

FAQs and Decision Guide for Chlorinated Solvents

(ESTCP ER-0530)

Tom Sale
Colorado State University

Chuck Newell
GSI Environmental Inc.

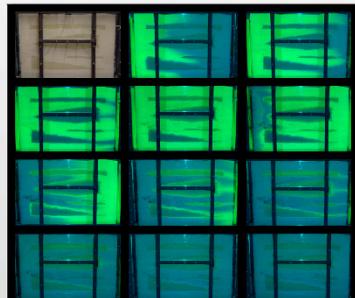
CLU-IN
Internet Seminar

March, 24, 2009

1

ESTCP ER-0530

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



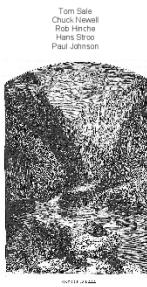
Frequently Asked Questions Regarding
Management of Chlorinated Solvents in
Soils and Groundwater

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



Coming Soon (2009)

Guide for Selecting Remedies for
Subsurface Releases of Chlorinated
Solvents



Google - Chlorinated Solvents FAQs

2

Opportunity

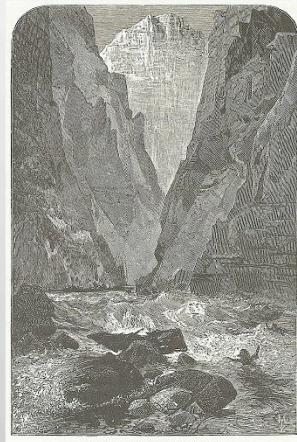
Highlight current knowledge in support of sound decision for releases of chlorinated solvents



Better use of resources



Better environment



3

Audience

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...

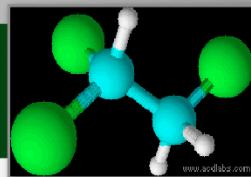
...we can be more successful in the future than we have been in the past



1950s chlorinated solvent disposal area

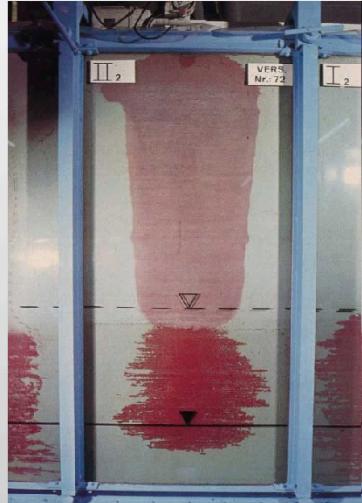
5

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



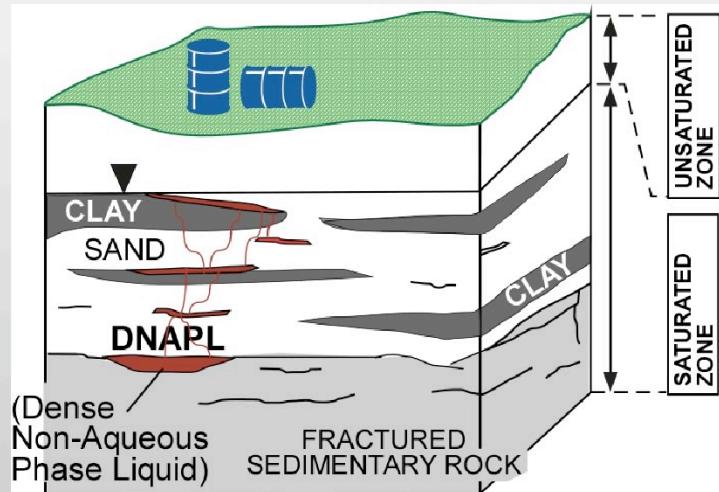
Attributes	Industrial Values	Environmental Challenges
Volatile	Good for cleaning	Readily form vapor plumes in soils
Chemically stable under typical aerobic conditions	Easy to store	Often slow to degrade in aerobic soils and groundwater systems
Non-flammable	Safe from a fire and explosion hazard perspective	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?



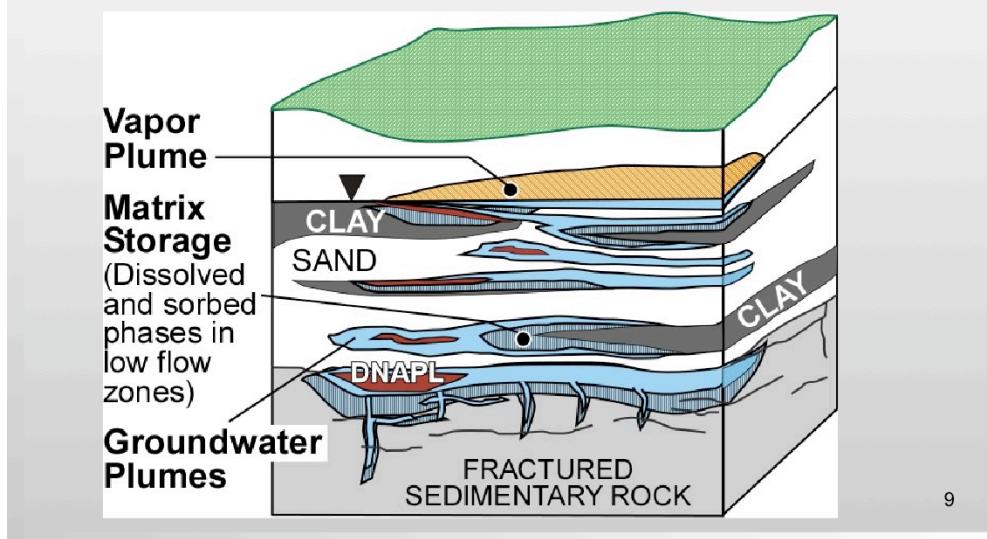
- Dense Chlorinated Solvents in Porous and Fractured Media:
Model Experiments By Friedrich Schwille (Translated by [James F. Pankow](#))

Early Stage

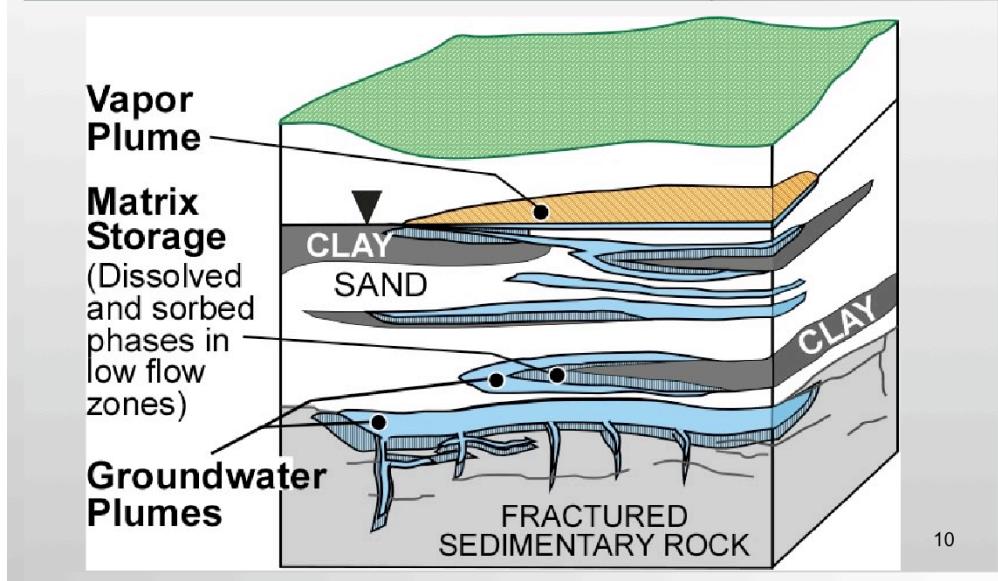


8

Middle Stage



Late Stage



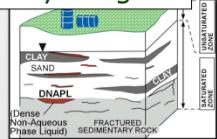
14 Compartment Model

Phase/Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL	1 2 3		NA	NA
Aqueous		6	7	6
Sorbed	5			

11

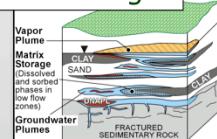
Mapping contaminant distribution and technology performance using the 14-compartment model

Early Stage



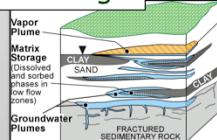
Zone/Phase	SOURCE		PLUME	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	LOW	MODERATE	LOW	LOW
DNAPL	LOW	HIGH		
Aqueous	LOW	MODERATE	MODERATE	LOW
Sorbed	LOW	MODERATE	LOW	LOW

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

12

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.

