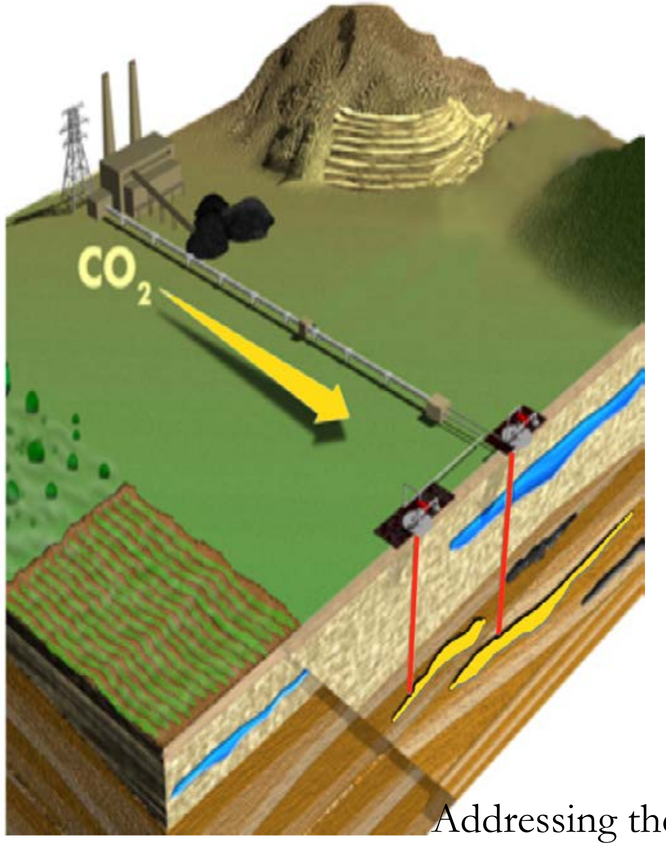
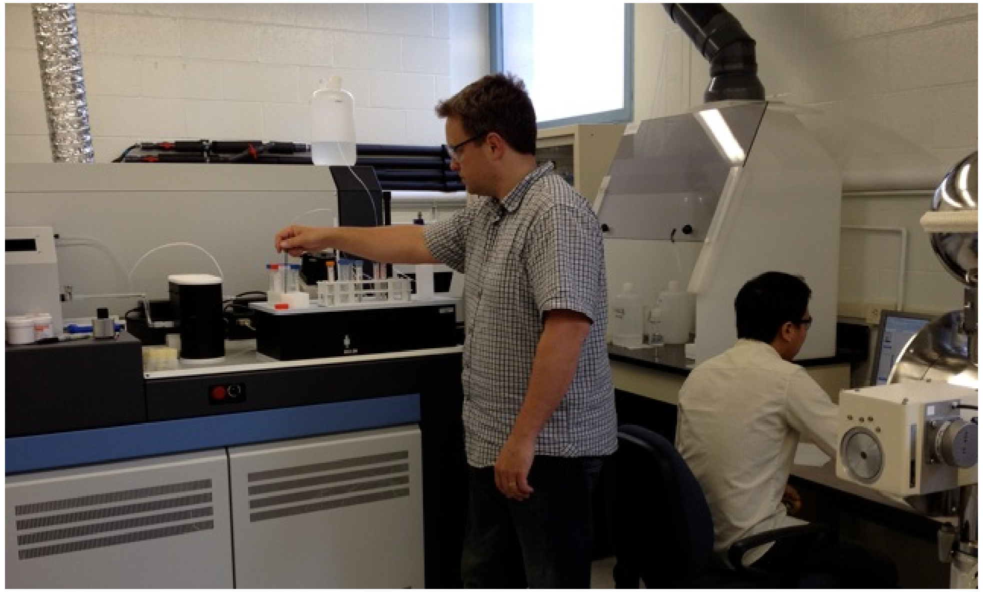
Geochemical Impacts and Signals of CO_2 on Groundwater

Task 20/21 FY2019

J. Alexandra Hakala & Christina L. Lopano
NETL-Research and Innovation Center





U.S. Department of Energy

National Energy Technology Laboratory

Addressing the Nation's Energy Needs Through Technology Innovation – 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting

August 26-30, 2019

Project Team Members (FY2019)

Task 20: Novel Geochemical Signal Methodologies

- NETL-RIC: Alexandra Hakala (PI), Christina Lopano, Harry Edenborn; LRST - James Gardiner, Randal Burton Thomas, Mengling Stuckman, ORISE – Brandon McAdams, Thai Phan
- University of Pittsburgh: Rosemary Capo, Brian Stewart,
- West Virginia University: Shikha Sharma

