Thank you for signing in early

The webinar will begin promptly at
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SERDP and ESTCP Webinar Series

The webinar will begin promptly at 12:00 pm ET, 9:00 am PT

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“Long Term Monitoring Issues at Chlorinated Solvent Sites”

April 21, 2016

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions

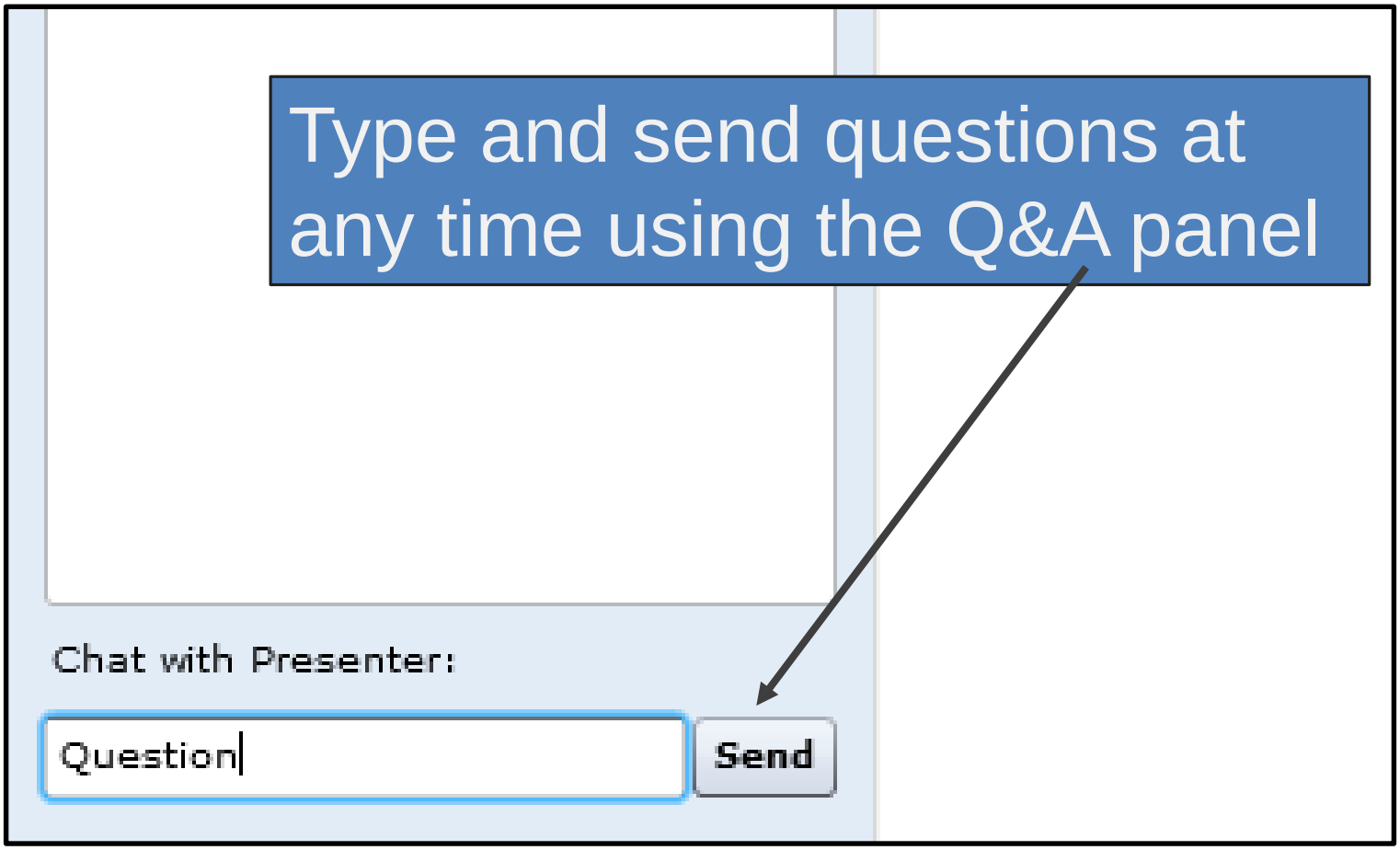
Jennifer Nyman, Ph.D., P.E.
Webinar Facilitator

SERDP DOD • EPA • DOE | ESTCP

Agenda

- **Webinar Logistics**
  Dr. Jennifer Nyman, Geosyntec Consultants (5 minutes)
- **Overview of SERDP and ESTCP**
  Dr. Andrea Leeson, SERDP and ESTCP (5 minutes)
- **A Practical Approach for Modeling Matrix Diffusion Effects in Low Permeability Zones**
  Dr. Ron Falta, Clemson University (25 minutes + Q&A)
- **Methods to Minimize and Manage Variability in Groundwater Monitoring Results**
  Ms. Poonam Kulkarni and **Dr. Thomas McHugh**, GSI Environmental Inc. (25 minutes + Q&A)
- **Final Q&A session**

How to Ask Questions



In Case of Technical Difficulties

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  - Click the mute/connect button
  - Wait 3-5 seconds
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- Submit a question using the chat box

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Environmental Restoration
Program Manager

SERDP

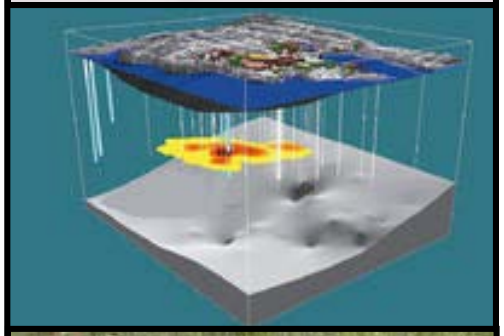
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

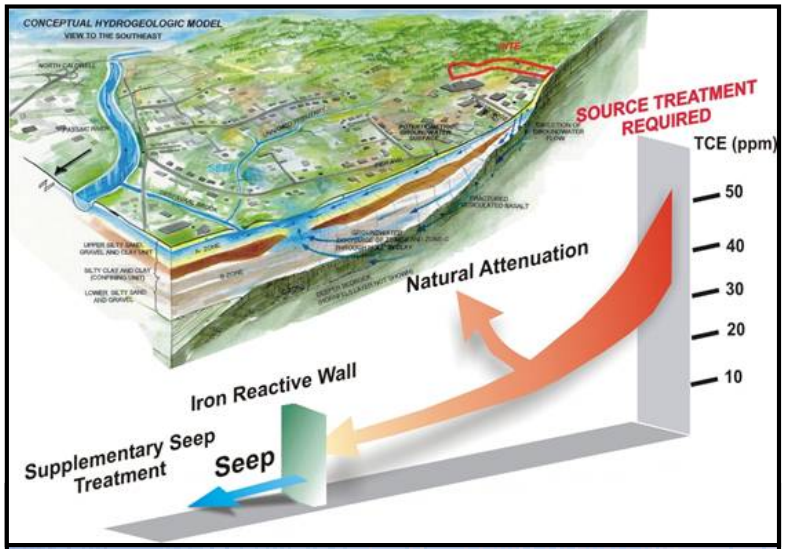
Program Areas

1. Energy and water
2. Environmental restoration
3. Munitions response
4. Resource conservation and climate change
5. Weapons systems and platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



SERDP and ESTCP Webinar Series

DATE	Topics
May 05, 2016	Cost Effective and Resilient Building-Scale Microgrid Solutions for Increased Energy Security
May 19, 2016	Quality Assurance Project Plan (QAPP) for Geophysical Classification Investigations – Part 1
June 02, 2016	Insensitive Munitions
June 16, 2016	Quality Assurance Project Plan (QAPP) for Geophysical Classification Investigations – Part 2
June 30, 2016	Geophysics 101 – Realistic Expectations for Geophysics When Used for Site Characterization and Remediation Monitoring
July 14, 2016	Remote Methods for Water Conservation
July 28, 2016	An Environmentally Acceptable Alternative for Fast Cook-off Testing, Demonstration, Validation and Implementation Efforts

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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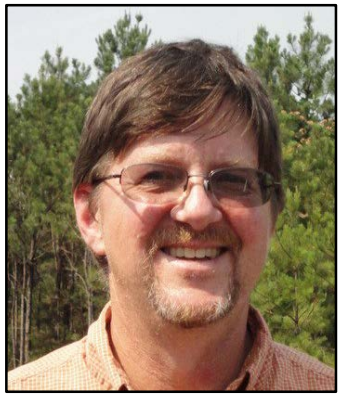
A Practical Approach for Modeling Matrix Diffusion Effects in Low Permeability Zones

Ron Falta, Ph.D.
Clemson University



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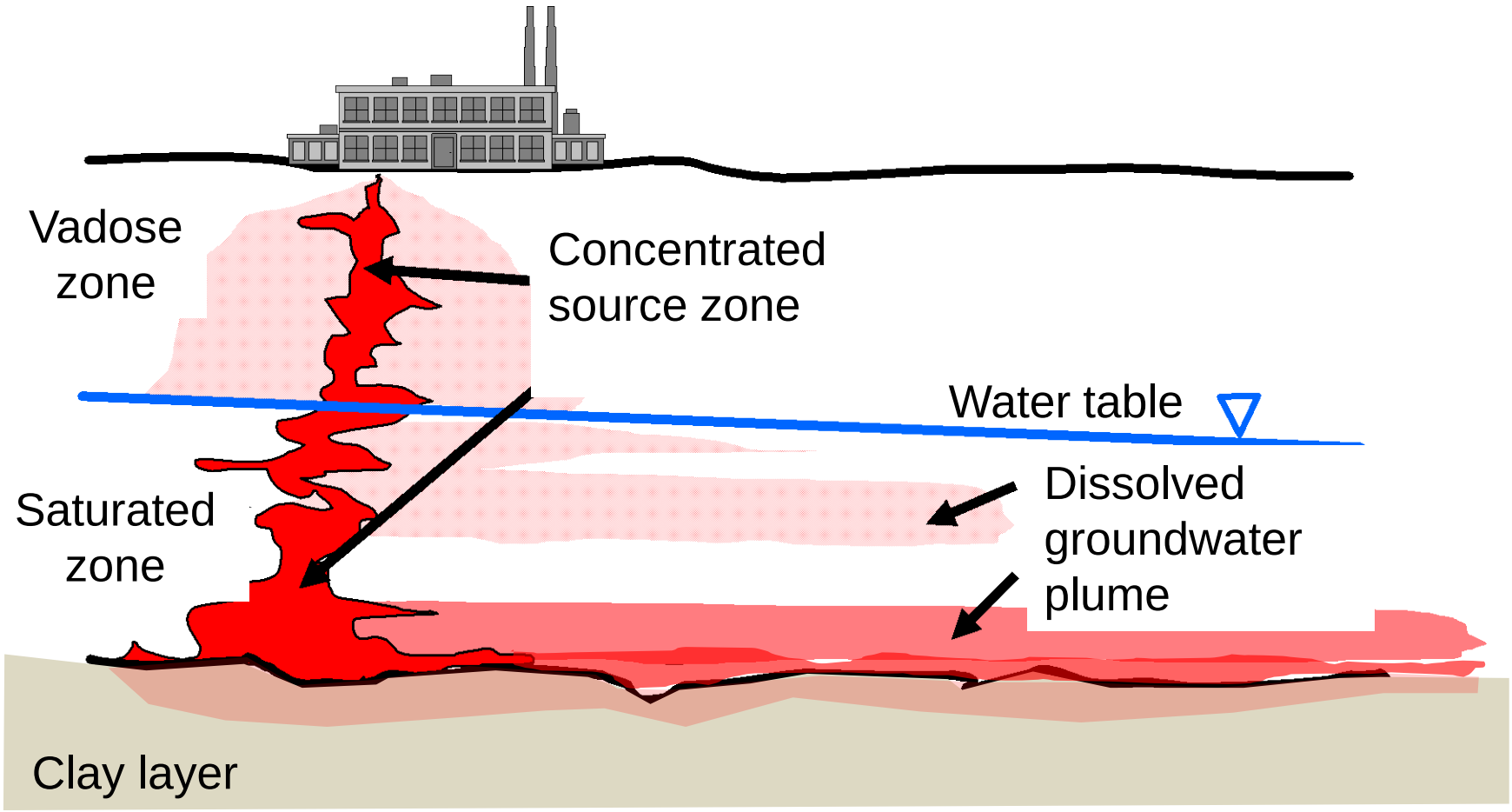
Agenda

