Persistent Groundwater Contaminant Plumes: Processes, Characterization, and Case Studies

UA-SRP & USEPA Seminar Series- Webinar

February 24, 2014

Mark L. Brusseau

School of Earth & Environmental Sciences

University of Arizona

Contaminant Transport Group University of Arizona

Superfund Research Program The University of Arizona

THE UNIVERSITY OF ARIZONA. Arizona's First University.

Constrained Mass Removal & Plume Persistence

"**significant limitations with currently available remedial technologies persist that make achievement of MCLs throughout the aquifer unlikely at most complex groundwater sites in a time frame of 50-100 years.**"*

"Complex" groundwater sites are defined as those that have DNAPL present (e.g., chlorinated solvents) and that have substantial subsurface heterogeneity, including the presence of extensive lower-permeability units or fractured media.

- Why does this situation exist?
- What options are available?

*National Research Council (NRC). 2013. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. Wash., DC

Outline

- Chlorinated-solvent sites- prevalence and issues
- Constrained mass removal and plume persistence: Impact of DNAPL source zones
- Constrained mass removal and plume persistence: Impact of mass storage in lower-K zones & hydraulic factors
- Constrained mass removal and plume persistence: Impact of sorbed mass
- Summary

~1600 SUPERFUND Sites

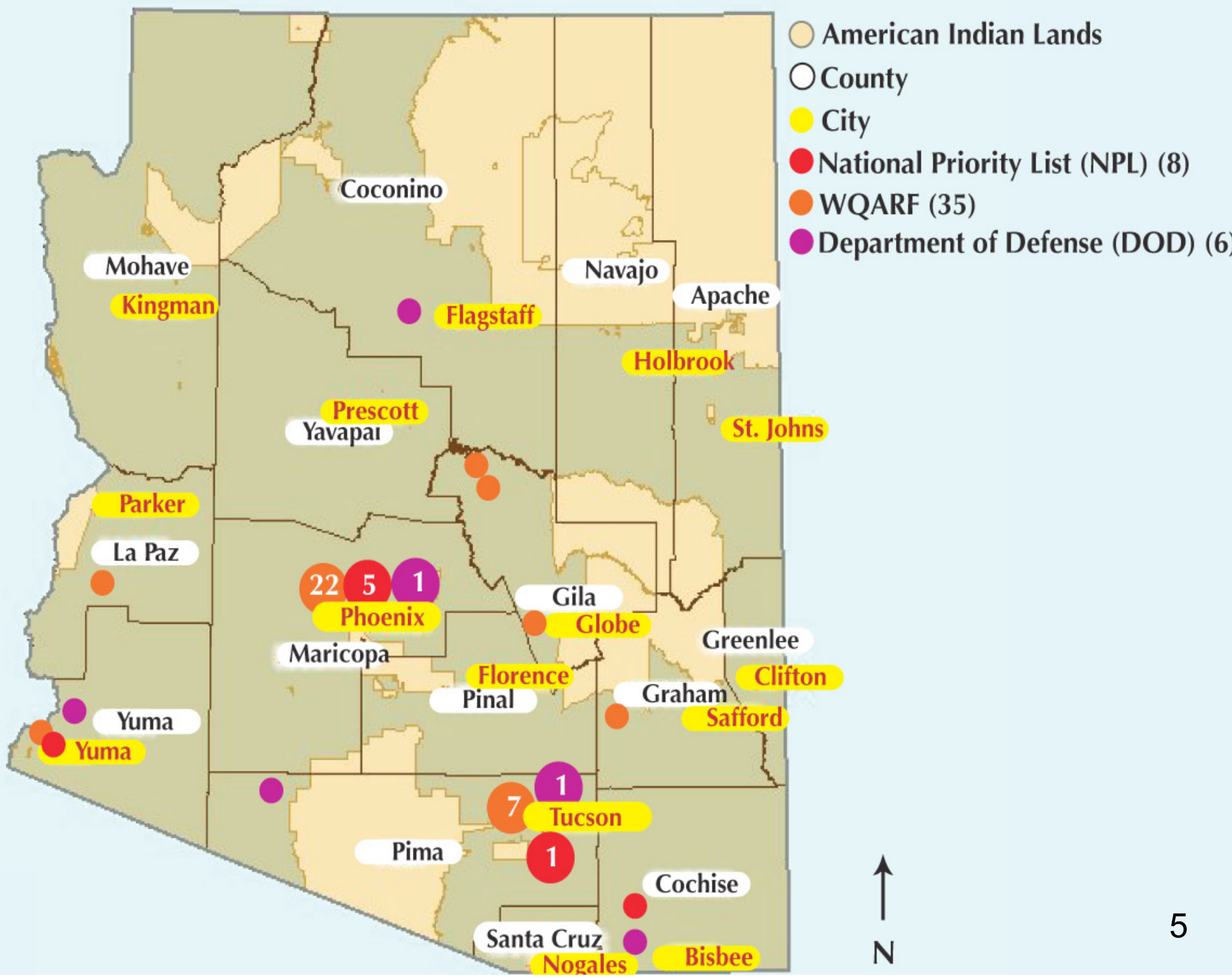
~80% have Chlorinated-Solvent Contaminants

Arizona Sites

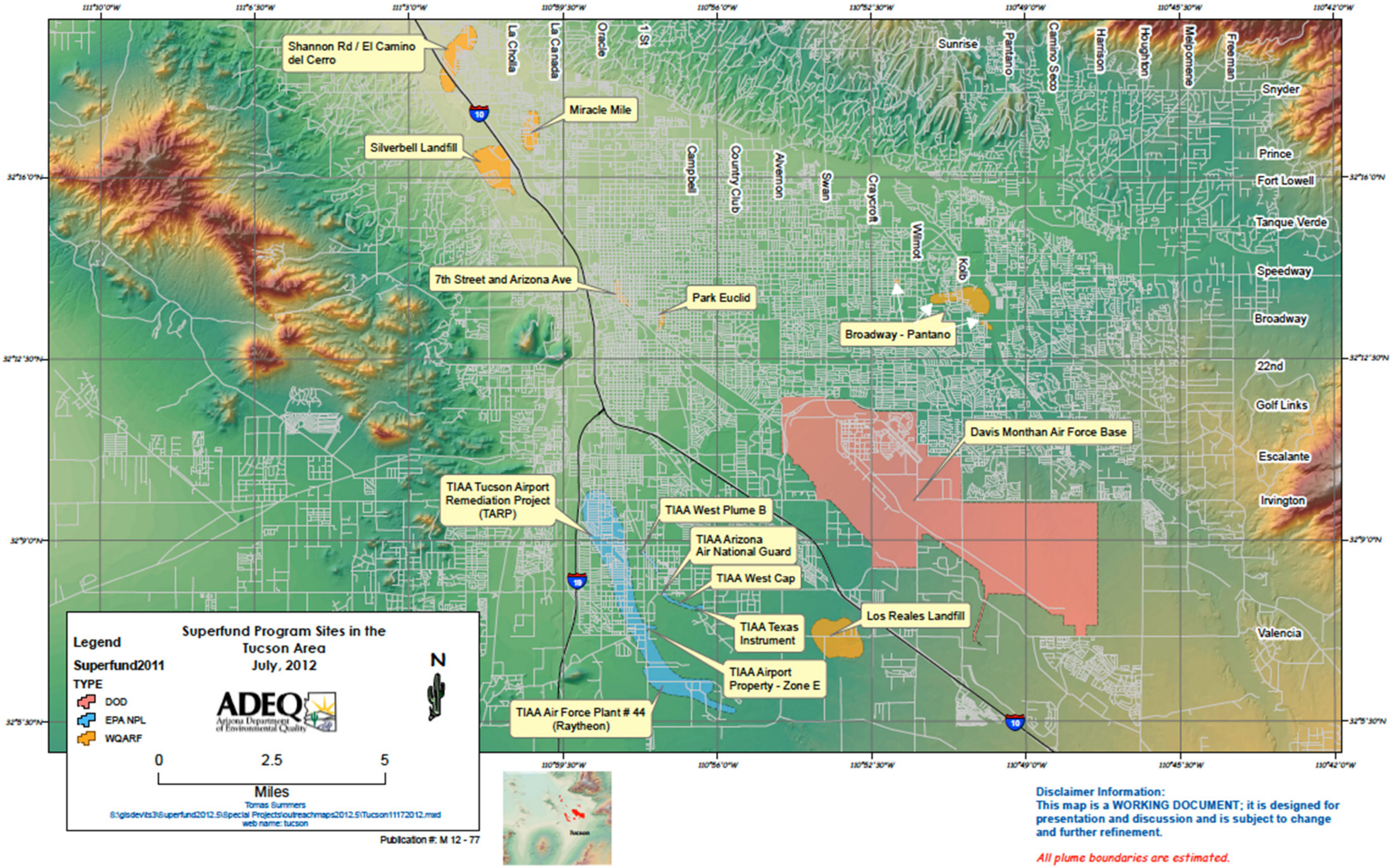
Chlorinated-Solvents Presence:

State: 31/35

Federal: 13/15



Groundwater Contamination Sites in Tucson



Disclaimer Information:
This map is a WORKING DOCUMENT; it is designed for presentation and discussion and is subject to change and further refinement.

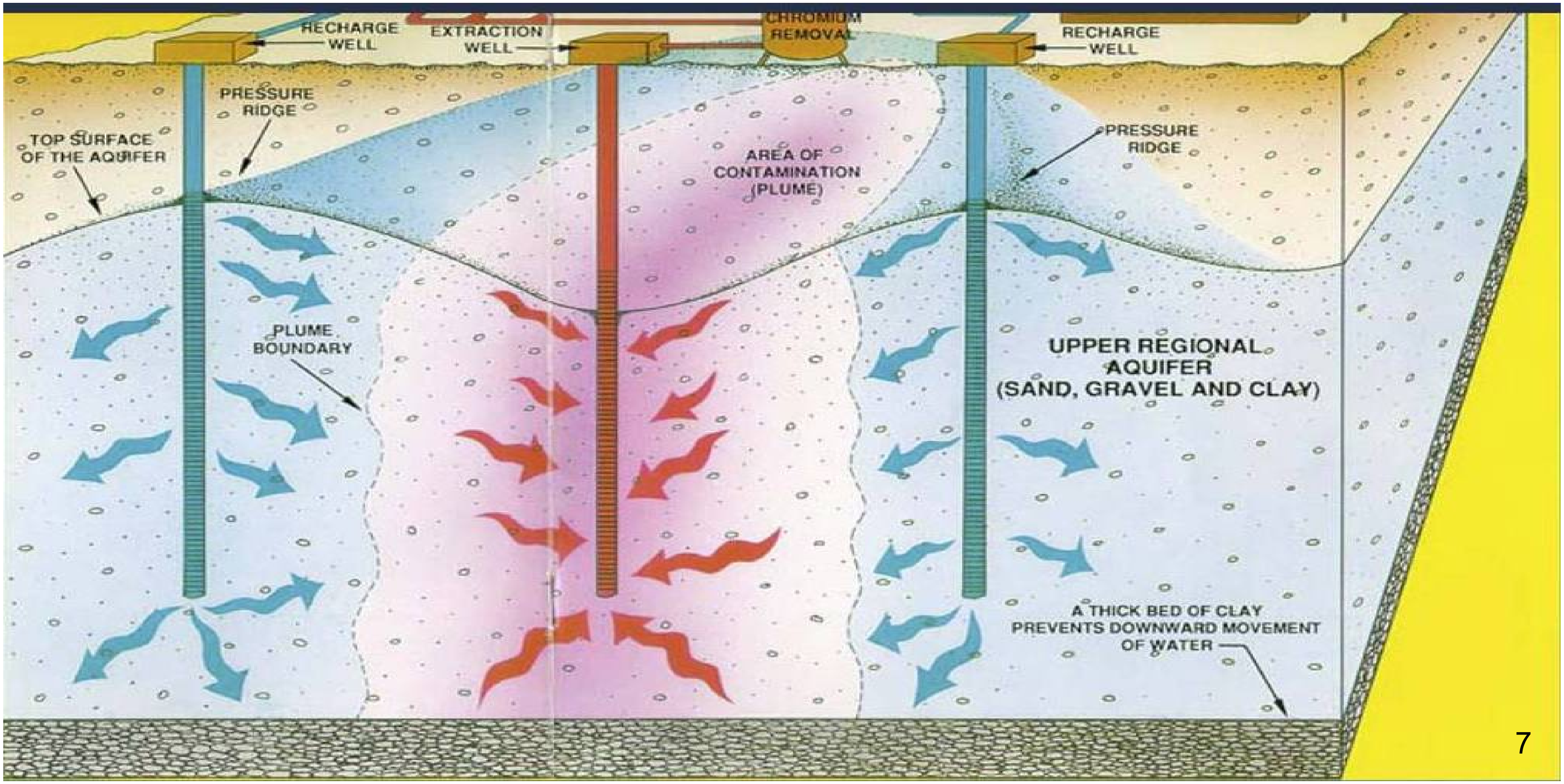
All plume boundaries are estimated.