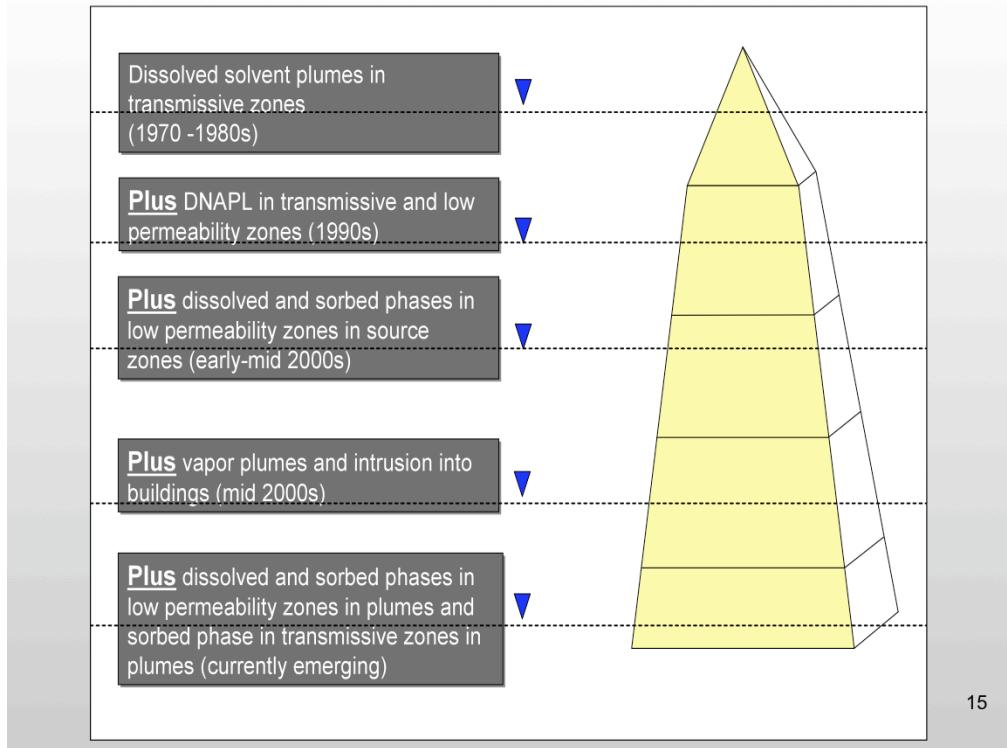
13

5. Why do we keep finding new challenges?

1960 Problem - Submerged?



14



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...

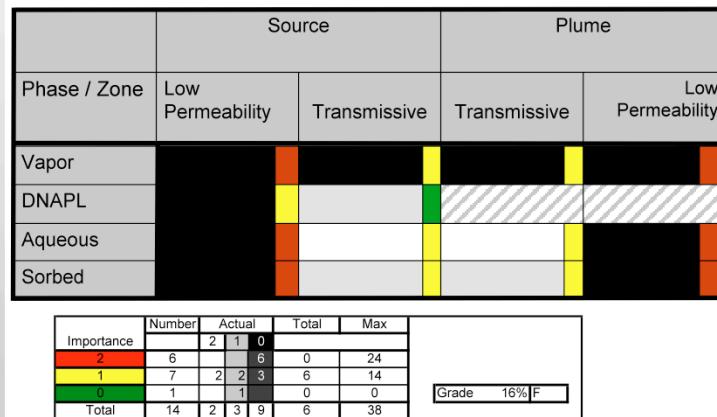


Source Delineation is Difficult

16

Comment on monitoring wells for site characterization

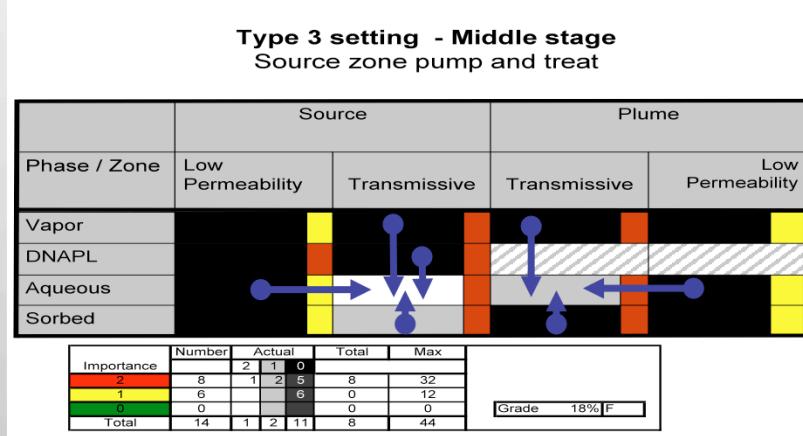
Characterization of a Type 3 setting at late stage using conventional monitoring wells



17

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

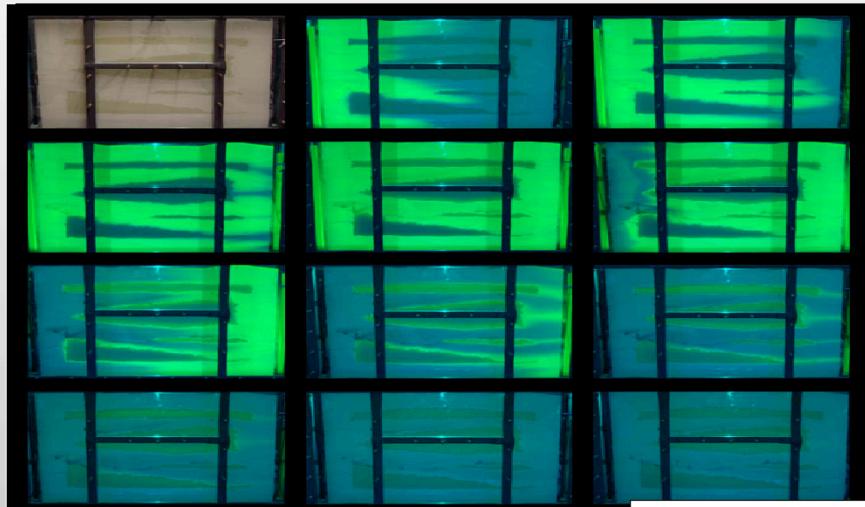
The National Research Council's 1994 report on groundwater clean-up alternatives concluded:
"Remediation by pump-and-treat processes is a slow process. Simple calculations for a variety of typical situations show that predicted clean-up times range from a few years to tens, hundreds, or even thousands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



18

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

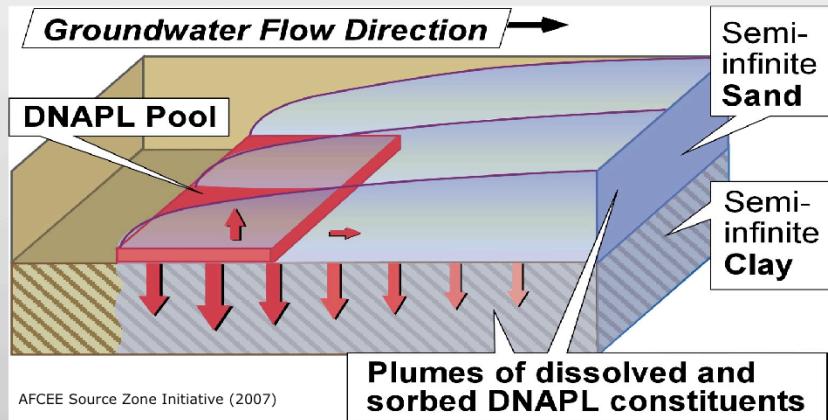
Tom Sale / Colorado State University



20

Thought Experiment 1 (Part A)

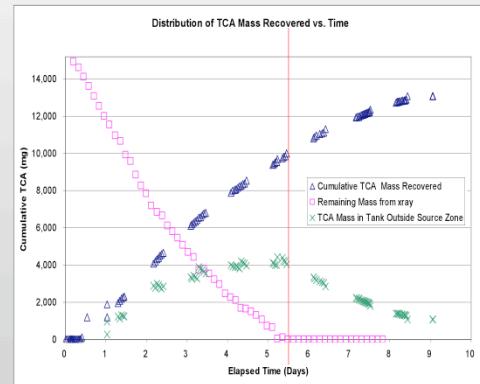
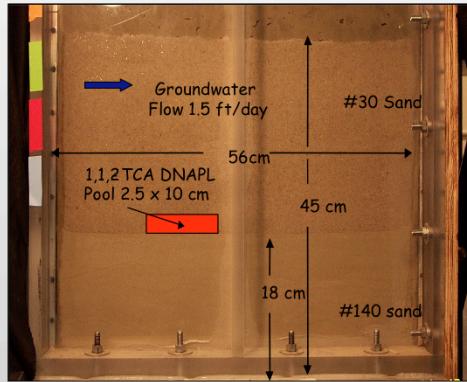
How much of the contaminant move into
the low permeability layer?



21

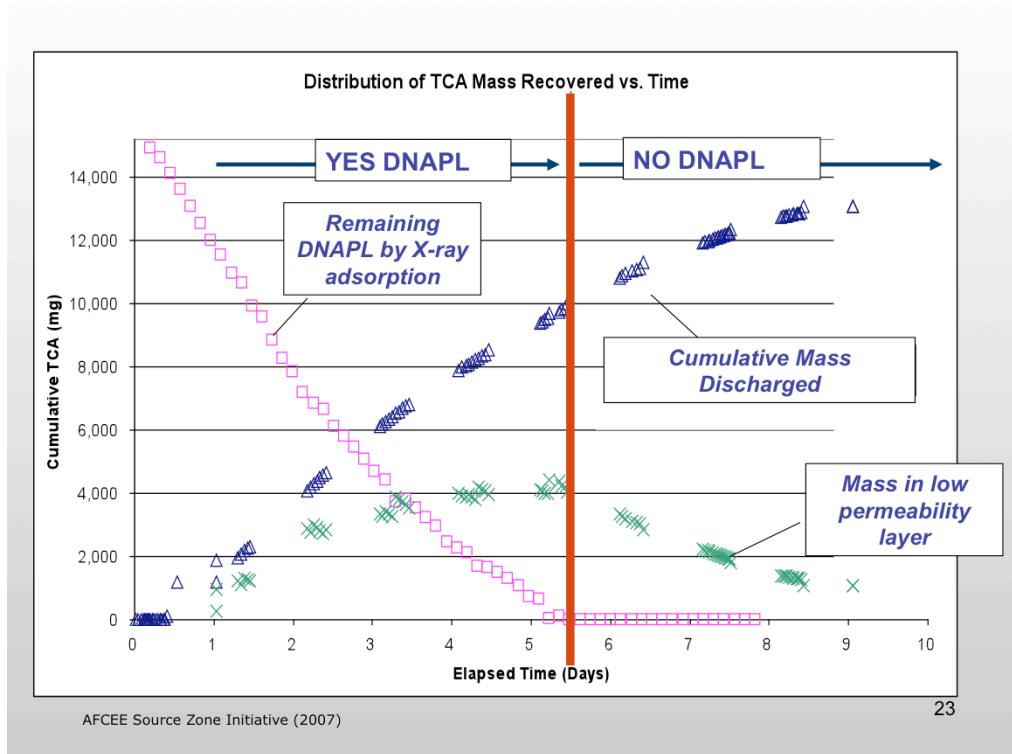
Two layer sand tank study

Colorado School of Mines (Tissa Illangasekare and Bart Wilkins)

