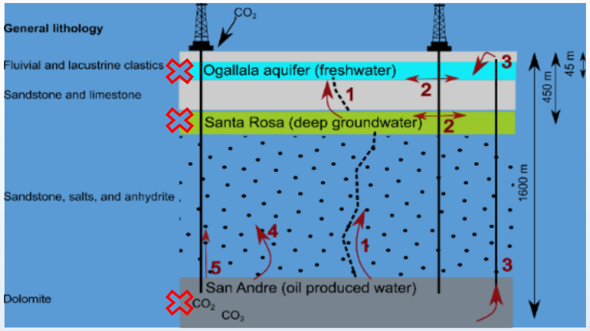
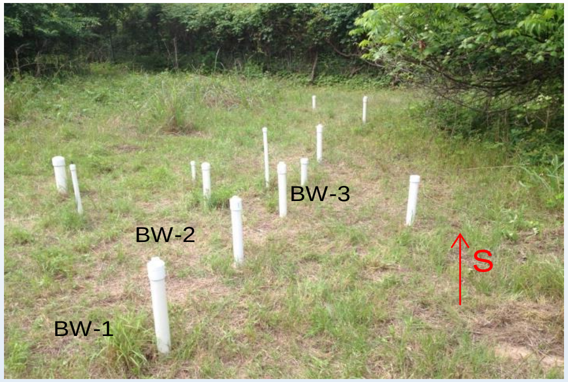
MVA Field Activities



Hank Edenborn

NETL - RIC



U.S. Department of Energy
National Energy Technology Laboratory
Mastering the Subsurface Through Technology, Innovation and Collaboration:
Carbon Storage and Oil and Natural Gas Technologies Review Meeting
August 16-18, 2016

NETL Research Presentations and Posters

WEDNESDAY, AUGUST 17, 2016

- 12:30 PM MVA Field Activities – Hank Edenborn
- 2:35 PM Resource Assessment – Angela Goodman
- **2:35 PM Understanding Impacts to Air Quality from Unconventional Natural Gas – Natalie Pekney**
- **4:05 PM Improving Science-Base for Wellbore Integrity, Barrier Interface Performance – Nik Huerta**
- **5:20 PM Wellbore Integrity and Mitigation – Barbara Kutchko**

THURSDAY, AUGUST 18, 2016

- **1:00 PM Advances in Data Discovery, Mining, & Integration for Energy (EDX) – Kelly Rose**
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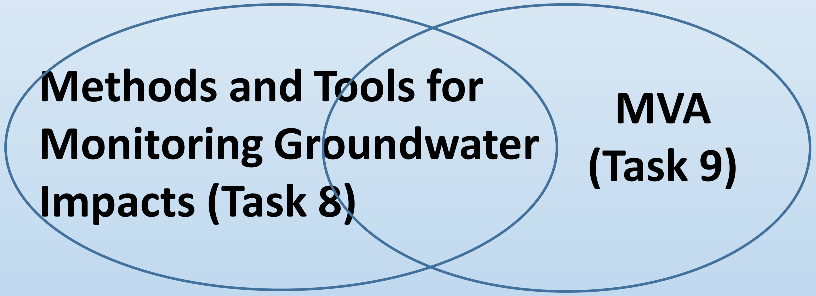
https://edx.netl.doe.gov/carbonstorage/
https://edx.netl.doe.gov/offshore/
https://edx.netl.doe.gov/ucr/

Monitoring, Verification and Accounting - MVA (Task 9): Field verification of tools and techniques to monitor leakage to groundwater

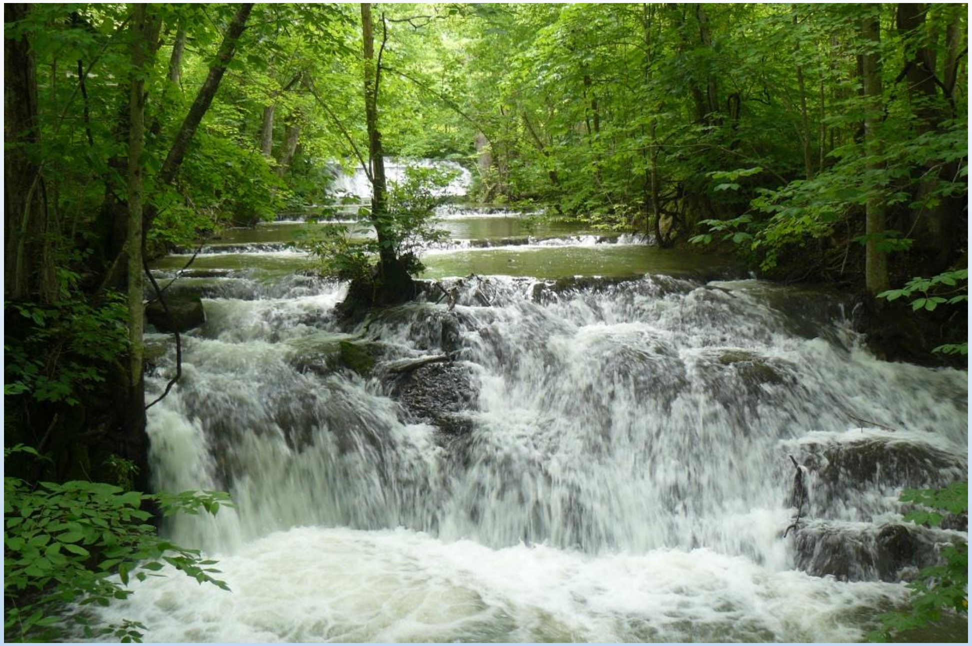
FY 2016 Team

- J. Rodney Diehl, NETL-RIC
- Hank Edenborn, NETL-RIC
- Djuna Gulliver, NETL-RIC
- Ale Hakala, NETL-RIC
- Christina Lopano, NETL-RIC
- James Gardiner, ORISE-NETL
- Thai Phan, ORISE-NETL
- Sean Sanguinito, ORISE-NETL
- Mengling Stuckman, ORISE-NETL
- Brian Stewart, U.Pitt, ORISE
- Shikha Sharma, WVU, ORISE
- Jinesh Jain, AECOM - NETL
- R. Burt Thomas, AECOM - NETL

