Monitoring of Geological CO_2 Sequestration Using Isotopes and Perfluorocarbon Tracers

Project Number FEAA-045

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U.S. Department of Energy

National Energy Technology Laboratory

Mastering the Subsurface Through Technology Innovation, Partnerships and Collaboration: Carbon Storage and Oil and Natural Gas Technologies Review Meeting

August 13-16, 2018

Presentation Outline

- Tracers & their applications to C storage
- Cranfield CO_2 storage pilot site
  - PFT simulations
  - CH_4 exsolution tracer
- Coupling reaction modeling with transport simulations
- Hydrocarbon interference with PFT analysis
- Accomplishments & Synergies

Candidate Tracers
(substances used to follow the course of a process)

Brines: Native non-conservative tracers that respond to changes

pH, alkalinity, electrical conductivity

Cations: Na, K, Ca, Mg, ΣFe, Sr, Ba, Mn

Major anions: Cl, HCO_3, SO_4, F, Br

Organic acids: acetate, propionate, formate, oxalate, etc.

Other organics: DOC; methane, CO_2, benzene, toluene

Gases: Native conservative tracers or added conservative tracers

Gases: N_2, H_2, O_2, CO_2, CO, CH_4, $C_2 – C_{n+}$

Noble gas tracers: Ar, Kr, Xe, Ne, He (and their isotopes)

Perfluorocarbon tracers (PFTs):

PMCP, PECH, PMCH, PDCH, PTCH (SF_6)

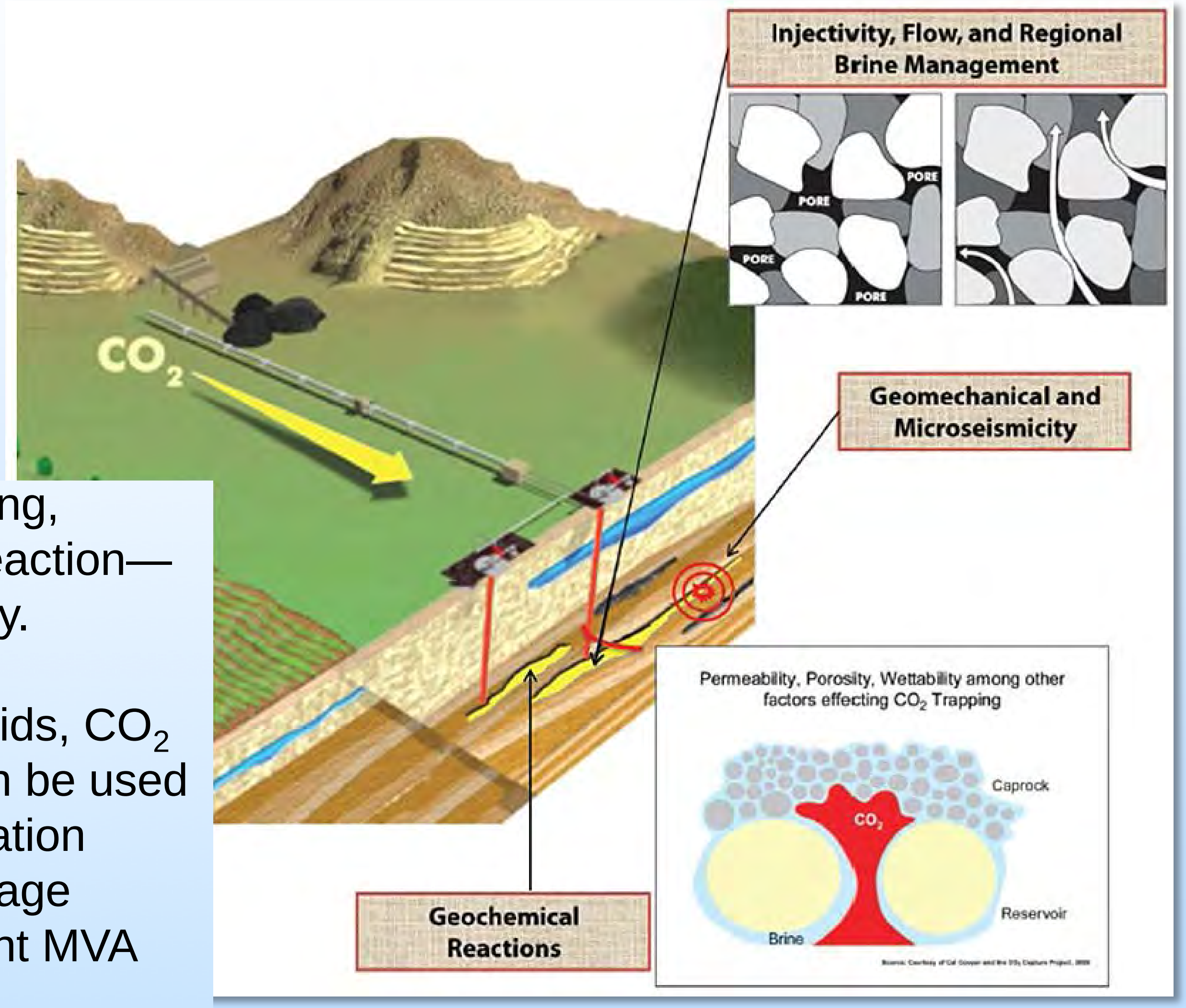
Isotopes: D/H, $^{18}O/^{16}O$, $^{87}Sr/^{86}Sr$ in water, DIC, minerals;

$^{13}C/^{12}C$ in CH_4, CO_2, DIC, DOC, carbonates

Benefit to Program

Geologic Storage, Simulations, and Risk Assessment

- Provide information on physical and geo-chemical changes in reservoir, ensuring CO_2 storage permanence.
- Facilitate fundamental understanding of processes impacting behavior of fluids —diffusion, dispersion, mixing, advection, capillarity, and reaction— to improve storage efficiency.
- Ground-truth behavior of fluids, CO_2 transport properties that can be used to constrain reservoir simulation models, predicting CO_2 storage capacity & designing efficient MVA programs.



