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Retardation of 1,4-Dioxane, NDMA, and Perchlorate in Fractured Sedimentary Rock

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University of Guelph
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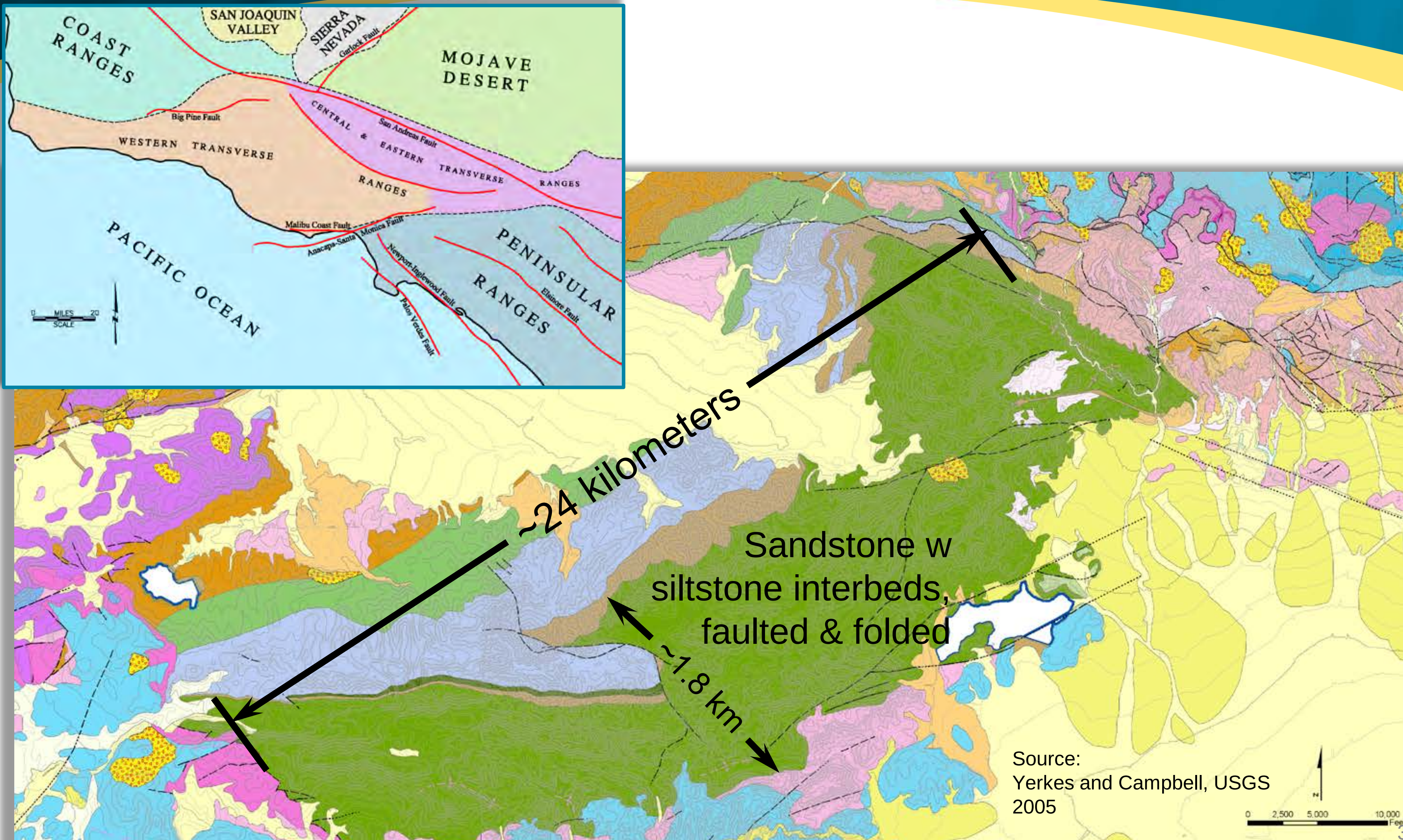
By: Richard Andrachek, P.E.
in collaboration with
Dr. Beth Parker & Steven Chapman, M.Sc., P.E.

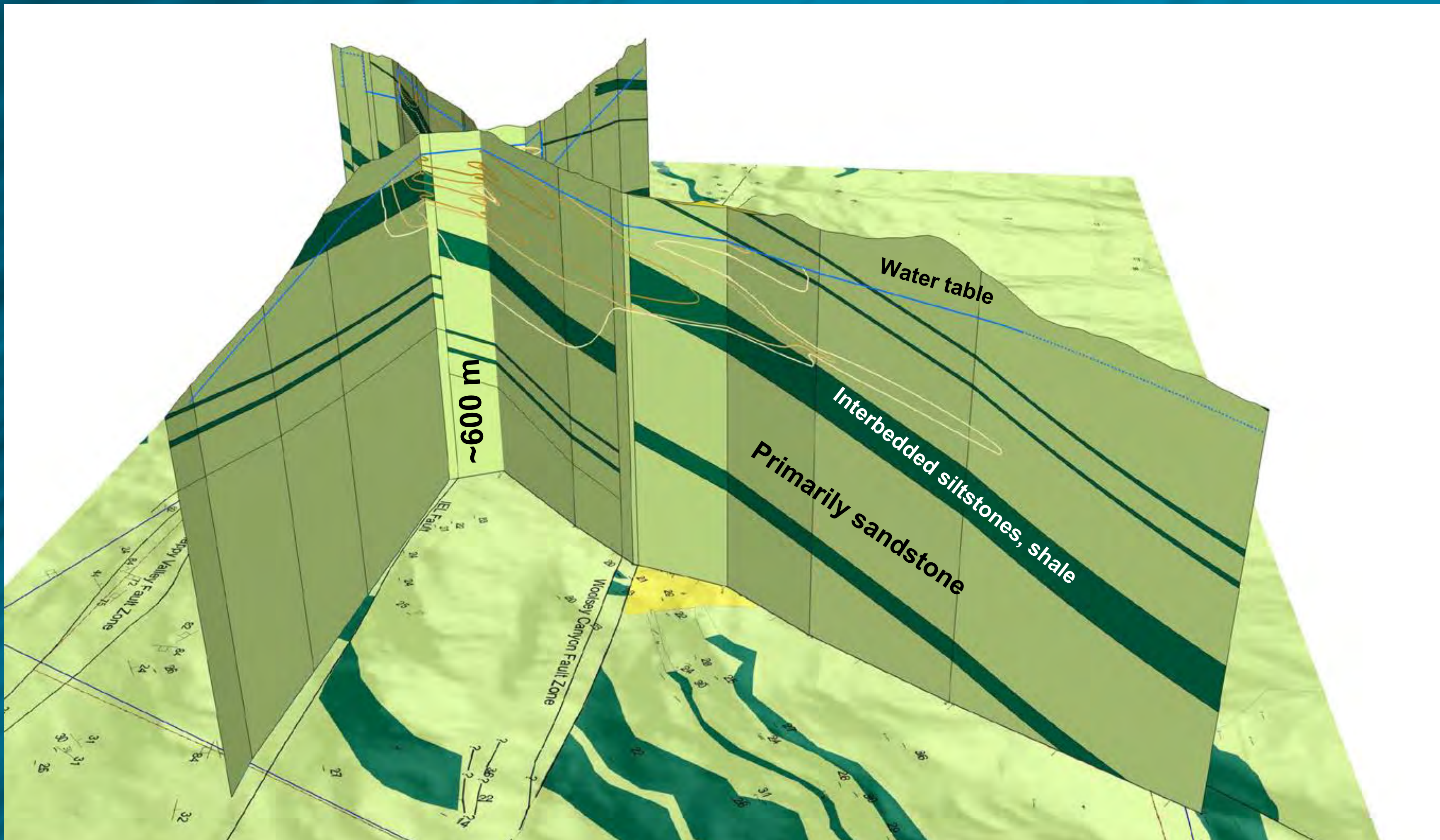
Topics:

1. Background
2. Approach
3. Results

Bedrock Geology of So Cal Location



Background



Water table
~600 m
Interbedded siltstones, shale
Primarily sandstone
Woolsey Canyon Fault Zone

Spectacular Setting

Strike: ~N70°E

ϕ_m: ~13% ($1 \times 10^{3,\,4}$x ϕ_f)

K_m: ~1×10^{-6} cm/s

Dip: 25°-30° NW

ϕ_f: ~0.01 to 0.001%

K_b: ~5×10^{-5} cm/s (50x K_m)

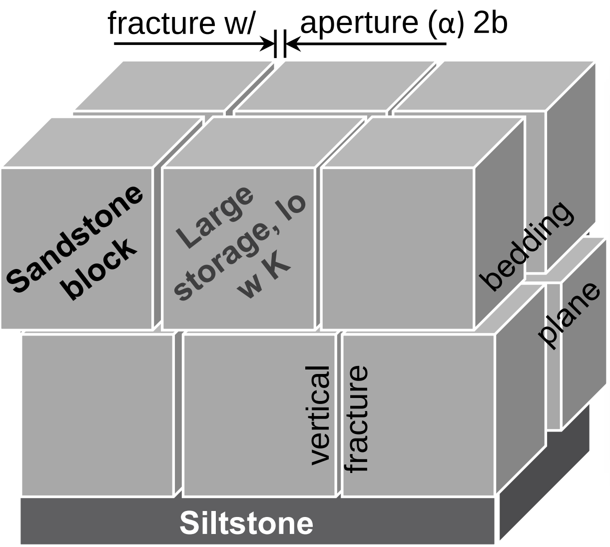
Hydrogeologic Conundrum (simplified)

