Research on Fate, Transport, and Remediation of Chlorinated Solvents in Fractured Sedimentary Rocks at the former Naval Air Warfare Center, West Trenton, NJ

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USGS

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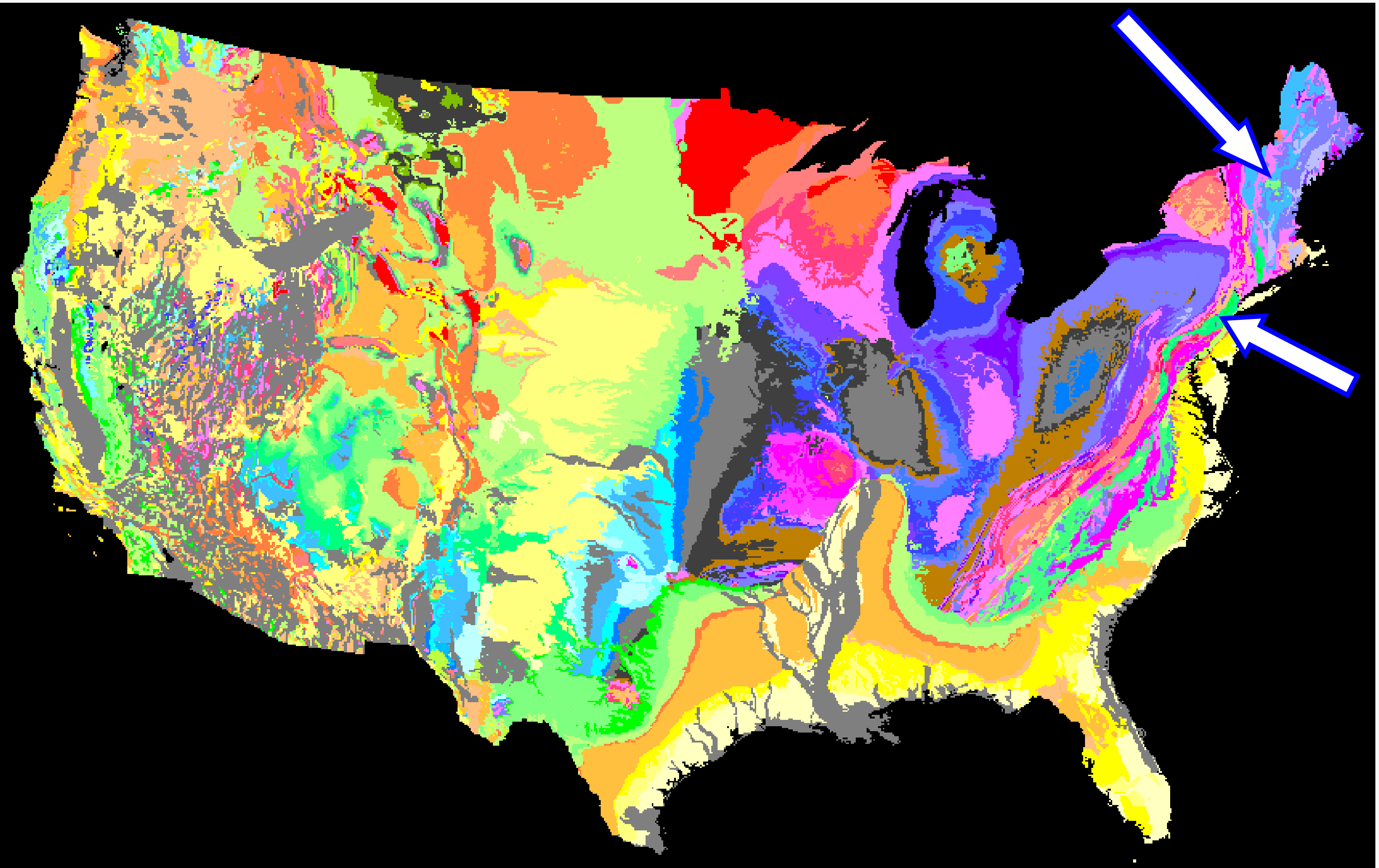
USGS Research in Fractured Rock Aquifers

Mirror Lake, New Hampshire:
Crystalline rocks of White Mountains

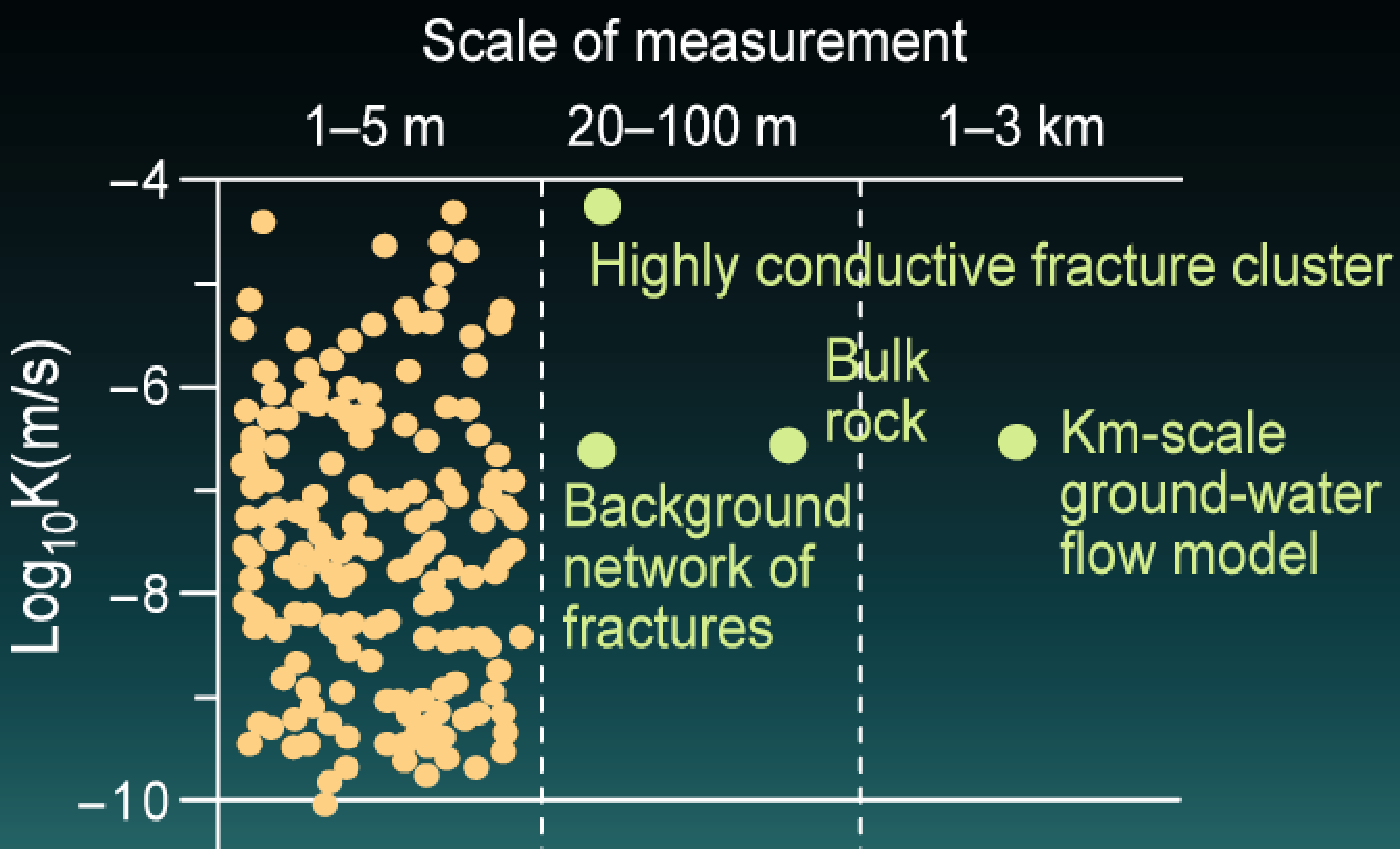


NAWC,
New Jersey:
Sedimentary rocks of Newark Basin

USGS Research on Flow and Transport in Fractured Rock Aquifers

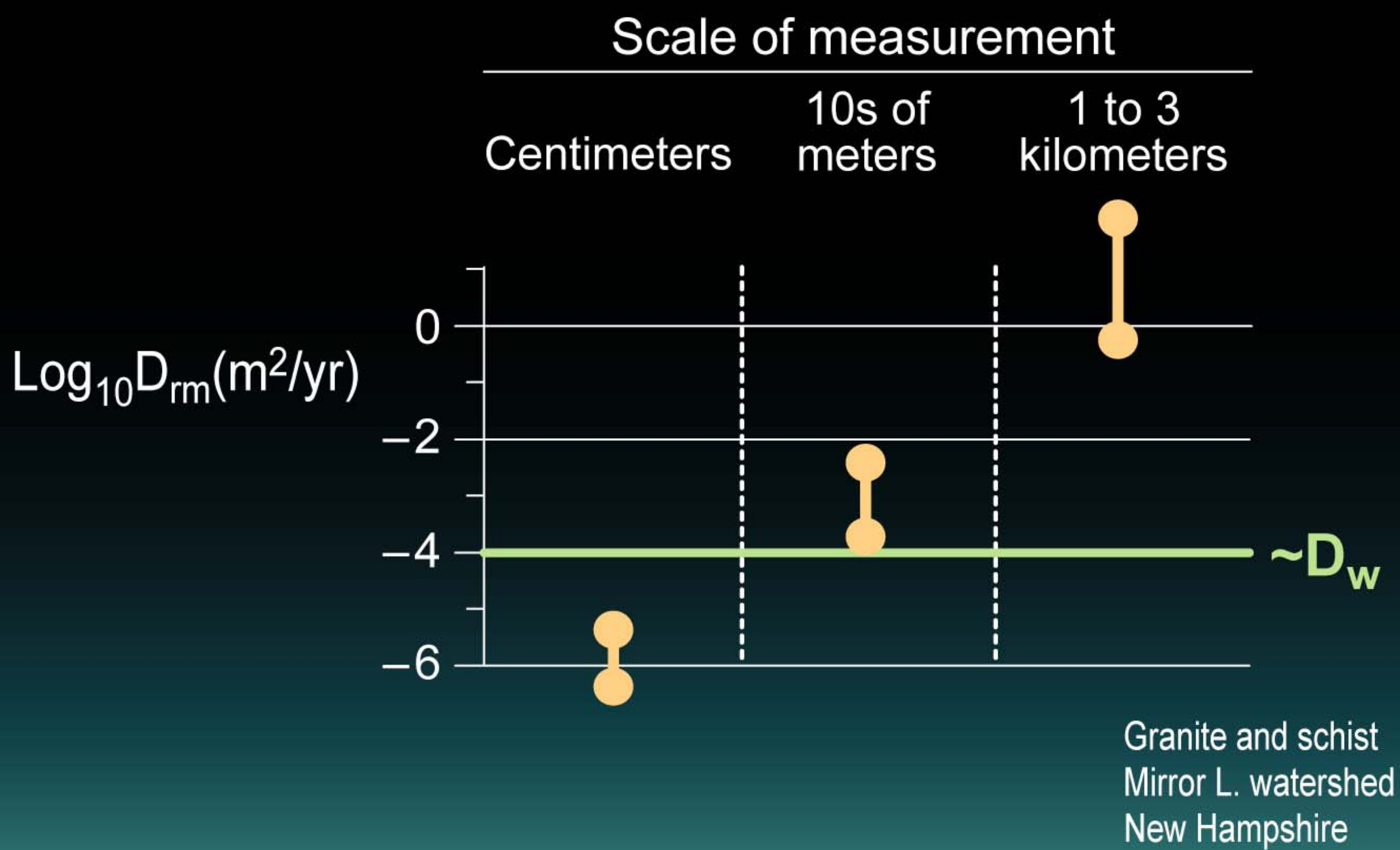
- Mirror Lake, NH: Previous site for research in fractured rock hydrology.
- Characterization methods and research findings have been used to understand ground-water flow and chemical transport at many other fractured rock sites.

Mirror Lake: Hydraulic Conductivity from Boreholes to Kilometers



Hsieh, Shapiro, Tiedeman

Mirror Lake: Matrix Diffusion



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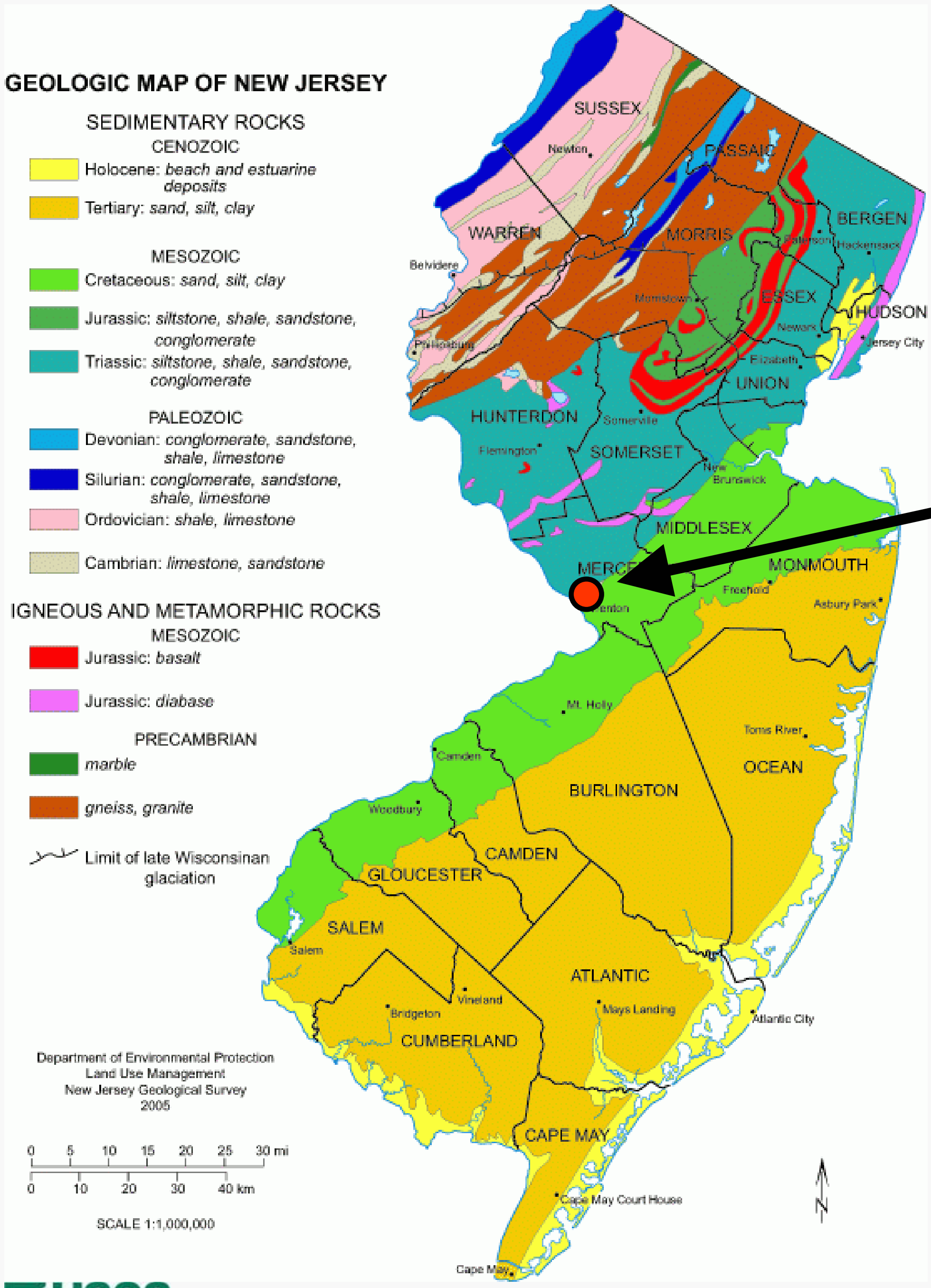
Becker & Shapiro (2000, 2003); Shapiro (2001)

Building on 20 Years of USGS Work in Fractured Aquifers

- Naval Air Warfare Center, NJ: Fractured rock site with ground-water contamination.
- NAWC chosen as current study site because:
  - Extensive TCE, DCE, vinyl chloride contamination in ground water.
  - Geologic framework well characterized.

