Field Test Analysis of Trichloroethene Abiotic & Bio-Degradation Rates, Sorption and Diffusion Coefficients for Low Permeability Fractured Rock

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April 17, 2019

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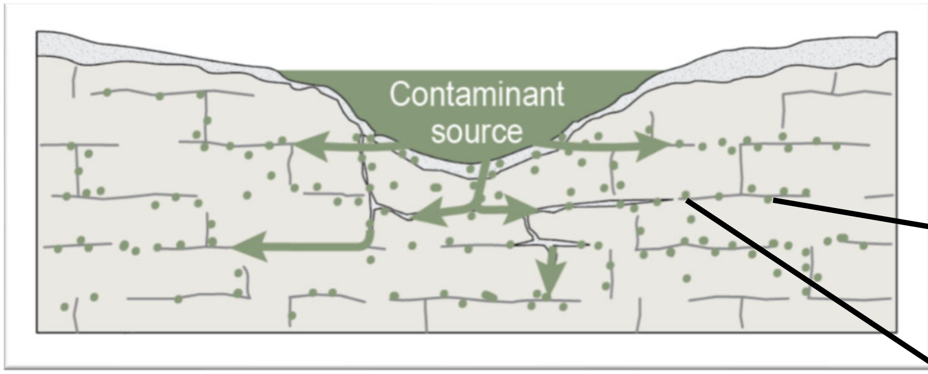
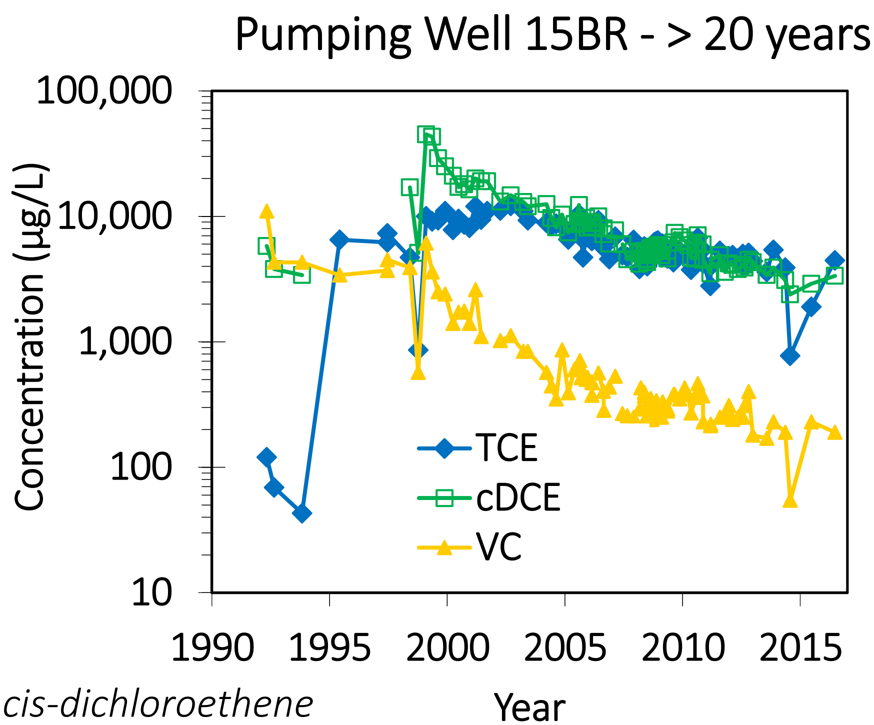
The State University of New York

Matrix contamination => long term secondary source





cDCE *cis-dichloroethene*
VC vinyl chloride or chloroethene

- DNAPL (dense nonaqueous phase liquid) dissolves & diffuses into matrix
- "Back diffusion" from matrix to fractures can sustain contaminant concentrations & limit remediation effectiveness

Project Objective:

Develop and test a field method capable of concurrently quantifying site-specific trichloroethene (TCE) “transport coefficients” in the matrix (slow)

- diffusion coefficient (tortuosity factor)
- sorption coefficients
- **degradation coefficients (*abiotic in matrix***, biotic in borehole)

