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Natural and Enhanced Biotic and Abiotic Attenuation of TCE in Fractured Sandstone

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Background

- Fractured rock aquifers are common in the US. Remediation of trichloroethene (TCE) in fractured rock can occur via biotic and abiotic pathways. [1,2]
- Predicting transformation rates within low permeability media is challenging. Crushed rock microcosms can be used, but it is unclear how the rates are impacted by crushing. Intact rock core microcosms offer a more realistic assessment of transformation rates but are more difficult to construct and monitor.
- How well do the results from crushed rock microcosms compare to intact microcosms? Can geochemical and geophysical properties be use as surrogates to predict rates? (Fig. 2).

Study Site Characteristics

- A fractured sandstone aquifer in southern California.
- Contaminated by TCE to depths in excess of 244 m.
- Reduction of TCE to *cis*-1,2-dichloroethene (cDCE).
- Trace levels of vinyl chloride (VC), ethene and acetylene.

Figure 1: Fractured sandstone site in southern California.

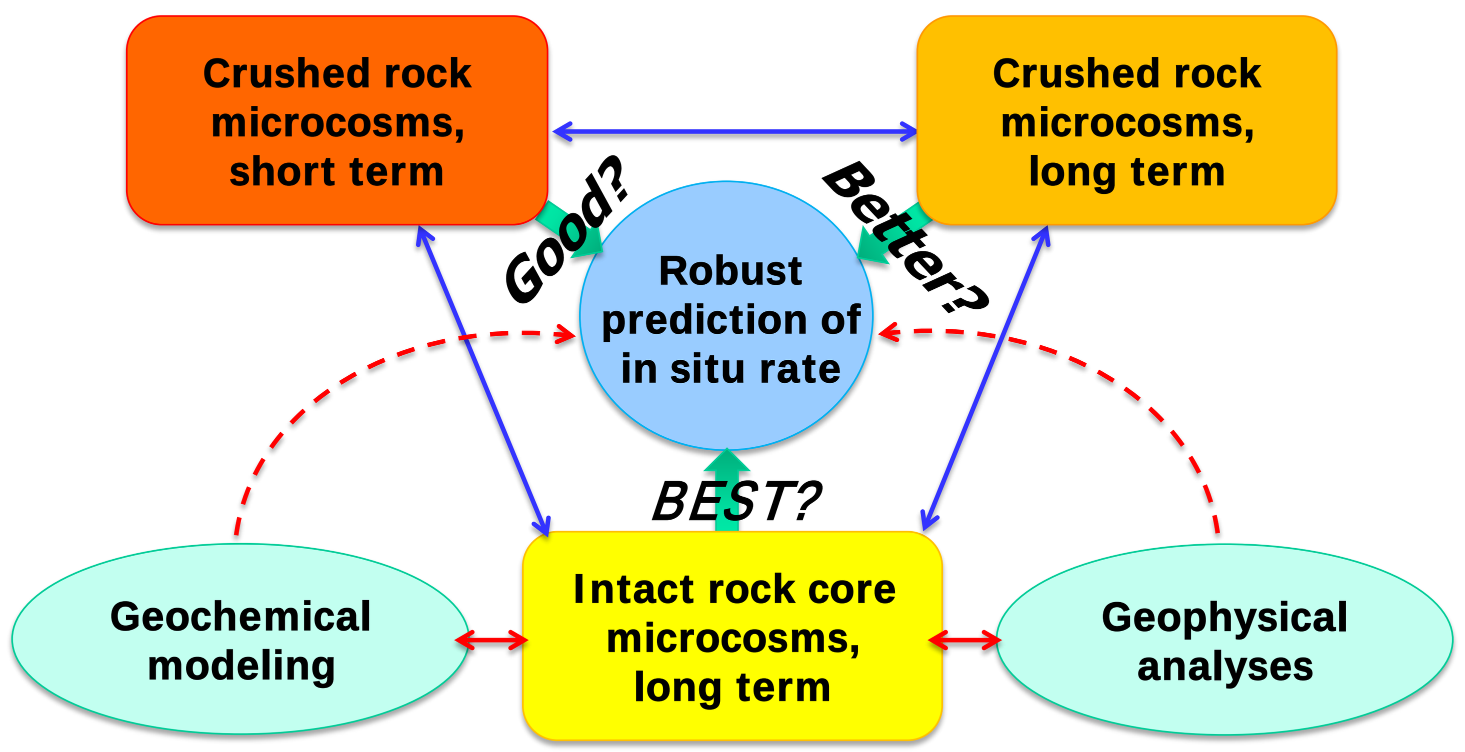

Figure 2: Approaches to predicting transformation rates in low permeability media.