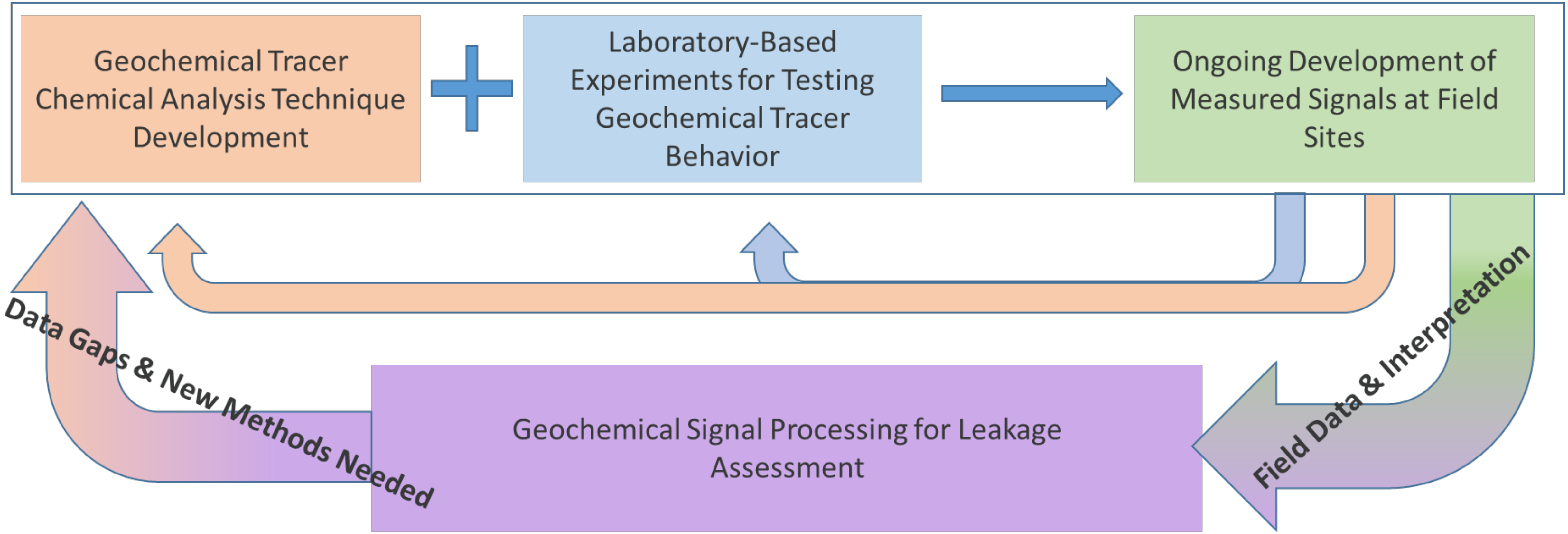
Task 21: Geochemical Signal Processing for Leakage Assessment

- NETL-RIC: Christina Lopano (PI), Alexandra Hakala, Robert Dilmore; LRST - James Gardiner, Randal Burton Thomas
- Carnegie Mellon Univ.: Mitchell Small, Jiaan Wang, Turner Cotterman
- UT BEG – Katherine Romanak

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

Carbon Storage Task 20 & 21 (FY2019)

Novel Geochemical Signal Methodologies



Task 20: Novel Geochemical Signal Methodologies

Task Technical Approach and Project Relevancy (PI: Ale Hakala)

Objective: Deliver geochemical tracers that can be **applied towards monitoring carbon storage systems for ensuring 99 percent carbon storage permanence**, as well as in situ or laboratory **analytical techniques for high-throughput and low-cost analysis of field samples**.

Rapid-Analysis Techniques for Trace Analytes in High-TDS Fluids

Proof-of-Concept Testing with Readily-accessible CO_2-Rich Natural Waters

Field Sampling for Comprehensive Monitoring at Active CO_2-EOR Site

Benefit: Monitoring fluids and gas for **chemical tracers that serve as precursor indicators for carbon storage reservoir leaks** allows for development and implementation of leak-specific mitigations.

Task 20: Novel Geochemical Signal Methodologies

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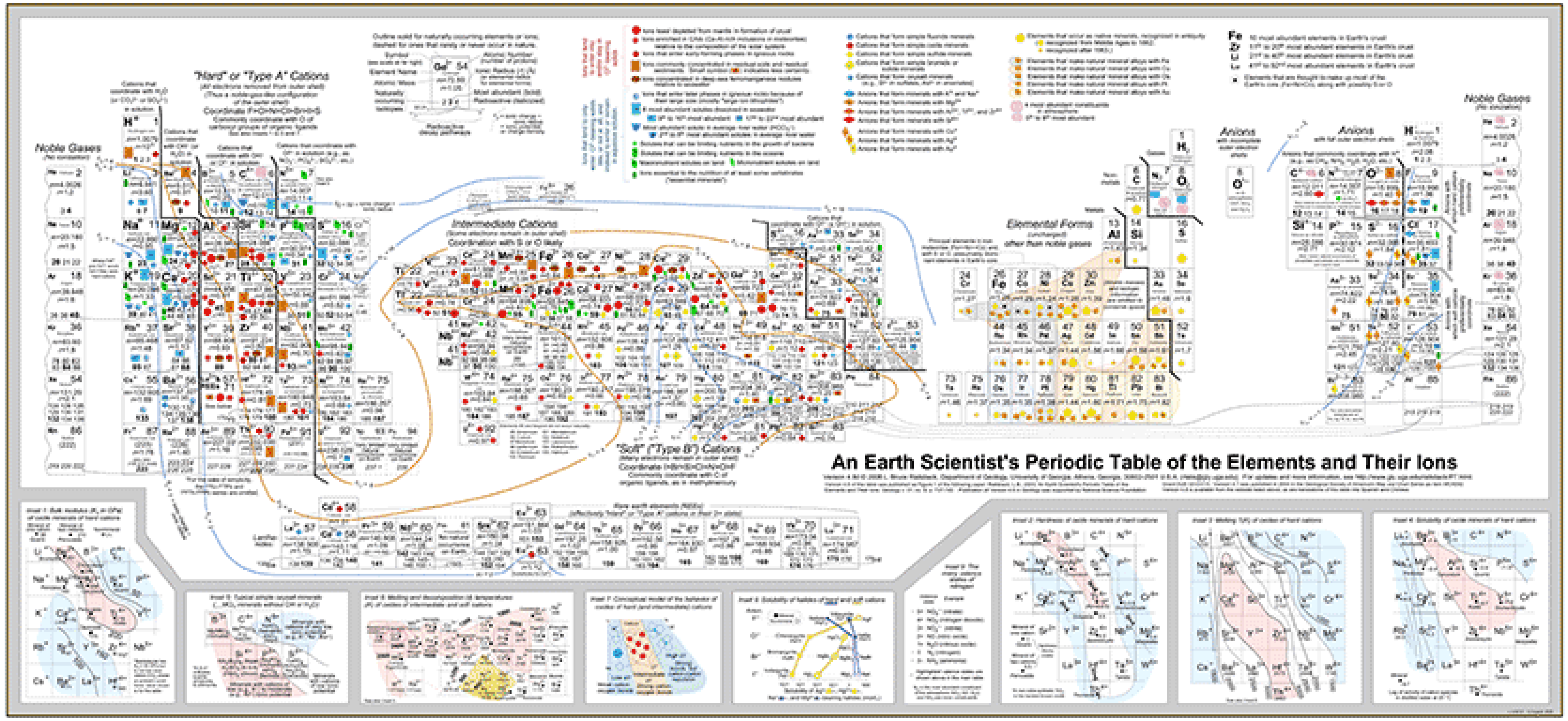
Task Technical Approach and Project Relevancy (PI: Ale Hakala)

Challenges:

- Identifying appropriate chemical signals to monitor for different types of geologic systems and leak types.
- Developing rapid laboratory analytical techniques for high-volume sample processing and analysis.
- Deploying sampling and direct analysis protocols for appropriate characterization of geochemical signal changes in the field for introduced and naturally occurring tracers.