Modified from NETL Carbon Storage GSRA Technology Research Areas Illustration

Project Overview

Current Goals and Objectives

Provide methods to interrogate the subsurface that will allow direct improvement of CO_2 storage

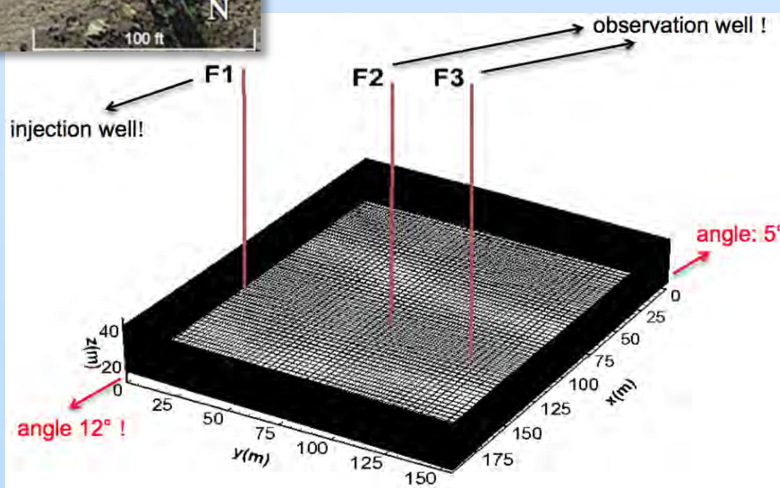
- Incorporate CO_2-brine chemical and isotopic reactions and transport into simulations
- Assess efficiency of perfluorocarbon tracer analysis using capillary adsorption tubes in a hydrocarbon-rich matrix

Cranfield Pilot Site, Mississippi

Carbon Storage Project: Detailed Area of Study

Extracted from > 60 million element model by UTBEG Hosseini et al., *IJGCC* (2013)

- $155 \times 195 \times 24$ m^3, inclined in *x* and *y*
- $64 \times 51 \times 79 = 257{,}856$ unstructured grid cells,
- F2 and F3 well locations (70, 100 m) from Ajo-Franklin et al., *IJGGC*, 2013
- Petro-physical properties for 8 facies

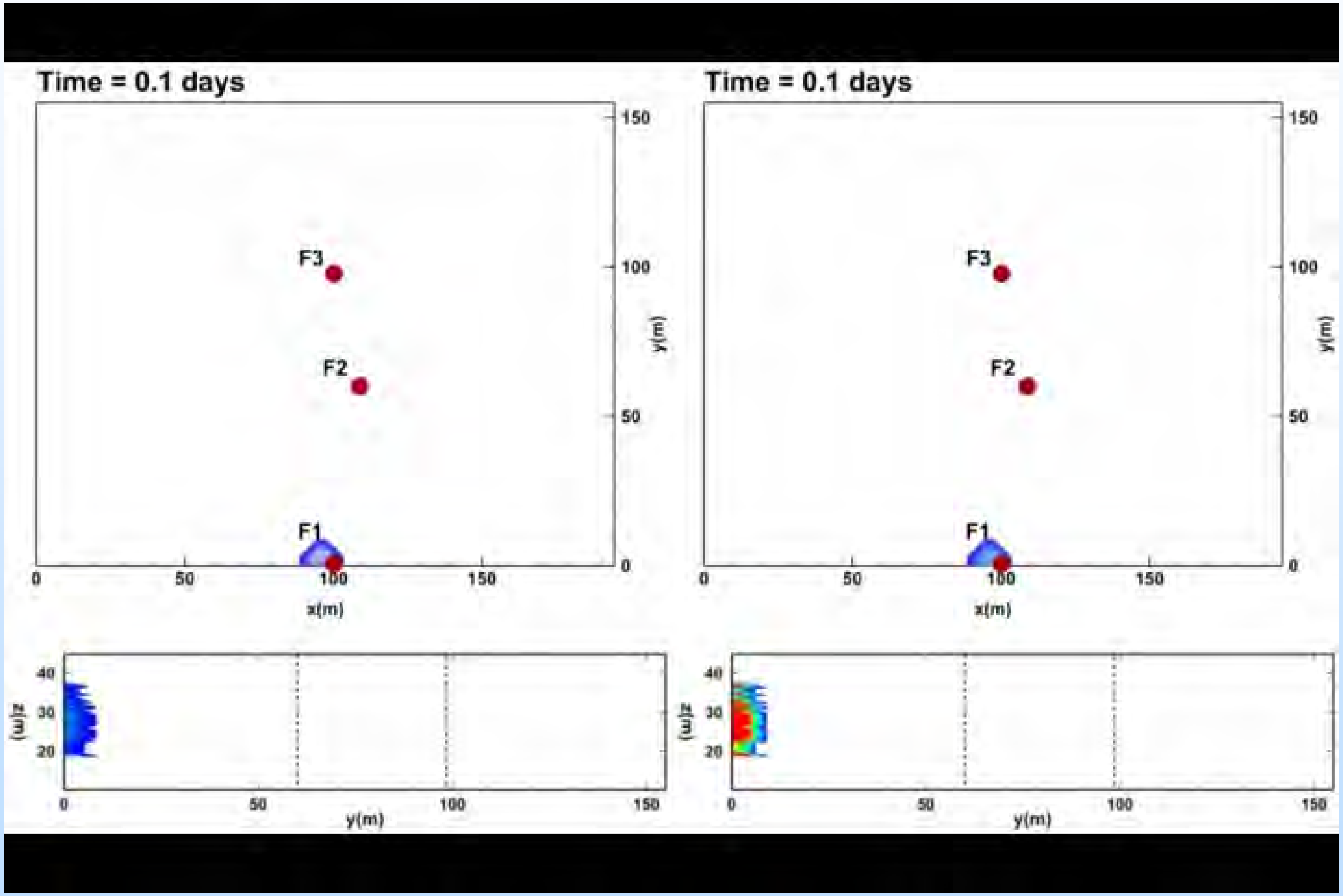


Thanks to:

- Hovorka & Hosseini @UT BEG
- LBNL, SECARB
- Sandia Technology
- Denbury Resources

