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**FAQs and Decision Guide for Chlorinated Solvents**  
(ESTCP ER-0530)

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GSI Environmental Inc.

CLU-IN  
Internet Seminar

March, 24, 2009

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# ESTCP ER-0530

Tom Sale, Chuck Newell, Hans Stroo, Rob Hinchee, and Paul Johnson

**Coming Soon  
(2009)**



Frequently Asked Questions Regarding  
Management of Chlorinated Solvents in  
Soils and Groundwater

August 2008  
Tom Sale, Charles Newell,  
Hans Stroo, Robert Hinchee, and  
Paul Johnson



Guide for Selecting Remedies for  
Subsurface Releases of Chlorinated  
Solvents

Tom Sale  
Chuck Newell  
Rob Hinchee  
Hans Stroo  
Paul Johnson



Google - Chlorinated Solvents FAQs

# Opportunity

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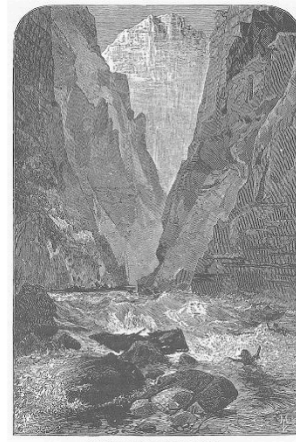
Highlight current knowledge in support of sound decision for releases of chlorinated solvents



Better use of resources



Better environment



WRECK AT DISASTER FALLS.

# Audience

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Parties participating in the process of selecting remedies for chlorinated solvent releases

- DoD staff,
- Consultants,
- Industry
- Regulators, and
- Community Representatives
- .....

CLU-IN Webinar Audience

- Background
  - Regulators
  - Industry
  - Consultants
  - US DoD
- Geographic Dist.
  - 38 States
  - 6 Countries

# 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...

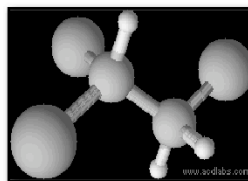
... the science and engineering on which remediation practice is based has improved dramatically...

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



1950s chlorinated solvent disposal area

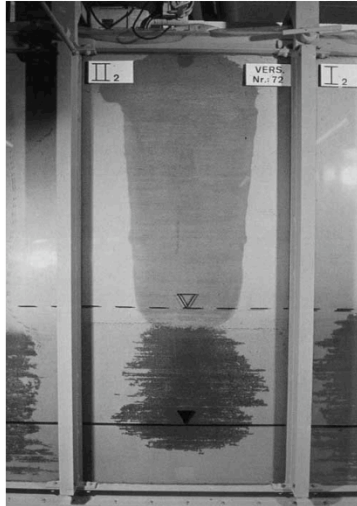
## 2. What are chlorinated solvents and why are they of concern?



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

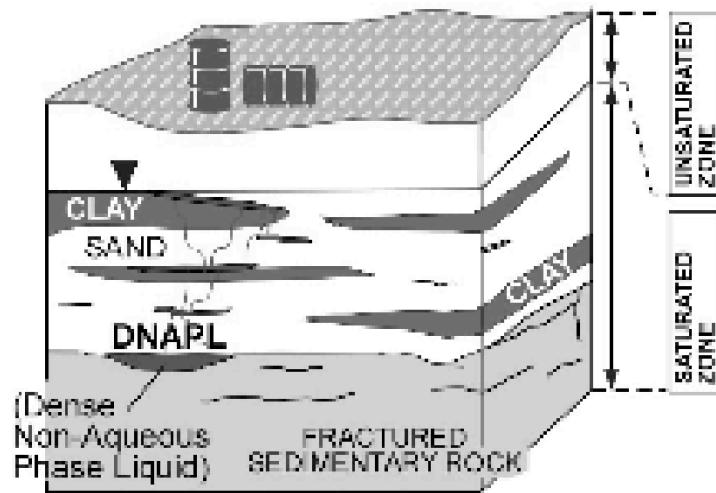
### 3. What happens when chlorinated solvents are released into the subsurface?

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- Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments By Friedrich Schuille (Translated by James F. Pankow)

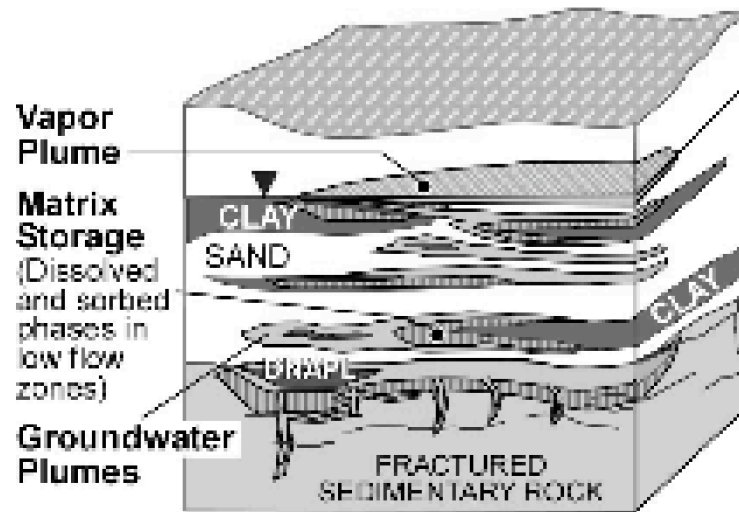
## Early Stage



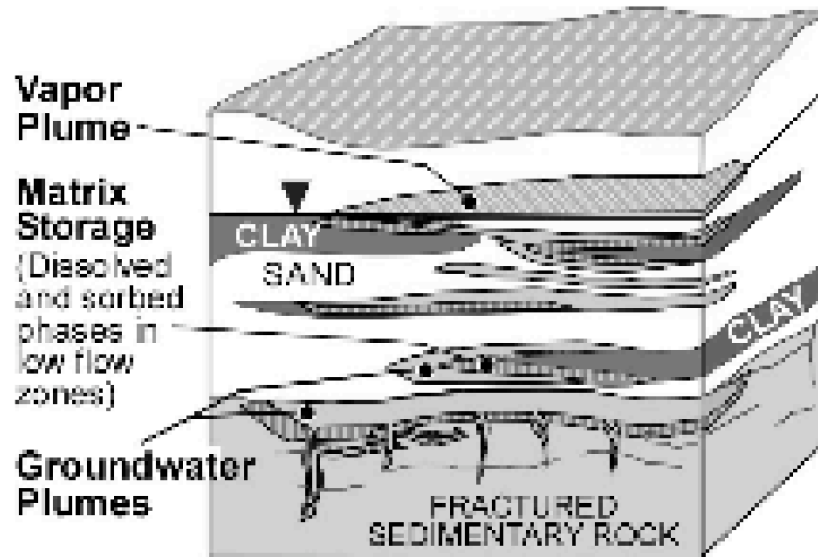
8



# Middle Stage

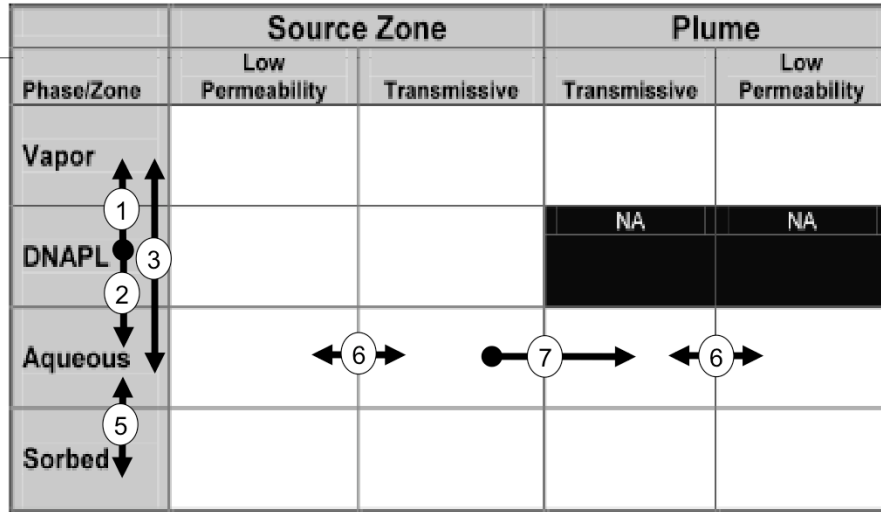


## Late Stage



10

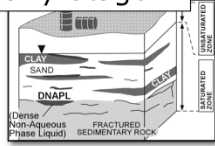
# 14 Compartment Model



11

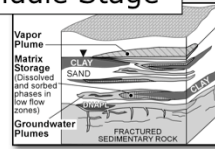
# Mapping contaminant distribution and technology performance using the 14-compartment model

## Early Stage



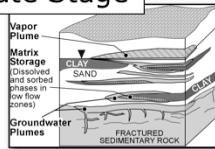
Zone/Phase	SOURCE		PLUME	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	LOW	MODERATE	LOW	LOW
DNAPL	LOW	HIGH		
Aqueous	LOW	MODERATE	MODERATE	LOW
Sorbed	LOW	MODERATE	LOW	LOW

## Middle Stage



Zone/Phase	SOURCE		PLUME	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	MODERATE	MODERATE	MODERATE	MODERATE
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

## Late Stage



Zone/Phase	SOURCE		PLUME	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	LOW	LOW	LOW	LOW
DNAPL	LOW	LOW		
Aqueous	MODERATE	LOW	LOW	MODERATE
Sorbed	MODERATE	LOW	LOW	MODERATE

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#### 4. What is a chlorinated solvent “source zone”?