- Introduction to matrix diffusion
- Current modeling approaches
- New high resolution semi-analytical method used in REMChlor-MD
- Matrix diffusion simulations in aquitards and fractured rock
- Summary

Project Objective and Benefits

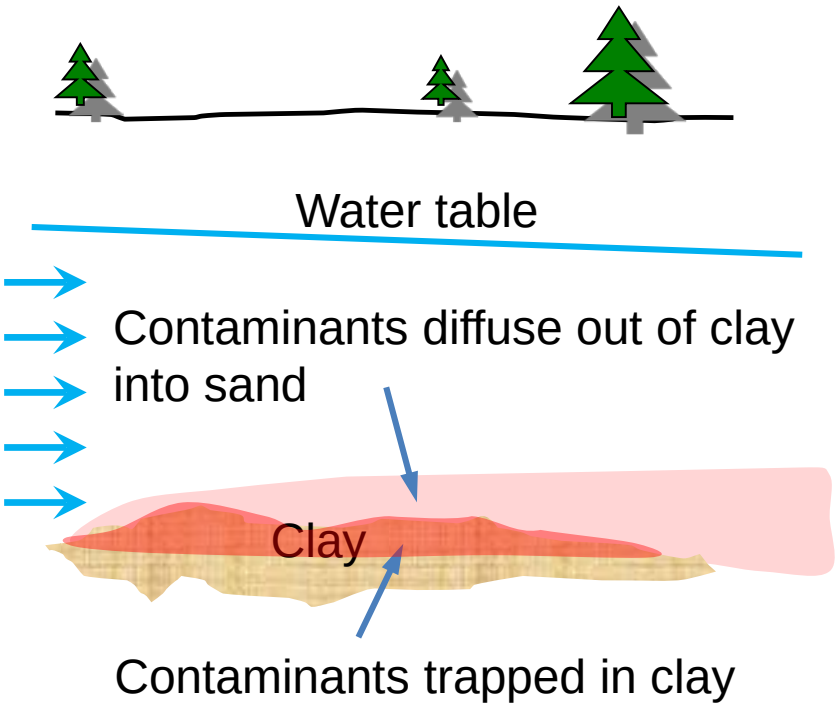
- Develop a new groundwater source/plume remediation screening model (REMChlor-MD) that considers matrix diffusion in the plume
- Enable site managers and stakeholders to assess likely impacts of source and plume remediation schemes (including natural attenuation)
- Improve decision-making to reduce costs and ensure effective use of limited resources for site remediation

Typical Chlorinated Solvent Contamination Scenario



Matrix Diffusion in Low K Zones

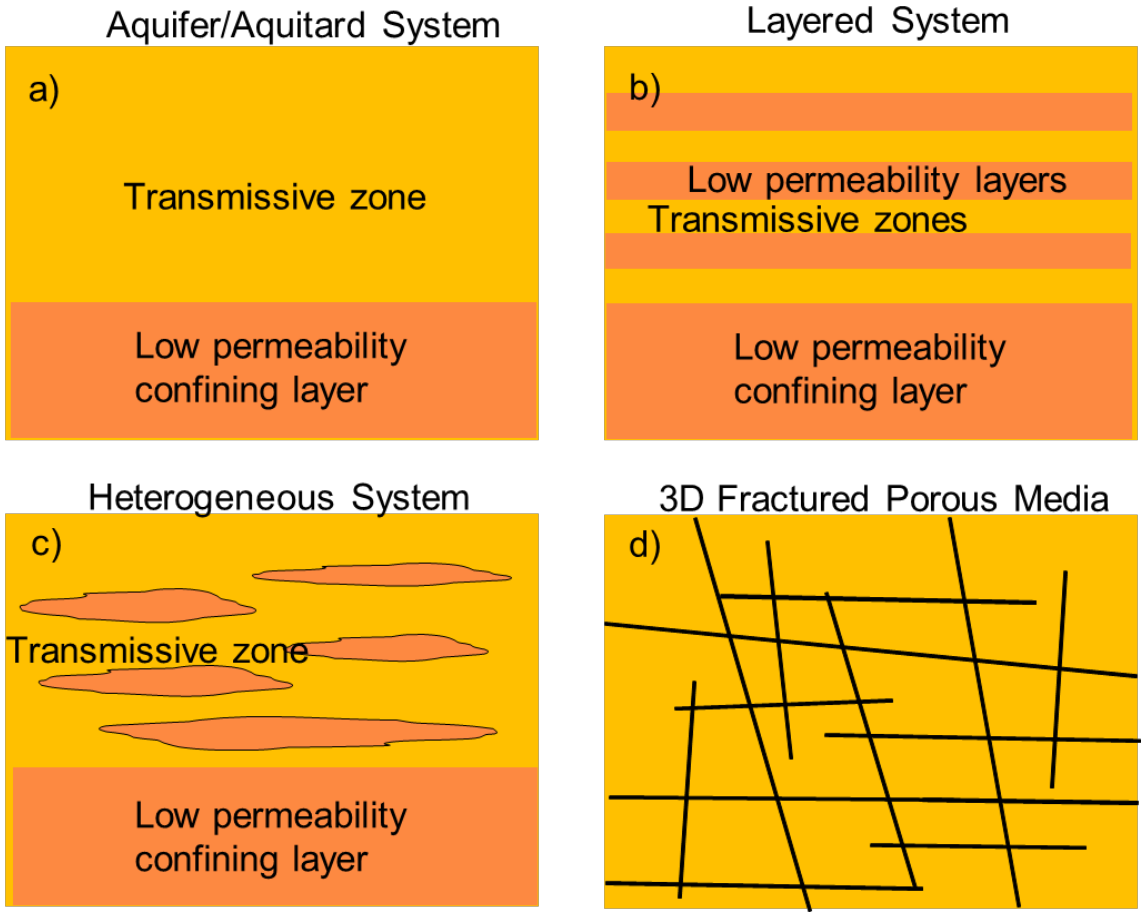
- Over time, dissolved contaminants in the plume can diffuse into clay zones
- After sandy zones are remediated, contaminants diffuse out of the clays, contaminating the groundwater again
- Back-diffusion process may last for decades to centuries*



** Chapman, S.W., and B.L. Parker (2005)*
Parker, B.L., S.W. Chapman, and M.A. Guilbeault (2008)

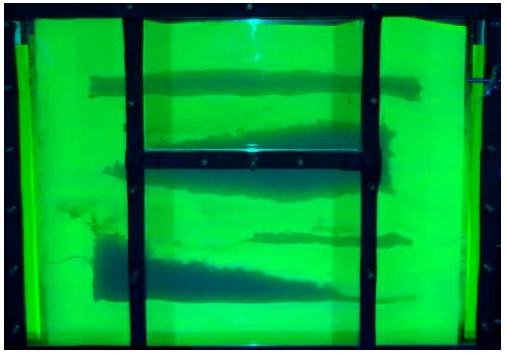
Matrix Diffusion

- Simulating matrix diffusion in these types of sites is very difficult with current models

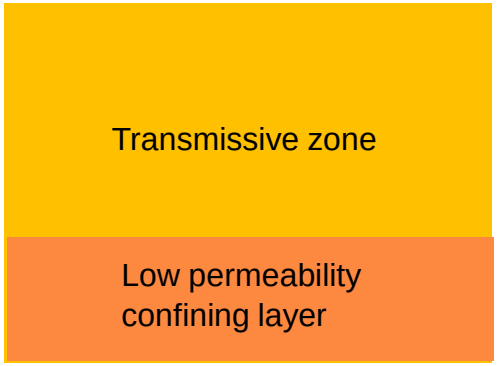


Numerical Models Can Simulate Matrix Diffusion Using High Resolution Grids

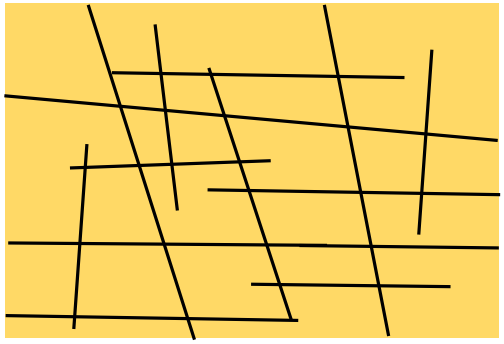
Examples of 2D models (Doner, 2008)



Chapman et al., 2012



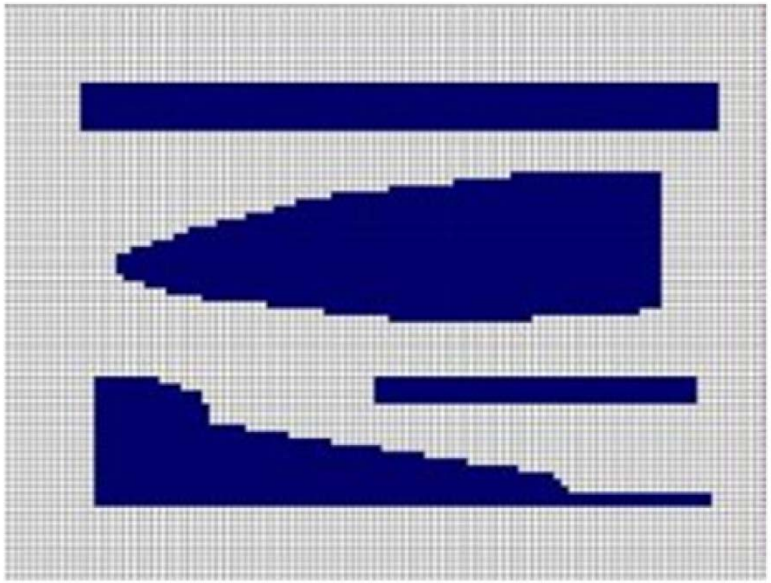
Parker et al., 2008



Chapman and Parker, 2013

“High Resolution” Method may not be Practical for 3-D Field Scale Simulations

- Matrix diffusion is controlled by gradients at the millimeter to centimeter range
- Field scale gridblock sizes are on the order of tens of centimeters to several meters
- Key matrix diffusion processes occur at the sub-gridblock scale



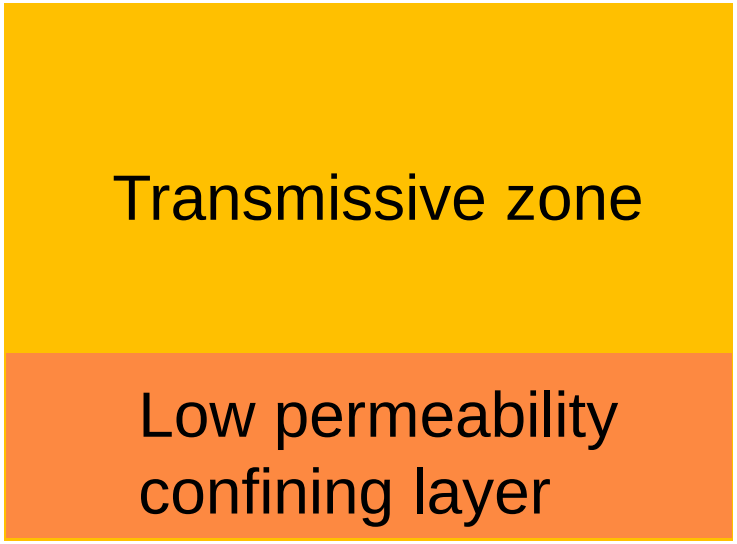
From Chapman et al., 2012

New Model: REMChlor-MD

- Screening level source/plume remediation model based on REMChlor framework
- Simple flow field (like Biochlor), but includes advection, dispersion, retardation and first-order decay with daughter products
- Source and plume remediation are independent and occur at different times and locations
- Key difference with REMChlor and Biochlor is the addition of matrix diffusion in the plume
- Matrix diffusion is modeled using a new semi-analytical technique (the rest of this talk)

Semi-Analytical Heat Conduction Method (Vinsome and Westerveld, 1980)

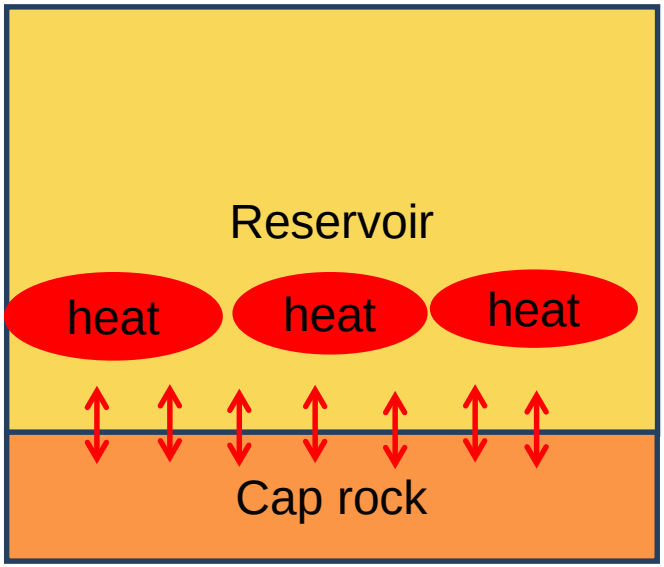
- Originally developed to calculate conductive heat flux from a reservoir into caprock
- Represents vertical temperature profile below each reservoir gridblock as an analytical function with two adjustable parameters: p and q
- Find algebraic expressions for p and q by satisfying the differential equation for heat conduction
- Parameters are updated at each time-step of a numerical simulation



$$T(z,t) = \left(T_{aq}(t) + pz + qz^2\right)e^{-z/d}$$

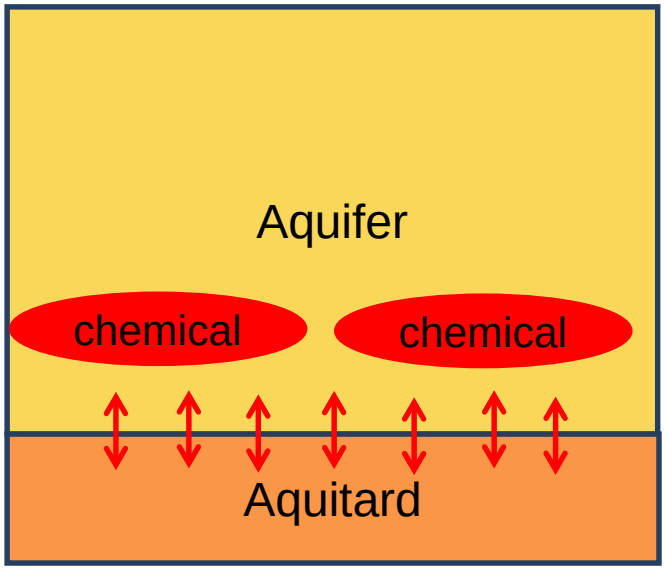
Adapt Method to Chemical Diffusion with First Order Decay

Heat conduction



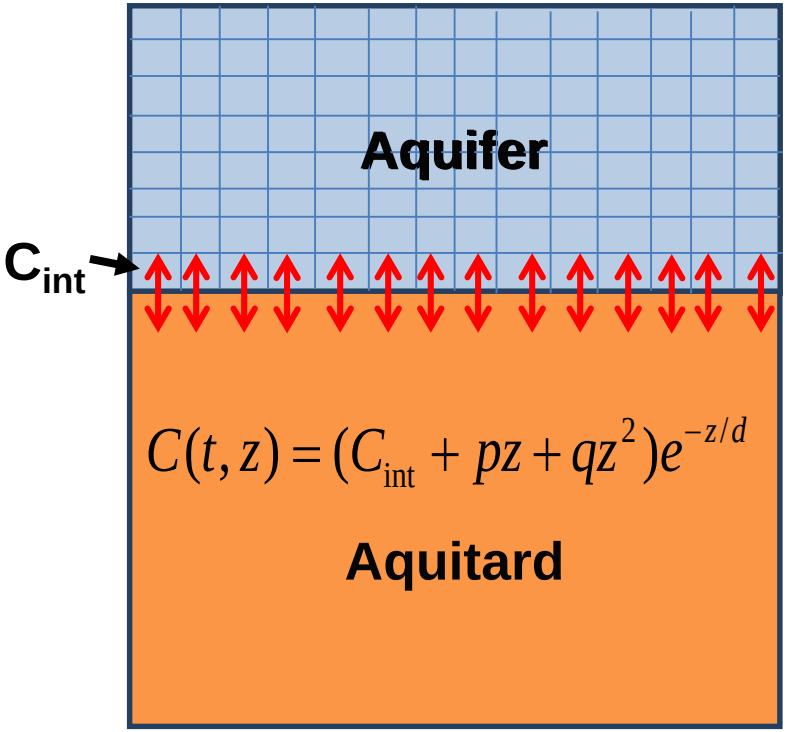
$$\rho C_r \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2}$$

Chemical diffusion



$$R \frac{\partial C}{\partial t} = \tau D_w \frac{\partial^2 C}{\partial z^2} - \lambda C$$

Semi-Analytical Method: Aquifer/ Aquitard Case

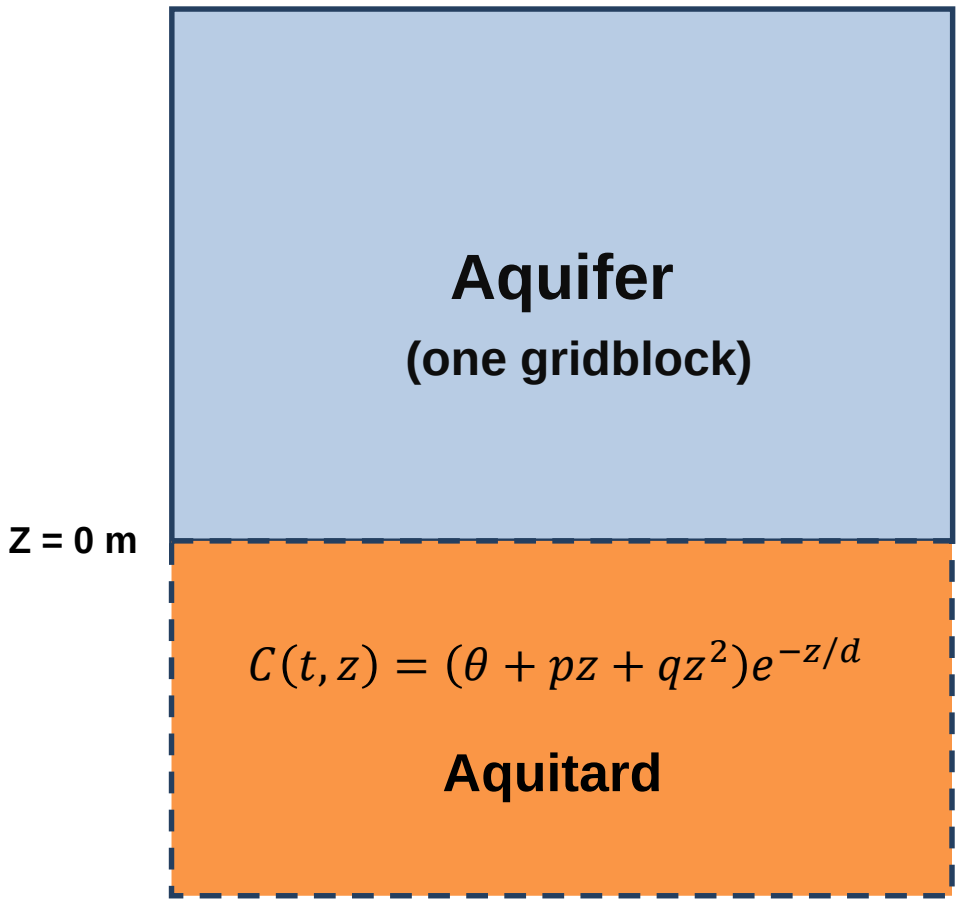


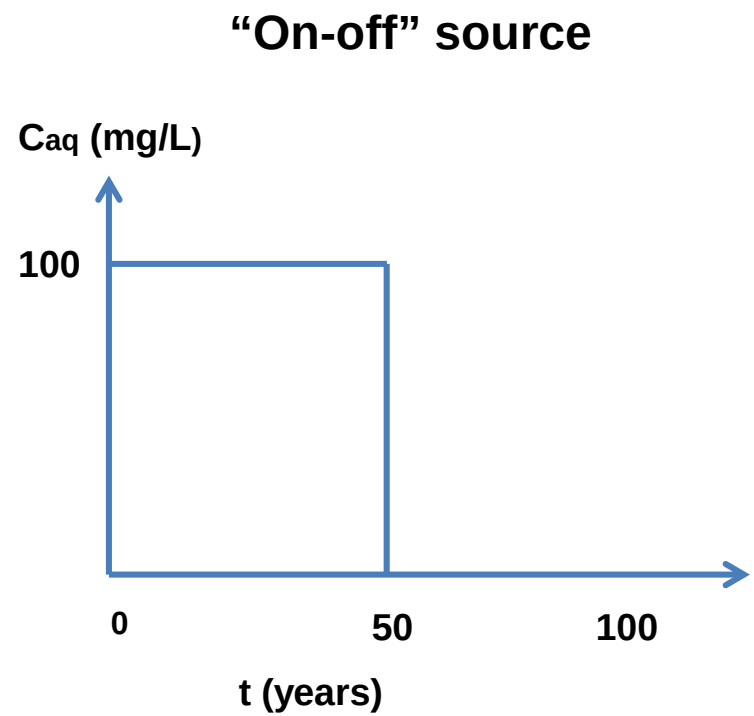
- Numerical modeling: Discretize only the aquifer
- C(t,z) = trial function approximating the concentration in low K zone adjacent to gridblock
- C_{int} = concentration in gridblock adjacent to aquitard at current time-step
- p, q = variable parameters determined by mass balance constraints
- d = time-dependent diffusion distance, $\frac{\sqrt{\tau D_w t / R}}{2}$

Determining “p” and “q” is Key Step

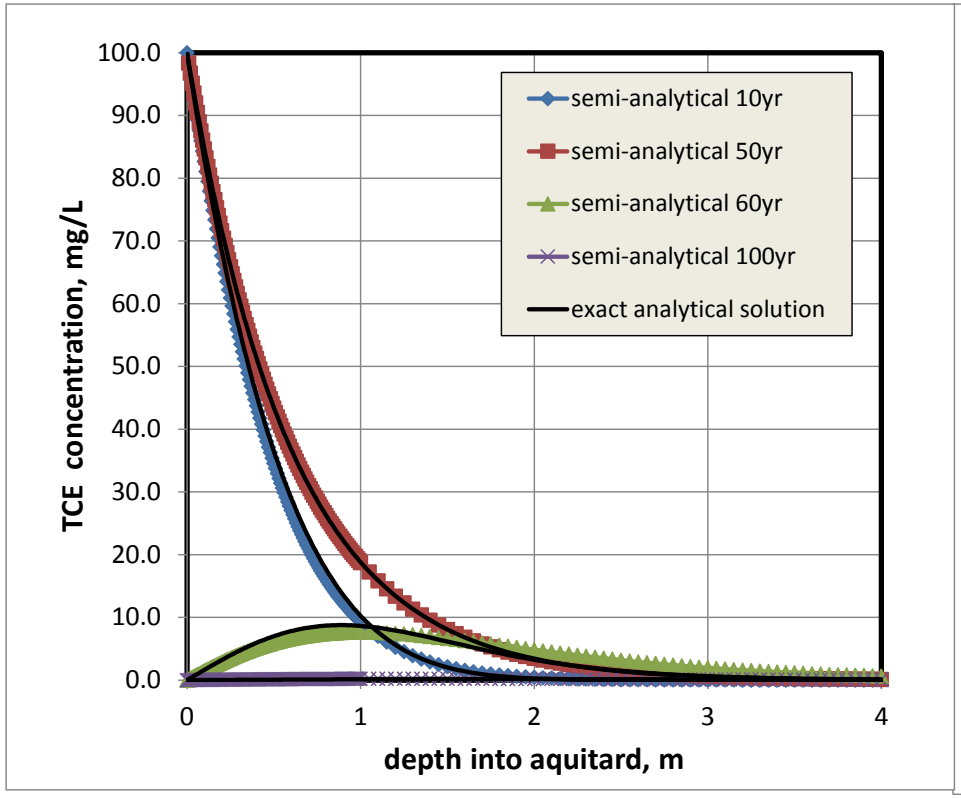
- Use two constraints
  - Differential equation for transient diffusion with reactions is exactly satisfied at the interface
  - Rate of change of mass in the low K zone obeys conservation of mass
- Exact form of p and q depend on the diffusion geometry and chemical reactions considered

