Monitoring of Geological CO_2 Sequestration Using Isotopes and Perfluorocarbon Tracers

Project Number FEAA-045

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U.S. Department of Energy

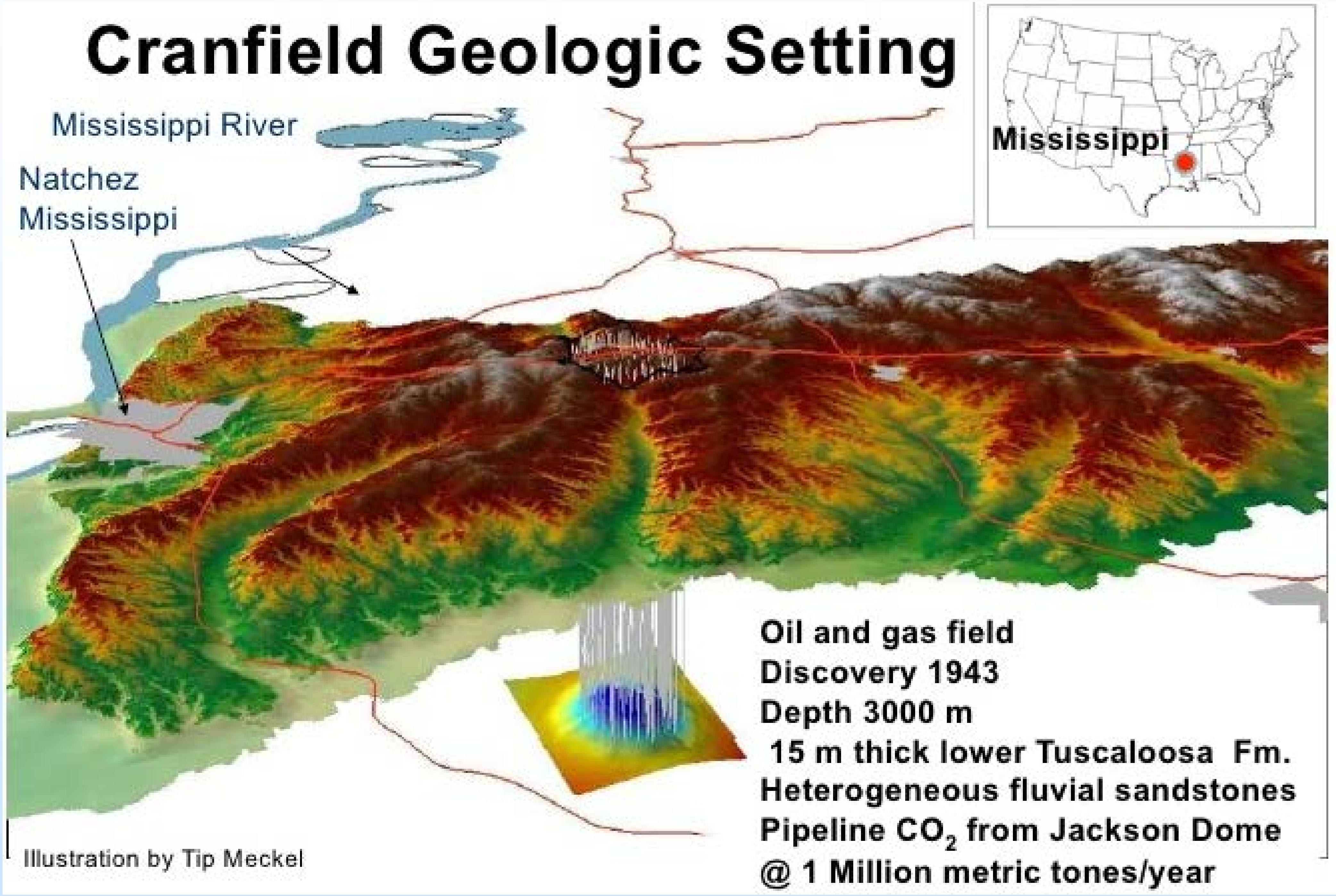
National Energy Technology Laboratory

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

August 1-3, 2017

Presentation Outline

- Benefits to program
- Perfluorocarbon tracer (PFT) analyses
- Reservoir simulations for CO_2 & tracers
- Conclusions
- Future work & Synergies
- Appendix

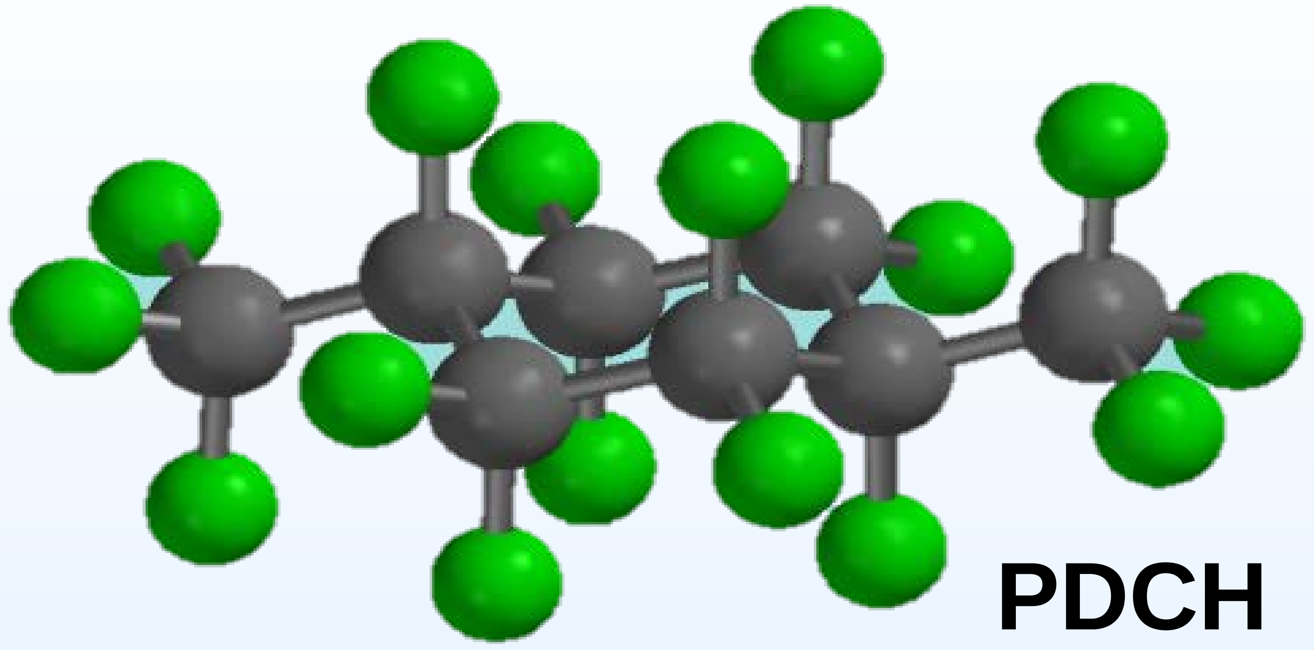


Modified from
slideshare.net/globalccs/cranfield-large-scale-co2-injection-usa

Introduced by Susan Hovorka this morning.

Conservative Perfluorocarbon Tracers (PFTs)

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



PDCH

Benefit to Program

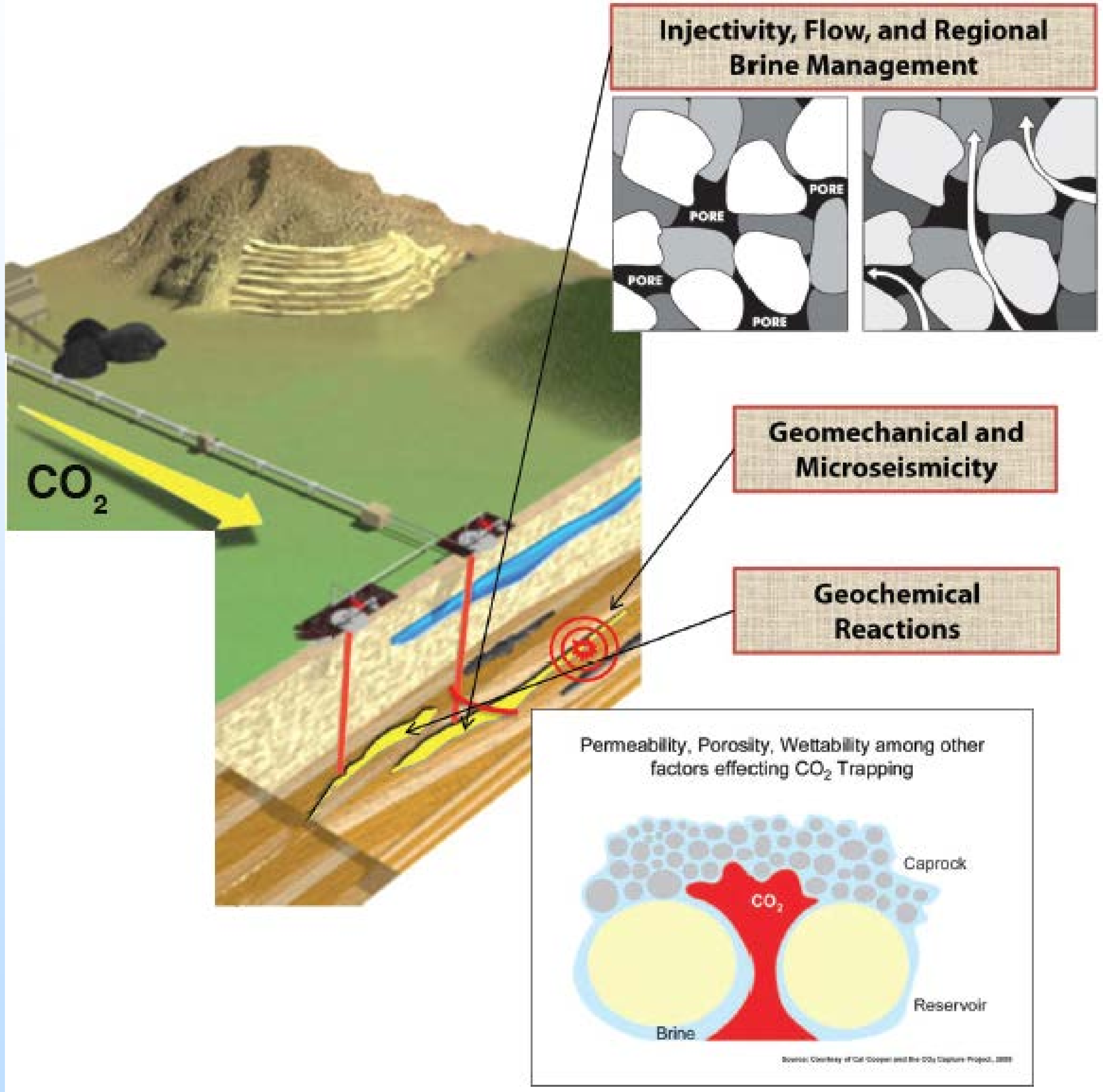
Use tracers to monitor & validate (99%) CO_2 **storage permanence**

New subsurface signal to monitor physical & chemical processes affecting **storage efficiency:**

- Alter porosity & permeability, e.g., fracturing (SubTER)
- Control fluid flow, e.g., diffusion, mixing, advection, capillarity, and reaction

Equally applicable to EOR and geothermal.

Complimentary tool to traditional geophysics.

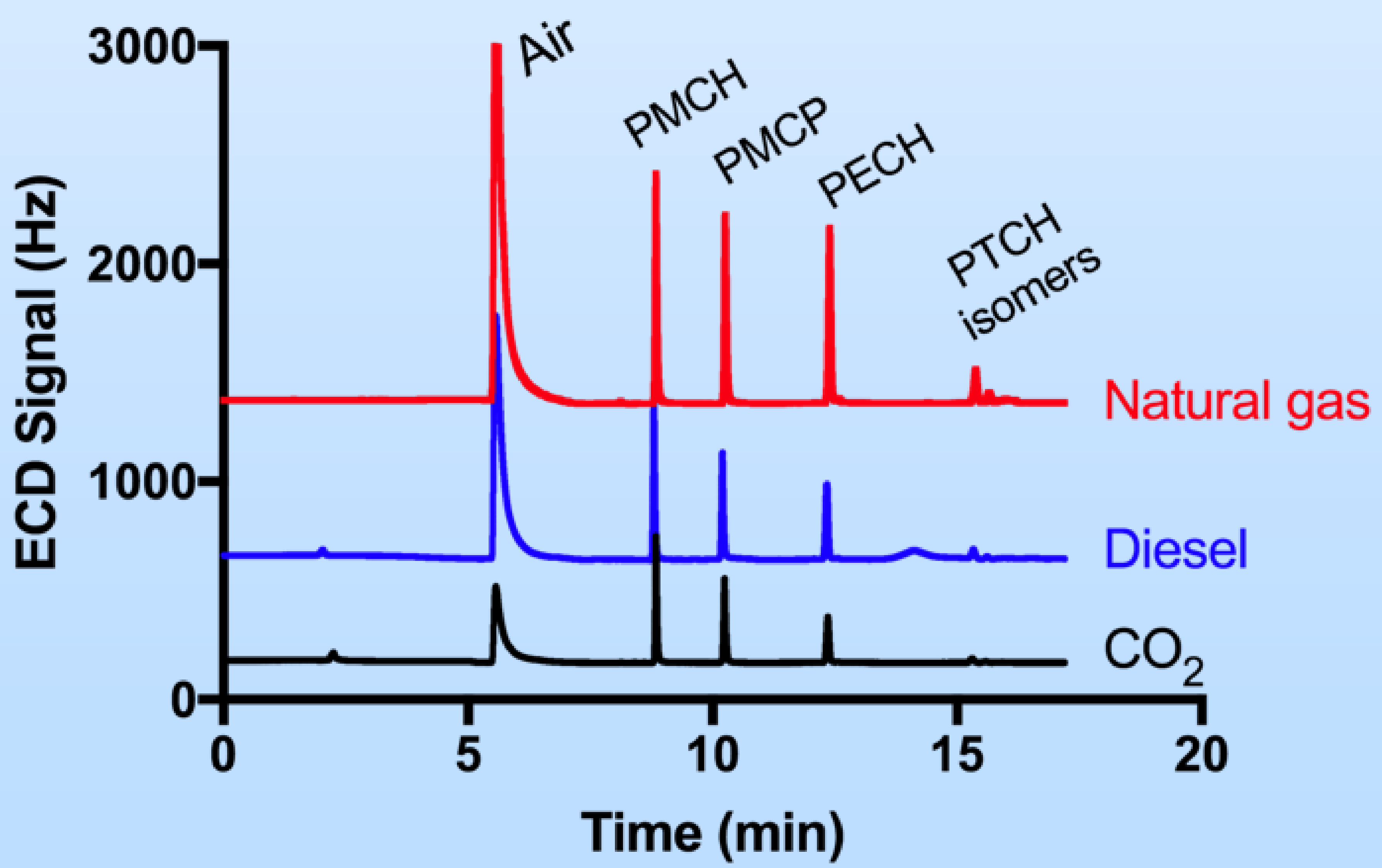


Modified from NETL Carbon Storage GSRA Technology Research Areas Illustration

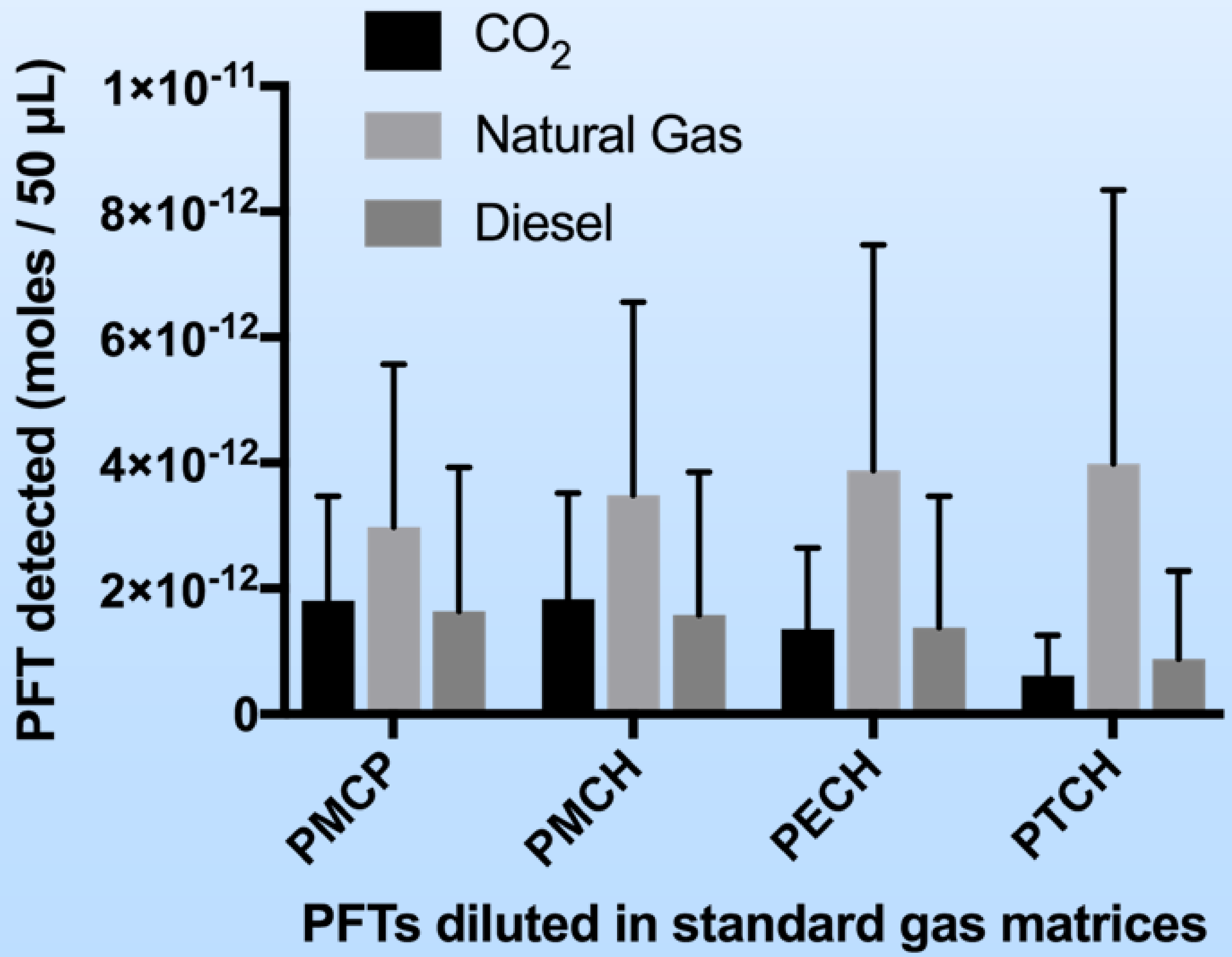
Hydrocarbons may have a small to insignificant effect on PFT analysis by direct injection GC-ECD

- *How does a hydrocarbon-rich sample matrix affect PFT sorption and analysis?*
- PFT standards diluted in 3 matrices: CO_2, natural gas, and CO_2 and diesel liquids.

