



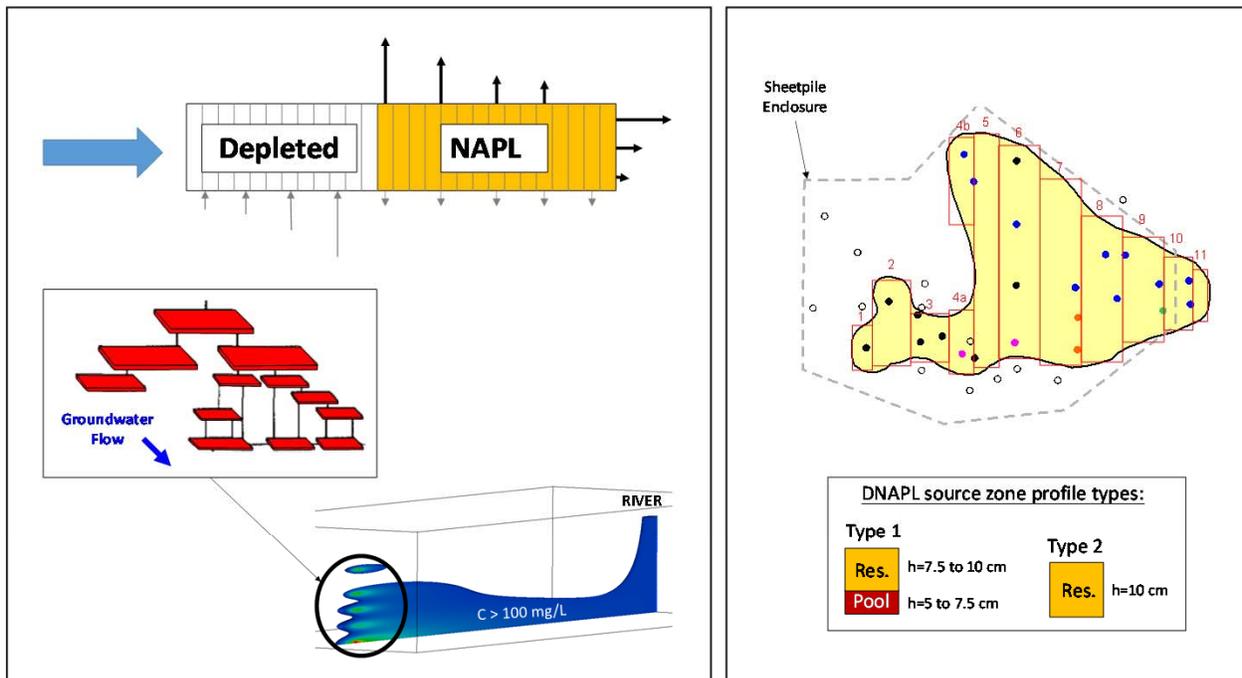
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Using the NAPL Depletion Model (NDM) for Estimating Natural and Enhanced Attenuation Timeframes

By Grant R. Carey, Ph.D.

Porewater Solutions
Ottawa, Ontario, Canada



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Bioremediation and Sustainable Technologies

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ABSTRACT:

Mass discharge from DNAPL source zones (i.e. *source strength*) will decline naturally over time as a result of dissolution and other processes occurring in the source zone. Although the naturally-occurring decline in source strength may be relatively fast, some form of in-situ treatment is often a regulatory requirement to reduce the source strength to the extent practicable. A target reduction in source strength is used at some sites as an interim compliance goal, for determining when to transition from active to passive source treatment.

Alternatives which may be used to enhance DNAPL dissolution, and accelerate the reduction in mass discharge from a source zone into a downgradient plume, include enhanced in-situ bioremediation (EISB), in-situ chemical oxidation (ISCO), and strategic pump-and-treat (SP&T). The selection of a technology for treating a DNAPL source zone is based in part on a cost-benefit-risk reduction analysis.

Two key questions arise when evaluating the relative benefit associated with enhanced DNAPL dissolution alternatives:

1. What is the attainable source strength reduction for an enhanced dissolution alternative?
2. How long will it take for an enhanced dissolution remedy to reach an interim compliance goal for source strength reduction?

Comparing the efficacy of MNA with that of enhanced remediation for a DNAPL source zone requires the estimation of attainable mass discharge reduction goals, and of the timeframe needed to achieve a target level of source strength reduction. This course presents fundamental concepts and hands-on exercises with a screening-level NAPL Depletion Model (NDM). The model is a Fortran-based program that enables users to better understand how key site characteristics influence attainable interim remedial goals and remediation timeframes.

NDM is useful as a screening tool for evaluating the relative timeframes for DNAPL source zone remedial alternatives, including MNA, EISB, ISCO, and SP&T to enhance dissolution. In addition, NDM may be used to provide input to solute transport models (e.g., REMCHLOR or MT3DMS) or to conduct a forensic analysis that helps refine the understanding of DNAPL architecture at a specific site.

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LEARNING OBJECTIVES:

After this course, participants will be able to:

1. Explain why mass discharge from DNAPL source zones declines over time, and identify the type of model (e.g. linear, exponential, or power) which is typically used to represent this source strength decline.
2. Identify the average source strength reduction attained during implementation of ISCO, EISB, and thermal remedies at other sites, which may be used as the basis for estimating an attainable site-specific interim compliance goal.
3. Use simple spreadsheet models to estimate mass discharge and mass remaining trends for a mixed DNAPL source zone (e.g. Falta et al., 2005), or for surface dissolution from a single DNAPL pool (Johnson and Pankow, 1992), and list the main limitation associated with each of these models with respect to remediation timeframe estimation.
4. Use the NAPL Depletion Model to simulate naturally-occurring and enhanced attenuation timeframes for mixed DNAPL source zones (i.e. “box model”), DNAPL pools, and/or layers of residual DNAPL.
5. List at least three site characteristics which have a significant influence on the naturally-occurring or enhanced DNAPL depletion timeframe.
6. Identify the typical range for DNAPL pool thickness observed at the field-scale for aged chlorinated solvent sites.
7. Use a spreadsheet model to estimate how the relative water permeability varies with NAPL saturation.
8. Use various regression equations to estimate NAPL Depletion Model input parameters for a wide range of soil textures (based on hydraulic conductivity) including: effective and total porosity, tortuosity coefficient, transverse dispersivity, irreducible water saturation, and the pore size distribution index and entry pressure-based parameters for the Van Genuchten permeability model.

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	Section 3b	Single DNAPL Pool
	Section 3c	Multiple Pools
	Section 3d	Residual DNAPL Layer
	Section 3e	Multicomponent NAPL Dissolution
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TAB 5	Section 5	Summary and References
TAB 6	Appendix A	Curriculum Vita
TAB 7	Appendix B	NAPL Depletion Model (NDM) Governing Equations
TAB 8	Appendix C	REMTEC 2015 Presentation: ISR-MT3DMS for Estimating Back-Diffusion Remediation Timeframe

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BIOGRAPHY:

Grant Carey is President of Porewater Solutions, and specializes in litigation, modeling, DNAPL, and chemical fate. Grant has worked on hundreds of projects across North America over the past twenty-five years. Grant has a B.A.Sc. degree from the University of Waterloo, a Masters degree in Civil Engineering from Carleton University (Ottawa, Ontario), and recently completed his Ph.D. at the University of Guelph, with a focus on quantifying the relative cost, benefit, and limitations associated with partial DNAPL remediation alternatives.

Grant has developed public domain and commercial software used for modeling and visualization of reactive transport in groundwater, including the NAPL Depletion Model, BioRedox-MT3DMS and the Remediation ToolKit (SEQUENCE, BioTrends, and BioTracker). Grant is currently developing a state-of-the-art reactive transport model called In Situ Remediation (ISR-MT3DMS), which includes a novel method for simulating back-diffusion remediation timeframes. Grant has published more than 90 courses, presentations, and papers, and is currently a trainer for the ITRC web seminars on Mass Flux and Mass Discharge, and Remediation of Contaminated Sediments.

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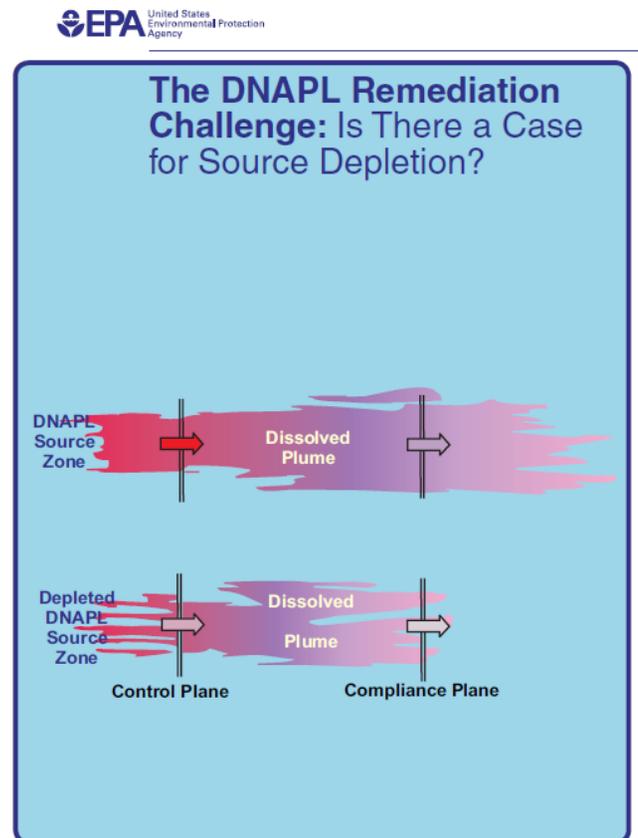
Course Overview

Section 1



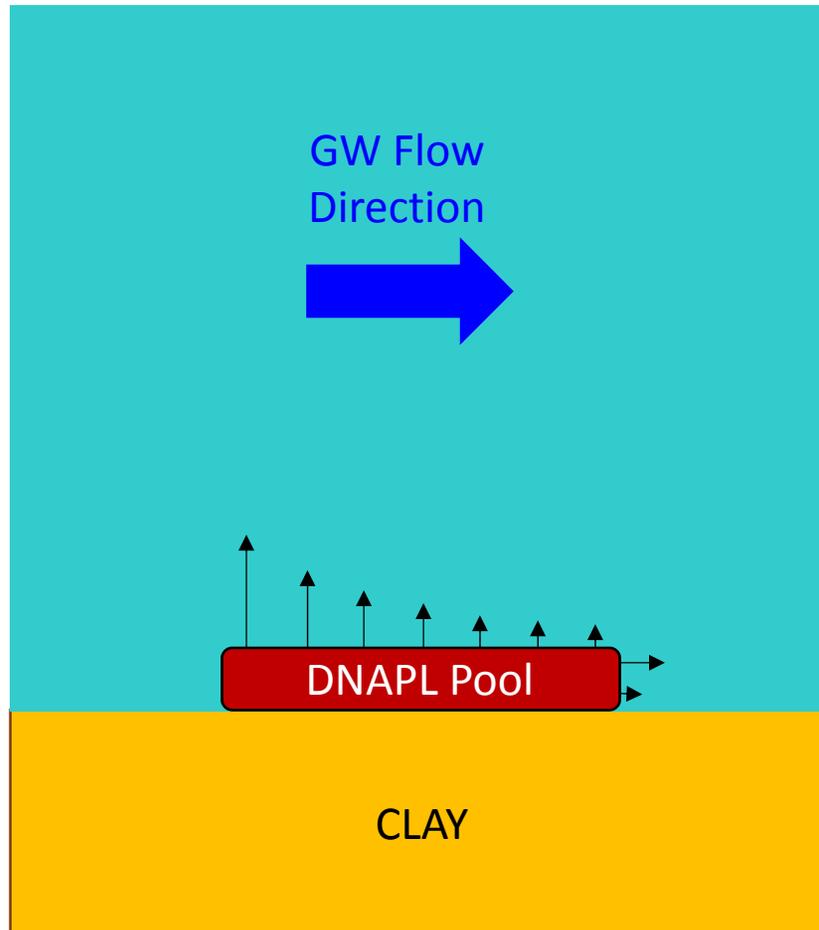
NAPL Source Depletion

- Thousands of contaminated sites
 - NAPL is or was present
 - Naturally-occurring dissolution
 - Years to centuries before depleted
 - Regulated treatment or containment
 - Diffusion – decades to centuries+
- DNAPL Remediation challenges:
 1. Attainable Goals, Timeframe
 2. Source cleanup versus MNA+plume mgt
- **Need for NAPL screening models**
 - Improved understanding
 - **More reliable estimates – time and \$\$\$**



Kavanaugh et al., 2003

DNAPL Source Zones – Single Pool Sub-zone

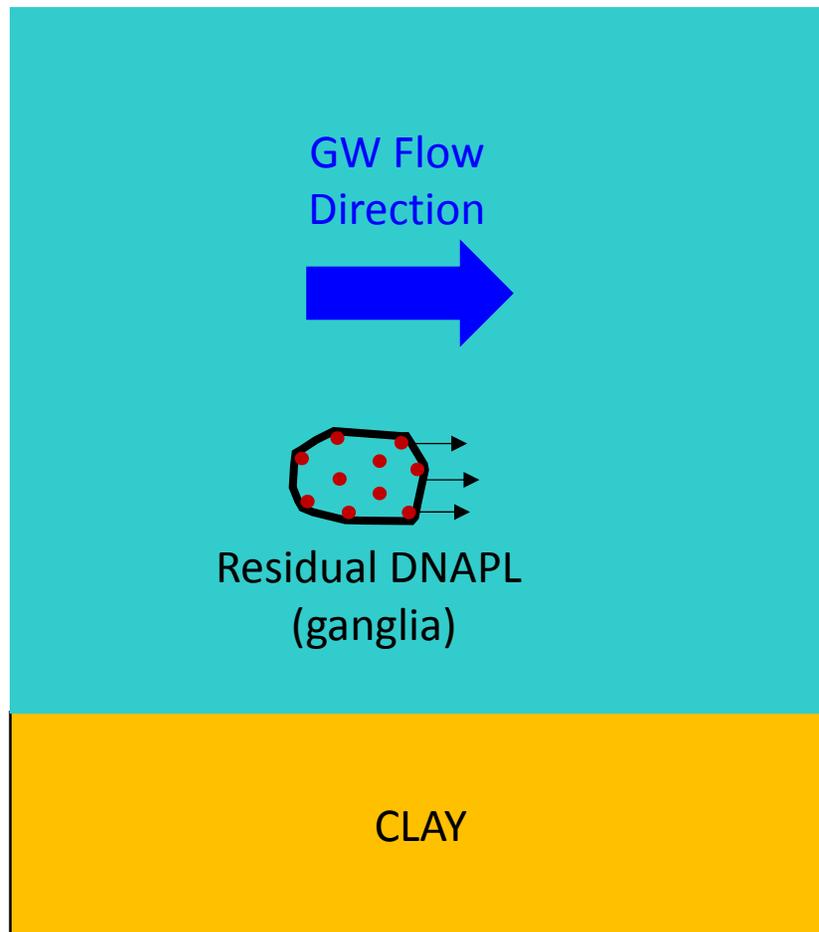


Source strength decline due to:

- Decline in NAPL-water interfacial area (i.e. pool length)



DNAPL Source Zones: Residual Sub-zone



Source strength decline due to:

- Decline in NAPL-water interfacial area
- Intra-source by-passing
 - Decline in mass removal efficiency

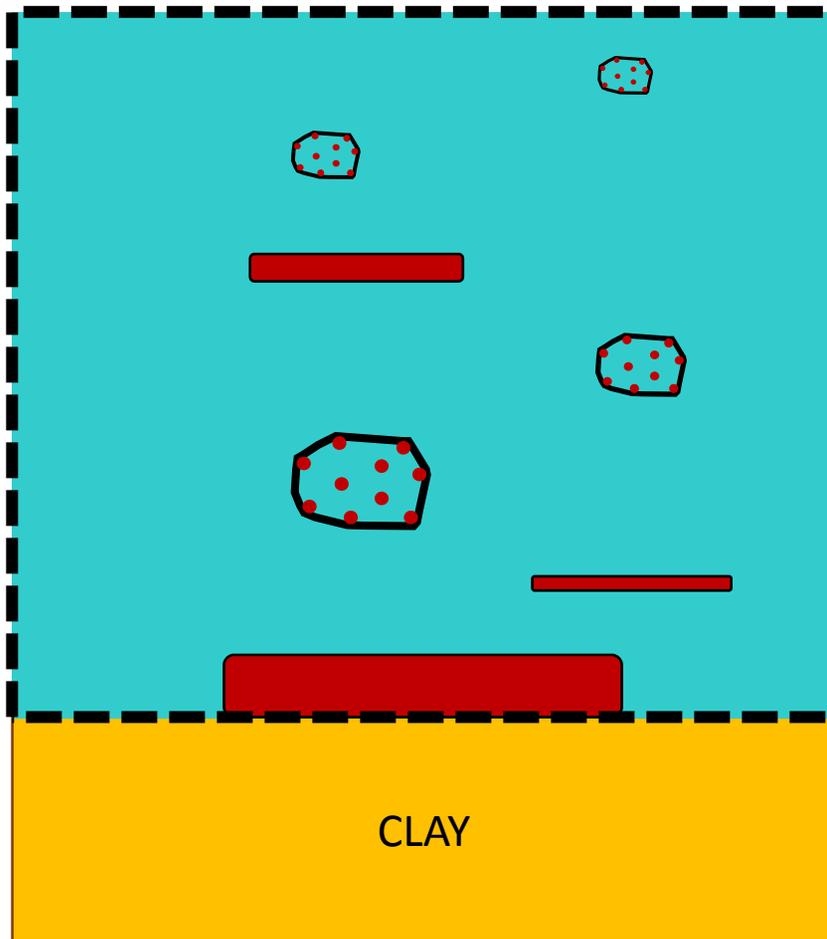


DNAPL Source Zones

- A source zone may consist of one or more sub-zones
- Each sub-zone → single pool or residual layer
- Plumes derived from each sub-zone are thin vertically
 - May be modeled individually, with a combined mass discharge (source strength) calculated over all sub-zones



DNAPL Source Zones: Mixed (Box Model)



Mixed source zones:

- Unable to distinguish smaller sub-zones
- Includes portions of aquifer without DNAPL (vertically and horizontally)
- Only able to model overall behavior
 - Mass discharge and mass remaining



DNAPL Depletion Models

- Academic – dissolution rate that declines with time
 - Parker and Park, 2004; Zhu and Sykes, 2004; Christ et al., 2006 and 2010
 - Predict mass discharge at each time step
 - Field-scale dissolution rates not predictable based on lab experiments

- Simple exponential decline rate: $Md = e^{-\lambda t}$

- Falta et al. (2005) Power Law Model: $Md/Md_o = (M/M_o)^\beta$

Md = mass discharge at time t (kg/y)

Md_o = mass discharge at time t (kg/y)

M = mass discharge at time t (kg)

M_o = mass discharge at time t (kg)

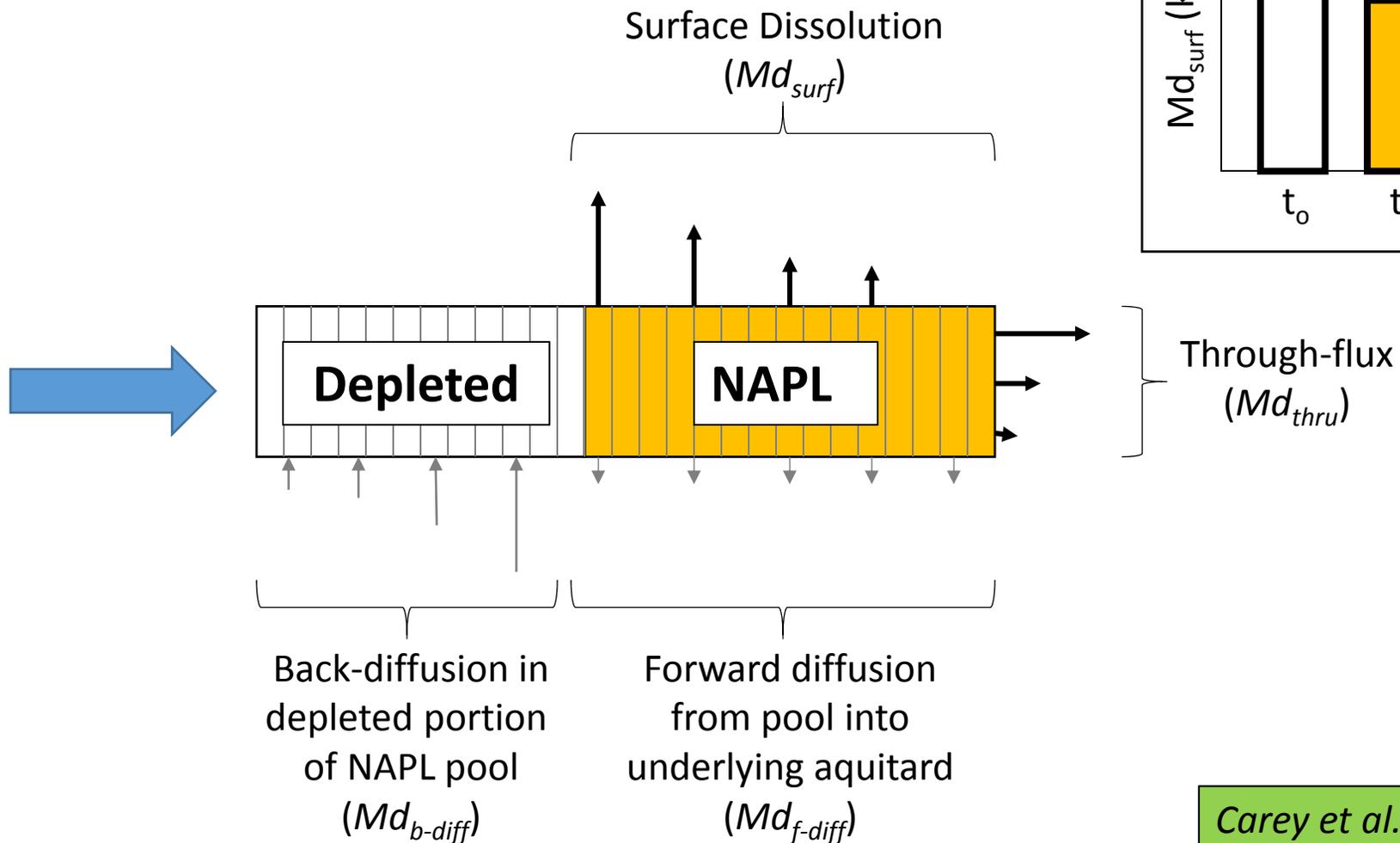
λ = source strength exponential decline rate (per time)

β = mass discharge at time t (dimensionless)



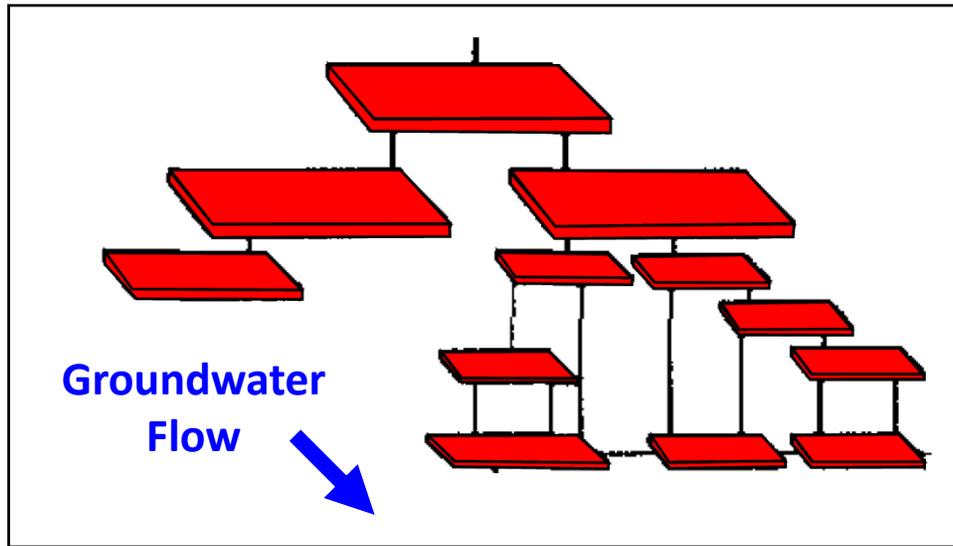
NAPL Depletion Model (NDM)

NAPL SUB-ZONE (i.e. layer)

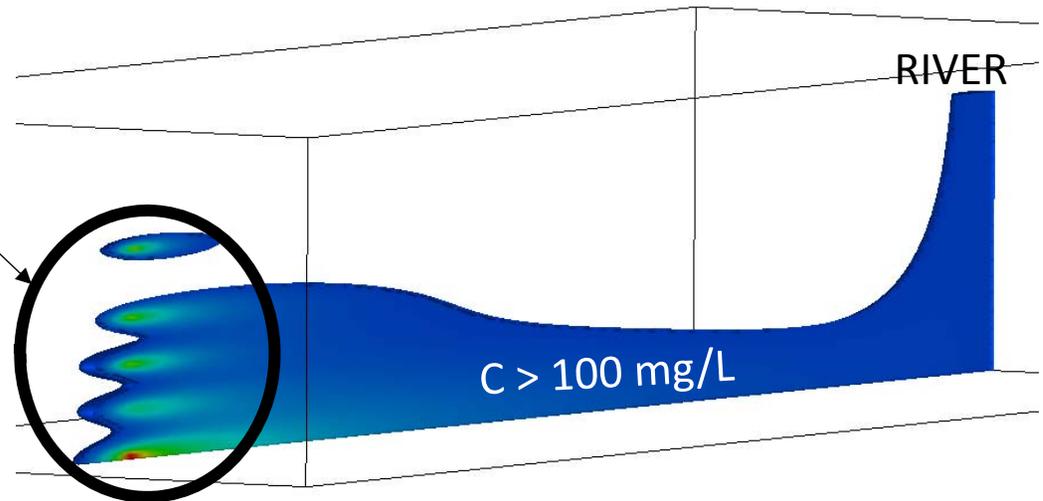


Carey et al. (2014a)

Source Zone Architecture



Modified from Anderson et al., 1992

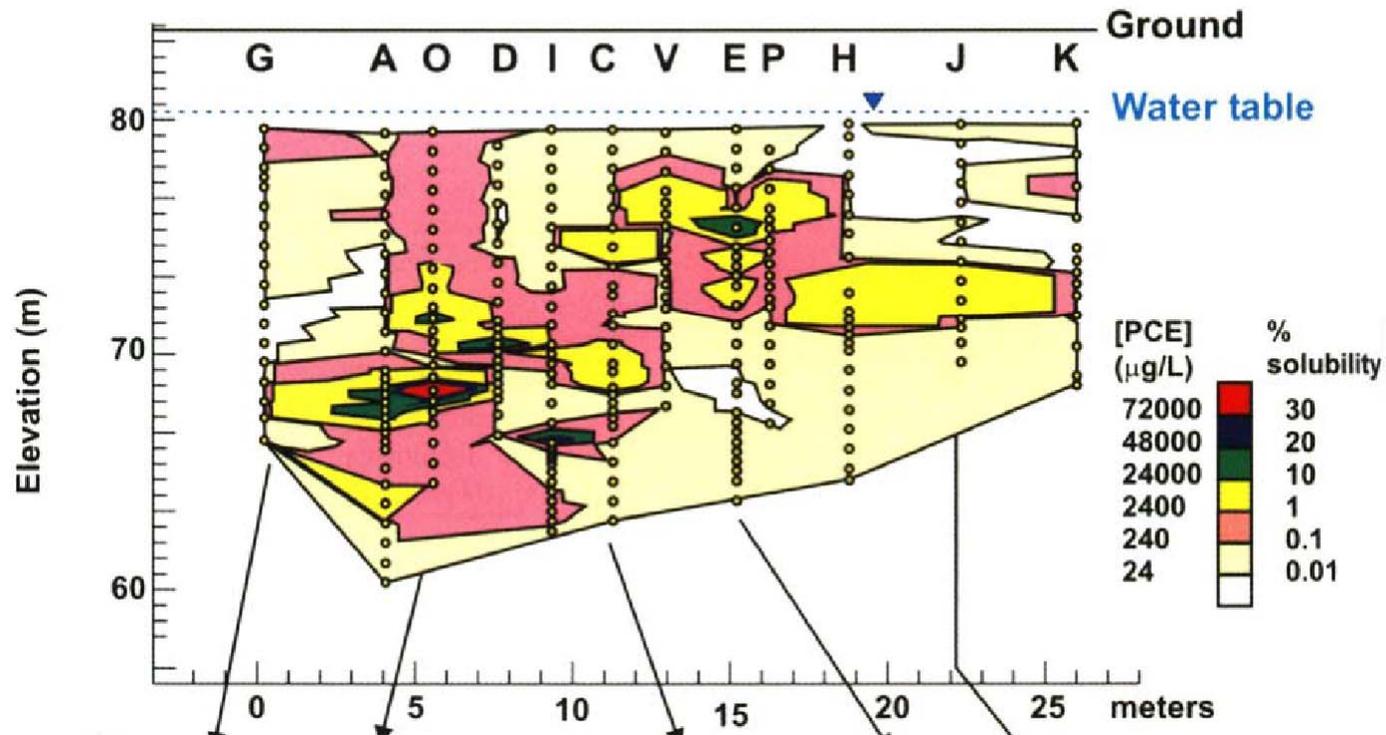


Carey et al. (2015e)



Source Zone Transect Example

New Hampshire PCE Site



Guilbeault et al. (2005)



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NDM Uses

- Depletion timeframes – natural and enhanced
 - Relative benefit of enhanced treatment
 - Input for cost calculations
- Identify critical properties that need additional characterization or investigation to reduce uncertainty
- Improved understanding of factors influencing NAPL depletion
- Interpretive model – calibrate / eliminate architecture scenarios (model vs. observed source strength trends)
- Input for transport models
 - MT3DMS: source strength vs. time
 - REMchlor: Power law model, timeframe for enhanced attenuation



2014/2015 Publications List

Carey, G.R., E.A. McBean, and S. Feenstra, **2014a**, DNAPL Source Depletion: 1. Predicting Rates and Timeframes, *Remediation Journal*, Summer 2014, p. 21-47.

Carey, G.R., E.A. McBean, and S. Feenstra, **2014b**, DNAPL Source Depletion: 2. Attainable Goals and Cost-Benefit Analyses, *Remediation Journal*, Autumn 2014, p. 79-106.

Carey, G.R., E.A. McBean, and S. Feenstra, **2015a**, Estimating Tortuosity Coefficient based on Hydraulic Conductivity, submitted to *Ground Water* (in review).

Carey, G.R., E.A. McBean, and S. Feenstra, **2015b**, Estimating Transverse Dispersivity Based on Hydraulic Conductivity, in preparation for submittal to *Transport Processes in Porous Media*.

Carey, G.R., E.A. McBean, and S. Feenstra, **2015c**, Through-Discharge Decline Rate for Layers of Residual DNAPL: 1. Field-scale multicomponent source, in preparation for submittal to *Water Resources Research*.

Carey, G.R., E.A. McBean, and S. Feenstra, **2015d**, Through-Discharge Decline Rate for Layers of Residual DNAPL: 2. Empirical Regression, in preparation for submittal to *Water Resources Research*.

McGregor, R. and G. Carey, **2015**, Long Term Study of Oxidant Injection into a Fractured Limestone Aquifer Impacted by Petroleum Hydrocarbons, in preparation for submittal to *Remediation Journal*

Carey, G.R. and R. McGregor, **2015**, ISR-MT3DMS for Modeling Back-Diffusion Remediation Timeframe, in preparation for submittal to *Remediation Journal*.

Carey, G.R., E.A. McBean, and S. Feenstra, **2015e**, NAPL Depletion Model Development and Case Studies: 1. Natural Dissolution, in preparation.

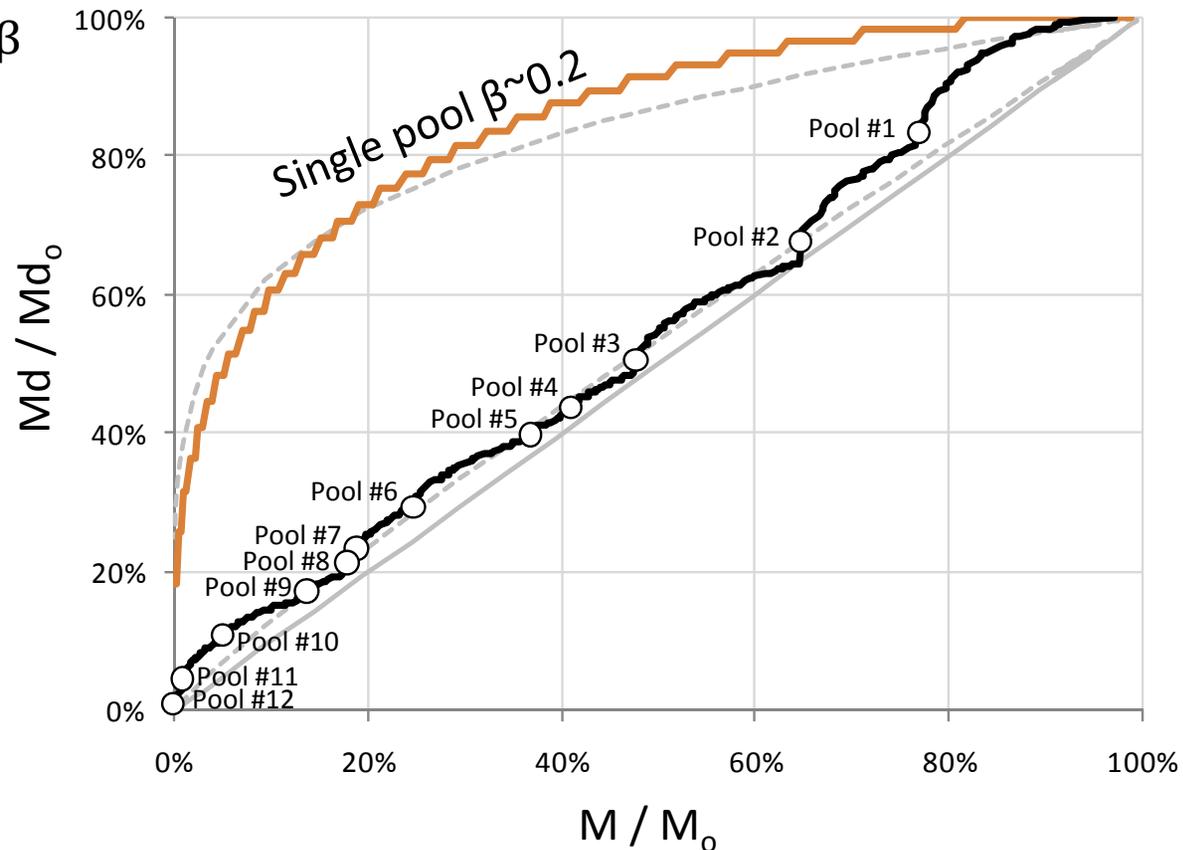
Carey, G.R., E.A. McBean, and S. Feenstra, **2015f**, NAPL Depletion Model Development and Case Studies: 2. Enhanced Dissolution, in preparation.



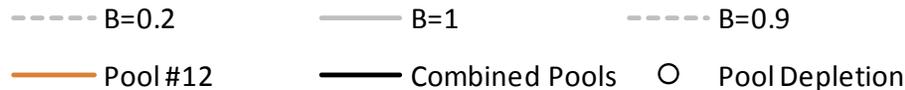
MdR vs. MR for Single & Multiple Pools

Multiple pools with heterogeneous thickness → exponential Md decline

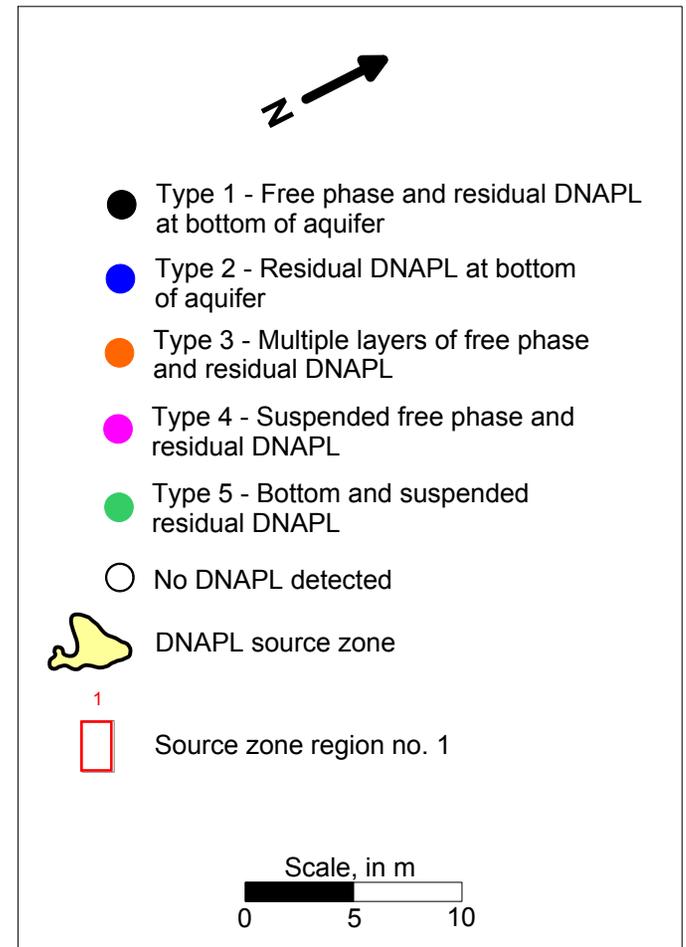
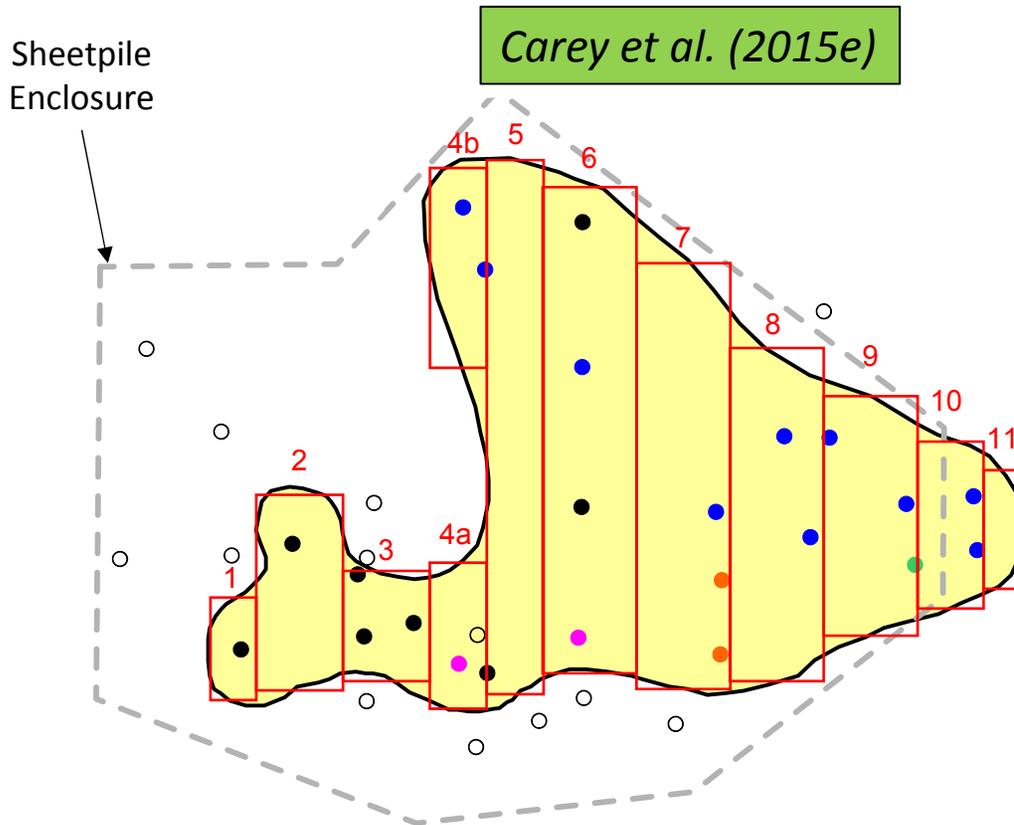
$$\frac{Md}{Md_o} = \left(\frac{M}{M_o} \right)^\beta$$



Carey et al. (2015e)

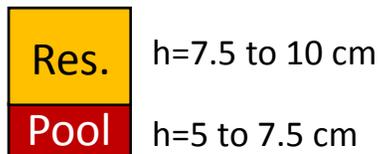


Example - CT Site Sub-Zones (plan view)

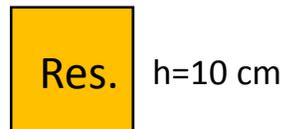


DNAPL source zone profile types:

Type 1

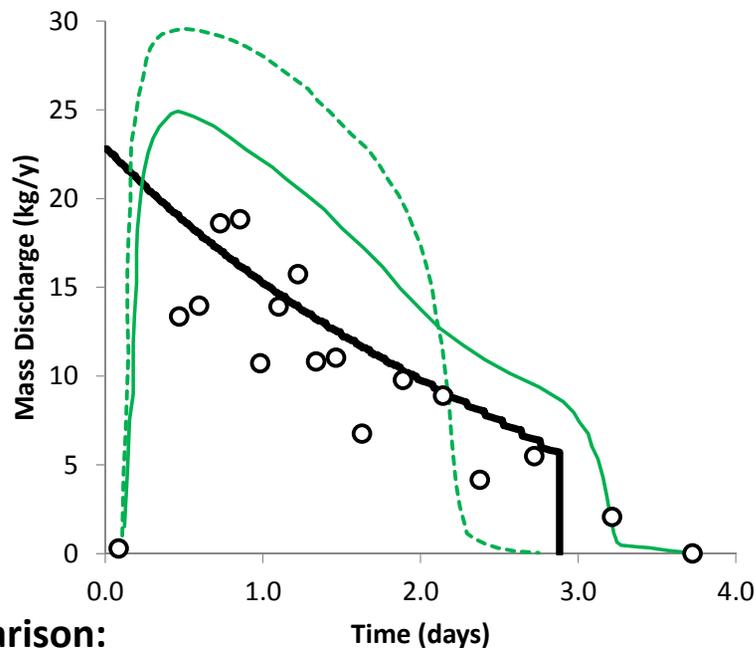


Type 2

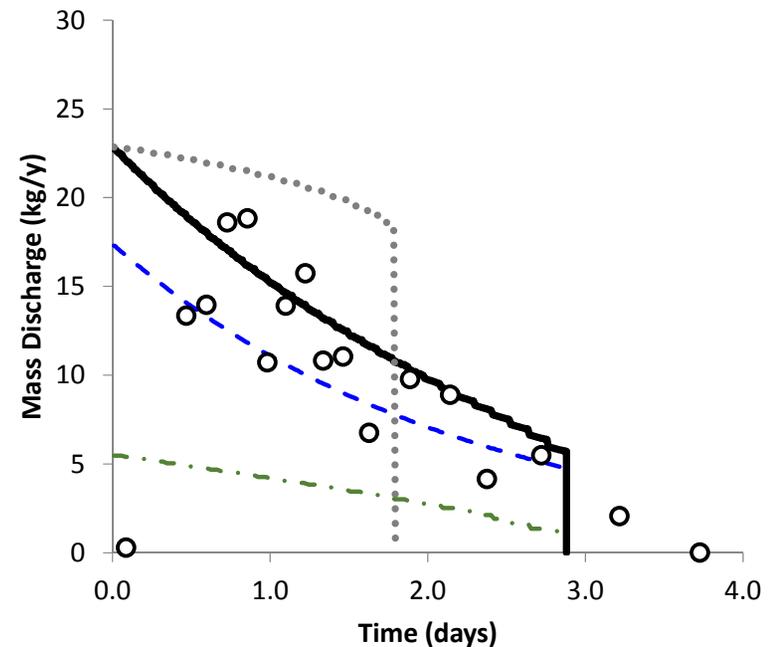


Model of Brusseau et al. (2002) Experiment

(a) Comparison of NDM and Brusseau et al. (2002) numerical results



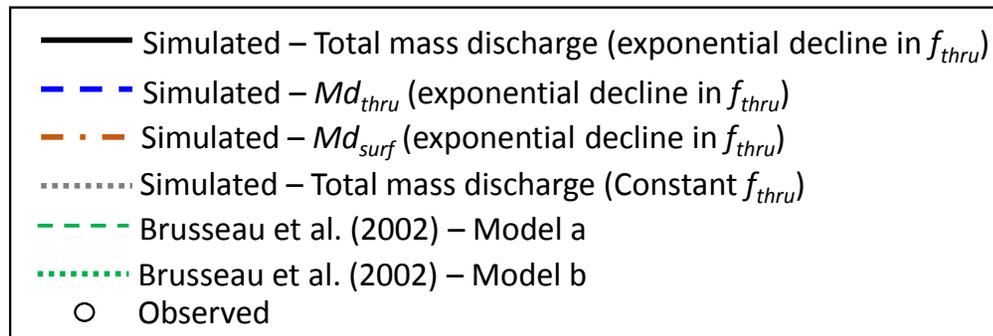
(b) NDM simulation results – Md_{tot} , Md_{surf} and Md_{thru}



Model comparison:

Carey et al. (2015d)
1D NDM model: 33 cells
Calibrated input: none

Brusseau et al. (2002)
3D model: 18,000 cells
Calibrated input: diss. rate

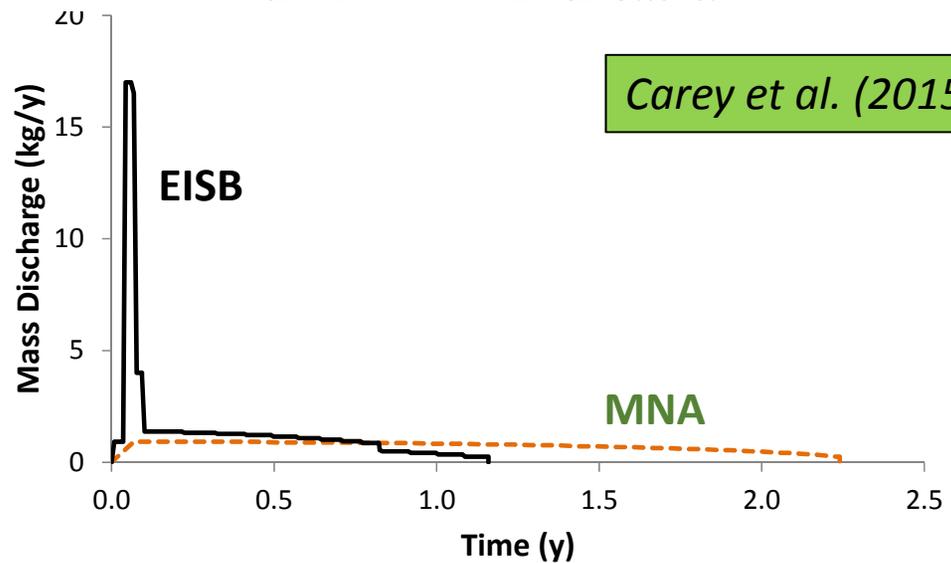
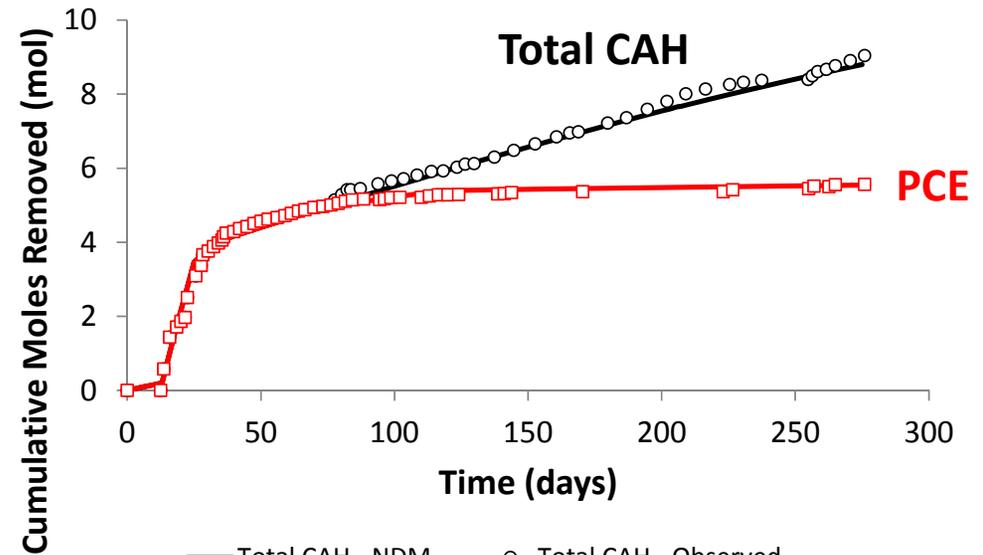


NDM Validation to Lab Studies

Ward et al., 2009 (EISB of PCE Pool)

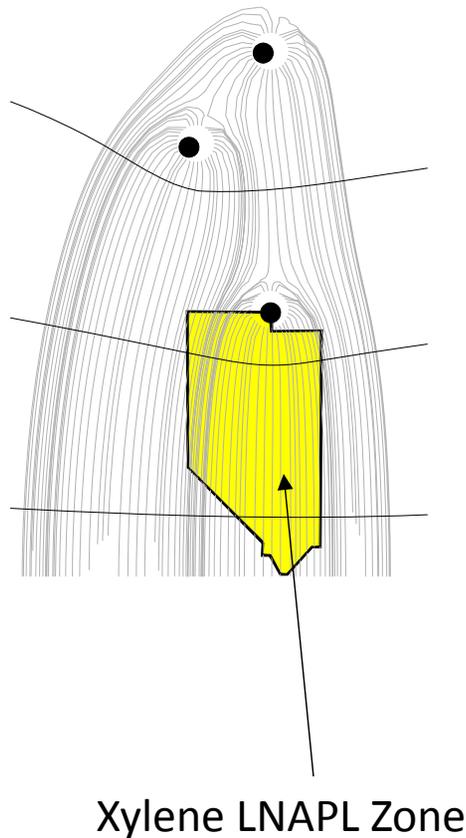


Ward, 2009, ESTCP ER-0438



Carey et al. (2015f)

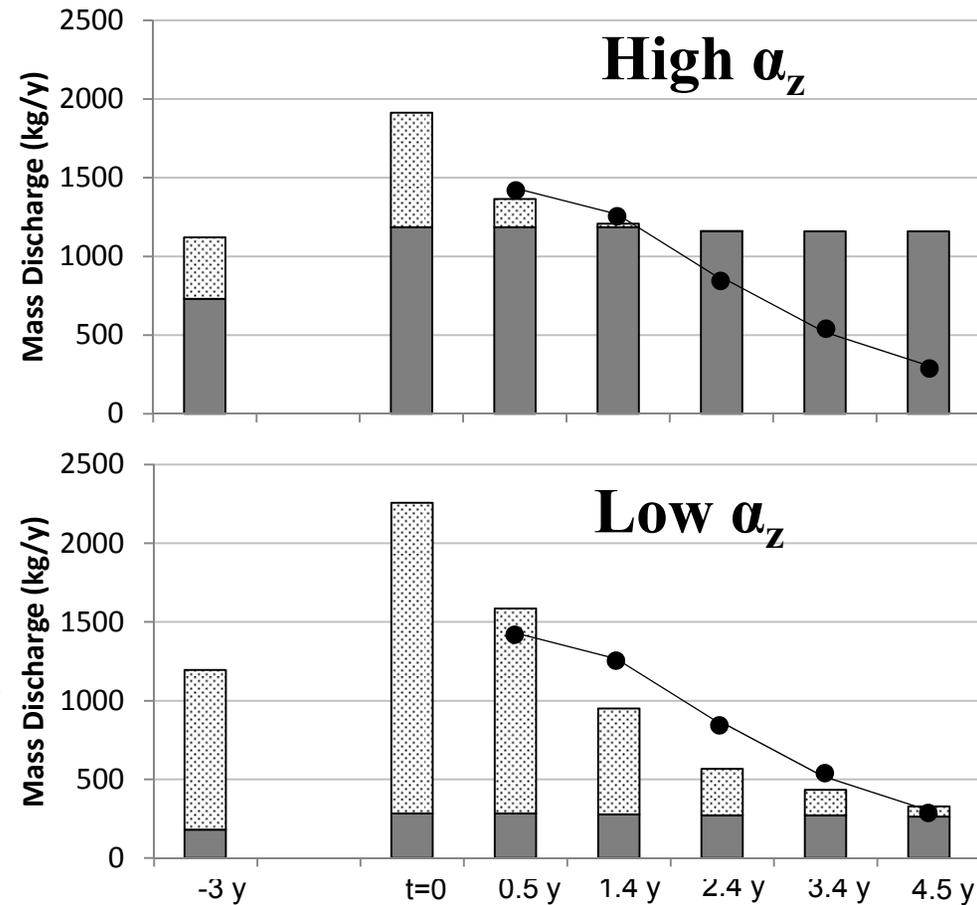
NDM for Forensic Analysis of LNAPL Architecture Schafer and Therrien, 1995 Field Study



Case I:
Initially thin
with fast decline
in thickness

Case II:
Initially thick
with slow decline
in thickness

Carey et al. (2015f)



Md_{surf}

Md_{thru}

Observed Total Md

Course Overview

- DNAPL concepts (***)
- Spreadsheet analytical models
- NAPL Depletion Model (NDM)
 - Input parameter estimation
 - Model input and output files
- Example applications
- Influence of various properties on depletion timeframe
 - Focus investigations to support depletion modeling



DNAPL Concepts

Section 2



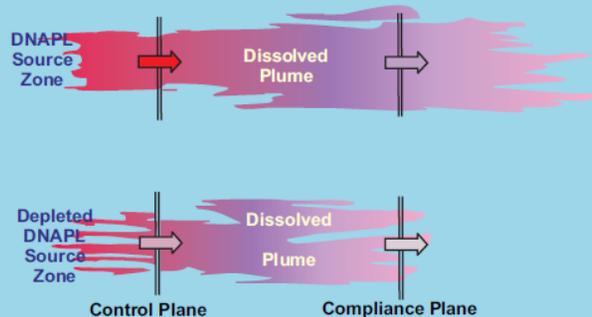
DNAPL Sites: A Decade of Reflection

2003

2012



The DNAPL Remediation Challenge: Is There a Case for Source Depletion?

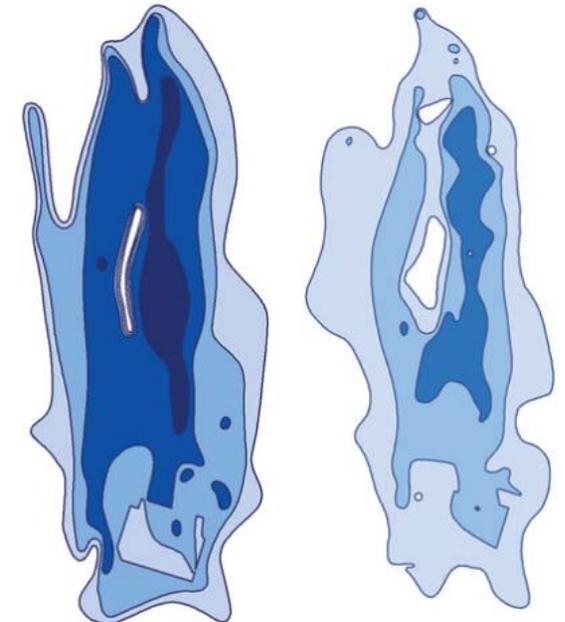


Research and Guidance

- DoD / DOE research
- ITRC
 - Mass Flux
 - DNAPL Strategies
 - Alternative End Points
- EPA
 - TI Waivers
 - Site closure
 - DNAPL Delineation
- States
 - CA – Low Threat Closure

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2.2

The New Paradigm

Site Characterization Tools

- *Mass flux and Mass discharge*
- *Modeling back-diffusion timeframe*

Remediation

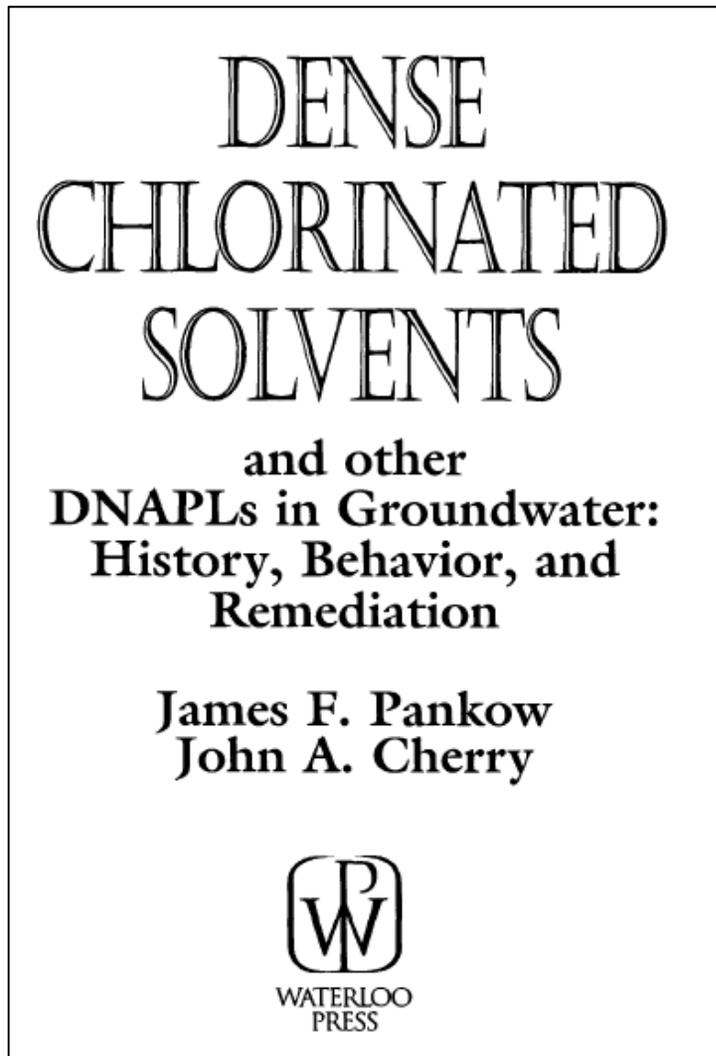
- *Mass discharge → Attainable interim goal*
- *Focus, Focus, Focus on the mass (Biggest Bang for \$\$\$)*

Management framework

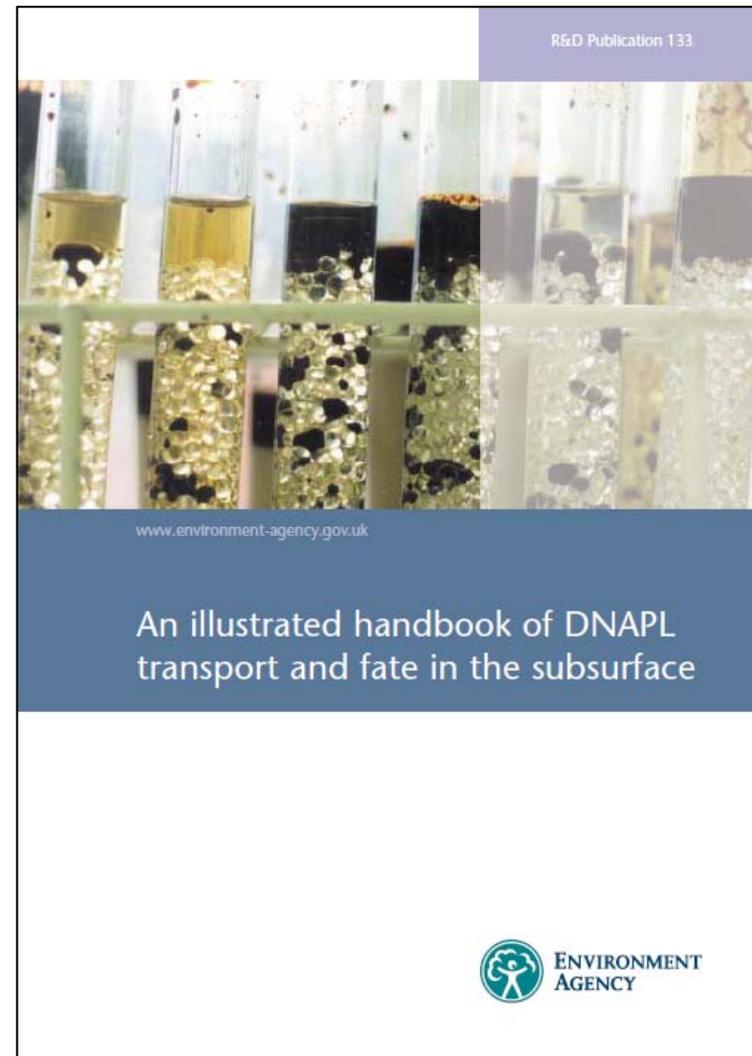
- *Integrated source-plume management*
- *Transition from active to passive source treatment*



DNAPL References (Course USB)



Pankow and Cherry (1996)



Kueper et al. (2003)

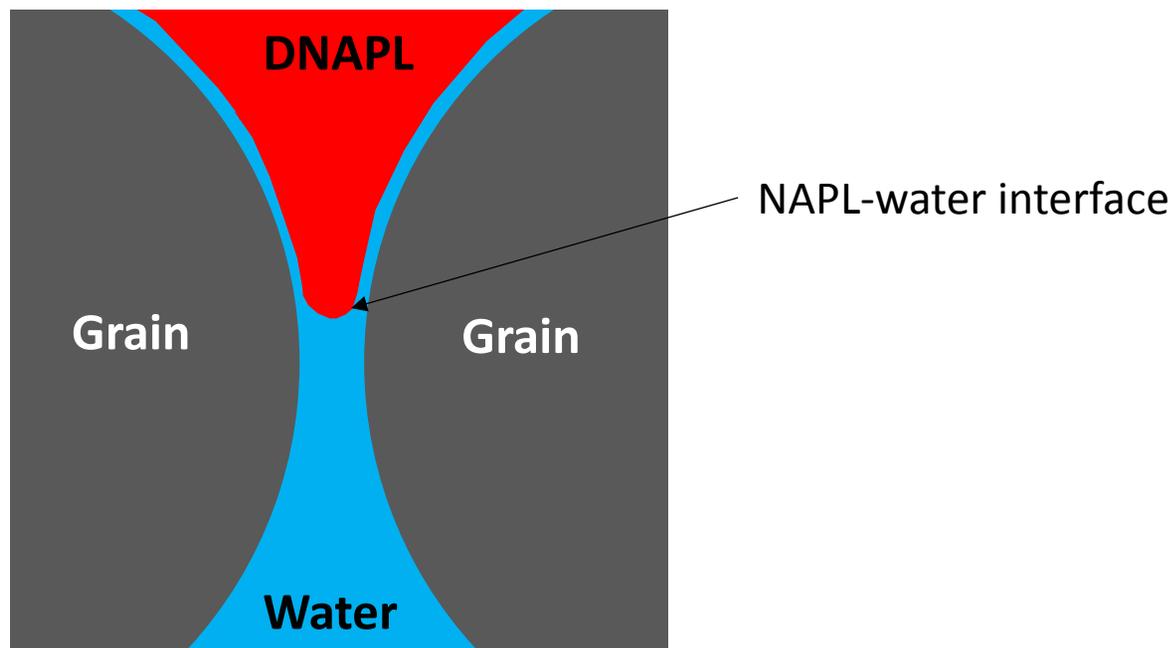


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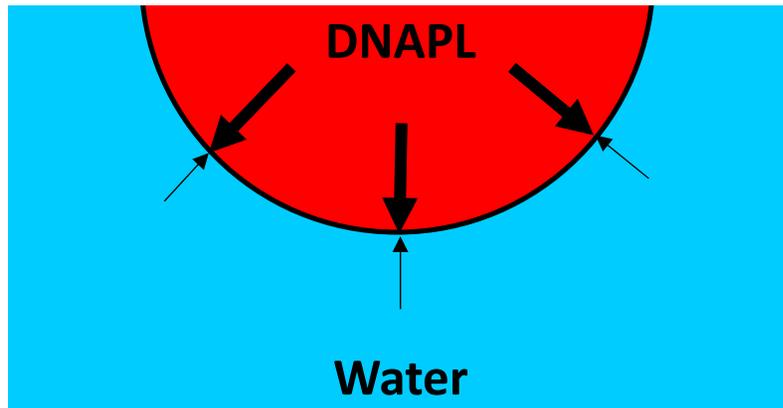
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Dense Non-Aqueous Phase Liquid (DNAPL)

- DNAPLs are immiscible in groundwater
 - Separate phase
 - Dissolves slowly over time



Dense Non-Aqueous Phase Liquid (DNAPL)



NAPL-water interface (curved):

- Under tension
- Pressure drop across interface (ΔP)
- Higher pressure on DNAPL side

- Interfacial tension is a property of NAPL-water or air-water systems

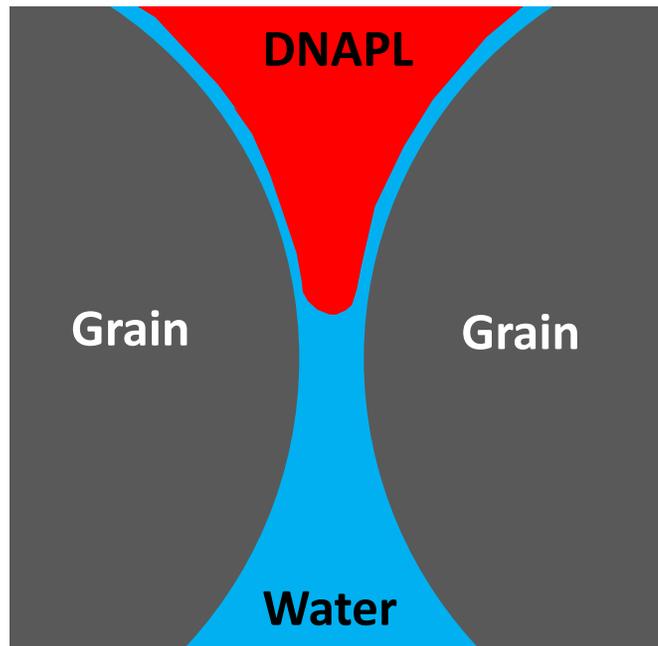
$$\sigma_{\text{air-water}} = 72 \text{ dynes/cm}$$

$$1 \text{ N/m} = 1,000 \text{ dynes/cm}$$

$$\sigma_{\text{NAPL-water}} = 20 \text{ to } 50 \text{ dynes/cm}$$

Wetting vs. Non-Wetting Phase

- Below the water table, water is **wetting** phase
 - Preferentially spreads over sand grains
 - Tends to occupy smaller, constricted pore spaces



- DNAPL is **non-wetting** phase
 - Occupies larger pore spaces
 - Needs to overcome entry pressure threshold (P_e) to invade a pore space



Capillary Pressure

- Capillary pressure (P_c) is the difference in pressure between NAPL and water at the interface

$$\begin{aligned} P_c &= \Delta P = P_{non-wetting} - P_{wetting} \\ &= P_{NAPL} - P_{water} \end{aligned}$$

- Entry pressure (P_e) is the minimum capillary pressure needed for DNAPL to invade a pore space:

$$\text{DNAPL-water } P_e = 2 \sigma_{nw} / r$$

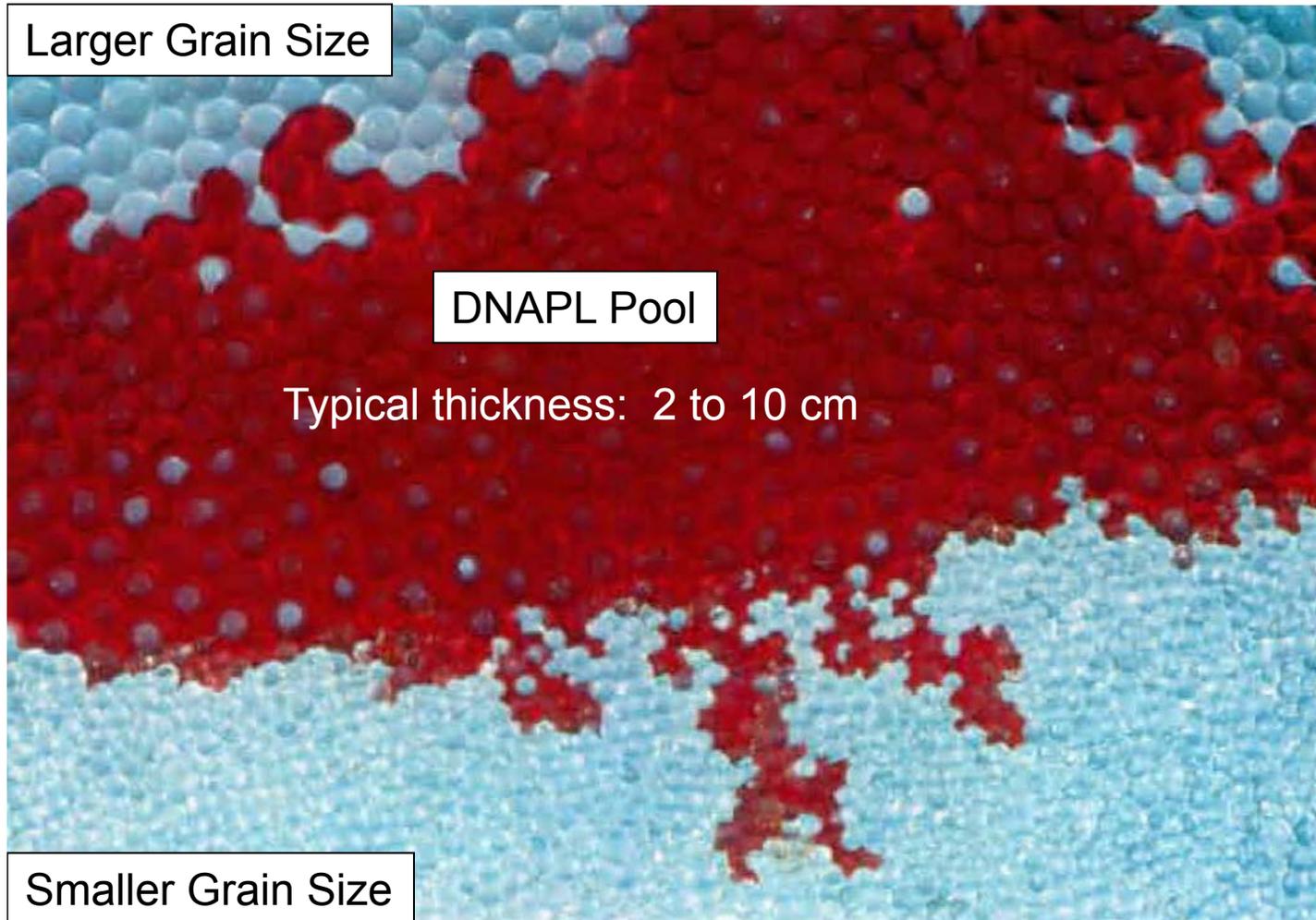
where r is the pore radius.

$$\begin{aligned} \text{Air-water } P_e &= 2 \sigma_{aw} / r \\ \text{DNAPL-water } P_e &= (\sigma_{nw} / \sigma_{aw}) \times \text{Air } P_e \end{aligned}$$

DNAPL will first invade the largest pore spaces.



DNAPL Pool (Free Phase / Product)



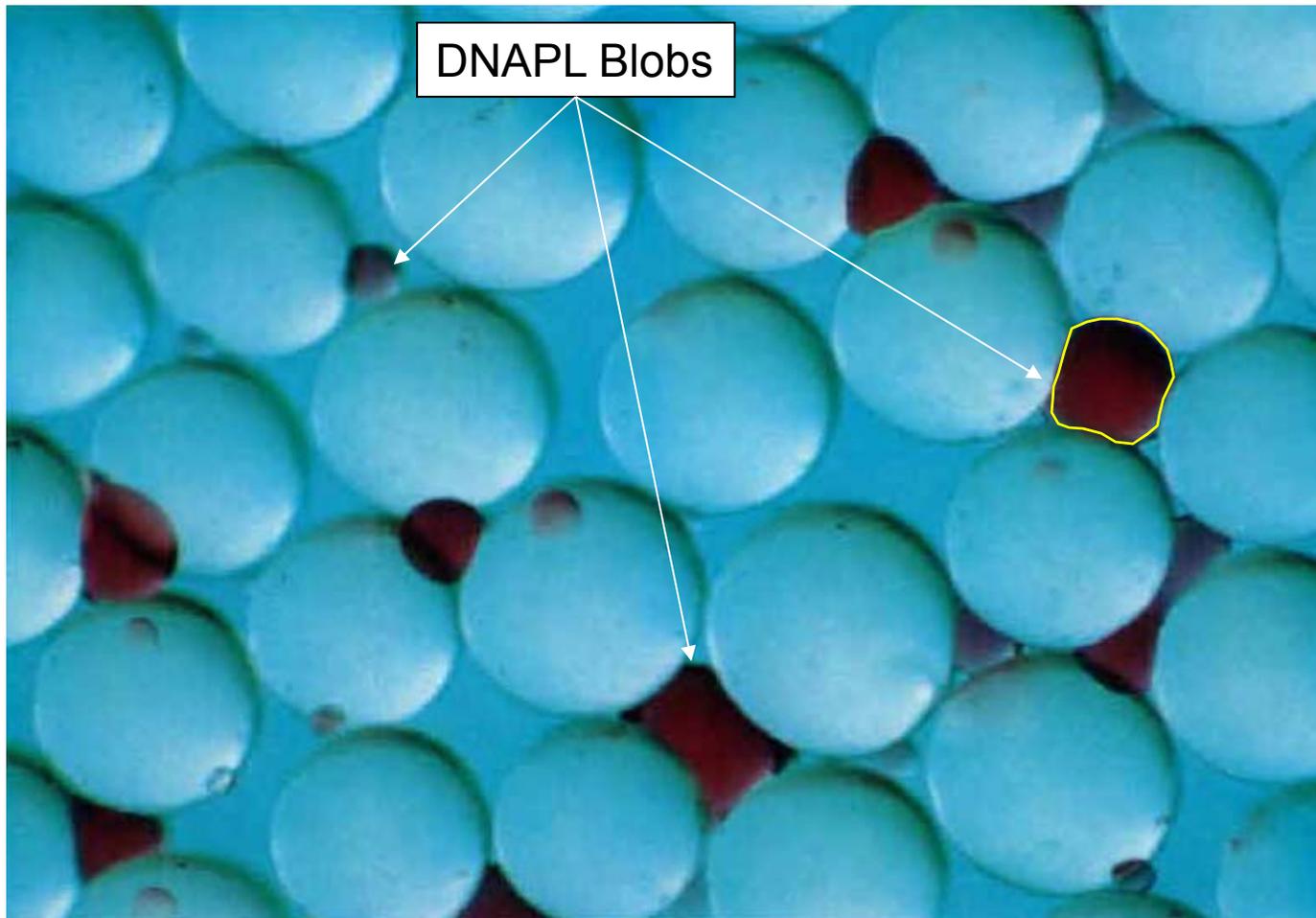
Source: Schwille, 1988

DNAPL Pools

- Large mass
- Continuous
- Potentially mobile
- Dissolve slowly
- Water present throughout pool layer



Residual DNAPL



Residual DNAPL

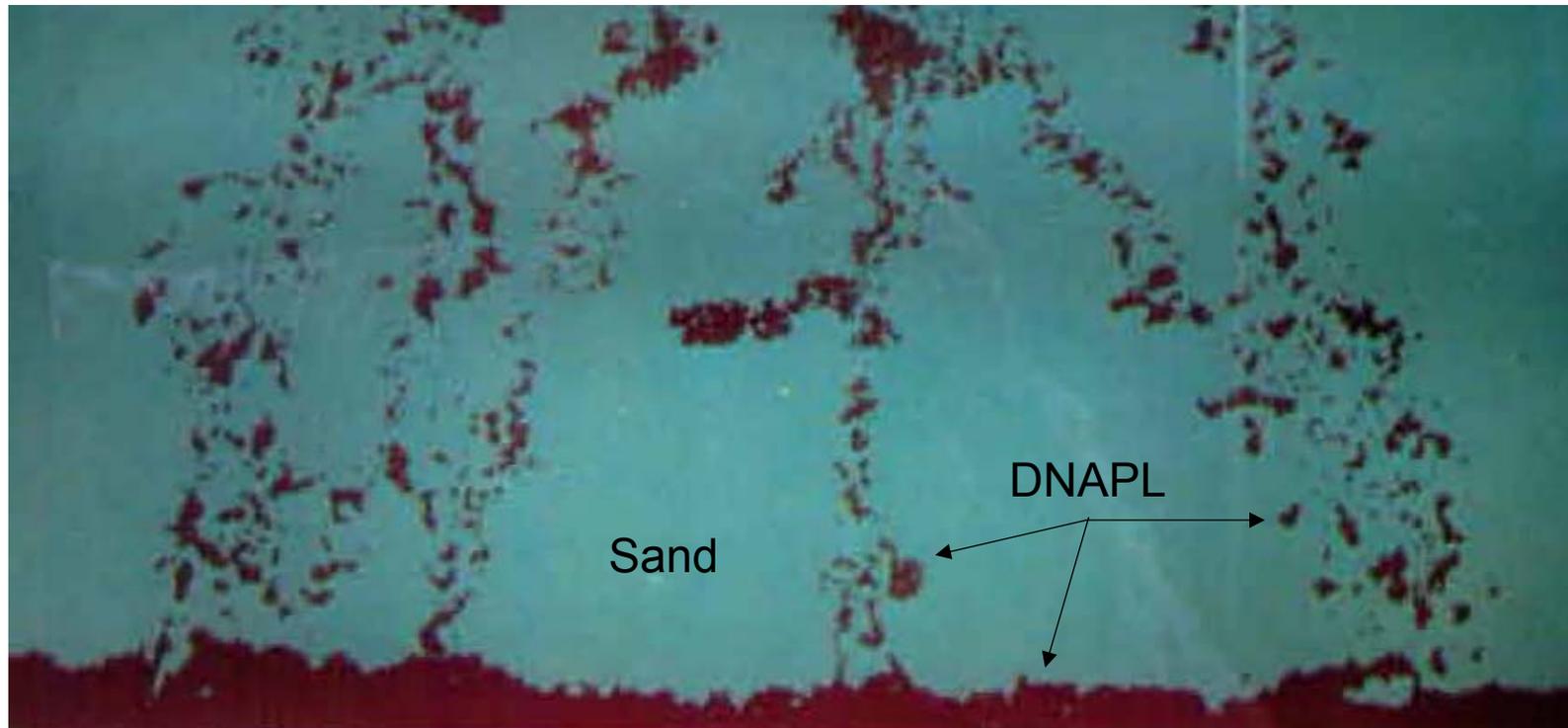
- Small mass
- Discontinuous
- Ganglia extend over 1 to 10 pore spaces
- Immobile
- Dissolves quickly

Source: *Schwille, 1988*



Chlorinated Solvent Sites

Initially released as DNAPL (oil-like) into subsurface.
DNAPL migrates chaotically – difficult to find after a release.



Source: *Schwille, 1988*



NAPL and Water Saturation Below Water Table

- Saturation is averaged over a volume of soil
- If no NAPL present
 - Pores completely filled with water
 - Water saturation (S_w) = 100%
 - NAPL saturation (S_n) = 0%
- Irreducible water saturation, S_{wr} = minimum water saturation

EXAMPLE:

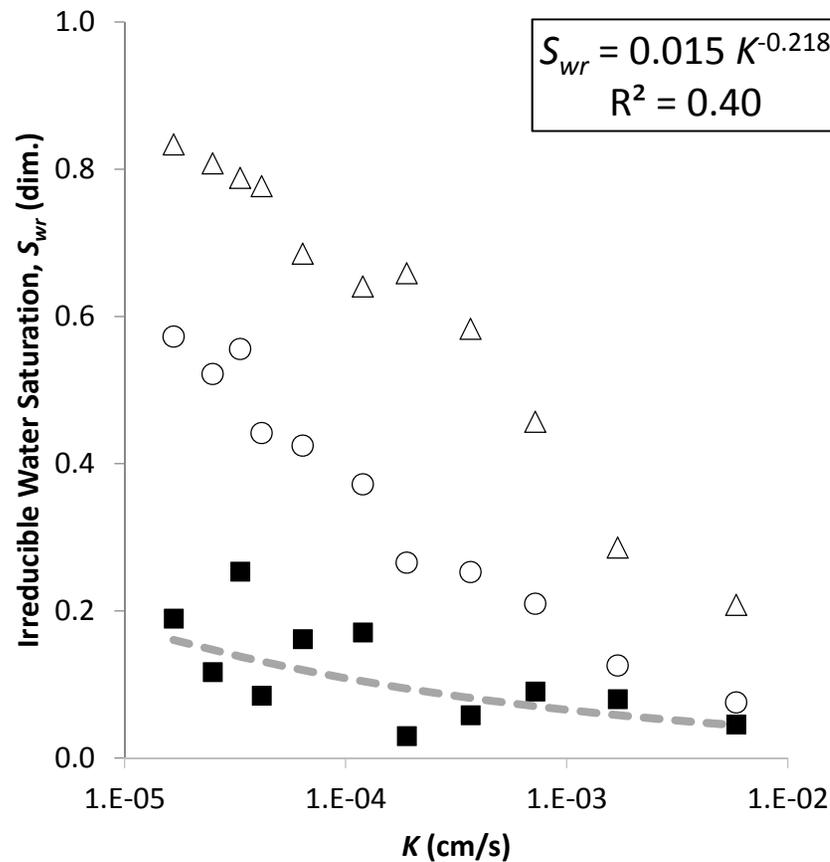
$$\theta_t = 0.40$$

$$\theta_w = 0.20$$

$$S_w = \theta_w / \theta_t = 50\%$$



Irreducible Water Saturation (S_{wr}) vs. K



(K units: cm/s)

- Rawls (1982), S_{wr}
- Rawls (1982), S_w at -15 bar
- △ Rawls (1982), S_w at -0.33 bar

K (cm/s)	S_{wr}
10^{-5}	18%
10^{-4}	11%
10^{-3}	7%
10^{-2}	4%

Carey et al. (2015e)

NAPL Saturation (S_n) Below Water Table

- $S_n = 1 - S_{wr}$
- Minimum $S_n = 0\%$
- Maximum $S_n = 1 - S_{wr}$
e.g. if $S_{wr} = 10\%$, max. $S_n = 90\%$

Input for NDM

Based on initial DNAPL mass in mixed source zone:

$$S_n = \frac{M_o}{V_{sz} \theta_t \rho_{NAPL}}$$

M_o = Initial DNAPL mass (kg)

V_{sz} = Volume of source zone (m^3) = L x W x H

θ_t = total porosity

ρ_{NAPL} = DNAPL density (kg/m^3)



Residual Saturation

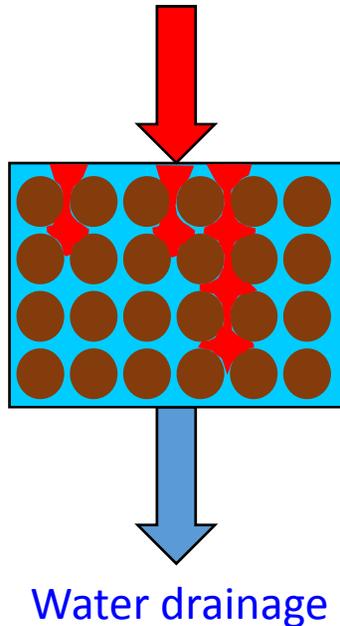
- “Residual Saturation” refers to a threshold NAPL saturation, above which the NAPL is present as a continuous, potentially mobile pool
 - Also referred to as free phase NAPL
- Below this threshold – DNAPL is not continuous, and is immobile (ganglia) – Residual DNAPL
- Common residual saturation for TCE in the literature is 15% to 20%
- General range of 20% to 50% has been cited in other literature
- Residual saturation threshold depends on initial release conditions

S_m = maximum water saturation = 1 – residual saturation threshold



Capillary Pressure Saturation Curve

DNAPL imbibition



Experiment: Measure P_c at different S_w

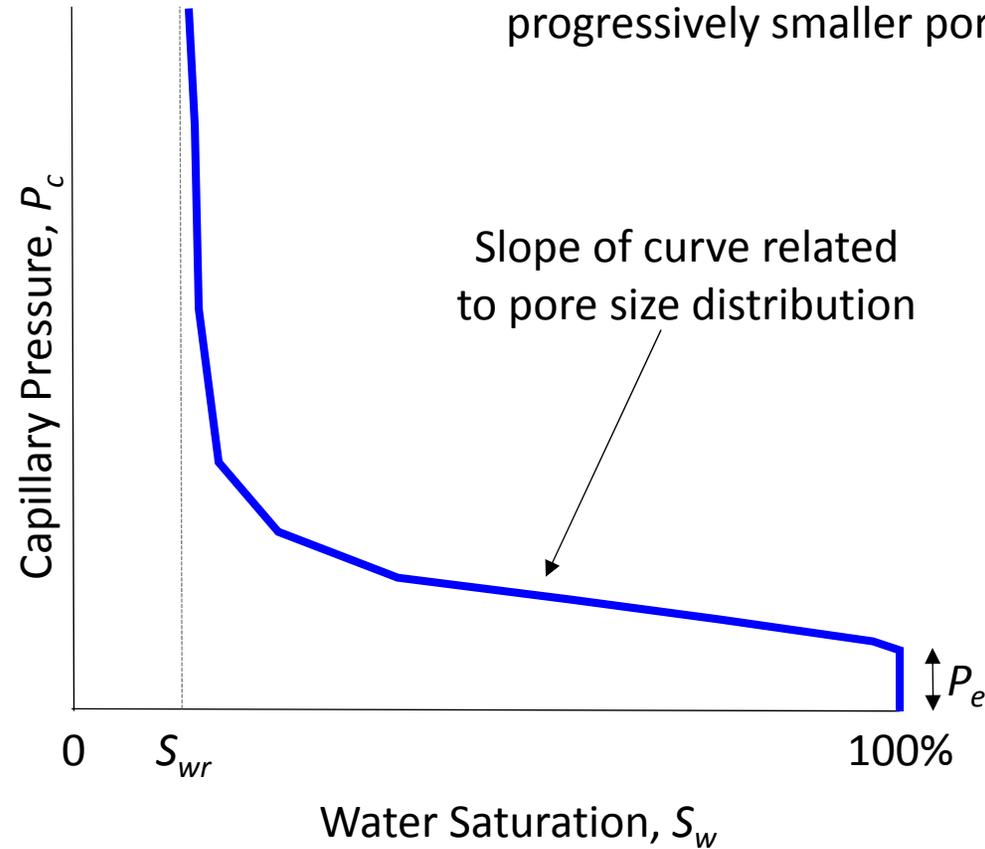
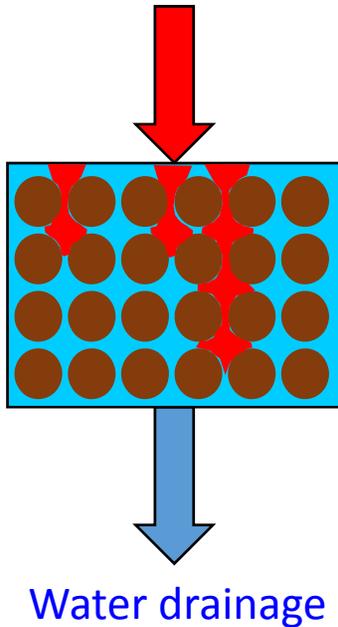
1. Start with $S_w=100\%$, $S_n=0$.
2. Slowly increase P_c until P_e exceeded (NAPL enters soil sample) $\rightarrow P_e$ est.
3. Incrementally increase P_c and measure corresponding S_w as water drains and DNAPL imbibes (enters).
4. Plot P_c-S_w points, and estimate curve characteristics
 - P_e , and pore size distribution

Capillary Pressure Saturation Curve

$$P_c = 2 \sigma_{nw} / r$$

- As P_c increases, DNAPL invades progressively smaller pore spaces (r)

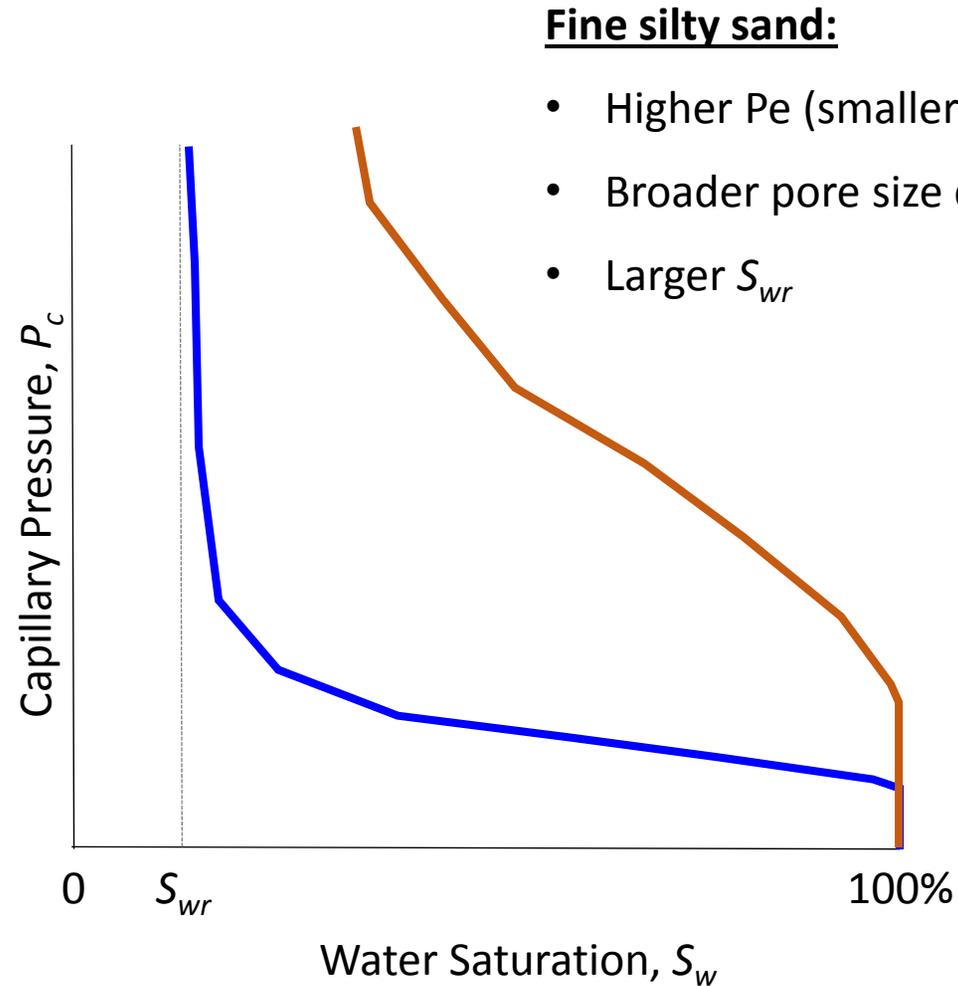
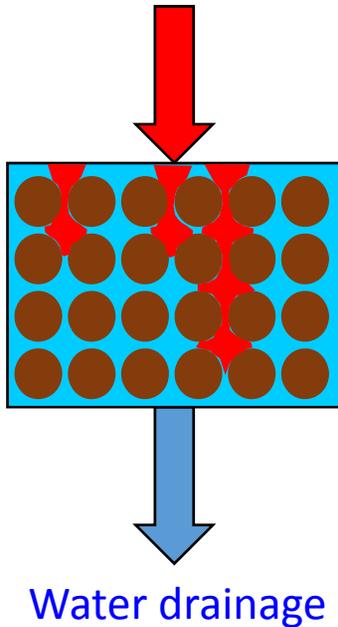
DNAPL imbibition



Example: — Coarse sand

Capillary Pressure Saturation Curve

DNAPL imbibition

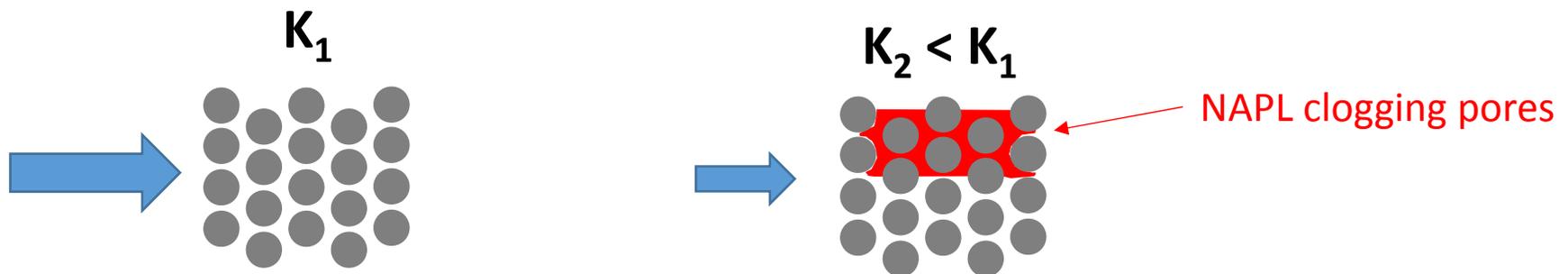


Example:

- Coarse sand
- Fine silty sand

Relative Water Permeability

- Intrinsic permeability (k) of soil is proportional to pore size
 - Larger pores \rightarrow Larger k and K , because more space for water to flow
- If NAPL partially clogging pores – reduced space for water to flow, & reduced permeability
- Relative water permeability (k_{rw}) – depends on NAPL saturation (S_n)



p. 106-107 in Pankow and Cherry, 1996; and Appendix B of course notes

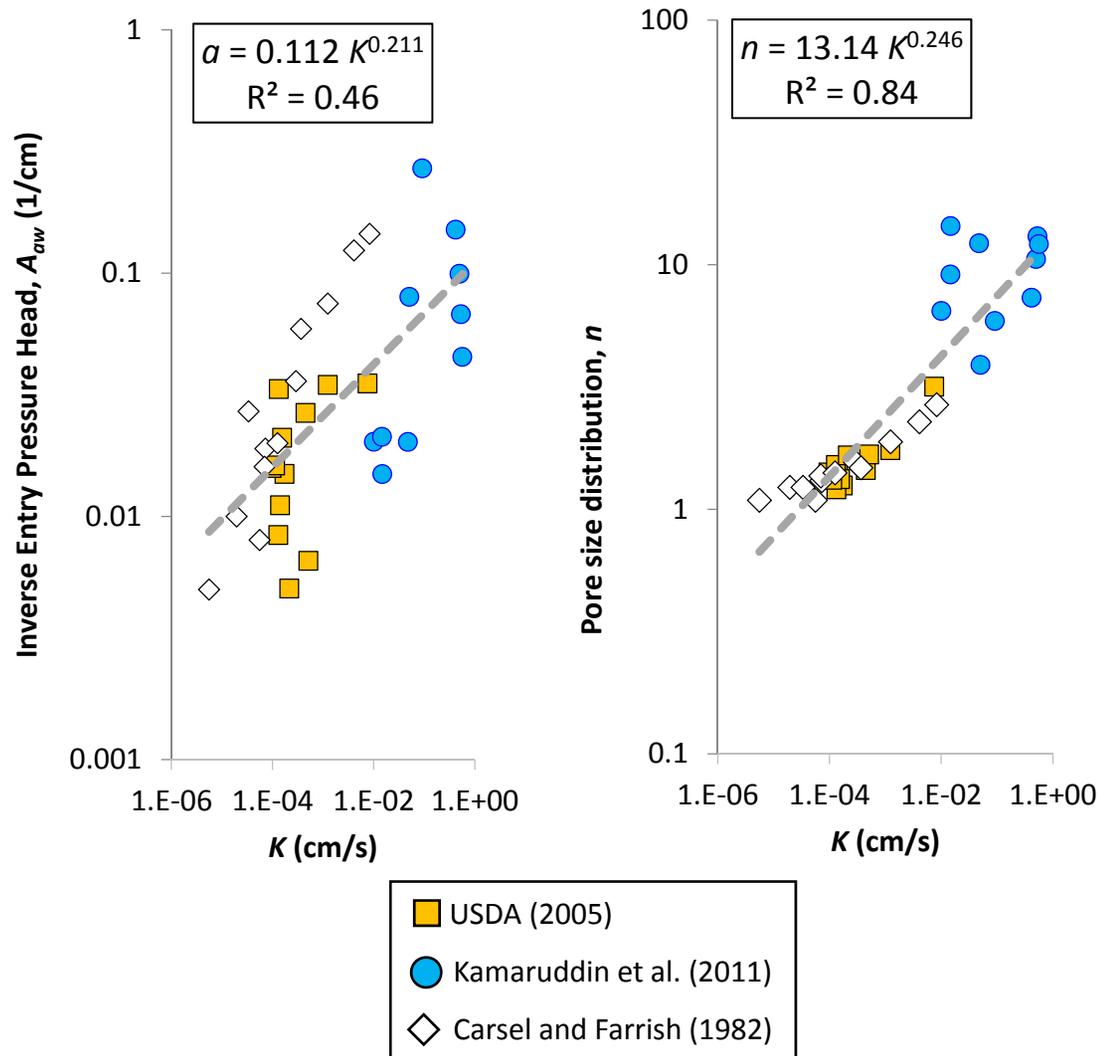


Relative Water Permeability

- Van Genuchten (1980) and Mualem (1976)
- Two parameters used to estimate shape of $P_c(S_w)$ curve, and k_{rw} based on S_w
 - Alpha, $\alpha = 1 / P_e$
 - Pore size distribution (n) $m=1-1/n$
- NDM – based on Van Genuchten model
- Also see Brooks-Corey and Burdine models in Pankow and Cherry (1996)

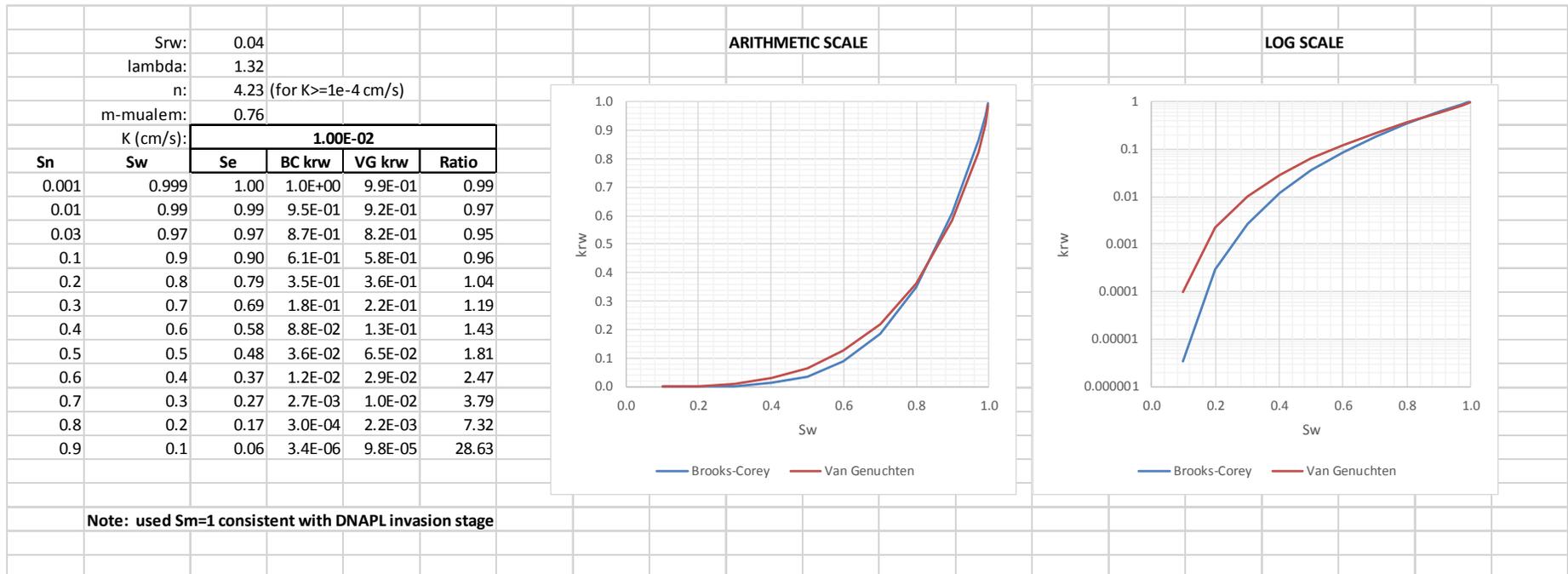


Regression of Pc(Sw) Characteristics vs. K



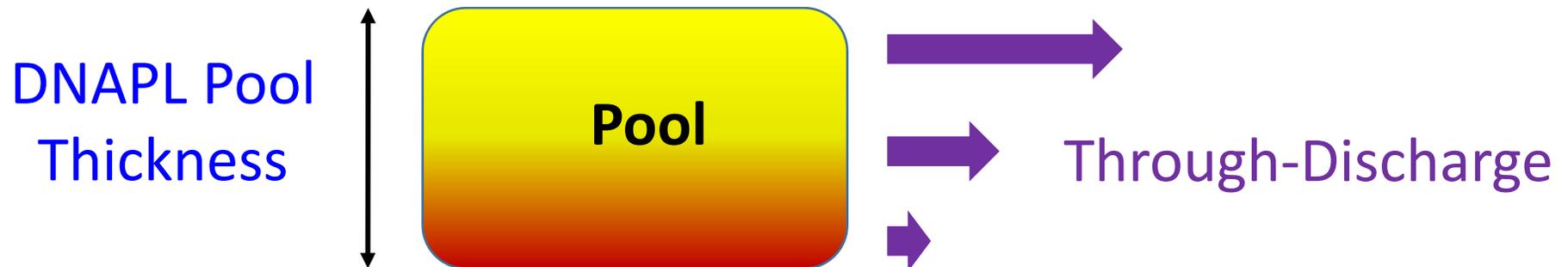
Krw(Sn) Estimation Spreadsheet

USB:\Models\krw comparison.xlsx



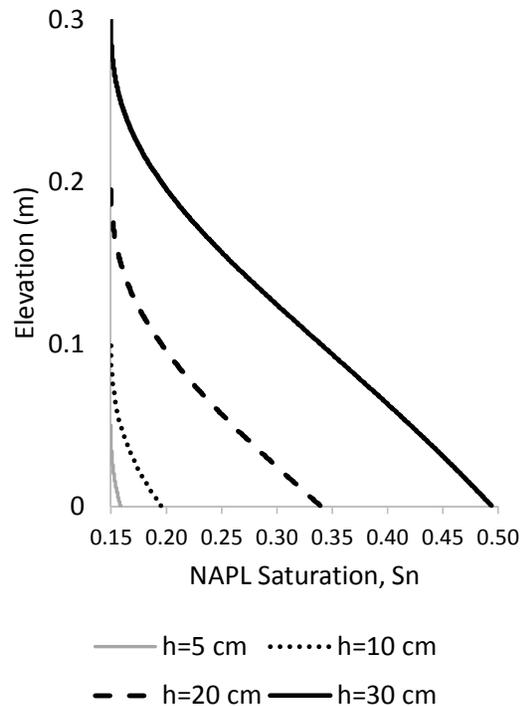
Transition Zones in DNAPL Pools

- Some DNAPL pools may have varying S_n with depth, and thus varying k_{rw} with depth
 - Lowest S_n is at the top of the pool (McWhorter and Kueper, 1996)
- Moreno-Barbero & Illangasekare, 2006 – refer to this upper zone with higher k_{rw} as the transition zone

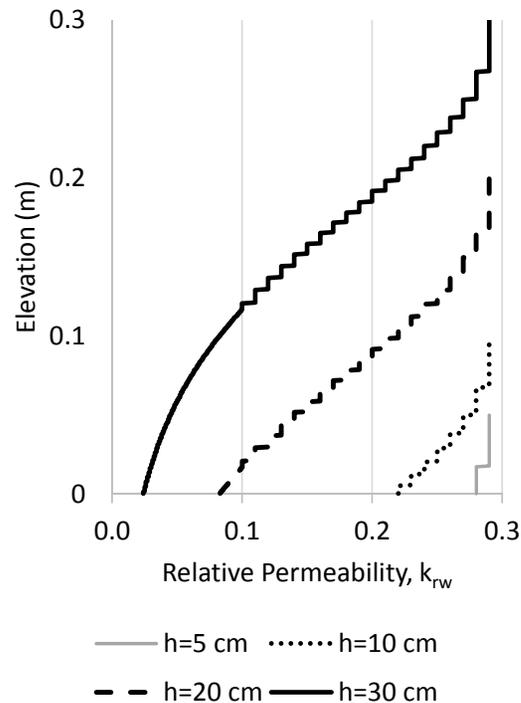


Transition Zone in DNAPL Pools

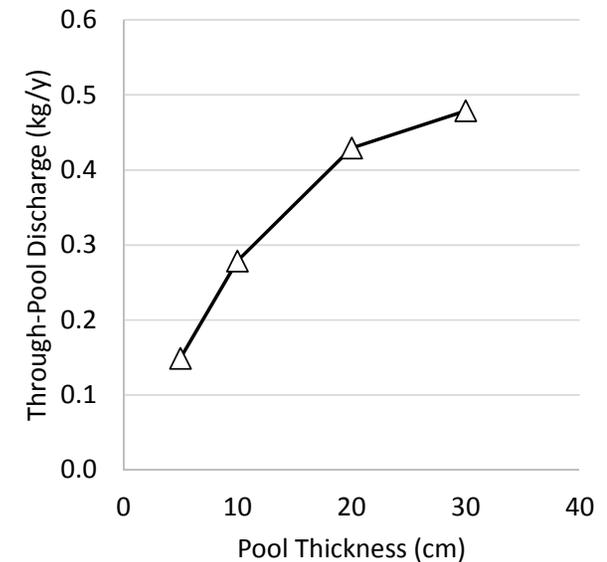
a) Elevation vs. NAPL saturation



b) Elevation vs. relative permeability



c) Through-pool discharge vs. pool thickness



Carey et al. (2014a)

Vertical distribution of DNAPL in pool – above calculations based on Eq. 3.18 in McWhorter and Kueper (1996) and Eq. B-8 in Appendix B (assumes $P_c=0$ at the top of the pool).

