Monitoring of Geological CO_2 Sequestration Using Isotopes & PFTs

Project Number FEAA-045

David E. Graham[1], Joachim Moortgat[2]

DR Cole[2], SM Pfiffner[3], TJ Phelps[3]

1 Oak Ridge National Laboratory

2 The Ohio State University

3 The University of Tennessee Knoxville

U.S. Department of Energy

National Energy Technology Laboratory

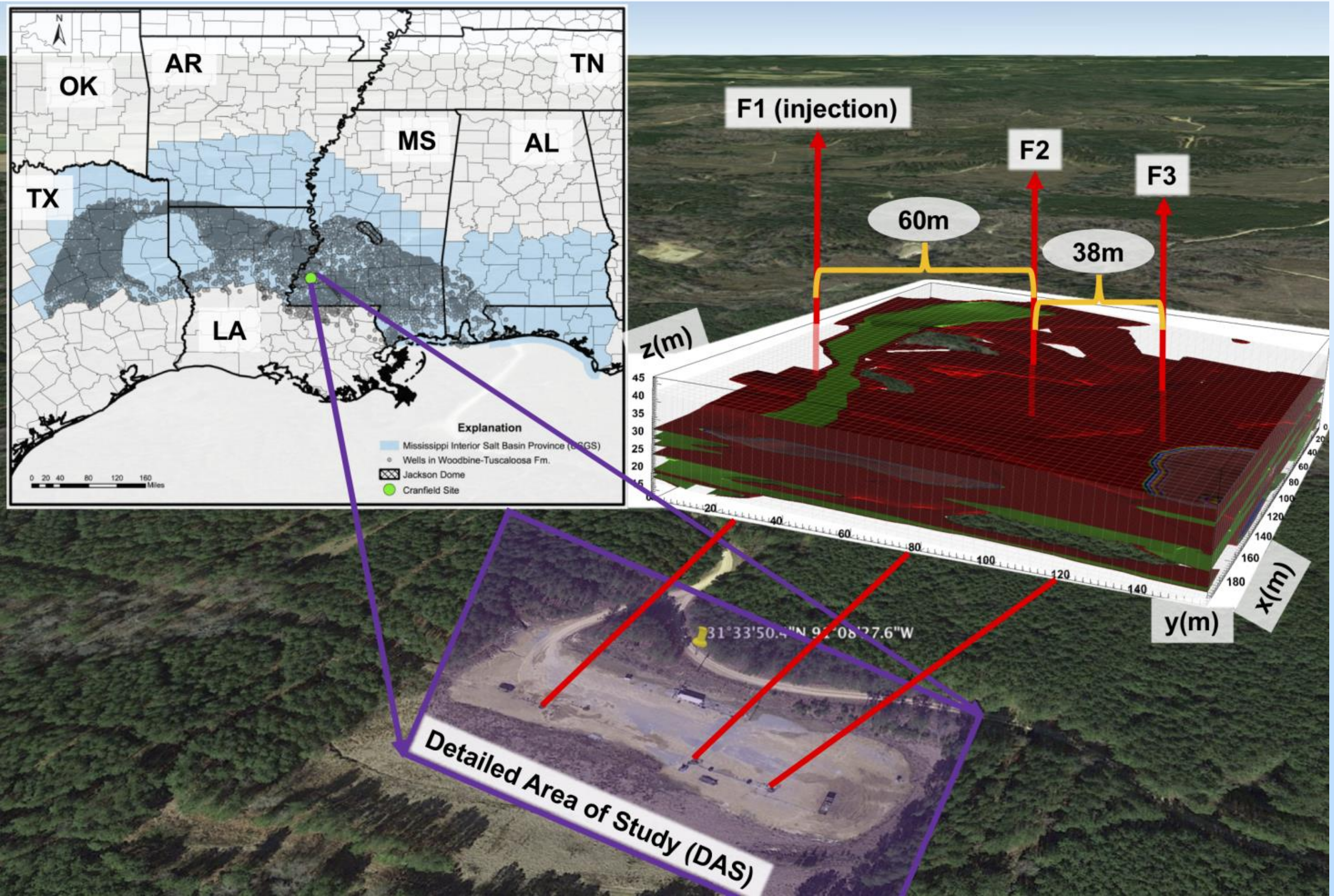
Carbon Storage Project Review Meeting

2020 Virtual Review Webinar

September 10, 2020

Project Overview

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



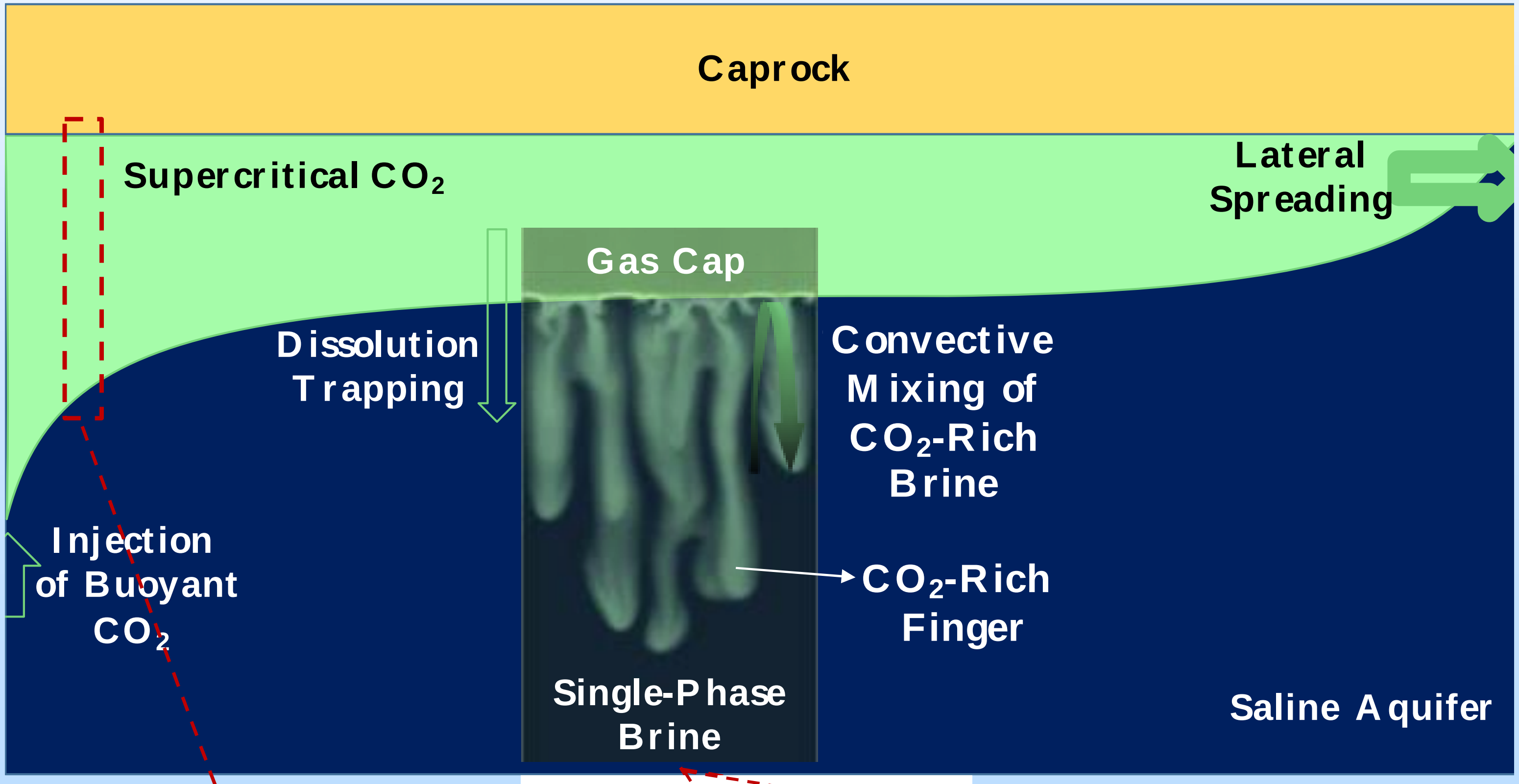
Tasks

1. Numerical Modeling of Reactive Transport at Cranfield and Other CCS Site(s) to
   - *Better interpret field data*
   - *Predict long-term evolution of fluids & formation*
   - *Apply lessons learned to other projects*
2. Assess efficiency of PFT analysis using capillary adsorption tubes in a hydrocarbon-rich matrix

Task 1 Objective

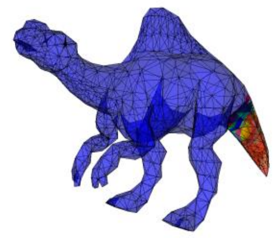
- Constrain **structural, solubility, and chemical** trapping mechanisms that guarantee storage permanence, through novel subsurface signals & modeling.
  - Non-trivial migration patterns in heterogeneous formations
  - Diffusion driven convection and cross-flow into low-perm. facies
  - Chemically driven mineralization of CO_2 and formation alterations

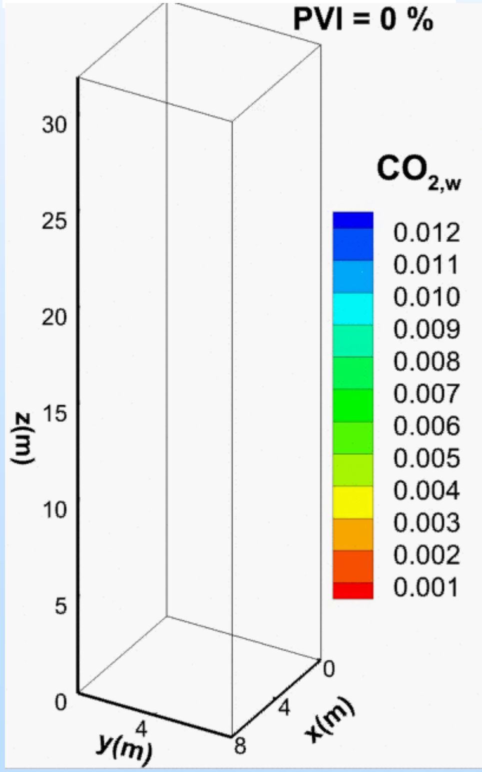
- Iteratively coupled workflow of field data and modeling



Modeling Tools

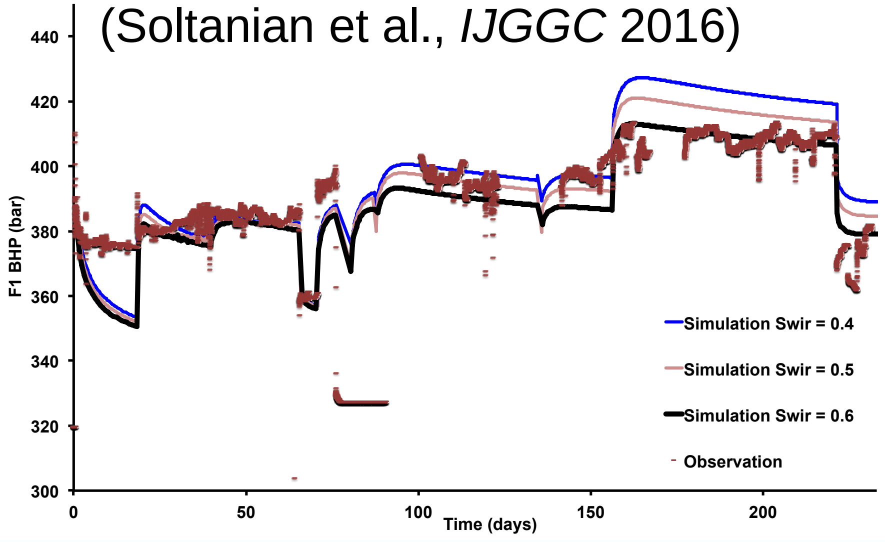
- Unique combination of capabilities in **Osures**:
  - Higher-order finite element (FE) methods for flow and transport: allow unstructured grids, tensor permeability, discrete fractures, strong heterogeneity
  - Low numerical dispersion (e.g., resolves small-scale onset of instabilities)
  - Cubic-plus-association (CPA) equation of state (non-ideal) phase behavior modeling of water, CO_2, hydrocarbons, tracers (capture, e.g., competitive dissolution and brine compressibility)
  - Fickian diffusion with self-consistent composition + T + p -dependent full matrix of diffusion coefficients for multicomponent multiphase fluids
  - Capillary-driven flow with composition + p -dependent surface tension
  - ***New*** Reactive transport by coupling to iPHREEQC geochemistry (2019-2020) and **PhreeqcRM** (2020-2021), which is faster / parallelizable.



