

# **SHORT COURSE**

## **Tools for Management of Chlorinated Solvent – Contaminated Sites**

3 December 2009



**SERDP**



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# Short Course Agenda



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

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# **Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents**

## **ER-0530**

Tom Sale, Chuck Newell,

Hans Stroo, Rob Hinchee, and Paul Johnson

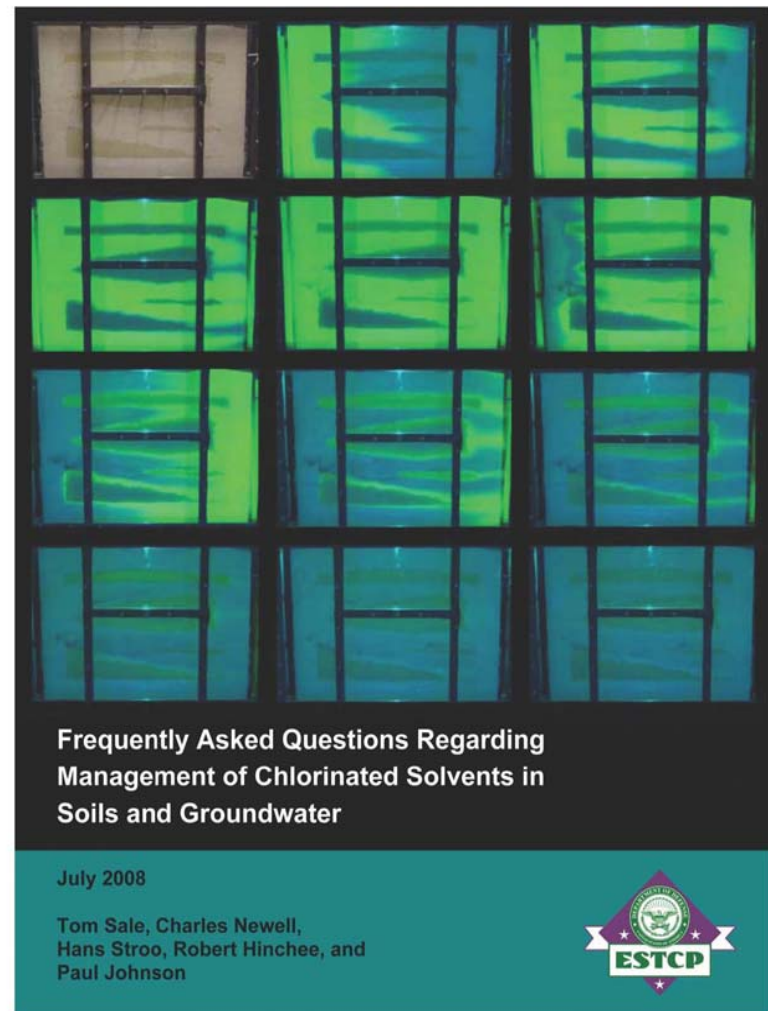


**SERDP**



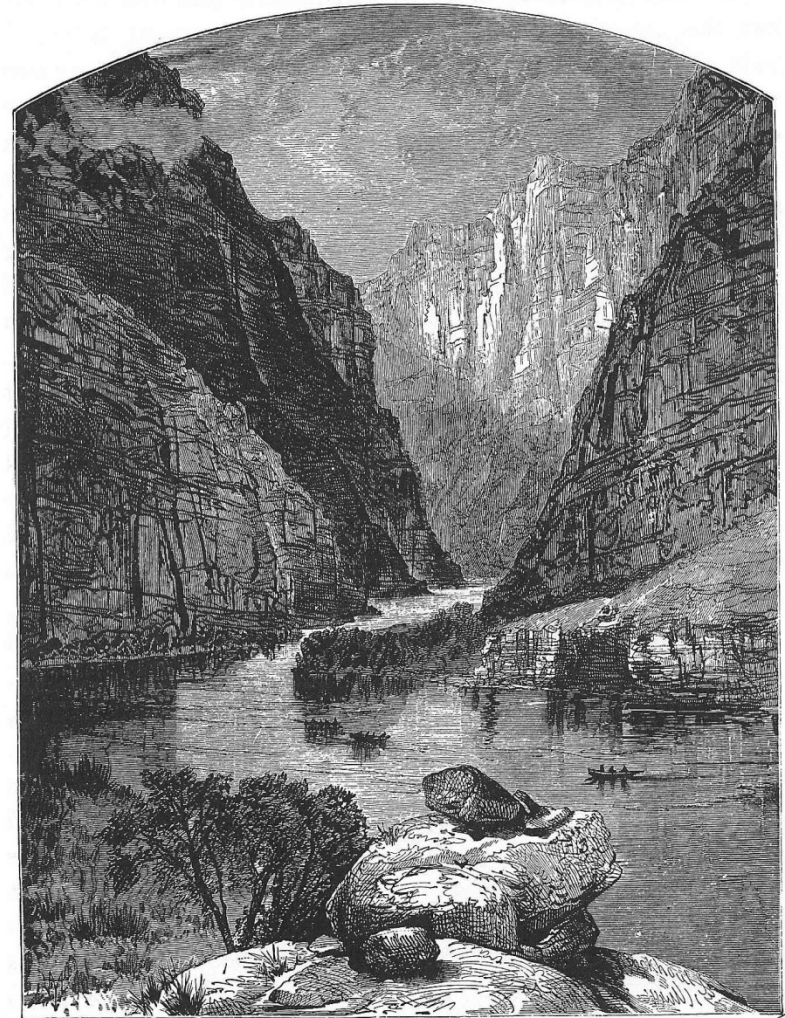
# Frequently Asked Questions

- Provides quick access to key concepts and references for those who need to know more
- August 2008
- Google - Chlorinated Solvents FAQs
- <http://www.estcp.org/Technology/upload/ER-0530-FAQ.pdf>



# Decision Guide

- Supports
  - ◆ Understanding site specific conditions,
  - ◆ Developing goals,
  - ◆ Selecting technologies, and
  - ◆ Packaging site remedies

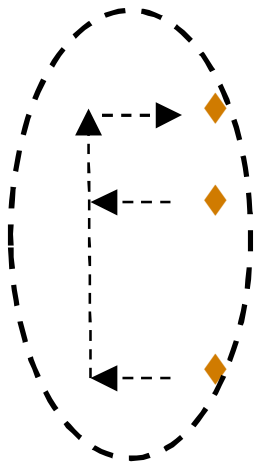


GATE OF LODORE.



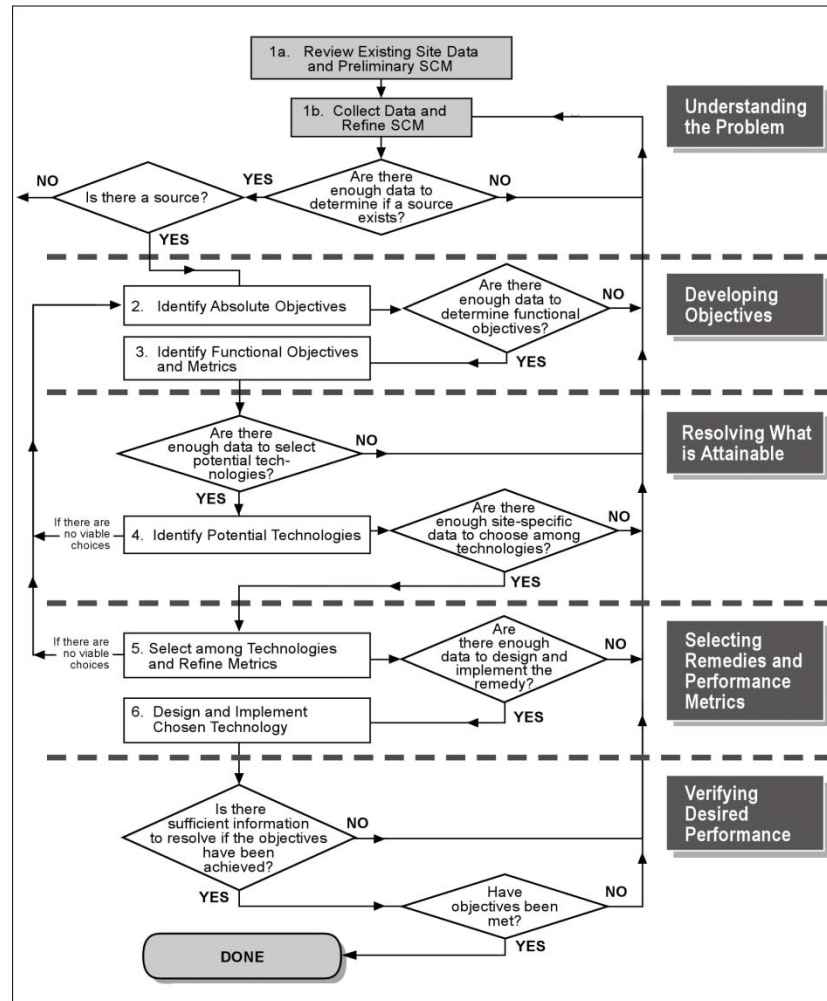
# Decision Guide

- Supports
  - ◆ Understanding site specific conditions,
  - ◆ Developing goals,
  - ◆ Selecting technologies, and
  - ◆ Packaging site remedies



GATE OF LODORE.

# Following NRC 2005



# **Understanding site specific conditions**



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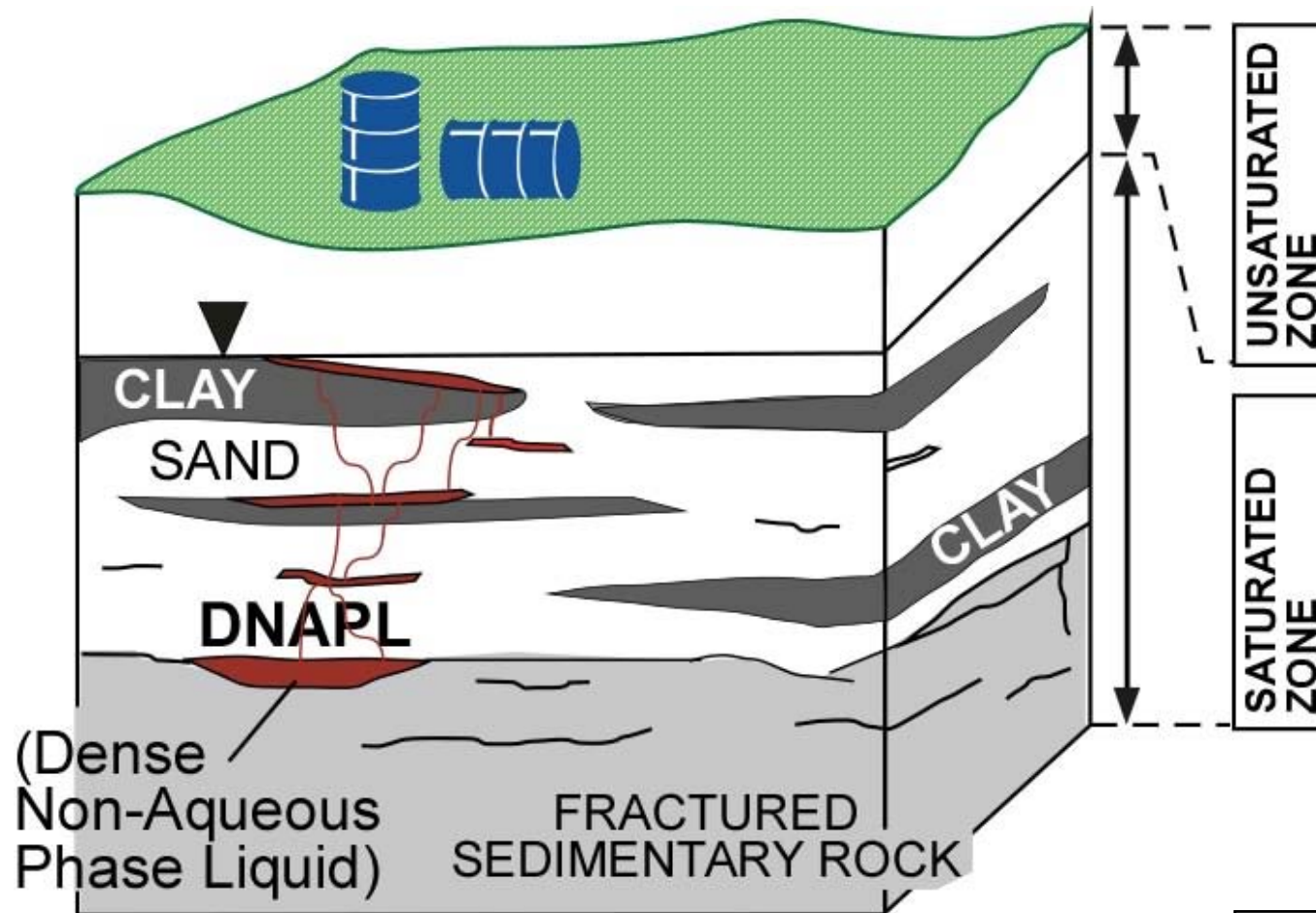


# **Inadvertent releases reflecting past practices...**





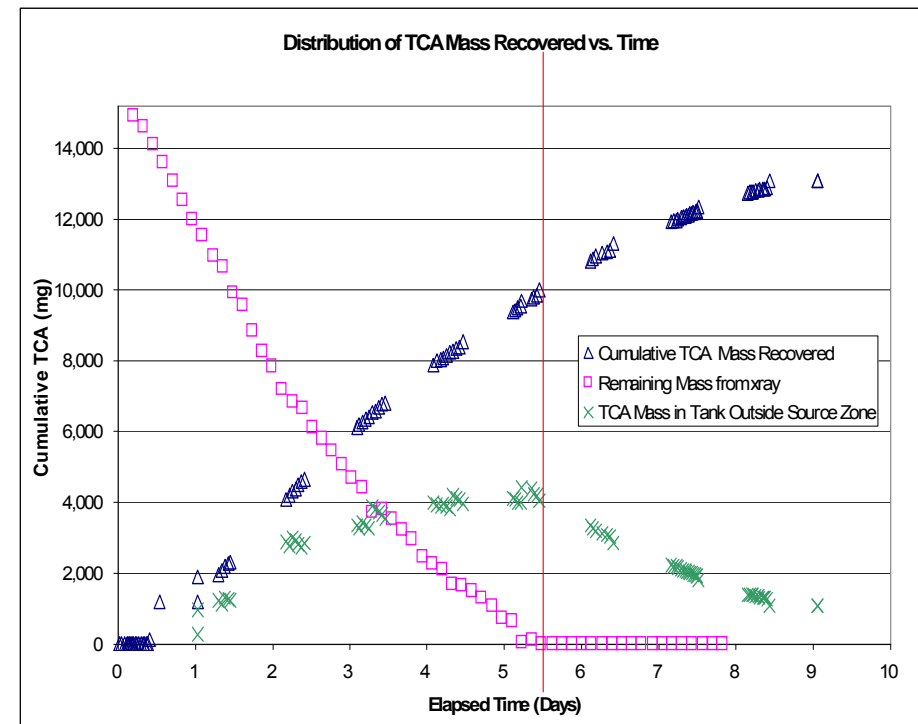
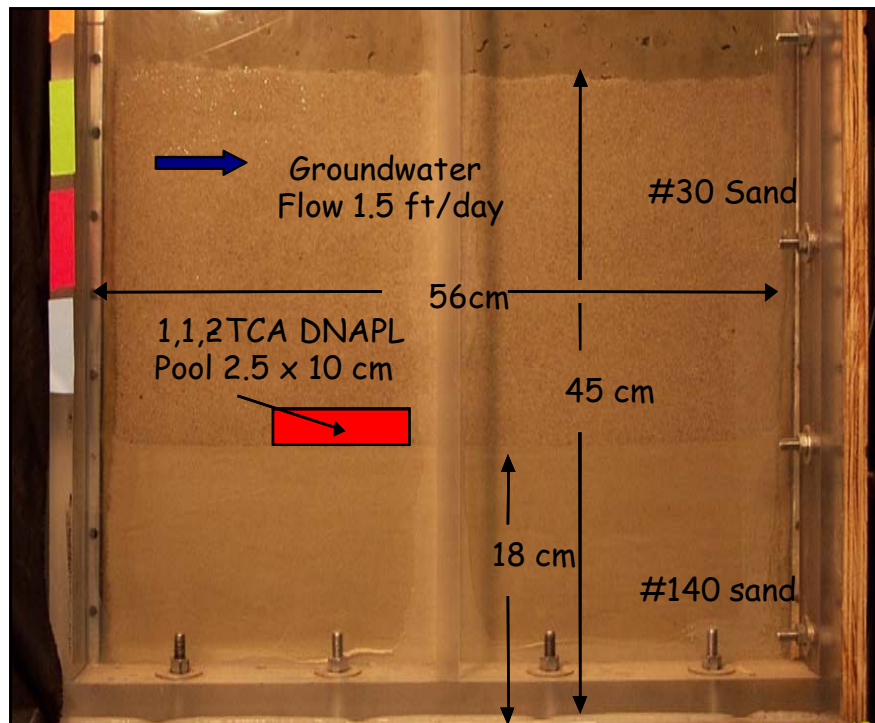
## Early Stage





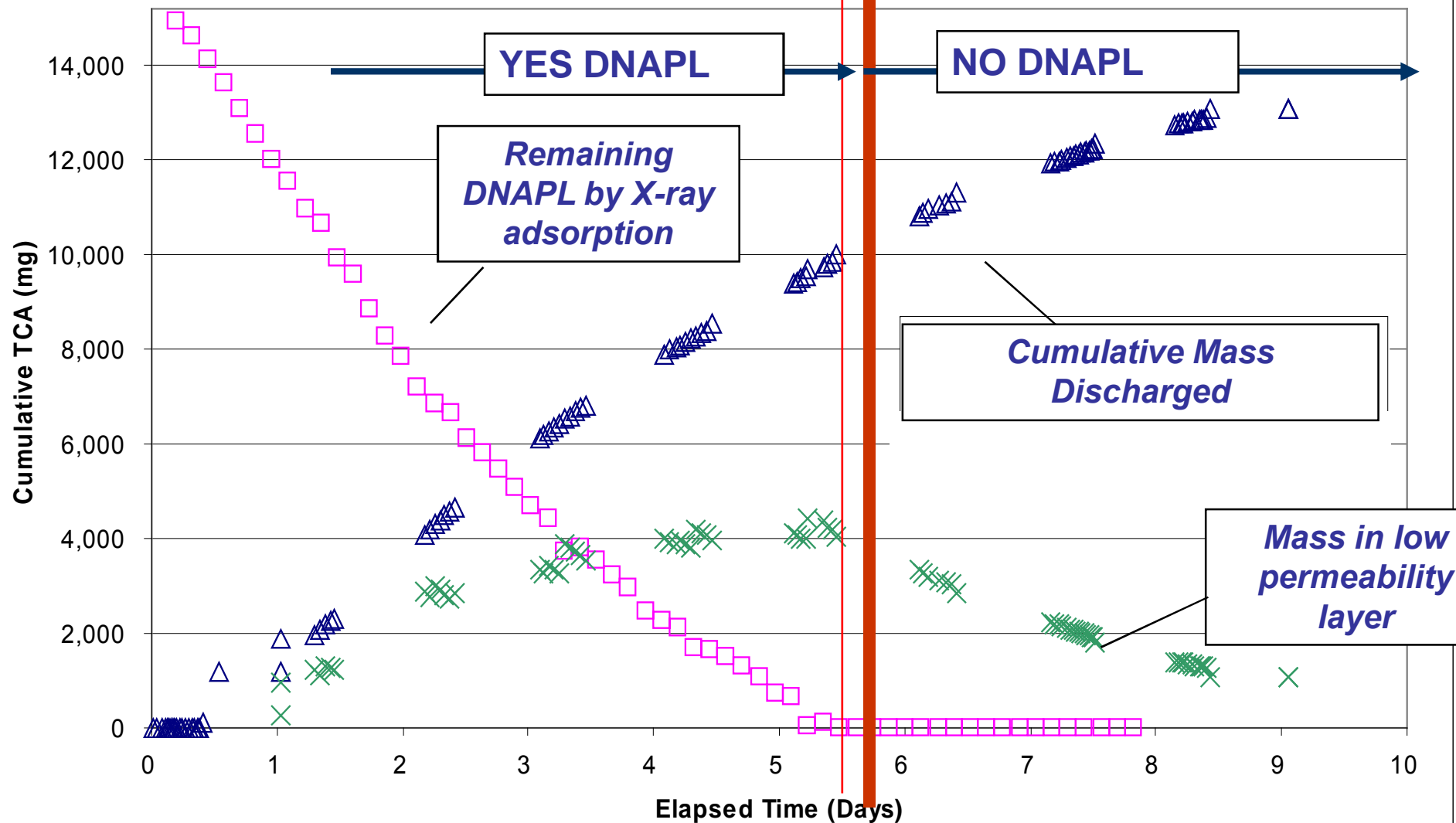
# Two layer sand tank study

Colorado School of Mines (Tissa Illangasekare and Bart Wilkins)



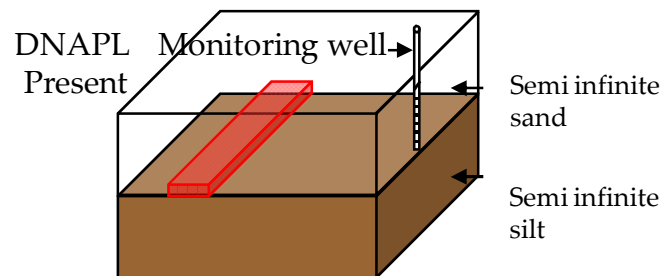
AFCEE Source Zone Initiative (2007)

Distribution of TCA Mass Recovered vs. Time

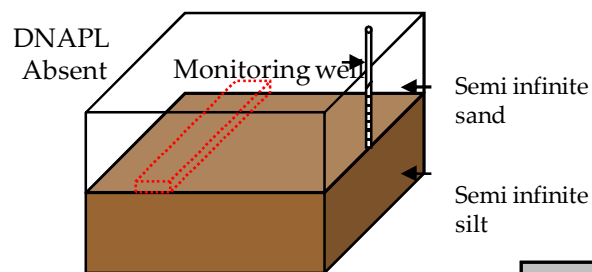


AFCEE Source Zone Initiative (2007)

# Aqueous and sorbed phases in transmissive and low permeability zone

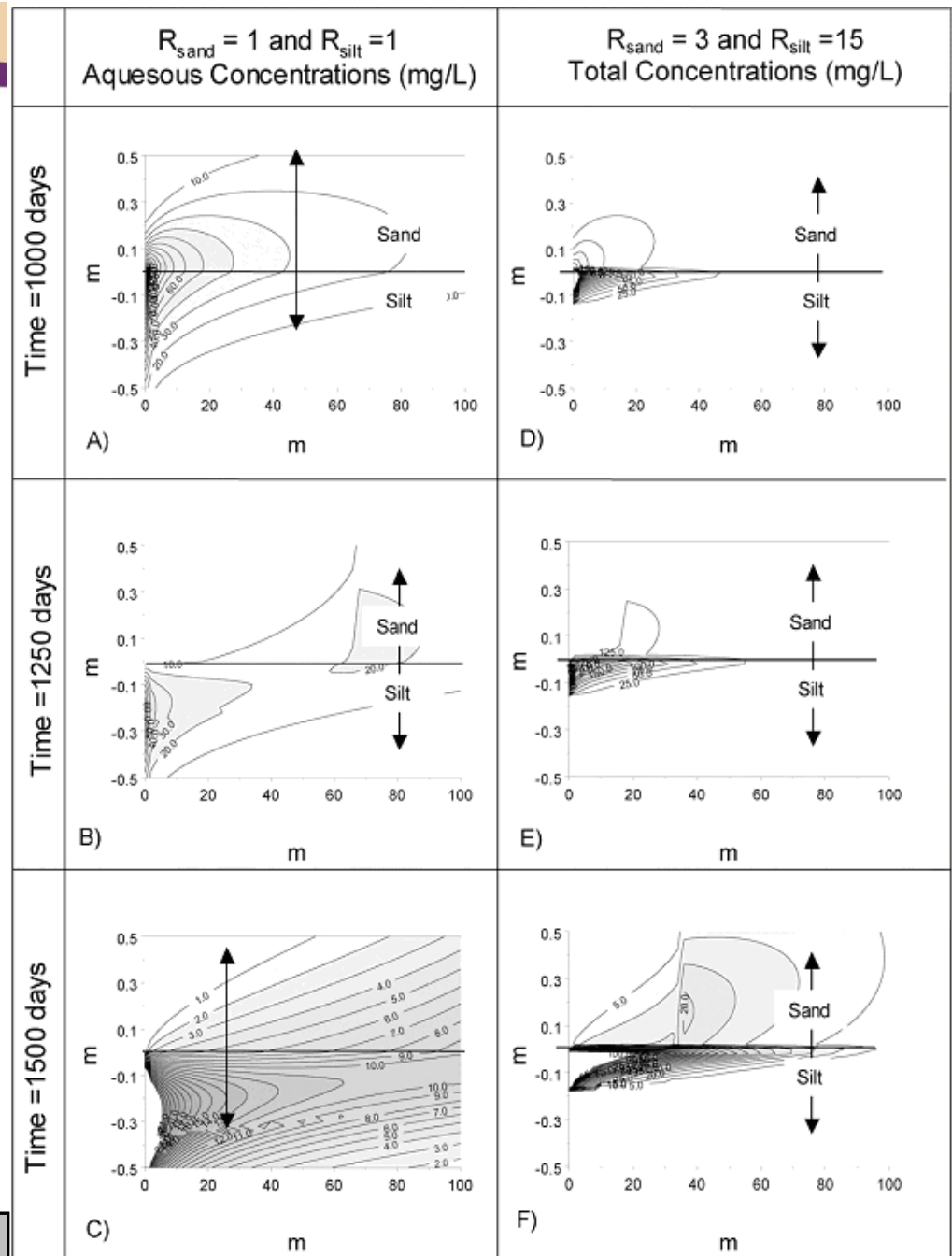


On for 1000 days



Off

Sale et al., 2008



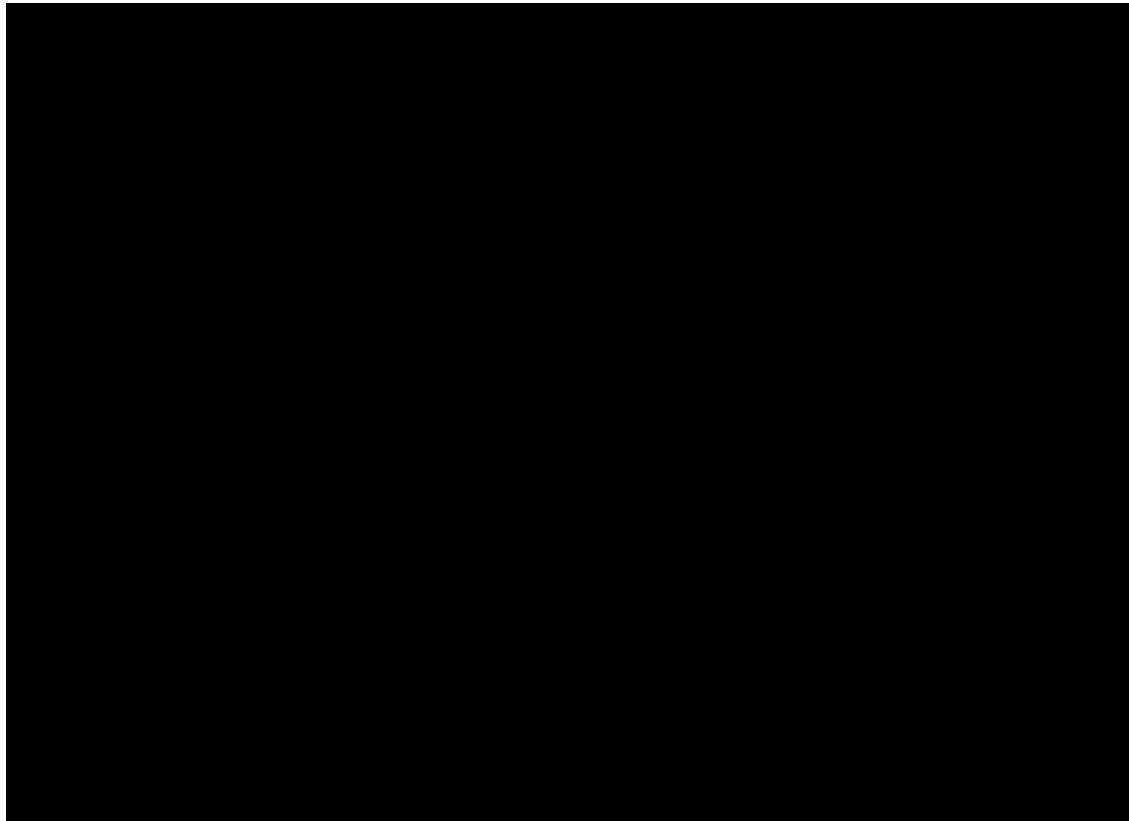


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# **Back Diffusion – The Movie**

**Lee Ann Doner – (2008) MS CSU**





# “Sandy aquifers”



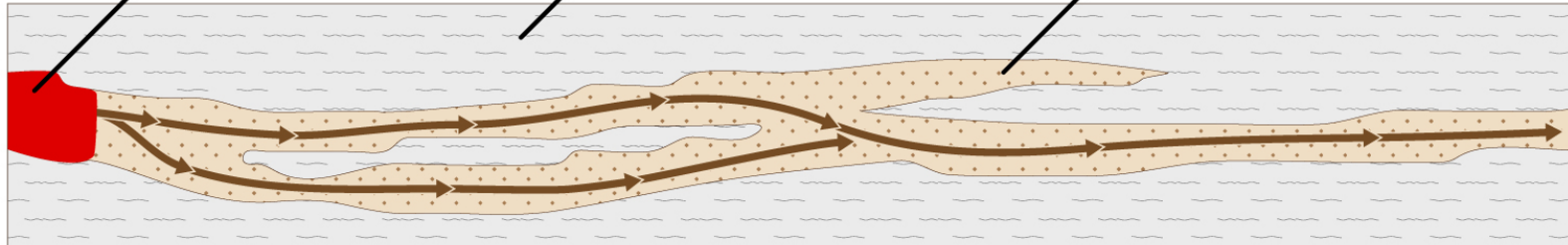
Image from Fred Payne /ARCADIS



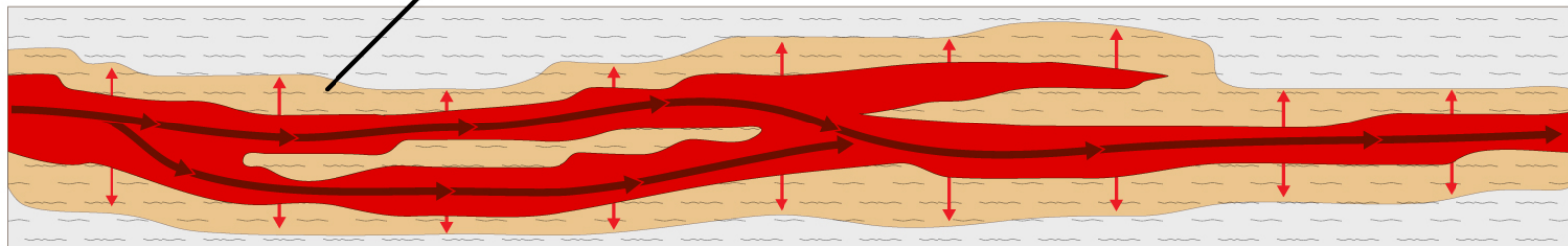
# New Paradigm



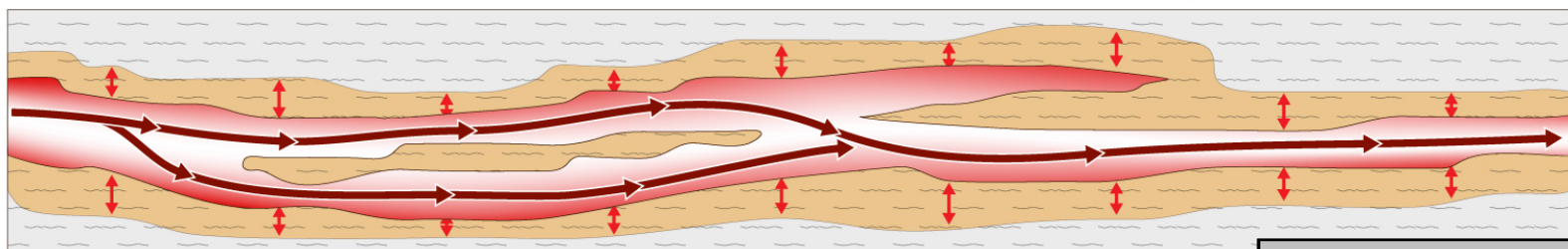
Advancing solvent plume      Low permeability silts      Transmissive sand



Expanding diffusion halo in stagnant zone

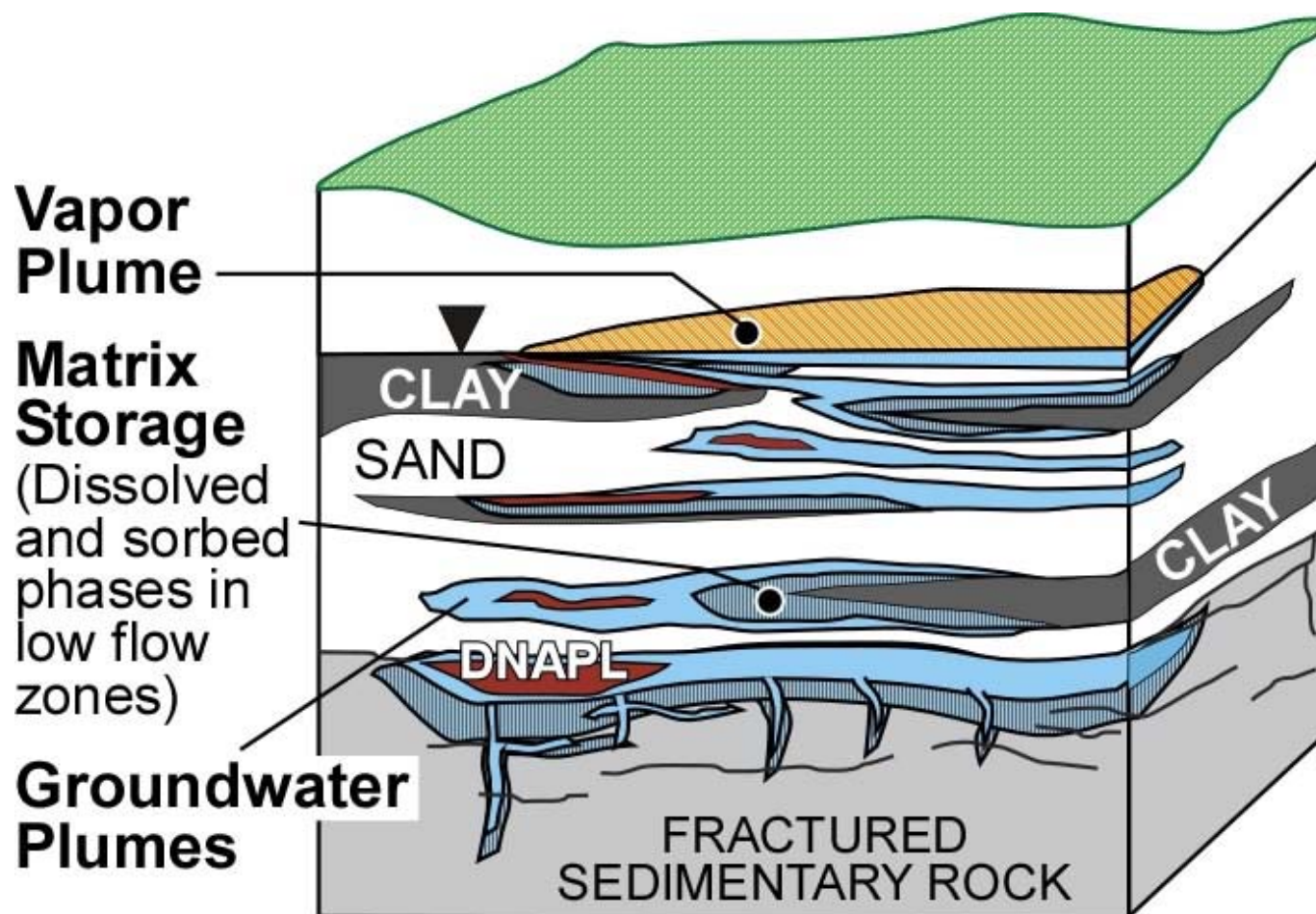


Simultaneous inward and outward diffusion in stagnant zones

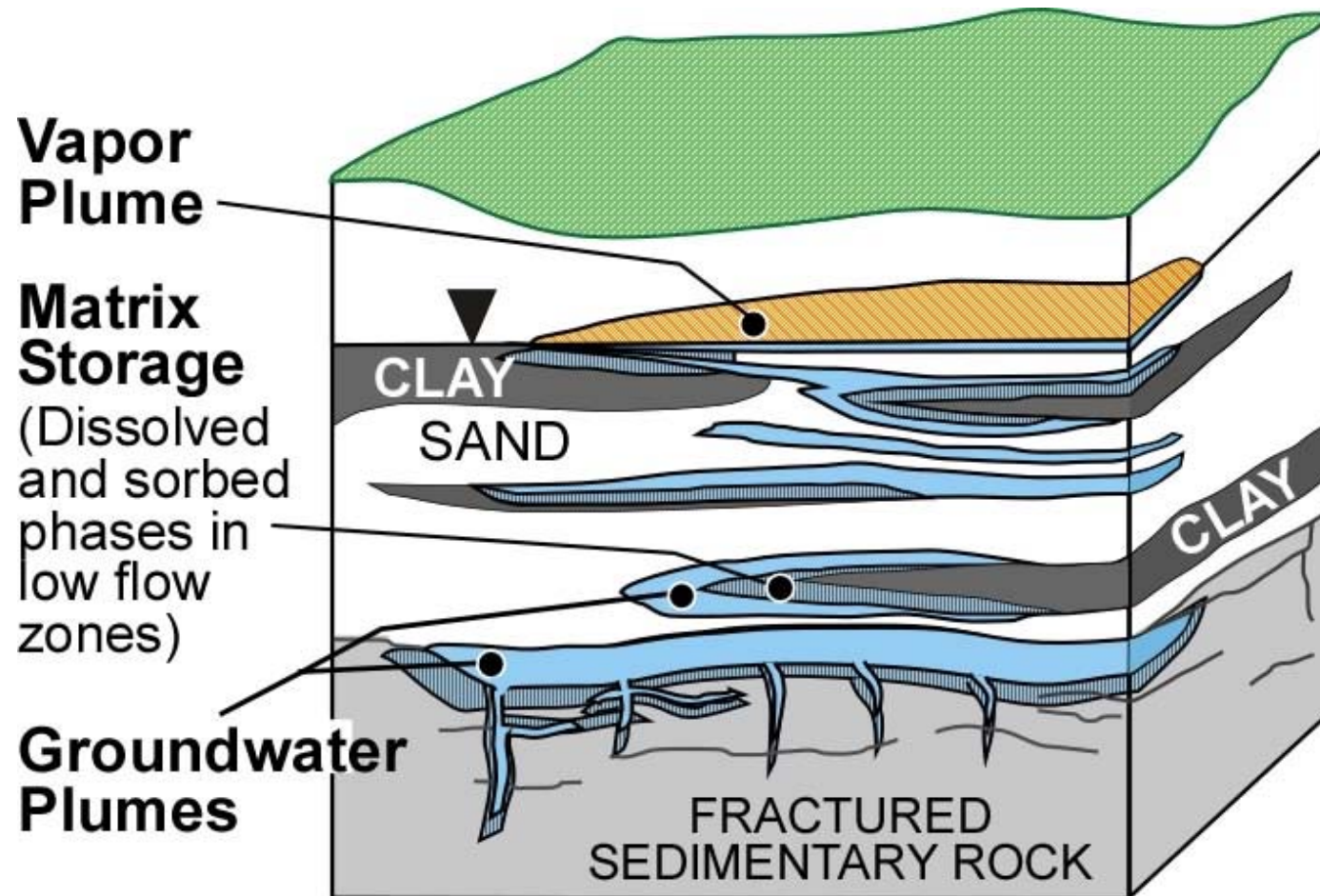


After NRC 2005

## Middle Stage



## Late Stage



Sale et al., 2008



# The 14 Compartments Model

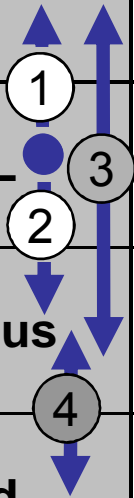
(a holistic perspective)

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

Sale et al., 2008

# With interdependencies (Option 1)

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				



# With interdependencies (Option 2)

Lattice of 17 potentially relevant fluxes

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

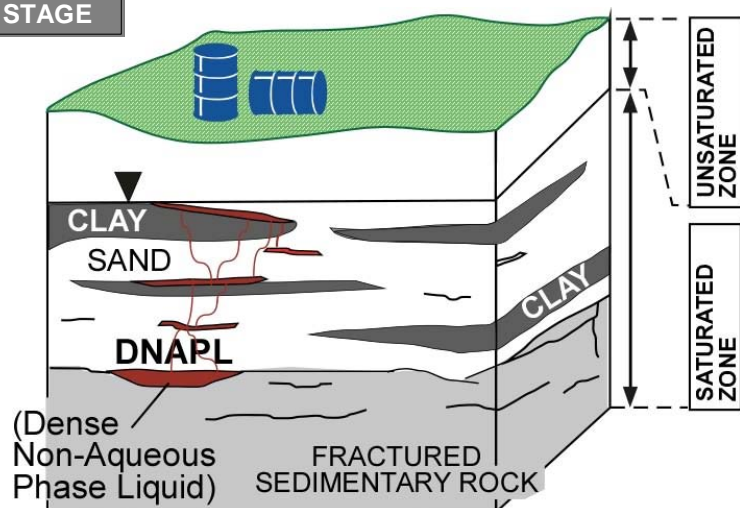
# With interdependencies (Option 2)

Lattice of 17 potentially relevant fluxes

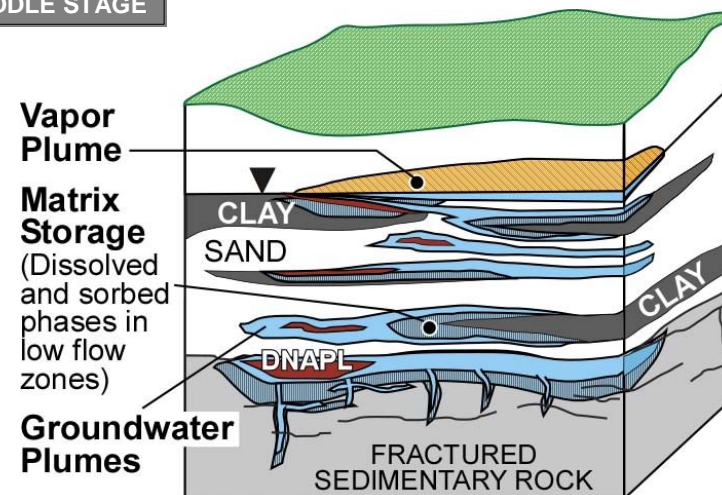
	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

# Mapping the evolution of a chlorinated solvent release

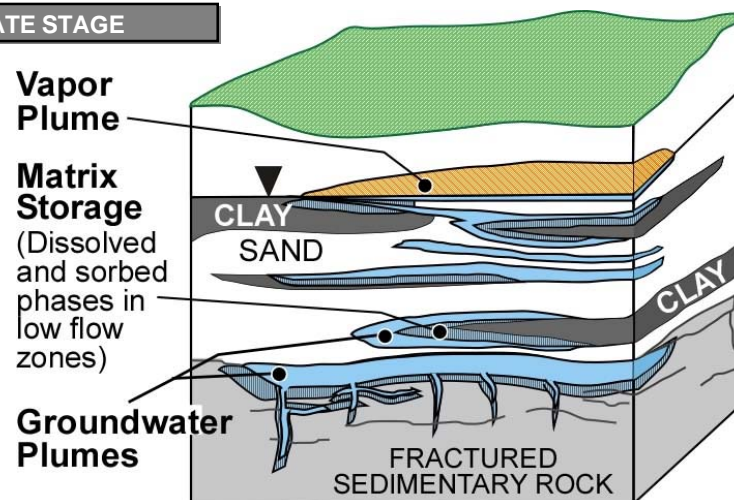
EARLY STAGE

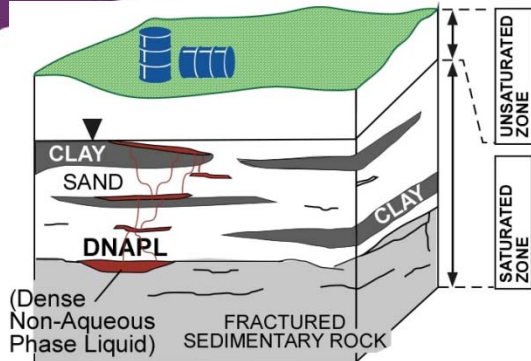


MIDDLE STAGE



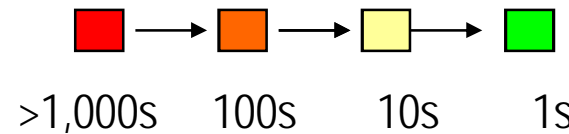
LATE STAGE



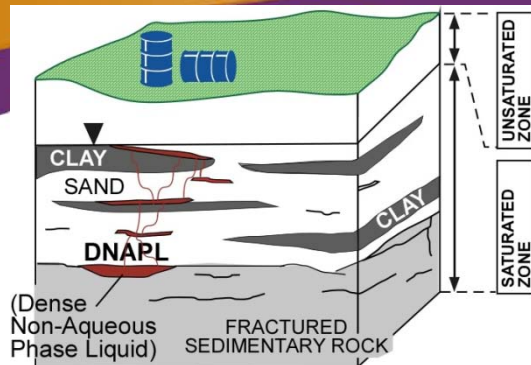


# Early Stage

Gw. or equivalent gw. conc.



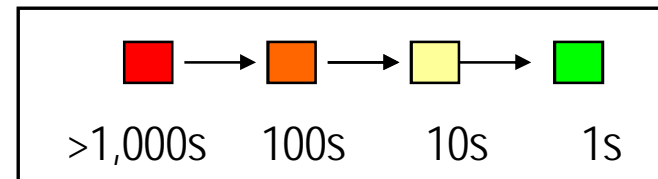
	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	Yellow	Orange	Green	Green
DNAPL	Yellow	Red	NA	NA
Aqueous	Yellow	Orange	Yellow	Green
Sorbed	Yellow	Yellow	Green	Green



SERDP

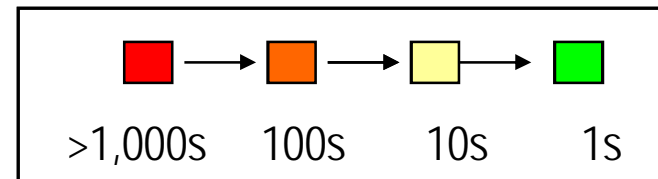
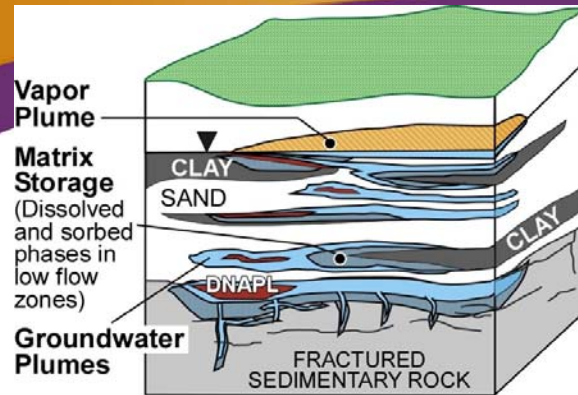


## Early Stage



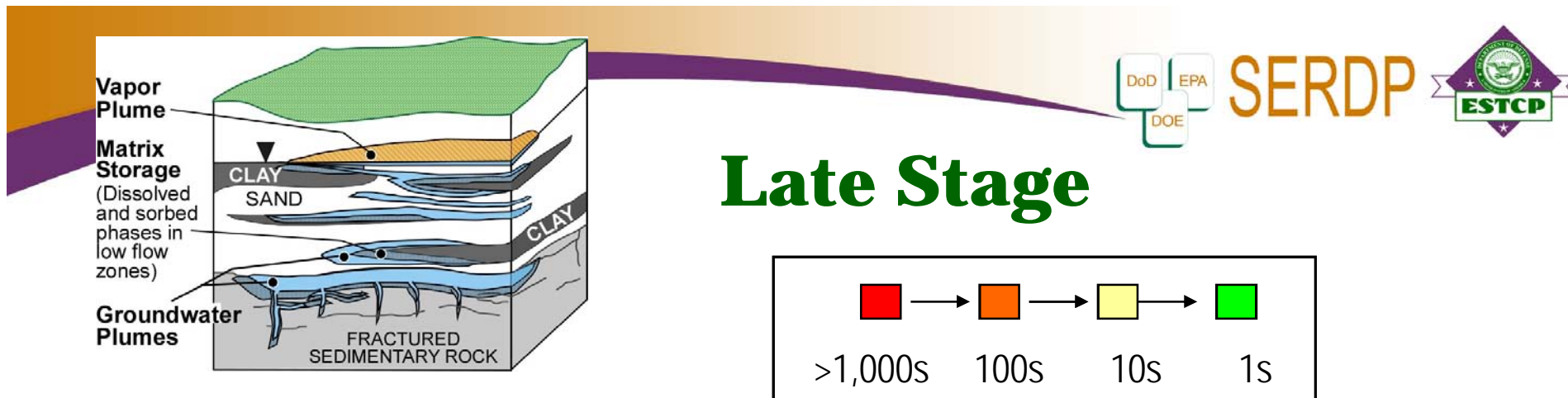
	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	Yellow	Orange	Green	Green
DNAPL	Yellow	Red	NA	NA
Aqueous	Yellow	Orange	Yellow	Green
Sorbed	Yellow	Yellow	Green	Green

# Middle Stage



	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	Orange box with vertical and horizontal blue arrows.	Orange box with vertical and horizontal blue arrows.	Orange box with vertical and horizontal blue arrows.	Yellow box with vertical and horizontal blue arrows.
DNAPL	Red box with vertical and horizontal blue arrows.	Red box with vertical and horizontal blue arrows.	Black box with 'NA'.	Black box with 'NA'.
Aqueous	Orange box with vertical and horizontal blue arrows.	Orange box with vertical and horizontal blue arrows.	Orange box with vertical and horizontal blue arrows.	Yellow box with vertical and horizontal blue arrows.
Sorbed	Orange box with vertical and horizontal blue arrows.	Orange box with vertical and horizontal blue arrows.	Orange box with vertical and horizontal blue arrows.	Yellow box with vertical and horizontal blue arrows.

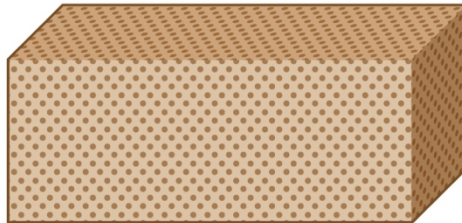




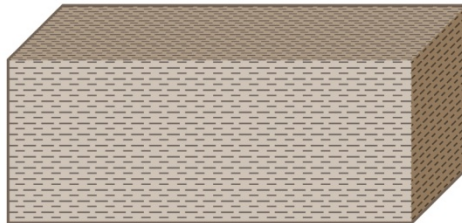
	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

# Type Setting

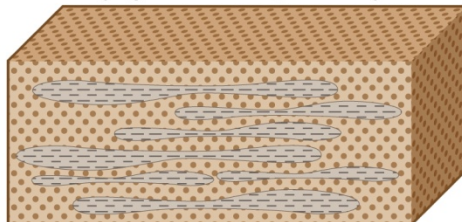
(I) Granular Media with Mild Heterogeneity and Moderate to High Permeability (e.g. eolian sands)



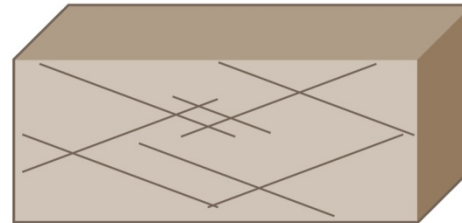
(II) Granular Media with Mild Heterogeneity and Low Permeability (e.g. lacustrine clay)



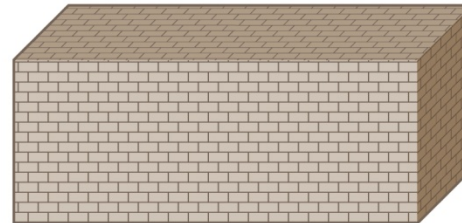
(III) Granular Media With Moderate to High Heterogeneity (e.g. deltaic deposition)



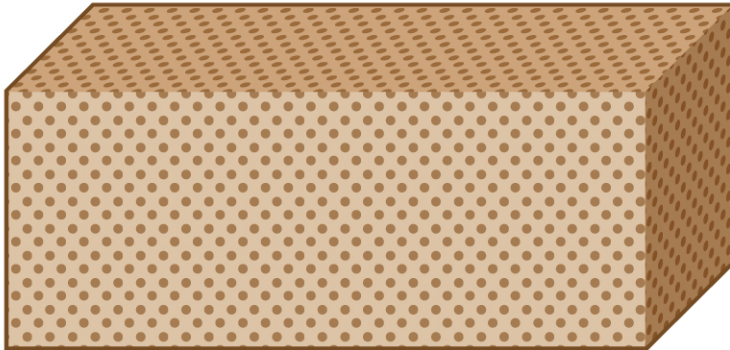
(IV) Fracture Media with Low Matrix Porosity (e.g. crystalline rock)



(V) Fracture Media with High Matrix Porosity (e.g. limestone, sandstone or fractured clays)



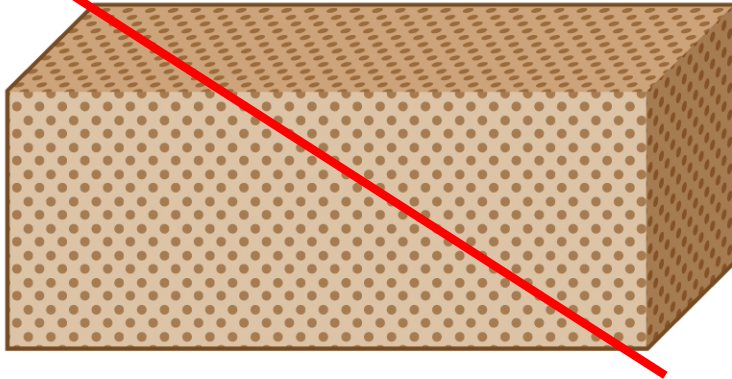
**(I) Granular Media  
with Mild Heterogeneity and  
Moderate to High Permeability  
(e.g. eolian sands)**



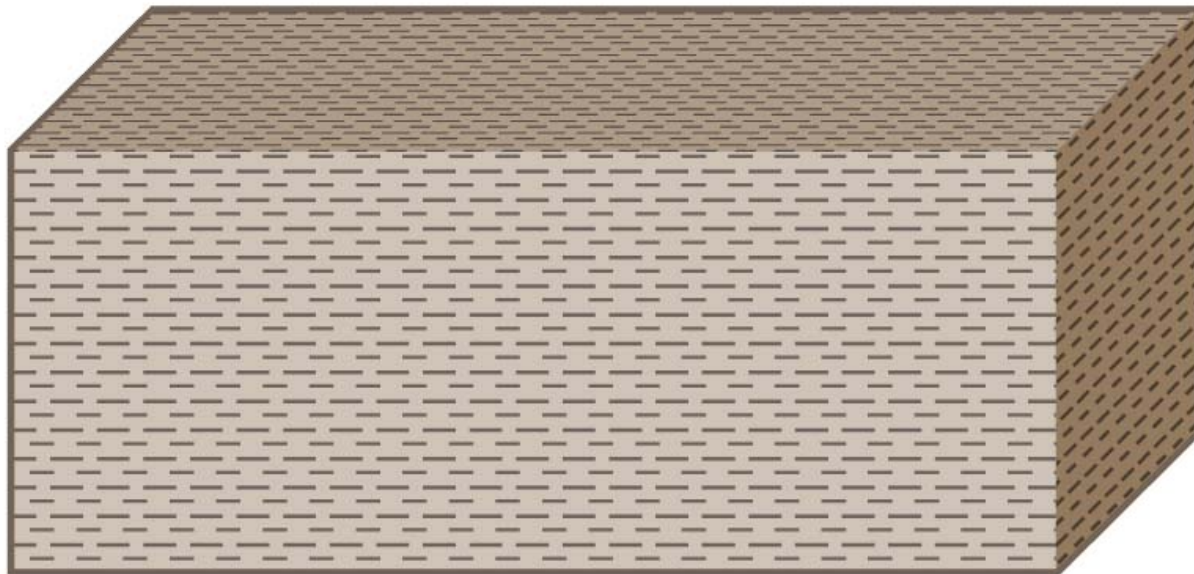
Great Sand Dunes National Park (Source <http://www.nps.gov/grsa>)



**(I) Granular Media  
with Mild Heterogeneity and  
Moderate to High Permeability  
(e.g. eolian sands)**

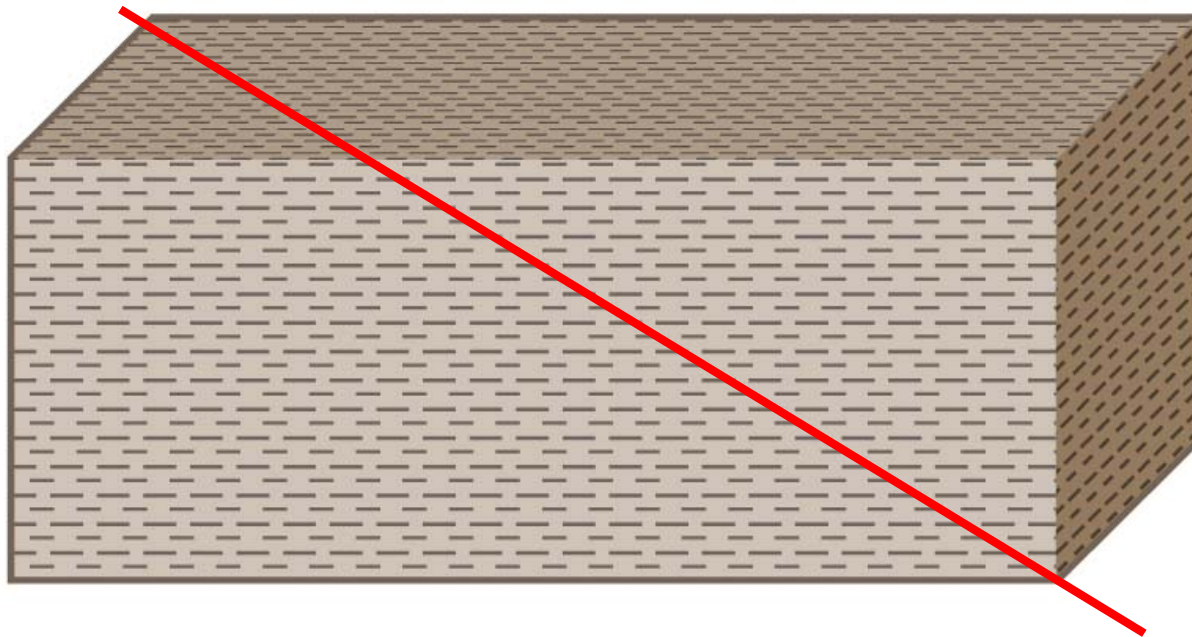


## **(II) Granular Media with Mild Heterogeneity and Low Permeability (e.g. lacustrine clay)**

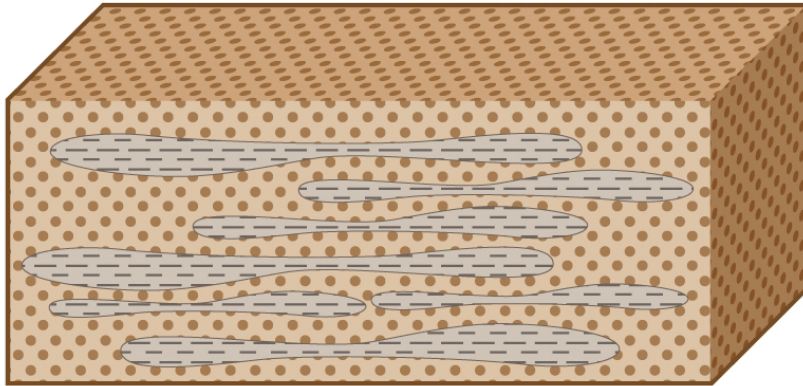




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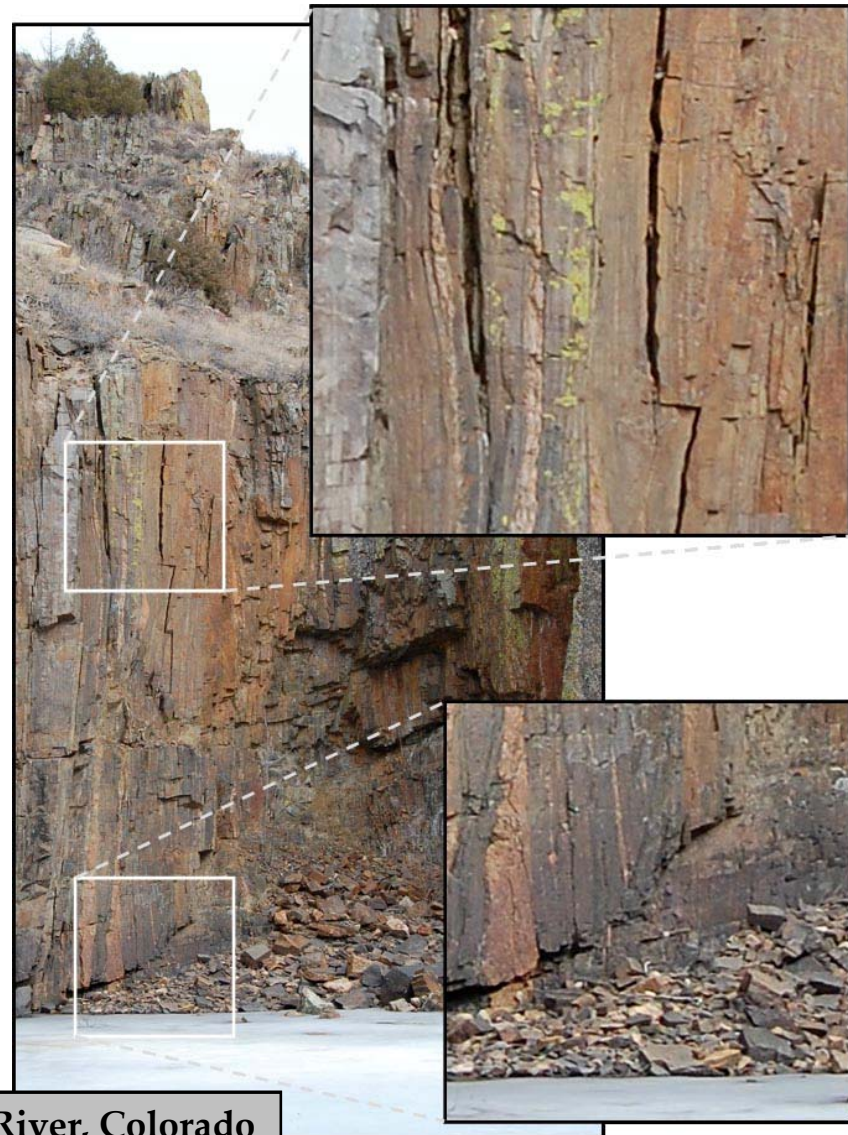
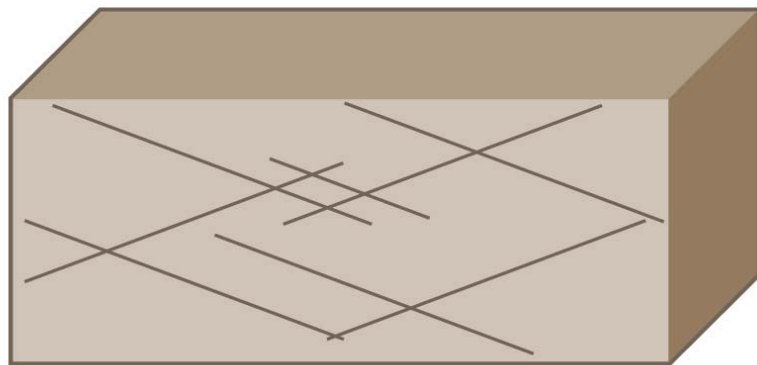


**(III) Granular Media With Moderate to High Heterogeneity  
(e.g. deltaic deposition)**





**(IV) Fracture Media  
with Low Matrix Porosity  
(e.g. crystalline rock)**



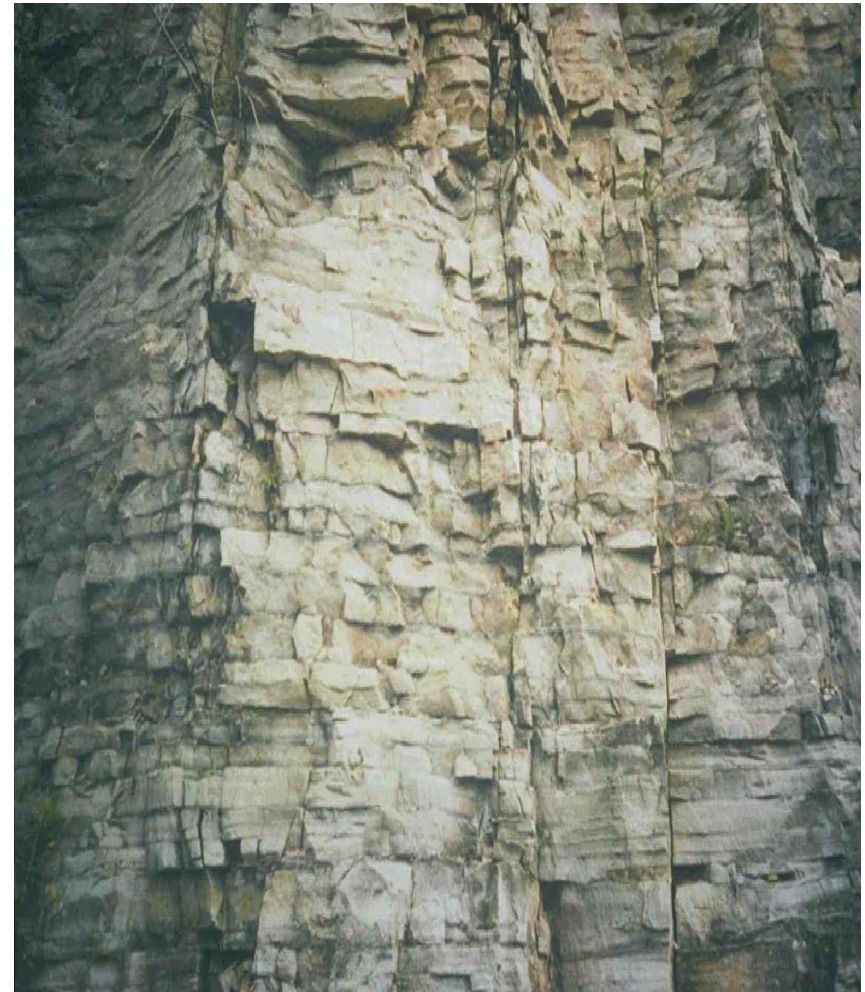
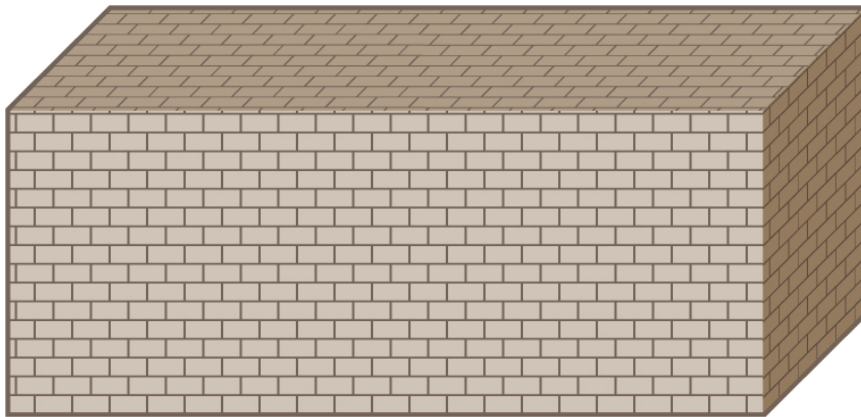
Cache La Poudre River, Colorado



Cache La Poudre River, Colorado



**(V) Fracture Media  
with High Matrix Porosity  
(e.g. limestone, sandstone  
or fractured clays)**

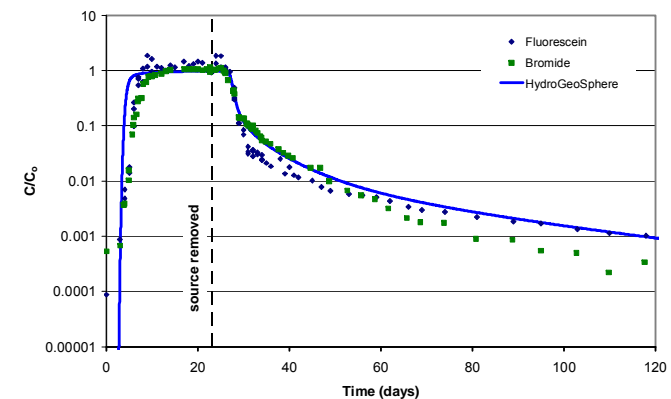
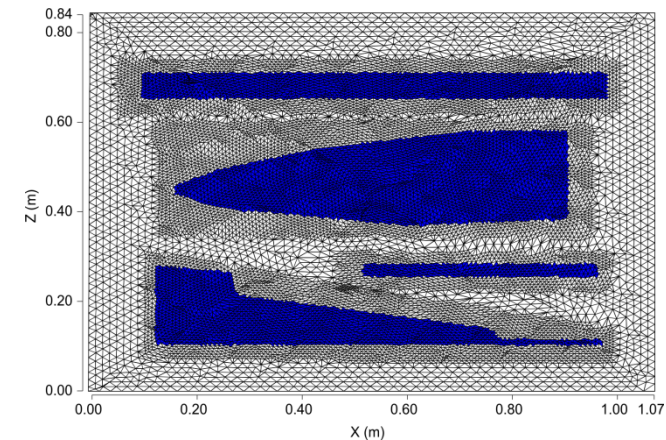
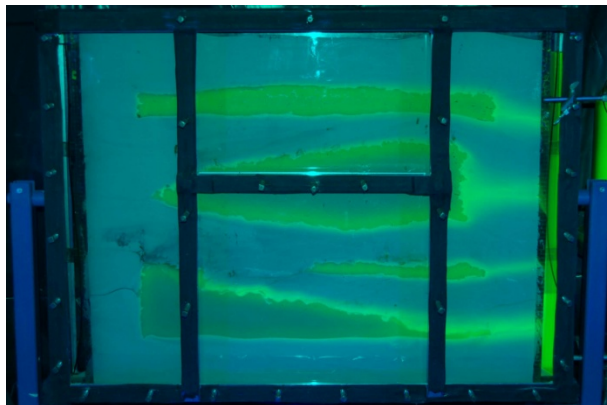
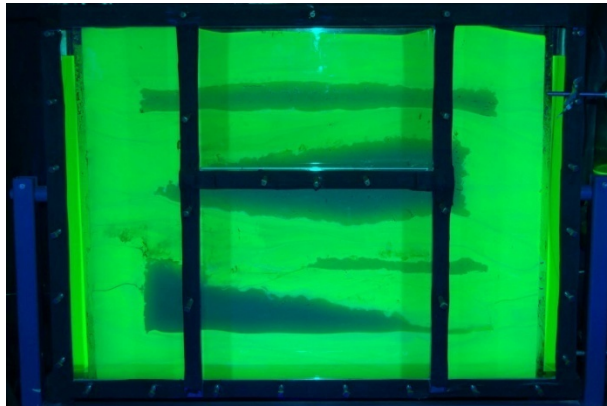


Bedding planes, joints, and vertical fractures in carbonate rock,  
Southern Ontario, Canada (Courtesy of Dr. Beth Parker)



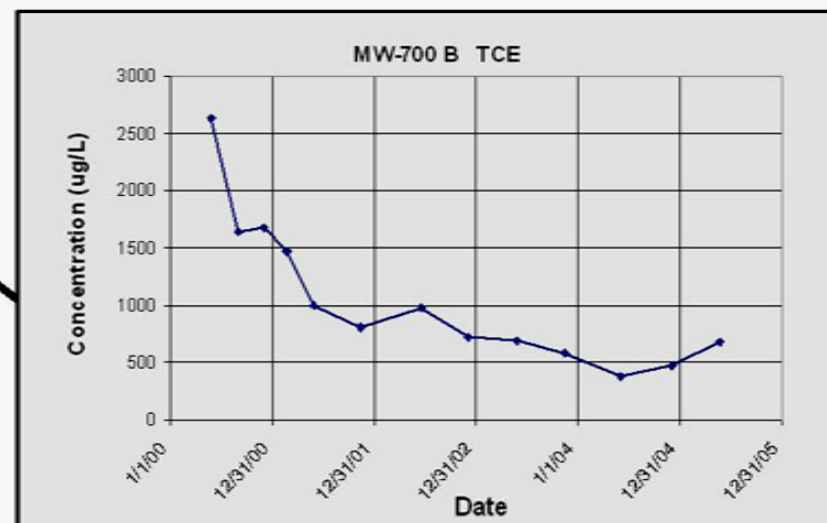
# Modeling

With proper grid discretization and time-stepping constraints, standard finite element numerical models can be used to evaluate contaminants in low permeability zones.