Test Semi-Analytical Method Using Only One Gridblock

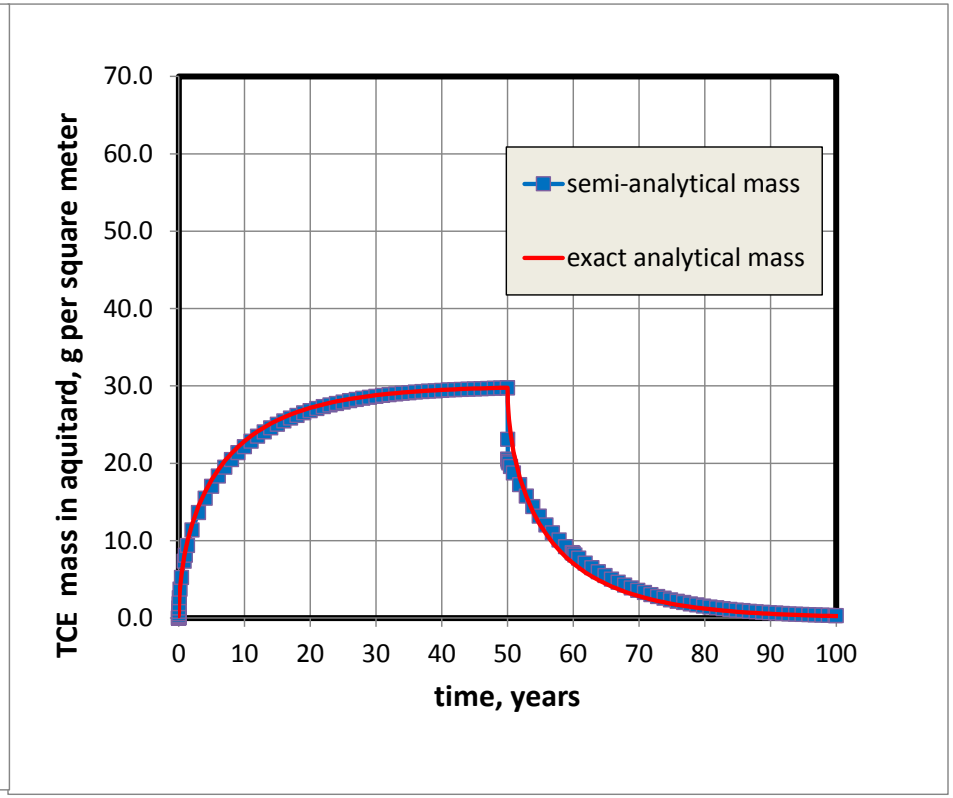




Case with 10-Year Half-Life in Aquitard



TCE concentration profiles in aquitard at different times



TCE mass in aquitard at different times

Solid lines are exact solutions for this problem. Simulation took 2/100 of a second

Tested with Two-Layer Dandy-Sale Solution (Sale et al., 2008)

DSM Data Input Screen

Matrix Diffusion Toolkit — *Version 1.2*

Site Location and ID: Industrial Site

1. SYSTEM UNITS

◉ SI Units ○ English Units

2. HYDROGEOLOGY

Transmissive Zone Description		Sand	Sand	
Transmissive Zone Effective Porosity	n_e	0.35	(-)	
Low-k Zone Description		Silt	Silt	
Low-k Zone Total Porosity	n'	0.45	(-)	
Transmissive Zone Seepage Velocity	V	3.70E+00	(m/d)	Calculate V ?

3. TRANSPORT

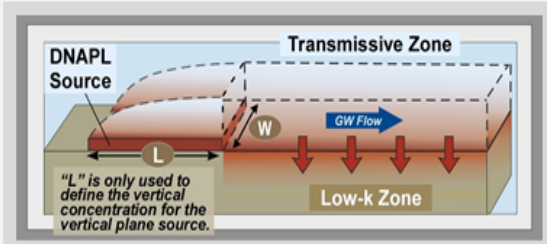
Key Constituent (enter directly or choose from drop down list)		TCE	TCE
Plume Loading Concentration Immediately Above Low-k Zone in Vertical Plane Source During Loading Period	C_o	1100	(mg/L)
Molecular Diffusion Coefficient in Free Water	D_o	9.10E-10	(m2/sec)
Transmissive Zone Apparent Tortuosity Factor Exponent	p	0.33	(-)
Low-k Zone Apparent Tortuosity Factor Exponent	p'	0.42	(-)
Bulk Density of Transmissive Zone	ρ_b	1.70	(g/mL)
Bulk Density of Low-k Zone	ρ'_b	1.50	(g/mL)

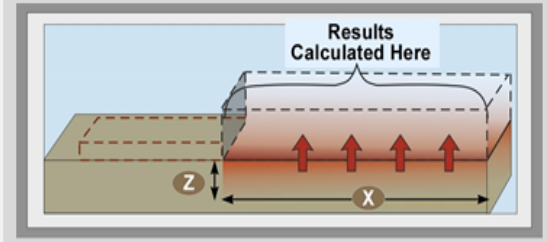
				Calculated R
Distribution Coefficient	K_d		(mL/g)	
or				
Transmissive Zone Fraction of Organic Carbon	f_{oc}	3.80E-04	(-)	1.17
Low-k Zone Fraction of Organic Carbon	f'_{oc}	5.40E-04	(-)	1.17
Organic Carbon Partitioning Coefficient	K_{oc}	9.33E+01	(L/kg)	

DATA INPUT INSTRUCTIONS

Enter value directly.

Value calculated by Toolkit. Do not enter data.





4. SOURCE ZONE CHARACTERISTICS

Source Zone Length	L	40	(m)	
Source Zone Width	W	40	(m)	
Transverse (Vertical) Hydrodynamic Dispersivity	α_t	1.00E-03	(m)	Restore
Source Loading Starts in Year		1990	(format: yyyy)	
Source Removed in Year		2040	(format: yyyy)	

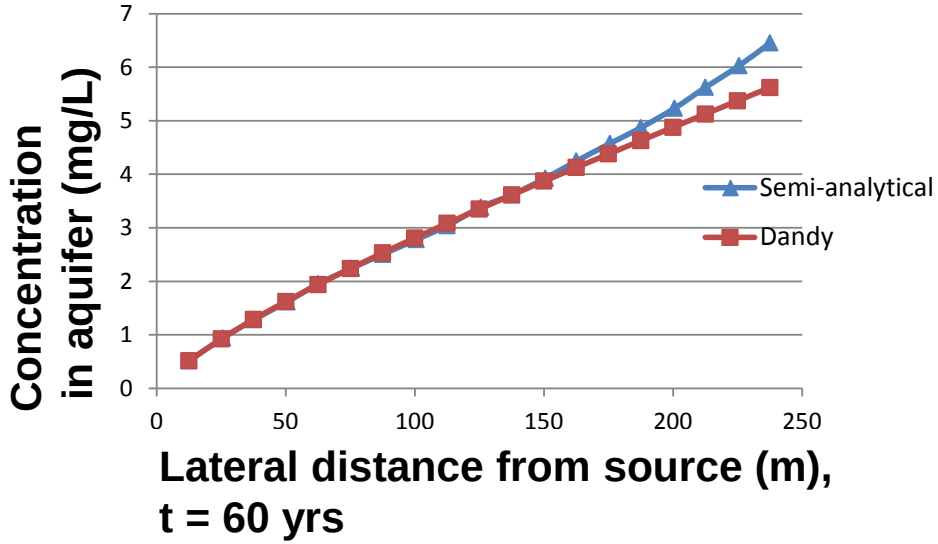
5. GENERAL

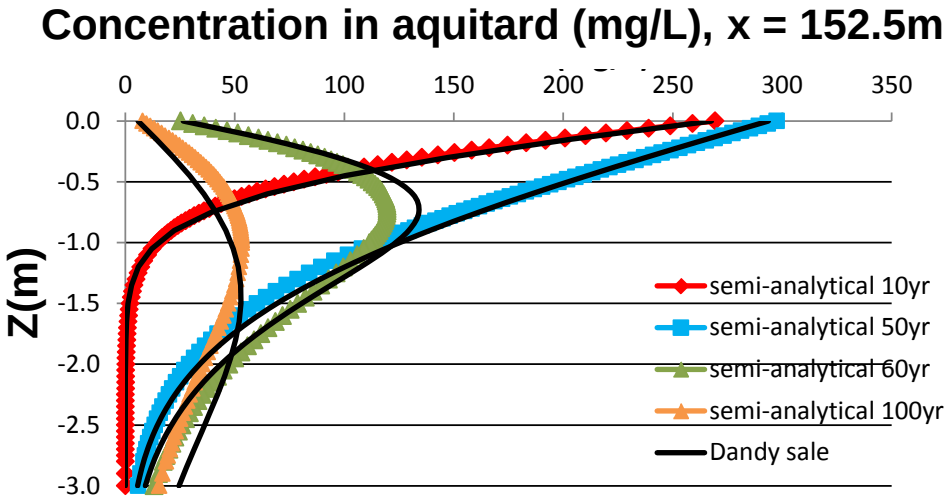
See Release Period Results for:

Year		2040	(format: yyyy)
Lateral Distance from Source	x	250	(m)
Depth into Low-k Zone	z	3	(m)

Testing Two-Layer Solution

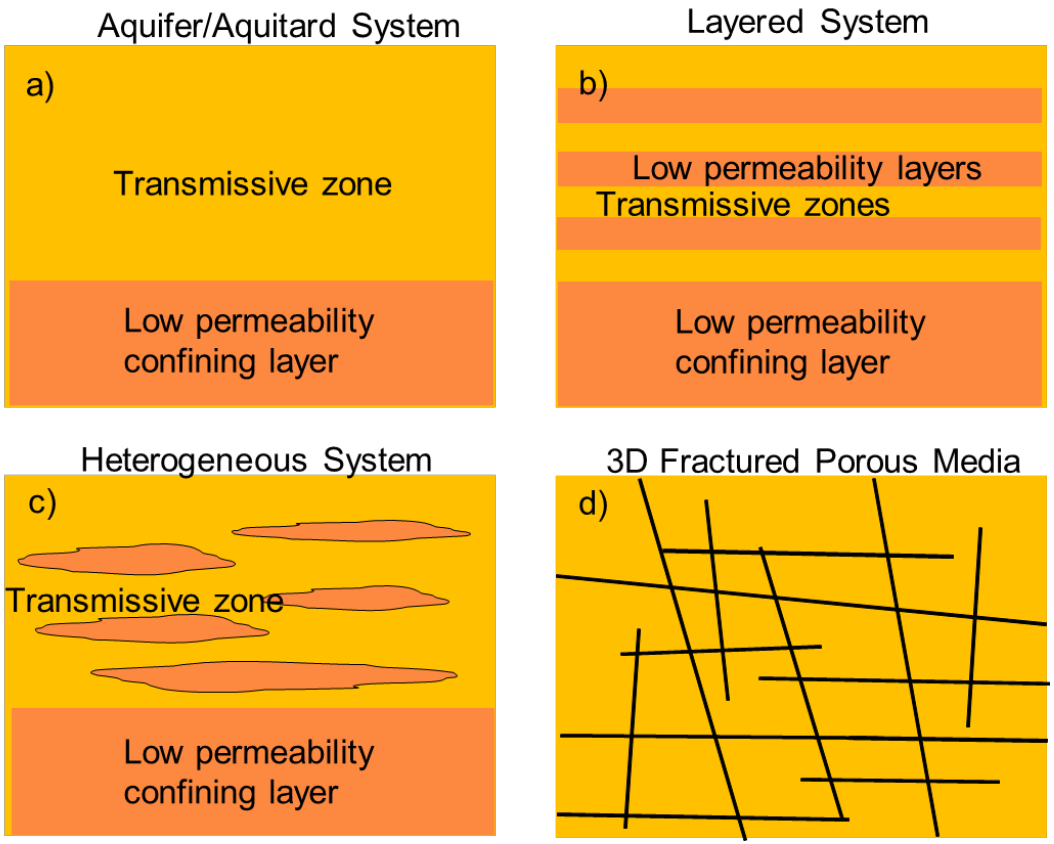
- 2D cross-section model
- Semi-analytic method used for aquitard
- Simulated DNAPL source at bottom of aquifer
- Source removed at 50 years followed by period of back diffusion





