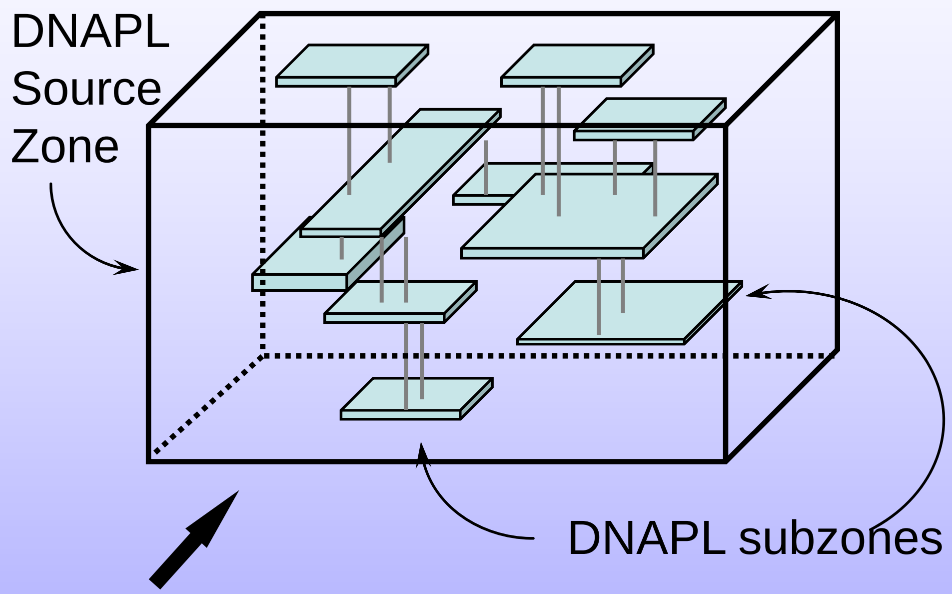
After NRC (2005)



The Nature of the Problem – How will source depletion or plume interception affect downgradient water quality?



Source Function



Any mass depletion will decrease subsequent loading to plumes

What remains can cause exceedances of standards for extended periods

The key issues are mass discharge and longevity

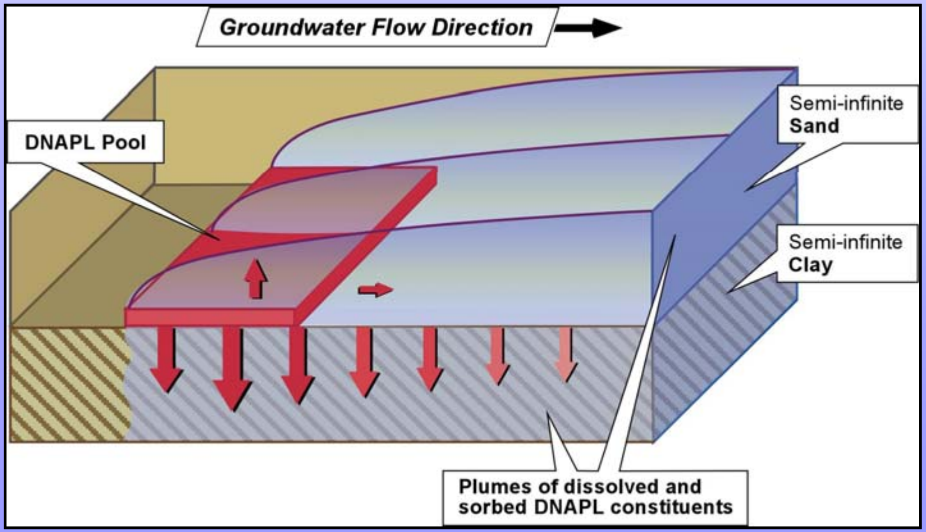
- ✓**Freeze and McWhorter (1997)**
- ✓**Sale and McWhorter (2002)**
- ✓**Rao and Jawitz (2003)**
- ✓**USEPA (2003)**
- ✓**NRC (2005)**
- ✓ **Suchomel and Pennel (2006)**
- ✓ **McGuire et al., (2006)**
- ✓ **Page, Soga, and Illangasekare (2007)**

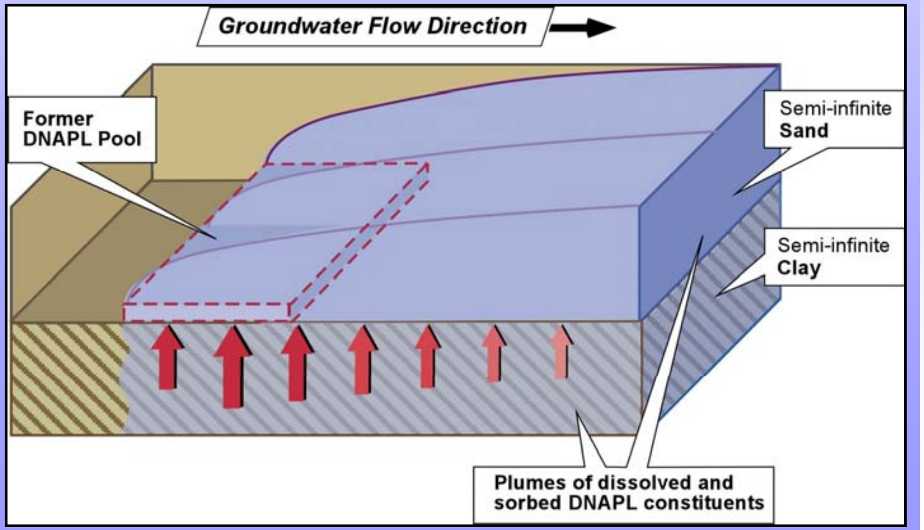
It is not just about Dense Nonaqueous Phase Liquids (DNAPLs)

Per Cohen and Mercer (1991) the total contaminant mass at in a volume of porous media is the sum of the nonaqueous, aqueous, vapor, and sorbed phases. At any point in space each of the phases is trying to equilibrate with the other phases.

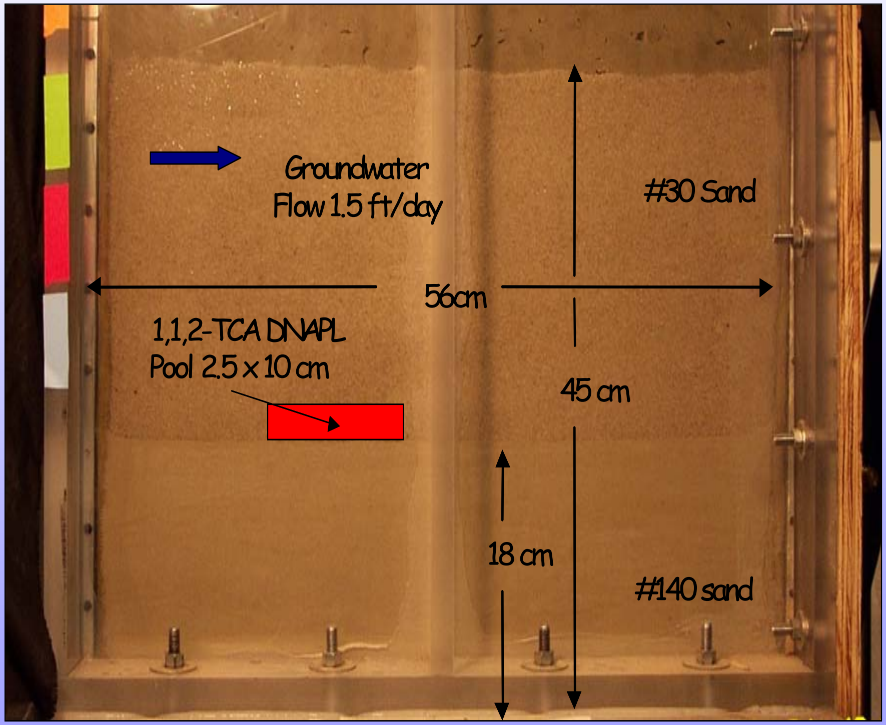
$$\omega_{Total} = \omega_{DNAPL} + \omega_{aqueous} + \omega_{vapor} + \omega_{sorbed}$$

