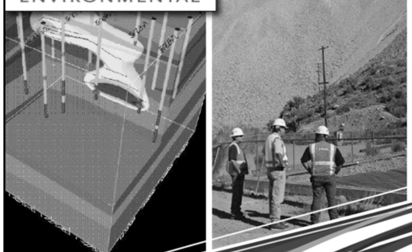


Decision Support System for Matrix Diffusion Modeling

Charles Newell and Shahla Farhat
GSI Environmental Inc.

EPA United States Environmental Protection Agency

Fall 2014 NARPM Presents Series

Acknowledgements

- Dr. Tom Sale, Colorado State
- Dr. Beth Parker, U. of Guelph
- SERDP/ESTCP
- Schlumberger, Geosyntec
- USEPA TIO

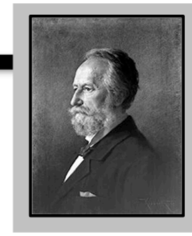
Road Map

- Introduction
- **Matrix Diffusion Background**
- Options for Modeling Matrix Diffusion
- Introduction to MDT – Square Root Model
- Dandy-Sale Model in the MDT
- Case Study 1
- Case Study 2
- Wrap-up and Open Discussion

Mini Road Map

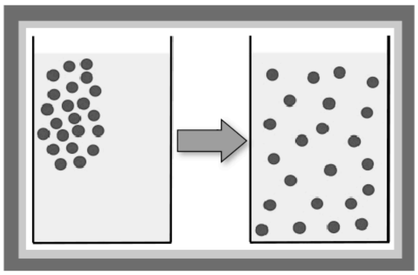
- **Matrix Diffusion Background**
- Lines of Evidence
- New Conceptual Model
- Collecting Field Samples

What is Diffusion?



Diffusion describes the spread of particles through random motion from regions of higher concentration to regions of lower concentration.

Key people: Fourier (1822), Fick (1855), Einstein (1905), Smoluchowski (1906)



$$J = D \frac{dC}{dx}$$

J = Diffusive flux flowing though a particular cross section (mg/ meter^2 / sec)

D = Diffusion coefficient (meter^2 / sec)

$\frac{dC}{dx}$ = Concentration gradient (mg / liter / meter)

Coffee Cup: **Convection + diffusion**

Laminar Groundwater: **Molecular diffusion - movement of molecules only**

Incomplete History of Matrix Diffusion in Groundwater

Foster (1975): Chalk system in England.

Where is the tritium going?

Goodall and Quigley (1977): Core analysis.

Matrix diffusion (30 cm penetration in clay) vs. advection in clay (4 cm).

Matrix Diffusion "overwhelms" advection..

5

Incomplete History of Matrix Diffusion in Groundwater

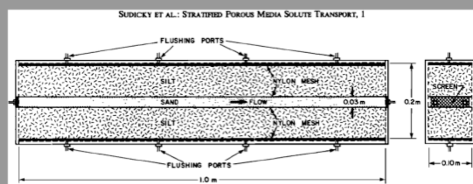


Fig. 1. Laboratory model.

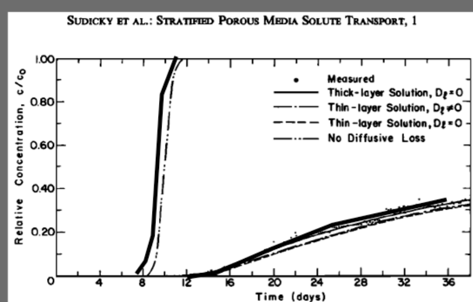
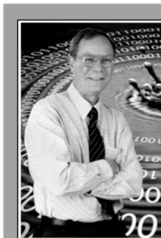


Fig. 2. Comparison between measurements and simulations for low-velocity case.

Sudicky, Gillham, and Frind (WRR: 1985):

"…these effects are the result of a transient redistribution of the tracer across the strata by transverse molecular diffusion …"



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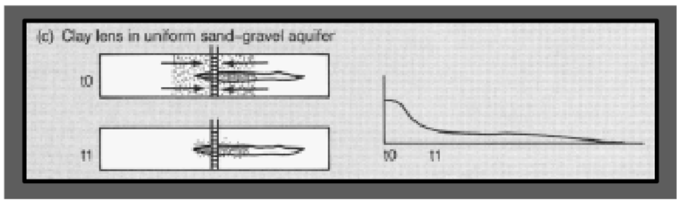
Incomplete History of Matrix Diffusion in Groundwater

Mackay and Cherry (ES&T: 1989)

"As plumes spread through aquifers, the dissolved contaminants move quickly through more permeable zones while they slowly invade the less permeable ones by flow or diffusion."

"Over the years and decades, this invasion can cause the plume to occupy large volumes of low permeability material. To obtain clean water from wells, it is generally necessary for the lower permeability parts of the aquifer system to be cleaned as well as the high permeability zones.



7

Incomplete History of Matrix Diffusion in Groundwater

Parker, Gillham, Cherry (G. W.: 1994):

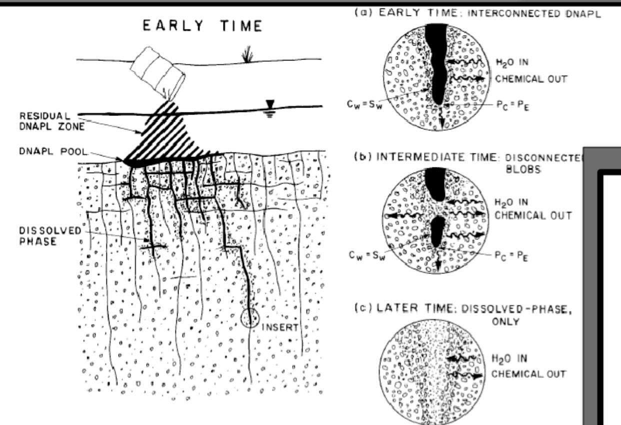


Fig. 1. Revised conceptual model for dense, immiscible organic liquid distribution at the individual fracture scale in fractur porous media: (a) Early time conditions with the DNAPL (nonwetting fluid) invading the fracture and dissolution occurring into the water film (wetting fluid) and subsequent diffusion into the adjacent porous matrix. (b) Intermediate time conditions illustrating disconnected DNAPL blobs in rough-walled fractures resulting from mass loss by diffusion into the matrix. (c) Later time conditions when all immiscible phase has dissolved and diffusion haloes exist around previous, DNAPL-filled fractures.

Matrix diffusion can soak up DNAPL in fractures – sometimes really quickly (days to weeks).

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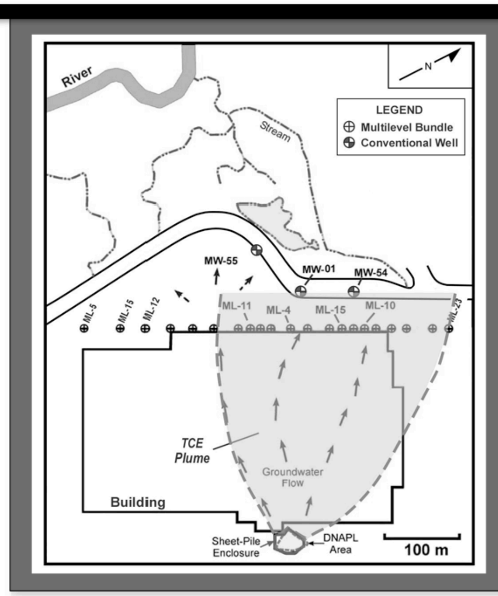
Incomplete History of Matrix Diffusion in Groundwater

Chapman and Parker (WRR: 2005).

"Vertical back diffusion from the aquitard combined with horizontal advection and vertical transverse dispersion account for the TCE distribution in the aquifer and that the aquifer TCE will remain much above the MCL for centuries."



Modified from figure in Chapman and Parker, 2005.

9

Frequently Asked Questions (Sale et al, 2008)

- Provides quick access to key concepts and references for those who need to know more
- Matrix-diffusion centric
- Tom Sale, Chuck Newell, Hans Stroo, Rob Hinchee, and Paul Johnson

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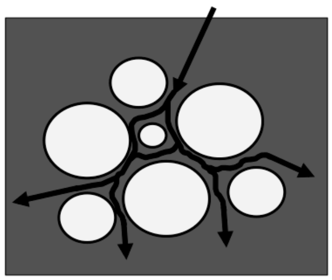
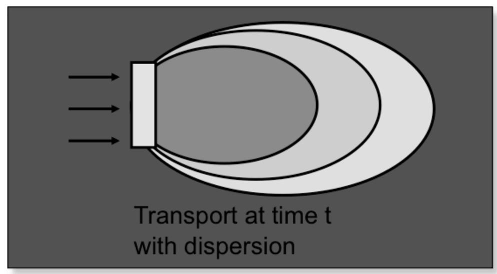
Old Plume Paradigm? Advection Dispersion Model

- Advection
- Dispersion
- Adsorption
- Biodegradation



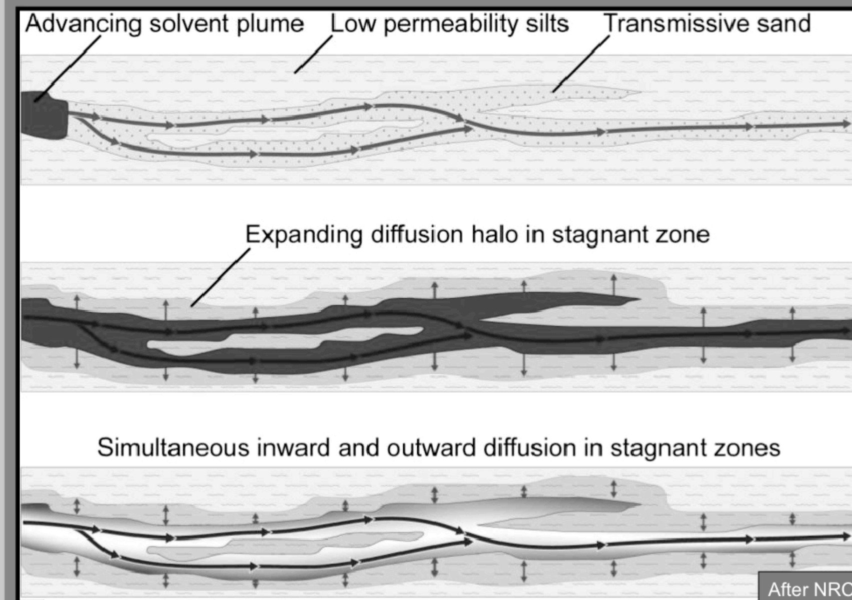


New Plume Paradigm
Heterogeneity Rules, Even in “Sandy Aquifers”

Image from Fred Payne /ARCADIS

Matrix Diffusion Paradigm:
Remediation Hydraulics (CRC Press)
Fred Payne, Joseph Quinnan, Scott Potter

New Plume Paradigm Matrix Diffusion



After NRC 2005

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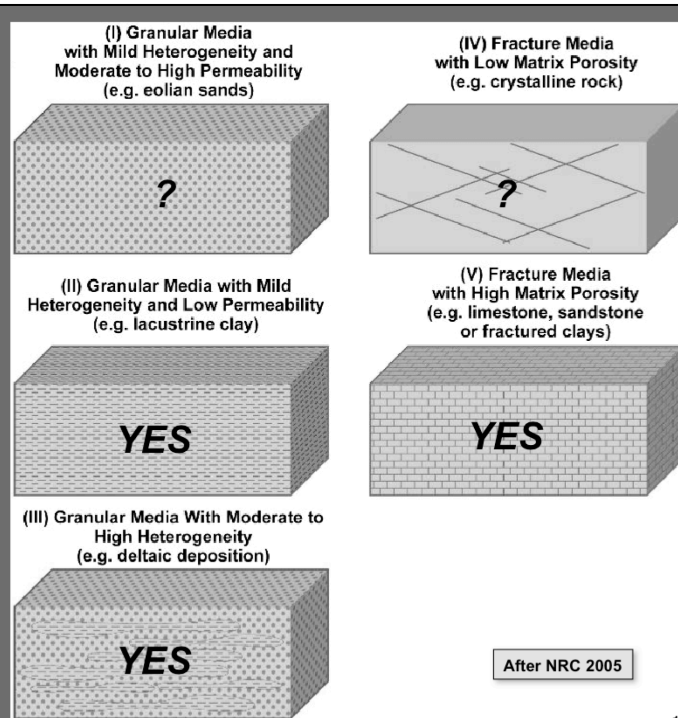
Where is Matrix Diffusion Important?