Relative Water Permeability

- Mixed source zones: large areas without NAPL
 - Assume $k_{rw} = 1$
- Distinct NAPL layers (sub-zones) – estimate k_{rw} if through-discharge is simulated
 - DNAPL pools may have higher through-discharge than typically believed, due to transition zone at top of pool



NAPL Source Zone Delineation

Kueper and Davies, 2009



Ground Water Issue

Assessment and Delineation of DNAPL Source Zones at Hazardous Waste Sites

Bernard H. Kueper* and Kathryn L. Davies**

1.0 - Introduction

Groundwater contamination from classes of chemicals such as chlorinated solvents, polychlorinated biphenyls (PCBs), creosote, and coal tar is frequently encountered at hazardous waste sites (40, 43). These types of contaminants have low solubilities in water and have densities greater than that of water. Therefore, they can exist in the subsurface as Dense, Non-Aqueous Phase Liquids (DNAPLs) and have the potential to migrate as a separate liquid phase to significant distances below the water table in both unconsolidated materials and fractured bedrock. Because of the physicochemical properties associated with DNAPLs, they migrate through the subsurface in a very selective and tortuous manner (13, 27, 29). Thus, the majority of DNAPL present in the subsurface may not be found immediately below the entry location and directly encountering DNAPLs with conventional drilling techniques may be difficult.

Determining the presence or absence of a DNAPL is an important component of the conceptual site model and is critical to the proper selection of the remediation approach. Subsurface DNAPL acts as a long-term source for dissolved-phase contamination and determines the spatial distribution and persistence of contaminant concentrations within the dissolved-phase plume. Once it has been determined that DNAPL exists within the subsurface, subsequent characterization activities are typically conducted to better delineate the boundaries of the DNAPL source zone. The DNAPL source zone is the overall volume of the subsurface containing residual and/or pooled DNAPL. It should be recognized that there will be uncertainty associated with the delineation of the DNAPL source zone. In addition to the DNAPL, there may be significant amounts of contaminant mass that have diffused into low permeability zones. Back diffusion of contaminant mass from these zones may sustain dissolved-phase plumes for significant periods of time, even after DNAPL has been removed. Establishing the presence and locations of such non-DNAPL sources is beyond the scope of this document.

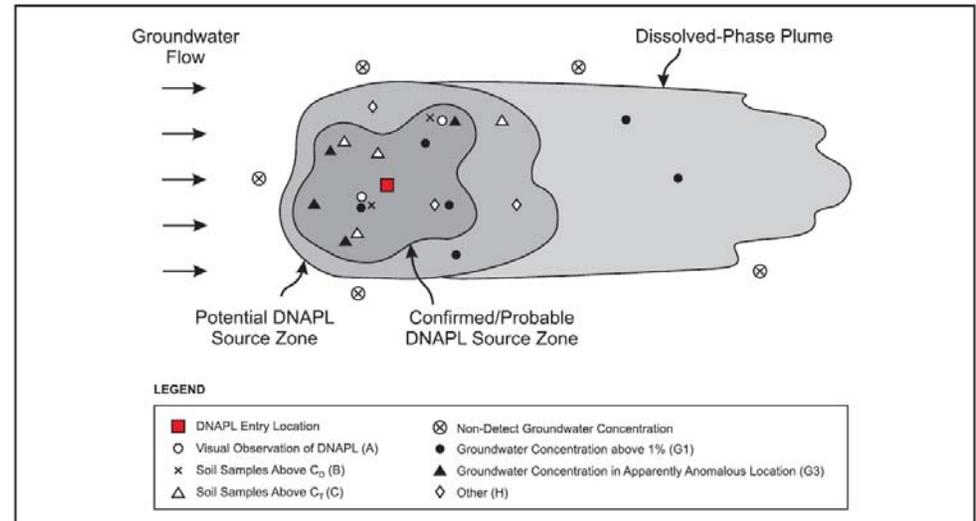
In January 1992, EPA published a Fact Sheet entitled 'Estimating Potential for Occurrence of DNAPL at Superfund Sites' (42) with the goal to help site personnel determine if DNAPL-based characterization strategies should be employed at a particular site. In September 1994, EPA issued a subsequent Fact Sheet entitled 'DNAPL Site Characterization' (39) discussing direct and indirect methods to assess the presence of DNAPL in the subsurface. Since

the publication of the initial fact sheets, there have been advancements in characterization tools, site investigation approaches (1-4) and knowledge of DNAPL source zone architecture within the subsurface. This document builds on information from the previous fact sheets to provide a framework for not only assessing the presence of DNAPL, but also for delineating the spatial extent of the DNAPL source zone, a priority at many sites due to the more prevalent use of *in-situ* remediation technologies (38). The strategy described in the present document utilizes converging lines of evidence that incorporate the scientific advancements in the field and expands the applicability of the document to include both unconsolidated deposits and fractured bedrock. An iterative, flexible site investigation approach (7) is encouraged.

2.0 - Nature of the DNAPL Source Zone

Upon release to the subsurface, DNAPL will distribute itself in the form of disconnected blobs and ganglia of organic liquid referred to as residual DNAPL, and in connected distributions referred to as pooled DNAPL (Figure 1). Residual DNAPL is found both above and below the water table within the pathways of DNAPL migration, and typically occupies between 5% and 30% of pore space in porous media (6, 27, 44) and in rock fractures (21). Residual DNAPL is trapped by capillary forces, and typically will not enter an adjacent monitoring well, even under the influence of aggressive groundwater pumping (6, 27).

Pooling of DNAPL can occur above capillary barriers, which are typically layers and lenses of slightly less permeable material (Figure 1). Pooling can therefore occur at any elevation in the subsurface, and not just at the base of permeable zones. Absence of pooling above clay aquitards and bedrock may be due to the presence of dipping fractures, bedding planes, joints and faults which may allow the continued downward migration of the DNAPL. Pools represent a continuous distribution of DNAPL, and typically correspond to DNAPL saturations of between 30% and 80% of pore space in both porous media and fractures. The frequency of pool occurrence and the thickness of pools are increased by the presence of horizontal capillary barriers, lower DNAPL density, higher interfacial tension, and an upward component to groundwater flow (17, 22). The thickness of pools typically ranges from fractions of an inch to a few feet, depending on fluid and media properties (36) as well as the volume released. Because pools represent a connected distribution of DNAPL, the pooled DNAPL is susceptible to mobilization through drilling activities and can short-circuit along existing monitoring wells and piezometers. In addition, pools may also be mobilized in response to changes in hydraulic gradient. The gradient required to mobilize a pool is a function of the DNAPL-water interfacial



- Lines of evidence approach
- Confirmed NAPL zones
 - Treatment
- Potential NAPL zones
 - Containment

* Queen's University, Kingston, Ontario CANADA

** U.S. EPA, Region 3



Porewater Solutions
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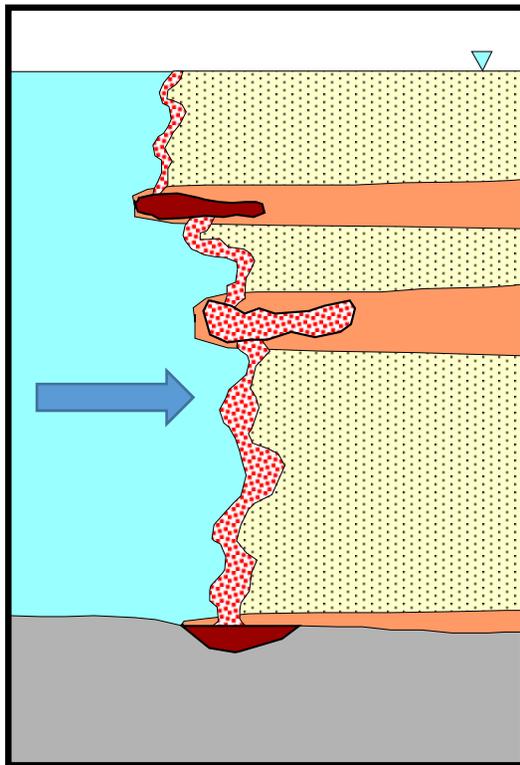
Examples of NAPL Indicators

- Saturation Threshold ($S_n \geq 5\%$) (confirmed)
- Visible NAPL (confirmed)
- Dye testing – confirmed if positive (potential for false negatives e.g. $S_n < 1\%$ or 2% , or fine-grained soils)
- Partitioning threshold – soil and GW
- Stain or sheen with supporting evidence (e.g. elevated PID, odor, or other evidence of contamination)
- GW or vapor concentration trends, anomalies
- Site use/history (e.g. release locations)

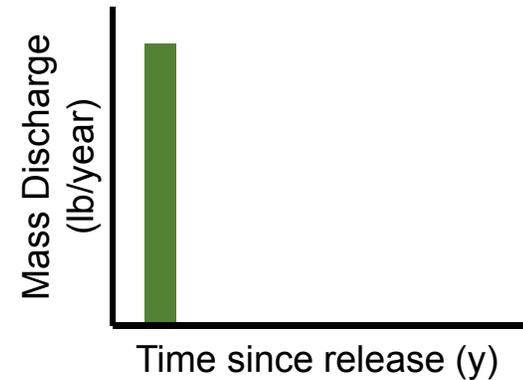


Mass Discharge Trends

Fresh Source



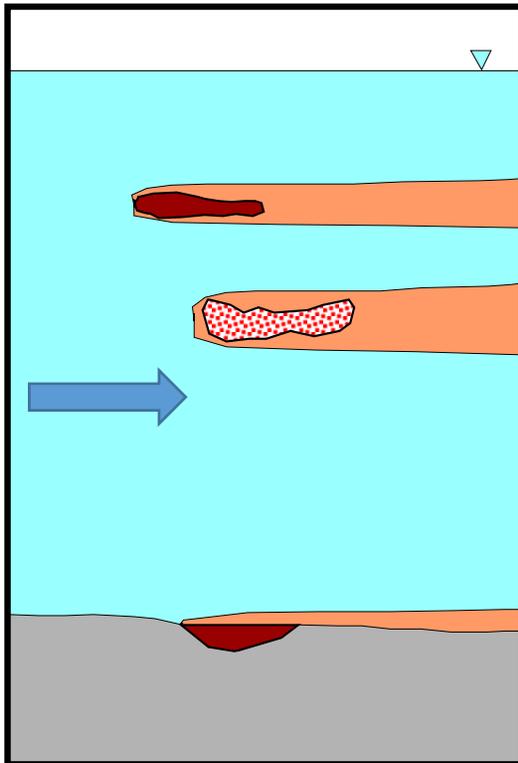
Mass discharge
from source zone
(kg/y)



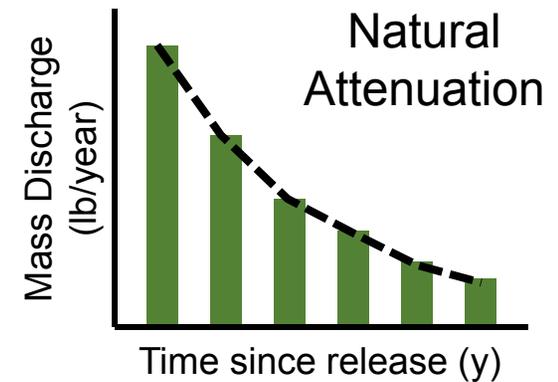
Modified from Parker et al., 2003

Mass Discharge Trends

Aged Source



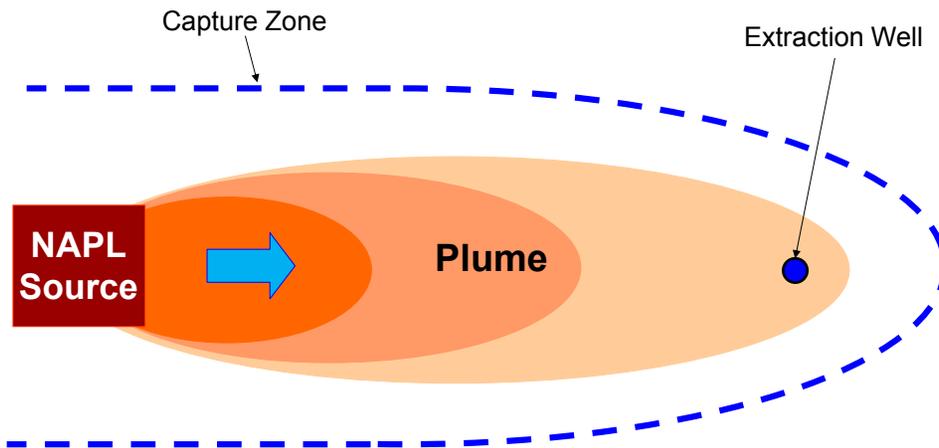
Typical source zone mass discharge = 1 to 100 kg/year



Newell et al., 2006:
Median TCE DNAPL half-life of 6 years

Mass discharge reduction 30x in 30 years

Mass Flux / Mass Discharge



Mass discharge affects plume length, risk.

Easily estimated with pumping wells.

Example: If need 90% reduction in risk, then goal is 90% reduction in mass discharge from source.

Technology Overview

Use and Measurement of Mass Flux and Mass Discharge

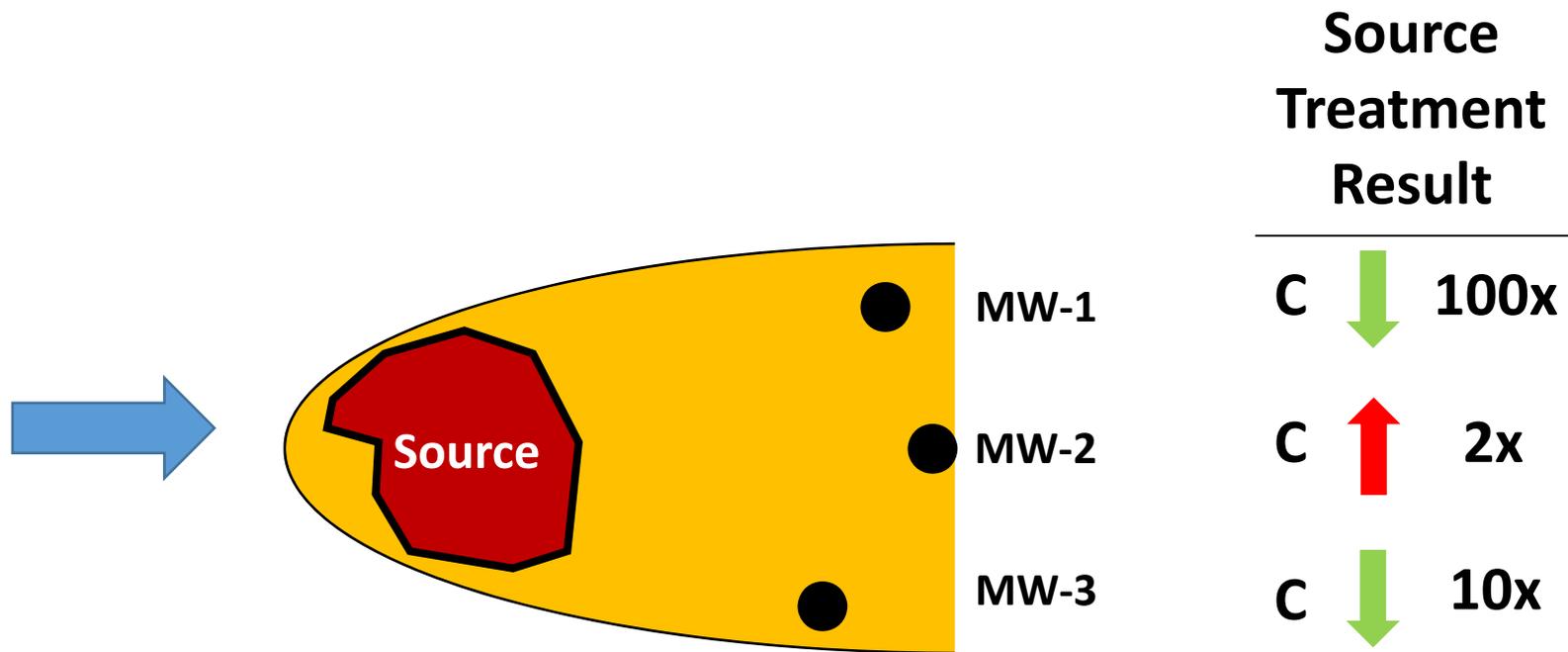
Mass Discharge (M_d) = Sum of Mass Flux (J) Estimates

The diagram shows a cross-section of the ground with a water table. A source on the left is shown with a plume extending to the right. Two vertical cross-sections, "Transect A" and "Transect B", are shown. At Transect A, a grid is overlaid on the plume, with an arrow labeled "Flux $J_{A,j}$ " and "Mass Discharge M_{dA} ". At Transect B, another grid is overlaid, with an arrow labeled "Flux $J_{B,j}$ " and "Mass Discharge M_{dB} ".

www.ITRCweb.org

August 2010

Concentration Trends Highly Variable

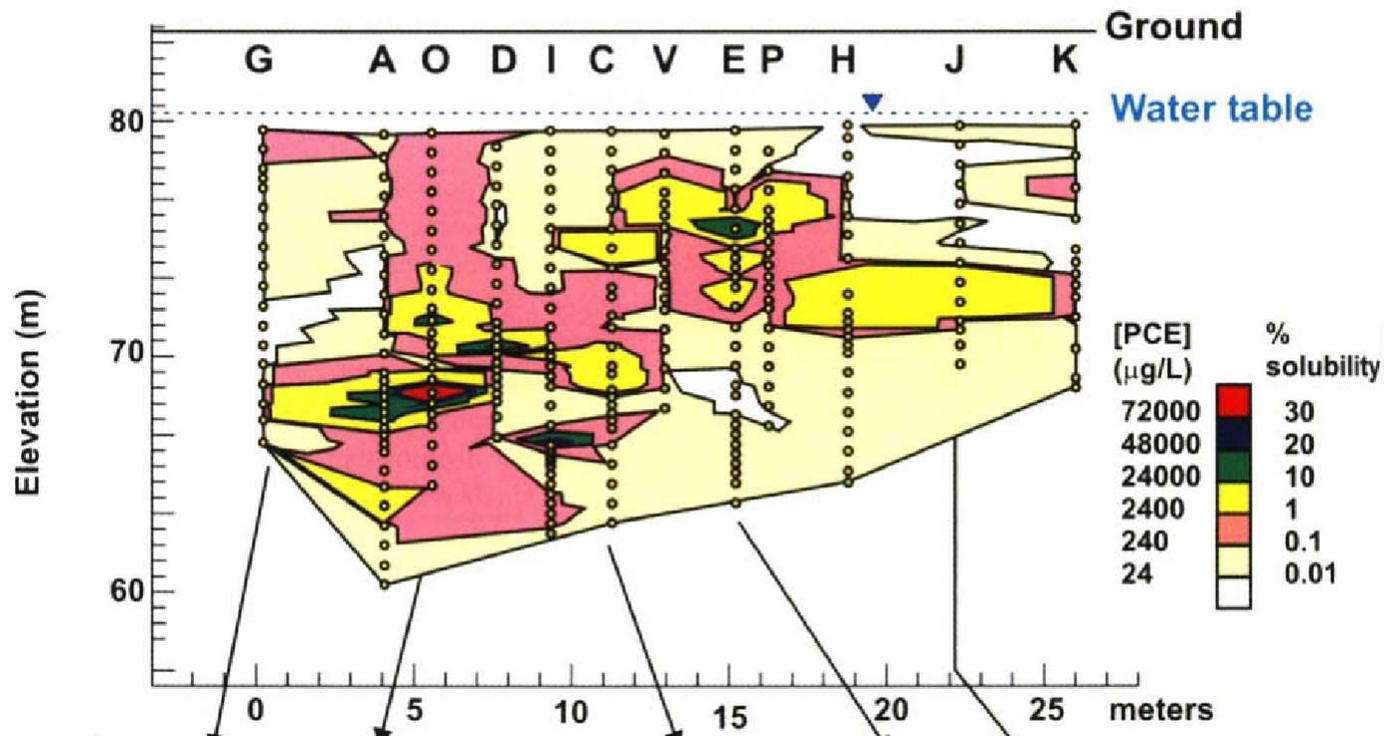


Note: Mass discharge is a single metric – easier to evaluate overall performance.

Source Mass Flux - Guilbeault et al., 2005

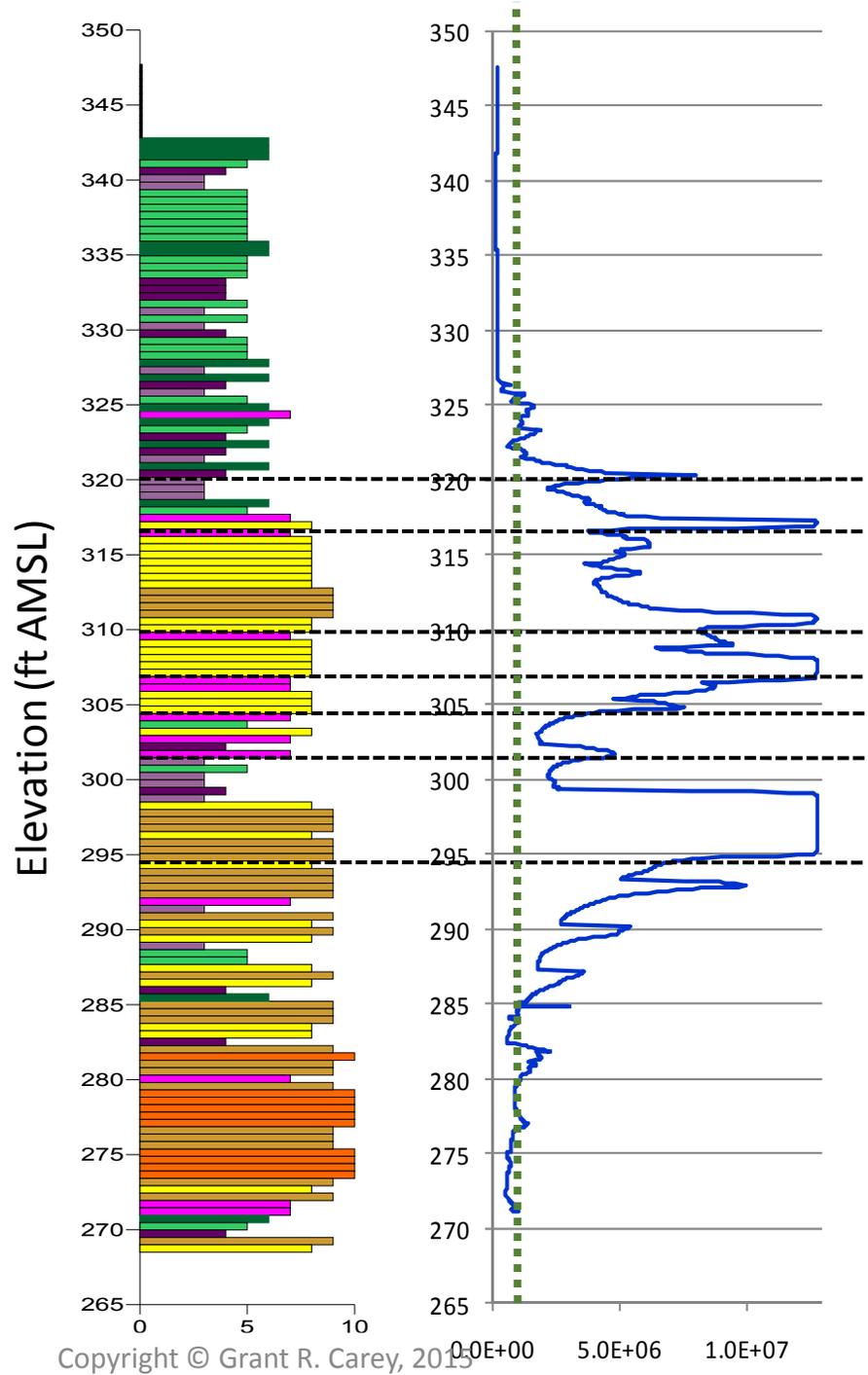
If we can see where the mass is coming from, we can focus remediation.

New Hampshire PCE Site



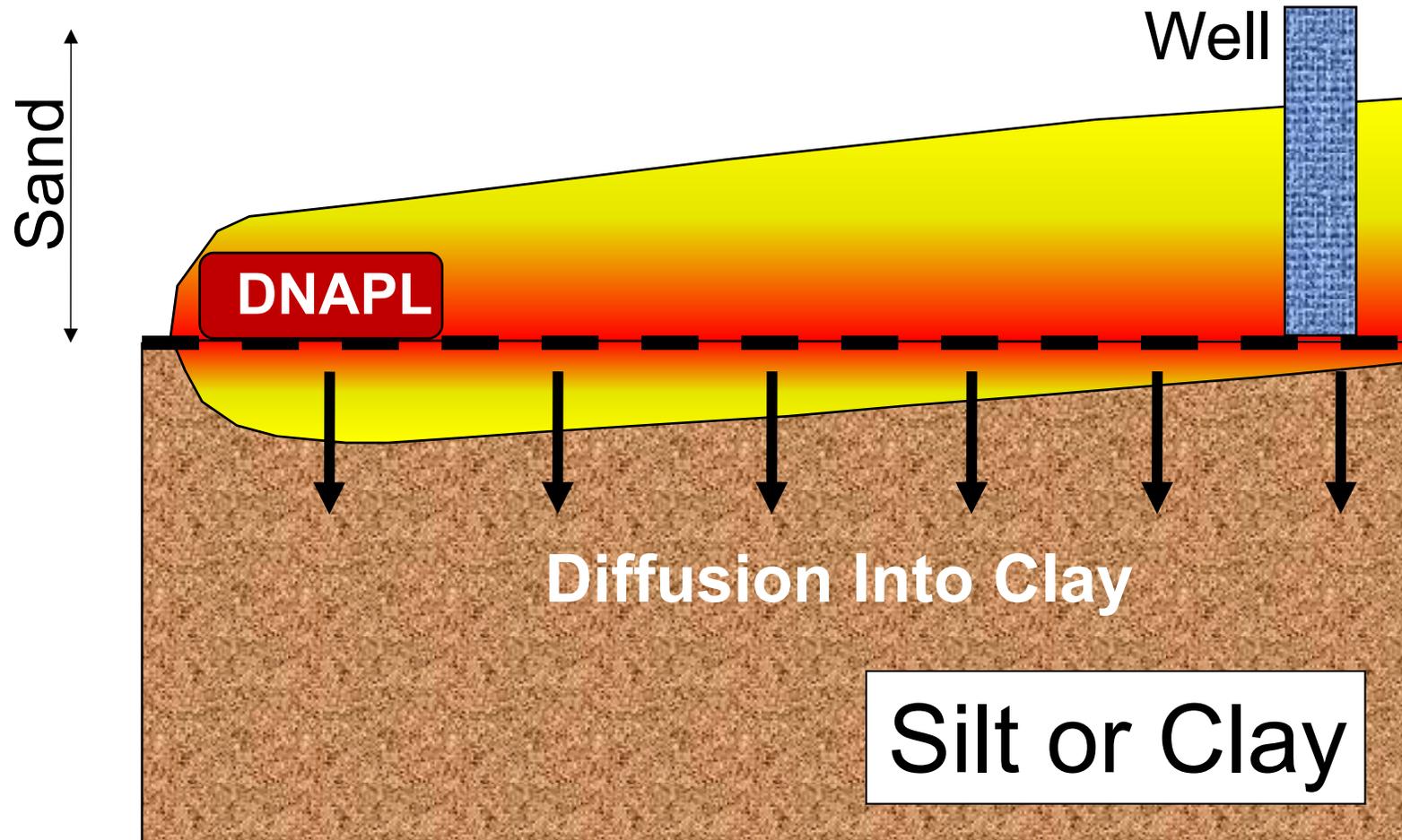
Source: Guilbeault et al. (2005)

CPT-MIP

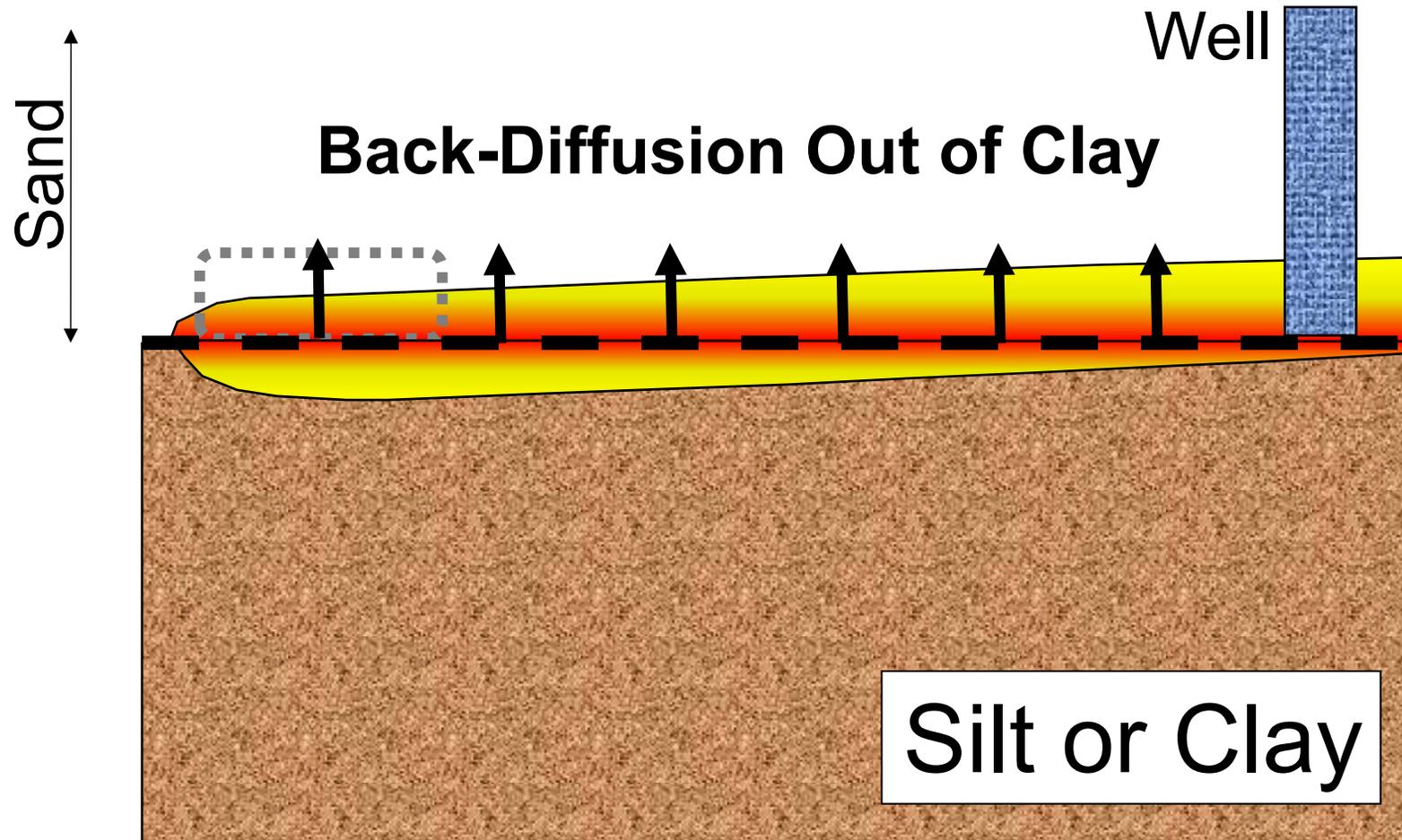


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Back-Diffusion



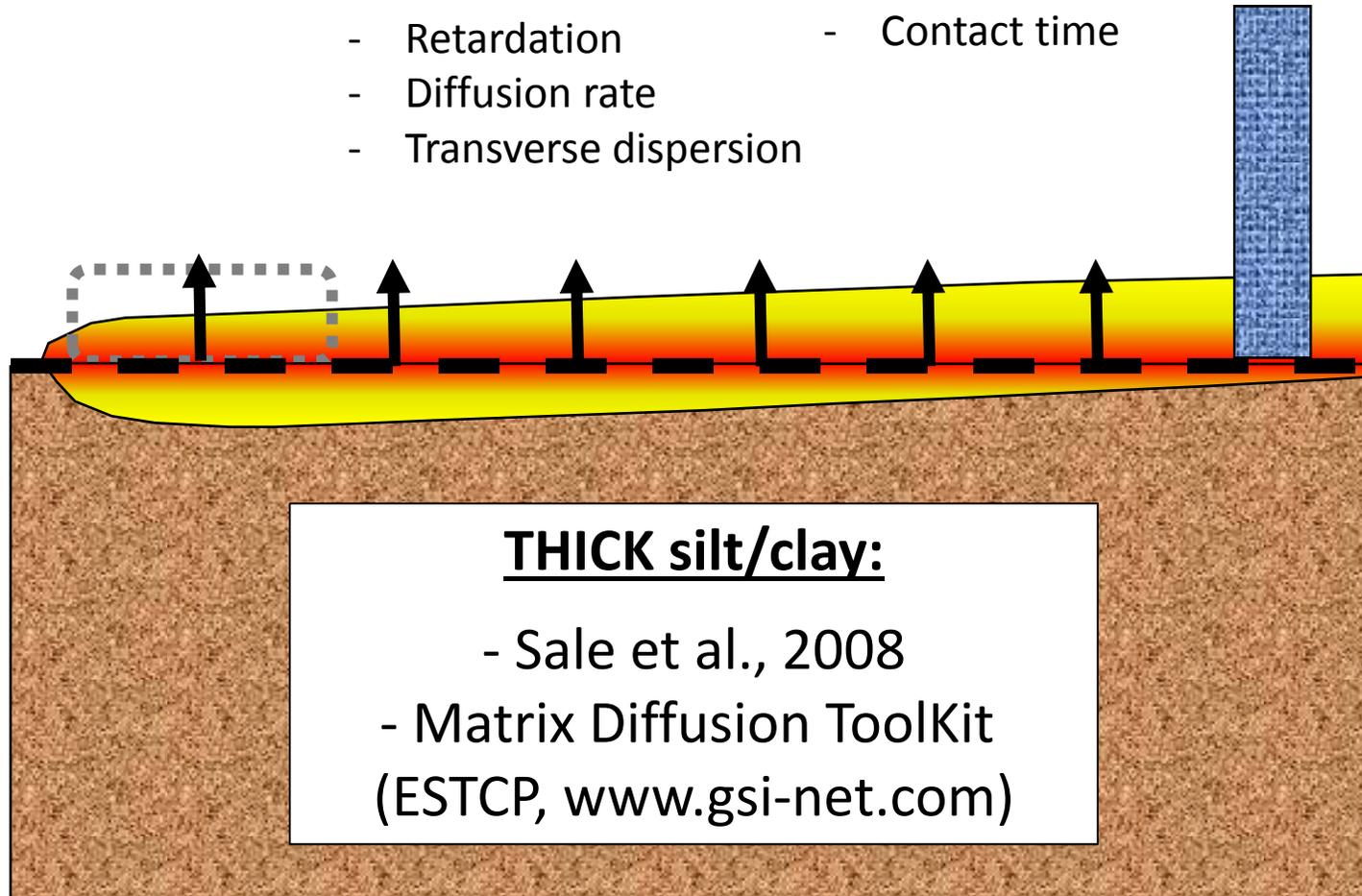
Back-Diffusion



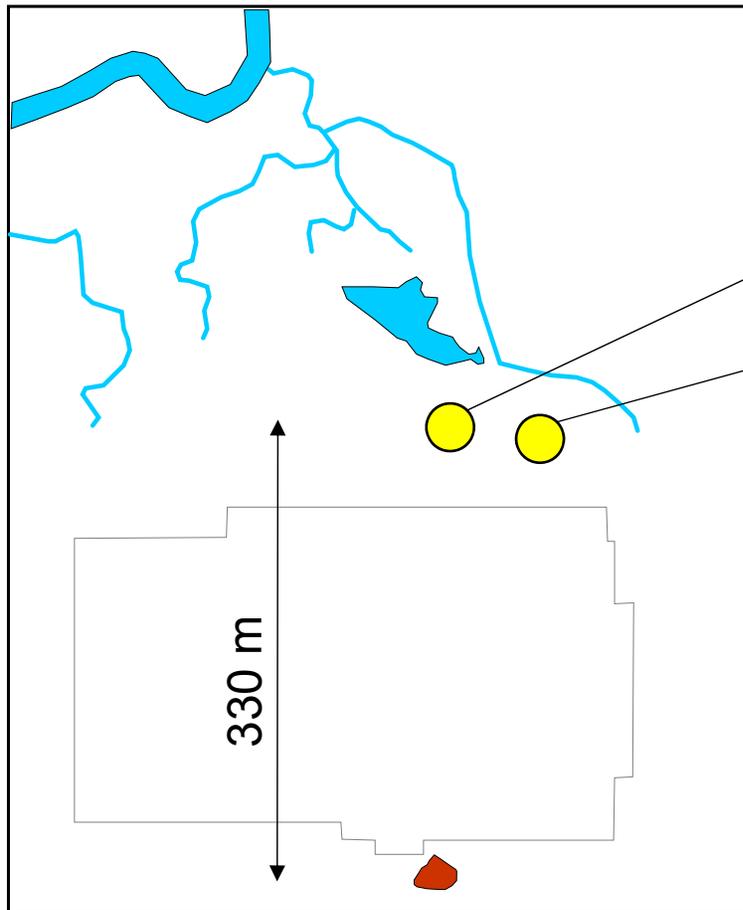
Back-Diffusion

Influencing factors:

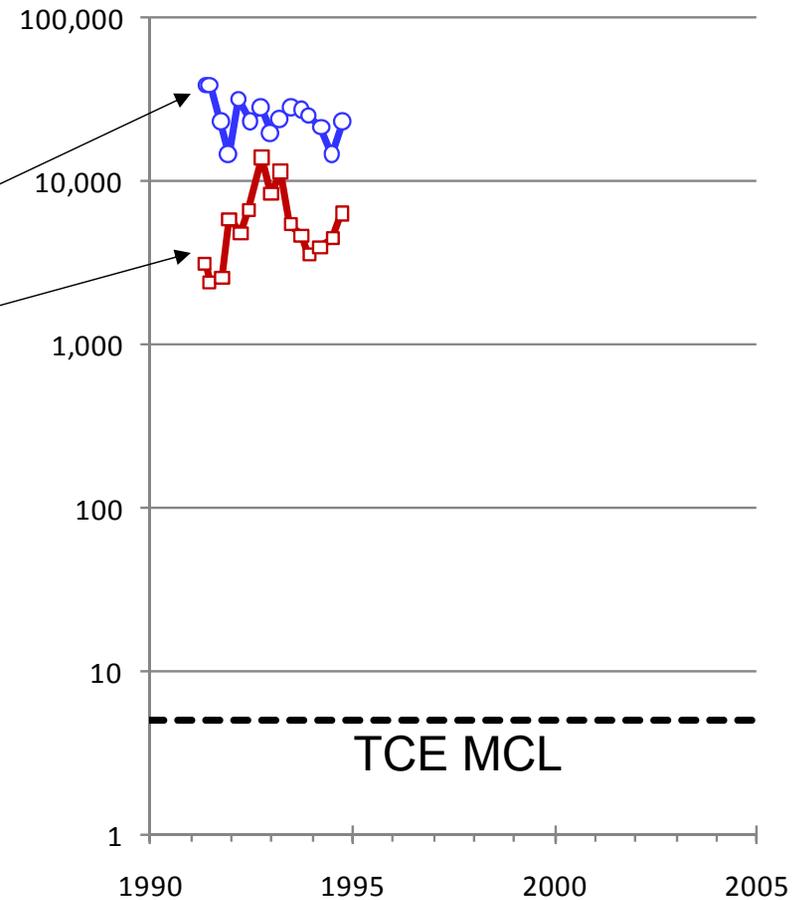
- Velocity
- Thickness
- Retardation
- Diffusion rate
- Transverse dispersion
- Length of clay lens
- Biodegradation
- Contact time



Connecticut Site (Chapman & Parker, 2005)

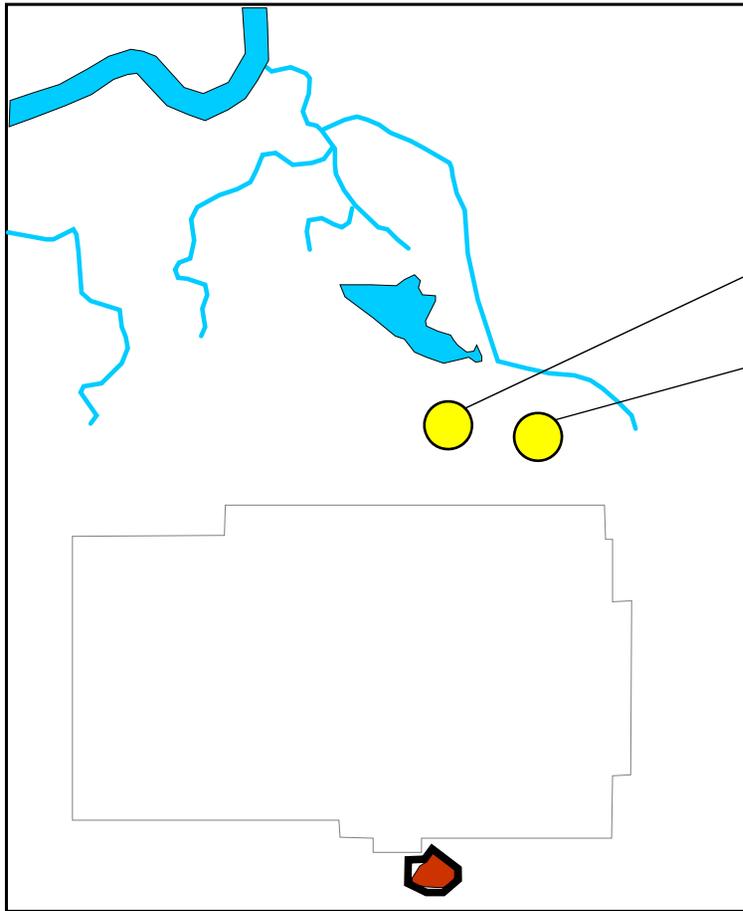


DNAPL Source Zone

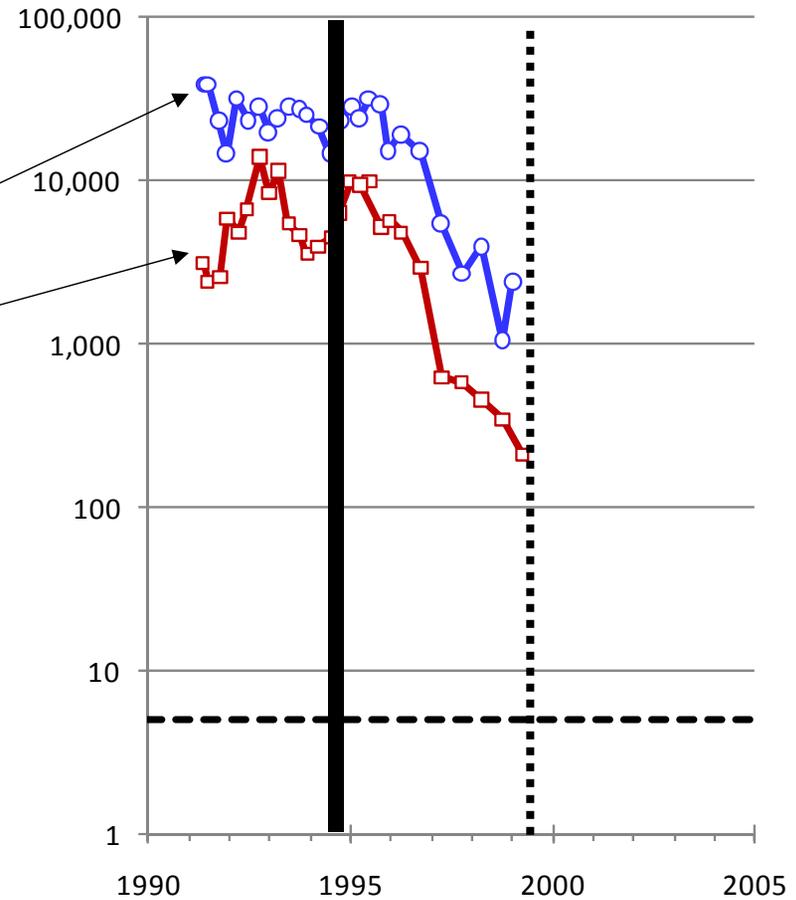


Source: Modified from Chapman and Parker (2005)

Connecticut Site (Chapman & Parker, 2005)

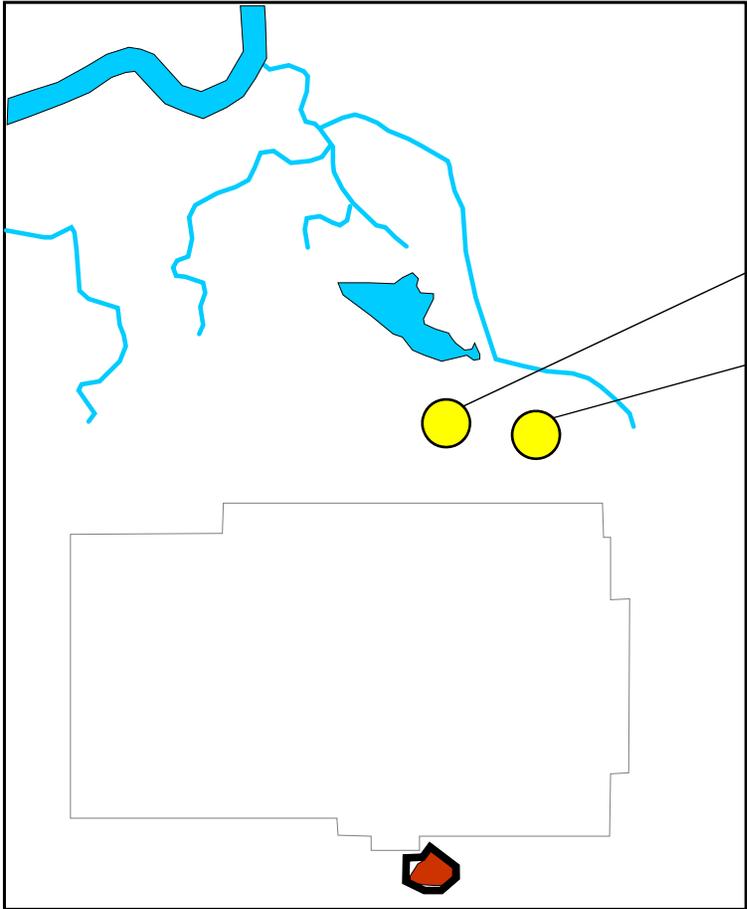


DNAPL Source Zone

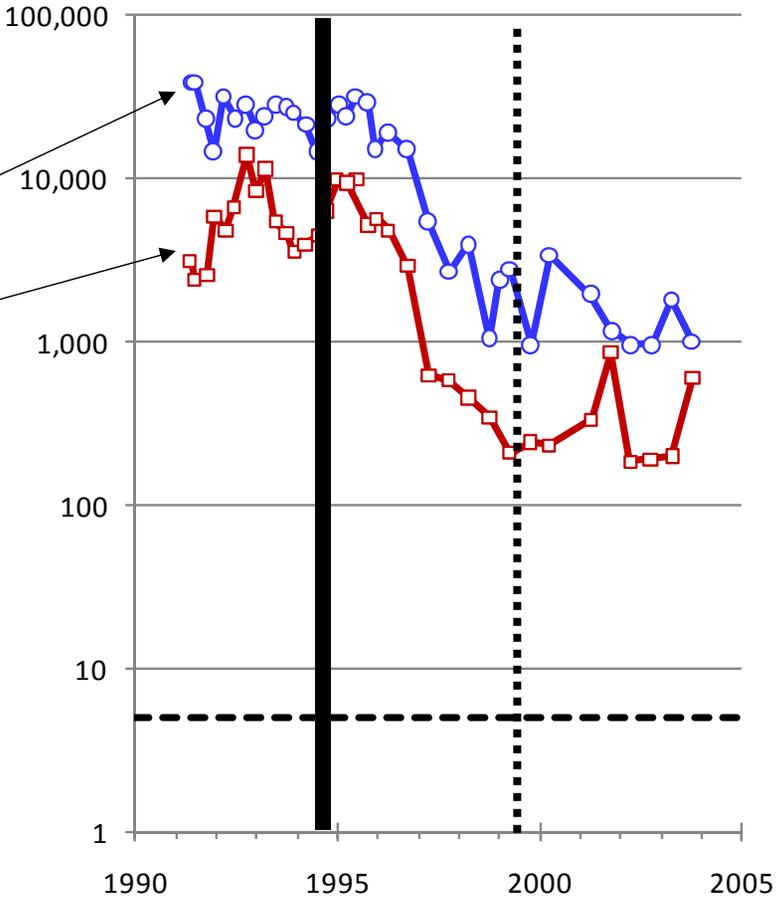


Source: Modified from Chapman and Parker (2005)

Connecticut Site (Chapman & Parker, 2005)



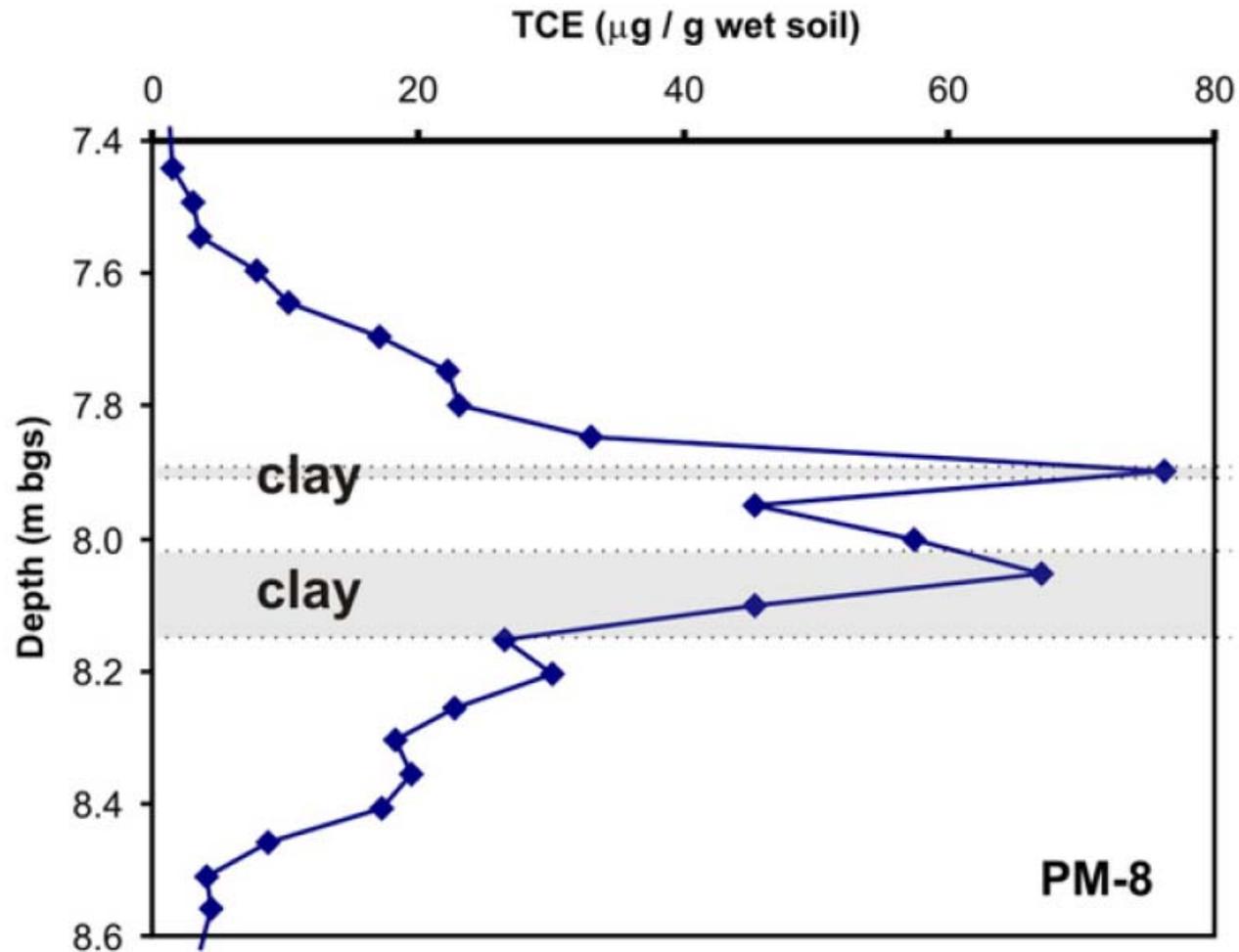
DNAPL Source Zone



Concentration reduction stalled at 93% (15x)

High Resolution Soil Sampling

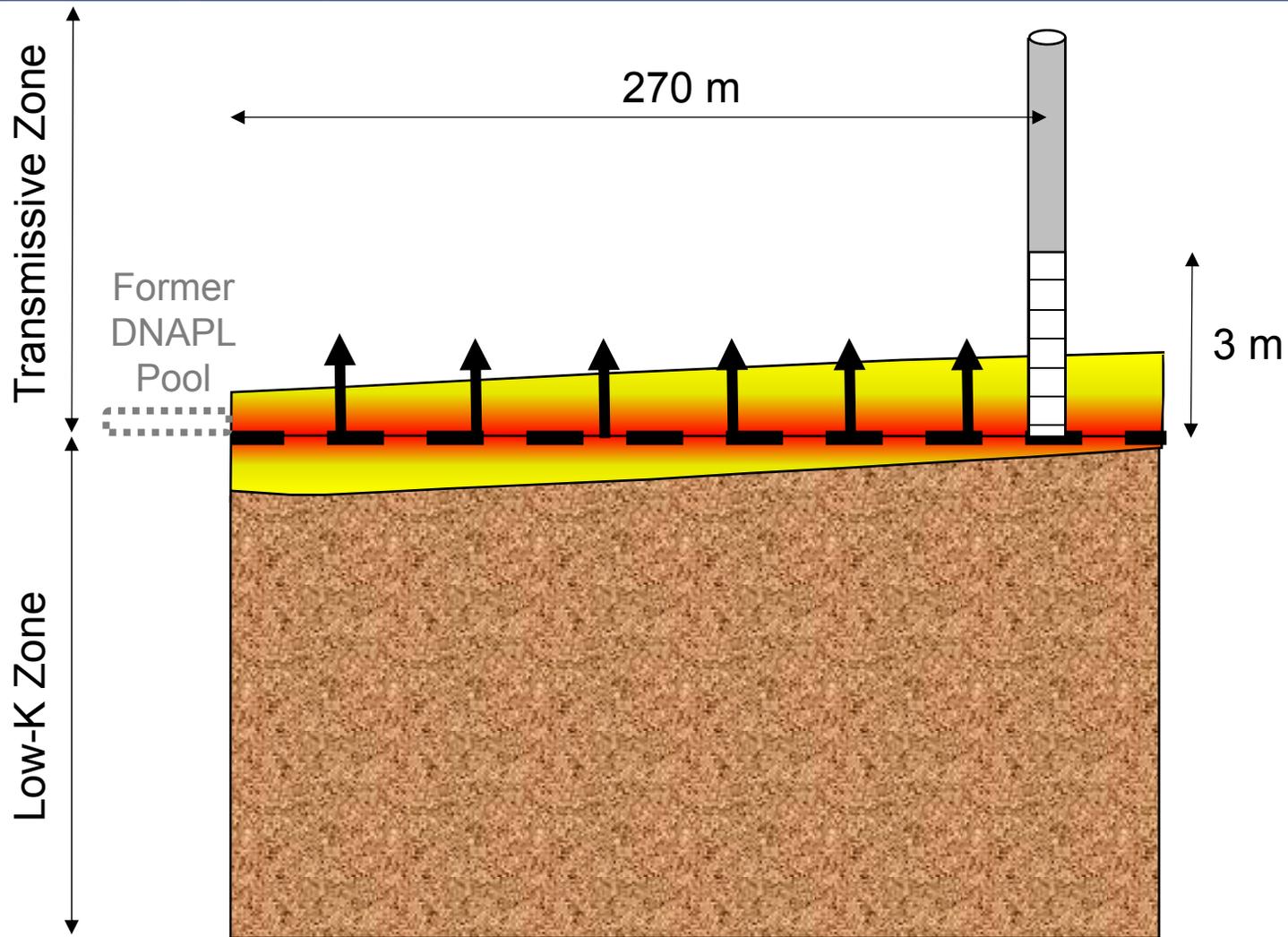
Note – convert soil to GW concentrations to confirm if back-diffusion profile with depth.



Parker et al., 2008, J. Cont. Hydrol., 102: 86-104



Back-Diffusion Modeling Example

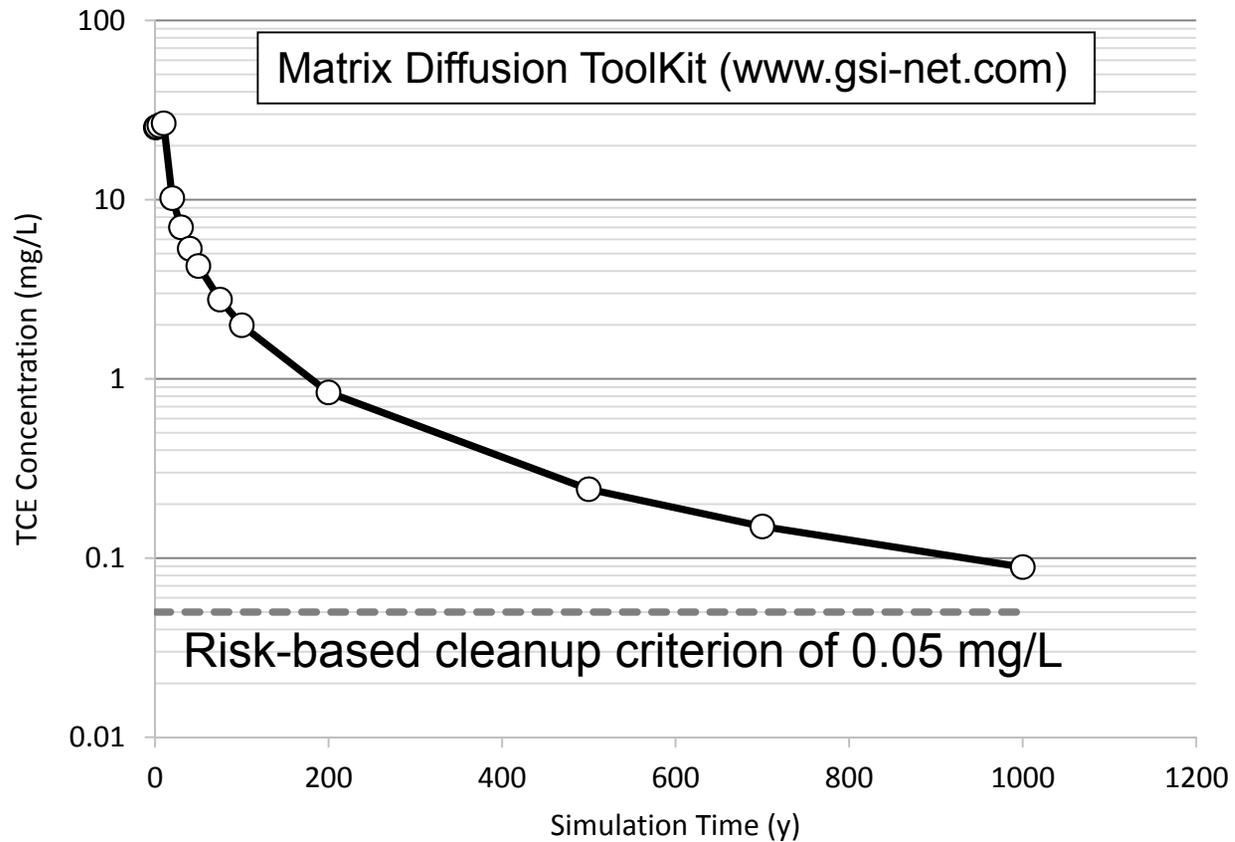


Source: Carey et al. (2014b)



Back-Diffusion Modeling Example

Distance of well from source: 270 m



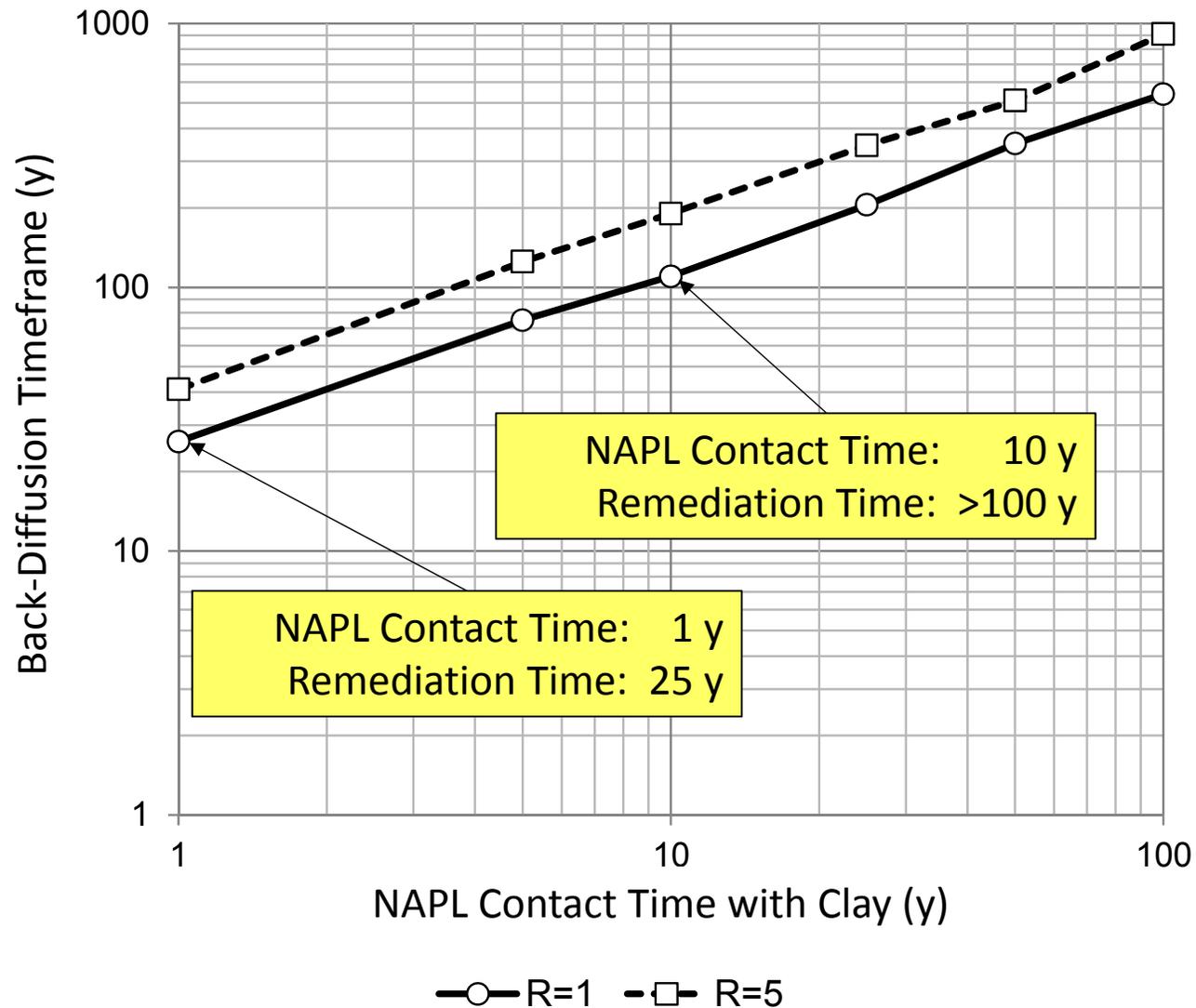
Source: Carey et al. (2014b)

Mass Discharge In/Out of Fine-Grained Layer (THICK)

- Seyedabbasi et al. (2012)
 - See Eq. B-23 and B-24 in Appendix B of course notes
- Small flux into clay from NAPL, relative to surface or through-discharge
 - May be ignored for NAPL depletion modeling purpose
- Mass discharge from fine-grained layers in plume cause substantially bigger influence on timeframe

Back-Diffusion Timeframe vs. NAPL Contact Time

Note – based on thick aquitard assumption.



In Situ Remediation (ISR-MT3DMS)

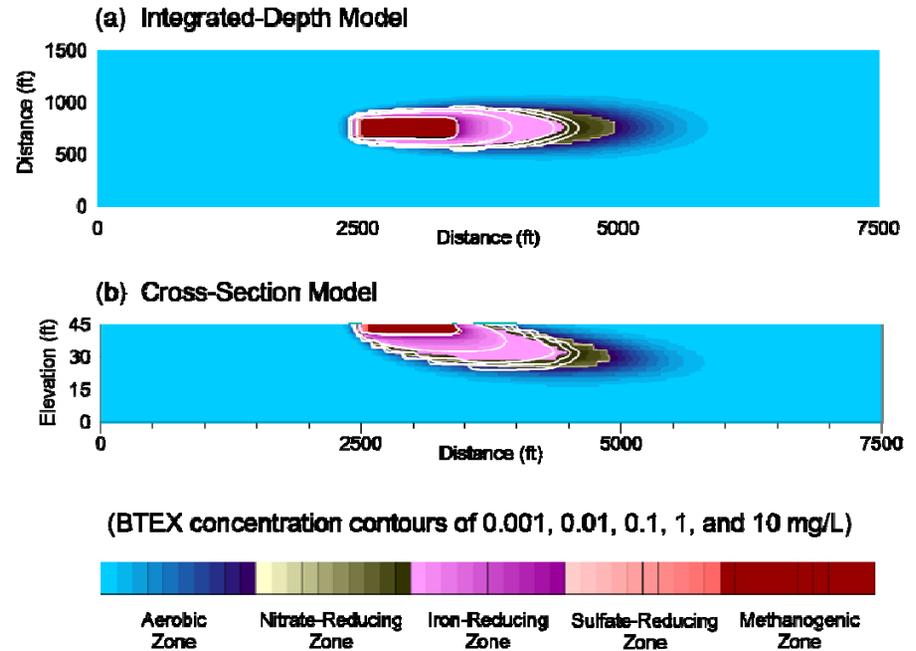
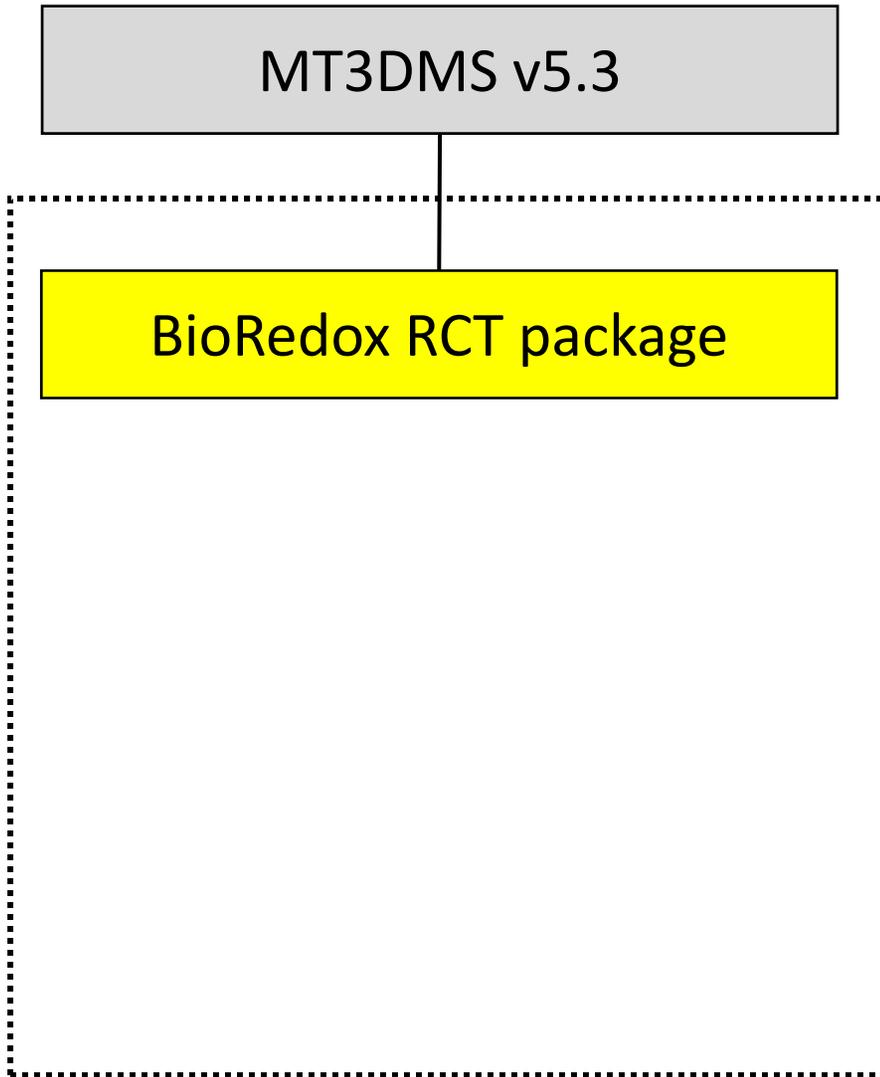
MT3DMS v5.3

Dr. Chunmiao Zheng

PUBLIC DOMAIN

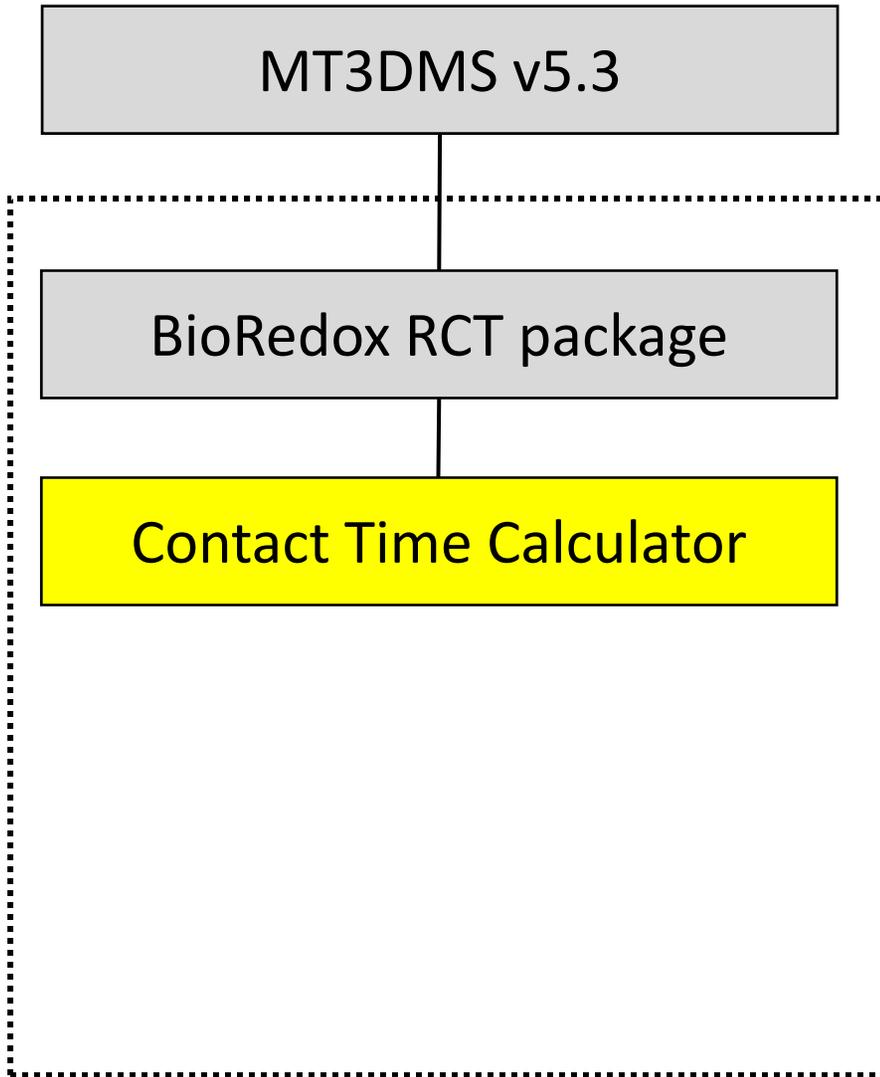


In Situ Remediation (ISR-MT3DMS)



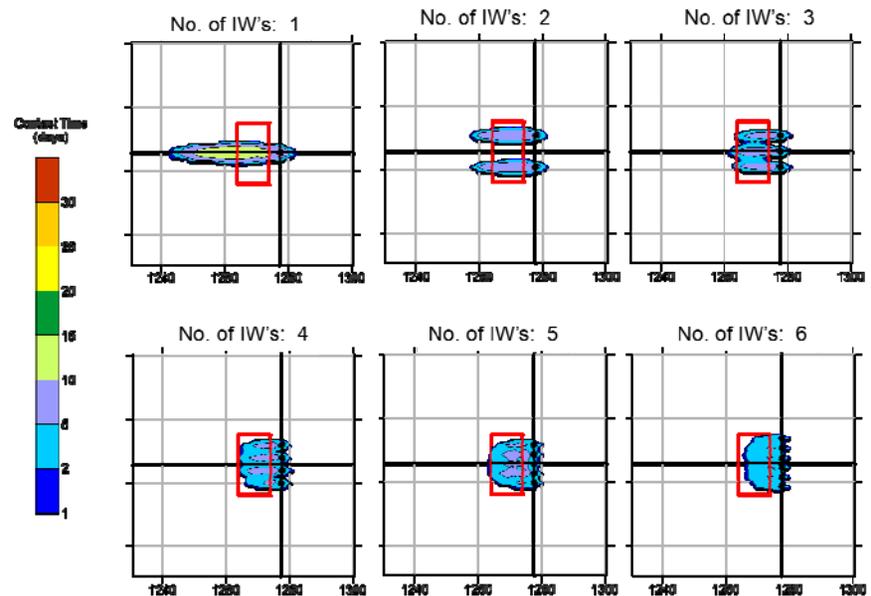
- Flexible reaction framework
- Redox zone visualization
- Mineral precip./dissolution
- Rate stimulation/inhibition

In Situ Remediation (ISR-MT3DMS)

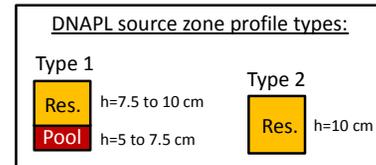
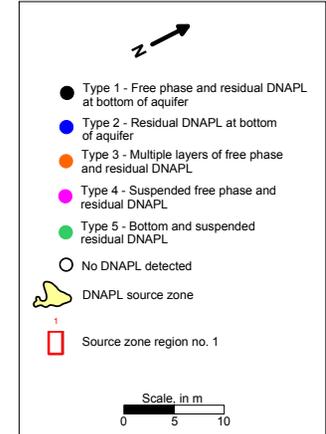
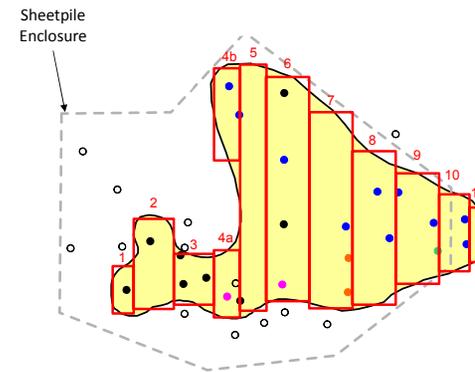
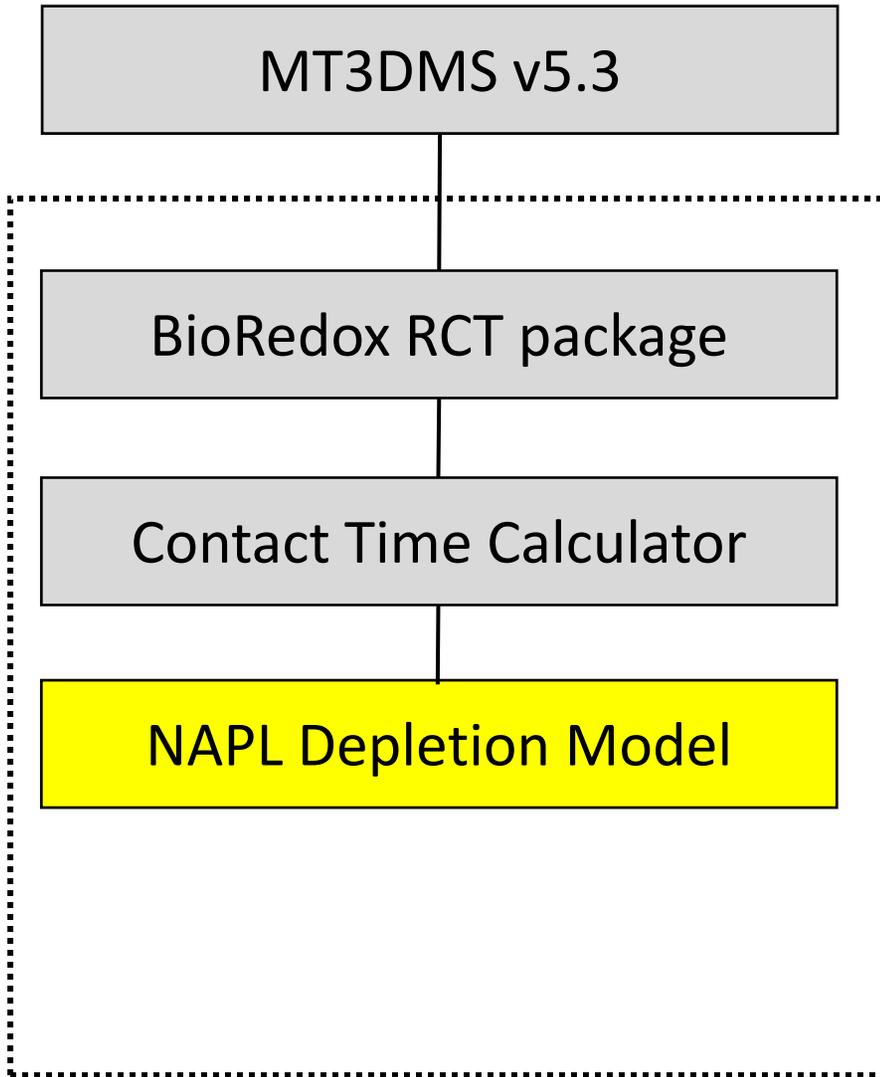


Optimization Metric

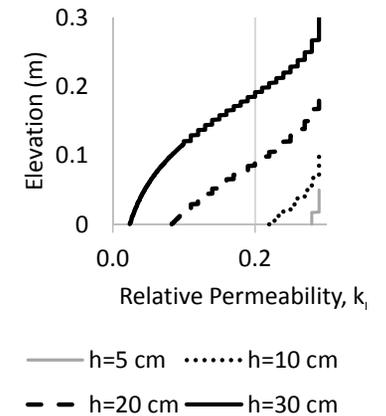
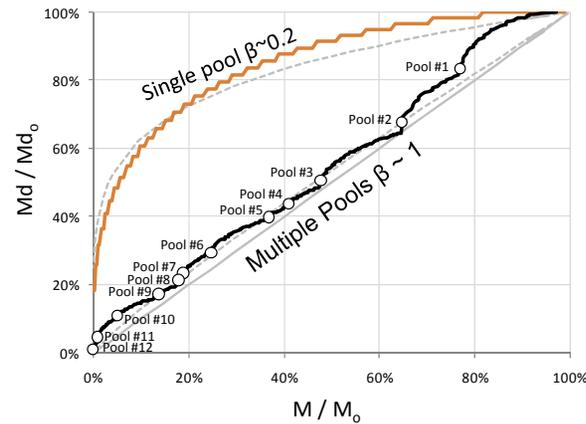
Injected Volume: 2000 L



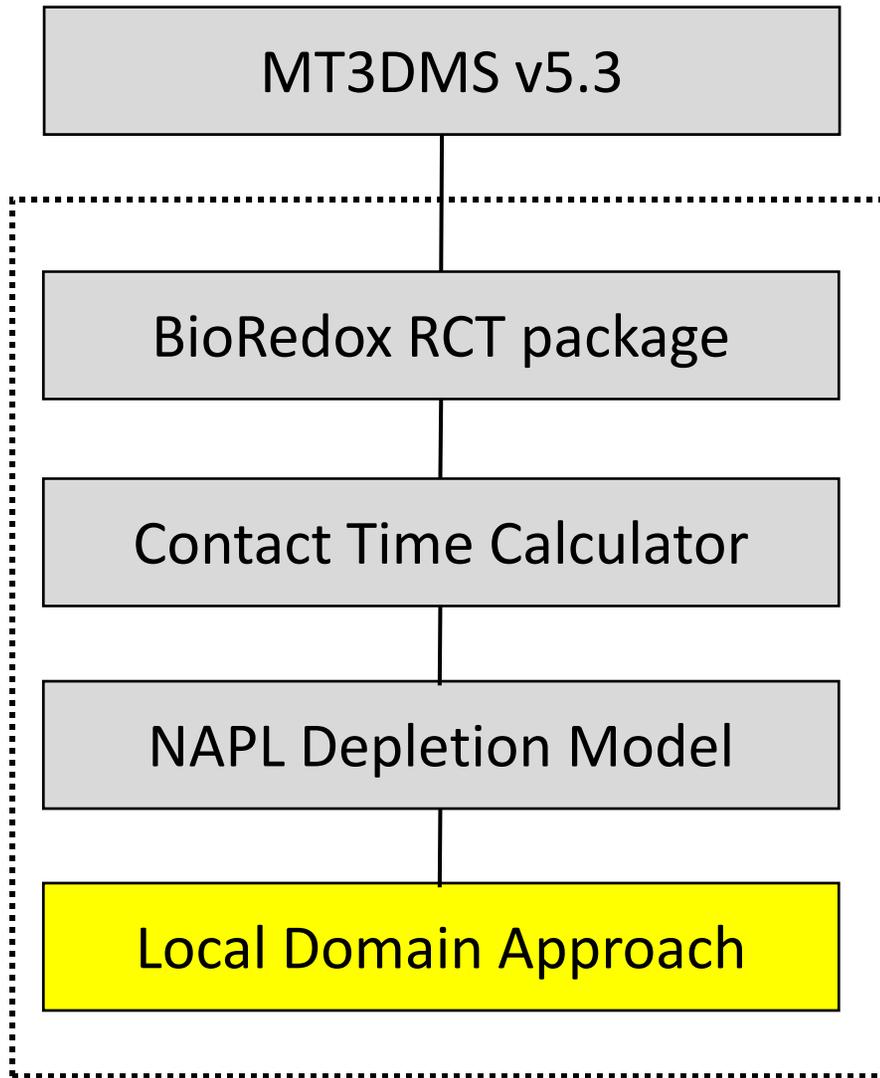
In Situ Remediation (ISR-MT3DMS)



Parker et al., 2003
 Parker et al., 2004
 Chapman and Parker, 2005
 Stewart, 2002



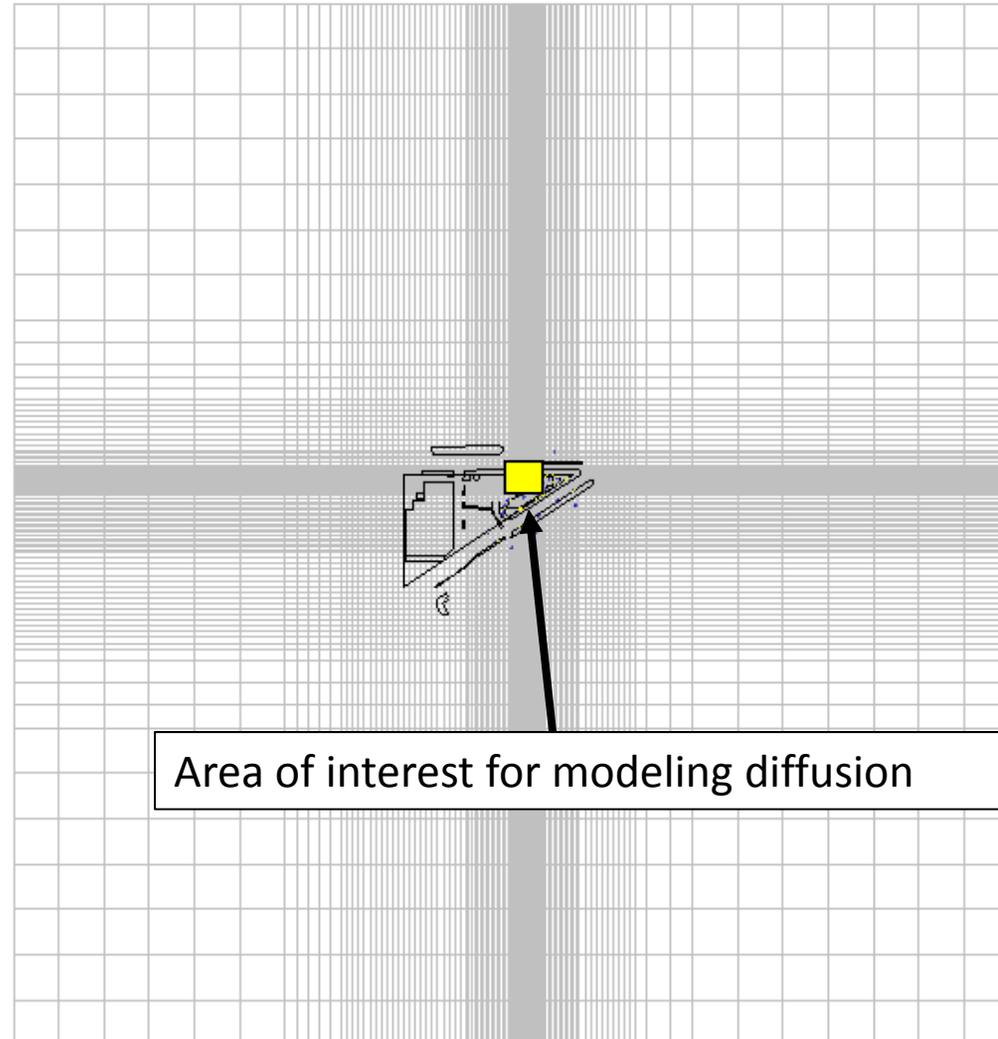
In Situ Remediation (ISR-MT3DMS)



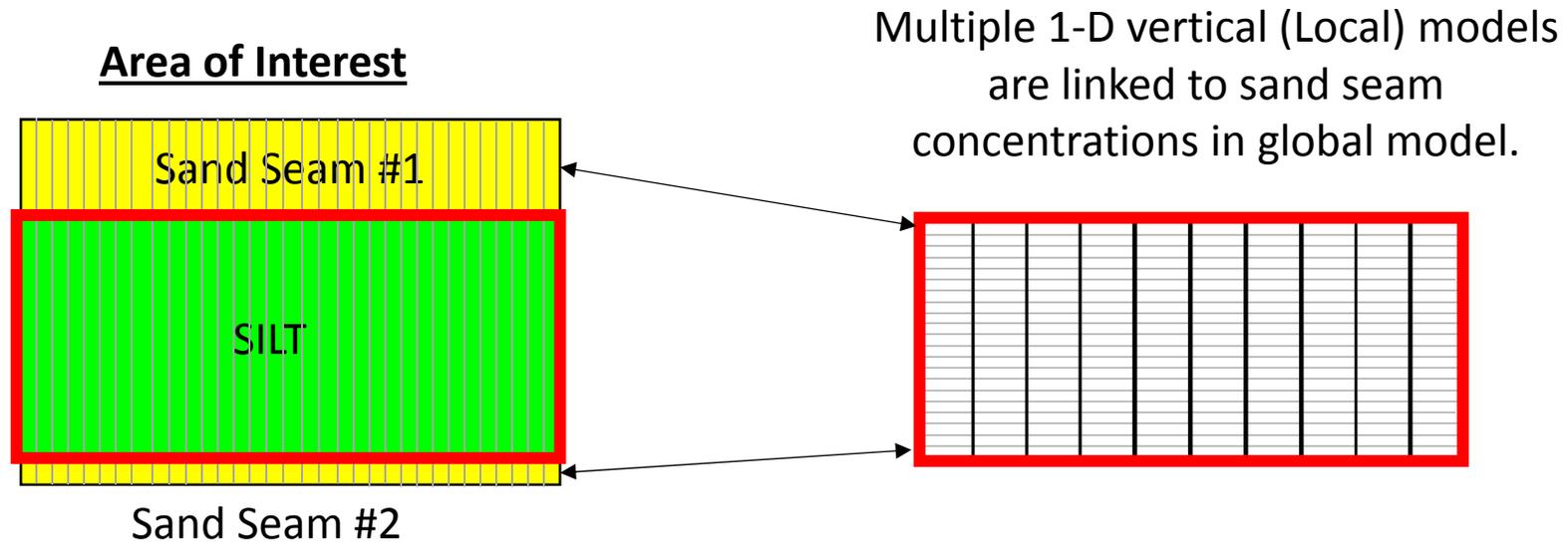
Large model linked to local 1-D model(s).