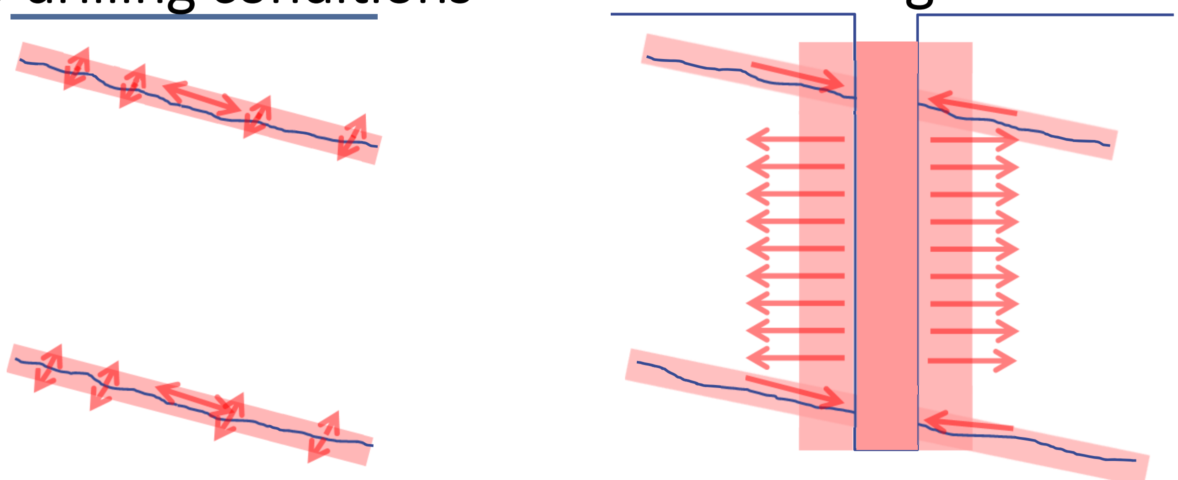
What characteristics of ‘back diffusion” cause it to effectively sustain contaminant concentrations?

Field Test Overview: Borehole provides matrix interface with long term contaminant exposure

Pre-drilling conditions | Post-drilling conditions

Pink=TCE

Schematics not to scale

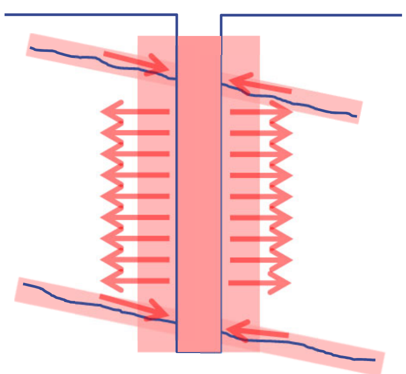


Permeable fractures feed TCE into wellbore water (post-drilling)

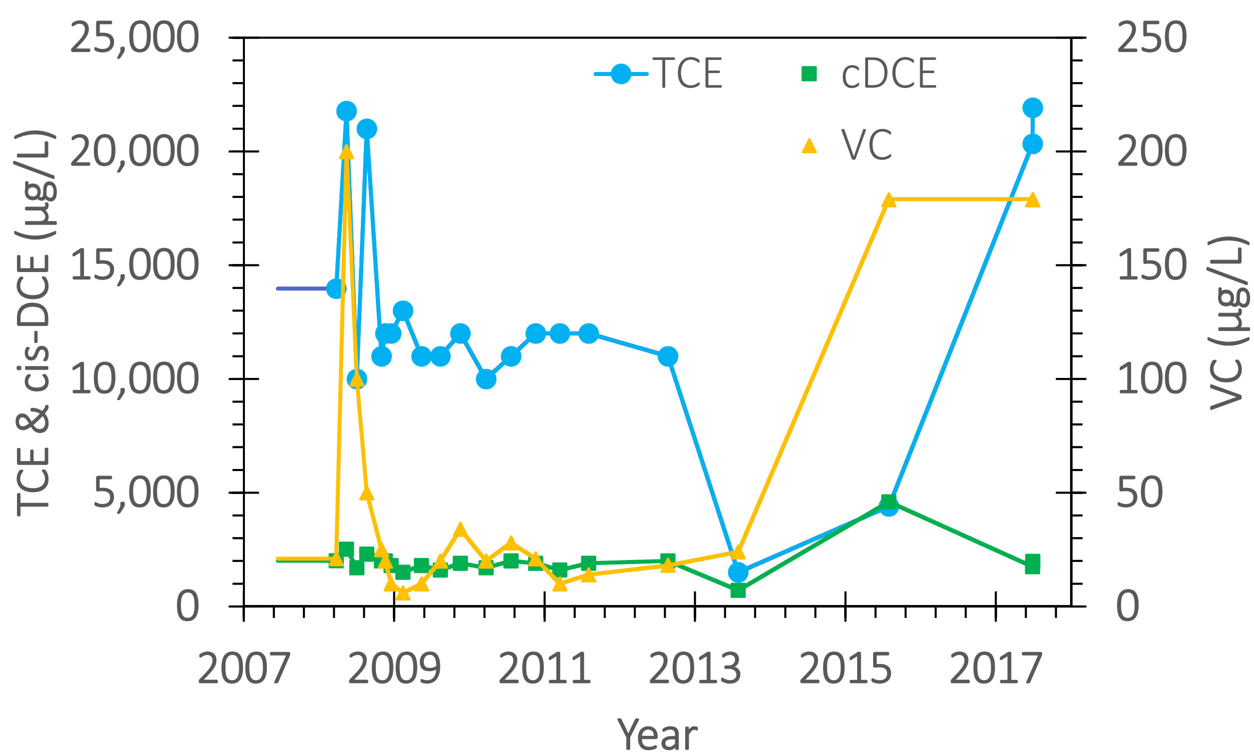
TCE diffuses from borehole into low-permeability matrix where sorption & abiotic reaction occur.