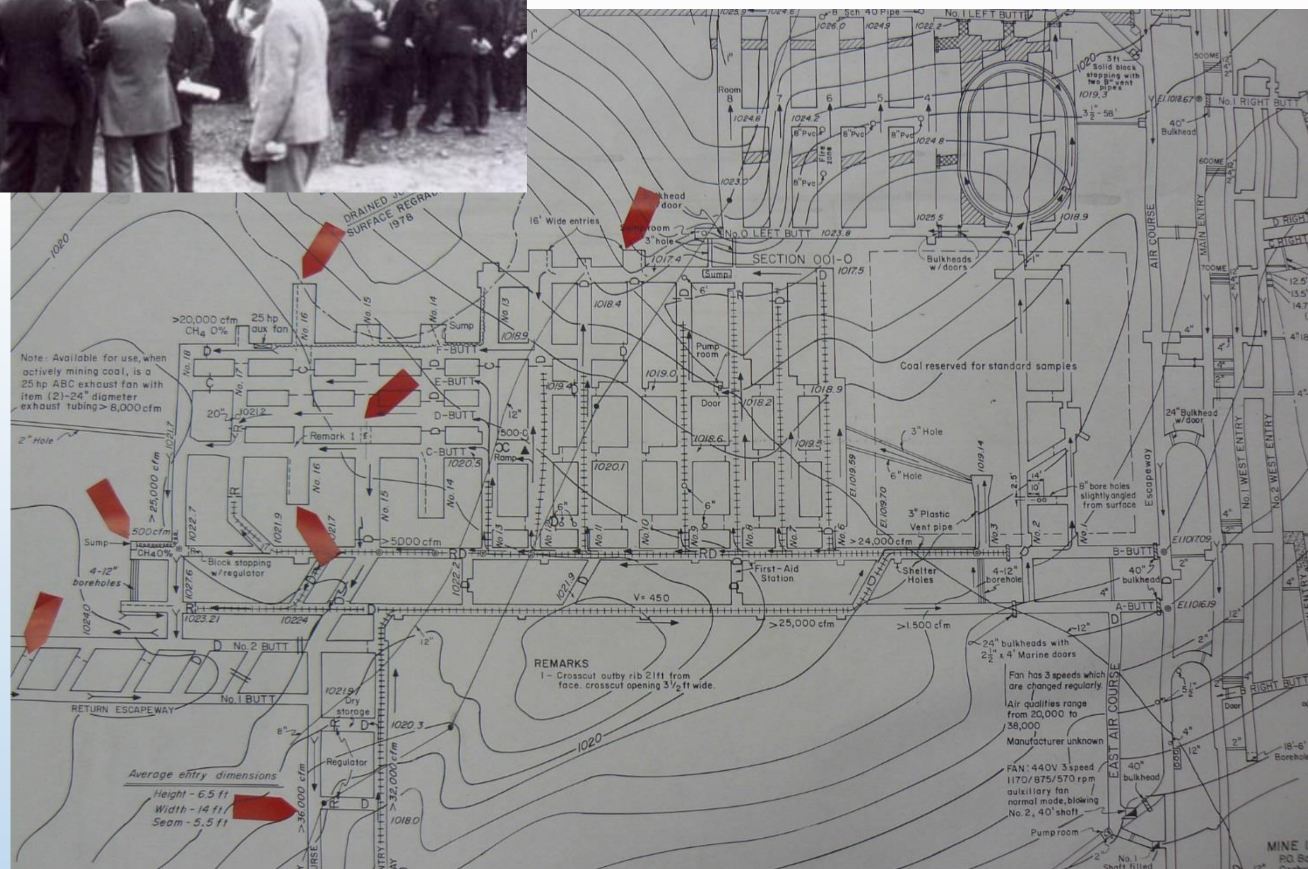


Technical approach employs a multidisciplinary team (chemists, geologists, microbiologists, materials engineers) to develop and demonstrate novel tools and techniques for MVA





U.S. Bureau of Mines Experimental Mine



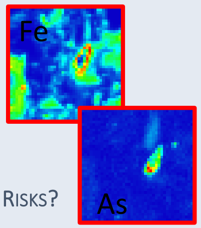
Benefit to the Program

- Program Goals:
  - Validate/ensure 99% storage permanence.
  - Develop best practice manuals for monitoring, verification, accounting, and assessment; site screening, selection and initial characterization…
- Project benefits:
  - *There is a need to be able to quantify leakage of CO_2 to the near surface and identify potential groundwater impacts. This project works to develop a suite of complementary monitoring techniques to identify leakage of CO_2 or brine to USDW's and to quantify impact.*

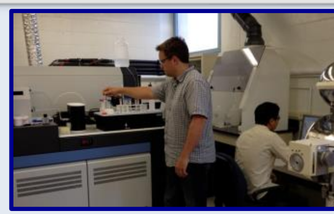
Monitoring Groundwater Impacts

Project Overview: Goals and Objectives

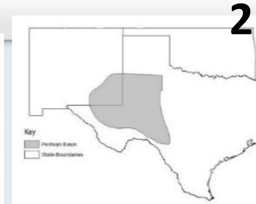
1 Understand natural Background variability



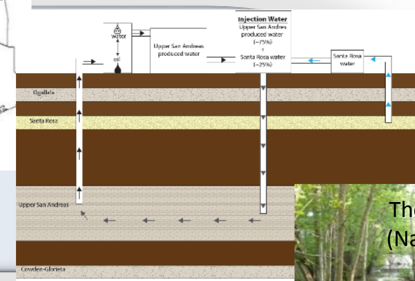
Risks?



Methods – complex waters



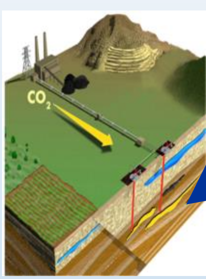
2 Establish the utility of isotopes to track migration of a CO_2 plume



Thermal springs (Natural Analog)

EOR Field Site

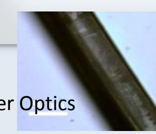
Demonstrate a suite of geochemically-based monitoring strategies for groundwater systems, and develop a statistical understanding of natural groundwater variability in CO_2 storage systems.



Migration into Shallow Aquifers

Migration into other Deep Formations

Validate/ensure 99% storage permanence



Fiber Optics

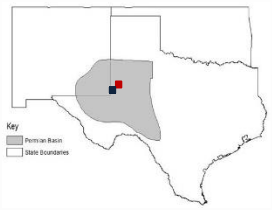
Continuous CO_2 Monitoring Devices

LIBS

3 Test and validate the use of CO_2 monitoring devices under field conditions

Groundwater Monitoring:
Enhanced Oil Recovery sites in Texas

Study sites: Seminole and Emma (Texas, USA)



Two sites are within 40 km in proximity

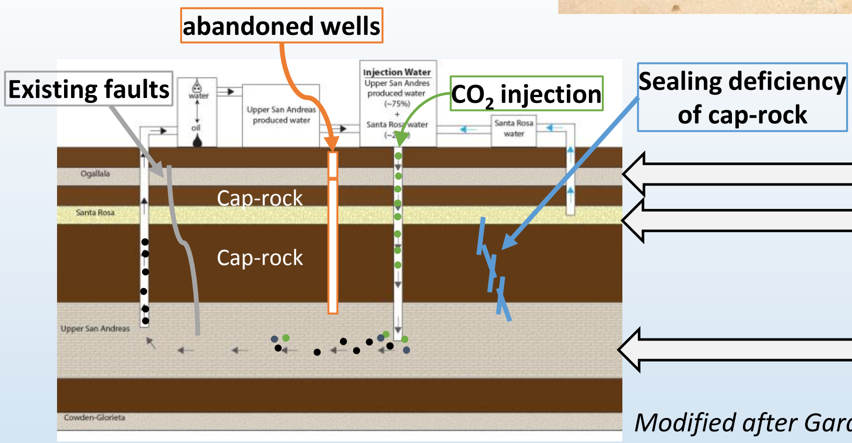
Pre- and post-CO_2 injection water samples analyzed for:

- Cation and anion concentrations
- Stable isotopes (C, H, and O) (including injected CO_2 gas)
- Metal isotopes (Li, Sr, and B)

To investigate:

- Potential CO_2 and brine migration to shallow groundwater aquifer
- Sub-surface water-CO_2-rock interactions

