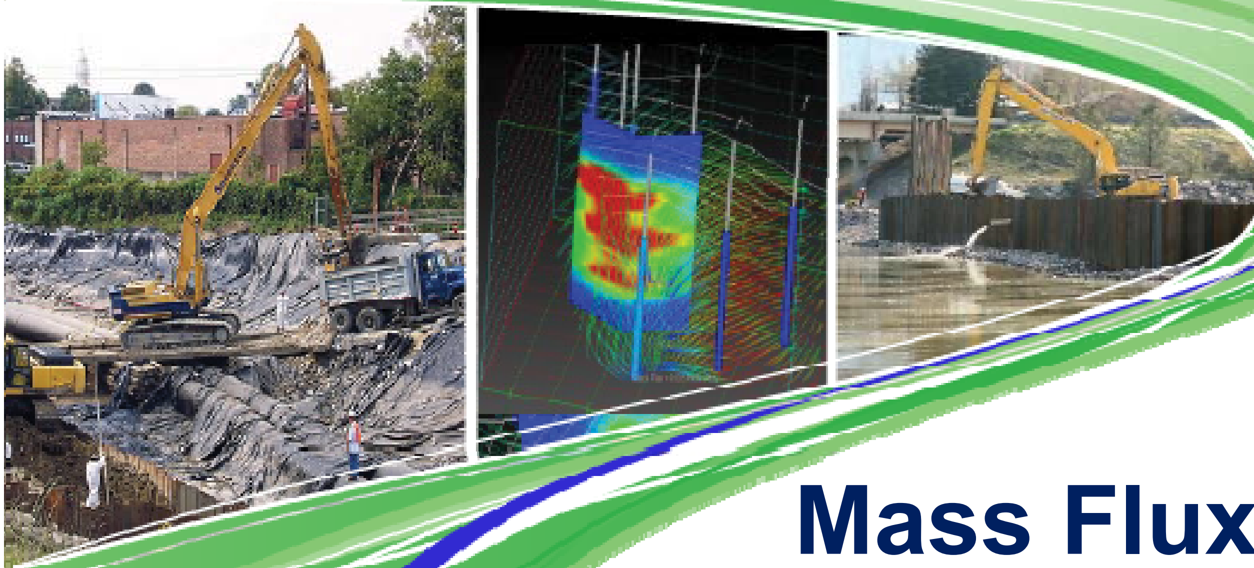

Mass Flux/Discharge: DNAPL and Back-Diffusion

Dr. Grant R. Carey

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Porewater Solutions
Expertise Experience Innovation

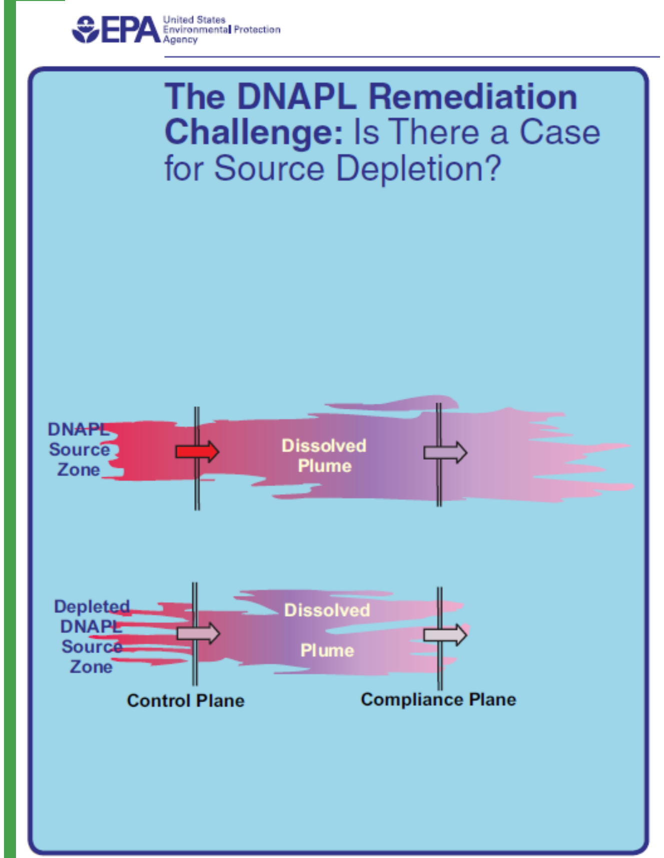
United States Environmental Protection Agency

24th Annual NARPM Training Program

NAPL Sites: A Decade of Reflection

Einerson and MacKay (2001) – Classic paper on mass flux and discharge.

Kavanaugh et al, 2003

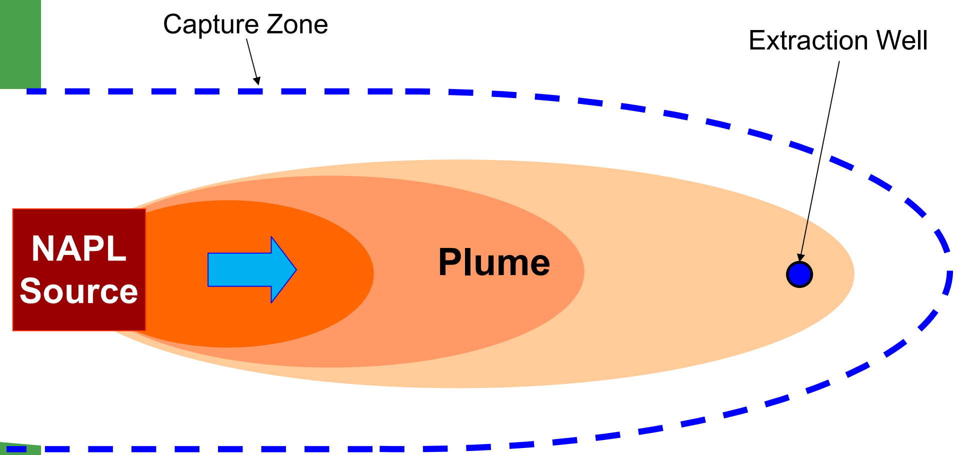


Research and Guidance

- DoD / DOE research
- ITRC
  - LNAPL Remediation
  - Mass Flux
  - DNAPL Strategies
  - DNAPL Characterization
- EPA
  - TI Waivers
  - Site closure
  - DNAPL Delineation
- States
  - CA – Low Threat Closure

Kavanaugh et al, 2013

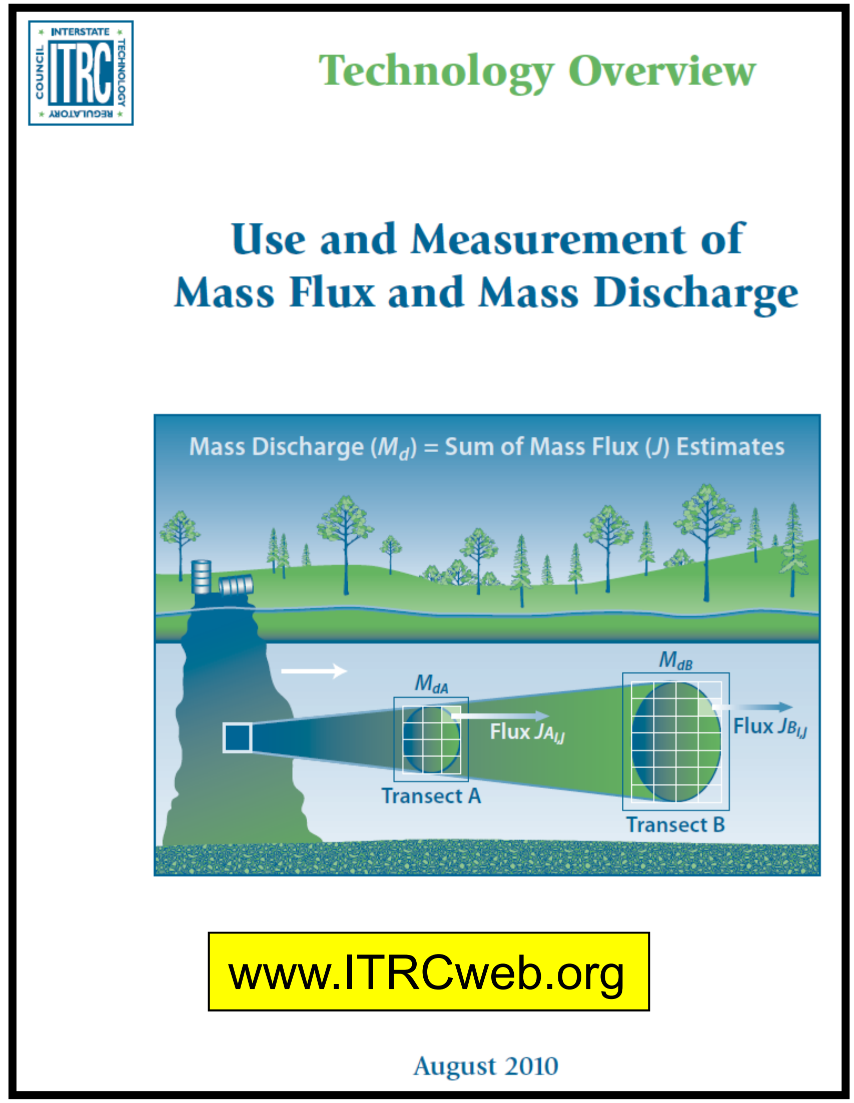
Mass Flux / Mass Discharge



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.



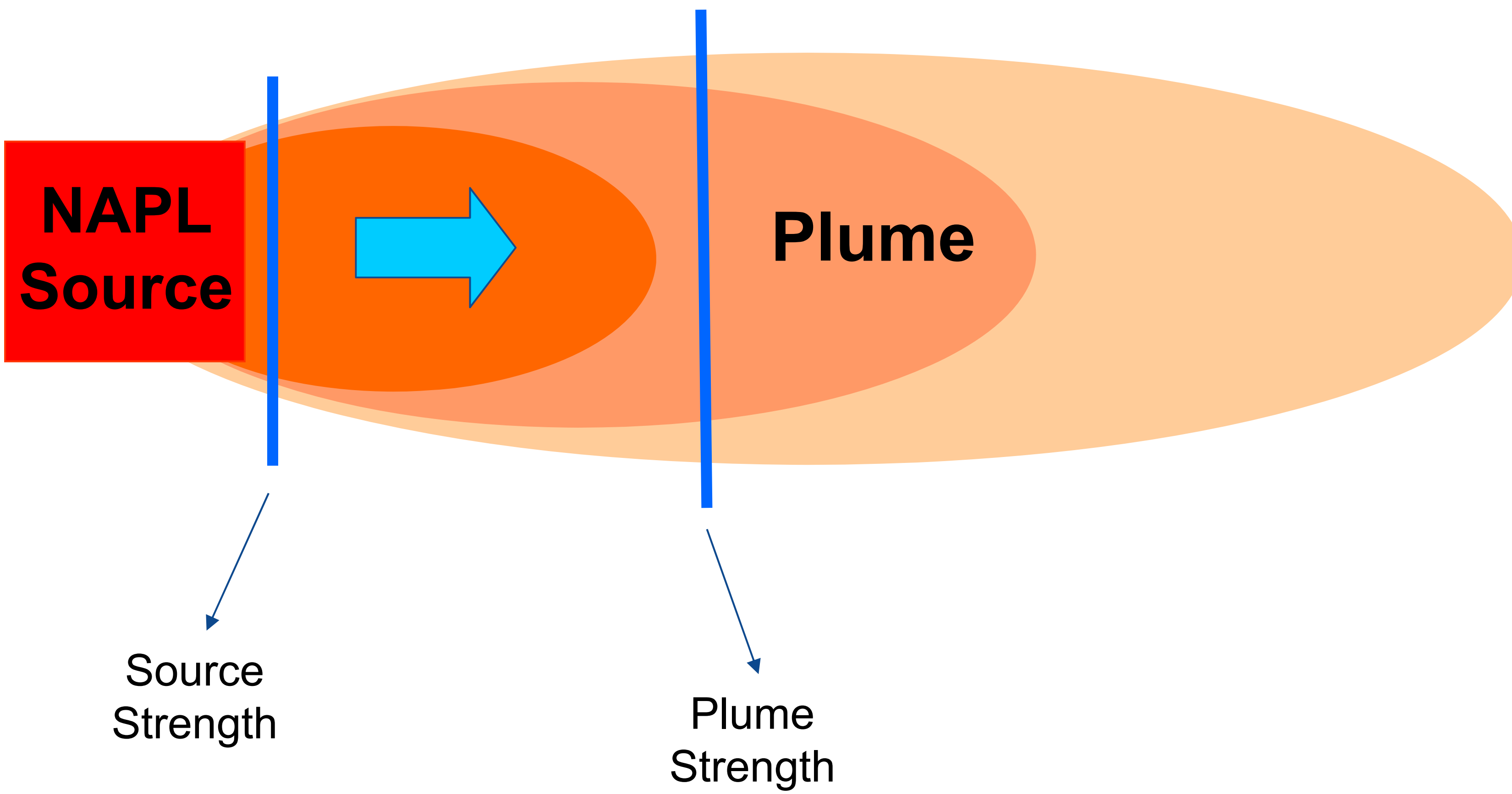
Outline

1. Concepts
   - Mass flux / Mass discharge
   - DNAPL architecture
   - Back-diffusion
2. Site Characterization Methods
3. Case Studies
4. Appendices

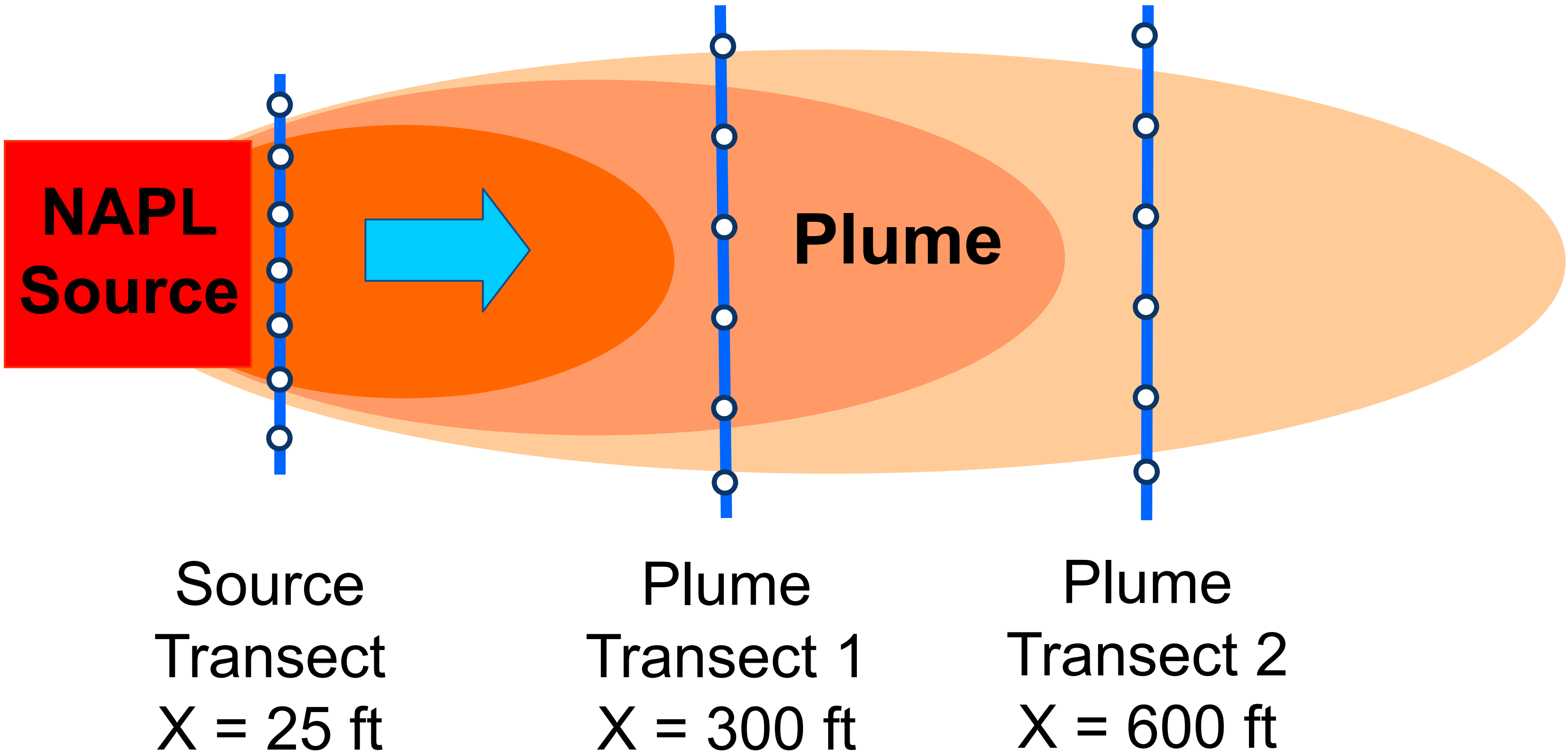
CONCEPTS

1.1 MASS FLUX / DISCHARGE

Mass Discharge = Source / Plume Strength

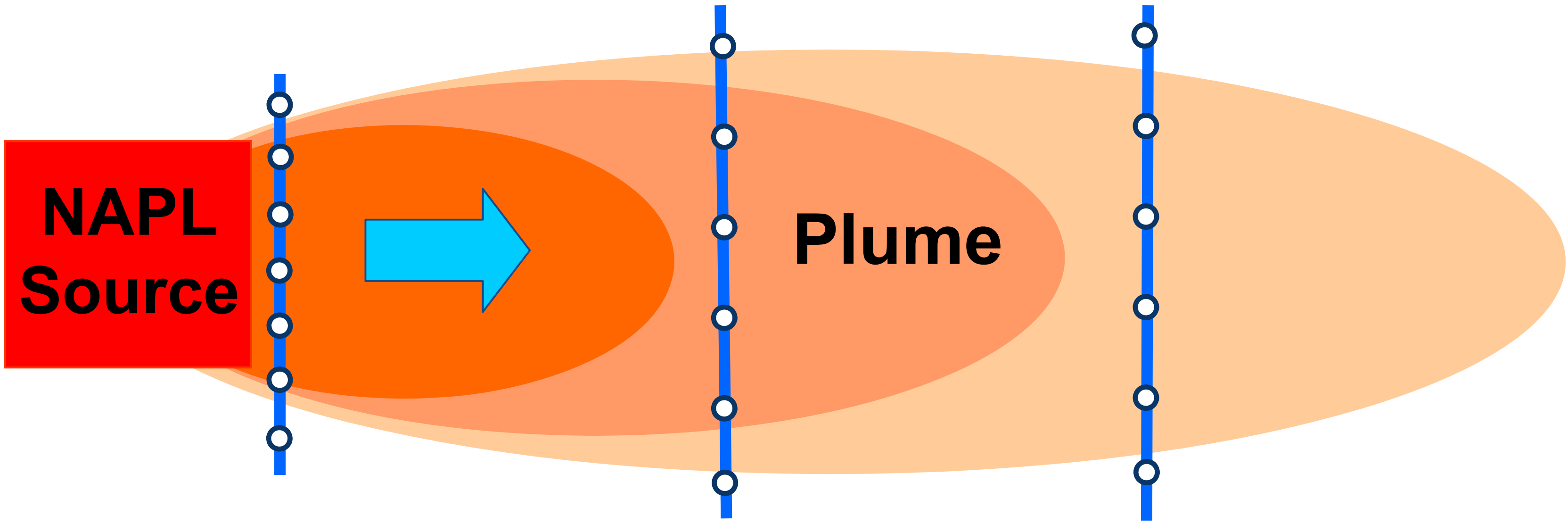


Mass Discharge = Source / Plume Strength



Mass Discharge = Source / Plume Strength

ITRC, 2016



Across any Transect, a Contaminant Plume Conveys:

Groundwater Discharge, **Q** (e.g., L/day)

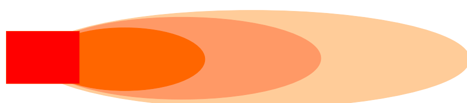
Contaminant **Mass Discharge**, **Md** (e.g., g/day or kg/year)

Md = Q x C **(L/day x mg/L = mg/day)**

Source Strength Affects Plume Length

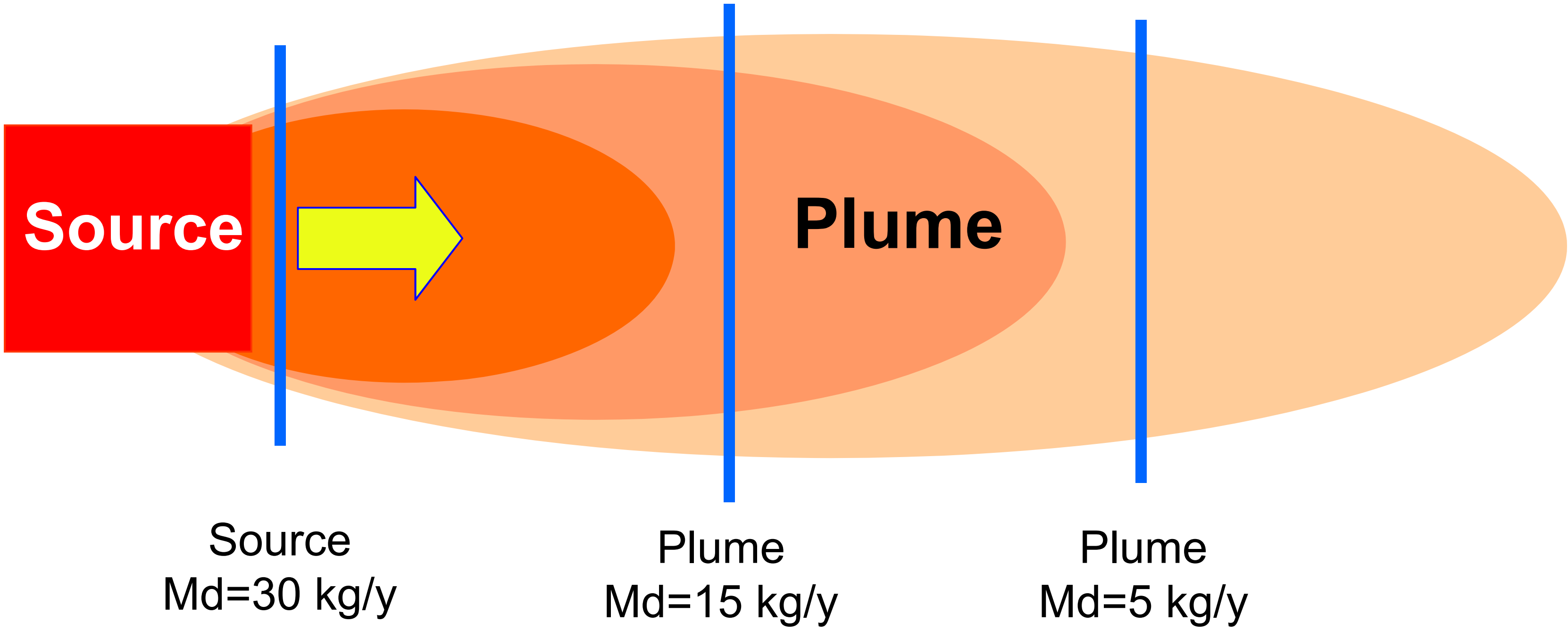
Site A: Source Strength = 30 kg/y

Site B: Source Strength = 10 kg/y



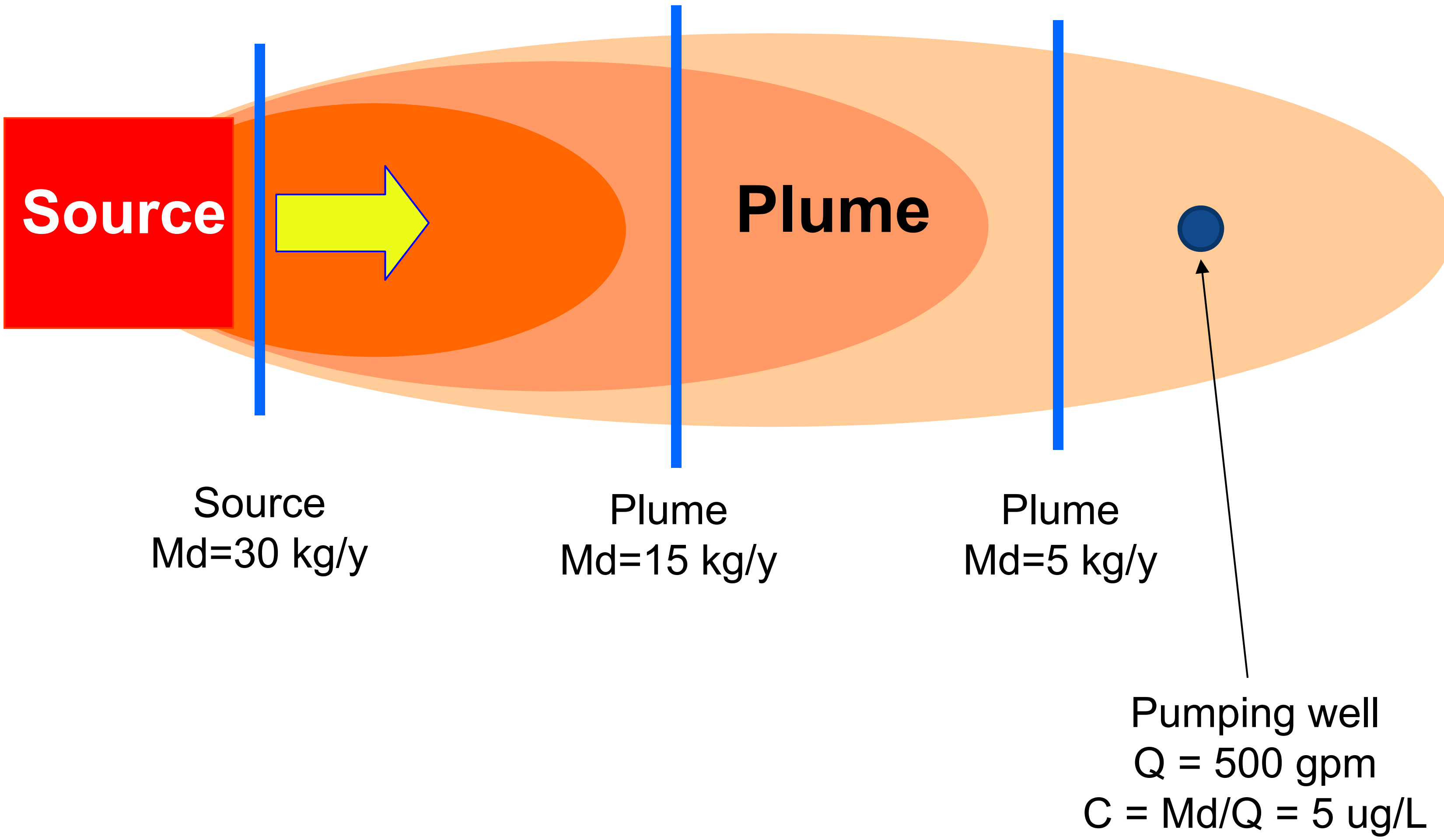
Note: all other conditions are equal for the two sites.

Mass Discharge Example

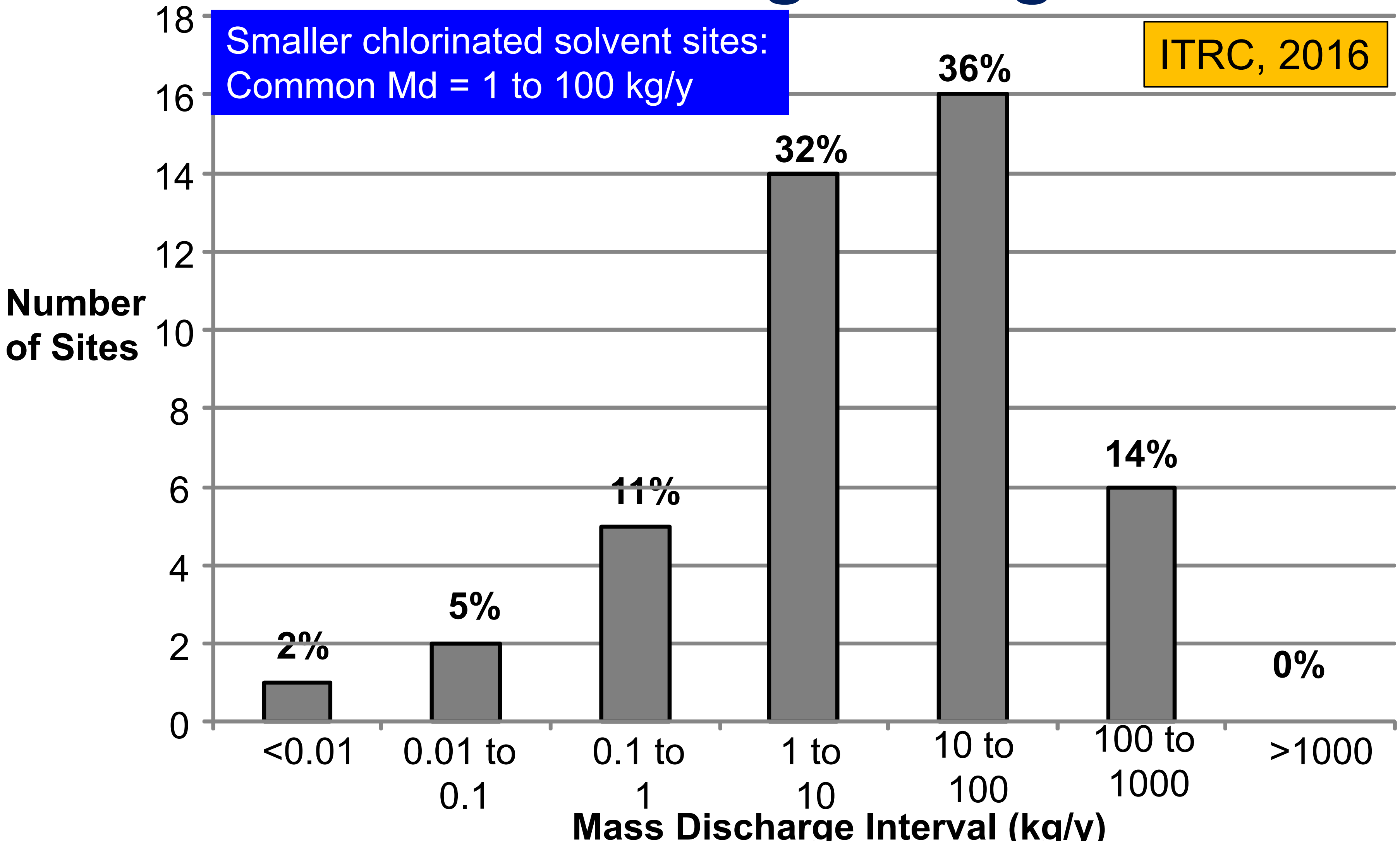


Biodegradation occurring along flowpath.

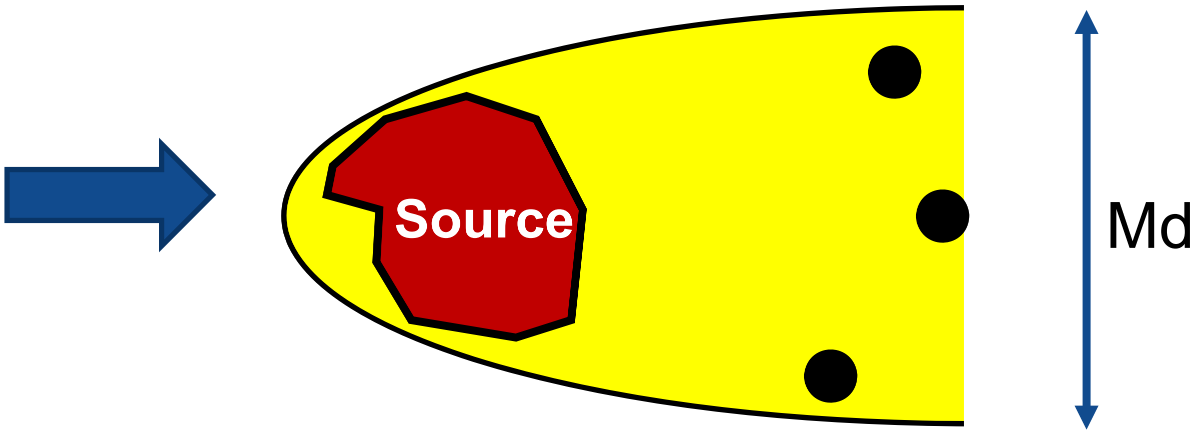
Mass Discharge Example



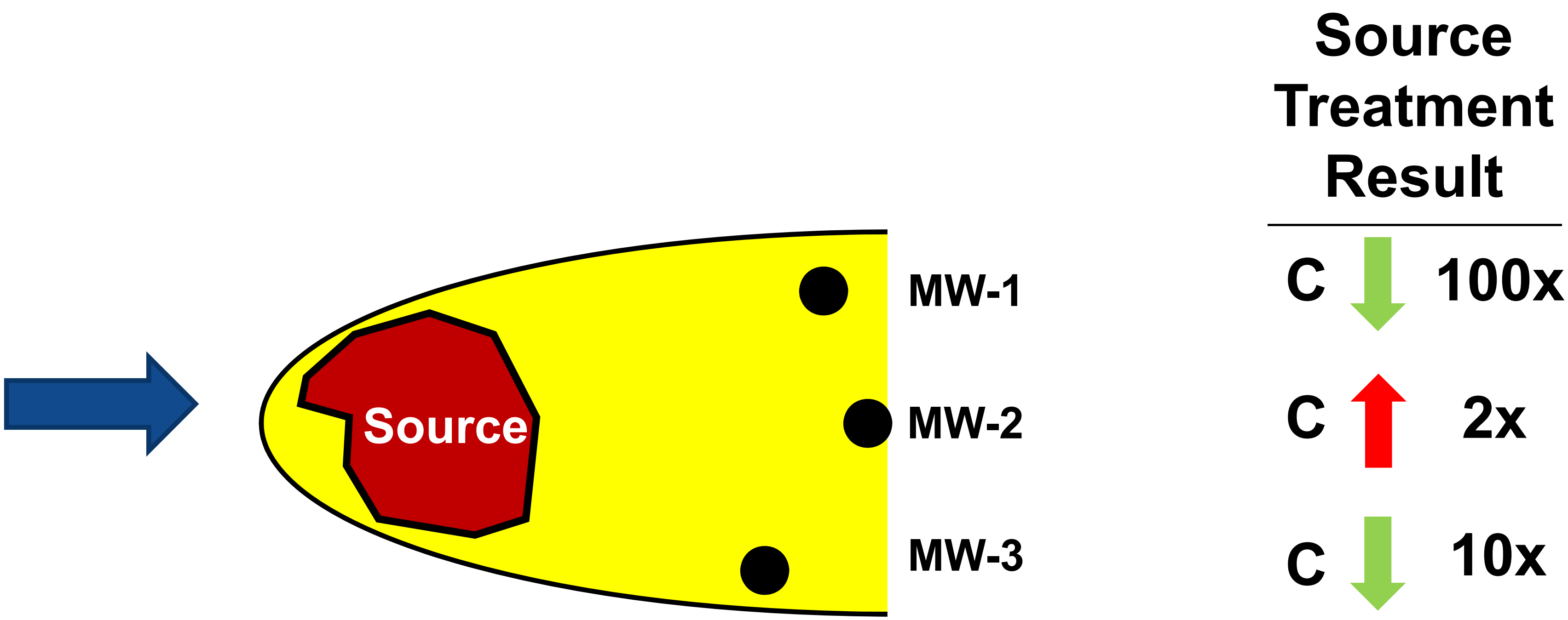
Frequency of Sites with VOC/SVOC Mass Discharge Ranges



Remedial Performance Monitoring



Remedial Performance Monitoring



Concentration Trends
– large variability between wells

Mass Discharge Trend
– Single metric, overall / average indicator
- Directly proportional to risk reduction

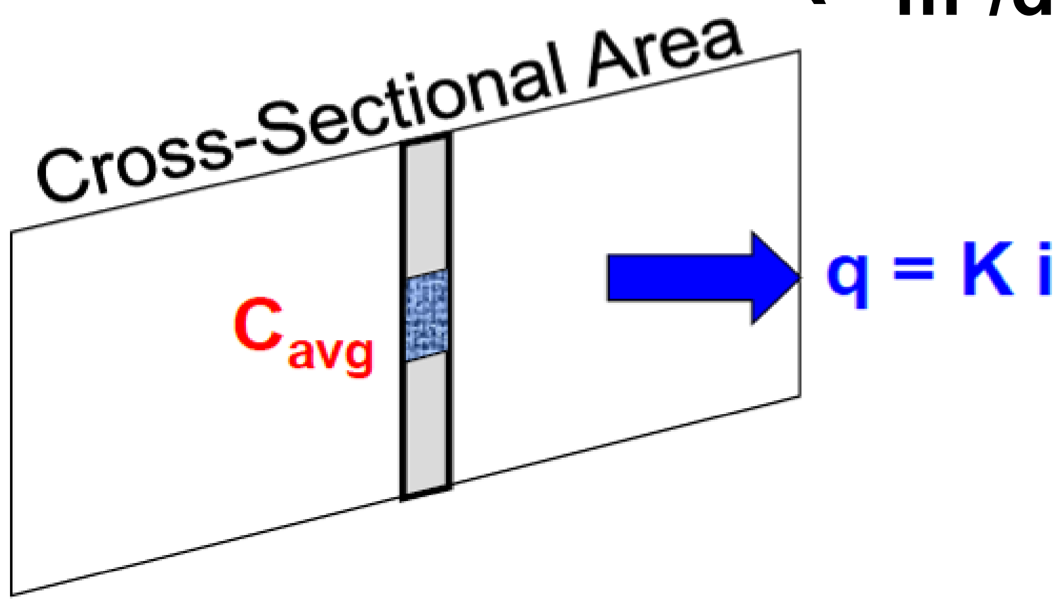
What Is Mass Flux?

ITRC, 2016

1. Specific Discharge, $q = K \times i$ $\left(\dfrac{L}{m^2/day}\right)$

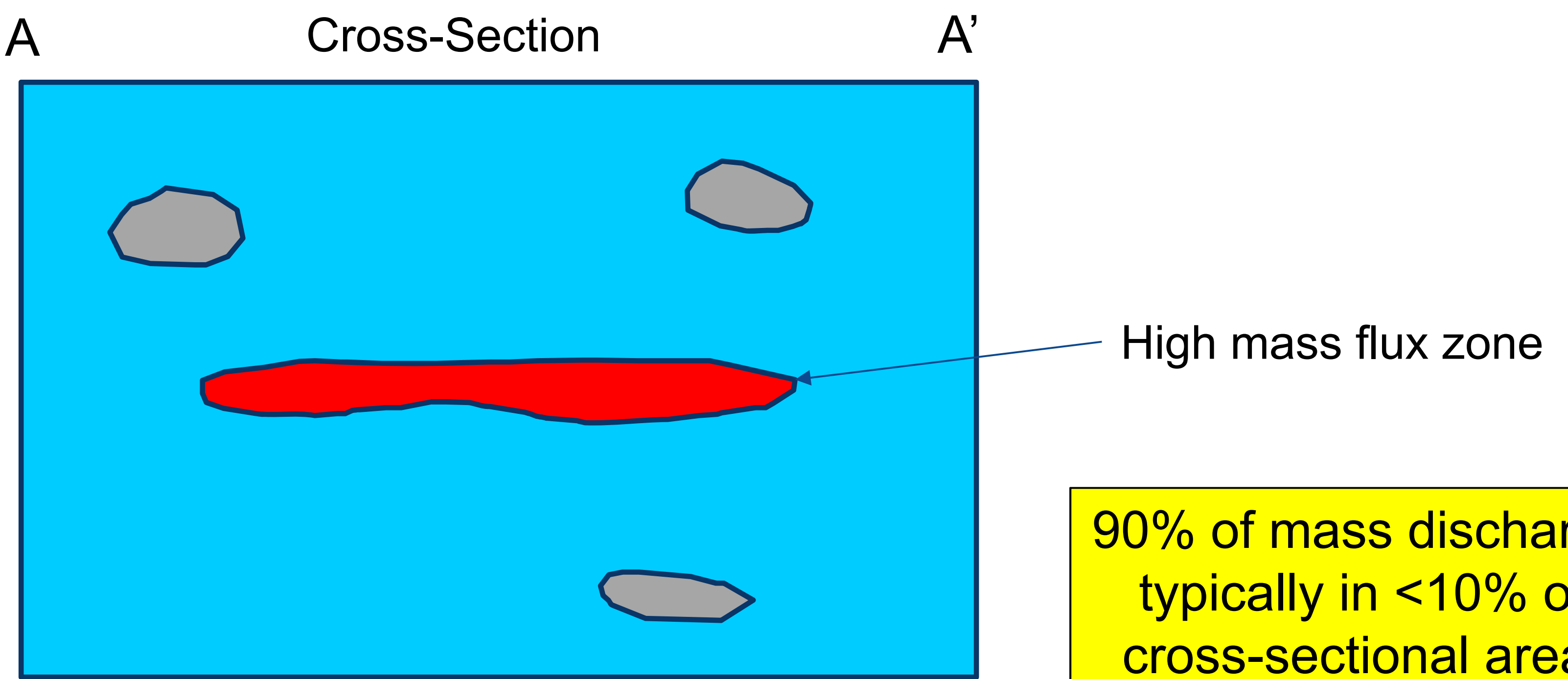
2. Average concentration, C_{avg} (g/L)

3. Mass Flux, $(J) = q \times C$ $\left(\dfrac{g}{m^2/day}\right)$

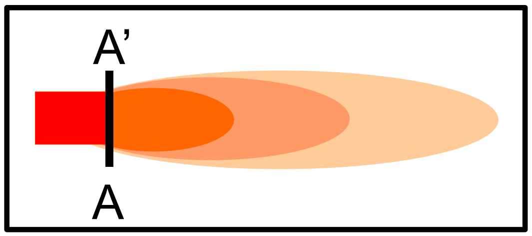


Mass Discharge Uses at NAPL Sites

- Focus remediation – high mass flux zones

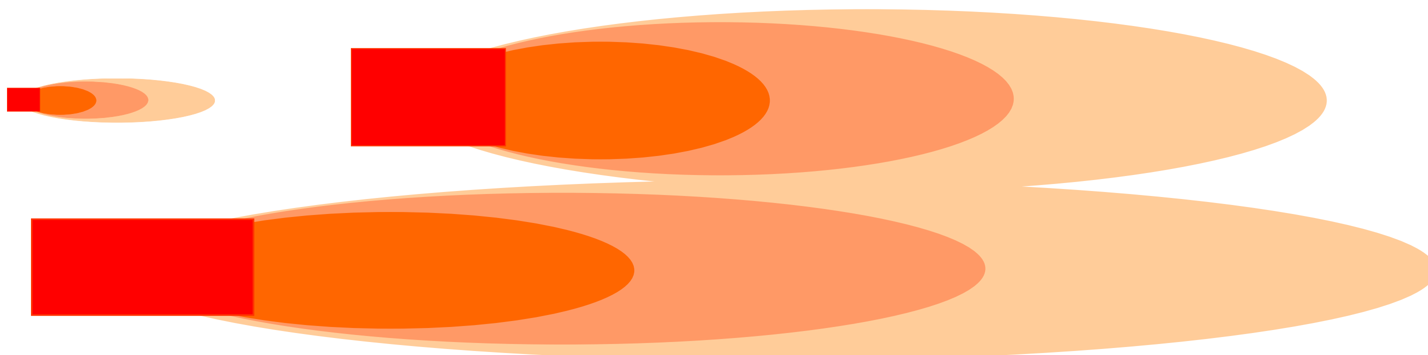


90% of mass discharge typically in <10% of cross-sectional area.



Mass Discharge Uses at NAPL Sites

- Focus remediation – high mass flux
- Prioritize - multiple zones or sites



Mass Discharge Uses at NAPL Sites

- Focus remediation – high mass flux
- Prioritize - multiple zones or sites
- Interim remedial goal
  - Risk reduction goal

Case Studies Section 3.1, and Carey, McBean, and Feenstra (2014b)

	Mean MdR	MdR Interval
EISB:	105x	(20x to 556x)
ISCO:	21x	(4x to 110x)
Thermal:	31x	(6x to 150x)

MdR = Mass discharge reduction

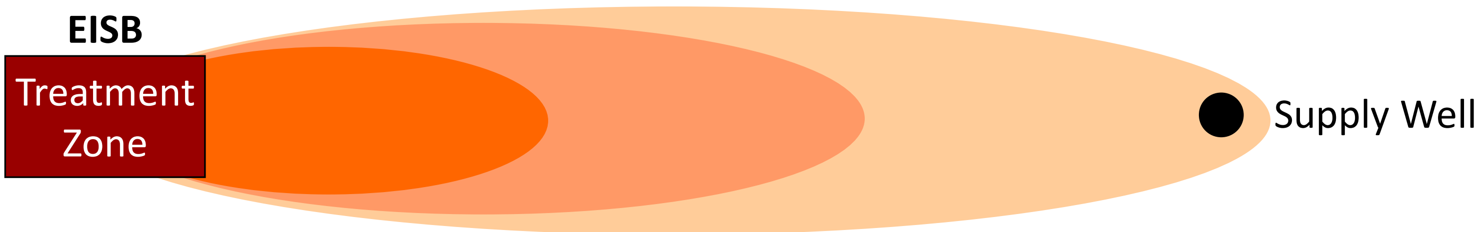
Mass Discharge Uses at NAPL Sites

- Focus remediation – high mass flux
- Prioritize - multiple zones or sites
- Interim remedial goal
  - Risk reduction goal
  - Empirical databases – What's attainable?
- Relative timeframes
- Plume response to treatment
- Performance monitoring

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.

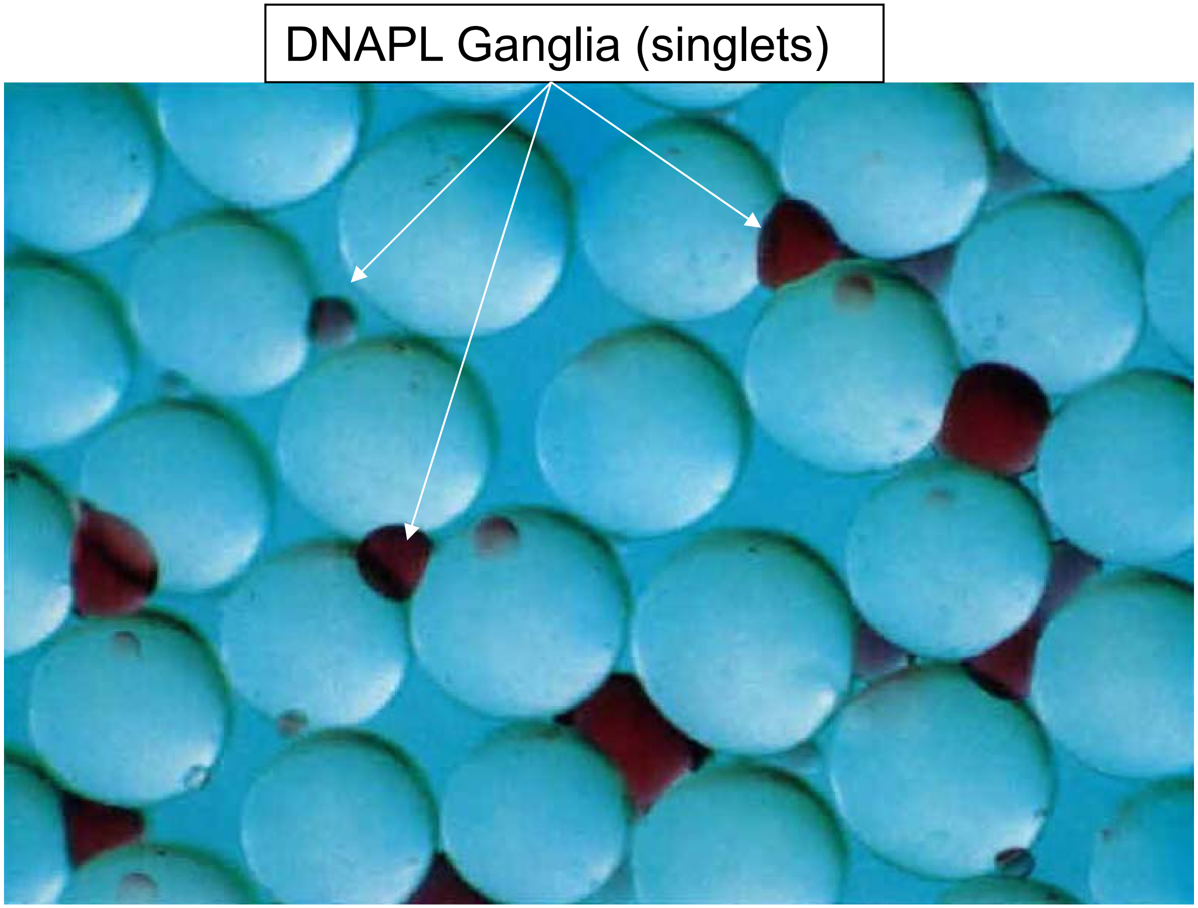


STEP 2: After this goal is achieved, transition to MNA in source zone

CONCEPTS

1.2 DNAPL TRENDS

Residual NAPL (Ganglia)

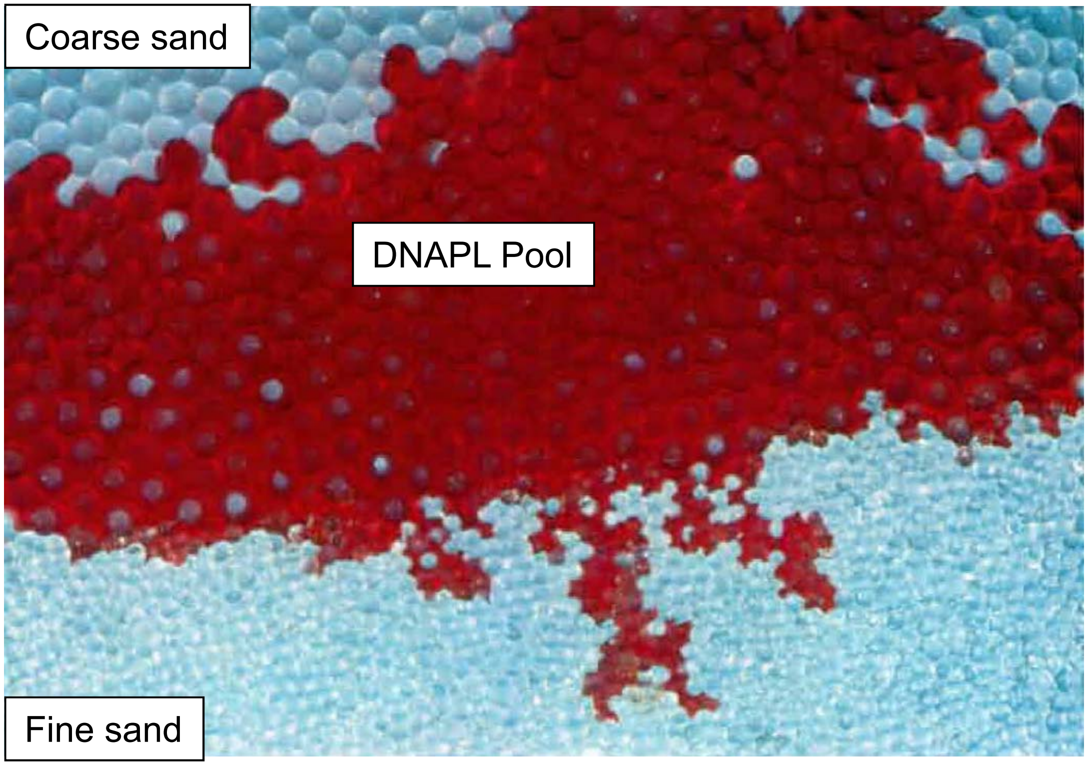


Source: *Schwille, 1988*

Residual NAPL

- Small
- Discontinuous
- Immobile

NAPL Pool (Free Phase)

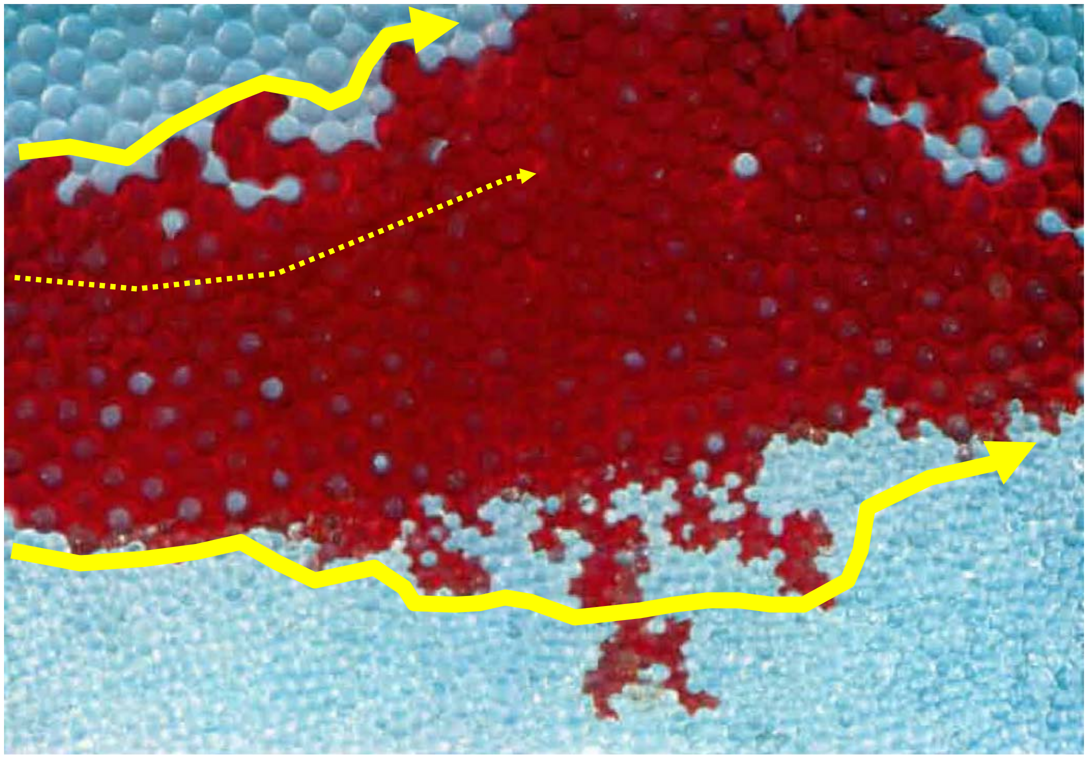


Source: *Schwille, 1988*

NAPL Pools

- Above low-K soil
- Horizontal NAPL layer
- Large mass

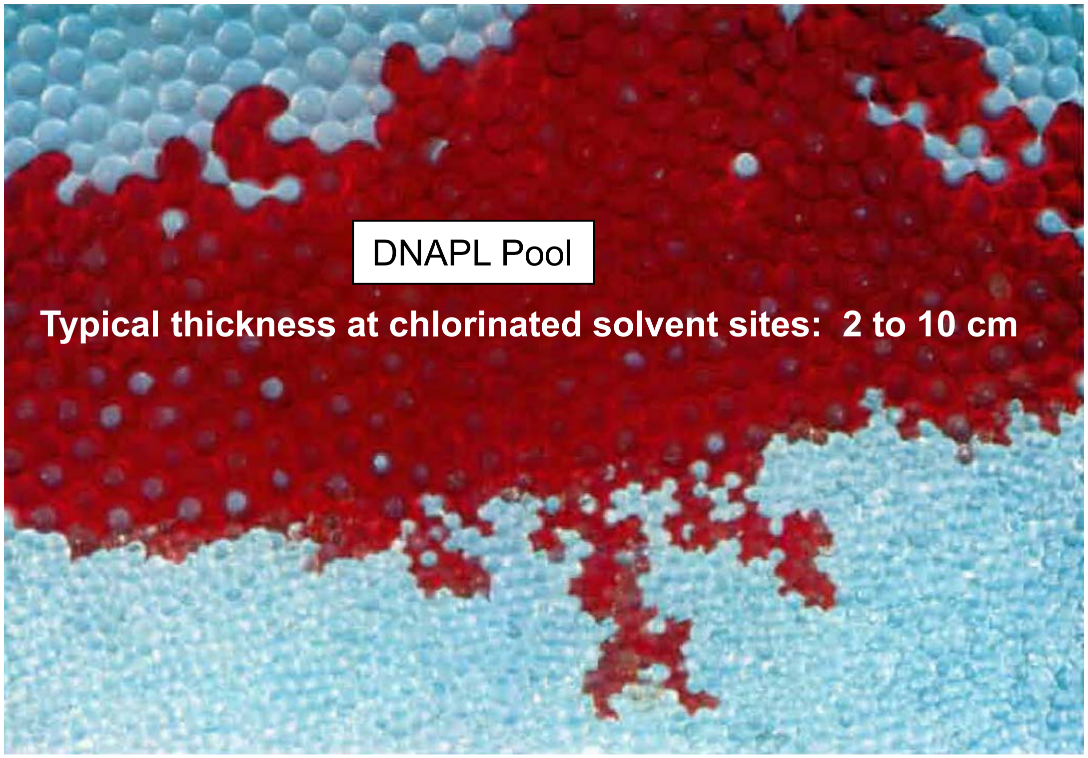
NAPL Pool (Free Phase)



Source: *Schwille, 1988*

NAPL below pool surface is generally not available to groundwater flow.