Monitoring data supplies pre-test concentration history

Post-drilling conditions



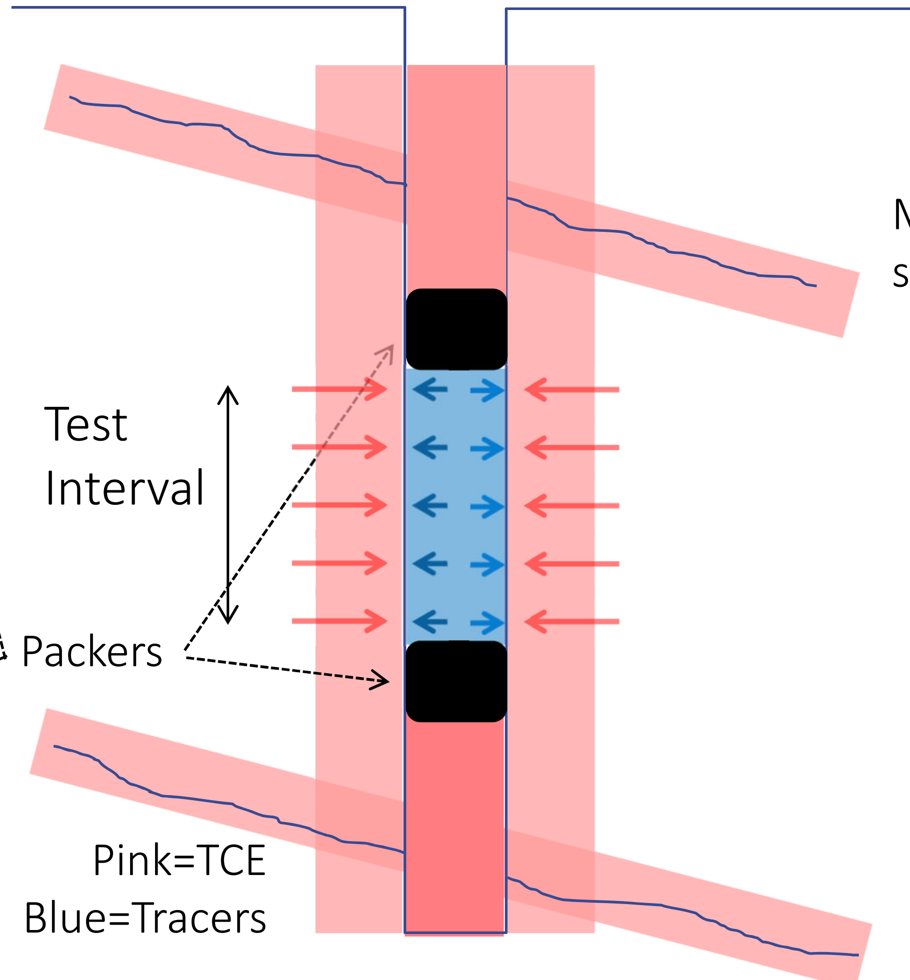
~Borehole drilled ~10 years prior to test