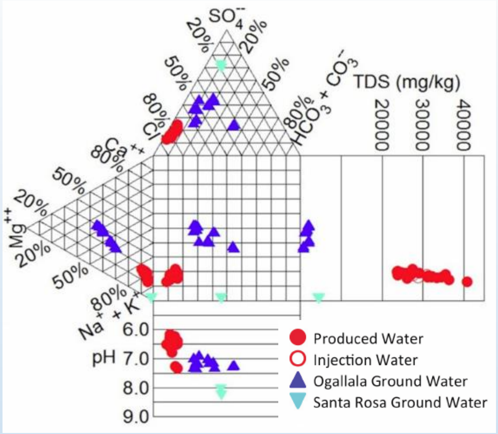
CO_2/Brine leakage scenarios:



Modified after Gardiner, 2014

San Andres produced water:

- Na-Cl type
- TDS: 24,400 to 42,200 mg/kg
- pH: circumneutral (6.2-7.4)



Pre-CO_2 injection

Analyze water samples from three stratigraphic formations including **Ogallala (shallow)**, **Santa Rosa (intermediate)**, and **San Andres (deep formation water)** collected prior to and after CO_2 break-through

Seminole Sampling Trip May 2016

East Seminole Oil Field

·Active CO_2 injection

·16 Wells Sampled

·Producing fm., deep groundwater, shallow groundwater

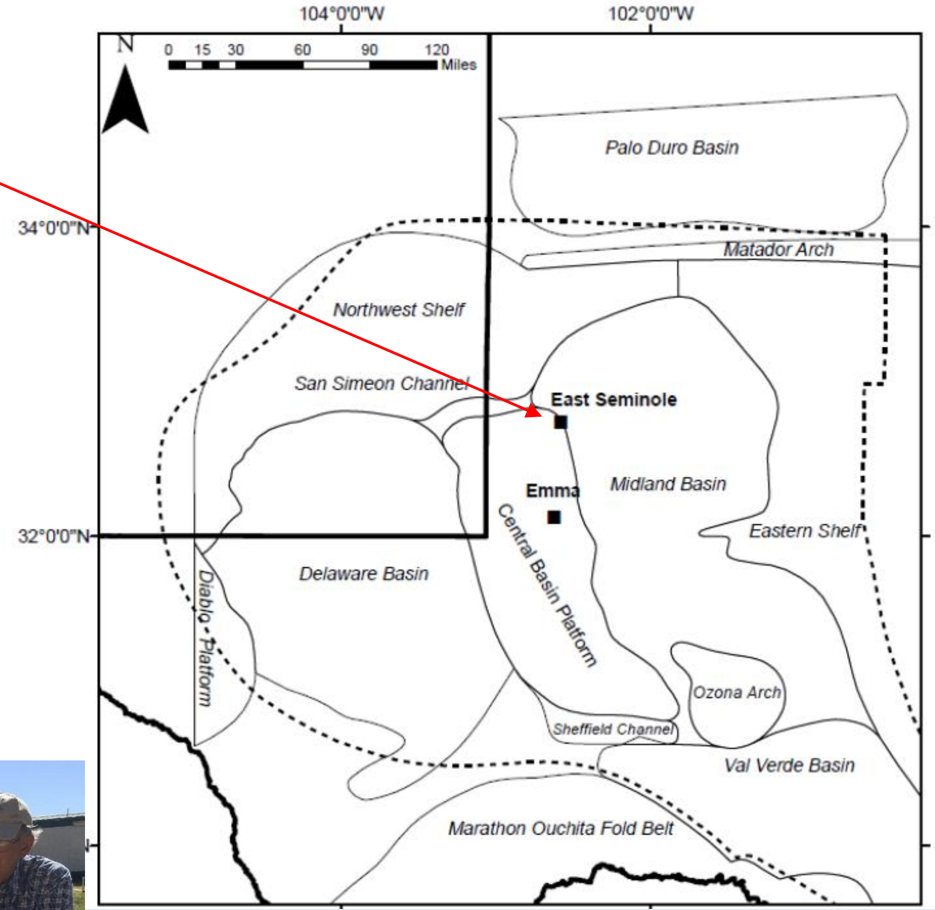
Well Blowout at East Seminole Site

·Occurred on December 7, 2015

·Packer failure followed by wellhead failure

→Failure between casing + tubing

·Lost an estimated 1.8 billion cubic ft of CO_2



Left: Thai Phan and Burt Thomas filtering produced waters at East Seminole; Above: Rodney Diehl measuring field parameters of Ogallala fresh water near East Seminole

Field Sampling Team
Rodney Diehl
James Gardiner
Thai Phan
Burt Thomas

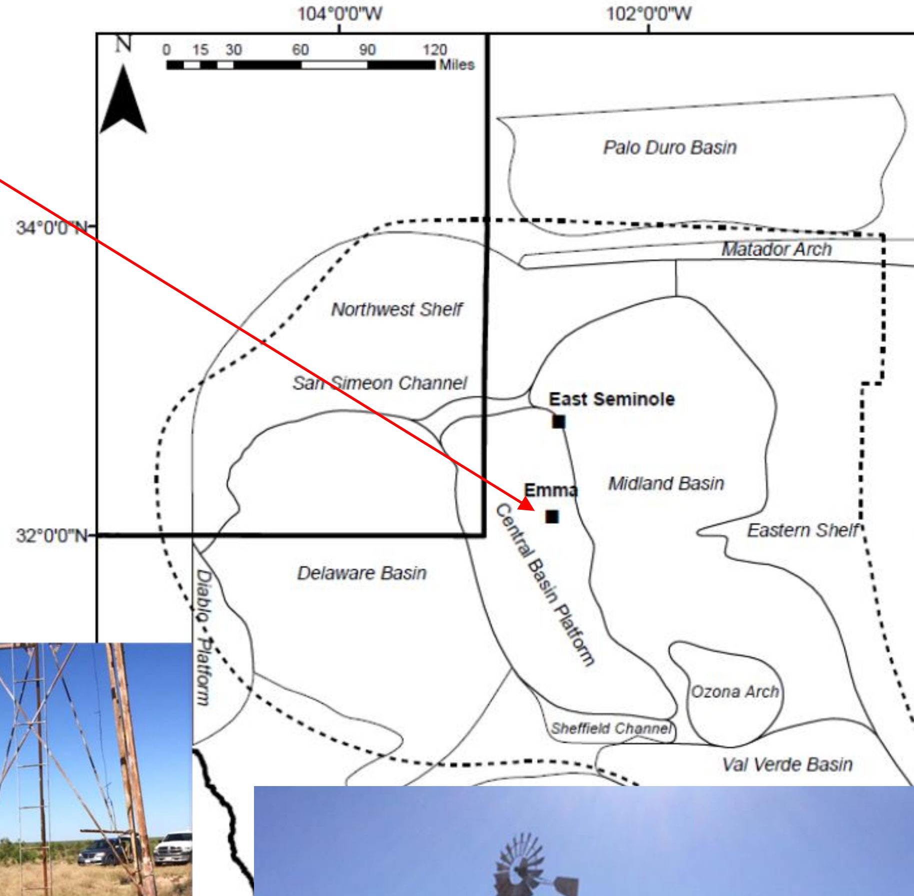
Seminole Sampling Trip May 2016

Emma Oil Field

- Active water injection
- 6 Wells Sampled
  - Producing fm. and shallow groundwater
- Comparison for CO_2 injection at Seminole
  - Influence of CO_2 on water-rock reactions

