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

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Project Overview

Current Goals and Objectives

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

1. Incorporate CO_2-brine chemical and isotopic reactions and transport into simulations.

2. Assess efficiency of perfluorocarbon tracer (PFT) analysis using capillary adsorption tubes in a hydrocarbon-rich matrix.

Presentation Outline

- Tracers & their applications to C storage
- Cranfield CO_2 storage pilot site
  - PFT simulations
- Hydrocarbon interference with PFT analysis
- Improved adsorbent tube sampling for PFTs
- Towards best practices for PFT tests

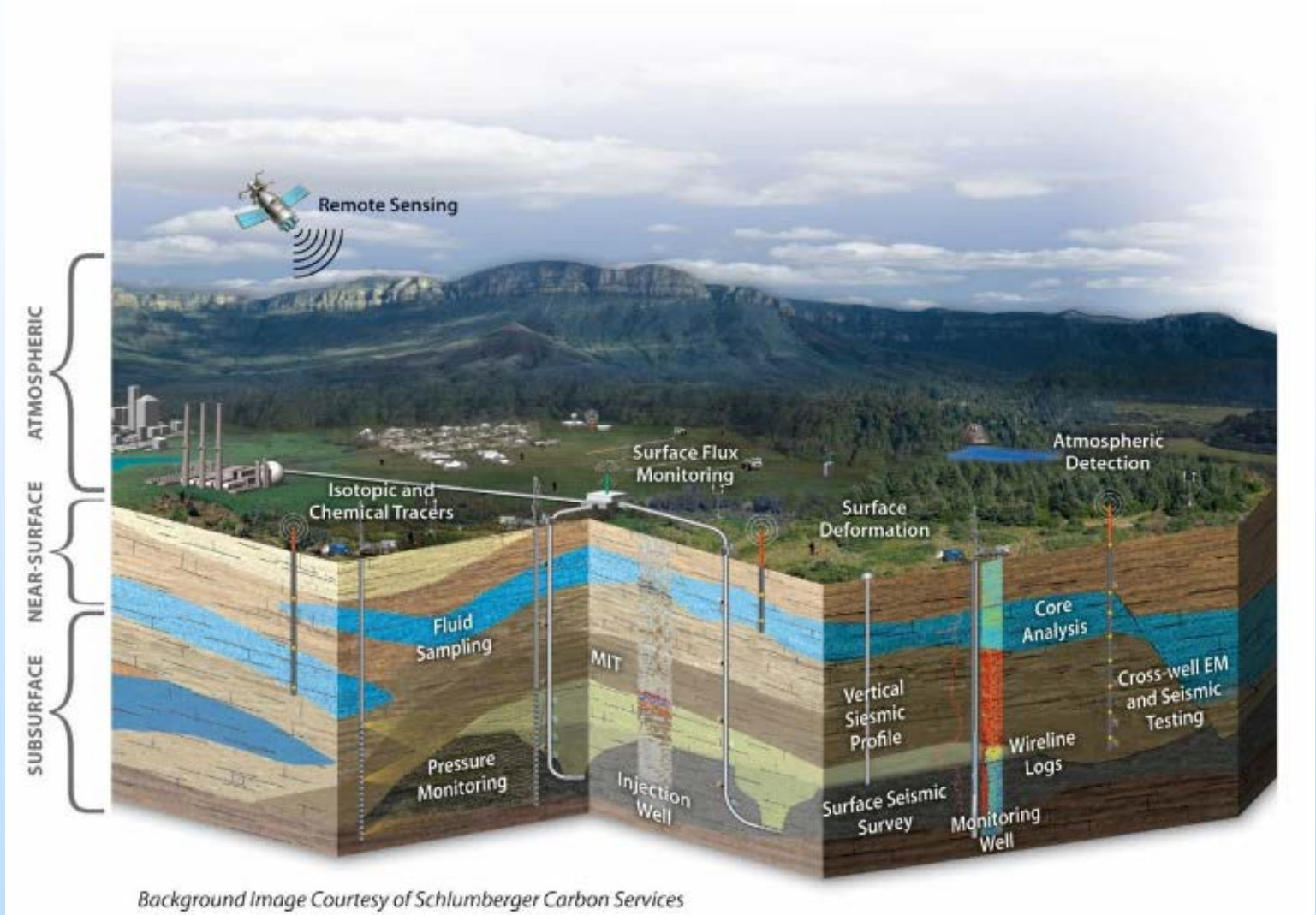
Benefit to Program

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

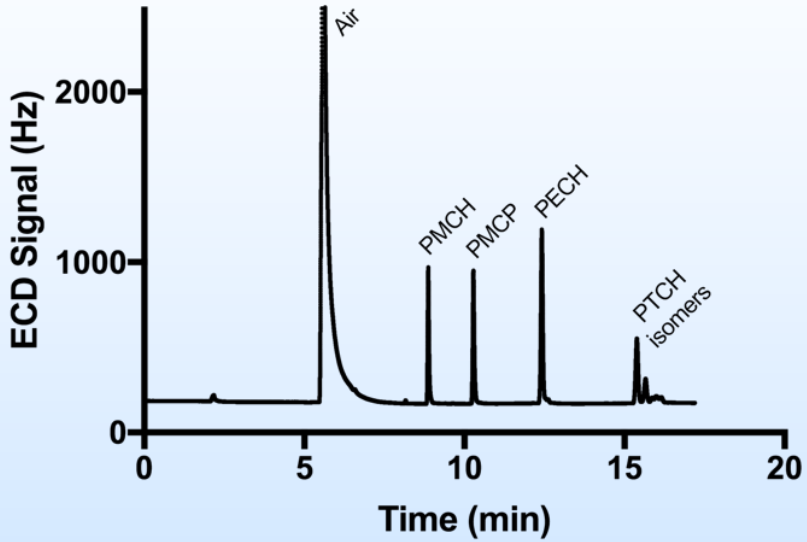


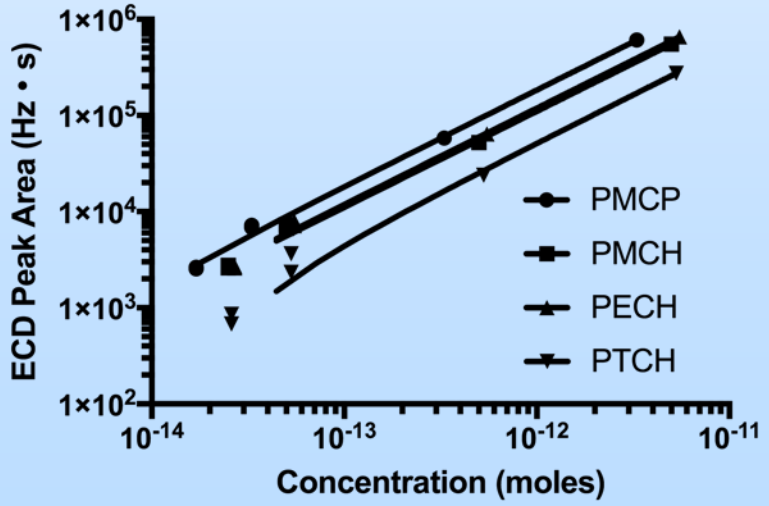
From NETL Carbon Storage MVA Tools Available for Monitoring CCS Projects

Conservative Perfluorocarbon Tracers (PFTs)

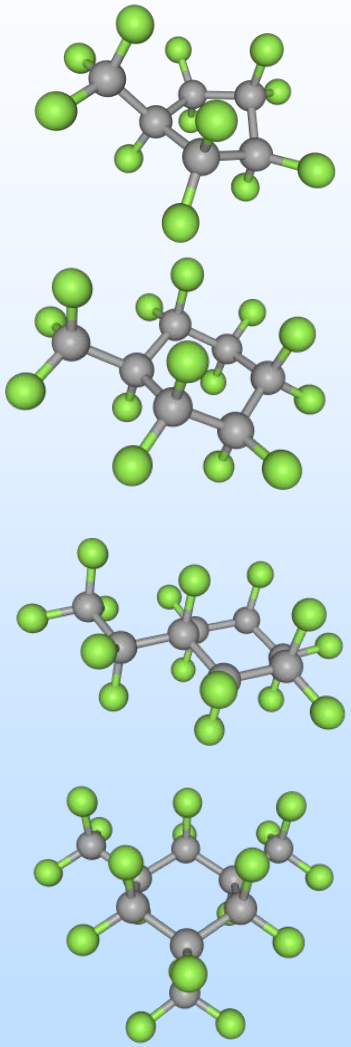
- Non-reactive, non-toxic, inexpensive and stable to 500°C
- Several PFTs can be quantified in a single analysis
- Detectable at pg-fg levels (fmoles)
- Different PFT "suites" (PMCP, PMCH, PECH, PDCH, PTCH), and SF_6, assess multiple breakthroughs
  → *flow regime indicator*