NAPL Pool (Free Phase)



Source: *Schwille, 1988*

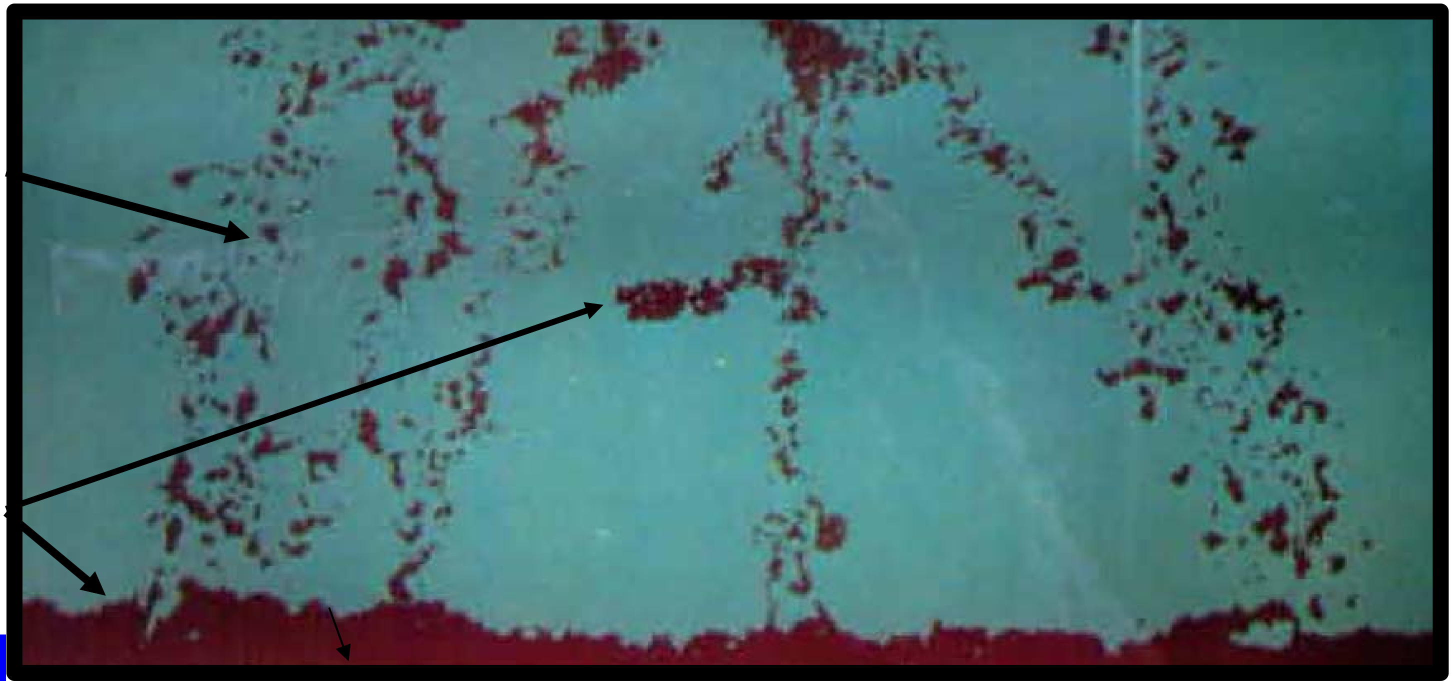
Fresh DNAPL Source Zone

Ganglia (residual NAPL)

Timeframe: Years

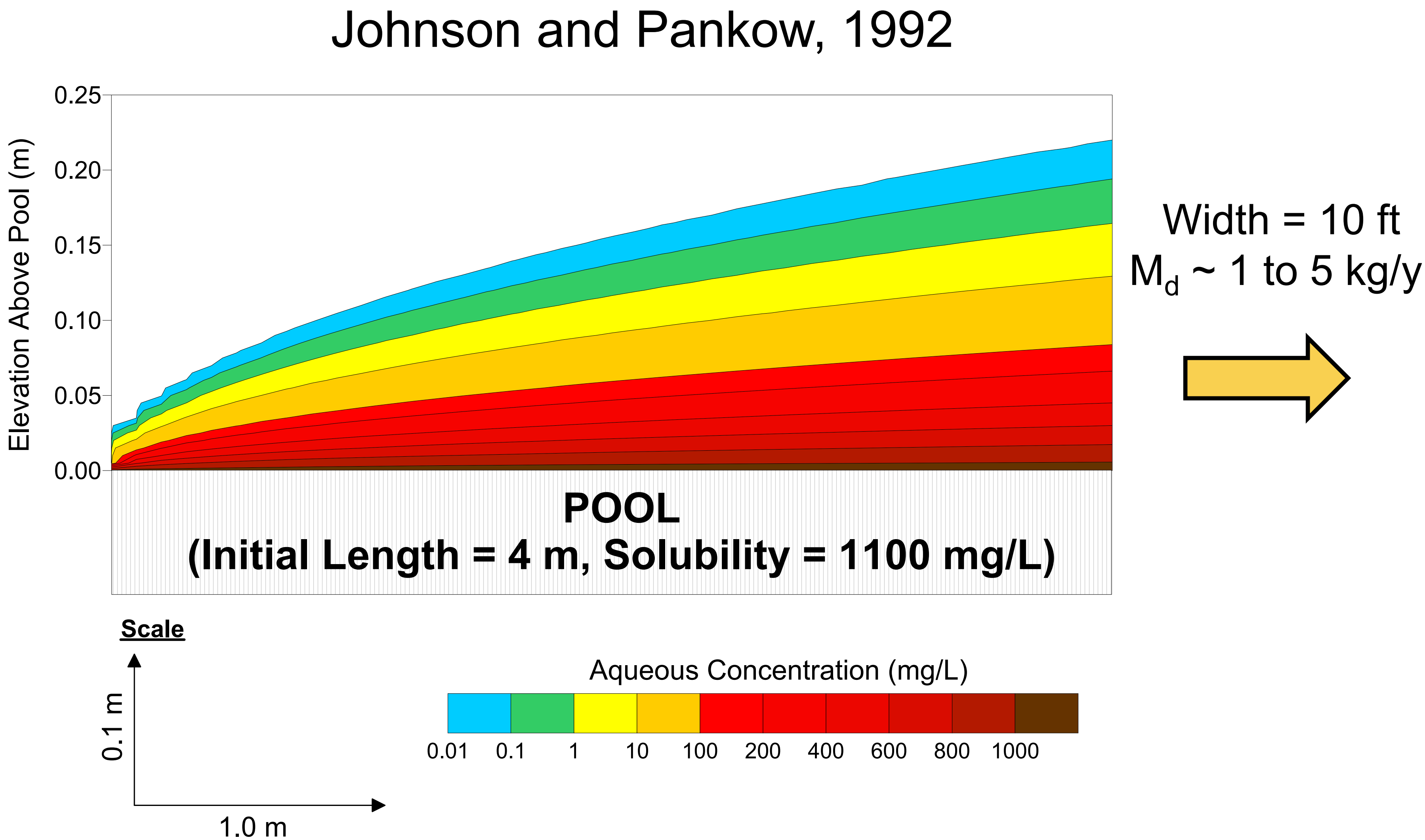
Pools (free phase NAPL)

Timeframe: Decades +

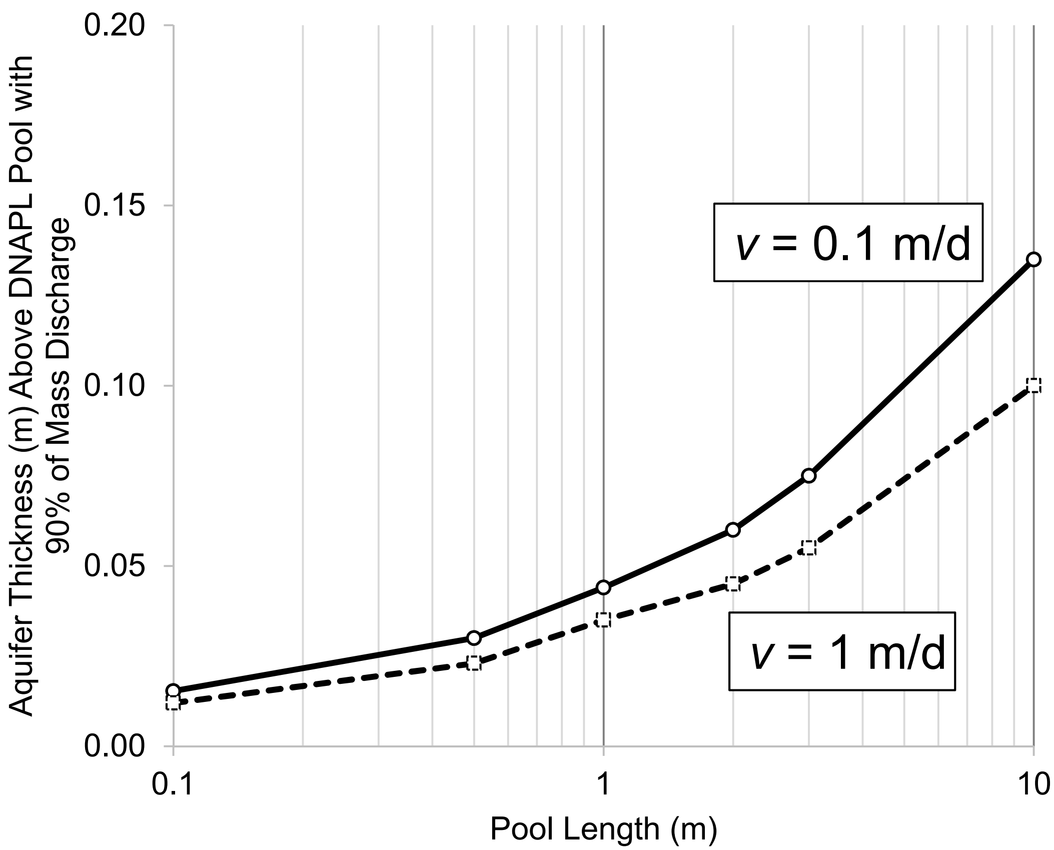


Source: *Schwille, 1988*

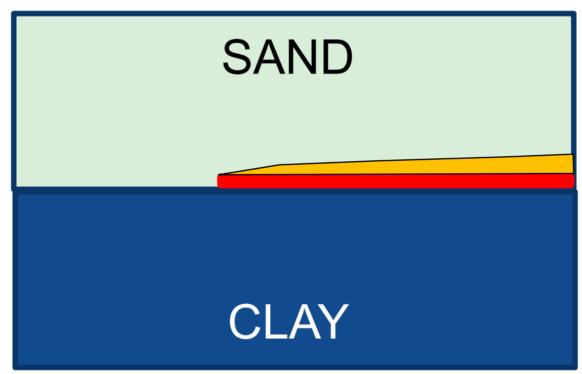
Concentration Profile Above Pool



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.



High intensity plumes over 1 to 6 inches above silt/clay layers.

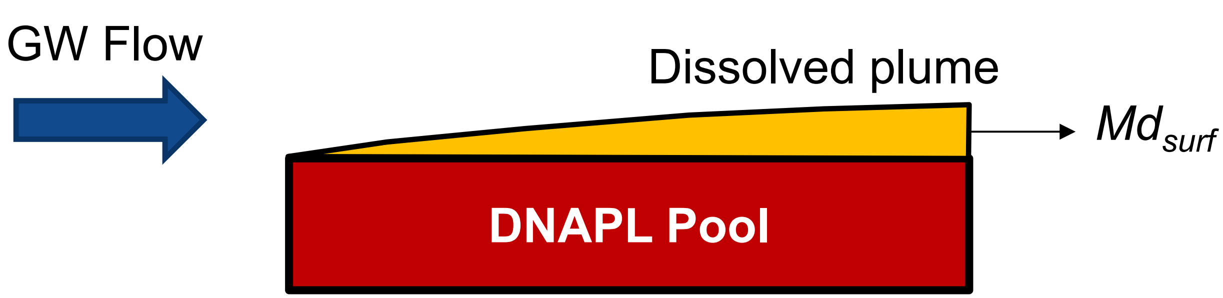
Surface Discharge from a DNAPL Pool

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

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 ($m^3/m^2/y$)
α_{TV} = transverse dispersivity (m)
θ_t = total porosity
τ = tortuosity coefficient
D_o = free-water diffusion coefficient (m^2/y)

Md proportional to:

- GW velocity
- Solubility
- Pool length, width



Surface Discharge from a DNAPL Pool

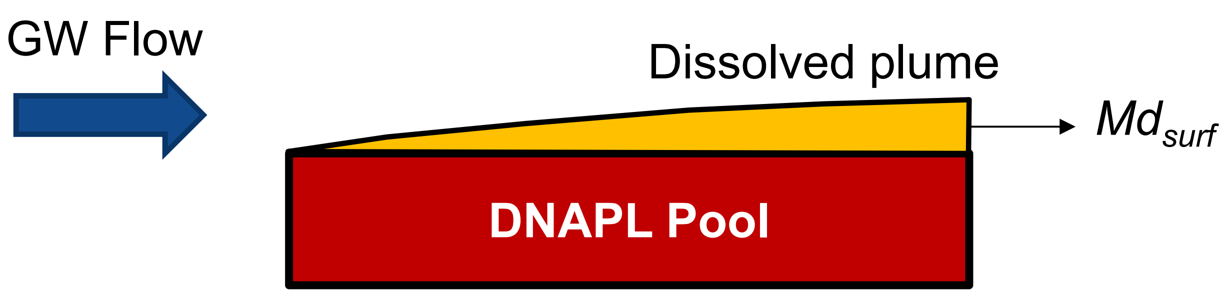
Solubility

1,2-DCA:	8,500 mg/L
TCE:	1,400 mg/L
PCE:	200 mg/L

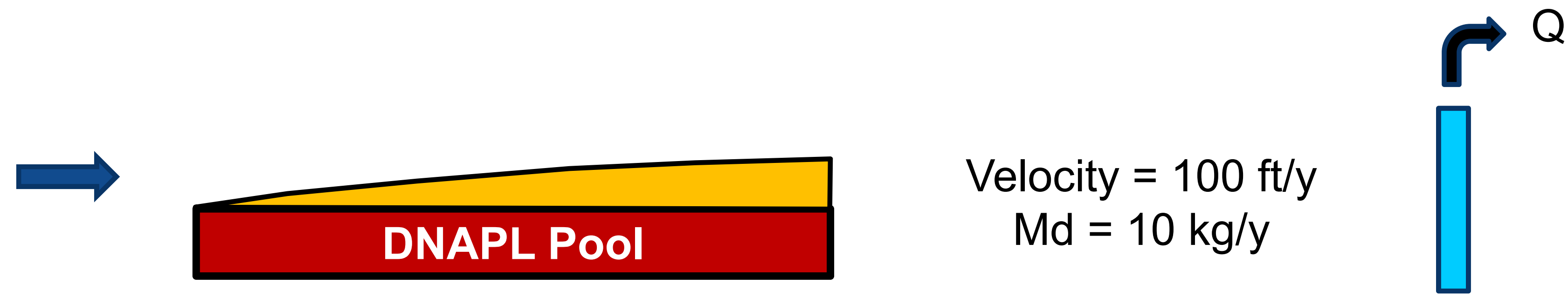
Higher C → Higher Md
Faster NAPL depletion

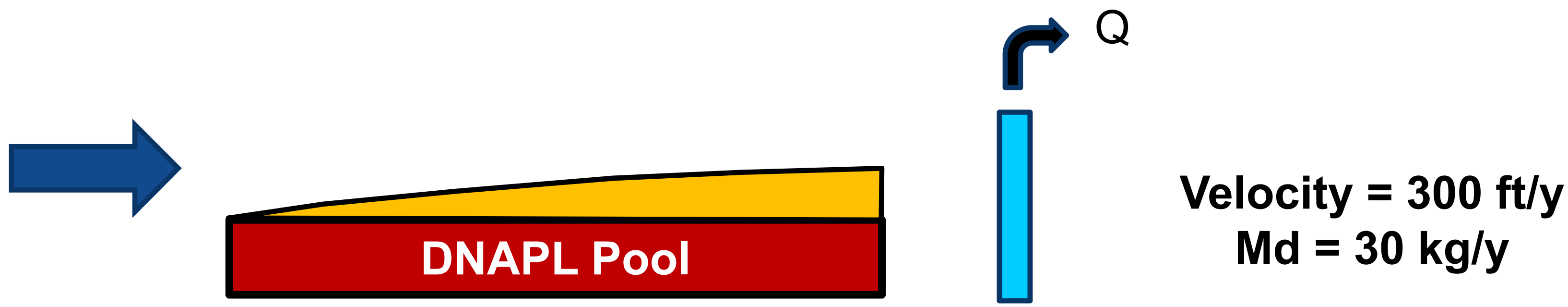
Md proportional to:

- GW velocity
- Solubility
- Pool length, width



Surface Discharge from a DNAPL Pool





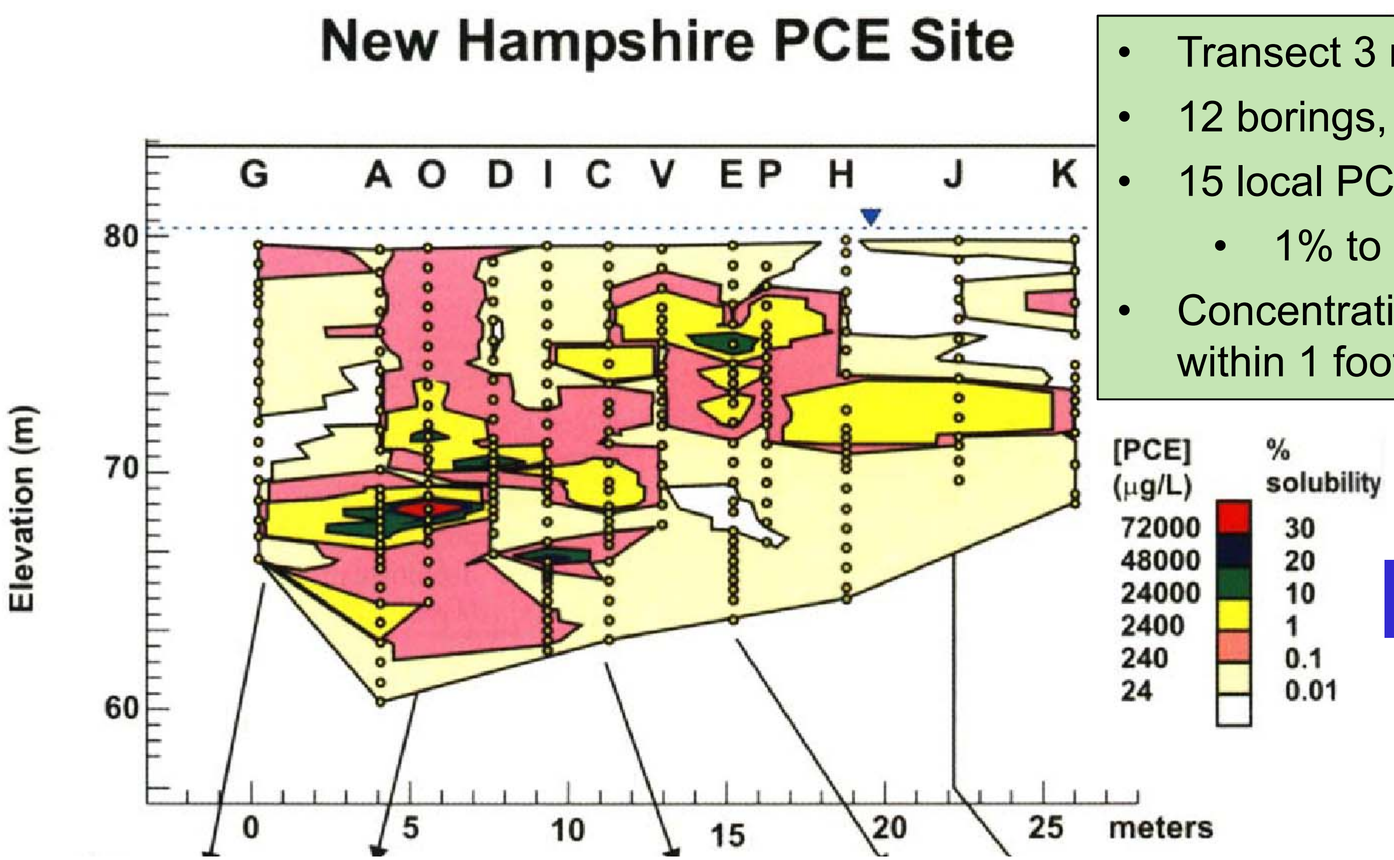
“Strategic Pump-and-Treat “(SP&T) may increase mass discharge from a NAPL zone, and reduce remediation timeframe.

Carey, McBean, and Feenstra (2014b)

ITRC (2016) – Reese Air Force Base

Source Mass Flux - Guilbeault et al., 2005

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

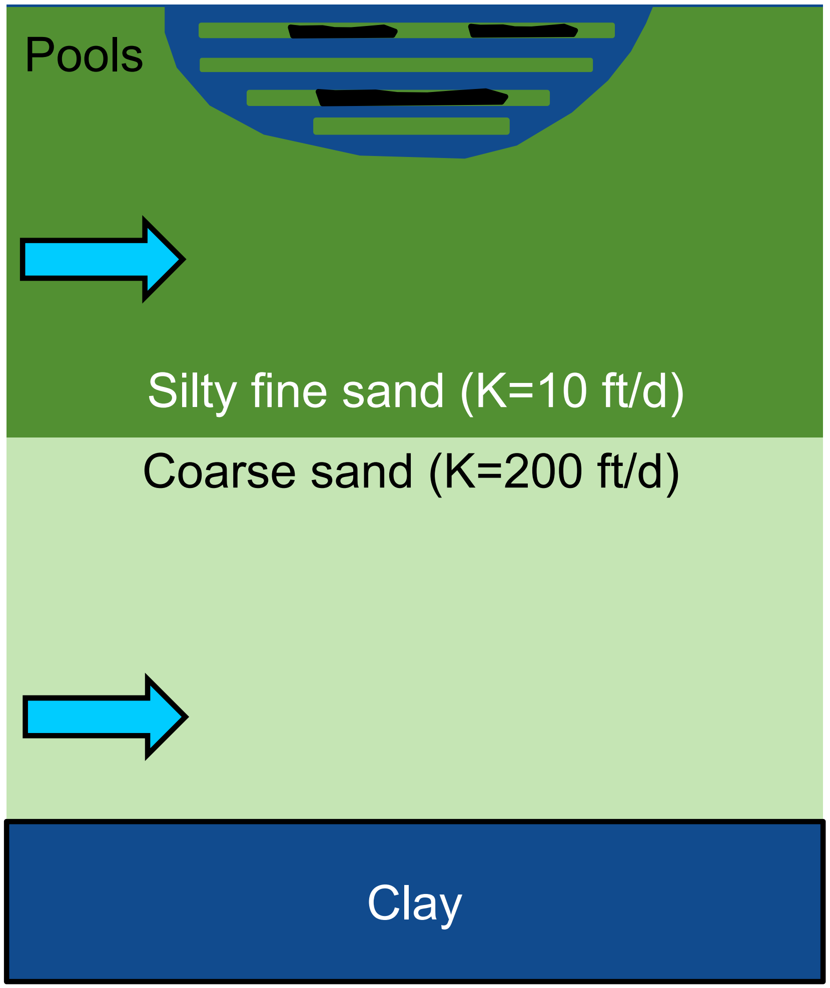


- Transect 3 m d/g of source
- 12 borings, 257 samples
- 15 local PCE maximae
  - 1% to 62% of solubility
- Concentrations vary up to 100x within 1 foot of soil core

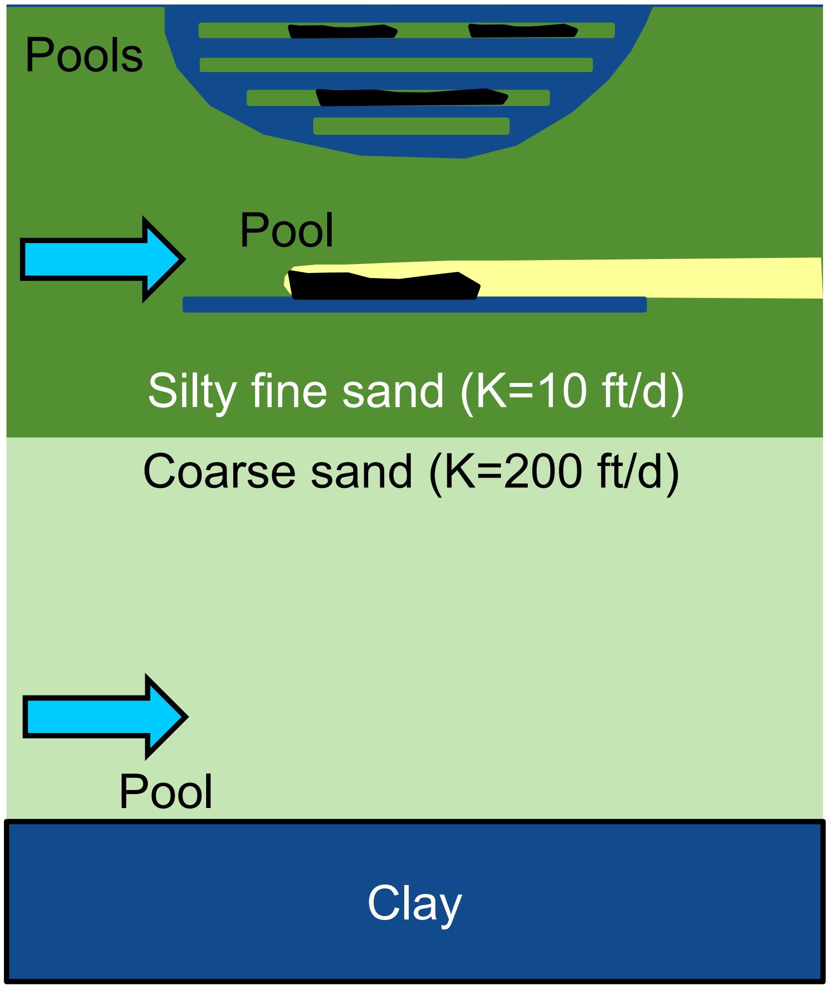
Md = 15 kg/y

Data indicate multiple, thin DNAPL layers present, several meters wide

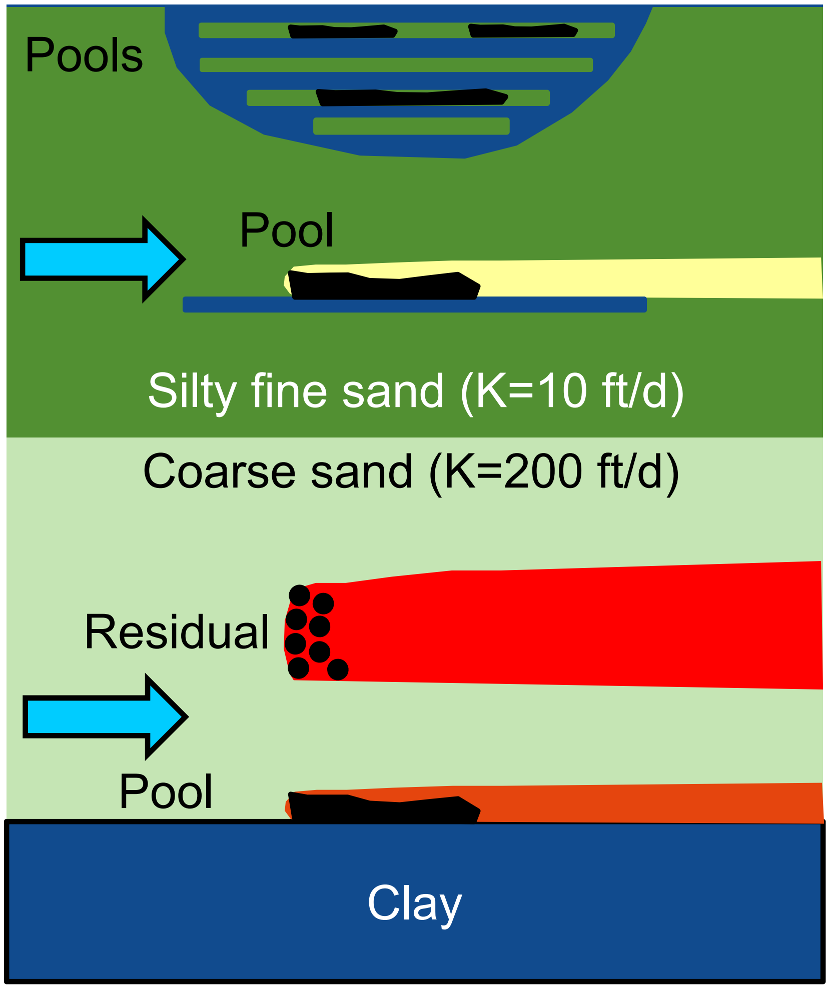
NAPL Accessibility vs. Mass Discharge



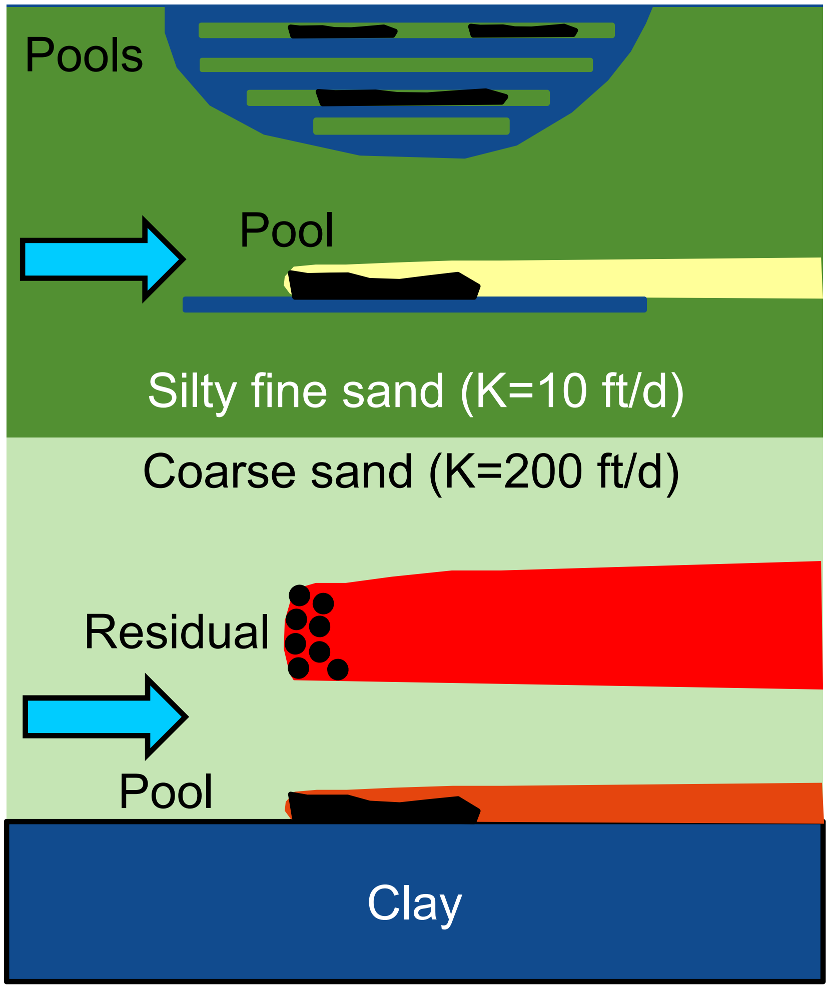
NAPL Accessibility vs. Mass Discharge



NAPL Accessibility vs. Mass Discharge



NAPL Accessibility vs. Mass Discharge



Relative Mass Discharge

Negligible

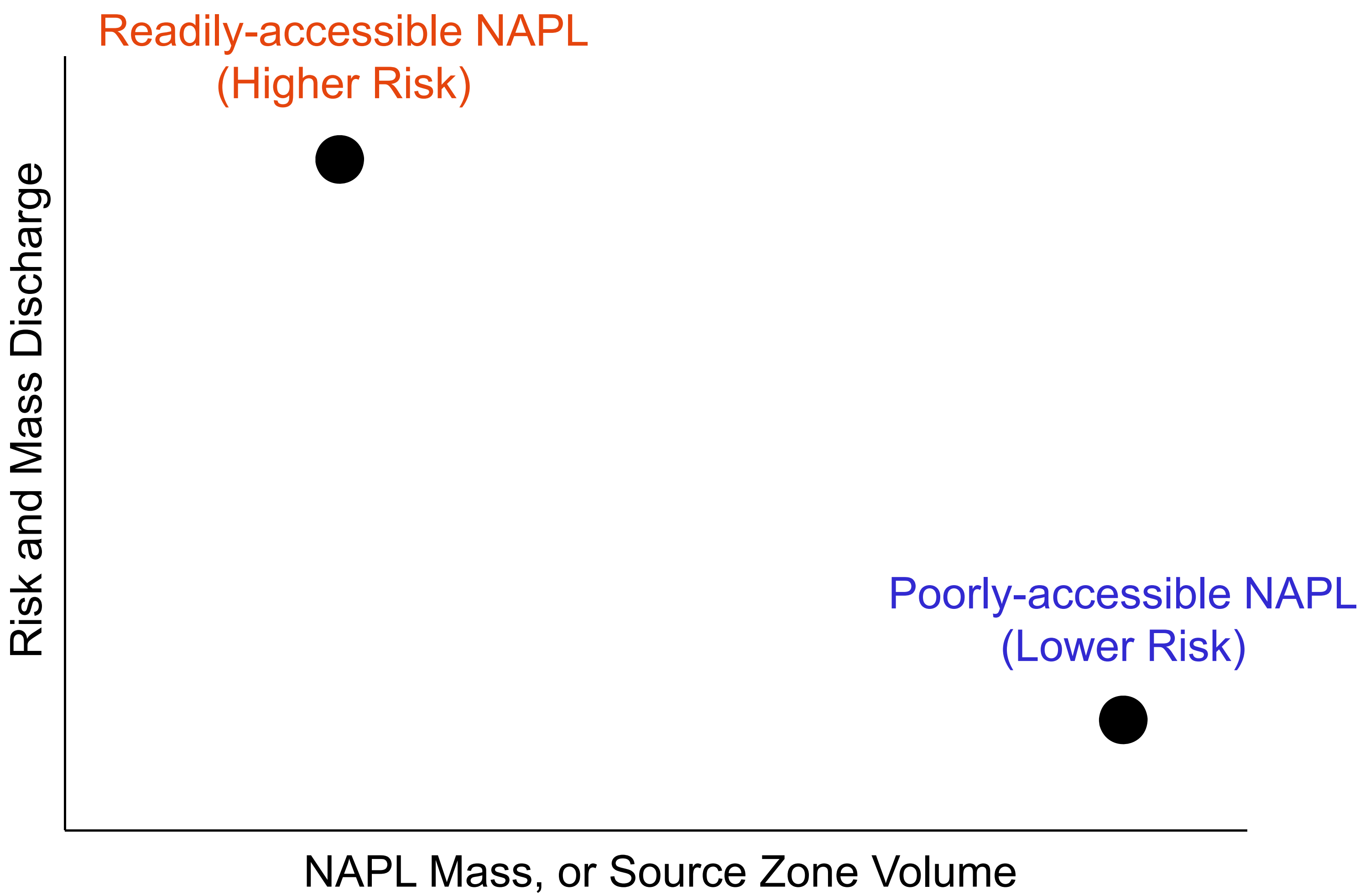
Low

Highest

Moderate to High

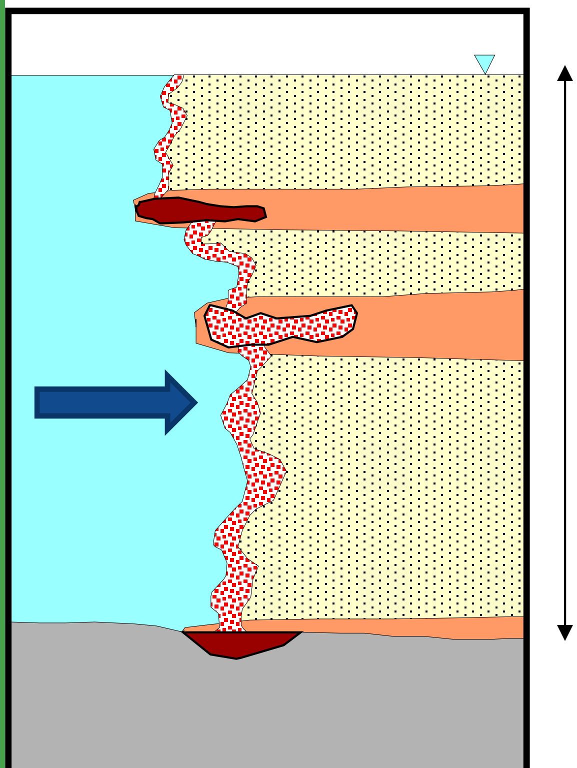
Note: Rate of NAPL depletion is inversely proportional to accessibility.

Mass Discharge vs. NAPL Mass



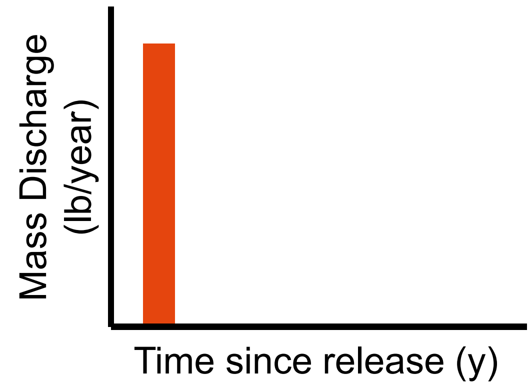
Mass Discharge Trend with Time

Fresh Source



Modified from Parker et al., 2003

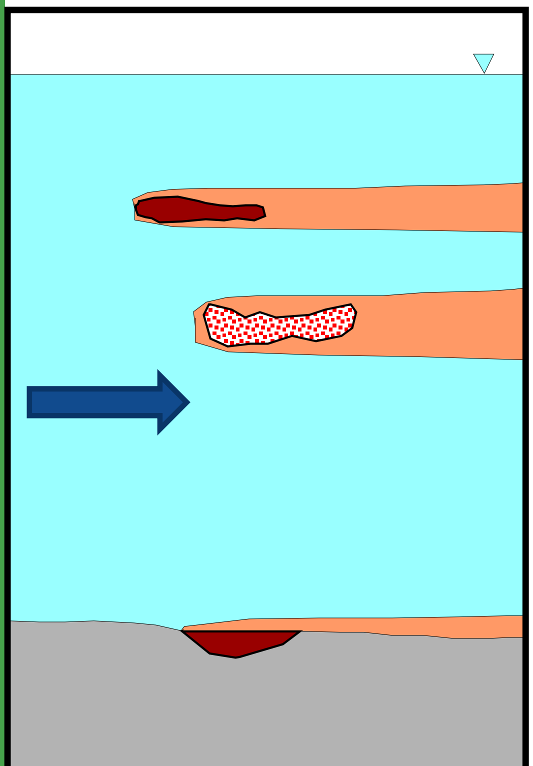
Mass discharge from source zone (kg/y)

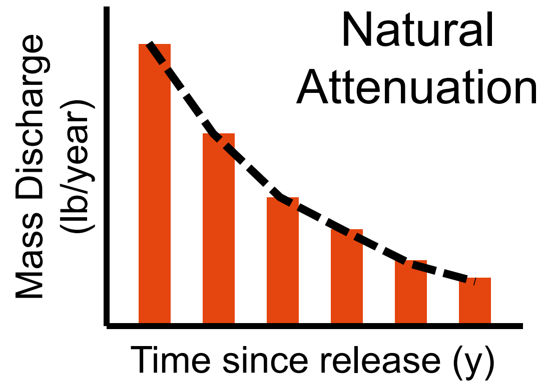


Mass Discharge Trend with Time

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

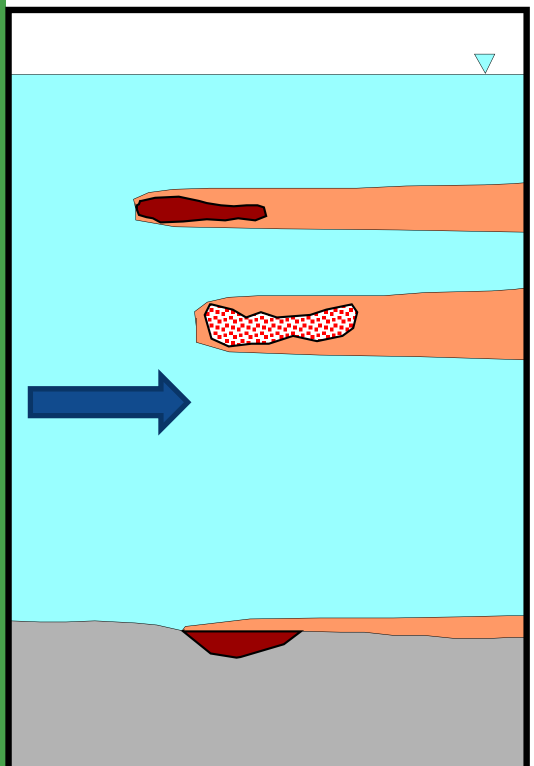
Aged Source





Mass Discharge Trend with Time

Aged Source



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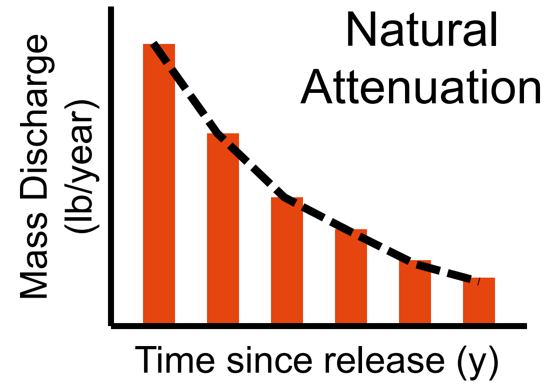
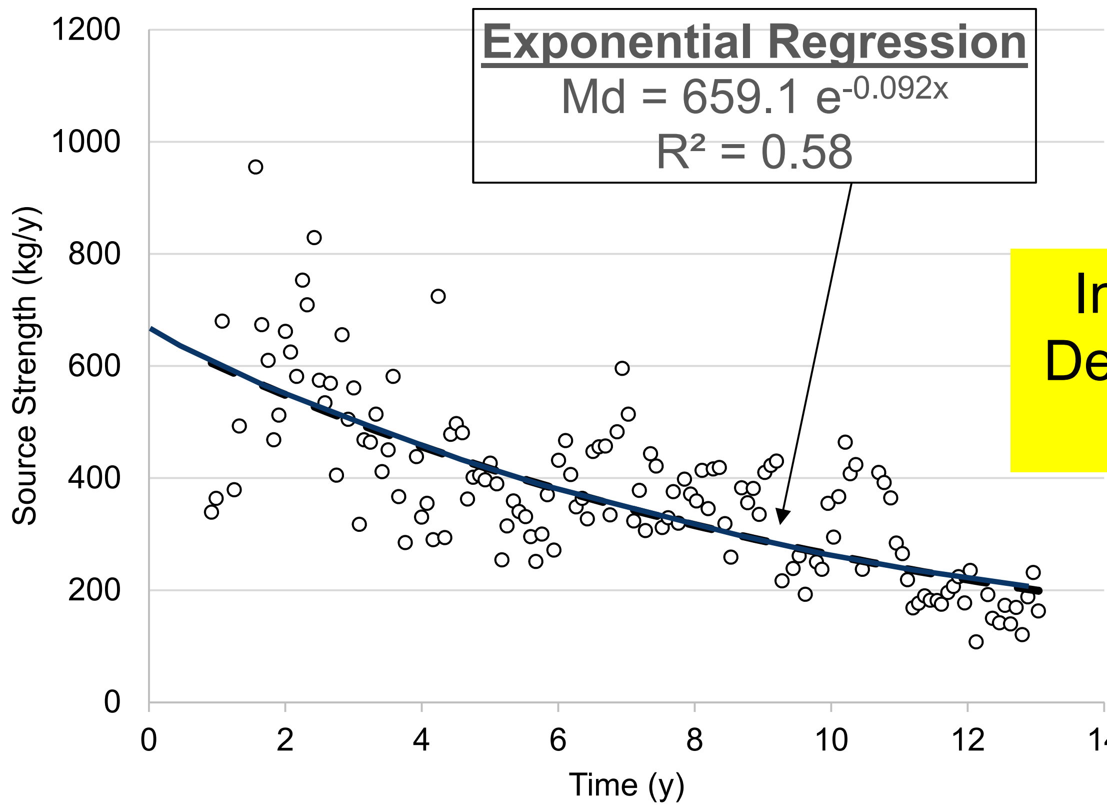


Newell et al., 2006:
Median TCE DNAPL half-life of 6 years

Mass discharge reduction 30x in 30 years

Naturall-Occurring Source Strength Decline at Tuscon Airport Site

Mass discharge estimates based on pumping wells near source zones.



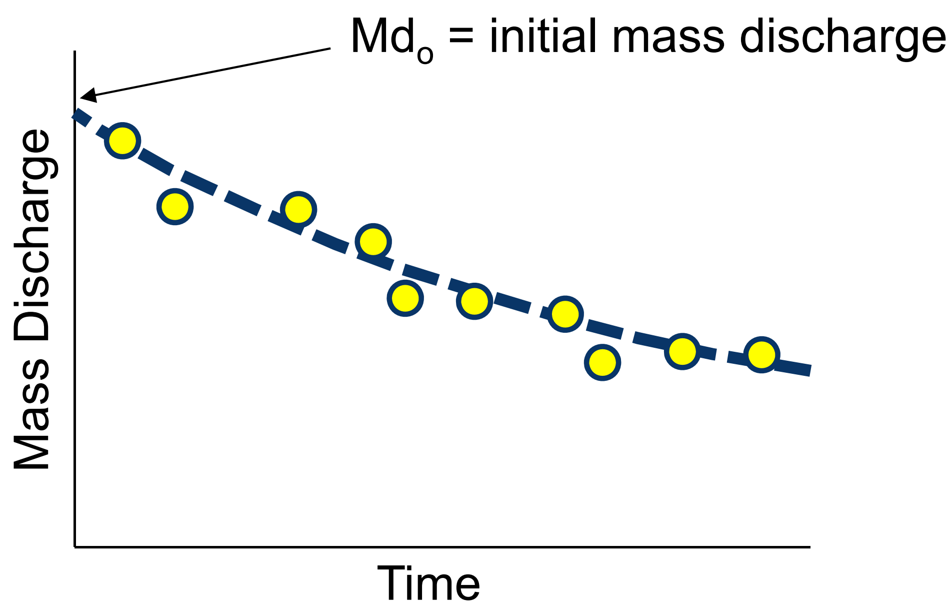
Initial Md (Md_o) = 660 kg/y
Decline rate (λ_{Md}) = 0.092 y^{-1}
Decline half-life = 7.5 y

Modified from Brusseau et al. (2011)

Estimating Mass: Mass Discharge Method

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

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



Estimating Mass: Mass Discharge Method

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

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

Example calculation for Tuscon Airport Site:

$$M_o = (660\ kg/y) / (0.092\ y^{-1})$$
$= 7{,}164$ kg ~ **Minimum NAPL mass in subsurface**

(Readily-accessible NAPL)

Calculation assumes uniform decline rate, and is based on readily-accessible NAPL mass.

May underestimate mass in pool-dominated source zones.