Bruce Ralisback, 2003, *Geology*

Task 20: Novel Geochemical Signal Methodologies

Task Technical Approach and Project Relevancy (PI: Ale Hakala)

Approach:

- Identify geochemical indicators to pursue for monitoring purposes.
- Develop laboratory analytical techniques to measure the identified geochemical indicators.
- Perform laboratory-based experiments as proof-of-concept for characterizing tracer behavior in carbon storage field settings.
- Pursue field-based studies to test field applicability of the naturally occurring and/or introduced chemical tracer for monitoring carbon storage permanence.

Laboratory Chemical Analysis Techniques

- Benchtop Ion Chromatography Methods
- B and Ba Isotope Geochemistry

Direct Field Monitoring Techniques

- Direct CO_2 Sensing in Groundwater
- Robust Redox Microelectrodes

New methods for off-the-shelf ion chromatography equipment allows for trace component analysis in high-TDS fluids

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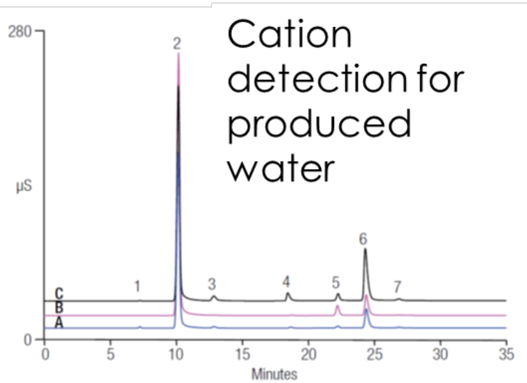
Benchtop Ion Chromatography Methods

Detection	Detector	Analytes
Cations	Conductivity	Li+[1], Na+[2], NH4+[3], K+[4], Mg+[5], Ca+[6], Sr2+[7], Ba2+ [8]

Detection	Detector	Analytes
Anions	Conductivity	fluoride[2], chloride[13], nitrite[14], nitrate[17], bromide[16], bromate[12], phosphate[24], chromate[27], iodide[29], **sulfate[21]**, **thiosulfate[26]**, **sulfite[20]**
Organic Acids	Conductivity	acetate[4], lactate[3], formate[6], butyrate[3], propionate[4], pyruvate[8], succinate[15], oxalate[22], citrate[28]

Detection	Detector	Analytes
Transition metals	UV-vis	Fe3+, Fe2+, Mn2+, Co2+, Ni2+, Zn2+, Cd2+
Rare earths	UV-vis	La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
Sulfides	Electro-chemical	**Sulfide** and cyanide

Intergion



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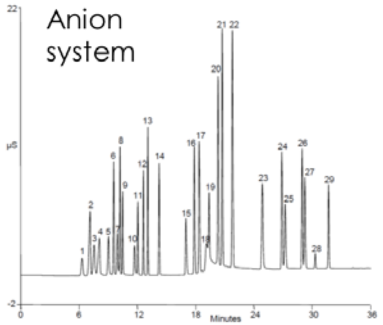
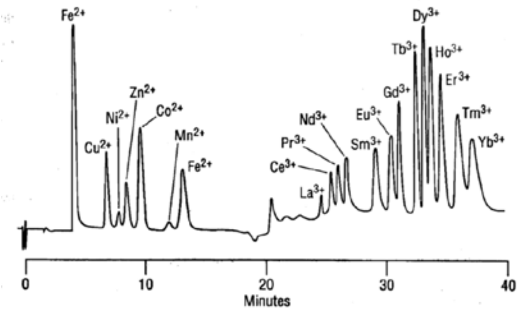


Reduces dilution effects for many trace components of natural brines.

Most field sample sets (1-20 wells) analyzed within a few days

UV-vis detector

Electro-chemical detector (Ag-AgCl)



Capability for analysis of B and Ba isotope fractionation in natural samples is on-line

Application of isotope geochemistry to source-identify geologic fluids and reactions

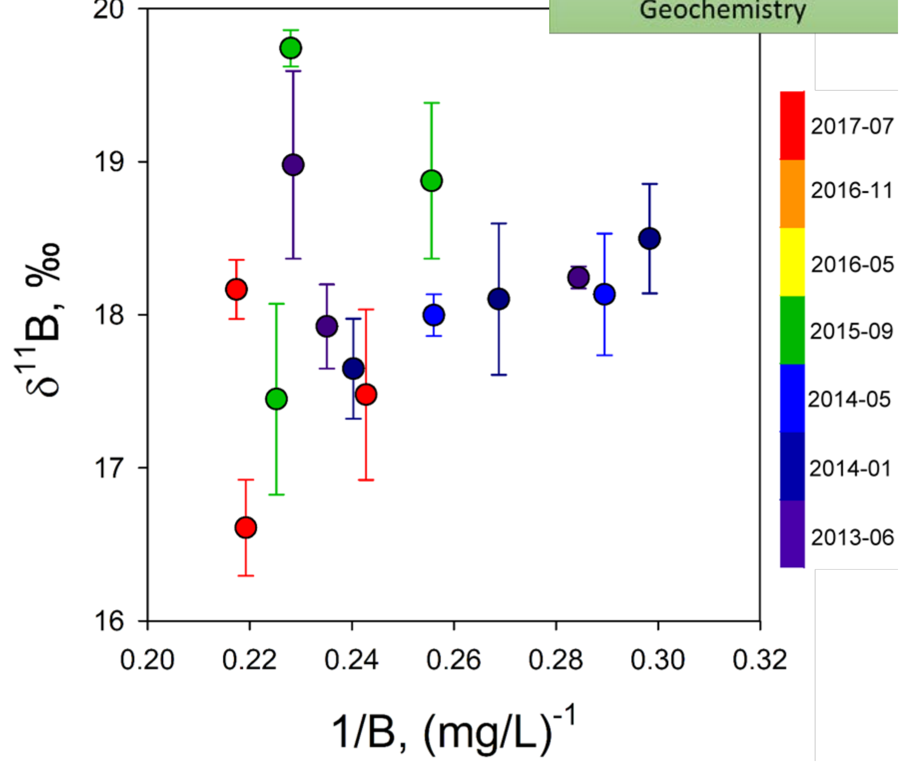
$^{11}B/^{10}B$	Identify whether leaked CO_2 contacted brine, or if it came directly from the sc-CO_2 plume
$^{138}Ba/^{134}Ba$	Characterize the potential for scale-forming minerals to develop within wells and geologic formations