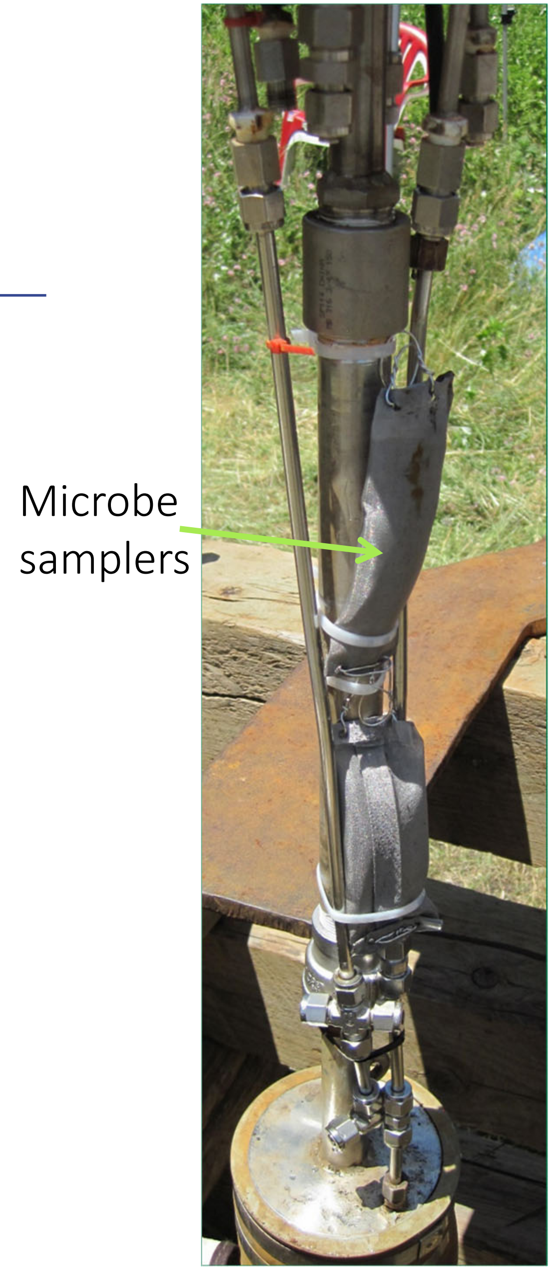


Sparging (N_2) to remove VOCs

Dosing bromide & trichlorofluoroethene (TCFE) tracer sol'n

Field Test Overview: Test Conditions





Simulations to Estimate Parameters

Processes simulated:

- Matrix diffusion
- Retardation from sorption (local equilibrium)
- Biodegradation only in borehole
- Abiotic degradation only in matrix