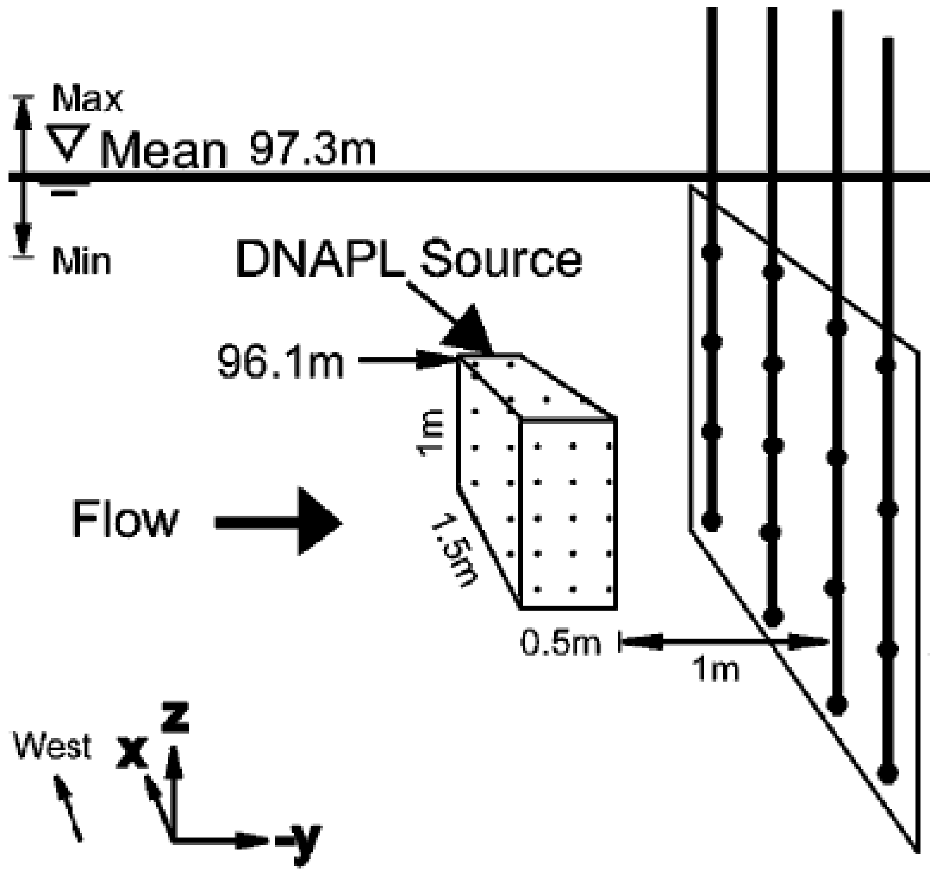
Multicomponent DNAPL Dissolution

- More soluble compounds preferentially depleted
- Less soluble compounds persist for longer time

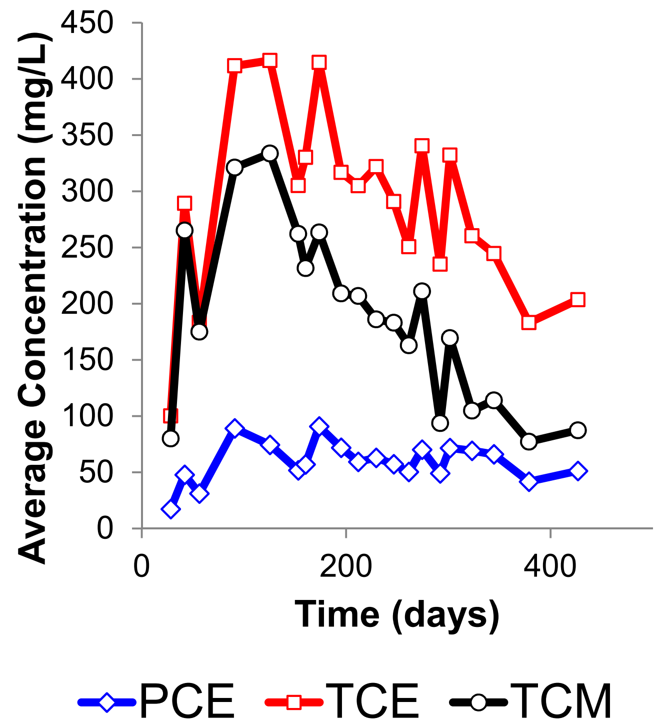
Multicomponent DNAPL Dissolution

- 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 in weathered DNAPL
  - Increasing conc. for less soluble compounds, as mole fraction (and effective solubility) increase over time

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

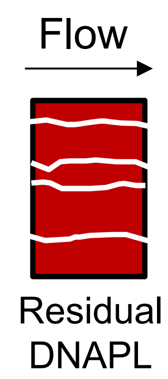


Source: Rivett and Feenstra (2005)



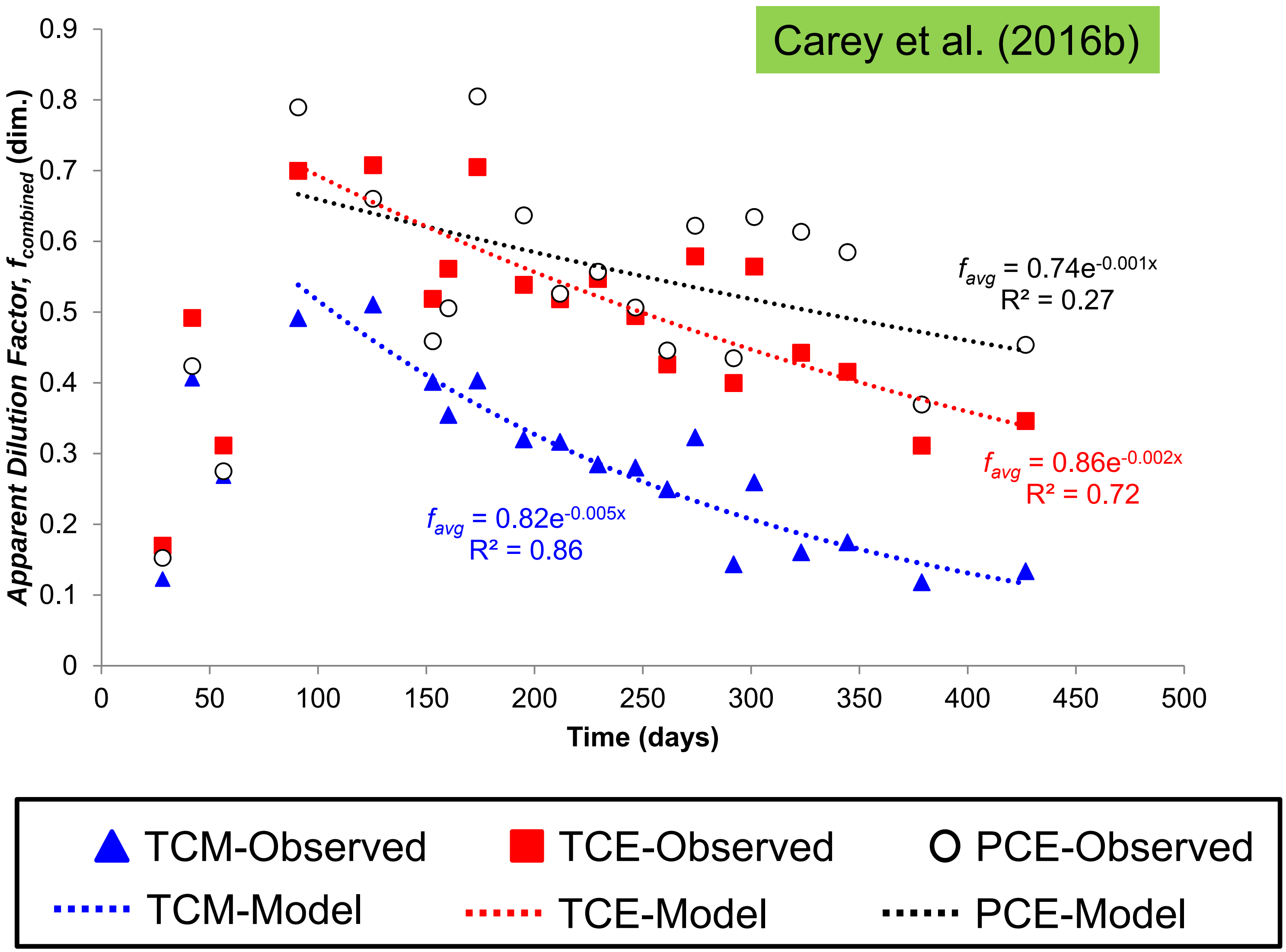
Emplaced Source Experiment Model

- 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



Carey et al. (2016b)

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



Enhanced NAPL Depletion and Mass Discharge Decline

- Enhanced Dissolution
  - Enhanced In-Situ Bioremediation (EISB)
  - In-Situ Chemical Oxidation (ISCO)
  - Strategic Pump-and-Treat
- Enhanced Volatilization – Thermal, SVE

	Mean MdR	**MdR Interval**
EISB:	105x	(20x to 556x)
ISCO:	21x	(4x to 110x)
Thermal:	31x	(6x to 150x)

Complex sites

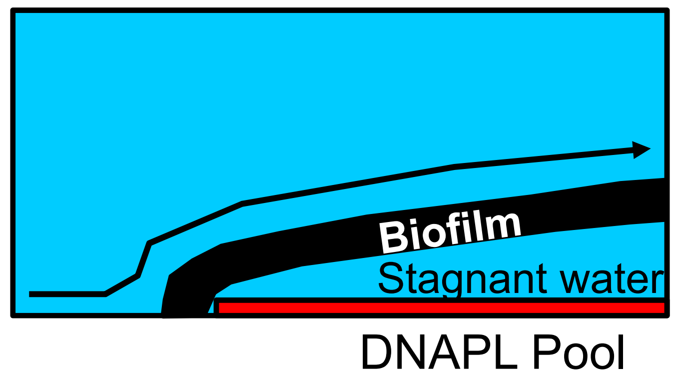
Chu et al. (2003) EISB Model Results

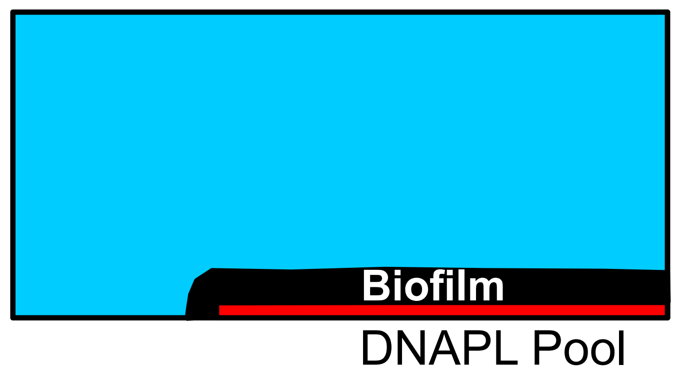
Case 1:

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

Case 2:

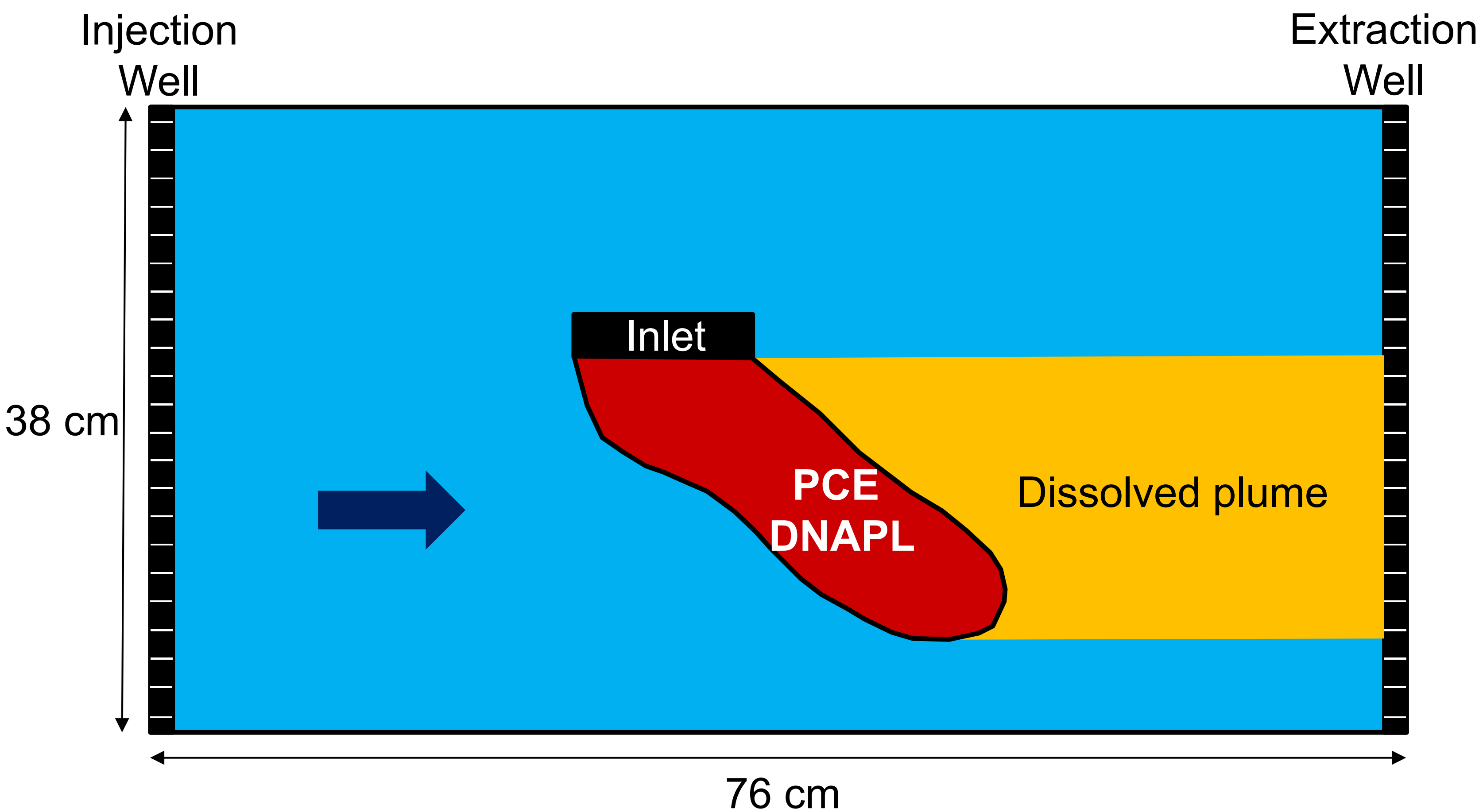
- Unlimited electron donor
- Biofilm grew adjacent to NAPL-water interface
- Most effective enhancement due to maximum concentration gradient





Modified from Chu et al. (2003)

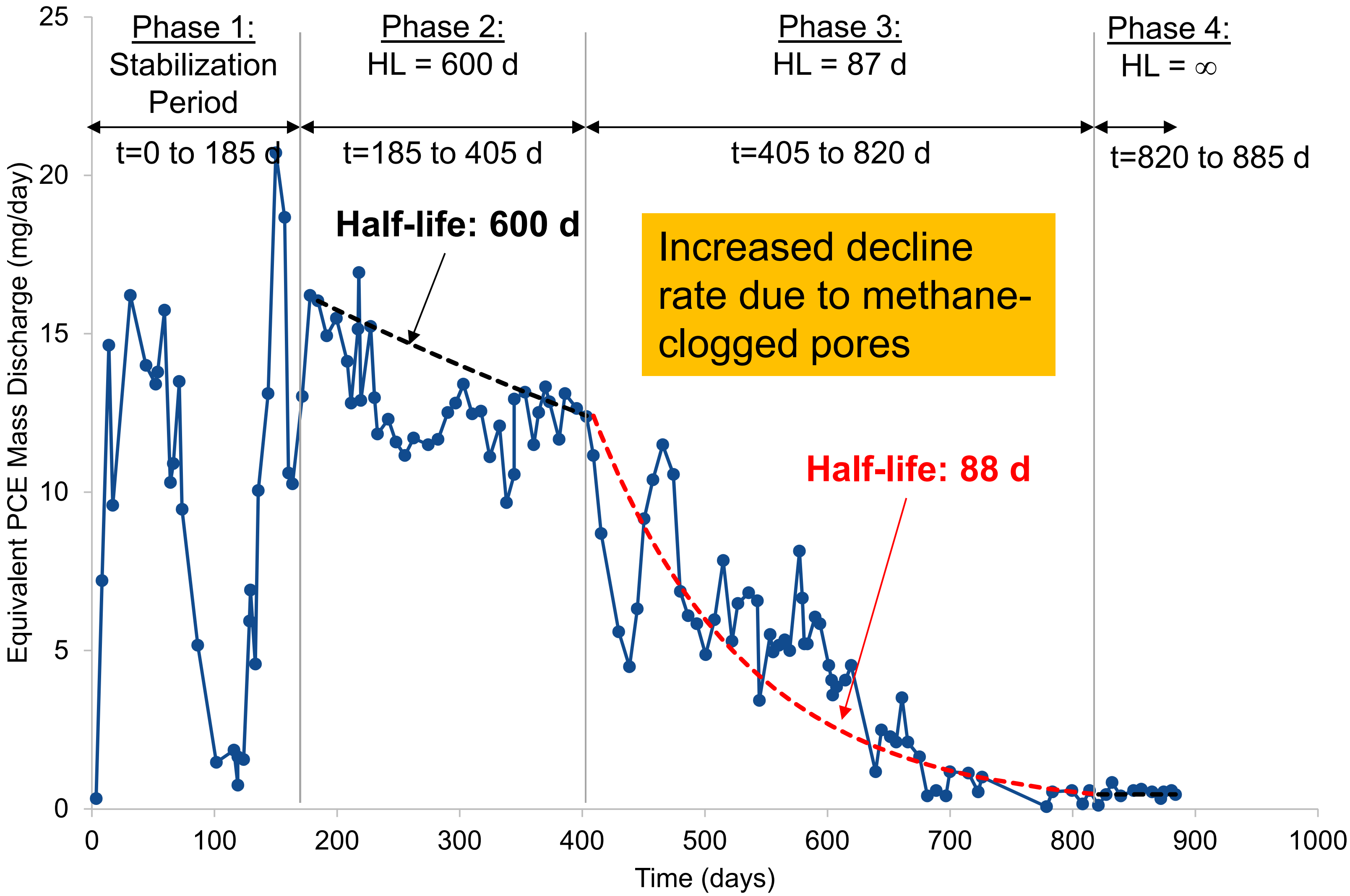
Sleep et al. (2006) DNAPL EISB Study



Modified from Sleep et al. (2006)

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

EISB in Lab Experiment

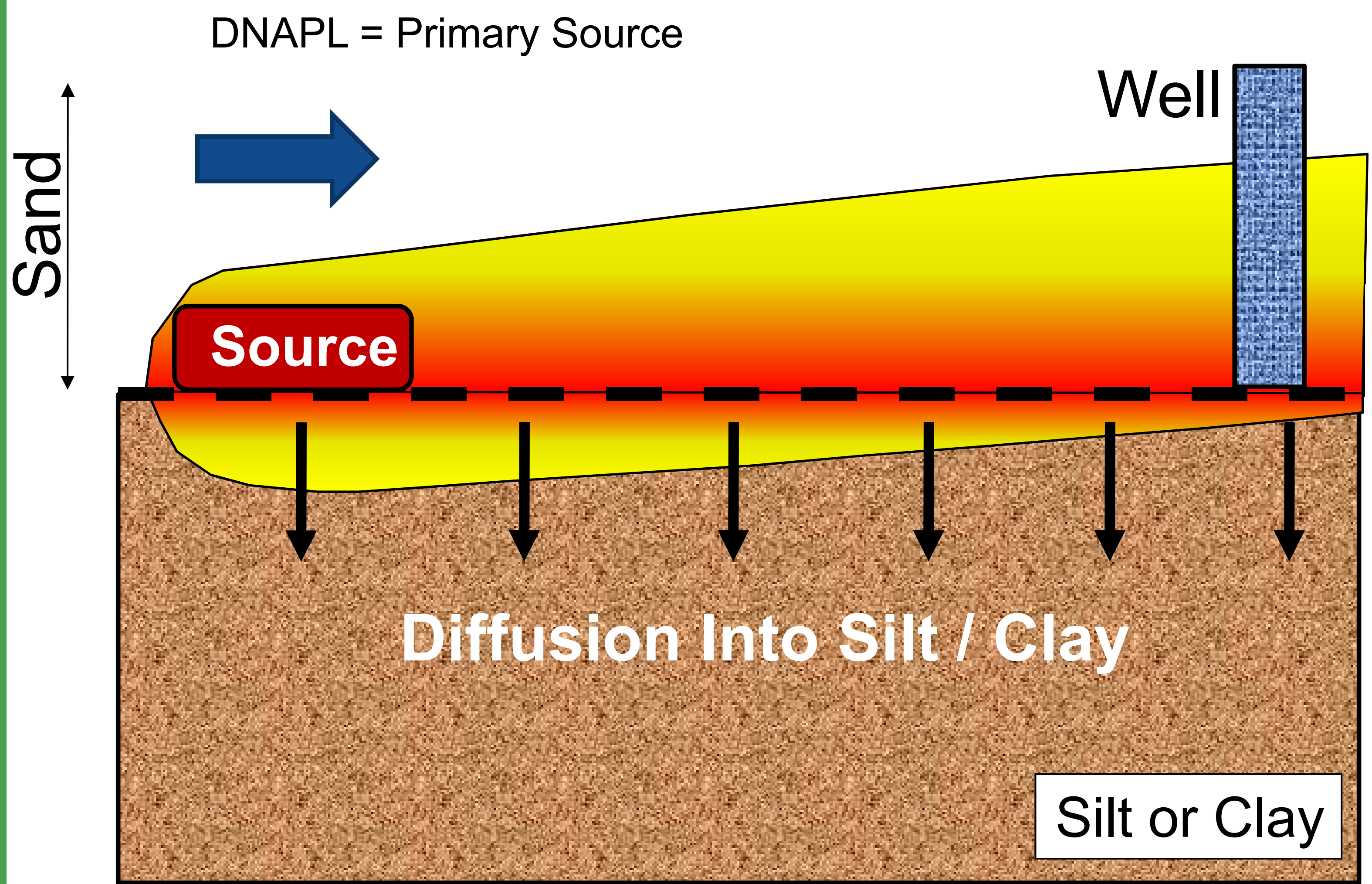


Mass discharge data from Sleep et al. (2006).

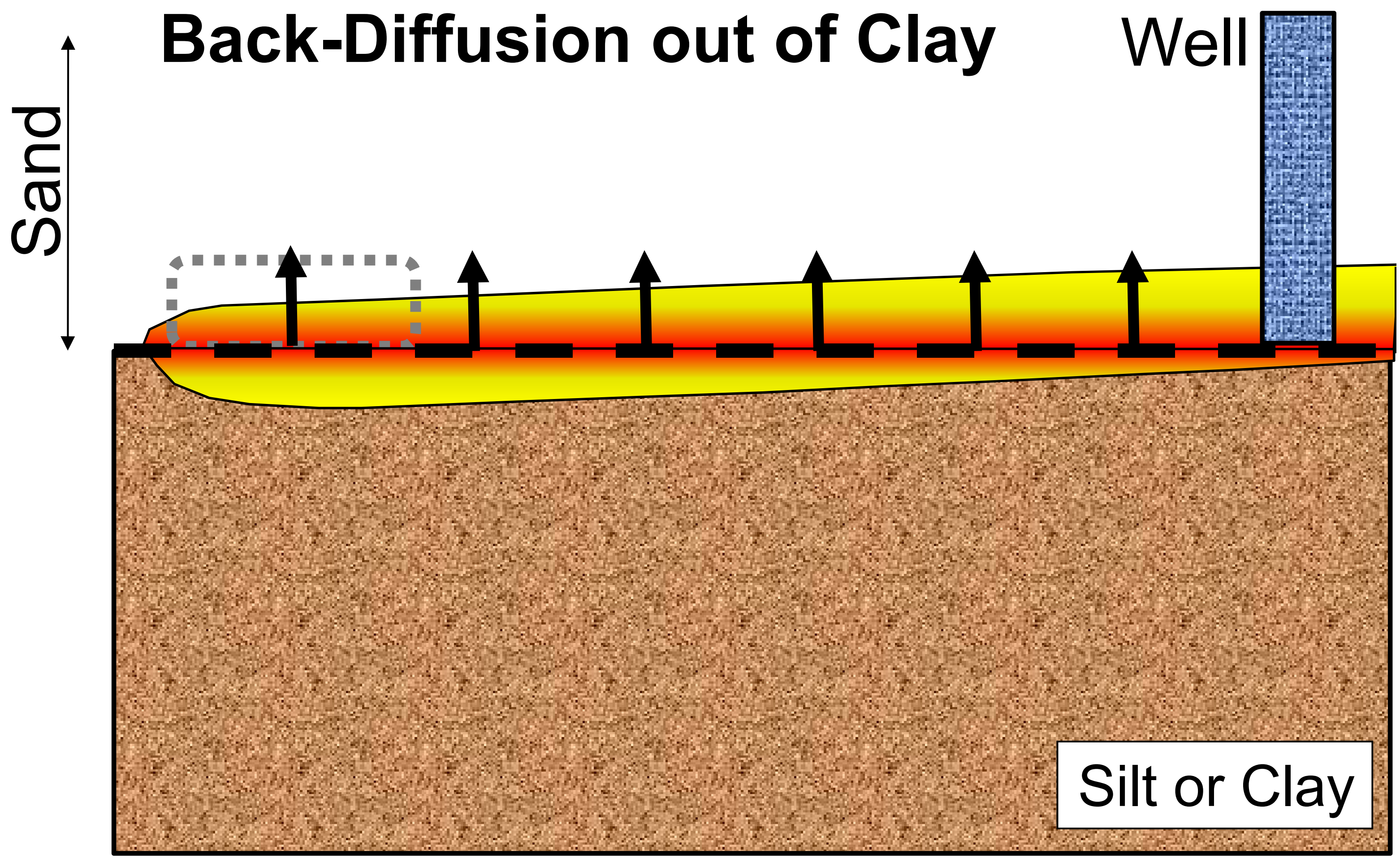
CONCEPTS

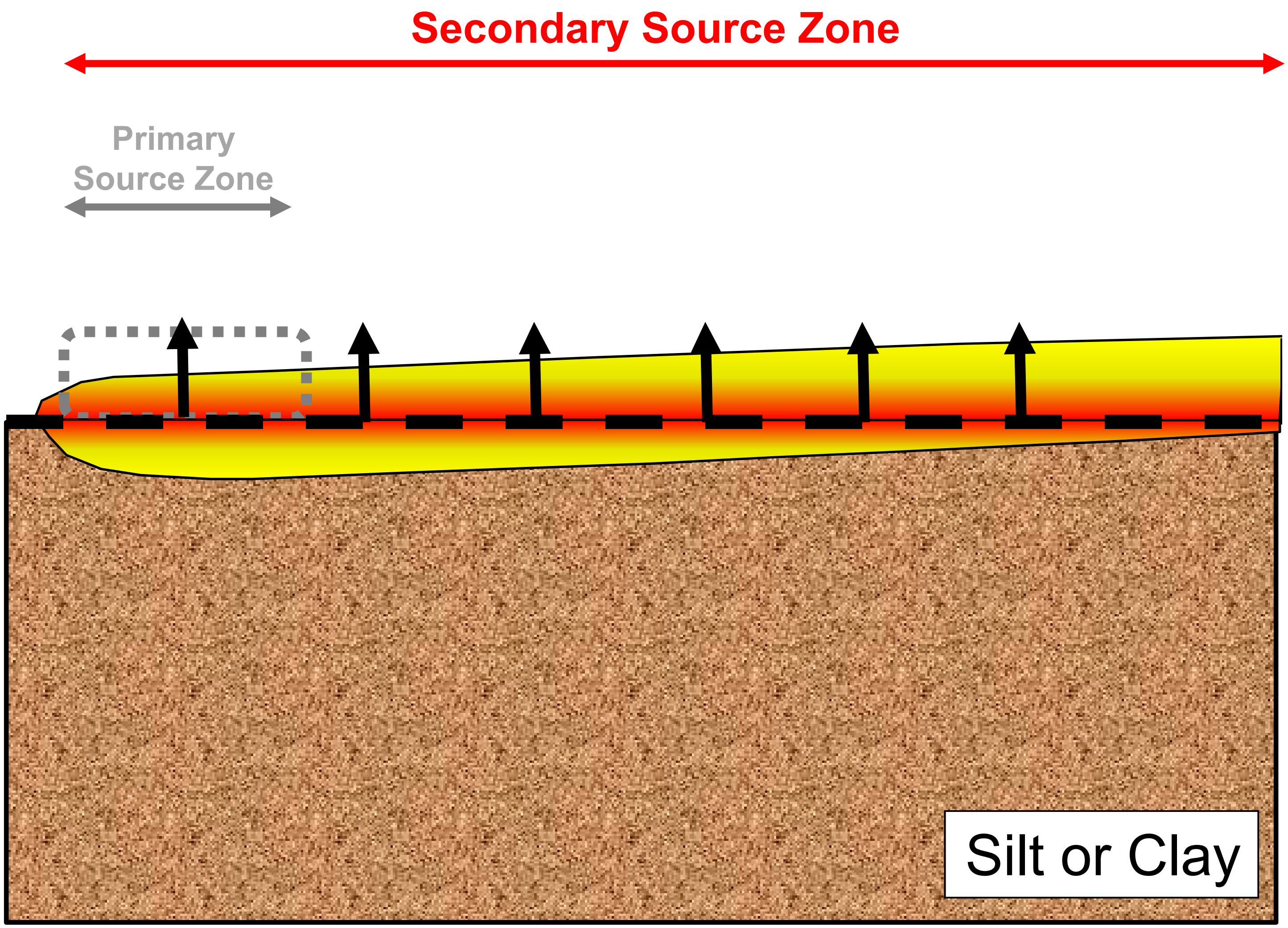
1.3 BACK-DIFFUSION TRENDS

Conceptual Model of Forward Diffusion



Conceptual Model of Back-Diffusion

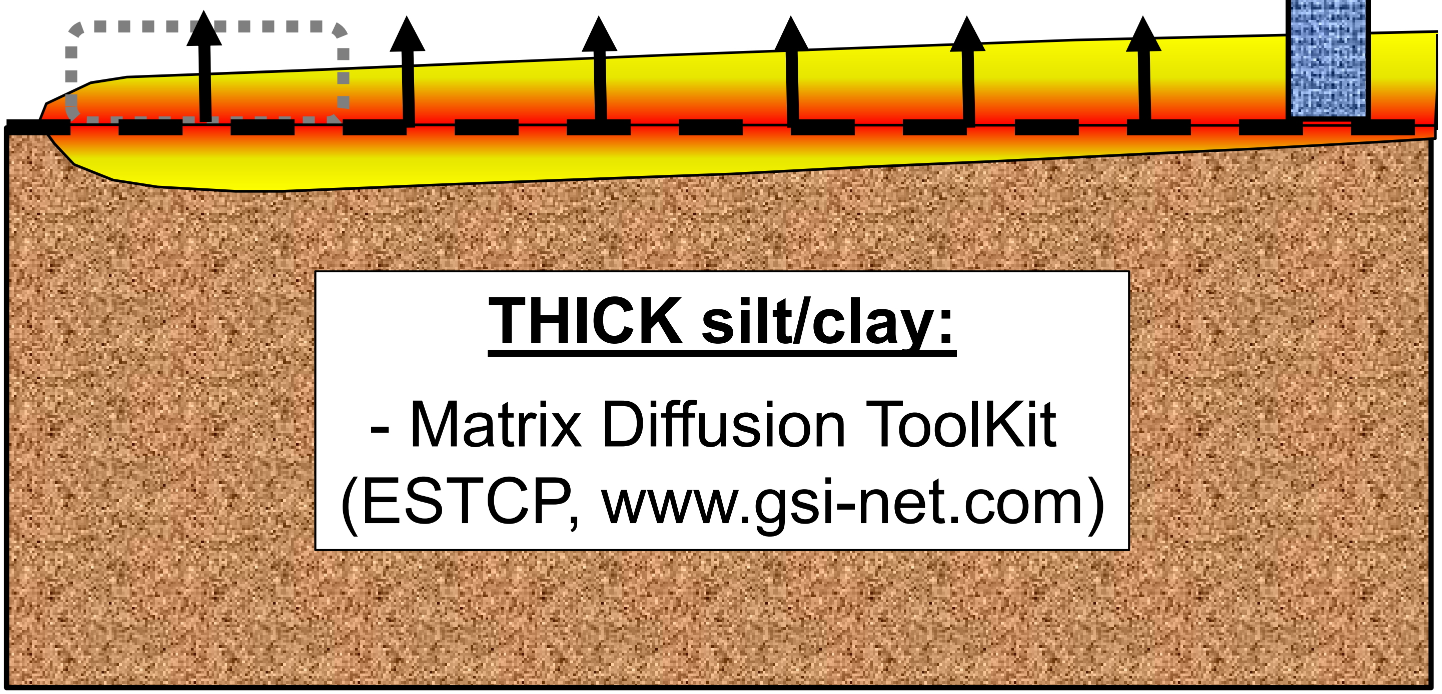



Secondary Source Zone
Primary
Source Zone
Silt or Clay

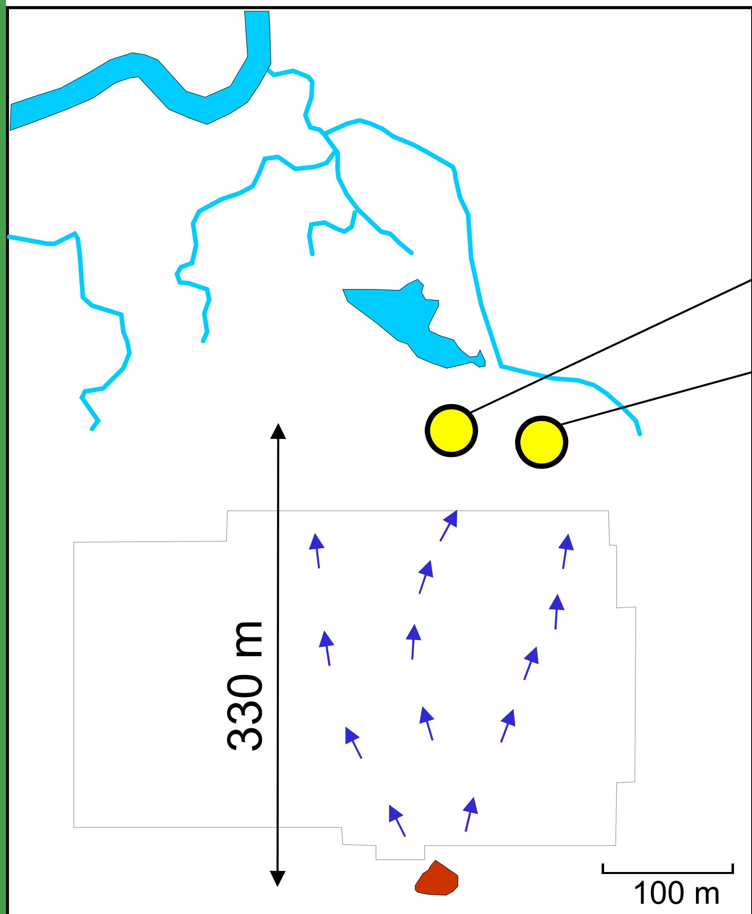
Factors Influencing Remediation Timeframe

Influencing factors:

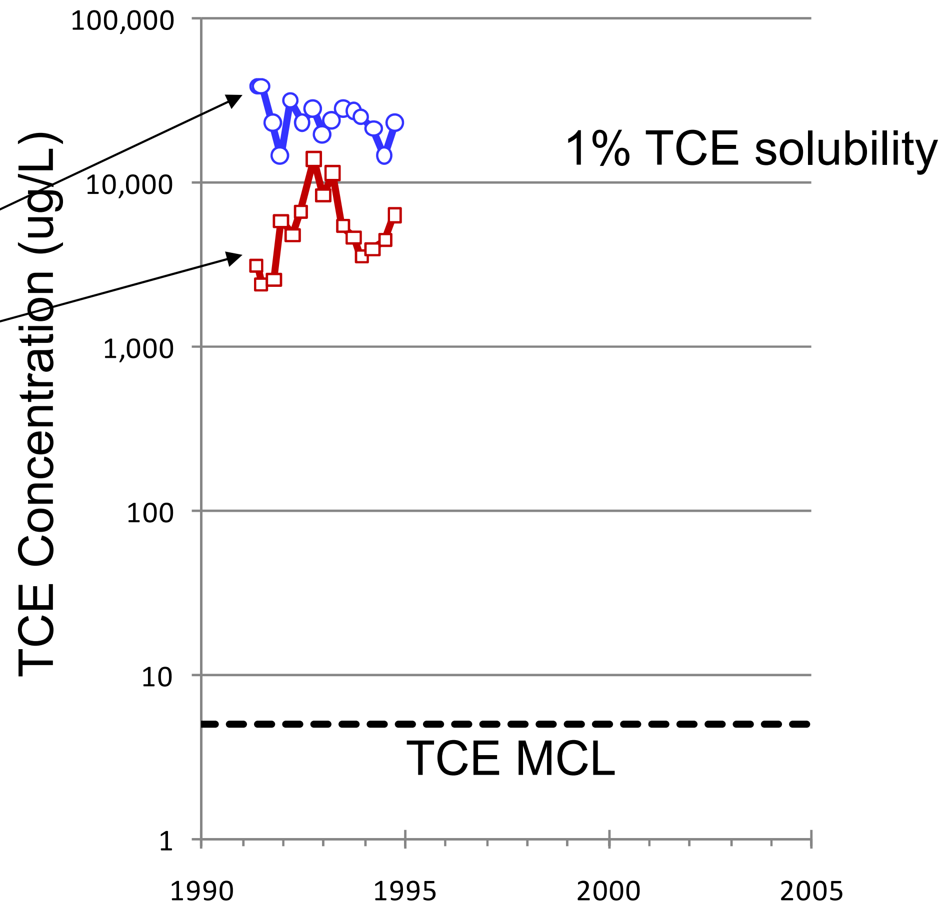
- Velocity
- Thickness
- Retardation
- Diffusion rate
- Transverse dispersion
- Length of clay lens
- Biodegradation
- Contact time



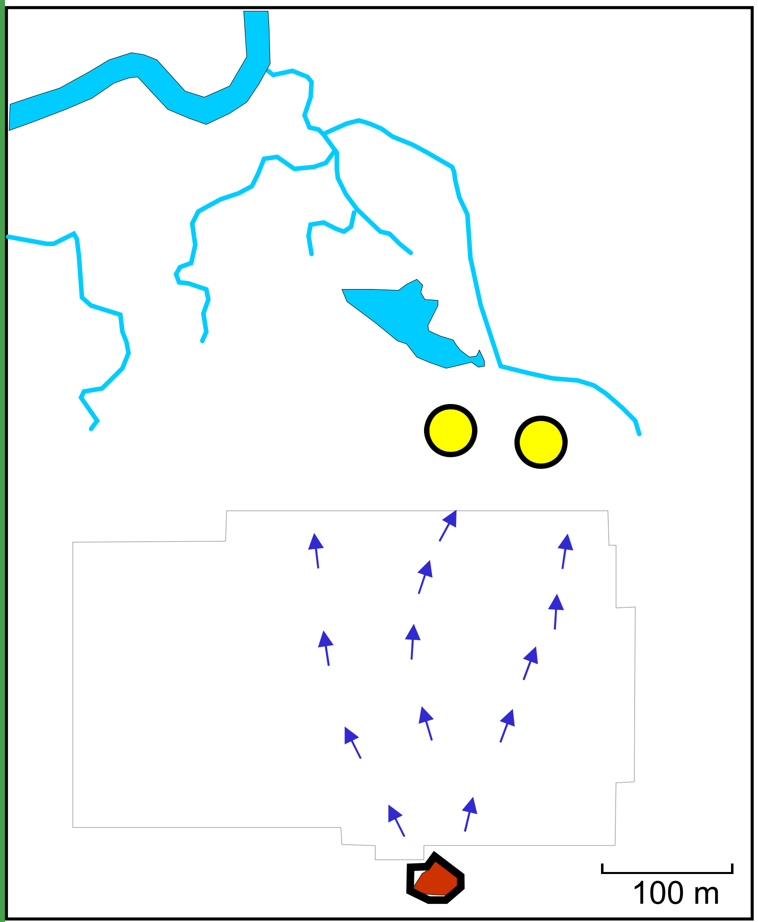
Connecticut Site (Chapman & Parker, 2005)



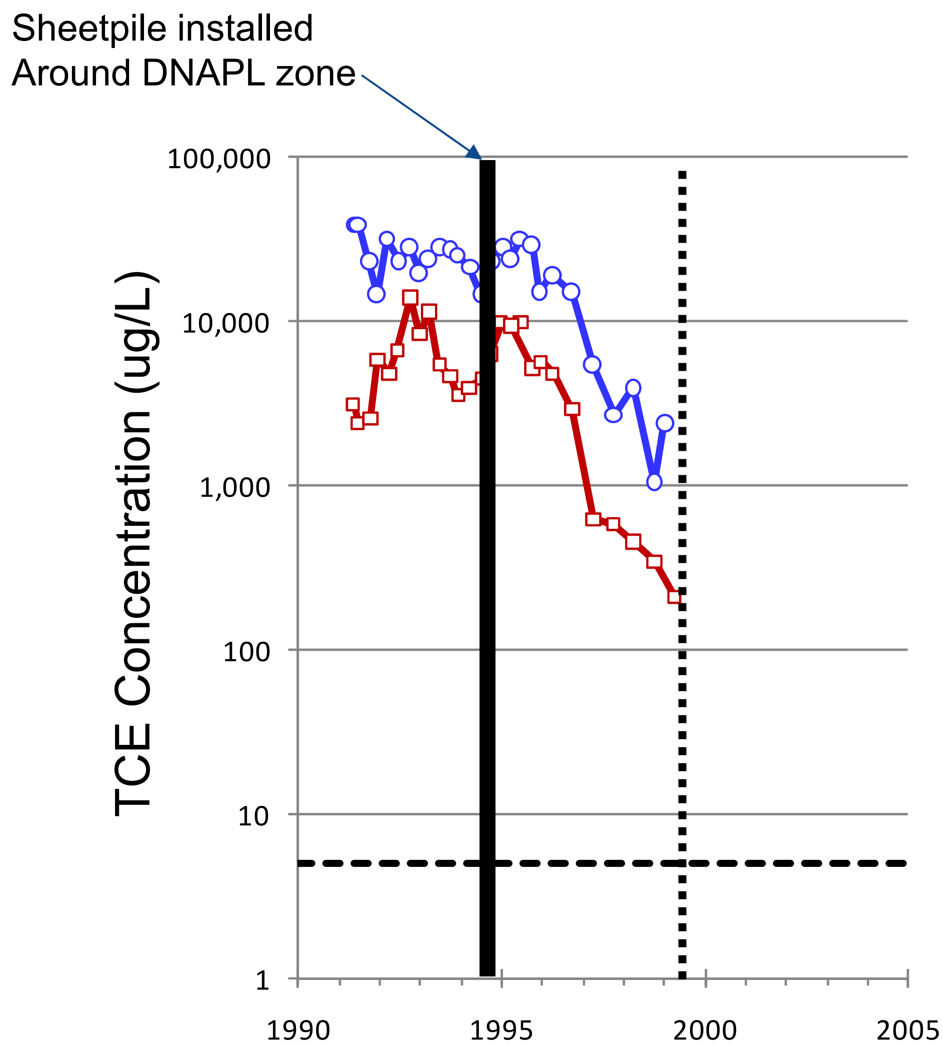
DNAPL Source Zone



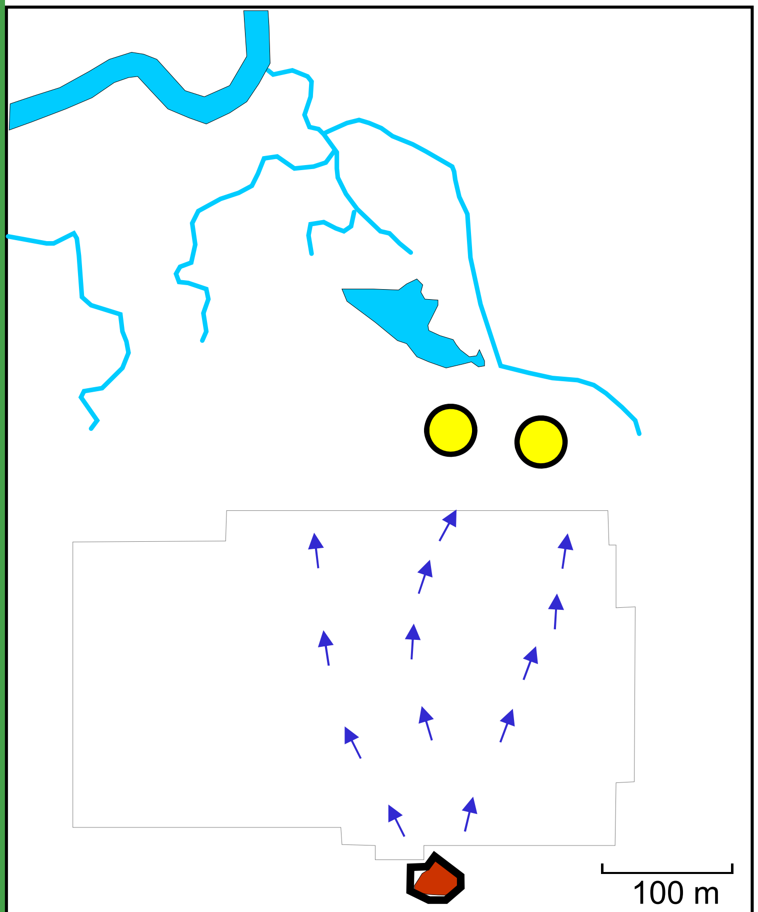
Connecticut Site (Chapman & Parker, 2005)



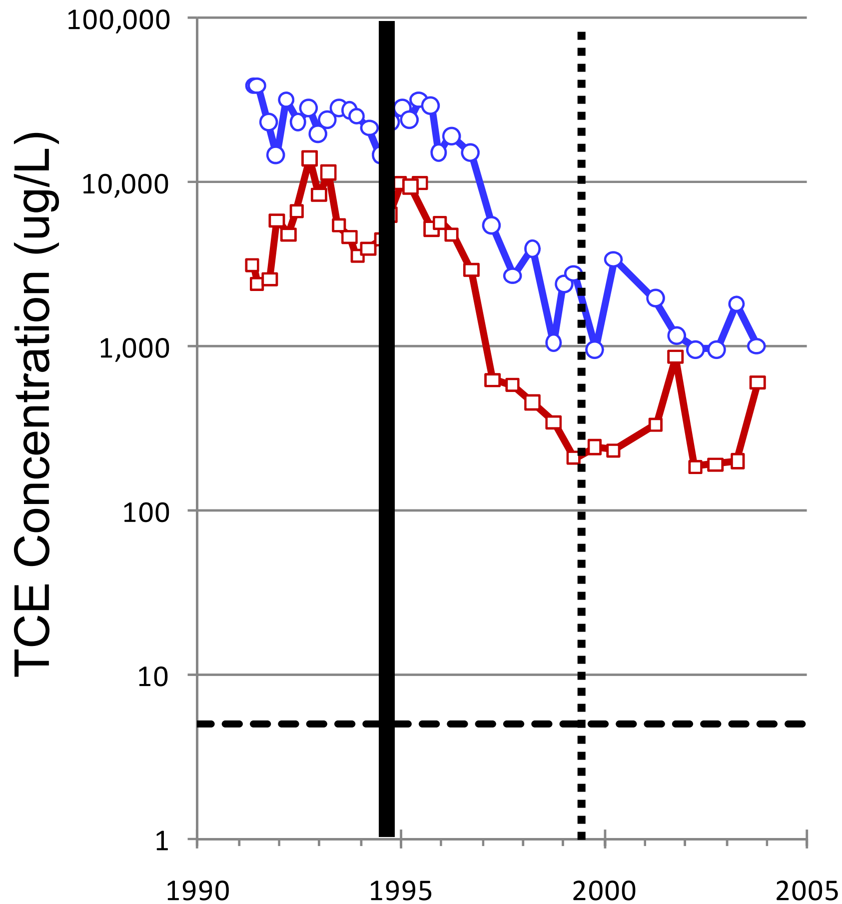
DNAPL Source Zone



Connecticut Site (Chapman & Parker, 2005)



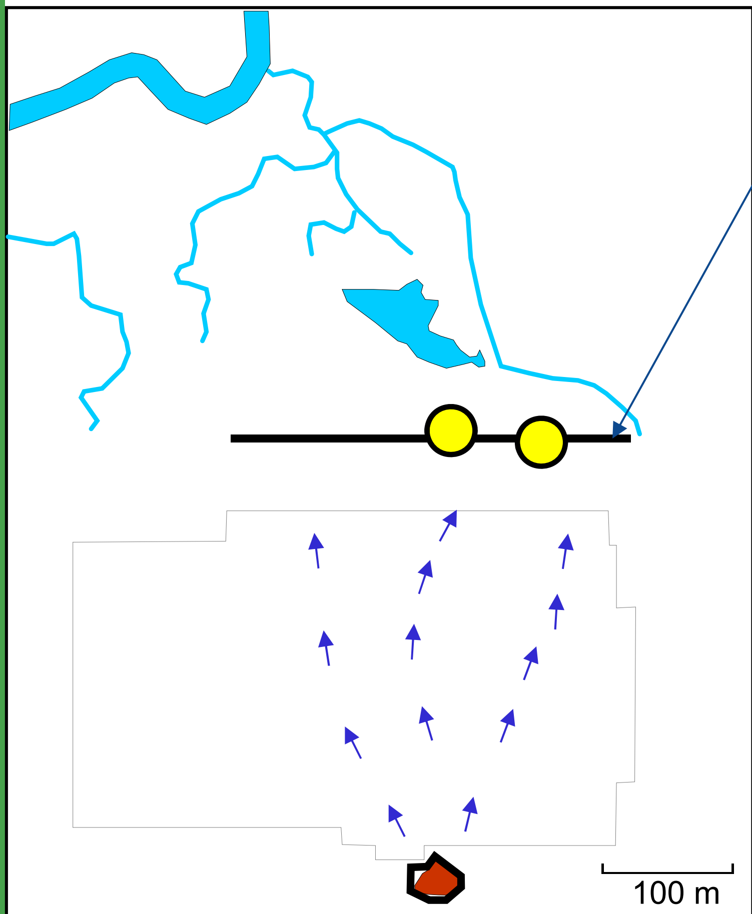
DNAPL Source Zone



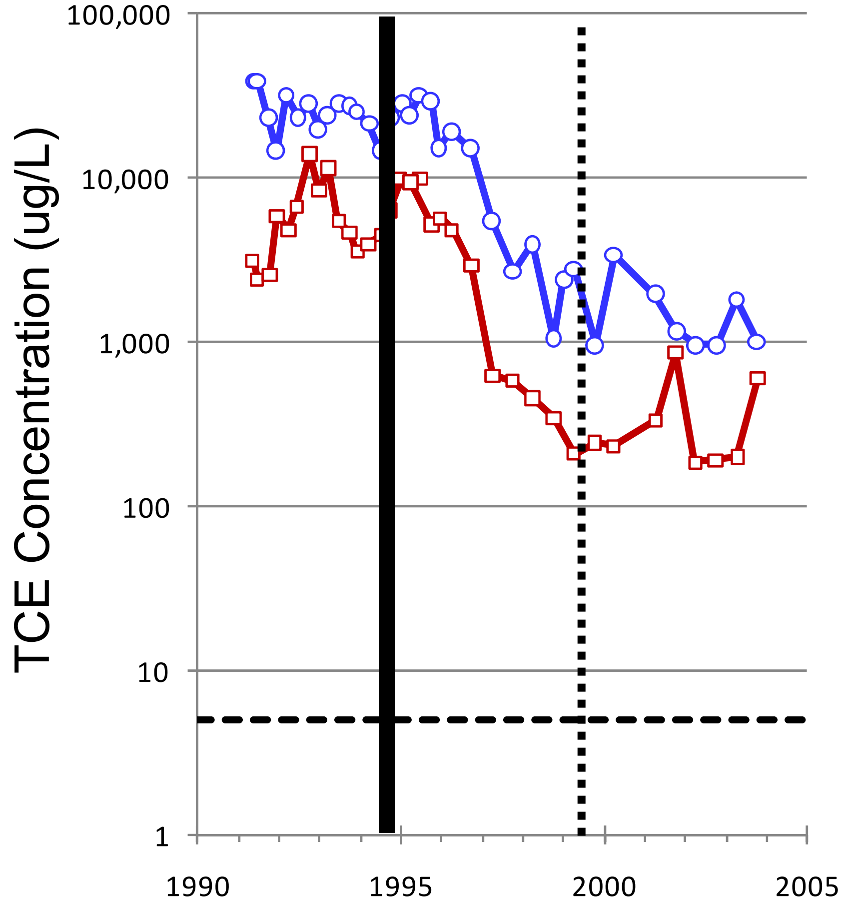
Concentration reduction stalled at 93% (15x)