Local Domain Approach

Global Model Domain

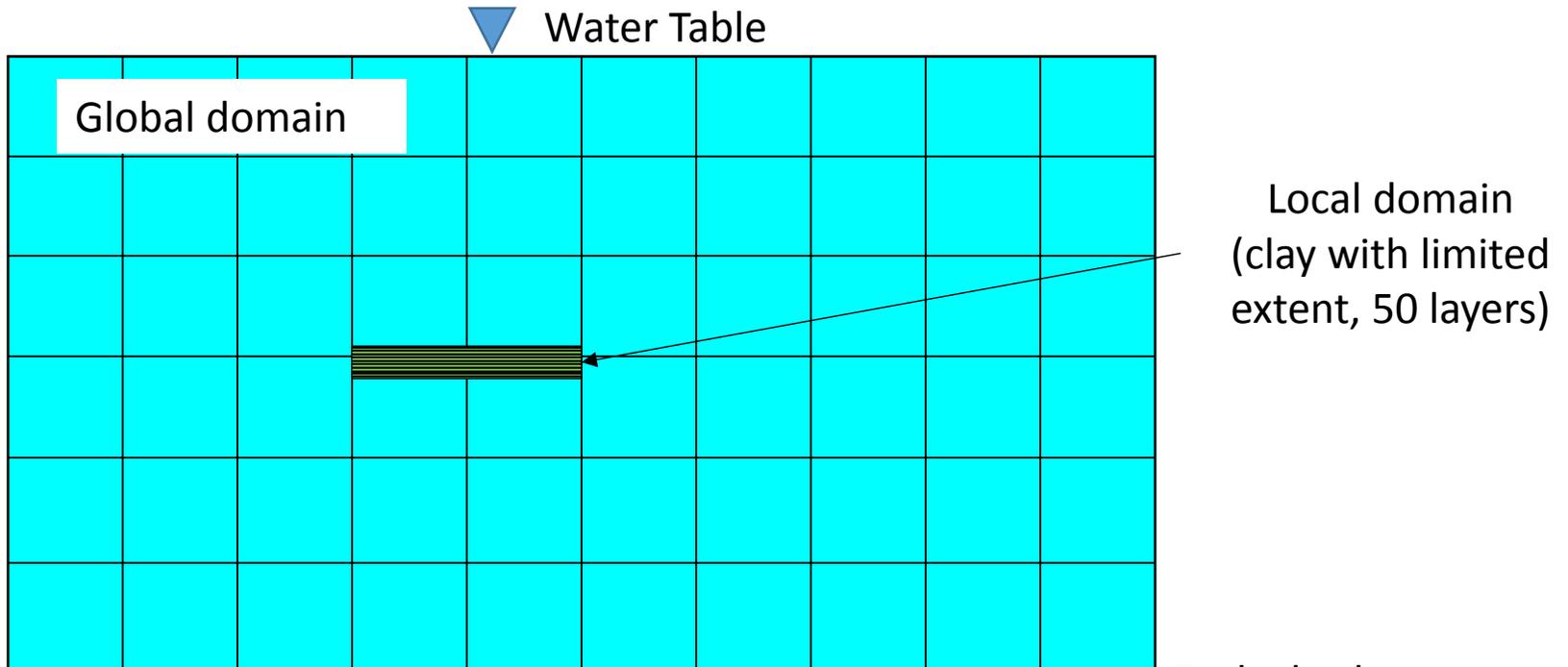


Local Model Domains for Silt (1-D Diffusion)



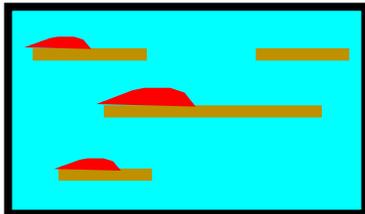
Silt layer is inactive to transport in global model.

Local Domain Approach



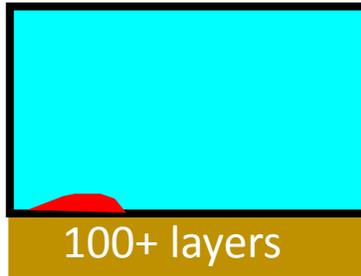
Each clay lens:
20 to 100+ layers

1

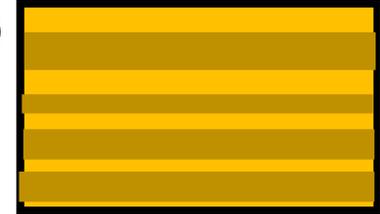


Each clay lens:
10 to 100+ layers

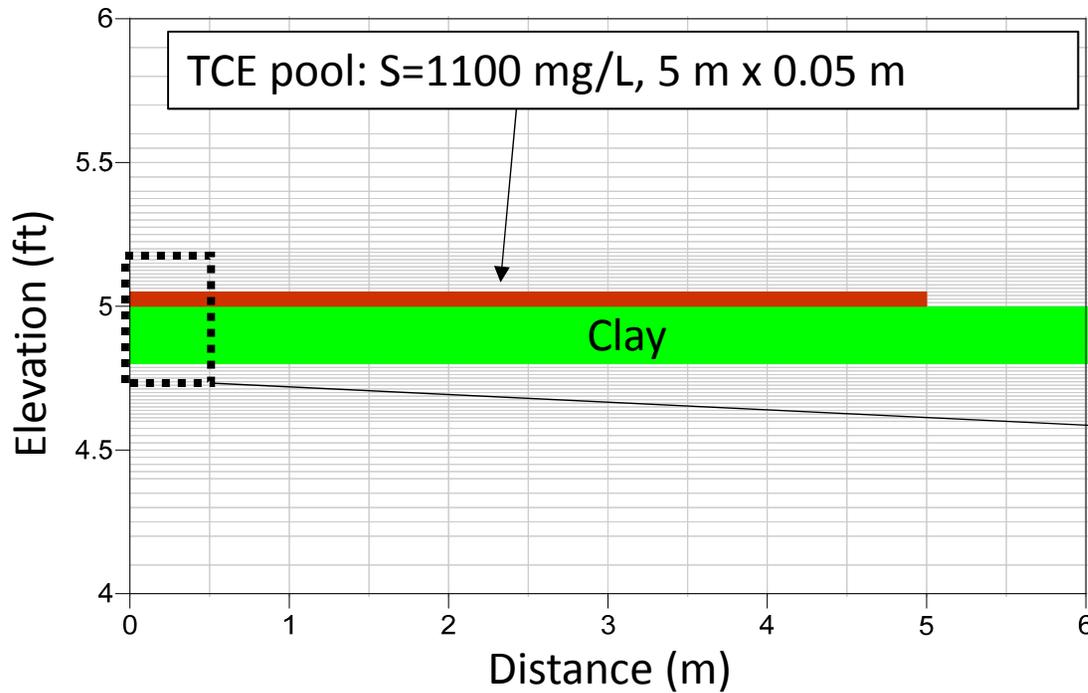
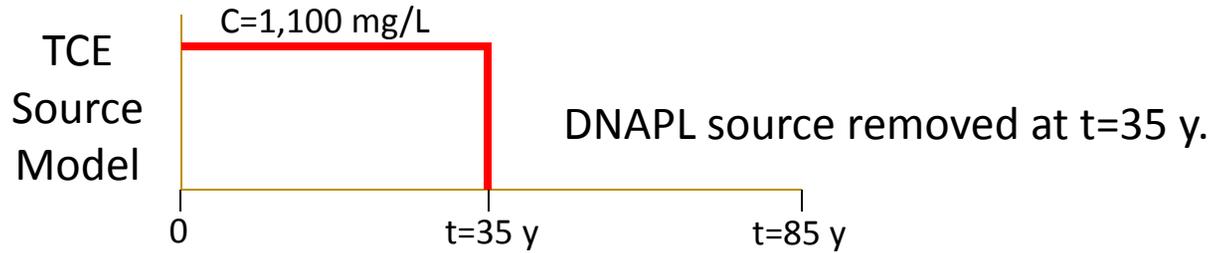
2



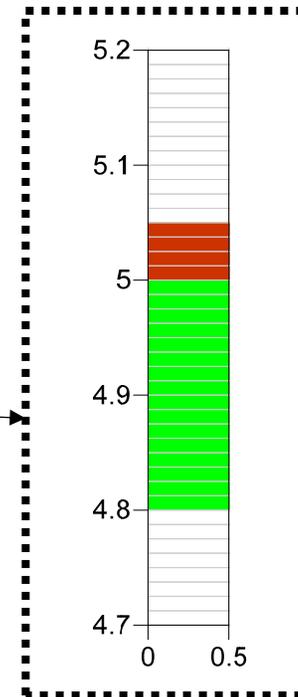
3



2-D Model Grid

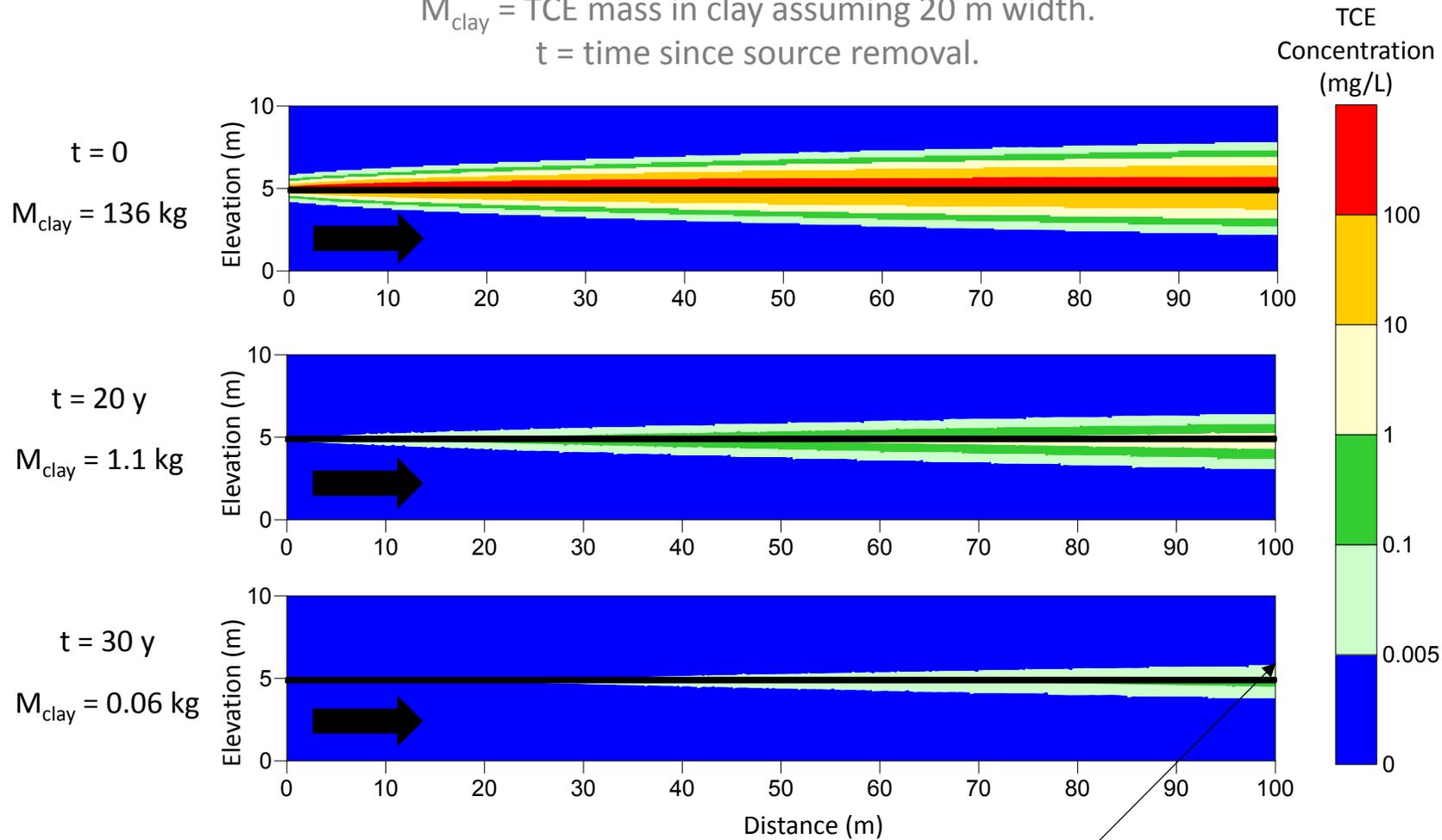


16 layers
in clay



Simulated TCE After Source Removal

M_{clay} = TCE mass in clay assuming 20 m width.
 t = time since source removal.

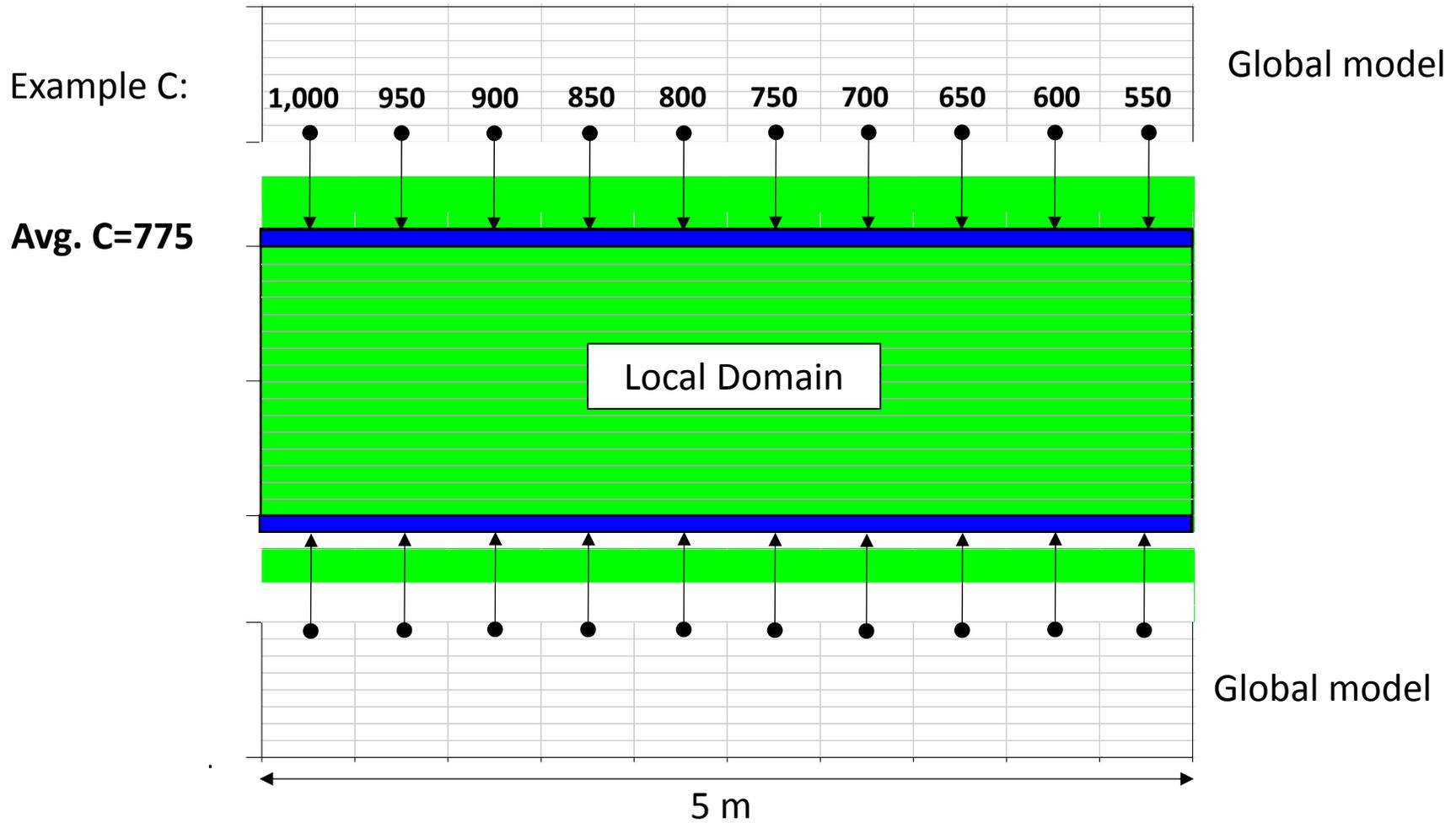


30 years after source removal:
 99.96% mass depletion in clay, avg. $C_{\text{well}} = 12 \text{ to } 126 \text{ ug/L}$

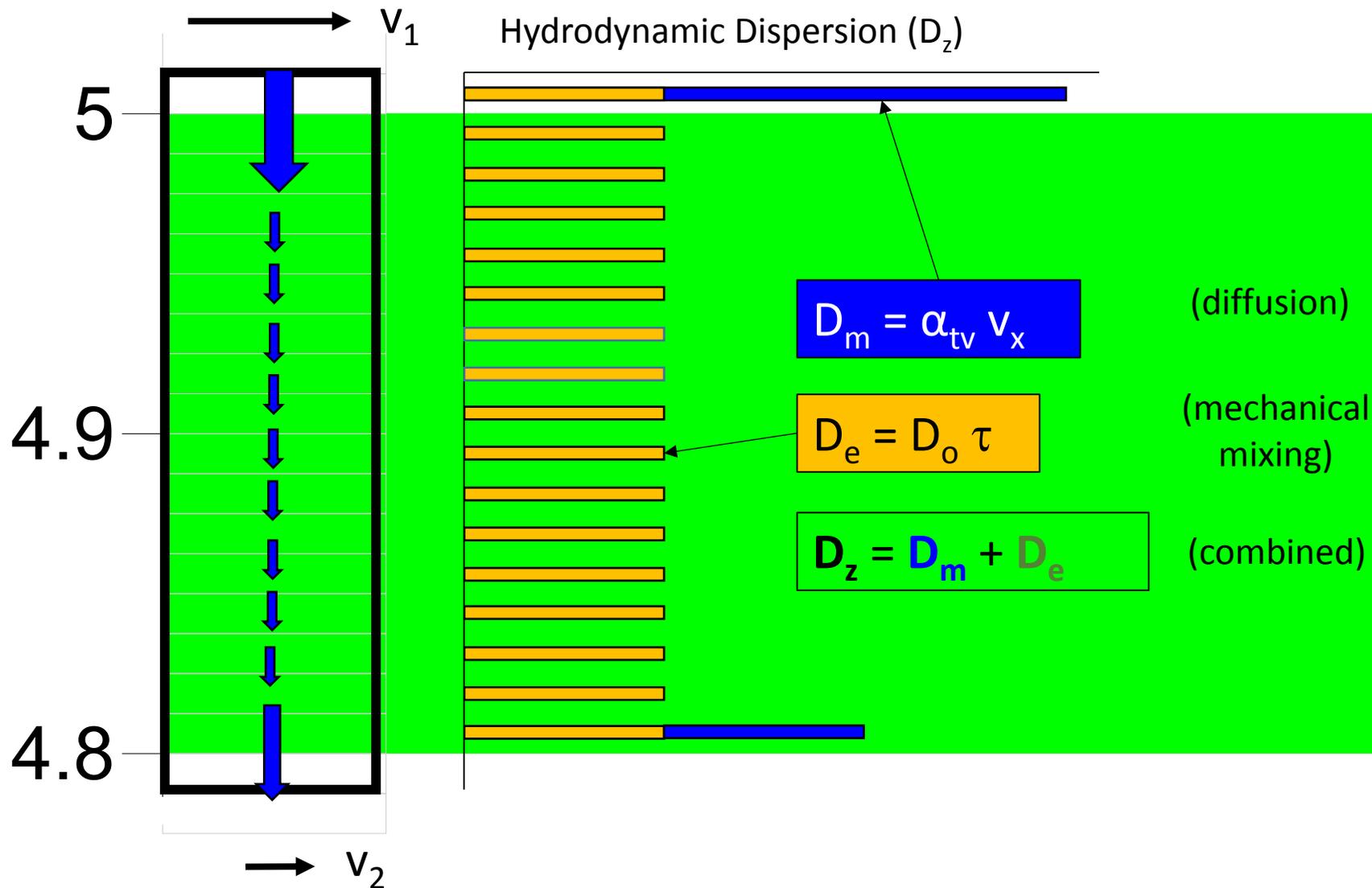
Md into top of clay = 15% to 40% of Md from DNAPL pool.

Local Domain Approach

Local domain $\Delta x = 5$ m, clay thickness varied.



Local Domain Dispersion



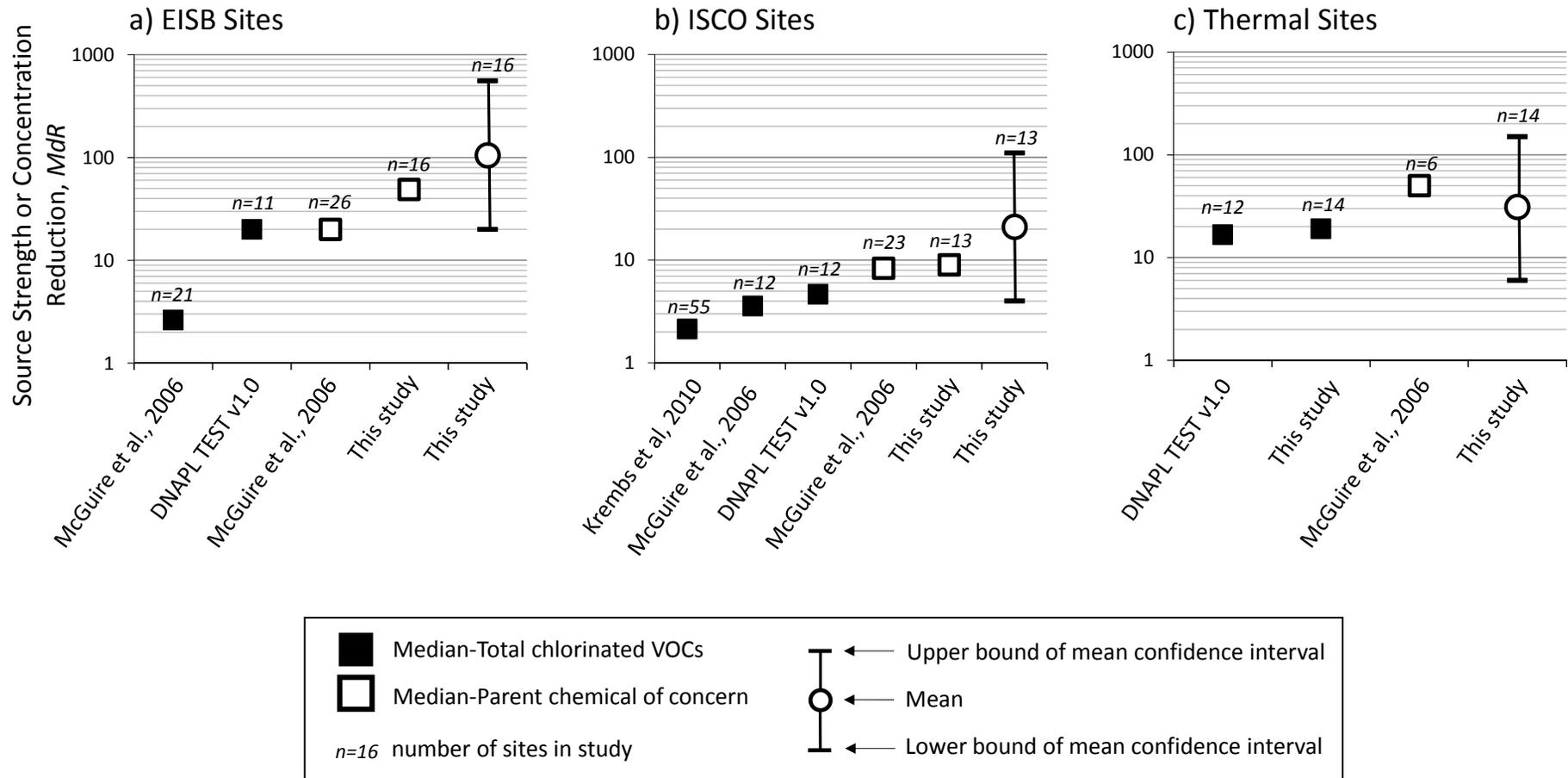
DNAPL Source Remediation

- MNA
- Enhanced dissolution
 - ISCO, EISB, Strategic P&T
- Thermal

Question: How much reduction in mass discharge can we expect to attain?



Mass Discharge Reduction: Interim Goal



Source: Carey, McBean, and Feenstra, 2014

Goal Attainability Depends on:

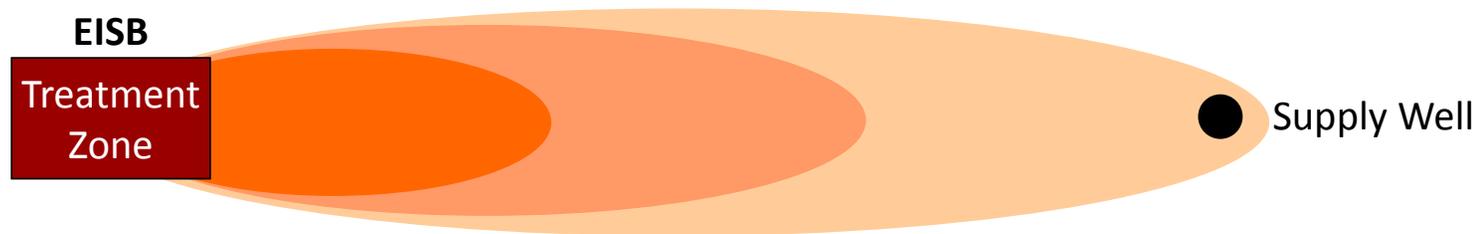
- Conceptual Site Model
 - Where is plume mass coming from?
- Heterogeneity – geology and DNAPL
 - **Site complexity is an important factor.**
- DNAPL chemical properties
- DNAPL accessibility to groundwater flow



Transition from Active to Passive Treatment

Case Study – Well 12A Superfund Site, Washington

STEP 1: Active source treatment until interim source strength reduction goal is achieved.



STEP 2: After this goal is achieved, transition to MNA in source zone



Upcoming transition checklist: ITRC – Remediation Management of Complex Sites

Integrated Source-Plume Management

- Source treatment – recognize limitations in:
 - DNAPL removal
 - Attainable, interim reduction in mass discharge
 - Use interim goal to transition to passive src treatment
 - Plume restoration (back-diffusion)
 - Characterize mass stored in silts/clays, and time to deplete once source treated or contained
 - Plume area larger than source – governs timeframe
- Ideally cost of source treatment is balanced with limitations in plume restoration
- Regulatory mechanisms – alternative end points



Initial Framework for DNAPL Remedy Evaluation

1. Site characterization

- DNAPL architecture – ganglia vs. pools
- Mass discharge (Md) history
- Potential for back-diffusion

2. Define attainable interim goals for DNAPL source zone

e.g. Realistic mass discharge reduction based on comparison to other sites

3. Evaluate back-diffusion timeframe in plume

4. Predict time to attain interim goals for DNAPL treatment, to support cost-benefit analysis



Questions?



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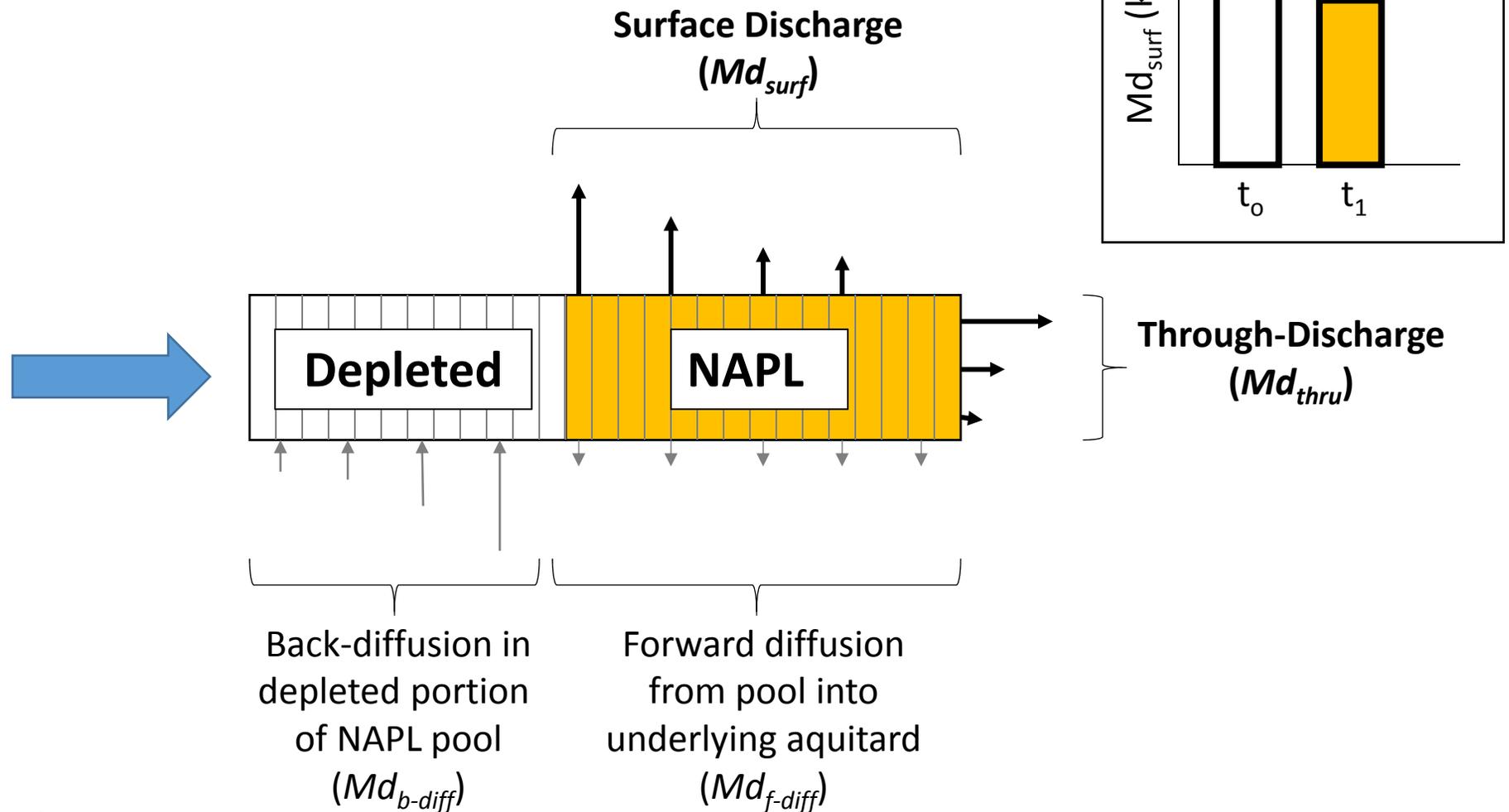
Introduction to NAPL Depletion Model (NDM)

Section 3



NAPL Depletion Model (NDM)

NAPL SUB-ZONE (i.e. layer)



Forward and Back-Diffusion

- Seyedabbasi et al. (2012) – analytical solution for forward and back-diffusion in silt/clay below DNAPL pools
 - Forward diffusive discharge from pool is negligible in pool mass balance – much smaller than surface discharge
- In terms of NAPL depletion, forward diffusion will not be considered in this course but can be easily modeled for discrete NAPL sub-zones using the solution in Seyedabbasi et al. (2012)
- Back-diffusion is a bigger problem for the downgradient plume relative to the source zone, because plumes occur over a larger area than source zones



NAPL Depletion Model (NDM)

NAPL Sub-zone

- Length
- Width
- Thickness
- C_{eff} , S_{no} , ρ_n
- K_{sat}
- Gradient
- Total porosity
- Column Δx
- Temporal discretization

Md_{surf}

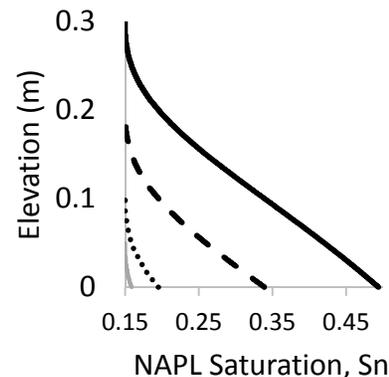
- Tortuosity
- D_o
- α_{tv}
- U/G sub-zone?
- f_{surf} multiplier
= 1 or 2

Md_{thru}

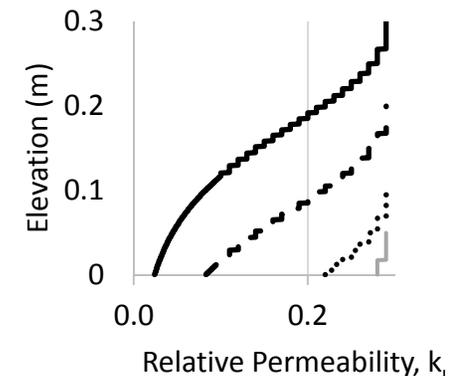
- Column application (first or uniform to all)
- Efficiency factor
- Optional Pool $S_n(z)$, $k_{rw}(z)$
 - Van Genuchten α_{aw} , n
 - σ_{nw} , σ_{aw}
 - S_{wr} , S_m
 - Layer Δz
- Residual layer dilution factor $f_{thru}(t)$
- U/G sub-zone?

Enhanced Attenuation

- f_{ed} (enhanced dissolution factor)
- f_{grad} (enhanced hydraulic gradient)
- f_{bio} (enhanced biodegradation)
- Daughter product ratios



— h=5 cm h=10 cm
- - h=20 cm ——— h=30 cm



— h=5 cm h=10 cm
- - h=20 cm ——— h=30 cm

NAPL Depletion Model (NDM)

NAPL Sub-zone

- Length
- Width
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- Gradient
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- Temporal discretization

Md_{surf}

- Tortuosity
- D_o
- α_{tv}
- U/G sub-zone?
- f_{surf} multiplier
= 1 or 2

Md_{thru}

- Column application (first or uniform to all)
- Efficiency factor
- Optional Pool $S_n(z), k_{rw}(z)$
 - Van Genuchten α_{aw}, n
 - σ_{nw}, σ_{aw}
 - S_{wr}, S_m
 - Layer Δz
- Residual layer dilution factor $f_{thru}(t)$
- U/G sub-zone?

Multi-component NAPL (X_{io})

Enhanced Attenuation

- f_{ed} (enhanced dissolution factor)
- f_{grad} (enhanced hydraulic gradient)
- f_{bio} (enhanced biodegradation)
- Daughter product ratios





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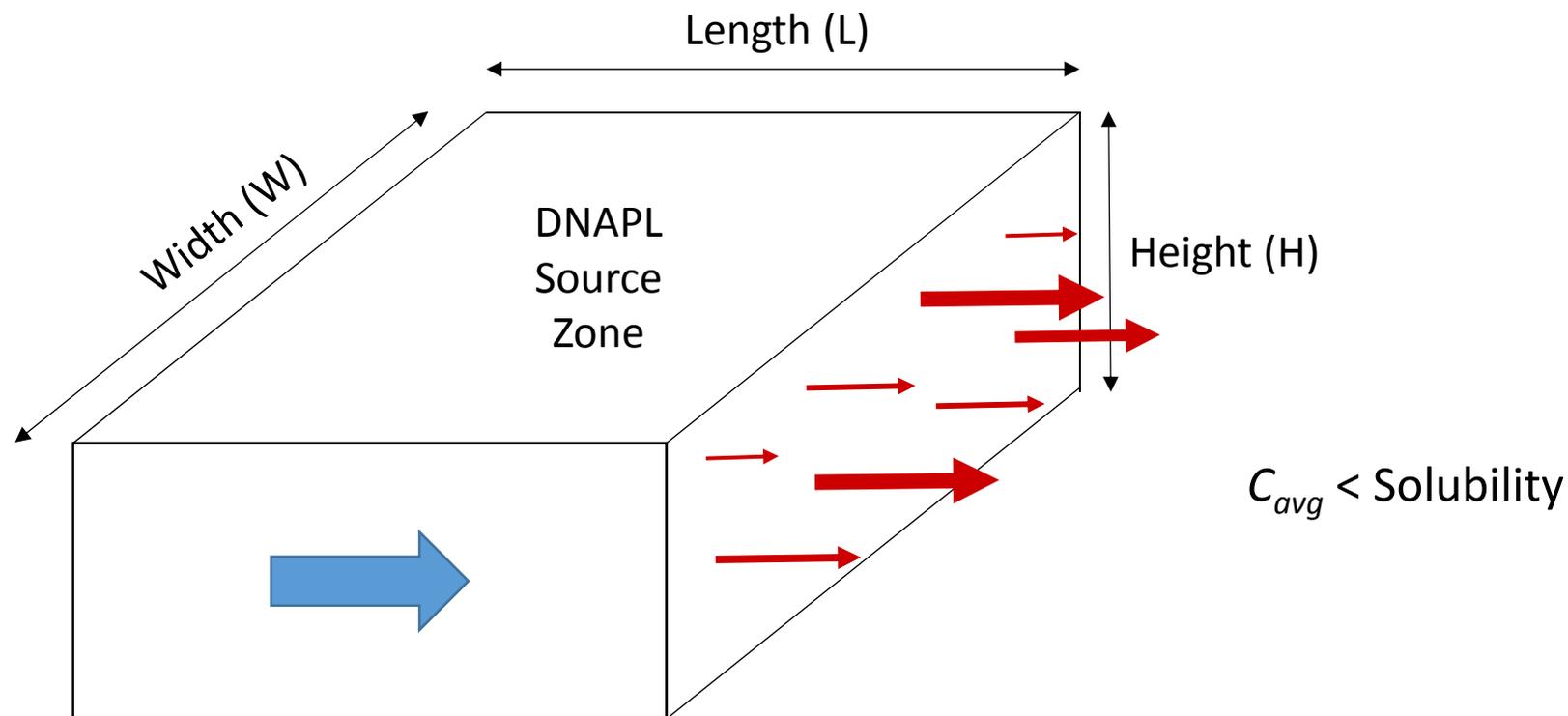
Example No. 1: Mixed Source Zone

Section 3a



Example No. 1: Mixed Source Zone

- Mixed source zone – encompasses soil volume with DNAPL pools and/or residual DNAPL, and includes soil where DNAPL is absent



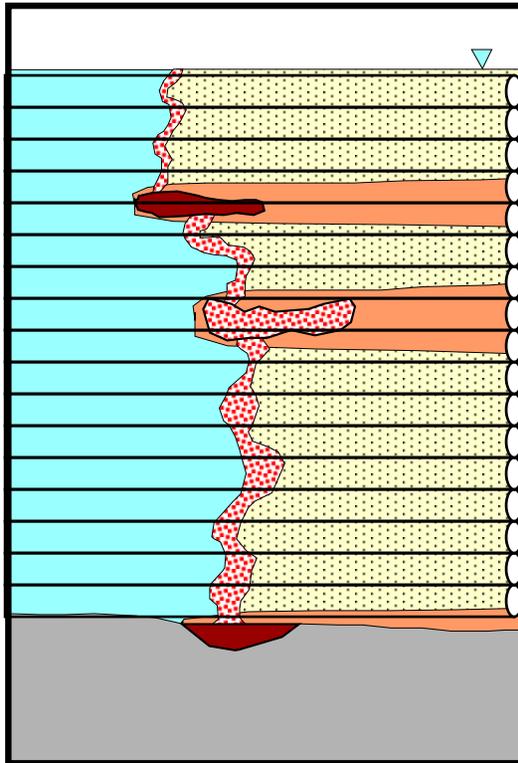
e.g. TCE $C_{avg} = 140 \text{ mg/L}$ (10% of solubility)



Average Concentration Example

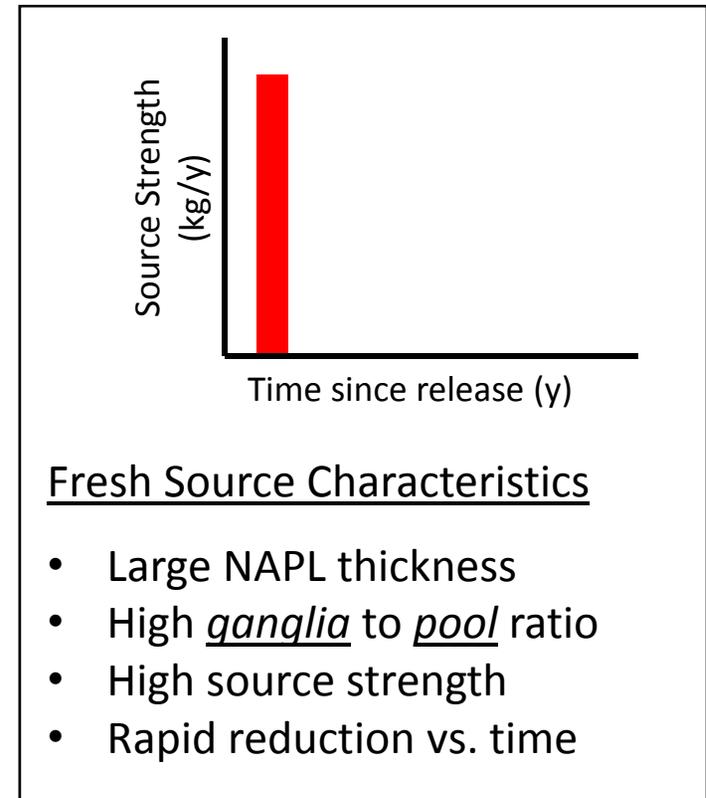
Fresh Source

$$C_{avg_o} = 88\% \text{ of Solubility}$$



Multilevel Samplers

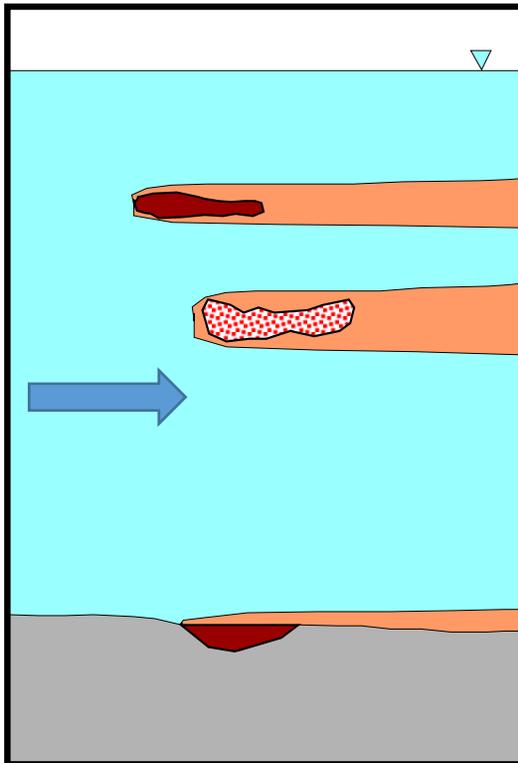
- C = Solubility
- C = 0
- C = Solubility
- C = 0
- C = Solubility
- C = Solubility
- C = Solubility



17 multilevel samplers, all with concentrations equal to solubility because all screens are situated directly downgradient of a DNAPL sub-zone (pool or ganglia).

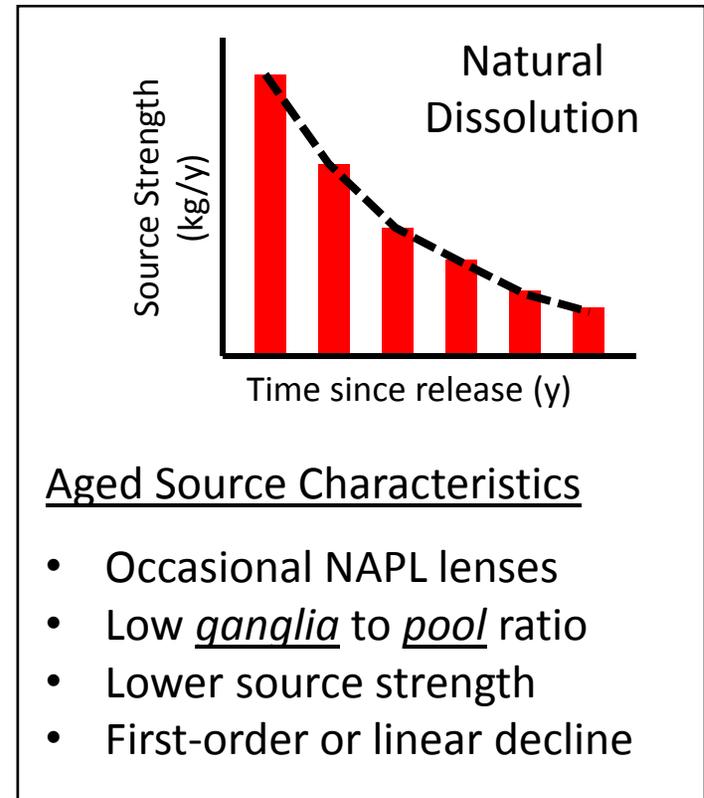
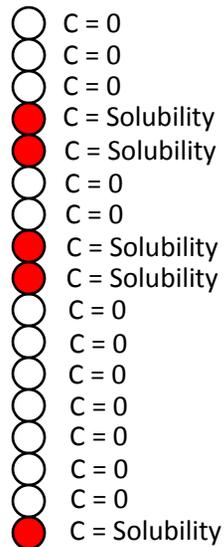
Average Concentration Example

Aged Source



$$C_{avg} = 30\% \text{ of solubility}$$

Multilevel Samplers



Note – C_{avg} is a flux-weighted average calculation. If K is uniform then it may be as simple as calculating the arithmetic average concentration at a monitoring transect of wells directly downgradient of the source zone; otherwise the calculation is more complicated.

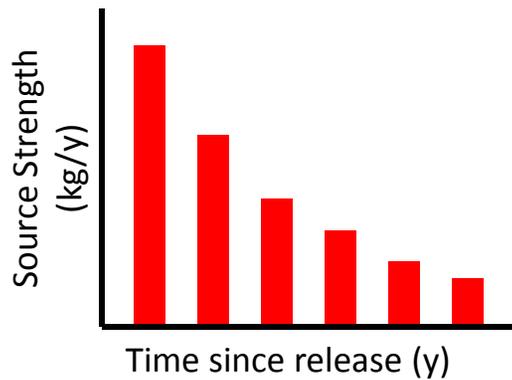


Average Concentration Example

- The average concentration at the downgradient source zone boundary is indicative of the relative number of streamtubes through the source zone that pass through NAPL
- In a large source zone, C_{avg} will decline over time
- Initial dilution factor, $f_{i0} = C_{avg_0} / \text{Solubility}$
- For example, if C_{avg_0} after a large release is 140 mg/L and solubility is 1400 mg/L, then $f_{i0} = 10\%$.
- Over time, the dilution factor will continue to decline as NAPL becomes depleted



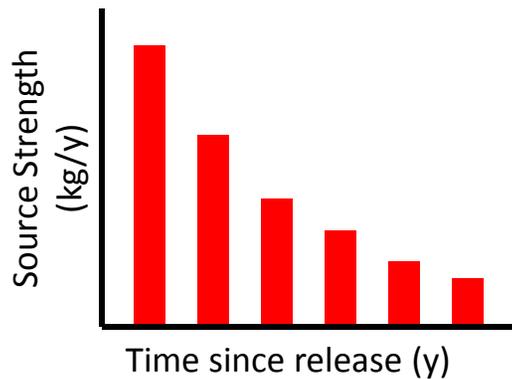
Dilution Factor Concept



Source Strength = mass discharge, or $Md = q A C_{avg}$

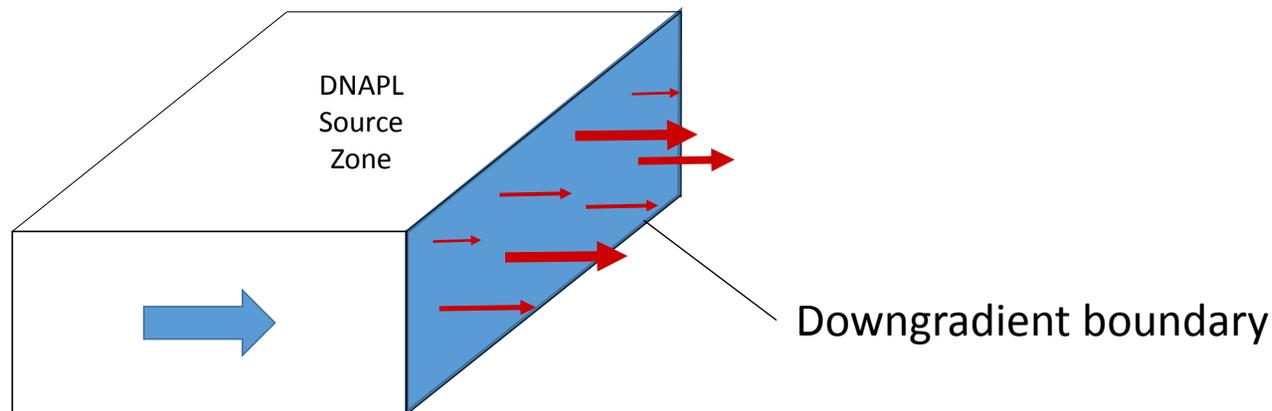


Dilution Factor Concept

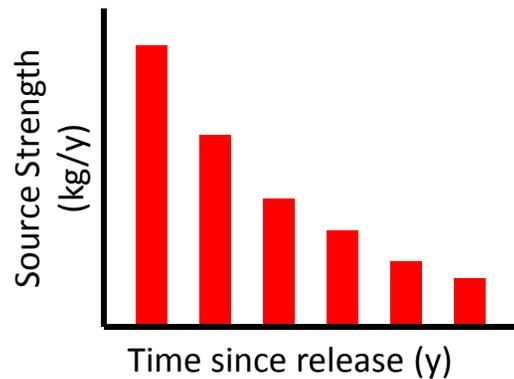


Source Strength = mass discharge, or $Md = q A C_{avg}$

C_{avg} = average concentration at source zone boundary



Dilution Factor Concept



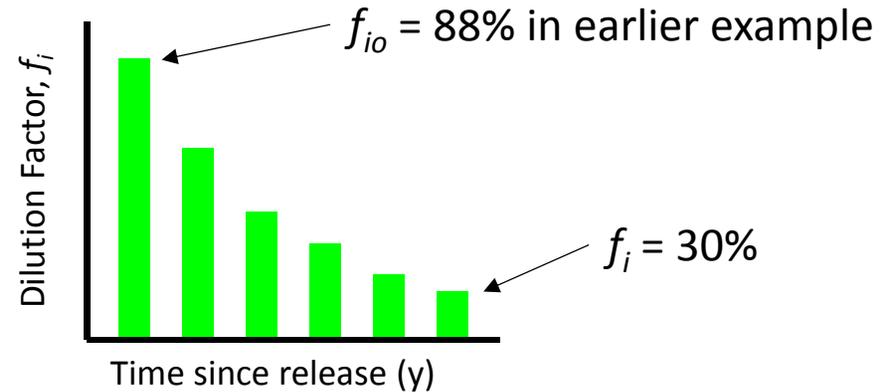
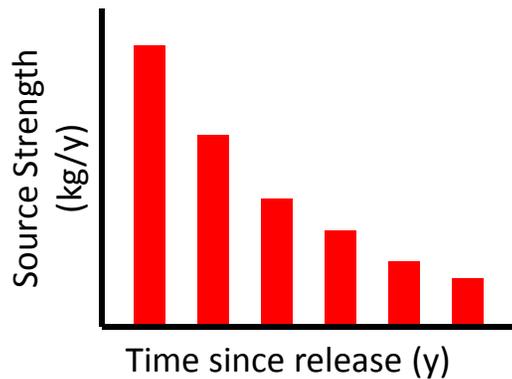
Source Strength = mass discharge, or $Md = q A C_{avg}$

C_{avg} = average concentration at source zone boundary

C_{avg_0} = initial average concentration



Dilution Factor Concept



Source Strength = mass discharge, or $Md = q A C_{avg}$

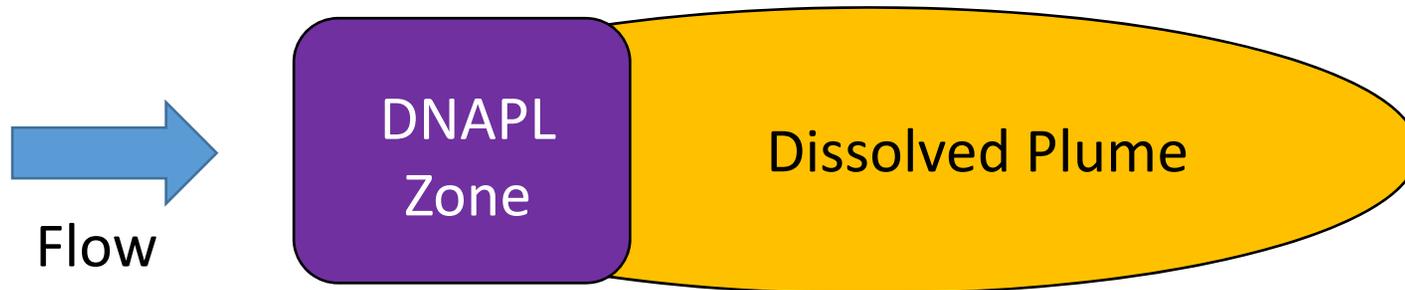
C_{avg} = average concentration at source zone boundary

C_{avg_0} = initial average concentration

f_i = dilution factor at time $t = C_{avg} / \text{Solubility}$

The dilution factor represents the relative number of streamtubes in a source zone that pass through NAPL.

Source Zone Transect with Streamtubes



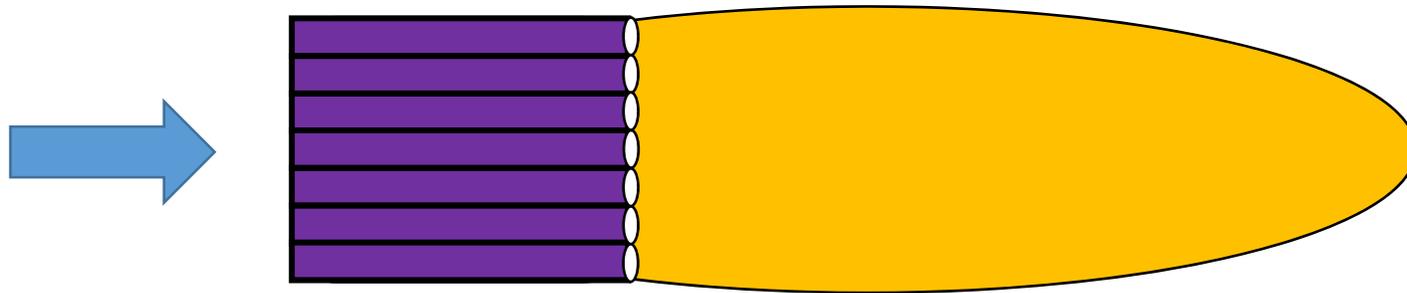
In case of a mixed DNAPL source zone, there are portions of the source zone where DNAPL is not present.

This is the simplest representation – a “black box” that averages conditions over the entire source zone.

This simplest case is used when individual DNAPL sub-zones (e.g. pools, or zones of residual DNAPL) are not readily identifiable.

Source Zone Transect with Streamtubes

Streamtube concept:



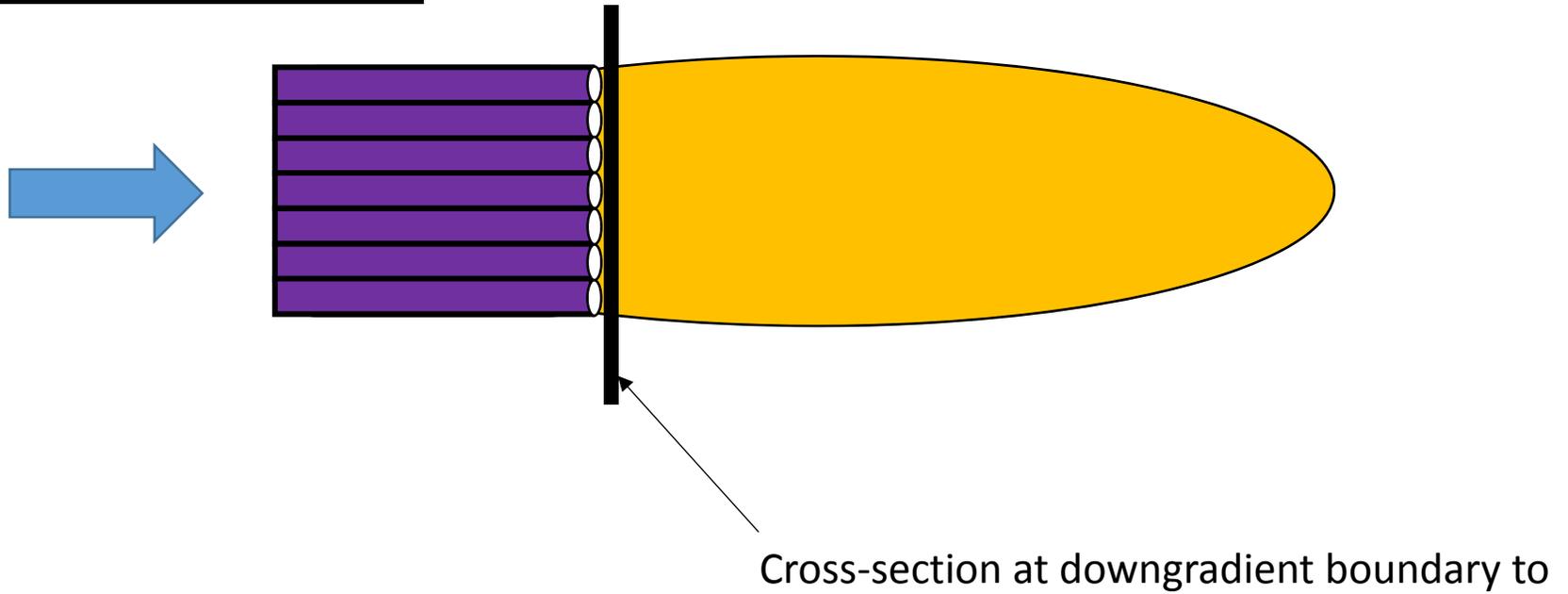
- Streamtubes through source zone (like pipes).
- Any streamtube intercepting DNAPL has $C = \text{Solubility}$.
e.g. for TCE, $C_{sol} = 1,400 \text{ mg/L}$.
- Any streamtube that does not intercept DNAPL has $C = 0$.

References: Jawitz et al. (2005); Fure et al. (2006)

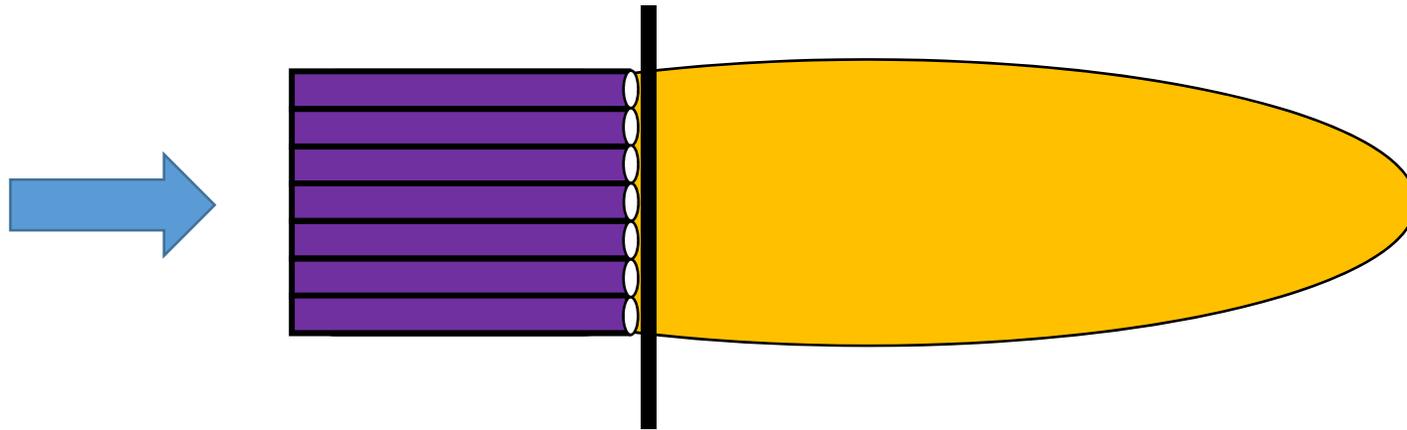


Source Zone Transect with Streamtubes

Streamtube concept:

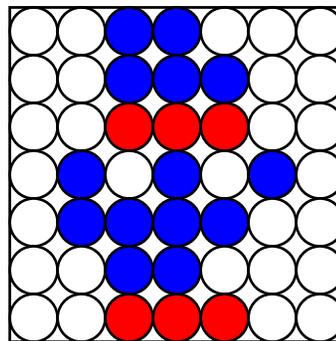
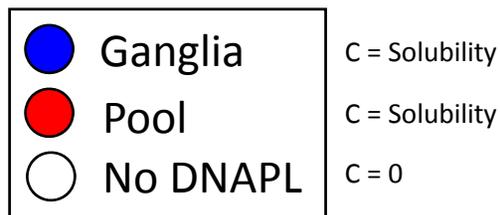


Source Zone Transect with Streamtubes



Cross-section looking upgradient into the source zone:

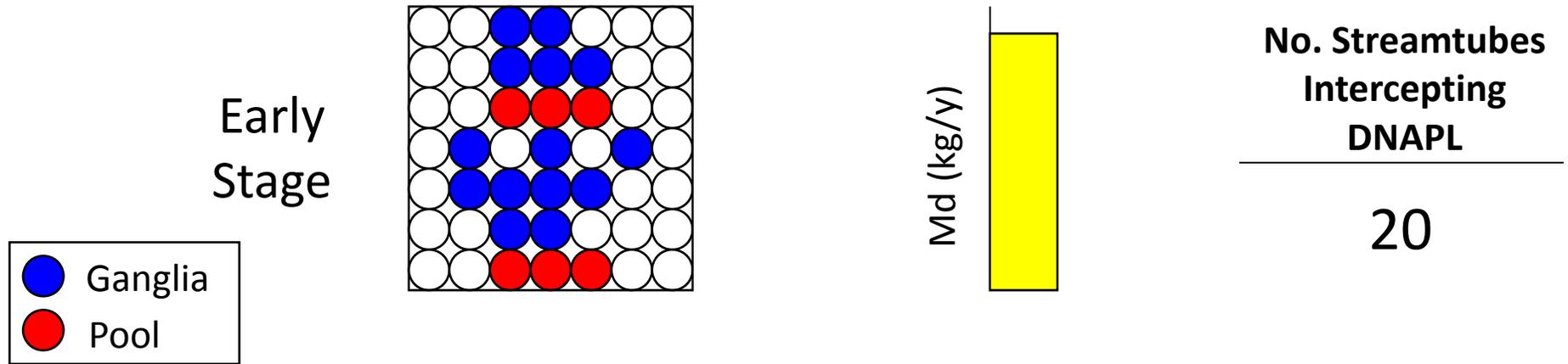
*Streamtubes
Intercepting:*



Early Stage

Note – streamtube concentrations are the same for ganglia and pools. They are distinguished here because streamtubes that intercept a DNAPL pool will persist for a longer period of time.

Source Zone Transect with Streamtubes



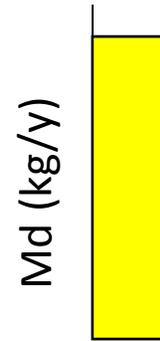
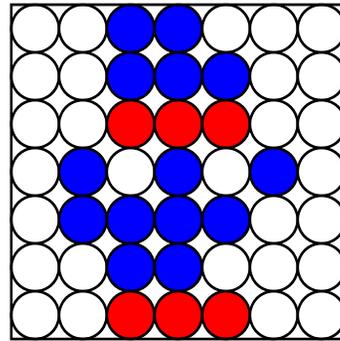
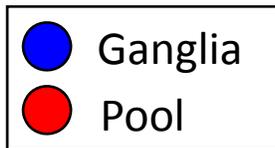
Total number of streamtubes in section = 49.

20 streamtubes intercept DNAPL.

$$C_{avg} = ?$$

Source Zone Transect with Streamtubes

Early Stage



No. Streamtubes Intercepting DNAPL

20

Total number of streamtubes in section = 49.

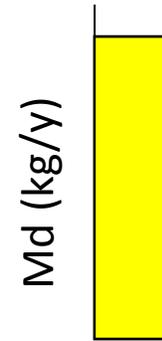
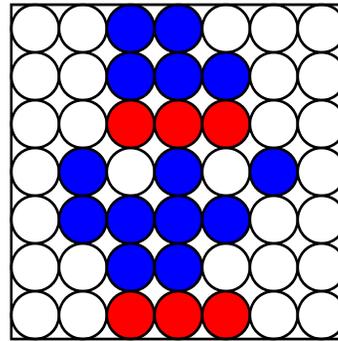
20 streamtubes intercept DNAPL.

$$C_{avg} =$$

$$\frac{(20 \times \text{Solubility}) + (29 \times 0)}{49}$$

Source Zone Transect with Streamtubes

Early Stage



No. Streamtubes Intercepting DNAPL
20

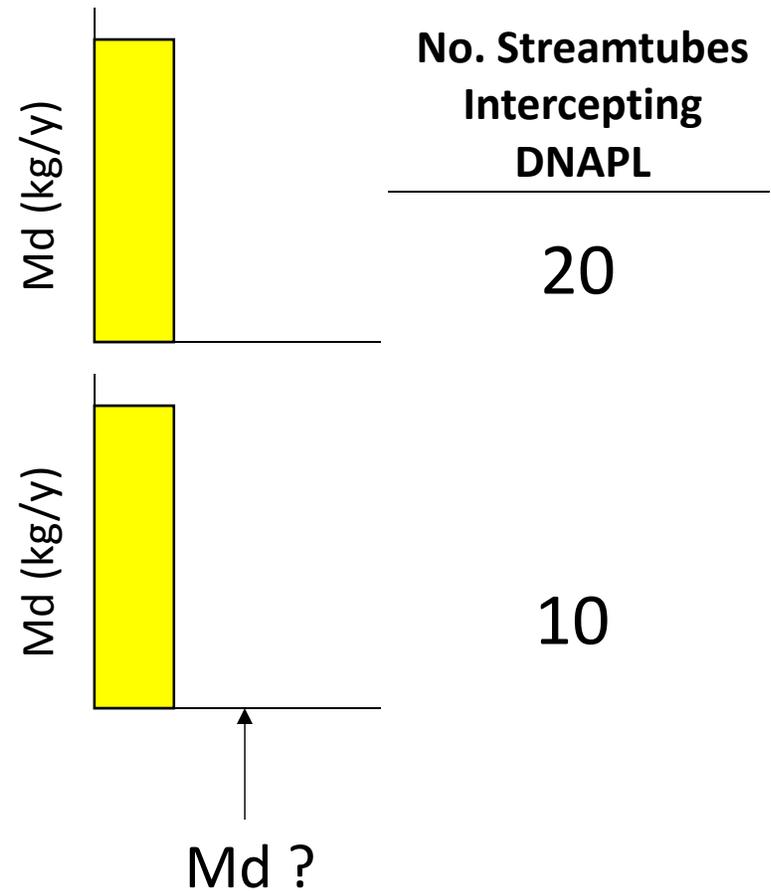
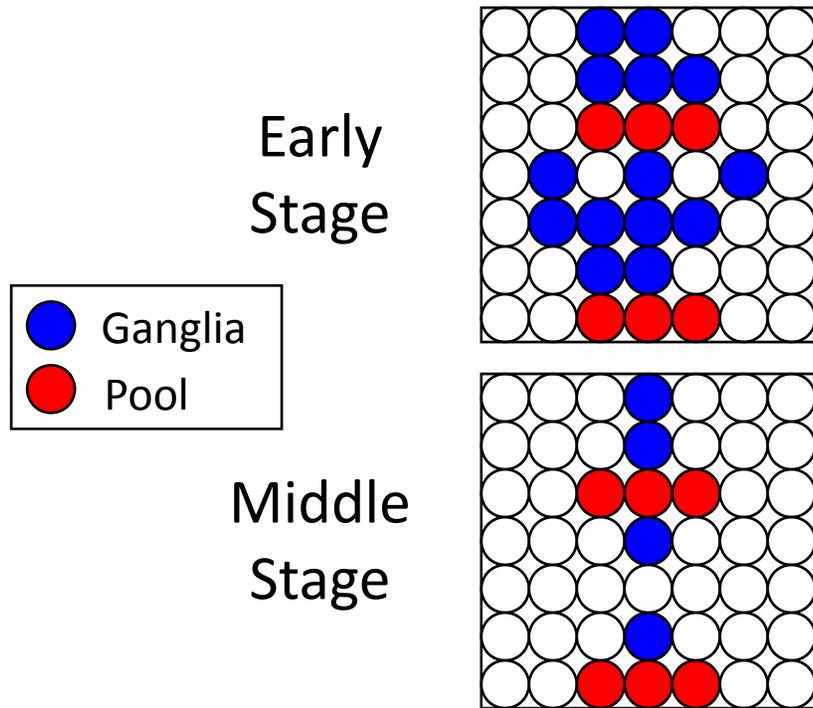
Total number of streamtubes in section = 49.

20 streamtubes intercept DNAPL.

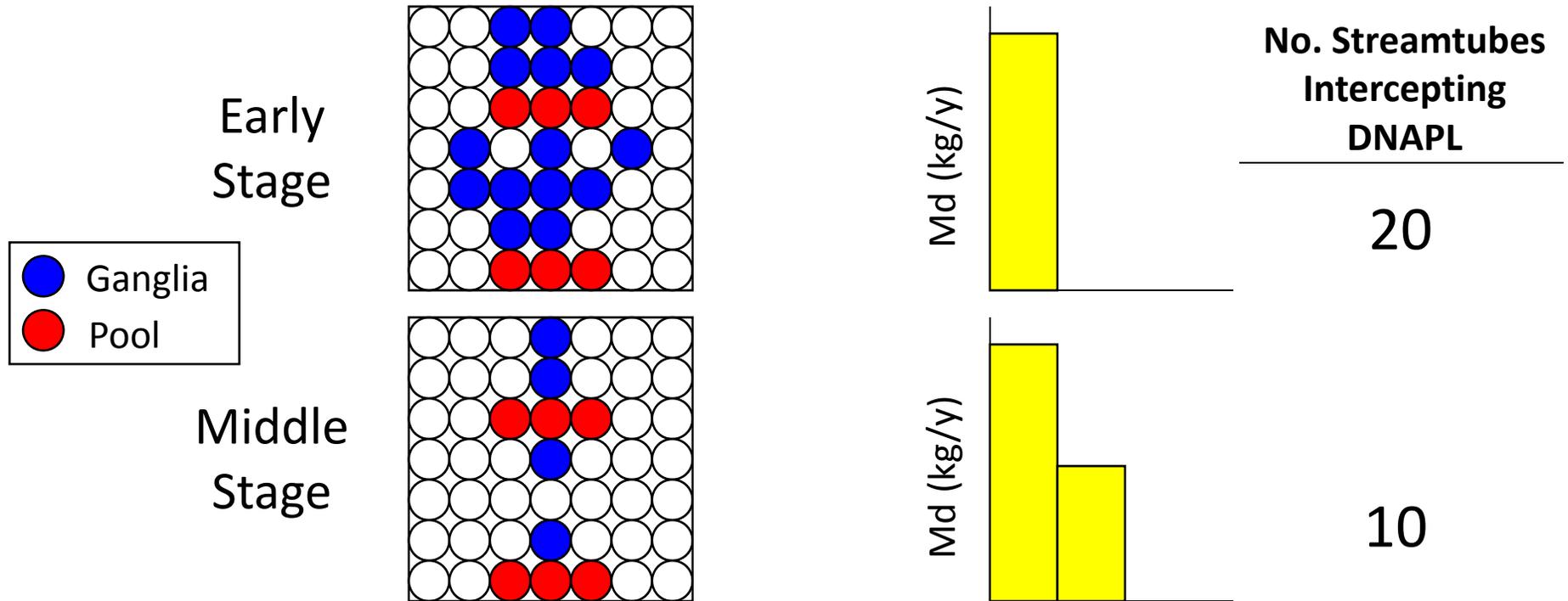
$$C_{avg} = 40\% \text{ of Solubility}$$

$$f_{io} = \text{initial dilution factor} = ?$$

Source Zone Transect with Streamtubes



Source Zone Transect with Streamtubes



$$f_i = ?$$

$$C_{avg} =$$

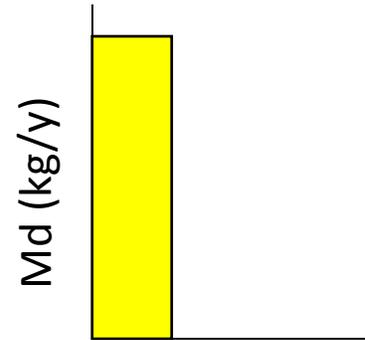
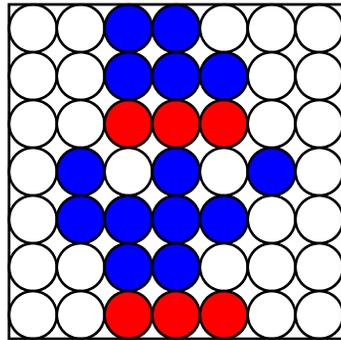
20% of Solubility

f_i = dilution factor
 = proportion of streamtubes passing through NAPL

Source Zone Transect with Streamtubes



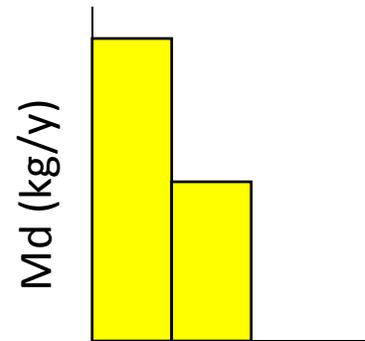
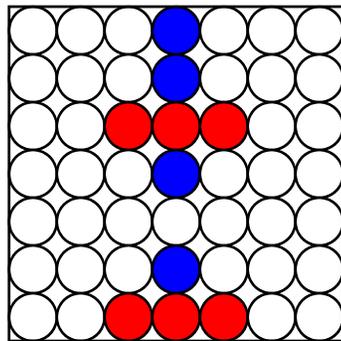
Early Stage



No. Streamtubes Intercepting DNAPL

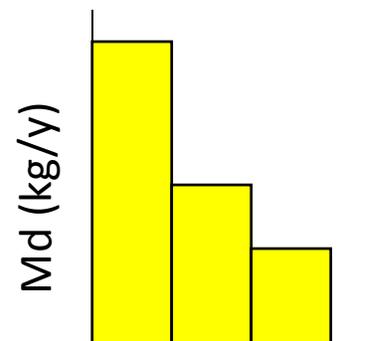
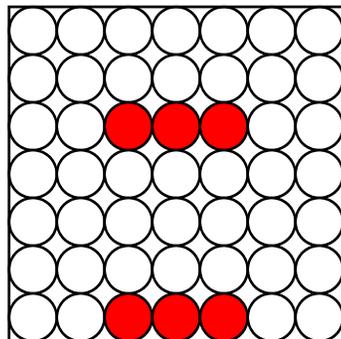
20 $f_{io} = 40\%$

Middle Stage



10 $f_i = 20\%$

Late Stage

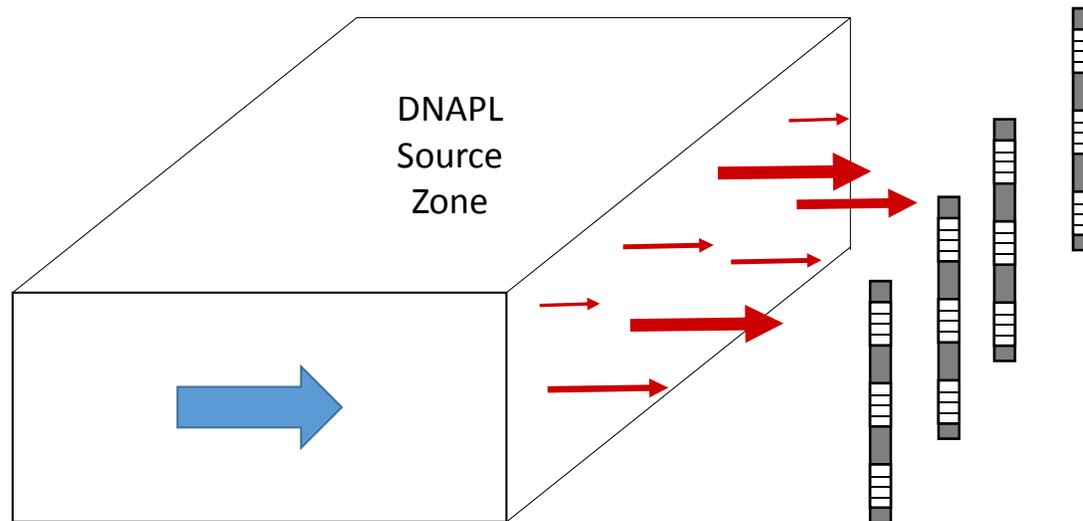


6 $f_i = 12\%$



Mass Discharge Monitoring

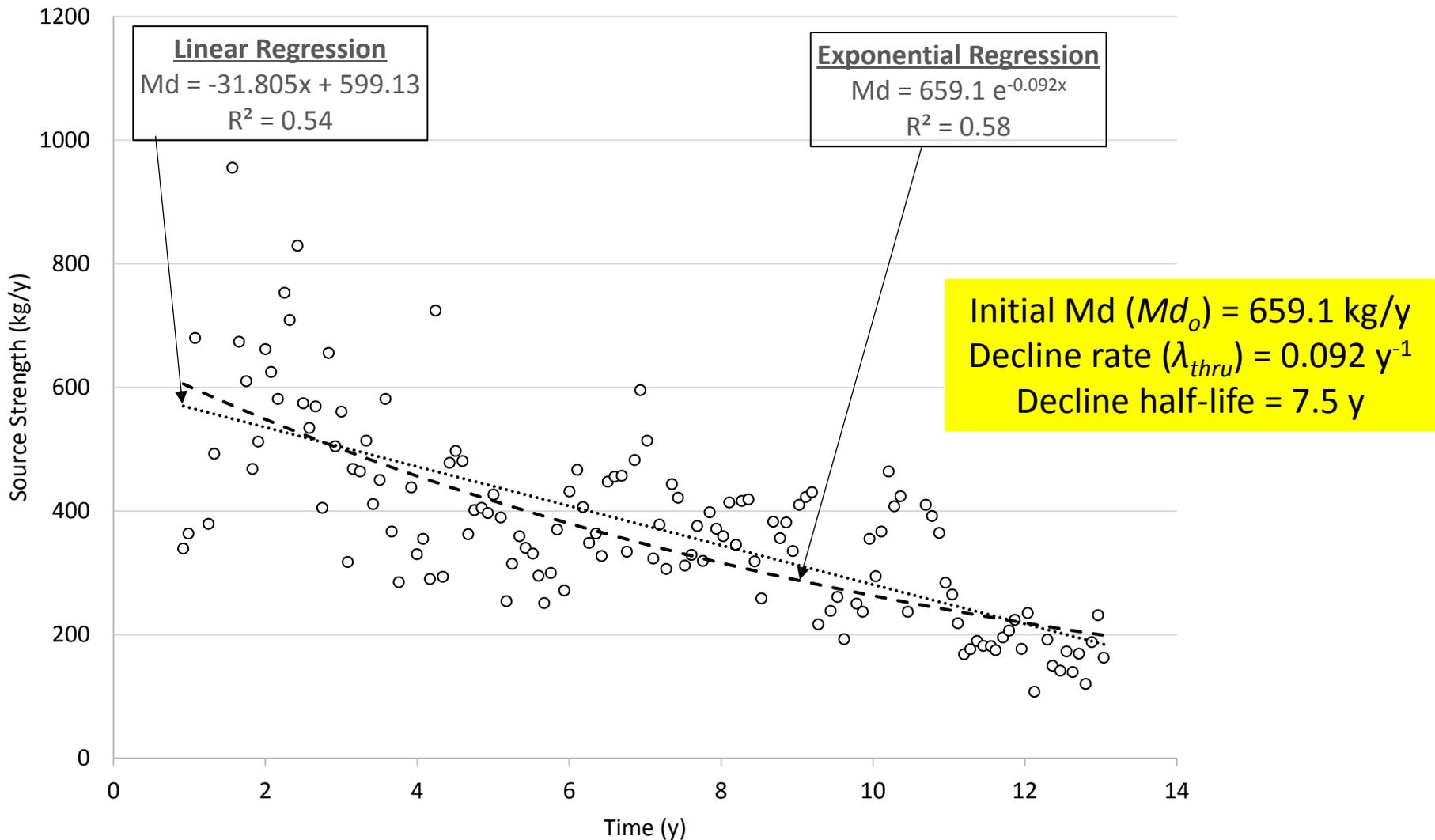
- Mass discharge (i.e. source strength) – overall metric of source behavior, directly tied to downgradient risk. (ITRC, 2010)



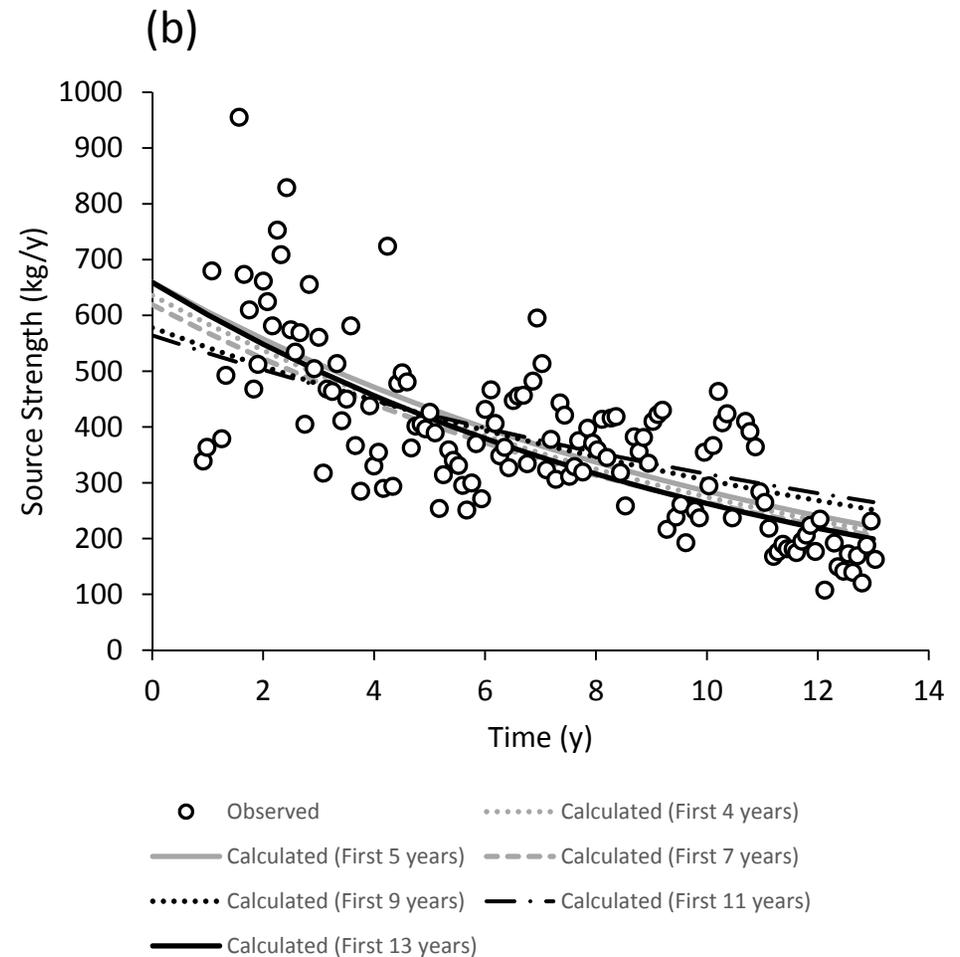
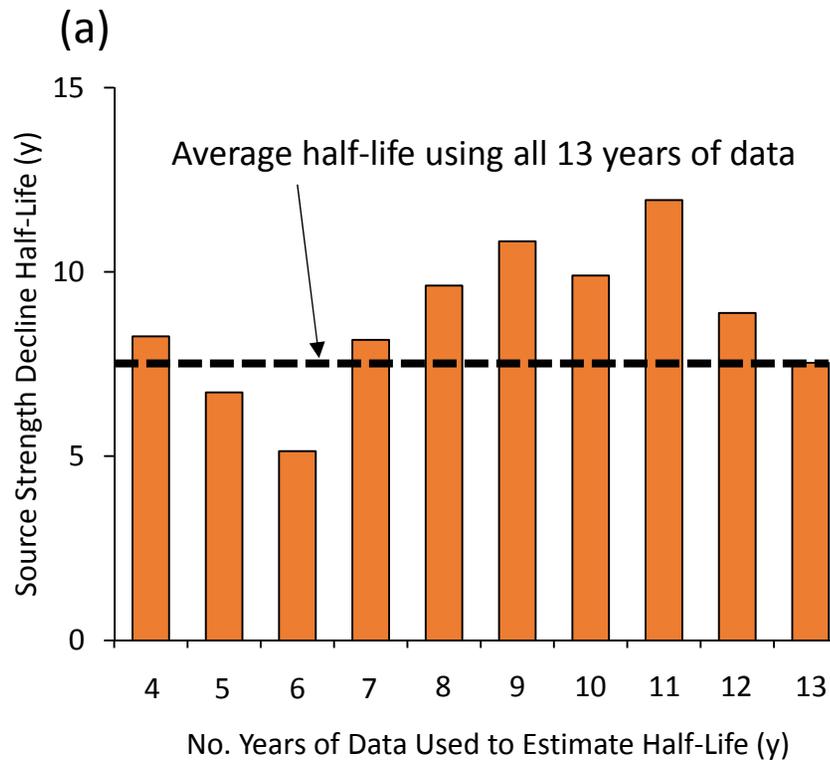
- Concentrations – vary between wells and over time, more difficult to predict point-specific behavior.
- NAPL depletion screening models – predict average concentration or mass discharge.

Tuscon Airport (Brusseau et al., 2011)

Note: Source strength = mass discharge (Md) at downgradient source zone boundary.



Half-Life Based on Length of Monitoring



Observed and estimated source strength decline at Tucson Airport Site prior to in-situ chemical oxidation. (a) Estimated source strength decline half-life based on varying number of years of initial monitoring data. (b) Observed and estimated source strength based on exponential decline model, with half-lives calculated based on 4, 5, 7, 9, 11, and 13 years of monitoring data. Observed source strength data were presented in Brusseau et al., 2011.

Mass Discharge Decline Models

- Newell et al., 2005 – natural attenuation trends matched using either linear or exponential models.
 - Exponential models, with tailing in longer term, more representative of mass discharge and concentration trends in DNAPL source zones.
- Carey et al., 2014a – exponential models clearly a better fit for mass discharge decline under EISB and ISCO, relative to a linear decline model.
 - Less than half of the monitoring wells in a multi-site dataset illustrated clear decline trends during EISB and ISCO.



Simple Approach for Estimating Mass in a DNAPL Source Zone

Estimating initial mass (M_o) in source zone (Newell et al., 2005):

$$M_o = Md_o / \lambda_{thru} \quad [M_o \text{ in kilograms, } Md_o \text{ in kg/y, and } \lambda_{thru} \text{ in } y^{-1}.]$$

Example calculation for Tuscon Airport Site:

$$\begin{aligned} M_o &= (659.1 \text{ kg/y}) / (0.092 \text{ y}^{-1}) \\ &= 7,164 \text{ kg} \end{aligned}$$

Then use a simple mass discharge decline model to estimate cumulative mass removed over time, and current mass remaining.

Calculation assumes uniform decline rate. May overestimate mass when substantial DNAPL pools present.