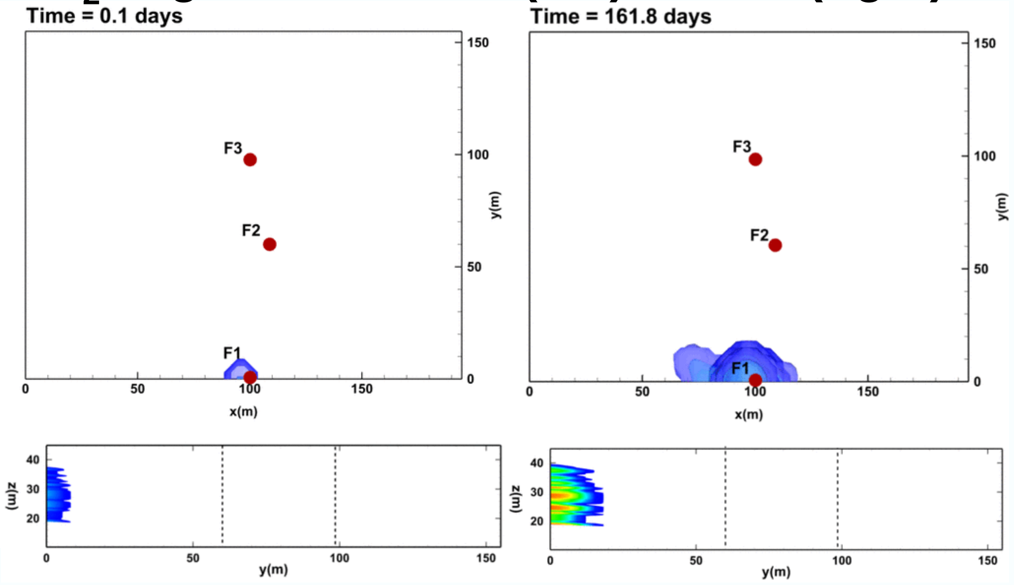


Prior Accomplishments

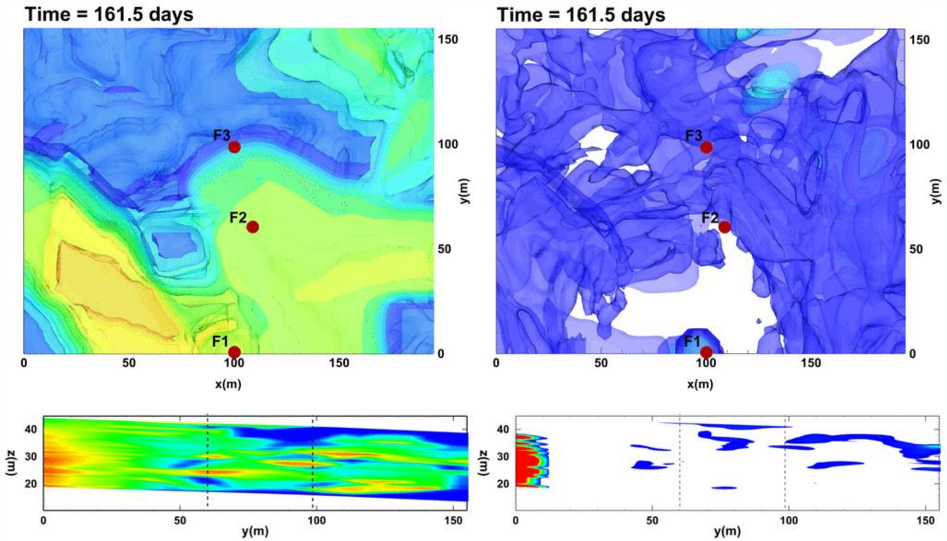
Pressure response in injection well (Soltanian et al., *IJGGC* 2016)

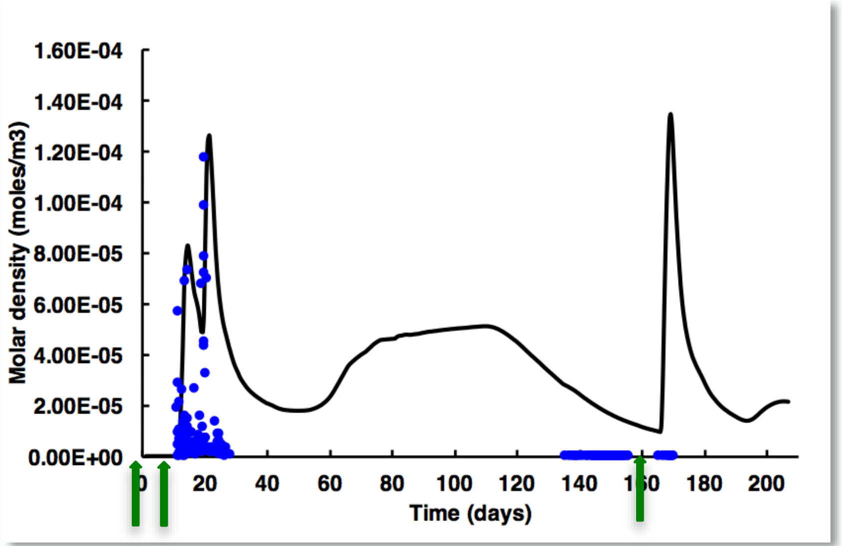


CO_2 migration in 2009 (left) & 2010 (right)



CO_2 and PFC tracer migration (Soltanian et al., *GGST* 2018)





Technical Status

- 2020: Coupled **Osures**, higher-order FE simulator for 3D multiphase multicomponent compositional (Equation of State-based) convection, diffusion, capillarity, gravity, dispersion, fractures to **iPHREEQC** and **PhreeqcRM** for geochemistry.

- PHREEQC (USGS) is open source, well validated, offers interface to other flow simulators (only 1D transport itself).

- Currently, full Osures capabilities and 1-phase chemistry fully validated[1]. Multiphase in initial testing, completed later in FY2021.

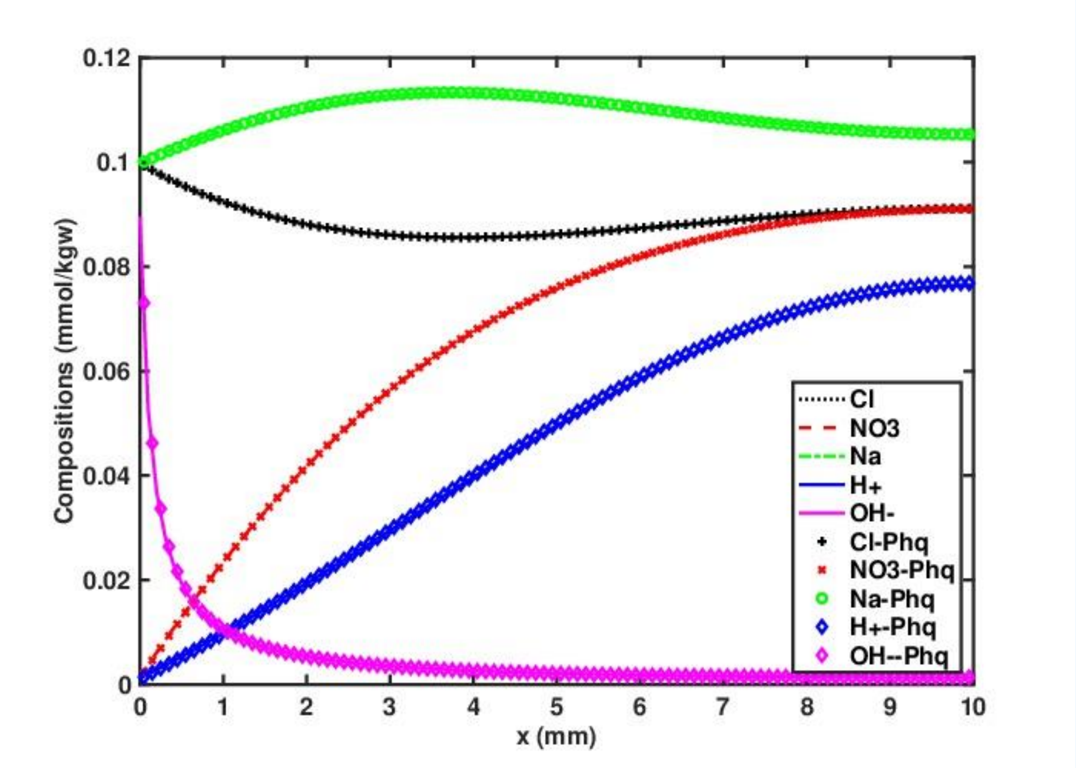
1. SCIENTIFIC REPORTS nature **A Higher-Order Finite Element Reactive Transport Model for Unstructured and Fractured Grids**

Joachim Moortgat[1,*], Mengnan Li[1], Mohammad Amin Amooie[2], and Di Zhu[3]

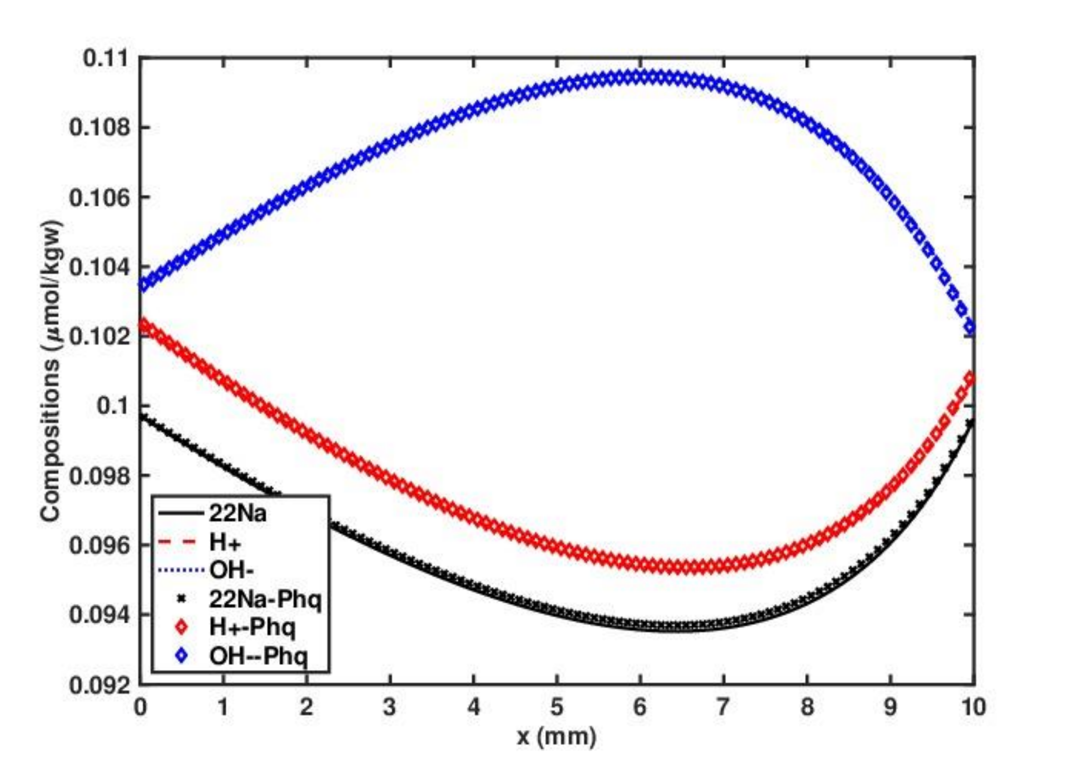
[1]School of Earth Sciences, The Ohio State University, Columbus, OH 43210, USA
[2]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[2]Occidental Petroleum Corporation, Houston, TX 77046, USA
[*]moortgat.1@osu.edu

Benchmarking

1. Electrochemical migration (Nernst-Planck diffusion[1]) of Na^+, Cl^-, H^+, NO_3^-.
   Modeled with CrunchFlow, MIN3P, PHREEQC (symbols), **Osures** (solid).