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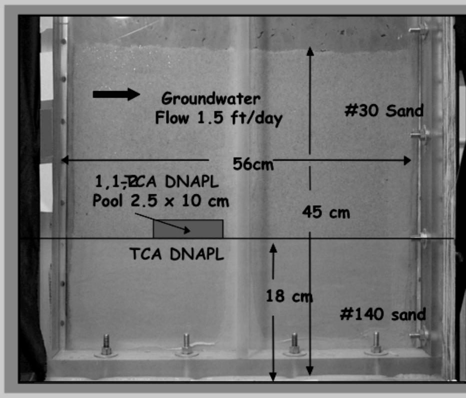
Mini Road Map

- **Matrix Diffusion Background**
- **Lines of Evidence**
- New Conceptual Model
- Collecting Field Samples

Two layer sand tank study Colorado School of Mines (Tissa Illangasekare and Bart Wilkins)



AFCEE Source Zone Initiative (2007)

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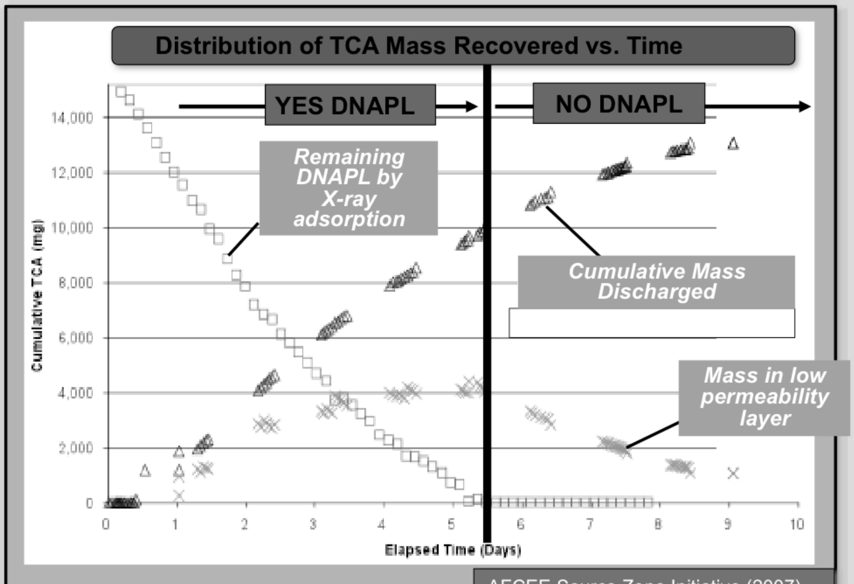
Distribution of TCA Mass Recovered vs. Time



AFCEE Source Zone Initiative (2007)

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Matrix Diffusion Movie
Doner and Sale, Colorado State University

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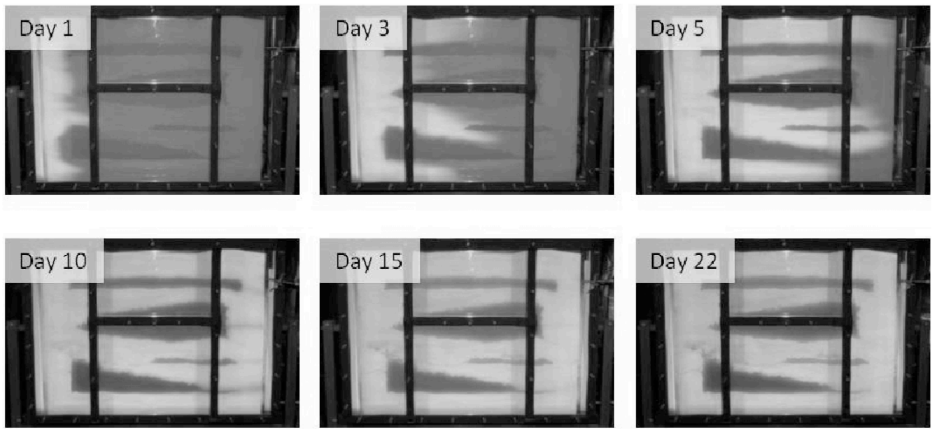
Matrix Diffusion Movie
Doner and Sale, Colorado State University

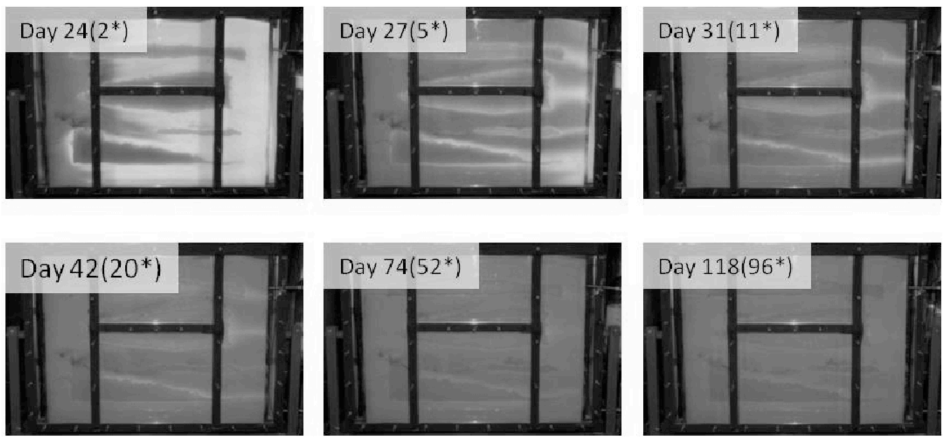
Loading Phase



To Download: www.gsi-net.com

Matrix Diffusion Movie
Doner and Sale, Colorado State University

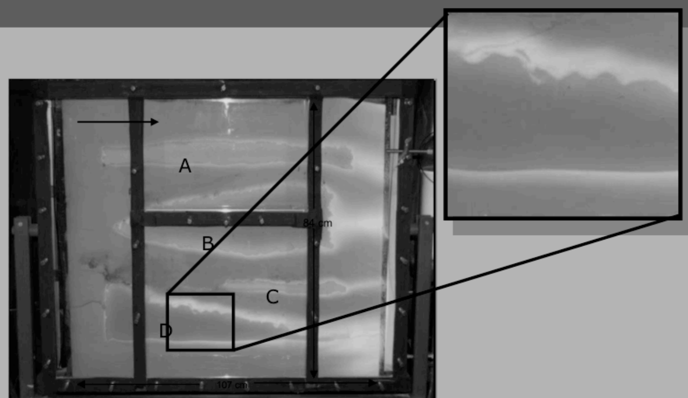
Flushing Phase



To Download: www.gsi-net.com

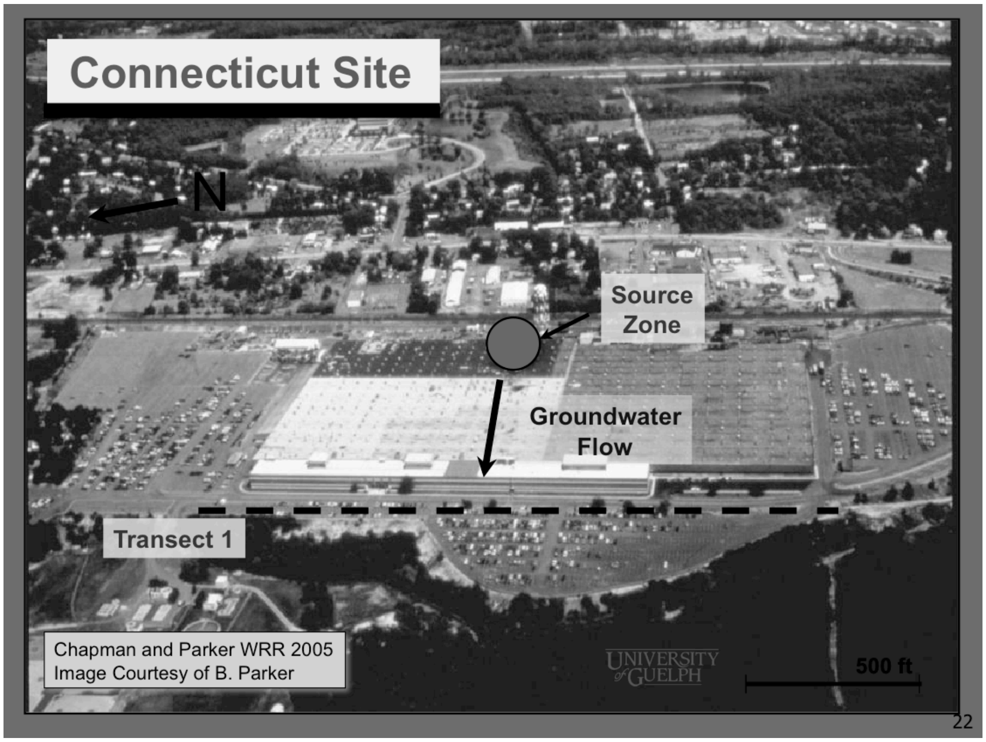
Key Point – Matrix Diffusion is a Small Scale Phenomena

Matrix diffusion governed by concentrations gradients that occur at scales of *centimeters to millimeters.*



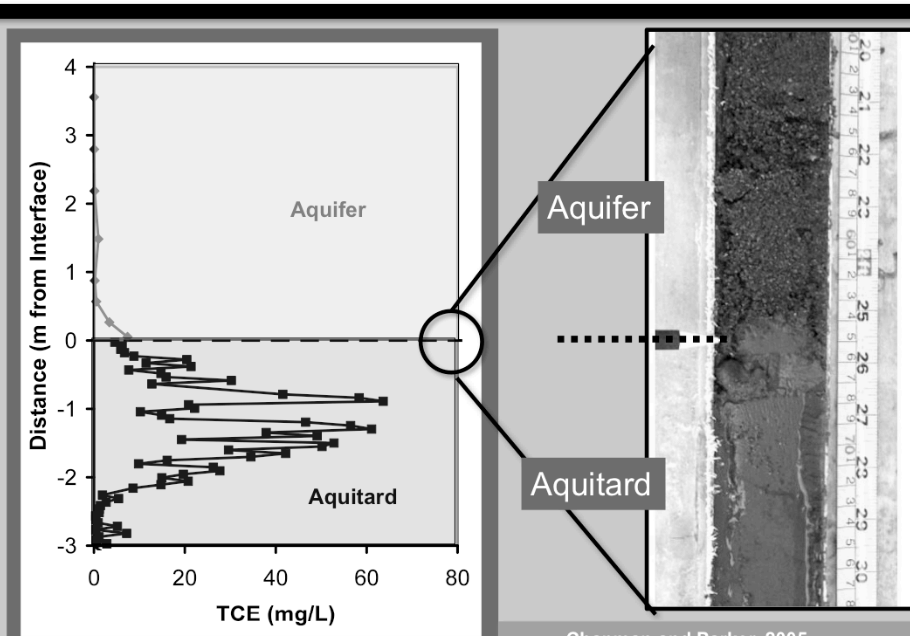
Day 28

21

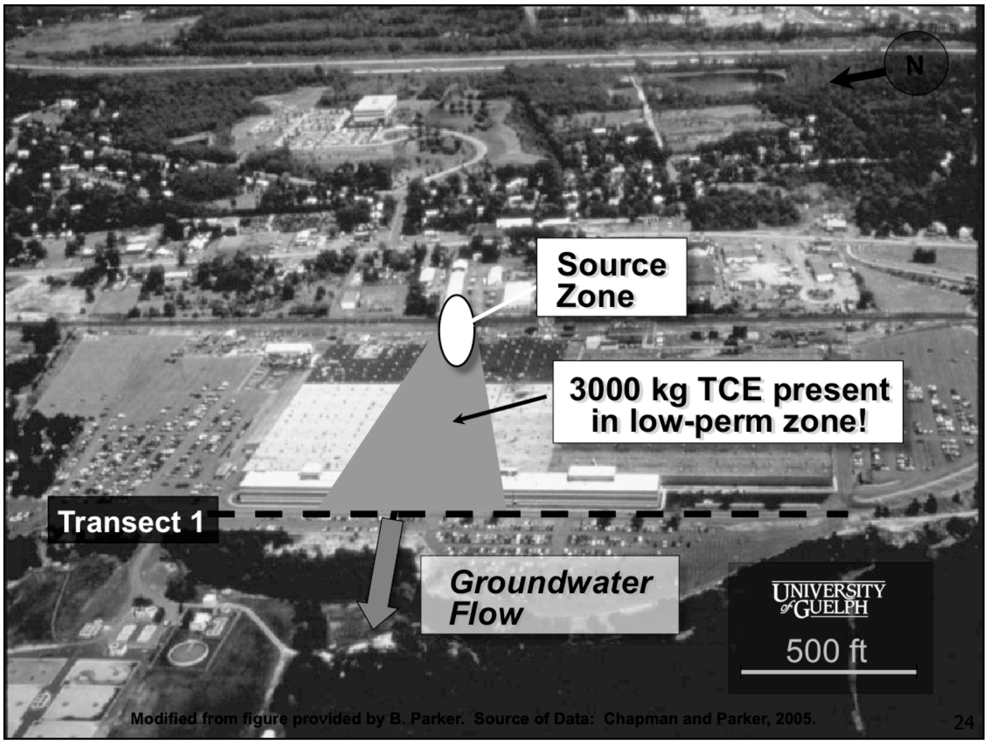


Aerial photograph – source area east of facility, monitoring transect along west side of facility 900 ft from source along entire width of facility (~1400 ft).

High-Resolution Data from Core

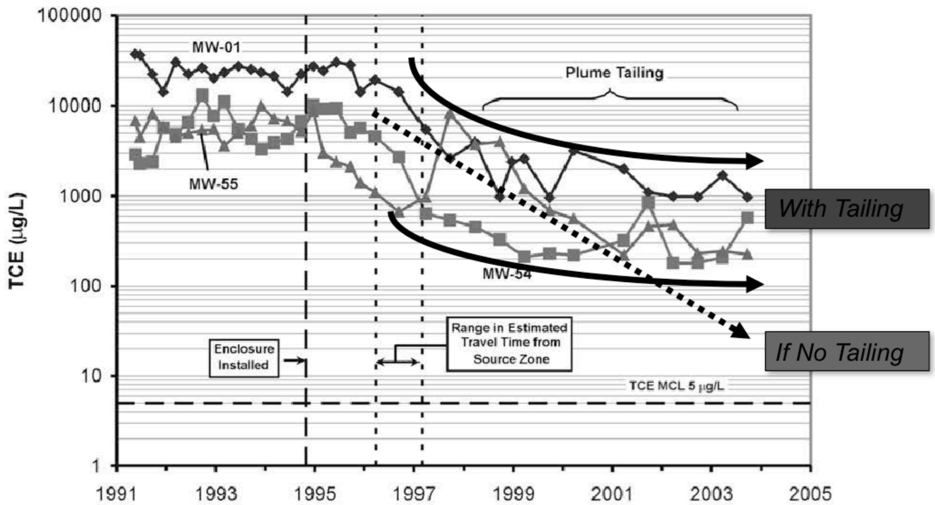


Chapman and Parker, 2005



Aerial photograph – source area east of facility, monitoring transect along west side of facility 900 ft from source along entire width of facility (~1400 ft).

Concentration vs. Time from Monitoring Wells



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

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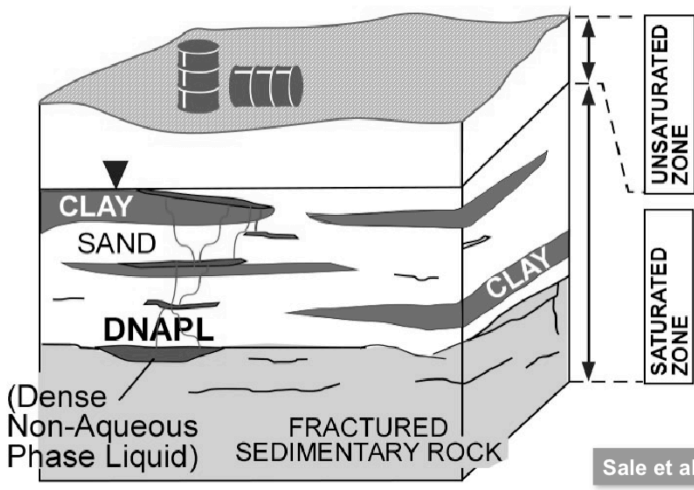
Mini Road Map

- **Matrix Diffusion Background**
- Lines of Evidence
- **New Conceptual Model**
- Collecting Field Samples

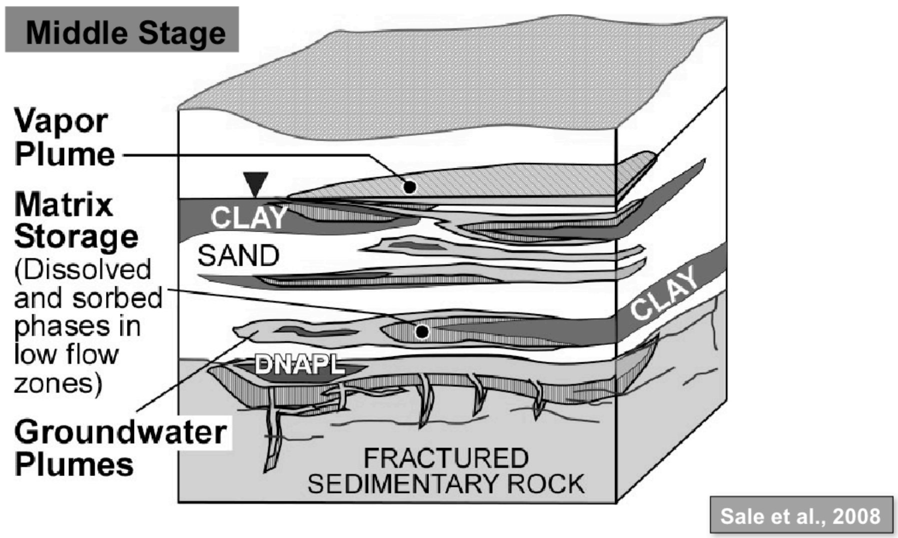
Life Cycle of a Chlorinated Solvent Site

Early Stage



Sale et al., 2008

Life Cycle of a Chlorinated Solvent Site



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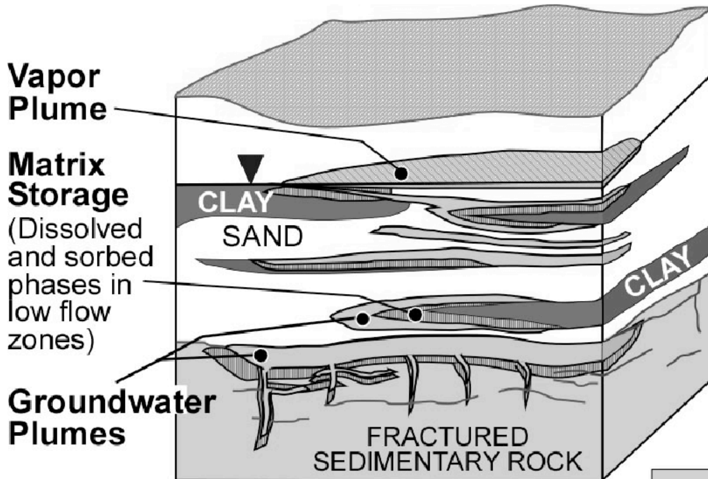
Life Cycle of a Chlorinated Solvent Site

Late Stage



Sale et al., 2008

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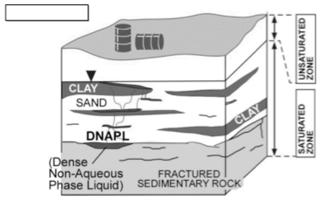

Early Stage

GW. or equivalent GW. conc.

>1,000s → 100s → 10s → 1s

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

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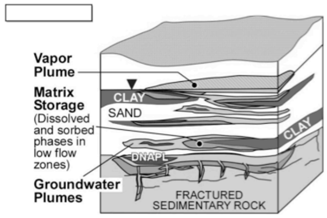


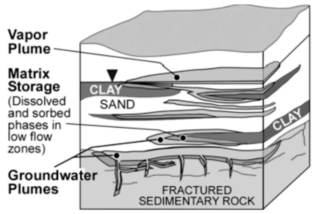
Middle Stage

GW. or equivalent GW. conc.

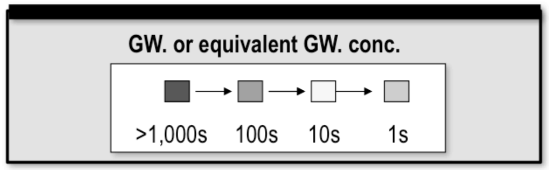
>1,000s → 100s → 10s → 1s

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

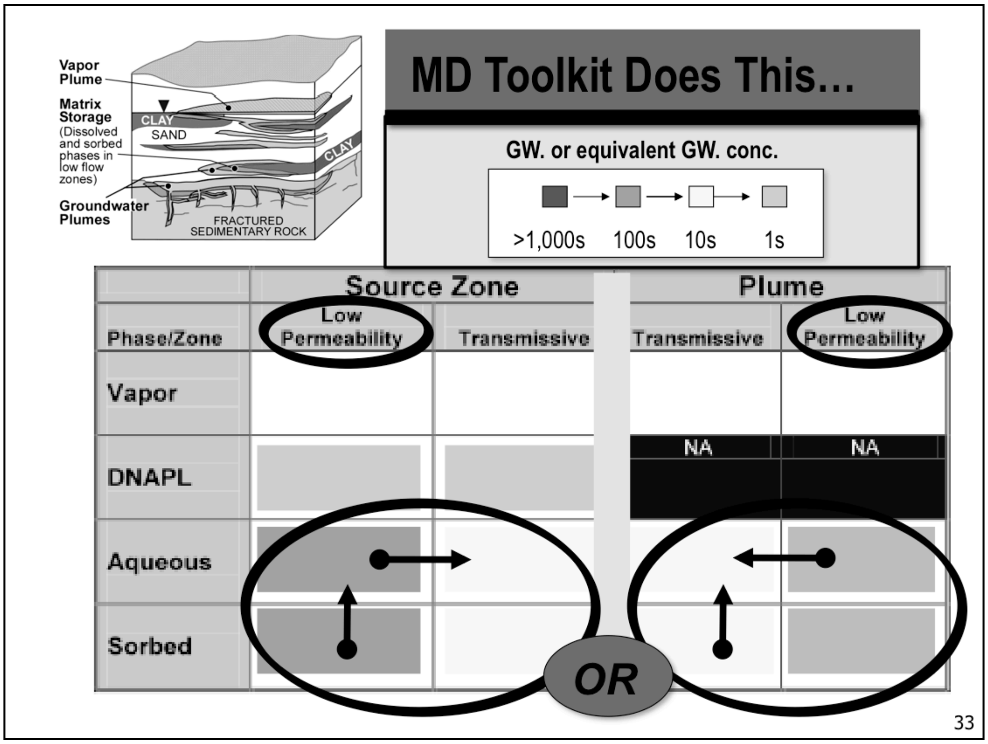
31



Late Stage



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

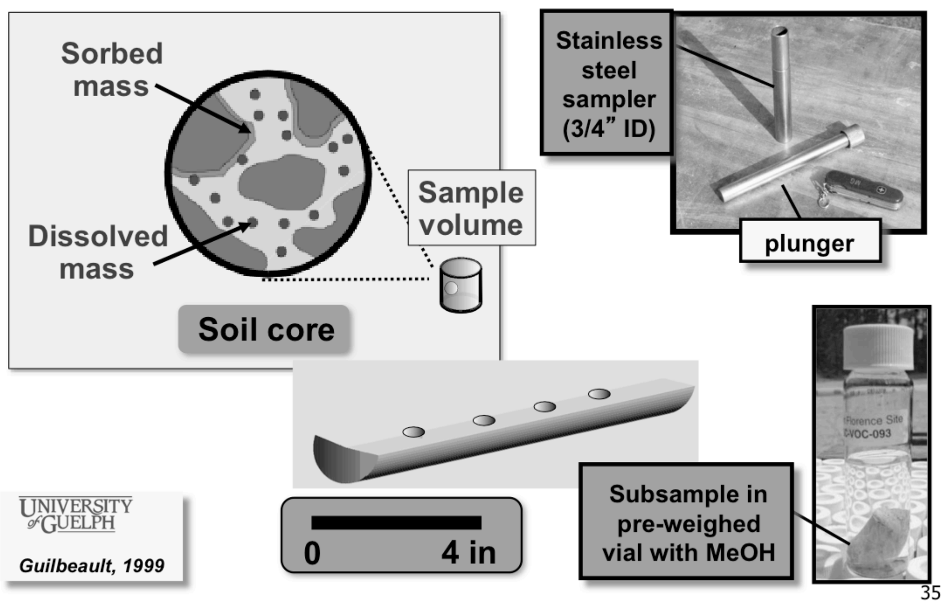


Vapor Plume
Matrix Storage
(Dissolved and sorbed phases in low flow zones)
Groundwater Plumes
CLAY
SAND
CLAY
FRACTURED SEDIMENTARY ROCK
MD Toolkit Does This…
GW. or equivalent GW. conc.
>1,000s
100s
10s
1s
Source Zone
Plume
Phase/Zone
Low Permeability
Transmissive
Transmissive
Low Permeability
Vapor
DNAPL
NA
NA
Aqueous
Sorbed
OR
33

Mini Road Map

- **Matrix Diffusion Background**
- Lines of Evidence
- New Conceptual Model
- **Collecting Field Samples**

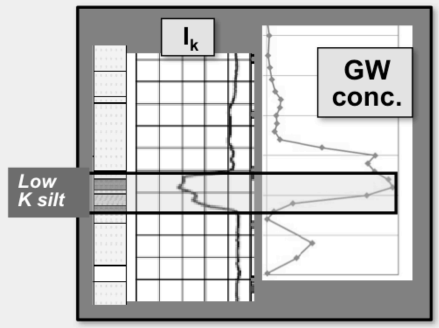
High-Resolution Soil Core Subsampling



Field Sampling
Step 1. Real-time Profiling to Identify Intervals of Interest

Several tools available, including Waterloo^{APS} (from Stone Environmental Inc.)

- **Index of Hydraulic Conductivity (I_k)**
- **Contaminant concentration and physical-chemical properties through GW sample collection**



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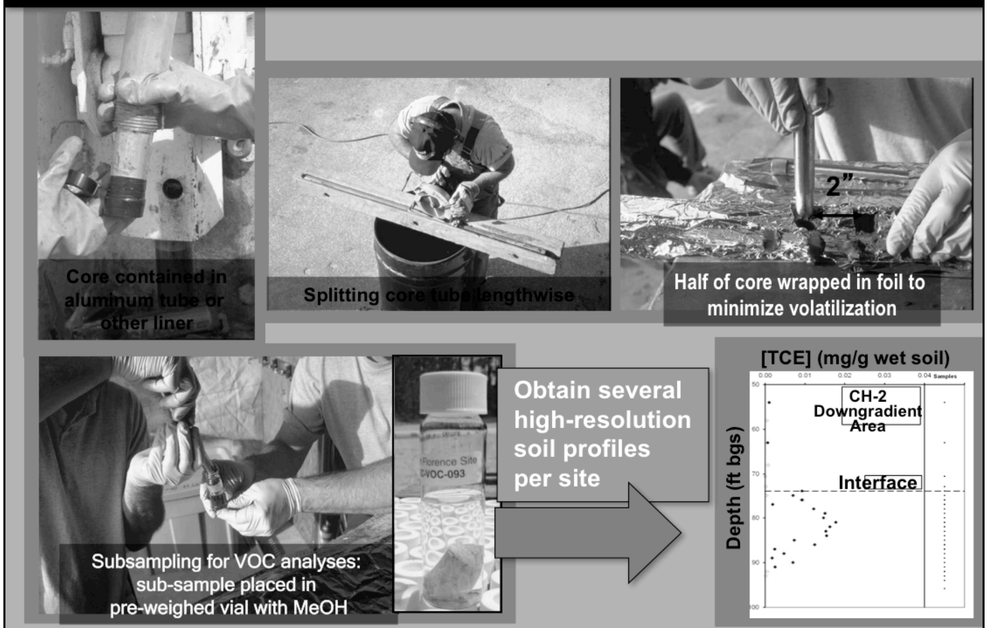
Step 2. Soil Subsampling



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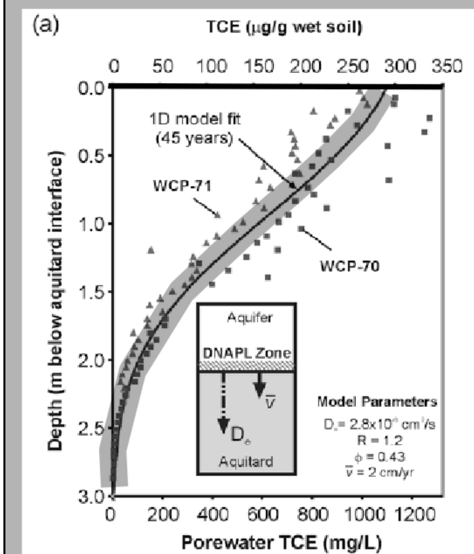
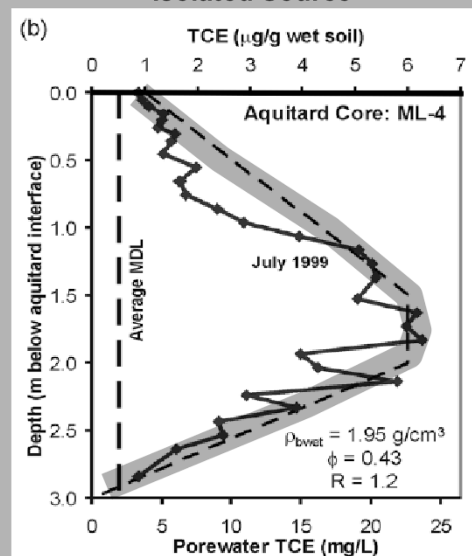
Constant Loading vs. Declining Aquifer Concentration

Zone with DNAPL



Downgradient of Isolated Source



Chapman and Parker, 2005

Exercise

NUMBER 1

Diffusion Curves

♦

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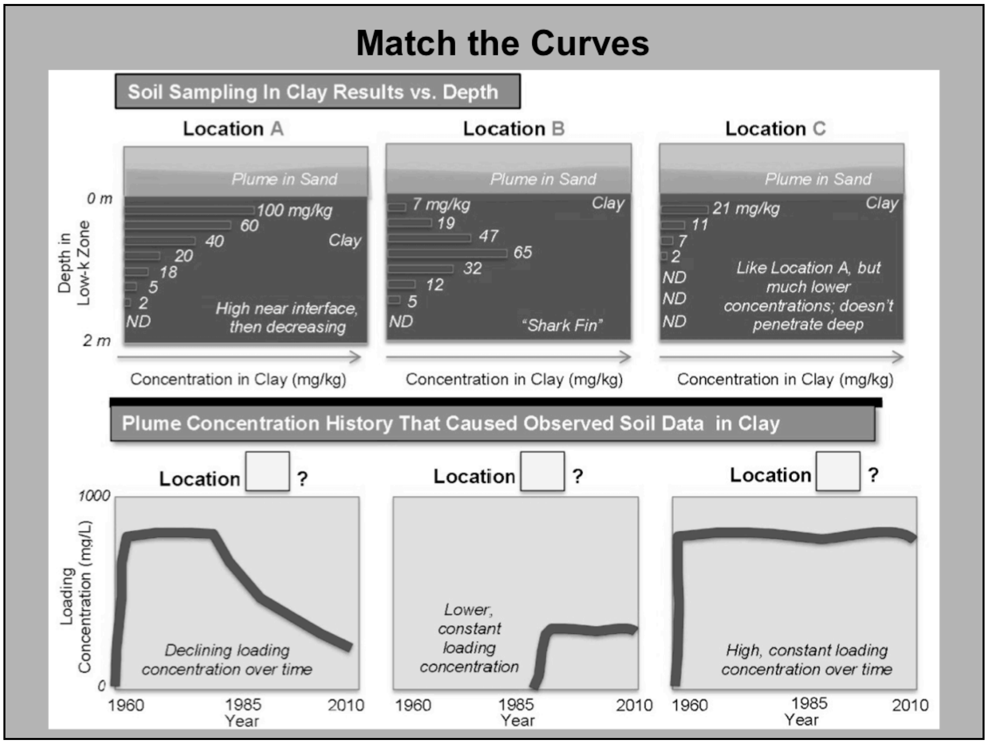
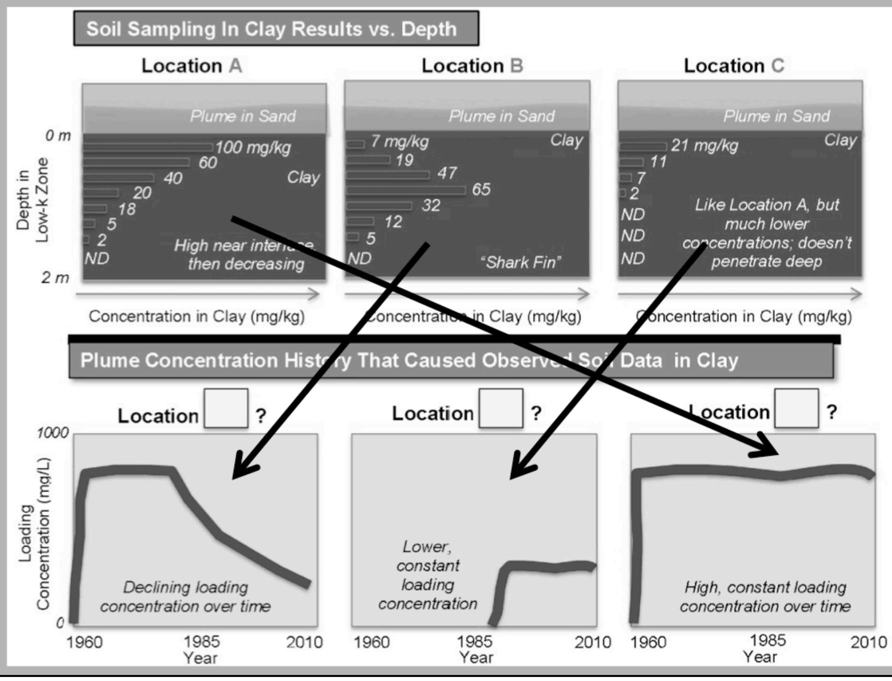
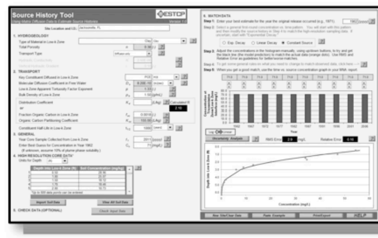

Match the Curves
Soil Sampling In Clay Results vs. Depth
Location A
Location B
Location C
Plume in Sand
Depth in Low-k Zone
0 m
2 m
100 mg/kg
60
40
20
18
5
2
ND
Clay
High near interface, then decreasing
7 mg/kg
19
47
65
32
12
5
ND
"Shark Fin"
21 mg/kg
11
7
2
ND
ND
ND
Like Location A, but much lower concentrations; doesn't penetrate deep
Concentration in Clay (mg/kg)
Plume Concentration History That Caused Observed Soil Data in Clay
Location ?
Loading Concentration (mg/L)
1000
0
Declining loading concentration over time
Lower, constant loading concentration
High, constant loading concentration over time
1960
1985
2010
Year

Match the Curves - Answers



Modeling Historical Impacts – Source History Tool

WHAT:	**Analytical groundwater model that estimates source concentration over time, i.e., a "source history"**
WHERE:	**Free download from:** • **http://www.serdp.org (soon)** • **http://www.gsi-net.com (now)**
WHO:	**S. Farhat, P. de Blanc, C. Newell, and D. Adamson** *GSI Environmental Inc.* **Project Team: B. Parker and S. Chapman** *University of Guelph* **T. Sale** *Colorado State University* ***Funded by ESTCP (ER-201032)***



Road Map

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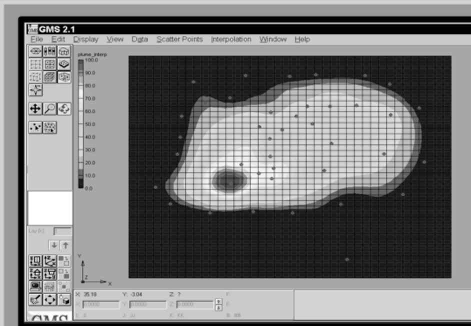
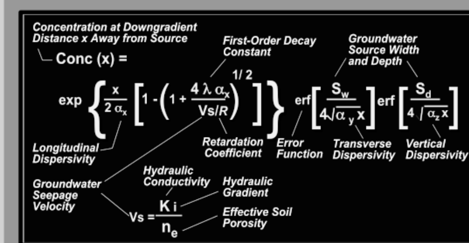
- Matrix Diffusion Background
- **Options for Modeling Matrix Diffusion**
- Introduction to MDT – Square Root Model
- Dandy-Sale Model in the MDT
- Case Study 1
- Case Study 2
- Wrap-up

Types of Groundwater Models

- Flow vs. Transport Models
- Numerical Models
- Analytical Models





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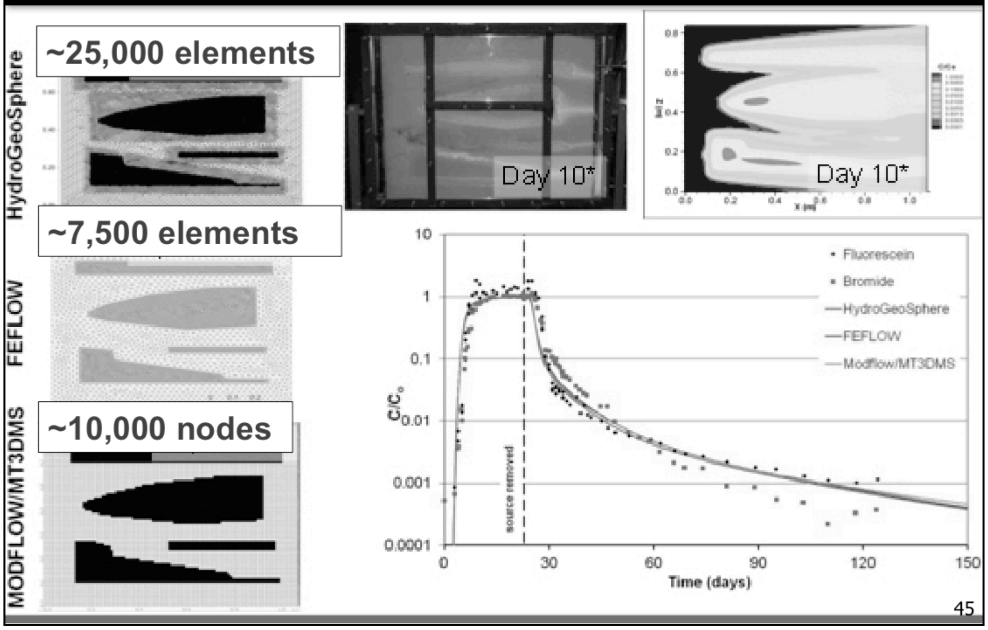
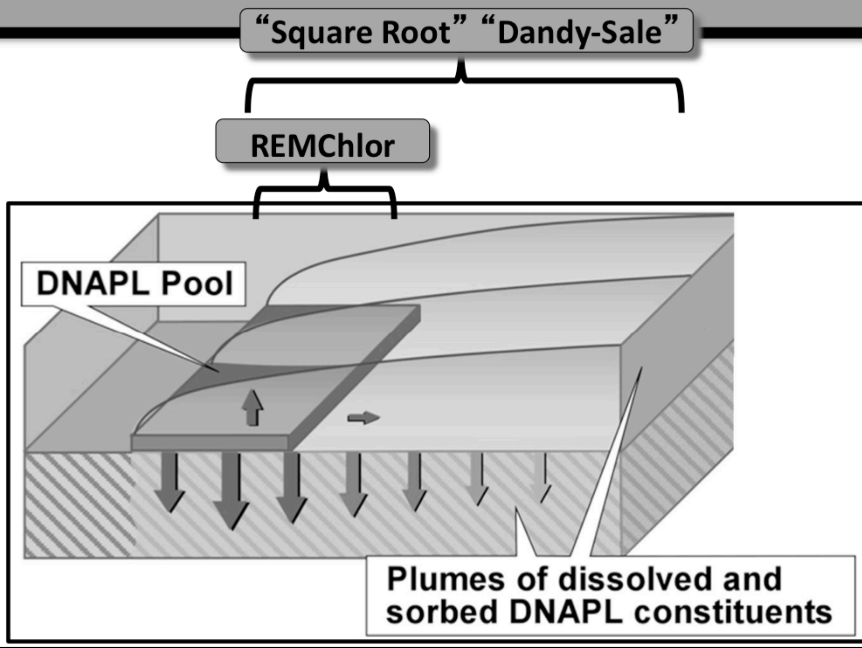
Numerical Models: It takes a lot of grid cells to model this….

(Chapman, Sale, Doner, Parker, 2012)



Three Simple Analytical Matrix Diffusion Models



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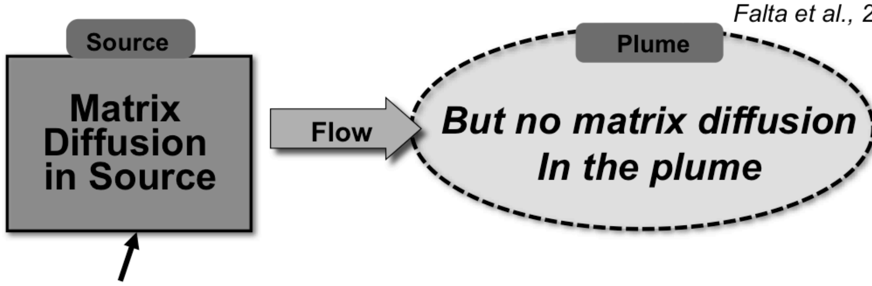
REMChlor and REMFuel Source/Plume/Remediation Models

Falta et al., 2007



You enter source mass, concentration leaving source

You decide how mass leaves over time with "gamma"

A high gamma (>1.0) can simulate matrix diffusion

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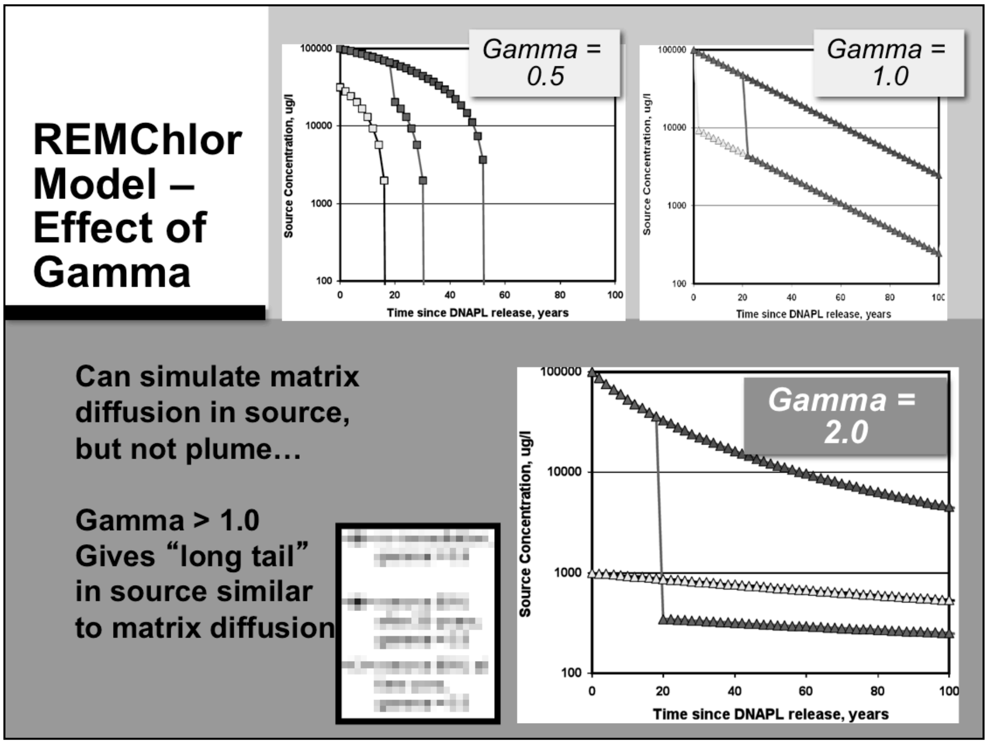
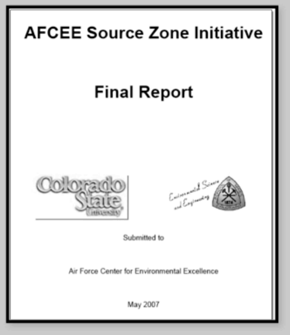

REMChlor Model – Effect of Gamma
Gamma = 0.5
Gamma = 1.0
Gamma = 2.0
Source Concentration, ug/l
Time since DNAPL release, years
Can simulate matrix diffusion in source, but not plume…
Gamma > 1.0 Gives “long tail” in source similar to matrix diffusion

“Square Root Model” for Matrix Diffusion

“On-Off” Source

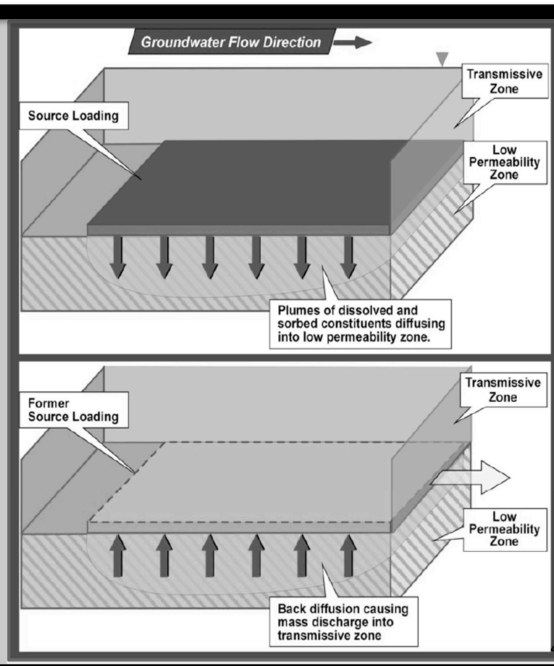

AFCEE Source Zone Initiative

Final Report

Submitted to

Air Force Center for Environmental Excellence

May 2007



Dr. Tom Sale
Dr. Tissa Illangasekare

Adapted from
Parker et al., 1995

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“Square Root” Matrix Diffusion Model

$$M_D = \varphi_{LP} C_S L_p \left[\sqrt{\frac{R_{LP} D_e}{\pi t}} - \sqrt{\frac{R_{LP} D_e}{\pi \left(t - t' \right)}} \right]$$

- M_D: **Mass Discharge** from Low Perm. Unit (grams per day) *assuming no concentration in transmissive zone*

- φ_{LP} - Low Permeability Unit Porosity
- D_e - Effective Diffusion Coefficient of Low Perm Unit,
- R - Retardation Factor of Low Perm Unit
- t - Time Loading Started, years before simulation time
- t’ - Time Loading was Removed, years before simulation time
- C_s - Concentration at interface during loading period

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MEW Site
Mountain View, California

Team members: Schlumberger, GSI, Geosyntec

- Seyedabbasi et al., Remediation, 2013
- McDade et al., Remediation, 2013

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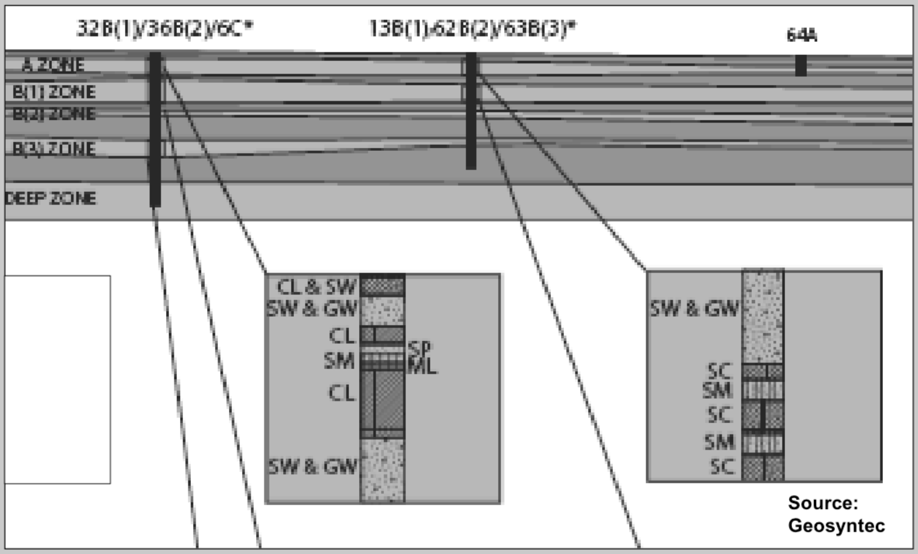
MEW Site: Site Hydrogeology



Source: Geosyntec

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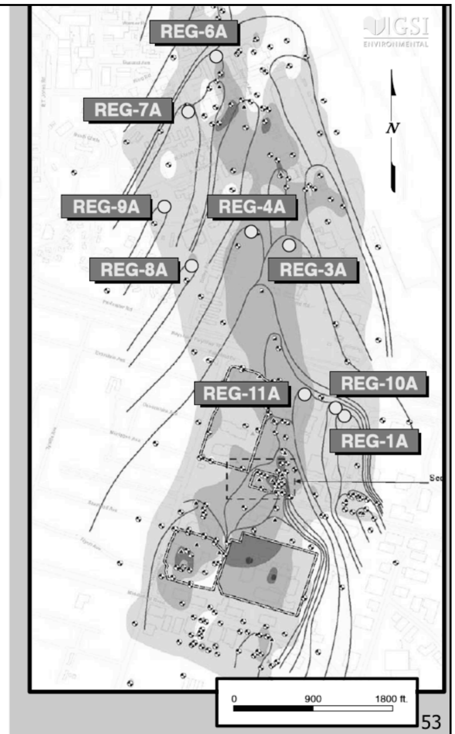
Pump & Treat System at MEW Site

- Middlefield–Ellis–Whisman Site
- Three Zones: A/A1, B1/A2, B2
- 1980s: Slurry Walls, Pump & Treat
- Today ~100 recovery wells, ~500 gpm
- Removal: ~97,000 pounds VOCs
- Reduction: Approximately 1 OoM decrease in average TCE concentration 1992-2009



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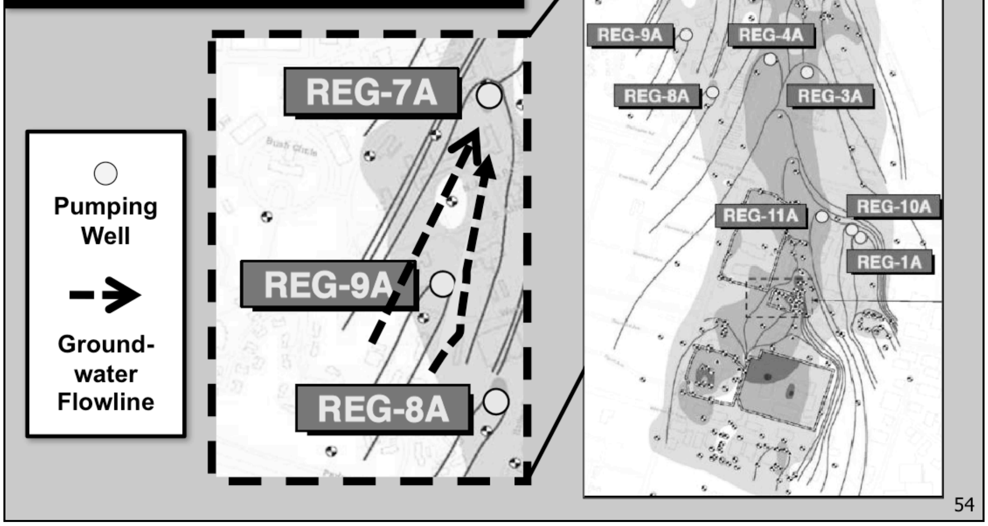
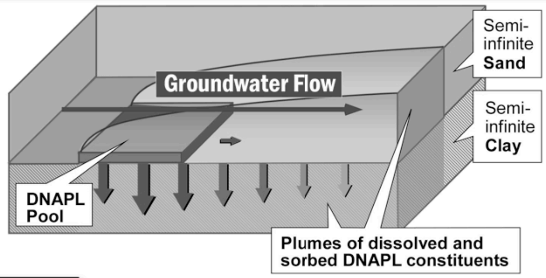
Example A: MEW Site Pump and Treat Capture Zones



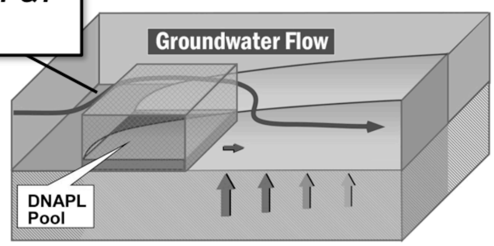
Matrix Diffusion Model Applied to MEW Site

"Charging Period"



Then Build Slurry Walls, P&T Wells, Contain Sources

"Back Diffusion Period"



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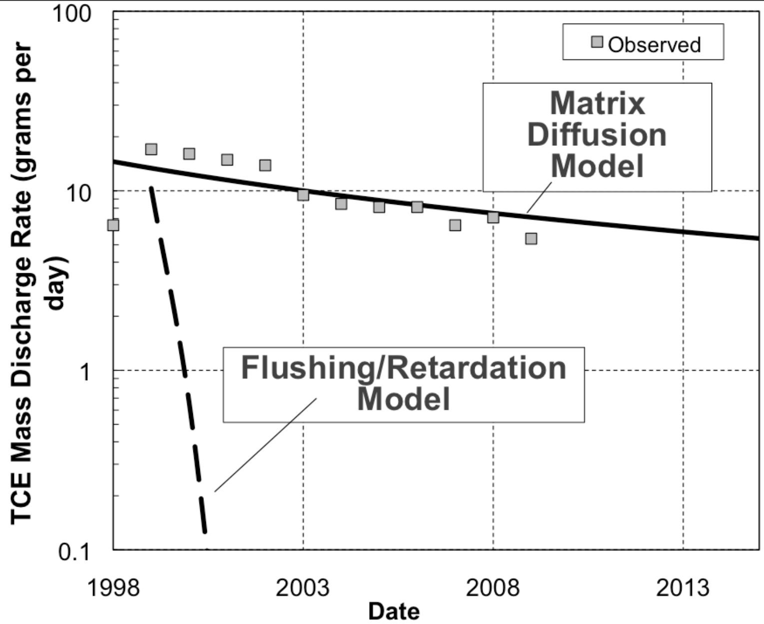
Results:
Recovery Well REG-8A: 30 Pore Volumes



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Dandy-Sale Model

Contents lists available at ScienceDirect

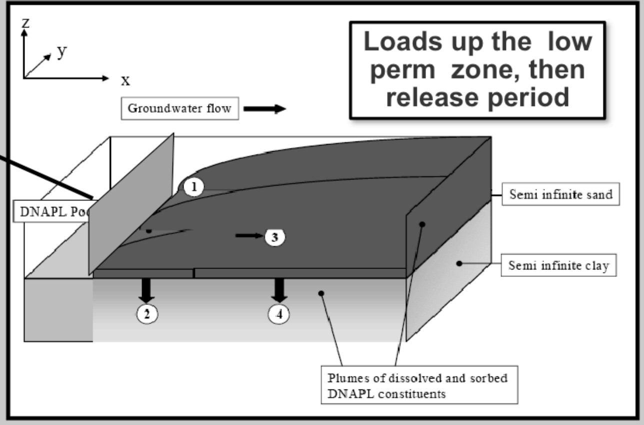
Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Effects of reduced contaminant loading on downgradient water quality in an idealized two-layer granular porous media

Tom C. Sale[a,*], Julio A. Zimbron[a,1], David S. Dandy[b]

Loads up the low perm zone, then release period



Vertical Plane Source

(Higher concentration near bottom)

SERDP
DOD • EPA • DOE

Sale, Zimbron, Dandy, 2008

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Dandy-Sale Analytical Matrix Diffusion Model

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Effects of reduced contaminant loading on downgradient water quality in an idealized two-layer granular porous media

Tom C. Sale [a,*], Julio A. Zimbron [a,1], David S. Dandy [b]

[a] Department of Civil & Environmental Engineering, Colorado State University, Fort Collins, CO, 80523-1320, United States
[b] Department of Chemical & Biological Engineering, Colorado State University, Fort Collins, CO, 80523-1320, United States

$$\frac{C'}{C_0}=\frac{\phi^2}{2\pi}e^{-kx/v}\int_0^x\int_0^{t-x/v}\frac{e^{-\hat{k}u}}{\sqrt{u}(x-\xi)^{3/2}}\left[\frac{1}{\sqrt{\pi\xi}}-\frac{b}{\phi}e^{b^2\xi/\phi^2}erfc\left(\frac{b}{\phi}\sqrt{\xi}\right)\right]\frac{e^{-Y^2B^2/(\gamma^2+4B^2u)}}{\left(\gamma^2+4B^2u\right)^2}\times\left[4YB^2ue^{-Y^2\gamma^2/4u(\gamma^2+4B^2u)}+\sqrt{\pi}\gamma\left(4B^2u-2Y^2B^2+\gamma^2\right)\sqrt{\frac{u}{\gamma^2+4B^2u}}erfc\left(\frac{Y\gamma}{2u}\sqrt{\frac{u}{\gamma^2+4B^2u}}\right)\right]du\,d\xi \quad (10)$$