MW-173 B TCE

Date	Concentration (ug/L)
1/1/00	190
12/31/00	105
12/31/00	60
12/31/01	98
12/31/01	95
12/31/01	25
12/31/02	24
12/31/02	20
1/1/04	32
1/1/04	15
12/31/04	10
12/31/05	10
12/31/05	8





# Connecticut Site

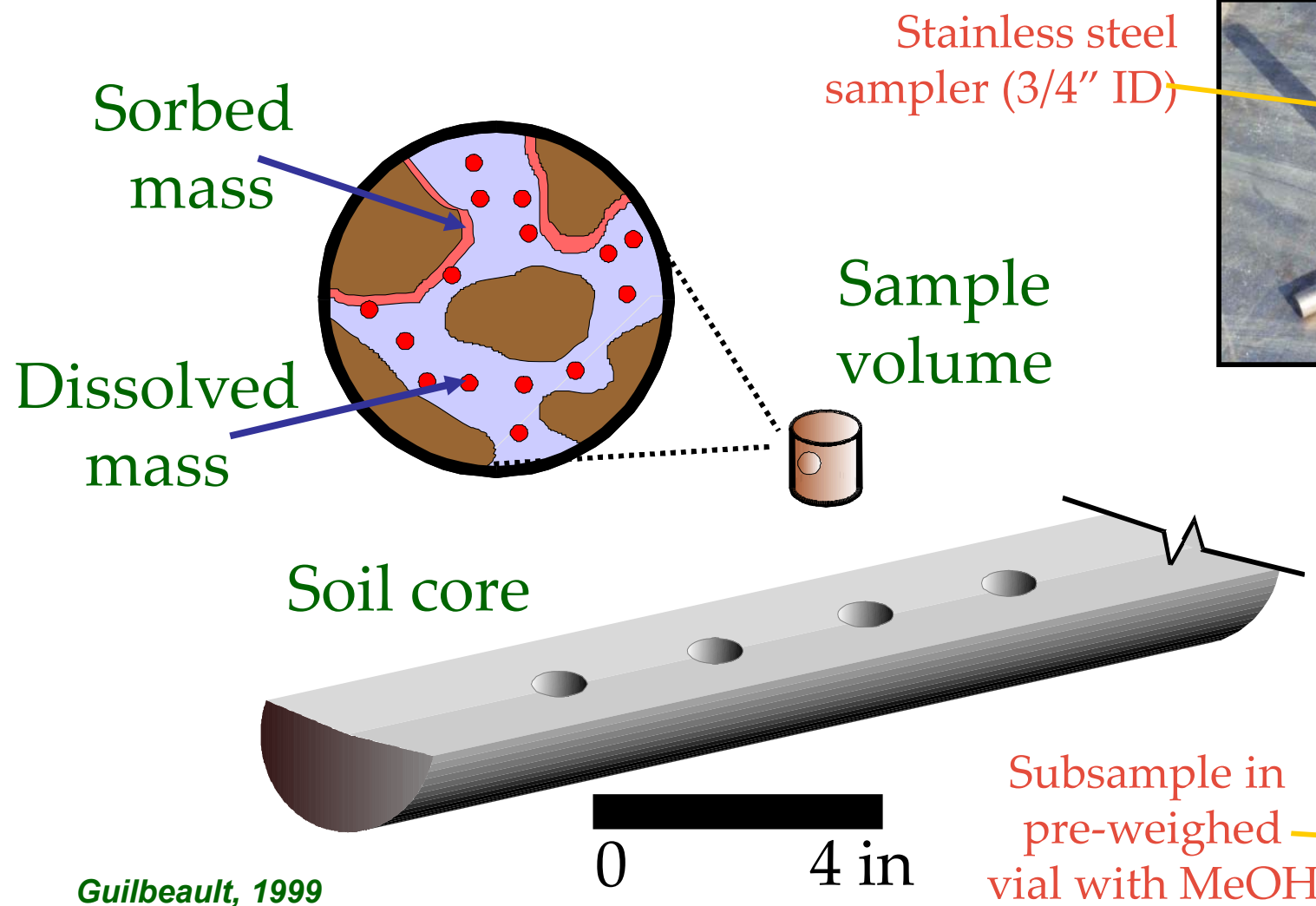


Chapman and Parker 2005  
Image Courtesy of B. Parker

UNIVERSITY  
of GUELPH

500 ft

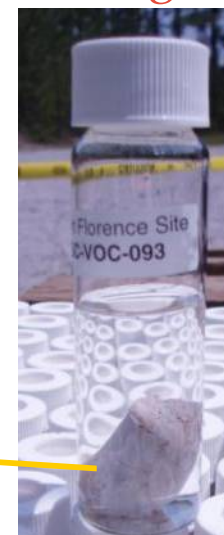
# Technical Approach: Soil Core Subsampling (Task 2)



Stainless steel  
sampler (3/4" ID)



Plunger



Guilbeault, 1999



# Aquifer – Aquitard Contact

Stratigraphic  
Column

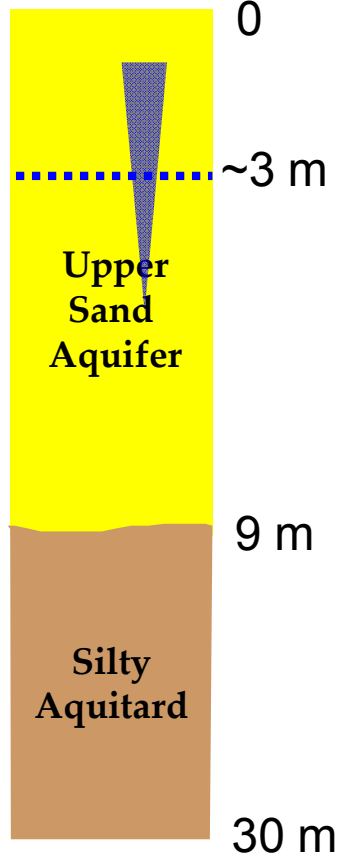
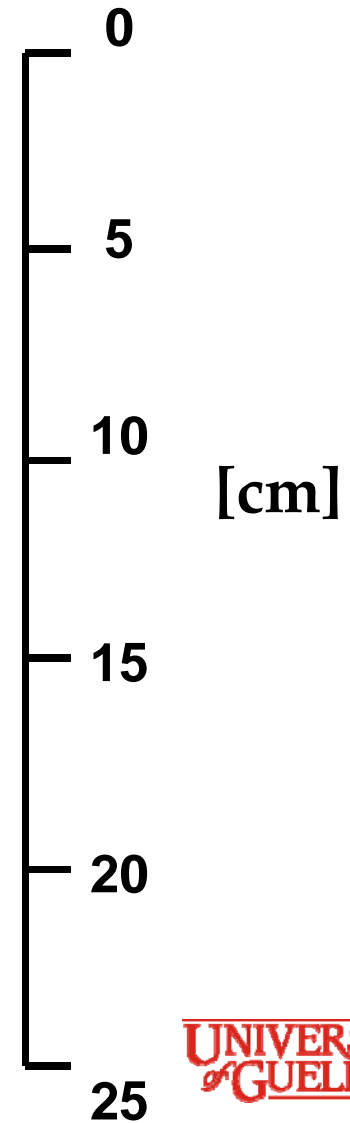
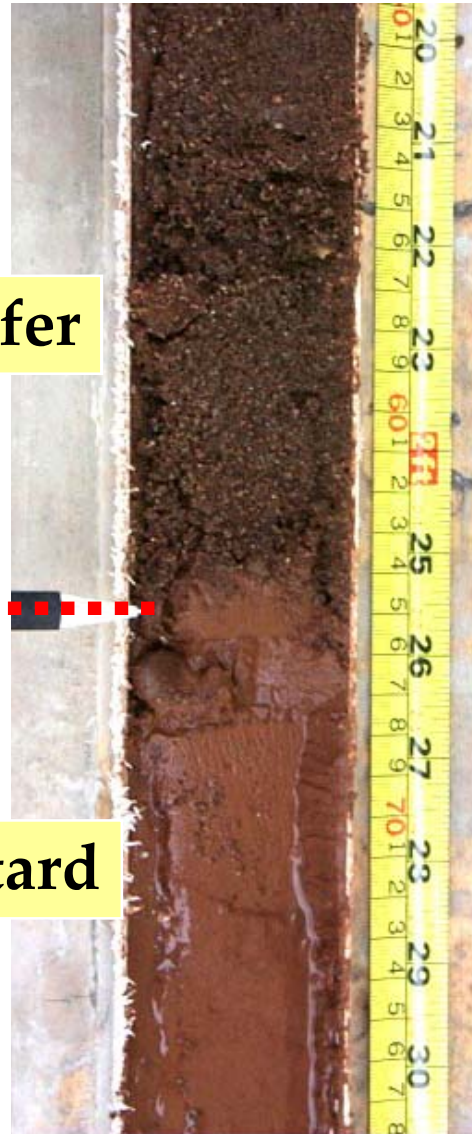


Image Courtesy of B. Parker

Aquifer

Aquitard

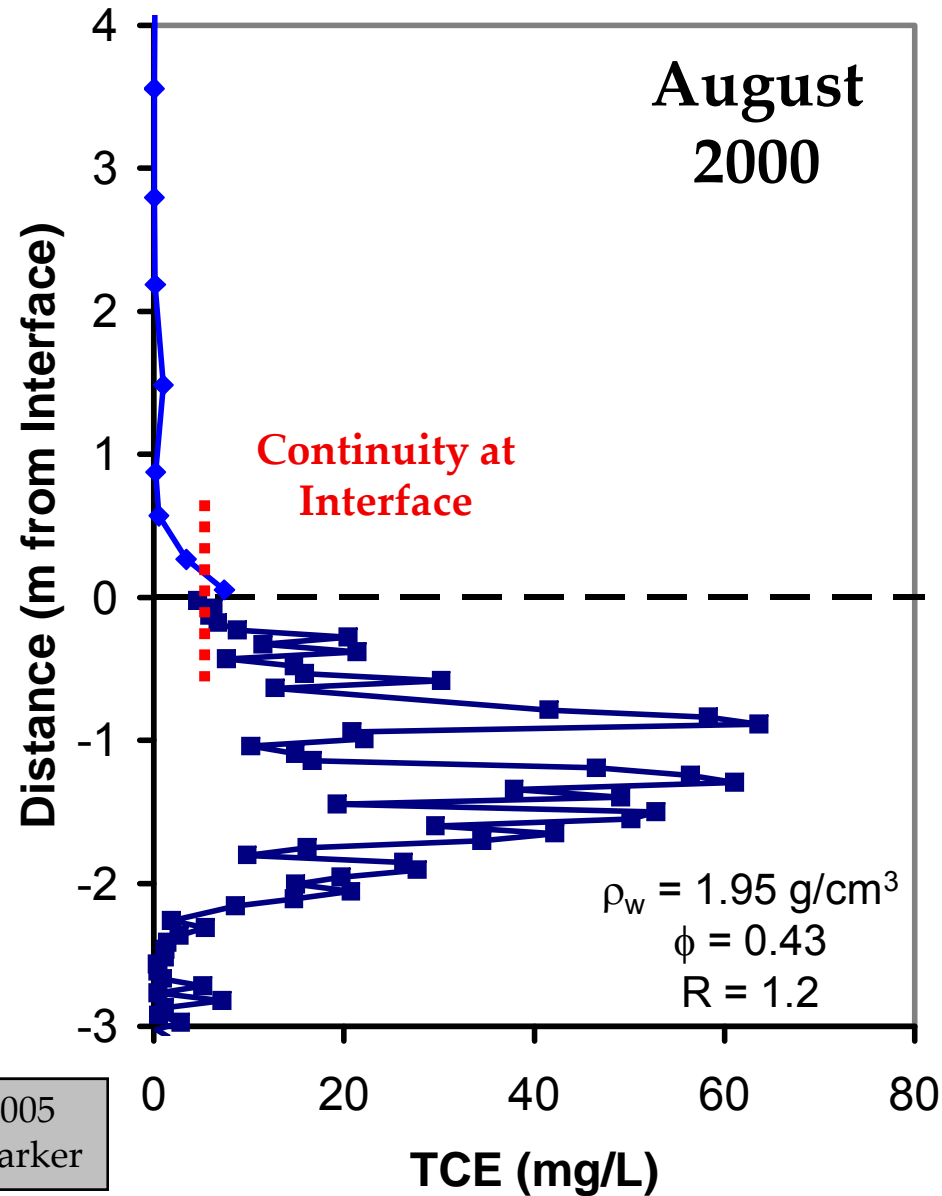




# High-Resolution Data from Core

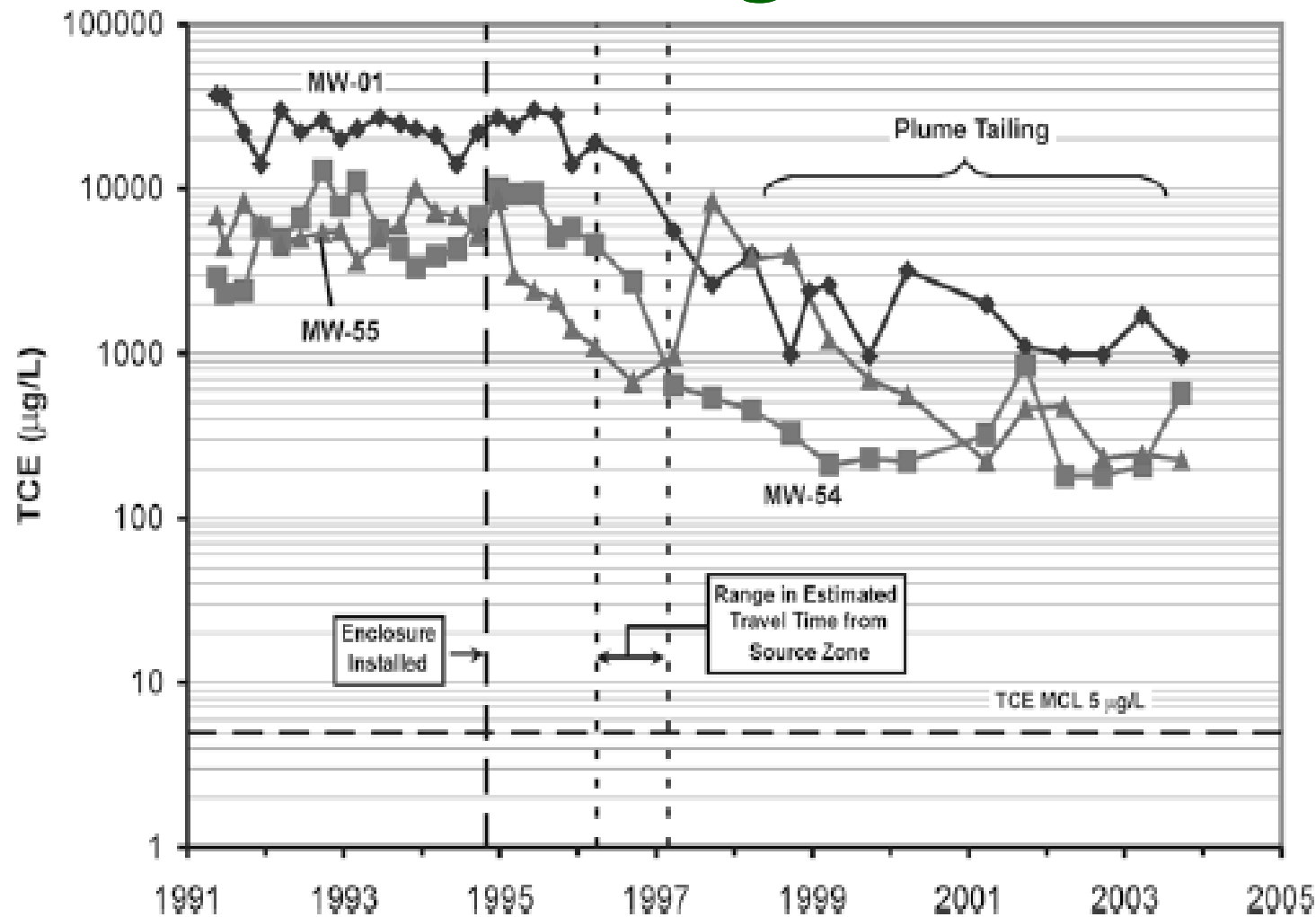


Most Mass  
is in the  
Aquitard !



Chapman and Parker 2005  
Image Courtesy of B. Parker

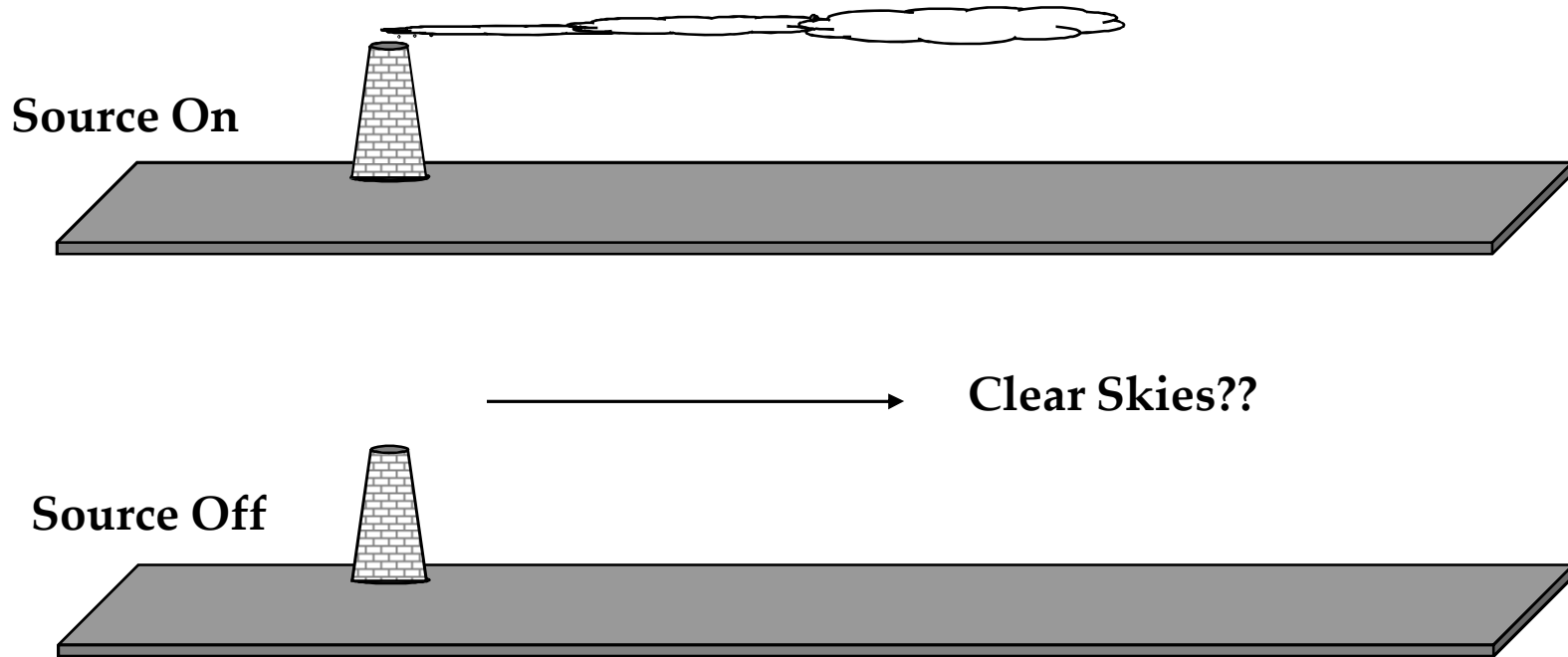
# Concentration vs. Time from Monitoring Wells



Source: Chapman and Parker, 2005 Copyright 2005 American Geophysical Union. Reproduced/modified by permission of AGU.

**Key Concepts about L&D Plumes**

# What happens after the “source” is addressed?





# Setting Objectives

Tom Sale, Chuck Newell

University Consortium for Field-Focused Groundwater  
Contamination Research

University of Guelph, Ontario

May 19-20, 2009



## **NRC (2005) observations regarding objectives**

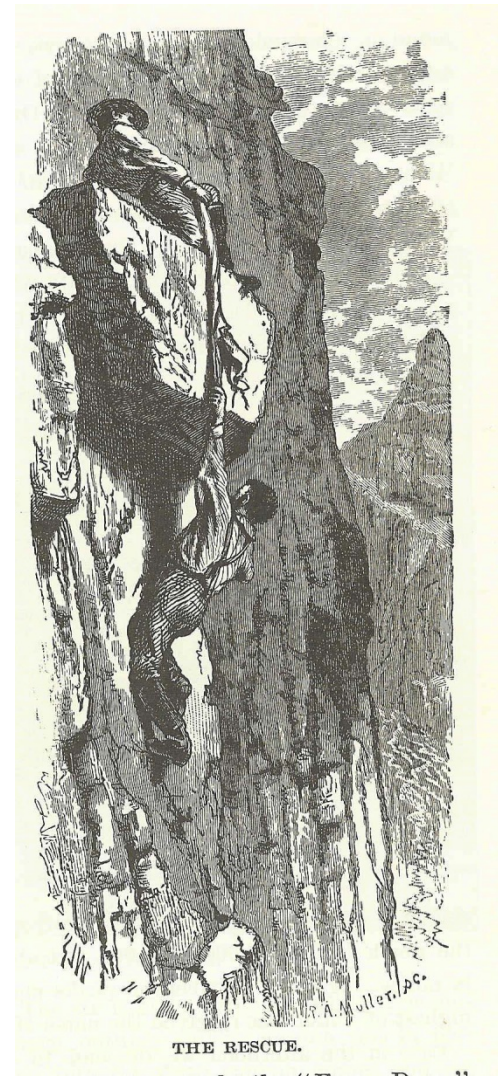
*Failure to explicitly state remedial objectives appears  
to be a significant barrier ...*

and

*Vagueness of objectives for remedial projects can  
preclude effective decision making*

# Yoggi Berra

- “if you don’t know where you are going you might end up someplace else”
- “if you don’t know where you are going you might not get there”



John Wesley Powell, Exploration of the Colorado River and its Tributaries

## Objectives (NRC 2005)

- Absolute – Broad
- Functional - Specific

## Comments on goals

- Set by participating parties
- Reflects the values of the participants
- Site specific
- Different priorities for different participants
- Should not be dictated
- Should be SMART\*
  - ◆ Specific
  - ◆ Measureable
  - ◆ Attainable
  - ◆ Relevant (or Realistic)
  - ◆ Timely

Should be BAV

- ◆ Beneficial
- ◆ Attainable
- ◆ Verifiable

\*Peter Drucker "The Practice of Management"



# Shopping List - Absolute Objectives

- Protection of human health and the environment
- Conservation of natural resources
- Mitigate adverse community impacts
- Minimize the burden of past practices on future generations

# Shopping List – Functional Objectives

- Risk
  - ◆ Human Health
  - ◆ Ecological receptors
  - ◆ Worker
- Extent
  - ◆ Limit expansion
  - ◆ Reduce footprint
- Reduce Longevity
  - ◆ Source
  - ◆ Plume
- Regulatory
  - ◆ Compliance
- Community
  - ◆ Beneficial land use
  - ◆ Avoidance of undue disruptions
- Economics
  - ◆ Practical costs
  - ◆ Limit economic interruptions
  - ◆ Sustain property value
- Sustainability
  - ◆ Net environmental benefit
  - ◆ Passive solutions
  - ◆ Effectiveness of combinations
- Resource Conservation
  - ◆ Limit future losses
  - ◆ Renovation of impacted resources
  - ◆ Protect habitat

← Absolute Objectives →

Functional Objectives

	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
<b>Risk</b>				
Prevent active adverse human exposure via groundwater or soil gas				
Prevent active ecological exposure via groundwater or soil gas				
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor				
<b>Extent</b>				
Prevent expansion of source zones and plumes				
Reduce the extent of source zones and plumes				
<b>Longevity</b>				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.				
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.				
<b>Regulatory</b>				
Comply with local, state, and federal regulations				
<b>Community</b>				
Address adverse (non-health) impacts to communities				
<b>Land use</b>				
Restore beneficial use of impacted lands				
<b>Economic</b>				
Select actions that have a practical near terms capital costs and minimal life cycle cost				
Avoid undue interruptions to communities, government, and industry activities				
Redress adverse impacts to property values				
<b>Sustainability</b>				
Select measures that have a net positive environmental benefit				
Progress to a state in which passive remedies will be sufficient to address residual impacts				
Enhance the effectiveness of complementary technologies				
<b>Resource Conservation</b>				
Limit future degradation of resources				
Restore impacted groundwater to standards needed for beneficial use				
Protect sensitive biological habitat				

# The Perfect Remedy

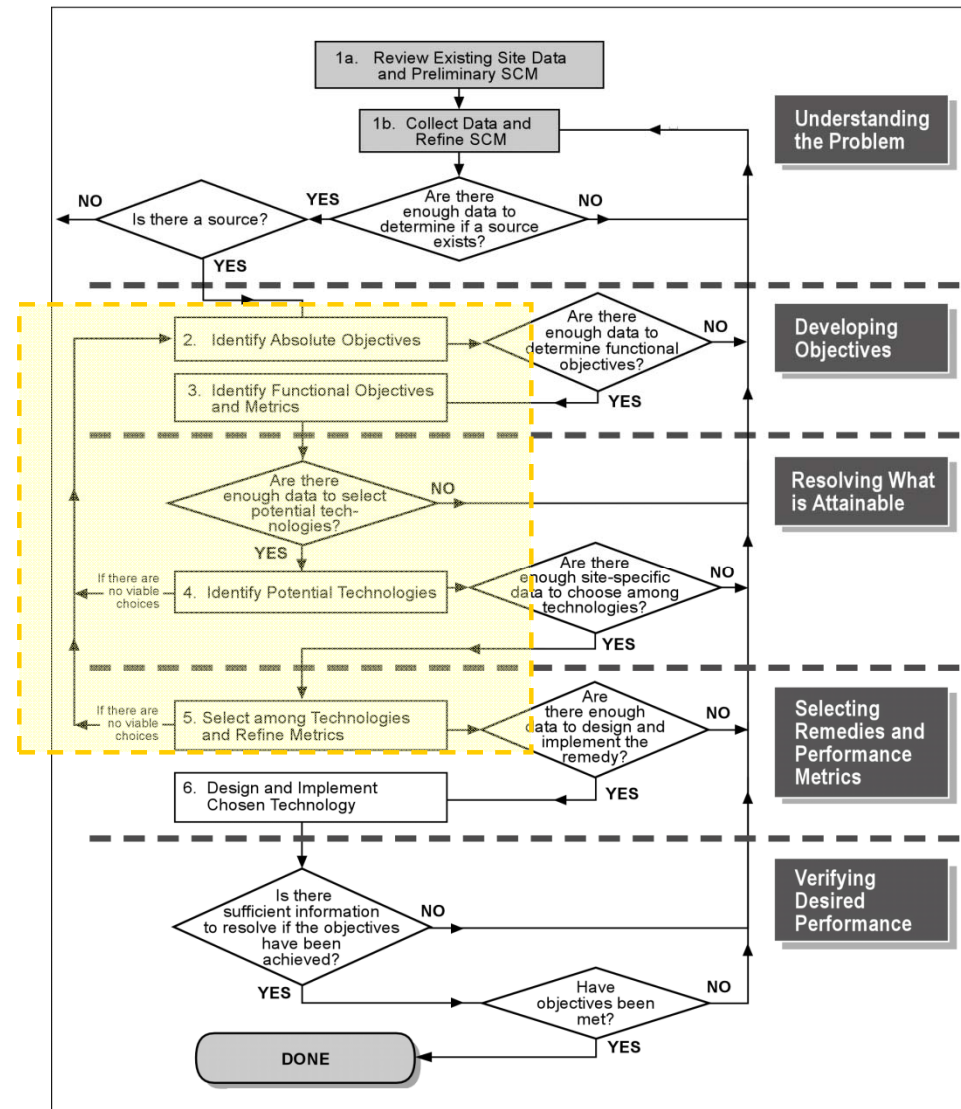
← Absolute Objectives →

↑  
Functional Objectives  
↓

	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
<b>Risk</b>				
Prevent active adverse human exposure via groundwater or soil gas				
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Select measures that have a net positive environmental benefit				
Progress to a state in which passive remedies will be sufficient to address residual impacts				
Enhance the effectiveness of complementary technologies				
<b>Resource Conservation</b>				
Limit future degradation of resources				
Restore impacted groundwater to standards needed for beneficial use				
Protect sensitive biological habitat				

# Iterative Nature of Setting Goals

- Desired outcome
- Remedy Selection
- Prediction of outcome
- Comparison to goals
- ...





# Selecting technologies

# What technologies do

- Treatment
  - ◆ Flux reduction
  - ◆ Longevity reduction
- Containment
  - ◆ Flux reduction

# **General classes of proven treatment technologies addressed include**

- Physical Processes
- In Situ Chemical Oxidation
- In Situ Chemical Reduction
- In Situ Biological Reduction
- Thermal

# **General classes of proven containment technologies addressed include**

- Hydraulic Containment (Pump and Treat)
- Hydraulic barriers
- Coupled Hydraulic-Physical Containment
- In Situ Stabilization
- Permeable Reactive Barriers



# Combined Remedies

Engineered Element  
 $A+B+C+\dots$





Institutional Element  
 $I+II+III+\dots$

# OoM Rules of Thumb

- Well implemented in-situ remediation remedies are likely to reduce source zone groundwater concentrations by **about one order-of-magnitude (90% reduction)** from pre-treatment levels.
- One order-of-magnitude source reduction...
  - ♦ gives one order-of-magnitude improvement downgradient water quality.
- But with fast groundwater flow, low mass storage, and/or active attenuation...
  - ♦ potentially gives 2-3 orders-of-magnitude improvement downgradient over several years

# **Mapping technology performance using the 14 compartment model**





# Pump & Treat

	Source Zone		Plume	
Phase / Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	Extraction of contaminated groundwater from transmissive zones is likely to have little effect on vapor in the vadose zone.			
DNAPL	Depletion of aqueous phase from transmissive zones will cause slow release from low permeability zones	DNAPL has the potential to be a long term source of aqueous phase	Not Applicable	
Aqueous		 Pumping groundwater from the source zone will cause direct depletion of aqueous phase in transmissive zones	Pumping groundwater from the source zone will drive direct depletion of aqueous phase in transmissive zones	 Depletion of aqueous phase from transmissive zones will drive slow release from low permeability zones in plumes
Sorbed		 Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process		

How Does PUMP AND TREAT\* Affect Contaminants in the 14 Different Compartments?

\* (when used for treatment, not containment)

**Key:** Technology has this effect on contaminants in this compartment

	Direct depletion
	Depletion but as a secondary effect
	Limited secondary effect
	Largely unaffected



# Orders of Magnitude (OoM)

DEGREE OF CONTAMINATION	
Degree of Contamination	Level described by equivalent concentrations in water
3 = Very High	1 – 10s (plus) mg/L in water
2 = High	100 -1000 ug/L in water
1 = Moderate	10-100 ug/L
0 = Low	1-10 ug/L

Anticipated Performance	
Description	Approximate Removal
3 = Direct	> 90%
2 = Secondary	90-10 %
1 = Limited	< 10% -1%
0 = Largely Unaffected	<1%

# Distribution of chlorinated solvents in a late stage Type IV setting (Fractured rock with low matrix porosity)

	Source Zone		Plume	
Zone/Phase	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0	0	0	0
DNAPL	0	0		
Aqueous	0	1	1	0
Sorbed	0	1	1	0

Distribution of chlorinated solvents in a late stage  
Type 4 setting (Fractured Rock with Low Matrix Porosity)

# Pump and treat in a late stage Type IV setting

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	0	0	0	0	0	0	0
DNAPL	1	0	1	0				
Aqueous	1	0	3	1	3	1	1	0
Sorbed	1	0	2	1	2	1	1	0

Maxium	12	Actual	10	Score	83
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# Screening pump and treat in a middle stage Type III setting.

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	2	0	2	0	1	0	1
DNAPL	1	2	1	3				
Aqueous	1	2	3	3	3	2	1	1
Sorbed	1	2	2	3	2	2	1	1

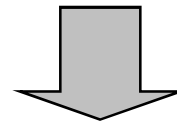
Maximum	81	Actual	36	Score	44
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# Outcome from pump and treat


	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	2	0	2	0	1	0	1
DNAPL	1	2	1	3				
Aqueous	1	2	3	3	3	2	1	1
Sorbed	1	2	2	3	2	2	1	1

Maxium	81	Actual	36	Score	44
--------	----	--------	----	-------	----



	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	2	0	2	0	1	0	1
DNAPL	1	2	1	3				
Aqueous	1	2	3	3	3	2	1	1
Sorbed	1	2	2	3	2	2	1	1

# Source Excavation

	Source Zone		Plume	
Phase / Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	<p>Assuming that the entire source zone is removed, and properly backfilled, no contamination should remain in the source zones</p> 		May reduce vadose zone vapor concentrations	
DNAPL			Not Applicable	
Aqueous			<p>Removal of the upgradient source should yield 1 to 3 order of magnitude improvements in downgradient water quality</p>	<p>Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones</p>
Sorbed			<p>Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.</p>	

# Source excavation as a function of age

Source excavation in an early stage Type 3 setting.

Zone/Phase	Source Zone				Plume			
	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	3	1	3	2	1	0	1	0
DNAPL	3	1	3	3				
Aqueous	3	1	3	3	2	1	1	0
Sorbed	3	1	3	3	2	0	1	0

Maximum	48	Actual	47	Score	98
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Source excavation in a late stage Type 3 setting.

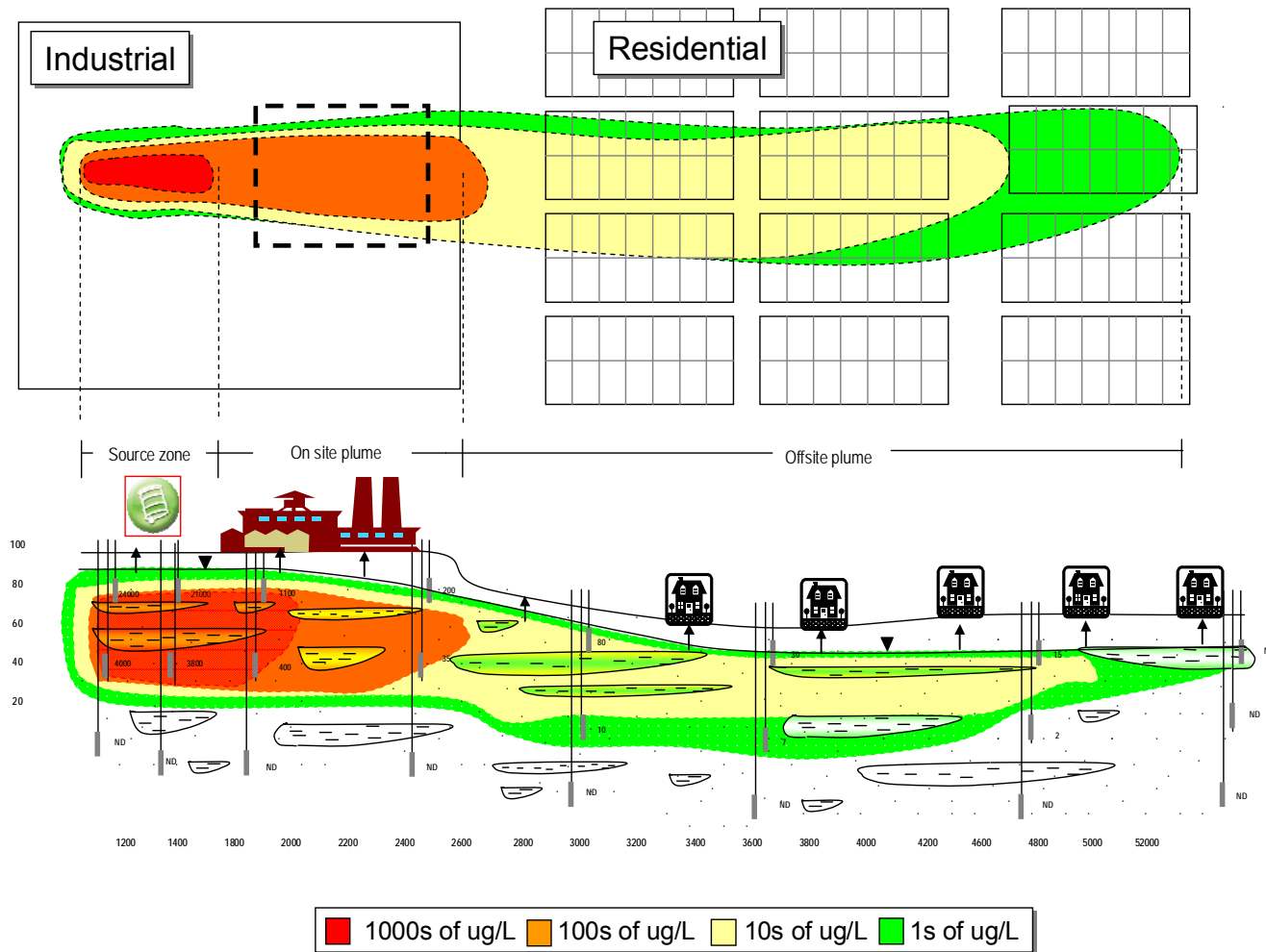
Zone/Phase	Source Zone				Plume			
	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	3	1	3	1	1	1	1	1
DNAPL	3	0	3	0				
Aqueous	3	2	3	1	2	1	1	2
Sorbed	3	2	3	1	2	1	1	2

Maximum	48	Actual	34	Score	71
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# Packaging Remedies

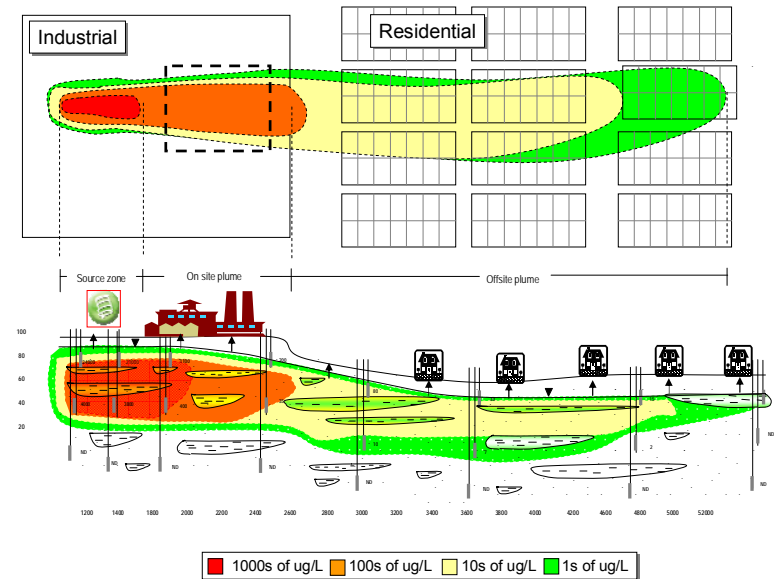


# Example NO. 1



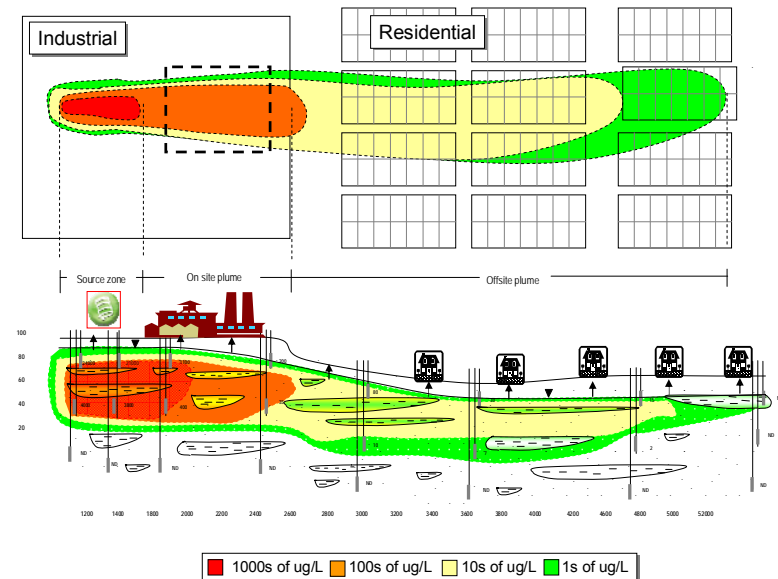
# Site attributes

- 30 year old release of chlorinated solvent
- ~ 1 mile plume in a sandy aquifer
- 1000s of ug/L in the source area to 1s of ug/L at the end of the plume
- No DNAPL observed in the source zone
- Stable plume with active degradation
- Lower permeability media (clays layers) are accumulating contaminant via inward diffusion
- Indoor air is a concern in the residential area



# Drivers

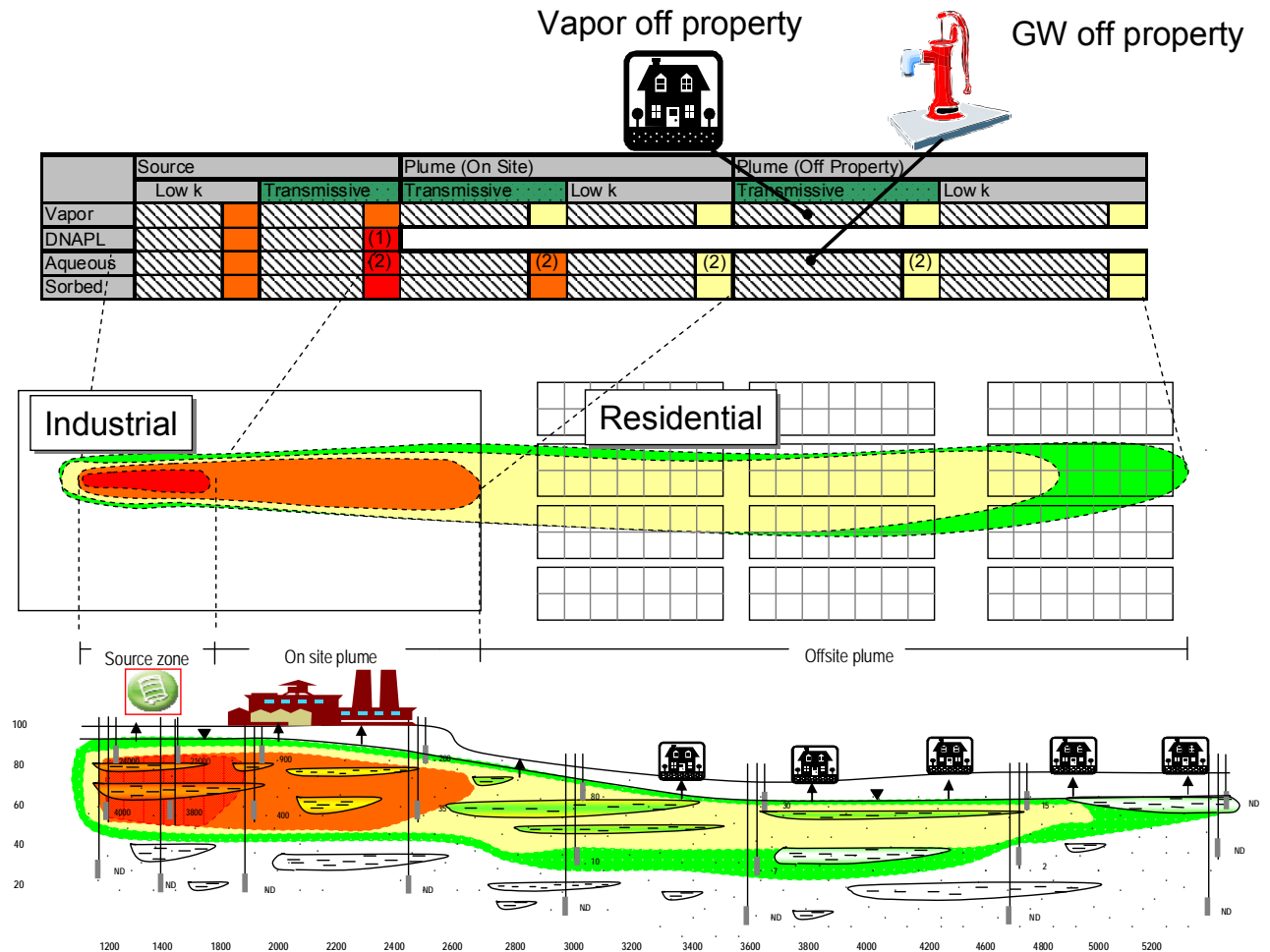
- Home owners are concerned about health effects, property values, and disruptions in the neighborhood.
- Regionally, the community is committed to a clean environment while wanting to preserve jobs.
- Facility is committed to immediately addressing exposure pathways and meeting all other obligations with constraints of –
  - ♦ a preference for actions with consequential benefits
  - ♦ economically feasibility
- Regulators support the interests of the community, provide technical support, and pursue compliance.



# Before Treatment



- Setting
  - ◆ Middle stage
  - ◆ Type II
  - ◆ Cont. in low k zones
- With potential exposure via
  - ◆ Vapor
  - ◆ Groundwater
  - ◆ Onsite worker



# Consensus goals

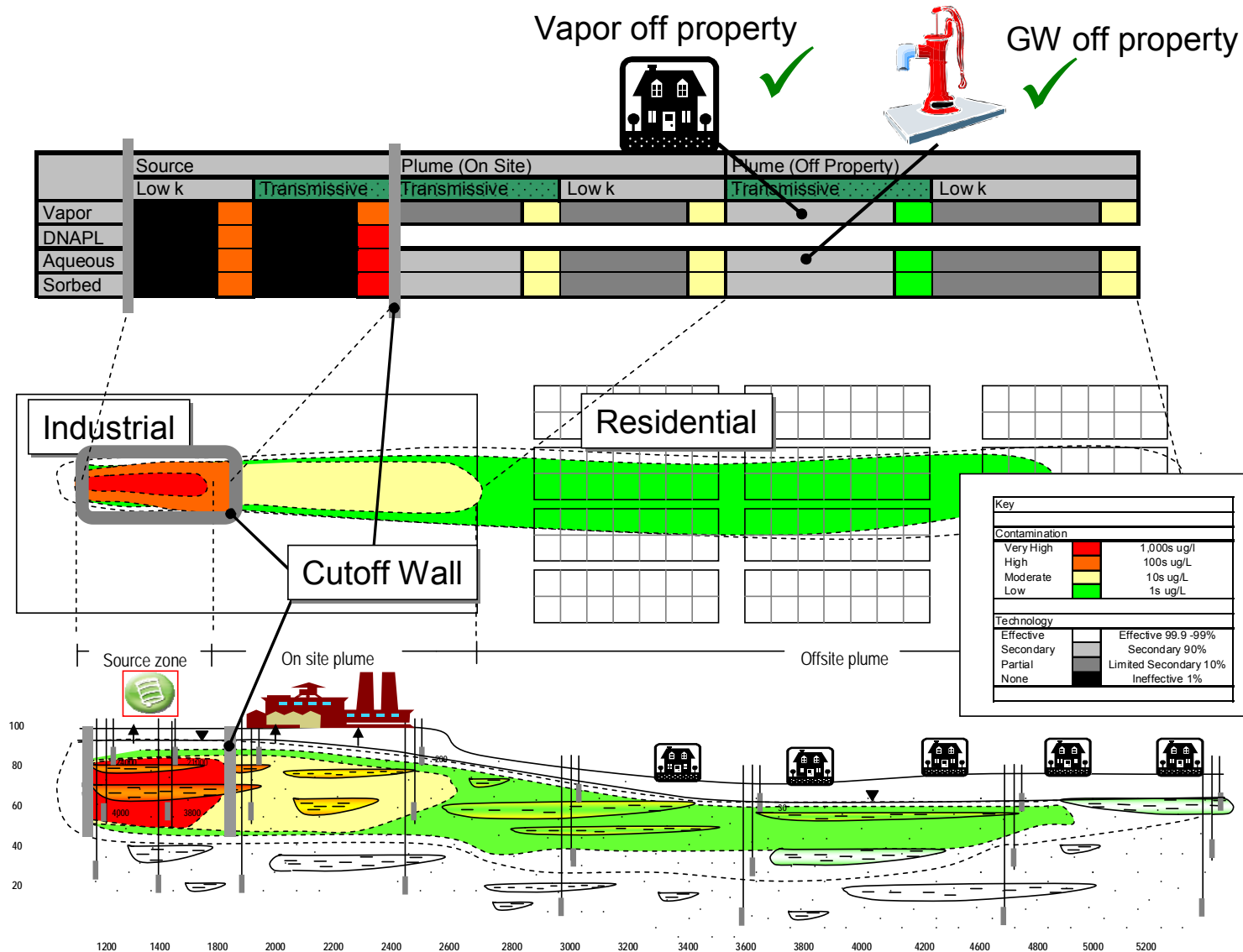
Not Applicable

	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
<b>Risk</b>				
Prevent active adverse human exposure via groundwater or soil gas				
Prevent active ecological exposure via groundwater or soil gas				
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor				
<b>Extent</b>				
Prevent expansion of source zones and plumes				
Reduce the extent of source zones and plumes				
<b>Longevity</b>				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.				
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.				
<b>Regulatory</b>				
Comply with local, state, and federal regulations				
<b>Community</b>				
Address adverse (non-health) impacts to communities				
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Restore beneficial use of impacted lands				
<b>Economic</b>				
Select actions that have a practical near terms capital costs and minimal life cycle cost				
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Redress adverse impacts to property values				
<b>Sustainability</b>				
Select measures that have a net positive environmental benefit				
Progress to a state in which passive remedies will be sufficient to address residual impacts				
Enhance the effectiveness of complementary technologies				
<b>Resource Conservation</b>				
Limit future degradation of resources				
Restore impacted groundwater to standards needed for beneficial use				
Protect sensitive biological habitat				

To be defined



# Source containment with institutional controls for GW



# Source Containment + GW Institutional Controls

 good
  ok
  marginal
  no eff.

Current Conditions	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
<b>Risk</b>				
Prevent active adverse human or ecological exposure via groundwater	good	no eff.	good	good
Prevent active adverse human or ecological exposure via soil gas	ok	ok	ok	ok
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor	marginal	no eff.	marginal	marginal
<b>Extent</b>				
Prevent expansion of source zones and plumes	good	good	good	good
Reduce the extent of source zones and plumes	ok	ok	ok	ok
<b>Longevity</b>				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.	no eff.	no eff.	no eff.	no eff.
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.	ok	ok	ok	ok
<b>Regulatory</b>				
Comply with local, state, and federal regulations	marginal	marginal	marginal	marginal
<b>Community</b>				
Address adverse (non-health) impacts to communities	marginal	marginal	marginal	marginal
<b>Land use</b>				
Restore beneficial use of impacted lands	no eff.	ok	ok	ok
<b>Economic</b>				
Select actions that have a practical near terms capital costs and minimal life cycle cost	no eff.	no eff.	good	good
Avoid undue interruptions to communities, government, and industry activities	no eff.	no eff.	good	good
Redress adverse impacts to property values	no eff.	ok	ok	ok
<b>Sustainability</b>				
Select measures that have a net positive environmental benefit	good	good	good	good
Progress to a state in which passive remedies will be sufficient to address residual impacts	no eff.	no eff.	no eff.	marginal
Enhance the effectiveness of complementary technologies	no eff.	no eff.	no eff.	ok
<b>Resource Conservation</b>				
Limit future degradation of resources	good	good	good	good
Restore impacted groundwater to standards needed for beneficial use	marginal	marginal	marginal	marginal
Protect sensitive biological habitat	no eff.	marginal	marginal	marginal

## Other Examples

- Plume without natural attenuation
- Fracture rock without matrix porosity
- Fracture rock with matrix porosity

# Closing

## Key Points

- Holistic evaluation of all compartments
- The nature of the problem evolves with time
- Goals need to be SMART
- Single Technologies rarely address all compartments
- Many goals compete with each other
- Learning to value what is achievable and live with what remains



# Discussion

- Value of compromise
  - ♦ Finding ways to go forward with what is beneficial, attainable, and verifiable
  - ♦ Learning to live with what will remain
- Alternatives to strict numerical standards
- Challenge of non-degradation policies
- Ways to break the log jam
- Time frames

# Short Course Agenda



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

# Short Course Agenda



**SERDP**



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# ***Development Of A Protocol And Screening Tool For Selection Of DNAPL Remedial Technologies***

## **ER-0424**

**Carmen A. Lebrón**  
NAVFAC ESC

**Dr. David Major**  
**Dr. Julie Konzuk**  
*Geosyntec Consultants*

**Dr. Bernard Kueper**  
*Queen's University*

**Dr. Jason Gerhard**  
*University of Western Ontario*



**SERDP**



## ***Seminar Outline:***

Thursday, December 3, 2009		
Start	End	Topic
10:25 AM	10:40 AM	<b>Background, Objectives and Introduction to Screening Tool Development</b> <i>(Presented by Ms. Carmen A. Lebrón)</i>
10:40 AM	11:05 AM	<b>Numerical Modeling: Simulations &amp; Conclusions/Generalizations from Simulations</b> <i>(Presented by Dr. Bernard Kueper)</i>
11:05 AM	11:20 AM	<b>Conclusions/Generalizations from Case Studies</b> <i>(Presented by Dr. Julie Konzuk)</i>
11:20 PM	11:30 AM	<b>Screening Tool Demonstration</b> <i>(Presented by Dr. Julie Konzuk )</i>
11:30 PM	11:45 AM	<b>Questions &amp; Answers</b>



# ***DNAPL Remediation Paradigm***

- Uncertainties in DNAPL remediation technology selection:
  - ◆ How do different technologies perform in various geological/chemical environments?
  - ◆ What are reasonable expectations in terms of mass removal and concentration reductions?
  - ◆ What technology best meets our goals/needs?



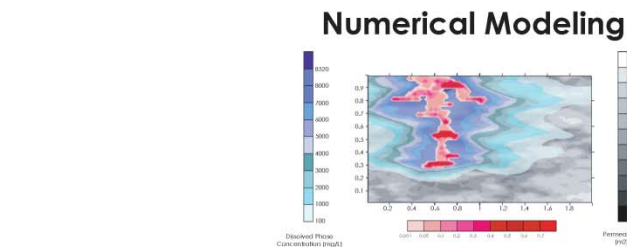
## ***Project Objectives***

- Develop a screening tool that can be applied at DNAPL source zone sites to:
  - ◆ Reduce uncertainty in estimating remedial outcomes
  - ◆ Evaluate potential technology performance
  - ◆ Aid RPMs in technology selection based on desired performance metrics
- Screening tool developed using a modular approach, which allows for:
  - ◆ Incorporating other features in the future
  - ◆ Periodic updates of information in the screening tool database without reprogramming the screening tool

~~Prediction  
Tool~~

Expectation  
Management  
Tool

# Technical Approach



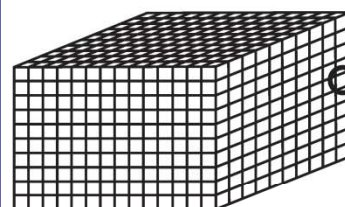
## Literature Review



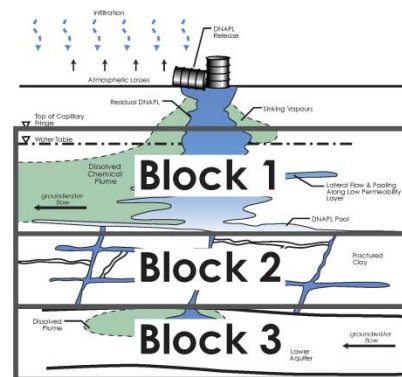
- DNAPL panel reports
- Refereed literature (journal publications)
- Non-refereed literature (conference proceedings)
- Guidance documents
- Other print sources
- Web databases
- SERDP & ESTCP projects



## Database Interface Forms



## Database/Protocol



## Site Parameters

Input

## Screening Tool

User-Friendly Interface

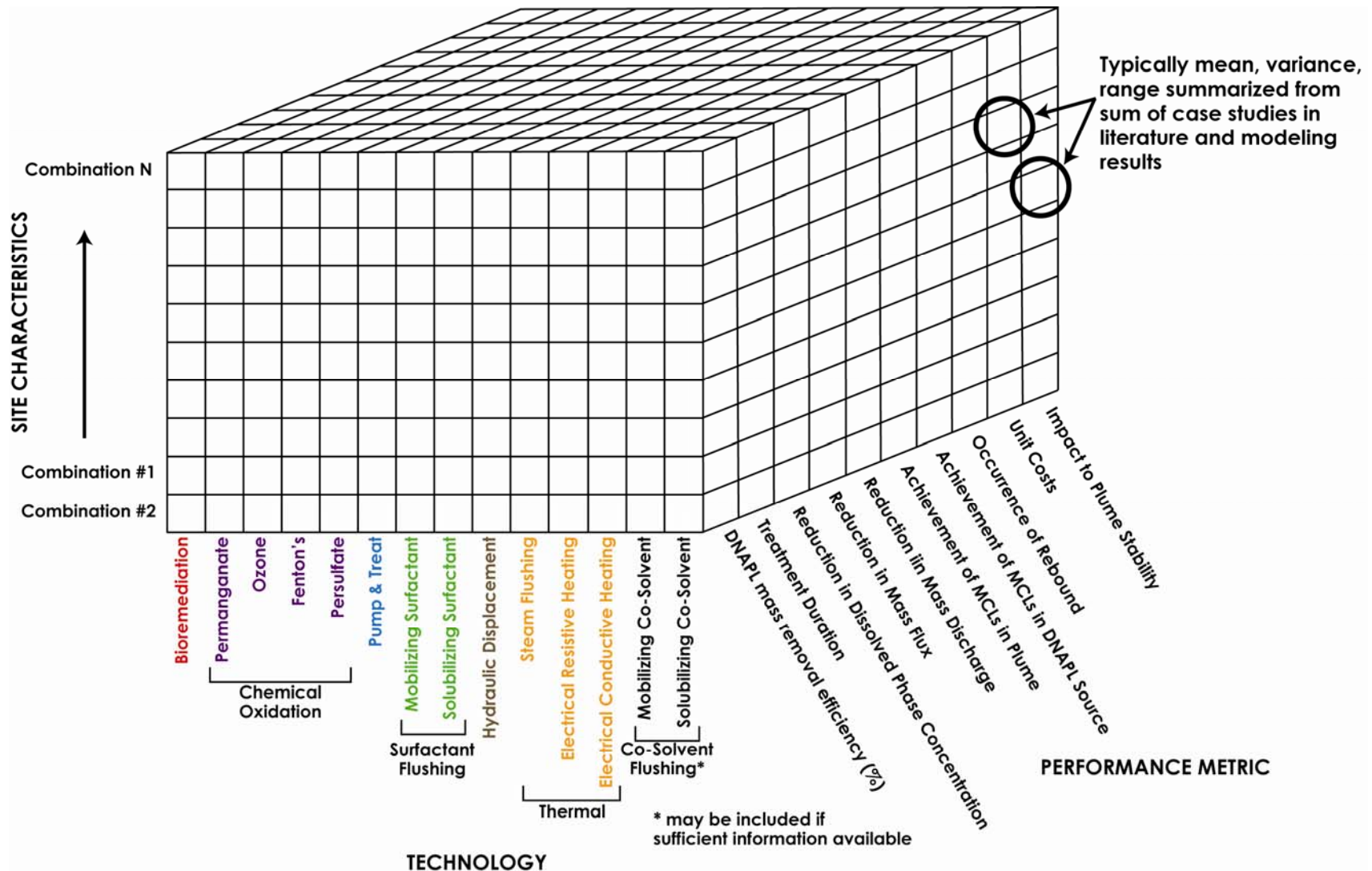


Output



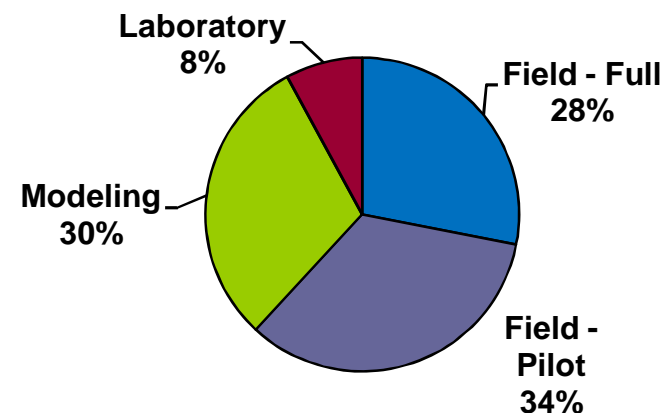
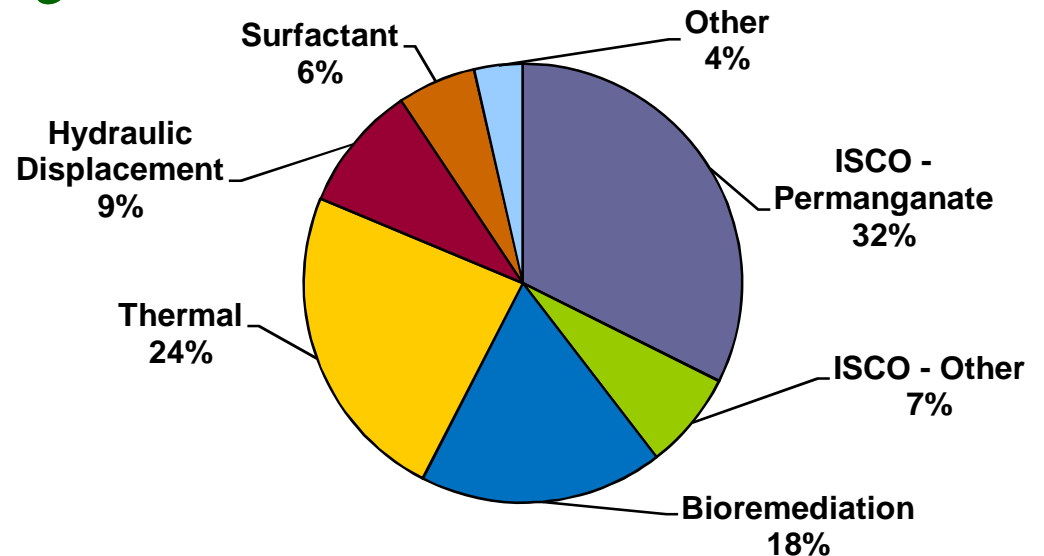
## DNAPL Remedial Technology Screening Tool Report

# *The Matrix, a.k.a. Database*



# Case Study Collection

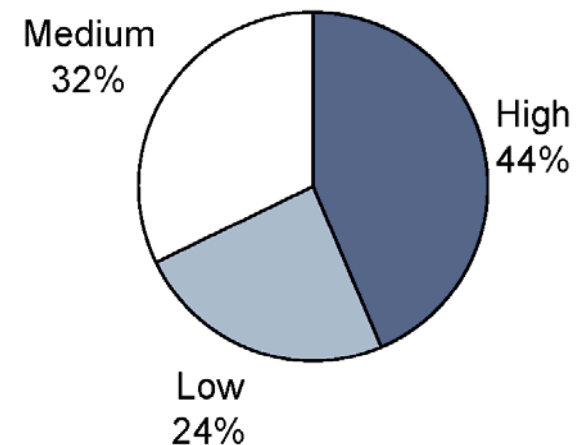
- Case studies entered into database to date:
  - 42 modeling case studies
  - 11 lab studies
  - 86 field case studies
- An additional 76 field case studies identified and >70 modeling case studies still to be entered into database





# *Case Study Quality Control*

- **Data Quality Rankings (DQRs) developed for each case study**
  - ◆ Value between 1 (low) and 3 (high)
- **Weighted average of ratings for:**
  - ◆ Information source (low weighting)
  - ◆ Age of study (medium)
  - ◆ Methods used to characterize DNAPL (medium)
  - ◆ Completeness of pre-treatment data set (high)
  - ◆ Completeness of post-treatment data set (high)
- **In screening tool, users can filter data based on DQRs**

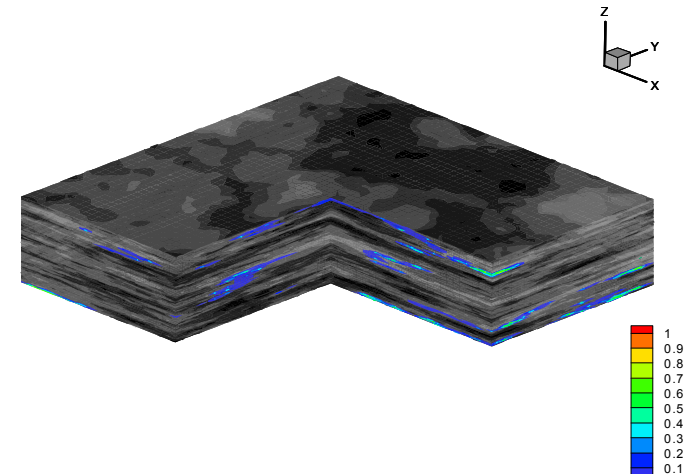


# ***Modeling/Simulations***

## ✓ ***Why Modeling?***

## ✓ ***Allows us to:***

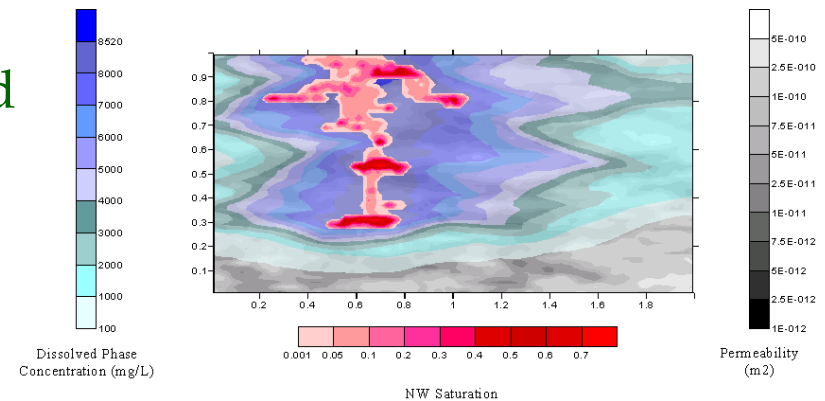
- ◆ Simulate DNAPL releases in various geologic settings and create different architectures
- ◆ Compare technology performance
- ◆ Evaluate impact of various factors on tech performance
- ◆ Assess source removal long-term impacts on groundwater quality



# Modeling/Simulations

## Step 1. Creating template sites

- Simulate a range of geological, hydrogeological, and chemical environments
- Simulate a range of DNAPL releases and architectures



## Step 2. Modeling DNAPL Treatment

- Simulate treatment with selected technologies
- Metrics evaluated include DNAPL mass reduction, source zone concentration reduction, mass flux reduction, plume length

Template Site	+	Remediation Technology	=	Case study in Screening Tool
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SERDP



# Simulations/Template Sites

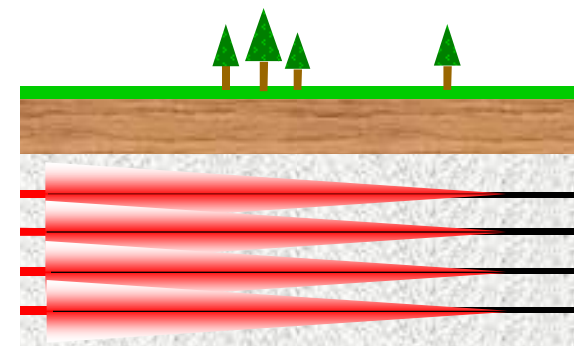
*Porous Media Template Site Parameters*

Template Site	DNAPL Type	DNAPL Release Volume	Hydraulic Conductivity	Soil Heterogeneity
Low Heterogeneity	TCE	7.57 m <sup>3</sup>	10 <sup>-3</sup> cm/s	<b>ln k = 1</b>
Low K	TCE	7.57 m <sup>3</sup>	<b>10<sup>-4</sup> cm/s</b>	ln k = 2
Low DNAPL Volume	TCE	<b>1.89 m<sup>3</sup></b>	10 <sup>-3</sup> cm/s	ln k = 2
Lower Density DNAPL	<b>1,1,1-TCA</b>	7.57 m <sup>3</sup>	10 <sup>-3</sup> cm/s	ln k = 2
<b>Base Case</b>	<b>TCE</b>	<b>7.57 m<sup>3</sup></b>	<b>10<sup>-3</sup> cm/s</b>	<b>ln k = 2</b>
Higher Density DNAPL	<b>PCE</b>	7.57 m <sup>3</sup>	10 <sup>-3</sup> cm/s	ln k = 2
High DNAPL Volume	TCE	<b>18.9 m<sup>3</sup></b>	10 <sup>-3</sup> cm/s	ln k = 2
High K	TCE	7.57 m <sup>3</sup>	<b>10<sup>-2</sup> cm/s</b>	ln k = 2
High Heterogeneity	TCE	7.57 m <sup>3</sup>	10 <sup>-3</sup> cm/s	<b>ln k = 4</b>

# Simulations/Template Sites

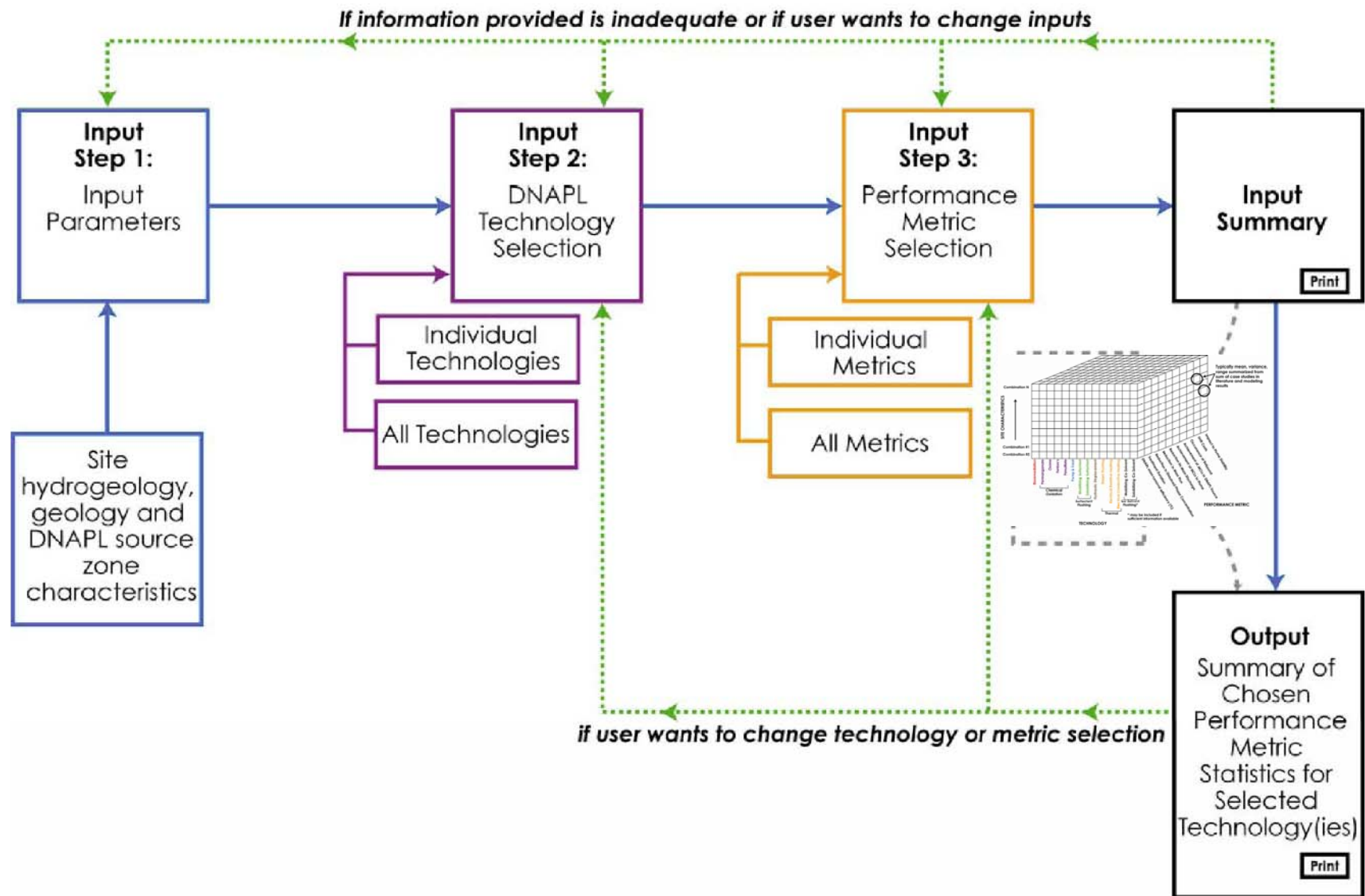
## Fractured Clay Template Site Parameters

Template Site	DNAPL Type	Fracture Aperture	Matrix Porosity	Fraction Organic Carbon	Fracture Spacing
Low Organic Carbon	TCE	75 $\mu\text{m}$	30%	0.0015	1.0 m
Low Matrix Porosity	TCE	75 $\mu\text{m}$	15%	0.003	1.0 m
Low Fracture Aperture	TCE	37.5 $\mu\text{m}$	30%	0.003	1.0 m
Low Density DNAPL	1,1,1-TCA	-	-	-	-
<b>Base Case</b>	<b>TCE</b>	<b>75 <math>\mu\text{m}</math></b>	<b>30%</b>	<b>0.003</b>	<b>1.0 m</b>
High Density DNAPL	PCE	75 $\mu\text{m}$	30%	0.003	1.0 m
High Fracture Aperture	TCE	150 $\mu\text{m}$	30%	0.003	1.0 m
High Matrix Porosity	TCE	75 $\mu\text{m}$	45%	0.003	1.0 m
High Organic Carbon	TCE	75 $\mu\text{m}$	30%	0.006	1.0 m



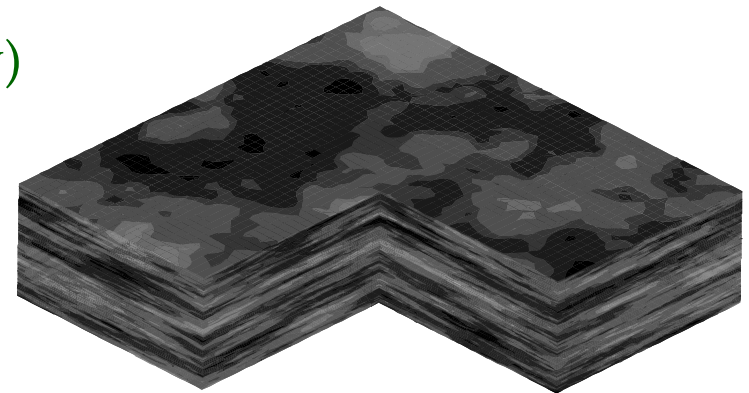


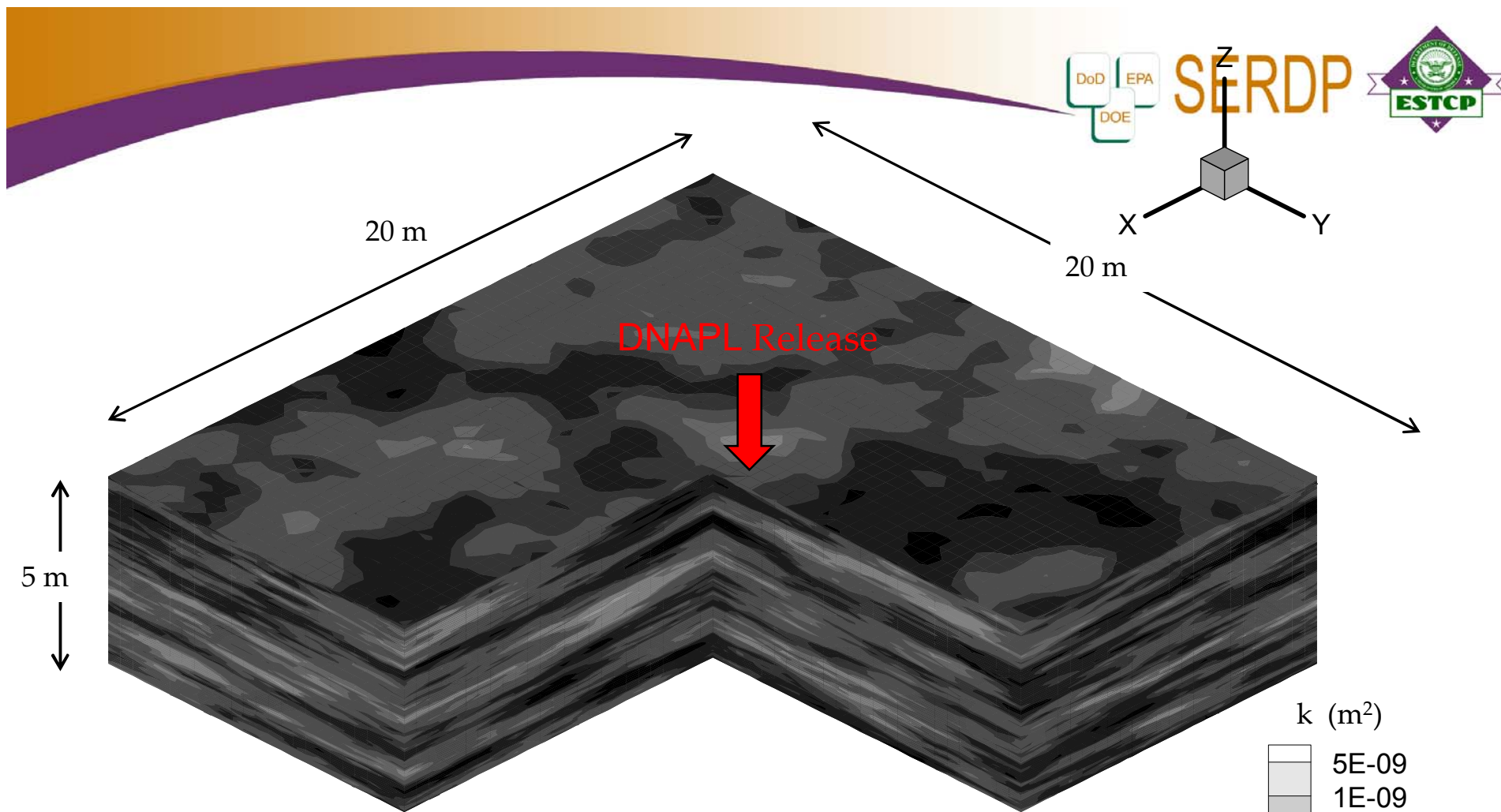
# Screening Tool Structure



# ***Numerical Modeling***

- Numerical simulation of DNAPL source zone remediation in porous and fractured media
- Technologies considered:
  - ◆ Hydraulic Displacement (PM only)
  - ◆ Pump-and-Treat
  - ◆ In Situ Chemical Oxidation
  - ◆ Enhanced In Situ Bioremediation
  - ◆ Surfactant Flushing
- Technologies applied to 'Template Sites'





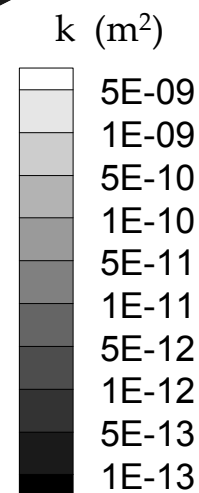
Spatially correlated random  $k$  field:

$$\lambda_x = \lambda_y = 3.0 \text{ m} \quad \Delta x = \Delta y = 0.40 \text{ m}$$

$$\lambda_z = 0.2 \text{ m}$$

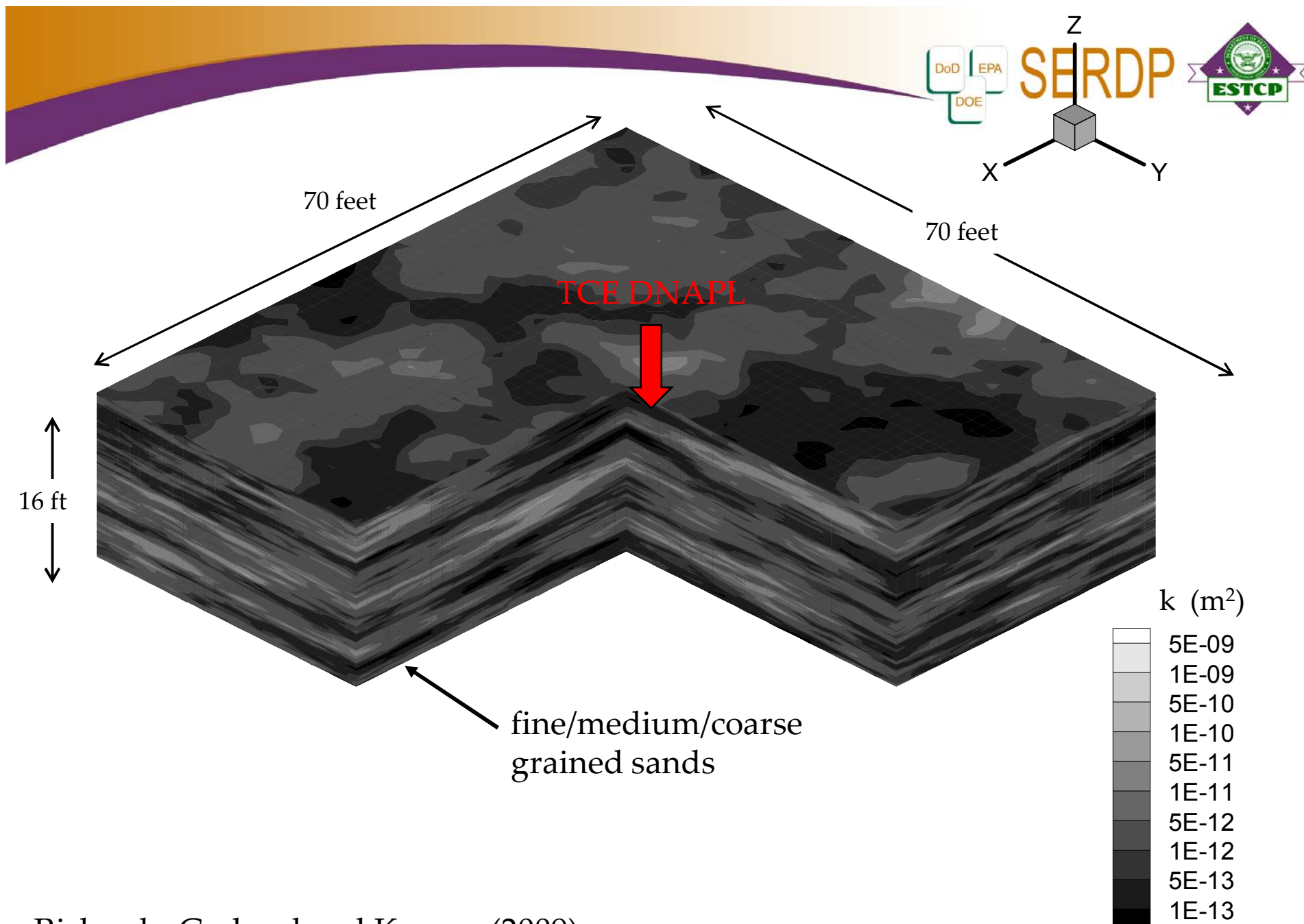
$$\Delta z = 0.05 \text{ m}$$

$$NN = 250,000$$



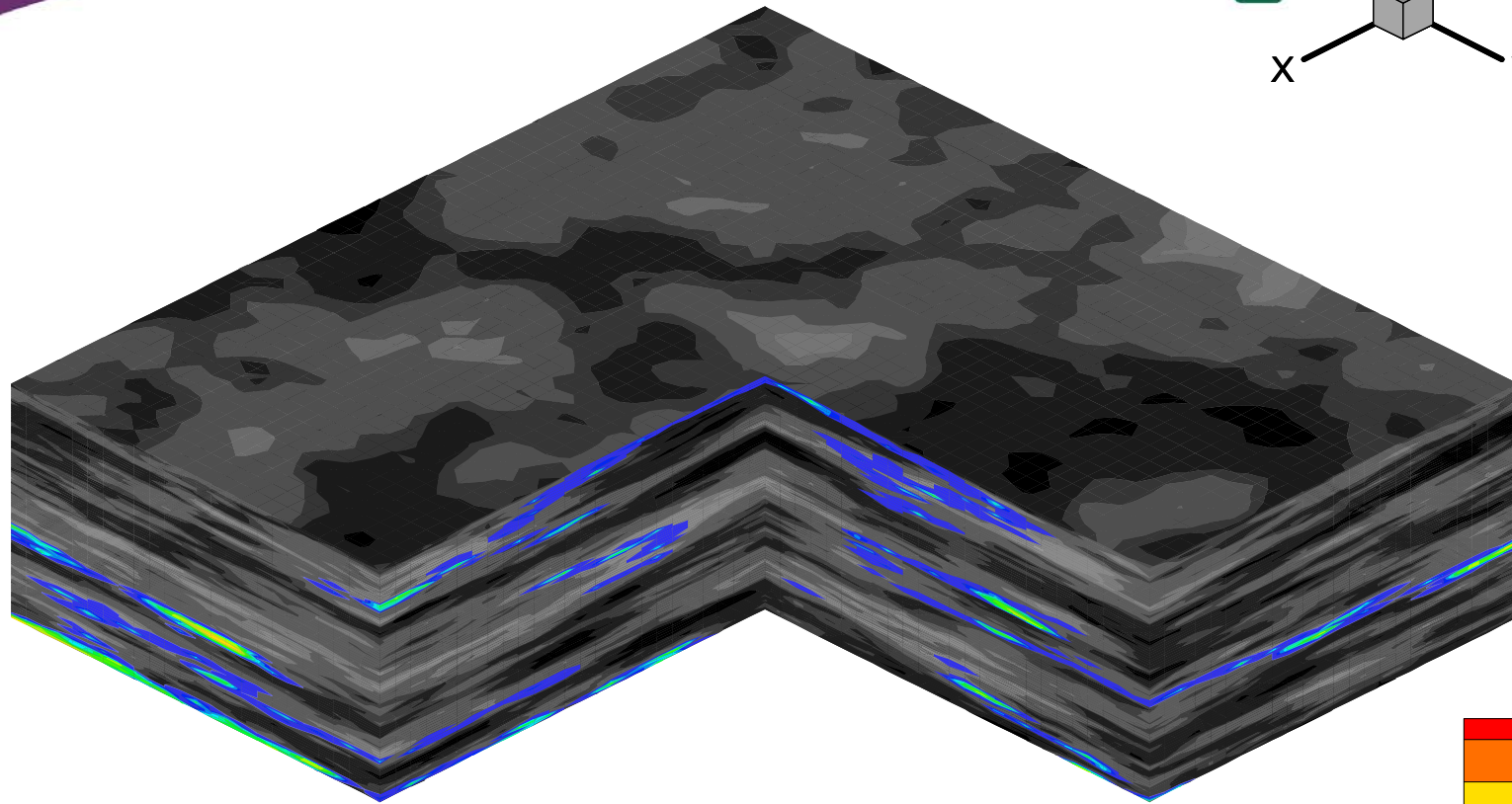
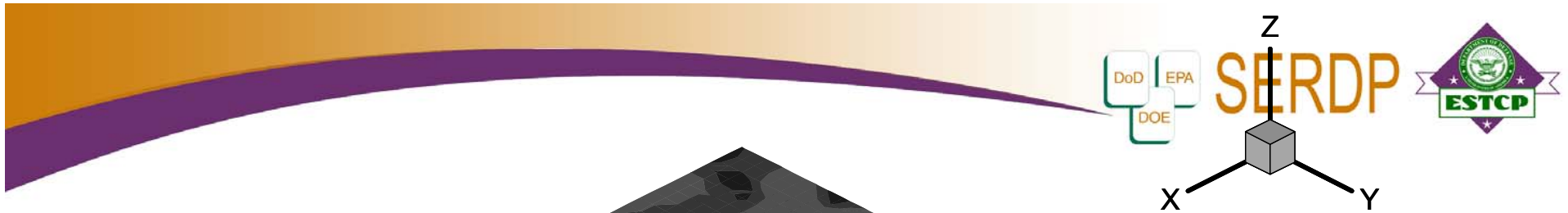
## ***Porous Media Template Sites***