Objectives

- Compare abiotic transformation rates for TCE and cDCE in crushed rock and intact core microcosms.
- Evaluate biostimulation in crushed rock and intact core microcosms.

Crushed Sandstone Microcosms

- **Microcosms**: 50 mL groundwater + 20 g crushed sandstone
- **Biostimulation:** Lactate
- **Controls**: Unamended live microcosms
- Each treatment prepared with and without ^{14}C-TCE or ^{14}C-cDCE. Addition of ^{14}C permitted tracking of CO_2 and nonvolatile products, while microcosms without ^{14}C permitted analysis of δ^{13}C enrichment.

Intact Rock Core Microcosms (Fig. 3 and 4)

- Sandstone core (3" long, 2.375" diameter) sandwiched between two stainless steel end caps. Top cap hollowed out to create a 14.5-mL reservoir that simulated a fracture. Encased in heat-shrinkable Teflon and inserted in a stainless steel pipe, the ends of which were TIG welded to the caps.

Figure 3: Intact core microcosms

- Cores initially saturated with groundwater containing TCE; bromide served as conservative tracer.
- Reservoir initially filled with TCE and bromide-free groundwater; 2 mL of groundwater exchanged weekly via Mininert valves to simulate fracture flow and to collect samples.
- Six pairs of cores, each included two cores collected from the same depth. One received groundwater with lactate, the other received just groundwater and served as controls.