Top View – Cranfield DAS 2009 CO_2 and PFT Injection Campaign

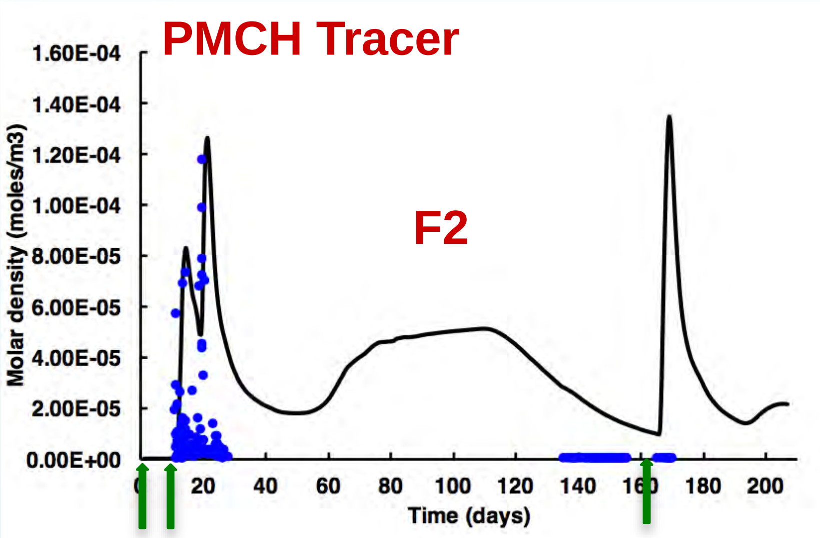
CO_2 **PMCH Injection (0 & 11 days)**

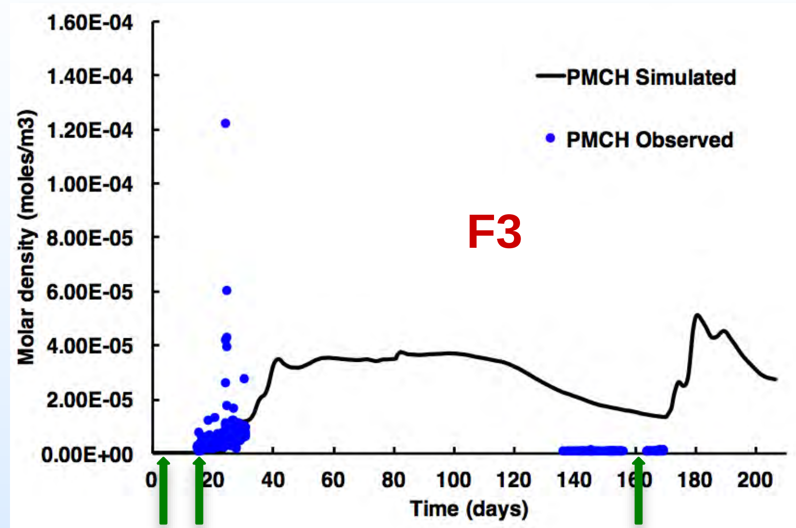


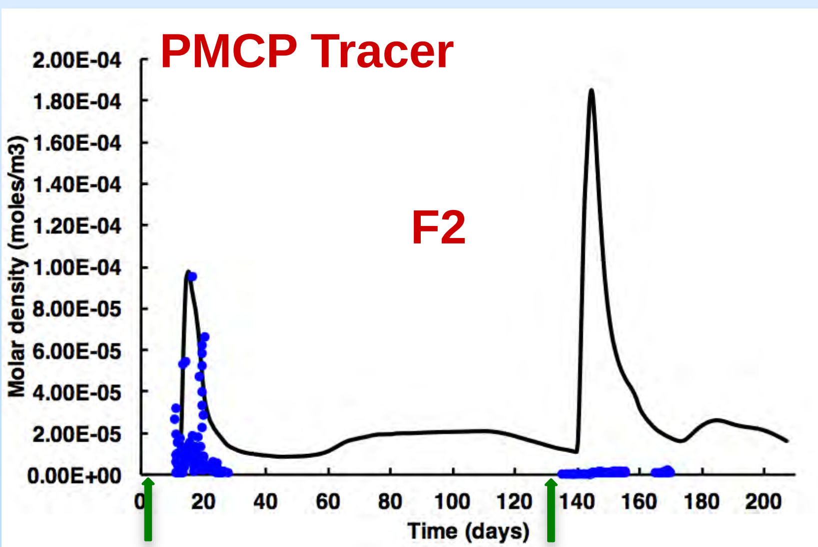
Soltanian MR, Amooie MA, Cole D, Graham D, Pfiffner S, Phelps T, Moortgat J (2018) Transport of perfluorocarbon tracers in the Cranfield Geological Carbon Sequestration Project. Greenhouse Gases: Science and Technology 8(4):650-671