Average linear groundwater velocity (Freeze & Cherry, 1979):

$$\bar{v} = K * i / \phi$$

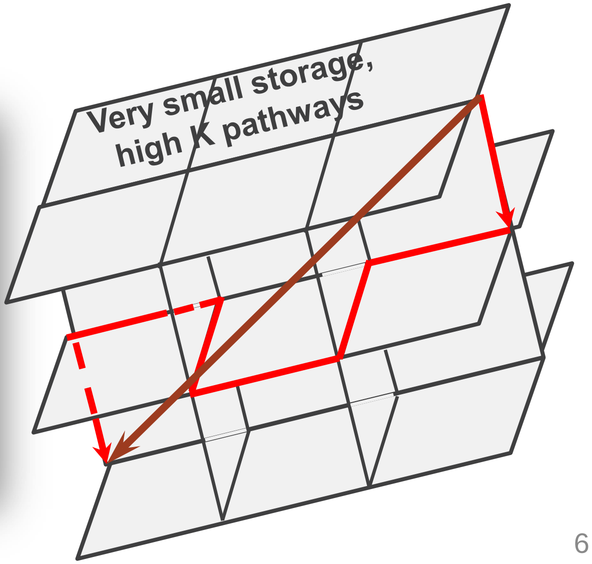
$$= K_b * i / \phi_f$$, **substitution yields: ~1 - 2 km/yr**

Conceptualized Bedrock Matrix Blocks with Fracture Network



Physical System in Outcrop

Conceptualized Fracture Network with Bedrock Matrix Blocks Removed



Hydrogeologic Implications on Transport of Conservative Contaminants (simplified)

Retardation

(sorption on fracture faces):

$R_f = 1 + [A * K_a]$, **Small number**

A = fracture surface area / fracture void space volume, and

K_a = mass sorbed to solid phase (per unit area) / dissolved concentration

....so by extension with $\bar{v} \approx 1 - 2$ km/yr, transport distances should be long...

But another transport process is at play that has retardation effect: diffusion

THE CHALK GROUNDWATER TRITIUM ANOMALY — A POSSIBLE EXPLANATION

1975

S.S.D. FOSTER

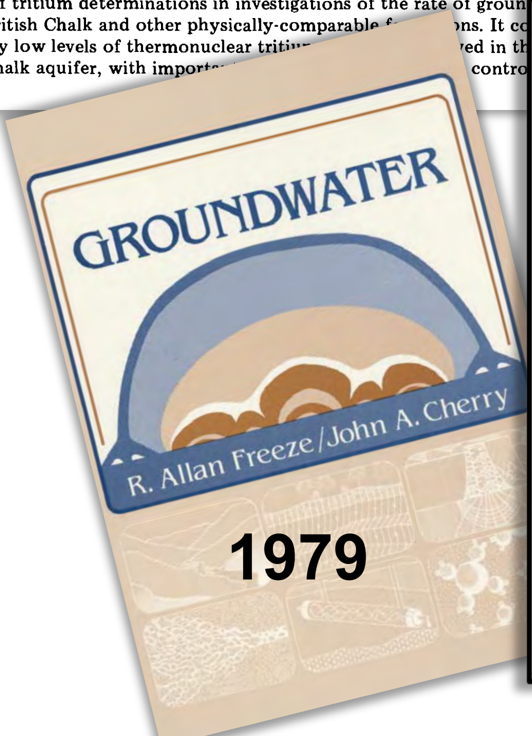
Hydrogeological Department, Institute of Geological Sciences, London (Great Britain)

(Received August 30, 1974; accepted September 3, 1974)

ABSTRACT

Foster, S.S.D., 1975. The Chalk groundwater tritium anomaly a possible explanation. J. Hydrol., 25: 159—165.

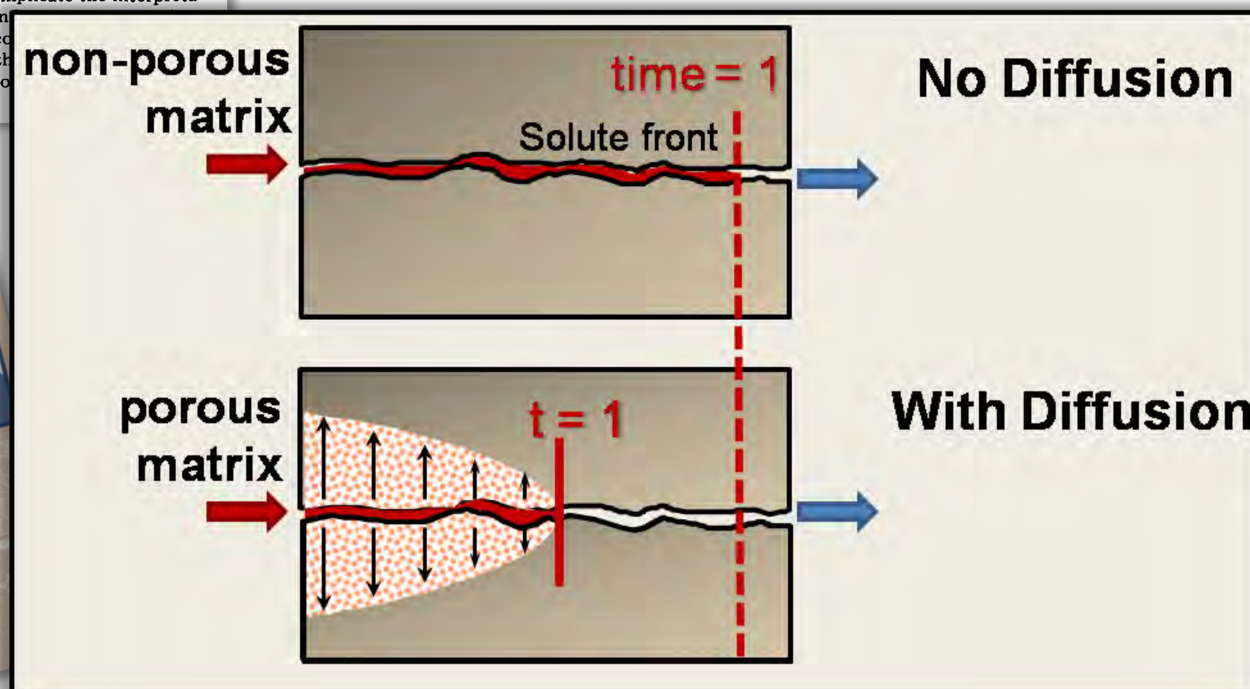
Attention is drawn to a mechanism which could profoundly complicate the interpretation of tritium determinations in investigations of the rate of groun
the British Chalk and other physically-comparable f ons. It co
alously low levels of thermonuclear tritiu ved in th
the Chalk aquifer, with import contro