Template Site	DNAPL	Initial Mass (kg)	Initial Volume (m <sup>3</sup> )	Mean $k$ (m <sup>2</sup> )	Variance In $k$
Base case	TCE	3520	2.41	$3.03 \cdot 10^{-12}$	1.74
High mean $k$	TCE	3496	2.39	$3.02 \cdot 10^{-11}$	1.74
Low mean $k$	TCE	3535	2.42	$3.04 \cdot 10^{-13}$	1.74
Low heterogeneity	TCE	3355	2.30	$1.87 \cdot 10^{-12}$	0.87
High heterogeneity	TCE	3186	2.18	$7.41 \cdot 10^{-12}$	3.48
Small DNAPL volume (post HD)	TCE	785	0.54	$3.03 \cdot 10^{-12}$	1.74
Small DNAPL volume (pre HD)	TCE	803	0.55	$3.03 \cdot 10^{-12}$	1.74
Large DNAPL volume	TCE	7343	5.03	$3.03 \cdot 10^{-12}$	1.74
High density DNAPL	PCE	3871	2.37	$3.03 \cdot 10^{-12}$	1.74

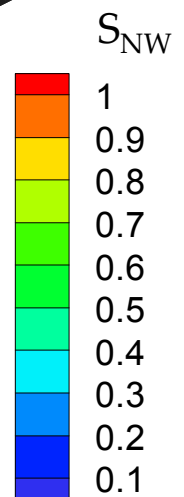


Richards, Gerhard and Kueper (2009)

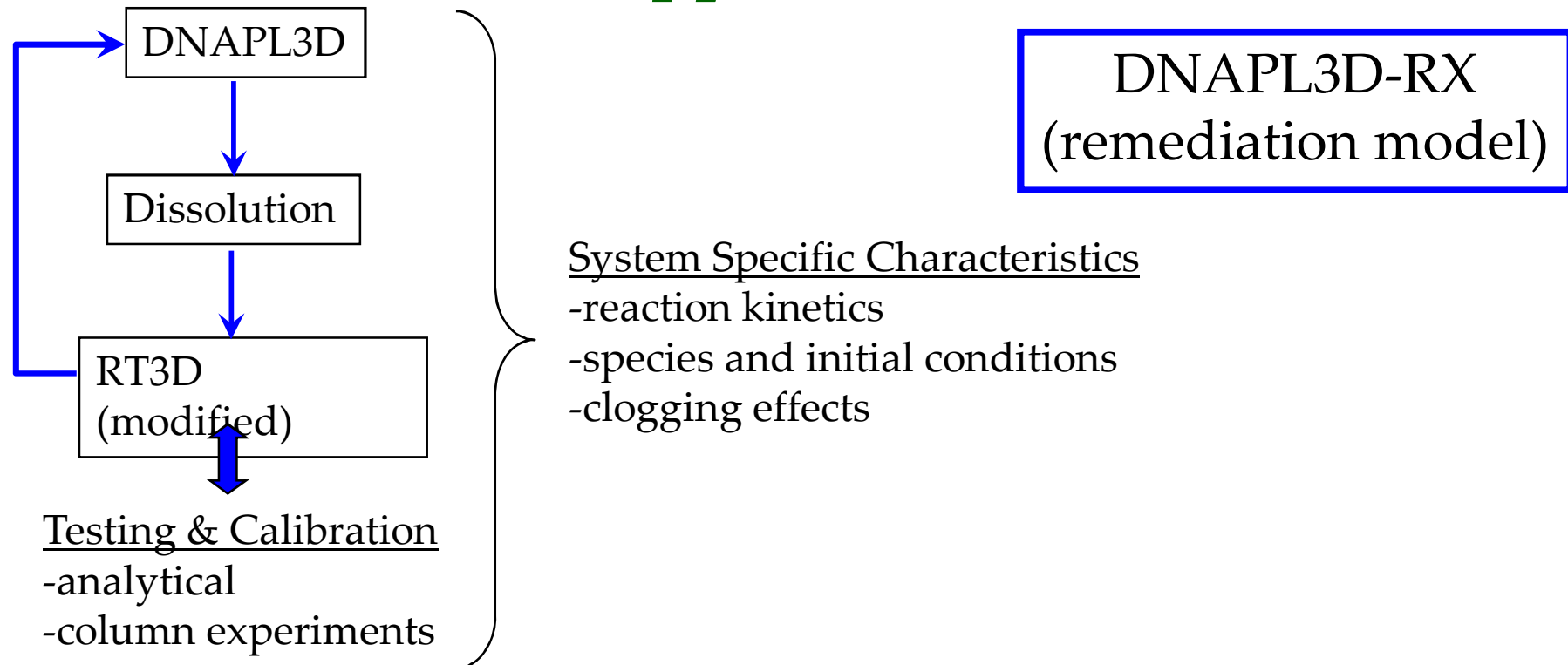




15.0 years, source off



# ***Remediation Model Development & Application***

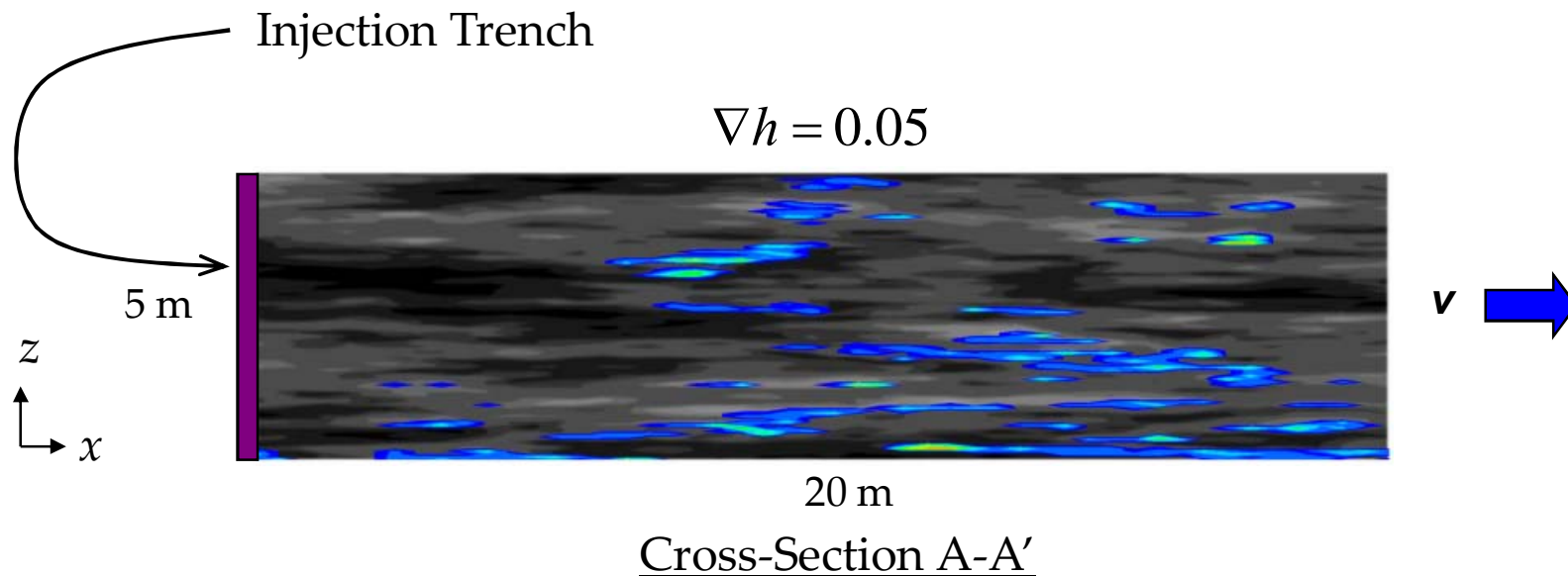
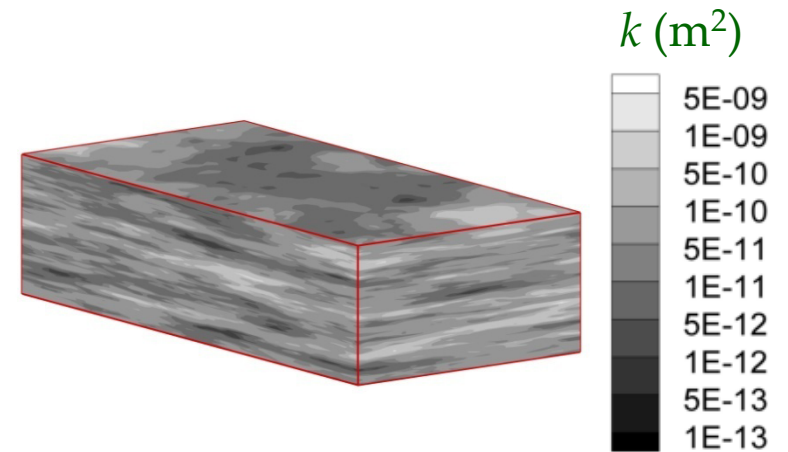
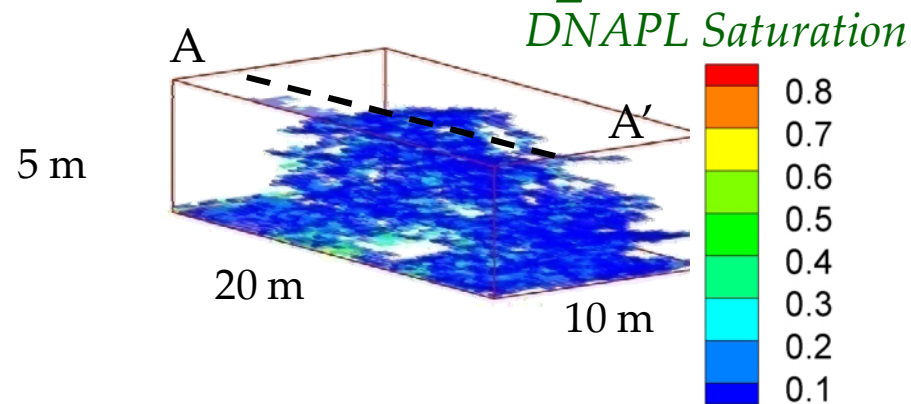


## **Field Scale Applications**

**9 Template Sites (geology, TCE/PCE/111-TCA, DNAPL volume)**

**5 technologies (HD, P&T, ISCO, EISB, SEAR )**

# Base Case Modeling Domain (Template Site 1)



# ***In-Situ Chemical Oxidation (ISCO) with Potassium Permanganate***

- Stoichiometry, kinetics and rate constants from literature
- 2<sup>nd</sup> order reactions for TCE/PCE and OAM with  $\text{MnO}_4^-$
- $\text{KMnO}_4$  injected at 2,500 mg/L
- Species specific diffusion coefficients (TCE and  $\text{MnO}_4^-$ )
- OAM cross-correlated with  $k$  (negative)
- Pore clogging due to rind formation (*West et al., 2008, AWR*)
- Perfectly buffered system assumed
- Local equilibrium dissolution of DNAPL

# ISCO Simulations



Simulation	Description	Injection Duration (days)	KMnO <sub>4</sub> Breakthrough at Exit Face?
1	Base case	849	No
2	High mean $k$	83	No
3	Low mean $k$	3650	No
4	Low heterogeneity	1086	No
5	High heterogeneity	575	No
6a	Small DNAPL volume (post HD)	163	No
6b	Small DNAPL volume (pre HD)	166	No
7	Large DNAPL volume	2251	Yes
8	PCE DNAPL	724	No
9	Base case, no Rind	849	No
10	Base case, no NOD	849	Yes
11	Base case, no NOD & no Rind	849	Yes

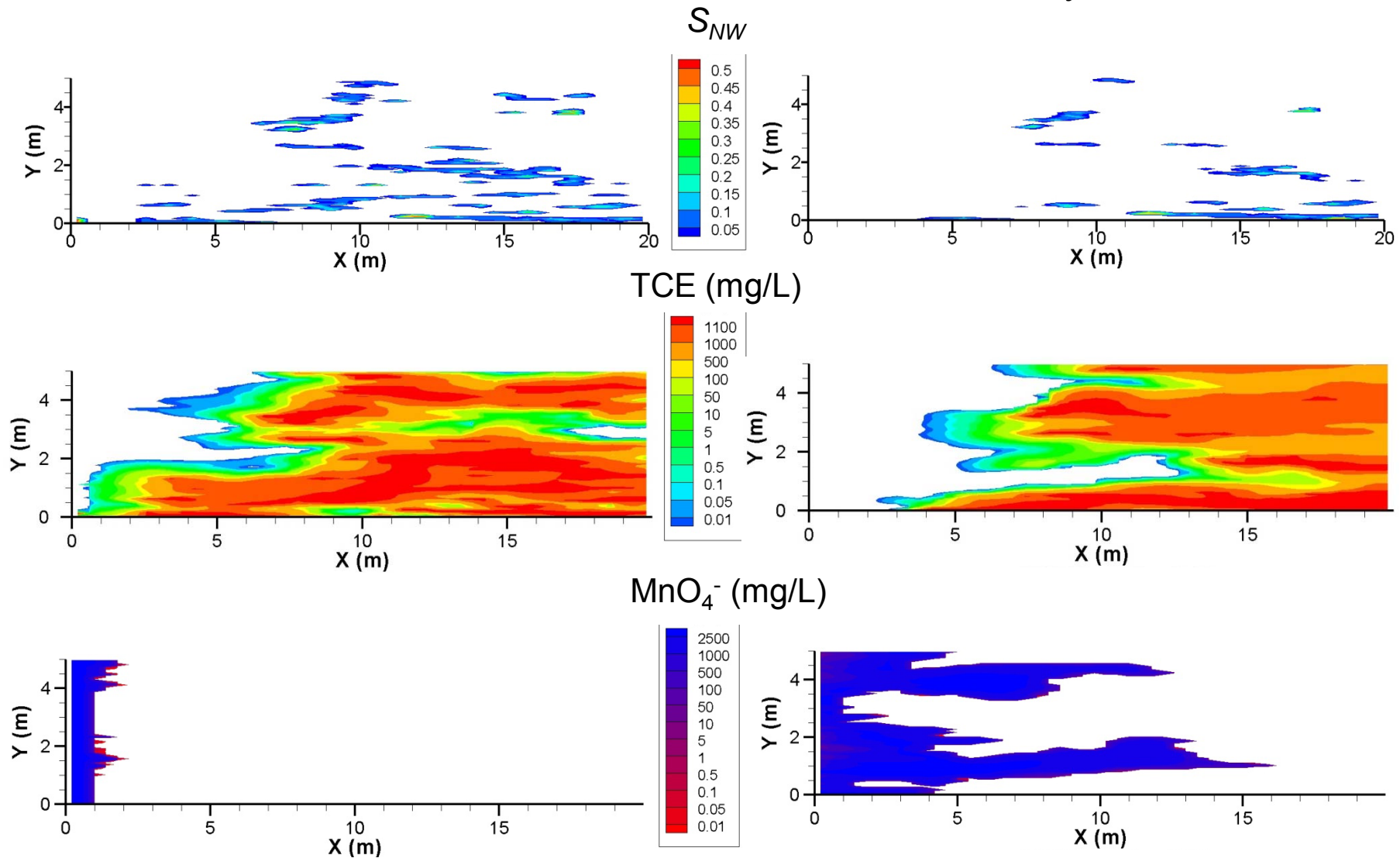


# Comparison of ISCO Output – Base Case

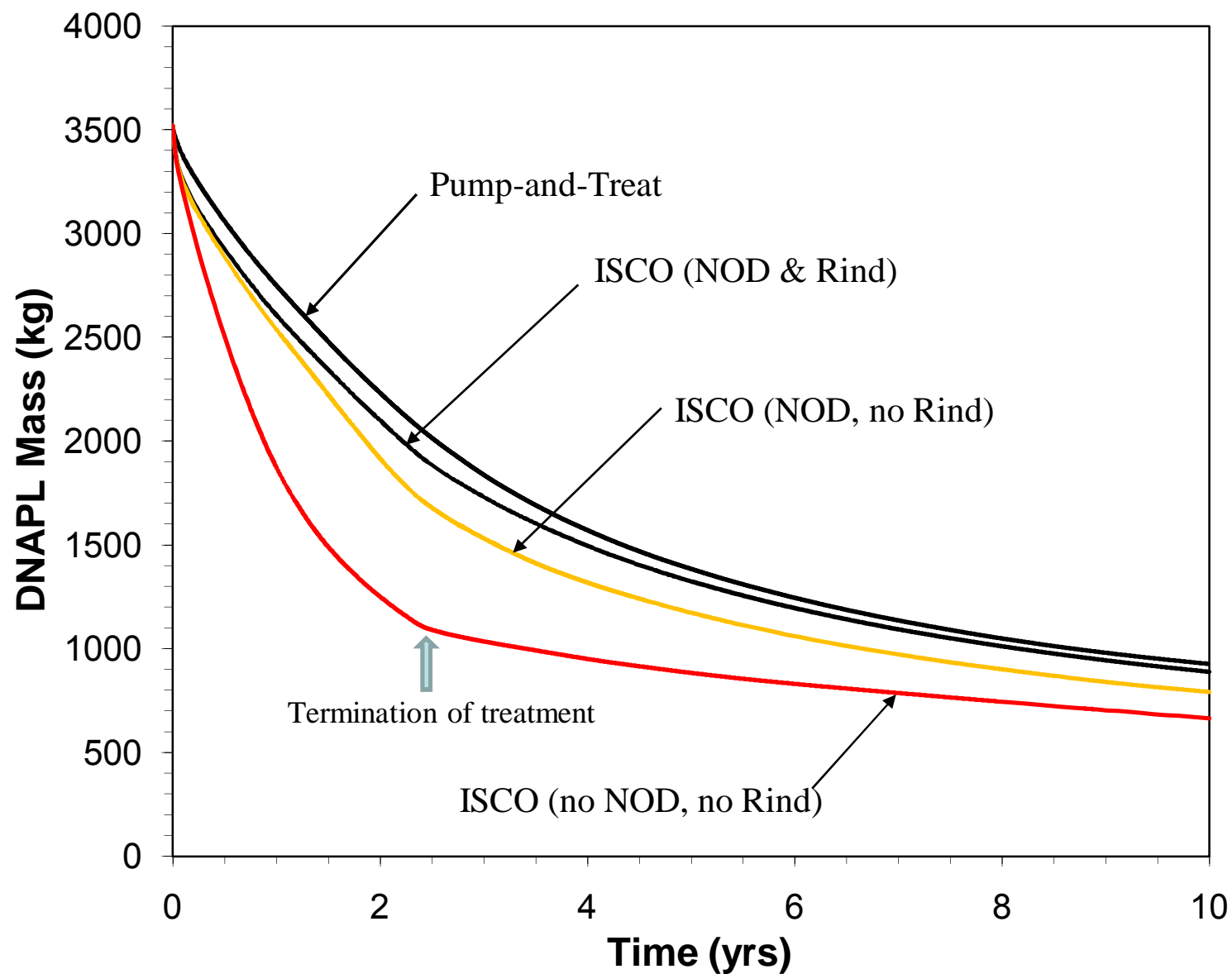


1 month

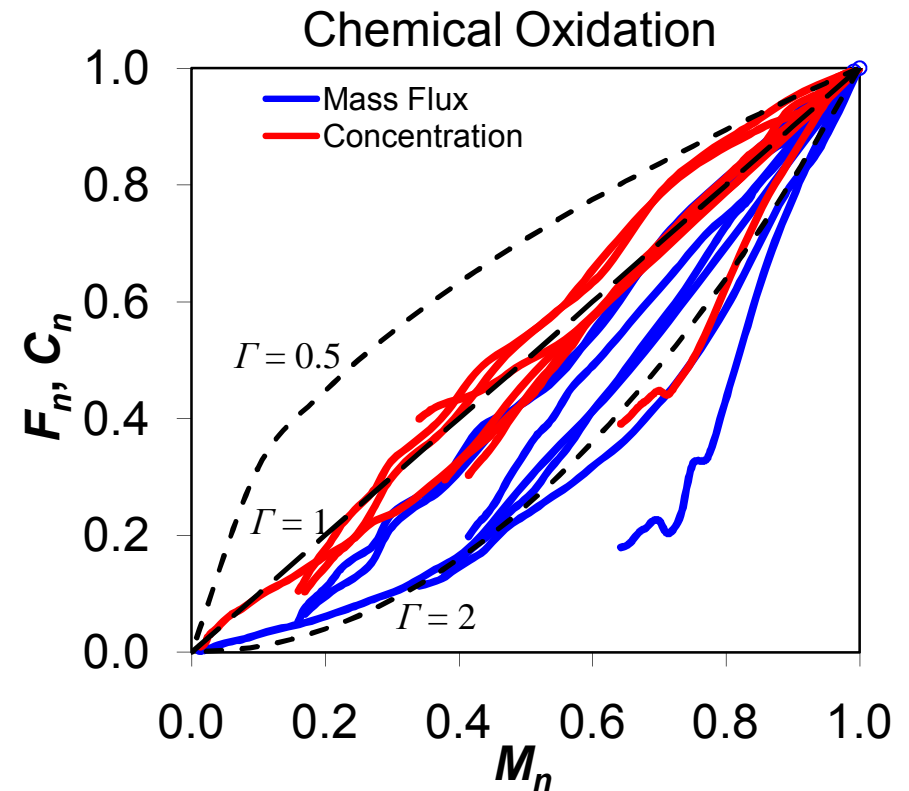
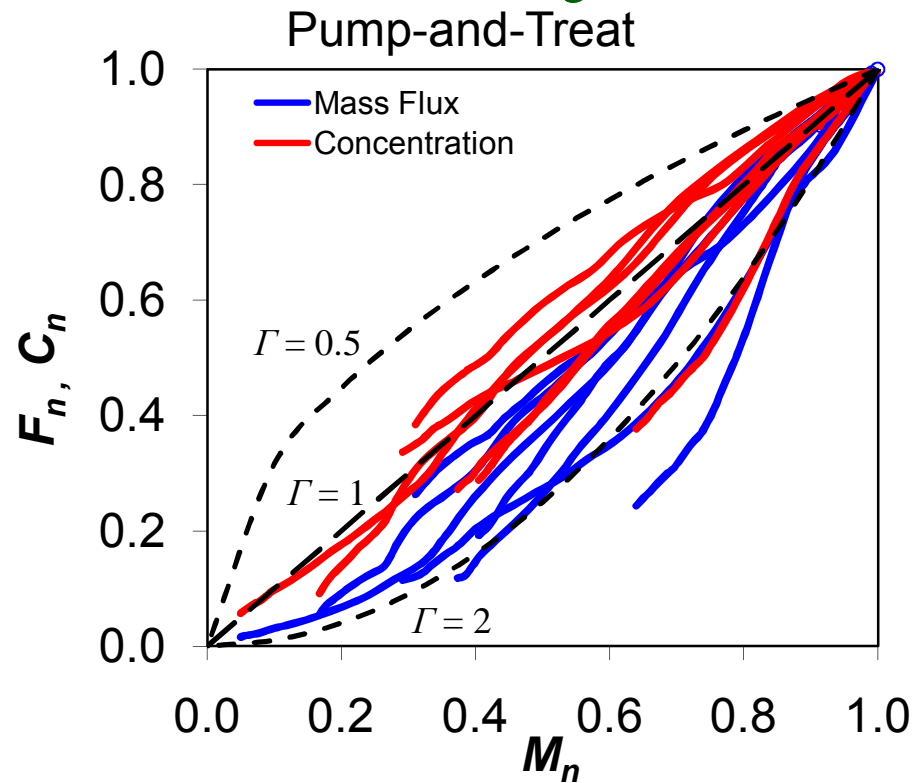
2.33 years



# *ISCO Base Case Template*



# Pump-and-Treat vs Chemical Oxidation (Boundary Flux and Concentration)



$$C_n = \frac{C(t)}{C(t_0)} \quad F_n = \frac{M_f(t)}{M_f(t_0)} \quad M_n = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right) \quad C_n = \frac{C(t)}{C(t_0)} = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right)^\Gamma$$

# ***Enhanced In-Situ Bioremediation (EISB)***

- Stoichiometry, kinetics and rate constants from literature
- TCE (or PCE) degrades to *cis*-DCE
- Monod-type kinetics
- First-order decay of biomass
- Lactate injected @ 1 day/week for 2.5 years
- 3 biologic species: fermentors, dechlorinators, & methanogens (competitors)
- All microbes initially uniformly distributed
- Lactate converted to H<sub>2</sub> by fermentors
- H<sub>2</sub> consumed by both dechlorinators & methanogens
- Bioclogging due to dechlorinator & methanogen biomass

# ***EISB Simulations***



**SERDP**



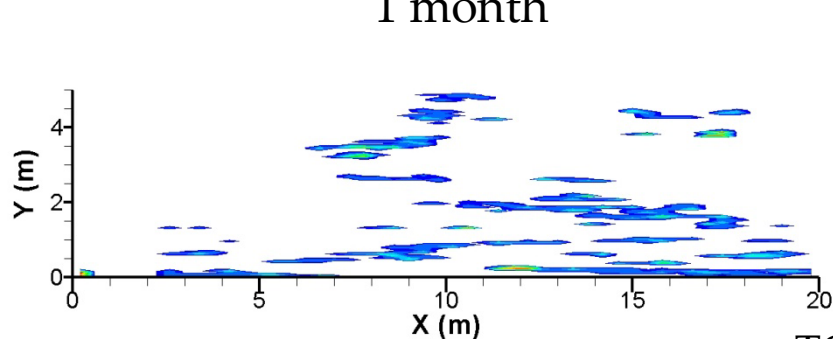
Simulation	Description	Lactate injection concentration (mg/L)
1	Base case	39130
2	High mean $k$	39130
3	Low mean $k$	39130
4	Low heterogeneity	39130
5	High heterogeneity	39130
6a	Small DNAPL volume (post HD)	39130
6b	Small DNAPL volume (pre HD)	39130
7	High DNAPL volume	39130
8	PCE DNAPL	39130 or 7511
BC1	Base case, no bioclogging	39130
BC2	Base case, no competition	39130
BC3	Base case, no bioclogging & no competition	39130
PS1	Base case, 1 hour/day lactate pulse	134160
PS2	Base case, 1 week/month lactate pulse	24113



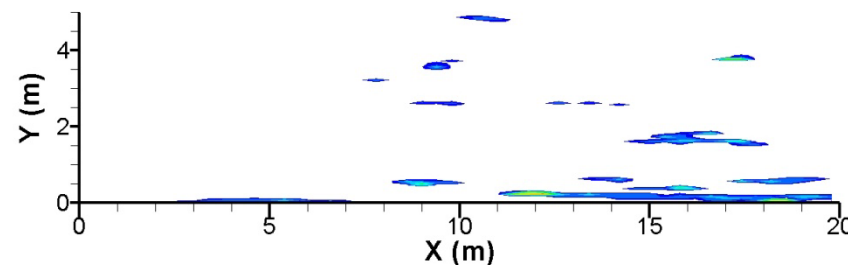
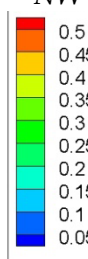
# Comparison of EISB Output – Base Case

1 month

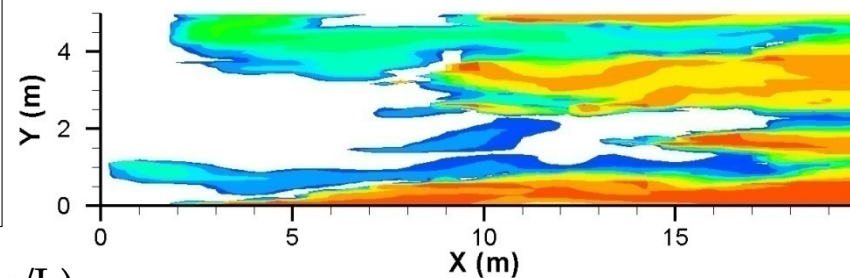
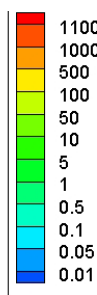
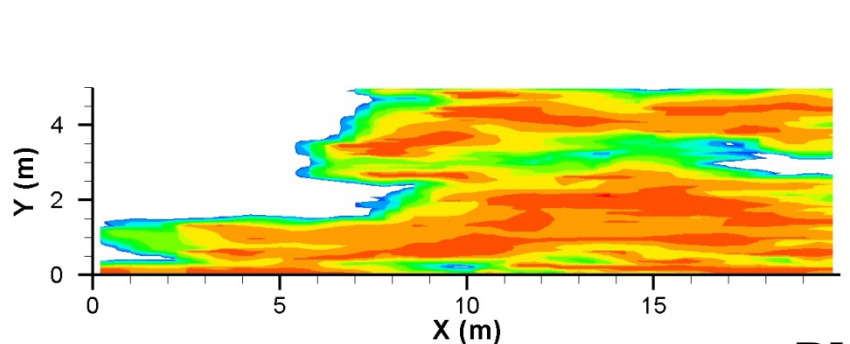
2.5 years



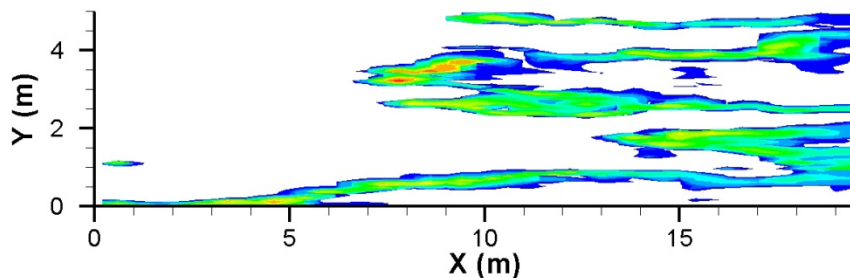
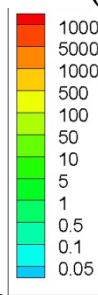
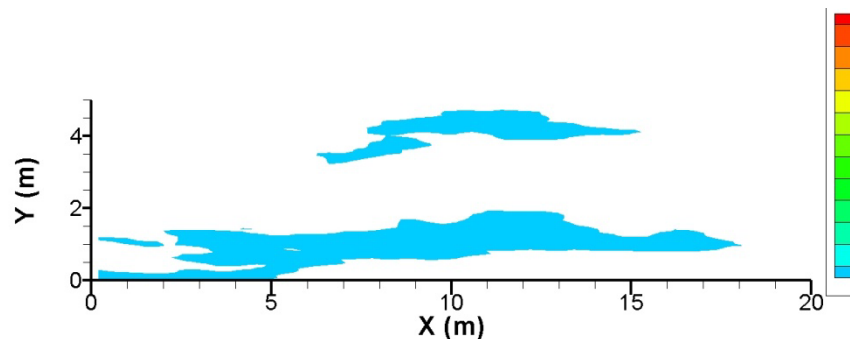
$S_{NW}$



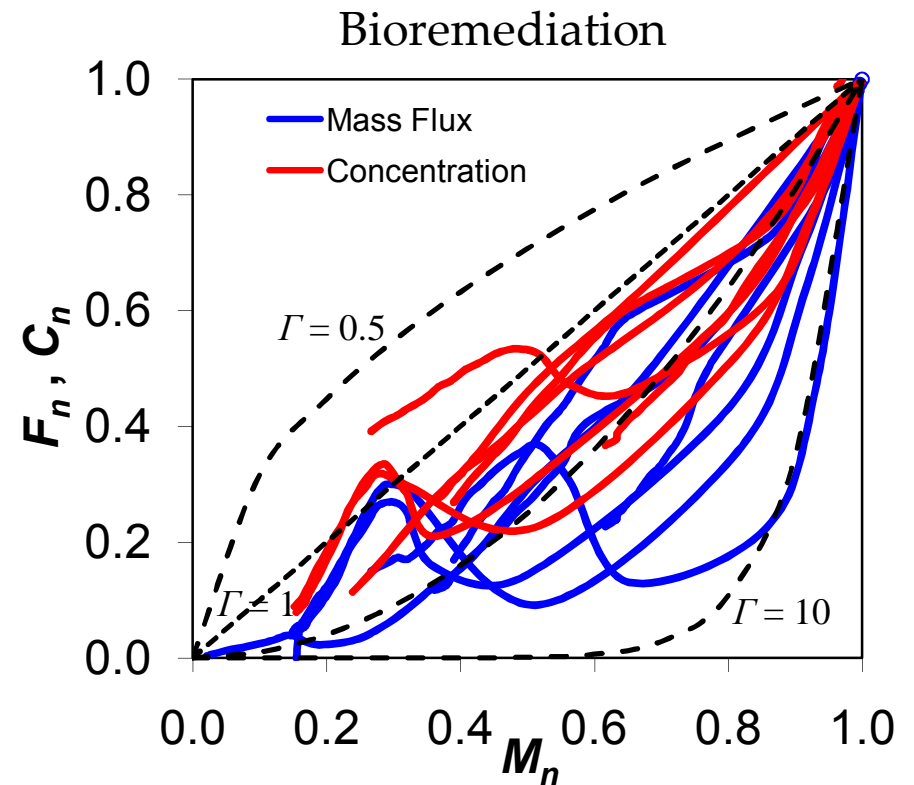
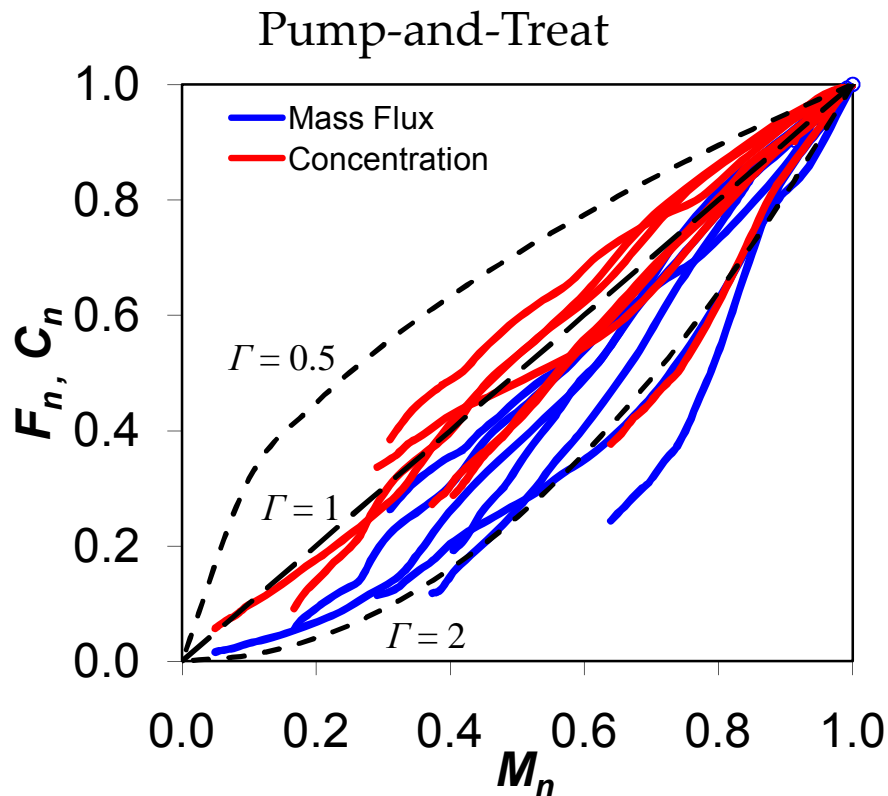
TCE (mg/L)



DHC (mg/L)



# Pump-and-Treat v. Bioremediation (boundary flux and concentration)



$$C_n = \frac{C(t)}{C(t_0)} \quad F_n = \frac{M_f(t)}{M_f(t_0)} \quad M_n = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right) \quad C_n = \frac{C(t)}{C(t_0)} = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right)^\Gamma$$

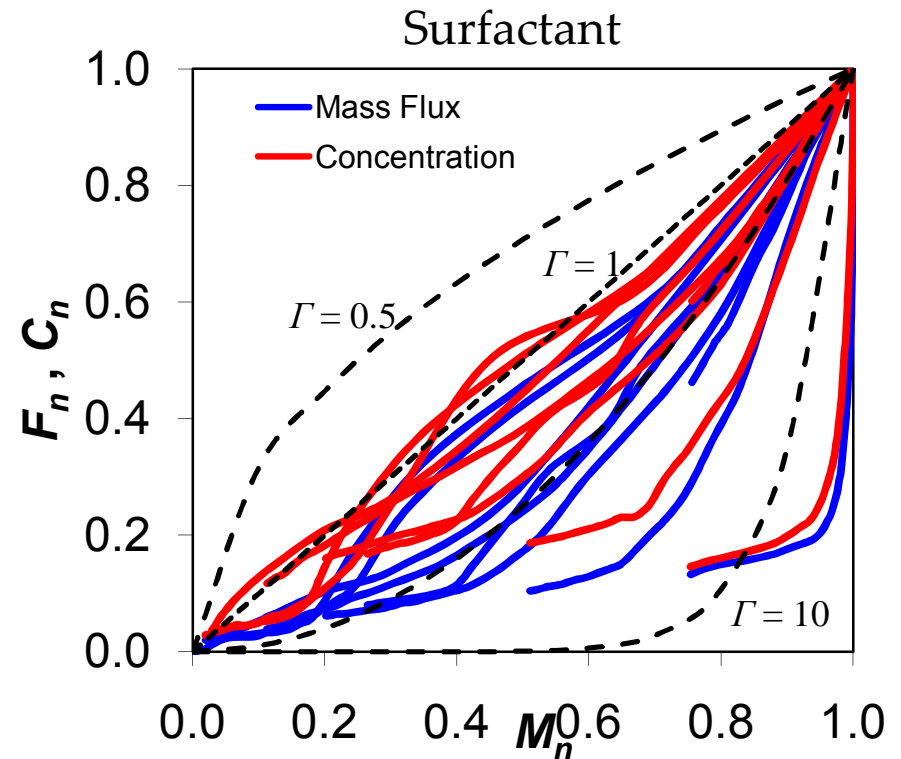
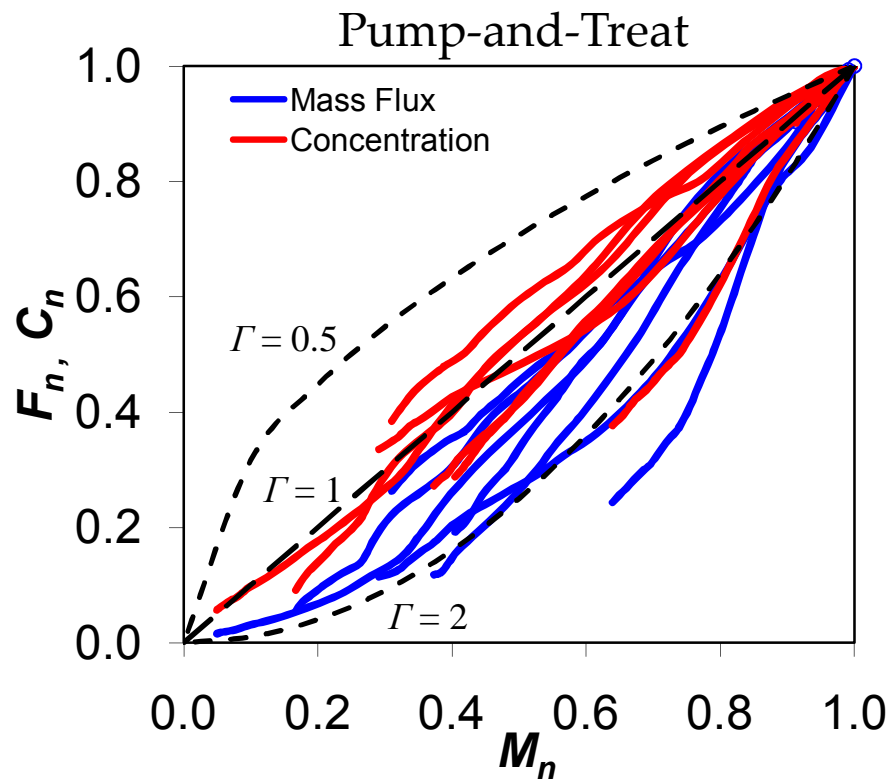
# ***Surfactant Enhanced Aquifer Remediation (SEAR)***

- Dissolution kinetics and rate constants from literature
- Tween 80 injected at 40,000 mg/L for 22 days (base case)
- 3 species: TCE/PCE solute, Tween 80 micelles, and pseudo micro-emulsion
- Enhanced dissolution by linear driving function
- Interfacial tension reduction not simulated
- Model tested against published column experiments

# ***SEAR Simulations***

<b>Simulation</b>	<b>Template site</b>	<b>SEAR injection time (days)</b>
1	Base case (TCE)	22
2	High mean $k$	2
3	Low mean $k$	223
4	Low heterogeneity	29
5	High heterogeneity	11
6a	Small DNAPL volume (post-HD)	5
6b	Small DNAPL volume (pre-HD)	5
7	Large DNAPL volume	48
8	PCE DNAPL	35

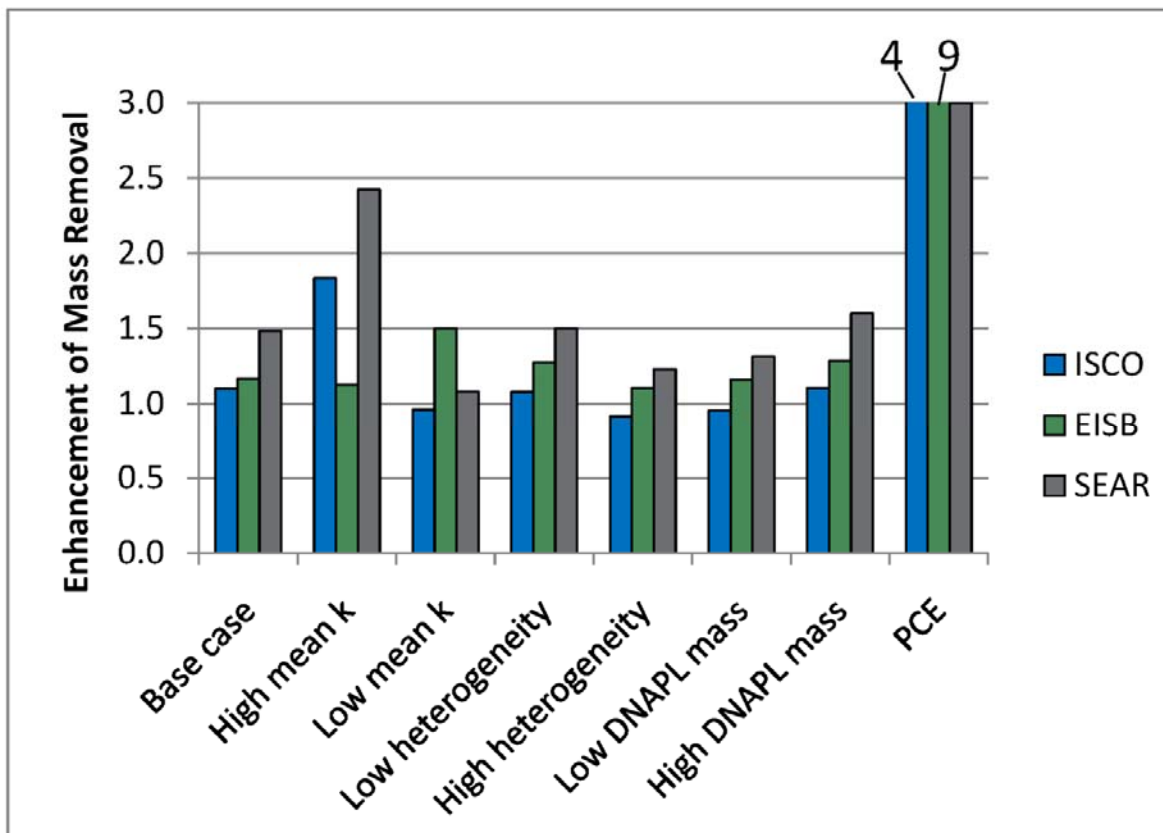
# Pump-and-Treat vs SEAR (boundary flux and concentration)



$$C_n = \frac{C(t)}{C(t_0)} \quad F_n = \frac{M_f(t)}{M_f(t_0)} \quad M_n = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right) \quad C_n = \frac{C(t)}{C(t_0)} = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right)^\Gamma$$

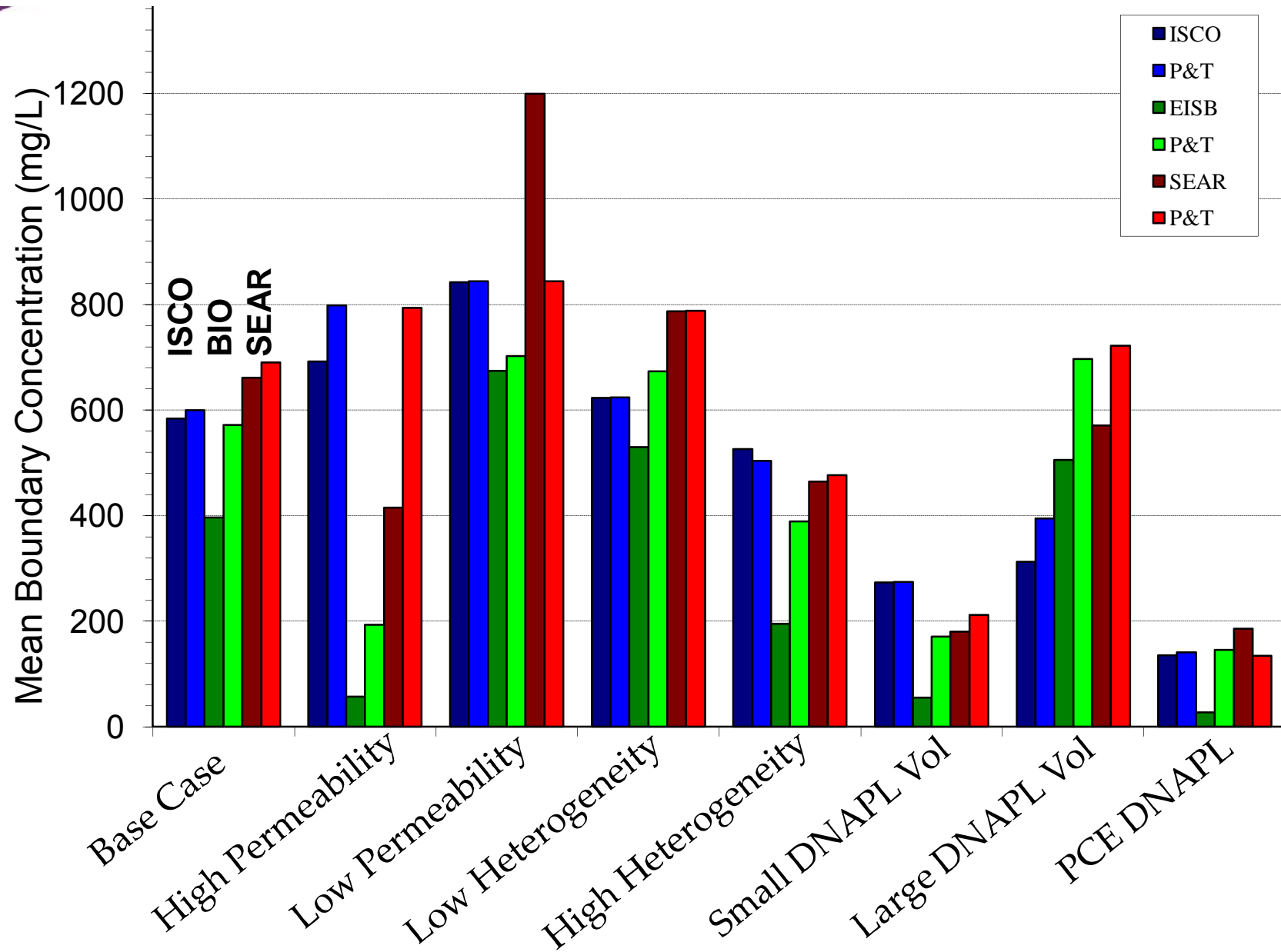


# Comparative Enhancement of DNAPL Mass Removal at End of Treatment

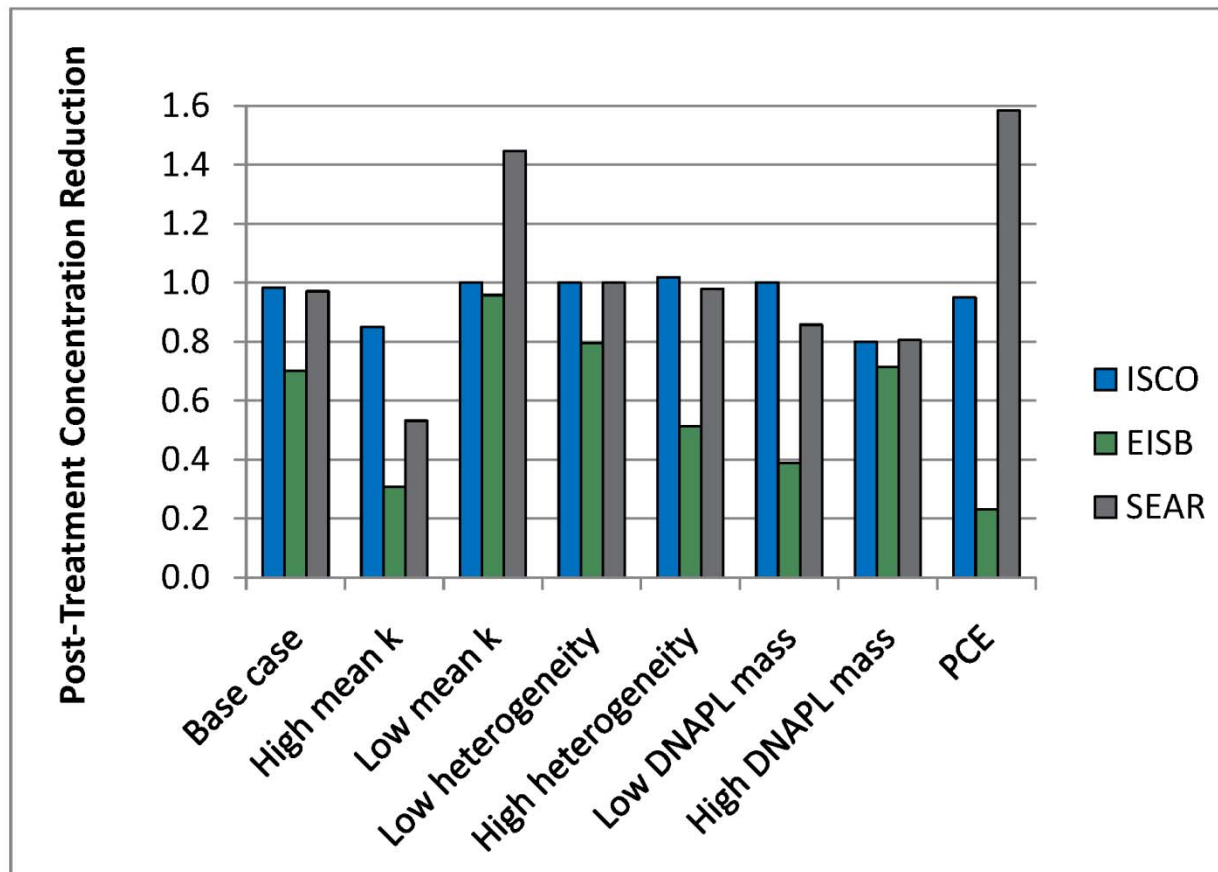


- Enhancement of mass removal greatest where dissolution is not a significant mass removal factor:
  - Lower solubility DNAPLs (PCE)
- ISCO (MnO<sub>4</sub>) only technology where incomplete treatment reduces mass removal efficiency below doing P&T

# *Mean Boundary Concentration at End of Treatment*

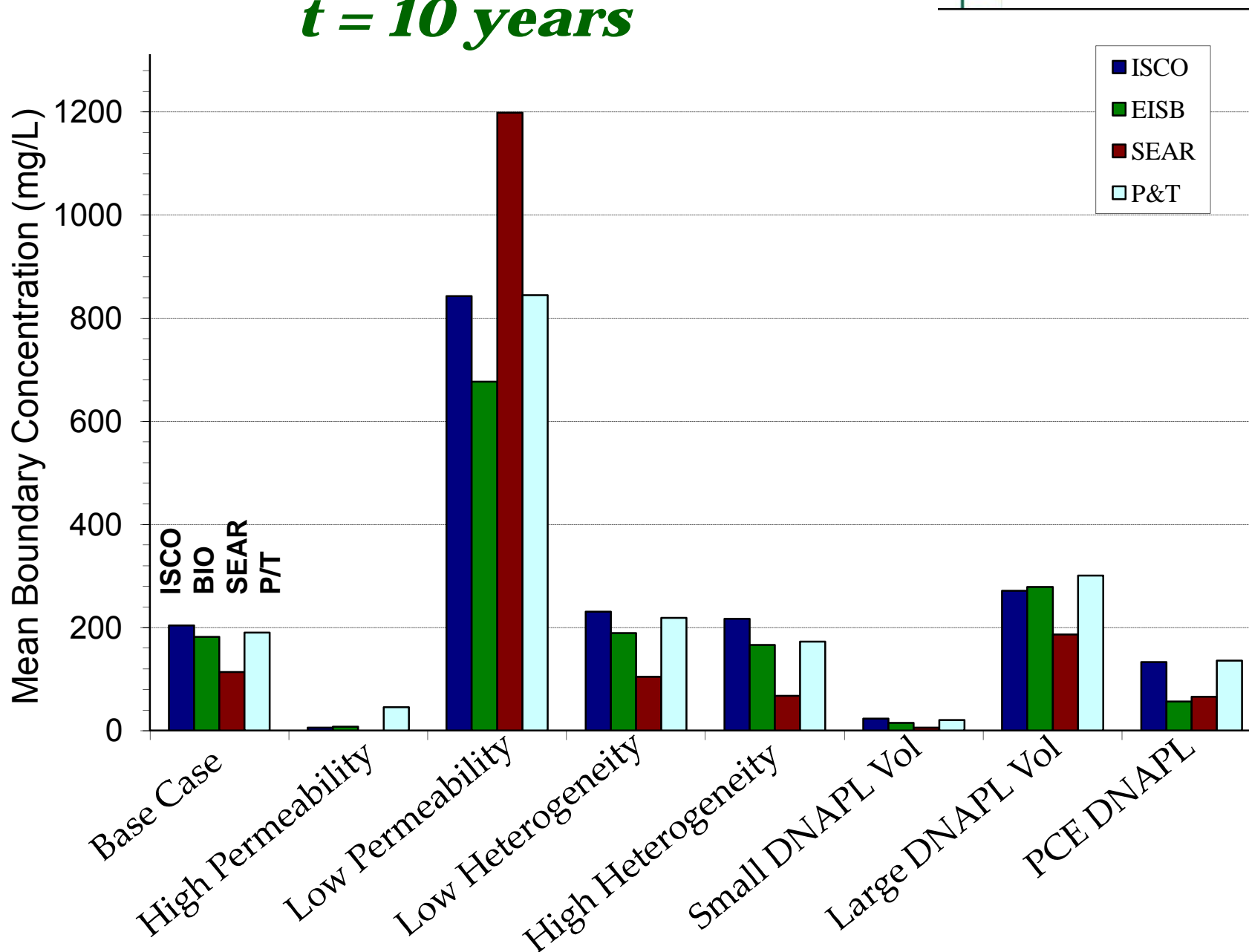


# ***Concentration Reduction Enhancement Normalized to P&T – at End of Treatment***

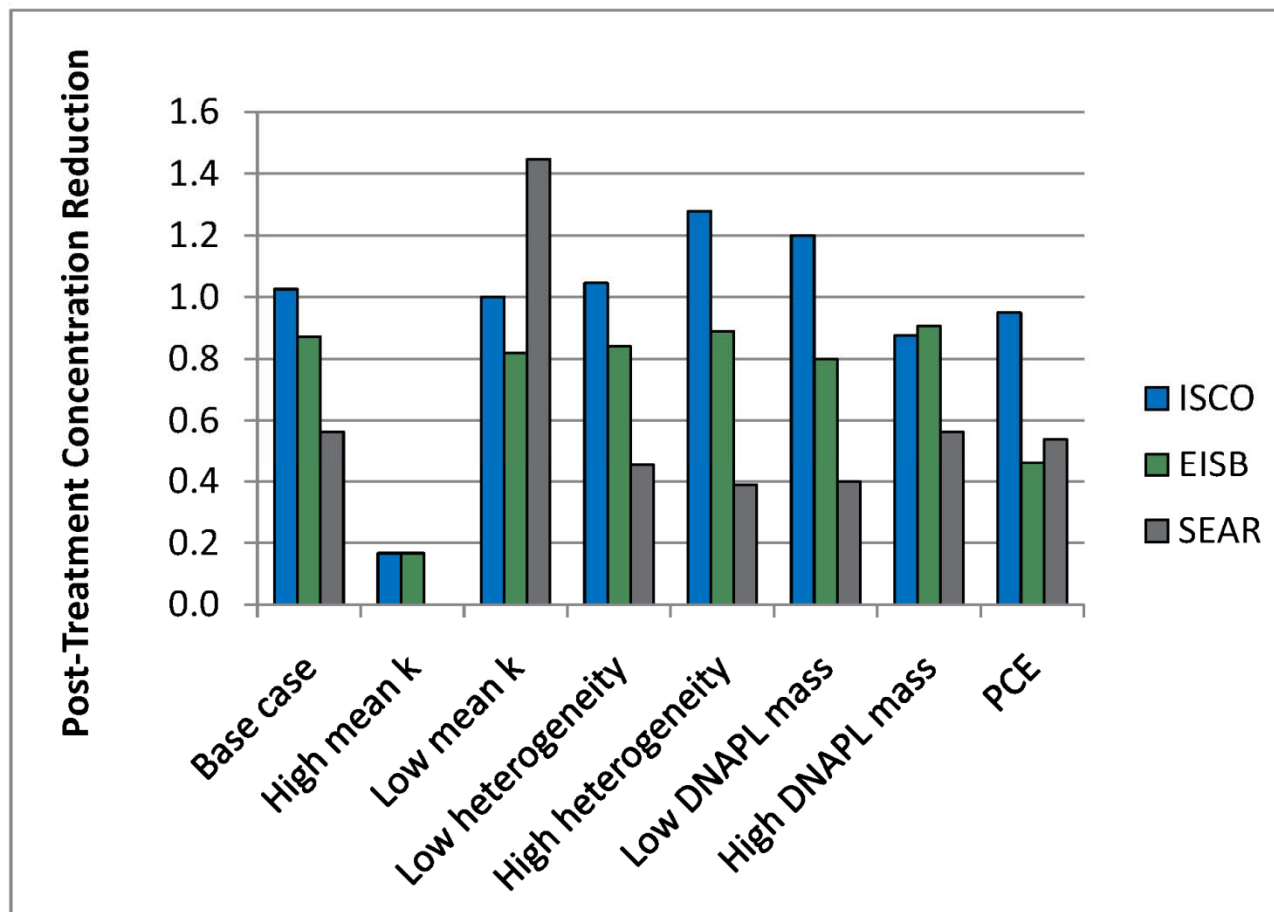


- Reduction factor  $>1$  = concentrations higher than seen for dissolution only
- EISB has greatest enhancement in concentration reductions at treatment termination
- ISCO reductions were minimal

# *Mean Boundary Concentration* *t = 10 years*



# Concentration Reduction Enhancement Beyond P&T – After 10 Years



- SEAR enhancement of concentration reduction continues to improve, except for low permeability soils
- EISB concentrations still lower than P&T for all, but enhancement in reduction is reduced
- ISCO enhancement still minimal, and worsened in some cases



## ***Conclusions – Porous Media Modeling***

- Technology performance (DNAPL mass, flux and concentration reduction) is site specific (geology, DNAPL volume)
- Flux decreases faster than concentration
- Low permeability generally not conducive to injection technologies
- Important to arrive at accurate estimate of DNAPL mass to optimize design

## ***Conclusions – Porous Media Modeling***

- P/T & ISCO ( $\text{MnO}_4$ ) typically lead to near-linear reduction in concentration with mass removal, while EISB and SEAR have greater proportion of concentration reduction with DNAPL mass removal
- Partial mass removal will not achieve MCLs in groundwater concentrations
- Demand from natural organic matter can result in significantly more oxidant demand compared to stoichiometric DNAPL mass requirements
  - ◆ Cost issue

## Case Study Trend Analysis

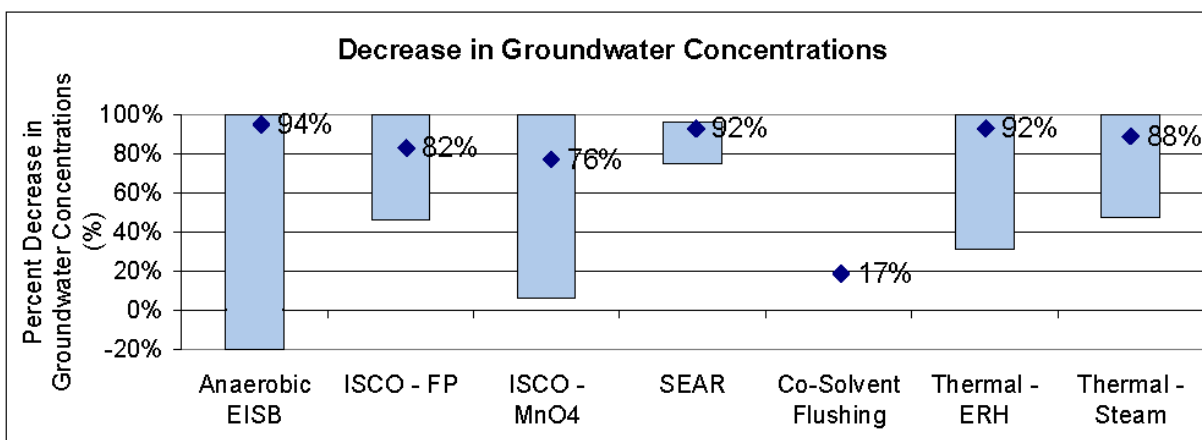
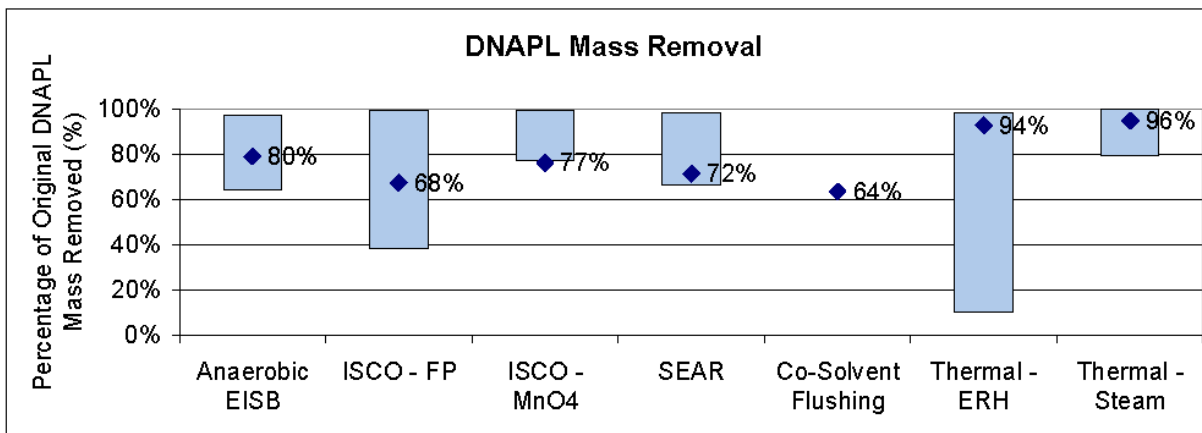
- Linear and non-linear multivariate regression used to evaluate influence of site parameters on technology performance:

- Correlations between site parameters and performance metrics
- Determine the 'key' site & technology parameters correlated to performance

Performance Metric	Treatment Area	Saturated Thickness	Soil Heterogeneity	Pooled DNAPL	Electrode Spacing
Decrease in Groundwater Concentrations	<i>Equally good performance in nearly all case studies</i>				
Decrease in Soil Concentrations	---			--	
Removal of DNAPL Mass	----				
Treatment Duration (ERH)		++			++++
Treatment Duration (Steam)	+++		++++		
Rebound of Groundwater Concentrations	<i>Equally good performance in all case studies</i>				
Unit Cost (\$/m <sup>3</sup> )		+++		++	
Achievement of MCLS	<i>No apparent influence from site parameters</i>				

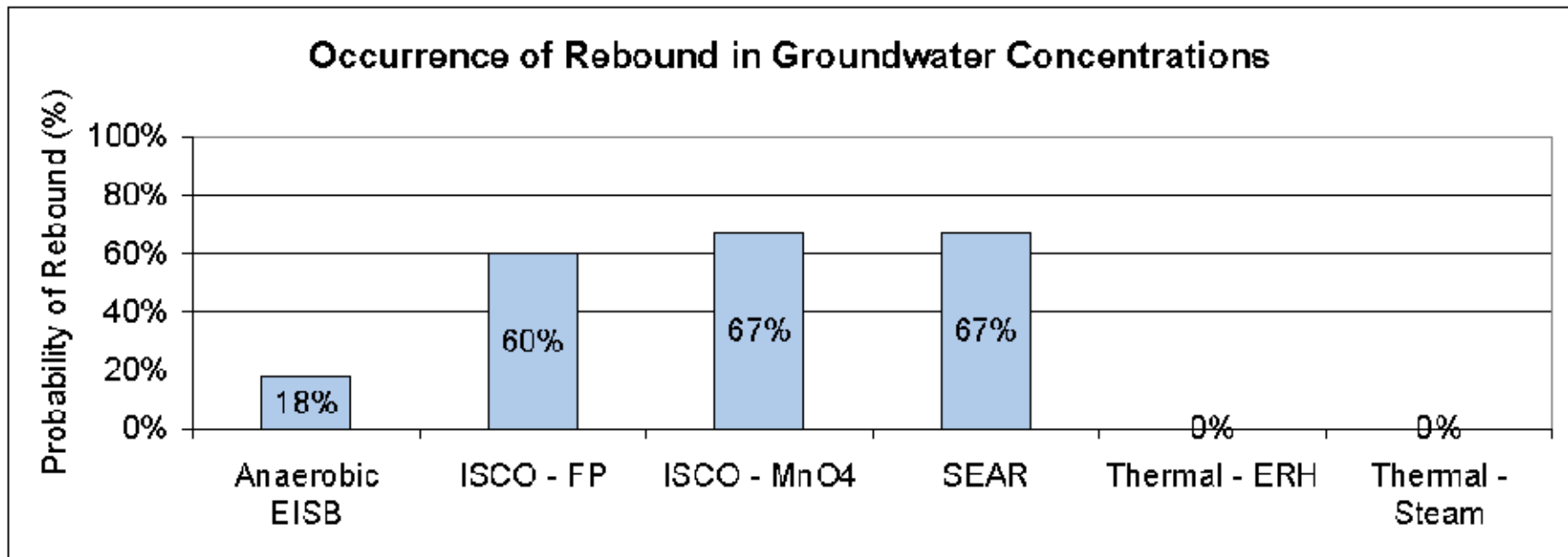
- indicates weakest negative correlation, ---- indicates strongest negative correlation  
 + indicates weakest positive correlation, ++++ indicates strongest positive correlation

# Technology Performance Comparison



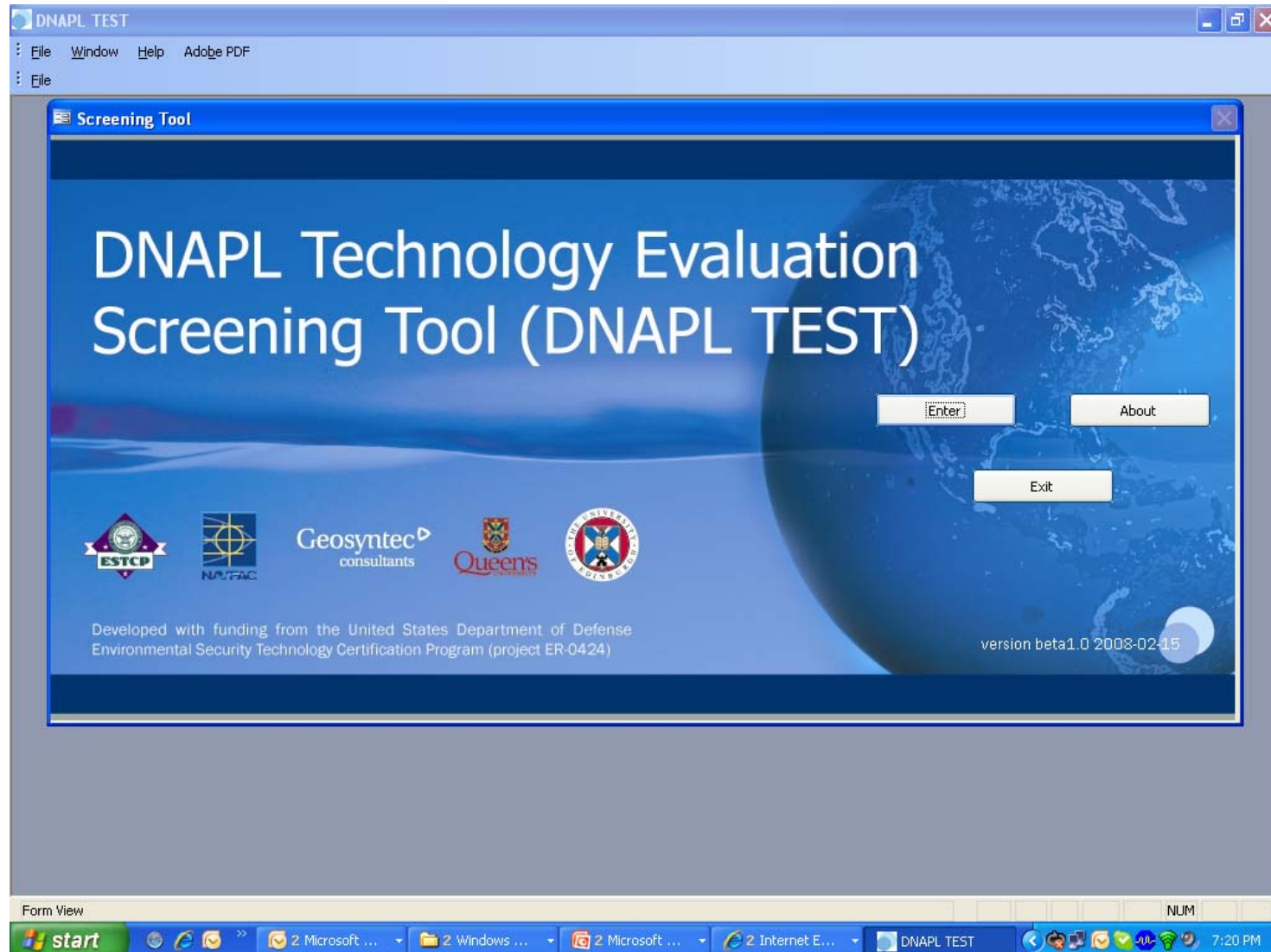
- Thermal typically better at removing DNAPL mass, other technologies more likely to have partial mass removal
- Temporary increases in flux/ concentrations may be seen during EISB due to increased dissolution of the DNAPL and production of more soluble daughter products

# ***Long-Term Impact on Concentrations***



- Extent of mass removal impacts long-term groundwater concentrations
  - ◆ Thermal most likely to have near complete mass removal, others more likely to be partial mass removal

# ***Screening Tool Demonstration***





# ***Screening Tool Demonstration***



## **General Analysis**

- ◆ General trends in tech performance
- ◆ Filter out various factors to narrow analysis, evaluate changes

## **Site-Specific Analysis**

- ◆ User inputs site parameters of interest
- ◆ Tools searches for statistically similar case studies, and outputs technology performance info

# General Analysis Demo



SERDP



DNAPL TEST

GA Step 2

Analysis Name: General Analysis Demo

## Step 2 Technology Selection

\* Select one or more DNAPL remediation technologies of interest:

Select All Clear All ?

- ☒ Cosolvent
- ☒ ISCO - Permanganate
- ☒ ISCO - Fenton's or Peroxide
- ☒ ISCO - Ozone
- ☒ EISB - Anaerobic
- ☒ EISB - Aerobic
- ☒ SEAR
- ☒ Thermal - ERH
- ☒ Thermal - Conductive
- ☒ Thermal - Steam
- ☒ Thermal - Other
- ☒ Hydraulic Displacement
- ☒ Other

\* required field

Acronyms

DNAPL	Dense non-aqueous phase liquid
EISB	Enhanced in situ bioremediation
ERH	Electrical resistance heating
ISCO	In-situ chemical oxidation
SEAR	Surfactant-enhanced aquifer remediation

Step 1 Analysis Overview → Step 2 Select Technology → Step 3 Constrain Data Quality, Study Type, Treatment Area → Step 4 Constrain Site Geology, Chemistry → Step 5 View Output

Studies Remaining: 139 Average DQR: 2.24 ?

Exit Restart FAQs

version beta 1.0 2008-02-15

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ER0424 Lebron SERDP Seminar.ppt [Read-Only] [Compatibility Mode]

Ready

start

2 Microsoft ... 2 Windows ... 2 Microsoft ... 2 Internet E... DNAPL TEST

NUM

7:24 PM

# General Analysis Demo



DNAPL TEST

GA Step 2

## Step 2 Technology Selection

\* Select one or more DNAPL remediation technologies of interest:

Select All Clear All ?

- ☒ Cosolvent
- ☒ ISCO - Permanganate
- ☒ ISCO - Fenton's or Peroxide
- ☒ ISCO - Ozone
- ☒ EISB - Anaerobic
- ☒ EISB - Aerobic
- ☒ SEAR
- ☒ Thermal - ERH
- ☒ Thermal - Conductive
- ☒ Thermal - Steam
- ☒ Thermal - Other
- ☒ Hydraulic Displacement
- ☒ Other

\* required field

Step 1 Analysis Overview → **Step 2 Select Technology** → Step 3 Constrain Data Quality, Study Type, Treatment Area → Step 4 Constrain Site Geology → Step 5

Studies Remaining: 139 Average DQR: 2.24 ?

Exit

Studies Remaining: 139 Average DQR: 2.24 ?

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ER0424 Lebron SERDP Seminar.ppt [Read-Only] [Compatibility Mode]

start 2 Microsoft ... 2 Windows ... 2 Microsoft ... 2 Internet E... DNAPL TEST NUM 7:24 PM

# General Analysis Demo

DNAPL TEST

GA Step 3

Analysis Name: General Analysis Demo

## Step 3 Constrain Data Quality, Study Type, and Treatment Area

**Select data quality rankings (DQR):**  
Each case study entered into the database has been assigned a Data Quality Ranking (DQR) based on criteria including the completeness of the data record, the age of the study, etc. If you wish to refine your analysis to higher quality data, please select the

DNAPL TEST

GA Step 4

Analysis Name: General Analysis Demo

## Step 4 Constrain Site Geology and Chemistry

**Select case studies reporting the following geologies:**

<input type="button" value="Select All"/> <input type="button" value="Clear All"/> <input <="" td="" type="button" value="?"/> <td> <b>Unconsolidated</b>  <input checked="" type="checkbox"/> Gravel  <input checked="" type="checkbox"/> Sand  <input checked="" type="checkbox"/> Silt  <input checked="" type="checkbox"/> Clay  <input checked="" type="checkbox"/> Till  <input checked="" type="checkbox"/> Other Unconsolidated       </td> <td> <b>Consolidated</b>  <input checked="" type="checkbox"/> Igneous  <input checked="" type="checkbox"/> Metamorphic  <input checked="" type="checkbox"/> Sedimentary  <input checked="" type="checkbox"/> Other Consolidated       </td>	<b>Unconsolidated</b> <input checked="" type="checkbox"/> Gravel <input checked="" type="checkbox"/> Sand <input checked="" type="checkbox"/> Silt <input checked="" type="checkbox"/> Clay <input checked="" type="checkbox"/> Till <input checked="" type="checkbox"/> Other Unconsolidated	<b>Consolidated</b> <input checked="" type="checkbox"/> Igneous <input checked="" type="checkbox"/> Metamorphic <input checked="" type="checkbox"/> Sedimentary <input checked="" type="checkbox"/> Other Consolidated
---	---	--

**Site Chemistry:**

<input type="button" value="Select All"/> <input type="button" value="Clear All"/> <input <="" td="" type="button" value="?"/> <td> <input checked="" type="checkbox"/> Chlorinated Ethenes (e.g., tetrachloroethene, trichloroethene)  <input checked="" type="checkbox"/> Chlorinated Ethanes (e.g., tetrachloroethane, trichloroethane, dichloroethane)  <input checked="" type="checkbox"/> Chlorinated Methanes (e.g., carbon tetrachloride)       </td>	<input checked="" type="checkbox"/> Chlorinated Ethenes (e.g., tetrachloroethene, trichloroethene) <input checked="" type="checkbox"/> Chlorinated Ethanes (e.g., tetrachloroethane, trichloroethane, dichloroethane) <input checked="" type="checkbox"/> Chlorinated Methanes (e.g., carbon tetrachloride)
---	---

Step 1 Analysis Overview → Step 2 Select Technology → Step 3 Constrain Data Quality, Study Type, Treatment Area → Step 4 Constrain Site Geology, Chemistry → Step 5 View Output

Studies Remaining: 139 Average DQR: 2.24

Exit Restart FAQs

version beta1.0 2008-02-15

Filter by:

- DQR
- Case study type
- Treatment area
- Geology
- Chemistry

# General Analysis Demo

GA Step 5

Analysis Name: General A

## Step 5 View Output Reports

Click below to view reports on the specified information: ?

DNAPL Mass Removal	Treatment Duration
Groundwater Concentration Decrease	Unit Cost of Source Zone Treatment
Soil Concentration Decrease	DQR Summary and Case Study Reference Report
Achievement of MCLs	Summary of Input Selections
Rebound	

Note: If there is no data available for a particular performance metric for a specific technology, that technology will not appear.

Step 1 Analysis Overview → Step 2 Select Technology → Step 3 Constrain Data Quality, Study Type, Treatment Area → Step 4 Constrain Site Geology, Chemistry →

Studies Remaining: 139 Average DQR: 2.24 ?