Connecticut Site (Chapman & Parker, 2005)

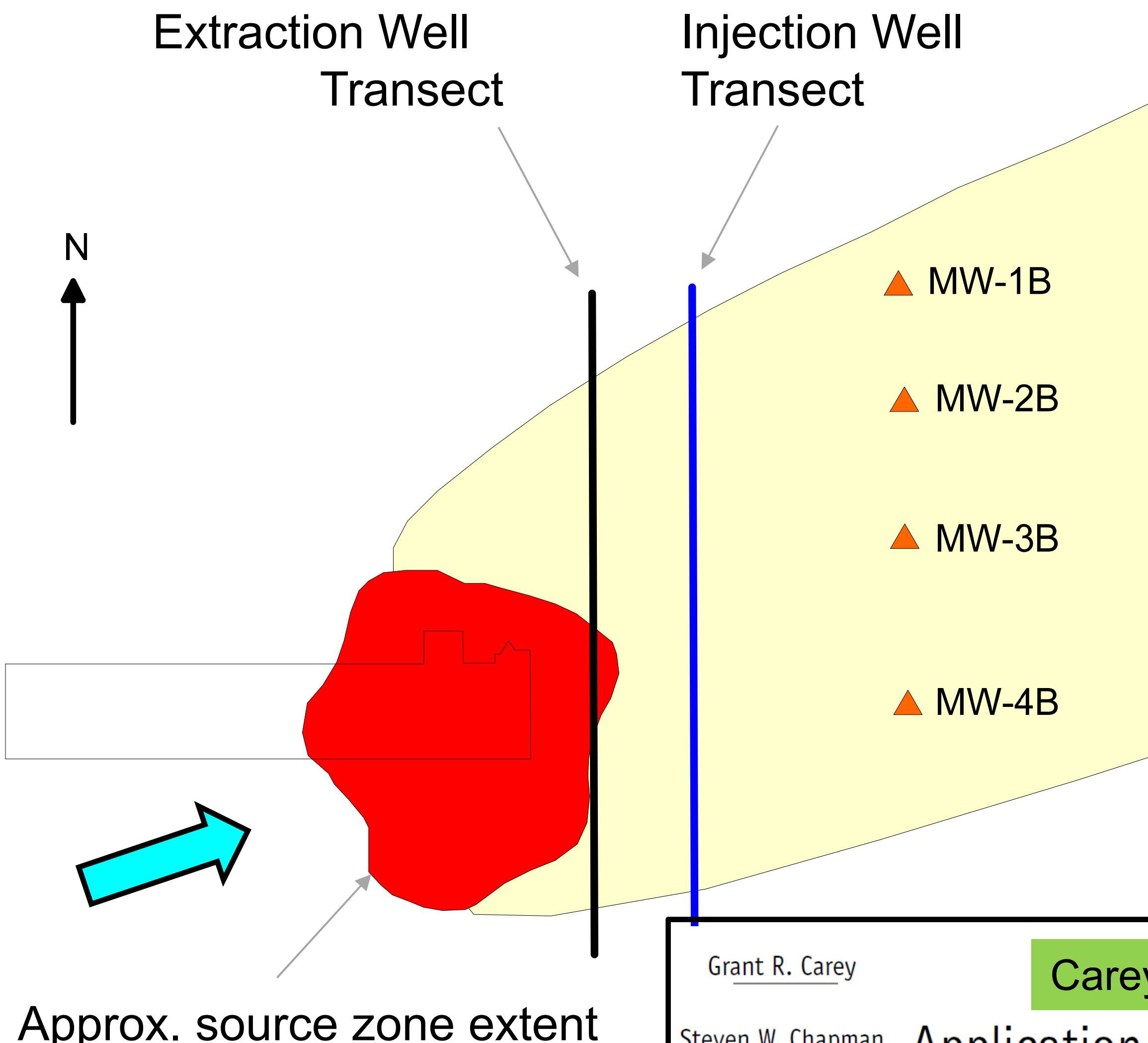
Plume strength due to back-diffusion in 2000: 36 kg/y



DNAPL Source Zone



Case Study – Florida Site



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

Carey et al. (2015)

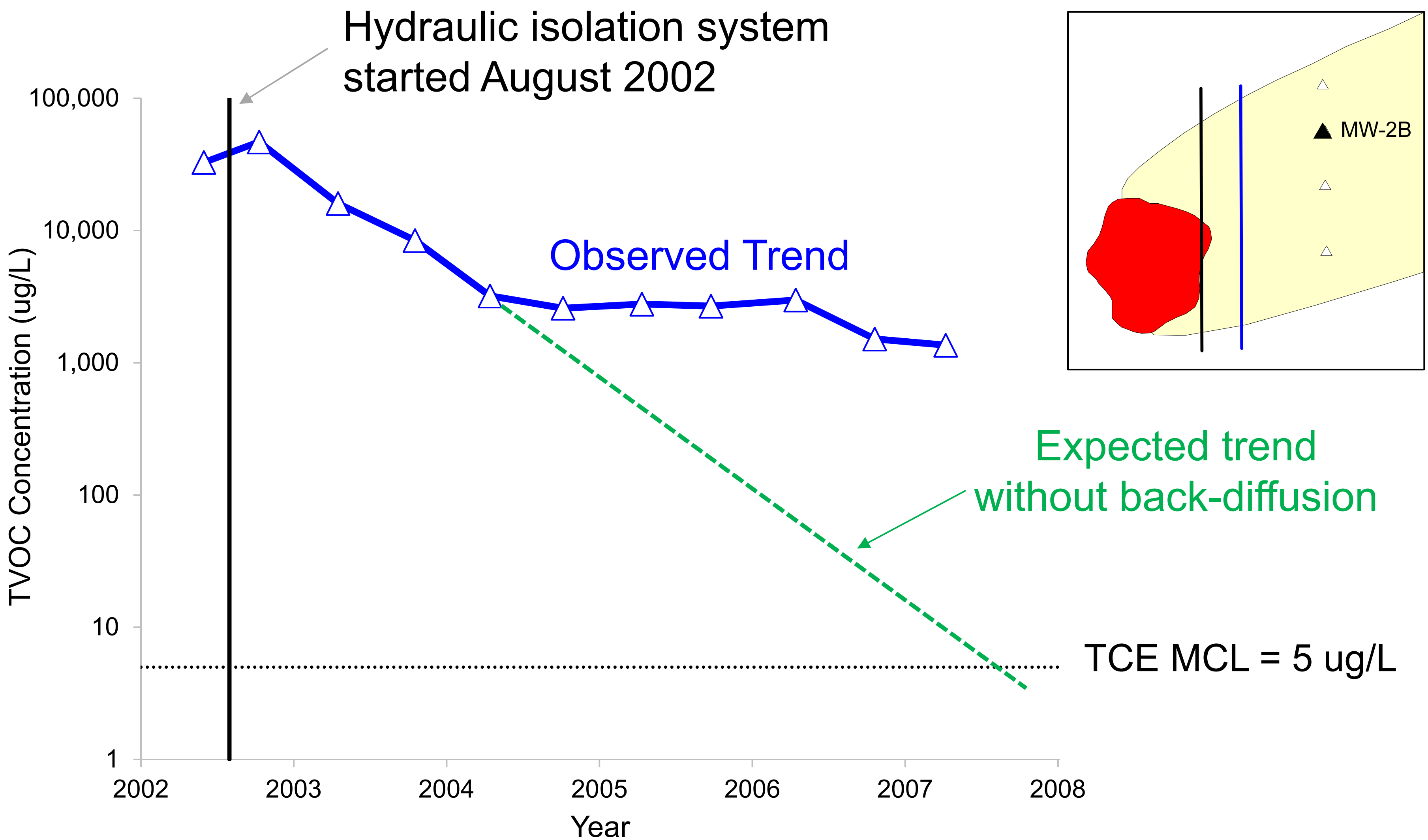
REMEDIATION Autumn 2015

Grant R. Carey
Steven W. Chapman
Beth L. Parker
Rick McGregor

Application of an Adapted Version of MT3DMS for Modeling Back-Diffusion Remediation Timeframes

Modified from Parker et al., 2008

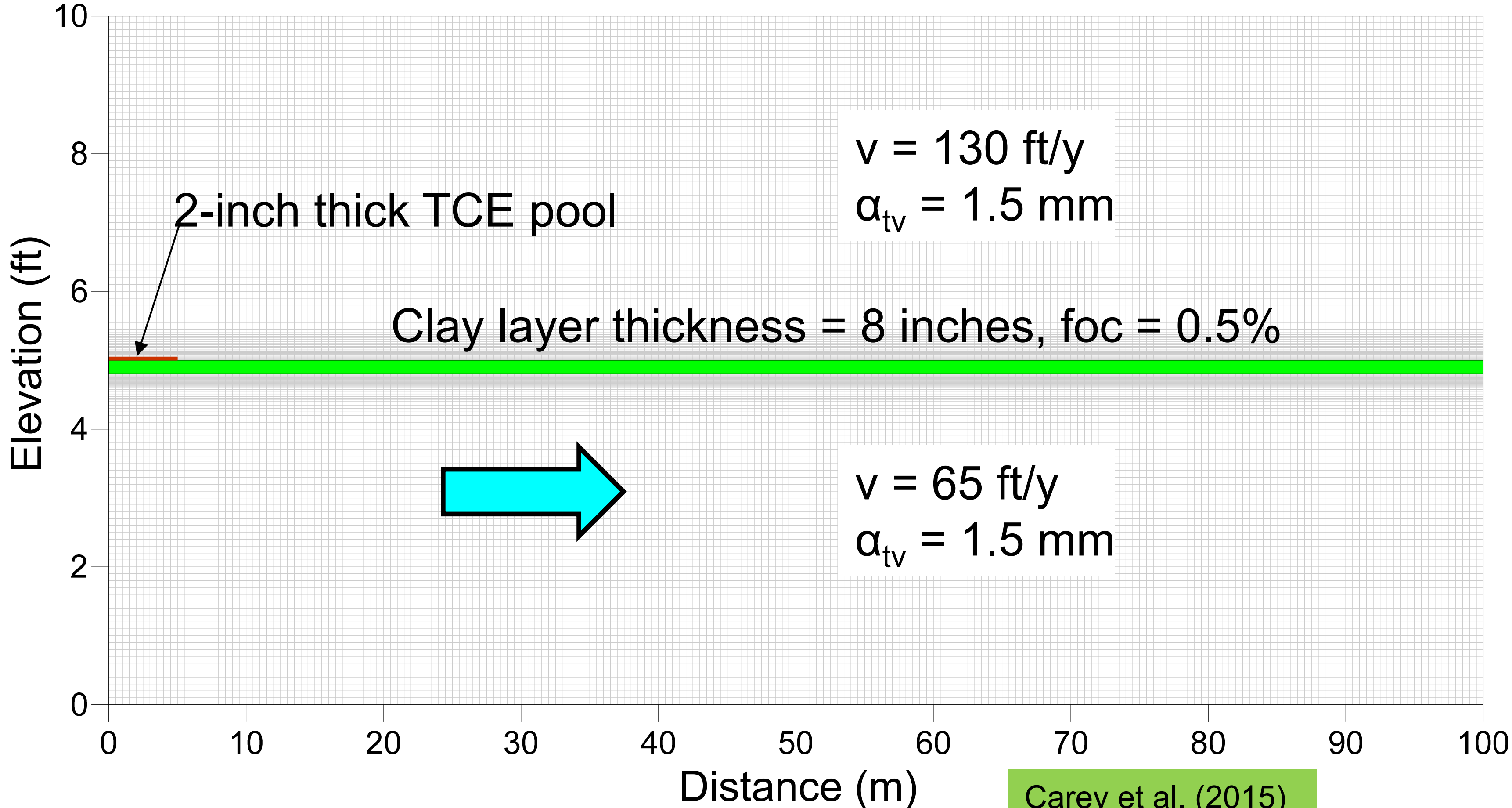
TVOC Trend After Source Containment



Modified from Parker et al., 2008

2-D Model Grid

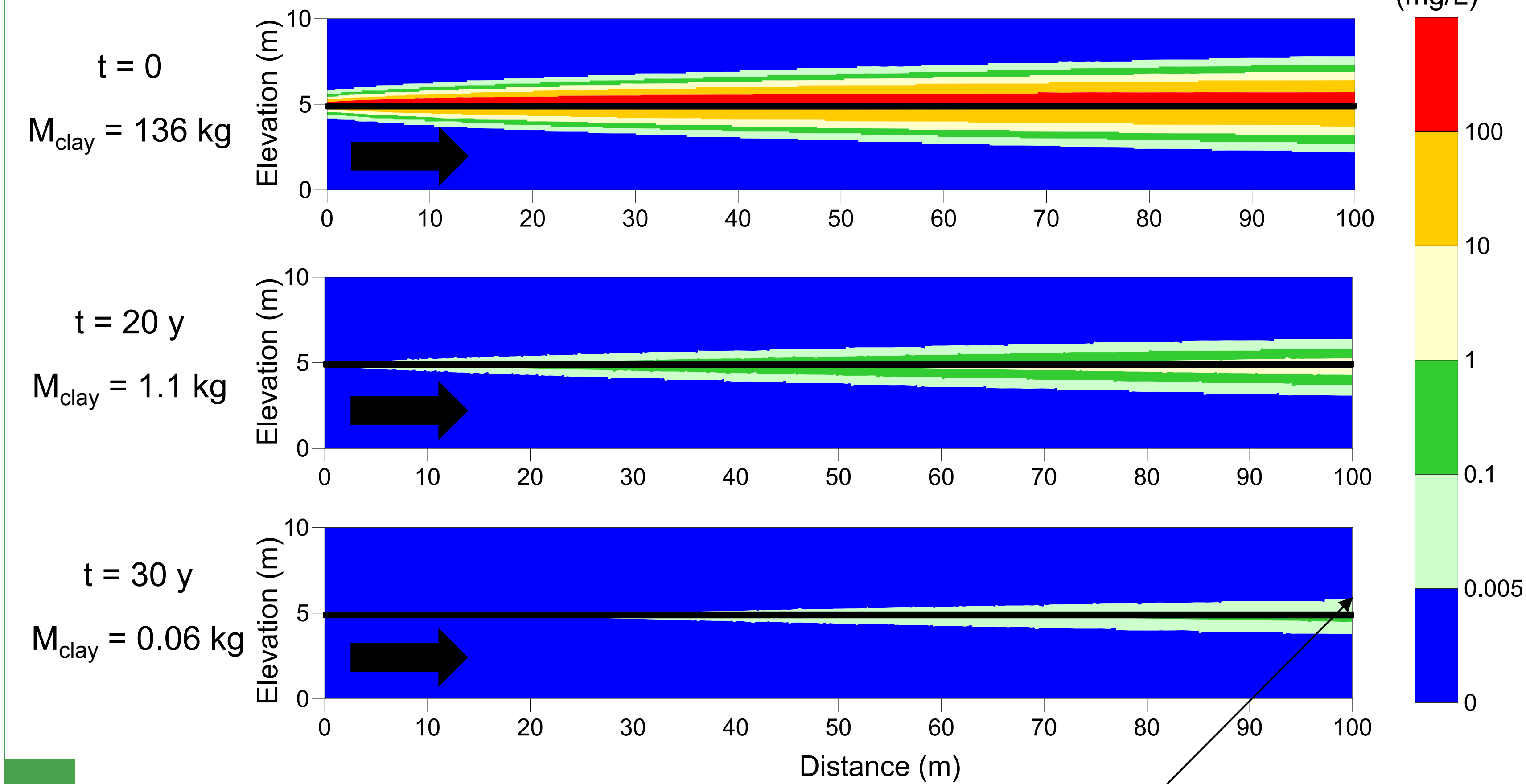
200 columns, 158 rows (layers)
Minimum grid spacing: Δz = 1.25 cm, Δx = 0.5 m
Run-time = 45 minutes for 85-y simulation (Δt = 0.24 d)



Carey et al. (2015)

Simulated TCE After Source Removal

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

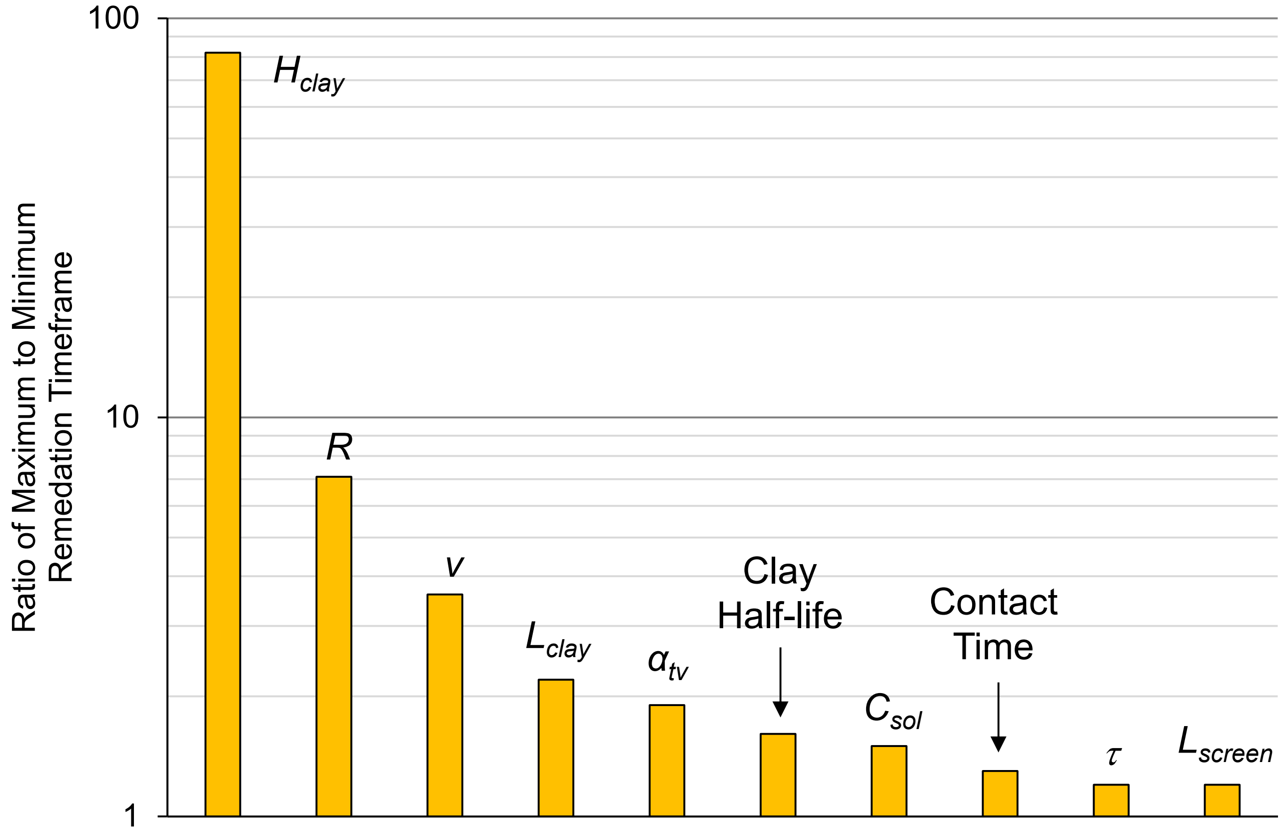


30 years after source removal:
99.96% mass depletion in clay, avg. C_{well} = 12 to 126 ug/L

Carey et al. (2015)

Remediation Timeframe Sensitivity Analysis

See Appendix A



H_{clay} = silt/clay layer thickness

R = retardation coefficient

v = groundwater velocity

L_{clay} = silt/clay layer length

α_{TV} = transverse dispersivity

Half-life → biodegradation

C_{sol} = solubility

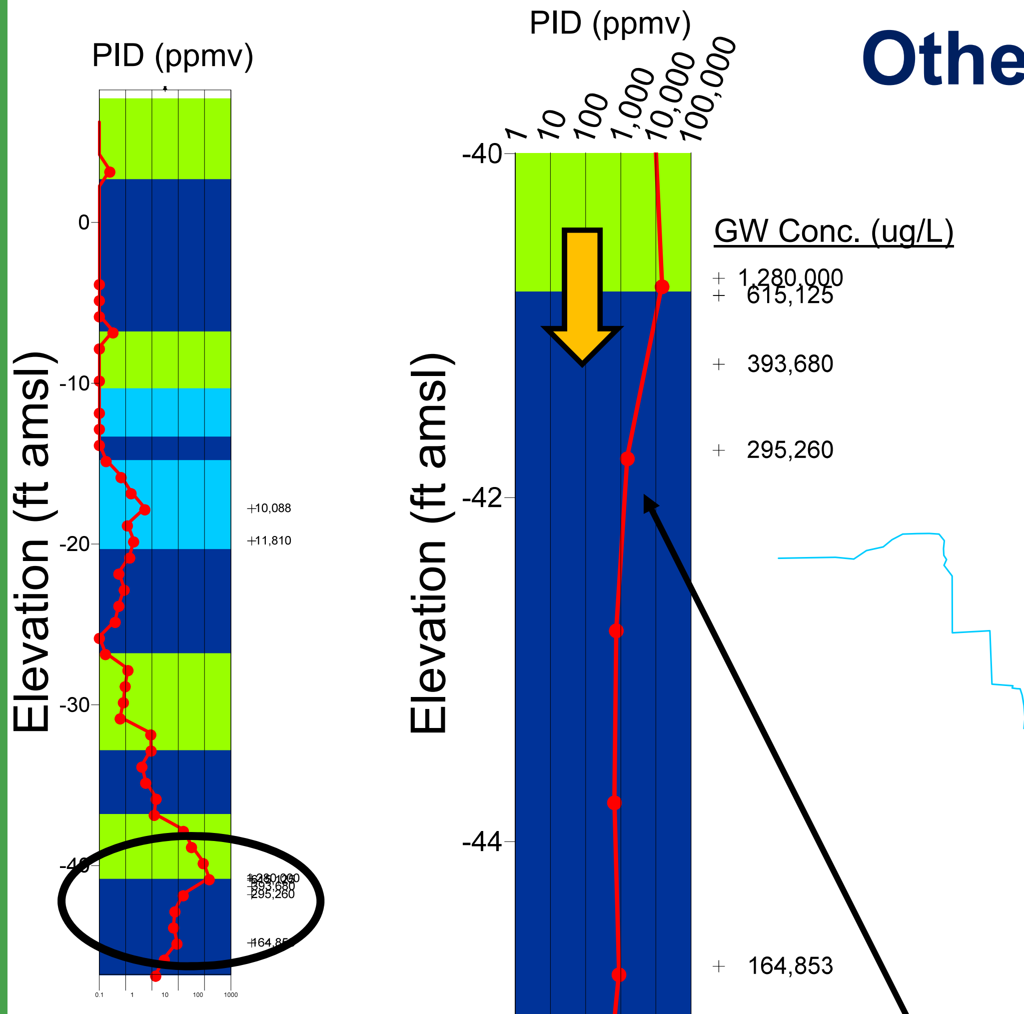
Contact time – between NAPL and silt/clay

τ = tortuosity coefficient

L_{screen} = well screen length

Carey et al. (2015)

Other site - TCE in silt/clay



PID may be used to supplement soil samples for evaluating diffusion direction, and vertical penetration depth in silt/clay.

(**Order-of-magnitude**)

Classic diffusion profile through silt/clay (forward diffusion from overlying sand). High concentrations in aquitard will cause long remediation timeframe.

+ Soil sample with calculated GW TCE concentration (ug/L)

1,700 Hydropunch GW TCE concentration (ug/L)

PID (ppm) – log scale

Silt/clay/organic matter

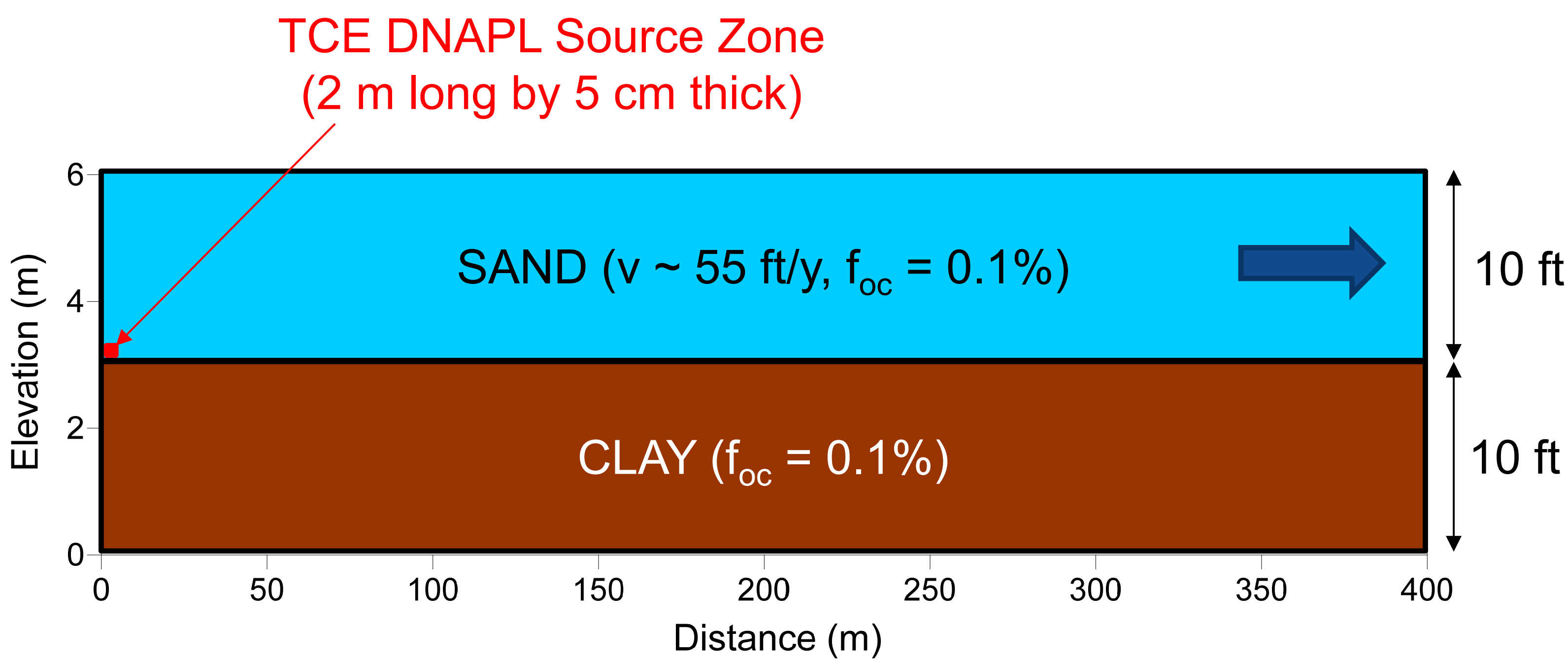
Sandy silt

Fine sand, silty/clayey sand

Medium to coarse sand

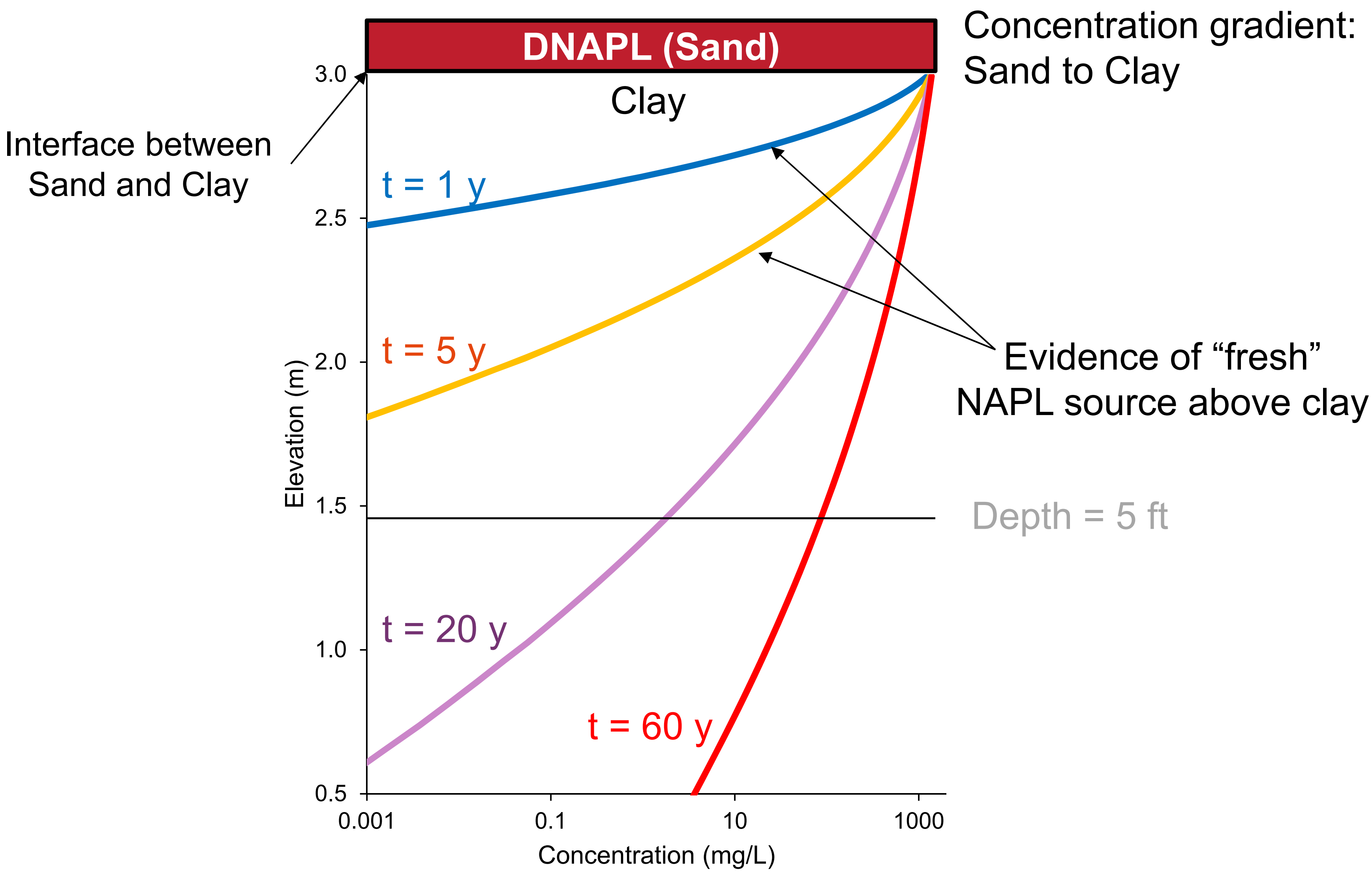
Fill

Back-Diffusion Example

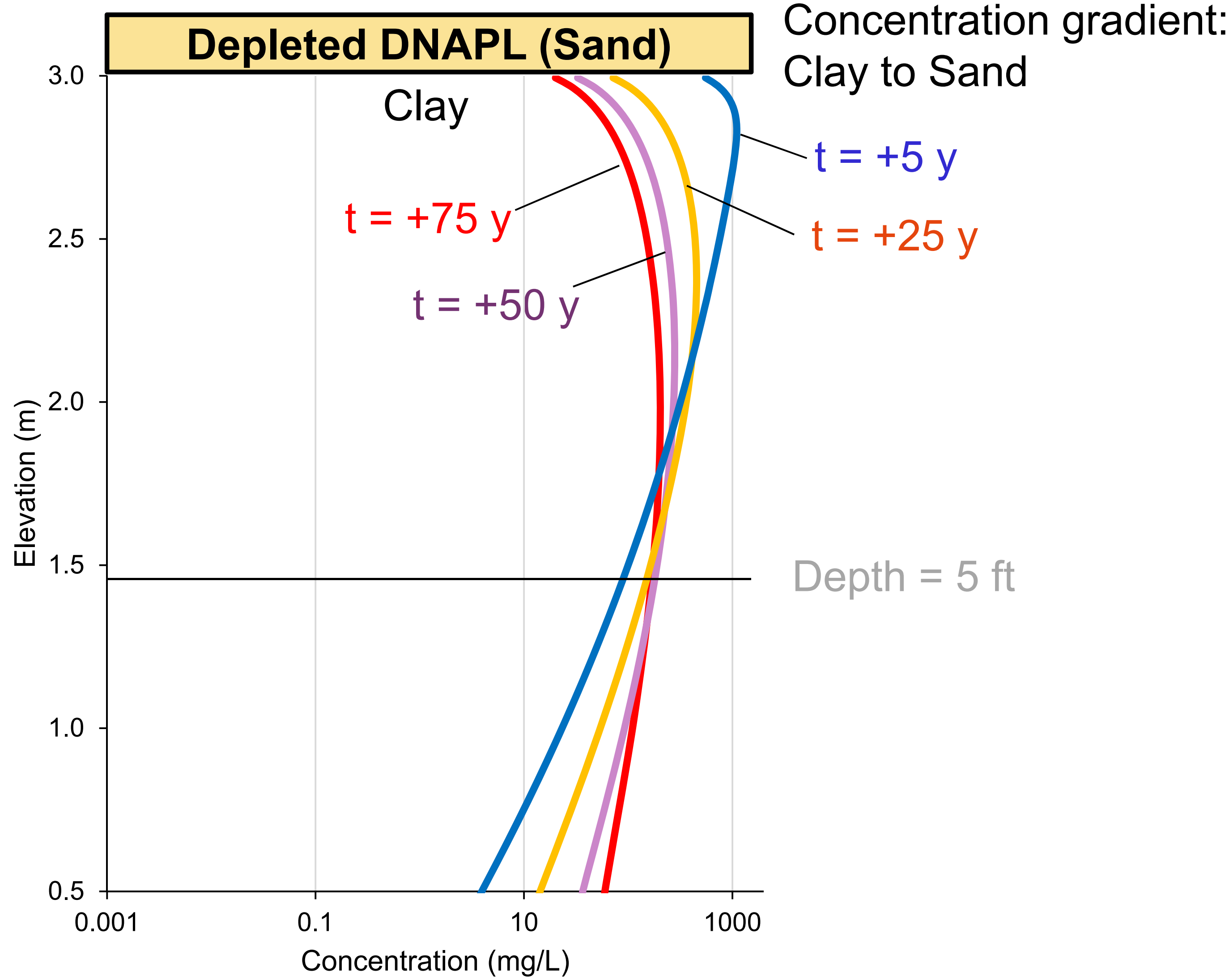


1. Numerical model – minimum vertical grid spacing: 1.25 cm
2. NAPL source 1955 to 2015, then depleted.
3. Model run for 100 years after source depletion (to 2115).

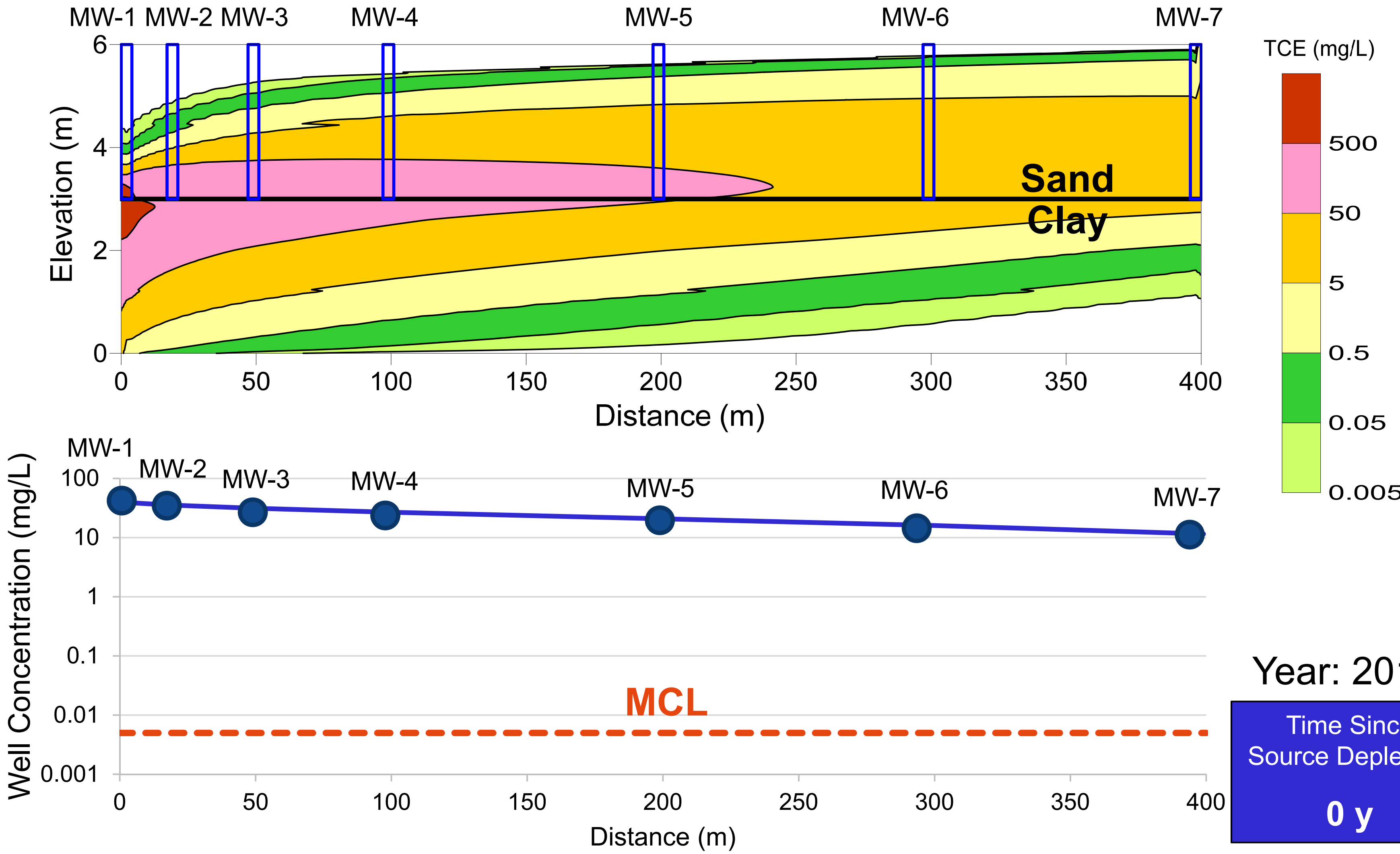
Profile Below DNAPL: Forward-Diffusion



Profile Below DNAPL: Back-Diffusion



Back-Diffusion Example – Case 1: Minimal Attenuation Along Flowpath

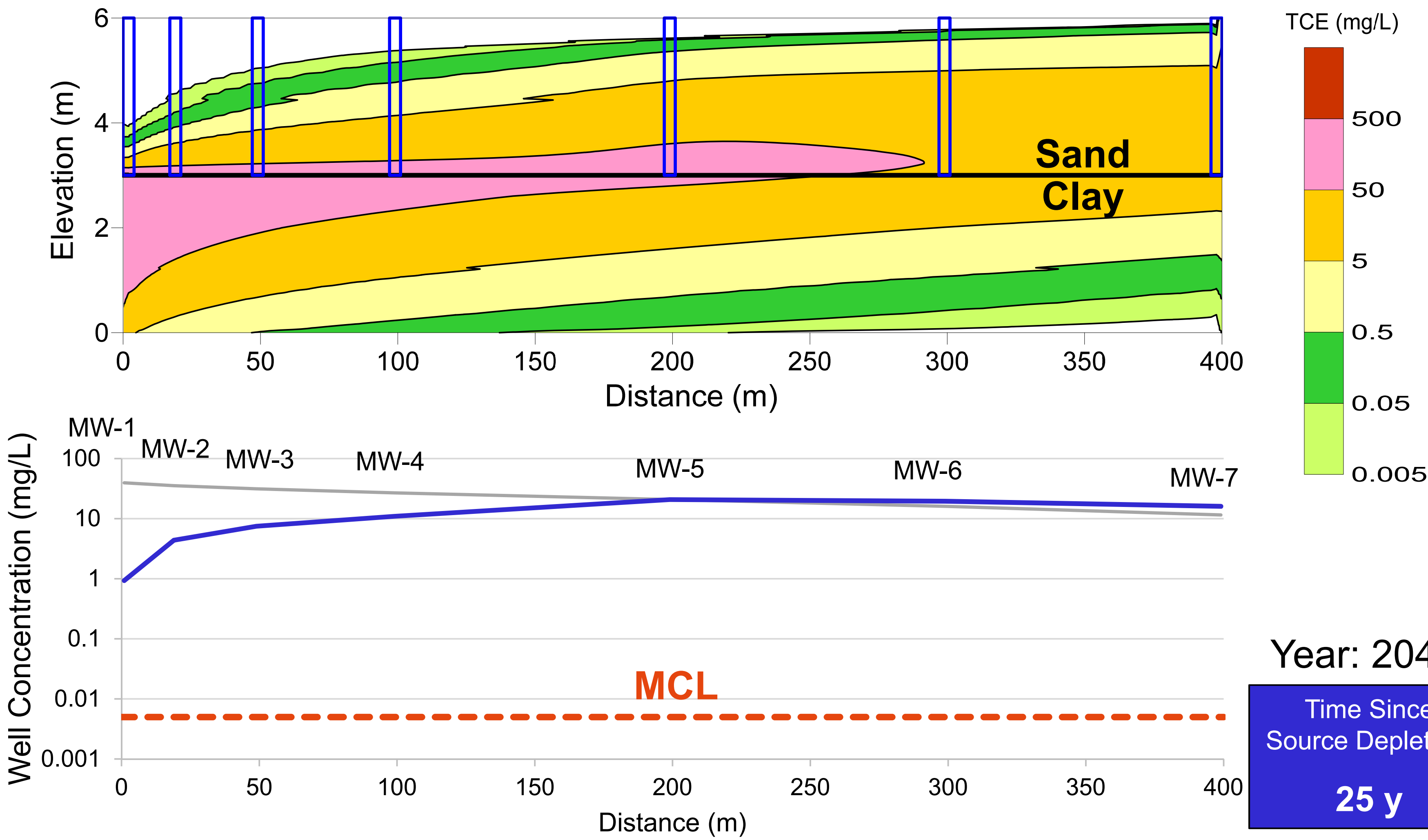


Year: 2015

Time Since Source Depletion:

0 y

Back-Diffusion Example – Case 1: Minimal Attenuation Along Flowpath

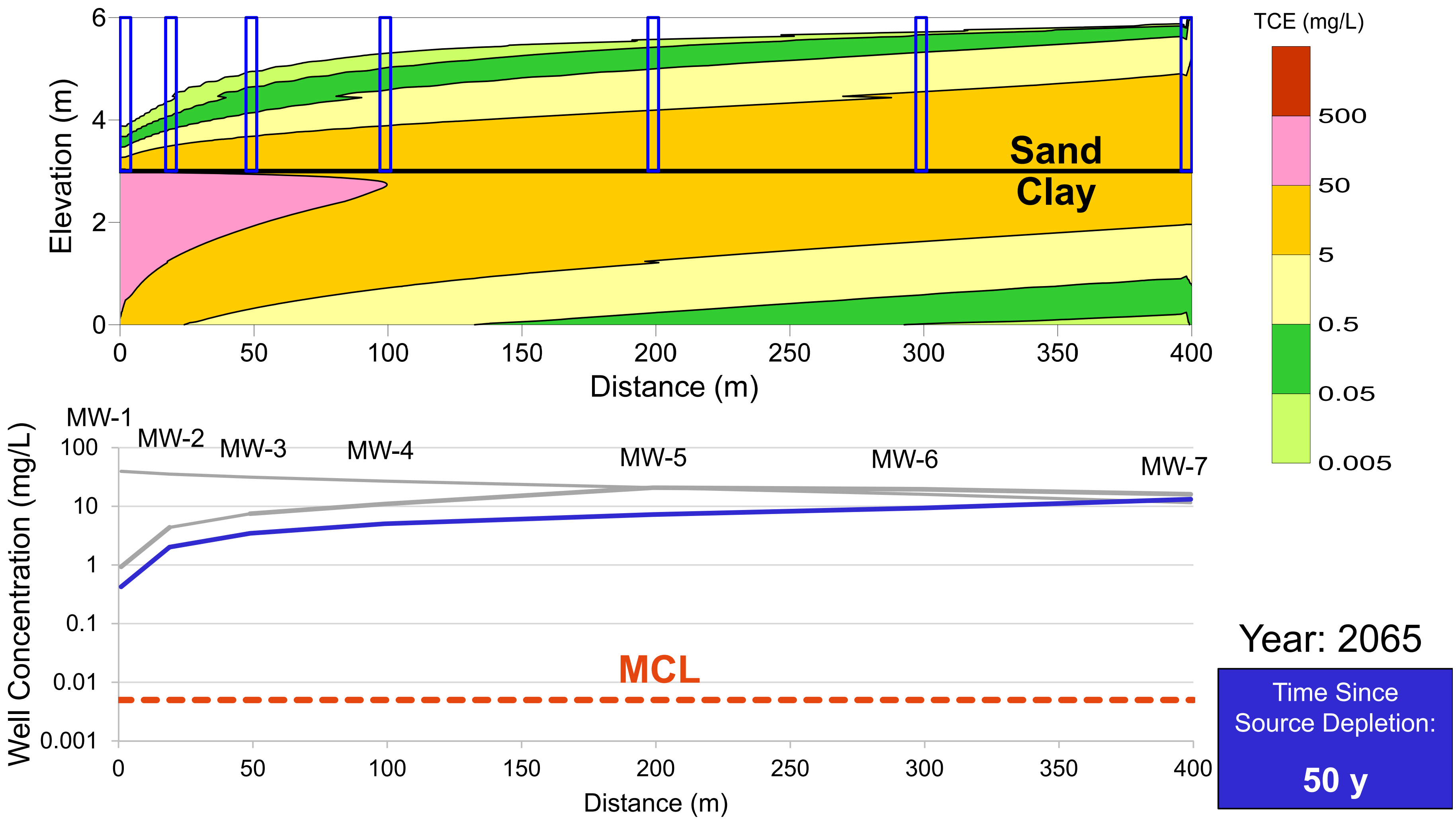


Year: 2040

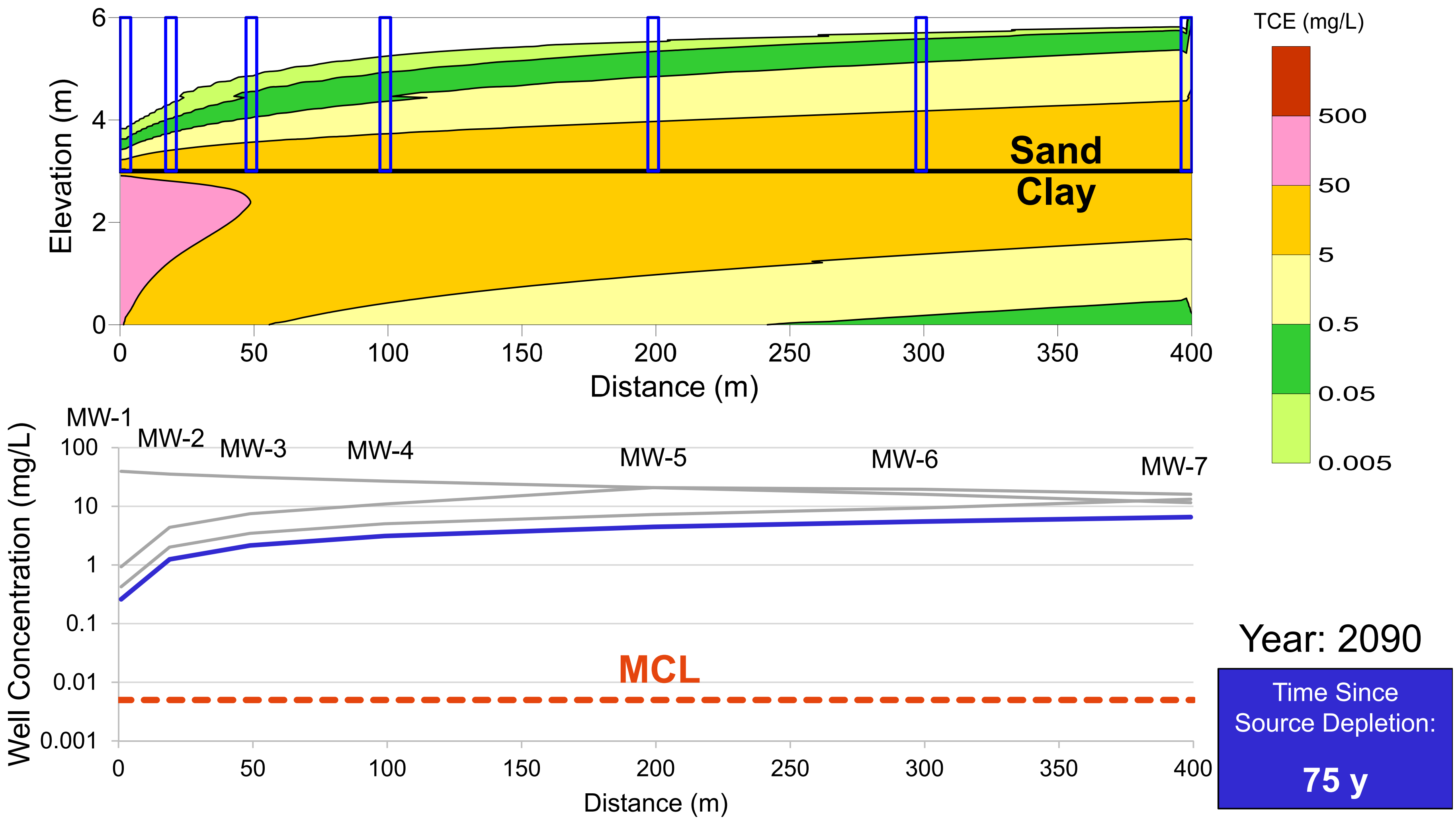
Time Since Source Depletion:

25 y

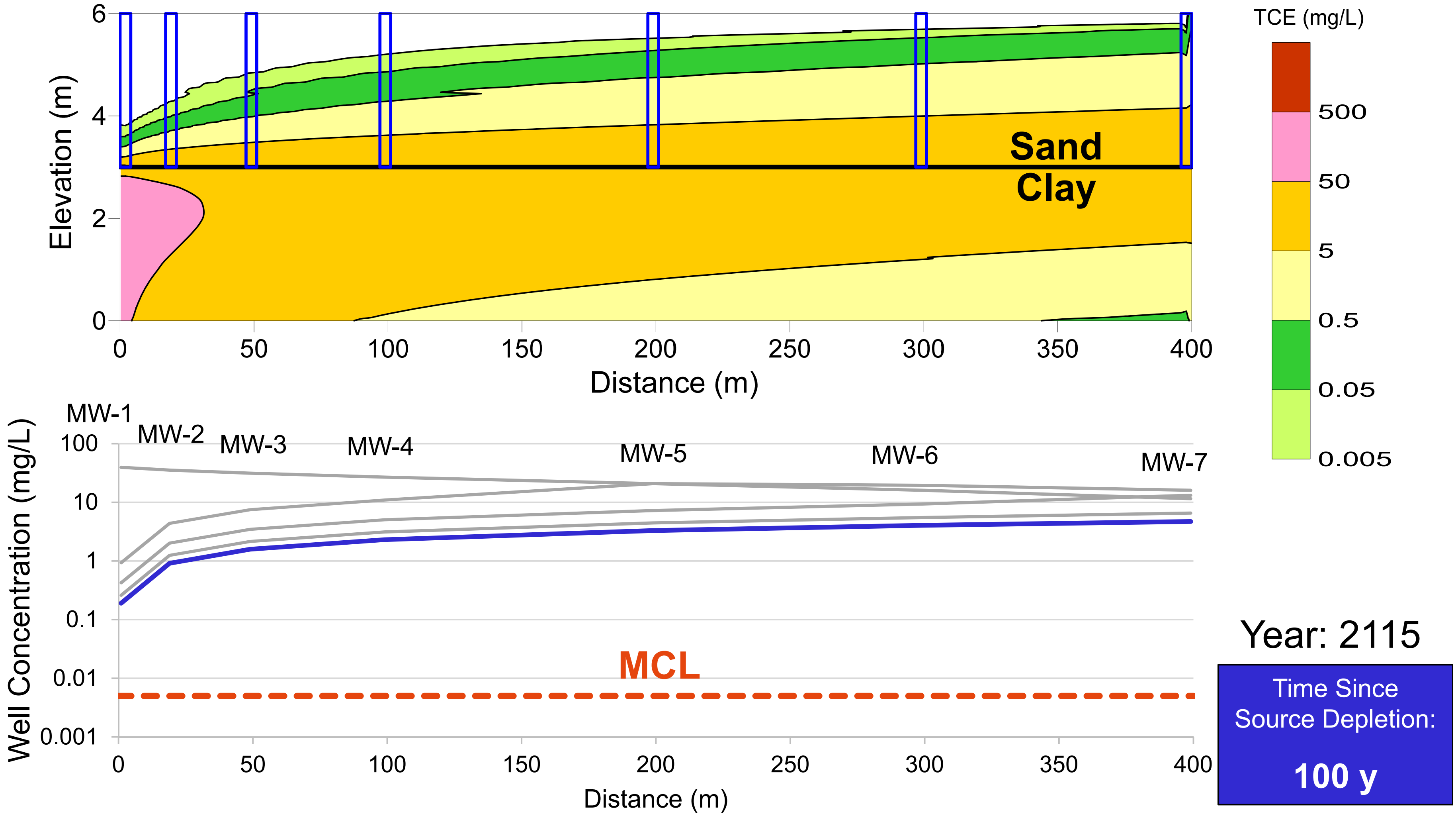
Back-Diffusion Example – Case 1: Minimal Attenuation Along Flowpath



