Monitoring of Geological CO_2 Sequestration Using Isotopes & Perfluorocarbon Tracers

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

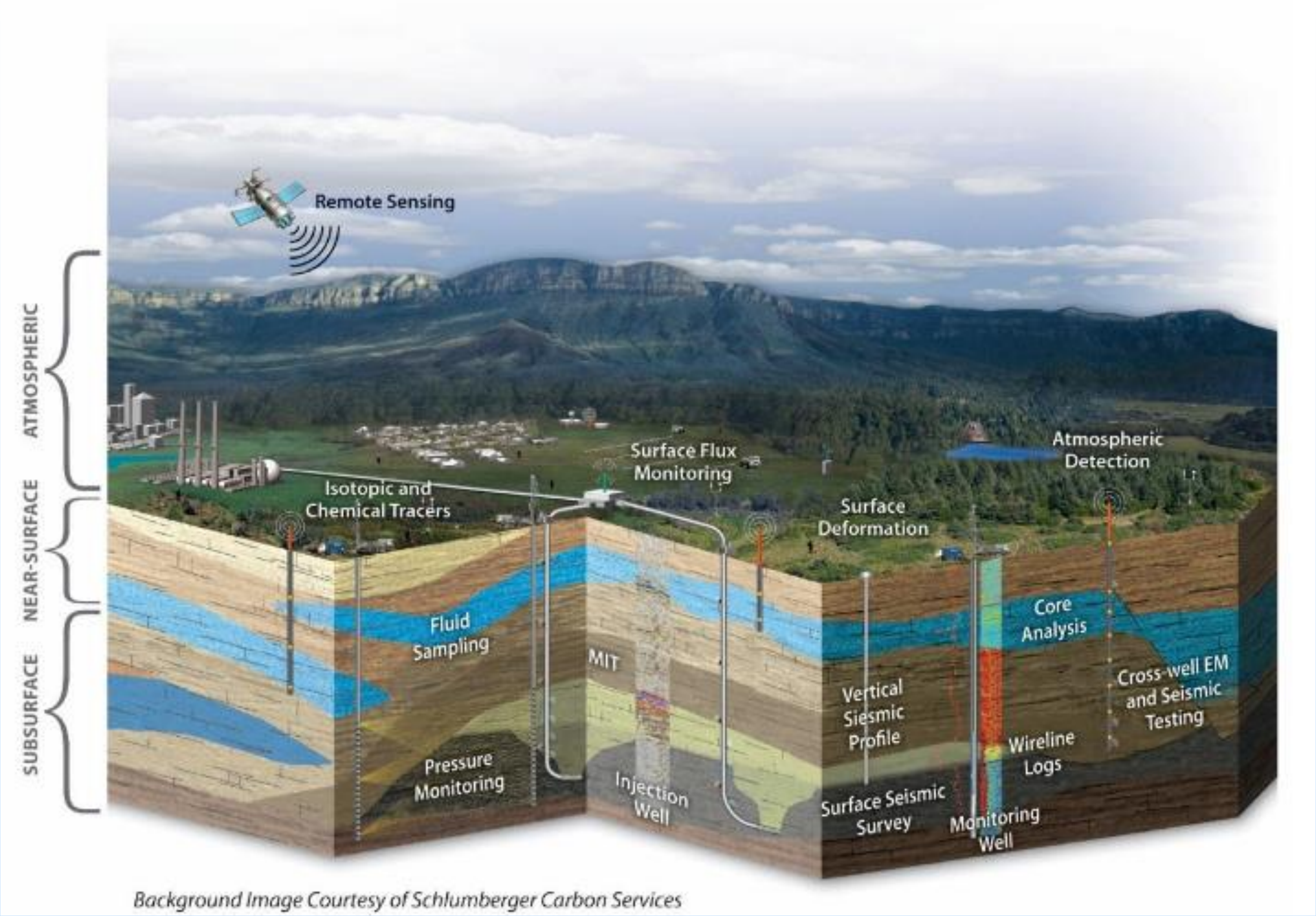
Carbon Management Project Review Meeting

August 15, 2022

Benefit to Program

Monitoring, Verification, Accounting and Assessment

- Provide information on physical and geo-chemical changes in reservoir, ensuring CO_2 storage permanence.
- Ground-truth behavior of fluids, CO_2 transport properties to constrain reservoir simulation models, predicting CO_2 storage capacity & designing efficient MVA programs.
- Address CCUS Priority Research Directions:
- Optimizing Injection of CO_2 by Control of the Near-Well Environment
- Realizing Smart Monitoring to Assess Anomalies and Provide Assurance



From NETL Carbon Storage MVA Tools Available for Monitoring CCS Projects

FEAA-045 Timeline

< 2009 Frio Brine pilot site tracer tests

2009-2015 Cranfield CO_2 storage project tracer tests and measurements (with SECARB)

2015-2022 Enhanced models integrating tracer results with CO_2 storage reservoir simulations

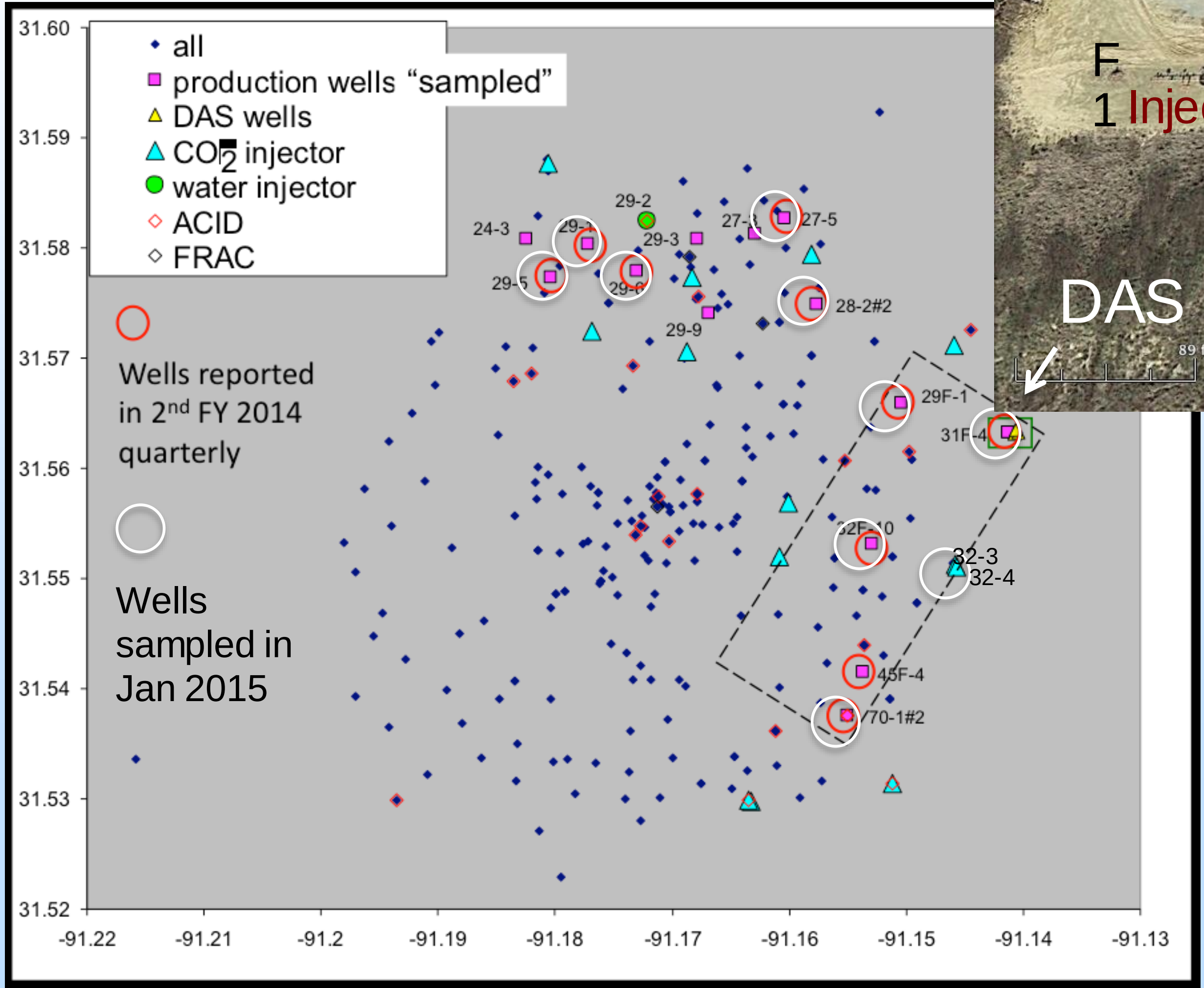
2020-2022 Chester-16 reef simulations (with MRCSP)

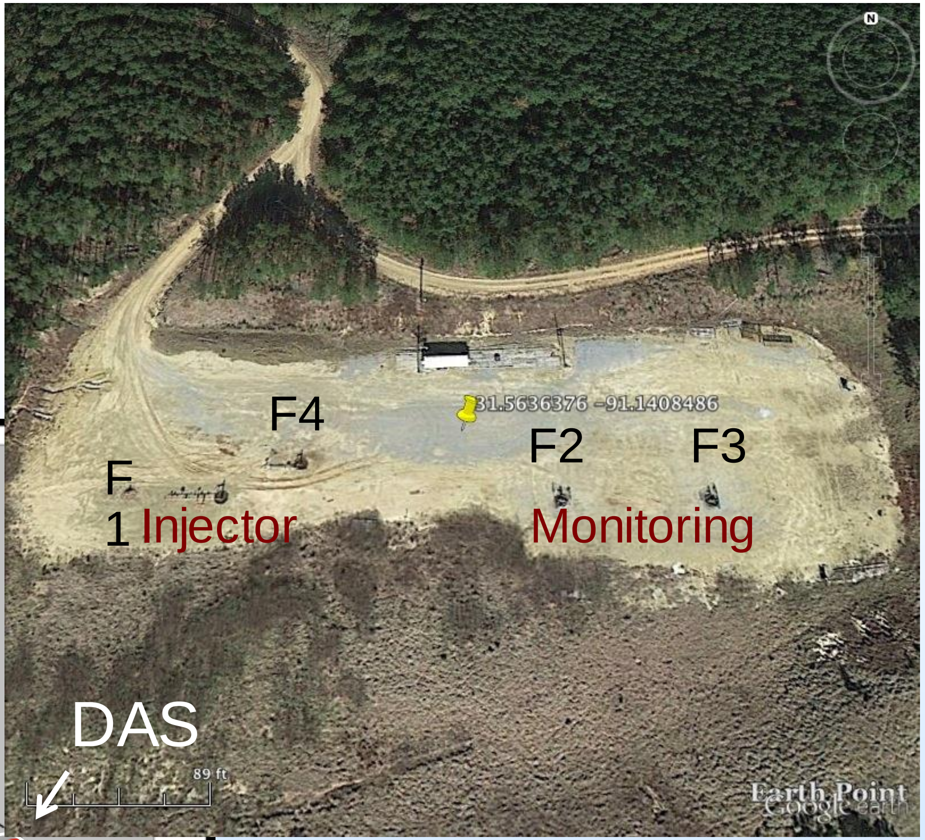
2015-2022 Improved perfluorocarbon analytical methods for tracer tests

Tracers for Evaluating CO_2 Storage in Brine Reservoirs

Trapping Mechanisms	Processes	Tracers
Migration, structural, and stratigraphic trapping of $scCO_2$	Advection, Dispersion, Mixing & Dilution	CO_2 isotopes Methane (CH_4) Perfluorocarbons (PFTs) Noble gases
Residual trapping in rock pores	Capillary Forces	(As above)
Dissolution of CO_2 into formation brine	Diffusion, Partitioning	Water isotopes CO_2 isotopes pH DIC, Alkalinity
Chemical trapping of CO_2 through fluid-rock geochemical reactions	Dissolution, Precipitation, Water-Rock Interactions	CO_2 isotopes Cations, Sr isotopes Anions

Cranfield, MS
Detailed Area of Study (DAS)

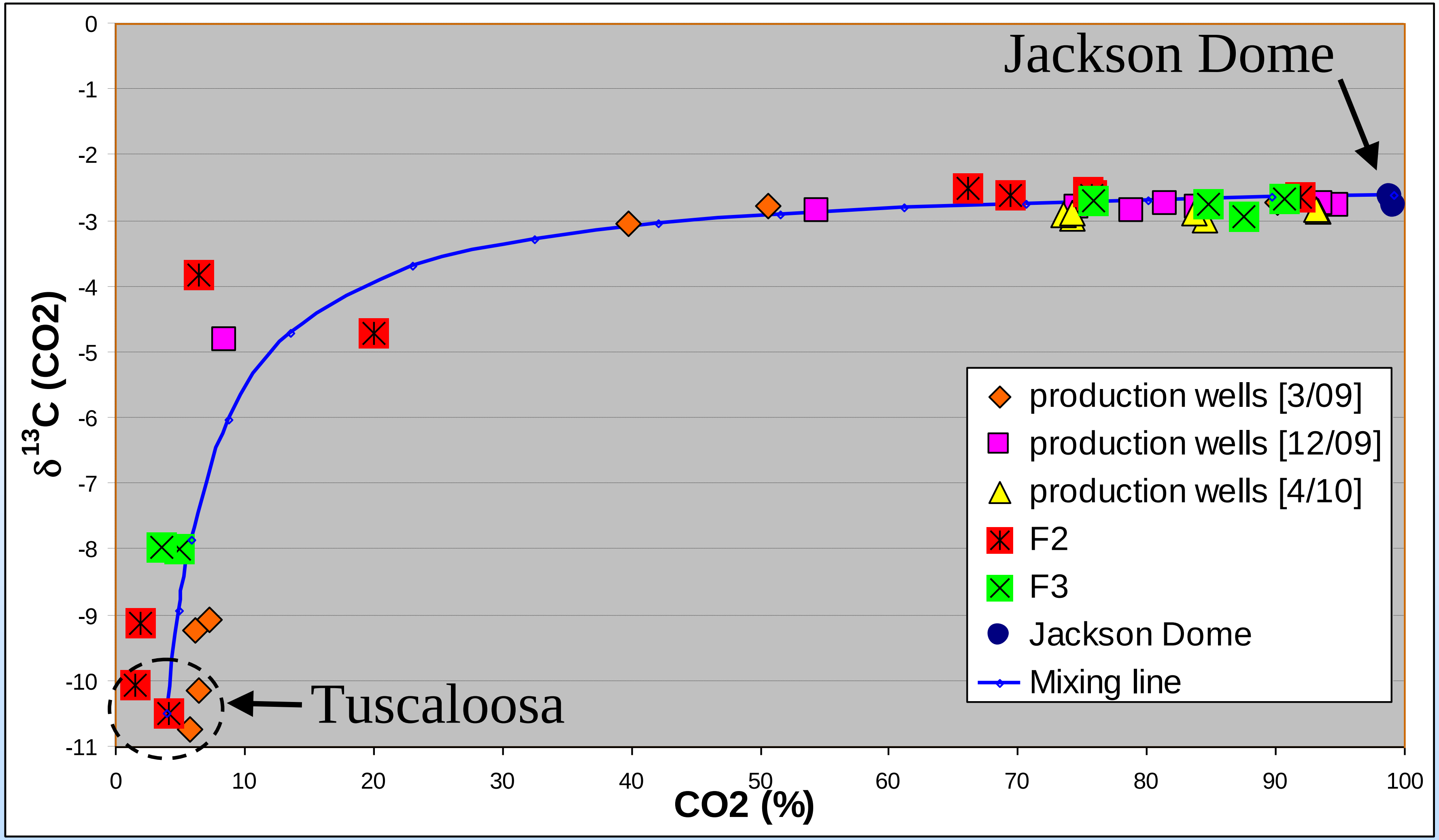




Thanks to:

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

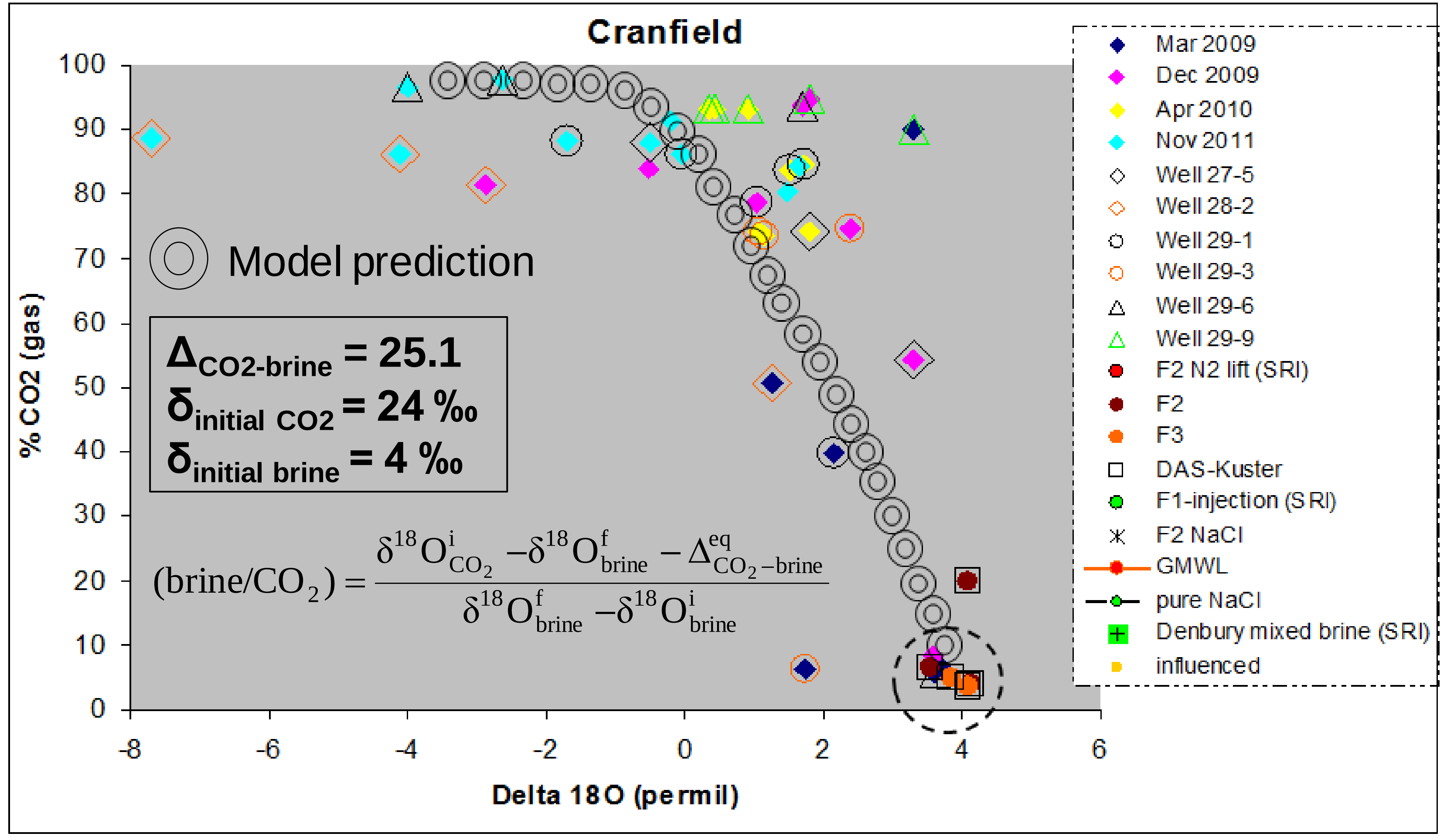
Carbon Isotopes ($^{13}C/^{12}C$) of Injected CO_2 Gas from Jackson Dome Show Good Mixing with Tuscaloosa CO_2



Simple two-component fluid mixing dominates at the DAS site

No obvious evidence of CO_2 reaction with reservoir rock carbonates

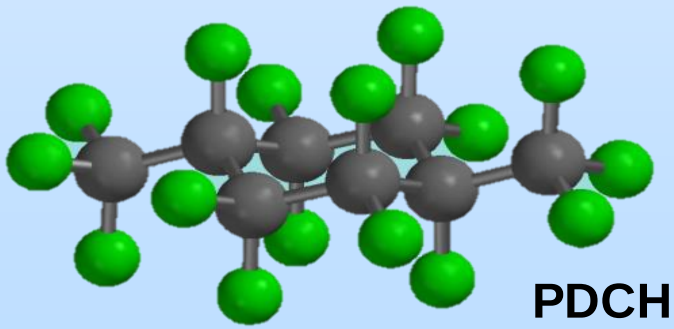
Modeling of O isotope shifts in CO_2



Magnitude of oxygen isotope shift largely a function of brine/CO_2 ratio vs carbon isotope variation due to mixing of formation CO_2 with injectate

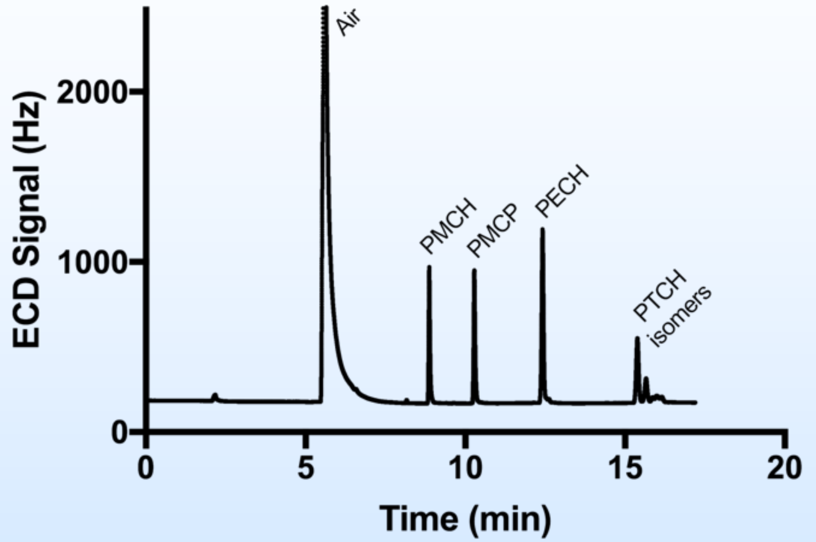
Conservative Perfluorocarbon Tracers (PFTs)

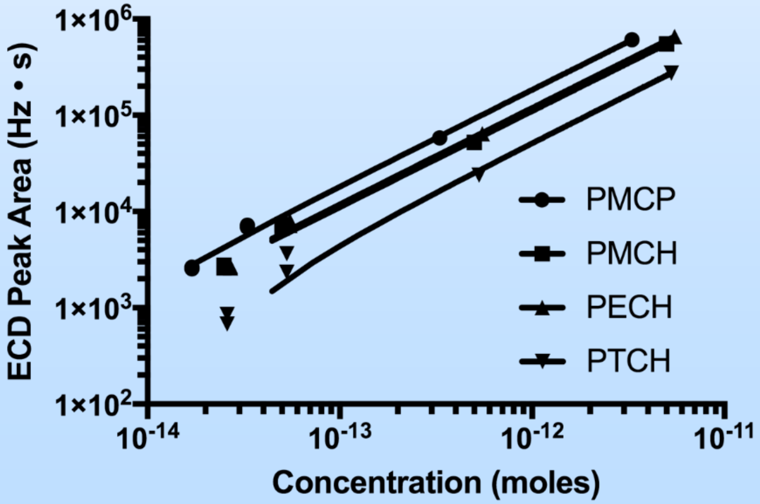
- Non-reactive, non-toxic, inexpensive and stable to 500°C
- Several PFTs can be quantified in a single analysis
- Detectable at pg-fg levels (fmoles)
- Different PFT "suites" (PMCP, PMCH, PECH, PDCH, PTCH), and SF_6, assess multiple breakthroughs
  → *flow regime indicator*



