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The Retention and Release of Groundwater Contaminants in Fractured Rock and Other Dual-Porosity Media by Matrix Diffusion and "Effective" Matrix Diffusion

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Acknowledgements:

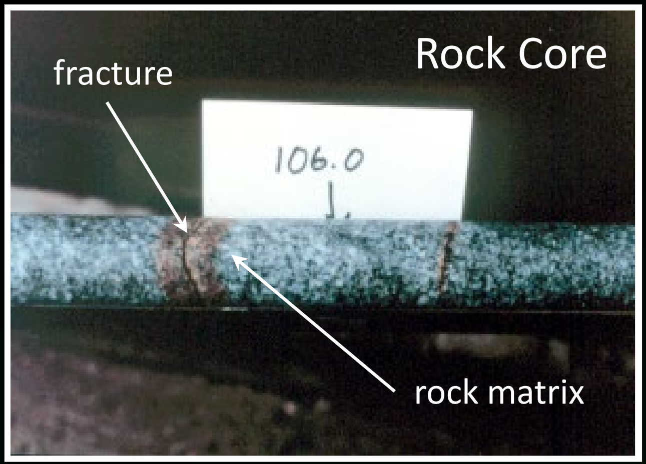
U.S. Geological Survey Toxic Substances Hydrology Program

SERDP DOD • EPA • DOE

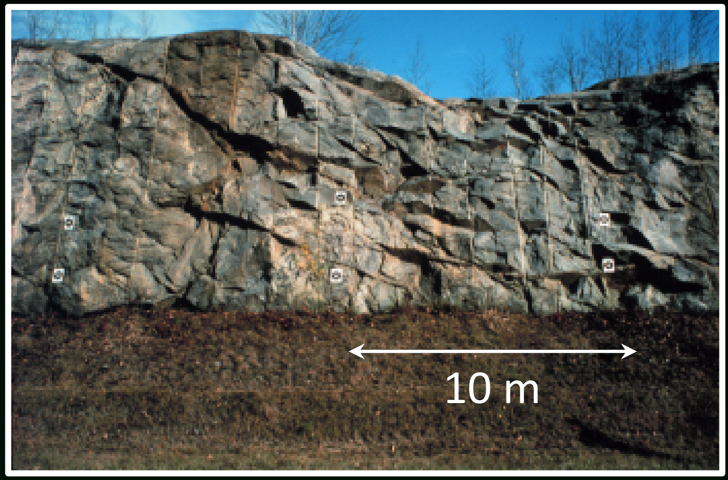
ESTCP

UNITED STATES NAVY

Hierarchy of void space



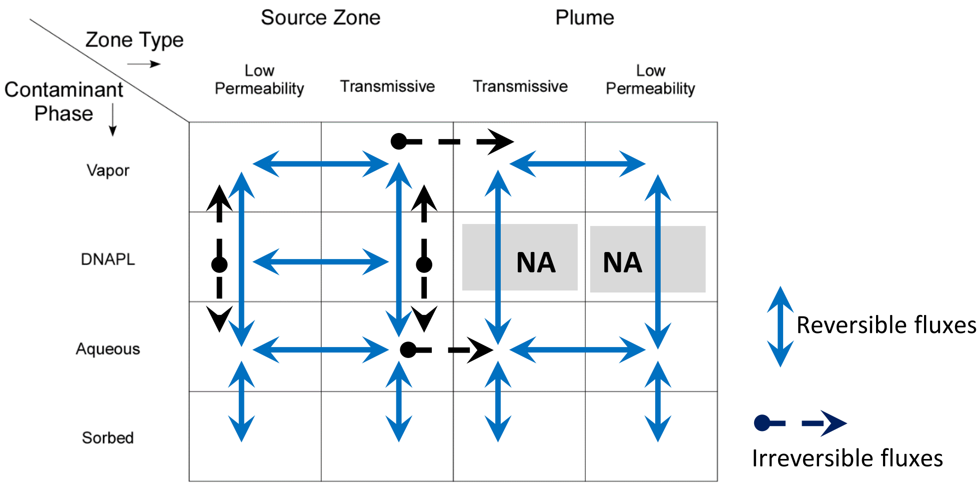
Fractured Rock



Shapiro et al., 2007

Organic Contaminants

14 - Compartment Model and Contaminant Fluxes between Compartments



(modified from Sale et al., 2008; Sale and Newell, 2011; ITRC 2011)

Low-permeability (flow-limited) regions of aquifer:

- Do not contribute to volumetric flow
- Act as reservoirs for contaminant storage
- Mass fluxes into and out of low-permeability regions defined via diffusive exchange with more permeable aquifer materials

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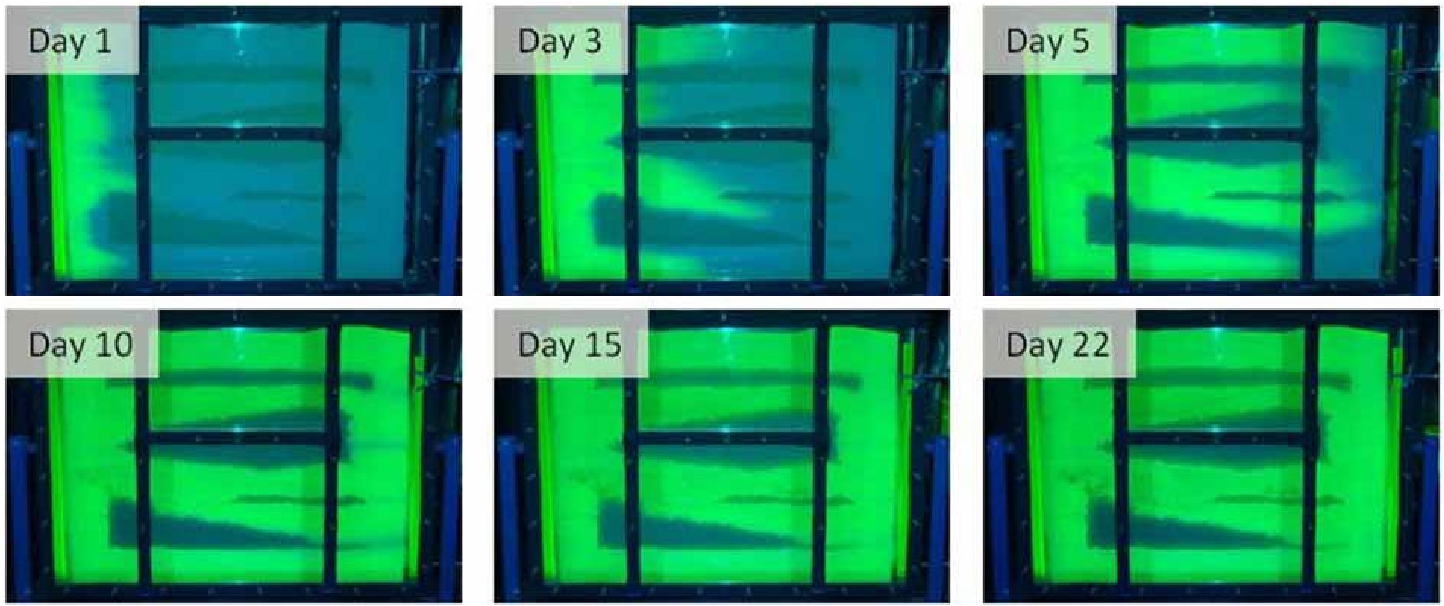
Flow-Limited Regions of an Aquifer

- *Low permeability material may not be significant with respect to volumetric groundwater flow. . .*
- *During contaminant "loading", dye diffuses from permeable pathways to low-permeability materials due to concentration gradient*
- *During "flushing", dye diffuses from low-permeability materials to permeable pathways due to concentration gradient*

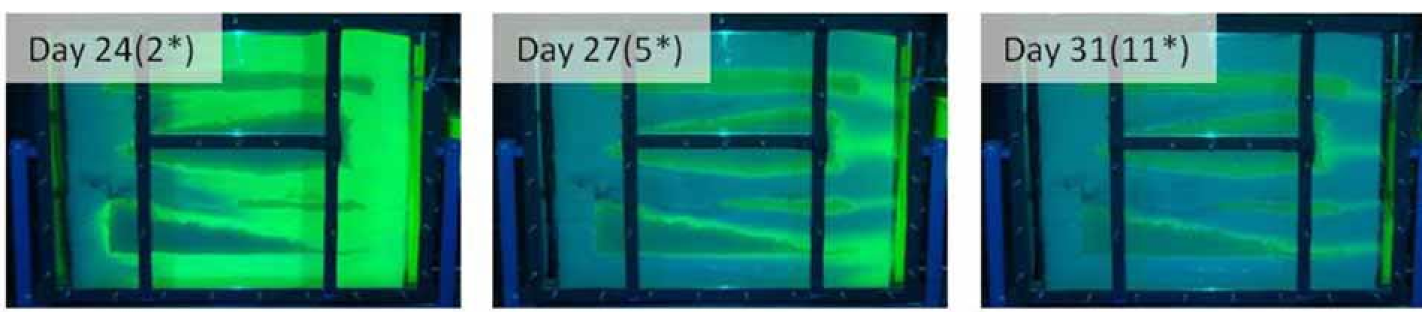
❑ Low-permeability material embedded in a permeable sand

Dye injection. . .

from Doner and Sale, Colorado State University



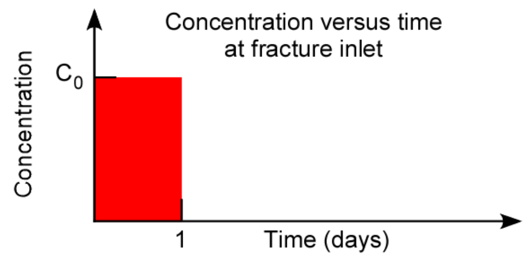
Flushing. . .