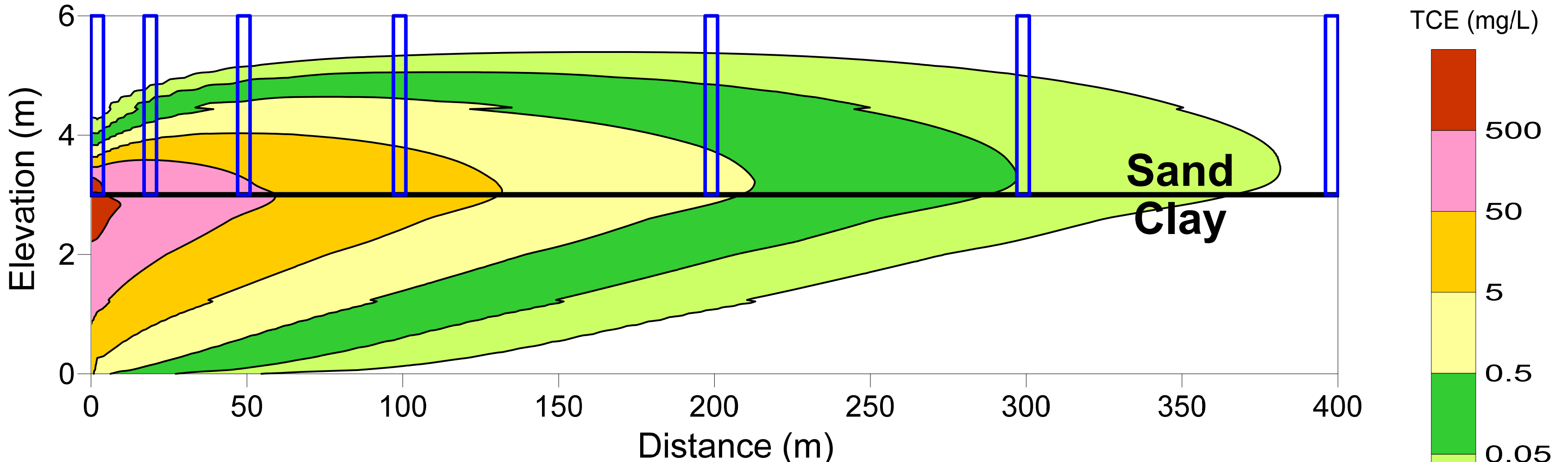
Back-Diffusion Example – Case 1: Minimal Attenuation Along Flowpath

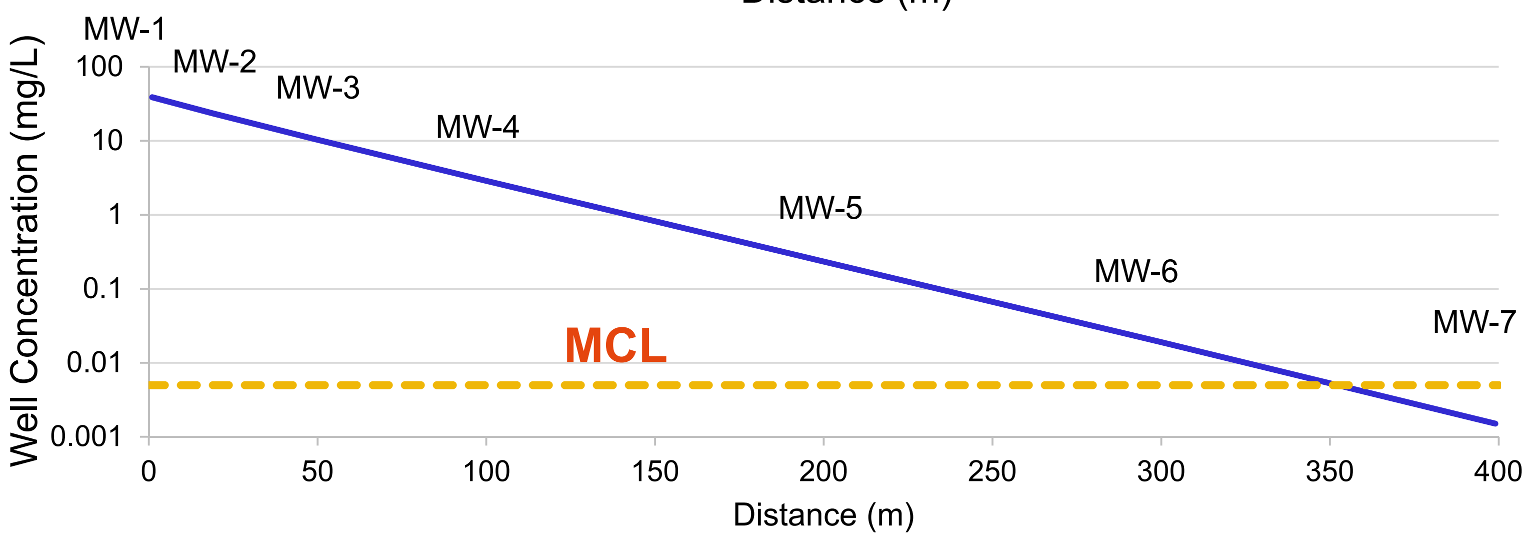


Back-Diffusion Example – Case 1: Minimal Attenuation Along Flowpath



Back-Diffusion Example – Case 2: Strong Attenuation Along Flowpath



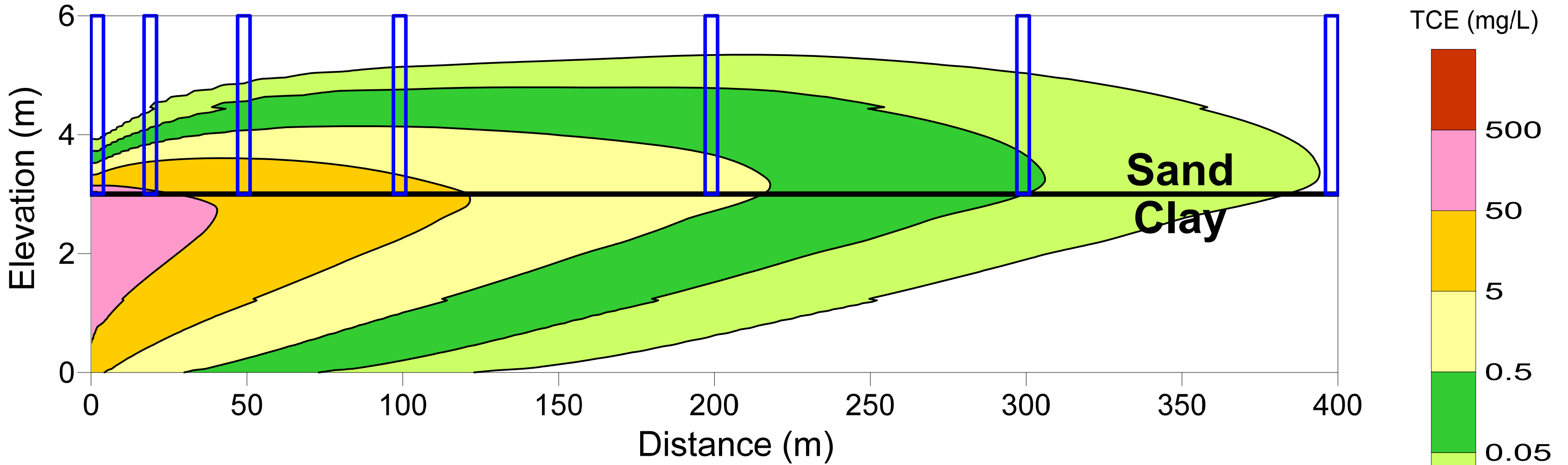


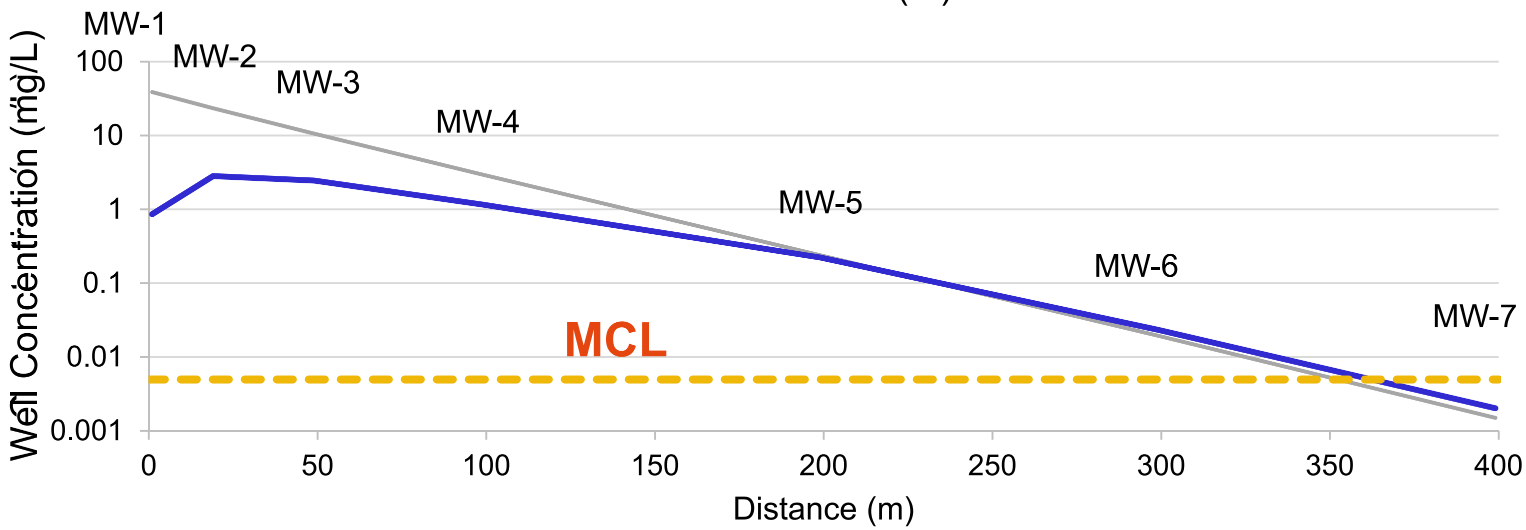
Year: 2015

Time Since Source Depletion:

0 y

Back-Diffusion Example – Case 2: Strong Attenuation Along Flowpath



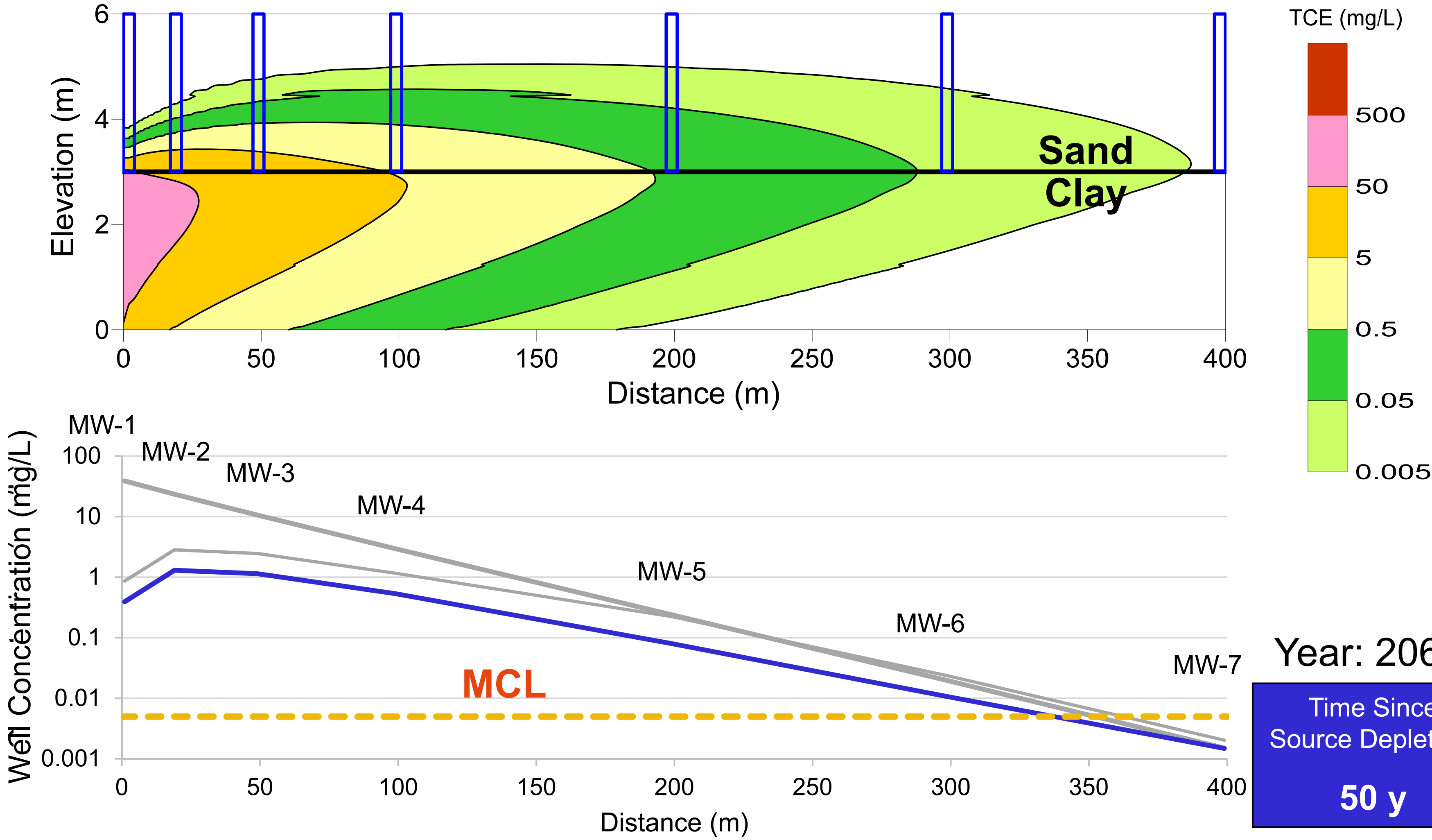


Year: 2040

Time Since Source Depletion:

25 y

Back-Diffusion Example – Case 2: Strong Attenuation Along Flowpath

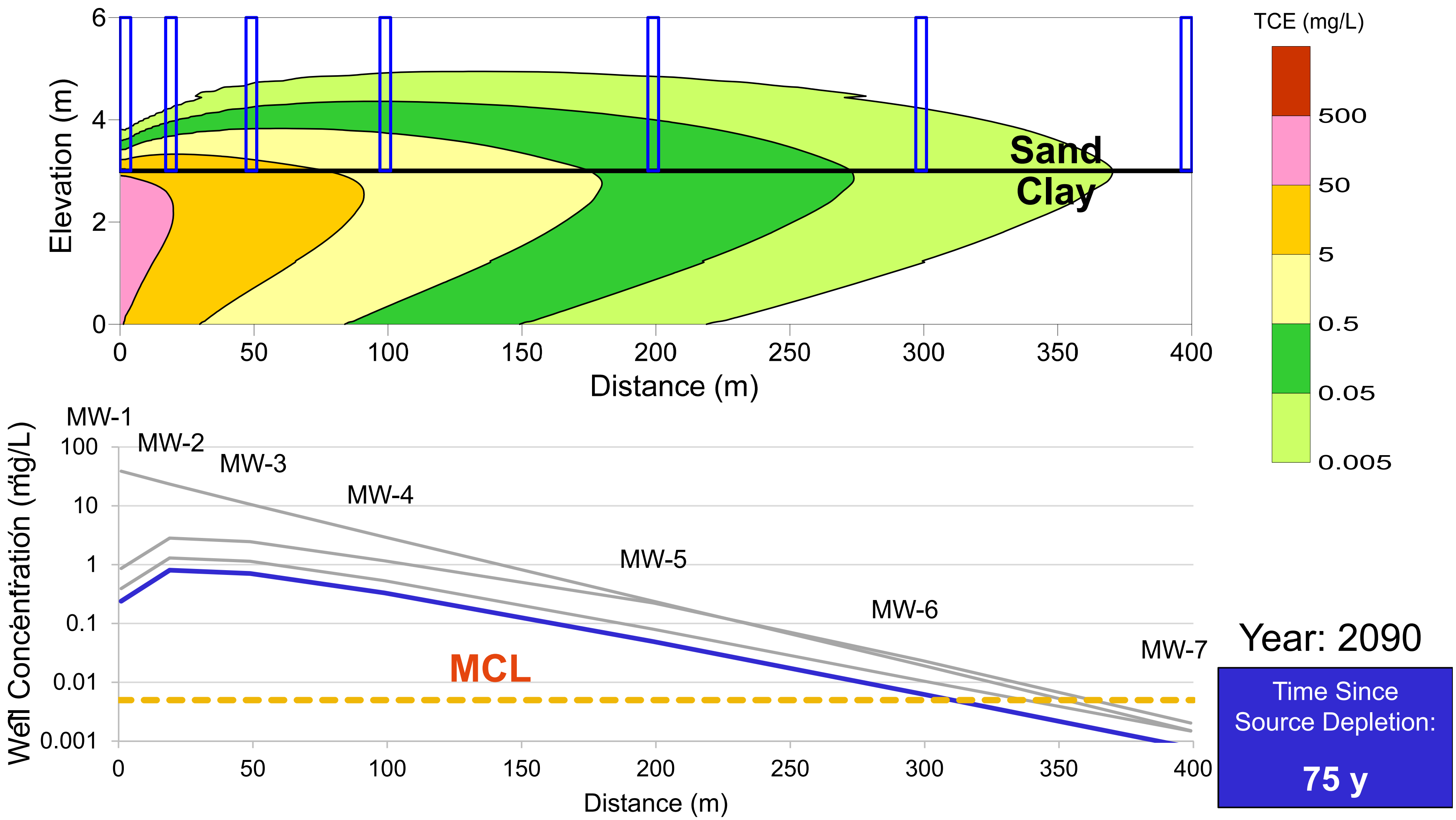


Year: 2065

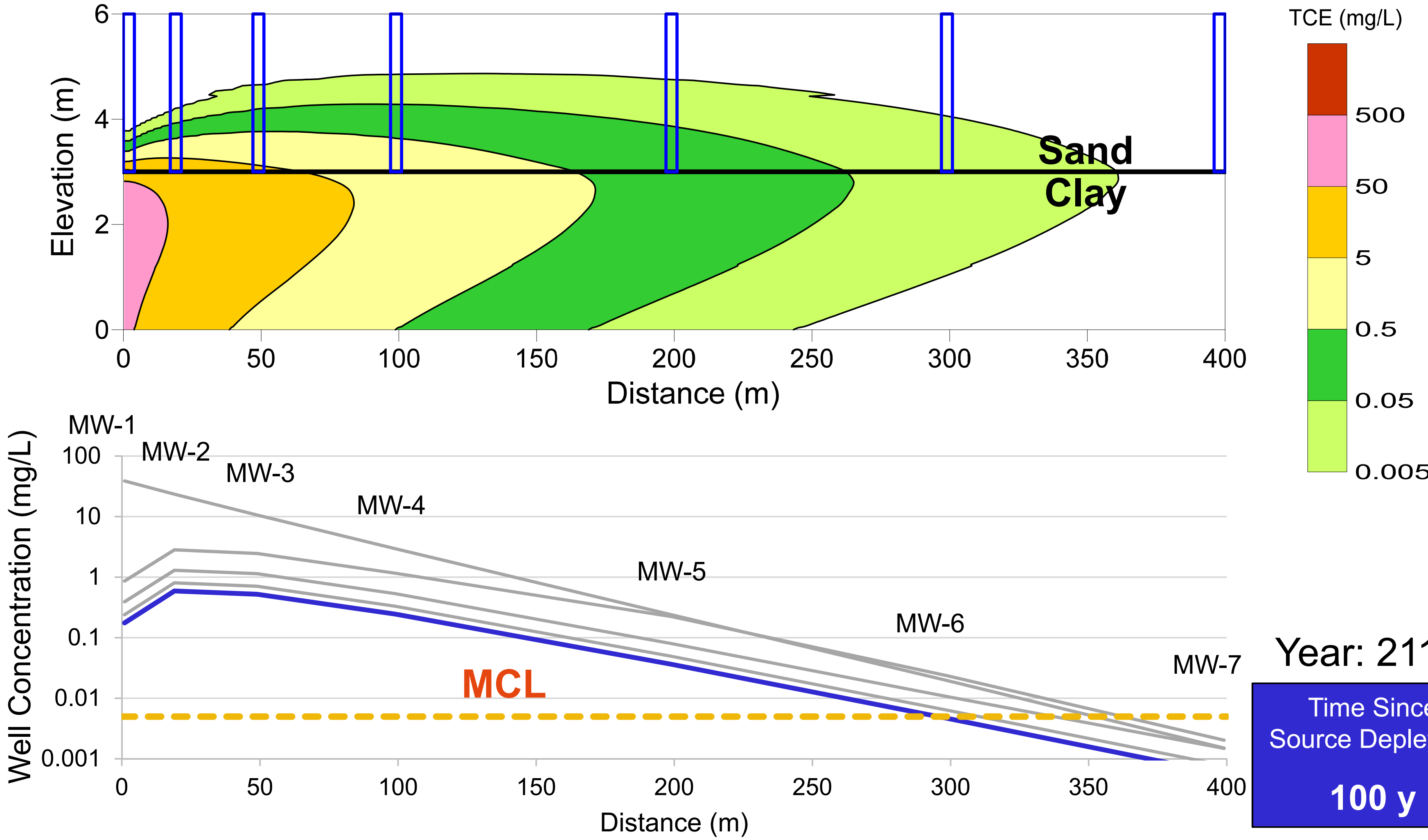
Time Since Source Depletion:

50 y

Back-Diffusion Example – Case 2: Strong Attenuation Along Flowpath



Back-Diffusion Example – Case 2: Strong Attenuation Along Flowpath



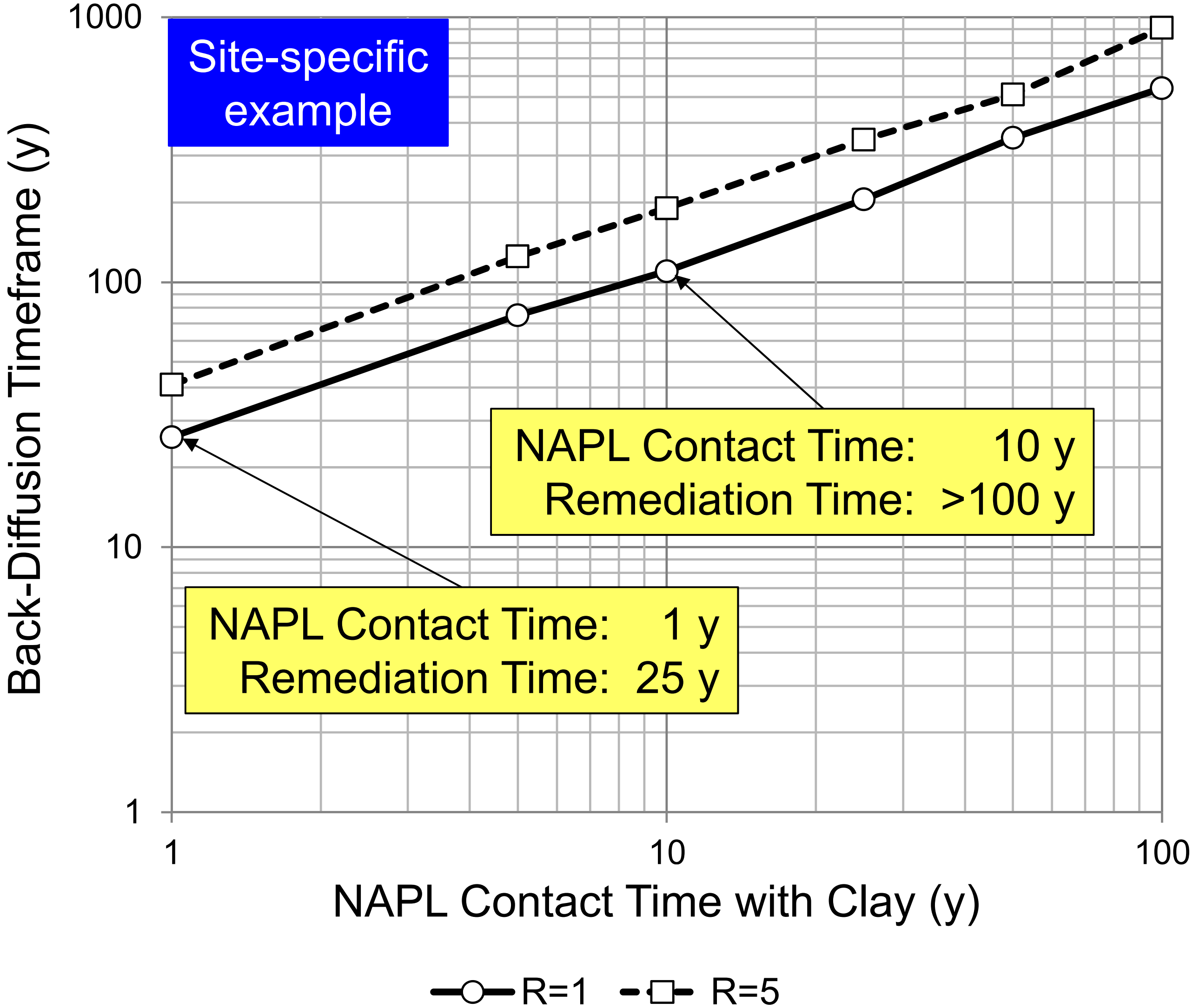
Year: 2115

Time Since Source Depletion:

100 y

Remediation Timeframe vs. Contact Time

Note – based on thick aquitard assumption.



Integrated Source-Plume Management

- Recognize potential limitations in:
  - DNAPL treatment
    - Attainable, interim reduction in mass discharge
    - Interim goal: Transition to passive source 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

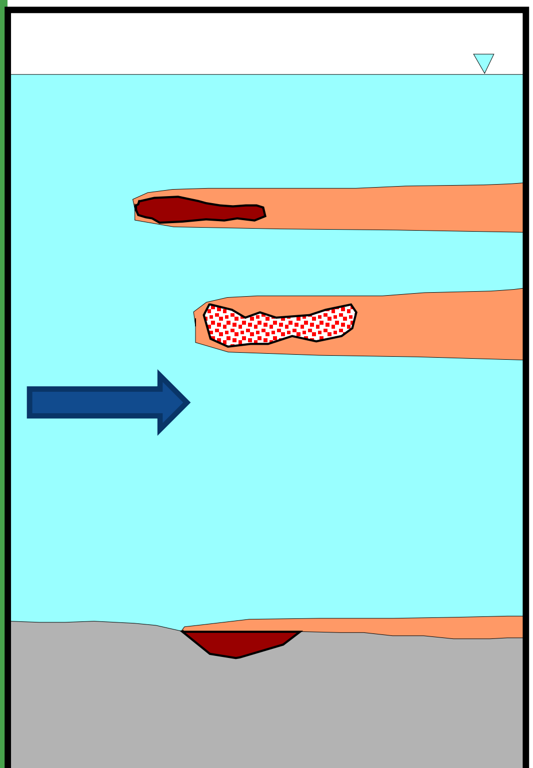
Initial Framework for DNAPL Remedy Evaluation

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. Mass discharge reduction?
3. Evaluate back-diffusion timeframe in plume
4. Predict time to attain interim goals for DNAPL treatment, and targets for plume strength reduction

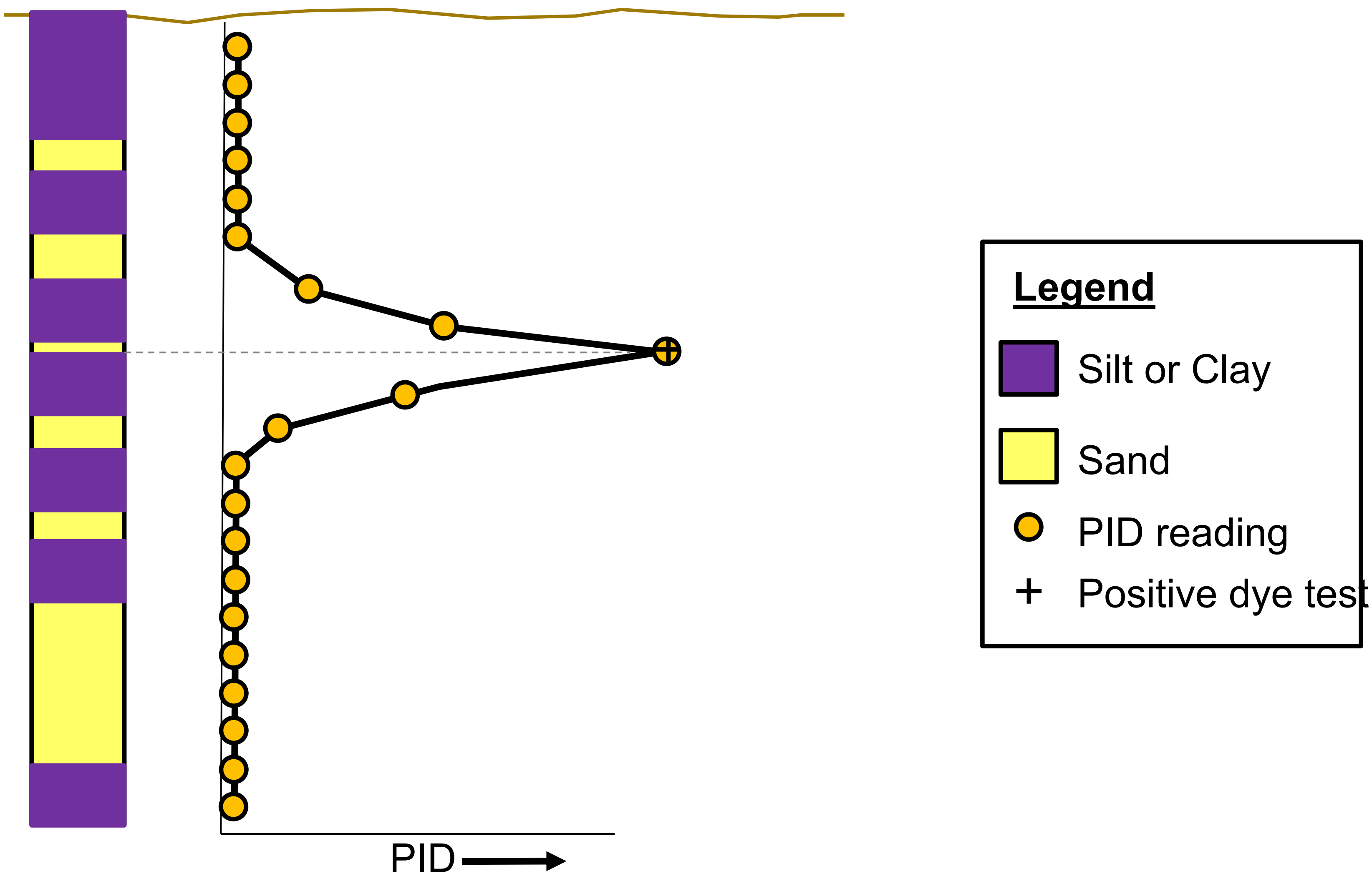
2. SITE CHARACTERIZATION

Conceptual Model – Aged Source Zones



- Pool / layer-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 DNAPLS Pools

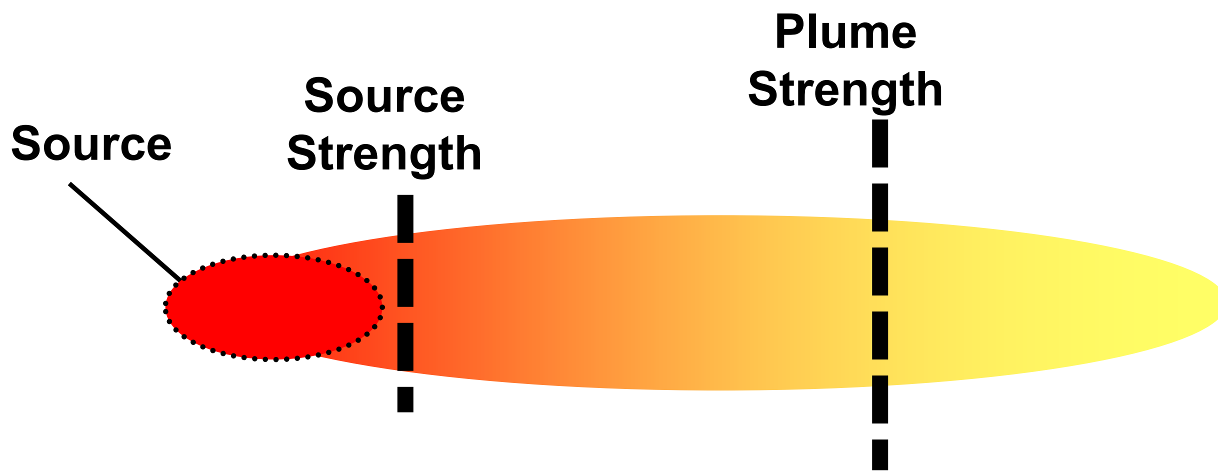
- Visible NAPL in wells (free phase)
- NAPL seeping from soil cores
- Persistently high concentrations in transmissive formation (>1% solubility in monitoring wells)
- Slow source strength decline rate
- Heterogeneous or layered geology in aged NAPL source zone
- Thin aqueous plumes downgradient of source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

Five Methods for Mass Discharge

ITRC, 2016

- *Method 1:* Transect Method
- *Method 2*: Well Capture/Pumping Methods
- *Method 3:* Passive Flux Meters
- *Method 4*: Using Existing Data (Isocontours)
- *Method 5*: Solute Transport Models

All methods are "ready to go"

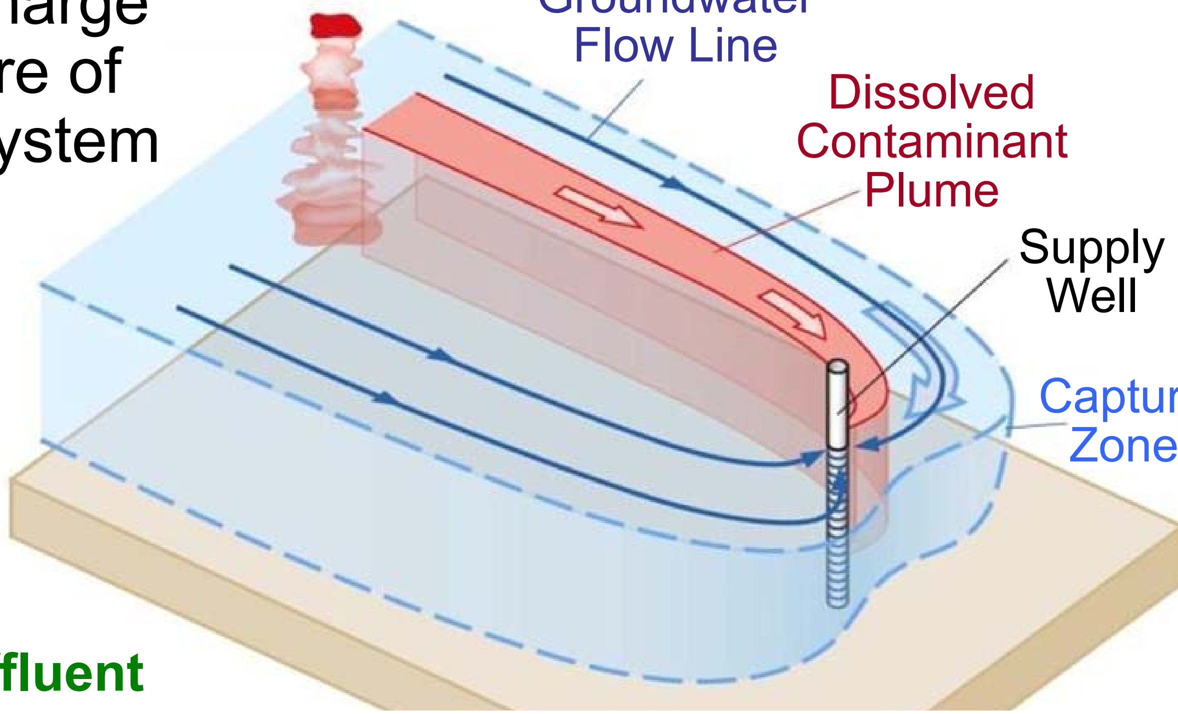


Well Capture Mass Discharge Calculation

Einarson and MacKay, 2001; ITRC, 2016

Nichols and Roth, 2004

Figure 4-8



Measure Q, C_{well} from well

Calculate mass discharge based on total capture of plume by pumping system

$$M_d = Q \times C_{well}$$

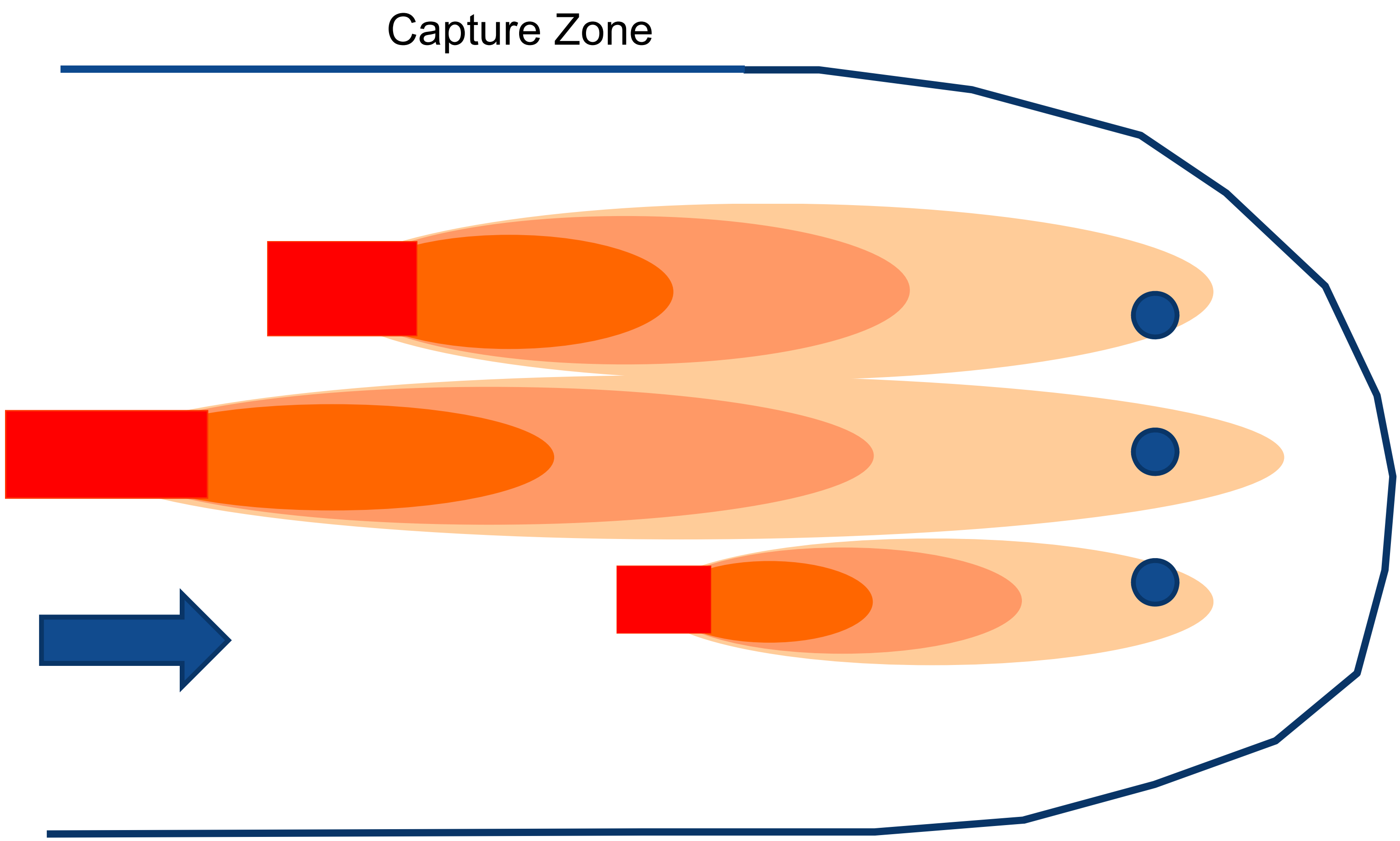
M_d = Mass discharge (grams per day)

C_{well} = concentration in recovery well effluent (grams per liter)

Q = Well pumping rate (liters per day)

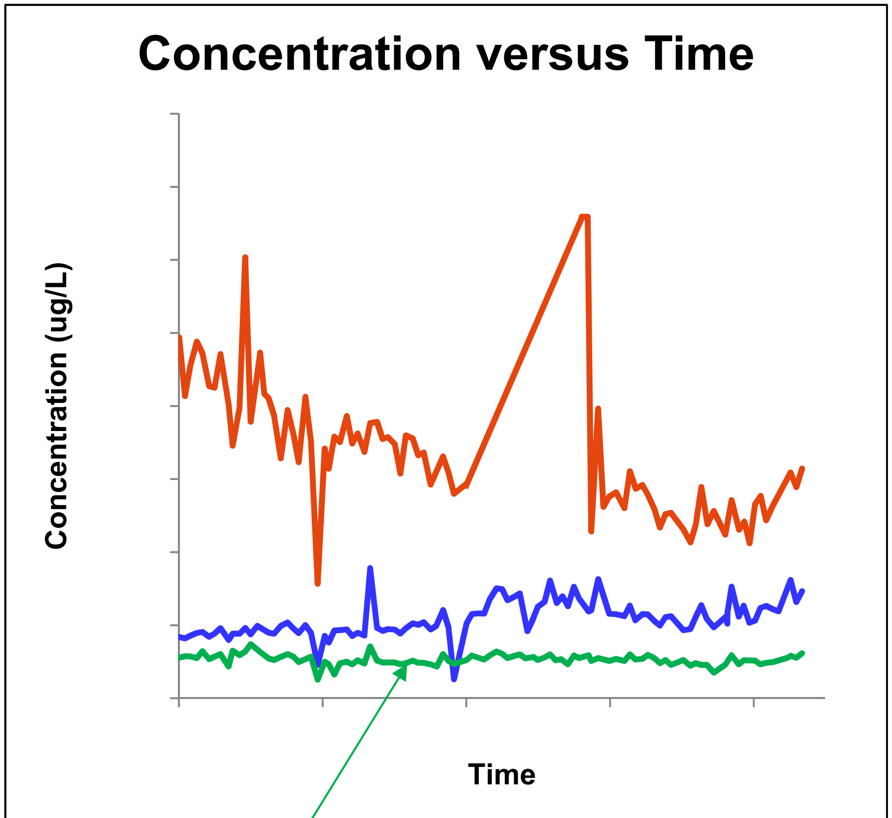
$$\frac{\text{gram}}{\cancel{\text{liter}}} \times \frac{\cancel{\text{liters}}}{\text{day}} = \frac{\text{grams}}{\text{day}}$$

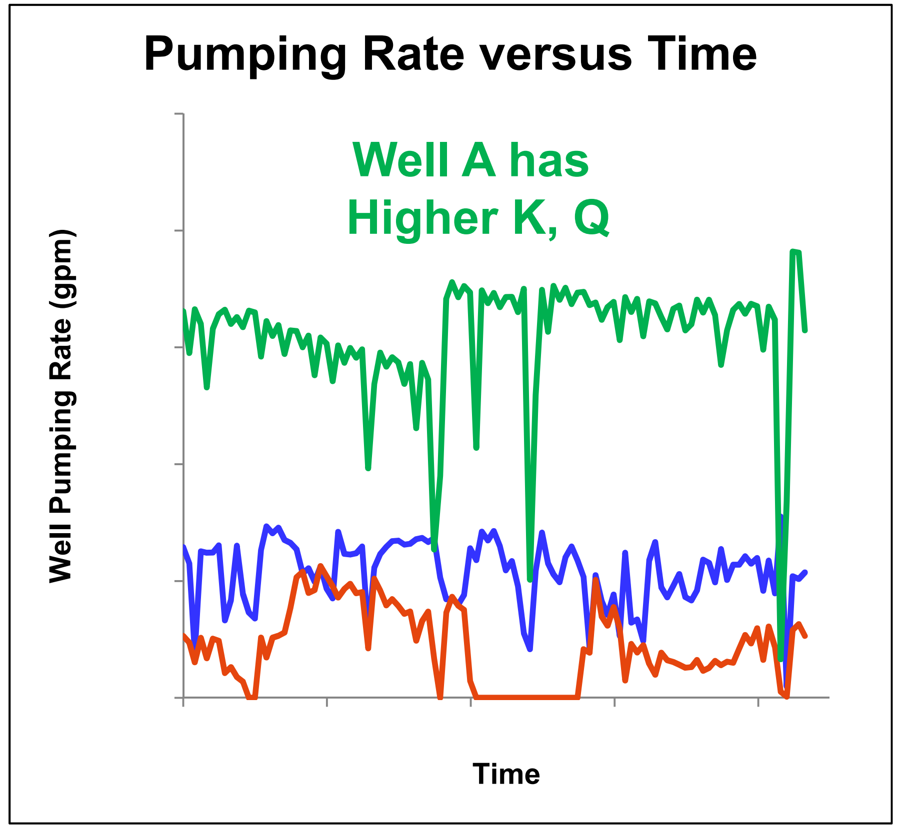
Hypothetical Example of Regional Supply Wells



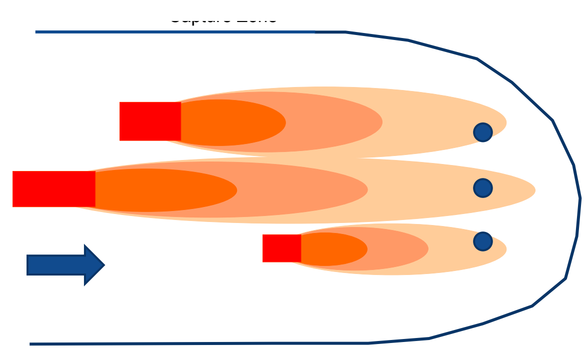
Water pumped to treatment plant.

Hypothetical Concentrations and Pumping Rates

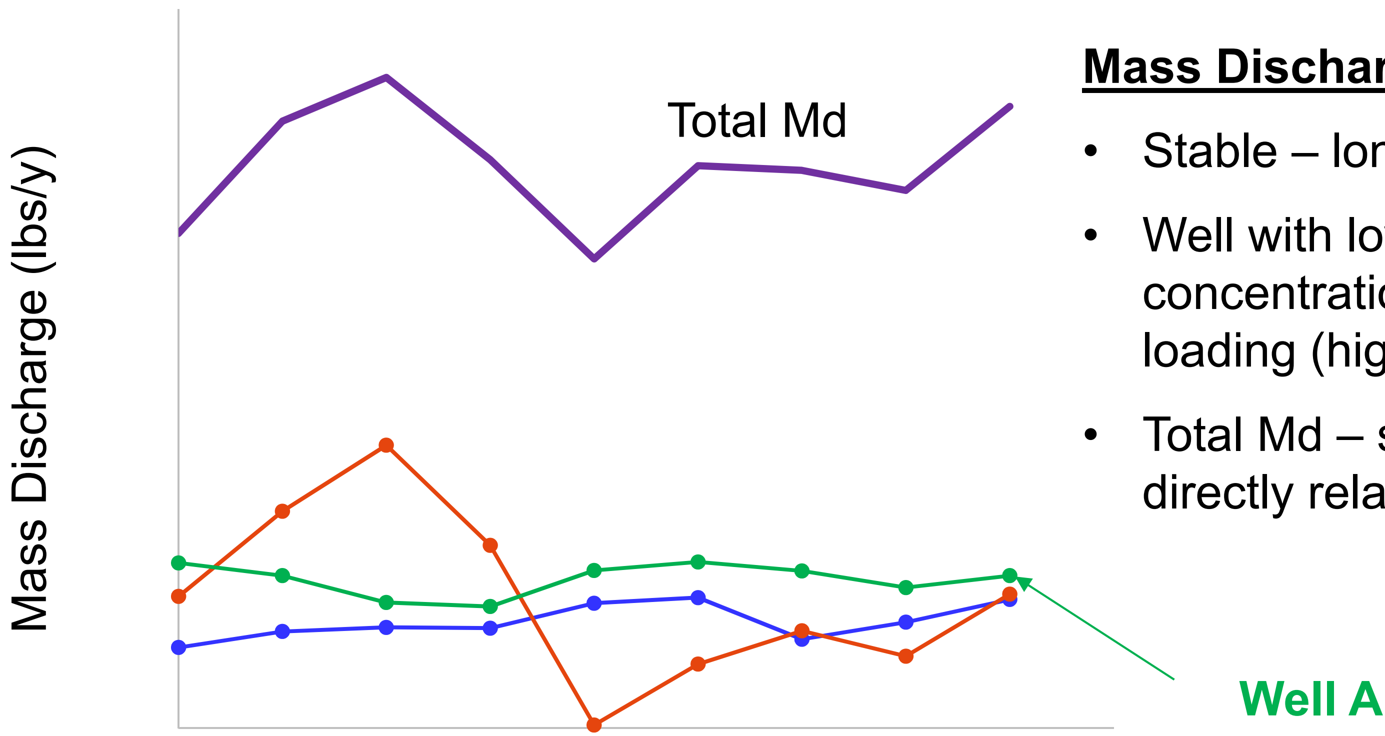




Well A has
Lowest concentration.