2. Tracer isotope ($^{22}Na^+$ vs Na^+) diffusion due to charge effects[1]
   PHREEQC (symbols), **Osures** (solid) steady-state $^{22}Na^+$ concentration



[1] Rasouli, Steefel, Mayer, Rolle; Benchmarks for multicomponent diffusion and electrochemical migration. Comput Geosci (2015)

Benchmarking

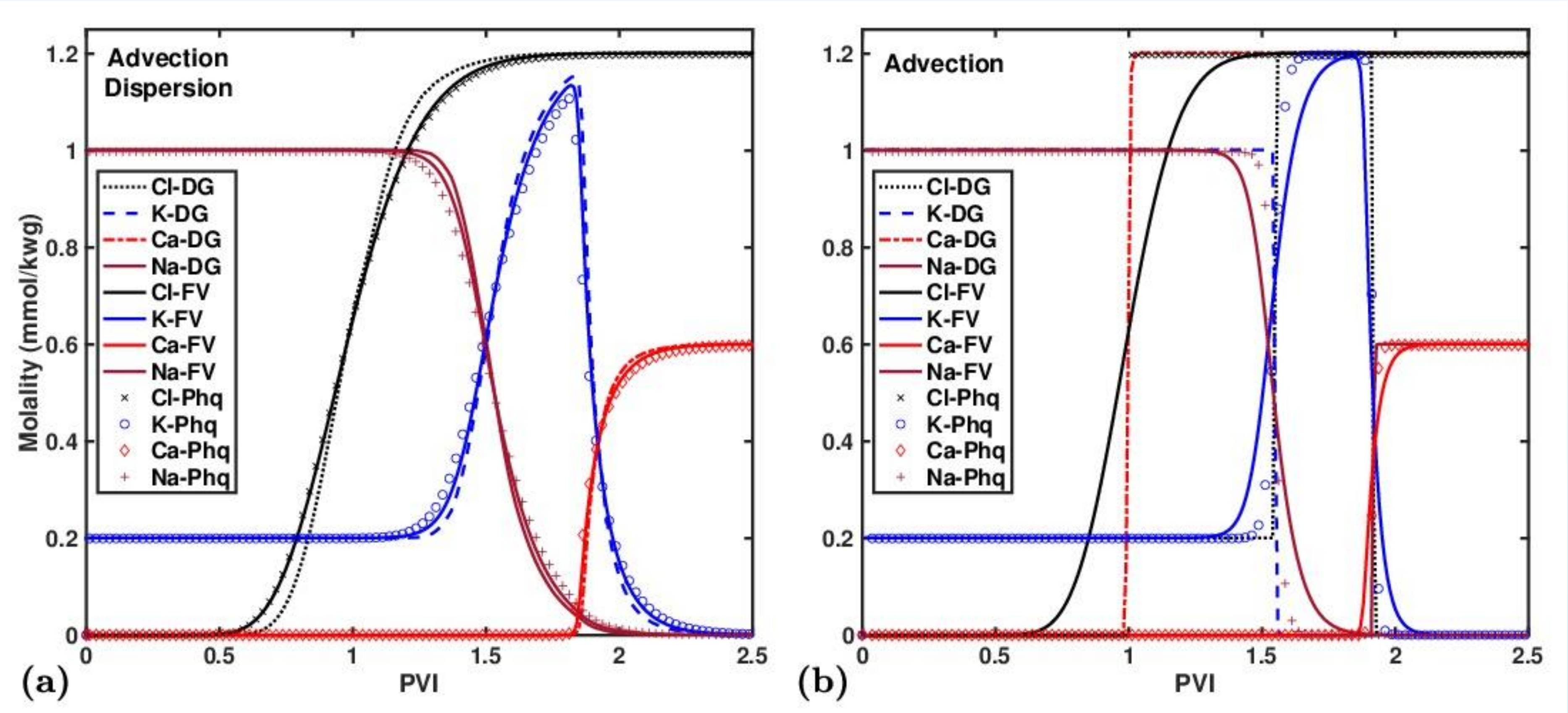
3. Rock-fluid cation exchange column (Ex. 11 PHREEQC manual)

$CaCl_2$ → Na^+ K^+ NO_3^- → ?

Ca-Cl injected into Na-K-NO_3 solution. Ca^{2+} exchanges with Na^+ and K^+

PHREEQC (symbols)

Osures (solid line)

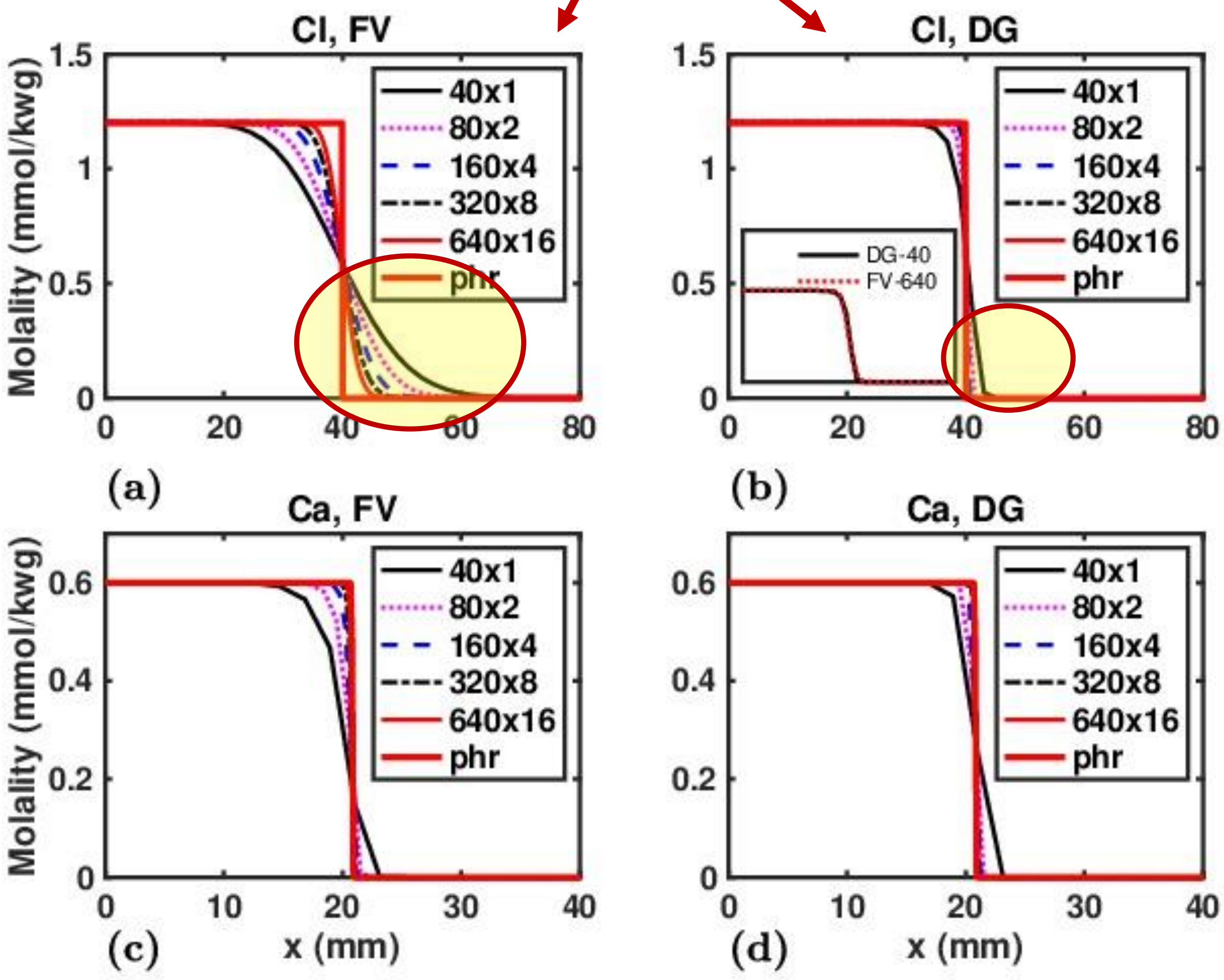


Higher-Order Methods

- Mixed (Hybrid) FE method for pressure & velocity field
- Multilinear Discontinuous Galerkin FE for reactive transport
- Unstructured, relatively coarse, 3D grids
- Accurate velocities and low numerical dispersion,

Breakthrough curves

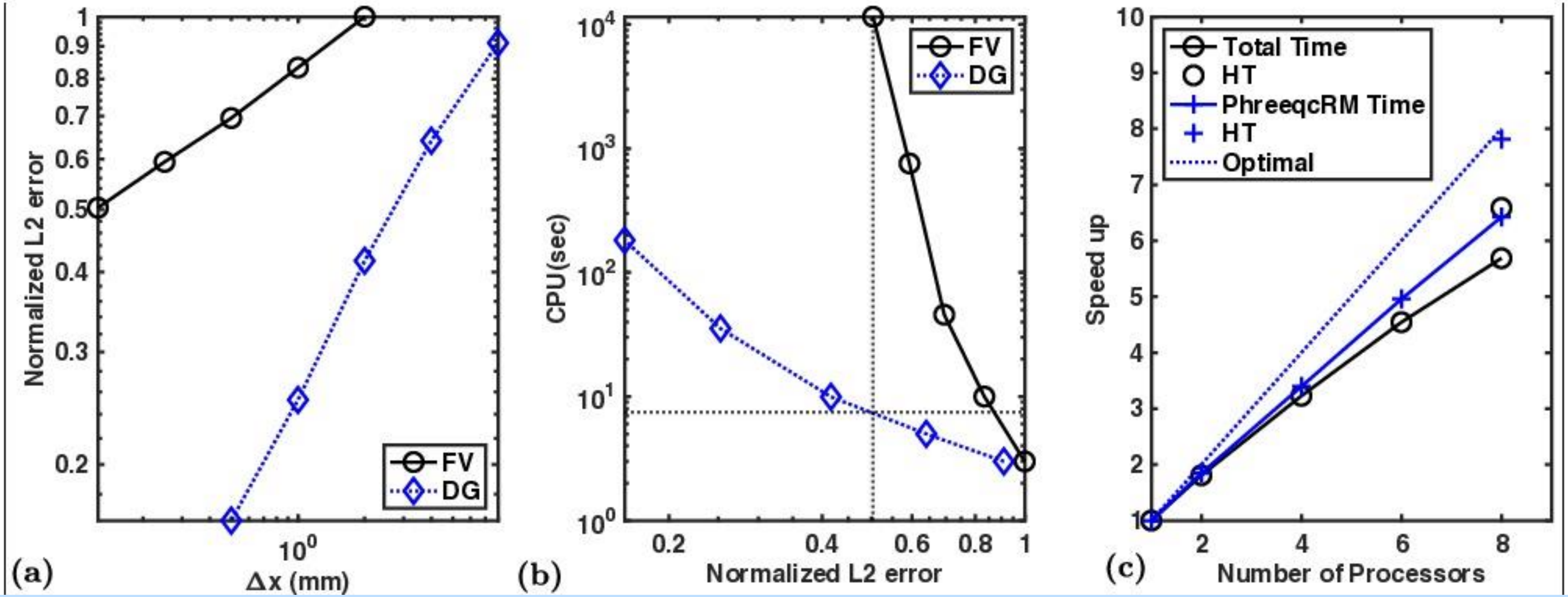
1st order **2nd order**



- which translates to…:

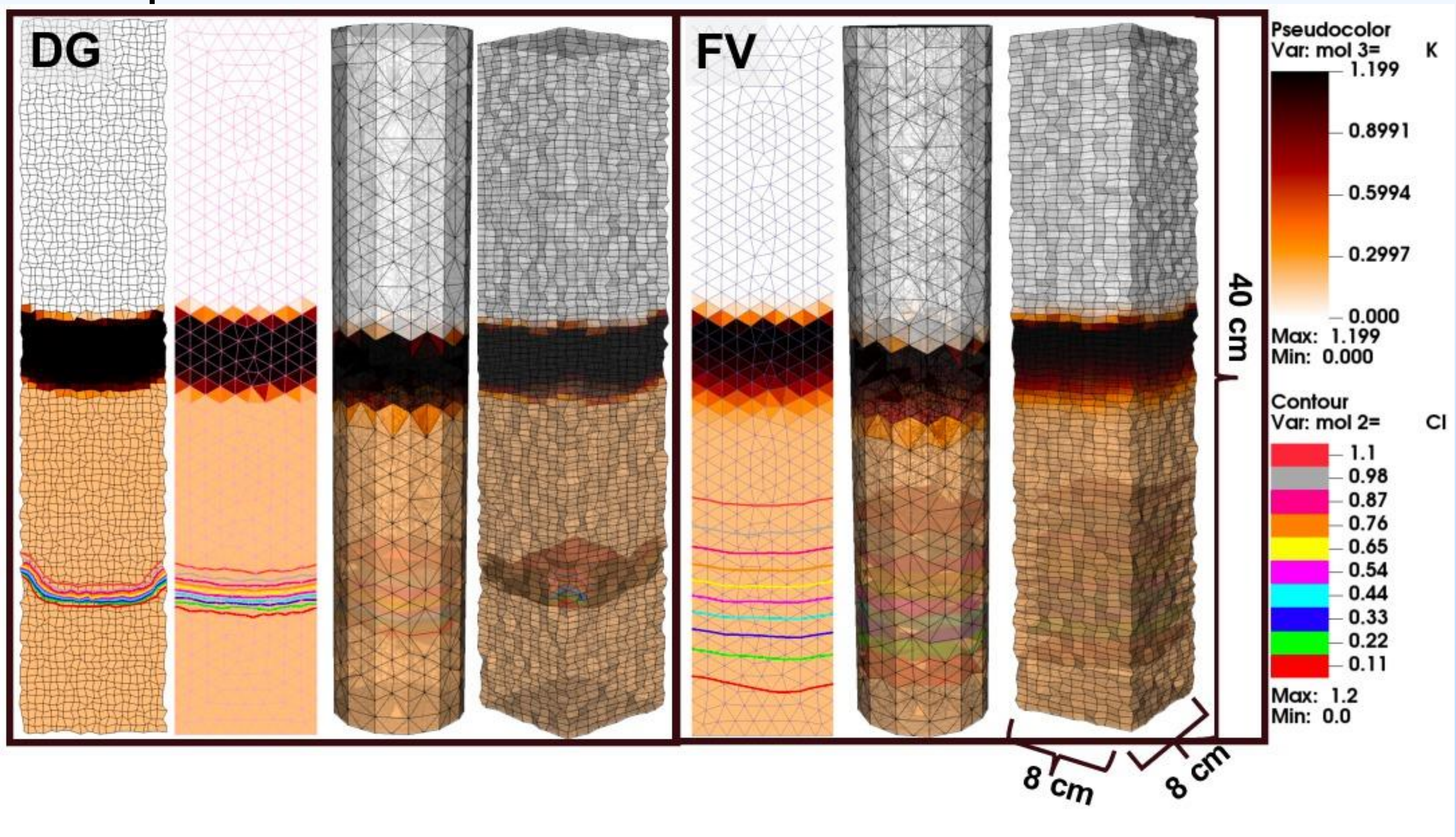
Higher-Order Methods

- Three orders of magnitude improvement in computational efficiency!
- More from good parallel scaling of PhreeqcRM.



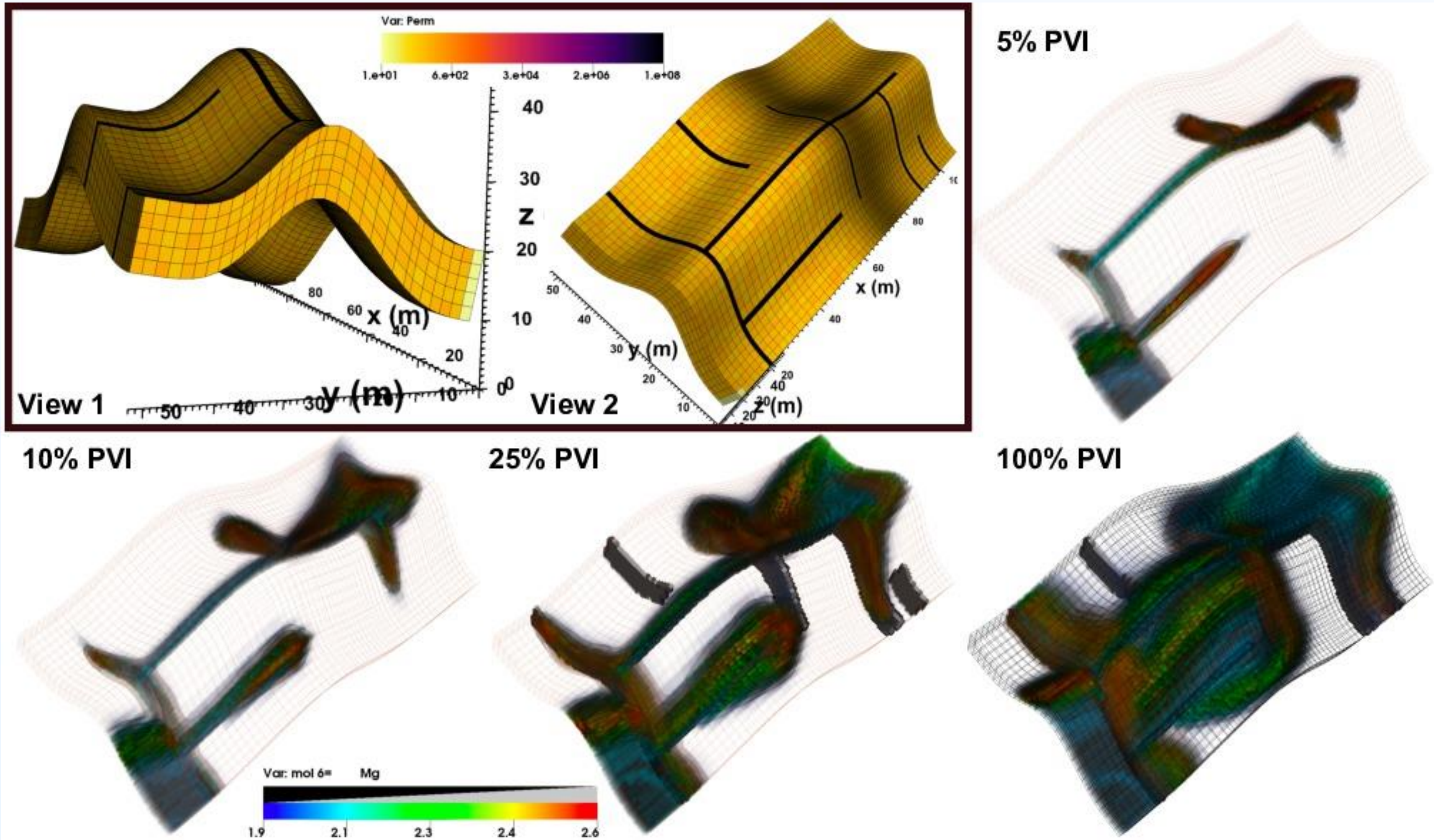
Unstructured Grids

- 2D: Quads & Triangles, 3D: Tetra- & Hexahedra
- Allows gridding of, e.g., cores and complex geological formations.
- Validated for both aqueous equilibrium and rock-fluid reactions on all 2D and 3D grid types.

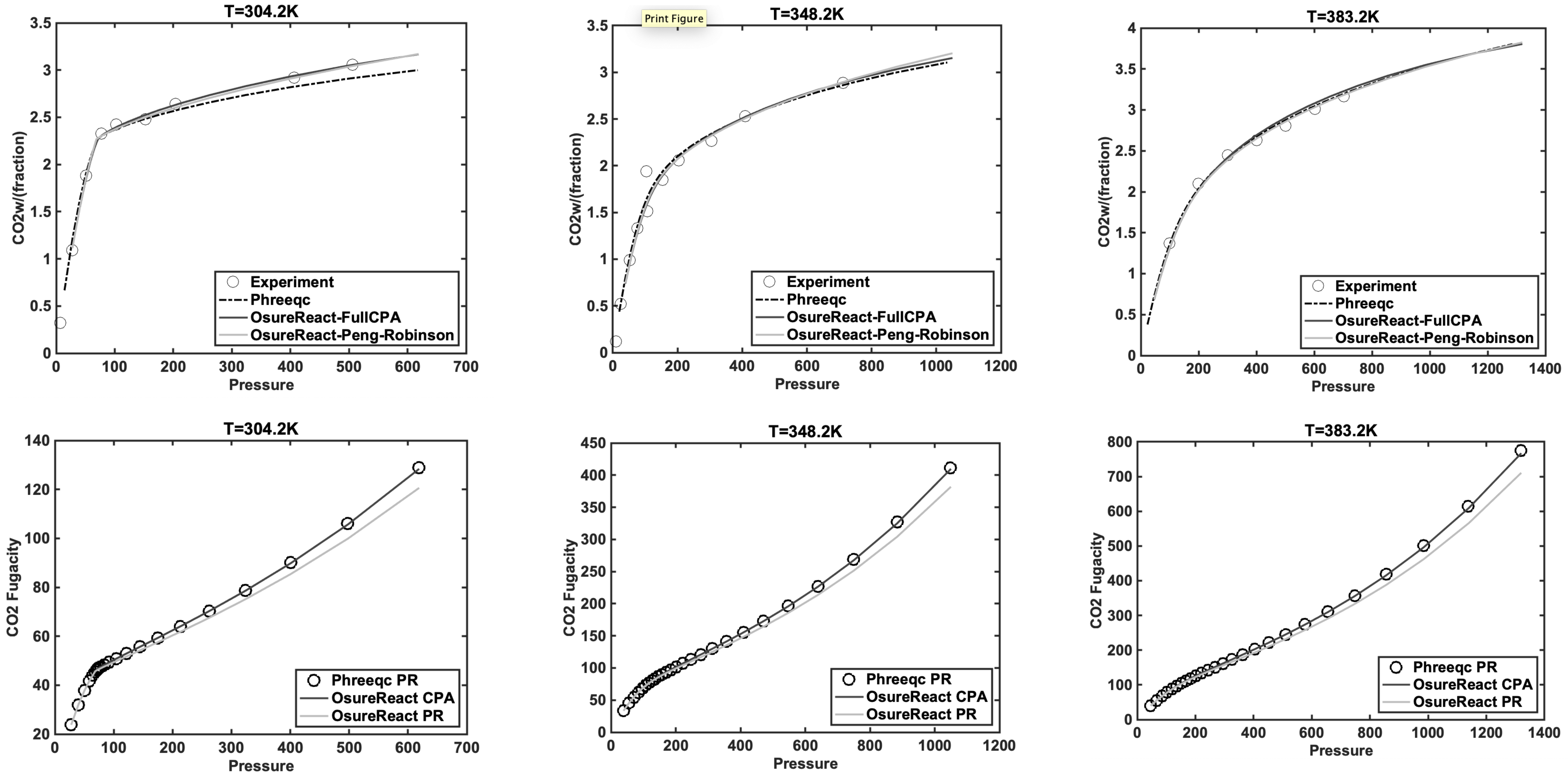


Discrete Fractures

FE discrete fracture example with convection, diffusion, and rock-fluid cation exchange reactions.