Emma Oil Field Update

- CO_2 injection stopped in October 2015
- Occurred for 1 month
  (1) CO_2 breakthrough occurred
  (2) Not economically feasible



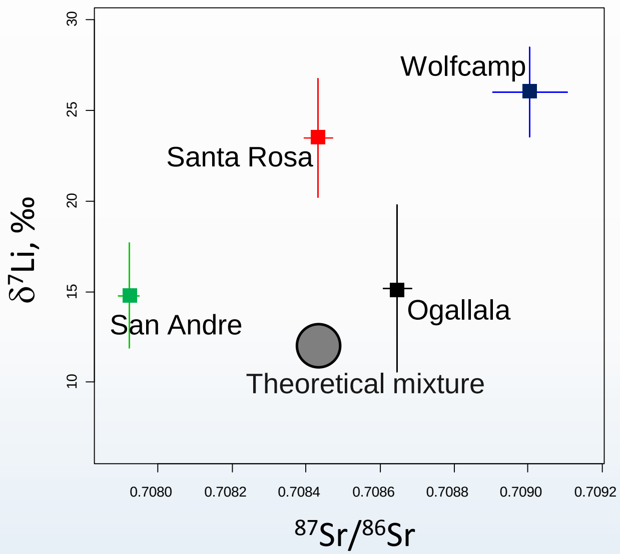
Field Sampling Team
Rodney Diehl
James Gardiner
Thai Phan
Burt Thomas

Burt Thomas and Rodney Diehl sampling Ogallala formation groundwater from windmill pump near Emma Oil Field

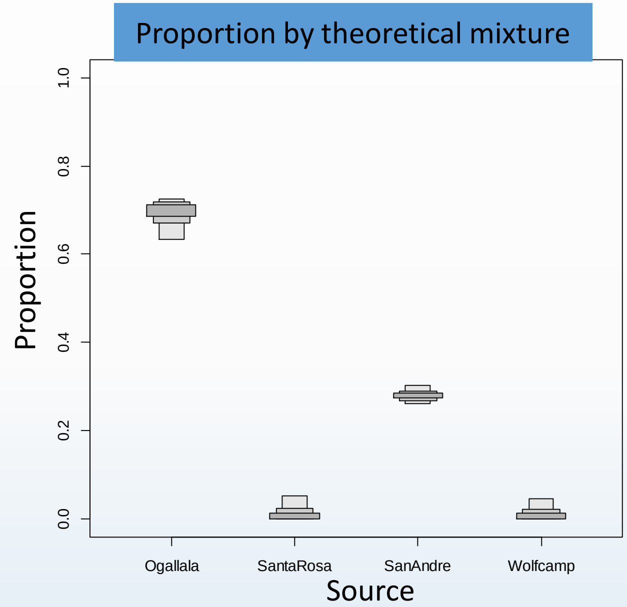
Windmill pump that taps Ogallala formation groundwater near Emma Oil Field

Evaluation of potential leaks using metal isotopes

- Developing statistical relationships for hypothetical Li and Sr isotope signatures based on end-member characteristics (Thai Phan).



Distinct isotopic compositions of four end-members



→ Bayesian isotopic mixing models predict source proportion of mixtures

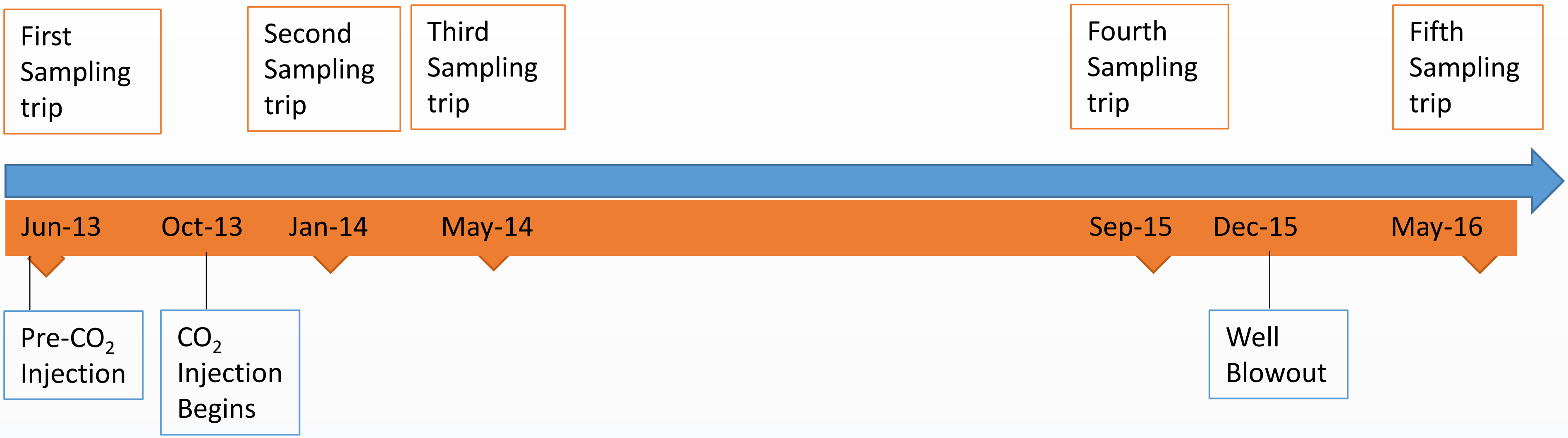
Theoretical mixture: Ogallala 70%, San Andres 30%

Modelled mixture: Ogallala 68%, San Andres 28%

→ ***Sr and Li isotopes are effective geochemical tracers of potential brine migration from the subsurface upward to shallow groundwater system***

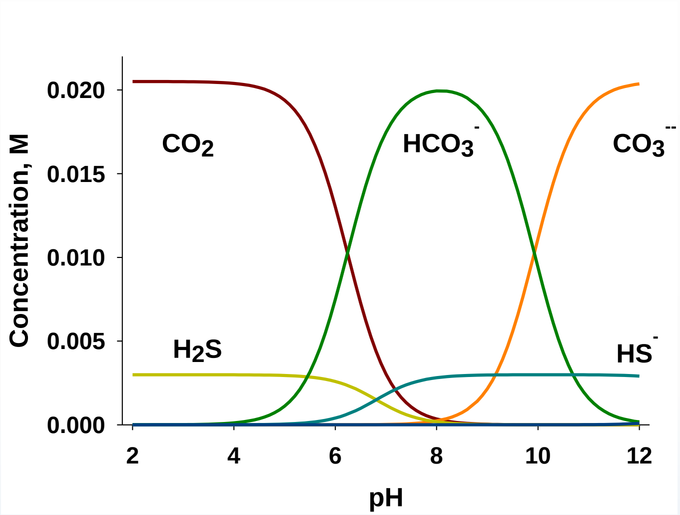
→ ***Future samples can undergo analysis to evaluate if fluid migration occurs***