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



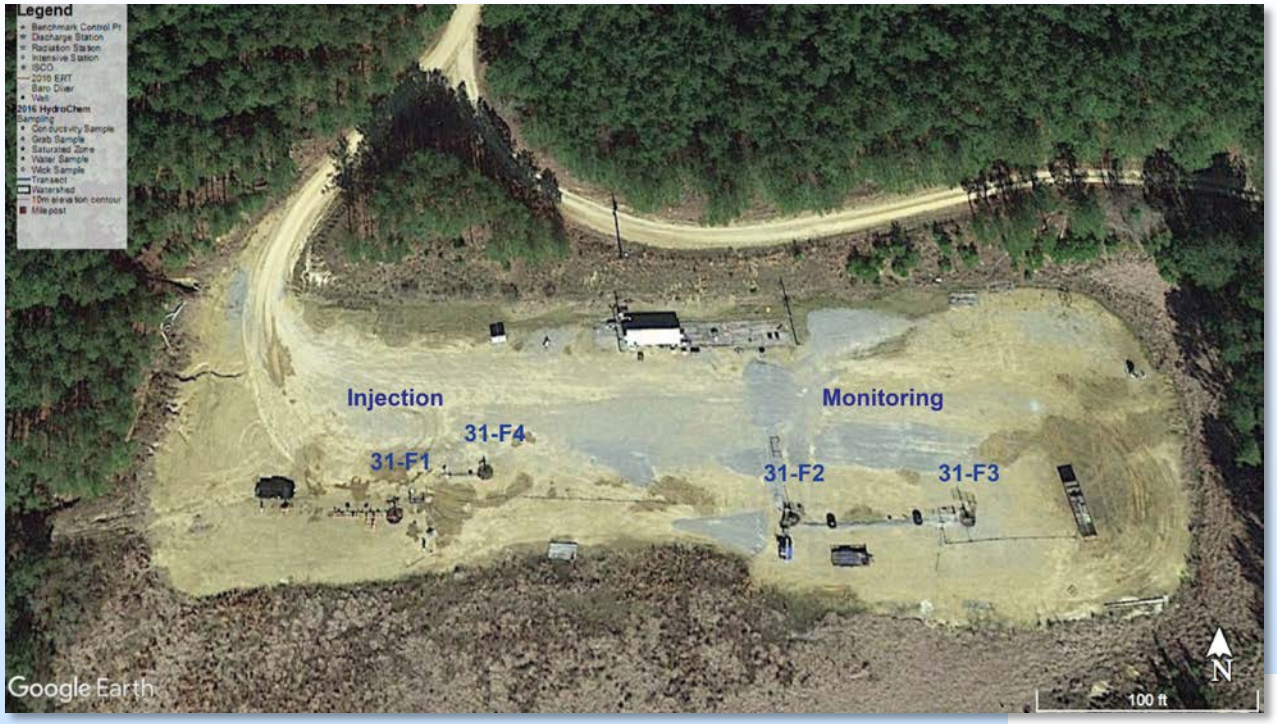


Compound	Mol. Wt.	Boiling Point	LogP (est)
PMCP Perfluoromethylcyclopentane	300	48 °C	3.4
PMCH Perfluoro(methylcyclohexane)	350	76 °C	4.1
PECH Perfluoroethylcyclohexane	400	102 °C	5.4
PTCH Perfluoro-1,3,5-trimethylcyclohexane	450	126 °C	6



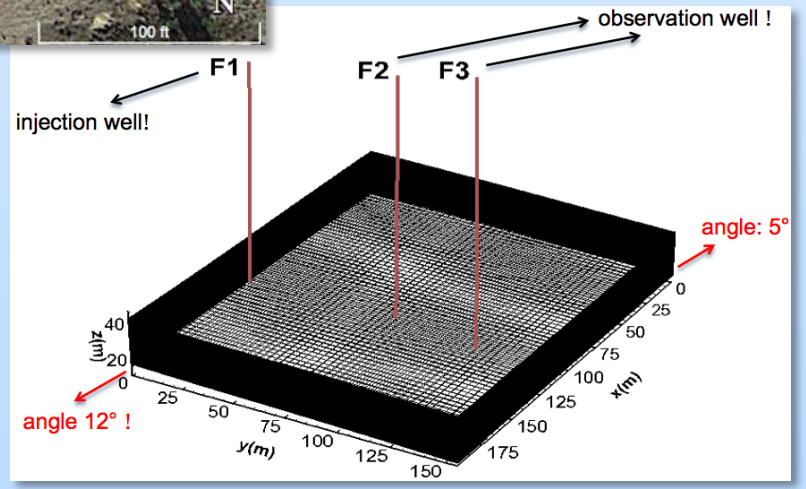
Cranfield Pilot Site, Mississippi

Carbon Storage Project: Detailed Area of Study



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

- 155 × 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

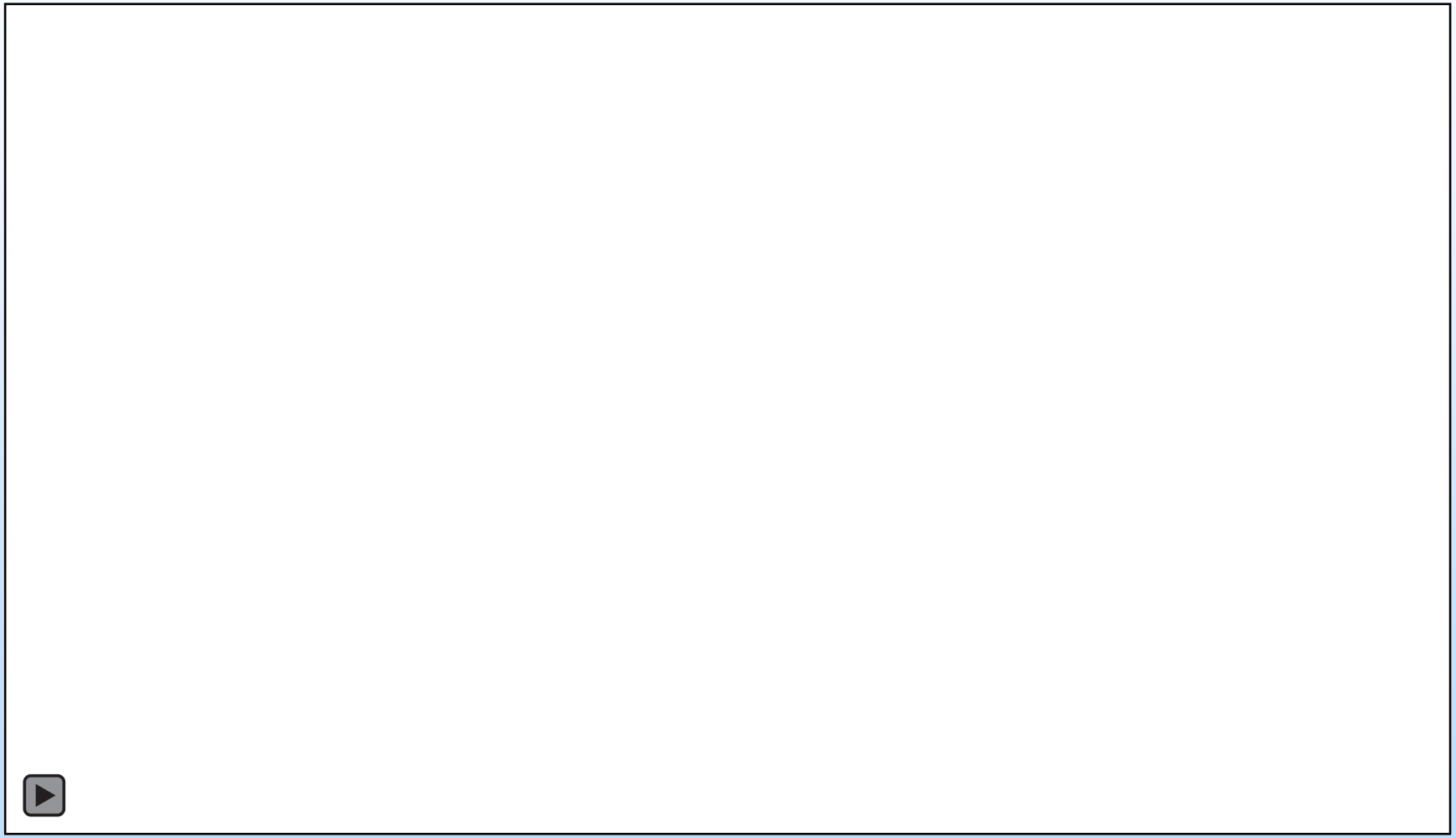


Thanks to:

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

Top View – Cranfield DAS 2009 CO_2 and PFT Injection Campaign

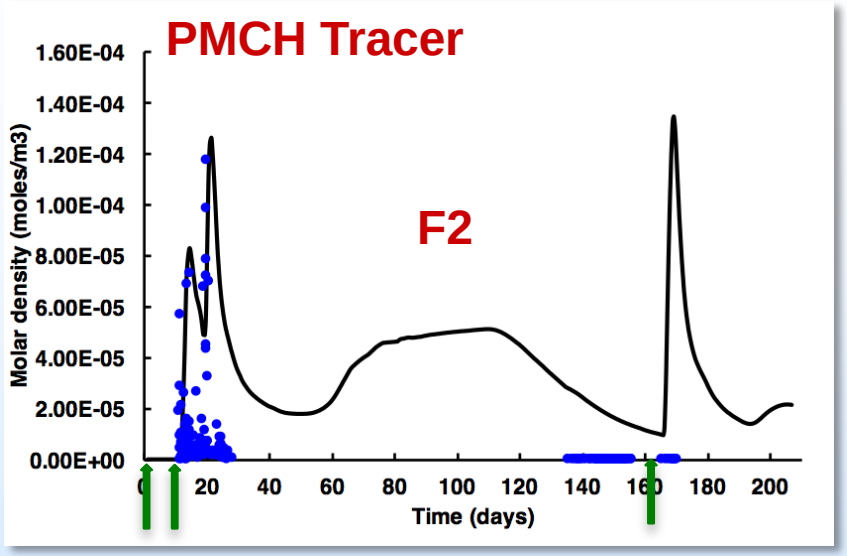
CO_2 **PMCH Injection (0 & 11 days)**

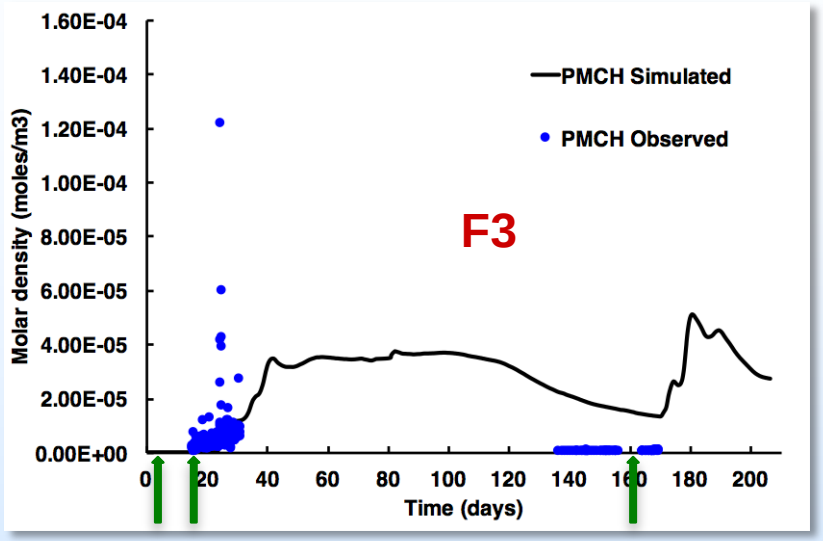


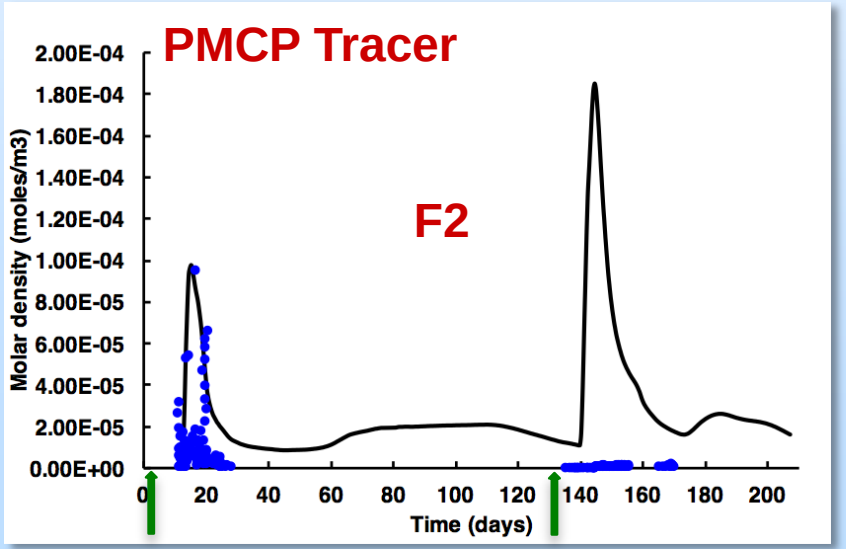
Soltanian MR, Amooie MA, Cole D, Graham D, Pfiffner S, Phelps T, Moortgat J (2018) Transport of perfluorocarbon tracers in the Cranfield Geological Carbon Sequestration Project. Greenhouse Gases: Science and Technology 8(4):650-671