Chlorinated-Solvent Contaminants are Primary Concern at all 9 Sites

Groundwater Remediation

Standard Method = Pump and Treat

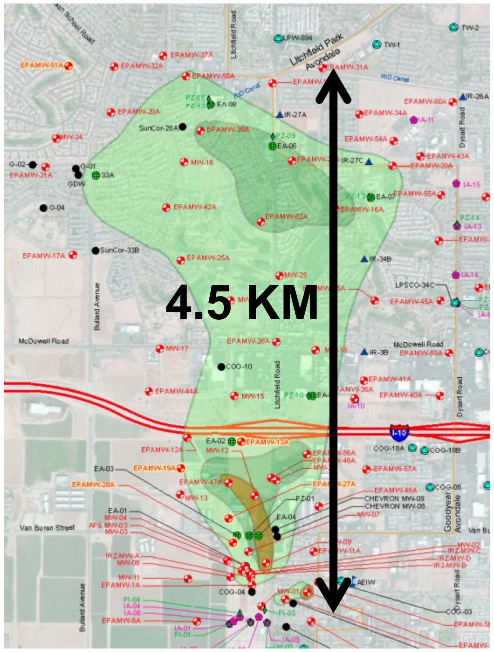
Very effective for plume containment



Impact of P&T on Water Resources

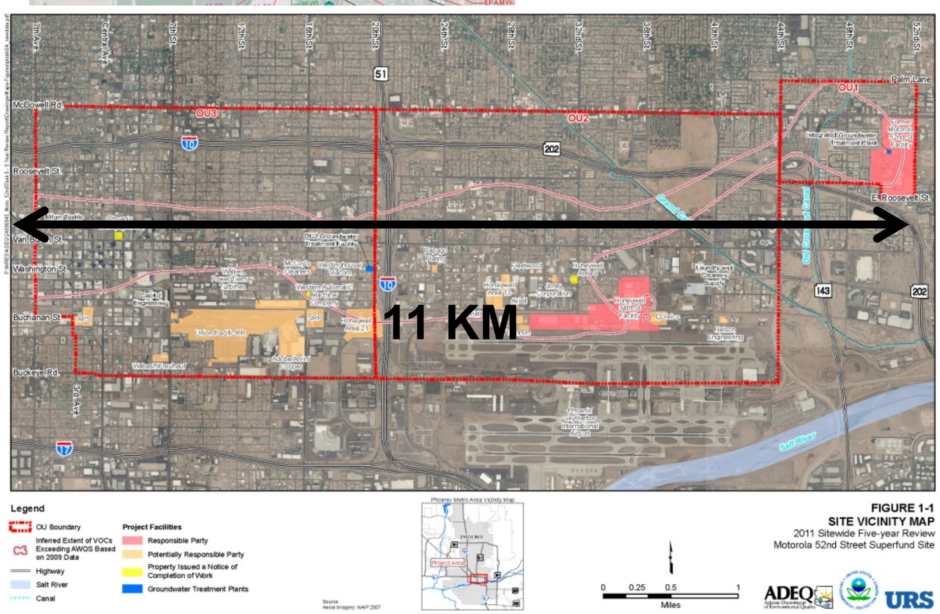
- Analysis for Tucson [Brusseau & Narter, 2013]- year 2010
- Compare aggregate volume of groundwater extracted for all P&T systems to total metropolitan groundwater withdrawal
- Total groundwater withdrawal for all P&T systems = 16.6 M m^3
- This is ~20% of the total groundwater withdrawal in Tucson
- Treated water used primarily for potable water or re-injection
- Represents ~6% of total potable water supply

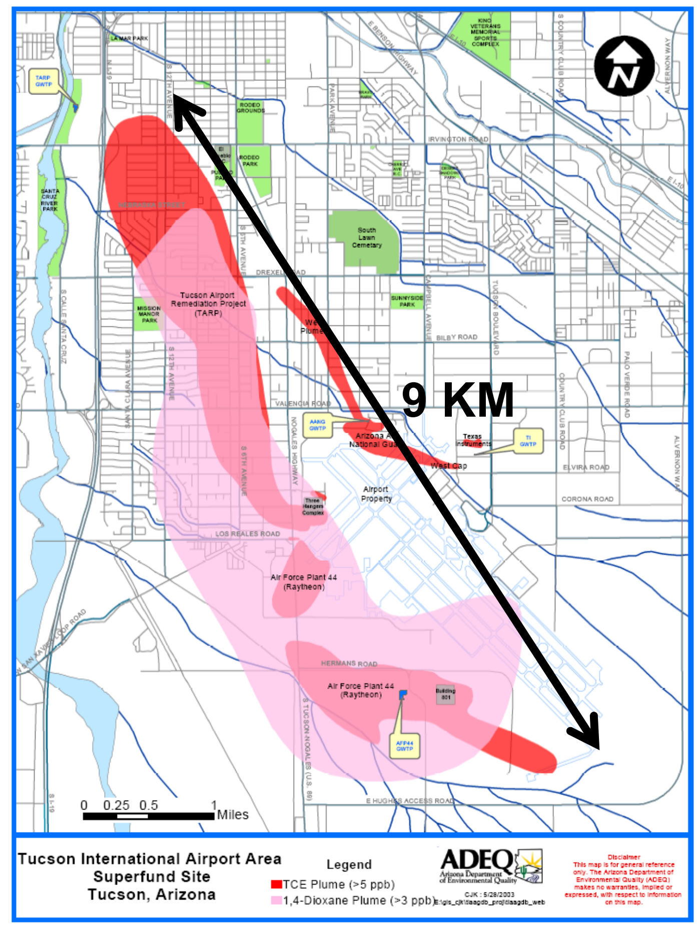
Three Chlorinated-Solvent Sites in Arizona



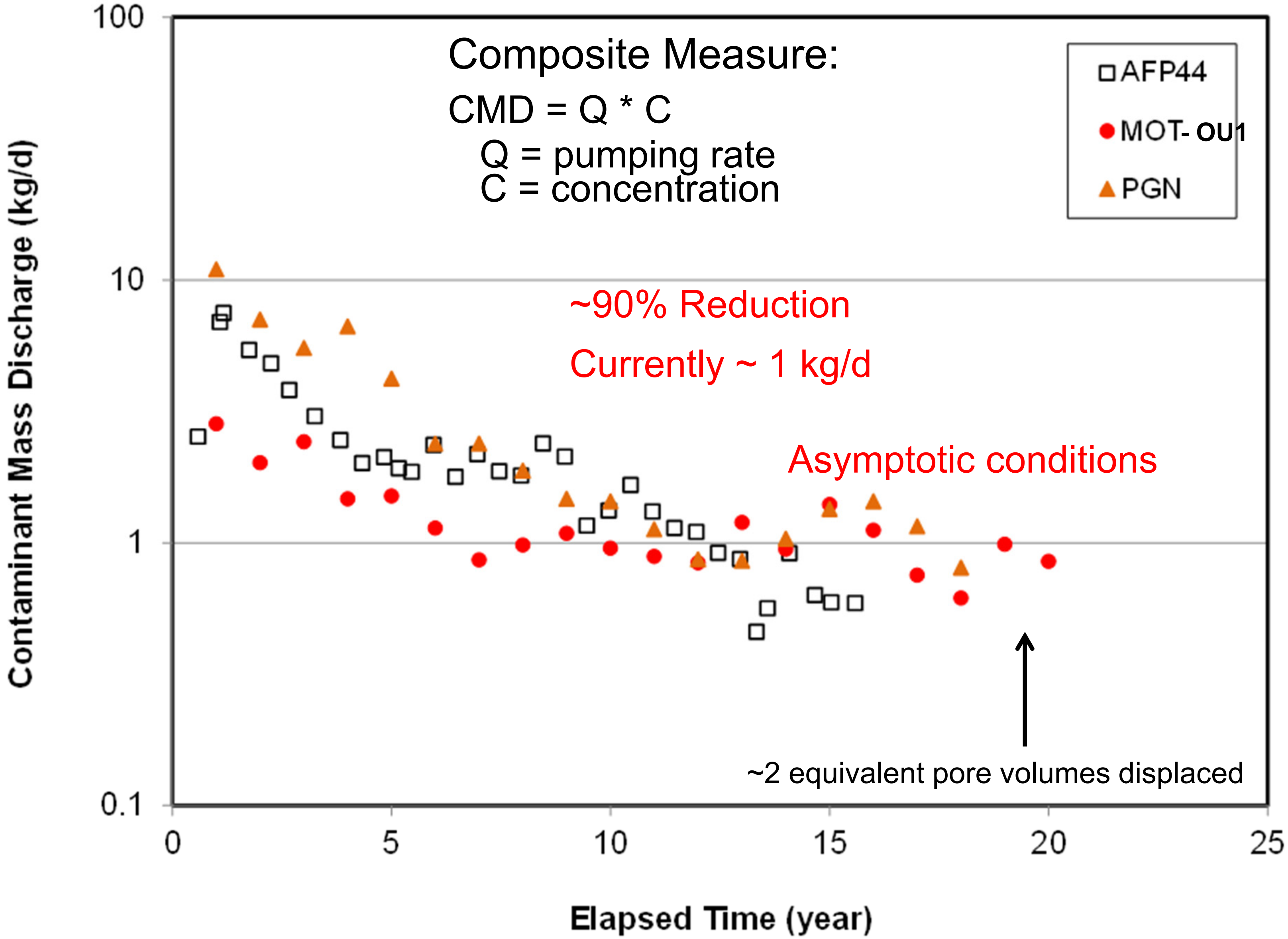
- TCE is Primary COC
- Very Low Retardation (R<2)
- No Measurable Transformation Processes
- V. Low Biogeochemical Attenuation Capacity

★ Large Plumes
(several km long)





Pump & Treat CMD Data



Constrained Mass Removal & Plume Persistence

Potential Factors:

- Uncontrolled DNAPL Sources
- Plume-scale Lower-K Zones and Mass Storage (diffusive mass transfer- “back diffusion”)
- Plume-scale Sorbed-phase Mass Storage (sorption/desorption processes)
- Hydraulic Factors (P&T well-field, etc)
- Low Attenuation Capacity
- Other (Institutional, Analytical, etc)

Constrained Mass Removal & Plume Persistence

Long Known:

United States Environmental Protection Agency | Office of Research and Davelopment | Office of Solid Waste and Emergency Response | EPA/540/4-89/005

E P A **Ground Water Issue**

1989

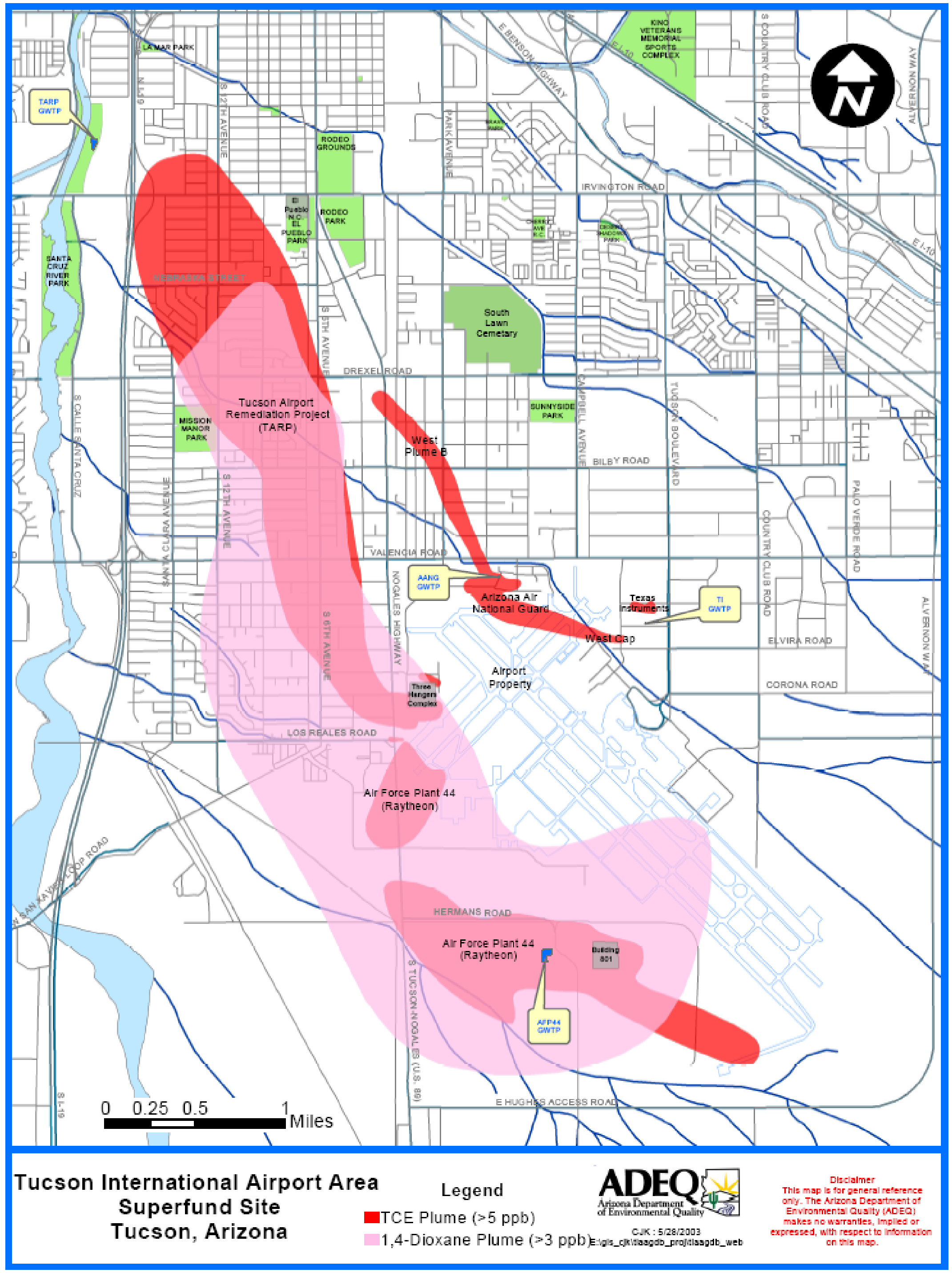
Performance Evaluations of Pump-and-Treat Remediations

Joseph F. Keely

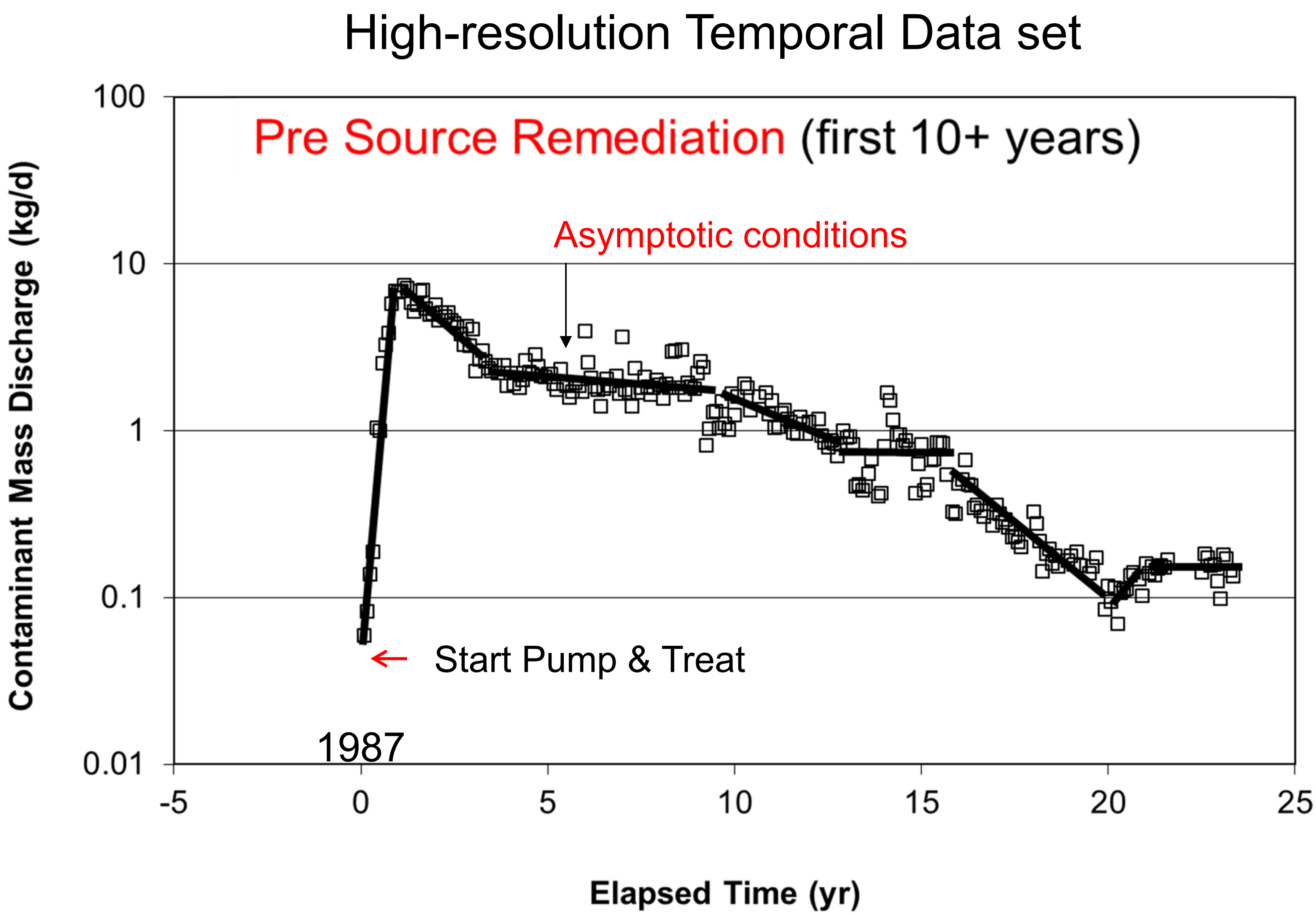
Need to Determine Relative Significance of Each Factor, and Site-dependent Functionality

Tucson International Airport Area Superfund Site

- TCE/DCE Contamination Identified in 1981
- Site Placed on Superfund NPL in 1983
- Pump and Treat started in 1987 (south plume)
- Source-zone Remediation efforts [SVE, ISCO]
- UA Collaboration since 1993



Composite CMD: AFP44



Constrained Mass Removal & Plume Persistence

Question: What is the relative significance of each of the various Persistence/Attenuation factors for this site?