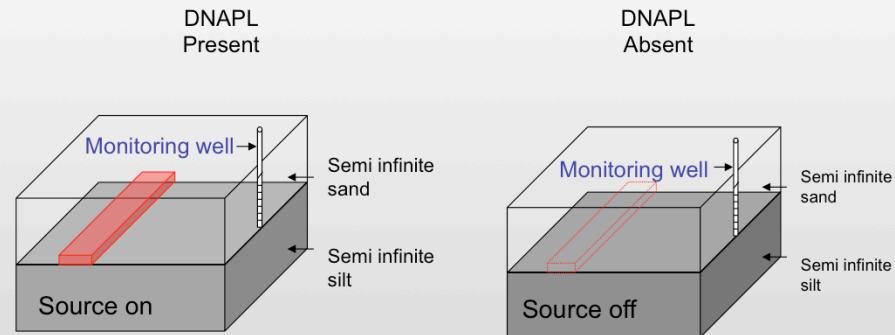


AFCEE Source Zone Initiative (2007)

22



2 layer model scenario



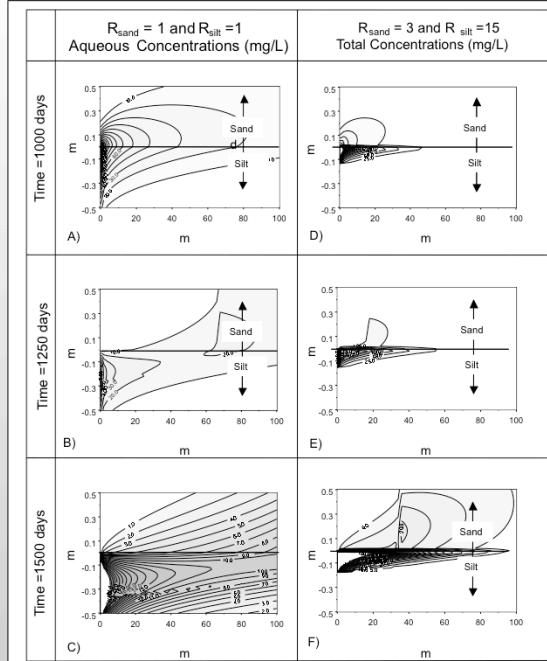
AFCEE Source Zone Initiative (2007)

24

Concentration profiles in cross-section

1 m by 100 m domain

Sale, Zimbron, and Dandy JCH (2008)

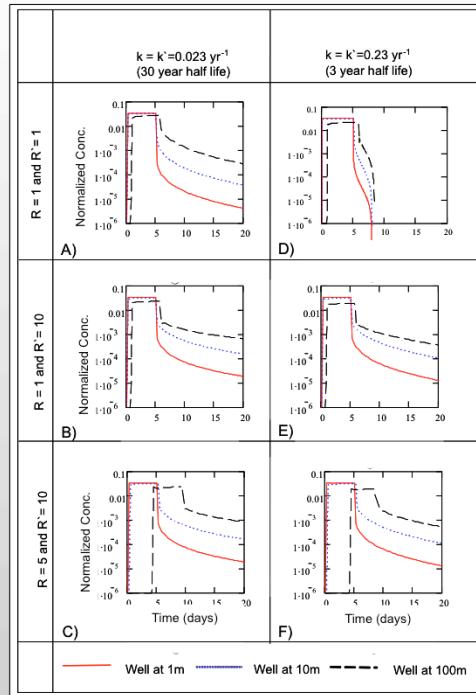


25

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

Sale, Zimbron, and Dandy JCH (2008)

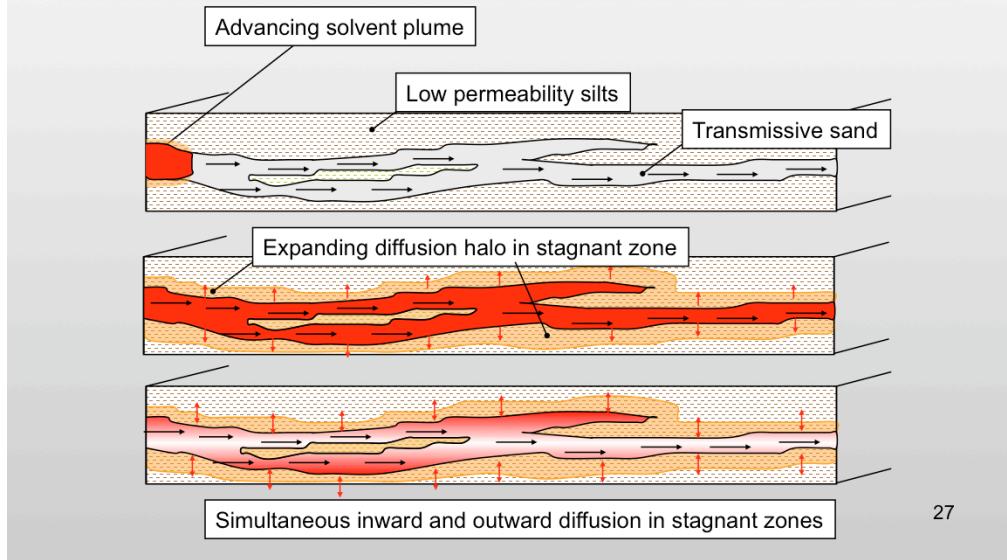
See Also Chapman and Parker (2005)



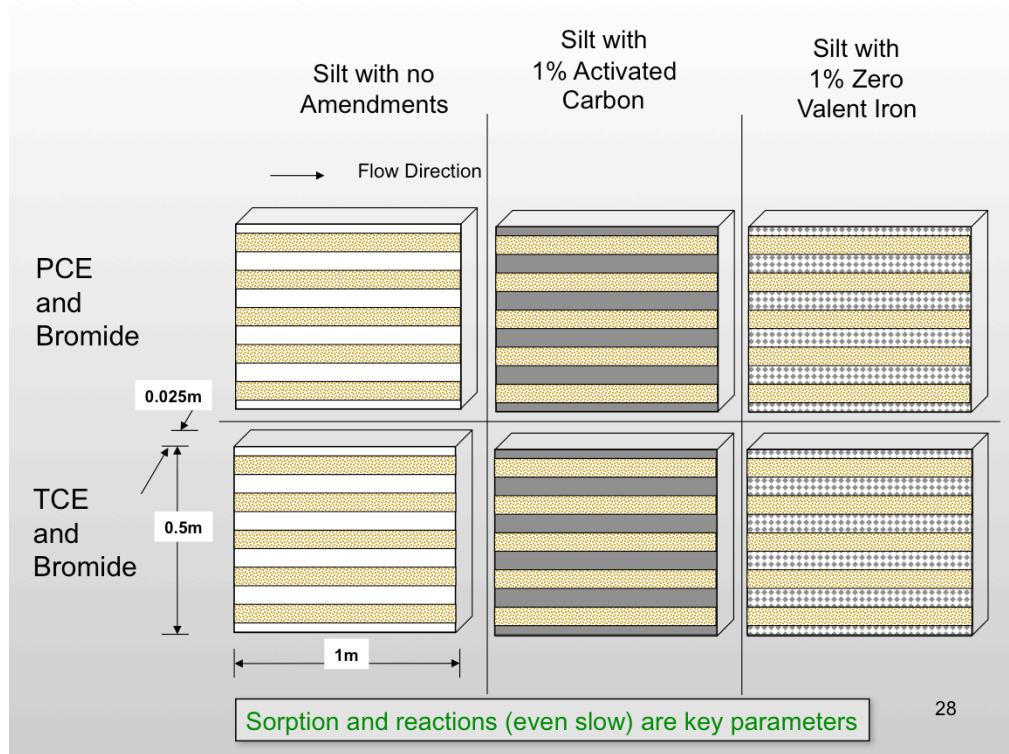
26

Thought Experiment 2)

What is the effect of upgradient flux reduction on downgradient water quality?