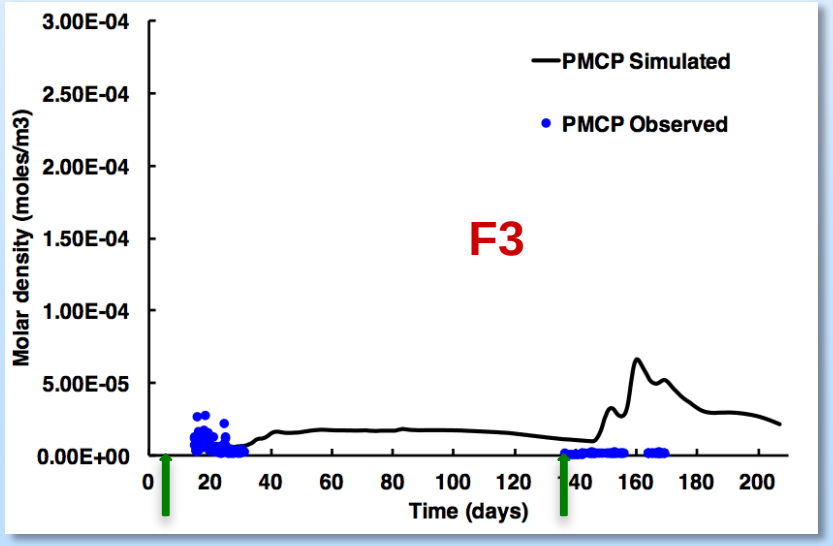
Simulating PFT Injection Campaign

2009-2010 Breakthrough Curves









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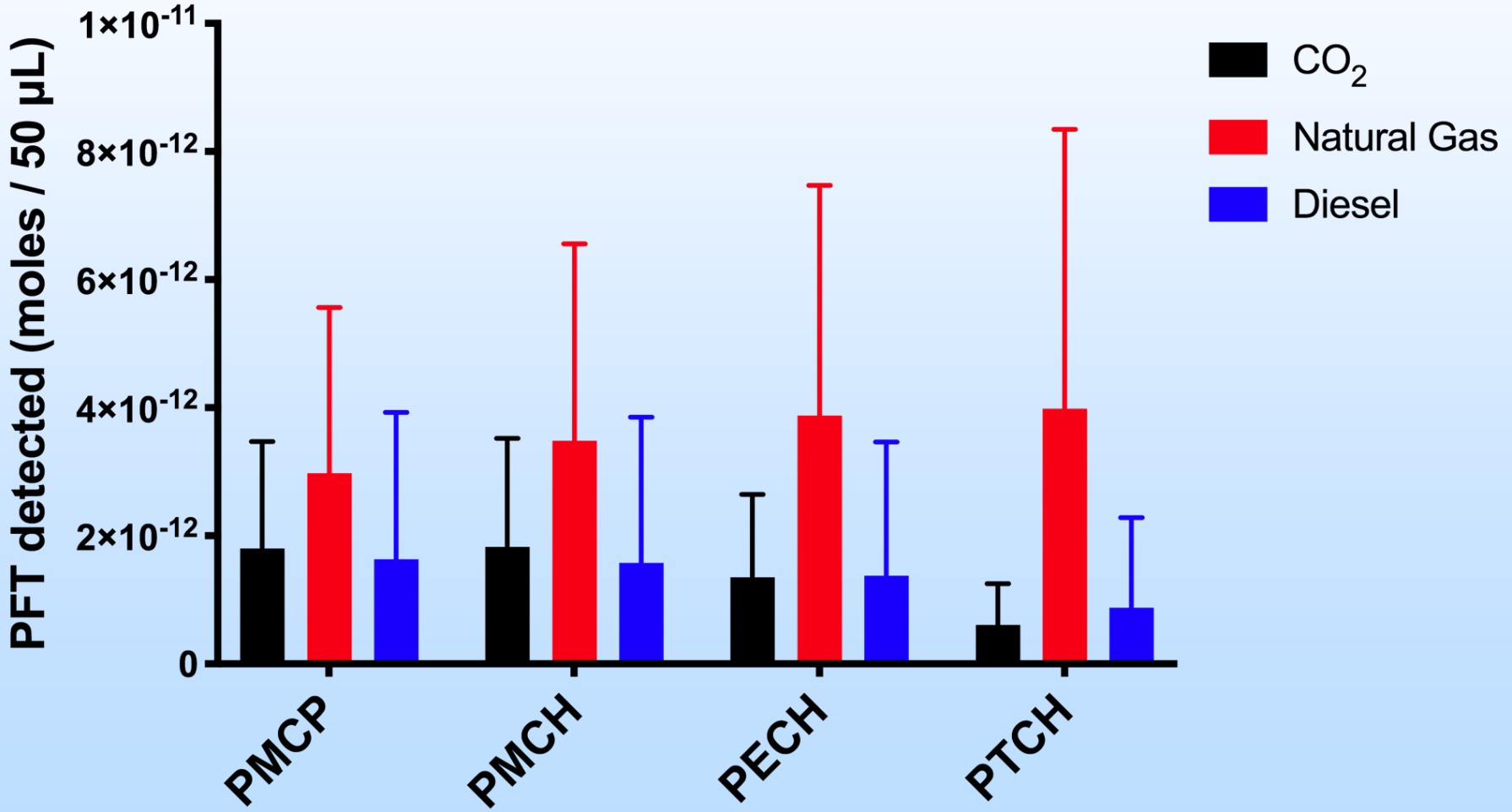
Improving PFT Tests

- 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
- Analyze by thermal desorption and gas chromatography
- Hydrocarbon interference?

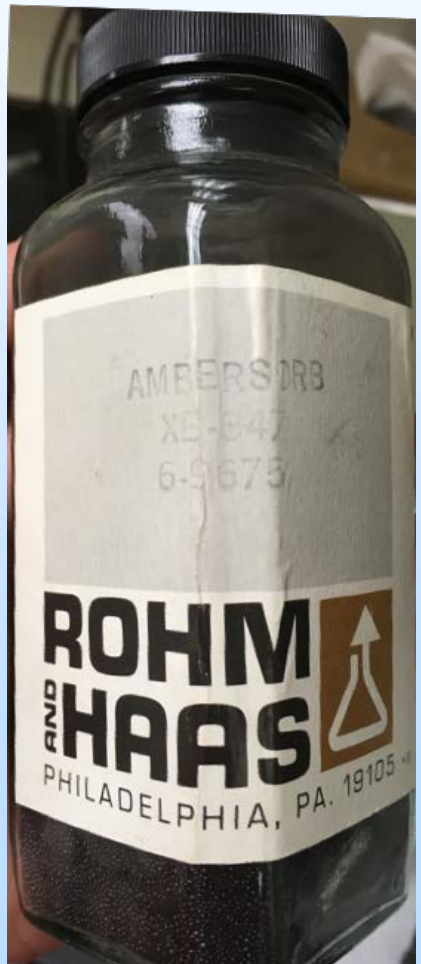
No significant interference for PFTs diluted into gas matrices and analyzed directly by GC-ECD



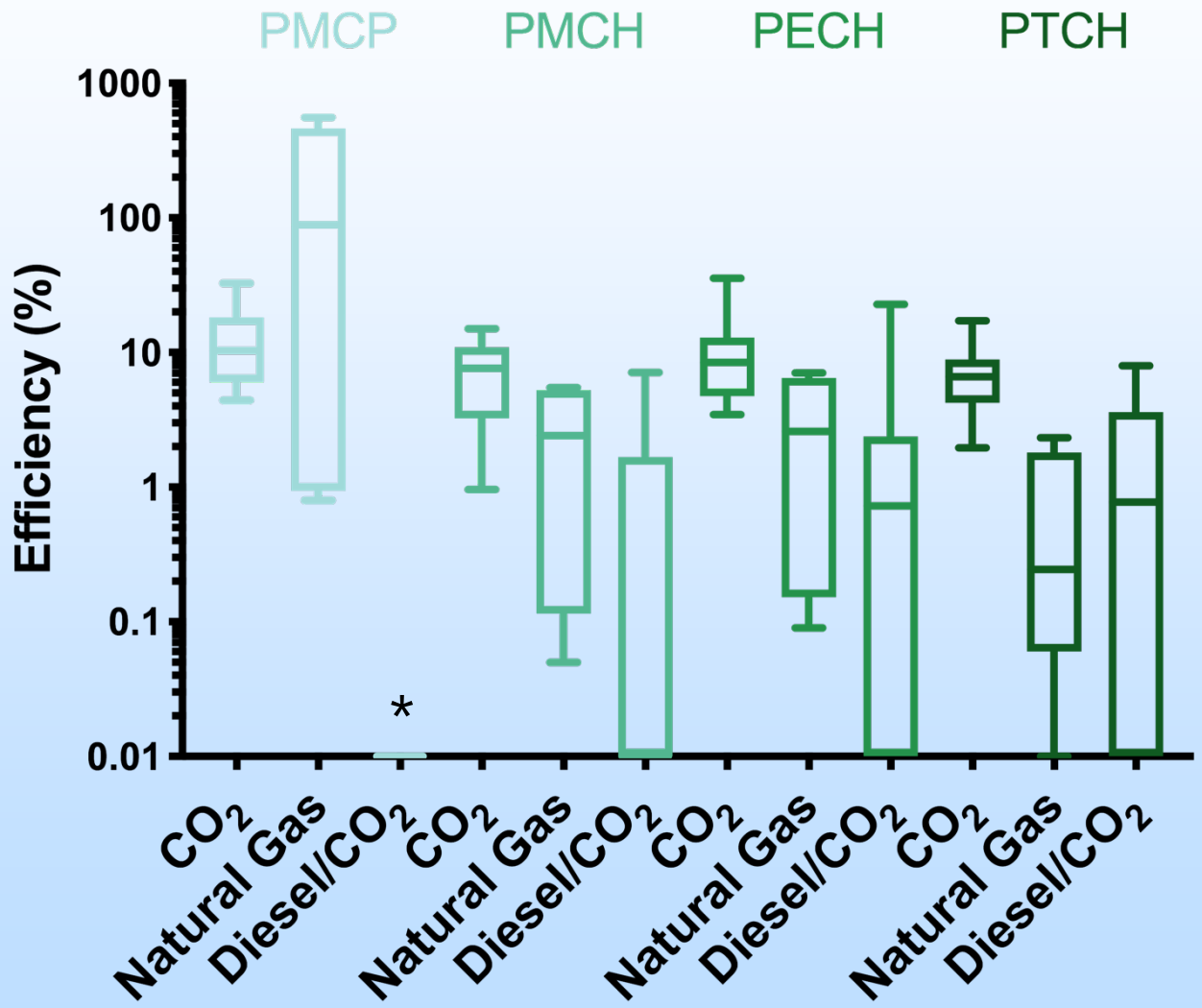
Thermal Desorption Tubes

Do hydrocarbons interfere with PFT sampling & analysis?