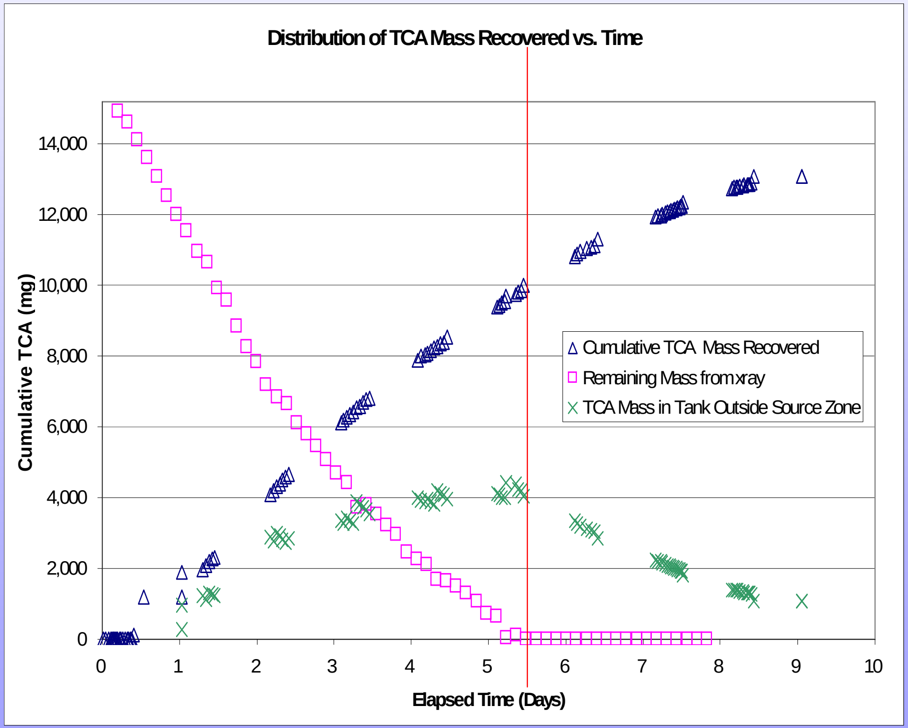
Where ω is the mass of contaminant (e.g. chlorinated solvent) per unit mass porous media.



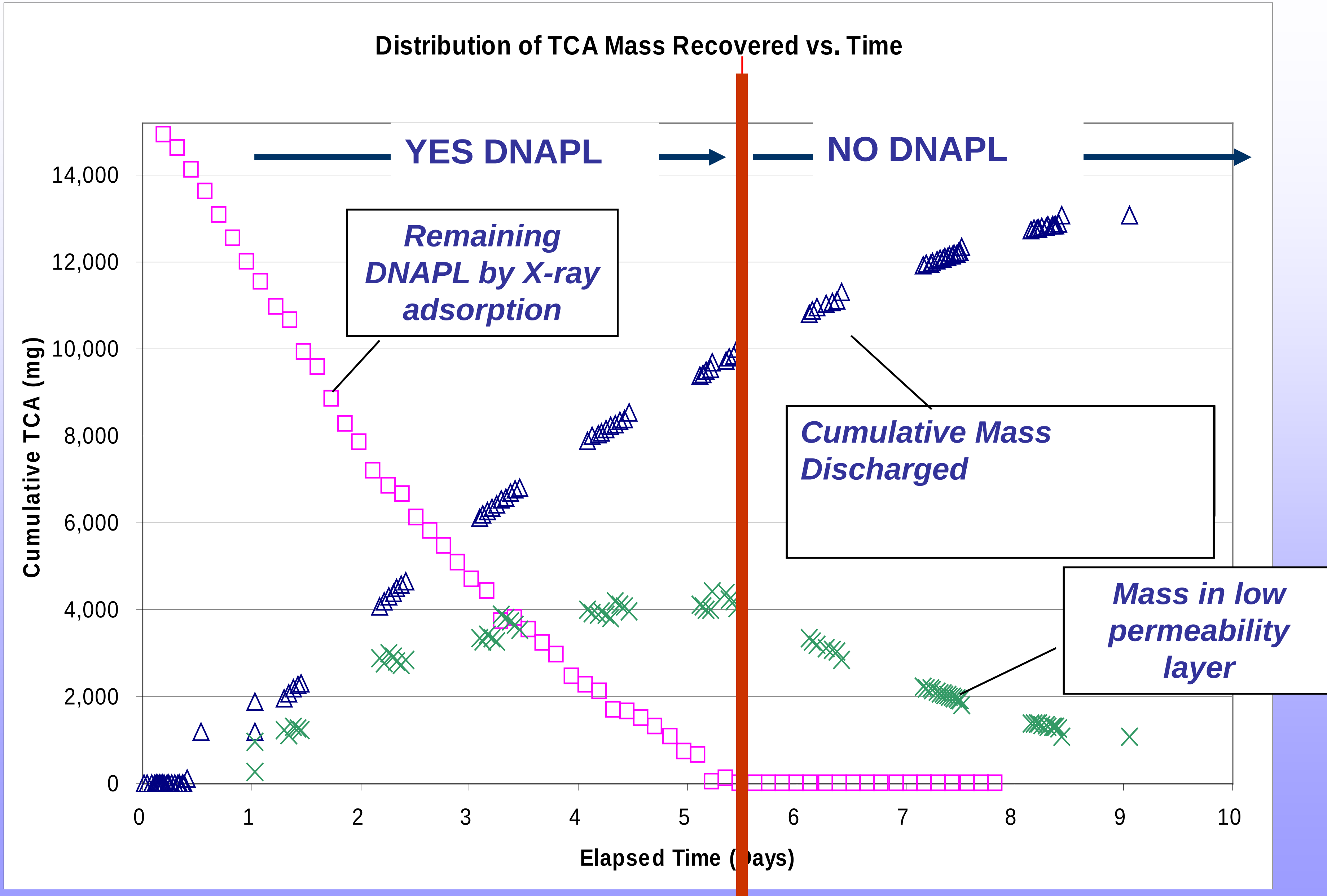


AFCEE Source Zone Initiative (2007)





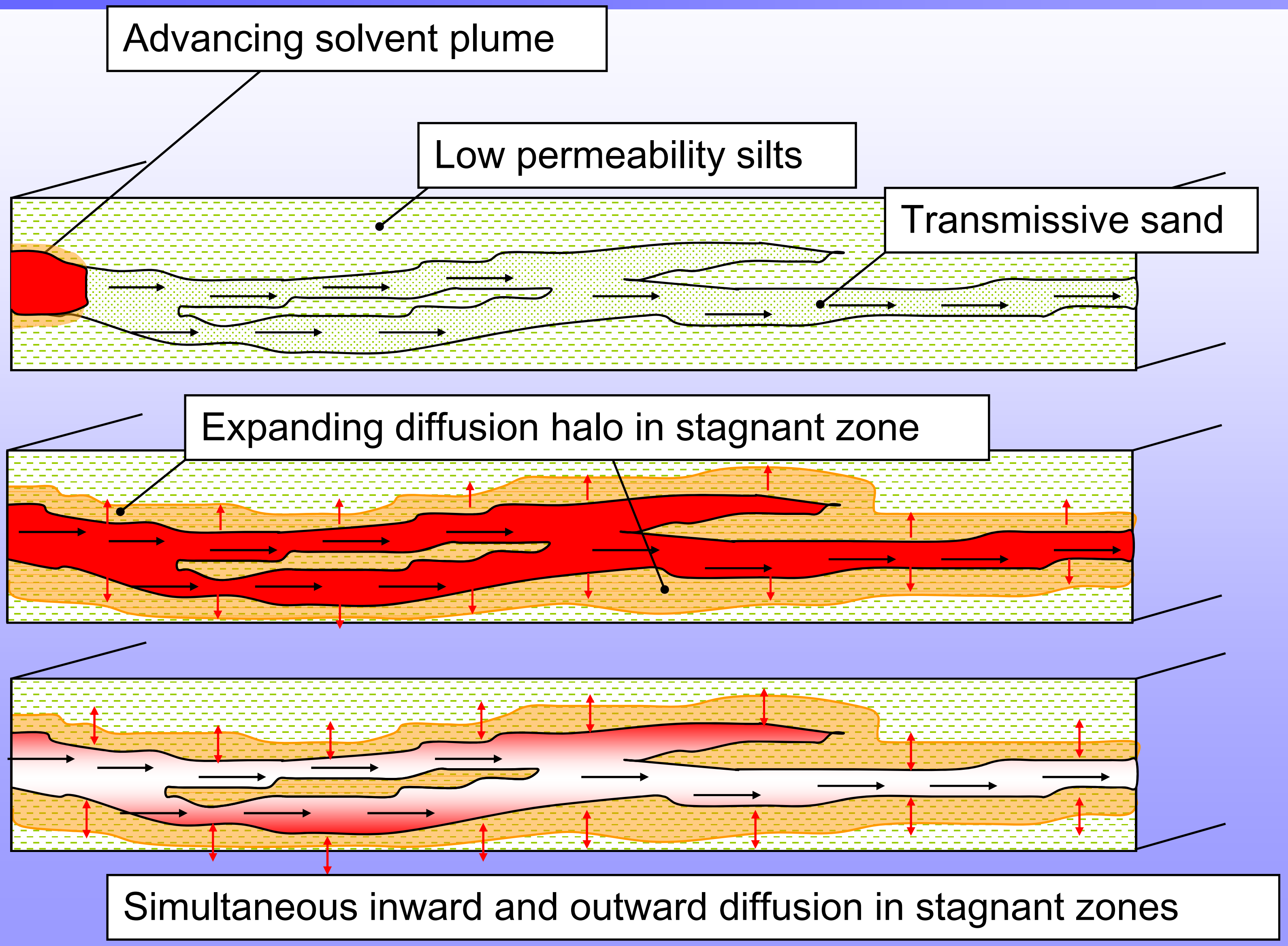
Wilking, Illangasekare, and Sale



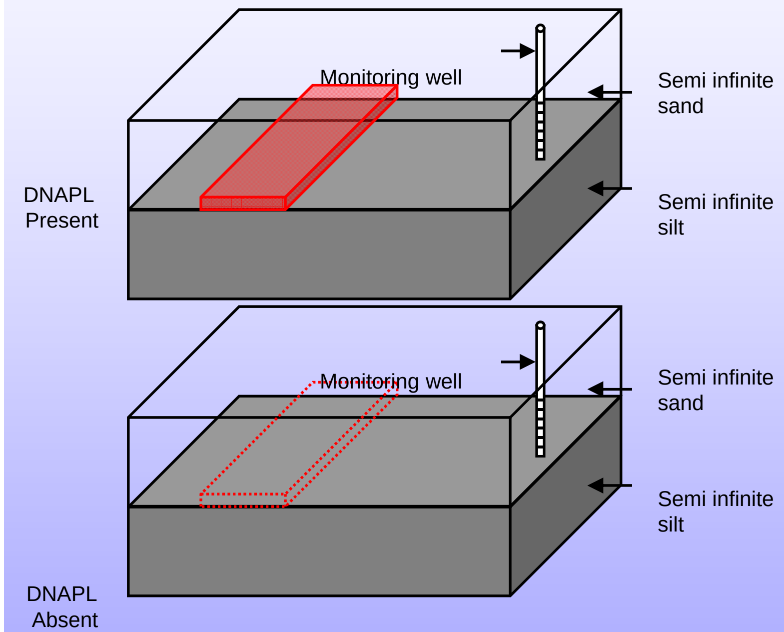
Distribution of TCA Mass Recovered vs. Time
YES DNAPL
NO DNAPL
Remaining DNAPL by X-ray adsorption
Cumulative Mass Discharged
Mass in low permeability layer
Cumulative TCA (mg)
0
2,000
4,000
6,000
8,000
10,000
12,000
14,000
0
1
2
3
4
5
6
7
8
9
10
Elapsed Time (Days)

AFCEE 2007

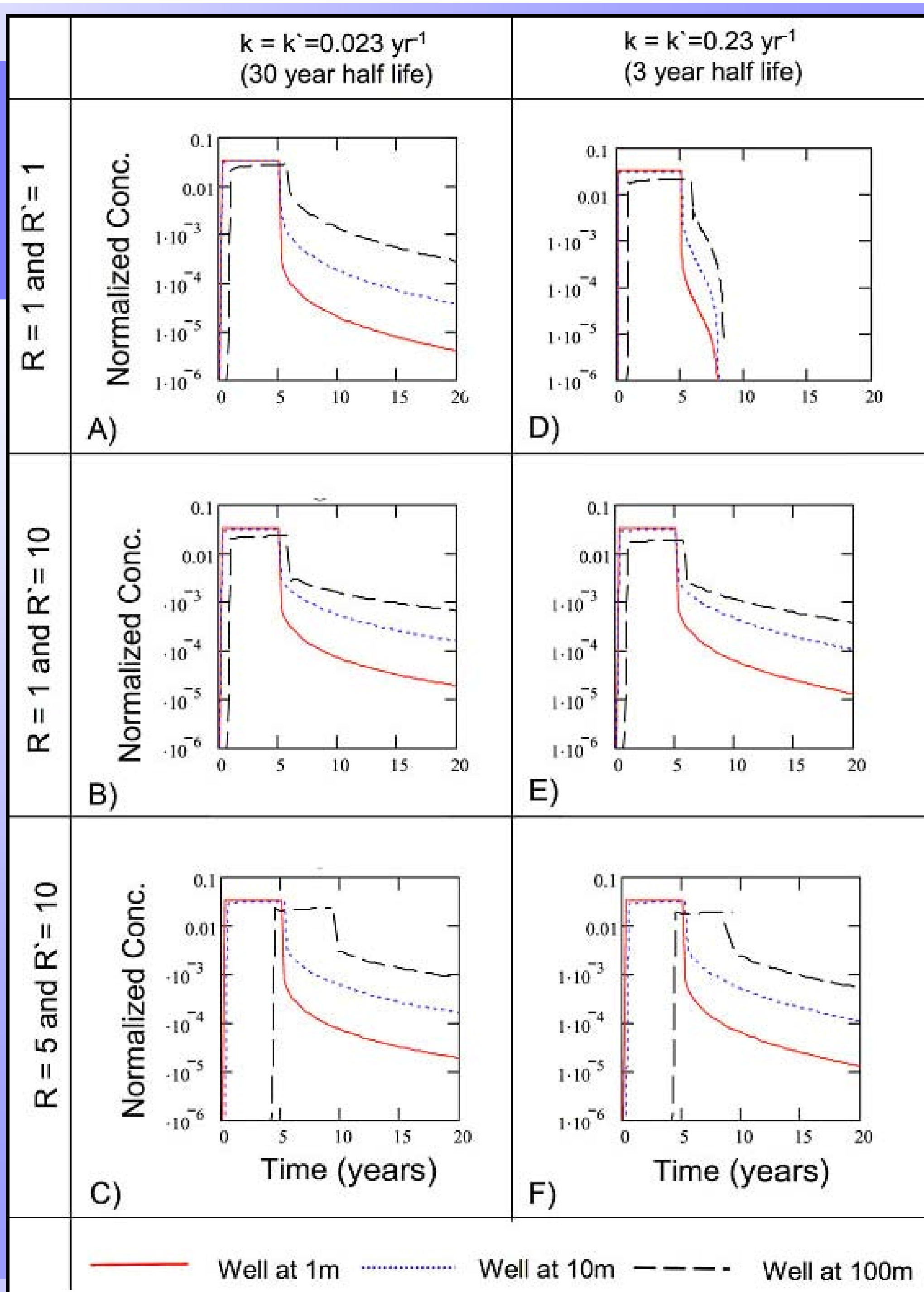
AFCEE (2007) Contaminant storage-release in plumes



AFCEE (2007)



See also - Chapman and Parker, Water Resources Research, December 2005

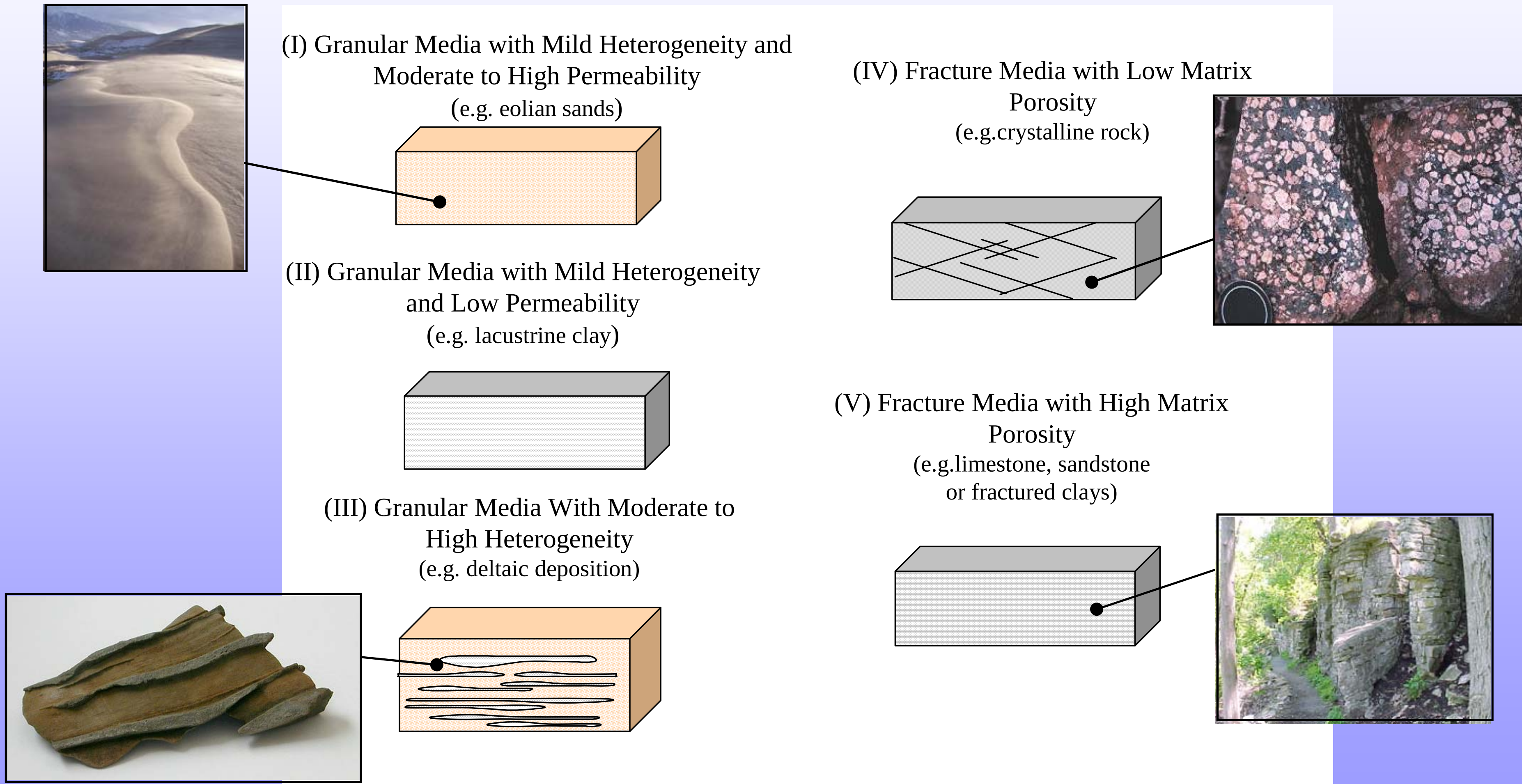


Plume Function

- Chapelle, F., Bradley, P., and Casey, C., 2004, Accelerated cleanup follows Fenton's ISCO and substrate addition: USEPA Technology News and Trends, no. December 2004.

  - Given active degradation in the plume
    - Limited storage
    - Rapid downgradient response

Type setting for contaminant storage and release (following USEPA 2003 & NRC 2005)



14 subsurface compartments potentially containing chlorinated solvents

	Source		Plume	
	Transmissive	Low Permeability	Transmissive	Low Permeability
DNAPL	√	√		
Aqueous	√	√	√	√
Sorbed	√	√	√	√
Vapor	√	√	√	√

The problem we face is dependent on the setting and the age of the release

Early Stage → Middle Stage → Weathered Stage

Type 1

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	LOW		
Aqueous	MODERATE	LOW	MODERATE	LOW
Sorbed	MODERATE	LOW	MODERATE	LOW
Vapor	MODERATE	LOW	MODERATE	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	LOW	MODERATE	LOW
Sorbed	LOW	LOW	MODERATE	LOW
Vapor	LOW	LOW	MODERATE	LOW

Type 2

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW
Sorbed	LOW	MODERATE	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW
Sorbed	LOW	MODERATE	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW
Sorbed	LOW	MODERATE	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Type 3

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	MODERATE	HIGH	MODERATE	HIGH
Sorbed	MODERATE	HIGH	MODERATE	HIGH
Vapor	MODERATE	LOW	MODERATE	LOW

Type 4

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	HIGH	MODERATE	HIGH	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	MODERATE	MODERATE	MODERATE

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	HIGH	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	MODERATE	MODERATE	MODERATE

Type 5

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	MODERATE	HIGH	MODERATE	HIGH
Sorbed	MODERATE	HIGH	MODERATE	HIGH
Vapor	MODERATE	LOW	MODERATE	LOW

High, moderate and low relative fractions of CVOC in the 14 compartments

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Primary fields of interest

Early Stage → Middle Stage → Weathered Stage

Type 1

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	LOW		
Aqueous	MODERATE	LOW	MODERATE	LOW
Sorbed	MODERATE	LOW	MODERATE	LOW
Vapor	MODERATE	LOW	MODERATE	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	LOW	MODERATE	LOW
Sorbed	LOW	LOW	MODERATE	LOW
Vapor	LOW	LOW	MODERATE	LOW

Type 2

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW
Sorbed	LOW	MODERATE	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW
Sorbed	LOW	MODERATE	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW
Sorbed	LOW	MODERATE	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Type 3

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	MODERATE	HIGH	MODERATE	HIGH
Sorbed	MODERATE	HIGH	MODERATE	HIGH
Vapor	MODERATE	LOW	MODERATE	LOW

Type 4

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	HIGH	MODERATE	HIGH	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	MODERATE	MODERATE	MODERATE

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	LOW	MODERATE	HIGH	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	MODERATE	MODERATE	MODERATE

Type 5

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

Weathered Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	LOW	LOW		
Aqueous	MODERATE	HIGH	MODERATE	HIGH
Sorbed	MODERATE	HIGH	MODERATE	HIGH
Vapor	MODERATE	LOW	MODERATE	LOW

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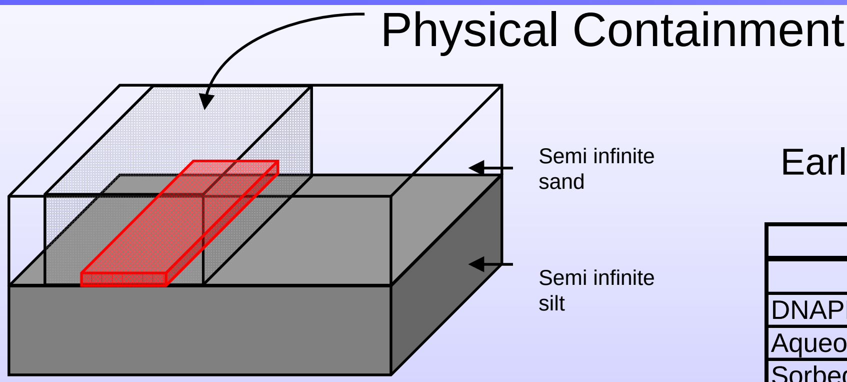
Chapman and Parker, WRR (2005)



~70,000kg released

Early Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	HIGH	LOW		
Aqueous	LOW	LOW	LOW	LOW
Sorbed	LOW	LOW	LOW	LOW
Vapor	LOW	LOW	LOW	LOW

5,000-20,000kg, remaining isolated source zones

~3,000kg downgradient in low k zones

Middle Stage

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

~62,000-47,000 kg in transmissive zones in the plume or degraded?

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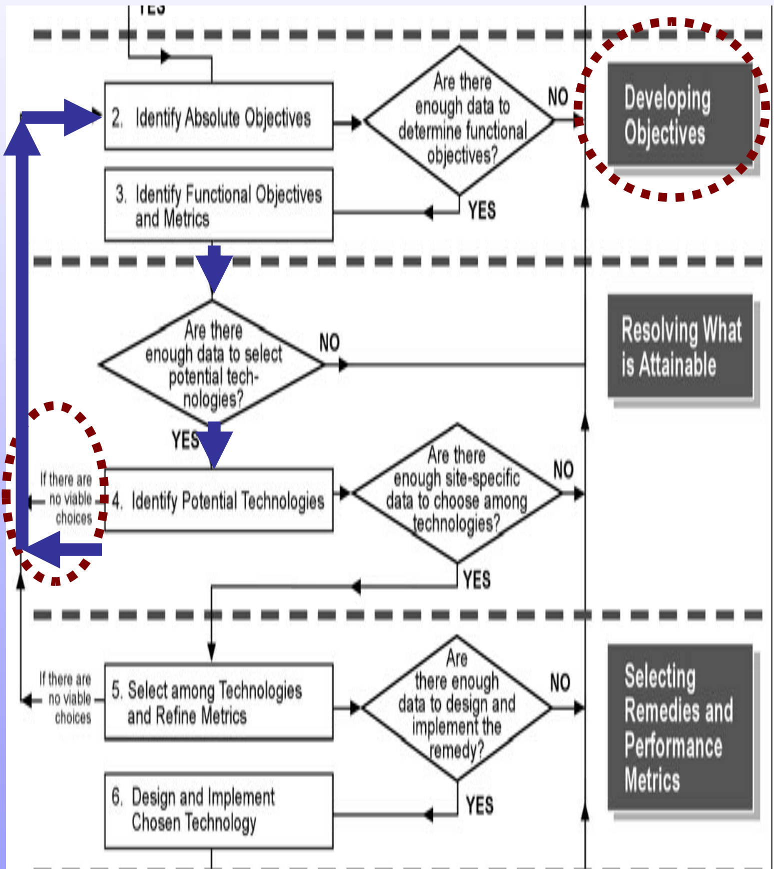
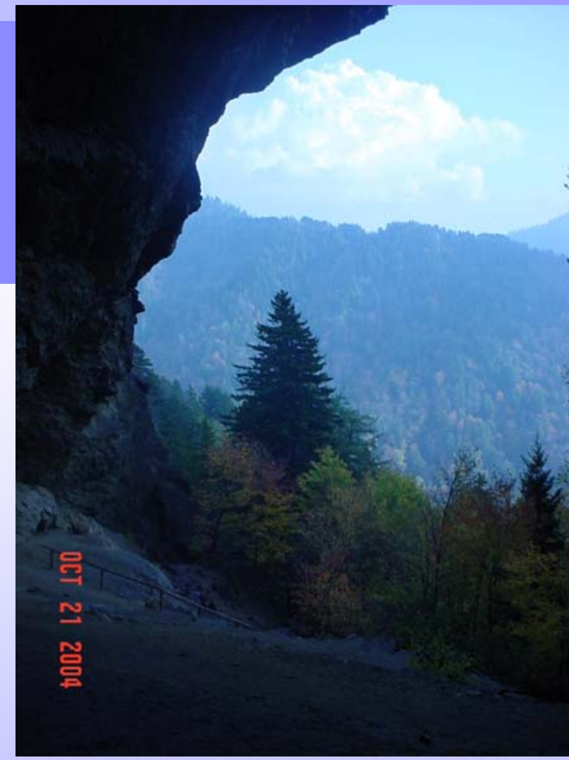
Resolving Objectives



After NRC 2005

Establishing goals that are **attainable** and **beneficial**

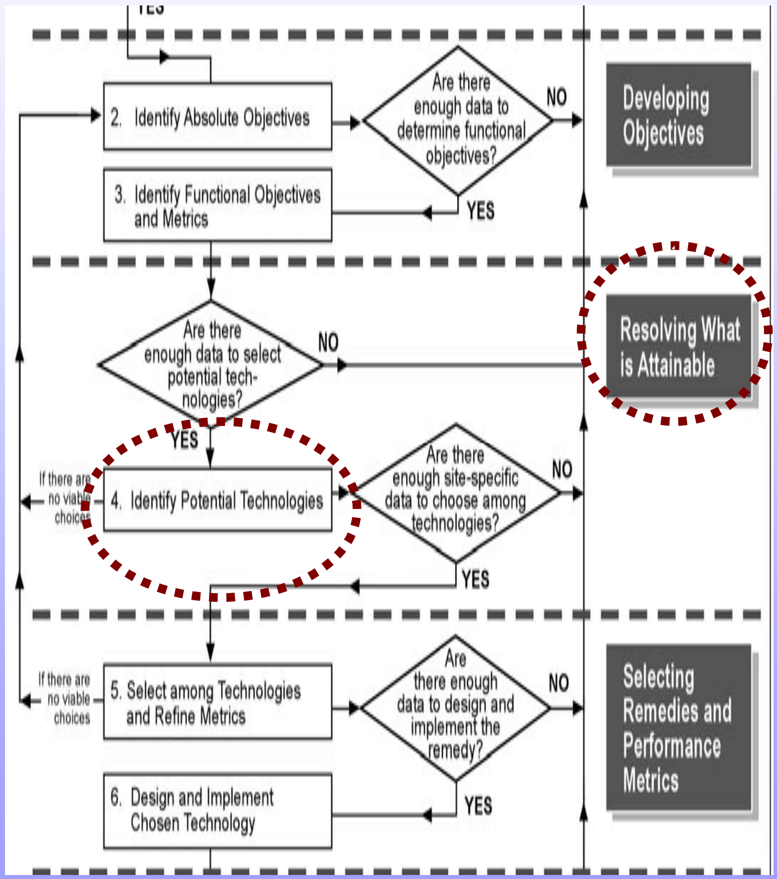
Making decisions requires balancing priorities