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

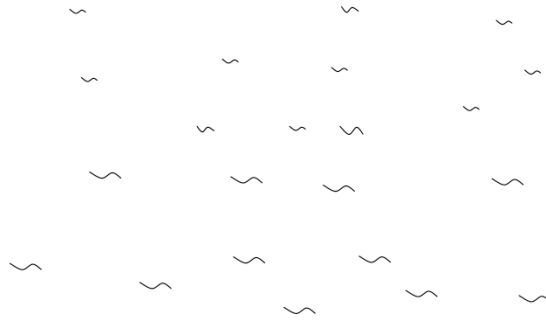
- ... a subsurface reservoir that sustains a plume (primarily dissolved groundwater plumes...
- ... the DNAPL-containing region is initially the primary reservoir... also includes high concentration dissolved- and sorbed-phase halos about the DNAPL-containing region...
- ... acknowledges that some chlorinated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

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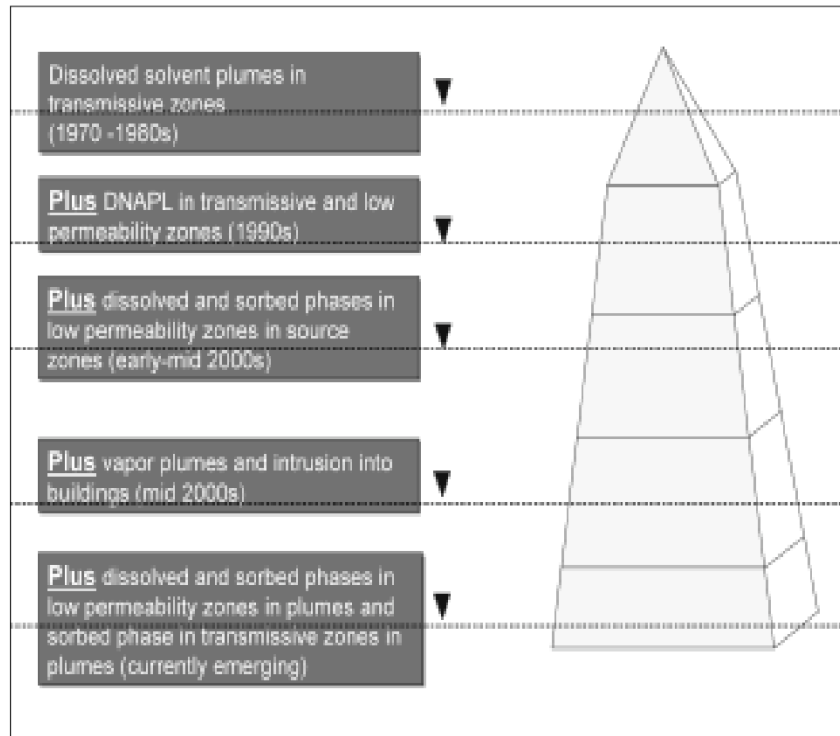
## 5. Why do we keep finding new challenges?

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1960 Problem - Submerged?



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

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- ... 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**

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# Comment on monitoring wells for site characterization

Characterization of a Type 3 setting at late stage using conventional monitoring wells

Phase / Zone	Source		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	Black	Black	Black	Black
DNAPL	Black	White	Diagonal	Diagonal
Aqueous	Black	White	White	Black
Sorbed	Black	White	White	Black

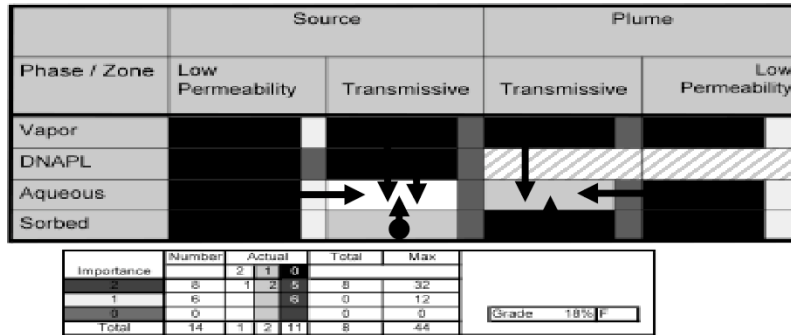
Importance	Number	Actual			Total	Max
3	8	2	1	0	0	24
2	7	2	2	3	6	14
1	1	1	1	0	0	0
0	1	1	1	0	0	0
Total	14	2	3	9	6	38

Grade 16% F

## 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."*

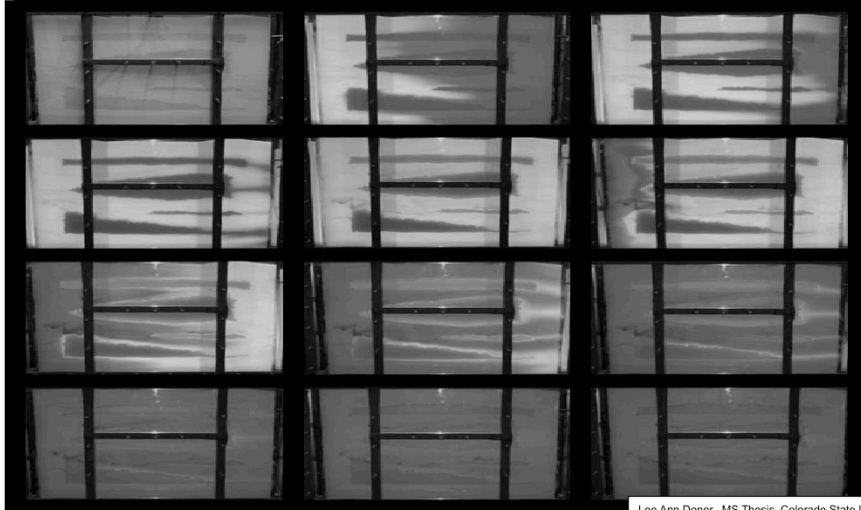
**Type 3 setting - Middle stage**  
Source zone pump and treat



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## 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.

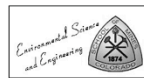


19

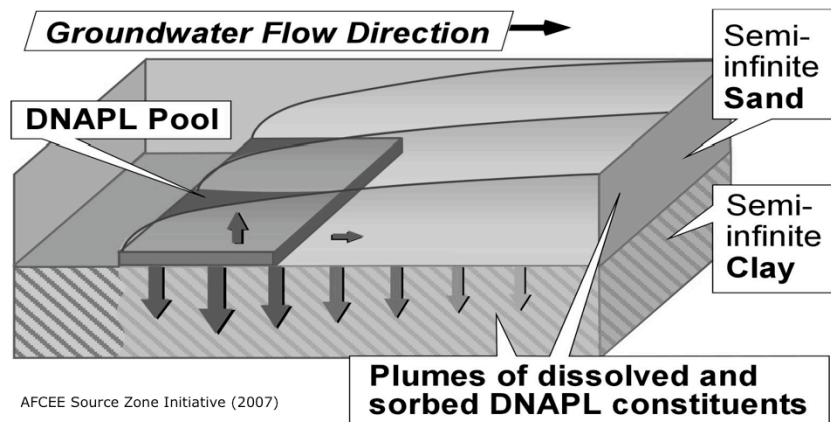
Lee Ann Doner, MS Thesis, Colorado State University

Excerpts from  
Recent AFCEE and DuPont Funded  
Research

Tom Sale / Colorado State University



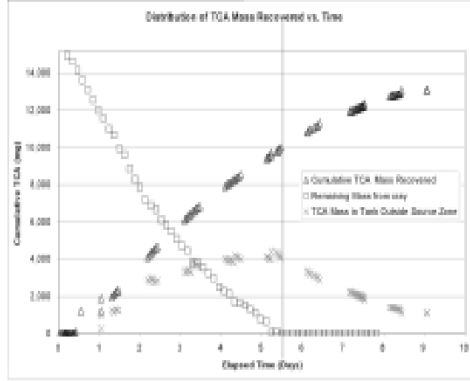
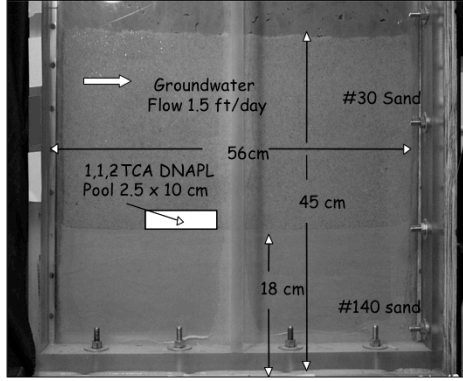
Thought Experiment 1 (Part A)  
How much of the contaminant move into  
the low permeability layer?