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

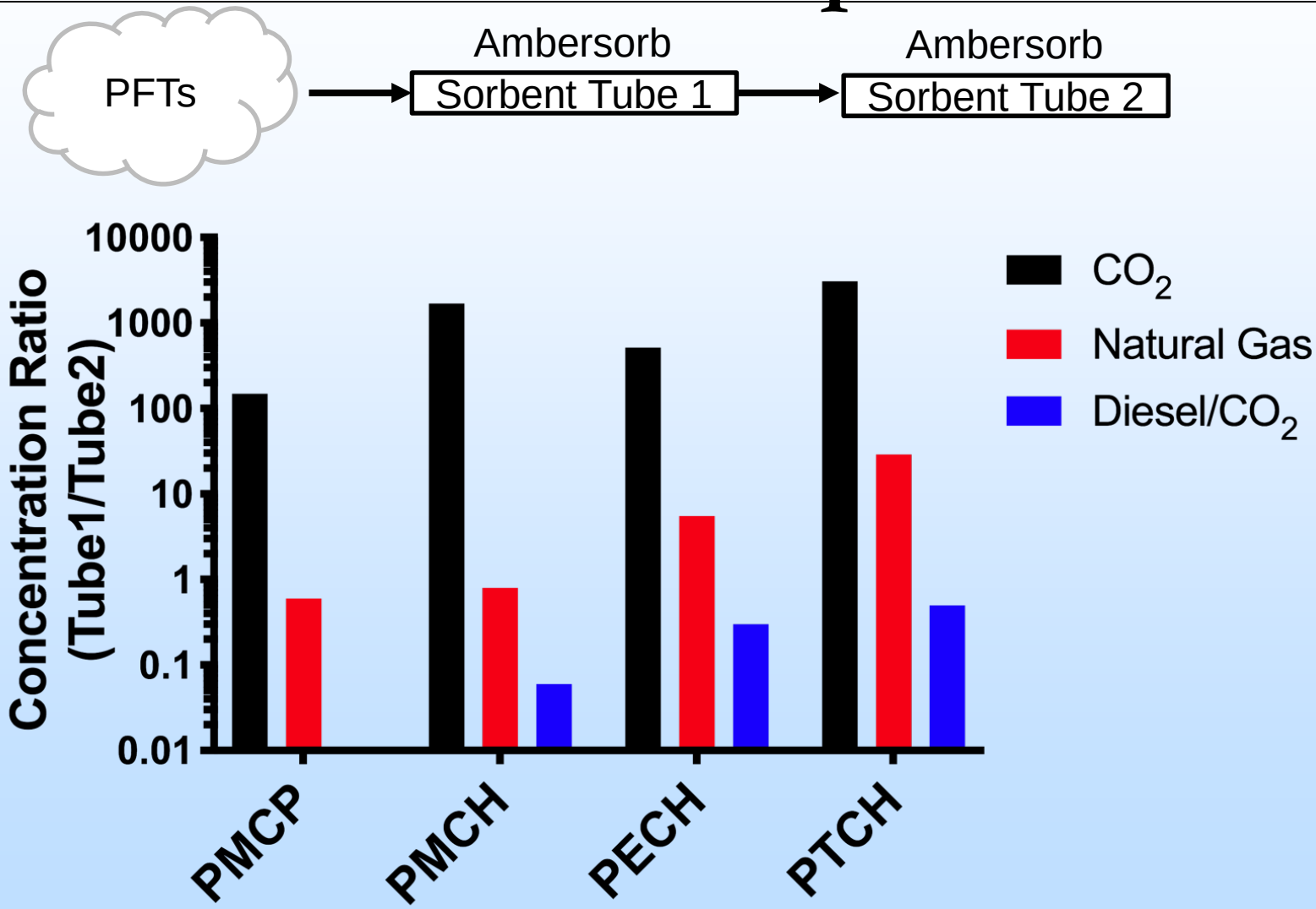


Decreased Efficiency of PFT Analysis by Sorption Tube Sampling



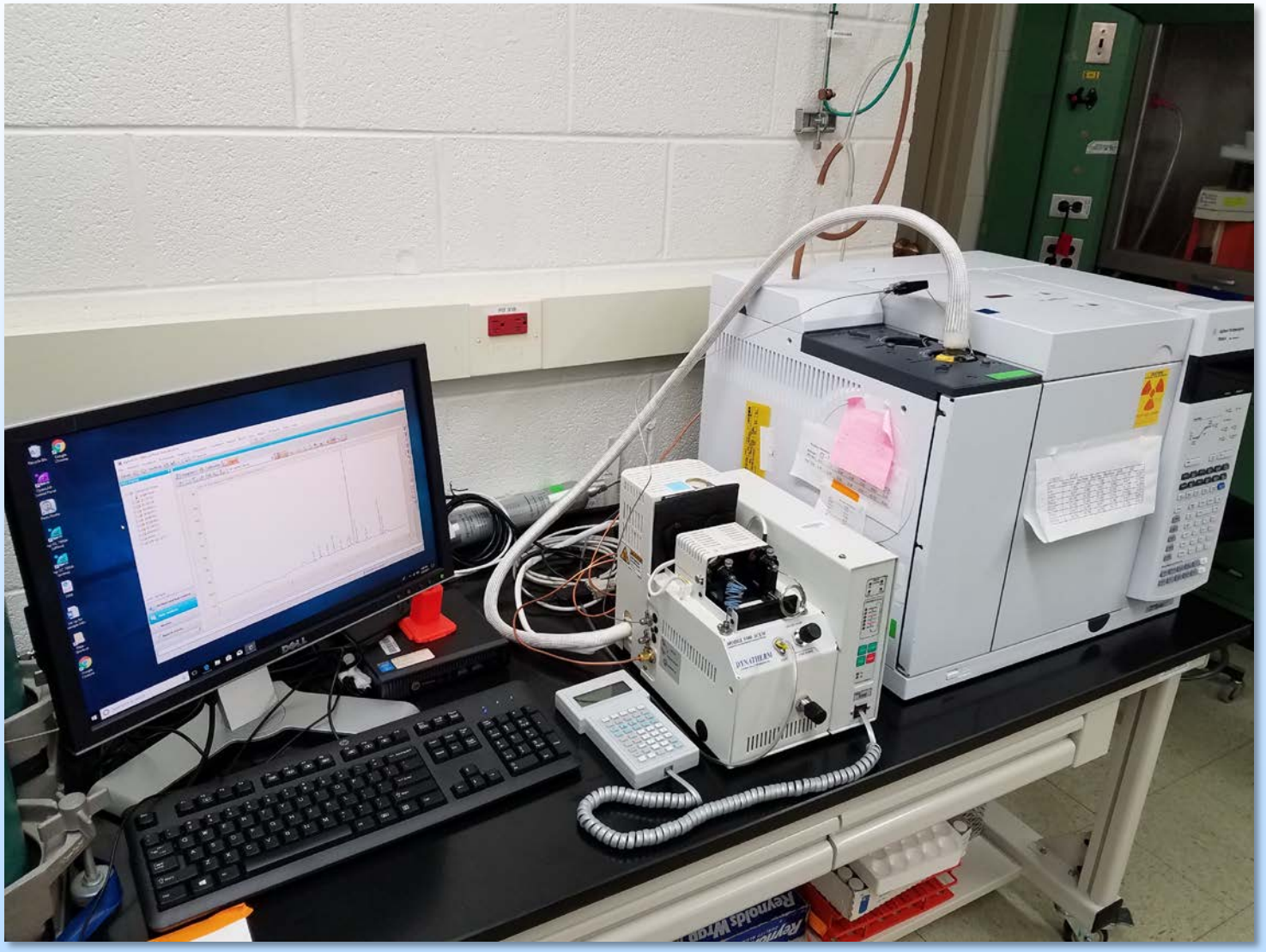
AMBERSORB matrix. GC-MS Analysis by Sean Sanguinito, NETL