PDCH

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

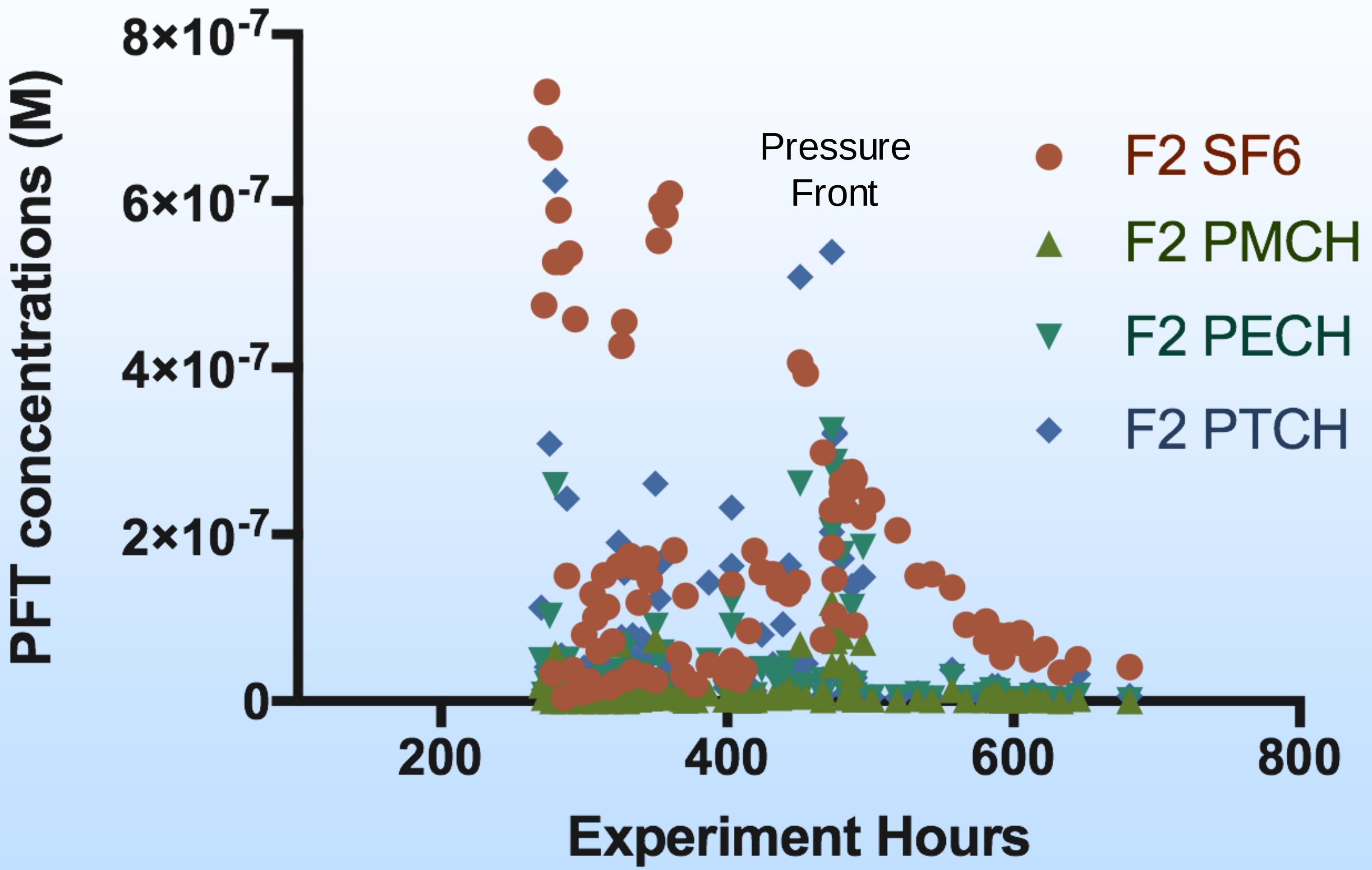




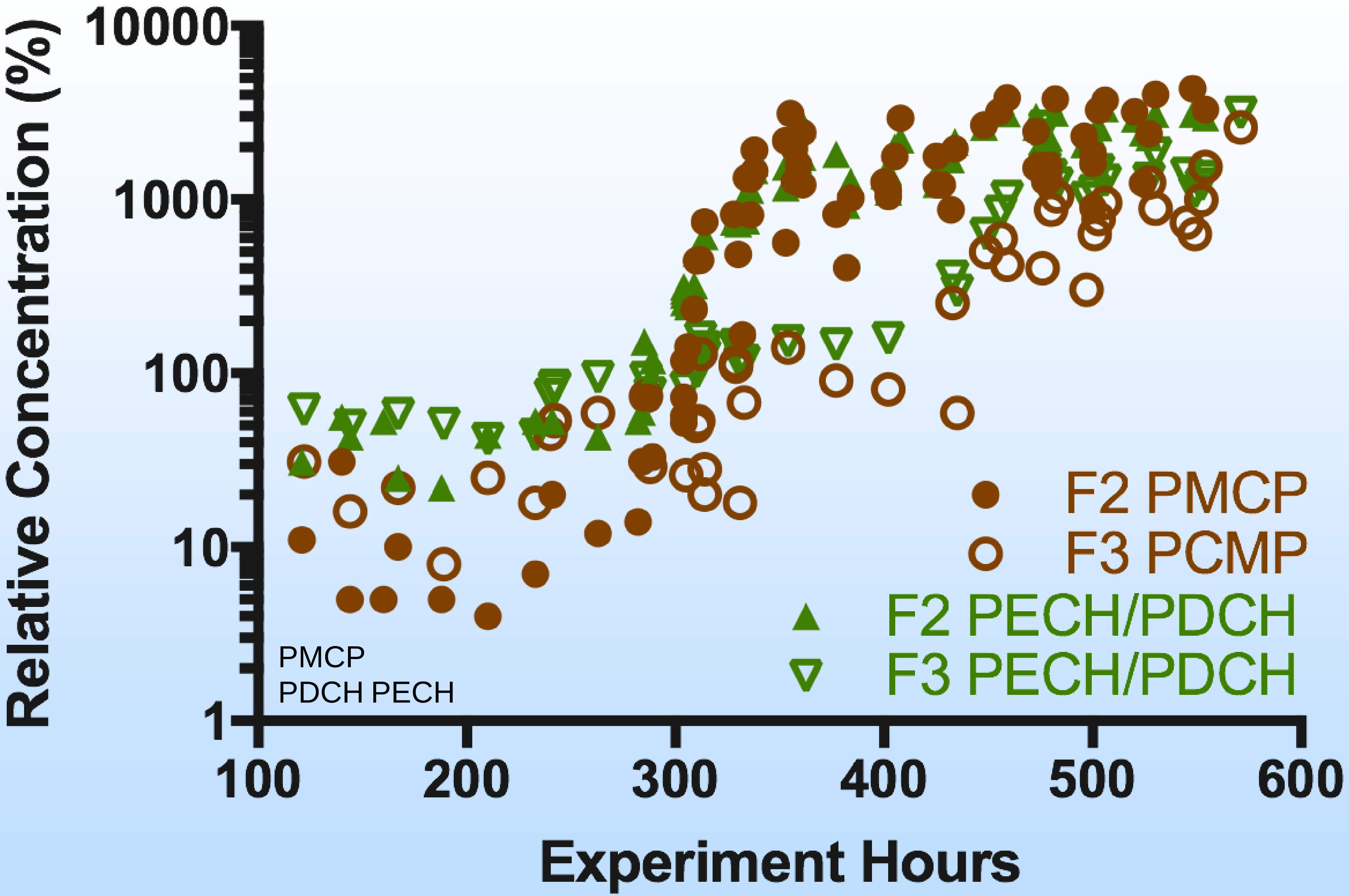
2009 Campaign PFTs at F2

Injections

Time	PFT
0	PMCH
6	PTCH
31	PECH
33	SF_6
75	PDCH
269	PMCH
436	PTCH

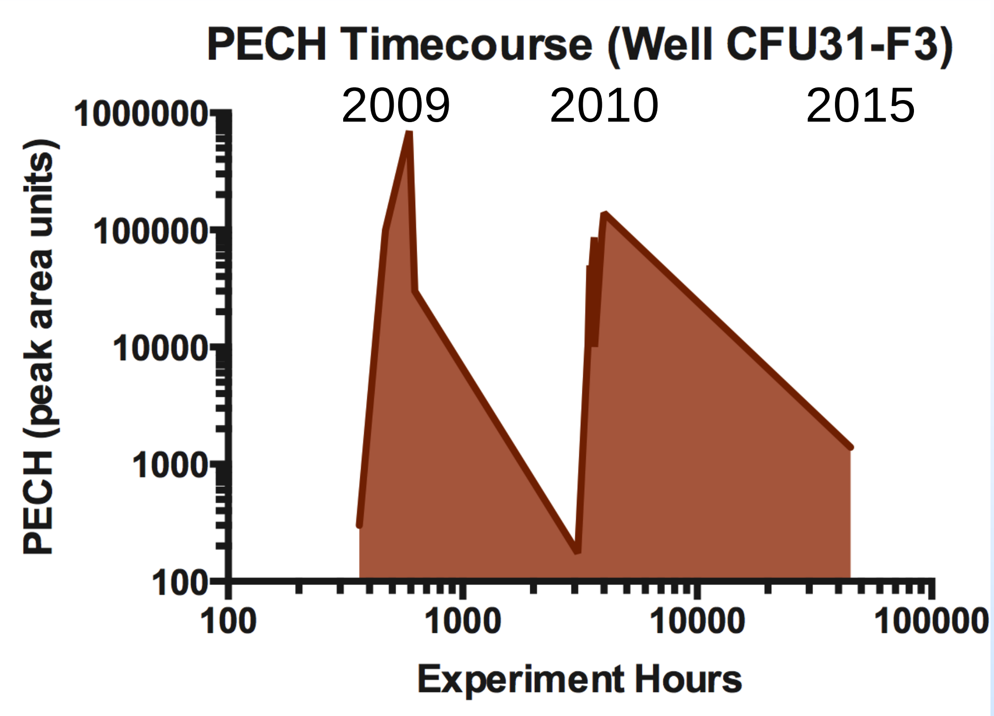


2010 Campaign PFTs Relative to PTCH



PFTs Present After 5 Years of Experiment!

- Long-term diffusive tail (50 X longer than Frio)
- Tracer reservoir in F3 vicinity (>20,000 hr of previous inactivity)
- Revealed differential transport of SF_6 and PECH (and others)



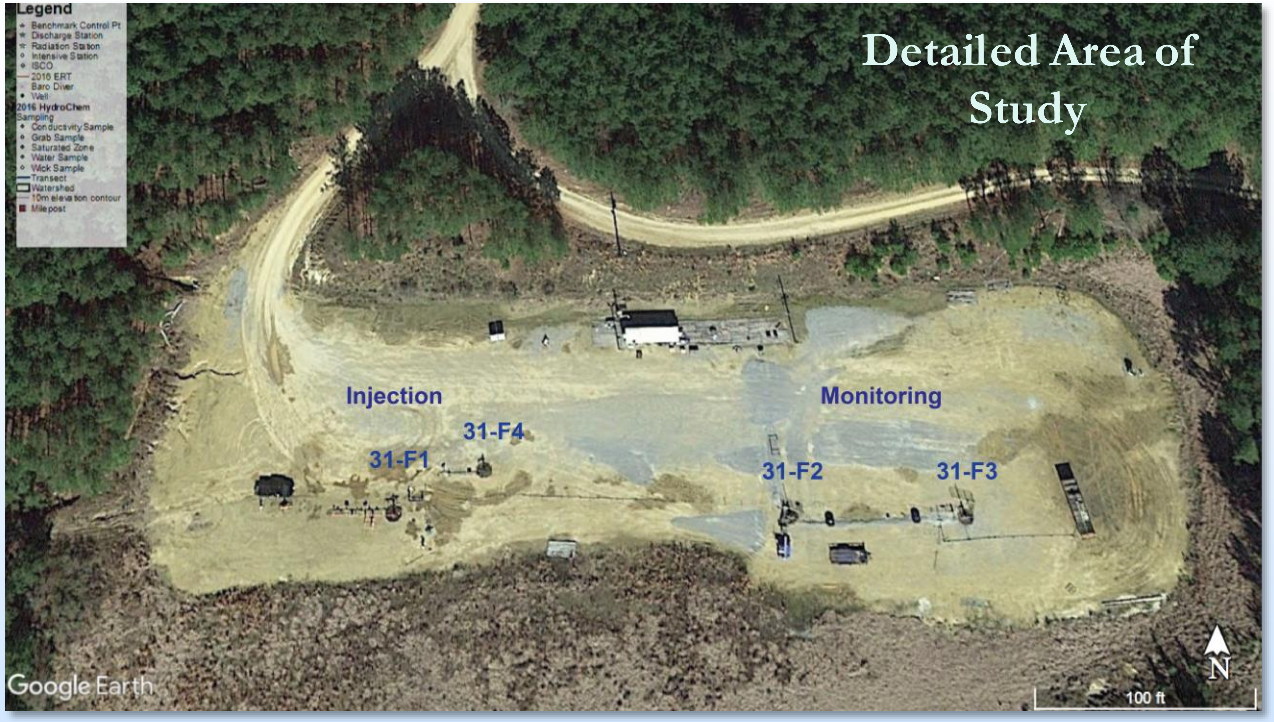
PFTs Observed as Peak Area Units for the F3 Observation Well

PFT	F3 Pre-Vent 01-13-15	F3 Post Vent 01-23-15	F3 Post Vent 01-26-15
SF6	185,245	0	0
PMCP	571	173	37
PMCH	1079	428	121
PECH	2017	1233	377
PTCH	541	376	107

Lessons Learned

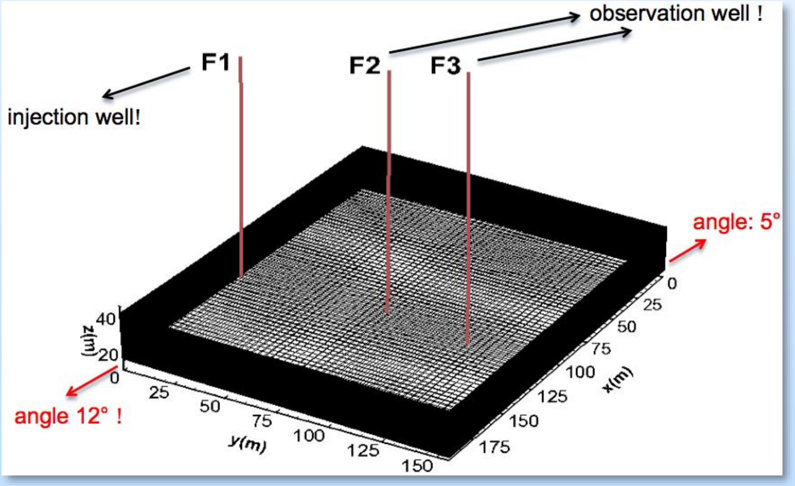
- Long-term experiments are important (long-tail)
- Carbon isotopes are valuable for mixing models
- Flow paths evolve in the reservoir
- Sensitive tracer detection is critical
- Suites of tracers are essential for interpreting flow
- Multiple suites of tracers are required for monitoring with repeated injections
- Models & simulations help to interpret tracer results

Modeling CO_2 Injection at the Cranfield Pilot Site



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

- 155 × 195 × 24 m^3, inclined in *x* and *y*
- 64 × 51 × 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

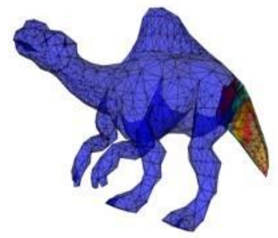


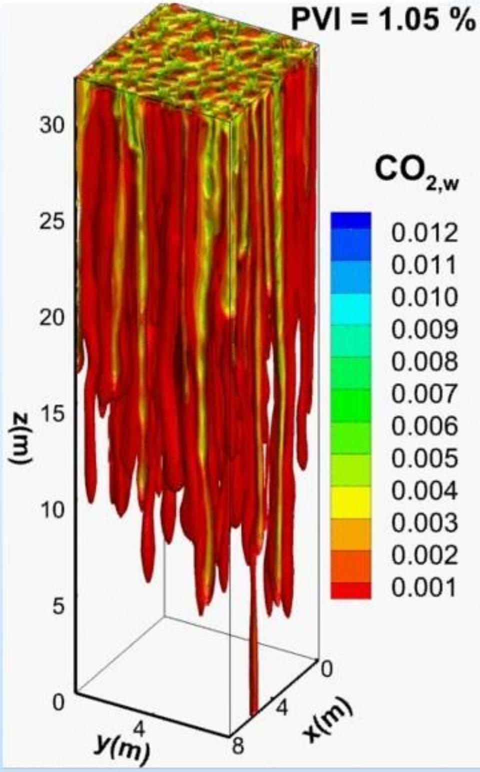
Numerical Modeling of Reactive Transport

- *Better interpret Cranfield field data*
- *Predict long-term evolution of fluids & formation*
- *Simulate critical CO_2 transport and reaction processes*
- *Apply lessons learned to other projects*

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, 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
  - Reactive transport by coupling to iPHREEQC geochemistry (2019-2020) and **PhreeqcRM** (2020-2021), which is faster / parallelizable.



