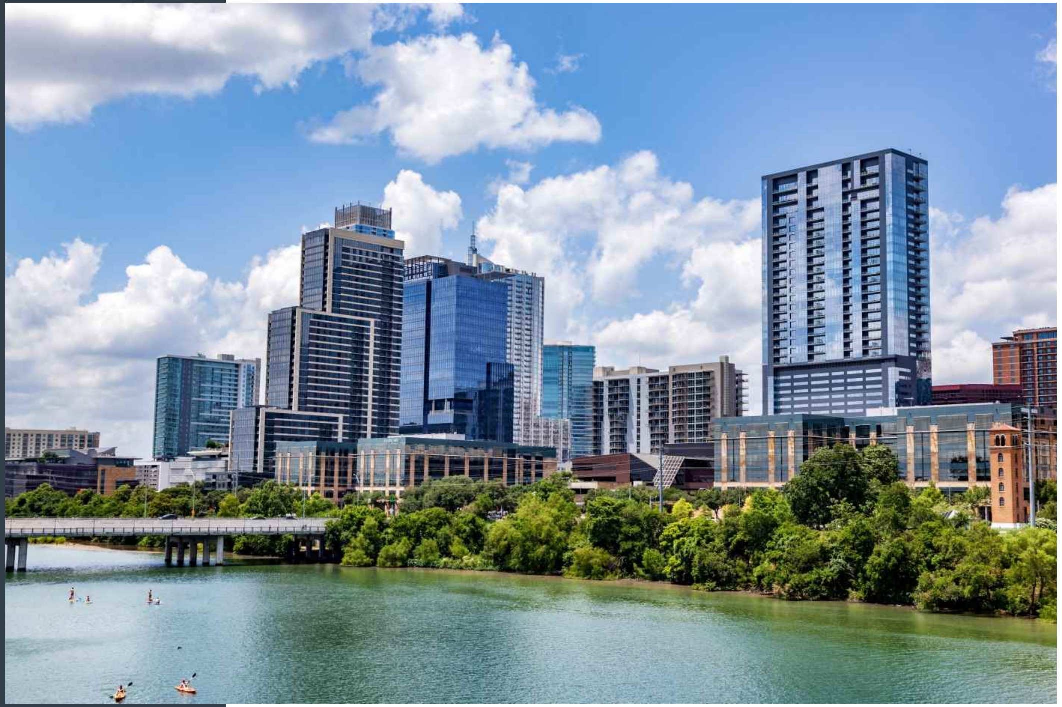
Geosyntec consultants

CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

Microcosm Evaluation of TCE Degradation in Fractured Rock in Response to Amendments

Hao Wang



Team Efforts

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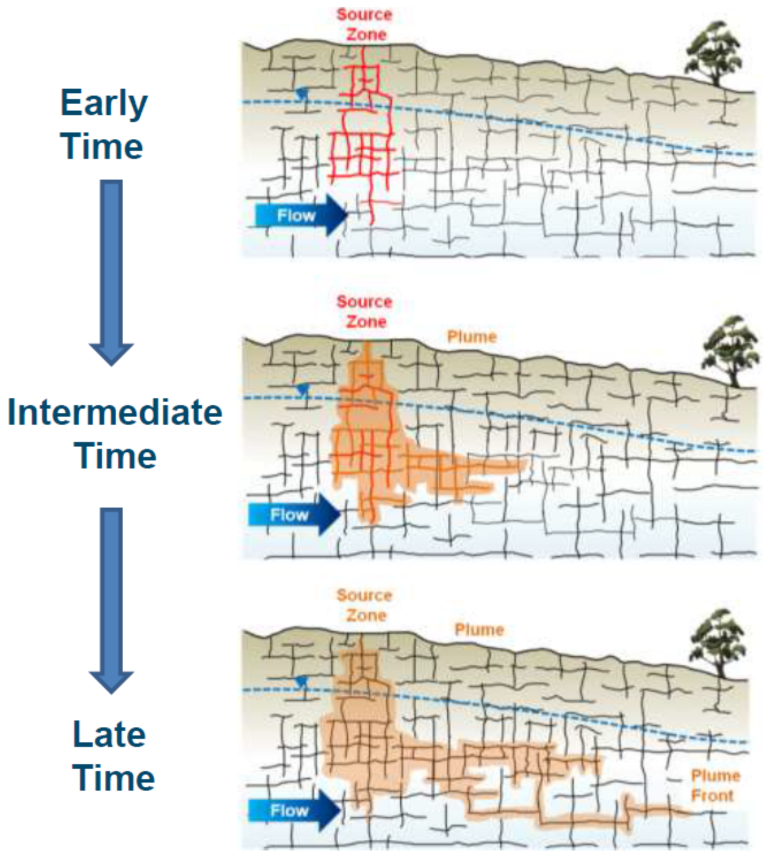
Ramona Darlington Iery (NAVFAC EXWC)

- Rong Yu (Synterra)

Project #ER-2622

Background

TCE contamination of **low permeability media (fractured bedrock aquifer)** occurs in three phases:



DNAPL reaches stationary phase in fractures

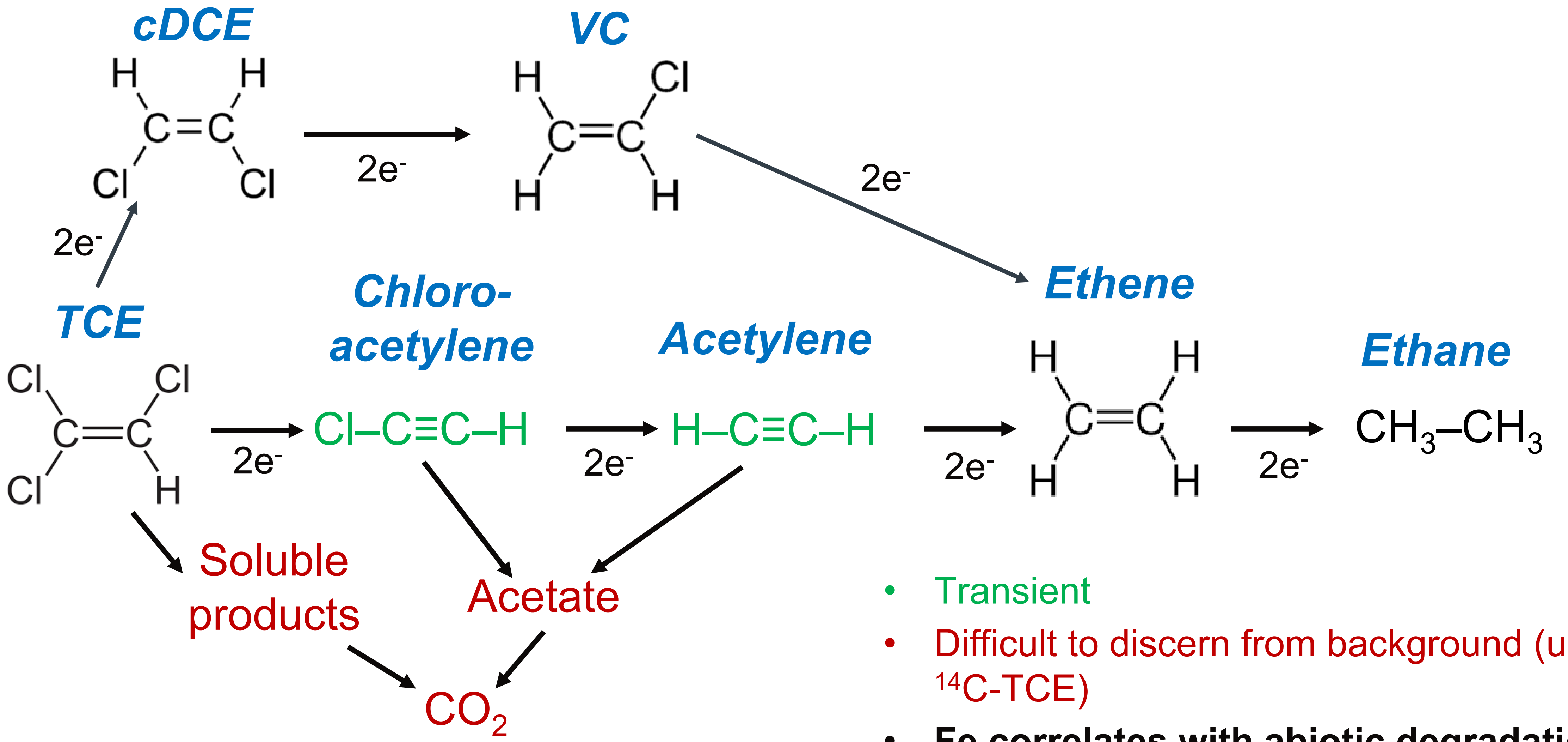
Much DNAPL gone, diffusion into matrix in source and plume zones

All DNAPL gone, most mass resides in matrix; back diffusion contributes to persistent groundwater contamination

Parker et al. 2012

The remainder: Does TCE in the matrix undergo abiotic or biotic degradation?

TCE Degradation Pathways



- Transient
- Difficult to discern from background (use ^{14}C-TCE)
- **Fe correlates with abiotic degradation**