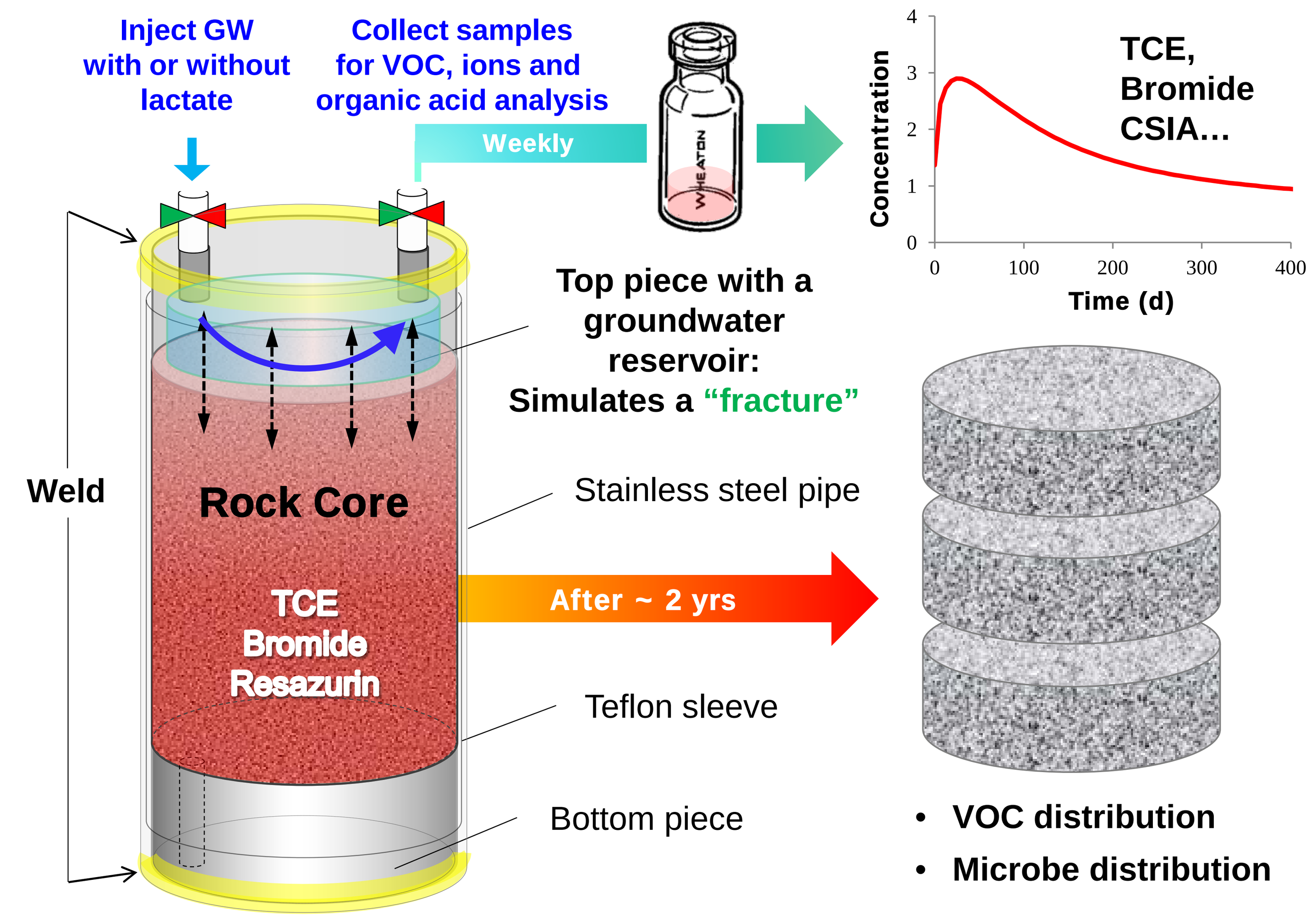

Figure 4: Experimental design for the intact core microcosms

Results: Diffusion and Reaction

- TCE and bromide diffused out of the core in all microcosms (Fig. 5a-5f).
- Reductive dechlorination of TCE to cDCE was complete in 1 unamended and 5 lactate-amended microcosms (Fig. 5e and 5f) after 600 days of incubation; no VC or ethene detected.
- Among the pairs of microcosms, the ones with cDCE production showed significantly more total chlorinated ethene removal than their diffusion-only analogue (Fig. 6).
- Enrichment in δ^{13}C-TCE and cDCE suggested the occurrence of other transformations (Fig. 5g-5i).
- Complete sulfate reduction occurred in lactate-amended units while none occurred in unamended controls (data not shown); lactate was transformed to acetate which was subsequently consumed (data not shown).

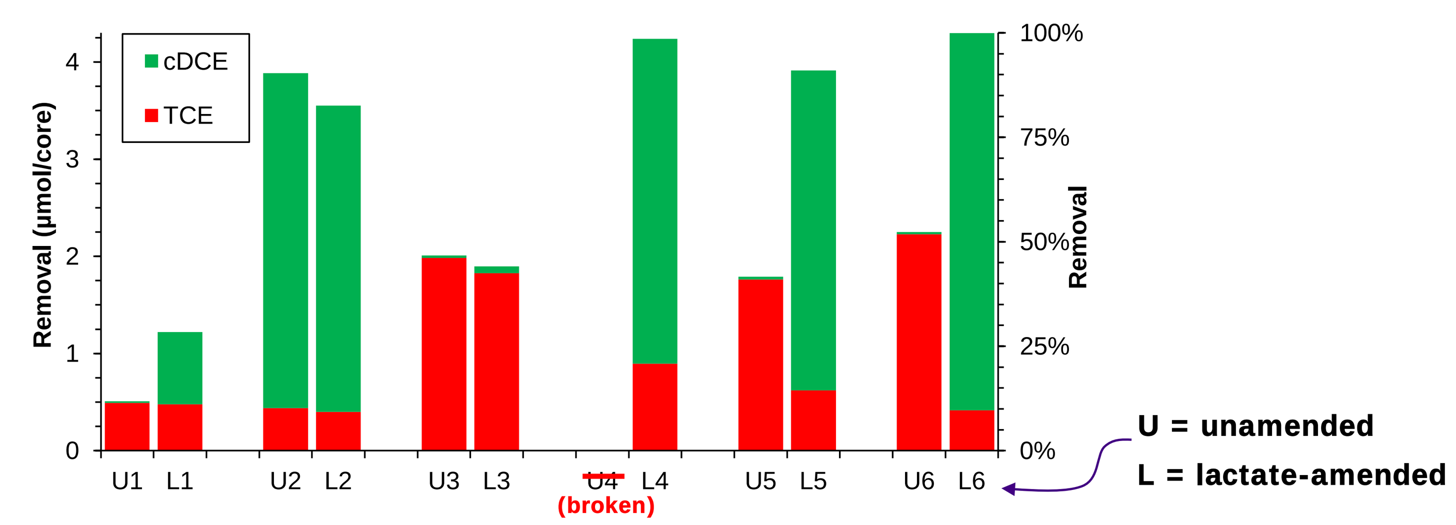

Figure 6: Cumulative removal of TCE and cDCE from rock core microcosms after 600 days.

Table 1: Comparison of crushed rock microcosms and intact core microcosms.