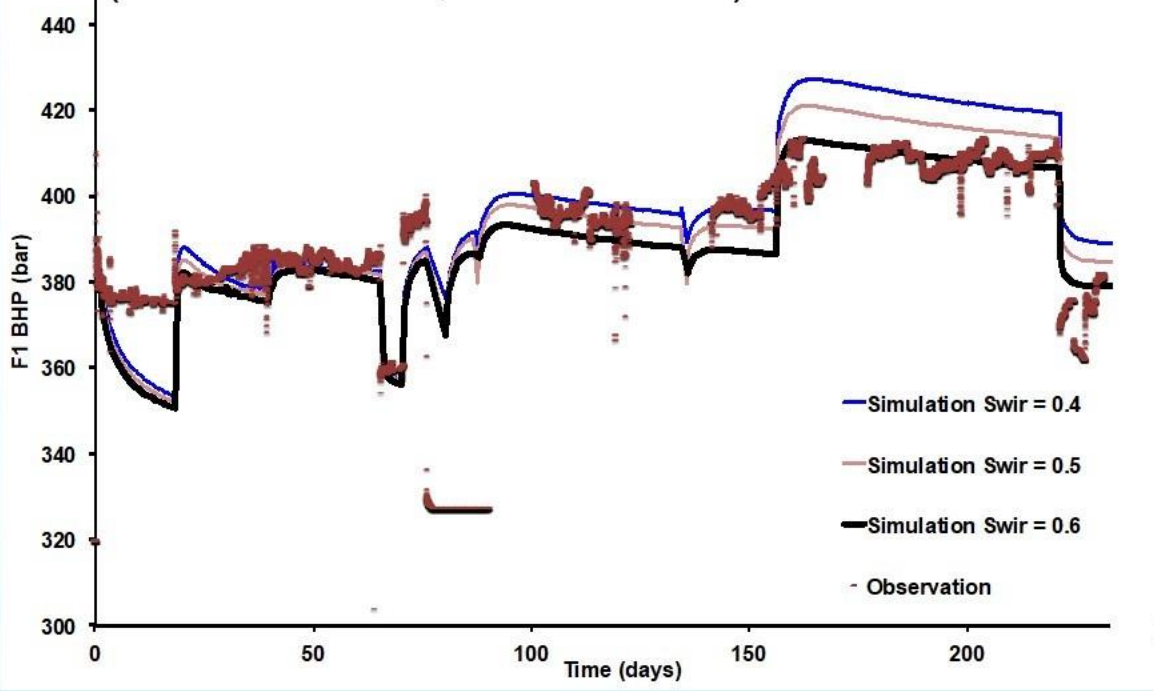


Modeling of pure CO_2 injection into brine at Cranfield

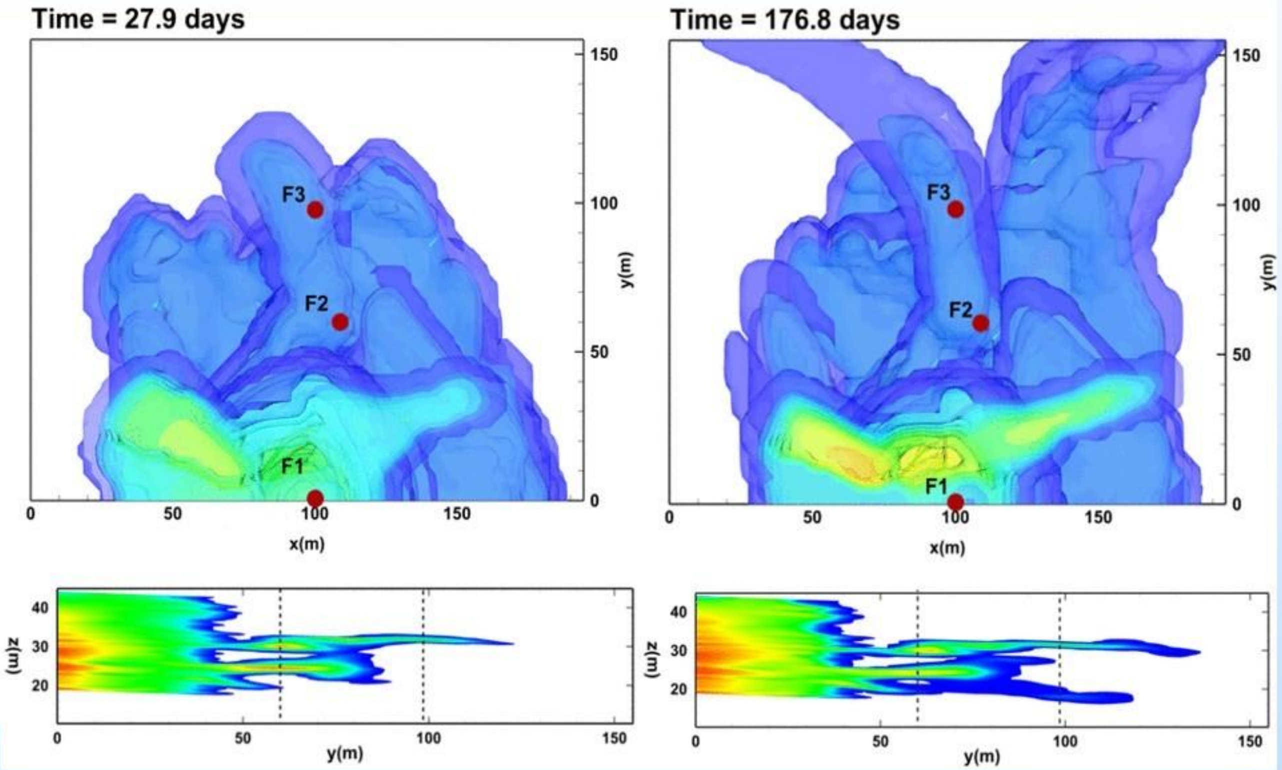
Excellent match to observed pressure response and CO_2 breakthrough times in observation wells.

Pressure response in injection well

(Soltanian et al., *IJGGC* 2016)

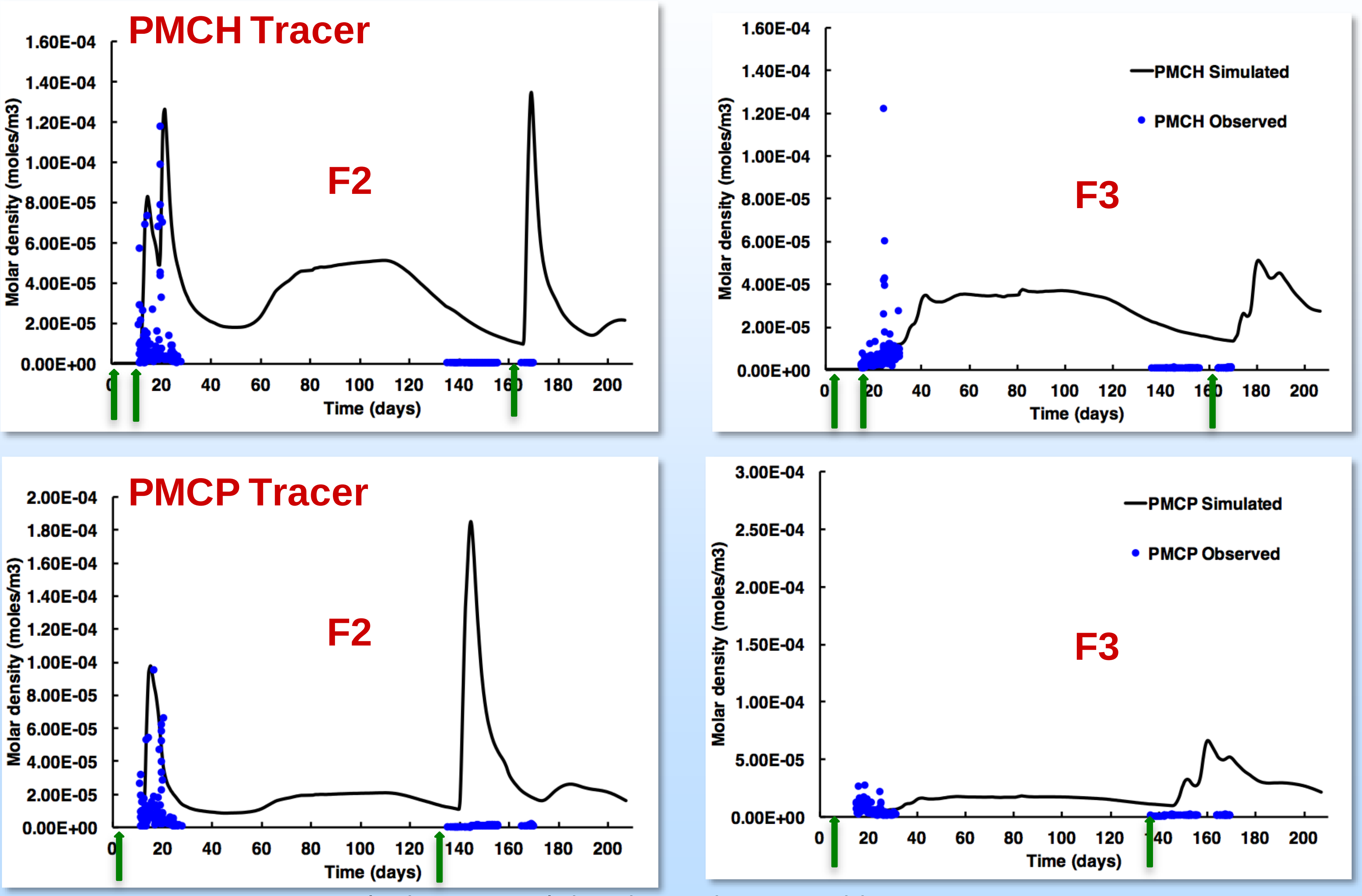


CO_2 migration in 2009 (left) & 2010 (right)



Simulating PFT Injection Campaign

2009-2010 Breakthrough Curves

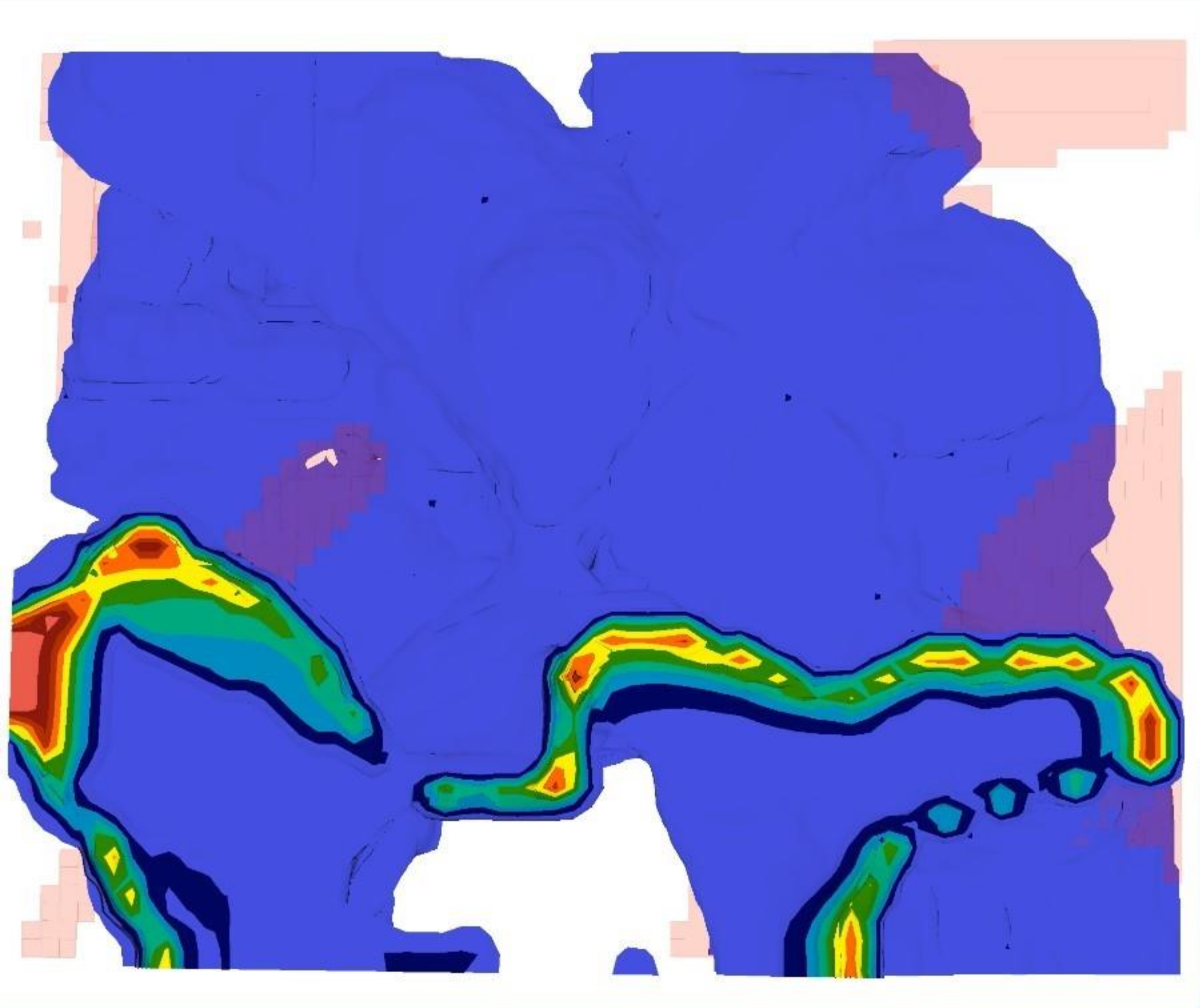


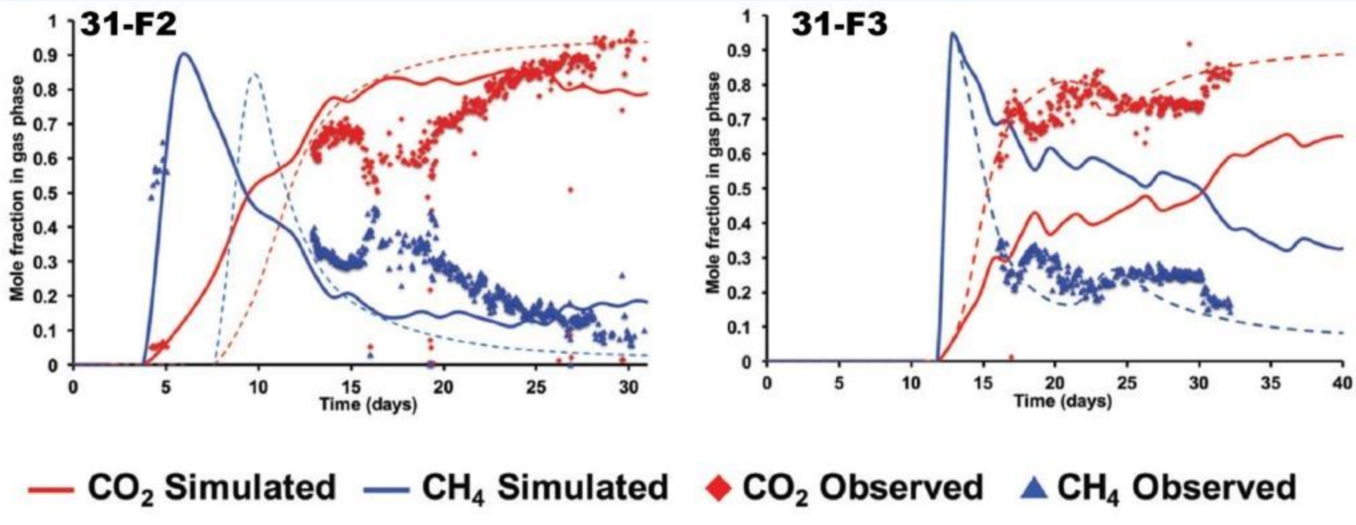
Soltanian MR, et al. (2018) Greenh. Gases 8(4):650-671

Conclusions from Simulations

- Qualitative agreement with previous studies, but closer to field data due to high-resolution static model, higher-order FE methods, and robust physics
- Agreement (mostly) on static model and wettability
- However, pressures at highest rate and CO_2 breakthrough in F3 overestimated in all models
- Most likely cause: missing fluvial conduits of flow
- Tracer breakthrough in F3 before F2 suggests the same

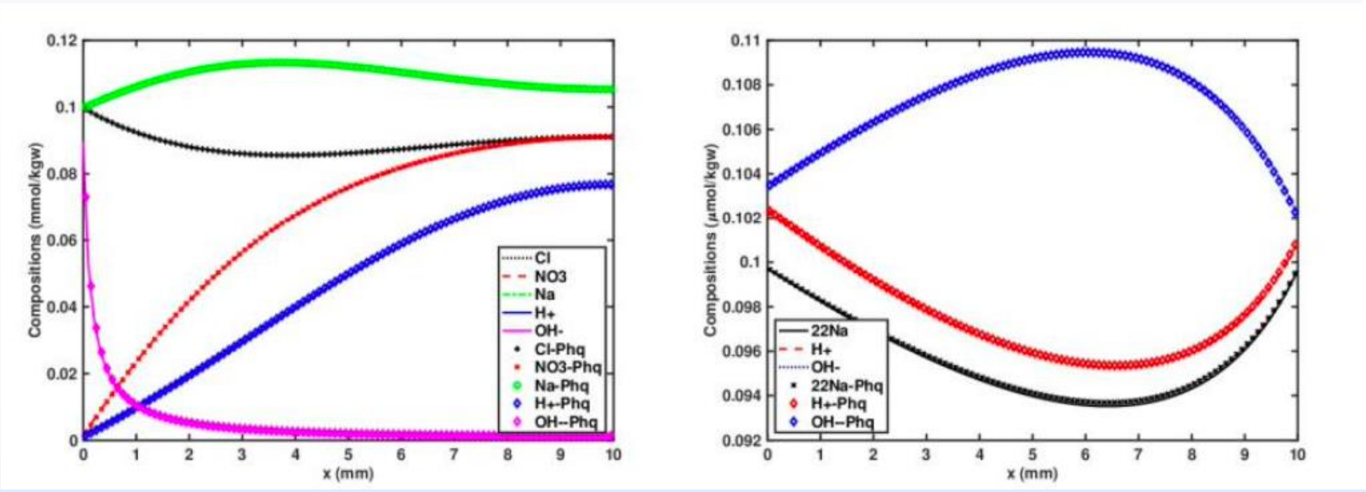
Modeling of the exsolution of methane dissolved in formation brine