- Development of matrix separation techniques for complex matrices
- Rapid analysis with ICP introduction system

Collaboration with the Department of Geology and Environmental Science, University of Pittsburgh

Boron Sublimation Technique Successfully Applied on CO_2-EOR Field Samples

B and Ba Isotope Geochemistry



CO_2 injection does not affect the $\delta^{11}B$ values produced water from the target CO_2-EOR reservoir (San Andres formation, west TX)

Direct Sensing of CO_2 In Shallow Monitoring Wells

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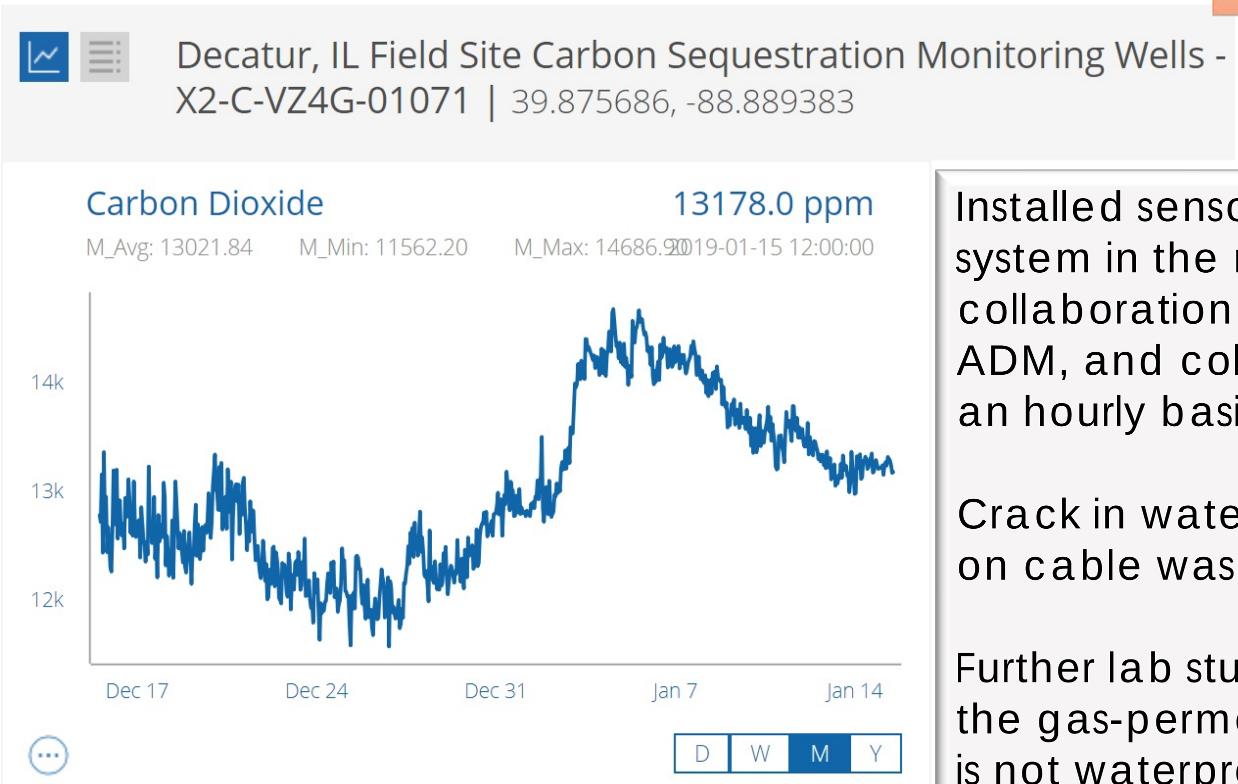
Direct CO_2 Sensing in Groundwater

Decatur, IL carbon sequestration monitoring wells

NETL-modified new generation NDIR sensor with solar-powered data collection and transmission system



Installed sensor and telemetry system in the monitoring well, in collaboration with ISGS and ADM, and collected data on an hourly basis

Crack in waterproof insulation on cable was observed

Further lab studies suggest that the gas-permeable membrane is not waterproof below a relatively shallow depth

Fabrication of robust microelectrodes for *in situ* monitoring of Fe and S speciation in produced water