Processes	Crushed Rock Microcosms	Intact Rock Core Microcosms
Reductive Dechlorination	TCE → cDCE → VC → ethene (stimulated by lactate)	TCE → cDCE (stimulated by lactate)
Abiotic Transformation	^{14}C products + δ^{13}C enrichment	δ^{13}C enrichment
Half life (abiotic)	cDCE: 11~31 yr TCE: 11~21 yr (Determined based on ^{14}C data)	cDCE: 40~80 yr TCE: 25~44 yr (Model fitting)

Results: Modeling in COMSOL Multiphysics

- Due to its symmetry, a 3D microcosm can be represented by a 2D model, whose results can be transformed back into 3D via revolution (Fig. 4).
- Governing equations were assigned to diffusion, biodegradation and abiotic transformation processes. Evolution of δ^{13}C compounds was calculated based on their kinetic isotope effect as previously described [3 – 4].
- Parameters were selected from preliminary experiments or based on the literature, and optimized through data fitting.

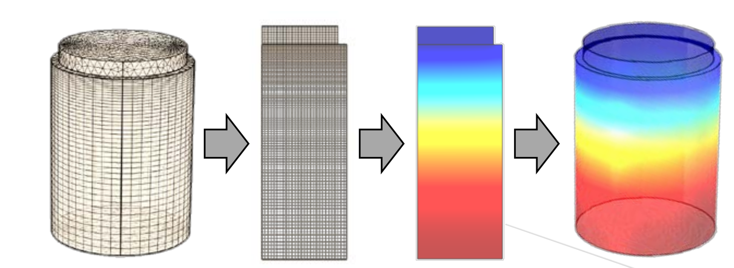

Figure 4: Transformation between 3D and 2D.

Processes Name	Governing Equations	Kinetic Isotope Effect
Diffusion from matrix to fracture	$\frac{\partial C_i}{\partial t} = \varepsilon \tau_{\mathrm{eff,i}} D_{\mathrm{F,i}} \frac{\partial^2 c_i}{\partial x^2} - K_i/R_i$	$D^h = D^l(1+\varepsilon)$
Reductive dechlorination (Monod)	$\frac{dS}{dt} = -\frac{\hat{\mu}X}{Y} \cdot \frac{S}{K_s + S} \quad \left(\hat{q} = \frac{\hat{\mu}}{Y}\right)$	$\hat{\mu}^h = \hat{\mu}^l(1+\varepsilon)$
Microbial growth (Monod)	$\frac{dX}{dt} = -\frac{dS}{dt}Y - K_d X = \frac{\hat{\mu}S}{K_s + S}X - d_H X$	
1st order abiotic transformation	$\frac{dC_i}{dt} = -kC_i$	$k^h = k^l(1+\varepsilon)$