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1. REMChlor	2. Square Root Model	3. Dandy-Sale Model
Simple	Very simple	Complex Function
Vertical plane source	Horizontal source is directly over low perm zone	Vertical plane source upgradient of low perm zone
No matrix diffusion in plume	• On-off source • Unimpeded back diffusion	• On-off source • More accurate back diffusion
Concentration or Mass Discharge	• Mass discharge • Mass in low perm • Concentration in Well	Same as Square Root, but with Conc. in Low Perm.
U.S. EPA CSMoS (Google: "EPA" and "REMChlor")	ESTCP Matrix Diffusion Toolkit (www.gsi-net.com)	

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Road Map

- Introduction
- Matrix Diffusion Background
- Options for Modeling Matrix Diffusion
- **Introduction to MDT – Square Root Model**
- Dandy-Sale Model in the MDT
- Case Study 1
- Case Study 2
- Wrap-up

EPA United States Environmental Protection Agency

Matrix Diffusion Toolkit

ESTCP

WHAT: Analytical groundwater transport models that estimates matrix diffusion effects

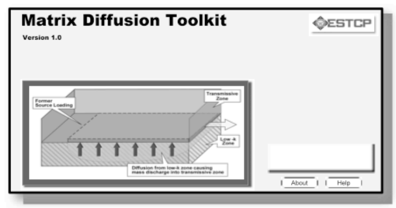
WHERE: Free download from:

- http://www.serdp.org
- http://www.gsi-net.com

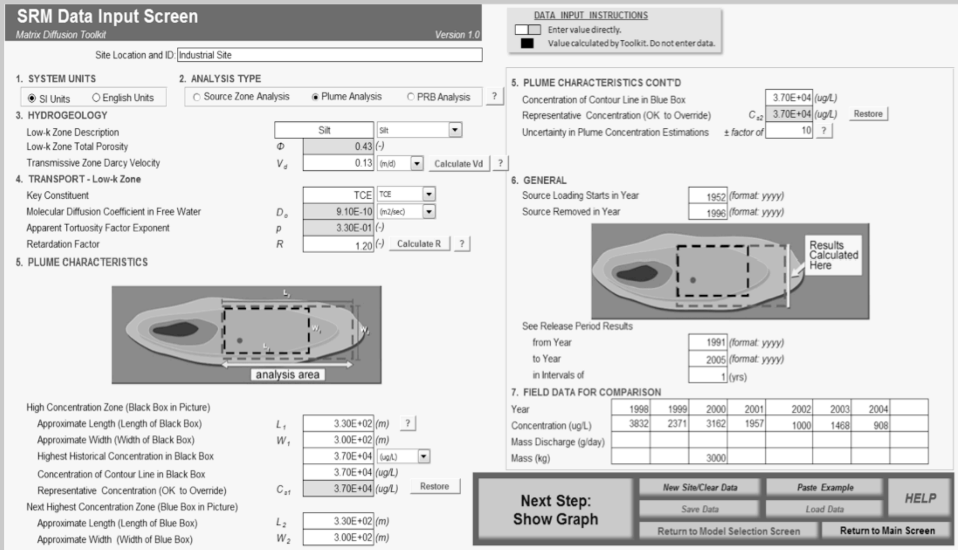
WHO: S. Farhat and C. Newell
GSI Environmental Inc.

T. Sale, D. Dandy, and J. Wahlberg
Colorado State University

Funded by ESTCP



Square Root Model: *Data Input Screen*



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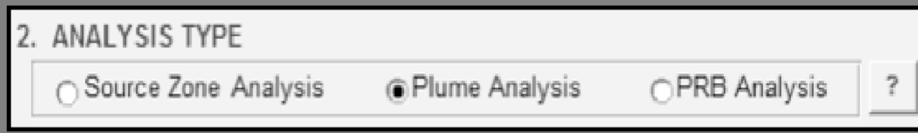
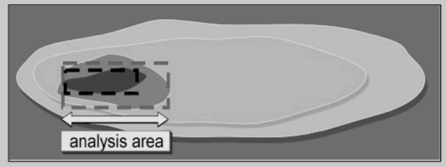
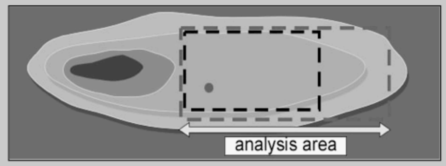


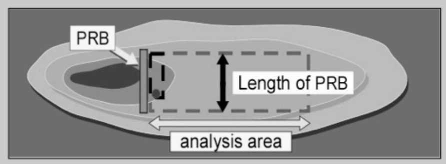
Select "Source Zone Analysis" to see matrix diffusion impacts in a source zone:



Select "Plume Analysis" to see matrix diffusion impacts in a downgradient plume:



Select "PRB Analysis" to see matrix diffusion impacts downgradient of a PRB:



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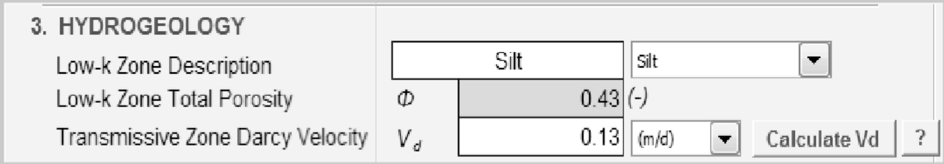

Low-k Zone Description	**Choose from dropdown menu or enter directly**
Low-k Zone Total Porosity	**Keep Toolkit default or enter directly.** • **Based on Pankow and Cherry (1996)** • **Domenico and Schwartz (1999)** • **Davis (1969) and Johnson and Morris (1962)**
Transmissive Zone Darcy Velocity	**Enter directly or use Toolkit to calculate**

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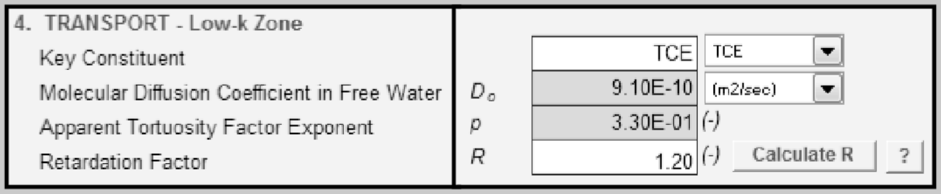
Square Root Model: *Transport*



Parameter	Description
Molecular Diffusion Coefficient in Free Water	**Keep Toolkit default or enter directly** • **From TRRP (2008)** • **TCE =** 9.1E-06 cm^2/s • **PCE =** 8.2E-06 cm^2/s • **Benzene =** 9.8E-06 cm^2/s • **Other refs: Pankow and Cherry (1996), Wiedemeier *et al.* (1999), etc.**

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Apparent Tortuosity Factor Exponent

Parameter	Description
Apparent Tortuosity Factor Exponent	**Keep Toolkit default or enter directly**

tortuosity → $\tau = n^p$ ← **porosity**

p varies:

- 1/3: Millington, 1959
- 0.3 to 1.5: Charbeneau, 2000
- 1.3 to 4.5: Pankow and Cherry, 1997
- 0.33 for Clay: Parker et al., 1994

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GSI's Decision Support for Tortuosity

(1) Pick Material

- Gravel
- Sand
- Silt
- Clay
- Sandstone/Shale
- Granite

(2) Software Produces

If no porosity value is entered:

- Default Porosity
- Tortuosity factor

If porosity value is entered:

- Tortuosity factor

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Current Look-up Table

Soil Type	Default Porosity	Relationship*	Estimated Tortuosity
Fine Sand	0.20	$\tau = n^{0.33}$	0.59
Silt	0.48	$\tau = n^{1.1}$	0.45
Clay	0.47	$\tau = n^{1.1}$	0.44
Sandstone/ Shale	0.10	$\tau = n$	0.10
Granite	0.006	$\tau = n^{0.55}$	0.06

*** From Parker et al. (2004); Millington and Quirk (1961); and Pankow and Cherry (1996)**

Retardation Factor

Parameter	Description
Retardation Factor	**Enter directly or use Toolkit to calculate** • **Transmissive zones** 1-3 (typical for BTEX) 2-5 (typical for CVOC) • **Low-k zones** Thought to be > trans zones. Currently, few sites with data

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Calculating Retardation Factor

Parameter	Description
K_{oc}	**Keep Toolkit default or enter directly** • **From TRRP (2008)** • **TCE =** 93 mL/g • **PCE =** 155 mL/g • **Benzene =** 66 mL/g • **Other refs: Pankow and Cherry (1996), Wiedemeier *et al*. (1999), etc.**

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Calculating Retardation Factor Cont'd

Parameter	Description
Low-k zone fraction organic carbon	**Enter directly** • Likely range: 0.0002 - 0.10 • Chapman and Parker (2005): silts and clays = 0.0024 to 0.00104 • Adamson (2012): clay = 0.001; silts = <0.0005 to 0.0022
Soil bulk density of low-k zone	**Enter directly** • Typical value = 1.7 g/mL • Lovanh et al. (2000) and Domenico and Schwartz (1990): Clay = 1.0 to 2.4 Sandstone = 1.6 to 2.68 • Koerner (1984): Stiff glacial clay = 2.07 organic clay = 1.43

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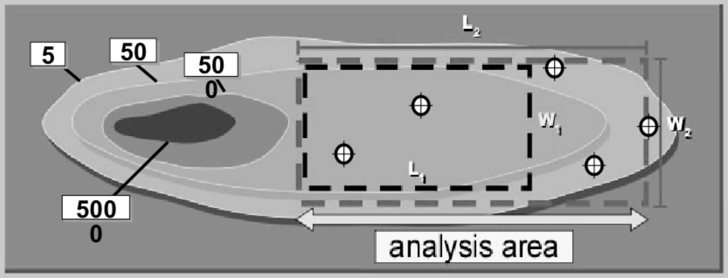
Square Root Model: *Plume Charac.*



High Concentration Zone (Black Box in Picture)			
Approximate Length (Length of Black Box)	L_1	3.30E+02	(m)
Approximate Width (Width of Black Box)	W_1	3.00E+02	(m)
Highest Historical Concentration in Black Box		3.70E+04	(ug/L)
Concentration of Contour Line in Black Box		3.70E+04	(ug/L)
Representative Concentration (OK to Override)	C_{s1}	3.70E+04	(ug/L)

Restore

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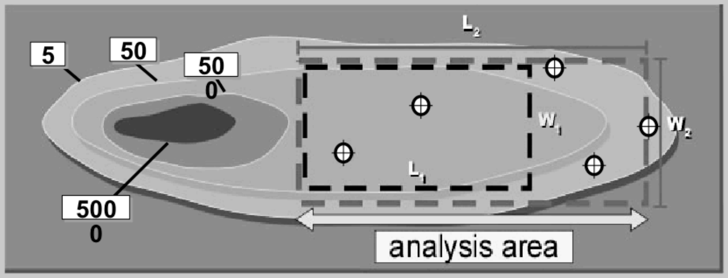
Plume Characteristics Cont'd



Next Highest Concentration Zone (Blue Box in Picture)				
Approximate Length (Length of Blue Box)	L_2	3.30E+02	(m)	
Approximate Width (Width of Blue Box)	W_2	3.00E+02	(m)	
Concentration of Contour Line in Blue Box		3.70E+04	(ug/L)	
Representative Concentration (OK to Override)	C_{s2}	3.70E+04	(ug/L)	Restore
Uncertainty in Plume Concentration Estimations	± factor of	10	?	