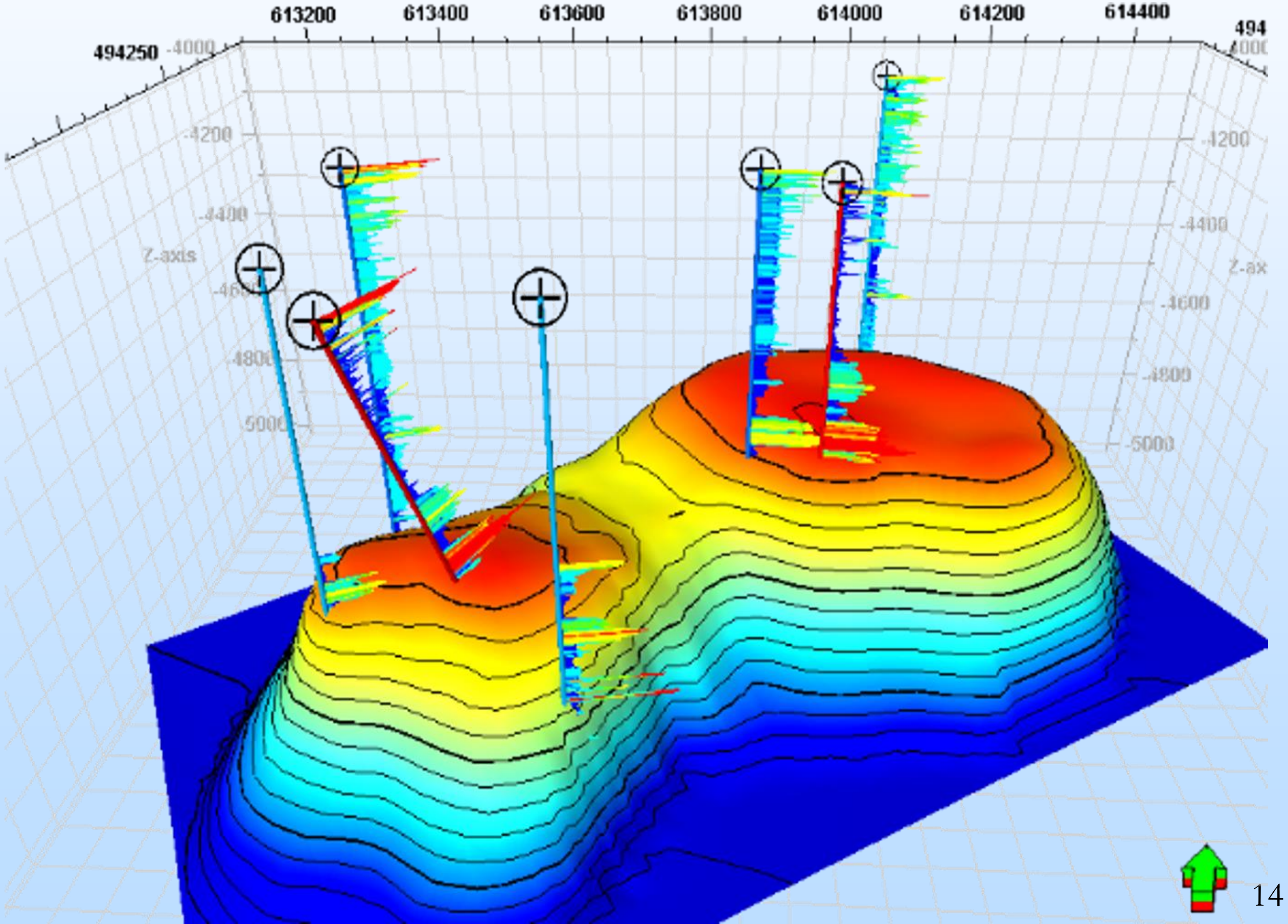
Preliminary Two-Phase Testing



Chester 16

New synergistic collaboration developed with Battelle to model CO_2 transport in challenging Chester 16 reef system (MRCSP)

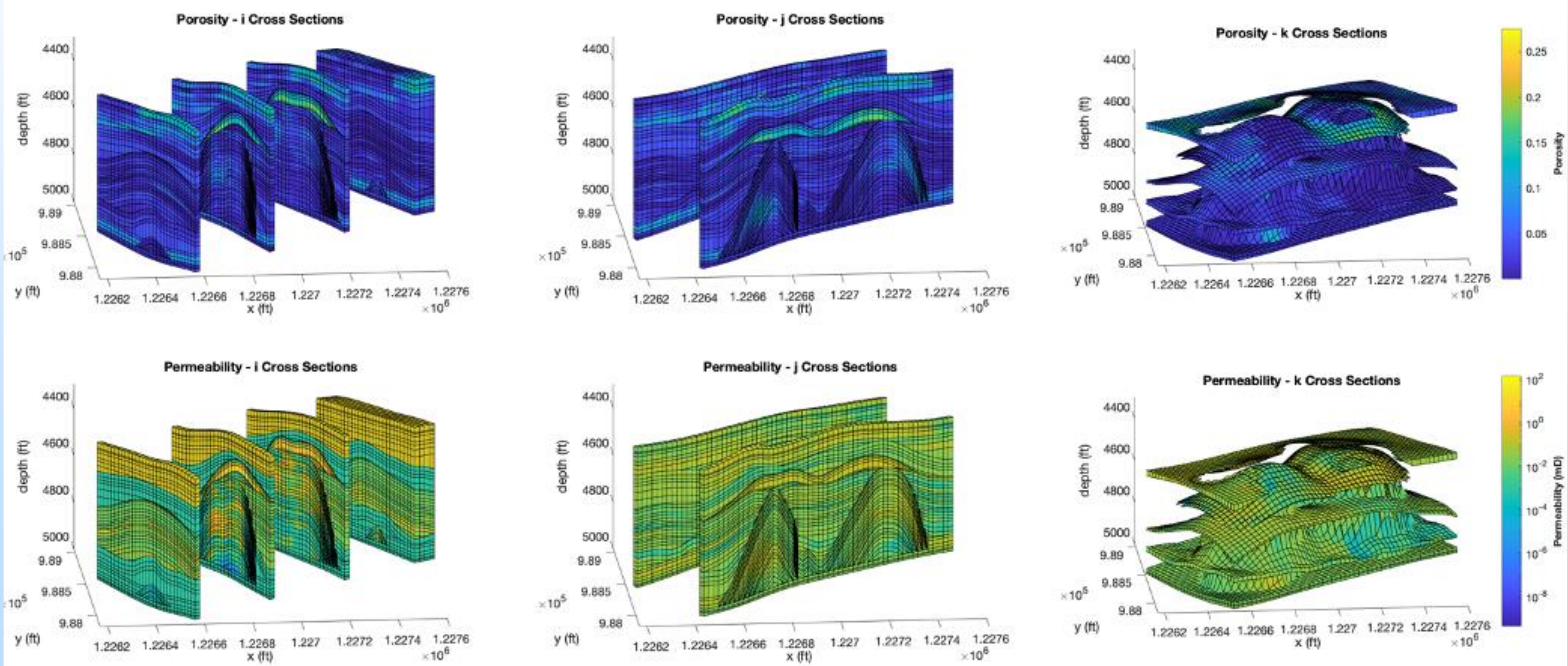
- First milestone: develop alternative static model



BATTELLE
It can be done

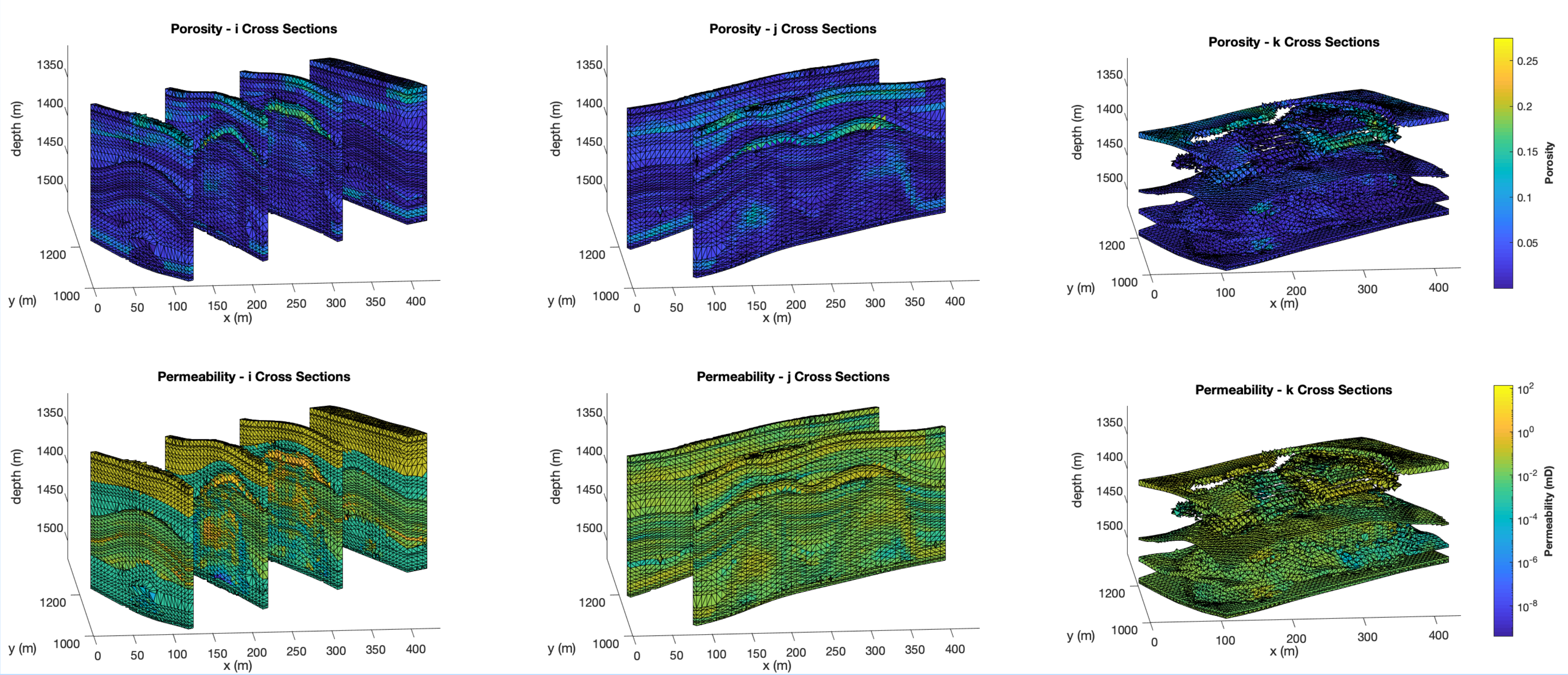
Chester 16

- Industry-standard is logically Cartesian corner-point grids.
- For complex geometry, like domes, many dead and pinched cells.
- Can truly unstructured, e.g. tetrahedral, grids offer advantages?



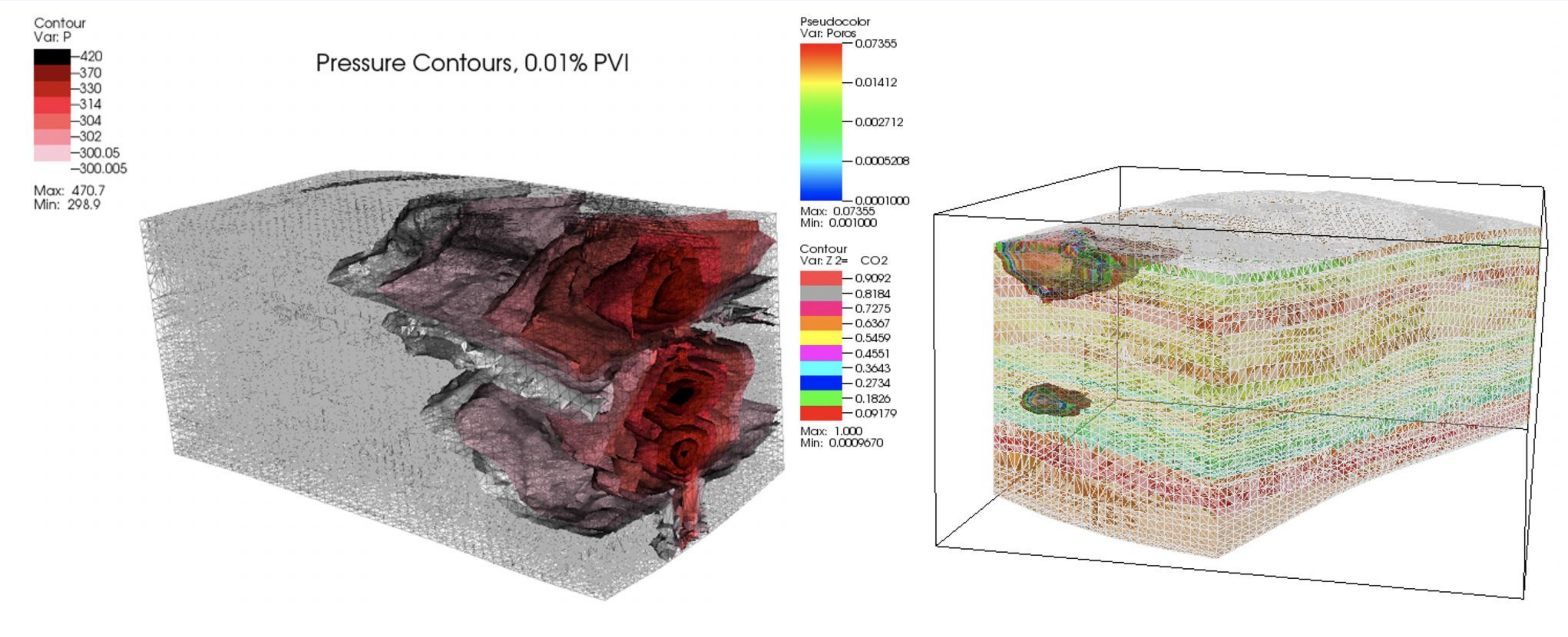
Chester 16

- Preliminary tetrahedral static model for Chester 16 reported in FY2020Q1 report.