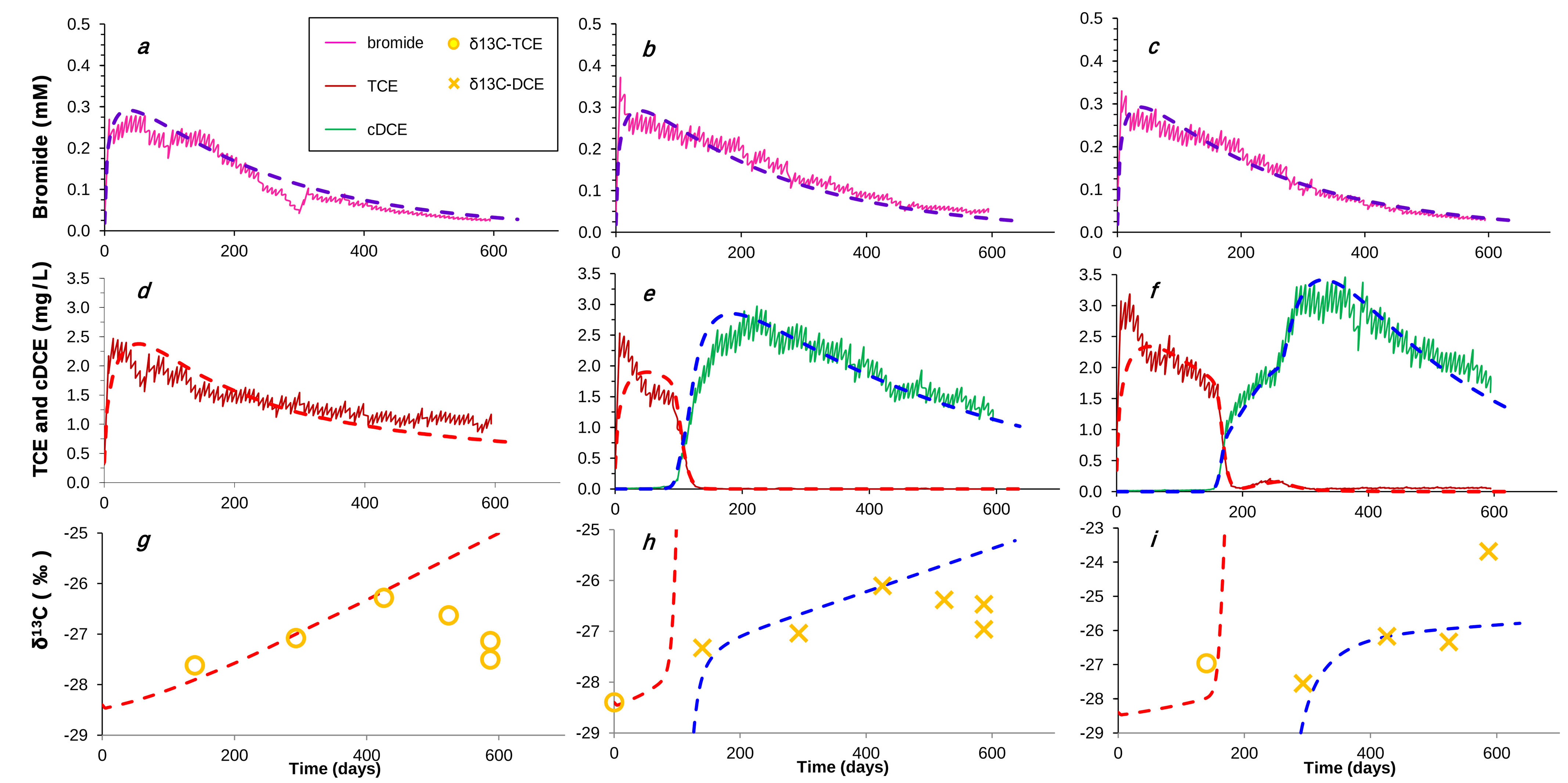

Figure 5: Monitoring results and COMSOL simulation for bromide (*a-c*), TCE and/or cDCE (*d-f*) and δ^{13}C-TCE and/or δ^{13}C-cDCE (*g-i*) in unamended microcosm #3 (left panel), lactate-amended #2 (middle panel) and lactate-amended #4 (right panel). Dashed lines represent COMSOL model simulation.

Conclusions

- **Crushed rock microcosms (Table 1)** suggested that biostimulation with lactate is effective in enhancing reductive dechlorination in fractured sandstone.
- Occurrence of abiotic transformation was confirmed based on increase in $^{14}CO_2$ and ^{14}C-NSR as well as δ^{13}C enrichment; half lives were calculated as **11~31 yr** for cDCE and **11~21 yr** for TCE.
- In **intact rock core microcosms (Table 1)**, reductive dechlorination of TCE to cDCE was complete in 5 of the lactate-amended and 1 of the unamended units, but VC was not detected. VOC removal was significantly higher in cores with TCE → cDCE.
- Abiotic processes for TCE and cDCE confirmed by enrichment in δ^{13}C.
- A 2D numerical model developed in COMSOL successfully simulated diffusion, abiotic and biotic reactions of bromide, TCE and cDCE.
- Evolution of δ^{13}C during diffusion, biodegradation and abiotic transformation processes was successfully modeled and calibrated using δ^{13}C-TCE and δ^{13}C-cDCE data.
- Half lives were **40~80 yr** for cDCE and **25~44 yr** for TCE, lower than rates in crushed rock microcosms. Intact rock core microcosms should be more representative of the rate of *in situ* transformation.
- Intact rock core microcosms plus numerical modeling are useful tools in understanding the effects of natural attenuation and biostimulation on contaminants in sedimentary rock.

References

1) **Darlington R, Lehmicke L, Andrachek RG, Freedman DL.** 2008. Biotic and abiotic anaerobic transformations of trichloroethene and cis-1,2-dichloroethene in fractured sandstone. Environ. Sci. Technol. **42:**4323-4330.
2) **Darlington R, Lehmicke LG, Andrachek RG, Freedman DL.** 2013. Anaerobic abiotic transformations of *cis*-1,2-dichloroethene in fractured sandstone. Chemosphere **90:**2226-2232.
3) **Bouchard D, Cornaton F, Höhener P, Hunkeler D.** 2011. Analytical modelling of stable isotope fractionation of volatile organic compounds in the unsaturated zone. J. Contamin. Hydrol. **119:**44-54.
4) **Cretnik S, Bernstein A, Shouakar-Stash O, Löffler F, Elsner M.** 2014. Chlorine isotope effects from isotope ratio mass spectrometry suggest intramolecular C-Cl bond competition in trichloroethene (TCE) reductive dehalogenation. Molecules **19:** 6450-6473.

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