Objectives need to reflect the values of the impacted parties

- Clean water
- Clean air
- Net benefit
  - Beneficial land use
  - Sustainability
- Stewardship of Resources
- Compliance

Screening Technologies



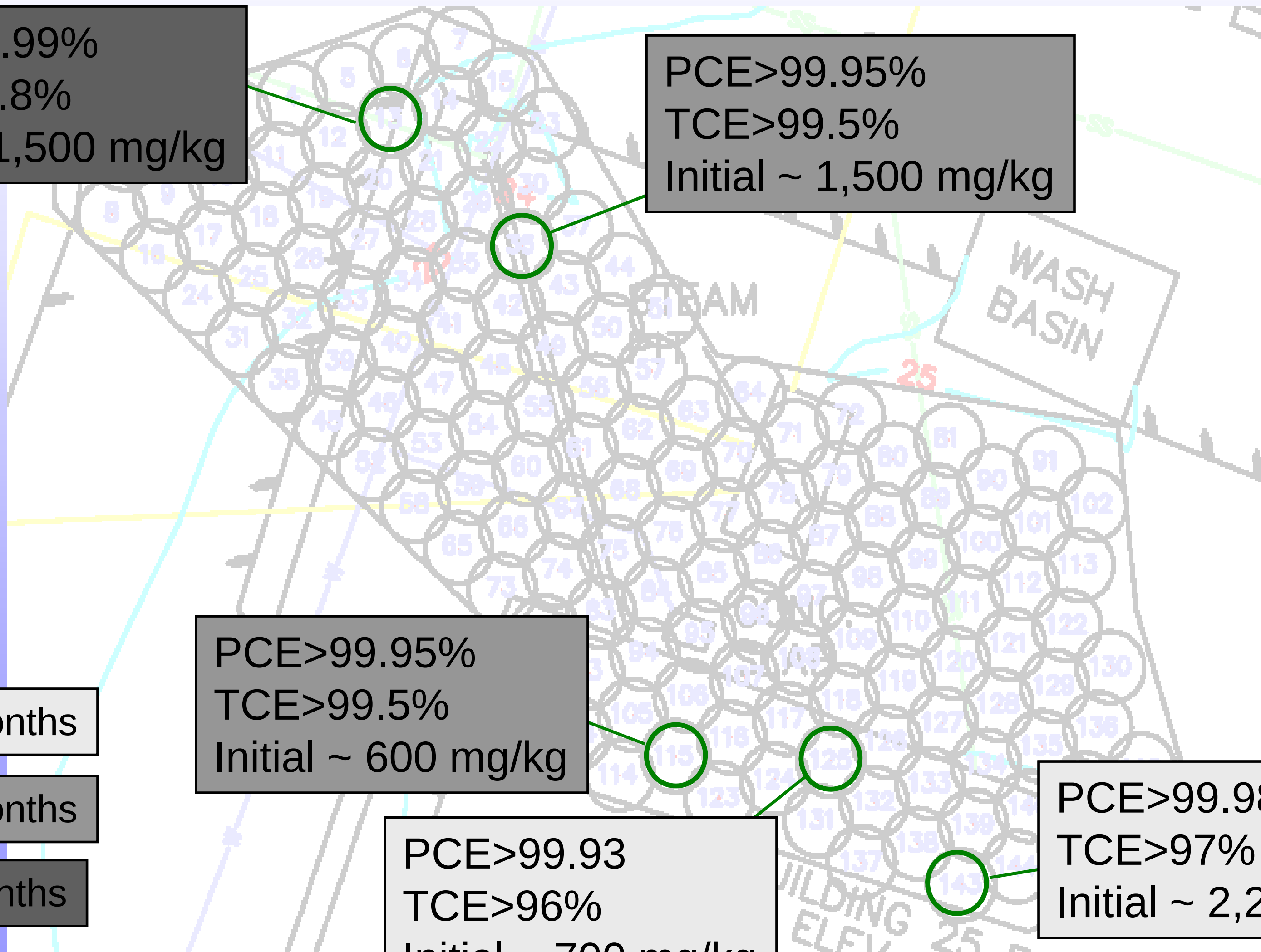
After NRC 2005

Source Zone Technologies

- Excavation
  - Disposal
  - Treatment
- *In situ*
  - Stabilization
  - Flushing
    - SVE
    - Surfactants
  - Destruction
    - **Thermal**
    - **Chemical Oxidation**
    - **Biological Reduction**
    - **Chemical Reduction**

14 tons of PCE

ZVI-Clay - Percent removal in soils at 15 ft



PCE>99.99%
TCE>99.8%
Initial ~ 1,500 mg/kg

PCE>99.95%
TCE>99.5%
Initial ~ 1,500 mg/kg

PCE>99.95%
TCE>99.5%
Initial ~ 600 mg/kg

PCE>99.93
TCE>96%
Initial ~ 700 mg/kg

PCE>99.98%
TCE>97%
Initial ~ 2,200mg/kg

0 to 30 months

0 to 12 months

0 to 7 months

Technology Effectiveness – Type III geology, Middle stage system

Pump and Treat

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	Addressed?	MODERATE	Addressed?	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

Conductive Heating or ZVI-Clay

	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	Addressed	Addressed		
Aqueous	Addressed	Addressed	Addressed?	MODERATE
Sorbed	Addressed	Addressed	MODERATE	MODERATE
Vapor	Addressed	Addressed	MODERATE	LOW

DRAFT

Containment Technologies

- Containment
  - Hydraulic barriers
  - Physical barriers
  - Reactive barriers
    - Sparge
    - Iron
    - Biological