Seminole Sampling Summary



- **Compilation of Major Chemistry Data from 5 Sampling Trips over 3 years is near completion**
- **MVA: Comparison of major and isotopic chemistry data from groundwaters and produced waters**
  - **·Pre-CO_2 injection baseline**
  - **·CO_2-injection pre-blowout**
  - **·CO_2-injection post-blowout**
- **Results will collectively be used to evaluate chemical signals that could serve as indicators of fluid or CO_2 migration into aquifers overlying the EOR reservoir**

CarboQC determination of CO_2 - H_2S interference



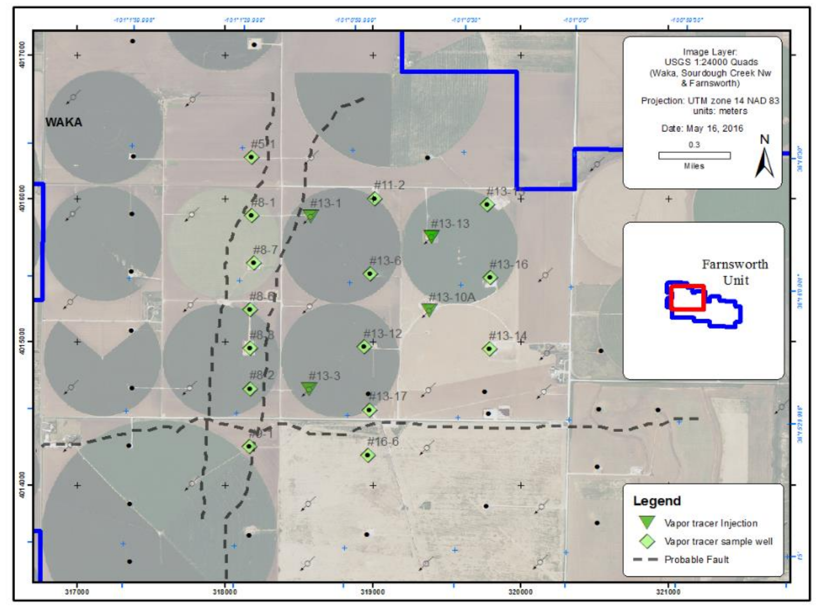
- CarboQC – volumetric expansion of sealed water sample
- H_2S the only significant gas with similar solubility to CO_2 in water
- Seminole concentrations dissolved sulfide: 500-1000 mg/L
- High concentrations of H_2S interfere with volumetric expansion method
- Success eliminating H_2S using Cu or Zn to precipitate
- Metal sulfide precipitation also changes pH, driving HCO_3^- to CO_2

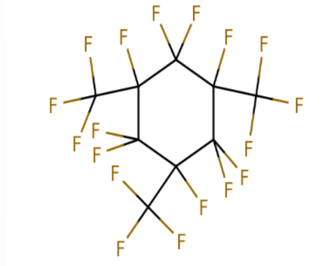
Perfluorocarbon Tracers – Farnsworth Unit MVA

Monitoring the extent of CO_2 plume and pressure perturbation

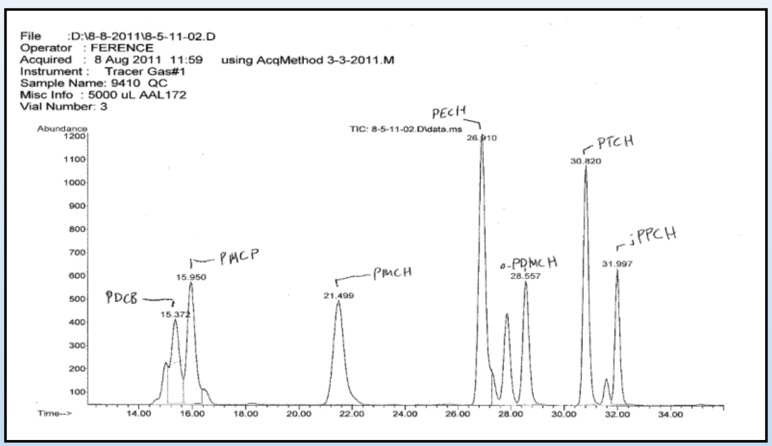
- **Purpose**
  - Monitor CO_2 plume migration from injection wells
  - Analytical support for measurement of vapor-phase perfluorocarbon tracers
- **Collaboration Partners**
  - National Energy Technology Laboratory (NETL)
  - Southwest Regional Partnership (SWP)
  - Chaparral Energy
- **Project Details**
  - Using CO_2 for enhanced oil recovery within the Farnsworth Unit
  - Injection into the Upper Morrow Formation (produced >19 million barrels of oil and >44 billion cubic feet of gas
  - CO_2 storage estimates exceed 25 million metric tons

Perfluorocarbon Tracers – Farnsworth Unit MVA





Perfluorotrimethylcyclohexane (PTCH)



- 4 injection wells
  - Well 13-13 injected PTCH in May 2015
  - Well 13-10A injected PDCB in November 2015
  - Well 13-1 injected PMCH in May 2016
  - Well 13-3 injected PECH in May 2016

- 15 production/sampling wells

Perfluorocarbon Tracers – Farnsworth Unit MVA

- Sample tubes shipped to NETL for sample preparation and analysis

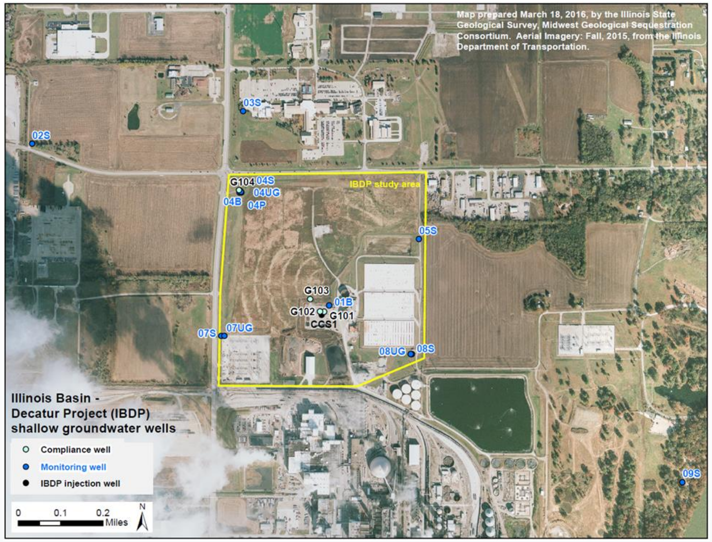
- Thermal desorption with cryogenic focusing gas chromatography/mass spectrometry (GC/MS) with chemical ionization (CI) and selected ion monitoring (SIM)

To Date:

- >300 samples analyzed since March 2016
- Breakthrough demonstrated for at least one well

Illinois Basin – Decatur Project (IBDP)

- Midwest Geological Sequestration Consortium large-scale carbon capture and storage site in Decatur, Illinois



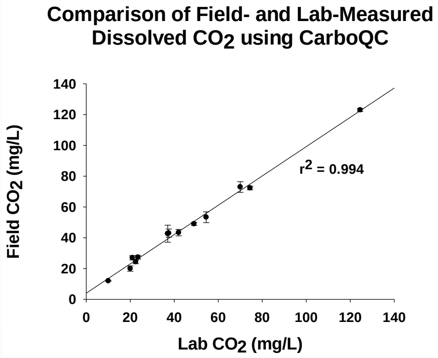
- Seventeen shallow groundwater monitoring wells ranging in depth from 6 to 90 meters (20 to 300 feet) have been installed and monitored for groundwater levels and chemistry since March 2009

- Accompanied Illinois State Geological Survey personnel during groundwater sampling trips in October 2015 and May 2016

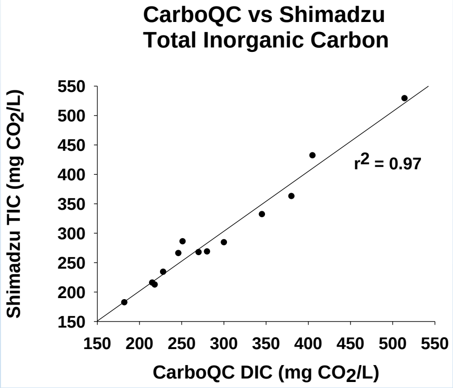
- Goal was to **field test and troubleshoot** the CarboQC and NDIR CO_2 methods on sampled water at an active sequestration site

Illinois Basin – Decatur Project
CarboQC method

CarboQC Volumetric Expansion Method



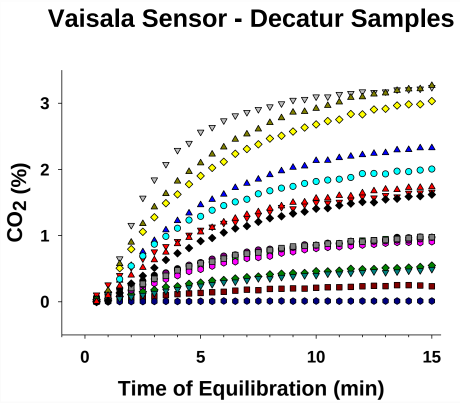
- CarboQC was tested extensively at natural analogue sites (springs and mine drainage)
- Compare and contrast with water collected at well heads and analyzed in lab
- Compare CarboQC-derived TIC with that measured using total carbon analyzer
- Design and test pressure valve design that allows CO_2 measurement during continuous pumping

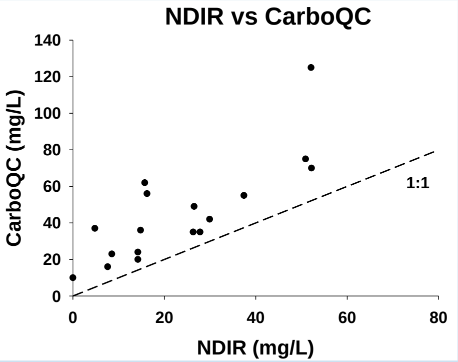


Illinois Basin – Decatur Project
NDIR Sensors

- Test gas-permeable NDIR sensors using flow-through system in the field
- Troubleshoot field methods and optimize
- Compare data obtained using alternative methods (CarboQC, alkalinity, etc.) with NDIR sensor-collected data

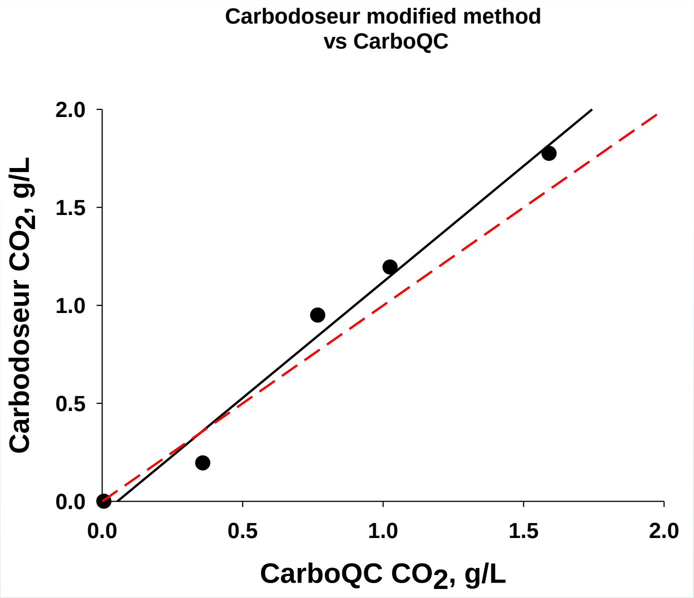
- Initial results showed that lengthy equilibration periods (> 15 min) were required for NDIR CO_2 measurements in lab and field
- Even longer equilibration time may be required for accurate measurements
- Occasional anomalies seen that may be related to water chemistry





"Carbodoseur"

- Simple method used by wineries to determine CO_2
- Liquid is shaken and amount displaced by CO_2 is measured
- Best at high CO_2 concentrations, but surprisingly effective

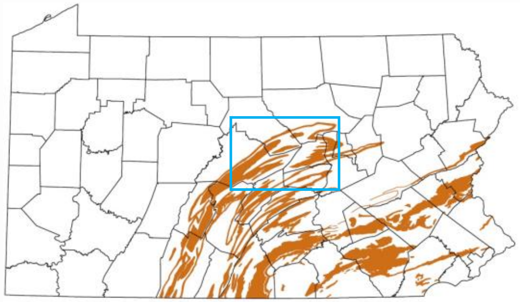


Commercial Carbodoseur $200

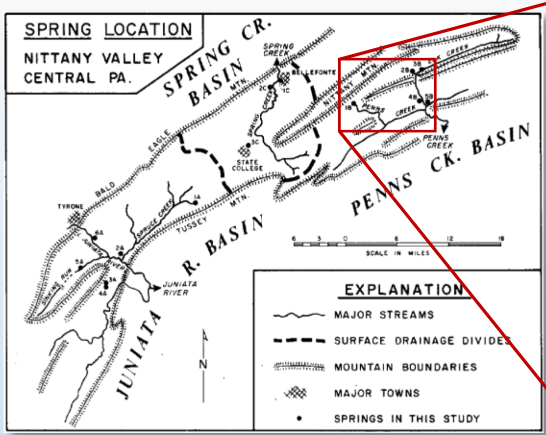
1.5 L adaption using 2 L soda bottle ca. $10

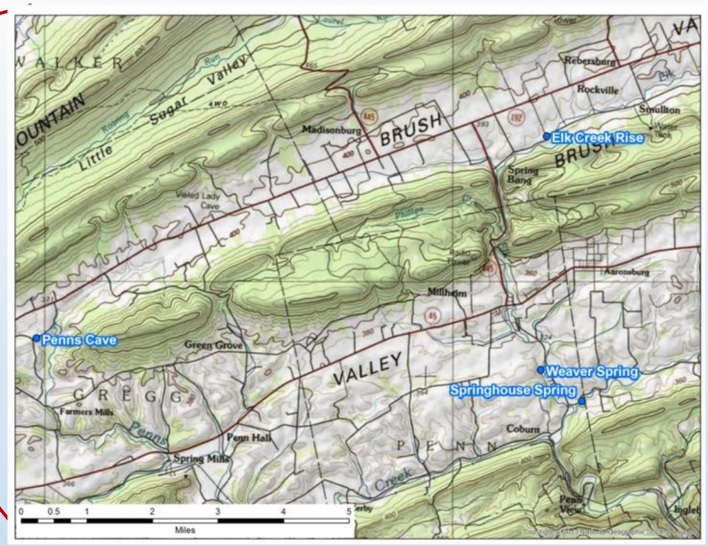
New Field Work for FY17

Storm hysteresis - Long-term karst aquifer monitoring



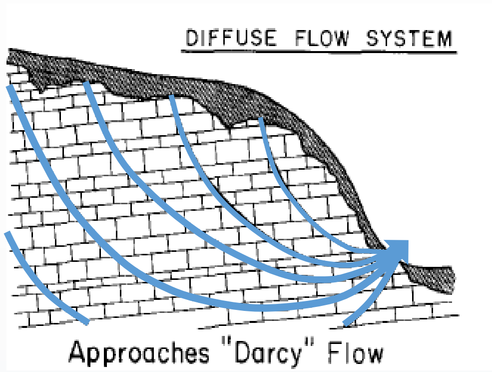
- NSF study by Bucknell and Temple University examining the influence of storm systems on groundwater flow and recharge in karst environments
- Karst = 20% of ground surface and 40% of groundwater supply in U.S.
- Ridge and Valley region of central PA has a complex karst hydrology
- Follow-up on 1971 study using contemporary monitoring methods