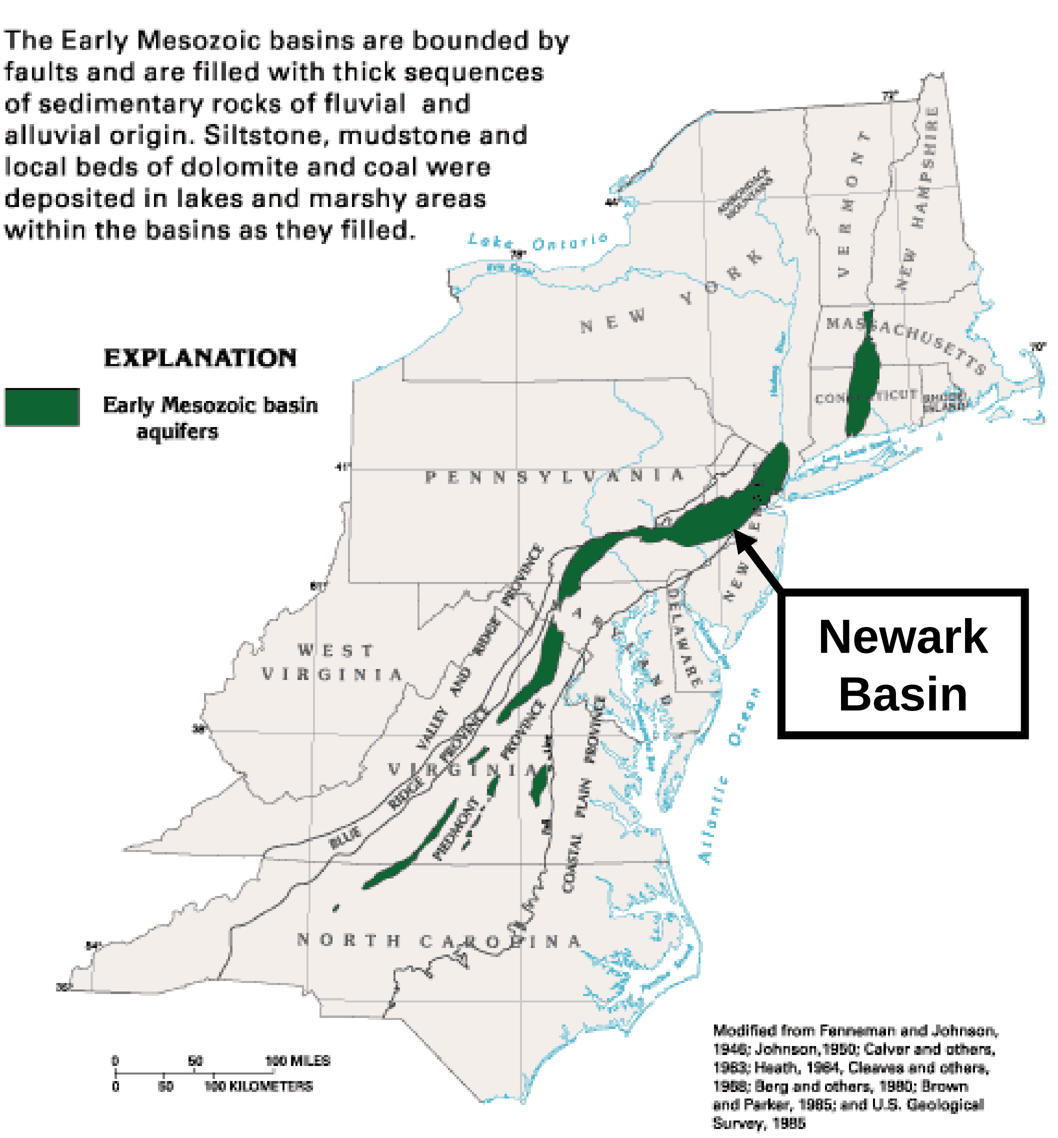


Former Naval Air Warfare Center (NAWC) West Trenton, NJ

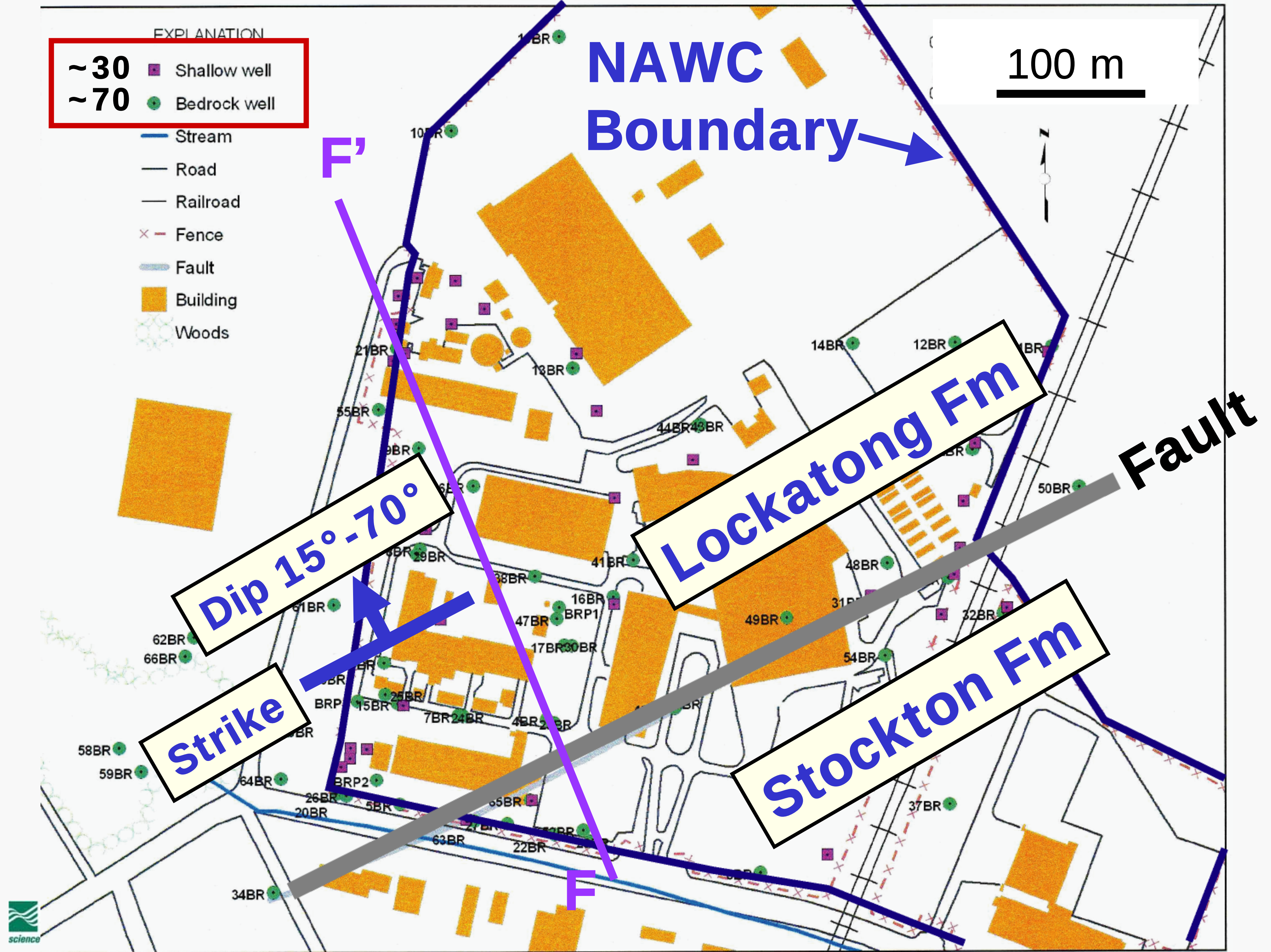
Site History

- Navy jet engine testing facility, 1950's to 1990's
- TCE & jet fuel leaked into subsurface
- Facility was closed in 1998
- Pump & treat since mid-1990's

NAWC Underlain by Fractured Dipping Sedimentary Rocks of Newark Basin

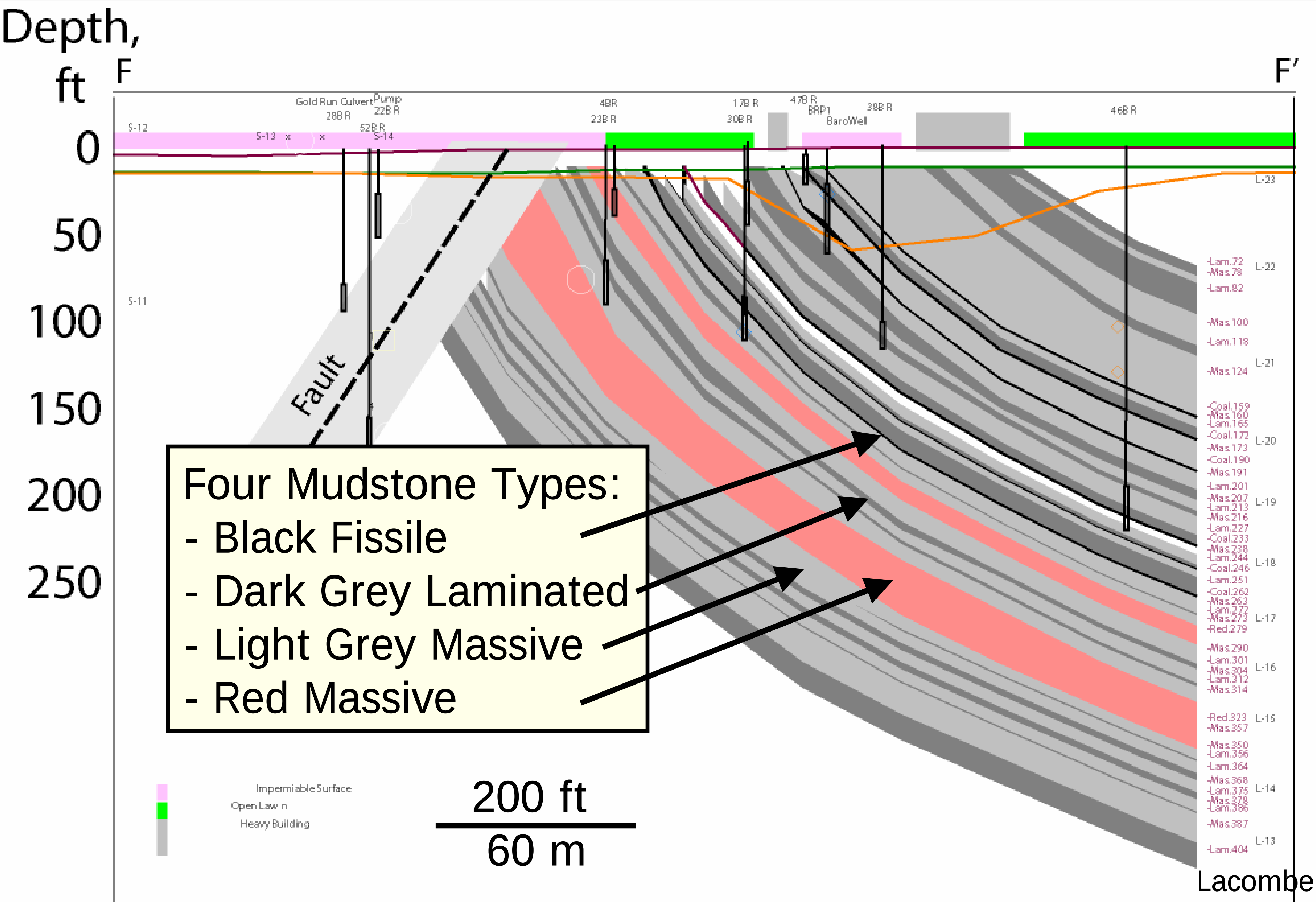


- Rift basin deposited in Triassic (early Mesozoic), about 200 to 250 million years ago.
- In vicinity of NAWC, rocks are gently dipping mudstones and sandstones.

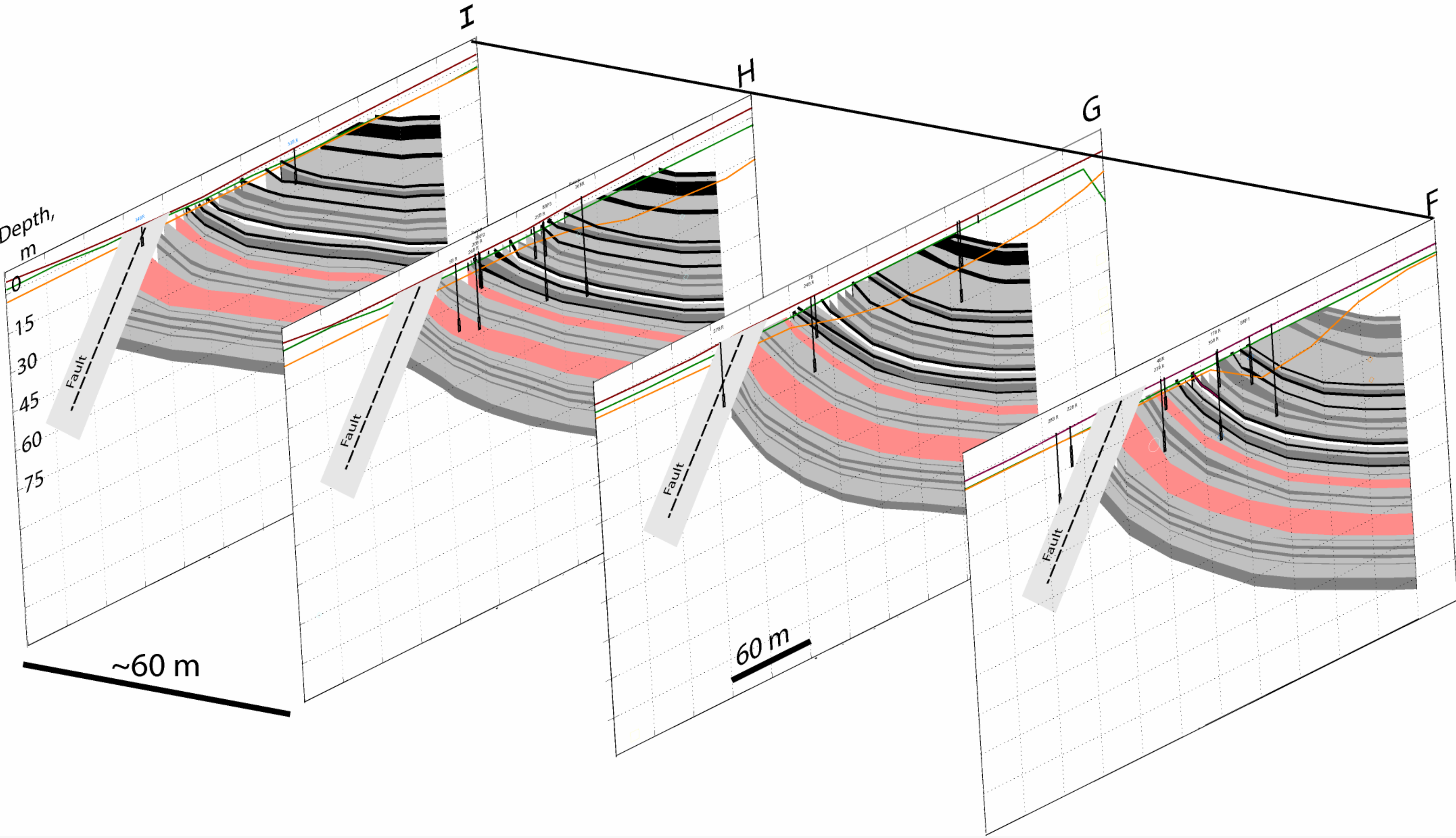


EXPLANATION
~30 Shallow well
~70 Bedrock well
Stream
Road
Railroad
Fence
Fault
Building
Woods
NAWC
Boundary
100 m
F'
F
Dip 15°-70°
Strike
Lockatong Fm
Stockton Fm
Fault

Dipping Bedded Lockatong Mudstones



Dipping Bedded Lockatong Mudstones



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Highly weathered rock

Competent Black & grey mudstone

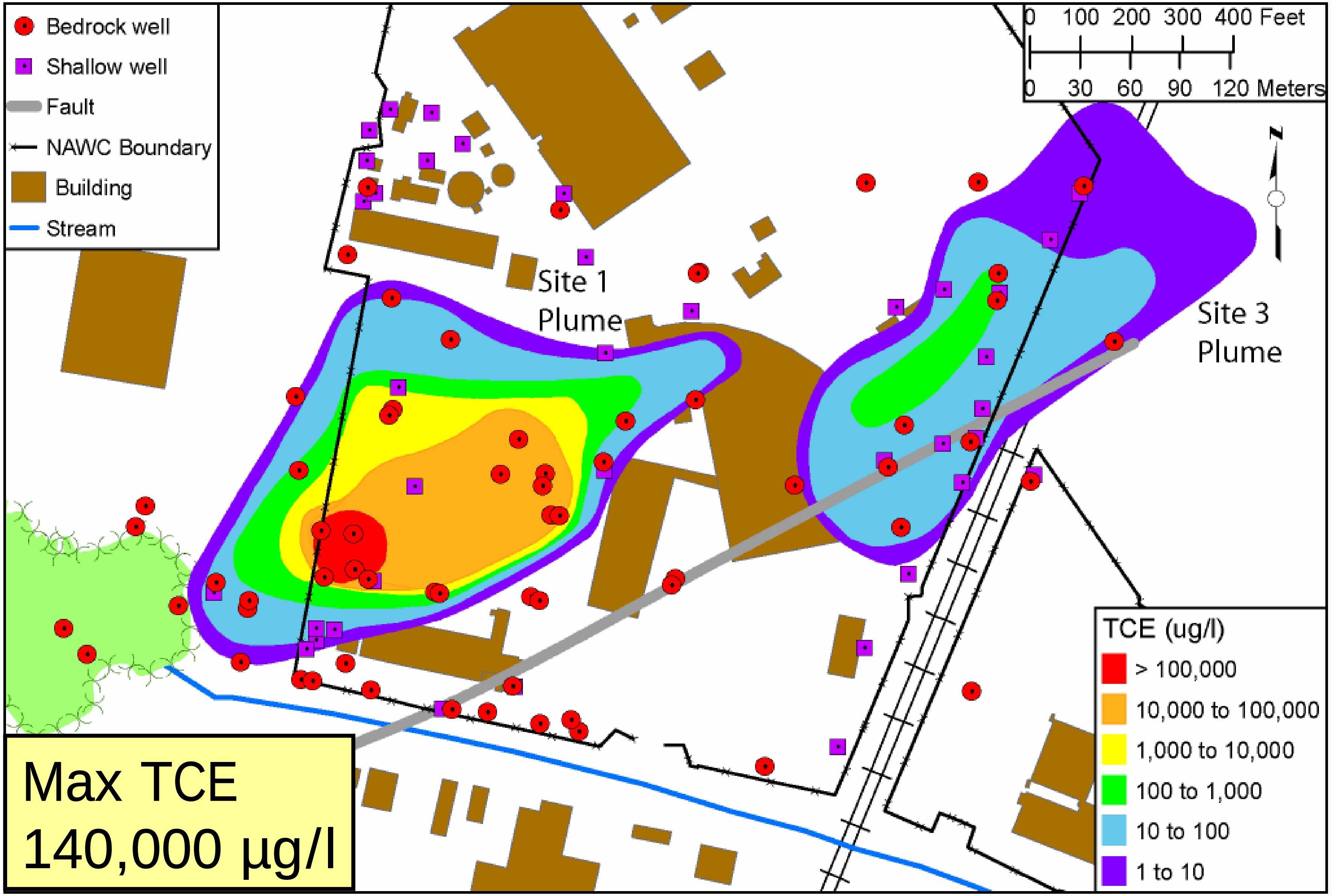
Ground-Water Contamination: Trichloroethene, Dichloroethene, Vinyl Chloride

- TCE used as heat transfer agent at jet engine testing facility.
- Leaked into subsurface in many locations, in pure and dissolved phases.
- Has anaerobically biodegraded (reductive dechlorination) under natural conditions to form DCE and vinyl chloride.

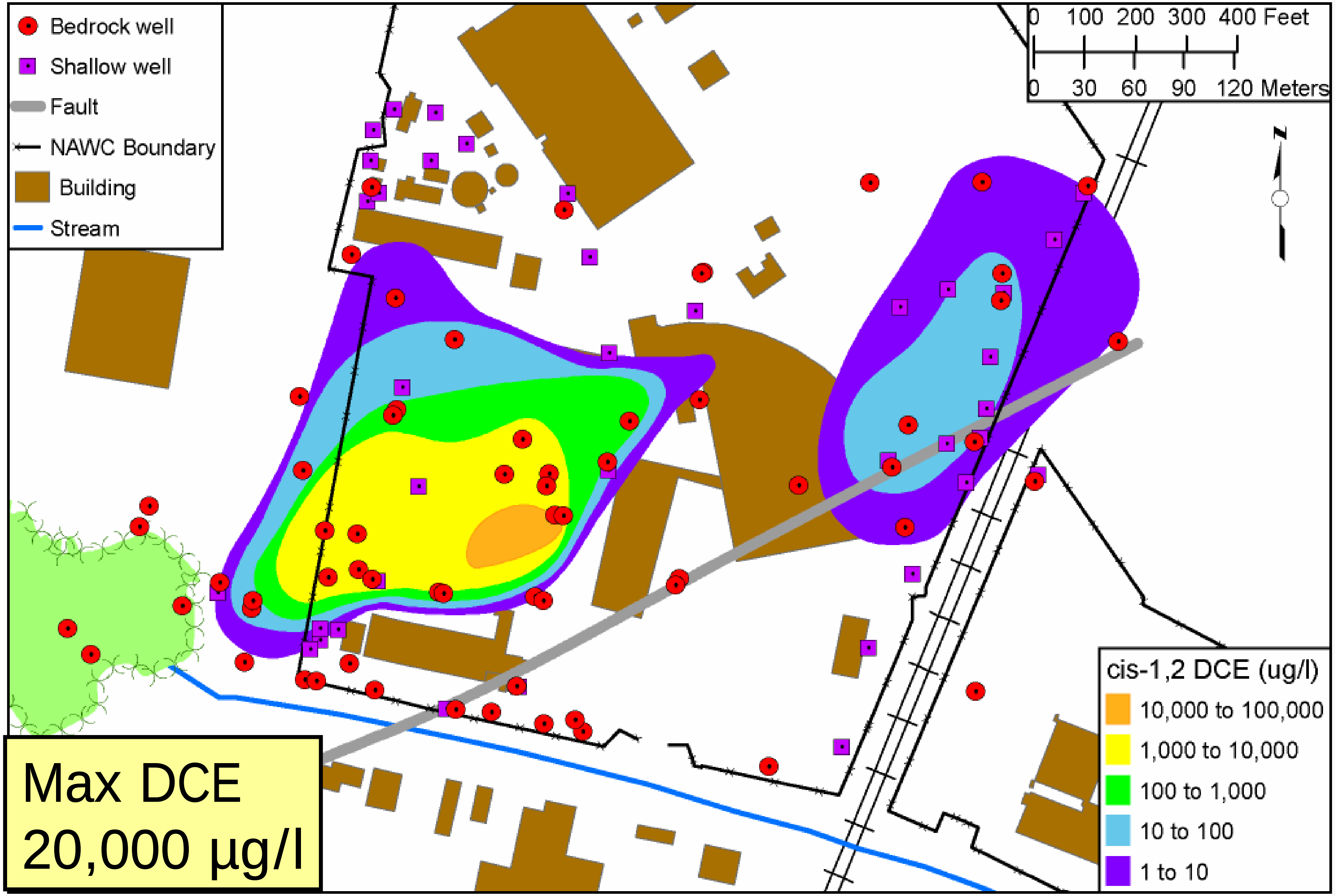
TCE →	**DCE** →	**VC** →	**Ethene**
3 Cl^-	2 Cl^-	1 Cl^-	0 Cl^-