Chester 16

- Preliminary modeling of CO_2 injection indicates necessity for further improvements in grid refinement and computational efficiency.



Lessons Learned

- Critical uncertainties in modeling/predicting two-phase migration of supercritical CO_2 into brine-saturated formation:
  - Subsurface heterogeneity,
  - Relative permeability & capillary pressure relations: especially facies-dependence.

- Convective mixing of dissolved CO_2 relatively insensitive to multimodal facies heterogeneity when porosity and permeability are correlated. Simple scaling laws in terms of formation/fluid properties apply broadly.

- Rock-fluid reactions likely modest on short time-scales but may affect long-term storage. Predictions require costly (parallelized) numerical modeling & further research.

Project Summary (Task 1)

- Completed:
  - Modeling of CO_2, brine, and various tracers at Cranfield.
  - Fundamental analyses of solubility trapping (mixing and spreading of dissolved CO_2).
  - Initial implementation and benchmarking of coupled flow and reactive transport with Osures+iPhreeqc/PhreeqcRM

- Ongoing & Future work:
  - Investigation of *multiphase* flow and *reactive* transport at Cranfield
  - Technology improvements (specifically parallelization / HCP)
  - Modeling of independent Chester 16 field site to stress-test modeling tools.

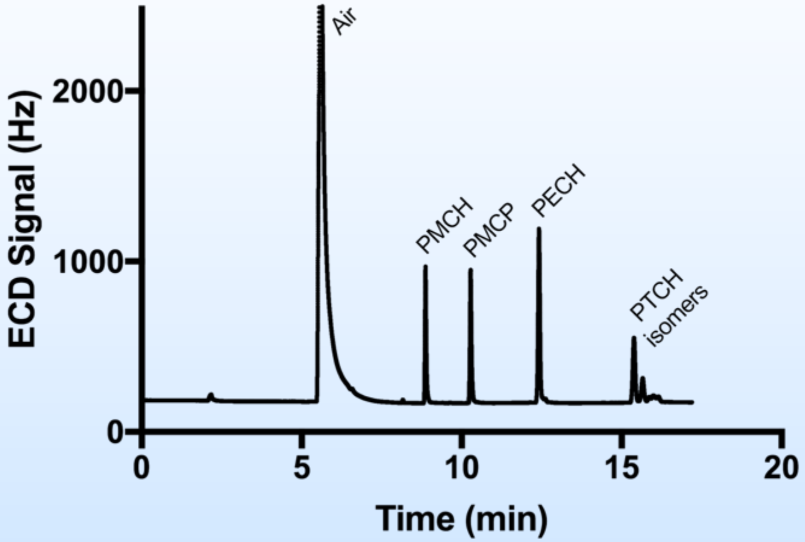
Task 2 Objective

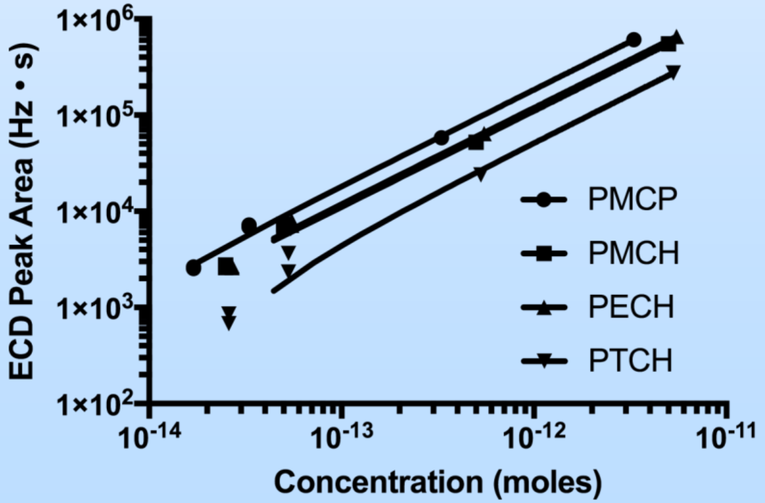
Develop methods to improve the analysis of perfluorocarbons in a hydrocarbon-rich matrix, found in many EOR and EGR monitoring well samples.

<u>Conservative Perfluorocarbon Tracers (PFTs)</u>

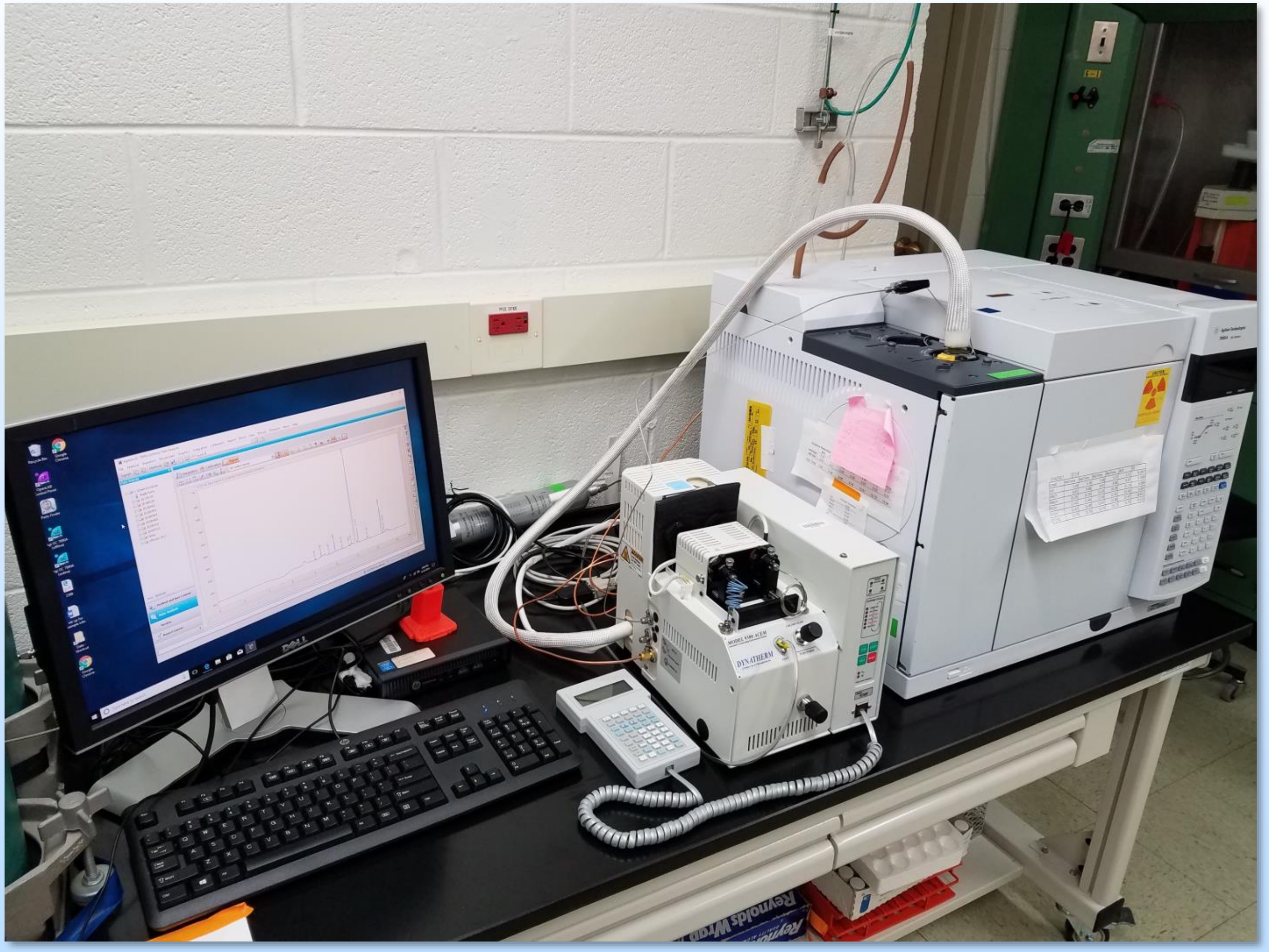
- Non-reactive, non-toxic, inexpensive and stable to 500°C
- Several PFTs can be quantified in a single analysis
- Detectable at pg-fg levels (fmoles)
- Different PFT "suites" (PMCP, PMCH, PECH, PDCH, PTCH), and SF_6, assess multiple breakthroughs
  → *flow regime indicator*

GC-ECD analysis of 20-30 fmoles (5-10 pg) each PFT in air



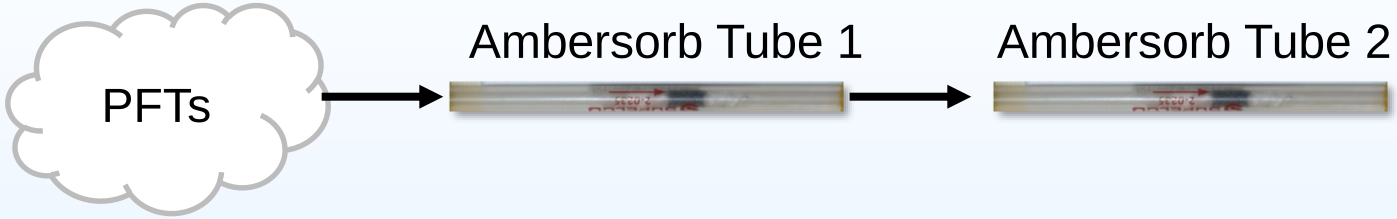


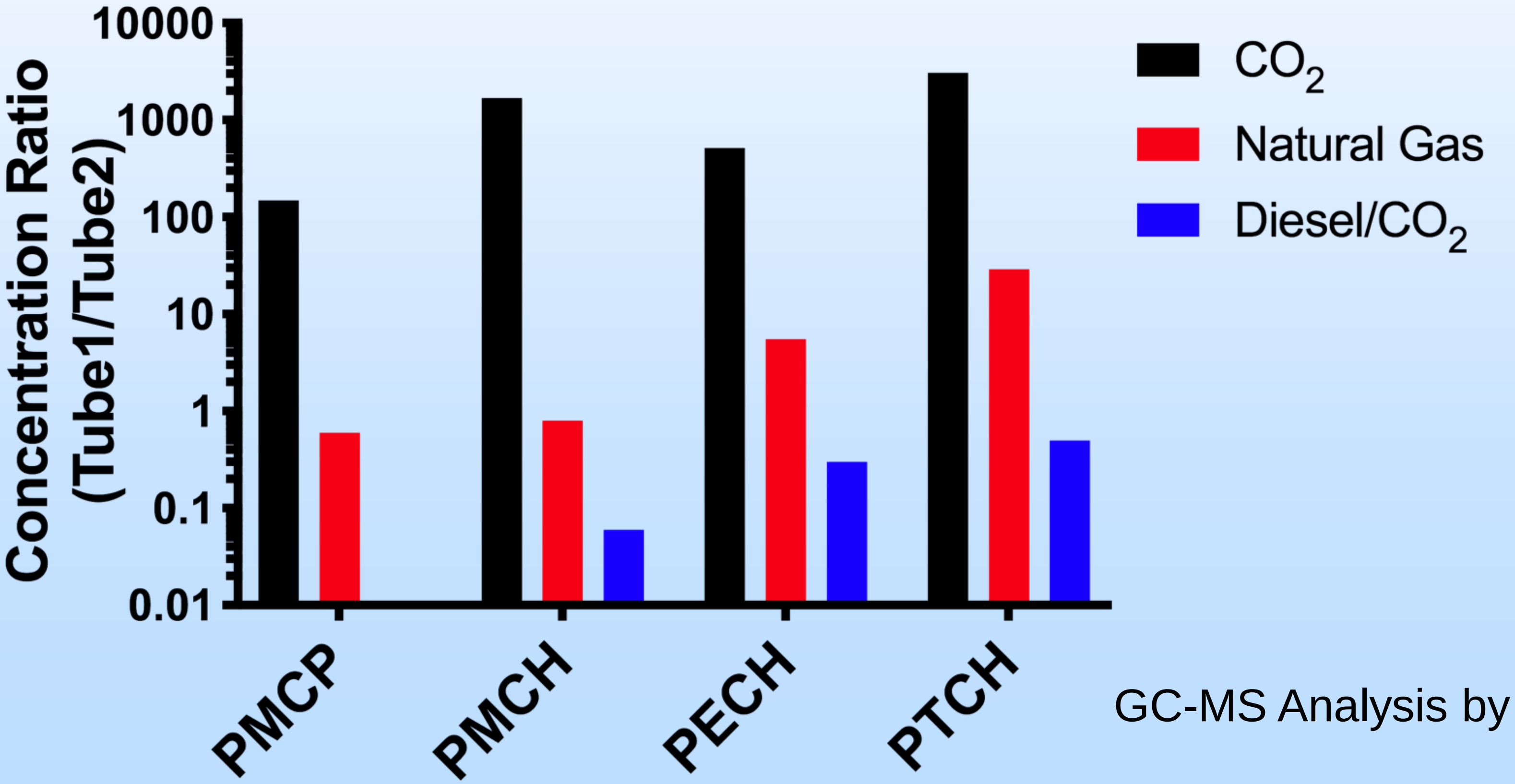
Thermal Desorption-Gas Chromatography with Electron Capture Detection