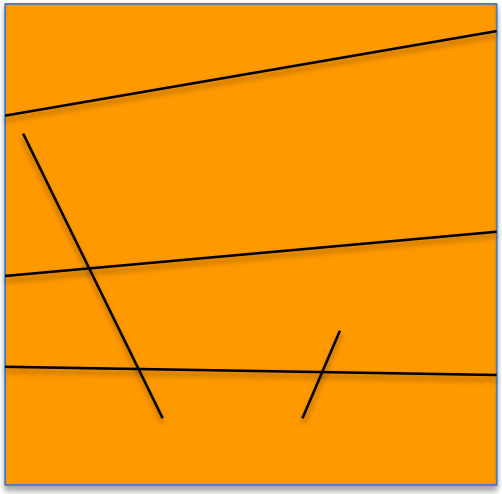
Generalized Method Can Apply to Heterogeneous or Fractured System

- Modified semi-analytical approach to apply to embedded gridblock heterogeneities (layers, lenses, fractured rock)
- Allowed for coupled parent-daughter decay reactions in matrix (PCE-TCE-DCE-VC)



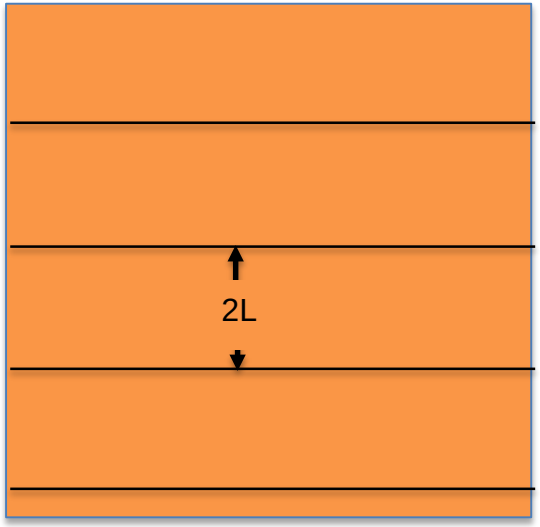
Testing Matrix Diffusion in Fractured Rock

- "Worst case" for matrix diffusion due to small volume of fractures and large surface area
- Exact analytical solution called CRAFLUSH is available for the case of parallel fractures (Sudicky and Frind, 1982)
- Analytical solution assumes 1D advection-dispersion-retardation-decay in fracture coupled with perpendicular diffusion and decay in matrix



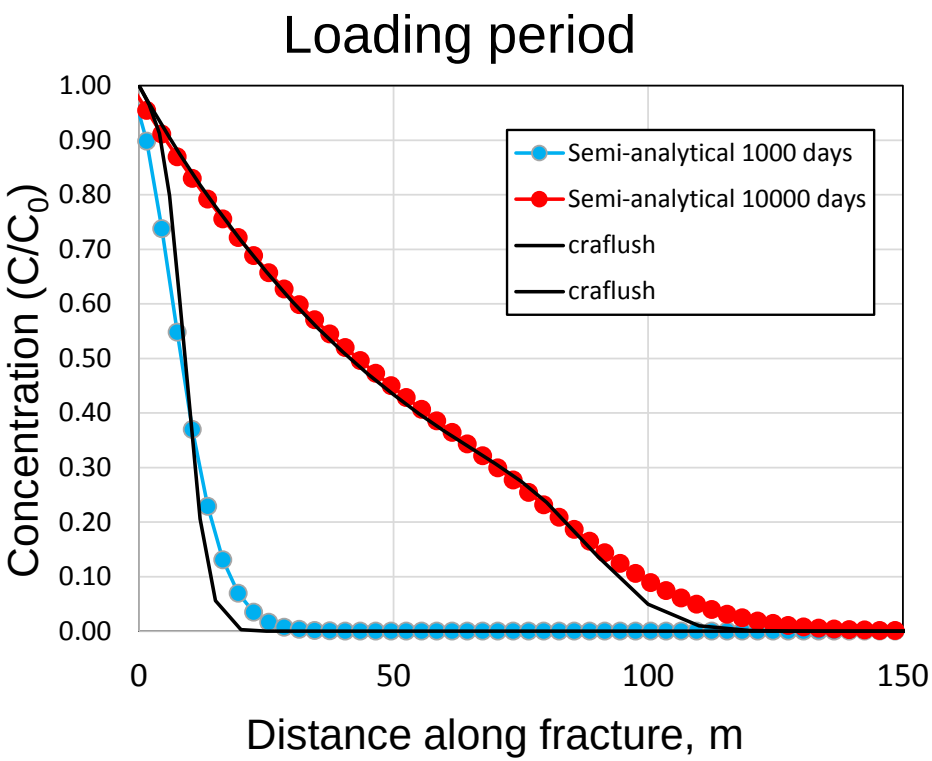
Fractured Rock Matrix Diffusion Test Case

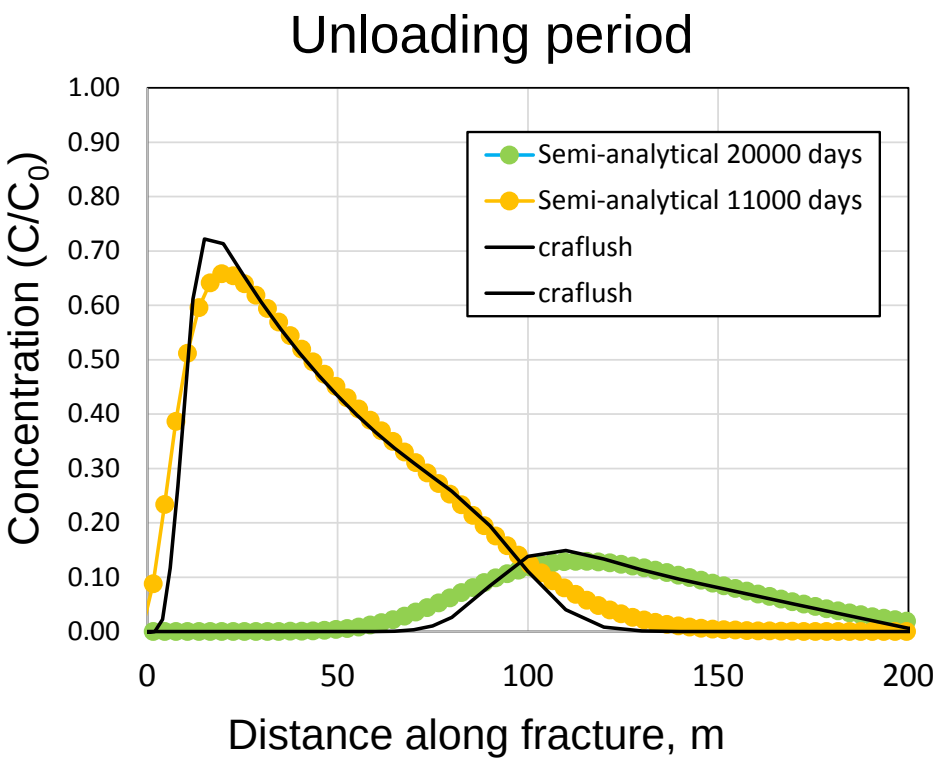
- Fracture spacing (2L) of 0.1 m
- Fracture aperture of 100 µm
- First order decay in both fracture and matrix with half-life of 12.35 years
- Velocity in fracture is 0.1 m/d
- Introduce contaminant for 10,000 days, then follow with clean water for 10,000 days
- Without matrix diffusion, the solute would travel 1000m in 10,000 days, and would be flushed out by clean water



Fractured Rock Matrix Diffusion Test Case

- Matrix diffusion from parallel fractures with a fracture spacing of 0.1 m





Summary

- Screening-level model called REMChlor-MD developed for source/plume remediation that includes matrix diffusion
- Tool is designed to allow site managers and stakeholders to quickly assess impacts of source and plume remediation schemes (including natural attenuation)
- Model will include graphical user interface (similar to Biochlor and Matrix Diffusion Toolkit) and a user's guide
- Web-based training, FREE public distribution of code

Acknowledgments

ESTCP Project ER-201426 Team

- Chuck Newell, GSI Environmental Inc., Houston, TX
- Shahla Farhat, GSI Environmental Inc., Houston, TX
- Kira Lynch, US EPA Region 10 ORD, Seattle, WA

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201426/ER-201426

Speaker Contact Information

faltar@clemson.edu; 864-656-0125

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Q&A Session 1

SERDP DOD • EPA • DOE | ESTCP

Methods to Minimize and Manage Variability in Groundwater Monitoring Results – Part I

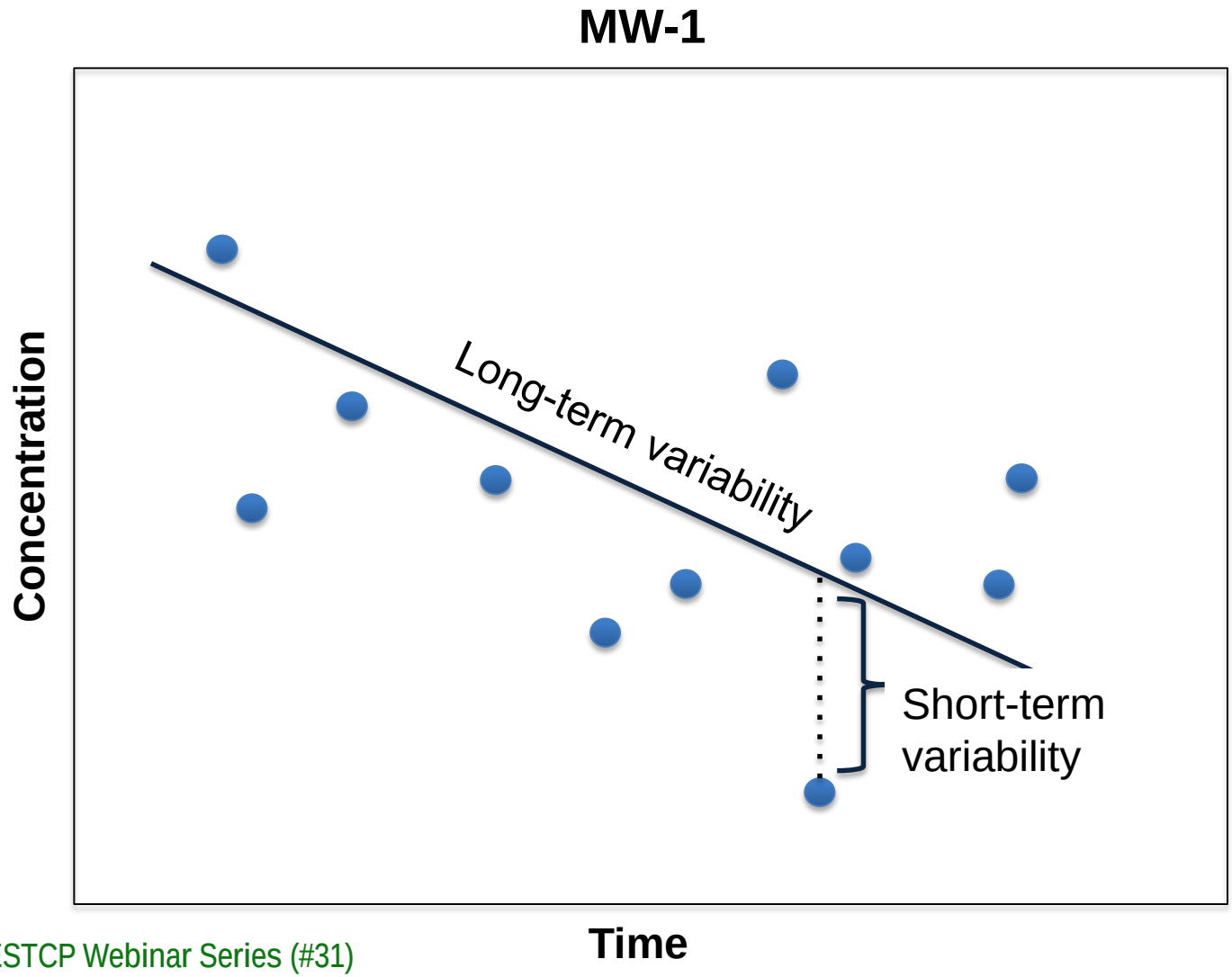
Poonam Kulkarni, P.E.
GSI Environmental, Inc.