Coupling TCE Degradation and Back-diffusion

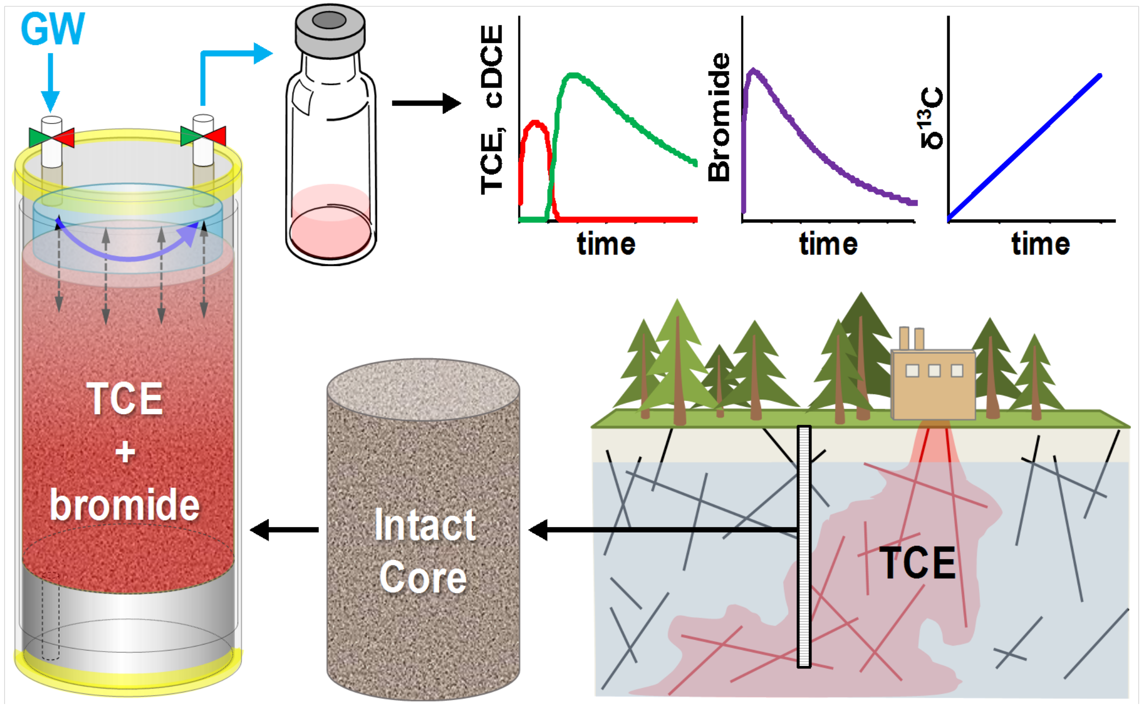
- Crushed rock microcosms:
  - Crushed rock & groundwater in serum bottles: evaluation of results subject to rock surface change; fast (~40 days) and less expensive.
  - Tracking acetylene + ethene + ethane, ^{14}C-labeled products.

- Intact core microcosms:
  - Less rock surface change and disturbance on degradation chemistry;
  - Mimic back-diffusion processes;
  - More complex but comprehensive.

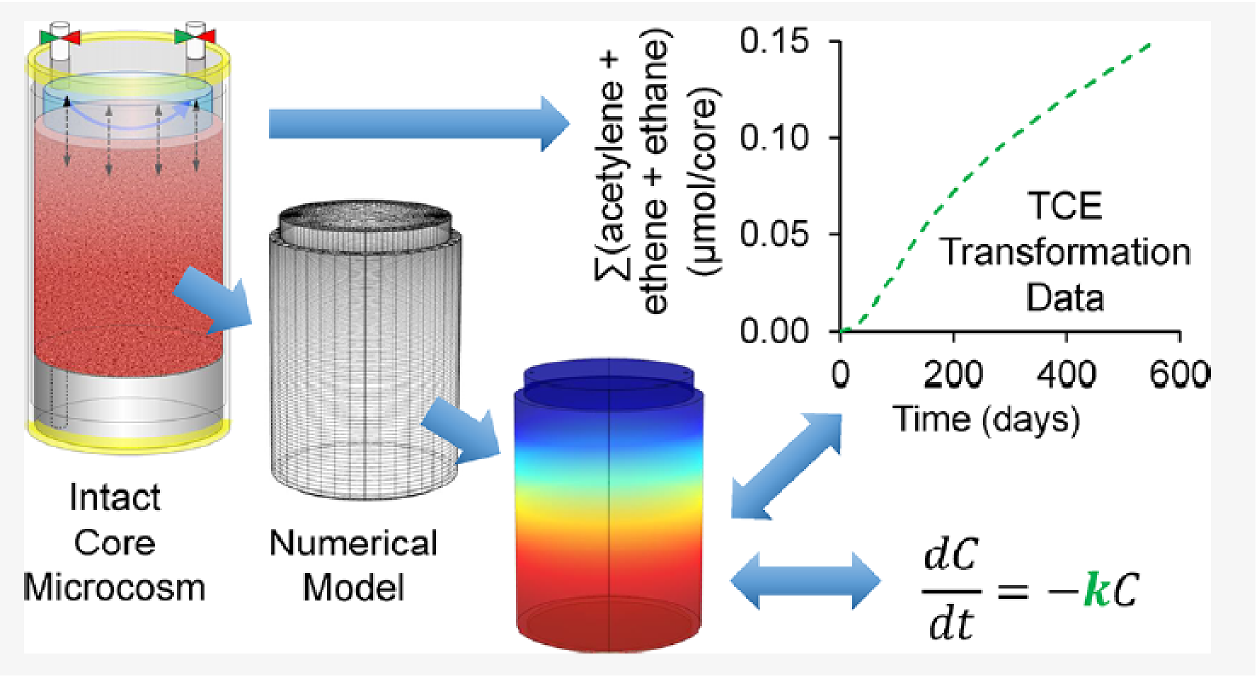
Intact core microcosm study tracks product accumulation and back-diffusion to provide a line of evidence for monitored natural attenuation