USGS science for a changing world

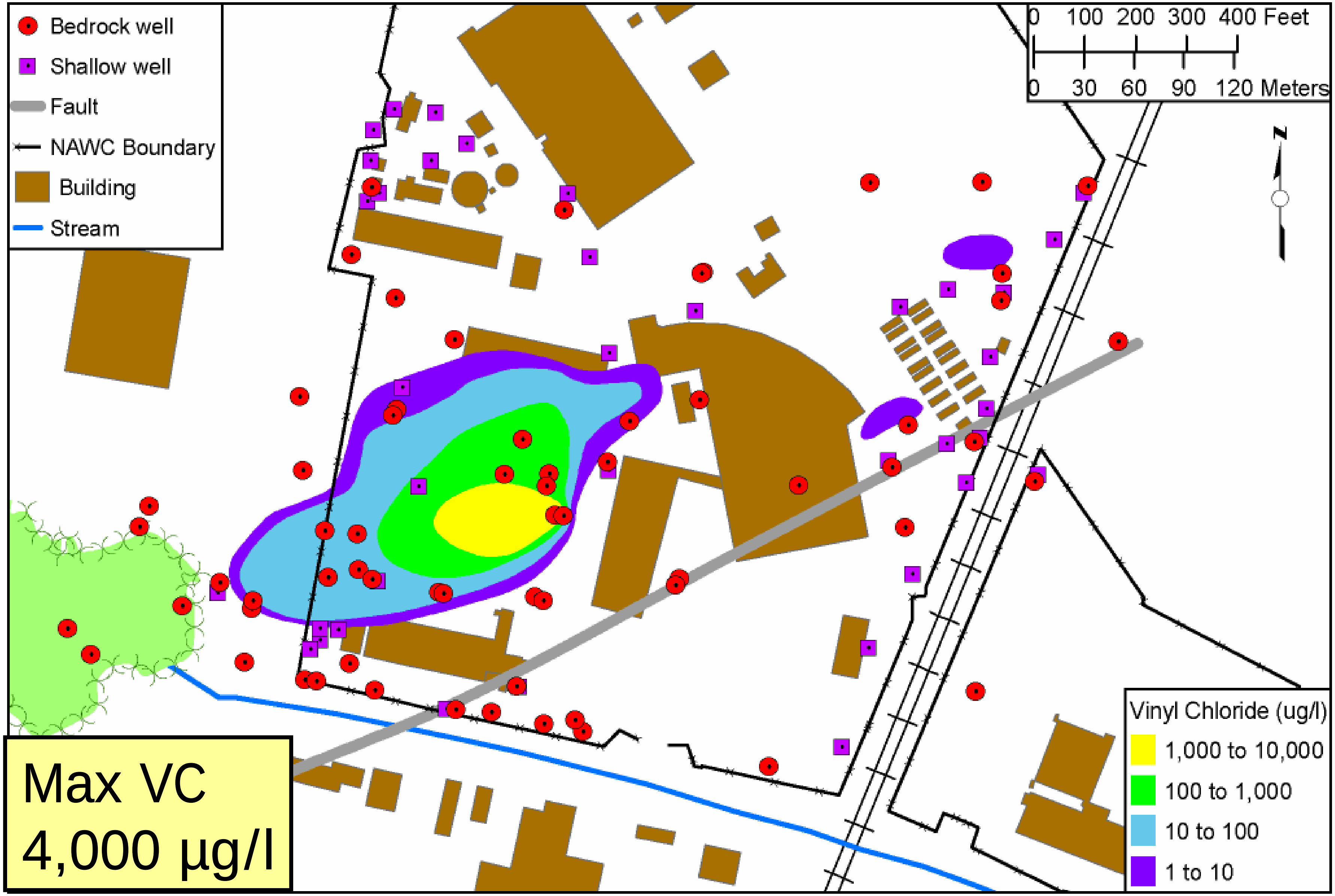
Trichloroethene at depth of 30 m



Dichloroethene at 30 m depth



Vinyl Chloride at 30 m depth



Max VC
4,000 µg/l

Approach of Investigations Under USGS Toxics Substances Hydrology Program

- Conduct detailed, **long-term**, **multidisciplinary** investigation at a ‘focus site’.
- Generalize and transfer results from focus site to other contaminated aquifers.

NAWC: Research Objectives

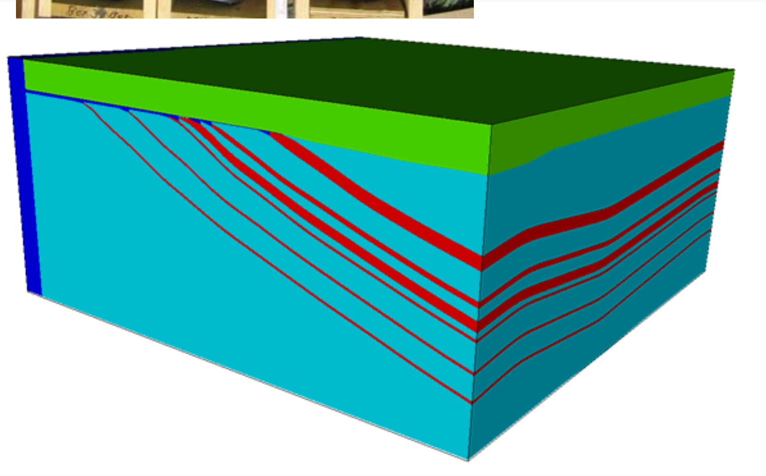
- Understand physical, chemical, and microbiological **processes and properties** affecting contaminant fate and transport in fractured rocks.
- Investigate processes of natural **contaminant removal** and evaluate methods to enhance this removal.
- Develop and test **models** to help improve understanding of the properties and processes.
- **Transfer** knowledge, processes, and methods.

NAWC: Research Themes

1. Finding flow and transport paths
2. Monitoring contamination, geochemistry, and microbiology
3. Evaluating remediation effectiveness

Theme 1: Finding Flow and Transport Paths

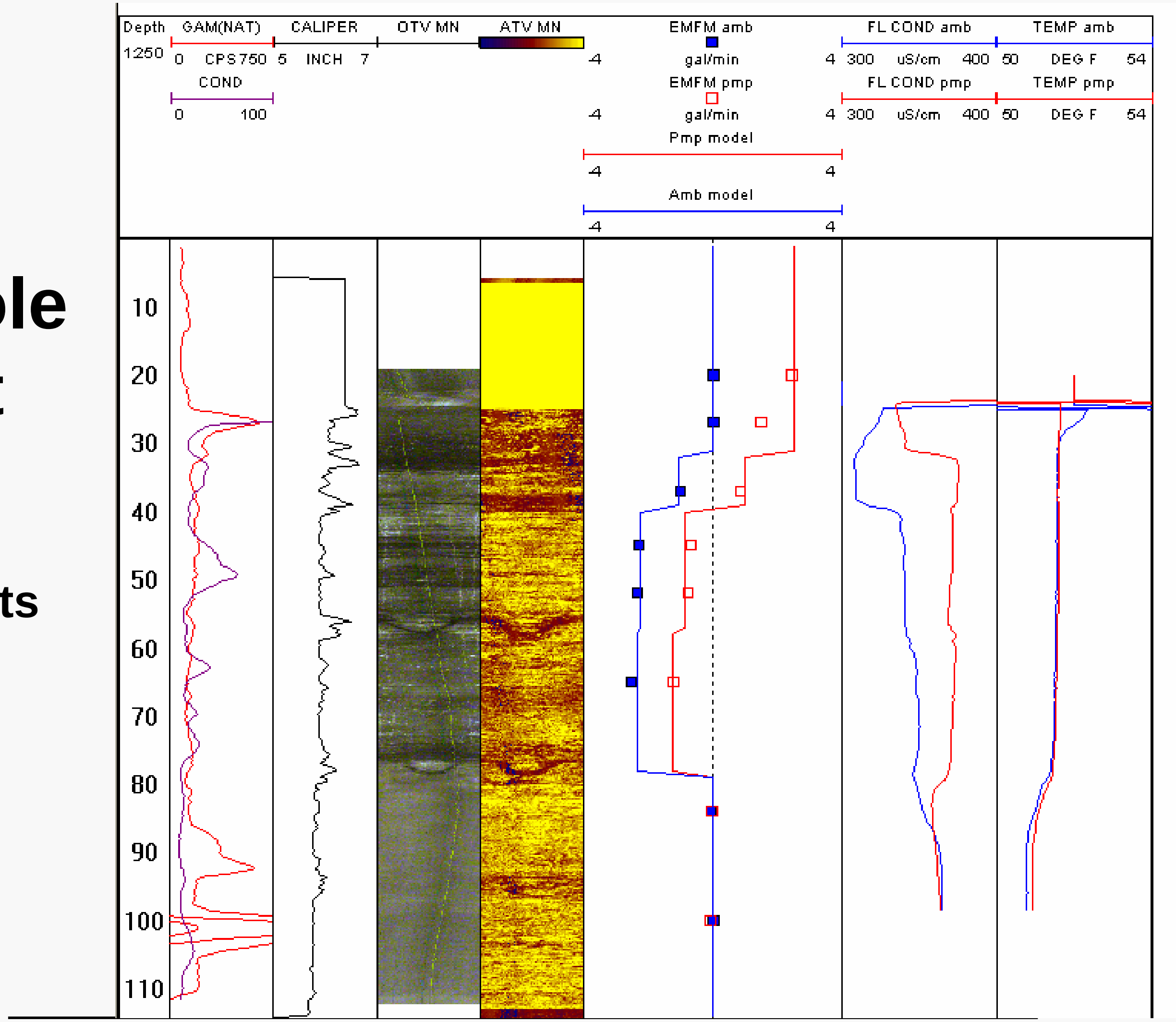
- **Understanding the fate of chlorinated solvents in fractured rock . . .**
- **and designing effective remediation strategies first requires . . .**
- **a detailed understanding of the paths of fluid and chemical movement.**



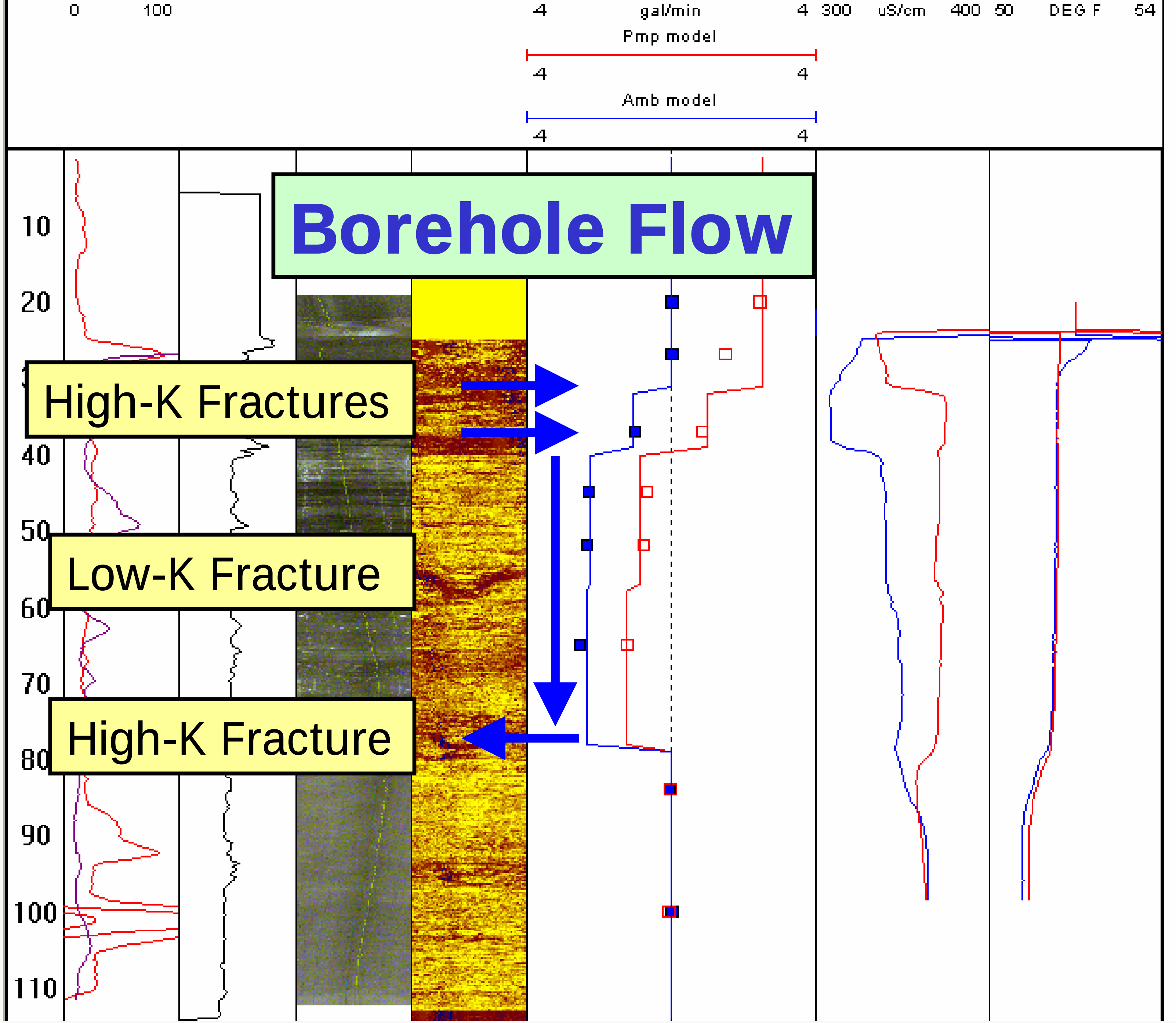
Borehole Flow Logging To Identify Permeable Fractures

Single-Hole Flow Test

Measured and Modeled Results



Williams, Anderson, Johnson



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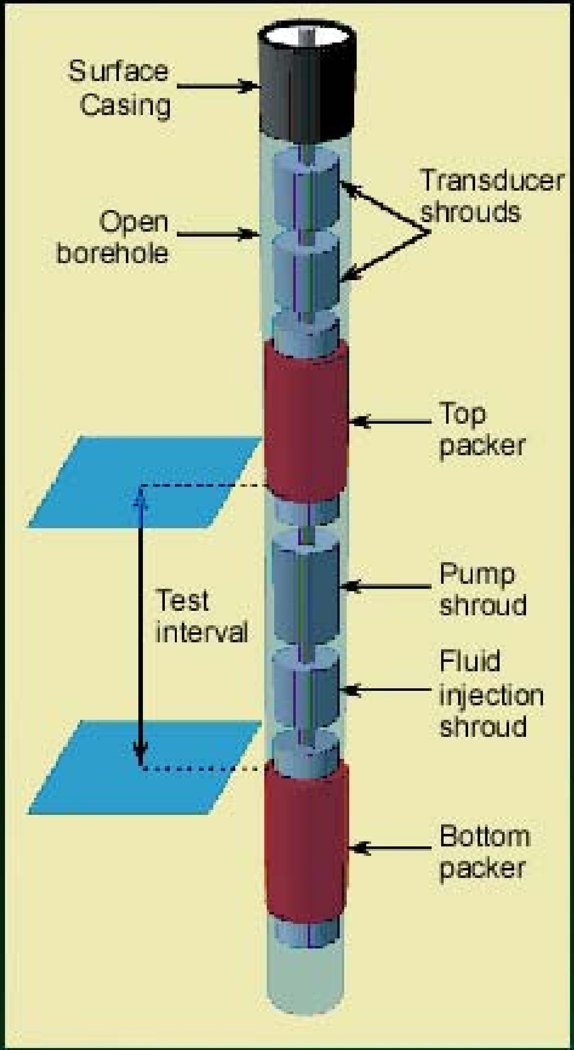
Straddle Packer System: Hydraulic Testing, Geochemical Sampling



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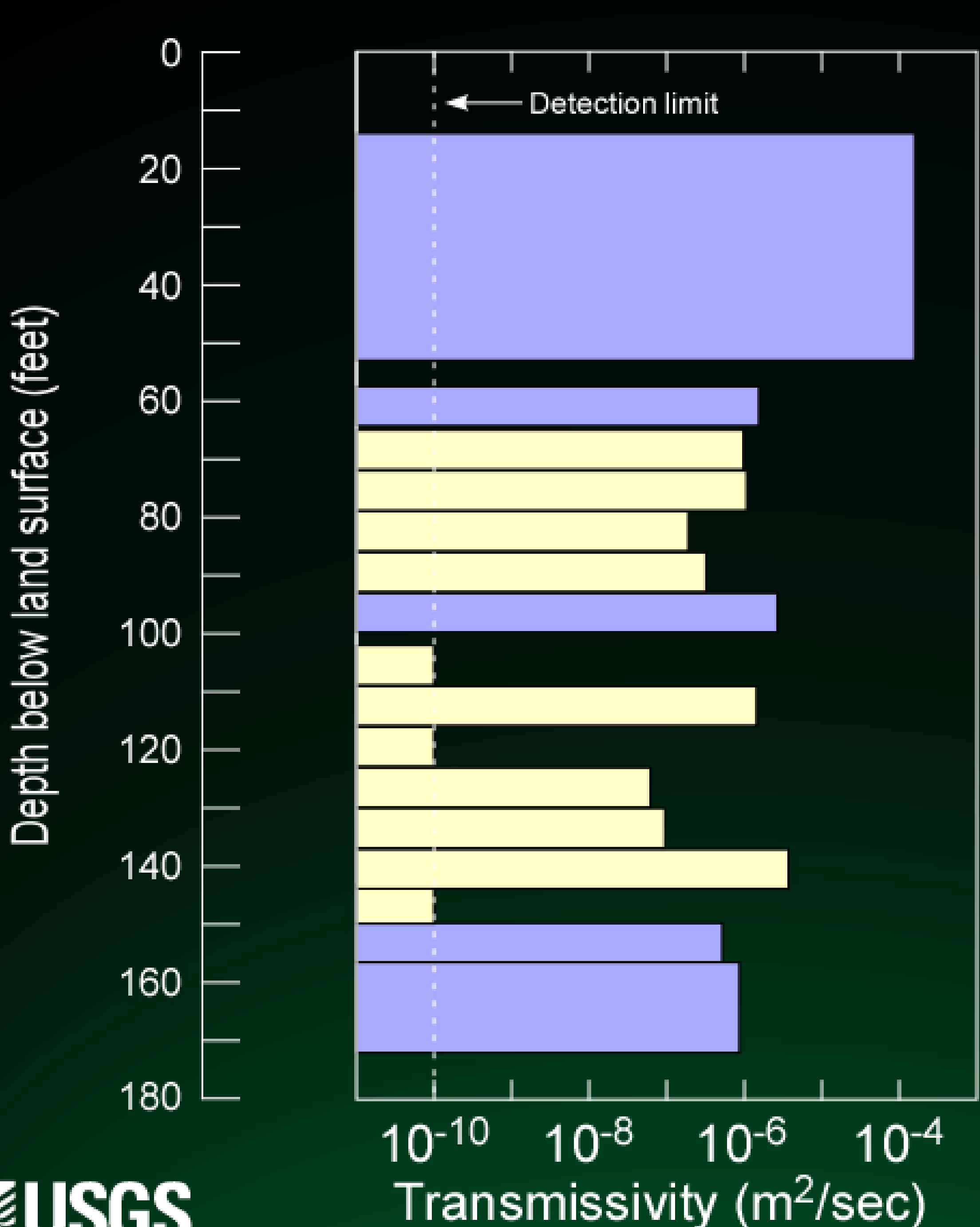