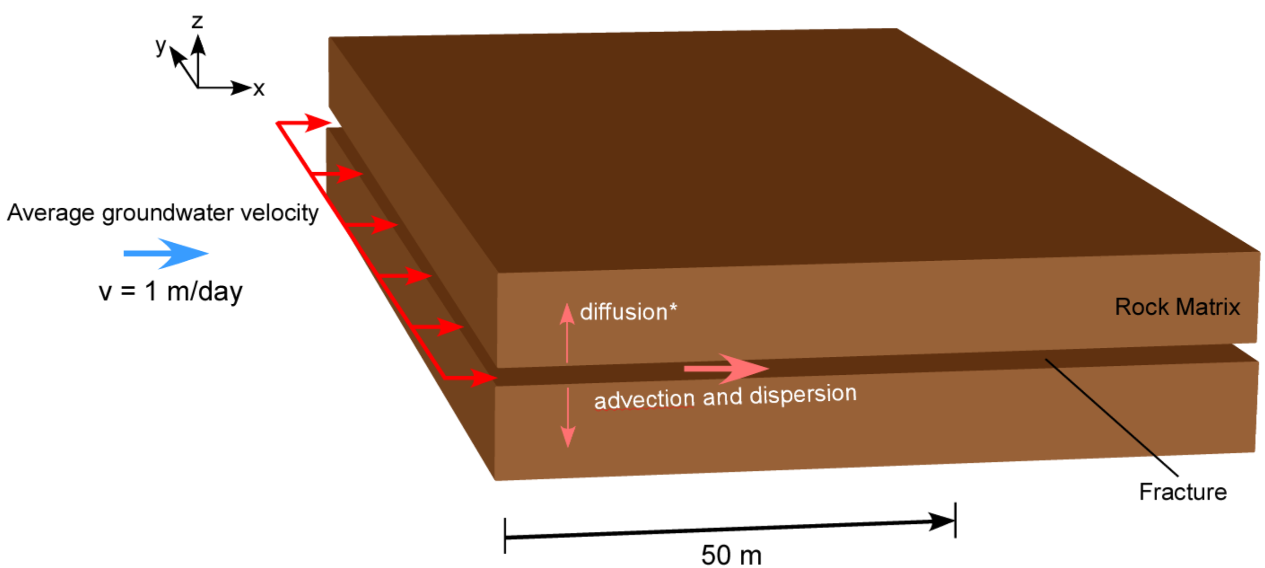


(* denotes days since flushing started)

Matrix Diffusion in Fractured Rock: Contaminant Retention and Release

Example of chemical transport and matrix diffusion in a single fracture. . .





Dispersion: $D = \alpha_L |v|$

Matrix diffusion: $D_m = n \gamma D_w$

*direction of diffusion depends on the local concentration gradient in the z-direction

Longitudinal dispersivity: α_L

Matrix porosity: n

Matrix formation factor: γ

Free water diffusion: D_w

Shapiro et al., 2007

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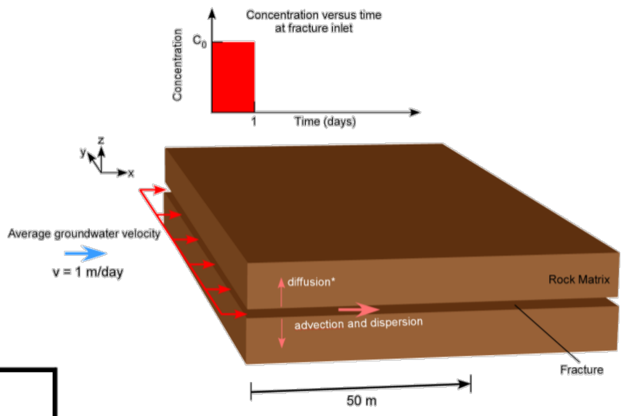
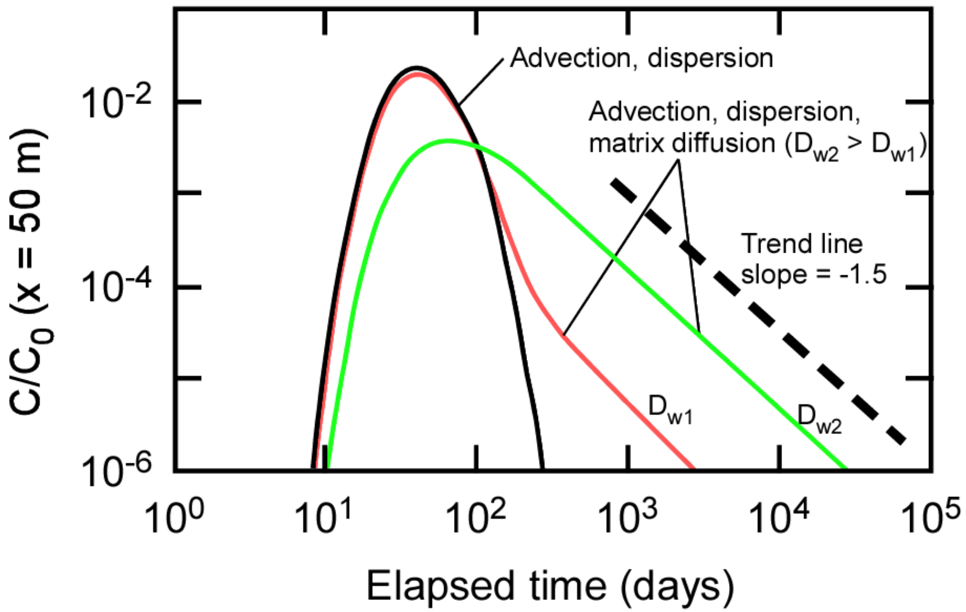
Matrix Diffusion in Fractured Rock: Contaminant Retention and Release

Example of chemical transport and matrix diffusion in a single fracture. . .

Chemical response in the fracture (50 m downgradient). . .





Dispersion: $D = \alpha_L \, |v|$

Matrix Diffusion: $D_m = n \, \gamma \, D_w$

Longitudinal dispersivity: α_L

Matrix porosity: n

Matrix formation factor: γ

Free-water diffusion: D_{w1}, D_{w2}

Shapiro et al., 2007

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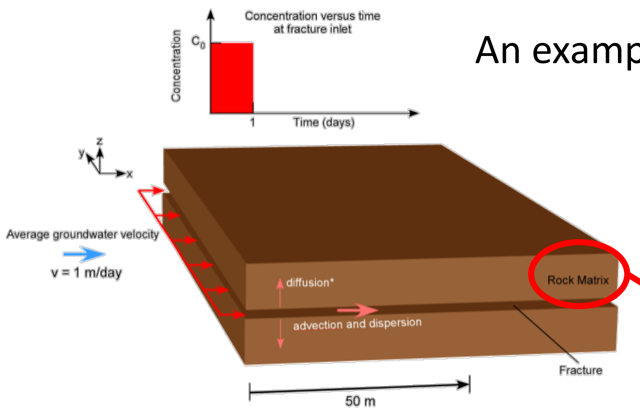
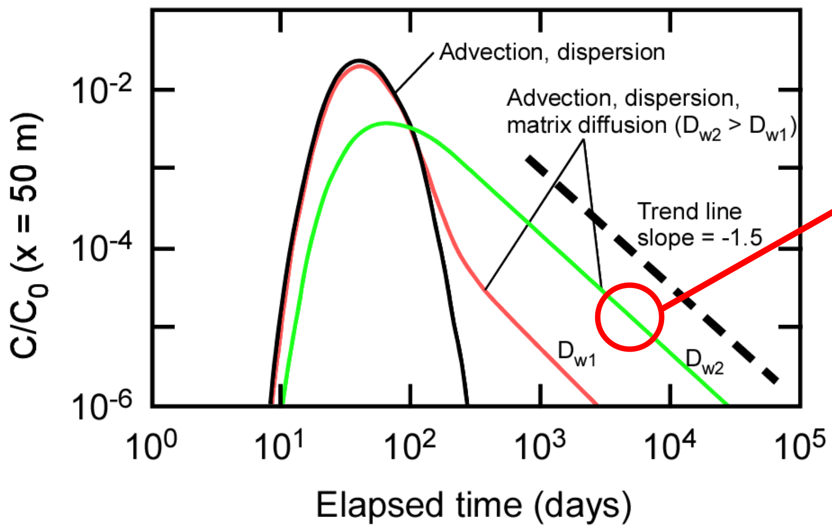
Matrix Diffusion in Fractured Rock: A Blessing or a Curse ?

The "curse" of matrix diffusion. . .

An example: Pulse injection and monitoring 50 m downgradient





<u>the curse</u>. . .retention of contaminants in flow limited regions of the aquifer. .

<u>limiting access to remediation amendments</u>

<u>slow release of contaminants to permeable pathways yields a long-term contaminant source</u>

Shapiro et al., 2007

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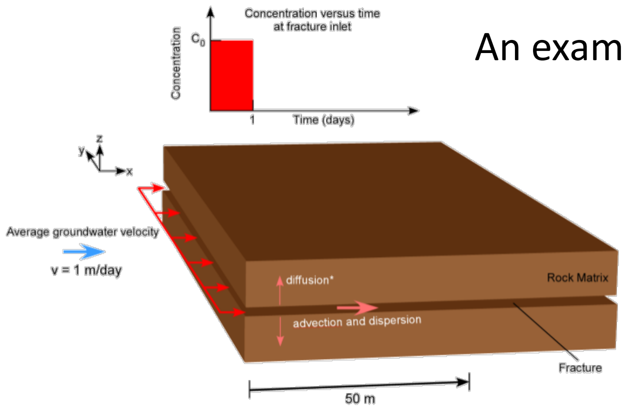
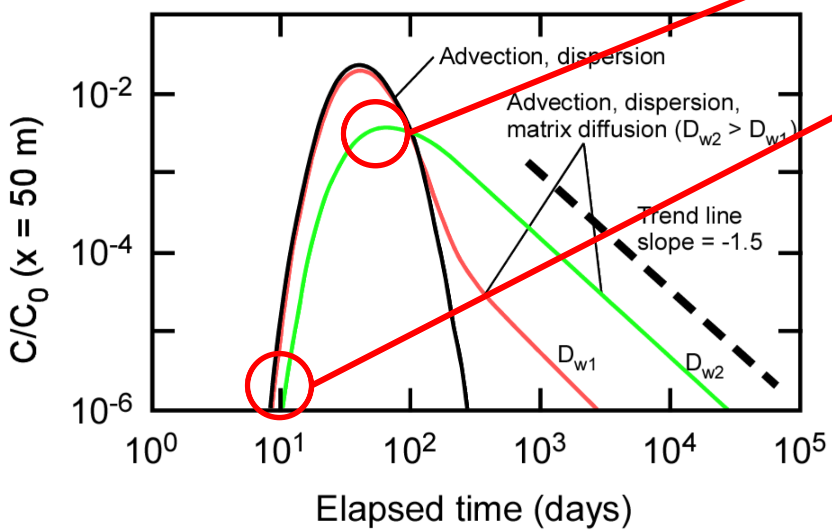
Matrix Diffusion in Fractured Rock: A Blessing or a Curse ?