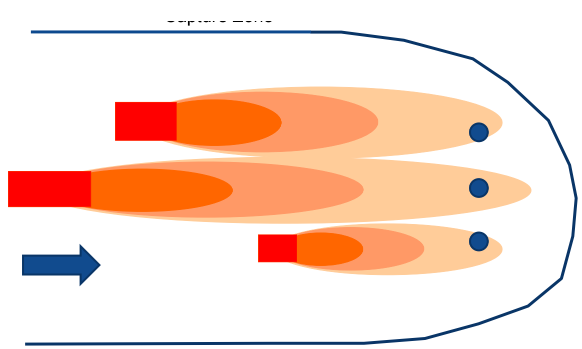


Mass Discharge (Md)

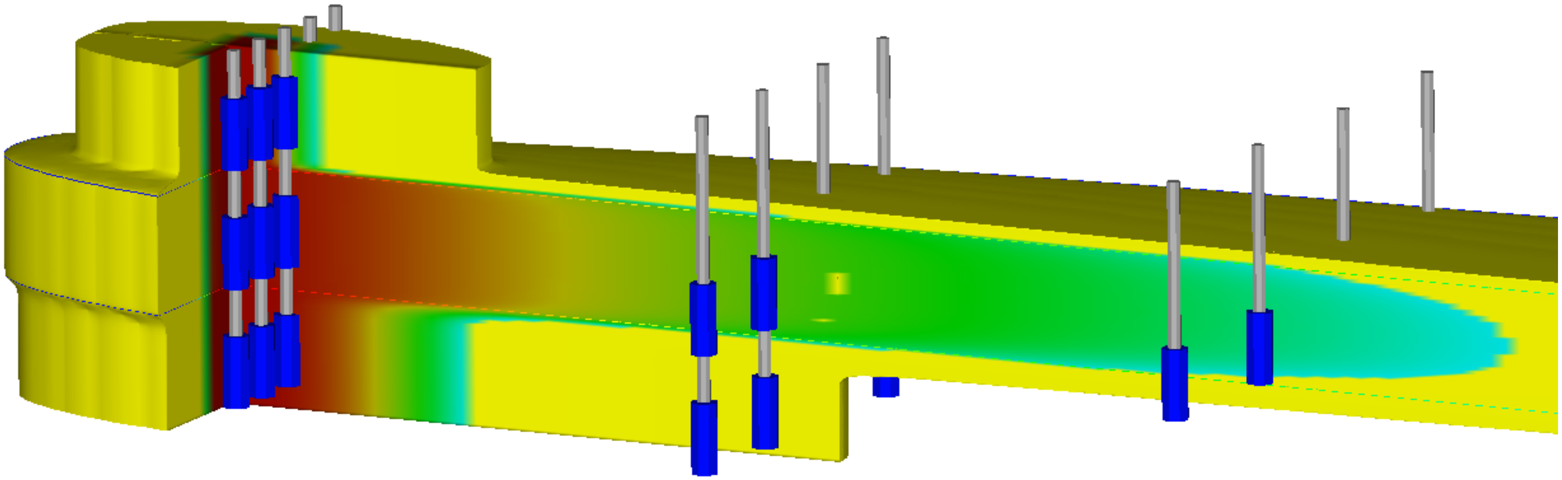


Mass Discharge Evaluation

- Stable – long-term impact
- Well with lowest concentration has highest loading (higher K, Q)
- Total Md – simple metric that directly relates to risk

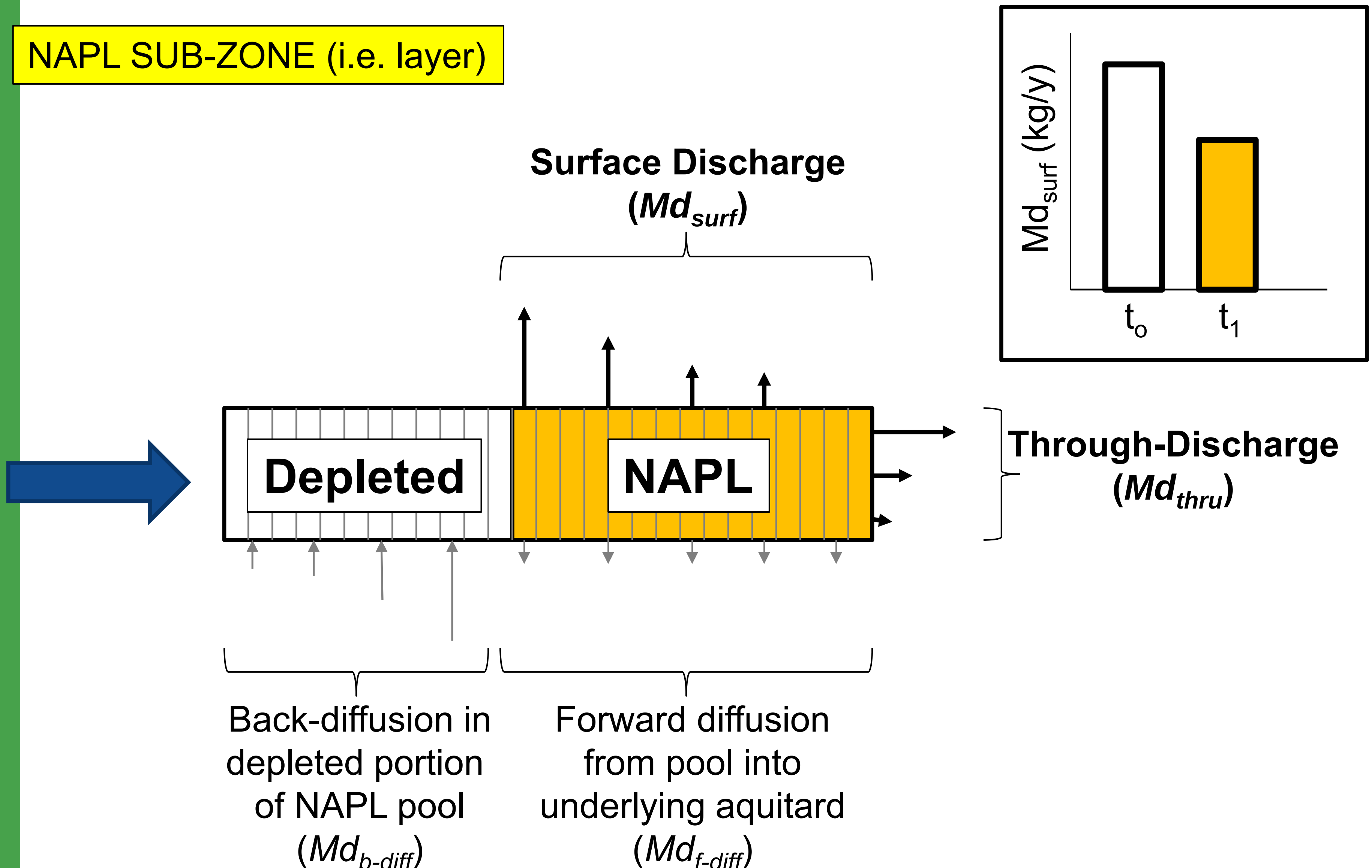


Transect Method



- General trends
  - Closer spacing at source, wider downgradient
  - 5-10 ft screens vs. multilevel samplers
    - % of transect area being monitored
    - Mass discharge vs. mass flux monitoring
    - Value of pre-characterization work (e.g. MIP)

NAPL Depletion Model (NDM)



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}

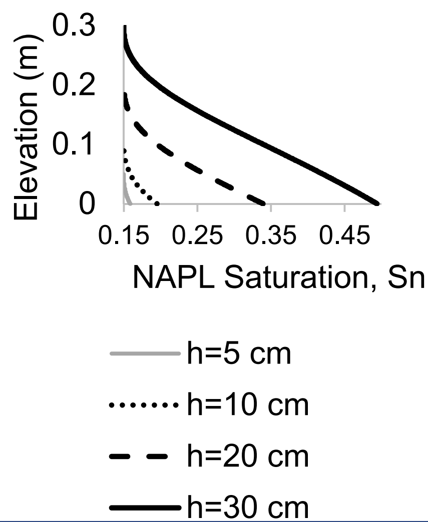
- Tortuosity
- D_o
- α_{tv}
- U/G sub-zone?
- f_{surf} multiplier
  = 1 or 2

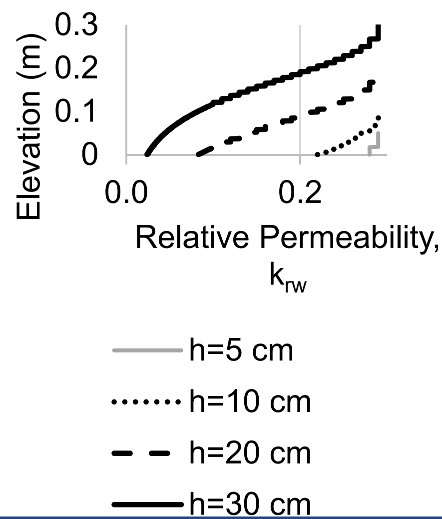
Md_{thru}

- 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



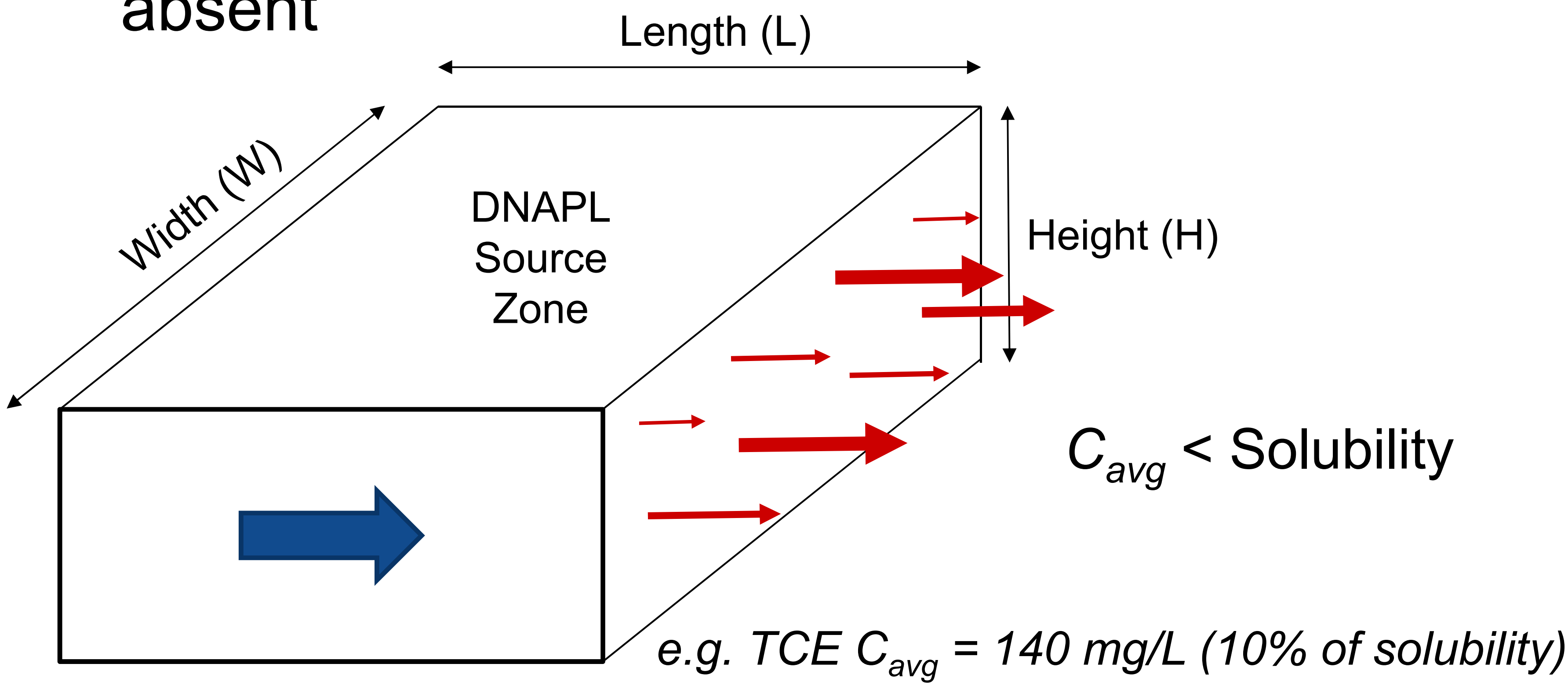


Estimating Input Parameters Based on K

Reference	Empirical Relationship (K in m/s)	
Carey et al., 2016a	$\tau = 0.60\ K^{0.030}$	(i)
Carey et al., 2016c	$\theta_t = 0.30\ K^{-0.026}$	(ii)
	$\theta_e = 0.41\ K^{0.064}$, $K \leq 1x10^{-2}$ m/s	(iii)
	$\theta_e = (0.29\ K^{-0.026}) - 0.03$, $K > 1x10^{-2}$ m/s	(iv)
Carey et al., 2016c	$\alpha_{TV} = 0.08\ K^{-0.16}$, $v \leq v_c$	(v)
	$\alpha_{TV} = 0.08\ K^{-0.16}\ (v_c/v)^{0.5}$, $v > v_c$	(vi)
Carey et al., 2016e	$\alpha_{aw} = 0.112\ (100\ K)^{0.211}$	(vii)
	$n = 13.14\ (100\ K)^{0.246}$ $K \geq 1x10\text{-}4$ m/s	(viii)
	$S_{wr} = 0.015\ (100\ K)^{-0.218}$	(ix)

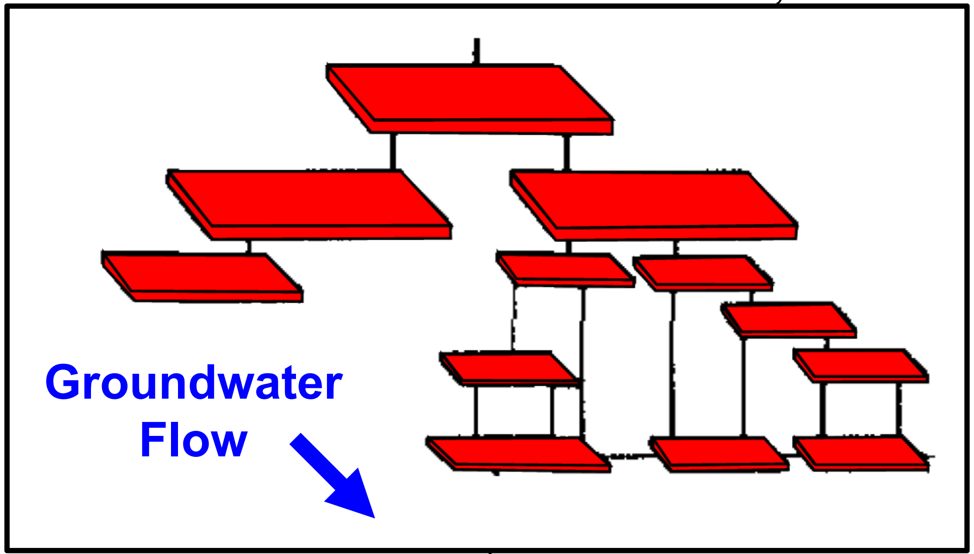
Example No. 1: Mixed Source Zone

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

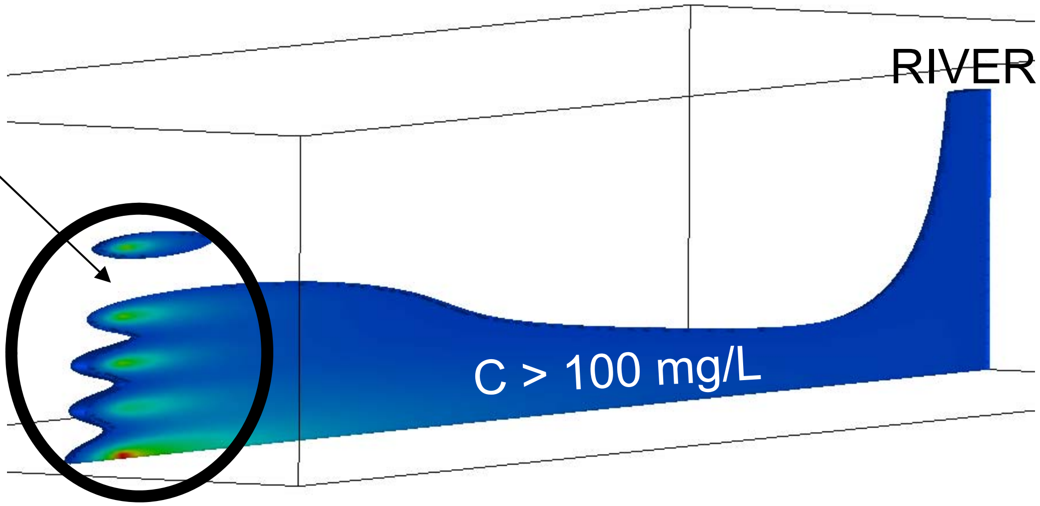


Example No. 2: Defined NAPL Layers

Modified from Anderson et al., 1992



See Appendix B for LNAPL Site Case Study

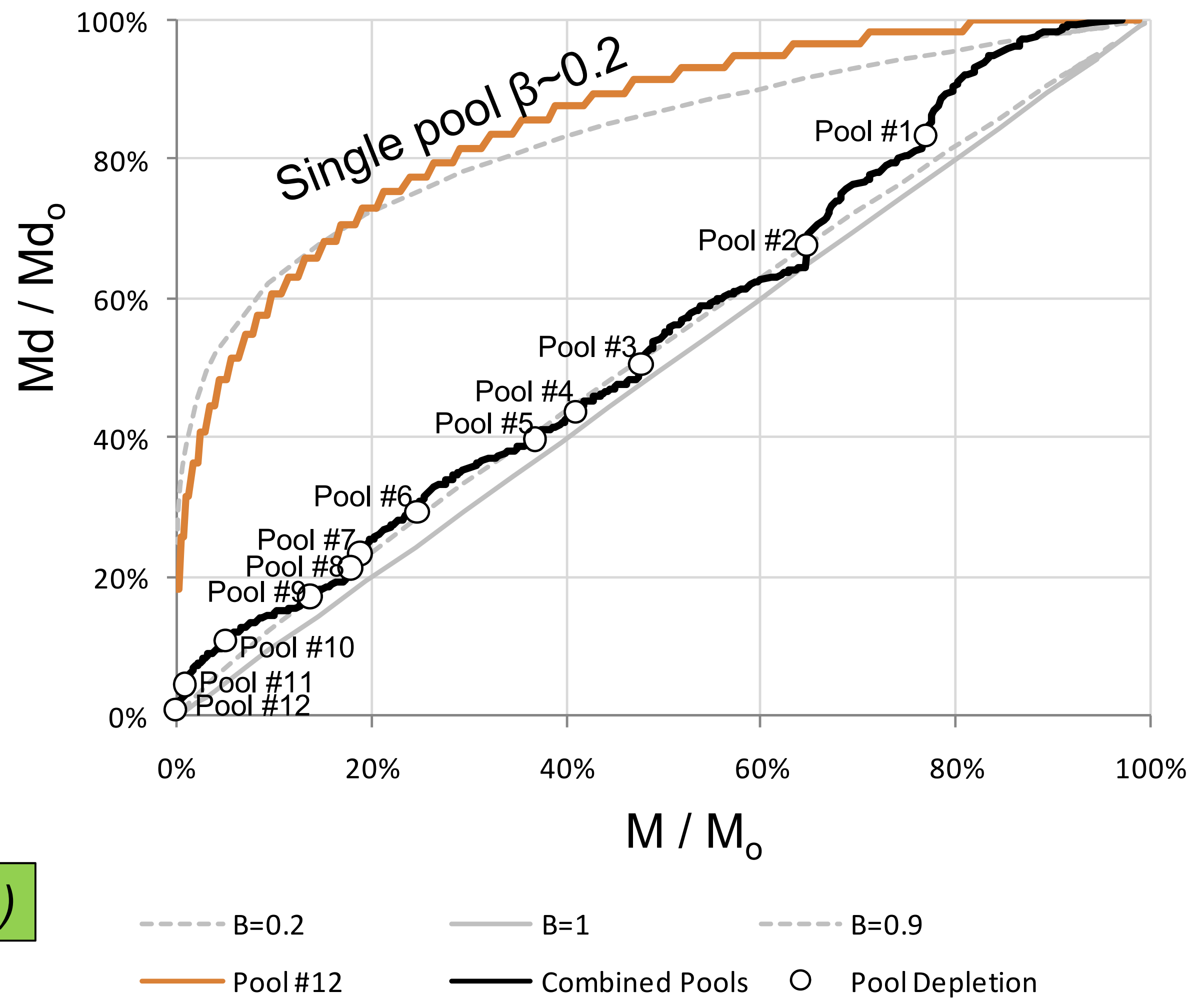


Carey et al. (2014b)

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. (2016e)

Carey et al. (2014b)

REMEDIATION Autumn 2014

Grant R. Carey

Edward A. McBean

Stan Feenstra

DNAPL Source Depletion: 2. Attainable Goals and Cost–Benefit Analyses

CASE STUDIES

3.1 PREDICTING Md REDUCTION

Empirical-Based Attainable Goals

- Objective: To estimate attainable source strength (Md) reduction goal for DNAPL zones at:
  - Complex sites
  - More simple sites
- Technologies: EISB, ISCO, Thermal

Empirical Databases

- McGuire et al. (2006) – concentration reduction at individual wells for EISB and ISCO at DNAPL sites
  - Some wells had low starting concentrations
  - Median reduction of all wells
- SERDP/ESTCP TEST
  - Median concentration reduction at individual wells
- Stroo et al. (2012):
  - 1 to 2 orders-of-magnitude (OOM) reduction

Md Reduction (MdR) at DNAPL Sites

$$MdR = \frac{\text{Pre-treatment Md}}{\text{Post-treatment Md}}$$

Md = mass discharge (source strength)

MdR = 5x → 80% reduction
MdR = 10x → 90% reduction
MdR = 20x → 95% reduction
MdR = 100x → 99% reduction
MdR = 1,000x → 99.9% reduction

MdR better indication of order-of-magnitude change than % reduction

Md Reduction (MdR) at DNAPL Sites

- Started with McGuire et al. (2006) dataset for EISB and ISCO
- Filtered out wells with C < 1% solubility (less likely to be directly downgradient of source)

  → Focus on "Source Wells" trends
- Calculated site MdR based on mean of all "Source Well" concentration trends
- Calculated mean and confidence interval of all site MdR (log-normal)

Note: Medians from other studies ignore influence of sites with poor and excellent performance.

Thermal Studies based on Triplett-Kingston (2008)

Triplett Kingston (2008) Site ID (Table 5.5)	Pre-Treatment Source Strength (kg/y)	Post-Treatment Source Strength (kg/y)	Ratio of Pre- to Post-Treatment Source Strength, MdR	MdR%	Geometric Mean Site MdR
Site 1	51.5	0.187	275.4	99.6%	275.4
Site 2	59.9	4.94 / 20.7	4.7	78.6%	4.7
Site 3	48	0.125	384.0	99.7%	384.0
Site 4	31.8	2.11	15.1	93.4%	15.1
Site 5	684	82.3	8.3	88.0%	8.3
Site 6	4.64	0.0734	63.2	98.4%	63.2
Site 7	9.42	0.0267	352.8	99.7%	33.0
	4.93	1.6	3.1	67.5%	
Site 8	1.71	0.595	2.9	65.2%	2.7
	2.43	0.969	2.5	60.1%	
Site 9	0.40	0.03	13.1	92.4%	13.1
Site 10	0.0192	1.78E-07	107,865.2	100.0%	16,979.8
	2.86E-04	1.07E-07	2,672.9	100.0%	
Site 11	0.0968	0.0607	1.6	37.3%	1.6
Site 12	1.24	0.0535	23.2	95.7%	23.2
Site 13	9.27	0.017	545.3	99.8%	495.9
	7.35	0.0163	450.9	99.8%	
Site 14	1.31	2.84	0.5	-116.8%	0.5

Carey et al. (2014b)

MdR Mean and Confidence Interval

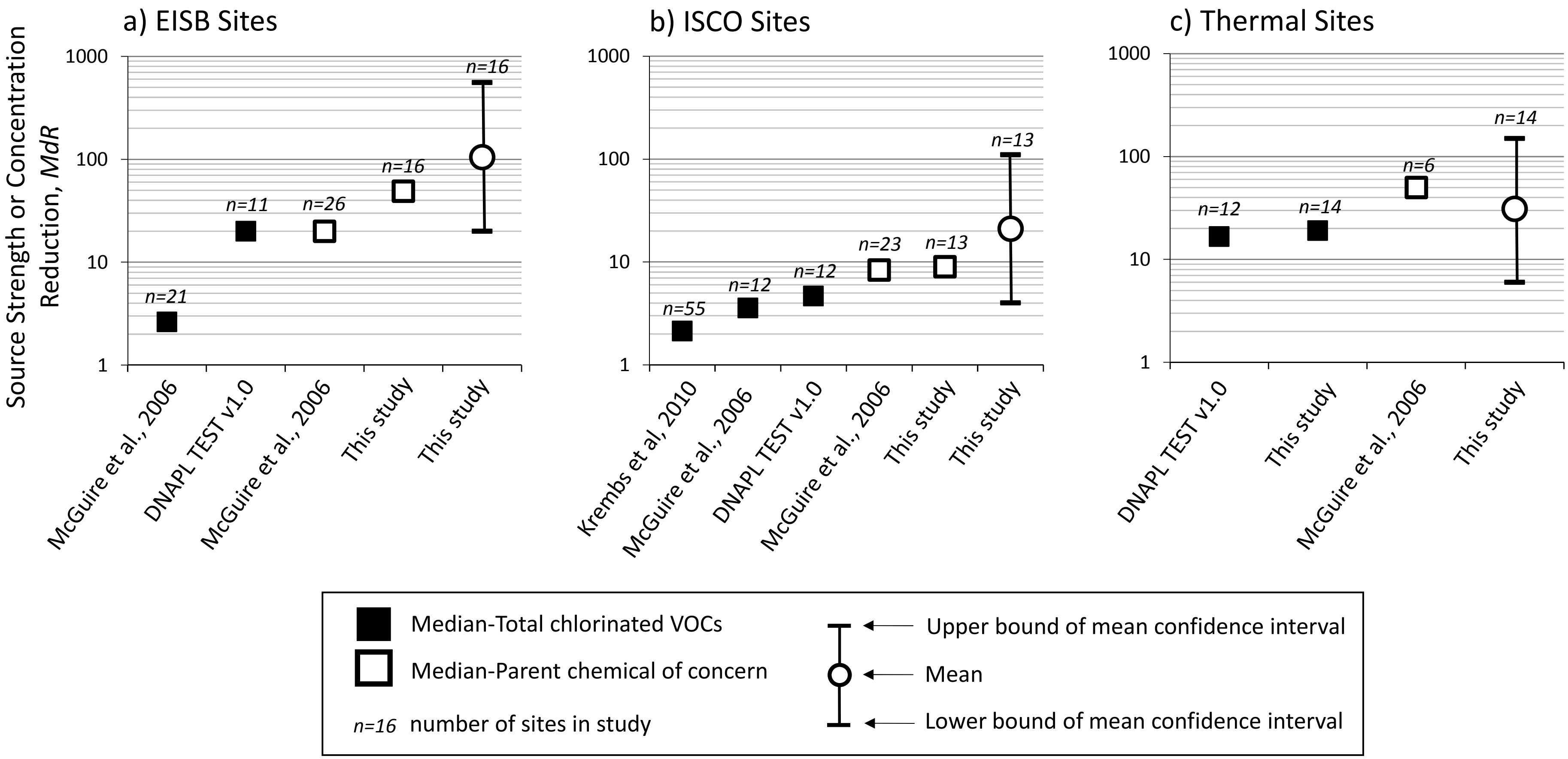
	Mean MdR	Conf. Int.
EISB:	105x	(20x to 556x)
ISCO:	21x	(4x to 110x)
Thermal:	31x	(6x to 150x)

Complex sites:

- **Use low end of confidence Interval**

Carey et al. (2014b)

Average Mass Discharge Reduction

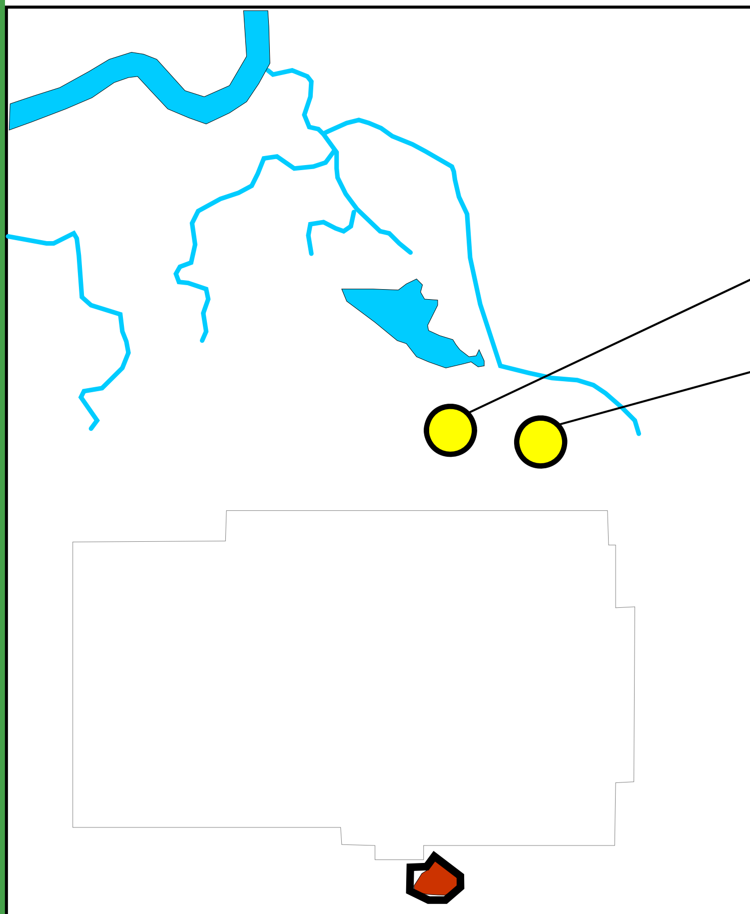


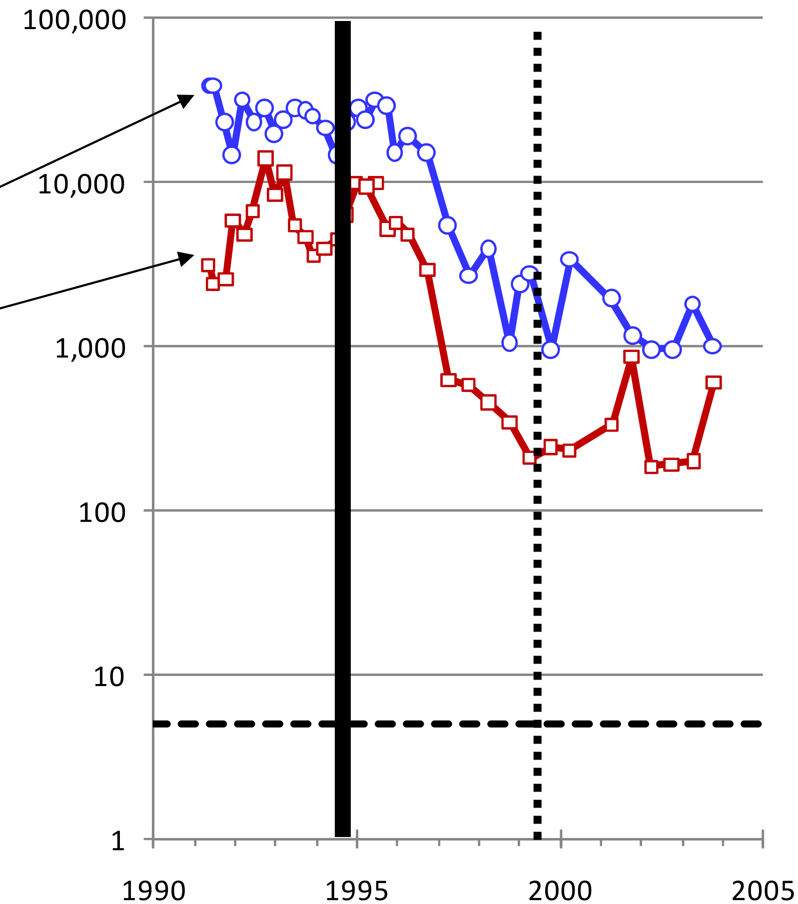
Carey et al. (2014b)

CASE STUDIES

3.2 CONNECTICUT SITE

Connecticut Site (Chapman & Parker, 2005)



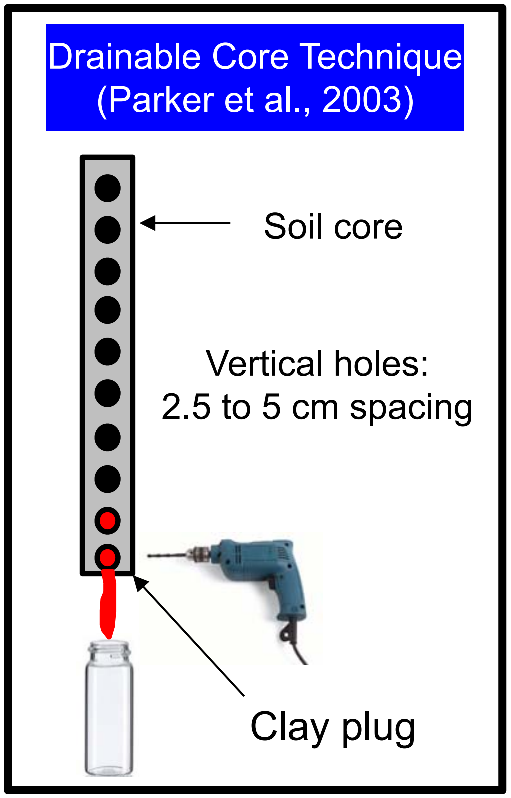


DNAPL Source Zone

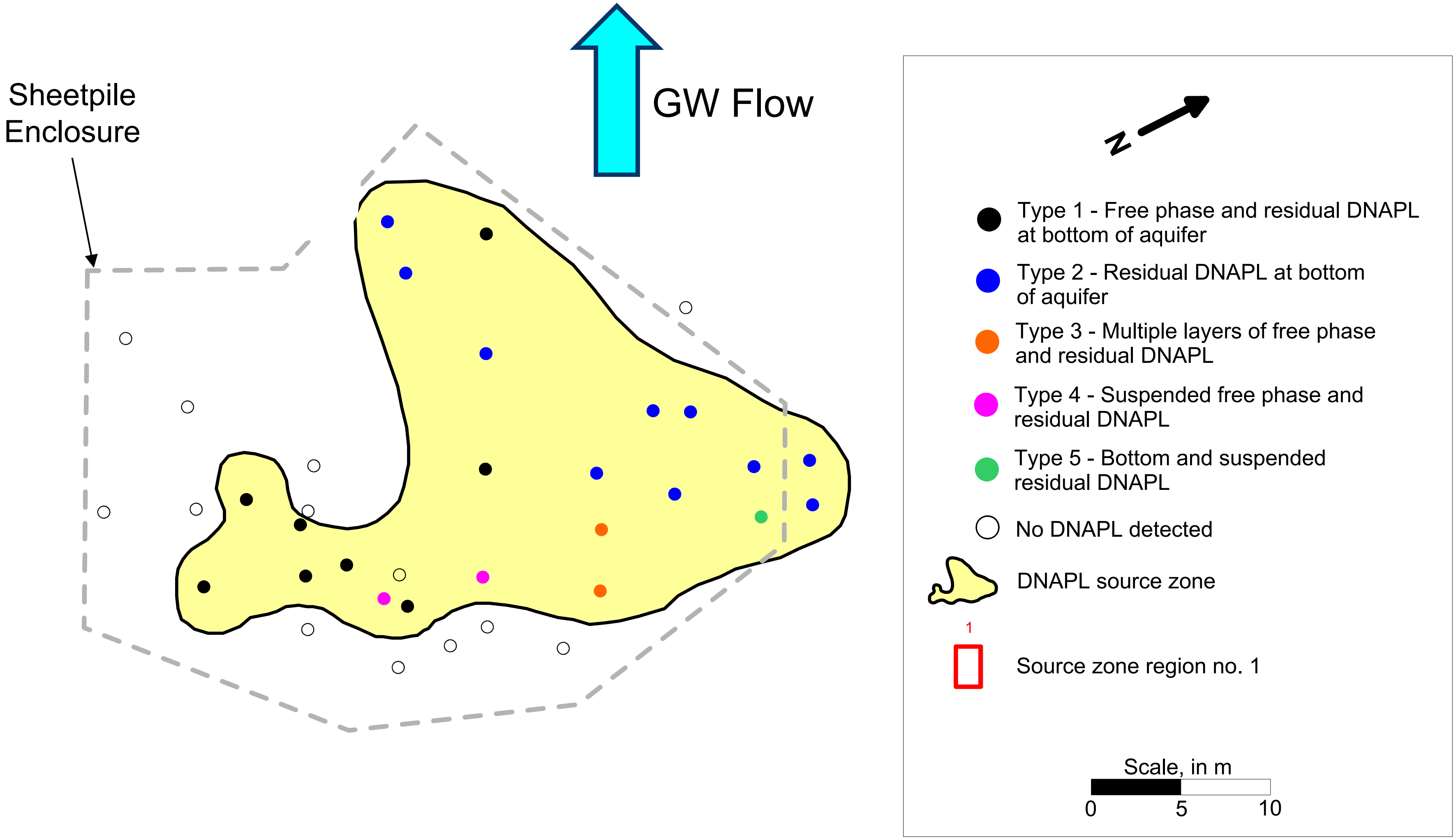
Concentration reduction stalled at 93% (15x)

Case Study: Beth Parker et al. (2003)

- Connecticut site
- Large DNAPL source zone
  - Bottom of sand aquifer, above aquitard
- Multiple lines of evidence
  - Visual inspection
  - Soil samples – close vertical spacing
    - Partitioning threshold, S_n, & layer thickness
  - Dye tests (Sudan IV)
  - Drainable core technique → Pool thickness



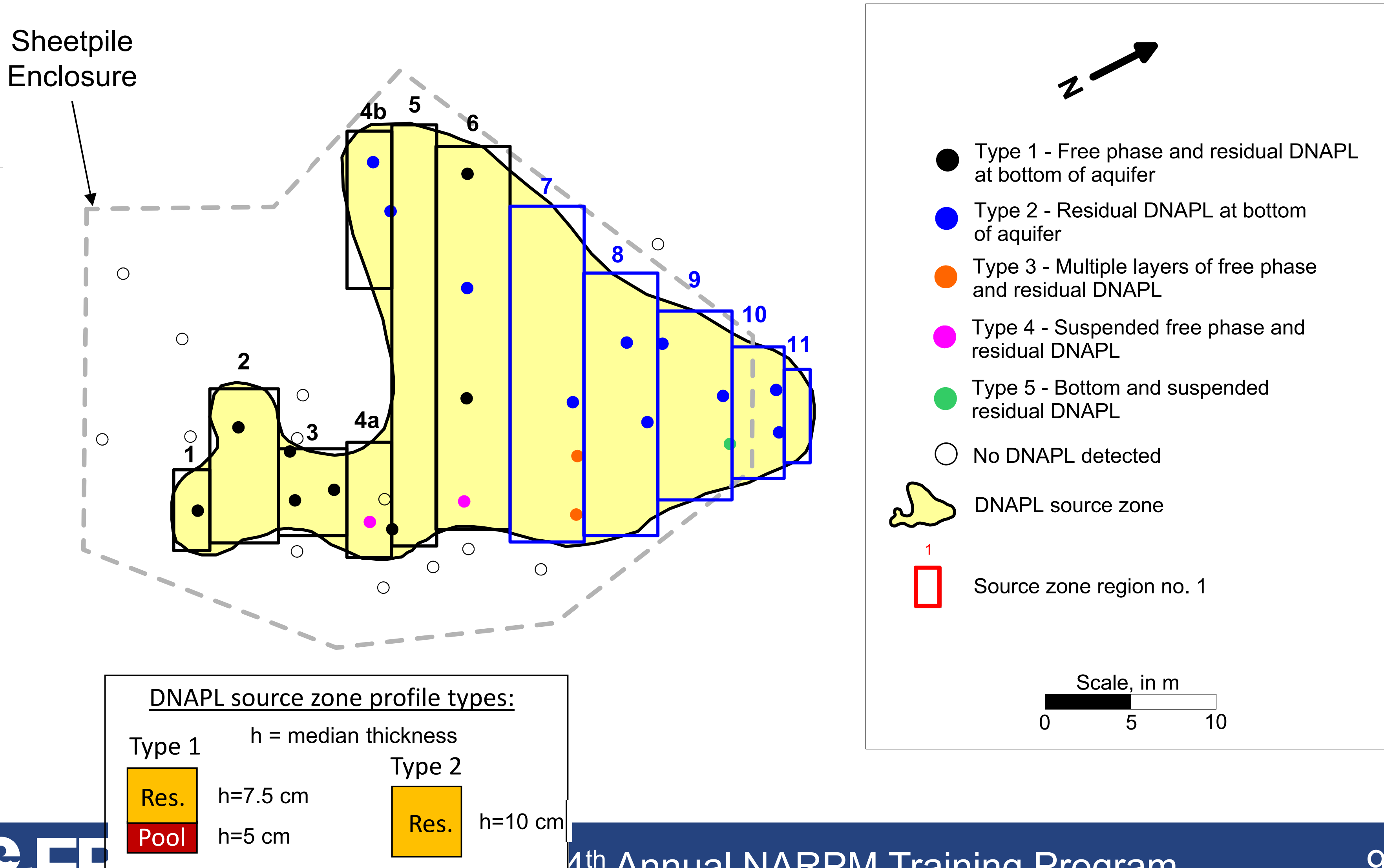
1996/97 Source Zone



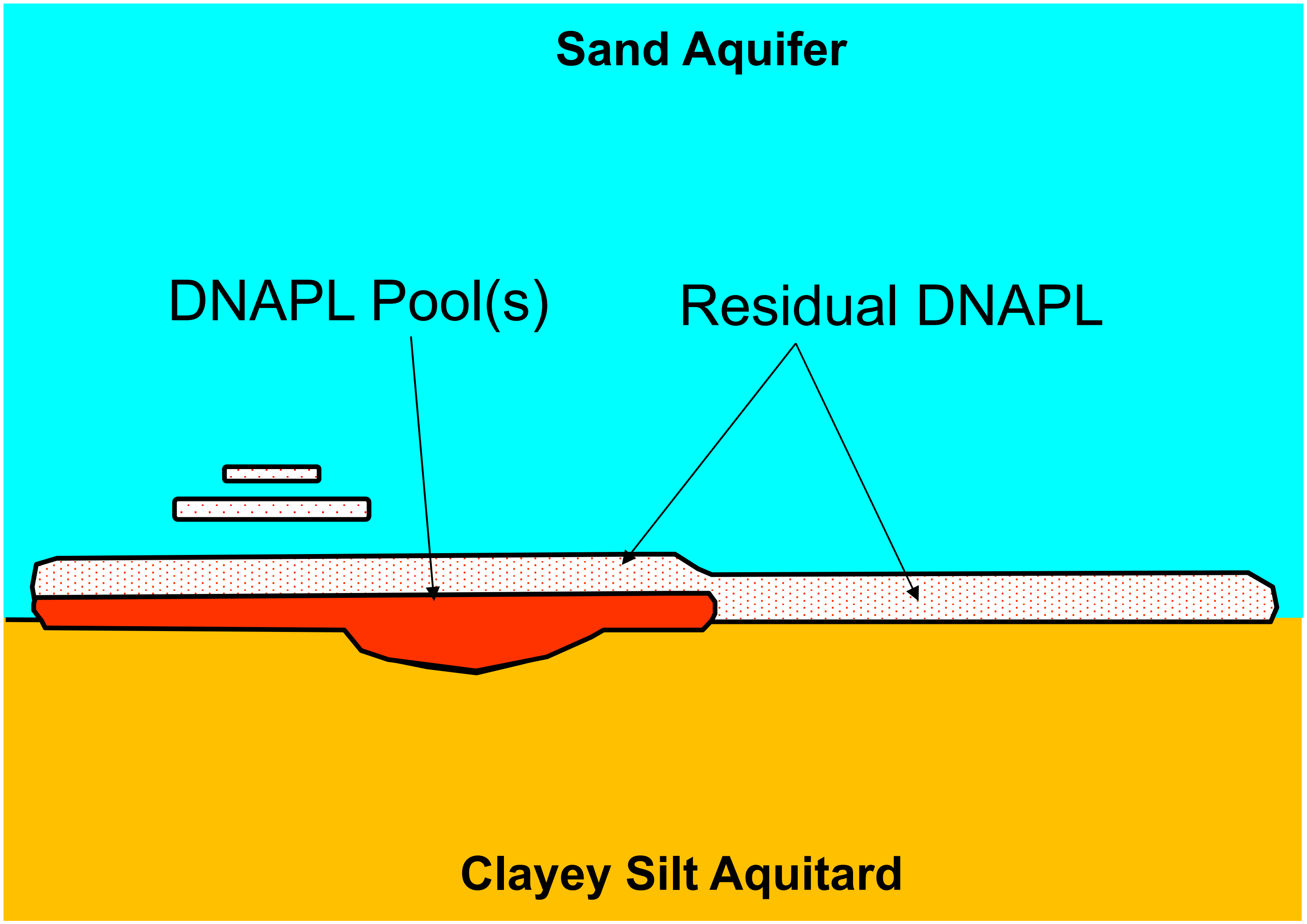
Field Data summarized in Stewart (2002) and Parker et al. (2003)

DNAPL Sub-Zones

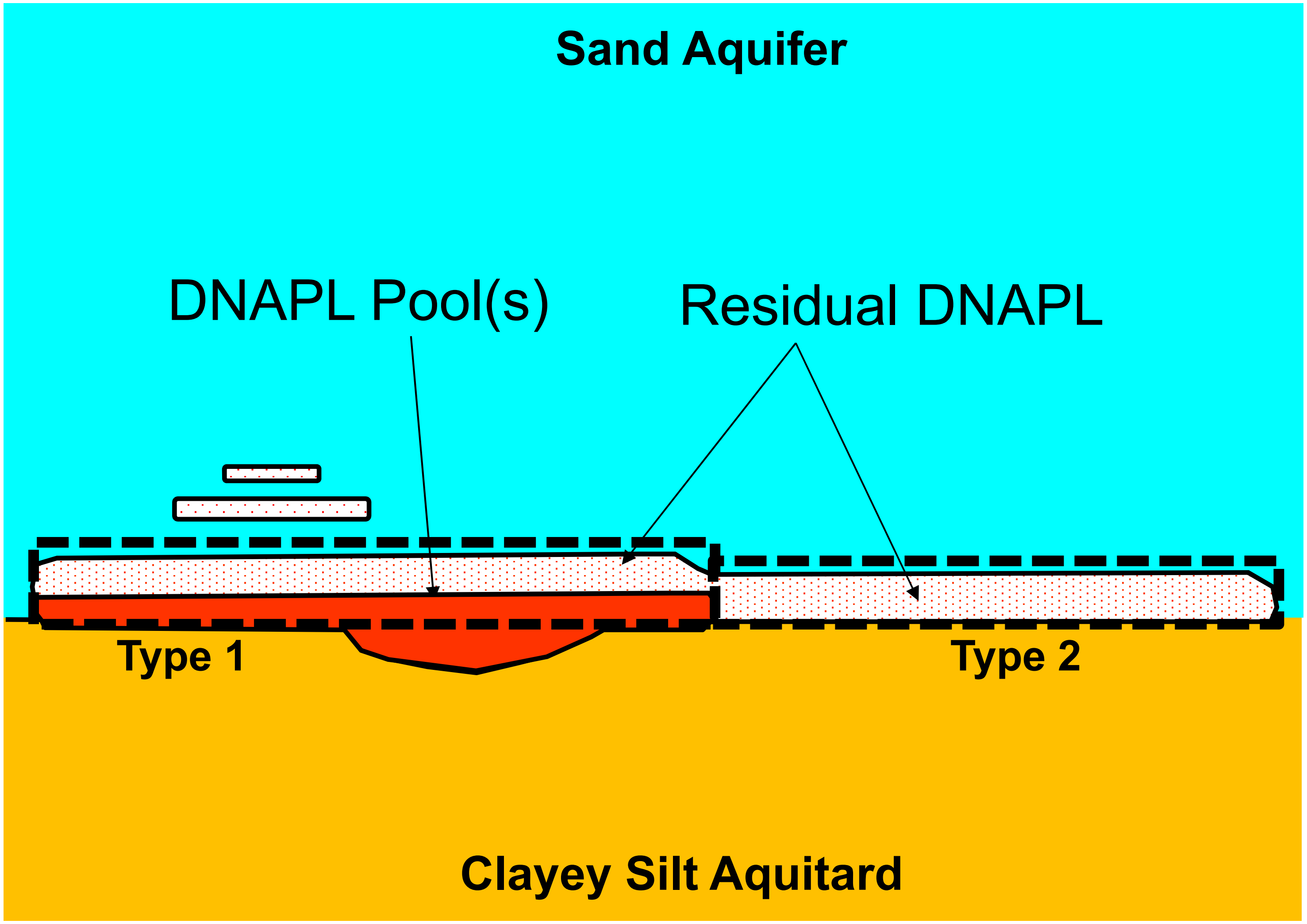
Carey et al. (2016e)



Typical DNAPL Architecture

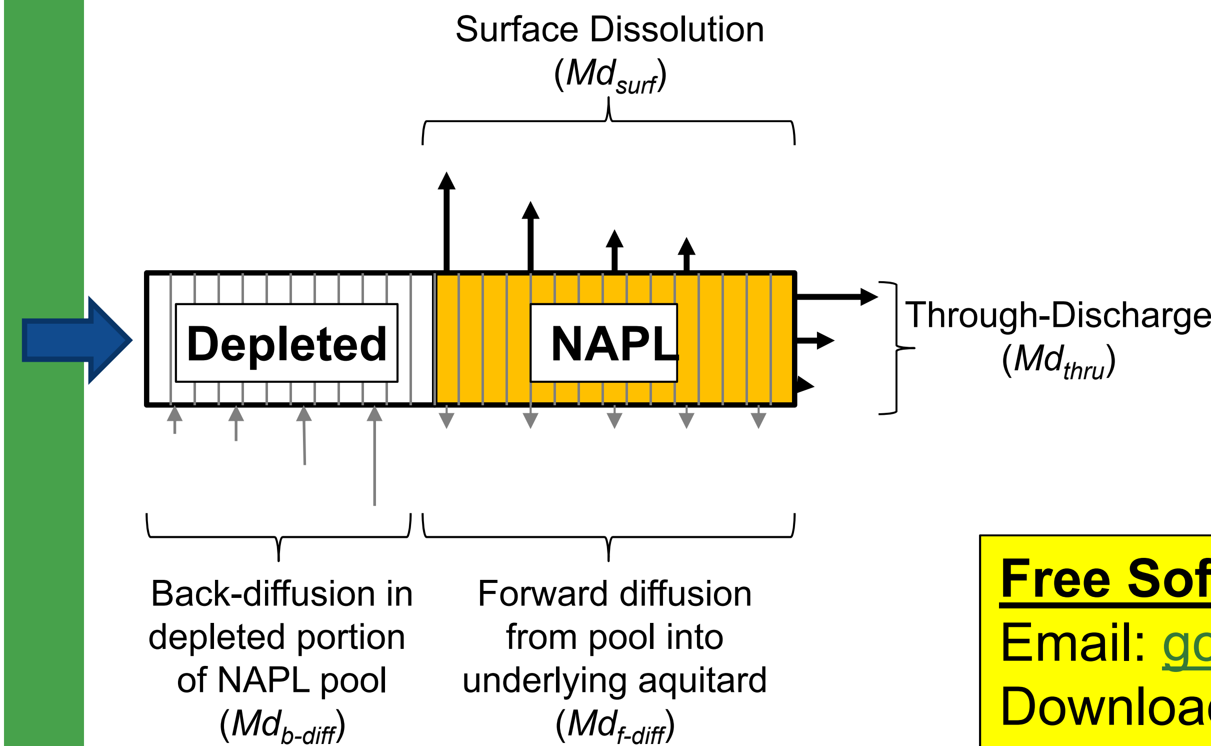


Typical DNAPL Architecture



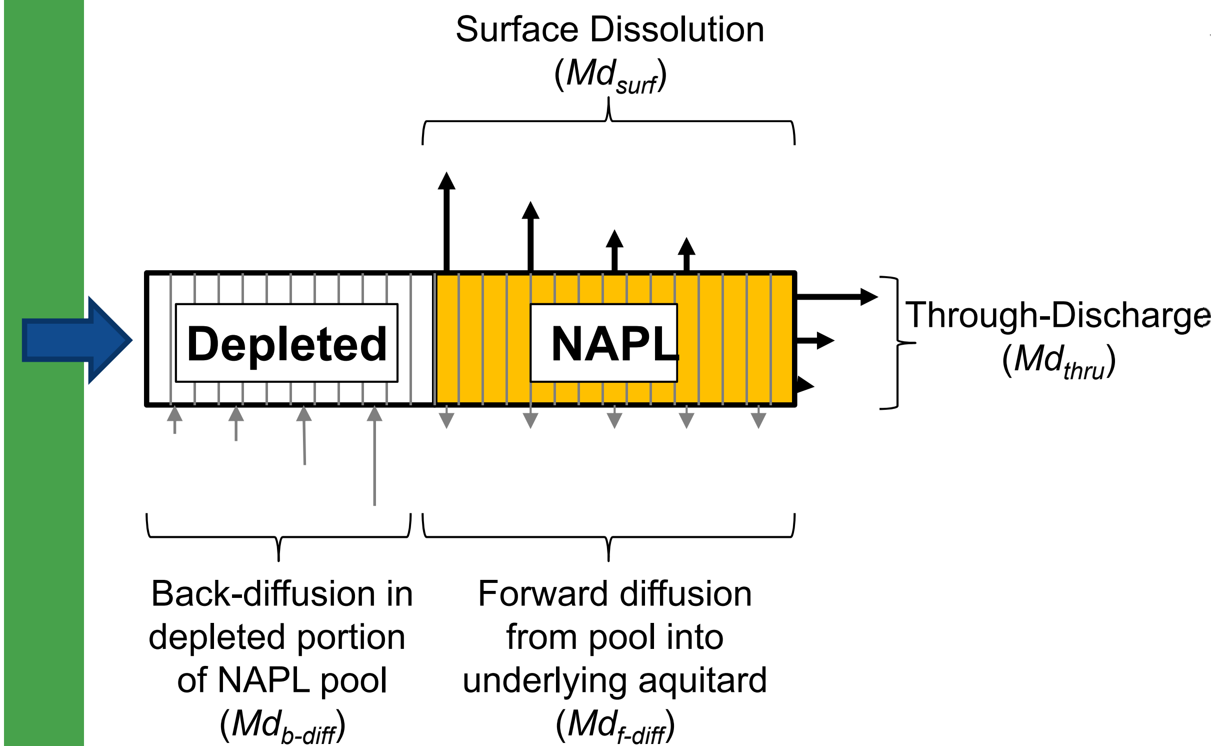
NAPL Depletion Model (NDM): Mass Discharge-Based

Carey et al. (2014a)



Free Software and course:
Email: gcarey@porewater.com
Download: www.porewater.com

NAPL Depletion Model (NDM): Mass Discharge-Based



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

Carey et al. (2016a,c,e)

Model Validation Goals

1. DNAPL mass in simplified source zone consistent with Chapman and Parker (2005).
2. Simulate Initial (1994) Mass discharge – estimated to be 360 to 720 kg/y.
3. Predicted mass discharge decline half-life – estimated to be about 10 years (Chapman and Parker, 2005).