Conducted an integrated Laboratory, Field, and Modeling study

Plume-scale Modeling Effort

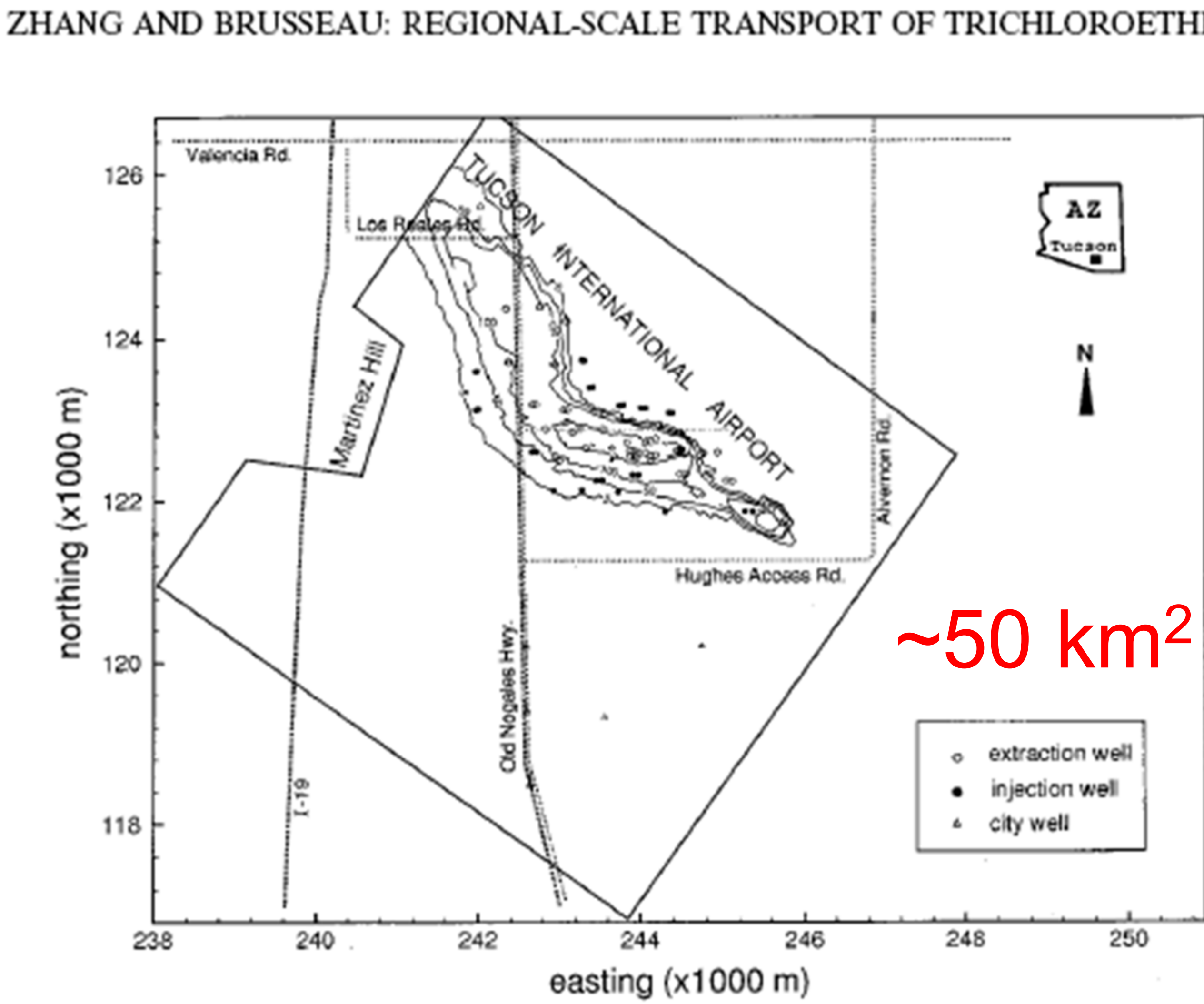


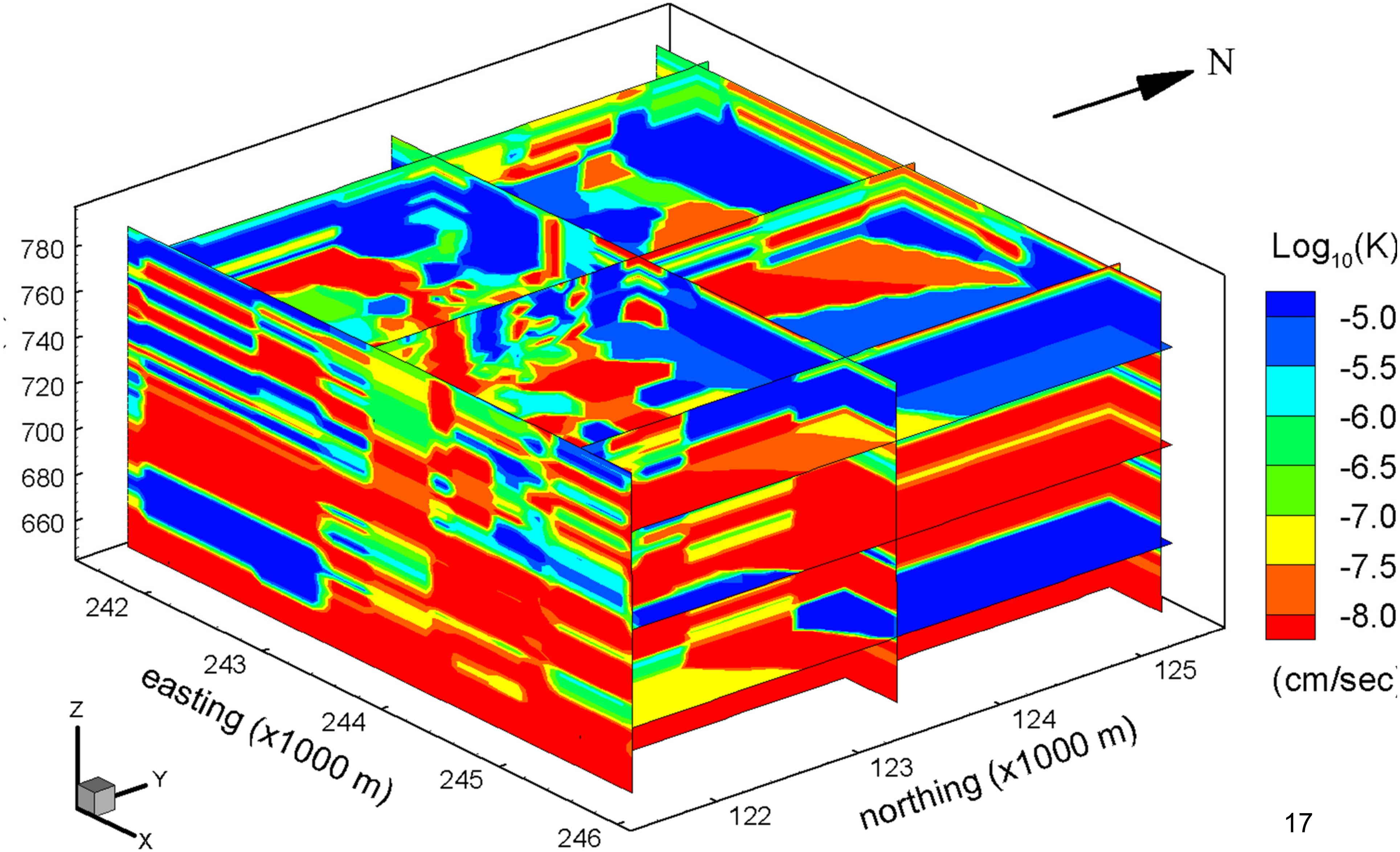
Figure 1. Study domain and trichloroethene plume as of 1987 (concentration units are $\mu g\ L^{-1}$).

Known Inputs

Conduct series of scenario-testing sensitivity analyses

~50 km^2

Three-Dimensional Distribution of Hydraulic Conductivities at AFP-44 Site



Impact of Transport Processes

K Variability & Diffusive Mass Transfer (back diffusion)

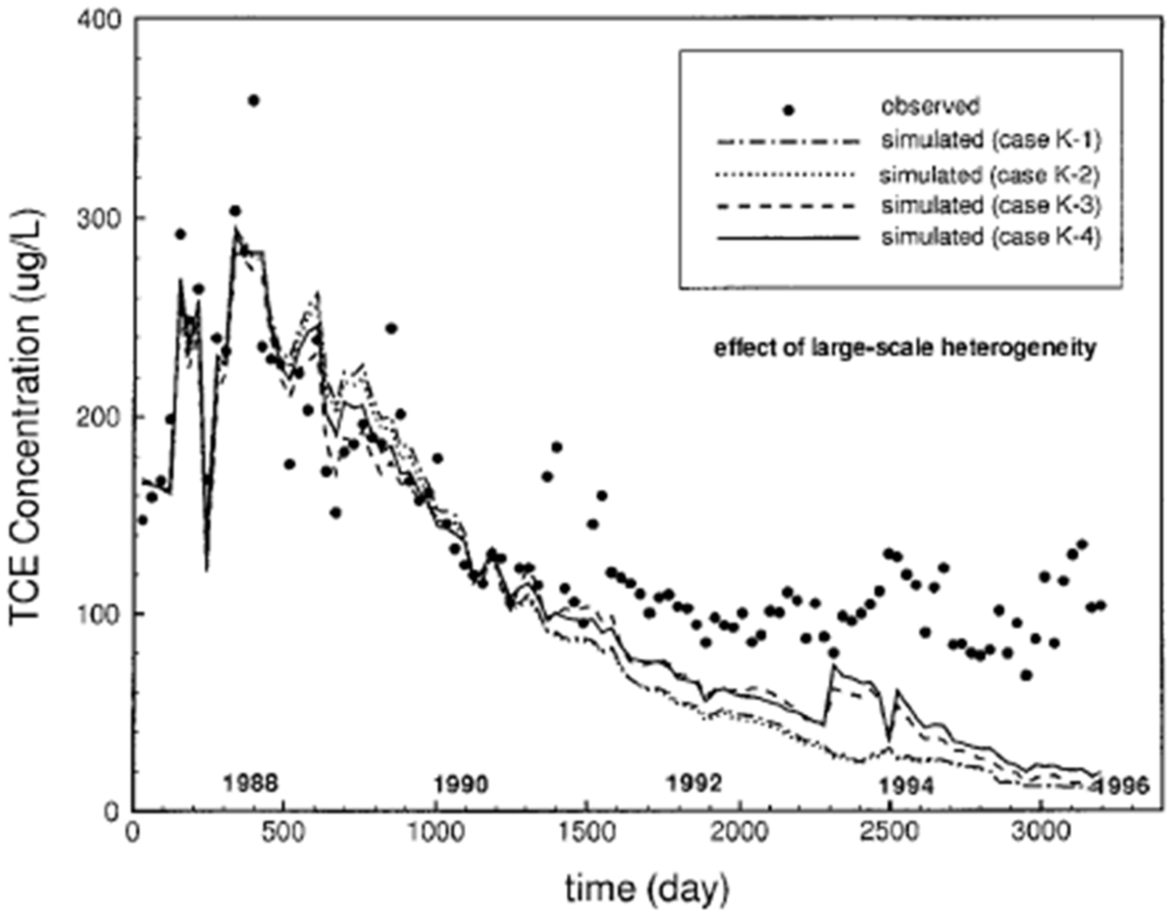


Figure 5. The impact of spatially variable hydraulic conductivity on simulated influent trichloroethene concentrations: case K-1, homogeneous; case K-2, heterogeneous vertically but homogeneous areally; case K-3, heterogeneous areally but homogeneous vertically; and case K-4, heterogeneous areally and vertically.