The “blessing” of matrix diffusion. . .



An example: Pulse injection and monitoring 50 m downgradient



the blessing. . .retention of contaminants in flow limited regions of the aquifer. . .

attenuating the downgradient concentrations. . .

delaying downgradient migration of contaminants. .

. . .matrix diffusion is the rationale for the licensing of selected geologic environments as sites for waste isolation (e.g., WIPP site, New Mexico, USA)

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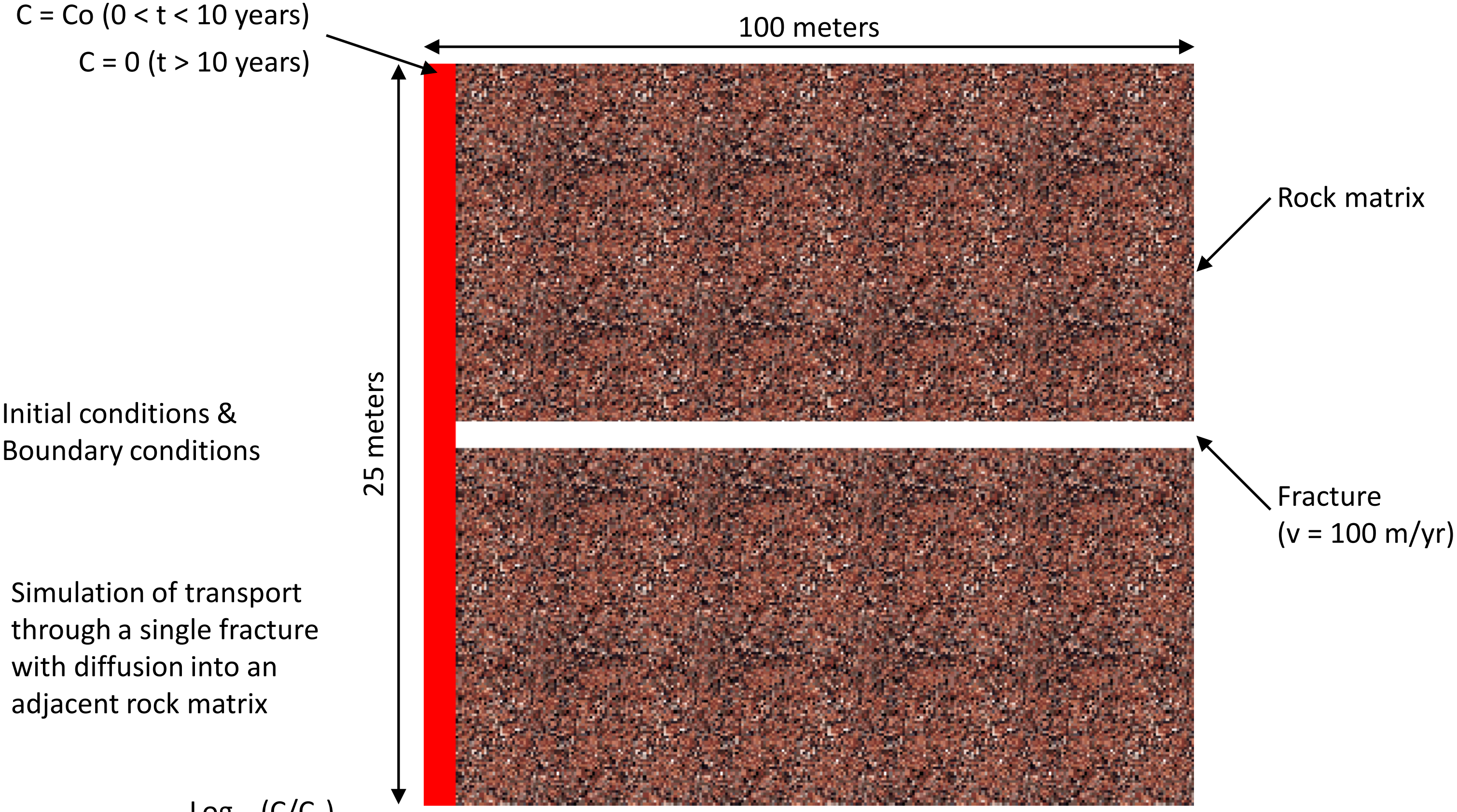
Shapiro et al., 2007

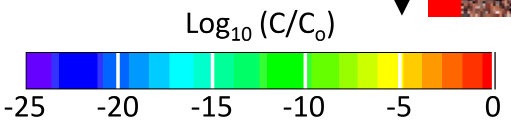
Matrix Diffusion in Fractured Rock: Why do we see extended residence times?

Although fractures are highly permeable groundwater pathways, contaminants introduced into fractures have extended residence times. . .



Initial conditions & Boundary conditions

Simulation of transport through a single fracture with diffusion into an adjacent rock matrix



Vertical exaggeration x 4

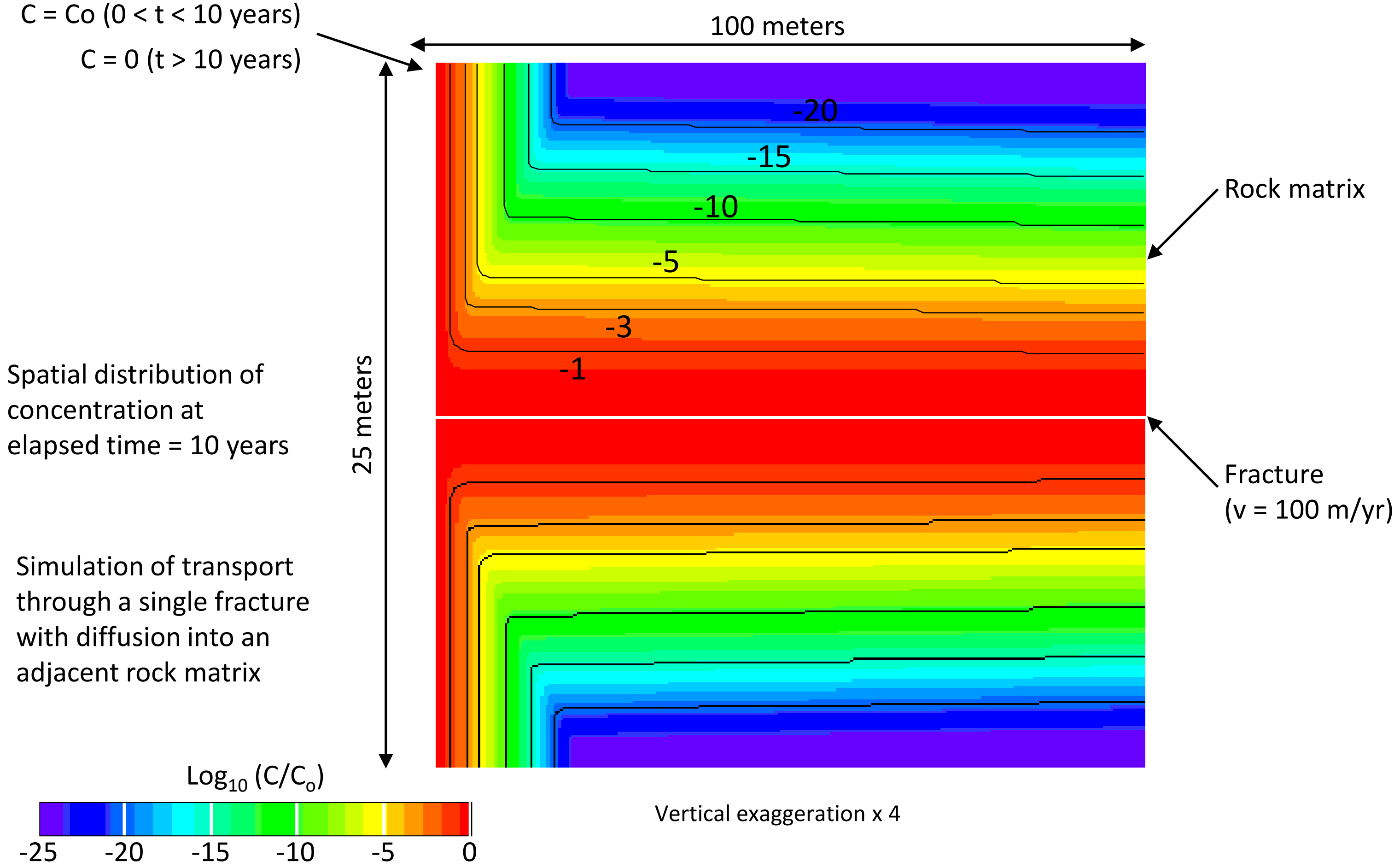
Matrix Diffusion in Fractured Rock: Why do we see extended residence times?

Although fractures are highly permeable groundwater pathways, contaminants introduced into fractures have extended residence times. . .

C = Co (0 < t < 10 years)
C = 0 (t > 10 years)

Spatial distribution of concentration at elapsed time = 10 years

Simulation of transport through a single fracture with diffusion into an adjacent rock matrix



Matrix Diffusion in Fractured Rock: Why do we see extended residence times?