Increased PFT Breakthrough to Downstream Sampler Tube

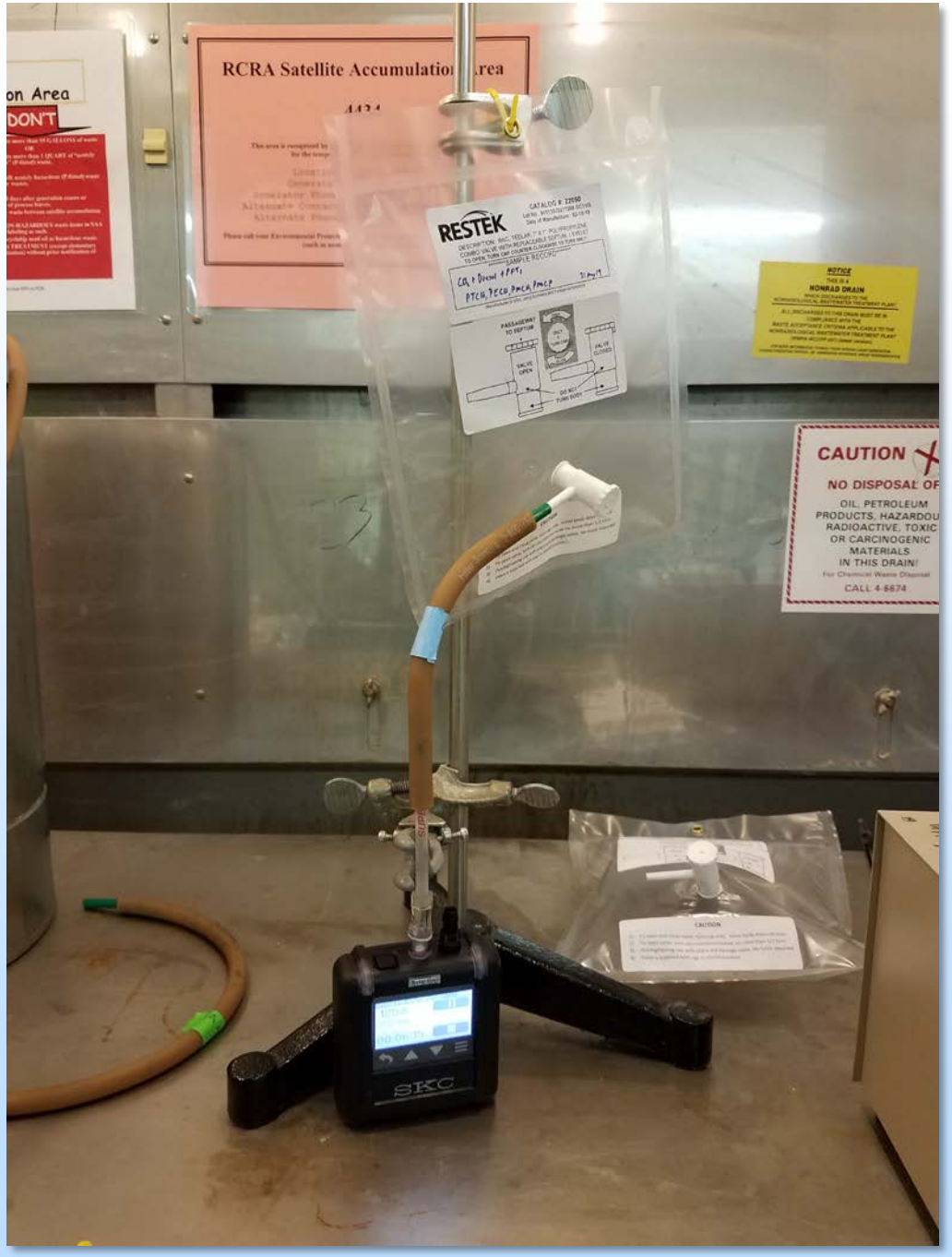


GC-MS Analysis by Sean Sanguinito, NETL

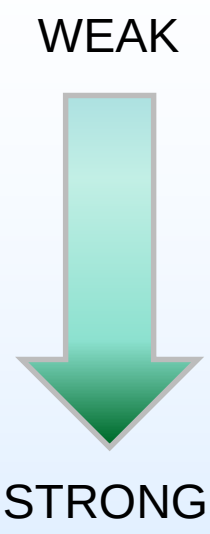
Thermal Desorption-Gas Chromatography with Electron Capture Detection



Mixture of 4 PFTs (20-40 pmoles) in CO_2 + diesel volatiles loaded onto a thermal desorption tube

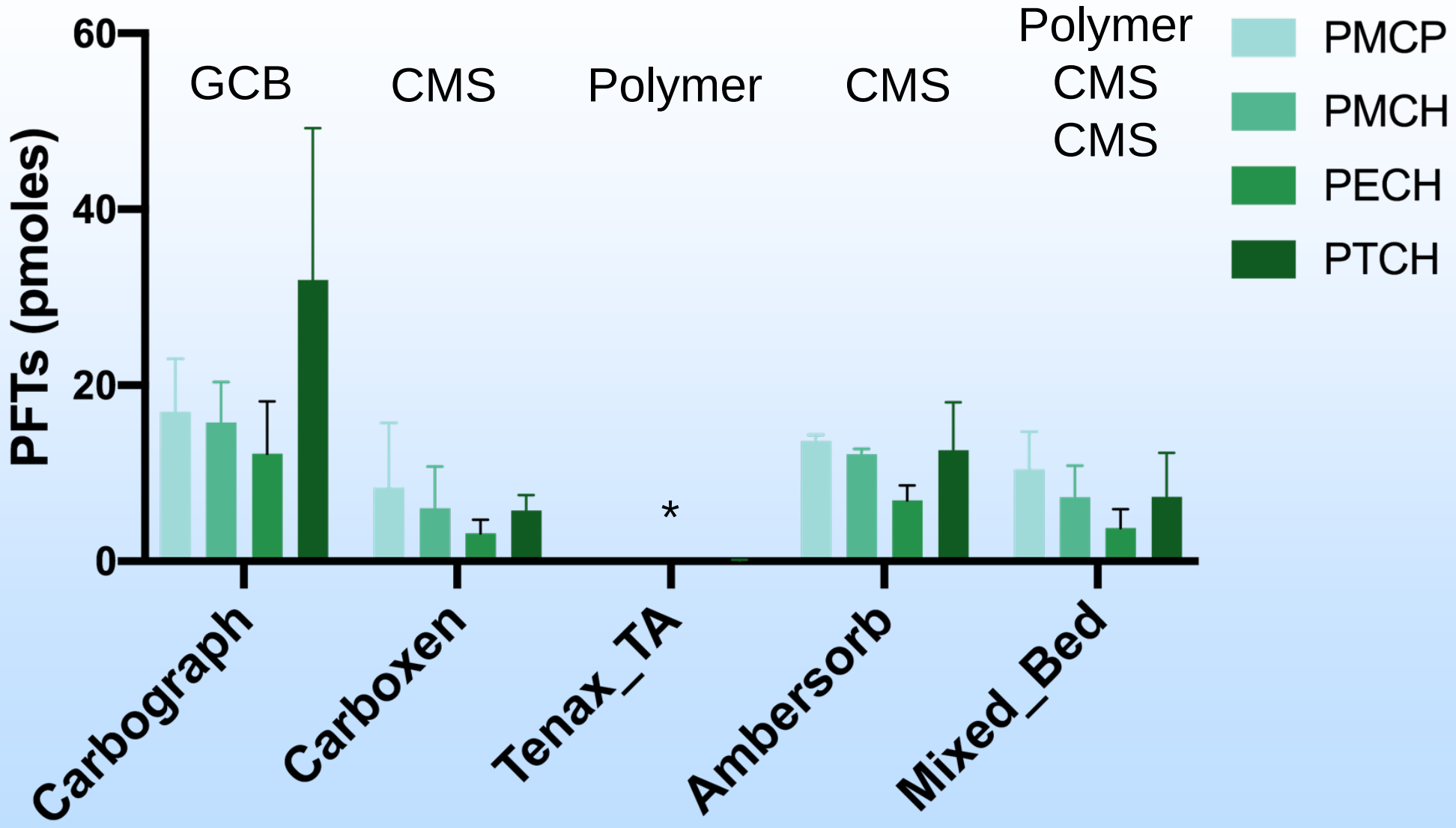


Adsorbent	Type[1]
Tenax TA	Porous polymer
Carbograph 1	GCB
Carbopack B	GCB
Ambersorb XE-347	CMS
Carboxen 569	CMS
Tenax TA/Carboxen 1000/ Carbosieve S-III	Mixed bed: Porous polymer, CMS, CMS
Carbopack B/Carbosieve S-III "Air Toxics"	Mixed bed: **GCB**, CMS
Carbopack B/Carbosieve S-III "Inverse Air Toxics"	Mixed bed: GCB, **CMS**