Impact of Transport Processes

Sorption-desorption (nonlinear, rate limited)

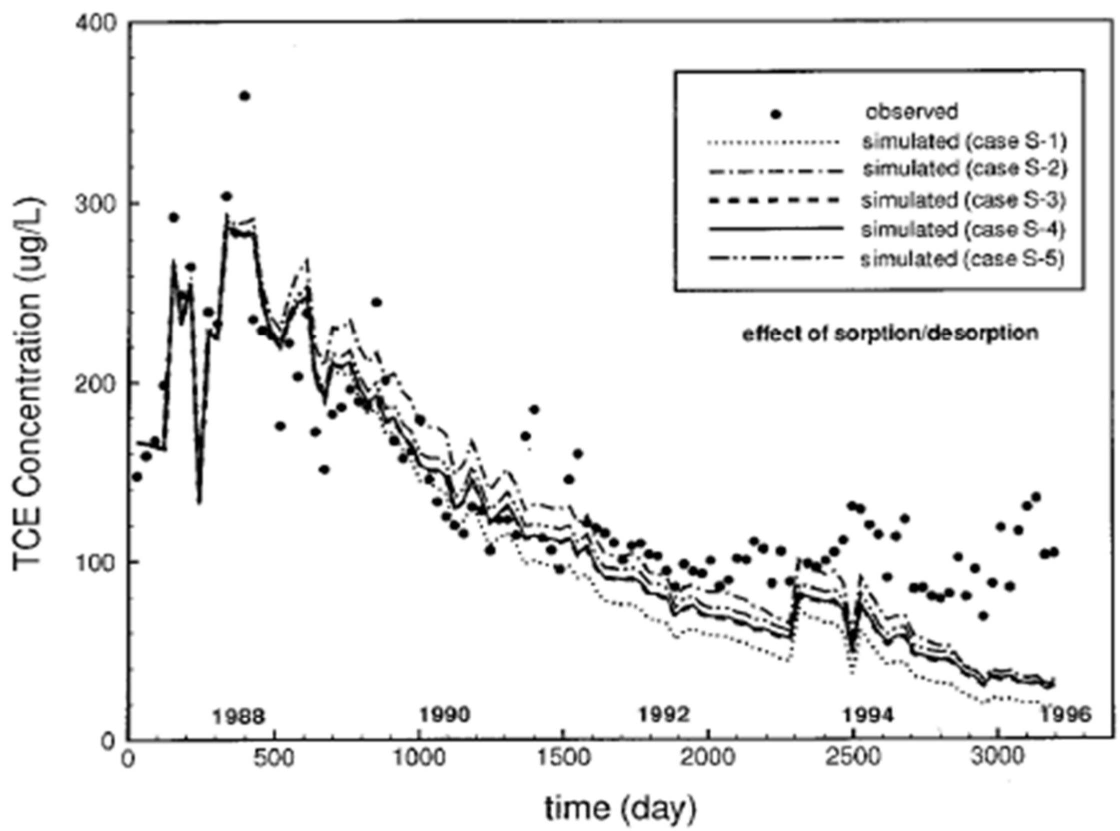
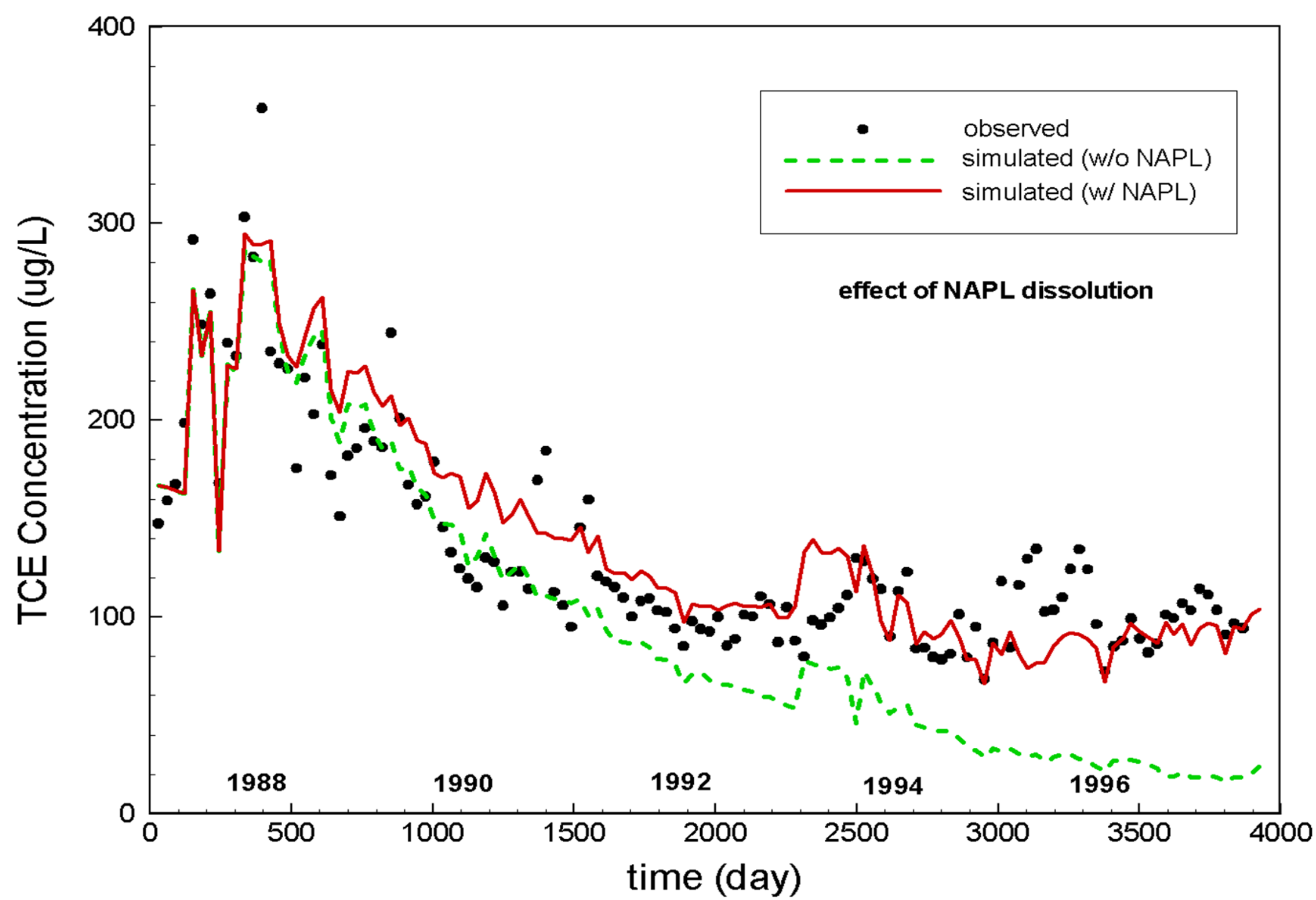


Figure 6. The impact of nonideal sorption/desorption on simulated influent trichloroethene concentrations: case S-1, no sorption/desorption; case S-2, linear, instantaneous sorption/desorption; case S-3, linear, rate-limited sorption/desorption; case S-4, nonlinear, rate-limited sorption/desorption; and case S-5, linear, rate-limited sorption/desorption with contaminant aging. [Sims include physical heterogeneity]

Impact of Transport Processes

DNAPL in Source zones ★ Controlling Factor for Early Phase

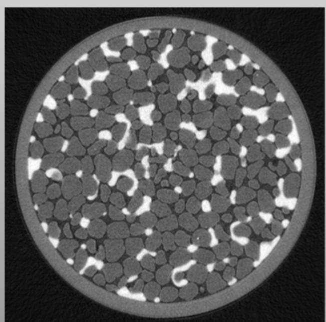


Comparison of the Simulated Influent TCE Conc. at Treatment Plant with the Observed Data