1979

Fick's 1st Law

$J = -D \, \underline{\partial C}$

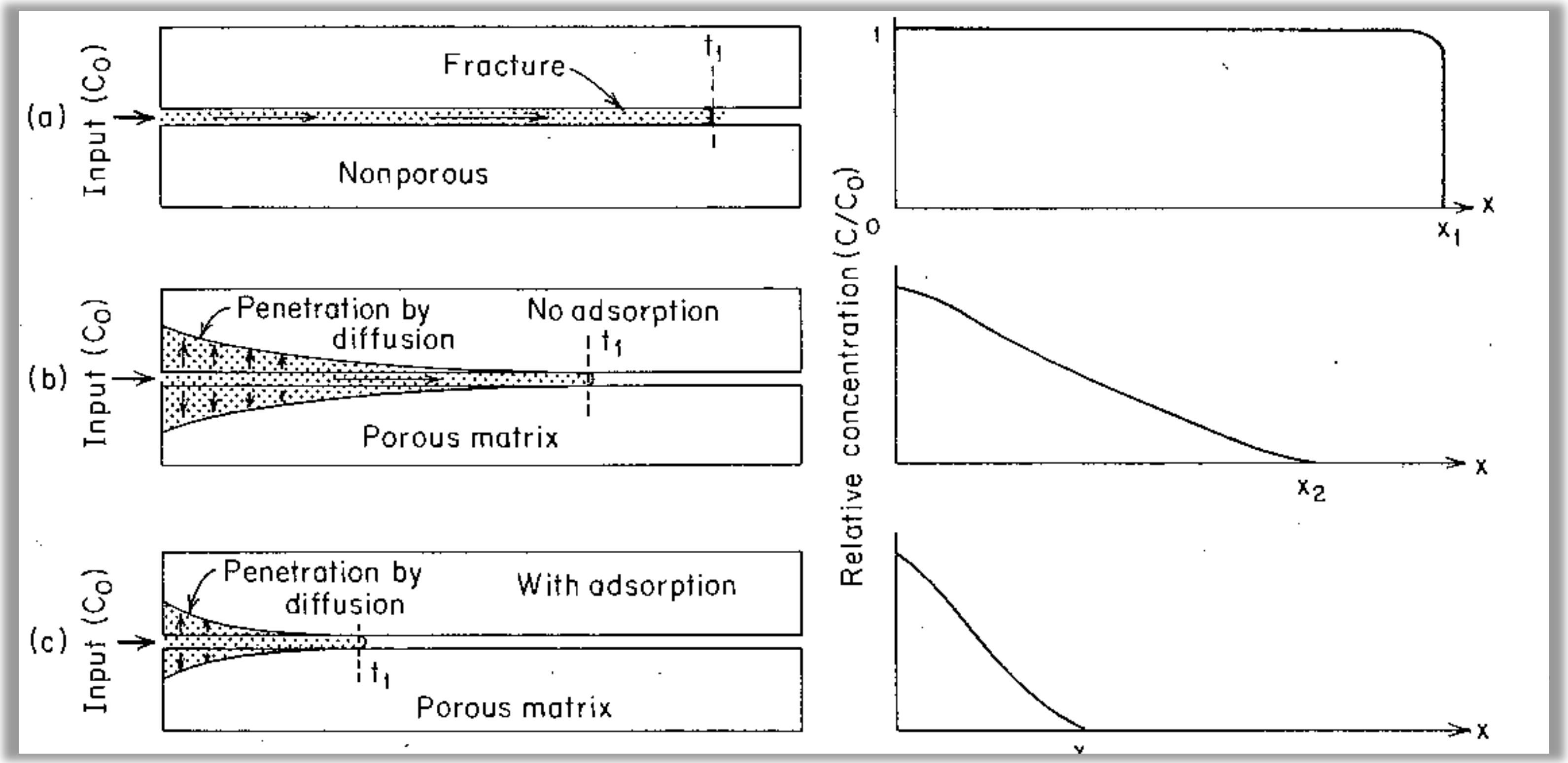


Apparent retardation of plume fronts due to diffusion

$R_a = D_{gw} / D_s$

D_{gw} = distance of groundwater travel

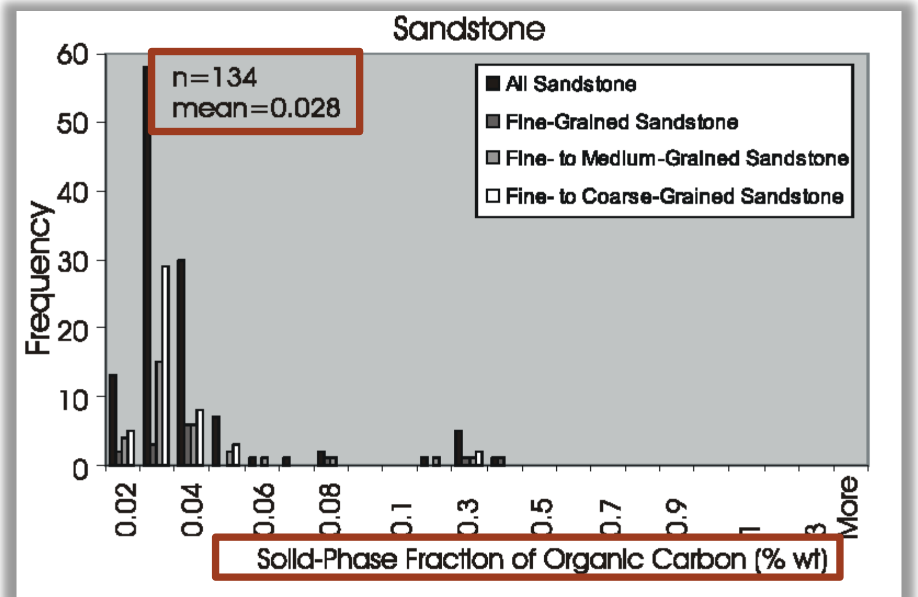
D_s = distance of solute travel at plume front



Properties Related to Contaminant Transport

Chemical	K_{oc}	R_s	Pure-Liquid Aqueous Solubility (mg/L)	Concentration of Interest (mg/L)	Free-Solution Diffusion Coefficient ,D_0 ($x10^{-5}$ cm^2/s)
1,4-Dioxane	2.61	1	666,000	0.001	1.01
NDMA	12.9	1.1	1,000,000	0.00001	1.06
Perchlorate	none		2,090,000	0.006	1.80
TCE	126	1.8	1,100	0.005	1.01

Values of K_{oc}, solubility and D_0 are from a compilation of sources

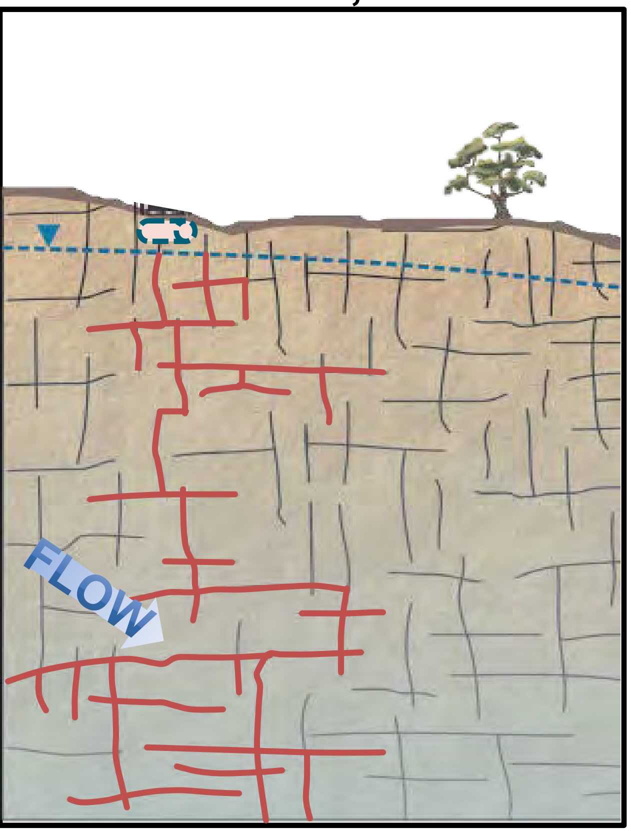


and $D_e = \tau * D_0$

τ = tortuosity

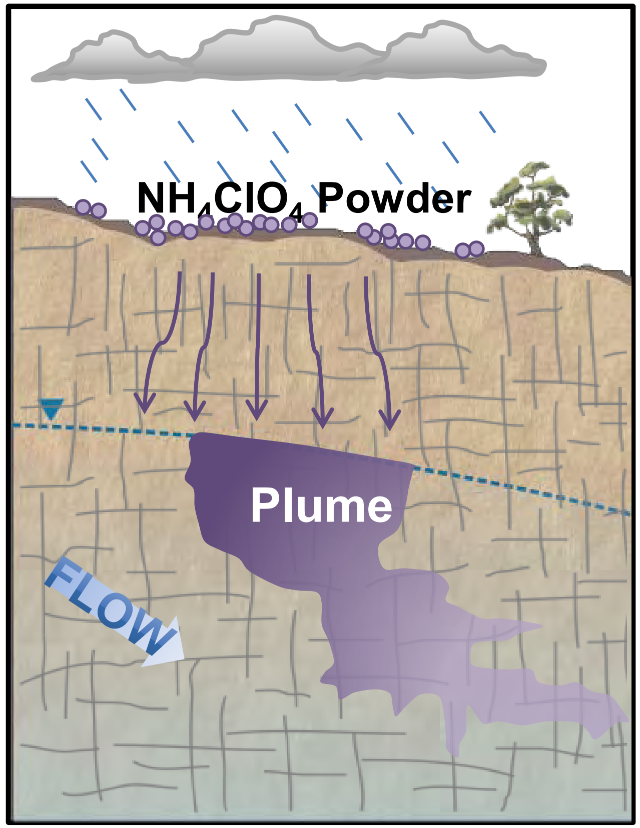
How Did These Chemicals Enter Groundwater?

1,1,1-Trichloroethane → 1,4-dioxane



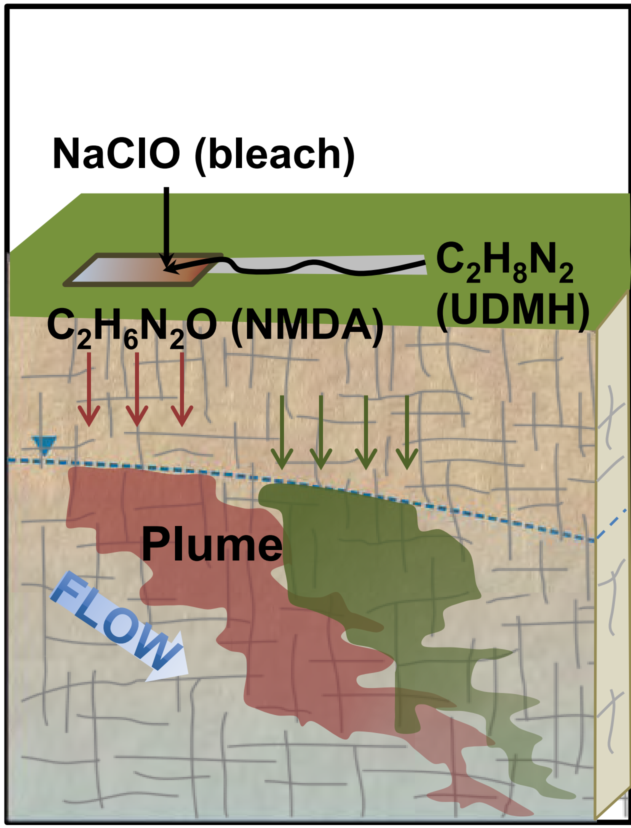
DNAPL Infiltration

Perchlorate (ClO_4)