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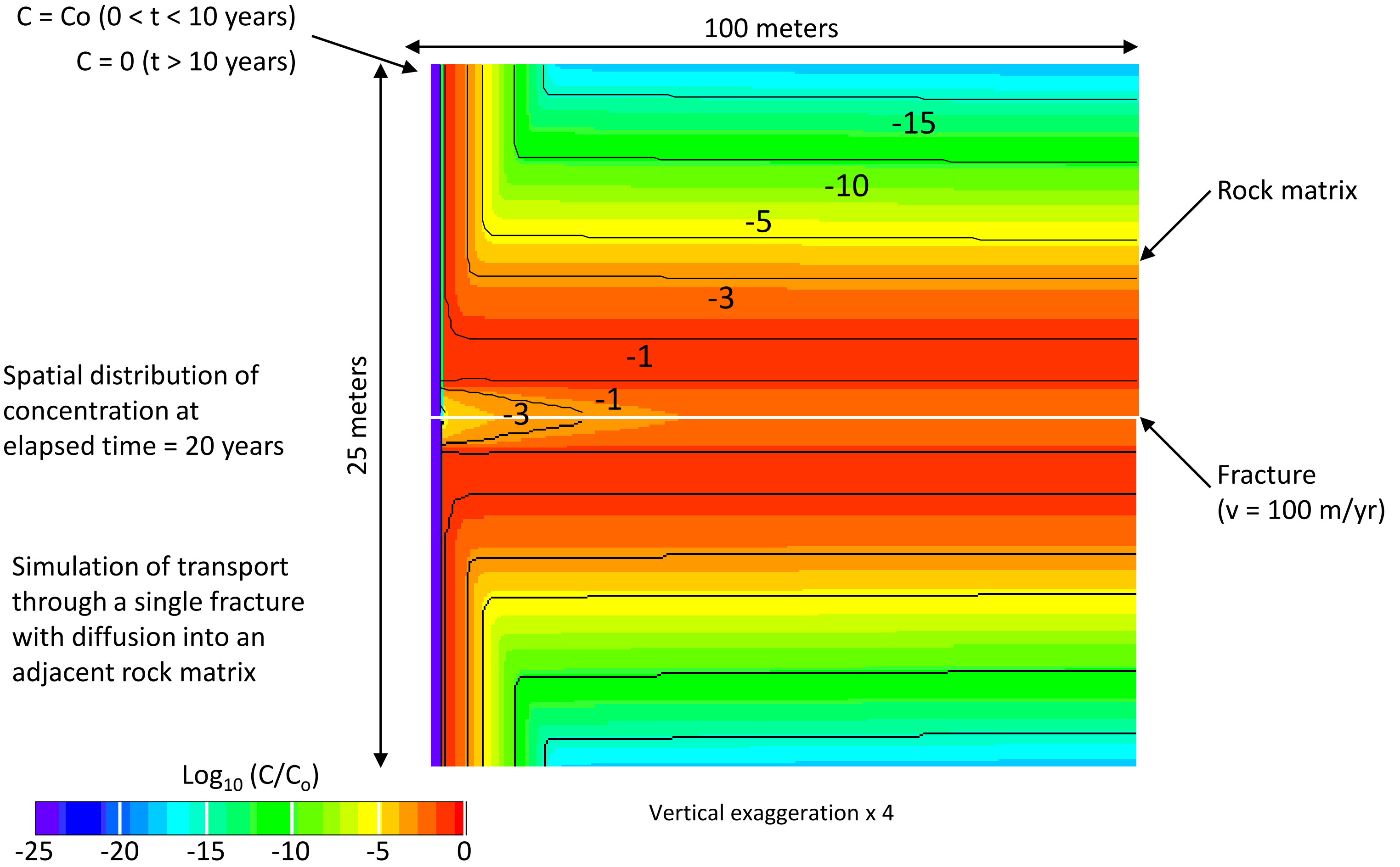

Spatial distribution of concentration at elapsed time = 20 years

Simulation of transport through a single fracture with diffusion into an adjacent rock matrix

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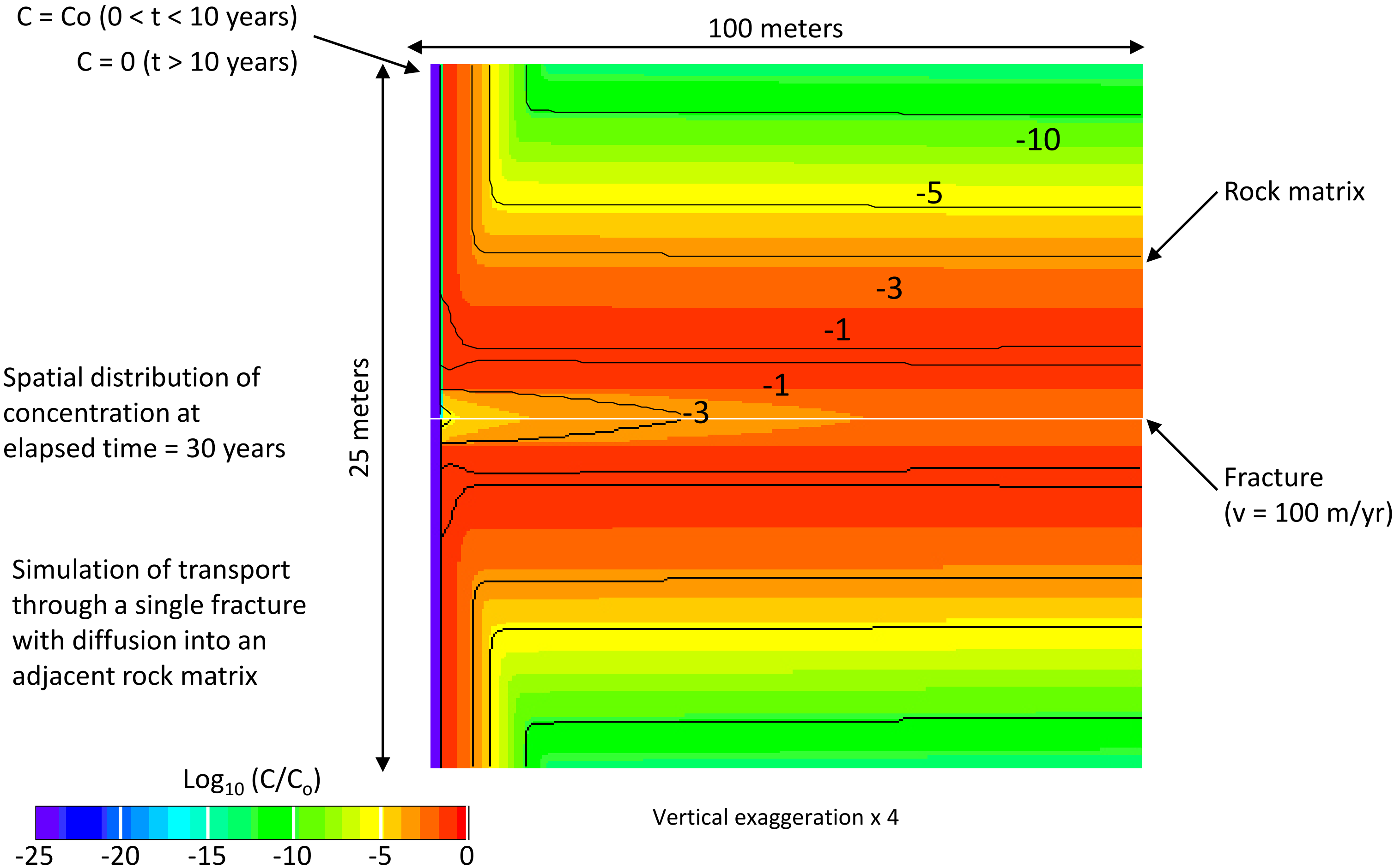
Matrix Diffusion in Fractured Rock: Why do we see extended residence times?

Although fractures are highly permeable groundwater pathways, contaminants introduced into fractures have extended residence times. . .



Spatial distribution of concentration at elapsed time = 30 years

Simulation of transport through a single fracture with diffusion into an adjacent rock matrix

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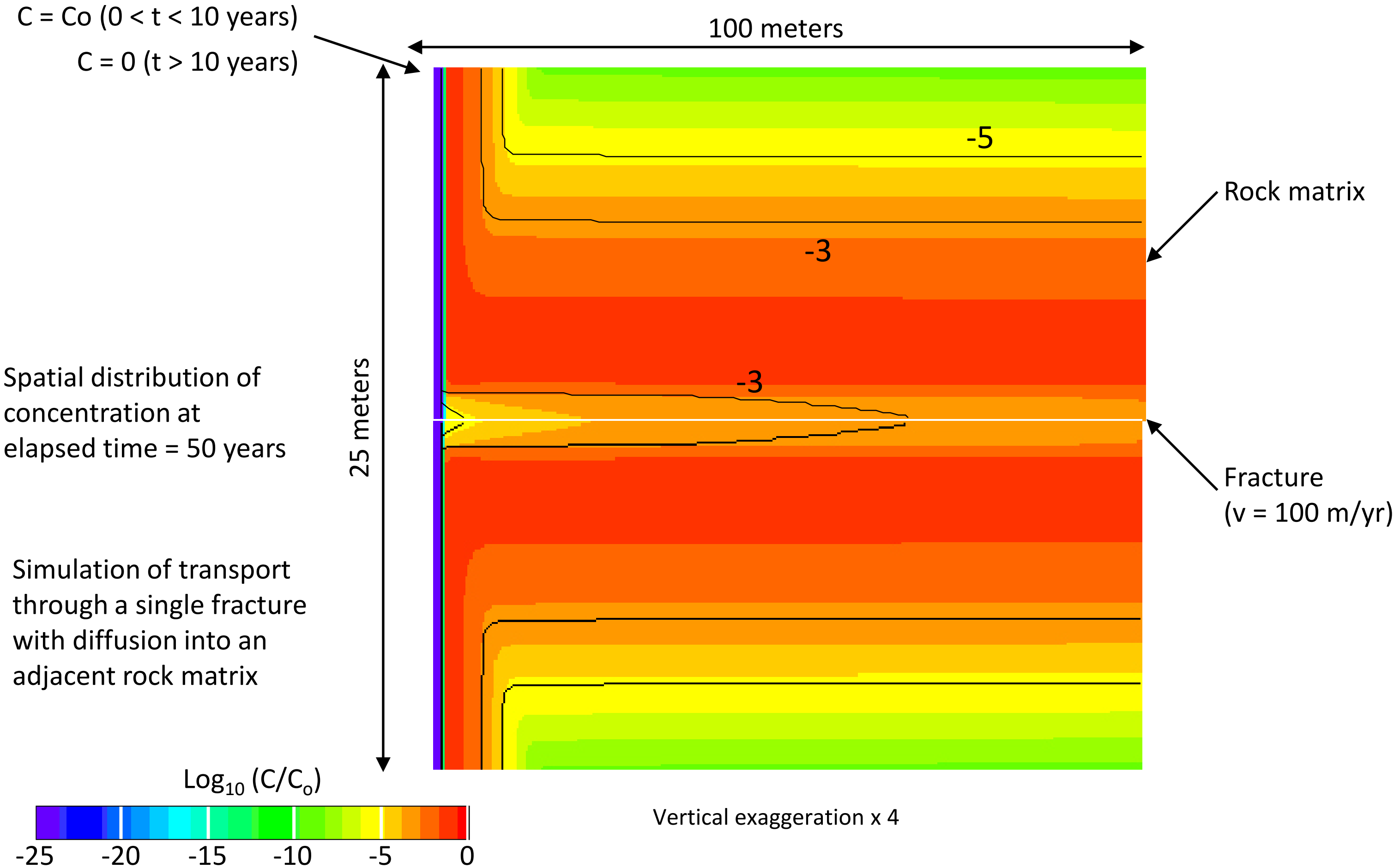
Matrix Diffusion in Fractured Rock: Why do we see extended residence times?