Source-zone Architecture, DNAPL Dissolution, and Mass Removal

Multi-scale Investigations of Systems

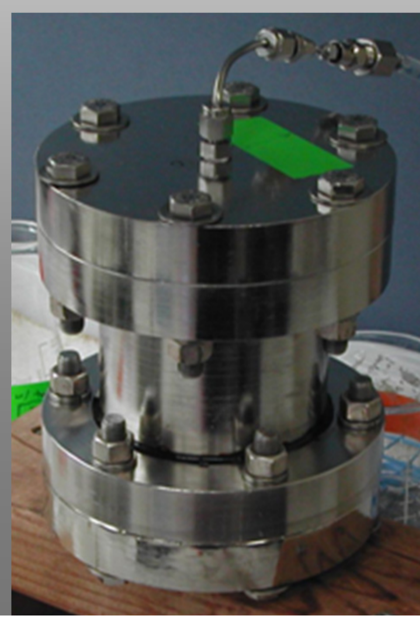
Pore



~6 mm

Core

~10 cm

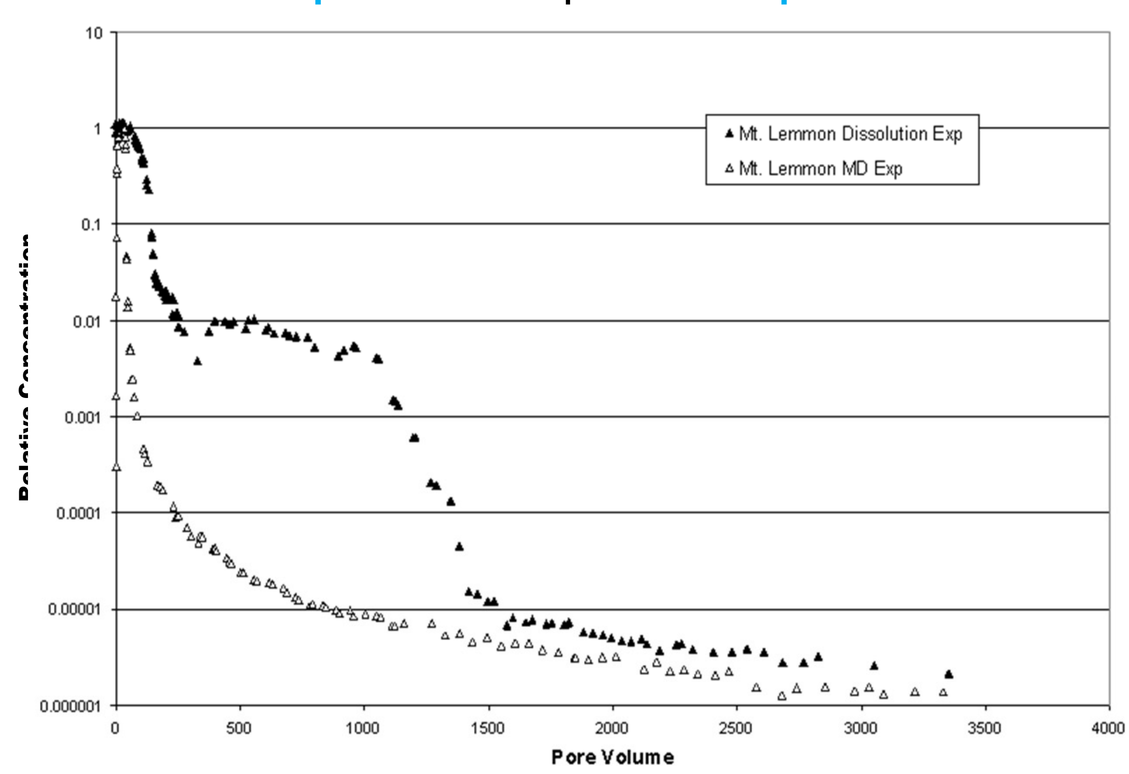


Intermediate

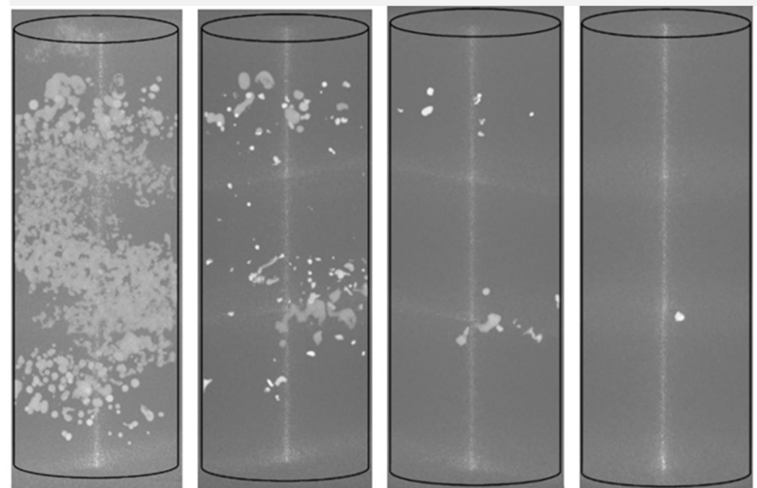
~2 m

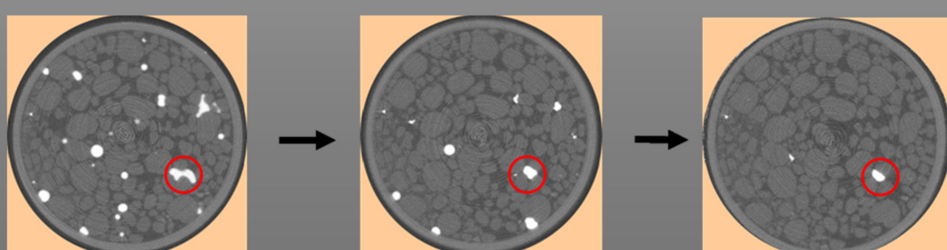
DNAPL Source Behavior

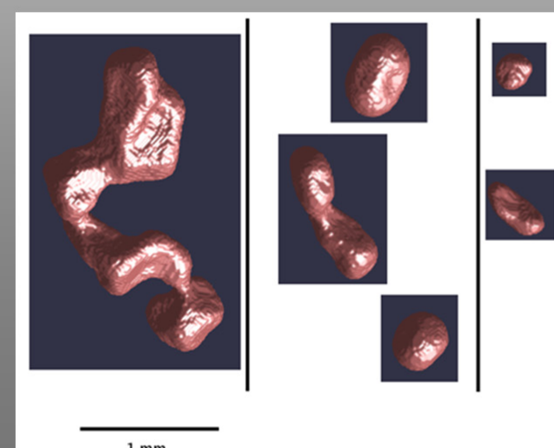
Column Experiments



Pore-scale Imaging: 10 μm resolution



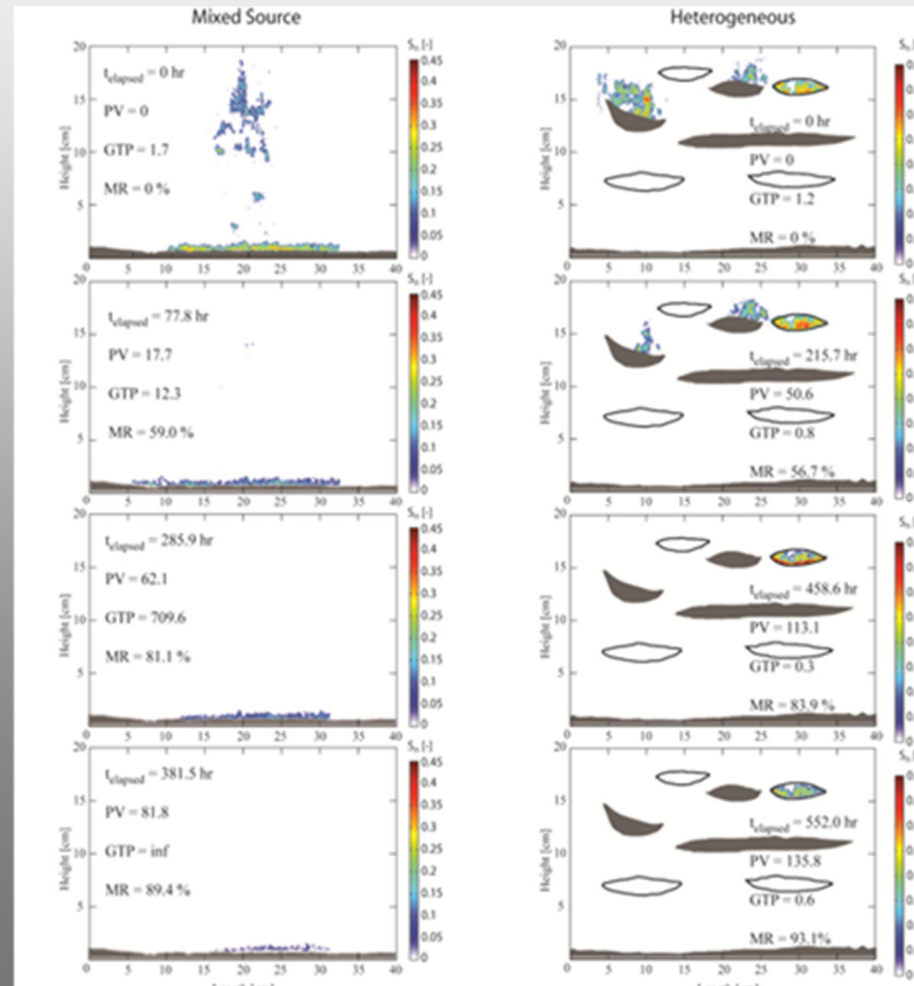




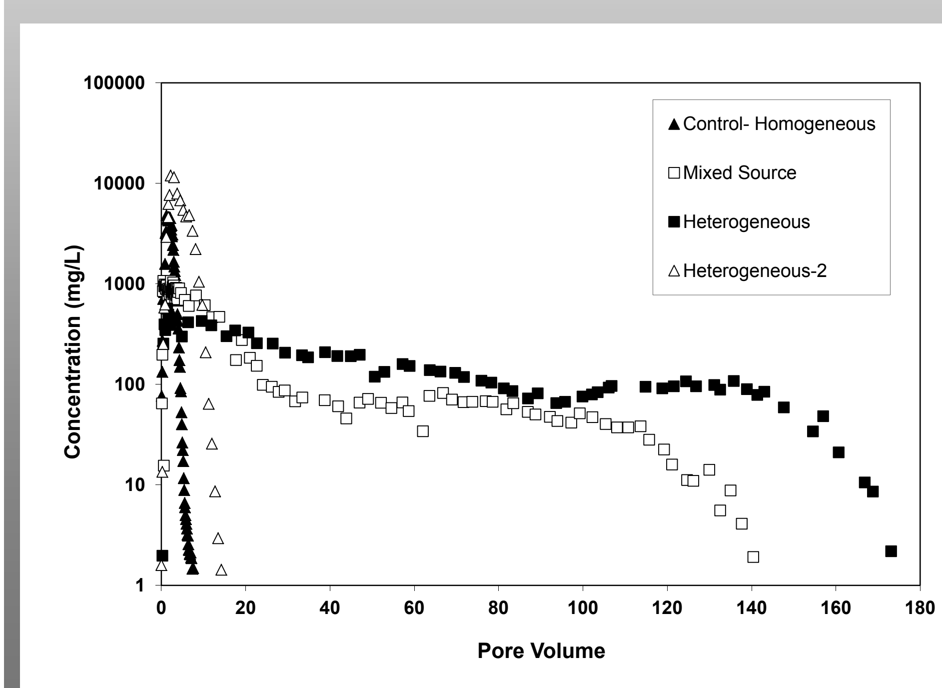
DNAPL Source Behavior

Laboratory Experiments
- Known DNAPL distributions
- Permeability variability
- Measure DNAPL in situ

DNAPL S_n Imaging



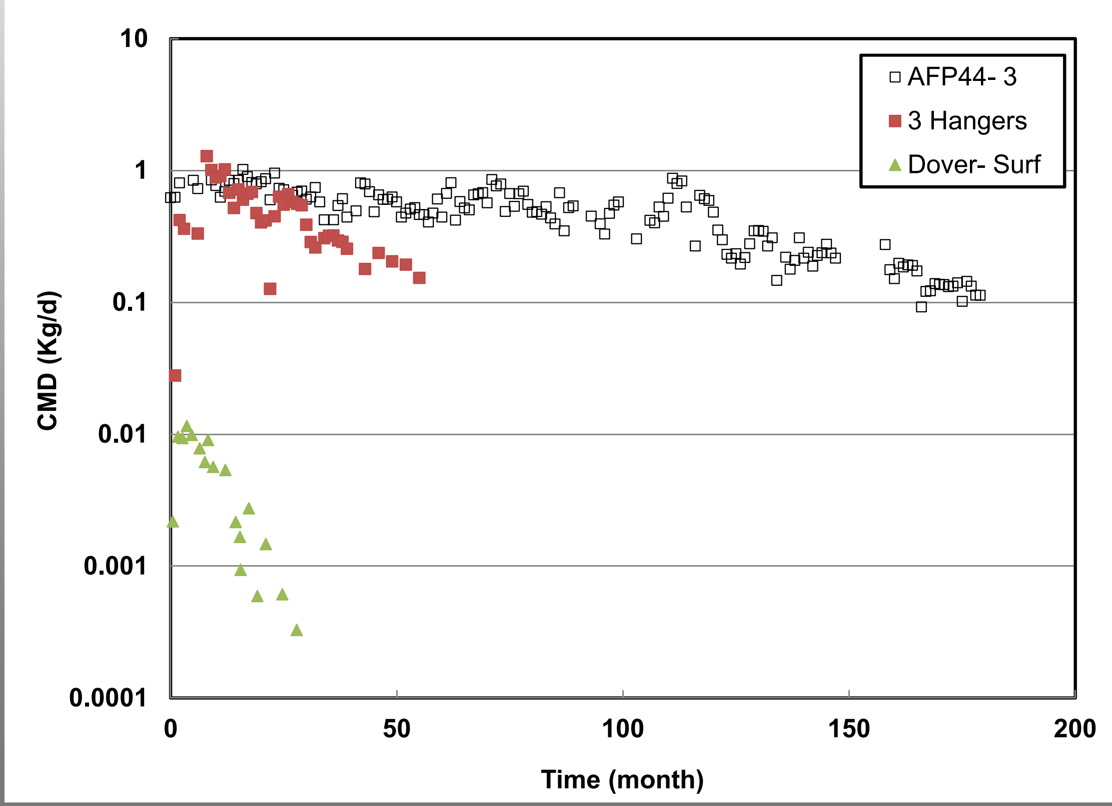
Flow-cell Experiments



DNAPL Source Behavior

Difficult to conduct comparative analysis

Field Data



Variables:

- Domain size

  [20 vs 10,000 m^2]

- Gradient & Q

  [natural vs induced]

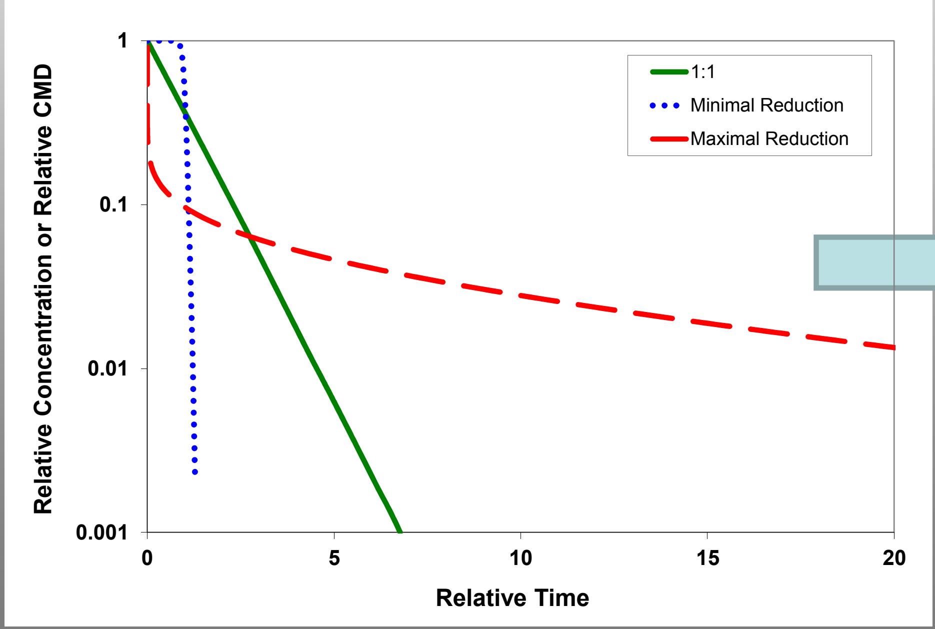
- Initial DNAPL Mass

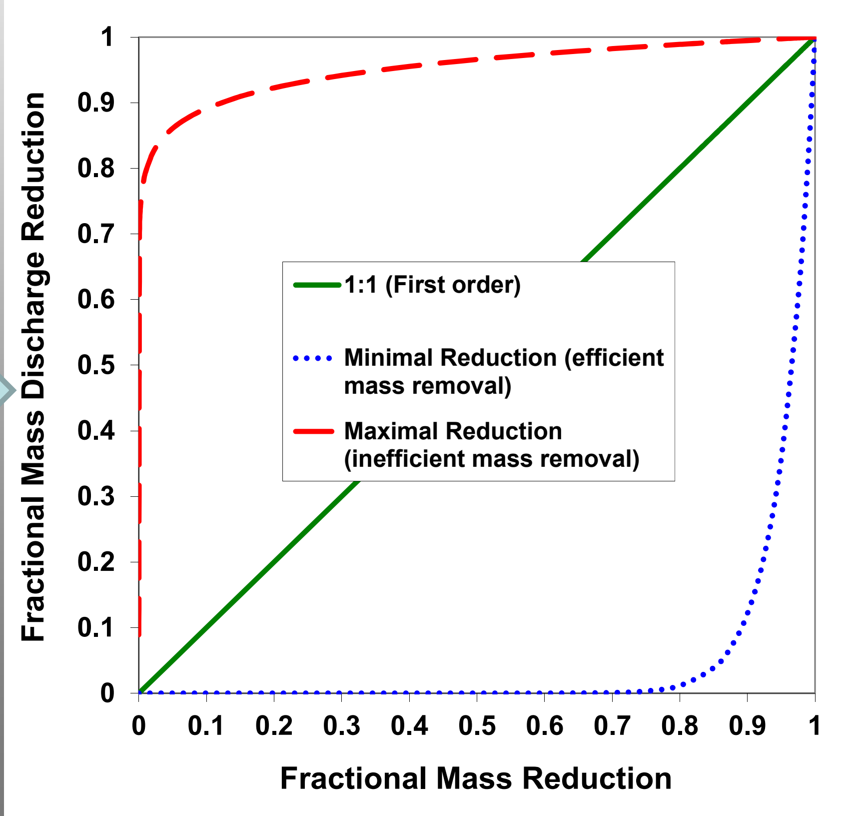
Data Analysis & Interpretation

- Employ contaminant mass discharge (CMD) metric

- Determine relationship between reduction in mass discharge and reduction in mass

- Enhances comparative analysis



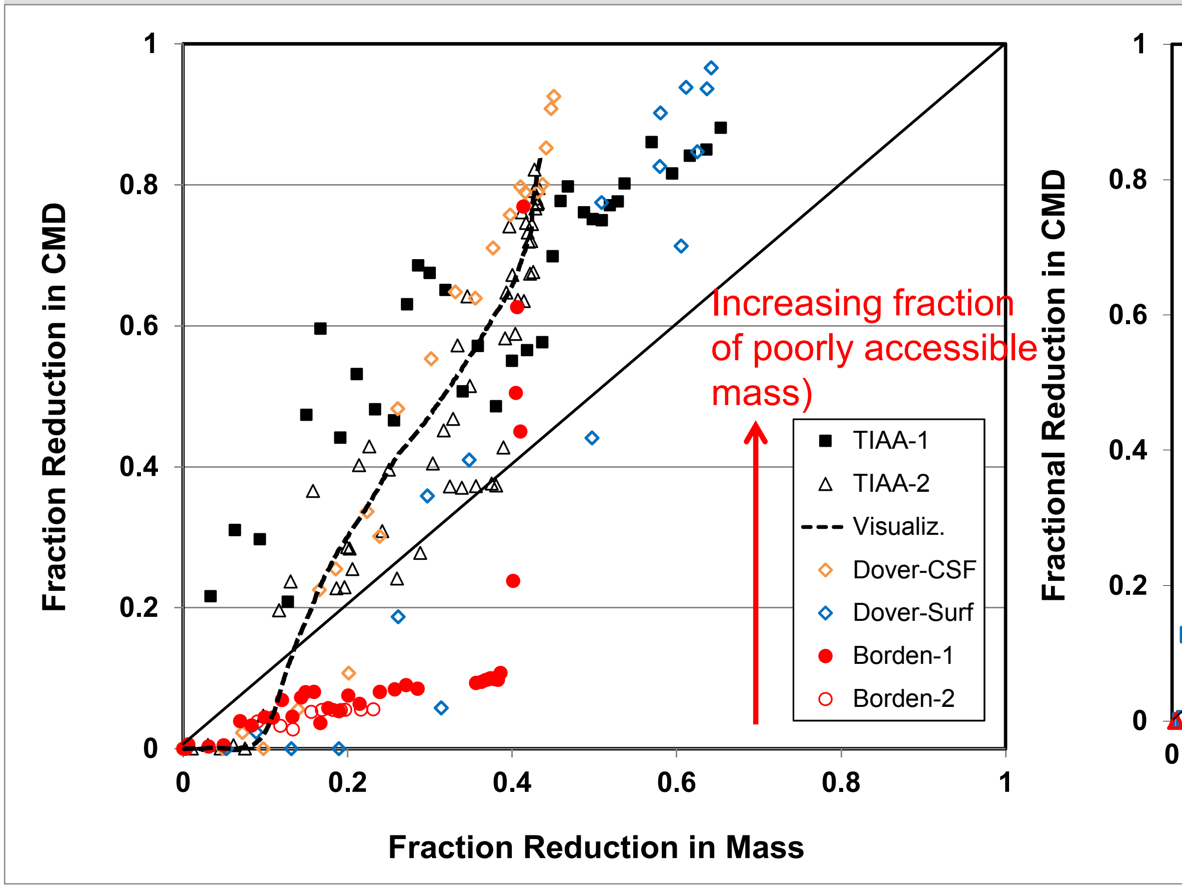


DNAPL Source Behavior

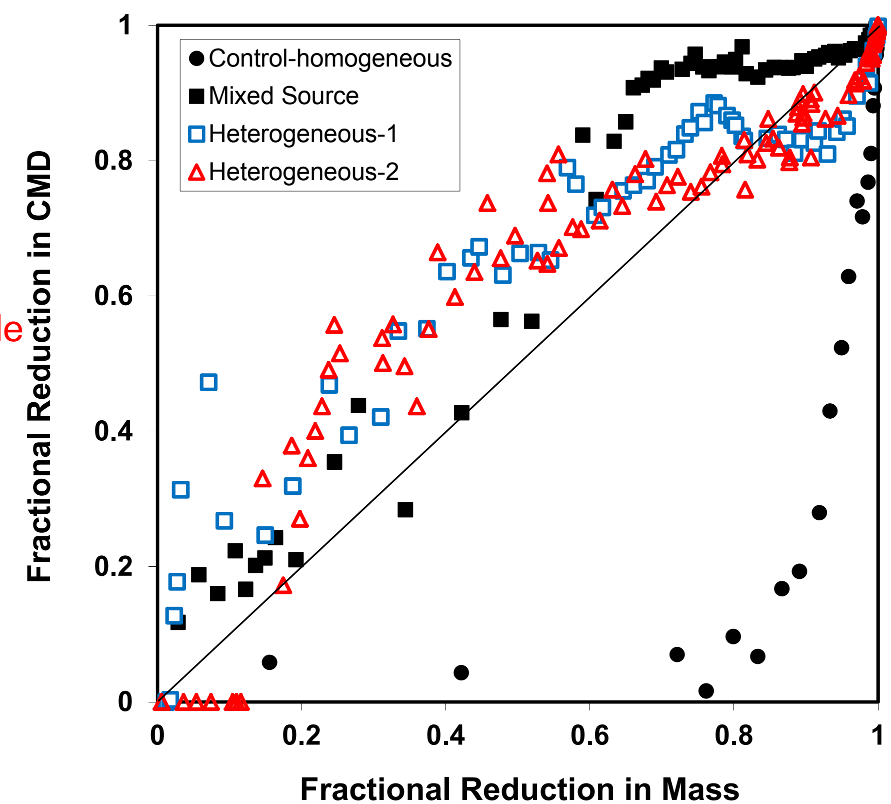
★ Contaminant Mass Distribution [Accessibility]