Determine Rate Constants with Intact Core Microcosms

Monitor Br⁻ diffusion and TCE attenuation



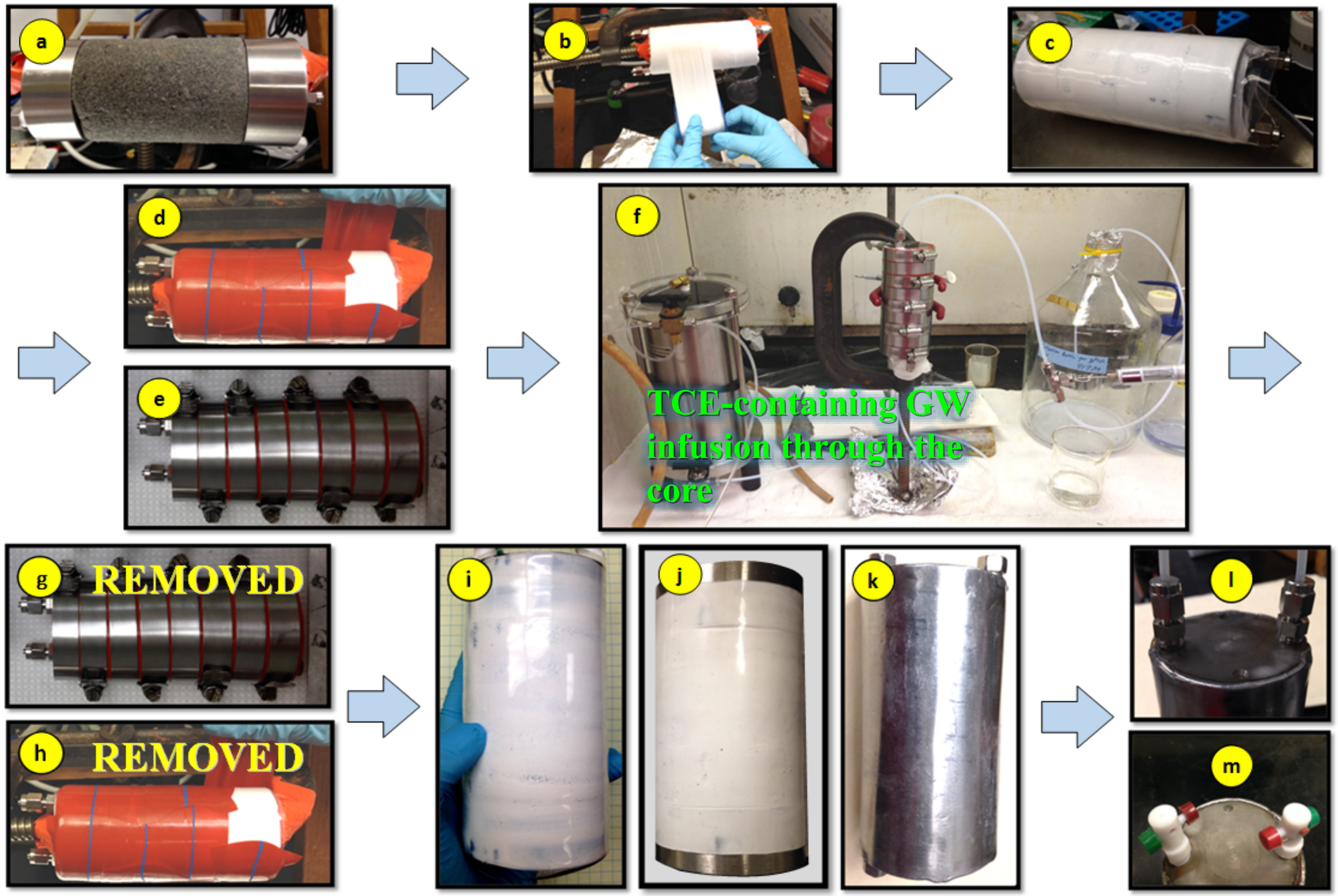
Observation-based Inverse Modeling for rate constants



Objectives

- Compare the effects of lactate and lactate + sulfate amendments on
  - biotic, and
  - biologically mediated abiotic degradation (BMAD) of TCE
- Evaluate TCE degradation rate
  - by natural attenuation processes,
  - using novel intact rock core microcosms

Microcosm Preparation



Key points:

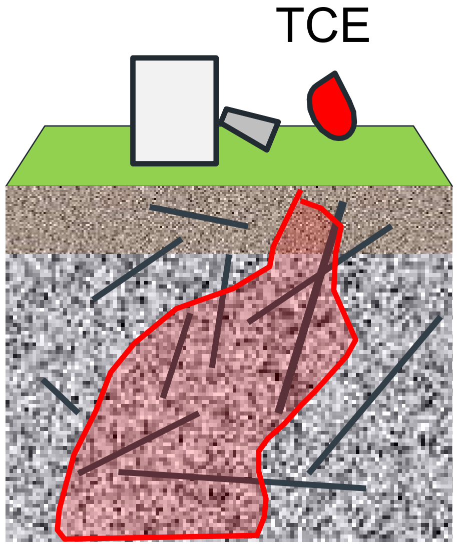
- ❑Reproduce the contamination process within the intact rock core;
- ❑Mimic pump-and-treat with clean GW flushing.