Electrolytic reactive barriers
ER-0112 and ER-0519

Technology Effectiveness – Type III geology, Middle stage system

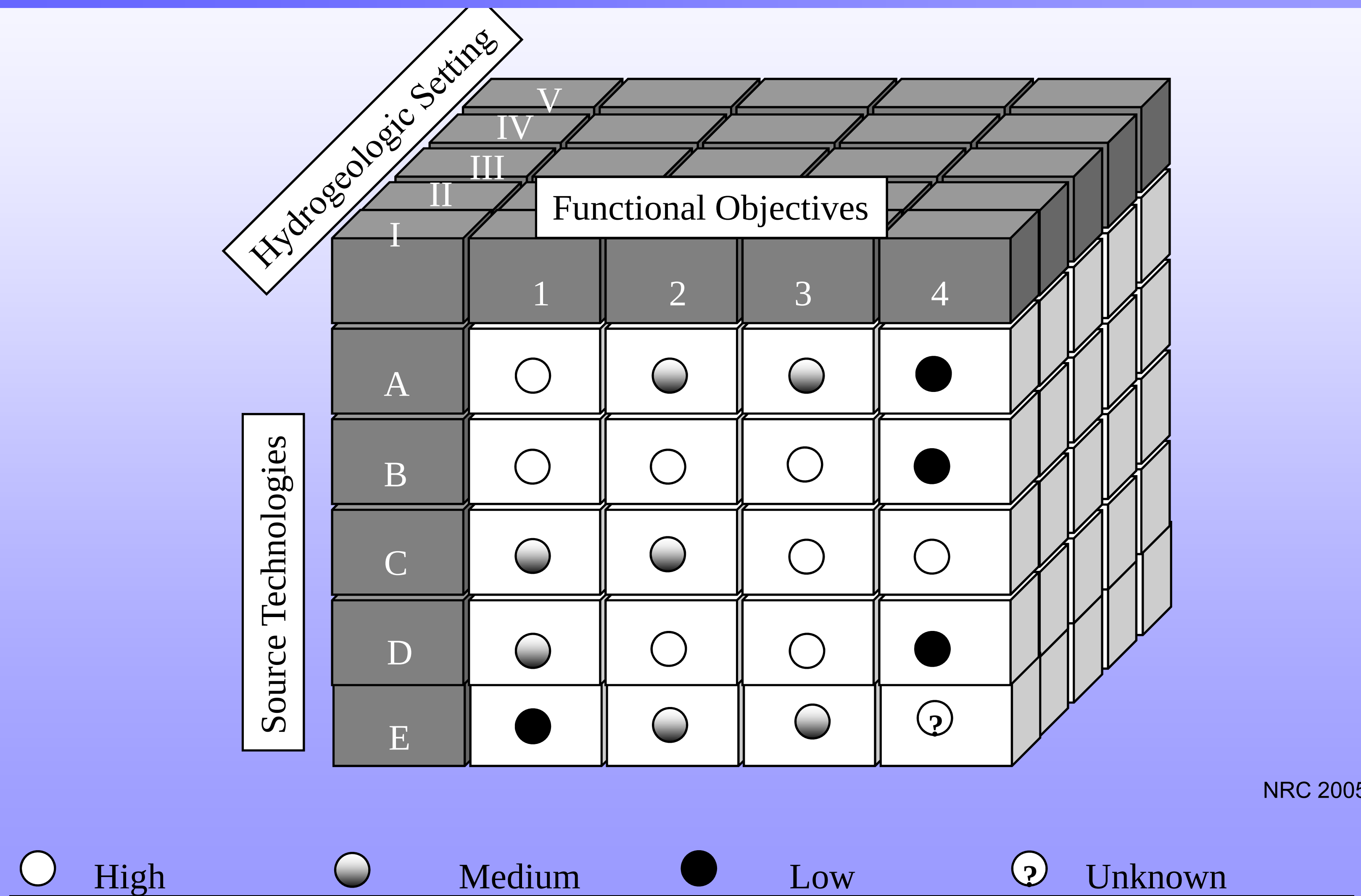
Containment

Zero dissolved flux to plume

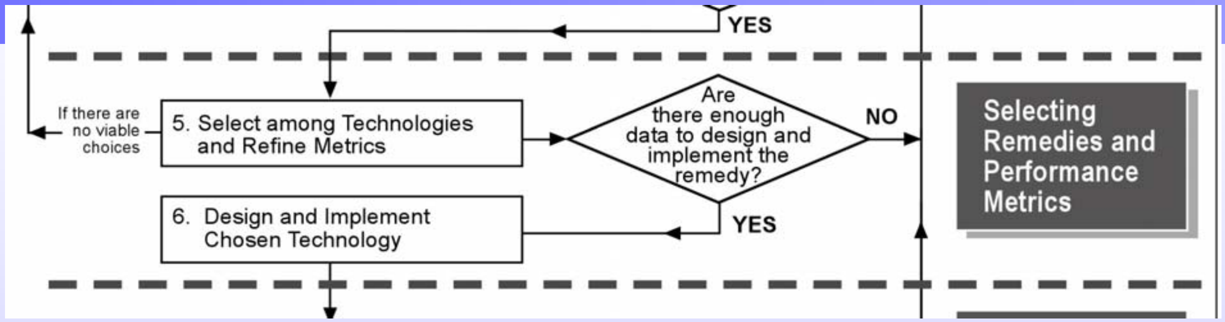
	SOURCE		PLUME	
	Transmissive	Stagnant	Transmissive	Stagnant
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	Addressed?	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE
Vapor	MODERATE	LOW	MODERATE	LOW

DRAFT

Potential for success also depends on the objectives

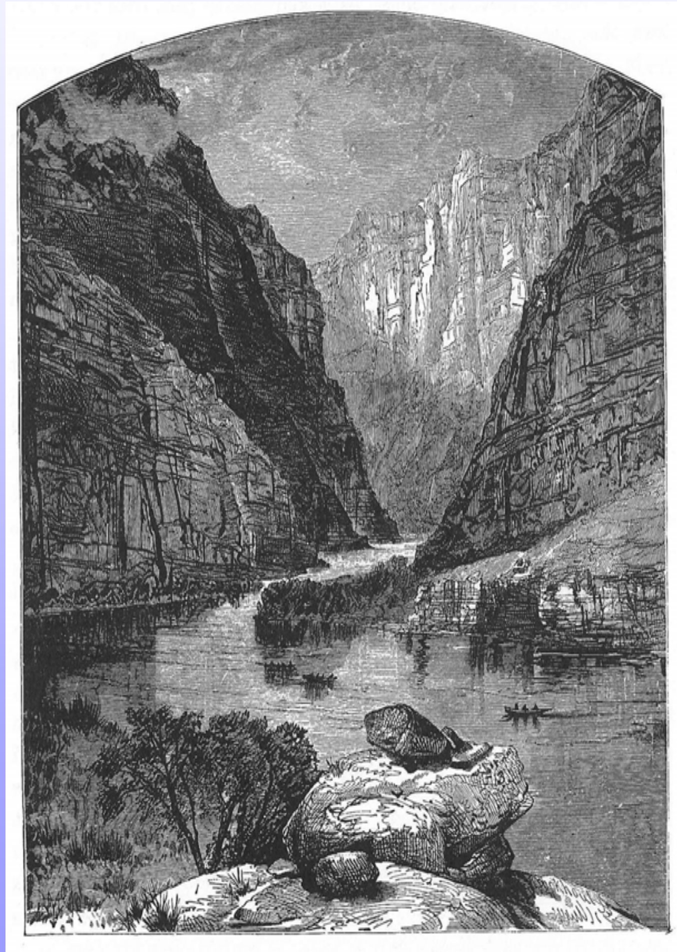


Remedial Packages



- Technologies
- Plans for subsequent land use
- Focused monitoring
- Contingency Plans
- …

Closing



GATE OF LODORE.