NDM Use of the Dilution Factor

- NAPL Depletion Model (NDM) predicts mass discharge (Md) as the global variable
 - Source strength = Md
- λ_{thru} is the rate of decline in mass discharge and the dilution factor (f_i)

$$Md_{thru} = q A C_{sol} f_i$$

Single component NAPL: C_{sol} = solubility

Multicomponent NAPL: C_{sol} = effective solubility

$$f_i = f_{i0} e^{-\lambda_{thru} t}$$

f_i = dilution factor = C_{avg} / C_{sol}

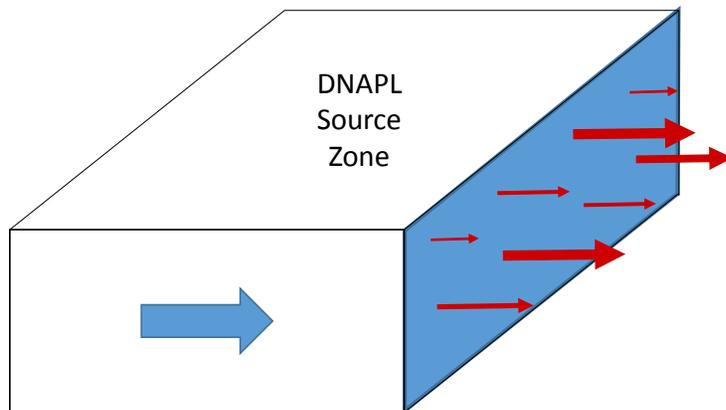
= proportion of streamtubes passing through NAPL



Falta et al. (2005a) Model

Power Law Model:

$$\frac{C_{avg}}{C_{avg_o}} = \frac{Md}{Md_o} = \left(\frac{M}{M_o}\right)^\beta$$



Input Parameters:

- Specific discharge, q ($\text{m}^3/\text{m}^2/\text{y}$)
- Initial NAPL mass, M_o (kg)
- Initial C_{avg_o} (mg/L)
- Area, $A = W \times H$ (m^2)

Calculated from Inputs:

- Initial mass discharge, Md_o (kg/y)
$$Md_o = q A C_{avg_o}$$
- Mass (M) and C_{avg} at time t

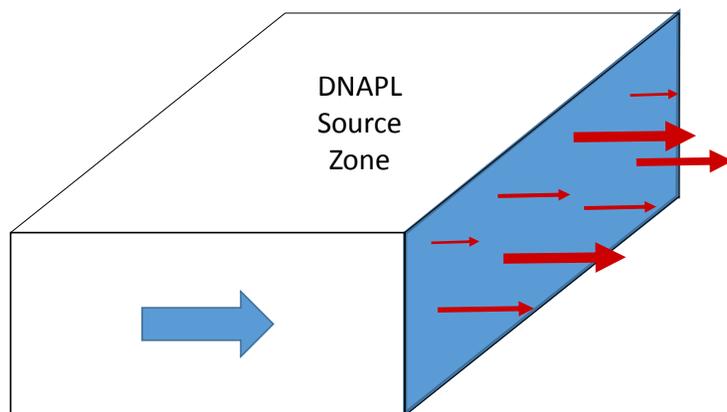
Note: The Falta et al. (2005a) model incorporates a mass degradation rate (λ_s), which is different from the depletion rate due to NAPL dissolution. This can be specified to be very low (e.g. half-life of 10,000 y) when mass degradation is negligible. (**RECOMMENDED**)



Falta et al. (2005a) Model: $\beta < 1$

$$M = \left[\frac{Md_o}{\lambda_s M_o^\beta} + \left(M_o^{1-\beta} + \frac{Md_o}{\lambda_s M_o^\beta} \right) e^{(\beta-1)\lambda_s t} \right]^{\frac{1}{1-\beta}}$$

$$C_{avg} = \frac{C_{avg_o}}{M_o^\beta} \left[\frac{Md_o}{\lambda_s M_o^\beta} + \left(M_o^{1-\beta} + \frac{Md_o}{\lambda_s M_o^\beta} \right) e^{(\beta-1)\lambda_s t} \right]^{\frac{\beta}{1-\beta}}$$

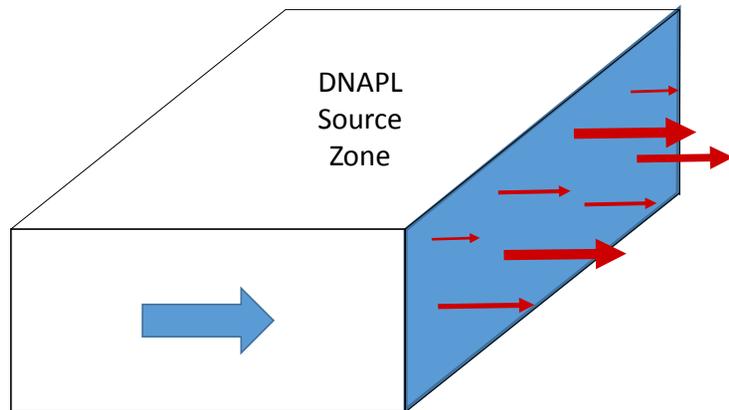


Falta et al. (2005a) Model: $\beta=1$

$$M = M_o e^{-(\lambda_{thru})t}$$

$$C_{avg} = C_{avg_o} e^{-(\lambda_{thru})t}$$

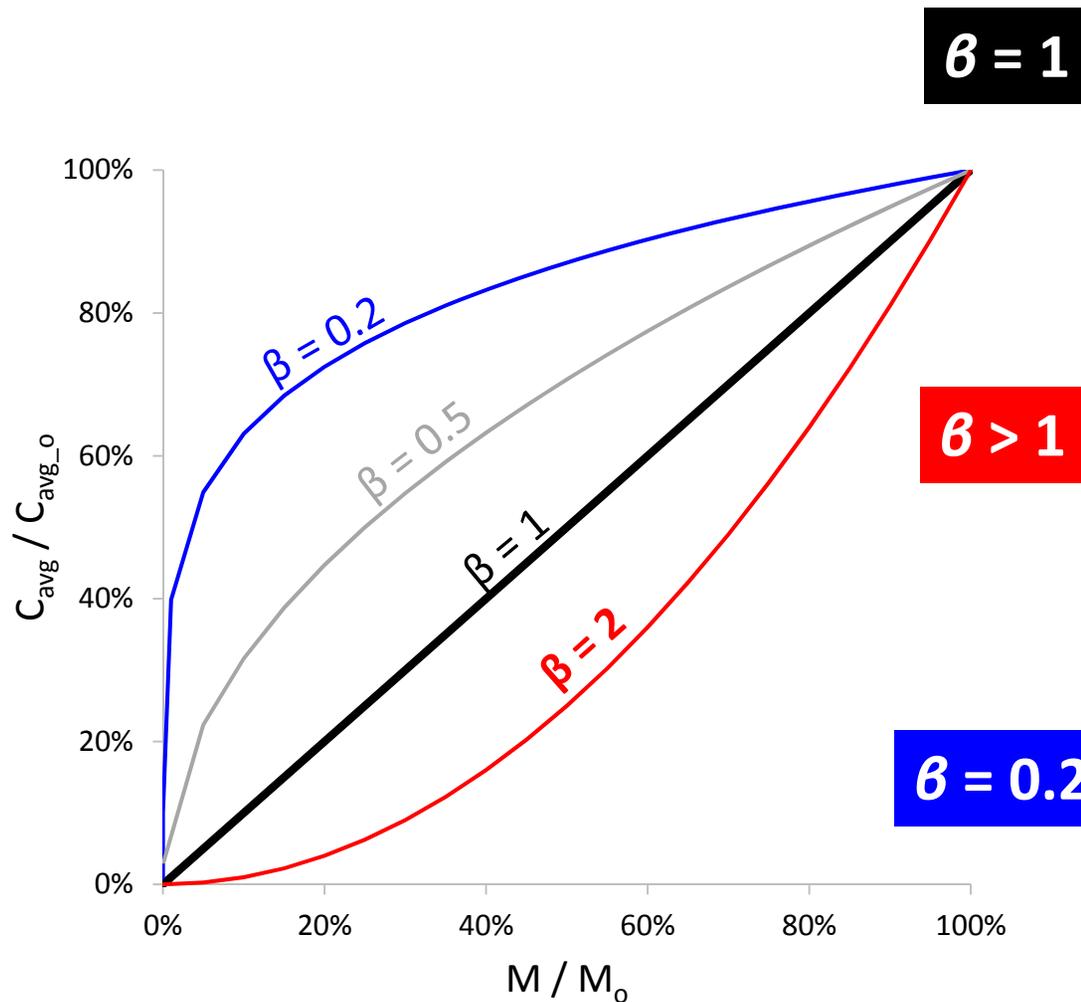
$$\lambda_{thru} = \frac{Md_o}{M_o} = \text{rate of decline in } M \text{ and } Md$$



Through-discharge = Md through source zone

$$\text{Half-life} = \frac{\ln 2}{\lambda_{thru}}$$

Influence of β



$\beta = 1$

- M_d and M have same exponential decline rate (Falta et al., 2005)
- Typical for natural attenuation of mixed source zones with mass mainly in transmissive zone (Falta et al., 2005) and heterogeneous distribution

$\beta > 1$

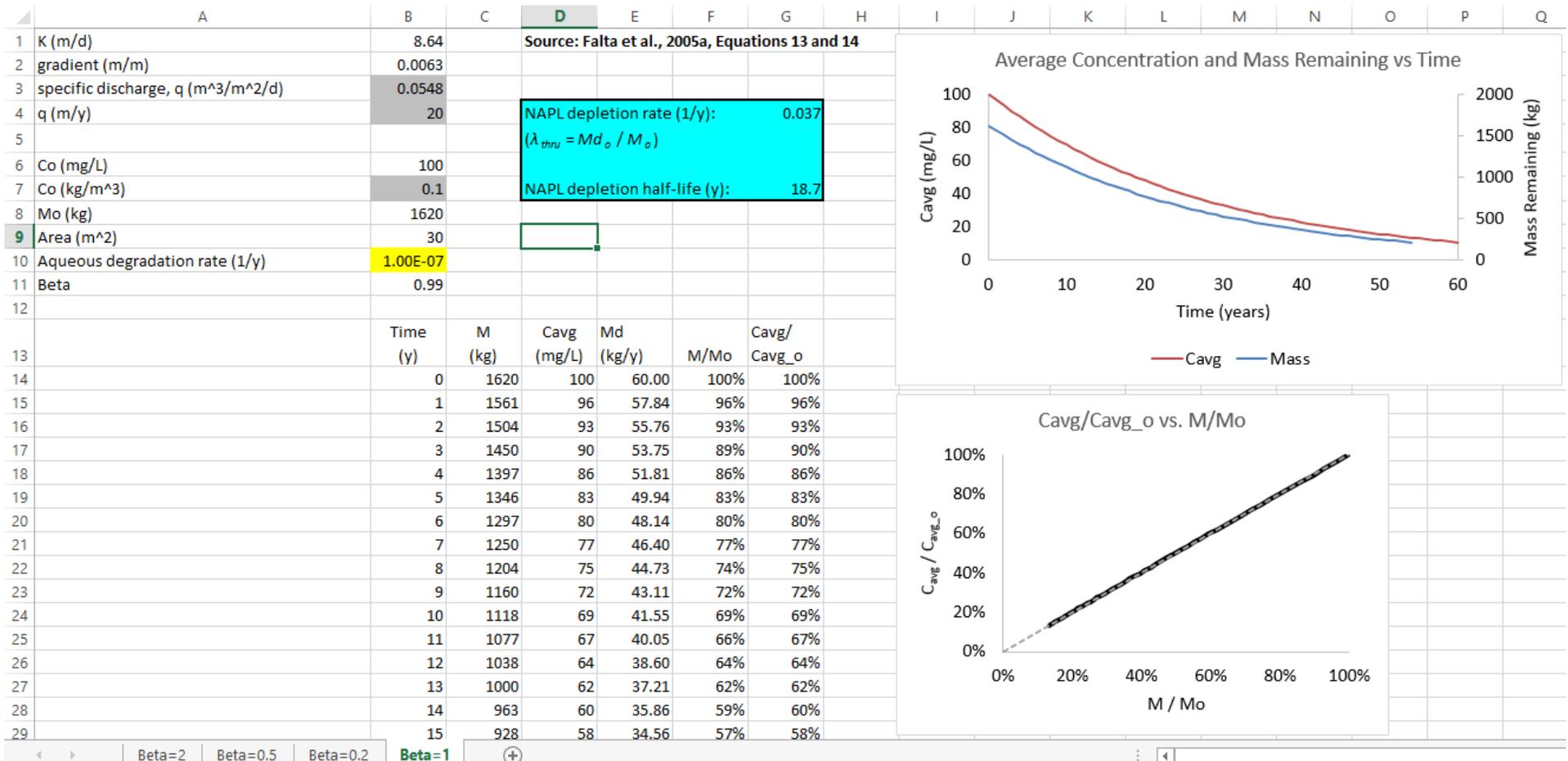
- Large reduction in source strength for small mass reduction
- Large portion of NAPL mass in low-K zone, or caused by pore clogging during in-situ remediation

$\beta = 0.2$

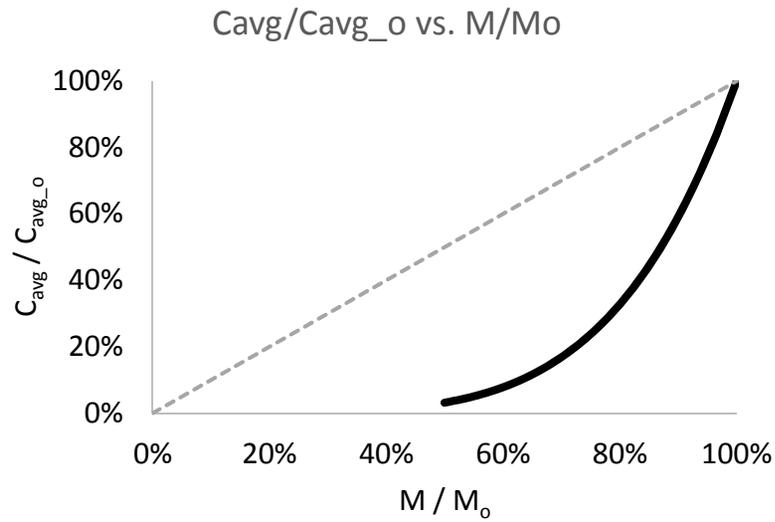
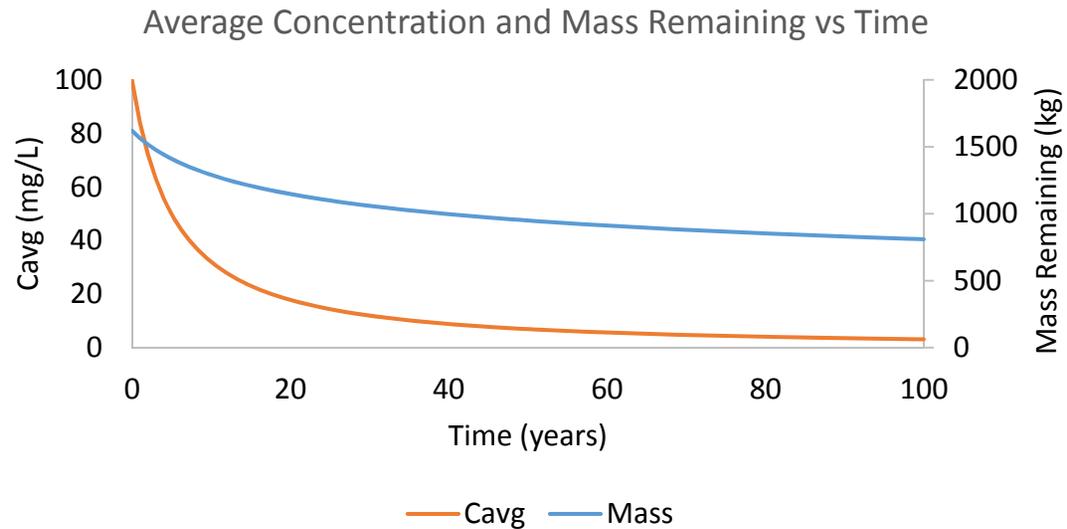
- Single DNAPL pool
- Small reduction in source strength for large mass reduction



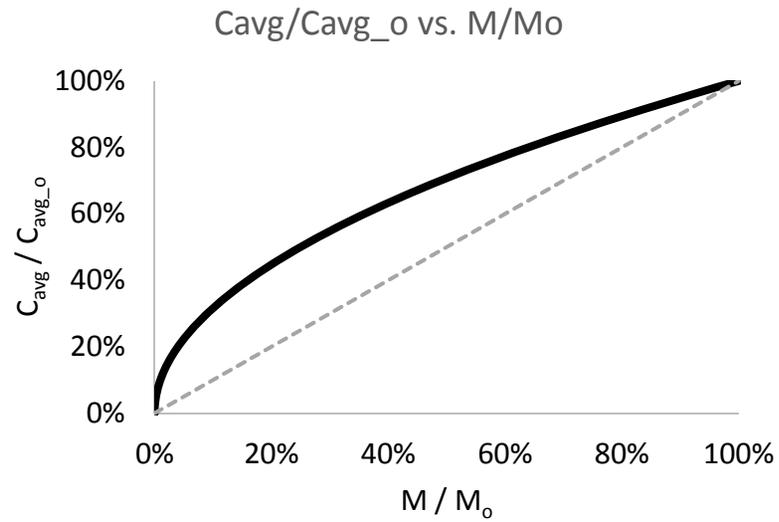
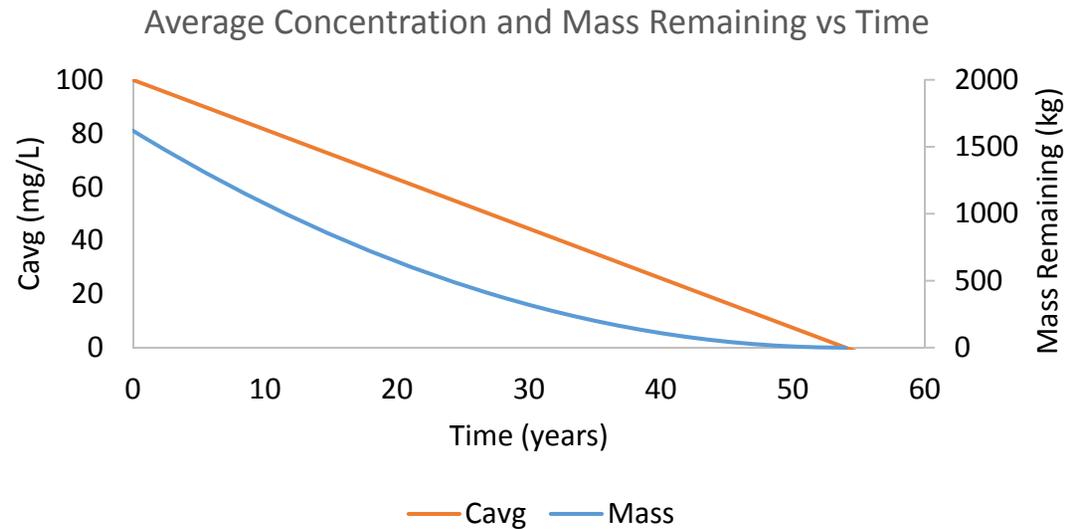
Example from Falta et al. (2005a): $\beta=1$



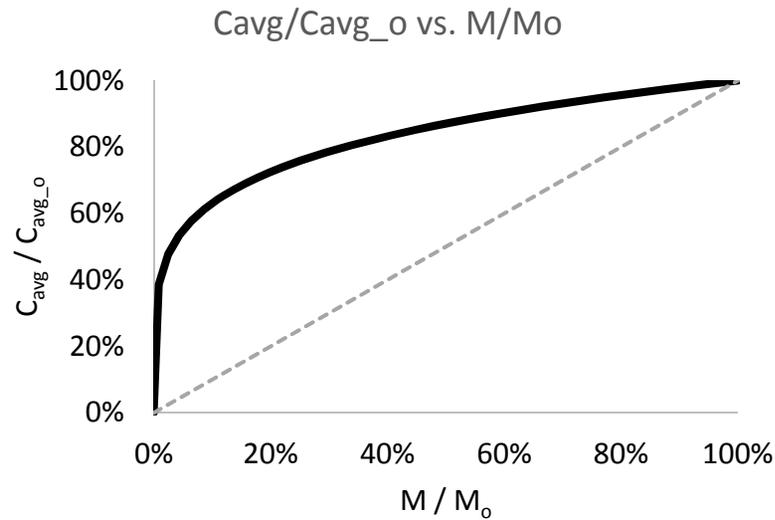
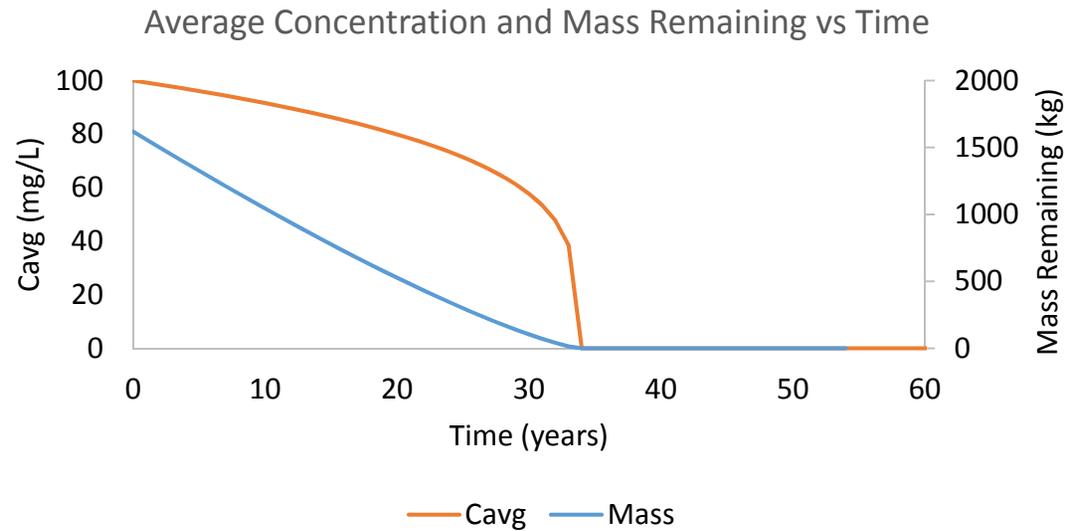
Example from Falta et al. (2005a): $\beta=2$



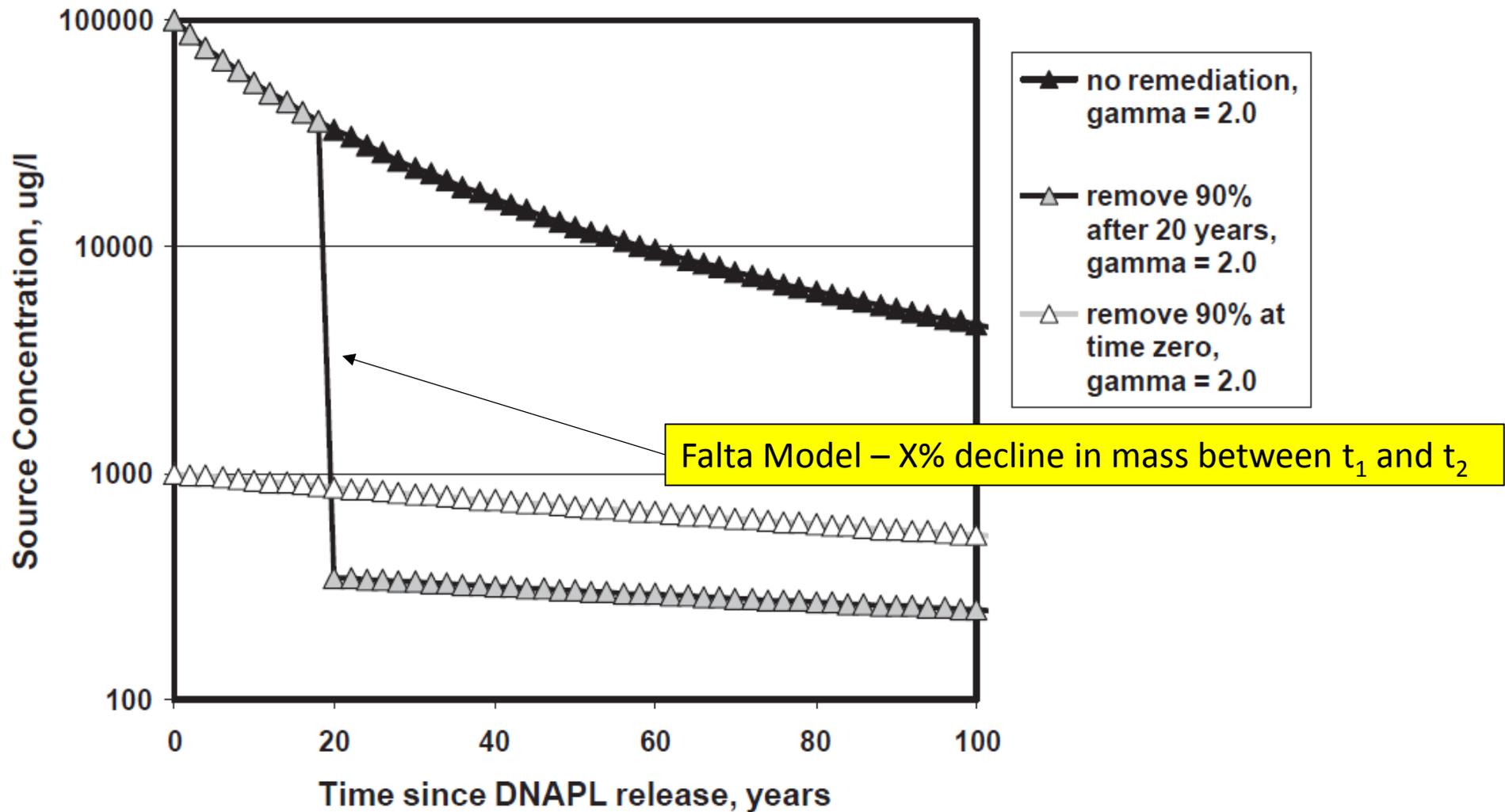
Example from Falta et al. (2005a): $\beta=0.5$



Example from Falta et al. (2005a): $\beta=0.2$



Falta et al. (2005a) – Remediation Model



Source: Falta et al. (2005a)



NAPL Depletion Model vs. Falta et al. Model

	NAPL Depletion Model	Falta et al. (2005)
Remediation timeframe:	Output	Input (Time for X% decline in mass)
Influence of Δv_{gw} :	Output	n/a
Mass discharge decline rate:	Input (site-specific or literature)	Output (Trend analysis for $\beta = 1$)
Beta (β):	Output (influence from enhanced rem.)	Input
Types of source zones:	Mixed, or discrete sub-zones (pools, res.)	Mixed only

General Concept for Mass Discharge (Md)

$$Md_{thru}^t = Md_o \left(e^{-\lambda_{thru} t} \right) f_{ed}^t$$

where Md_{thru}^t = source strength at time t

Md_o = initial source strength

λ_{thru} = mass discharge exponential decline rate

f_{ed}^t = enhanced dissolution factor at time t

Notes:

1. Through-discharge refers to the mass discharge through the downgradient boundary of the DNAPL source zone, otherwise known as *source strength*.
2. For a one-block source zone, this simple model can easily be entered into Microsoft Excel.



General Concept for Mass Discharge (Md)

$$Md_{thru}^t = Md_o (e^{-\lambda_{thru} t}) f_{ed}^t$$

Based on historical monitoring data
e.g. Tuscon Airport Site:

$$Md_o = 659 \text{ kg/y}$$

$$\lambda_{thru} = 0.092 \text{ y}^{-1}$$

Based on literature data
e.g. EISB $f_{ed} = 2$ to 3 (ITRC, 2008;
Stroo et al., 2012)



NDM Simulation of Through-Discharge

$$Md_{thru}^t = (k_{rw} q_x^t C_{sol}^t W H) f_i^t f_{ed}^t \quad \text{(Attachment A)}$$

where k_{rw_i} is the relative water permeability, q_x^t is the average specific discharge at time step t , C_{sol}^t is the effective solubility (which is the same as solubility for a single component NAPL), w_i and h_i represent the width and height of source zone i , f_i^t is a multiplier representing the proportion of the source zone cross-section which has streamtubes containing NAPL at time step t , and f_{ed}^t is a multiplier for mass discharge through the zone representing potential enhanced dissolution at time step t as a result of active remediation. The current version of NDM does not consider transient k_{rw_i} during source depletion; further study is warranted to determine when transient representation of this parameter may be helpful.

As discussed above, NDM represents three types of decline models for the f_i^t term to provide a surrogate representation for the rate of decline in NAPL-water interfacial area (IA) in the source zone:

- Exponential decline, $f_i^t = f_{io} e^{-\lambda_{thru,i} t}$ where f_{io} represents the initial proportion of the source zone cross-section which has streamtubes containing NAPL, and $\lambda_{thru,i}$ represents the first-order rate of decline of the proportion of streamtubes containing NAPL at time step t ;
- Linear decline, $f_i^t = f_{io} - f_{io} m_i^t t$ where m_i^t represents the linear decline slope at time step t ; and
- Constant $f_i^t = f_{io}$.



Initial Dilution Factor

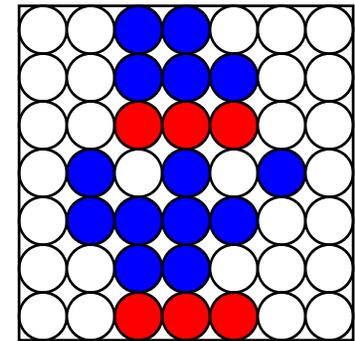
Note: for a mixed source zone, assume $k_{rw} = 1$

$$f_{io} = \frac{Md_o}{(k_{rw} q_{xo} C_{sol} W H)}$$

OR

$$f_{io} = \frac{C_{avg_o}}{C_{sol}}$$

e.g. $f_{io} \sim 40\%$



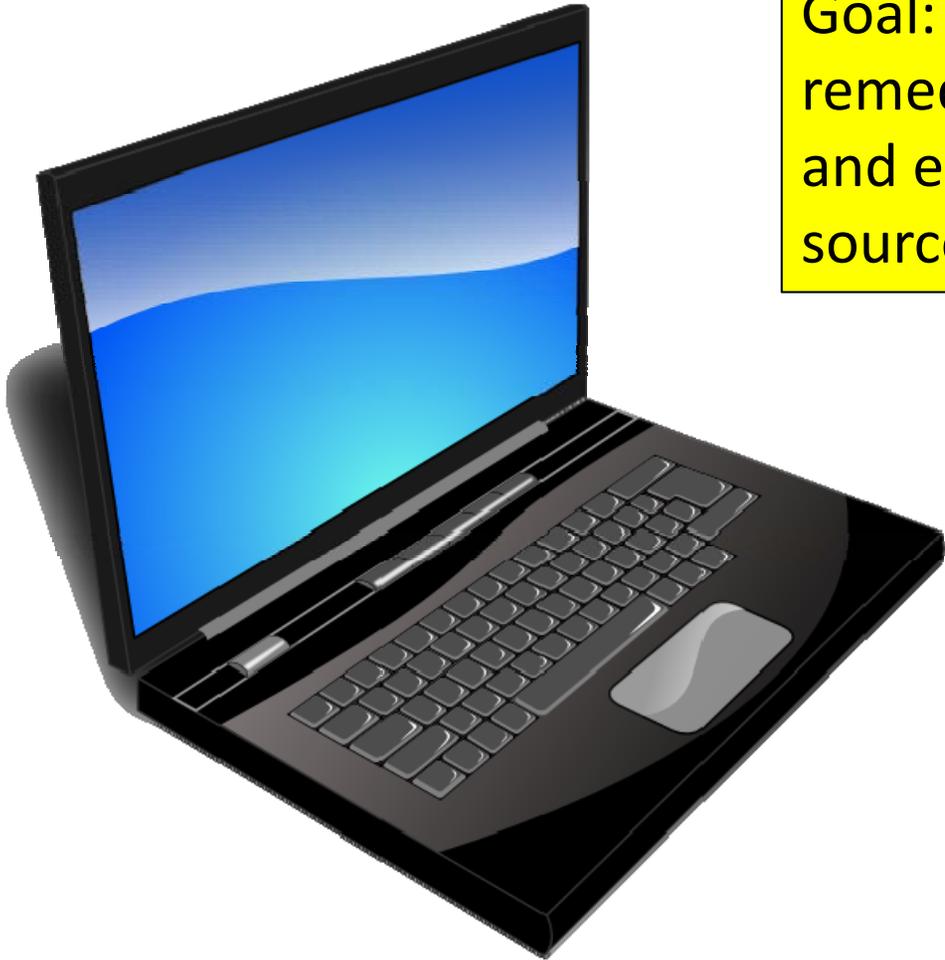
where f_{io} = initial dilution factor; and

C_{sol} = solubility for single component DNAPL



Exercise No. 1: Natural and Enhanced Dissolution in Mixed Source Zone

Goal: Use NDM to compare remediation timeframe for natural and enhanced dissolution of a mixed source zone.



Exercise No. 1 – Base Case Scenario

<u>Scenario Properties</u>	
* K (m/s)	1.00E-04
* Horizontal hydraulic gradient (m/m)	3.00E-03
q = Ki (m ³ /m ² /d)	0.026
GW velocity (m/d)	0.11
source zone length (m)	30
* source zone height (m)	5
* source zone width (m)	50
cross-sectional area (m ²)	250
source zone volume (m ³)	7500
total porosity	0.38
pore volume in source zone (m ³)	2850
Initial NAPL mass, M_o (kg)	7164
Initial source strength, Md_o (kg/y)	659
* Mass discharge decline rate, λ_{thru} (y ⁻¹)	0.092
* Relative water permeability, k_{rw}	1
* Initial dilution factor, f_{io}	19.9%
C_{avg_o} (mg/L)	279
Initial NAPL volume (m ³)	4.91
* initial NAPL saturation, S_n	0.1722%

<u>Parameters based on regression</u>	
* tortuosity coefficient	0.53
* transverse dispersivity (mm)	0.35
* total porosity	0.38
effective porosity	0.23
aw (1/cm)	0.04
n	4.23
Swr	0.04
<u>DNAPL Properties (TCE)</u>	
* Density (kg/m ³)	1460
* Solubility (mg/L)	1400
<u>Other Input Parameters</u>	
Average groundwater temperature (Celsius)	20
* Free-water diffusion coefficient (m ² /s)	8.40E-10
* Simulation time (days)	7300

Notes:

- * Input to NDM and used in exercise
- * Input to NDM and not used in exercise
- Yellow highlight is calculated value.



Model Scenarios ($\beta = 1$)

- Base case – natural attenuation
- Case $q \times 2$ – GW velocity $\times 2$
- Case $q \times 4$ – GW velocity $\times 4$
- Question: how does increasing velocity, via strategic pump-and-treat (SP&T), influence the remediation timeframe?
 - Strategic pump-and-treat involves placement of extraction wells in vicinity of source zone boundary, and pumping at rates higher than needed simply for hydraulic containment
 - Higher velocity \rightarrow faster NAPL depletion



NDM Input File – Natural Attenuation

```

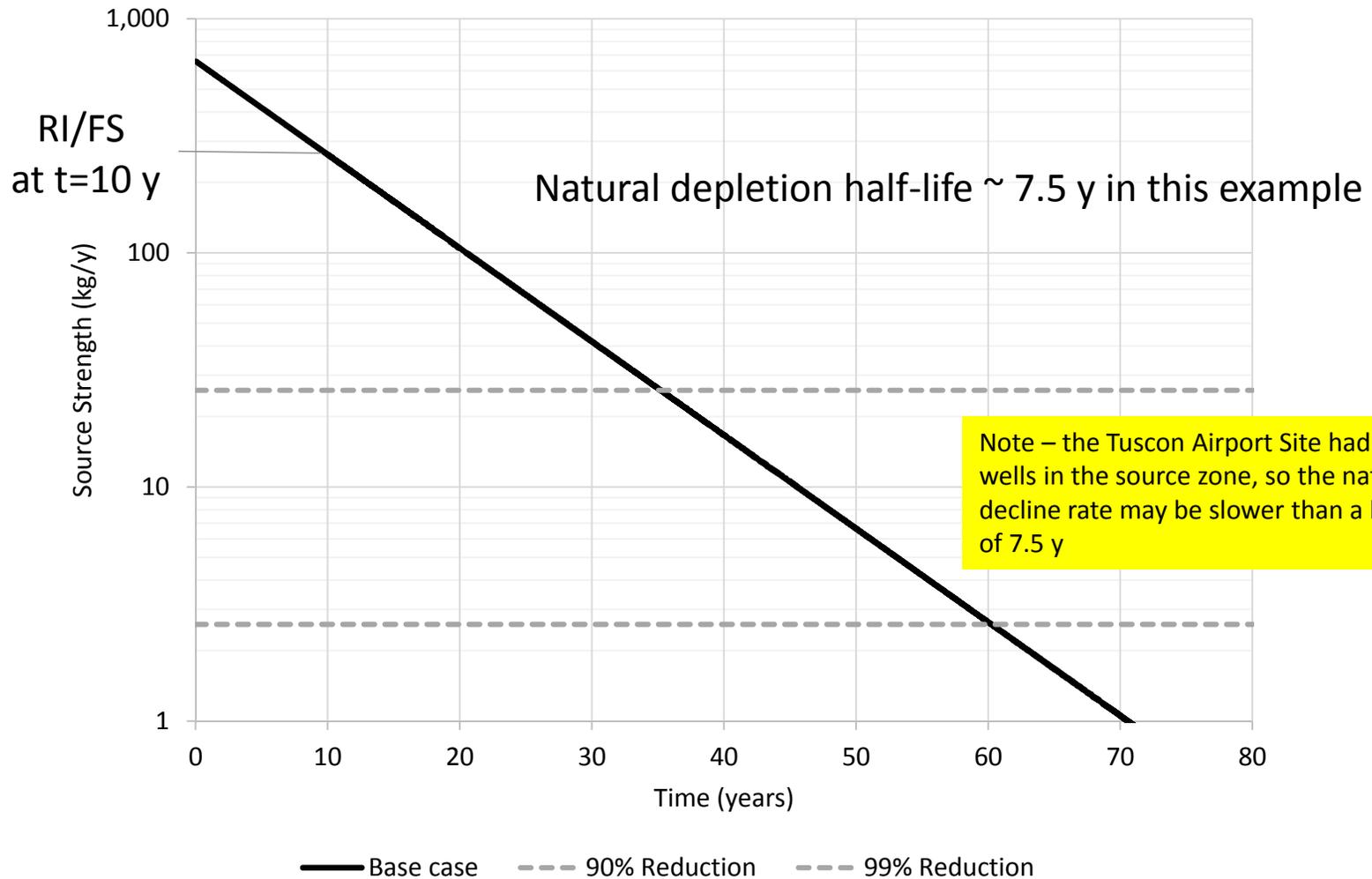
Base.IN - Notepad
File Edit Format View Help
|
3          'ipflux (0=no, 1=yes, flux from first seg only, 2=yes, flux uniform from all active pool segments, 3=yes, based on
1          'no. source zones
1 0        'source zone ID, ID of src affecting depletion rate
0.0 30.0 0.0 50.0 0.0 5.0 'x1,x2,y1,y2,z1,z2 in units of m)
0.0 1.     'fsurf,fsurfdep
0.1993 2 -2.52e-4 1.     'fio,jfeffmdl(0=constant; 1=linear; 2=exponential),feffm: slope of feff vs. time (units of per day, us
Base
1460.0     'density (kg/m^3)
1400.0     'solubility (mg/L)
8.4e-10    'free-water diffusion coefficient (m^2/s)
1.00e-4    'hydraulic conductivity (m/s)
0.0030     'hydraulic gradient (m/m)
0.38       'total porosity
0.00035    'transverse dispersivity (m)
0.53       'tortuosity
36500.0    'simulation time (d)
10.0000    'delta-t (d)
1.0000     'minimum delta-t (d)
30.0       'pool length discretization (m)
0          'nperiods for enhanced dissolution
1.000 0    'Fgrad, and flag to optionally re-calculate feffm (Md-thru decline rate) for exponential decline model (0=no, 1=yes)
0.00000 36500.0 'Fgrad time period
1          'itimeunit=2 (1=years, 2=days) - for output times (all time input in units of days)
0.001722 1.0 'source zone 1 - average Sn, krw
  
```

Source sub-zone properties

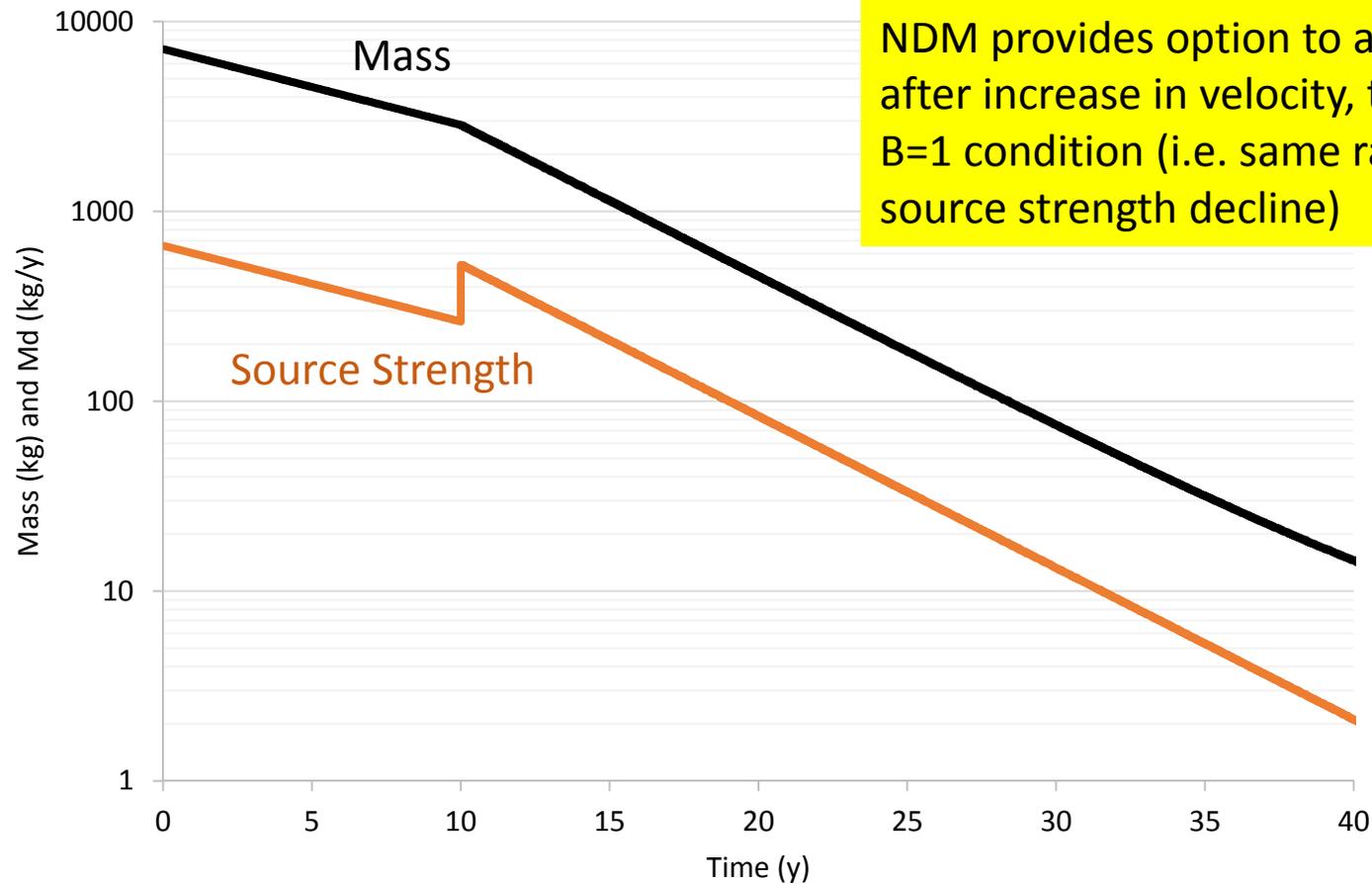
$$f_{effm} = \lambda_{thru} \text{ for exponential decline (per day)}$$

Gradient factor (multiplier) and associated time period (days)

NDM Simulation Results-Natural Attenuation



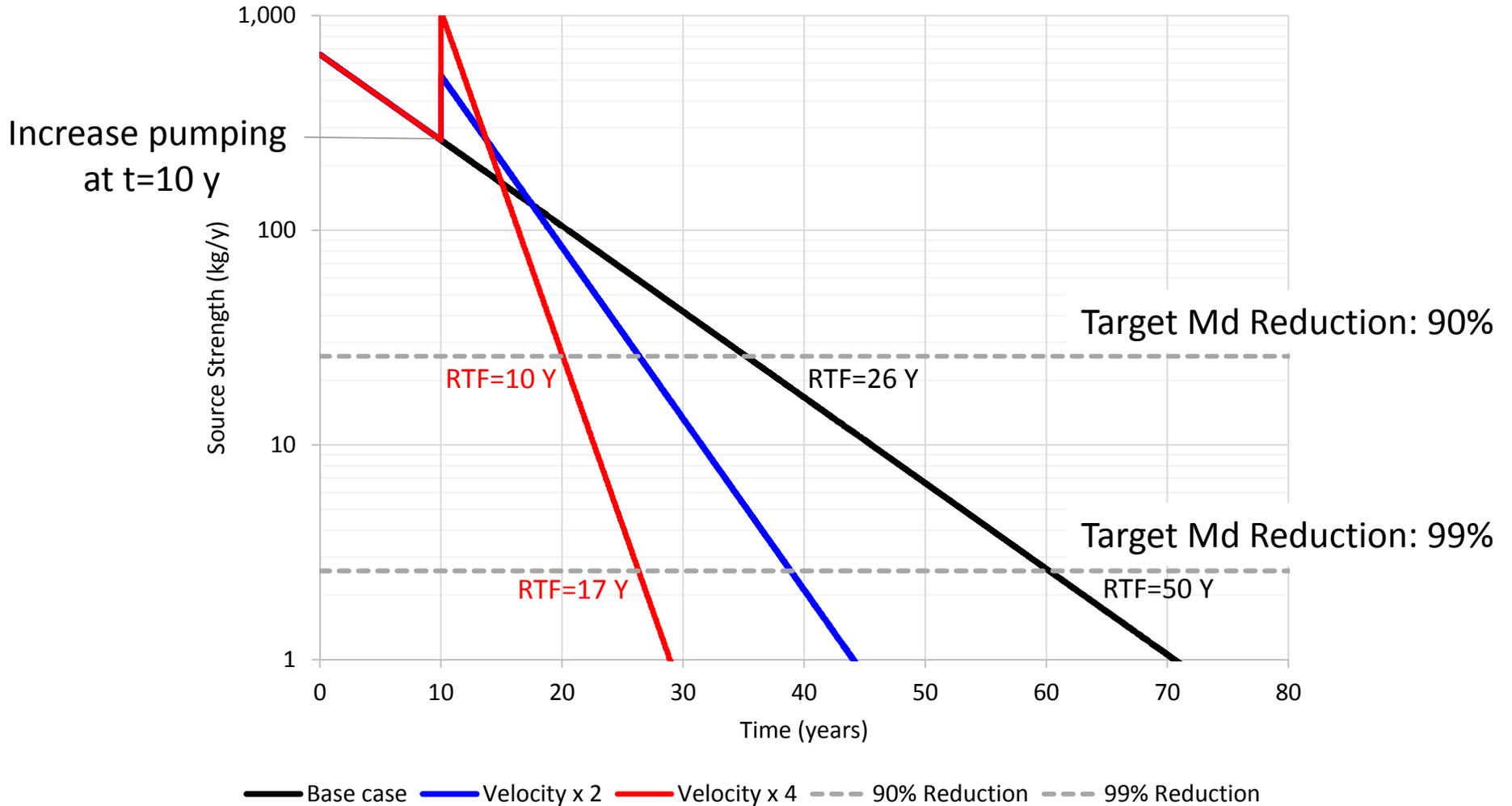
NDM Case: $q \times 2$



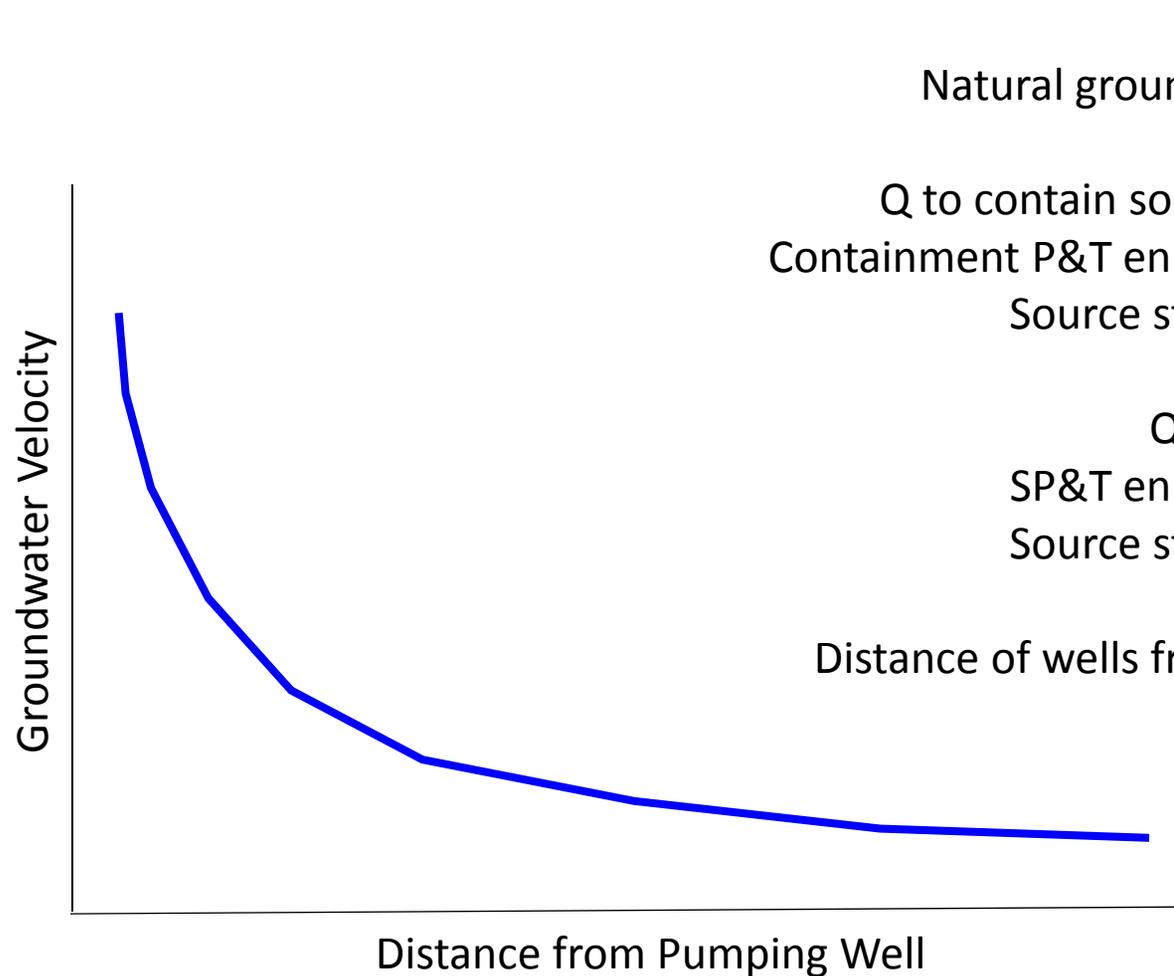
NDM provides option to adjust decline after increase in velocity, to maintain a $B=1$ condition (i.e. same rate for mass and source strength decline)

NDM simulated trends with decreases of more than 99% to 99.% become less accurate – small differences in 3rd or 4th decimal places of input parameters may influence simulated mass remaining.

NDM Simulation Results-Natural Attenuation



Groundwater Velocity vs. Distance from Pumping Well



Source width: 45 ft

Natural groundwater velocity: 350 ft/y

Q to contain source zone (gpm): 7

Containment P&T enhanced gradient: **1.5x**

Source strength increase: **50%**

Q for SP&T (gpm): 28

SP&T enhanced gradient: **3x**

Source strength increase: **200%**

Distance of wells from source zone: 30 ft



Questions?



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Ph: 613-270-9458



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Miscellaneous



Notes on Velocity

- Specific discharge, $q = K i$
 - Darcy Velocity
- Average linear groundwater velocity, $v = K i / \theta_e$
 - Seepage velocity
 - Interstitial velocity
 - Pore velocity
- Mass discharge – calculated using q , not v



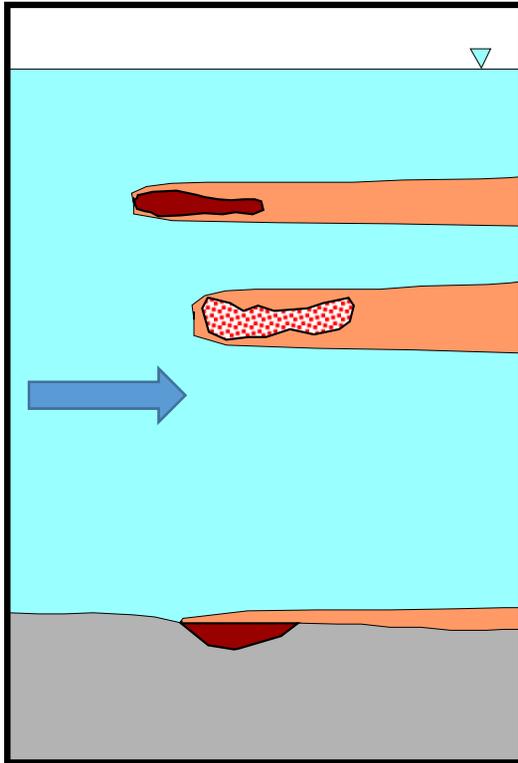
Example No. 2

Single DNAPL Pool

Section 3b

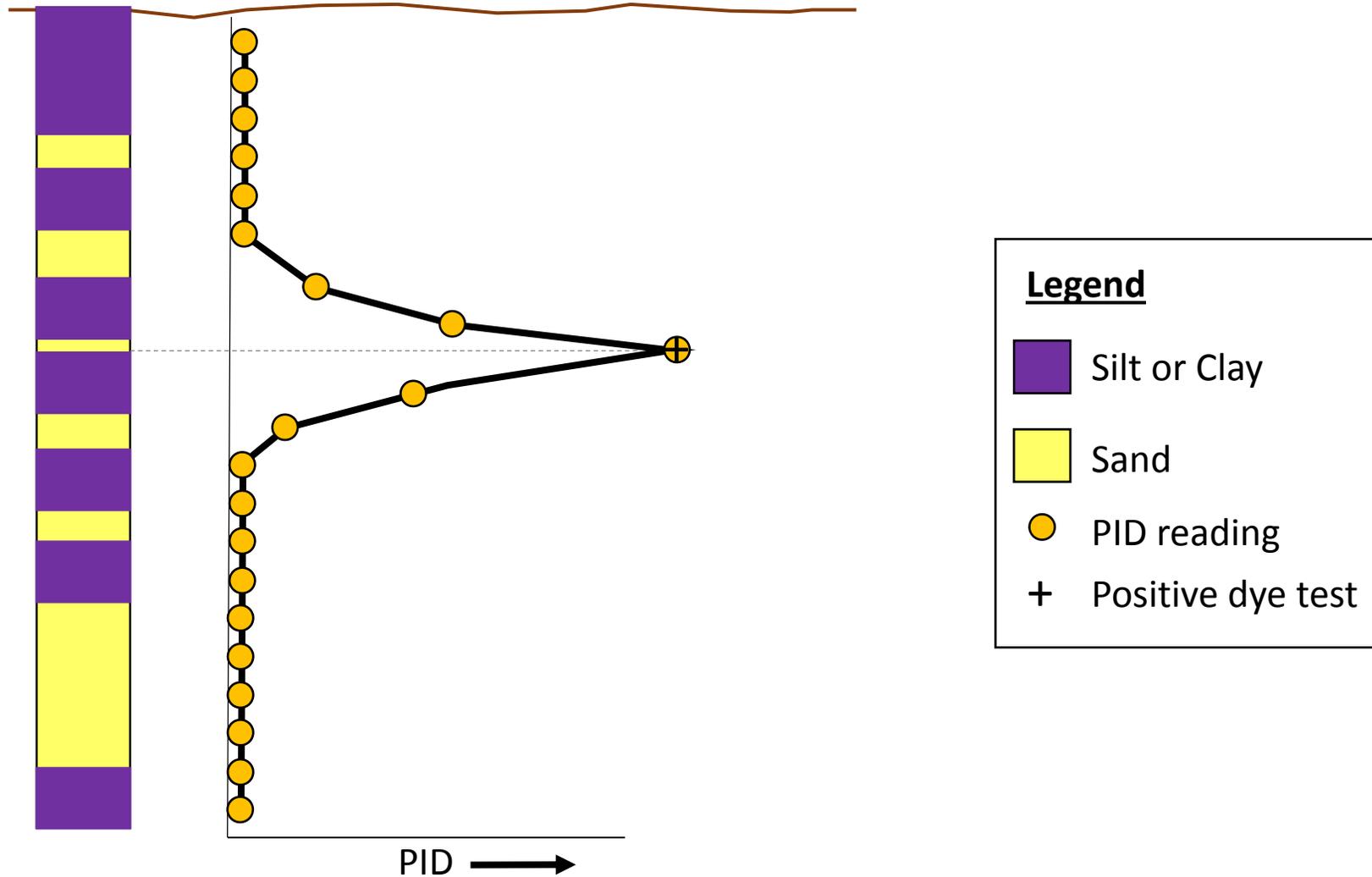


Conceptual Model – Aged Source Zones



- Pool-dominated
 - Particularly if highly heterogeneous geology
- Some thin pools may have depleted so average S_n is below residual saturation threshold
 - Horizontal layers of residual DNAPL
- Thin, high intensity GW plumes
- Persistent source strength with slow declines at discrete elevations

Example of DNAPL Pool Line of Evidence



Other lines of Evidence for Pools

- Visible NAPL in wells (free phase)
- NAPL seeping from soil cores
- Persistently high concentrations in transmissive formation ($>1\%$ solubility in monitoring wells)
- Slow source strength decline rate
- Heterogeneous or layered geology in aged NAPL source zone
- Thin aqueous plumes downgradient of source zone (pools or horizontal layers of residual DNAPL)
- Very high soil concentrations (\gg partitioning threshold)
- CPT-MIP profiles
- Parker et al. (2003) – core drainage method



Kueper and Davies, 2009

- Partitioning Threshold – soil concentration indicating NAPL presence
 - Higher than equilibrium conc. (dissolved, sorbed, and soil gas) at solubility
- e.g. TCE in soil sample below the water table

$$\begin{aligned}\theta_t &= \theta_w = 0.40 \\ \text{Specific gravity, } G_s &= 2.67 \\ \rho_b &= (1 - \theta_t) G_s = 1.60 \text{ g/mL} \\ f_{oc} &= 0.1\% \\ K_{oc} &= 125 \text{ mL/g} \\ C_{sol} &= 1400 \text{ mg/L}\end{aligned}$$

Partitioning Threshold, $C_t = 525 \text{ mg/kg TCE}$
(single component DNAPL)

Kueper and Davies, 2009 Appendix A

Calculation 2 – Threshold Chemical Concentration in Soil Based on Partitioning Relationships (see Ref. 11)

$$C_i^T = \frac{C_i}{\rho_b} (K_d \rho_b + \theta_w + H' \theta_a)$$

Partitioning Threshold

See Calculation #4 if multicomponent or unknown DNAPL composition.

- C_i^T = soil concentration (mg/kg) threshold for component i [calculated],
- C_i = effective solubility (mg/l) [see Calculation 3] of component i [calculated],
- ρ_b = dry soil bulk density (g/cc) [site specific measurement],
- K_d = soil-water partition coefficient (ml/g) [calculated using $K_d = K_{oc} f_{oc}$],
- θ_w = water-filled porosity (unitless) [calculated from site specific measurement of moisture content],
- H' = unitless Henry's constant [handbook],
- θ_a = air-filled porosity (unitless) [site specific measurement],
- K_{oc} = organic carbon - water partition coefficient (ml/g),
- f_{oc} = fraction organic carbon (unitless) [site specific measurement].

C_i^T represents the maximum amount of contaminant i that can be present in a porous media sample in the sorbed, aqueous, and vapor phases without a DNAPL phase present. The calculation can be applied below the water table by setting $\theta_a = 0$. Note that the water-filled porosity and the air-filled porosity sum to the total porosity. Note also that the calculation of C_i^T is typically more sensitive to f_{oc} than it is to the porosity values.

Kueper and Davies, 2009

- Saturation Threshold – soil concentration if NAPL present with $S_n = 5\%$.

Calculation 1 – Chemical Concentration in Soil Corresponding to Threshold DNAPL Saturation

$$C_D = \frac{S_r \phi \rho_N 10^6}{\rho_b} + C^T$$

- C_D = soil concentration (mg/kg) corresponding to threshold DNAPL saturation [calculated],
 S_r = threshold DNAPL saturation [set between 0.05 and 0.10],
 ϕ = effective porosity (unitless) [site specific measurement],
 ρ_N = DNAPL density (g/cc) [site specific measurement],
 ρ_b = dry soil bulk density (g/cc) [site specific measurement],
 C^T = amount of contaminant (mg/kg) present in the soil sample in the aqueous, vapor, and sorbed phases [see Calculation 2 to evaluate C^T].

Previous example:

TCE Saturation threshold = 18,750 mg/kg
(based on total porosity)

Example Calculation

PCE DNAPL ($\rho_N = 1.62$ g/cc) in a soil sample with $S_r = 0.05$, $\phi = 0.25$ and $\rho_b = 2.0$ g/cc corresponds to (ignoring the C^T fraction) $C_D = 10,125$ mg/kg. Note that the quantity C^T is typically negligible compared to the DNAPL saturation term. The above equation is applicable to single-component DNAPLs in unconsolidated porous media. See reference (25) for the relationship between C_D and DNAPL saturation for a multi-component DNAPL. It should be noted that $0.05 \leq S_r \leq 0.10$ is suitable for geologic deposits having typical ranges of f_{oc} values (i.e., less than 2%). In general, the value of S_r should be chosen such that the resulting C_D is at least an order of magnitude higher than the C^T in calculation 2 arrived at using the highest f_{oc} value measured at the site.



NAPL Soil Threshold Evaluation

- Partitioning threshold exceedance – potential NAPL
- Saturation threshold exceedance – confirmed NAPL
- In practice:
 - Soil samples may be diluted during sample collection, or off-gassing will result in underestimation of in-situ concentrations.
 - Given above, and that exceedances of saturation threshold are relatively rare even at pool-dominated sites – in some cases, exceedance of the saturation threshold may indicate presence of pooled NAPL (but not confirmed)

Previous example:

TCE 5% Saturation threshold = 18,750 mg/kg

TCE 15% saturation threshold (pool) = 56,250 mg/kg



Partitioning Calculations Spreadsheet

SOIL PARTITIONING THRESHOLDS FOR NAPL PRESENCE - SINGLE COMPONENT DNAPLs							Specific gravity	2.67
	PCE	TCE	1,2-DCA	111-TCA	CTET	CF	MC	
Saturation Threshold, Cd (mg/kg)	20,431	18,752	17,881	18,456	20,185	20,894	17,945	
Partitioning Threshold, Ct (mg/kg)	81	525	2,276	478	335	2,293	1,341	
Koc^{1,2} (mL/g) =	155	125	17.4	110	174	39.8	2.12	
foc =	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
Kd (mL/g) =	0.16	0.13	0.02	0.11	0.17	0.04	0.00	
Rho-b (g/mL) =	1.60	1.60	1.60	1.60	1.60	1.60	1.60	
Total porosity =	0.4	0.4	0.4	0.4	0.4	0.4	0.4	
Water Saturation	100%	100%	100%	100%	100%	100%	100%	
Porosity-water =	0.4	0.4	0.4	0.4	0.4	0.4	0.4	
Porosity-air =	0	0	0	0	0	0	0	
H¹ (dim.) =	0.75	0.42	0.04	0.70	1.24	0.15	0.36	
C_{sol} (mg/L) =	200	1,400	8,520	1,330	790	7,920	5,325	
Total Mass =	129.662	840.35	3645.4933	766.3726	536.21092	3672.97603	2148.071	
Sorbed =	38.3%	33.4%	6.5%	30.6%	41.1%	13.7%	0.8%	
Dissolved =	61.7%	66.6%	93.5%	69.4%	58.9%	86.3%	99.2%	
Air =	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Ct (mg/kg) =	81	525	2276	478	335	2293	1341	
NAPL density (g/mL) =	1.63	1.46	1.25	1.44	1.59	1.49	1.33	
Partitioning Calculations								
NAPL saturation	5.0%	5.0%	5.0%	5.0%	5.0%	5.0%	5.0%	
C _{npl}	20,350	18,227	15,605	17,978	19,850	18,602	16,604	
Ct (mg/kg)	81	525	2,276	478	335	2,293	1,341	
Cd (mg/kg)	20,431	18,752	17,881	18,456	20,185	20,894	17,945	
Mass distribution between phases								
Sorbed:	31	175	148	146	137	315	11	
Aqueous:	50	350	2,127	332	197	1,978	1,330	
Vapor:	0	0	0	0	0	0	0	
Total soil concentration, Ct (mg/kg)	81	525	2,276	478	335	2,293	1,341	

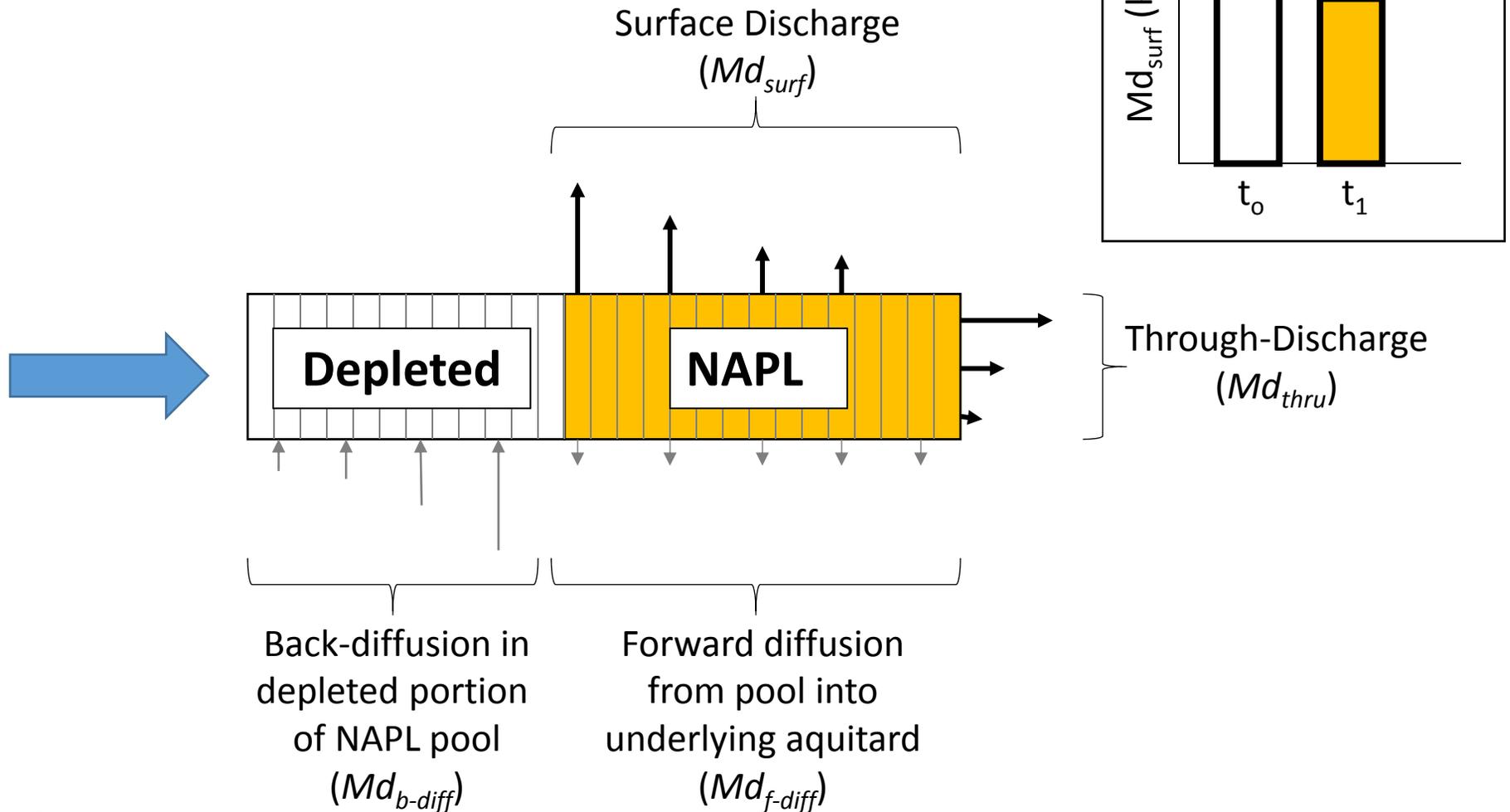


DNAPL Pool Dissolution Dynamics



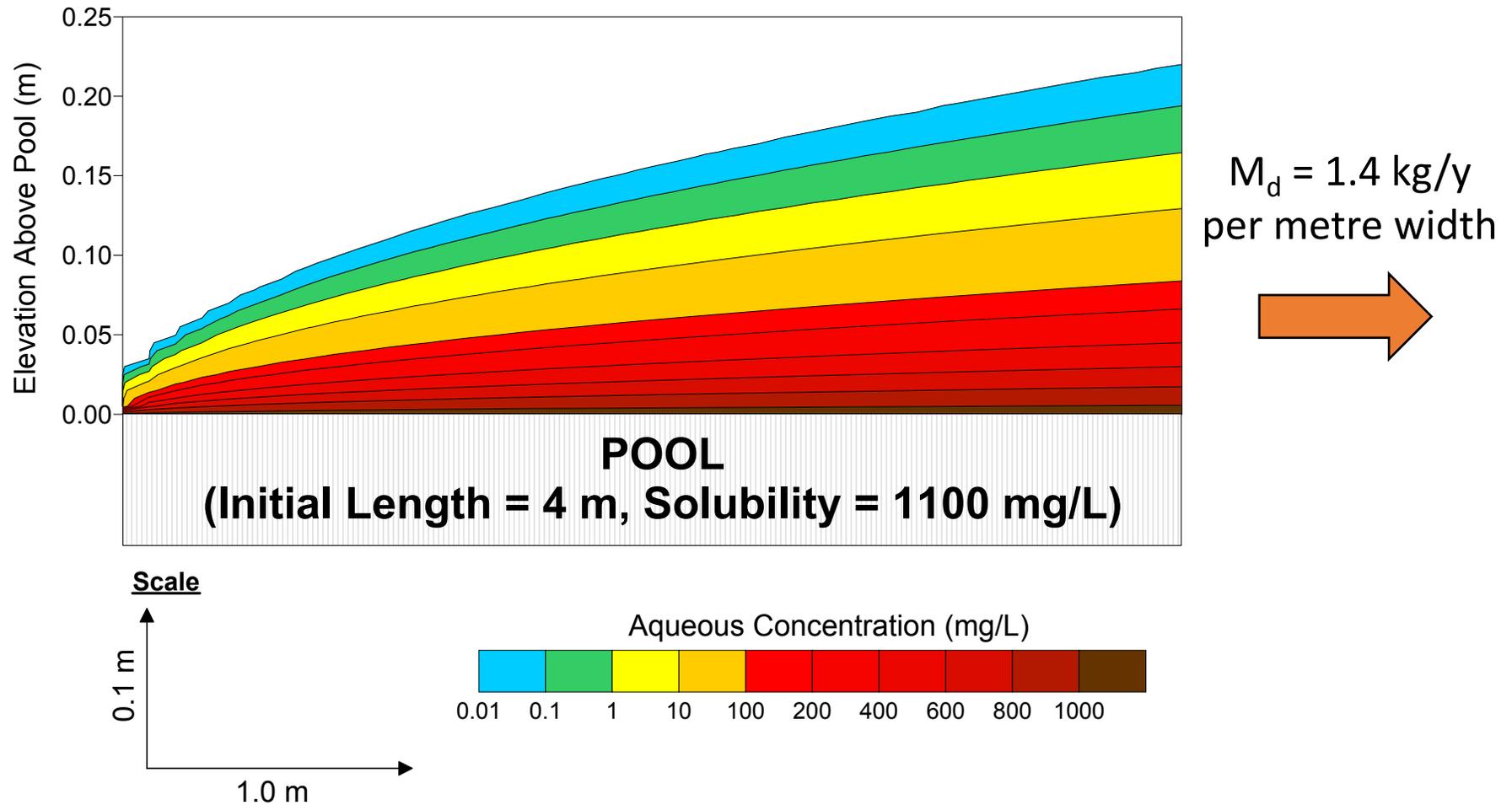
DNAPL Pool Mass Discharge Profile

NAPL SUB-ZONE (i.e. layer)

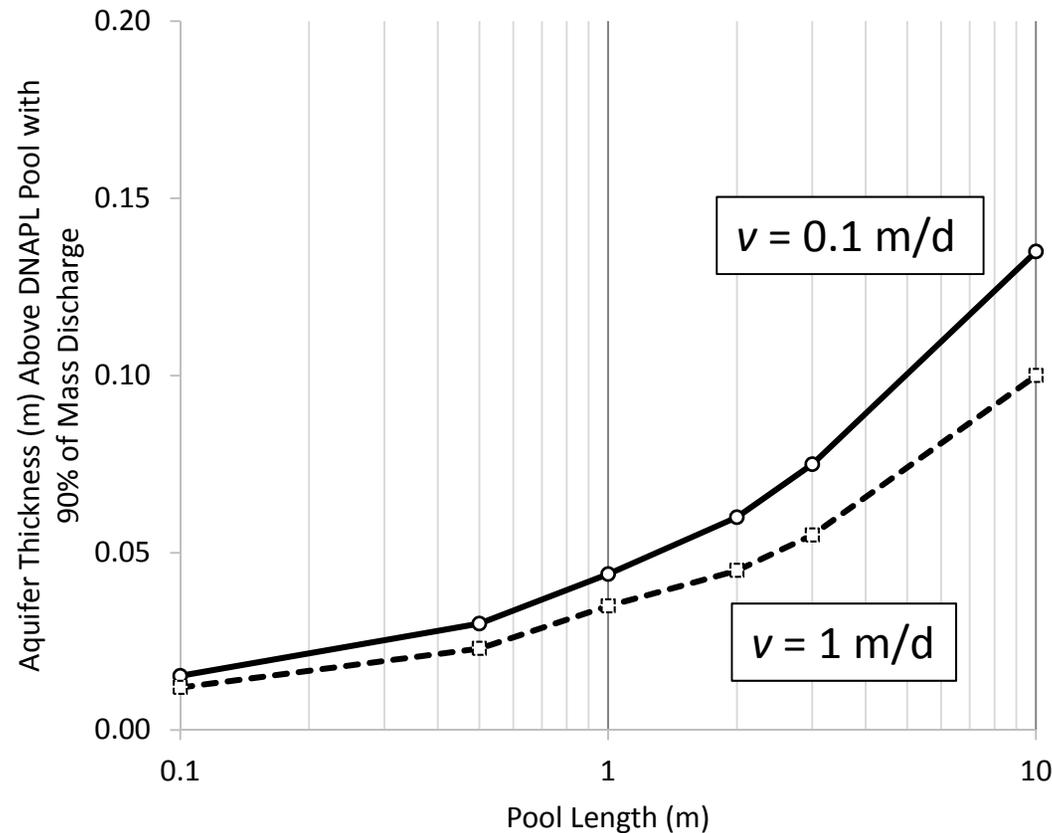


Concentration Profile Above Pool

Johnson and Pankow, 1992



Plume Thickness above a DNAPL Pool



Note – dissolved plumes above DNAPL pools are very thin and easily missed. High resolution PID, particularly in sand directly above silt/clay, may be helpful for identifying pool depths.

Thickness of aquifer above a DNAPL pool with 90% of the mass discharge from the pool, as a function of pool length.

Surface Discharge from a DNAPL Pool

$$Md_{surf} = \left(2L_p W_p (0.001 C_{sol}) \sqrt{\frac{q_x}{\pi L_p}} \right) \sqrt{\alpha_{TV} q_x + \theta_t \tau D_o}$$

Md_{surf} = surface discharge (kg/y)

L_p = pool length (m)

W_p = pool width (m)

C_{sol} = solubility (mg/L)

q_x = specific discharge (m³/m²/y)

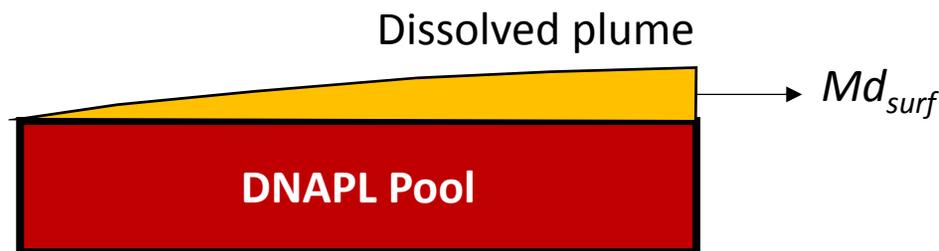
α_{TV} = transverse dispersivity (m)

θ_t = total porosity

τ = tortuosity coefficient

D_o = free-water diffusion coefficient (m²/y)

GW Flow



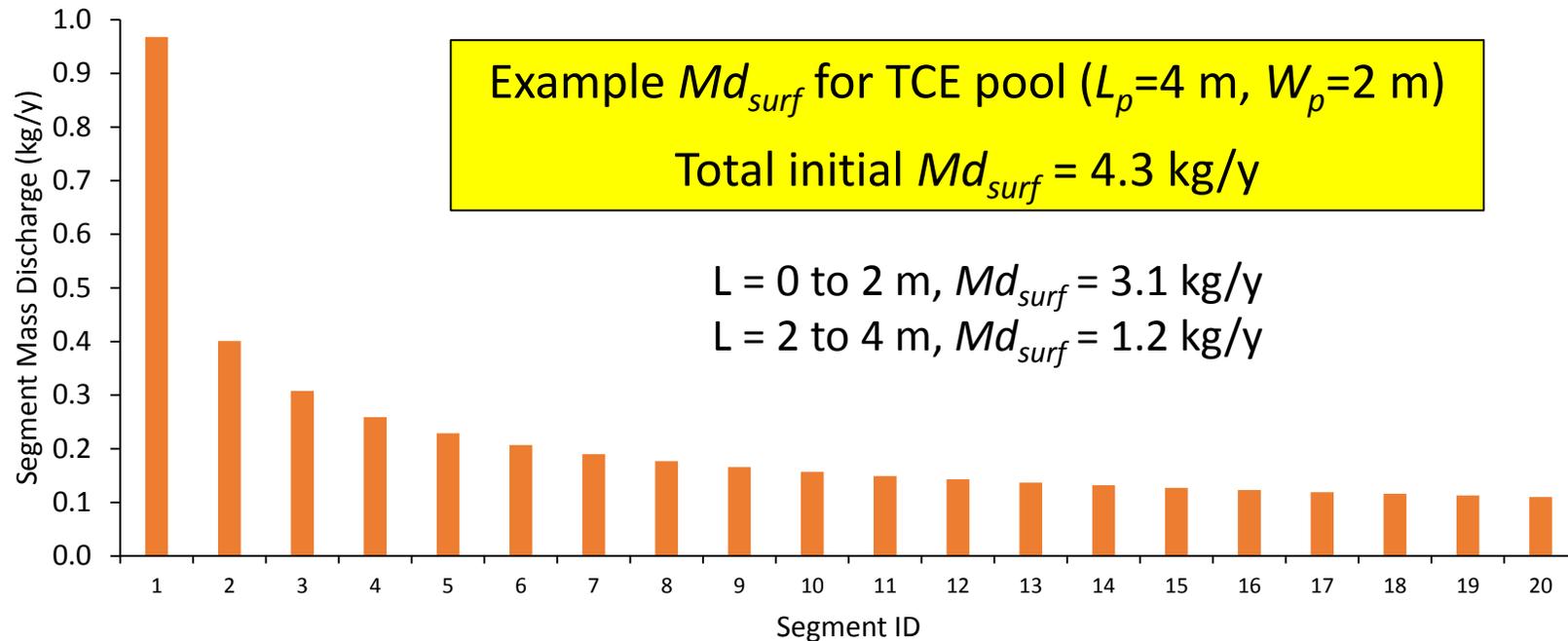
Analytical Solution: Constant-Length Model

USB\Models\Pool Constant-Length Model.xlsx

<u>Analytical solution for Surface Discharge from a DNAPL Pool</u>		
Chemical:	TCE	
Pool length, L_p (m):	4	
Pool width, W_p (m):	2	
Solubility, C_{sol} (mg/L):	1400	
Free-water diffusion coefficient, D_o (m ² /s):	7.0E-10	
Hydraulic conductivity, K (m/d):	8.64	
Horizontal hydraulic gradient, i (m/m):	0.01	
Specific discharge, q_x (m ³ /m ² /d):	0.09	
Total porosity, θ_t :	0.38	(regression equation, K in m/s)
Effective porosity, θ_e :	0.23	(regression equation, K in m/s, $K \leq 1$ cm/s)
Groundwater velocity, v (m/d):	0.38	
Tortuosity coefficient, τ (dim.):	0.46	(regression equation, K in m/s)
Transverse dispersivity, α_{TV} (mm):	0.35	(regression equation, K in m/s, $v < v_c$)
DNAPL density, ρ_{NAPL} (kg/m ³):	1460	
Average NAPL saturation, S_n :	0.15	
Pool height (m):	0.05	
Surface discharge, Md_{surf} (kg/y):	4.3	
Initial mass, M_o (kg):	33.4	
Constant-Length Model depletion time (y):	7.7	

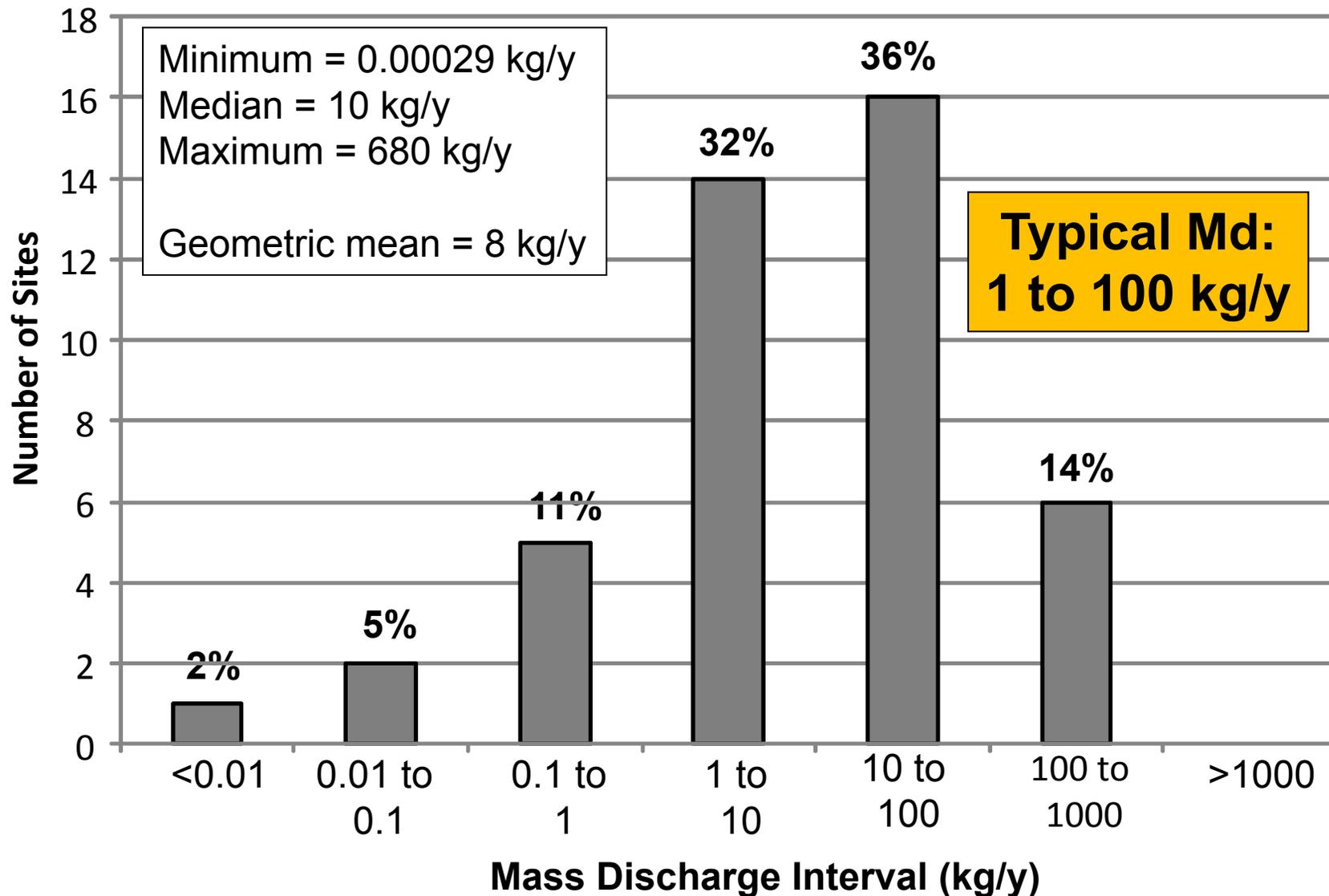


Mass Discharge vs. Distance Along Pool



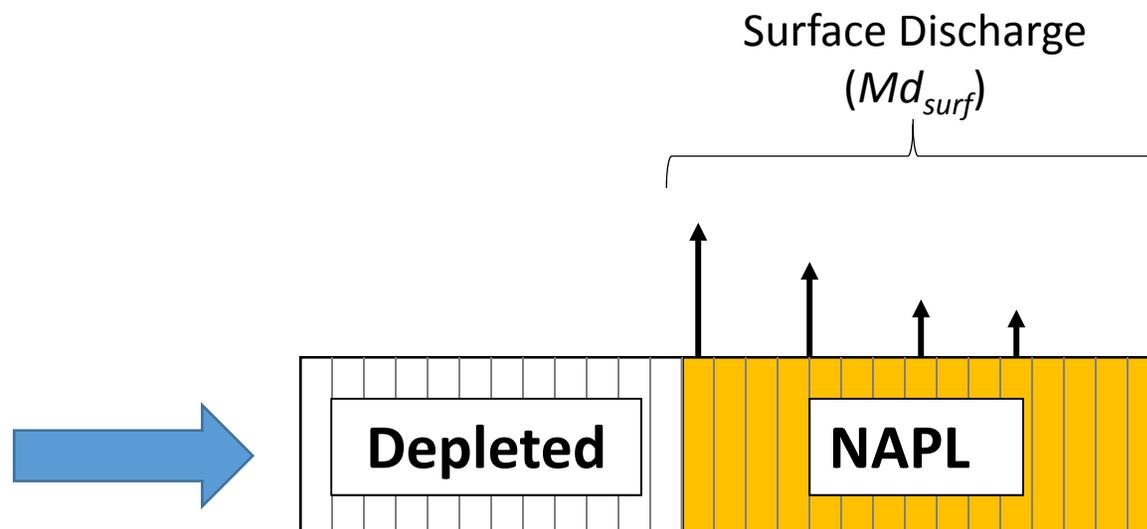
$L_p = 4$ m (Pool Segment $\Delta x = 0.2$ m)

Case Studies: Source Strength (ITRC, 2010)

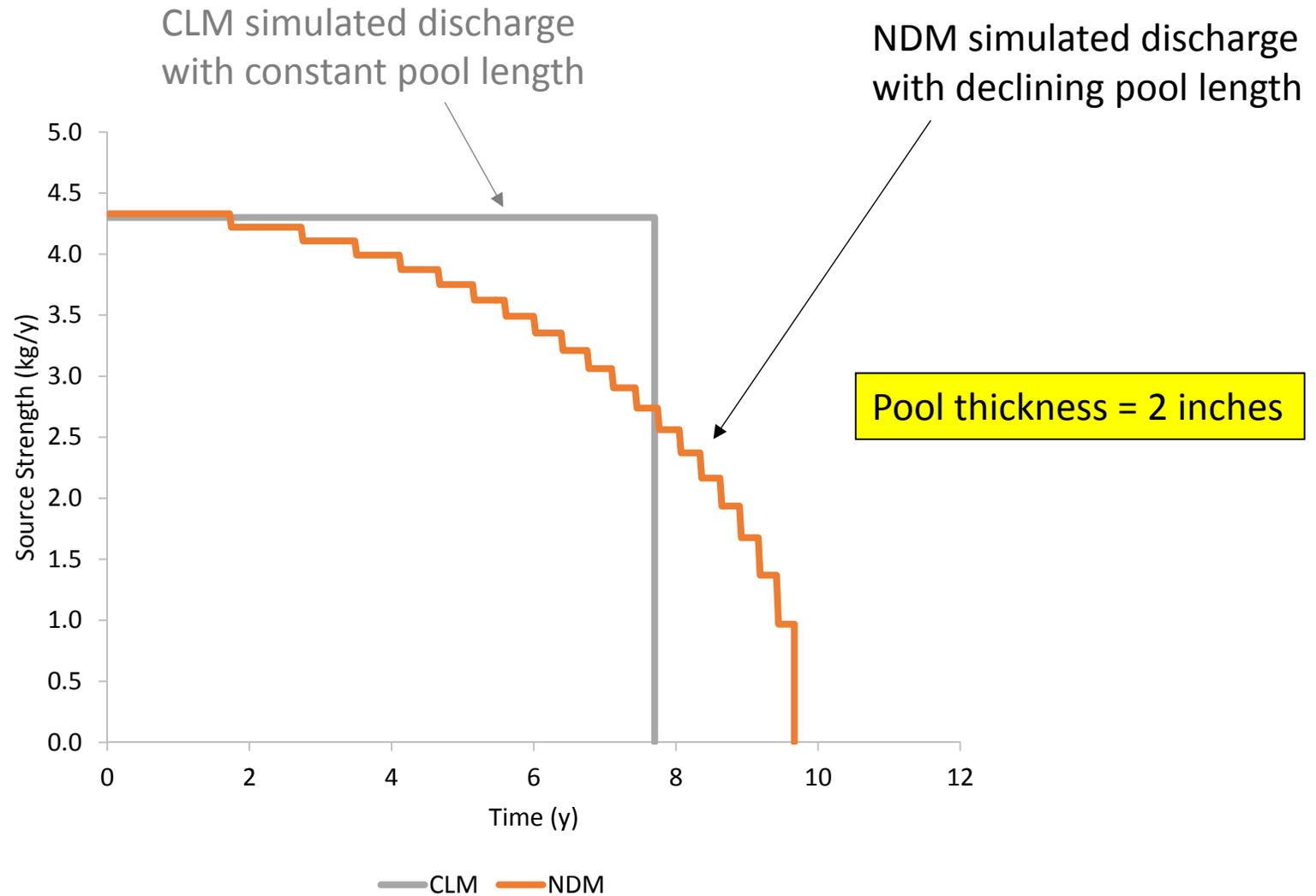


Pool Dissolution

- Pool length declines over time
 - Upgradient end dissolves first
- NAPL Depletion Model (NDM) – 1-D grid, segments become inactive when 100% depleted.
- Md_{surf} declines as pool length declines.



Mass Discharge Trends Over Time



Note: CLM refers to the Constant Length Model; NDM refers to the NAPL Depletion Model

Mass Discharge Decline

- One major reason for decline in source strength at NAPL source zones:
 - Decline in NAPL-water interfacial area (I.A.)
- For example – decline in pool length and area
- Ganglia vs. pool I.A. decline

Ganglia
● ● ● ●



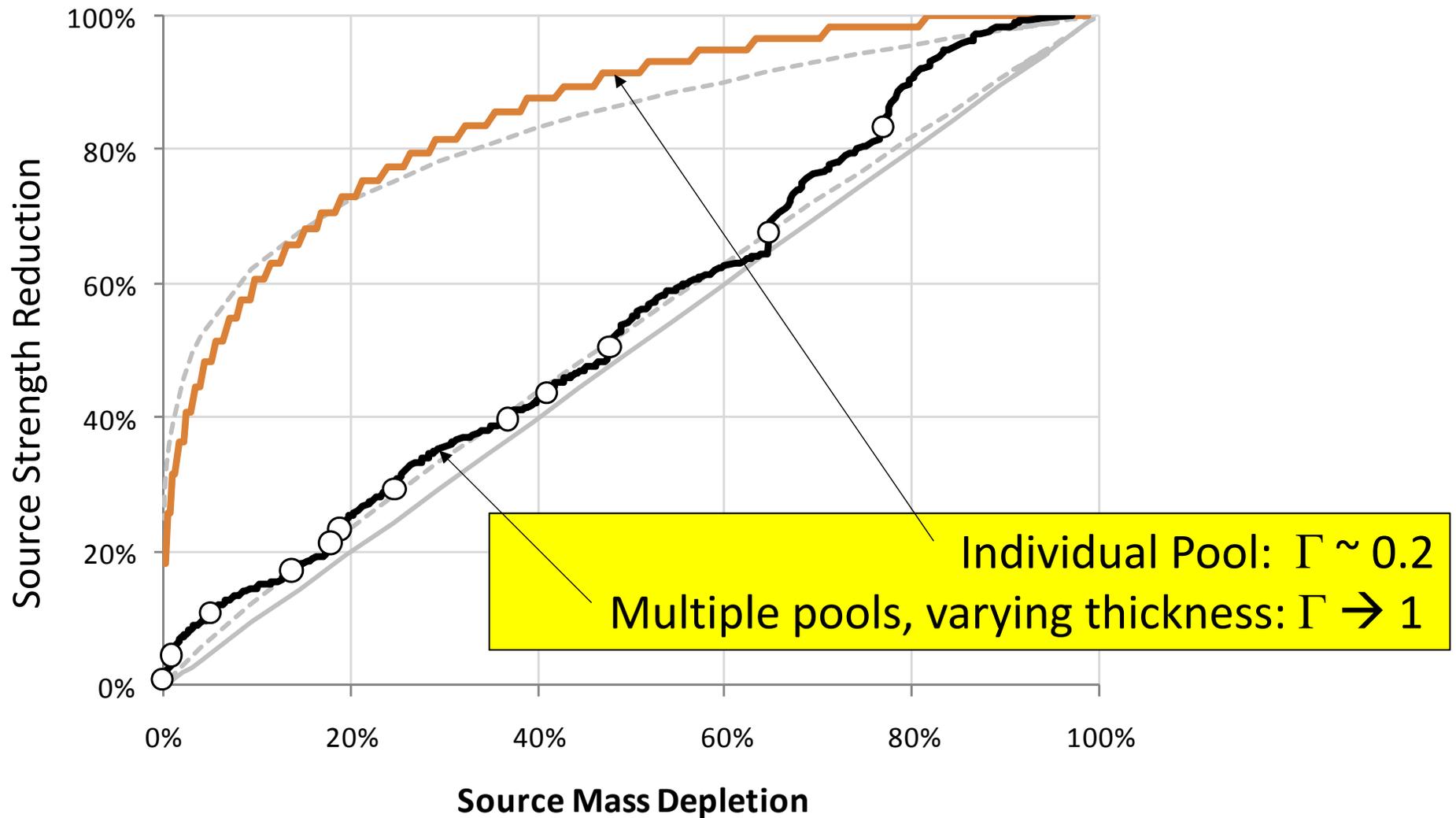
Most NAPL mass in pools is below the NAPL-water interface, and generally not available for dissolution.

Thicker pools → longer time to deplete.

Depletion timeframe \propto pool height = V/A

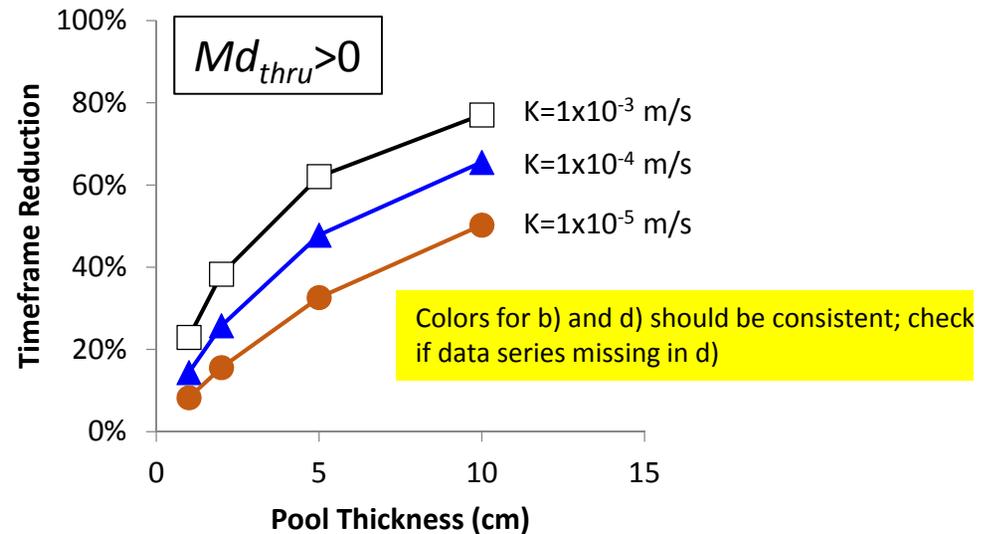
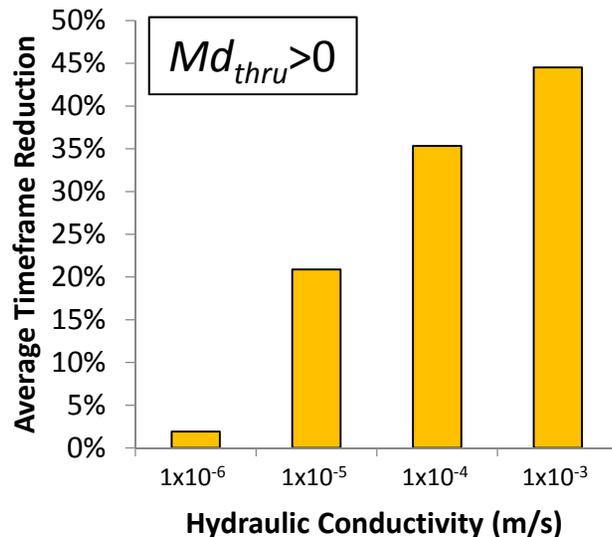
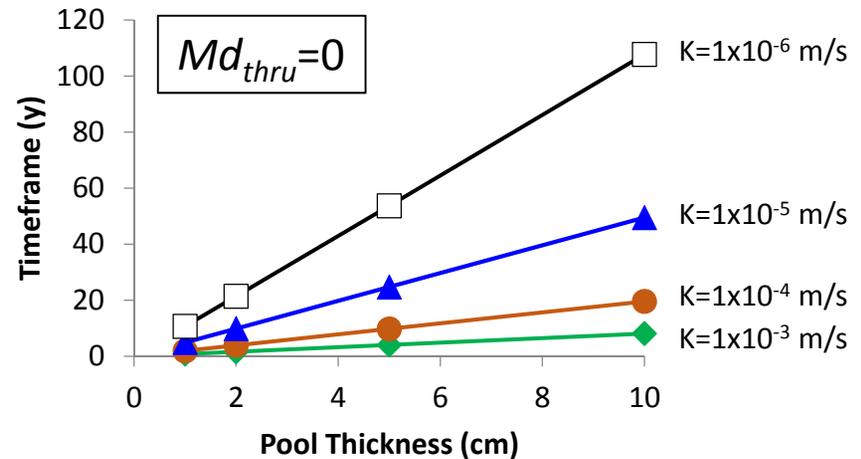
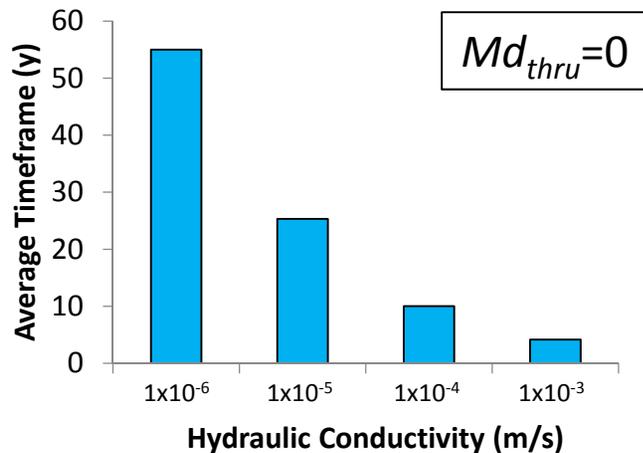


Source Strength vs. Source Mass



Pool Dissolution Sensitivity Analysis

Sensitivity analysis of remediation timeframe based on hydraulic conductivity, pool thickness, and DNAPL through-discharge.



Exercise No. 2: Pool Depletion Timeframe Sensitivity Analysis

Goal: Assess sensitivity of depletion timeframe to chemical properties.





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3b.24

Estimating Input Parameters for Md_{surf}

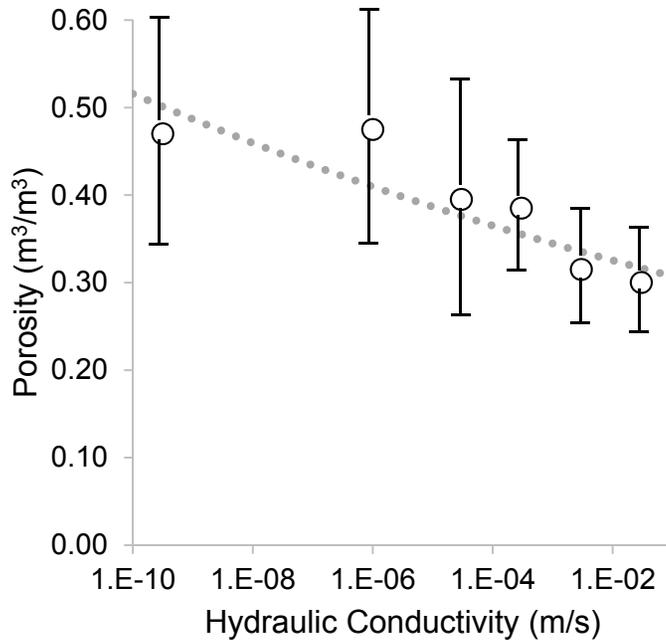


Estimating Input Parameters Based on K

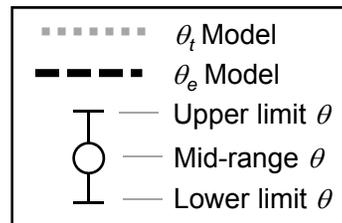
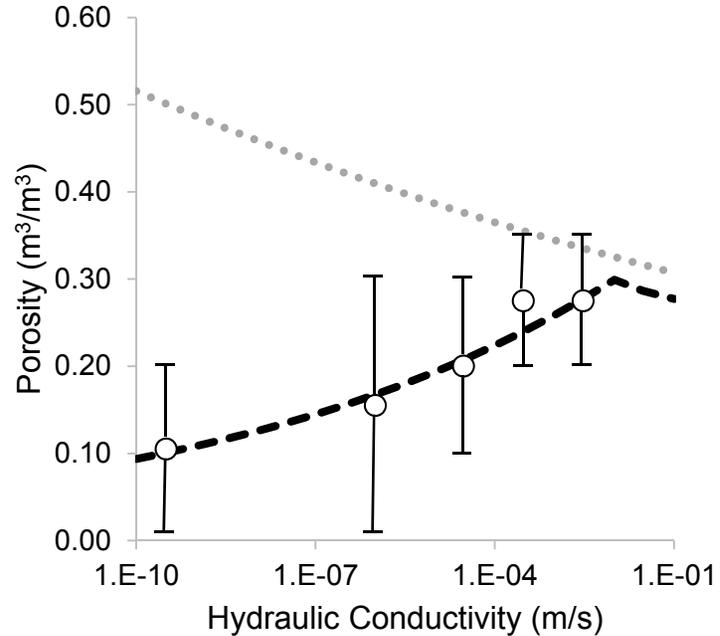
Reference	Empirical Relationship (K in m/s)
Carey et al., 2015a	$\tau = 0.60 K^{0.030}$ (i)
	$\theta_t = 0.30 K^{-0.026}$ (ii)
	$\theta_e = 0.41 K^{0.064}, K \leq 1 \times 10^{-2}$ m/s (iii)
	$\theta_e = (0.29 K^{-0.026}) - 0.03, K > 1 \times 10^{-2}$ m/s (iv)
Carey et al., 2015b	$\alpha_{TV} = 0.08 K^{-0.16}, v \leq v_c$ (v)
	$\alpha_{TV} = 0.08 K^{-0.16} (v_c/v)^{0.5}, v > v_c$ (vi)
Carey et al., 2015e	$\alpha_{aw} = 0.112 (100 K)^{0.211}$ (vii)
	$n = 13.14 (100 K)^{0.246} \quad K \geq 1 \times 10^{-4}$ m/s (viii)
	$S_{wr} = 0.015 (100 K)^{-0.218}$ (ix)

Total and Effective Porosity

a) Total porosity model (light dashed line) with mid-range and upper and lower θ_t limits for each soil texture.



a) Effective porosity model (dark dashed line) with mid-range and upper and lower θ_e limits for each soil texture.