SERDP DOD • EPA • DOE | ESTCP

Agenda

- Why is reducing variability important?
- Field demonstration
  - Comparison of sampling methods
- Monitoring optimization and trend analysis toolkit

Why is Reducing Variability Important?

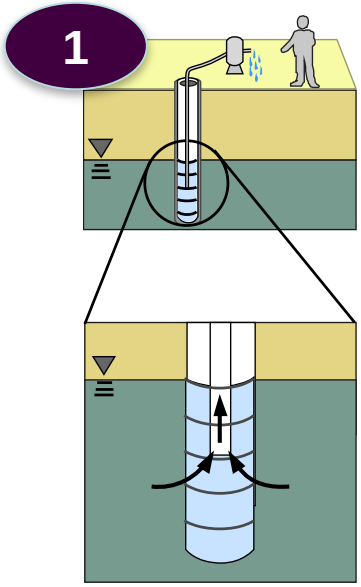


Why is Reducing Variability Important?

- Monitoring costs more than $100 million at Department of Defense (DoD) facilities across the country
- More than 40,000 wells are monitored
- Variability in contaminant concentrations increases costs and limits effective decision-making

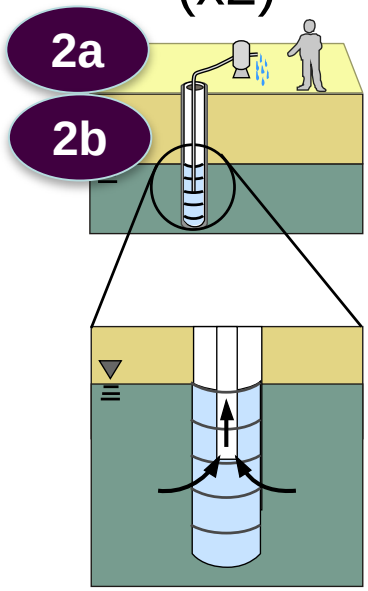
Compare Five Sampling Methods

Standard Low Flow



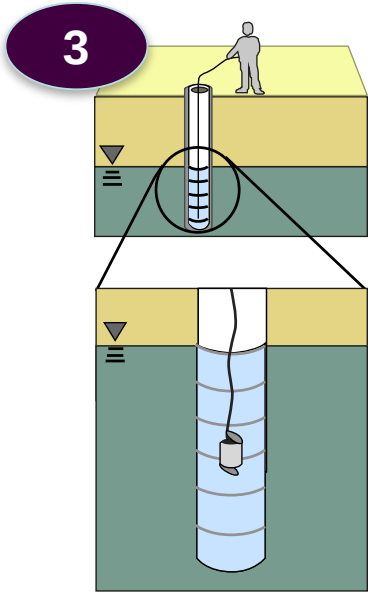
Low Flow Purge to Parameter Stability

Alternative Low Flow (x2)



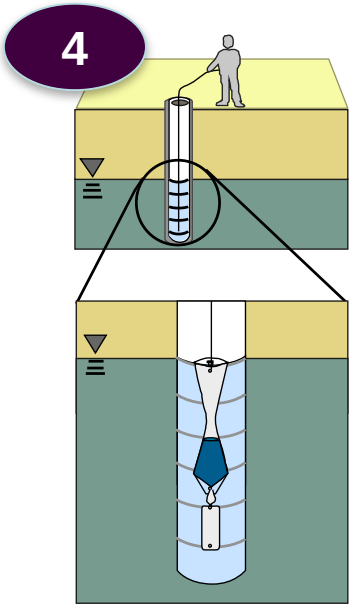
Low Flow Purge to Fixed Volumes

Passive No Purge



SNAP Samplers

Active No Purge



HydraSleeve

Alternative Sampling Procedures

	Std. Low Flow	Alt. Low Flow (x2)	Passive No Purge (SNAP)	Active No Purge (Hydra-Sleeve)
Dedicated Equipment		✓	✓	✓
Constant Intake Depth		✓	✓	✓
Fixed Volume Well Purge		✓		
Constant Flowrate (Purge and Sample)		✓		
Vial Fill: Bottom Fill		✓		✓
Vial Bubbles: <2 mL (5%) headspace OK		✓	✓	✓

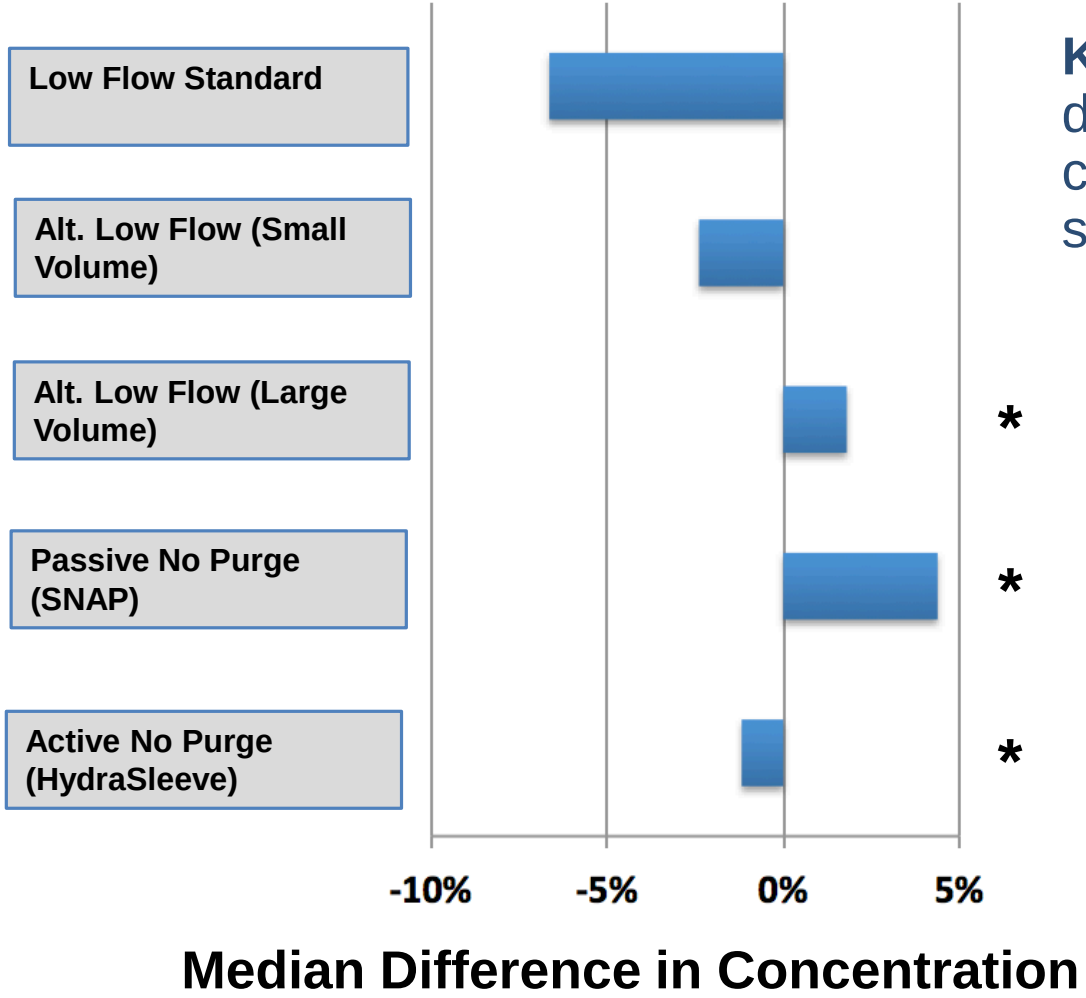
Field Demonstration Approach

Key statistics

2 Sites
8 Wells/site x 2 sites
6 Sample events/method (for each well)
480 Total samples
>3,200 Total concentration measurements

Sampling Event	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Program Week	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42	44	46	48
Method 1	●				●				●				●				●				●			
Methods 2a 2b		●				●				●				●				●				●		
Method 3			●				●				●				●				●				●	
Method 4				●				●				●				●				●				●

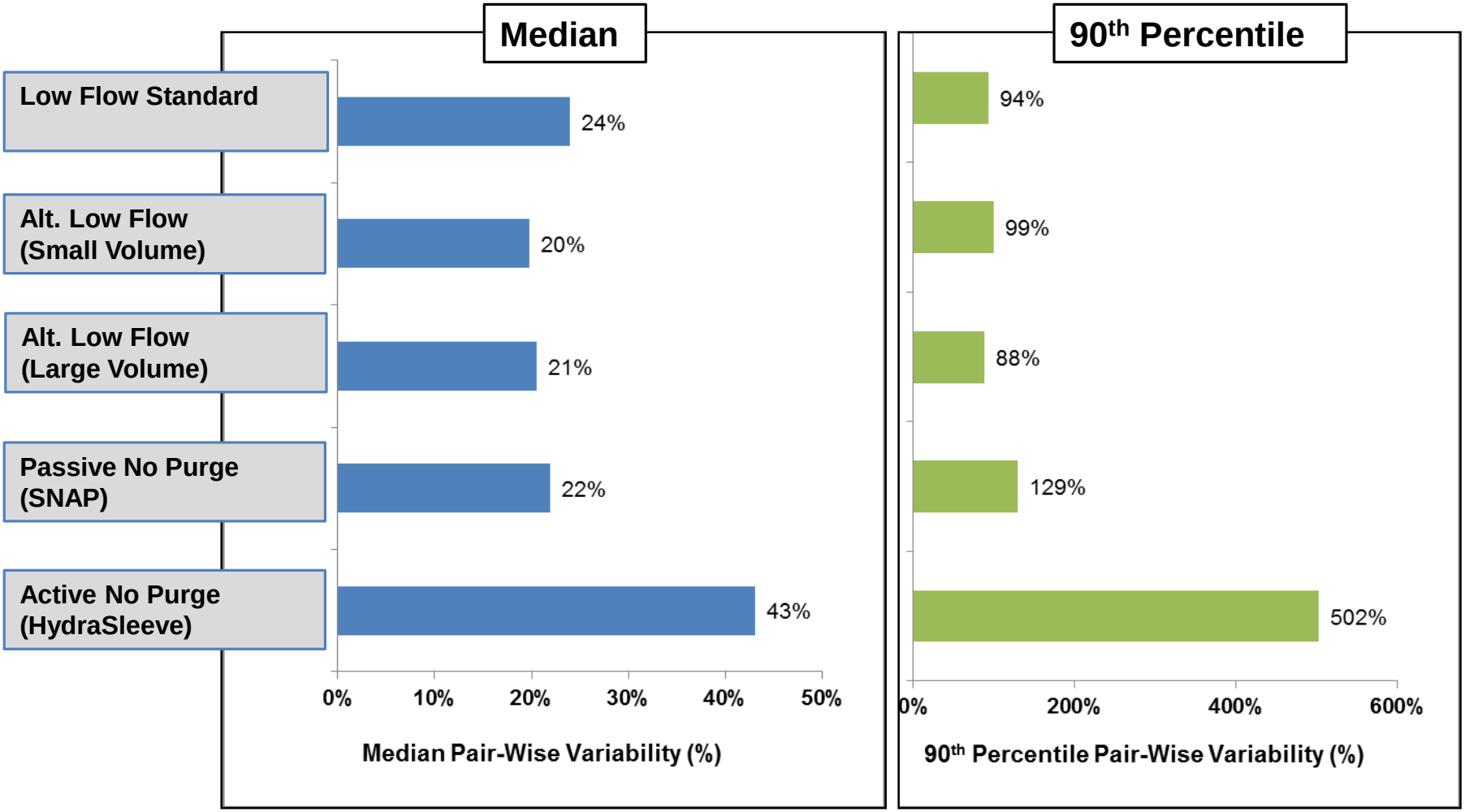
Effect of Sample Method: Bias



Key point: Small differences in median concentration between sample methods

* = Higher than Low Flow Standard ($p<0.05$)