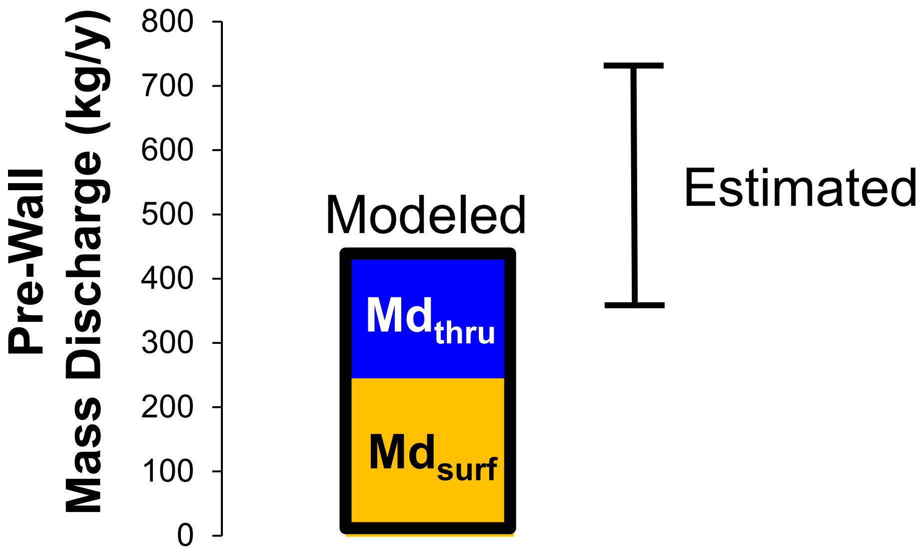
NDM Simulation Results

Simulated DNAPL mass = 4,250 kg

- Chapman and Parker (2005) estimated 5,000 to 20,000 kg
- Our simplified source zone ignored several large areas with thicker DNAPL
  - Limited contribution to overall mass discharge
  - Simulated DNAPL mass consistent with observed on that basis

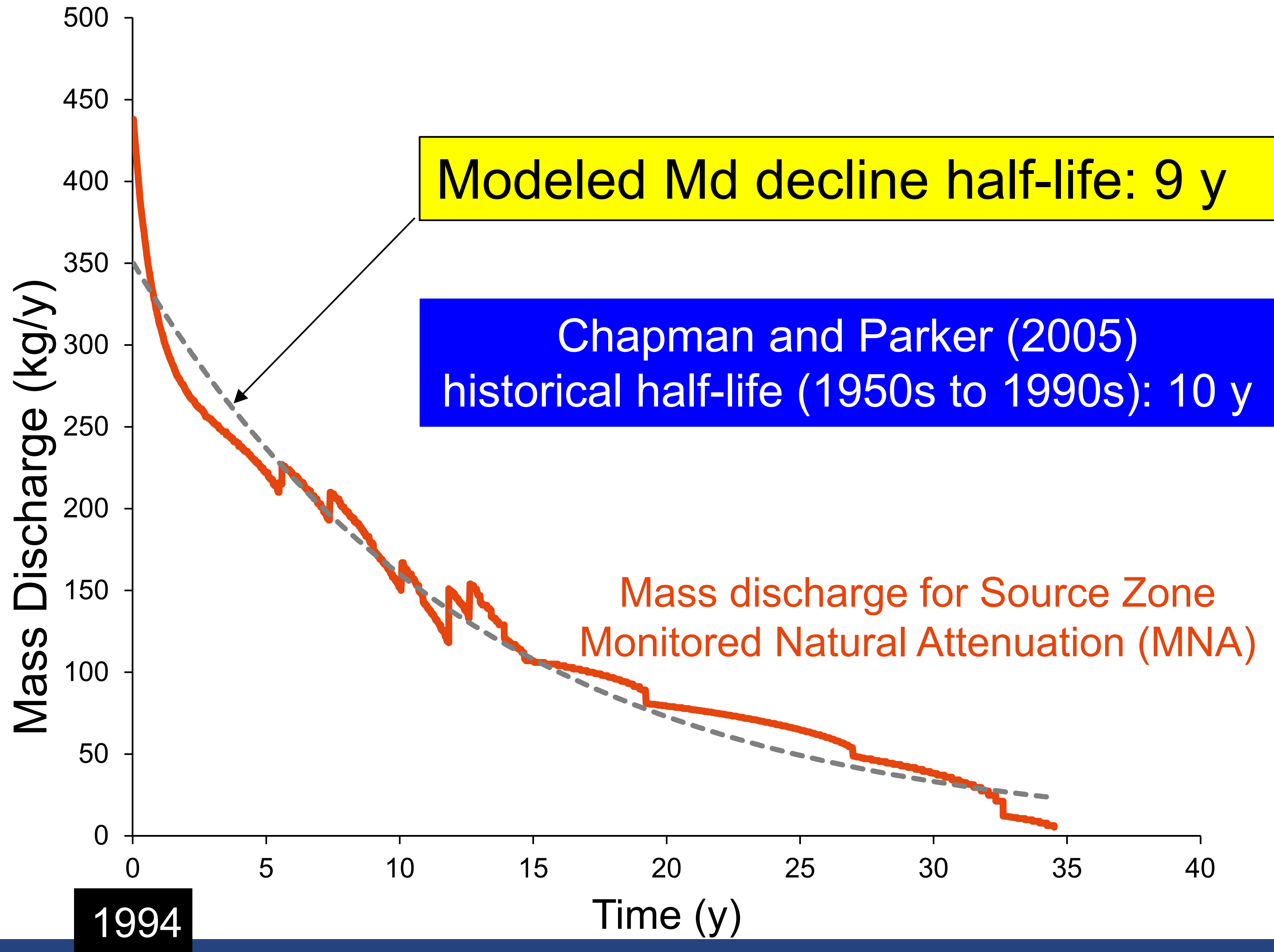
NDM Simulation Results

Simulated 1994 Mass Discharge

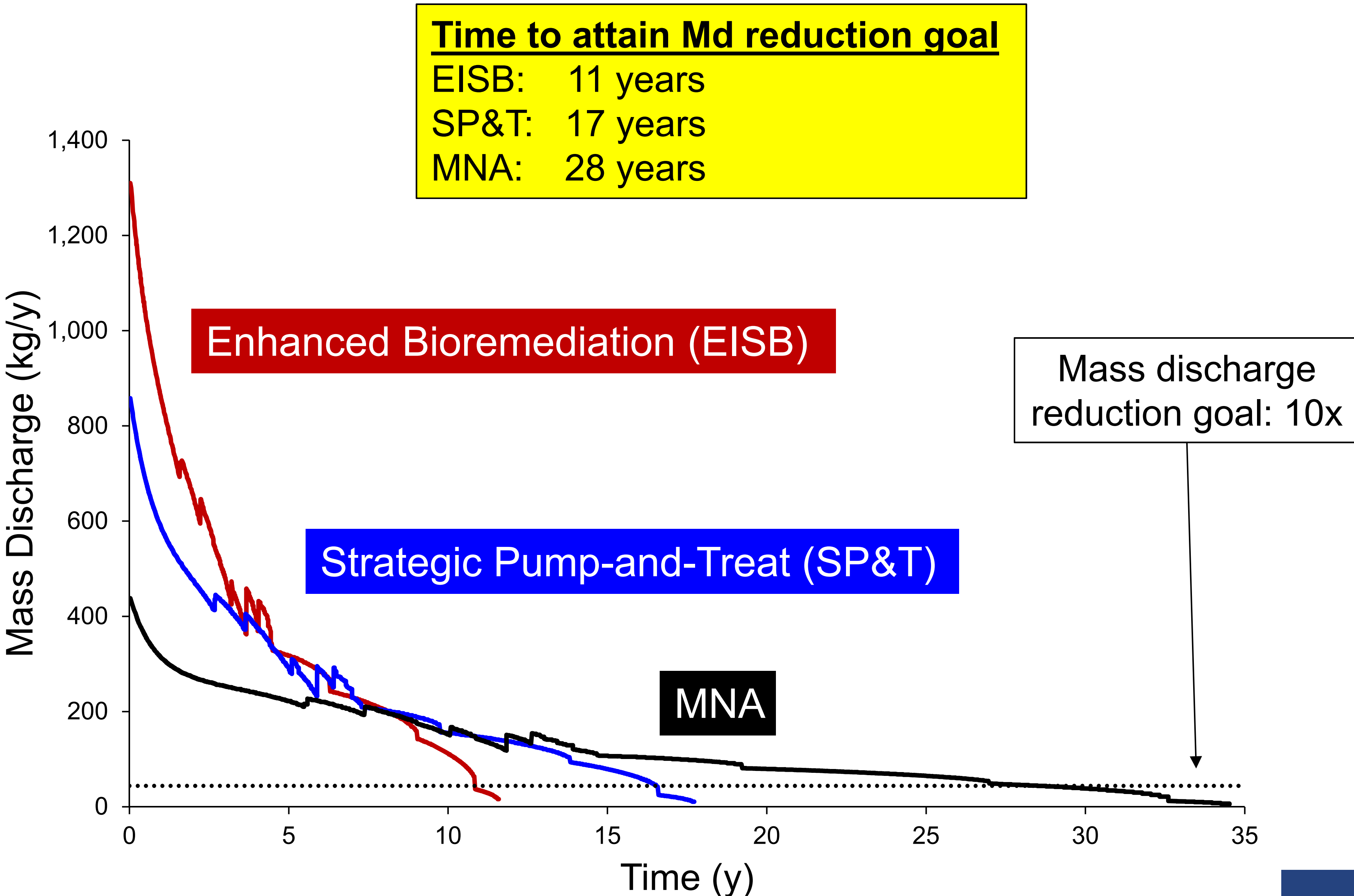


Modeled vs. Estimated Md Half-Life

Md = Mass discharge



Modeled Relative Depletion Timeframes



DNAPL Architecture Sensitivity Analysis

- Varied NAPL architecture and re-ran model – any other scenarios that match **1994 Md** and **half-life**?
  - Length / 2
  - Width / 2
  - Uniform thickness of 4”, 8”, or 1 ft
    - a) All pooled DNAPL; or
    - b) All residual DNAPL
  - Zero flux through all DNAPL sub-zones
  - Type 1 – residual zone is suspended above pool.
- No other scenarios matched **both** observations.
  - Half-life criteria: 10 years +/- 25%

Case Study Summary

1. We can use process-oriented NAPL depletion models when architecture well defined
   - Predict relative timeframes for natural and enhanced dissolution
   - Interpretive tool – improve our understanding
2. When architecture has higher uncertainty but still relatively well understood – may be able to use model as forensic tool
   - Evaluate range of potential architectures
   - Identify data gaps
3. Multiple goals needed to calibrate a NAPL depletion model

Section 4

SUMMARY

Summary

- Mass flux / Mass discharge
  - Improved site understanding, CSM
  - Improved remedial efficiency
  - Pumping well data → easy Md estimates
- NAPL Source Zones
  - Aged sites – mainly NAPL layers remaining
  - Exponential Md decline trends
    - Layer depletion, preferential channeling, weathering
  - Md used to predict interim goals and relative timeframes, focus remedy, monitor performance, etc.

Summary

- Back-diffusion
  - NAPL → Primary source
  - Diss. Mass in silt/clay → Secondary source
    - May extend timeframe by decades to centuries
  - Large area at some sites
    - Plume size >> Primary source zone
  - Site characterization - soil sampling, modeling
- Integrated framework for long-term site management (source + plume)

Questions?

Porewater Solutions
Expertise • Experience • Innovation

Grant Carey
Porewater Solutions

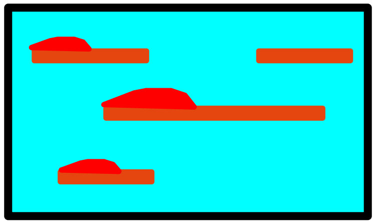
613-270-9458
gcarey@porewater.com
www.porewater.com

Appendix A

CASE STUDY OF BACK-DIFFUSION (FLORIDA)

Modeling Challenges

- Analytical solutions not available for:
  - Thin silt/clay lenses
  - Enhanced degradation rates



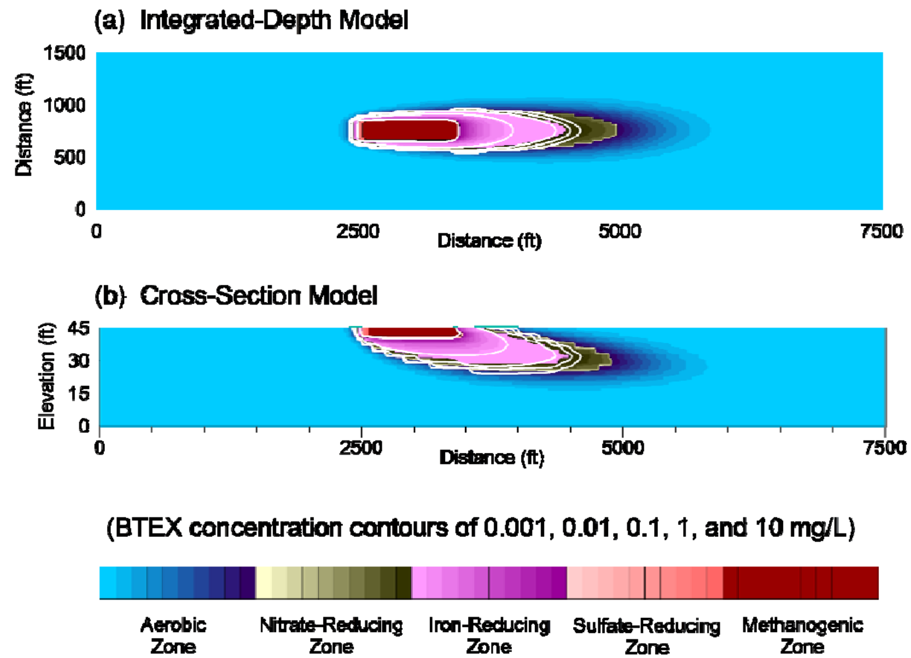
- Numerical models
  - Small grid spacing, time steps
  - Prohibitive for 3-D models
- **ISR-MT3DMS: new approach**

In-Situ Remediation (ISR-MT3DMS)

MT3DMS v5.3

BioRedox RCT package

Public domain – available 2017



- Reactions: **solvents, hydrocarbons, metals**
- **Unique visualization methods**
- Mineral precipitation/dissolution
- Rate stimulation/inhibition

Carey, Van Geel, and Murphy (1999)

In-Situ Remediation (ISR-MT3DMS)

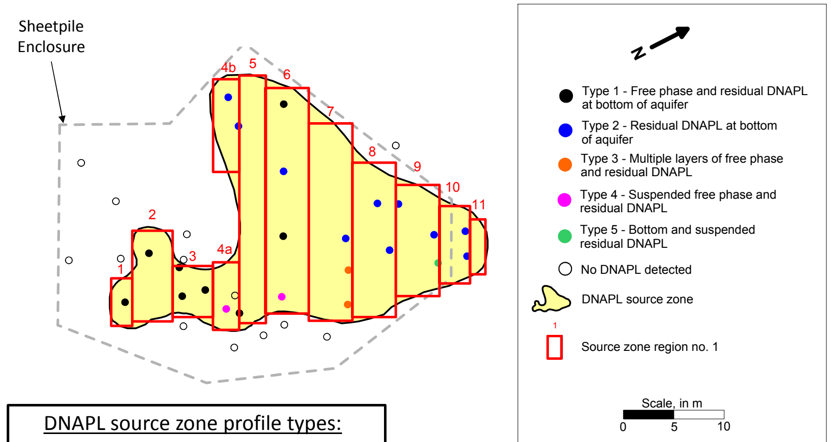
MT3DMS v5.3

BioRedox RCT package

Contact Time Calculator

NAPL Depletion Model

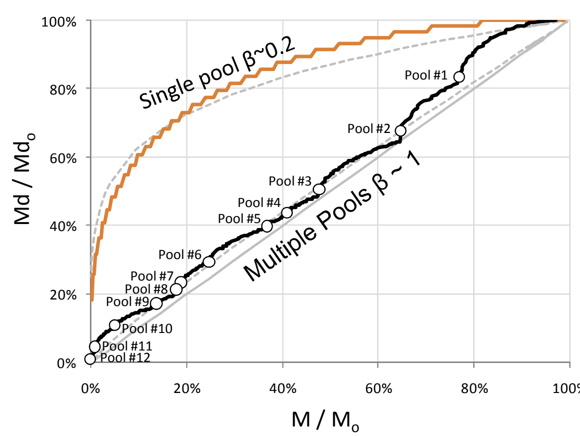
FREE (www.porewater.com)

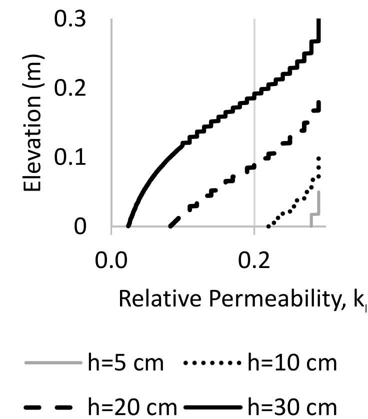


DNAPL source zone profile types:

Type 1		Type 2	
Res.	h=7.5 to 10 cm	Res.	h=10 cm
Pool	h=5 to 7.5 cm		

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





In-Situ Remediation (ISR-MT3DMS)

MT3DMS v5.3

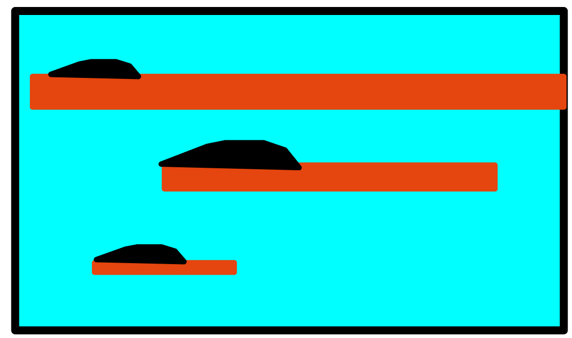
BioRedox RCT package

Contact Time Calculator

NAPL Depletion Model

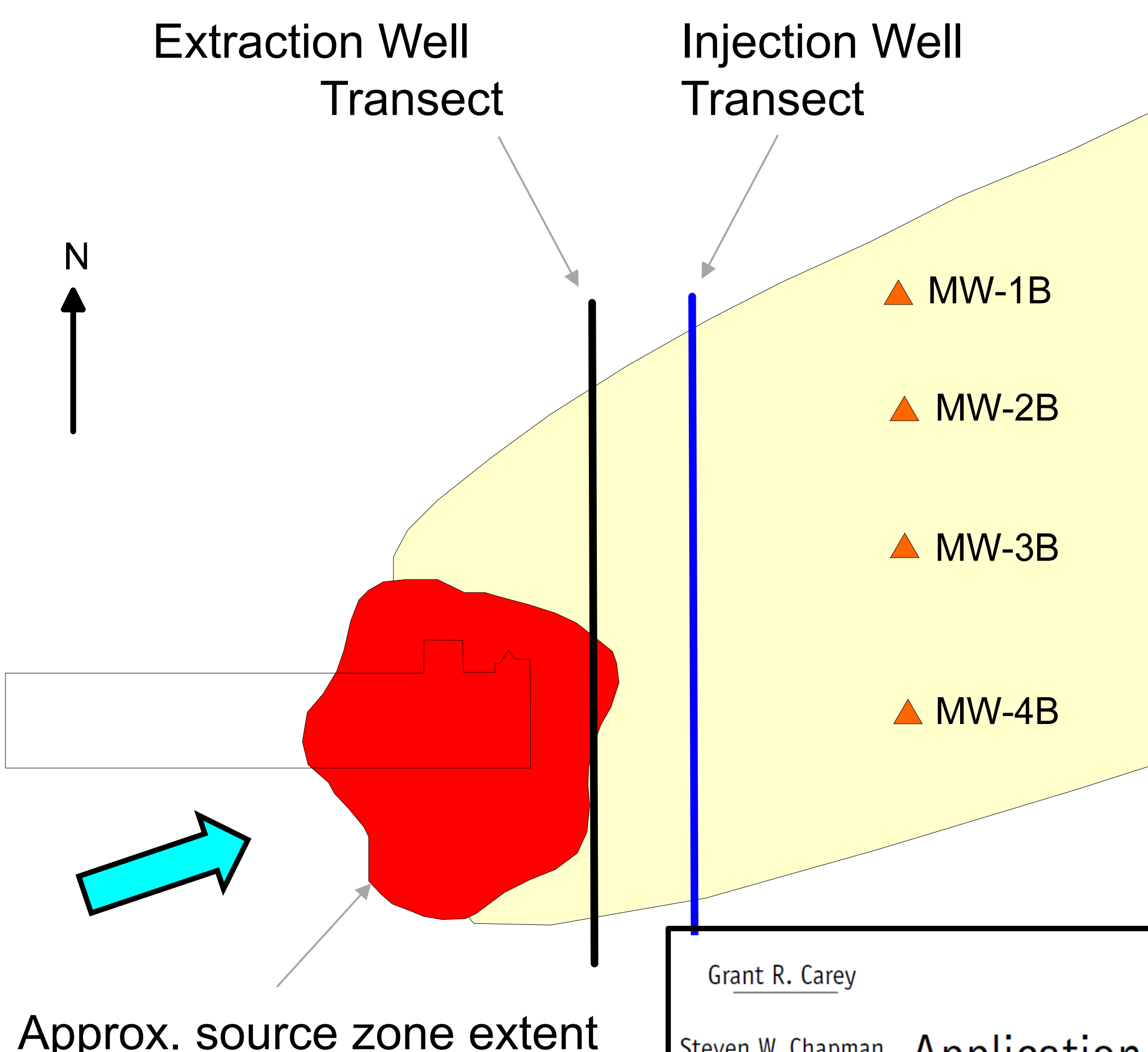
Local Domain Approach

<u>Collaborative research:</u>
- Dr. Brent Sleep (U. of Toronto)



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

Case Study – Florida Site



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

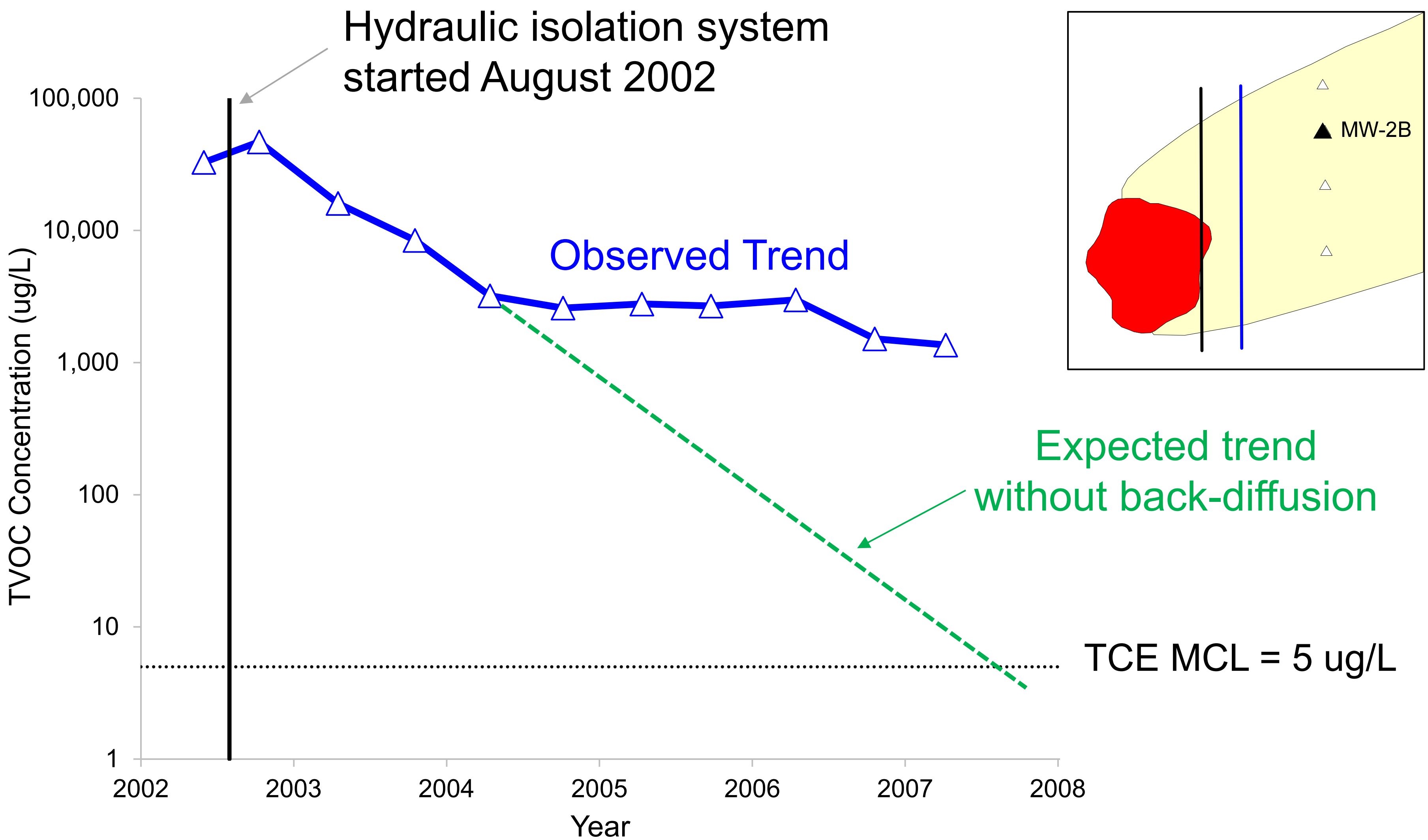
Modified from Parker et al., 2008

REMEDIATION Autumn 2015

Grant R. Carey
Steven W. Chapman
Beth L. Parker
Rick McGregor

Application of an Adapted Version of MT3DMS for Modeling Back-Diffusion Remediation Timeframes

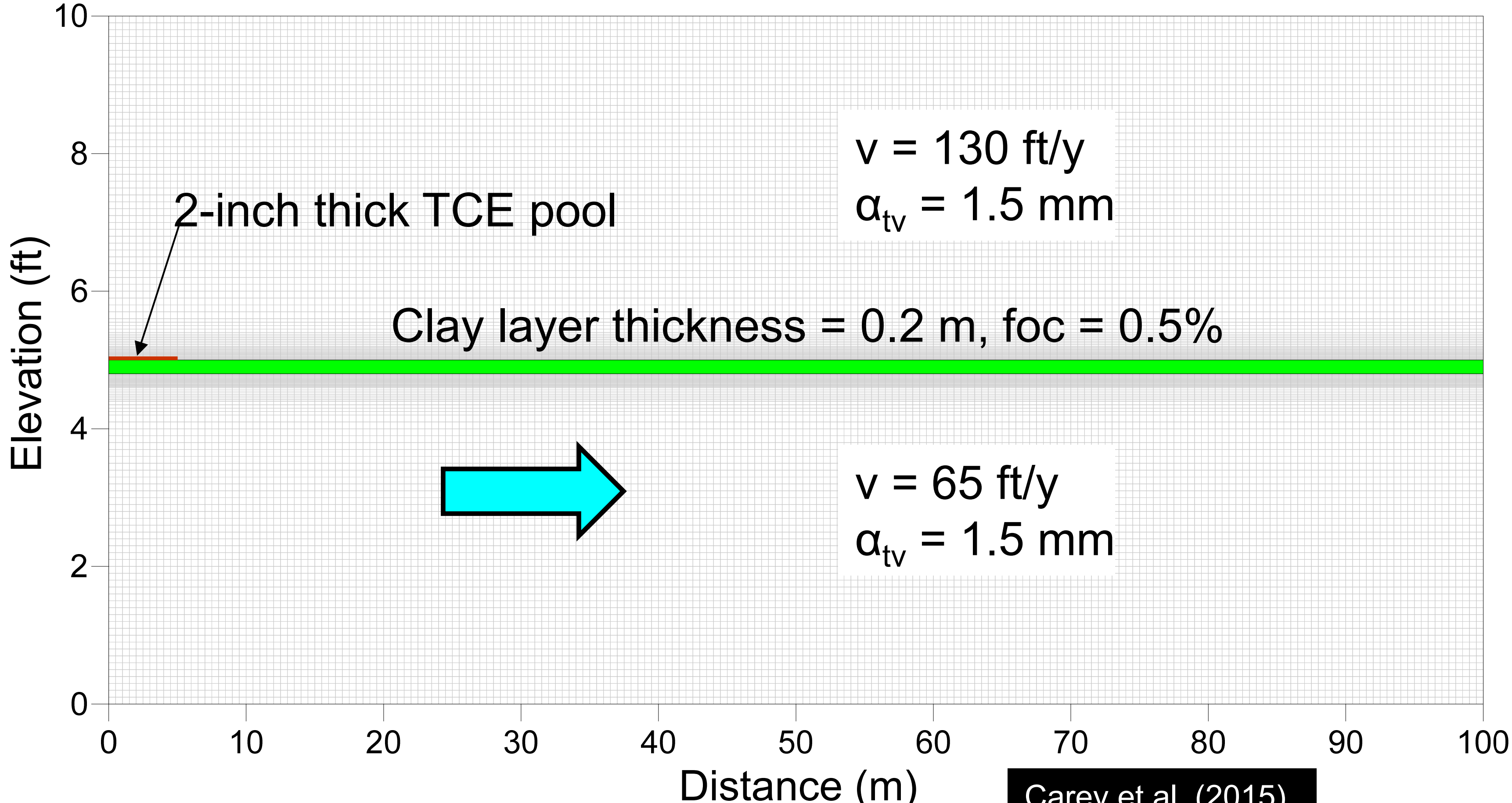
TVOC Trend After Source Containment



Modified from Parker et al., 2008

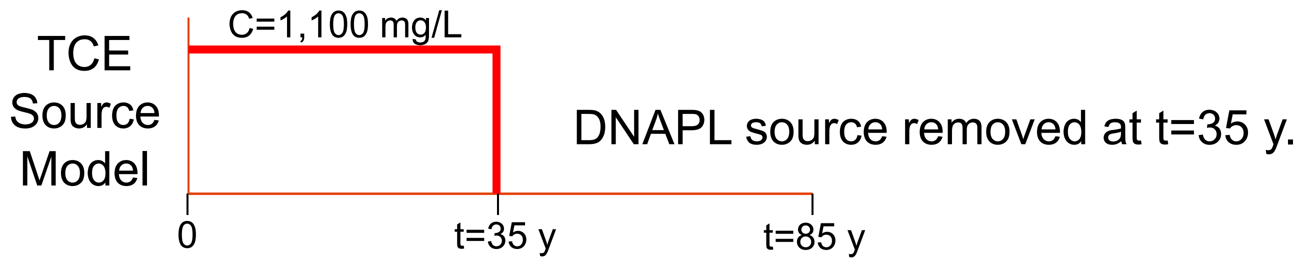
2-D Model Grid

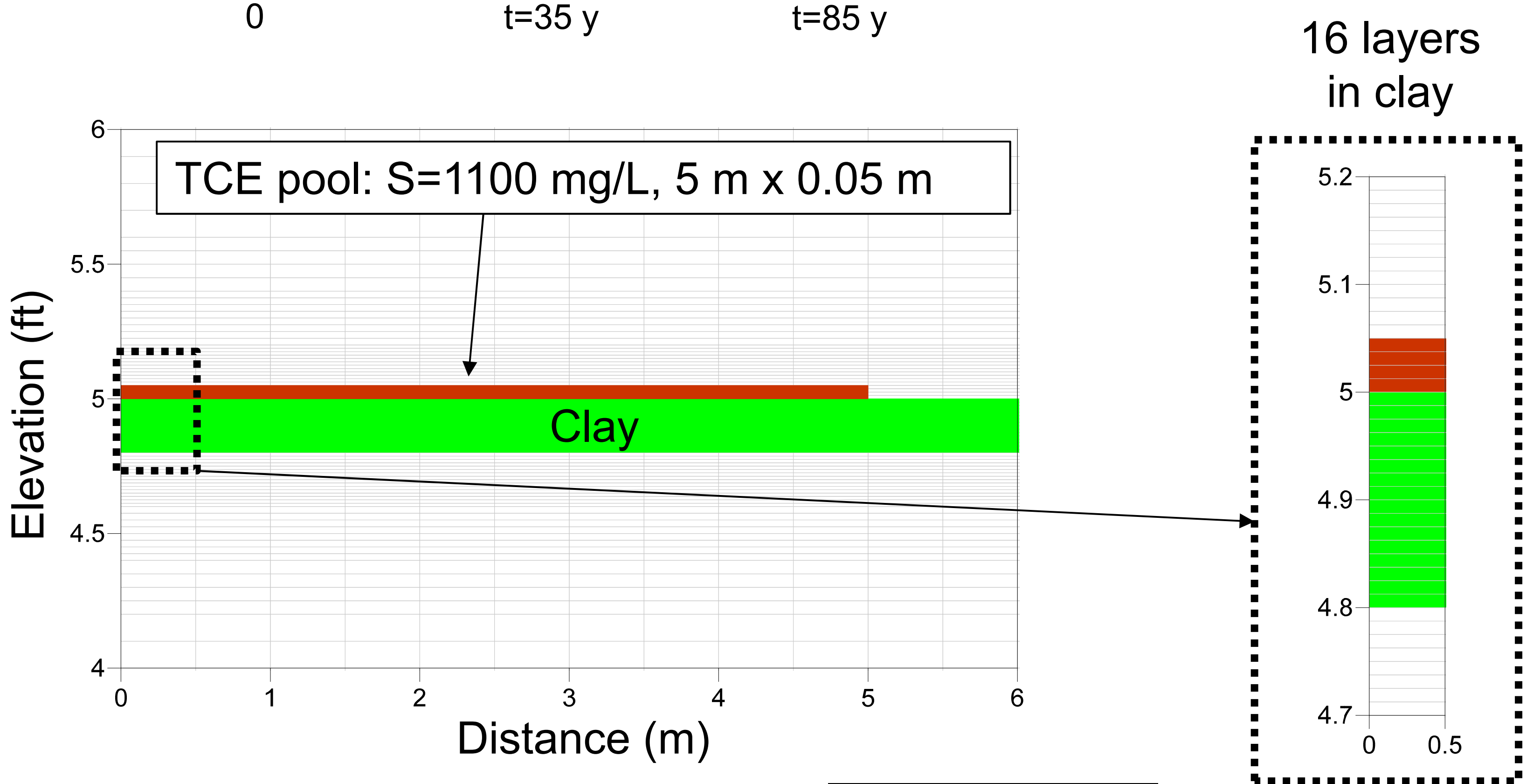
200 columns, 158 rows (layers)
Minimum grid spacing: Δz = 1.25 cm, Δx = 0.5 m
Run-time = 45 minutes for 85-y simulation (Δt = 0.24 d)



Carey et al. (2015)

Source Characteristics

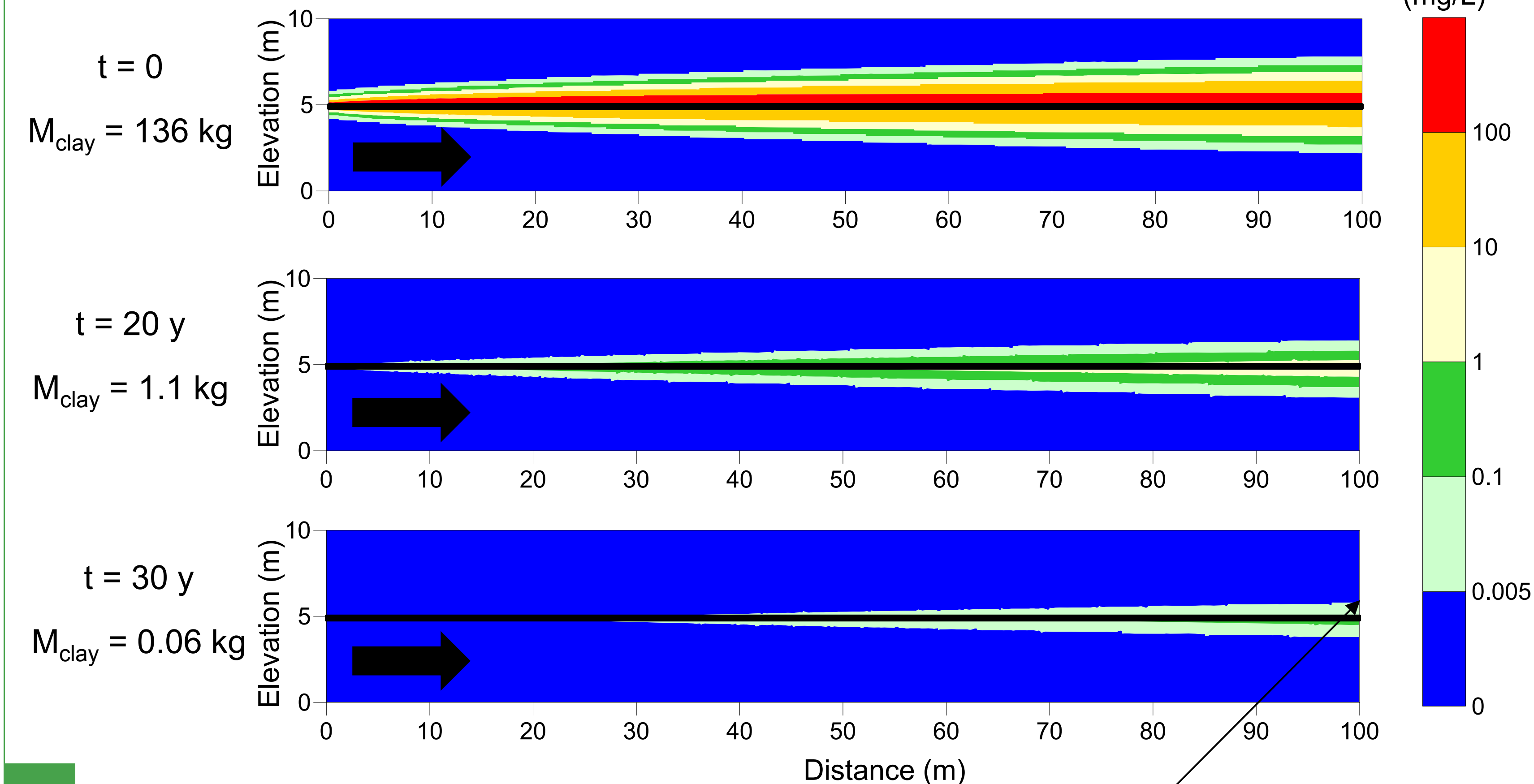




Carey et al. (2015)

Simulated TCE After Source Removal

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

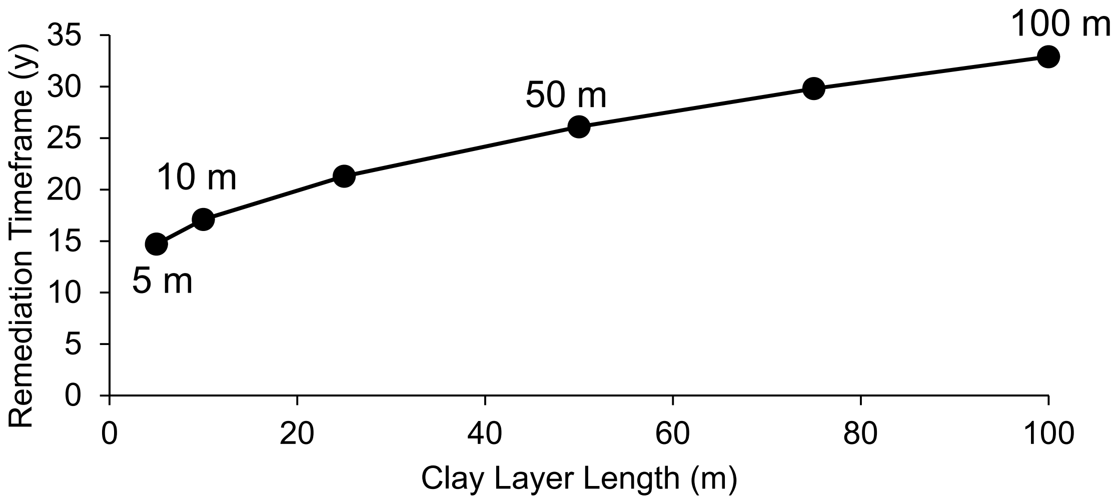


30 years after source removal:
99.96% mass depletion in clay, avg. C_{well} = 12 to 126 ug/L

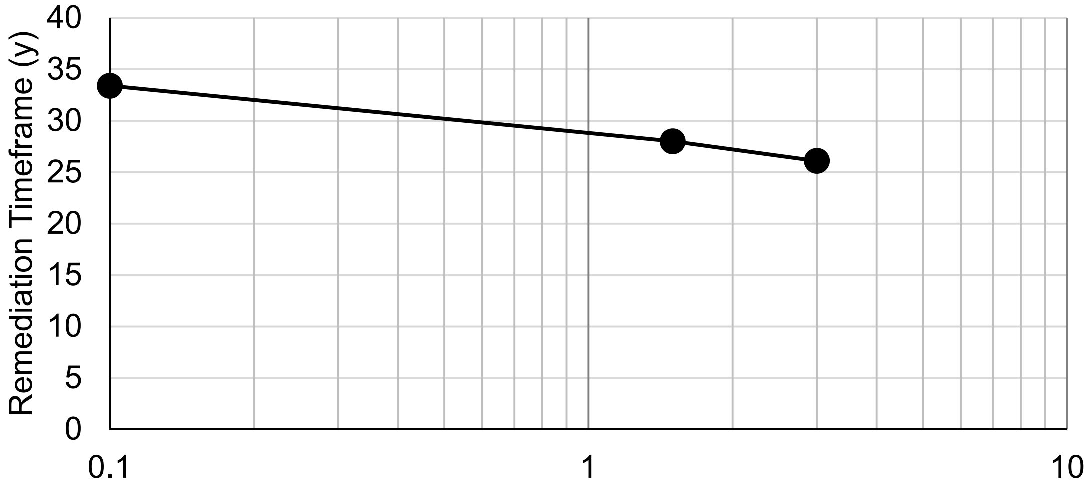
Carey et al. (2015)

Remediation Timeframe Sensitivity Analysis

(a) RTF vs. clay length
(Well screen=3 m)

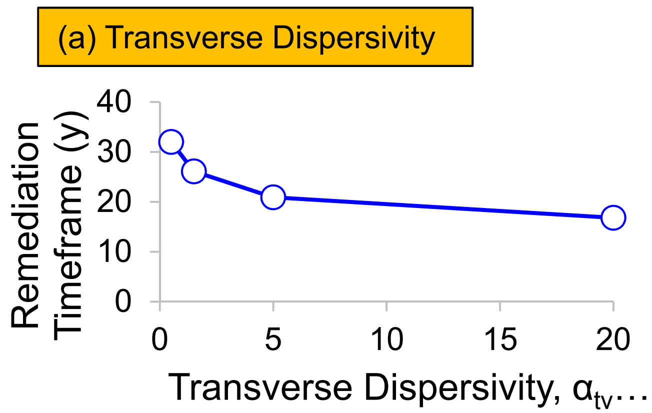


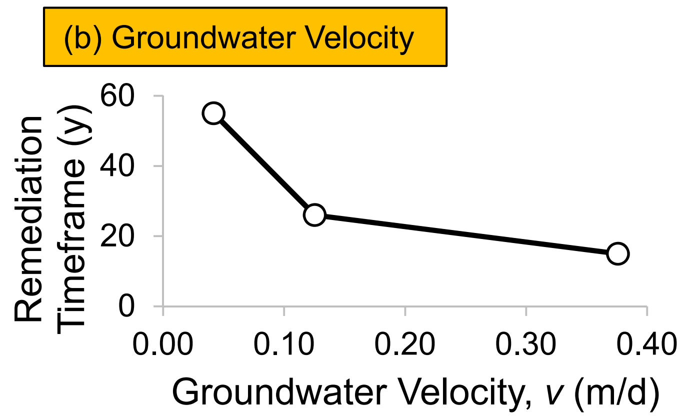
(b) RTF vs. screen length
(x = 50 m)



Carey et al. (2015)

Remediation Timeframe Sensitivity Analysis

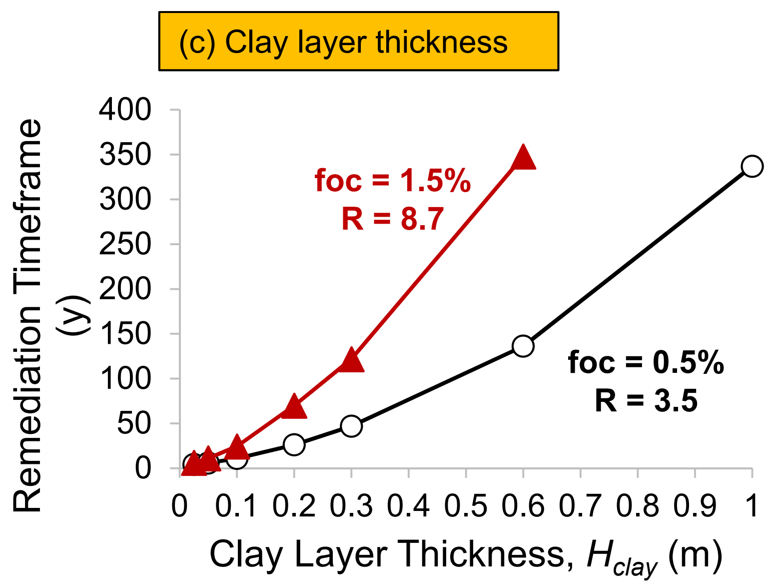


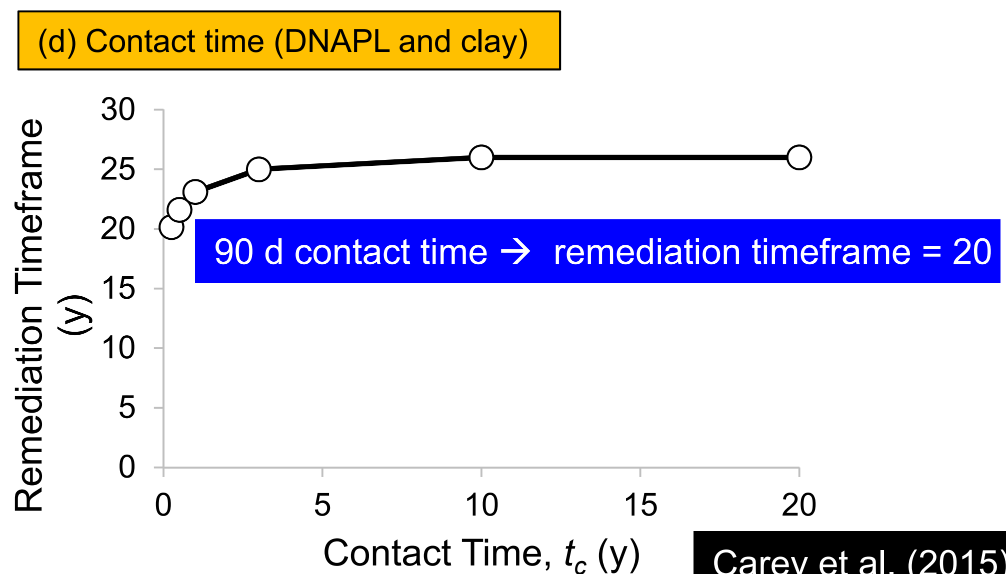


x = 50 m

L_{screen} = 3 m

H_{clay} = 0.2 m

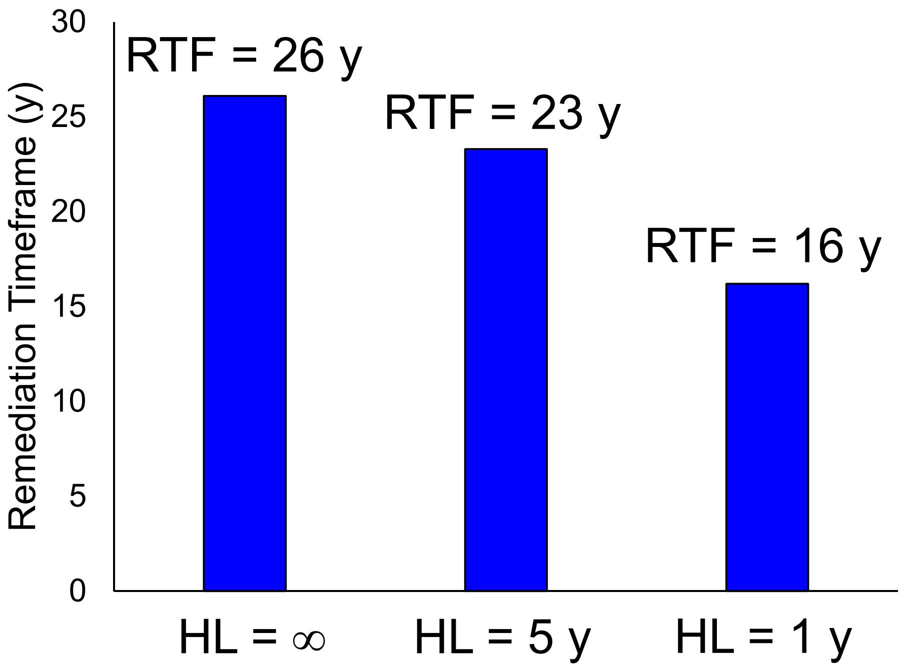




Carey et al. (2015)

Remediation Timeframe Sensitivity Analysis

a) Biodegradation Half-life in Clay Layer

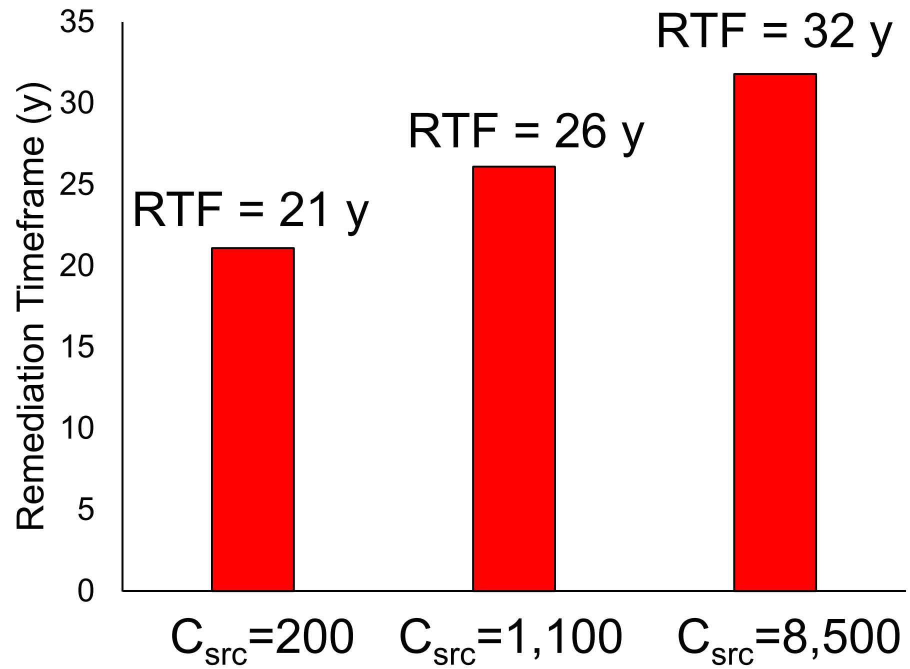


x = 50 m

L_{screen} = 3 m

H_{clay} = 0.2 m

b) Source Concentration (mg/L)

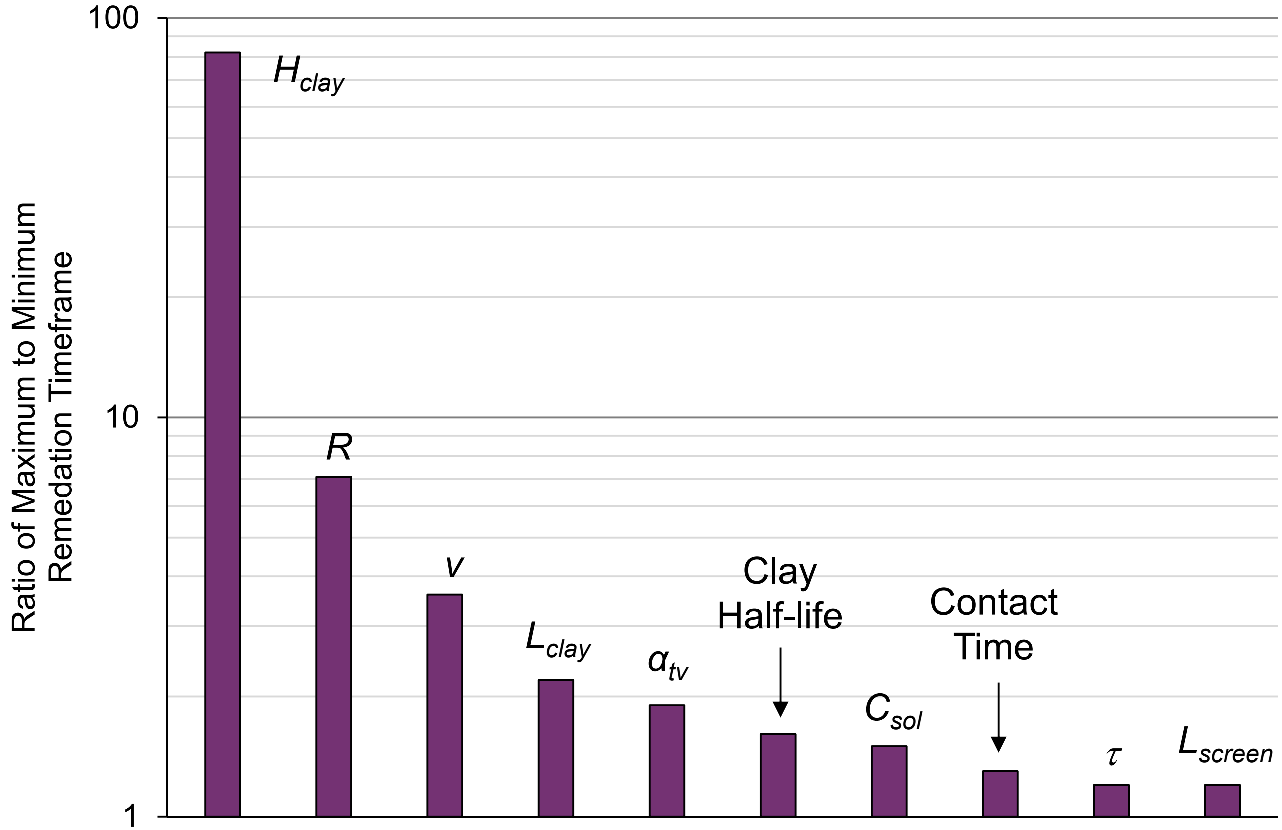


Note: K_d uniform

Source conc. increase: >4,000%
Timeframe increase: 50%

Carey et al. (2015)

Remediation Timeframe Sensitivity Analysis



H_{clay} = silt/clay layer thickness

R = retardation coefficient

v = groundwater velocity

L_{clay} = silt/clay layer length

α_{TV} = transverse dispersivity

Half-life → biodegradation

C_{sol} = solubility

Contact time – between NAPL and silt/clay

τ = tortuosity coefficient

L_{screen} = well screen length

Florida Site Conclusions

- **Characteristics with largest influence:**
  - Low-K layer thickness
  - Retardation coefficient (f_{oc})
  - Groundwater velocity

f_{oc} is critical for:

1. Mass stored in silt/clay
2. Soil → GW concerntrations

- **Characteristics with moderate sensitivity:**
  - α_{TV}, silt/clay length, biodegradation half-life

- **Back-diffusion timeframe least sensitive to:**
  - Solubility, NAPL contact time, τ, well screen length

Appendix B

CASE STUDY OF LNAPL DEPLETION MODEL (GERMANY)

Modeling LNAPL Depletion at a Former Xylene Processing Facility (Germany)

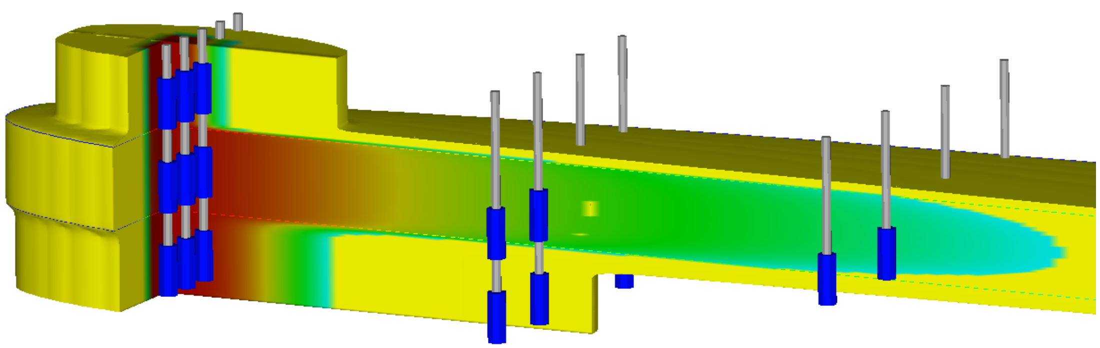
Originally presented at CleanUp 2015 (Melbourne, Australia)

by Grant R. Carey, Ph.D.

