Monitoring Geological CO_2 Sequestration Using Perfluorocarbon and Stable Isotope Tracers

Project FEAA-045

David E. Graham,[1*] Susan M. Pfiffner,[2] Tommy J. Phelps,[2] Yousif K. Kharaka,[3] James J. Thordsen,[3] and David R. Cole[4]

[1] Oak Ridge National Laboratory. [2] University of Tennessee Knoxville. [3]USGS, Menlo Park, CA. [4] The Ohio State University.

ABSTRACT

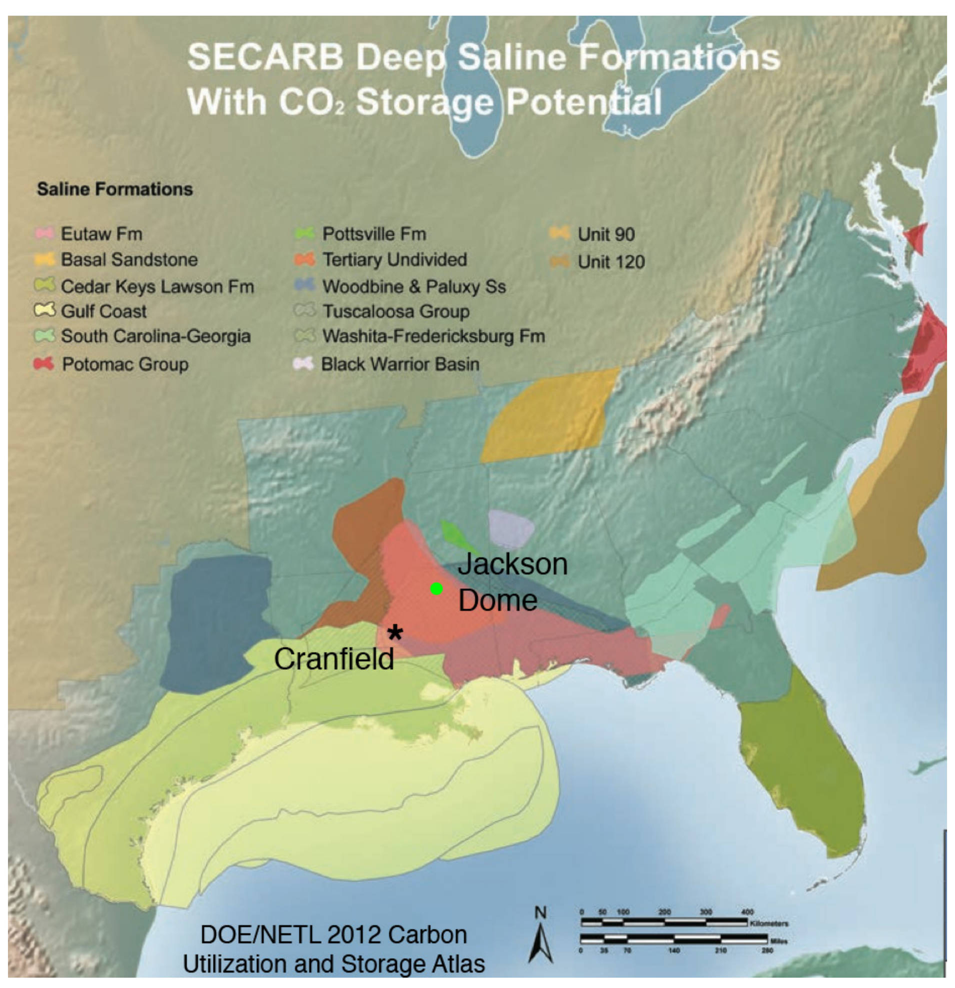
This project has developed and applied analytical methods to decipher the fate, breakthrough, transport, mixing and interactions of injected CO_2 with the brines and reservoir rock at the Frio, TX and Cranfield, MS sites of SECARB. We used a powerful combination of natural (isotopic) and introduced non-reactive tracers to decipher the fate and transport of CO_2 injected into the subsurface. Inert perfluorocarbon tracers (PFTs) measured at the ppt level by gas chromatography were complemented by gas chromatograph-isotope ratio mass spectroscopy analyses of the gas chemistry, including isotopic analyses of carbon, strontium, hydrogen and oxygen in the brine fluids. Samples from Cranfield monitoring wells obtained in campaigns from 2009 through 2015 enabled a comparison of baseline, injection and site-closing conditions. Results calibrate and validate predictive models used for (a) estimating breakthrough curves, CO_2 residence time, reservoir storage capacity, storage mechanisms, and transfer of injected carbon dioxide into nearby sedimentary units; (b) testing injection scenarios for process optimization, and (c) assessing potential leakage of CO_2 from the reservoir. Long-term monitoring techniques for stable isotopes and conservative tracers complement time-series geophysical measurements to provide an understanding of the behavior of injected CO_2. These results form a basis for developing new simulator modules in the future to improve the quantitative models of CO_2 plume activity in reservoirs for site management and Monitoring, Verification and Accounting (MVA). We are sharing best practices for PFT and geochemical analyses through technology transfer with university and regional partnership collaborators to facilitate method application and field-testing.

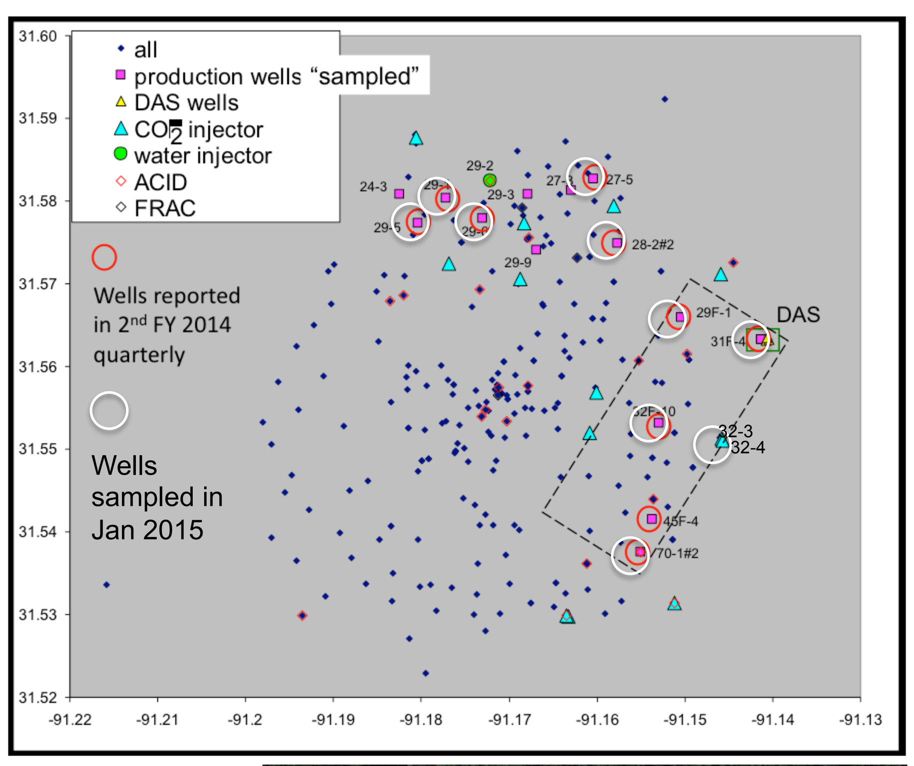
PROJECT GOAL & OBJECTIVES

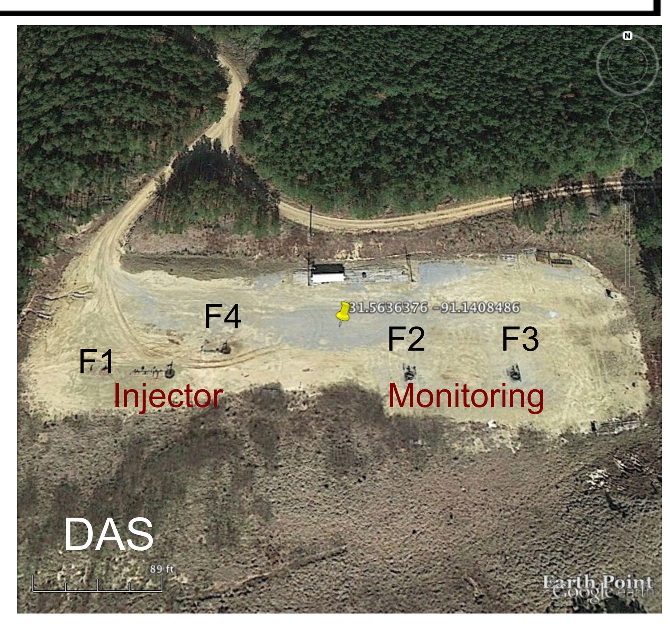
Develop complementary tracer methods to interrogate the subsurface for improved CO_2 storage efficiency and permanence.

- Completing geochemical and PFT analysis from 5-year Cranfield, Mississippi storage project (FY15)
- Transfering technology to storage project partners (Continuous)
- Improving ultra-trace detection methods for PFT mixtures (FY16-17)
- Integrating geochemical, isotope and PFT results into an advanced reservoir simulator for improved storage predictions (FY16-17)

CRANFIELD FIELD SITE







A map of well locations at the Cranfield, MS site indicates the latitude and longitude of those sampled for gas chemistry, gas isotopes, and brine oxygen, hydrogen and strontium isotopes highlighted by circles. Samples for PFT analysis were taken from wells in the DAS, at right.

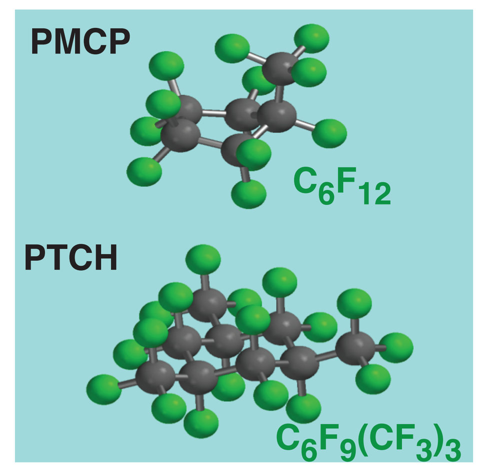
BENEFITS TO C STORAGE PROGRAM

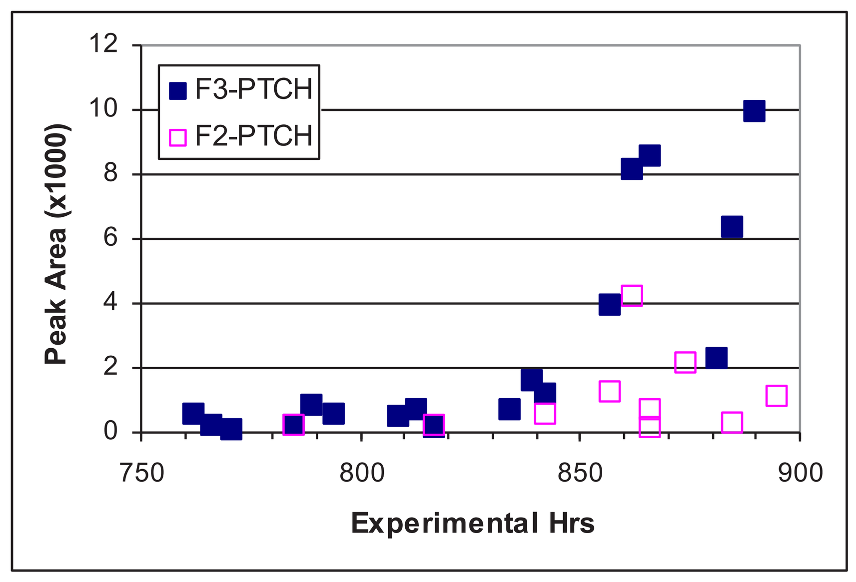
- Provide multi-scale information on physical and geochemical changes in the reservoir, ensuring CO_2 storage permanence
- Facilitate a fundamental understanding of processes impacting the behavior of fluids —diffusion, dispersion, mixing, advection, and reaction— to improve storage efficiency
- Ground-truth behavior of fluids and gases, CO_2 transport properties and CO_2 saturation that can be used to constrain reservoir simulations, predicting CO_2 storage capacity & designing efficient MVA programs

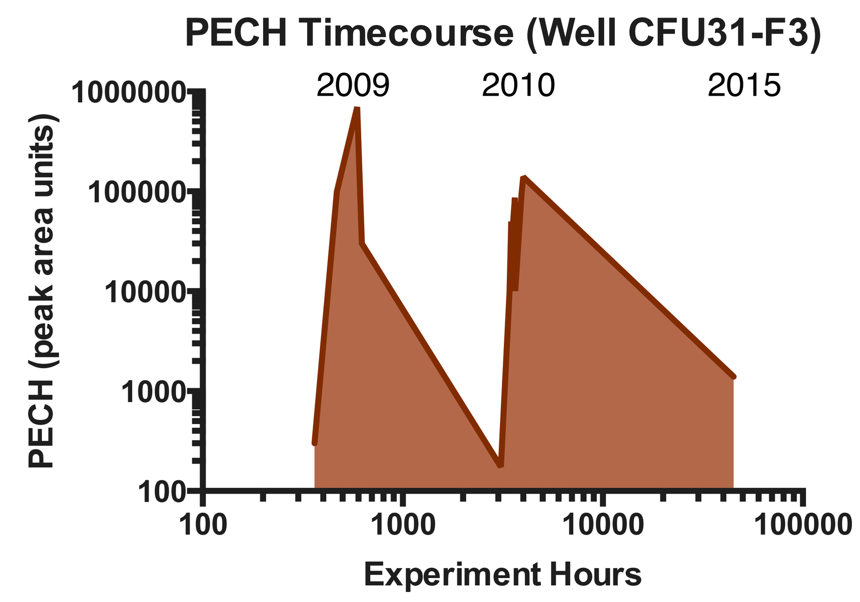
PERFLUOROCARBON TRACER RESULTS

Conservative perfluorocarbon tracers were introduced to decipher the fate, breakthrough, transport, mixing and interactions of injected supercritical CO_2 with the reservoir rock at Cranfield. The initial PFT breakthrough times at monitoring wells CFU 31-F2 and 31-F3 were little changed between Dec. 2009 and April 2010. However, the tracer breakthrough at the more distant F3 well ocurred before F2 following the second injection. Samples collected at the end of this 45,000-hr experiment contained significant levels of PECH at well F3, indicating a long tail of PFT migration through the reservoir system.

Using a suite of PFTs and SF_6 helps to identify breakthrough curves and resolve artifacts from repeated injections. Highly sensitive detection methods are essential.

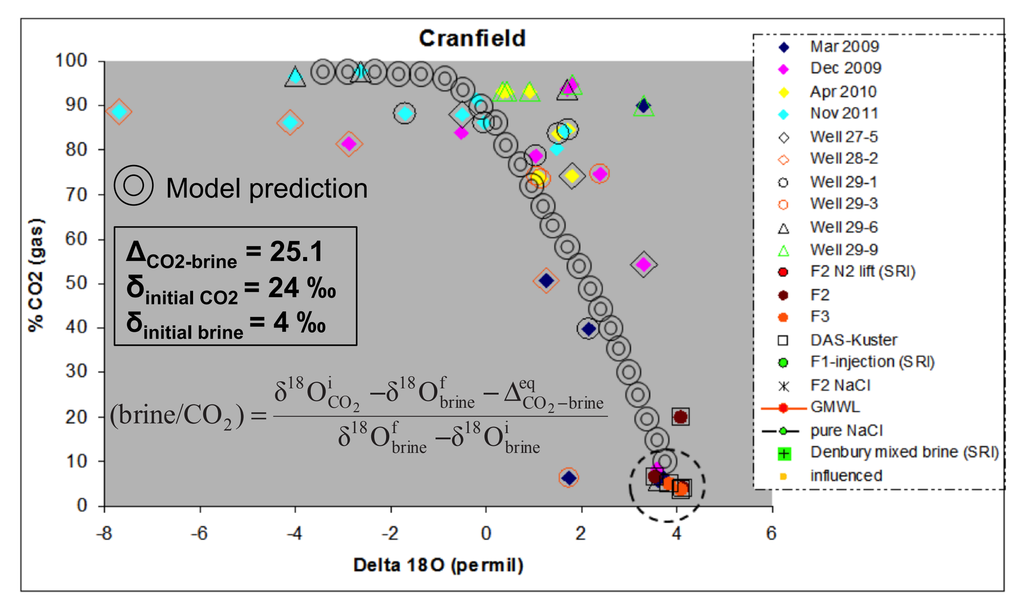






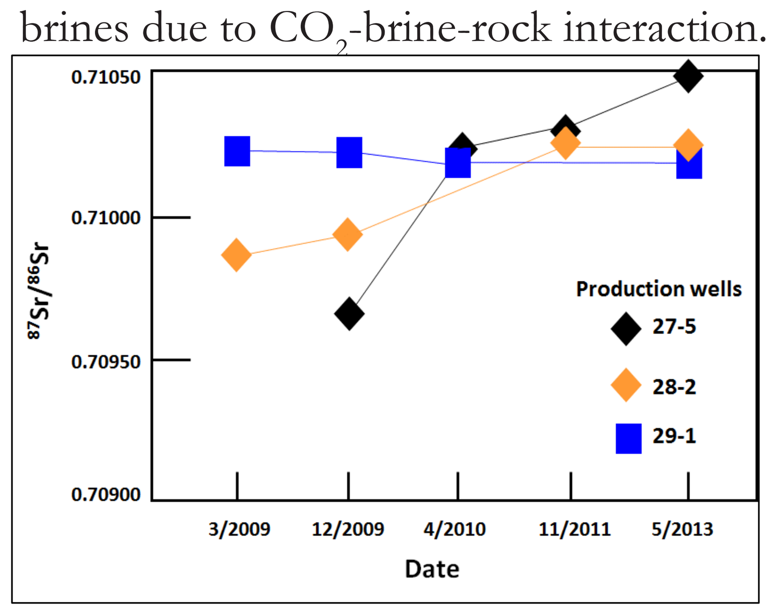
STABLE ISOTOPE RESULTS

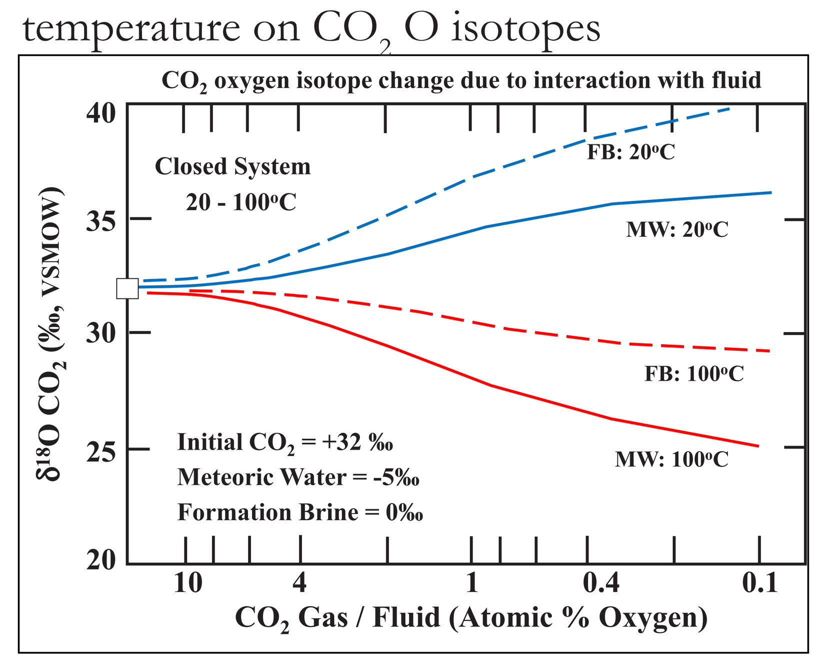
Oxygen and hydrogen isotopes were measured in brines from production wells and from the Brine Plant sampled in May of 2013. Typical O ($^{18}O/^{16}O$) and H (D/H) isotope values for this part of the Gulf Coast are 0±1 per mil and -24±3 per mil, respectively. Results show a depletion in ^{18}O, attributable to fractionation due to interaction with injected CO_2, which is consistent with modeled effects of brine O isotope composition and temperature on CO_2 isotopes.



Effect of brine O isotope composition and temperature on CO_2 O isotopes

^{87}Sr enrichment with time in Cranfield brines due to CO_2-brine-rock interaction.





SUMMARY

- Long-term experiments are essential to detect long tails of tracer injections and the evolution of flow paths in reservoirs.
- Sensitive tracer detection is critical —we plan to enhance sensitivity of current ultra-trace methods in FY16-17.
- Multiple suites of tracers are required for monitoring with repeated injections and interpreting subsurface flow.
- Increasing radiogenic Sr due to dissolution of sediment minerals (more $^{87}Sr/^{86}Sr$ measurements in progress)
- Mixing of CO_2 injectate and reservoir CO_2 revealed by carbon isotopes: ensure storage permanence, MVA
- Oxygen isotope shifts in CO_2 and brine yield estimates of CO_2/brine mass ratios complementary to RST
- Transferring technology to partners through collaboration & training
- Future interpretation of Cranfield tracer results in an advanced reservoir simulator

ACKNOWLEDGEMENTS

This project is supported by the U. S. Department of Energy's (DOE) Office of Fossil Energy funding to Oak Ridge National Laboratory under project FEAA-045. ORNL is managed by UT-Battelle for the U.S. DOE under Contract DE-AC05-00OR22725.

PI: David Graham (grahamde@ornl.gov)
FPM: Erik Albenze (Erik.Albenze@netl.doe.gov)

Oak Ridge National Laboratory · The Ohio State University · The University of Tennessee · U.S. Department of Energy