Depth below land surface (feet)
0
20
40
60
80
100
120
140
160
180
Detection limit
10^{-10}
10^{-8}
10^{-6}
10^{-4}
Transmissivity (m^2/sec)

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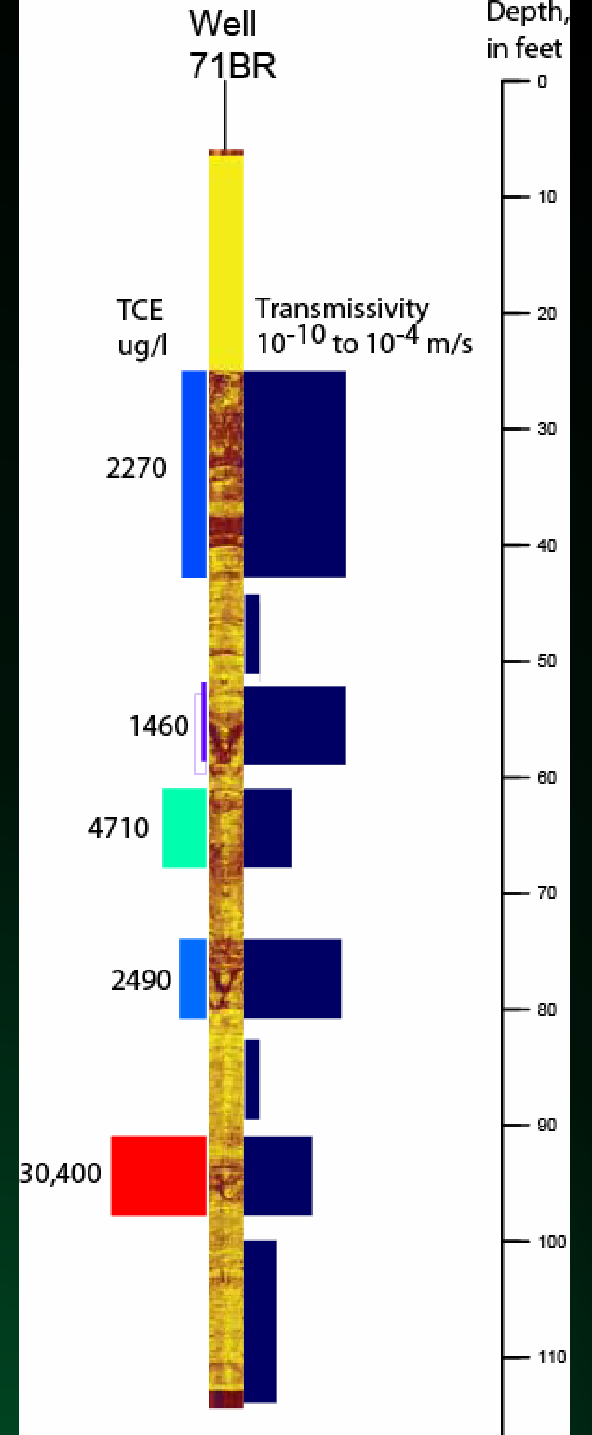
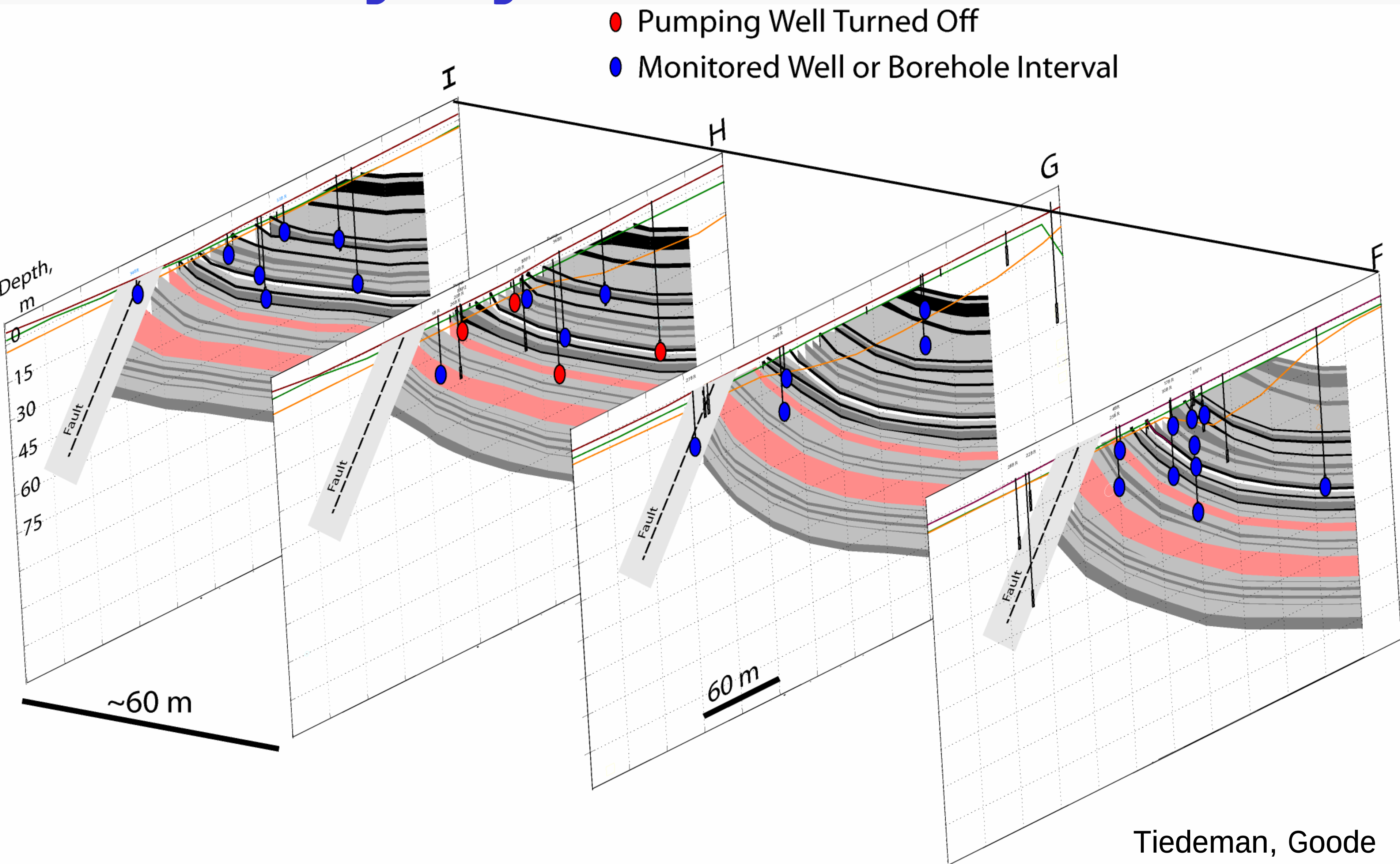
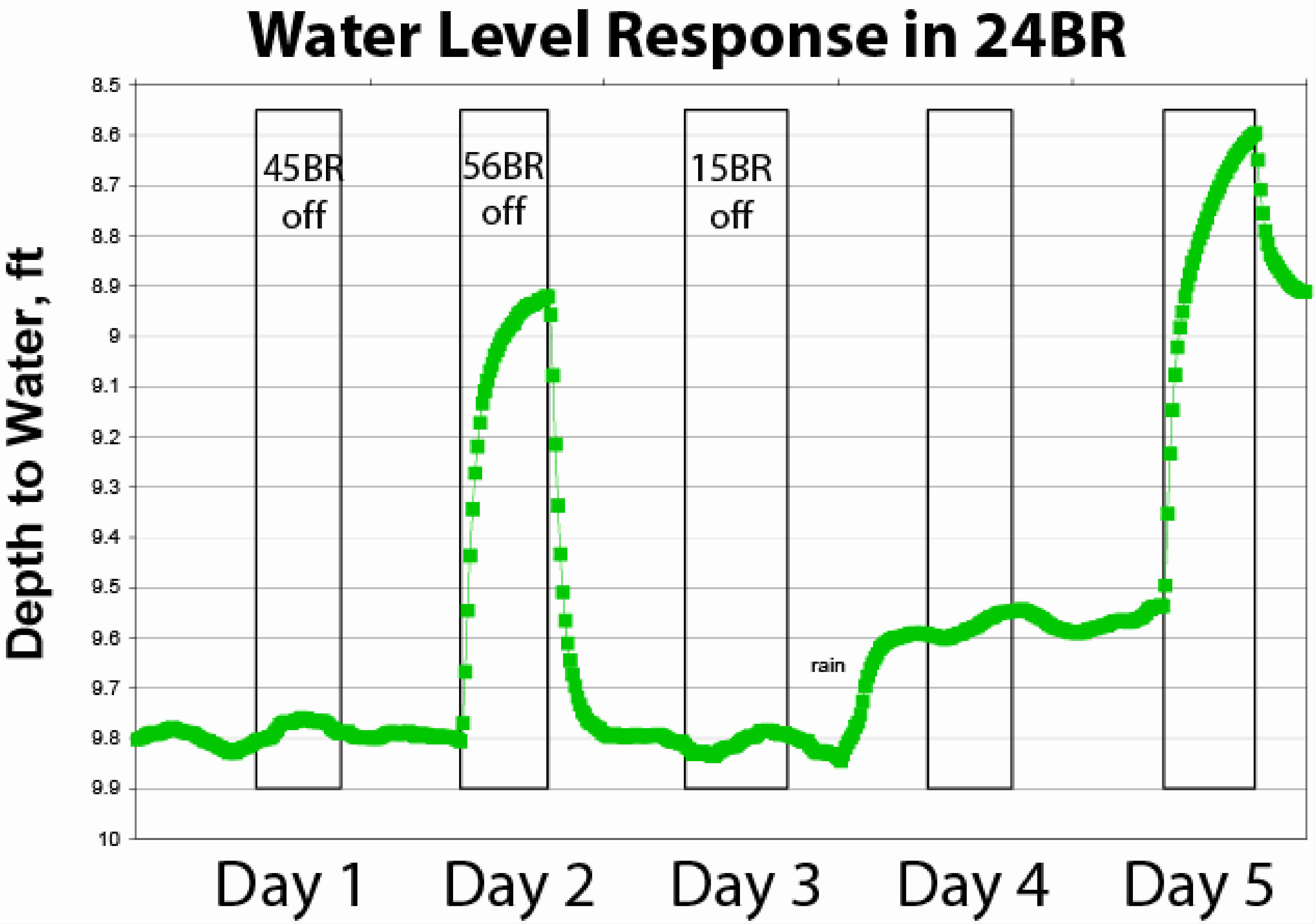


Well 71BR
Depth, in feet
0
10
20
30
40
50
60
70
80
90
100
110
TCE ug/l
Transmissivity 10^{-10} to 10^{-4} m/s
2270
1460
4710
2490
30,400

Short-Term Aquifer Tests To Identify Hydraulic Connections



Tiedeman, Goode



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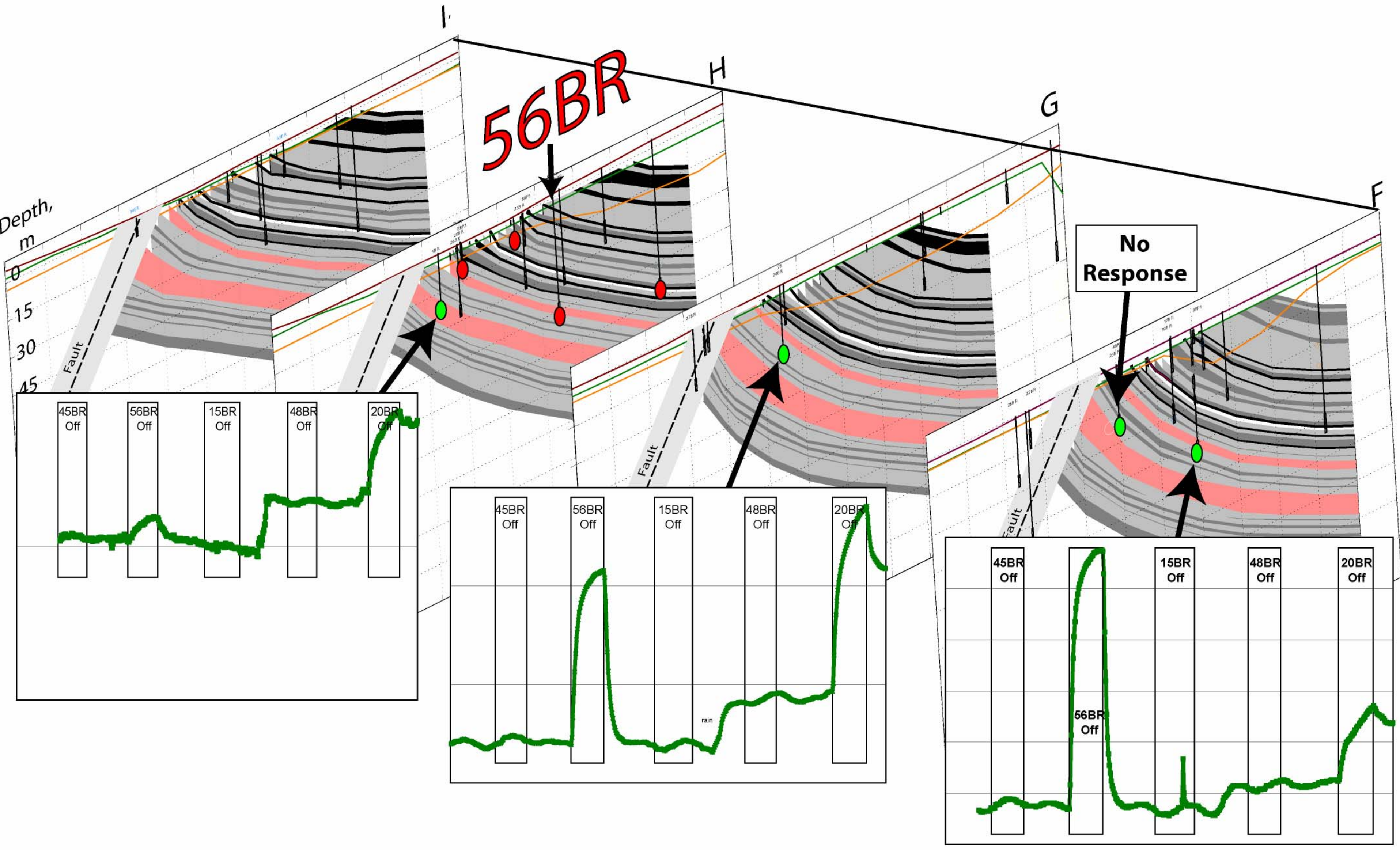
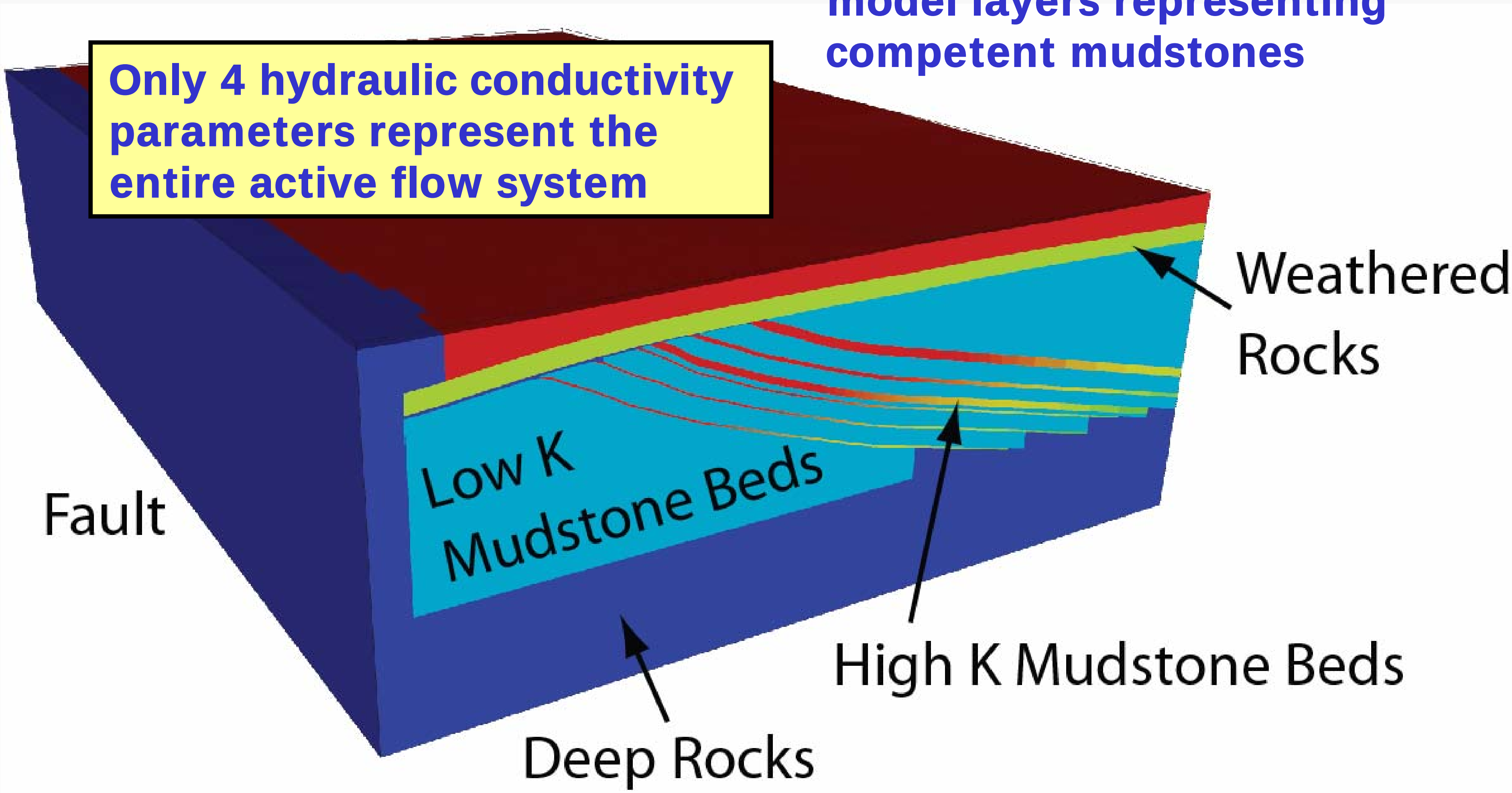
Response to Turning Pump Off at 56BR