Exit Restart FAQs

DNAPL Mass Removal

Groundwater Concentration Decrease

Soil Concentration Decrease

Achievement of MCLs

Rebound

Treatment Duration

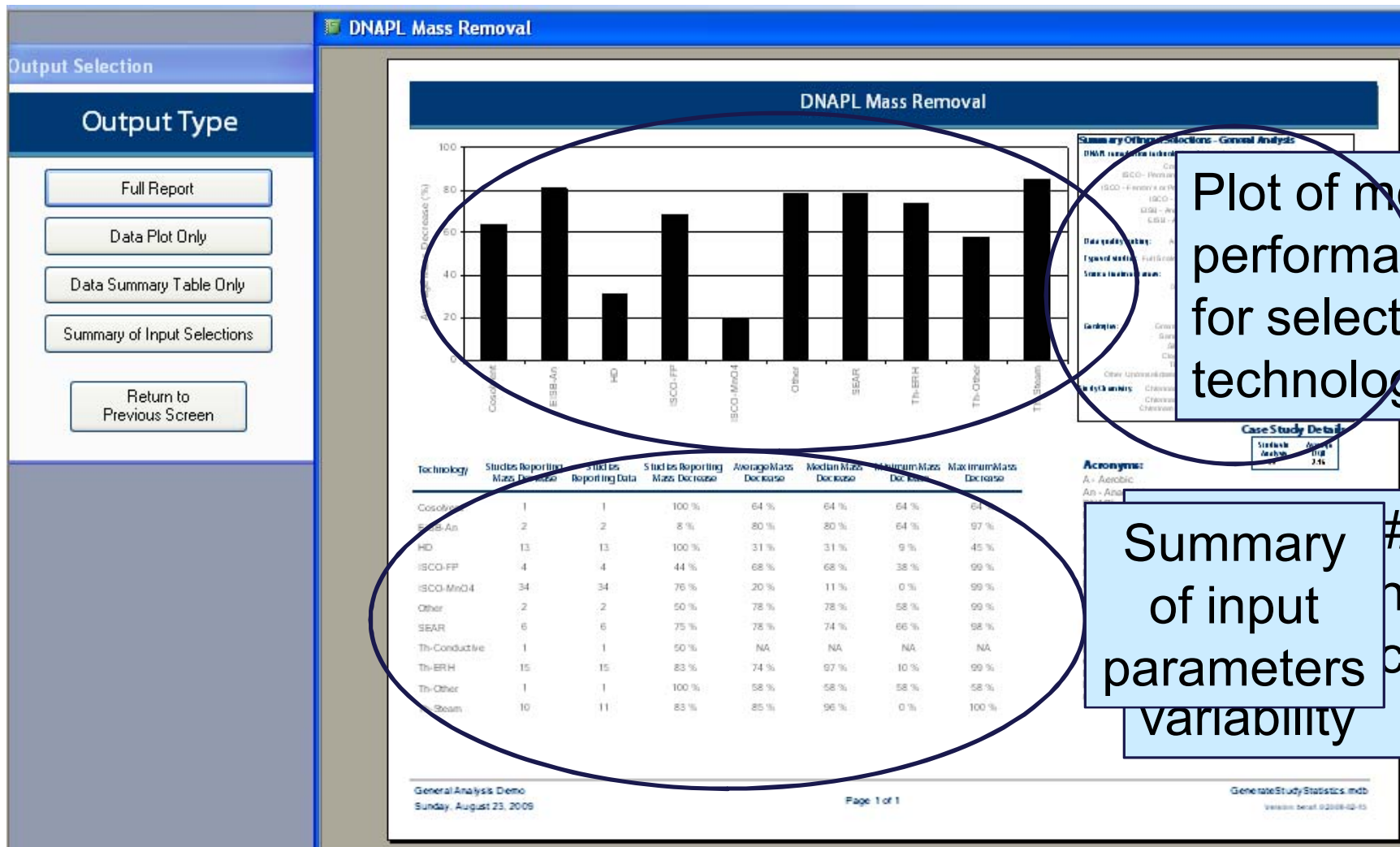
Unit Cost of Source Zone Treatment

DQR Summary and Case Study Reference Report

Summary of Input Selections



# General Analysis Demo





# General Analysis Demo

## DQR Summary and Case Study Reference General Analysis Demo

Technology	Case Study Identifier	DQR	Reference Type	Citation
Cosolvent	141	2.8	Journal	Jawitz JW, Sillan RK, Annable MD, Rao PSC, Warner K. In-Situ Alcohol Flushing of a DNAPL Source Zone at a Dry Cleaner Site. Environmental Science and Technology. 2000, 34: 3722-3729.
			Government	IRTC DNAPL Team Case Study Summary Report: Sages Dry Cleaners Jacksonville Florida. <a href="http://www.irtcweb.org/Documents/DNAPLs-3">www.irtcweb.org/Documents/DNAPLs-3</a>
		1.3	Conference	Lewis RF, Dooley MA, Johnson JC, and Murray WA. 1998. Sequential anaerobic/aerobic biodegradation of chlorinated solvents: Pilot-scale field demonstration. In Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, pp. 1-7, vol. C1-6: Physical, Chemical, and Thermal Technologies (Editors: Wickramanayake GB and Hinchee RE), Monterey CA, May 18-21.
EISB-An	19	2.1	ESTCP	Martin J and Sorenson K. Appendix E.1-Case study of enhanced bioremediation of a DNAPL source area: four years of data from Test Area North. INEEL. In: Principles

Individual case  
study  
reference  
information

# *Site-Specific Analysis Demo*

- Demo site characteristics:
  - ◆ Unconsolidated media, fine to medium-grained sand
  - ◆ 20,000 ft<sup>2</sup> DNAPL source area
  - ◆ Saturated aquifer thickness of 10 ft
  - ◆ DNAPL is present as both residual and pools
  - ◆ Moderate soil heterogeneity (3-5 order of magnitude variability)
- Technology of interest – thermal technologies
  - Statistically “similar” case studies in database identified by DNAPL TEST using relationships identified as part of the linear and non-linear multi-variate analysis

# Site-Specific Analysis Demo

DNAPL TEST

SSA Step 2

Analysis Name: Site-Specific Analysis Demo

## Step 2 Select Data Quality and Study Type

**Select data quality rankings (DQR):**

Each case study entered into the database has been assigned a Data Quality Ranking (DQR) based on criteria including the completeness of the data record, the age of the study, etc. If you wish to refine your analysis to higher quality data, please select the cut-off criteria for data quality to include in this analysis:

☐ All Data (low, medium, high)  
☐ Medium and High Quality  
☐ High Quality Only

[Explanation of Data Quality Rankings](#)

**Select the types of studies to include in this analysis:**

Field Case Studies: ☒ Full Scale ☒ Pilot Scale

☒ Laboratory ☒ Modeling

Step 1 Site Specific Analysis Overview → 
 Step 2 Select Data Quality and Study Type → 
 Step 3 Input Site Characteristics → 
 Step 4 Input Design Parameters → 
 Step 5 View Output

version beta1.0 2008-02-15

Form View (2) Microsoft Office PowerPoint FLTR NUM

start 2 Micro... 2 Wind... 2 Micro... 2 Inter... DNAPL T... Skype™ ... 7:52 PM

User Filters by:

- DQR
- Case study type

# Site-Specific Analysis Demo

SSA Step 3

Analysis Name: Site-Specific Analysis Demo

## Step 3 Input Site Characteristics

Please fill in the following criteria that describe your site. The site characteristics will be used for selection of studies with statistically similar technology performance. Please note: leaving input blank may restrict case studies available for the analysis.

SSA Step 4

## Step 4 Input Design Parameters

A statistical analysis of the influence of various design parameters unique to each technology on technology performance has been completed. Certain design criteria were found to be key to technology performance.

☐ If you wish to evaluate the impact of these key design parameters on technology performance, enter values for the noted parameters here, otherwise leave blank:

**Thermal Technologies:**  
Electrode Spacing  m

**Bioremediation:**  
In progress.

**Chemical Oxidation:**  
In progress.

**Surfactant/Cosolvent:**  
In progress.

**Hydraulic Displacement:**  
In progress.

**NOTE: In this beta version only thermal technologies are included. Other technologies will be incorporated in the full version of DNAPL TEST.**

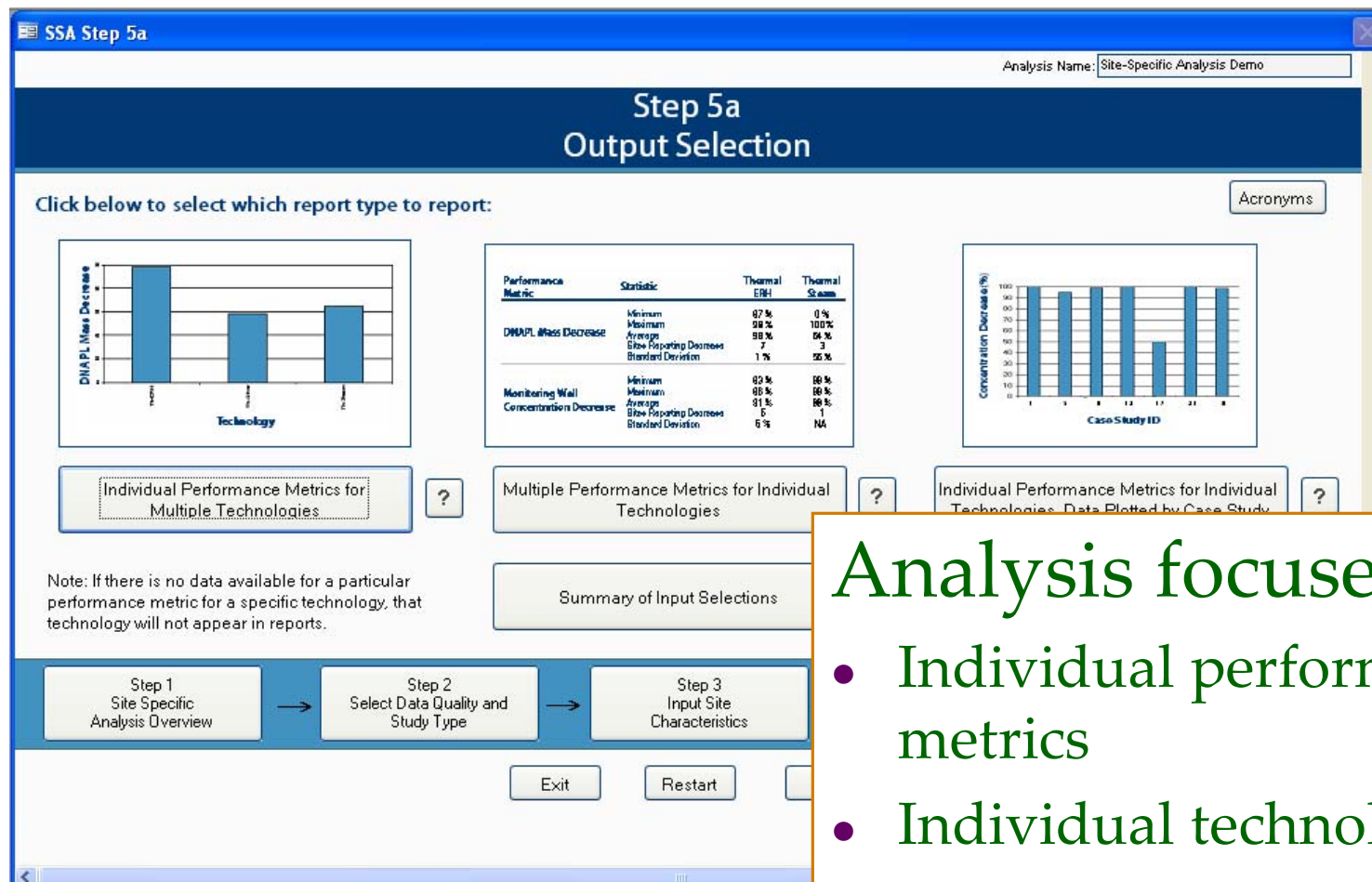
Step 1 Site Specific Analysis Overview → Step 2 Select Data Quality and Study Type → Step 3 Input Site Characteristics → Step 4 Input Design Parameters

Exit Restart FAQs

Input site and technology parameters:

- Geology
- Heterogeneity
- Treatment area
- Saturated thickness
- Mobility of DNAPL
- Electrode spacing, etc.

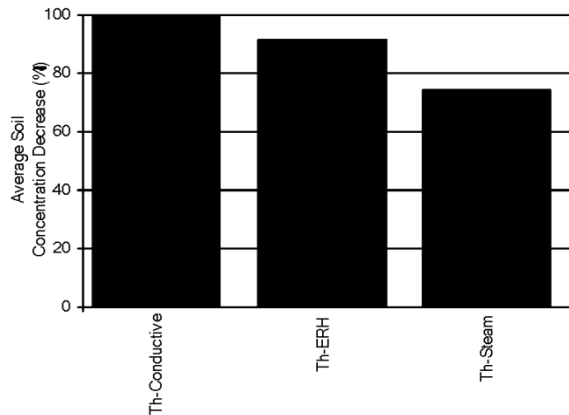
# Site-Specific Analysis Demo



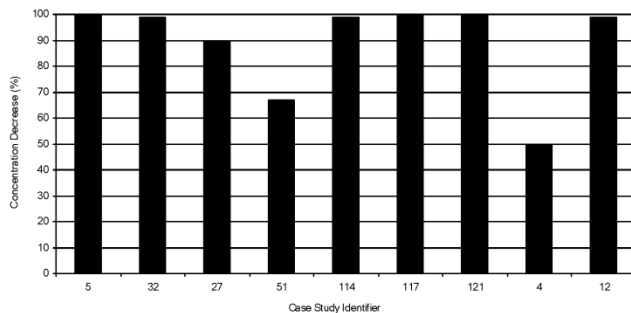
## Analysis focused on:

- Individual performance metrics
- Individual technologies, or
- Performance by case study

# Site-Specific Analysis Demo



DNAPL Mass Removal	Maximum	90 %	NA	NA
	Average	90 %	NA	NA
	Median	90 %	NA	NA
	Studies Achieving Decrease	3	NA	NA
	Studies Reporting Data	3	NA	NA
	Total Studies	3	NA	NA
Groundwater Concentration Decrease	Minimum	60 %	99 %	NA
	Maximum	99 %	99 %	NA
	Average	87 %	99 %	NA
	Median	91 %	99 %	NA
	Studies Achieving Decrease	10	1	NA
	Studies Reporting Data	10	1	NA
Soil Concentration Decrease	Minimum	67 %	50 %	99 %
	Maximum	100 %	99 %	100 %
	Average	91 %	75 %	100 %
	Median	99 %	75 %	100 %
	Studies Achieving Decrease	5	2	2
	Studies Reporting Data	5	2	2
	Total Studies	9	3	2



Performance Metric	Statistic	Thermal ERH	Thermal Steam	Thermal Conductive
DNAPL Mass Removal	Minimum	90 %	NA	NA
	Maximum	90 %	NA	NA
	Average	90 %	NA	NA
	Median	90 %	NA	NA
	Studies Achieving Decrease	3	NA	NA
	Studies Reporting Data	3	NA	NA
Groundwater Concentration Decrease	Minimum	60 %	99 %	NA
	Maximum	99 %	99 %	NA
	Average	87 %	99 %	NA
	Median	91 %	99 %	NA
	Studies Achieving Decrease	10	1	NA
	Studies Reporting Data	10	1	NA
Soil Concentration Decrease	Minimum	67 %	50 %	99 %
	Maximum	100 %	99 %	100 %
	Average	91 %	75 %	100 %
	Median	99 %	75 %	100 %
	Studies Achieving Decrease	5	2	2
	Studies Reporting Data	5	2	2
	Total Studies	9	3	2



# *Summary*

- This project has resulted in the creation of one of the most comprehensive database on source treatment technologies
- The modeling has shown to be a powerful means to:
  - ♦ Understand what factors affect performance,
  - ♦ Allow us to develop case studies for various situations where there are no documented cases, and
  - ♦ Increase our knowledge on how these technologies work in different environments
- The tool is infinitely scalable:
  - ♦ We can add more data,
  - ♦ Run analysis that allows "filtering" of knowledge
    - eg, new information that indicates rind dissolution, which can be modeled
- Screening Tool available by Spring 2010
- Periodic updates as warranted
  - ♦ New Case Studies or technologies
  - ♦ Enhancements to technologies
  - ♦ Continued site monitoring; i.e., Rebound

# Short Course Agenda



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

# Short Course Agenda



**SERDP**



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
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5:20 PM	Summary & Conclusion	Hans Stroo

# **Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty**

Presented by: Ronald Falta (Clemson University)  
and Charles Newell (GSI Environmental, Inc.)

## **ESTCP ER-0704**

- Ronald W. Falta and Hailian Liang  
Clemson University
- Charles J. Newell and Shahla Farhat, GSI  
Environmental, Inc.
- P. Suresh Rao and Nandita Basu Purdue  
University

# Model Objectives

**Develop a practical analytical tool that allows site managers to:**

- Quickly simulate changes in DNAPL source zones and dissolved plumes over time, with and without source remediation, source containment, and/or plume remediation
- Explore site management decisions in a probabilistic framework, so uncertainty becomes an integral part of the decision making process
- Compare the cost, risk, and performance of source treatment to plume treatment approaches



## Key Concept: Sources

- Most dissolved plumes can be traced back to a concentrated “source” area, where the original release occurred.
- The source area is usually small compared to the plume footprint
- The source may contain DNAPL, or it may consist of high concentrations of dissolved solvents in low permeability zones
- The **mass of contaminant** in the source zone, and the **mass discharge of contaminant** out of the source zone play a central role in the evolution of dissolved plumes

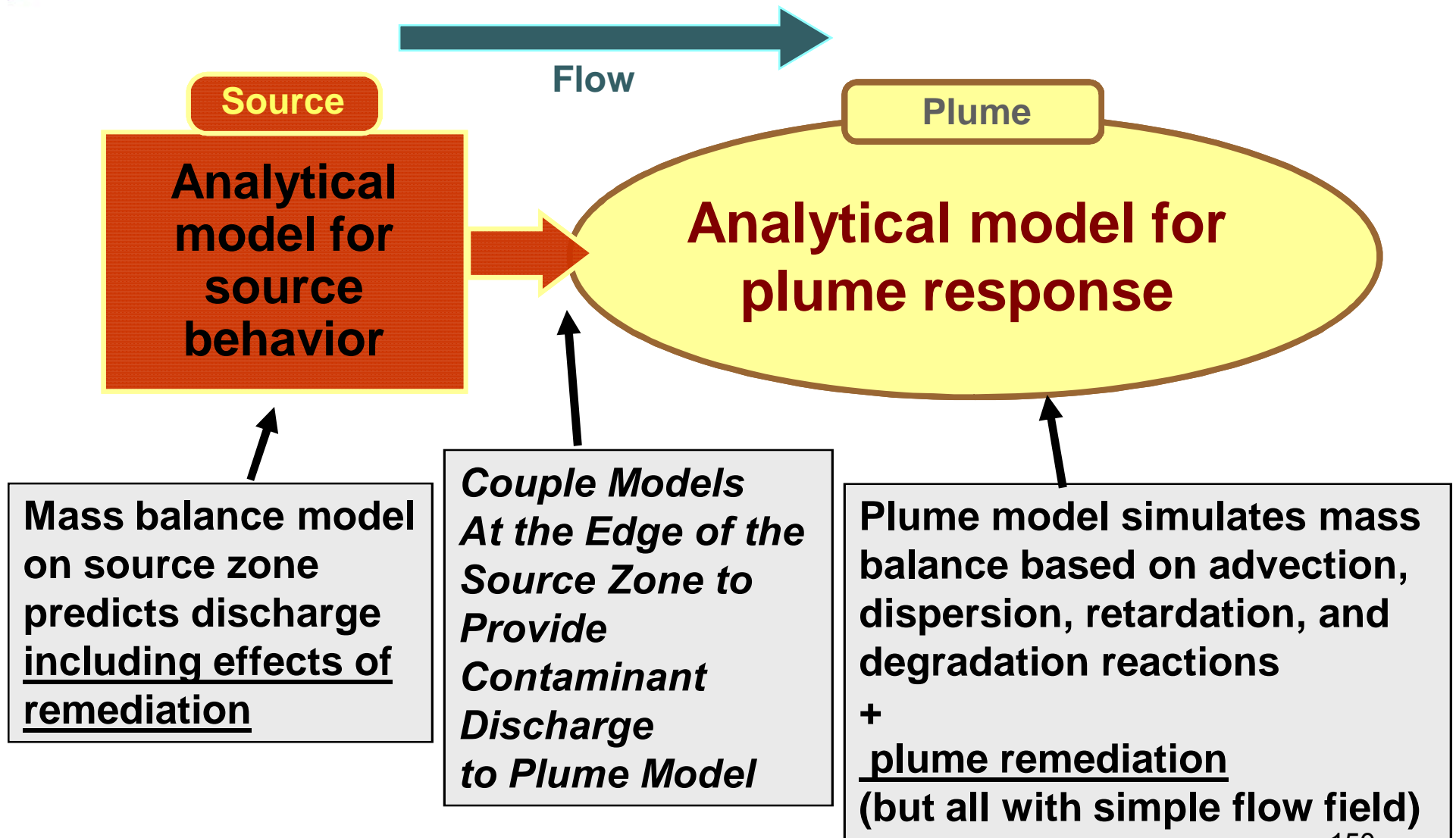
## Key Concept: Plumes

- Plumes are fed by the source, and move with the groundwater flow with some dispersion
- The dissolved contaminants may also adsorb or diffuse into aquifer materials
- The groundwater pore velocity (Darcy velocity divided by porosity) and the rate at which the chemical degrades play a central role the nature of the plume
- High velocities with low decay rates = large plumes
- Low velocities with high decay rates = small plumes

# Questions to be addressed by Mass Balance Type Modeling

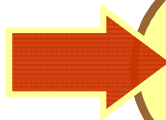
- What will happen if no action is taken?
- Will source remediation meet site goals?  
How effective must the source remediation be?
- Will enhanced biodegradation of the plume meet site goals? How effective (and long-lived) must the plume treatment be?
- Should I combine source and plume remediation?  
How much of each do I need before I get to transition to MNA?
- What is the remediation time-frame?
- What is a reasonable remediation objective?

# Core Model: REMChlor



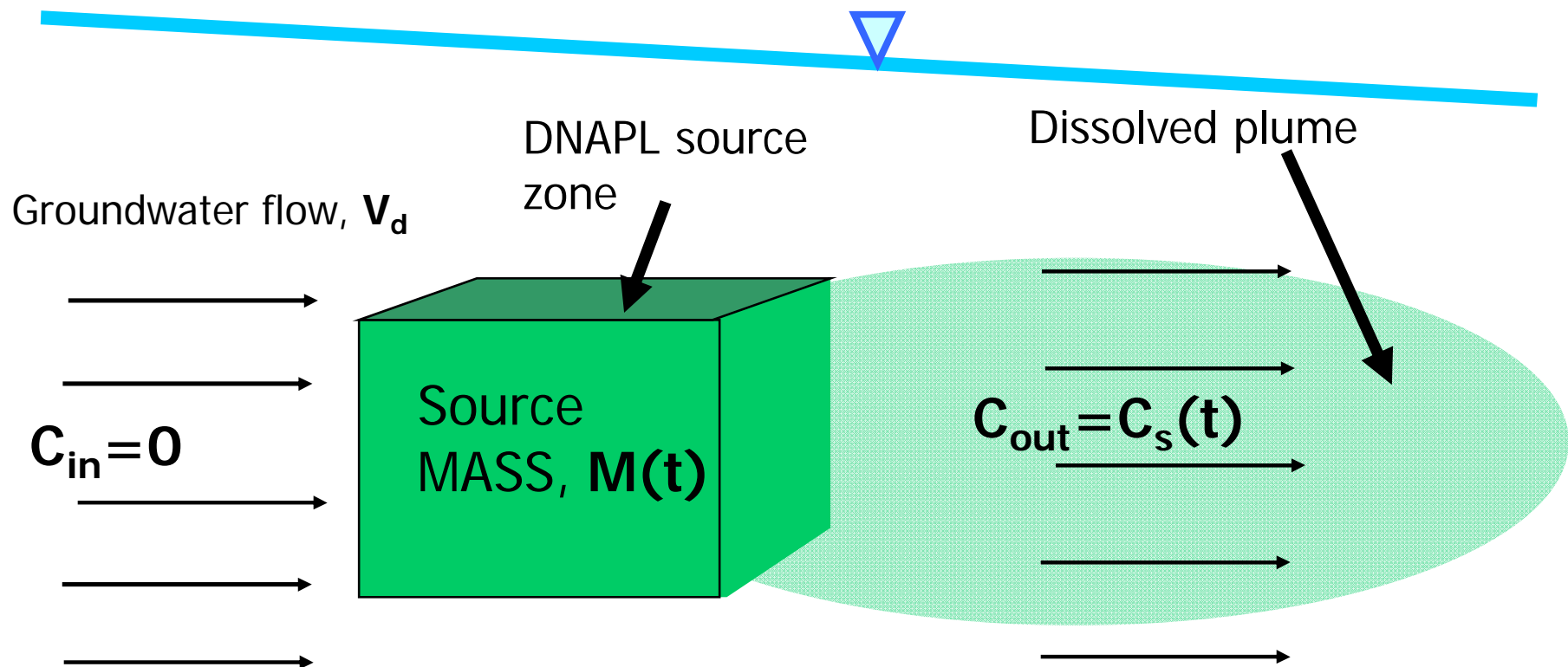
# Explanation of How the *Source Term* Works in REMCHLOR

**Analytical  
model for  
source  
behavior**



**Analytical model for  
plume response**

**Source conceptual model:** Mass is mainly removed by flushing. **The discharging concentration ( $C_s$ ) depends on the mass remaining in the source zone, ( $M$ )**



$$\frac{dM}{dt} = -Q(t)C_s(t) - \lambda_s M$$

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



**SERDP/EPA/Clemson  
Field Test of DNAPL  
Removal by Alcohol Flooding**

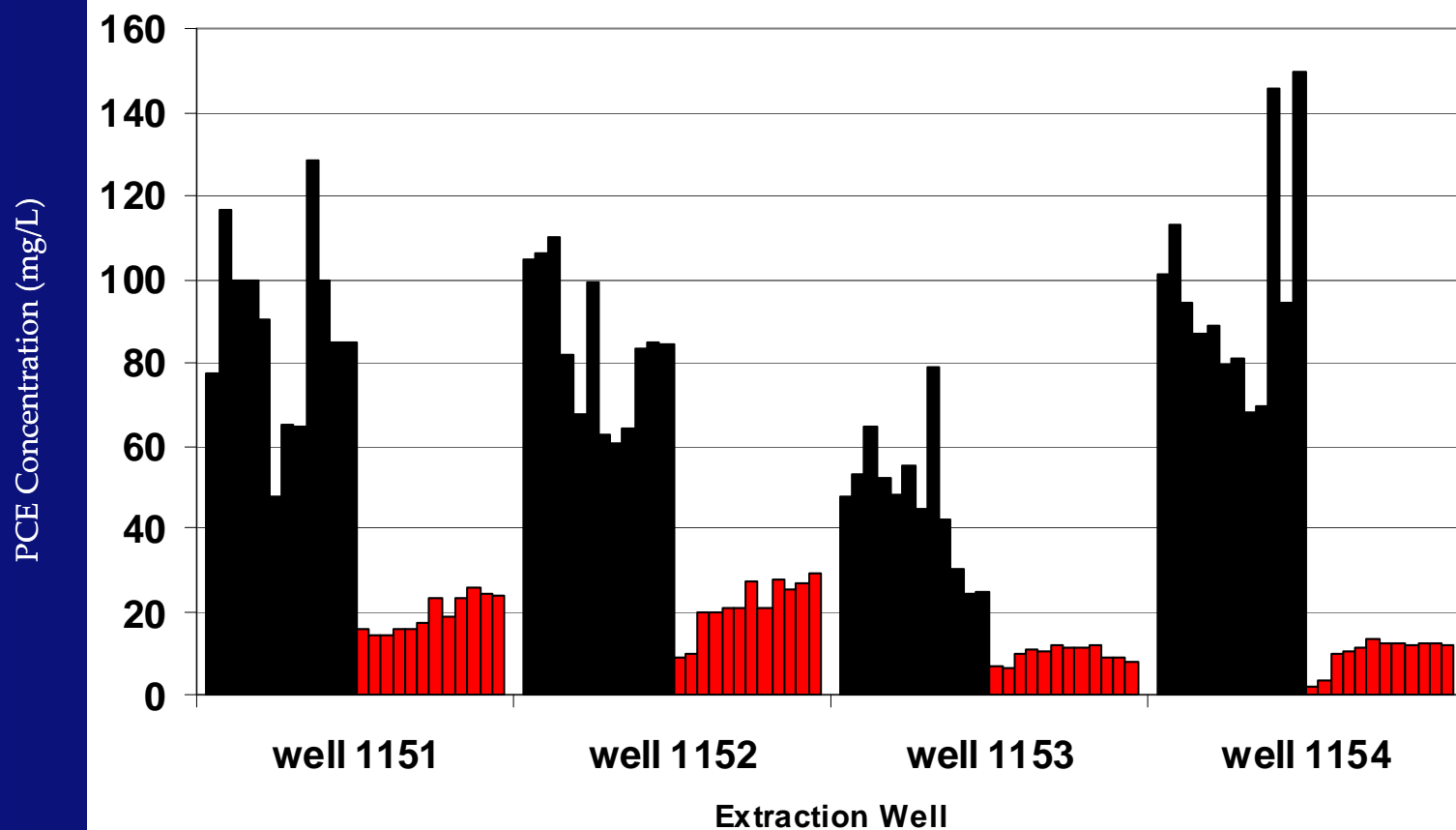
Dover Air Force Base, Delaware

**EPA released 92 kg of  
pure PCE into the test  
cell at a depth of 35'  
below the ground  
surface. A total of 73.5  
kg was removed  
during a 40 day alcohol  
flood**



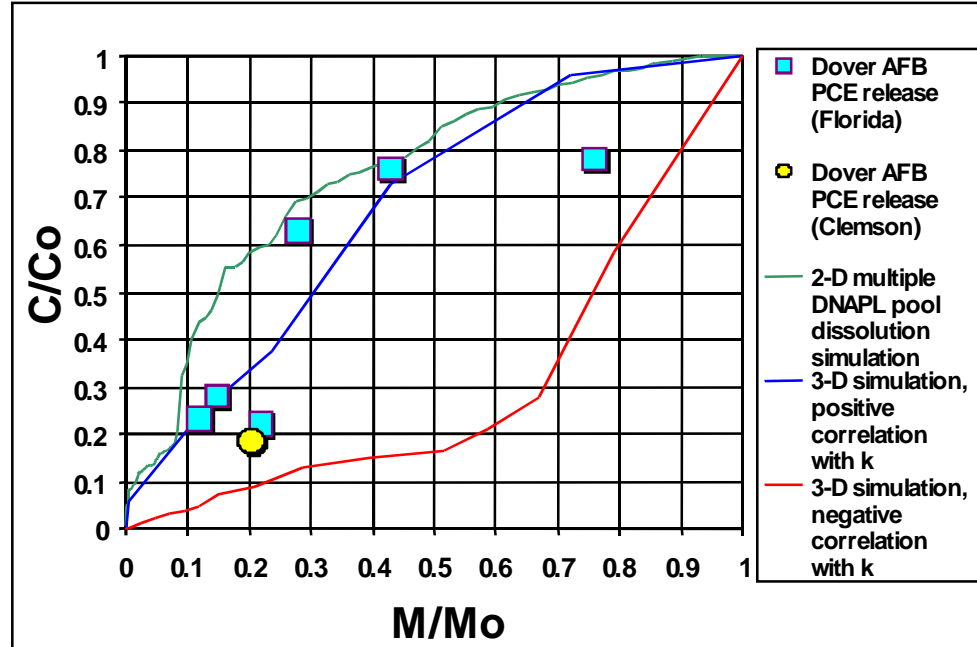
## 80% Source Removal Resulted in 81% Reduction in Groundwater Concentration

Pre-and Post-Cosolvent Flood PCE Concentrations

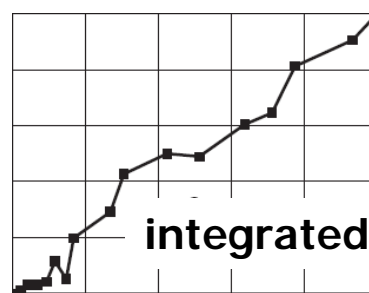
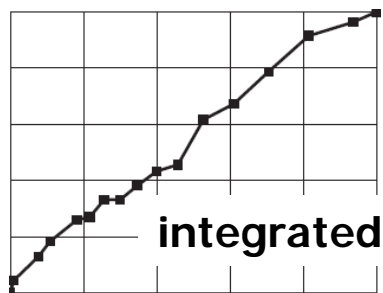


# Source Mass Reduction Leads to Discharge Reduction

## Field and Modeling Data



## Laboratory dissolution experiments

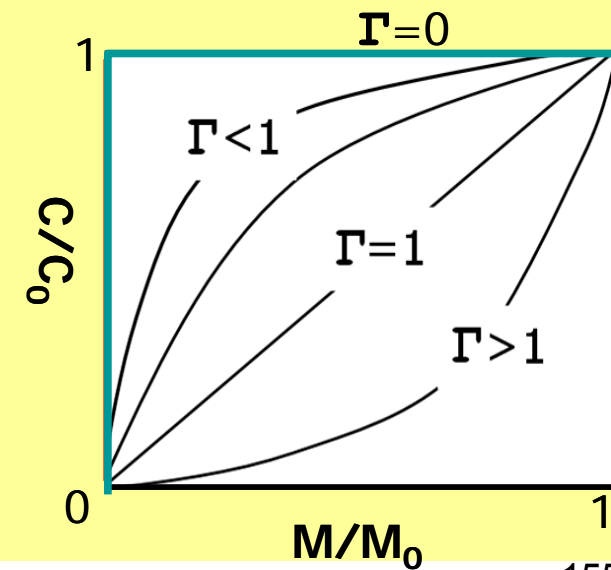


(Jawitz et al.)

## Power function model

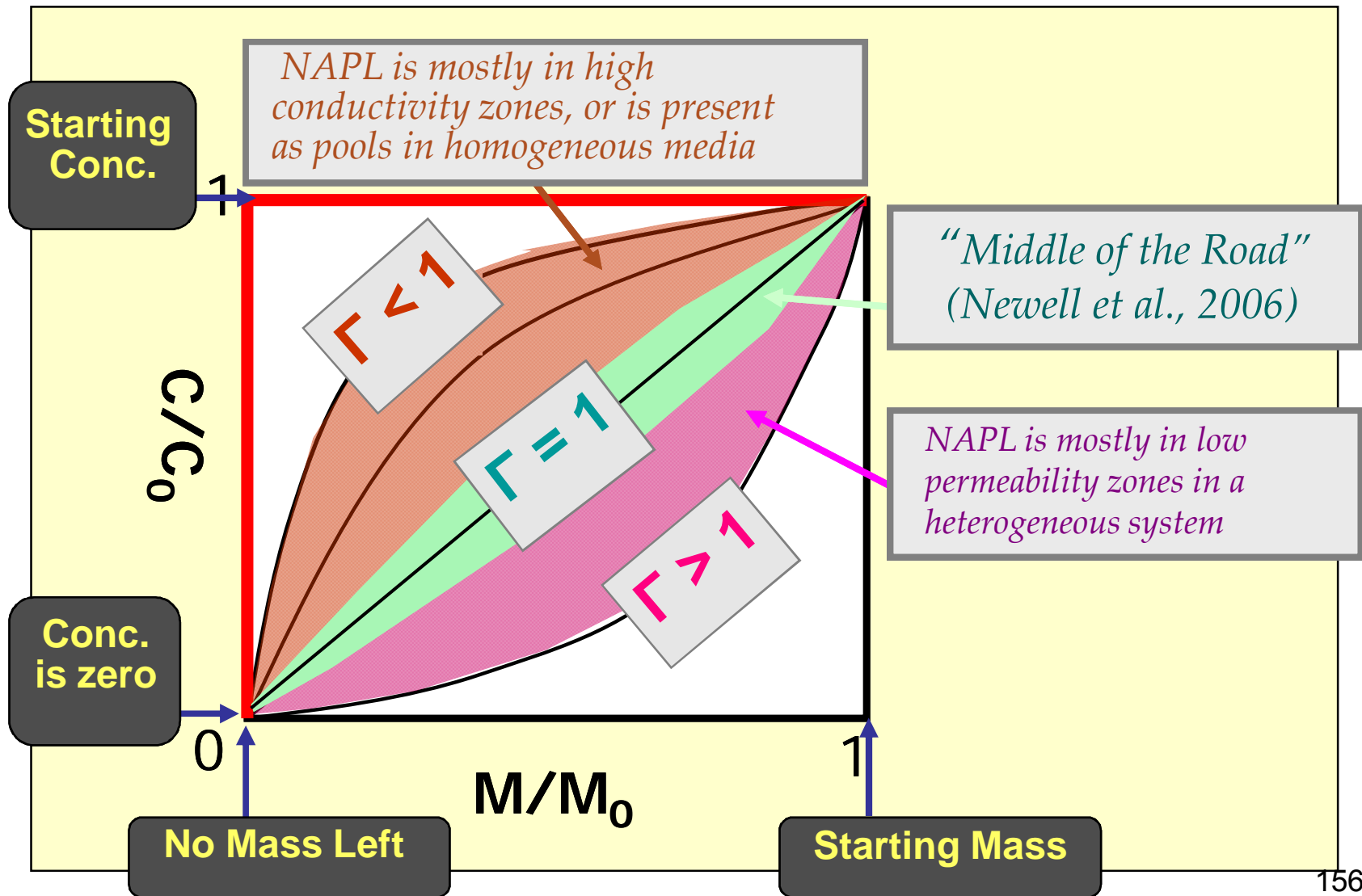
[Rao et al., 2001; Parker and Park, 2004; Zhu and Sykes, 2004]

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

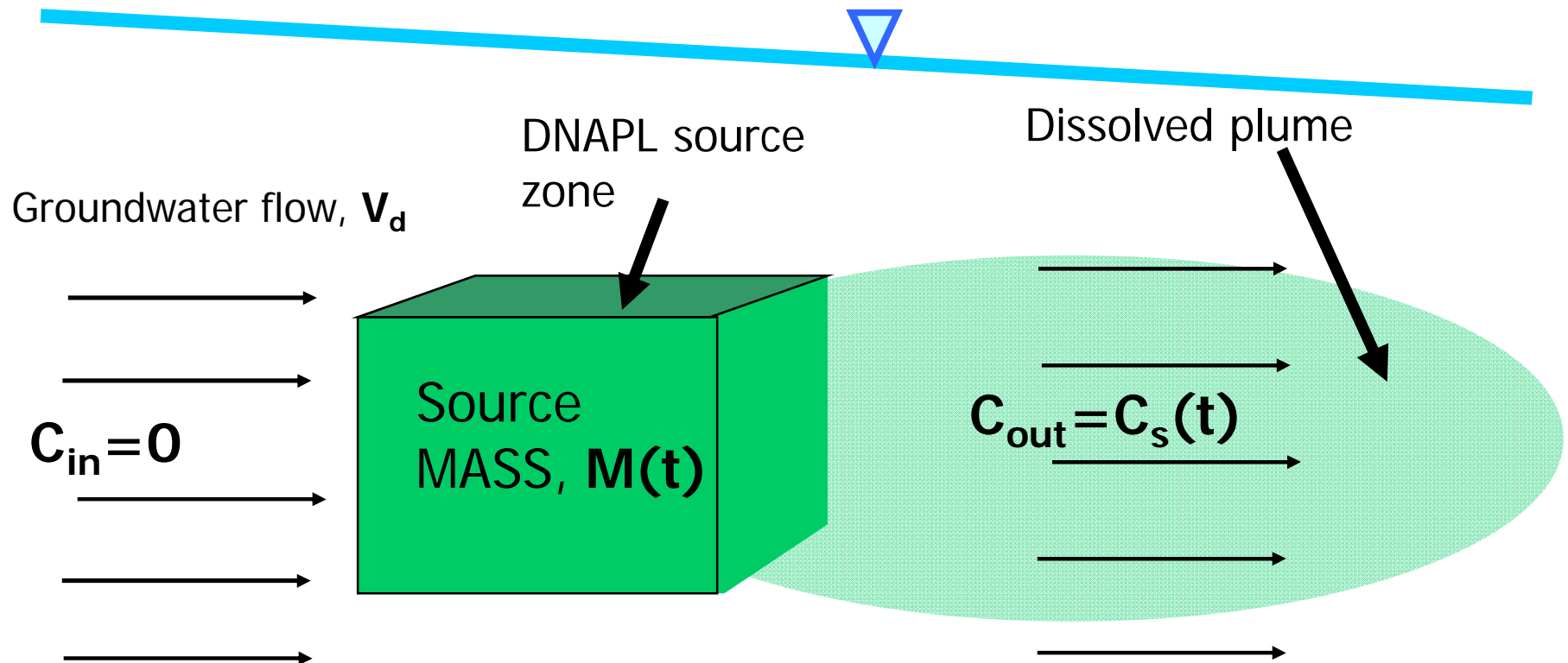




# Source Power Function - *What's That?*



**Source conceptual model: Remediation is simulated by removing a fraction of the source mass at the time of remediation**



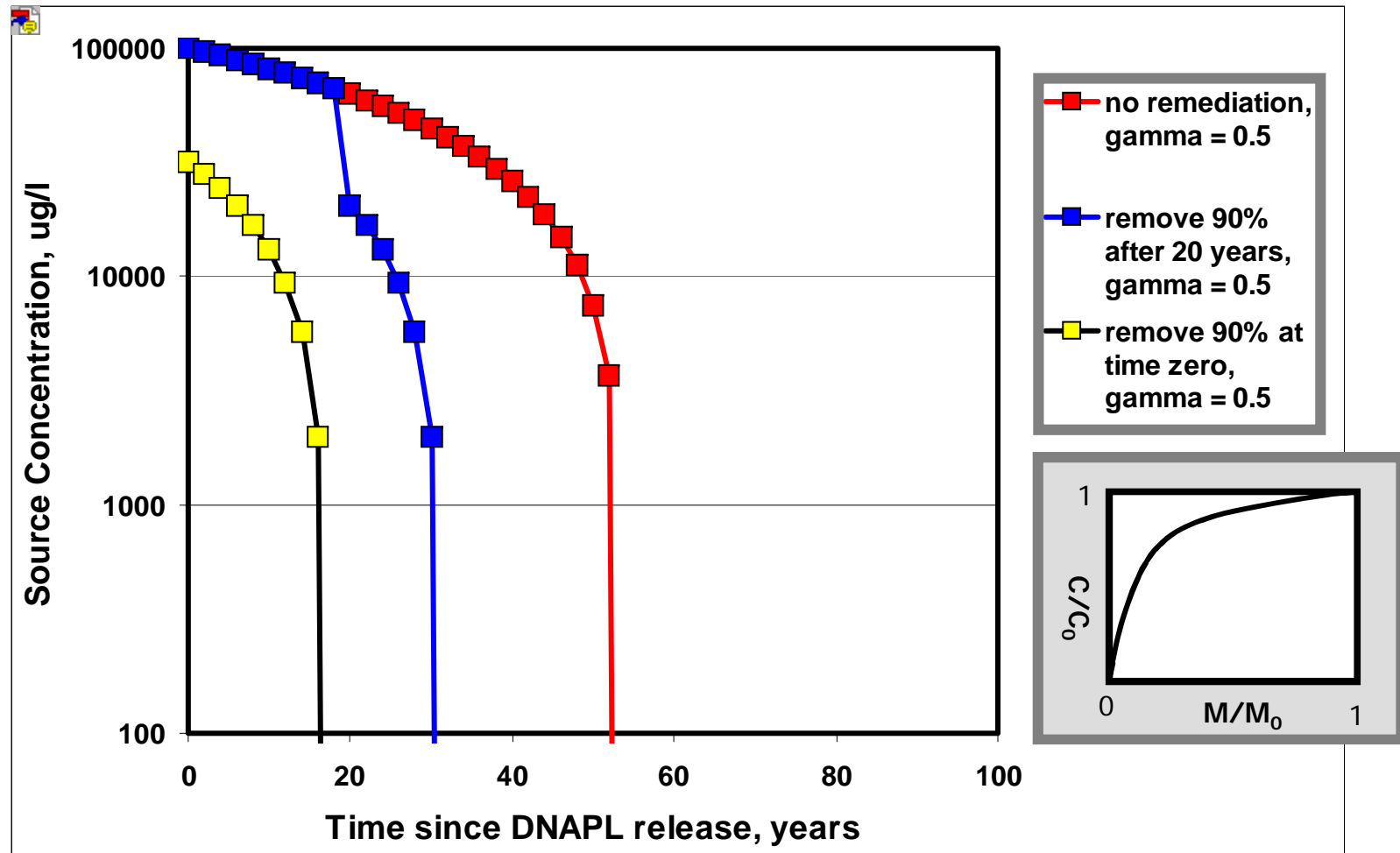
Remove a fraction  $X$  of  
The mass in source zone  
At time  $TR$  .

$$C_s = C_0 \left( \frac{(1-X)M_{TR}}{M_0} \right)^\Gamma \quad 157$$

## Source Behavior:

$\Gamma = 0.5$ ,  $M_0 = 1,620$  kg,

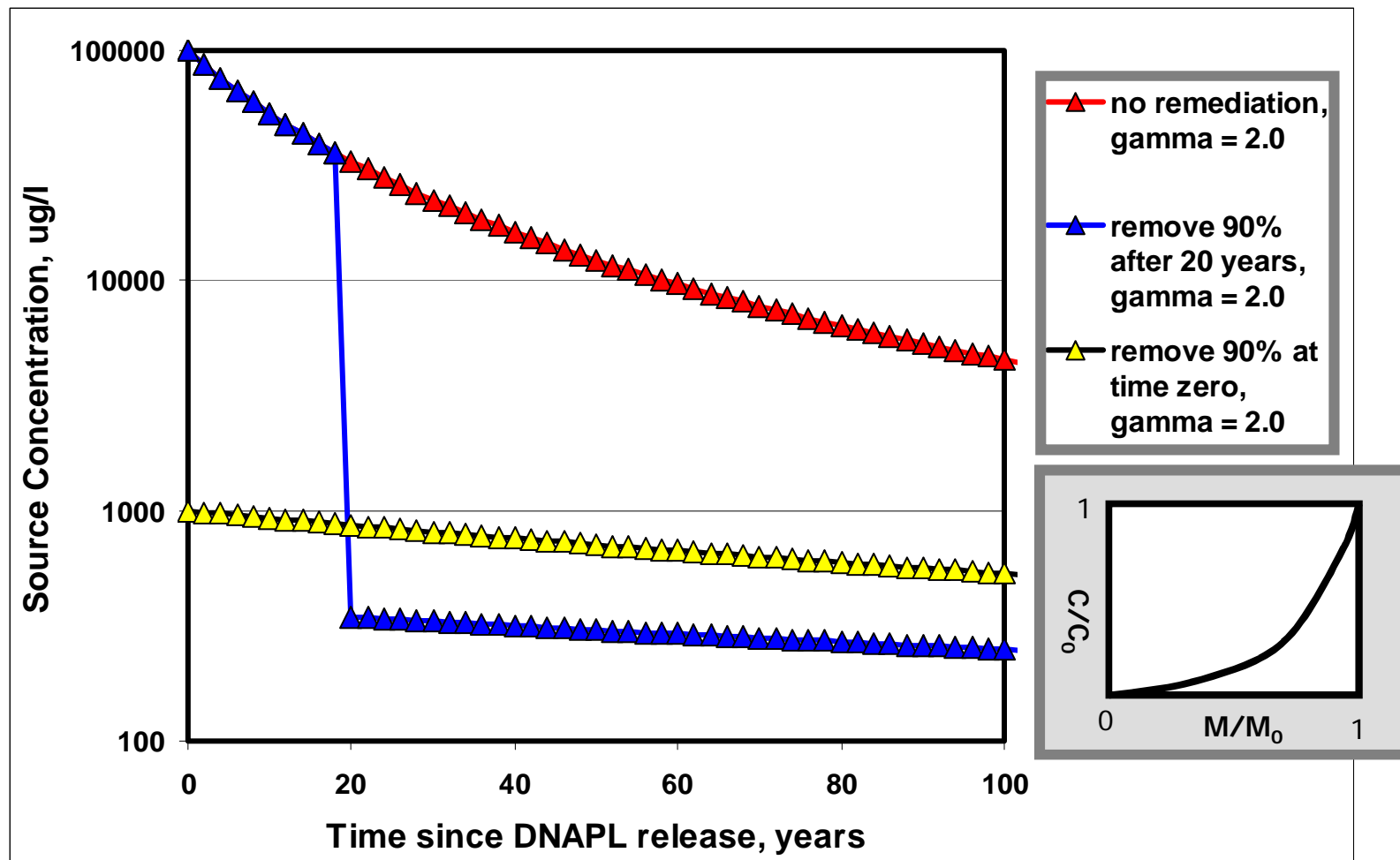
$V = 20$  m/yr,  $A = 10\text{m} \times 3\text{m}$ ,  $C_0 = 100$  mg/l





## Source Behavior:

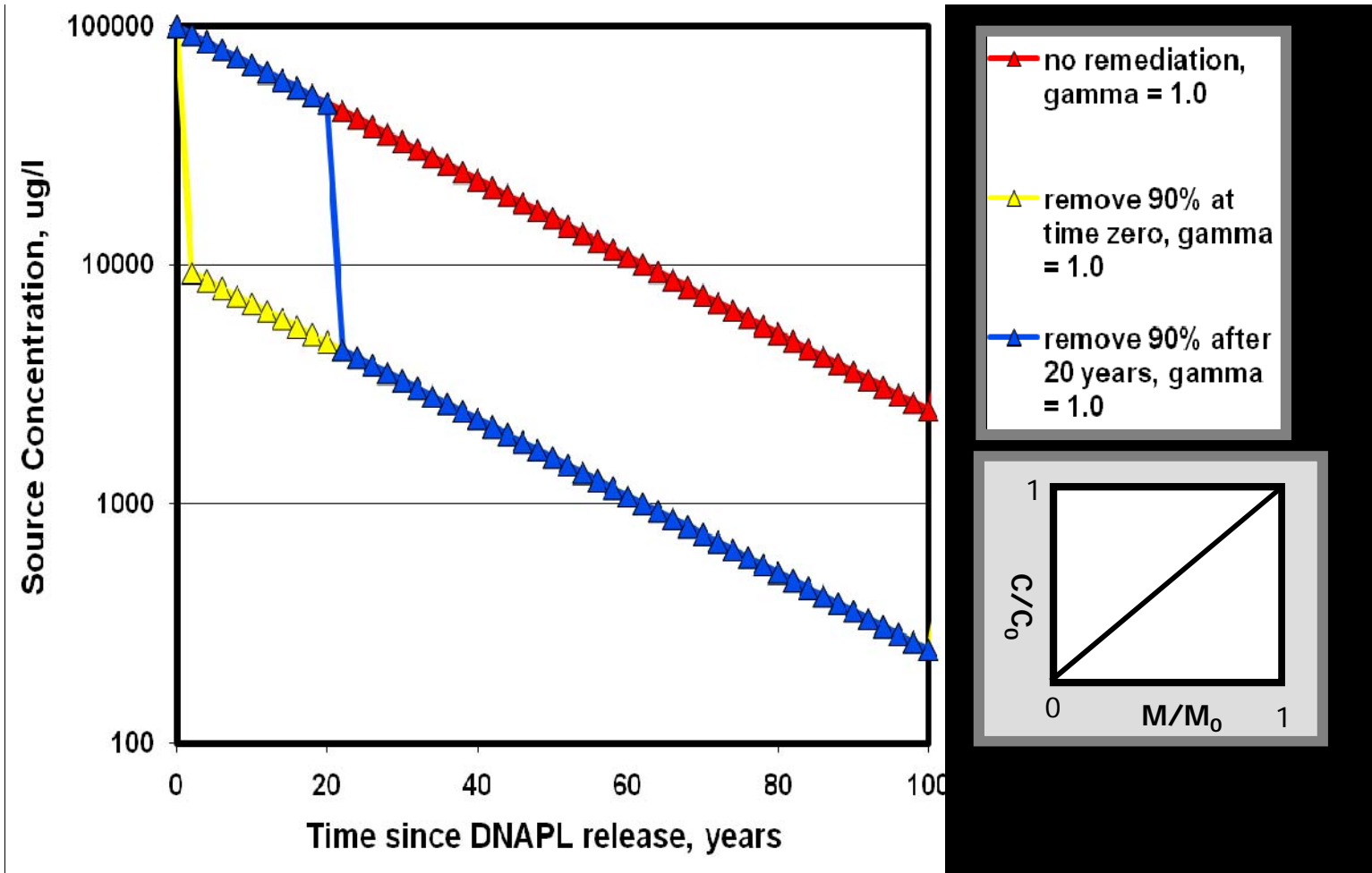
$\Gamma = 2.0$ ,  $M_0 = 1,620$  kg,  
 $V = 20$  m/yr,  $A = 10\text{m} \times 3\text{m}$ ,  $C_0 = 100$  mg/l



## Source Behavior:

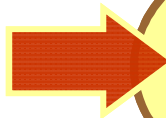
$$\Gamma = 1.0, \quad M_0 = 1620 \text{ kg},$$

$$V = 20 \text{ m/yr}, \quad A = 10\text{m} \times 3\text{m}, \quad C_0 = 100 \text{ mg/l}$$



# Explanation of How the *Plume* Works in REMCHLOR

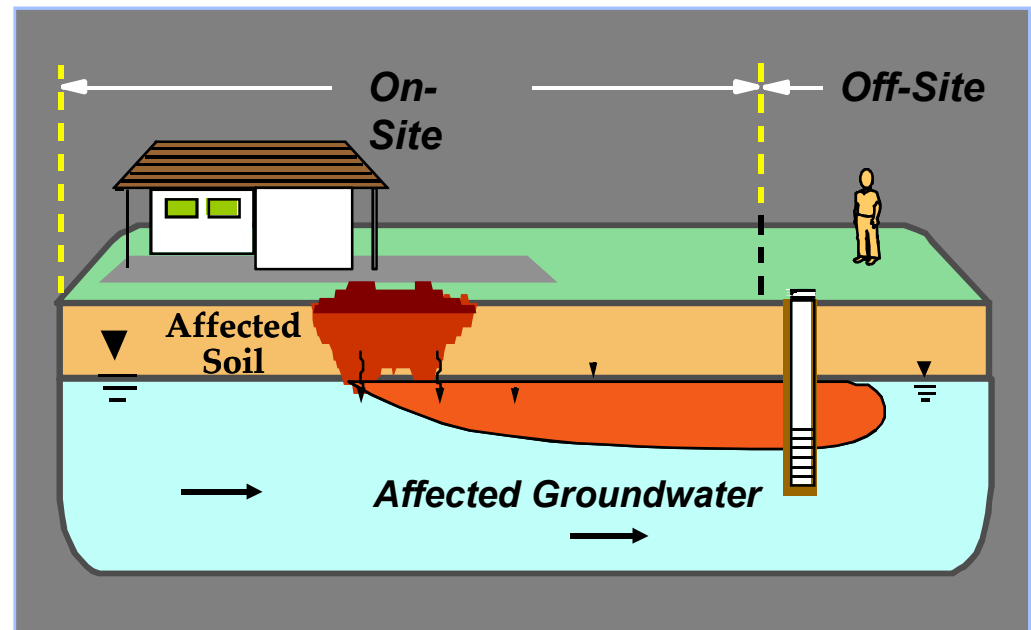
**Analytical  
model for  
source  
behavior**



**Analytical model for  
plume response**

# Key Process in REMChlor

- Source Term
- Advection
- Dispersion
- Adsorption
- Biodegradation



# Key Mass Balance Equations - *Plume*

*Plume equation solved for each species. Equations are linked through the chemical reaction terms*

*First-Order Decay reactions*

$$R \frac{\partial C_i}{\partial t} = -v \frac{\partial C_i}{\partial x} + \alpha_x v \frac{\partial^2 C_i}{\partial x^2} + \alpha_y v \frac{\partial^2 C_i}{\partial y^2} + \alpha_z v \frac{\partial^2 C_i}{\partial z^2} + rxn_i$$

**Retardation Coefficient**

**Longitudinal Dispersivity**

**Transverse Dispersivity**

**Vertical Dispersivity**

**Groundwater Seepage Velocity**

**Hydraulic Conductivity**

**Hydraulic Gradient**

$$v = \frac{K i}{n_e}$$

**Effective Soil Porosity**

## Groundwater Transport Processes - *Biodegradation*

Indigenous micro-organisms are capable of degrading many contaminants.

Need electron donor and electron acceptor.

***Fuels*** like benzene serve as electron donor.  
Oxygen, nitrate, sulfate, iron are electron acceptor.

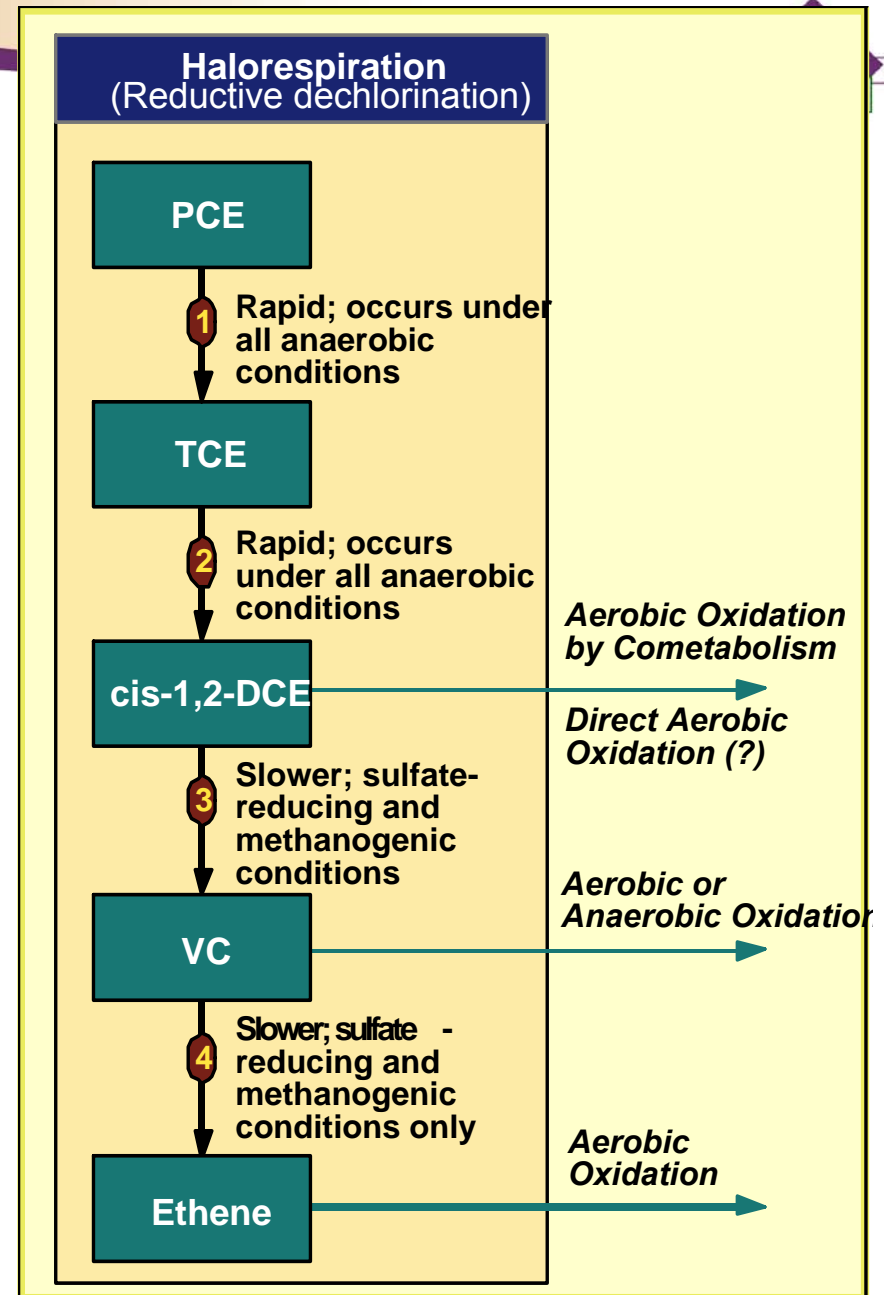
***Chlorinated solvents*** act as electron acceptor.  
Hydrogen/acetate serve as electron donor.



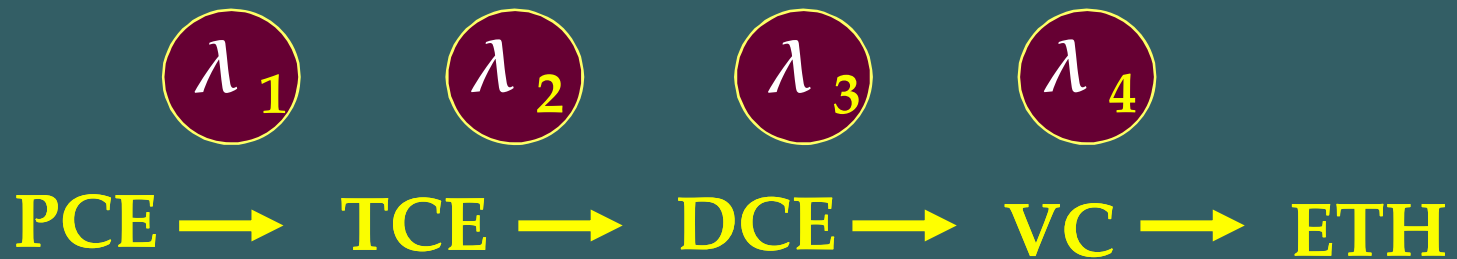
# Biodegradation Decay Chain for Chlorinated Ethenes

*Key footprints*  
*cis-DCE*  
*ethene or ethane*

(Adapted from RTDF, 1997)



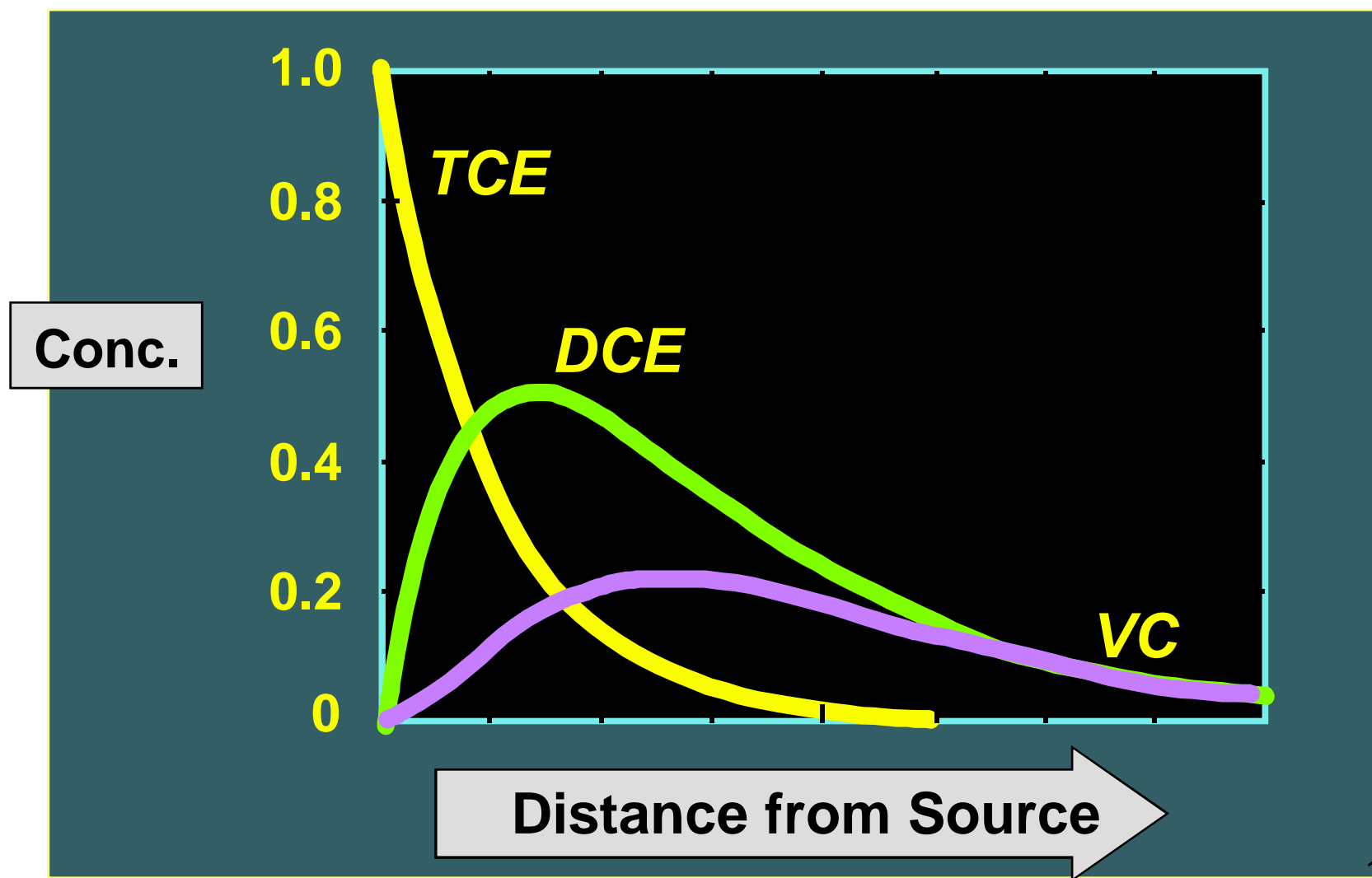
# Sequential Reactions



$$\text{Rate}_{\text{PCE}} = -\lambda_1 C_{\text{PCE}}$$

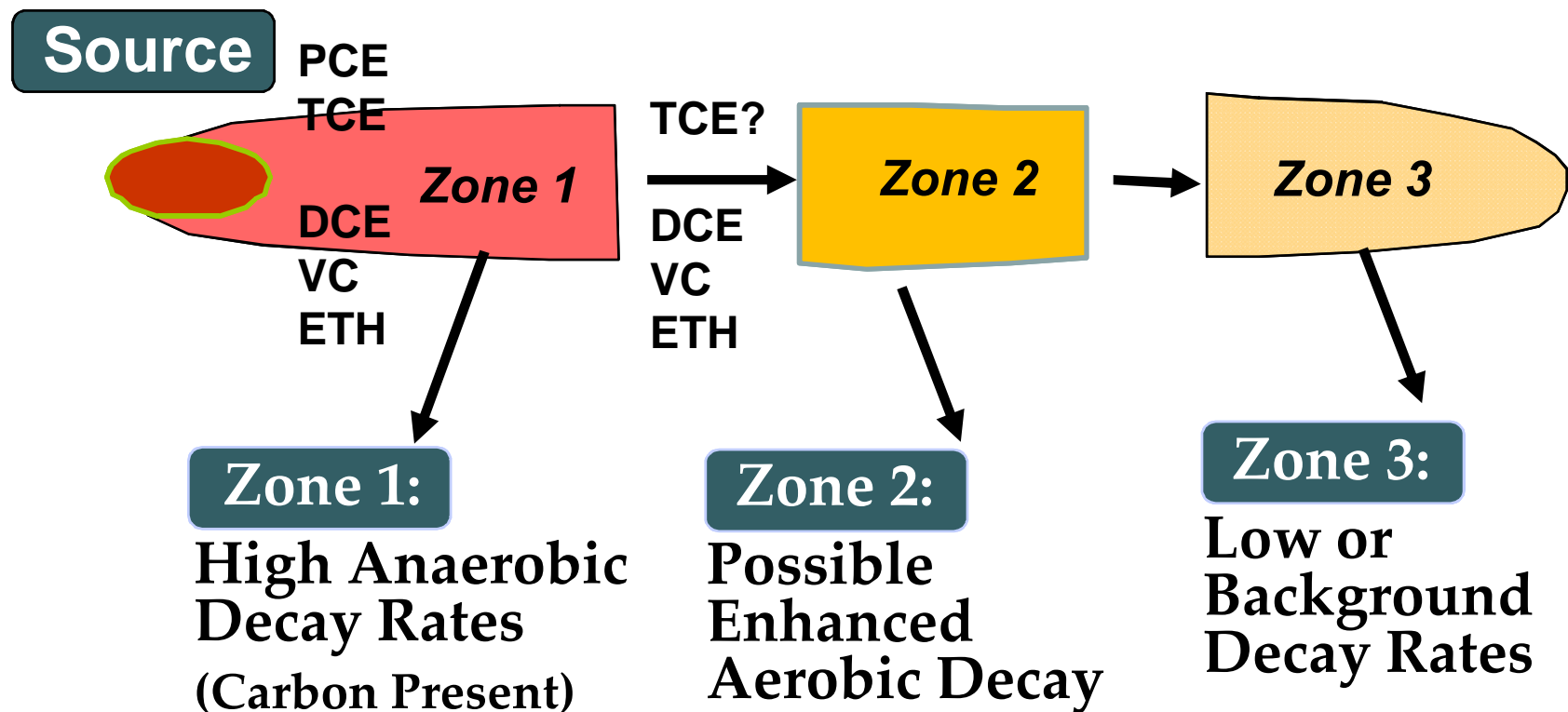
$$\text{Rate}_{\text{TCE}} = \lambda_1 y_1 C_{\text{PCE}} - \lambda_2 C_{\text{TCE}}$$

# Results of Sequential Reactions



# REMChlor Model: Other Features

## Three Reaction Zones for Mixed Sites

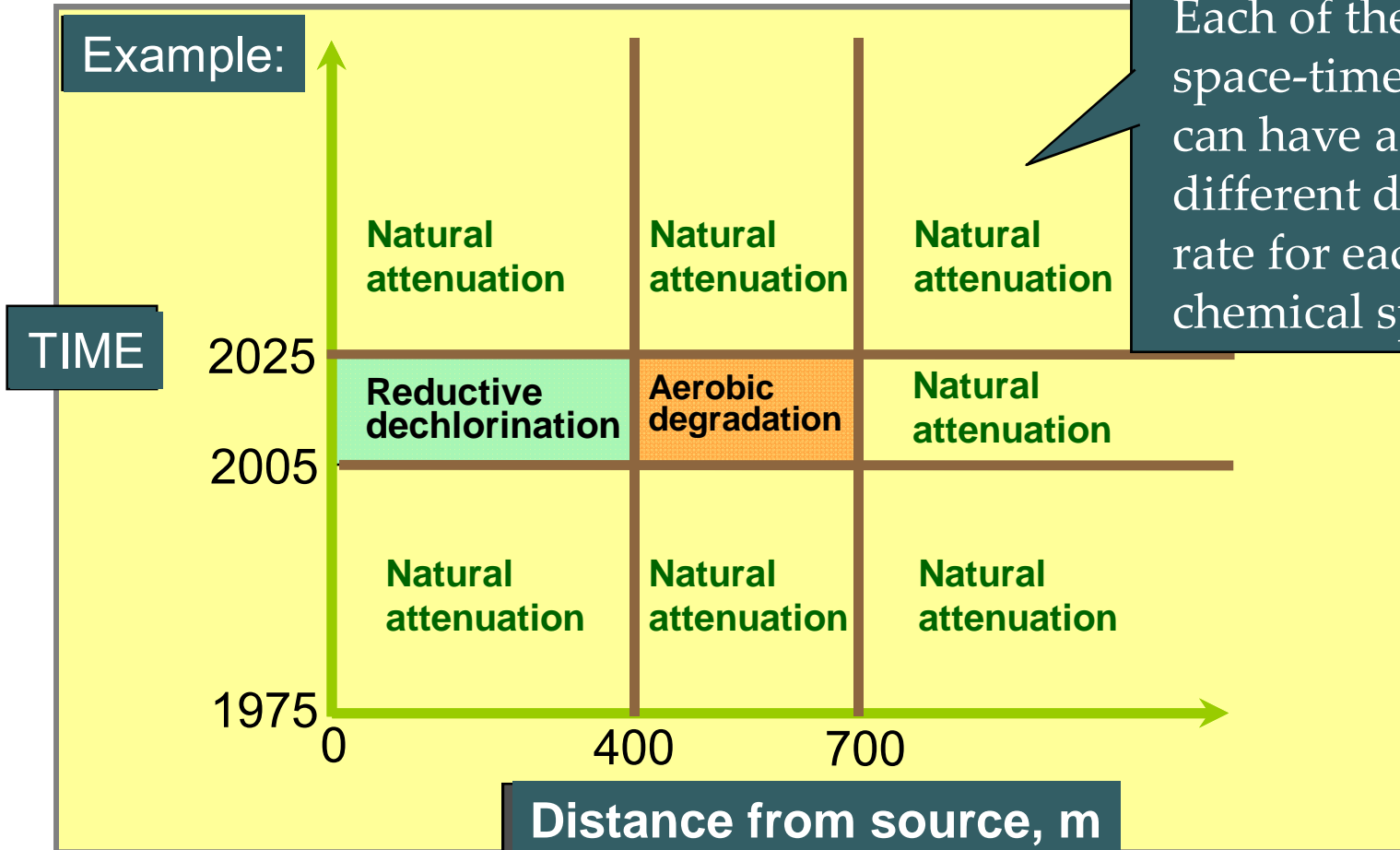


# Plume Remediation Model

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.

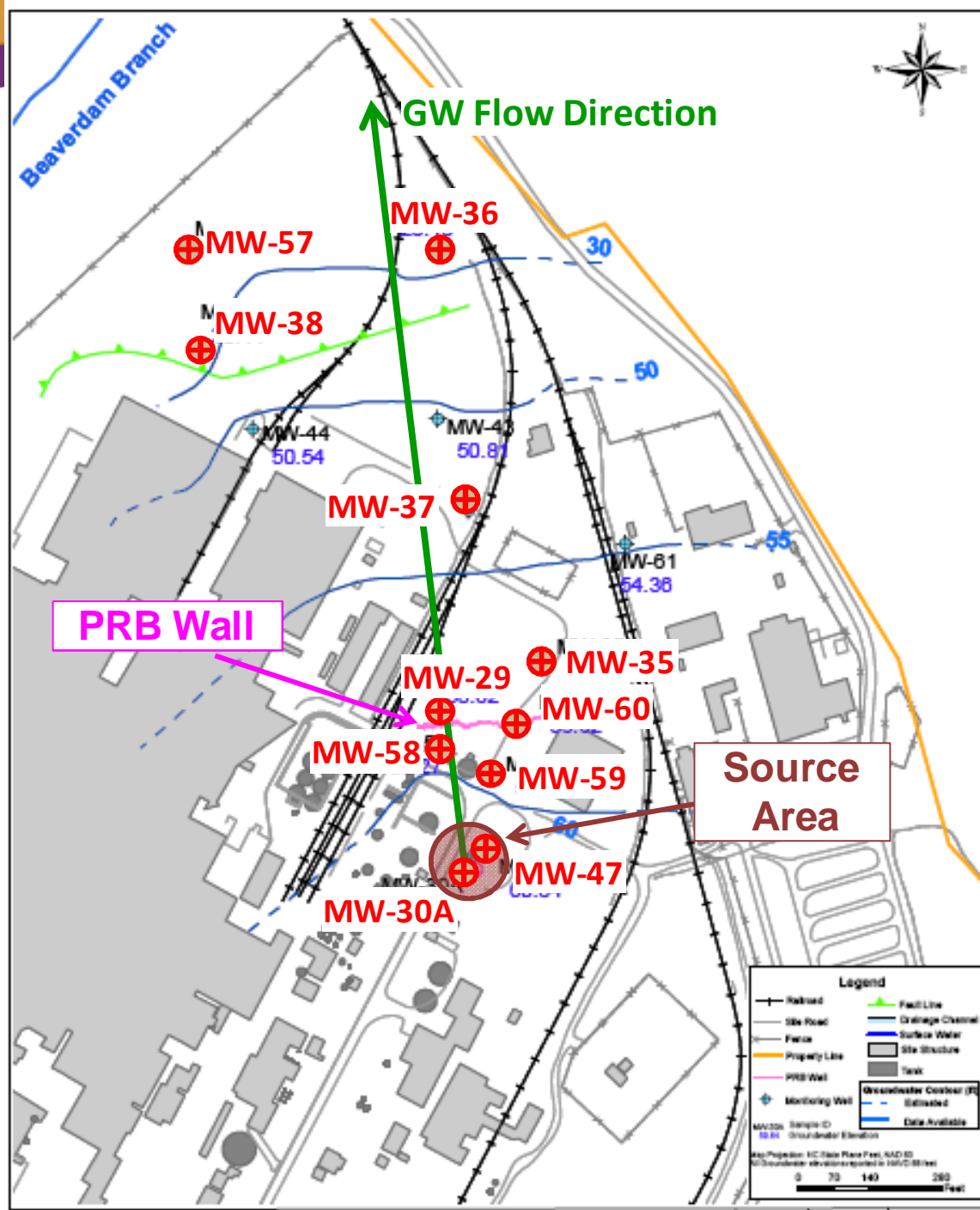
## **REMChlor Case Study: TCE plume at a manufacturing plant in North Carolina**

- DuPont Kinston Plant in eastern NC, currently produces Dacron polyester resin and fibers
- TCE contamination of groundwater discovered in the late 1980's; ~ stable plume about 1250 ft long (380 m).
- Release date unknown, but before 1980.
- Plume is dominated by TCE; small amounts of cis-1,2-DCE are present and VC is essentially absent
- Groundwater velocity is slow, less than 100 ft/yr pore velocity



## **REMChlor Case Study: TCE plume at a manufacturing plant in North Carolina**

- Source zone TCE mass estimated at 300 lbs (136 kg), source zone concentrations up to ~6,000 ug/l
- Source remediation took place in 1999, consisting of ZVI injection throughout the suspected source zone. Although source mass removal was reported as 95%, wells in the source zone have not seen large reductions in concentration.
- A 5 inch thick permeable reactive barrier (PRB) using ZVI was installed 290 ft downgradient of the source in 1999.