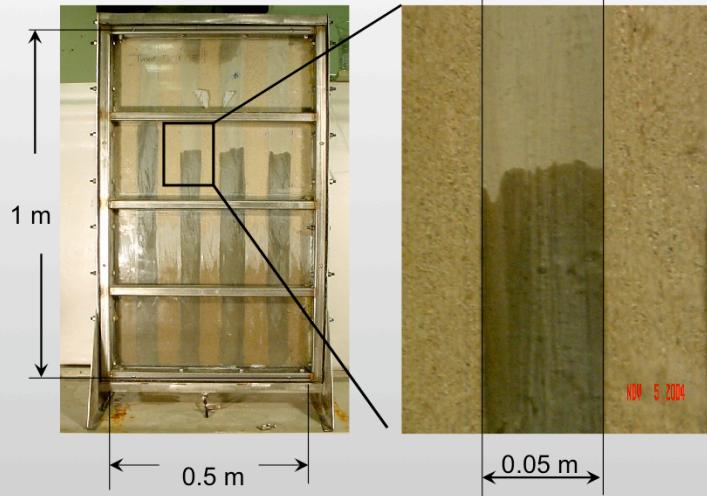
27



28

Multiple Layer Studies

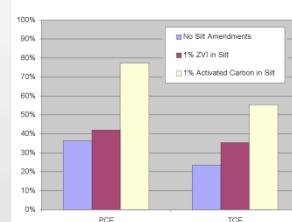
Source on for 25 days, Flushing with no source for an additional 53 day, Retained mass at 83 days



Colorado State University - Julio Zimbron, Leigh Neary, and Rachel Garcia

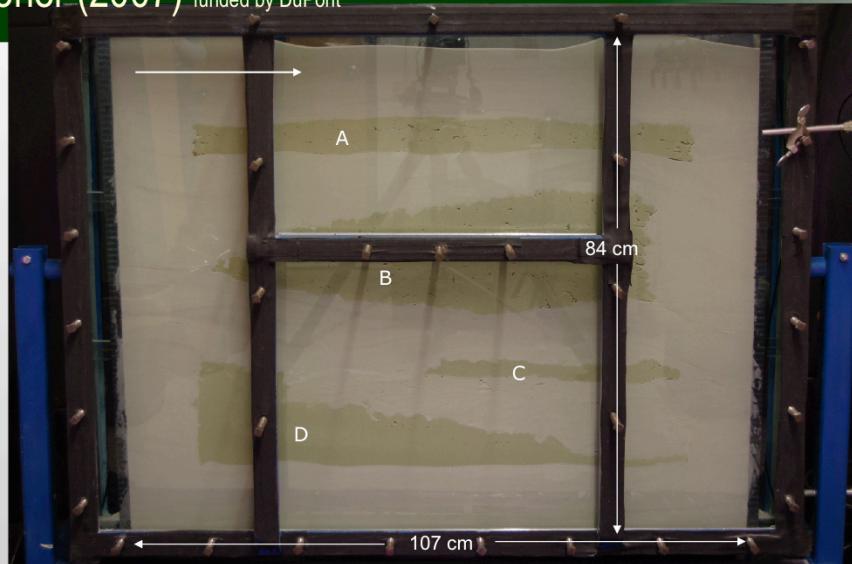
29

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



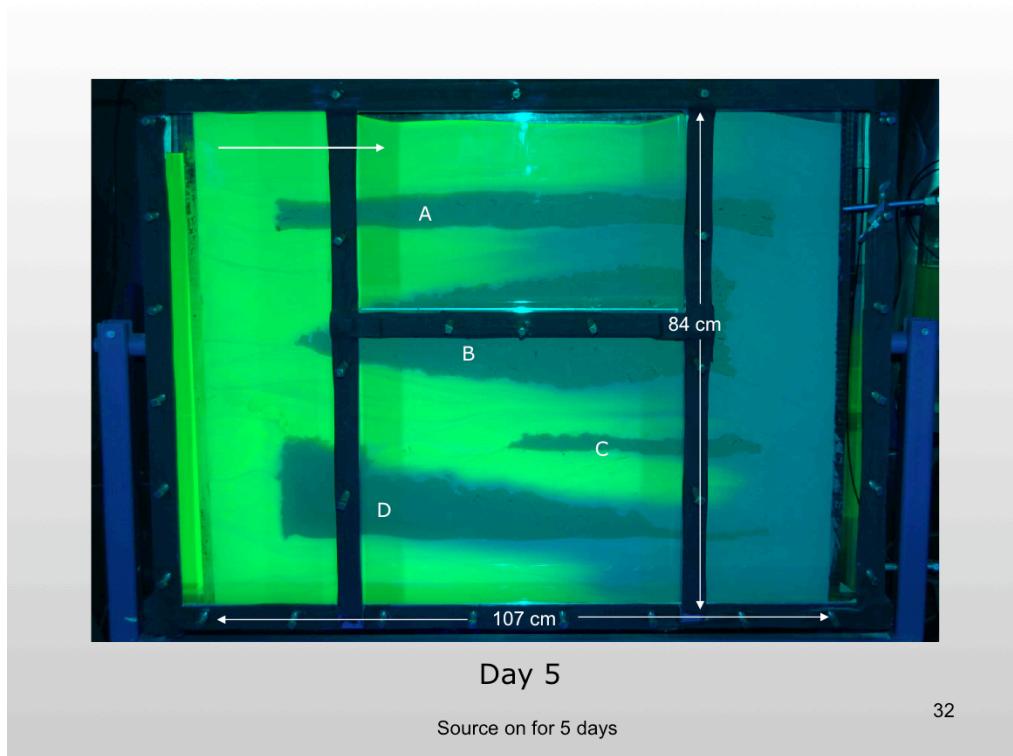
30

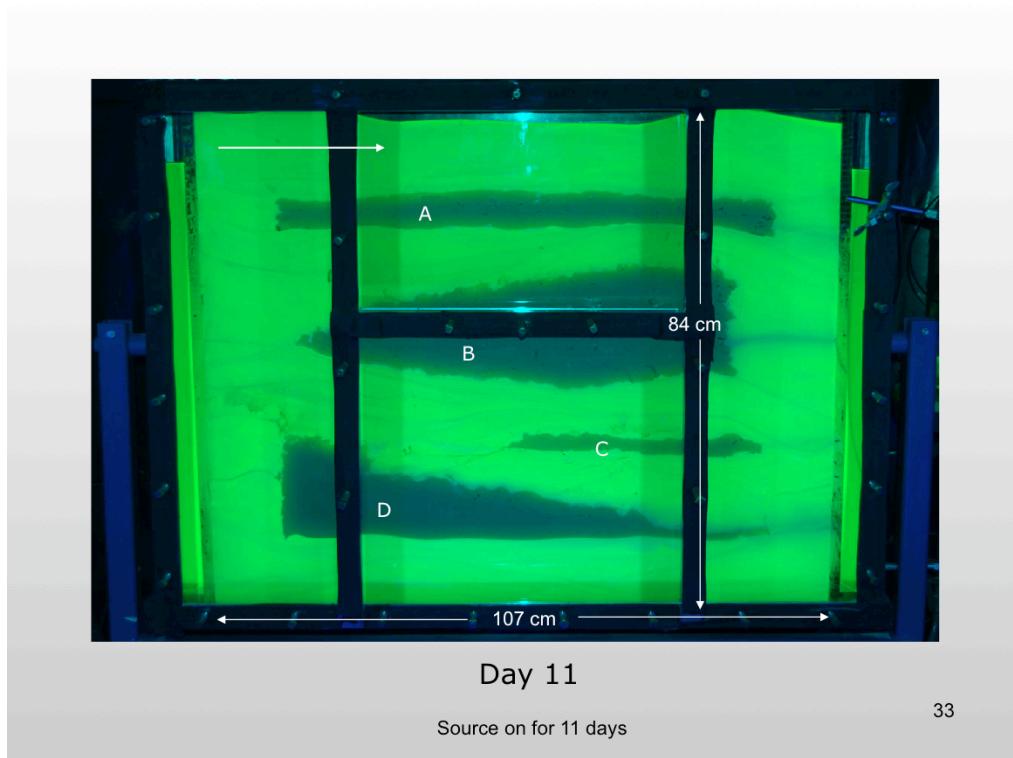
CSU Sand Tank Study Lee Ann
Doner (2007) funded by DuPont

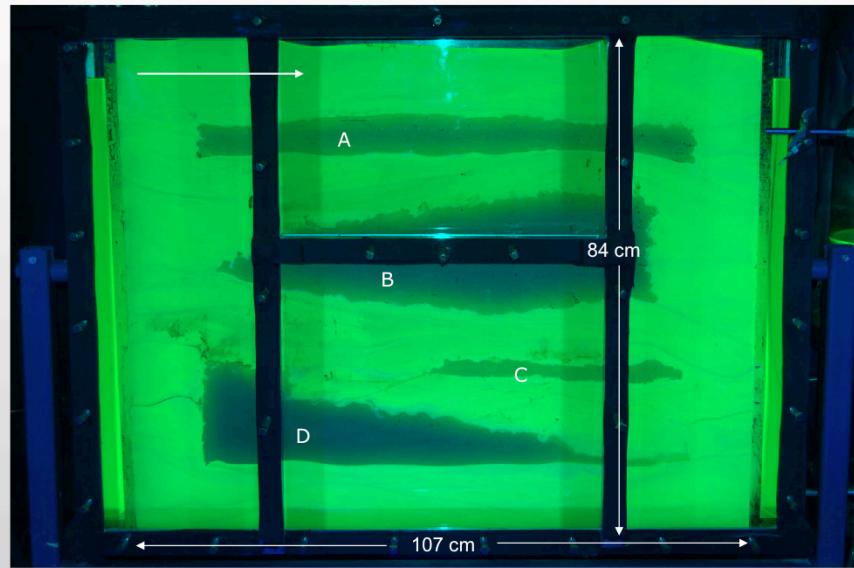


Day 1

31



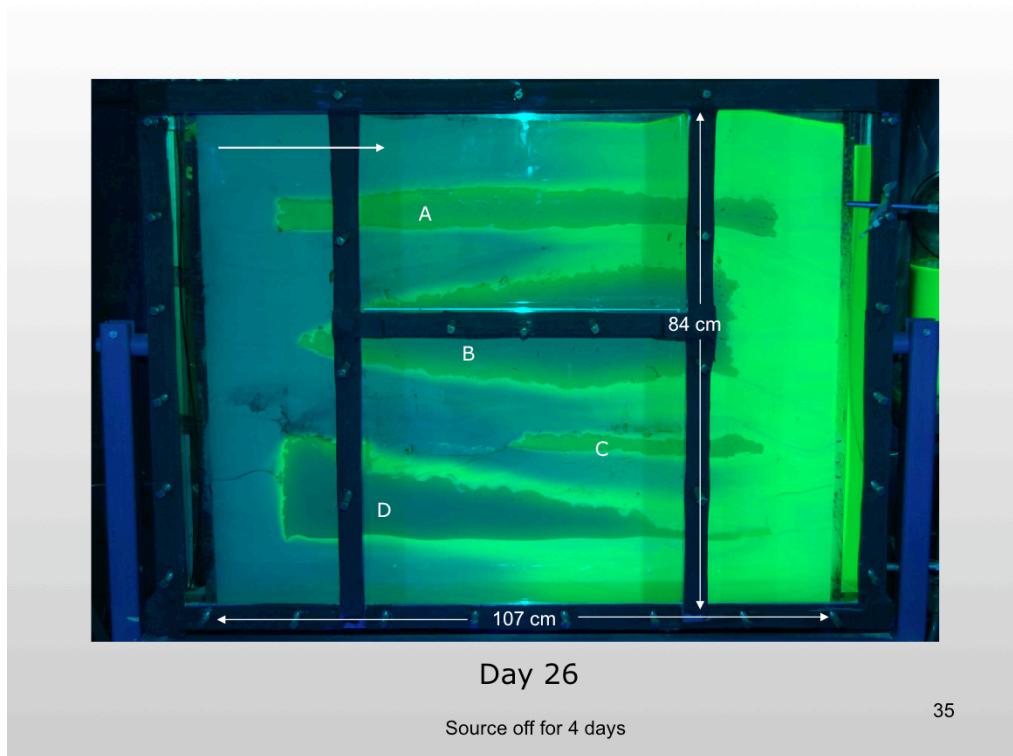


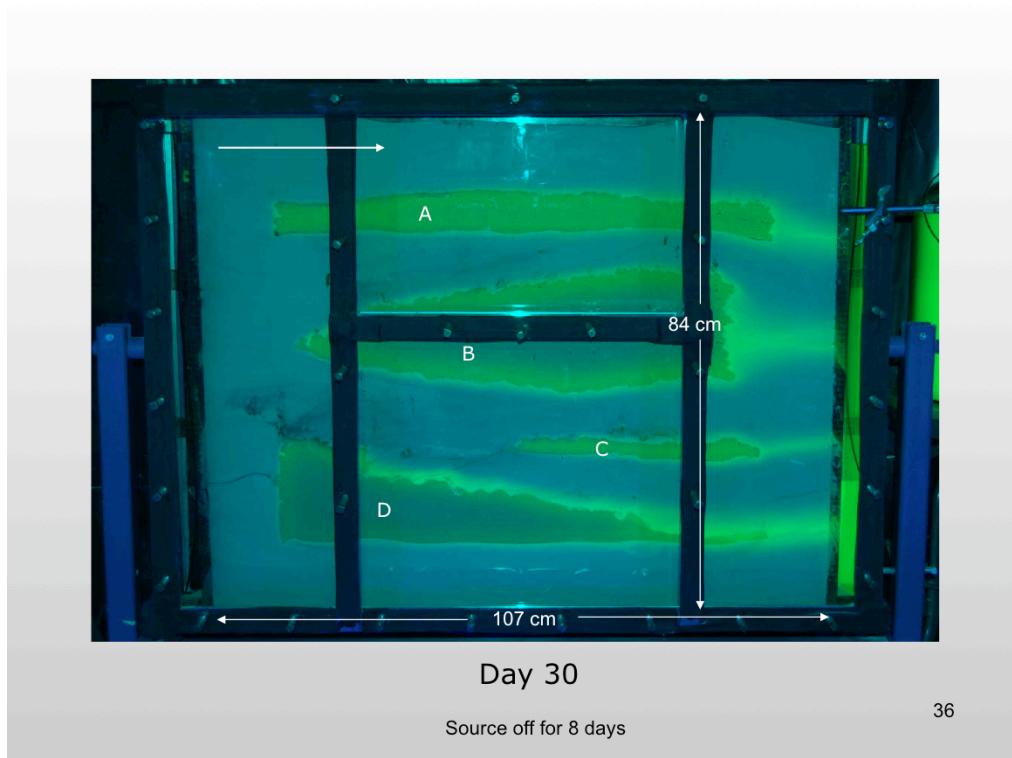


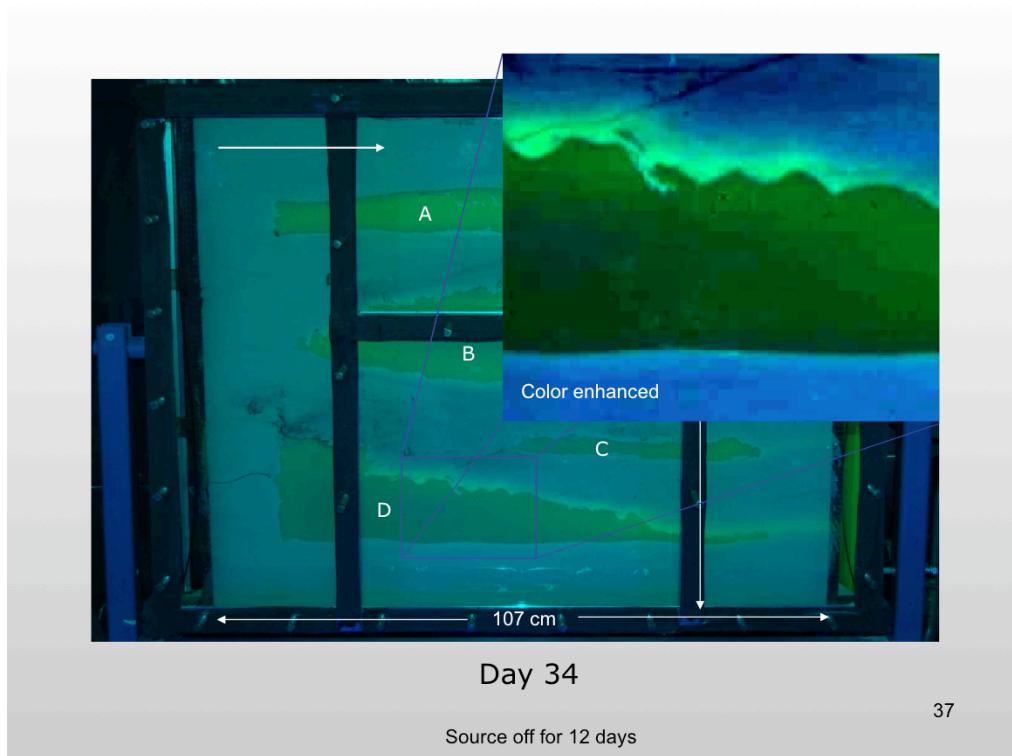
Day 23

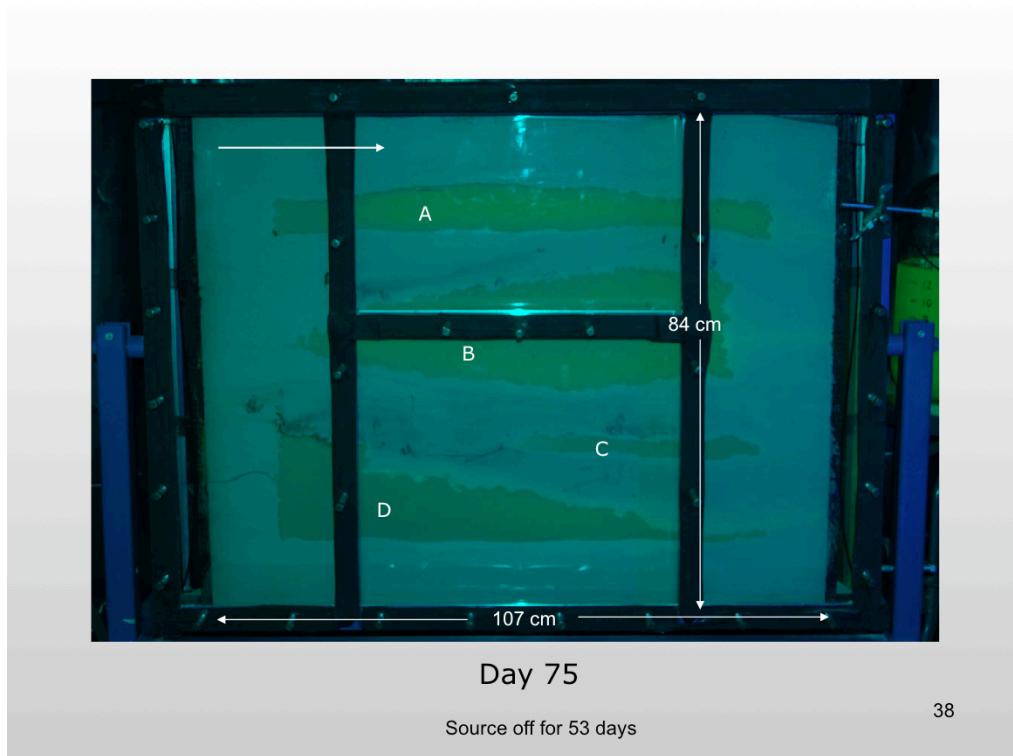
Source on for 23 days & shut off this day