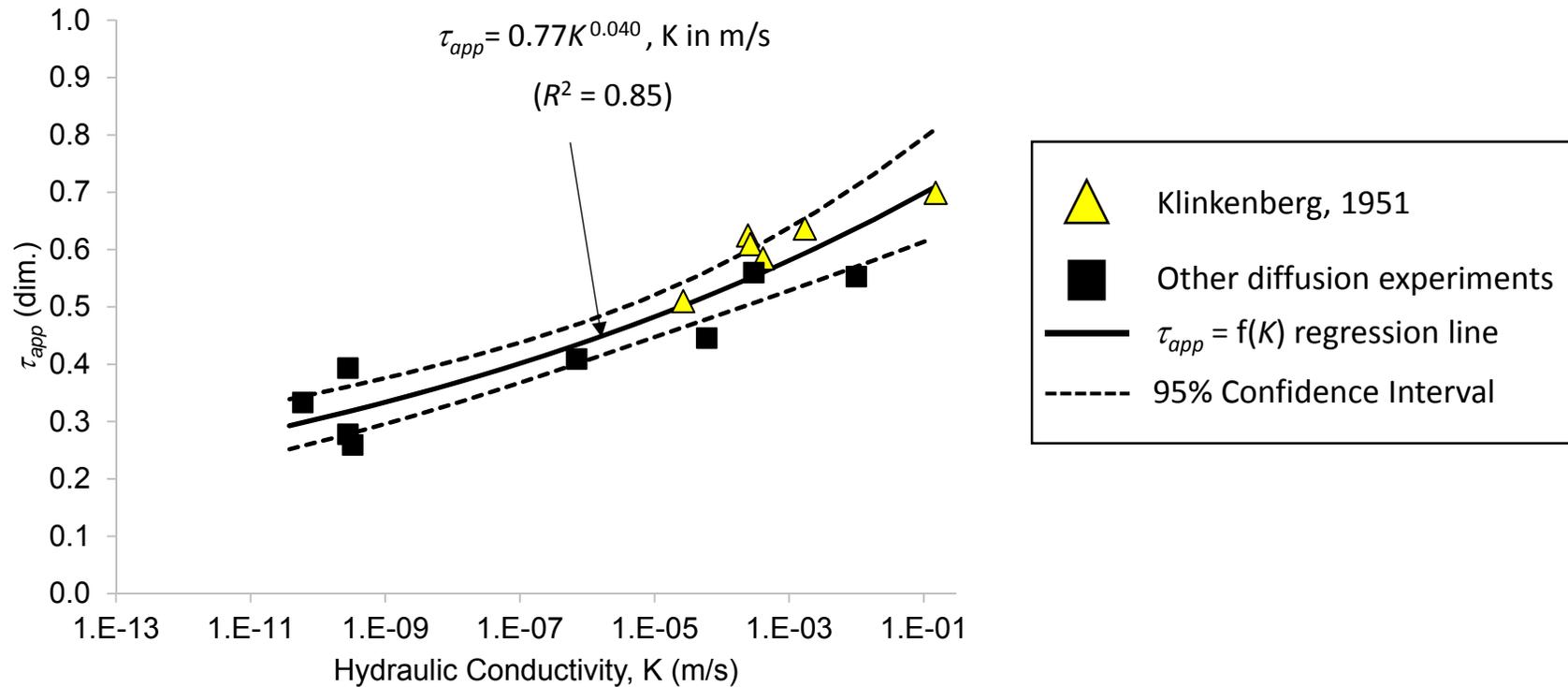
Porosity Models

$$\theta_t = 0.3 K^{-0.025}, K \text{ in m/s}$$

$$\theta_e = 0.40 K^{0.063}, K \leq 1 \times 10^{-2} \text{ m/s}$$

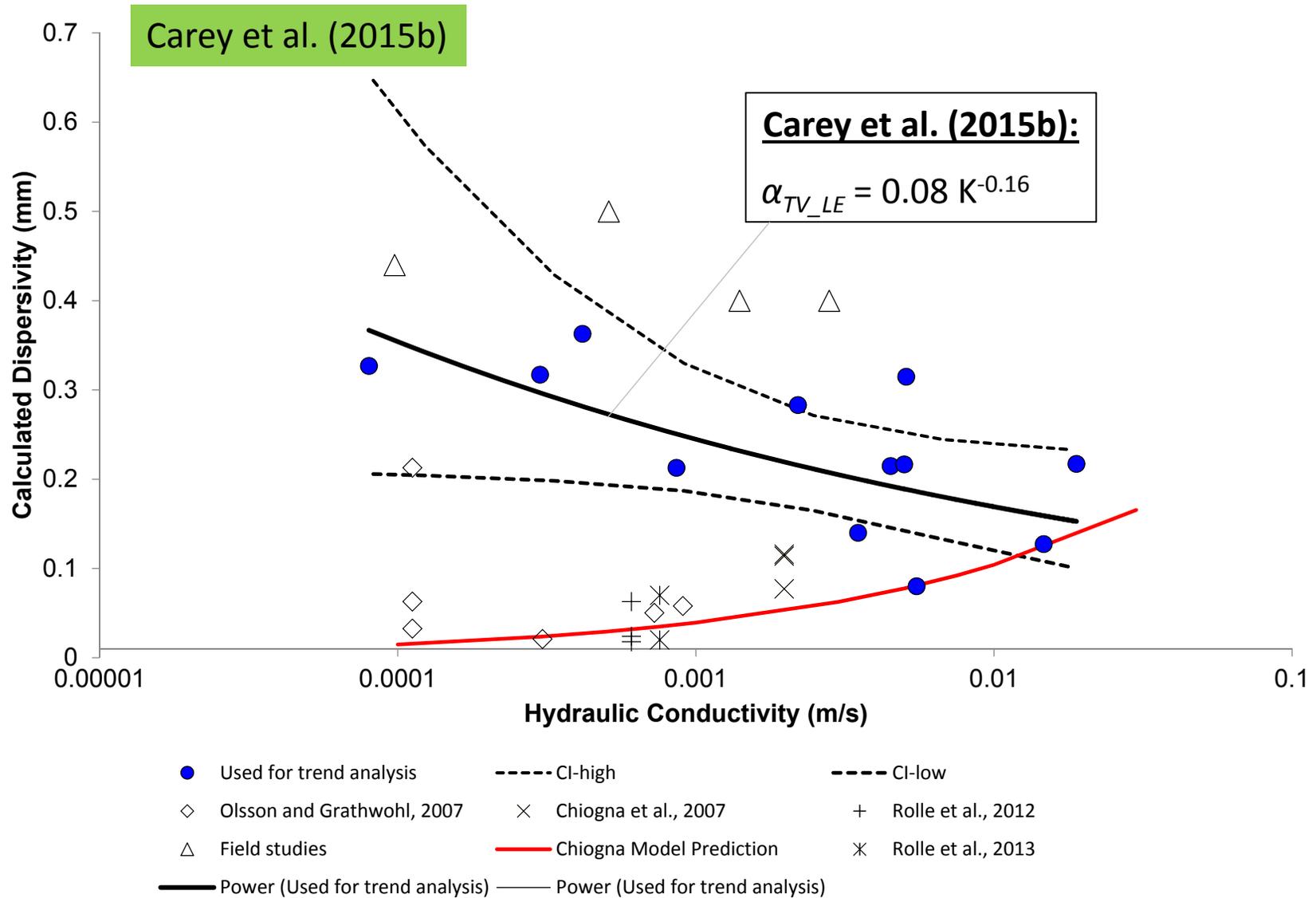
$$\theta_e = (0.3 K^{-0.025}) - 0.03, K > 1 \times 10^{-2} \text{ m/s}$$

Tortuosity Coefficient



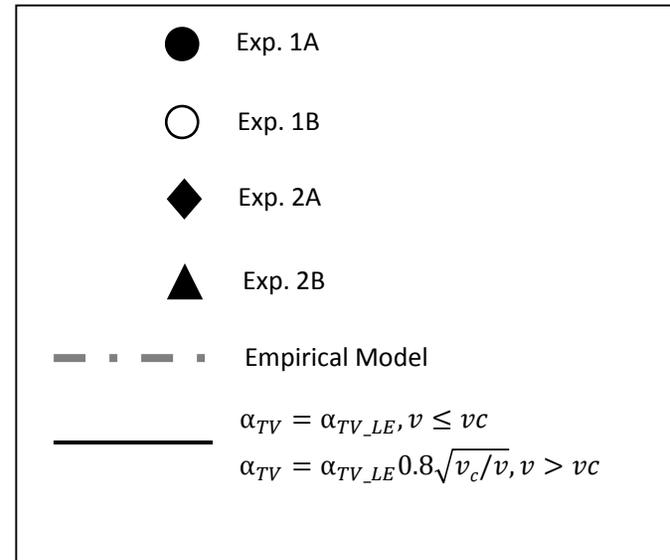
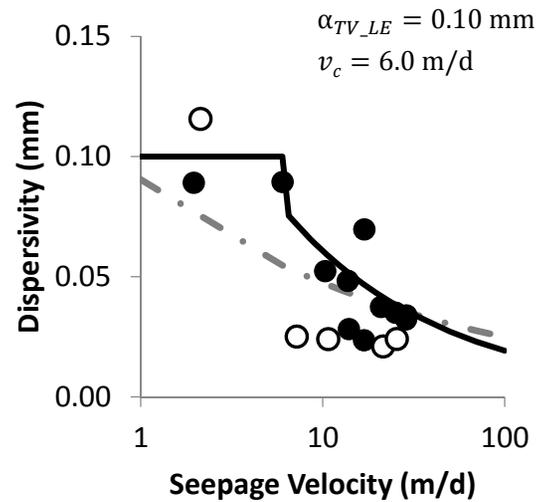
Carey et al. (2015a)

Transverse Dispersivity



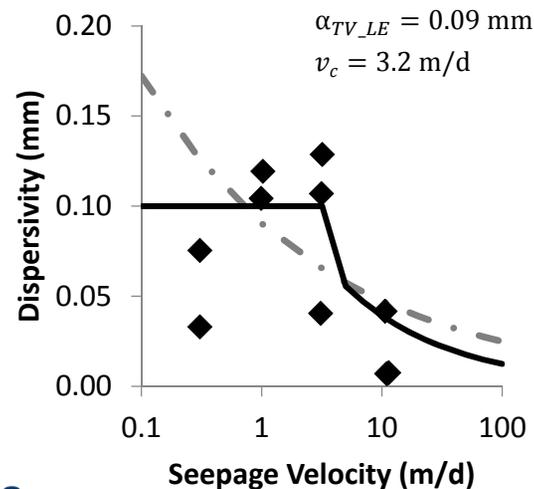
Velocity Influence on α_{tv}

(a) Experiment 1A/1B

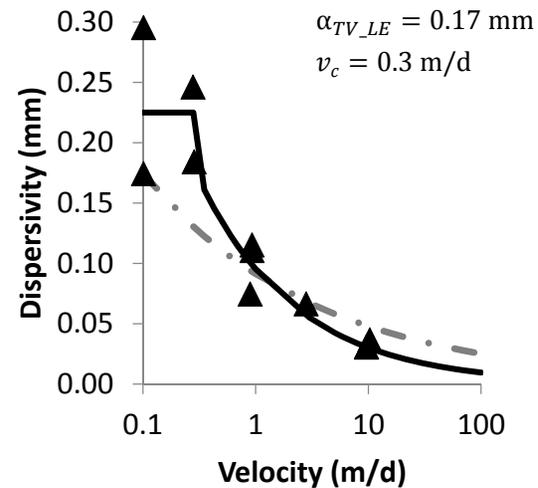


Carey et al. (2015b)

(b) Experiment 2A

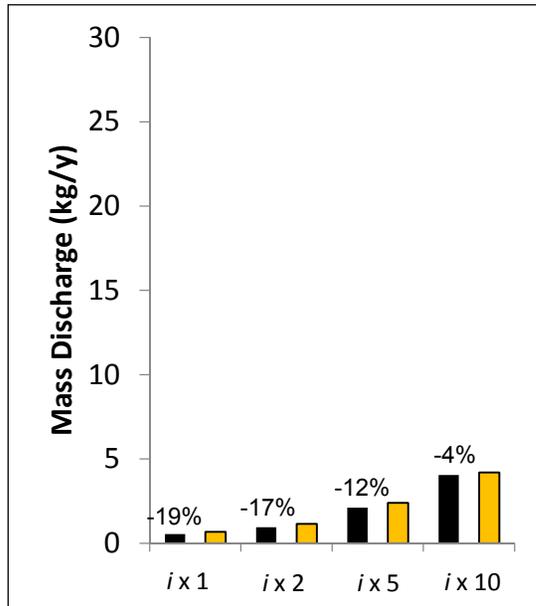


(c) Experiment 2B

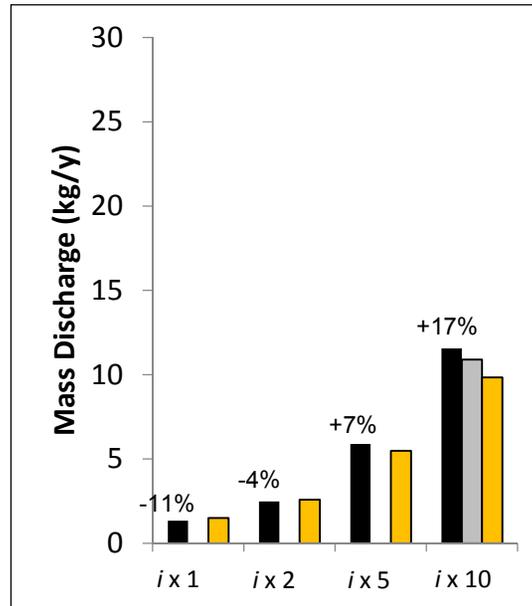


Influence of Velocity and α_{tv} on DNAPL Pool Source Strength

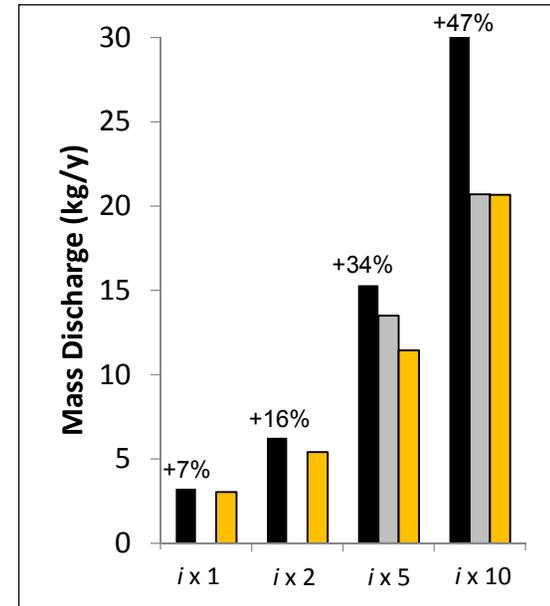
a) $K = 1 \times 10^{-5}$ m/s



b) $K = 1 \times 10^{-4}$ m/s



c) $K = 1 \times 10^{-3}$ m/s



Notes:

- i represents the horizontal hydraulic gradient, and $i \times 1$ represents the natural (i.e. pre-remedy) gradient.
- Percentages shown above the LE(K) Model result represent the difference in mass discharge relative to simulations based on the Empirical Model.

Carey et al. (2015b)

Influence of Velocity and α_{TV} on DNAPL Pool Source Strength

K (m/s)	d10 (mm)	Hydraulic Gradient (m/m)	Effective Porosity (m ³ /m ³)	Total Porosity (m ³ /m ³)	Groundwater Velocity, v (m/d)	v > 3 m/d?	α_{TV} (mm)		
							LE(K) Model	NE Model	Empirical Model
1.E-05	0.0125	0.03	0.2	0.42	0.13	no	0.36	--	0.75
1.E-05	0.0125	0.06	0.2	0.42	0.26	no	0.36	--	0.61
1.E-05	0.0125	0.15	0.2	0.42	0.65	no	0.36	--	0.48
1.E-05	0.0125	0.3	0.2	0.42	1.30	no	0.36	--	0.39
1.E-04	0.054	0.01	0.25	0.38	0.35	no	0.28	--	0.38
1.E-04	0.054	0.02	0.25	0.38	0.69	no	0.28	--	0.31
1.E-04	0.054	0.05	0.25	0.38	1.73	no	0.28	--	0.24
1.E-04	0.054	0.1	0.25	0.38	3.46	yes	0.28	0.25	0.20
1.E-03	0.24	0.003	0.3	0.33	0.86	no	0.22	--	0.19
1.E-03	0.24	0.006	0.3	0.33	1.73	no	0.22	--	0.16
1.E-03	0.24	0.015	0.3	0.33	4.32	yes	0.22	0.17	0.12
1.E-03	0.24	0.03	0.3	0.33	8.64	yes	0.22	0.10	0.10

Carey et al. (2015b)

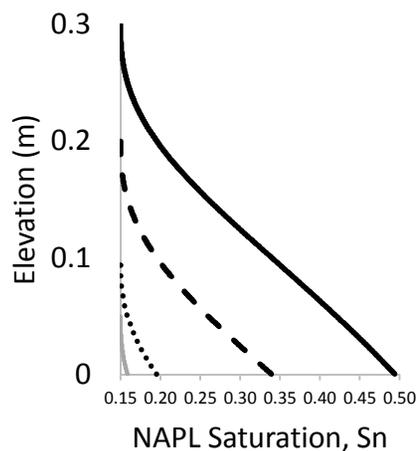
Through-Discharge



Through-Discharge (Md_{thru})

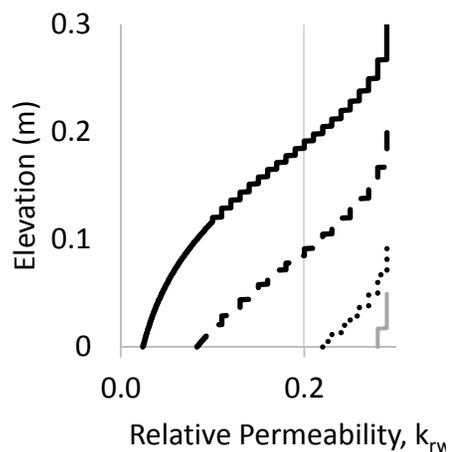


a) Elevation vs. NAPL saturation



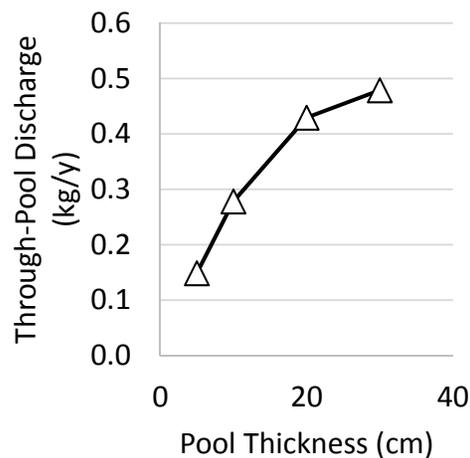
— h=5 cm h=10 cm
 - - h=20 cm ——— h=30 cm

b) Elevation vs. relative permeability



— h=5 cm h=10 cm
 - - h=20 cm ——— h=30 cm

c) Through-pool discharge vs. pool thickness



NAPL Depletion Model (NDM) Options

- Model variable with options: IPFLUX
- **Option 0**: $Md_{thru} = 0$
- **Option 1**: S_n and k_{rw} vs. depth; applied at first active segment in pool.
 - Pool layer discretized into m layers. S_n , k_{rw} , and reduced q_x calculated in each layer.
 - Total q_x through pool used to estimate Md_{thru} .

NAPL Depletion Model (NDM) Options

- Model variable with options: **IPFLUX**
- **Option 0**: $Md_{thru} = 0$
- **Option 1**: S_n and k_{rw} vs. depth; applied at first active segment in pool.
- **Option 2**: Same as Option 1, except mass removed equally from all horizontal segments in pool.
- **Option 3**: User inputs average S_n and k_{rw} over entire pool thickness. Mass removed from segment 1 only.



Additional Input Parameters (IPFLUX = 1,2)

<u>Other parameters for <i>Mdthru</i> calculation</u>		
<i>Swr</i>	0.04	(regression equation, <i>K</i> in cm/s)
<i>Sm</i>	0.85	=(1 - residual saturation threshold)
α_{aw} (per m)	4.26	(regression equation, <i>K</i> in cm/s)
<i>n</i>	4.23	(regression equation, <i>K</i> in cm/s)
Water density (kg/m ³)	1000	
delta-z (m)	0.0025	
<i>Feff</i>	1	
IFT-aw (dynes/cm)	72	
IFT-nw (dynes/cm)	34	

Exercise No. 3: Pool Depletion Time Sensitivity to Pool Dimensions and Through-Discharge



NDM Scenarios:

- TCE pools
- Lengths: 1, 2, 5, 10 m
- Thickness: 2, 5, 10, 20 cm
- Through-flux: Option 0 or 1



Questions?



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Example No. 3

Multiple DNAPL Pools

Section 3c

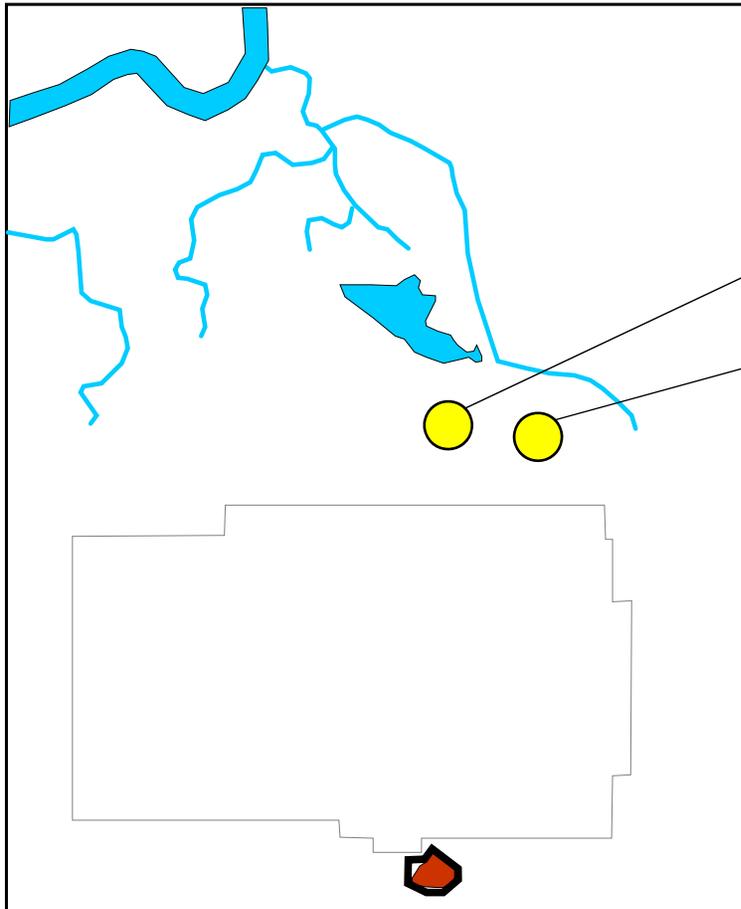


Connecticut Site Example

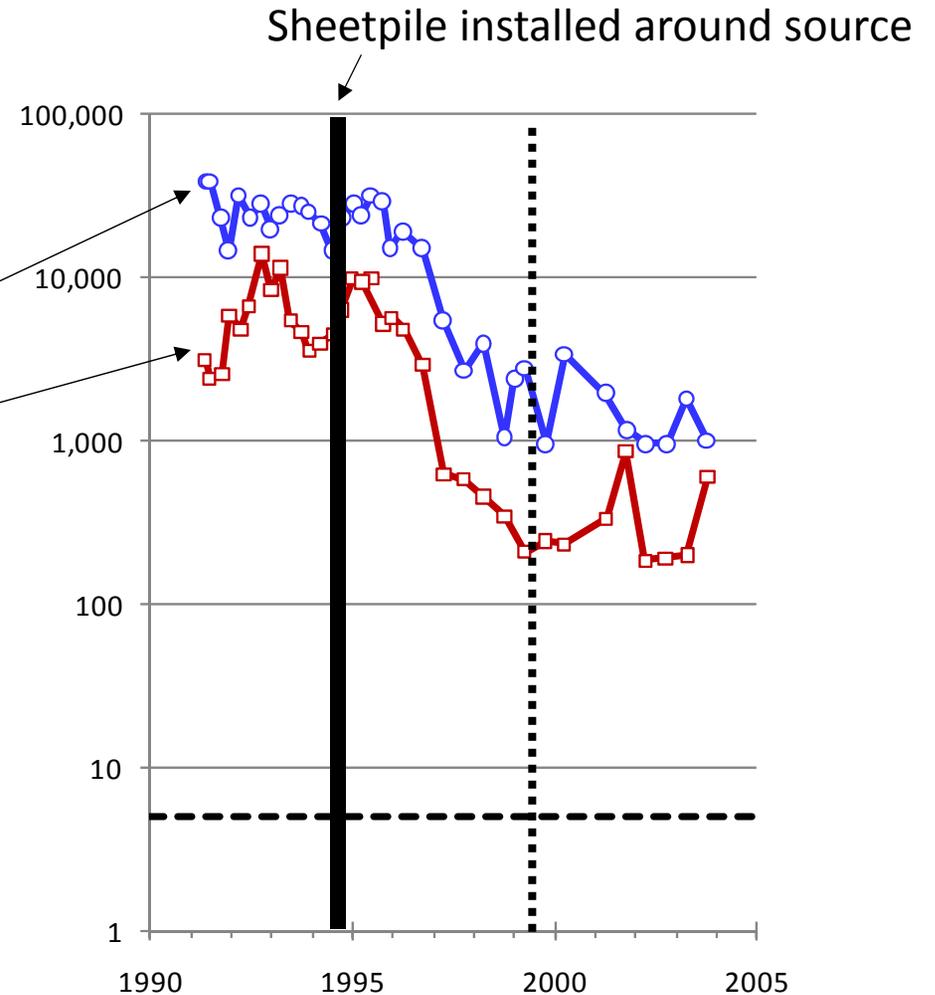
Carey et al. (2015e)



Connecticut Site (Chapman & Parker, 2005)



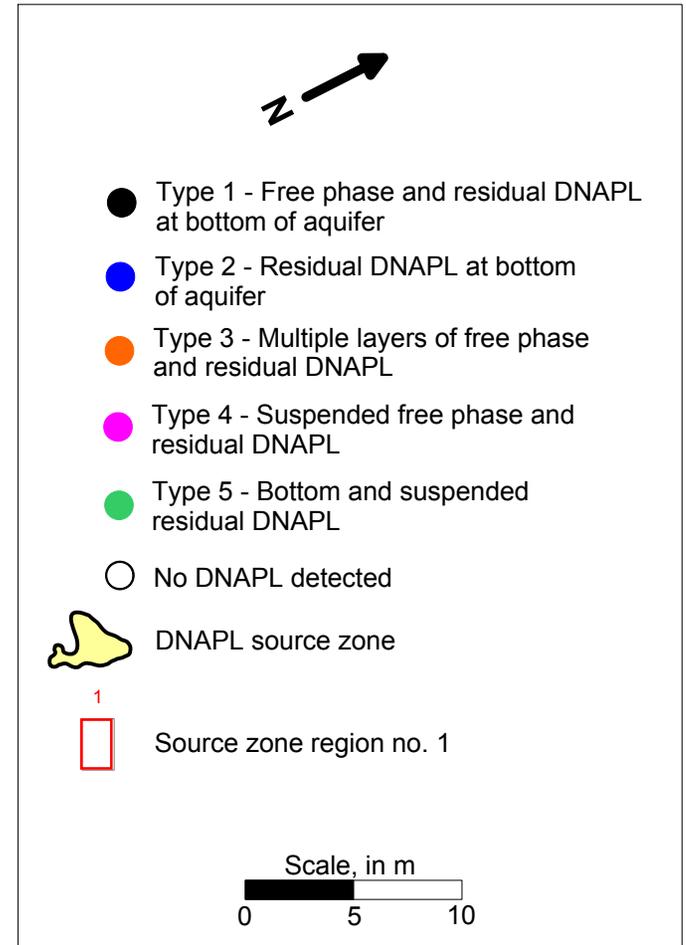
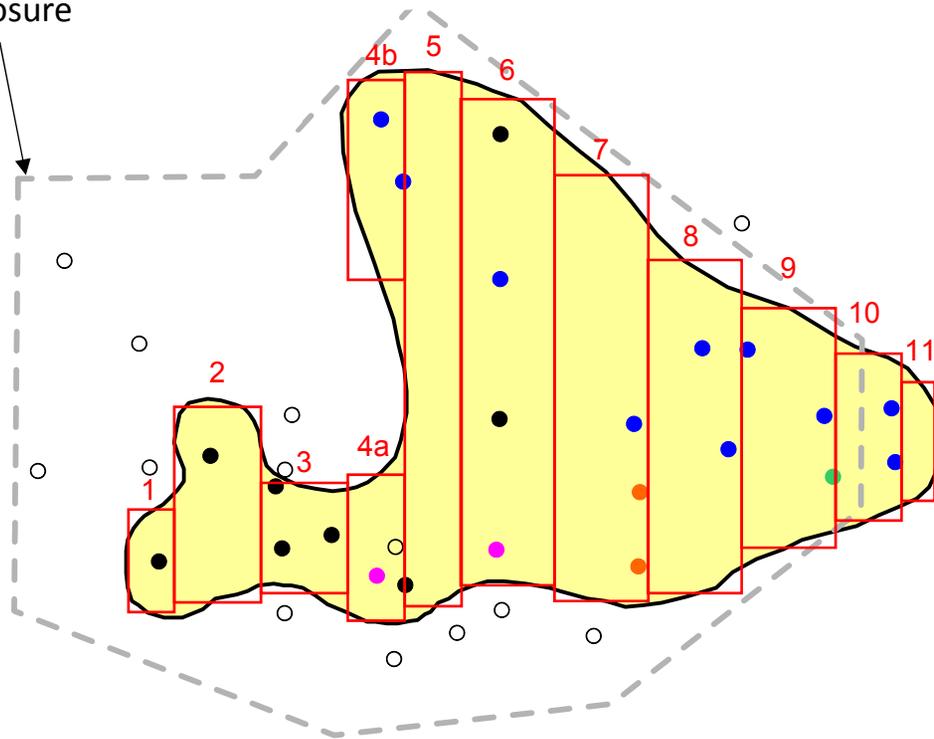
DNAPL Source Zone



Concentration reduction stalled at 93% (15x)

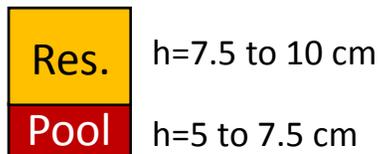
Example - CT Site Sub-Zones (plan view)

Sheetpile Enclosure

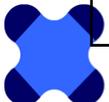
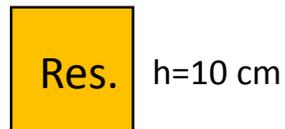


DNAPL source zone profile types:

Type 1



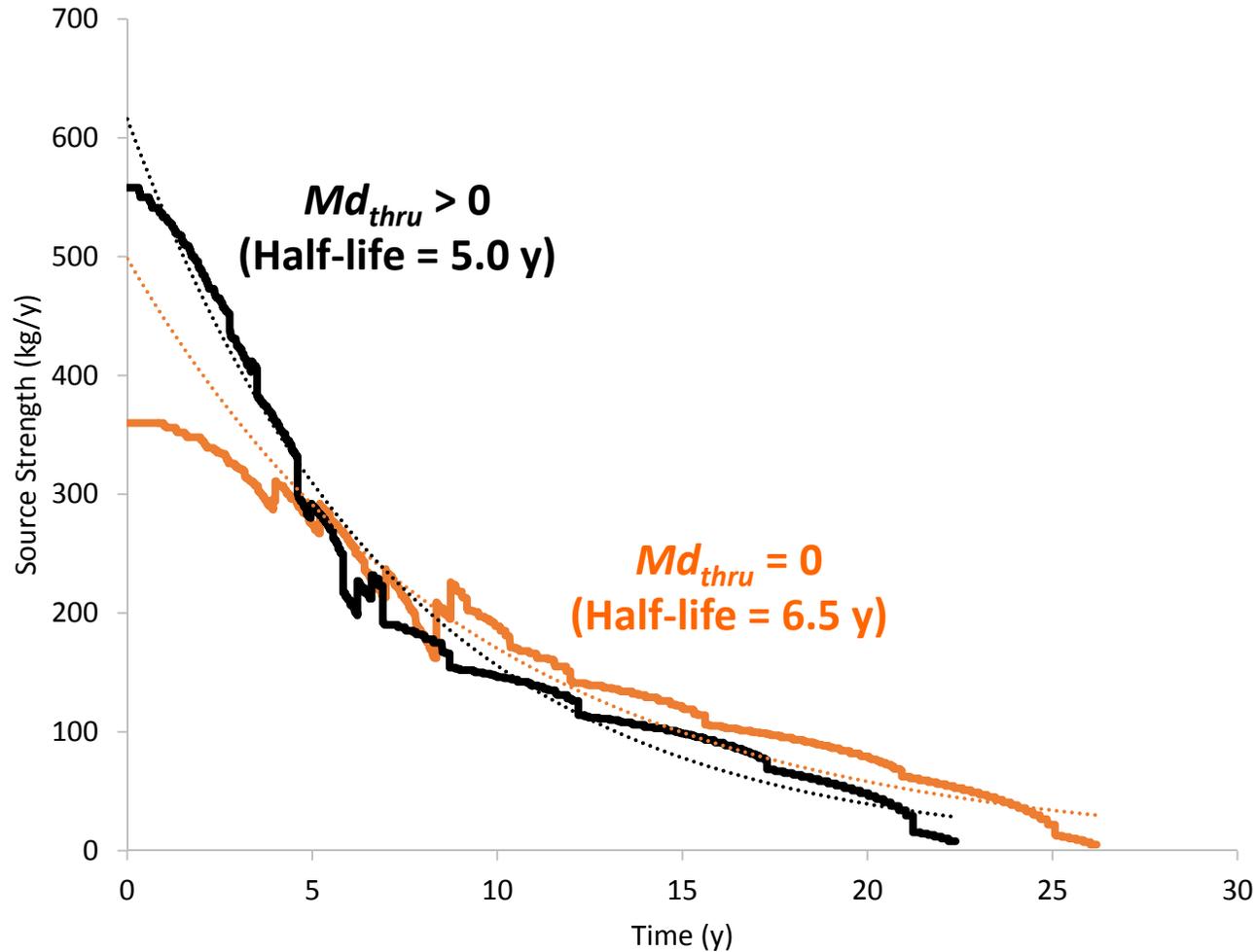
Type 2



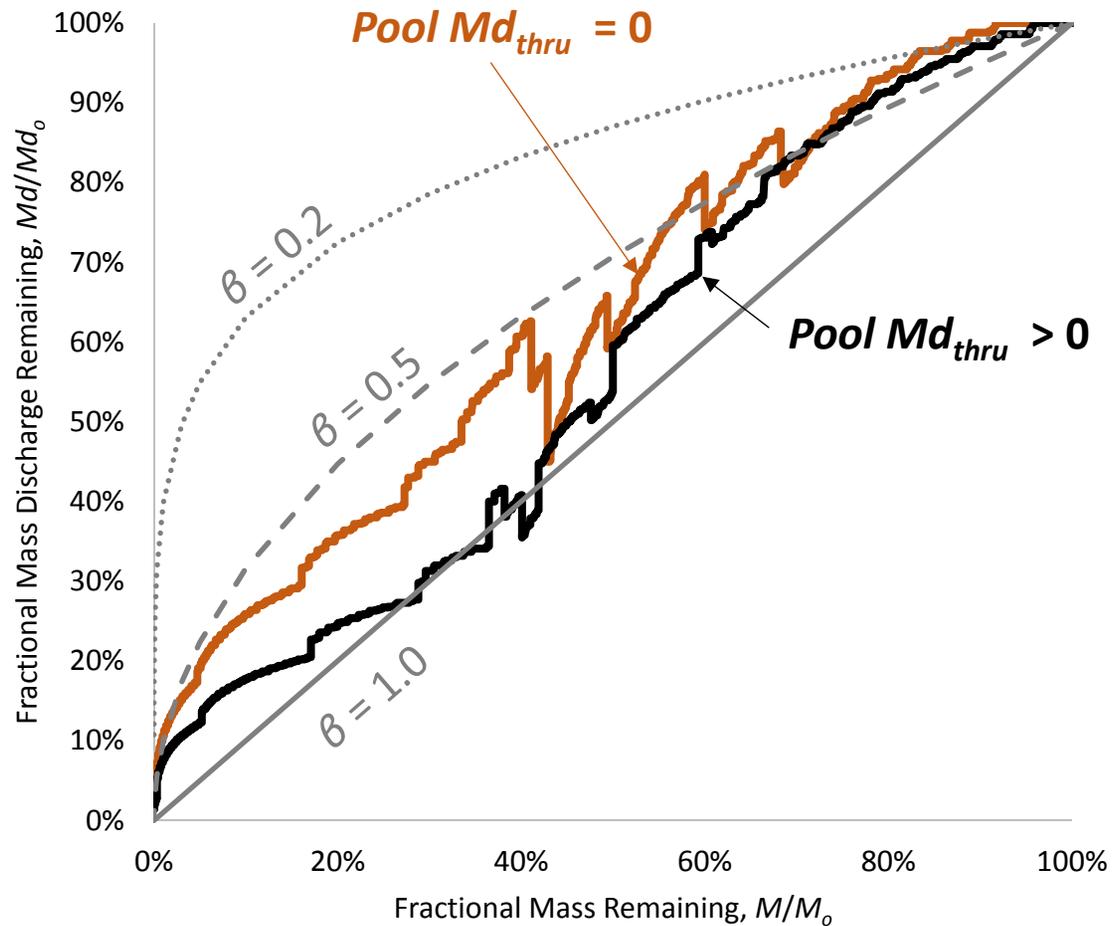
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Parker et al., 2003
Parker et al., 2004
Chapman and Parker, 2005
Stewart, 2002

Example – CT Site (NDM Model)



Example – CT Site (NDM Model)

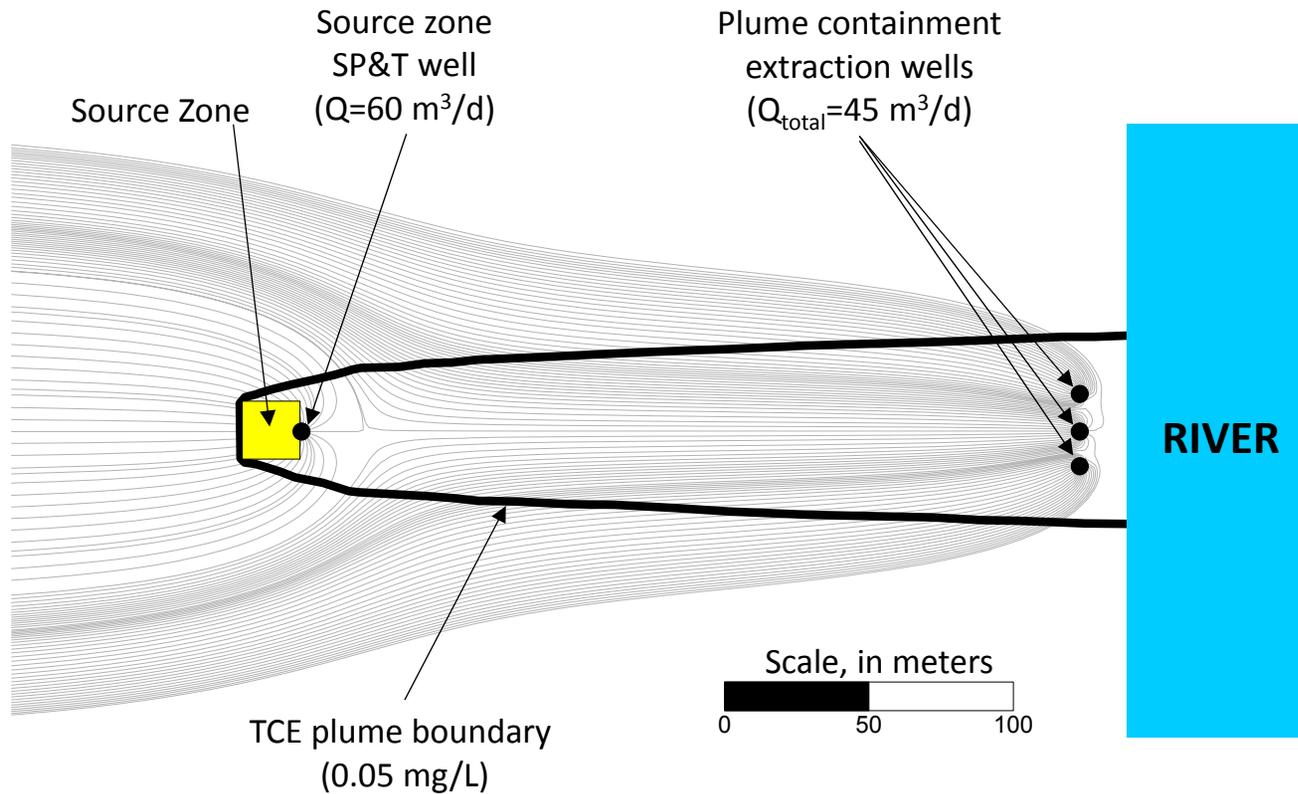


Example of a Feasibility Study

Carey et al. (2014b)

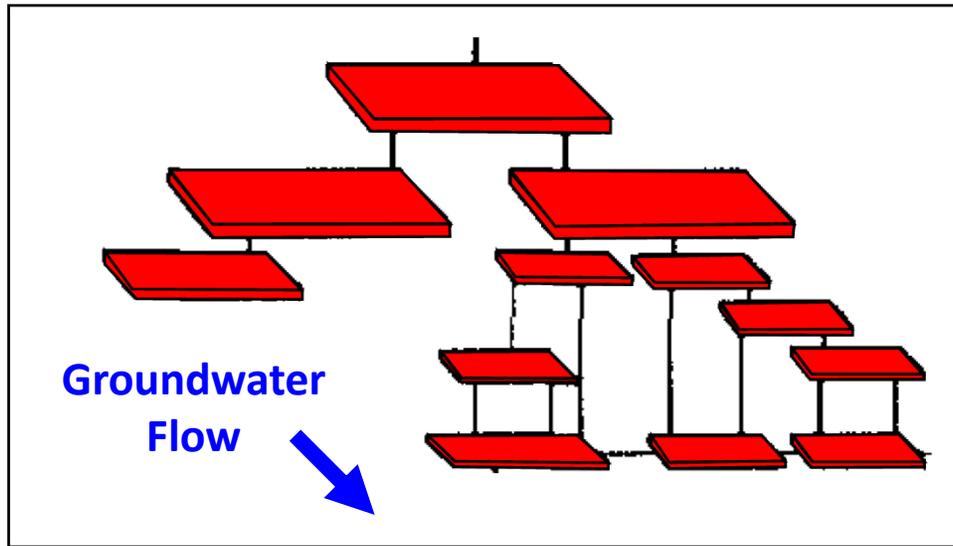


Example Scenario



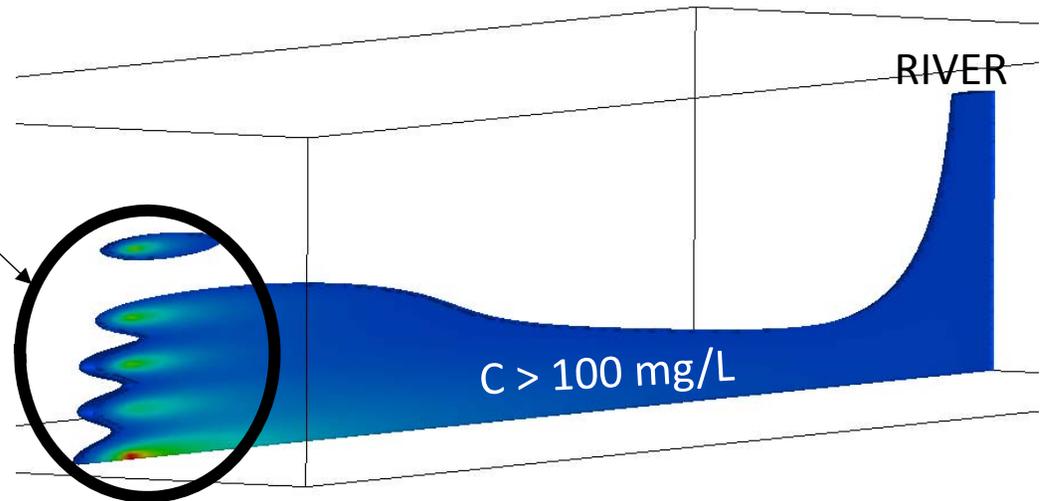
Simulated pre-treatment plume boundary (TCE 0.05 mg/L) and extraction well capture zones for alternative with SP&T for source zone treatment and P&T for plume containment.

How long to reach goals?



Modified from Anderson et al., 1992

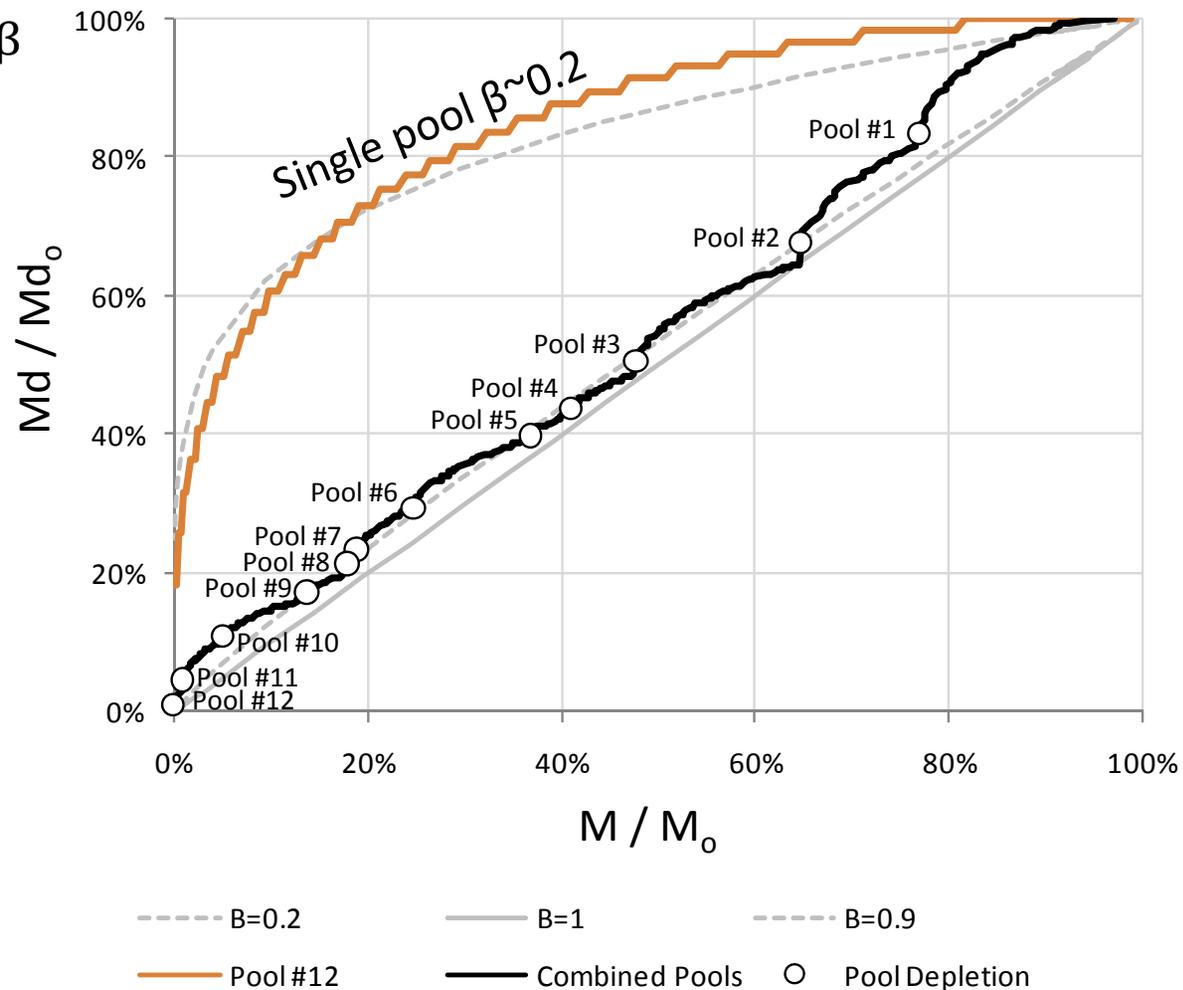
Which characteristics have the greatest influence on timeframe?



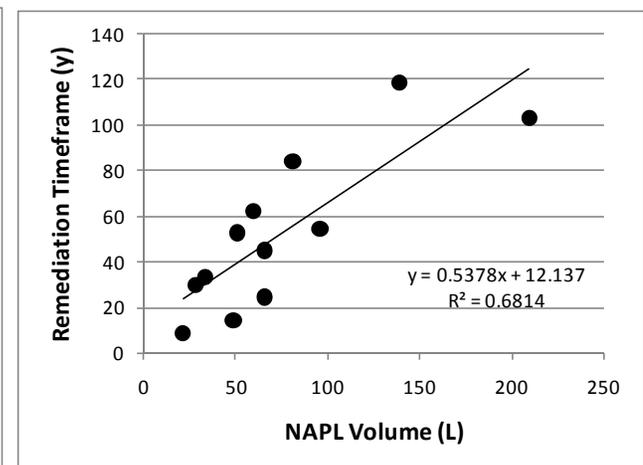
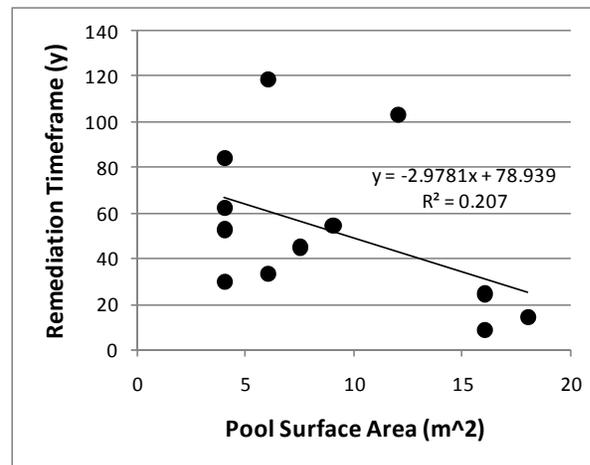
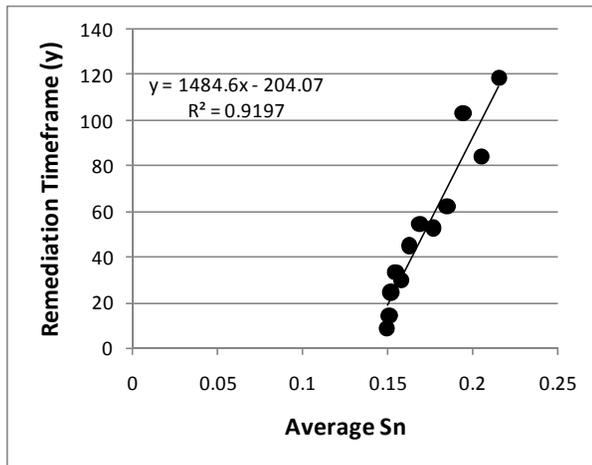
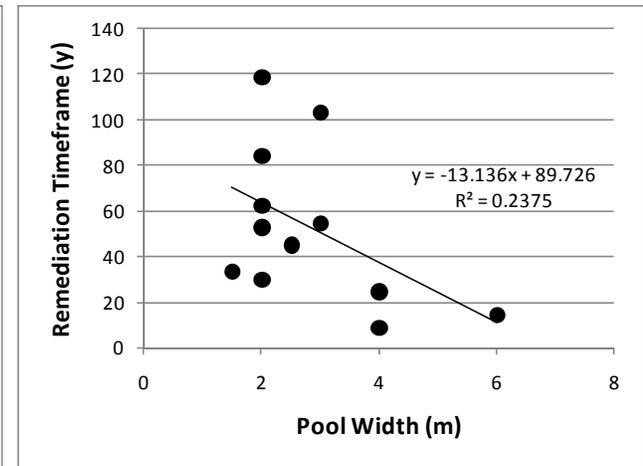
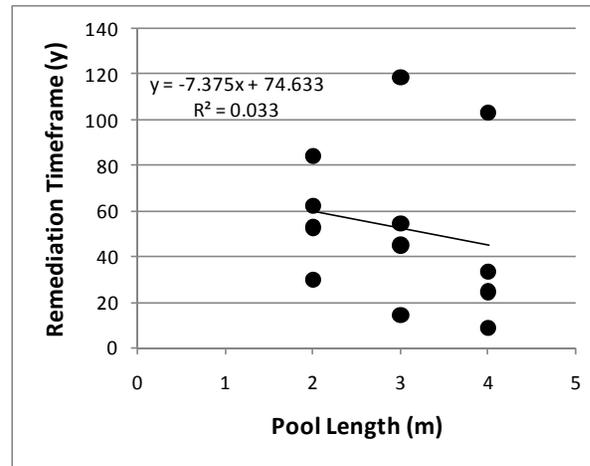
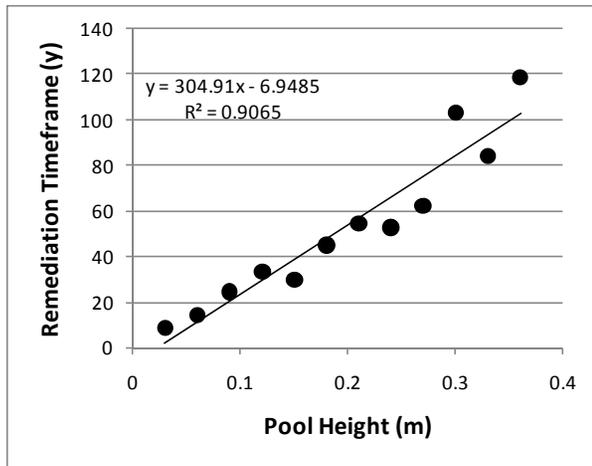
MdR vs. MR for Single & Multiple Pools

Multiple pools with heterogeneous thickness → exponential Md decline

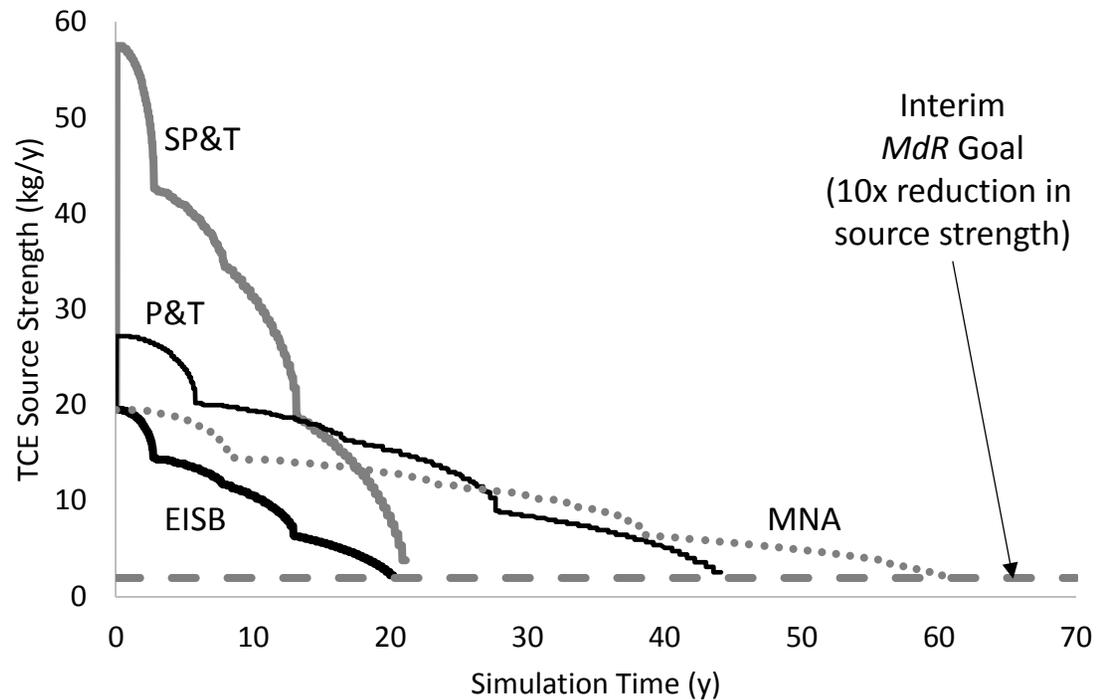
$$\frac{Md}{Md_o} = \left(\frac{M}{M_o} \right)^\beta$$



RTF Correlation with Pool Properties

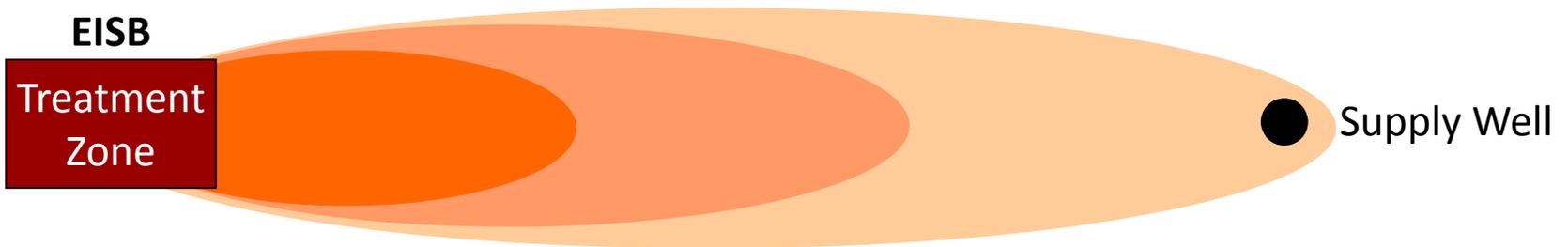


Simulated Source Strength vs. Time

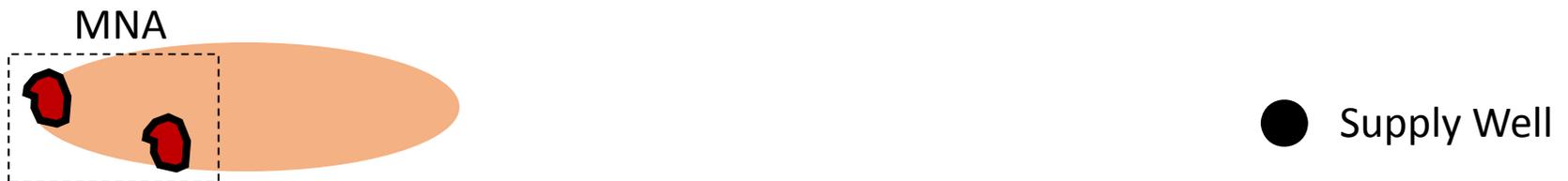


Cost-Benefit Analysis – Enhanced Dissolution

STEP 1: Active source treatment until interim source strength reduction goal is achieved.



STEP 2: After this goal is achieved, transition to MNA in source zone

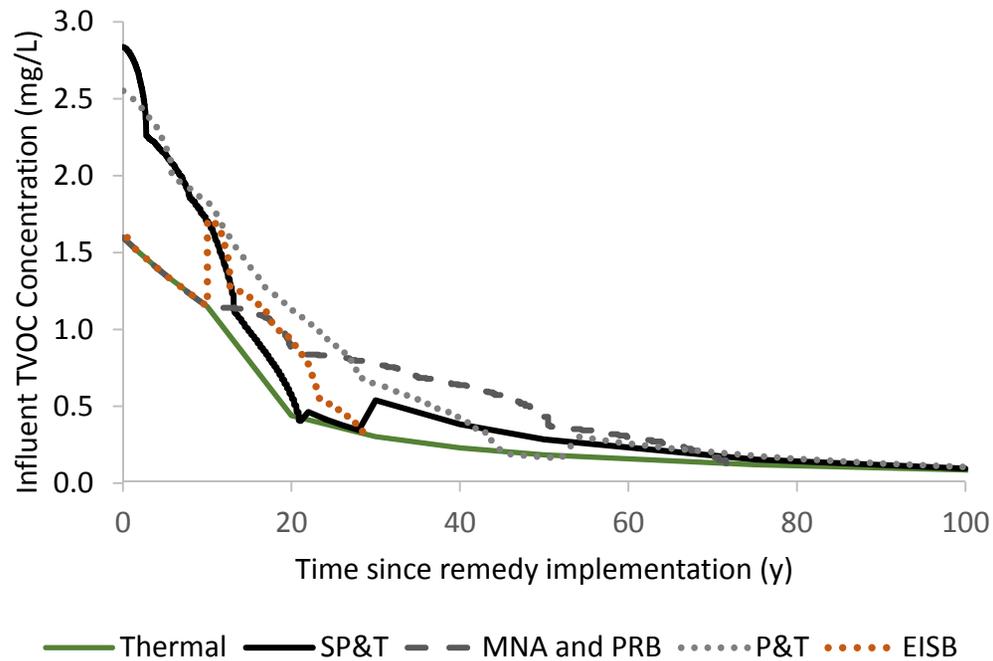


Conceptual example using source strength reduction as an interim goal to determine when to transition from active source treatment to a more passive alternative like MNA.

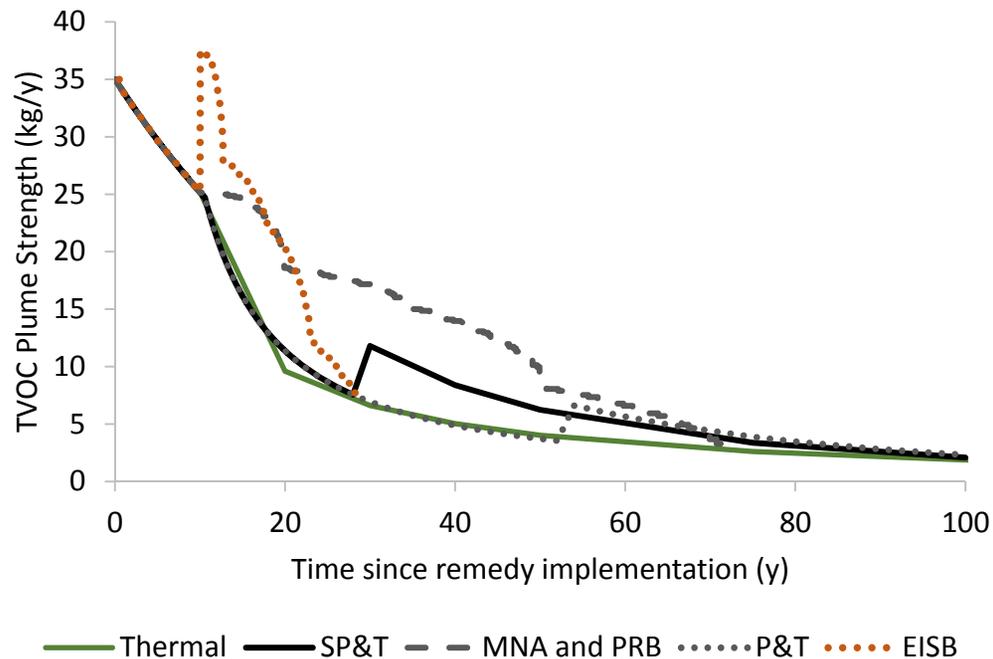
Unit Costs

I	II	III	IV	V	VI	VII
Alternative	Capital Cost	Deployment O&M ¹	Monitoring & Reporting ²	Total O&M	Periodic Cost ³	Comment
P&T - source zone (15 m ³ /d)	\$250,000	\$60,000	\$50,000	\$110,000		
P&T - plume (60 m ³ /d)	\$350,000	\$70,000	\$50,000	\$120,000		
P&T - source zone and plume (75 m ³ /d)	\$400,000	\$80,000	\$100,000	\$180,000		
SP&T - source zone (60 m ³ /d)	\$350,000	\$70,000	\$50,000	\$120,000		
SP&T - source zone; P&T - plume (105 m ³ /d)	\$500,000	\$100,000	\$100,000	\$200,000		
EISB - source zone	\$400,000	\$75,000	\$50,000	\$125,000		
ISCO - source zone	\$400,000	\$100,000	\$50,000	\$150,000		
Thermal - source zone	\$1,789,534	n/a	\$25,000	\$25,000		
PRB - source zone	\$680,000	\$0	\$25,000	\$25,000	\$226,667	media replacement every 10 y
PRB - plume	\$1,530,000	\$0	\$50,000	\$50,000	\$793,333	media replacement every 10 y
MNA - source zone	\$0	\$0	\$25,000	\$25,000		
Notes:						
¹ Deployment O&M costs do not include cost of monitoring and reporting						
² Annual monitoring and reporting costs are specified as follows: active source zone treatment, \$50,000; passive source zone treatment, \$25,000; plume containment, \$50,000 (including periodic river monitoring)						
³ Periodic cost not shown in table is \$125,000 for a five-year review, which is common to all site alternatives						

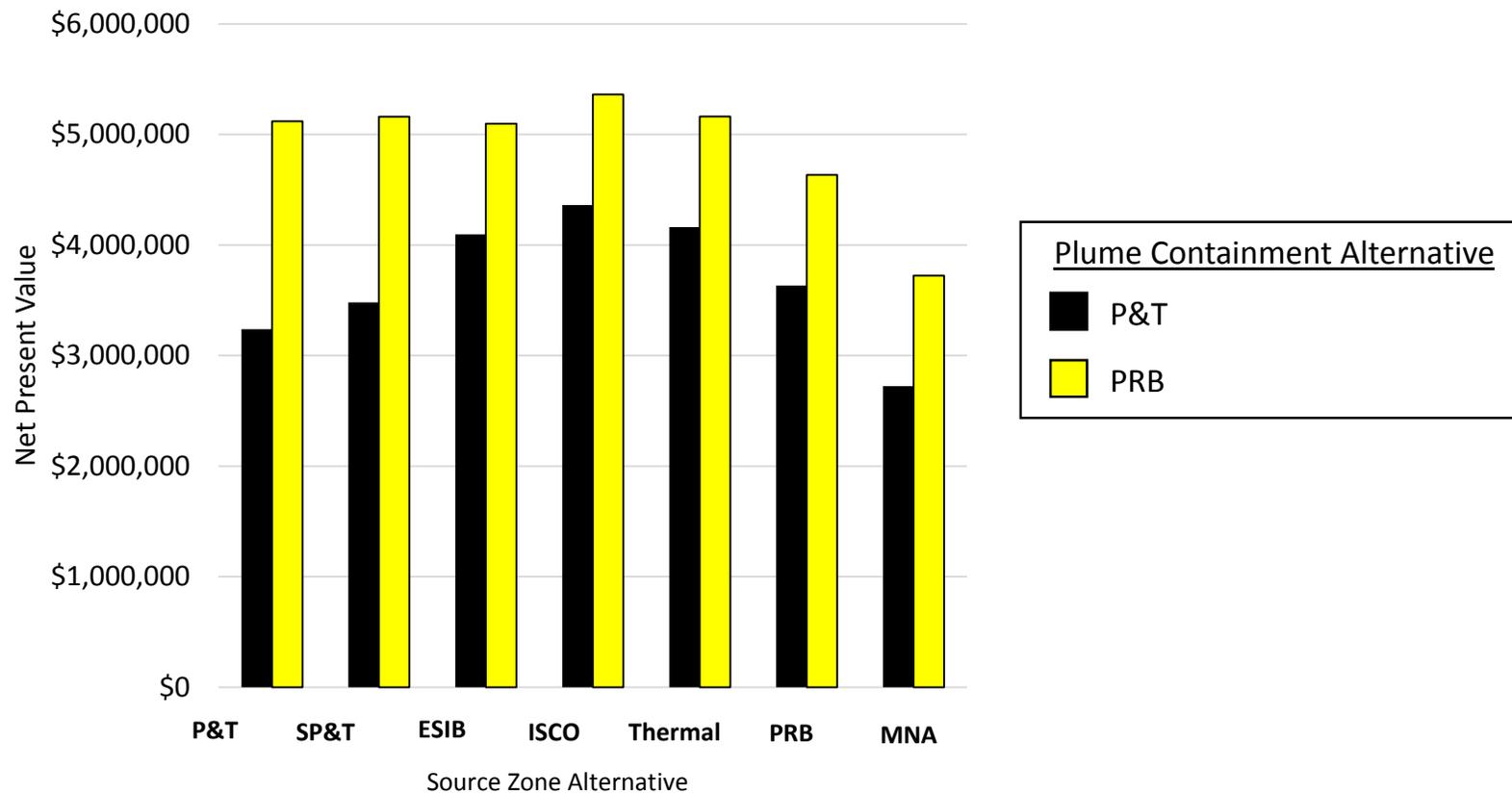
Simulated Influent TVOC Profiles



Simulated Plume Strength at X=270 m



Simulated Net Present Value



Influence of Pool Thickness Range

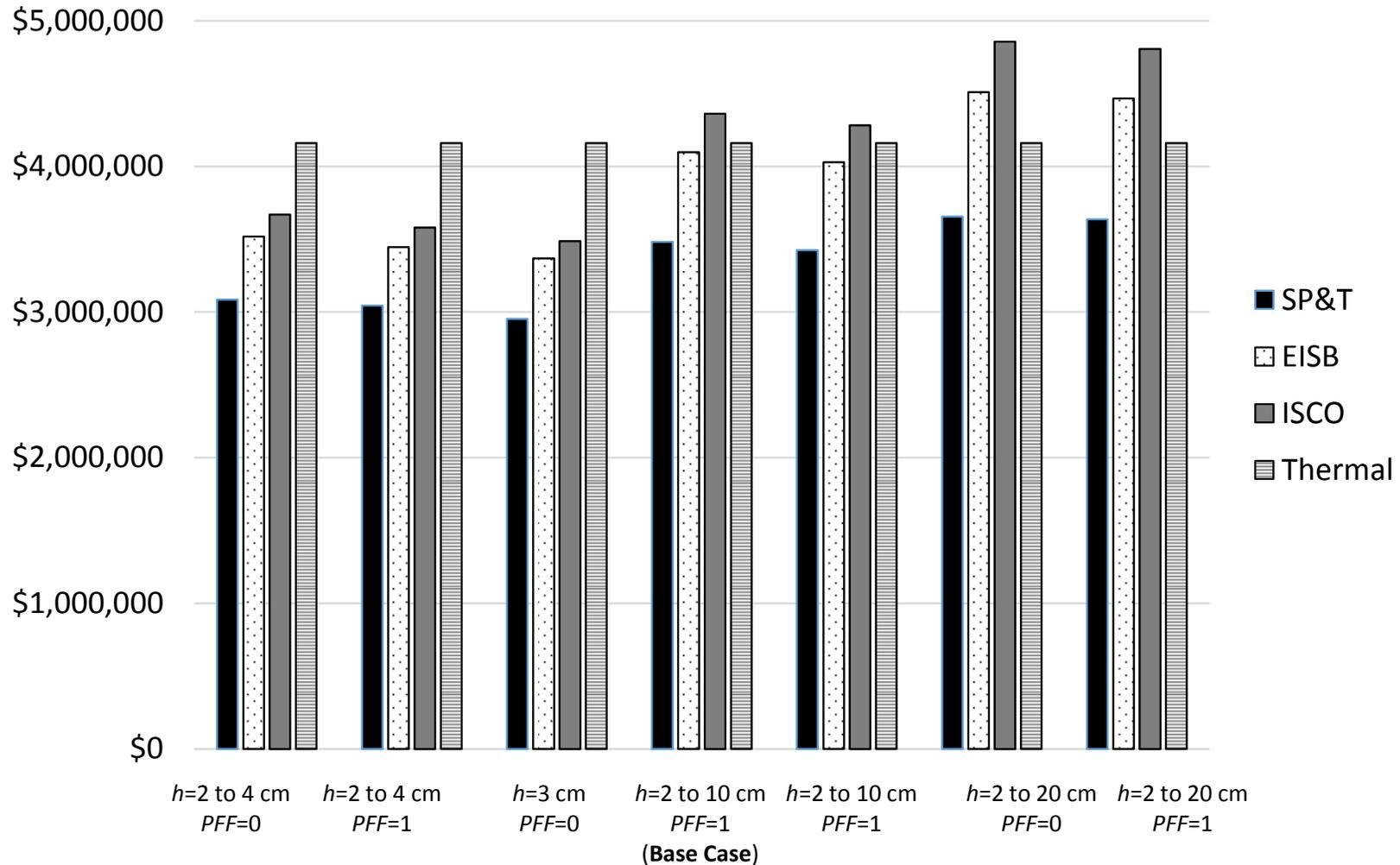
Pool Thickness, h (cm)	Pool Flux Factor PFF	Pre-treatment Conditions		Natural Decline Rate in Years 0 to 5 (1/y)	Natural Half-life in Years 0 to 5 (y)
		TCE Initial Mass, M_o (kg)	TCE Initial Source Strength, Md_o (kg)		
2 to 4	0	253	19.5	0.017	40.8
2 to 4	1	253	22.6	0.027	25.7
3	0	233	19.5	0.012	57.8
2 to 10	0	616	19.5	0.01	69.3
2 to 10	1	616	25.8	0.017	40.8
6	0	476	19.5	0.002	346.6
2 to 20	0	1500	19.5	0.01	69.3
2 to 20	1	1500	29.3	0.012	57.8
11	0	946	19.5	2.00E-15	∞



Influence of Pool Thickness Range

Range in Pool Thickness (cm)	Pool Flux Factor	Technology	TCE Initial Source Strength, Md _o (kg/y)	Time to Reach Interim Reduction Goal, MdR (y)
2 to 4	0	EISB	19.5	8
		MNA	19.5	22
		P&T	27.2	17
		SP&T	57.5	10
2 to 4	1	EISB	22.6	7
		MNA	22.6	19
		P&T	30.3	15
		SP&T	60.6	9
3	0	EISB	19.5	6
		MNA	19.5	17
		P&T	27.2	13
		SP&T	57.5	7
2 to 10	0	EISB	19.5	20
		MNA	19.5	61
		P&T	27.2	45
		SP&T	57.5	27
2 to 10	1	EISB	25.8	18
		MNA	25.8	43
		P&T	33.5	35
		SP&T	63.8	23
2 to 20	0	EISB	19.5	53
		MNA	19.5	158
		P&T	27.2	119
		SP&T	57.5	70
2 to 20	1	EISB	29.3	44
		MNA	29.3	94
		P&T	37.0	79
		SP&T	67.3	55

Cost-Benefit Analysis



Questions?



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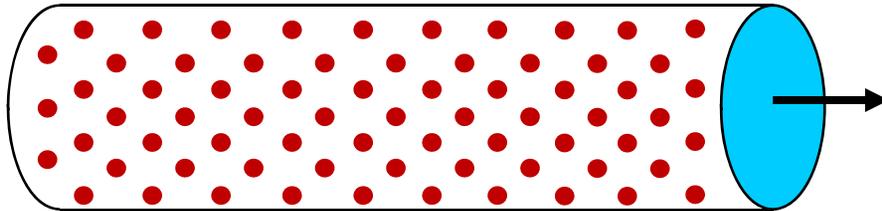
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Residual DNAPL Depletion

Section 3d

Effluent Trends

Time = 0



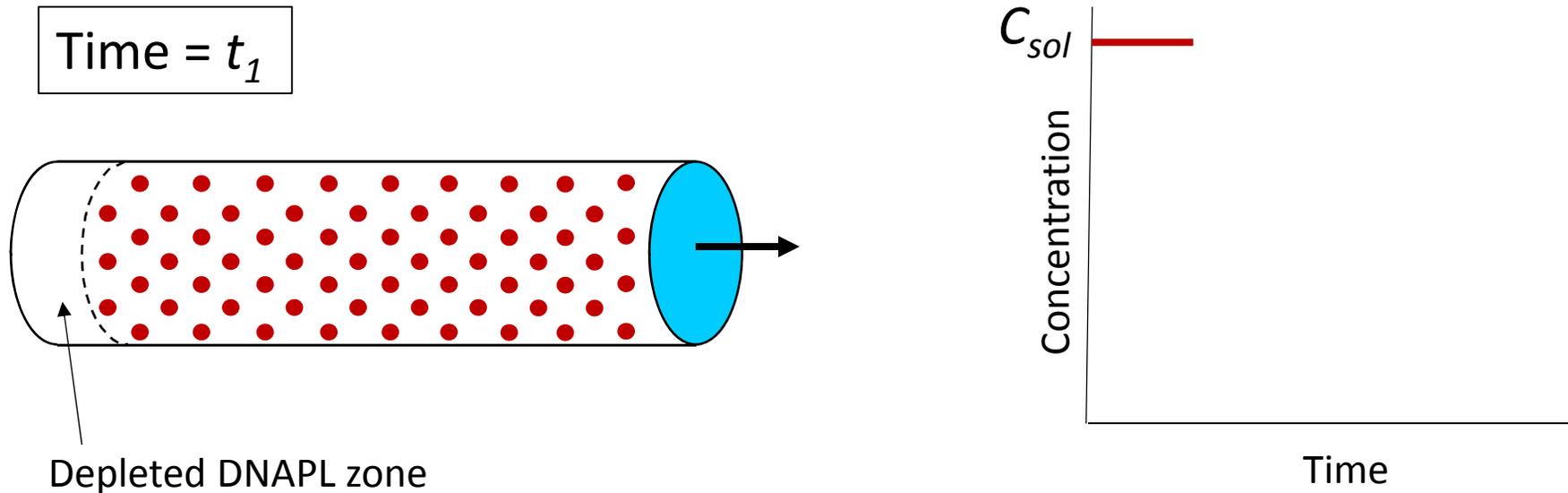
Concentration

Initial C?

Time

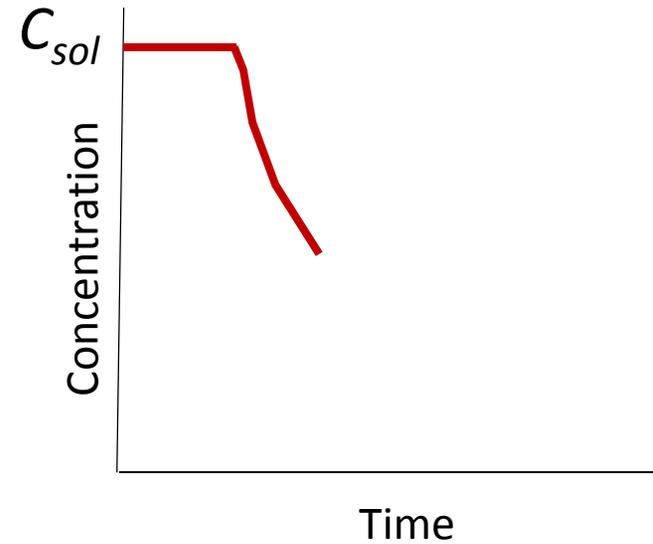
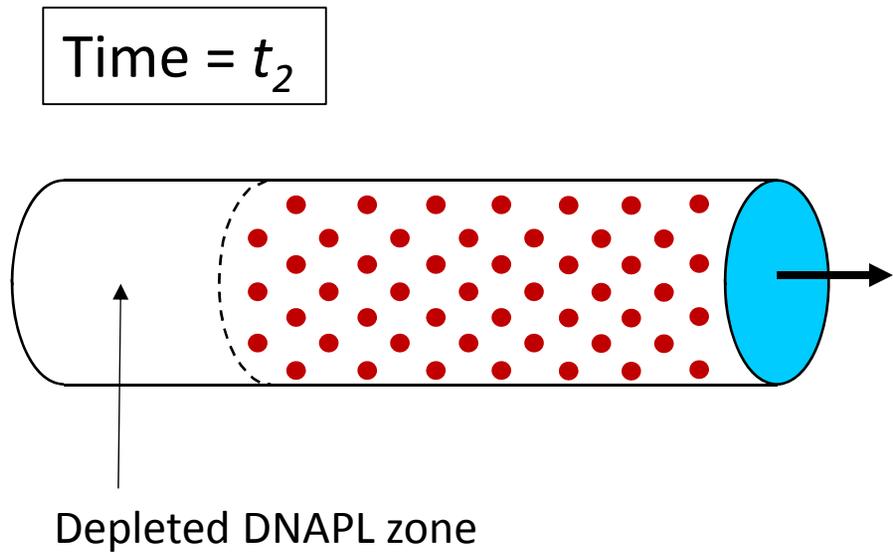
- Early 1990s – 1-D column studies by Powers et al. (1991, 1992, 1994), Imhoff et al. (1994)
- Relatively homogeneous (?) DNAPL, $S_n \sim 5$ to 7%

Effluent Trends



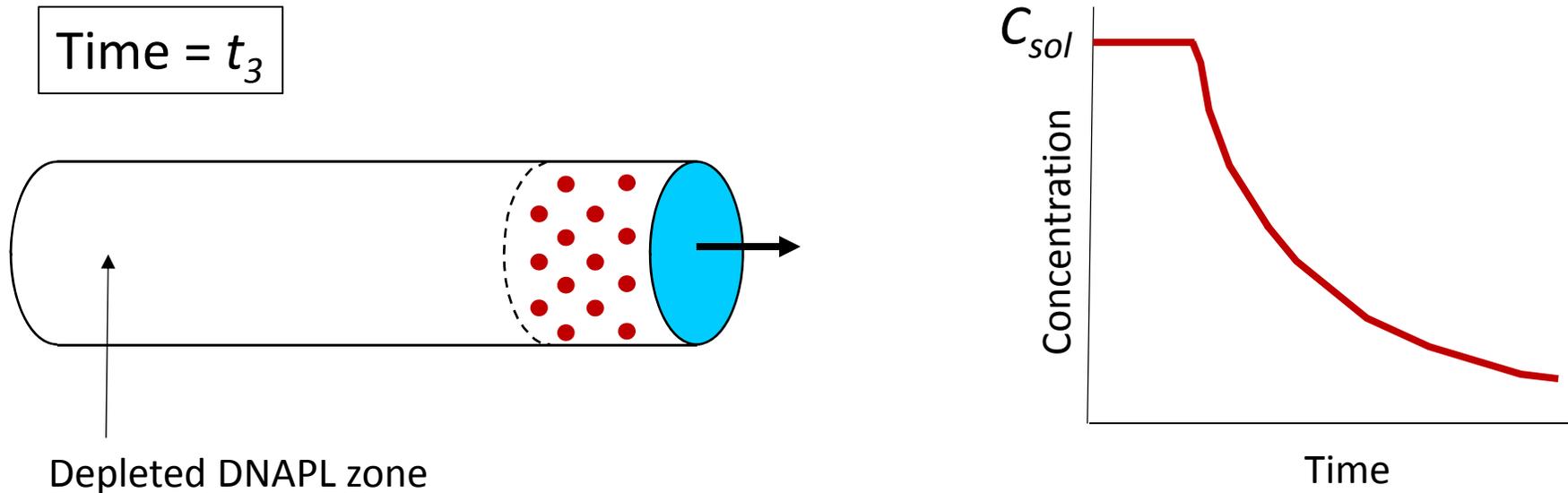
- Early portion of studies, effluent concentration at solubility level

Effluent Trends



- Then effluent concentration started to decline

Effluent Trends



- Early thinking was that decline caused by non-equilibrium dissolution at the NAPL-water interface of small ganglia
 - Rate-limited dissolution (K_{eff})

Md_{thru} Decline in Residual DNAPL

- More recent understanding (Imhoff et al., 1996; 2003), Rivett and Feenstra (2005), Farthing et al. (2012):
 - Heterogeneity in geology (K) and DNAPL distribution (S_n)
 - Causes fingering, preferential channeling in source zone
 - Referred to as **intra-source bypassing**
 - Apparent dilution effect → causes decline in source strength over time
 - Analogous to a decline in the number of streamtubes intercepting DNAPL within the source zone, caused by preferential flow channel development
 - Leads to inefficiency in mass removal ($\beta > 1$)



Concentration Decline Models

Powers et al., 1994

$$\frac{C_{avg}}{C_{eff}} = 1 - \exp\left(\frac{-K_{eff}L}{q}\right)$$

$$K_{eff} = K'_o \left(\frac{M}{M_o}\right)^\beta$$

$$K'_o = -\frac{q}{L} \ln\left(1 - \frac{C_{avg_o}}{C_{eff}}\right); \text{ or}$$

$$K'_o = 4.13 \left[\frac{v\rho_w d_{50}}{\mu_w}\right]^{0.60} \left[\frac{d_{50}}{d_M}\right]^{0.67} \left[\frac{d_{60}}{d_{10}}\right]^{0.37} \frac{D_o}{(d_{50})^2}$$

$$\beta = 0.518 + 0.114 \left(\frac{d_{50}}{d_M}\right) + 0.10 \left(\frac{d_{60}}{d_{10}}\right)$$



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Powers et al., 1994

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$$\beta = 0.518 + 0.114 \left(\frac{d_{50}}{d_M}\right) + 0.10 \left(\frac{d_{60}}{d_{10}}\right)$$

Limited lab scale, not applicable to field scale

Carey et al., 2015d

$$\frac{C_{avg}}{C_{eff}} = \frac{C_{avg_o}}{C_{eff}} \exp(-\lambda_{thru}t)$$

$$\lambda_{thru} = 0.8 \left(\frac{C_{eff}v}{M_o}\right)$$

C_{avg} used to estimate Md_{thru}

Applicable to lab scale, and small field-scale experiment.

Large field-scale uncertain.



Example – Brusseau et al. (2002) Experiment



1,2-DCA Residual DNAPL Zone
($S_n = 6.3\%$, $k_{rw} = 0.78$)

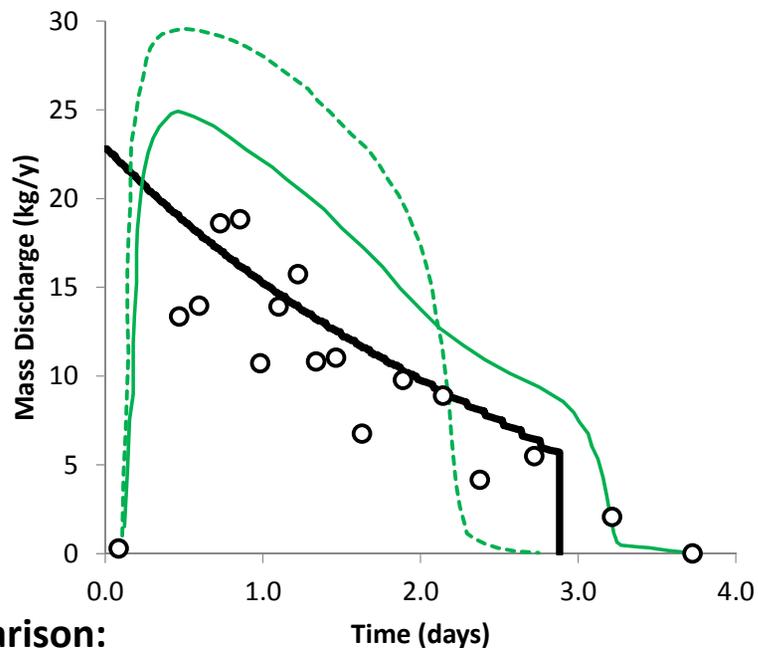
L = 0.66 m
W = 0.06 m
H = 0.10 m

- Used regression equations incl. λ_{thru} , and other measured parameters to estimate NDM inputs
 - No parameters were calibrated in model
- Compared to Brusseau et al. 3-D model
 - Similar approach, but calibrated part of dissolution rate based on column studies

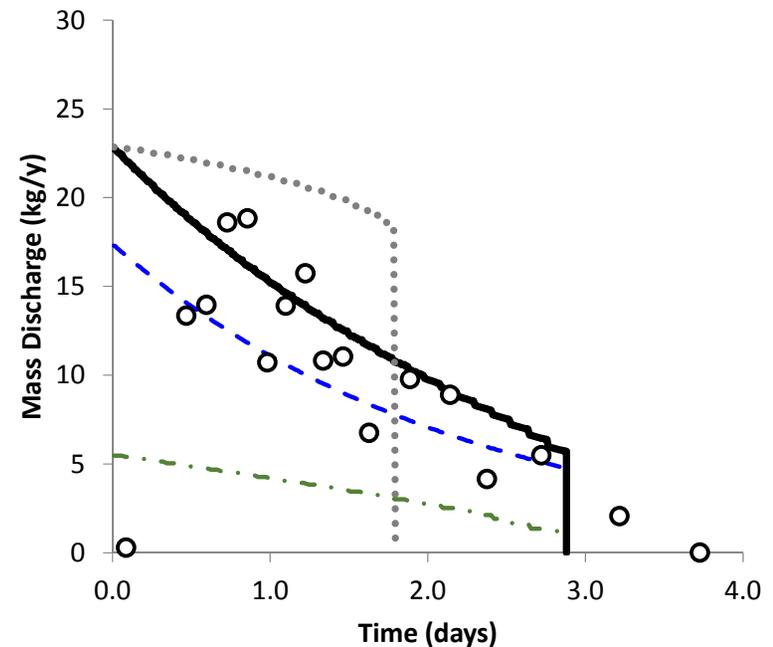


Model of Brusseau et al. (2002) Experiment

(a) Comparison of NDM and Brusseau et al. (2002) numerical results



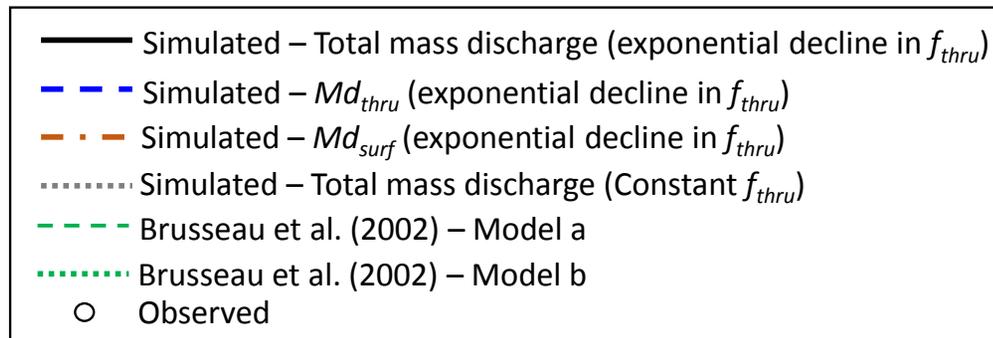
(b) NDM simulation results – Md_{tot} , Md_{surf} and Md_{thru}



Model comparison:

Carey et al. (2015d)
 1D NDM model: 33 cells
 Calibrated input: none

Brusseau et al. (2002)
 3D model: 18,000 cells
 Calibrated input: diss. rate



Carey et al. (2015d)

Summary

- Residual DNAPL depletion is more complex and less understood than pool depletion
- Infinite depletion timeframe when $\beta = 1$, which is inconsistent with conceptual model that ganglia deplete quickly.
- For field-scale NDM applications – rely on historical source strength trends to estimate λ_{thru}
- Be aware that layers of residual DNAPL may have longer depletion timeframes than modeled due to intra-source by-passing (i.e. preferential channeling)



Questions?



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Multicomponent DNAPL Depletion

Section 3e

Single vs. Multicomponent DNAPLs

- Single component – use pure solubility
e.g. TCE $C_{sol} = 1,400$ mg/L
- Multicomponent – solubility of each compound is reduced due to interference from other constituents
 - Reduced solubility at NAPL-water interface
 - Effective solubility: $C_{eff} = X_{mol} C_{sol}$
- For example, if a DNAPL has 50% TCE by mole fraction, then $C_{eff} = 50\%$ of 1400 = 700 mg/L

$$\begin{aligned} C_{eff} &= \text{effective solubility (mg/L)} \\ C_{sol} &= \text{pure solubility (mg/L)} \\ X_{mol} &= \text{mole fraction (dim.)} \end{aligned}$$



Multicomponent DNAPL Dissolution

- More soluble compounds preferentially depleted
- Less soluble compounds persist for longer time
- Evidenced by trends in dissolved concentrations downgradient of source zone
 - Declining conc. for more soluble compounds
 - Due to declining mole fraction as becomes depleted
 - Increasing conc. for less soluble compounds, as mole fraction (and effective solubility) increase over time



Calculating Mole Fraction (X_{mol})

- Based on soil sample(s) in NAPL sub-zone
- Use soil concentrations and assumption of unit soil mass (1 kg):

$$\textcircled{1} \quad \text{Total Moles} = \sum_{i=1}^n \frac{C_i}{1000 MW_i}$$

$$\textcircled{2} \quad X_{mol,m} = \frac{C_m / (1000 MW_m)}{\text{Total Moles}}$$

where *Total Moles* = total number of moles of all constituents in the NAPL (mol)

C_i = soil concentration of constituent i (mg/kg)

MW_i = molecular weight of constituent i (g/mol)

n = number of constituents in the multicomponent DNAPL

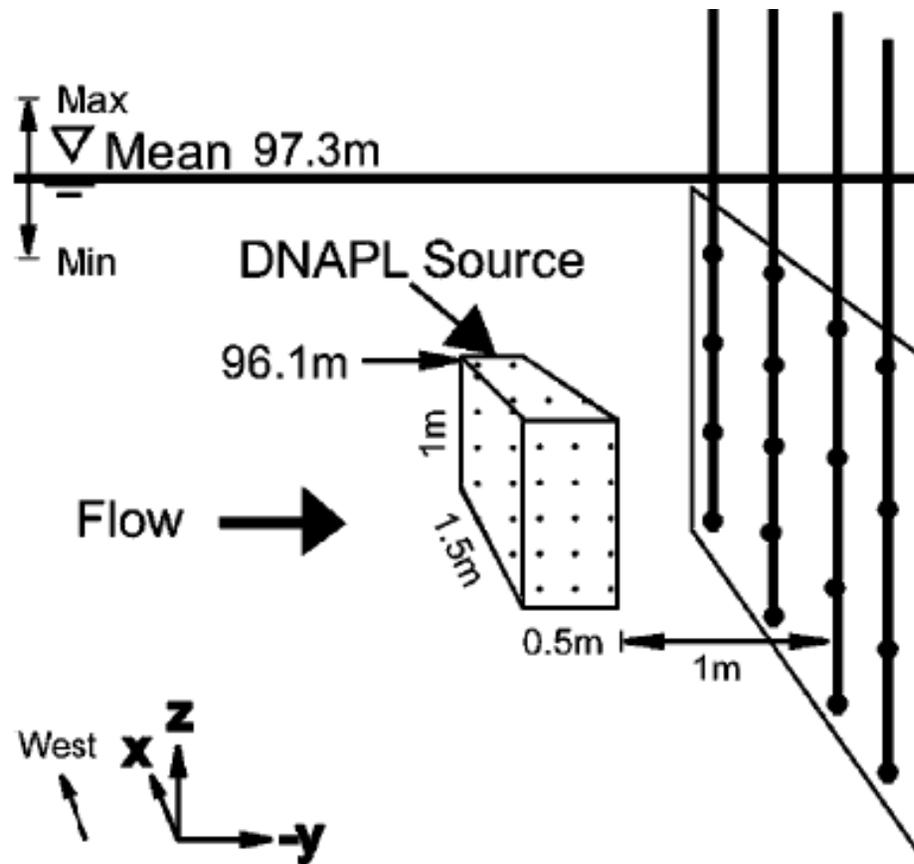
m = current constituent for X_{mol} calculation

$X_{mol,m}$ = mole fraction of constituent m

MW_m = molecular weight of constituent m (g/mol)



Emplaced Source Experiment – Borden (Rivett and Feenstra, 2005)



Source: Rivett and Feenstra (2005)



Emplaced Source Experiment (Borden)

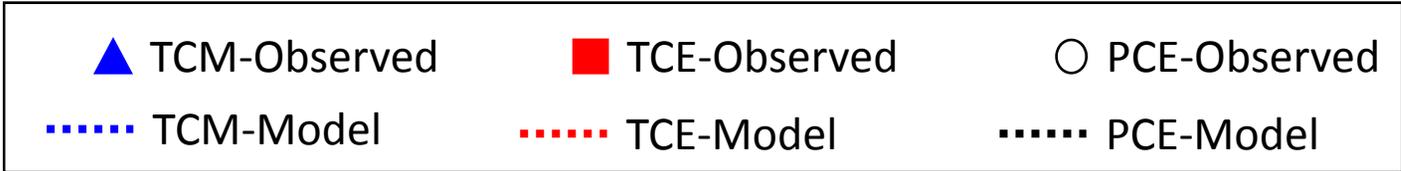
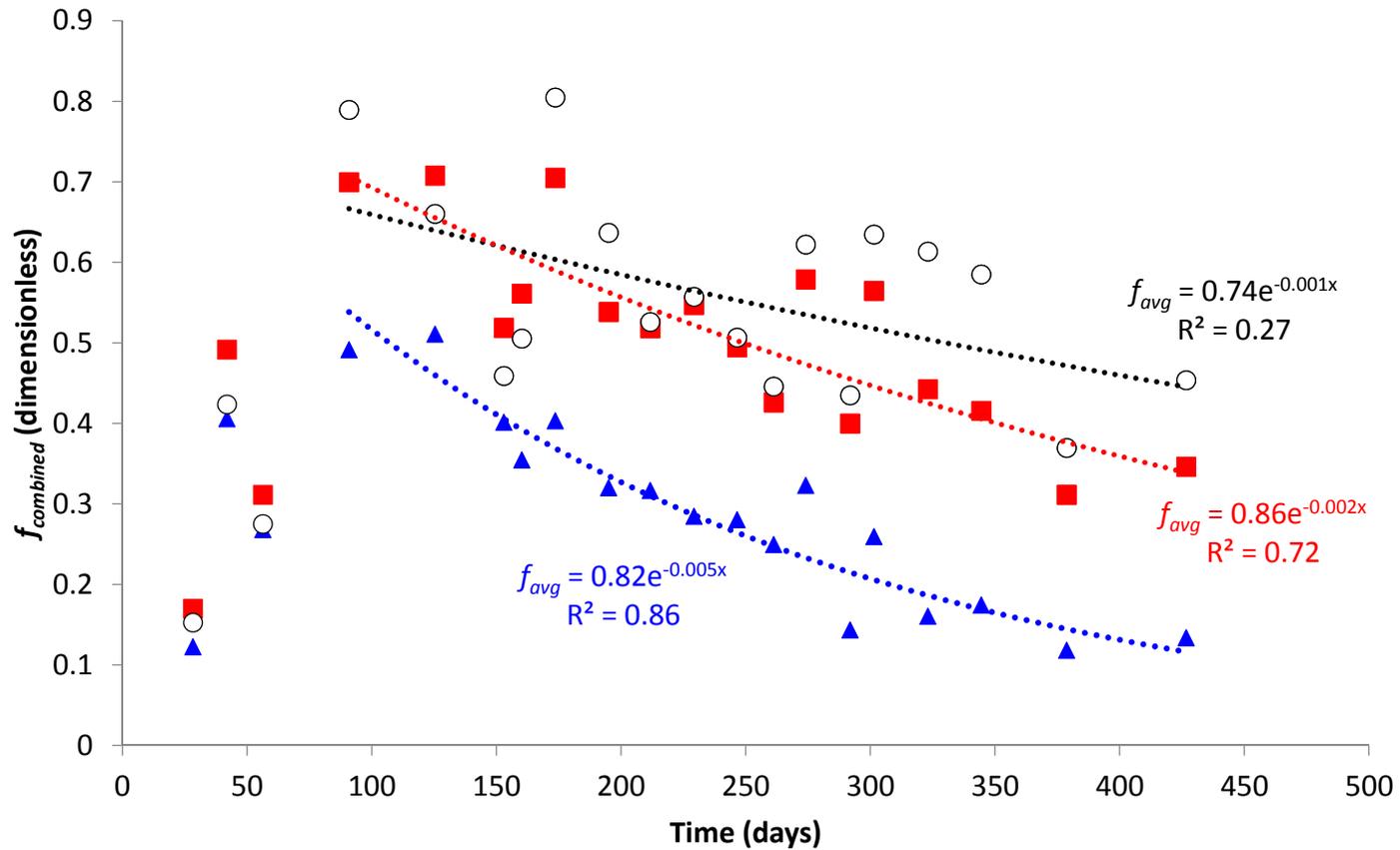
	TCM	TCE	PCE	Total			
Initial mass in DNAPL (kg)	2.68	11.83	13.2	27.71			
Mixed mass in 0-d core (kg)	1.45	8.93	12.6	22.98			
density (kg/m ³)	1472	1460	1600				
molecular weight (g/mol)	119.38	131.4	165.83				
# moles	12.15	67.96	75.98	156.09			
mole fraction	0.078	0.435	0.487				
solubility (mg/L) @ 23-24 C	8700	1400	240				
solubility (mg/L) @ 10 C	8395.5	1351	231.6				
effective solubility (mg/L) @ 23-24 C	677.00	609.56	116.83				
Rivett and Feenstra (2006) cite study by Horvath which suggests TCE solubility at 10 C is 3.5% lower than at 25C							
effective solubility (mg/L) @ 10 C	653	588	113				

Emplaced Source Experiment

- Mechanisms for declining source strength:
 1. Reduction in effective solubility (TCM)
 2. Intra-source bypassing i.e. preferential channeling
- NDM-MC (Multicomponent DNAPL dissolution)
 - Customized for 3-component DNAPL

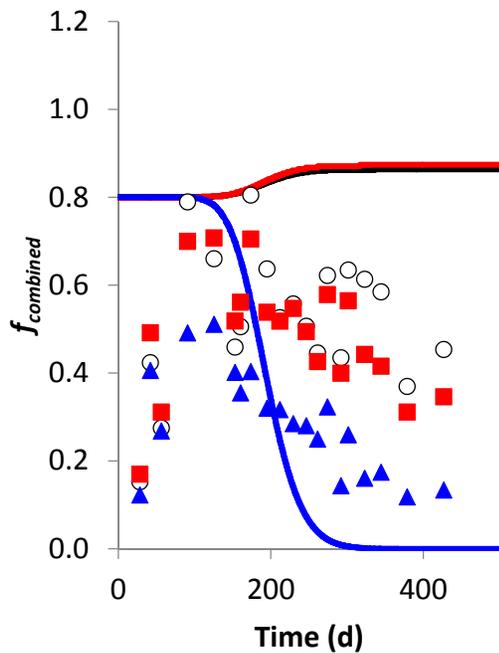


Calculation of the apparent f_{avg} versus time with exponential regression models for TCM, TCE, and PCE in the Emplaced Source experiment at Borden, Ontario.