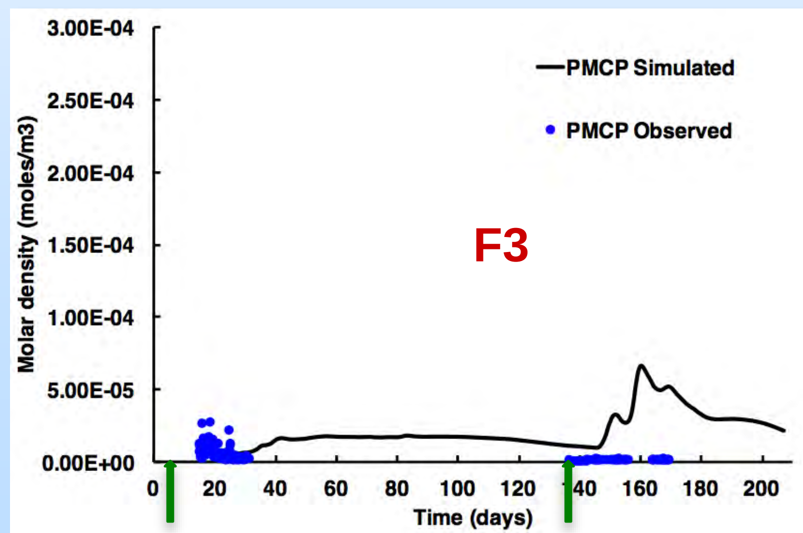
Simulating PFT Injection Campaign

2009-2010 Breakthrough Curves









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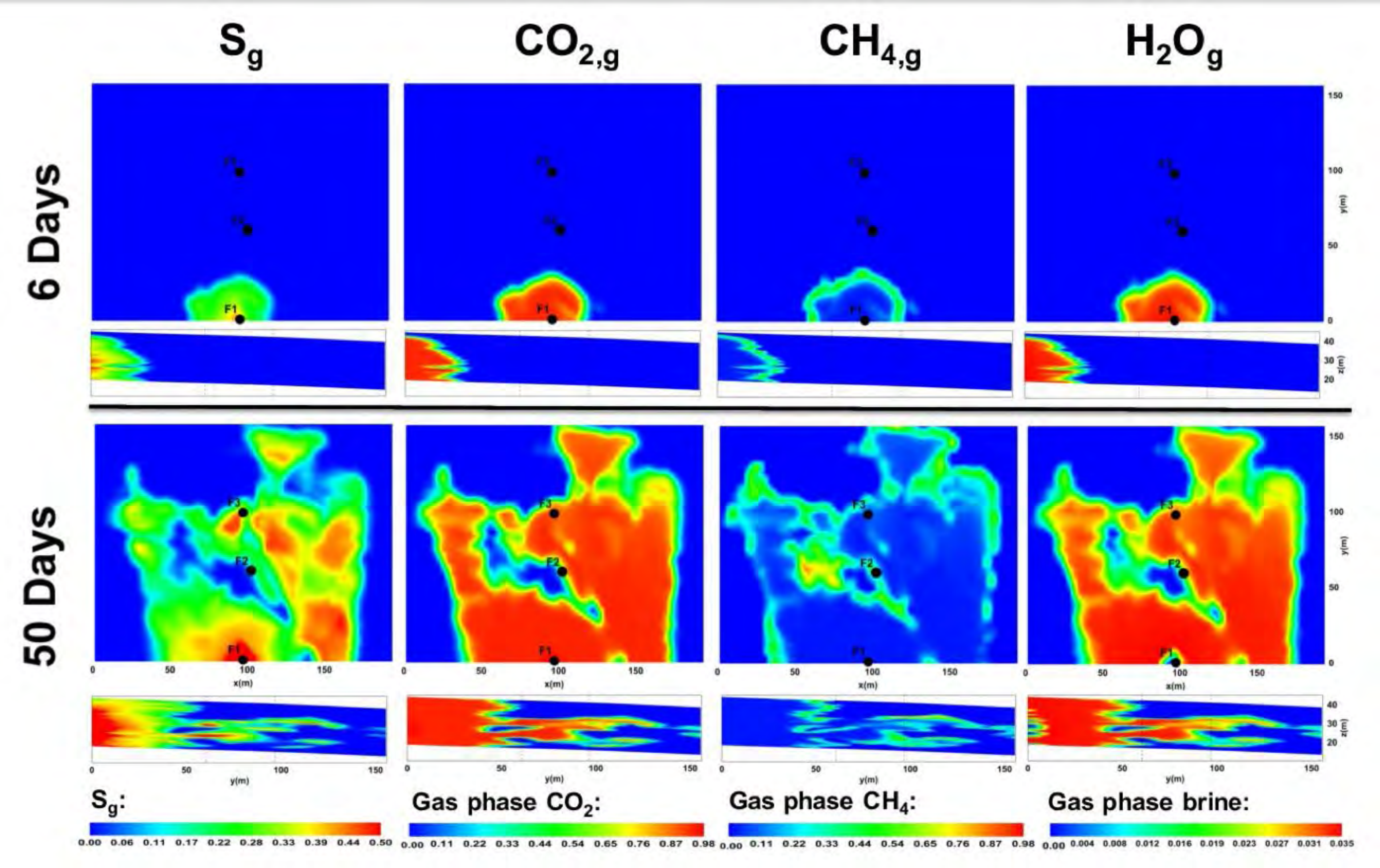
Competitive Dissolution of CO_2 Versus CH_4 in Brine



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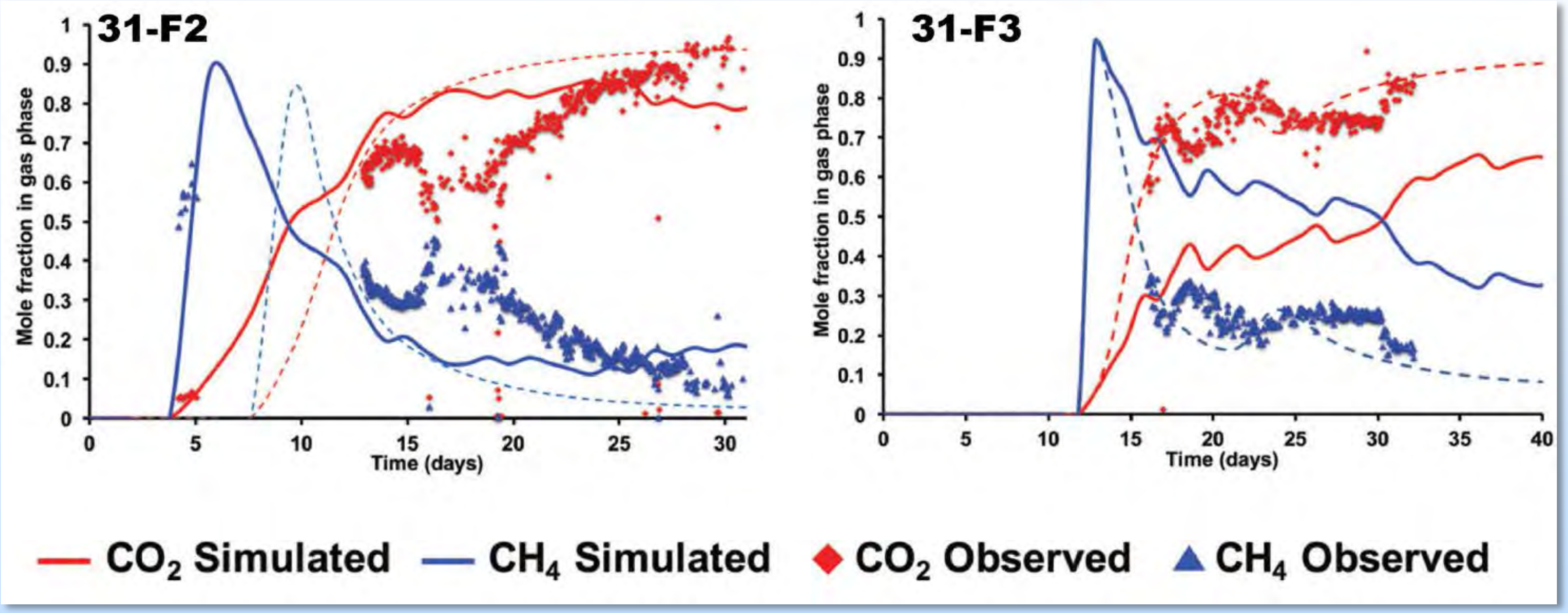
Simulated CH_4 Breakthrough Agrees With Field Data