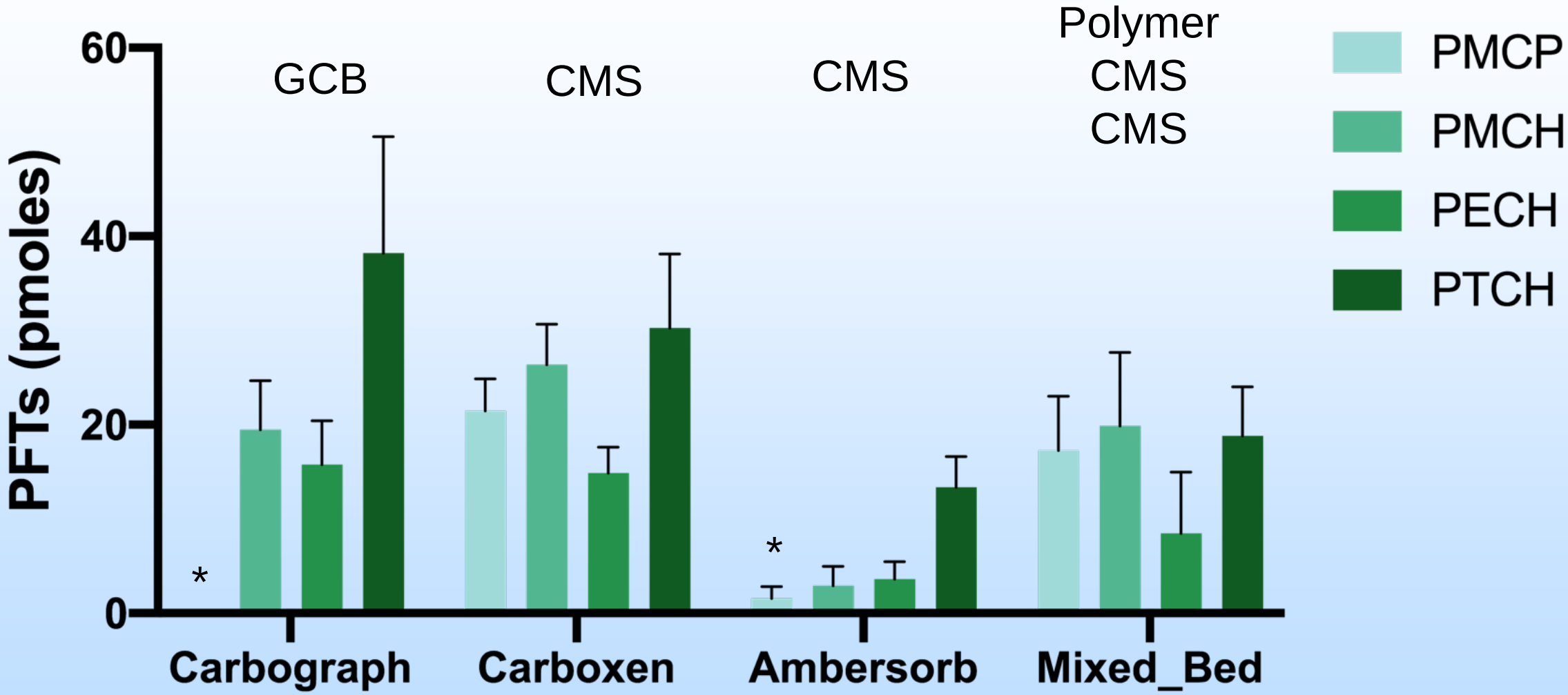
[1] GCB, Graphitized Carbon Black; CMS, Carbon Molecular Sieves.

PFTs in CO_2



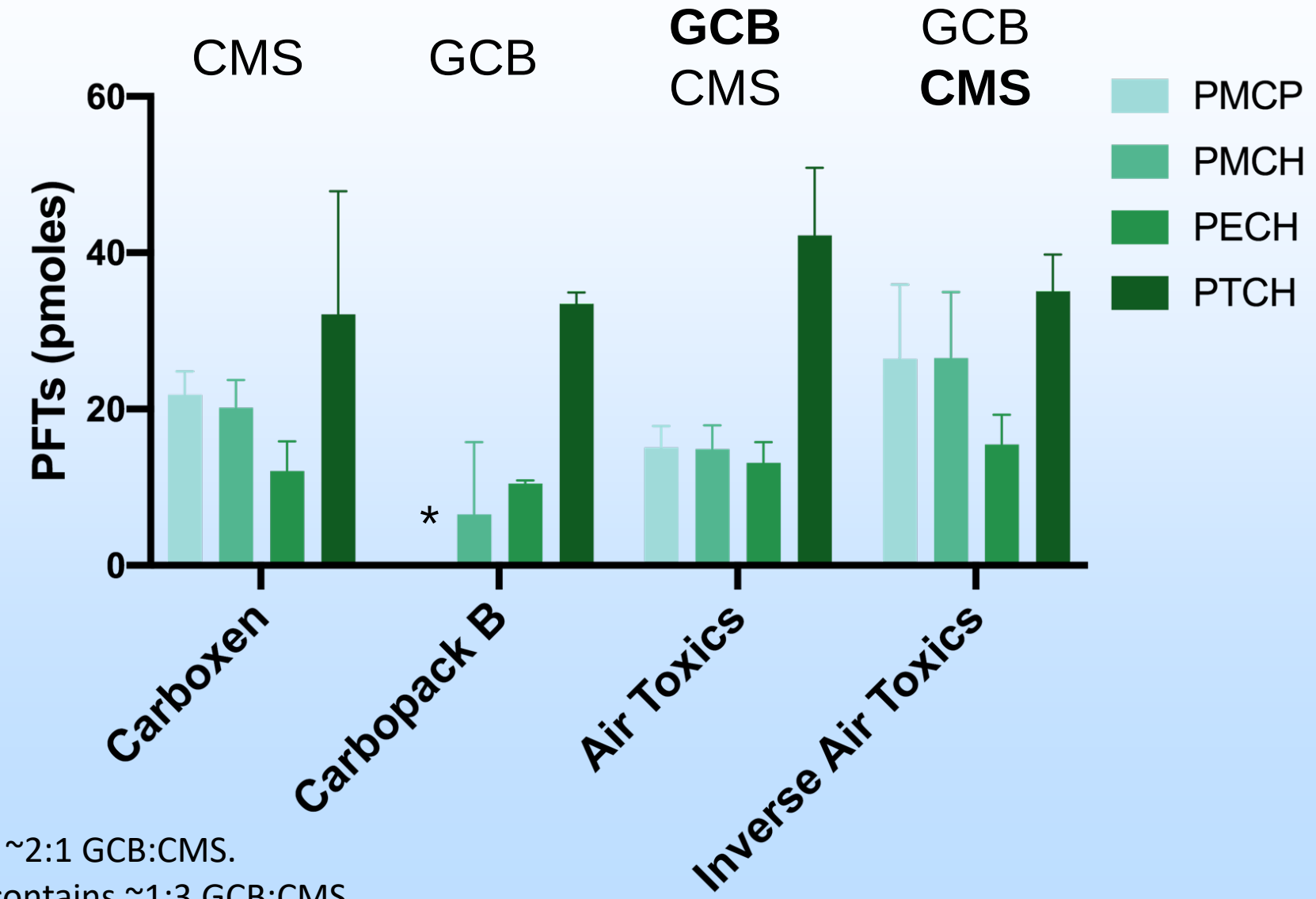
Five different types of sorbent tubes loaded with PFT standards in CO_2 were analyzed using thermal desorption with GC-ECD analysis. Measurements were performed on triplicate samples.