No change in retention times or baseline noise during analysis of 20-30 fmoles (5-10 pg) of each PFT in 3 matrices

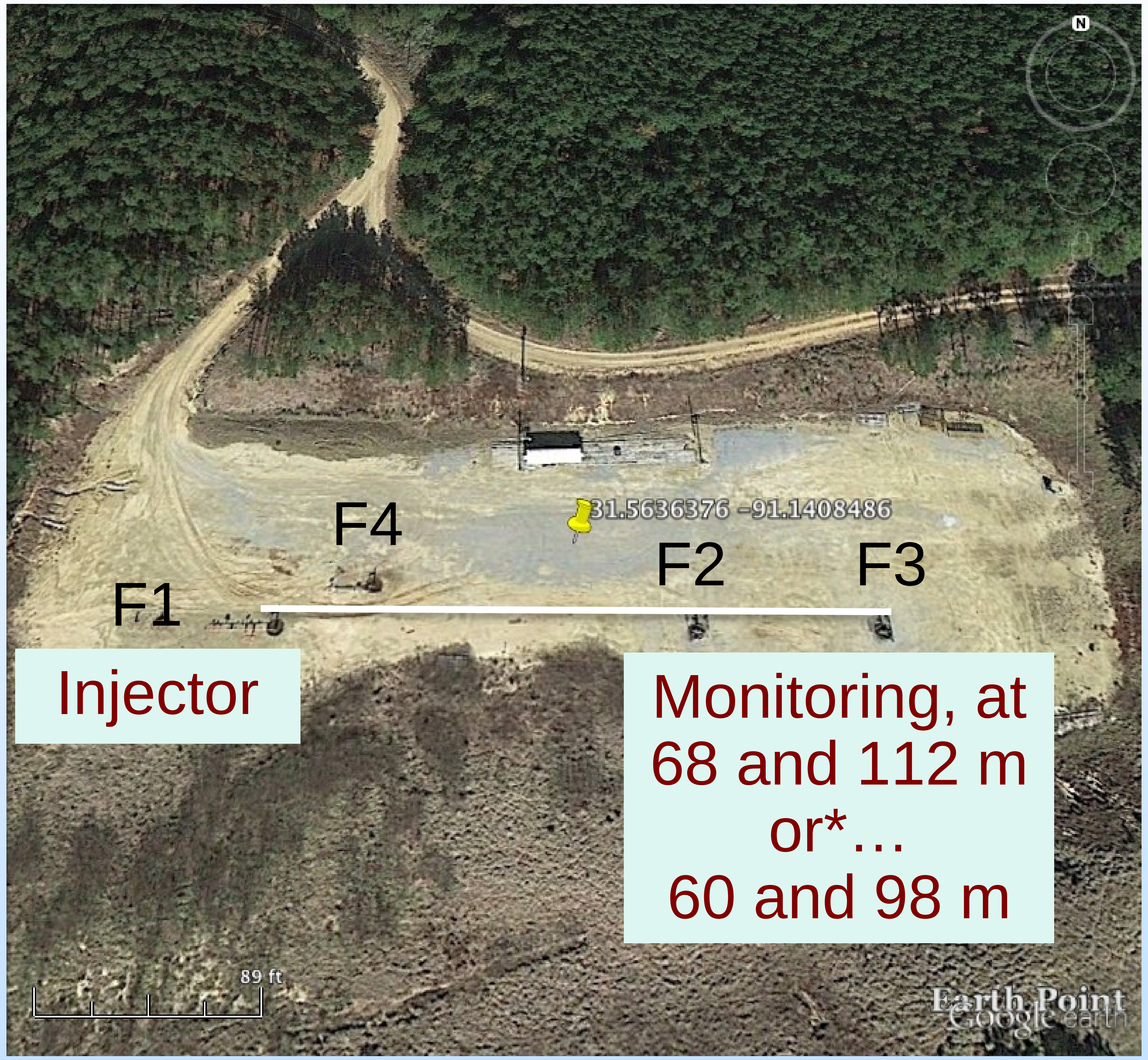


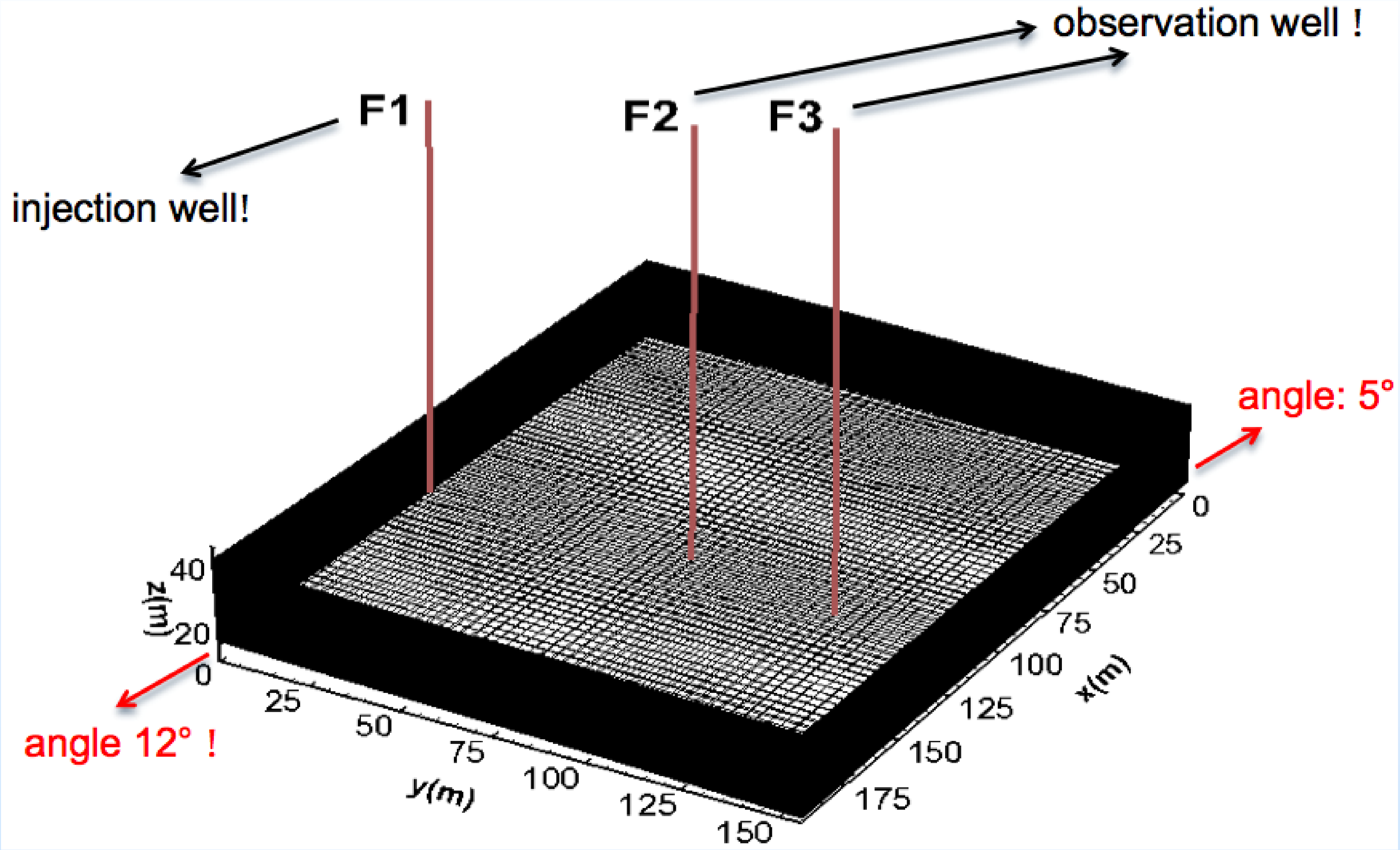
No significant difference in detecting pmole (ng) quantities of PFTs in 3 matrices



RESERVOIR MODELING & INTERPRETATION OF PFT FIELD DATA

Cranfield, SW Mississippi, near Natchez
Detailed Area of Study (DAS)





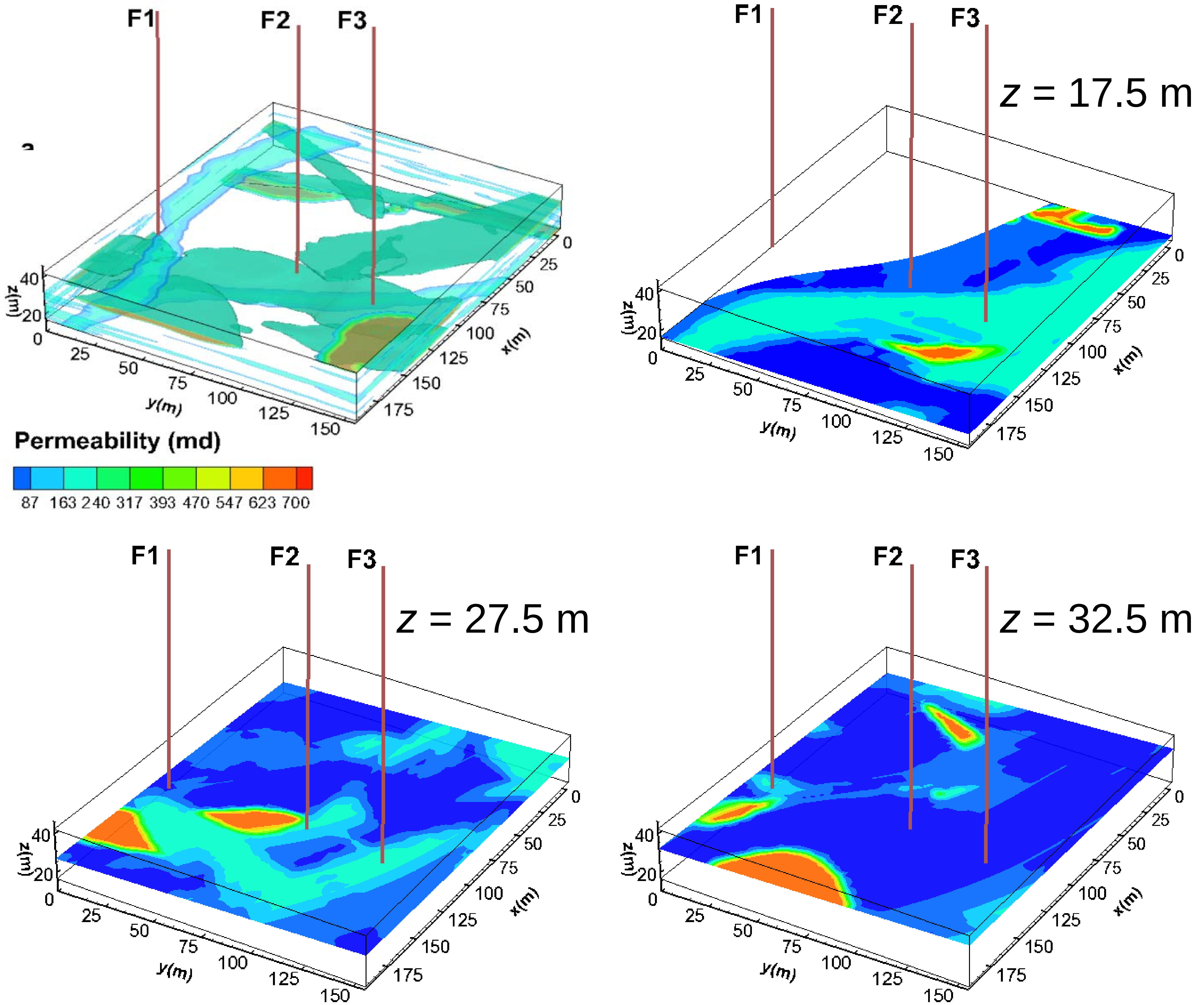
Extracted from > 60 million element model by UTBEG Hosseini et al., *IJGCC* (2013)

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

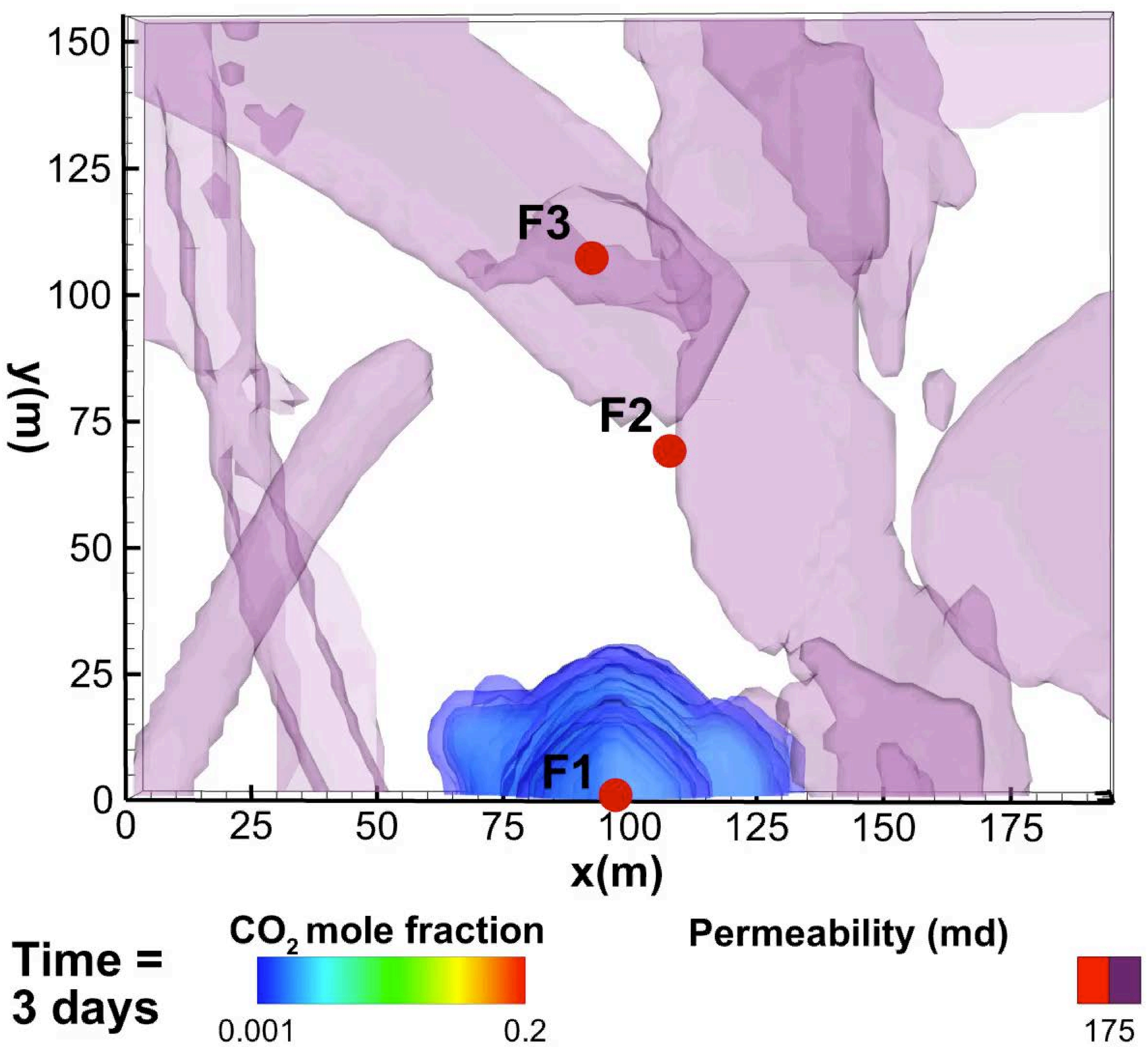
Thanks to:

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

Permeability



Fluvial depositional features: high permeability channels & tight shales

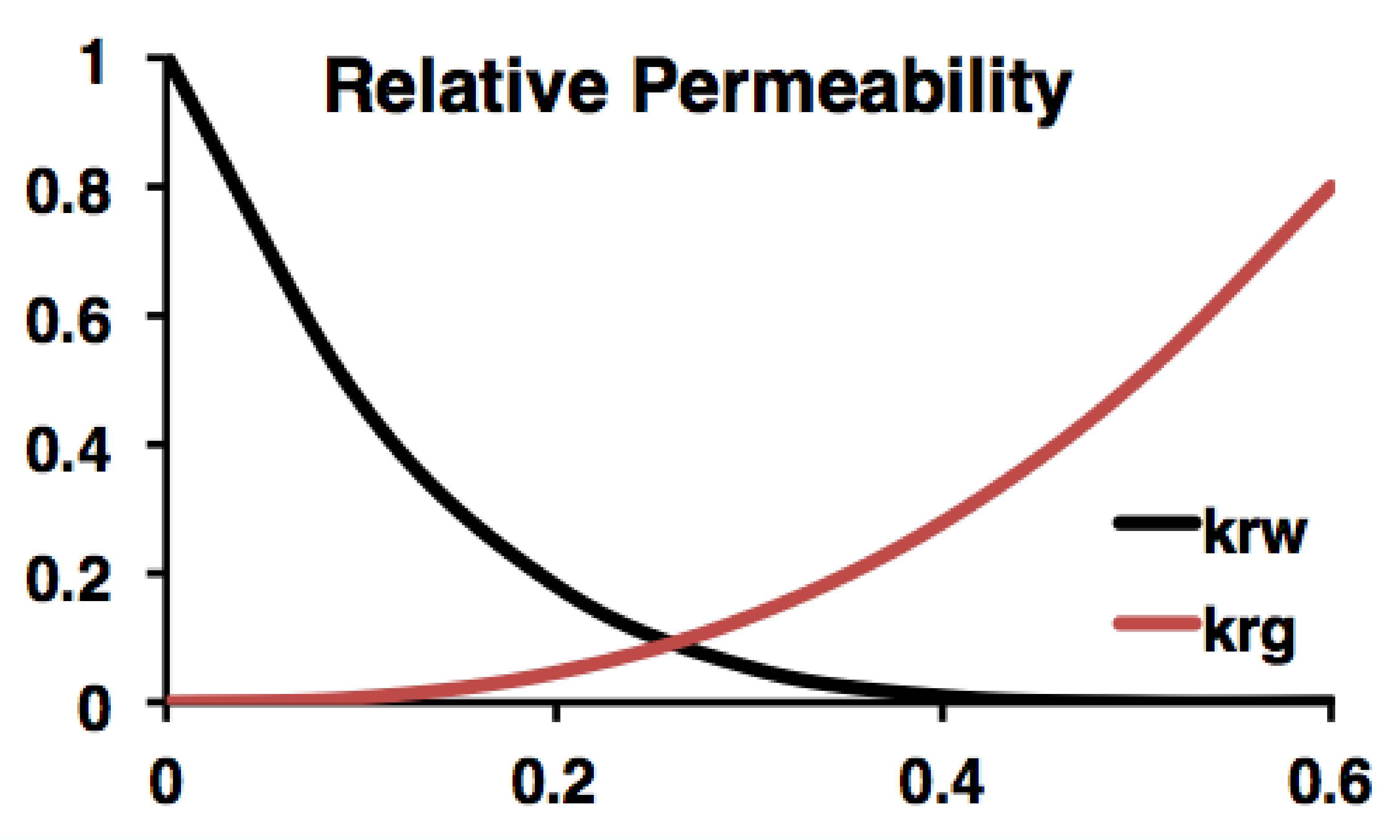


Osures Reservoir Simulator

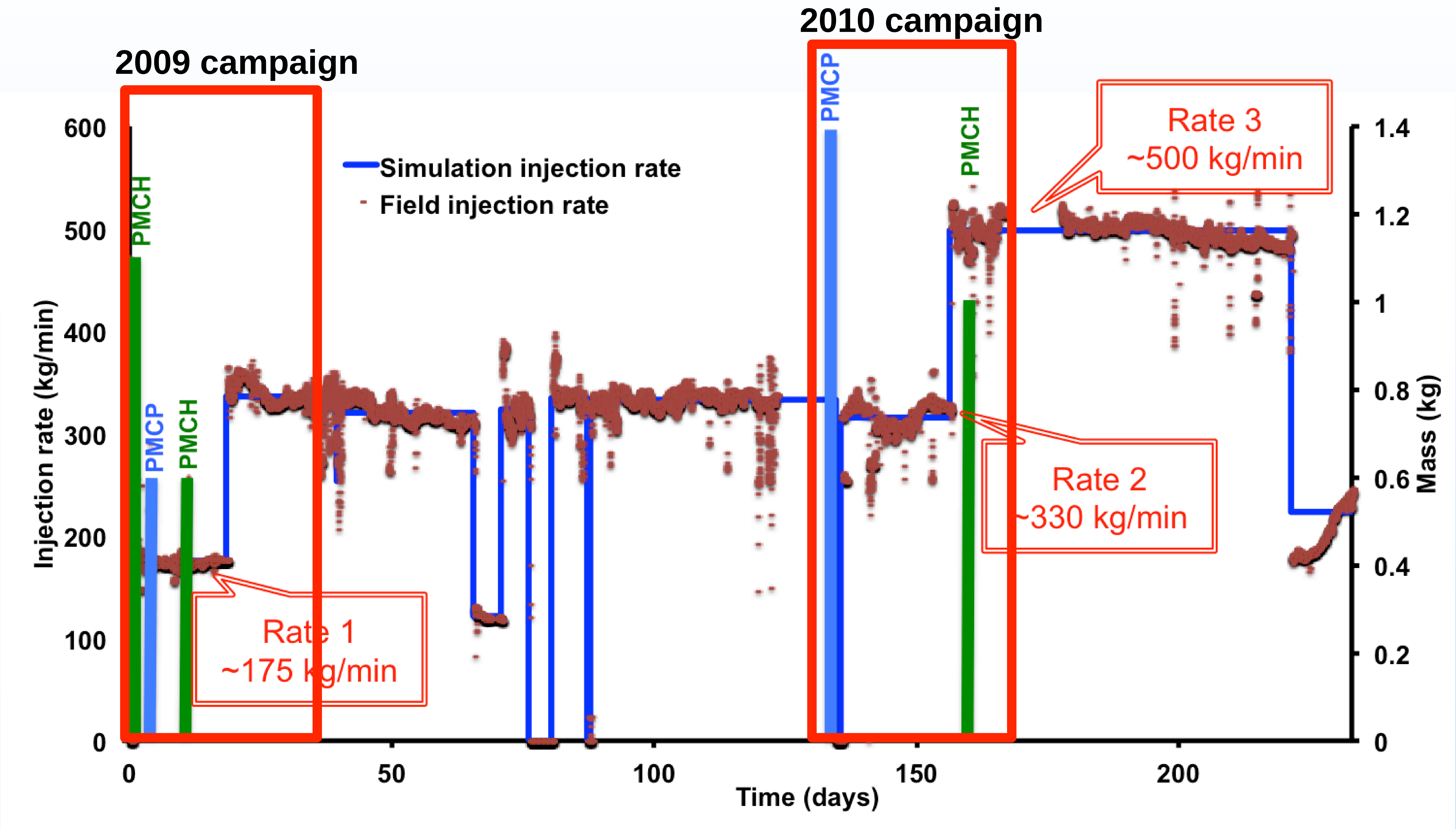
- Higher-order finite elements for flow and transport
- EOS-based phase-split computations, also for tracers
- Cubic-Plus-Association (CPA) EOS for water-CO_2 mixtures

- Fickian diffusion, mechanical dispersion, capillarity
- Brooks-Corey relative permeabilities with S_{wir} = 40% (or 60%)

- No-flow top and bottom (shale), constant p on outflow boundaries



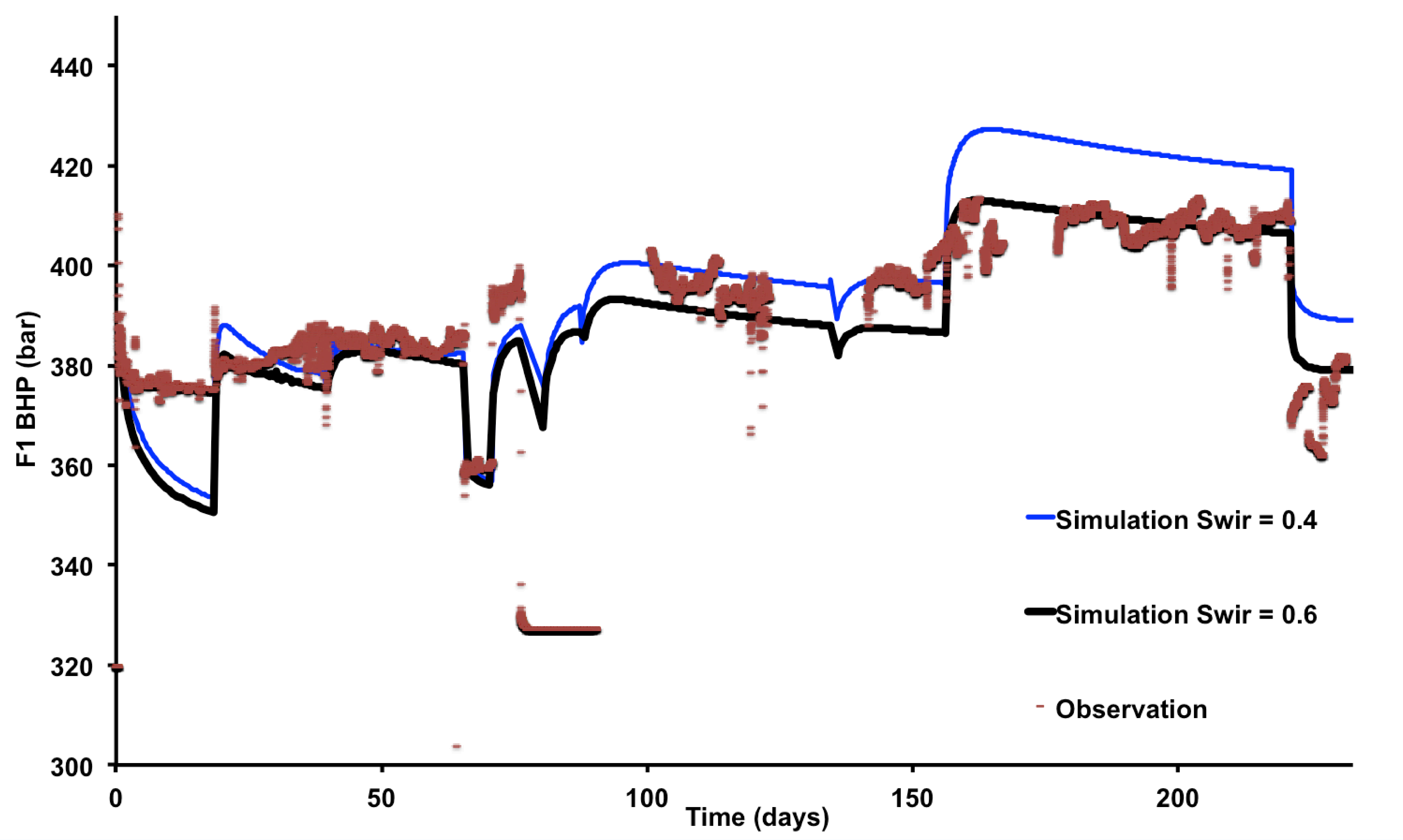
Injection Schedule



Data from UTBEG

(also PECH, PDCH, PTCH, and SF_6)

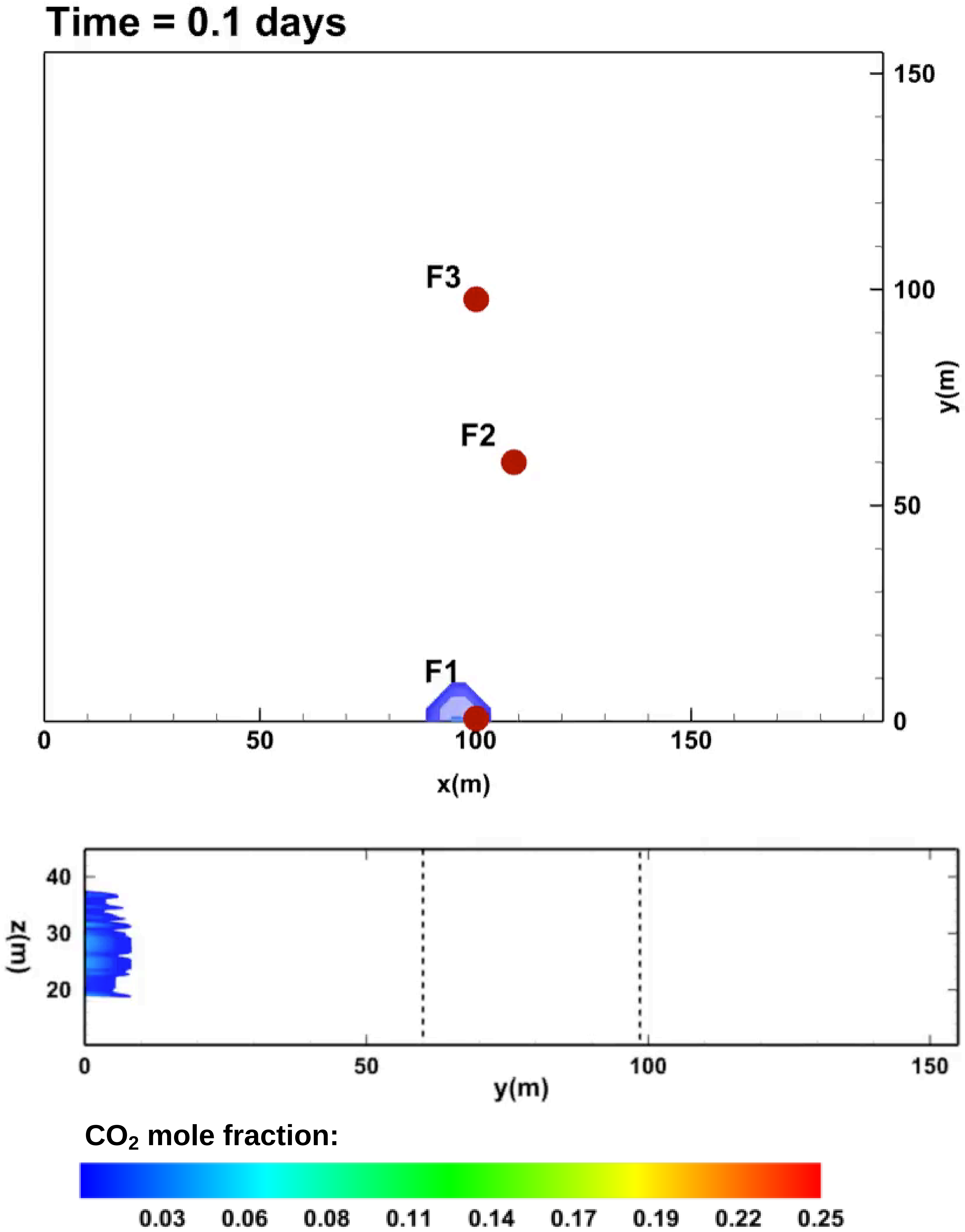
Pressure Response in F1



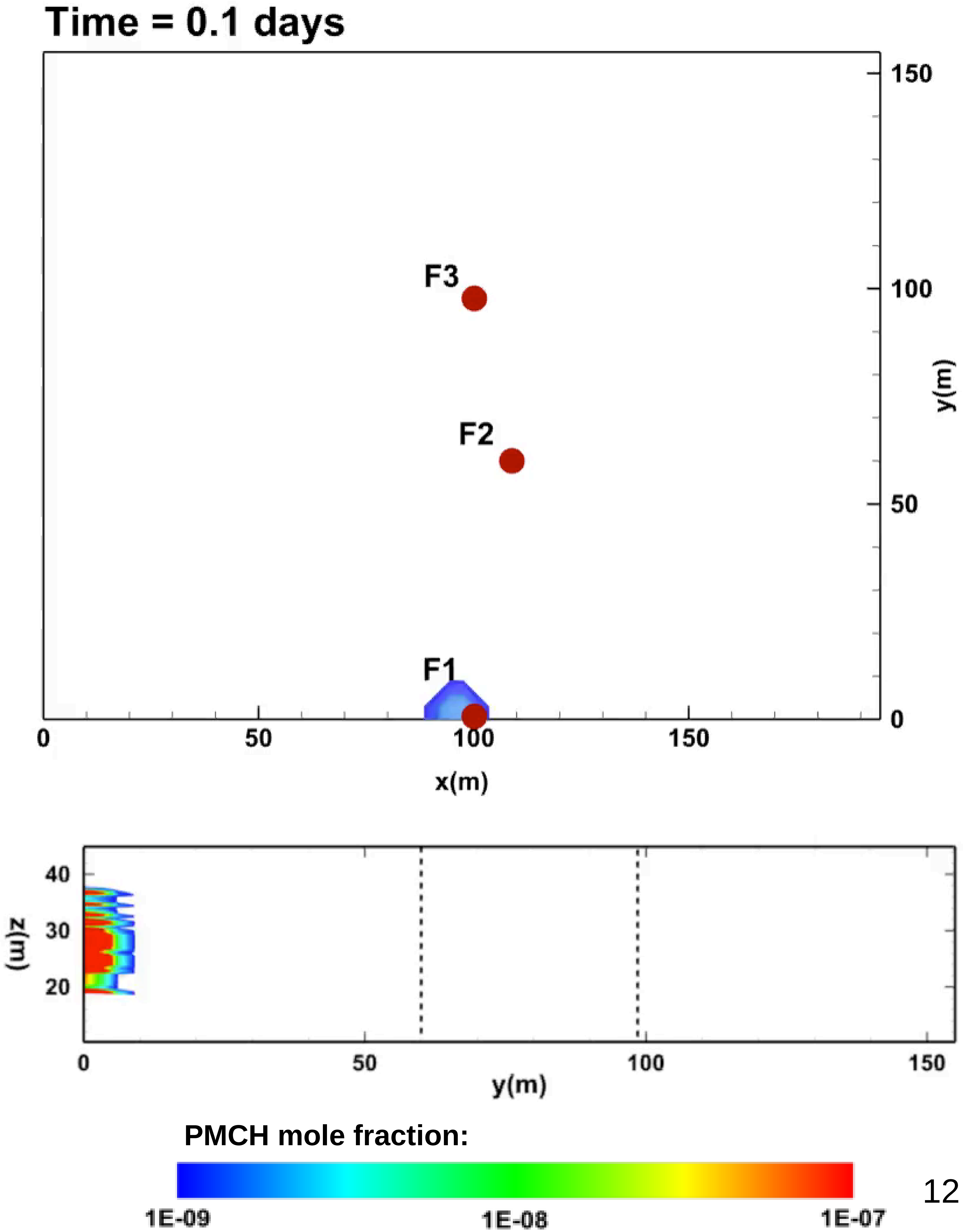
Data from UTBEG. Modeling in Soltanian et. al, *IJGGC* (2016)

2009 Campaign

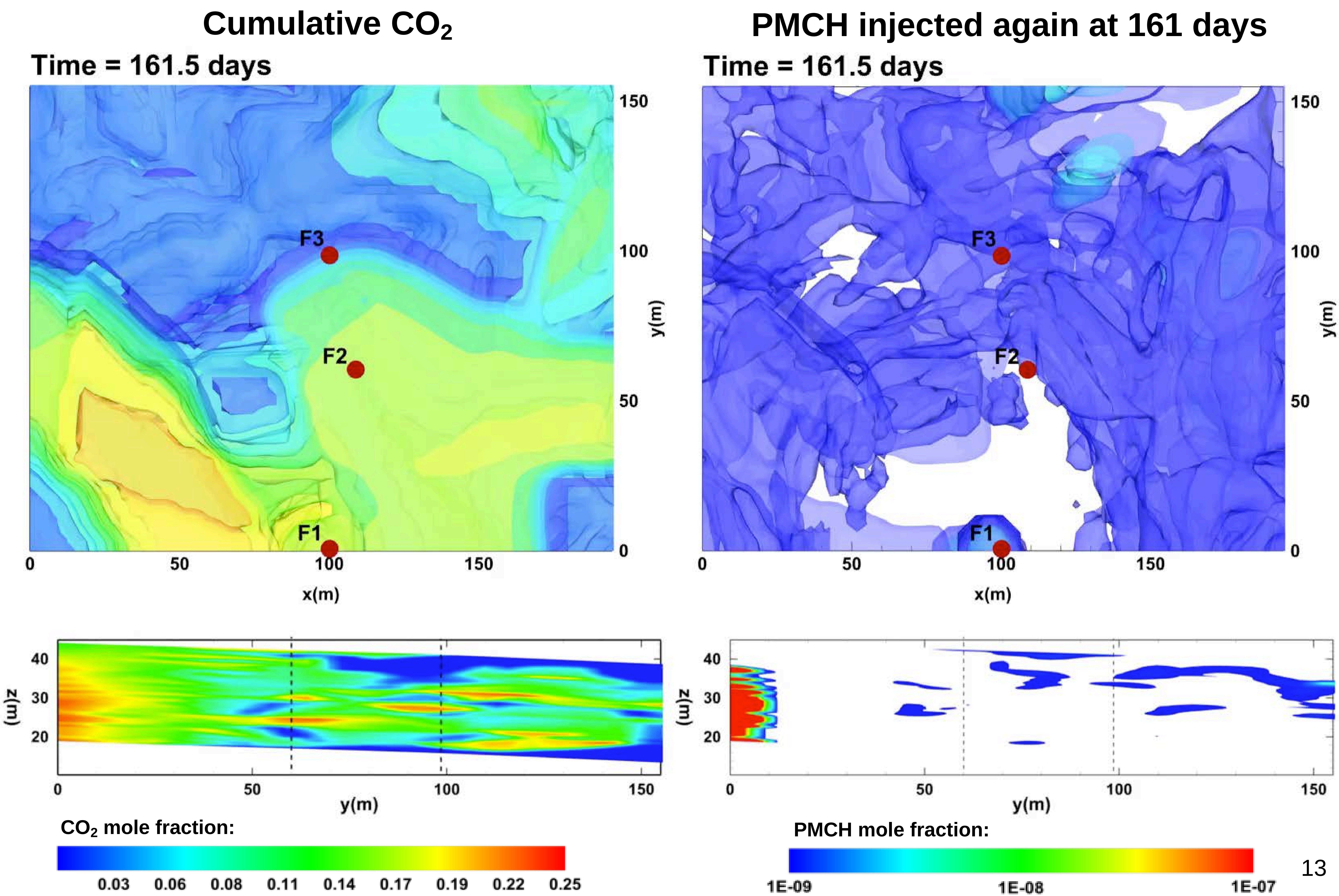
CO_2



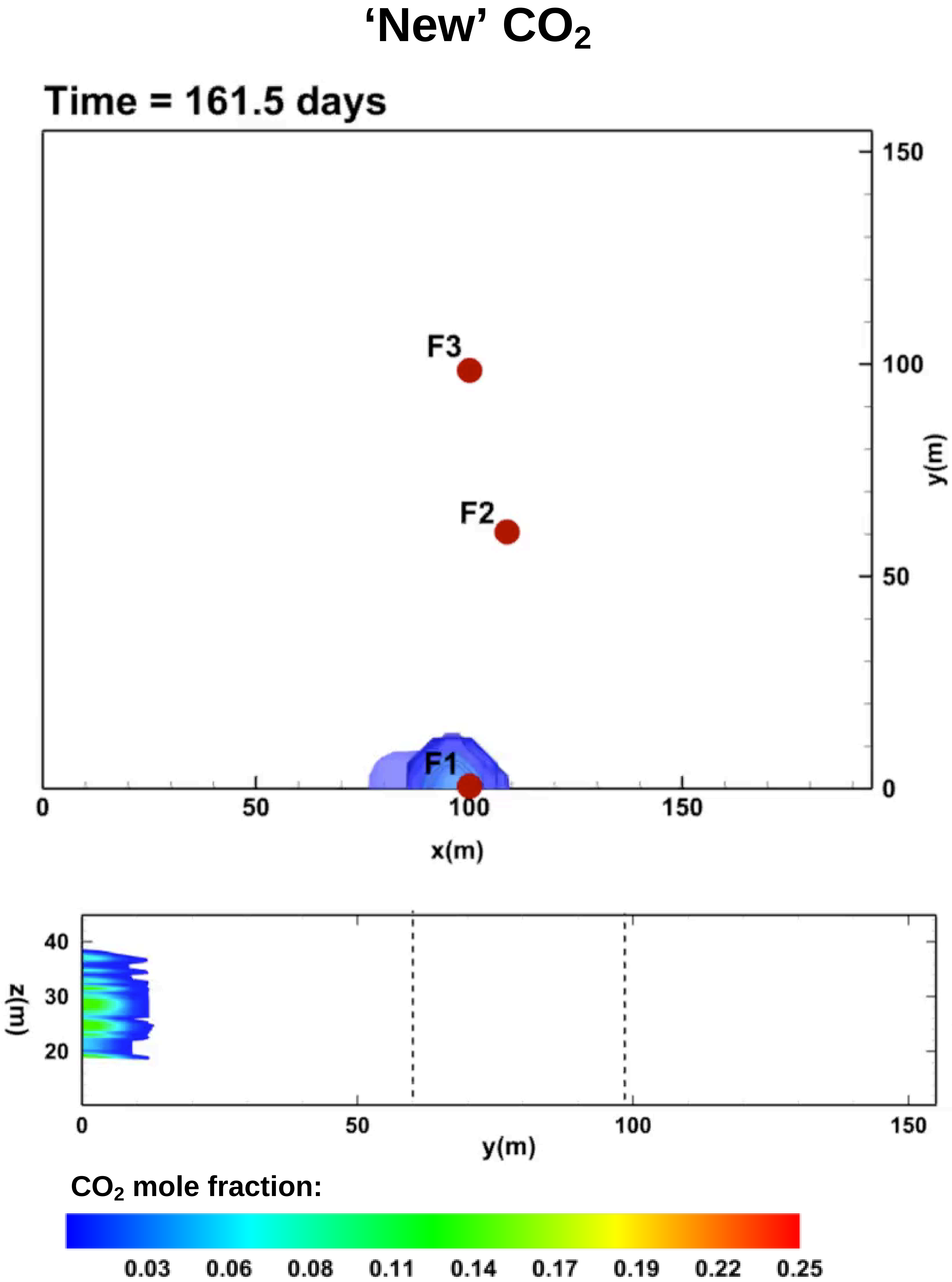
PMCH injected after 0 & 11 days

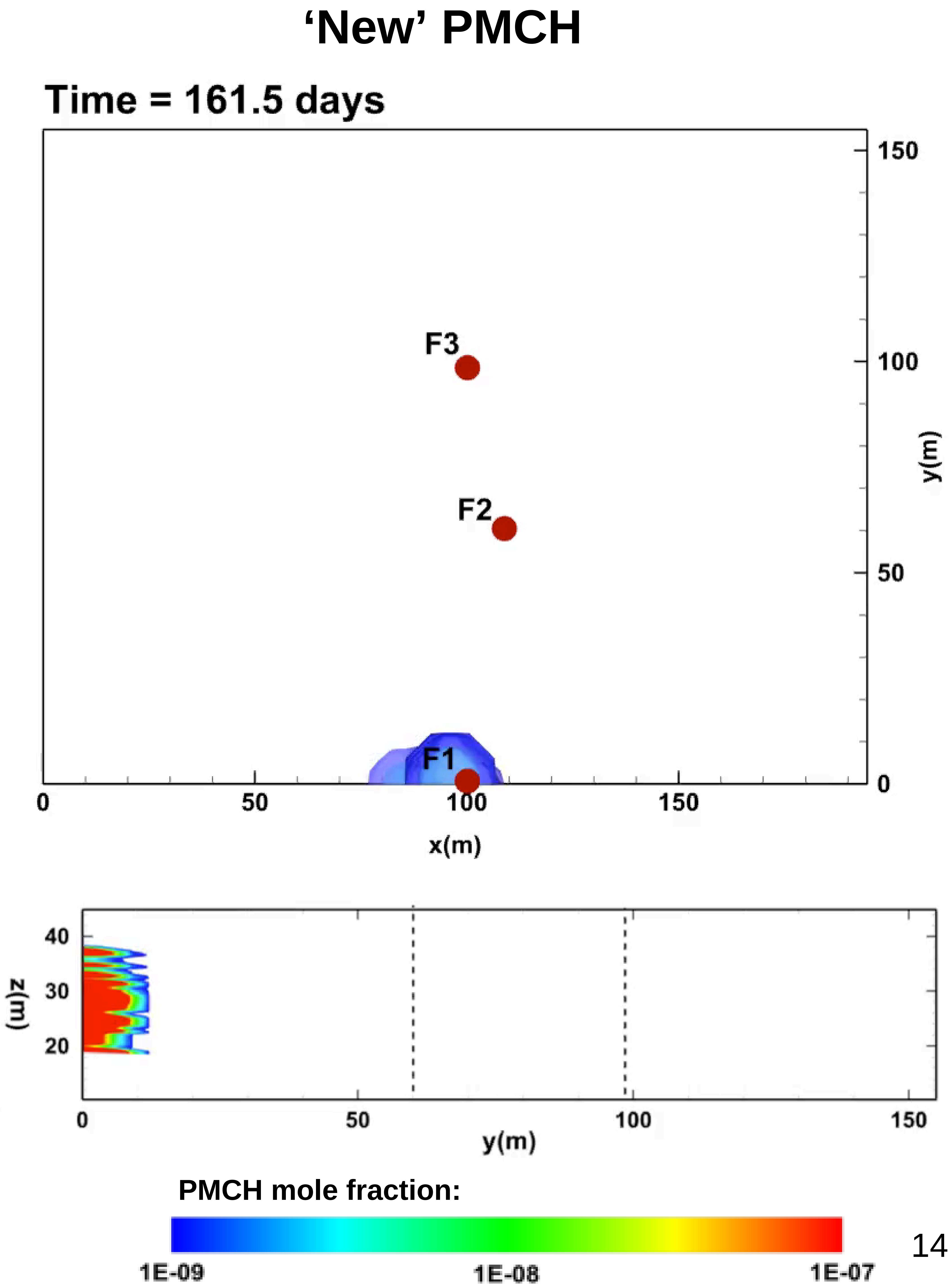


2010 Campaign



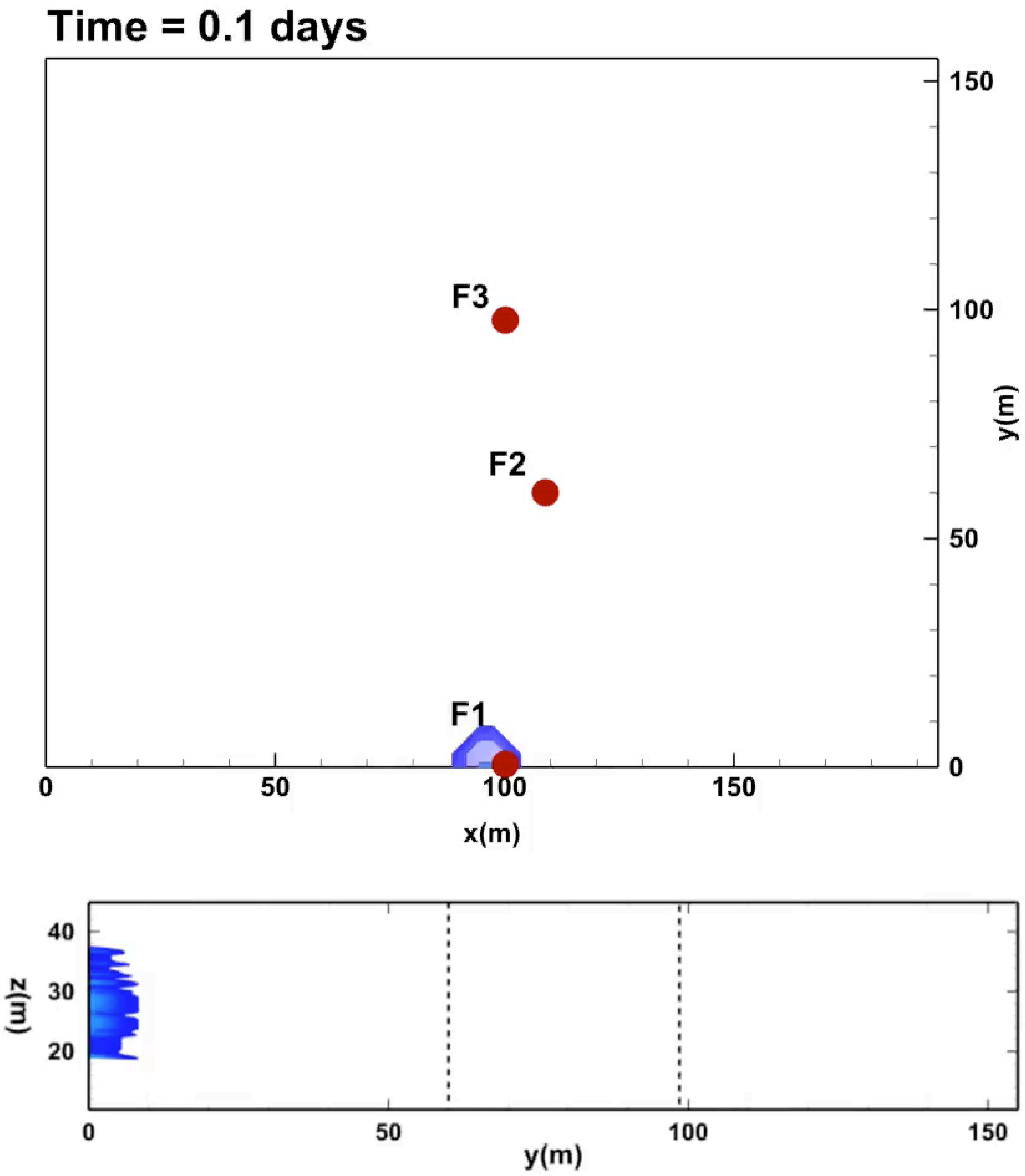
2010 Campaign



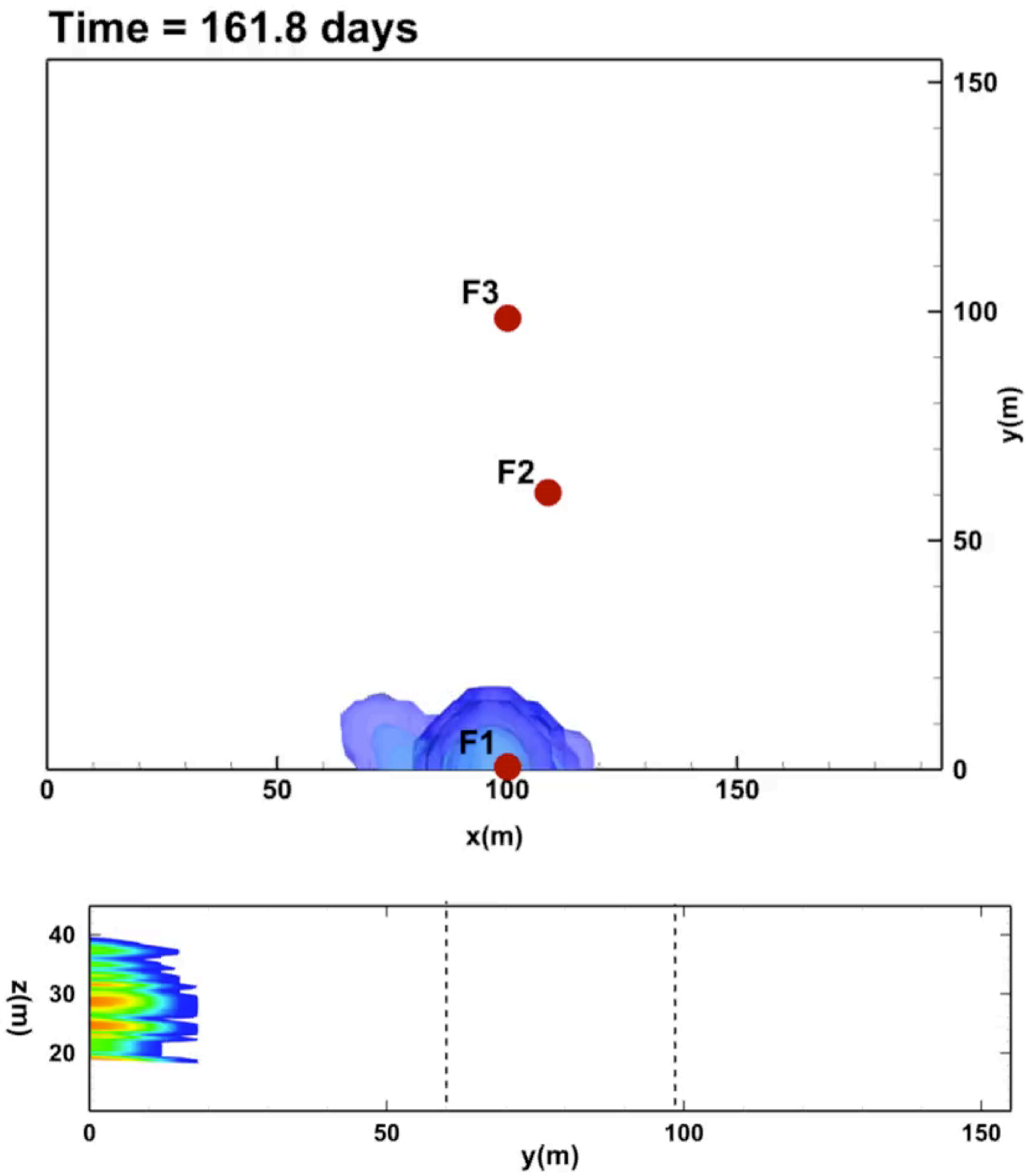


2009 vs 2010 (CO_2)

CO_2 in 2009

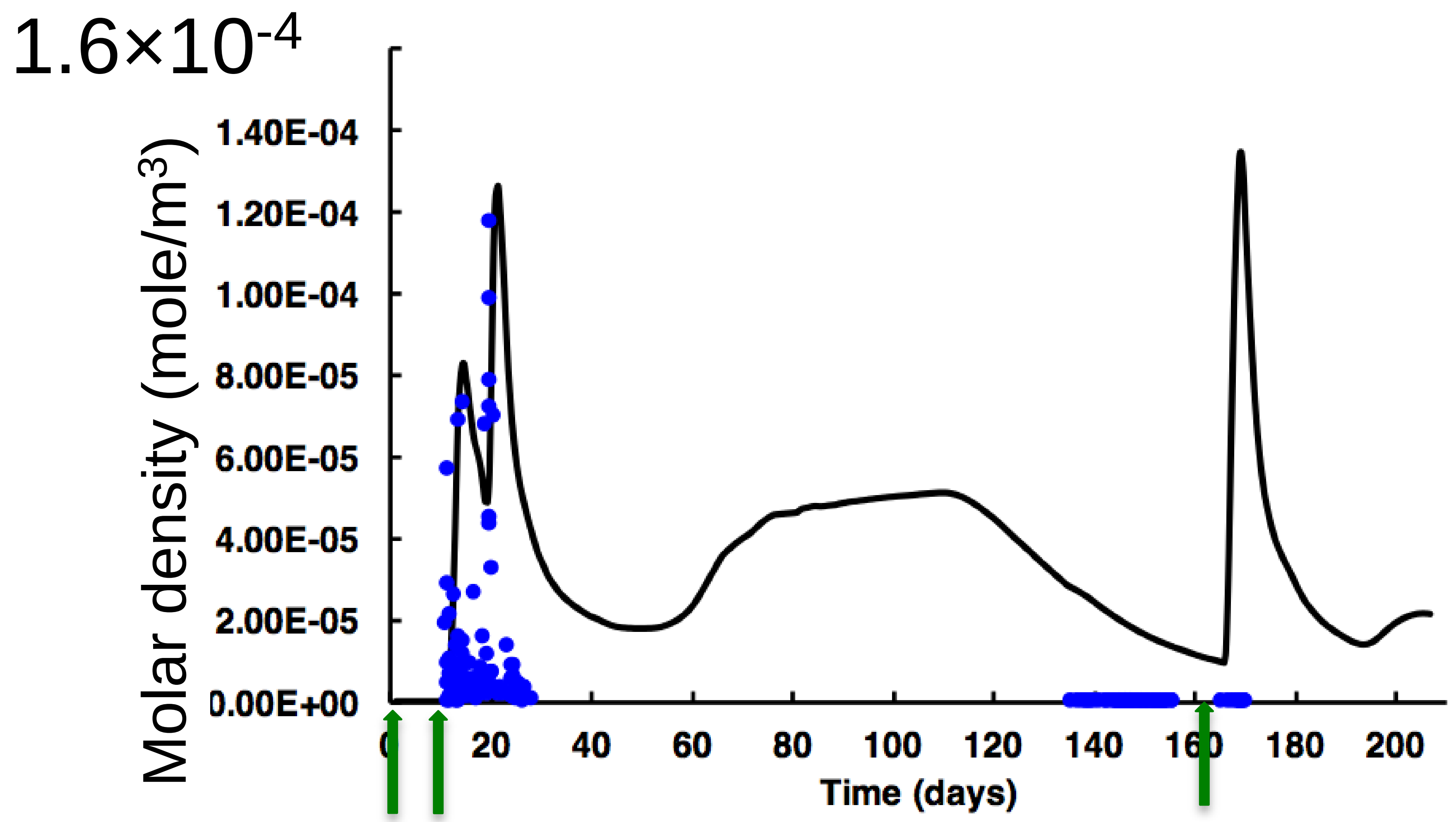


CO_2 in 2010

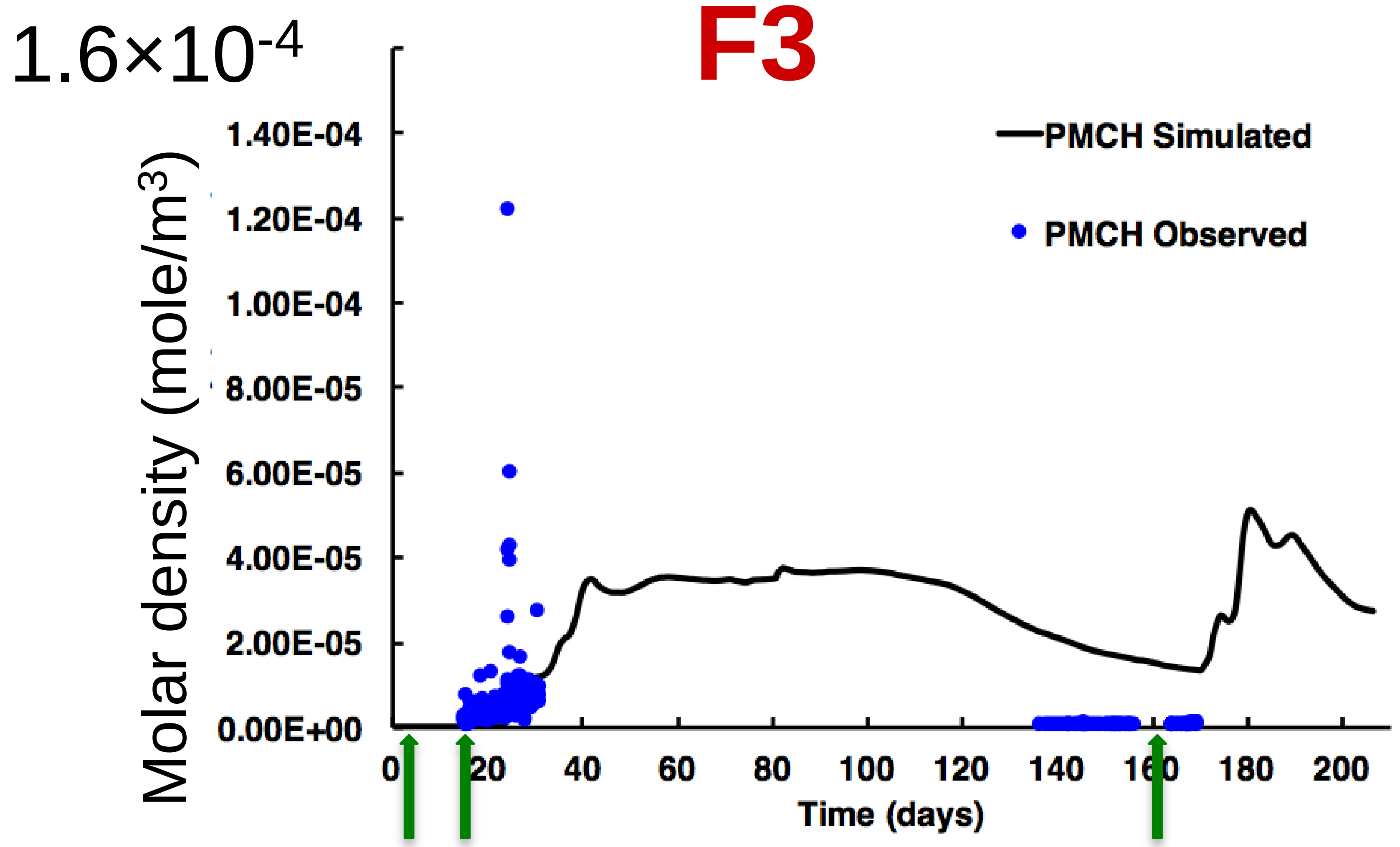


2009-2010 Breakthrough Curves

PMCH Tracer

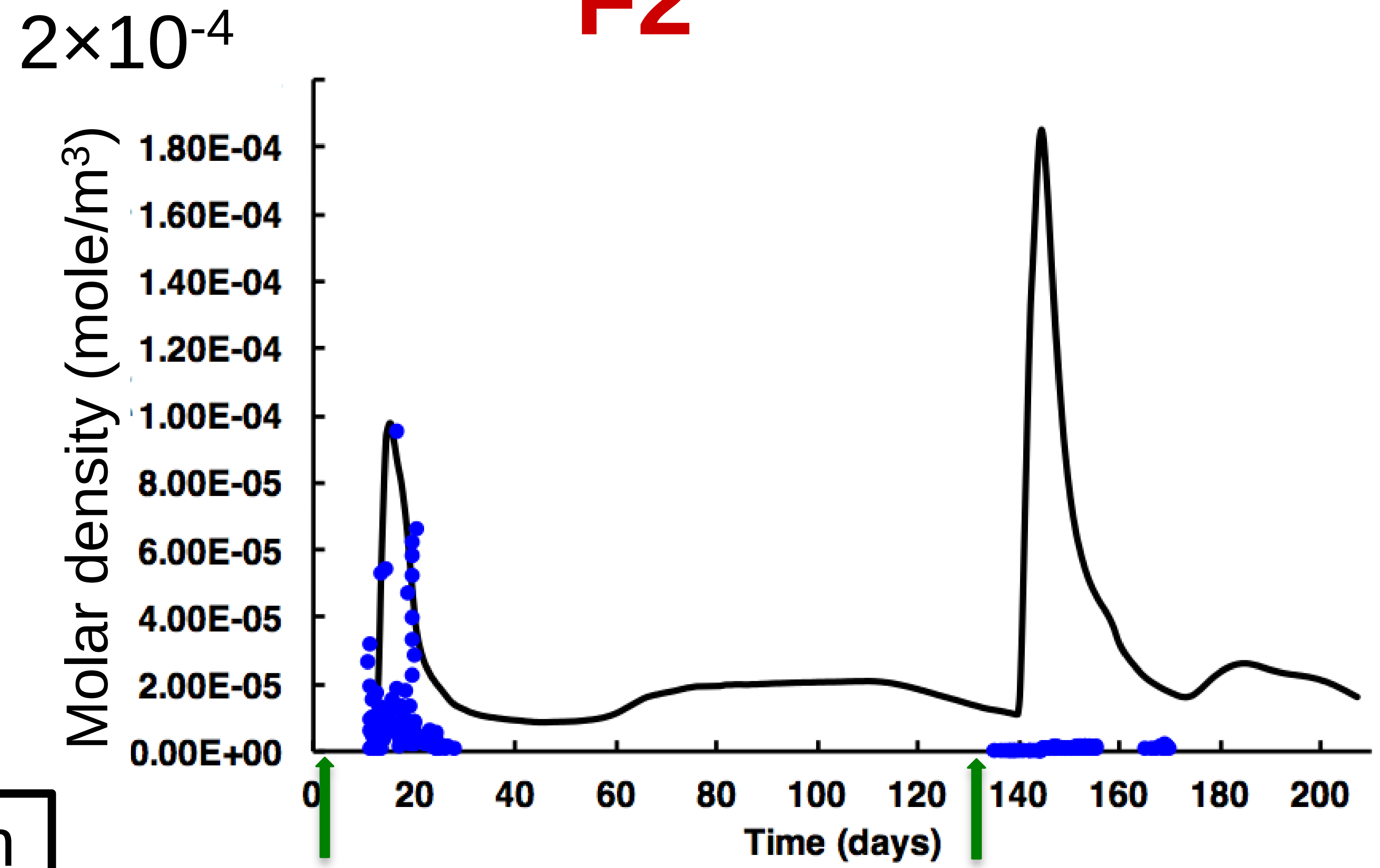


F3

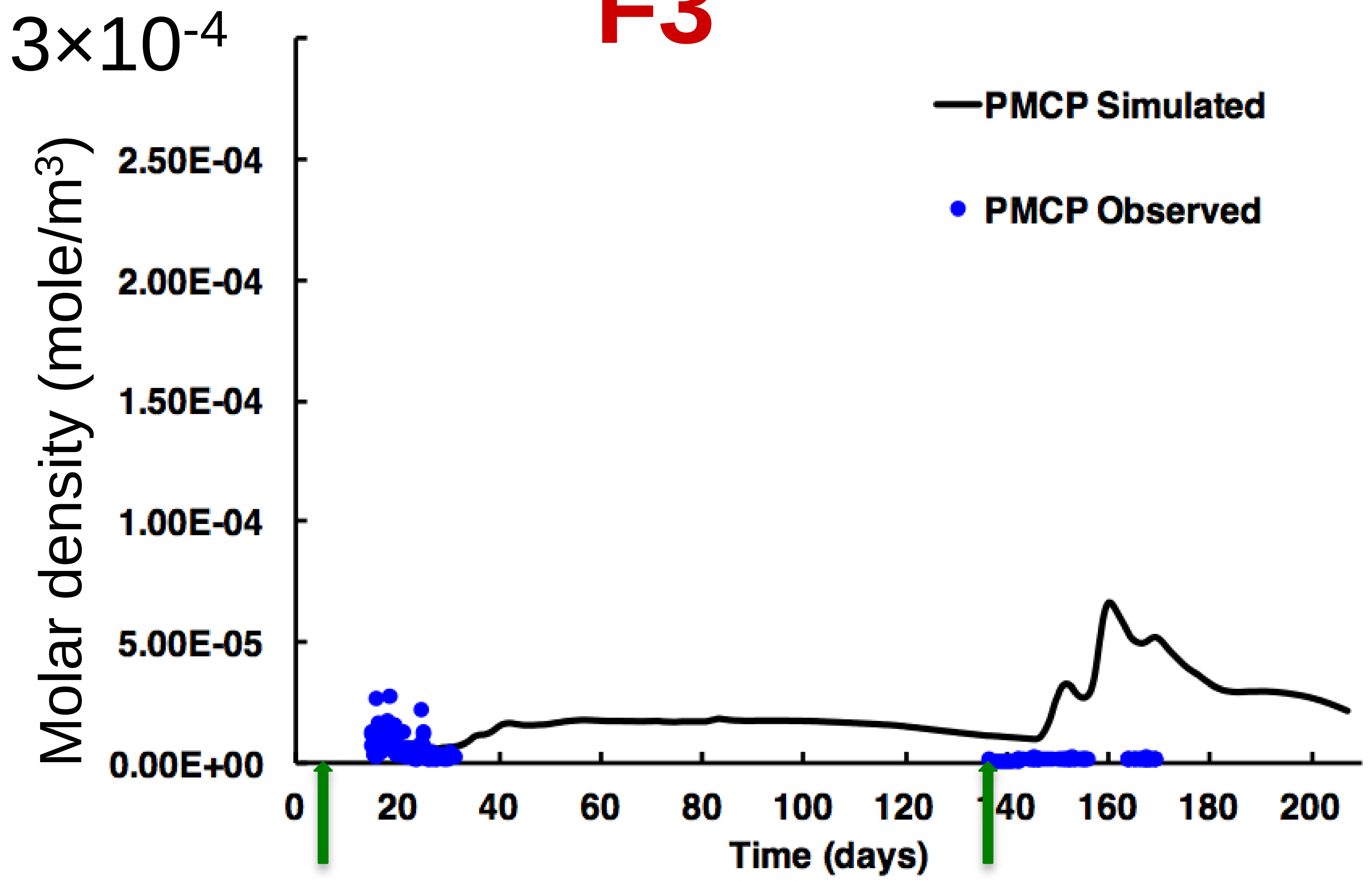


PMCP Tracer

F2



F3

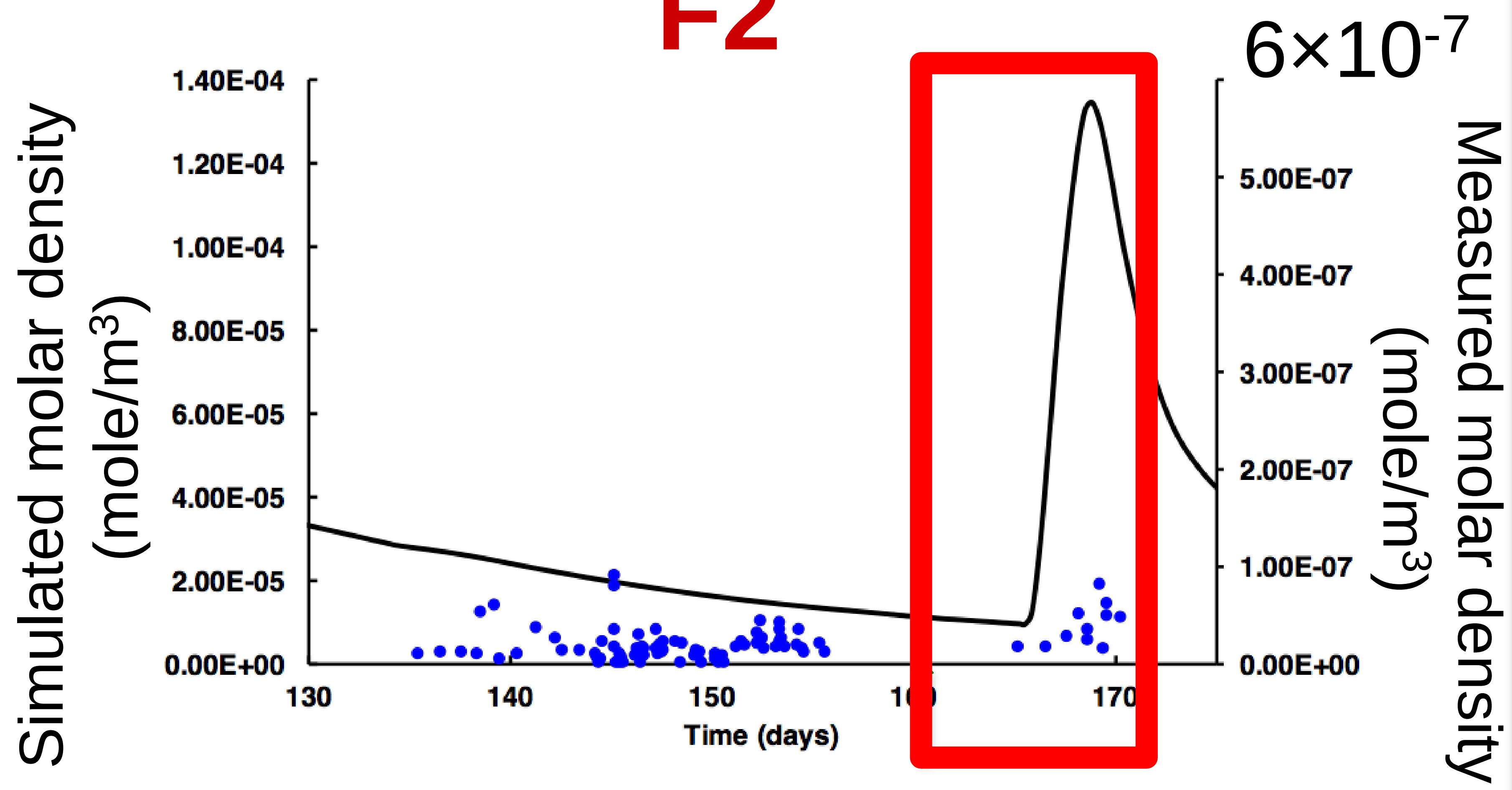


denotes injection

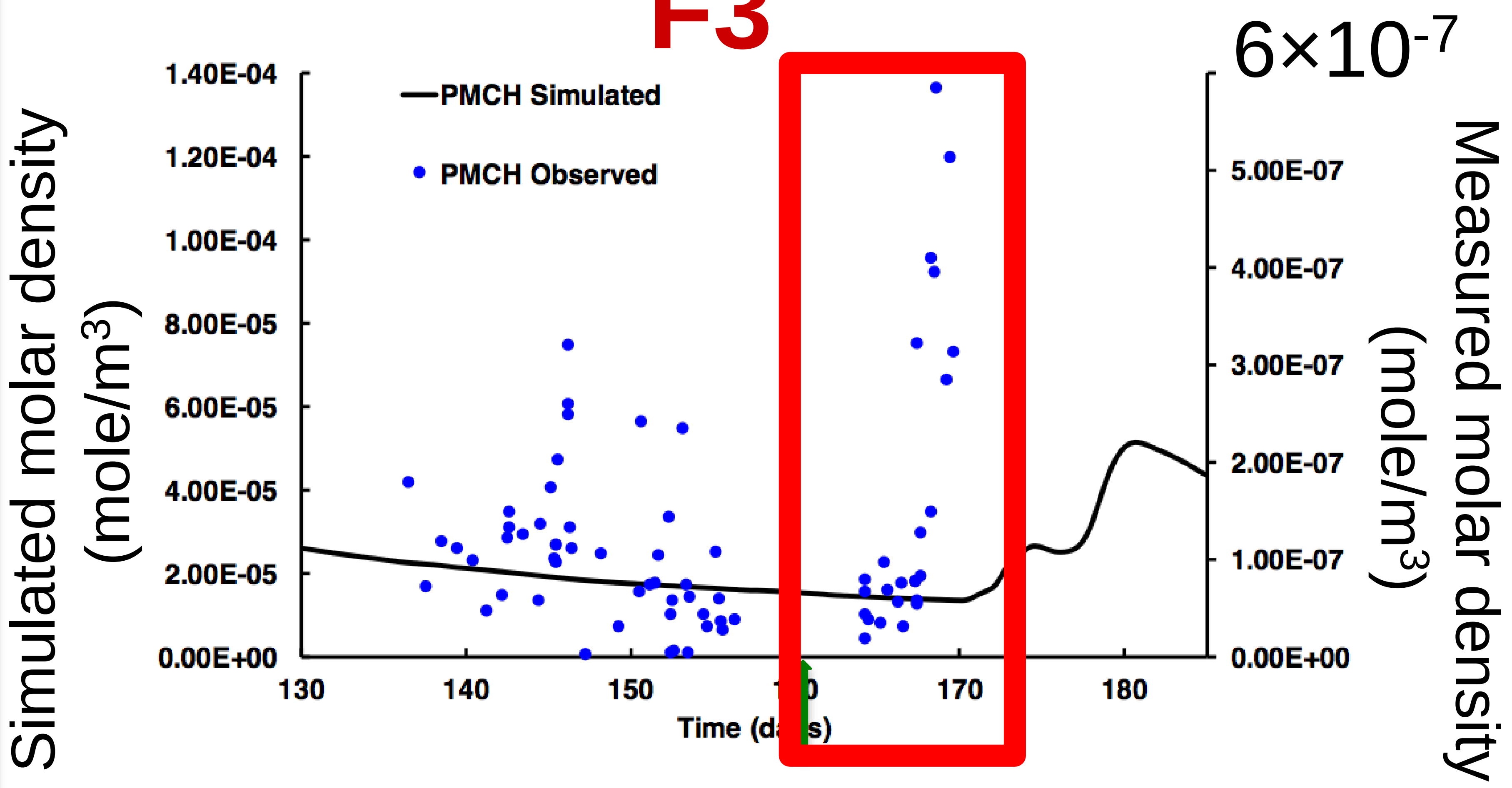
Only 2010 Campaign Breakthrough Curves

PMCH Tracer

F2

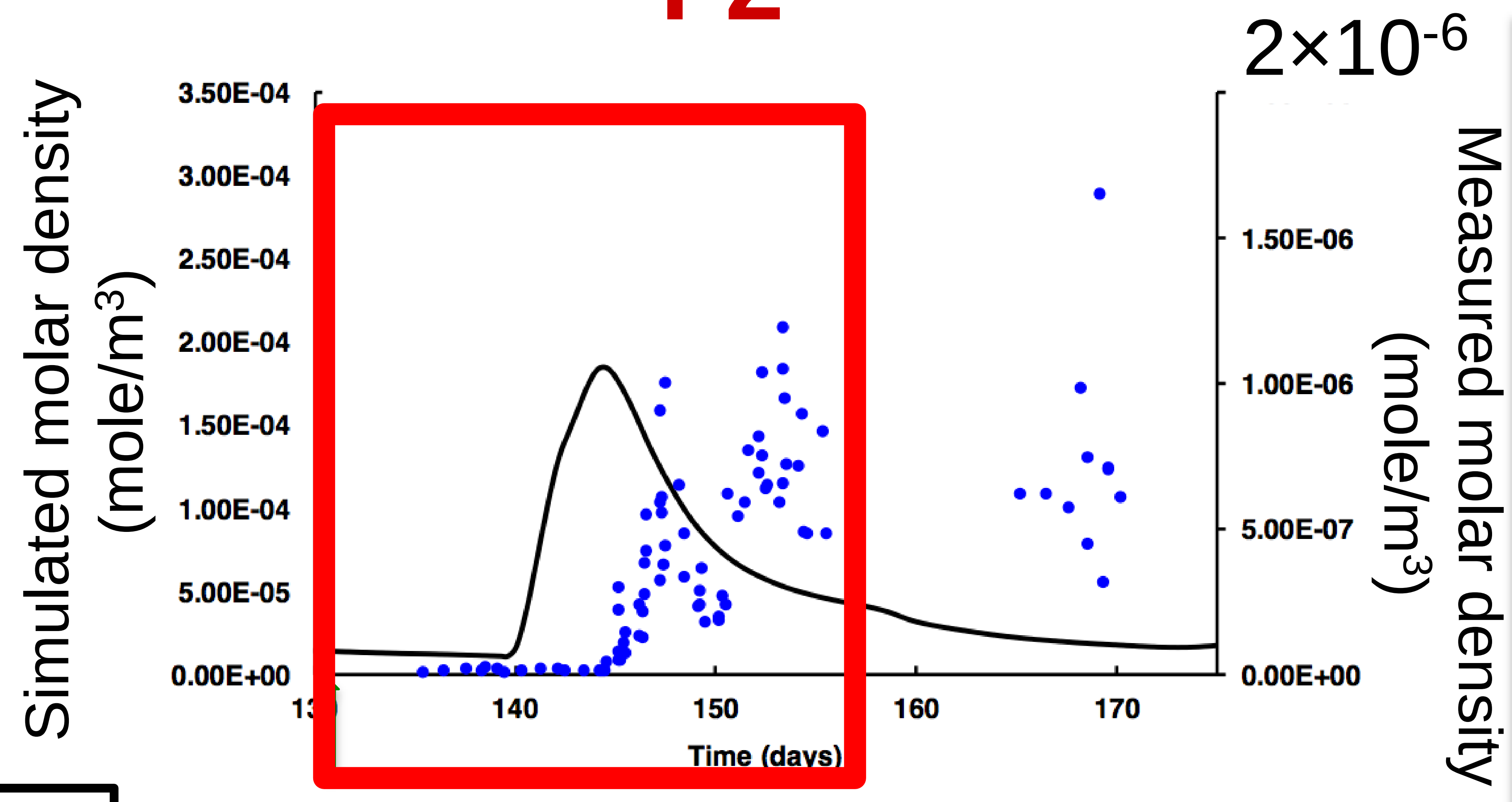


F3

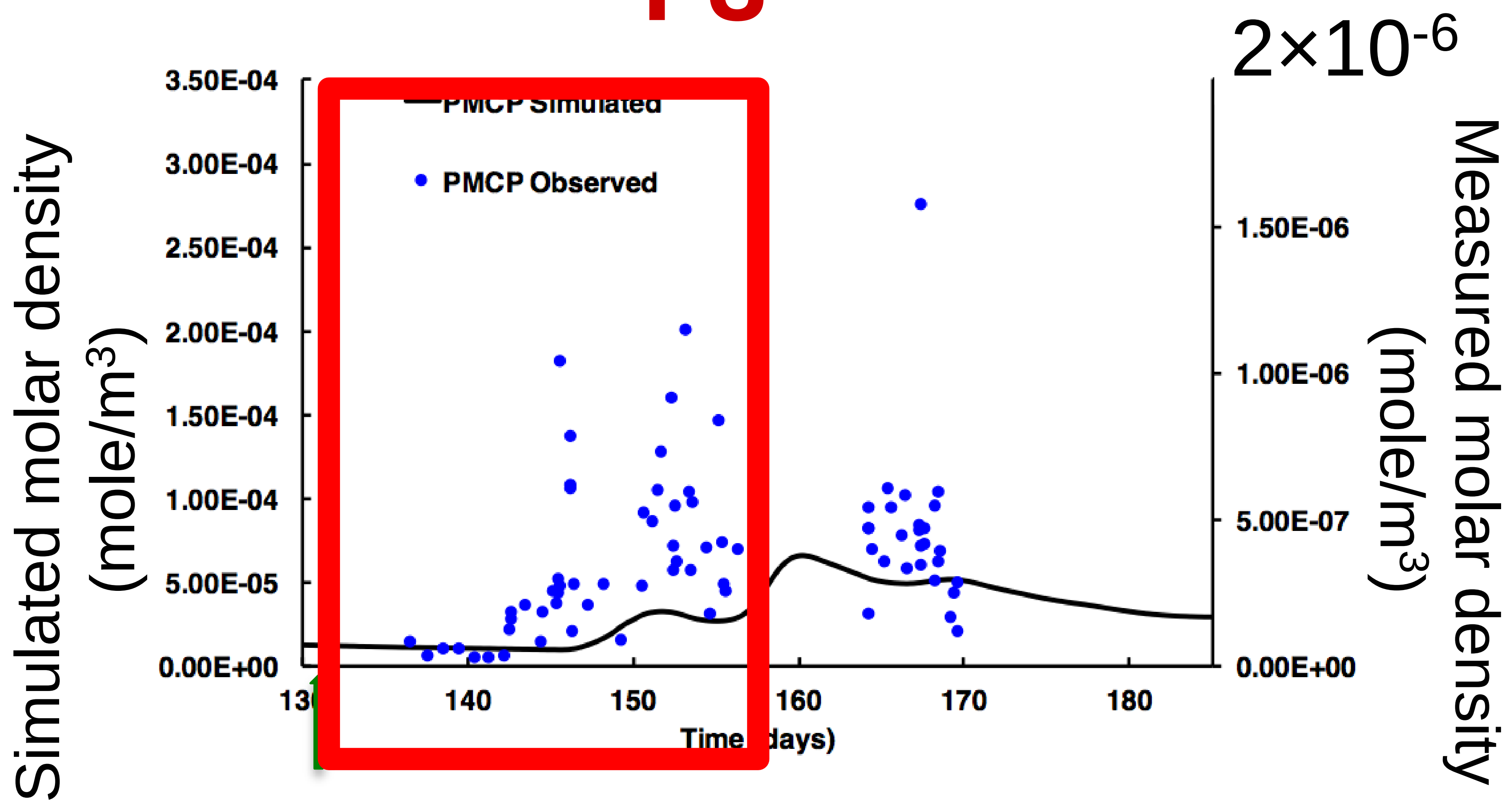


PMCP Tracer

F2



F3



Fracturing?

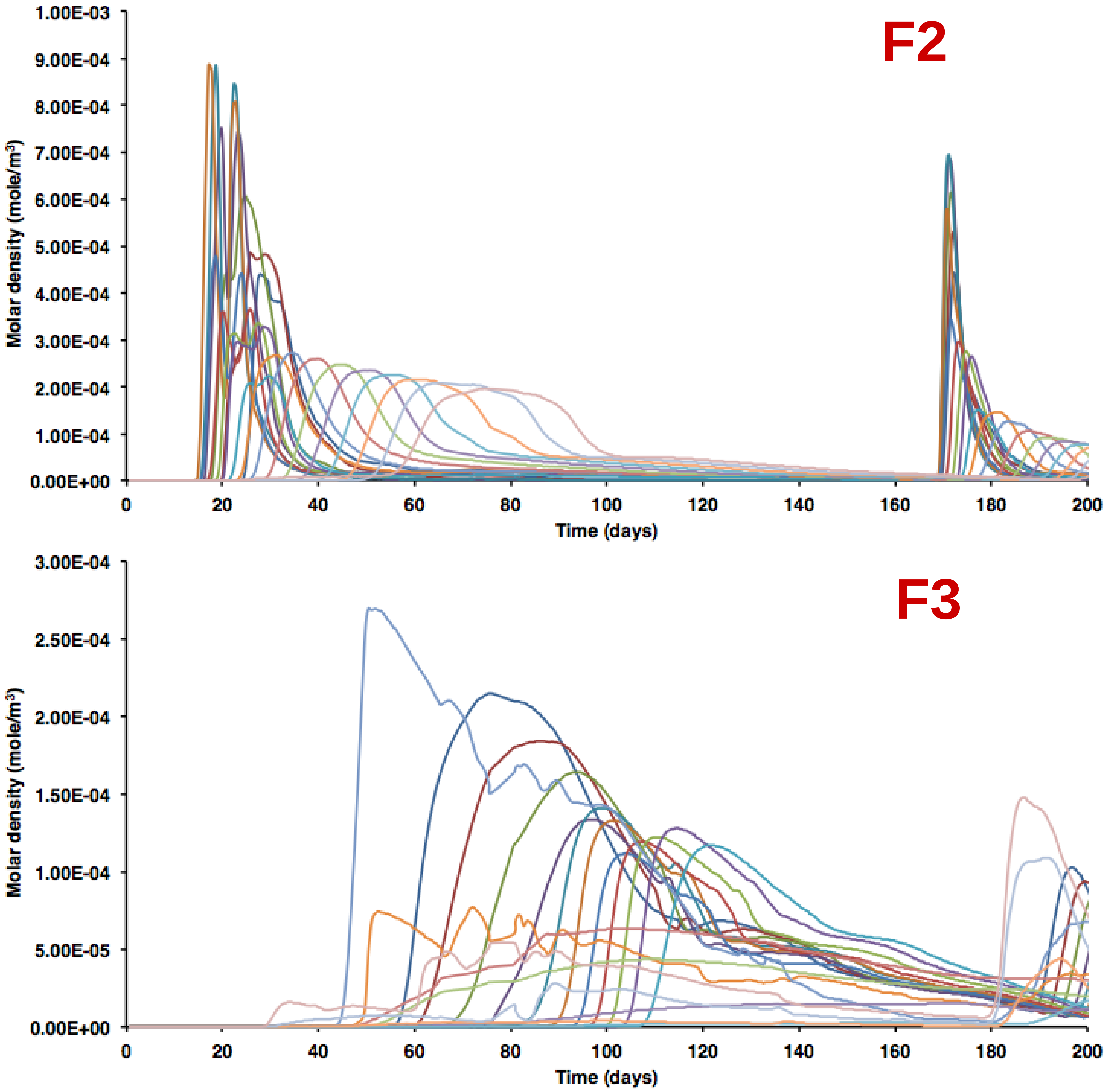
↑ denotes injection

Breakthrough Curves vs. Depth

20 grid cells throughout perforated intervals:

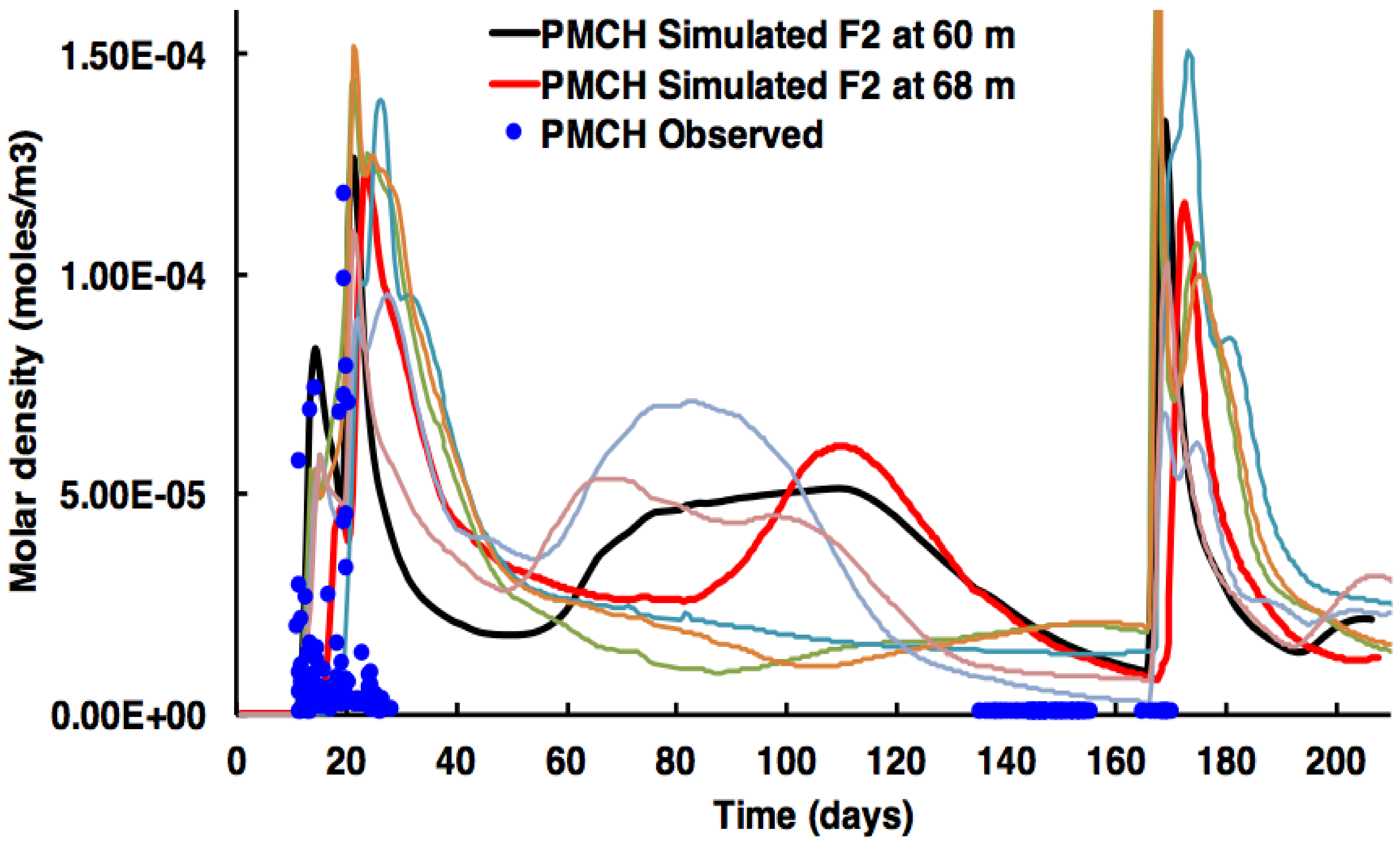
BTC/tailing highly variable with depth b/c of channelized permeability

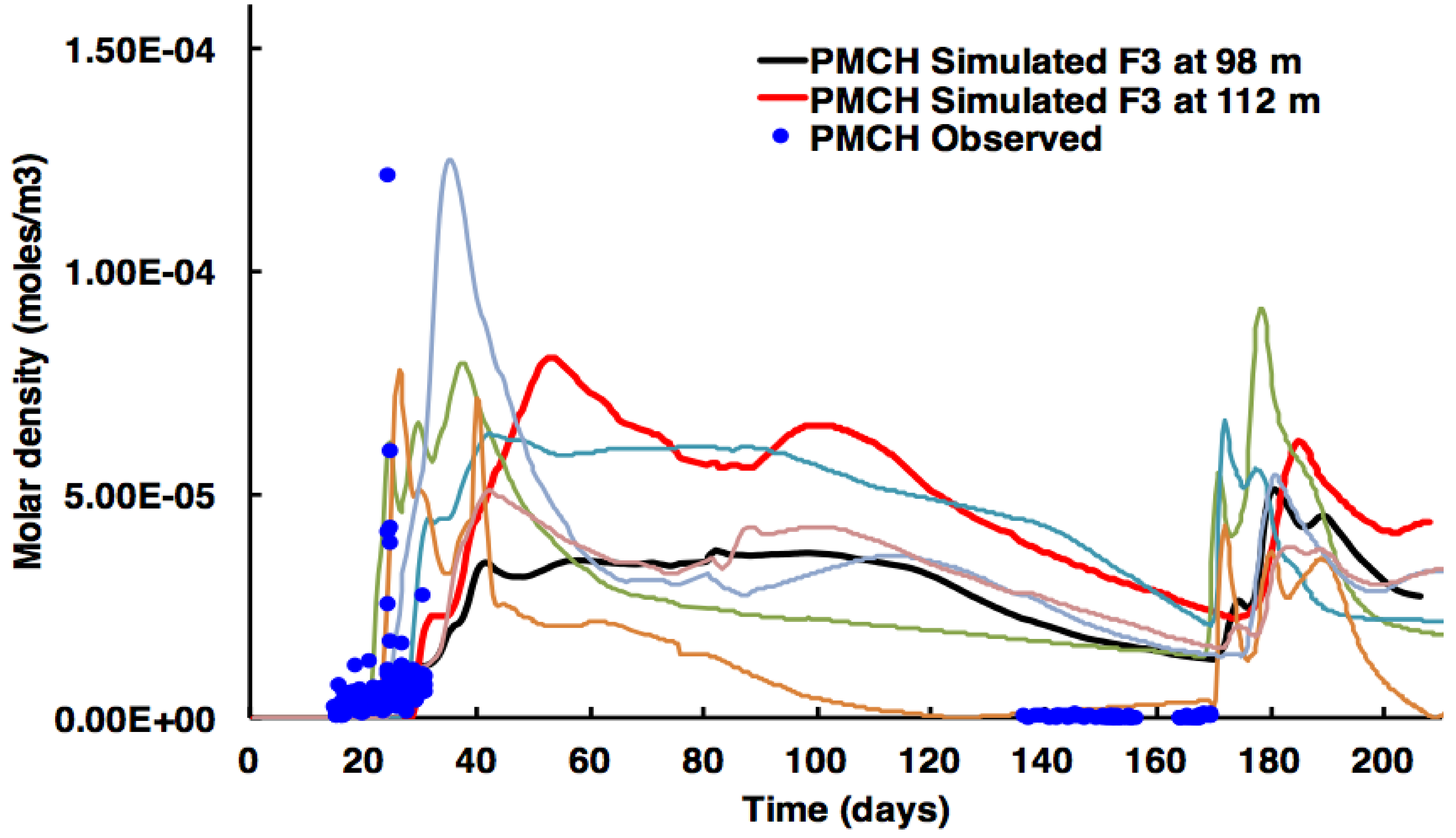
PMCH Tracer



Breakthrough Curves vs. Location of F2 and F3

- F2 and F3 placed at same distances from F1, but different lateral locations, i.e. in different fluvial channels
- Tailing/dilution highly variable
- **Heterogeneity critical** (also observed in Farnsworth Unit by Balch & McPherson's talk on Tuesday)





Conclusions

- 2016: Excellent match of pressure response and CO_2 breakthrough times
- Simulations match PFT field data remarkably well over short time-scales
- Larger discrepancy at later times due to the growing complexity of developing flow paths. Preliminary simulations could inform sampling times/duration.
- Tracer BTCs & simulations can constrain static reservoir properties (e.g., distribution of fluvial depositional features) and dynamic physical processes (e.g., advection, diffusion, viscous & gravitational fingering)
- Powerful tool to interrogate the subsurface *in-situ.* Complimentary to initial geophysical characterization, but also allowing *continuous* monitoring in time

Future Plans & Synergy

Modeling:

- Chemical trapping: Incorporate **water-rock reactions** in collaboration with **NETL**, validated through experimental facilities at NETL and field data.
- Solubility trapping: dissolution, mixing, spreading of injected CO_2.
- Capillary trapping: capillary snap-off and hysteresis trapping.
- Competitive dissolution/exsolution of CO_2 in methane saturated brine.

Evaluate effects of hydrocarbon-rich matrices on PFT capture and quantification in gas samples.

- Report on efficacy of sorbents to improve PFT capture and analysis. Coordination with **NETL** staff to compare methodologies and identify best practices for PFT analysis.

Synergistic opportunities not just in CSS, but also EOR, UOG, geothermal field development.

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2. Soltanian M.R., Amooie, M.A., Dai, Z., Cole, D., and Moortgat, J., *Critical Dynamics of Gravito-Convective Mixing in Geological Carbon Sequestration*. **Scientific Reports** (2016), **6**, 35921.
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Injected mass, injection schedule, observed, and simulated Breakthrough times

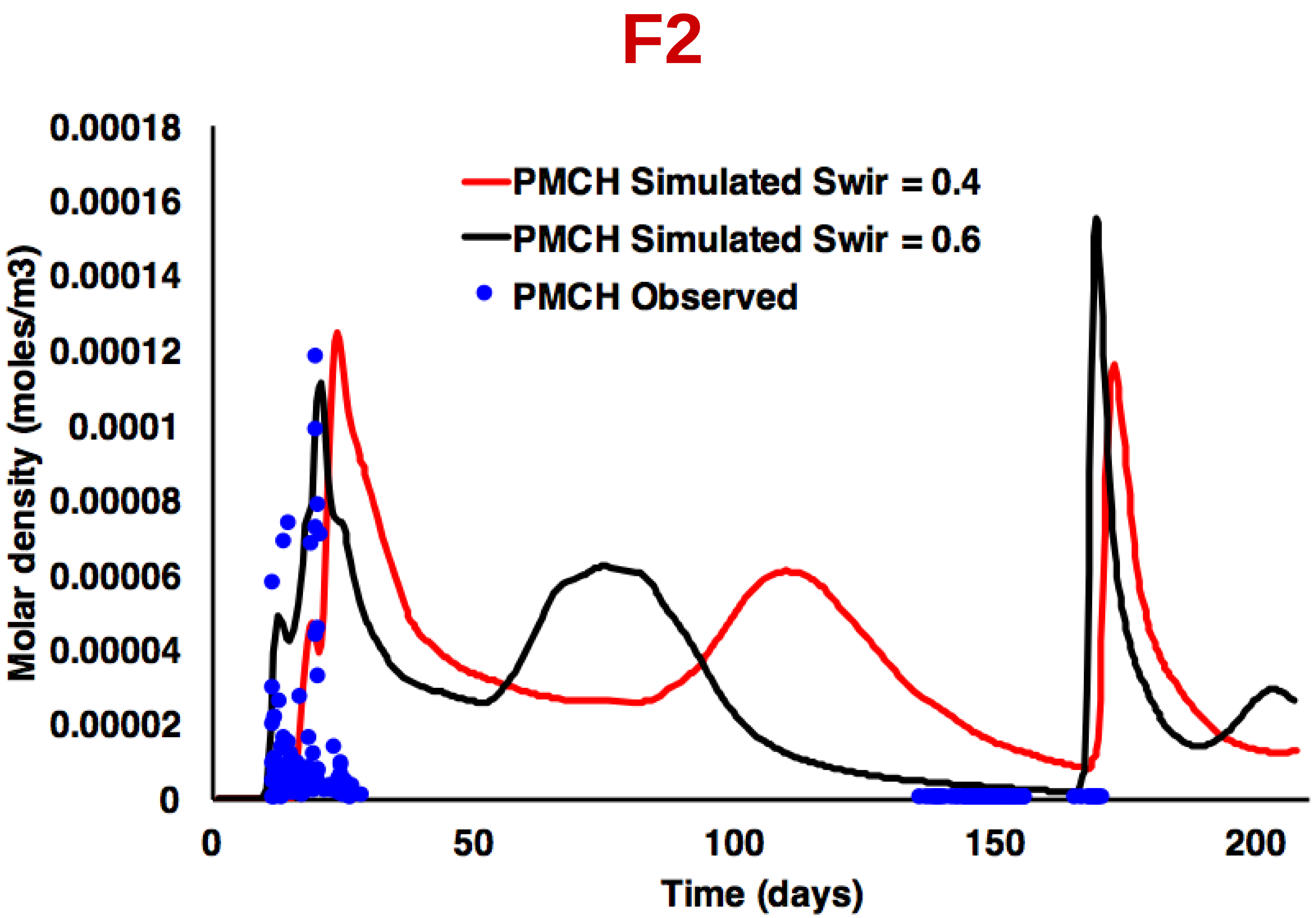
2009 campaign

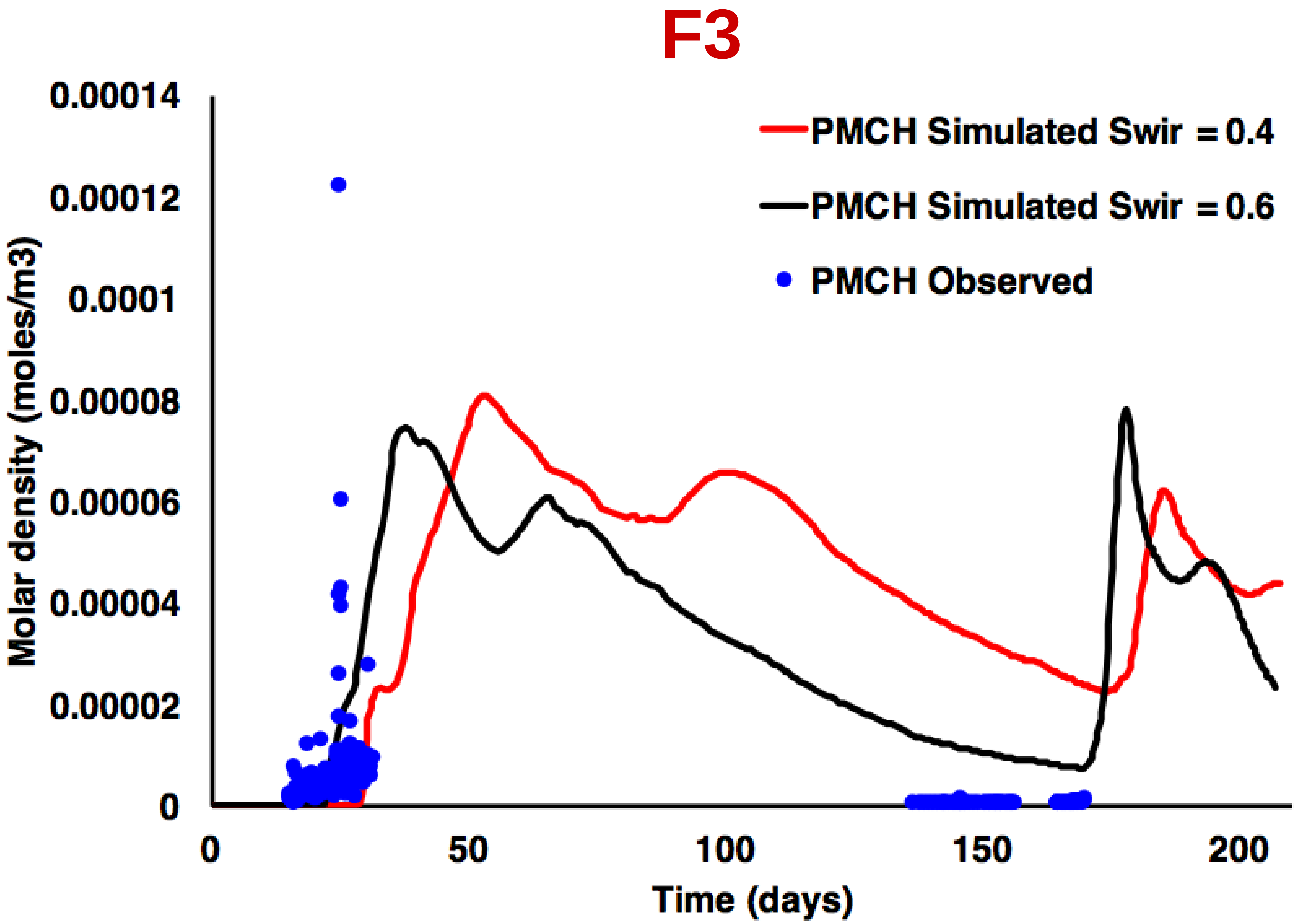
	Injected		Breakthrough time (days)			
			Observed		Simulated	
	Mass (kg)	Time (days)	F2	F3	F2	F3
CO_2		0	11	16	9-13	21-26
PMCP	0.6	3.125	13.7	15.6	11	23.2
PMCH	1.1	0	11.6	17.2	10	23.2
	0.6	11.2		23.7	-	31
PECH	0.6	1.3	11.4	15.6	10.2	23.2
	0.6	3.125		17.0	-	31.5
PTCH	1.1	0.25	11.1	16.5	10.4	23.5
	0.6	18.5		29.6	-	29
SF_6	40.4	2.5	12.0	14.8	10.8	23.2

2010 campaign

	Injected		Breakthrough time (days)			
			Observed		Simulated	
	Mass (kg)	Time (days)	F2	F3	F2	F3
PMCP	1.4	132.6	148.8	145.9	139.5	145.5
PMCH	1.0	161.5	-	168.5	165.5	170.5
PECH	1.3	132.7	146.3	145.5	139	144.5
	0.5	134.7	-	-	142	165.0
PTCH	1	161.5	-	168.5	165.5	170
SF_6	31.75	135	153.1	147.0	141	147

Residual Brine Saturation





Appendix

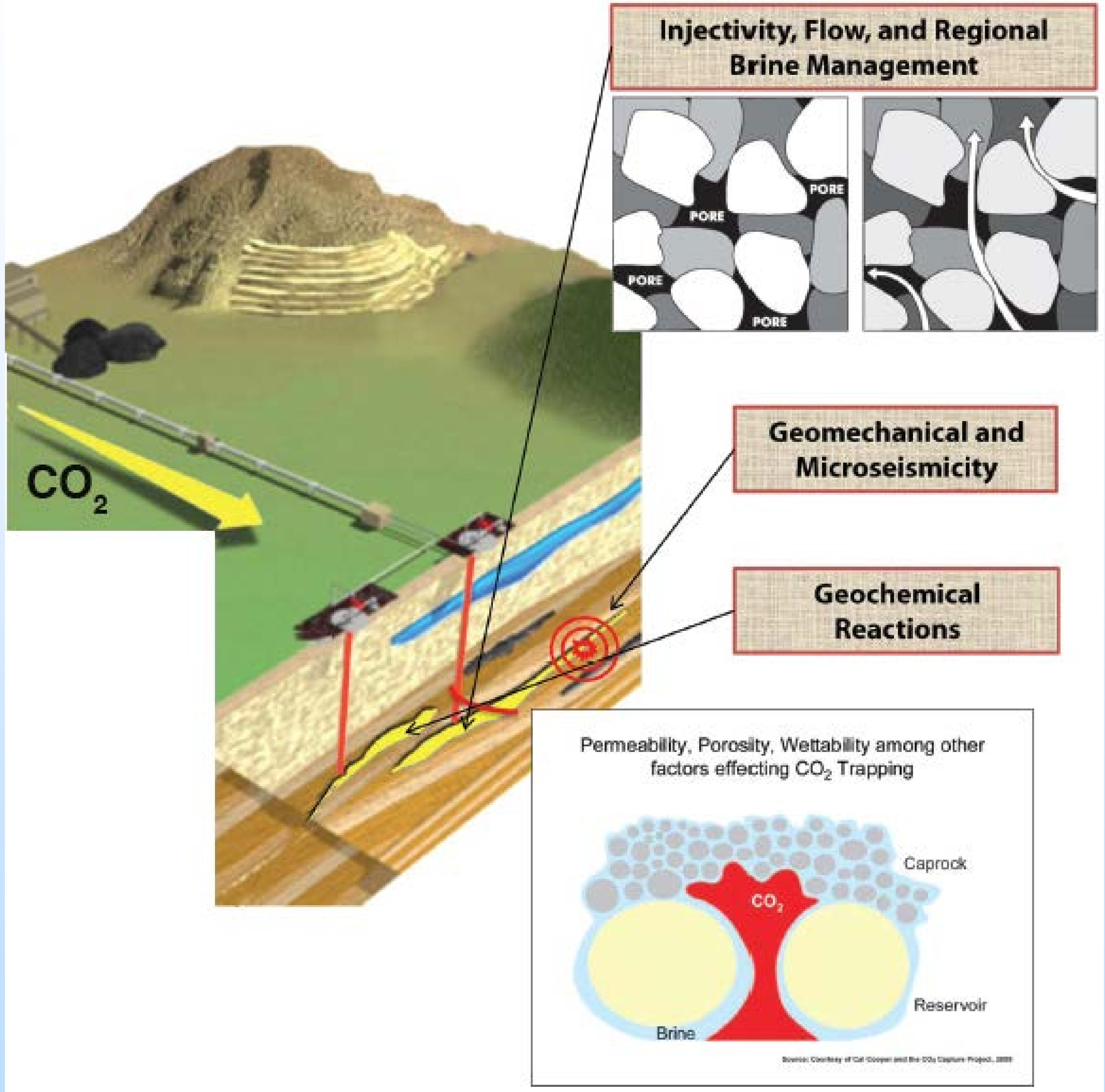
Benefit to Program

Use tracers to monitor & validate (99%) CO_2 **storage permanence**

New subsurface signal to monitor physical & chemical processes that can affect **storage efficiency:**

- Alter porosity & permeability, e.g., fracturing (SubTer)
- Control fluid flow, e.g., diffusion, mixing, advection, capillarity, and reaction

Couple tracers with reservoir modeling to predict storage capacity & effectiveness, aid future site selection & characterization.



Modified from NETL Carbon Storage GSRA Technology Research Areas Illustration

Project Overview

Develop complementary tracer methods to interrogate sub-surface for improved CO_2 storage efficiency & permanence

- Geochemical and PFT analysis from 5-year Cranfield, MS storage project
- Improved ultra-trace detection methods for PFT mixtures, improving sensitivity for leakage testing, and allowing large-scale field deployment
- Investigate potential effect of hydrocarbon matrix on PFT detection
- Integrate geochemical, isotope and PFT results into an advanced reservoir simulator for improved predictions
  - Step 1 (2016): Develop high-resolution petrophysical model & reproduce earlier simulations for pressure & CO_2
  - Step 2 (2017): Incorporate tracer data in simulations
  - Step 3 (2018): Incorporate reactions and study chemical, solubility, and capillary trapping.
- Transfer technology to storage project partners

Project Organization

U.S. DEPARTMENT OF ENERGY | NETL

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David Graham, PI

The University of Tennessee Knoxville

Tommy Phelps
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The Ohio State University

David Cole
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Collaborators:

RCSPs

National Energy Technology Laboratory

Bureau of Economic Geology — John A. and Katherine G. Jackson School of Geosciences

Berkeley Lab

USGS science for a changing world

Gantt Chart

Task	Milestone Description*	Fiscal Year 2017				Fiscal Year 2018			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.1	Preliminary simulation of perfluorocarbon and SF6 tracers	■	■						
3.2	Preliminary report on efficacy and operating parameters of GC systems for PFT analysis in hydrocarbon-rich matrices		■	■					
1.2, 1.3	Combined simulation of CO2 and tracer injection experiments, as well as methane evolution, for Cranfield DAS site			■	■				
1.5	Prioritization of reactive transport processes for simulation from discussions with NETL researchers				■	■			
3.1	Acquisition and installation of thermal desorption and cooled injection system hardware			■	■	■			
1.7	Universal dynamics of gravito-convective mixing of CO2 in 3D heterogeneous porous media and implications for geological carbon sequestration				■	■			
1.4	Initial incorporation of geochemical reactions and stable isotope tracers into the Osures reservoir simulator					■	■		
3.3	Report on efficacy of sorbents to improve PFT capture and analysis					■	■	■	
1.6	Detailed model of trapping mechanisms that guarantee the long-term permanence of injected CO2							■	■

Accomplishments and Benefits to Program

- Accomplishments
- **Assessing water-mineral-CO_2 interactions using geochemical modeling and isotopic signatures in baseline, during and post injection for multiple sites and campaigns.**
- **Determine behavior of perfluorocarbon tracer suites, breakthrough, development of reservoir storage over time at multiple sites.**
- **Delineate CO_2 fronts with PFT's, isotopes and on-line sensors (T, pH, Cond.).**
- **Established methods, proven successful, inexpensive, ongoing collaborations.**
- **Developed high-resolution Cranfield model to investigate CO_2 and tracer transport**
- ***Procedures for monitoring, verification and accounting (MVA) as tech transfer for larger sequestration demonstrations complementing other sites/partnerships.***
- **Established, successful, inexpensive, Technology Transfer collaborations.**
- **Publications: 17 journal/book articles, a dozen proceedings papers.**
- **Education: 4 Students and 2 postgraduates.**

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Lessons Learned

- Relative permeability parameters (e.g. S_{wir}) determined in lab for one (type of) core may not be applicable to all heterogeneous facies in reservoir, but critically affect predicted advective flow. Wettability/rel. perms. for multiple facies should be known.
- Continuously improving characterization of formation heterogeneity is paramount. Tracers can help:
  - Breakthrough curves (BTC) can be used in history matching.
  - BTCs vs. depth, if feasible, can improve characterization of layering.
- Complex channels can result in CO_2/tracers arriving in far observation wells before closer ones, as also observed in the Farnsworth Unit, SW-RPCS.
- Monitoring of BTCs should start early and continue long enough to measure tails. Simulations can help predict necessary sampling periods.
- Upscaled simulations predict much later breakthrough times than observed. Our fine grid simulations, though CPU expensive, accurately predict CO_2 and tracer BTCs.