21

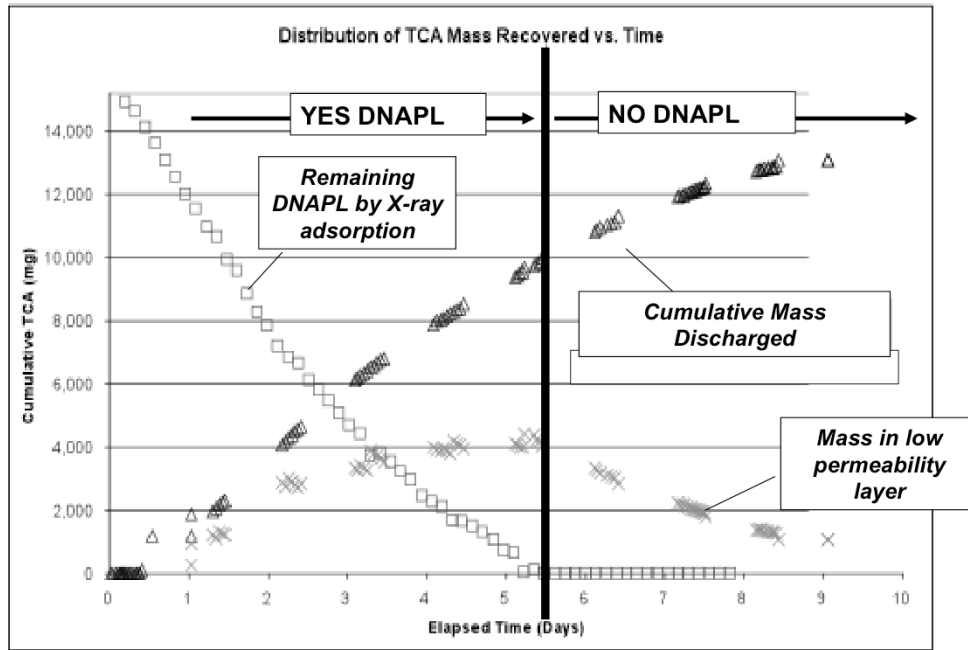
# Two layer sand tank study

Colorado School of Mines (Tissa Illangasekare and Bart Wilkins)



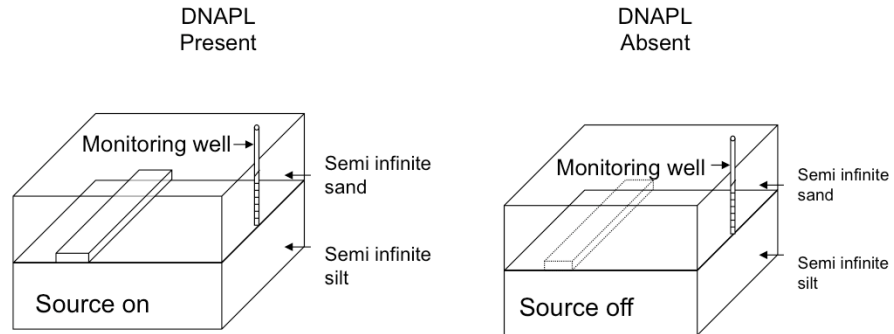
AFCEE Source Zone Initiative (2007)

22



AFCEE Source Zone Initiative (2007)

## 2 layer model scenario



AFCEE Source Zone Initiative (2007)

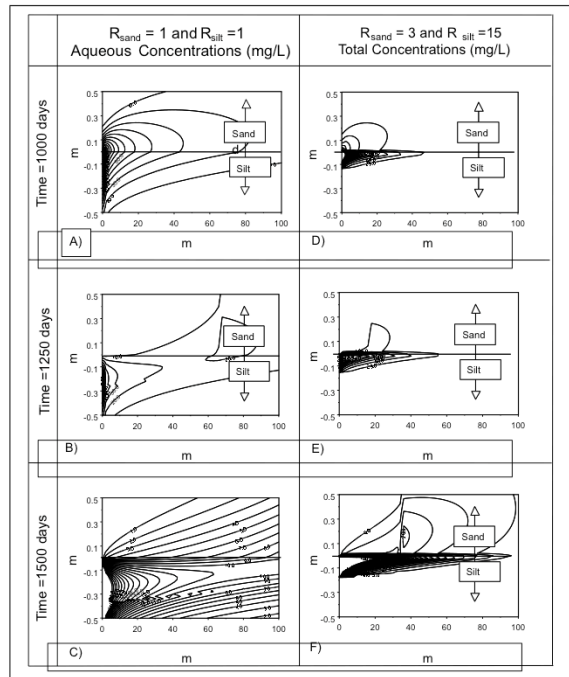
24



# Concentration profiles in cross-section

1 m by 100 m domain

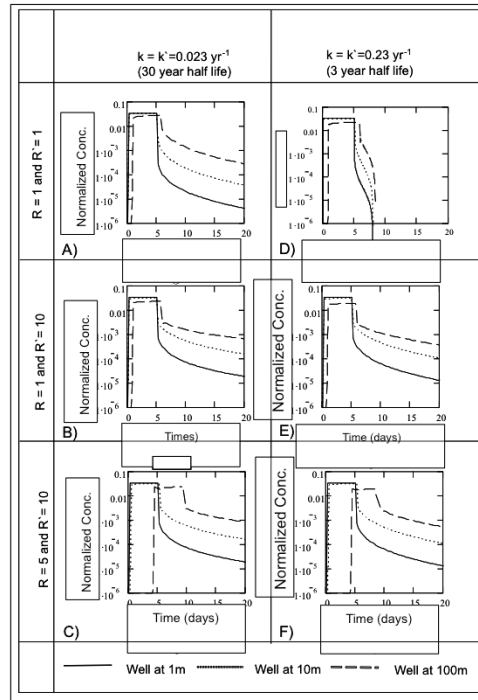
Sale, Zimbron, and Dandy JCH (2008)



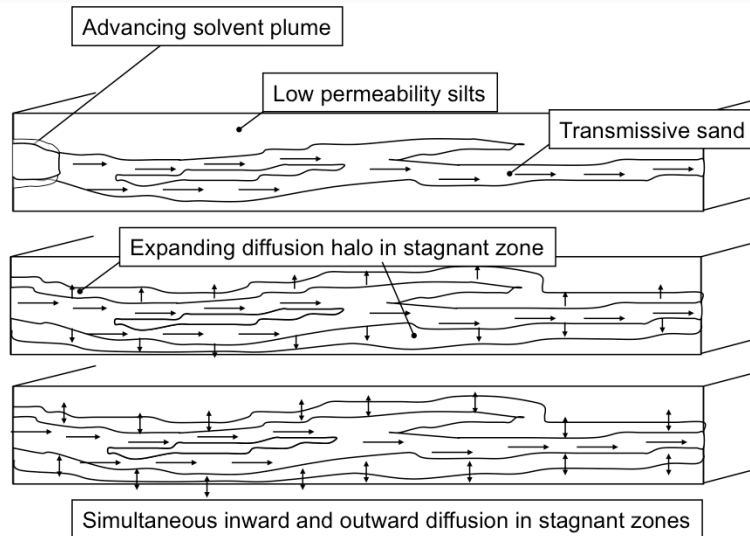
# Concentration at a downgradient well as a function of time, reactions rates and retardation

Sale, Zimbron, and Dandy JCH (2008)

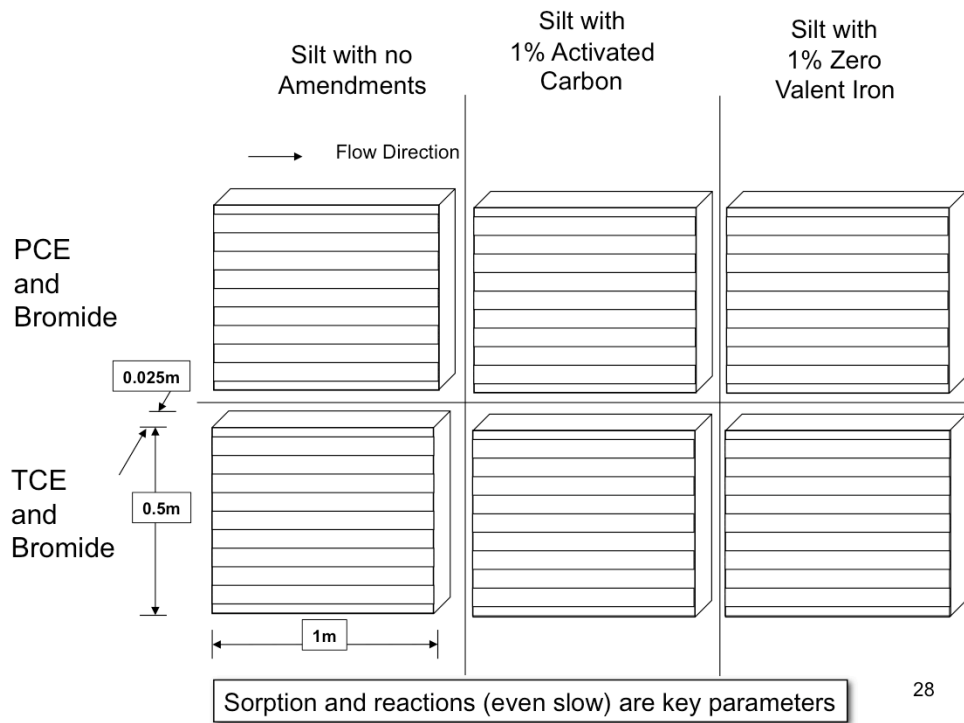
See Also Chapman and Parker (2005)



Thought Experiment 2)  
What is the effect of upgradient flux reduction on downgradient water quality?

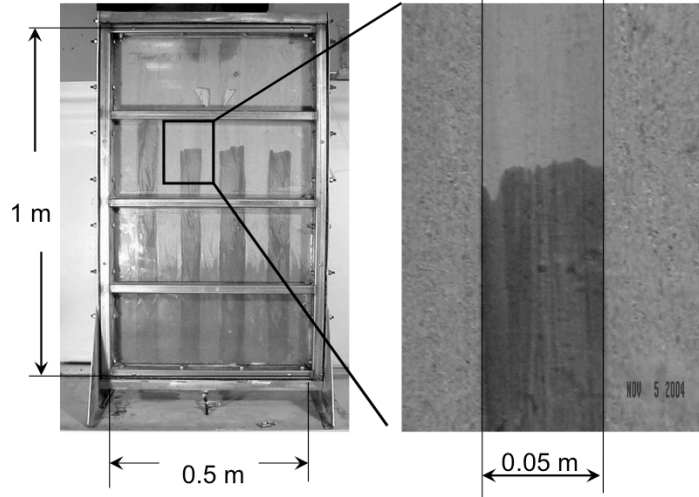


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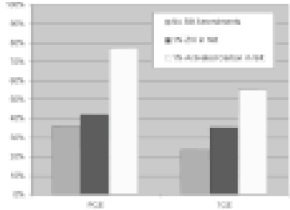
## Multiple Layer Studies

Source on for 25 days, Flushing with no source for an additional 53 day, Retained mass at 83 days

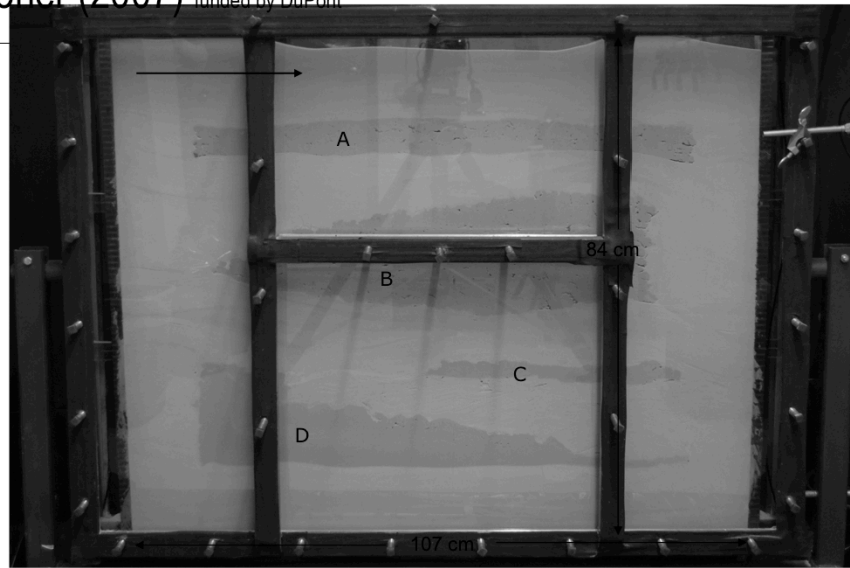


Colorado State University - Julio Zimbron, Leigh Neary, and Rachel Garcia <sup>29</sup>

Percentages of influent contaminant mass driven into the silt layers at the time the source is shut off.

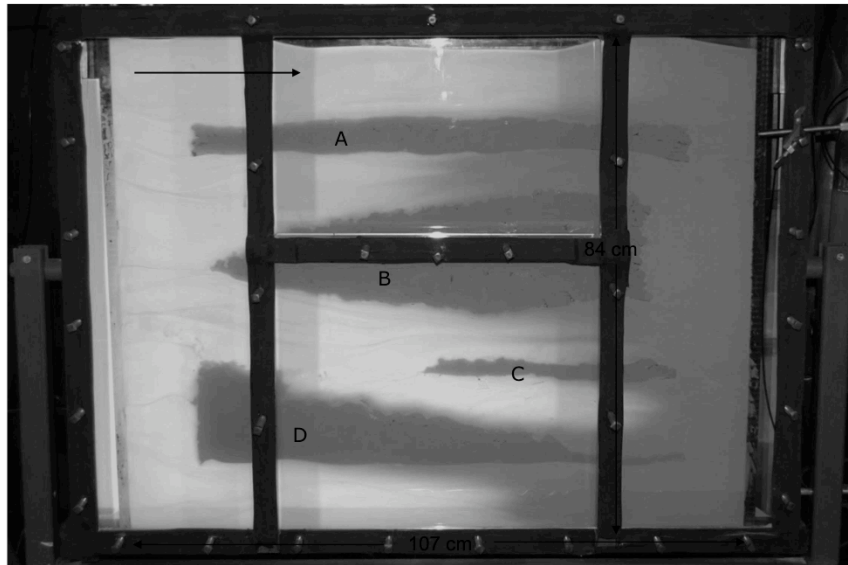


CSU Sand Tank Study Lee Ann  
Doner (2007) funded by DuPont



Day 1

31

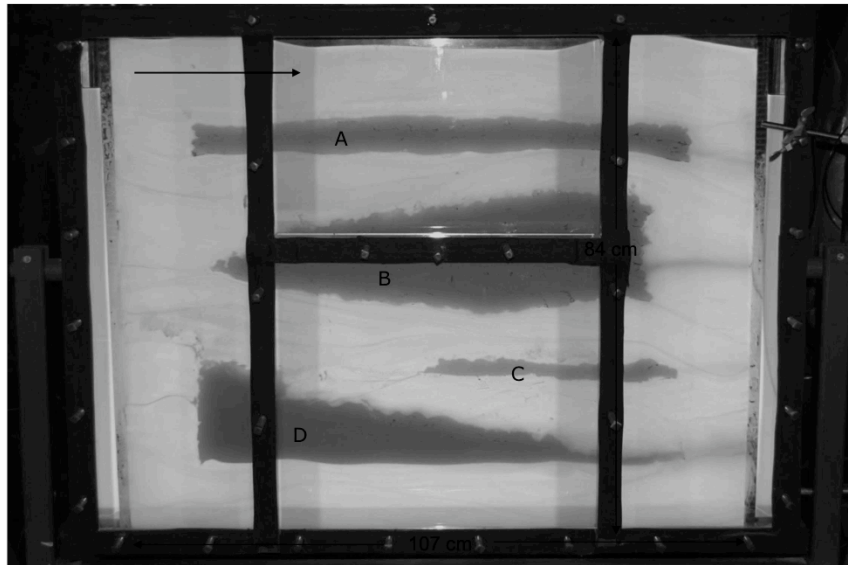


Day 5

Source on for 5 days

32

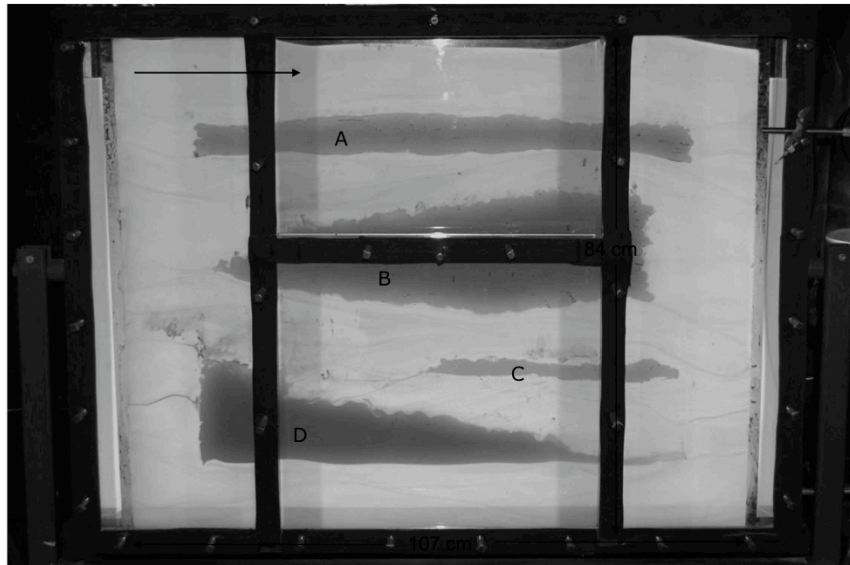




Day 11

Source on for 11 days

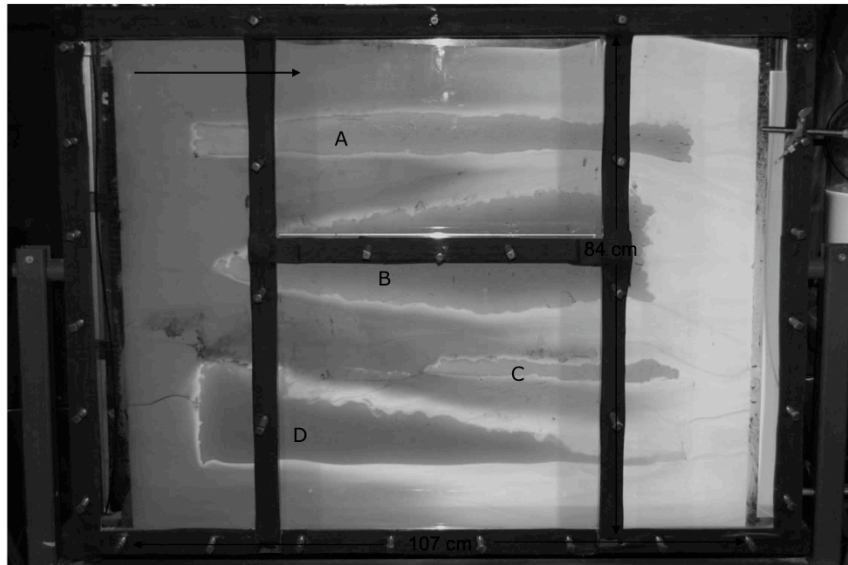
33



Day 23

Source on for 23 days & shut off this day

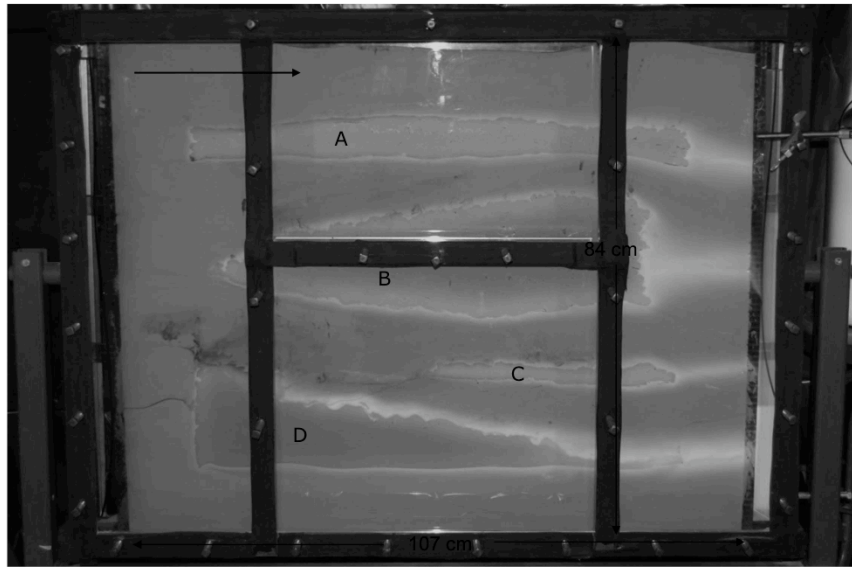
34



Day 26

Source off for 4 days

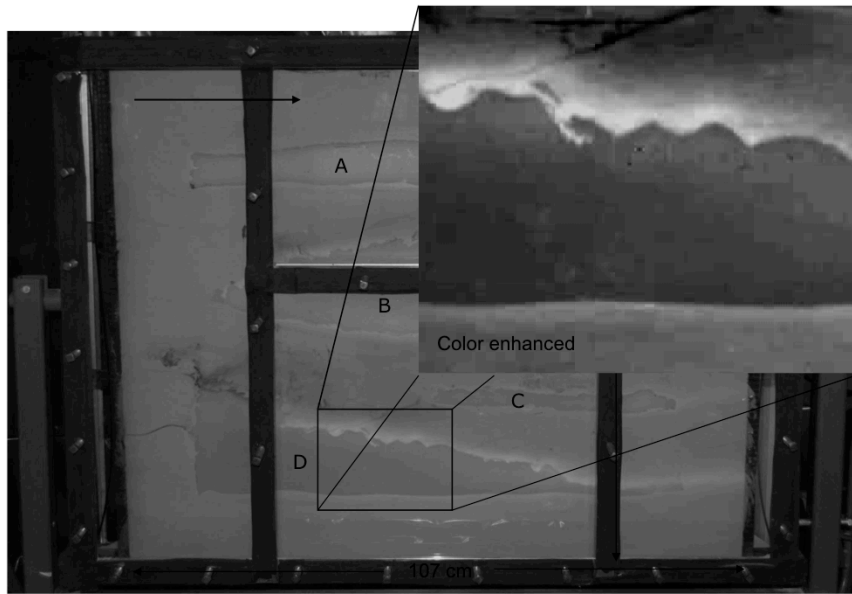
35



Day 30

Source off for 8 days

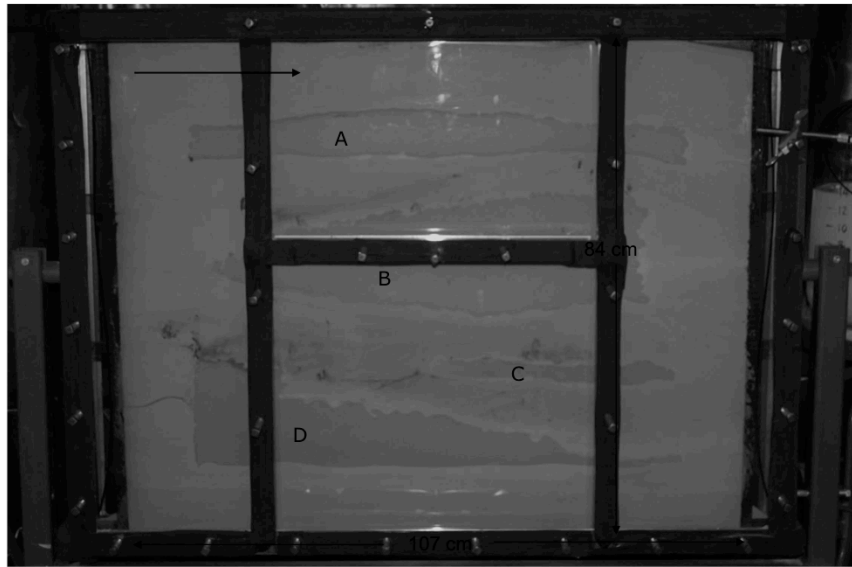
36



Day 34

Source off for 12 days

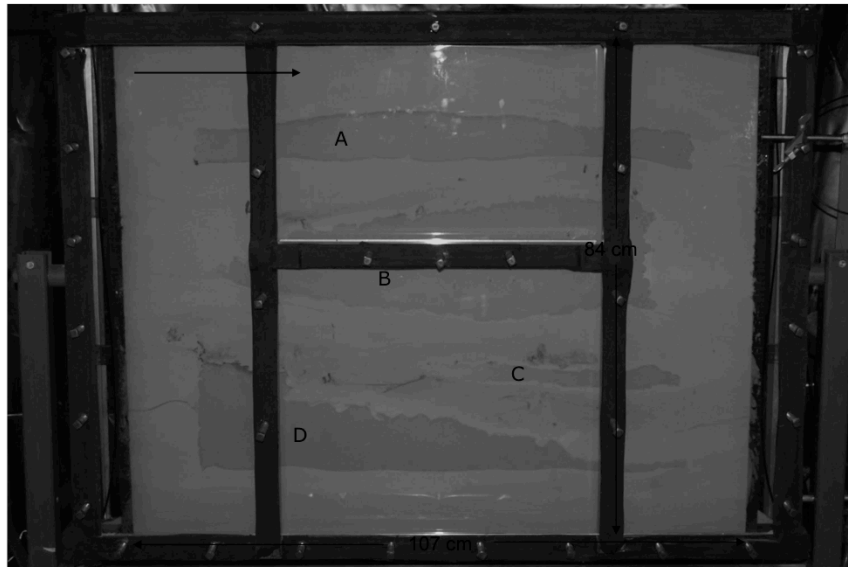
37



Day 75

Source off for 53 days

38



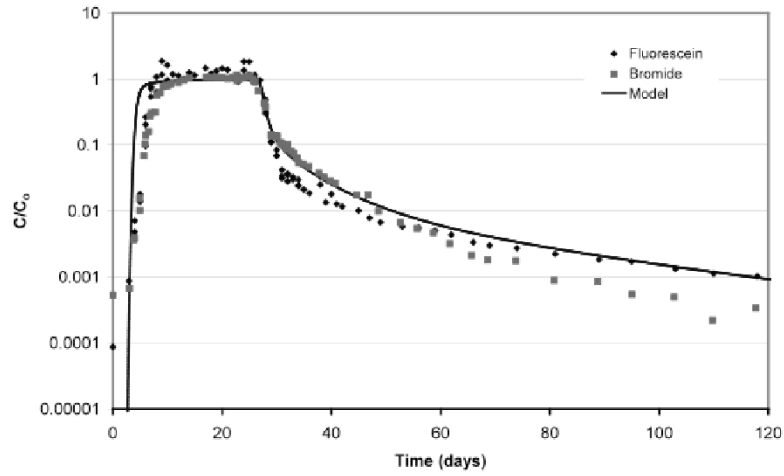
Day 132

Source off for 110 days

39

## Effluent Concentrations from Sand Tank With HydroGeosphere Modeling Results (Chapman and Parker UW)

Comparison of Lab versus Model Effluent Concentrations



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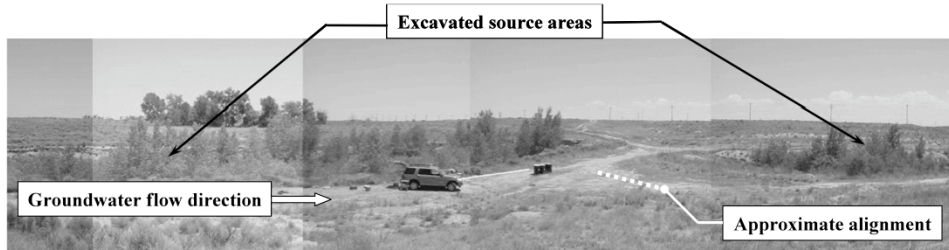
See Back Diffusion – The  
Movie

Available on CLU-IN Web site

# Example

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## Pueblo Chemical Depot



## Introduction

An electrolytic reactive barrier (e-barrier) was installed at the Pueblo Chemical Depot (Pueblo, CO, USA) in early 2006 to intercept a plume of groundwater contaminated with energetic compounds (Figure 1). The concept of an e-barrier is that of a permeable reactive barrier driven by low voltage direct current to affect electrolytic degradation of contaminant compounds.

The e-barrier was installed in 15 individual panels consisting of titanium – mixed metal oxide mesh electrodes mounted to vinyl sheet pile (Crane Materials International).



Figure 1. Installation of e-barrier through a plume containing RDX, 2,4,6-TNT, 2,4-DNT and 1,3,5-TNB

## Project Objectives

The primary objectives of the Demonstration/Validation are to provide the information necessary in terms of efficacy and cost to evaluate the potential of e-barriers for treatment of groundwater containing dissolved energetic compounds.

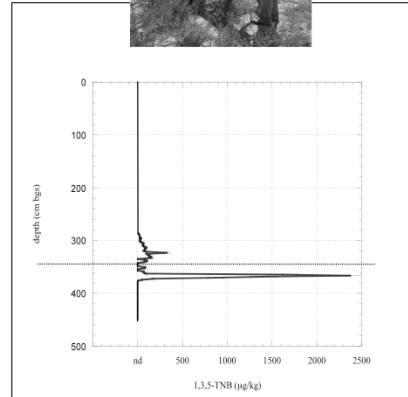
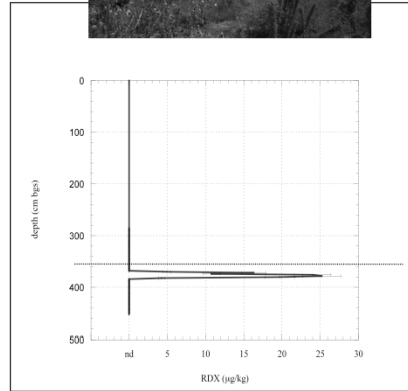
Secondary project objectives are to:

- 1) Evaluate the use of a four electrode set with respect to contaminant flux reduction,
- 2) Evaluate the use of commercially available off-the-shelf vinyl sheet pile as electrode support
- 3) Evaluate the use of a solar power supply
- 4) Provide the data necessary for Pueblo Chemical Depot to evaluate the use of e-barriers as a replacement alternative to the existing pump and treat system.

Figure 2. The e-barrier is powered by a 2 kW solar array consisting of 16 PV panels (BP Solar) and 3200 AHr battery array (MK Battery). Voltage applied to the e-barrier is controlled using DC-DC converters (Vicor). Power consumption by the e-barrier is currently approximately 350 W.



# Example



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## 9. Why are contaminants in the vadose zone important?

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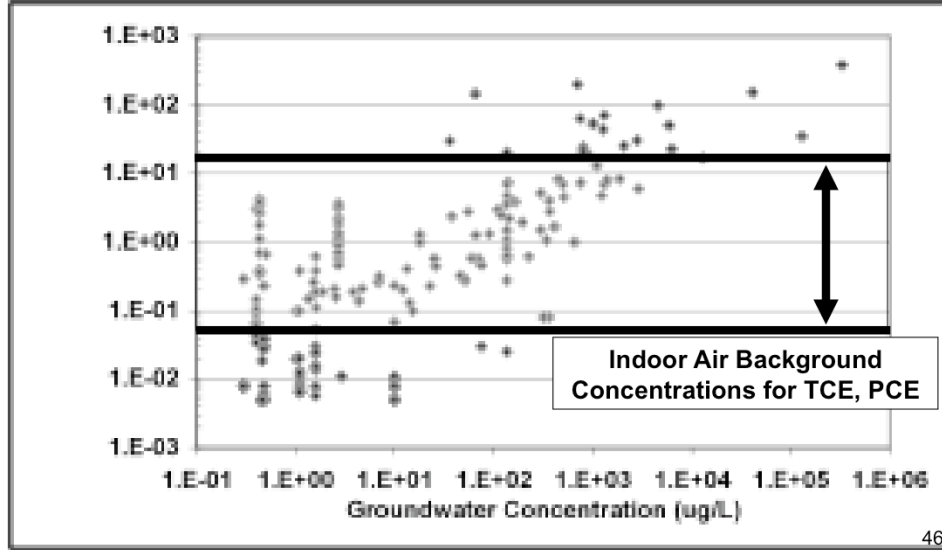
### Vadose Zone as *SOURCE*

- 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 key players

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



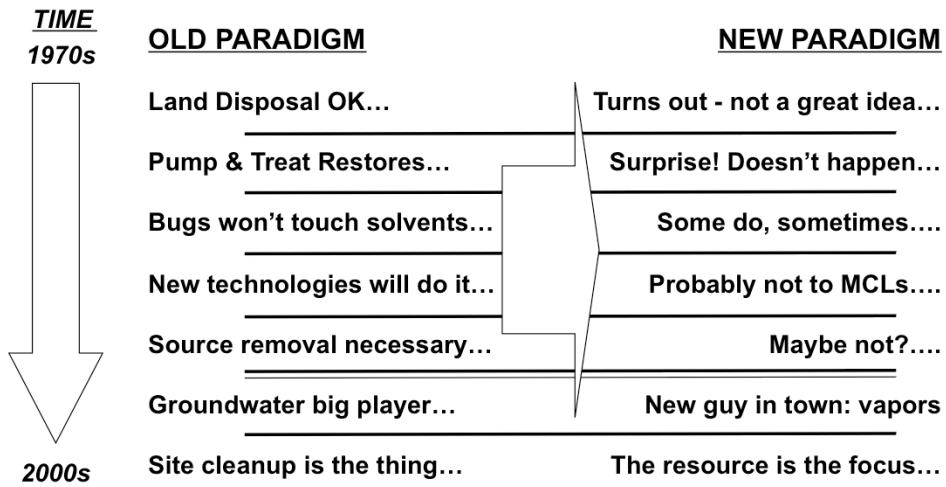
## 10. What have we learned in the last half century?