Leaching of Solids

NDMA



Water Infiltration

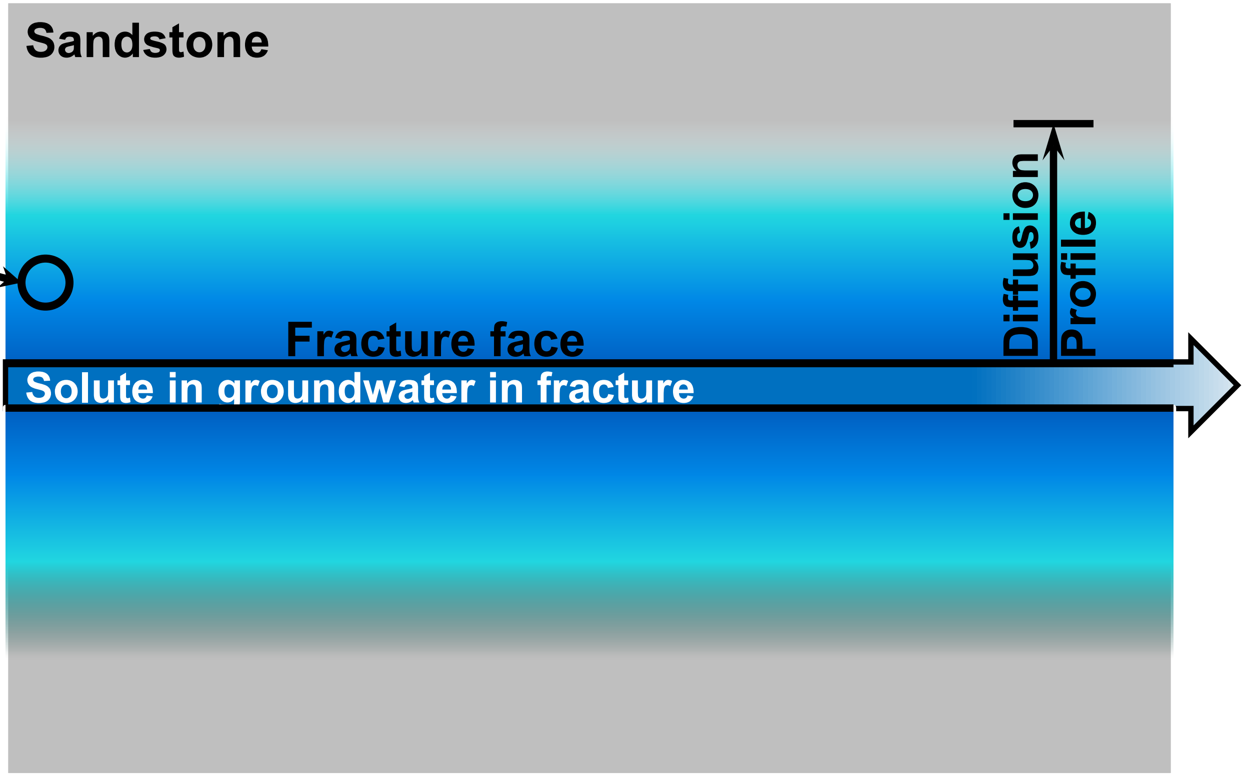
Retardation of 1,4-Dioxane, NDMA, and Perchlorate in Fractured Sedimentary Rock

Topics:

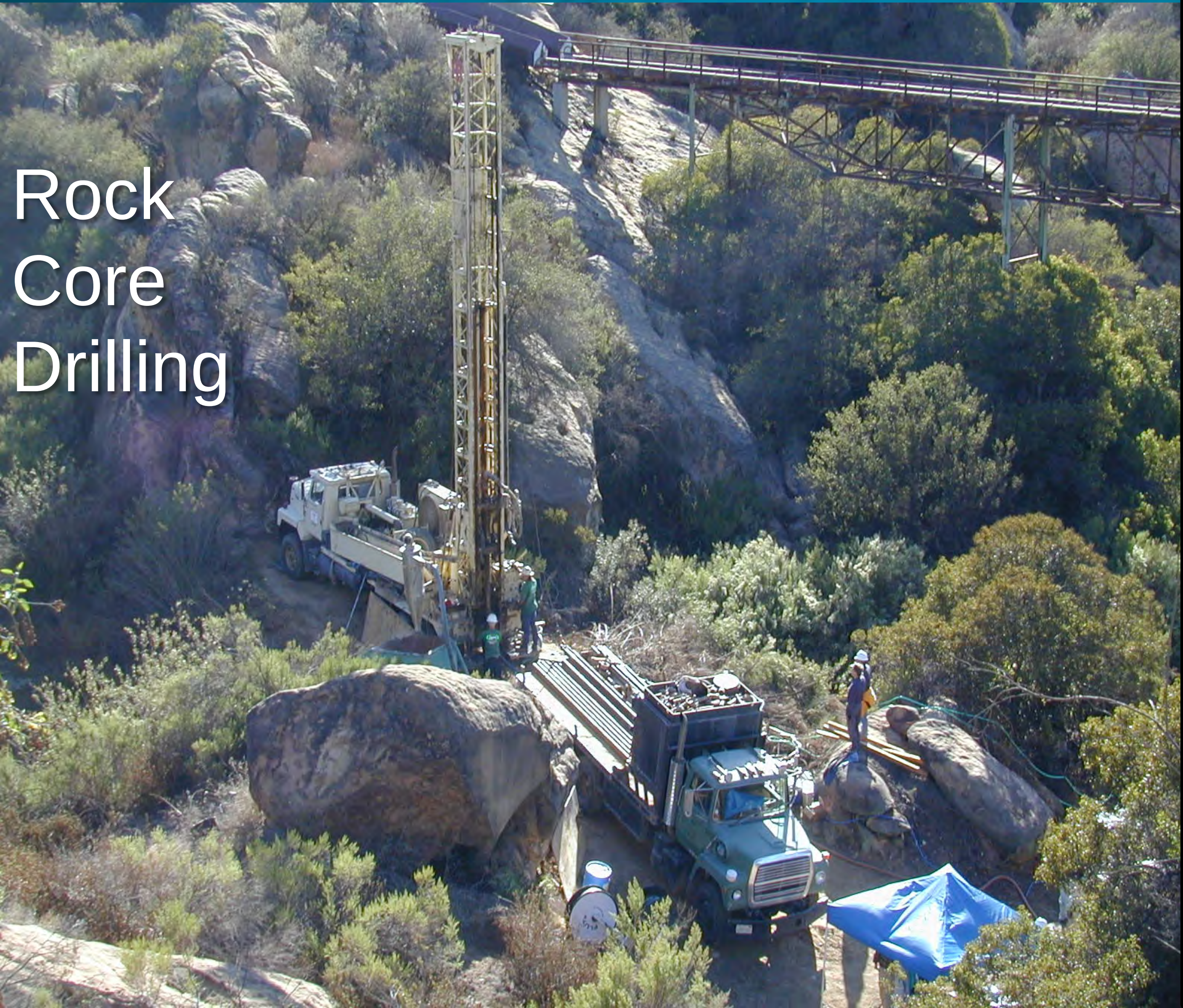
1. Background
2. **Approach**
3. Results

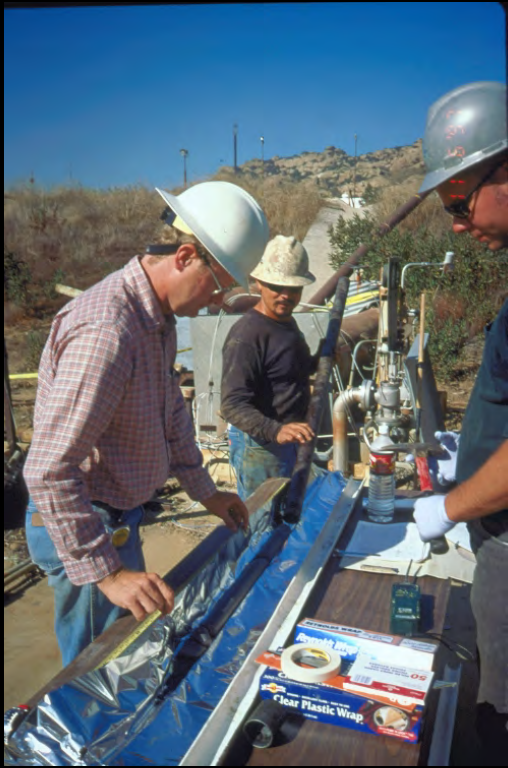
Validate diffusion through rock sampling