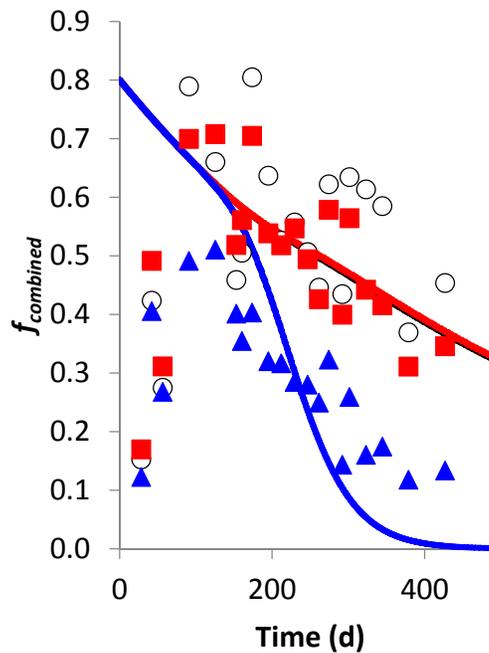


Simulated versus observed $f_{combined}$ with the source length discretized into 20 grid cells and three scenarios for the dilution factor.

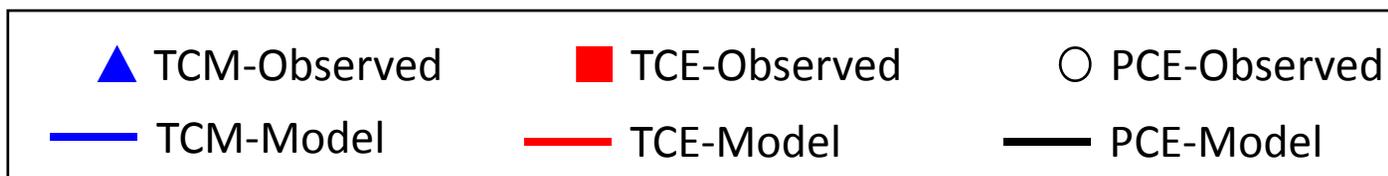
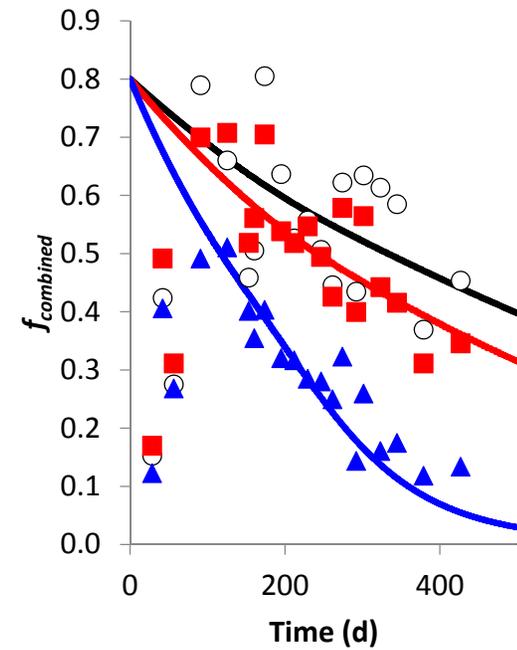
(a) Constant $f_{thru} = 0.8$



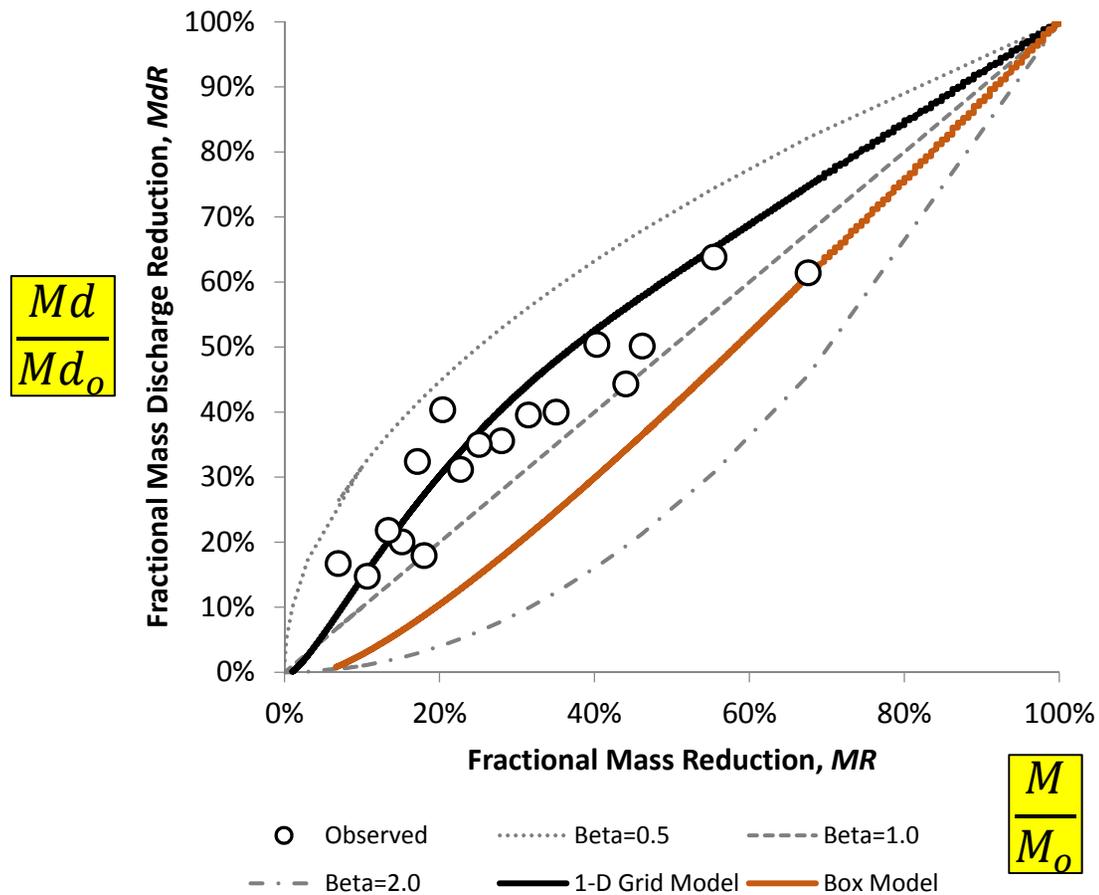
(b) f_{thru} half-life of 1 y



(c) f_{thru} half-life of 1.3 y for PCE, 1 y for TCE, and 0.5 y for TCM



Comparison of 1-D Grid to Box Model



Summary

- Cannot use analytical solution to estimate Md_{surf}
 - Effective solubility varies along length of pool in a multicomponent DNAPL
- 1-D Grid model more accurately represents reduced mass removal efficiency due to intra-source bypassing
- Even a residual source zone that appears to be relatively homogeneous, may have sufficient heterogeneity to cause preferential channeling.



Questions?



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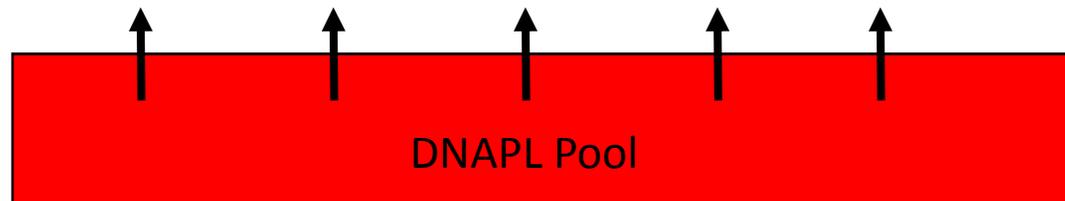
Ph: 613-270-9458

EISB in DNAPL Source Zones

Section 4

EISB Concept – DNAPL Dissolution Enhancement

Rate of dissolution depends on concentration gradient at NAPL-water interface.

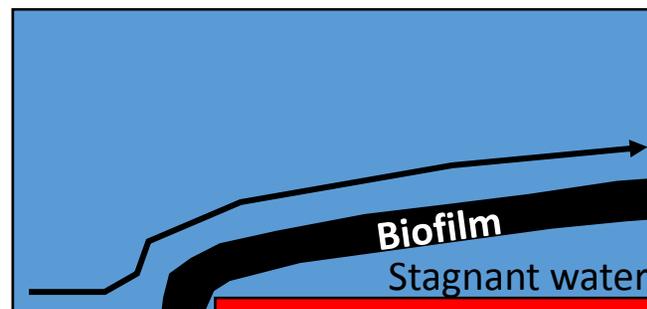


EISB: Larger concentration gradient → Faster dissolution

Chu et al. (2003) Model Results

Case 1:

- Low electron donor concentration
- Biofilm grew away from NAPL-water interface
- Less effective dissolution enhancement
- Created no-flow zone above NAPL



DNAPL Pool

Case 2:

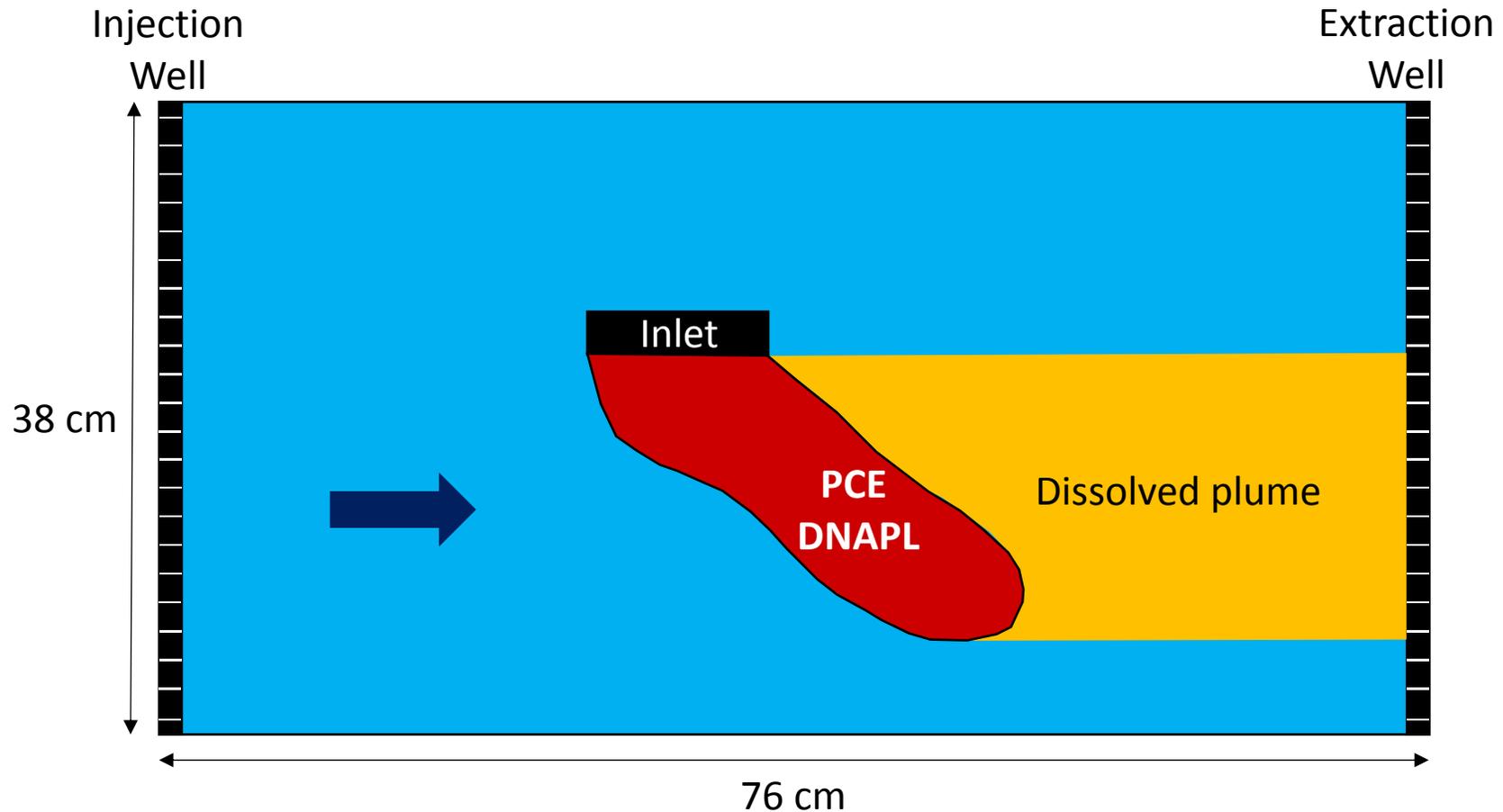
- Unlimited electron donor
- Biofilm grew adjacent to NAPL-water interface
- Most effective enhancement due to maximum concentration gradient



DNAPL Pool

Sleep et al. (2006) DNAPL EISB Study

Source: Modified from Sleep et al. (2006)

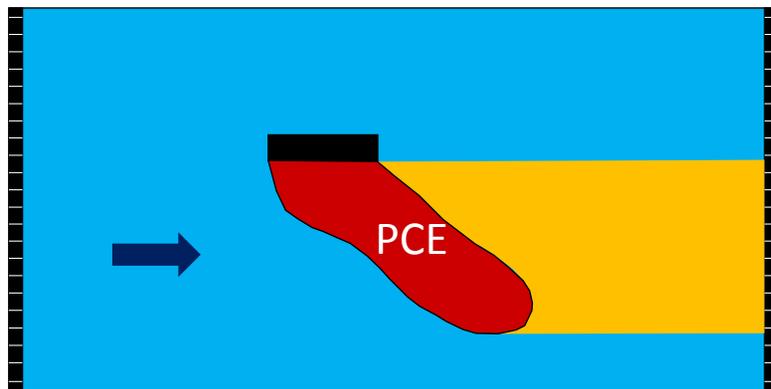


Source zone dimensions: 12 cm x 18 cm x 2.5 xm
Initial NAPL Saturation (S_n): 6.9% (residual DNAPL)

Sleep et al. (2006) DNAPL EISB Study

- PCE DNAPL introduced at $t=0$ (10 mL, 16.1 g)
- Soil from Dover AFB

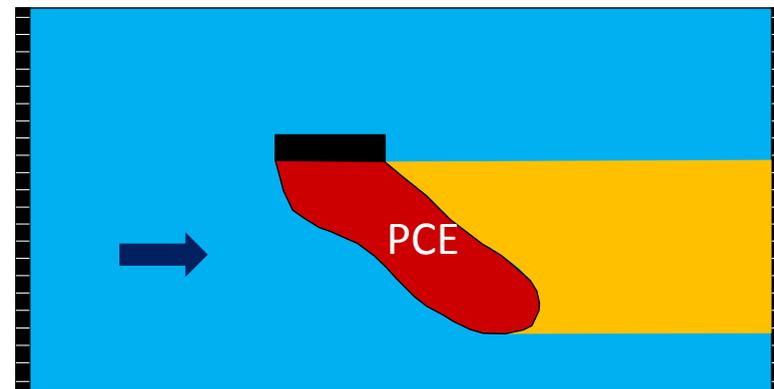
BOX 1



Biostimulation only

- PCE did not degrade
- Methane build-up

BOX 2



Biostimulation + Bioaugmentation

- PCE degraded to ethene
- Methane build-up



EISB Monitoring

- Molarity (M) = # moles per liter of water (mol/L)
- Total molarity of chlorinated ethenes (M_{CES})
 - PCE + TCE + cis-1,2-DCE + vinyl chloride + ethenes
- MW_{PCE} = molecular weight of PCE (g/mol)
- Equivalent PCE concentration (C_{PCE}) indicates total mass discharge from DNAPL
 - Represents amount of PCE dissolved from the DNAPL, based on measured PCE + daughter species conc.

$$C_{PCE} = 1000 M_{CES} MW_{PCE}$$

Units:

C_{PCE} in mg/L

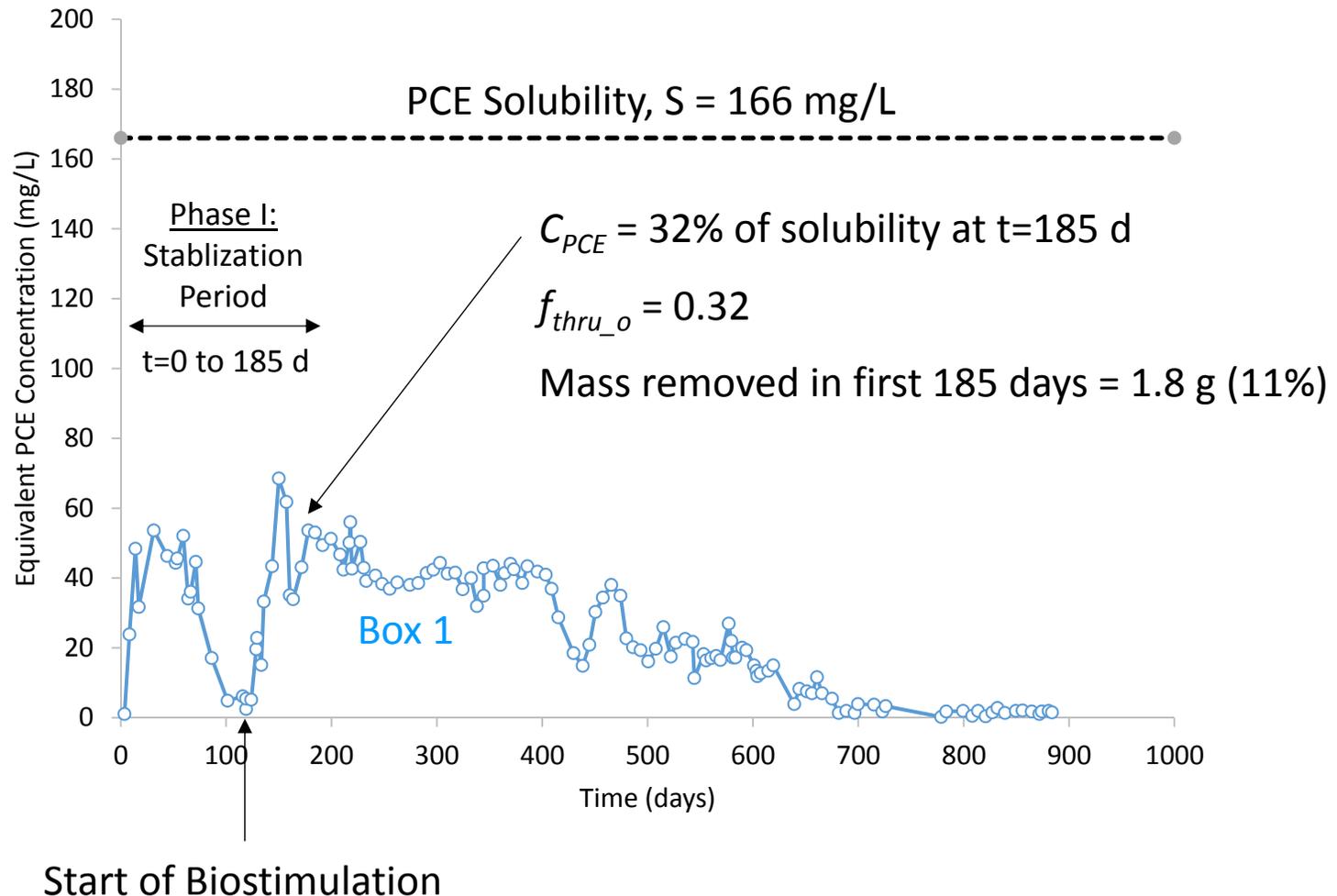
M_{CES} in mol/L

MW_{PCE} in g/mol

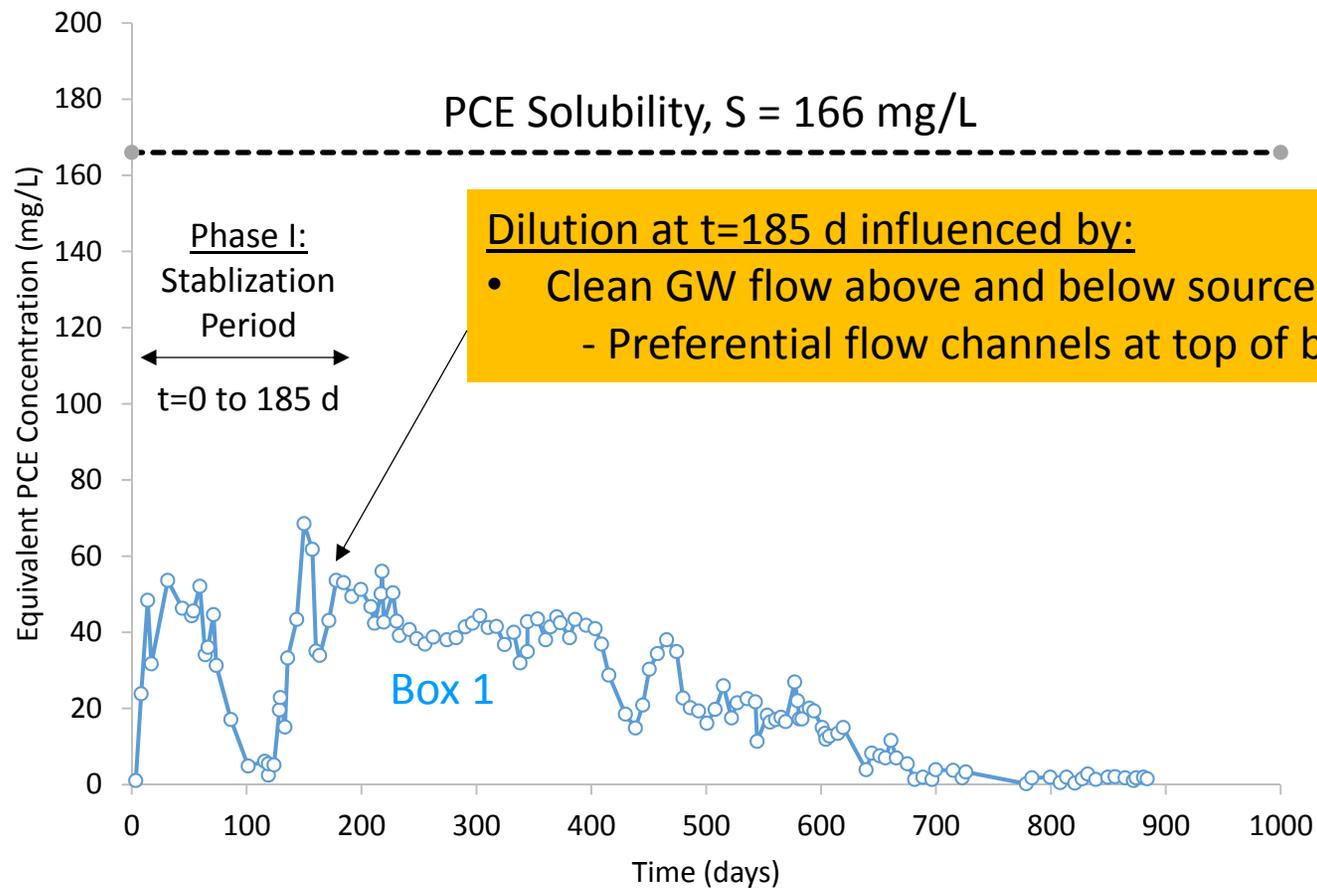


Effluent PCE Concentrations

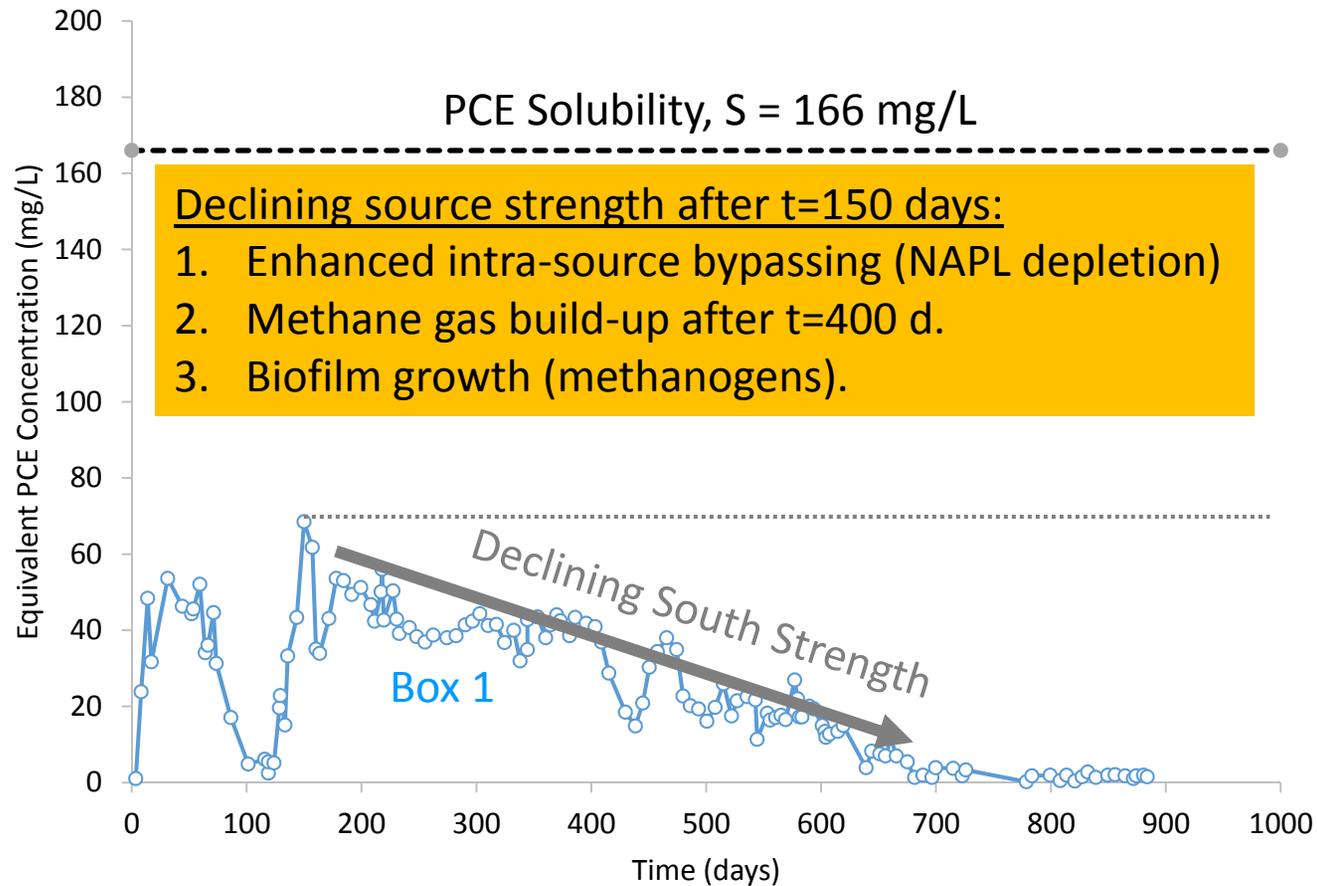
Source: Modified from Sleep et al. (2006)



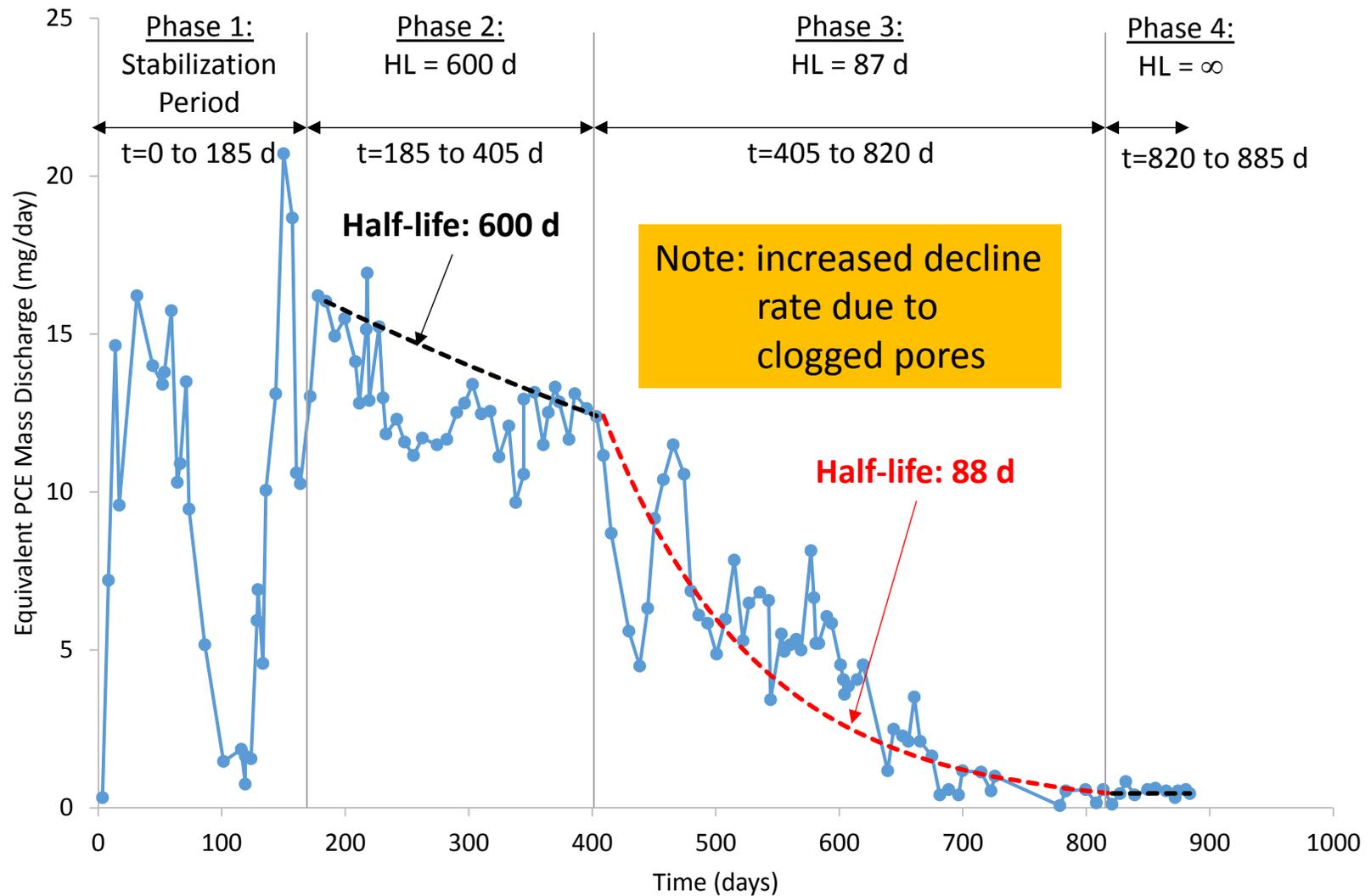
Effluent PCE Concentrations



Effluent PCE Concentrations

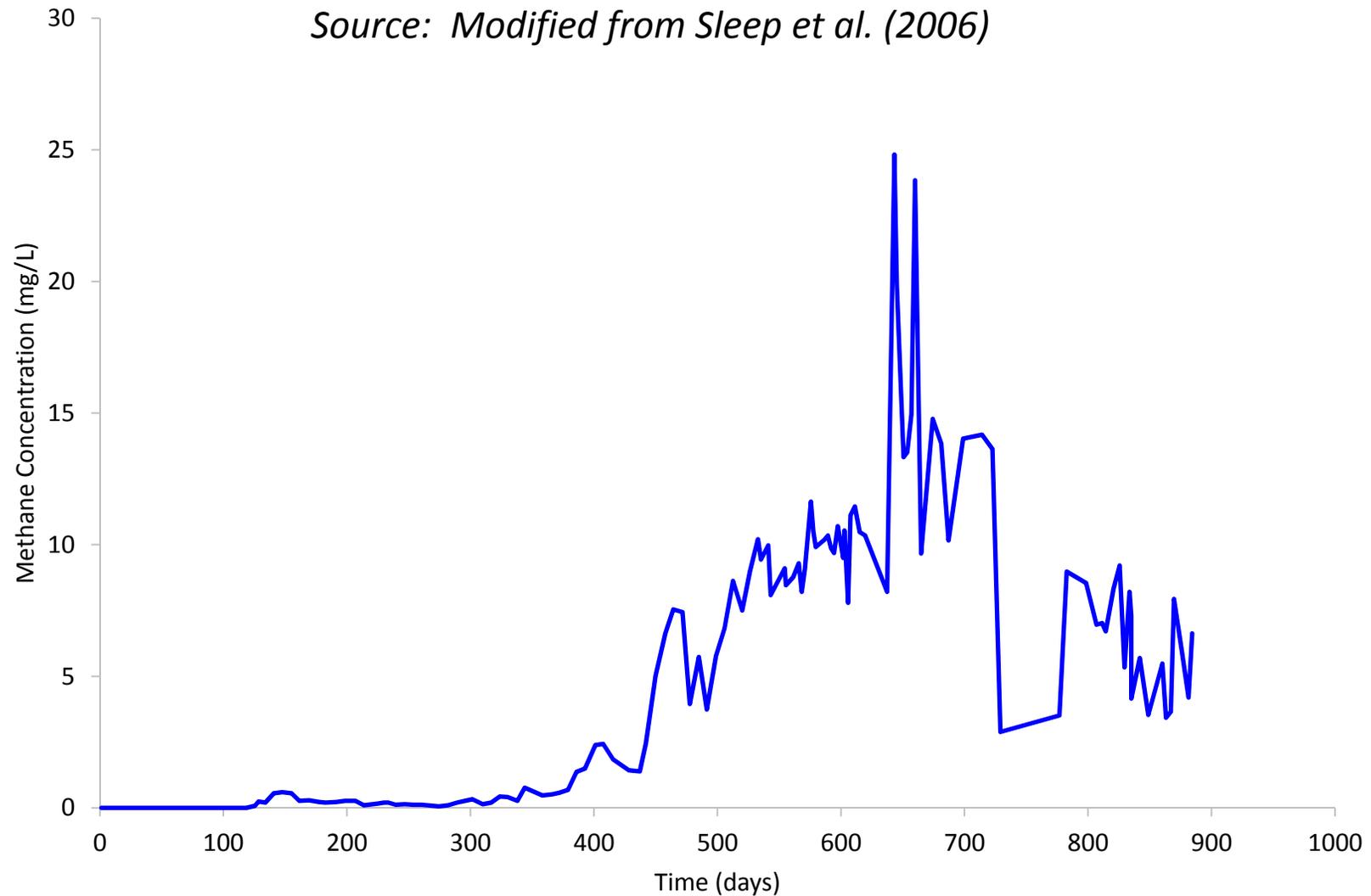


Through-Discharge Decline Half-Life

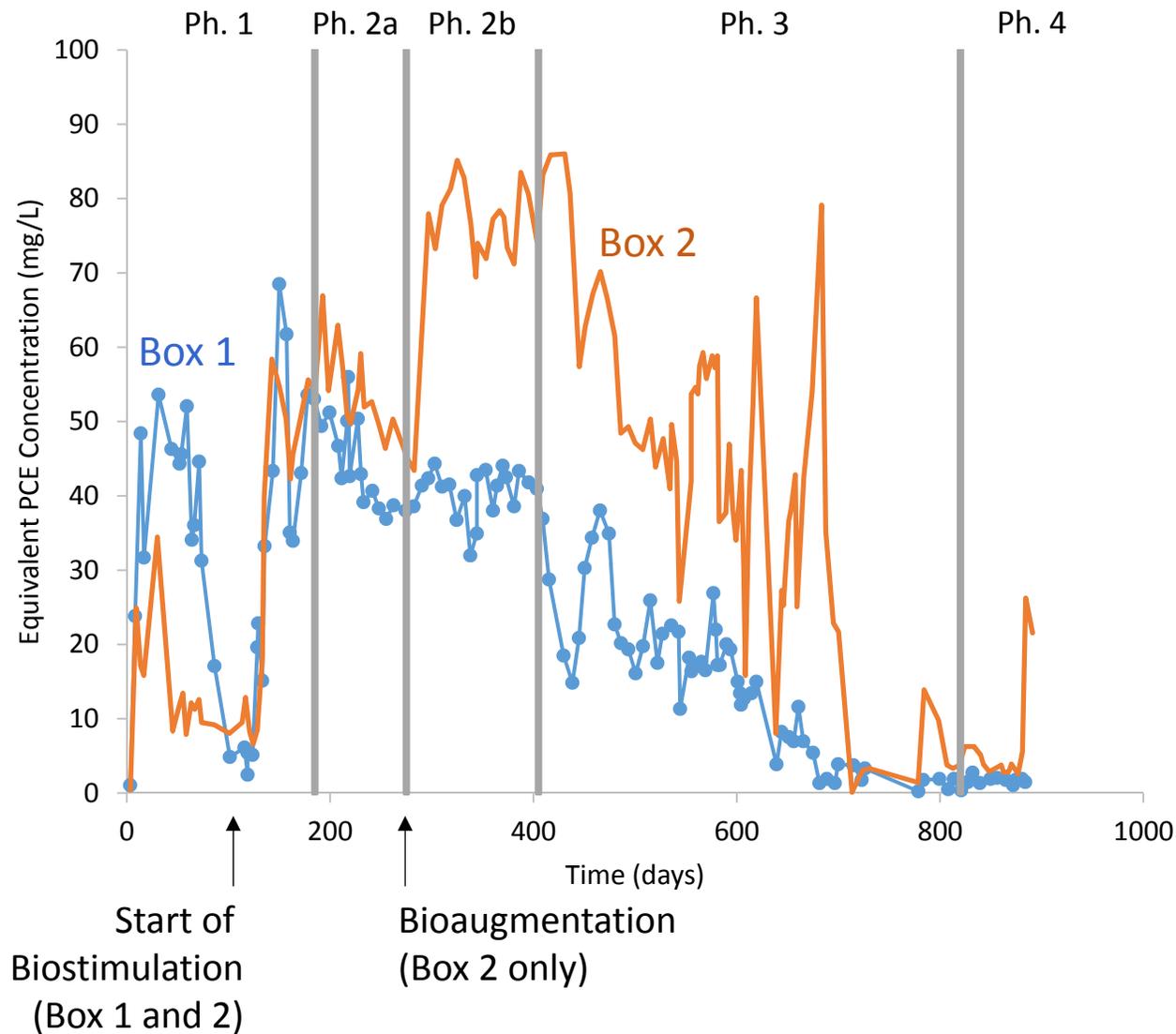


Effluent Methane Trends

Source: Modified from Sleep et al. (2006)

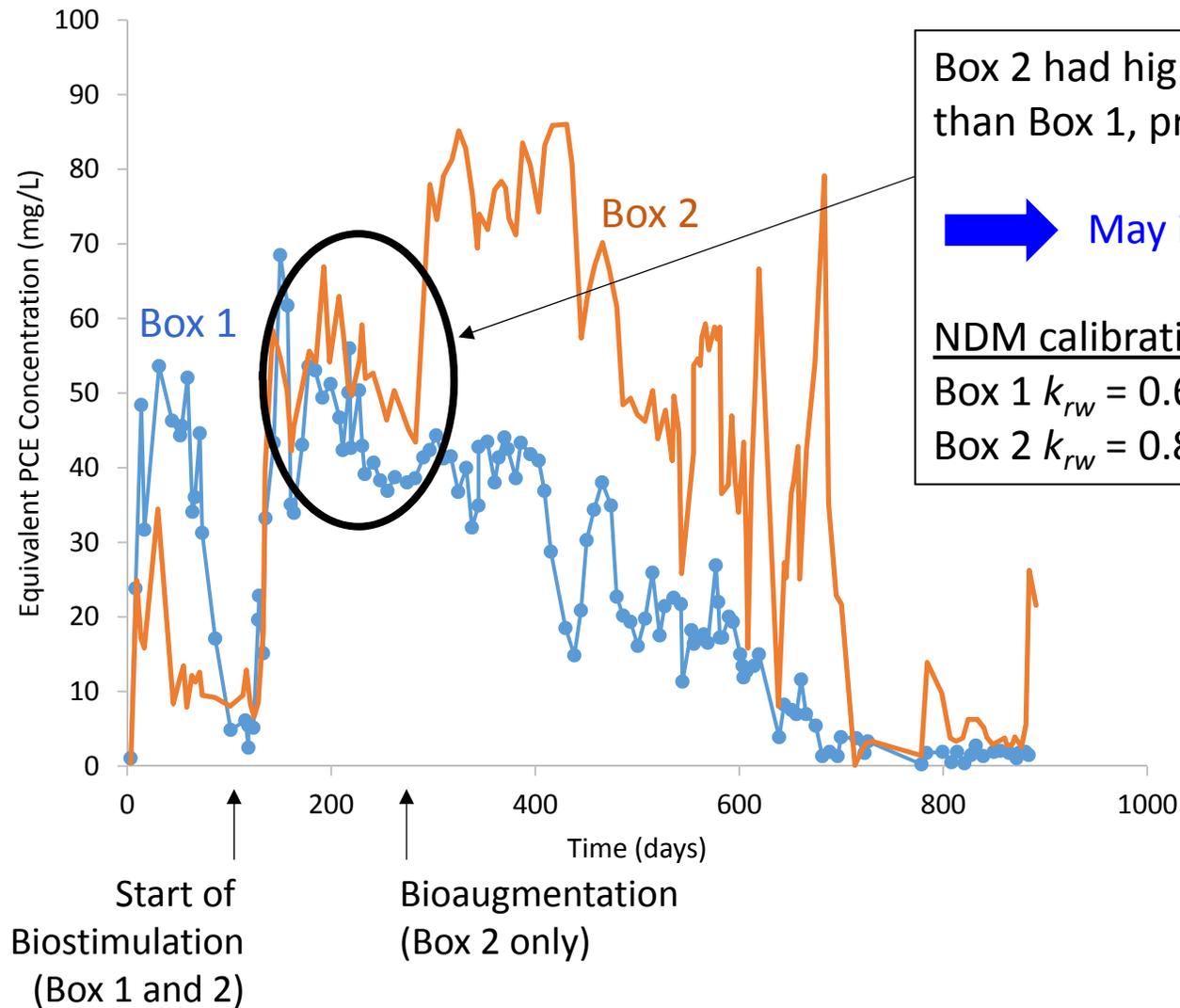


Box 2 with Bioaugmentation



<u>Phase</u>	<u>Time (d)</u>
1	0 to 185
2a	185 to 275
2b	275 to 405
3	405 to 820
4	820 to 885

Box 2 with Bioaugmentation



Box 2 had higher source strength than Box 1, prior to bioaugmentation.

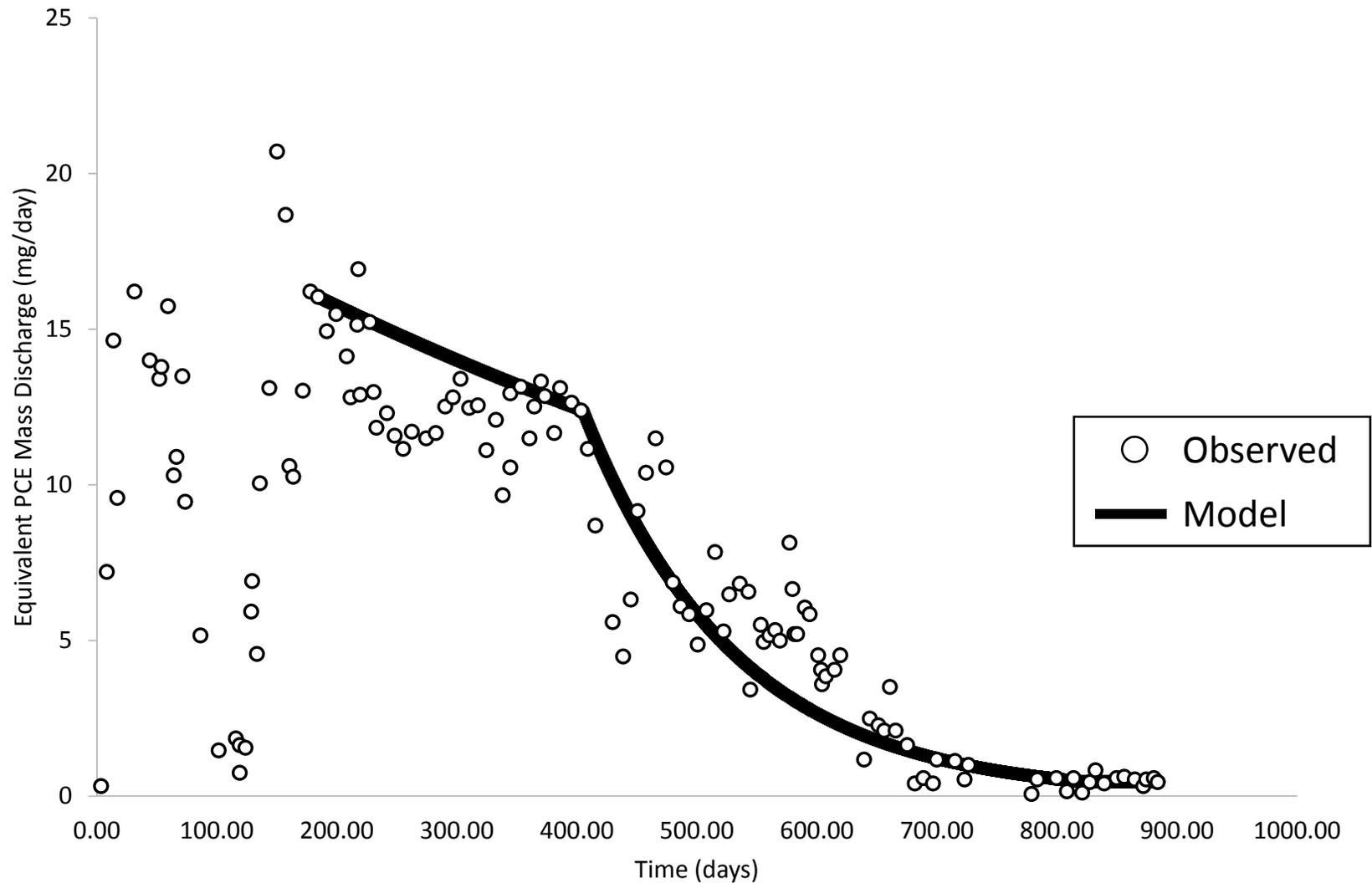
➡ May indicate higher k_{rw} for box 2.

NDM calibration:

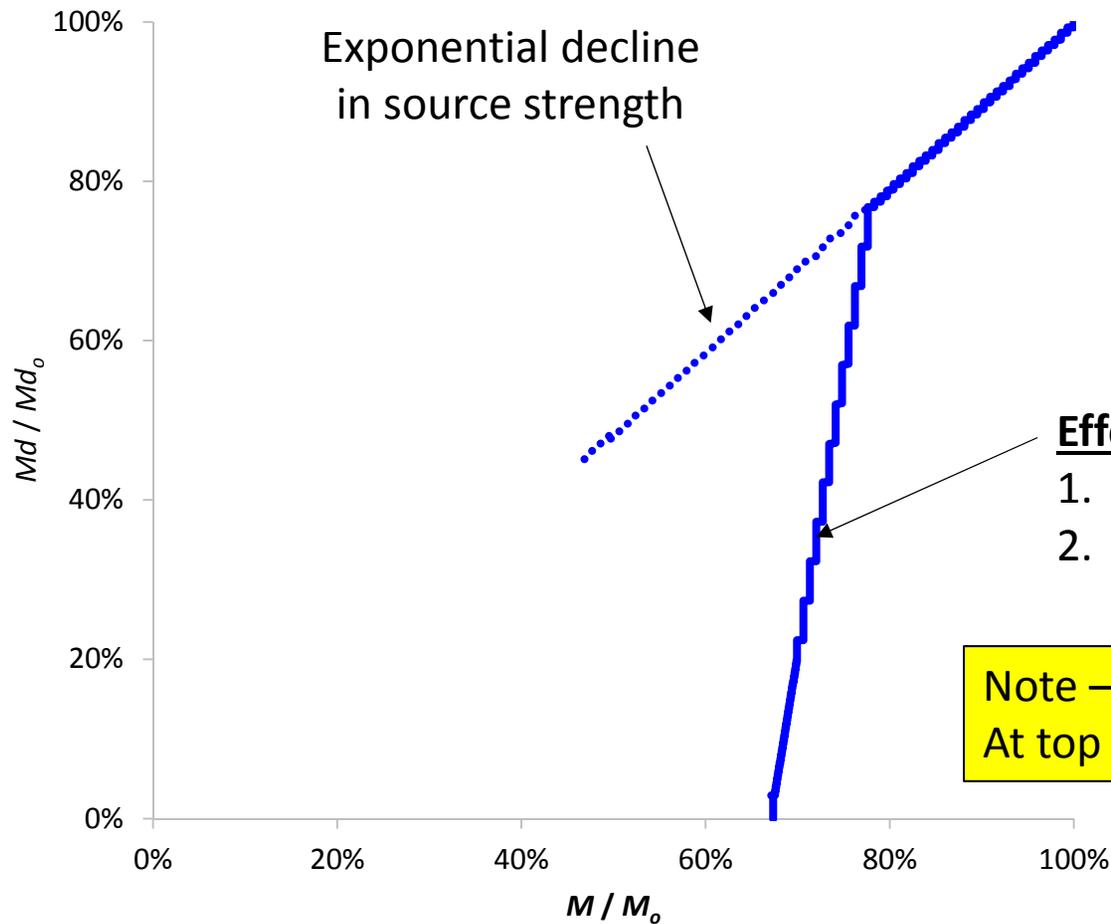
Box 1 $k_{rw} = 0.68$

Box 2 $k_{rw} = 0.85$

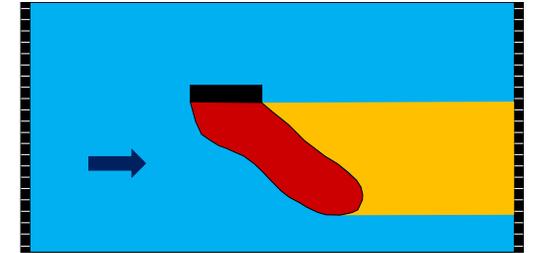
Box 1 – NDM Model vs. Observed



Box 1 Model Sensitivity Analysis



Box 1: Biostimulation only
(no PCE degradation)

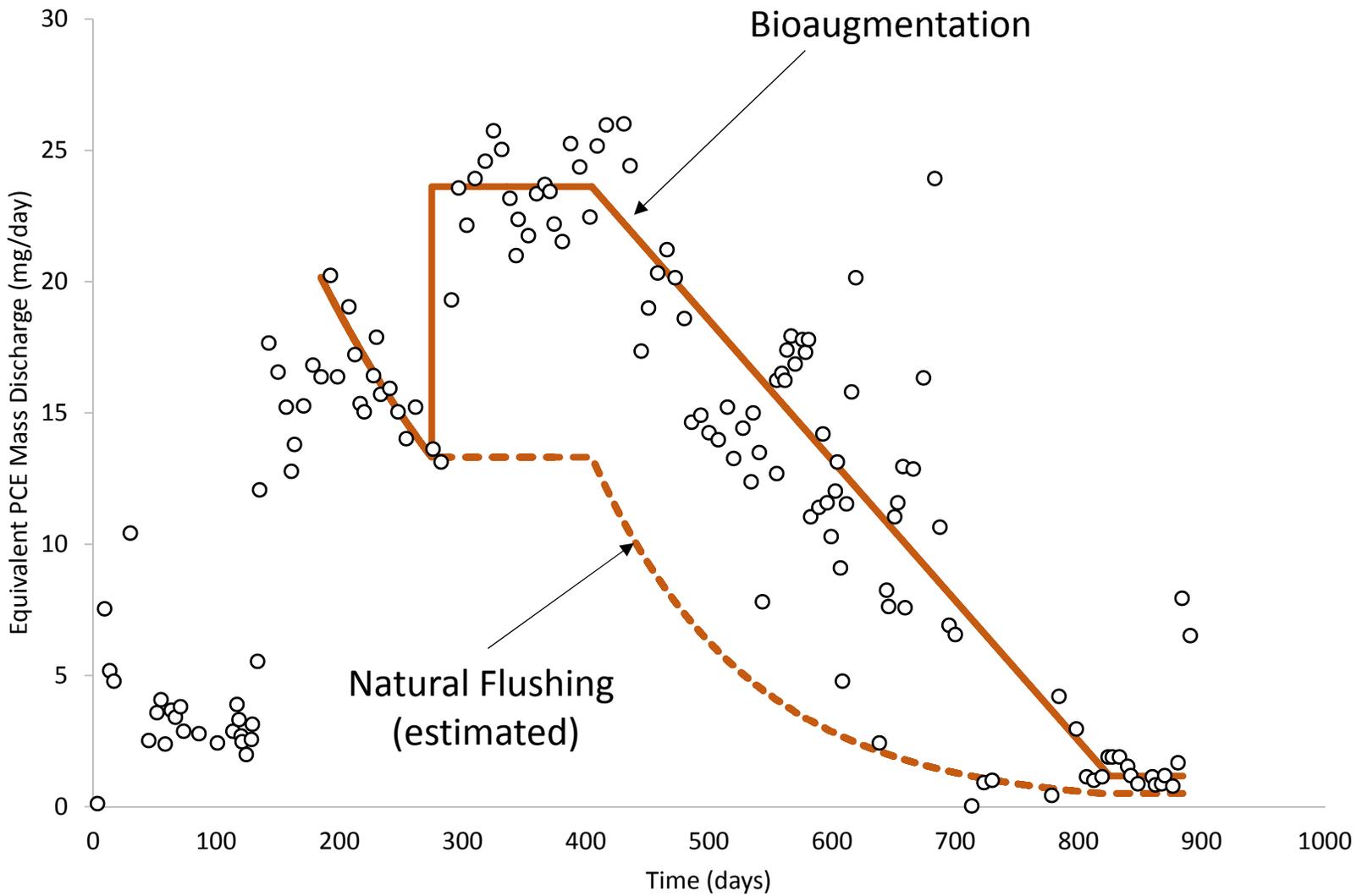


Effects of clogging from gas bubbles:

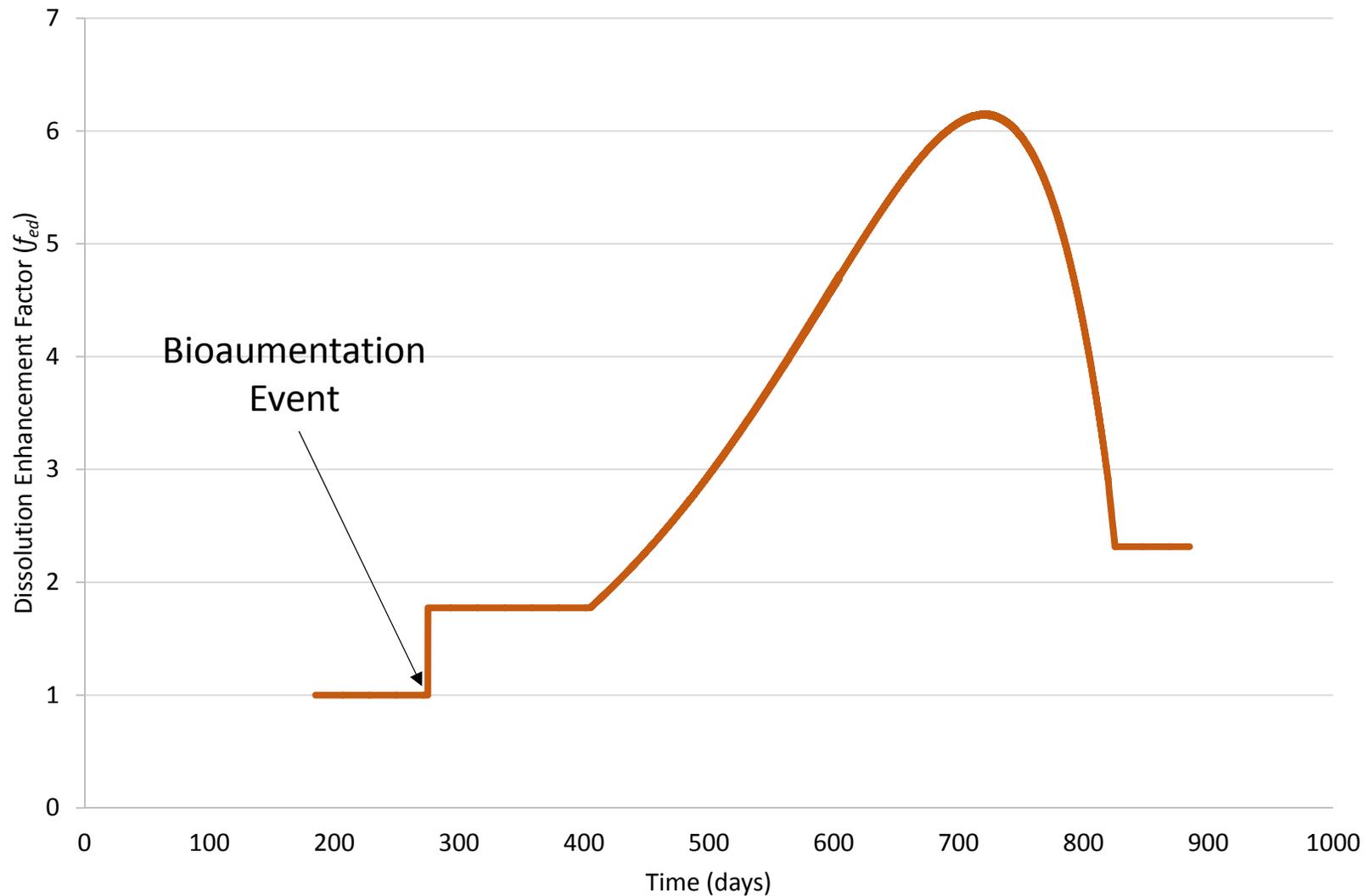
1. Poor mass removal efficiency
2. Increased risk reduction

Note – preferential channels observed
At top of tank (above NAPL source zone)

Box 2 – Natural and Enhanced Dissolution



Box 2 – Enhanced Dissolution Factor (f_{ed})



Competition for Electron Donor

- Sleep et al. (2006) estimated % of electron donor utilized for PCE degradation and other processes
- After bioaugmentation, dechlorination accounted for 1% to 7% of electron donor transformation
- Up to t=320 d: Fe-reduction 60% to 100
- After t=320 d: Methanogenesis 49% to 66% (when iron depleted)
- Competition for electron donors will reduce DNAPL dissolution enhancement



Summary

- EISB may enhance DNAPL dissolution
- Mass removal effectiveness limited by:
 - Pore clogging by biofilm and/or gas bubbles
 - May still result in significant source strength and risk reduction
 - Competition for electron donor
 - Inadequate supply of electron donor at DNAPL-water interface (e.g. pool)
 - Causes bioclogging above interface which inhibits water flow adjacent to DNAPL surface and limits DNAPL dissolution.



Questions?



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Course Summary

Section 5

DNAPL Concepts

- Aged DNAPL source zones
 - Pool-dominated
 - Typical thickness of 1 to 4 inches at chlorinated solvent sites
 - Declining source strength
 - a) Declining NAPL-water interfacial area (e.g. pool lengths)
 - b) Intra-source bypassing (preferential channelling) - streamtube analogy
 - MNA reasonable alternative if protective, based on cost-benefit analysis
- Strategic P&T may save significant \$\$ when treatment required, and infrastructure already exists at a site



Simple Approach for Estimating Mass in a DNAPL Source Zone

Estimating initial mass (M_o) in source zone (Newell et al., 2005):

$$M_o = Md_o / \lambda_{thru} \quad [M_o \text{ in kilograms, } Md_o \text{ in kg/y, and } \lambda_{thru} \text{ in } y^{-1}.]$$

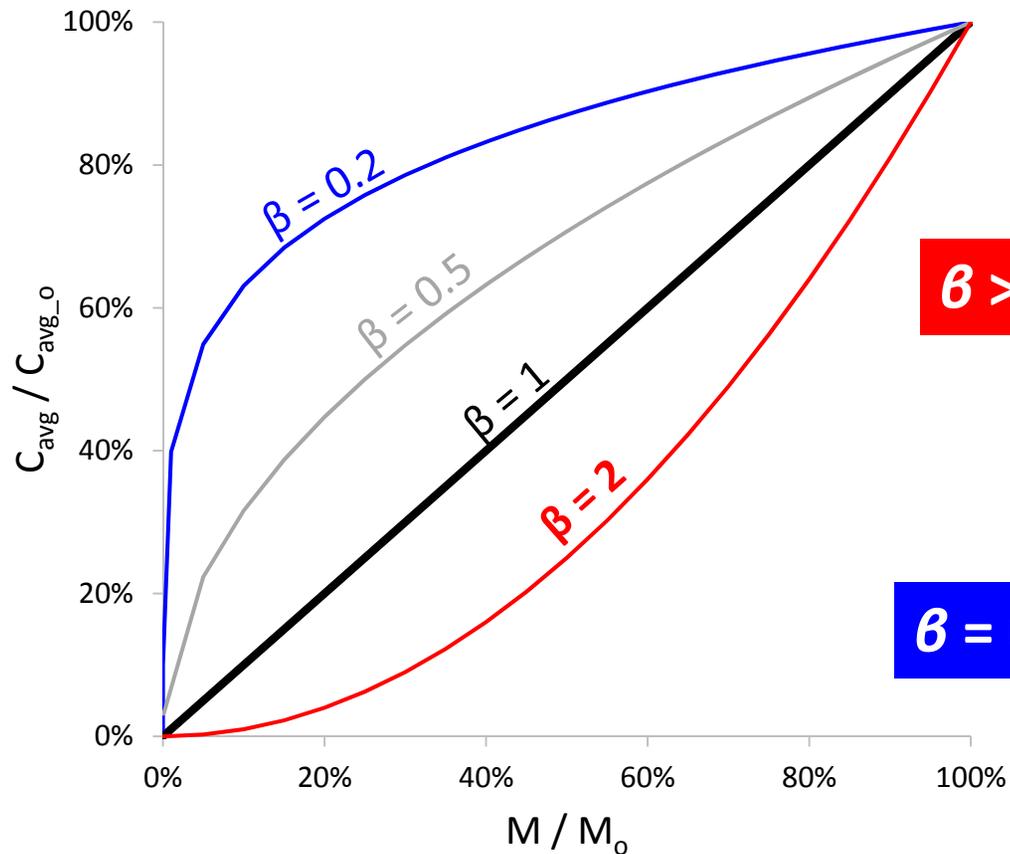
Example calculation for Tuscon Airport Site:

$$\begin{aligned} M_o &= (659.1 \text{ kg/y}) / (0.092 \text{ y}^{-1}) \\ &= 7,164 \text{ kg} \end{aligned}$$

Then use a simple mass discharge decline model to estimate cumulative mass removed over time, and current mass remaining.

Calculation assumes uniform decline rate. May overestimate mass when substantial DNAPL pools present.

Influence of β



$\beta = 1$

- M_d and M have same exponential decline rate (Falta et al., 2005)
- Typical for natural attenuation of mixed source zones with mass mainly in transmissive zone (Falta et al., 2005) and heterogeneous distribution

$\beta > 1$

- Large reduction in source strength for small mass reduction
- Large portion of NAPL mass in low-K zone, or caused by pore clogging during in-situ remediation

$\beta = 0.2$

- Single DNAPL pool
- Small reduction in source strength for large mass reduction

Site Management Approach

- Interim treatment goals – attainable Md reduction for various technologies (mean vs. median)
 - Even thermal remediation, on average, will only reduce source strength by a factor of 30x
- Integrated source treatment/plume management
 - Negligible benefit from “over-treating” the source zone if back-diffusion sustains downgradient plume
 - Long-term management may still be required regardless of source treatment effectiveness



NAPL Depletion Model (NDM) Uses

- Depletion timeframes – natural and enhanced
 - Relative benefit of enhanced treatment
 - Input for cost calculations
- Identify critical properties that need additional characterization or investigation to reduce uncertainty
- Improved understanding of factors influencing NAPL depletion
- Interpretive model – calibrate / eliminate architecture scenarios (model vs. observed source strength trends)
- Input for transport models
 - MT3DMS: source strength vs. time
 - REMchlor: Power law model, timeframe for enhanced attenuation



Types of Models

- Box model – mixed source zone
 - Overall behavior
 - Historical observed decline used to define λ_{thru}
 - Evaluate influence of velocity changes, or enhanced dissolution
- Process-oriented model (sub-zones)
 - Distinct layers of pooled or residual DNAPL
 - Interpretive model – which site characteristics influence depletion time?
 - Improved understanding



NDM Use of the Dilution Factor

- NAPL Depletion Model (NDM) predicts mass discharge (Md) as the global variable
 - Source strength = Md
- λ_{thru} is the rate of decline in mass discharge and the dilution factor (f_i)

$$Md = q A C_{sol} f_i$$

Single component NAPL: C_{sol} = solubility

Multicomponent NAPL: C_{sol} = effective solubility

$$f_i = f_{i0} e^{-\lambda_{thru} t}$$

f_i = dilution factor = C_{avg} / C_{sol}

= proportion of streamtubes passing through NAPL



Estimating Input Parameters

- See regression relationships (p. 3b.26)
- High resolution PID and/or soil measurements may help to:
 - Identify DNAPL pool locations
 - Provide evidence for back-diffusion timeframe analysis
- Key factors influencing pool depletion timeframe
 - Pool thickness
 - Groundwater velocity
 - Chemical solubility (or effective solubility)
- Other relevant factors: pool length, through-discharge, transverse dispersivity, intra-source bypassing



Model Limitations

- Simplified representation of complex conditions
- Screening model does not represent tailing below 90% to 99% source strength reduction
- Process-oriented models – need dimensions of DNAPL pools, layers (thickness key, length less critical)
 - Useful for relative alternative comparisons, and improving our understanding of factors which influence depletion timeframes
 - Some sites may benefit from probabilistic model to evaluate range of outcomes (e.g. Monte Carlo)
- Multicomponent model – does not simulate Md_{surf}



Questions?



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APPENDIX A

Grant R. Carey Curriculum Vita

Grant R. Carey, Ph.D., P.Eng.

EDUCATION

- Ph.D. University of Guelph, Guelph, Ontario, 2015
- M. Eng. Carleton University, Civil and Environmental Engineering, 2001
- 1997 One of two Canadian graduate students invited to a NATO Advanced Study Institute (Bioavailability of Organic Xenobiotics in the Environment) in the Czech Republic.
- B.A.Sc. University of Waterloo, Civil Engineering, 1993

EMPLOYMENT

- 2006- Present President and CEO
Porewater Solutions
- 2005-2006 Associate, and Director of Corporate Training
Conestoga-Rovers & Associates
- 2002-2004 Senior Engineer
Conestoga-Rovers & Associates
- 2000-2002 President and CEO
Environmental Institute for Continuing Education (EICE)
- 1996-2002 President and CEO
Environmental Software Solutions Inc. (ENSSI)
- 1996-1999 Carleton University Mediation Centre - Mediator, Conflict Resolution Program
- 1992-1996 Engineer
Conestoga-Rovers & Associates

PROFESSIONAL AFFILIATIONS

- California Groundwater Resources Association
- National Ground Water Association
- Ontario Professional Engineer

PROFILE OF PROFESSIONAL ACTIVITIES

Summary of Experience

Mr. Carey has worked on hundreds of projects across North America and has extensive experience in:

- Litigation
- Groundwater modeling
- DNAPL characterization
- Chemical fate and transport
- Groundwater and sediment remediation
- Forensic assessment of releases at chemical plants

- Assessment of tidal fluctuations and density effects on groundwater flow and contaminant transport
- Development of guidance manuals related to site characterization and remediation
- Source water protection
- Development of computer models for public domain and commercial use
- Training using blended solutions (e.g. classroom, interactive e-learning, correspondence, etc.).

Mr. Carey has published more than 90 courses, presentations, and papers. Mr. Carey is familiar with a wide range of models and visualization software including: MODFLOW, Modflow-Surfact, FEFLOW, SWIFT, T2VOC, VAPOR-2D, EVS, and ArcGIS. Representative project experience is described below.

Mathematical Modeling and Site Remediation

- Aerospace manufacturing facility, San Diego, California – Expert peer review for implementation of a remedial investigation, feasibility study, and development of a Remedial Action Plan.
- Cedar Chemical Site, Phillips County, Arkansas – Supported a PRP De Minimis evaluation.
- San Fernando Valley Superfund Site, Los Angeles, California – Expert peer review for implementation of a basin-scale investigation for delineation of hexavalent chromium, and groundwater modeling to evaluate capture zones for regional supply wells.
- Former manufacturing facility, Burbank, California – Expert peer review for monitoring and remediation of hexavalent chromium and chlorinated solvents.
- Chemical Manufacturing Facility, Kentucky – Expert support for implementation of a large RI/FS at a site with multiple DNAPL and LNAPL source zones.
- USA Petroleum site, San Jose, California – Hired as an expert witness to testify regarding the fate of MTBE from a gas station release near a regional drinking water supply well.
- Former rocket manufacturing facility, Southern California – Conducted a detailed investigation of chemical fate (perchlorate and chlorinated solvents) including validation of a three-dimensional basin-wide groundwater flow model for the San Bernadino Basin.
- Manufacturing Facility, Phoenix, Arizona – Developed a regional groundwater flow and chemical transport model for litigation, to evaluate source release timing for a TCE plume in a multi-aquifer system with regional supply wells.
- Canadian Tire Site, Toronto, Ontario – Developed a high resolution groundwater flow and multispecies reactive transport model to evaluate enhanced in-situ bioremediation of petroleum hydrocarbons.
- Confidential site, Ottawa, Ontario – Calibrated a groundwater flow and chemical transport model for evaluation of persulfate diffusion and reactivity in bedrock.
- Seaspans Site, British Columbia – Calibrated a three-dimensional transient (tidal oscillation) freshwater groundwater flow model for a coastal site and evaluated remedial design alternatives and sediment cap performance based on groundwater flow and chemical transport modeling;
- Union Bay Site, British Columbia – Calibrated a three-dimensional transient (tidal oscillation) groundwater flow model based on seasonal positions of the freshwater-seawater interface, and used a one-dimensional groundwater flow and chemical transport model to compare remedial alternative performance based on mass discharge reductions;

- Savannah River National Laboratory (SRNL) – Invited to conduct a reactive transport modeling study to evaluate the mass balance for a chlorinated solvent plume attenuation at Plattsburgh Air Force Base (New York) on behalf of SRNL’s research efforts related to natural and enhanced attenuation
- Vandenberg Air Force Base, California - Modeled tracer tests and bioremediation pilot tests to evaluate remedial performance as part of a Department of Defense (ESTCP) project related to the design of soluble substrate injection systems
- Texas Central Gulf Coast Aquifer Groundwater Availability Model – calibrated a regional groundwater flow model that covered an area that represents more than 10% of the drinking water supply for Texas, and used this model to predict water supply resources over a 50-year period in the future.
- Source Water Protection Study, Region of Waterloo, Ontario – Peer reviewed a regional groundwater flow model which was developed to evaluate three-dimensional groundwater directions, velocities, and to support a regional vulnerability assessment;
- Mine Exploration Project, Alaska – calibration of a 5,000 km² watershed-scale groundwater flow model to evaluate how future mining operations may influence groundwater and surface water resources, including a transient water balance calibration for 14 subwatersheds;
- Birkerød Site, Denmark – Developed a density-dependent soil vapor flow and transport model to evaluate the distribution of TCE mass flux and to evaluate the performance of a soil vapor extraction system.
- Sydney Tar Ponds, Sydney, Nova Scotia – Senior Modeler for groundwater flow and transport modeling in Phase II/III Environmental Assessment
- Superfund site in Tacoma, Washington – developed the conceptual and simulation models for a groundwater trench recirculation system in a tidally-influenced aquifer, including the simulation of tidal effects on time-varying groundwater extraction/injection rates using SWIFT/486
- ArvinMeritor Site, Allegan, Michigan – developed a groundwater flow model for a site next to the Kalamazoo River to evaluate the design of a permeable reactive barrier.
- Chemical manufacturing facility in Elmira, Ontario – developed groundwater flow model for designing a shallow aquifer extraction system adjacent to a surface water tributary, and assisted in the development of a phased approach for construction and testing of the extraction network.
- Former sand and gravel quarry, Maryland - Developed and calibrated a groundwater flow model to evaluate the range in dewatering pumping rates in support of a large excavation and bioremediation program
- Evaluated MNA for groundwater contaminated by chlorinated solvents and/or petroleum hydrocarbons at numerous sites
- Evaluated the influence of permeable and low-permeability landfill caps on the natural attenuation of chlorinated solvents such as TCE in an underlying aquifer
- Manufacturing Facility, Cambridge, Ontario – involved with regulatory negotiations and development of a field program to evaluate potential presence of an on-site solvent source and delineate contribution from an upgradient plume.
- Forest Waste Landfill Superfund Site, Michigan – developed a reactive transport model to simulate kinetic oxygen demand from various geochemical solutes, pyrite, DOC, and 20 organic chemicals of concern. The modeling of kinetic COD demonstrated that an in-situ oxygen curtain was a feasible remedy, which saved the client more than \$500,000.

- North Sanitary Landfill Superfund Site, Dayton, Ohio – managed the application of a multispecies reactive transport model to evaluate risks associated with natural attenuation of a landfill leachate plume, including representation of a number of chlorinated solvents, petroleum hydrocarbons, and inorganic chemicals of concern including manganese and arsenic.
- Rockwell Site, Cambridge, Ontario – conducted a modeling evaluation of matrix diffusion effects on TCE attenuation in groundwater using an analytical model (CRAFLUSH) and a one-dimensional numerical model (MT3DMS).
- Former Alsons Facility, Hillsdale, Michigan – evaluated potential for DNAPL migration in underground utilities and relative contributions from multiple sites.
- Fike Superfund Site, West Virginia – conducted a comprehensive assessment of MNA lines of evidence at a former pharmaceutical facility, including an evaluation of natural attenuation for 30 organic chemicals (chlorinated solvents and PAHs) and nine inorganic constituents.
- U.S. Navy flight facility, California – developed a custom subroutine for a redox-dependent transport model (BioRedox-MT3DMS) to evaluate the performance of a biosparging remedy for a BTEX plume.
- Municipal landfill, Waterloo, Ontario – Used a one-dimensional variably saturated flow and transport model to assess leachate migration potential through the vadose zone: 1) municipal landfill in Waterloo, Ontario, and 2) sludge lagoon in Cincinnati, Ohio
- Collaborated with a scientist from the U.S. Army Corps. Waterways Experiment Station to conduct a study of how BioRedox-MT3DMS could be applied to predict the natural attenuation of common explosives such as TNT and RDX
- Assisted researchers in the United States, Canada, the United Kingdom, and the Netherlands in applying BioRedox-MT3DMS to model conditions observed during field research studies involving the natural attenuation or enhanced bioremediation of various organic pollutants
- Former manufacturing facility, Illinois – chemical fingerprinting to delineate plumes from multiple sources and evaluated kinetics associated with 1,1,1-TCA degradation pathways to 1,1-DCE and 1,1-DCA in preparation for litigation.
- Douglas Autotech Facility – conducted a preliminary cost allocation assessment for TCE and DCE plumes involving numerous facilities, and presented results of this evaluation to opposition parties as part of a pre-litigation meeting.
- Manufacturing Facility, Barrie, Ontario – peer reviewed a fate and transport assessment conducted on behalf of a neighboring facility, and developed an alternate assessment of cost allocation that was used in litigation settlement discussions.
- Municipal landfill, Los Angeles, California – conducted a landfill gas modeling study and a critique of the proponent's groundwater modeling study, in support of an environmental hearing involving the closure of a municipal landfill site (affecting \$4 billion dollars in future revenue)
- Proposed municipal landfill in an abandoned quarry, Hamilton, Ontario – conducted a critique of proponent's groundwater modeling study in support of an environmental permit hearing
- Sand and gravel quarry, Caledon, Ontario – Conducted a detailed critical review of a groundwater modeling to assess the impact of water resource management alternatives in support of an environmental permit hearing

Soil/Landfill Gas

- Municipal landfill, Los Angeles, California – used a two-dimensional density-dependent vapor flow and transport model (Vapor-2D) to simulate the extent of landfill gas impact on underlying groundwater resources, and peer reviewed opposition report for a multi-billion dollar landfill impact assessment hearing
- Hazardous waste landfill, Phoenix, Arizona – used a two-dimensional density-dependent vapor flow and transport model to assess the extent of potential migration of 1,2-DCA from a spill
- Used a two-dimensional landfill gas model (Vapor-2D) to simulate the performance of vertical barrier walls in controlling gas migration from the landfill: 1) municipal landfill, Toronto, Ontario, and 2) municipal landfill, Mississauga, Ontario
- Developed three-dimensional vapor flow models to aid in the optimization of soil vapor extraction/injection systems: 1) hazardous waste landfill Superfund site in Phoenix, Arizona, and 2) municipal landfill and former drum disposal Superfund site in Lapeer County, Michigan
- Conducted feasibility studies and remedial designs for soil vapor extraction and/or injection systems: 1) Municipal landfill and former drum disposal Superfund site in Lapeer County, Michigan, 2) Hazardous waste landfill in Phoenix, Arizona, 3) former drum disposal Superfund site (once ranked 4th in priority among all NPL sites in the United States) Hardeman County, Tennessee, 4) Automobile manufacturing facility in Pontiac, Michigan, and 5) Manufacturing facility in Frewsburg, New York

Landfill Remediation

- Municipal landfill, Rhinelander, Wisconsin – developed a natural attenuation analysis used to successfully negotiate reduced scope in the landfill cap to an environmental hearing (cost savings of \$8 million)
- Municipal landfill and former drum disposal Superfund site, Lapeer County, Michigan - developed a \$600,000 field program to support remediation by natural attenuation at a municipal landfill site, coordinated the field work, managed the data analysis and participated in negotiations with the USEPA and state regulatory agency to reduce the scope of the groundwater remedy (cost savings of more than \$5 million)
- Municipal landfill, Allegan County, Michigan – evaluated the adverse influence of landfill cap installation on groundwater quality in the underlying aquifer
- Initiated the joint analysis of landfill natural attenuation at a Superfund site involving key scientists from the USEPA Office of Research and Development, and Thomas Christensen from the Technical University of Denmark

Guidance Manual Development and Peer Review

- Participated (and currently participating) on various ITRC teams to develop guidance manuals for site characterization and remediation including the following teams: Remediation of Complex Sites, DNAPL Site Characterization, Contaminated Sediments – Remediation, Integrated DNAPL Site Strategies (IDSS), and Enhanced Attenuation of Chlorinated Organics (EACO). Currently one of the internet-based training instructors for two ITRC seminars: Mass Flux and Mass Discharge, and

Remediation of Contaminated Sediments. Received the EACO team Industry Affiliates Program Award that recognizes outstanding contributions from industry members.

- Managed a contract with the Ministry of the Environment to edit the 2nd draft of the Ontario Phase II Environmental Site Assessment Technical Guidance Manual;

Model Development

Mr. Carey has developed a variety of commercial and public domain software tools, including:

In-Situ Remediation (ISR-MT3DMS) – three-dimensional reactive transport model based on the MT3DMS framework, for simulating the performance of in-situ remediation technologies, including enhanced in-situ bioremediation (EISB) and in-situ chemical oxidation. Model includes an innovative local domain approach for modeling forward and back-diffusion, and also includes the reaction package from BioRedox.

NAPL Depletion Model – semi-analytical screening model for simulating the depletion timeframe for LNAPL or DNAPL source zones.

BioRedox-MT3DMS (1999) – a three-dimensional finite difference model for simulating multispecies contaminant transport, including advection, dispersion, sorption, and coupled biodegradation-redox reactions between electron donors and electron acceptors. BioRedox-MT3DMS can simulate oxidation, reduction, and co-metabolic reactions, and is capable of modeling sequential transformation pathways for chlorinated solvents and petroleum hydrocarbons. BioRedox-MT3DMS is also capable of simulating equilibrium or rate-limited dissolution of light or dense NAPL sources, and includes a leachate composition model to represent time-varying landfill constituent concentrations leaching to underlying aquifers. BioRedox-MT3DMS was previously available in the public domain.

SEQUENCE (1999) – a visualization tool that uses a modified radial diagram approach to illustrate the effects of natural attenuation on groundwater redox conditions. SEQUENCE may also be used to evaluate spatial and temporal trends for chlorinated solvent species. The visual aids prepared using SEQUENCE provide convincing evidence for the effectiveness of remediation by natural attenuation. SEQUENCE integrates these radial diagram tools with a comprehensive data management system is available. SEQUENCE was previously sold as a commercial product.

BioTrends (1999) – a suite of tools for evaluating spatial and temporal trends using x-y charts with unique features that were specifically designed for evaluating chemical analytical data. Additional tools are provided for calculating first-order degradation rates between well pairs, or the average degradation rates along a flowpath based on a log-linear regression analysis, using the methods presented in the USEPA and AFCEE natural attenuation protocols. Another tool is provided to calculate the natural attenuation "score" for a site based on criteria presented in the USEPA protocol. BioTrends is integrated with a chemical properties database (CHEMbase), and the same project data management system used for the SEQUENCE visualization tool. BioTrends was previously sold as a commercial product.

BioTracker (1999) – a one-dimensional screening model that is integrated with visualization tools for transport model calibration and documentation. BioTracker utilizes a one-dimensional version of the BioRedox finite difference model to simulate multispecies transport processes including advection, dispersion, sorption, and single or sequential transformation reactions with optional

halogen accumulation. BioTracker incorporates a particle tracking tool that delineates flowpaths downgradient from one or more point source locations. The customized particle tracking routine utilizes Surfer contour maps of observed or simulated groundwater elevations as input. BioTracker is also integrated directly to the same project data management system used with BioTrends and SEQUENCE, and it is integrated with a chemical properties database (CHEMbase). BioTracker was previously sold as a commercial product.

Rate Inverse Models (1998) – two-dimensional and three-dimensional analytical solutions based on the Domenico solution for estimating first-order chemical biodegradation rates based on field-measured data. These models were previously distributed at short courses.

Vapor-2D (1992) – a two-dimensional finite element model that simulates multispecies, density-dependent vapor flow and transport. Vapor-2D was modified to predict the migration of gasoline vapors from a subsurface spill area, and includes a multicomponent NAPL source model. Vapor-2D was successfully validated by simulating laboratory experiments of vapor flow and transport of heptane in the vadose zone, and Vapor-2D has been used to assess density-dependent vapor migration at field sites. Vapor-2D is currently a proprietary model.

LEACHATE (1997) – developed a batch flushing model to simulate rate-limited mass transfer of leachate from a landfill with varying infiltration rates, including a component to quantify the effects of biodegradation for chlorinated solvents.

Training Services

- Toronto District School Board, Toronto, Ontario - Developed the outline and script for an interactive multimedia online course on Supervisor responsibilities that includes the development of a Health and Safety Action Plan for school Principals, Vice-Principals, and Superintendents.
- Walkerton Clean Water Centre, Walkerton, Ontario – designed and facilitated two think tank sessions involving provincial water quality experts and stakeholders representing all levels of government, First Nations groups, and training agencies. Also prepared the Operator Training Work Plan for the Walkerton Clean Water Centre based on feedback from the think tank sessions.
- Ontario Ministry of the Environment Vendor of Record for Technical Training – Project Manager for this Vendor of Record, and CRA was the only vendor selected in all four available training categories that included the development of classroom courses, instruction of classroom courses, development of technology assisted training, and development of correspondence courses)
- Ontario Ministry of the Environment Brownfields Legislation Training – designed and developed an interactive internet seminar that was broadcast to more than 20 MOE offices across Ontario, to provide training to provincial officers on the new Brownfield site legislation
- Ontario Ministry of the Environment Agriculture Training – designed and developed a four-week course for training new ministry agricultural enforcement officers.
- Ontario Ministry of the Environment Health and Safety Awareness for Water Treatment Plant Inspectors– Technical advisor for the development of a storyboard for an e-learning health and safety course targeted to MOE officers involved with water treatment plant inspections.
- Ontario Ministry of the Environment – attended the four-day MOE workshop “Effective Facilitation Techniques” with the Brownfields Transition Team, with an emphasis on collaborative and interactive learning exercises.

- Florida Department of Environmental Protection – provided technical advice for the design and development of a series of online courses to be delivered to professionals across Florida, involving risk assessment and remediation topics.
- CRA Institute Workforce Training – Director of Corporate training programs delivered to more than 2,000 staff in more than 60 offices in North America, South America, and Europe.
 - K-W Chamber of Commerce Award of Excellence for Workforce Training – Runner-up for the 2005 Award.
 - Managed corporate meetings broadcast utilizing webcast and teleconference software to more than 50 offices and involving more than 300 people.
 - Directed all business operations for the Environmental Institute for Continuing Education, including the delivery of more than 200 webcasts in a three-year period, sales of more than 100 asynchronous CD-ROM and web-based seminars, and certification of participation for professional engineers and scientists.
- Developed an easy-to-use e-learning interface that allows for cost-effective development of Flash-based multimedia courses.

Alternative Dispute Resolution

- received extensive training over a 3-year period in advanced mediation, facilitation, and coaching skills
- attended workshops on advanced mediation training, with an emphasis on diagnosing conflict, the transformative mediation model, and strategies for managing high-conflict mediations
- mediated disputes involving intercultural issues, organizational team-building and strategic planning
- provided professional coaching and role-playing services to the Graduate Certificate Program in Conflict Resolution, Carleton University (Department of Law)
- assisted in the development of several workshops related to alternative dispute resolution

SHORT COURSES, WORKSHOPS, AND TRAINING SEMINARS

- Invited Instructor for the ITRC webinar entitled "Remediation of Contaminated Sediments" offered from 2014 and 2015.
- Invited Instructor for the ITRC webinar entitled "Use and Measurement of Mass Flux and Mass Discharge" offered from 2010 through 2015.
- Instructor for a 4-hour short course entitled "Using the NAPL Depletion Model for Estimating Timeframes for Natural and Enhanced Attenuation", presented at the Third International Symposium on Bioremediation and Sustainable Environmental Technologies, Miami, Florida, May 18, 2015.
- Invited Instructor for 2015 Smart Remediation short course with presentation entitled "A New Paradigm for Managing Chlorinated Solvent Sites" in Ottawa, Ontario February 12, 2015.
- Invited Instructor for 2013 Smart Remediation short course with presentation entitled "Using Mass Discharge to Reduce Remediation Costs" in Ottawa, Ontario and in Toronto, Ontario, 2013.

- Instructor for a DNAPL workshop with presentation entitled “NAPL Dissolution and Fate of Groundwater Plumes”, Louisville, Kentucky, December 7, 2012.
- Invited instructor for the Smart Remediation short course with presentation entitled “The Influence of Back-Diffusion on Remediation Success”, Ottawa, Ontario, April 15, 2011.
- Instructor for the one-hour seminar entitled “Improving Groundwater Model Defensibility in Litigation”, San Francisco, California, May 21, 2014. (pre-approved for MCLE credit)
- Invited instructor on behalf of ITRC for a session entitled: Development of Remedial Goals Based on Mass Discharge Reductions, at the NEWMOA Enhanced In-Situ Bioremediation short course offered in Westford Massachusetts and Dayville Connecticut on October 5th and 6th, 2010.
- Instructor for a 4-hour short course entitled: Decision-Making Framework for DNAPL Sites Using a Cost-Risk-Benefit Analysis, presented at ConSoil 2010 September 23, 2010, Salzburg, Austria.
- Instructor for a 4-hour short course entitled: Decision-Making Framework for DNAPL Sites Using a Cost-Risk-Benefit Analysis, presented at Battelle 2010 Remediation of Chlorinated and Recalcitrant Compounds, May 26, 2010, Monterey, California.
- Invited instructor for a short course entitled: Approaches for the Remediation of DNAPL Sites and Tools for Measuring Mass Flux and Mass Discharge in the Remediation Process (An ITRC Short Course), presented at Battelle 2010 Remediation of Chlorinated and Recalcitrant Compounds, May 23, 2010, Monterey, California.
- Senior Instructor for the following seminars which were delivered by webcast or on CD-ROM to clients in North America, Europe, Australia, and Africa:
 - Application of SEQUENCE Radial Diagrams for Visualizing Natural Attenuation Trends for Chlorinated Solvents and Redox Indicators;
 - Avoiding Common Mistakes when Estimating First-Order Biodegradation Rates;
 - Arsenic Mobilization during Natural Attenuation of Organic Compounds;
 - Biodegradation Process and Biodegradability of Petroleum Hydrocarbons and Chlorinated Solvents;
 - Case Study of Innovative Techniques for Evaluating In-Situ Remediation;
 - Introduction to Biogeochemical Processes;
 - Overview of Bioremediation Transport Models for Evaluating Natural and Enhanced Bioremediation;
 - Overview of Monitored Natural Attenuation: Key Concepts and Regulatory Issues;
 - Overview of the Remediation ToolKit: Trend Analysis, Visualization, and Modeling Tools;
 - Reactive Transport Modeling for Evaluating Natural and Enhanced Bioremediation;
 - Visualizing the Effectiveness of MNA and Enhanced Attenuation Remedies Using SEQUENCE;
 - Visual Trend Analysis Methods for Evaluating Monitored Natural Attenuation Trends
- Senior instructor for a half-day short course “Evaluating the Effectiveness of Monitored Natural Attenuation and Enhanced Attenuation Remedies, delivered to the New Jersey Department of Environmental Protection, Trenton, New Jersey, June 28, 2006.

- Co-author of a half-day short course “Evaluating the Effectiveness of In-Situ Remediation”, which was delivered to CRA clients, regulators, and other consultants in Phoenix, Houston, Atlanta, and Princeton in 2005.
- Invited to co-present a seminar at the University of Waterloo Department of Earth Sciences, “Case Study of Innovative Modeling and Visualization Techniques for Evaluating In-Situ Remediation Technologies”, Waterloo, Ontario, December 3, 2004.
- Instructor for a two-hour seminar entitled “Summary of the Ontario Phase II Environmental Site Assessment Technical Guidance Manual”, which was delivered at an Ontario Ministry of the Environment workshop in Toronto, Ontario, March 13, 2003.
- Senior Instructor for a half-day short course “Visualization and Modeling of Monitored Natural Attenuation” Hartford, Connecticut, March 13, 2003.
- Senior Instructor for a half-day short course “Practical Reactive Transport Modeling for Evaluating In-Situ Bioremediation”, presented at the Sixth International Symposium on In Situ and On-Site Bioremediation, San Diego, California, June 4-7, 2001
- Senior Instructor for a 3-day short course “Advanced Ground Water Modeling Techniques for Evaluating Performance of Natural Attenuation and Enhanced Bioremediation: A computer workshop using the three-dimensional BioRedox model”, organized by the National Ground Water Association and offered in February 2000 (Albuquerque, New Mexico) and September 2000 (Toronto, Ontario).
- Senior instructor for a 3-day short course “Innovative Tools for the Analysis, Visualization, and Modeling of Natural Attenuation: Featuring the MoNA ToolKit and Visual Modflow”, organized by Waterloo Hydrogeologic and offered in Waterloo, Ontario, October 2-4, 2000
- Senior instructor for a 1-day short course “Innovative Tools for the Analysis, Visualization, and Modeling of Natural Attenuation: Featuring the MoNA ToolKit” Waterloo, Ontario, October 1, 2000.
- Instructor for a 2-day natural attenuation course organized by EPIC Education Program Innovations Centre: “Remediation by Natural Attenuation”, October 18-19, 1999, Etobicoke, Ontario
- Presented a seminar “Visualizing Natural Attenuation Trends” at the Groundwater Pollution and Hydrology short course organized by Princeton Groundwater, December 7-11, 1998, Las Vegas, Nevada

PUBLICATIONS

Book Contributions

Carey, G.R., P.J. Van Geel, E.A. McBean, and F.A. Rovers, 1999, Application of a Biodegradation-Redox Model for Predicting Bioremediation Performance, in P. Baveye, J.C. Block, and V.V. Goncharuk, (Eds.), *Bioavailability of Organic Xenobiotics in the Environment: Practical Consequences for the Environment*, Kluwer Academic Publishers, pp. 73-77

Refereed Journal Papers

Carey, G.R., E.A. McBean, and S. Feenstra, 2014, DNAPL Source Depletion: 1. Predicting Rates and Timeframes, *Remediation Journal*, Summer 2014, p. 21-47.

Carey, G.R., E.A. McBean, and S. Feenstra, 2014, DNAPL Source Depletion: 2. Attainable Goals and Cost-Benefit Analyses, *Remediation Journal*, Autumn 2014, p. 79-106.