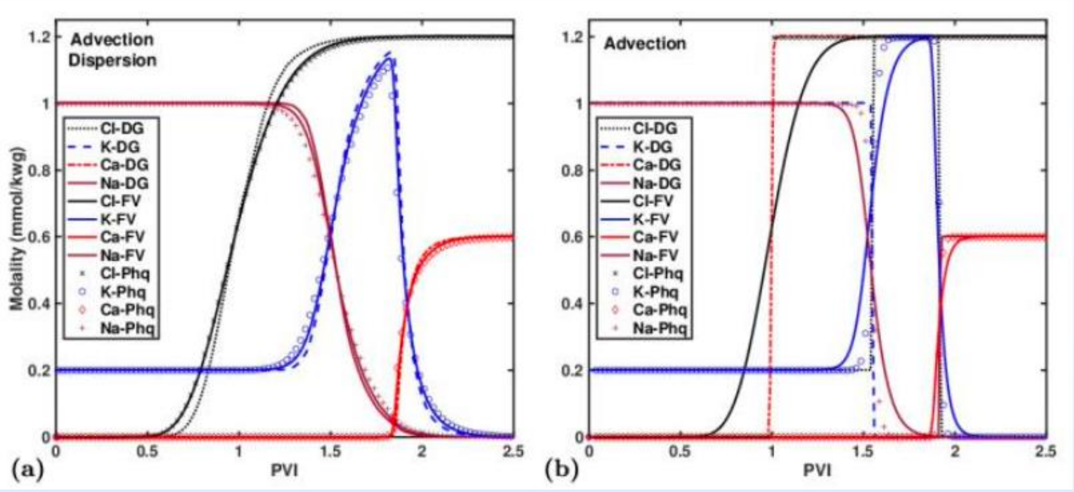




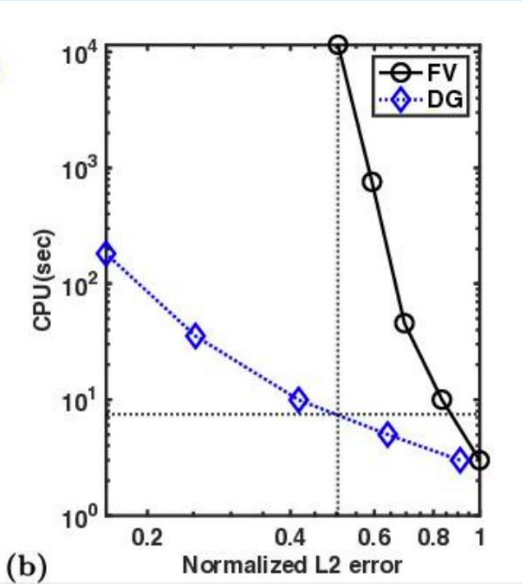
Match to observed breakthrough curves (Soltanian et al., (2018) *Groundwater* 56:176.

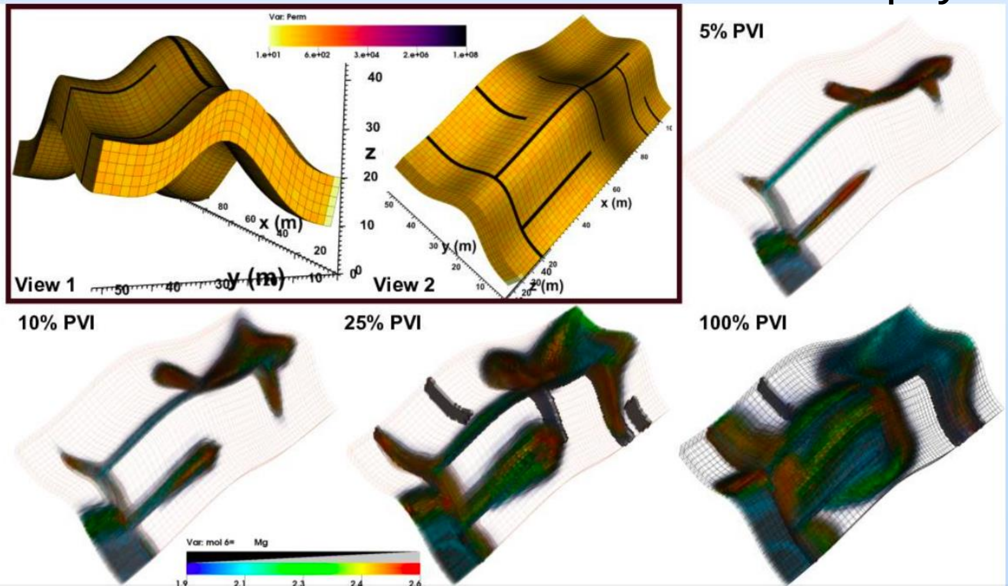
Reactive transport by coupling to iPhreeqc and PreeqcRM interfaces, only single-phase

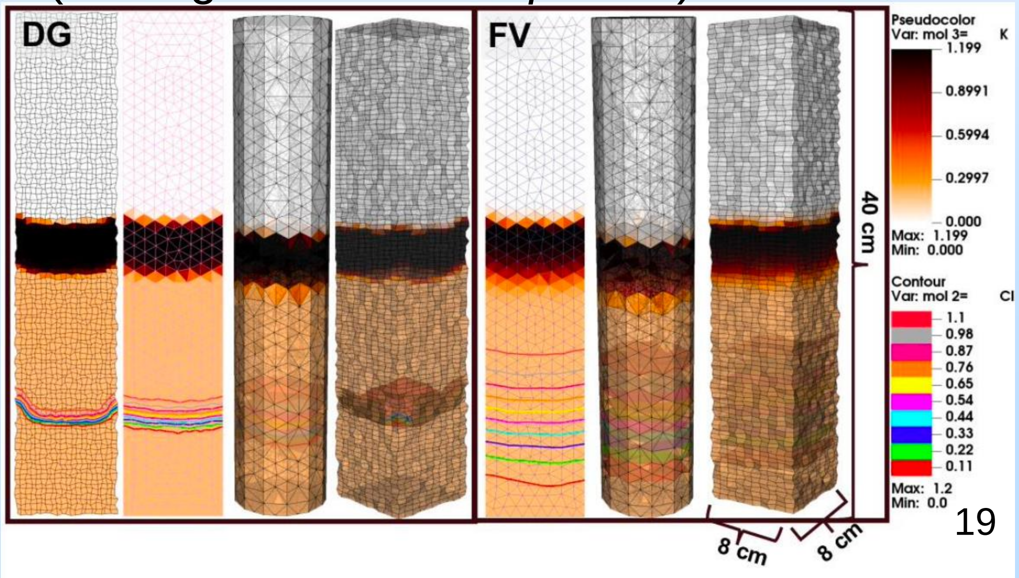




but now with advanced numerical methods and more physics (Moortgat et al. *Sci Rep* 2020):