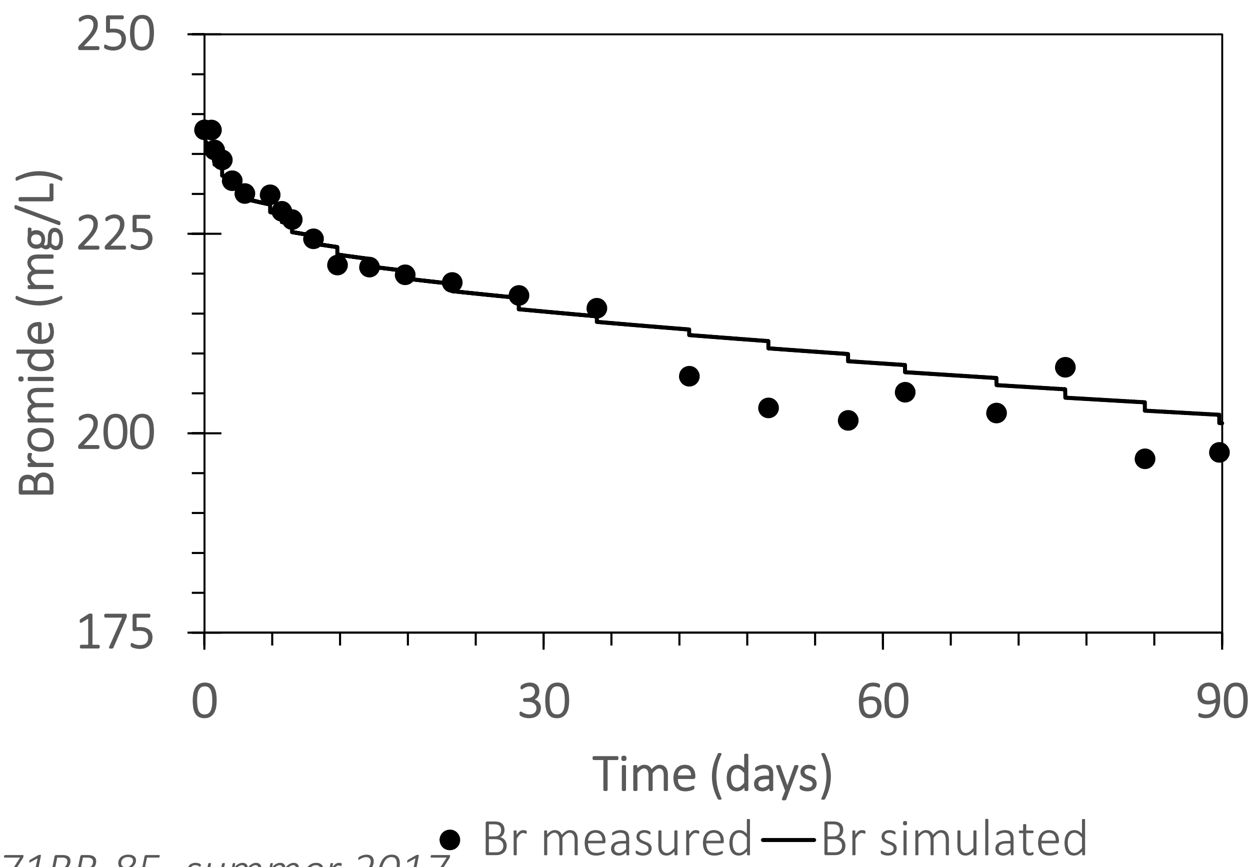
Simulation includes historical exposure

Effective diffusion coefficients from bromide tracer

- Tortuosity factor = 0.12

(porosity 0.05 assumed)

- Steps correspond to 'replacement water' during sampling



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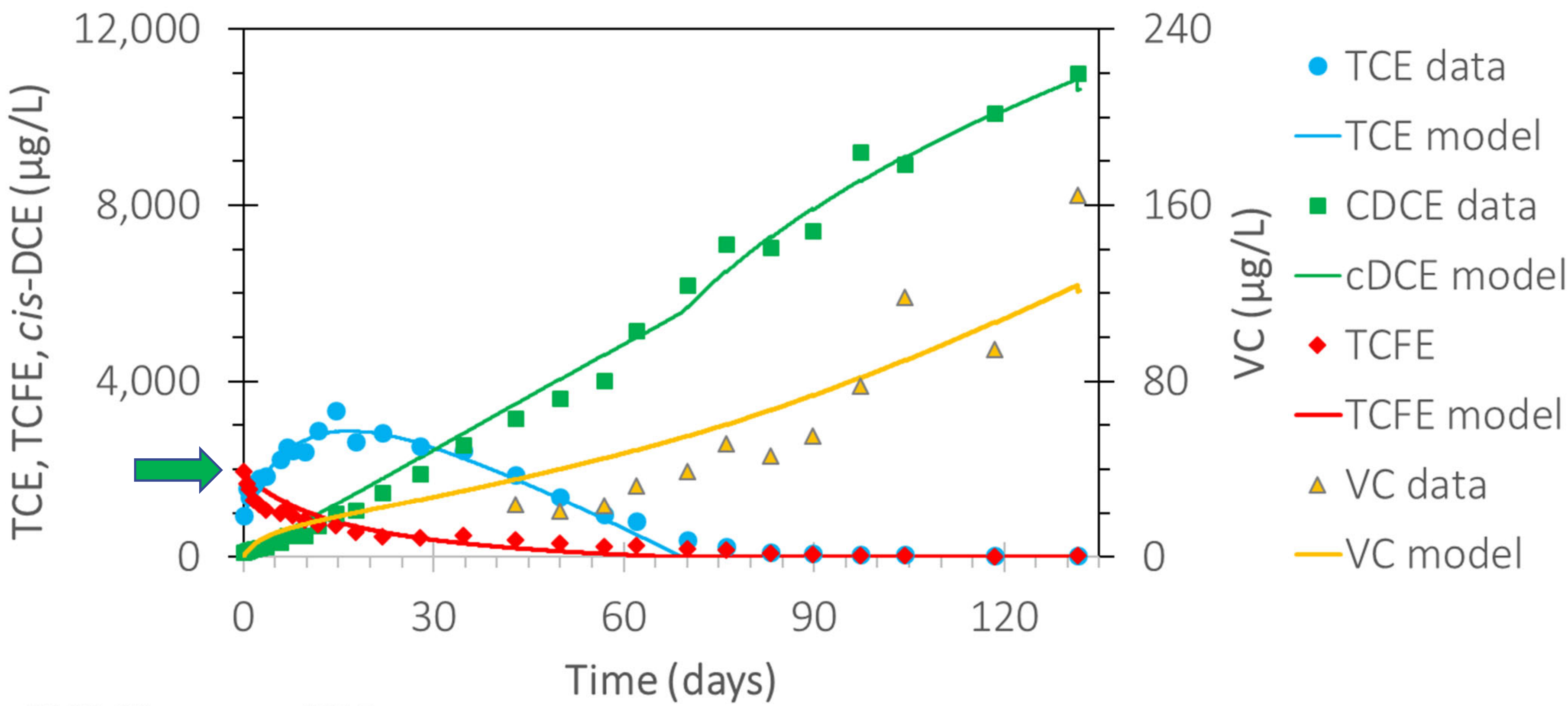
Observations

- TCE concentration << pre-test concentration (10-20 mg/L)
- *cis*-DCE concentration > pretest (➡) after ~30 days => rapid biodegradation in the borehole



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Degradation products not shown had very low or nondetectable concentrations, including acetylene, ethene, ethane or chlorofluoroethenes.