Porewater Solutions

Ottawa, Ontario, Canada

www.porewater.com gcarey@porewater.com



LNAPL Depletion Modeling

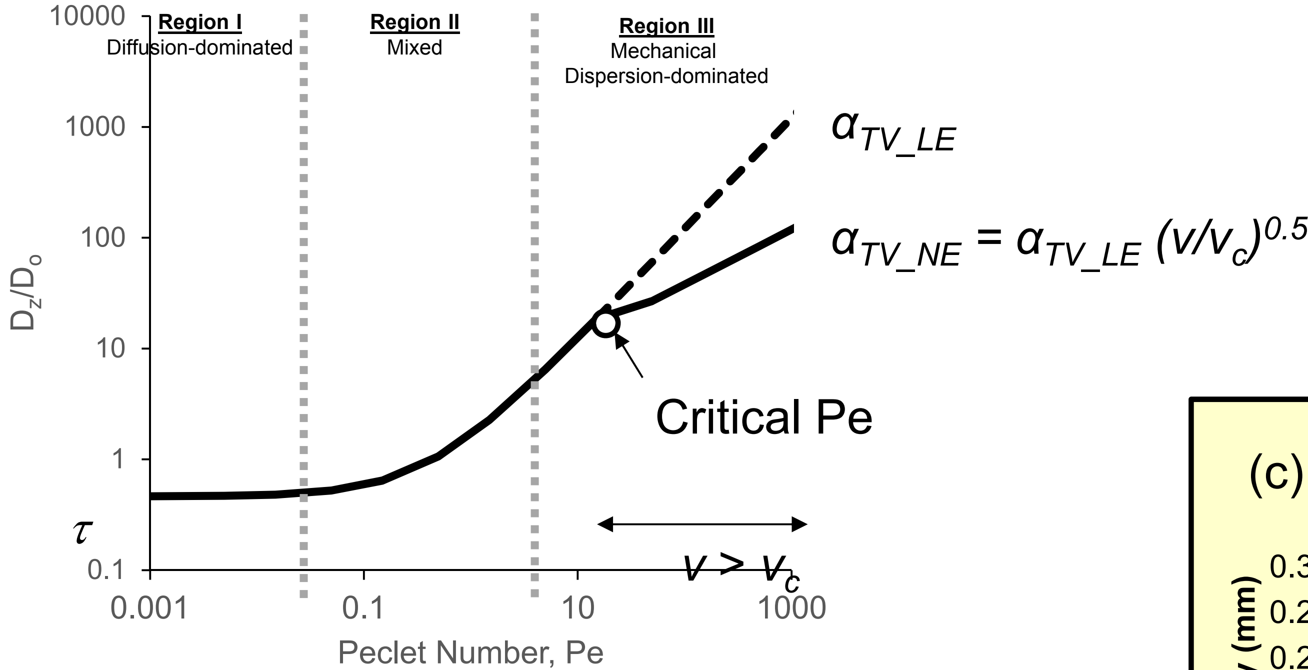
Through-Discharge, Md_{thru} based on average velocity at downgradient boundary (v_{DG_Bdy})

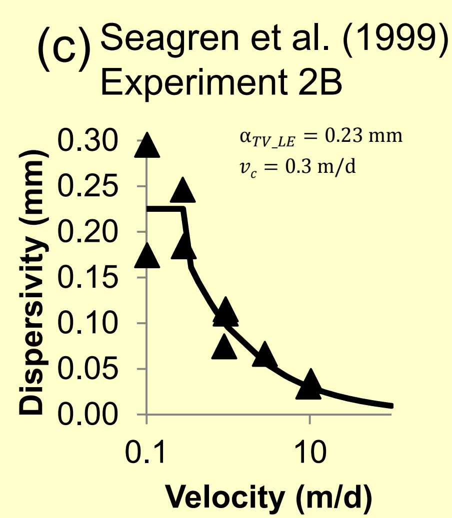
Surface Discharge, Md_{surf} based on average velocity across bottom surface area (v_{bot})

- **Model Uses**
  - Timeframe
  - Confirm CSM
  - Identify data gaps
  - Regulatory negotiations
- **Critical field properties**
  - LNAPL thickness
  - Transverse dispersivity
- **Case study example**

Transverse Vertical Dispersivity

Carey et al. (2016c)

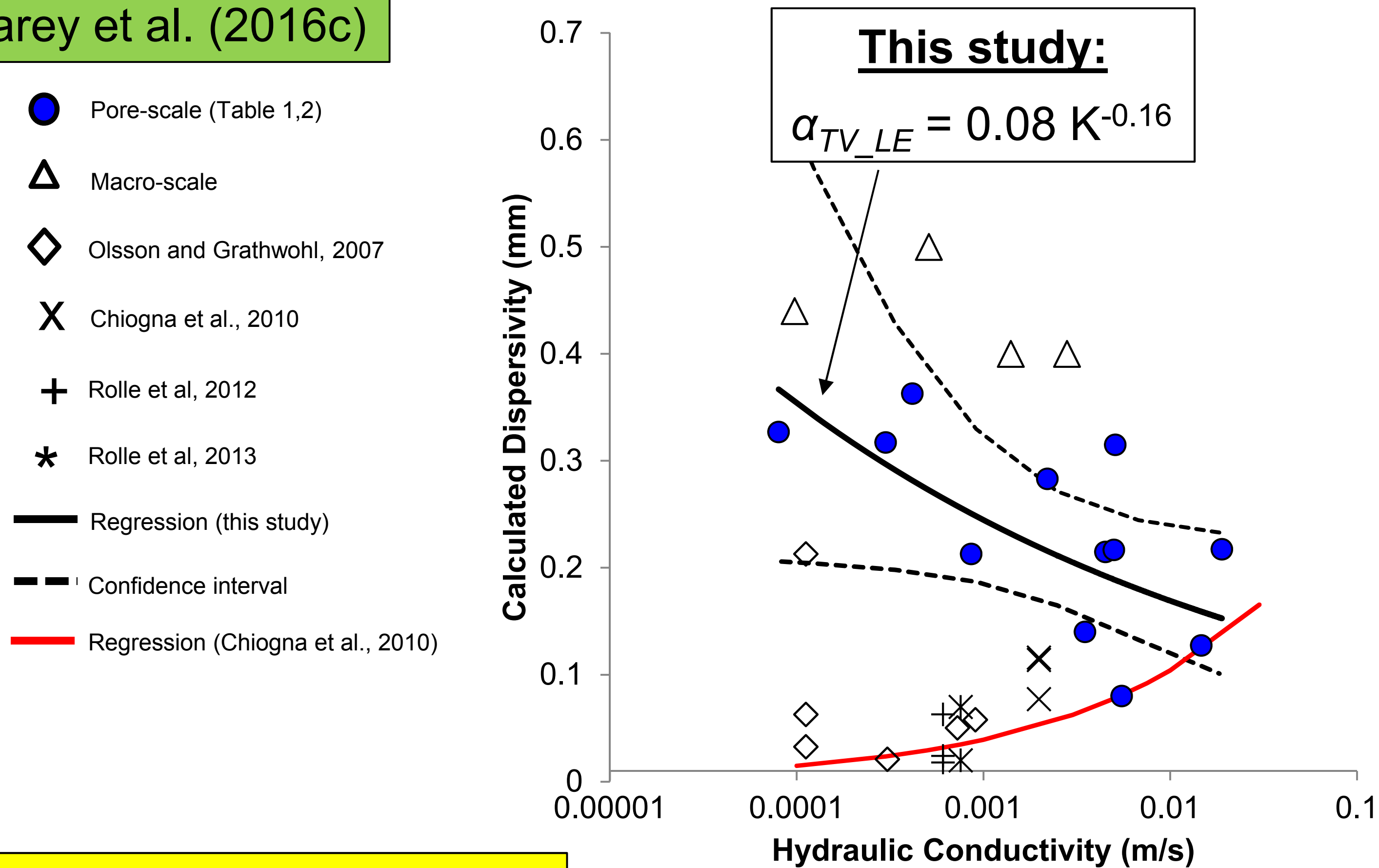




v_c ~ 3 to 5 m/d for pool dissolution

Transverse Vertical Dispersivity (LE) vs. K

Carey et al. (2016c)

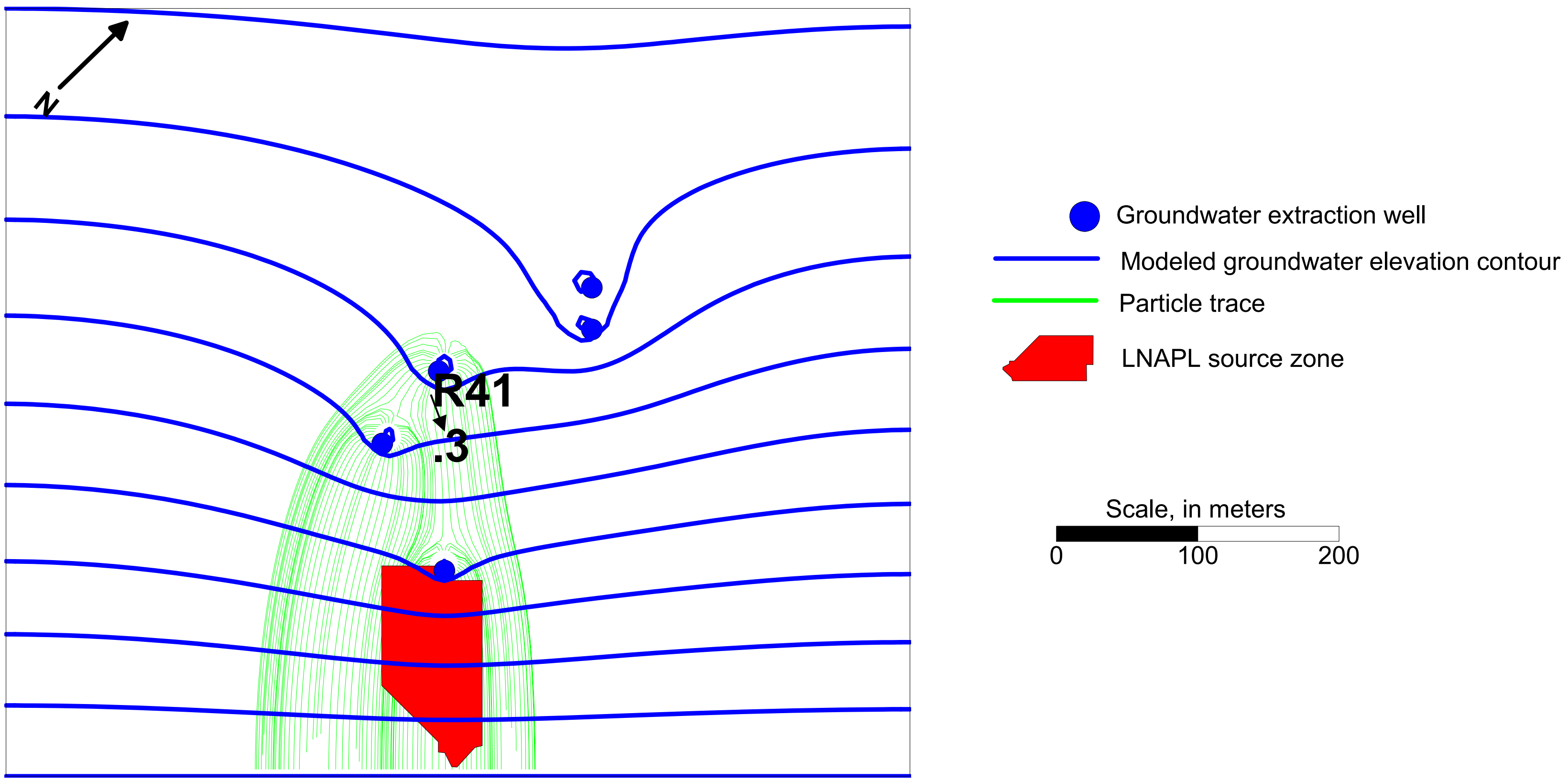


K = 0.2 cm/s

Schafer & Therrien: α_{TV_LE} = 10 mm
Small-scale: α_{TV_LE} = 0.22 mm
Larger-scale: α_{TV_LE} = 0.4 mm

Former Xylene Processing Facility (Germany)

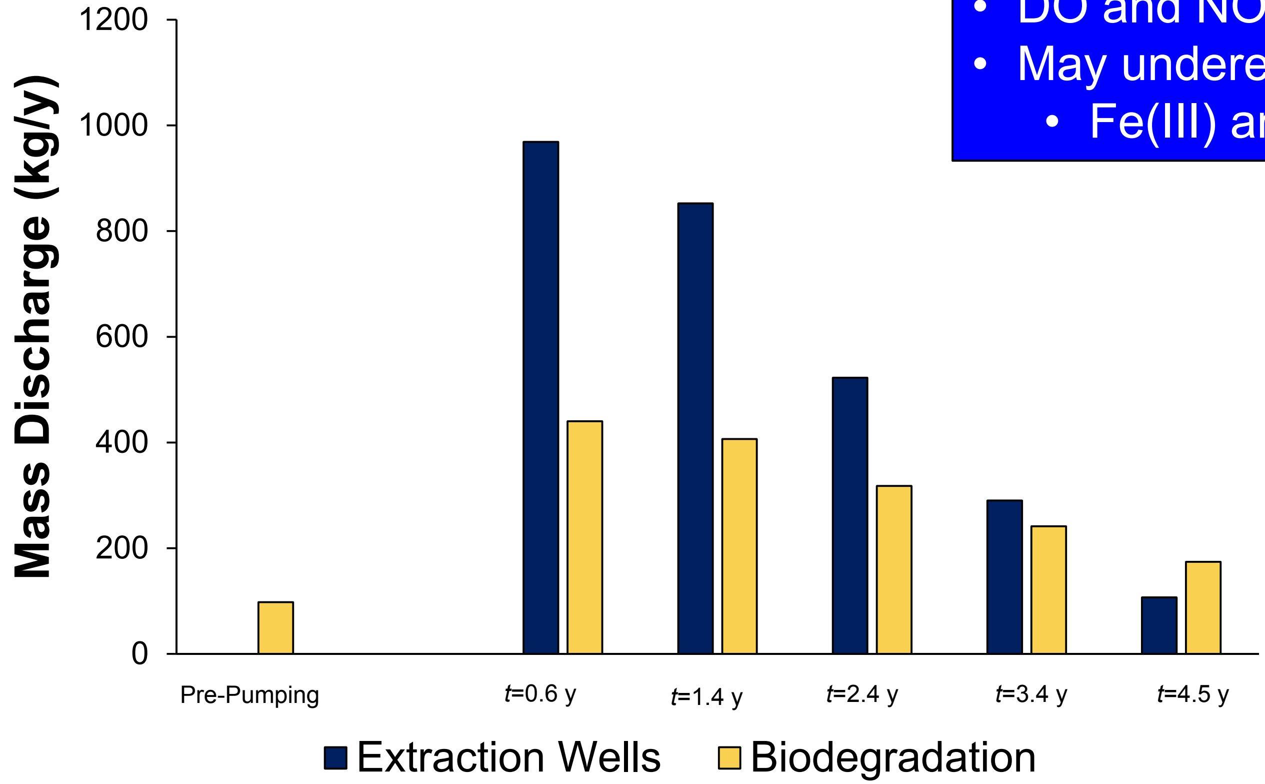
Modified from Schafer and Therrien (1995)



Estimated Mass Discharge Based on Schafer and Therrien (1995)

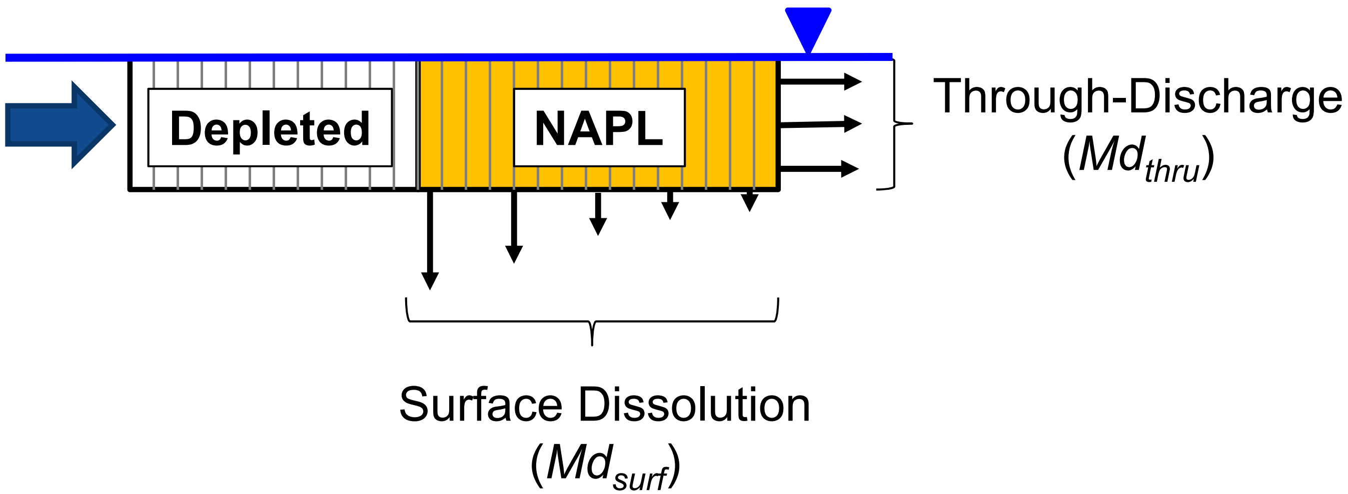
Modified from Schafer and Therrien (1995)

Modeled xylene biodegradation
- DO and NO3 reduction only
- May underestimate actual by 2x
  - Fe(III) and SO4 reduction



NAPL Depletion Model (NDM): Sub-zone Mass Discharge

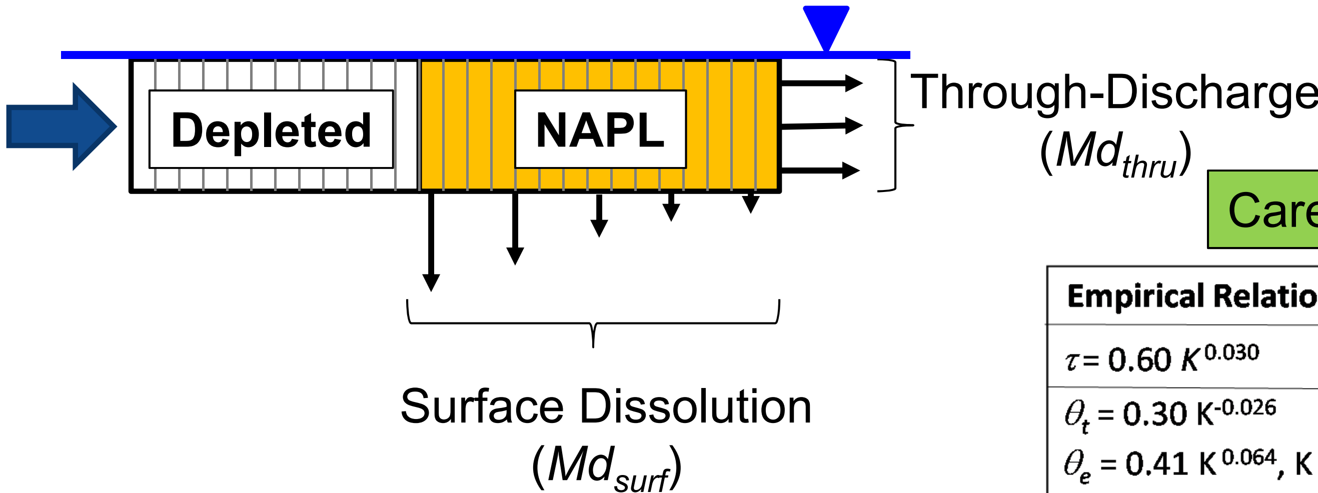
Carey et al. (2014a)



Free Software:
Email: gcarey@porewater.com
Download after Sep. 30th: www.porewater.com

NAPL Depletion Model (NDM): Sub-zone Mass Discharge

Carey et al. (2014a)

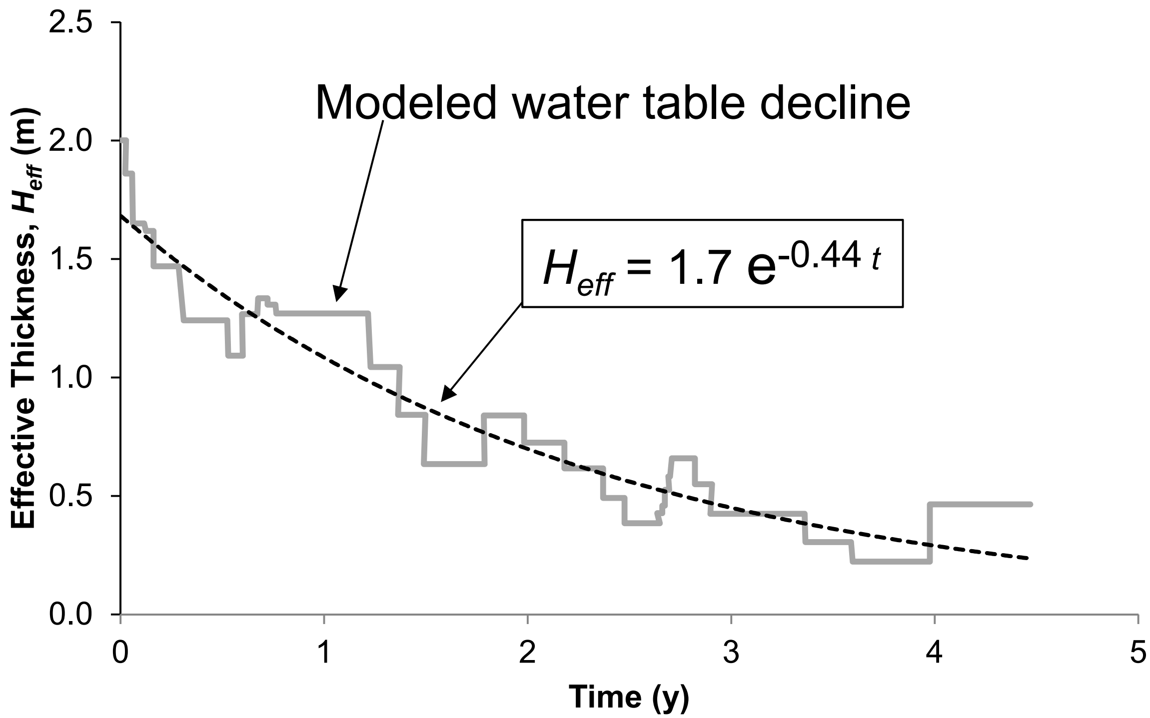


Carey et al. (2016a,c,e)

Empirical Relationship (*K* in m/s)	
$\tau = 0.60\ K^{0.030}$	(i)
$\theta_t = 0.30\ K^{-0.026}$	(ii)
$\theta_e = 0.41\ K^{0.064}$, $K \le 1\text{x}10^{-2}$ m/s	(iii)
$\theta_e = (0.29\ K^{-0.026}) - 0.03$, $K > 1\text{x}10^{-2}$ m/s	(iv)
$\alpha_{TV} = 0.08\ K^{-0.16}$, $v \le v_c$	(v)
$\alpha_{TV\_NE} = 0.08\ K^{-0.16}\ (v_c/v)^{0.5}$, $v > v_c$	(vi)
$\alpha_{aw} = 0.112\ (100\ K)^{0.211}$	(vii)
$n = 13.14\ (100\ K)^{0.246}$ $\quad K \ge 1\text{x}10\text{-}4$ m/s	(viii)
$S_{wr} = 0.015\ (100\ K)^{-0.218}$	(ix)

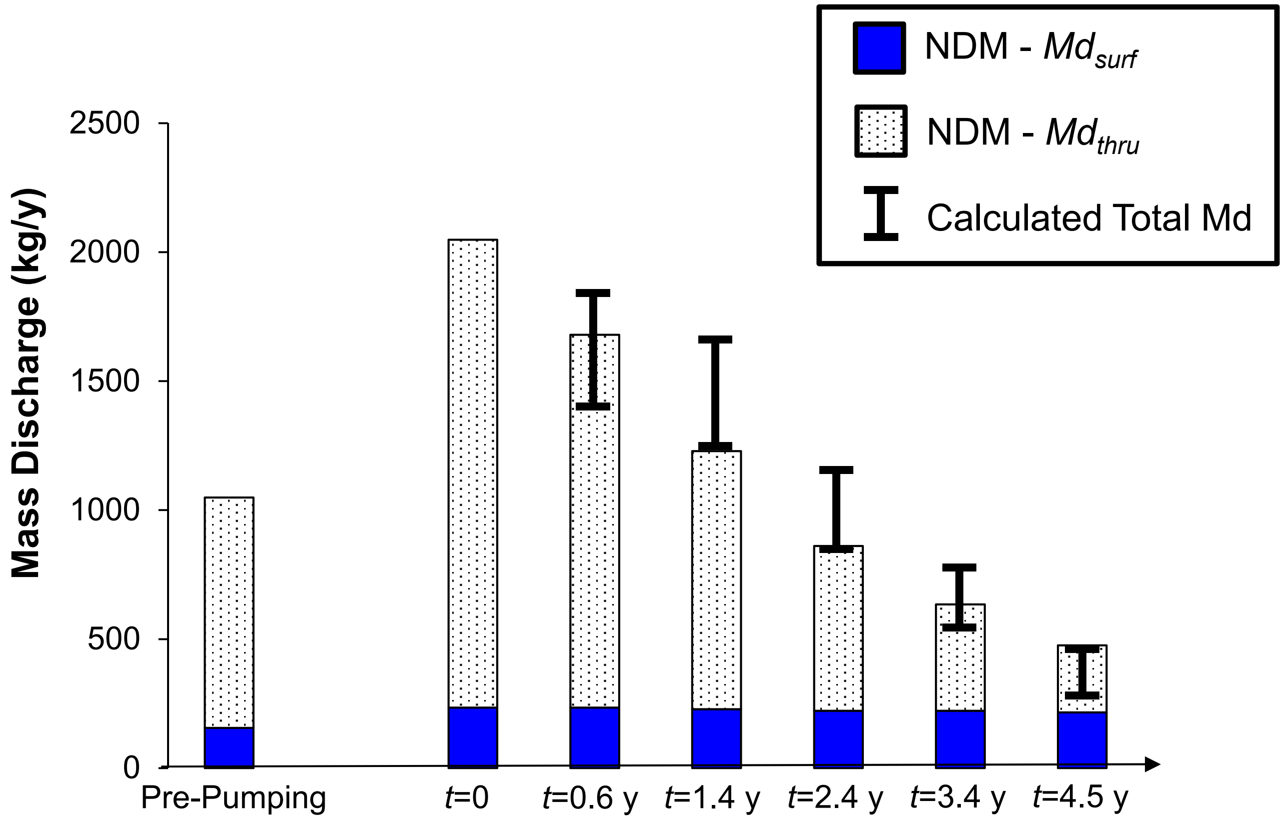
Saturated Source Zone Thickness vs. Time

Modified from Schafer and Therrien (1995)



Note: Effective thickness of the LNAPL source zone was determined based on an assumed source zone bottom elevation of 19.75 m, and the fluctuating water table elevation. t=0 corresponds to May 1, 1988.

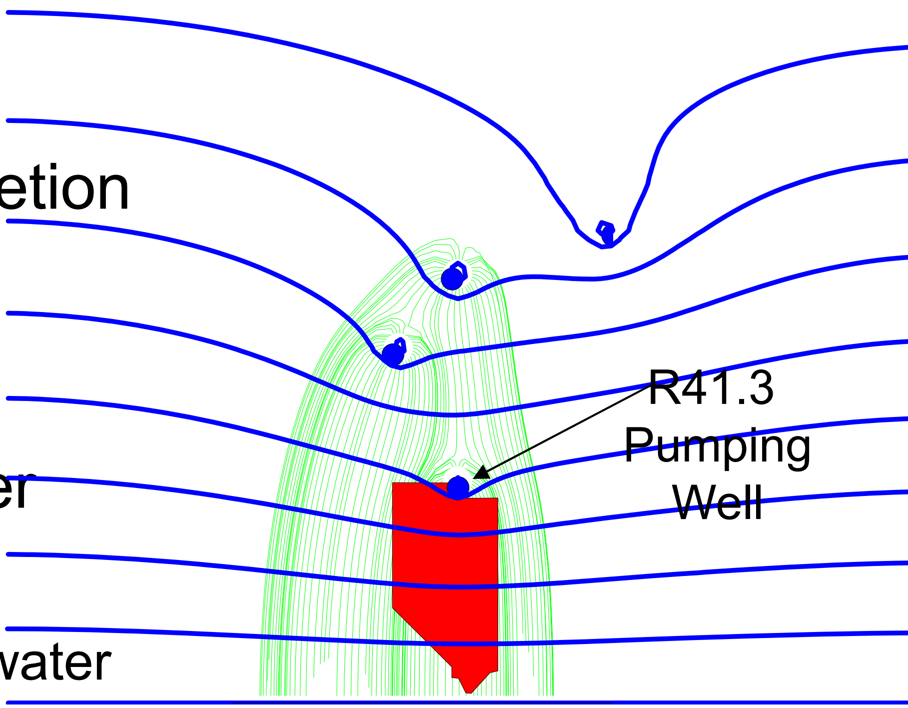
Modeled and Estimated Mass Discharge



Notes:

1. *Groundwater extraction system started at t=0.*
2. *Md = mass discharge.*
3. *Range in calculated total Md is based on the potential difference between including and excluding xylene biodegradation under manganogenesis, ferrogenesis, and sulfate reduction.*

Remediation Timeframe Analysis



Goal

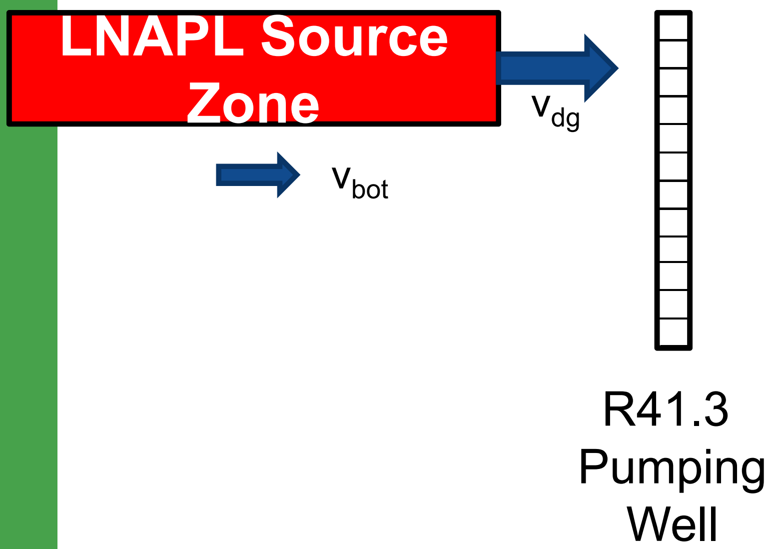
- Evaluate influence of Q on depletion timeframe

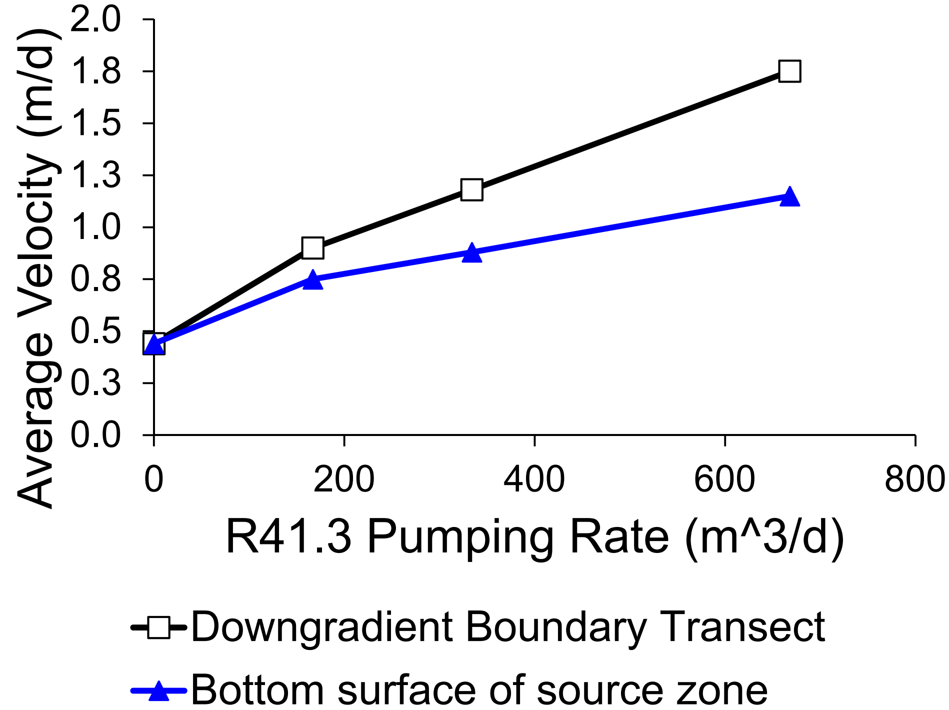
Approach

- Assume constant, average water table elevation
  - Source zone 0.85 m thick below water table
- Evaluate influence of increasing Q on GW velocity
- Model LNAPL depletion for each scenario

Scenarios
Q=0 (MNA)
Qx1 (system design)
R41.3 Qx2
R41.3 Qx4

Velocity vs. Pumping Rate

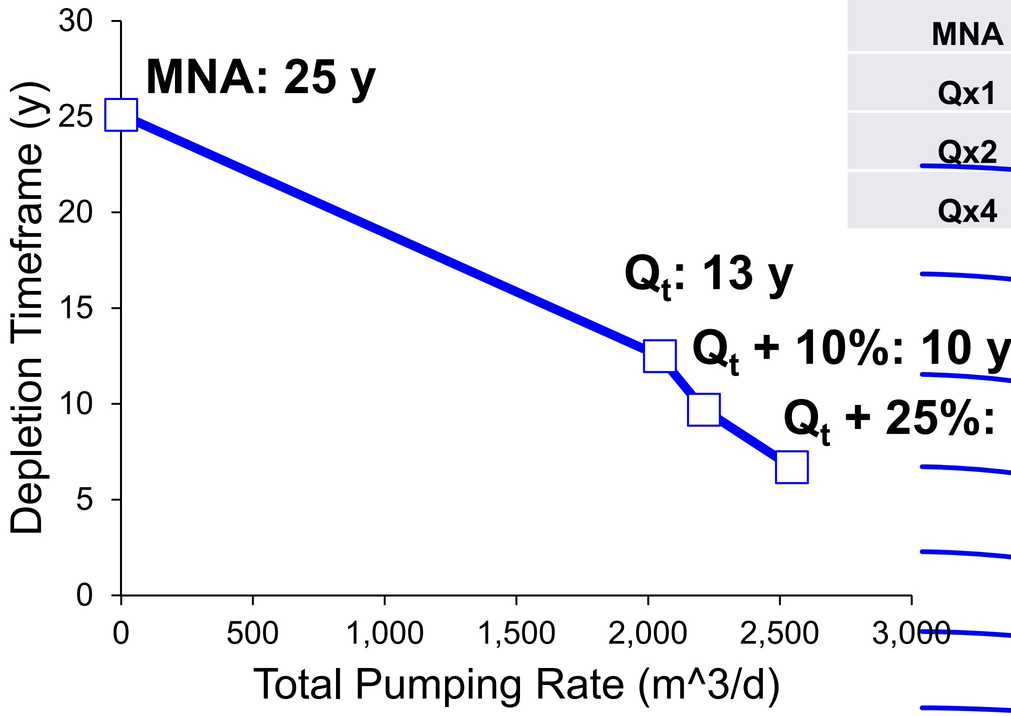




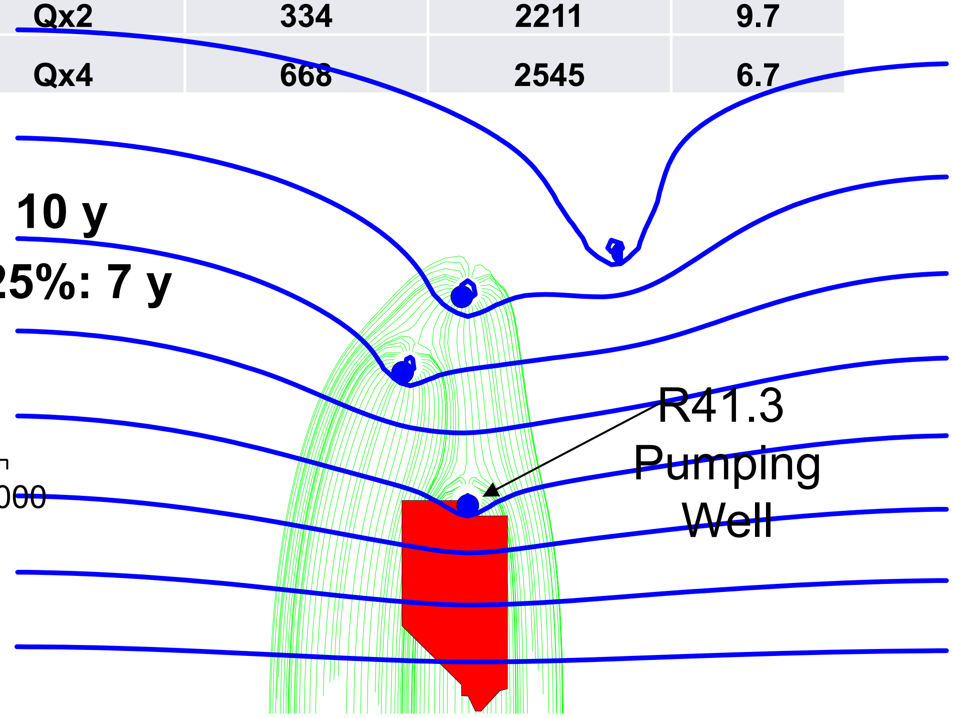
Note: Pumping rates at extraction wells R41.2, R41.4, R41.6, and R41.8 were simulated to be constant for all scenarios where the R41.3 well pumping rate was greater than zero.

Strategic Pump-and-Treat

Q_t = historical average pumping rate



Scenario	R41.3 Pumping Rate (m^3/d)	Combined Pumping Rate (m^3/d)	Remediation Timeframe (y)
MNA	0	0	25.1
Qx1	167	2044	12.5
Qx2	334	2211	9.7
Qx4	668	2545	6.7



Summary

- Transverse dispersivity based on K
- Model matched estimated mass discharge
  - Without any input calibration
- MNA may be appropriate if no receptors at risk
- Increased pumping rate at R41.3
  - Small incremental cost
  - Large reduction in remediation timeframe

Strategic Pump-and-Treat

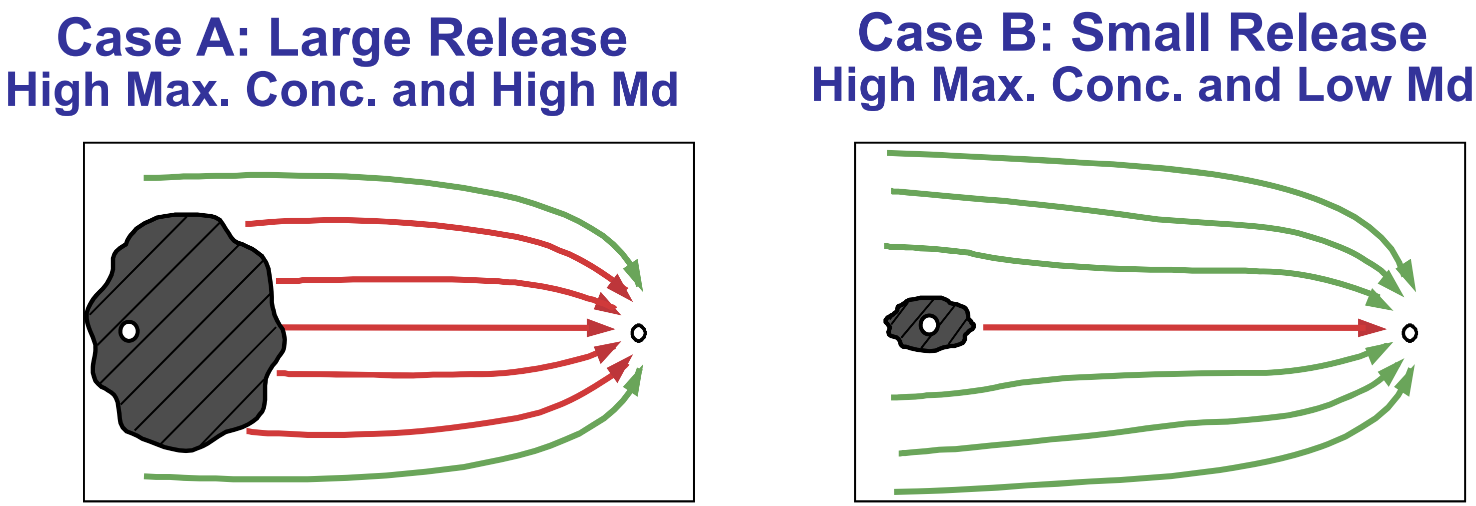
Appendix C

SUPPLEMENTAL SLIDES

Mass Discharge and Concentration

- Concentration-based approach may not account for important site characteristics
  - Large vs. small releases
  - Pumping rate at the receptor well

ITRC, 2016



KEY POINT: **Evaluation of mass discharge (M_d) can increase understanding of site and be an important component of the site conceptual model**

Mass Flux Can Be Highly Variable

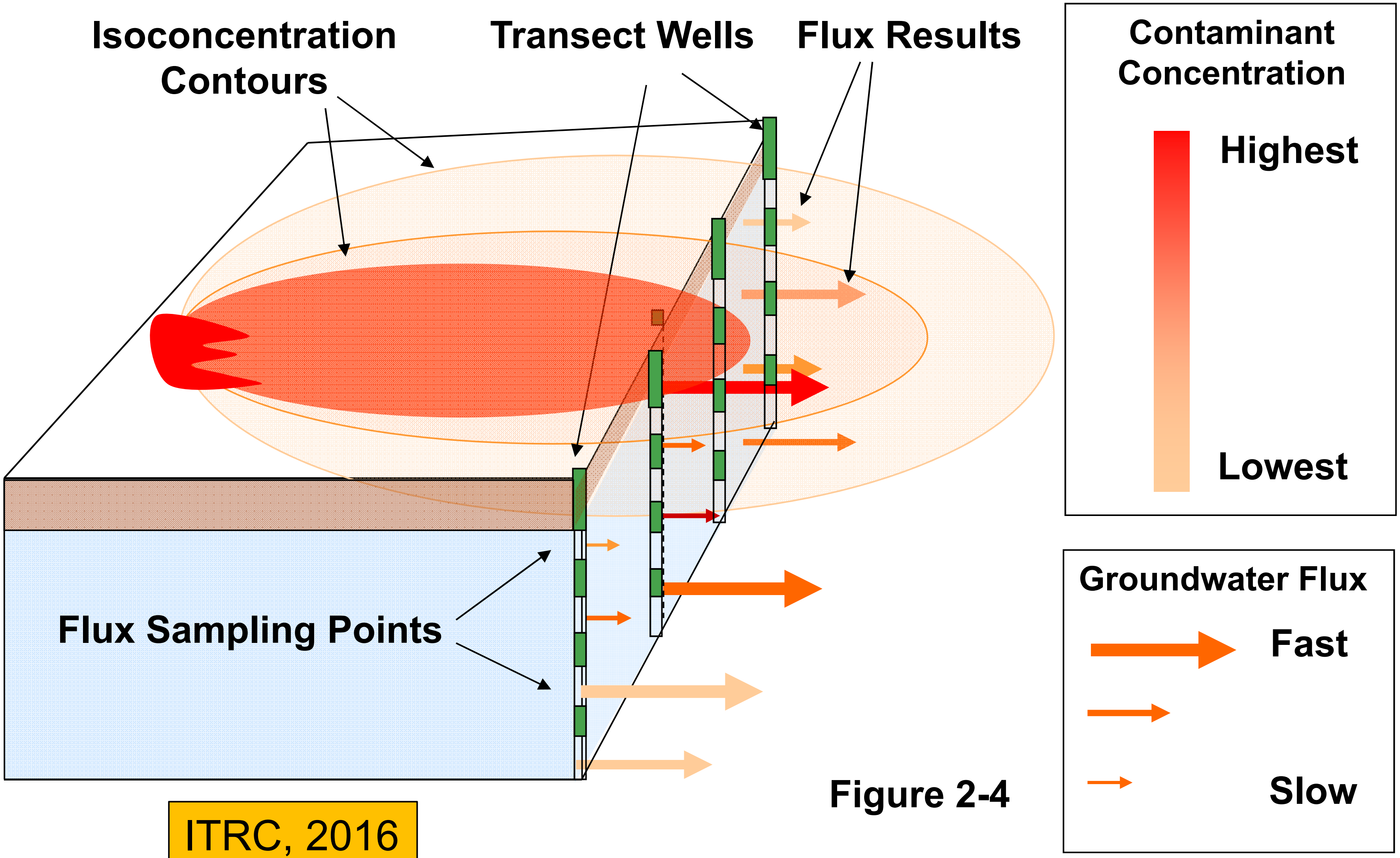


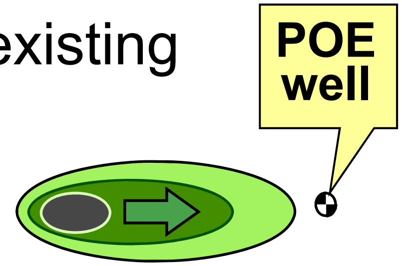
Figure 2-4

ITRC, 2016

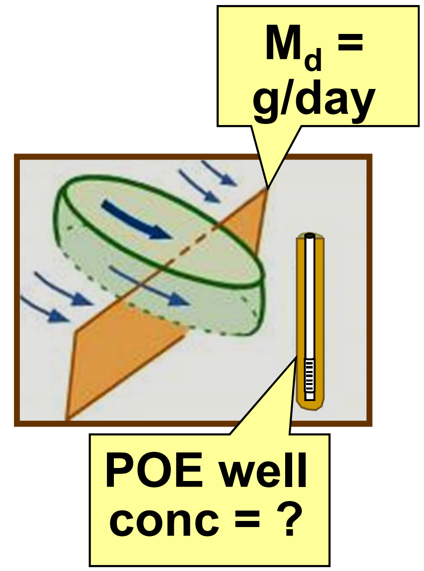
Mass Discharge vs. Traditional Approach

ITRC, 2016

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



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



KEY BENEFITS: **Mass discharge approach <u>sometimes</u> offers a better understanding of potential risks and attenuation rates, and can lead to sounder remediation strategies.**

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