PFTs in CO_2 + Diesel Volatiles



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.

PFTs in CO_2 + Diesel Volatiles



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

Accomplishments to Date

- Demonstrated application of repeated PFT tests in C storage project.
- Comparison with simulations of repeated PFT injections indicates reservoir changes.
- Confirmed hydrocarbon interference with standard sorbent tube sampling method for PFTs.
- Demonstrated >10X improvement in PFT detection in a hydrocarbon matrix using high specific surface area CMS or mixed-bed sorbents.

Lessons Learned & Next Steps

- PFT tests provide complementary information to geophysical methods to characterize CO_2 plume and reservoir development.
- Interpreting PFT results requires reservoir simulations.
- 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 CMS sorbents or mixed beds significantly and substantially improves detection.
- *Test effects of water on sorption efficiency.*
- *Compare thermal desorption on GC-ECD and GC-MS systems.*

Synergy Opportunities

- Collaborative PFT sorbent testing in hydrocarbon-rich matrices. Planned GC-MS experiments with NETL RIC.
- Sharing best practices for tracer analysis
- New tracer test campaigns for C storage/EOR

- Potential applications for CCUS Research Priority area:

  Locating, Evaluating, and Remediating Existing and Abandoned Wells
- Wellbore leakage, Environmental monitoring

Project Summary (Task 2)

– Completed PFT tests & simulations at Cranfield DAS

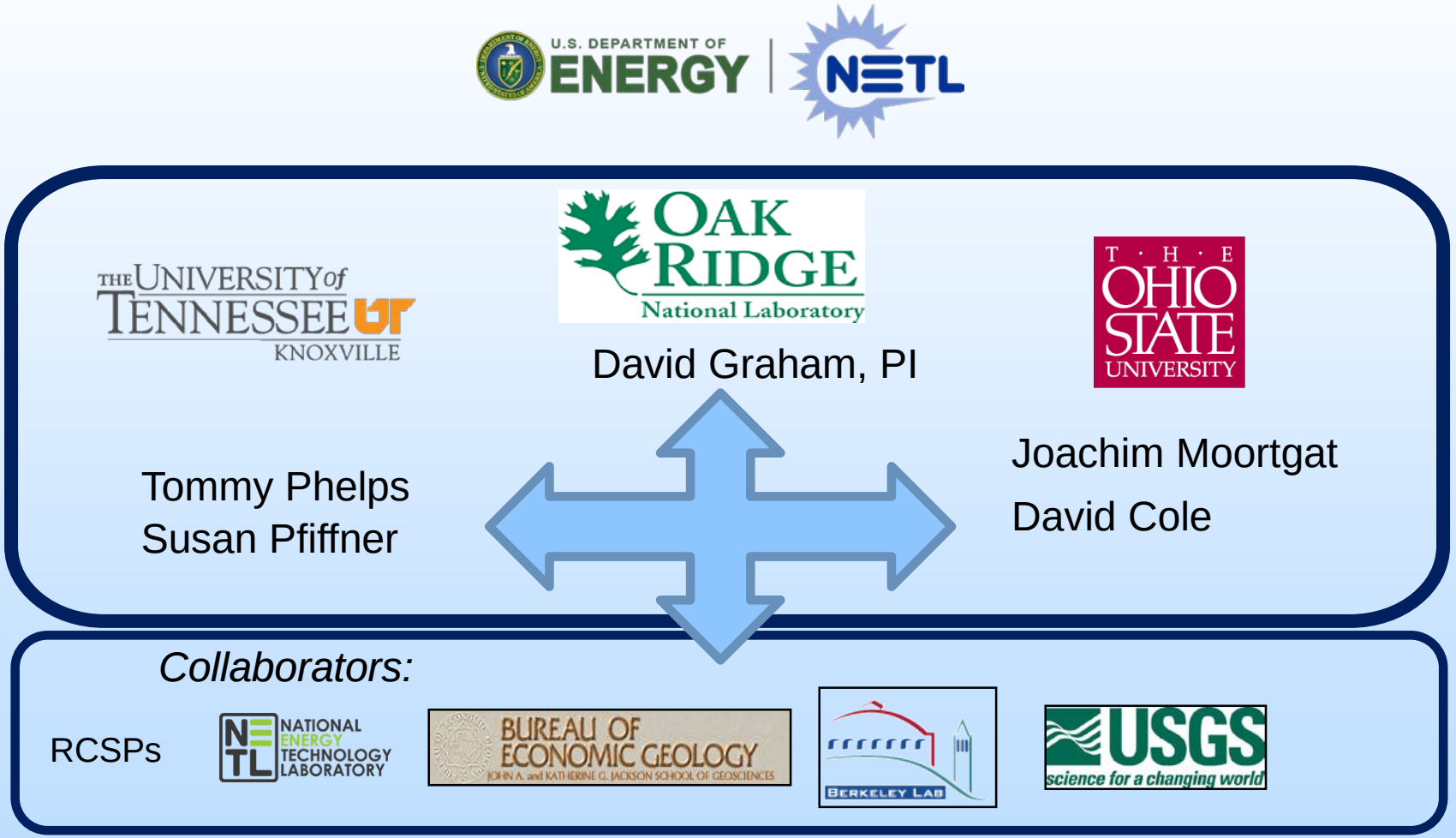
– Demonstrated significant hydrocarbon interference with sorption tube sampling of PFTs

– Identified >10X improvements in PFT detection in hydrocarbon matrices with new sorbent tubes

– Completing best practices for PFT tests.

Appendix

Project Organization

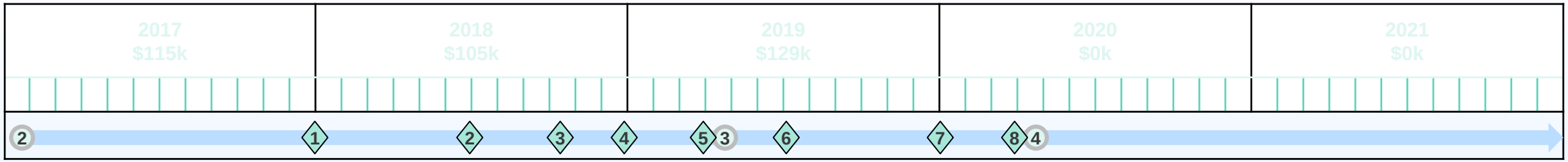


Gantt Chart

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

Task 2: Project Timeline Overview

Assess efficiency of PFT analysis using capillary adsorption tubes in a hydrocarbon-rich matrix



Milestones (2018-2020)

1. Prepare PFT standards in hydrocarbon (HC) matrices for sorbent tube test and GC-MS analysis at NETL
2. Report on efficacy of sorbents to improve PFT capture and analysis
3. Report on new adsorbent technology for PFT sampling
4. Survey field test opportunities for enhanced PFT sampling technology
5. Thermal desorption system installed on ORNL GC-ECD system
6. Sorbent selected for PFT-hydrocarbon experiments
7. Validation of PFT sorbent sampling method in HC matrices
8. Best practices identified for PFT sampling in HC-rich environments

Chart Key

TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Go / No-Go

Impact

Key Accomplishments/Deliverables (2017-2018)	Value Delivered
• Compiled and annotated Cranfield PFT data for modeling in Task 1. • Identified HC-rich sample matrices as a critical challenge for PFT methods due to potential interferences with sample collection and analytical instruments. • Demonstrated HC interference with sorbent tube sampling (NETL collaboration) • Developed a technology review and research plan to mitigate HC interference with new sorbent sampling methods.	• The initial application of this technology will be to monitor and delineate injected CO_2 breakthrough and features of developing plumes in a reservoir containing extractable hydrocarbons. Robust methods have the long-term potential to provide near-real-time information on process optimization, enabling adaptive control of CO_2 injections. The dataset collected from PFT measurements will be used to calibrate and validate predictive models.

Task 2 - Bibliography

- 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 8:650-671.