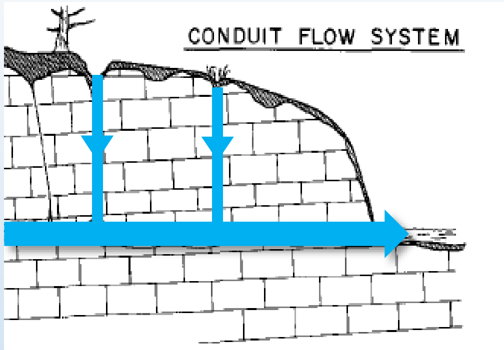




New Field Work for FY17

Storm hysteresis - Long-term karst aquifer monitoring





- Evaluate background CO_2 fluctuations due to storm events and recharge
- Field study provides opportunity to test NDIR sensor method under long-term data collecting conditions
- Data will be collected hourly over a one-year period of time at 3 springs
- Will allow us to evaluate long-term sensor performance (effects of biofilms, water level/pressure, power consumption, etc.)

NexSens data logging system

Effect of hydrostatic pressure on NDIR sensor detection of CO_2

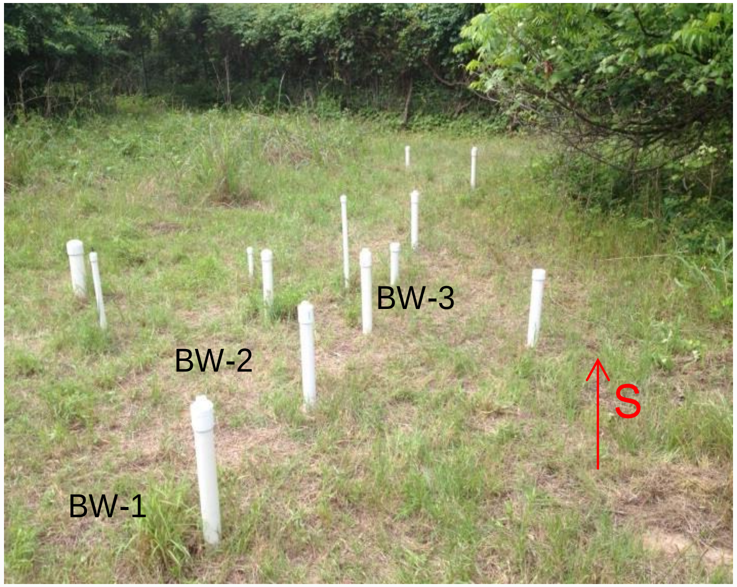
- Usefulness of NDIR method downhole may be severely limited by pressure effects
- Even in shallow water, both atmospheric and hydrostatic pressure need to be incorporated for greatest accuracy
- Natural thermal springs with high CO_2 in southern VA provide opportunities for controlled depth studies in former resort bathing pools

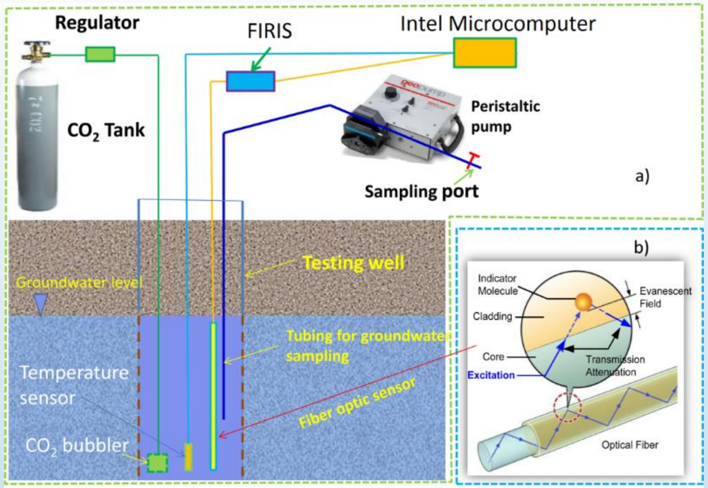
Old Sweet Springs, VA

New Field Work for FY17

CO_2 Pulse Tests
Brackenridge Field Laboratory, Austin, TX

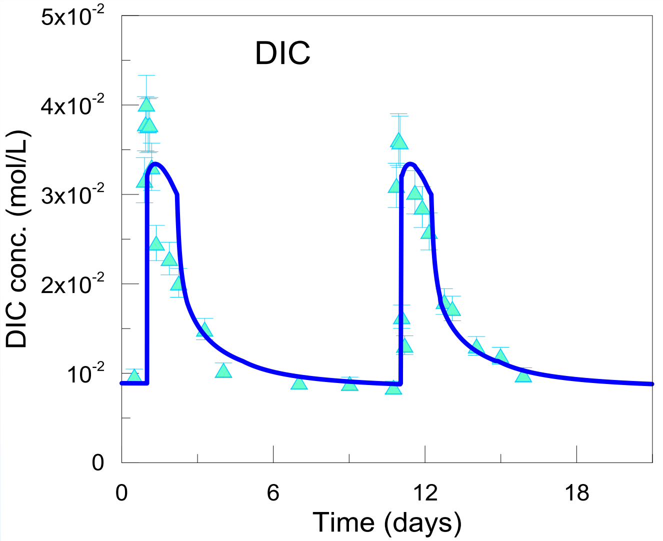
- Six shallow (10 - 20 ft) wells in unconfined aquifer
- Controlled CO_2 release
- Downhole fiber optic CO_2 sensor
- Groundwater sampling system
- Dr. Changbing Yang, Bureau of Economic Geology, UT-Austin