Although fractures are highly permeable groundwater pathways, contaminants introduced into fractures have extended residence times. . .

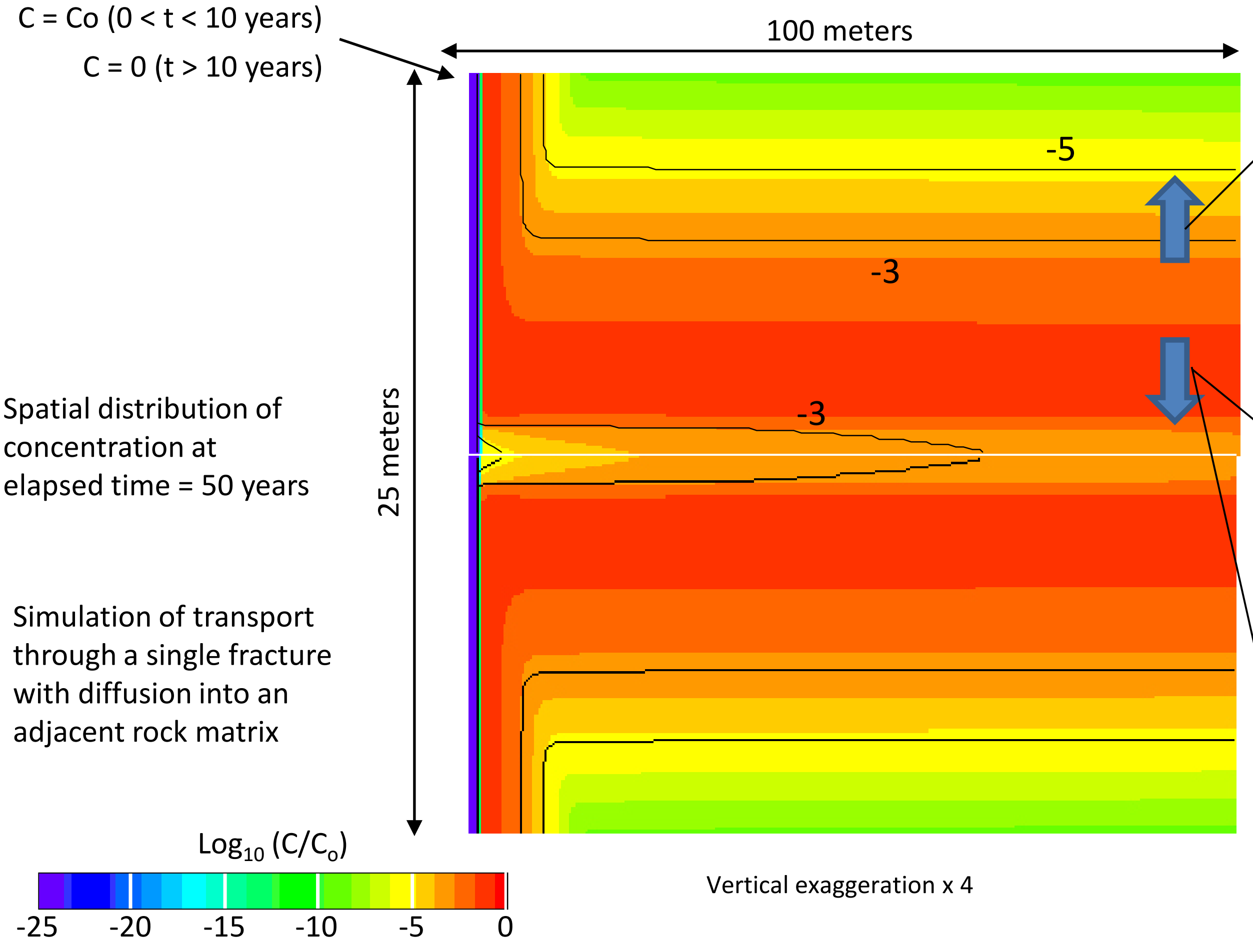


Matrix Diffusion in Fractured Rock: Why do we see extended residence times?

Although fractures are highly permeable groundwater pathways, contaminants introduced into fractures have extended residence times. . .

Spatial distribution of concentration at elapsed time = 50 years

Simulation of transport through a single fracture with diffusion into an adjacent rock matrix



Concentration gradient still driving contaminant mass away from the fracture. .

Concentration gradient driving contaminant mass toward the fracture. . ***. "back diffusion".*** . .

Over time, concentration gradient toward fracture decreases. . . reducing mass flux to the fracture.

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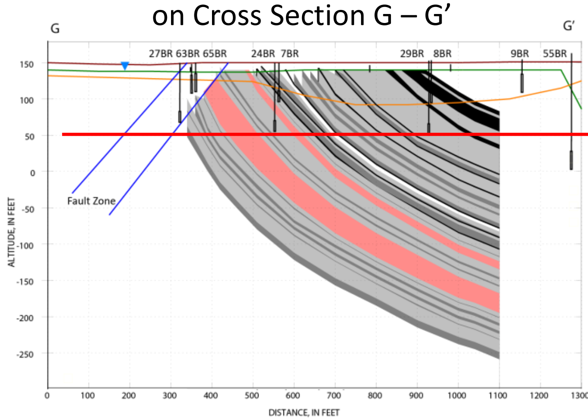
Characterizing contaminant mass in the subsurface

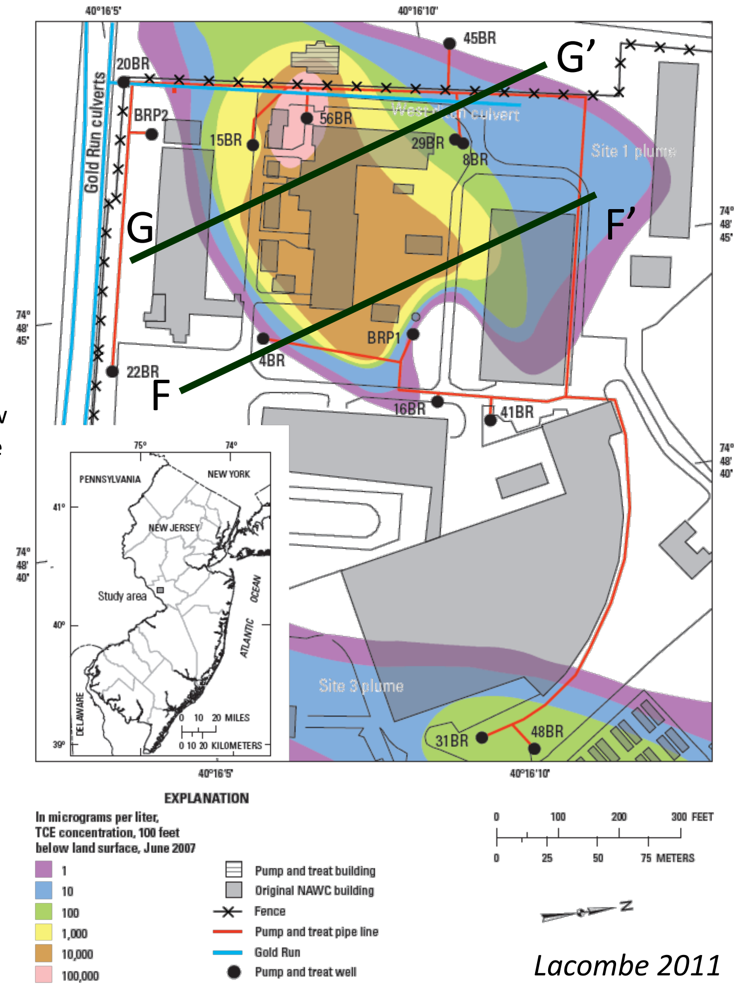
Naval Air Warfare Center, West Trenton, NJ

Interpretation of contaminant mass from ***mobile groundwater*** . . .water samples extracted from ***permeable fractures*** intersecting monitoring intervals (~20 ft sections of borehole)

Mudstone units of the Lockatong Formation on Cross Section G – G’



Isocontours of TCE concentration at 100 ft below land surface



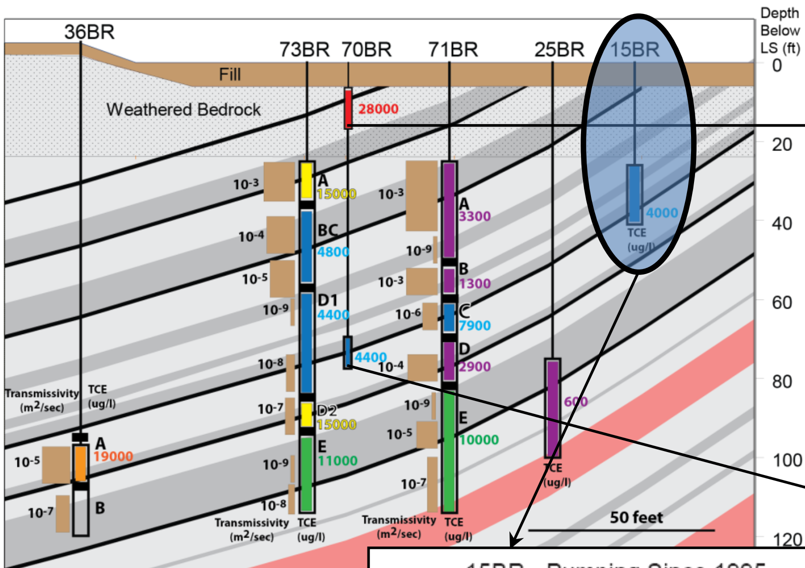
Lacombe 2011

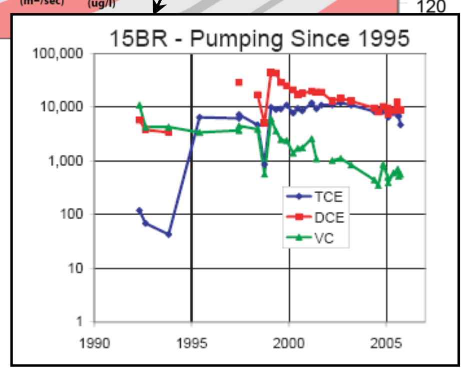
Are these isocontours of aqueous concentrations from fractures a physically meaningful way of characterizing contaminant mass in fractured rock ?