# REMChlor Model Parameters for Transport/Natural Attenuation

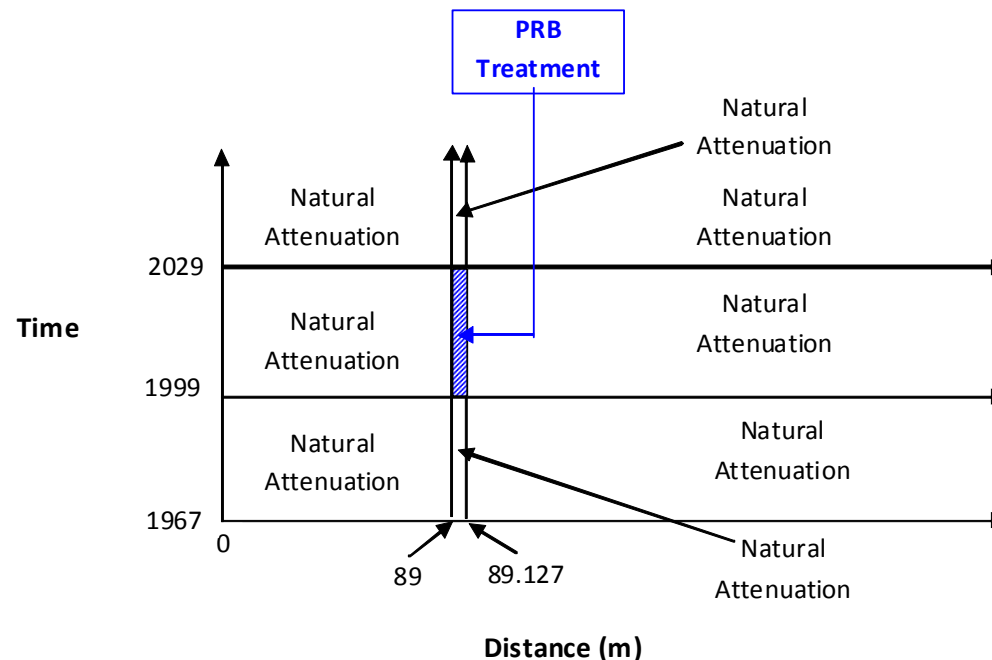


Parameter	Value	Comment
Initial Source Conc., $C_o$	6,000 ug/l	Estimated from source wells
Initial Source Mass, $M_o$	136 kg	From site reports; assume 1967 release date
Source function exponent, $\Gamma$	1	Estimated
Source Width, $W$	8m	From site reports
Source Depth, $D$	3.5m	From site reports
Darcy velocity, $V$	8m/yr	Calibrated; reports had estimated 1.5 to 4.6 m/yr
Porosity, $\phi$	0.33	From site reports
Retardation Factor, $R$	2	Estimated
Longitudinal dispersivity, $\alpha_l$	x/20	Calibrated
Transverse dispersivity, $\alpha_t$	x/50	Calibrated
Vertical dispersivity, $\alpha_v$	x/1000	Estimated
TCE decay rate in plume, $\lambda$	0.125/yr	Calibrated (equal to $t_{1/2}$ of 5.5 yrs)

# REMChlor Model Parameters for Source and Plume Remediation

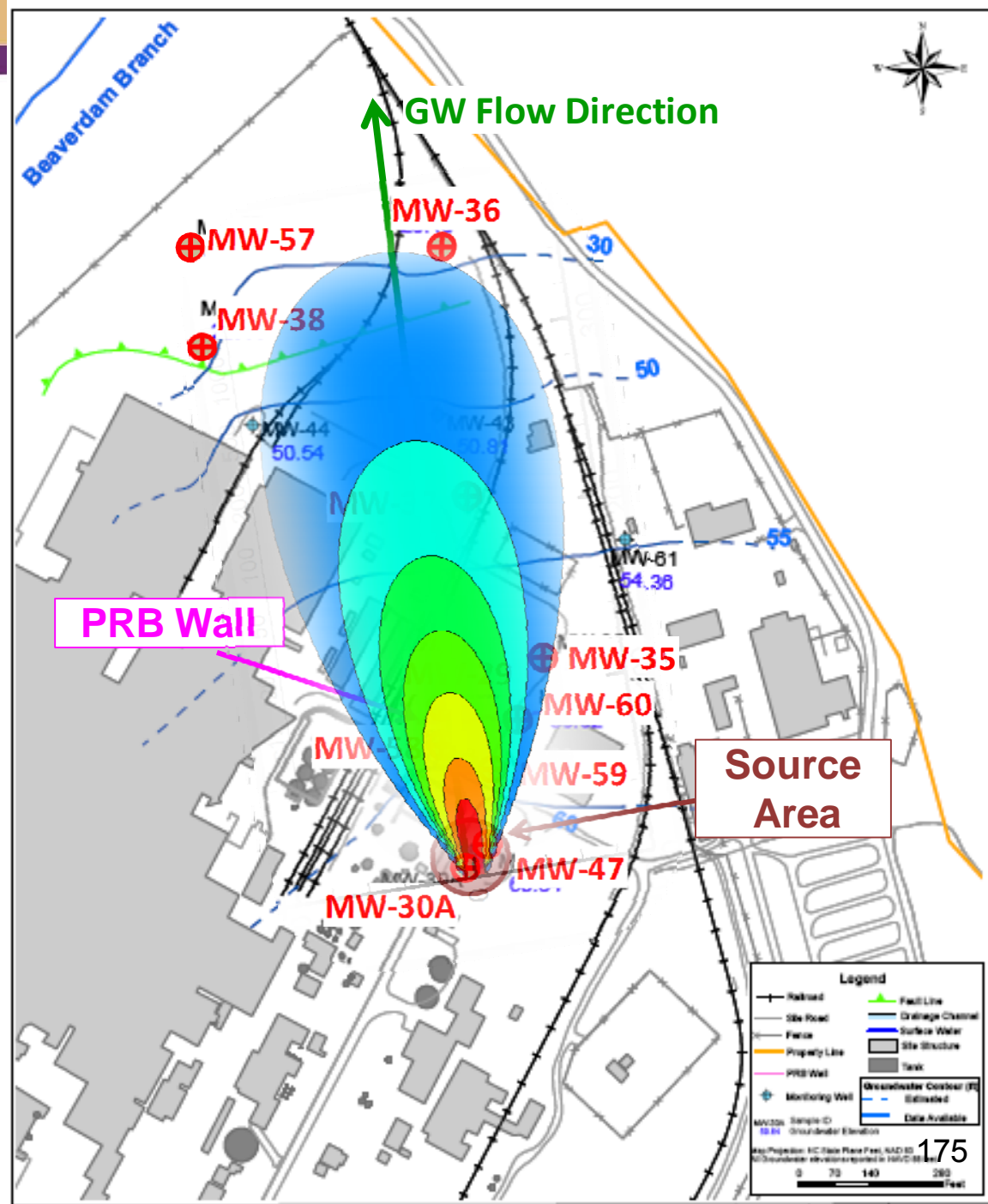


Parameter	Value	Comment
Fraction of source removed in 1999, X	95%	From site reports (but large uncertainty)
PRB wall thickness (after 1999)	0.127m (5")	From site reports
TCE decay rate in PRB	435/yr	Estimated from well data (equal to $t_{1/2}$ of 14 hours)



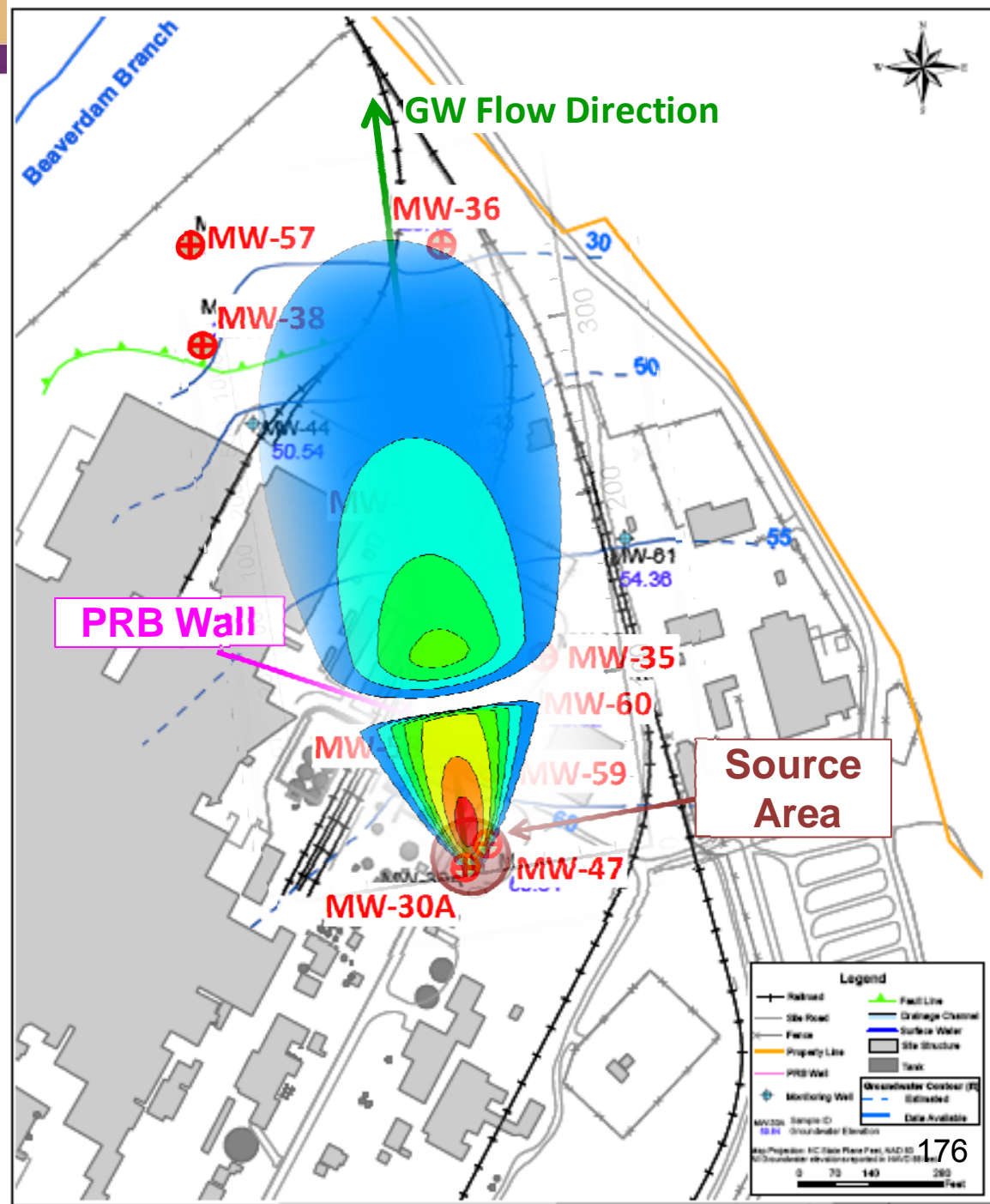
Simulated TCE concentrations  
In 1999 prior to  
source  
remediation or  
PRB wall  
installation

Contours at 5, 20,  
50, 100, 200, 500,  
and 1000 ug/l



Simulated TCE concentrations  
In 2001, 2 years  
after source  
remediation and  
PRB wall  
installation

Contours at 5, 20,  
50, 100, 200, 500,  
and 1000 ug/l

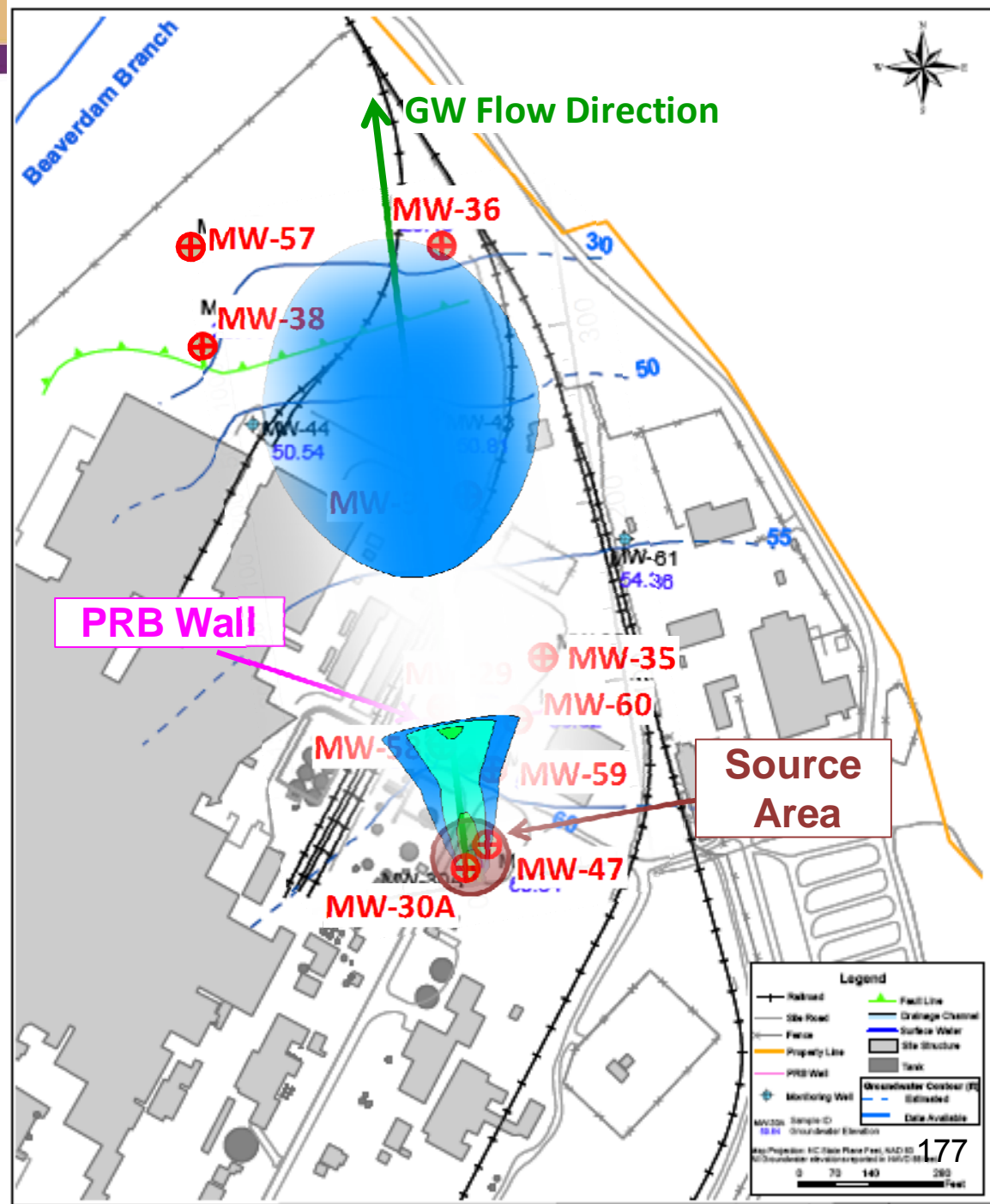


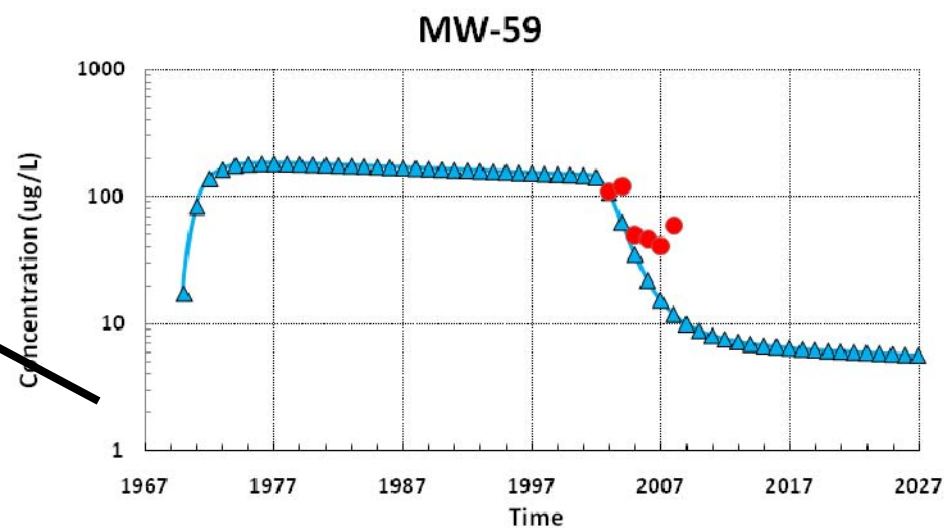
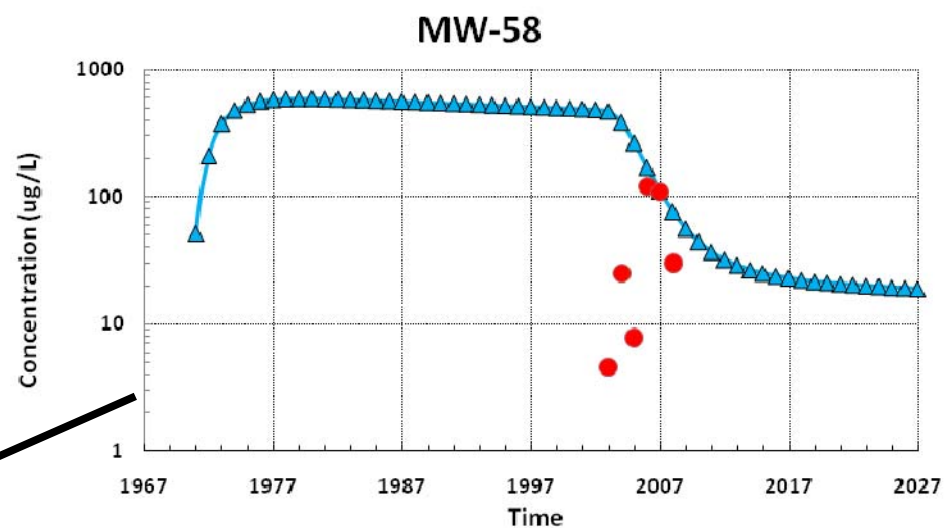
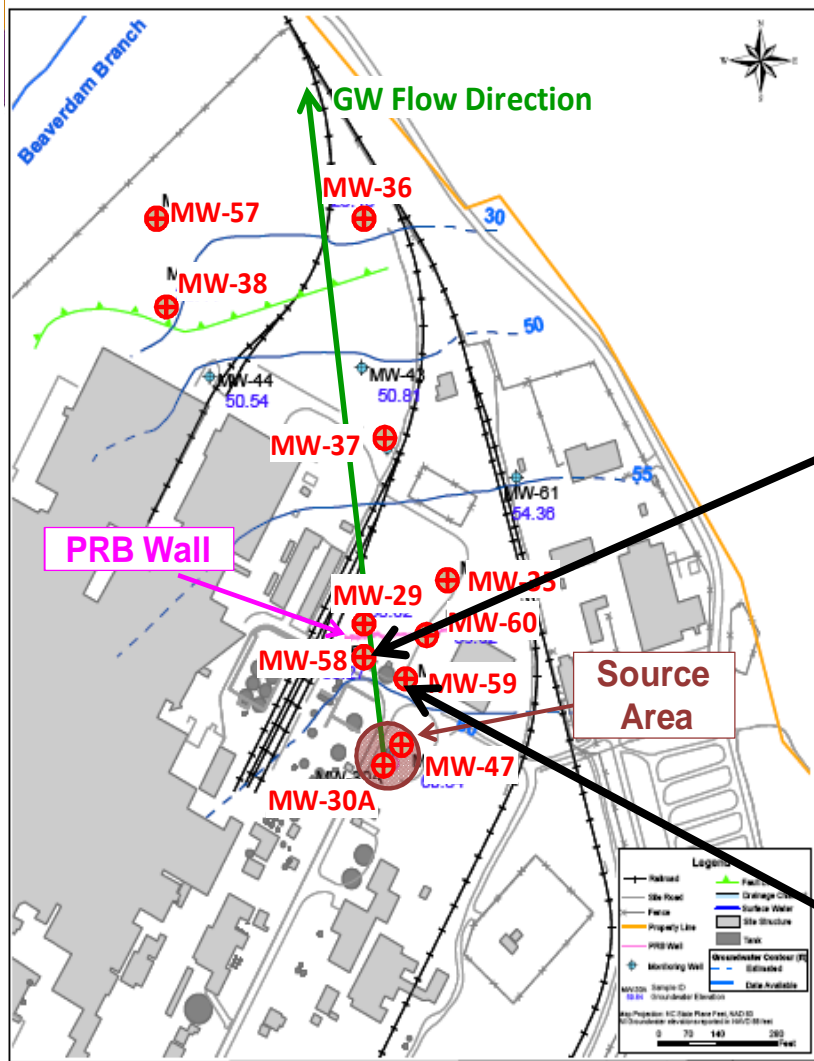


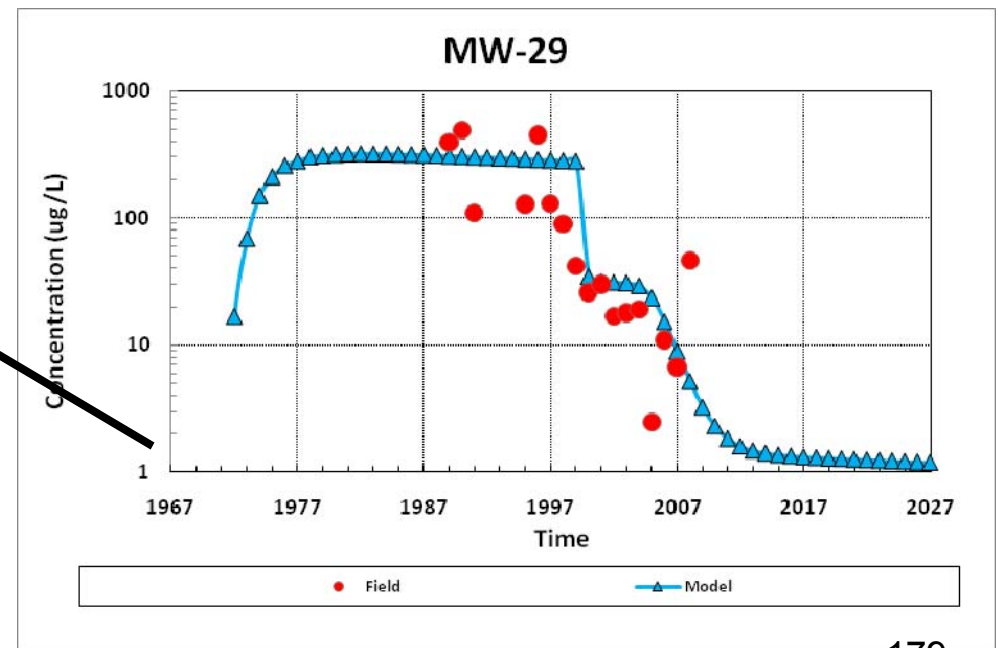
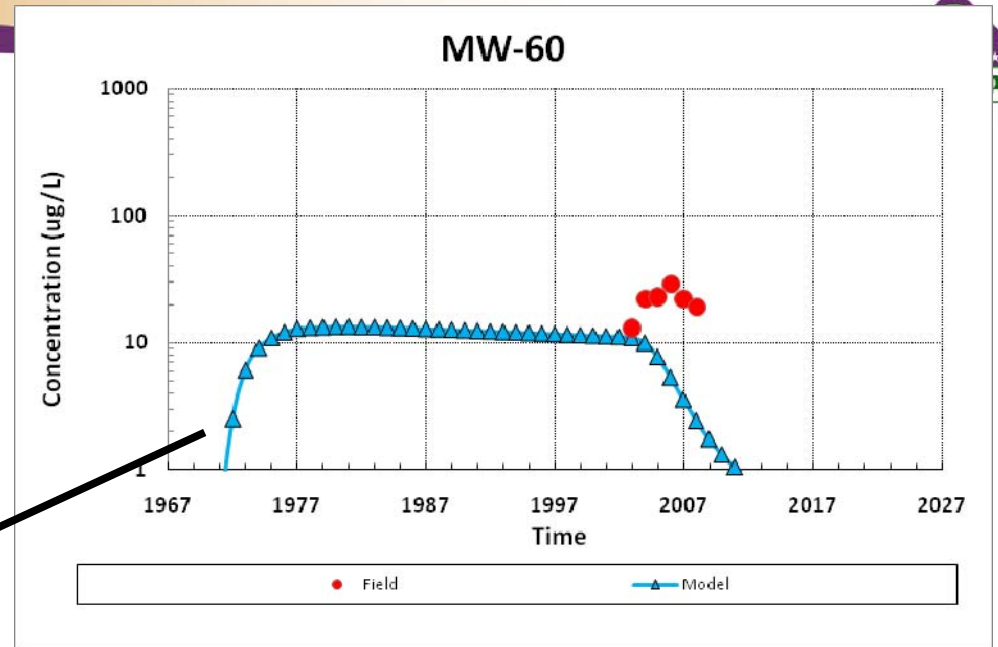
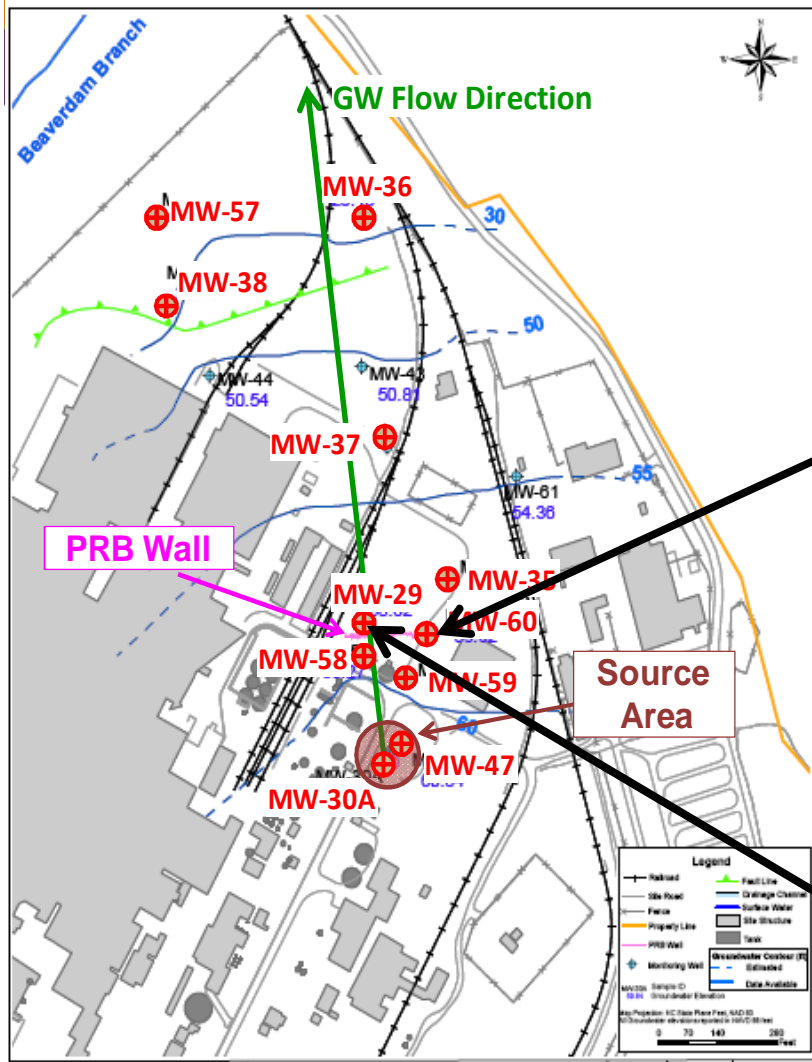


Simulated TCE

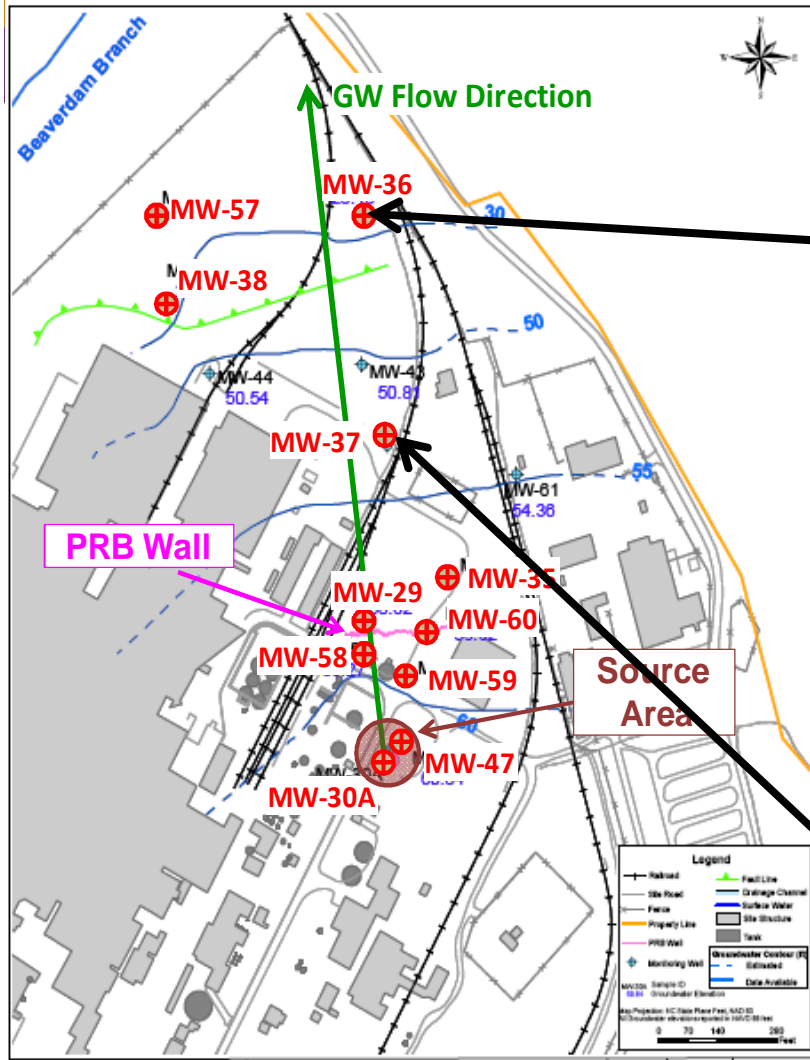
Contours at 5, 20,  
50, 100, 200, 500,  
and 1000 ug/l



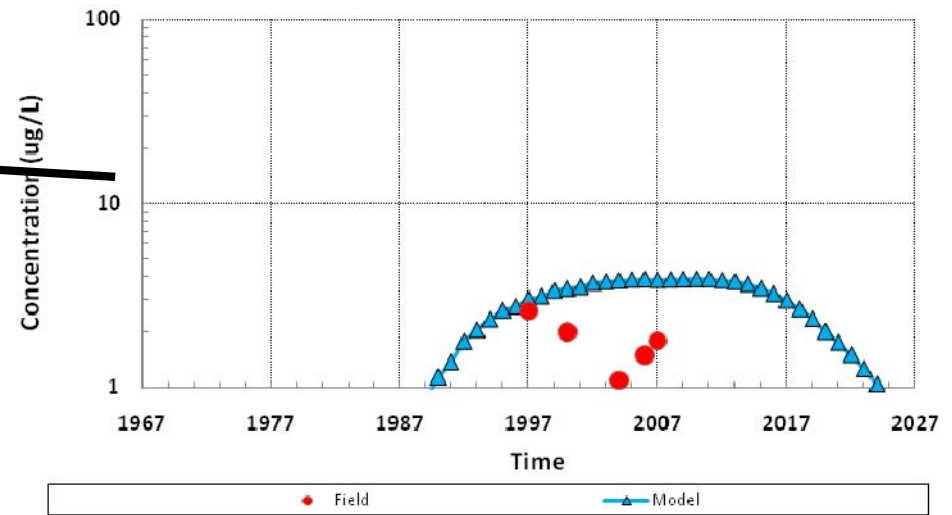




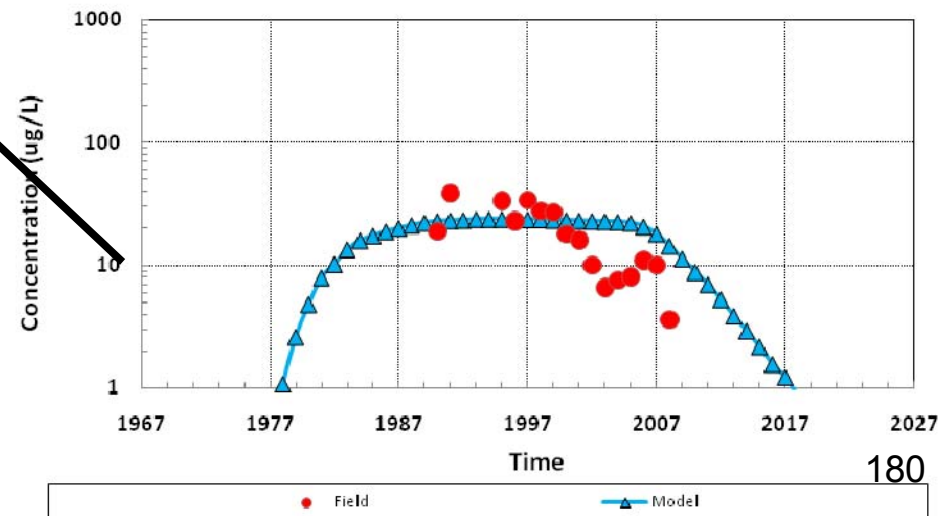
Well MW-29 is just downgradient of PRB wall



MW-36



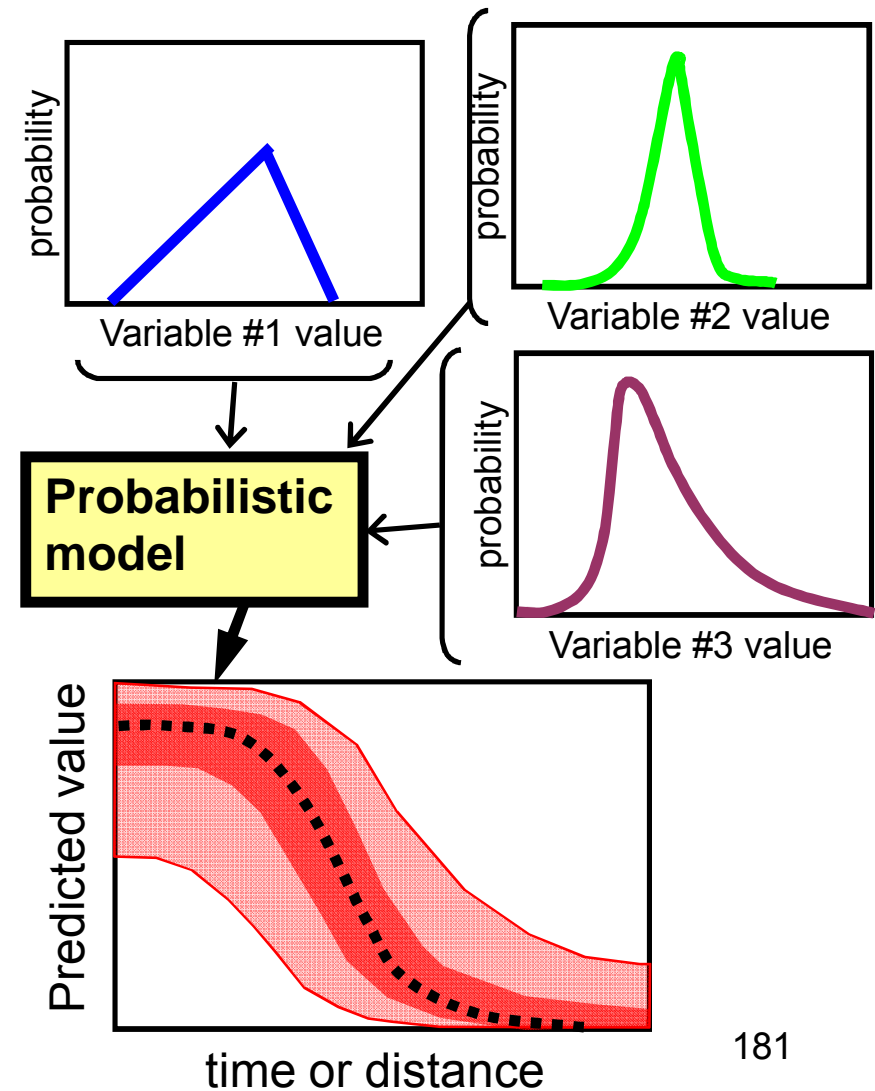
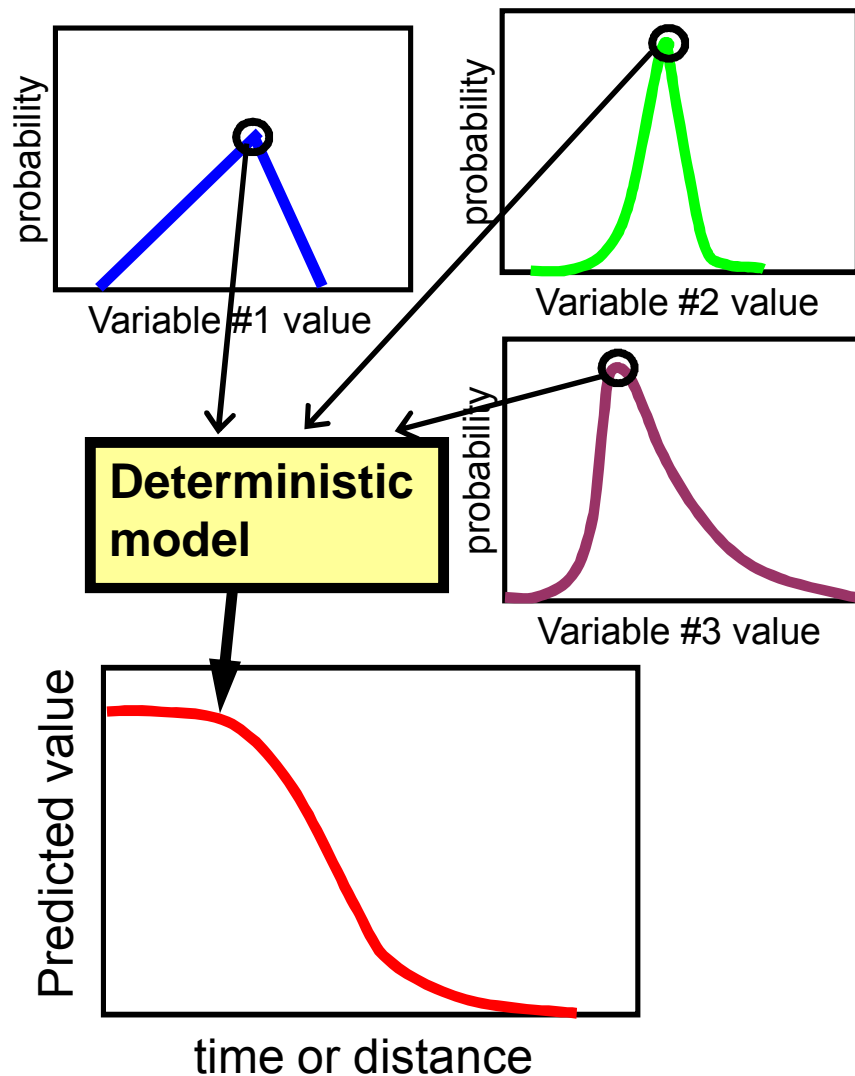
MW-37



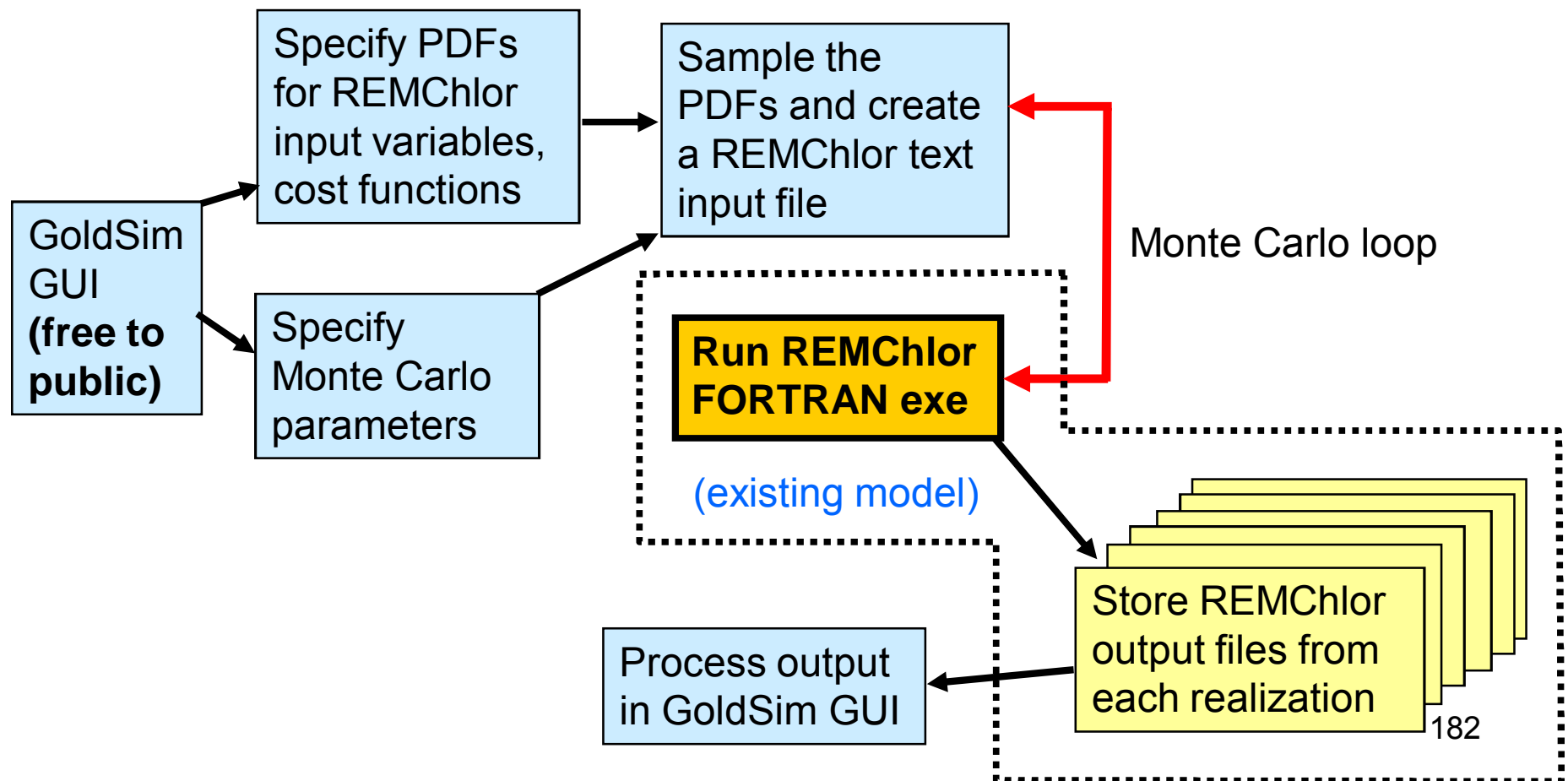
Well MW-29 is just downgradient of PRB wall



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



We have coupled the REMChlor FORTRAN code with the GoldSim probabilistic modeling software, and have produced graphical user interface using GoldSim. *We now have >70 probabilistic variables*

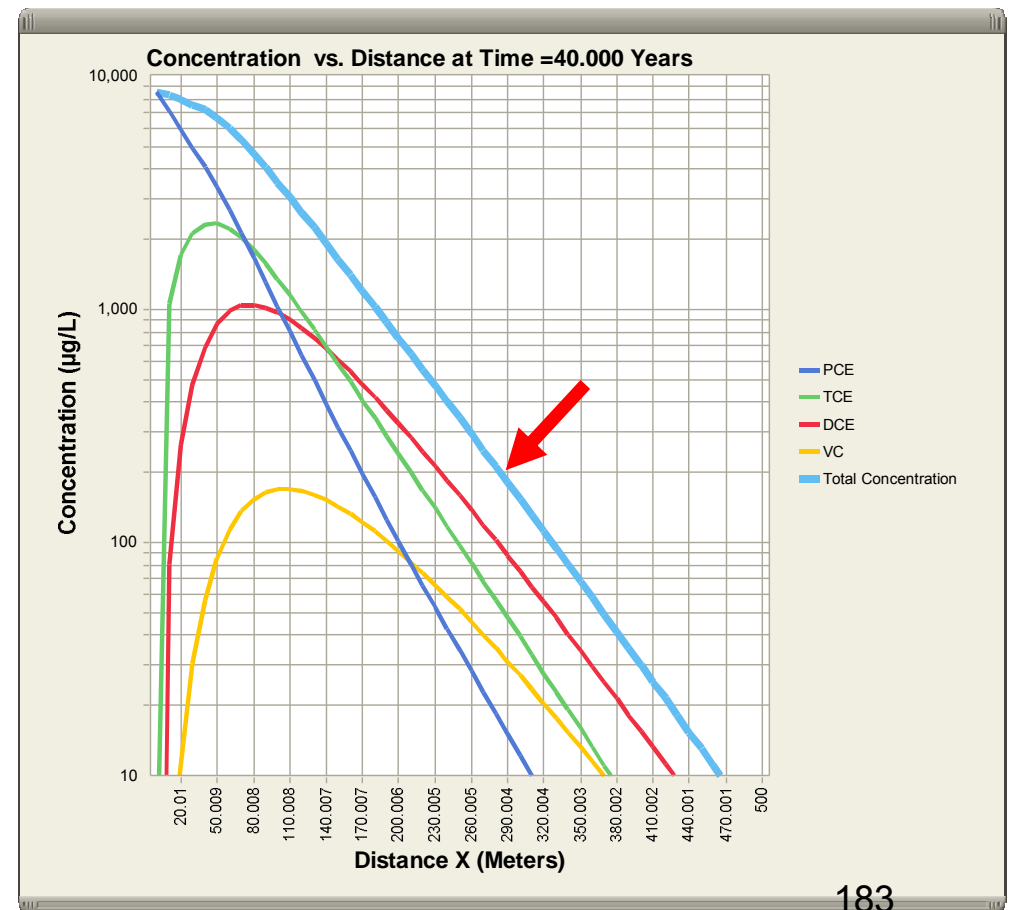




# Deterministic REMChlor Example

2023

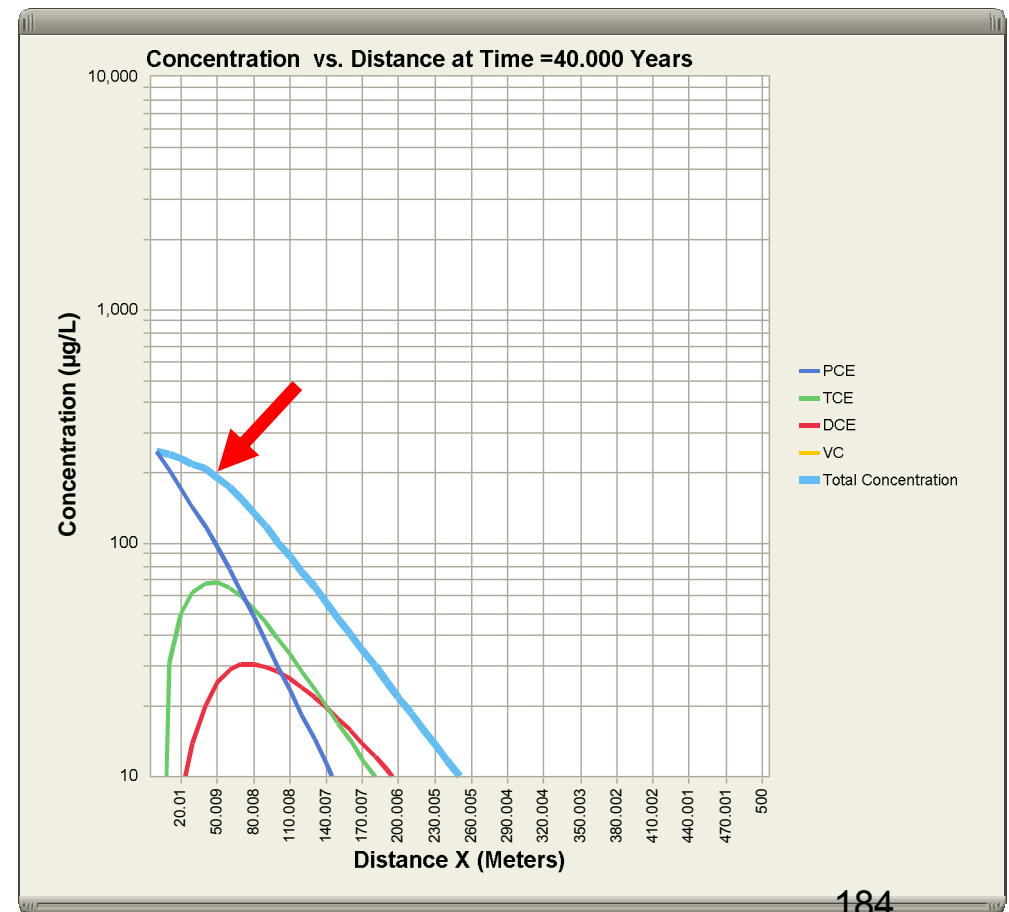
- 1600 kg release of PCE in 1983
- Plume stabilized in 2001, but is not shrinking
- The 200 ug/l total CVOC contour extends out to 290m in 2008.
- In the next 15 years, the plume will only shrink by 5m without remediation



# Deterministic REMChlor Example

- Simulate a very effective thermal remediation of the source that removes 97% of the source mass this year
- Remediation goal is to shrink the 200 ug/l contour to less than 100m in 15 years
- Maximum plume extent is only 50m, so this remediation should work

2023



# Setup REMChlor-GoldSim to run same problem



**source plume - risk cost function - Main**

Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty

Simulation Settings | Explore Model | Transport Parameters | Source Remediation | Plume Decay Rates | Sensitivity Analysis | Optimization

Observation Location  
X (m) 100 Y (m) 0 Z (m) 0  
Number of Stream Tube 100

**Run Model**

Results  
Total Concentration | Total Discharge | Total Cancer Risk | Total Cost | Source Cost | Plume Cost

References | Contact Information

ESTCP ER-0704 | CLUMSON UNIVERSITY | GSI ENVIRONMENTAL | PURDUE UNIVERSITY

**source plume - risk cost function - SourceParameters**

Source Parameters

Initial Concentration (g/L)  
Min 0.005 Likely 0.01 Max 0.02  
If checked, use Deterministic Value 0.01

Initial Mass (kg)  
Min 200 Likely 1020 Max 3000  
If checked, use Deterministic Value 1020

Gamma  
Min 1 Likely 1.40 Max 1.40  
If checked, use Deterministic Value 1

Source Dimensions  
Source Width (m)  
Min 3 Likely 10 Max 30  
If checked, use Deterministic Value 10

Source Depth (m)  
Min 0.5 Likely 3 Max 10  
If checked, use Deterministic Value 3

Source Length (m)  
Min 3 Likely 10 Max 30  
If checked, use Deterministic Value 10

Main Interface

**source plume - risk cost function - Component1\_Item**

Component 1 (Remediation)

Zone 1 Zone 2 Zone 3

Period 3  
Period 2  
Period 1

Decay Rate (1/yr)  
Min Likely Max  
0.8 1.1 2.4

Treatment Zone  
Treatment Discharge/Cost

Distance From Source, Meters  
X1 300 X2 600

Main Interface

**source plume - risk cost function - RemediationCost**

Source

Remediation Time Start Time 25 End Time 25.2  
Aqueous Phase  
Unit Cost \$/cubic meter  
Min Likely Max  
24.47 67.28 229.37

Fraction of Mass Removed  
Min Likely Max  
0.57 0.97 1

Thermal Methods  
Min Likely Max  
0.57 0.97 1

Surfactant Flooding  
Min Likely Max  
0.91 0.95 1

Chemical Oxidation  
Min Likely Max  
0 0.88 1

Bioremediation  
Min Likely Max  
0.29 0.95 1

Source  
Min Likely Max  
0.6 0.8 0.95

Main Interface

**source plume - risk cost function - TransportParameters**

Transport Parameters

Darcy Velocity (m/yr)  
Min Likely Max  
0.2 0.333 0.4

Porosity  
Min Likely Max  
0.2 0.333 0.4

Retardation Factor  
Min Likely Max  
0.01 2 20

Scale-dependent Dispersion Parameters  
Logitudinal Transverse Vertical  
Min Likely Max  
0.001 0.01 0.1

Main Interface

**source plume - risk cost function - Component1**

Component 1

Zone 1 Zone 2 Zone 3

Period 3  
Period 2  
Period 1

Decay Rate (1/yr)  
Min Likely Max  
0.8 1.1 2.4

Treatment Zone  
Treatment Rate

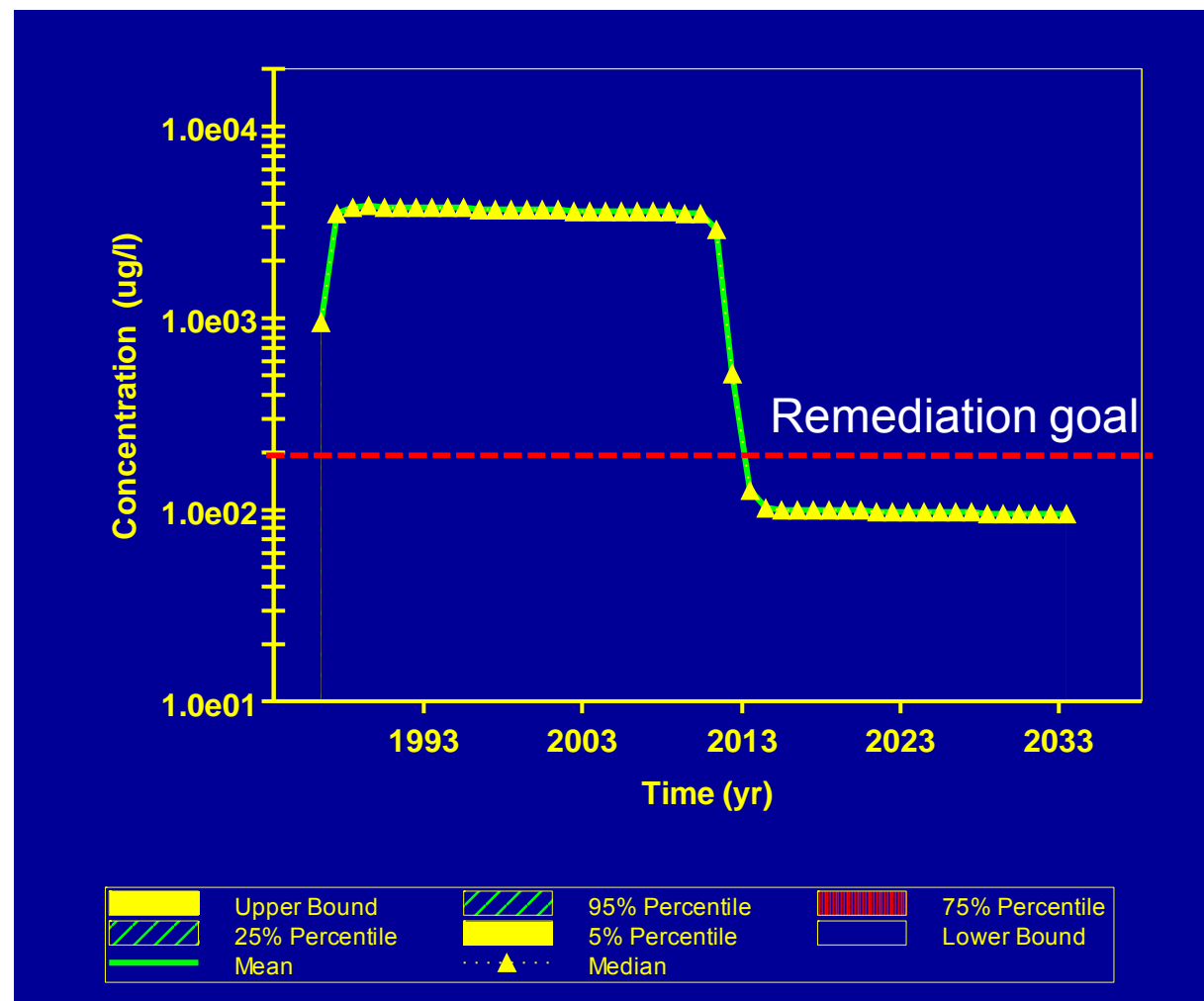
Distance From Source, Meters  
X1 300 X2 600

Cancer Risk Slope Factor  
Oral Inhalation  
Min Likely Max  
0.01 0.001 0.05

Main Interface

# Setup REMChlor-GoldSim to run same problem – deterministic result is the same

Concentration versus time at compliance point located 100m downgradient from source.



# Setup REMChlor-GoldSim to run same problem – make some source parameters uncertain

source plume risk cost function - SourceParameters

**Source Parameters**

Initial Concentration (g/L)

0.005	0.01	0.02
Min	Likely	Max

☒ If checked, use Deterministic Value 0.01

**Initial Mass (kg)**

500	1620	3000
Min	Likely	Max

☐ If checked, use Deterministic Value 1620

**Gamma**

1	1.21
Mean	Stdv

☐ If checked, use Deterministic Value 1

**Source Dimensions**

Source Width (m)

3	10	30
Min	Likely	Max

☒ If checked, use Deterministic Value 10

Source Depth (m)

0.5	3	10
Min	Likely	Max

☒ If checked, use Deterministic Value 3

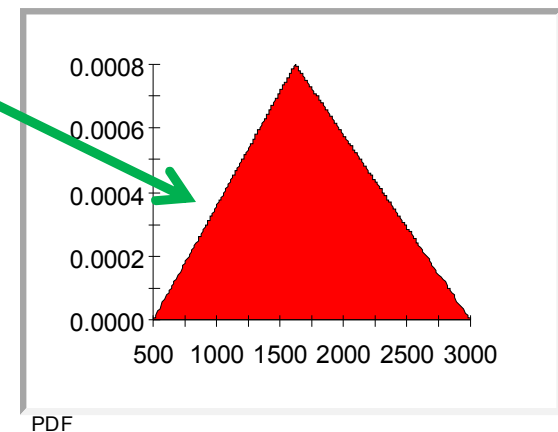
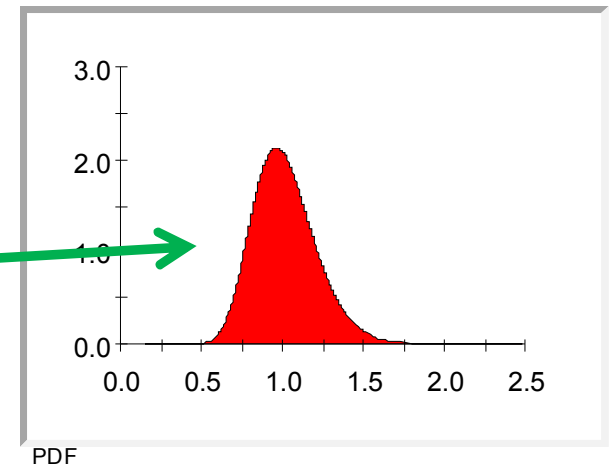
Source Length (m)

5	10	30
Min	Likely	Max

☒ If checked, use Deterministic Value 10

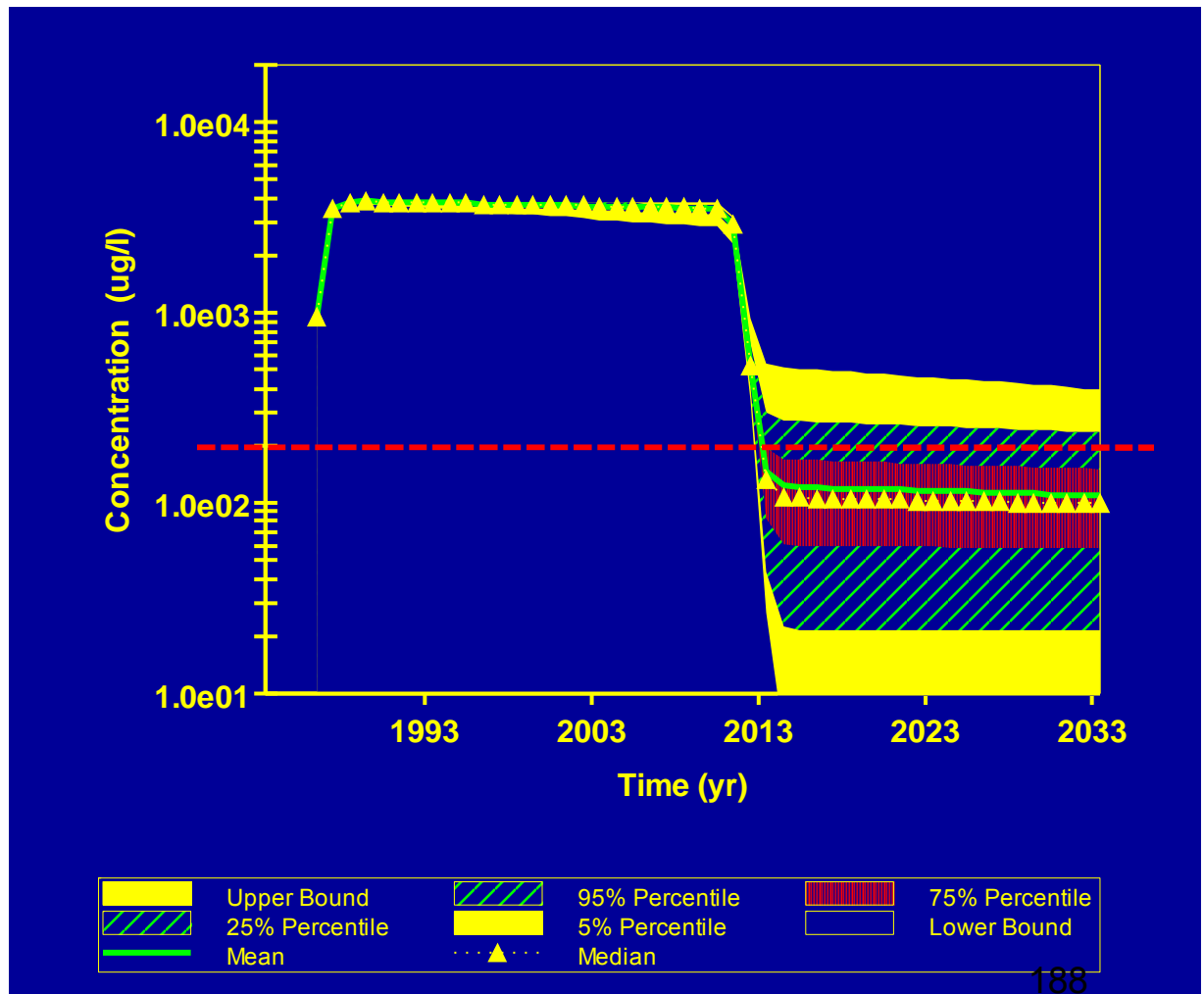
Main Interface

GoldSim Run Controller



# Probabilistic result

- Model predicts >75% chance of meeting concentration goal
- Upper bound concentration at 100m in 2023 is 460 ug/l.





# Add remediation efficiency uncertainty

source plume risk cost function - RemediationCost

**Source**

Remediation Time Start Time End Time Aqueous Phase Source Decay (1/yr)

Min Likely Max If checked, use Deterministic Value

25 25.2 0 0.01 0.1 ☒ 0

**Fraction of Mass Removed**

Min Likely Max If checked, use Deterministic Value

☒ Thermal Methods 0.8 0.97 1 ☐ 0.97

☐ Surfactant Flooding 0.91 0.95 1 ☐ 0.95

☐ Chemical Oxidation 0 0.88 1 ☐ 0.88

☐ Bioremediation 0.29 0.95 1 ☐ 0.95

If checked, use enhanced aqueous phase decay rate for

☐ Source

$t_r$  0.6 0.8 0.95 ☐ 0.8

$n$  0.6 0.8 0.95 ☐ 0.8

$Q_{in}$  0.6 0.8 0.95 ☐ 0.8

**Unit Cost ( \$/cubic meter )**

Min Likely Max If checked, use Deterministic Value

24.47 67.28 229.37 ☐ 67.28

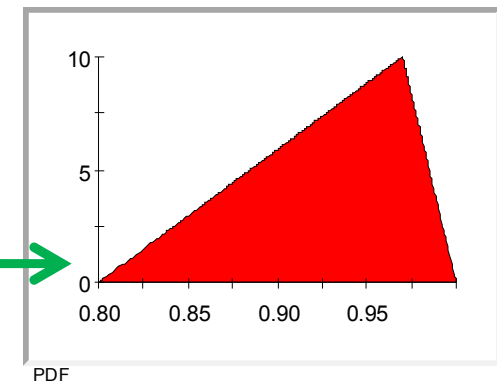
50.46 294.35 4205.05 ☐ 294.35

15.29 95.57 395.27 ☐ 95.57

1.53 22.17 172.02 ☐ 22.17

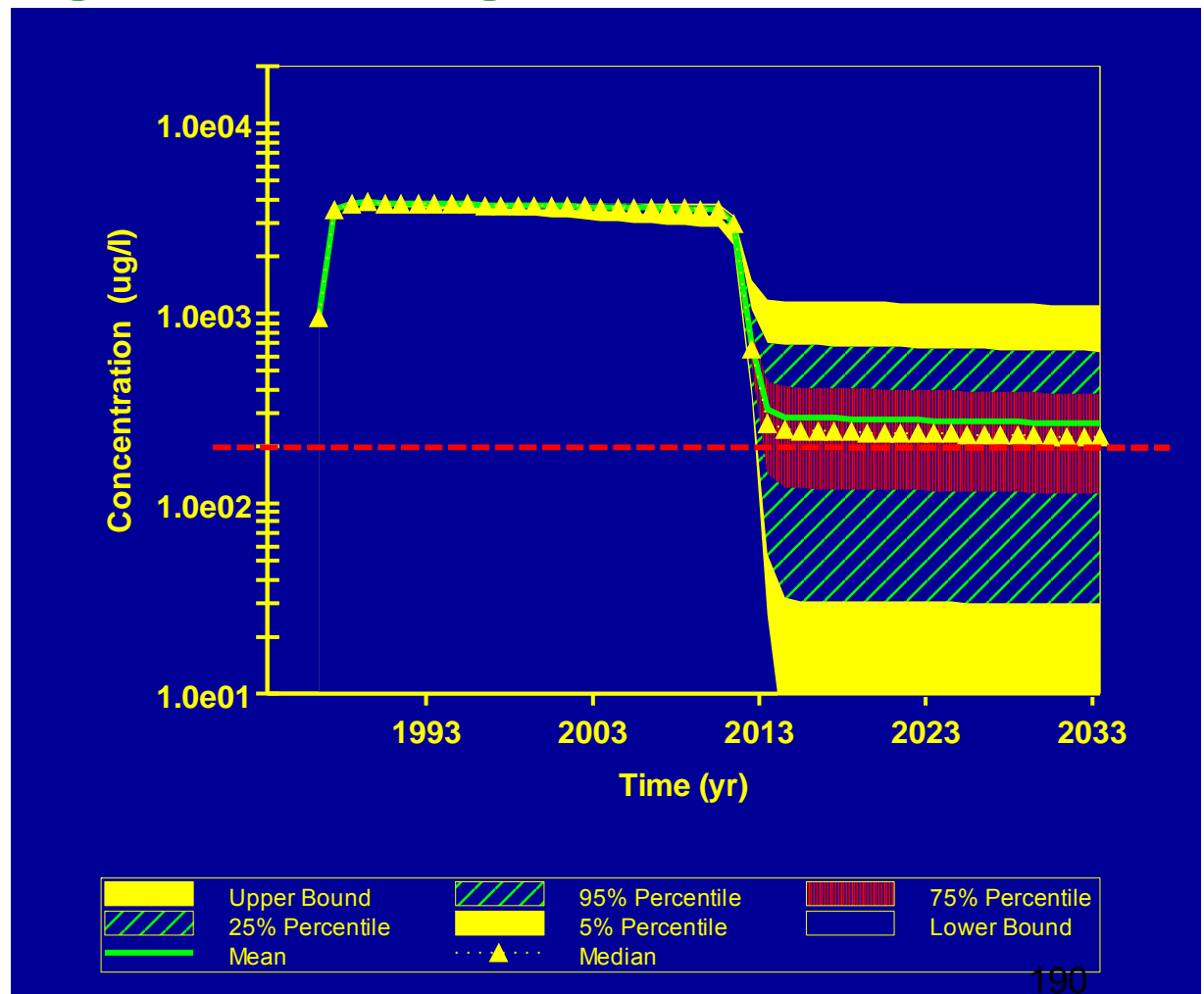
Main Interface

GoldSim Run Controller



# Model predicts possible failure of original design

- Remediation effort is predicted to meet goal only ~50% of the time given uncertainty
- Upper bound concentration at compliance point is 1130 ug/l



# Add enhanced bioremediation of the plume in the first 300m, sustained indefinitely

source plume risk cost function - Component1\_Rem

**Component 1 (Remediation)**

Component Name: 1

Time, Years

tpume 2 → 100

Period 3

Zone 1

Natural Attenuation

Period 2

Treatment Zone

Treatment Dimension/Cost

Decay Rate

Min Likely Max If checked, use Deterministic Value

1.1 2.4 4.8 ☐ 1.1

tpume 1 → 25

Period 1

Natural Attenuation

Min Likely

0.8 1.1

X 1 300

Distance From Source, Meters

Main Interface

Component 1\_Rem  
Component 2\_Rem  
Component 3\_Rem  
Component 4\_Rem

source plume risk cost function - Plume\_Treatment

**Plume Treatment**

Time, Years

tpume 2 → 100

Period 3

Zone 1

Natural Attenuation

Zone 2

Natural Attenuation

Zone 3

Natural Attenuation

Period 2

Treatment Zone

Treatment Width (m) 30

Treatment Depth (m) 5

Unit Cost ( \$/cubic meter

Min Likely Max If checked, use Deterministic Value

1 2 3 ☐ 0

Period 1

Natural Attenuation

Min Likely Max If checked, use Deterministic Value

1 2 3 ☒ 0

X 1 300

X 2 600

Distance From Source, Meters

Annual O&M Cost 10000

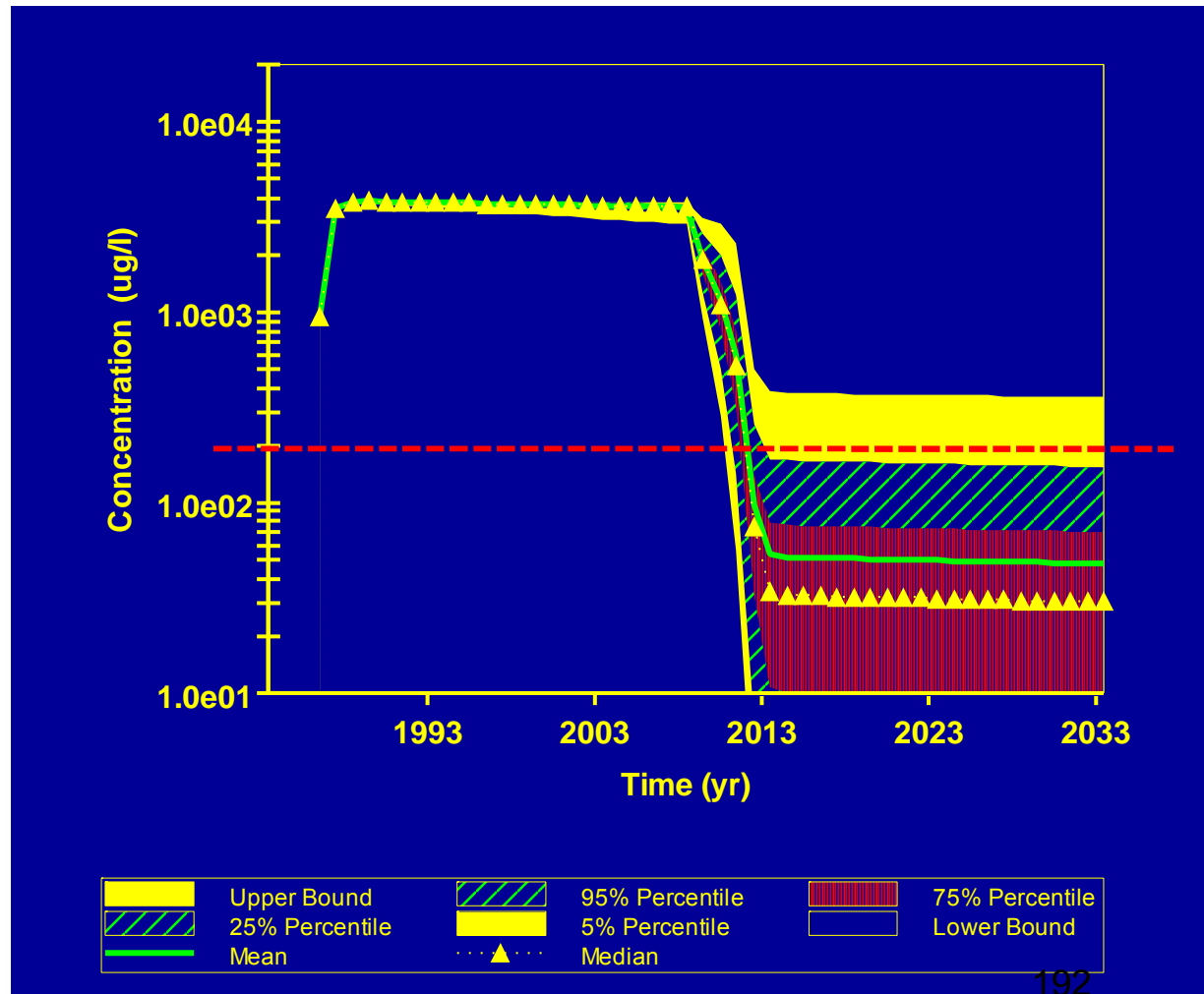
Treatment Period (tpume2 - tpume1) 75

Discount Rate ( 4

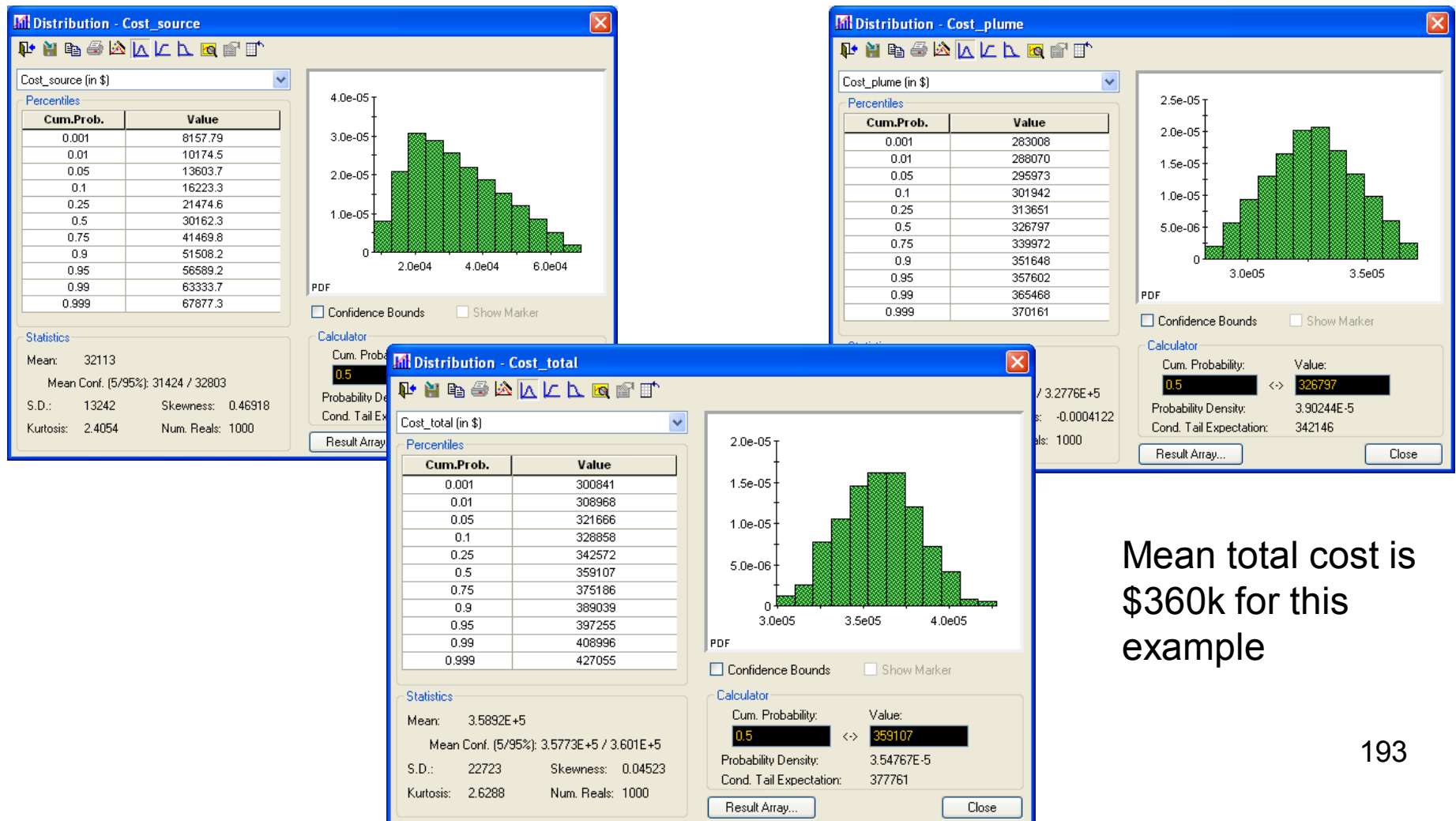
Main Interface

# New design appears to be robust

- Remediation will meet goal with >95% certainty
- Upper bound concentration at compliance point is 370 ug/l, which is less than a factor of 2 above the goal



# Estimated cost of remediation (using probabilistic cost functions)



Mean total cost is  
\$360k for this  
example

## **Now Revisit the Kinston, NC site**

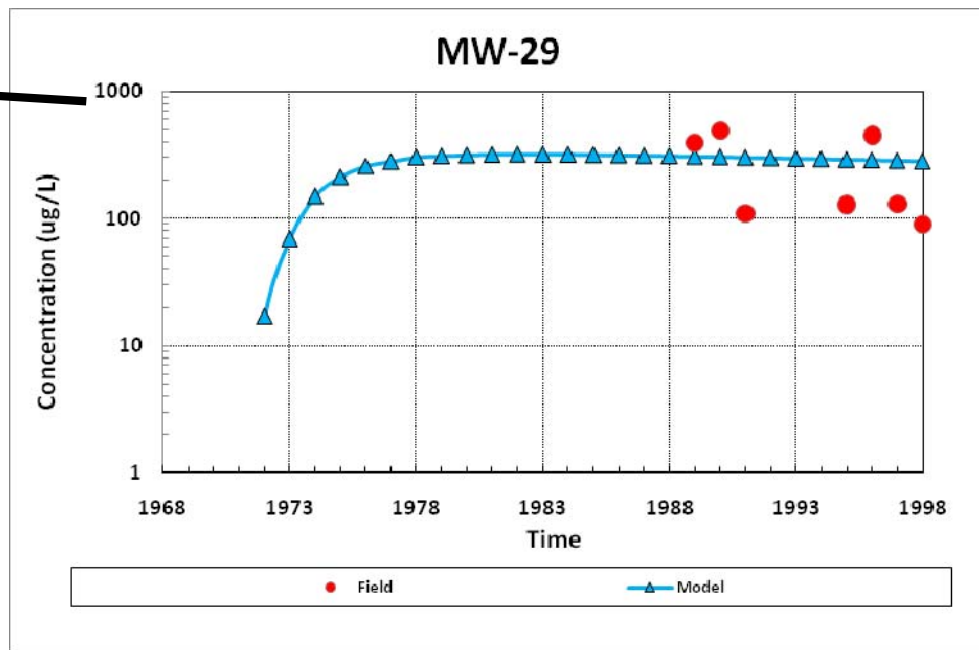
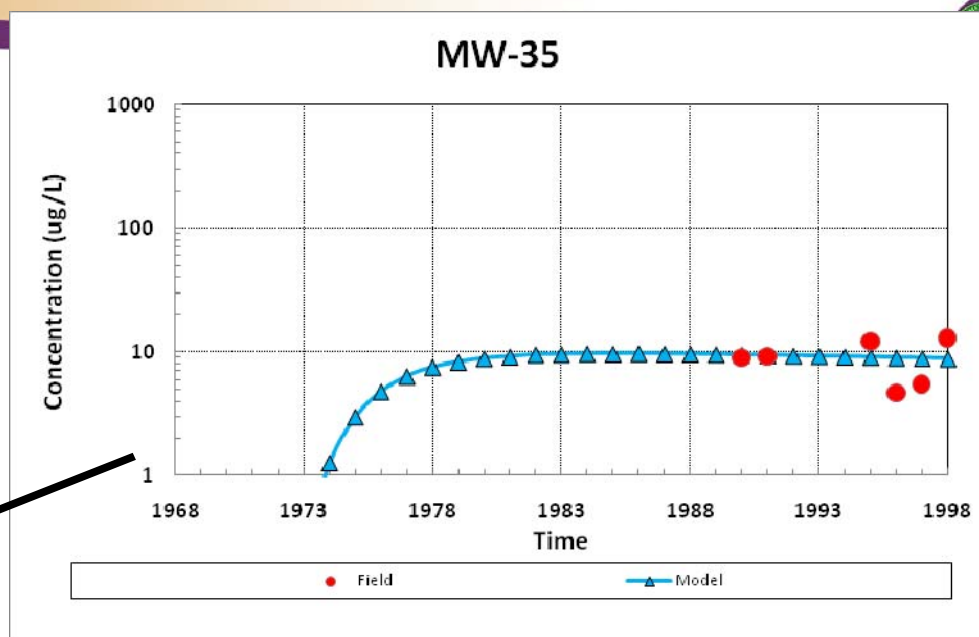
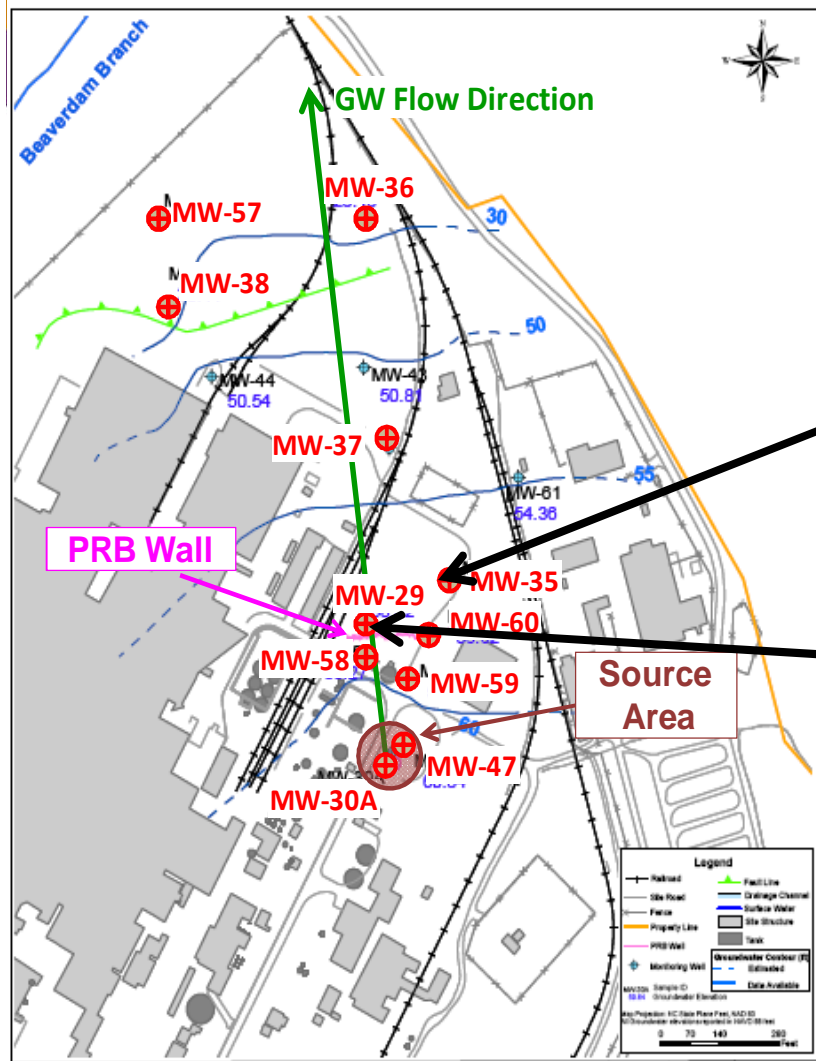
- The earlier example was a calibrated deterministic model
- What if we wanted to predict the response of the system to proposed remediation operations?
- Let's pretend that it is 1998. We have been monitoring this plume for 10 years, so we have some parameter estimates
- We'll use the probabilistic model to simulate the source and plume remediation considering uncertainty