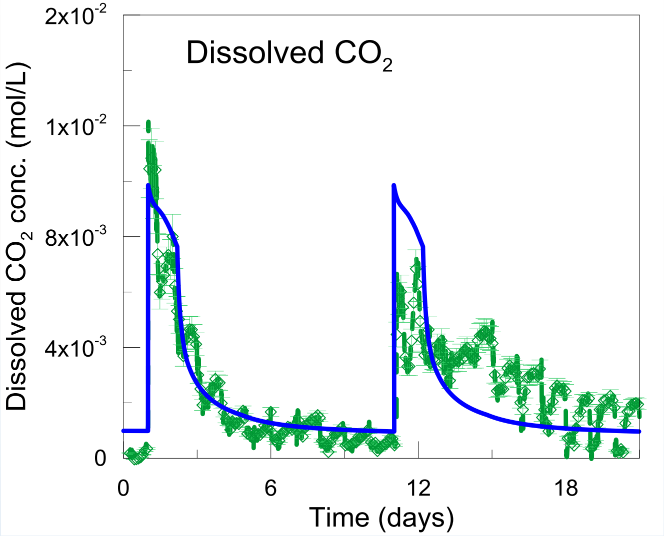


New Field Work for FY17

CO_2 Pulse Tests
Brackenridge Field Laboratory, Austin, TX



Lab analysis of DIC



Fiber optic sensor

- **<u>Goal</u>:** Compare downhole fiber optic sensor and geochemical data with CO_2 determined using CarboQC and NDIR methods

Key Accomplishments (2016)

- Team compiled groundwater quality data collected over 3 years for the Seminole EOR site, including before and after CO_2 injection, and after catastrophic blow-out of injection well
- Models were developed to predict isotopic signatures in groundwater under different leakage scenarios at Seminole EOR site
- Analytical support was provided for PFC tracer studies at the Farnsworth EOR site
- Direct CO_2 analytical methods were successfully adapted to the surface sampling of pumped groundwater at sequestration site monitoring wells
- CO_2 concentrations were determined directly in EOR produced water containing high levels of H_2S by sulfide precipitation/pH correction methods
- Field opportunities for sensor validation in PA and TX were identified and initiated
- Publication and presentation of field results

Synergy Opportunities

- Deployment of tested CO_2 sensing technologies at field sites where alternative methods are being used and environmental conditions differ will provide additional corroboration of collected data
- The NDIR method has the capability to measure aqueous CO_2 continuously downhole, but still needs to be tested in controlled, shallow well environments. Likely limited to shallow monitoring wells
- Collected data sets may be useful in identifying similar trends at other sites

Summary

- Collected data provide an excellent opportunity to examine a groundwater EOR data set generated pre- and post-CO_2 injection and after the occurrence of a well blow-out
- Preliminary attempts at modeling leakage scenarios using isotopic data are promising
- New field opportunities in more controlled environments (CO_2-injected shallow wells, high CO_2 thermal springs) will allow side-by-side testing with other detection methods and initial testing of influence of pressure on NDIR method
- Coordination and continuity of long-distance field work remains a challenge

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UCR Unconventional Resources

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https://edx.netl.doe.gov/ucr/

NETL Research Carbon Storage Program

Appendix

Organization Chart

9.1.1	Field Work Planning and Coordination (FY16)	Coordinate field sampling efforts for established collaborations with industry and university partners. This encompasses planning and coordination between other Subtasks for the collection of produced water samples in addition to overlying well water and/or groundwater samples. Future work may encompass the collection of gas samples and rock samples if feasible. Samples will be collected at EOR sites, for example, Texas, a coal storage site in West Virginia, and regional CO_2 storage partnership sites.	Hakala, Lopano, Edenborn
9.1.2	Comprehensive Groundwater Field Testing (FY16)	Performance of field testing and sample collection to evaluate methods for detecting CO_2 or brine leakage from storage formations into shallow systems. Research to be performed during FY16 will focus on sampling at the west Texas field sites to complete post-CO_2 injection monitoring, and field projects with RCSP sites as appropriate.	Diehl, Gardiner, Phan, Stuckman, Lopano, Sharma, Stewart
9.1.3	Field Validation of Direct CO_2 Sensors (FY16)	This element will implement the monitoring tools that have been developed for evaluating groundwater impacts in field settings ranging from natural analog to various CO_2 injection sites with different storage conditions to test the tools in a wide range of geologic settings. The techniques will be field tested and critically evaluated to develop a statistically based protocol for USDW monitoring. Baseline variability for key monitoring signals in groundwater will be documented for an aquifer prior to and during CO_2 injection.	Edenborn, Vesper (WVU), Jain
9.1.4	Statistical Evaluation of Baseline Field Data (FY16)	This element will document baseline variability for key monitoring signals in groundwater for aquifers prior to and during CO_2 injection. This element will also conduct statistical analysis on chemistry results to document baselines in potential source terms from the CO_2 reservoir.	Gardiner, Thomas

Organization Chart (cont'd)

9.1.5	Forward Modeling of Geochemical Leakage Signals (FY16)	This element will conduct forward geochemical modeling of what a leak to groundwater aquifers would look like under various field conditions.	Bromhal
9.2.1	PFT Analysis (FY16)	This element will continue to provide analytical support for the SW Partnership Farnsworth Field project to detect perfluorocarbon tracers (PFT) co-injected with CO_2 and other potential projects requesting support.	Diehl, Sanguinito

Gantt Chart

Task/Subtask	Project Dates for each Task/Subtask: Start	Project Dates for each Task/Subtask: Finish	FY16 (Q1, Q2, Q3, Q4)
8. Methods for Monitoring Migration of CO2/Brine Plumes and Groundwater Impacts	**10/01/2015**	**09/30/2019**	M1.16.8.A; M1.16.8.B
8.1 Geochemical Monitoring Tools and Protocols for Groundwater Systems	10/01/2015	09/30/2019	
8.1.1 Natural geochemical tracers in groundwater	10/01/2015	09/30/2016	
8.1.2 Continuous CO2 Monitoring Devices	10/01/2015	09/30/2016	
8.1.3 Development and Assessment of LIBS for Measurement of CO2 Impacts in Groundwater	10/01/2015	09/30/2016	
8.1.4 Fiber-Optic Technology for Downhole Measurement of Potential Groundwater Impacts	10/01/2015	09/30/2016	
8.2 Forward Modeling of Remote Sensing/Geophysical Monitoring Tools	10/01/2015	09/30/2018	
8.2.1 Evaluation of Non-wellbore Based Methods to Determine the CO2: Brine Interface Location in Storage Reservoir	10/01/2015	09/30/2016	
8.2.2 Routine Surveillance to Detect CO2 or Brine Incursions into USDW	10/01/2015	09/30/2016	
8.3 Fundamental Controls on Groundwater Composition	10/01/2015	09/30/2018	
8.3.1 CO2-Water-Rock impacts on groundwater signals	10/01/2015	09/30/2016	
8.3.2 Microbiological impacts and responses	10/01/2015	09/30/2016	
9. MVA Field Activities	**10/01/2015**	**09/30/2020**	M1.16.9.A; M1.16.9.B
9.1 Groundwater monitoring - Field Testing and Signal Validation	10/01/2015	09/30/2019	
9.1.1 Field work planning and coordination	10/01/2015	09/30/2016	
9.1.2 Comprehensive groundwater field testing	10/01/2015	09/30/2016	
9.1.3 Field validation of direct CO2 sensors	10/01/2015	09/30/2016	
9.1.4 Statistical Evaluation of Baseline Field Data	10/01/2015	09/30/2016	
9.1.5 Forward modeling of geochemical leakage signals	10/01/2015	09/30/2016	
9.2 Analytical Support for the SW Partnership Farnsworth Field Project	10/01/2015	09/30/2018	
9.2.1 PFT Analysis	10/01/2015	09/30/2016	

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Awards

- TechConnect Innovation Award “Compact Laser Spectroscopy for downhole sensing applications”