Effect of Sample Method: Variability

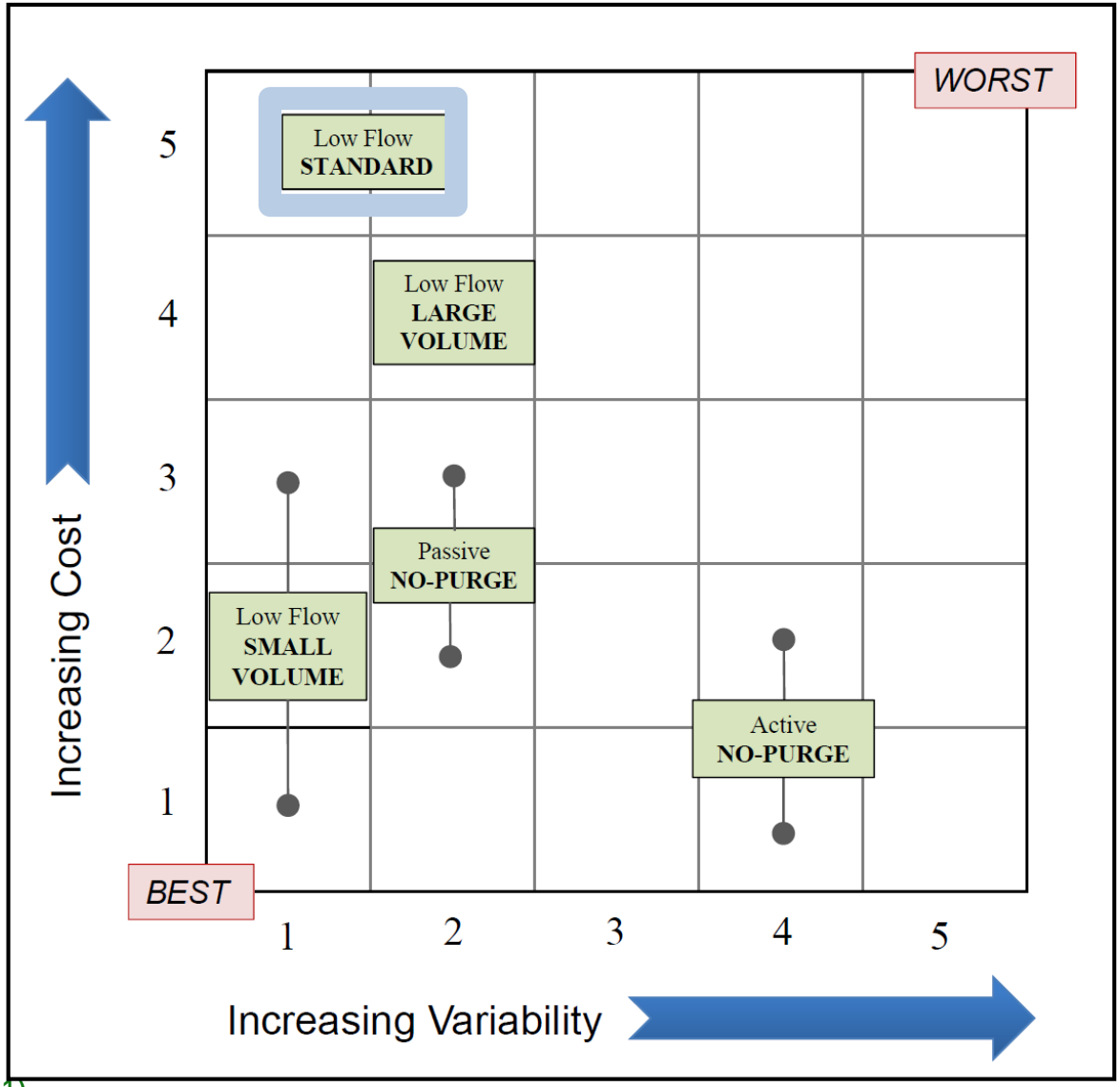


Key point: Alternative methods did not reduce short-term variability

Overview of Results

Example Site:

Changing from Std. Low Flow to Alt. Low Flow (Small Volume) can decrease total monitoring costs by 40-50%



Semi-Quantitative Ranking Analysis of Sampling Methods. *Gray dots indicate range of costs for shallow and deep wells.*

Overview of Results

- Sample method has little or no effect on concentration or variability*
- No apparent benefit to monitoring purge parameters compared to fixed volume purge
- Select sample method based on cost, ease of implementation and sample volume requirements

** Except for HydraSleeve at some sites*

More on HydraSleeve

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Negative Bias and Increased Variability in VOC Concentrations Using the HydraSleeve in Monitoring Wells

by Thomas E. McHugh, Poonam R. Kulkarni, Lila M. Beckley, Charles J. Newell, and Marilyn Zumbro

Abstract

The HydraSleeve is a sampling device for collecting groundwater from the screened interval of a monitoring well without purging that uses a check valve to take in water over the first 3 to 5 feet of an upward pulling motion. If the check valve does not perform as expected, then the HydraSleeve has the potential to collect water from an incorrect depth interval, possibly above the screened interval of the well. We have evaluated volatile organic chemical (VOC) results from groundwater samples collected with the HydraSleeve sampler compared to other methods for sampling monitoring wells at three sites. At all three sites, lower VOC concentration results were observed for samples collected using the HydraSleeve. At two of these three sites, the low concentration sample results were most strongly associated with monitoring wells with more than 10 feet of water above the monitoring well-screened interval. At the site with the largest dataset, the median bias for samples collected with HydraSleeve was −20% ($p < 0.001$). At this site, a bias of −26% ($p < 0.001$) was observed for the subset of monitoring wells with greater than 10 feet of water above the screened interval compared to a bias of −7% ($p = 0.21$) for wells screened across the top of the water table. In addition to lower VOC concentrations, the monitoring records obtained using the HydraSleeve were more variable compared to monitoring records obtained using purge sampling methods, a characteristic that would make it more difficult to determine the long-term concentration trend in the well.

Methods to Minimize and Manage Variability in Groundwater Monitoring Results – Part II

Dr. Thomas McHugh
GSI Environmental Inc.

SERDP DOD • EPA • DOE | ESTCP

Tool for Data Evaluation and Monitoring Optimization

- How much monitoring data needed to characterize concentration trends?
- What is trade off between monitoring frequency and duration?
- A tool for monitoring optimization

How Much Monitoring Data Needed to Identify Long-Term Trend?

Summary of Results from 20 Sites

Accuracy/Confidence Goal	Years of Quarterly Monitoring Required		
	Best Site	Median Site	Worst Site
Medium Confidence: Statistically-significant decreasing concentration trend ($p<0.1$) for 80% of monitoring wells	**2.8 yrs**	**7.3 yrs**	**30 yrs**
Medium Accuracy: Determine the long-term attenuation rate with an accuracy (i.e., 95% confidence interval) of +/- 50% or +/- 0.1 yr^{-1} (whichever is larger) for 80% of monitoring wells.	**4.0 yrs**	**7.4 yrs**	**14.5 yrs**

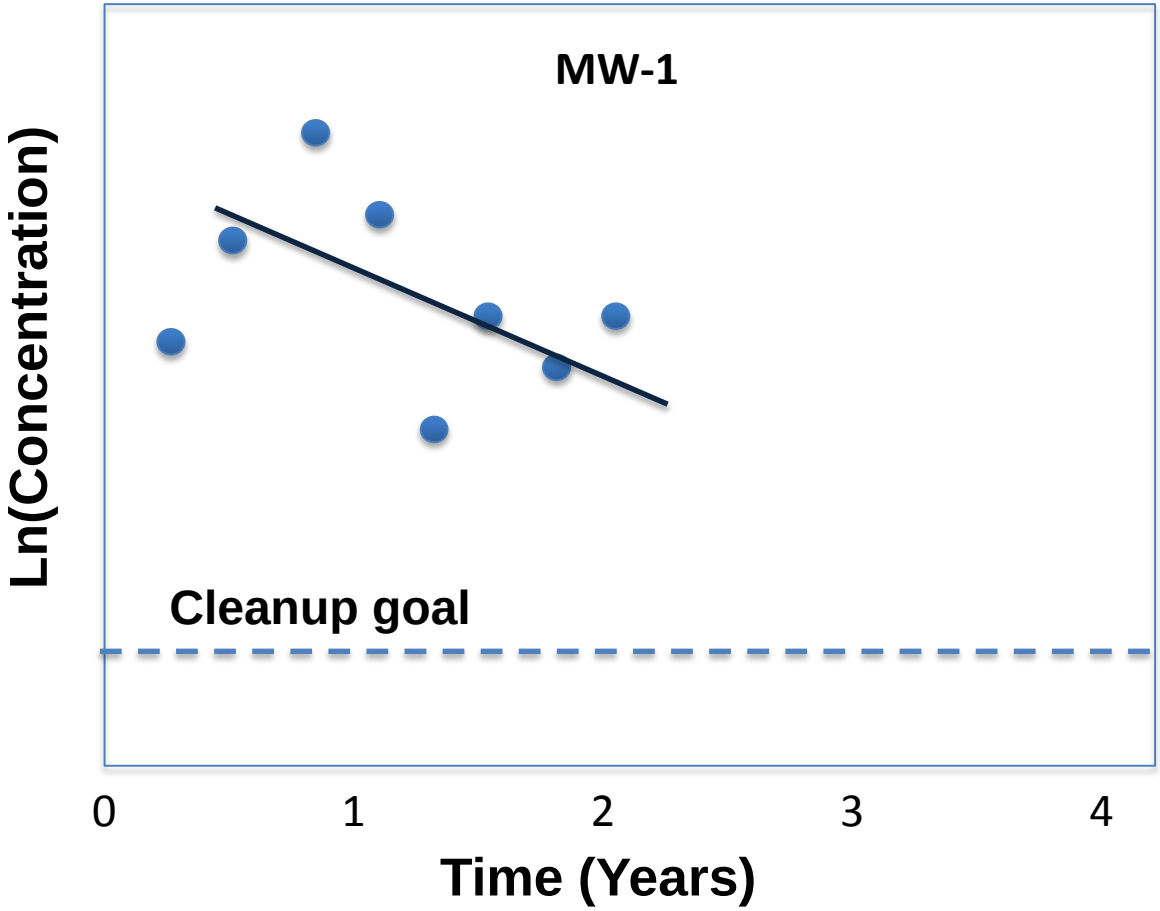
Key point: At most sites, it takes a long time to accurately characterize the long-term attenuation rate

How Much Monitoring Data Needed to Identify Long-Term Trend?

- It commonly takes seven years or more of quarterly monitoring data to characterize the attenuation rate with even a medium level of accuracy (i.e., +/- 50%)
- Making decisions (e.g., remedy effectiveness, remediation timeframe) based on insufficient data can result in incorrect decisions