Intact Core Microcosm Study #1

Chatsworth formation (California): Formation comprised of sandstone and interbedded siltstone and shale units.

Credit: NASA

Thousands of tests with liquid-fueled rocket engines from 1950s to 2005;
TCE used to clean the tested engines



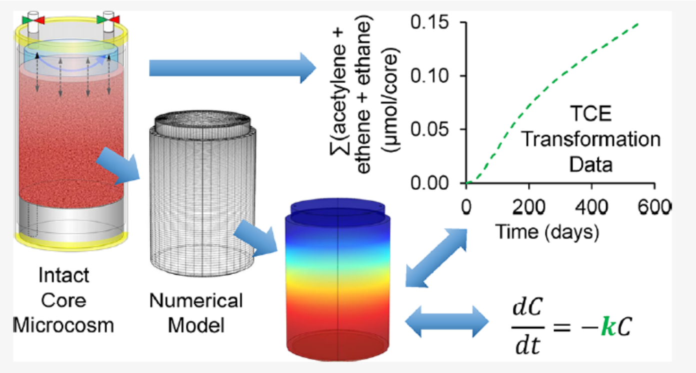
TCE DNAPL released:
Total ~500,000 gallons;
Up to 244 m (800 ft) bgs;
Up to 5,200 µg/L (ppb)

Microcosm Design

15 microcosms

- ❑ 5 unamended (1 broke)
- ❑ 6 lactate-amended
- ❑ 3 stainless steel vessel controls
- ❑ Operated for ~600 days

Transport & Reaction Model (2D r-z coordinate system)

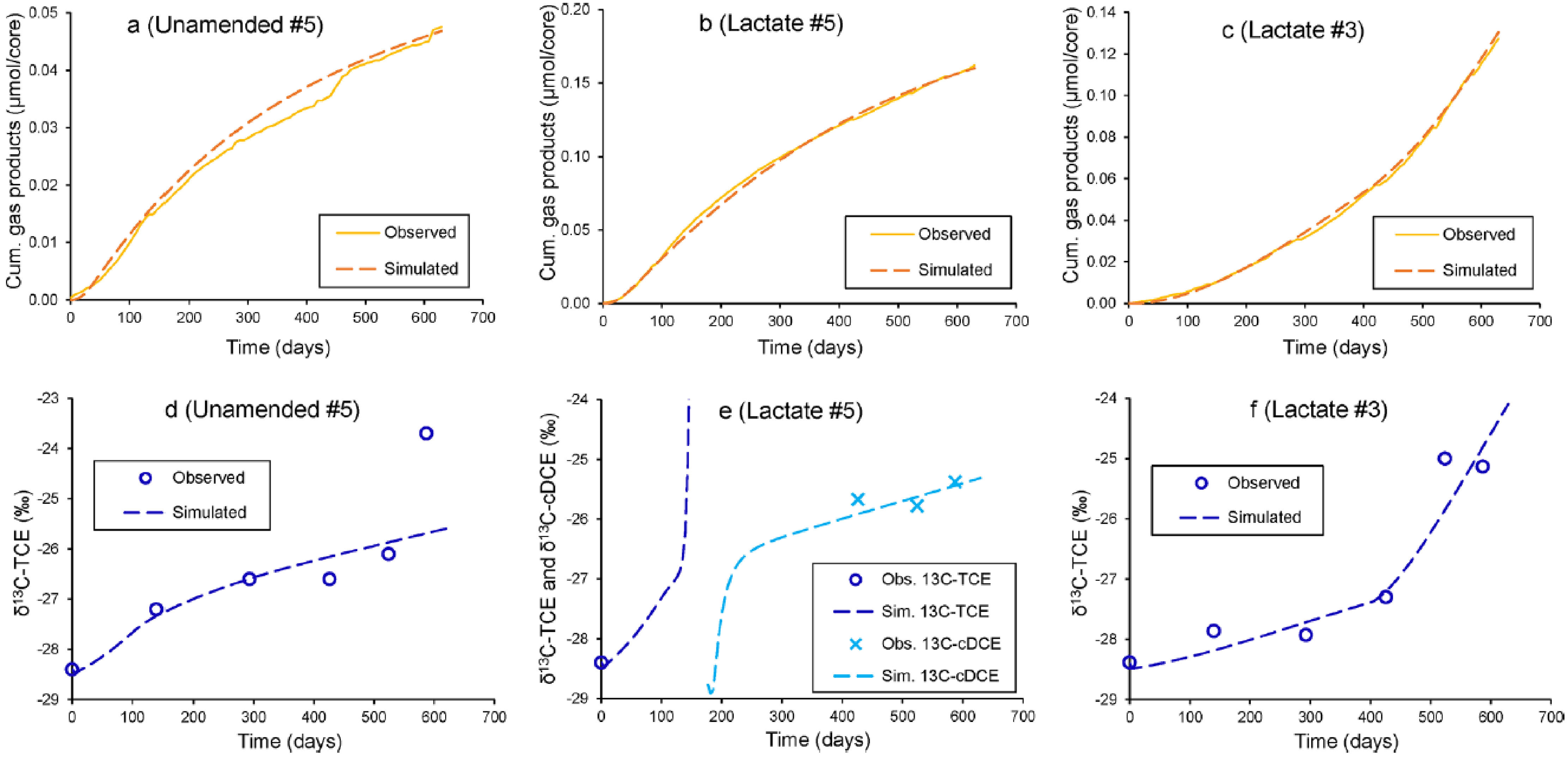


Mass Balance Equation:

Storage term | Transport term | Reaction terms

- C = TCE and Br^- concentration or $\delta^{13}C$ in microcosms
- t = time
- z = downstream distance between diffusion source and a specific depth of the core
- r = distance from the centerline
- κ = lumped diffusivity, $D_f^*\tau/R$
  - D_f = diffusion coefficient for the solute in water; τ = matrix tortuosity; R = retardation coefficient
- K_{CR} = apparent degradation rate for reductive dichlorination, $K_{CR} = k_{CR}{}^*C$
- K_{CA} = apparent degradation rate for abiotic degradation, $K_{CA} = k_{CA}{}^*C$

Results: Gas products and $\delta^{13}C$ enrichment



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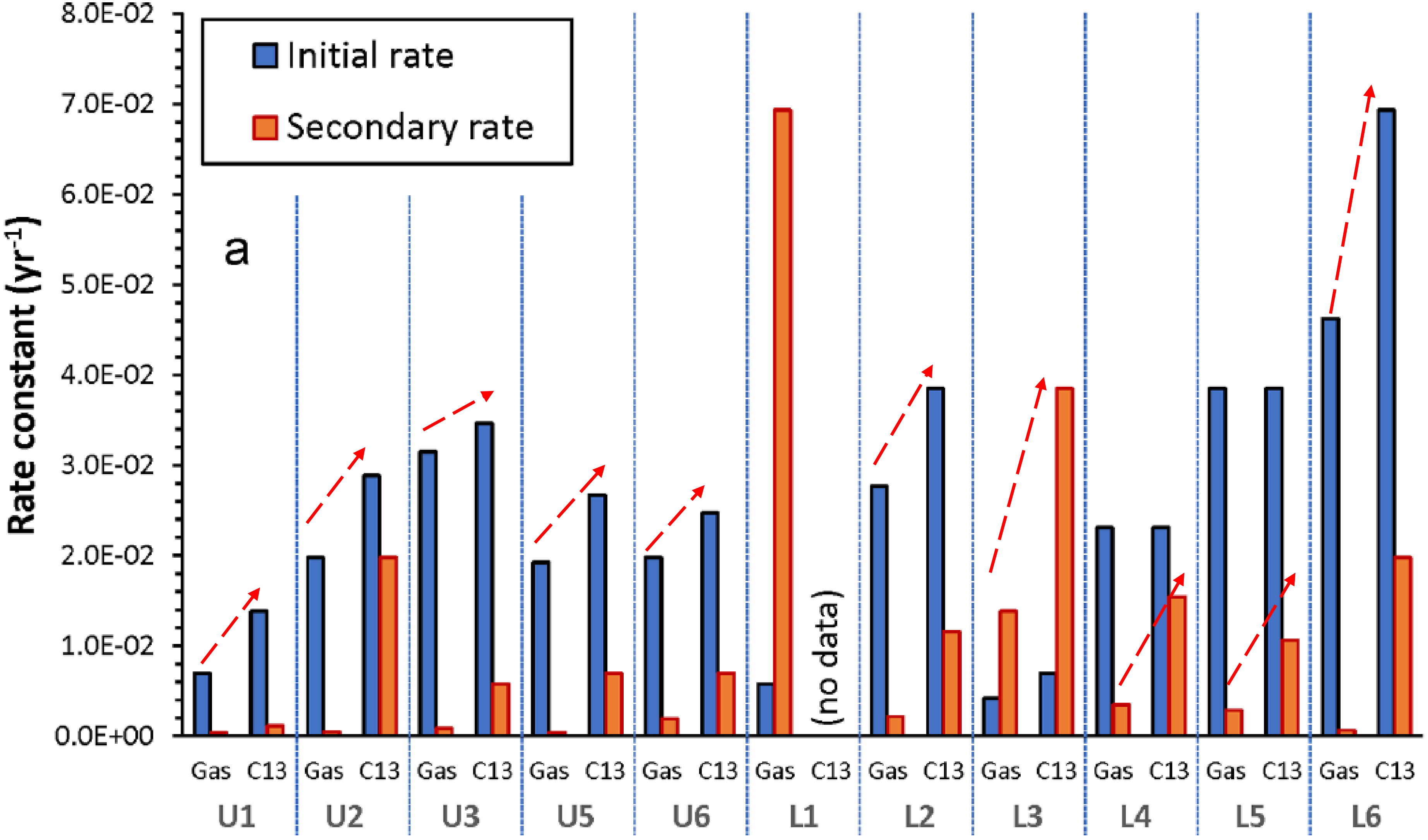


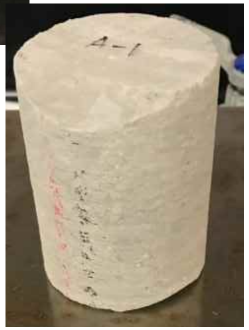
Key Points:

- ❑ Determined rate constants based on gases and $\delta^{13}C$ observations
- ❑ Lactate improved rates
- ❑ $k_{c13} > k_{gases}$; what are we missing?