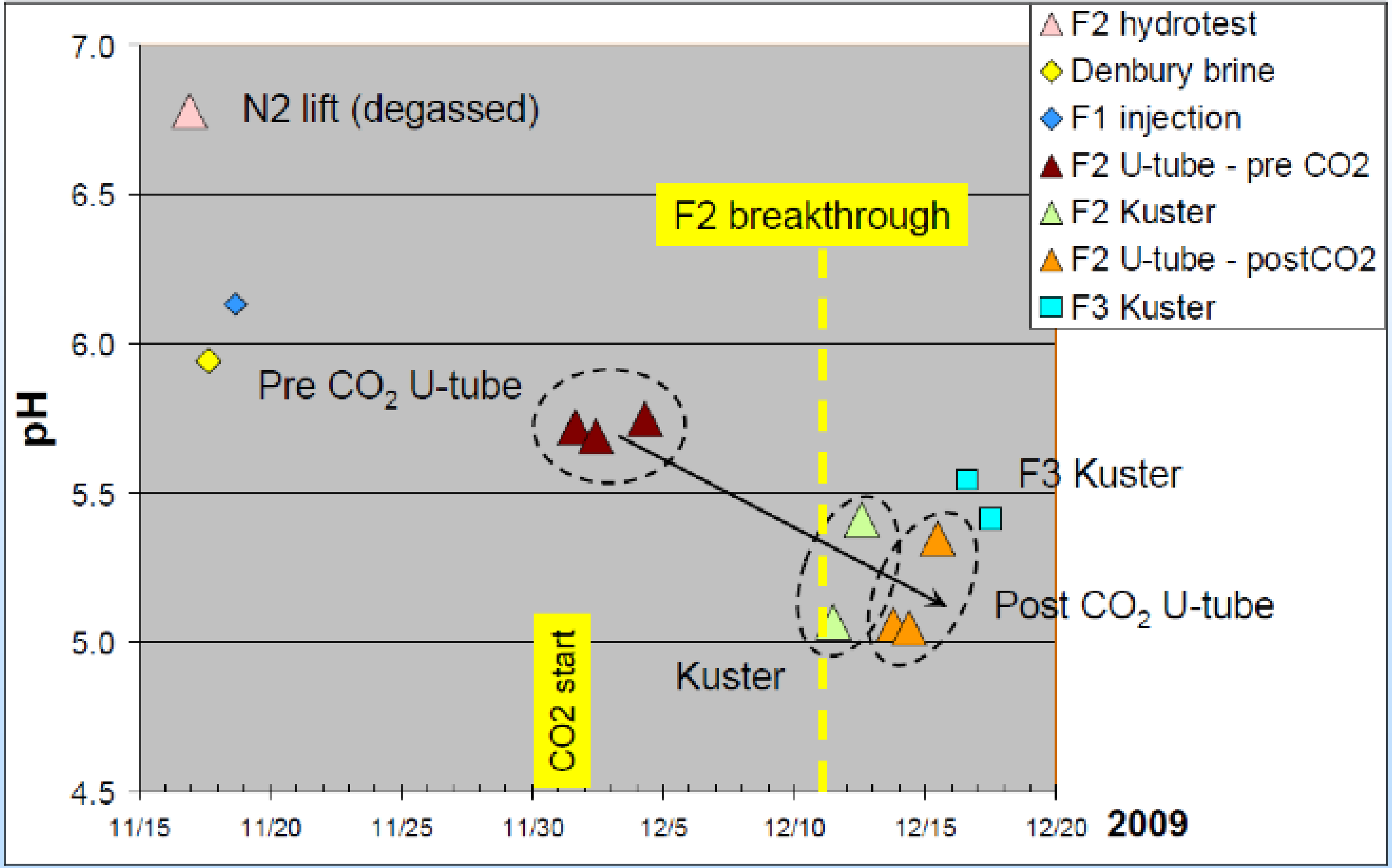






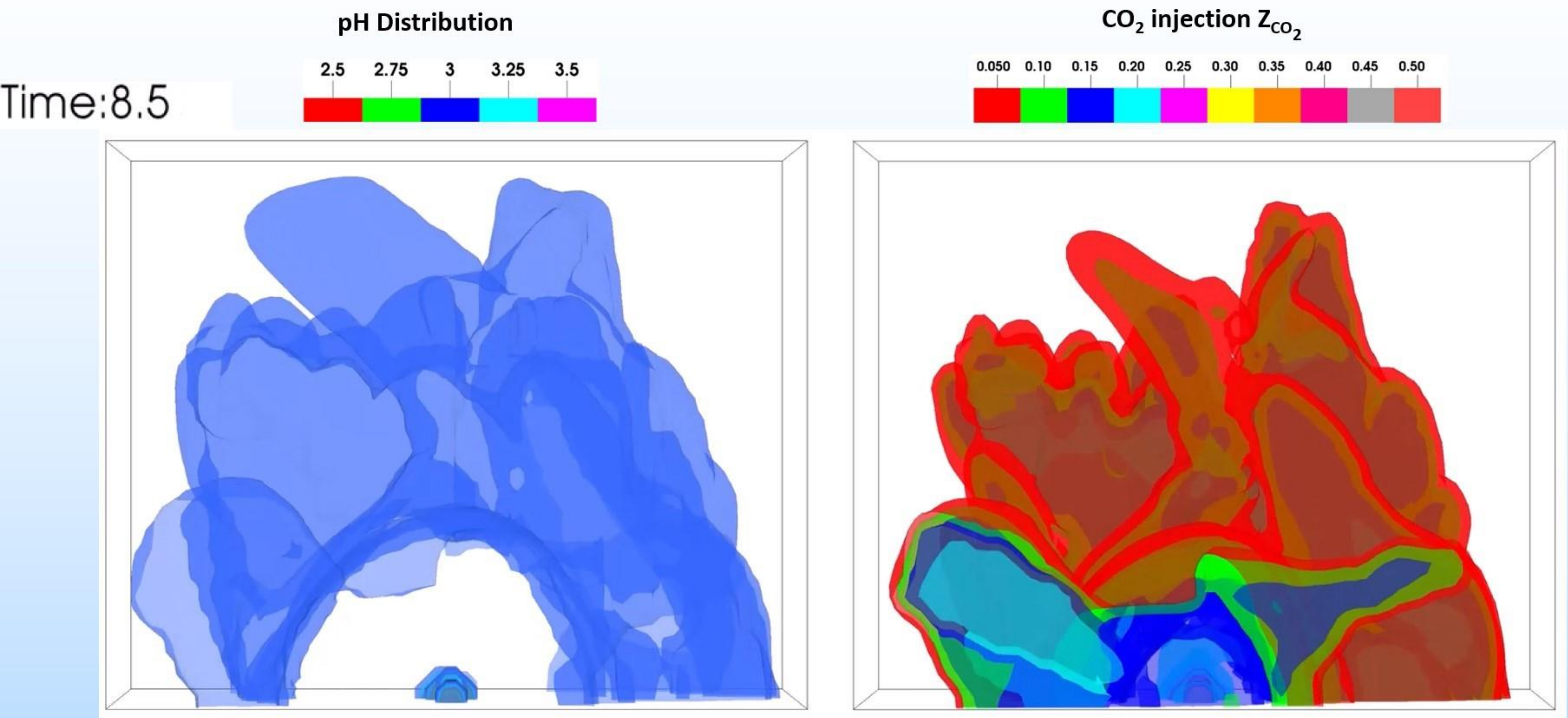
Two-Phase Geochemistry

Measured pH change in formation brine during CO_2 injection



Two-Phase Reactive Transport

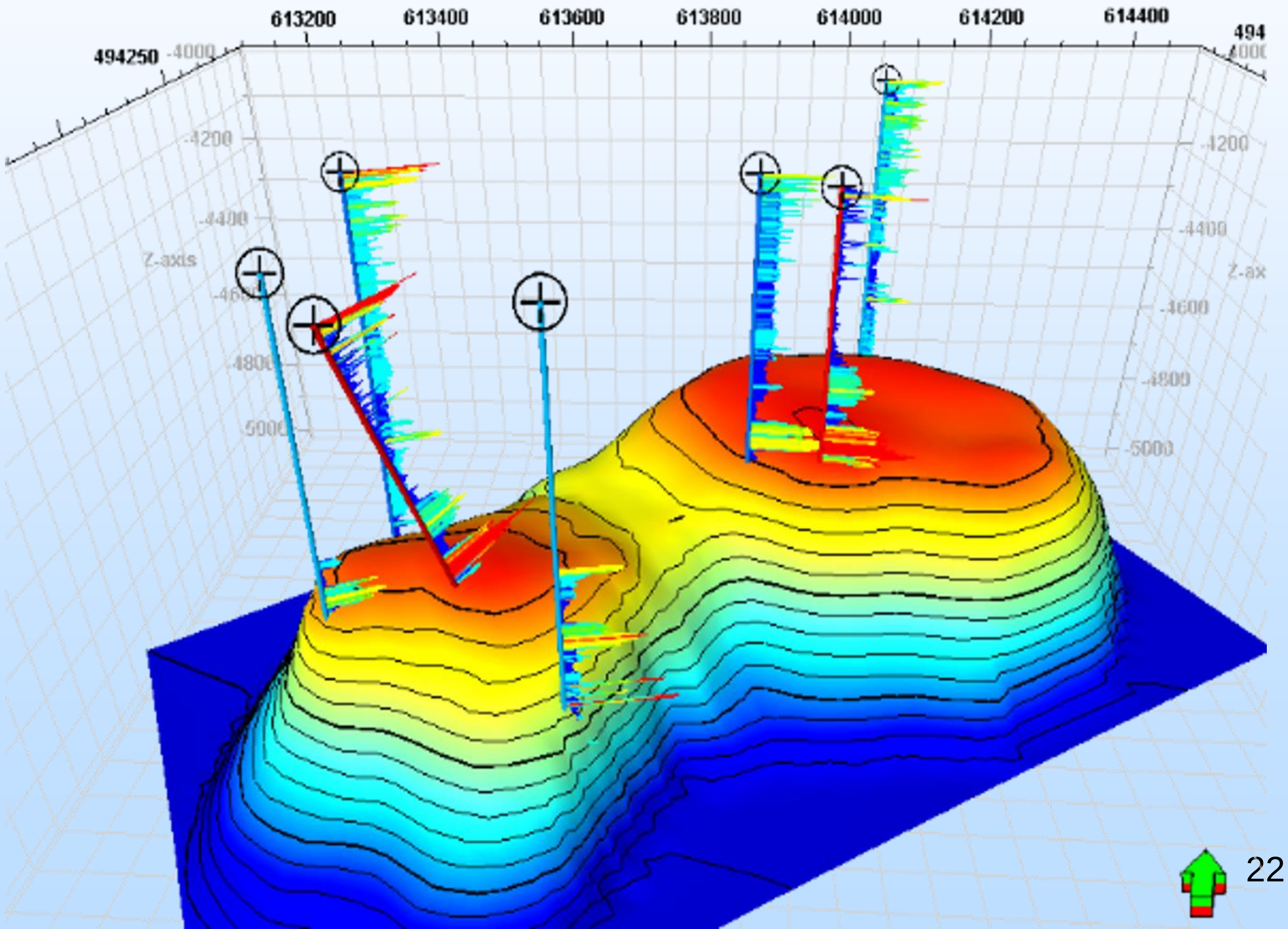
Modeling of the pH change in formation brine during CO_2 injection



Chester 16

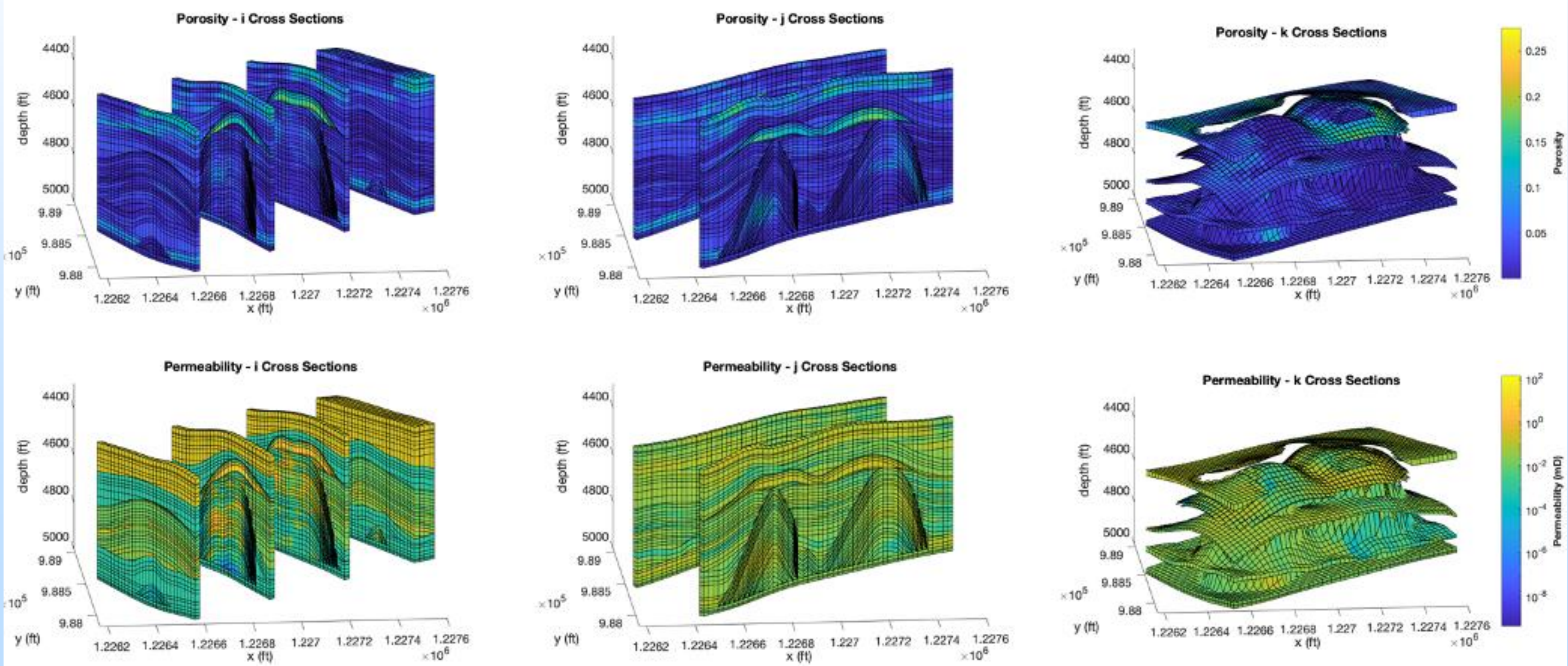
New synergistic collaboration developed with Battelle to model CO_2 transport in complex Chester 16 reef system (MRCSP)

- First milestone: develop alternative static model



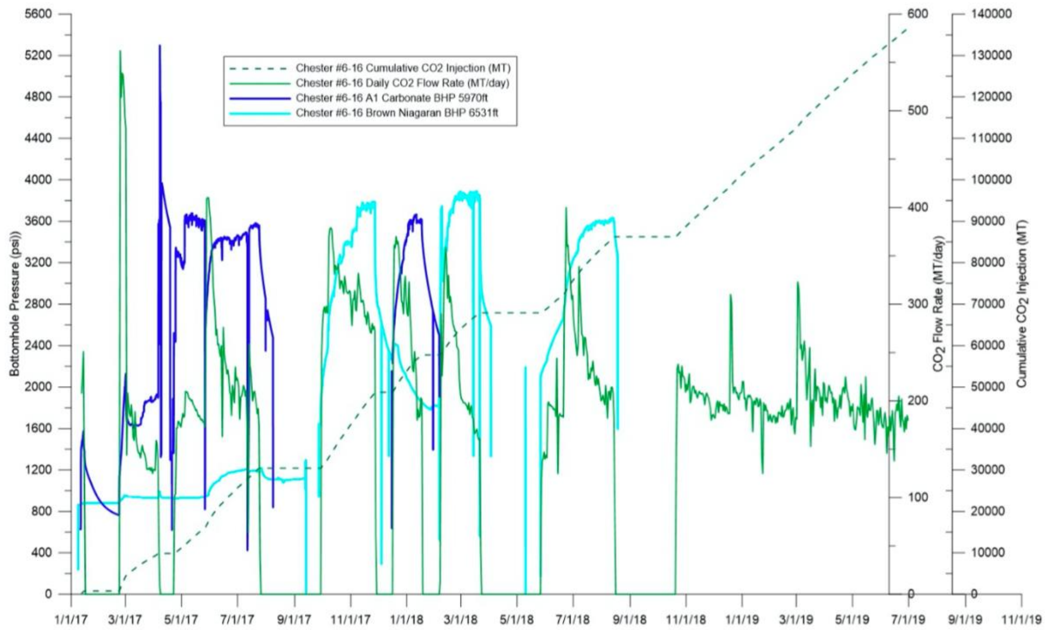
Chester 16

- Industry-standard is logically Cartesian corner-point grids.
- For complex geometry, like domes, many dead and pinched cells.
- Advantages of unstructured, e.g. tetrahedral, grids



Chester 16

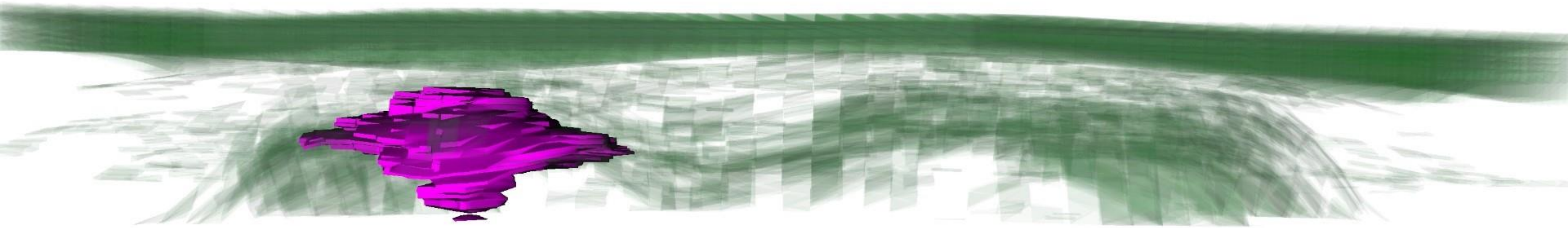
- Multiple injection and ‘soak’ periods
- Model CO_2 injection into water at BHP of 130 bar and T = 104 F where CO_2 is supercritical

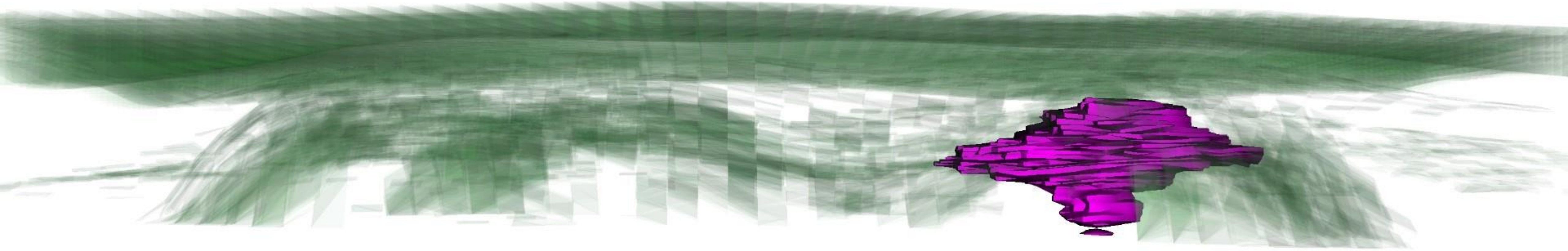


Injection Period	Date Range	Days Injected	Target Formation	CO_2 Injected (MT)
1	1/11/17 - 1/14/17	3	A1 Carbonate	804
2	2/22/2017 - 4/6/2017	43	A1 Carbonate	9,039
3	4/22/2017 - 7/24/2017	93	A1 Carbonate	20,585
4	9/29/2017 - 11/27/2017	59	Brown Niagaran	18,314
5	12/16/2017 - 1/16/2018	31	A1 Carbonate	9,010
6	2/5/2018 - 3/21/2018	44	A1 Carbonate and Brown Niagaran	10,178
7	5/26/2018 - 8/14/2018	80	A1 Carbonate and Brown Niagaran	18,320
8	10/20/2018 - 7/29/2019	Continuing	A1 Carbonate and Brown Niagaran	55,390

Chester 16

- Preliminary modeling of CO_2 injection (higher-order DG)
- Two viewing angles, 1 year of injection, 1 mol% CO_2 contours (and perm.)