- Carey, G.R., E.A. McBean, and S. Feenstra, 2015, Estimating Tortuosity Coefficient based on Hydraulic Conductivity, submitted to *Ground Water* (in review).
- Carey, G.R., E.A. McBean, and S. Feenstra, 2015, Estimating Transverse Dispersivity Based on Hydraulic Conductivity, in preparation for submittal to *Transport Processes in Porous Media*.
- Carey, G.R., E.A. McBean, and S. Feenstra, 2015, Through-Discharge Decline Rate for Layers of Residual DNAPL: 1. Field-scale multicomponent source, in preparation for submittal to *Water Resources Research*.
- Carey, G.R., E.A. McBean, and S. Feenstra, 2015, Through-Discharge Decline Rate for Layers of Residual DNAPL: 2. Empirical Regression, in preparation for submittal to *Water Resources Research*.
- McGregor, R. and G. Carey, 2015, Long Term Study of Oxidant Injection into a Fractured Limestone Aquifer Impacted by Petroleum Hydrocarbons, in preparation for submittal to *Remediation Journal*
- Carey, G.R. and R. McGregor, 2015, ISR-MT3DMS for Modeling Back-Diffusion Remediation Timeframe, in preparation for submittal to *Remediation Journal*.
- Carey, G.R., E.A. McBean, and S. Feenstra, 2015, NAPL Depletion Model Development and Case Studies: 1. Natural Dissolution, in preparation.
- Carey, G.R., E.A. McBean, and S. Feenstra, 2015, NAPL Depletion Model Development and Case Studies: 2. Enhanced Dissolution, in preparation.
- Schreiber, M., G.R., D. Feinstein, Carey and J. Bahr, 2004, Mechanisms of Electron Acceptor Utilization, *Journal of Contaminant Hydrology*, 73(1-4), p. 99-127.
- Carey, G.R., P.J. Van Geel, T.H. Wiedemeier, and E.A. Mcbean, 2003, A Modified Radial Diagram Approach for Evaluating Natural Attenuation Trends for Chlorinated Solvents and Inorganic Redox Indicators, *Ground Water Monitoring and Remediation*, 23(4): 75-81.
- Carey, G.R., T.H. Wiedemeier, P.J. Van Geel, E.A. McBean, J.R. Murphy, and F.A. Rovers, 1999, Visualizing Natural Attenuation Trends: Petroleum Hydrocarbons Attenuation at the Hill Air Force Base, *Bioremediation Journal*, 3(4): 379-393

Software Manuals

- Carey, G.R., 2015, NAPL Depletion Model (NDM): User's Guide, Porewater Solutions, Ottawa, Ontario, Canada.
- Carey, G.R., P.J. Van Geel, and J.R. Murphy, 1999, BIOREDOX-MT3DMS: A Coupled Biodegradation-Redox Model for Simulating Natural and Enhanced Bioremediation of Organic Pollutants – V2.0 User's Guide, Conestoga-Rovers & Associates, Waterloo, Ontario, Canada
- Carey, G.R., P.J. Van Geel, and J.R. Murphy, 1999, BIOREDOX-MT3DMS: A Coupled Biodegradation-Redox Model for Simulating Natural and Enhanced Bioremediation of Organic Pollutants – V2.0 Verification Manual, Conestoga-Rovers & Associates, Waterloo, Ontario, Canada
- Carey, G.R., 1999, BIOREDOX-MT3DMS Tutorial Guide: Modeling Natural Attenuation at the Plattsburgh Air Force Base, Conestoga-Rovers & Associates, Waterloo, Ontario, Canada
- Carey, G.R., 1999, The Remediation ToolKit (SEQUENCE, BioTrends, BioTracker) – User's Guide, Conestoga-Rovers & Associates, Waterloo, Ontario, Canada

Other Publications and Presentations

- Carey, G.R., 2015, ISR-MT3DMS for Modeling Back-Diffusion Timeframe, to be presented at Cleanup 2015 Conference, organized by CRC Care, Melbourne, Australia, September 13-16 (invited presentation).
- Carey, G.R., 2015, Case Studies of LNAPL and DNAPL Depletion Modeling Based on High Resolution Architecture Characterization, to be presented at Cleanup 2015 Conference, organized by CRC Care, Melbourne, Australia, September 13-16 (invited presentation).
- Carey, G.R., 2015, ISR-MT3DMS for Modeling Back-Diffusion Timeframe, presented at REMTEC Summit, Westminster, Colorado, March 3, 2015.
- Carey, G.R. and E.A. McBean, 2013, Predicting Achievable Mass Discharge Goals, Timeframes, and Back-Diffusion Contributions, presented at REMTEC Summit, Westminster, Colorado, March 4-6, 2013 (invited presentation).
- Carey, G.R., M. King, J. Christensen, and C. Pattersen, 2013, Modeling the Influence of Tidal Pumping on Naphthalene Transport through an AquaBlok Cap, presented at Battelle's Conference on Remediation of Contaminated Sediments, Dallas, Texas, February 4-7, 2013.
- Carey, G.R. and E.A. McBean, 2010, Uses, Benefits, and Limitations of Mass Flux and Mass Discharge: A Case Study Review, presented at Consoil 2010, Salzburg, Austria, September 22-24, 2010.
- Carey, G.R. and E.A. McBean, 2010, NAPL Depletion Model (NDM) for Predicting Remediation Timeframe, presented at Consoil 2010, Salzburg, Austria, September 22-24, 2010.
- Carey, G.R. and E.A. McBean, 2010, Validation of a Mass Balance Approach for Estimating DNAPL Remediation Timeframe, presented at Battelle 2010 Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 24-27, 2010.
- Carey, G.R. and E.A. McBean, 2010, A Mass Balance Approach for Estimating DNAPL Source Remediation Timeframe, presented at the 2010 RPIC Federal Contaminated Sites National Workshop in Montreal, QC May 10-13, 2010.
- Carey, G.R. and E.A. McBean, 2010, Back-Diffusion and Discount Rate Implications for DNAPL Remediation Strategies, presented at the 2010 RPIC Federal Contaminated Sites National Workshop in Montreal, QC May 10-13, 2010.
- Stroo, H. and G.R. Carey, 2010, Use and Measurement of Mass Flux and Mass Discharge, presented at the AFCEE Technology Transfer Workshop in San Antonio, Texas, April 6-9, 2010.
- Carey, G.R., 2006 Plattsburgh Mass Balance Modeling Case Study, invited to submit to Savannah River National Laboratory, 2006.
- Carey, G.R., J. Vaillancourt, M.G. Mateyk, and J. Maude, 2006, Case Study Feasibility Study for an In Situ Oxygen Curtain, presented at the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 22-25, 2006.
- Carey, G.R., 2006, "Overview of Monitored Natural Attenuation", excerpt from the "ITRC MNA and Enhanced Attenuation Resource Guide", available online in 2006.
- Kean, J., K. Wilson, J. Doyon, K.M. Vangelas, and G. Carey, 2006, Monitored Natural Attenuation and Enhanced Attenuation - A National Overview: Results of an ITRC Survey, in Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 22-25, 2006.

- Kean, J., K.M. Vangelas, K. Wilson, G.R. Carey, D. Green, J. Doyon, and P. Harrington, 2005, Monitored Natural Attenuation and Enhanced Attenuation – A National Overview: Results of an ITRC Survey, presented at the SERDP conference, Seattle, Washington, November 2005.
- Carey, G.R., “Visualizing the Effectiveness of MNA and Enhanced Attenuation Remedies Using SEQUENCE “, presented at the ITRC EACO team meeting, October 2005.
- Carey, G.R., D. Major, D. Verret, and M. Roworth, 2003, Visualization and Modeling of Bioaugmentation at Kelly Air Force Base, presentation at the Seventh International Symposium on In Situ and On-Site Bioremediation, Orlando, Florida, June 2-5, 2003
- Carey, G.R. and M. Roworth, 2003, Evaluating Remediation Timeframe for Combined Source Containment-MNA Remedies, presentation at the Seventh International Symposium on In Situ and On-Site Bioremediation, Orlando, Florida, June 2-5, 2003.
- King, M., G. Carey, D. Abbey and F. Baechler, 2003, Groundwater and Contaminant Transport Modelling at the Sydney Tar Ponds, in Proceedings of the 2003 IAHR Conference, Winnipeg, Canada.
- Carey, G.R., 2001, Case Study of New Techniques for Calculating Biodegradation Rates, presented at the Sixth International Symposium on In Situ and On-Site Bioremediation, San Diego, California, 2001.
- Carey, G.R., Derivation of Multi-Dimensional Inverse Models for Estimating First-Order Biodegradation Rates, Technical Note published online by the Environmental Institute for Continuing Education, July 17, 2001.
- Carey, G.R. and P.J. Van Geel, 2000, Calibration of a Leachate Natural Attenuation Model for the Vejen Landfill (Denmark), in Proceedings of the Groundwater 2000 Conference, Copenhagen, Denmark, June 2000
- Van Geel, P.J., K. Britton, and G.R. Carey, 1999, Impact of Biodegradation Rates on the Redox Zones Generated below Landfills, Proceedings of the 52nd Canadian Geotechnical Conference, Regina, Saskatchewan, October 24-27, 1999
- Carey, G.R., P.J. Van Geel, J.R. Murphy, E.A. McBean, and F.A. Rovers, 1999, Modeling Natural Attenuation at Plattsburgh Air Force Base, Presented at the Fifth International Symposium on In Situ and On-Site Bioremediation, San Diego, California, April 19-22, 1999
- Carey, G.R., E.A. McBean, and F.A. Rovers, 1999, Visualizing Natural Attenuation Trends, in Proceedings of the Fifth International Symposium on In Situ and On-Site Bioremediation, San Diego, California, April 19-22, 1999
- Carey, G.R., E.A. McBean, and F.A. Rovers, 1999, Risk Management Using Natural Attenuation Processes, presented at the 1999 Risk Management Symposium, Air Force Space Command, February 1999
- Carey, G.R., P.J. Van Geel, J.R. Murphy, E.A. McBean, and F.A. Rovers, 1998, Full-Scale Field Application of a Coupled Biodegradation-Redox Model (BIOREDOR), in Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998
- P.J. Van Geel, G.R. Carey, E.A. McBean, and F.A. Rovers, 1998, An Integrated Landfill Modeling System (ILMS) for Evaluating Remediation Alternatives, in Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998

- Harris, S.M., S. Day, E. Roberts, F.A. Rovers, and G.R. Carey, 1998, Applications of an Innovative Method for Visualizing Natural Attenuation, in Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998
- Carey, G.R., P.J. Van Geel, J.R. Murphy, E.A. McBean, and F.A. Rovers, 1998, Coupled Biodegradation-Redox Modeling to Simulate Natural Attenuation Processes at the Plattsburgh Air Force Base (New York), in Proceedings of MODFLOW'98, Golden, Colorado, October 5-7, 1998
- Carey, G.R., P.J. Van Geel, J.R. Murphy, and E.A. McBean, 1998, An Efficient Screening Approach for Modeling Natural Attenuation, in Proceedings of MODFLOW'98, Golden, Colorado, October 6-8, 1998
- Carey, G.R., P.J. Van Geel, E.A. McBean, and F.A. Rovers, 1997, An Innovative Modeling and Visualization Approach for Demonstrating the Effectiveness of Natural Attenuation, presented at the IBC Natural Attenuation '97 Conference, December 8-10, Scottsdale, Arizona
- Carey, G.R., P.J. Van Geel, E.A. McBean, F.A. Rovers, and G.T. Turchan, 1997, Modeling Landfill Cap Influence on Natural Attenuation, in Sardinia'97, Proceedings of the Sixth International Landfill Symposium, October 13-17, Cagliari, Italy
- Carey, G.R., P.J. Van Geel, E.A. McBean, F.A. Rovers, 1997, Effect of Landfill Cap Permeability on the Natural Attenuation of Chlorinated Solvents Below a Landfill, in 1997 Canadian Geotechnical Conference Proceedings, October 20-22, Ottawa, Ontario
- Carey, G.R., M.G. Mateyk, G.T. Turchan, E.A. McBean, F.A. Rovers, J.R. Murphy, and J.R. Campbell, 1996, Application of an Innovative Visualization Method for Demonstrating Intrinsic Remediation at a Landfill Superfund site, Proceedings of API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, Houston, Texas
- Carey, G.R., M.G. Mateyk, E.A. McBean, G.T. Turchan, J.R. Campbell, and F.A. Rovers, 1996, Multiple Lines of Evidence for Evaluating Intrinsic Remediation at a Landfill Site, Proceedings of the Nineteenth International Madison Waste Conference, Madison, Wisconsin
- Farquhar, G.J. and G.R. Carey, 1991, An Overview of Landfill Practices Now and in the Future, Municipal Solid Waste Management: Making Decisions in the Face of Uncertainty, University of Waterloo Press, Waterloo, Ontario, pp. 77-92

B. NAPL Depletion Model (NDM) Development

B.1 Conceptual Model

The NAPL Depletion Model (NDM) is a semi-analytical screening model which may be used to estimate NAPL depletion under conditions of naturally-occurring or enhanced dissolution. NDM is a process-oriented model, which means that it explicitly represents various porous media and NAPL characteristics which influence the rate of dissolution for one or more NAPL sub-zones within an overall source zone. A sub-zone refers to a NAPL body (e.g. layer) which is relatively continuous, and may not be further discretized into smaller sub-zones on the basis of geometry, porous media characteristics, and/or NAPL characteristics (e.g. chemical composition, NAPL saturation, or density). A NAPL source zone in NDM is comprised of one or more individual sub-zones.

NDM is an alternative to the use of simpler up-scaled models, which typically represent domain-averaged dissolution rates or decline rates for a uniform source zone. NDM may be used for LNAPL or DNAPL, and was developed with the flexibility to simulate NAPL pools, residual sub-zones, and/or mixed zones of NAPL. NDM simulates three types of dissolution or discharge processes: (a) surface dissolution at the top or bottom of a sub-zone; (b) reduced groundwater flow through a sub-zone based on a user-specified or model-calculated relative water permeability; and (c) flux into or out of lower-permeability zones adjacent to one or more NAPL sub-zones.

The key output variables for NDM are the mass discharge and NAPL mass remaining for each individual sub-zone, and the total metrics for the combined source zone. NDM does not simulate changes in aqueous concentrations outside of the NAPL sub-zones, although it is possible to use simple multipliers to simulate or calibrate the ratios of daughter product formation for mass discharge calculations.

Uses of NDM may include:

- Interpretation of NAPL architecture based on calibration of a model to historical discharge trends;
- Estimation of future mass discharge decline rates and depletion timeframes for an existing alternative;
- Evaluation of the relative performance of various potential alternatives as part of feasibility study;
- Quantifying the relative sensitivity of predicted trends (e.g. depletion timeframe) to various site characteristics, in order to identify those characteristics which require further investigation.

NDM is a Fortran-based program which offers a number of options for representing NAPL pools, residual NAPL sub-zones, and/or mixed NAPL zones. A simple mass balance approach is

used within NDM to simulate the mass discharge, and mass remaining, in each NAPL sub-zone of a simulation at the end of each time step. The analytical governing equations for NDM are described in more detail below. General functionality in NDM includes:

- Use of a one-dimensional grid to represent each NAPL sub-zone, with user-defined length, width, thickness, and average NAPL saturation (or depth-specific NAPL saturation calculations performed by the model for NAPL pools with a capillary pressure of zero at the top surface).
- NDM simulates dissolution from the upgradient end of each sub-zone, and upgradient grid cells that become depleted in mass during a simulation are defined to be inactive for the remainder of the simulation. In this manner, the pool-scale declining NAPL-water interfacial area may be represented, as well as the corresponding influence on mass discharge associated with surface dissolution.
- Option to apply through-discharge to the upgradient-most, active cell in a NAPL sub-zone, or uniformly to all cells within a NAPL sub-zone.
- A user-defined multiplier which allows for simulation of surface discharge for none, one, or both the top and bottom surfaces of a NAPL sub-zone, or for simulating an accelerated specific discharge adjacent to the NAPL-water interface.
- Option to make the start of surface and/or through discharge for a NAPL sub-zone to be dependent on the depletion of another zone (e.g. an upgradient sub-zone, or an overlying or underlying layer of NAPL).
- Option for constant, exponential or linear decline models to represent the transient influence of intra-source bypassing and other rate-limited kinetics on the through-discharge with a NAPL sub-zone;
- Quasi-2D representation of discharge through the transition zone in the upper portion of NAPL pools where the relative water permeability is sufficiently large to allow for significant mass discharge, and the NAPL saturation is optionally calculated at specific depths within the pool;
- Enhanced dissolution corresponding to temporal changes in hydraulic gradient (e.g. at the start of pumping near a source zone), or an enhanced dissolution factor associated with in-situ remedies such as enhanced in-situ bioremediation (EISB) or in-situ chemical oxidation (ISCO).
- Automated non-linear calibration of the β term in $Md/Md_o = (M/M_o)$ for each sub-zone;
- An adaptive time-stepping scheme to account for changing system dynamics when a sub-zone grid cell becomes inactive; and
- Option for through-discharge simulations for multicomponent NAPL (see Section A.6).
- Batch mode so that hundreds of simulations may be executed automatically. (A separate processor may be used to generate text input files and post-process output files for use with monte carlo or latin hypercube realizations.)

B.2 Sub-zone Mass Balance

As long as mass remains in NAPL sub-zone i , the total mass discharge related to NAPL dissolution to the aqueous phase is based on

$$Md_{i,diss}^t = Md_{i,thru}^t + Md_{i,surf}^t + Md_{i,diff}^t \quad (B-1)$$

where $Md_{i,diss}^t$ = total mass discharge from dissolution of NAPL to the aqueous phase in sub-zone i at time step t [ML⁻¹];

$Md_{i,thru}^t$ = mass discharge from dissolution of NAPL into groundwater flowing through sub-zone i at time step t [ML⁻¹];

$Md_{i,surf}^t$ = mass discharge from dissolution of NAPL into groundwater flowing across the top and/or bottom of sub-zone i at time step t [ML⁻¹]; and

$Md_{i,diff}^t$ = mass discharge from dissolution of NAPL and subsequent diffusion into a low-permeability unit above and/or below sub-zone i at time step t [ML⁻¹].

The mass remaining in each grid cell j of NAPL sub-zone i at the end of the time step t is calculated using

$$M_{ij}^t = M_{ij}^{t-1} - (Md_{ij,thru}^t + Md_{ij,surf}^t + Md_{ij,diff}^t)\Delta t \quad (B-2)$$

Where M_{ij}^{t-1} refers to the mass remaining in NAPL sub-zone i cell j at the end of the previous time step [M], and Δt represents the length of the time step [T]. The total NAPL mass remaining in sub-zone i at the end of the time step is calculated by summing the NAPL mass remaining in each cell of the sub-zone grid. The total mass added to storage in low-permeability unit(s) adjacent to each NAPL source zone is also accounted for in the mass balance.

The equations and potential uses of each of the individual mass discharge terms in Eq. B-1 are discussed further below.

Finally, the source strength contributing to the downgradient plume from NAPL dissolution is calculated as

$$Md_{i,source}^t = (Md_{i,thru}^t + Md_{i,surf}^t)f_{RXN1}^t \quad (B-3)$$

Where f_{RXN1}^t represents a multiplier for the reduction in source strength due to chemical transformations occurring in the source zone when NAPL is present. This term is useful for simple, quasi-representation of transformation reactions that may occur upon implementation of an active remedial technology such as EISB or ISCO.

When mass has been completely depleted in NAPL sub-zone i , mass discharge contributing to ongoing source strength via back-diffusion from adjacent diffusive source zones (if simulated) is then simulated for the time step using

$$Md_{i,source}^t = (Md_{b-diff}^t) f_{RXN2} \quad (B-4)$$

where f_{RXN2} represents a multiplier for the reduction in source strength due to chemical transformations occurring in the source zone once NAPL has been depleted. This term may be used to represent sustained transformation reactions which may occur after the cessation of EISB.

B.3 Sub-Zone Through-Discharge

Residual/Mixed Source Zones

For residual and mixed NAPL source zones, mass discharge due to dissolution of NAPL into groundwater flowing through sub-zone i is given by

$$Md_{i,thru}^t = (krw_i q_x^t C_{eff}^t w_i h_i) f_i^t f_{ed1}^t \quad (B-5)$$

where krw_i is the relative water permeability, q_x^t is the average specific discharge at time step t , C_{eff}^t is the effective solubility (which is the same as solubility for a single component NAPL), w_i and h_i represent the width and height of source zone i , f_i^t is a multiplier representing the proportion of the source zone cross-section which has streamtubes containing NAPL at time step t , and f_{ed1}^t is a multiplier for mass discharge through the zone representing potential enhanced dissolution at time step t as a result of active remediation. The current version of NDM does not consider transient krw_i during source depletion; further study is warranted to determine when transient representation of this parameter may be helpful.

As discussed above, NDM represents three types of decline models for the f_i^t term to provide a surrogate representation for the rate of decline in NAPL-water interfacial area (IA) in the source zone:

- Exponential decline, $f_i^t = f_{io} e^{-\lambda_i^t t}$ where f_{io} represents the initial proportion of the source zone cross-section which has streamtubes containing NAPL, and λ_i^t represents the first-order rate of decline of the proportion of streamtubes containing NAPL at time step t ;
- Linear decline, $f_i^t = f_{io} - f_{io} m_i^t t$ where m_i^t represents the linear decline slope at time step t ; and
- Constant $f_i^t = f_{io}$.

As an example, if a transect across the downgradient boundary of a source zone has 10% of the cross-sectional area with NAPL upgradient of the transect, f_{io} will be specified as 0.10. At field sites, it is expected that exponential decline models will typically be used to represent aged

sources and/or sources with a heterogeneous NAPL distribution, and the constant f_i^t model will be used to represent high-saturation portions of pools with relatively homogeneous distributions of NAPL.

For sites where an exponential decline model is applicable, the first-order rate (λ) may be estimated based on historical monitoring data. Of note is the relationship summarized by Newell and Adamson (2005) such that $\lambda = Md_o/M_o$, where Md_o represents the source strength at the time of characterization and M_o represents an estimate of initial source mass contributing to the this source strength. If the first-order rate can be estimated from site monitoring data, then an estimate of M_o and the corresponding average NAPL saturation (Sn_o) in a source zone can also be readily estimated. For residual and mixed source zones, the average NAPL saturation source zone (Sn_o) is an input parameter for NDM to facilitate estimation of the initial NAPL mass in a source zone.

To represent the influence of changes in the specific discharge rate which may occur during active remediation, the time-dependent exponential and linear decline rates are calculated respectively based on:

$$\lambda_i^t = \lambda_{io} q_x^t / q_{xo} \quad (B-6)$$

$$m_i^t = m_{io} q_x^t / q_{xo} \quad (B-7)$$

Pool Source Zones

Given the higher NAPL saturation in pools and the corresponding reduction in water permeability, as well as the occurrence of some pools that form in topographic depressions on the surface of a low-permeability layer, a relatively small flux of groundwater will occur through the body of the pool.

To facilitate a comparison of the mass discharge which may occur through pool sub-zones relative to the discharge arising from surface dissolution, NDM incorporates the flexibility of simulating the rate of reduced water flow at various depths within a NAPL pool. NDM also incorporates the option of specifying an average Sn_{io} and krw_i for use in estimating the initial mass discharge through the NAPL source zone based on Equation B-5, or to specify a mass discharge of zero based on the assumption that the relative permeability in the pool layer is negligible relative to the mass discharge from the surface of the pool.

McWhorter and Kueper (1996) document the following equation for estimating the elevation in a pool corresponding to an effective saturation:

$$z = T - \frac{P_o}{\Delta\rho g} \left[\left(\frac{S_w - S_{wr}}{S_m - S_{wr}} \right)^{-1/m} - 1 \right]^{1-m} \quad (B-8)$$

where z refers to an elevation in a pool layer with height T , P_o is the reference capillary pressure defined as $\rho_w g / \alpha$, where α [L^{-1}] and m [dim.] are capillary pressure-saturation curve coefficients defined by Van Genuchten (1980), ρ_w is the density of water [ML^{-3}], g is the gravitational acceleration constant [LT^{-2}], $\Delta\rho$ is the difference between NAPL and water density [ML^{-3}], S_w is the water saturation, S_{wr} is the irreducible water saturation, and S_m is the maximum water saturation.

Re-arranging the above equation and solving for $S_n=1-S_w$ at elevation z gives

$$S_n(z) = 1 - S_{wr} - (S_m - S_{wr}) \left[1 + \left(\frac{\alpha \Delta\rho (T-z)}{\rho_w} \right)^{\frac{1}{1-m}} \right]^{-m} \quad (B-9)$$

Van Genuchten (1980) defines the relative water permeability for a two-phase system as

$$krw = Se_{krw}^{1/2} \left[1 - (1 - Se_{krw}^{1/m})^m \right]^2 \quad (B-10)$$

where Se_{krw} , the effective saturation used to estimate relative water permeability, is given by

$$Se_{krw} = \frac{S_w - S_{wr}}{1 - S_{wr}} \quad (B-11)$$

To estimate the total mass discharge through a pool layer with variable $S_n(z)$, the pool layer is vertically discretized into m layers with uniform thickness Δz . The NAPL saturation in each layer (S_{nim}) is calculated by substituting the pool height (h_i) for T in Equation B-8. The effective saturation Se_{krw} is calculated by substituting $S_{wim}=1-S_{nim}$ for S_w in Equation B-11, and the relative water permeability in layer m of the pool source zone i (krw_{im}) is then calculated using Equation B-10. The mass discharge arising from NAPL dissolution into groundwater flowing through source zone i at time step t is then calculated by summing the depth-specific discharges using

$$Md_{i,thru}^t = \left(\sum_{m=1}^{nlay} krw_{im} q_x^t C_{eff}^t w_i \Delta z \right) f_i^t f_{ed1}^t \quad (B-12)$$

Equation B-12 includes a time-dependent enhanced dissolution multiplier, which may be used to represent enhanced dissolution periods within an overall model simulation (e.g. EISB or Strategic Pump-and-Treat). Note that NDM does not represent potential mobilization of NAPL that may occur with some in-situ remediation technologies. Care must be exercised during in-situ remediation to ensure that expansion of the source zone does not occur.

B.4 Sub-Zone Surface Discharge

NAPL pools are typically characterized by a relatively limited NAPL-water interfacial area at the surface of pools where dissolution into flowing groundwater occurs. Solute transport at this surface interface is driven by transverse vertical dispersion. The solute transport equation is

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$$\theta \frac{\partial C}{\partial t} = \theta D_z \frac{\partial^2 C}{\partial z^2} - q_x \frac{\partial C}{\partial x} \quad (\text{B-13})$$

where C is the solute concentration [ML^{-3}], D_z is the hydrodynamic dispersion coefficient [L^2T^{-1}], and q_x is specific discharge [$\text{L}^3\text{L}^{-2}\text{T}^{-1}$]. In this form of the advection-dispersion equation, the hydrodynamic dispersion coefficient is calculated using

$$D_z = \alpha_{TV} v_x + D_e, \quad \text{and} \quad D_e = \tau D_o \quad (\text{B-14})$$

where α_{TV} is the transverse vertical dispersivity [L], $v_x (=q_x/\theta)$ is the average linear groundwater velocity [LT^{-1}], D_e is the effective diffusion coefficient [L^2T^{-1}], τ is the tortuosity coefficient, and D_o is the free-water molecular diffusion coefficient [L^2T^{-1}].

In some cases, the above equation B-13 is written as

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_x \frac{\partial C}{\partial x} \quad (\text{B-15})$$

where the hydrodynamic dispersion coefficient and effective molecular diffusion coefficient are estimated based on Equation B-14. In contrast, Hunt et al. (1988) expressed the advection dispersion equation based on an alternative form of the governing equation

$$\theta \frac{\partial C}{\partial t} = D_z^* \frac{\partial^2 C}{\partial z^2} - q_x \frac{\partial C}{\partial x} \quad (\text{B-16})$$

where the adjusted hydrodynamic dispersion coefficient is calculated using

$$D_z^* = \alpha_{TV} q_x + D_e^*, \quad \text{and} \quad D_e^* = \theta \tau D_o \quad (\text{B-17})$$

In other words, when specific discharge is used in the advection term of the governing equation and for calculating mechanical dispersion, it is important to include a porosity term in the term representing the effective molecular diffusion coefficient.

Analytical Solution for Mass Discharge from a Pool Surface

Based on the analytical solution cited by Johnson and Pankow (1992) for the steady-state form of Equation B-15, mass discharge from dissolution along the surface of a pool with length L and width w is

$$Md = LwC_{eff}\theta \sqrt{\frac{4D_z v_x}{\pi L}} \quad (\text{B-18})$$

Hunt et al. (1988) present the analytical solution based on Equation E-16 as

$$Md = LwC_{eff} \sqrt{\frac{4D_z^* q_x}{\pi L}} \quad (\text{B-19})$$

Note that both Equations E-18 and E-19 yield the identical solution provided that θ is used to estimate v_x . Equation E-19 can be further re-arranged to yield

$$Md = \left(2LwC_{eff} \sqrt{\frac{q_x}{\pi L}} \right) \sqrt{\alpha_{TV} q_x + \theta \tau D_o} \quad (\text{B-20})$$

It is not clear whether θ should represent total or effective porosity, since both advection and diffusion contribute to solute transport to some degree during surface dissolution from a pool. From Equation B-20 it is clear that under high specific discharge conditions, mechanical dispersion will dominate over the effective molecular diffusion term and porosity will have a negligible influence on the mass discharge calculation. In low specific discharge environments, molecular diffusion is likely to dominate the hydrodynamic dispersion term and it is appropriate then to assign θ as total porosity. When considering the middle case where mechanical dispersion and effective molecular terms are equal in a fine sand, the total porosity may be twice as high as effective porosity (e.g. 0.40 vs. 0.20, respectively). In this case, mass discharge calculated using total porosity is approximately 20% higher than the discharge that would be calculated using effective porosity. There is a smaller range for total vs. effective porosity for a coarse sand (e.g. 0.35 to 0.275), resulting in a smaller difference for mass discharge calculated based on total versus effective porosity.

Given that these differences are relatively minor when compared to uncertainty in specific discharge or pool dimensions, and that total porosity is more directly measured at the site and more applicable under conditions of low specific discharge, it is recommended that the total porosity be used when estimating mass discharge on the basis of Equation B-20.

It is also recommended that the solution in Equation in B-20 be used for estimating mass discharge instead of Equation B-18, since v_x is typically calculating using effective porosity which is not the appropriate porosity to use in Equation B-18 for sites where transport is diffusion-dominated.

Based on the analytical solution presented in Equation B-20, NDM estimates the mass discharge from the surface of source zone i discretized in $j=1$ to grid cells using the equations

$$Md_{i,surf}^t = \left[\sum_{j=1}^{ncol} (Md_{i,surf,j}^t - Md_{i,surf,j-1}^t) \right] \quad (\text{B-21})$$

$$Md_{i,surf,j}^t = \left[x_{ij} w_i C_{eff}^t \sqrt{\frac{4D_z^t q_x^t}{\pi x_{ij}}} \right] f_{ed2}^t f_{surf} \quad (\text{B-22})$$

where x_{ij} is the length from the upgradient edge of the pool to the downgradient end of column j , $f_{ed2}^t \geq 1$ is a multiplier that is used during the portion of the simulation where a dissolution enhancement technology has been implemented, and f_{surf} is a multiplier that is equal to 0, 1, or 2

to represent the number of source zone surfaces where dissolution is occurring into overlying and/or underlying groundwater. f_{surf} may also be assigned a real number to represent a multiplier for accelerated specific discharge adjacent to the boundary surface of the NAPL sub-zone. For a pool source zone, typically $f_{surf}=1$ (e.g. when the pool is underlain by a low-permeability silt or clay). For a residual NAPL layer that has transmissive layers both above and below it, $f_{surf}=2$.

B.5 Diffusive Mass Discharge Into and Out of Low-Permeability Units

Seyedabbasi et al. (2012) present the analytical equations used to estimate mass discharge associated with both forward diffusion into the low-permeability unit (which is based on work presented in Parker et al., 1994), as well as for back-diffusion into the more transmissive unit.

Mass discharge from a single component NAPL source zone i to a low-permeability unit is estimated based on

$$Md_{i,diff}^t = \phi L_i w_i C_s \sqrt{\frac{R\tau D_o}{\pi t}} \quad ; \quad t < t_{depletion} \quad (B-23)$$

where ϕ is total porosity in the low-permeability unit [L^3L^{-3}], C_s is solubility [ML^{-3}], R is the retardation coefficient in the low-permeability unit, τ' is the tortuosity coefficient for the low-permeability unit, and $t_{depletion}$ is the simulation time at which all NAPL in the source zone has been depleted. This equation is based on the assumption that the low-permeability unit is a semi-infinite domain; therefore, this equation is only valid when the low-permeability unit is sufficiently thick that significant mass does not diffuse through the exit boundary of the low-permeability unit. This equation also assumes a constant solubility in time in the source zone and therefore is not applicable for multicomponent NAPLs when effective solubility changes significantly over time.

The analytical solution for estimating the time-varying mass discharge associated with back-diffusion from the low-permeability unit into the depleted source zone is presented in Seyedabbasi et al. (2012) as

$$Md_{i,b-diff}^t = \phi L_i w_i C_s \left(\sqrt{\frac{R\tau D_o}{\pi t}} - \sqrt{\frac{R\tau D_o}{\pi(t-t')}} \right) \quad ; \quad t > t_{depletion} \quad (B-24)$$

The reader is referred to Seyedabbasi et al. (2012) for an evaluation of the relative longevity of plumes sustained by back-diffusion relative to the initial NAPL dissolution period. These analytical models may be used to compare the magnitude of the diffusive discharge from a NAPL pool, to surface and/or through-discharge. Generally, the diffusive discharge is much lower in magnitude, on average, relative to the other two types of mass discharge from a NAPL pool.

B.6 Multicomponent NAPL Dissolution

A version of NDM has been prepared to simulate multicomponent NAPL dissolution (NDM-MC). The present version of NDM-MC is limited in that surface discharge is not simulated; only through-discharge may be simulated for a multicomponent NAPL, and the maximum number of species in this current version is limited to three.

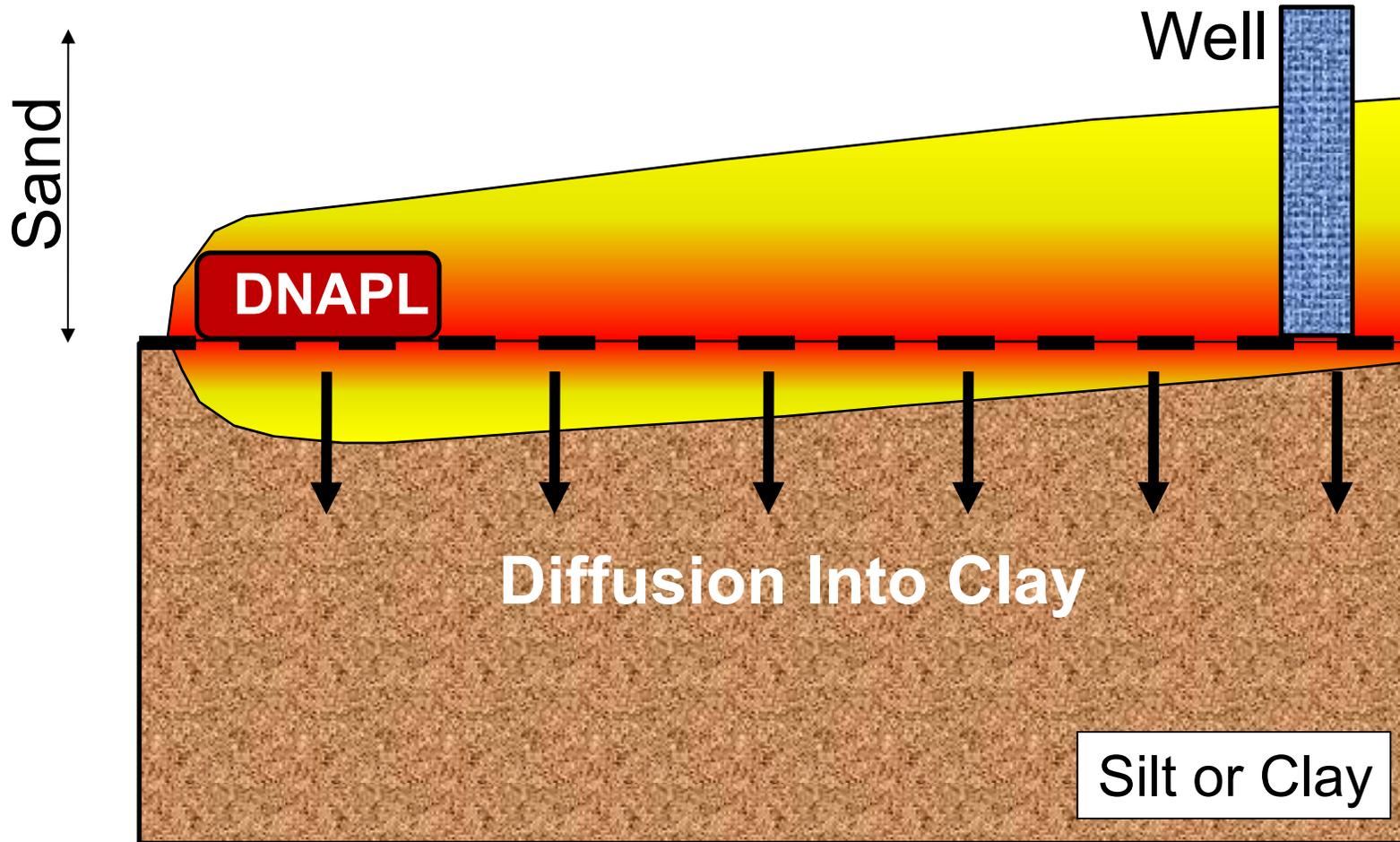
The model equations are similar to those described above for NDM, with the main difference being that the effective solubility for each species is calculated in each sub-zone grid cell at the end of each time step, based on an automated re-calculation of the species molar fraction in each cell. If an upgradient cell has a smaller effective solubility for a species than a downgradient cell, then mass will be dissolved from the downgradient cell to ensure that local equilibrium is achieved at the NAPL-water interface. Similarly, if an upgradient cell has a larger effective solubility than a downgradient cell, then mass will be re-dissolved into the NAPL in the downgradient cell to maintain equilibrium. The influence of intra-source by-passing may be simulated using one of the transient dilution factor equations (see Section A.3).

For further information regarding the availability of NDM-MC, please contact Grant Carey at Porewater Solutions (*email: gcarey@porewater.com; telephone: 613-270-9458*).

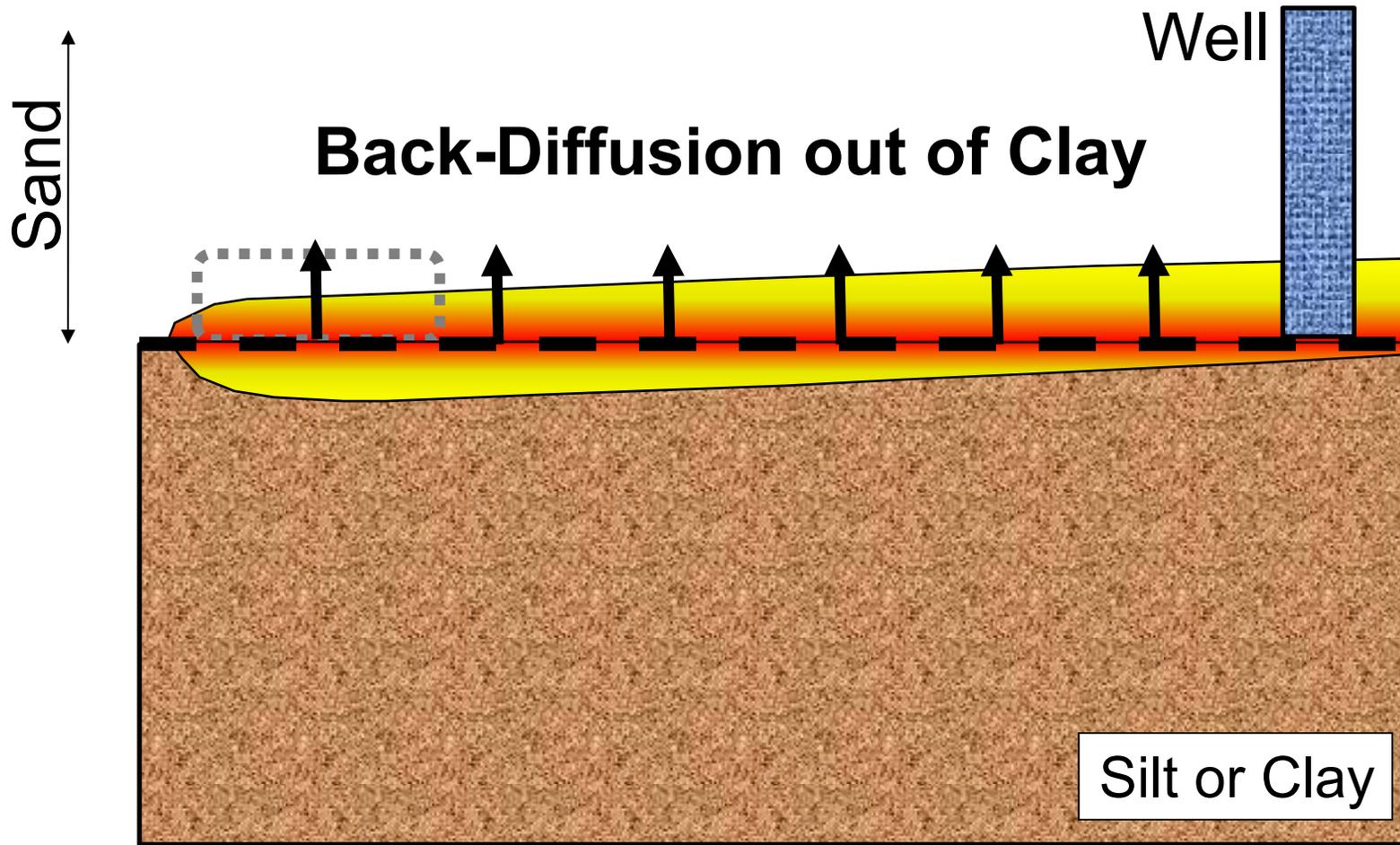
ISR-MT3DMS for Modeling Back-Diffusion Timeframe

Grant R. Carey
President
Porewater Solutions

Forward Diffusion

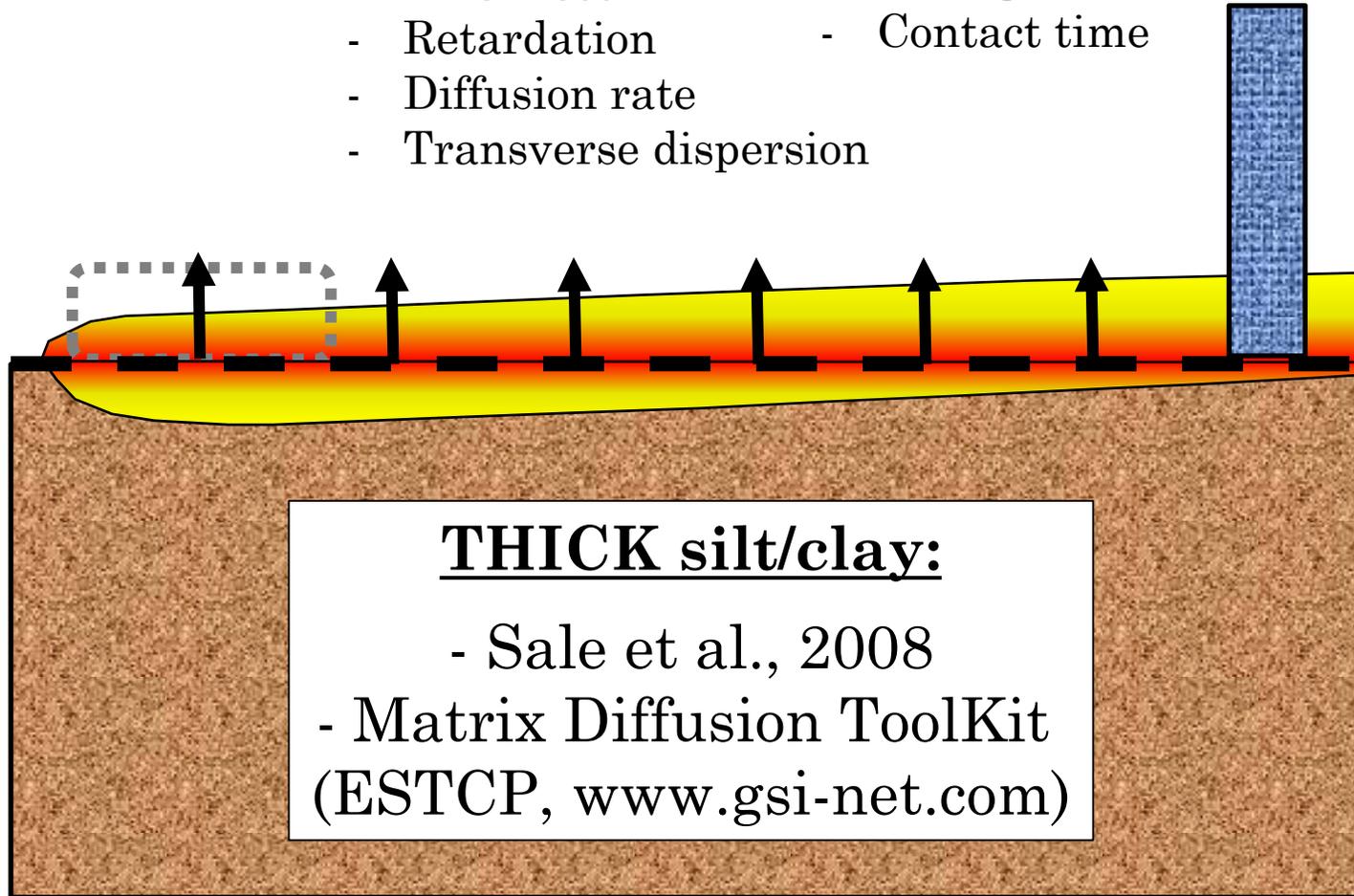


Back-Diffusion



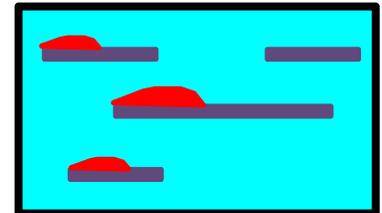
Remediation Timeframe?

- Influencing factors:
- Velocity
 - Thickness
 - Retardation
 - Diffusion rate
 - Transverse dispersion
 - Length of clay lens
 - Biodegradation
 - Contact time



Modeling Challenges

- Analytical solutions not available for:
 - Thin silt/clay lenses
 - Enhanced degradation rates
- Numerical models
 - Small grid spacing, time steps
 - Prohibitive for 3-D models
- ISR-MT3DMS: new approach



Introduction

- **Case Study #1** – Model limitations
- **ISR-MT3DMS** overview
- **Case Study #2** – Florida site (thin clay)
 - Model input estimation
 - ISR-MT3DMS proof of concept, verification
 - Timeframe sensitivity analysis

Case Study #1 – Ontario Site

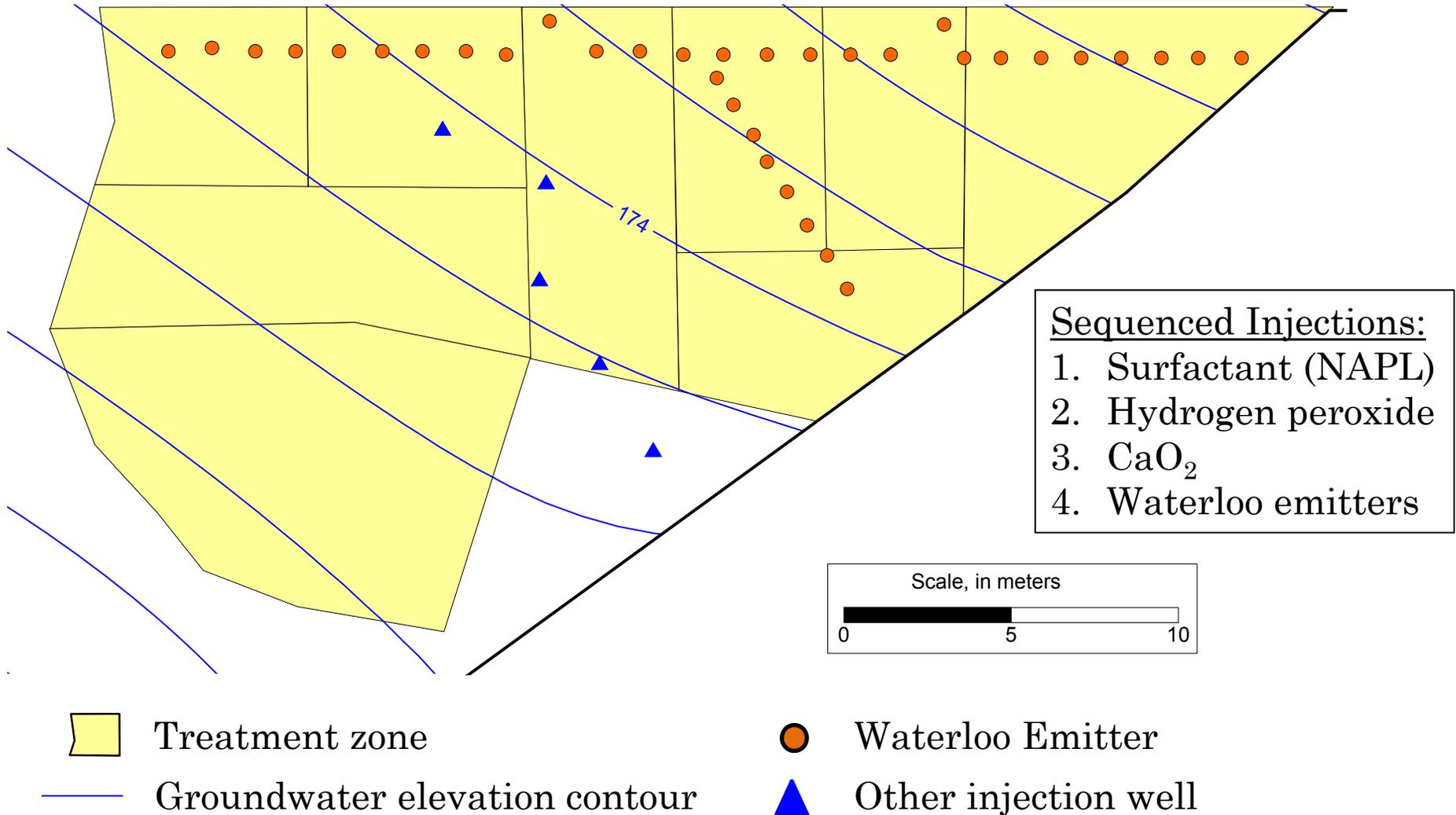


Acknowledgement:

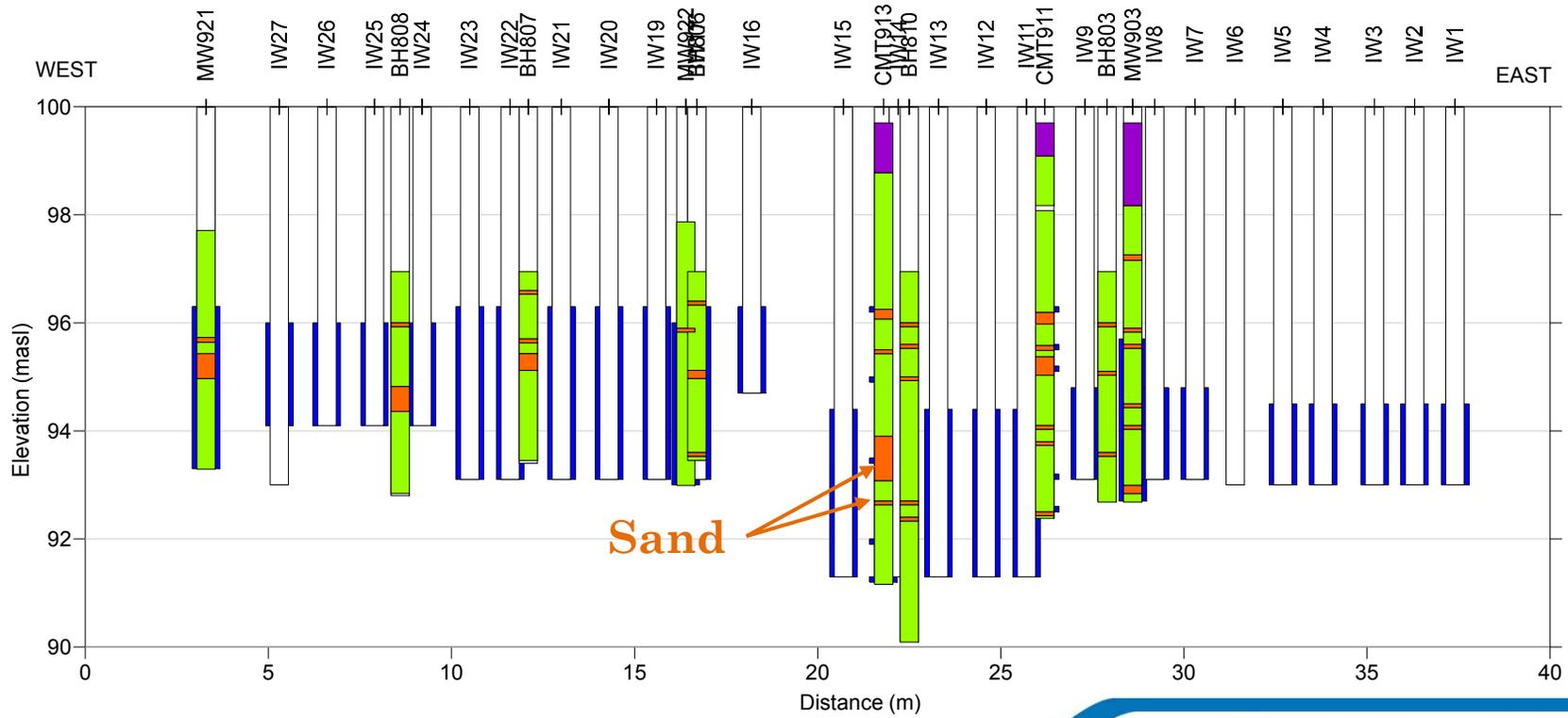
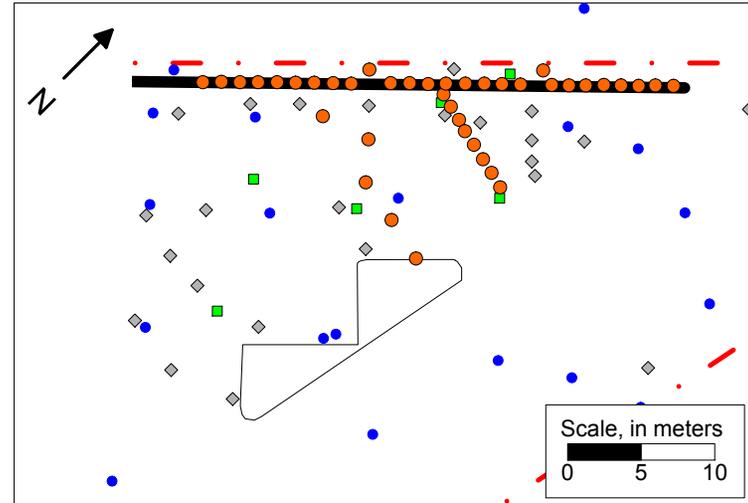
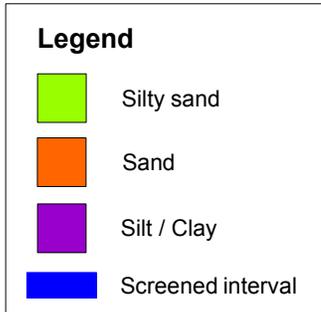
Rick McGregor, President
InSitu Remediation Services Limited

rickm@IRSL.ca

Case Study #1 – Ontario Site



Section K-K'



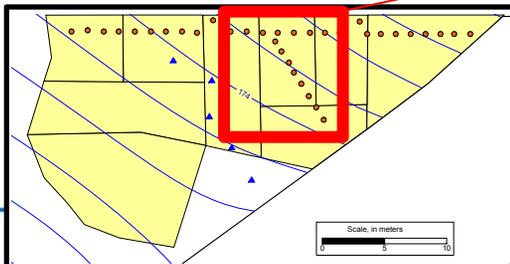
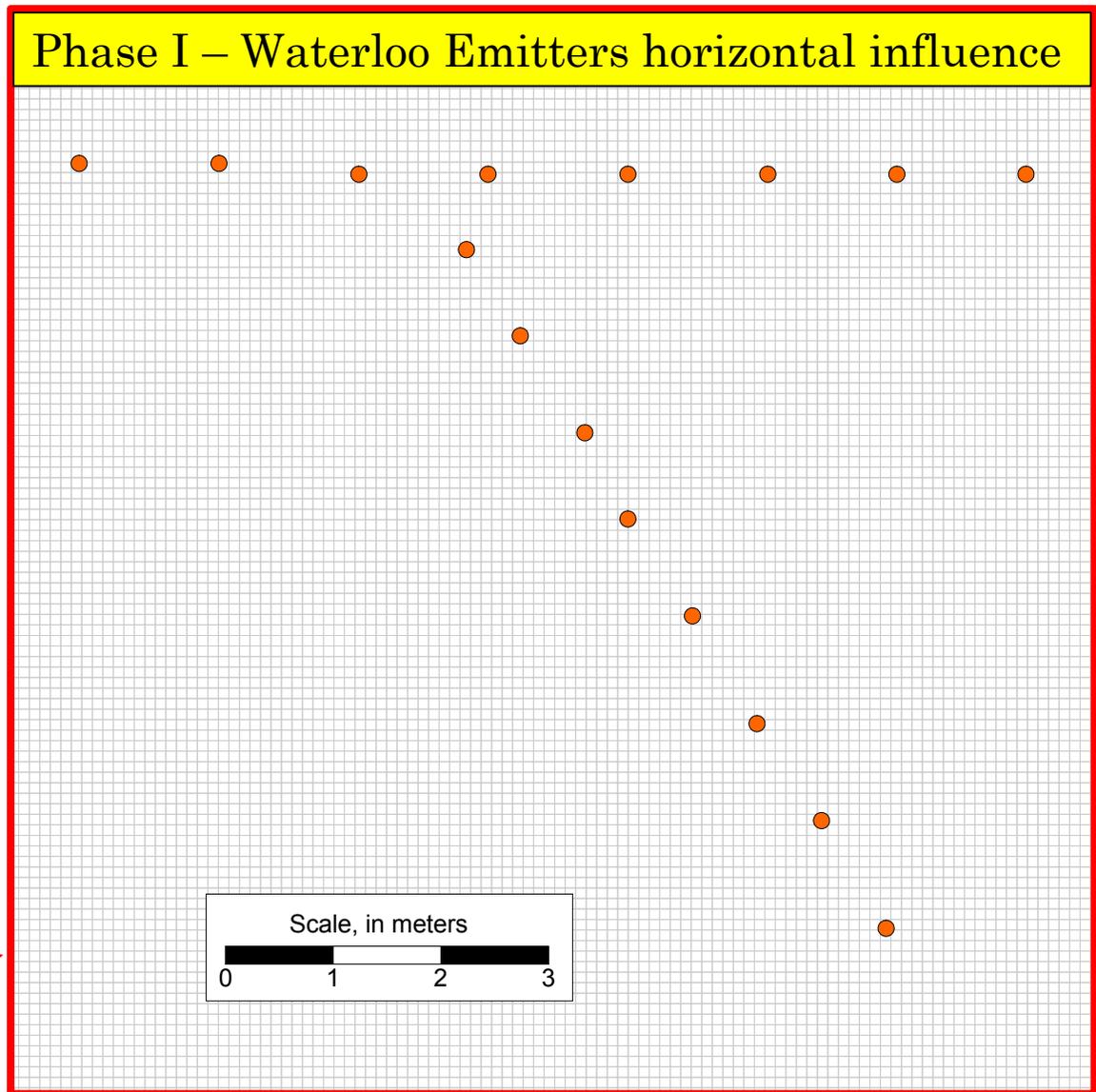
Model Grid

Minimum spacing = 4 inches
(Waterloo Emitter diameter)

2-D: 450 columns, 280 rows

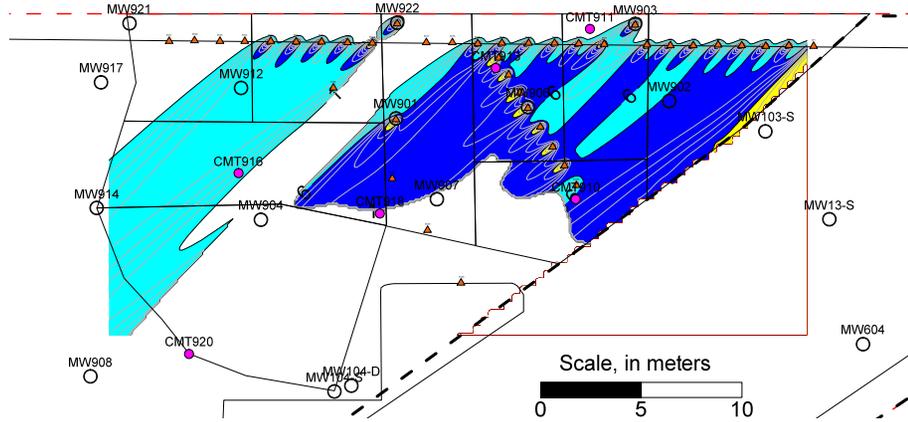
Time step = 0.05 d

Phase I – 5 solutes
(4-hour run-time)

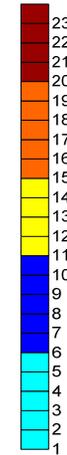


Phase I: Waterloo Emitters (t=3y)

Case 1: PHC $K_{oc} = 5,000 \text{ mL/g}$



DO (mg/L)



Electron Donors:

- GRO, DRO, Fe(II)

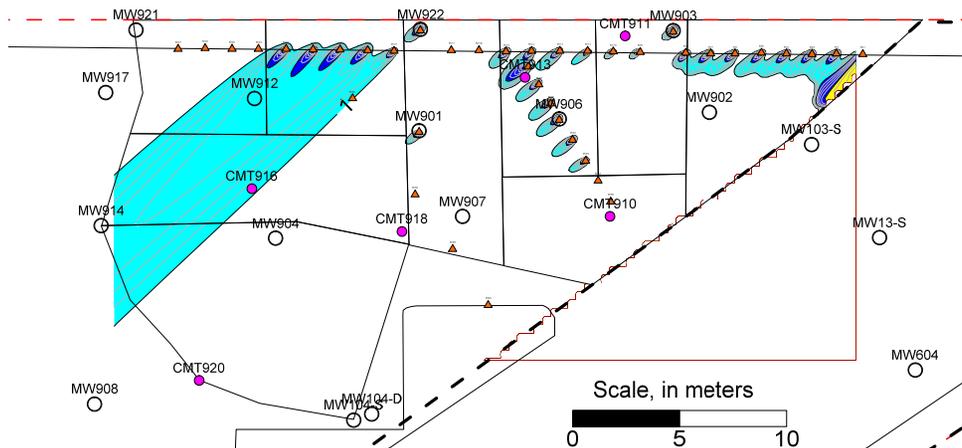
Electron Acceptors:

- DO, Fe(III)_s

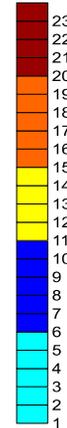
Reactions:

- Instantaneous or first-order
- Reductive dissolution

Case 2: PHC $K_{oc} = 50,000 \text{ mL/g}$



DO (mg/L)



Phase II model:

- Hydrogen peroxide
- CaPO
- GRO/DRO Conc. ↓
- **Diffusion into silt**

In Situ Remediation (ISR-MT3DMS)

MT3DMS v5.3

Dr. Chunmiao Zheng

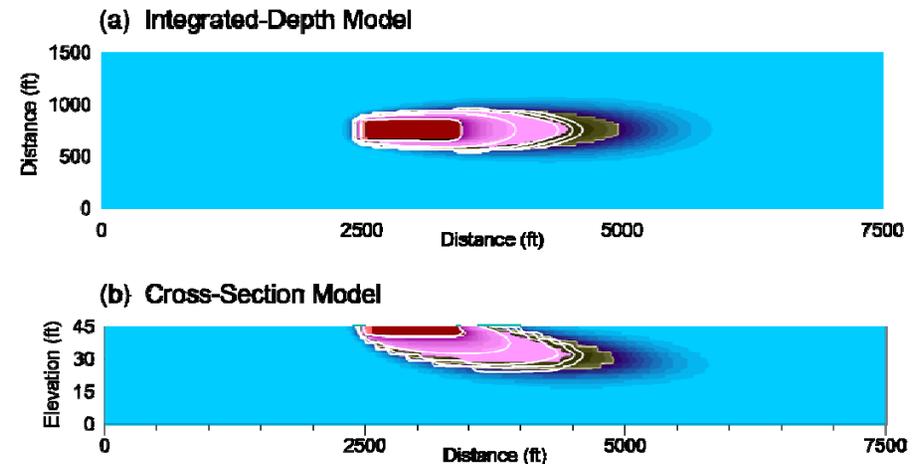
PUBLIC DOMAIN

Carey, Van Geel, and Murphy (1999)

In Situ Remediation (ISR-MT3DMS)

MT3DMS v5.3

BioRedox RCT package



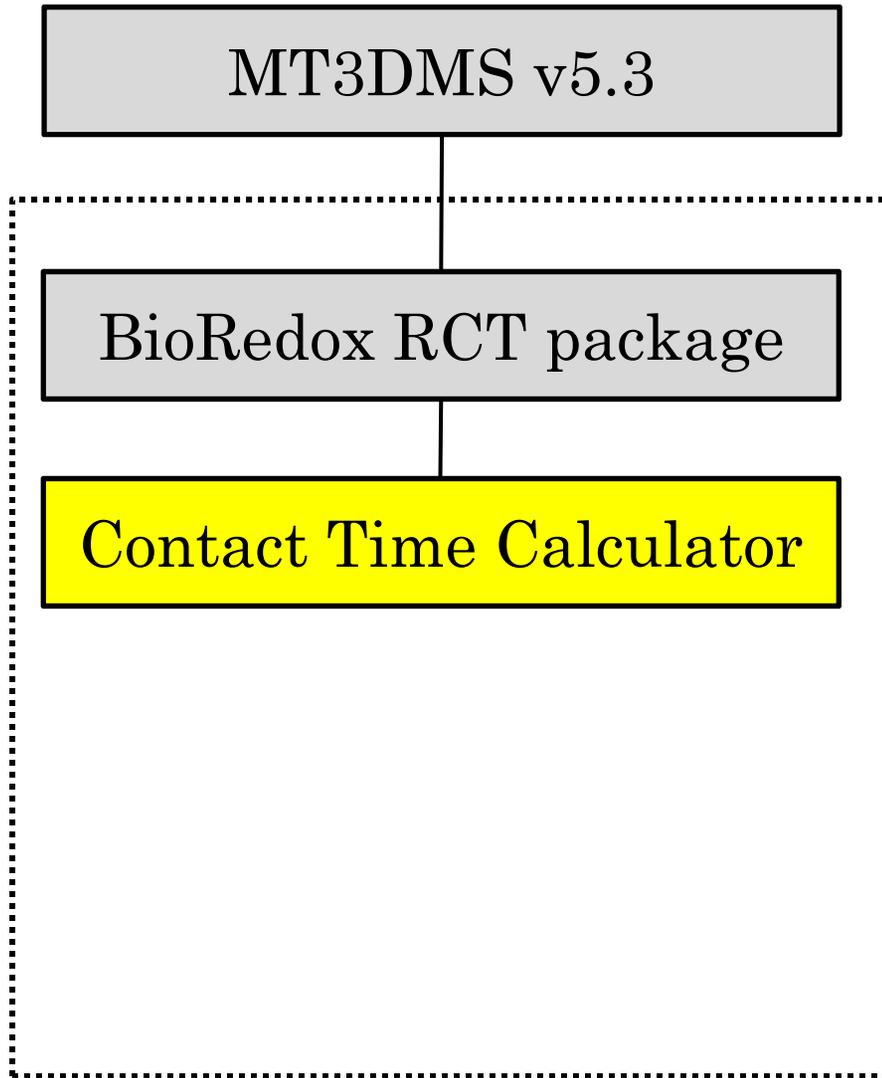
(BTEX concentration contours of 0.001, 0.01, 0.1, 1, and 10 mg/L)



- Flexible reaction framework
- Redox zone visualization
- Mineral precip./dissolution
- Rate stimulation/inhibition

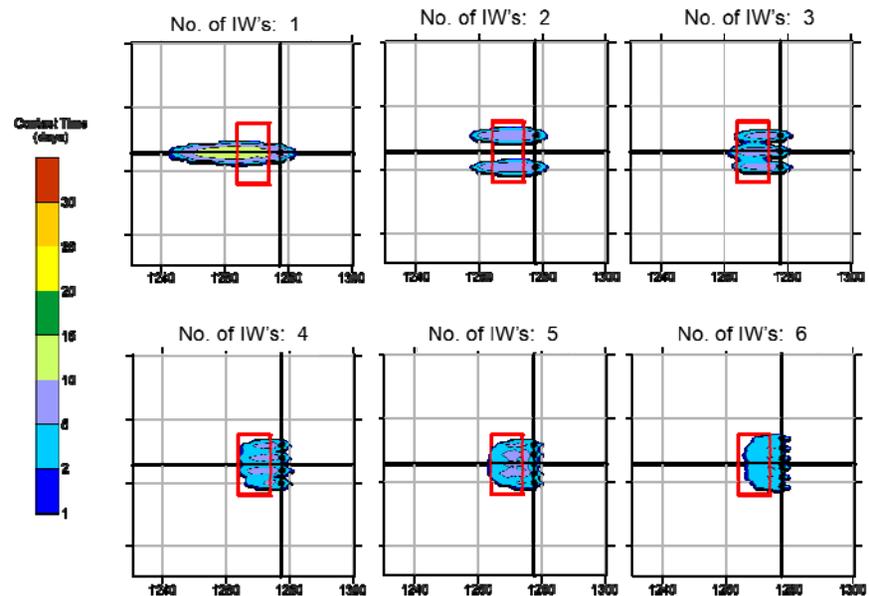
Carey, Van Geel, and Murphy (1999)

In Situ Remediation (ISR-MT3DMS)

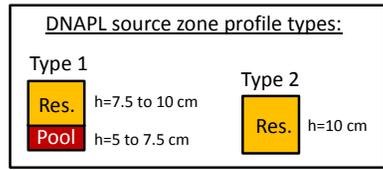
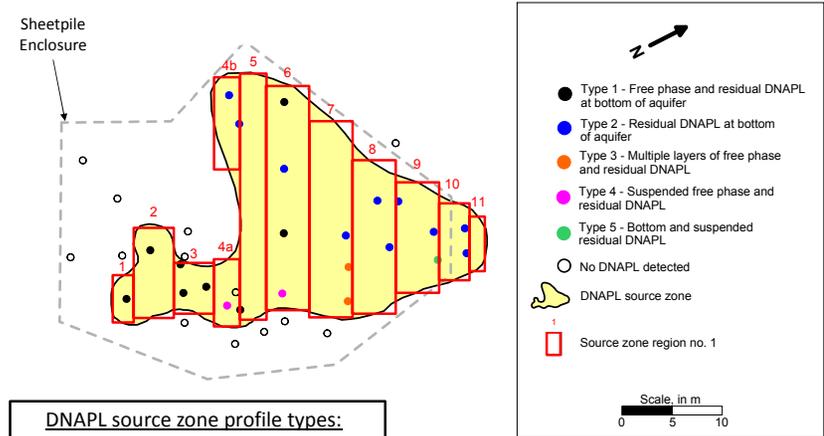
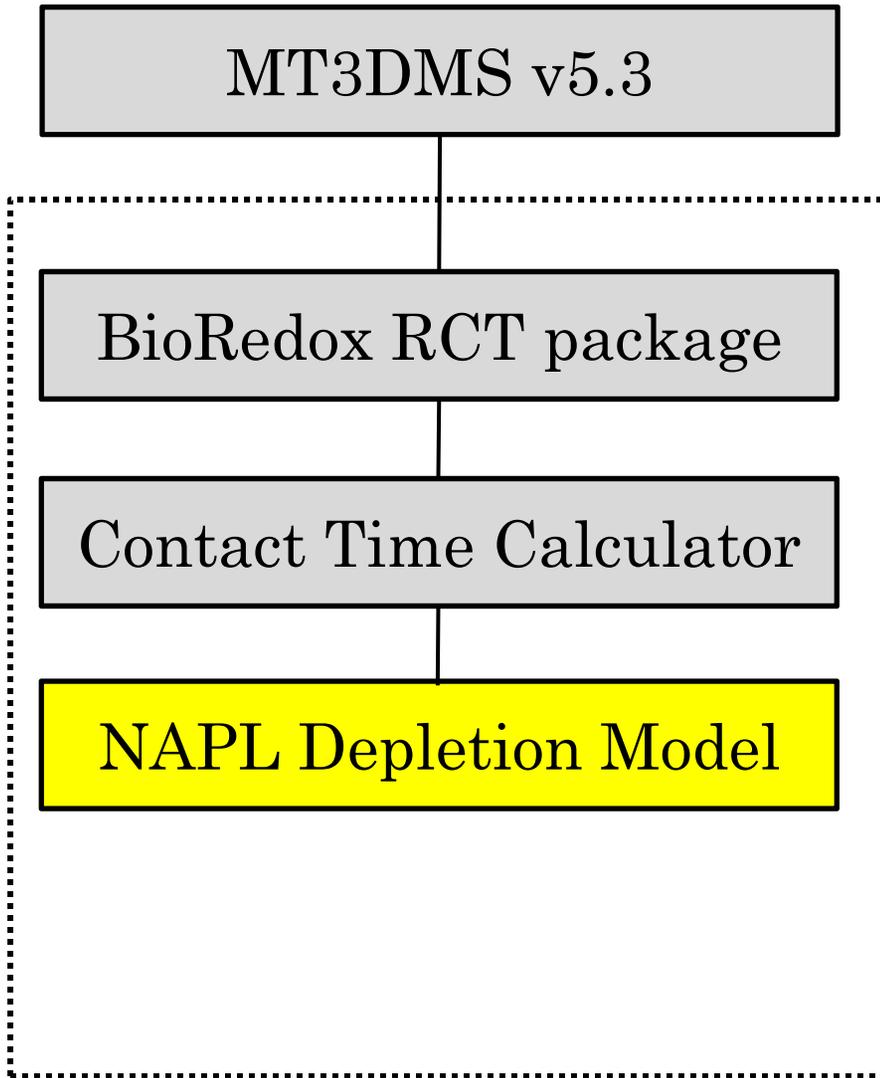


Optimization Metric

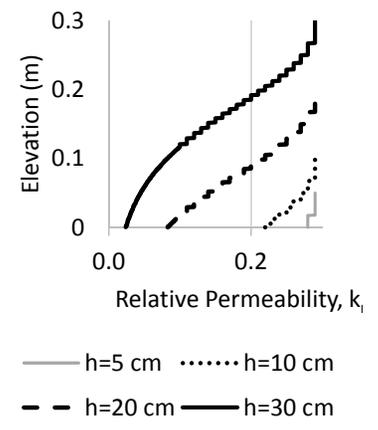
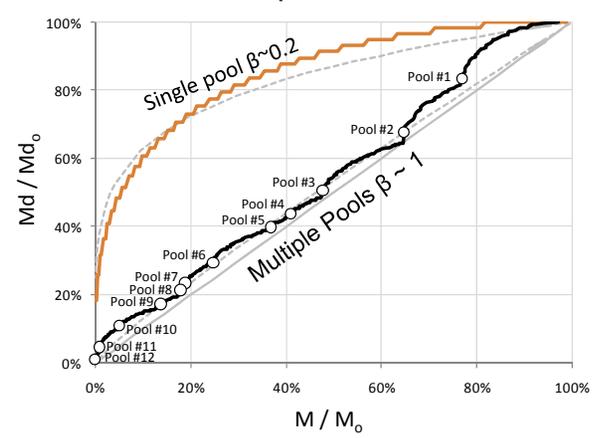
Injected Volume: 2000 L



In Situ Remediation (ISR-MT3DMS)



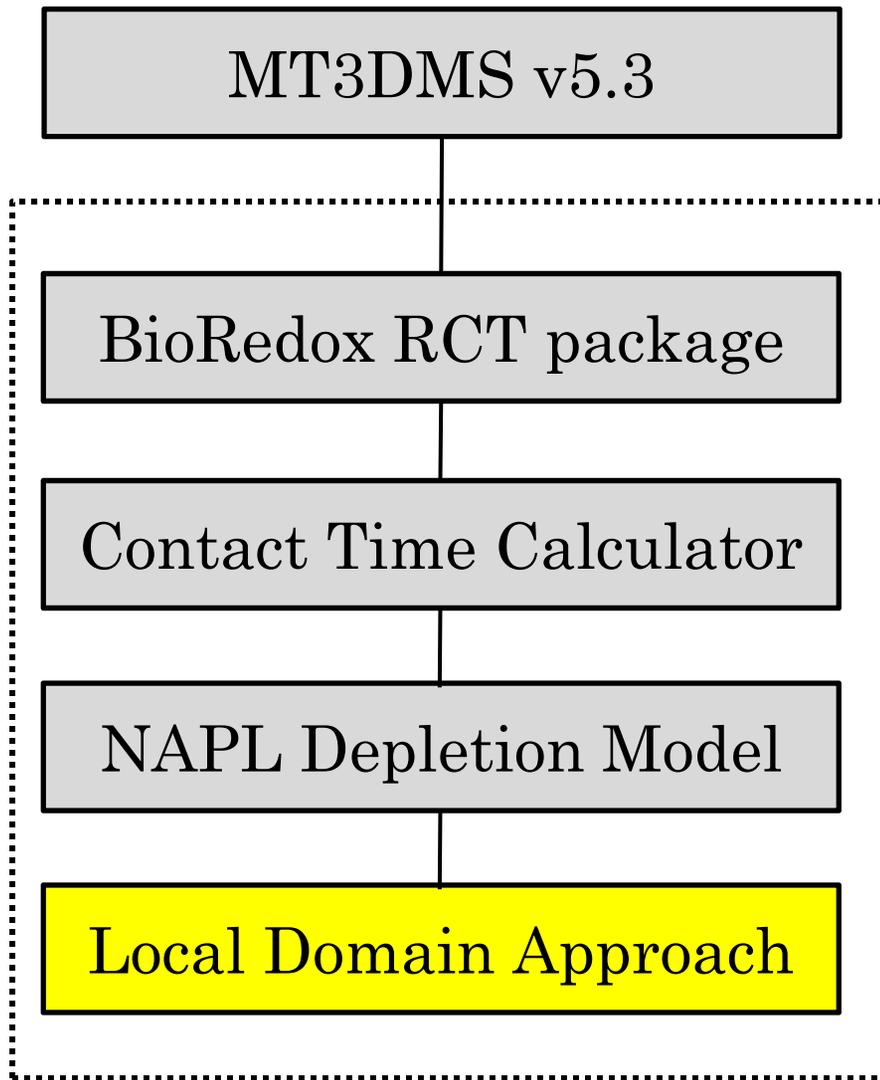
Parker et al., 2003
 Parker et al., 2004
 Chapman and Parker, 2005
 Stewart, 2002



Carey, McBean, and Feenstra (2014a,b; 2015a,b,c)



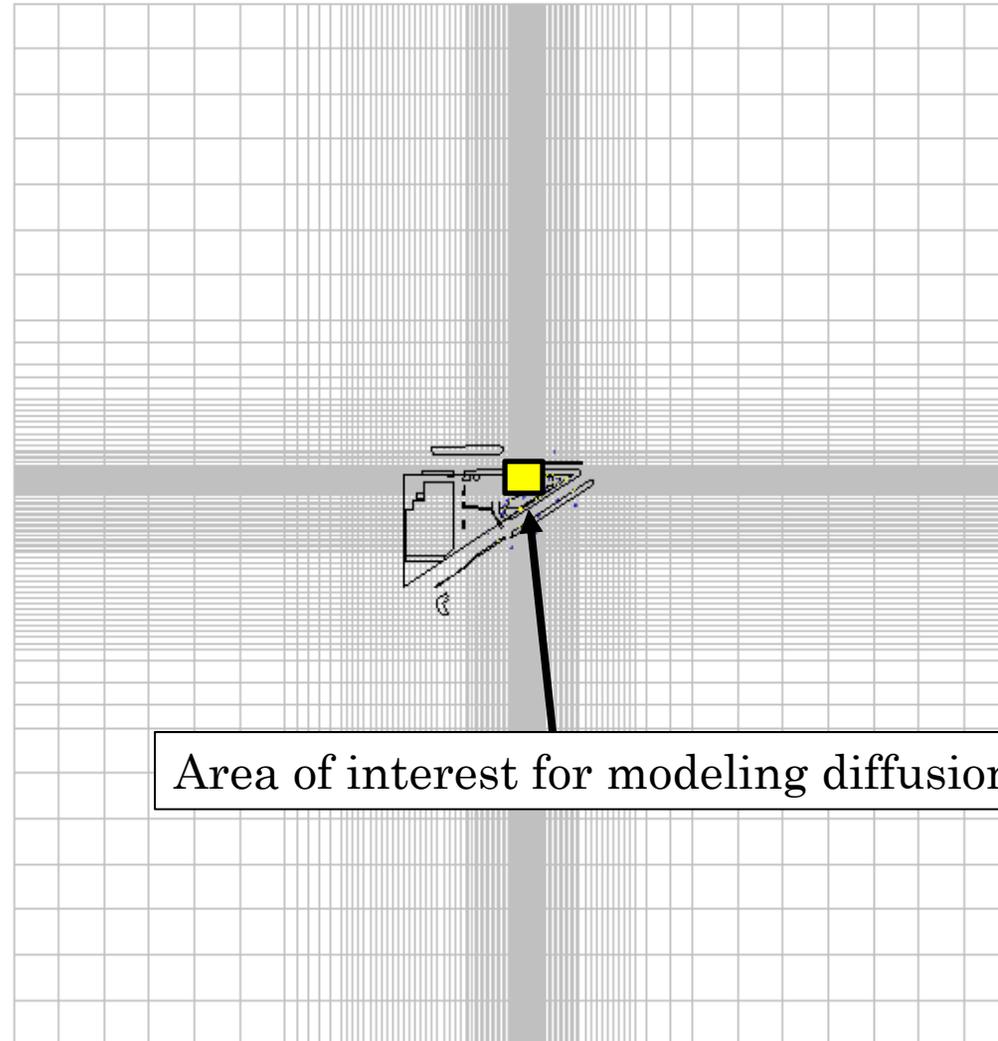
In Situ Remediation (ISR-MT3DMS)



Large model linked to local 1-D model(s).

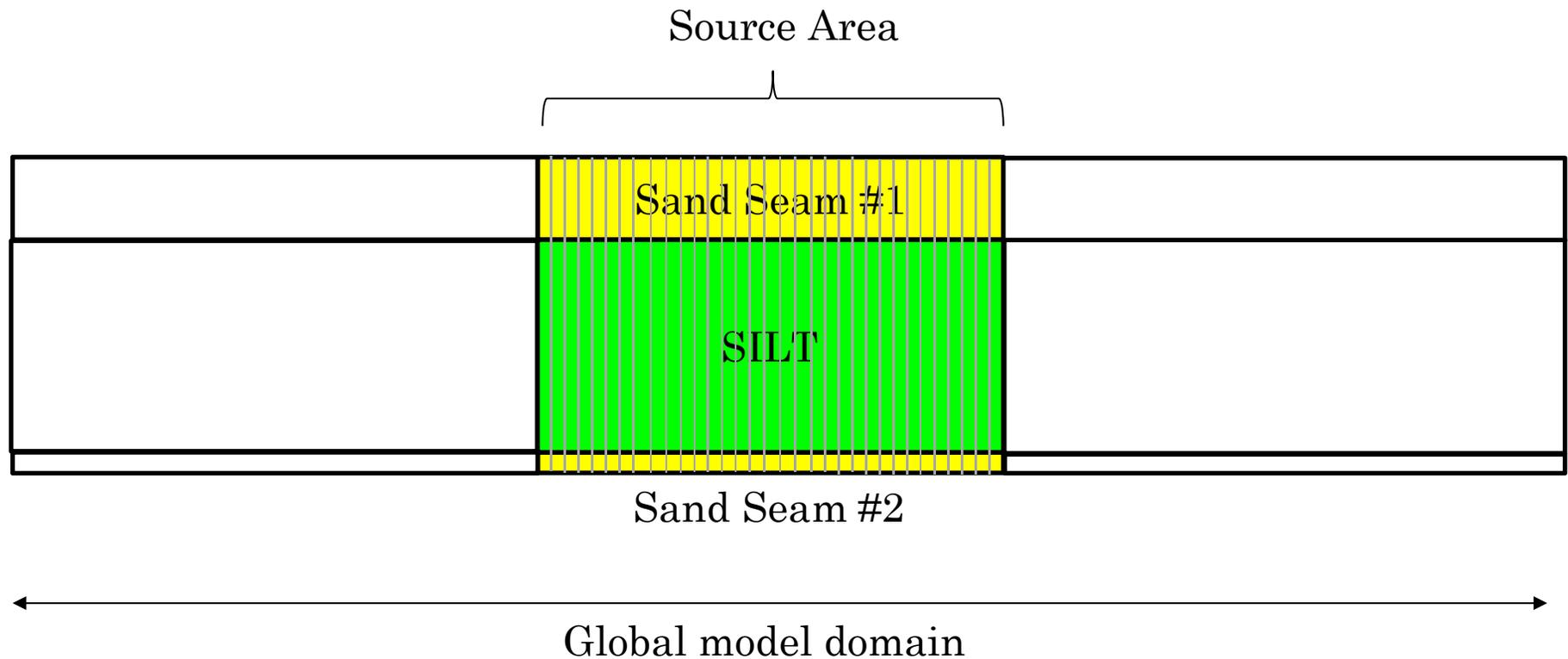
Local Domain Approach

Global Model Domain

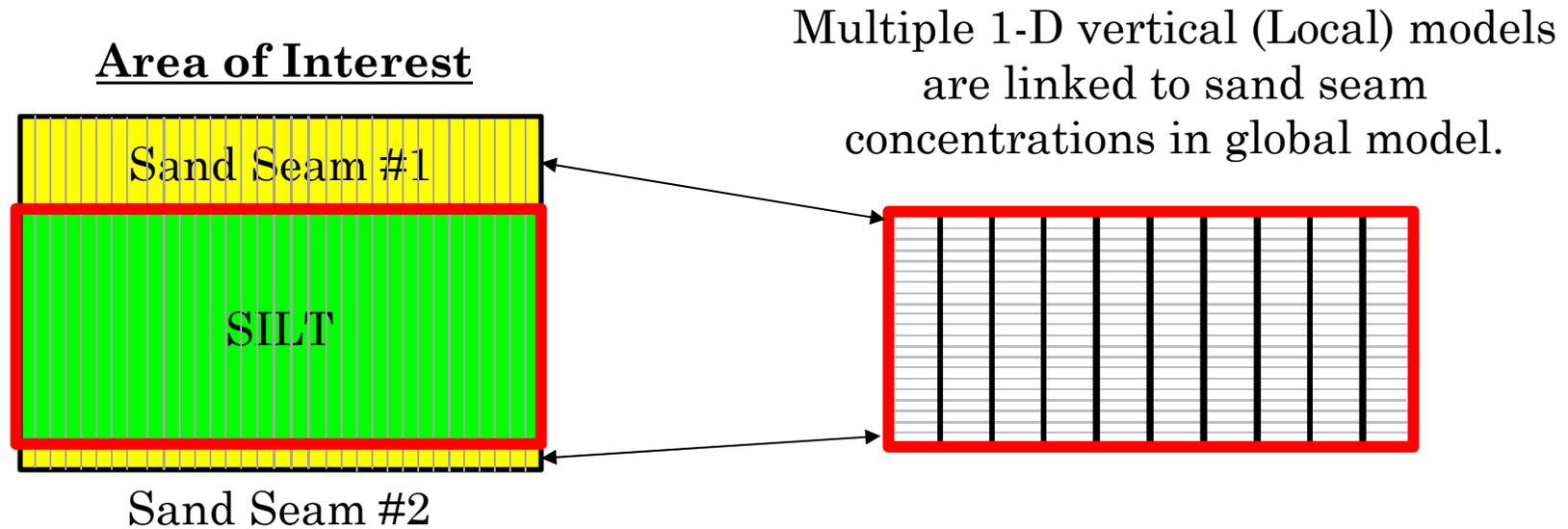


Area of interest for modeling diffusion

Cross-Section in Global Model (3 layers)¹⁸

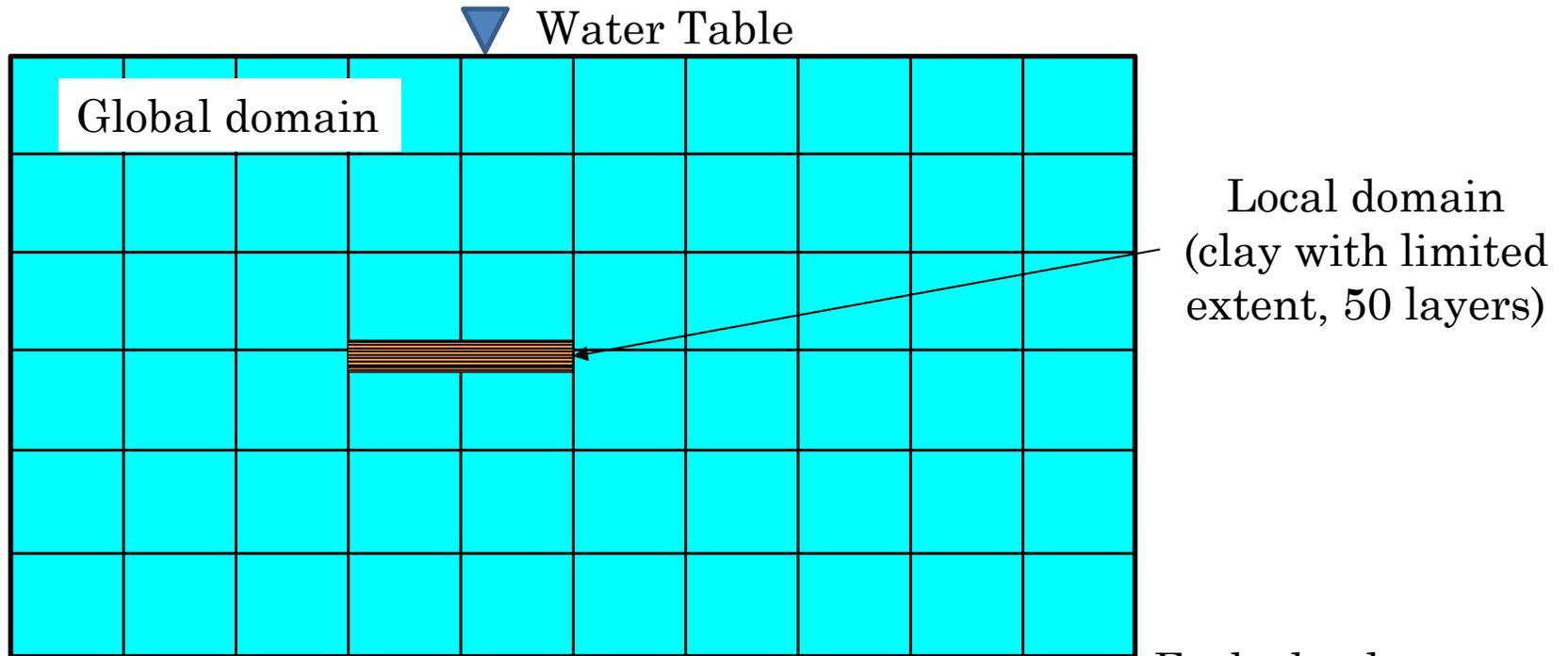


Local Model Domains for Silt (1-D Diffusion)

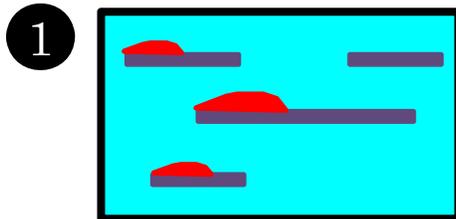


Silt layer is inactive to transport in global model.