Are they useful in designing remediation strategies ?

Characterizing contaminant mass in the subsurface

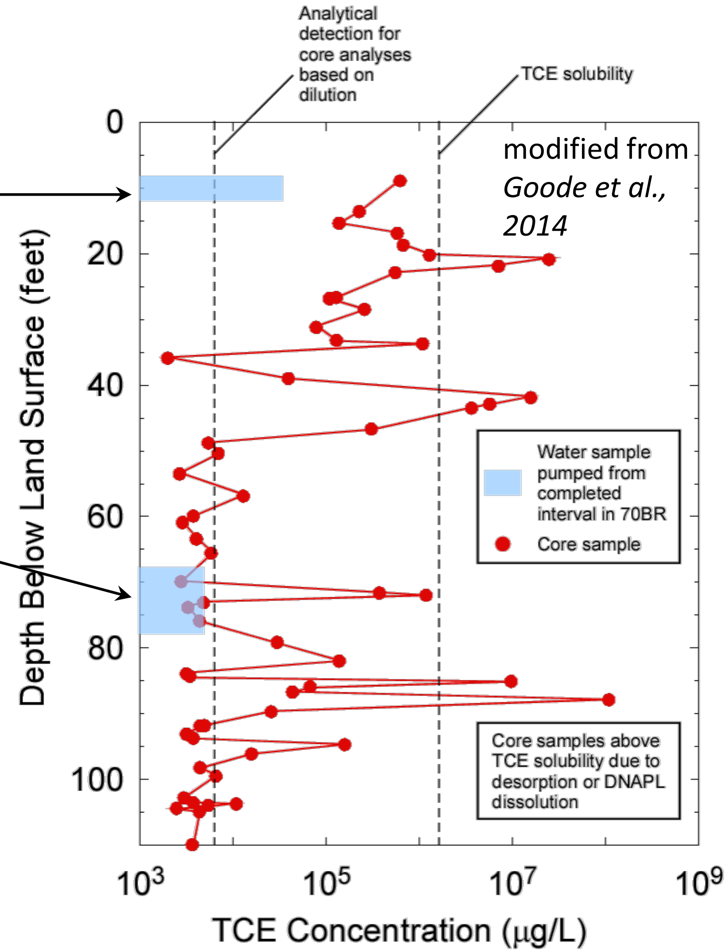
Water samples from mobile groundwater (fractures) do not provide an accurate picture of the contaminant distribution in the subsurface





. . .if pumping was terminated, mass of TCE in rock matrix would likely yield elevated concentrations in mobile groundwater (fractures). . .
“***contaminant rebound***”

TCE in fractures and the rock matrix



Equivalent Aqueous Phase TCE for Core Samples

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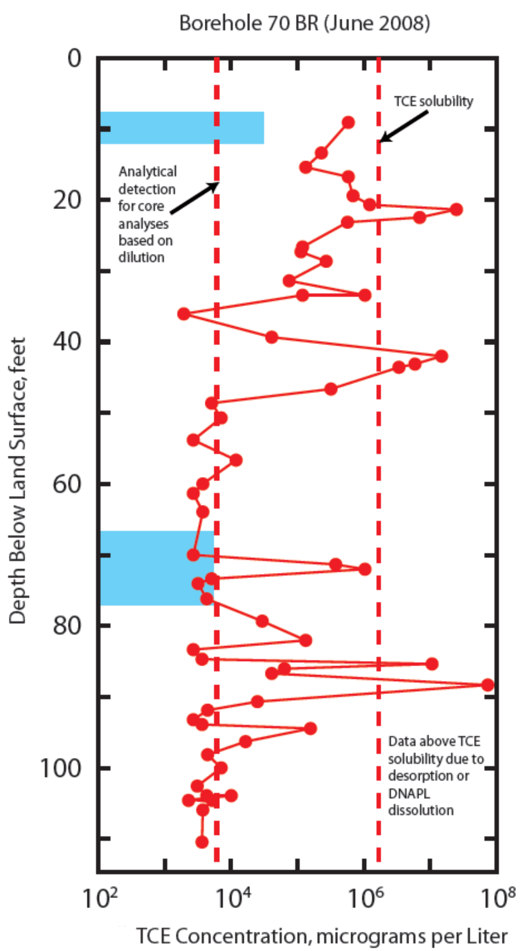
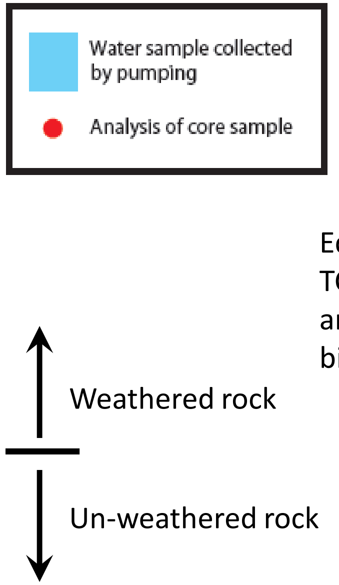
Characterizing contaminant mass in the subsurface



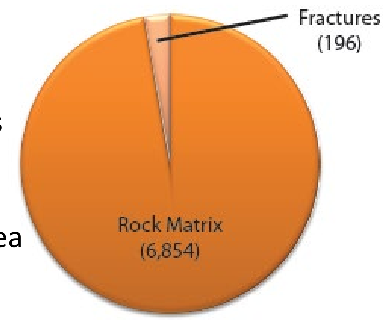
Equivalent Aqueous Phase TCE for Core Samples



modified from *Goode et al., 2014*

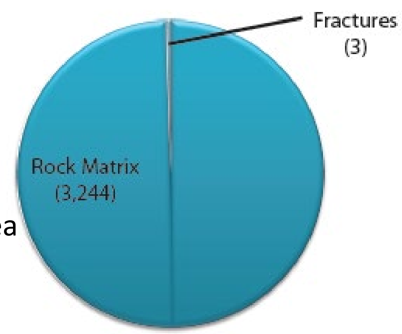
Distribution of organic contaminants between fractures and rock matrix

Equivalent kilograms TCE in fractures and rock matrix in bioaugmentation area



Weathered & Un-weathered Rock

Equivalent kilograms TCE in fractures and rock matrix in bioaugmentation area



Un-weathered Rock

Are water samples from mobile groundwater (fractures) a viable means of assessing contaminant distribution?

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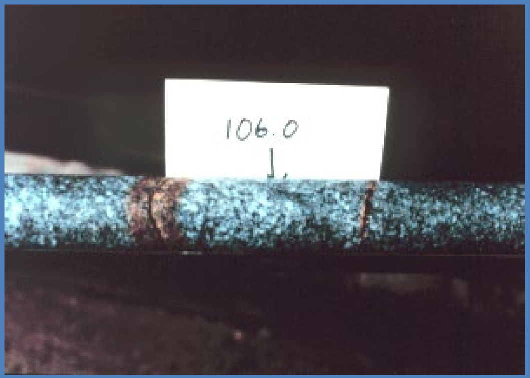
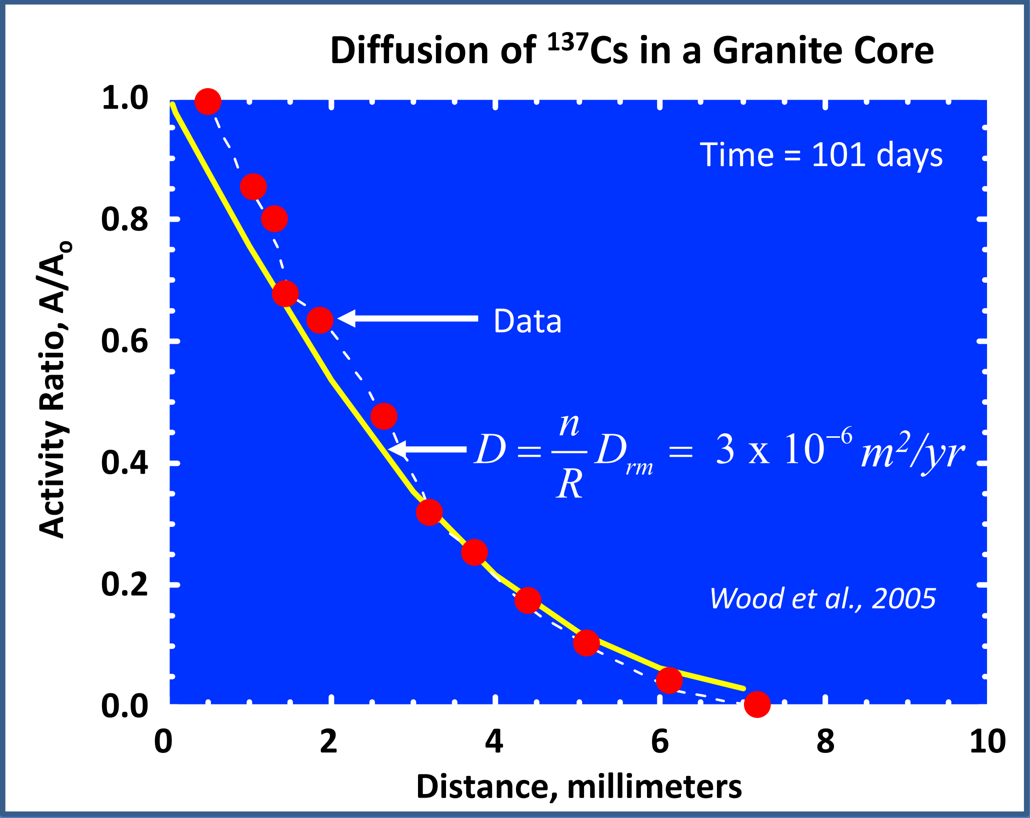
Quantifying Matrix Diffusion – Laboratory Analysis of Rock Core