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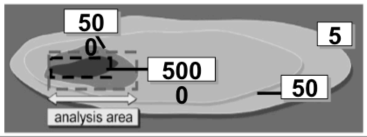
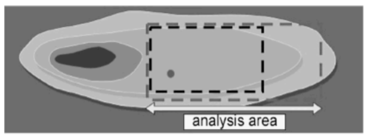
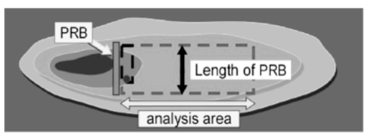
<table>
<tr><th>Type of Problem to Be Analyzed Using the Toolkit</th><th>Black Box in Drawing</th><th>Blue Box in Drawing</th></tr>
<tr><td>To see matrix diffusion impacts in a source zone:

</td><td>Is drawn around the highest contour in the source area.</td><td>Is drawn around the second highest contour in the source area.</td></tr>
<tr><td>To see matrix diffusion impacts in a downgradient plume:

</td><td>Is drawn around the highest contour downgradient of the source area.</td><td>Is drawn around the second highest contour downgradient of the source area.</td></tr>
<tr><td>To see matrix diffusion impacts downgradient of a PRB:

</td><td>Is drawn around the highest contour downgradient of the PRB. The width of the box is the width of the PRB.</td><td>Is drawn around the second highest contour downgradient of the PRB. The width of the box is the width of the PRB.</td></tr>
</table>

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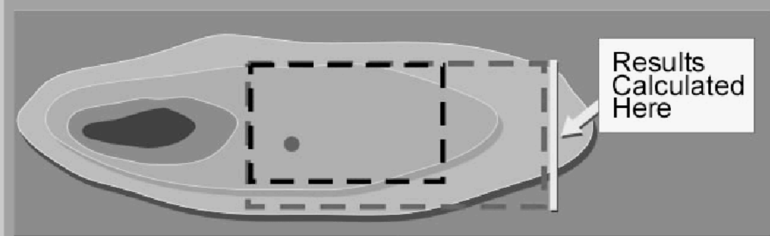
Square Root Model: *General*

6. GENERAL	
Source Loading Starts in Year	1952 *(format: yyyy)*
Source Removed in Year	1996 *(format: yyyy)*



See Release Period Results	
from Year	1991 *(format: yyyy)*
to Year	2005 *(format: yyyy)*
in Intervals of	1 (yrs)

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Square Root Model: *Field Data*

7. FIELD DATA FOR COMPARISON					
Year	1998	1999	2000	2001	
Concentration (ug/L)	3832	2371	3162	1957	
Mass Discharge (g/day)					
Mass (kg)			3000		

- **Can enter up to 8 values for comparison**
  - Helps with model calibration

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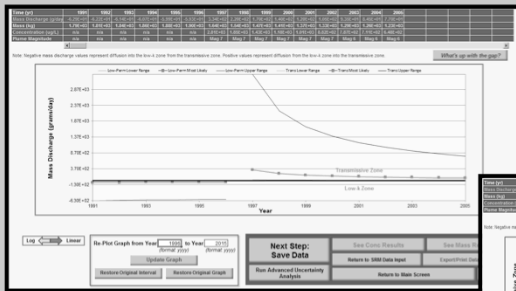
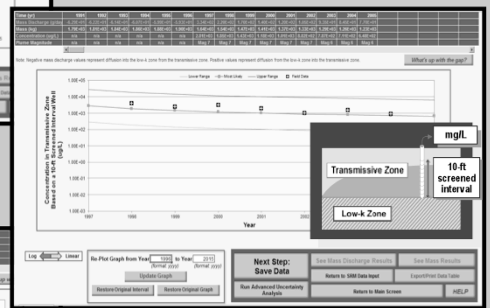
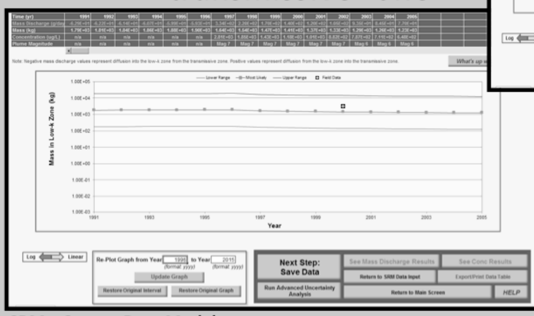
SRM Output



- Mass discharge



- Concentration in transmissive zone



- Mass in low-k zone

SRM = Square Root Model

Road Map

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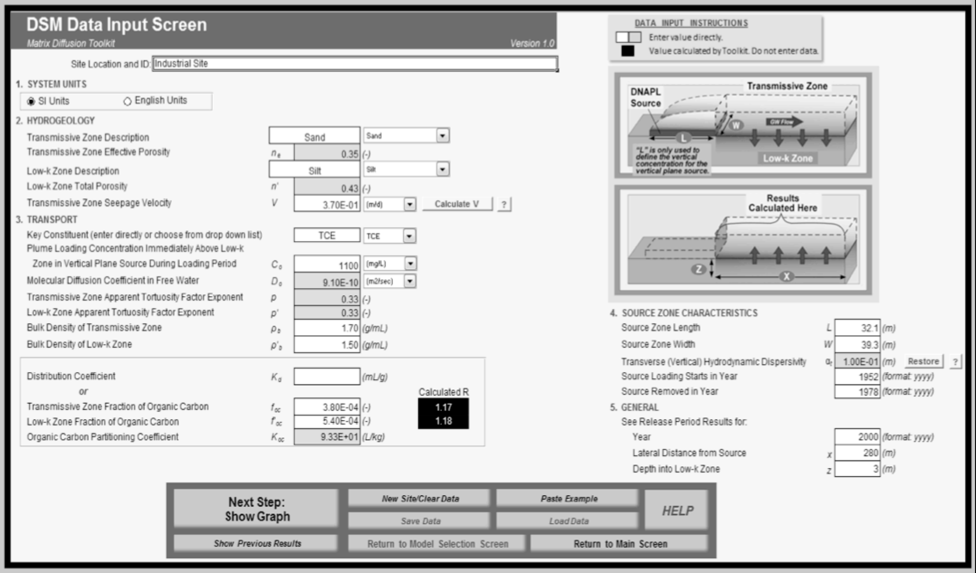
Dandy-Sale Model: *Data Input Screen*



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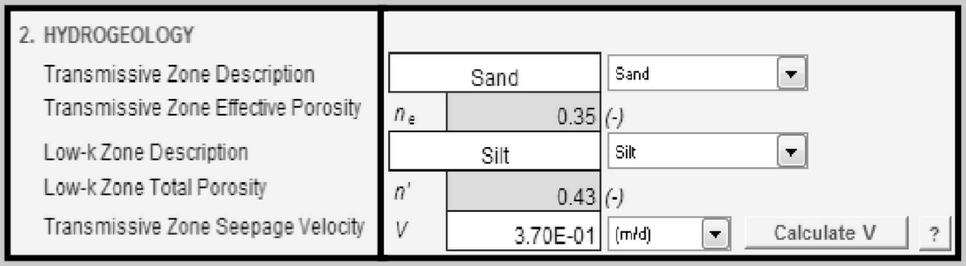
Dandy-Sale Model: *Hydrogeology*



- **Similar to SRM Data Input**
  - Choose from dropdown menu or enter directly
  - Keep Toolkit default or overwrite
  - Enter directly or use Toolkit to calculate value

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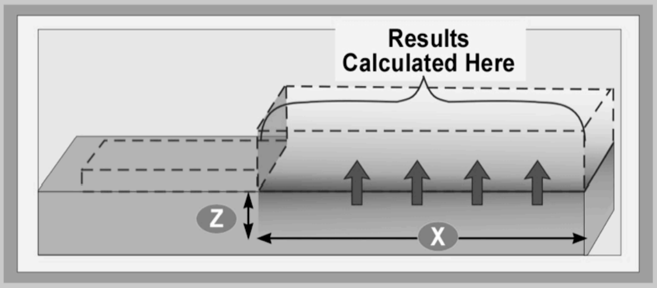
Dandy-Sale Model: *General*



5. GENERAL			
See Release Period Results for:			
Year		2000	*(format: yyyy)*
Lateral Distance from Source	*x*	280	*(m)*
Depth into Low-k Zone	*z*	3	*(m)*

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Dandy-Sale Model: *Outputs*

Low-k Zone

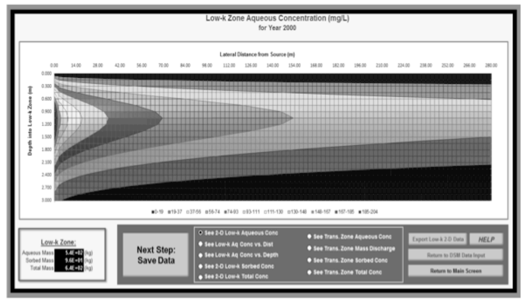
- **2-D aqueous concentration**
- **Aqueous concentration vs. distance**
- **Aqueous concentration vs. depth**
- **2-D sorbed concentration**
- **2-D total concentration**

Transmissive Zone

- **Aqueous concentration**
- **Mass discharge**
- **Sorbed concentration**
- **Total concentration**

Aqueous, Sorbed, and Total Mass

- **Low-k zone**
- **Transmissive zone**



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Road Map

- Introduction
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- **Case Study 1**
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WATER RESOURCES RESEARCH, VOL. 41, W12411, doi:10.1029/2005WR004224, 2005

Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation

Steven W. Chapman and Beth L. Parker

Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada

Received 28 April 2005; revised 18 July 2005; accepted 4 August 2005; published 6 December 2005.

[1] At an industrial site on a sand aquifer overlying a clayey silt aquitard in Connecticut, a zone of trichloroethylene dense nonaqueous phase liquid (DNAPL) at the aquifer bottom was isolated in late 1994 by installation of a steel sheet piling enclosure. In response to this DNAPL isolation, three aquifer monitoring wells located approximately 330 m downgradient exhibited strong TCE declines over the next 2–3 years, from trichloroethylene (TCE) concentrations between 5000 and 30,000 μg/L to values leveling off between 200 and 2000 μg/L. TCE concentrations from analysis of vertical cores from the aquitard below the plume and also from depth-discrete multilevel systems in the aquifer sampled in 2000 were represented in a numerical model. This shows that vertical back diffusion from the aquitard combined with horizontal advection and vertical transverse dispersion account for the TCE distribution in the aquifer and that the aquifer TCE will remain much above the MCL for centuries.

Citation: Chapman, S. W., and B. L. Parker (2005), Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation, *Water Resour. Res.*, *41*, W12411, doi:10.1029/2005WR004224.

1. Introduction

[2] It has long been recognized that DNAPL zones in aquifers cause persistent plumes composed of dissolved phase contaminants [*Schwille*, 1988; *Mackay and Cherry*, 1989]. Decades of experience indicates pump and treat fails to achieve permanent aquifer restoration due to the presence source removal or isolation if low-permeability zones are present within the aquifer, or at the top and/or bottom of the aquifer.

[3] A common situation at contaminated sites is the presence of a DNAPL accumulation zone at the bottom of unconfined sand or gravel aquifers underlain by clayey

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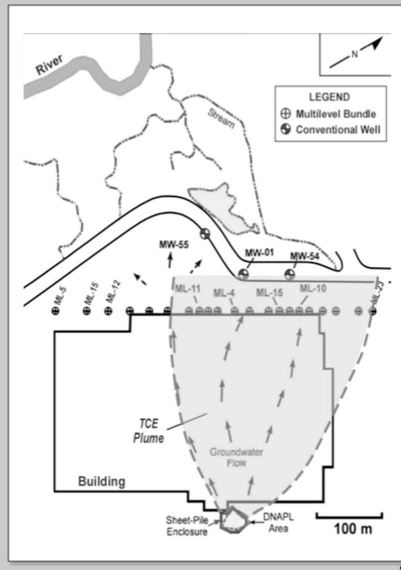
Case Study #1: *Industrial Site, CT*

Site from Chapman and Parker, 2005

- Metal product manufacturing site (1952 – 2001)
- TCE occurs in surficial sandy aquifer
  - overlying a clayey silt aquitard
- TCE DNAPL isolated in 1994 using steel sheet pile enclosure
- Historical industrial pumping resulted in a long-term downward hydraulic gradient across the aquitard
- In 2000, TCE observed in
  - Vertical cores collected from aquitard below plume
  - Depth-discrete multilevel sampling



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Case Study #1: *Industrial Site, CT*

Matrix Diffusion Toolkit used to:

- Estimate effects of diffusion into and from low-k zones
- Both SRM and DSM applied
  - **Step 1:** Initial values entered into the Toolkit
  - **Step 2:** Toolkit outputs compared to field observed TCE

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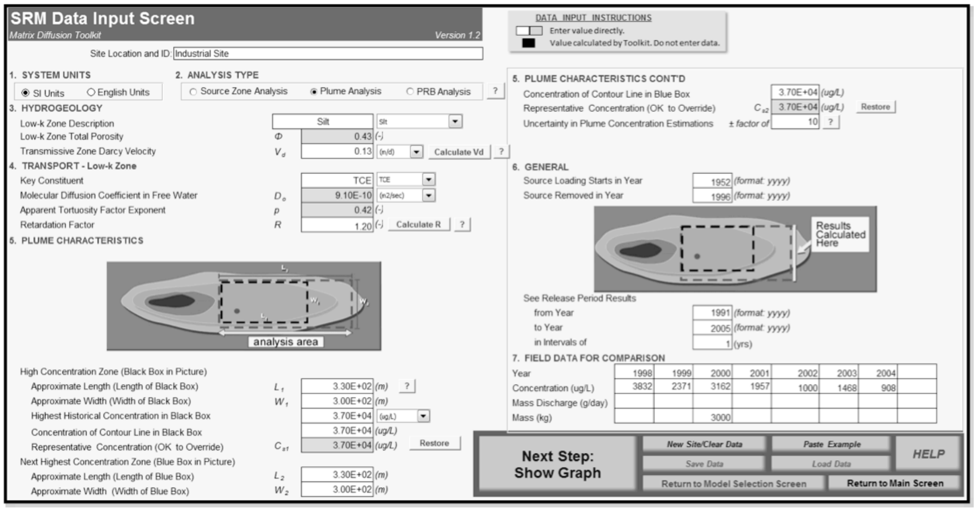
SRM: *Site-specific Parameters*

Parameter	Value
Low-k porosity	0.43
Darcy velocity	0.13 m/d
Retardation factor	1.2
Representative concentration	37,000 ug/L (max observed)
Conc. zone dimensions	330 m x 300 m
Source starts	1952
Source removed	1996 (“effective”)
Mol. Diff. coeff. (Toolkit default)	9.1 x 10^{-10} m^2/sec
App. tort. fac. exp.	0.42

SRM: *Input Screen*



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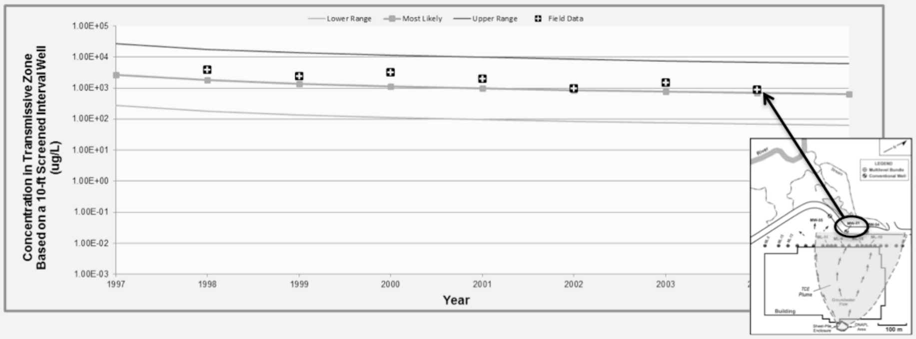
SRM: *Concentration Output*

Time (yr)	1991	1992	1993	1994	1995	1996	1997	1998
Mass Discharge (g/day)	-6.06E+01	-5.98E+01	-5.91E+01	-5.84E+01	-5.77E+01	-5.70E+01	3.22E+02	2.12E+02
Mass (kg)	1.73E+03	1.75E+03	1.77E+03	1.79E+03	1.81E+03	1.83E+03	1.58E+03	1.48E+03
Concentration (ug/L)	n/a	n/a	n/a	n/a	n/a	n/a	2.71E+03	1.78E+03
Plume Magnitude	n/a	n/a	n/a	n/a	n/a	n/a	Mag 7	Mag 7

Time (yr)	1999	2000	2001	2002	2003	2004	2005
Mass Discharge (g/day)	1.63E+02	1.35E+02	1.15E+02	1.01E+02	9.00E+01	8.13E+01	7.42E+01
Mass (kg)	1.42E+03	1.36E+03	1.32E+03	1.28E+03	1.24E+03	1.21E+03	1.18E+03
Concentration (ug/L)	1.37E+03	1.13E+03	9.69E+02	8.49E+02	7.57E+02	6.84E+02	6.24E+02
Plume Magnitude	Mag 7	Mag 7	Mag 7	Mag 7	Mag 6	Mag 6	Mag 6

Note: Negative mass discharge values represent diffusion into the low-k zone from the transmissive zone. Positive values represent diffusion from the low-k zone into the transmissive zone.