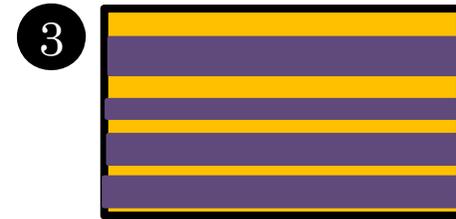
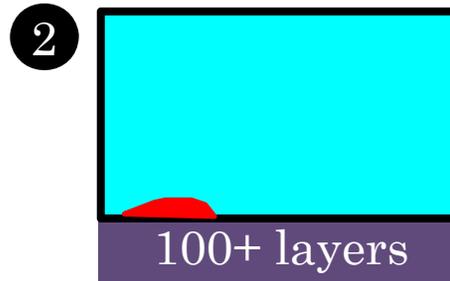
Local Domain Approach



Each clay lens:
20 to 100+ layers

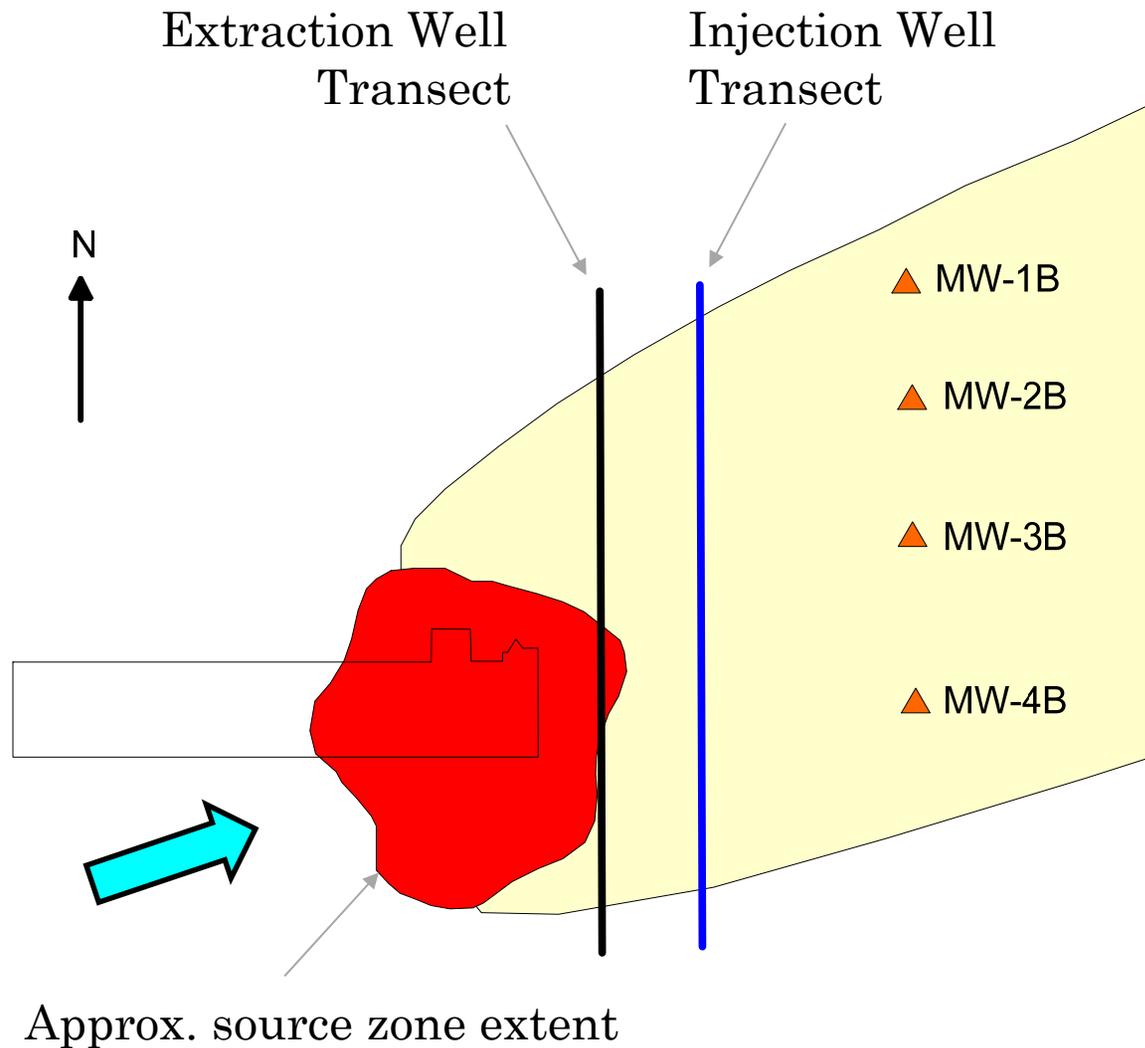


Each clay lens:
10 to 100+ layers



Case Study #2 – Florida Site

21

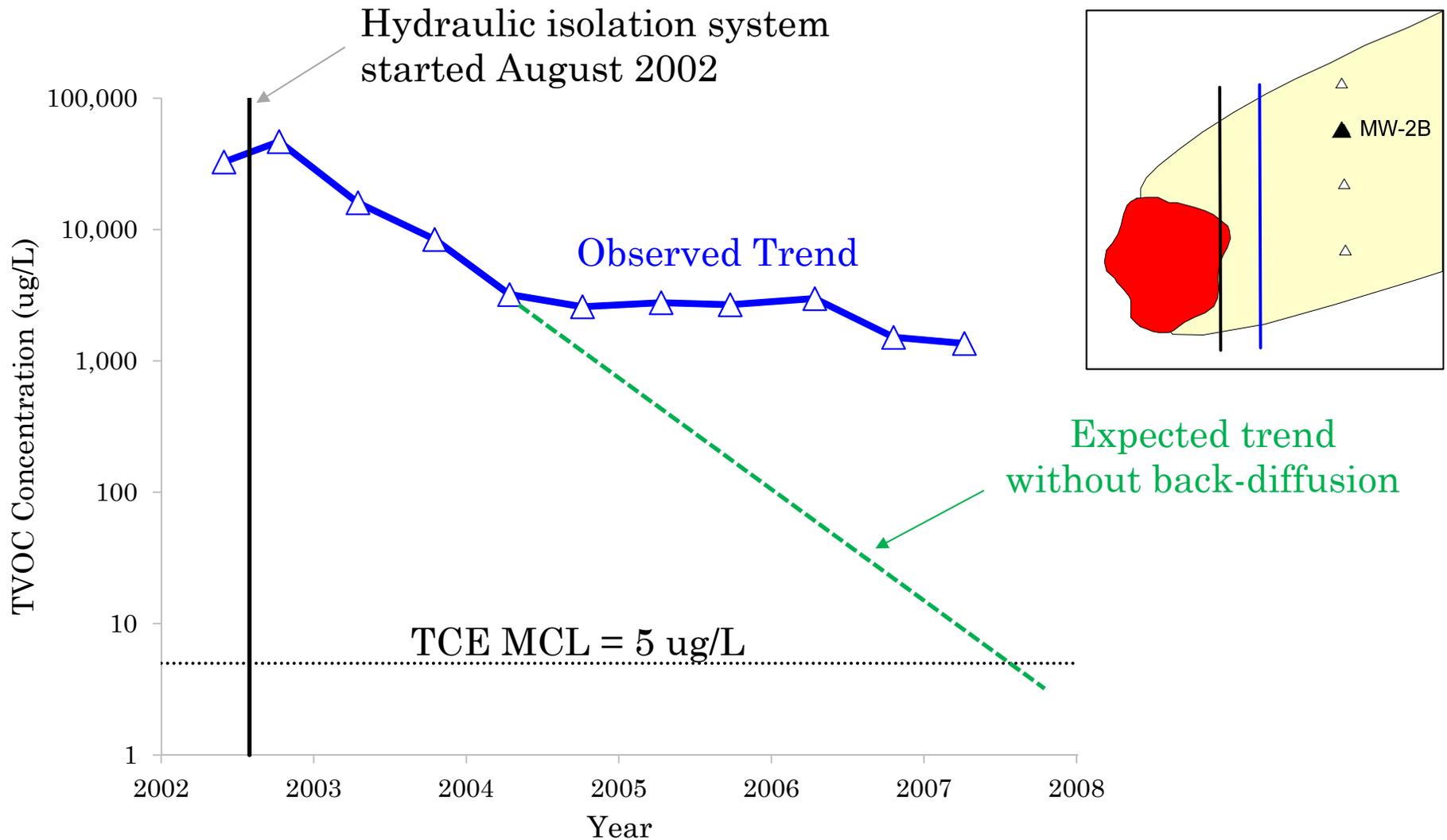


Site Characteristics

- Beach sand aquifer
- Continuous, thin clay layer across site
- Other discontinuous, thin silt/clay layers
- Multiple, thin suspended DNAPL layers in source zone

Source: Modified from Parker et al., 2008

TVOC Trend at MW-2B



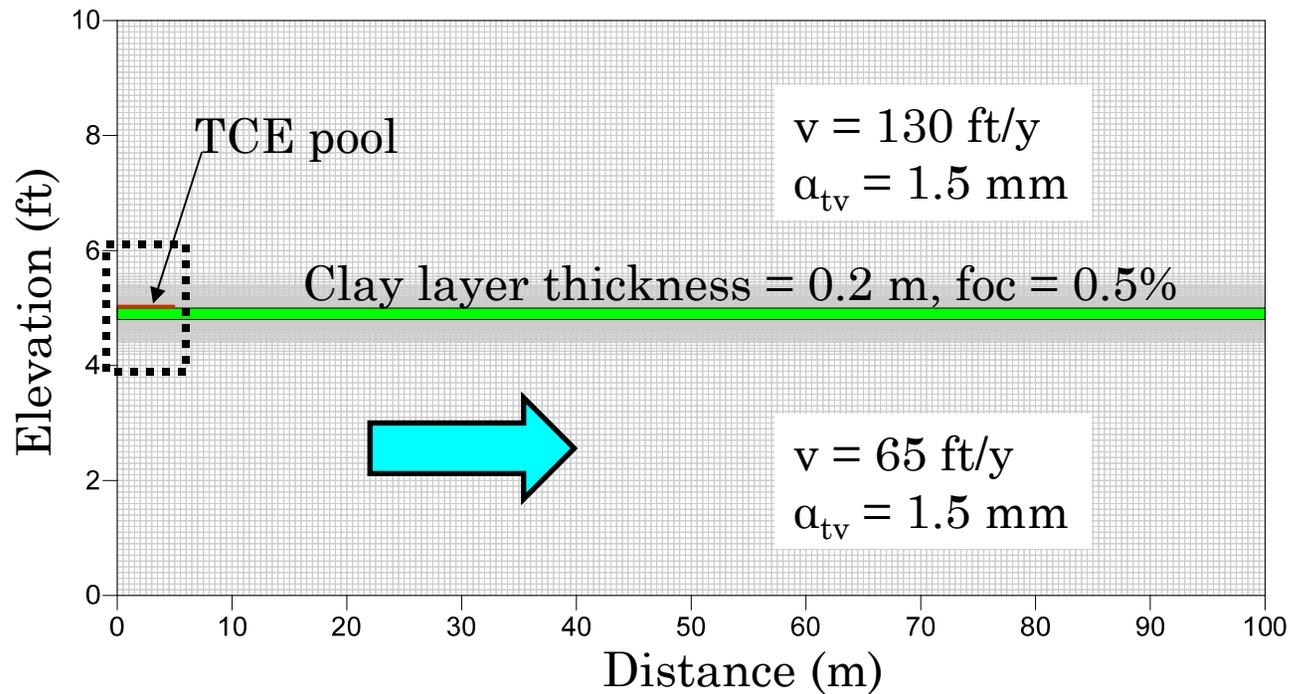
Source: Modified from Parker et al., 2008

2-D Model Grid

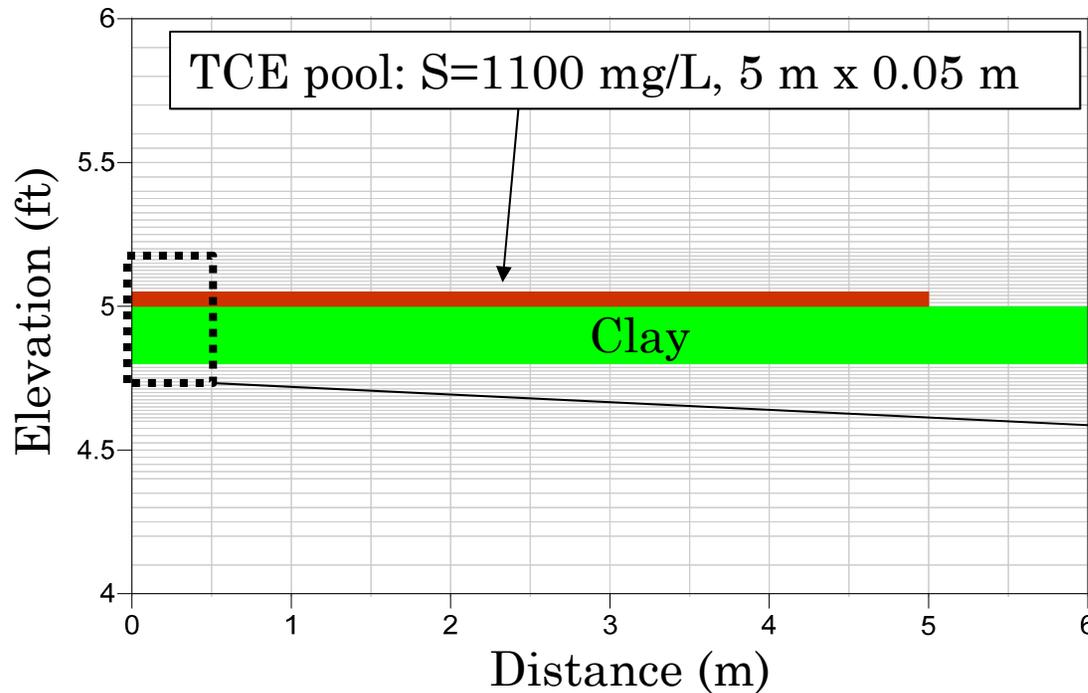
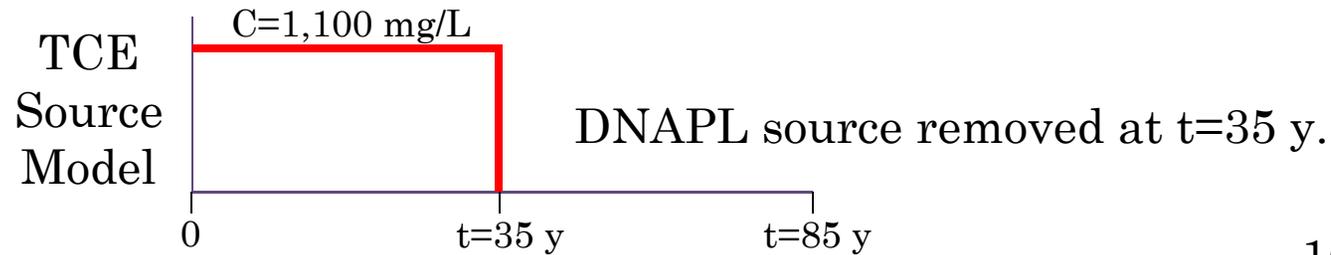
200 columns, 158 rows (layers)

Minimum grid spacing: $\Delta z = 1.25$ cm, $\Delta x = 0.5$ m

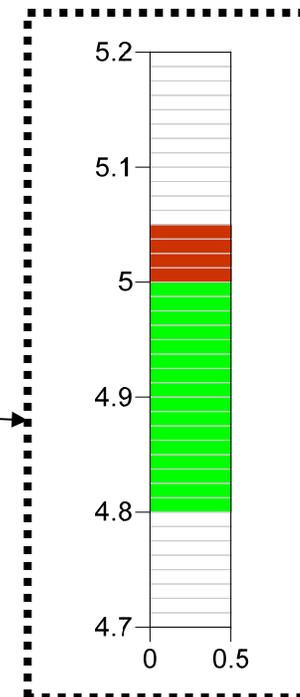
Run-time = 45 minutes for 85-y simulation ($\Delta t = 0.24$ d)



2-D Model Grid

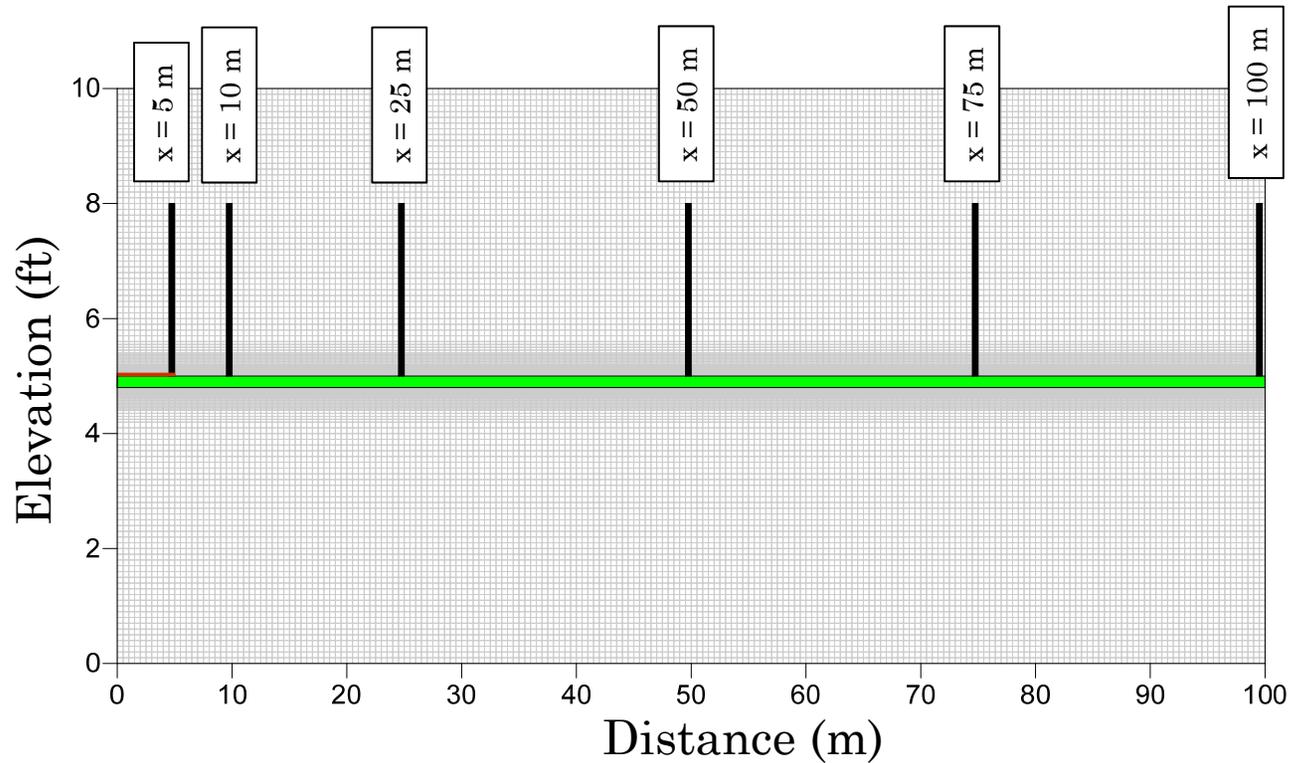


16 layers
in clay



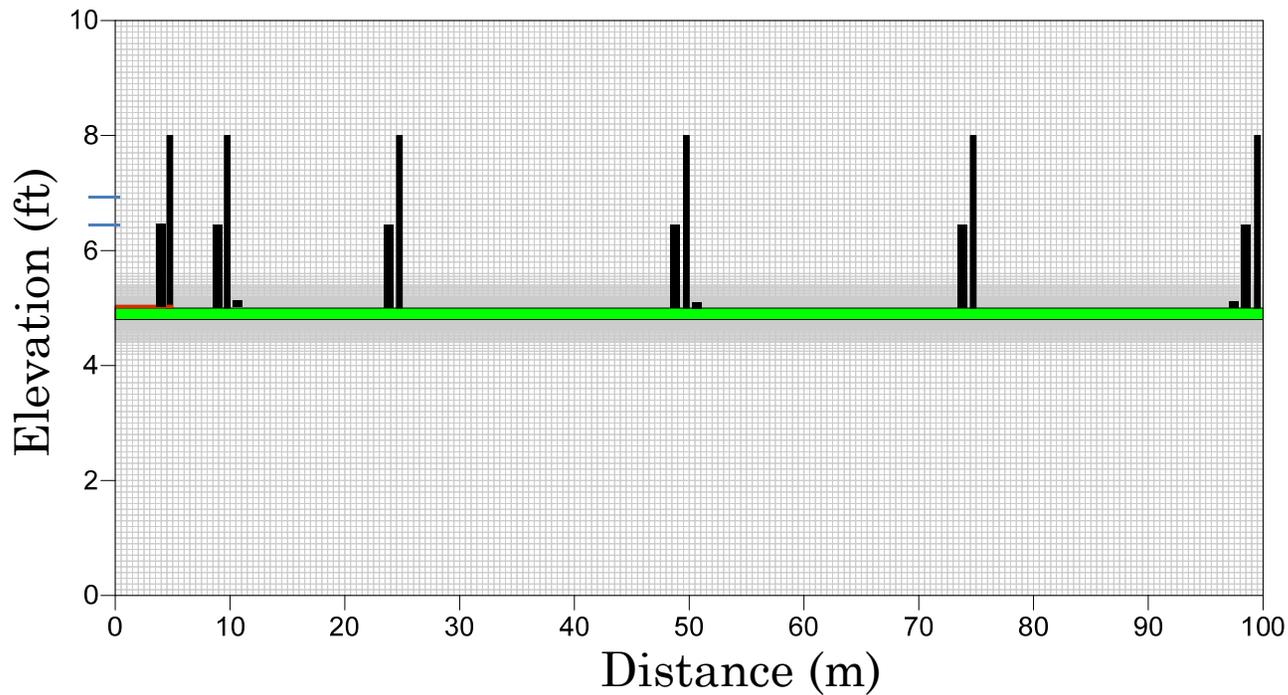
2-D Model: Horizontal Wells

RTF versus clay layer length? ($C < 0.005$ mg/L)



Multiple Well Screen Lengths

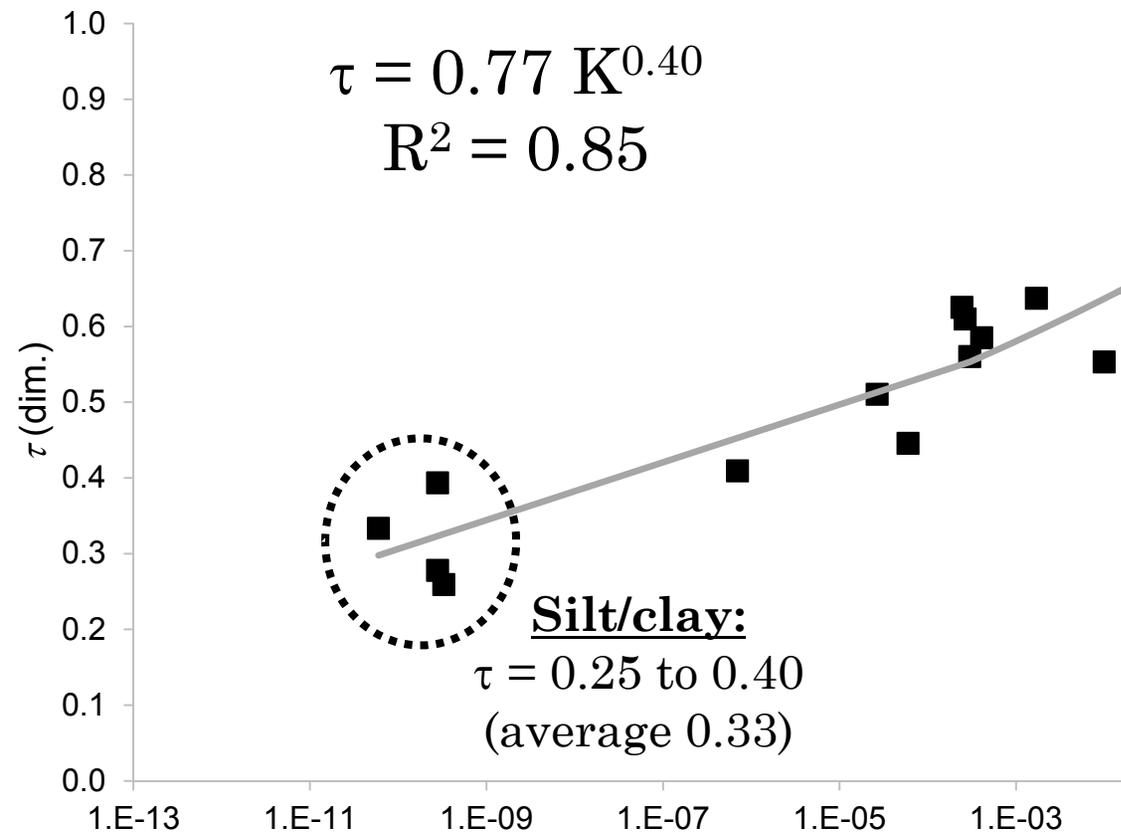
Influence of screen length on remediation timeframe?



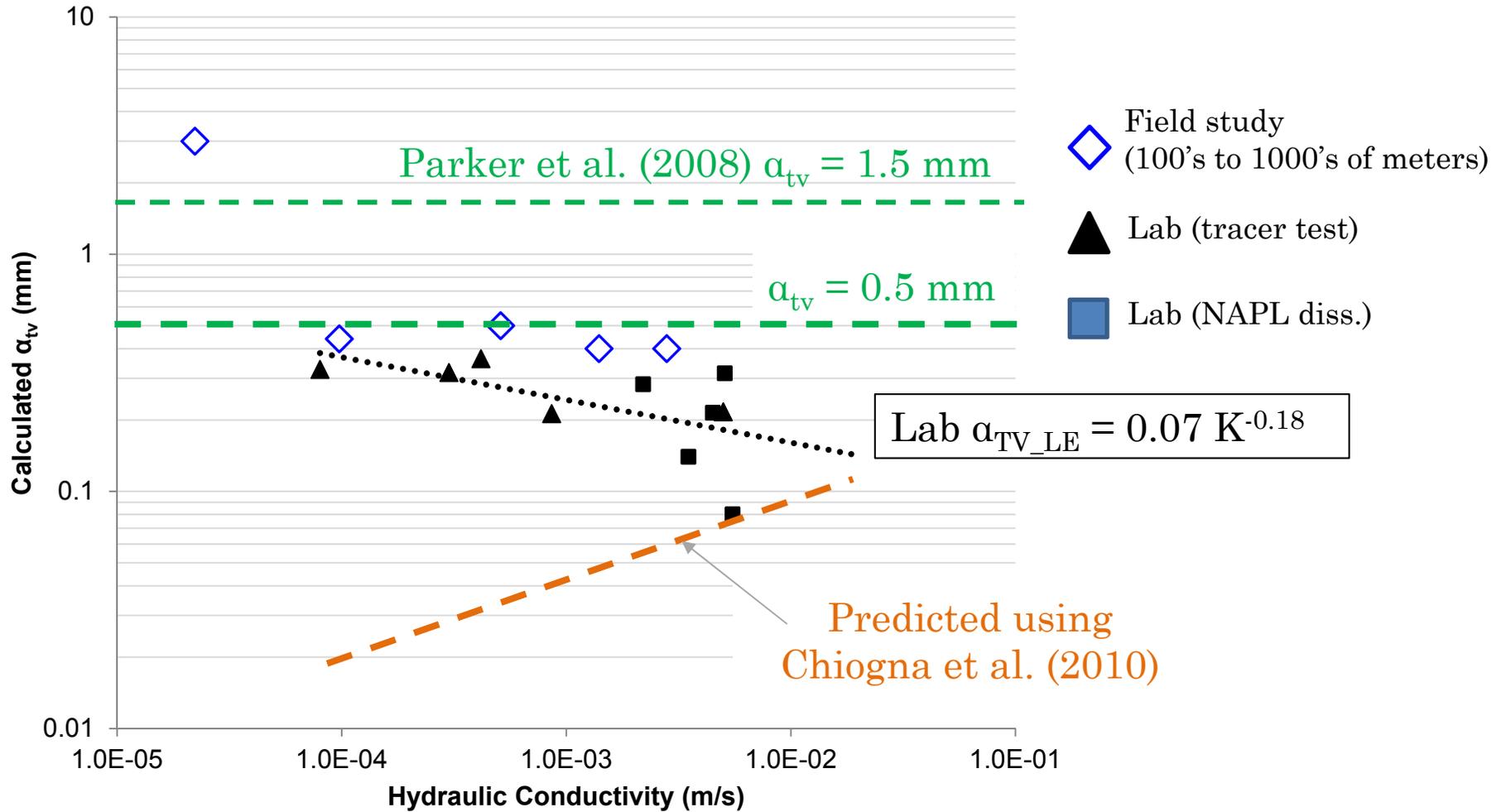
Well lengths = 0.1, 1.5, and 3 m

Tortuosity Coefficient

τ proportional to θ_e (not θ_t)



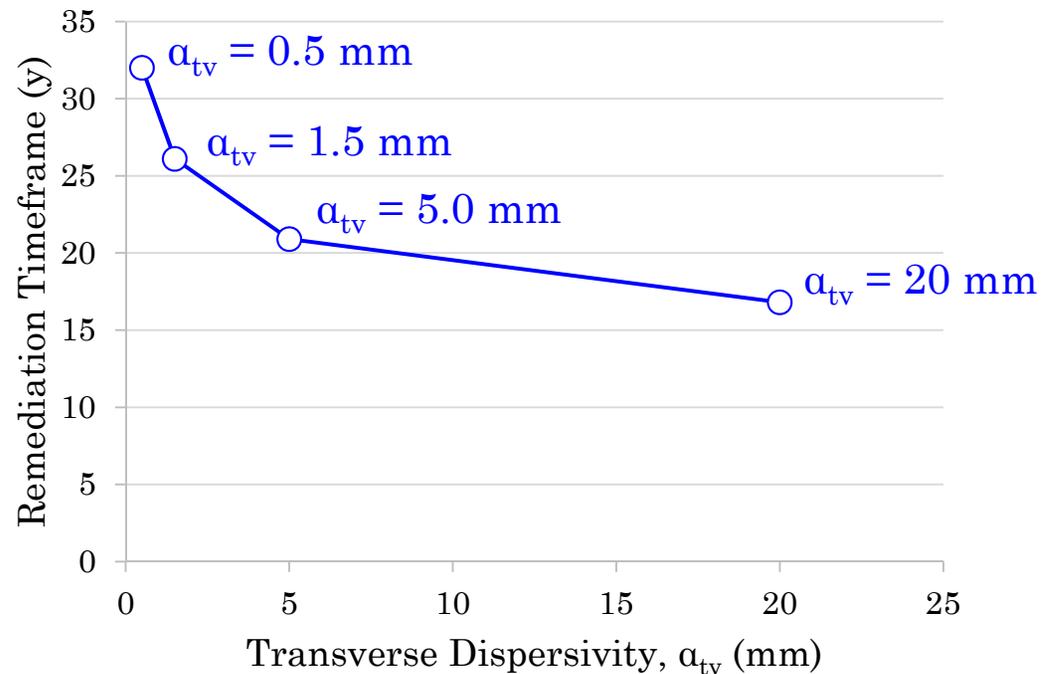
Transverse Dispersivity (LE) vs. K



Note – results not shown for glass bead studies.
LE = Local equilibrium.

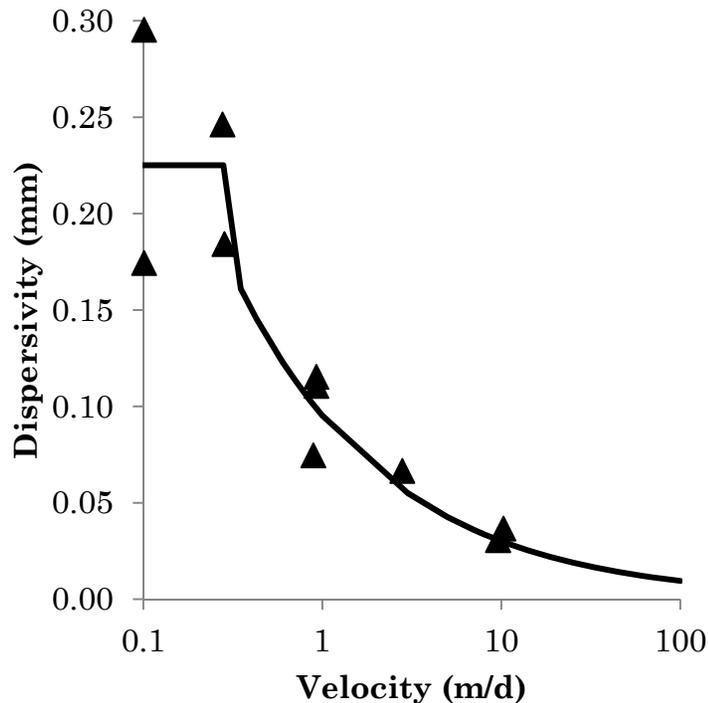
Dispersivity Influence on Remediation Timeframe

$X = 50$ m, Well screen length = 3 m



Transverse Dispersivity vs. Velocity³⁰

Re-calculated dispersivity based on Seagren et al., 1999 experiments.



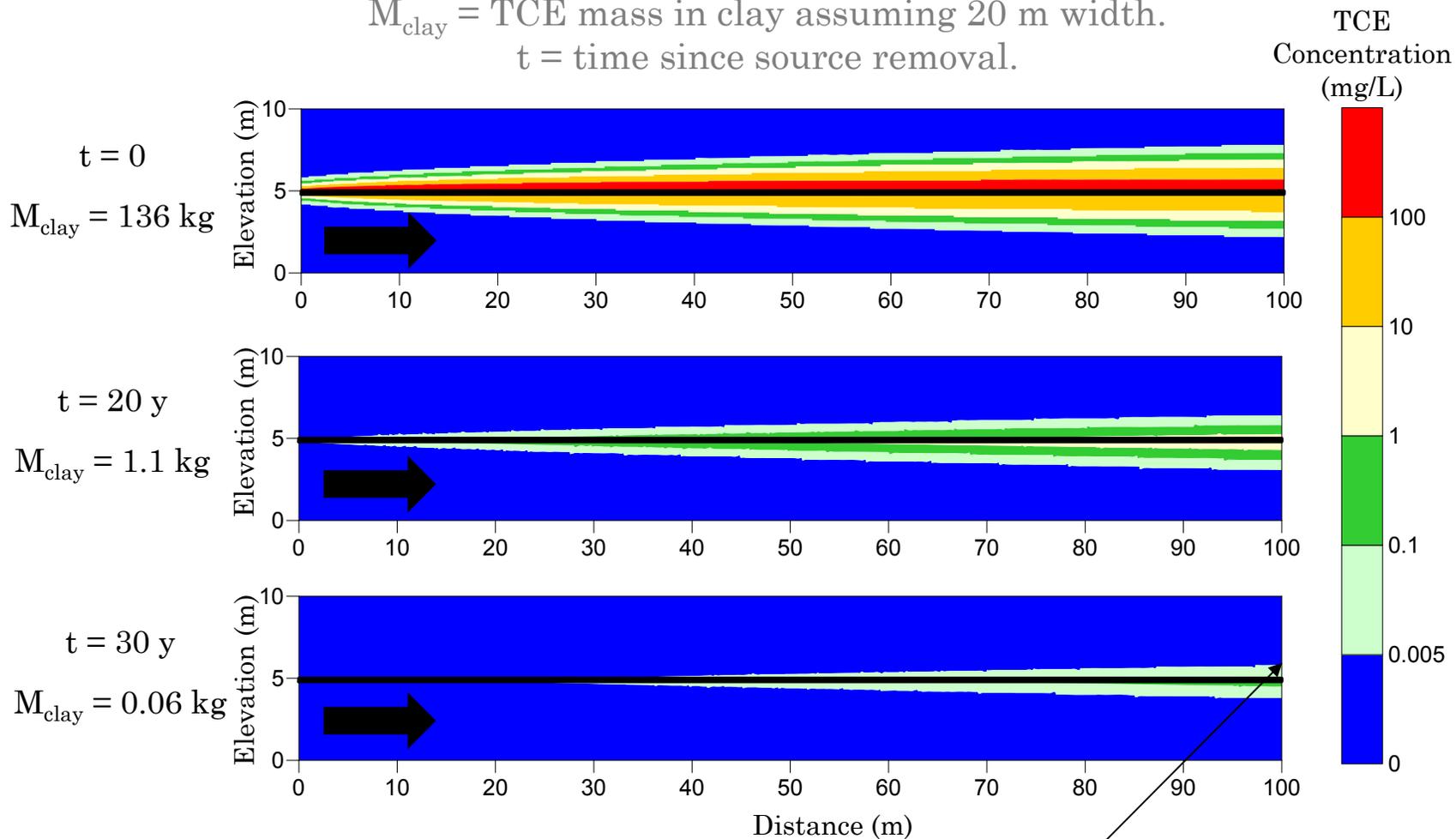
$$\alpha_{TV} = \alpha_{TV_LE}, v \leq v_c$$
$$\alpha_{TV} = \alpha_{TV_LE} 0.8 \sqrt{v_c/v}, v > v_c$$

Non-equilibrium transverse dispersion at high velocity:

- Klenk and Grathwohl, 2002
- Chiogna et al., 2010

Simulated TCE After Source Removal

M_{clay} = TCE mass in clay assuming 20 m width.
 t = time since source removal.

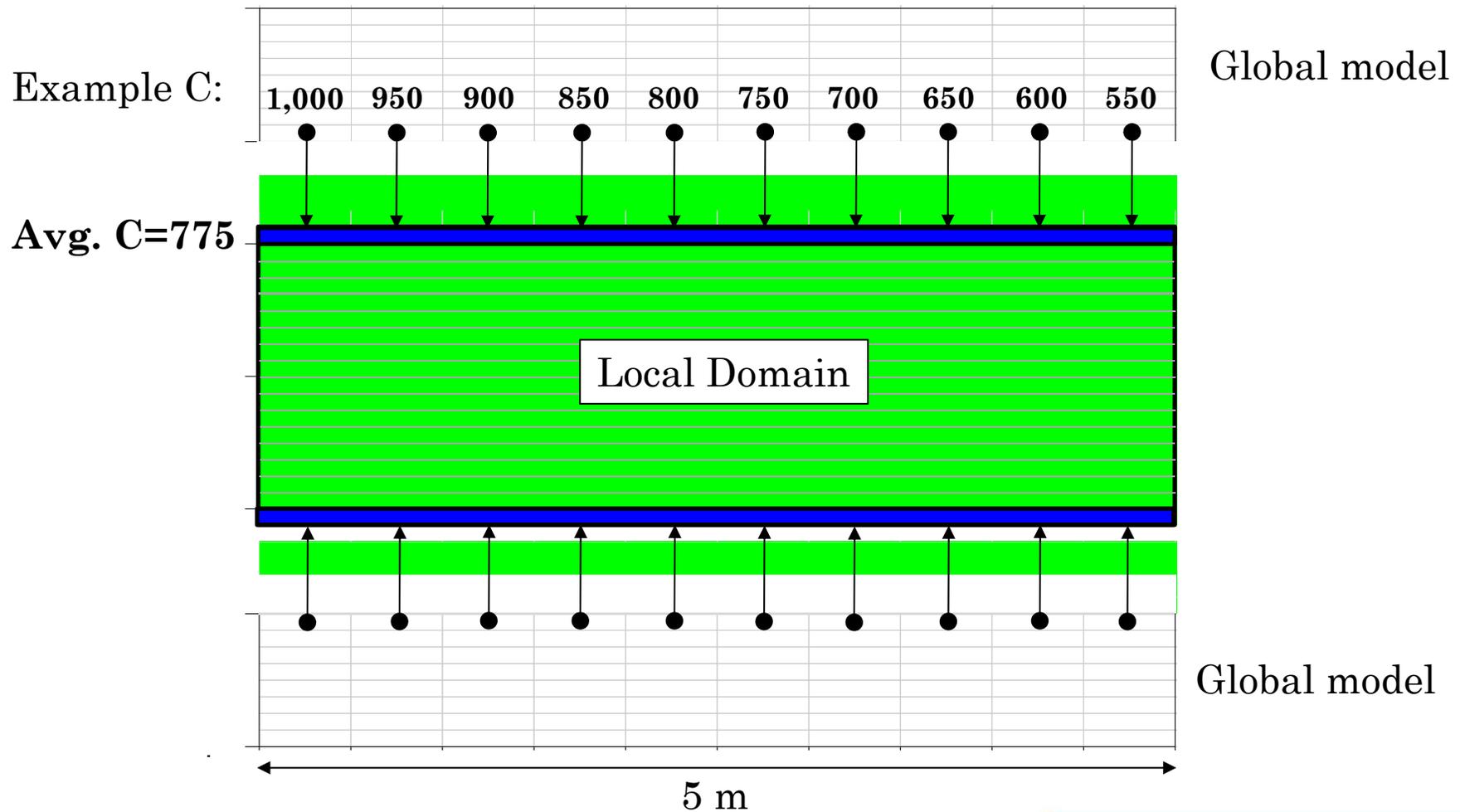


30 years after source removal:
 99.96% mass depletion in clay, avg. $C_{\text{well}} = 12 \text{ to } 126 \text{ ug/L}$

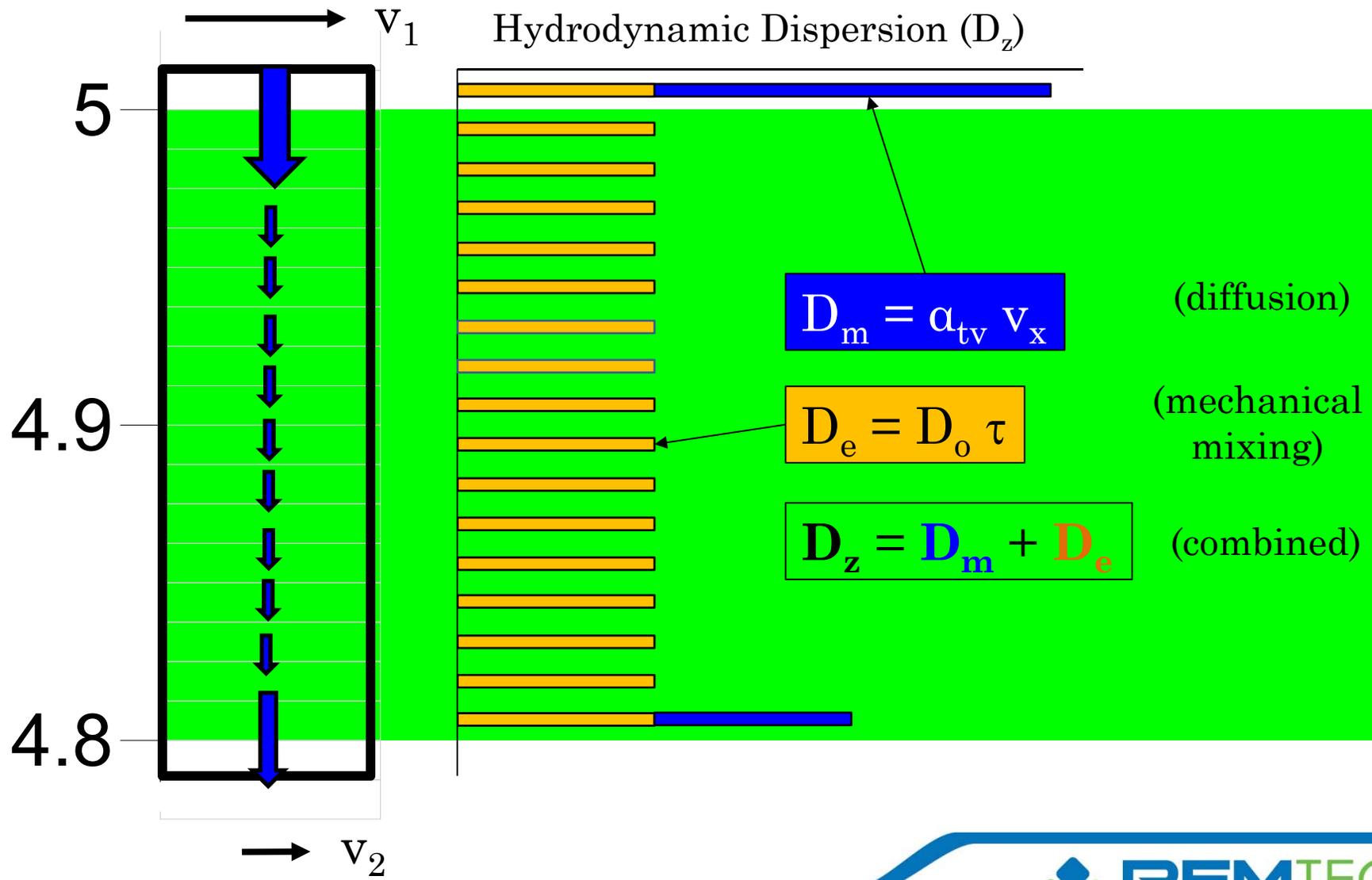
Md into top of clay = 15% to 40% of Md from DNAPL pool.

Local Domain Approach

Local domain $\Delta x = 5$ m, clay thickness varied.



Local Domain Dispersion



Influence of Mechanical Mixing

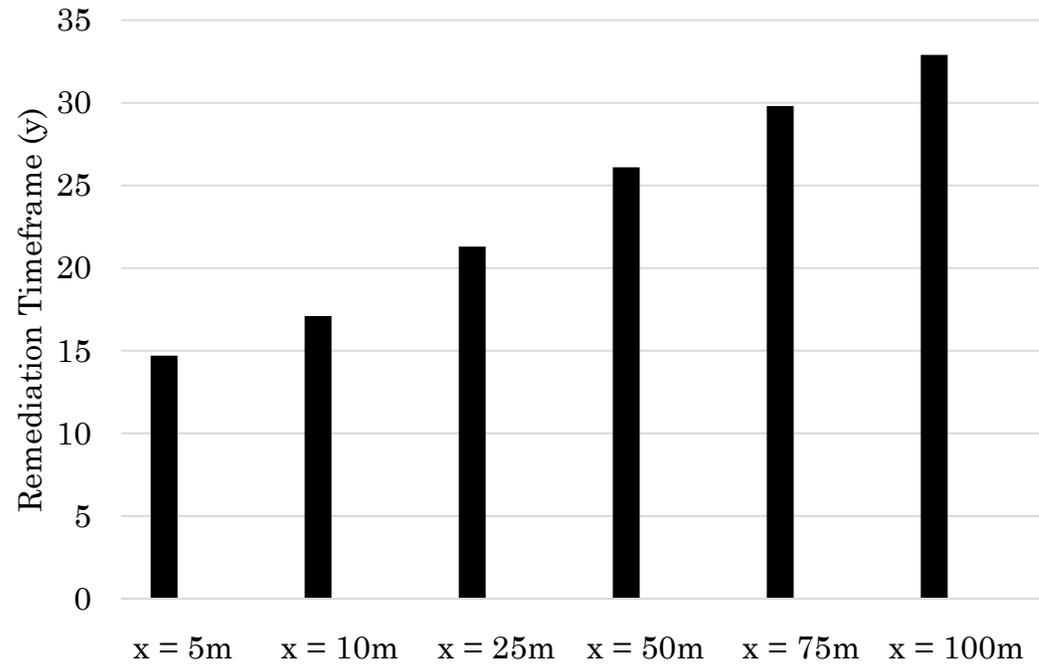
- Horizontal velocity above clay - increases transverse dispersion and mass flux into/out of clay (3x higher at this site)
- 1-D models or flux calculations typically based on D_e (D_m assumed to be zero)
 - May substantially underestimate mass flux into and out of clay

$$\text{Flux} = -D_z \theta \Delta C / \Delta x$$

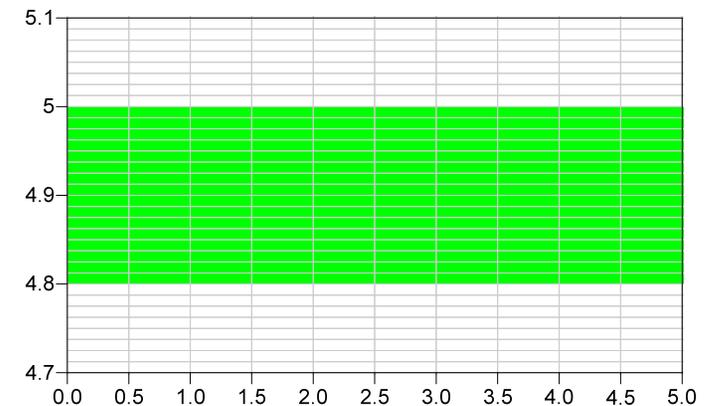
Remediation Timeframe

Mass balance = 0.04%

■ No Local domains



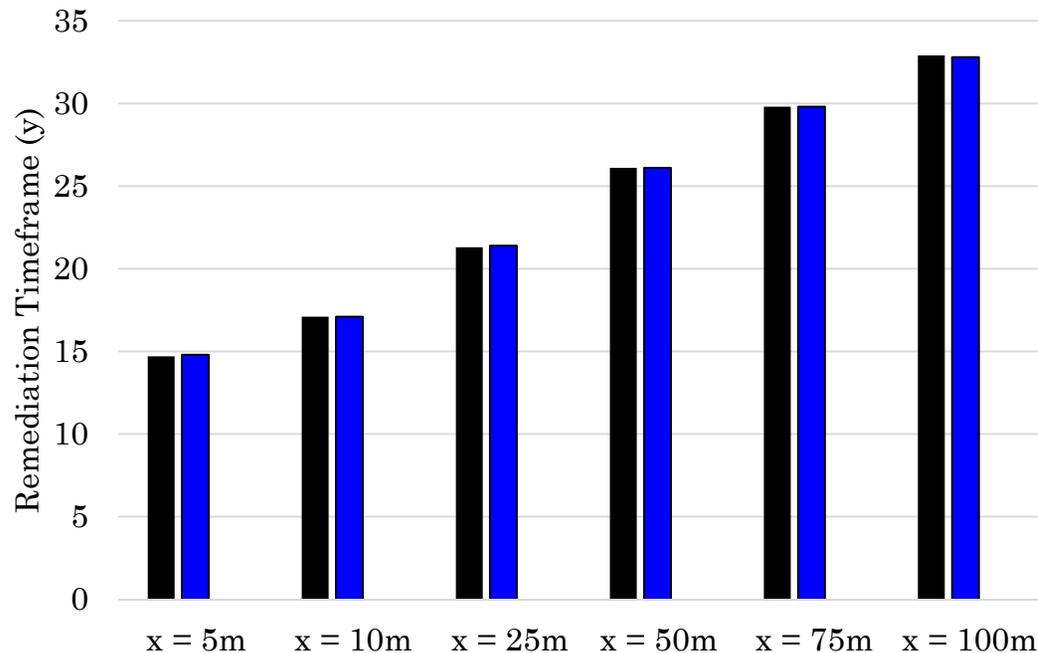
Global domain only



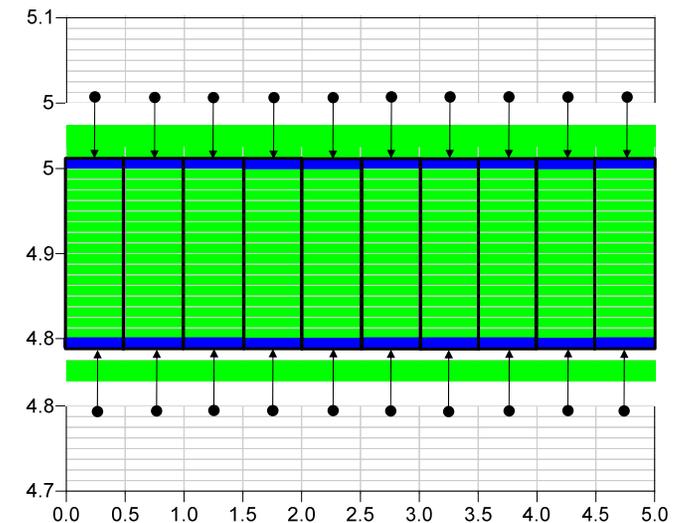
Remediation Timeframe

Mass balance = 0.04% Mass balance = 0.04%

■ No Local domains ■ 200 Local domains



200 Local domains, $\Delta x = 0.5$ m



Remediation Timeframe

Mass balance = 0.04%

Mass balance = 0.04%

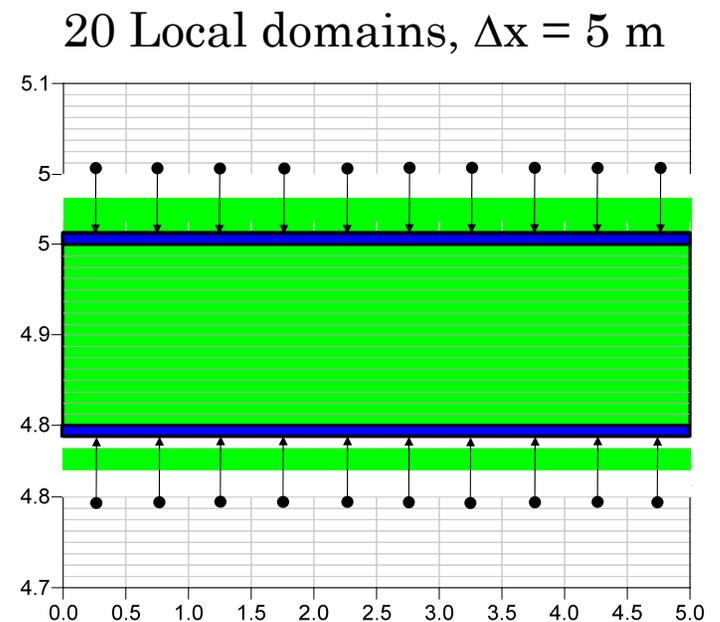
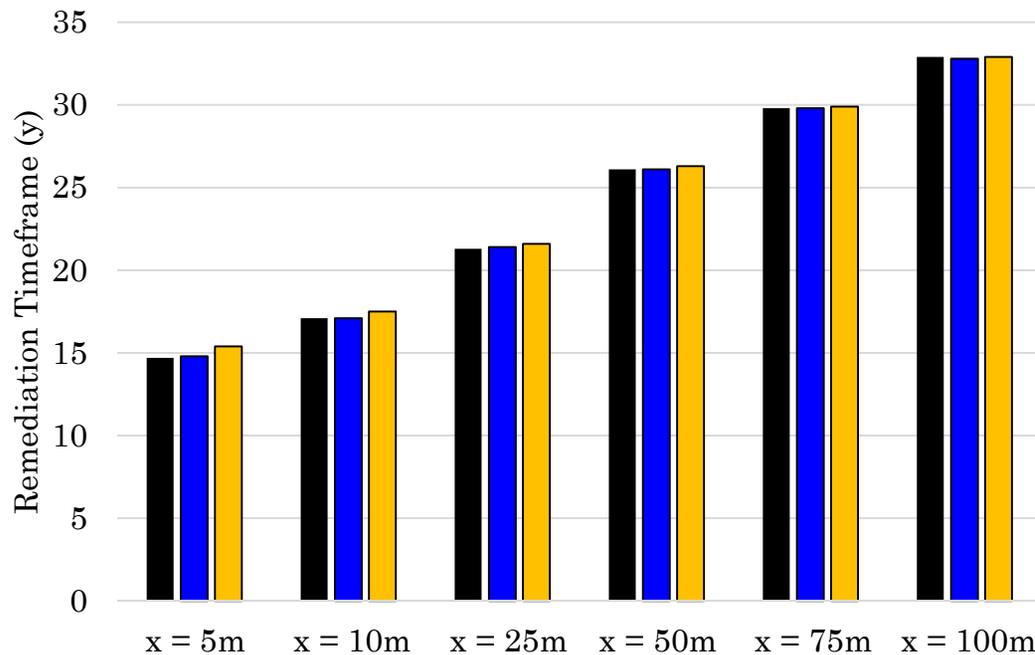
Mass balance = 0.07%

■ No Local domains

■ 200 Local domains

■ 20 Local domains

$\Delta x = 0.5 \text{ m}$

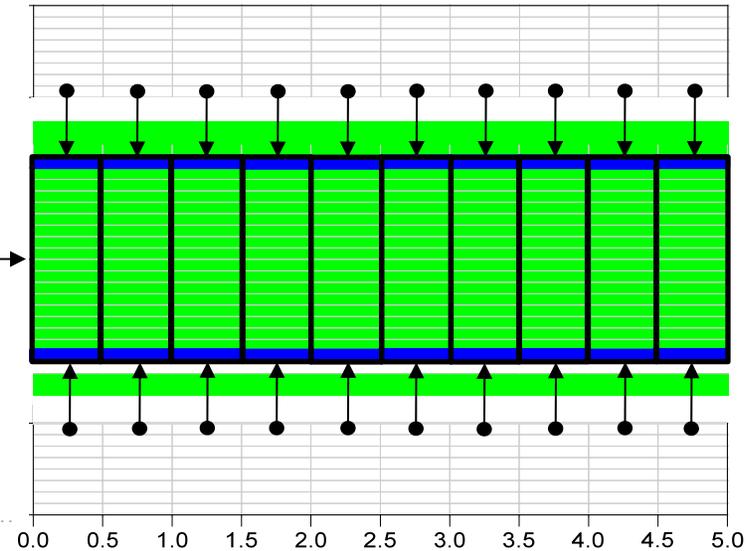


Influence of Thickness and R

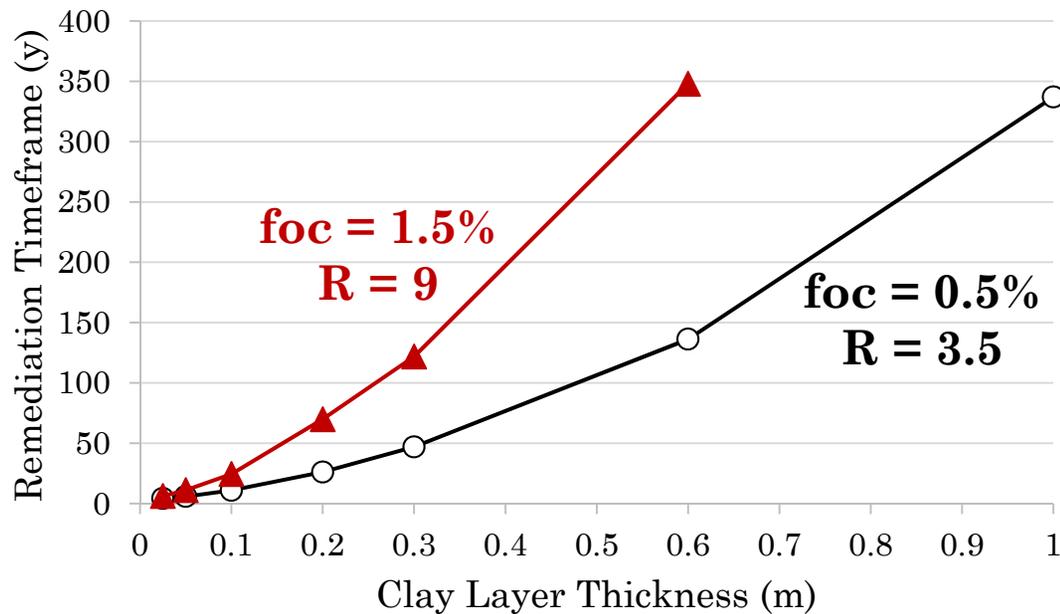
No. local domains = 200 ($\Delta x = 0.5$ m)

7 model runs with different clay thickness

- 0.025, 0.05, 0.1, 0.2, 0.3, 0.6, and 1 m



x = 50 m



Sensitivity Analysis: Length of Clay Layer

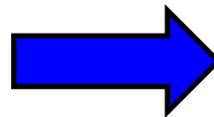
$L_1 \sim 30 \text{ ft}$



$L_2 \sim 300 \text{ ft}$



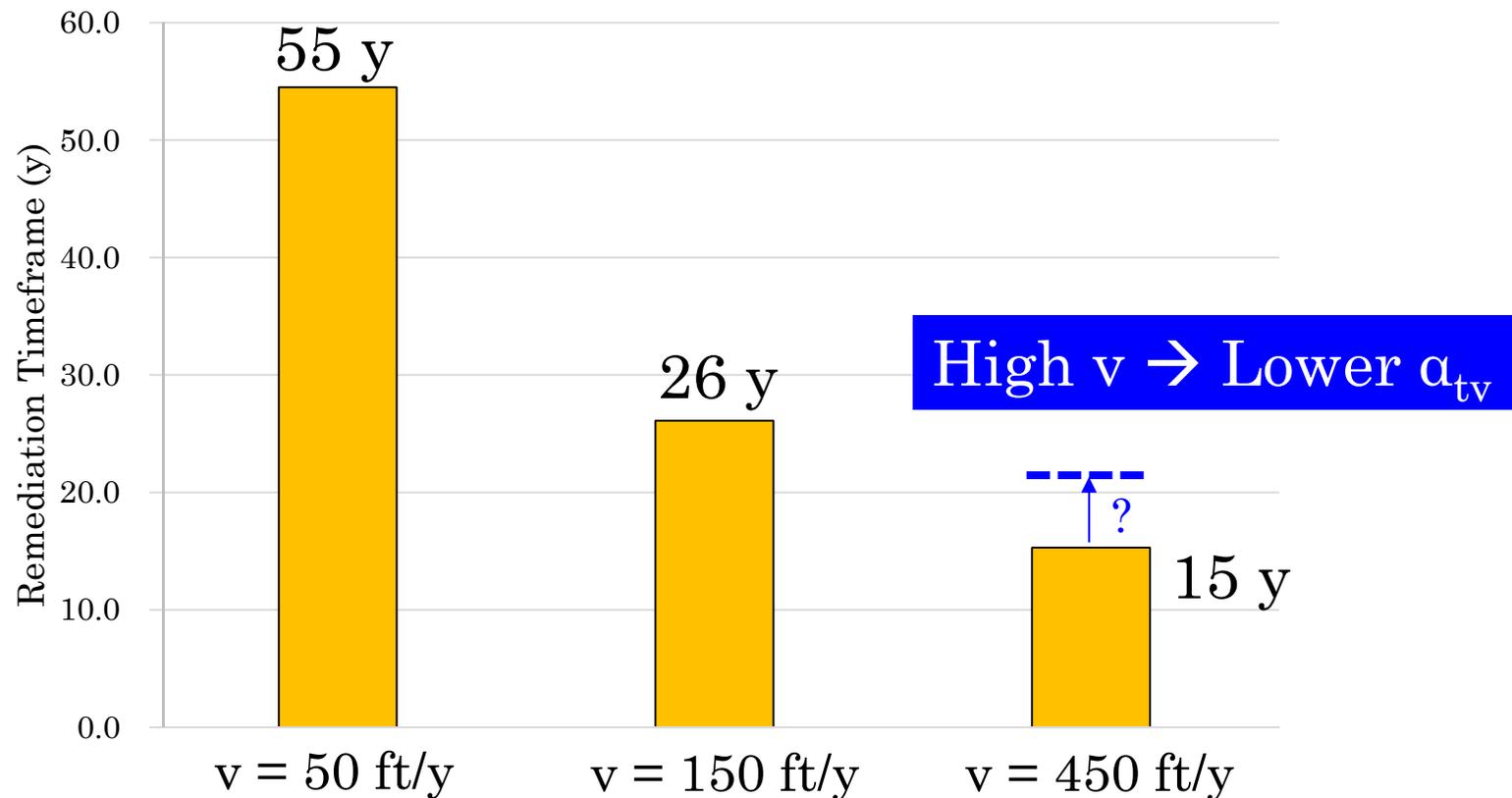
Length x 10



RTF x 2

Sensitivity Analysis:

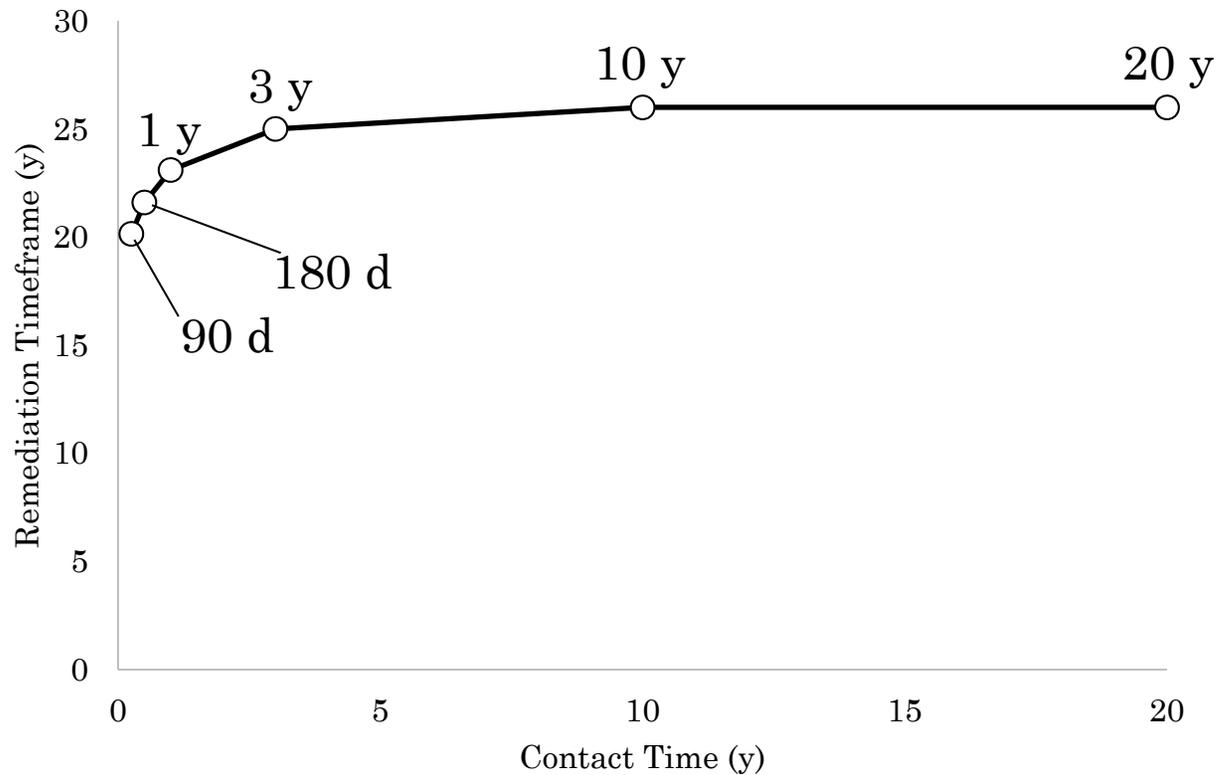
Velocity ($x=50$ m, screen $L=3$ m)



Note – ISR-MT3DMS simulation did not consider potential decrease in α_{tv} at higher velocity.

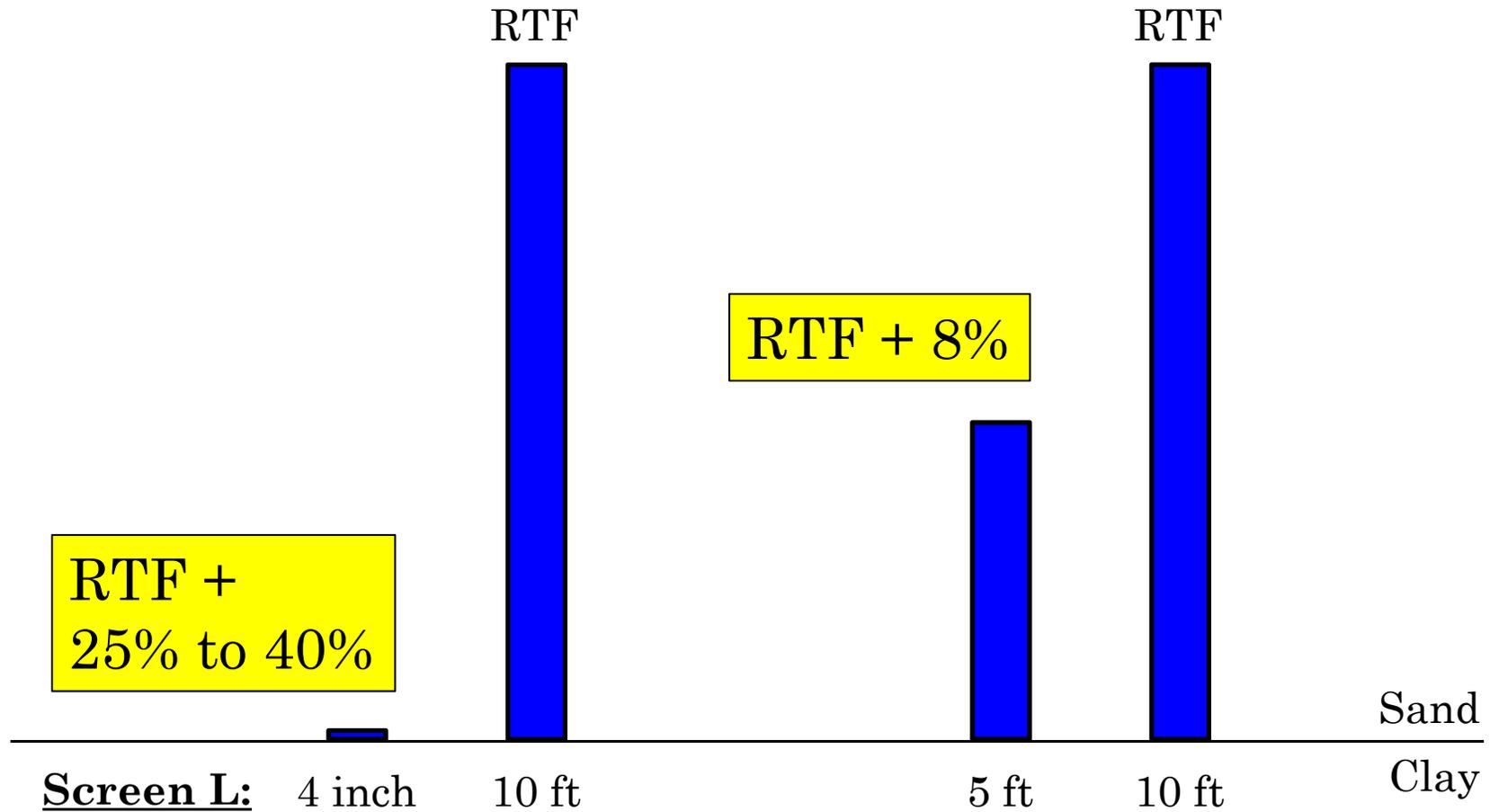
Influence of Contact Time (Thin Layer) ⁴¹

$x = 50$ m, Well screen $L = 3$ m



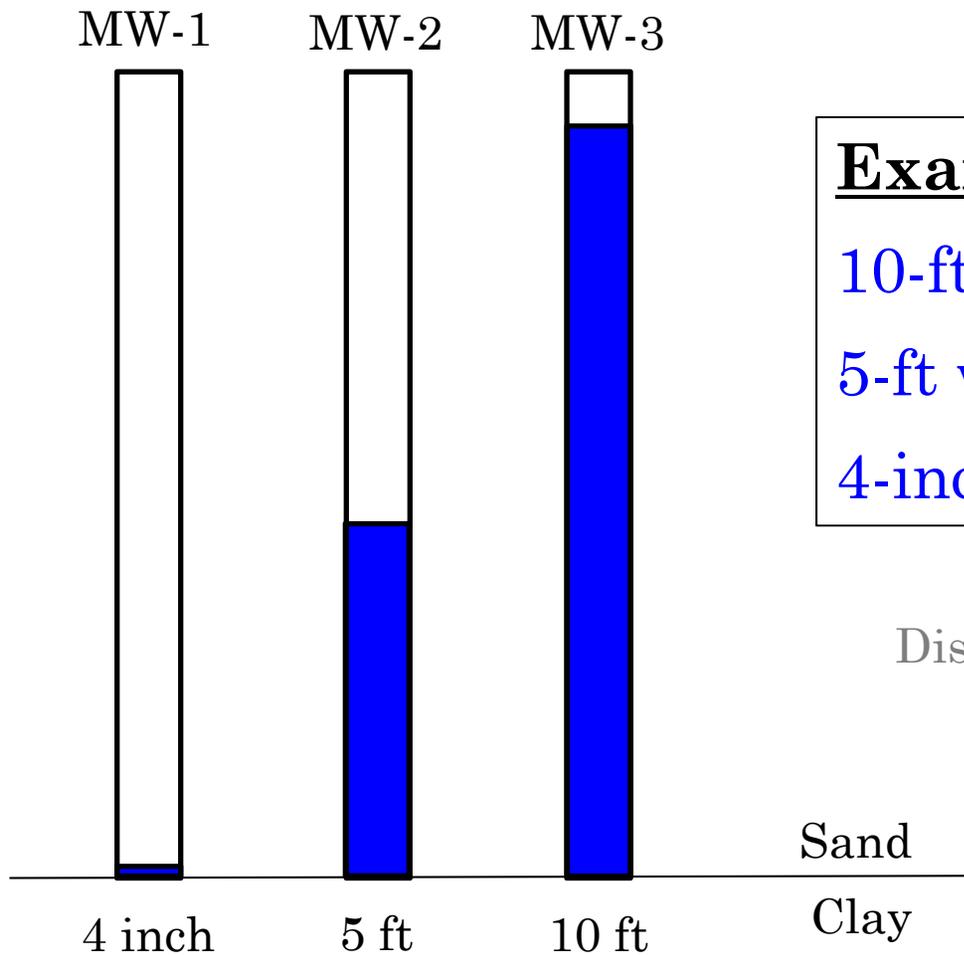
Contact time - between DNAPL and clay layer.

Sensitivity Analysis: Well Screen Length



Shorter screen → Longer RTF

Sensitivity Analysis: Well Screen Length



Example

10-ft well: $RTF = 30 y$

5-ft well: $RTF + 3 y$

4-inch well: $RTF + 8 \text{ to } 12 y$

Distance of 15 to 300 ft from source.

Conclusions

- ISR-MT3DMS – Local Domain
- Proof of concept, verification
- Model inputs: τ and α_{tv}
- Mechanical mixing vs. diffusion
- Back-diffusion in thin layers: RTF most sensitive to v , b , foc

ISR-MT3DMS Next Steps

- On-going development, verification

Demonstration sites (w/reactions) & beta testing

- Short course at Battelle symposium in May 2015
 - NDM and ISR-MT3DMS
 - Beta version release
- GUI Developers
- Target release date: 2016 (FREE)

Questions?



Porewater Solutions

Expertise • Experience • Innovation

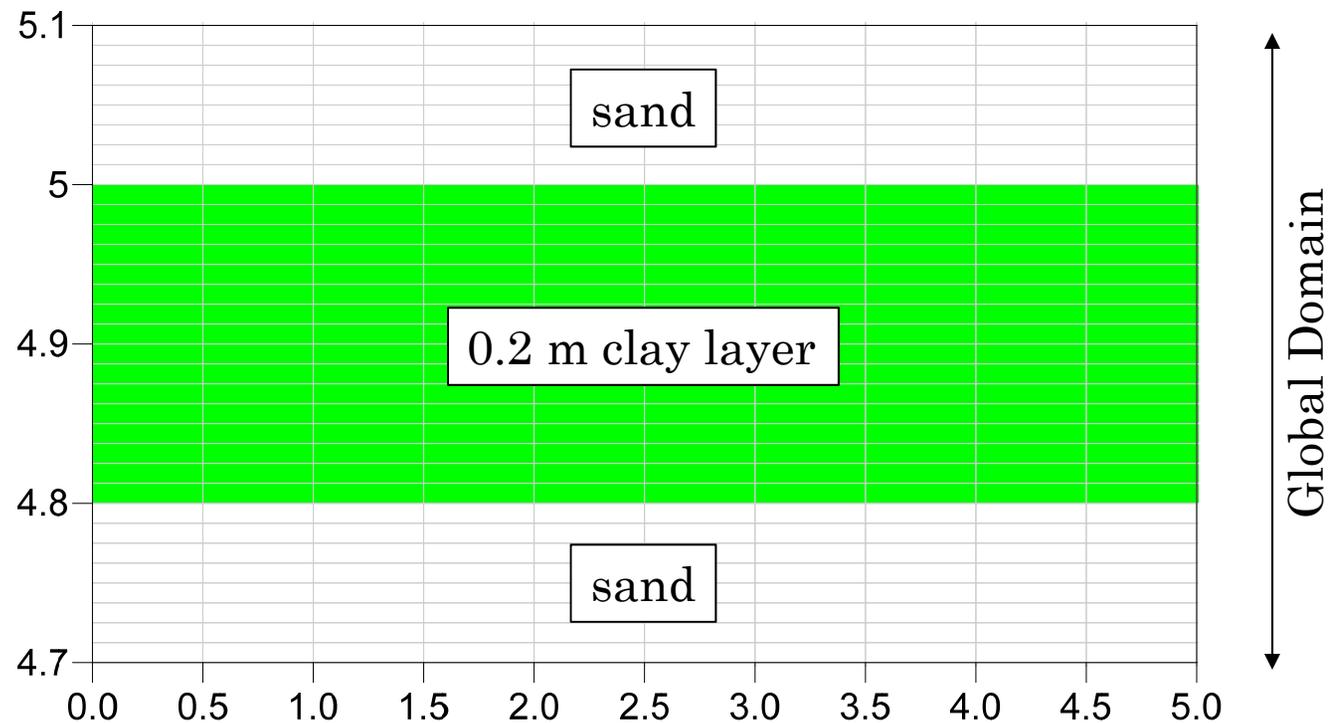
Grant Carey
Porewater Solutions

613-270-9458

gcarey@porewater.com

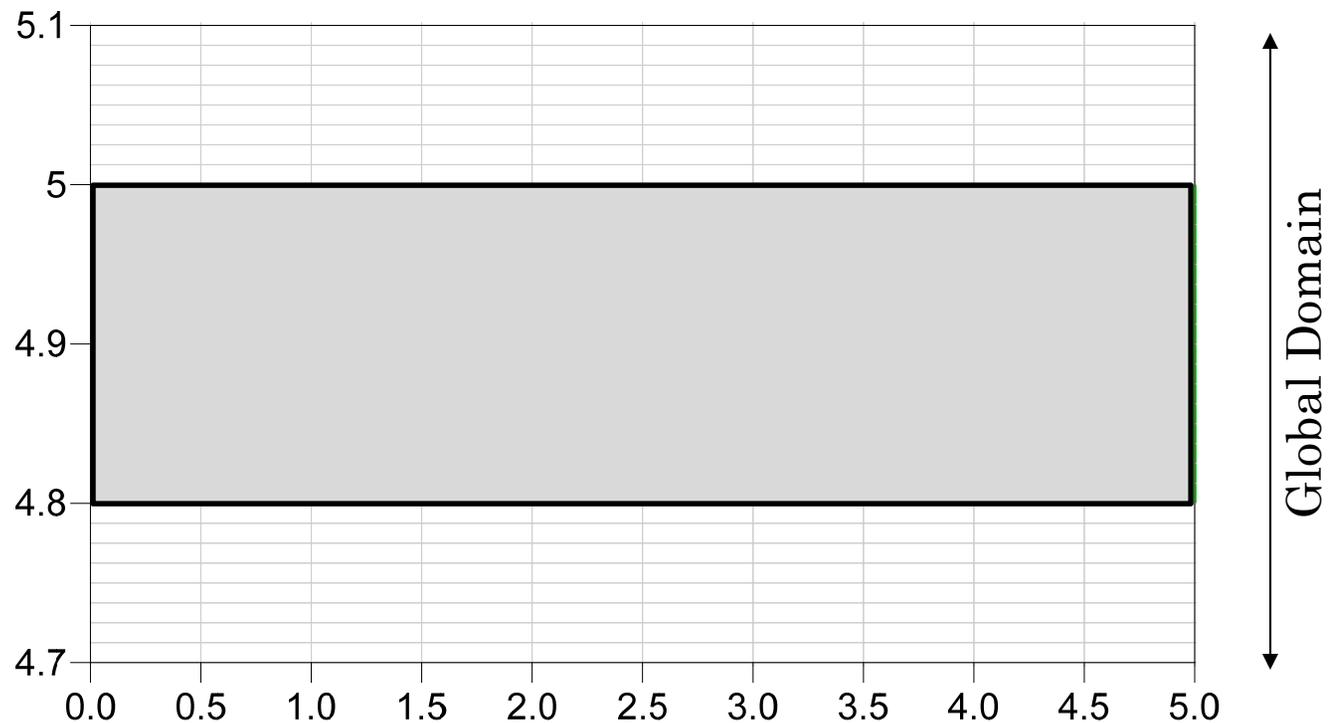
Local Domain Approach

1. Global domain section (example)



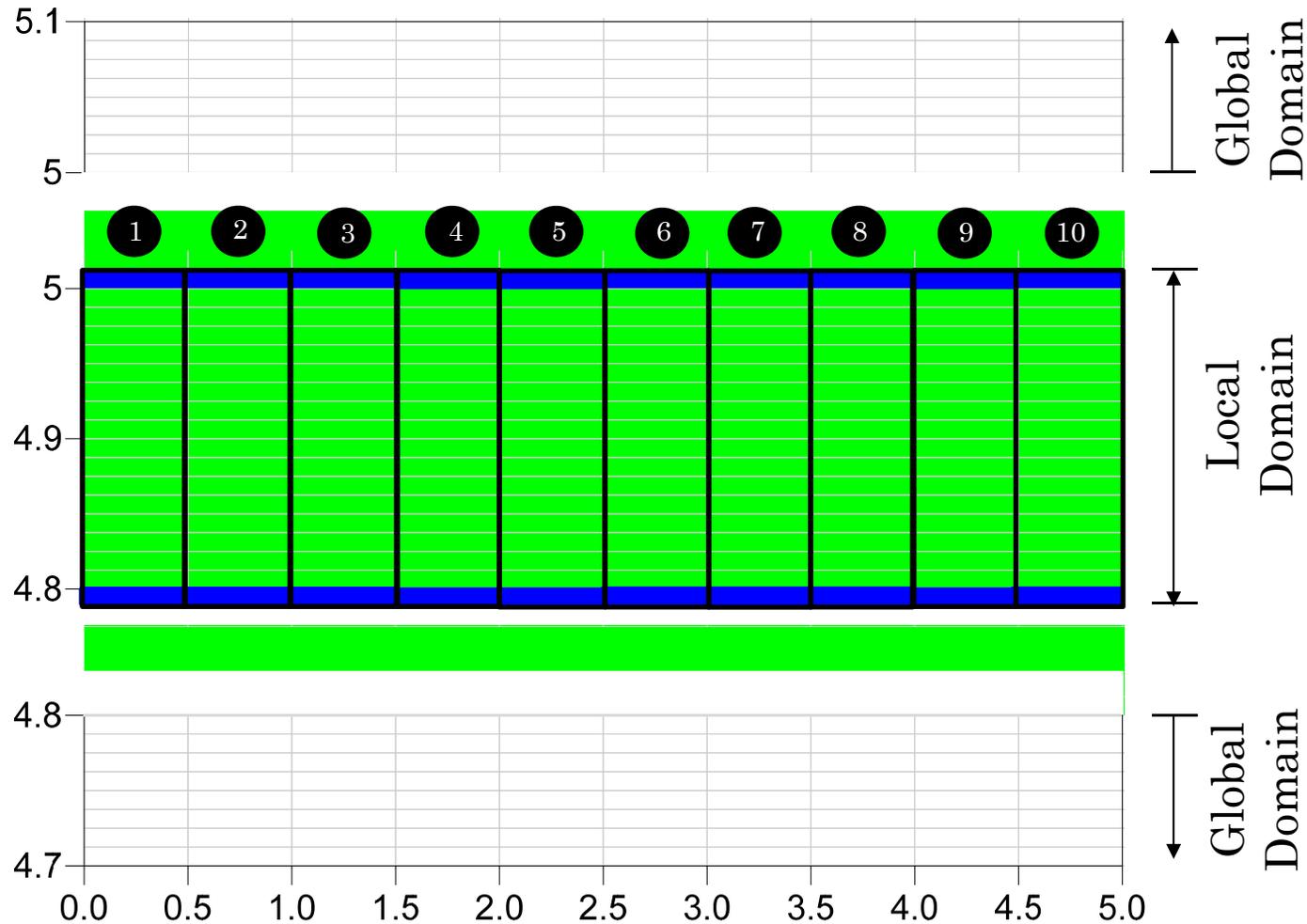
Local Domain Approach

2. Inactive transport in clay zone, in global domain.



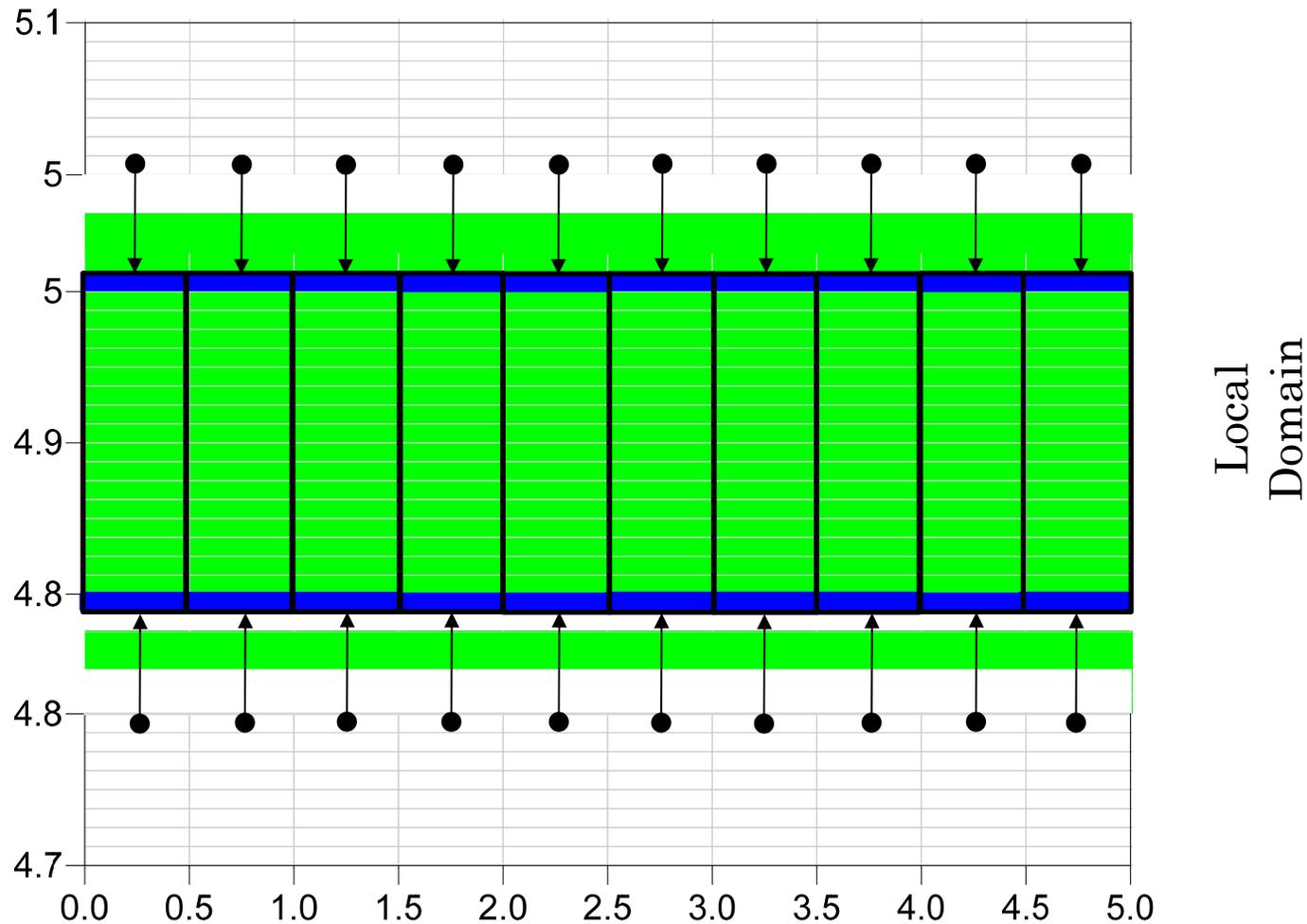
Local Domain Approach

3. Insert 200 local domains ($\Delta x = 0.5$ m, $\Delta z = 1.25$ cm).



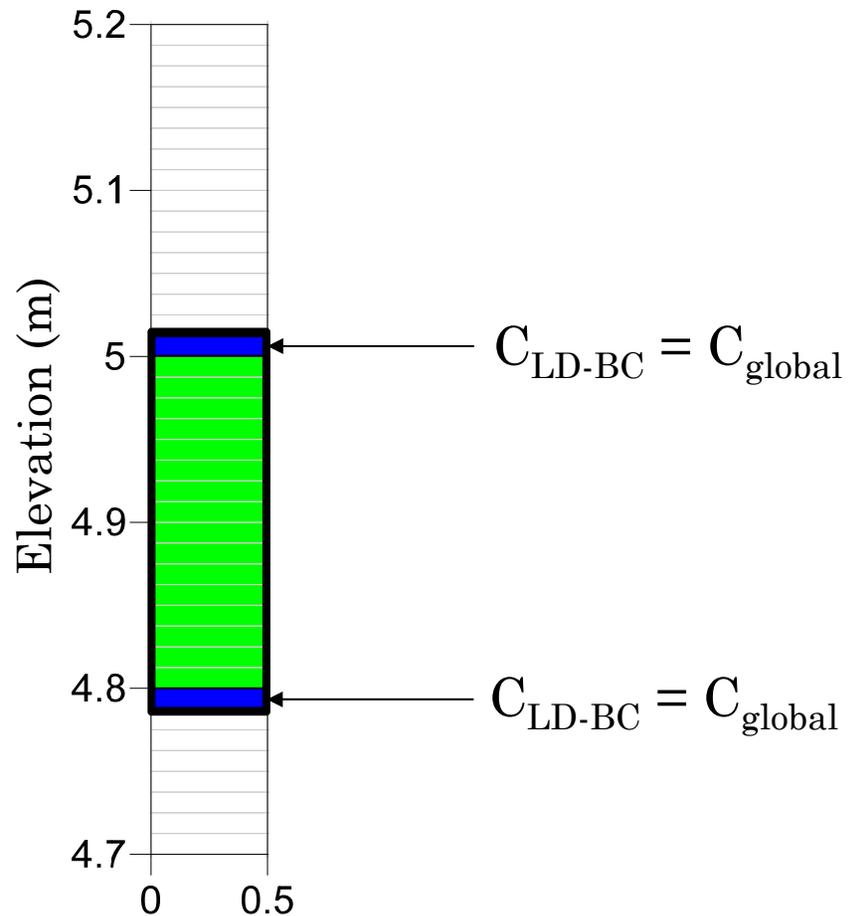
Local Domain Approach

4. Associate global domain conc. with local domain boundaries.



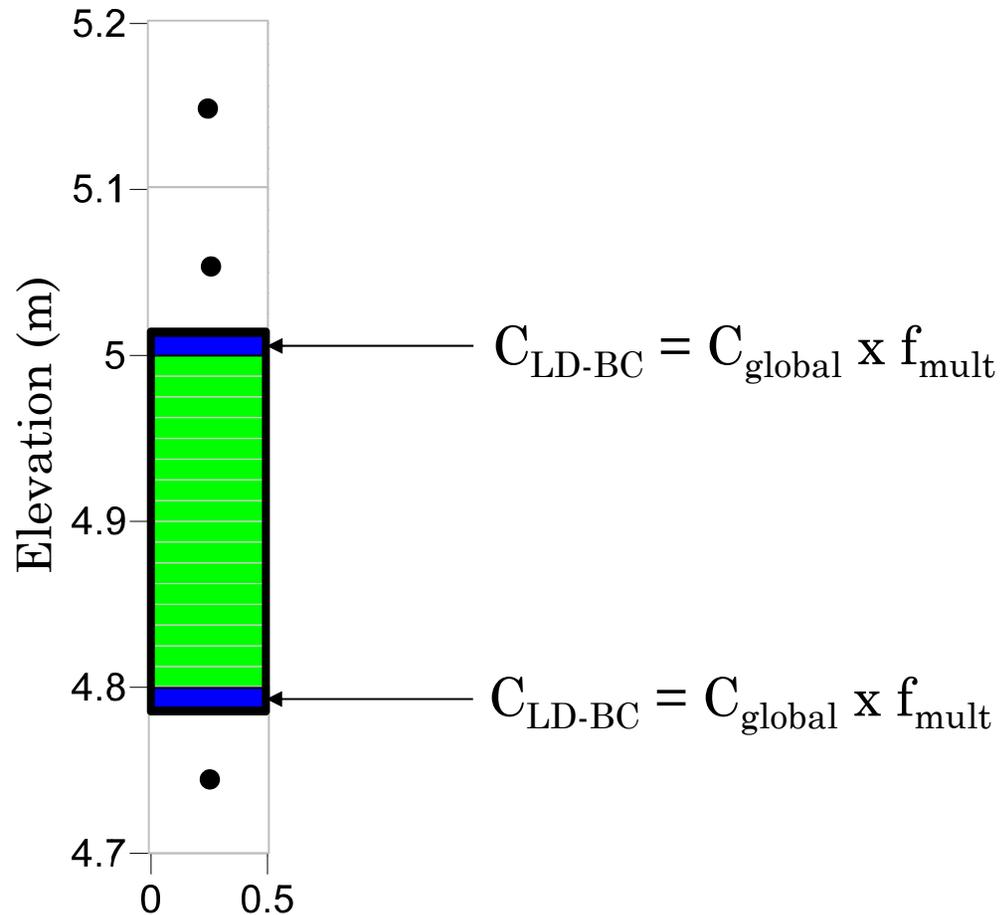
Local Domain Boundary Conditions

Scenario A – same vertical discretization in local and global domains



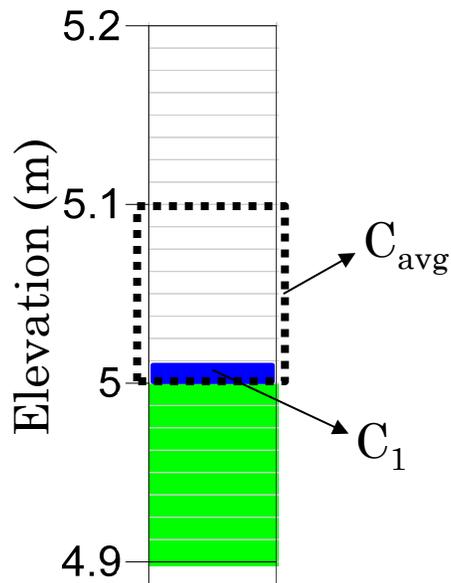
Local Domain Boundary Conditions

Scenario B – Global domain has larger vertical grid spacing.

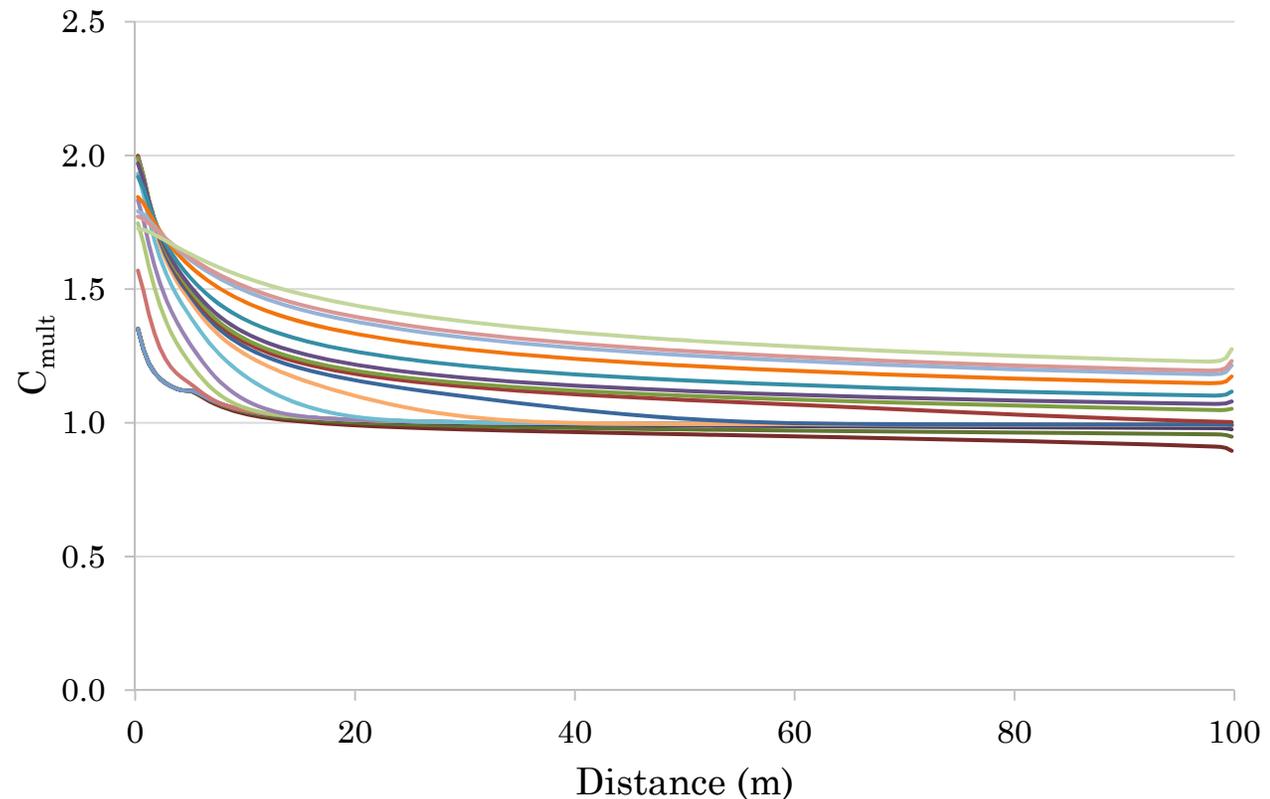


f_{mult} Trends (t = 3 to 85 y)

(travel time from source to d/g boundary ~ 2.5 years)

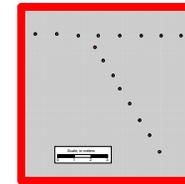
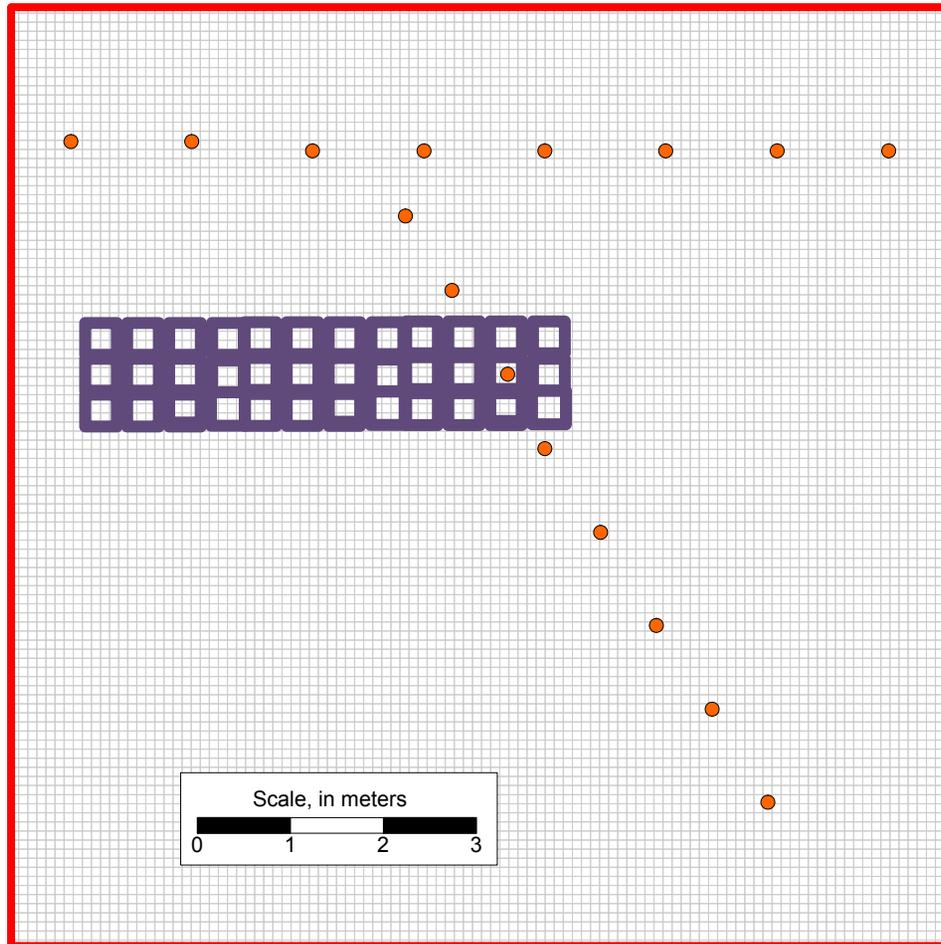


$$f_{\text{mult}} = C_1 / C_{\text{avg}}$$



Narrow range in f_{mult} over x and time – suggests average may be used to define local domain boundary condition with coarser global domain grid spacing (to be confirmed).

Example Applications

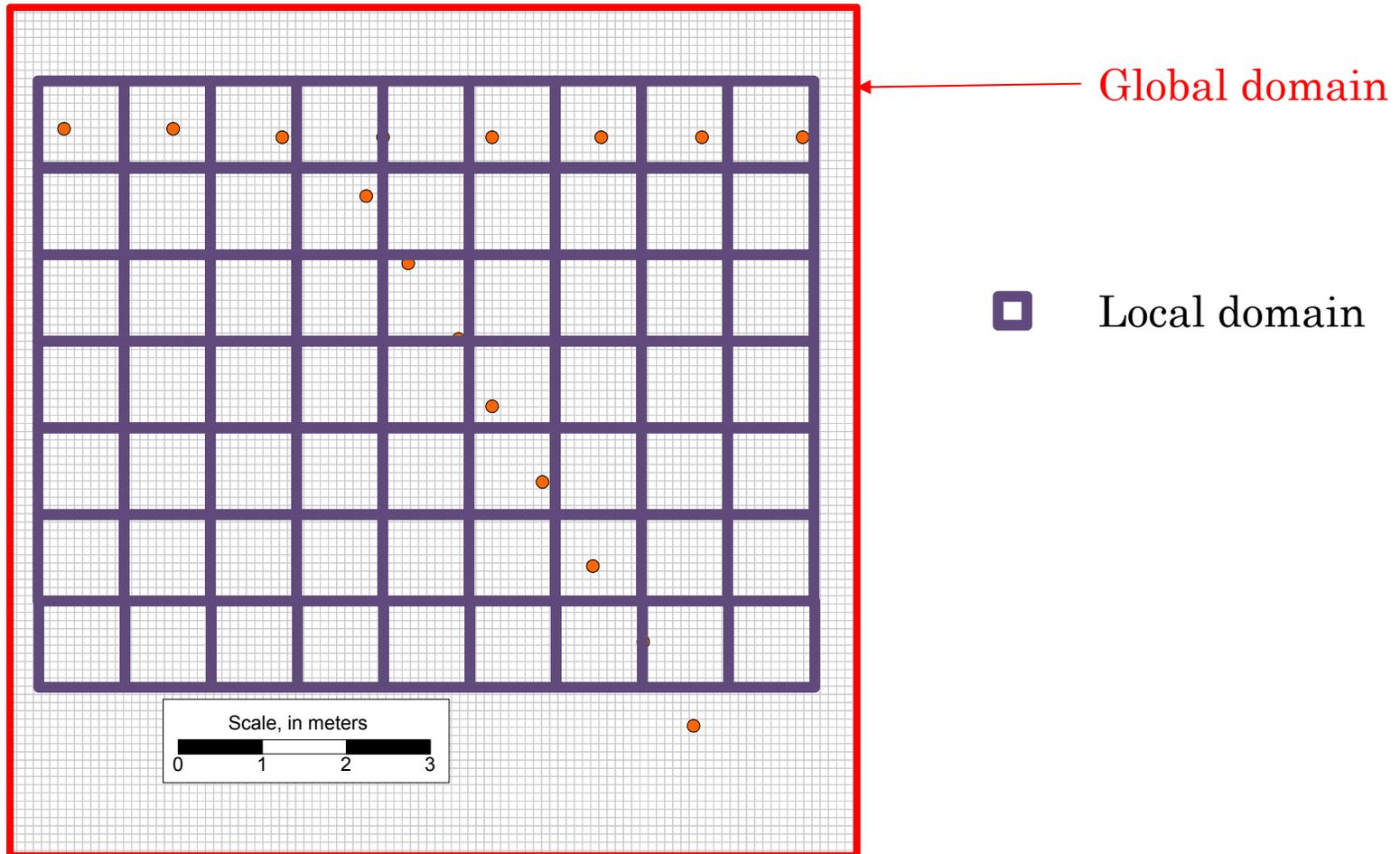


Global domain



Local domain

Example Applications



Modeling Goals at Complex Sites

- Improve process understanding

Interpretive Tool

- Optimize remediation performance
- Timeframe range (RTF)
 - Establish realistic expectations