Rock porewater should contain dissolved solute

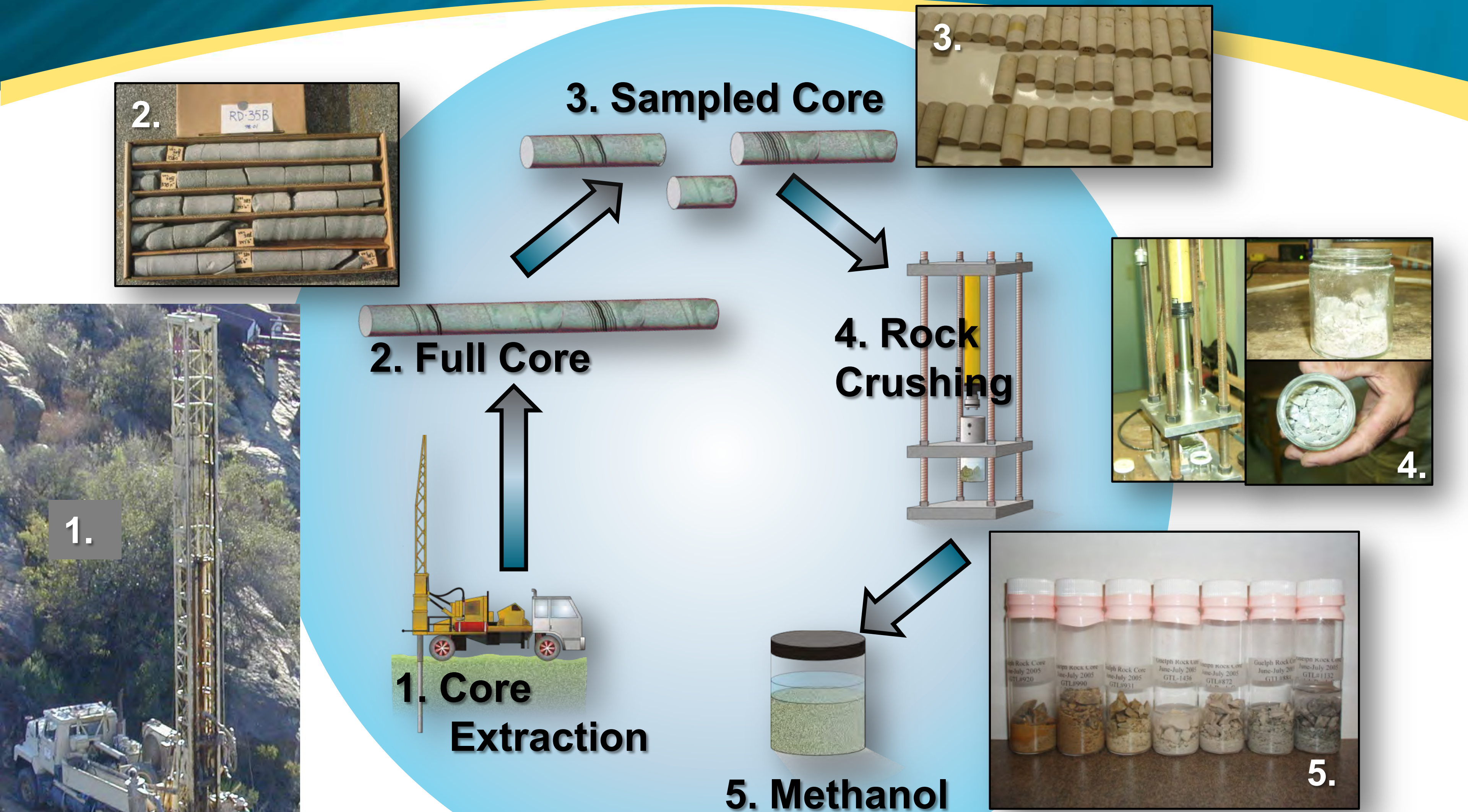


Rock Core Sampling and Analysis



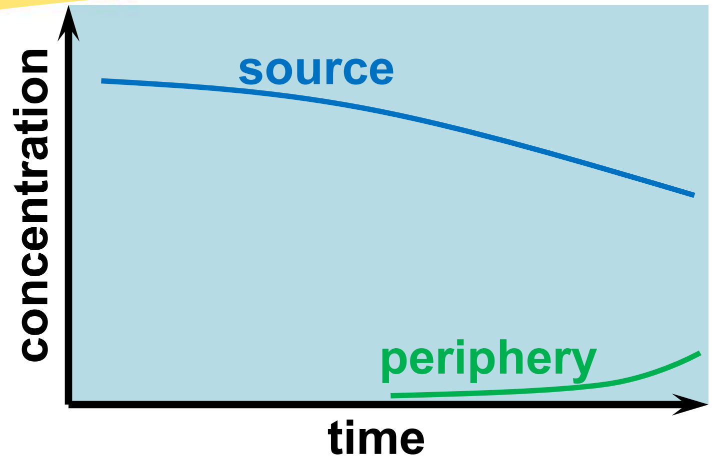


Rock Core Sample Prep Process

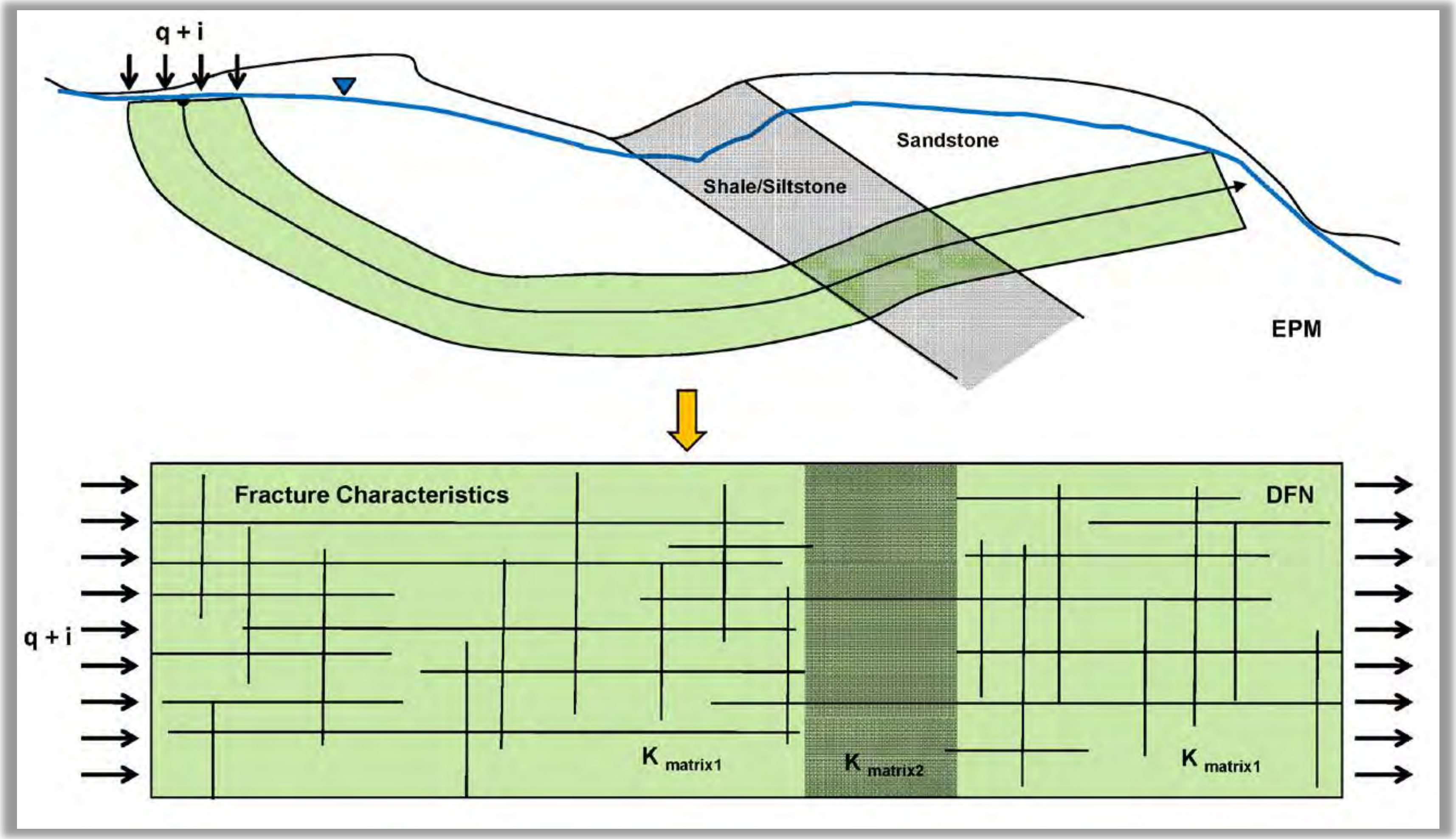


CORE DFN ™
DISCRETE FRACTURE NETWORK APPROACH

Time-series plots of concentrations from wells can be used to estimate magnitude of plume front R_a



Insights from transport modeling to help visualize and quantify effect



Retardation of 1,4-Dioxane, NDMA, and Perchlorate in Fractured Sedimentary Rock

Topics:

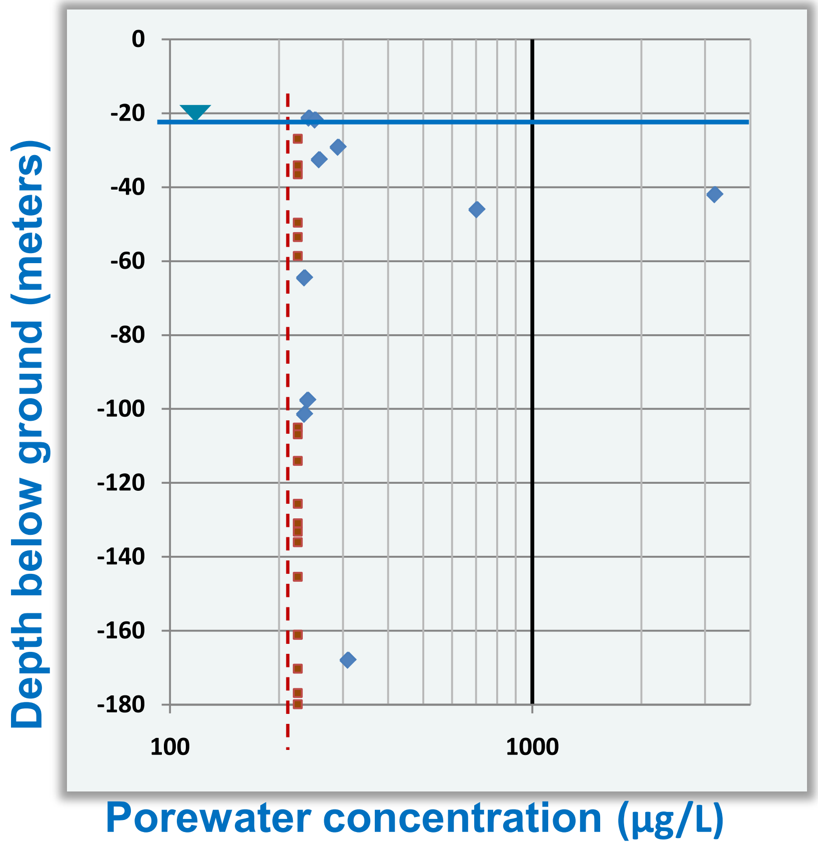
1. Background

2. Approach

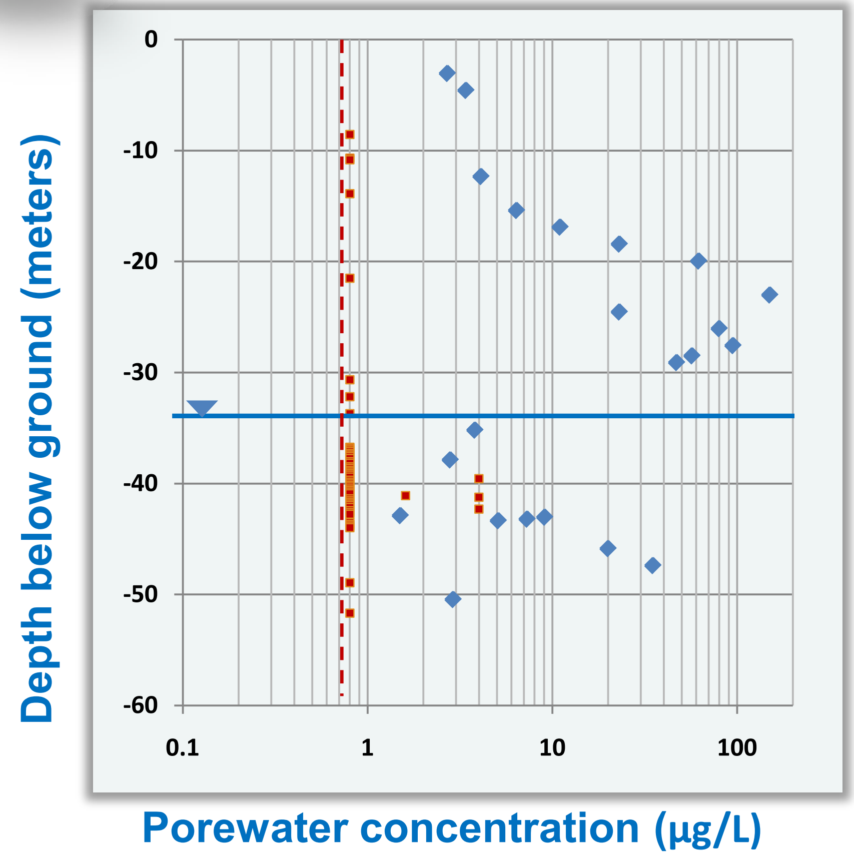
3. Results

1,4-dioxane & perchlorate results show extent of diffusion

Plot of 1,4-dioxane in rock core



Plot of perchlorate in rock core



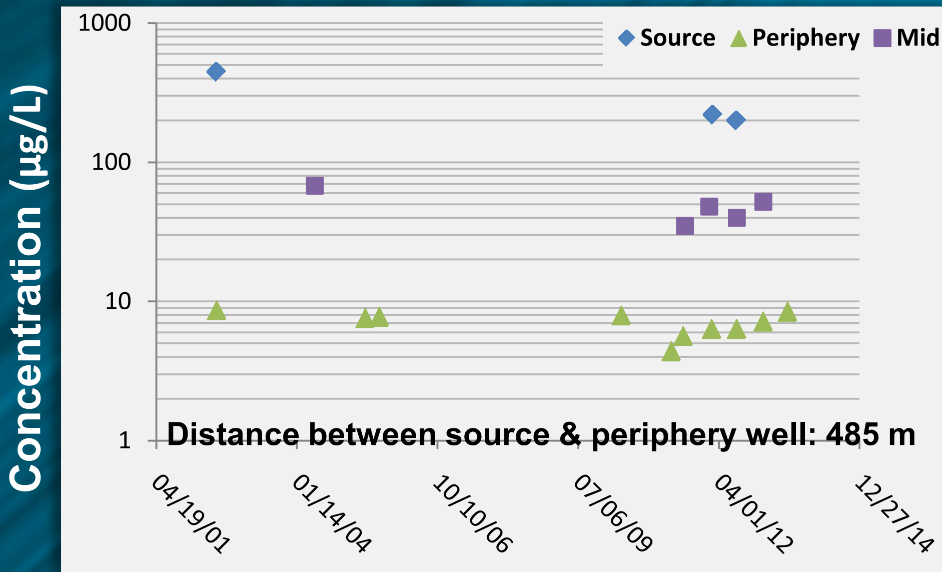
Location ~135 m from source input

Protocol: 5% of total # samples, 8260B, MRL: 225

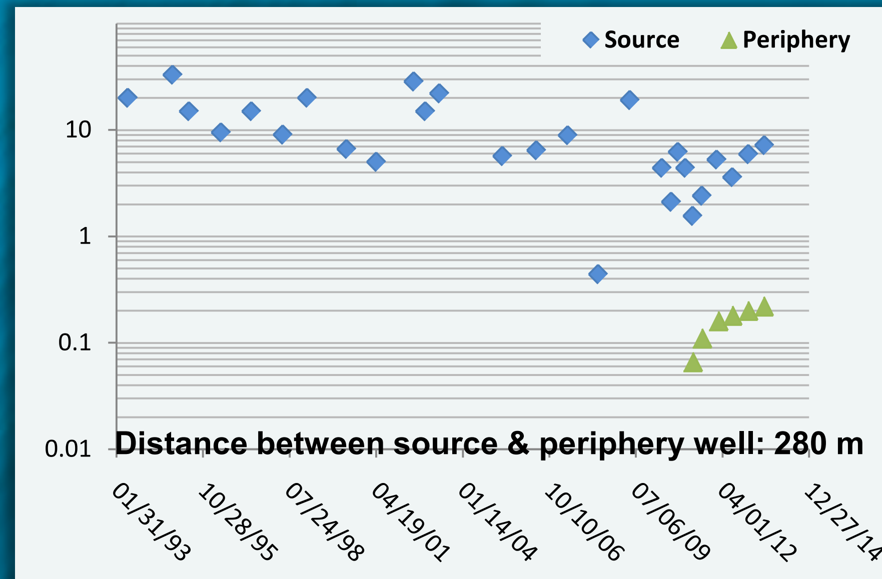
Location near broadly distributed source

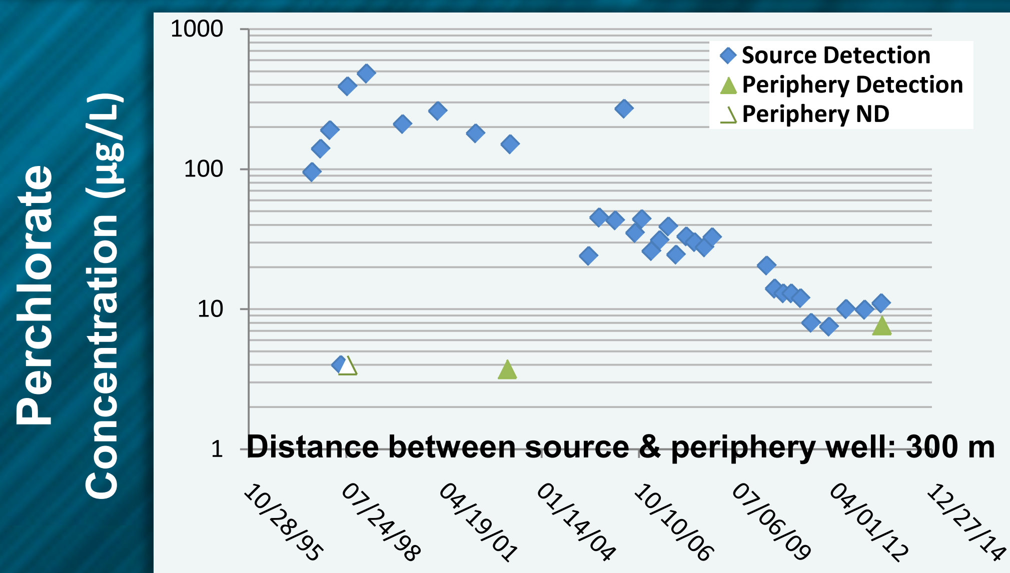
Samples from conventional wells show retardation effect