What's up with the gap?



Log | Linear

Re-Plot Graph from Year 1996 to Year 2015
(format: yyyy) (format: yyyy)

Update Graph

Restore Original Interval | Restore Original Graph

Next Step: Save Data

See Mass Discharge Results | See Mass Results

Return to SRM Data Input | Export/Print Data Table

Run Advanced Uncertainty Analysis

Return to Main Screen | HELP

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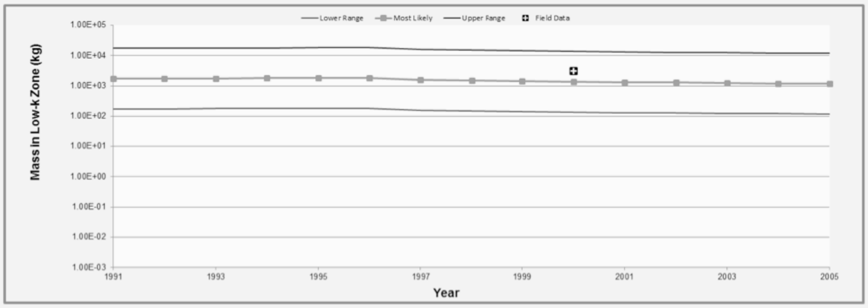
SRM: *Mass in Low-k Zone*

Time (yr)	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Mass Discharge (g/day)	-6.06E+01	-5.98E+01	-5.91E+01	-5.84E+01	-5.77E+01	-5.70E+01	3.22E+02	2.12E+02	1.63E+02	1.35E+02	1.15E+02	1.01E+02	9.00E+01	8.13E+01	7.42E+01
Mass (kg)	1.73E+03	1.75E+03	1.77E+03	1.79E+03	1.81E+03	1.83E+03	1.58E+03	1.48E+03	1.42E+03	1.36E+03	1.32E+03	1.28E+03	1.24E+03	1.21E+03	1.18E+03
Concentration (ug/L)	n/a	n/a	n/a	n/a	n/a	n/a	2.71E+03	1.78E+03	1.37E+03	1.13E+03	9.69E+02	8.49E+02	7.57E+02	6.84E+02	6.24E+02
Plume Magnitude	n/a	n/a	n/a	n/a	n/a	n/a	Mag 7	Mag 7	Mag 7	Mag 7	Mag 7	Mag 7	Mag 6	Mag 6	Mag 6

Note: Negative mass discharge values represent diffusion into the low-k zone from the transmissive zone. Positive values represent diffusion from the low-k zone into the transmissive zone.

What's up with the gap?



Log / Linear

Re-Plot Graph from Year 1996 (format: yyyy) to Year 2015 (format: yyyy)

Update Graph

Restore Original Interval | Restore Original Graph

Next Step: Save Data

See Mass Discharge Results | See Conc Results

Return to SRM Data Input | Export/Print Data Table

Run Advanced Uncertainty Analysis

Return to Main Screen | HELP

SRM: *Output*

Time (yr)	2535	
Mass Discharge (g/day)	6.27E-01	
Mass (kg)	2.57E+02	2
Concentration (ug/L)	5.28E+00	5.
Plume Magnitude	Mag 4	

4	2555	2556	2557
1	5.95E-01	5.93E-01	5.92E-01
2	2.52E+02	2.52E+02	.52E+02
	5.01E+00	4.99E+00	.98E+00
	Mag 4	Mag 4	Mag 4

- **Estimate of Time to Clean**
  - > 500 years to reach MCL of 5 ug/L

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Case Study #1: *SRM Key Points*

- Matrix Diffusion Toolkit reproduced observed concentrations within an order of magnitude
- No adjustment needed for Toolkit default parameters
- Matrix Diffusion Toolkit reproduced observed mass in low-k zone within an order of magnitude
- SRM modeling estimates >500 yr to reach MCL of 5 ug/L
  - Compares well to Chapman and Parker's more sophisticated modeling that indicated concentrations "will remain much above the MCL for centuries."
- Typical advection-dispersion type model would show no mass in the low-k unit, a fundamentally incorrect conceptual model

MCL = Maximum Contaminant Level

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Road Map

- Introduction
- Matrix Diffusion Background
- Options for Modeling Matrix Diffusion
- Introduction to MDT – Square Root Model
- Dandy-Sale Model in the MDT
- Case Study 1
- **Case Study 2**
- Wrap-up

Case Study #2: *DSM Modeling*

- Same site as Case Study #1
- DSM used to estimate effects of diffusion into and from low-k zones
- Estimate groundwater concentrations in the low-k zone
  - Source area
  - Plume area
- Modeling approach:
  - **Step 1:** Initial values entered into the Toolkit
  - **Step 2:** Toolkit outputs compared to field observed TCE values

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DSM: *Site-specific Parameters*

Parameter	Value
Low-k (silt) porosity	0.43
Trans zone (sand) porosity	0.35
Seepage velocity	0.37 m/d
Mean concentration	1100 mg/L (TCE solubility)
Trans zone bulk density	1.7 g/mL
Low-k zone bulk density	1.5 g/mL

DSM: *Site-specific Parameters*

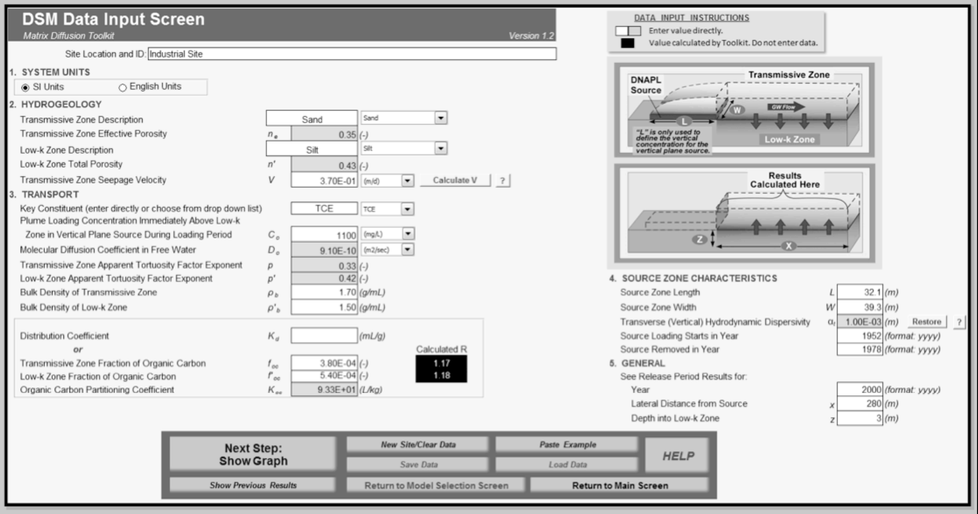
Parameter	Value
Trans zone foc	0.038%
Low-k zone foc	0.054%
Conc. zone dimensions	32 m x 39 m
Source starts	1952
Source removed	1997

foc = fraction organic carbon

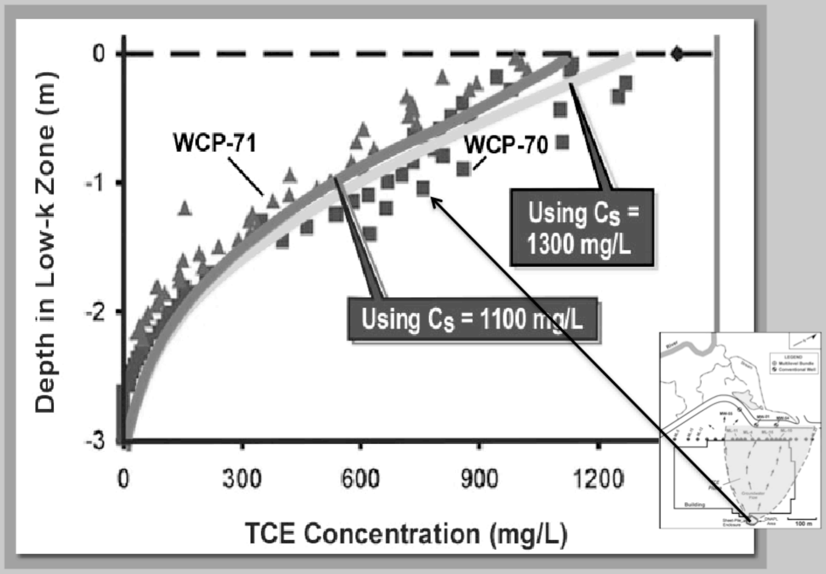
DSM: *Toolkit Default Parameters*

Parameter	Value
Mol. diff. coeff.	9.1×10^{-10} m^2/sec
Trans zone app. tort. fac. exp.	0.33
Low-k zone app. tort. fac. exp.	0.42
Organic carbon part. coeff.	93.3 L/kg
Coeff. Transverse hyd. disp	0.16

Source Evaluation



Comparison of DSM with Observed



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Case Study #2: *Key Points*

- **Matrix Diffusion Toolkit reproduced observed concentrations reasonably well**
- **Comparison using max reported source concentration of 1300 mg/L**
  - **Also reproduced observed concentrations reasonably well**
- **No adjustment needed for Toolkit default parameters**

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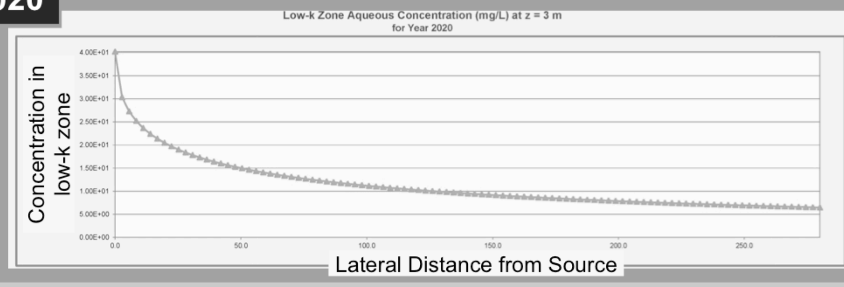
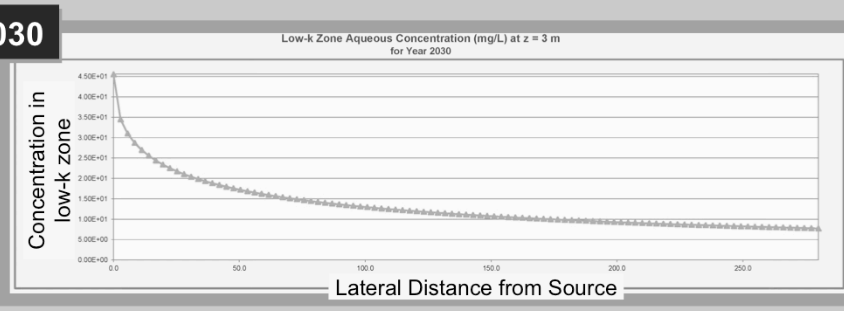
Future Predictions

2020



2030



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Road Map

- Introduction
- Matrix Diffusion Background
- Options for Modeling Matrix Diffusion
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- Case Study 1
- Case Study 2
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Which model should I use: SRM or DSM?

I Want the Following Information:	Which Model?	Output
1. Mass Discharge (sometimes called mass flux) data from a low-k zone to a transmissive zone in units of grams per day versus time (both past and future).	Square Root **OR** Dandy-Sale	Mass discharge vs. time plot
2. How much mass could be present in low-k zones at my site?	Square Root **OR** Dandy-Sale	Mass in low-k zone vs. time plot

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Which model should I use: SRM or DSM?

I Want the Following Information:	Which Model?	Output
3. If I install a permeable reactive barrier, will I have trouble achieving downgradient cleanup standards?	Square Root **OR** Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot
4. I want to know the concentration vs. depth profile in a low-k zone.	Dandy-Sale	Concentration* vs. depth plot or Concentration vs lateral distance plot

* Concentration assuming a monitoring well with a 10-foot screened interval (this cannot be changed in the model)

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Which model should I use: SRM or DSM?

I Want the Following Information:	Which Model?	Output
5. If I remove all the DNAPL in a source zone, is there a chance I'll still be above MCLs? How much longer might I have to wait for a source zone to achieve MCLs after the DNAPL is all gone?	Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot

* Concentration assuming a monitoring well with a 10-foot screened interval (this cannot be changed in the model)

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Which model should I use: SRM or DSM?

I Want the Following Information:	Which Model?	Output
6. I want to make sure the matrix diffusion model accounts for contaminant concentrations in the transmissive zone when calculating the release for low-k zones?	Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot

* Concentration assuming a monitoring well with a 10-foot screened interval (this cannot be changed in the model)

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Which model should I use: SRM or DSM?

I Want the Following Information:	Which Model?	Output
7. I want to account for the travel time of the plume in the transmissive zone so that the loading period for the downgradient low-k zones starts later than the loading period for the near-source low-k zones. (This is more important for plumes, such as plumes with long residence times, > 20 years).	Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot

* Concentration assuming a monitoring well with a 10-foot screened interval (this cannot be changed in the model)

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Model Demo