Prior Accomplishments

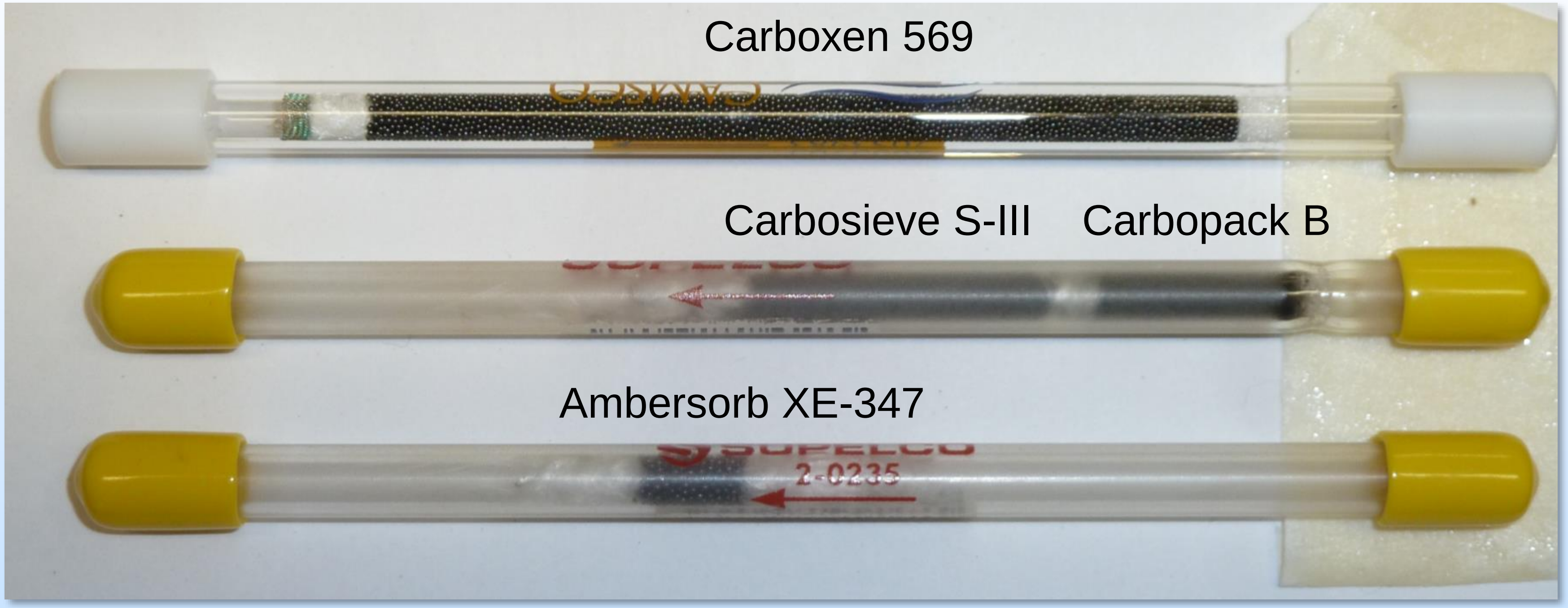
Increased PFT breakthrough to downstream tube in the presence of hydrocarbons





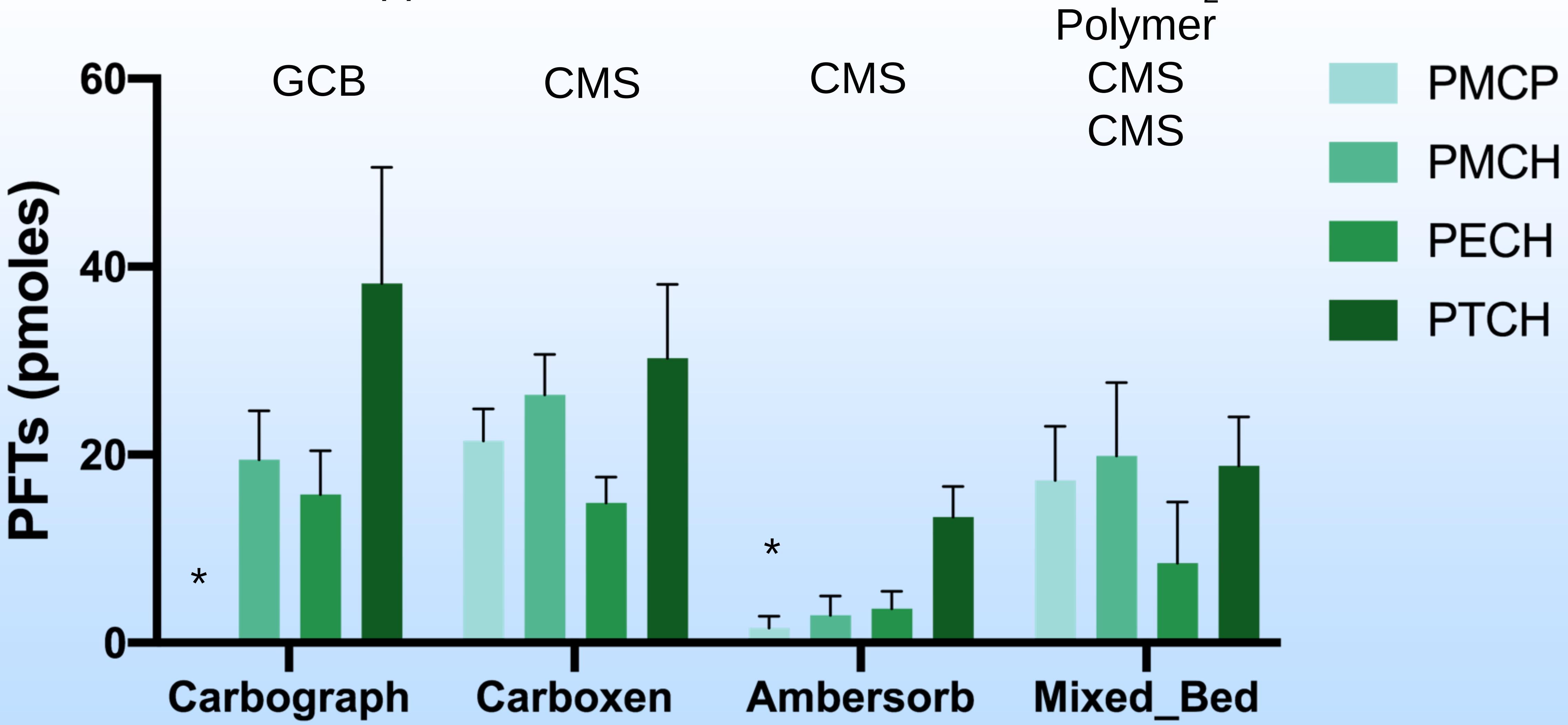
GC-MS Analysis by Sean Sanguinito, NETL

Alternative Thermal Desorption Tubes



Prior Accomplishments

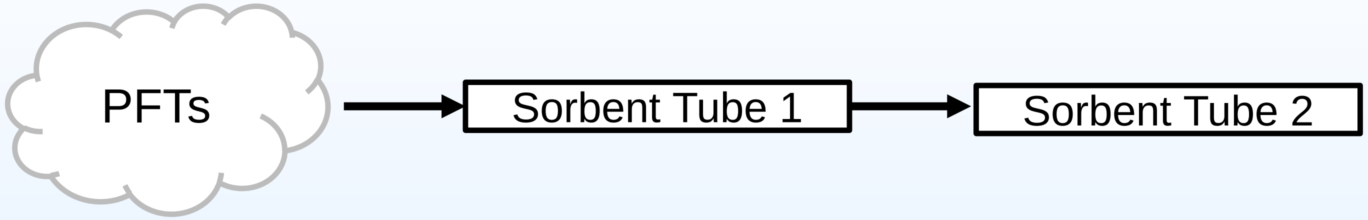
Alternative sorbents trapped more PFTs than Ambersorb with CO_2 & diesel volatiles