1,4-dioxane



NDMA





Well data yields apparent retardation estimates

Chemical	Transport Distance (m)	Time (yrs from release)	GW Travel Distance (m)	Apparent Retardation of Plume Front (C/C_0 = 2 OM)
1,4-dioxane	485	40	12,600	50
NDMA	280	50	15,800	110
Perchlorate	300	50	15,800	100

$K_b = 1x10^{-4}$ cm/s

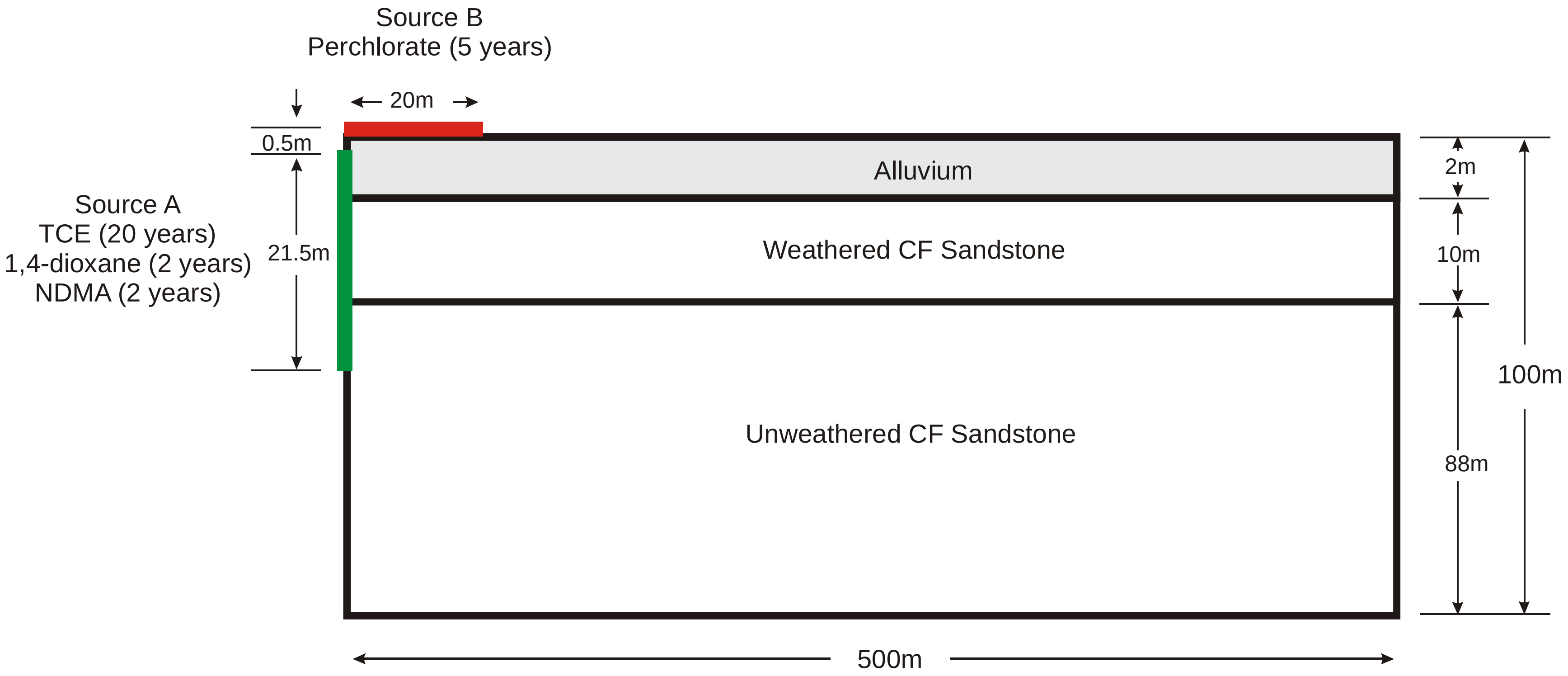
$\phi_f = 1x10^{-4}$

$i = .002$

$\overline{v} = 630$ m/yr

Results

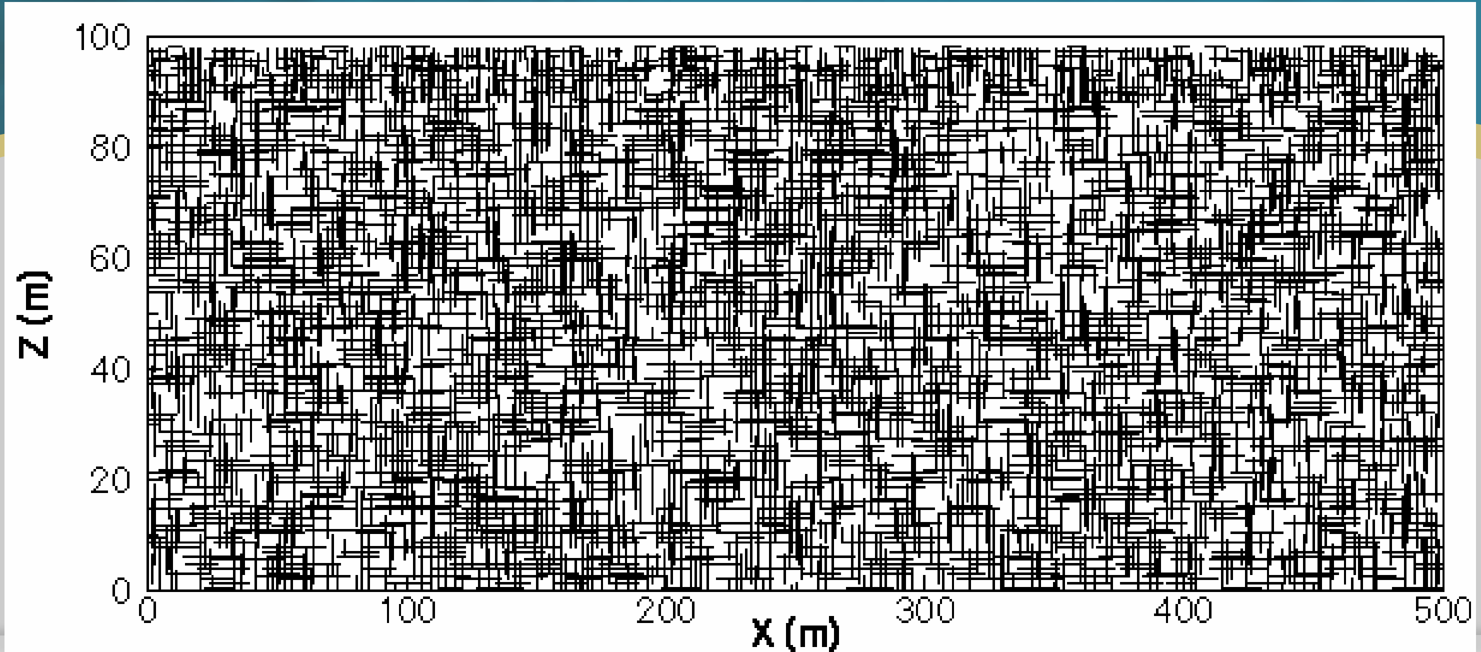
Insight from transport modeling? Conceptualization: vertical section

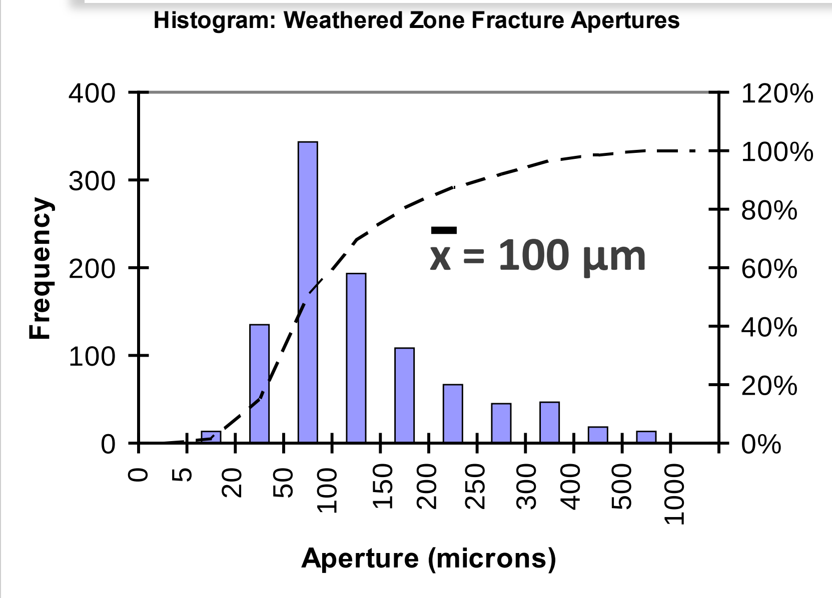


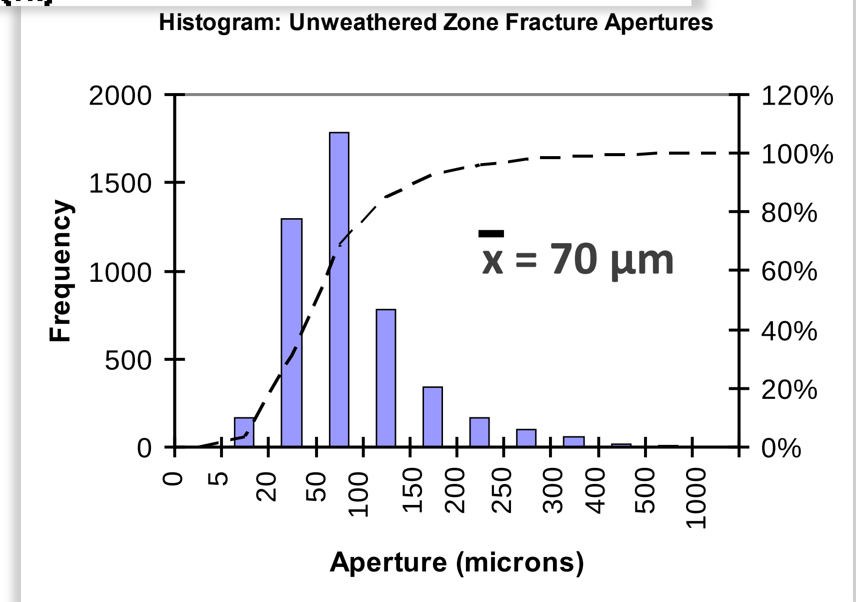
Fractran:
2-D discrete fracture network model
Steady-state flow, transient contaminant transport
Accounts for diffusion and sorption