Fast TCE biodegradation consistent with independent batch experiment results

Calibrated parameters

	K_d (L/kg)	λ_o** (µM/day)	$t_{1/2}$ (day)
TCE	4.6	1.1	
TCFE	8.9*		
cis-DCE	0.91*		3100

*Kd ratios TCFE:TCE & *cis*DCE:TCE fixed based on lab data or solubility

**Zeroth order (TCE+TCFE) biodegradation

Biodegradation kinetic form & rate constants

- TCE & TCFE either 0^{th} or 1^{st} order
- TCE & TCFE rate constants consistent lab (factor of 4)
- Fast TCE to *cis*DCE
  Slow *cis*DCE to VC

Sorption coefficients (K_d)

- Consistent with lab results
- High

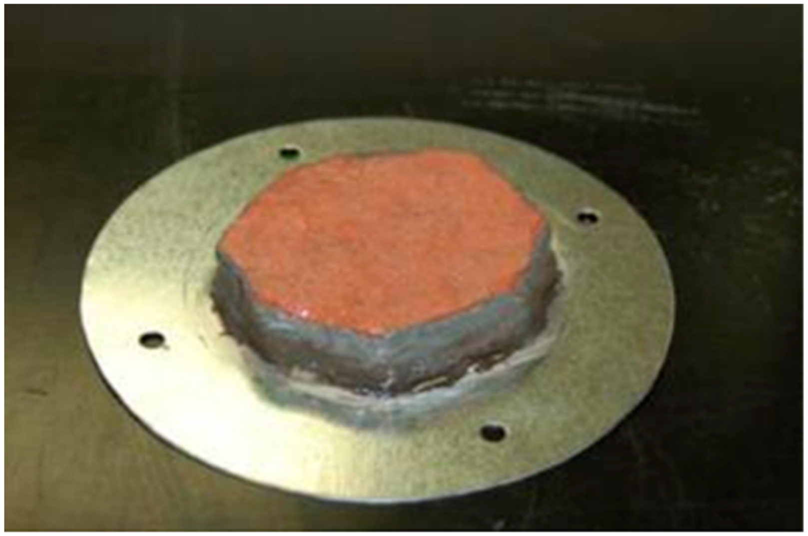
Abiotic degradation???

Approach to abiotic degradation

- Incorporate abiotic degradation in the matrix into model and refit experiments
- Use rate coefficient previously measured for rocks from this field site by Schaefer et al. (2013)*

$$k' = 5 \times 10^{-9}\ s^{-1}$$

- Schaefer et al. assumed that sorbed phase degraded
- Vary which phase -dissolved or sorbed - degrades



Rock mounted for diffusion experiment from Schaefer et al. (2013)

*Schaefer, et al., *Coupled Diffusion and Abiotic Reaction of Trichlorethene in Minimally Disturbed Rock Matrices.* ES&T, 2013. **47**(9): p. 4291-4298.

Diffusive transport equation with degradation of dissolved and sorbed contaminant

$$\mathrm{R}\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial^2 x} - \left(\lambda C + \frac{\rho k K_d}{\theta} C\right)$$

Degradation of dissolved & sorbed TCE

R –retardation factor

D-diffusion coefficient

C-dissolved concentration

ρ-bulk density

θ-porosity

λ-degradation rate coefficient for dissolved

k—degradation rate coefficient for sorbed

Assume linear, instantaneous, equilibrium sorption

Adjusting rate constant for dissolved or sorbed degradation

$k' = k\rho K_d$ =5x10−9 s^{-1}

- Representative value from Schaefer et al.