Diffusion through a rock face



$$J_x = -\frac{n\gamma D_w}{R}\frac{dC}{dx}$$



n – rock matrix porosity
J_x - diffusive mass flux in the x-direction per unit area ($ML^{-2}T^{-1}$)
γ - formation factor (inversely proportional to tortuosity)
D_w – ^{137}Cs free water diffusion coefficient (L^2T^{-1})
$D_{rm} = \gamma D_w$ – rock matrix diffusion coefficient (L^2T^{-1})
R – ^{137}Cs retardation factor
C – aqueous concentration (mass per unit volume, ML^{-3})
x – spatial coordinate (L)
L – units of length; M – units of mass; T – units of time

$$\frac{n}{R}\gamma D_w = \frac{n}{R} D_{rm}$$

Are laboratory interpretations appropriate for field scale characterization?

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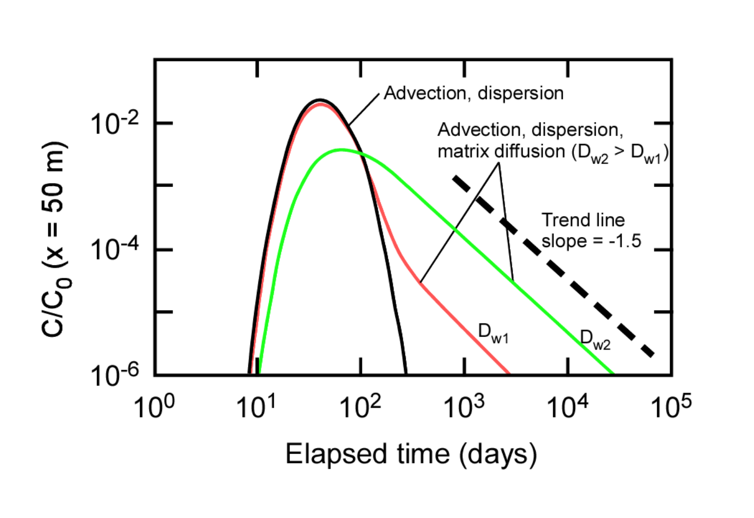
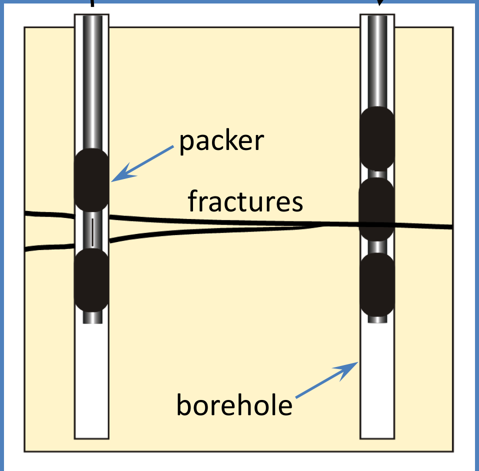
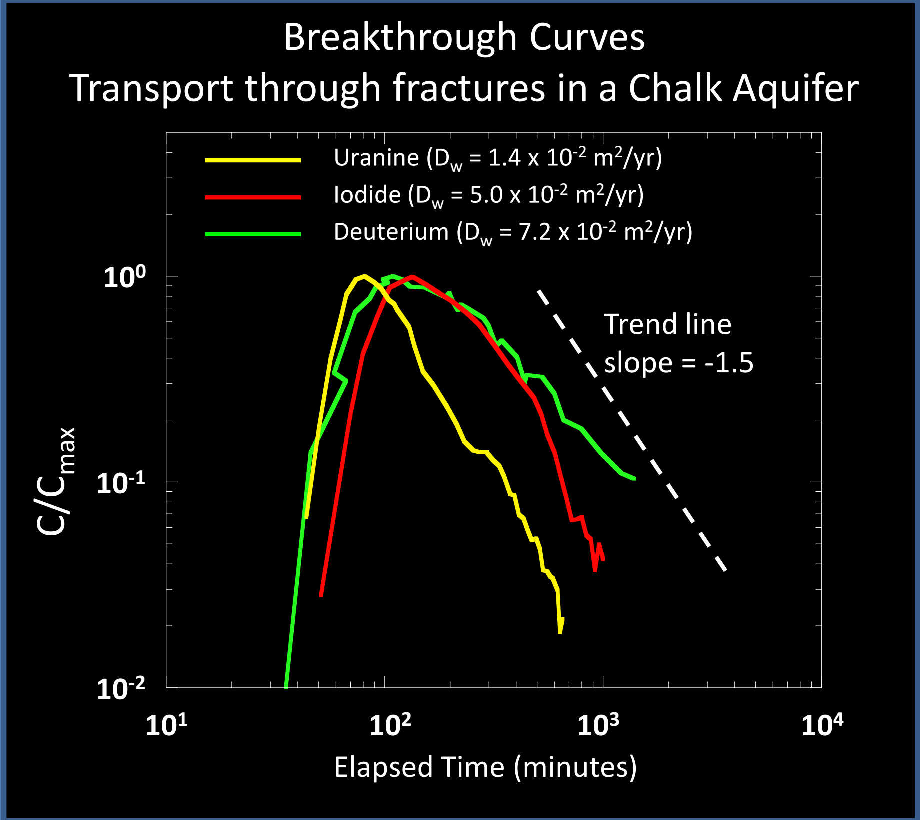
Quantifying Matrix Diffusion – Field Scale Testing (10's of meters)

Simulation – transport in a single fracture





Field Experiment:
Multiple tracers injected with different free water diffusion coefficients, D_w



Chalk Aquifer, Béthune, France, modified from *Garnier et al. 1985*

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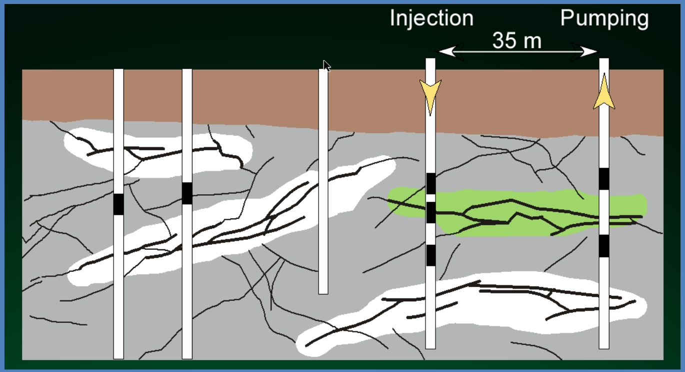
Quantifying Matrix Diffusion – Field Scale Testing (10's of meters)

Tracer Injection **Pumping**

Not all field scale tests support use of laboratory interpretations to characterize matrix diffusion at the field scale. . .

Granite and Schist – Mirror Lake, NH

Multiple tracers injected with different free water diffusion coefficients, D_w

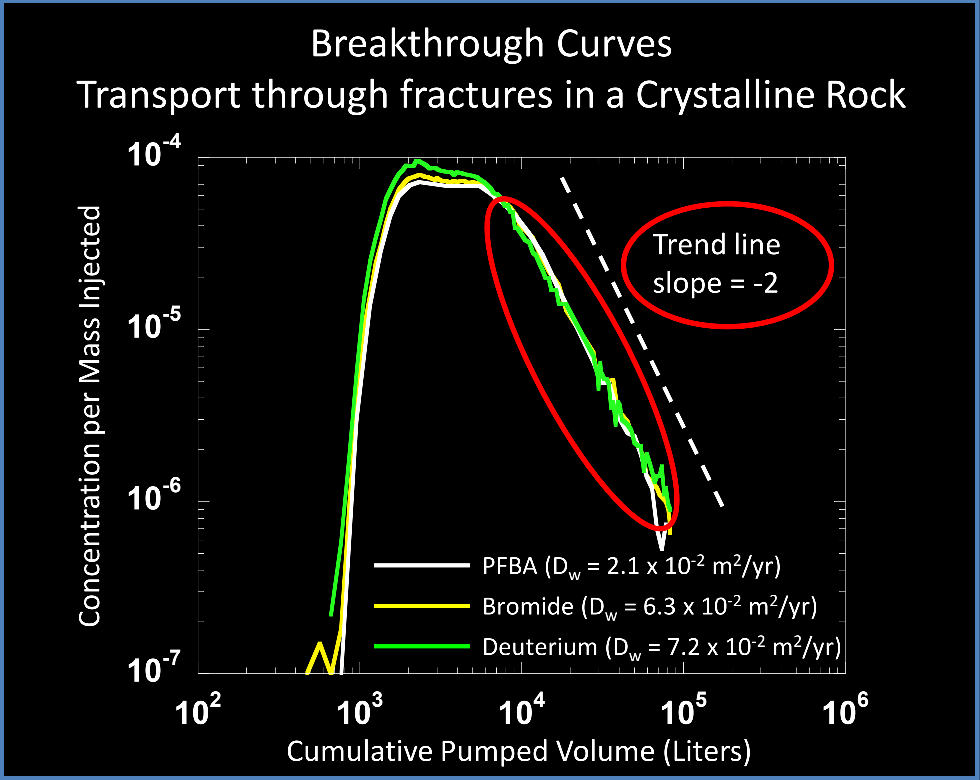


$$D = n\gamma D_w = nD_{rm}$$

However, from interpretation of breakthrough curves:

$$D_{rm} > D_w$$

Is this physically reasonable?