Project Summary (Task 1)

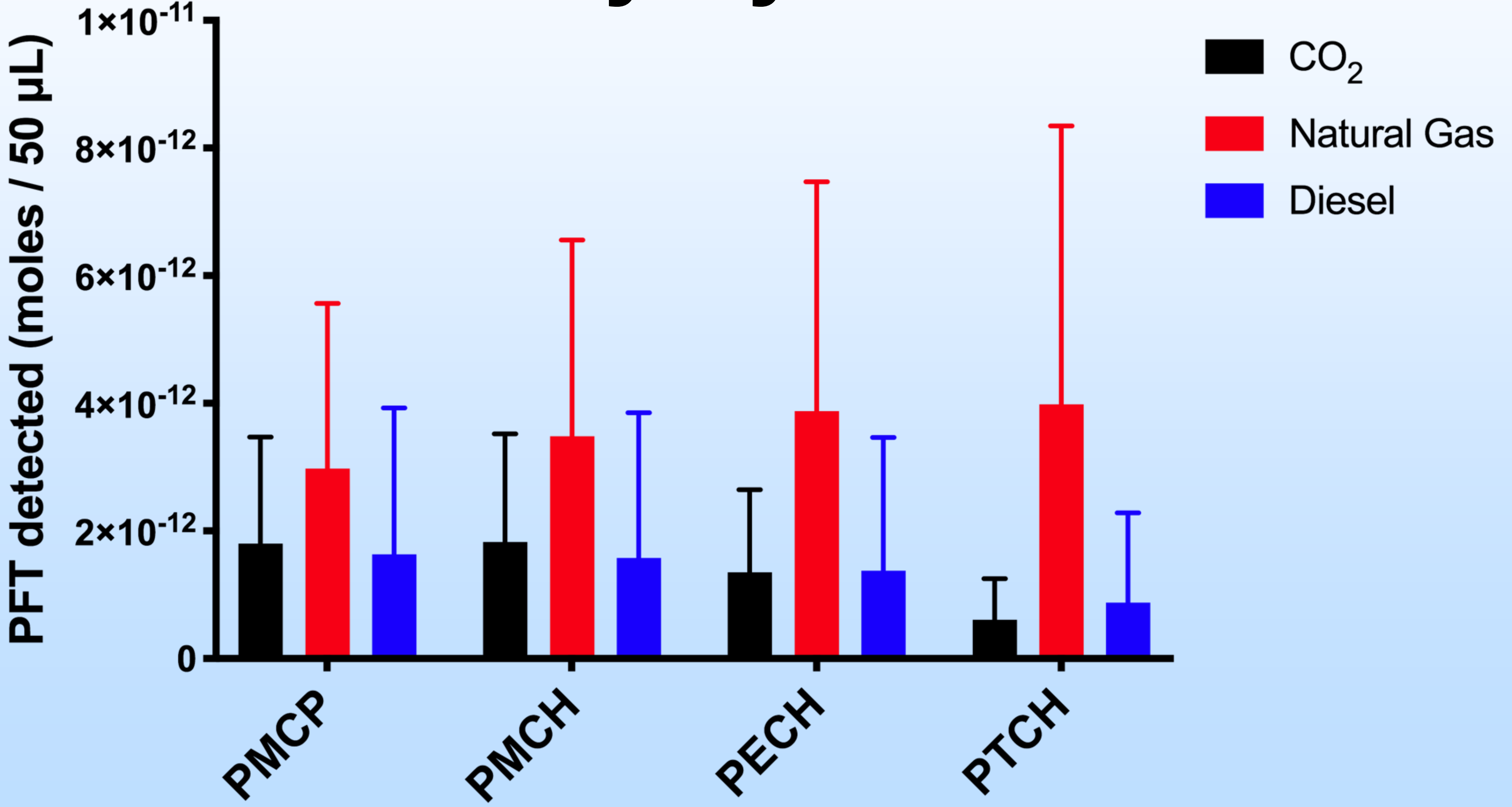
- Modeling of CO_2, CH_4, brine, and perfluorocarbon tracers at Cranfield
- Fundamental analyses of solubility trapping (mixing and spreading of dissolved CO_2)
- Initial implementation and benchmarking of coupled flow and reactive transport with Osures+iPhreeqc/PhreeqcRM
- Investigation of *multiphase* flow and *reactive* transport at Cranfield
- Modeling of independent Chester 16 field site
- Technology improvements (specifically parallelization / HCP)

Task 2. Improving PFT Tests

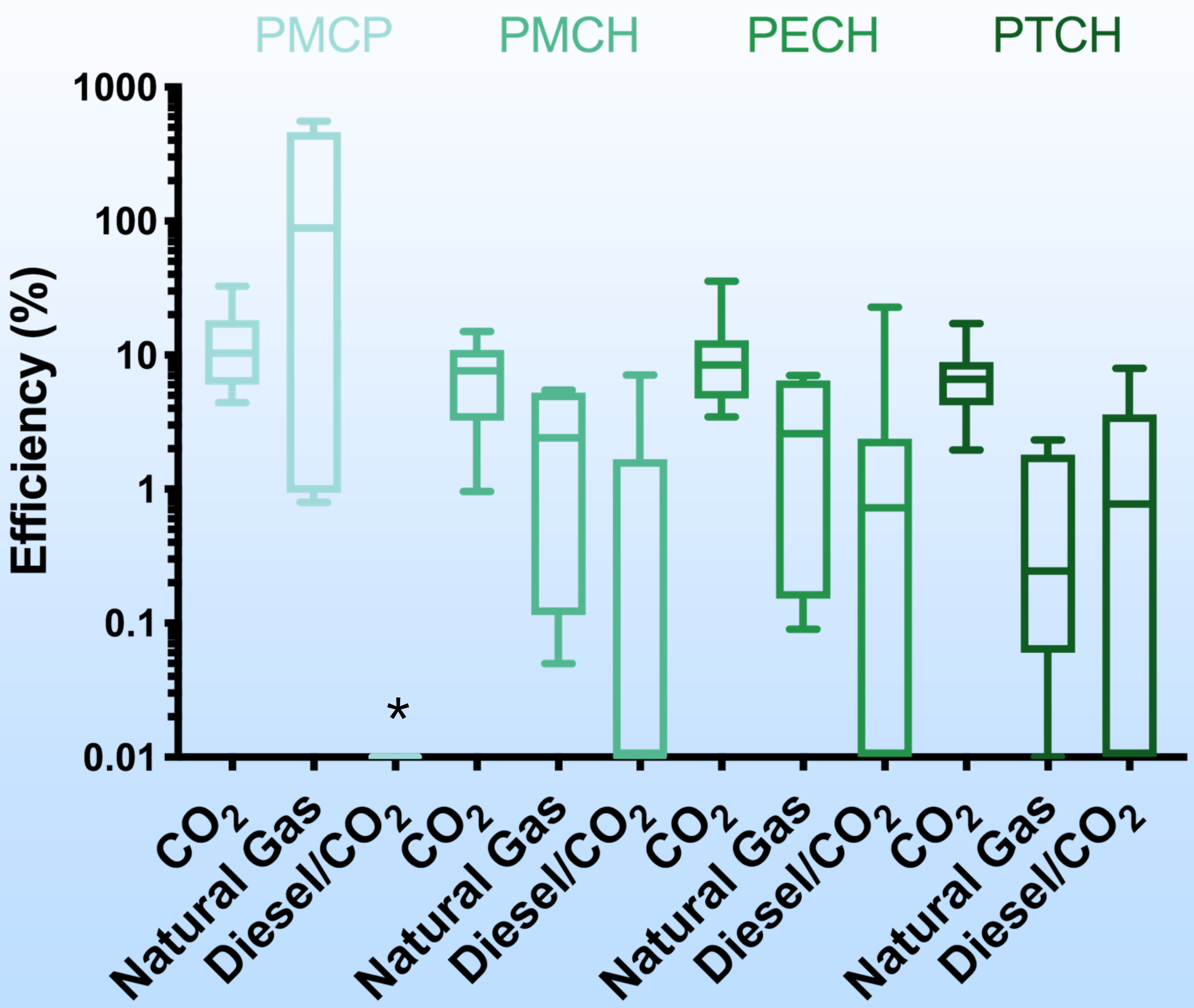
- Develop methods to improve the analysis of perfluorocarbons in a hydrocarbon-rich matrix, found in many EOR and EGR monitoring well samples.
- Detect lower concentrations in gas samples
- Reduce sampling frequency
- Simplify sample collection, transport and storage

- BNL researchers (Senum et al) in the 1980’s sampled PFTs with capillary adsorbent tracer samplers (~60 mg AMBERSORB™)
- Concentrates PFTs from a large gas volume on a single sorption tube

No significant interference for PFTs diluted into gas matrices and analyzed directly by GC-ECD

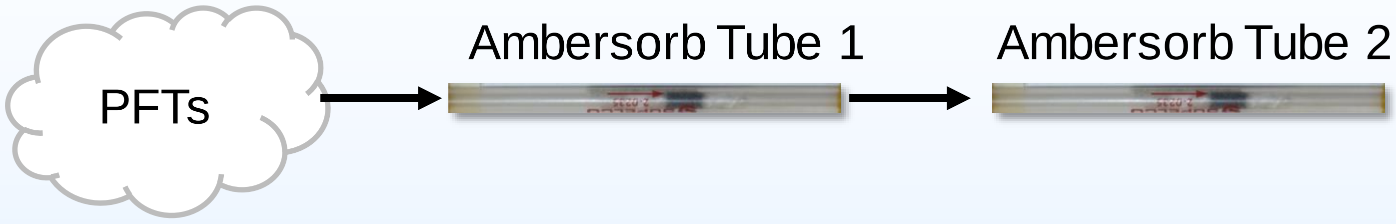


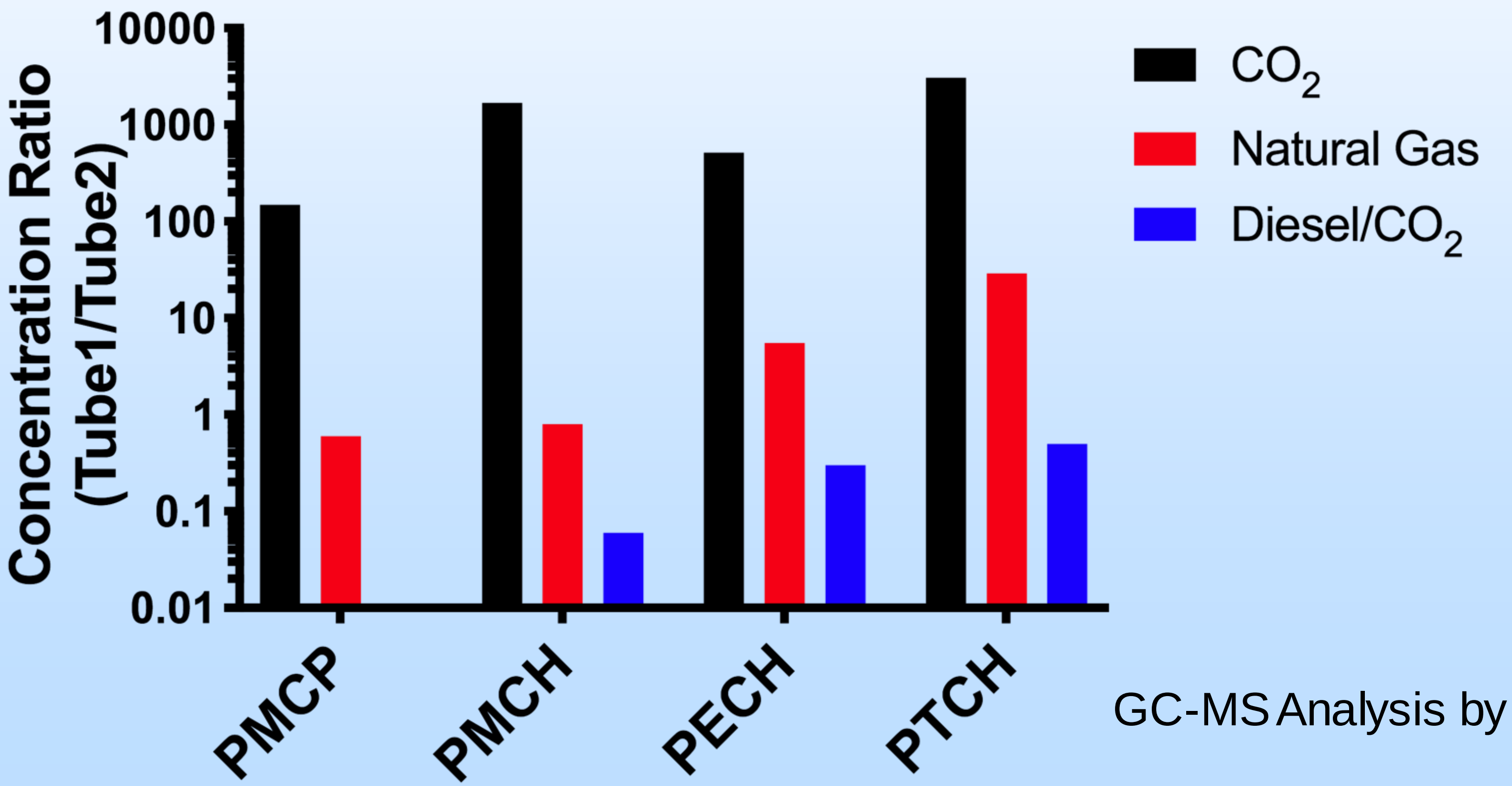
Decreased Efficiency of PFT Analysis by Sorption Tube Sampling



AMBERSORB matrix. GC-MS Analysis by Sean Sanguinito, NETL

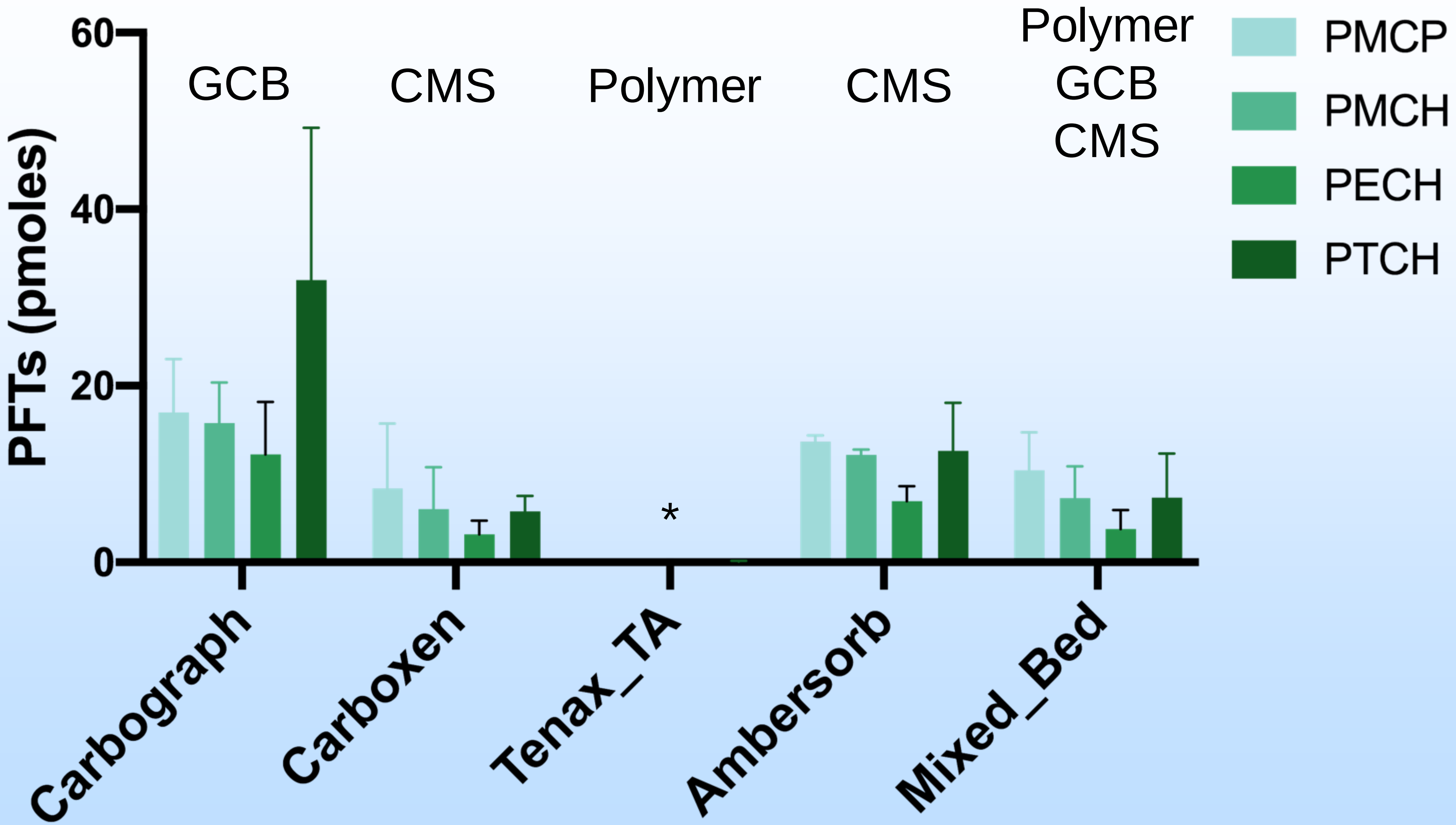
Increased PFT breakthrough to downstream tube in the presence of hydrocarbons