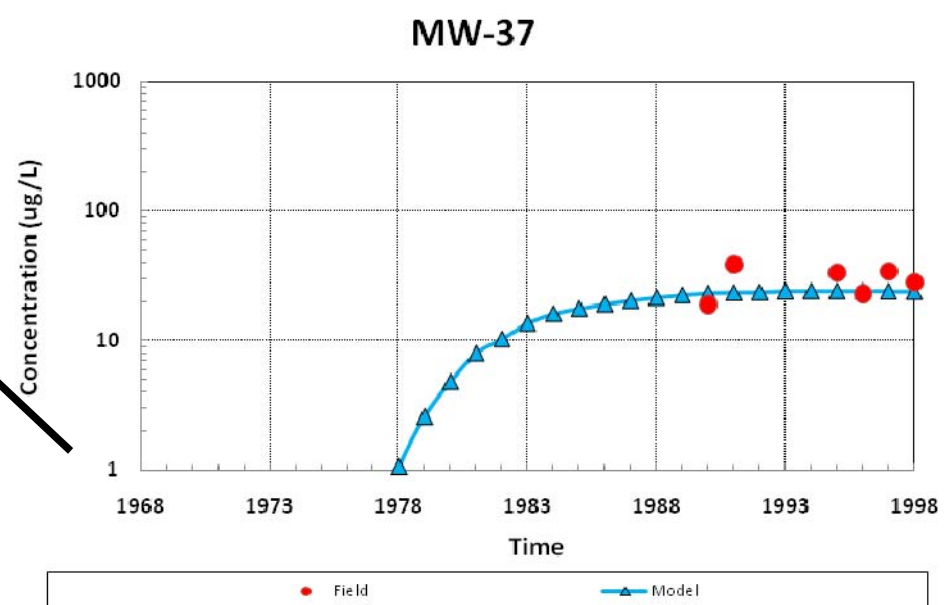
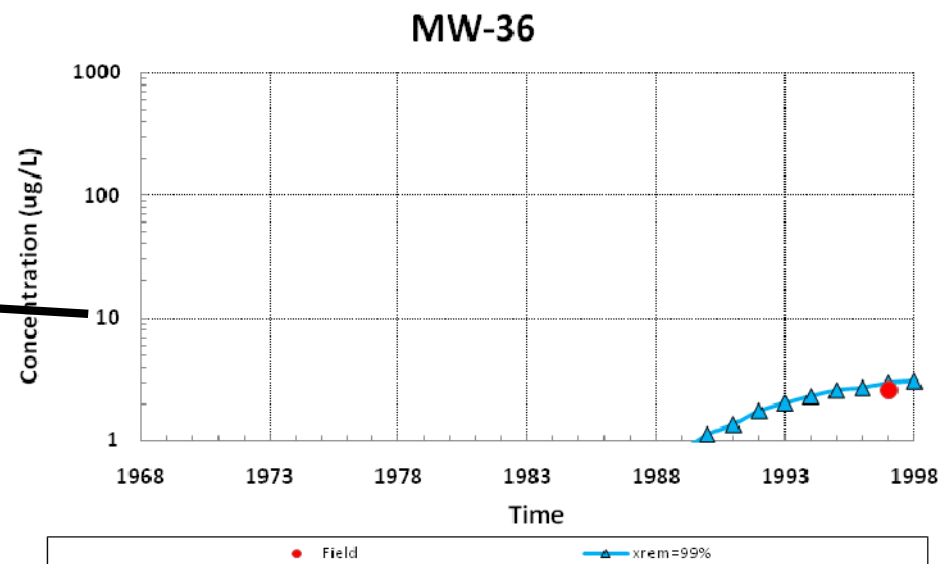
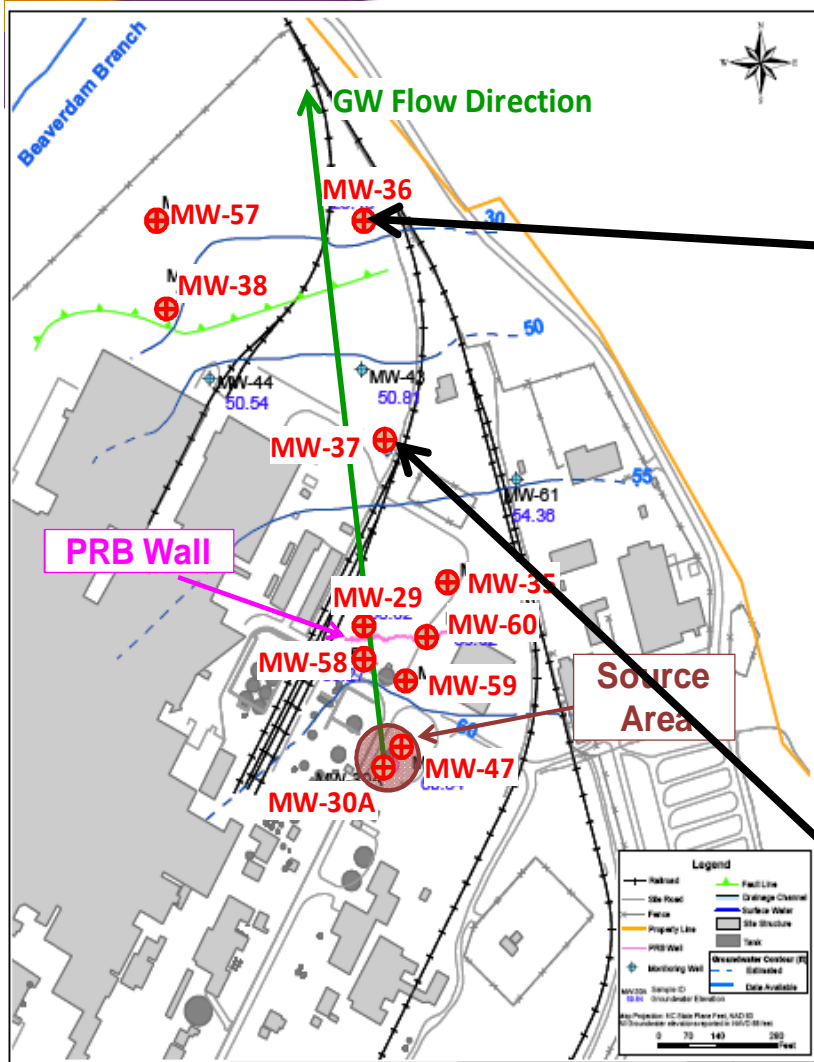


# Step 1: Calibrate transport model using pre-1998 data



Parameter	Value	Comment
Initial Source Conc., $C_0$	6,000 ug/l	Estimated from source wells
Initial Source Mass, $M_0$	136 kg	From site reports; assume 1967 release date
Source function exponent, $\Gamma$	1	Estimated
Source Width, $W$	8m	From site reports
Source Depth, $D$	3.5m	From site reports
Darcy velocity, $V$	8m/yr	Calibrated; reports had estimated 1.5 to 4.6 m/yr
Porosity, $\phi$	0.33	From site reports
Retardation Factor, $R$	2	Estimated
Longitudinal dispersivity, $\alpha_l$	x/20	Calibrated
Transverse dispersivity, $\alpha_t$	x/50	Calibrated
Vertical dispersivity, $\alpha_v$	x/1000	Estimated
TCE decay rate in plume, $\lambda$	0.125/yr	Calibrated (equal to $t_{1/2}$ of 5.5 yrs)

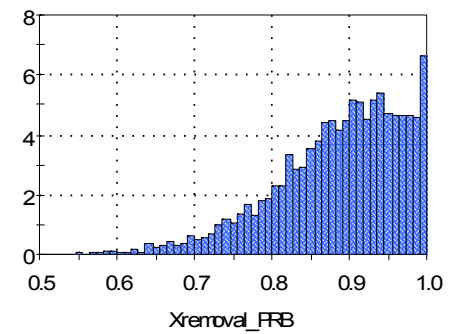
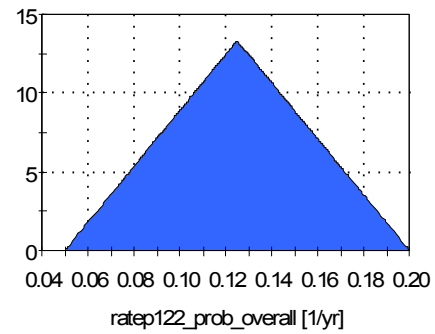
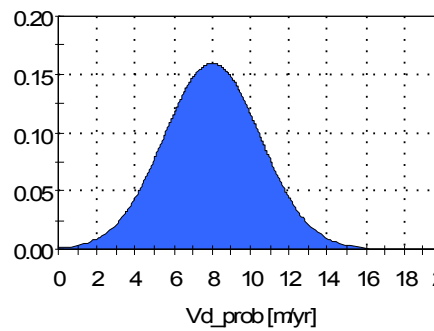
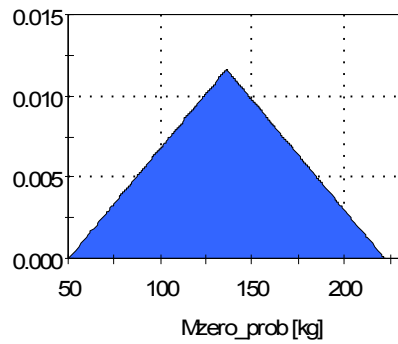
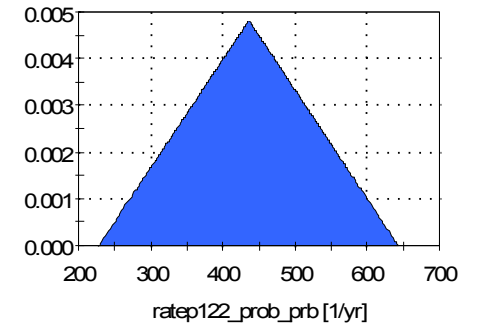
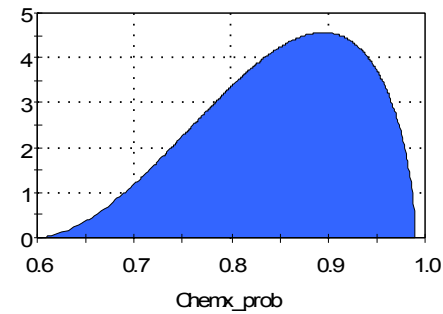
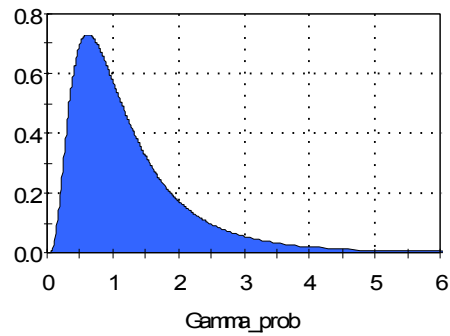
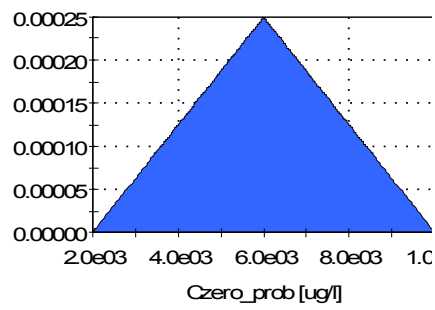




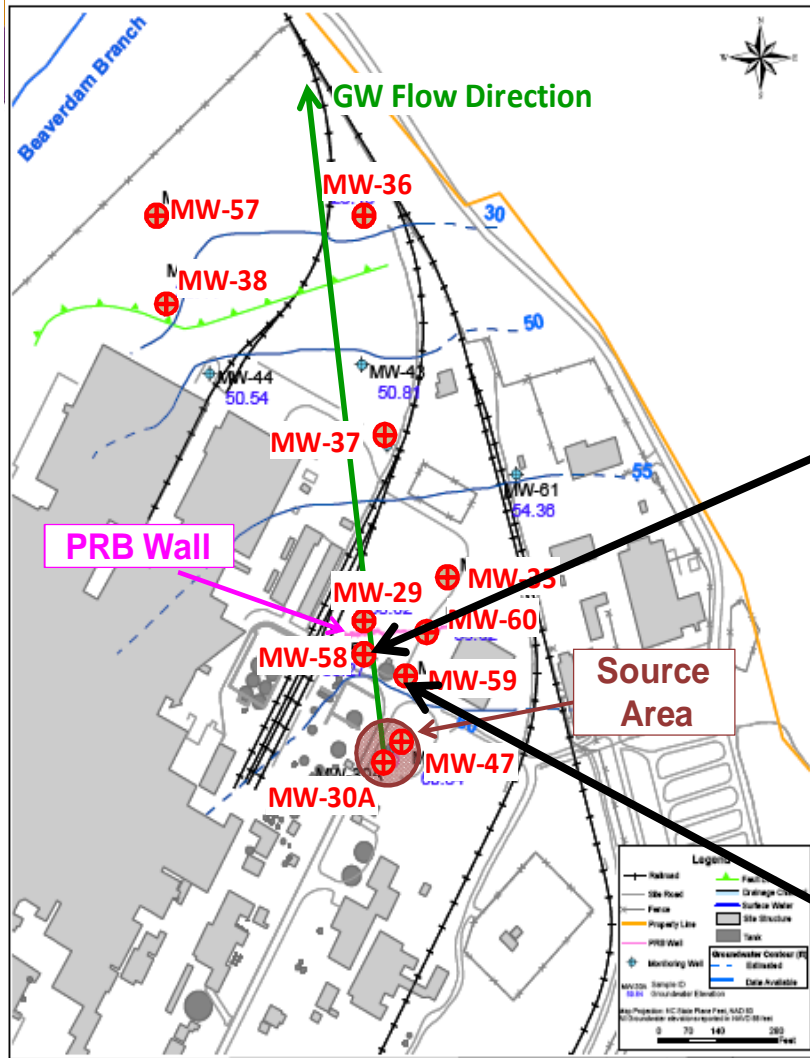
# Add Probabilistic Inputs

Parameters	Distribution	Distribution Parameters	Reference
Initial source concentration (ug/l)	Triangular	most likely=6000, min=2000, max=10,000	estimated
Initial source mass (kg)	Triangular	most likely=136, min=50, max=222	estimated
Power function exponent	Log-normal	geo. Mean =1, geo stdv=2	
Darcy velocity (m/yr)	Normal	mean=8, stdv=2.5	
Overall plume natural attenuation rate for TCE (1/yr)	Triangular	most likely=0.125, min=0.05, max=0.2	
Fraction of source mass removal (%)	Beta	mean=0.85, stdv = 0.08, min=0.6, max=0.99	McGuire et al, 2006
PRB enhanced decay rate (1/yr)	Triangular	most likely=436, min=228, max=643	

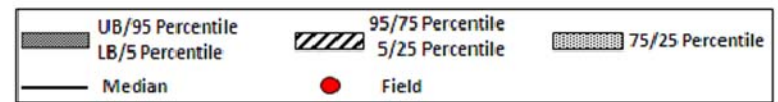
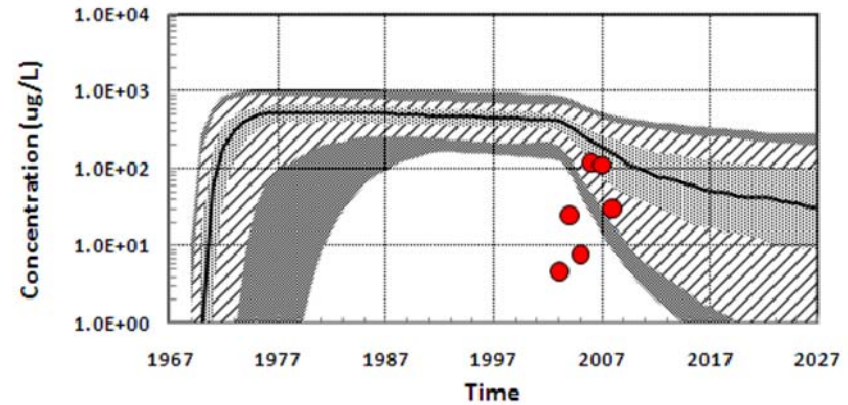
# PDFs



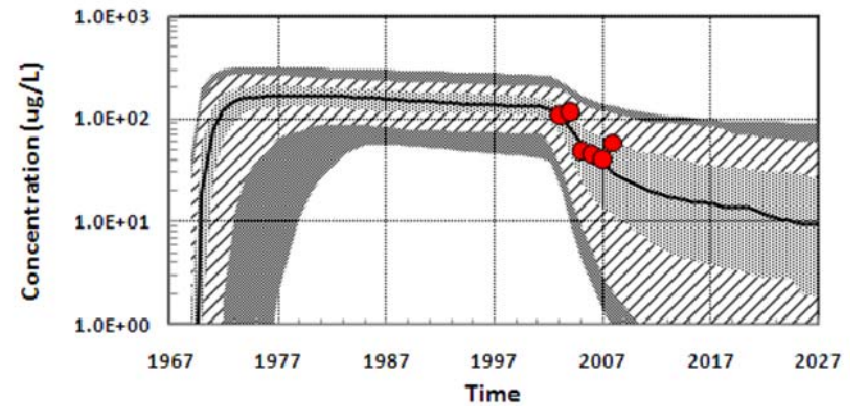




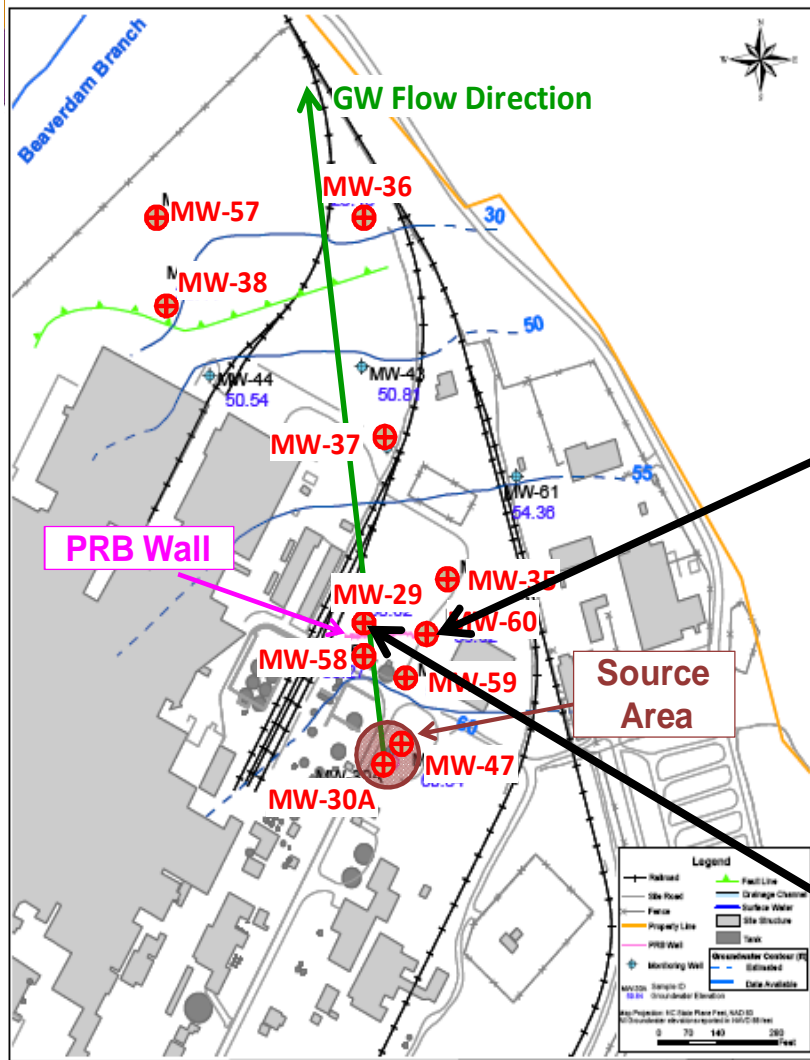
MW-58



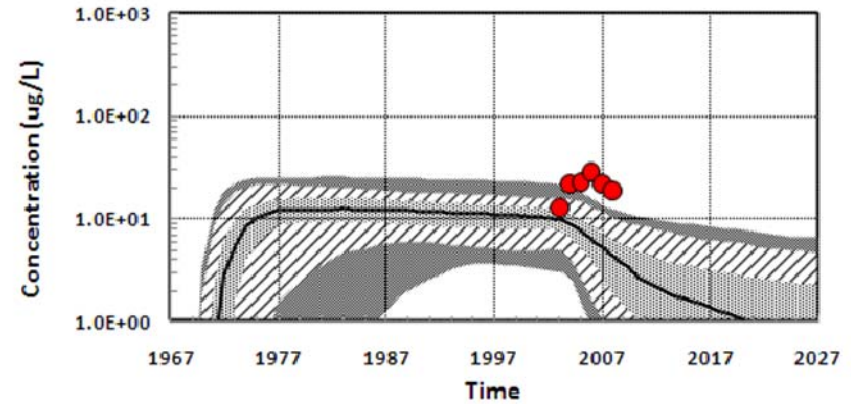
MW-59



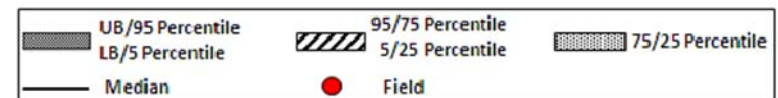
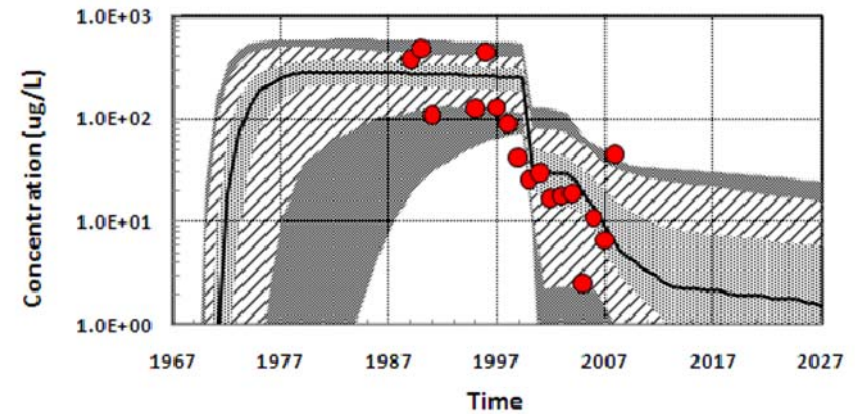




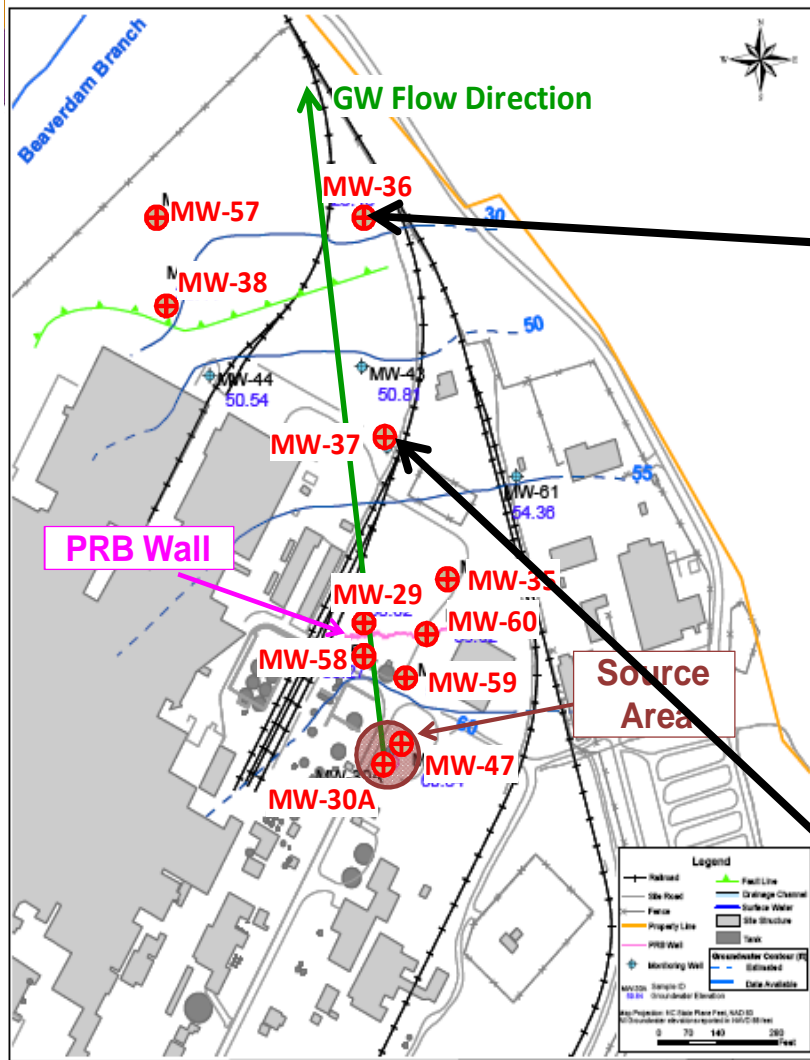
MW-60



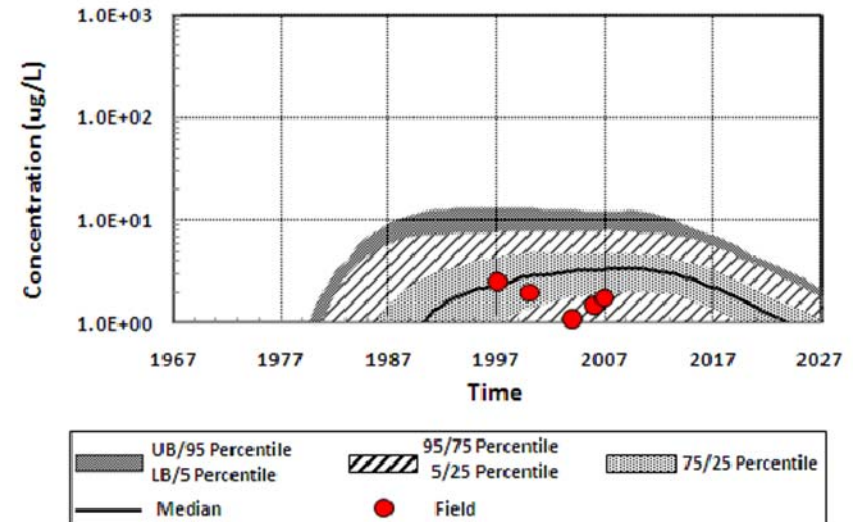
MW-29



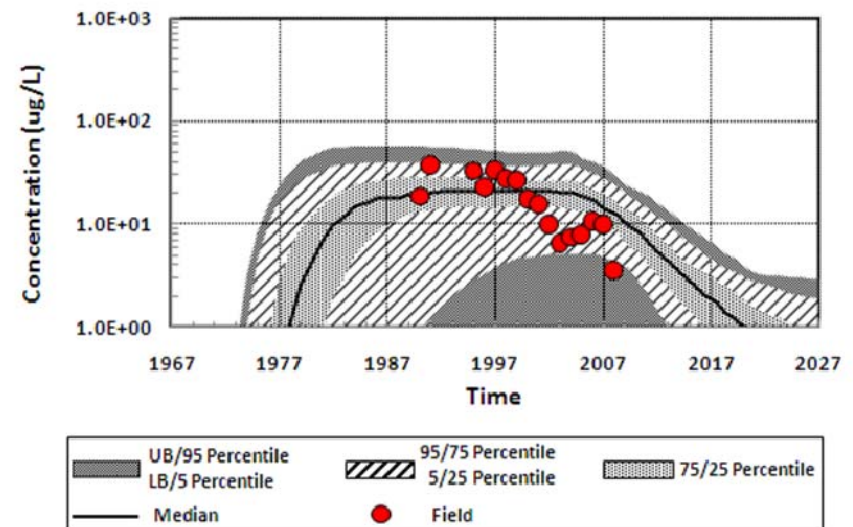
Well MW-29 is just downgradient of PRB wall



MW-36



MW-37



# How to get Probabilistic REMChlor

- See handout.
- Download dll and player files from Clemson FTP site;
- Download GoldSim Player executable from GoldSim site (free)

# Short Course Agenda



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo



# Planning and Design of Emulsified Oil Injection Systems



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M. Tony Lieberman



Aaron Weispfenning  
Matthew Clayton

NC STATE UNIVERSITY

Thomas Simpkin



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(Robert Borden, Aaron Weispfenning, and Matt Clayton)
  - Solutions-IES (M. Tony Lieberman)
  - CH2M Hill (Tom Simpkin)
- Financial and technical support from ESTCP
- NCSU is not sponsoring or endorsing this presentation



# Emulsified Oil Process

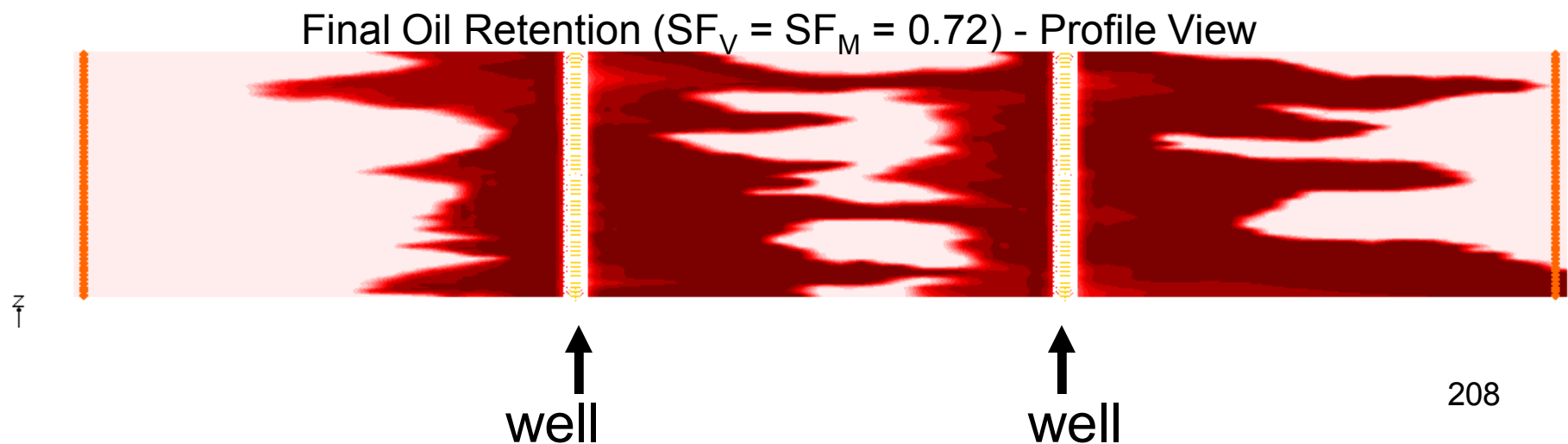
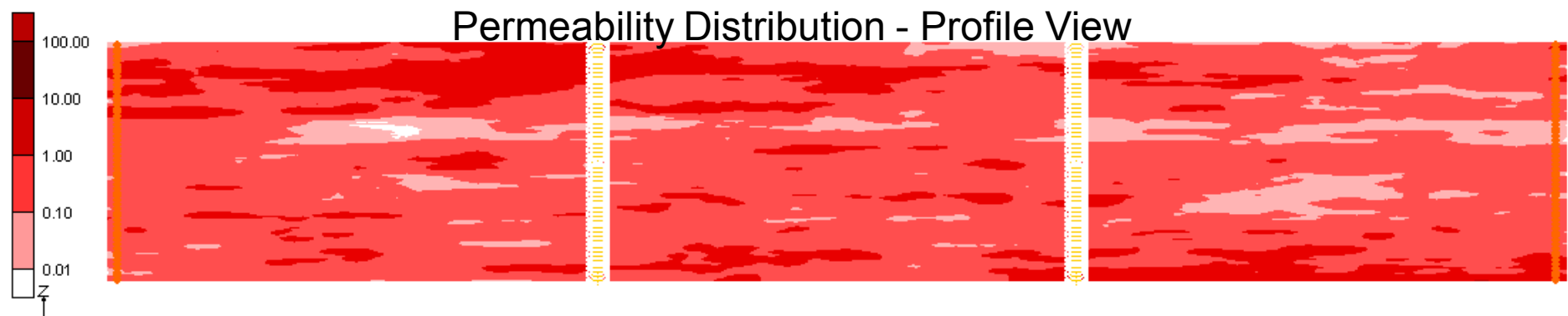
- Install temporary or permanent injection points
  - ◆ Grids or barriers
- Prepare and inject emulsion
- Inject water to distribute emulsion throughout treatment zone
- Oil droplets eventually stick to sediment surfaces
- Oil slowly ferments to  $H_2$  and acetate
- $H_2$  and acetate drive anaerobic biodegradation processes
- Bioaugment if needed
- Monitor and wait



# Numerical Modeling of Emulsified Oil Distribution



- MODFLOW/RT3D
- 3D heterogeneous aquifer



# How to Improve Treatment?

- Good treatment requires good contact
  - How to improve contact
    - ♦ Inject more emulsified oil → more \$\$\$
    - ♦ Inject more water to distribute oil → more \$\$\$
    - ♦ Install more closely spaced wells → more \$\$\$
- Problem: Which do I focus on?
- Solution: ESTCP Project ER-0626  
Development of a Design Tool for Planning  
Aqueous Amendment Injection Systems

# Injection System Design Tool – Injection Only

- Input

- Site Data

- Aquifer characteristics
    - Contaminants
    - Biogeochemical data

- Costs

- Fixed
    - Drilling
    - Substrate
    - Labor for injection

- Design Info

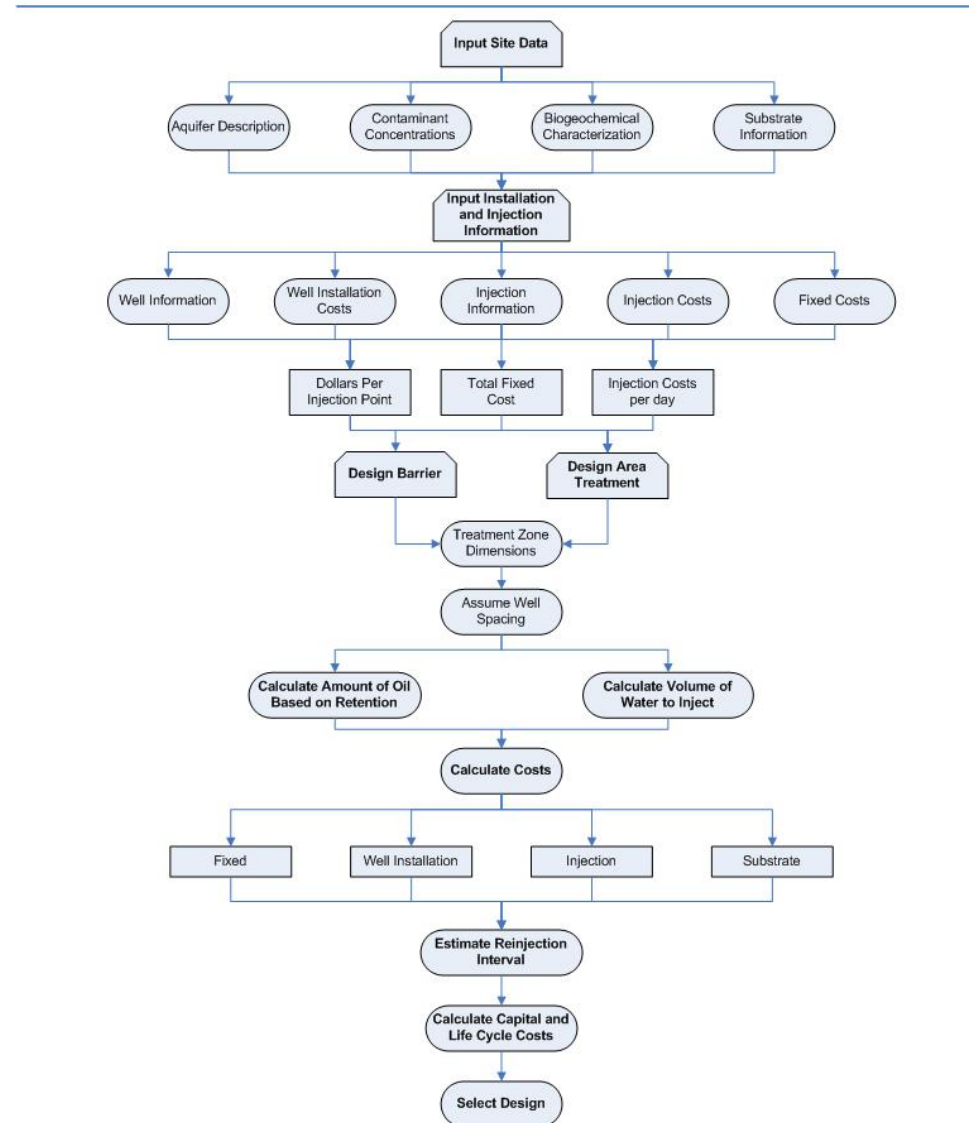
- Treatment zone dimensions
  - Contact time
  - Design life
  - Scaling factors

- Output

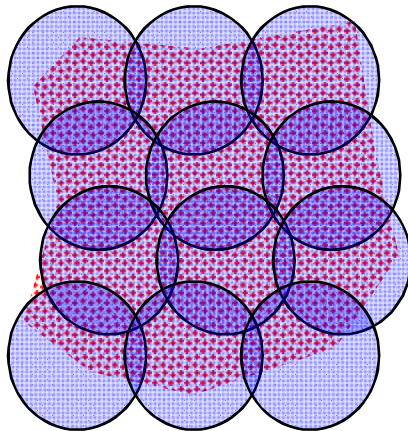
- Contact efficiency
  - Capital costs
  - Life cycle costs

## Emulsified Oil Design Tool

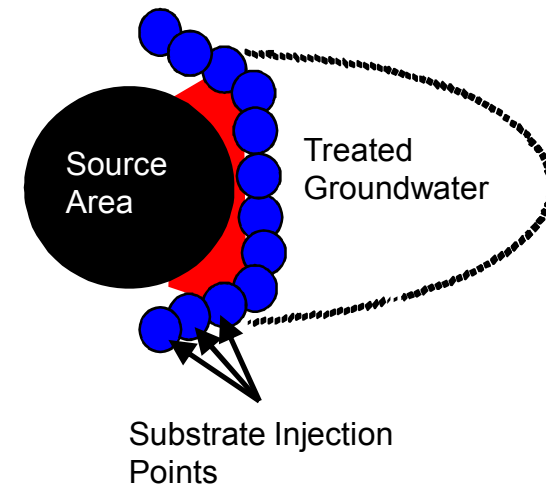
Flowchart



# Injection System Layout



- **Source Area**
  - ◆ Grid of injection wells to 'saturate' source area
  - ◆ Requires
    - More wells
    - More substrate
  - ◆ Can displace contaminants
  - ◆ Treatment most effective in high K zones

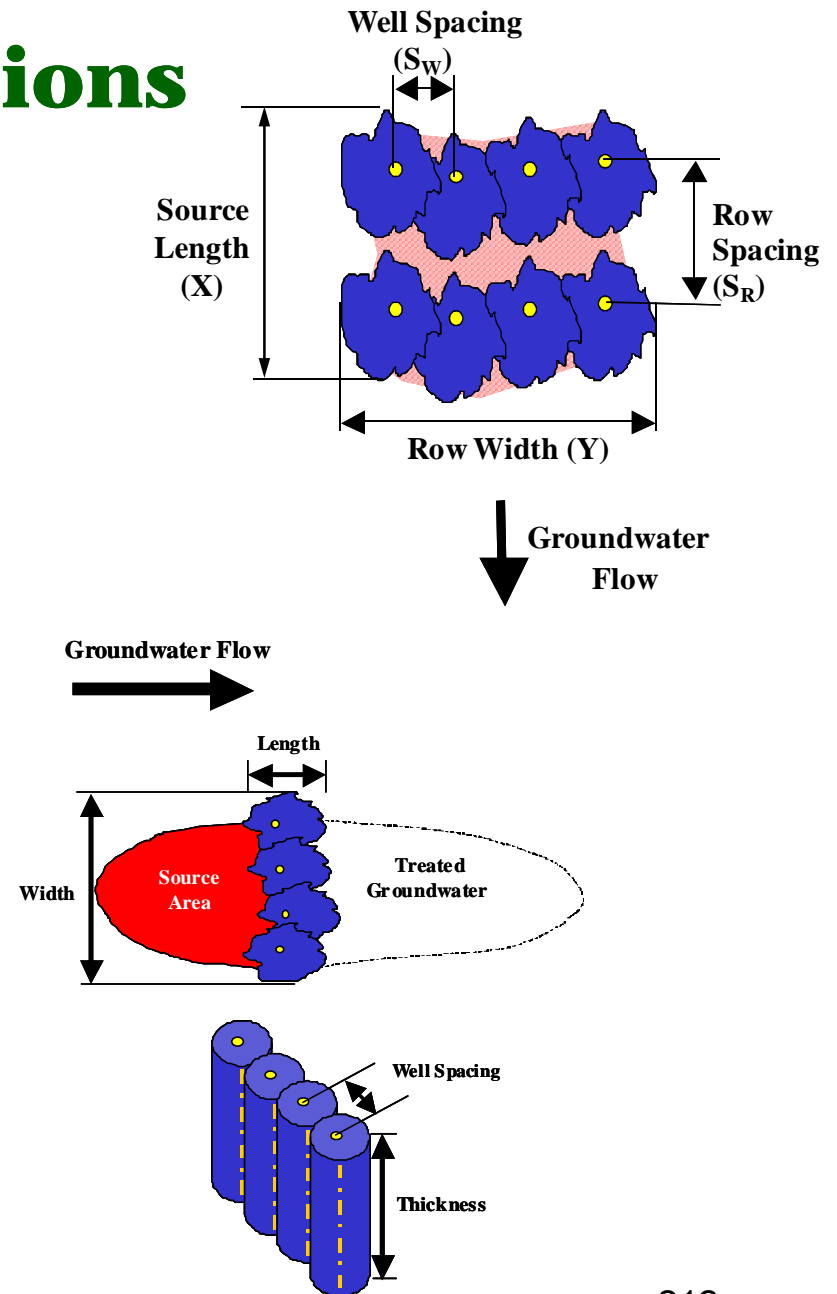


- **Barrier(s)**
  - ◆ Row of injection wells to intercept plume
  - ◆ Lower cost
    - Fewer wells
    - Less substrate
  - ◆ Lower potential for contaminant displacement
  - ◆ Does not eliminate source



# Treatment Zone Dimensions

- Width perpendicular to GW flow (Y)
  - ♦ Source width
  - ♦ Barrier width
- Length parallel to GW flow (X)
  - ♦ Source length
  - ♦ In barriers, provide enough contact time
- Vertical Thickness (Z)
  - ♦ Use effective thickness when visibly different units are present
- Wells arranged in rows perpendicular to flow
  - ♦ Wider spacing between rows to allow for downgradient drift
- $S_W$  = spacing of wells within a row
- $S_R$  = spacing of rows
  - ♦ Design tool has an allowable ratio of  $S_R$  to  $S_W = 1:1$  or  $2:1$
- Design tool will help select optimum  $S_W$





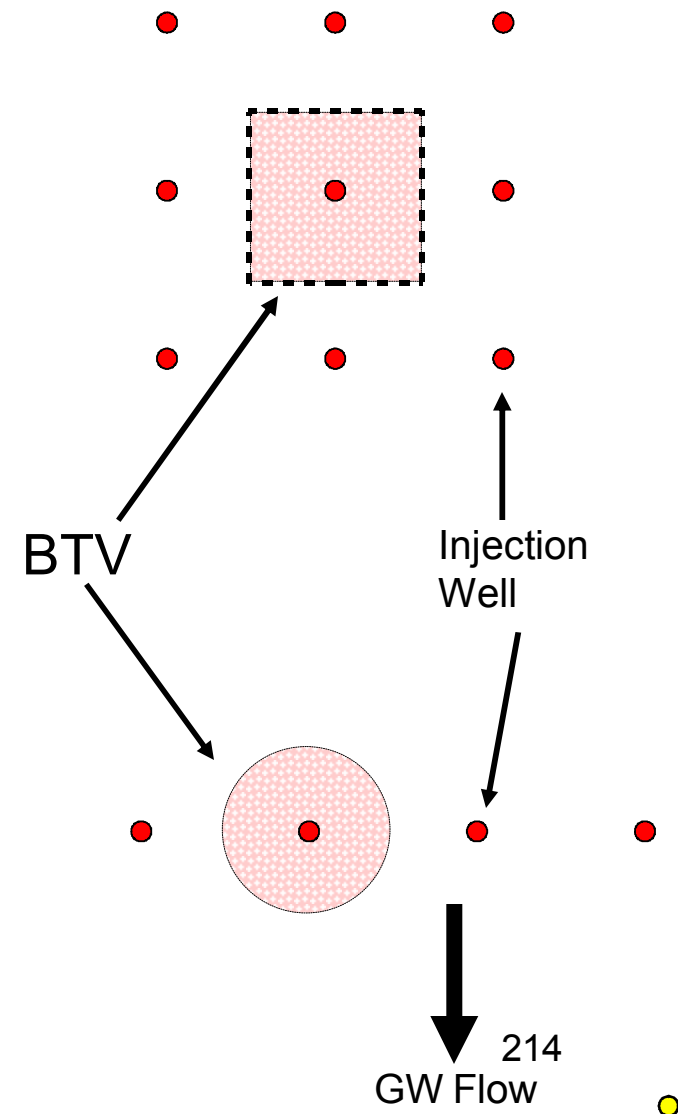
# How to Design an Injection System

- Fluid Volume =  $BTV * n_e * SF_V$   
BTV = Base Treatment Volume  
 $n_e$  = Effective Porosity (dimensionless)  
 $SF_V$  = Volume Scaling Factor (dimensionless)  
 $SF_V$  typically 0.2 to 0.6 for area treatment
- Oil Requirement =  $OR_M * BTV * \rho_B * SF_M$   
 $OR_M$  = Maximum Oil Retention (lb oil / lb soil)  
 $\rho_B$  = Soil Bulk density (lb/ft<sup>3</sup>)  
 $SF_M$  = Mass Scaling Factor (dimensionless)  
 $SF_M$  typically 0.2 to 0.6 for area treatment

# Base Treatment Volume (BTV)



- BTV = 'standard' volume around each well used to scale treatment quantities
- For Area Treatment  
BTV = volume of rectangular prism surrounding each well  
$$\text{BTV} = S_W * S_R * Z$$
- For Barrier Treatment  
BTV = volume of cylinder surrounding each well  
$$\text{BTV} = \frac{1}{4} \pi S_W^2 * Z$$



# Oil Retention (OR) by Sediment

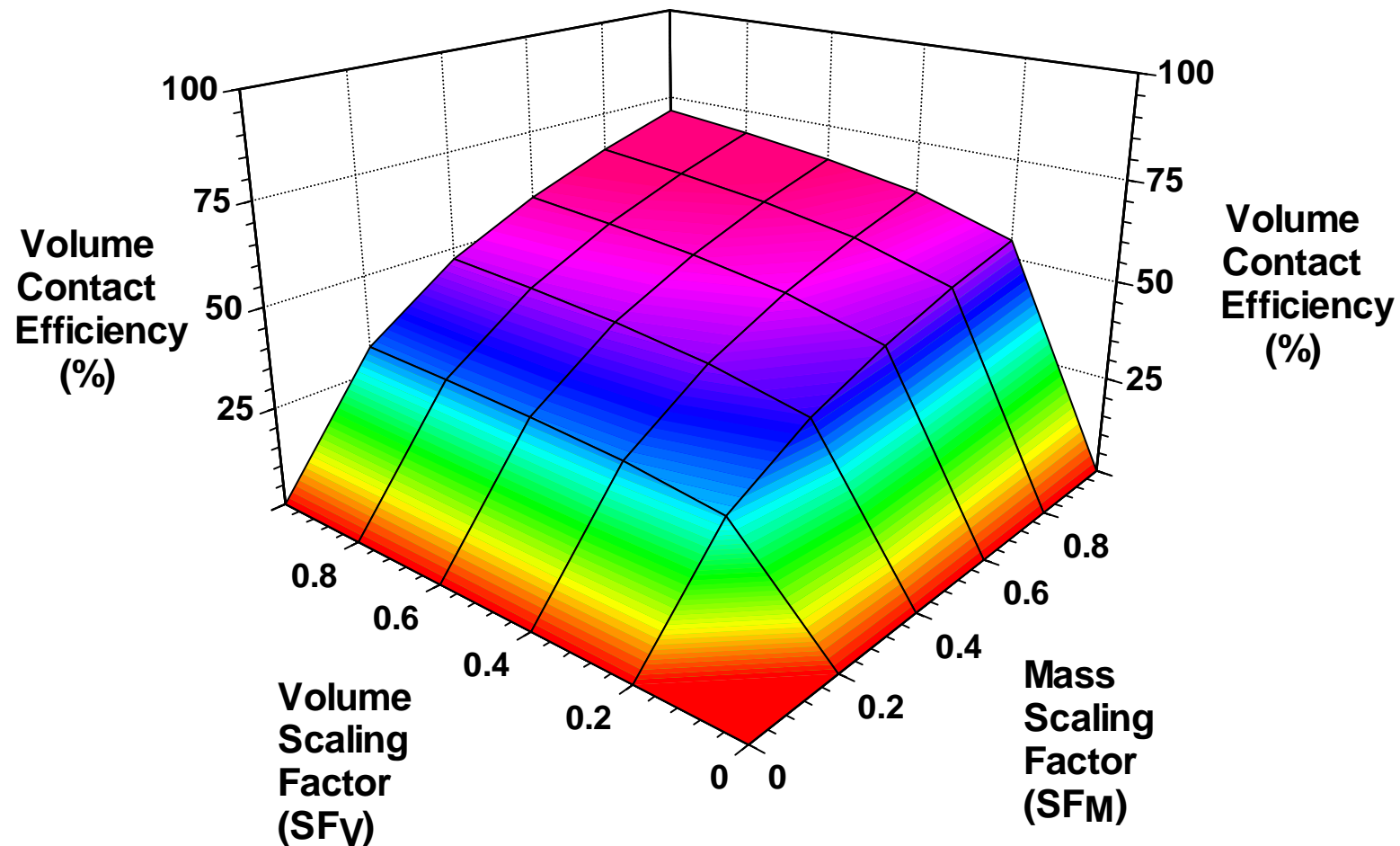
Oil retention is a function of

- ♦ Droplet size
  - Oil droplets should be smaller than sediment pores for easy transport
  - $\sim 1 \mu\text{m}$  easily pass through most pores (30 - 100  $\mu\text{m}$ )
- ♦ 'Capacity' of soil to hold oil droplets
  - Silts and clays have more charged sites  $\rightarrow$  hold more oil
- ♦ Surfactant type
  - Non-ionics typically have lower sorption
  - Ionics have higher sorption (lecithin sorption is very high)
- ♦ Surface charge (zeta potential) of sediments and droplets
  - Most clays have a net negative charge
  - Negatively charged droplets will have lower retention

# Maximum Oil Retention ( $OR_M$ )

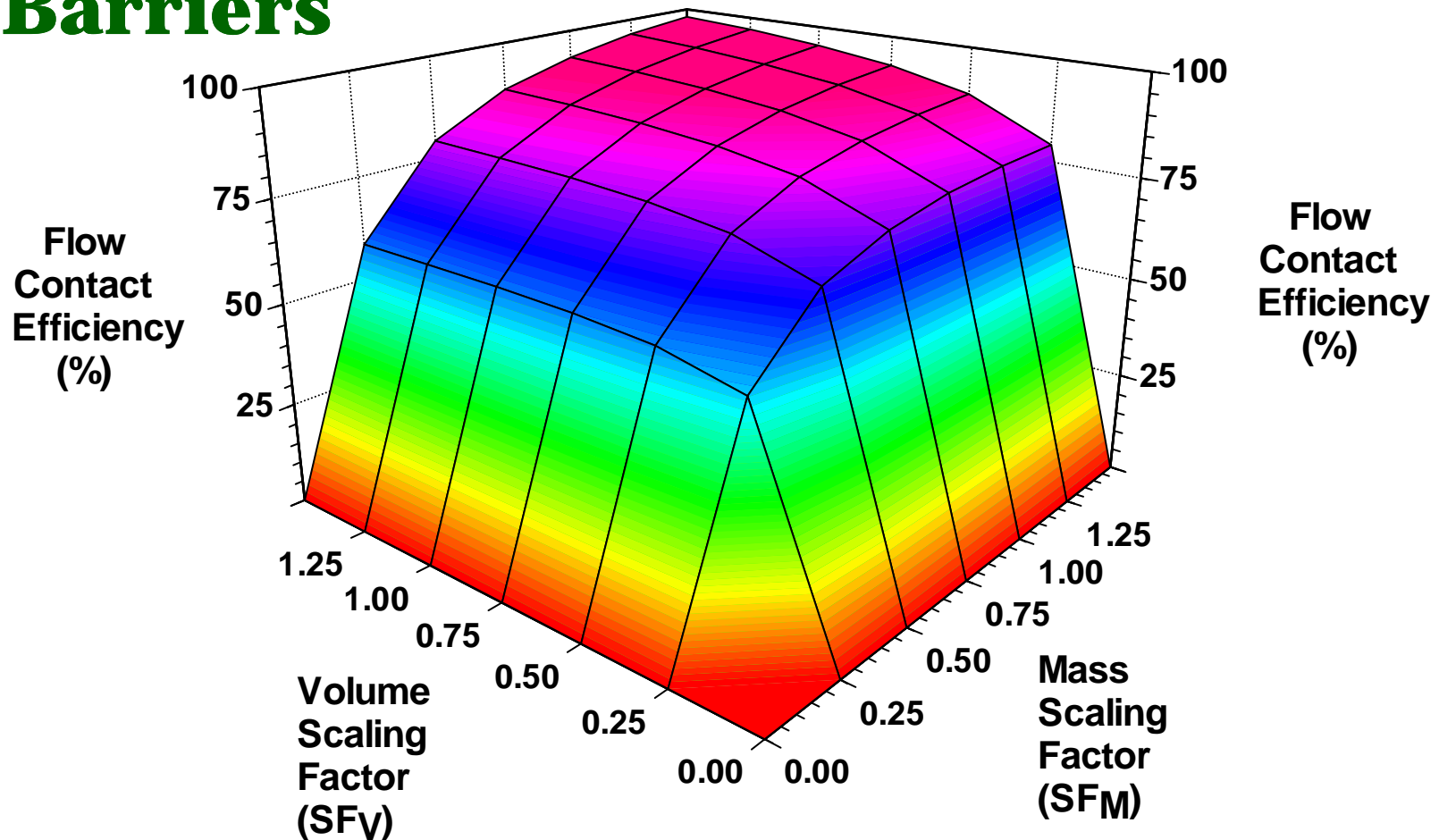
Aquifer Material	Emulsion	Test Condition	Maximum Retention (g/g)
Blended sand (7% Silt+Clay)	Homemade	Column	0.0054
Blended sand (9% Silt+Clay)	Homemade	Column	0.0061
Blended sand (12% Silt+Clay)	Homemade	Column	0.0095
Alluvium (clayey sand)	EOS <sup>®</sup>	Column	0.0037
Low K, weathered rock (sandy clay)	EOS <sup>®</sup>	Field	0.003 (estimated)
High K, gravelly sand	EOS <sup>®</sup>	Field	0.0004 (estimated)

# Volume Contact Efficiency for Area Treatment (Row Spacing = Well Spacing)



Clayton, M. H., and R. C. Borden, Numerical Modeling of Emulsified Oil Distribution in Heterogeneous Aquifers, Ground Water, 47(2): 246–258, 2009.

# Flow Contact Efficiency for Barriers



Clayton, M. H., and R. C. Borden, Numerical Modeling of Emulsified Oil Distribution in Heterogeneous Aquifers, Ground Water, 47(2): 246–258, 2009.



# Barrier Contact Time

- Contact time ( $C_t$ ) between oil and contaminants
  - ♦ Provide 60 – 120 days for satisfactory chlorinated solvent removal
  - ♦ Use longer  $C_t$  for:
    - High sulfate loading
    - 'Unknown' high K layers that could cause short-circuiting through oil treated zone
    - High contaminant concentrations
    - High removal efficiency required
- Barrier length along flow direction (x)  
(length parallel to flow)

$$X = C_t * v$$

$v$  = non-reactive transport velocity

# How to Estimate Oil Reinjection Frequency

- Calculate oil required for biodegradation
  - ♦ Background Electron Acceptors
    - $O_2$ ,  $NO_3$ ,  $SO_4$
  - ♦ Contaminant to be treated
    - TCE,  $ClO_4$ , etc.
  - ♦ Organic carbon released to downgradient aquifer
    - Based on chemical composition of oil and microbiology
    - Typically assume average of 50-100 mg/L over project life for EOS<sup>®</sup>
  - ♦ Reduced compounds produced
    - Dissolved Fe, Mn,  $CH_4$
- Oil Demand (D) is substrate consumed per volume of water that flows through each treatment row

# Treatment Performance in Barriers as Substrate is Consumed

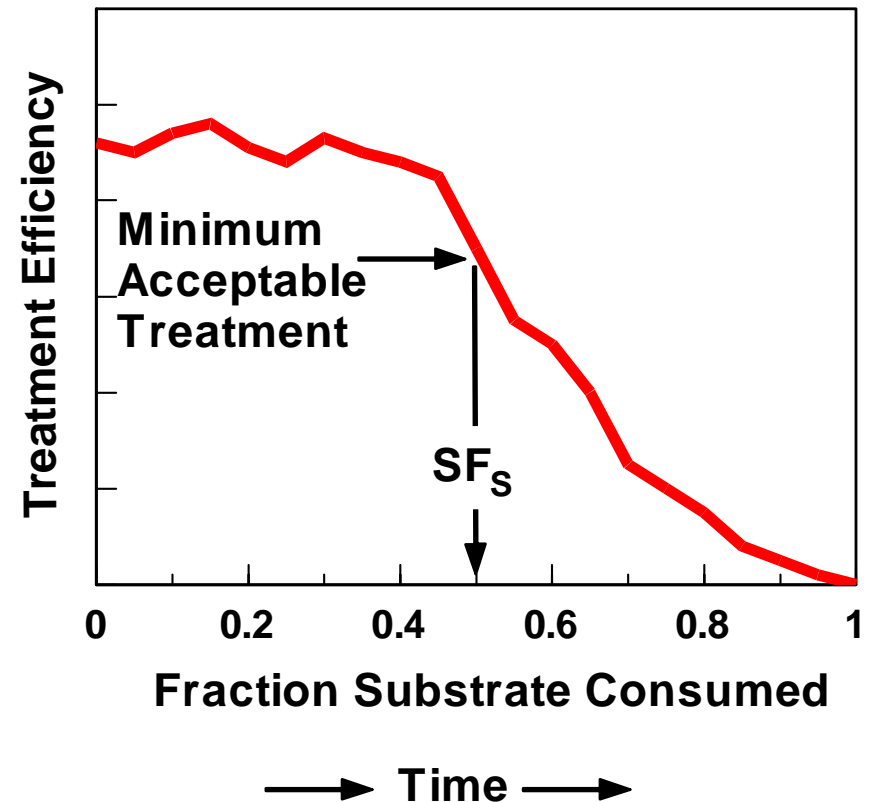


## Treatment efficiency

- ♦ maximum when excess substrate is present
- ♦ will drop as substrate is consumed

## Substrate Scaling Factor ( $SF_S$ )

- ♦  $SF_S$  = fraction of substrate consumed when treatment < acceptable
- ♦  $SF_S \rightarrow$  time to reinject
- ♦  $SF_S$  typically varies from 0.3 to 0.6



# Determine Injection Frequency for Barriers



- Theoretical life of single injection (T)
  - ♦  $T = \text{Oil Injected} / (D * Q)$
  - ♦  $\text{Water Flux (Q)} = Y * Z * K * i$ 
    - Y = Width perpendicular to flow
    - Z = Effective treatment zone thickness
    - K = Hydraulic conductivity
    - i = Hydraulic gradient
  - ♦ D = Oil Demand (mg of oil / L of water)
- Reinjection Interval (RI) =  $T * SF_s$ 
  - ♦ Design tool has maximum allowable period between reinjections that will over-ride calculation

# Design Tool

## Table of Contents

- Four sections
- Click on button to navigate to a page
- Each page has a button to go forward, backward, or back to table of contents
- Reset buttons reset all pages within a section
- Start with Aquifer Description

**Emulsified Oil Design Tool**  
Version 33 - 2/13/2008

This tool is intended to assist engineers with the design of injection only systems for distributing emulsified oils for enhancing the anaerobic bioremediation of groundwater contaminants. More specifically, this tool allows users to evaluate the use of emulsified oils applied in barriers and area treatments. This design tool requires the user to provide all necessary information for site data and information for at least one installation and injection method. The model uses this information to evaluate the costs of various designs using different well spacings. Graphical representations of the effect of well spacing on project costs are generated. Users should have a good understanding of enhanced anaerobic bioremediation using emulsified oils before using this tool.

**Table of Contents**

<i><u>Site Data</u></i>	<i><u>Installation and Injection</u></i>	<i><u>Barrier Treatment</u></i>	<i><u>Area Treatment</u></i>
Aquifer Description	Injection Through Direct Push Rods	Design Information	Design Information
Contaminant Concentrations	DPT Well Installation	Capital Cost Analysis	Capital Cost Analysis
Biogeochemical Characterization	Well Installation by Conventional Drilling	Life Cycle Analysis	Life Cycle Analysis
Substrates and Reagents	Installation and Injection Summary	NPV for Selected Design	NPV for Selected Design
Reset Site Data	Reset Installation and Injection	Summary of Selected Design	Summary of Selected Design
		Reset Barrier Treatment	Reset Area Treatment

# Aquifer Description



- Enter information in the cells outlined in red
- White cells outlined in black are for additional information and do not need to be completed

**Site Data - Aquifer Description**

Information on the physical characteristics of the aquifer is entered on this page. This information will later be used to calculate injection volumes and costs for barrier and area treatments.

**1 Site Information**

a Name			
b Description (e.g., project number)			
c Location			

**2 Hydraulic Characteristics**

a Depth to water table		ft	0.00	m
b Depth to top of injection zone		ft	0.00	m
c Depth to bottom of injection zone		ft	0.00	m
d Hydraulic Gradient		ft/ft	0	m/m
e Hydraulic Conductivity		ft/day	0.00E+00	cm/s
f Estimated Total Porosity				
g Estimated Effective Porosity				
h Seepage Velocity	#DIV/0!	ft/day	#DIV/0!	cm/s
	#DIV/0!	ft/yr	#DIV/0!	m/yr

**3 Soil Characteristics**

a Description of Soil Lithology				
b Bulk Density		lbs/ft <sup>3</sup>	0.0	g/cm <sup>3</sup>
c Maximum Oil Retention by soil (see Table 4.2 in design manual). This value has a critical impact on cost and treatment performance.		lbs oil/lbs soil	0	kg oil/kg soil

Return to Table of Contents      Go Back to Previous Page (Introduction)      Go Forward to Next Page (Contaminant Concentrations)



# Contaminant / Biogeochemical Characterization

- Enter concentrations for contaminants and background electron acceptors
- Additional contaminants can be included by specifying the concentration, molecular weight, and the electron equivalents per mole

**Data - Contaminant Concentrations**

Information on the concentration of common contaminants are entered on this page. This information is used to calculate the number of electron equivalents (e- equiv) required to biodegrade these contaminants. Several of the more common contaminants are listed below along with their molecular weight (MW) and e- equiv/mole. Blank cells in rows m, n, and o allow the user to enter information on additional contaminants. For these additional contaminants, the user must enter the contaminant concentration, MW and e- equiv/mole.

	ug/L	MW (g/mole)	e- equiv/ mole	e- equiv demand (e- equiv/L)
a Tetrachloroethene (PCE), C <sub>2</sub> Cl <sub>4</sub>		155.8	8	
b Trichloroethene (TCE), C <sub>2</sub> HCl <sub>3</sub>		131.4	6	
c cis-1,2-dichloroethene (c DCE), C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>		96.9	4	
d Vinyl Chloride (VC), C <sub>2</sub> H <sub>3</sub> Cl		62.5	2	
e Carbon tetrachloride, CCl <sub>4</sub>		153.8	8	
f Chloroform, CHCl <sub>3</sub>		119.4	6	
g sym-tetrachloroethane, C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>		167.8	8	
h 1,1,1-Trichloroethane (TCA), CH <sub>3</sub> CCl <sub>3</sub>		133.4	6	
i 1,1-Dichloroethane (DCA), CH <sub>3</sub> CHCl <sub>2</sub>		99.0	4	
j Chloroethane, C <sub>2</sub> H <sub>5</sub> Cl		64.9	2	
k Perchlorate, ClO <sub>4</sub> <sup>-</sup>		99.4	8	
l Hexavalent Chromium, Cr(VI)		52.0	3	
m				
n				
o				
p e- equiv demand from contaminant concentrations	0.00E+00 e- equiv/L			

**Data - Biogeochemical Characterization**

Information on the concentration of background electron acceptors is entered on this page. This information is used to calculate the number of electron equivalents (e- equiv) required to deplete these materials. The total e- equivalent is then calculated from the contaminant demand and the background electron acceptor demand. This value is later used to calculate the annual substrate demand.

	mg/L or mg/Kg	MW (g/mole)	e- equiv/ mole	e- equiv demand (e- equiv/L)
a Background Dissolved Oxygen (mg/L)		32.0	4	
b Background Nitrate (mg/L as N)		14.0	5	
c Background Sulfate (mg/L)		96.1	8	
d Estimated methane produced (mg/L)		16.0	8	
e Soil Manganese Content (mg/Kg) (not used in calculation)				
f Estimated Mn <sup>2+</sup> produced (mg/L)		54.9	2	
g Soil Iron Content (mg/Kg) (not used in calculation)				
h Estimated Fe <sup>2+</sup> produced (mg/L)		55.8	1	
i pH (not used in calculation)				
j Alkalinity (mg/L) (not used in calculation)				
k e- equiv demand from biogeochemical characterization	0.00E+00 e- equiv/L			
				<b>Total e- equiv demand (e- equiv/L)</b> 0.00E+00

# Well Installation Method

- Approach assumes temporary or permanent wells are installed using direct push equipment
- Multiple wells are manifolded together for emulsion injection
- Select the method on the Installation and Injection Summary page

## Summary of Installation and Injection Costs

This page provides a summary of the total fixed cost, dollars per injection point and dollars per gallon of fluid injected for the three different injection approaches. Click on the radio button to select the injection approach to be used in design and costing. Users can return to this page to evaluate alternative injection approaches.

### 1 Injection through Direct Push Rods

a	Total fixed cost	1,475 \$
b	Dollars per injection point	371 \$/boring

☐ Select this method

c	Injection rate to be used in Design	4.0 gpm/well
d	Injection costs per day	2,885 \$/day

### 2 Well Installation by Direct Push followed by Emulsion Injection

a	Total fixed cost	8,000 \$
b	Dollars per injection point	1,157 \$/well

☒ Select this method

c	Injection rate to be used in Design	1.5 gpm/well
d	Injection costs per day	2,600 \$/day

### 3 Well Installation by Conventional Drilling followed by Emulsion Injection

a	Total fixed cost	8,500 \$
b	Dollars per injection point	1,350 \$/well

☐ Select this method

c	Injection rate to be used in Design	3.0 gpm/well
d	Injection costs per day	2,850 \$/day

[Return to Table of Contents](#)

[Go Back to Previous Page  
\(Well Installation by  
Conventional Drilling\)](#)

[Go Forward to Design a Barrier  
Treatment](#)

[Go Forward to Design an Area  
Treatment](#)

Results of the analysis are broken into:

- ♦ Total fixed cost
- ♦ Dollars per injection point
- ♦ Injection rate
- ♦ Injection costs per day

# Barrier Design Information

- User enters information on:
  - ♦ Treatment zone dimensions
  - ♦ Treatment zone contact time
  - ♦ Targeted carbon released
  - ♦ Design life
  - ♦ Mass, volume and substrate scaling factors
- Model calculates expected contact efficiency

## Single Permeable Reactive Barrier - Design Information

Design criteria for installation of a single permeable reactive barrier is entered on this page. This criteria is later used to determine material quantities and estimate costs for a variety of design alternatives.

### 1 Treatment Zone Dimensions

a	Width (perpendicular to groundwater flow)	<input type="text"/>	ft	0.00	m
b	Effective Treatment Zone Thickness	<input type="text"/>	ft	0.00	m
i.	Top of Treatment Zone	<input type="text"/>	ft	0.00	m
ii.	Bottom of Treatment Zone	<input type="text"/>	ft	0.00	m
c	Seepage Velocity	<input type="text"/>	#DIV/0! ft/day	#DIV/0!	cm/s
d	Groundwater Flux through Treatment Zone	<input type="text"/>	#DIV/0! gal/yr	#DIV/0!	L/yr

### 2 Treatment Zone Contact Time

A minimum contact time of 2 to 4 months is typically required for effective treatment of chlorinated solvents in emulsified oil barriers. Longer contact times may be needed for difficult to degrade contaminants, with higher contaminant concentrations, and/or high concentrations of competing electron acceptors. Shorter contact times may be acceptable for easily treated contaminants (e.g. nitrate or perchlorate) or when only partial treatment is required.

a	Minimum Allowable Contact time	<input type="text"/>	days		
b	Minimum Allowable Contact length	<input type="text"/>	ft	0.00	m
c	Minimum length to be used in design	<input type="text"/>	#DIV/0! ft	#DIV/0!	m

### 3 Targeted Carbon Released

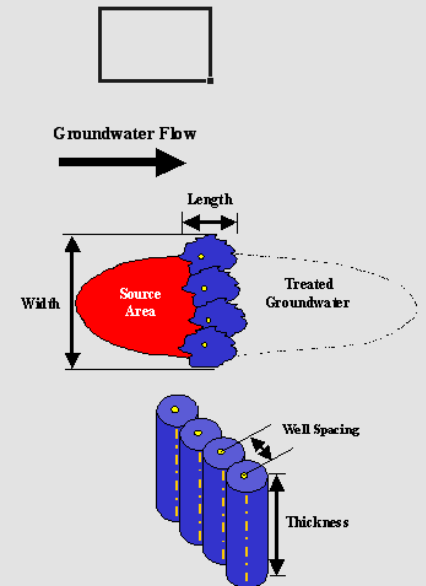
Emulsified oil barriers release dissolved organic carbon (DOC) over the life of the barrier. This DOC released is in excess of that required for contaminant biodegradation and consumption of competing electron acceptors. Field monitoring data indicates that DOC released from barriers declines from hundreds mg/L shortly after emulsion injection to tens of mg/L near the end of the operating life. Long-term average DOC concentrations are typically in the range of 40 - 100 mg/L.

a	Average Amount of DOC Released	<input type="text"/>	mg/L		
b	DOC Released per year	<input type="text"/>	#DIV/0! lb	#DIV/0!	kg

### 4 Design Life

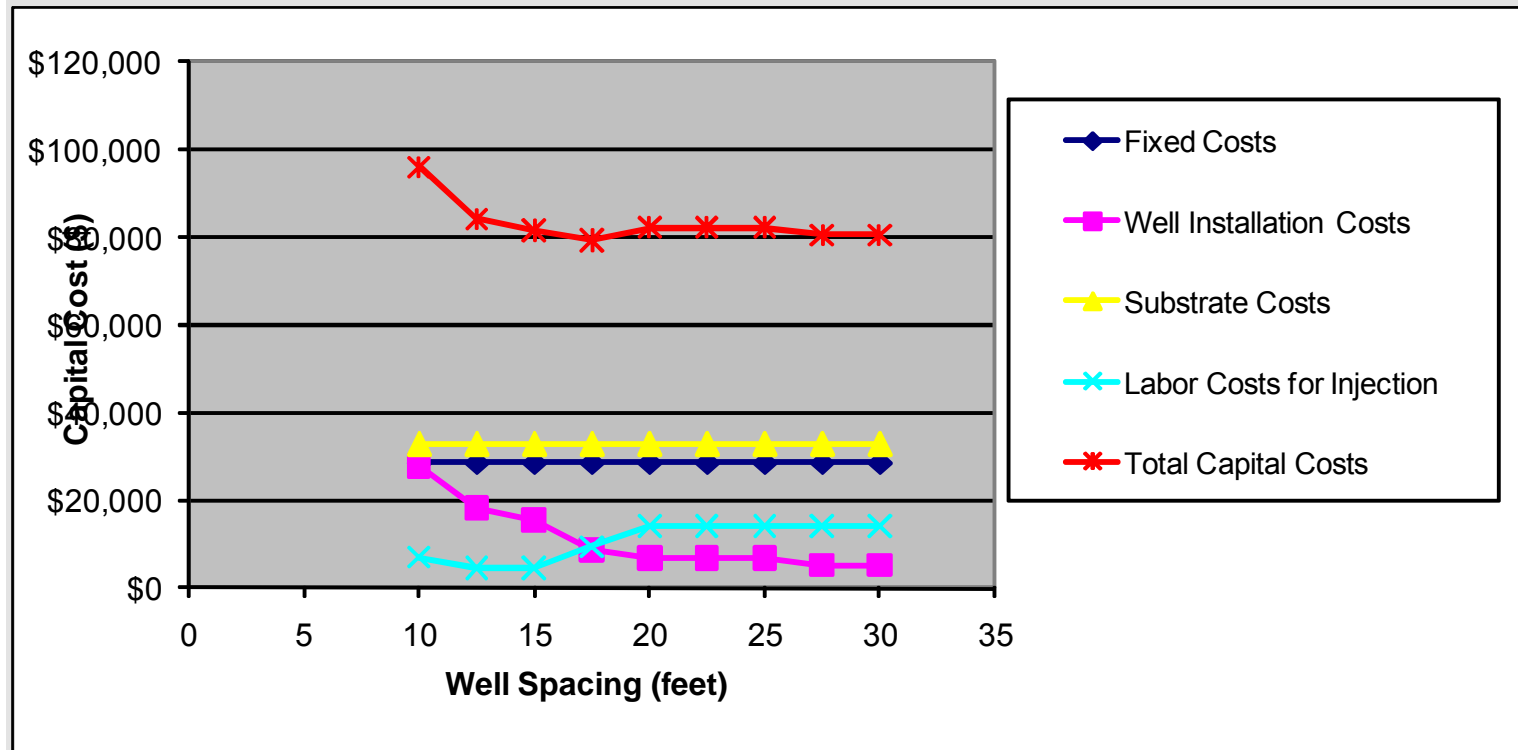
The design tool estimates reinjection frequency based on amount of substrate injected, the annual substrate consumption rate, and fraction of initial substrate consumed when treatment performance declines. However, users may specify a maximum time between reinjections. The design tool will then use the smaller of these two values. Life cycle costs are calculated based on the reinjection frequency and other ongoing costs (monitoring, etc.)

a	Total Project Life (Max of 30 years)	<input type="text"/>	years		
b	Substrate Scaling Factor (typically 0.3 to 0.6)	<input type="text"/>			
c	Maximum Time between Reinjections	<input type="text"/>	years		



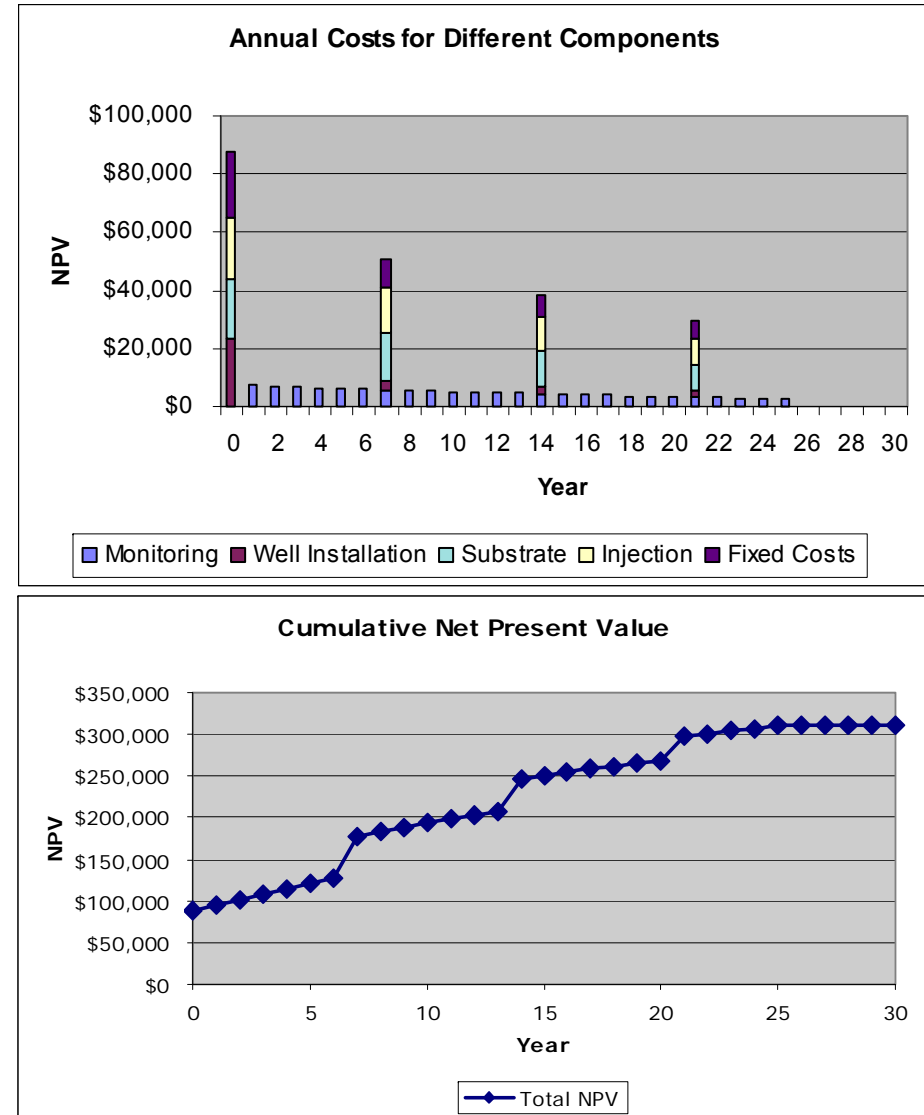
# Capital Cost Analysis

- Enter minimum well spacing and incremental increase
- Enter planning and engineering costs
- Look at capital cost vs well spacing



# Life Cycle Cost Analysis

- Enter information on:
  - Annual interest rate
  - Engineering costs for each future event
  - Well replacement / rehabilitation for future injections
  - Annual monitoring and reporting costs
  - Results are presented as lifetime Net Present Value (NPV) vs well spacing
  - Select a design (15 ft) to see additional information



# Print Out Design Summary

## Area Treatment Using a Series of Barriers - Selected Design

This sheet shows a summary of the selected design that can be saved or printed before looking at alternative designs.