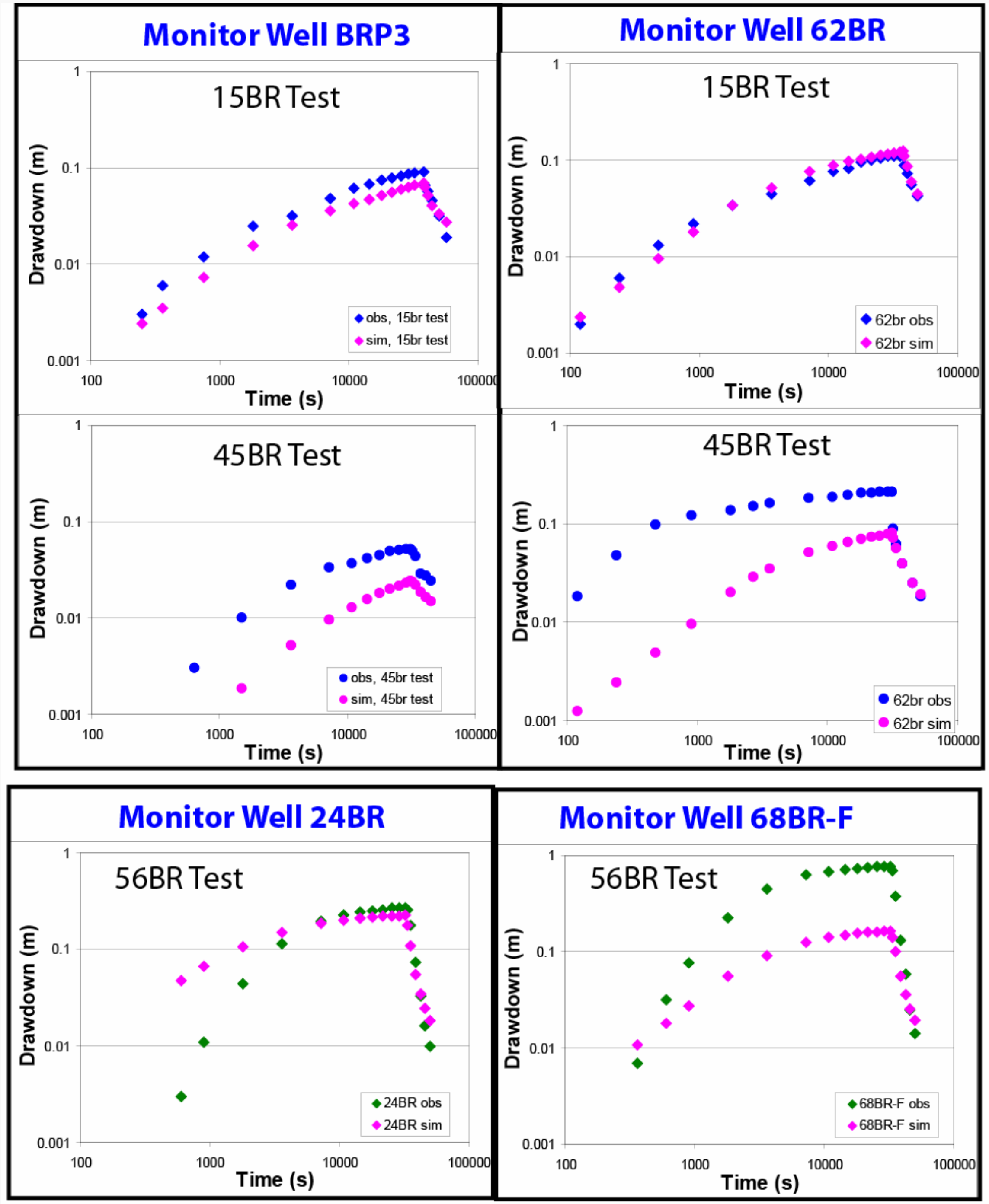
Site-Scale Ground-Water Flow Model

MODFLOW-2000 with dipping model layers representing competent mudstones

Only 4 hydraulic conductivity parameters represent the entire active flow system

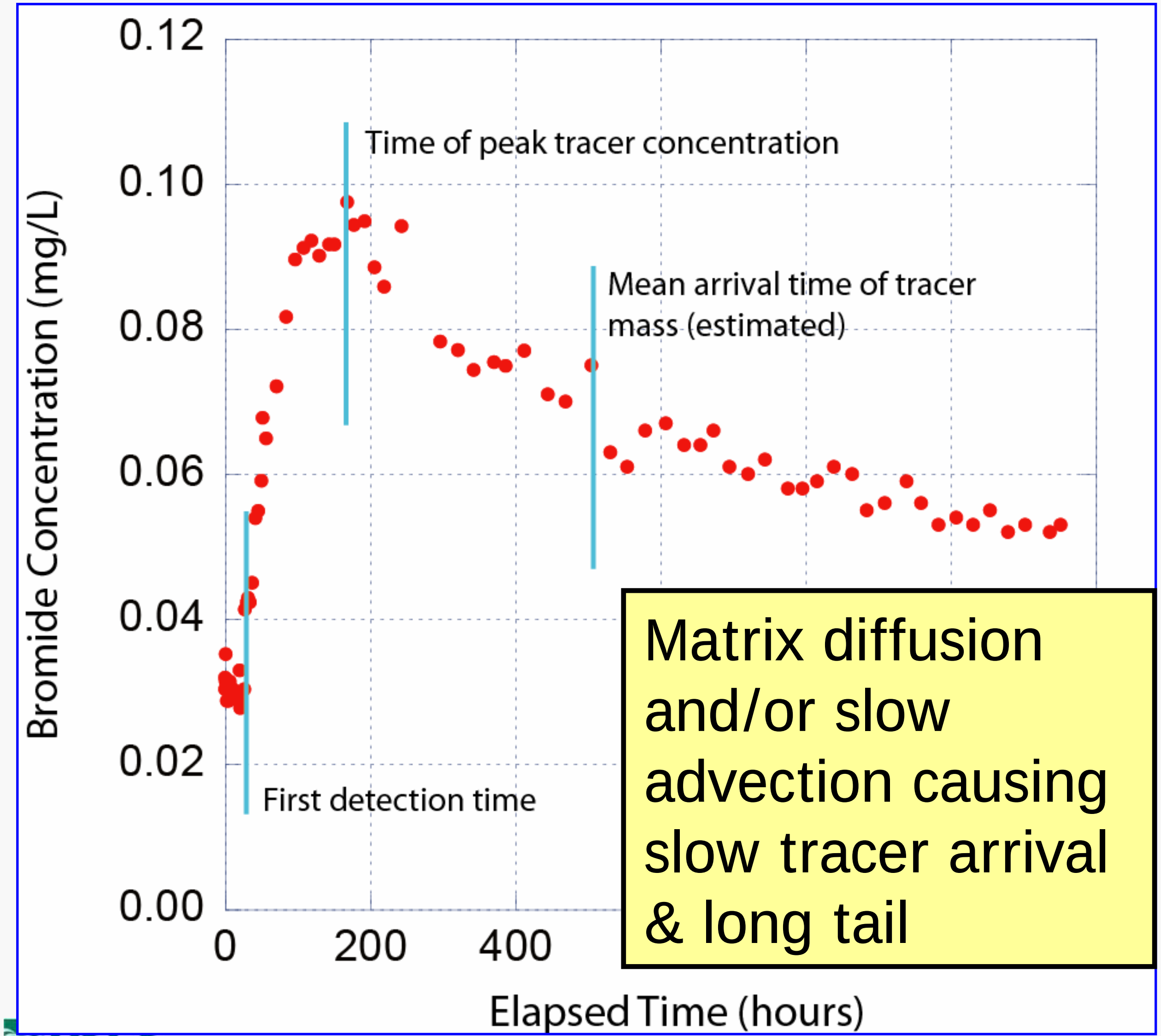


MODFLOW-2000 model with simple parameterization produces a reasonable fit to many of the aquifer test responses.



Tracer Testing

Converging radial test; wells 130' apart



Matrix diffusion and/or slow advection causing slow tracer arrival & long tail

First detection: 1.5 days

(Hydraulic response: 3 minutes)

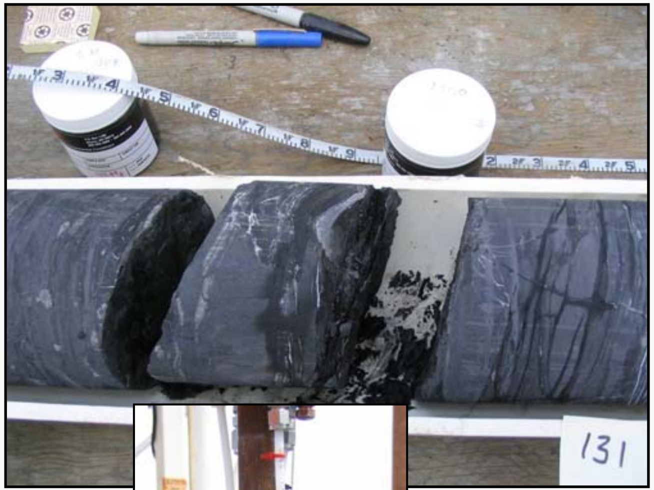
Peak arrival: 7 days

Tail still above background after two months

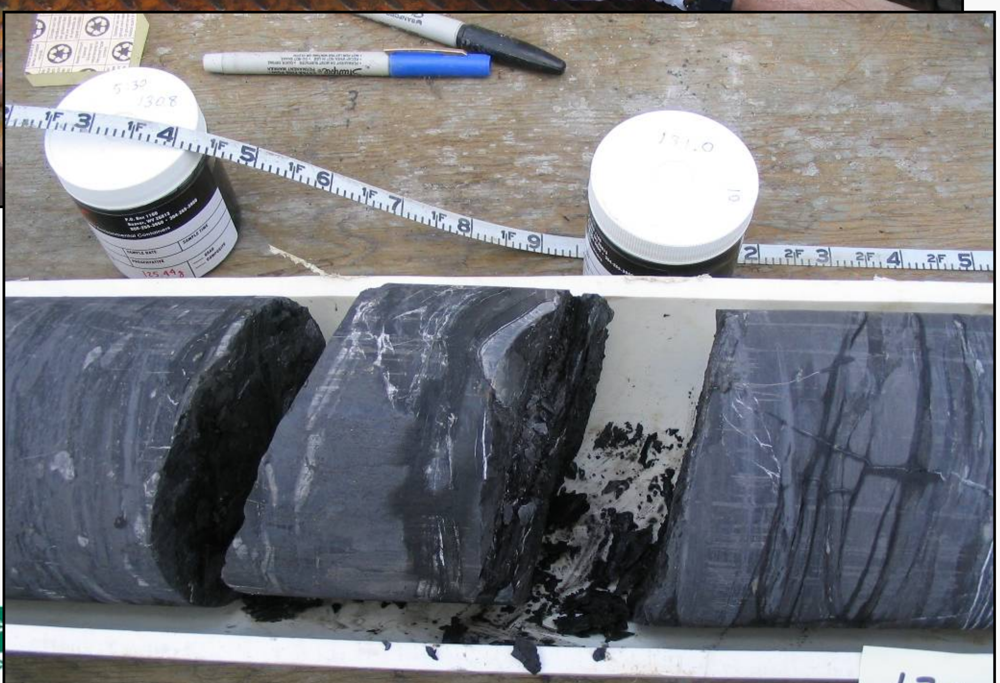
Shapiro, Hsieh, Goode

Theme 2: Monitoring Contamination, Geochemistry, and Microbiology

- In fractured rock, water chemistry and redox conditions can vary dramatically over short distances …
- … resulting in significant spatial variability in contaminant concentrations and in-situ microbial ecology.



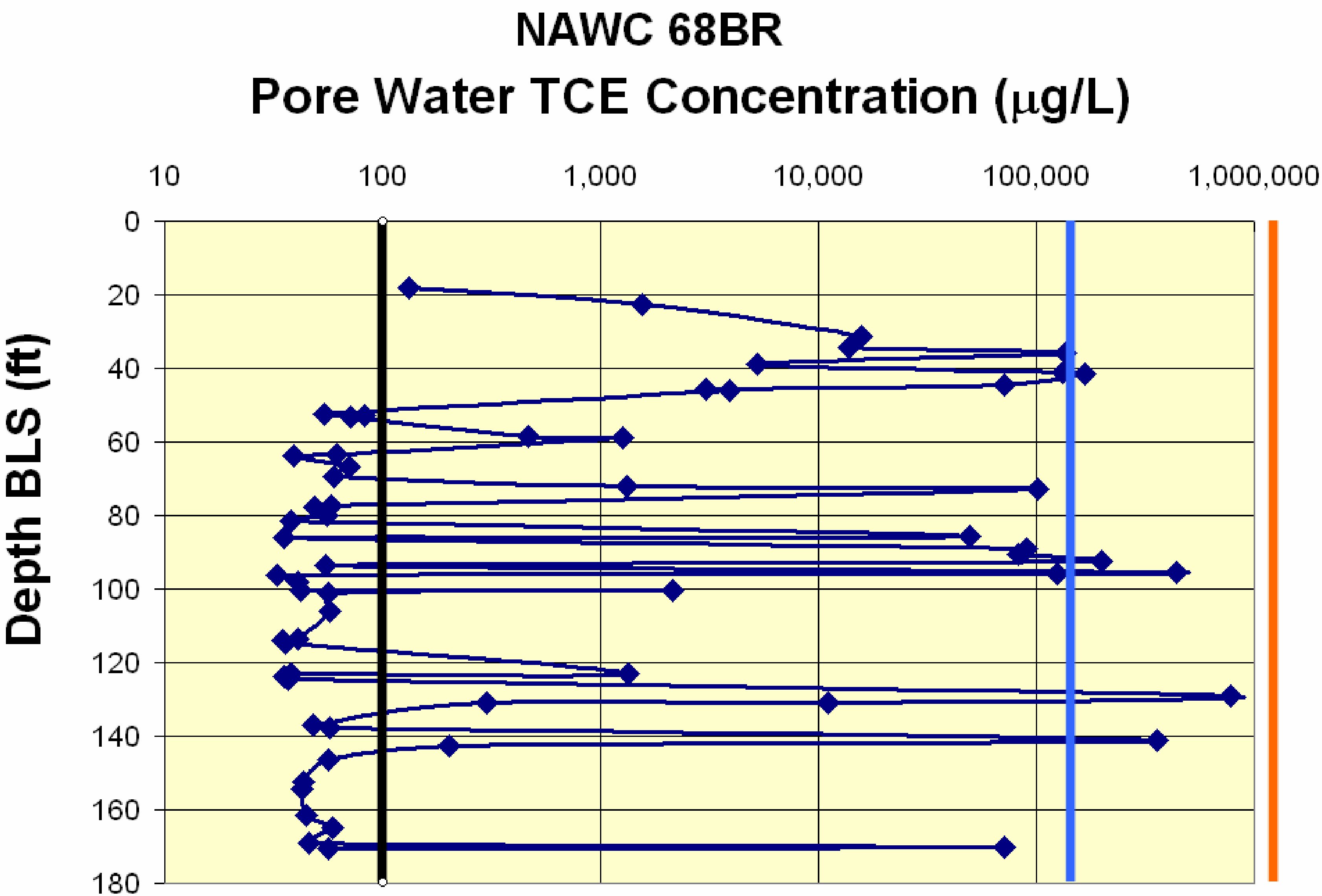
Contaminant Distribution in Primary Porosity (Rock Matrix)



- Rock core samples collected, placed in methanol, and stored for several months.
- VOC concentrations in methanol measured.
- Converted to concentration in pore water, using value of rock porosity.

Goode

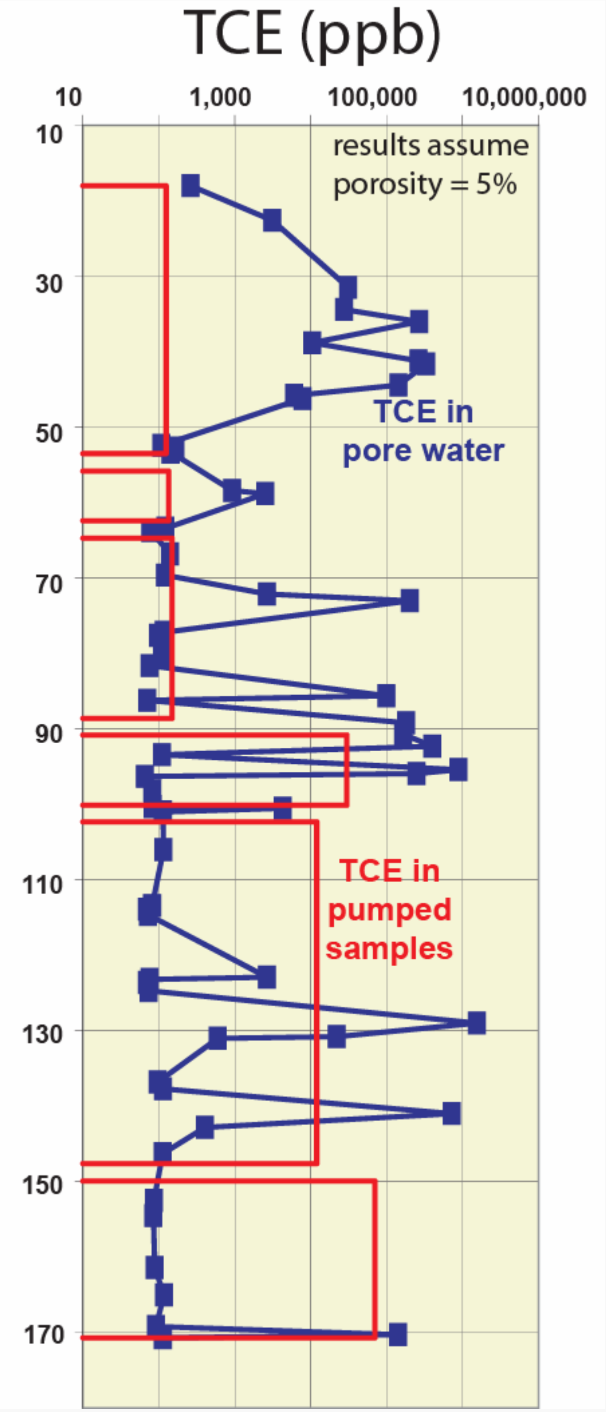
Extreme Variability with Depth



High TCE concentrations generally associated with weathered, fissile, or laminated mudstones.

TCE in Core and in Pumped Samples

TCE concentrations in pumped samples can show little or no relation to concentrations in pore waters of the adjacent rock.



Monitoring Biodegradation

- In unconsolidated aquifers, efficiency of chloroethene (e.g., TCE, DCE) biodegradation depends on:
  - concentration & bioavailability of the **contaminant** and of the **electron donor**
  - concentration & activity of a **microbial community** that degrades chloroethenes
- Research at NAWC: showing that this finding also applies to fractured rock aquifers.
- Key to determining biodegradation efficiency: To **monitor the spatial distribution of the contaminants, electron donor, and microbial community**.

How to Monitor Biodegradation in Fractured Rock?

- Isolate short borehole intervals using inflatable packers.
- Sample **hydrogen & dissolved organic carbon** (electron donors)**,** **contaminant concentrations,** and **microbial DNA** in the borehole intervals.
- Use in-situ samplers as well as pumped samples.

In-Situ Samplers:
Emplaced Downhole for 1 year

Passive Diffusion Samplers:
Inorganics, VOCs, dissolved gases, dissolved hydrogen.

Microcosms of Crushed Rock:
Microbial DNA.