Intact Core Microcosm Study #2

Site #	Location	Prevailing Geology	Porosity (%)	Fe (ppm)	MS (m^3/kg)
1	Coastal Atlantic	Limestone (mud)	3.6 ± 1.4	1,209 ± 93	2.4E-9 ± 2.3E-9
2	Mid-South	Limestone (mildly Karstic)	16.6 ± 0.7	1,554 ± 151	3.9E-9 ± 3.7E-9
3	Coastal Atlantic	Shale	6.1 ± 3.3	34,299 ± 1,129	-

DOD Sites

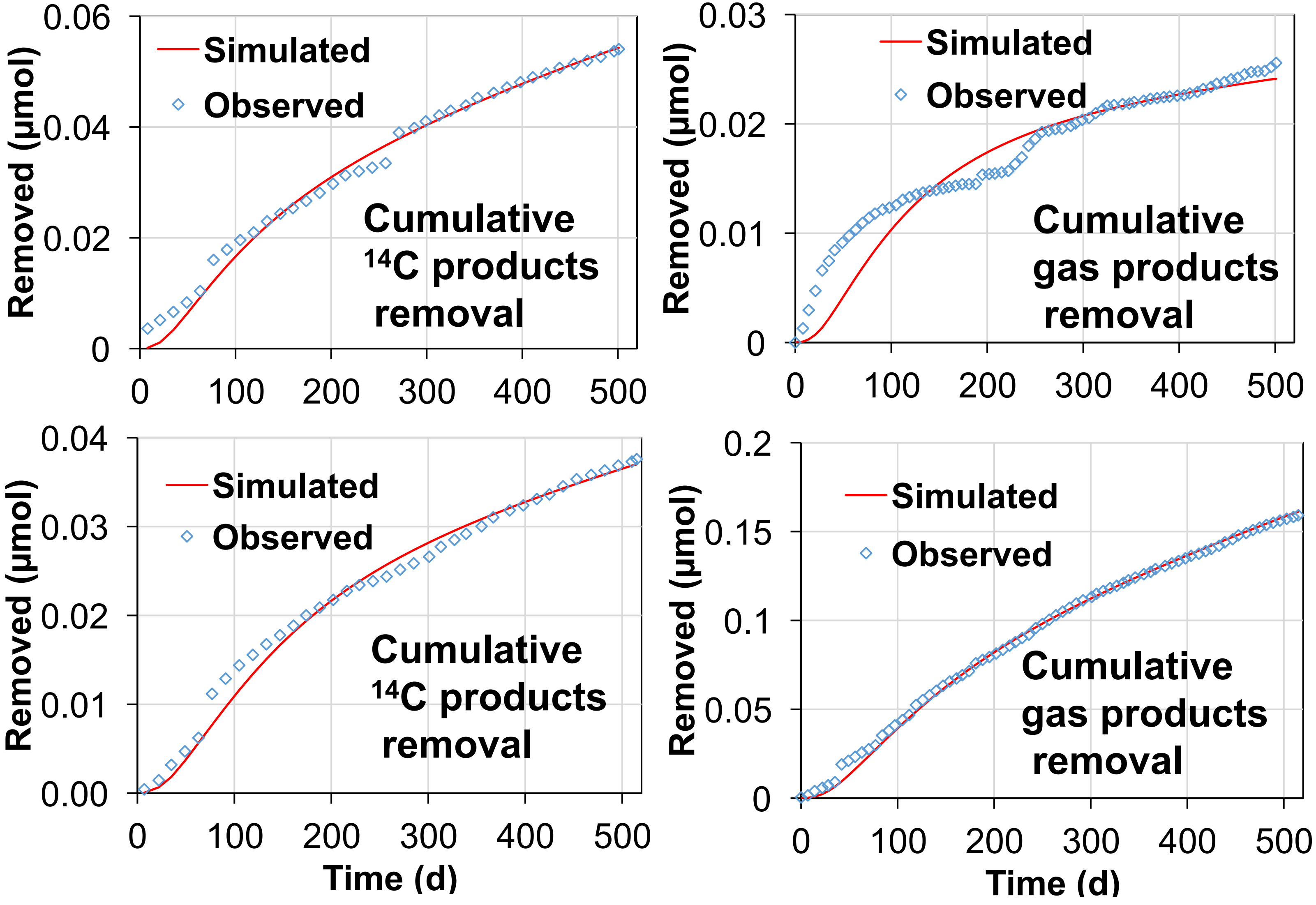


Microcosm Design

- Key advance: Addition of ^{14}C-TCE and non-labeled TCE into one half of the microcosms; the other half received non-labeled TCE only
- Weekly monitoring of ^{14}C-products, VOCs, bromide, sulfate, VFAs; periodic samples for $\delta^{13}C$
- ~38 microcosms per site
- Incubation time: 300~530 days