We set out on a journey into the unknown

Paradigm shifts of the last half century

Old School Paradigm (Period of prevalence)	New School Paradigm (Time of broad acceptance)
Given the volatility of chlorinated solvents, land disposal is an appropriate practice. *(1940s through 1970s)*	Releases of chlorinated solvents to subsurface environments can create big problems. Few things are more important than limiting future releases. *(Beginning in the 1980s)*
Aquifers may be restored by pumping out the contaminated water (pump-and-treat). *(1970s through 1980s)*	Solvents sorbed to solids, present as DNAPL, and stored in stagnant zones can sustain groundwater concentrations in transmissive zones for long periods. *(1990s through 2000s)*
Chlorinated solvents are recalcitrant. *(1970s through 1990s)*	Chlorinated solvents will degrade under a range of natural and engineered conditions. *(Beginning late 1990s)*
New technologies hold promise of achieving MCLs in source zones. *(early through mid 1990s)*	In many settings (most) available technologies will not achieve MCLs and long-term management will be needed. *(Beginning mid 1990s)*
Primary risks and site care costs can be addressed by removal and/or depletion of source zones. *(1970s through early 2000s)*	Contaminants can remain after source zone treatment in matrix storage or in dissolved plumes, and these can sustain exceedances of MCLs and may necessitate site care for long periods of time. *(mid 2000s)*
Source zone remediation is a necessary component of corrective action. *(1970s through ???)*	Source zone remediation should be considered, but is not always a necessary component of corrective action. Long-term management, containment, and MNA may be more effective strategies at some sites. *(2000s)*
Groundwater represents the primary pathway and media of concern. *(1970s through late 1990s)*	Vapor intrusion is recognized as a pathway of concern of the same order as groundwater. *(2000s)*
Regulators focus on site cleanups. *(1980s and 1990s)*	Some regulators begin to bring natural resource damage (NRD) issues into the site management process, such as filing NRD lawsuits. *(2000s)*

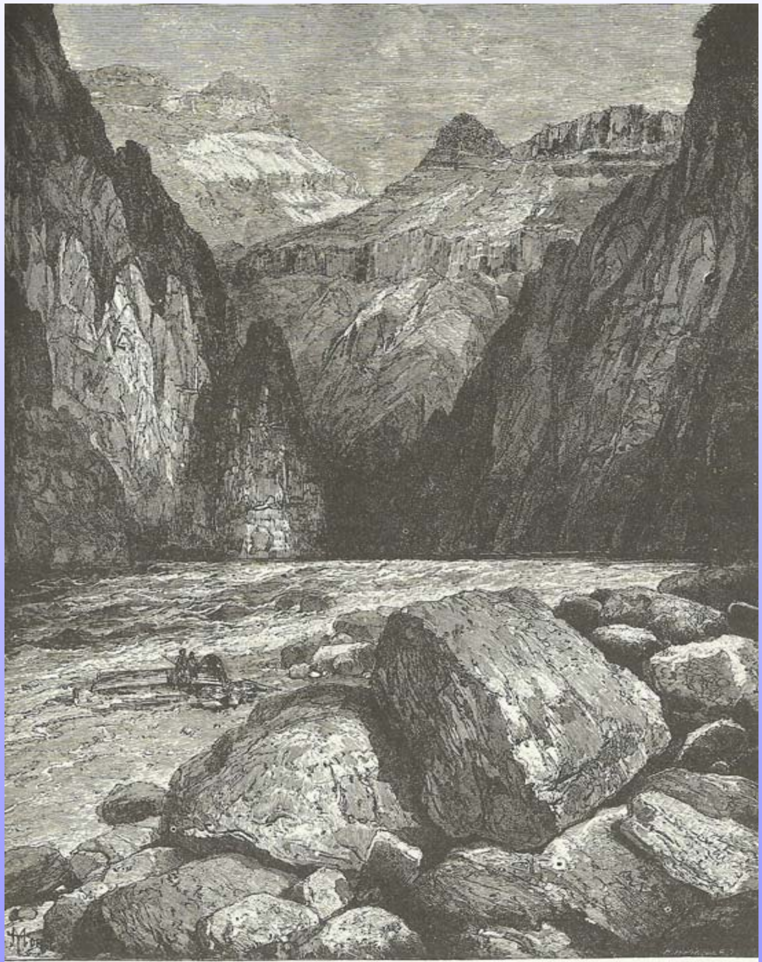
Closing

We have encountered unanticipated challenges

In contemplating this problem, a landmark 1994 National Research Council (NRC) study, *Alternatives for Groundwater Cleanup*, observed "*the nation may be wasting large amounts of money on ineffective remediation efforts.*"

WRECK AT DISASTER FALLS.

Closing



GRANITE FALLS, KIABAB DIVISION, GRAND CANYON.

We have come a long way. Today, given new knowledge, we are far better prepared to meet the challenges that lie before us.

DoD EPA DOE SERDP Strategic Environmental Research and Development Program

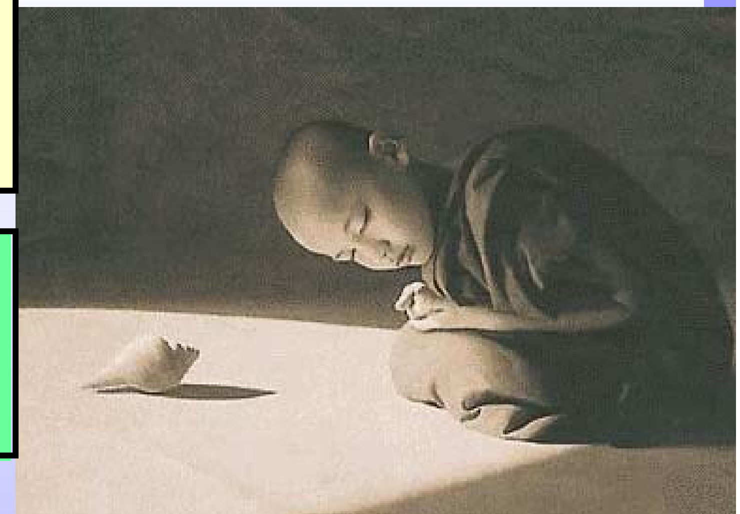
ESTCP Environmental Security Technology Certification Program

Discussion

Key Findings - Characterization

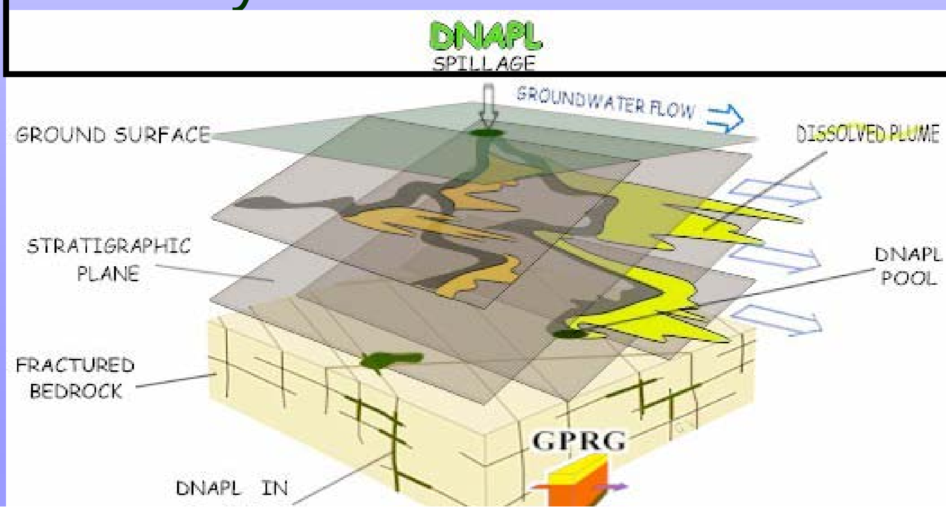
"It isn't that they can't see the solution.
It's that they can't see the problem"

G.K. Chesterton



Need To Use The "Observational Approach"

Trade High Spatial Data Density for Time Data?



Sources, & People, Age & Change Morphology