{source architecture, site age (mass removed)}

Field Data



Flow-cell Experiments



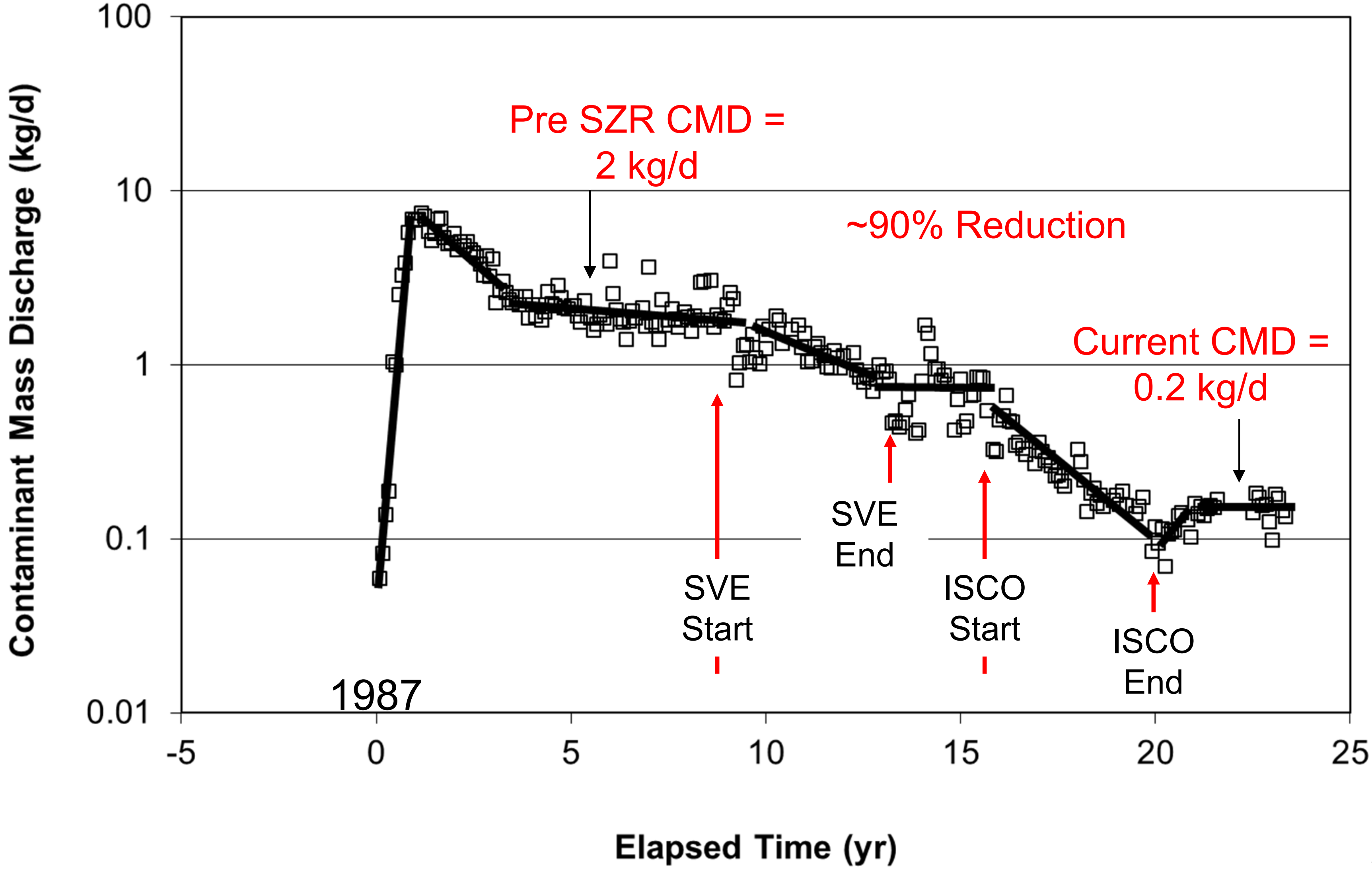
Post Source-zone Remediation

Persistence Factors:

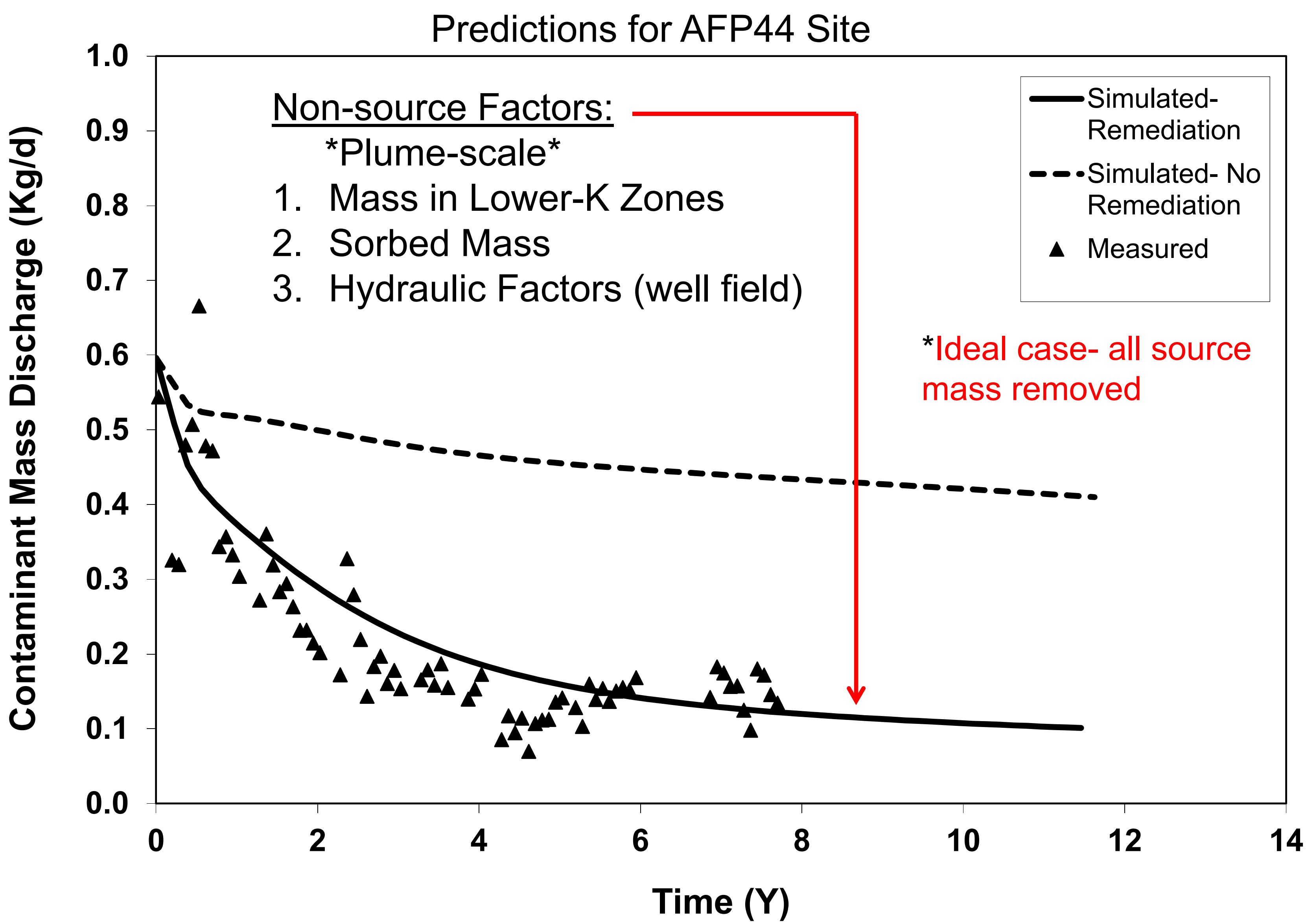
- Residual DNAPL Sources (incomplete removal/containment)
- Plume-scale Lower-K Zones and Mass Storage (diffusive mass transfer- “back diffusion”)
- Plume-scale Sorbed-phase Mass Storage (sorption/desorption processes)
- Hydraulic Factors (P&T well-field, etc)
- Other (Institutional, Analytical, etc)

Composite CMD: AFP44

Impacts from Source Remediation efforts



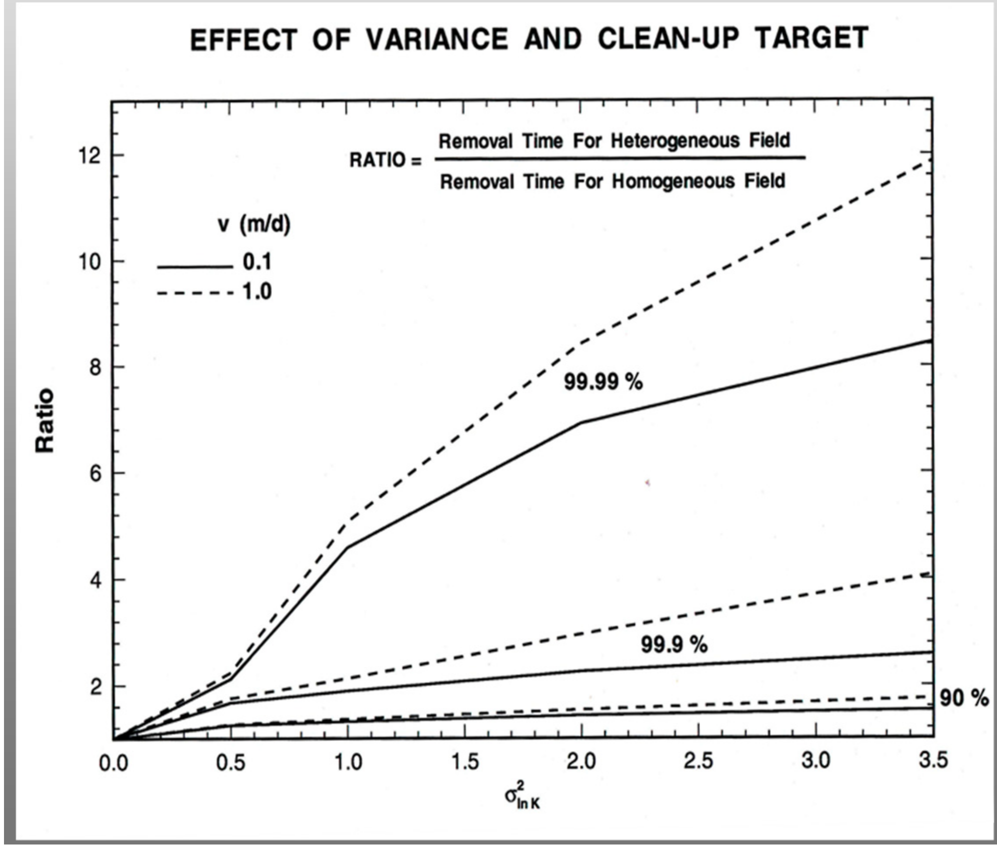
Plume Persistence after Source Remediation