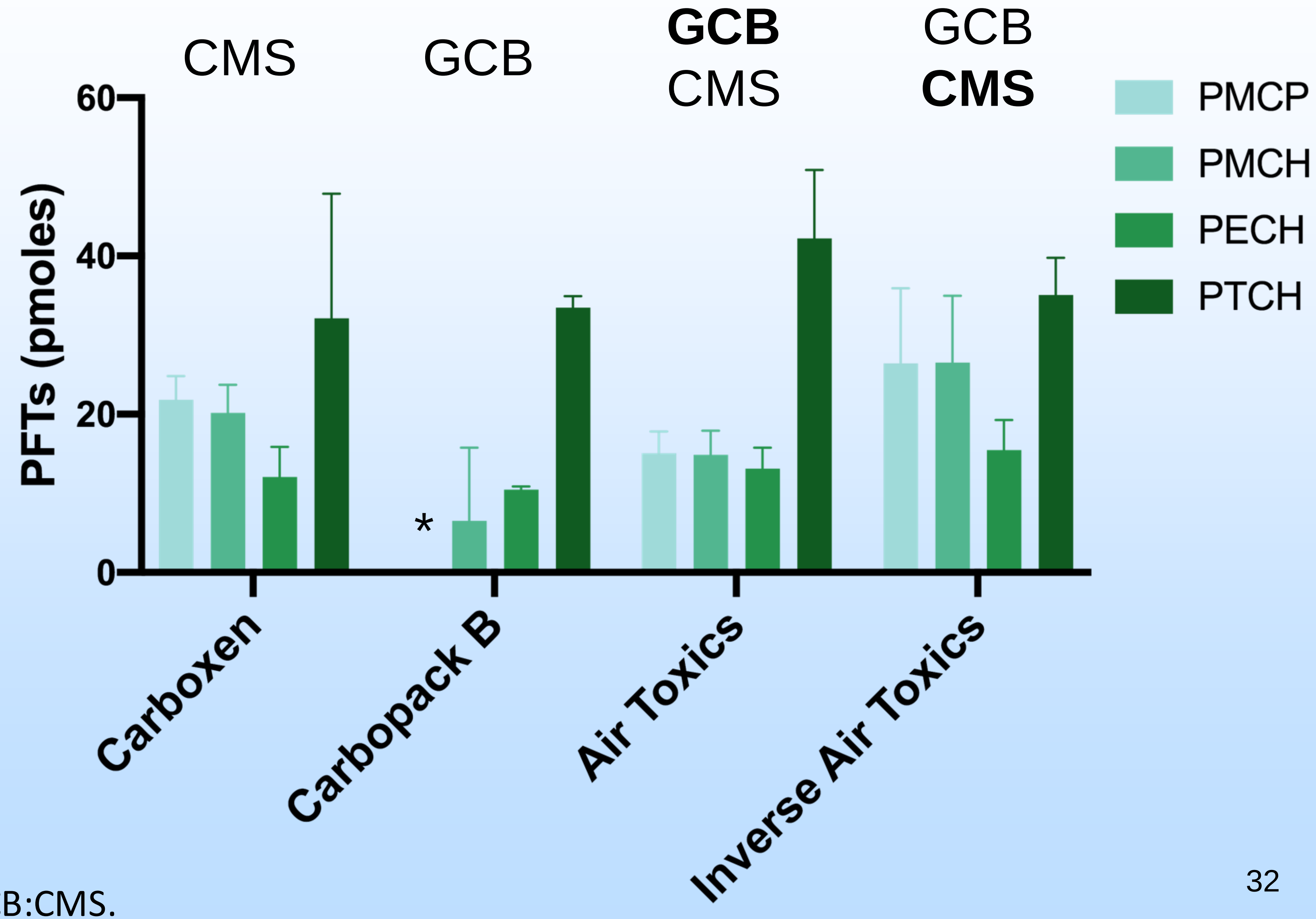
GC-MS Analysis by Sean Sanguinito, NETL

PFTs in CO_2



Five different types of sorbent tubes loaded with PFT standards in CO_2 were analyzed using thermal desorption with GC-ECD analysis. Measurements were performed on triplicate samples.

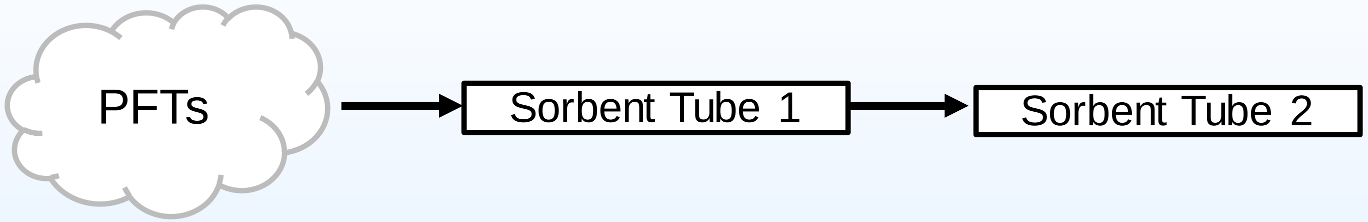
PFTs in CO_2 + Diesel Volatiles



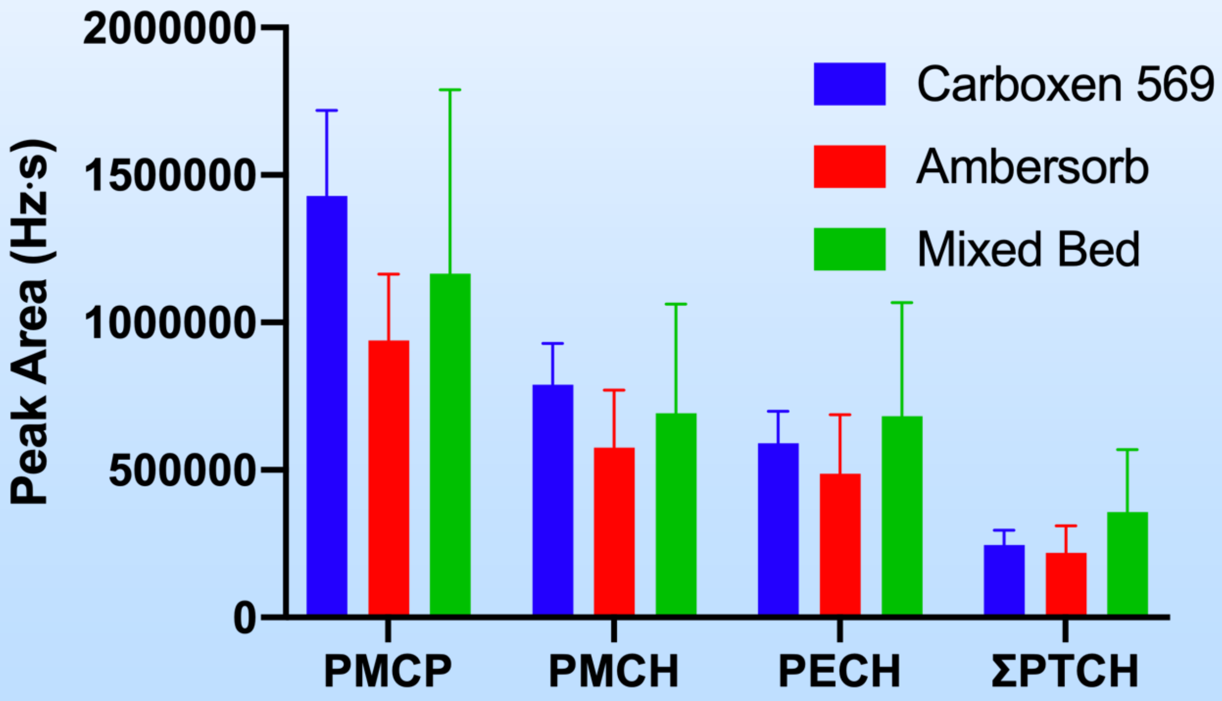
Air Toxics tube contains ~2:1 GCB:CMS.
Inverse Air Toxics tube contains ~1:3 GCB:CMS.

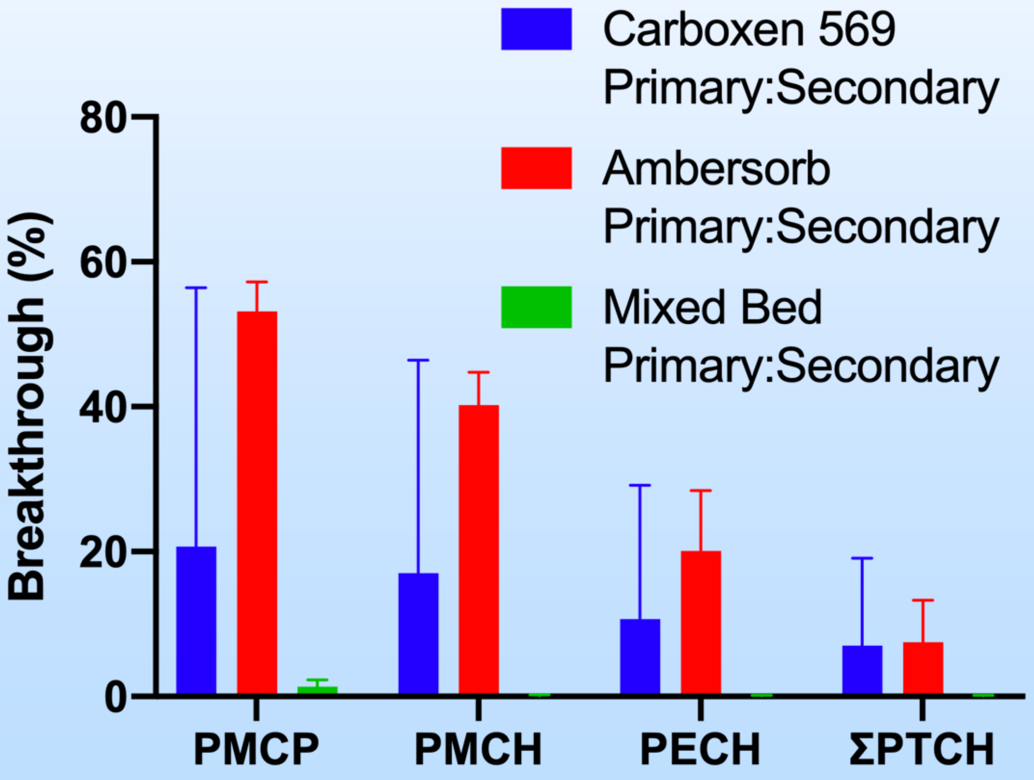
New Sorbents Reduced Breakthrough

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

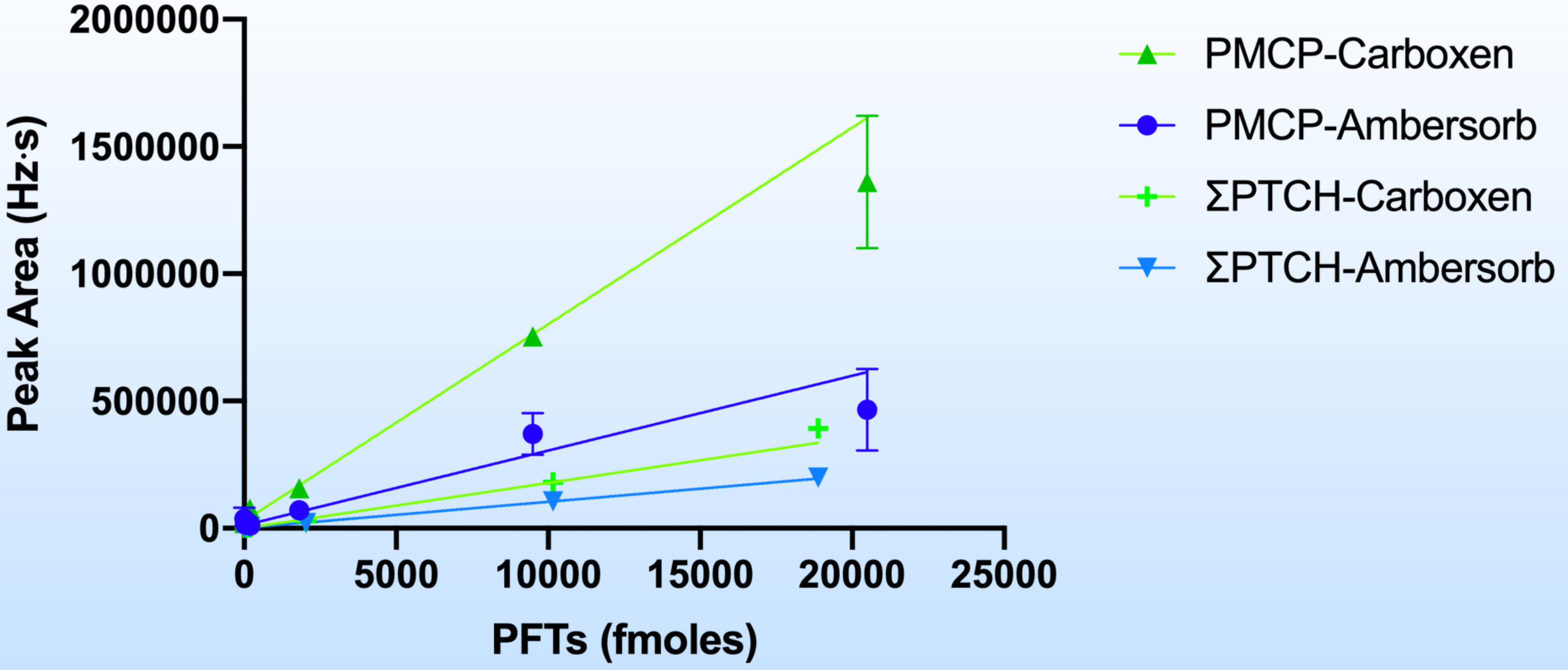


Sum of both tubes





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.

APPENDICES

Organization Chart

U.S. DEPARTMENT OF ENERGY | NETL

Oak Ridge National Laboratory

David Graham, PI

The University of Tennessee Knoxville

Tommy Phelps
Susan Pfiffner

The Ohio State University

Joachim Moortgat

David Cole

Postdocs: Soltanian, Zhu, Li

Collaborators:

National Energy Technology Laboratory | Bureau of Economic Geology | Berkeley Lab | USGS science for a changing world | Battelle

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.

Synergies

- Established collaborative simulation opportunities with MRCSP regarding complex 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