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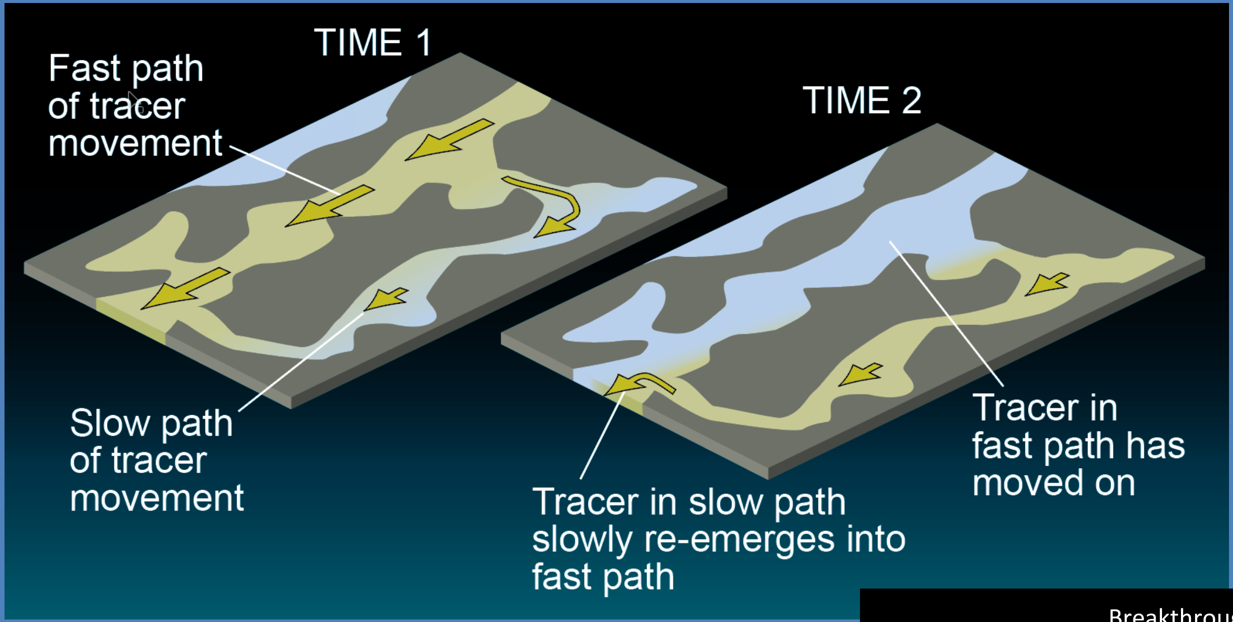
Becker and Shapiro, 2000 *Shapiro et al., 2007*

“Effective” Matrix Diffusion

Diffusion-like tailing ($D_{rm} > D_w$), leading to extended residence times. . .
An artifact of “extreme” variability in fluid advection



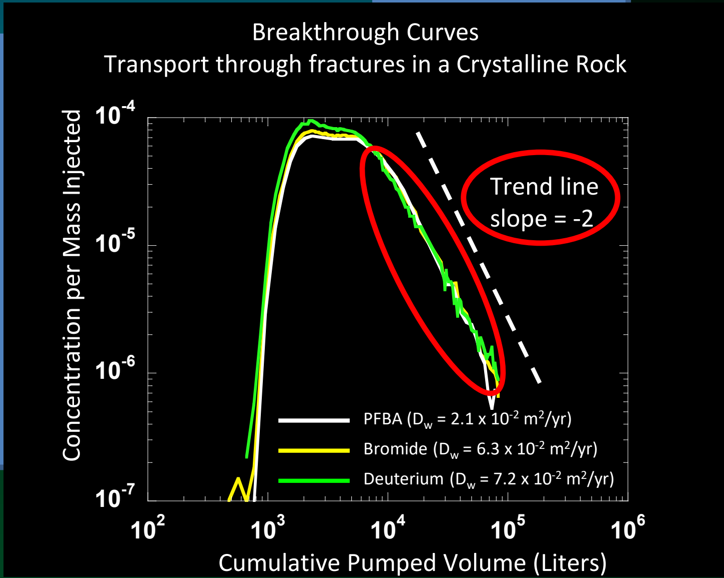
Becker and Shapiro, 2000

Shapiro 2001

Shapiro et al., 2007

Shapiro et al., 2008

- Hydraulic conductivity of fractures varies over more than 6 orders of magnitude
- Large range of velocity is not consistent with the conceptualization of hydrodynamic dispersion
- Slow advection leads to a diffusion-like process – small travel distance over extended period time, similar to diffusion into and out of flow-limited aquifer material



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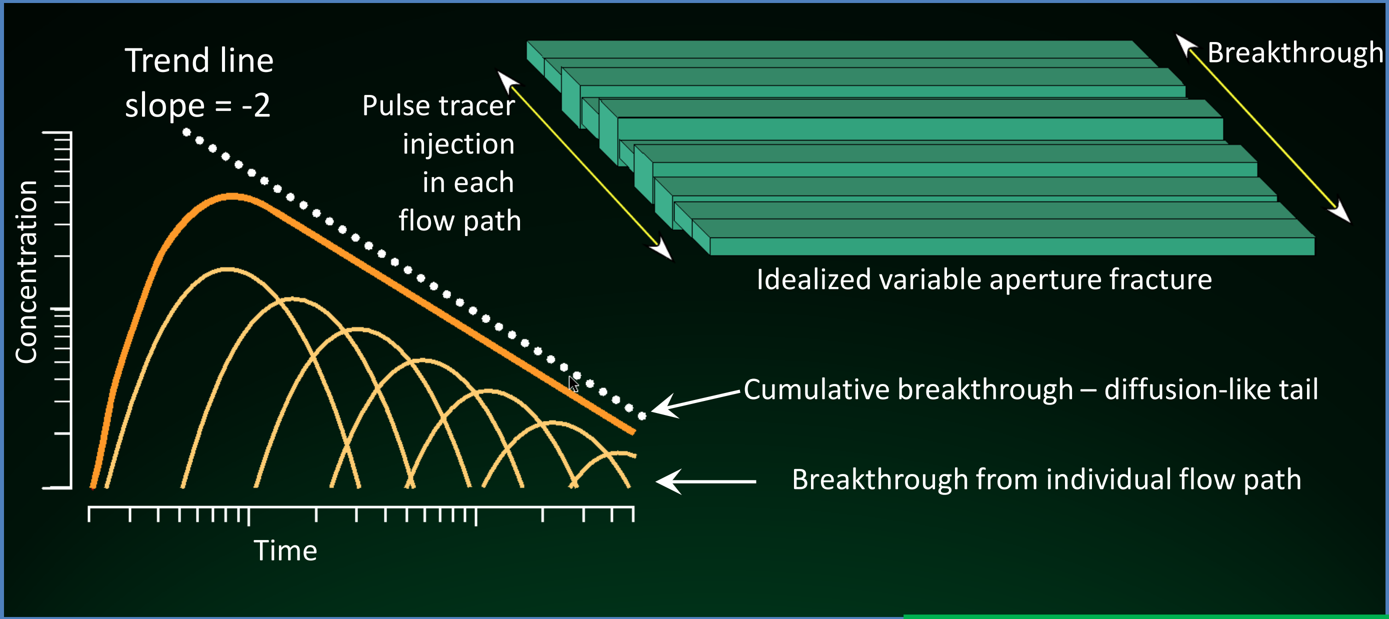
"Effective" Matrix Diffusion



Becker and Shapiro, 2000

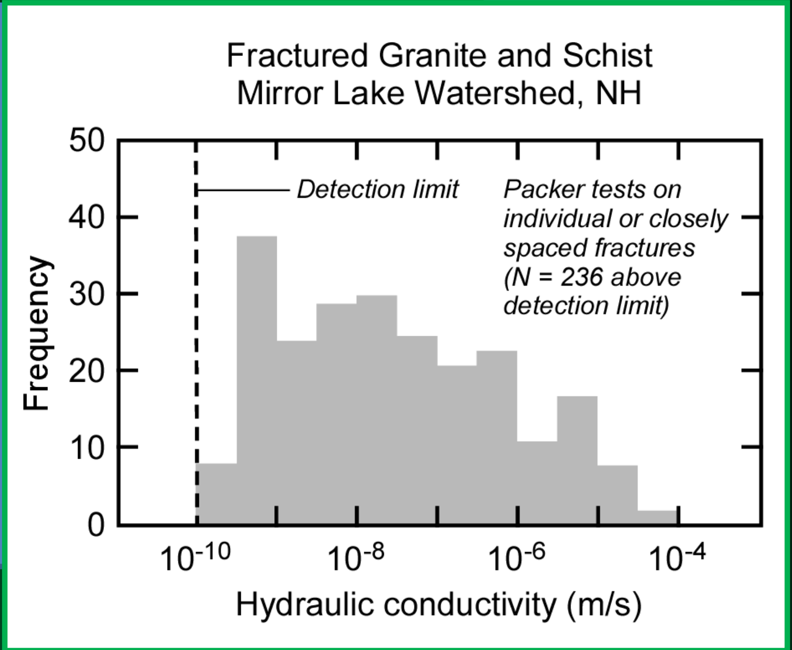
Shapiro 2001

Shapiro et al., 2007

"Effective" diffusion impacts calculations of the longevity of contamination. . .

. . .contaminant storage and release exists not only in the rock matrix. . .

. . .but also, in low-permeability fractures. . .



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The Significance of the Rock Matrix at Sites of Groundwater Contamination

- Do not underestimate the significance of the rock matrix in retaining contaminant mass. . .a critical element of source zone delineation. . .and contaminant longevity. . .
- Even crystalline rocks exhibit matrix retention. . .e.g., nuclear waste isolation (e.g., Swedish Nuclear Fuel and Waste Management Program)
- The retention of contaminant mass in the rock matrix can be of significance in both the source zone and the downgradient plume
- Large concentration gradients "drive" contaminant mass into the rock matrix "rapidly". . .
- Rate of "back diffusion" diminishes as the concentration gradient in the rock matrix decreases over time. . .
- Surface chemical processes (sorption) must also be considered in evaluating retention and release of contaminants in the rock matrix. . .

Shapiro et al., 2017

Shapiro and Brenneis, 2018

Shapiro et al., 2019

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