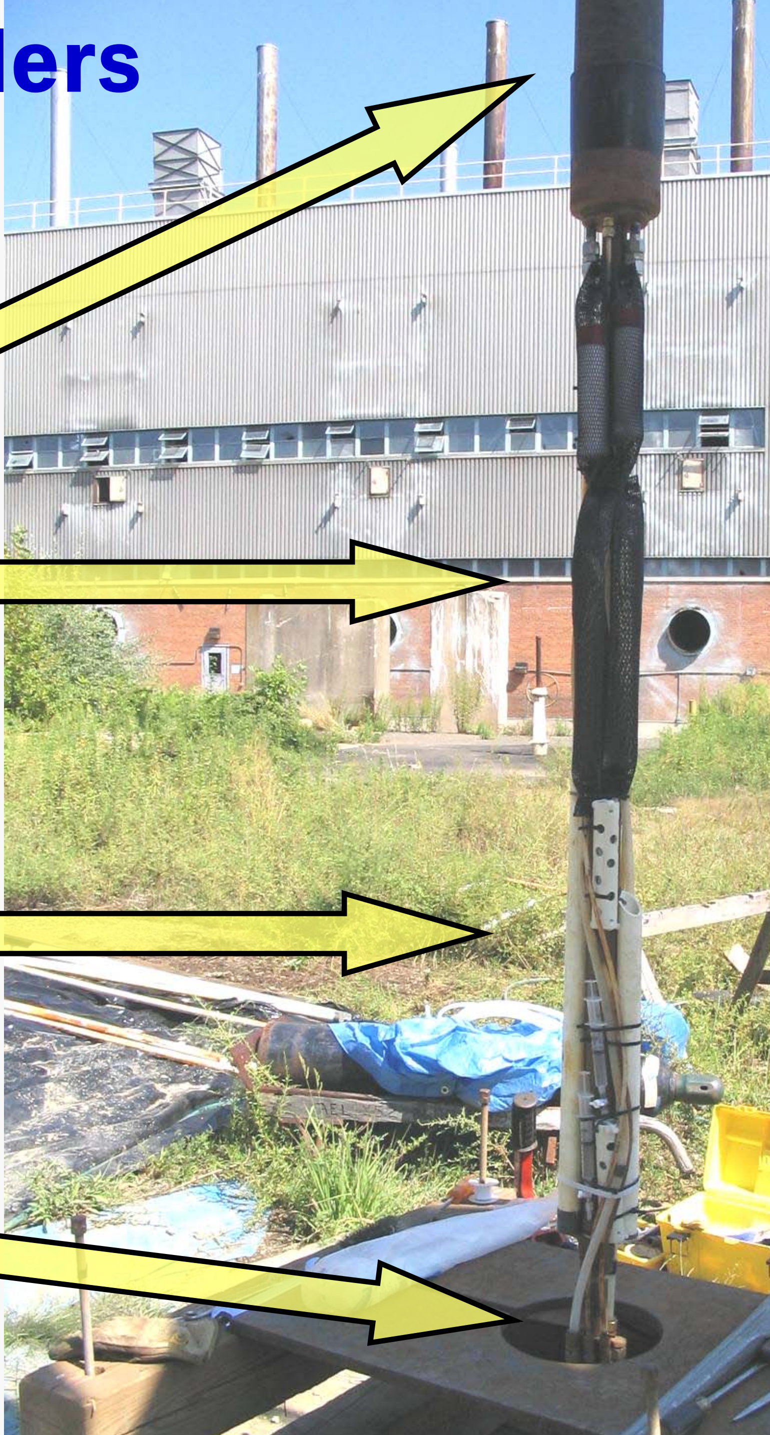
Packers and In-Situ Samplers for Long-Term Monitoring

Upper Packer

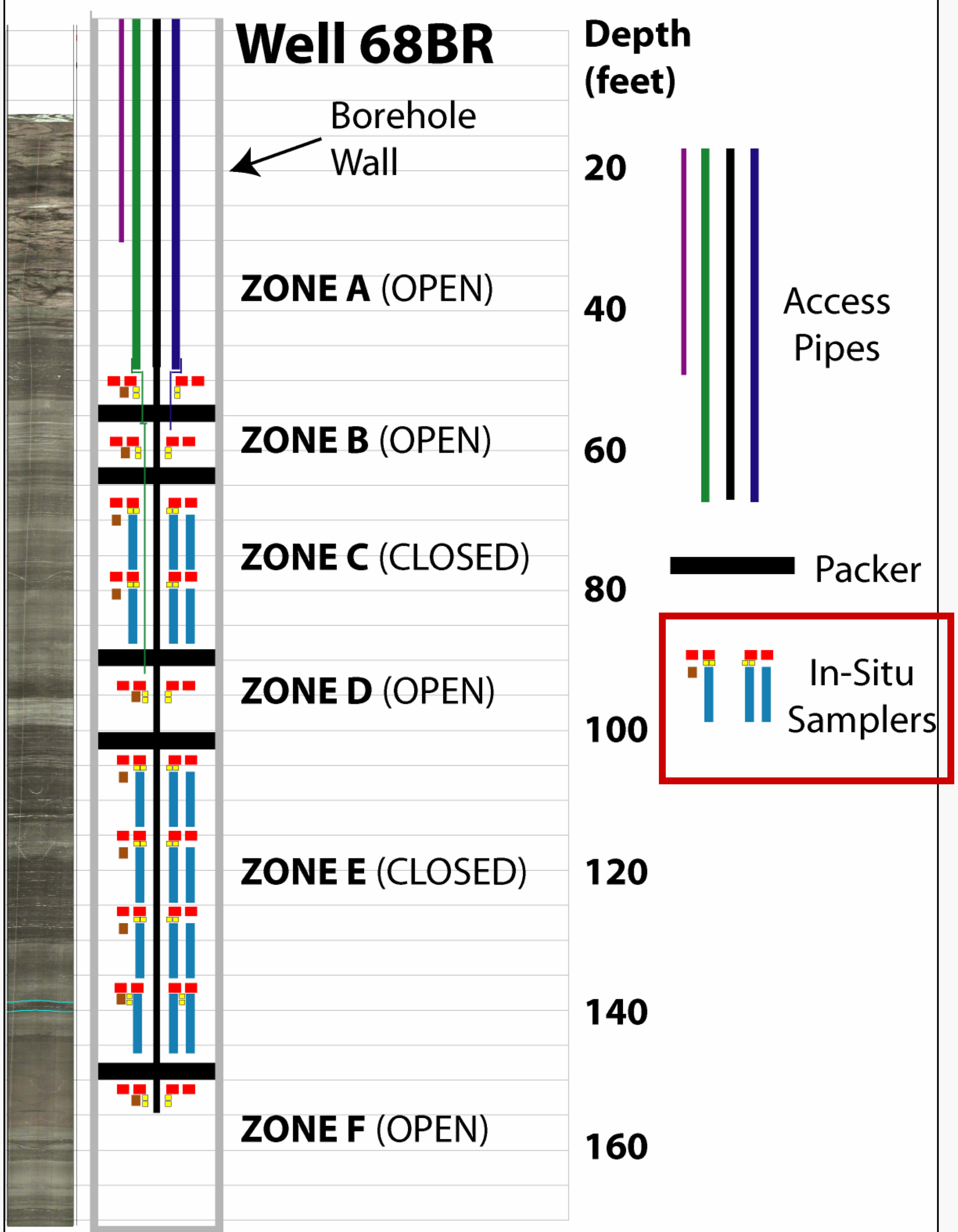
Diffusion Samplers

Crushed Rock Microcosms

Lower Packer



Schematic of Packers and In-Situ Samplers Inside the Borehole



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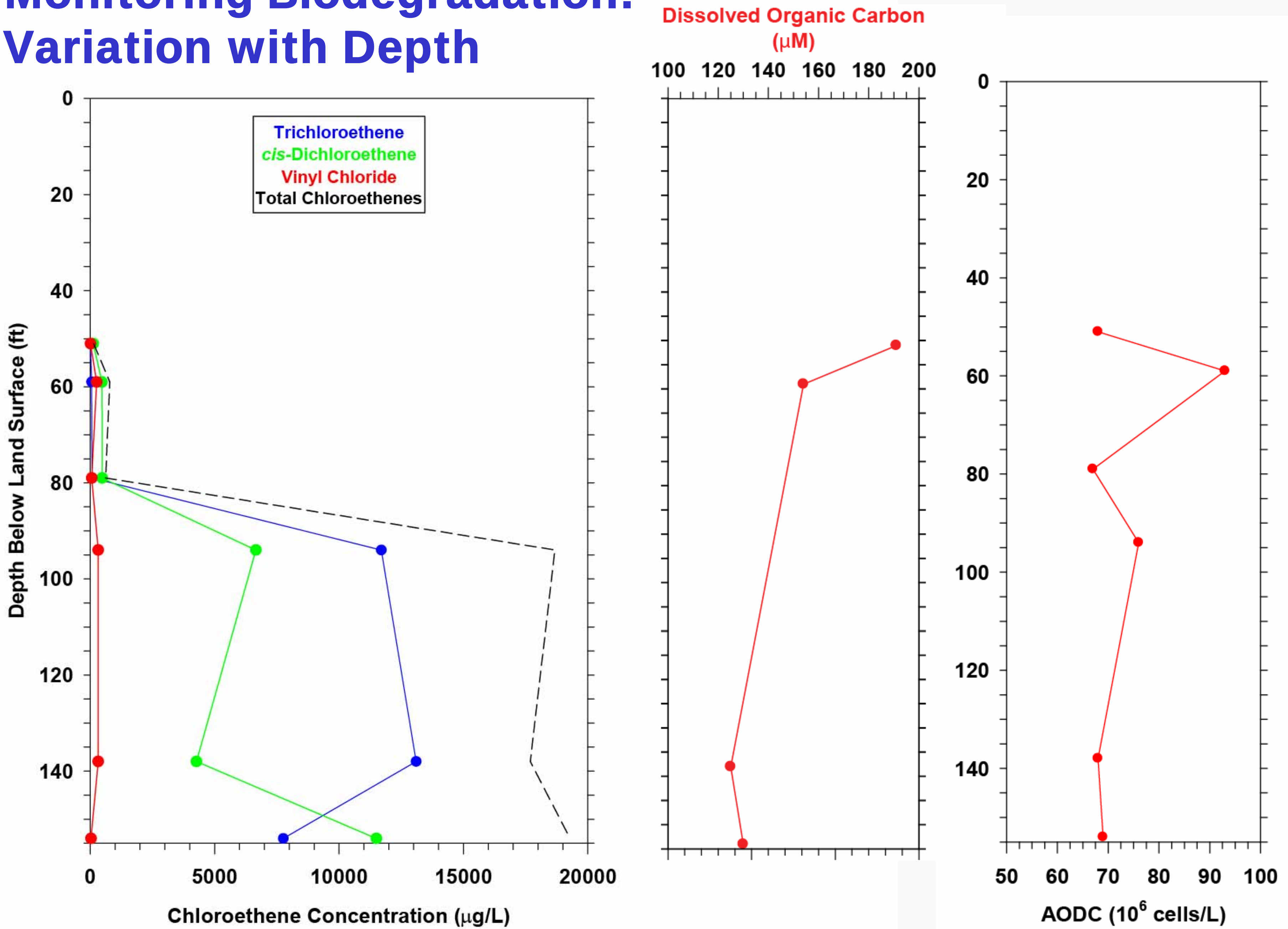
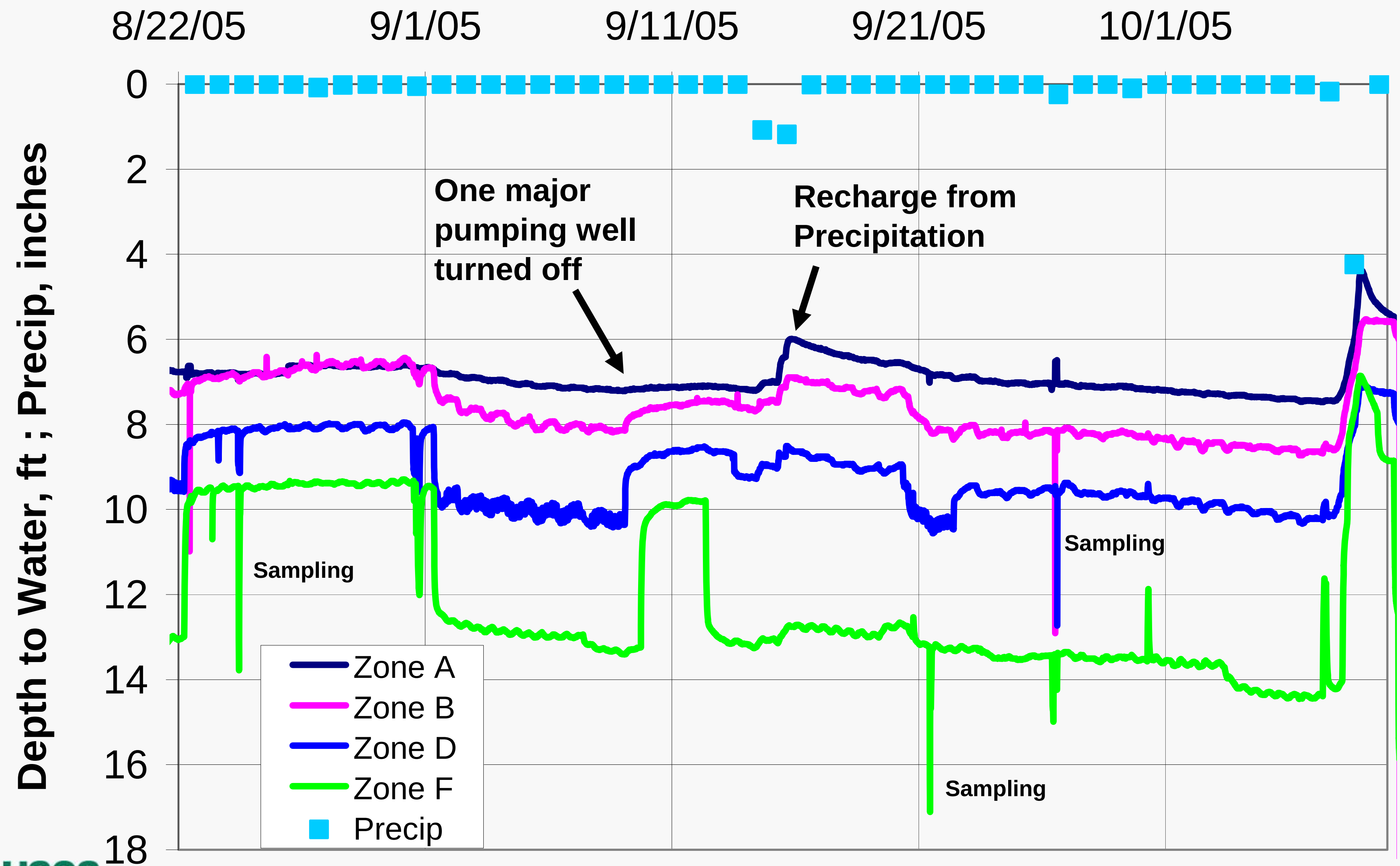
Monitoring Biodegradation: Variation with Depth



Bradley, Chapelle

Water Levels in Packed Intervals: Information about GW Hydraulics



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Theme 3: Evaluating Remediation Effectiveness

- Assessing remediation effectiveness is challenging in any GW system
- The hydrologic uncertainties and spatial variabilities associated with fractured-rock aquifers makes this even more challenging

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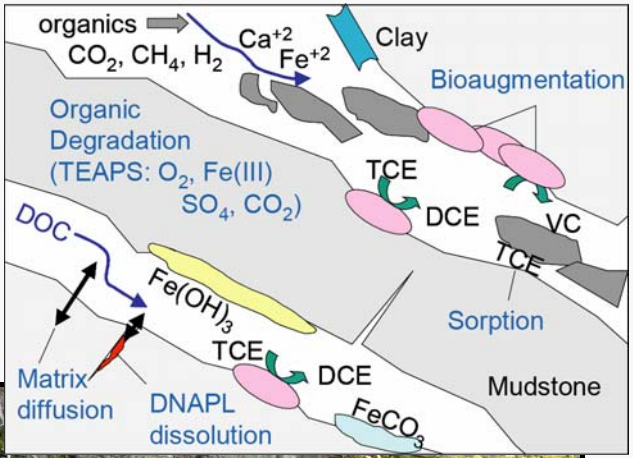
Remediation in Fractured Rocks: Challenges

- Complexity of physical, chemical, and microbiological processes and their interactions.
- Complexity of individual fractures & fracture connectivity
- Flow-limited regions of the aquifer (rock matrix, low-K fractures) act as continuing contaminant sources

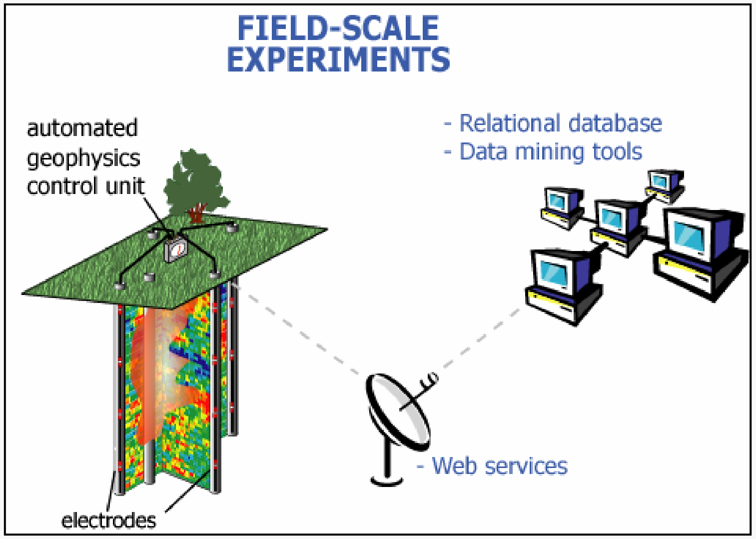


Shapiro

Remediation in Fractured Rocks: Directions

- Identify thermal, microbial, and other technologies that can access contaminants in the flow-limited regions.

- Identify geophysical and direct sensing methods to evaluate spatial and temporal changes in contaminant concentrations, microbiology, etc.



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Shapiro

Evaluating Remediation Effectiveness

- **Pump & Treat, Monitored Natural Attenuation, Enhanced Biodegradation**
- **Understand processes** that control remediation and **estimate contaminant mass removed**, using:
  - **Empirical methods** – field monitoring of contaminants, geochemistry, redox processes, microbiology.
  - **Reactive transport modeling** to synthesize data, test hypotheses about controlling processes, and simulate mass removed.

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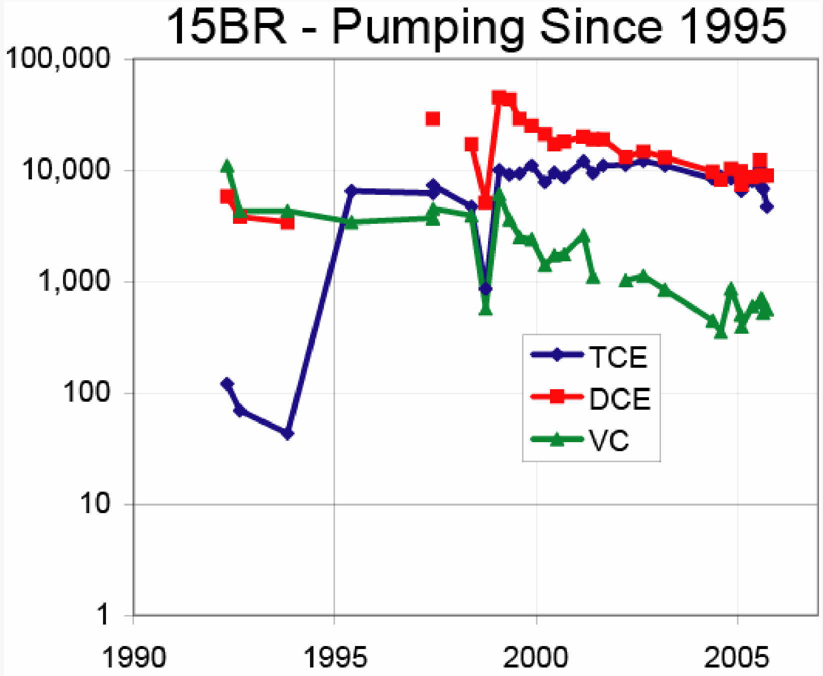
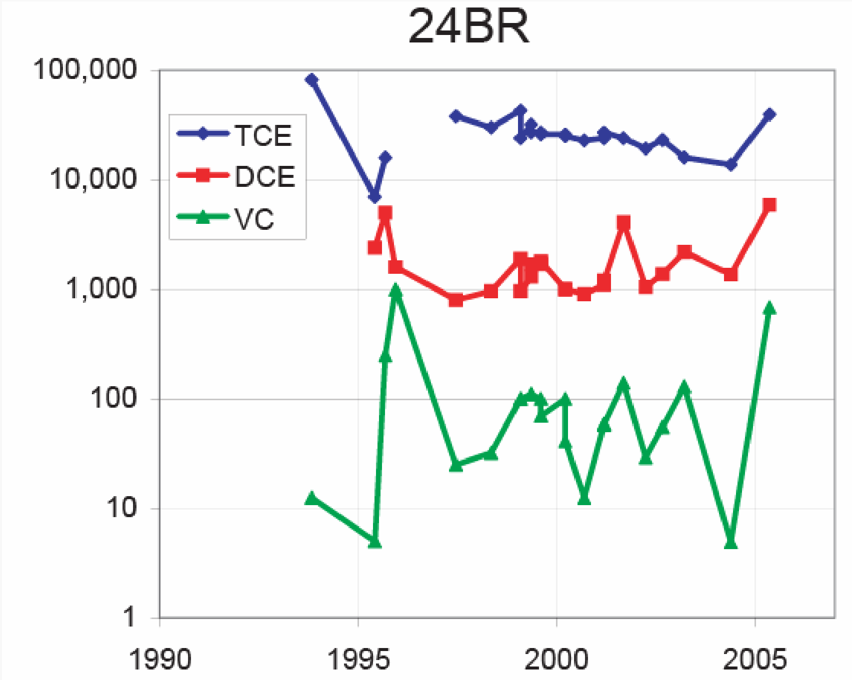
Contaminant Removal by Pump and Treat: Inefficient

- Pump and treat operating for 10 years, but contaminant concentrations have not significantly decreased.
- Likely that large amount of contaminant mass resides in the primary porosity and in low K fractures.