$k = k'/\rho K_d$=2x10^{-8} s^{-1}

- ρ=2.6 kg/L, assume 0.1 L/kg from data 0.081-0.17 L/kg

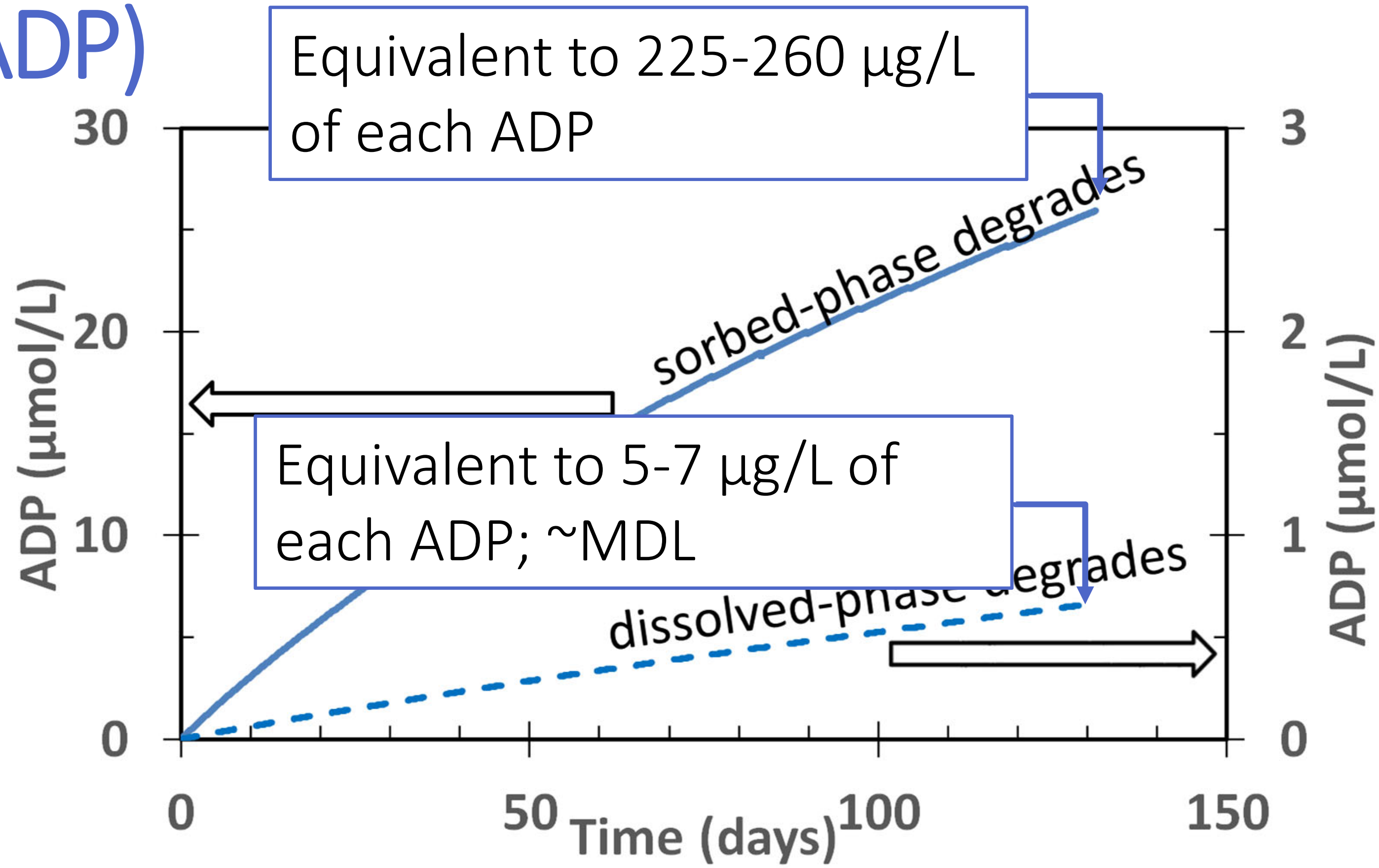
$\lambda = k'/\theta$= 6.6x10^{-8}s^{-1}

- Fit Schaefer et al. results assuming only dissolved phase degrades, θ=0.076

Results of simulations with abiotic degradation

- Quality of TCE and cisDCE fits unaffected
- Degradation of dissolved phase only
  - parameters same as base case (=case with no abiotic degradation)
- Degradation of sorbed phase
  - sorption coefficient approximately doubled from base case, small change in biodegradation rate

Model of Abiotic Degradation Products (ADP)



ADP are ethene, ethane, acetylene

No ADPs were observed during experiment. . .

EXPECTED	OBSERVED
Sorbed TCE abiotic degradation:	
225-260 µg/L of each of 3 ADP	XX
Dissolved TCE (in matrix):	ND- acetylene, ethane
5-7 µg/L of each of the 3 ADP	Trace ethene at end of experiment

Provisional Conclusion: Abiotic degradation below detection limit?