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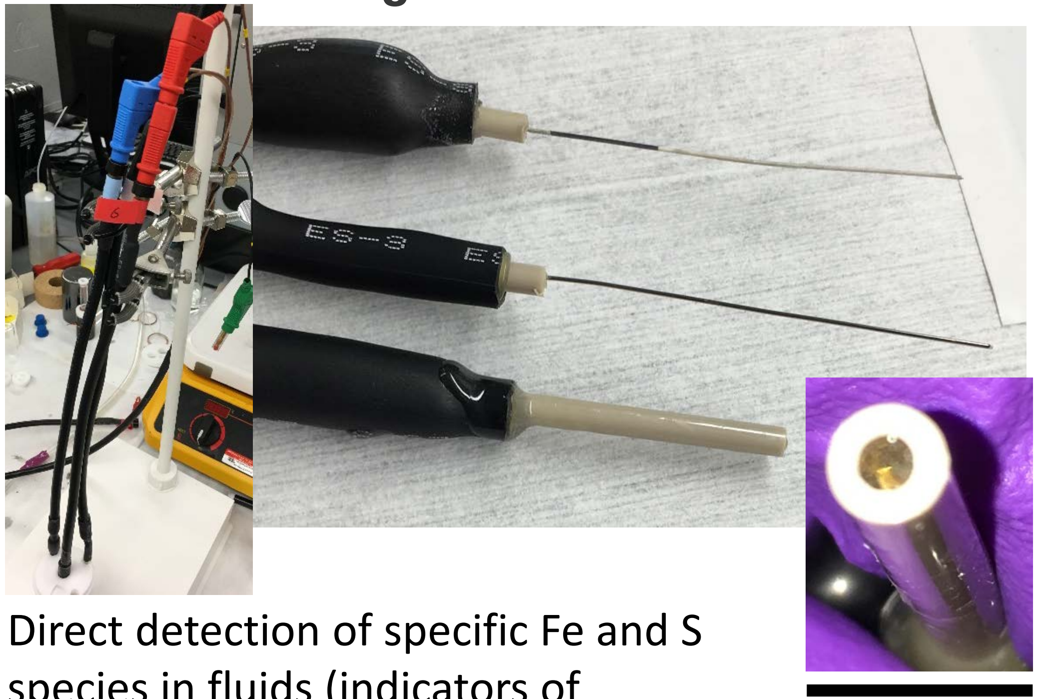
Direct Monitoring of Fe and S speciation in high-TDS Fluids



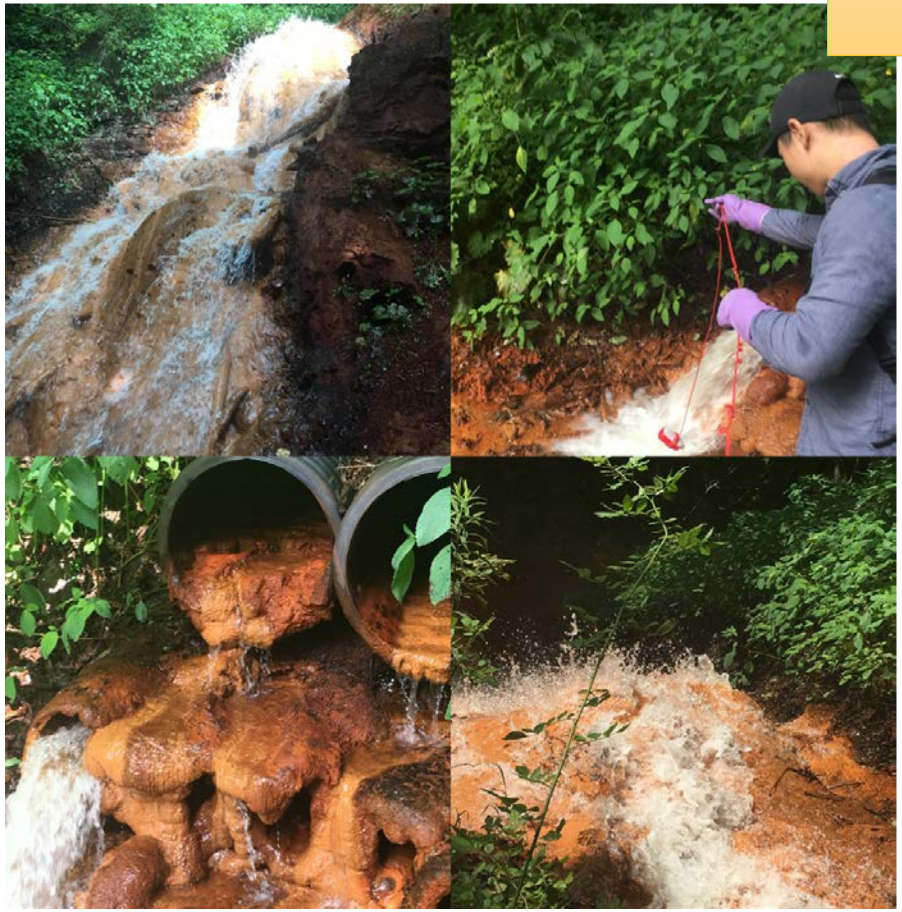
5 mm

Direct detection of specific Fe and S species in fluids (indicators of subsurface redox reactions)

Future goal is to develop down-hole monitoring capability

Electrodes Tested on Fluids from a CO_2- and Fe-Rich Waterfall

Robust Redox Microelectrodes

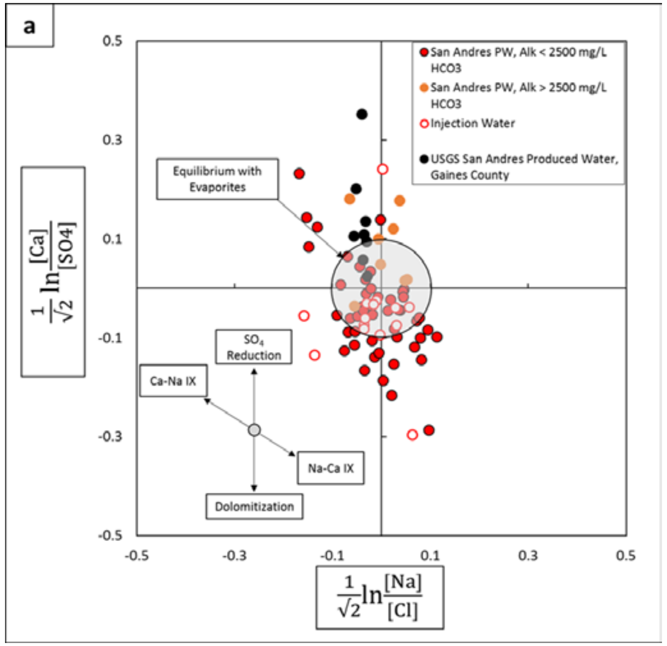


Analysis of Fe speciation is in progress

Task 21: Geochemical Signal Processing for Leakage Assessment

Task Technical Approach and Project Relevancy (PI: Christina Lopano)

Objective: Need exists for a **low-cost, easily implemented monitoring strategy for carbon storage reservoir leak detection in different geologic regions**. Geochemistry-based methods for tracking brine or CO_2 migration from carbon storage formations into other geologic units can provide early detection of well or reservoir integrity issues and inform of leakage pathways.