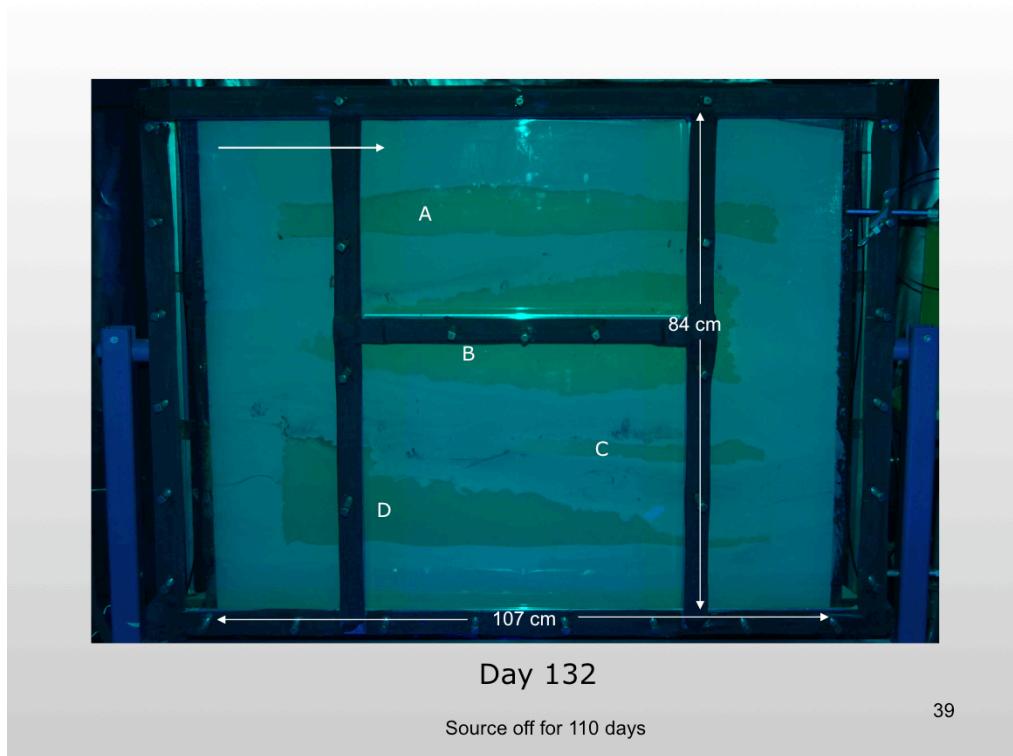
34





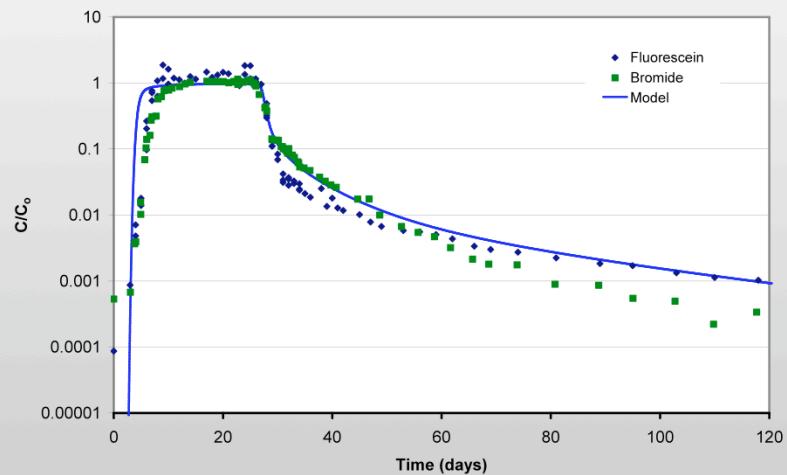






Effluent Concentrations from Sand Tank With HydroGeosphere Modeling Results (Chapman and Parker UW)

Comparison of Lab versus Model Effluent Concentrations



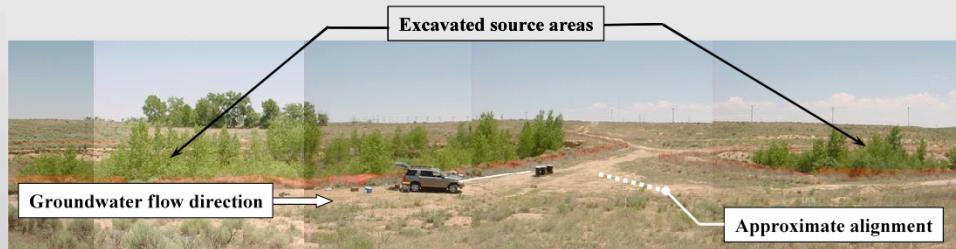
40

See Back Diffusion – The
Movie

Available on CLU-IN Web site

Example

Pueblo Chemical Depot



42

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 ebarriers for treatment of groundwater containing dissolved energetic compounds.

Secondary project objectives are to:

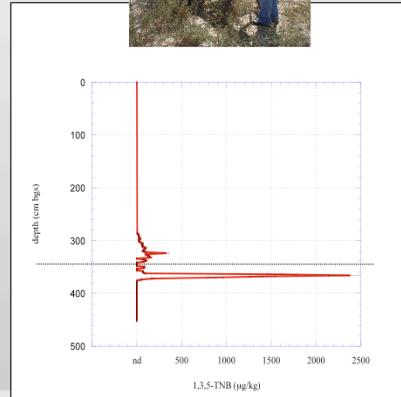
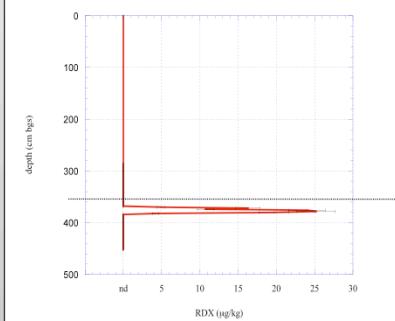
- 1) Evaluate the use of a four electrode set with respect to contaminant flux reduction,
- 2) Evaluate the use of commercially available off-the-shelf vinyl sheet pile as electrode support
- 3) Evaluate the use of a solar power supply
- 4) Provide the data necessary for Pueblo Chemical Depot to evaluate the use of ebarriers 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 Ah battery array (MK Battery). Voltage applied to the ebarrier is controlled using DC-DC converters (Vicor). Power consumption by the ebarrier is currently approximately 350 W.



43

Example



9. Why are contaminants in the vadose zone important?

Vadose Zone as *SOURCE*

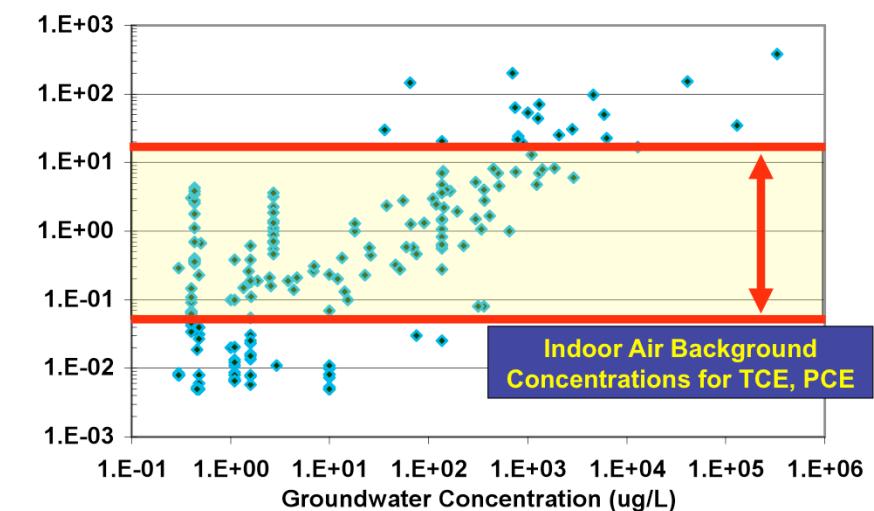
- Source compartments from 14 compartment model
- Most but not all sites dominated by saturated zone sources
- SVE: soil moisture key performance factor

Vadose Zone as *PATHWAY*

- Indoor air pathway - empirical studies and model development
- Confirming impacts difficult
- ESTCP and SERDP key players

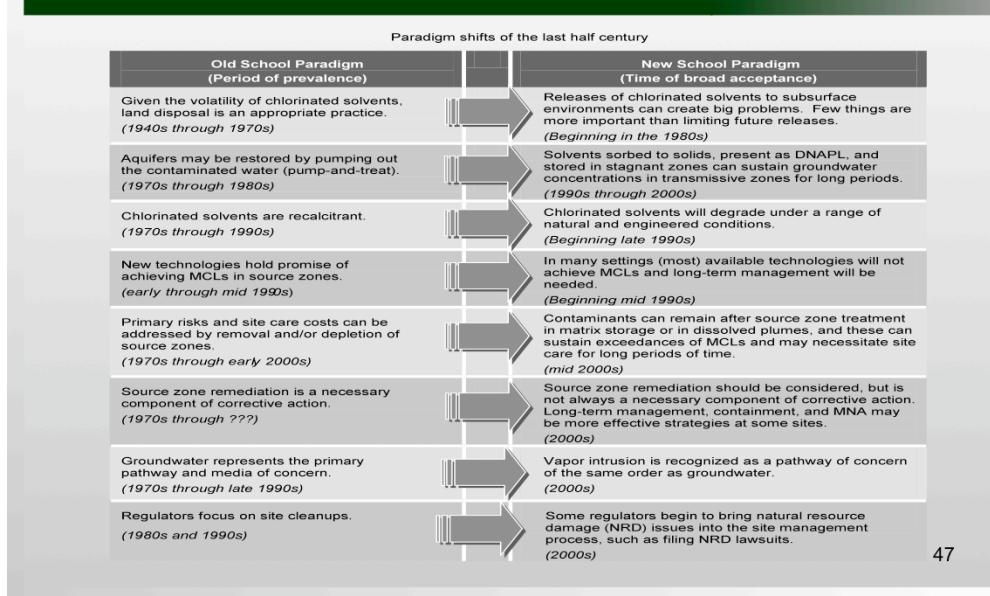
45

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



46

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



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?

•Chemical Oxidation

- *Permanganate*
- *Peroxide*
- *Persulfate*

•Thermal

- *Conductive*
- *Electrical*

50

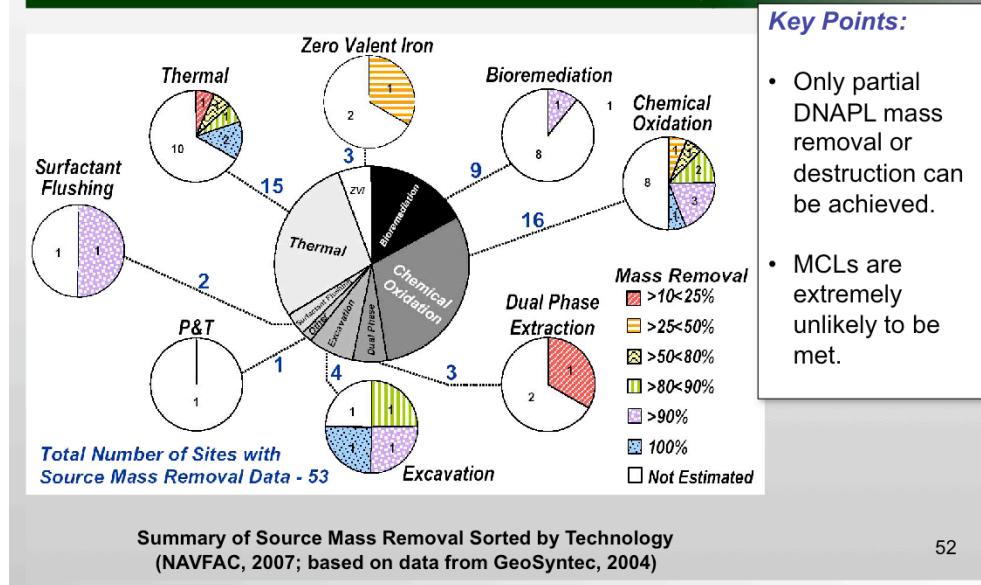
12. Which *in-situ* source treatment technologies are receiving the widest use?

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

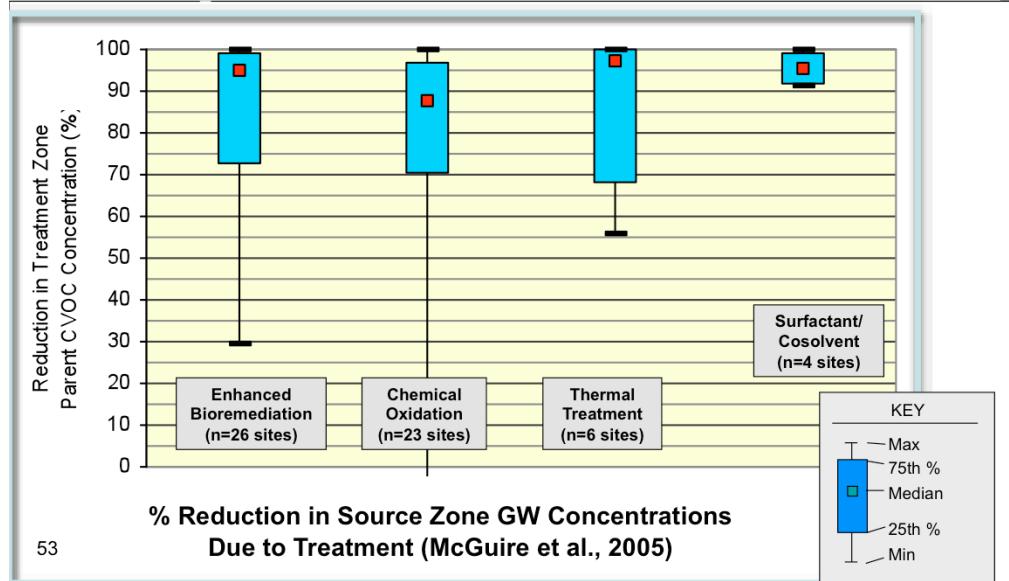


51

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



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



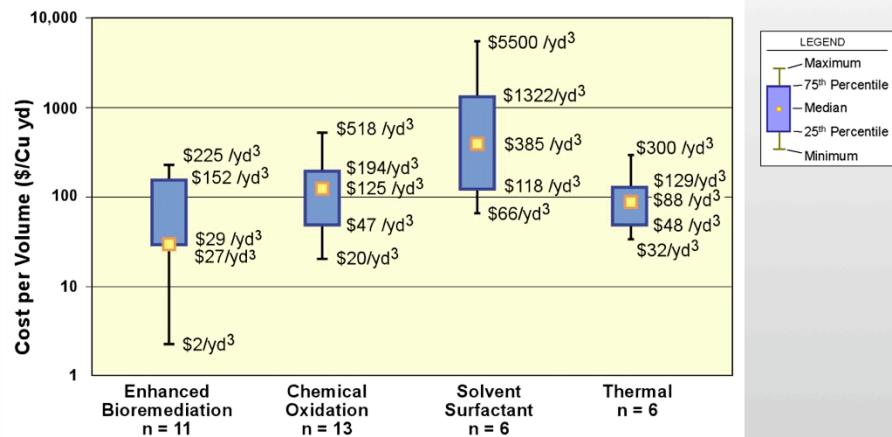
13. What can we expect from common source treatment technologies? (cont'd)

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)

55

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

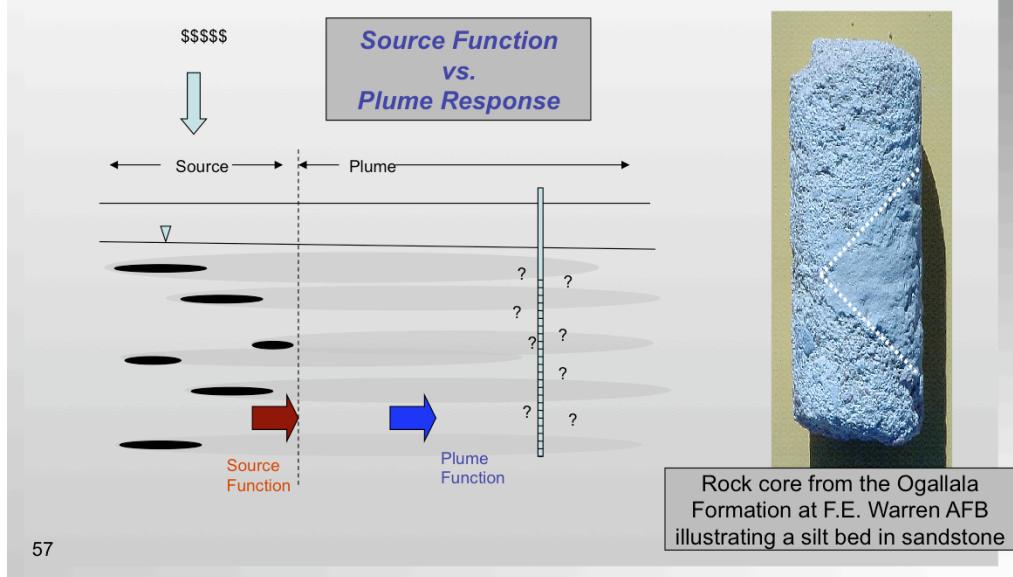
Very General Rule of Thumb

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.



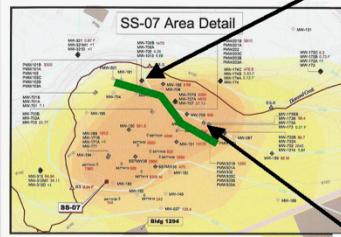
56

15. How will reduced loading from sources affect plumes?

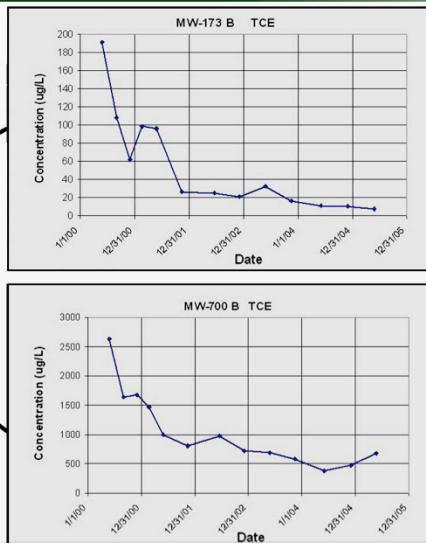


15. How will reduced loading from sources affect plumes? (cont'd)

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

58

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.**

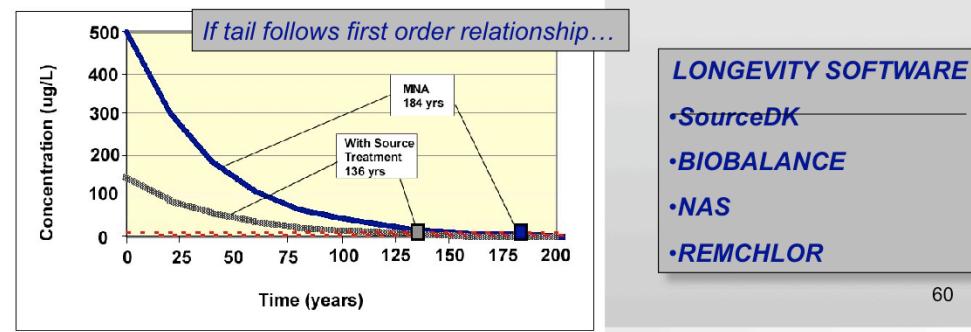
But with fast groundwater flow, low mass storage, and/or active attenuation...

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

59

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

- One benefit 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”



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**



61

17. What can we expect from containment measures?

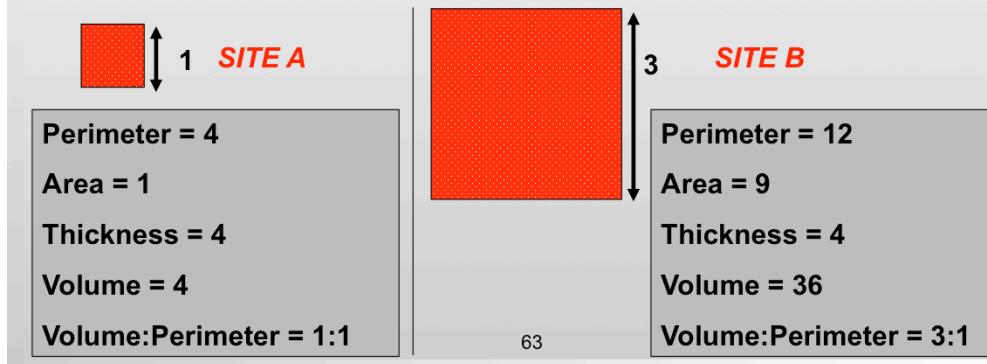
- 43 of 52 full scale ZVI barriers are “meeting regulatory expectations”
- 25 of 29 sites with physical barriers have “acceptable performance” in medium term (10 years or less)
- MNA sole remedy (no source treatment) at 30% of 191 MNA sites



62

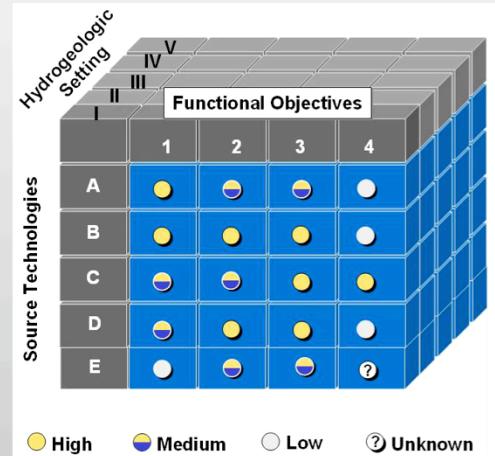
20. How does one compare treatment vs. containment?

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



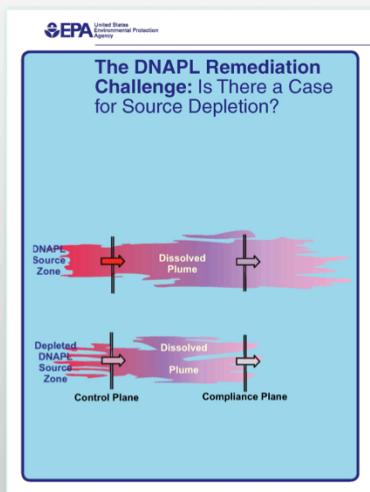
20. How do site characteristics affect clean-up decisions?

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



64

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.

65

Qualitative Decision Chart: *RC Approach*

Yes, Source Depletion



No, Source Depletion



GLADIATOR



66

Key Factors for Deciding

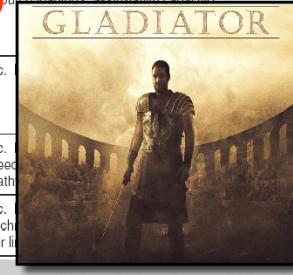


■ Source Zone:	<i>Expanding</i>	<i>Immobile</i>
■ Plume Status:	<i>Expanding</i>	<i>Stable</i>
■ Resource Value:	<i>High</i>	<i>Low</i>
■ Containment Cost:	<i>High</i>	<i>Low</i>
■ Will Reduce Remed. Timeframe?	<i>A Lot</i>	<i>A Little</i>
■ Need for Rapid Cleanup?	<i>Yes</i>	<i>No</i>

67

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	<ul style="list-style-type: none"> 1a. Expanding P_L Zone (probably care at chlorinated solvent sites problem too)  	<ul style="list-style-type: none"> 1b. Free-Phase DNAPL present but stable in stratigraphic traps 1c. Immobile, residual DNAPL Zone
Reduce source longevity, and reduce long-term management requirements	<ul style="list-style-type: none"> 2a. High life-cycle containment cost (for example, containment Net Present Value (NPV) >> cost of remediation) 3a. Low reliability containment system 4a. High probability of loss due to DNAPL (for example, sole-source aquifer OR Well Yield < 1000 mg/L with TDS > 3000 mg/L) 5a. High probability of meaningful reduction in time to reach MCLs (for example, small sites with low complexity) 	<ul style="list-style-type: none"> 2b. Moderate life-cycle containment cost 3b. Moderate probability of containment system 4b. Moderate resource value 5b. Moderate probability of a meaningful reduction in time to MCLs
Near-term enhanced natural attenuation due to reduced dissolved phase loading	<ul style="list-style-type: none"> 6a. Expanding dissolved phase plume (source loading > assimilative capacity)  	<ul style="list-style-type: none"> 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)	<ul style="list-style-type: none"> 7a. Receptor in or impacted soon (for example, < 2 years)  	<ul style="list-style-type: none"> 7b. Potential longer-term risk to receptor (for example, >2 years travel time) 7c. Receptor in or impacted soon (for example, < 2 years) 
Near-term attainment of MCLs	<ul style="list-style-type: none"> 8a. Need for rapid cleanup (for example, pending property sale) 	<ul style="list-style-type: none"> 8b. Limited need for rapid cleanup 8c. Need for long-term path
Intangibles	<ul style="list-style-type: none"> 9a. Desire for active remedy; desire to test new technologies; desire to recuse stewardship burden on future generations 	<ul style="list-style-type: none"> 9b. Neutral on intangible issues. 9c. Desire for long-term path



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

69

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

NRC Philosophy:

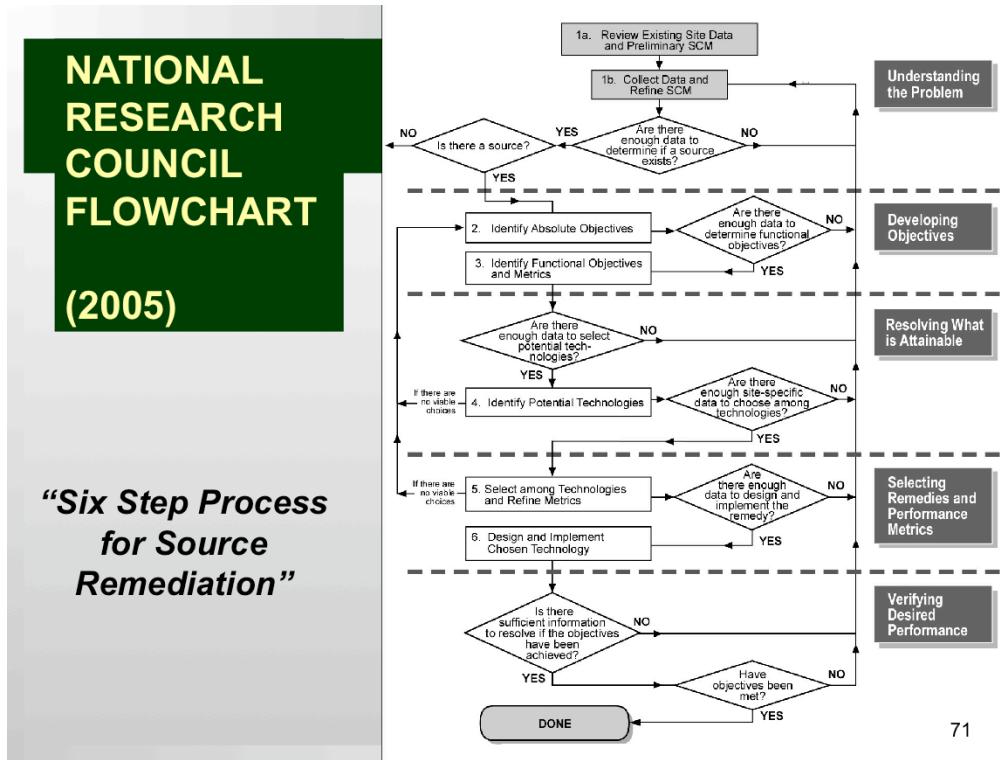
Two different *categories* of objectives:

- *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.

70

NATIONAL RESEARCH COUNCIL FLOWCHART (2005)

“Six Step Process for Source Remediation”



71

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

72

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

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

74

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 (**SERDE**) 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://gwf.clini.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



Aqueous phase in transmissive zones
DNAPL in transmissive zones

Sorbed phase transmissive zones
Aqueous phase in low permeability zones
Sorbed phase in low permeability zones
DNAPL in low permeability
Vapor in transmissive zones
Vapor in low permeability zones

76

Discussion



77

Thank You

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

[Links to Additional Resources](#)

[Feedback Form](#)