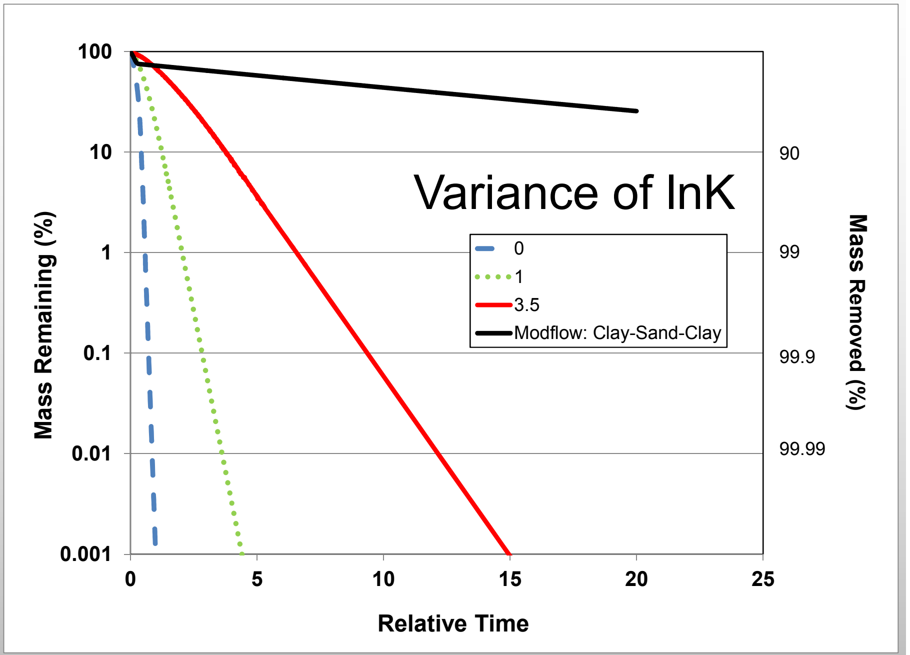


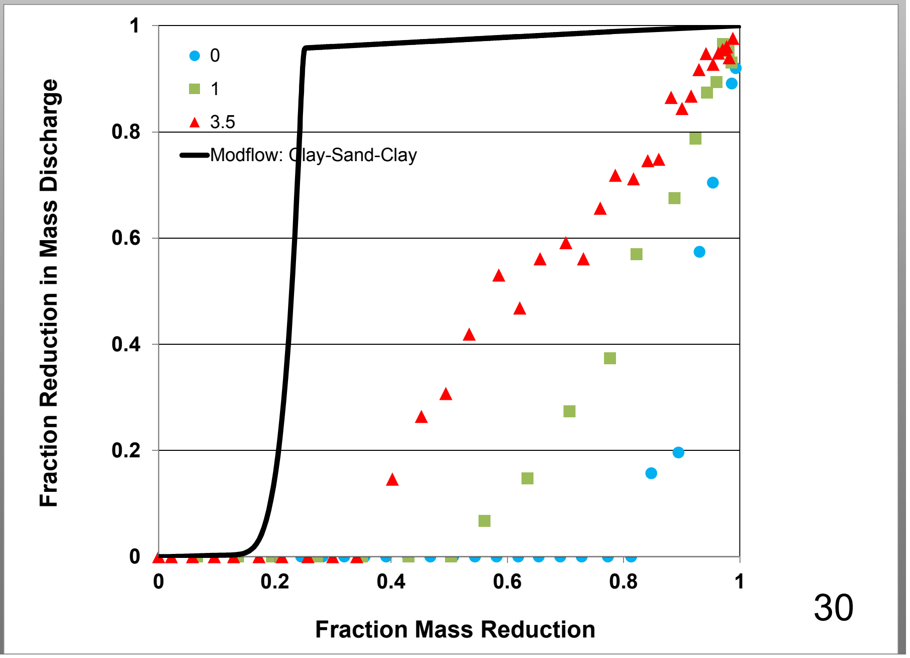
Lower-permeability Zones & Diffusion

Model Simulations

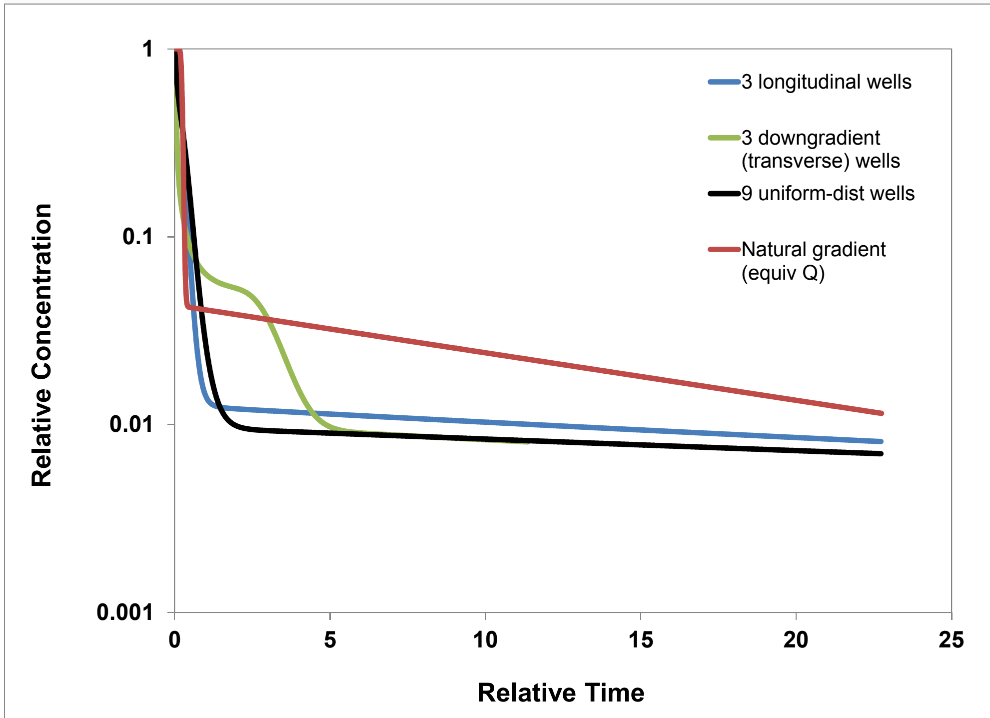
Stochastic (random K fields)
vs.
Discrete (homogeneous, orthogonal) layers (MODFLOW)





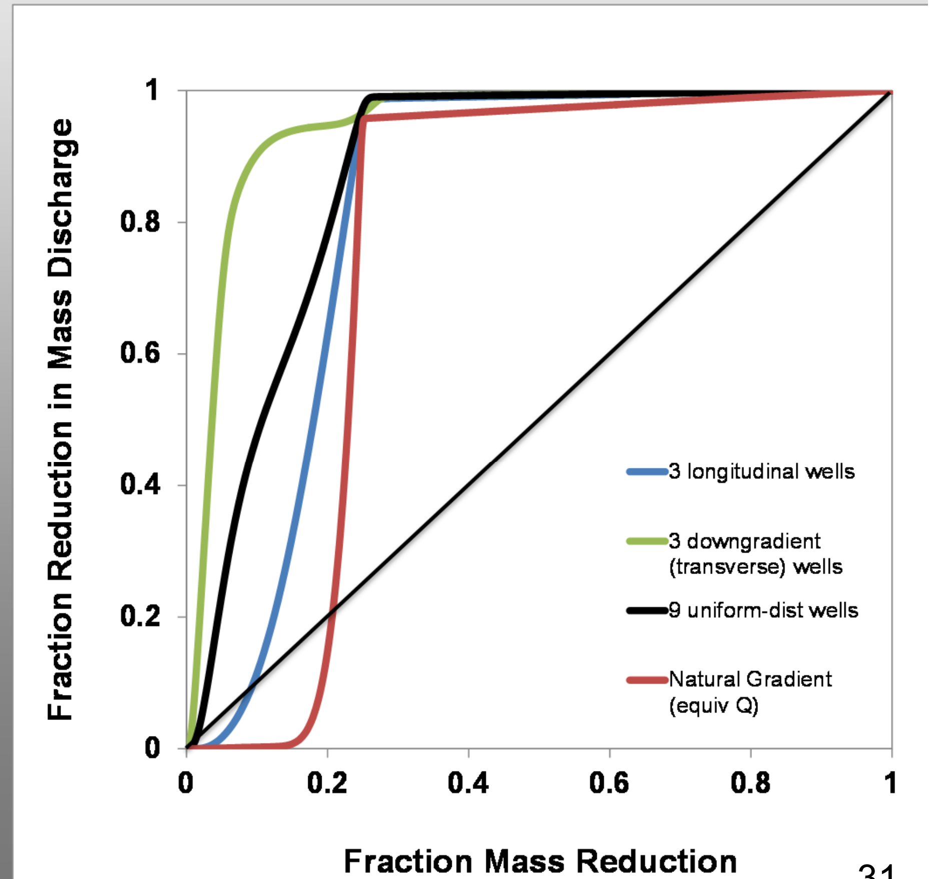


Well-field Configuration



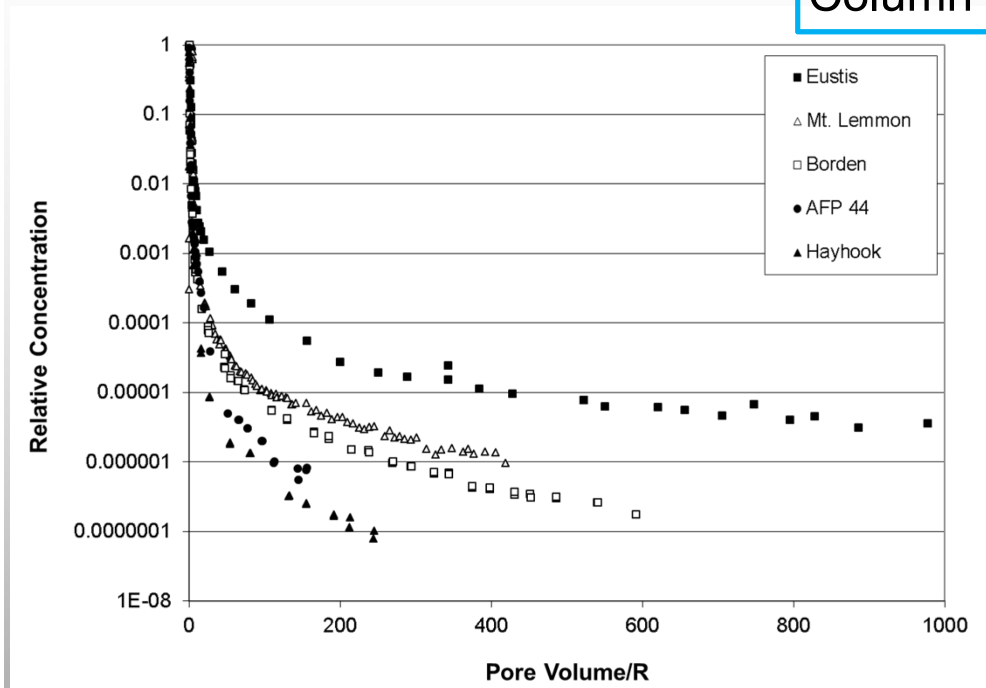
Model Simulations

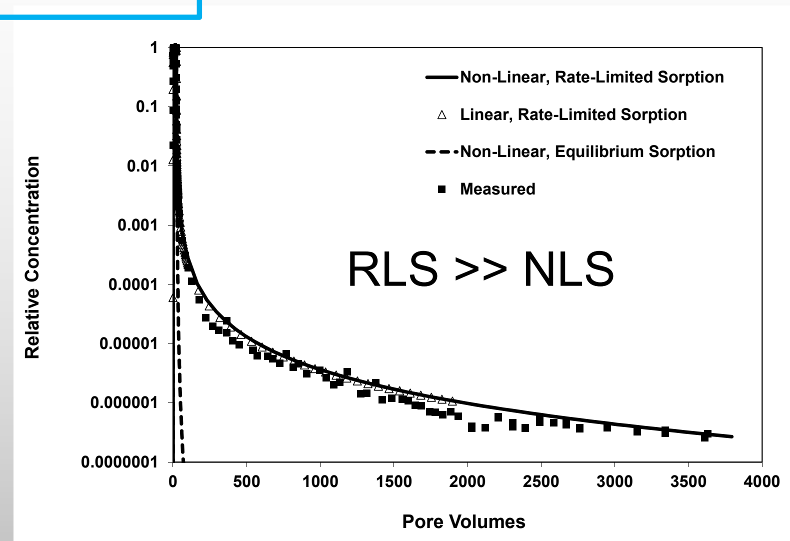
3–Layer system (Clay-Sand-Clay) [MODFLOW]



Sorption-Desorption Processes

Column Experiments





Extensive Elution Tailing

- Observed for all media
- Occurs with short contact times
- Need continuous-distribution domain model

★ Causative Mechanisms?

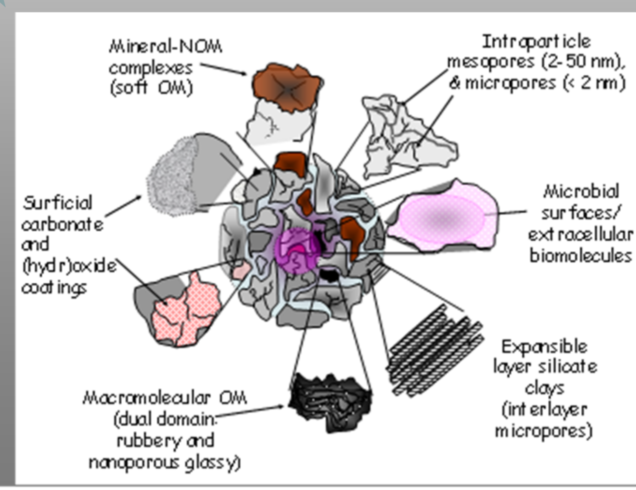
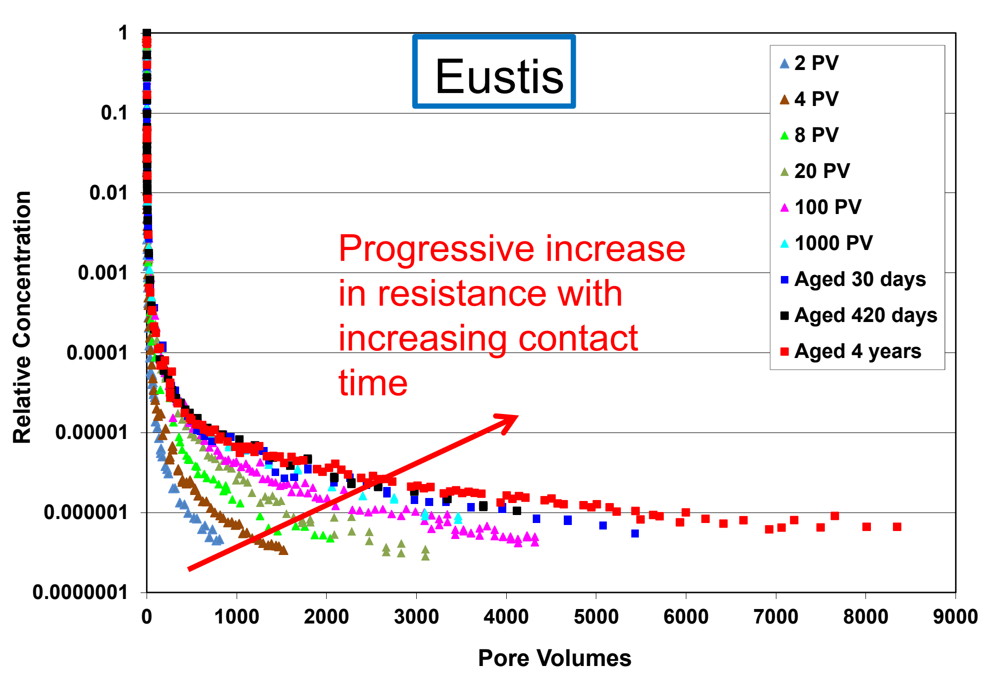


Figure A. Biogeochemically-reactive solid-water interfaces present in natural and waste-impacted geomedia (from Chorover and Brusseau, 2008)