Benefit: Process-based approach in conjunction with real-field signal data for better prediction, or earlier detection, of a problem.

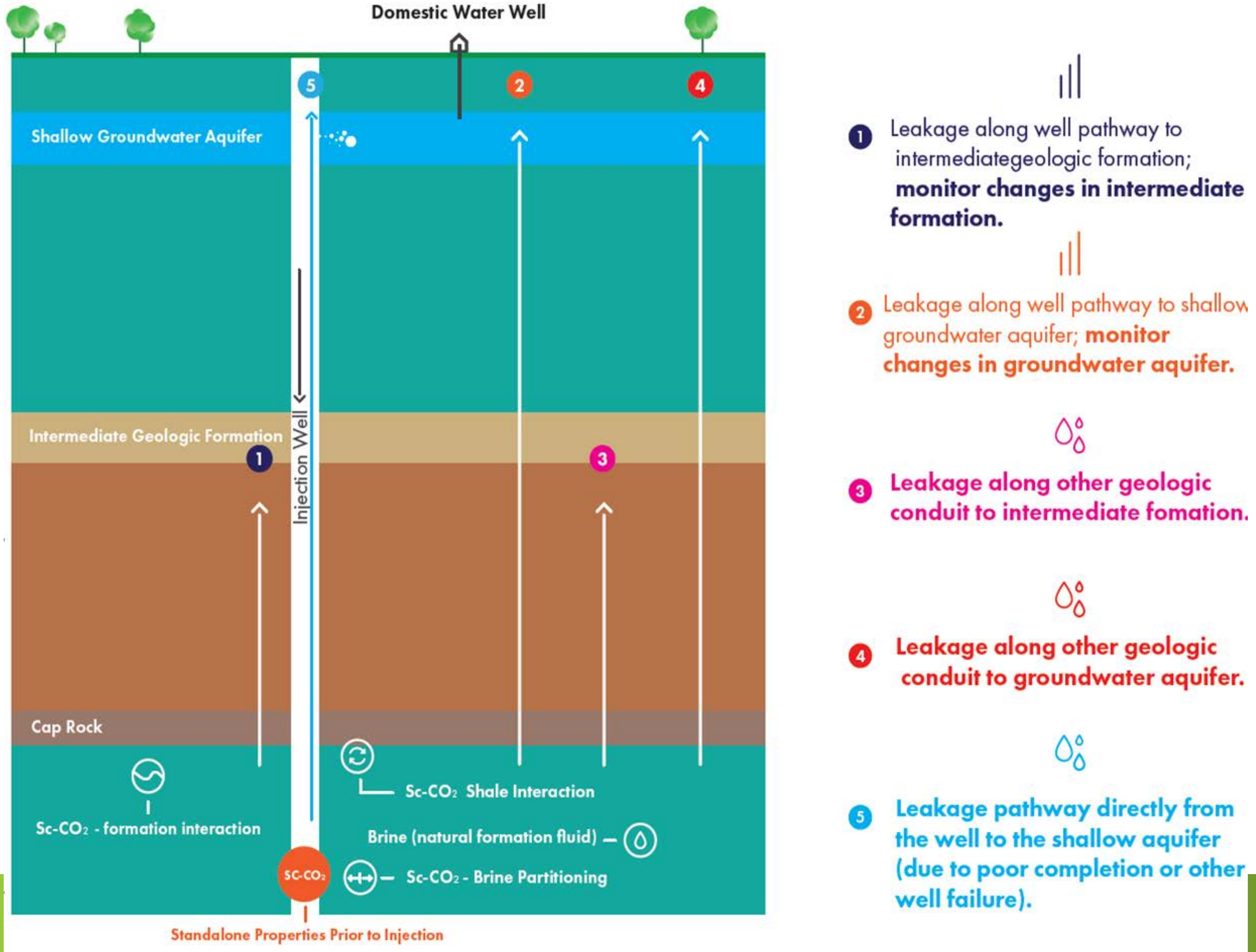
Task 21: Geochemical Signal Processing for Leakage Assessment

Task Technical Approach and Project Relevancy (PI: Christina Lopano)

Challenges:

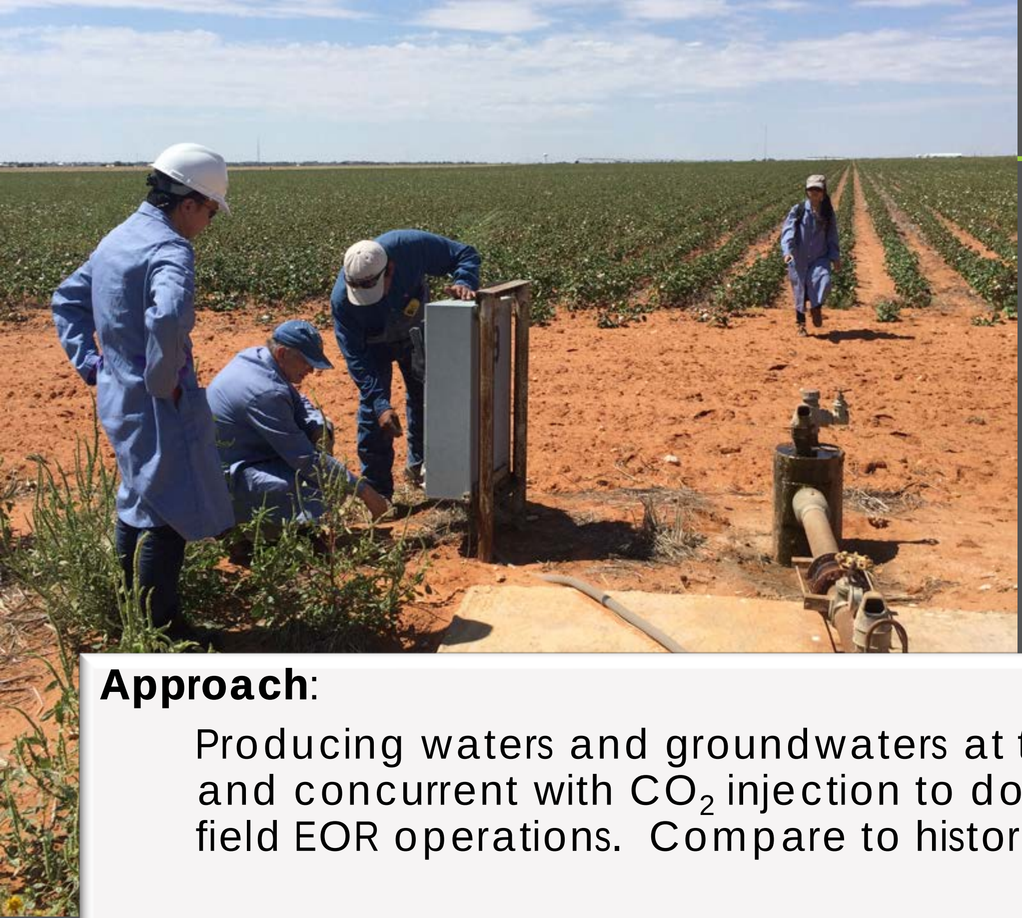
Distinguishing whether geochemical variance is due to **formation reactions**, common **oil field practices** (EOR), or **natural mixing** phenomena.

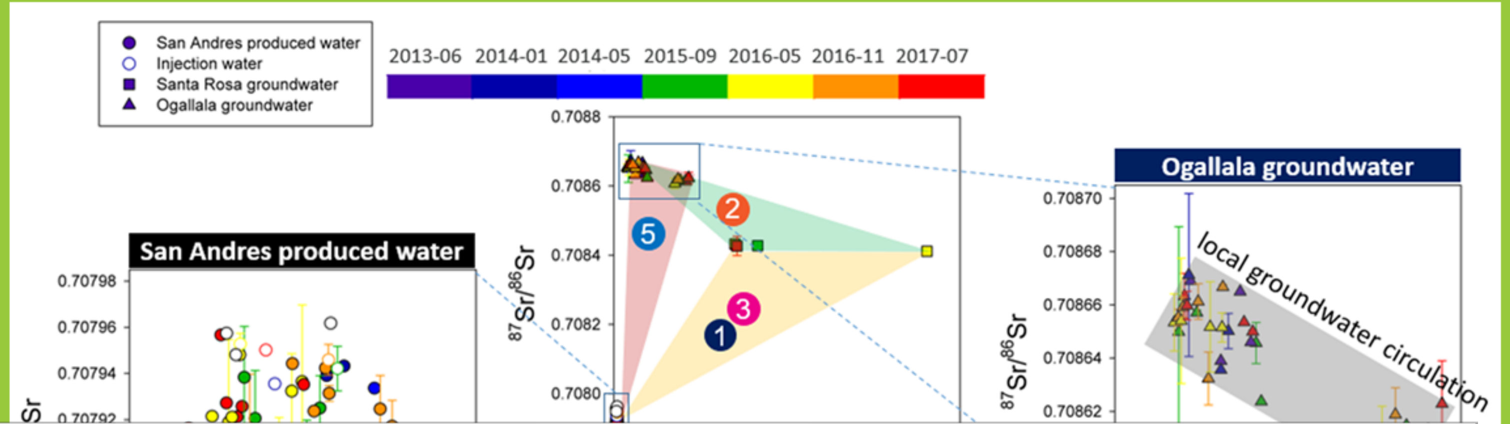
What is a baseline?



Monitoring CO_2-EOR Operational Baseline in the Permian Basin

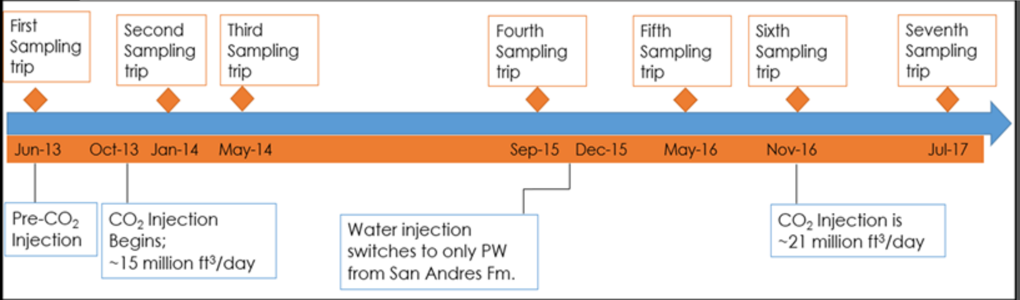
Multi-year sampling for activities including transition from water flooding to water-alternating-gas techniques





Approach:

Producing waters and groundwaters at two Permian Basin field areas will be sampled and analyzed prior to and concurrent with CO_2 injection to document geochemical variation in produced waters during normal oil field EOR operations. Compare to historical geochemistry data.