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





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?

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•Chemical Oxidation

- *Permanganate*

- *Peroxide*

- *Persulfate*

•Thermal

- *Conductive*

- *Electrical*

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

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- **Bioremediation**

- *High Solubility Substrate*

- *Low Solubility Substrate*

- **Chemical Reduction**

- *ZVI Injection*

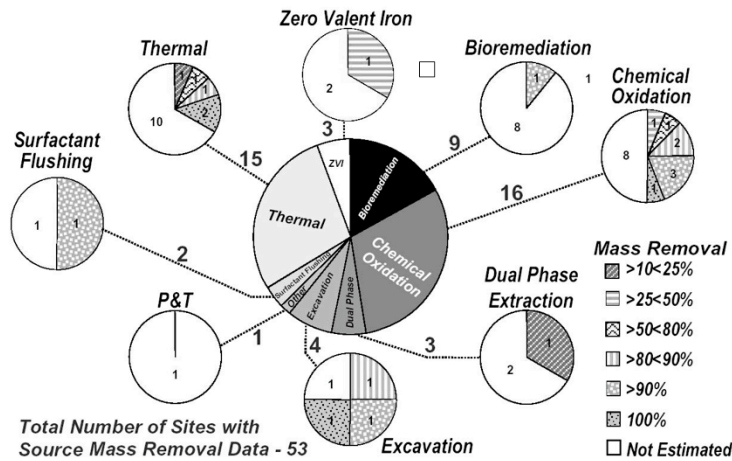
- *ZVI Soil Mixing*

- **Monitored Natural Attenuation**

- **Soil Vapor Extraction**

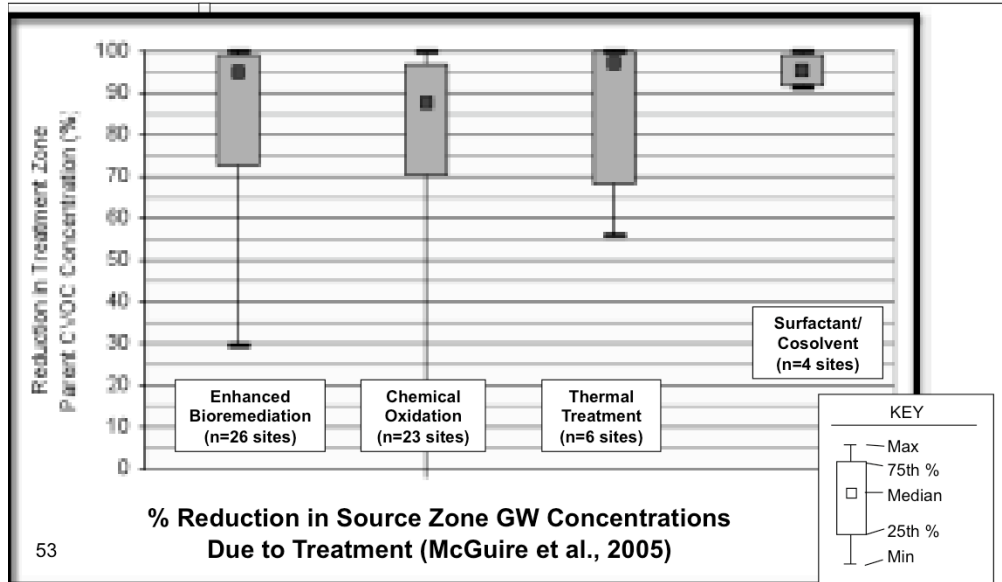


### 13. What can we expect from common source treatment technologies?



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

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



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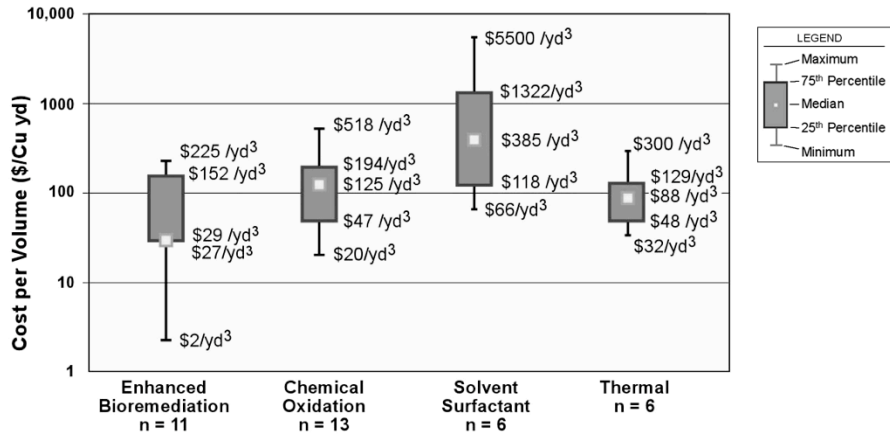
### 13. What can we expect from common source treatment technologies? (cont'd)

#### 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)

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

### *Very General Rule of Thumb*

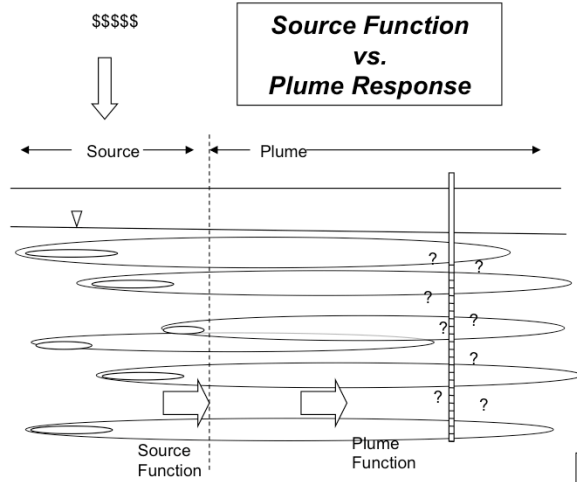
Investments on the order of **millions of dollars per acre** appear to have the potential to achieve **one order of magnitude** reductions in chlorinated solvent mass and concentration in source zones.



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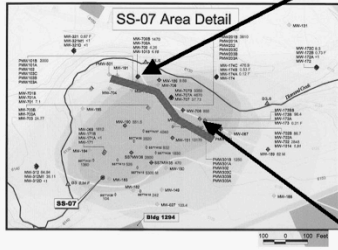
# 15. How will reduced loading from sources affect plumes?



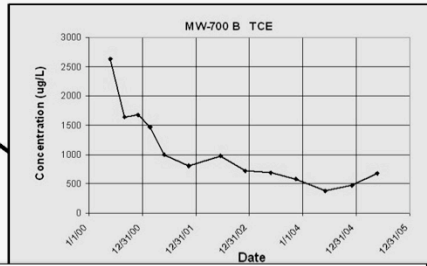
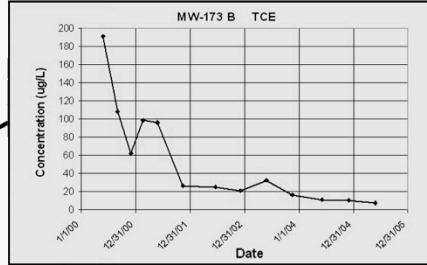
Rock core from the Ogallala Formation at F.E. Warren AFB illustrating a silt bed in sandstone

# 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:***

**One order-of-magnitude source reduction...**

- gives one order-of-magnitude improvement downgradient.

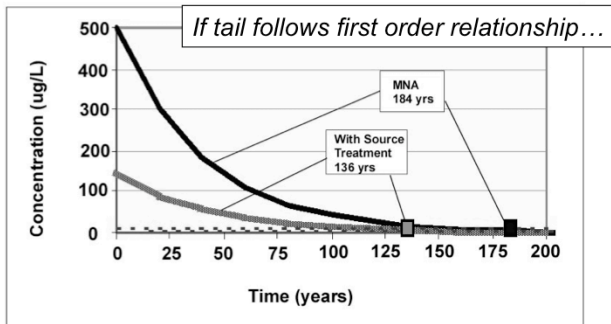
**But with fast groundwater flow, low mass storage, and/or active attenuation...**

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

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## 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 how much is difficult.
- Must account for likely “tails” to source concentration
- May not get “equal benefit for equal work”



### LONGEVITY SOFTWARE

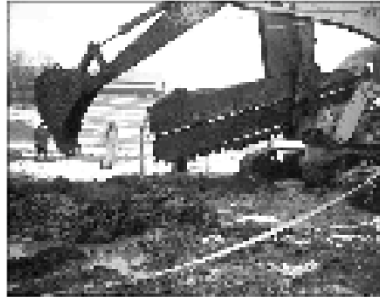
- SourceDK
- BIOBALANCE
- NAS
- REMCHLOR

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17. Which containment measures are receiving the widest use?