Sorption-Desorption Processes

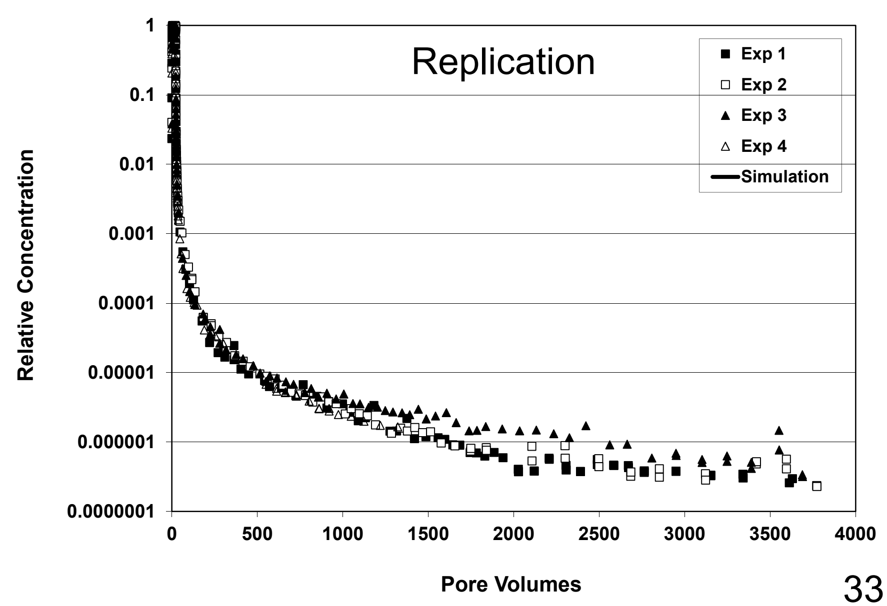


★ Interaction with Hard Carbon

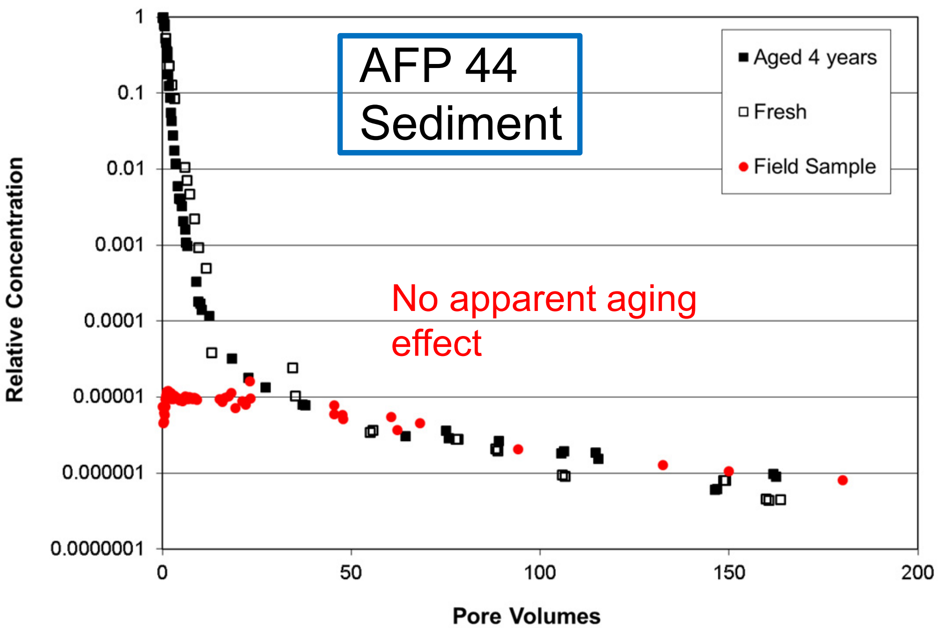
[sorbate permeation within, and sorbate-induced deformation of, the HC matrix]

98% quartz sand
2% clay (kaolinite- non-expanding)
0.38% organic carbon
0.14% hard carbon (kerogen, bc)

Non-linear sorption
Competitive sorption



Sorption-Desorption Processes



XRD Analysis: several AFP44 samples and 2 (mont) specimen controls

Clay inter-layer d-spacing = ~0.3-0.6 nm

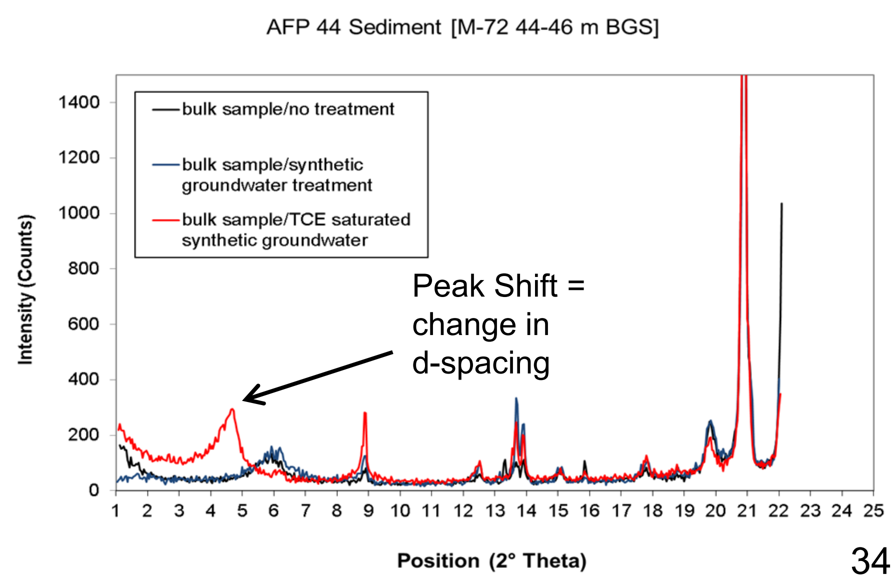
TCE thickness = ~0.3 nm

Increase in d-spacing for TCE treatment = ~0.4 nm

★ TCE Intercalation [+ HCl]

98-80% quartz, feldspars
2-20% clay (montmorillonite- expanding)
0.03% organic carbon
0.02% hard carbon (kerogen, bc)

Non-linear sorption



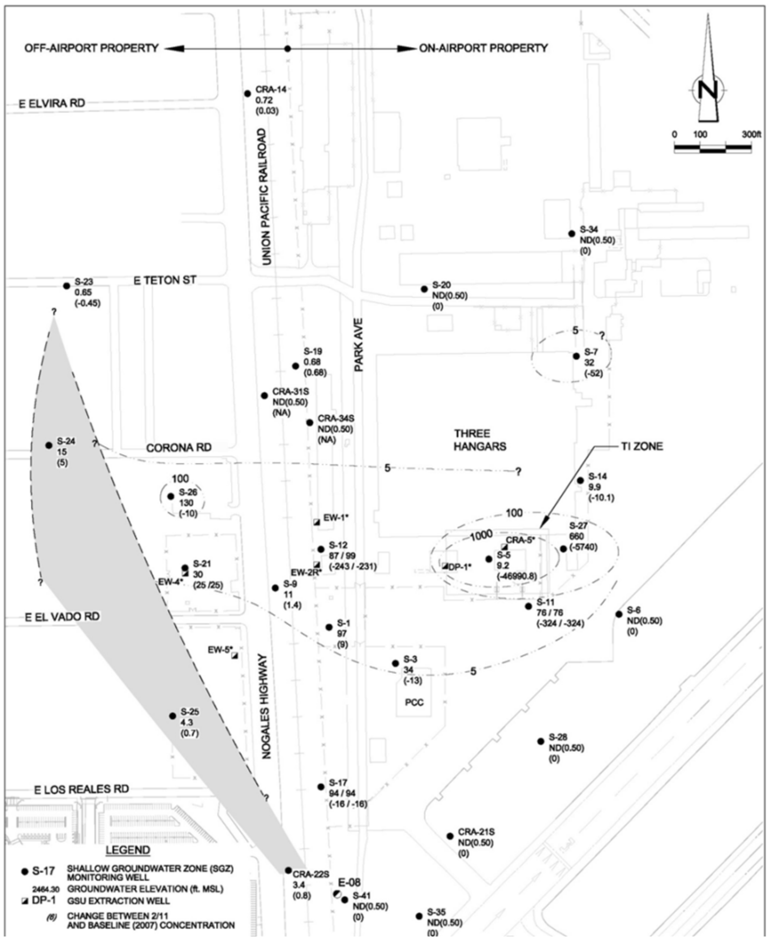
Summary: 3 Hanger Site at TIAA

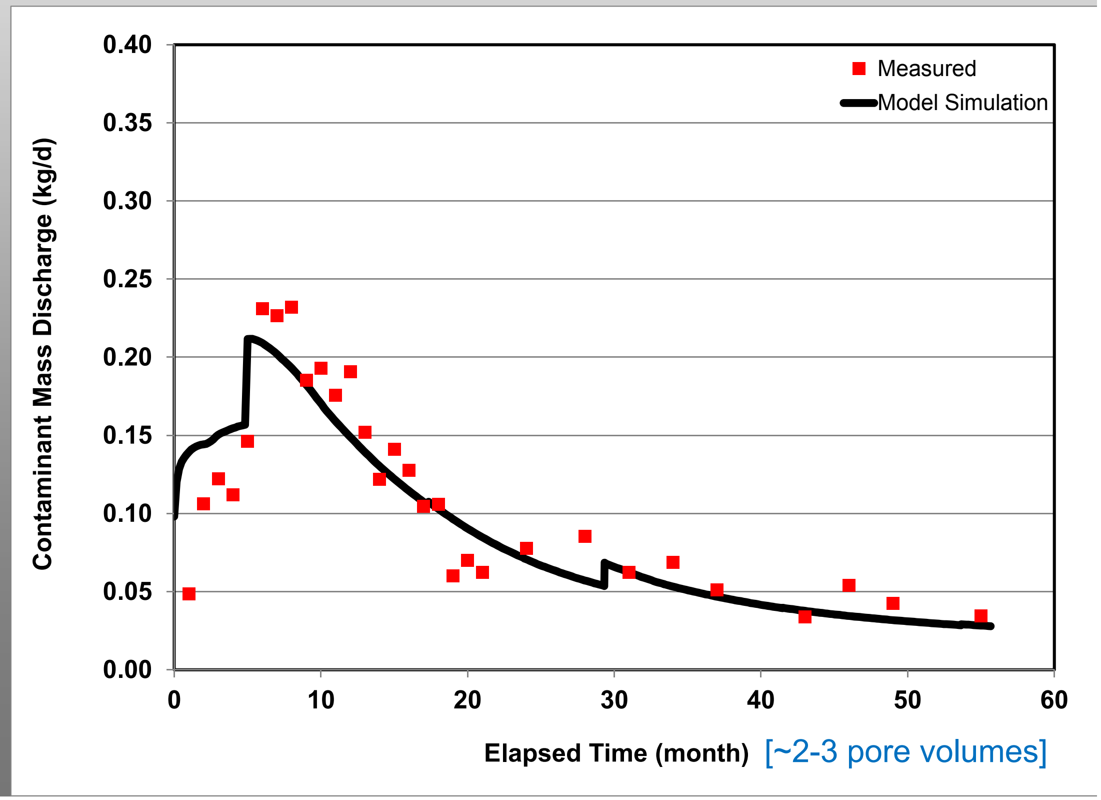
Hydraulic Source Control

Plume Reduction = ~50%

Identify Relevant Factors:

1. Low-K Zones and DMT
2. Source Residual
3. Well-field Configuration





Summary: continued

- Source Zones- incomplete removal/containment of contamination, continuing source
- Large, Persistent Plumes- contributing factors
- Site “Architecture” and “Age” key factors
  - Subsurface properties (permeability field, flow field)
  - Contaminant distribution (phases, relative accessibility)
  - Change in contaminant distributions and accessibility as sites age
- Alternatives to P&T ?
- Long-term Site Management

Acknowledgements

- The many students and post-docs who have contributed to this research; our collaborators and partners with EPA, AECOM, US Air Force, CRA, Tucson Airport Authority, ADEQ.

- Financial support provided by the National Institute of Environmental Health Sciences Superfund Research Program (ES04940), the US Department of Defense Strategic Environmental Research and Development Program (ER-1614), the US Air Force, and the Tucson Airport Authority

References

- Brusseau, M.L.; Nelson, N.T.; Zhang, Z.; Blue, J.E.; Rohrer, J.; Allen, T. 2007. Source-Zone Characterization of a Chlorinated-Solvent Contaminated Superfund Site in Tucson, AZ. J. Contam. Hydrol., 90:21-40.
- Brusseau, M.L., Hatton, J., and DiGuiseppi, W. 2011. Assessing the Impact of Source-Zone Remediation Efforts at the Contaminant-Plume Scale: Application to a Chlorinated-Solvent Site. J. Contam. Hydrol., 126:130-139.
- Brusseau, M.L., Carroll, K.C., Allen, T., Baker, J., DiGuiseppi, W., Hatton, J., Morrison, C., Russo, A., and Berkompas, J. 2011. The Impact of In-situ Chemical Oxidation on Contaminant Mass Discharge: Linking Source-zone and Plume-scale Characterizations of Remediation Performance. Environ. Sci. Technol., 45:5352-5358.
- Brusseau, M.L., Russo, A.E., and Schnaar, G. 2012. Nonideal Transport of Contaminants in Heterogeneous Porous Media: 9- Impact of Contact Time on Desorption and Elution Tailing. Chemosphere, 89:287-292.
- Brusseau, M.L. 2013. Use of Historical Pump-and-Treat Data to Enhance Site Characterization and Remediation Performance Assessment. Water Air Soil Poll., 224: article 1741.
- Brusseau, M.L. and Narter, M. 2013. Assessing the Impact of Chlorinated-Solvent Sites on Metropolitan Groundwater Resources. Groundwater, 51(6): 828-832.
- Brusseau, M.L.; Matthieu III, D.E.; Carroll, K.C.; Mainhagu, J.; Morrison, C.; McMillan, A.; Russo, A.; Plaschke, M. 2013. Characterizing Long-term Contaminant Mass Discharge and the Relationship Between Reductions in Discharge and Reductions in Mass for DNAPL Source Areas. J. Contam. Hydrol., 149: 1-12.
- Chorover, J. and Brusseau, M.L. 2008. Kinetics of Sorption-Desorption, pgs 109-149 in *Kinetics of Water-Rock Interaction*, S.L. Brantley, J. Kubicki, and A.F. White, Editors, Springer, New York, NY.
- DiFilippo, E.L. and Brusseau, M.L. 2008. Relationship Between Mass Flux Reduction and Source-zone Mass Removal: Analysis of Field Data. J. Contam. Hydrol., 98:22-35.
- DiFilippo, E.L., Carroll, K.C., and Brusseau, M.L. 2010. Impact of Organic-Liquid Distribution and Flow-Field Heterogeneity on Reductions in Mass Flux. J. Contam. Hydrol., 115:14-25.
- Johnson, G.R., Norris, D.K., and Brusseau, M.L. 2009. Mass Removal and Low-concentration Tailing of Trichloroethene in Freshly-amended, Synthetically-aged, and Field-contaminated Aquifer Material. Chemosphere, 75:542–548.
- Matthieu III, D.E., Brusseau, M.L., Johnson, G.R., Artiola, J.L., Bowden, M.L., Curry, J.E. 2013. Intercalation of Trichloroethene by Sediment-Associated Clay Minerals. Chemosphere, 90:459-463.
- Russo, A., Johnson, G.R., Schnaar, G., and Brusseau, M.L. 2010. Nonideal Transport of Contaminants in Heterogeneous Porous Media: 8. Characterizing and Modeling Asymptotic Contaminant-Elution Tailing for Several Soils and Aquifer Sediments. Chemosphere, 81:366-371.
- Schnaar, G. and Brusseau, M.L. 2006. Characterizing pore-scale dissolution of organic immiscible liquid in natural porous media using synchrotron X-ray microtomography. Environ. Sci. Technol., 40:6622-6629.
- Zhang, Z. and Brusseau, M.L. 1999. Nonideal Transport of Reactive Solutes in Heterogeneous Porous Media: 5. Simulating Regional-Scale Behavior of a Trichloroethene Plume During Pump-and-Treat Remediation. Water Resour. Res., 35: 2921-2935.