### 1 Site Information

a	Name	Example Site
b	Description (e.g., project number)	AFB
c	Location	Florida
d	Maximum Oil Retention	0.009 lbs oil/lbs soil

### 2 Treatment Design Criteria

a	Reinjection Interval	4 years
b	Timeframe in which all groundwater in targeted area should theoretically flush through active treatment zones.	8 years

### 3 Well Layout

a	Well Spacing	13 ft	3.81 m
b	Number of Wells per Row	3 wells/row	
c	Row Spacing	12.5 ft	3.81 m
d	Number of Rows	7 rows	
e	Total Number of Wells	21 wells	

### 4 Logistics for Each Injection Event

a	Total Mass of Oil Injected	5,891 lbs	2,672 kg
b	Total Injection Volume	9,425 gallons	35,679 L
c	Total Injection Volume per well	449 gal/well	1,699 L/well
d	Estimated Injection Rate	1.0 gpm/well	
e	Number of wells injected simultaneously	10 wells	

### 5 Costs for Initial Installation and Injection

a	Fixed Costs (planning and installation)	\$28,570
b	Well Installation Costs	\$18,200
c	Injection Costs	\$7,050
d	Substrate Costs	\$32,725
e	Total Installation and Injection Costs	\$86,545

### 6 Costs for Future Injection Events

a	Fixed Costs (engineering and installation)	\$13,570
b	Well Rehabilitation and/or Installation Costs	\$4,550
c	Labor Cost for Injection	\$7,050
d	Substrate Costs	\$32,725
e	Total Installation and Injection Costs	\$57,895

### 7 Total Life Cycle Costs

a	Annual Interest Rate	5%
b	Monitoring and Reporting	\$64,632
c	Total Injection Costs (fixed, well installation, labor for injection, and substrate)	\$173,361
d	Project Life NPV	\$237,993

### 8 Design Parameters

a	Volume Scaling Factor	0.5
b	Mass Scaling Factor	0.5
c	Estimated Contact Efficiency for Injection	40%

to 54%



# Additional Resources

- Software Download
  - ◆ <http://docs.serdp-estcp.org/> (search for Design Tool )
  - ◆ [http://www4.ncsu.edu/~rcborden/Design\\_Tool.html](http://www4.ncsu.edu/~rcborden/Design_Tool.html)
- Manual
  - ◆ Emulsified Oil Design Tool USERS MANUAL
  - ◆ Tutorial included in Manual Appendix
- Websites
  - ◆ SERDP/ESTCP ([www.serdp-estcp.org](http://www.serdp-estcp.org))
    - A Treatability Test for Evaluating the Potential Applicability of the Reductive Anaerobic Biological In Situ Treatment Technology to Remediate Chloroethenes”
    - “Protocol for Enhanced In Situ Bioremediation Using Emulsified Edible Oil”
  - ◆ AFCEE (<http://www.afcee.brooks.af.mil/products/techtrans/>)
    - “Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents”
    - “Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil”

# Short Course Agenda



SERDP



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:20 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

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# Planning and Design of Permanganate Injection Systems



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([rcborden@eos.ncsu.edu](mailto:rcborden@eos.ncsu.edu))

**M. Tony Lieberman**



**Ki Young Cha**

**NC STATE UNIVERSITY**

**Thomas Simpkin**



# Acknowledgements



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  - North Carolina State University
    - Robert Borden
    - Ki Young Cha
  - Solutions-IES
    - M. Tony Lieberman
  - CH2M Hill
    - Tom Simpkin
- Financial and technical support from ESTCP
- NCSU is not sponsoring or endorsing this presentation



# ISCO using $\text{MnO}_4$

DoD EPA SERDP  
 $\text{NaMnO}_4$  feed system.



- Target Contaminants
  - ♦ Chlorinated Ethenes (PCE, TCE, DCE, VC)
  - ♦ RDX, HMX, TNT
- Not Effective for
  - ♦ Chlorinated ethanes (e.g., 1,1,1-TCA)
  - ♦ Carbon tetrachloride
  - ♦ Benzene, MTBE
- Injection Procedure
  - ♦ Install injection points
  - ♦ Prepare  $\text{MnO}_4$  solution
  - ♦ Inject water to distribute  $\text{MnO}_4$  solution throughout treatment zone
- $\text{MnO}_4$  is consumed by
  - ♦ Natural Oxidant Demand (NOD)
  - ♦ Target contaminant



automatic  $\text{KMnO}_4$  feed system





# What is the Secret to making ISCO Work?

**“Success is achieved by  
having enough oxidant in contact with the  
contaminant for a long enough period of  
time to react effectively”**

*ISCO Technology Practices Workshop  
Colorado School of Mines, March 2007*

- Design Tool Performance Criteria
  - ◆ Reagent distributed throughout target zone
  - ◆  $\text{MnO}_4$  concentration > \_\_\_\_\_ mg/L after \_\_\_\_\_ days
    - Target  $\text{MnO}_4$  Concentration ~ 100 to 1000 mg/L
    - Target contact time ~ 10 to 100 days

# Permanganate Design Tool Development



- Develop reaction kinetics to simulate  $\text{MnO}_4$  consumption by NOD
- Implement model as:
  - ♦ RT3D
  - ♦ simple spreadsheet model (CDISCO)
- RT3D sensitivity analysis
  - ♦ 3-D heterogeneous aquifer
  - ♦ Range of injection volumes,  $\text{MnO}_4$  loading and model parameters
- Use RT3D results to 'calibrate' CDISCO spreadsheet model

# Modeling Approach

- Standard Advection – Dispersion Equations for Contaminant (C) and  $\text{MnO}_4$  (M) transport

$$\frac{1}{R} \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) - F(C, M)$$

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial M}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i M) - F(C, M, N_I, N_S)$$

- Reaction Kinetics

- Instantaneous reaction between C and M
- Instantaneous reaction between M and  $\text{NOD}_I$
- 2<sup>nd</sup> Order reaction between M and  $\text{NOD}_S$  ( $N_S$ )

$$\frac{dM}{dt} = -K_S M N_S \rho_B / n$$

- Equations coded into
  - RT3D reaction module
  - Spreadsheet as series of CSTRs
- Model assumes No NAPL present

# RT3D Simulations



Simulate small part of  
large injection grid

3-D Heterogeneous K distribution

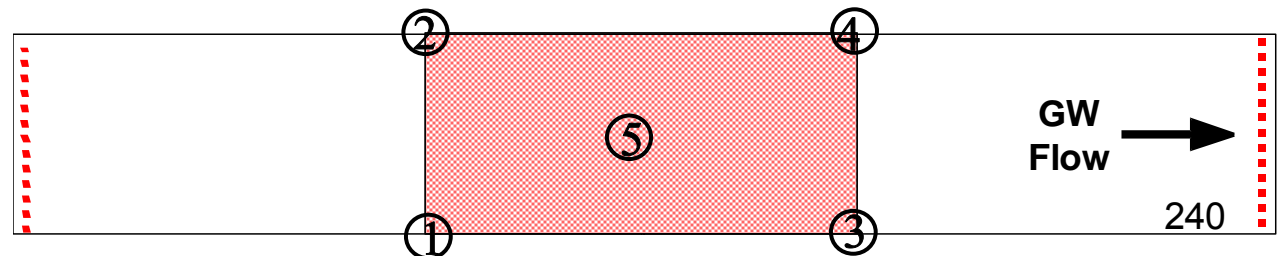
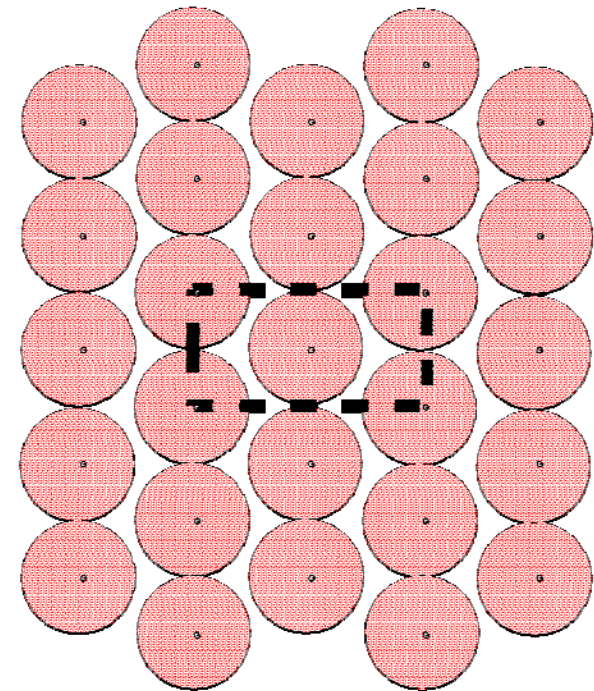
- ♦ Low, medium and high heterogeneity

Vary

- ♦ Mass of  $\text{MnO}_4$  injected
- ♦ Volume of water injected
- ♦ Well spacing
- ♦ Injection sequence
- ♦ NOD kinetic parameters

Examine contact efficiency in  
target zone

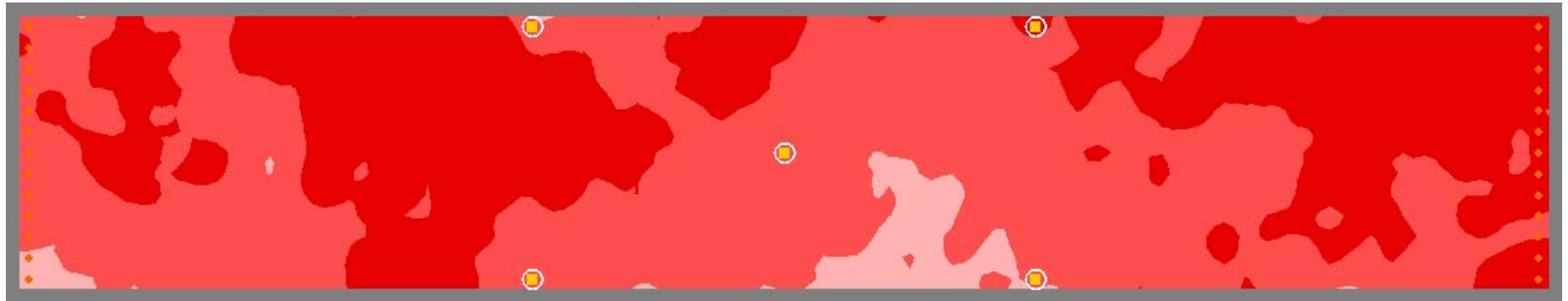
GW Flow →



# Typical Simulation Results for Stochastic Permeability Distribution - 'Medium Heterogeneity'



Permeability Distribution - Plan View



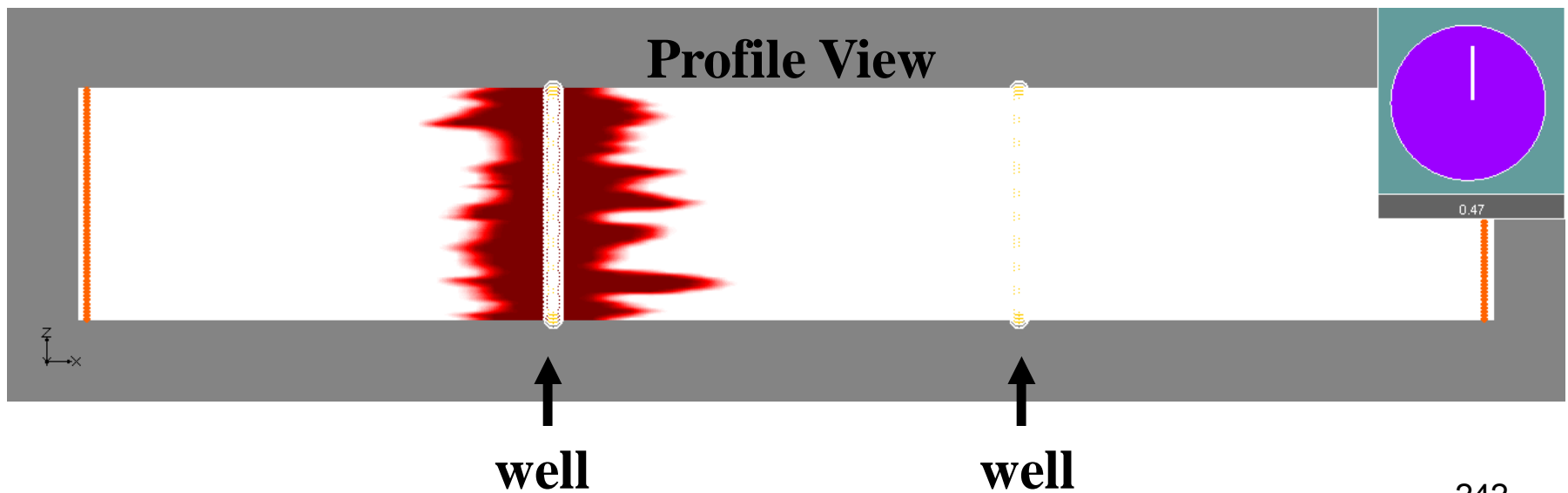
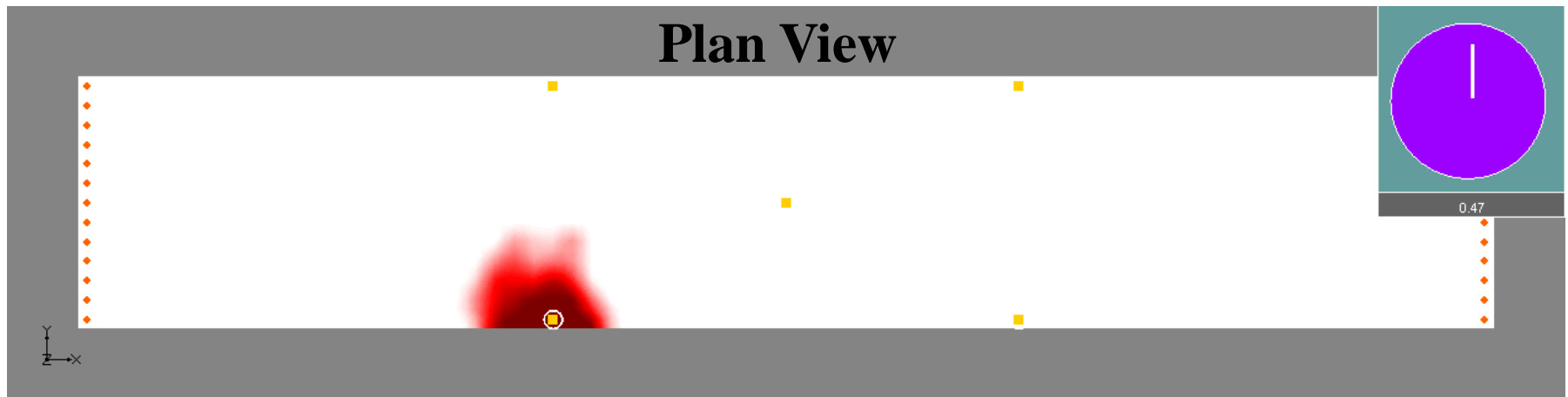
Permeability Distribution - Profile View



↑  
well

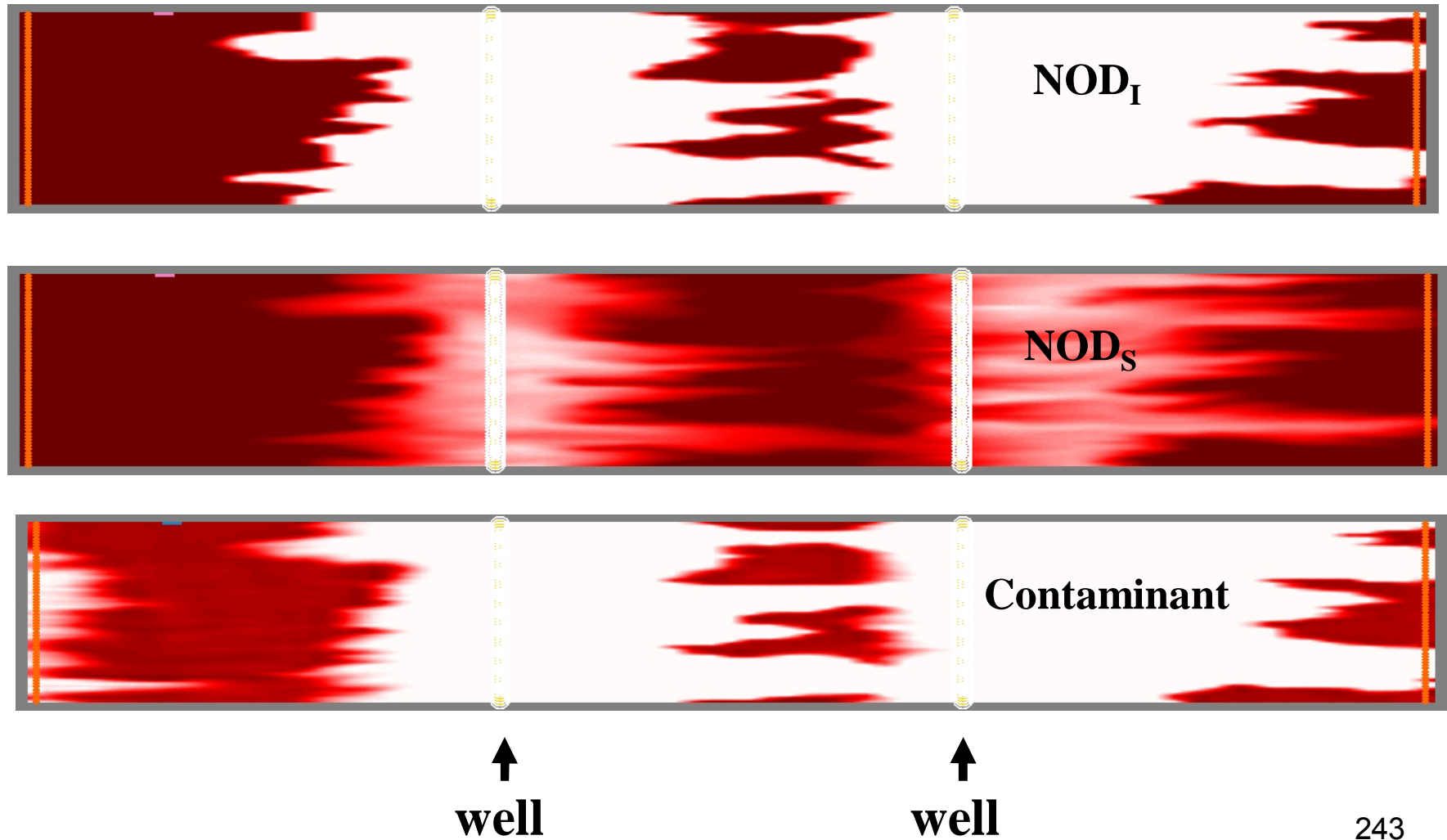
↑  
well

# Simulated $\text{MnO}_4^-$ Distribution



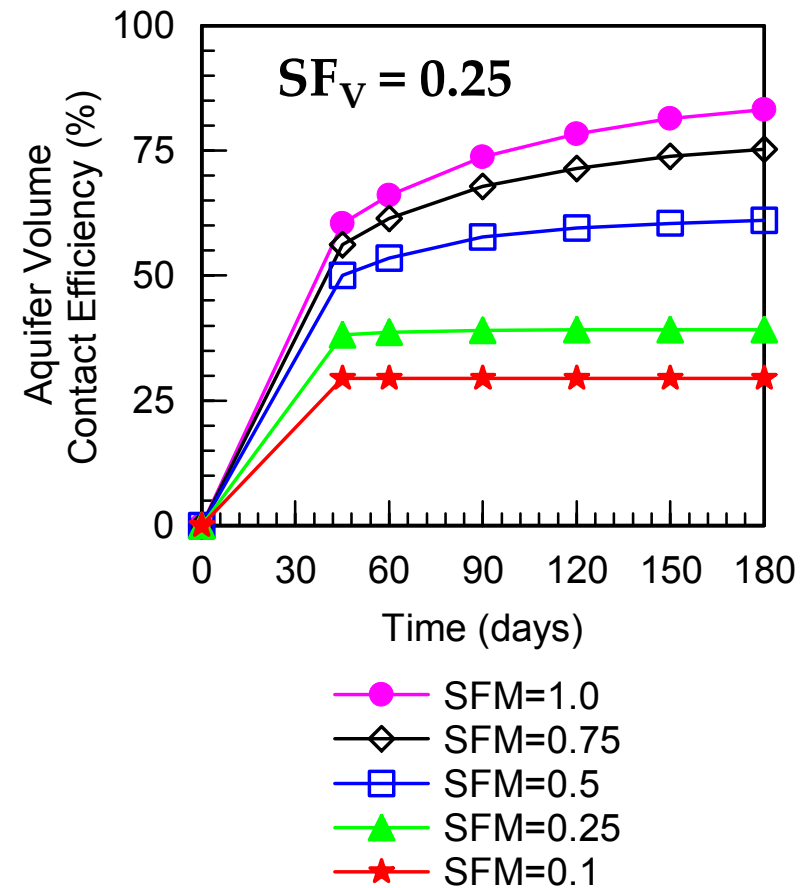


# Simulation Results – Profile View – 180 Days after Injection



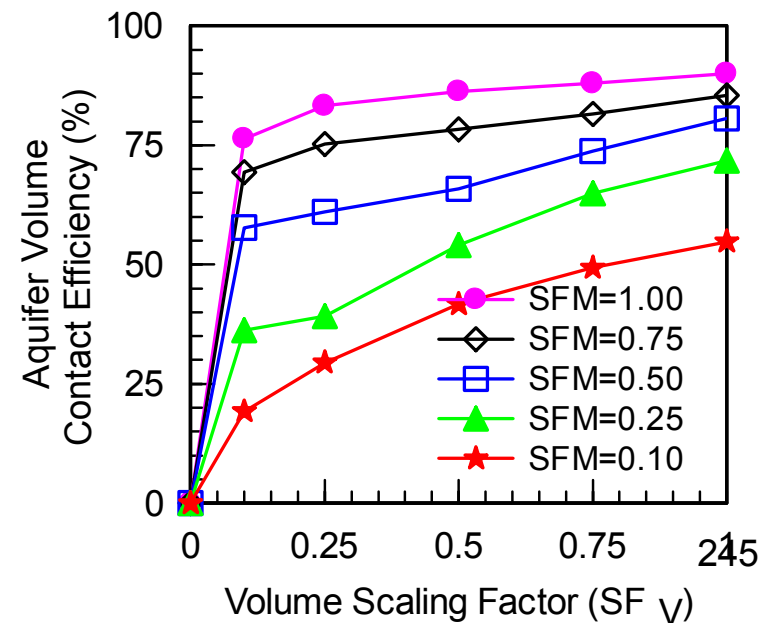
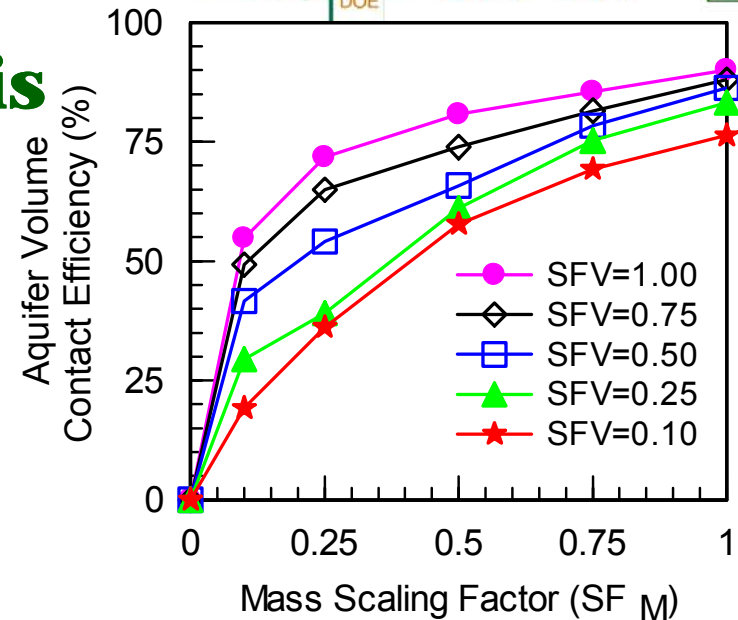
# RT3D Sensitivity Analysis

- Design Parameters
  - ◆ Mass scaling factor ( $SF_M$ )  
 $SF_M = \text{MnO}_4 \text{ applied} / \text{ultimate demand}$
  - ◆ Volume scaling factor ( $SF_V$ )  
 $SF_V = \text{Volume water} / \text{pore volume}$
- Performance Measure
  - ◆ Aquifer Volume Contact Efficiency ( $E_V$ )
- Results
  - ◆  $E_V$  increase with time for large  $SF_M$ 
    - Downgradient drift of  $\text{MnO}_4$
    - Diffusion into low K zones
  - ◆  $E_V$  at 180 days will be used as primary performance measure



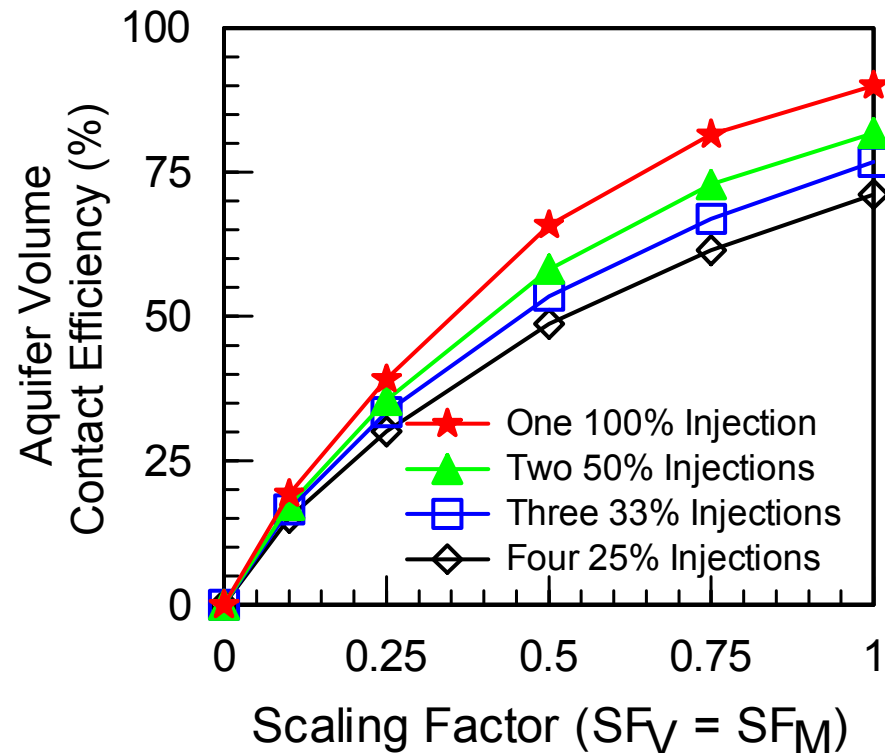
# RT3D Sensitivity Analysis

- Effect of  $\text{MnO}_4$  Mass Injected
  - Increasing  $\text{SF}_M$  (more  $\text{MnO}_4$ ) increases contact efficiency
  - Caution: too much  $\text{MnO}_4$  can cause downgradient release of  $\text{MnO}_4$
- Effect Water Injection Volume
  - Increasing  $\text{SF}_M$  (more  $\text{MnO}_4$ ) increases contact efficiency
  - For  $\text{SF}_M > 0.5$ , large injection volumes have less benefit



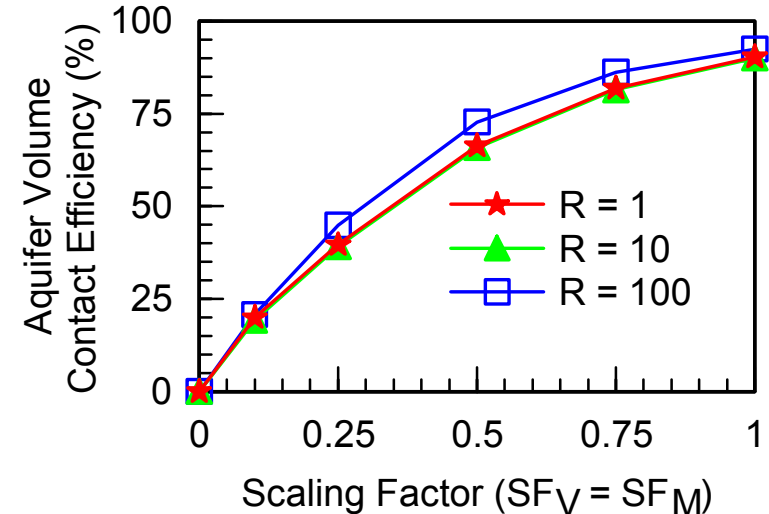
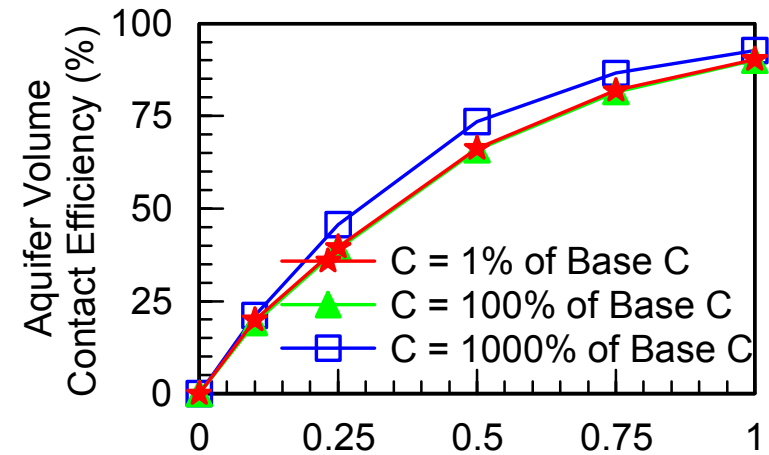
# RT3D Sensitivity Analysis

- Evaluate Impact of Multiple Injections
  - ♦ Total volume constant
  - ♦ Total  $\text{MnO}_4$  constant
- Results
  - ♦ One large injection slightly more effective than four small injections
  - ♦ Four small injections much more effective than one small injection
  - ♦ Multiple injections has lower risk of downgradient migration



# RT3D Sensitivity Analysis

- Initial Contaminant Concentration
  - Minimal effect on  $E_v$
  - Assumes you provide enough  $MnO_4$
  - No NAPL in model
- Contaminant Retardation Factor
  - Minimal effect on  $E_v$
  - Assumes you provide enough  $MnO_4$



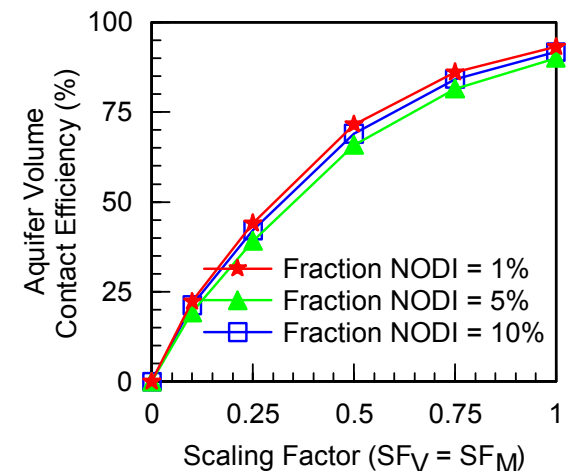
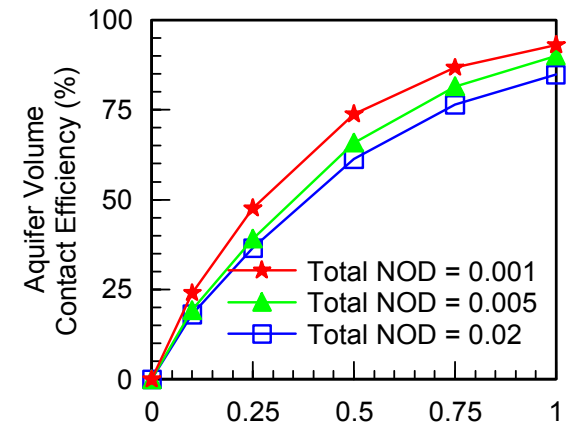
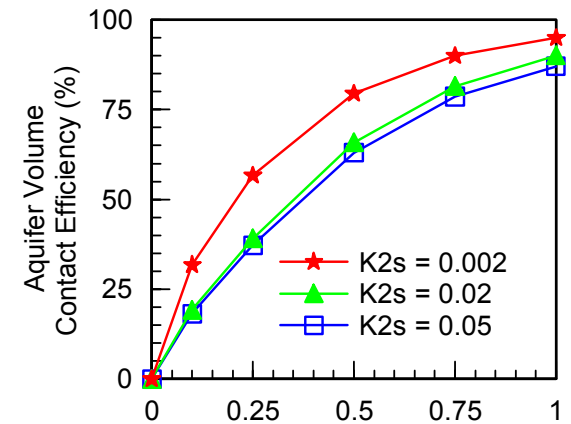
# RT3D Sensitivity Analysis

- NOD Kinetics

- ◆ Slow NOD rate
  - ◆ Total NOD
  - ◆ Fraction  $\text{NOD}_I$

- Results

- ◆ Contact efficiency sensitive to both Total NOD and NOD kinetics
  - ◆ Cannot use simple design curves to estimate contact efficiency
  - ◆ Need 'simple' spreadsheet model for design

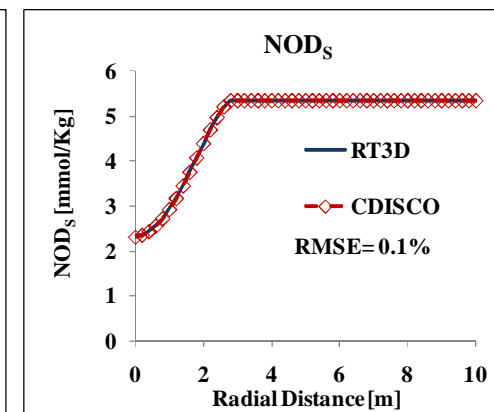
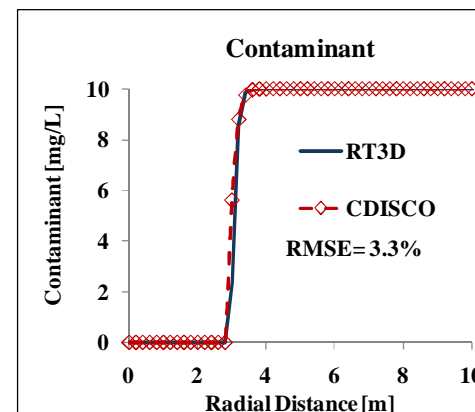
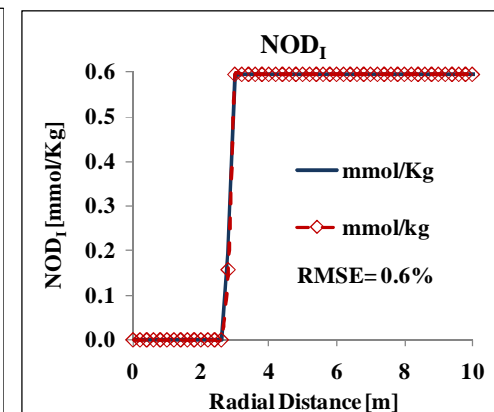
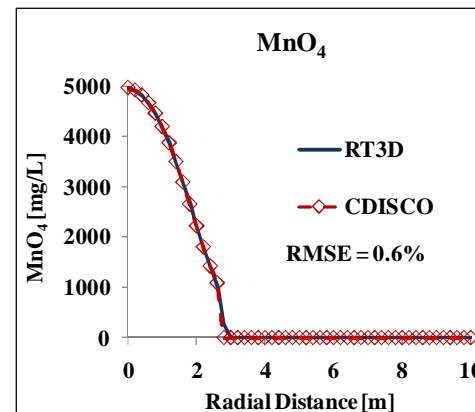




# Spreadsheet Design Tool



- CDISCO –  
Conceptual Design of ISCO
  - ♦ MS Excel based Numerical Model
  - ♦ Developed jointly with ER-0623
- Mechanics
  - ♦  $\text{MnO}_4$  transport and consumption
  - ♦ Based on series of CSTRs
  - ♦ NOD kinetics identical to RT3D
  - ♦ Includes cost estimating tool to aid in comparing alternatives
- Model Validation
  - ♦ Results 'identical' to full RT3D for homogeneous aquifers

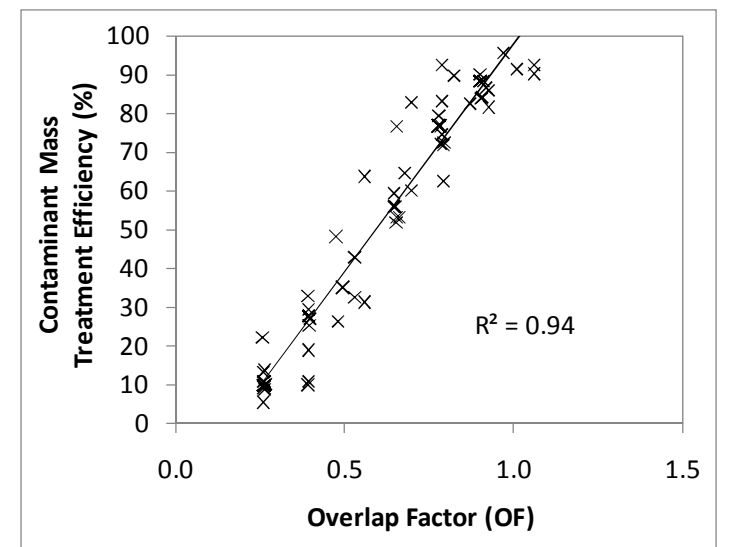
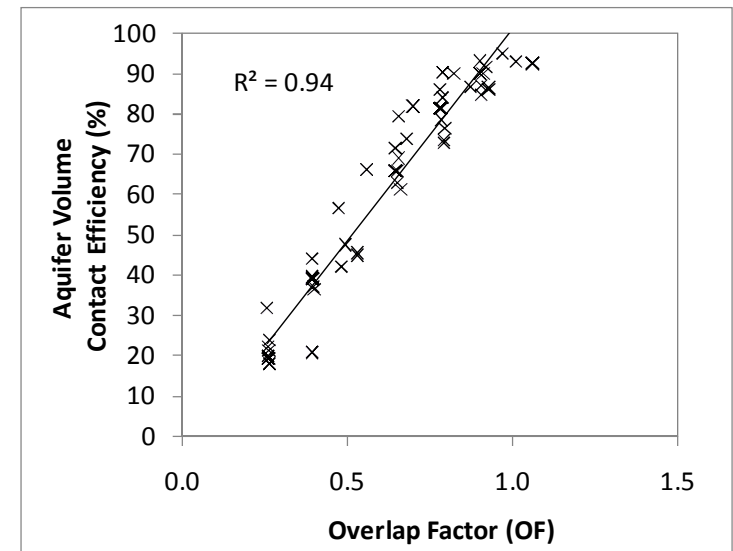


# How to Design an Injection System

1. Enable Macros
2. Enter site data
3. Enter Design Criteria
  - a. Target  $\text{MnO}_4$  concentration (typical ~ 100 – 1000 mg/L)
  - b. Target contact time (typical ~ 10 – 100 days)
  - c. Overlap Factor (OF)
4. Click 'calculate' (run  $\text{MnO}_4$  transport model)
5. Enter cost data
6. Review cost summary
7. Revise design and repeat model run

# Overlap Factor (OF)

- Overlap Factor (OF)
  - ◆ Well Spacing =  $2 \cdot \text{ROI} / \text{OF}$
  - ◆ ROI = radius of influence
- CDISCO calculates ROI
  - ◆ Minimum  $\text{MnO}_4$  concentration after \_\_\_ days
- User must pick OF
  - ◆ Currently, no guidance on correct OF
  - ◆ Increasing OF increases cost
- Comparison of RT3D and CDISCO
  - ◆ Obtain  $E_v$  and  $E_M$  from 3D heterogeneous simulations
  - ◆ Obtain ROI from CDISCO
- Conclusion
  - ◆ OF between 1.0 and 1.5 generates good results



# Site Data



SERDP



1. Model run parameters
  - a. simulation duration
  - b. time step
2. Hydrogeologic characteristics
  - a. Permeability
  - b. Porosity
  - c. effective thickness
3. NOD parameters
  - a. Total NOD
  - b. Fraction instantaneous
  - c. Slow NOD rate coefficient
4. Oxidant and contaminant info
5. Injection info
  - a. Injection well diameter and design flow per well
  - b. Hours per day of injection and days of injection
6. Design criteria
  - a. Target oxidant concentration and contact time
  - b. Radius of influence overlap factor (OF)

Hydrogeologic Characteristics		
Top of Injection Interval	30	ft bgs
Bottom of Injection Interval	40.00	ft bgs
Aquifer Thickness	10	ft
Thickness of Mobile Zone (Z)	10.0000	ft
Porosity	0.20	L/L
Longitudinal Dispersivity	2.0000	ft
Hydraulic Conductivity (k)	50.00	ft/day
Depth to Water Table	15	ft
Soil and NOD Characteristics		
Bulk Density	1.60	Kg/L
NOD	1	g/Kg
Fraction Instantaneous	0.20	
Second Order Slow NOD Consumption Rate (Ks)	0.1000	L / mmol - d
Oxidants Information		
Name of Oxidant	Permanganate (MnO <sub>4</sub> <sup>-</sup> )	
Molecular Weight of Oxidant	118.94	g/mol
Initial Oxidant Concentration	0.00	mg/L

# Cost Data

## Installation and Injection Costs for: Injection through Direct Push Probes

Information on the labor and materials required for ISCO injection by direct push injection (DPI) is entered on this page. Drilling and injection is assumed to be performed by a subcontract driller with supervision by the prime contractor. In this approach the oxidant is injected in a single operation where the DPI equipment drives the rod to the desired depth immediately followed by oxidant injection over an aquifer thickness equal to the injection screen length. The rod is moved to a different depth and the operation is repeated. Once injection is complete over the entire injection interval, the rod is removed, the boring grouted and the DPI equipment is shifted to a new location. DPI injections can be performed into a single probe or into multiple probes simultaneously.

### 1. Categories

- a. Prime contractor  
(mobe, hourly labor, expenses)
- b. Subcontractor  
(mobe, hourly labor, expenses)
- c. Reagent, materials and equipment rental

### 2. Activities

- a. Fixed costs  
(design, permitting, etc.)
- b. Injection well or probe installation
- c. Reagent injection

#### 1 Injection Information

a	Top of Injection Interval	30	ft
b	Bottom of Injection Interval	50	ft
c	Injection rate to be used in Design	3,000	gpd/probe
d	Number of probes injected simultaneously, or number of probes drilled and injected per day	5	

#### 2 Fixed Costs

a	Prime contractor mobilization	500	\$
b	Subcontractor mobilization	2,000	\$
c	Water Supply	500	\$
d	Piping and other equipment for oxidant preparation and injection	2000	\$
e	Time required for equipment setup and removal	8	person - hr
f	Average labor rate for equipment setup and removal	100	\$/hr
g	Labor cost for setup and removal	800	\$
h	<b>Total fixed cost</b>	<b>5,800</b>	<b>\$</b>

0

#### 3 Prime Contractor Information and Daily Costs

a	Prime contractor personnel on-site each day of injection	1	person(s)
b	Average labor rate of prime contractor personnel	100	\$/hr
c	Hours billed per person per day	10	hr/person/day
d	Per Diem (e.g., meals, travel, vehicle rental, lodging)	200	\$/person/day
e	Additional costs (consumables, H&S, and monitoring equipment)	200	\$/day
f	Injection equipment rental costs (pumps, tanks, hoses, etc.)	200	\$/day
g			
h	<b>Total daily cost for prime contractor</b>	<b>1,600</b>	

4,800

#### 4 Subcontractor Information and Daily Injection Costs

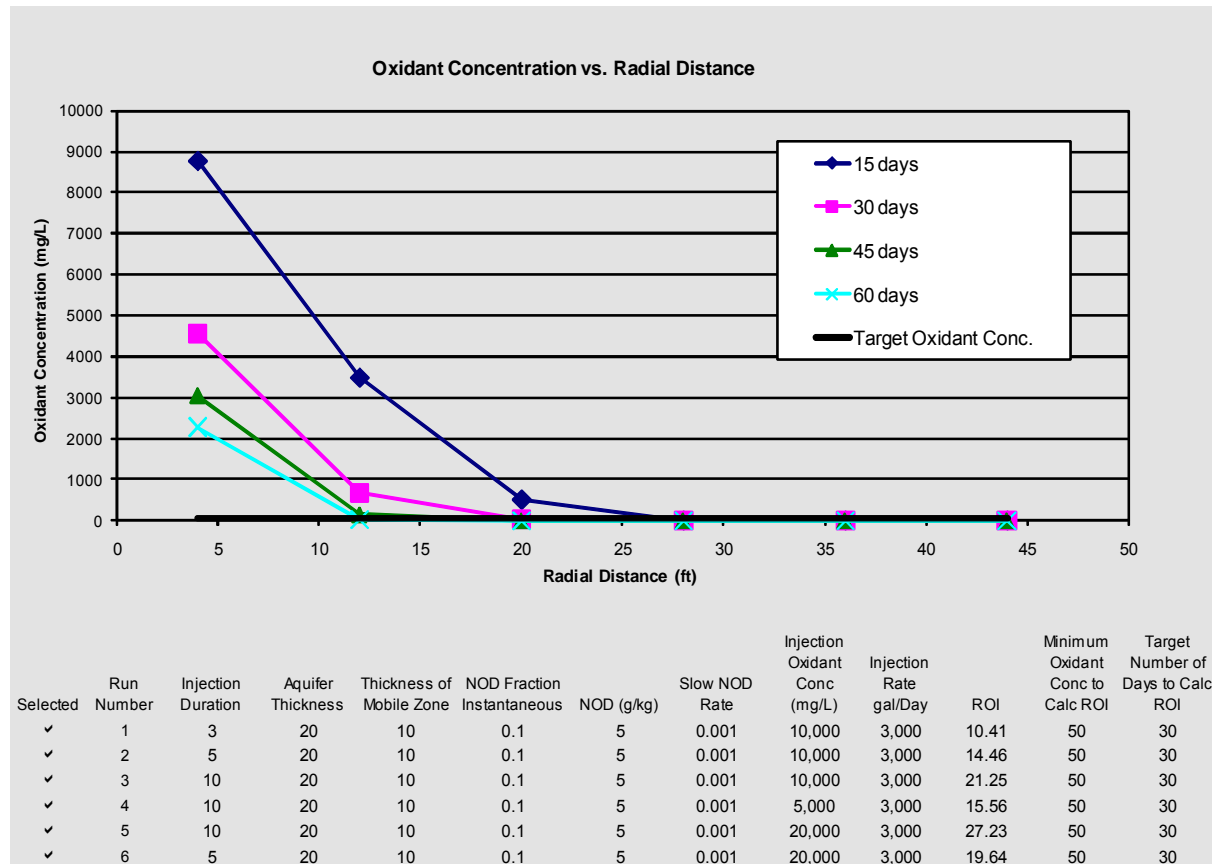
a	Drilling Equipment to be used		
b	Daily cost for DPT equipment and operator	3000	\$/day
f	Additional material and IDW daily costs	200	\$/day
g	<b>Total daily cost for subcontractor</b>	<b>3,200</b>	<b>\$/day</b>

#### 5 Daily Costs for Injection using DPT Equipment

a	<b>Injection costs per day</b>	<b>4,800</b>	<b>\$/day</b>
---	--------------------------------	--------------	---------------

# Permanganate Design Tool

- Typical CDISCO Results
  - Generates graphs of  $\text{MnO}_4$  conc. vs distance for different injection conditions
- Determines effective Radius of Influence (ROI) based on
  - Minimum  $\text{MnO}_4$  Conc.
  - Contact Time
- Determines injection well spacing based on
  - ROI
  - Overlap factor





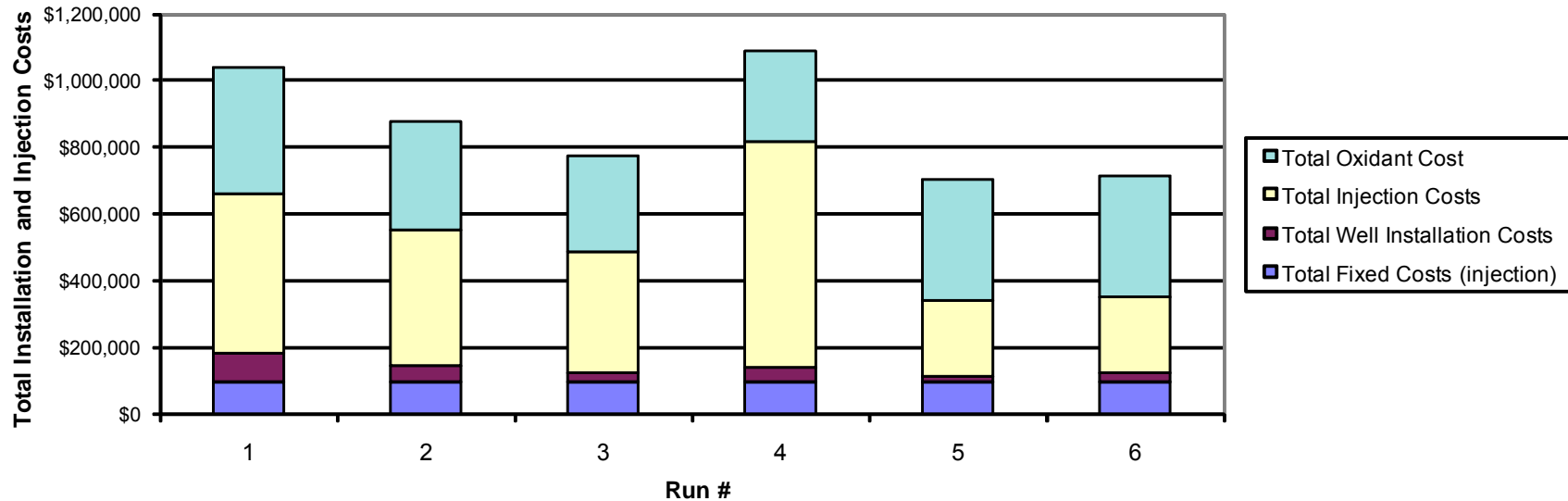
# Design Tool Summary



SERDP



Run	1	2	3	4	5	6
Total Fixed Costs (injection)	\$94,800	\$94,800	\$94,800	\$94,800	\$94,800	\$94,800
Total Well Installation Costs	\$85,667	\$47,700	\$25,367	\$41,000	\$18,667	\$29,833
Total Injection Costs	\$478,800	\$410,400	\$364,800	\$684,000	\$228,000	\$228,000
Total Oxidant Cost	\$378,547	\$324,469	\$288,417	\$270,391	\$360,521	\$360,521
Total Installation and Injection Costs	\$1,037,814	\$877,369	\$773,384	\$1,090,191	\$701,988	\$713,155
Number of probes or wells required	35	18	8	15	5	10
NOD (g/kg)	5	5	5	5	5	5
Injection Oxidant Concentration	10000	10000	10000	5000	20000	20000
Injection Oxidant Mass (lbs)	26288	22533	20029	18777	25036	25036
Injection Duration (days)	3	5	10	10	10	5
Volume Injected per Day (gal/d)	3000	3000	3000	3000	3000	3000
Thickness of Mobile/Target Thickness	0.5	0.5	0.5	0.5	0.5	0.5



# Additional Resources

- Software Download
  - ◆ <http://docs.serdp-estcp.org/> (search for Design Tool )
  - ◆ [http://www4.ncsu.edu/~rcborden/Design\\_Tool.html](http://www4.ncsu.edu/~rcborden/Design_Tool.html)
- Technical Report
  - ◆ Design Tool for Planning Permanganate Injection Systems
- Websites
  - ◆ SERDP/ESTCP (<http://docs.serdp-estcp.org>)
    - In Situ Chemical Oxidation Initiative
    - Decision Support Tools for In Situ Chemical Oxidation
  - ◆ ITRC ([http://www.itrcweb.org/gd\\_ISCO.asp](http://www.itrcweb.org/gd_ISCO.asp) )  
Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Ed.
  - ◆ USEPA,  
In-Situ Chemical Oxidation - Engineering Issue  
<http://www.epa.gov/ada/download/issue/600R06072.pdf>

# Short Course Agenda



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

# Improved Field Evaluation of NAPL Dissolution and Source Longevity

**Dr. Michael Kavanaugh**  
Malcolm Pirnie, Inc.

**Dr. Mark Widdowson**  
Virginia Tech

**Dr. Rula Deeb**  
Malcolm Pirnie, Inc.

**Dr. Lloyd “Bo” Stewart**  
Praxis Environmental  
Technologies, Inc.

## Project Team: ER-0833

- Malcolm Pirnie, Inc.
  - ◆ Michael Kavanaugh, Ph.D., P.E. (PI)
  - ◆ Rula Deeb, Ph.D. (Project manager)
  - ◆ Jennifer Nyman, Ph.D. (Deputy project manager)
- Praxis Environmental Technologies, Inc.
  - ◆ Lloyd “Bo” Stewart, Ph.D., P.E. (co-PI)
- Virginia Polytechnic Institute and State University
  - ◆ Mark Widdowson, Ph.D. (co-PI)
- GeoTrans, Inc.
  - ◆ Jim Mercer, Ph.D.

# Acknowledgements

- Air Force (funding of the TEE pilot study)
  - ◆ Mr. Bill Lopp, AFCEE
- BEM (contractor at the site)



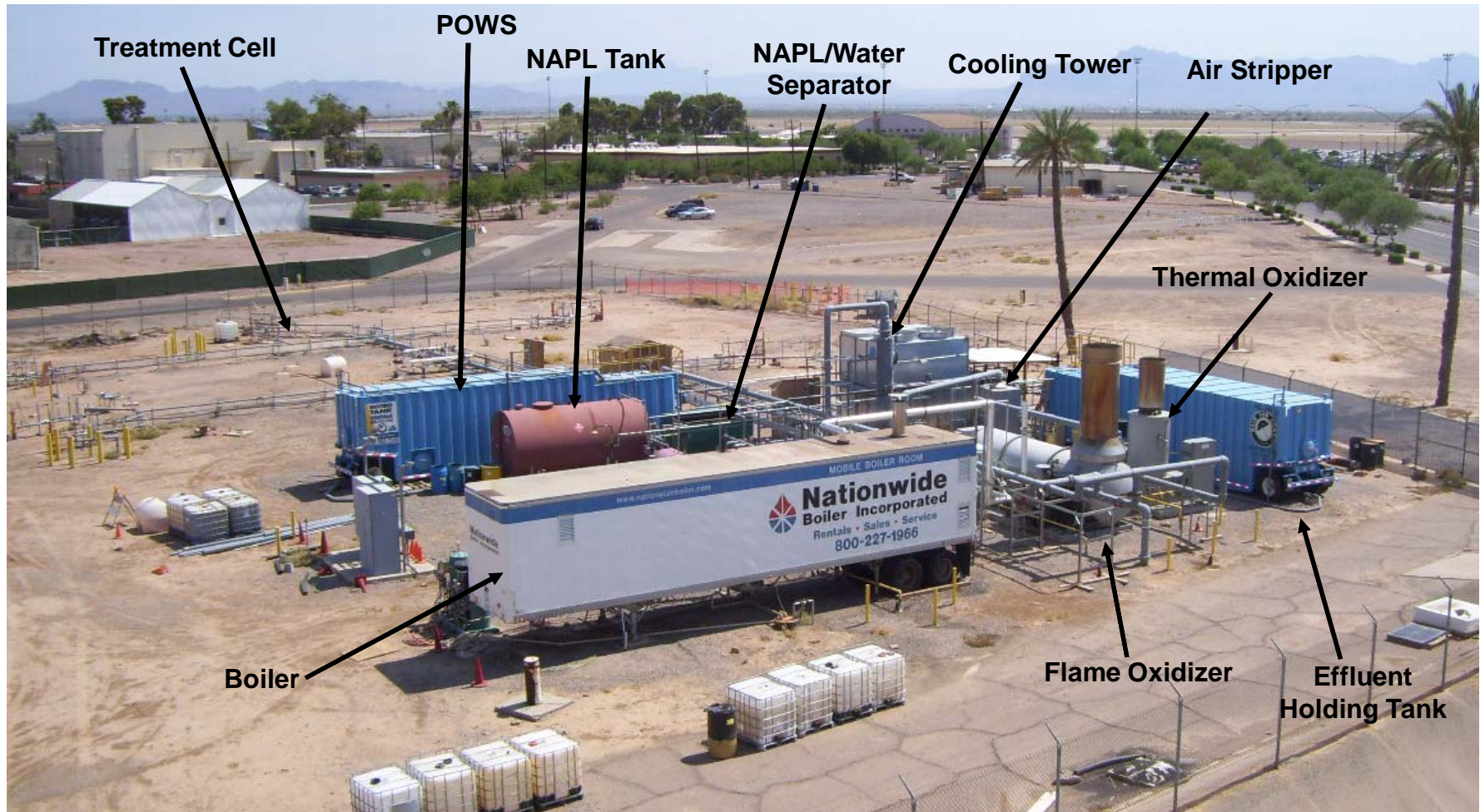
# Decision-Making Tool for NAPL Source Zones

- Key challenge: Determining magnitude of NAPL source depletion needed to meet site Remedial Action Objectives (RAOs) at defined point of compliance.
- Technical challenges
  - ◆ Rate of LNAPL dissolution as function of time
  - ◆ Accurate prediction of transformation processes for chemicals of concern (e.g., benzene, naphthalene)
- Proposed approach
  - ◆ Field determination of pre and post remediation rates of dissolution based on field estimates of mass transfer coefficients
  - ◆ Application of SEAM3D fate and transport model combined with flow model to assess the potential effectiveness of source removal scenarios

## Demonstration Site

- Site ST012, former Williams AFB, AZ
- Multi-component NAPL source zone
  - ◆ JP-4 fuel, BTEX, naphthalene
- Variety of NAPL architectures
  - ◆ Extensive smear zone from rising water table; dispersed ganglia
  - ◆ Pooled NAPL below low permeability, semi-confining units
- Pilot test of Thermal Enhanced Extraction (TEE) by USAF
  - ◆ Duration: October 2008 – May 2009
  - ◆ Mass transfer tests before and after TEE
  - ◆ Data interpretation and simulation of various source depletion options using SEAM3D

# Demonstration Site



*View facing northeast across Site ST012 (July 2, 2008)*

# Multi-Scale Measures of Mass Dissolution Rate

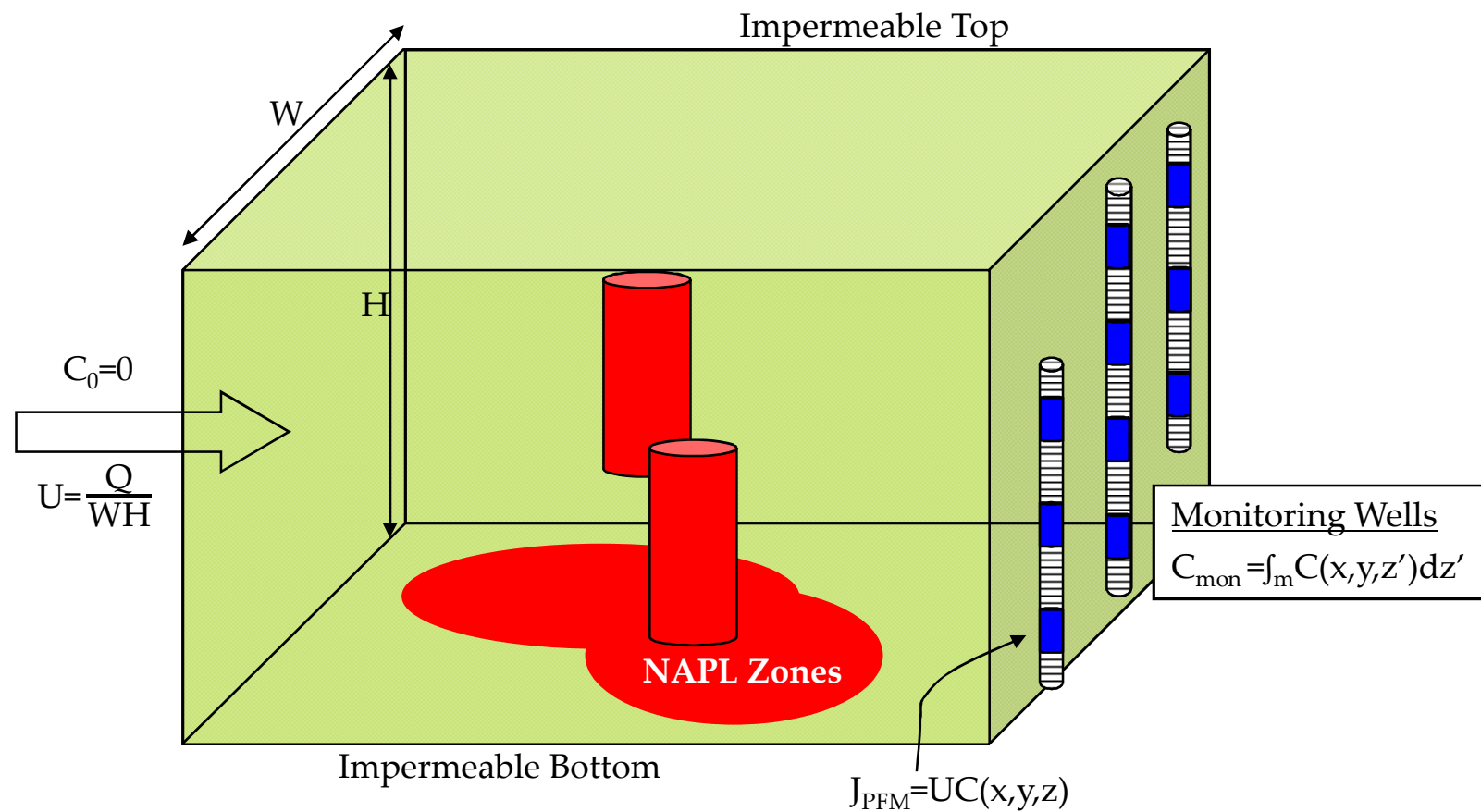
- Sweep the NAPL source zone with clean water
- Collect multi-scale data for water movement through the source zone
- Collect multi-scale data for concentrations and mass flux of target chemicals

# Field Technologies

- Conventional Monitoring Well Data
  - ◆ Concentration
  - ◆ Water level
  - ◆ NAPL thickness and recharge rate
- Integrated Pumping Test (IPT)
  - ◆ Modified to include water injection
  - ◆ Modified to include tracer test (e.g., bromide)
  - ◆ No new capital if Pump & Treat system is in place
- Passive Flux Meters (PFMs)
  - ◆ Vertically segmented within multiple monitoring wells



# Conventional Data with PFMs Collected Downgradient





# Nomenclature

$W$  = width of flow cross-section through NAPL zone

$H$  = height of flow cross-section through NAPL zone

$Q$  = volumetric flow rate through cross-section

$U$  = velocity of groundwater

$C_0$  = ambient concentration entering NAPL zone

$C(x,y,z)$  = concentration at position  $x,y,z$

$C_{\text{ext}}$  = concentration in extracted groundwater

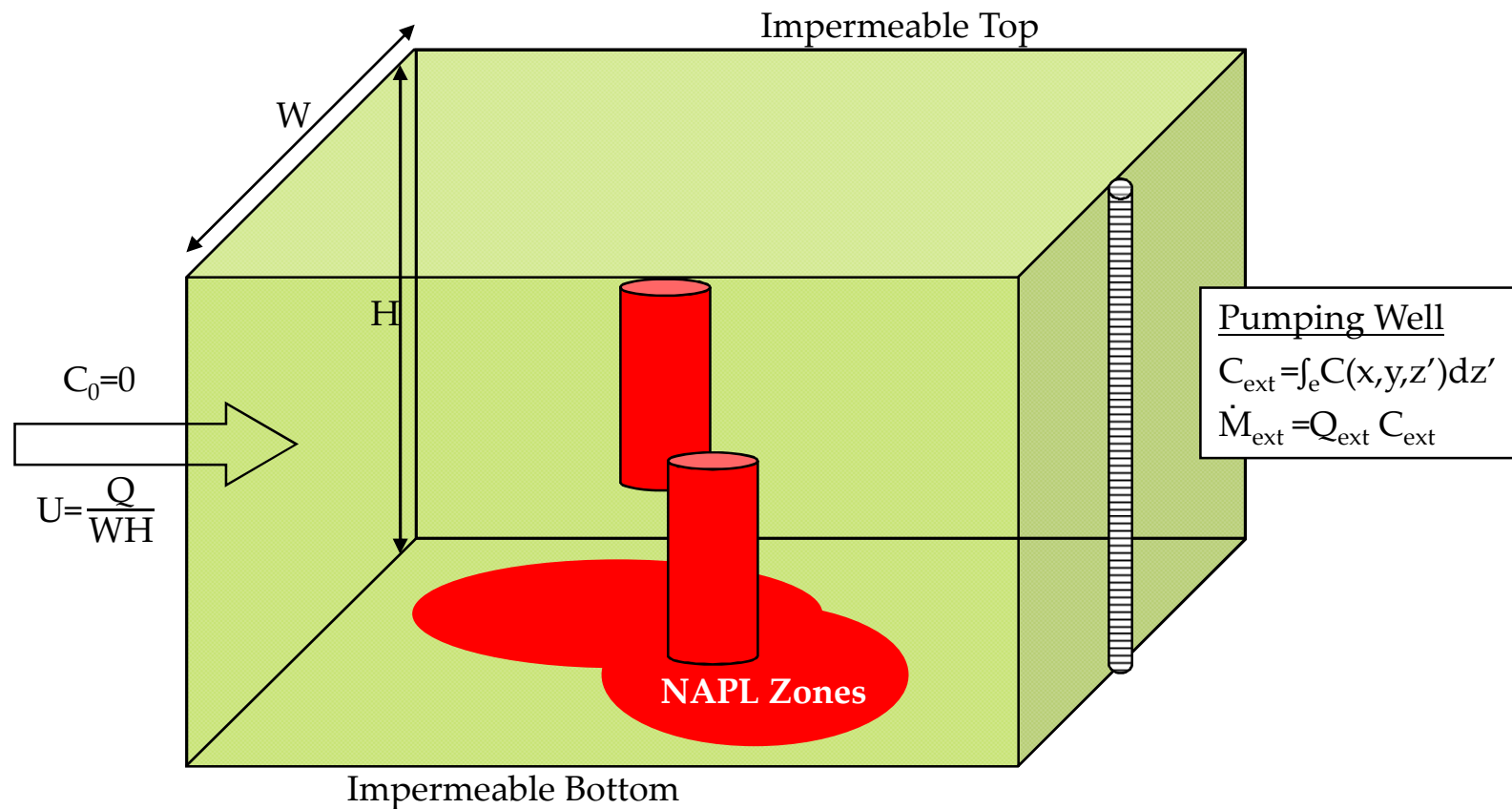
$Q_{\text{ext}}$  = volumetric extraction rate

$M_{\text{ext}}$  = mass extraction rate of contaminant

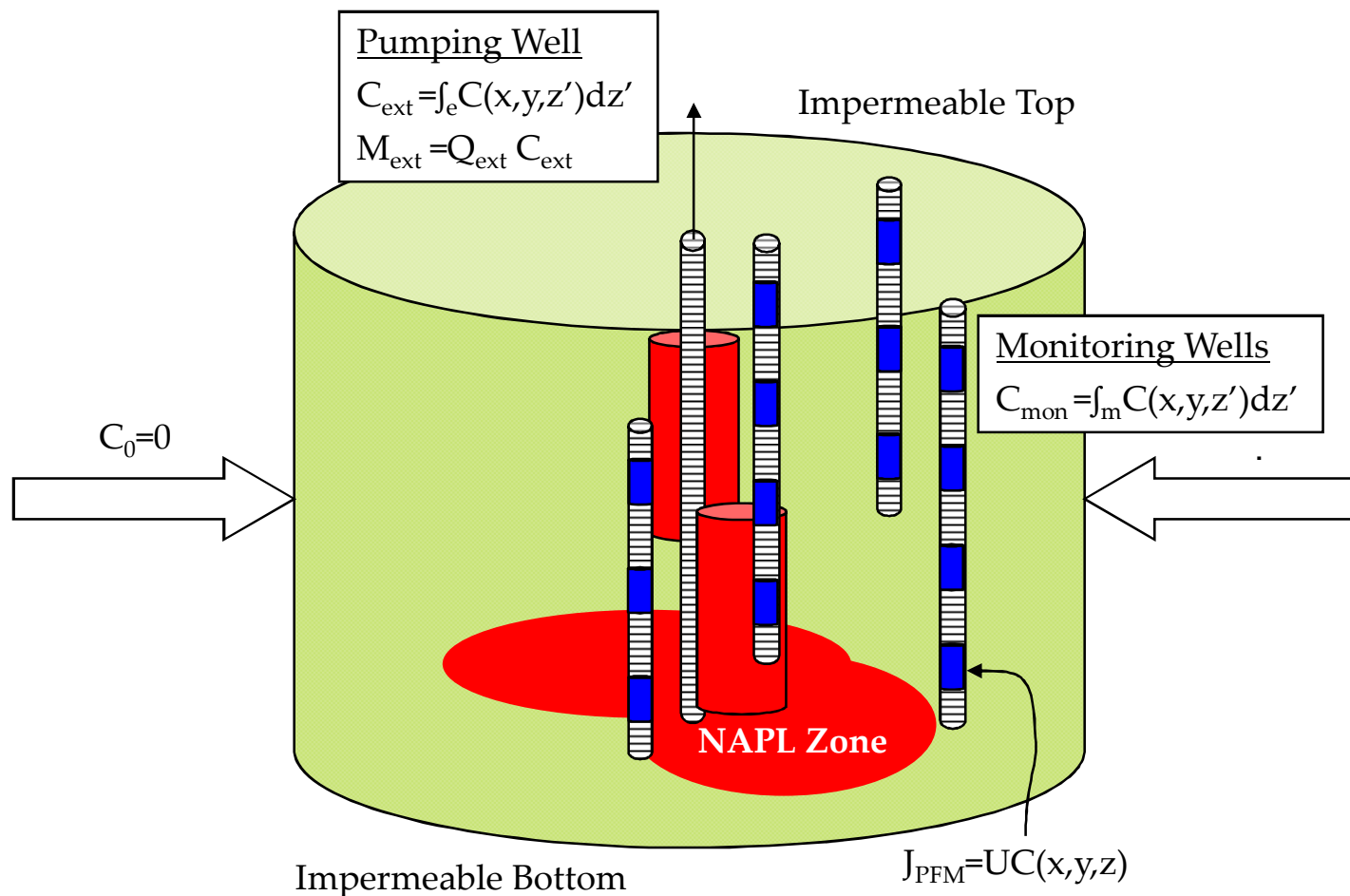
$C_{\text{mon}}$  = concentration in monitoring well

$J_{\text{PFM}}$  = contaminant flux measured by PFM at  $x,y,z$

# Mass Dissolution from IPT Collected Downgradient



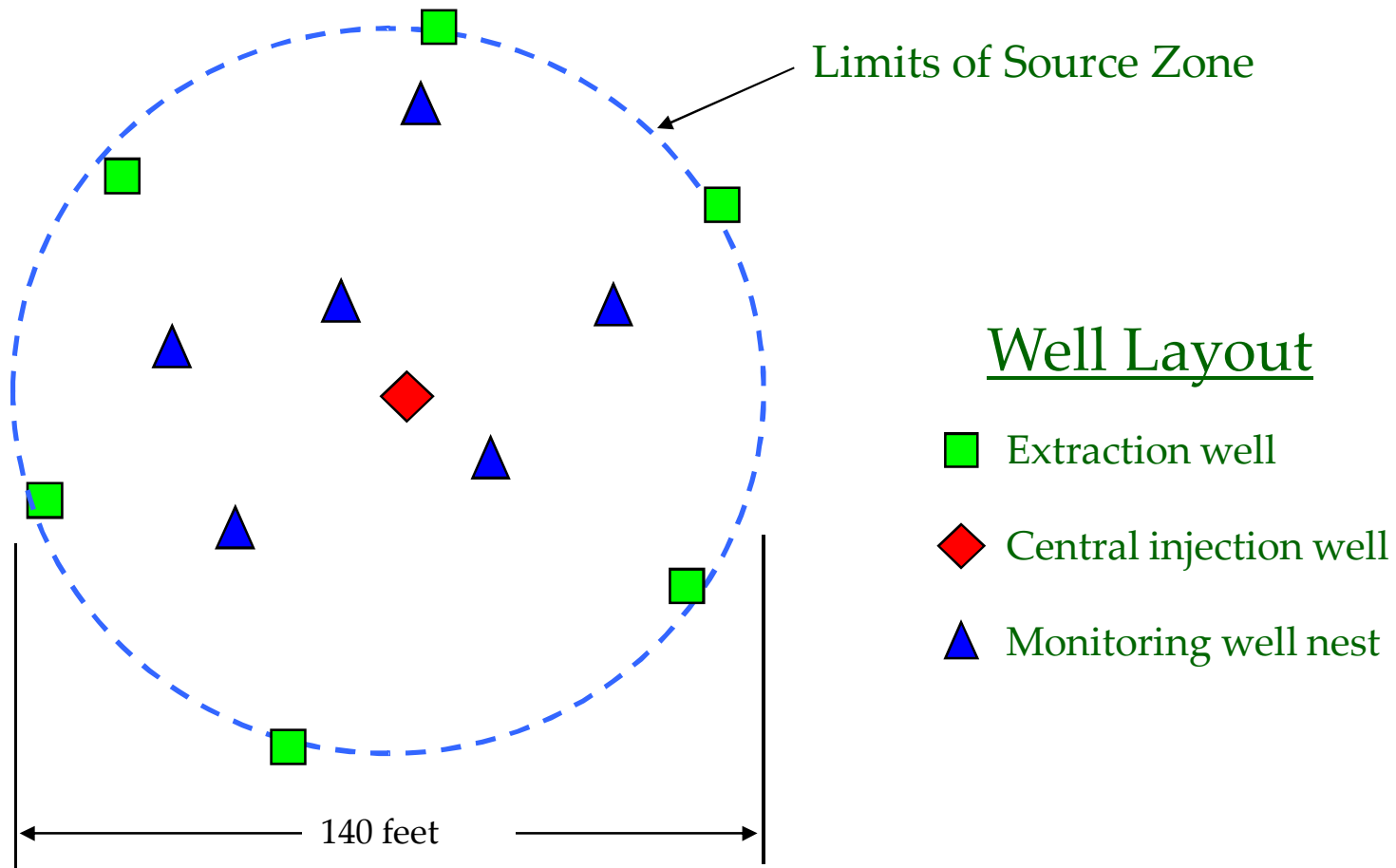
# Multi-Scale Mass Dissolution Measurements in Source Zone



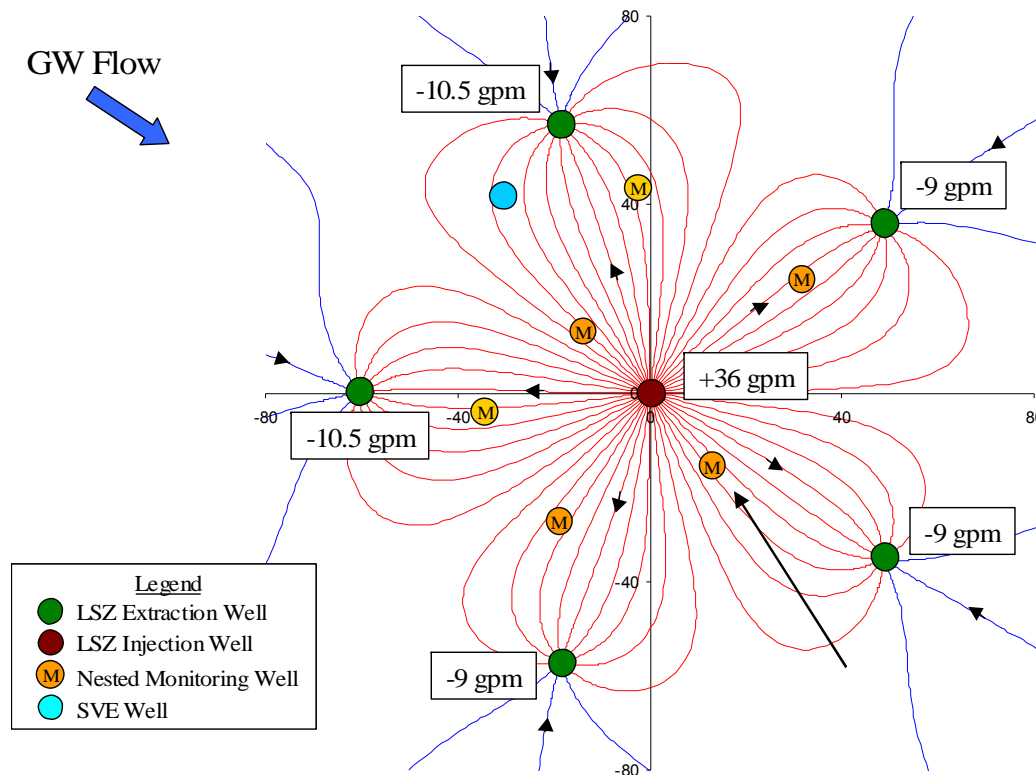
# Integrated Pumping Test

- Water Injection to Sweep Source Zone
- Tracer Test to Define Flow Intervals
  - ♦ Bromide
  - ♦ Multi-Level Sensors
- Defines Mass Dissolution on a Large Scale
  - ♦ Imposed flow rate higher than ambient groundwater flow
  - ♦ Yields a maximum mass dissolution rate
  - ♦ Mass dissolution on the scale of the DNAPL source dimensions