Results

2-D discrete fracture network (Fractran)

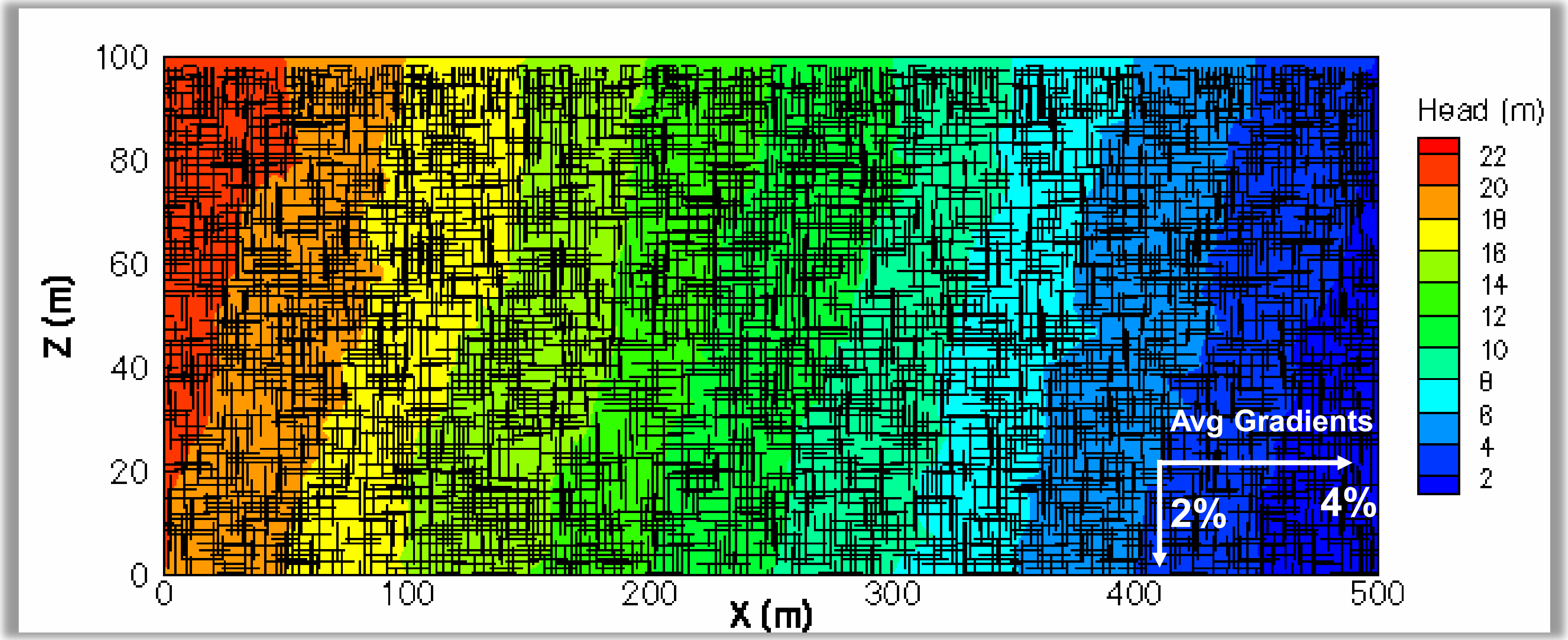






Results

2-D DFN Flow Solution (steady state)



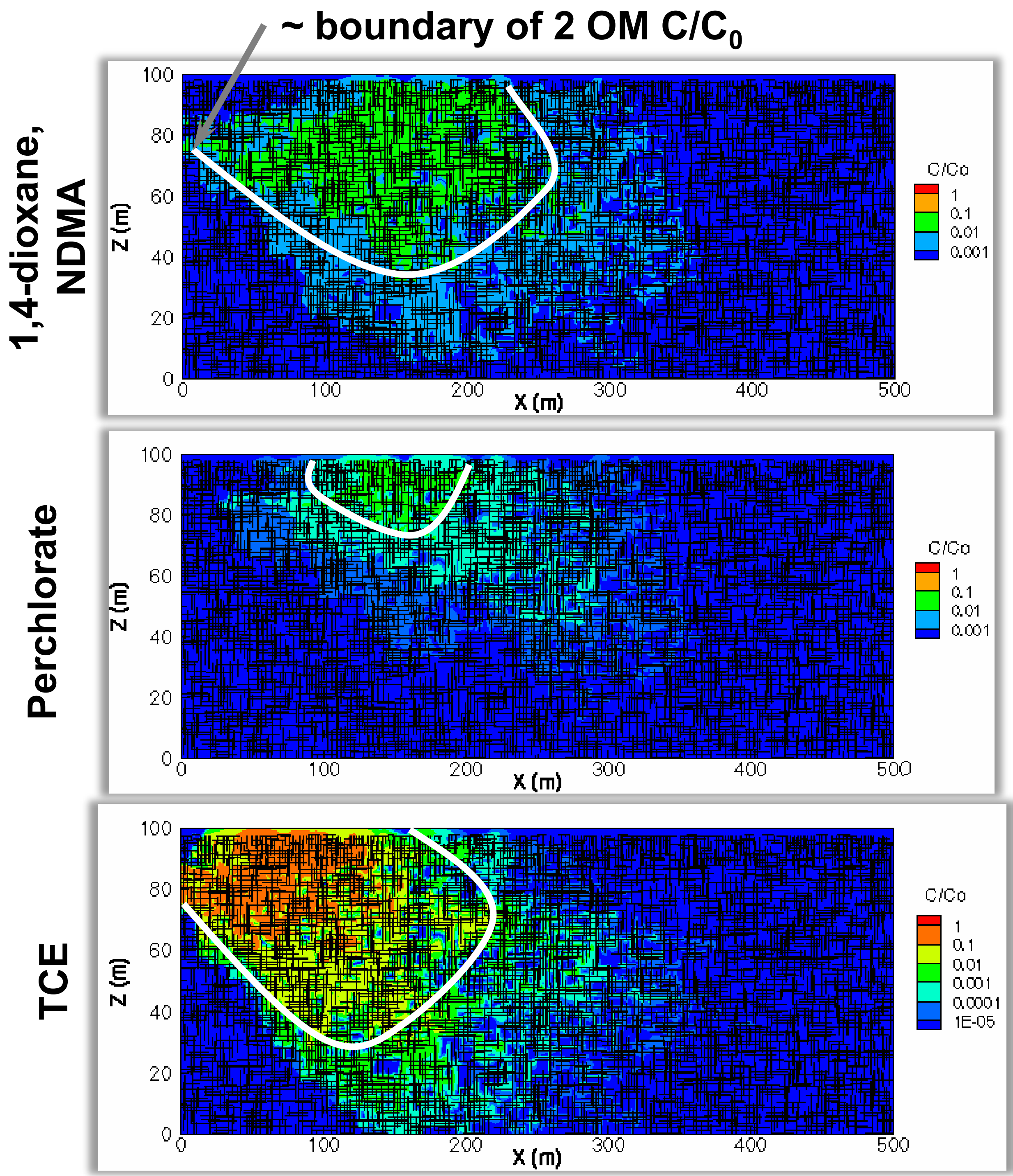
K_b = $2x10^{-5}$ cm/s

ϕ_f = $7x10^{-5}$

i = as shown

Transport Simulations at time 50 years after release

Chemicals remain within a few hundred meters of input



Summary

- **Average Linear Groundwater Velocities are High**
  - **In the range of kilometer/year**
- **Matrix Diffusion Causes Strong Retardation**
  - **Local plume front R_a ranges from 50 to ~100, at t = 50 years, C/C_0 = 2 OM**
  - **Sorption in rock matrix, if applicable enhances retardation**
- **All Dissolved Chemicals Diffuse**
  - **Diffusion coefficients fall within narrow range**

Retardation of 1,4-Dioxane, NDMA, and Perchlorate in Fractured Sedimentary Rock

Thank you!

By:
Andrachek, Parker, and Chapman

UNIVERSITY of GUELPH
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TCE Removal from Rock Matrix Controlled by Diffusion