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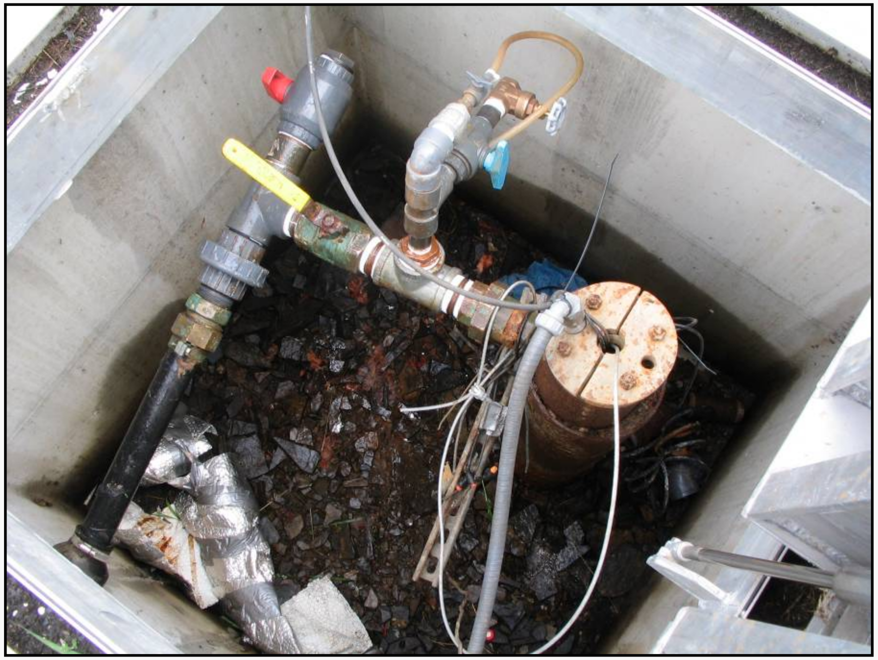
Empirical Estimates: Contaminant Mass Removed by Pump & Treat

- Calculate using
  - Flow rates and concentrations from recovery wells
  - Treatment plant data



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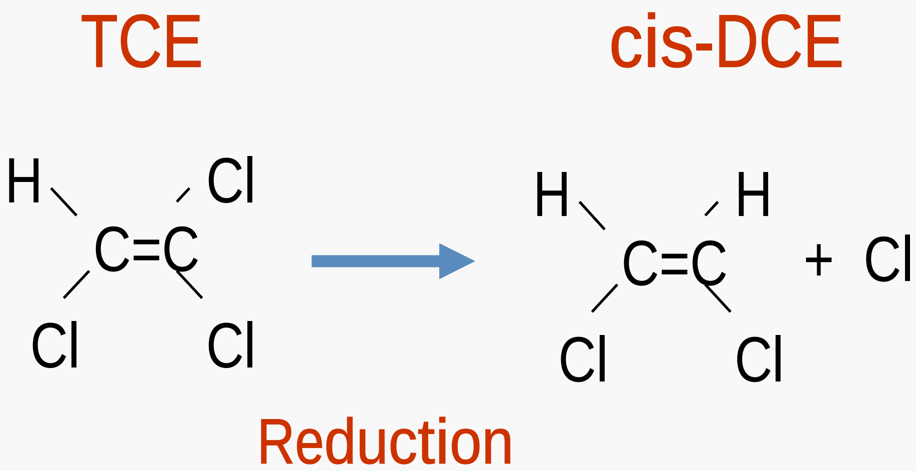
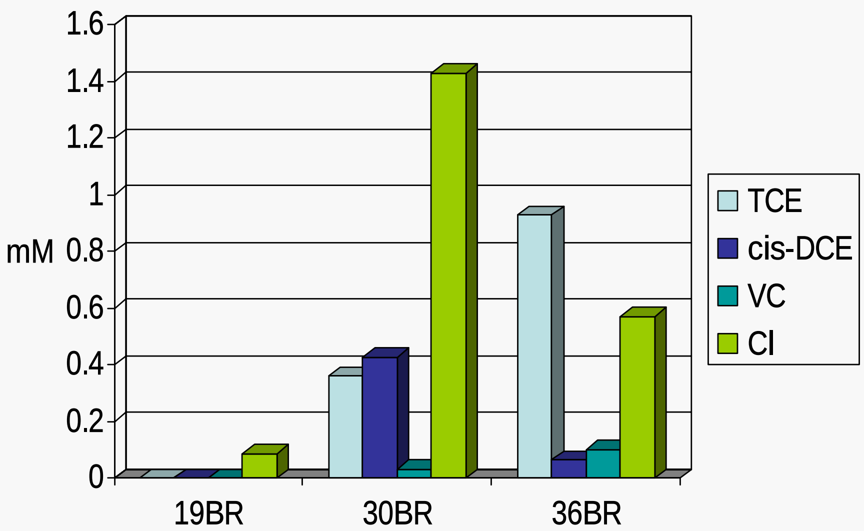
Empirical Estimates: Mass Removed by Monitored Natural Attenuation

- Chloride as tracer of TCE transformation





- Carbon isotopes as tracers of TCE transformation – TCE becomes enriched in heavier carbon isotope

Chapelle

Biostimulation/Bioaugmentation Study Conducted by Navy and GeoSyntec

- Goal: investigate potential for enhancing natural biodegradation.
- July 2005: Injected electron donor and microbe culture.
- Concentrations of TCE in injection wells ranged from 206 to 15,800 µg/L.

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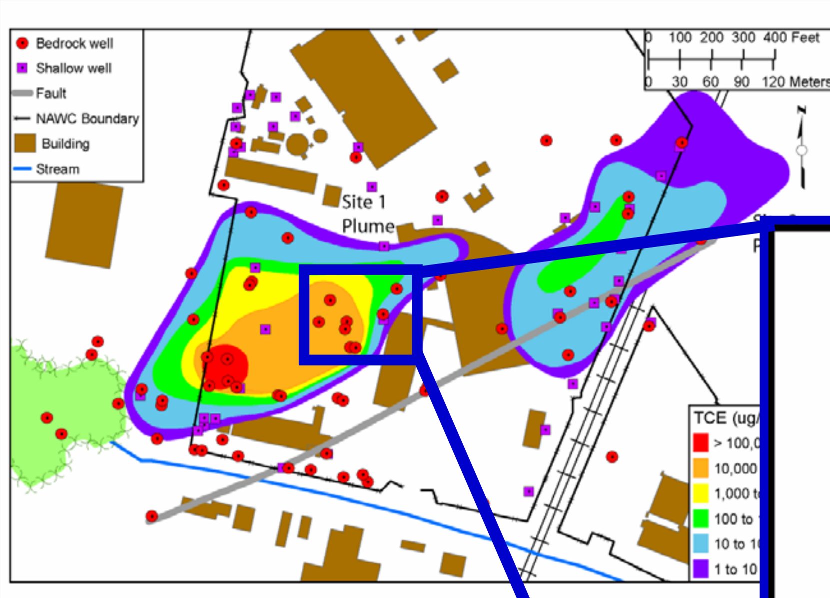
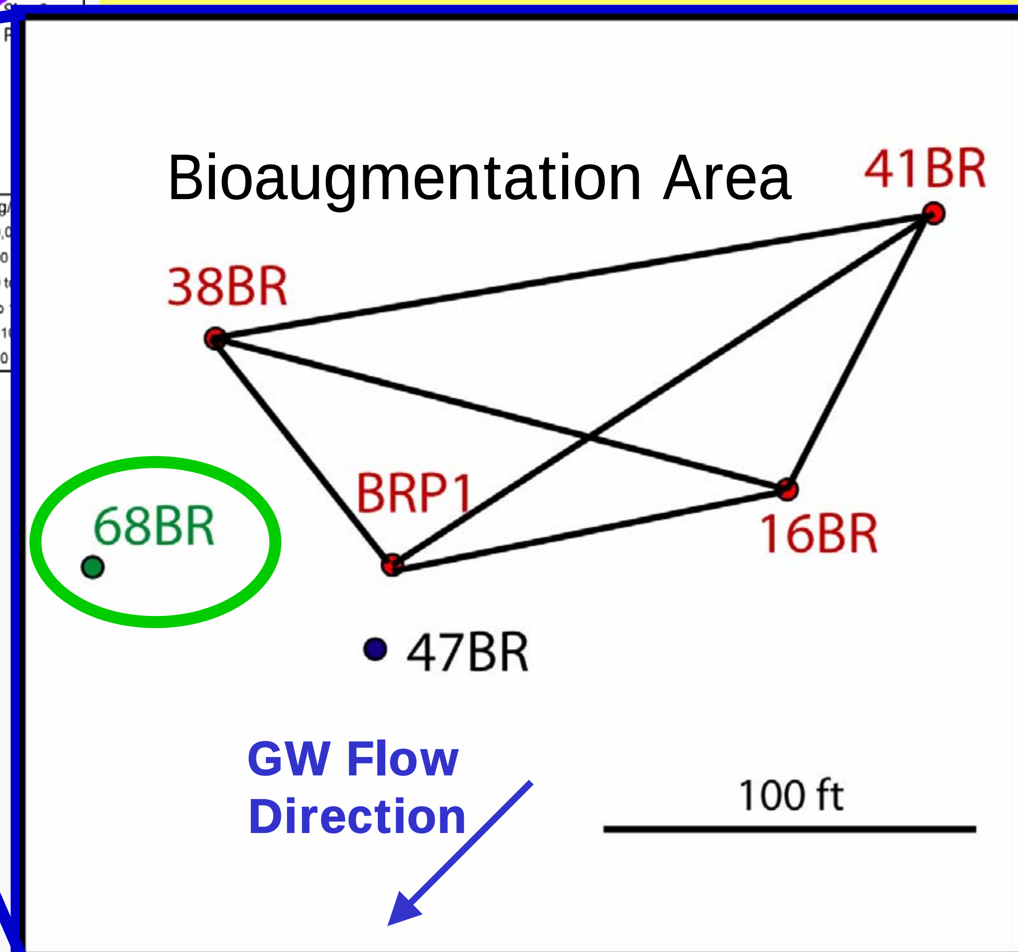
Amendments Injected in Four Wells



TCE at 30 m depth

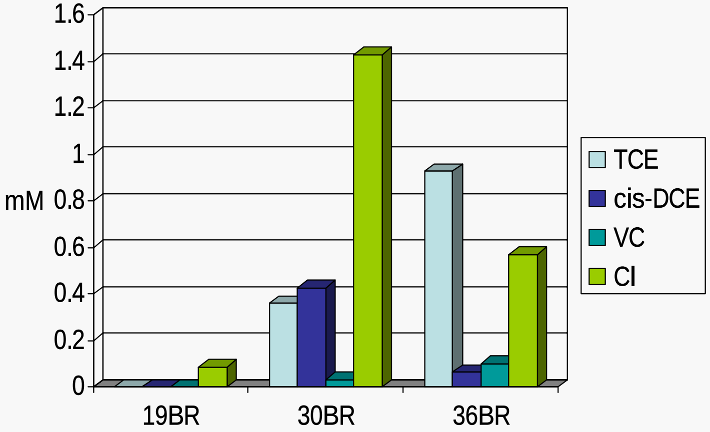
VOC concentrations decreased to ~0 in the 4 injection wells.

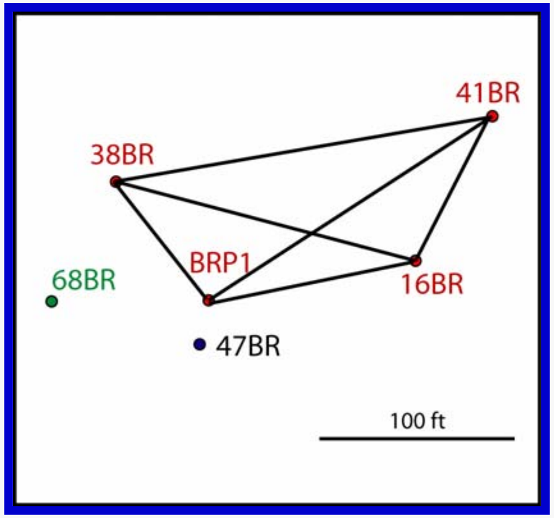


Not yet resolved whether enhanced bio has affected downgradient well.

Empirical Estimates: Contaminant Mass Removed by Enhanced Biodegradation

- Similar techniques as for Monitored Natural Attenuation: Chloride; carbon isotopes
- Also can monitor bioaugmentation amendments; make assumptions about volume of aquifer treated





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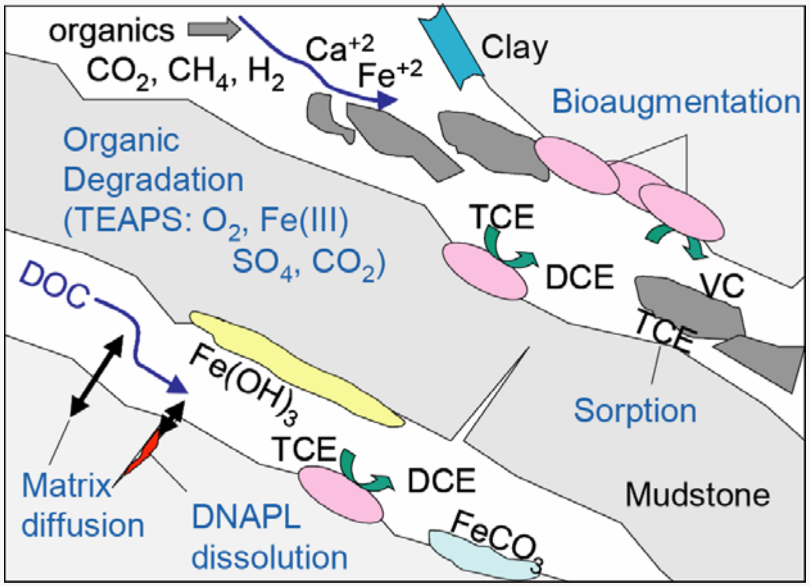
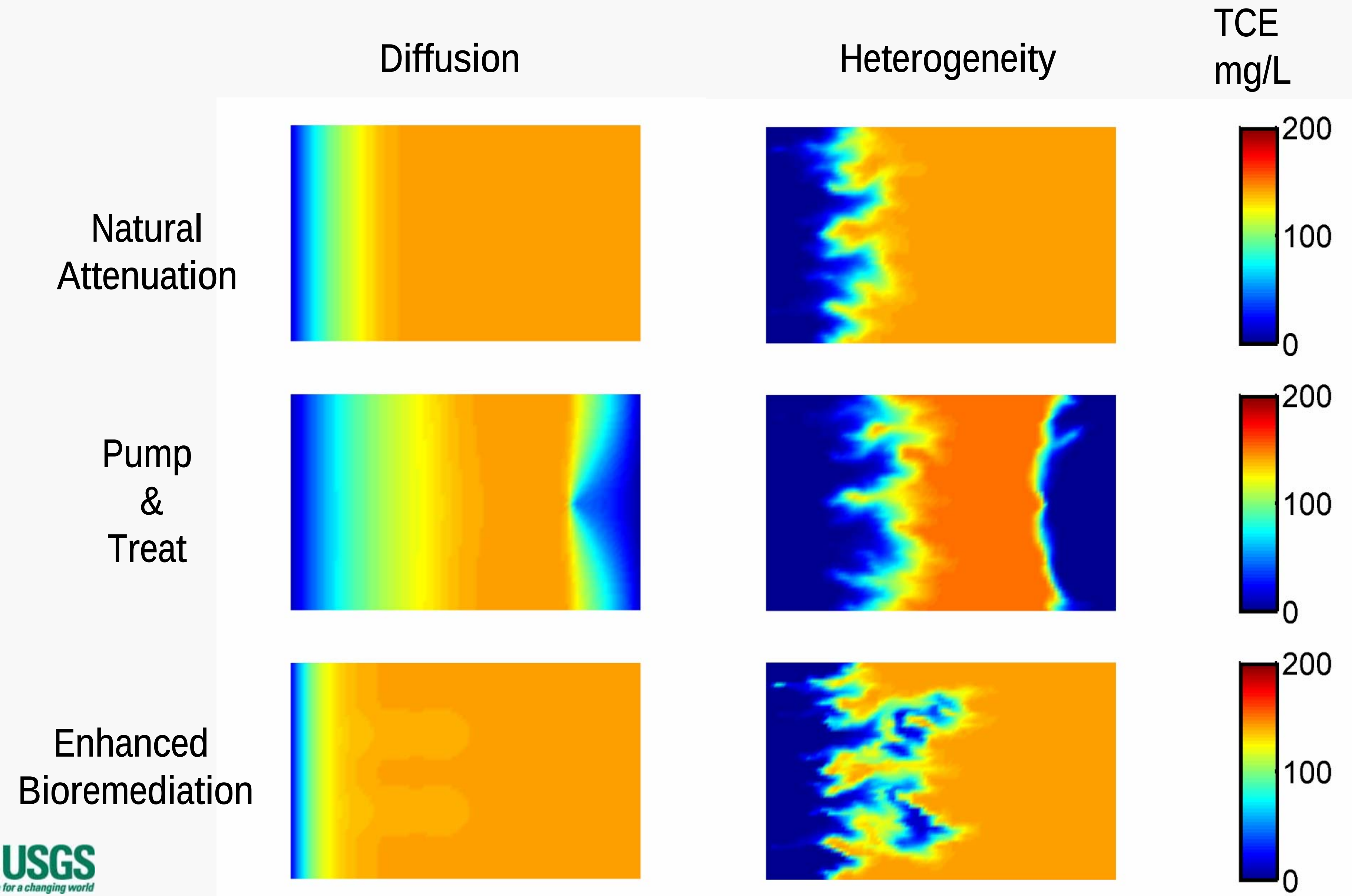
Reactive Transport Modeling to Understand Processes Controlling Remediation

- **Reactive Transport Models**
  - **synthesize** physical, geochemical, and microbiological data
  - **test hypotheses** about dominant processes controlling the transport and biotransformation of chlorinated solvents