## Plan View of Wells



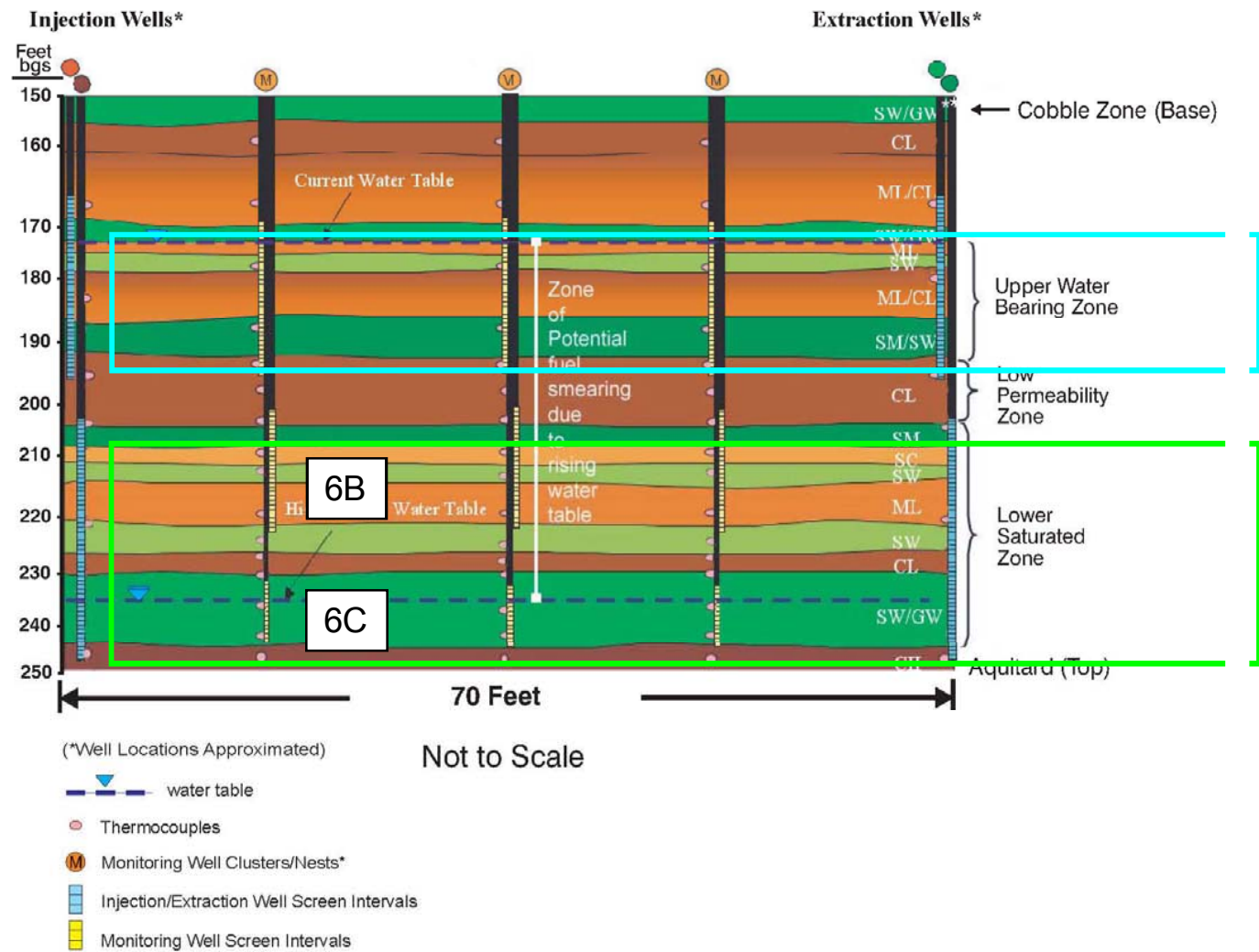
# Idealized Streamlines during IPT



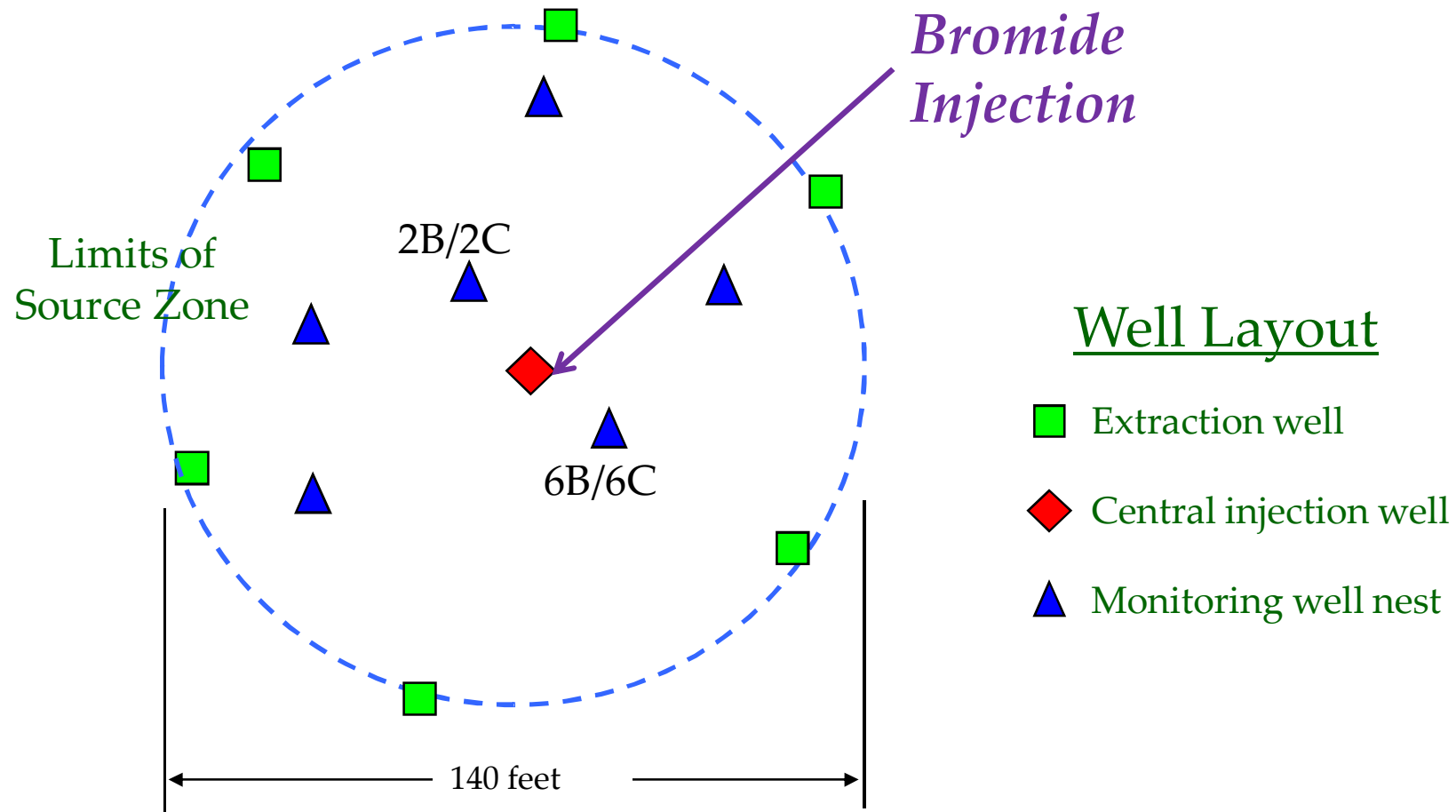
Streamlines Depicting Idealized Groundwater Flow During Mass Transfer Test



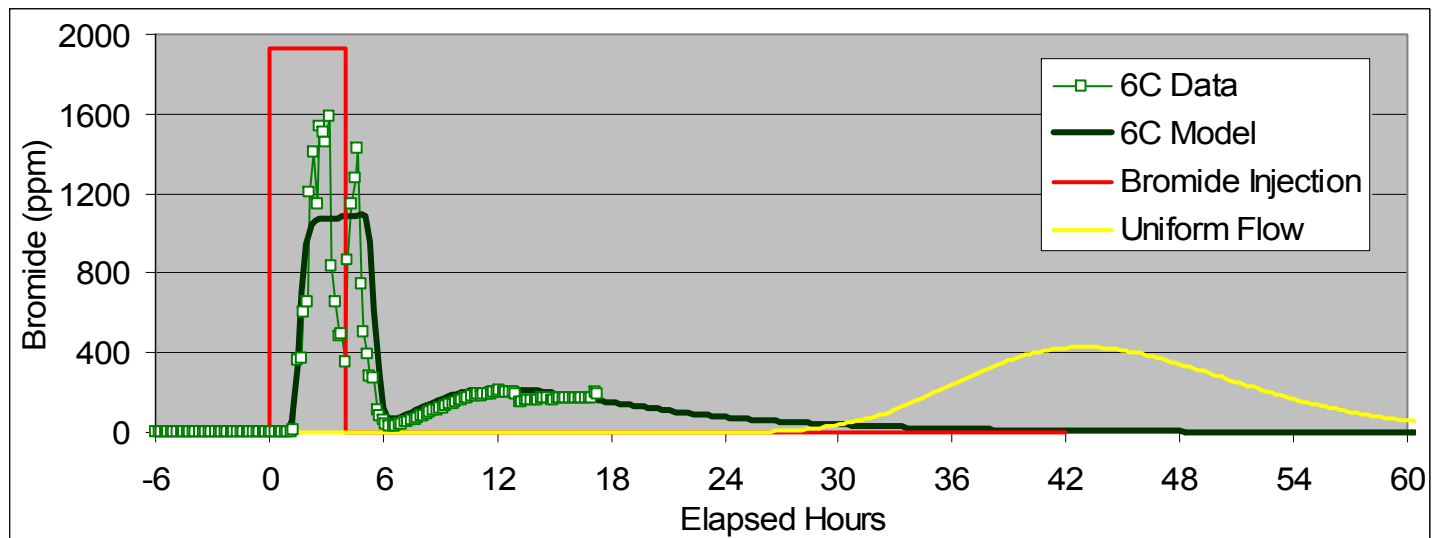
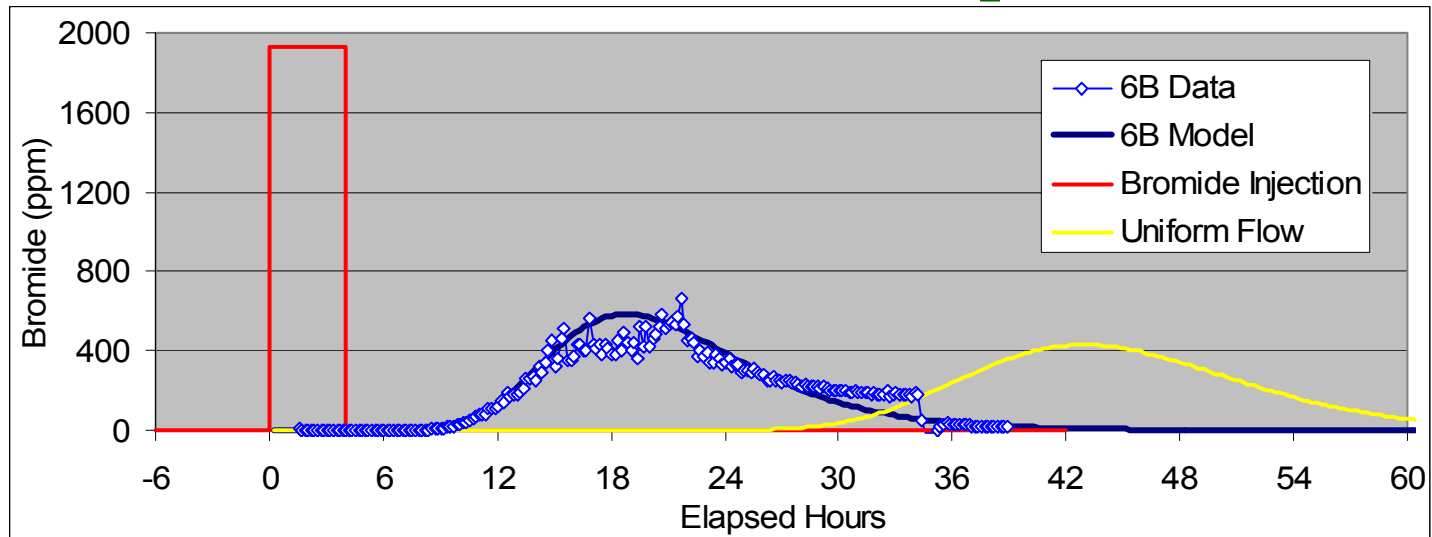
# Conceptual Cross-Section



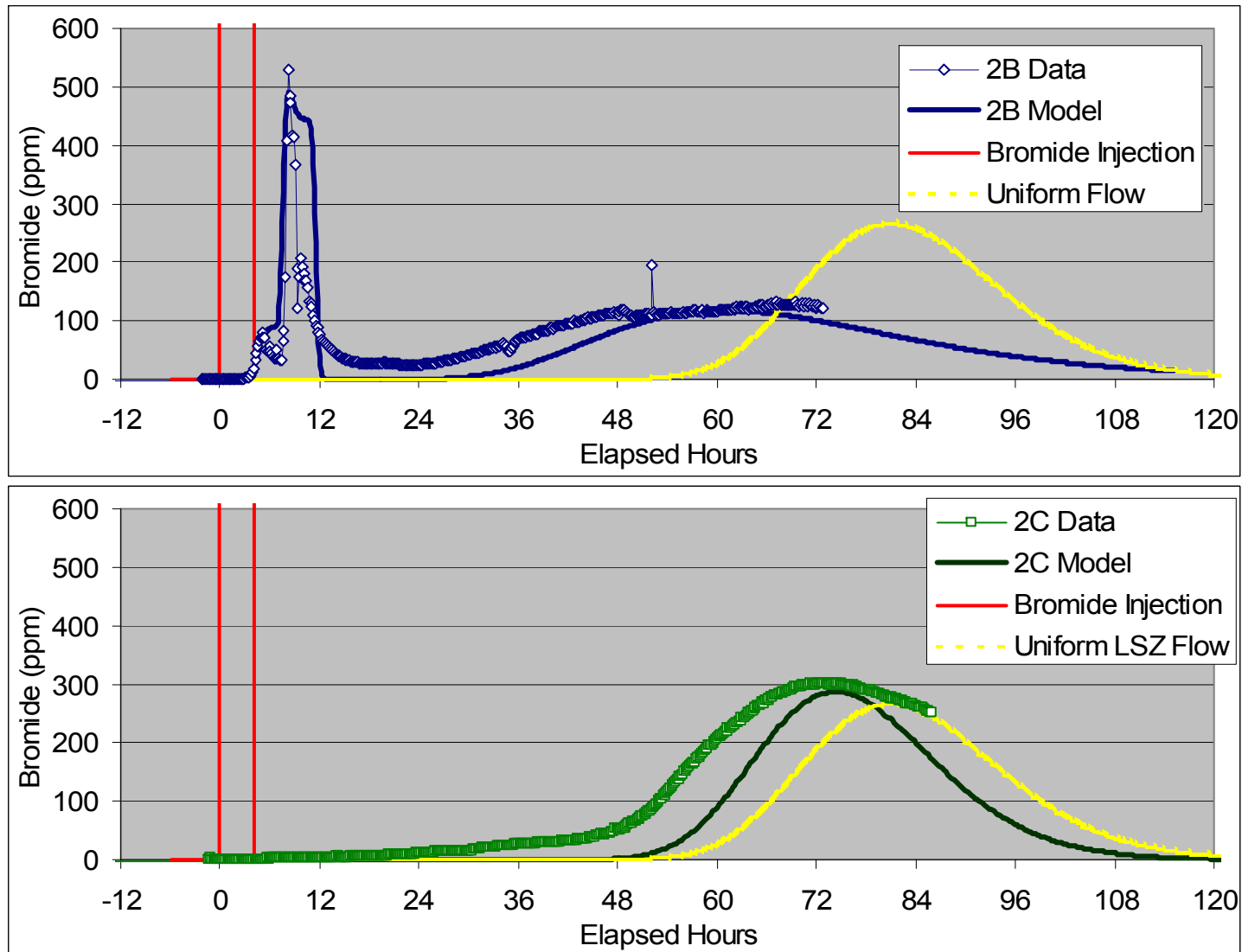
# Tracer Test Layout



# Bromide Tracer Responses



# Bromide Tracer Responses

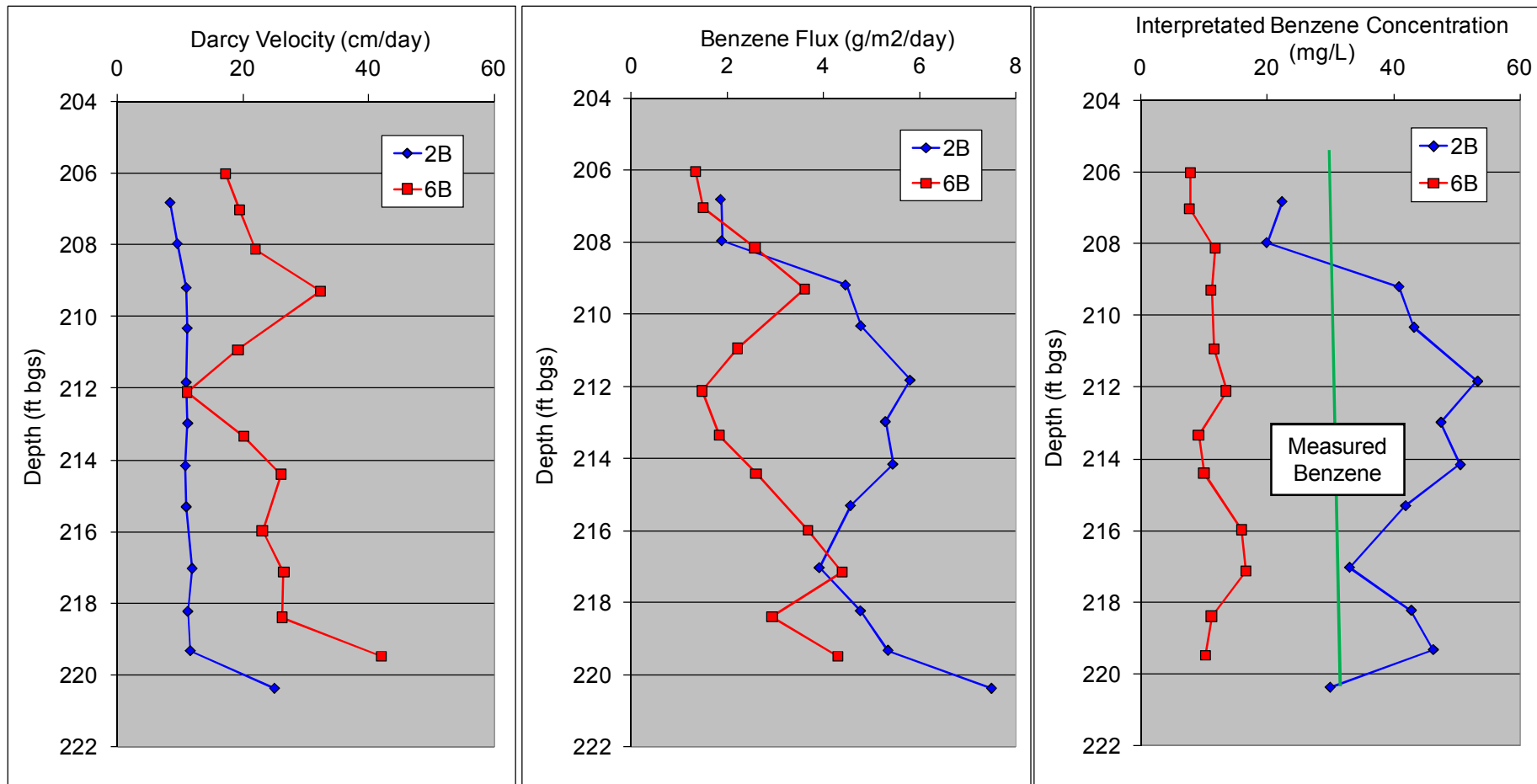


## Passive Flux Meters (PFMs)

- PFMs are segmented nylon mesh tubes filled with a sorbent/tracer mixture
- Inserted into monitoring wells to passively intercept groundwater flow
- Permeable sorbent (e.g., GAC) retains dissolved contaminants
- Preloaded alcohol tracers are leached as groundwater flows through the PFM
- PFM provides vertical profiles of horizontal water and contaminant fluxes

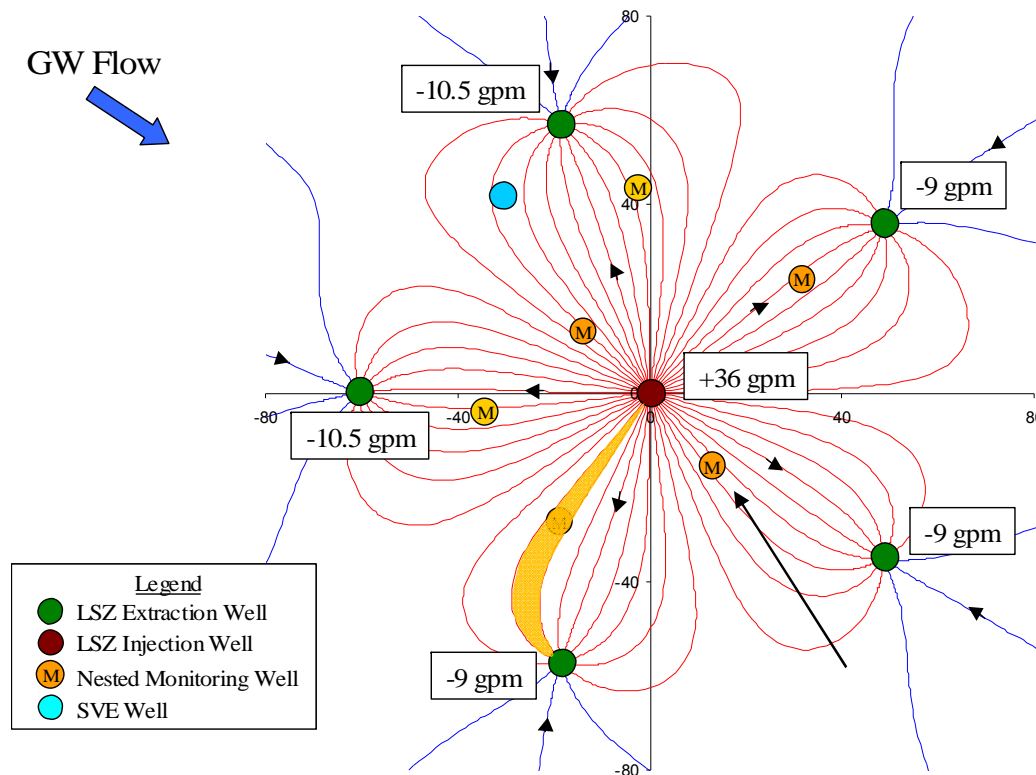


# Passive Flux Meters





# Idealized Streamlines during IPT



Streamlines Depicting Idealized Groundwater Flow During Mass Transfer Test

## Interpretation of IPT

- Large-scale bulk mass transfer coefficient determined from the IPT (yields a maximum value):

$$M_{source,i}^{NAPL} = K_{i,IPT} C_i^{eq} V_{IPT} = QC_{i,ext}$$

$$K_{i,IPT} = \frac{QC_{i,ext}}{C_i^{eq} V_{IPT}}$$

- ♦  $M^{NAPL}$  = total mass extraction/dissolution rate of component  $i$
- ♦  $Q$  = total extraction rate
- ♦  $C_i^{eq}$  = equilibrium aqueous concentration
- ♦  $C_{i,ext}$  = concentration of  $i$  in extracted groundwater
- ♦  $K_{i,IPT}$  = bulk mass transfer coefficient
- ♦  $V_{IPT}$  = sweep volume

## Interpretation of PFMs

- Streamtube-scale bulk mass transfer coefficient determined from the IPT and PFM:

$$K_{i,streamtube} = \frac{J_{i,PFM} A_{PFM}}{V_{streamtube} C_i^{eq}}$$

- ♦  $J_{i,PFM}$  = contaminant flux measured by the PFM
- ♦  $A_{PFM}$  = streamtube cross-sectional area at the PFM
- ♦  $V_{streamtube}$  = volume of soil flushed by clean water intersected by the PFM
- ♦  $C_i^{eq}$  = equilibrium aqueous concentration
- ♦  $K_{i,streamtube}$  = streamtube-scale bulk mass transfer coefficient

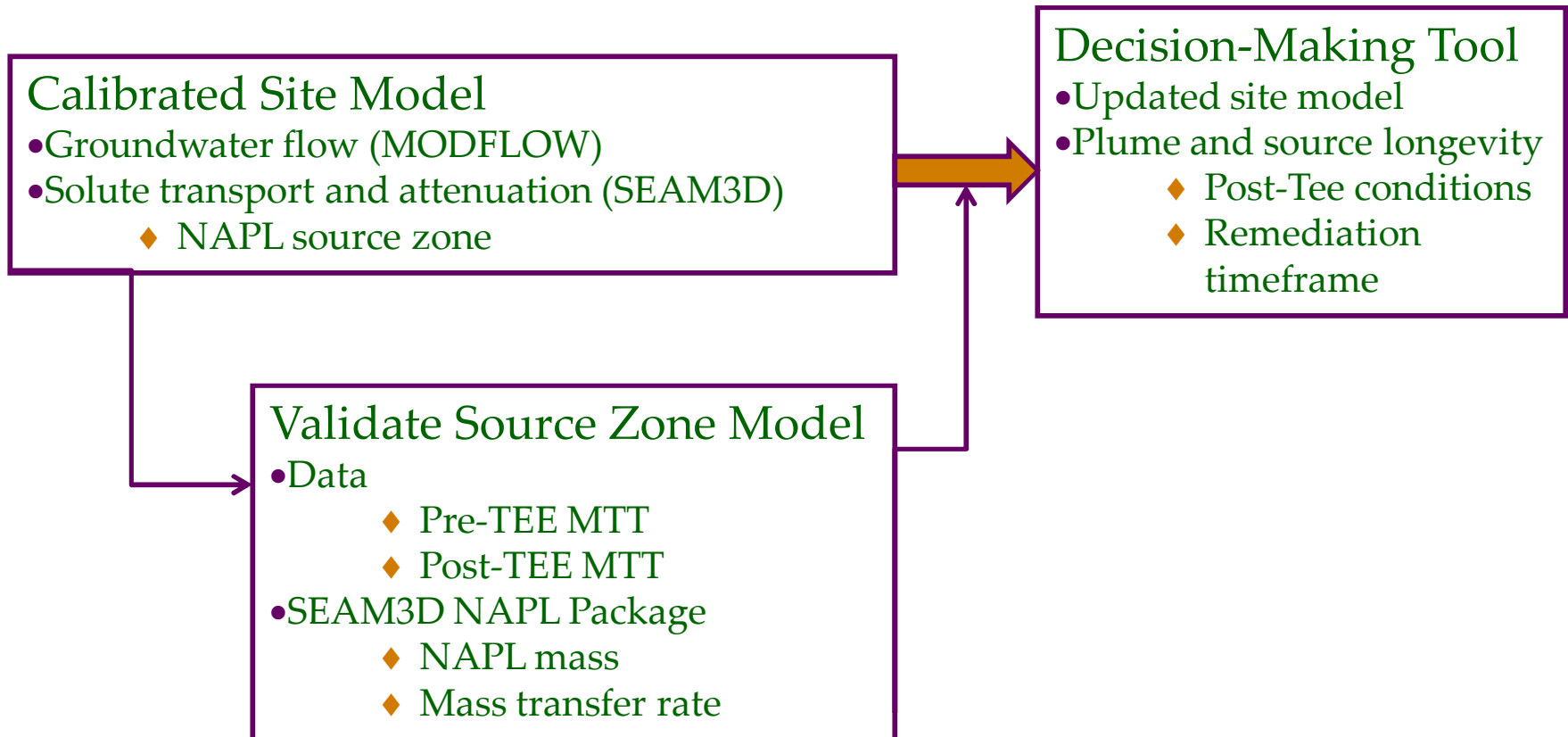
# HOW DO WE USE THE MULTI-SCALE MASS DISSOLUTION MEASUREMENTS?

Modeling

# Modeling Objectives

- Validate results of MMT data interpretation
  - ◆ Source zone parameters
- Predict post-TEE conditions
  - ◆ New equilibrium plume size and concentrations
- Quantify time of remediation estimates for source longevity in support of decision making
  - ◆ Remedial action work plan
  - ◆ Evaluate range of uncertainty
  - ◆ Additional mass removal scenarios

# Tools and Steps



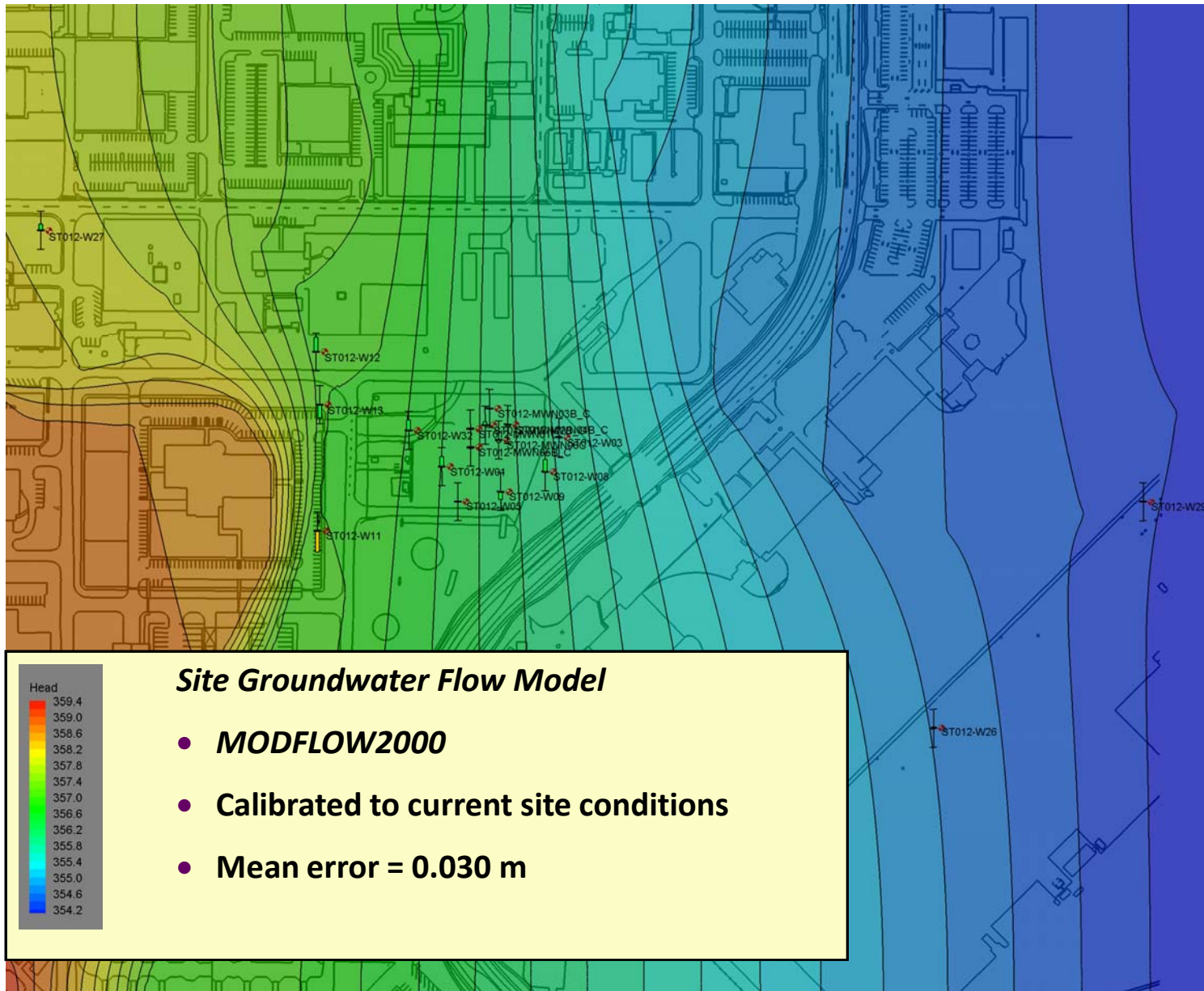


# Calibrated Site Model

- Groundwater flow – MODFLOW 2000
- Solute transport and attenuation – SEAM3D
  - ◆ Physical transport
  - ◆ Biodegradation
    - Aerobic
    - Anaerobic
  - ◆ NAPL dissolution
    - Multi-component
    - Upscaled mass transport coefficient

# MNA Modeling Objective

- Objective - Simulate current site conditions, including historical data
  - ◆ PHC transport coupled to NAPL dissolution and aerobic/anaerobic biodegradation
- Approach
  - ◆ Construct and calibrate groundwater flow model to match observed historical water level data
  - ◆ Calibrate a solute transport model to historic PHC concentrations and TEAP/redox conditions



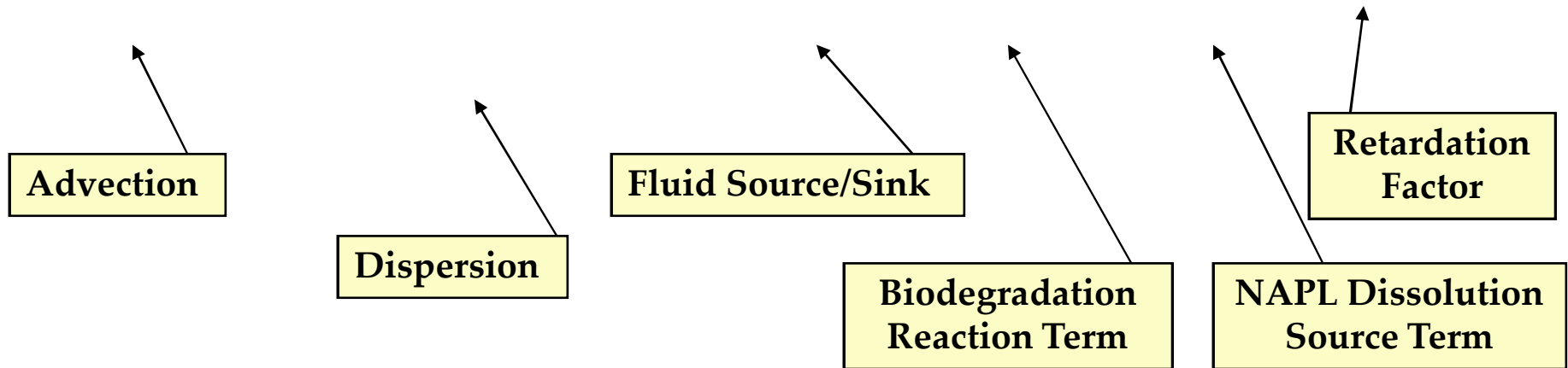
# Model Variables

- Hydrocarbon Compounds – NAPL
- Electron Acceptors (aq)
  - ◆ Oxygen
  - ◆ Nitrate
  - ◆ Sulfate
- Electron Acceptors (s)
  - ◆ Bioavailable Fe(III)
- End Products
  - ◆ Fe(II)
  - ◆ Sulfide
  - ◆ Methane

# Solute Transport

Hydrocarbon Compounds:  $C_i$

$$-\frac{\partial}{\partial x}(q_s C_i) + \frac{\partial}{\partial x}\left(\theta D \frac{\partial C_i}{\partial x}\right) + Q_s C_i^* - M_{snk,i}^{Bio} + M_{source,i}^{NAPL} = \theta R \frac{\partial C_i}{\partial t}$$

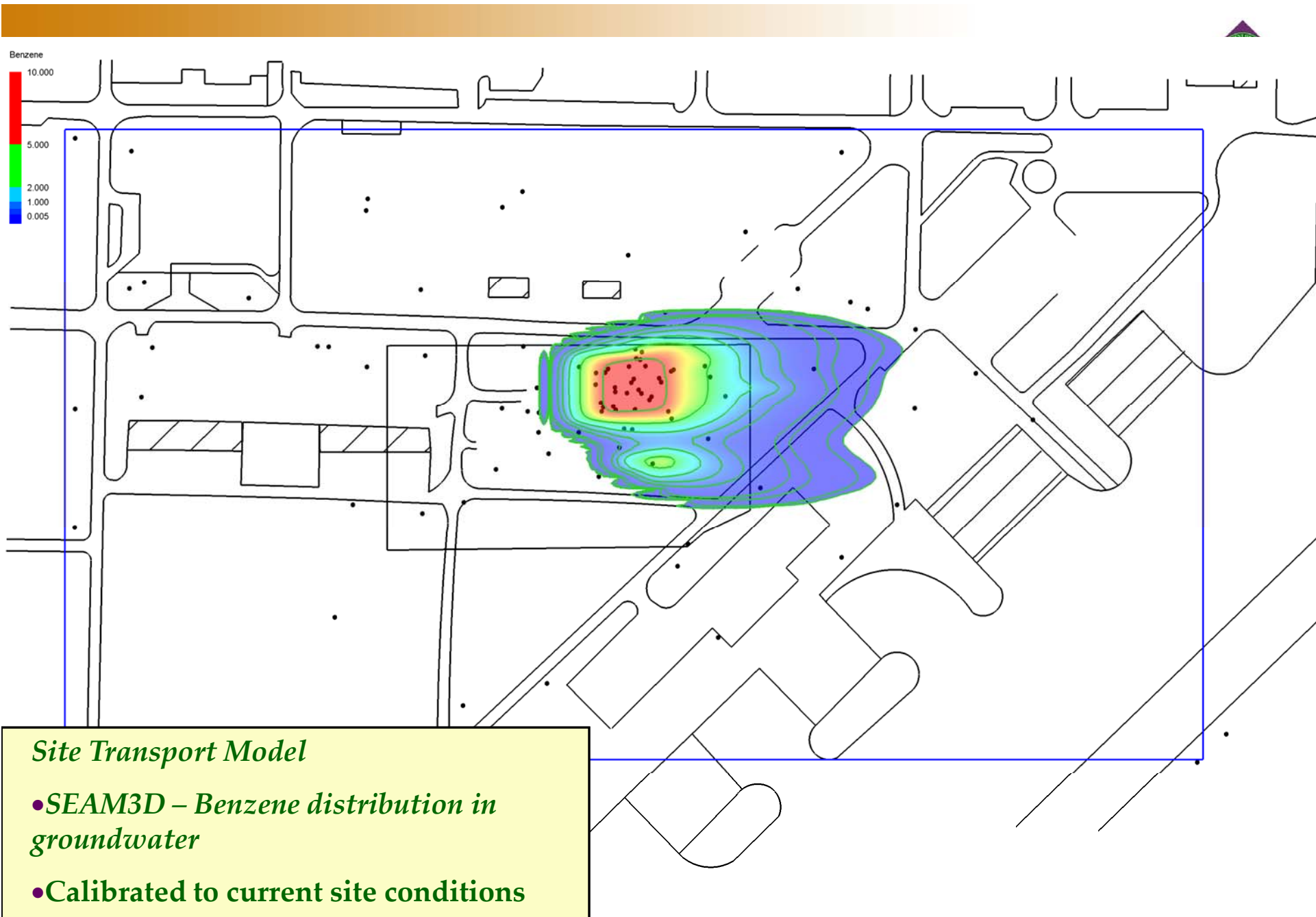


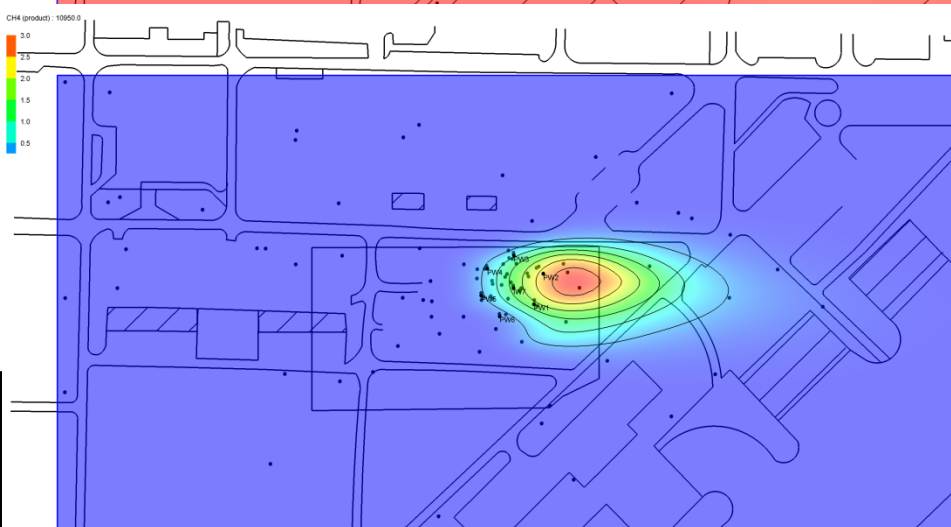
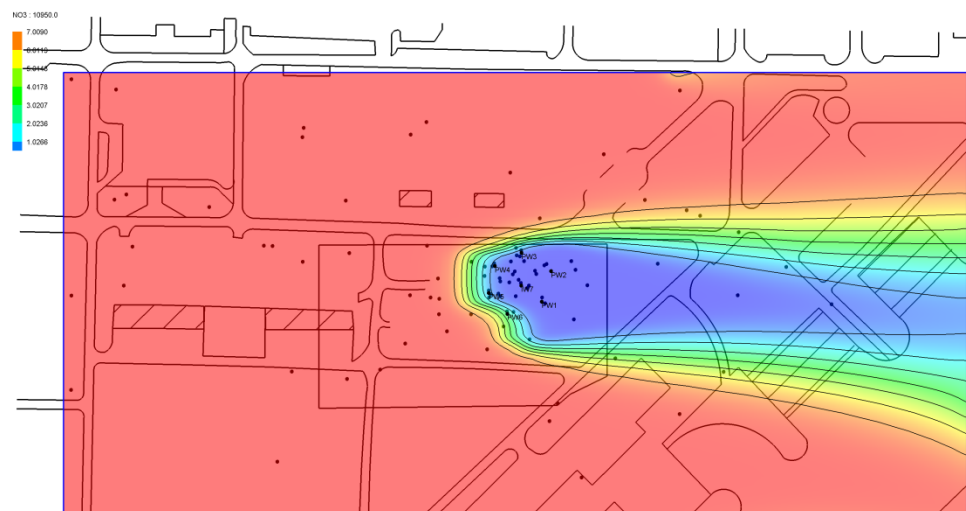
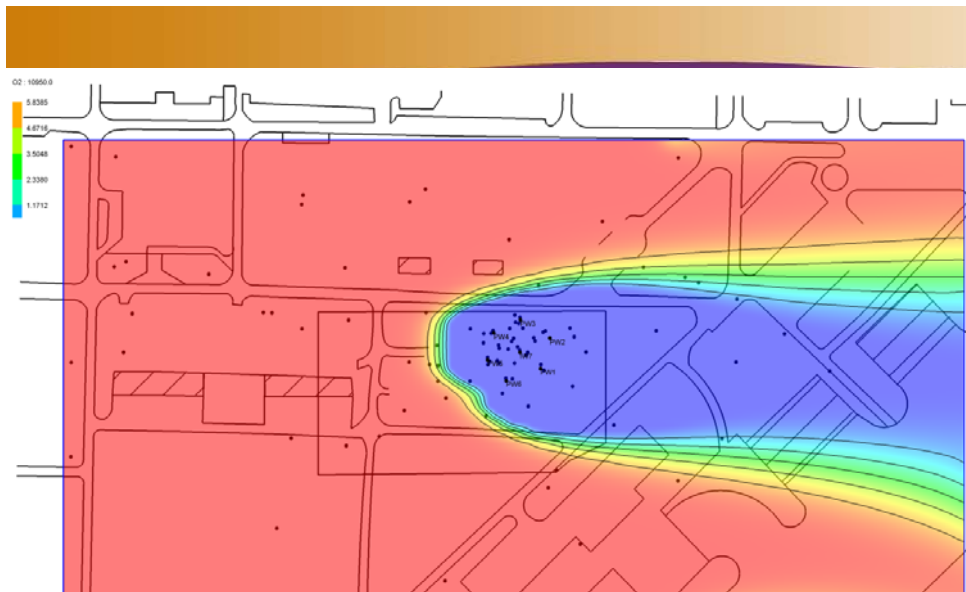
# Biodegradation

- Hydrocarbon Biodegradation Sink Term
  - ◆ Sum of all applicable terminal electron-accepting processes (TEAPs)
  - ◆ Utilization rates for compound,  $i$  (TEAP-specific)

$$M_{snk,i}^{Bio} = \sum_{ea} v_{x,i,ea}^{\max} \left[ \frac{C_i}{K_{x,i,ea}^{ed} + C_i} \right] \left[ \frac{E_{ea}}{K_{x,le}^{ea} + E_{ea}} \right] I_{ea,li}$$







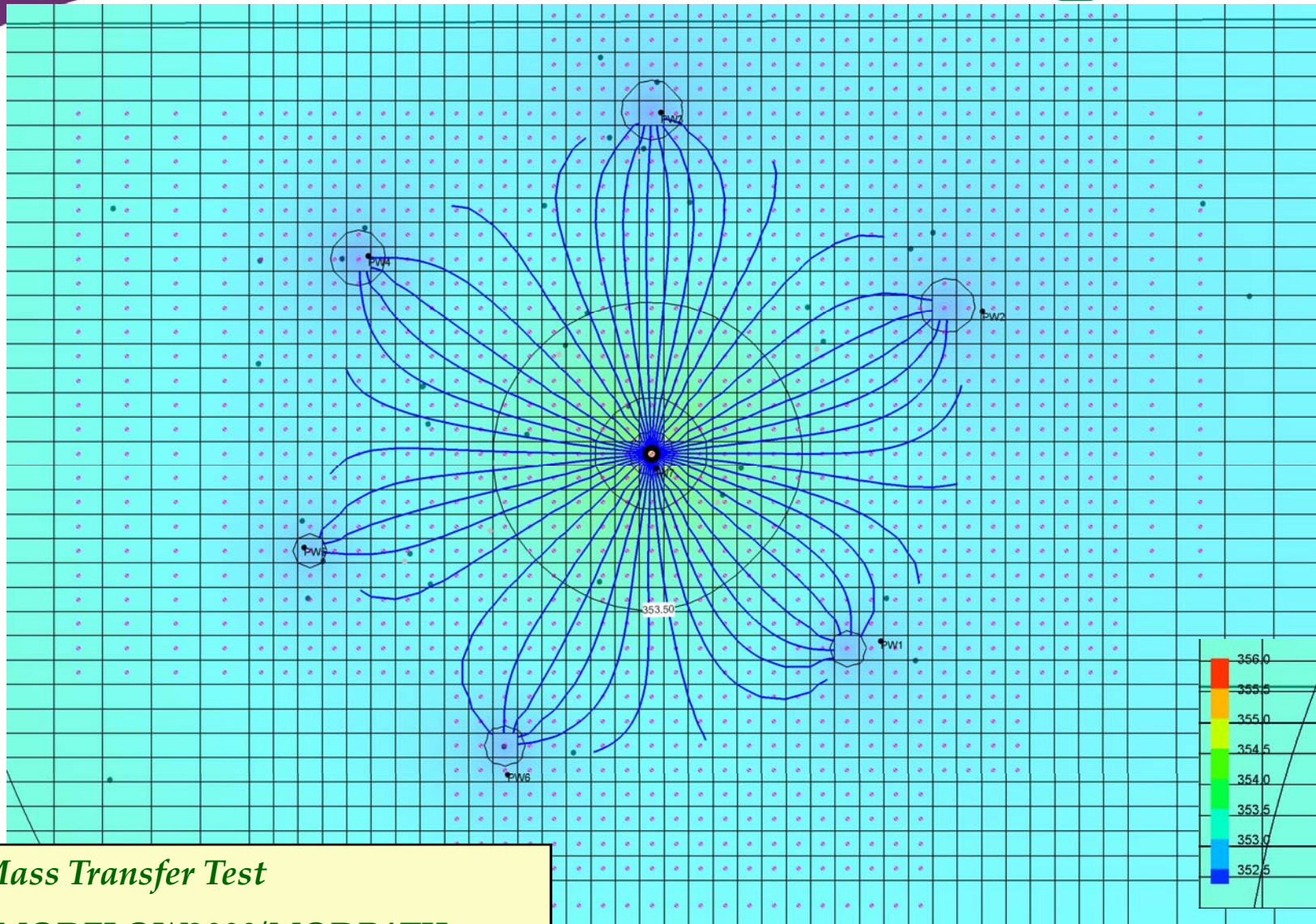
### Site Transport Model – SEAM3D

- Electron Acceptors (DO, NO<sub>3</sub>, SO<sub>4</sub>)
- Methane

## Model Validation - MTT

- Validation of the source zone model is accomplished by simulating the mass transfer test using MODFLOW and SEAM3D
- Steps
  - ◆ Improve resolution of model grid
  - ◆ Validate flow model
    - Injection/pumping data
    - Water level data
  - ◆ Refine NAPL mass estimates and mass transfer parameters
    - Estimates constrained by results of MTT data interpretation





### *Mass Transfer Test*

- MODFLOW2000/MODPATH
- Calibrated to Pre-TEE MTT

## Source Zone Model

- NAPL Dissolution – Hydrocarbon mass transfer is modeled using a first order mass transfer function:

$$M_{source,i}^{NAPL} = K(C_i^{eq} - C_i)$$

- K is a time-dependent mass transfer coefficient based on the upscaled mass transfer function

$$K(t) = k^{NAPL} \left( \frac{V}{V_o} \right)^{\Gamma}$$

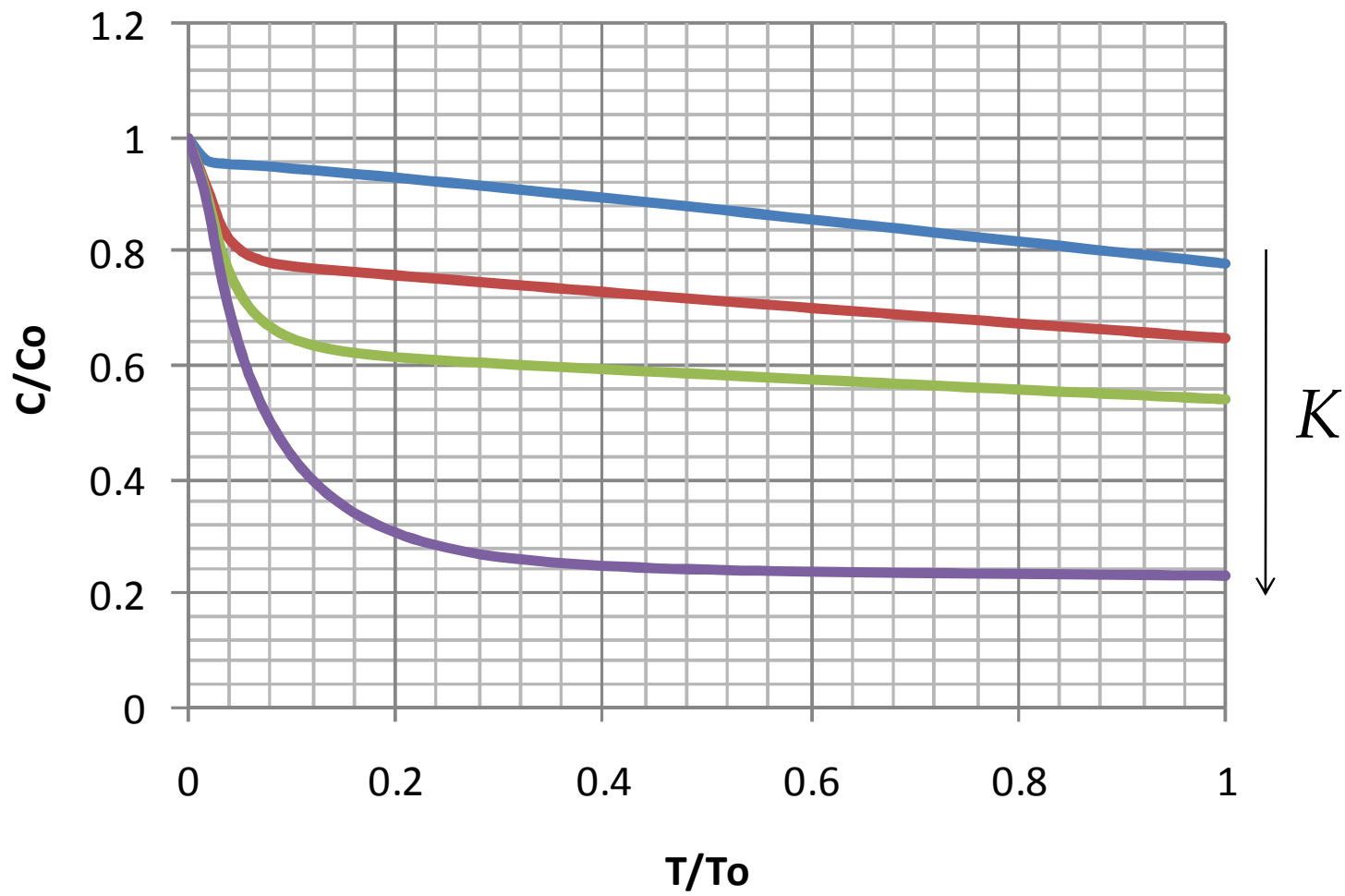
- ♦ V = volume of NAPL
- ♦  $k_{NAPL}$  = field-scale mass transfer coefficient
- ♦ G = upscaled mass transfer parameter
- ♦  $C_i^{eq}$  = equilibrium aqueous concentration

## Source Model – Initial Parameter Estimates

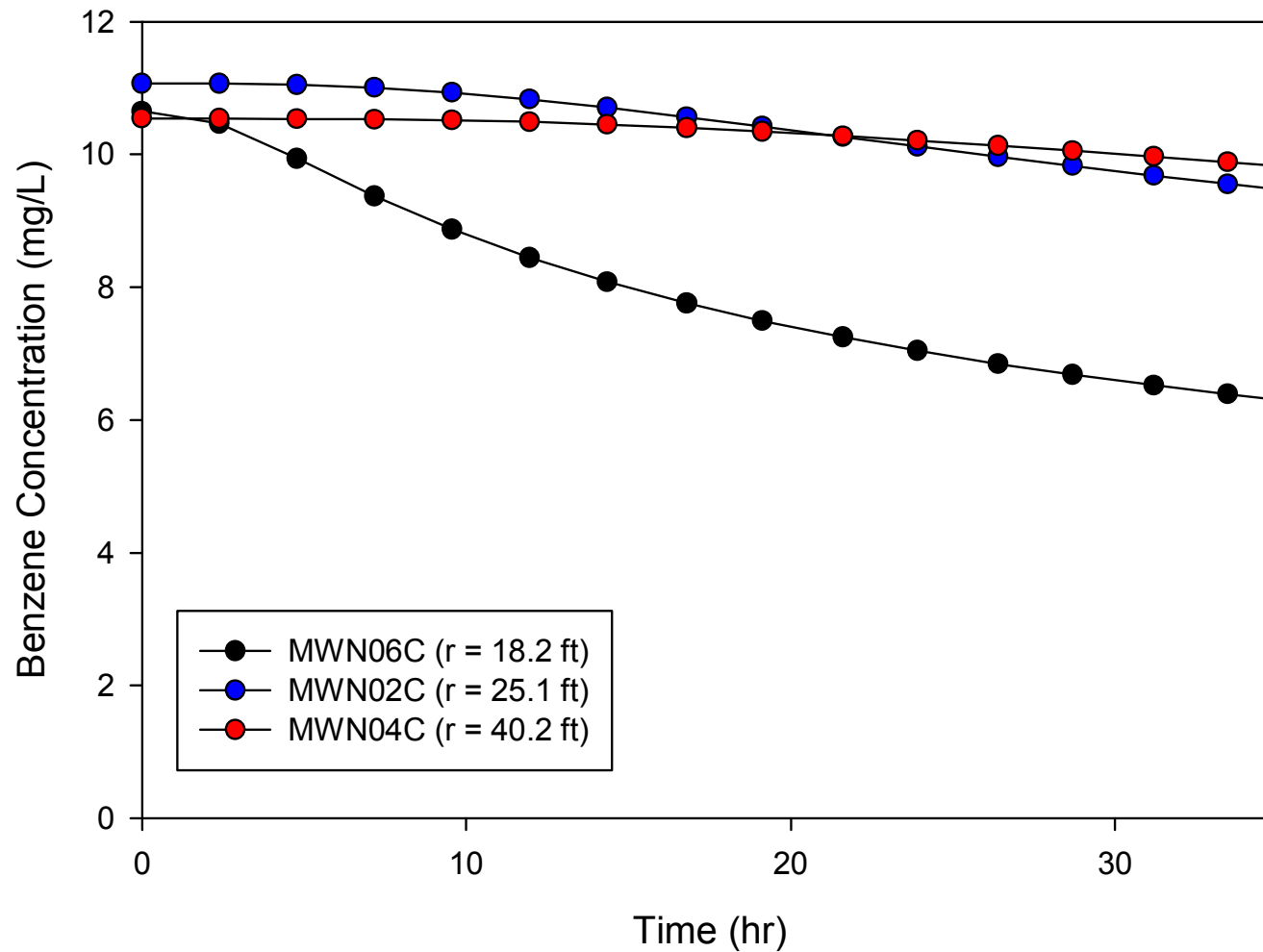
- Calibrated STA model input parameters
- Pre-test monitoring well data – contaminant concentrations
  - ♦ NAPL source components – equilibrium concentrations
  - ♦ Composition of NAPL
- Results of MMT analysis
  - ♦ NAPL mass and distribution
  - ♦ Mass transfer rate



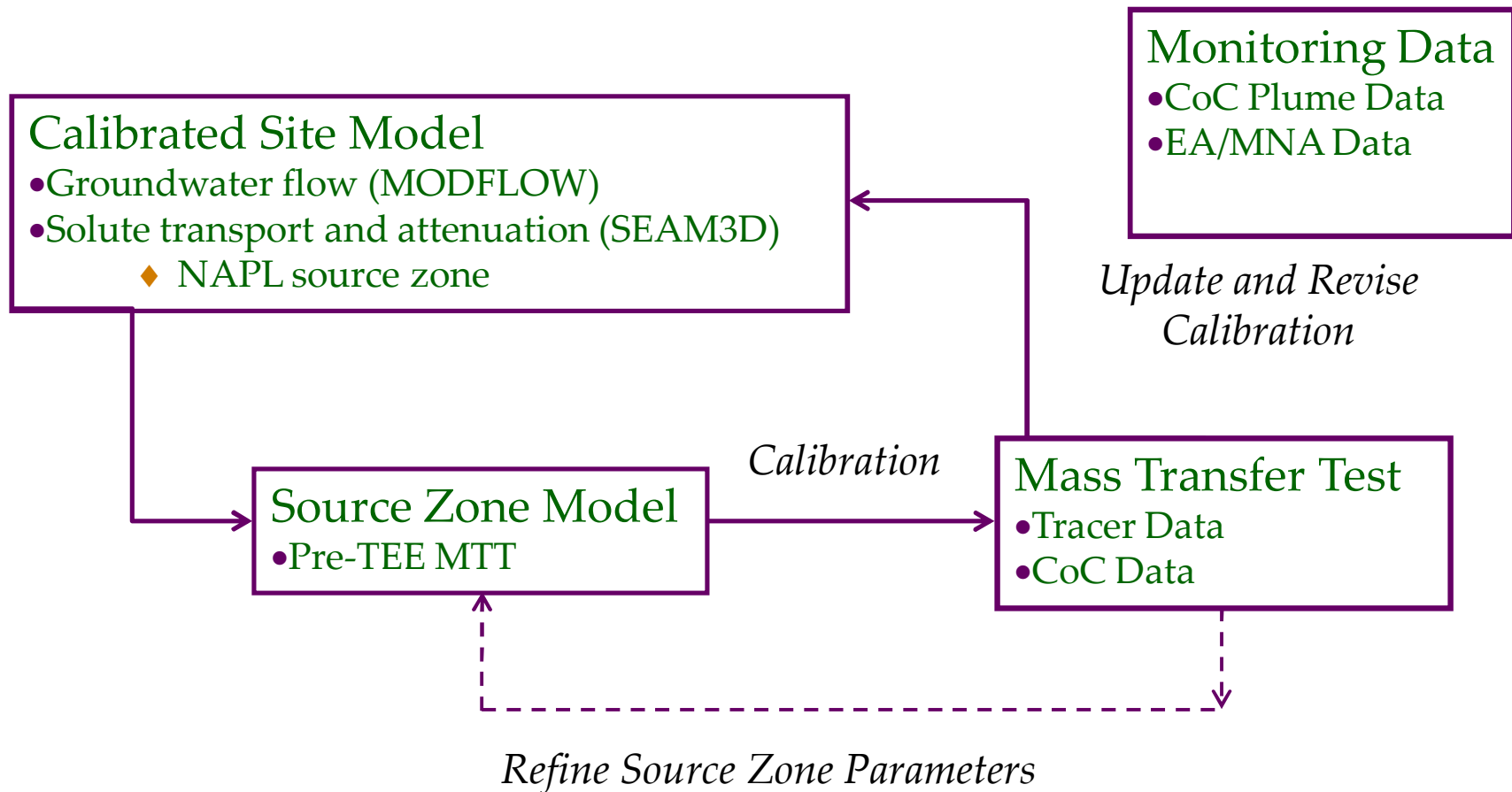
## Breakthrough Curves (Pre-TEE)



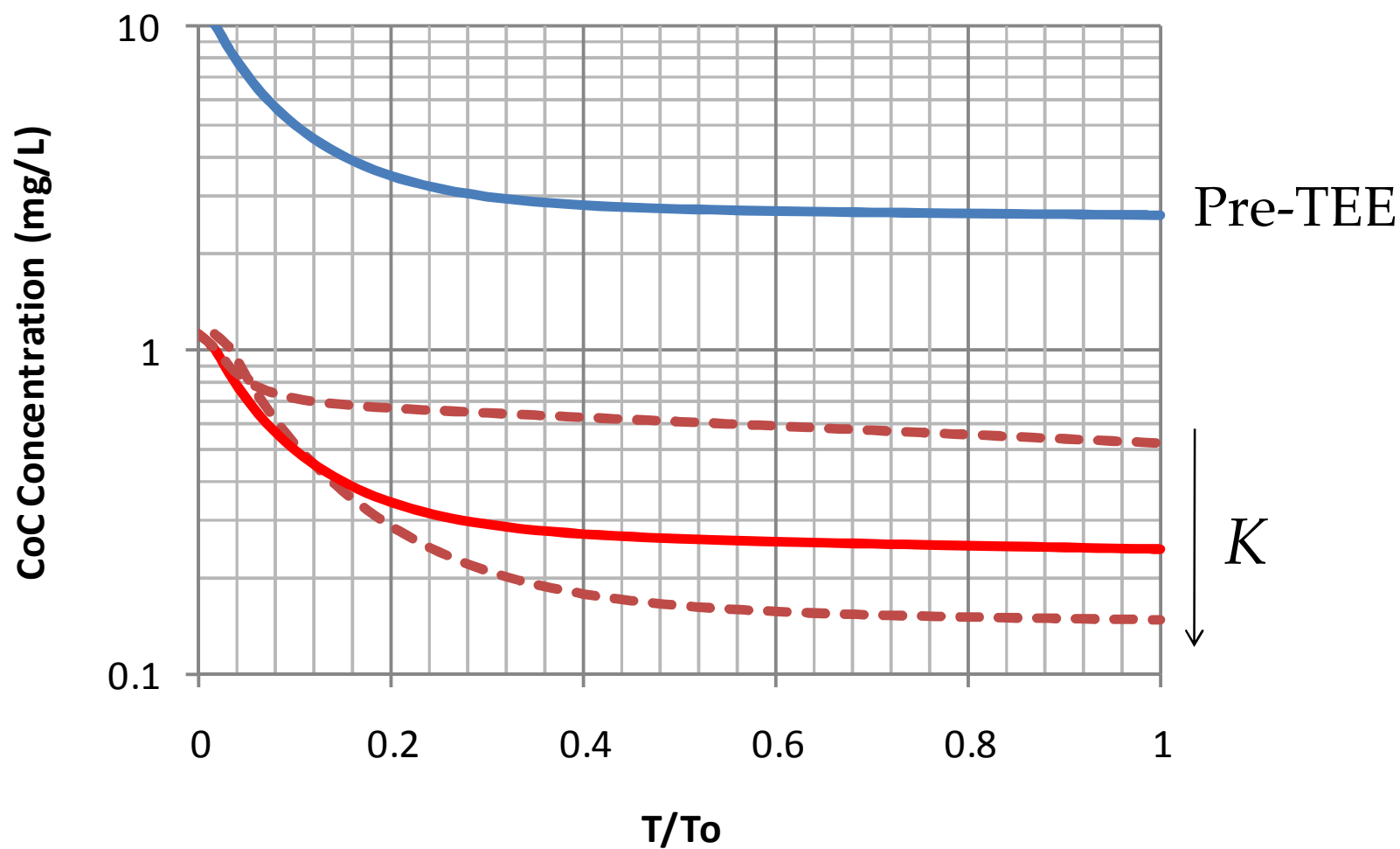
## Breakthrough Curves (Pre-TEE)



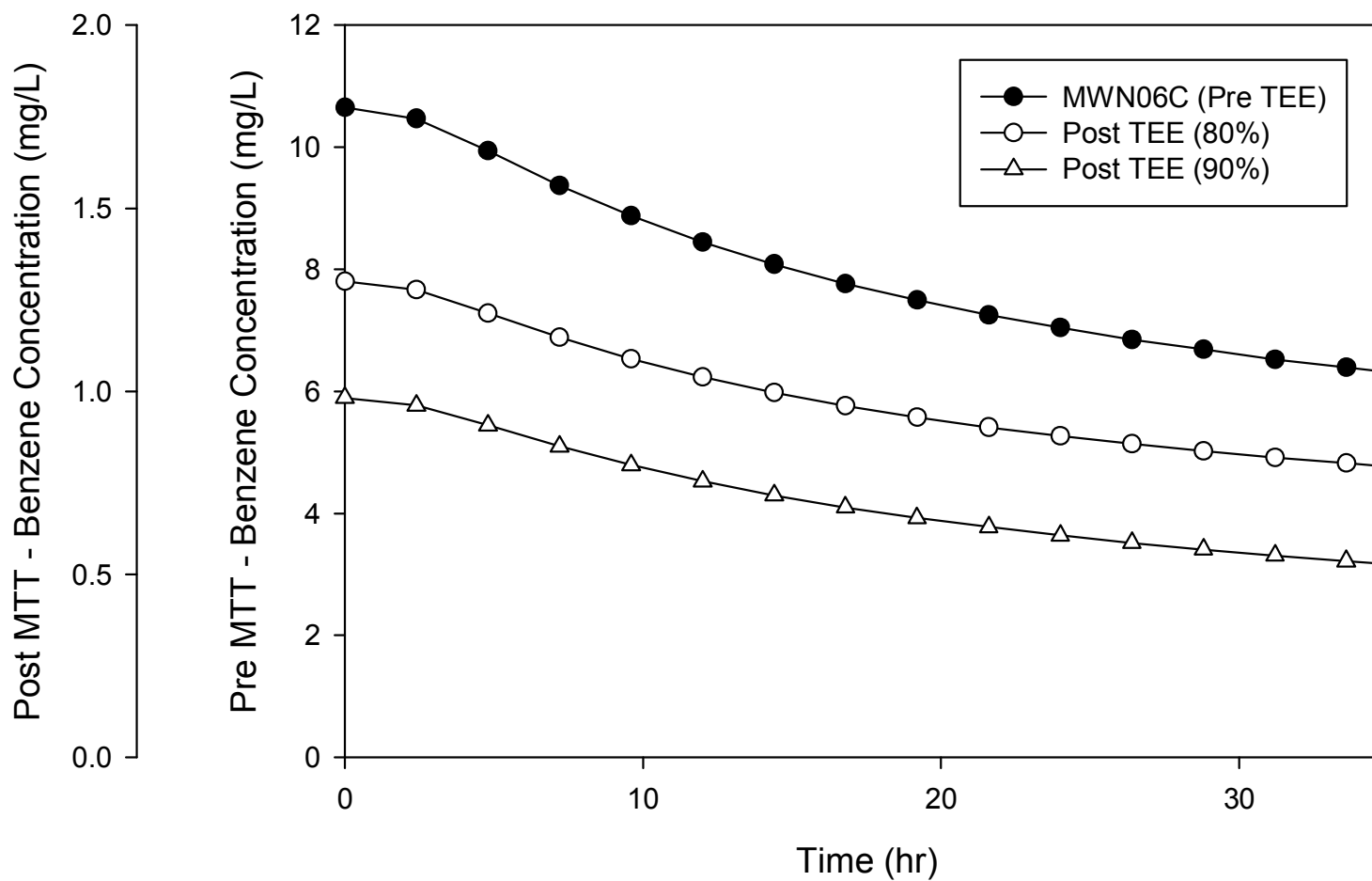
# Source Model – Parameter Revision



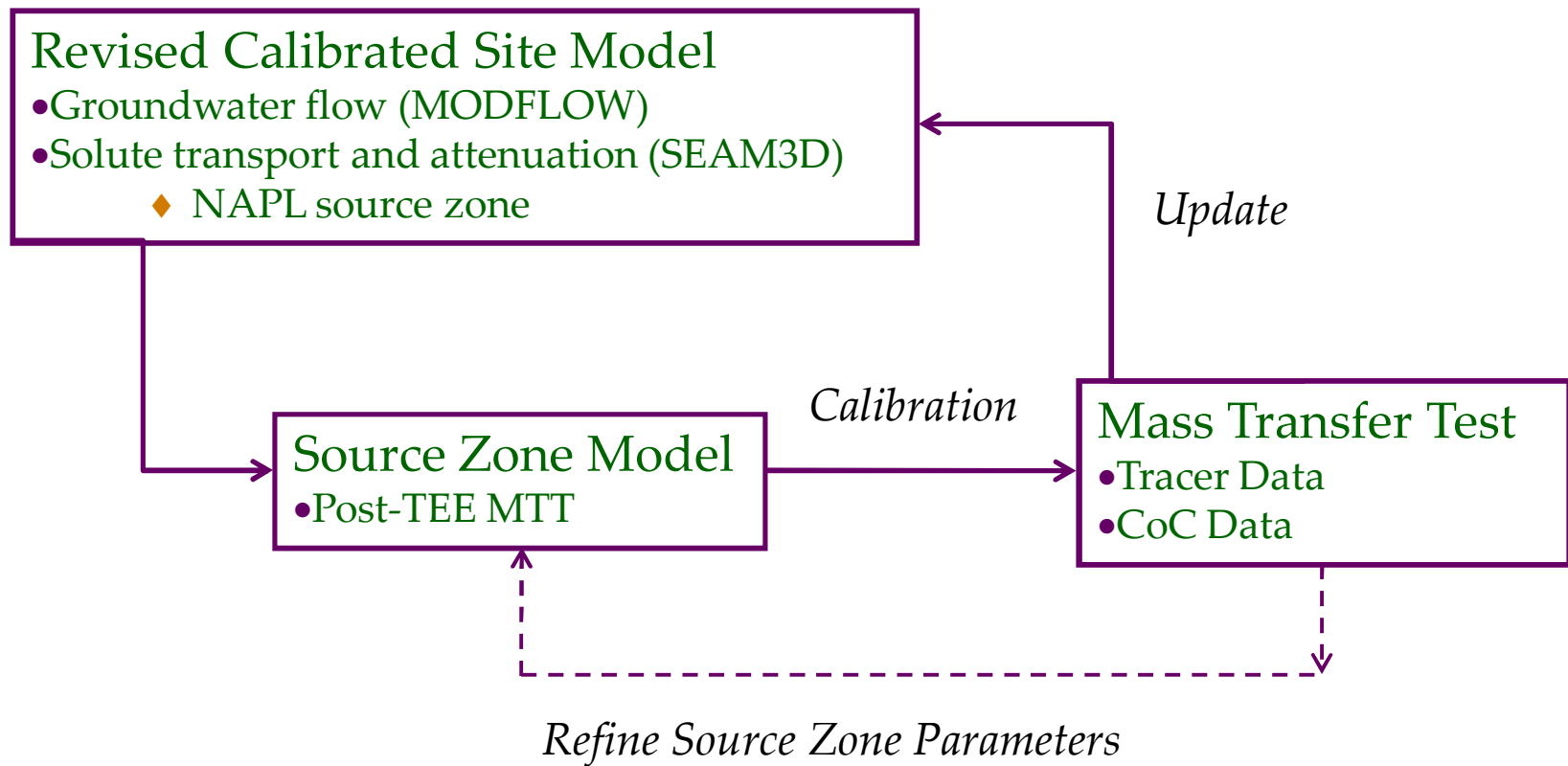
## Breakthrough Curves (Post-TEE)



## Breakthrough Curves (Post-TEE)



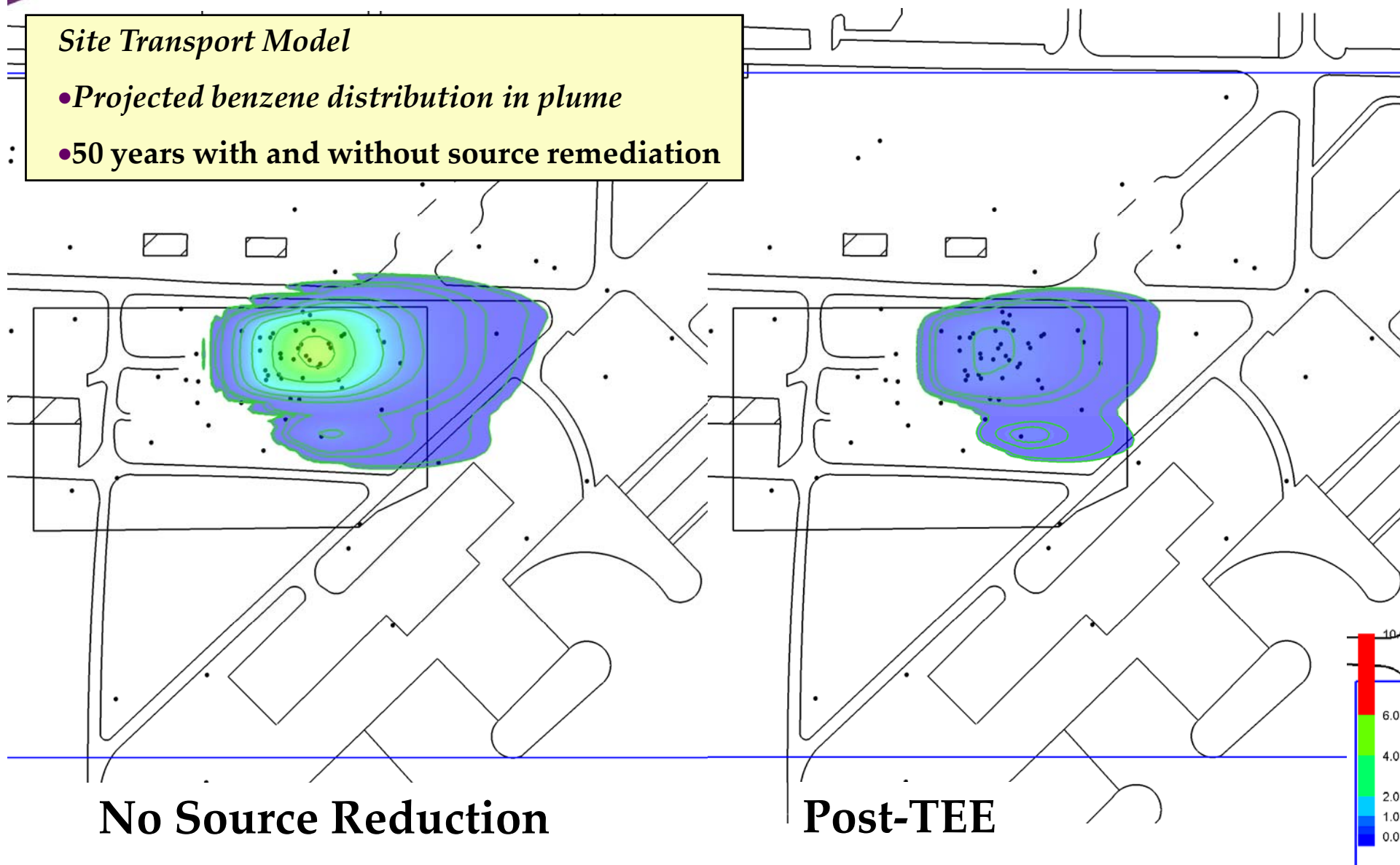
# Source Model – Post Remediation





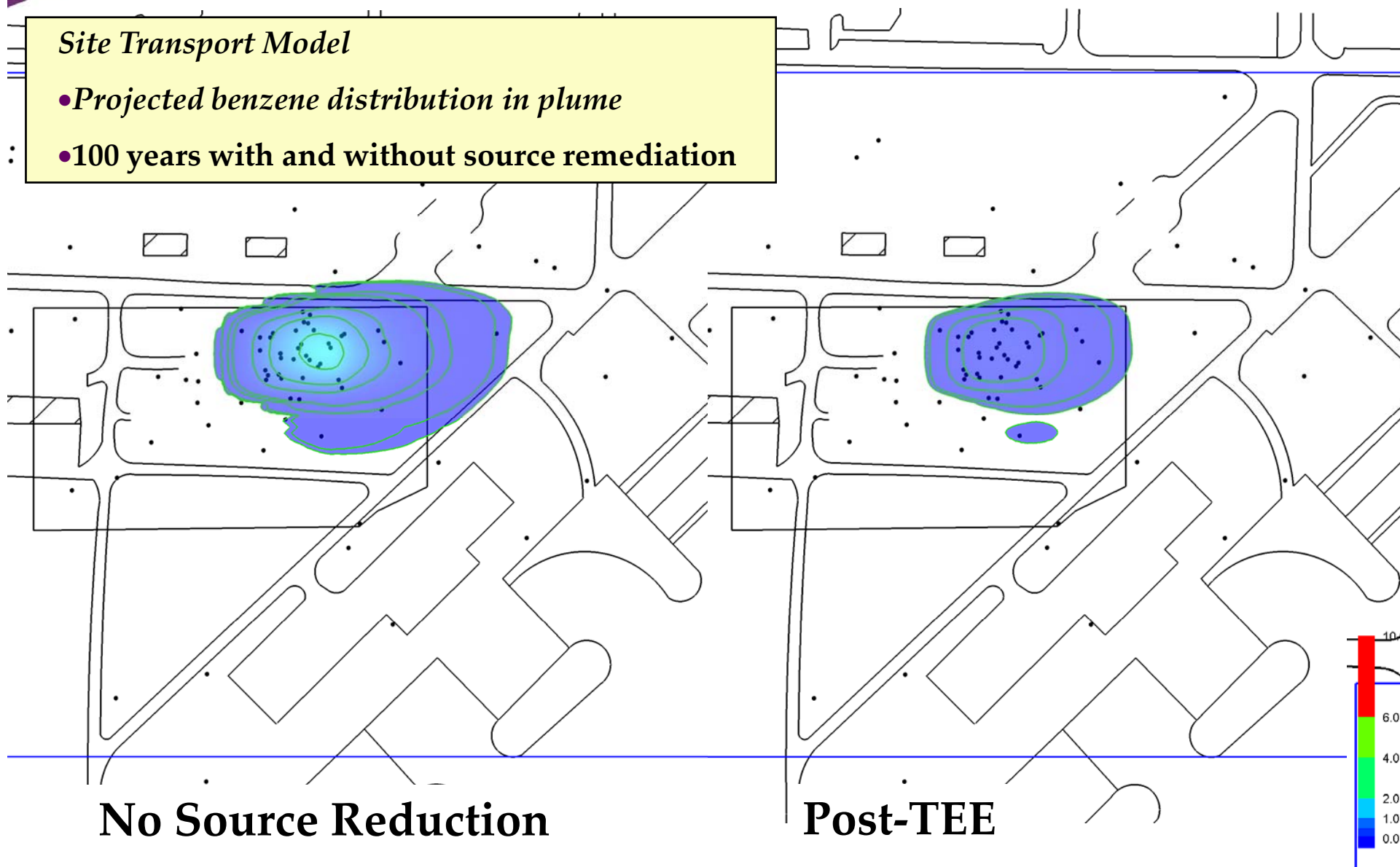
### Site Transport Model

- *Projected benzene distribution in plume*
- 50 years with and without source remediation



### Site Transport Model

- *Projected benzene distribution in plume*
- 100 years with and without source remediation



# Conclusions: Decision-Making Tool for NAPL Source Zones

- Overview of tool
  - ◆ Combination of innovative field measurements and interpretation using a computational model
  - ◆ Measurement of mass dissolution rate from the source zone
  - ◆ Modeling source term to predict future mass dissolution rates and plume longevity
- Advantages
  - ◆ Testing and analytical tool for evaluating multiple scenarios for source zone reduction and plume longevity
  - ◆ Reduces uncertainty associated with remedial timeframe estimates – additional data collection constrains model input parameters that control source depletion and plume longevity

# Conclusions: Decision-Making Tool for NAPL Source Zones (Continued)

- Limitations
  - ◆ Mass transfer coefficients may not be applicable across a site
    - Does the test accurately measure mass transfer from low permeability units?
  - ◆ Model predictions are dependent on NAPL mass estimates that may vary widely within the source zone
- Cost
  - ◆ Application of this tool will require a monetary investment
  - ◆ Cost saving may be realized by use of available test infrastructure

# Short Course Agenda



SERDP



8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:20 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo