Characterizing Contaminant Mass in the Rock Matrix

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with Tom Imbrigiotta, Allen Shapiro, Claire Tiedeman, and others

USEPA-USGS Fractured Rock Workshop

EPA Region 10

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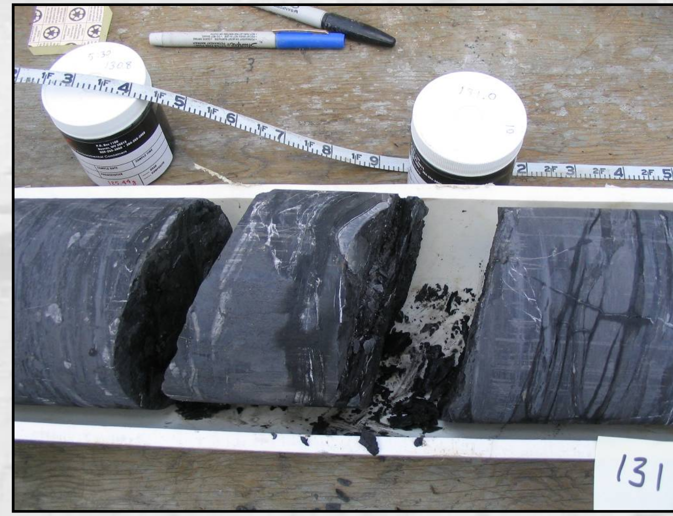
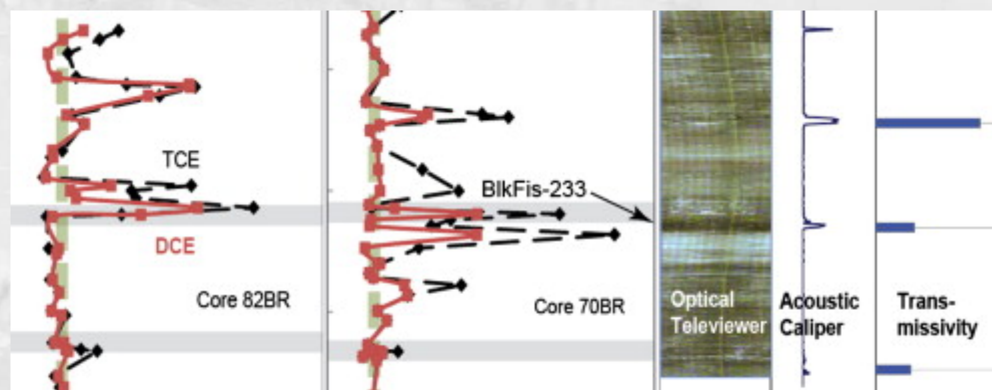
Outline

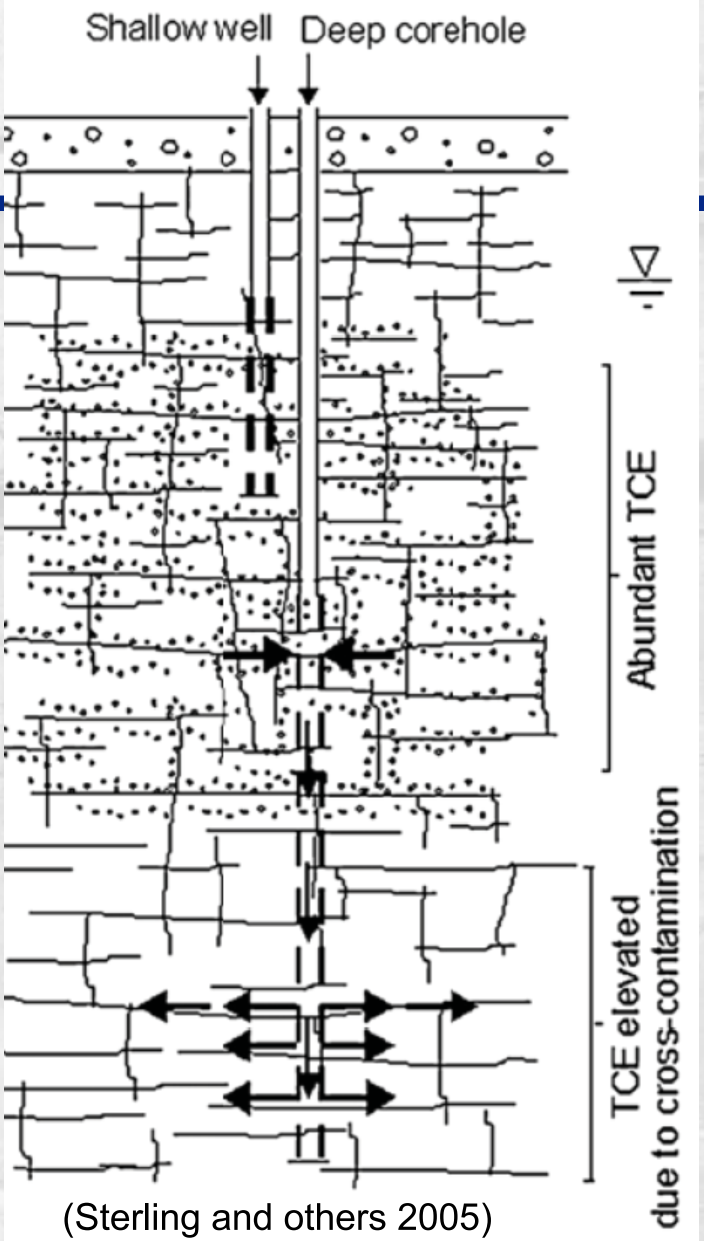
- Why Delineate CVOCs in Matrix?
- Rock Core Sampling for CVOCs
  - Synthesis with Other Characterization
- Case study
- Commercial Vendor





Why Delineate CVOCs in Matrix?

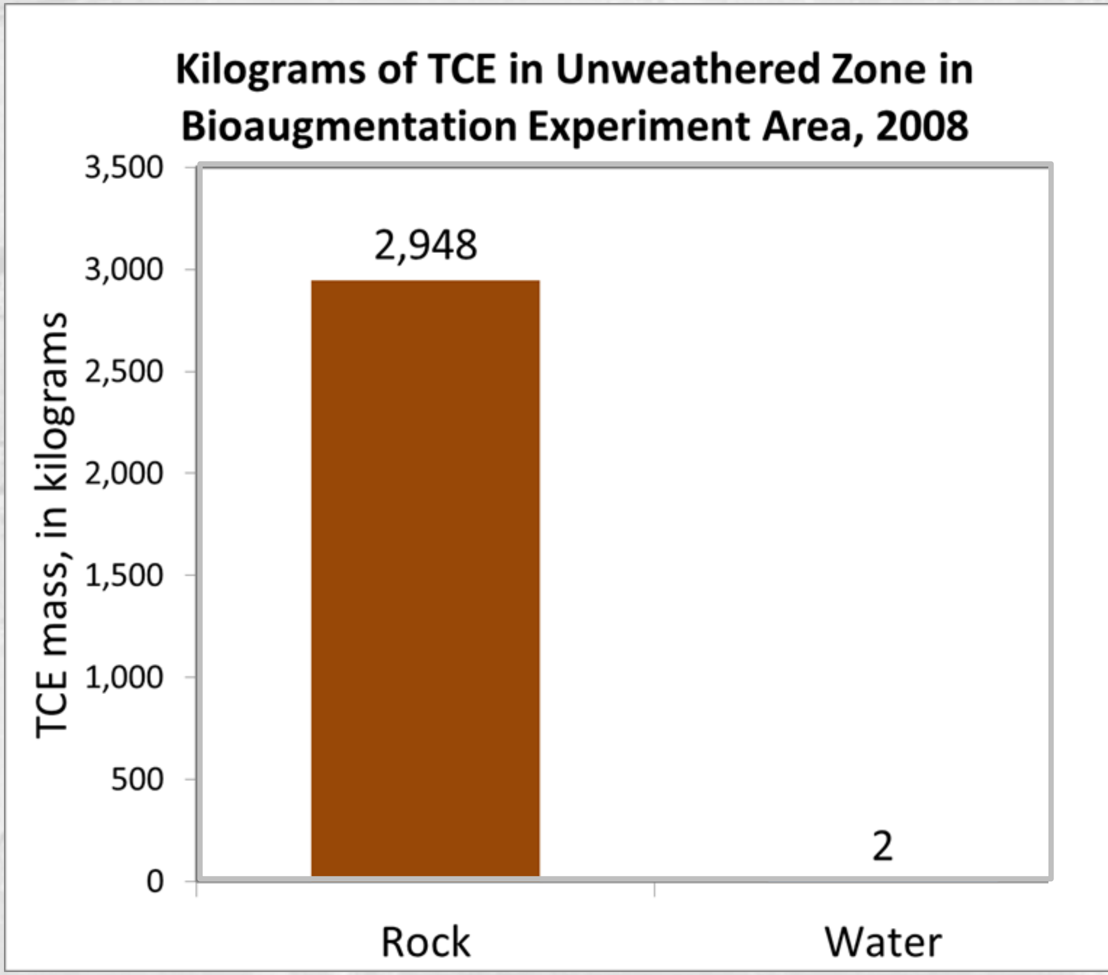
- Core samples much less affected by migration during and after drilling
  - Gravity pulls Dense-NAPL downward
  - Downward borehole flow carries solutes (advection)



(Sterling and others 2005)

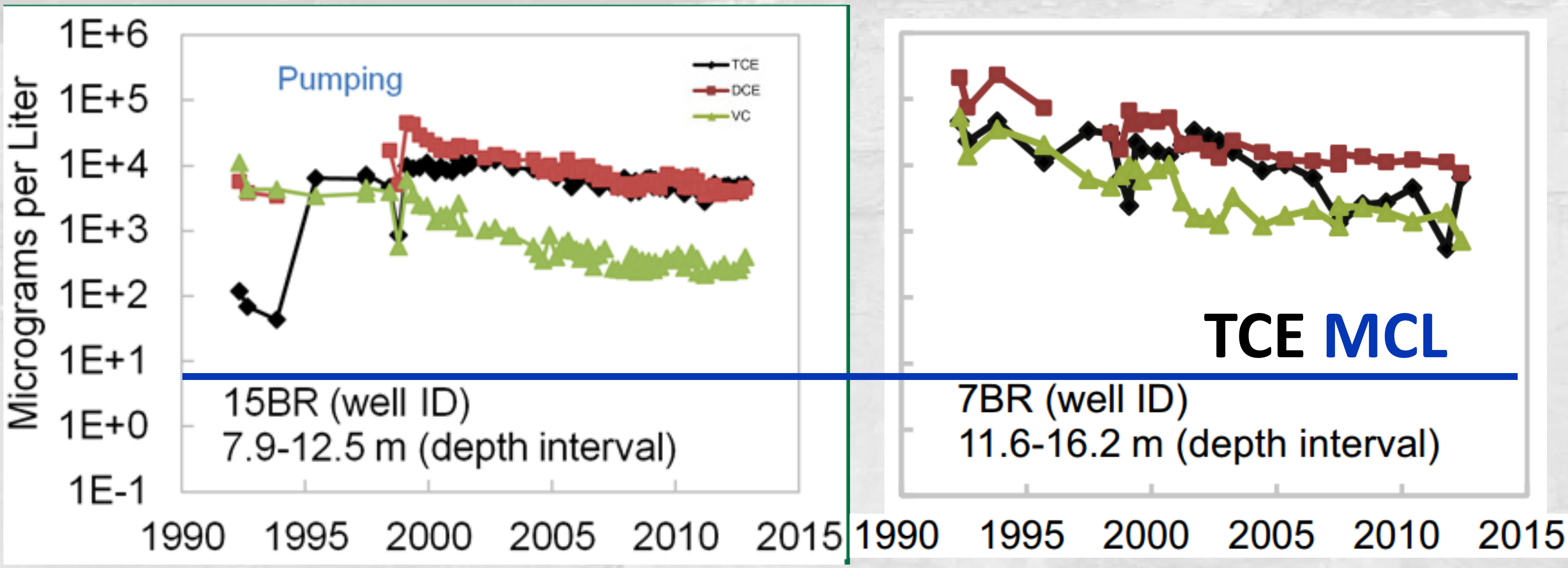
Why Delineate CVOCs in Matrix?

- **CVOCs often reside mostly in or on rocks, not in water in fractures**
- **Water in fast-flowing fractures contains a small portion of the CVOCs**



Why Delineate CVOCs in Matrix?

- **Slow release by diffusion and de-sorption causes long-term exceedance of MCLs**

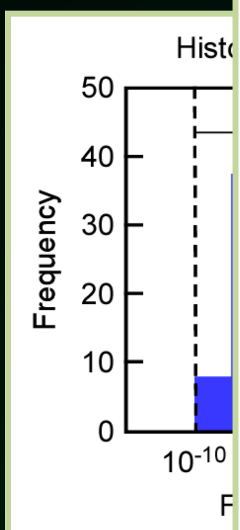


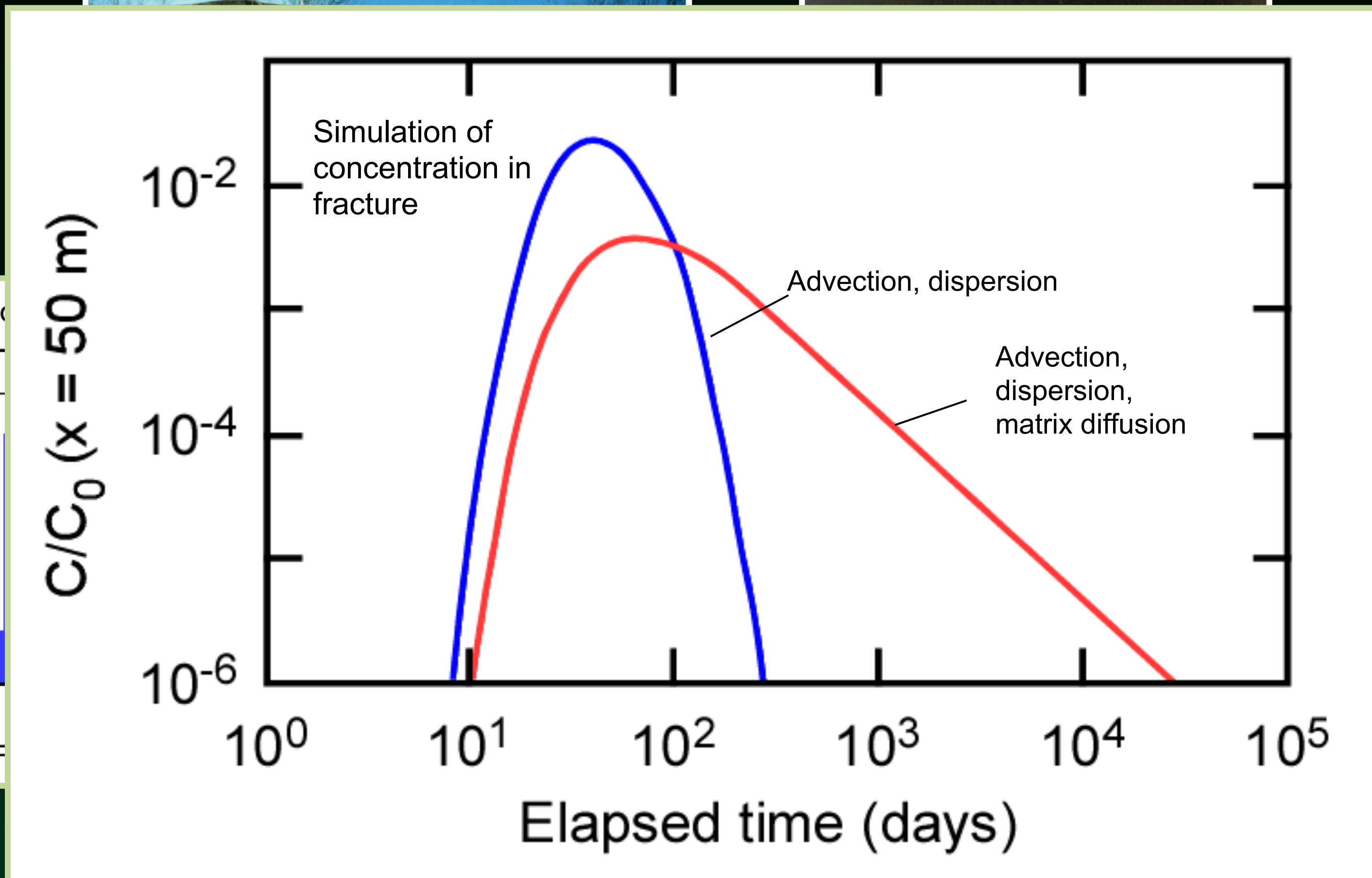
(modified from Goode and others 2014)

Fractured Rock: A Challenging Environment for Groundwater Remediation

1. Convoluted groundwater flow paths and complex spatial distribution of contaminants

2. Diffusion into and out of primary/intrinsic porosity (rock matrix)



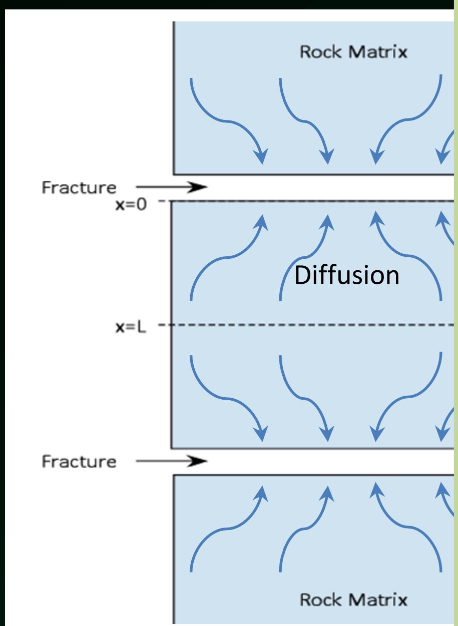


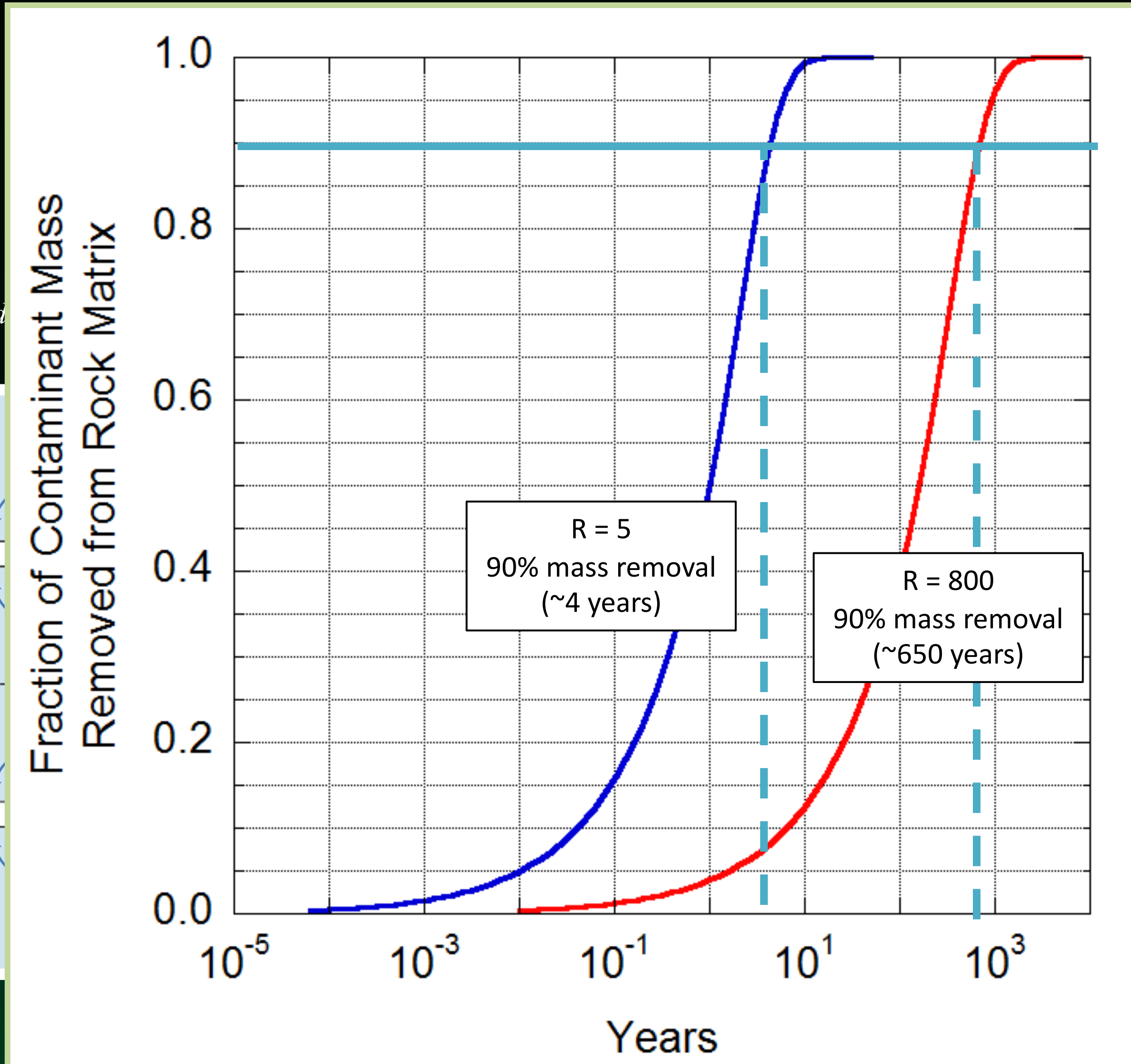
A Simple Evaluation of TCE Retention in the Rock Matrix

$$R\frac{\partial C}{\partial t} - D_d\frac{\partial^2 C}{\partial x^2} =$$

$$R = 1 + \frac{\rho_b K_d}{n} \qquad K_d$$

rption
rock matrix
er

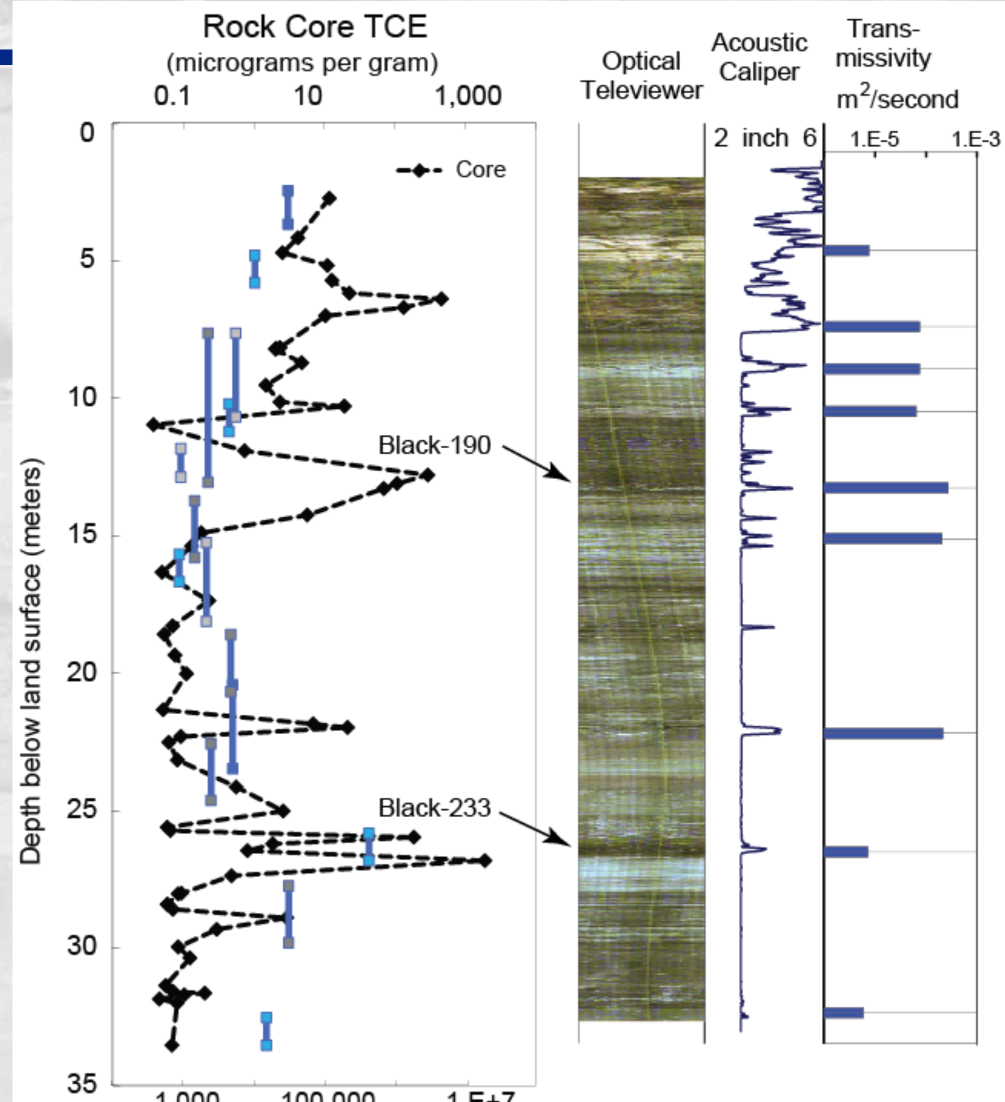




USGS

Why Delineate CVOCs in Matrix?

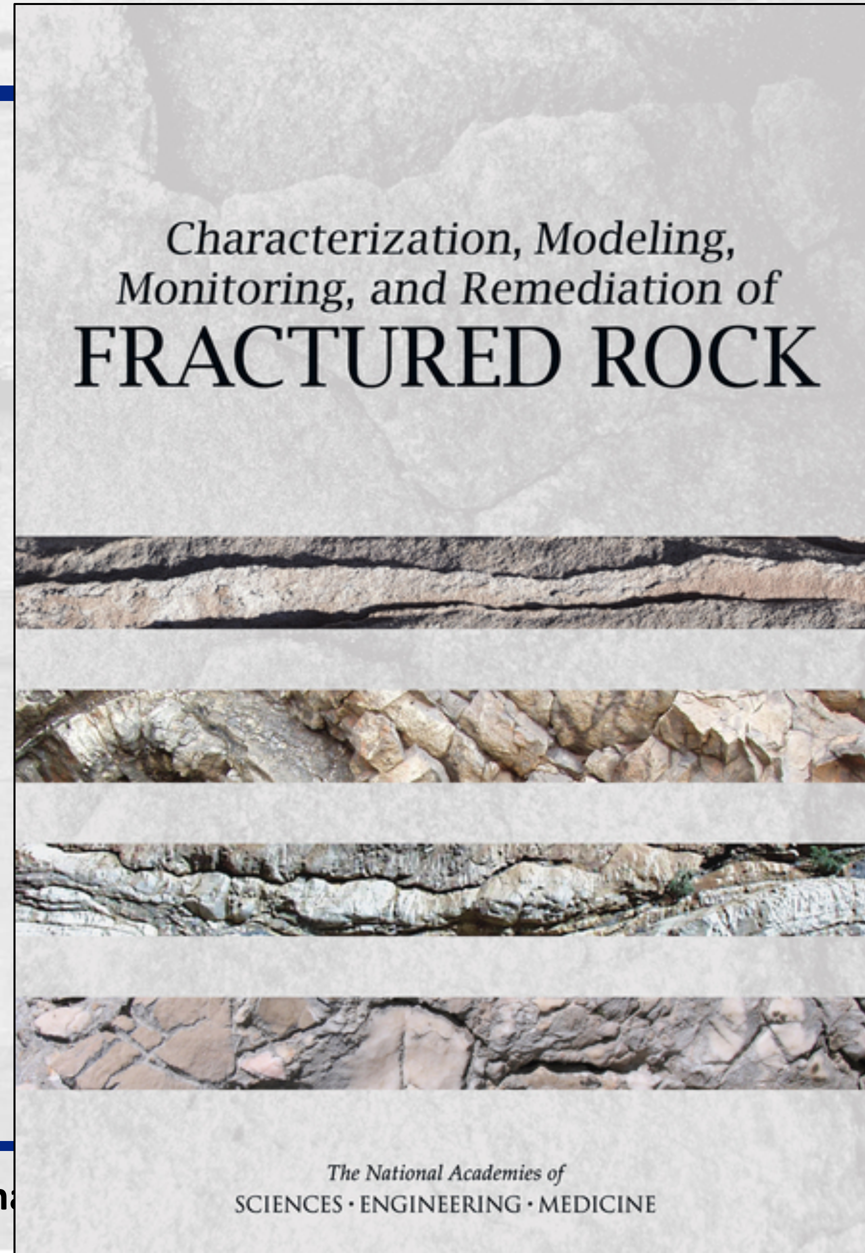
- Bioaugmentation amendments limited to thin permeable strata around injection well, and . . .
- Contaminants constrained near permeable fractures



(modified from Goode and others 2014)

Why Delineate CVOCs in Matrix?

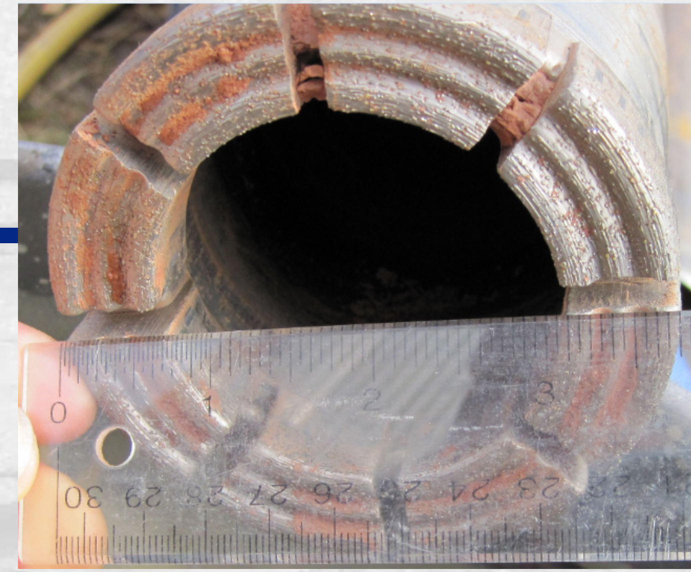
- Recommendation 2 [of 10]:
- "Estimate the potential for contaminant to be transported into, stored in, and transported back out of rock matrix over time."



Rock Coring Methods

- **Rotary Coring – Best method for collecting relatively undisturbed cores; minimal polymer added, only if necessary, to help remove cuttings; minimal chemical effects**
  - **Triple barrel (inner split barrel) improves sample integrity**

- **Sonic Coring – Can be used, but not preferred because it may create new fractures; high-pressure water introduced to remove cuttings, probable vertical cross-contamination effects**



Analysis of Rock Core for CVOCs

- Developed from sediment coring and methanol extraction technologies
- Initial rock-core applications and refinement by Beth Parker, John Cherry, and colleagues (e.g. Sterling, et al., 2005)
- Parker's Trademarked "CORE^{DFN}" approach licensed to Stone Environmental
- Stone Environmental and/or Beth Parker's group (now at Guelph U., Canada) have worked on many EPA sites

Analysis of Rock Core for CVOCs

- **USGS began using similar methods in Region 3 in 2001 (e.g. Sloto, 2002)**
- **A “bulk” analysis, includes all CVOC phases in sample**

SECTION OF CORE (UNWEATHERED SANDSTONE) SAMPLED FOR VOLATILE ORGANIC COMPOUNDS

Analysis of Rock Core for CVOCs

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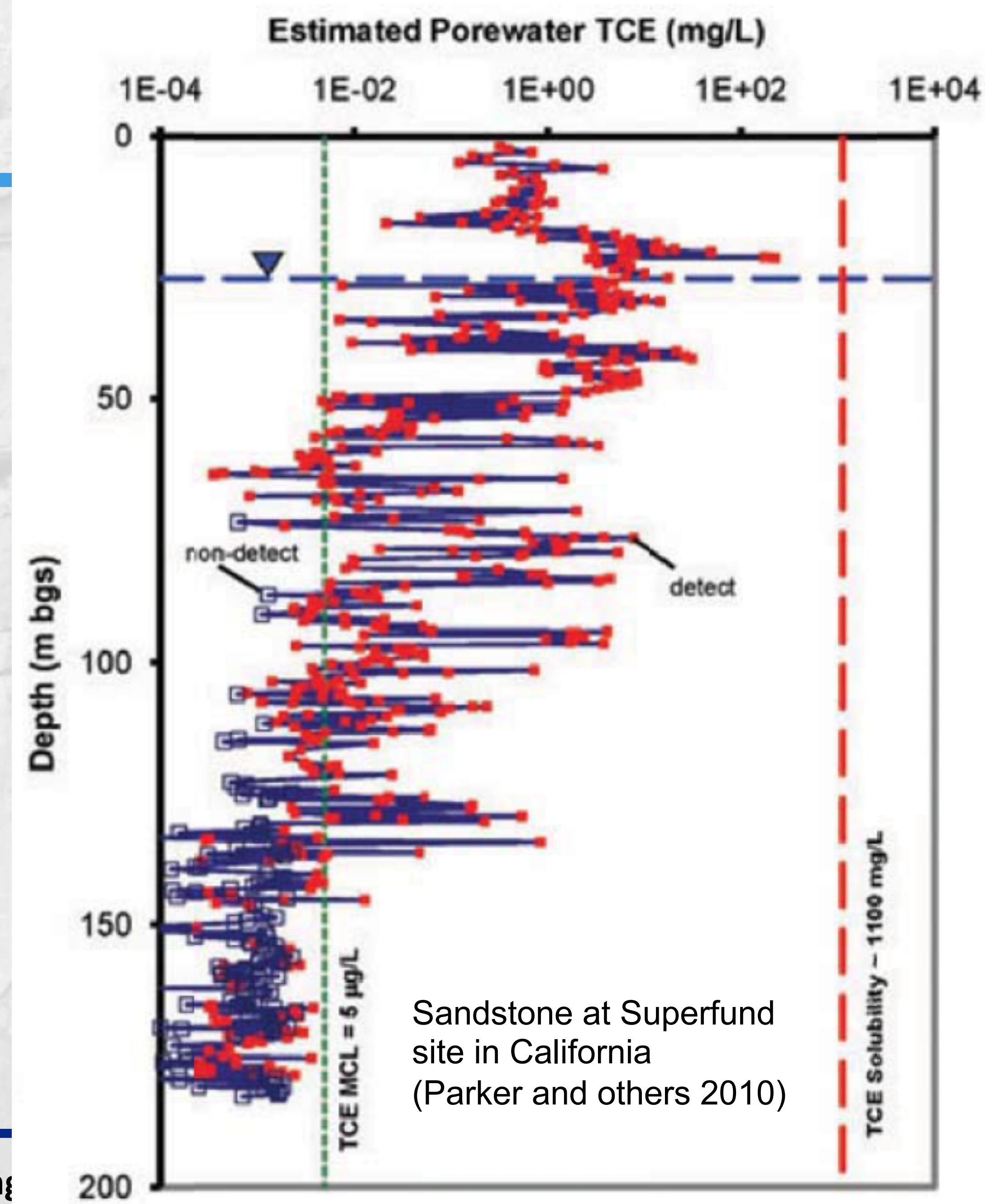
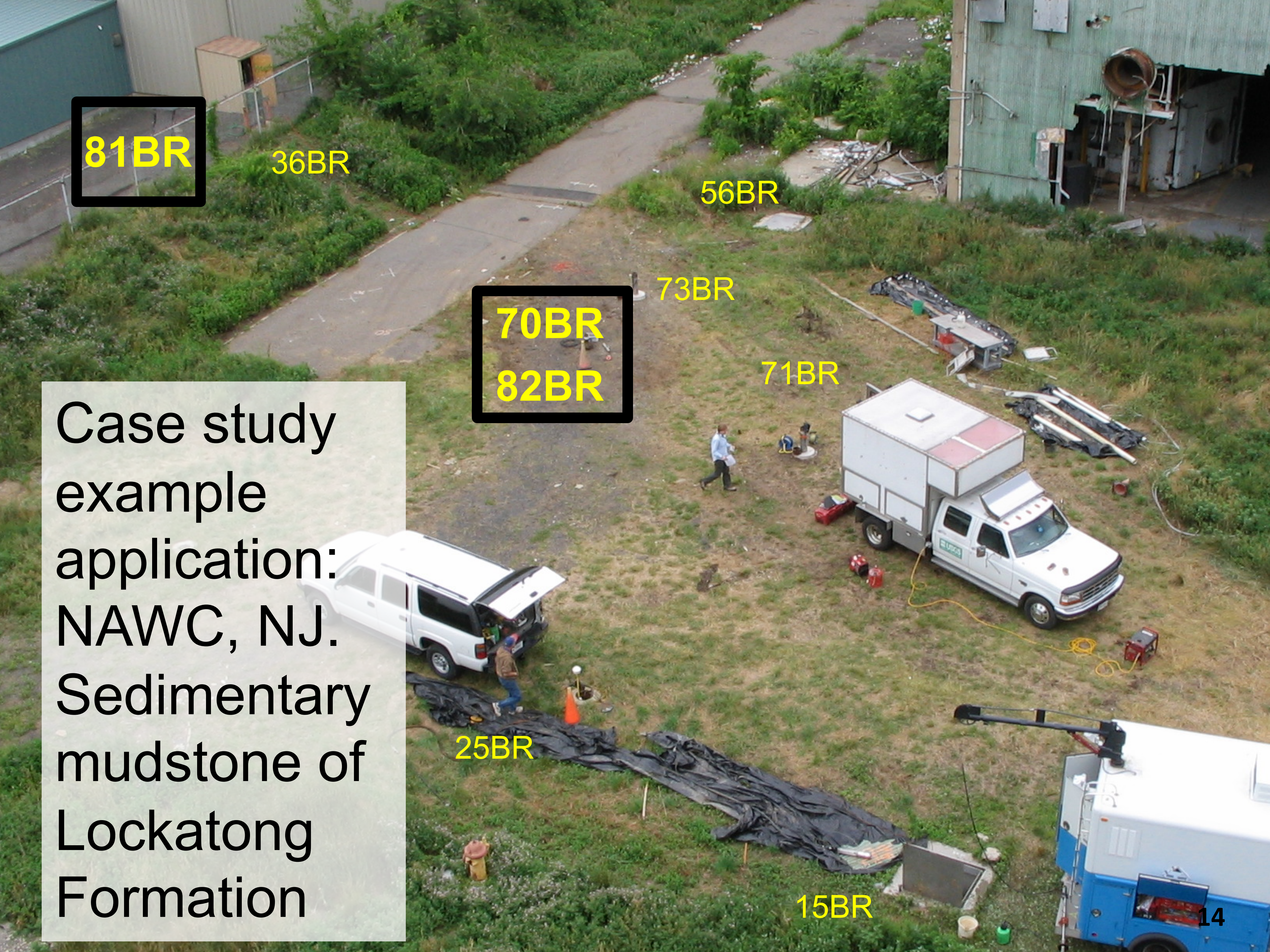
- A "bulk" analysis, includes all CVOC phases in sample

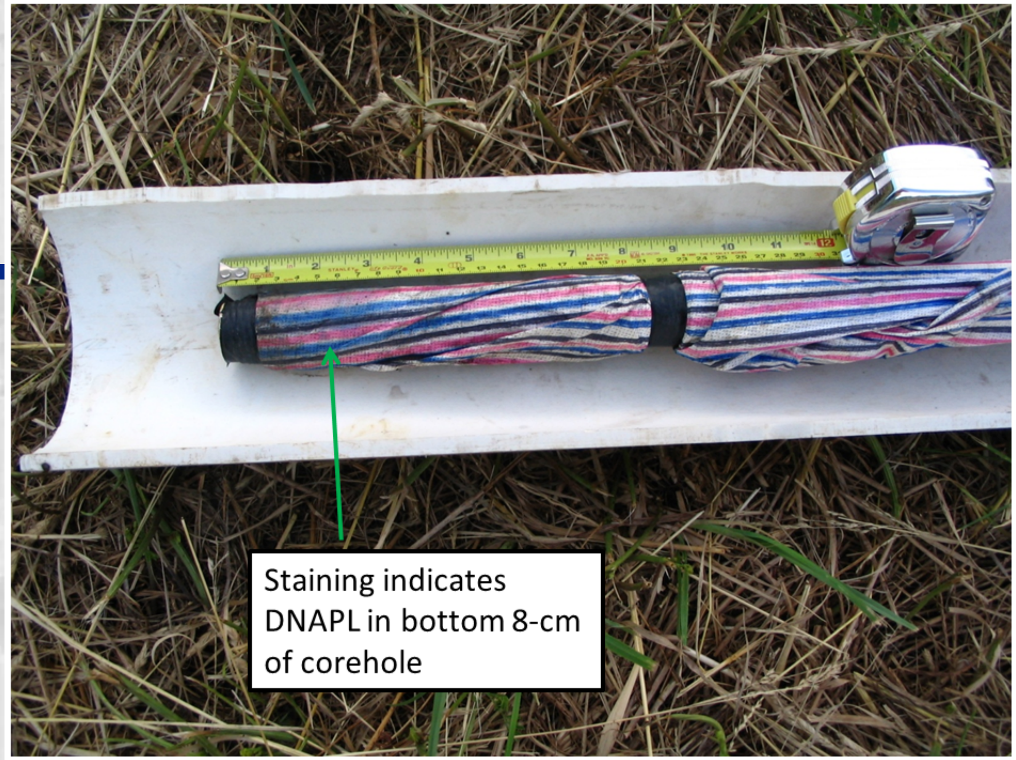


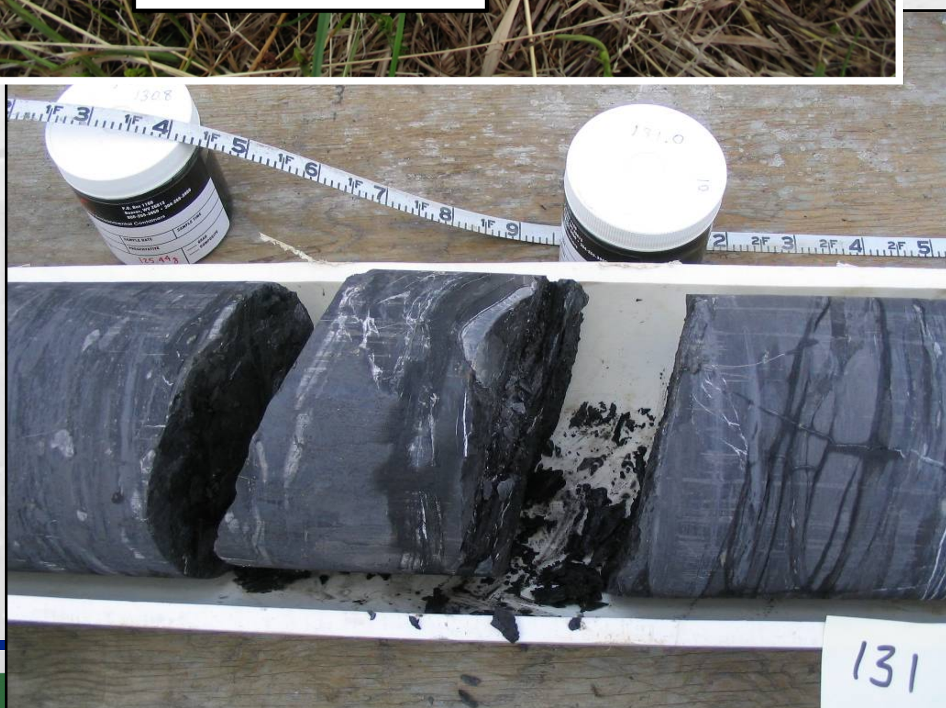
Sandstone at Superfund site in California (Parker and others 2010)

Case study example application: NAWC, NJ. Sedimentary mudstone of Lockatong Formation



Methods





- DNAPL screening during coring – Hydrophobic-Dye Cloth (FLUTe)
- Rock Core VOC sampling and analysis (Sterling, Parker, Cherry and others 2005)

5-ft core in PVC trough prior to sub-sampling. Sledge hammer, chisels, jars, zip-loc bags on hand. Sampler wearing gloves (level D PPE).

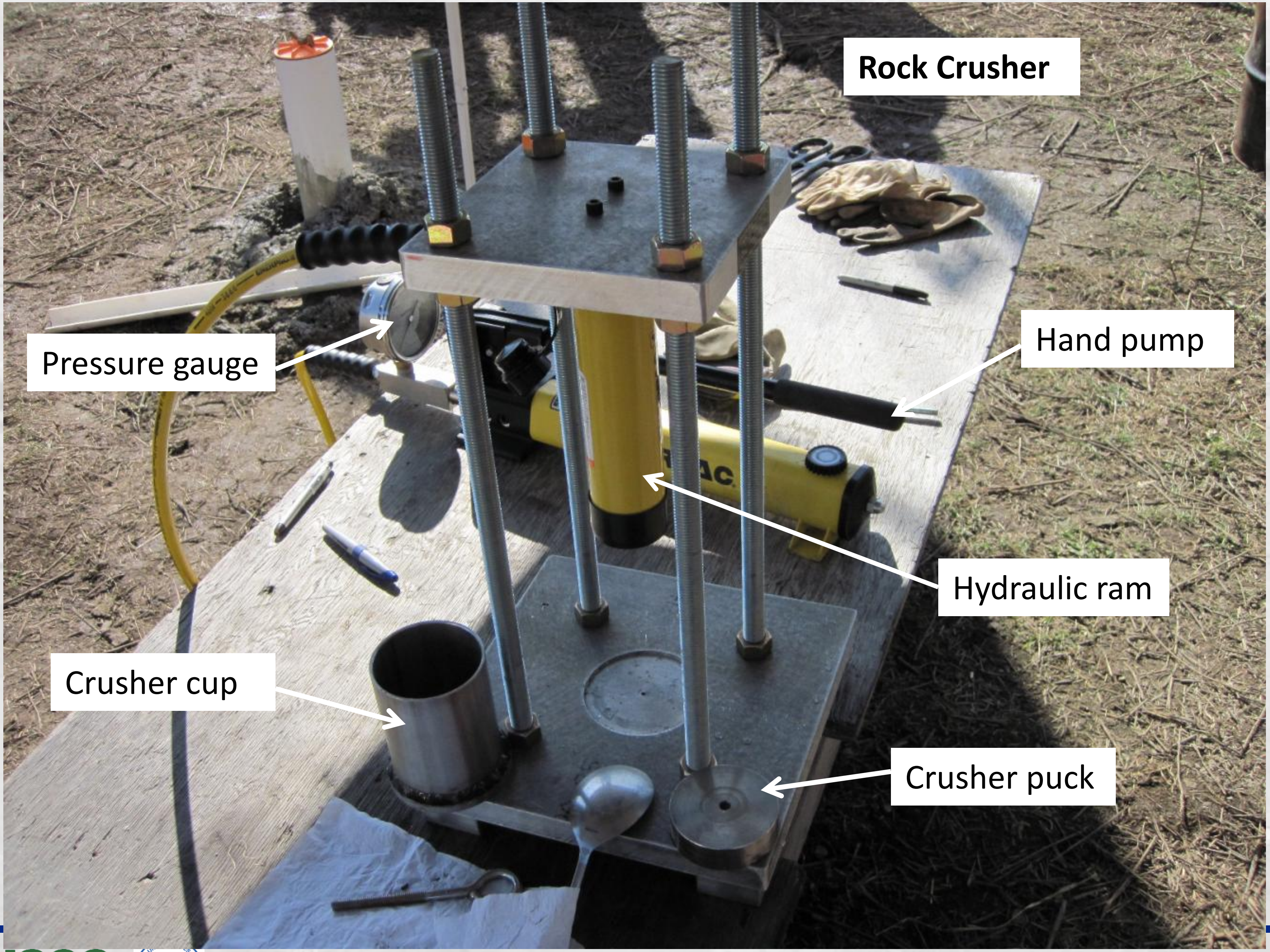
Core length is measured.

Chisel and hammer used to cleave off a section of core ½ to 1 inch thick.

First sample placed in crusher cup. Crushed immediately.

Additional samples from same core wrapped in aluminum foil and stored in zip-loc bags until they can be crushed. Septa jars labeled the same as the bags.

Typical 5-ft core with wooden spacers labeled and placed in the spaces where the core sub-samples were obtained.


Rock Crusher
Pressure gauge
Hand pump
Hydraulic ram
Crusher cup
Crusher puck

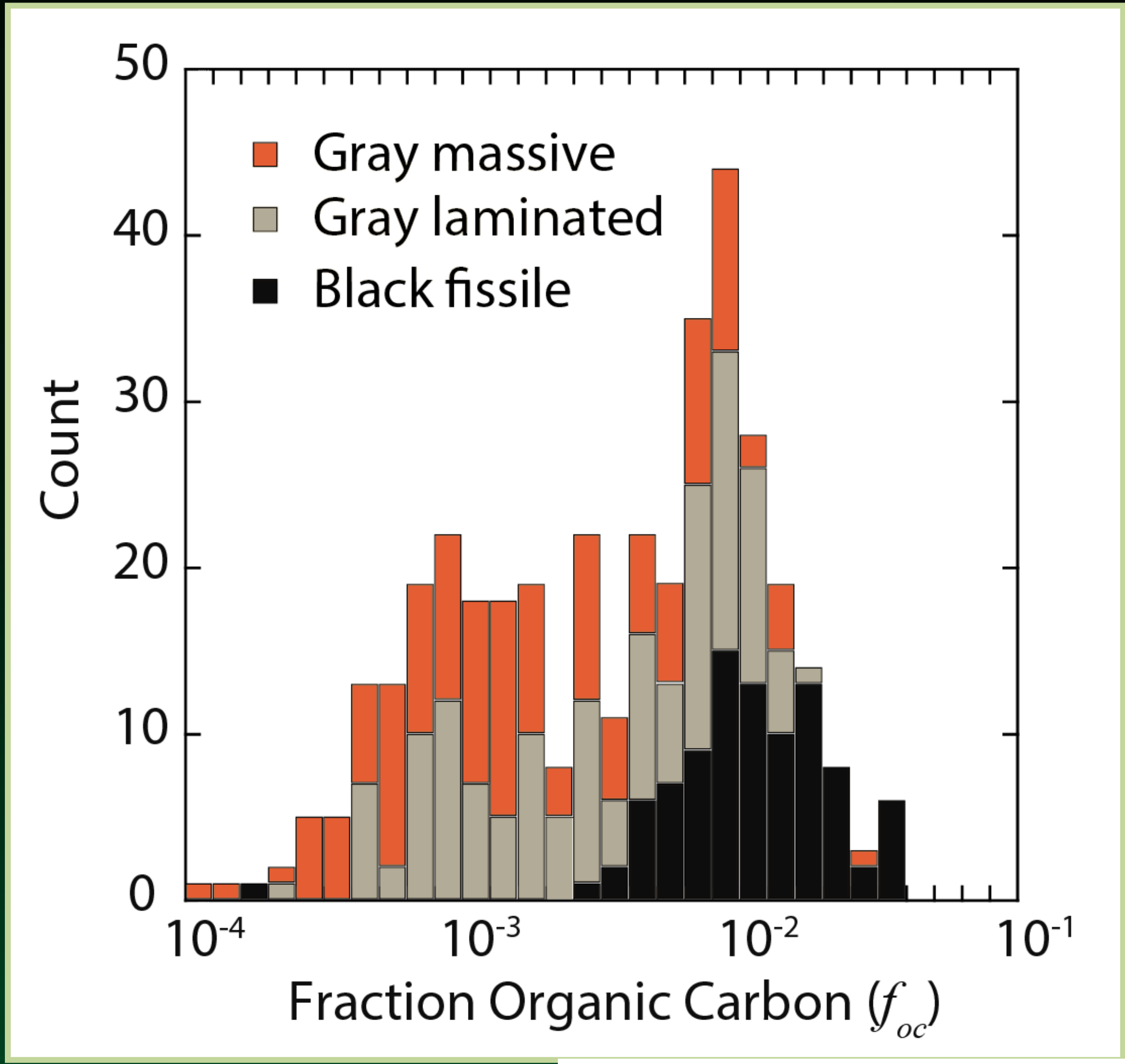
Rock crusher in use. Extra rock core samples being saved. In background, core being stored in core boxes and field lab vehicle with scale to weigh bottles containing core samples and methanol.

Adding 50 mLs of methanol to the bottle containing the crushed rock core sample.

Crusher cup, crusher puck, spatula, chisel cleaning buckets – 1 tap water, 2 tap water rinse, 3 deionized water rinse.

Variability of Organic Carbon Content in Mudstone

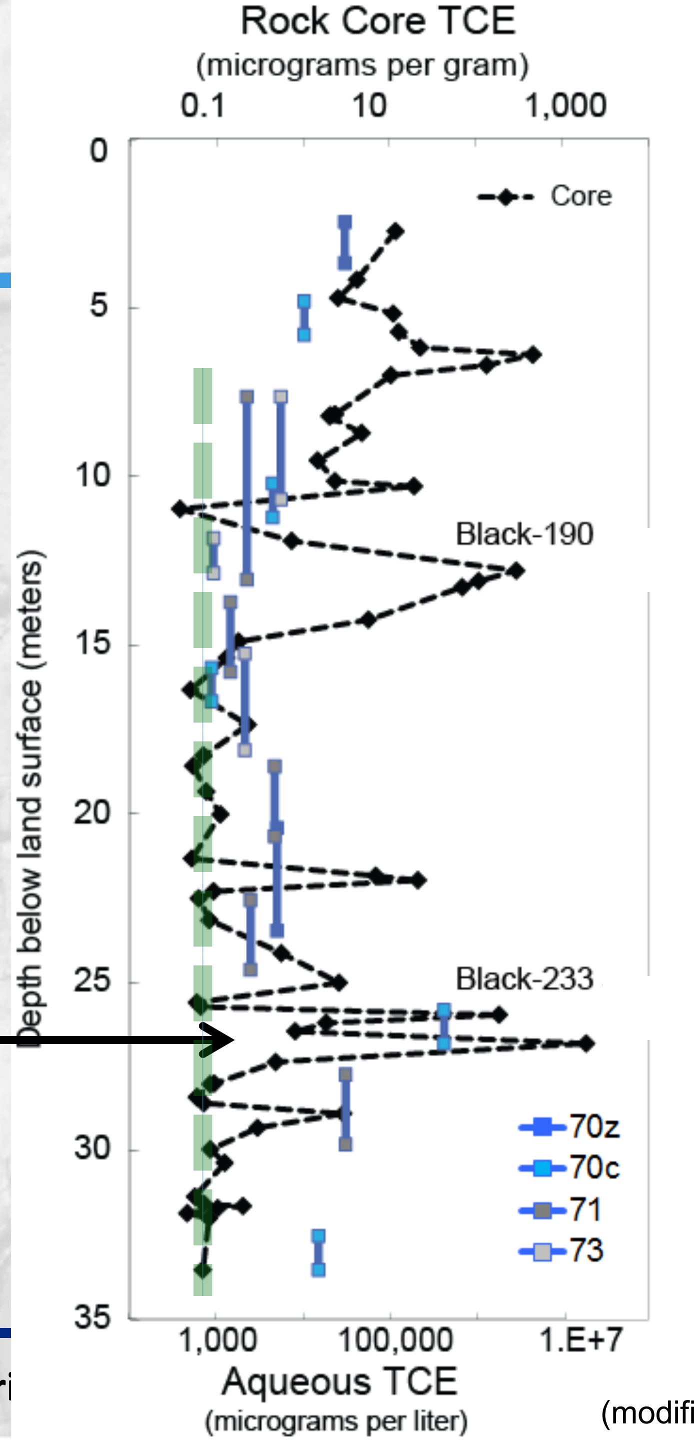
- Continuous rock core from 7 boreholes
- Lithologic description of cores
- Sections of core analyzed for:
  - TCE, DCE, VC
  - Organic Carbon
  - Porosity
  - Bulk density



(modified from Shapiro and Brenneis 2018)

Results 70BR

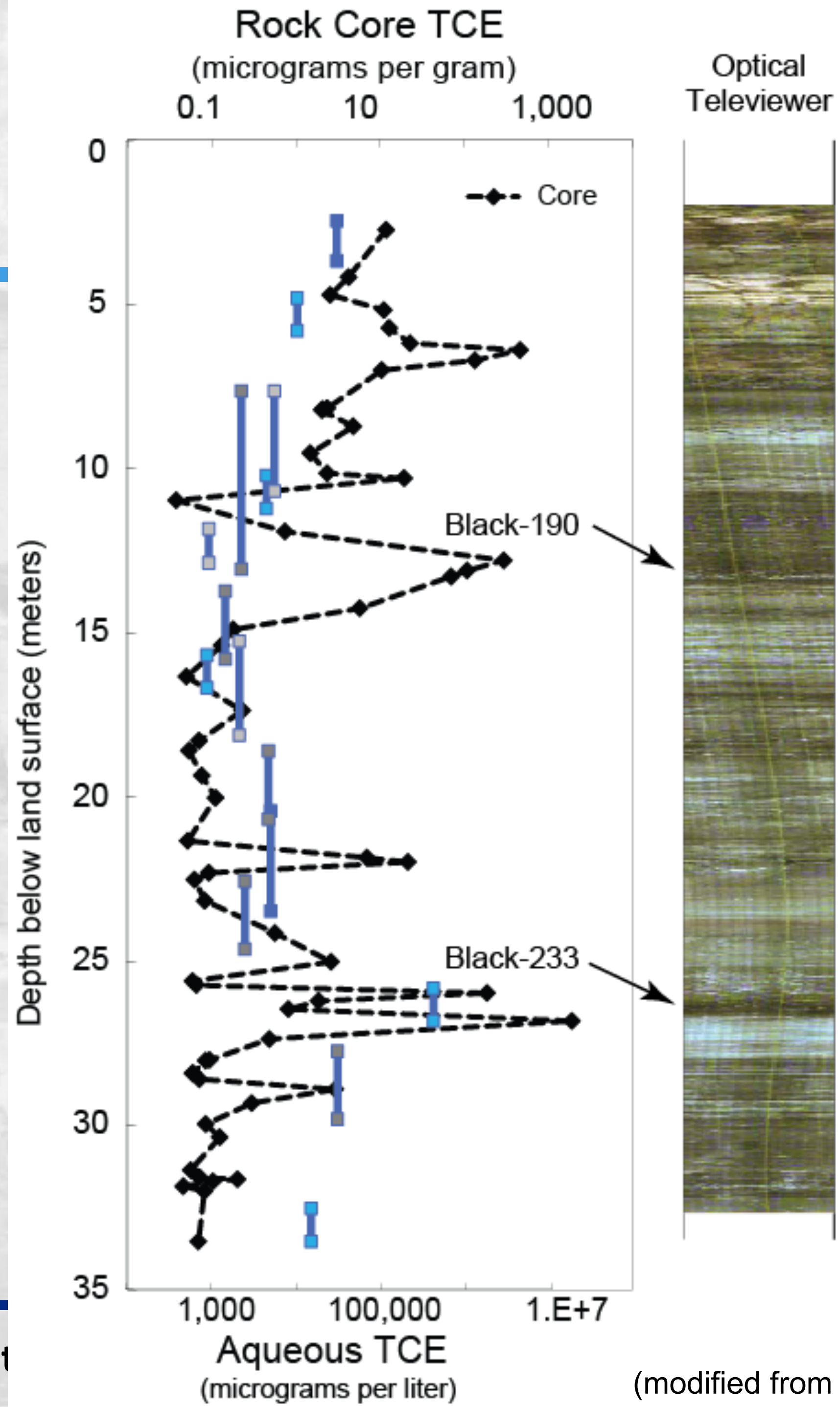
- Rock Core TCE (black, top)
- TCE in all but 1 sample < 15 m
- Non-detect in most samples > 15 m
- Aqueous TCE (blue, bottom) much less variable than core
- DNAPL detected at 27 m during coring (after >12 years of P&T)



(modified from Goode and others 2014)

Results
70BR

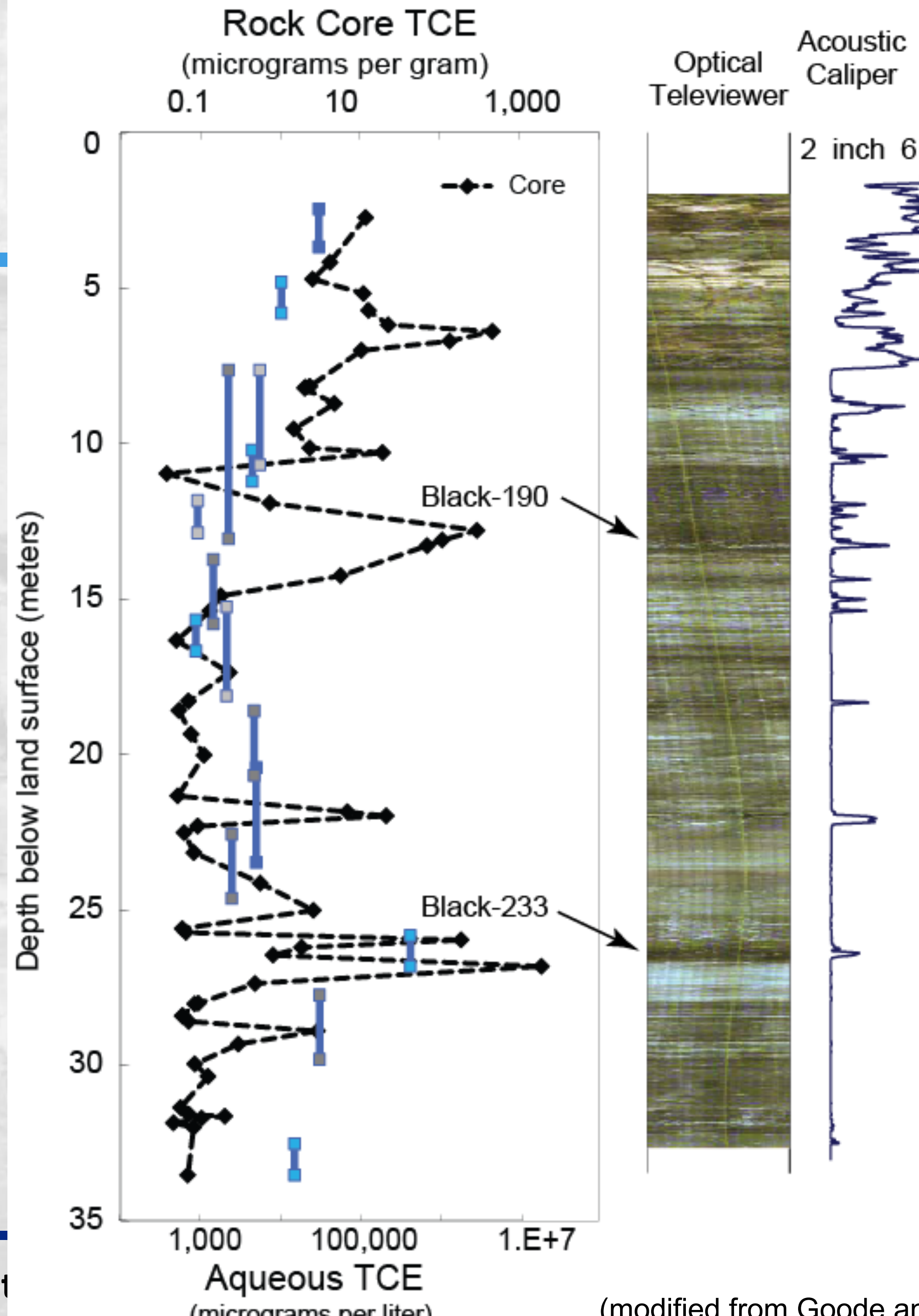
- Optical Televiewer – Color lithology
- High-carbon Black fissile strata
- Gray laminated strata
- Light-gray massive strata



(modified from Goode and others 2014)

Results 70BR

- Acoustic Caliper
- Highly fractured shallow weathered zone
- Isolated fractures below 15 m depth in Black, and other, strata



(modified from Goode and others 2014)

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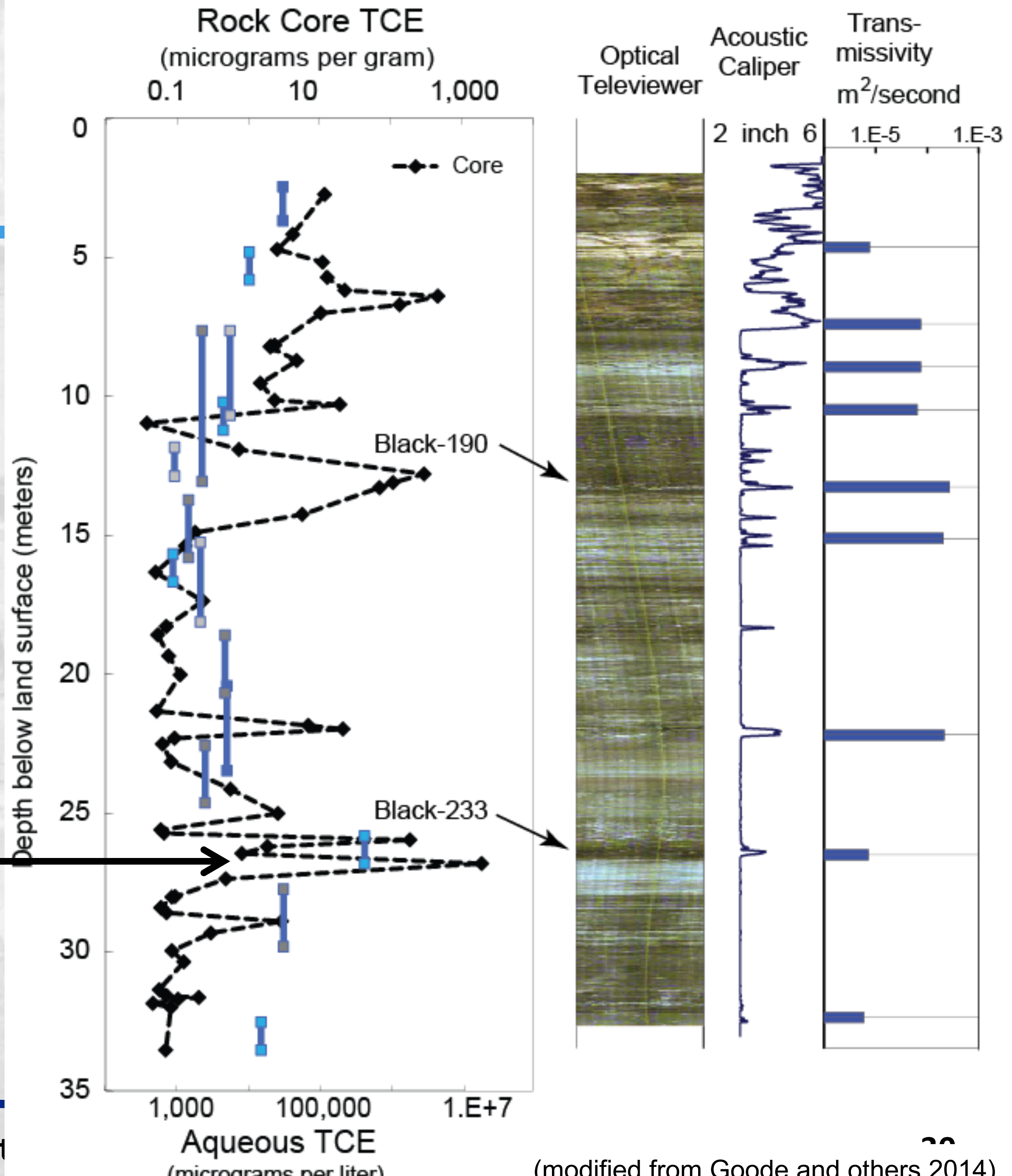
Results
70BR

- Transmissivity from Borehole Flowmeter Johnson & Anderson
- Several high-T zones 7-15 m depth
- Isolated high-T zones below 15 m
- DNAPL detected at 27 m during coring (after >12 years of P&T)



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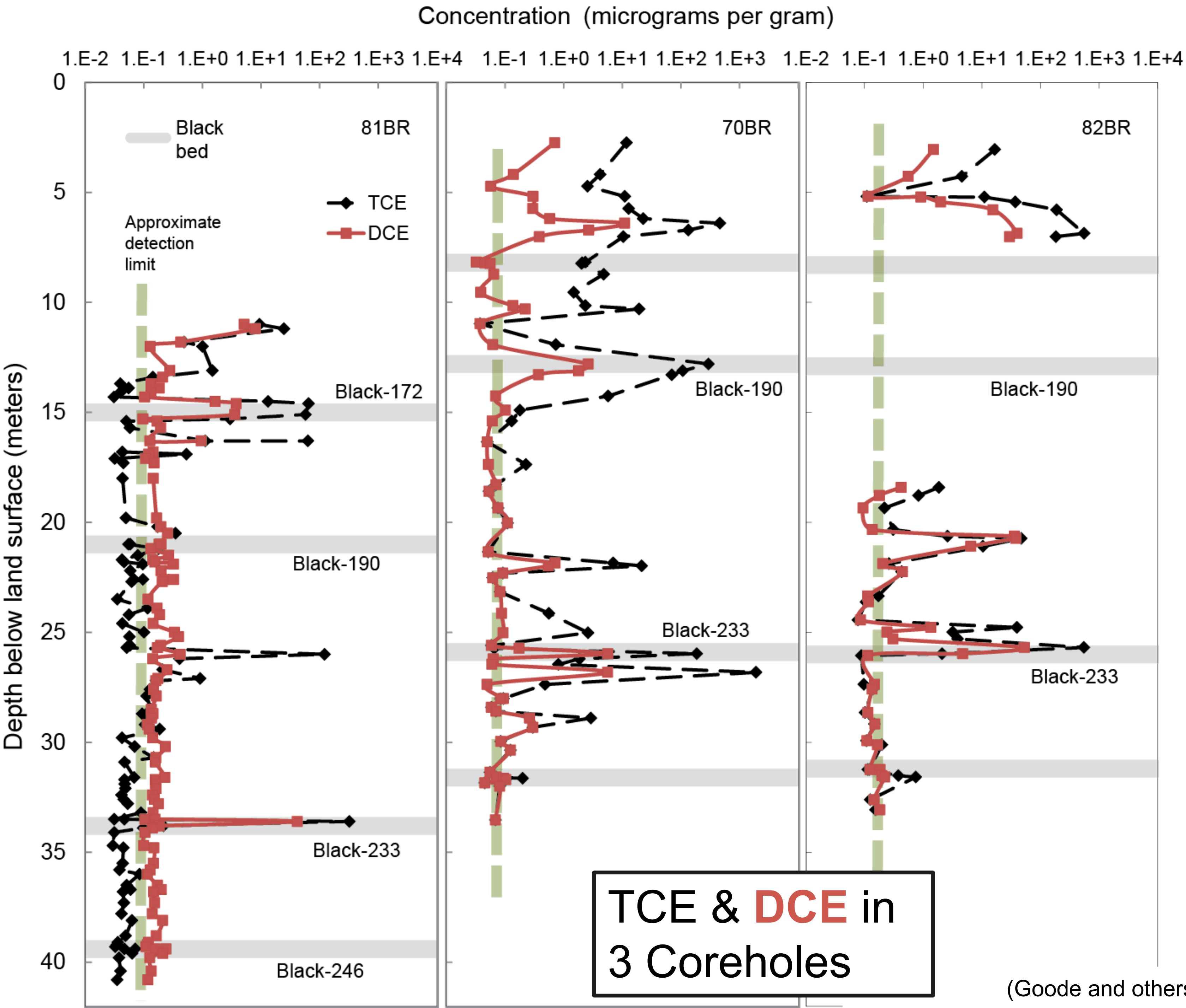
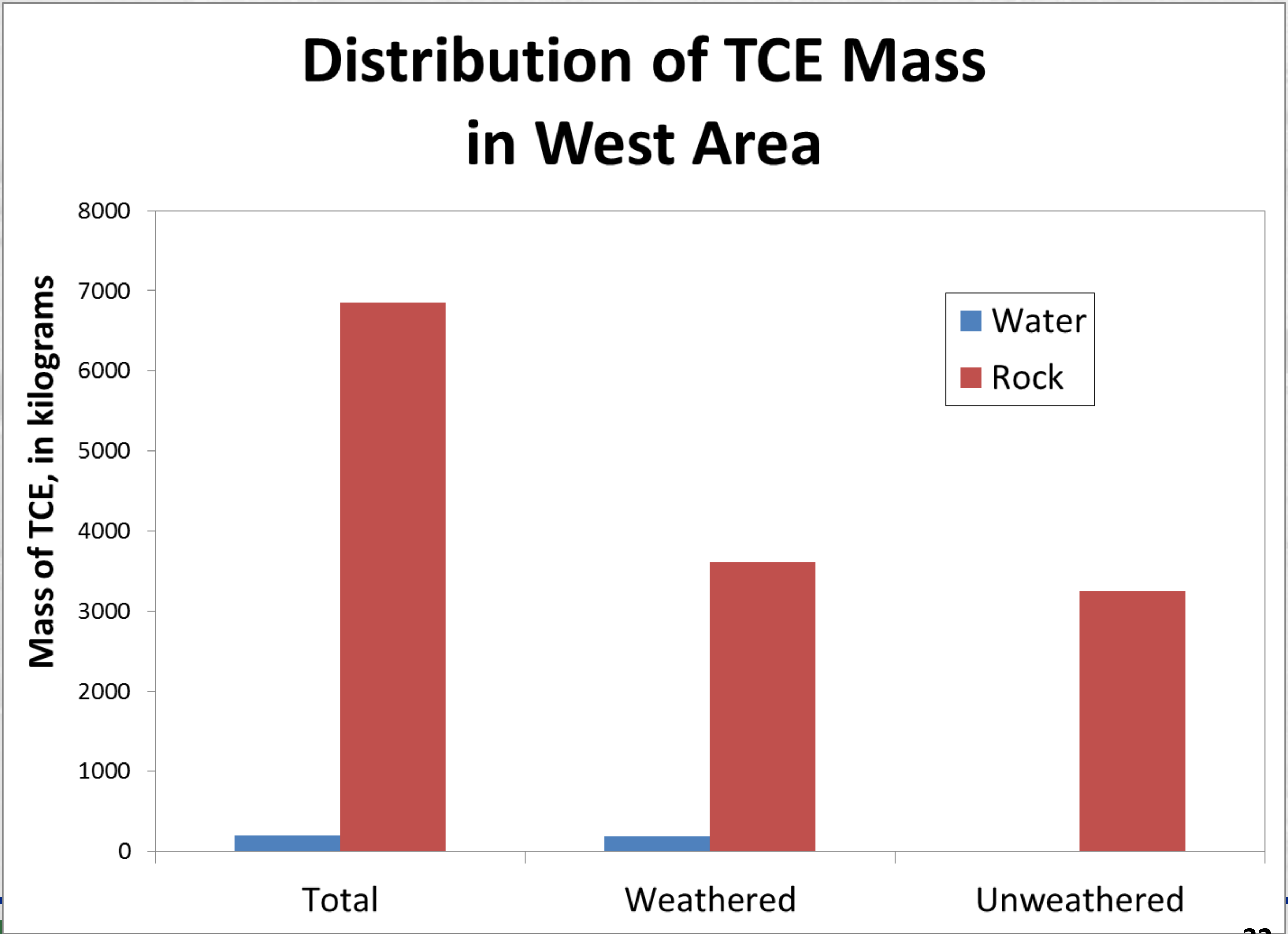


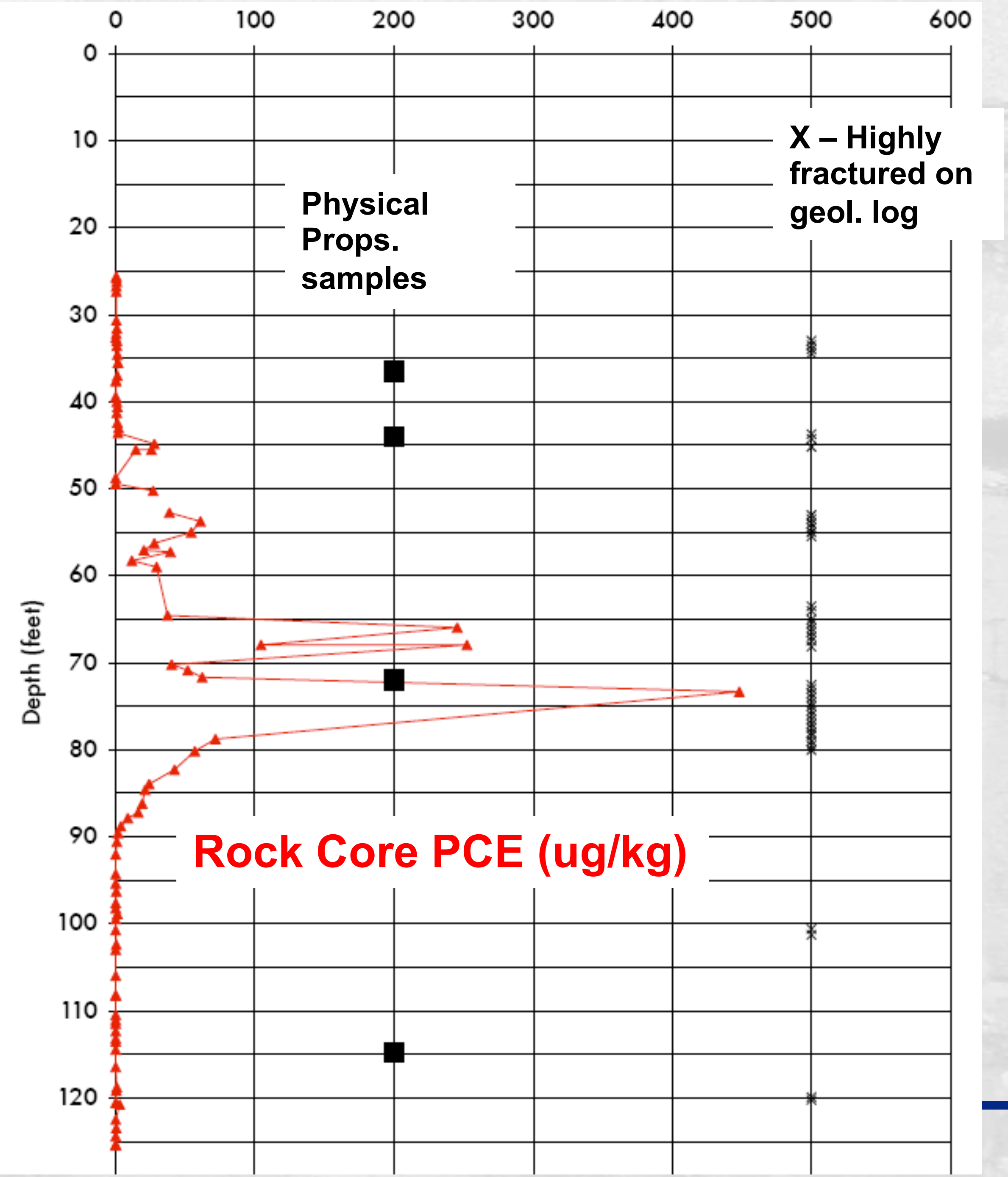
TCE & DCE in 3 Coreholes

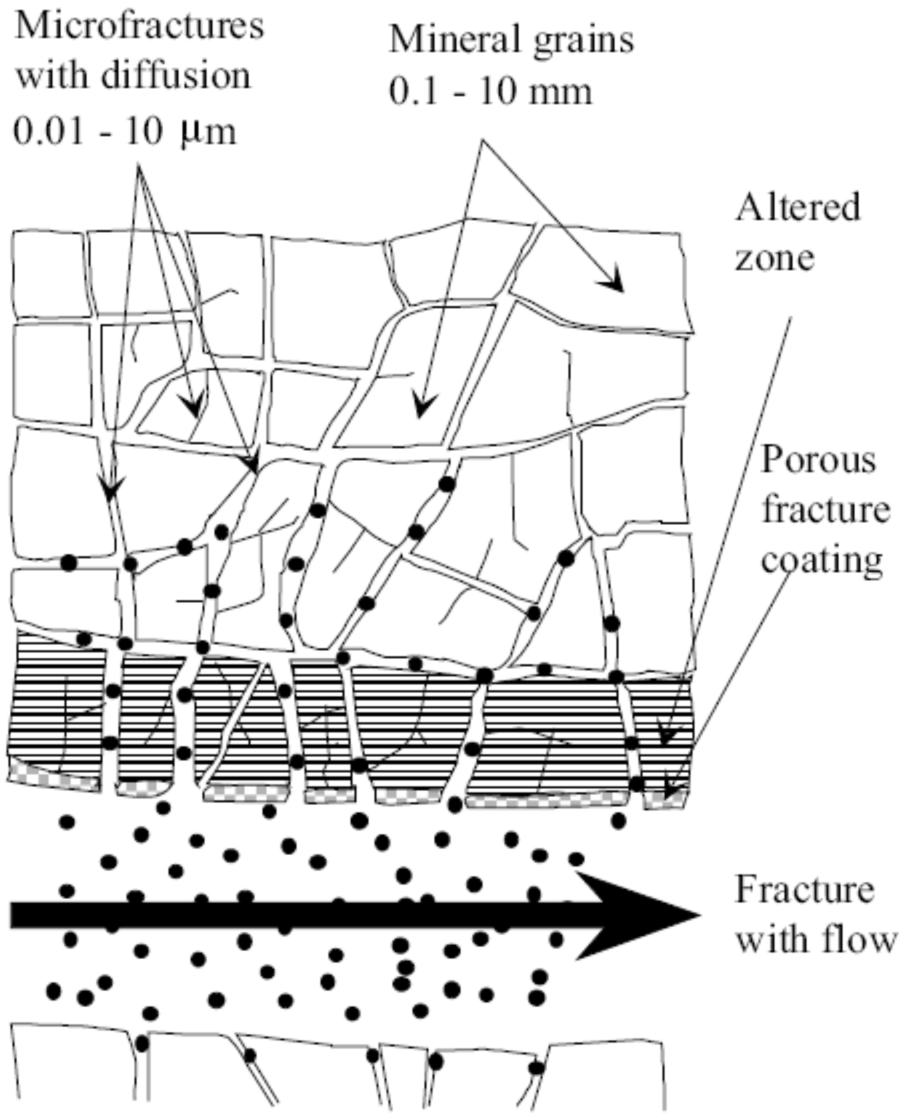
(Goode and others 2014)


Distribution of TCE Mass
in West Area
Mass of TCE, in kilograms
0
1000
2000
3000
4000
5000
6000
7000
8000
Water
Rock
Total
Weathered
Unweathered

- CVOCs in Crystalline Rock
- Shenandoah Road Groundwater Contamination Superfund Site, East Fishkill, NY

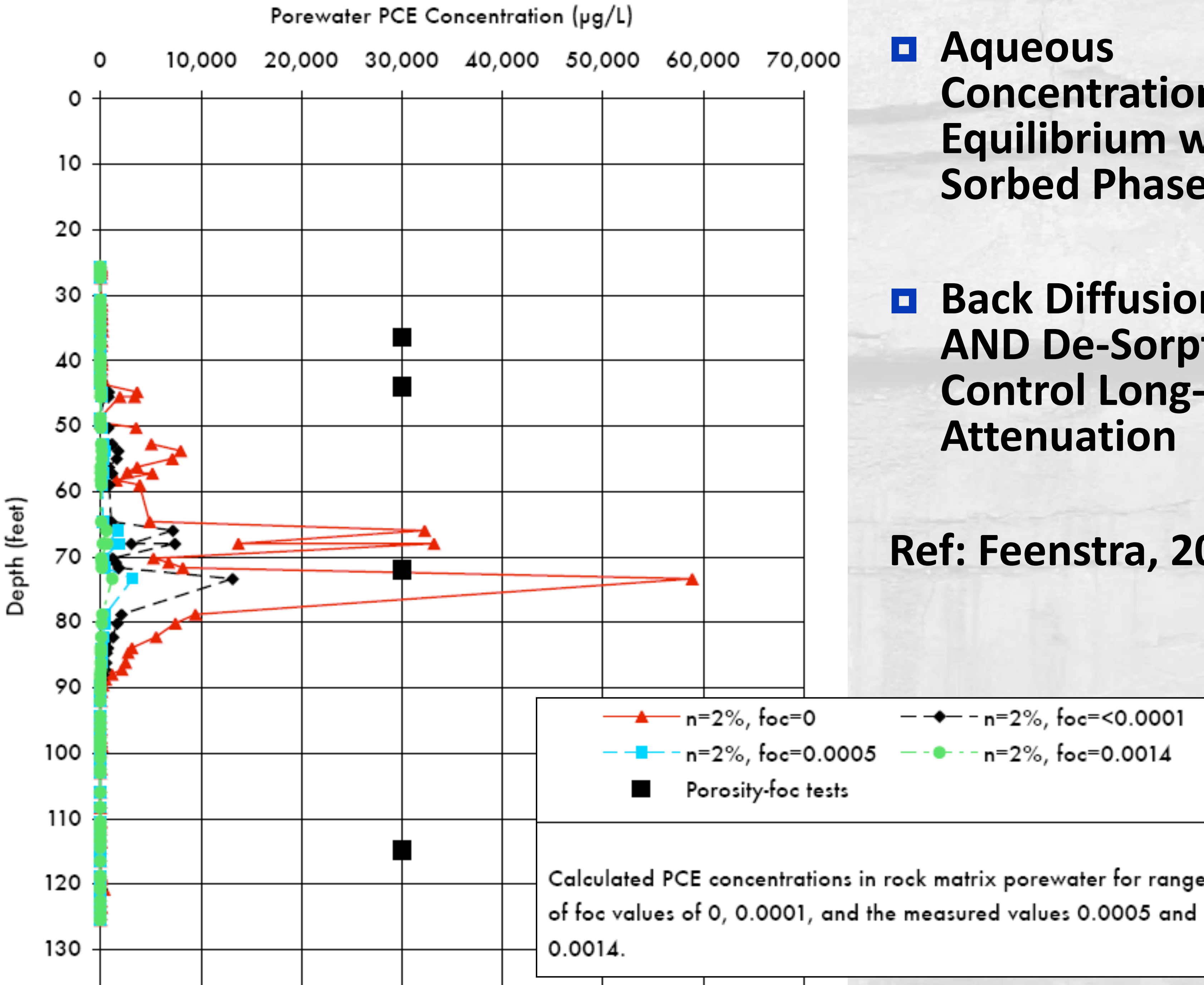
Ref: Feenstra, 2012





Heterogeneous structure of the crystalline rock matrix (Rasilainen 1997).

Rasilainen, K. (1997). Matrix Diffusion Model, In SItu Tests Using Natural Analogues.
Ph.D. Thesis, Helsinki University of Technology, Espoo, Finland.



Calculated PCE concentrations in rock matrix porewater for range of foc values of 0, 0.0001, and the measured values 0.0005 and 0.0014.

- **Aqueous Concentrations in Equilibrium with Sorbed Phase**
- **Back Diffusion AND De-Sorption Control Long-Term Attenuation**

Ref: Feenstra, 2012

Commercial Vendor Available

- Parker's Trademarked "CORE^{DFN}" approach licensed to Cascade Environmental (previously to Stone Environmental)
- Stone Environmental and/or Beth Parker's group (now at Guelph U., Canada) have worked on several sites
- Parker and colleagues continue to refine methods
  - E.g. Microwave heated methanol extraction (speeds analysis) & vacuum-sealed crusher (reduces VOC loss prior to extraction)

Take Home

- Long-term CVOCs in groundwater at many fractured-rock sites controlled by gradual release from rocks (diffusion, sorption, etc.)
- Rock Core Sampling for CVOCs
  - Represents pre-drilling distribution (mediates open-hole effects)
  - Synthesis with Other Characterization !!
- Commercial Vendor available
- Becoming more widely applied as part of Superfund program

Stop here.

Following slides included in handouts

Thank You

Pierre Lacombe
Allen Shapiro
Claire Tiedeman
Alex Fiore
Steven Walker
Matt Miller
& others . .

USGS

Toxic Substances Hydrology Program
New Jersey Water Science Center
Hydrologic Research & Development Program
Office of Ground Water
National Assoc. Geoscience Teachers/USGS Intern Program

Office of Superfund Remediation and Technology Innovation
Region 3

Naval Facilities Engineering Command

Watermark

Geosyntec

SERDP
DOD • EPA • DOE

ECOR Solutions, Inc.

References

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Sloto, R. A., 2002, Hydrogeological Investigation at Site 5, Willow Grove Naval Air Station/Joint Reserve Base, Horsham Township, Montgomery County, Pa., *USGS WRIR Report* 01-4263, 37 p.