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



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17. What can we expect from containment measures?

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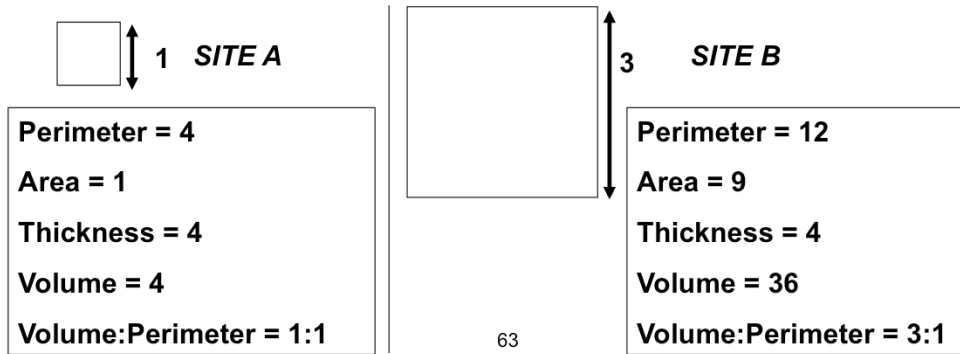
- 43 of 52 full scale ZVI barriers are “meeting regulatory expectations”
- 25 of 29 sites with physical barriers have “acceptable performance” in medium term (10 years or less)
- MNA sole remedy (no source treatment) at 30% of 191 MNA sites



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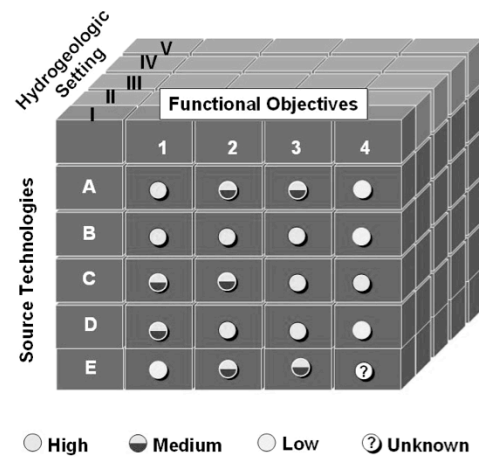
20. How does one compare treatment vs. containment?

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



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

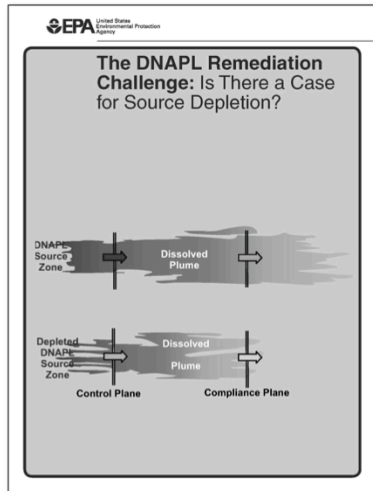
- NRC “Cube”
  - Objectives
  - Settings
  - Technologies
- Series of Tables



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



EPA / 600-R-031/143, 2003

### Decision Matrix

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

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**Qualitative Decision Chart: *RC Approach***

***Yes, Source  
Depletion***



***No, Source  
Depletion***



## Key Factors for Deciding

Yes



No



■ Source Zone:	<i>Expanding</i>	<i>Immobile</i>
■ Plume Status:	<i>Expanding</i>	<i>Stable</i>
■ Resource Value:	<i>High</i>	<i>Low</i>
■ Containment Cost:	<i>High</i>	<i>Low</i>
■ Will Reduce Remed. Timeframe?	<i>A Lot</i>	<i>A Little</i>
■ Need for Rapid Cleanup?	<i>Yes</i>	<i>No</i>

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## Weight of Evidence: **More Likely** to Benefit from Tmt.

DESIRED REMEDIAL BENEFITS <sup>1</sup>	MORE NEED FOR SOURCE DEPLETION	LESS NEED FOR SOURCE DEPLETION
Reduce potential for DNAPL migration as separate phase	1a. Expanding DNAPL Zone (probably due to chlorinated solvents) <i>(containment addresses this problem too)</i>	1b. Free-Phase DNAPL present but stable in stratigraphic traps
Reduce source longevity, and reduce long-term management requirements	2a. High life-cycle containment cost (for example, containment Net Present Value (NPV) >> cost of remediation) 3a. Low reliability of containment system 4a. High resource value (for example, resource used to DNAPL (for example, multi-source aquifer OR Wall Yield > 1000 mg/L or 2500 mg/L) <sup>2</sup> 5a. High probability of meaningful reduction in time to reach MCLs (for example, 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 reach MCLs
Near-term enhanced natural attenuation due to reduced dissolved phase loading	6a. Expanding dissolved phase plume (source loading > assimilative capacity) <i>(containment addresses this problem too)</i>	6b. Stable 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 impacted or impacted soon (for example, < 2 years) <i>(containment addresses this problem too)</i>	7b. Potential longer-term risk to receptor (for example, >2 years travel time)
Near-term attainment of MCLs	8a. Need for rapid cleanup (for example, impending property sale)	8b. Limited need for rapid cleanup
Intangibles	9a. Desire for active remedy; desire to test new technologies; desire to reduce stewardship burden on future generations	9b. Neutral on intangible issues.



□

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

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- 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?

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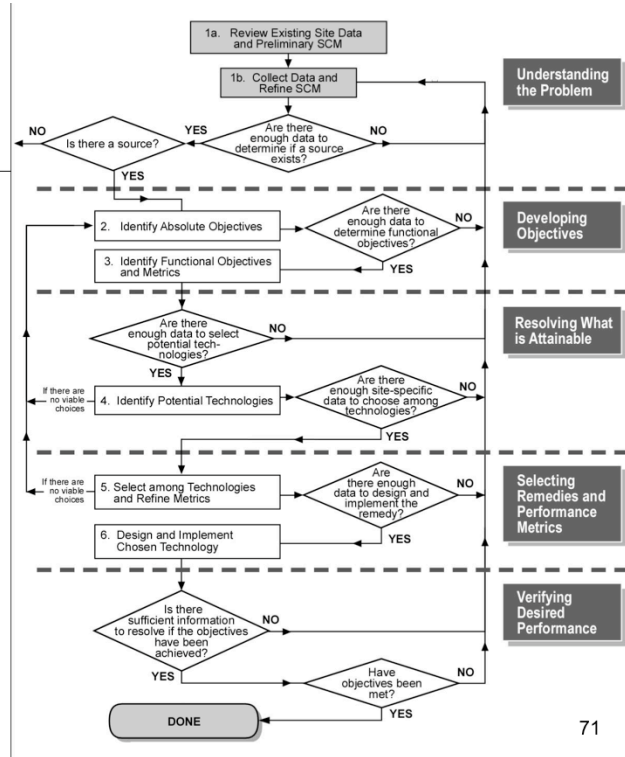
NRC Philosophy:

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?

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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?

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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?

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### ***The Observational Approach:***

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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

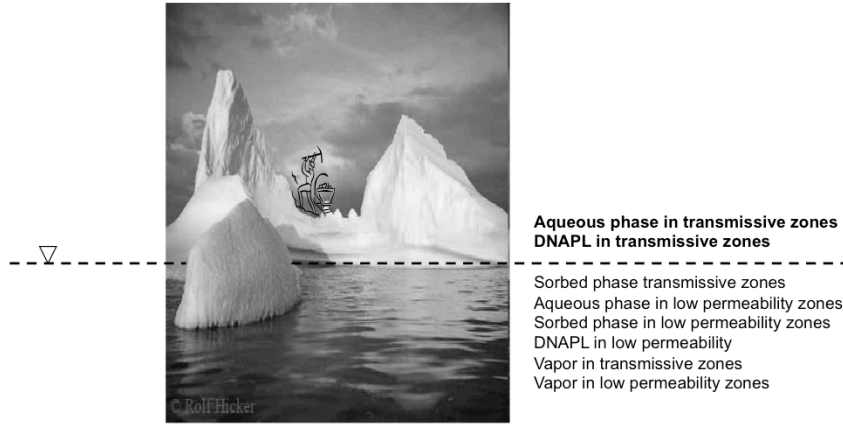
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## 25. Where can I find more information?

- 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](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/>

□

We need to look at the entire problem...  
including the parts that are less apparent



# Discussion

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# Thank You

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After viewing the links to additional resources,  
please complete our online feedback form.