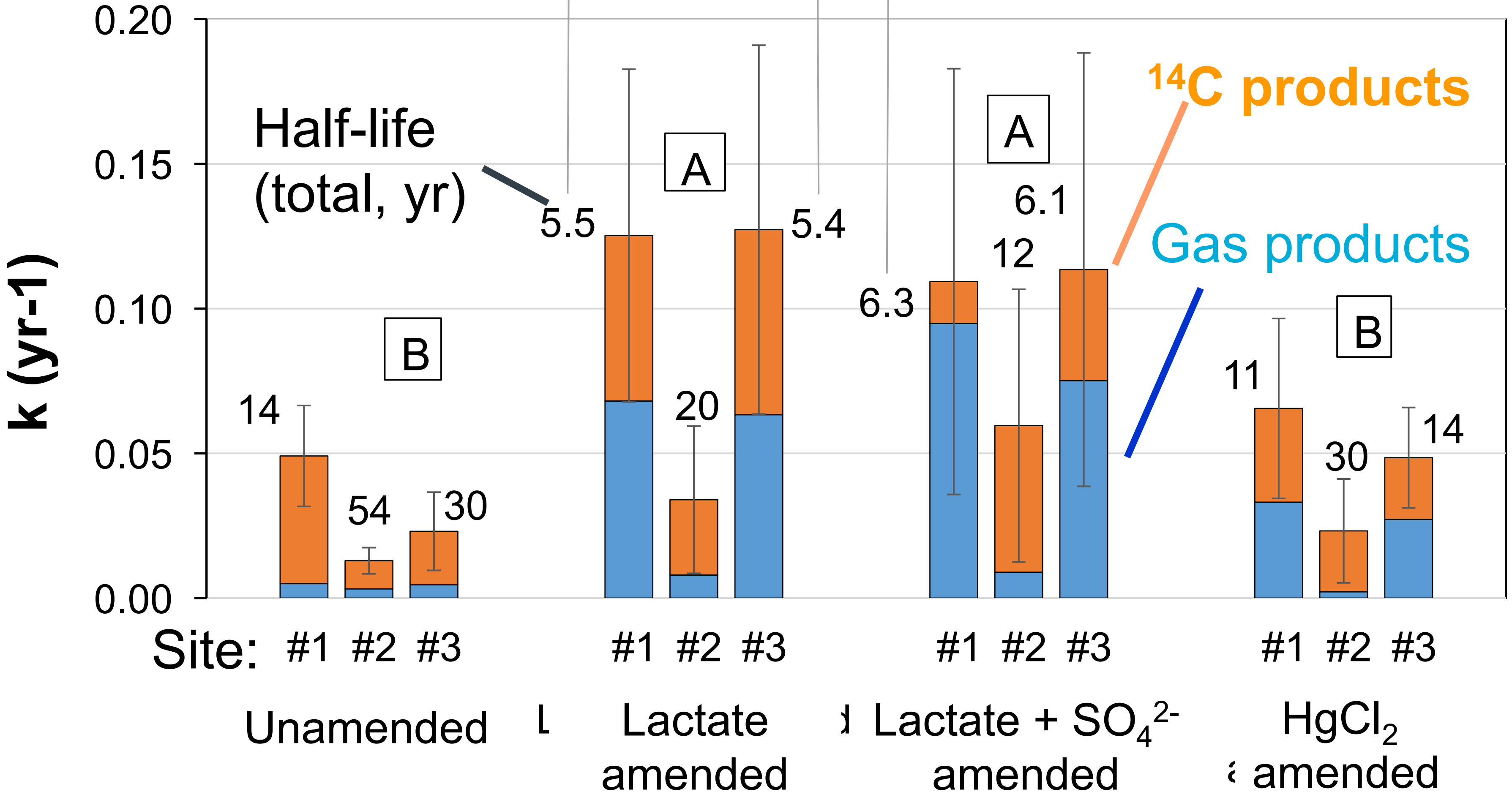
4 Unamended
4 Lactate Amended
4 Lac + SO_4^{2-} Amended
4 $HgCl_2$ amended
3 Container Control

Results: Unamended and L+S Treatment



	Unamended (Site #1)	Lactate + Sulfate (Site #1)
Final Phase	**31-501 d**	**40-515 d**
k_{14C} (yr^{-1})	0.046	0.014
k_{gases} (yr^{-1})	0.0051	0.15
k_{total} (yr^{-1})	0.051	0.17

Overall Results: Abiotic k_{final}



Final Phase:

- *n = 8 for gases*
- *n = 4 for ^{14}C*

Comparison of sites:

#1 = #3 > #2

- *Comparison of treatments:*

(Lac = L+S) > (UN = Abiotic)

Summary

- Lactate and lactate + sulfate amendment enhanced TCE degradation. Electron donor delivery cost-effectiveness needs evaluation;
- Involving ^{14}C-TCE allowed more complete tracking estimations of TCE degradation, especially for those treatments where TCE abiotic degradation > biotic degradation;
- Intact rock core provided a test environment to reproduce TCE back-diffusion and degradation; the rate estimation was consequently more realistic;
- Future studies: Correlation between the TCE abiotic degradation rate constants and mineralogical properties (Fe contents) and geophysical measurements (magnetic susceptibility, electrical resistivity).


Questions