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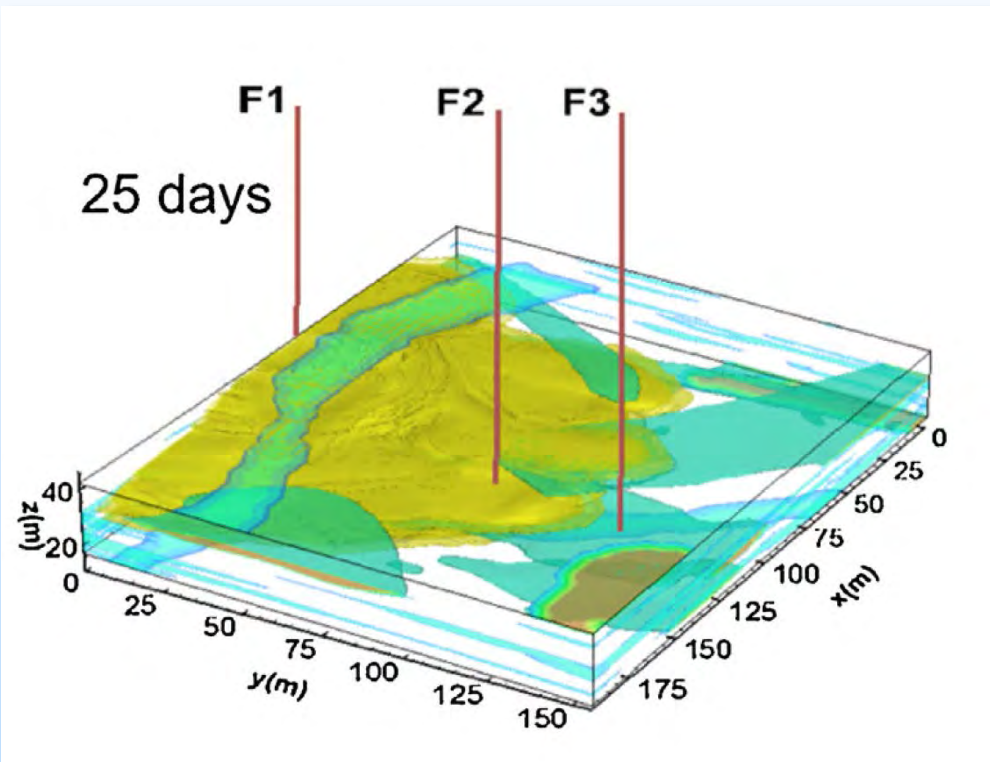
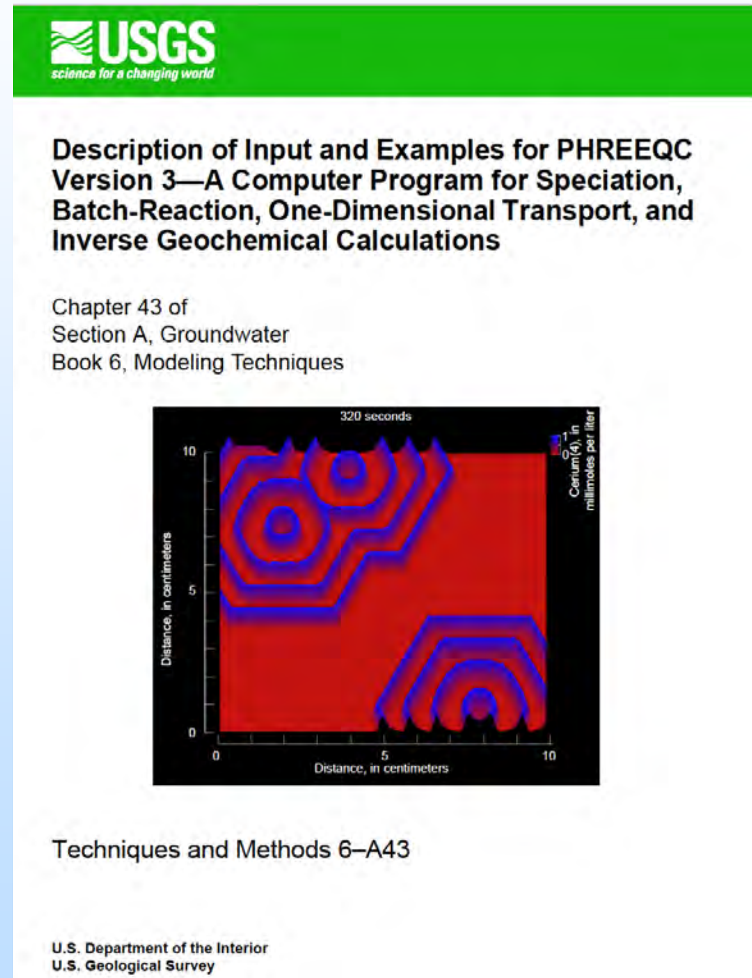
Coupling Flow & Transport with Geochemical Reactivity

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Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations

Chapter 43 of
Section A, Groundwater
Book 6, Modeling Techniques

Techniques and Methods 6–A43

U.S. Department of the Interior
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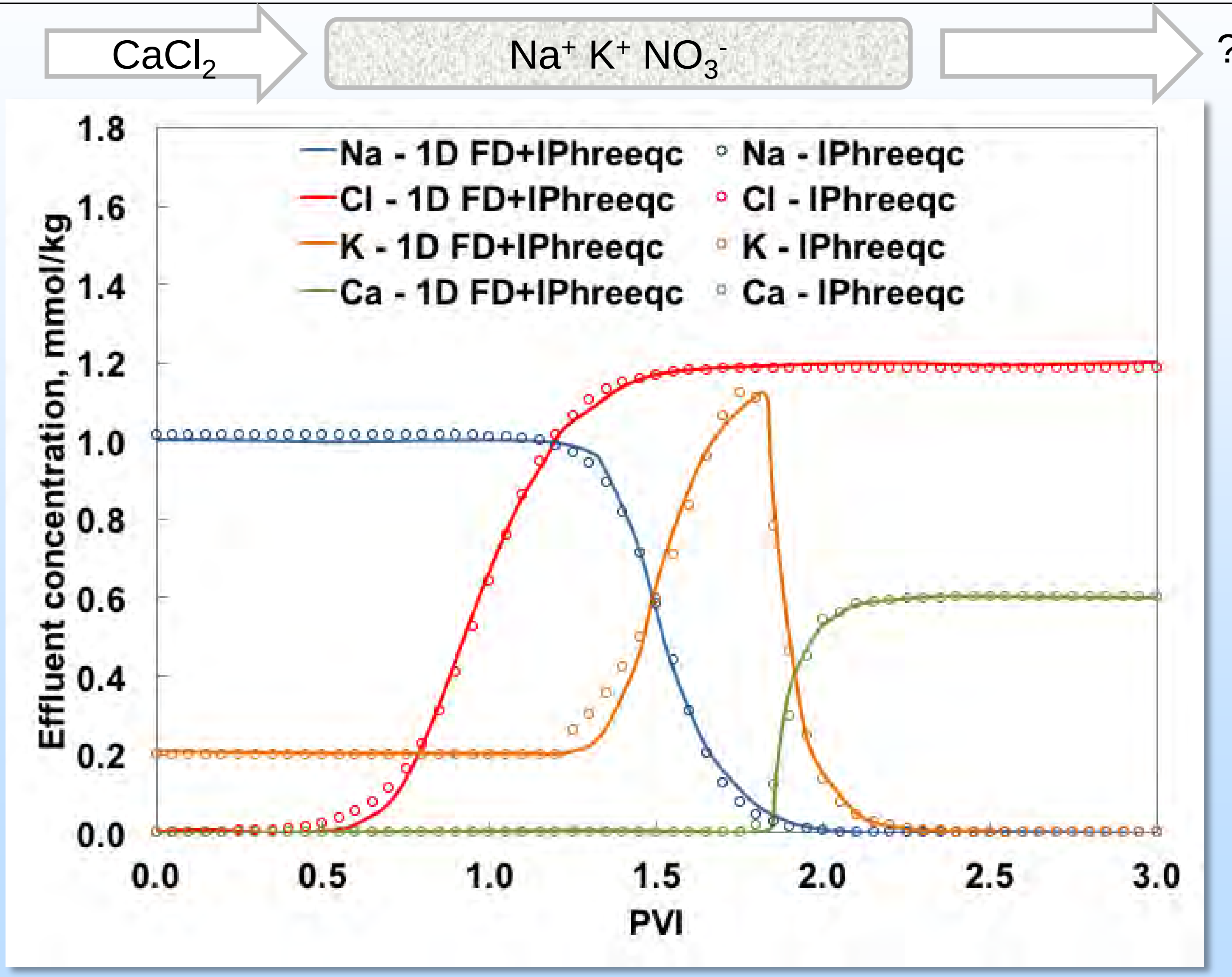
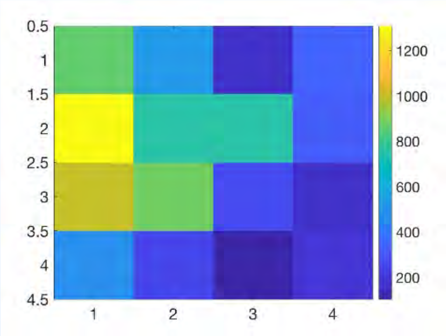
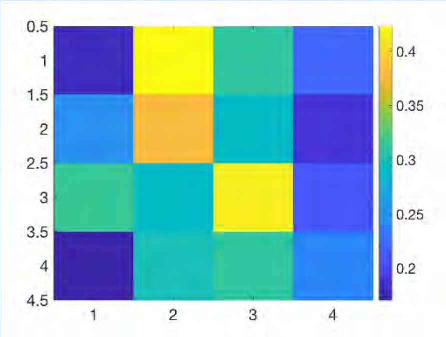
Validation Example:
Transport & Cation Exchange



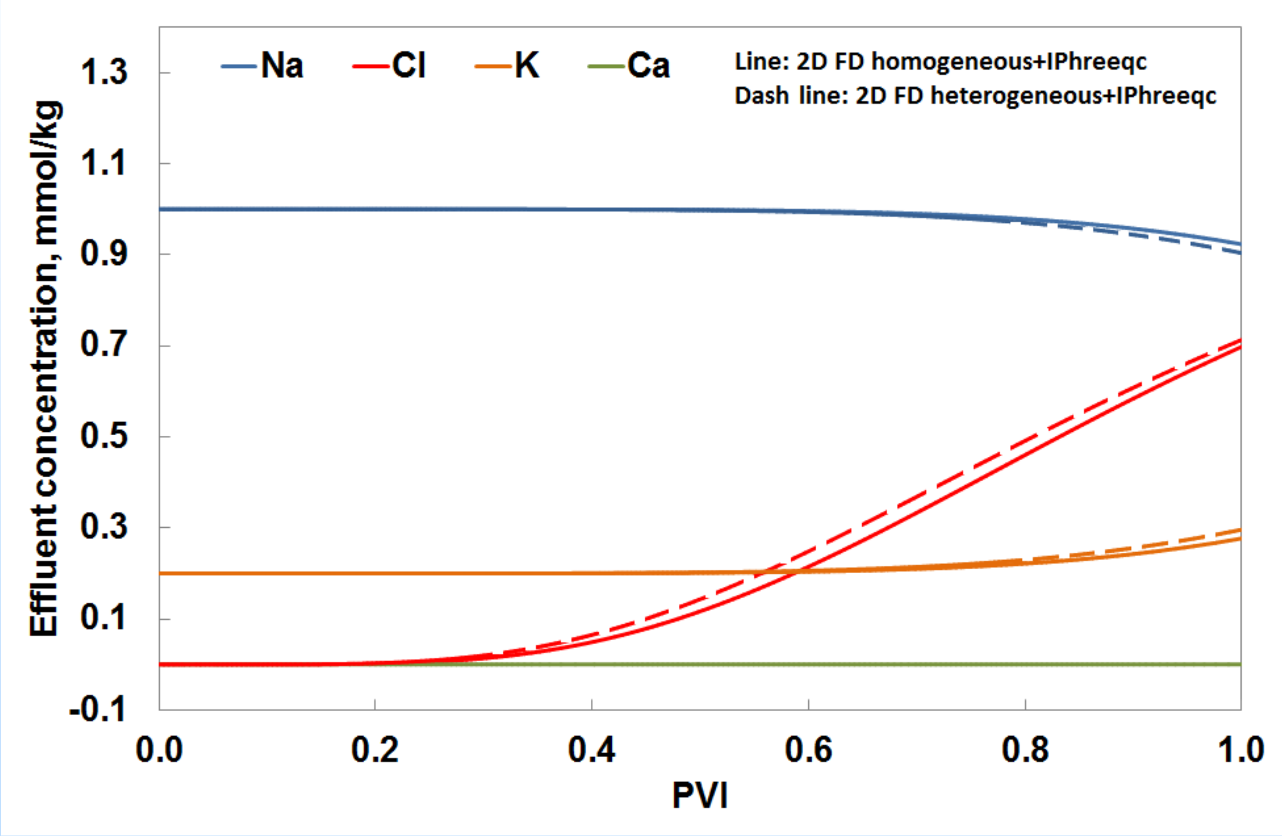
Same Problem in 2D Homogeneous & Heterogeneous Domains



Permeabilities field (mD)



Porosity field

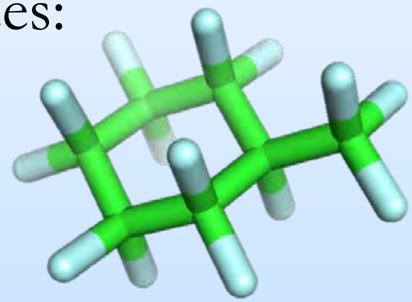


Modeling Overview & Next Steps

- 2016: CO_2-H_2O flow & transport in high-resolution static model of DAS with advanced EOS.
- 2017: Addition of perfluorocarbon and SF_6 tracers.
- 2018 (early): Addition of CH_4 to study competitive dissolution/exsolution, formation of free gaseous CH_4. Excellent agreement with field data for all above.
- 2018 (late): Addition of reactive transport to complete comprehensive model of all trapping mechanisms.
- 2018-2019: Collaborate with NETL RIC to validate geochemistry and then use model to interpret lab-to-field data (e.g., Mt Simon core to Cranfield DAS).
- Consider reactive transport both in target formation but also in potential cap-rock failures.