Site specific findings using the testing apparatus & method at NAWC

Biodegradation (TCE to cisDCE) fast in borehole under experiment (no flow) conditions

- Maintains low TCE concentration compared to matrix
- Consistency between model and results suggests biodegradation occurs at the interface, not in the matrix
- cisDCE to VC degradation rate increased in later part of test – increased residence time

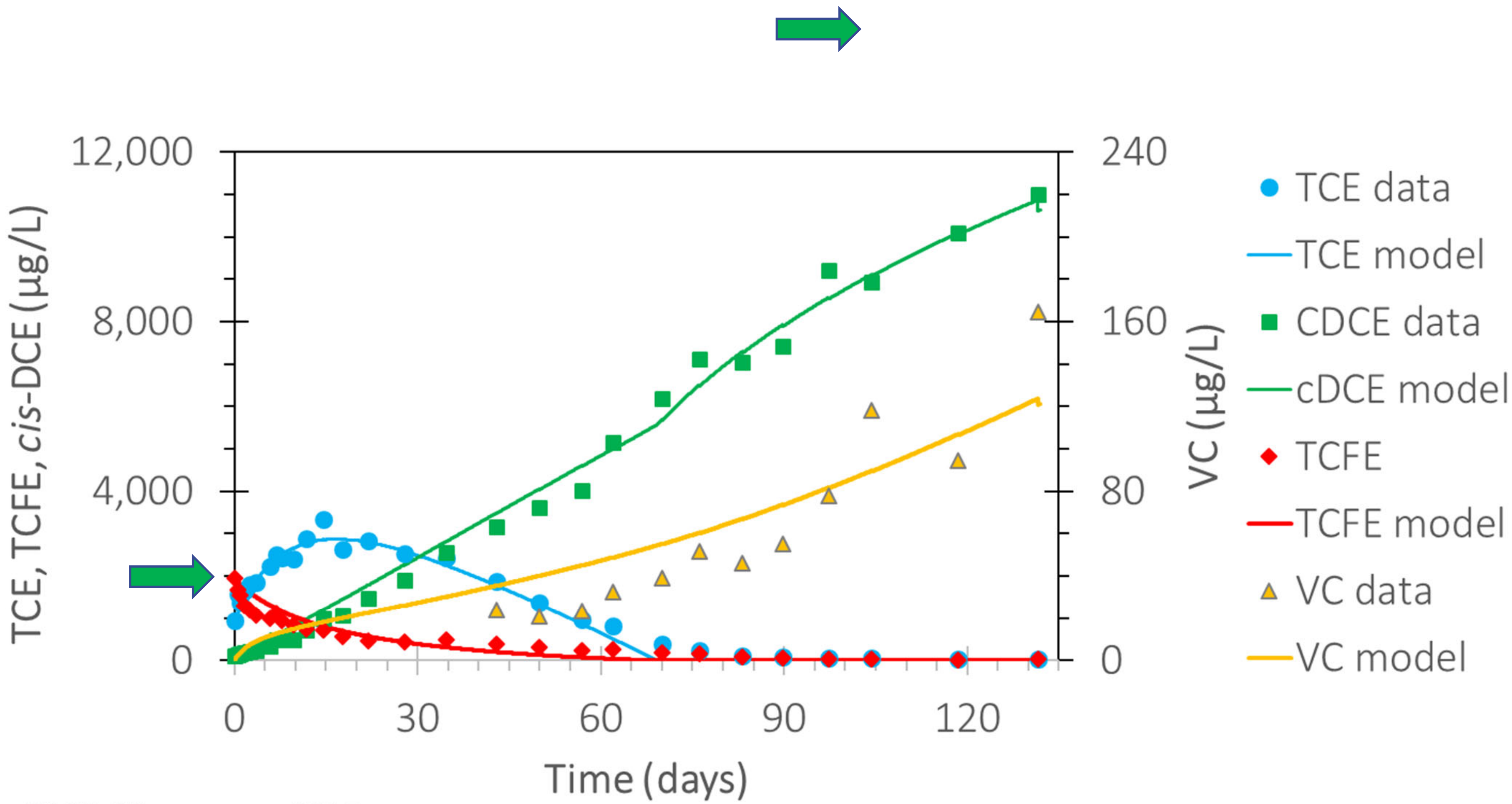
Sorption retains CVOC mass near interface between high & low permeability

- Borehole wall in experiment; fracture interface in field conditions
- "High Kd" in these sedimentary rocks is consistent with overmature organic matter

No evidence of abiotic degradation in this or other tests

- If dissolved phase degrades, impact on overall mass negligible

TCE biodegradation *fast* & cis DCE degradation rate increasing



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Acknowledgements

FINANCIAL SUPPORT

SERDP Project no. ER-2533

& the following USGS programs:

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

SERDP
DOD ▪ EPA ▪ DOE

SITE ACCESS & HISTORIC DATA

US Navy

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