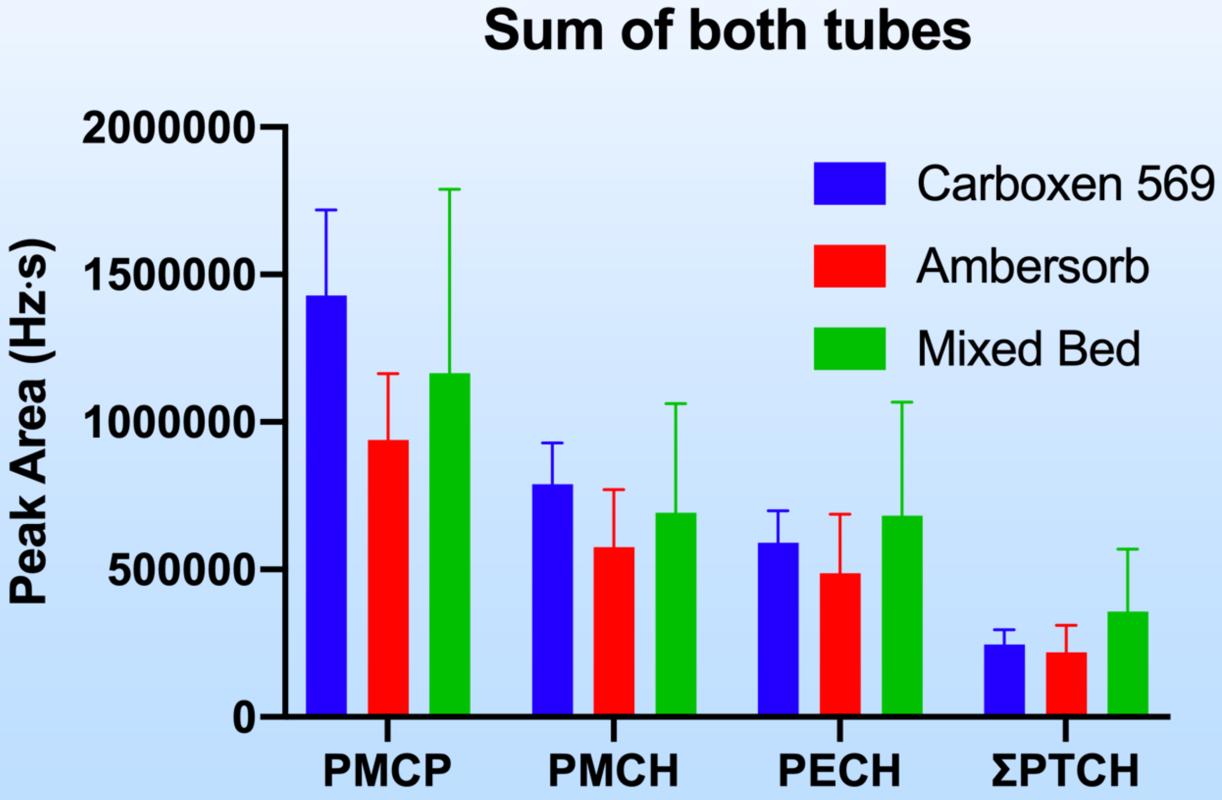


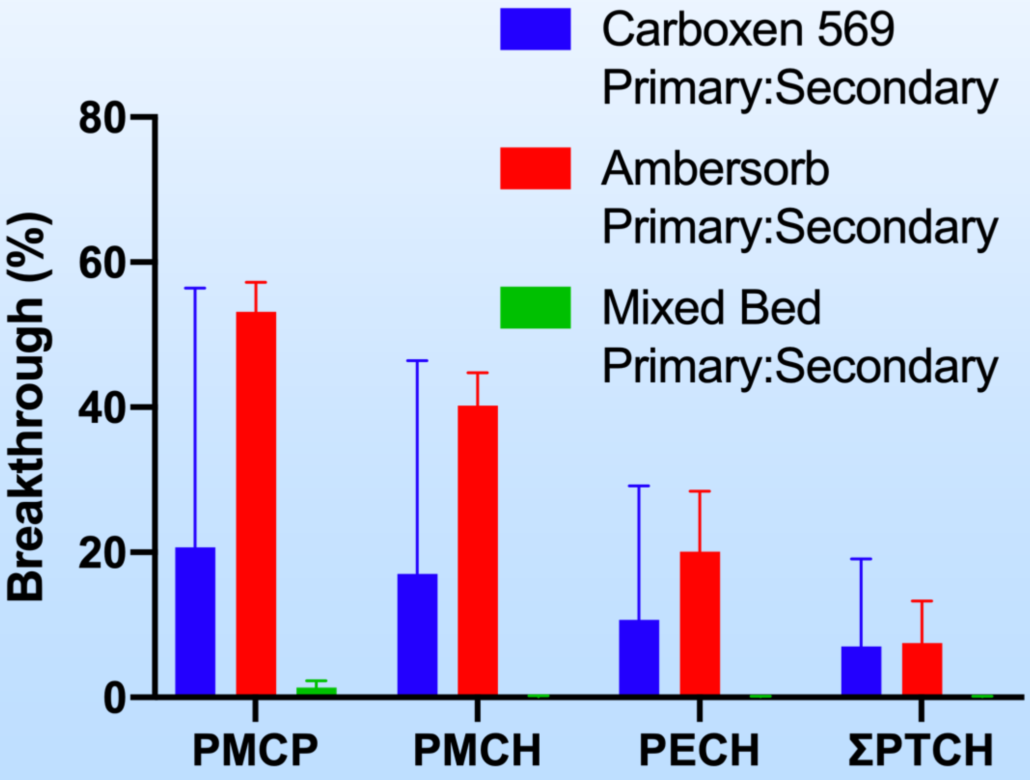
Tubes containing four sorbents were loaded with PFT standards in CO_2 saturated with diesel and analyzed using TDS with GC-ECD analysis. The mixed bed tube contains Tenax TA, Carboxen 1000 and Carbosieve S-III.

New Sorbents Reduced Breakthrough

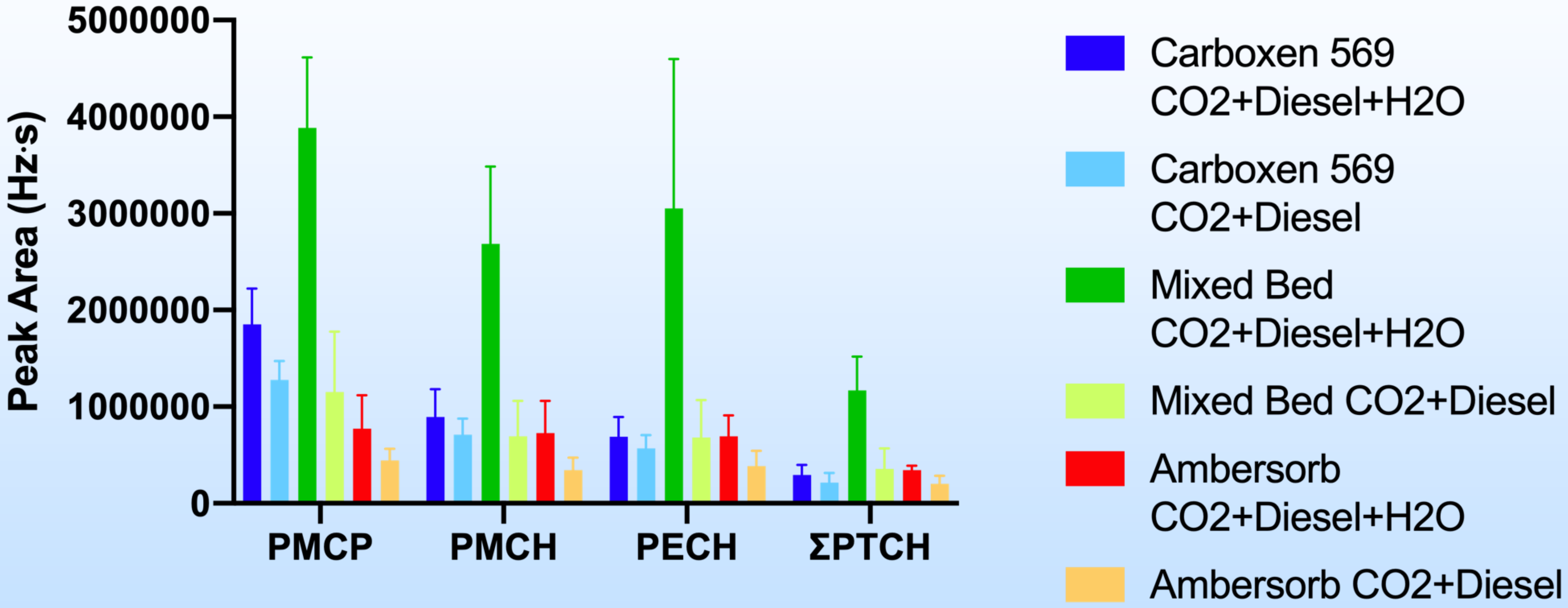
Alternative sorbents trapped more PFTs than Ambersorb with CO_2 & diesel volatiles





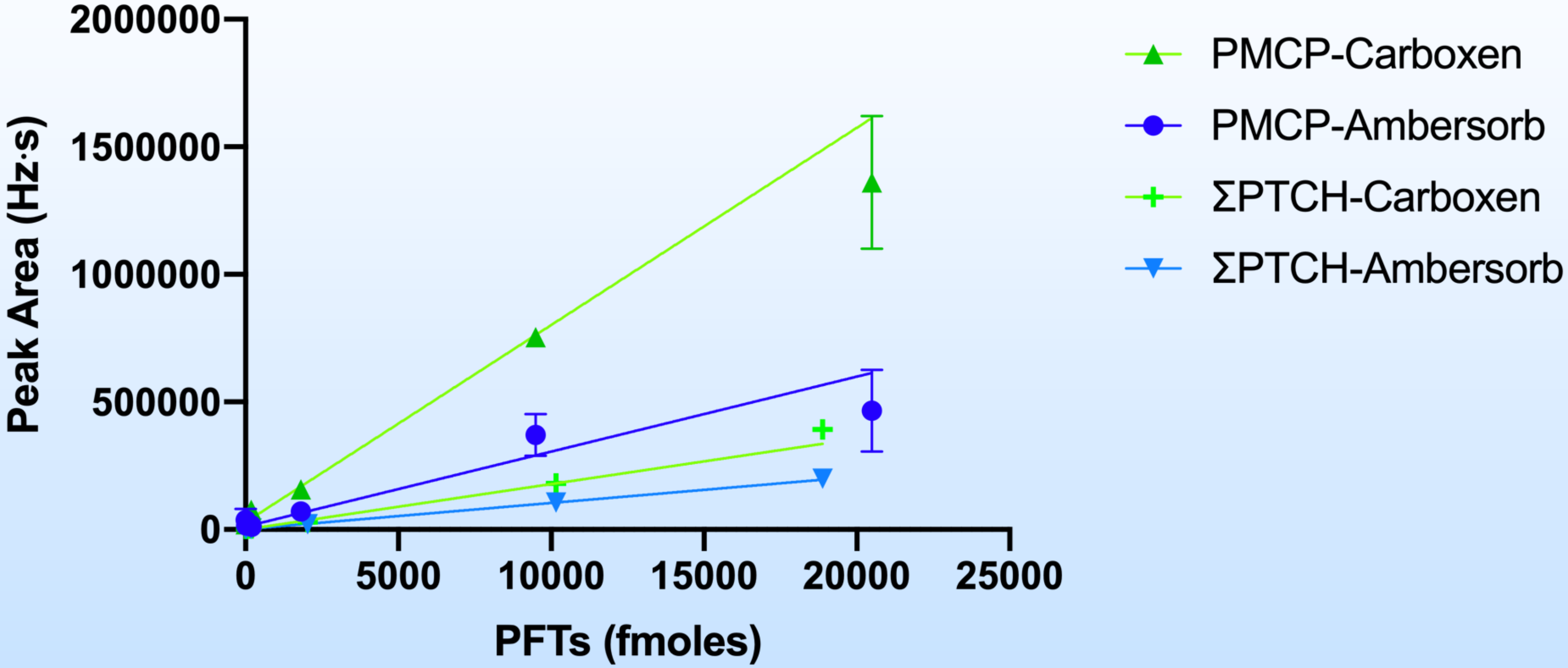


Water Does Not Inhibit PFT sorption



Water did not have a significant effect on PFT recovery from Carboxen 569 or Ambersorb .
Unexpected increase in the mixed-bed sorbent's sensitivity to PMCP, PMCH and PECH (P_{adj} < 0.001 for each)

Improved Sensitivity and LOD with Carboxen 569 Sorbent Tubes



PFT	Ambersorb XE-347 LOD (pmoles/L)	Carboxen 569 LOD LOD (pmoles/L)
PMCP	5.8	0.5
PMCH	1.6	0.1
PECH	0.7	0.1
PTCH	1.3	0.3

Summary (Task 2)

- Hydrocarbons substantially reduce the efficiency of perfluorocarbon adsorption to AMBERSORB™.
- The most volatile PFT (PMCP) may not be adsorbed in the presence of HCs using some sampling tubes.
- Larger bed volumes of high specific surface area carbon molecular sieve sorbents or mixed beds significantly and substantially improves detection.
- Carboxen 569 is a recommended replacement for AMBERSORB in sorbent tubes for PFT sampling.
- PFT response factors (sensitivities) vary significantly, but LOD is similar and limited by background contamination.

Synergies

- Established collaborative simulation opportunities with MRCSP regarding challenging reef systems.
- Open to other partnerships, incl. future large-scale projects.
- Addressing priority research directions:
  - PRD S-1: Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gton/yr Capacity
  - PRD S-2: Understanding Dynamic Pressure Limits for Gigatonne-scale CO_2 Injection
  - PRD S-6: Improving Characterization of Fault and Fracture Systems
- Collaborative PFT sorbent testing in hydrocarbon-rich matrices. Planned GC-MS experiments with NETL RIC.
- Sharing best practices for tracer analysis
  - Potential applications for CCUS Research Priority areas: Locating, Evaluating, and Remediating Existing and Abandoned Wells & Wellbore leakage

APPENDICES

Organization Chart

David Graham, PI

Tommy Phelps
Susan Pfiffner

Joachim Moortgat
David Cole
Postdocs: Soltanian, Zhu, Li

Collaborators:

Gantt Chart

Task	Milestone Description*	Fiscal Year 2019				Fiscal Year 2020				Fiscal Year 2021				Planned Start Date	Planned End Date	Actual Start Date	Actual End Date
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4				
2.1	Survey field test opportunities for enhanced PFT sampling technology													9/18	12/18	9/18	12/18
2.1	Thermal desorption system installed on ORNL's gas chromatography system													2/19	3/19	2/19	3/19
2.1	Sorbent selected for PFT-hydrocarbon experiments													3/19	6/19		7/19
1.1	Initial transport modeling of aqueous equilibrium reactions with Osures+iPhreeqc													3/19	9/19	3/19	9/19
1.2	Data sharing planned with partner institution(s) for future modeling of a CCS project independent of the Cranfield DAS													3/19	12/19		12/19
2.1	Validation of PFT sorbent sampling method in hydrocarbon matrices													7/19	12/19		3/20
2.1	Best practices identified for PFT sampling in hydrocarbon-rich environments													9/19	12/20		
1.2	Static model developed for a modeling benchmark study of an independent CSS project													7/19	6/20		8/20
1.1	First demonstrations of reactive transport modeling of the multiphase brine-CO2-rock system using higher-order accurate methods													7/19	12/20		
1.2	Modeling of CO2-brine flow and transport for a field site different from Cranfield DAS													1/20	3/21		
1.1	Final model of geochemistry and reactive transport at Cranfield													7/20	6/21		
1.1	Complete CO2-brine-rock geochemistry and reactive transport incorporated into CSS simulations													10/20	9/21		
3	Final report on Monitoring of Geological CO2 Sequestration Using Isotopes and Perfluorocarbon Tracers													1/20	9/21		