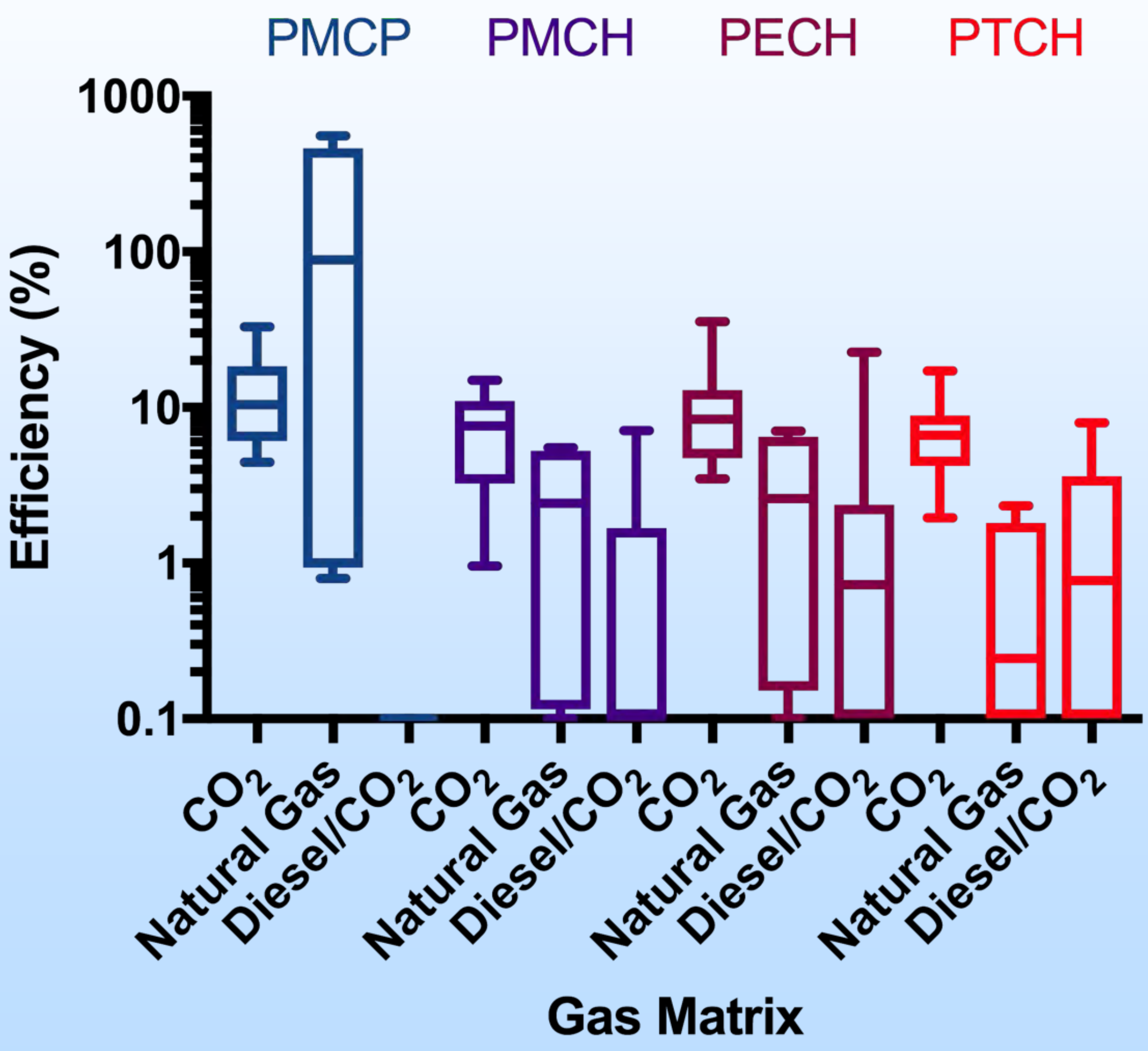
Do Hydrocarbons Interfere with PFT Sampling & Analysis?

- Minimal interference with GC-ECD analysis by direct injection
- Sorbent tubes can be used to concentrate PFTs from gas samples.
- Potential competition in sorbent tube sampling
- Created a set of PFT standards in 1-L gas matrices:
  - CO_2
  - Natural gas
  - Diesel-saturated CO_2