Curtis

Reactive Transport Modeling To Simulate Contaminant Mass Removed



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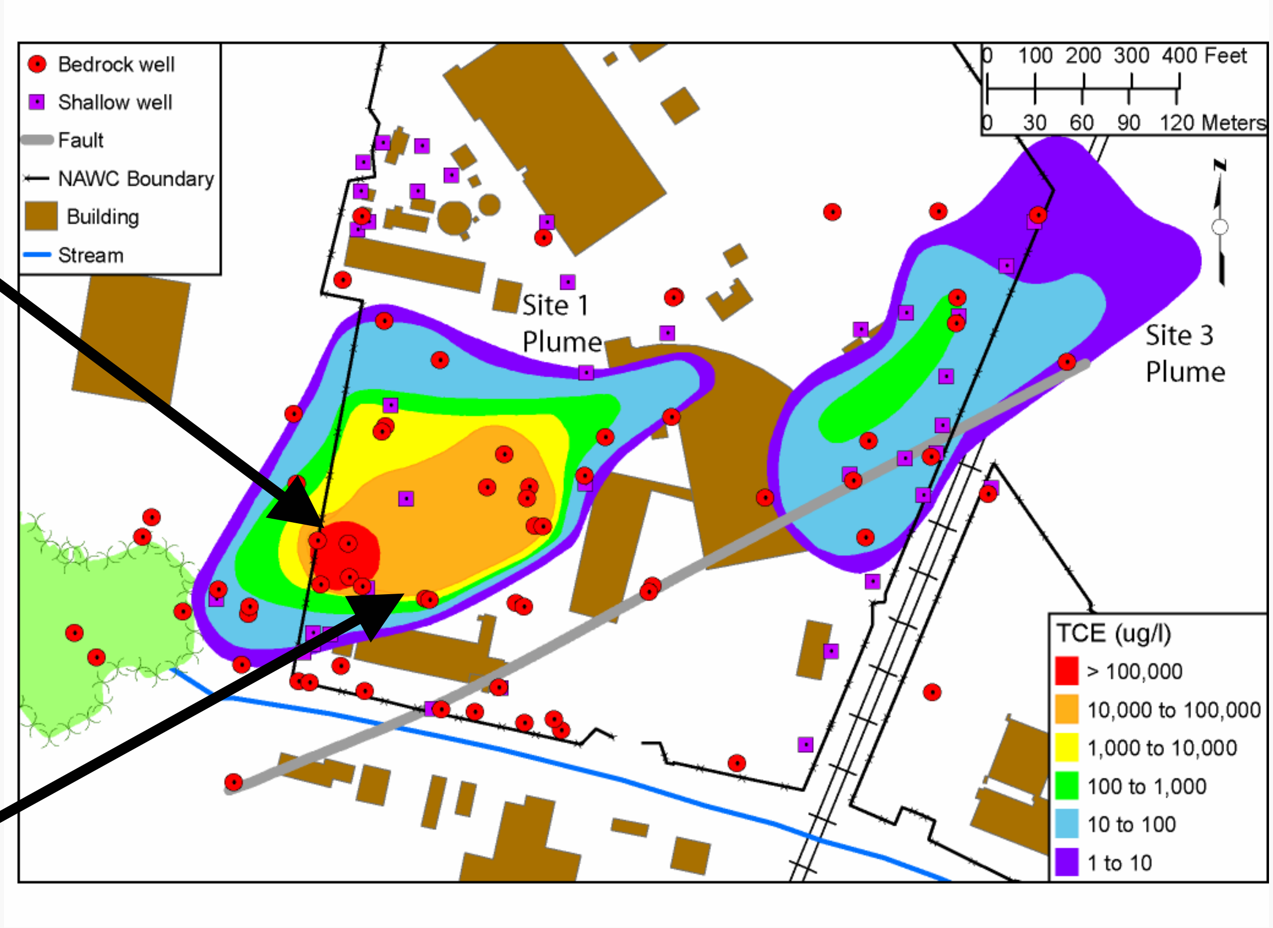
Evaluating Remediation Effectiveness

Bioaug 2008

Thermal 2008

(Keuper et al)



USGS Fact Sheet

Lists web sites where you can obtain additional information about activities at NAWC

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SERDP
Strategic Environmental Research and Development Program

Contamination in Fractured-Rock Aquifers—Research at the former Naval Air Warfare Center, West Trenton, New Jersey

The U.S. Geological Survey and cooperators are studying chlorinated solvents in a fractured sedimentary rock aquifer underlying the former Naval Air Warfare Center (NAWC), West Trenton, New Jersey. Fractured-rock aquifers are common in many parts of the United States and are highly susceptible to contamination, particularly at industrial sites. Compared to "unconsolidated" aquifers, there can be much more uncertainty about the direction and rate of contaminant migration and about the processes and factors that control chemical and microbial transformations of contaminants. Research at the NAWC is improving understanding of the transport and fate of chlorinated solvents in fractured-rock aquifers and will compare the effectiveness of different strategies for contaminant remediation.

The U.S. Navy tested jet engines at the Naval Air Warfare Center, West Trenton, New Jersey, from the mid-1950s until the late 1990s. Fractured bedrock at the site was contaminated with trichloroethylene (TCE) used during the testing operations.

Complex Fractured-Rock Aquifers and Contamination

Toxic chemicals such as chlorinated solvents pose a serious threat to the Nation's ground-water resources. Many industrial sites in the Eastern United States are located in the Piedmont physiographic region, where fractured rock aquifers are common. Improper disposal methods, leaking tanks and pipes, and chemical spills have contaminated fractured-rock aquifers in and around these sites.

The restoration and protection of ground-water quality at these sites depend on knowledge of the physical, chemical, and microbiological processes that affect the transport and fate of these toxic chemicals. To gain this knowledge, the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program, in cooperation with other Federal, State, and private-sector organizations, is conducting multidisciplinary research on contamination in fractured sedimentary rock underlying the former Naval Air Warfare Center (NAWC) in West Trenton, New Jersey.

Why Is There Contamination at the NAWC?

The U.S. Navy tested jet engines at the NAWC in West Trenton, New Jersey, from the mid-1950s until the late 1990s. Fractured bedrock at the site was contaminated with trichloroethylene (TCE) used during the engine testing operations. It is likely that heavier-than-water TCE has flowed vertically downward and in the down-dip direction of the fractured sedimentary rocks. An aqueous-phase plume of dissolved TCE has flowed along the strike and in the up-dip directions. There is evidence of microbial transformation (biodegradation) of TCE to dichloroethylene (DCE) and vinyl chloride (VC). Investigations of the ground-water contamination at the site began in the late 1980s, and a pump and treat operation that has successfully limited offsite migration was started in the mid-1990s.

Multidisciplinary and Cooperative Research

One objective of the cooperative research at the NAWC is to improve scientific understanding of physical, chemical, and microbial processes affecting the transport and fate of chlorinated solvents, including the role of dense nonaqueous phase liquid (DNAPL) TCE as a long-term source. The research also will develop methods for cost effective subsurface monitoring and will compare different strategies for cleaning up TCE in fractured-rock aquifers. The NAWC site was chosen for this research because the general hydrogeologic framework is well defined and the site contains extensive contamination over a range of geochemical conditions.

In 1993, the USGS began studies at the NAWC in cooperation with the U.S. Navy.

Rock cores from a borehole at the NAWC, showing the dipping mudstone strata that are pathways for ground-water flow and chemical transport.

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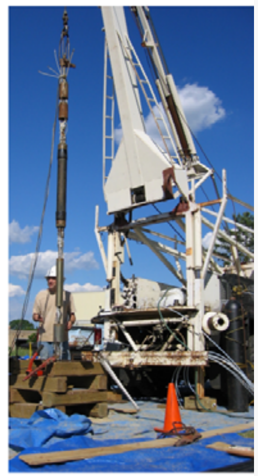
NGWA Workshop Flyer

NGWA/EPA Fractured Rock Conference: State of the Science and Measuring Success in Remediation

Workshop on Fate, Transport, and Remediation of Chlorinated Solvents in Fractured Sedimentary Rocks at the former Naval Air Warfare Center, West Trenton, NJ

Wednesday September 26, 10:20 am to 3:00 pm.



This workshop will present results of multidisciplinary investigations conducted by the U.S. Geological Survey (in cooperation with the U.S. Navy, Geosyntec Consultants, and ECOR Solutions) of trichloroethene (TCE) distribution, transport, and biodegradation in fractured mudstones underlying the former Naval Air Warfare Center (NAWC), West Trenton, NJ. Beginning in the 1950's, TCE was released to land surface in dissolved and pure phases, and has been observed in ground water as deep as 60 m. Natural microbial reductive dechlorination has partially transformed TCE to cis-1,2-dichloroethene (cDCE), vinyl chloride (VC), and ethene. A pump and treat system has operated for about a decade, but dissolved contaminant concentrations remain high (up to ~140 mg/L TCE, ~20 mg/L cDCE, and ~4 mg/L VC), suggesting that substantial contaminant mass remains in the low-permeability part of the rock. A bioaugmentation pilot study was conducted to investigate enhanced biodegradation of TCE and its daughter products.

Oral and poster presentations, computer displays, rock core, and field equipment will be used to illustrate methods, results, and interpretation of field investigations at NAWC. Presentations will focus on three themes:

Finding flow and transport paths: Understanding the fate of chlorinated solvents in fractured rock and designing effective remediation strategies first requires a detailed understanding of the paths of fluid and chemical movement. At NAWC, results of hydraulic and tracer tests and geologic and geophysical characterization have been used together with flow modeling to identify these paths.

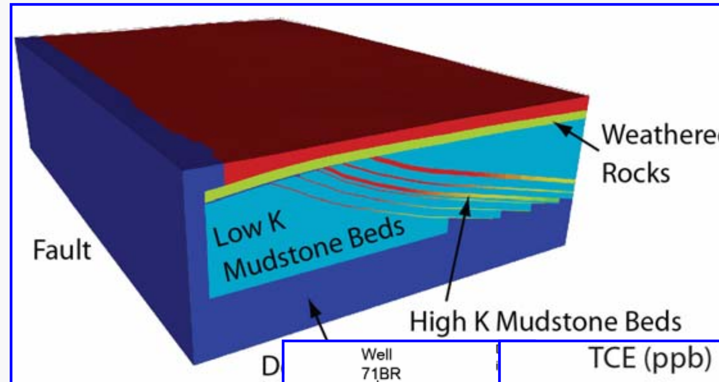
Monitoring contaminants, geochemistry, and microbiology: Innovative approaches to monitoring contaminant concentrations, water chemistry, and redox conditions have shown significant spatial variability of these constituents, reflecting the highly heterogeneous geologic and geochemical environment. This variability is a critical factor in designing remediation strategies.

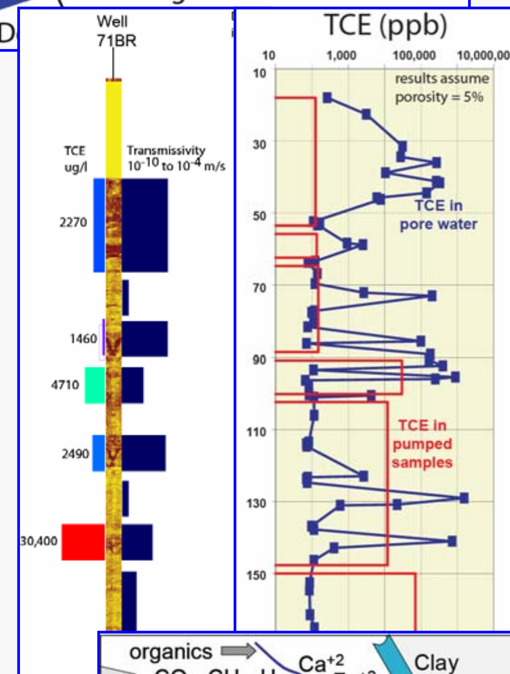
Evaluating remediation effectiveness: Pump and treat has been relatively inefficient, in terms of contaminant mass removed per volume pumped. Bioaugmentation shows promise for increasing natural degradation rates and enabling complete transformation of TCE. Reactive transport modeling that synthesizes multidisciplinary subsurface data is being used to compare remediation strategies.

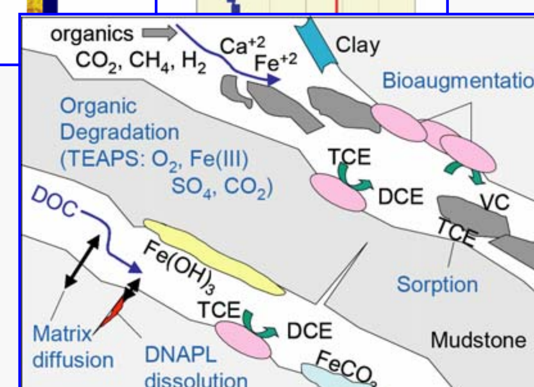
Workshop Schedule

Introduction		
10:20 – 10:40	Oral presentation: **Multidisciplinary studies of flow, transport, and remediation at the former Naval Air Warfare Center**	C.R. Tiedeman
Finding flow and transport paths		
10:40 – 11:00	Oral presentation: **Finding flow and transport paths**	D.J. Goode
11:00 – 11:40	Poster presentations:	
	Mapping the 3D distribution of subsurface sedimentary strata	P.J. Lacombe, W.C. Burton
	Delineating geologic heterogeneity with surface geophysics	K.J. Ellefsen
	Using borehole flow logging to identify permeable fractures and local-scale hydraulic connections	J.H. Williams, C.D. Johnson
	Identifying site-scale hydraulic connections and properties through aquifer testing and flow modeling	C.R. Tiedeman, D.J. Goode
	Using tracer tests to discern transport paths and properties	A.M. Shapiro, P.A. Hsieh
Monitoring contaminants, geochemistry, and microbiology		
11:40 – 12:00	Oral presentation: **Monitoring contaminants, geochemistry, and microbiology**	A.M. Shapiro
12:00 – 1:20	**LUNCH: on your own** **(Note: Lunch time has changed from that printed in the Conference Program)**	
1:20 – 1:50	Poster presentations:	
	Monitoring the vertical variability of contaminants and geochemistry using multi-level borehole packers	T.E. Imbrigiotta, C.R. Tiedeman
	Characterizing the distribution of chlorinated solvents in the rock matrix	D.J. Goode, A.M. Shapiro
	Understanding the site-scale distribution of chlorinated solvents in relation to the geologic framework	P.A. Hsieh
	Characterizing natural biodegradation by monitoring redox conditions and microbiology	P.M. Bradley, F.H. Chapelle
Evaluating remediation effectiveness		
1:50 – 2:10	Oral Presentation: **Evaluating remediation effectiveness**	F. H. Chapelle
2:10 – 2:40	Poster Presentations:	
	Estimating the contaminant mass removed by pump and treat operations	P.J. Lacombe
	Pilot-scale implementation of bioaugmentation to remediate chlorinated solvents	M.F. DeFlaun
	Monitoring natural biodegradation by analyzing light stable isotopes of different compounds	K.M. Revesz
	Using reactive transport modeling to compare remediation strategies	G.P. Curtis
Wrap-Up and Discussion		
2:40 – 3:00	**Workshop summary, audience questions, and discussion**	All workshop presenters

Summary: USGS Research in Contaminated Fractured Rocks







- Finding flow and transport paths
- Monitoring contamination, geochemistry, microbiology
- Evaluating remediation effectiveness

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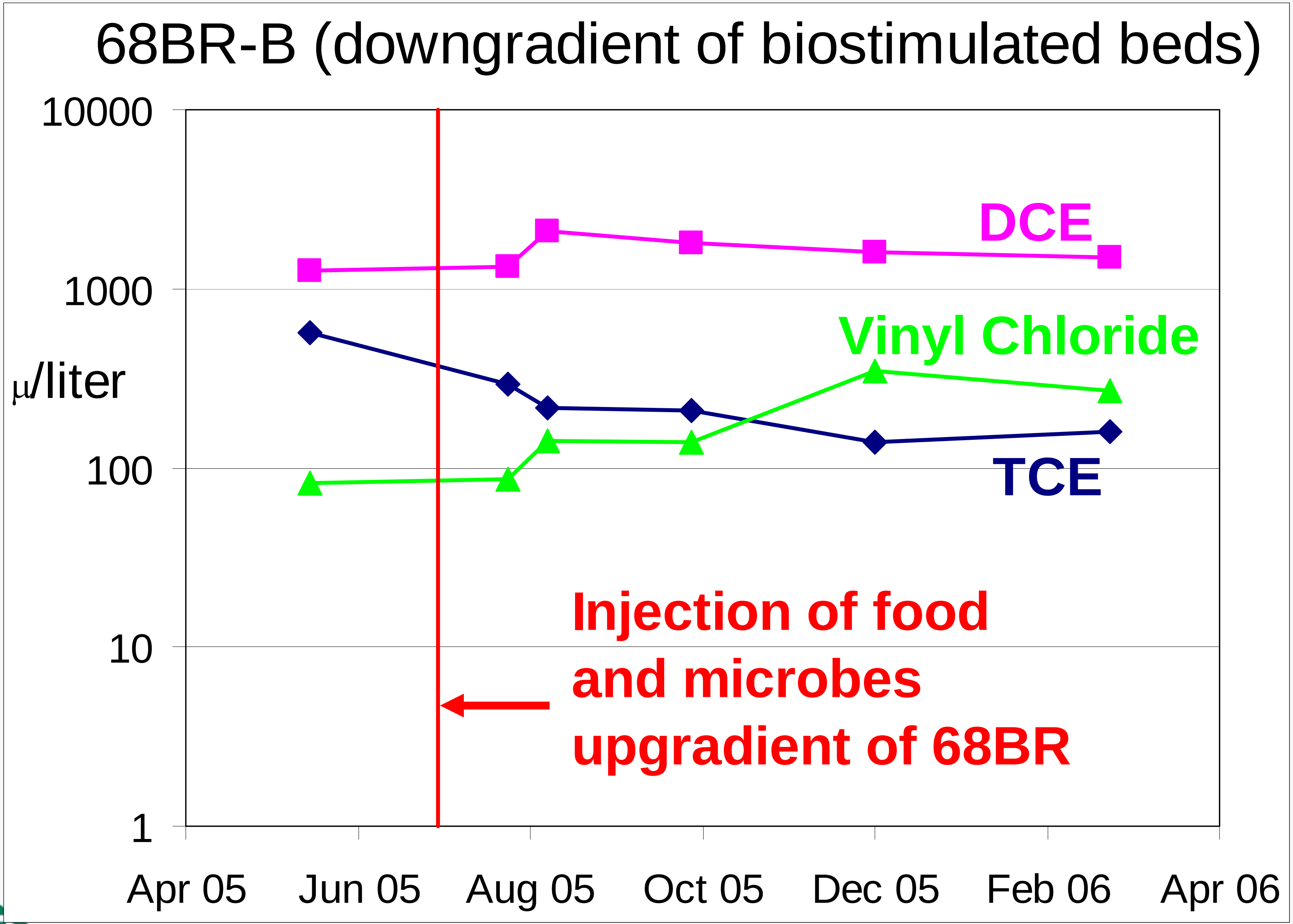
Questions, Comments, Requests?

Possible evidence of enhanced biodegradation in 68BR



Empirical Estimates of Mass Removed

- Pump & Treat
  - 400 liters TCE removed in 2006
  - 8000 liters TCE removed 1997-2006
- Monitored Natural Attenuation
  - 700 liters over unknown time period
- Enhanced Biodegradation
  - 3 to 5 liters
  - Much less than P & T in 1 year because bioaugmentation took place in a rock volume with low to moderate TCE concentrations
- Compare to mass remaining in system:
  - Highly dependent on assumptions about percent of primary porosity containing DNAPL
  - 2000 to 46,000 liters TCE

TCE Released to GW: Highly Uncertain

- ~100,000 liters in ‘closed’ heat transfer system
- Estimates of loss per year: 4000 to 20,000 liters (highly uncertain)
- Using low end of this range, 160,000 liters released over 40 years (1955 – 1995)
- Compare to estimates of TCE removed and remaining:
  - Removed: 8000 liters by P & T + 700 liters by MNA = 8,700 liters
  - Remaining: 2000 to 46,000 liters
  - Sum of these << 160,000 liters
- Does this mean less TCE released than estimated, or we aren’t accounting for some mass remaining in the GW system? TCE likely discharged to creek prior to P & T system coming on line; estimate of amount is unknown but could be large.

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