Effect of Monitoring Frequency

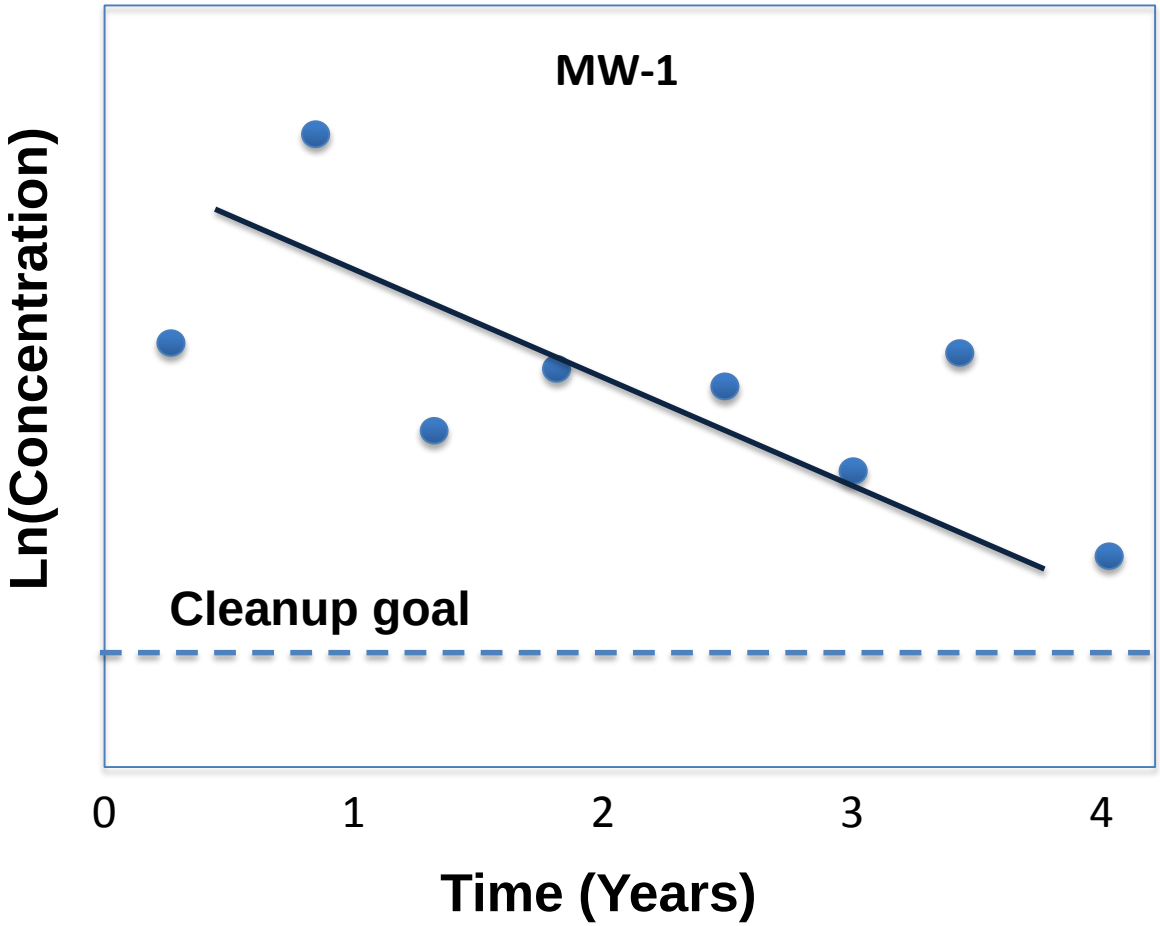
Eight Quarterly Monitoring Events



How does monitoring frequency affect confidence and accuracy of the attenuation rate?

Effect of Monitoring Frequency

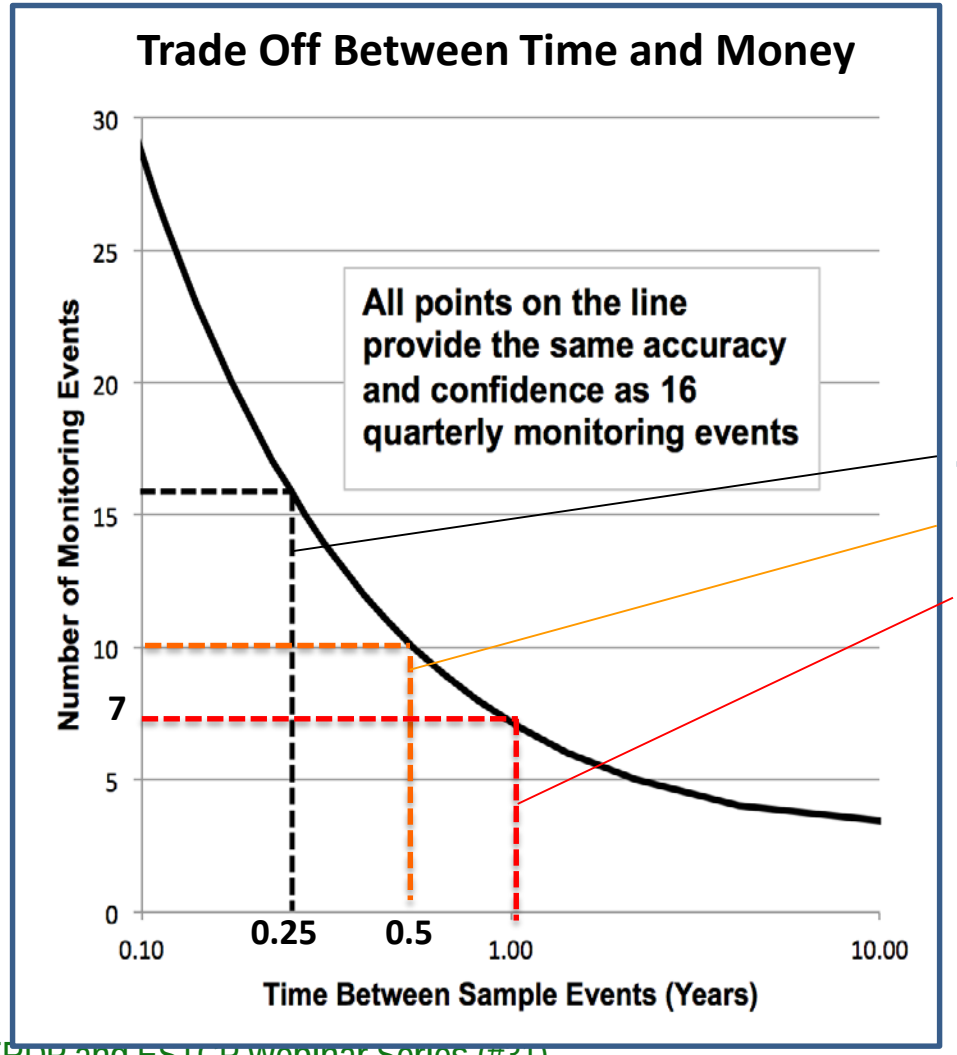
Eight Semiannual Monitoring Events



Key point:
Increasing time between monitoring events will increase CONFIDENCE and ACCURACY of long-term attenuation rate…

By how much?

What is Trade-Off between Monitoring Frequency and Duration?



Same answer for all site:

4 years of quarterly monitoring =
5 years of semiannual monitoring =
7 years of annual monitoring

What is Trade-Off Between Monitoring Frequency and Duration?

Groundwater

Open Source – free to download - doi: 10.1111/gwat.12407

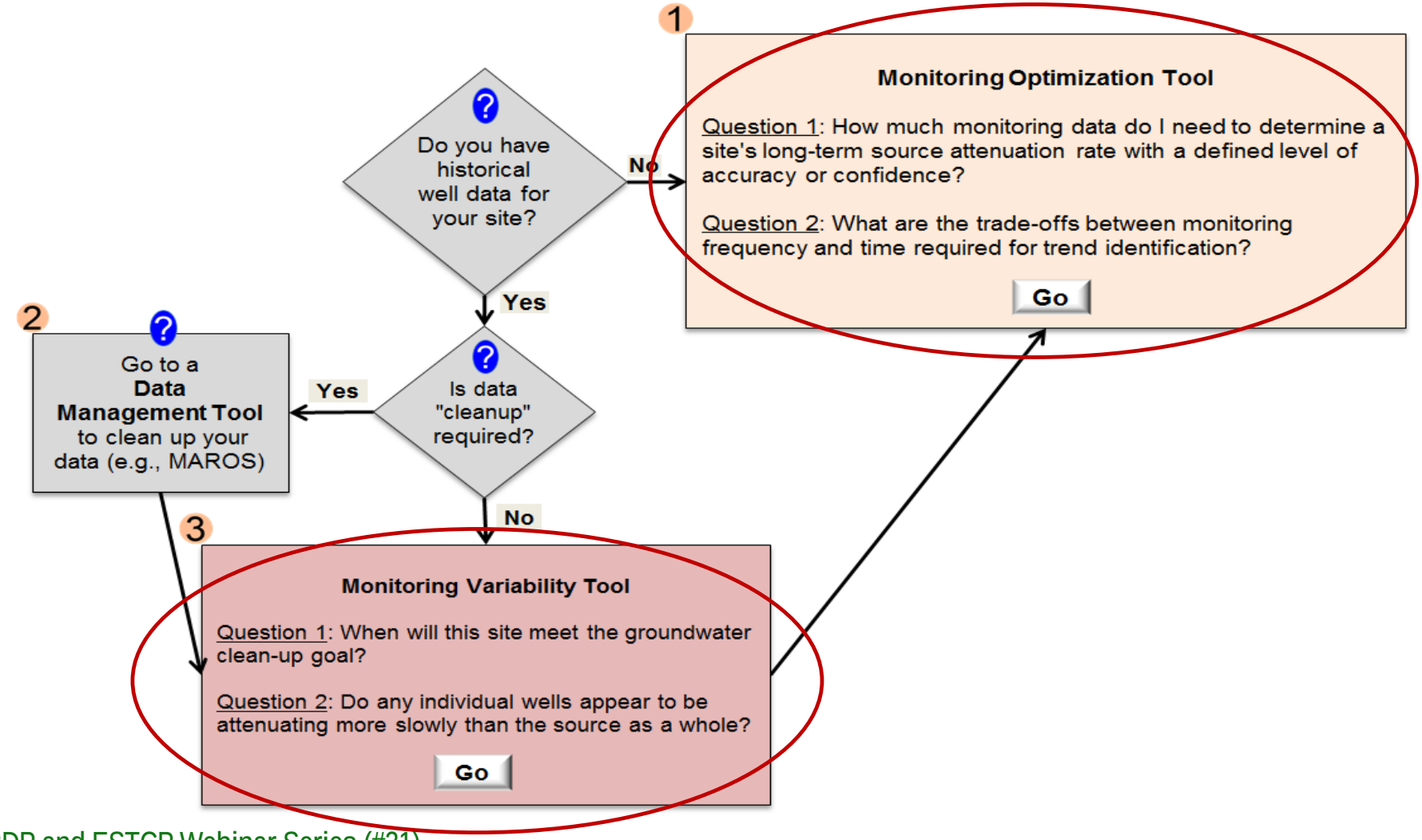
Time vs. Money: A Quantitative Evaluation of Monitoring Frequency vs. Monitoring Duration

by Thomas E. McHugh[1,2], Poonam R. Kulkarni[2], and Charles J. Newell[2]

Abstract

The National Research Council has estimated that over 126,000 contaminated groundwater sites are unlikely to achieve low ug/L clean-up goals in the foreseeable future. At these sites, cost-effective, long-term monitoring schemes are needed in order to understand the long-term changes in contaminant concentrations. Current monitoring optimization schemes rely on site-specific evaluations to optimize groundwater monitoring frequency. However, when using linear regression to estimate the long-term zero-order or first-order contaminant attenuation rate, the effect of monitoring frequency and monitoring duration on the accuracy and confidence for the estimated attenuation rate is not site-specific. For a fixed number of monitoring events, doubling the time between monitoring events (e.g., changing from quarterly monitoring to semi-annual monitoring) will double the accuracy of estimated attenuation rate. For a fixed monitoring frequency (e.g., semi-annual monitoring), increasing the number of monitoring events by 60% will double the accuracy of the estimated attenuation rate. Combining these two factors, doubling the time between monitoring events (e.g., quarterly monitoring to semi-annual monitoring) while decreasing the total number of monitoring events by 38% will result in no change in the accuracy of the estimated attenuation rate. However, the time required to collect this dataset will increase by 25%. Understanding that the trade-off between monitoring frequency and monitoring duration is not site-specific should simplify the process of optimizing groundwater monitoring frequency at contaminated groundwater sites.

Monitoring Optimization and Trend Analysis Toolkit



Monitoring Optimization and Trend Analysis Toolkit

- Trend analysis questions
  - When will this site meet the groundwater clean-up goal?
  - Do any wells appear to be attenuating more slowly than the source as a whole?

Monitoring Optimization and Trend Analysis Toolkit

- Monitoring optimization questions
  - How much monitoring data is needed to determine site's long-term source attenuation rate with a defined level of accuracy or confidence?
  - What are trade-offs between monitoring frequency and time required for trend identification?

Option	Sample Frequency	Total Sampling Events	Cost Per Well ($K)
Option 1:	Sample weekly for 1.6 years	82	123
Option 2:	Sample monthly for 2.7 years	33	49
Option 3:	Sample quarterly for 4.1 years	16	25
Option 4:	Sample semiannually for 5.0 years	10	15
Option 5:	Sample annually for 6.5 years	7	10
Option 6:	Sample every 2 years for 9.0 years	5	7
Option 7:	Sample every 5 years for 18.4 years	4	6

Benefits to DoD

- Groundwater sampling methods
  - Determine method based on cost and ease of implementation
  - No benefits to purge-to-parameter stability
- Monitoring Optimization and Trend Analysis Toolkit
  - Helps site managers evaluate site conditions for better decision making
  - Optimize monitoring frequency and duration
  - More accurate trend analysis

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-201209/ER-201209

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Q&A Session 2

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