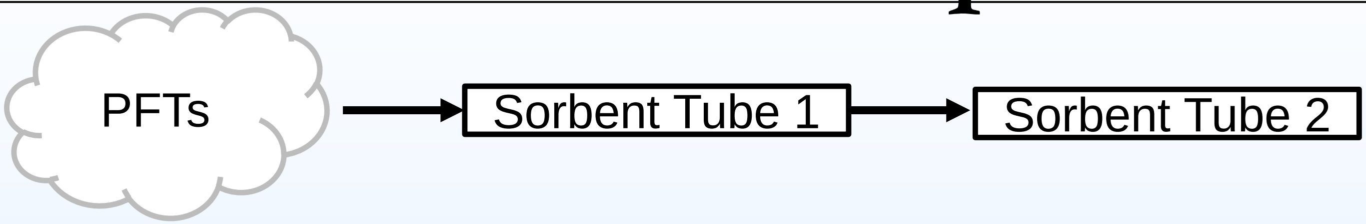


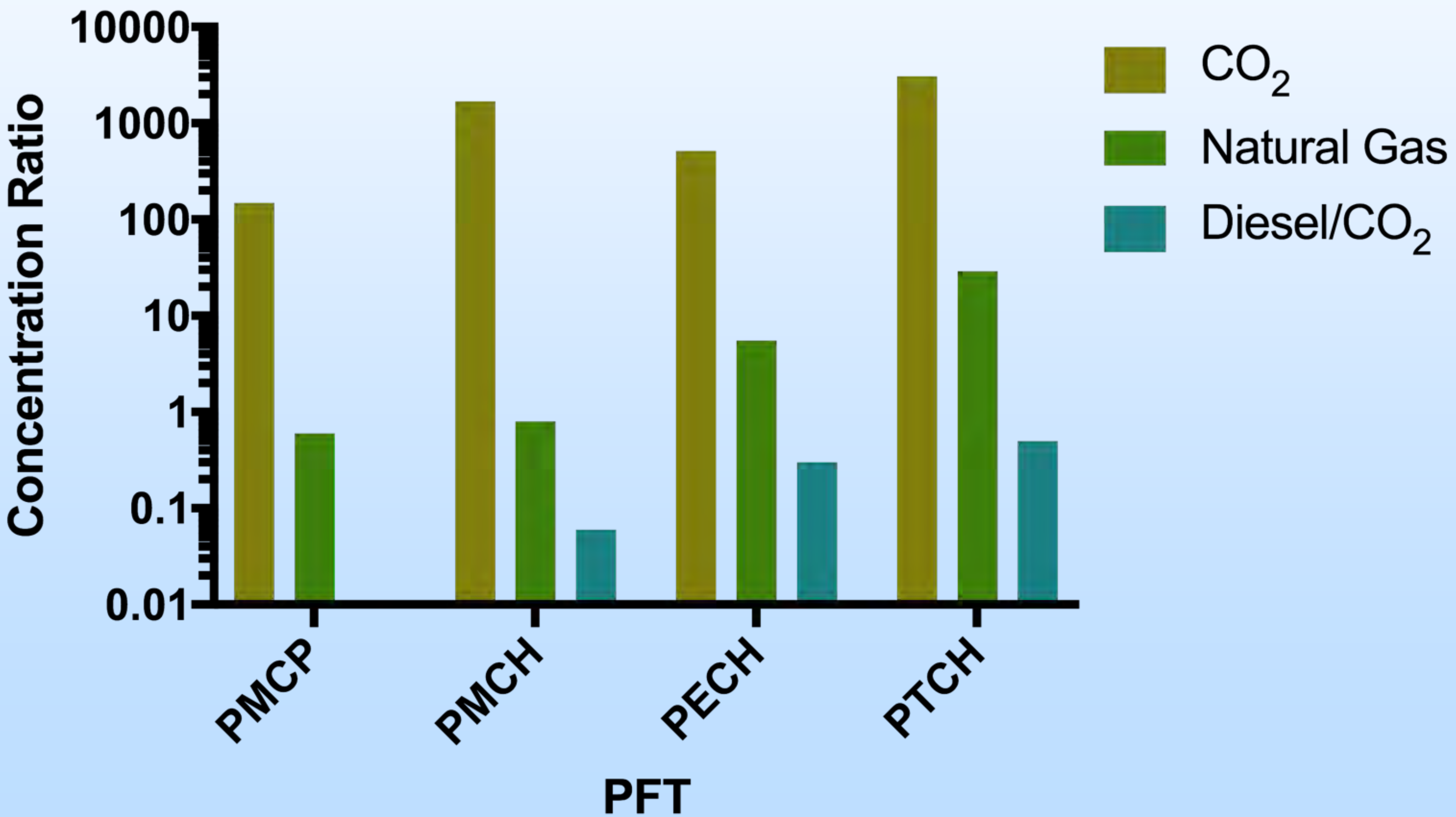
- Loaded on AMBERSORB™ in quartz sorbent tube
- Analysis at NETL RIC (Sean Sanguinto) using thermal desorption and GC-NICI-MS

Decreased Efficiency of PFT Adsorption, Desorption and Analysis



Increased PFT Breakthrough to Downstream Sampler Tube





Lessons Learned & Next Steps

– Hydrocarbons substantially reduce the efficiency of perfluorocarbon adsorption to AMBERSORB™.
– The most volatile PFT (PMCP) dissolved in a CO_2 matrix saturated with diesel could not be detected on sorption tube samples using GC-NICI-MS.
– Diesel matrix also caused early breakthrough of samples during active sampling with sorption tubes, introduced high variability in sorption tube samples, and substantially reduced the sensitivity of analysis for all PFTs.
– Research and development activities are needed to identify new sorbents and PFT capture strategies that are more robust to hydrocarbons in reservoir gas matrices.

Synergy Opportunities

- Collaborate with NETL RIC to validate geochemistry and then use model to interpret lab-to-field data (e.g., Mt Simon core to Cranfield DAS).
- Collaborative PFT sorbent testing in hydrocarbon-rich matrices
- New tracer test campaigns
- Sharing best practices for tracer analysis

Project Summary

- Simulated both PFT experiments at Cranfield DAS
- Validated CH_4 exsolution modeling with excellent match to field measurements
- Coupling geochemical reaction modeling with transport modeling for dynamic 3-D reservoir simulations
- Demonstrated significant hydrocarbon interference with sorption tube sampling of PFTs
- Assessing options to reduce interference and increase selectivity using advanced sorbents
- We welcome collaborations

Appendix

Project Organization

David Graham, PI

Tommy Phelps
Susan Pfiffner

Joachim Moortgat

David Cole
Reza Soltanian
Judy Zhu

Collaborators:

RCSPs

Gantt Chart

Task	Milestone Description*	Fiscal Year 2018				Fiscal Year 2019				Planned Start Date	Planned End Date	Actual Start Date	Actual End Date	Comment (notes, explanation of deviation from plan)
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4					
1.1	Prioritization of reactive transport processes for simulation from discussions with NETL researchers	■								8/17	12/17	8/17	1/18	
2.1	Prepare PFT standards in hydrocarbon matrices for sorbent tube test and GC-MS analysis at NETL	■								9/17	12/17	9/17	12/17	
FY17	Universal dynamics of gravito-convective mixing of CO2 in 3D heterogeneous porous media and implications for geological carbon sequestration	■								6/17	12/17	5/17	12/17	
2.1	Report on efficacy of sorbents to improve PFT capture and analysis	■	■							1/18	6/18			
1.2	Report on how pattern formation and its evolution can provide unique and easy-to-use predictive tools for the long-term dissolution-trapping of CO2, enhanced by gravito-convective mixing	■	■	■	■					10/17	9/18			
1.3, 1.4	Initial incorporation of geochemical reactions and stable isotope tracers into the Osures reservoir simulator			■	■					6/18	9/18			
2.2	Report on new adsorbent technology for PFT sampling		■	■	■					1/18	9/18			
2.2	Survey field test opportunities for enhanced PFT sampling technology				■	■				8/18	12/18			
1.5	Final report on CO2 trapping mechanisms, with a focus on capillary trapping					■	■			10/18	6/19			
1.6	Assess the role of fractures on CO2 trapping mechanisms					■	■	■	■	10/18	9/19			

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