Central Basin Platform Group/Formation	Lithology	Average Depth (m) of Samples at field area
Alluvium	Silty sand	
Ogallala	Fluvial and lacustrine clastics	~45-55
Fredericksburg	Limestone	
Antler / Paluxy	Sandstone	
Dockum Group / Santa Rosa Fm.	Fluvial-deltaic and lacustrine clastics	~460
Dewey Lake		
Rustler	Halite, Anhydr., Sylvite	

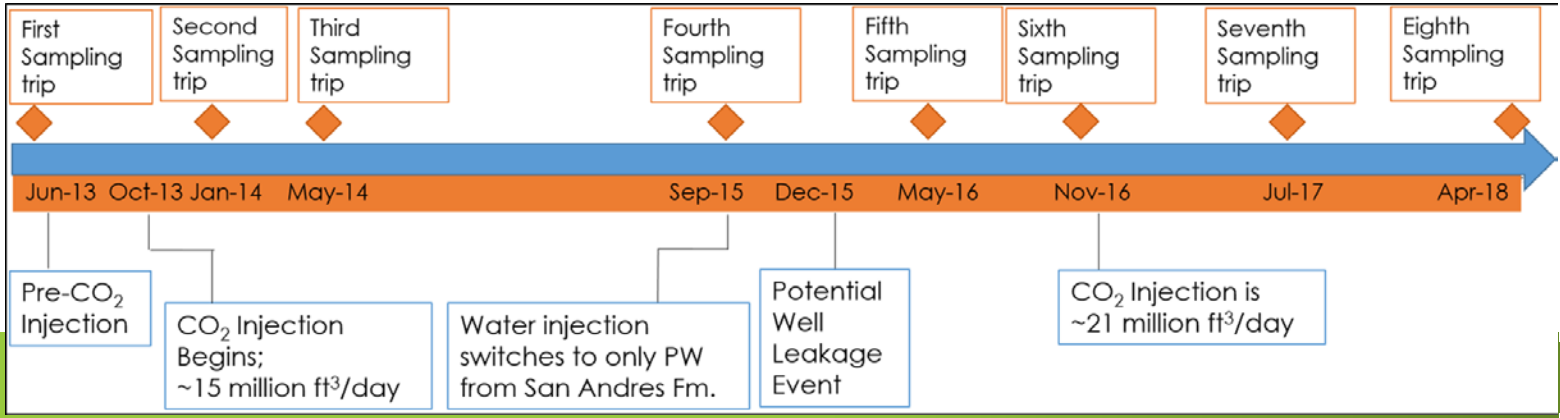
Gardiner et al *In prep*

Geochemistry Data at E. Seminole Site

Knowledge Gaps: What is a baseline?

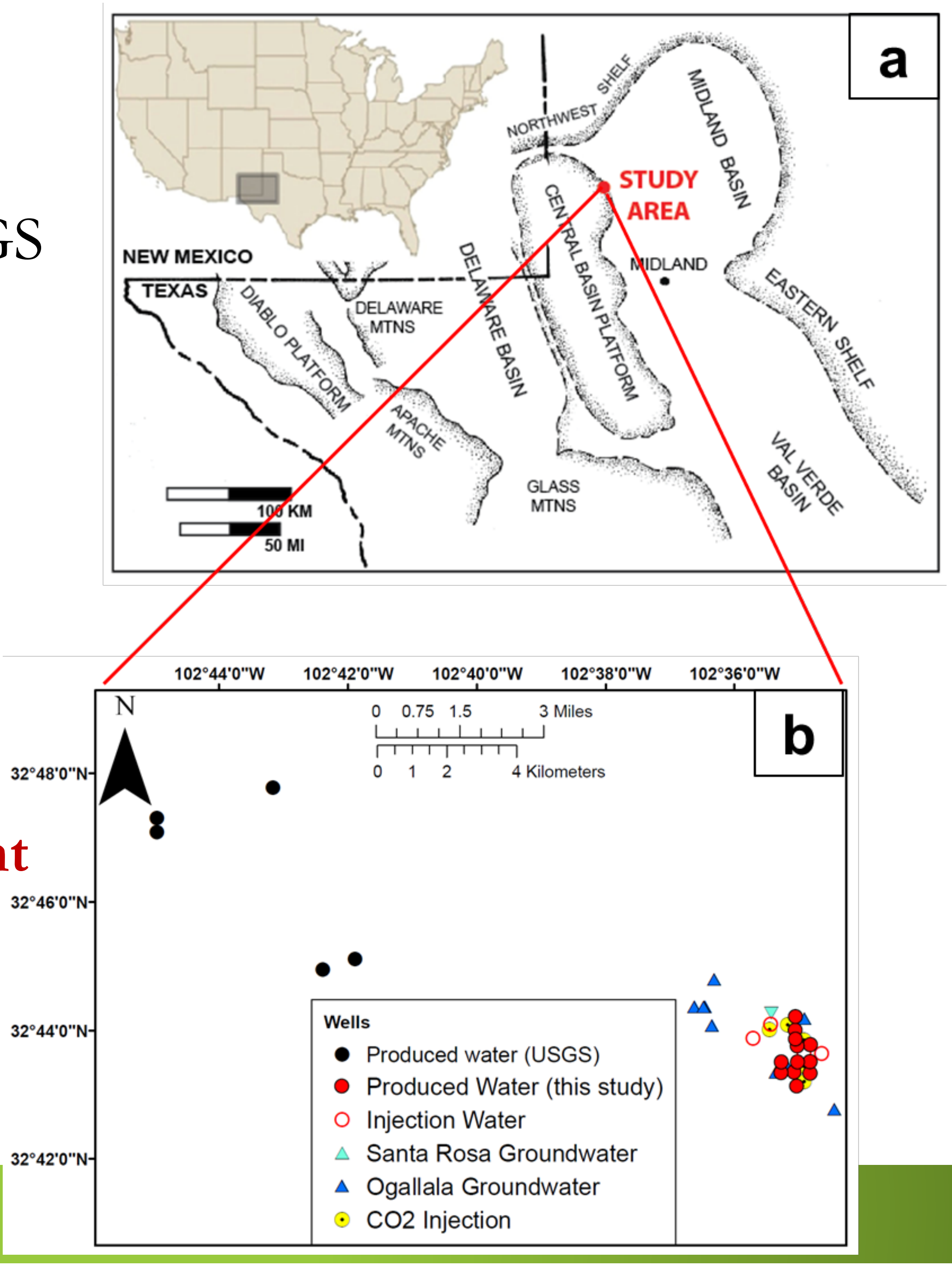
1) Does injected CO_2 affect produced water chemistry?
2) Do produced waters have a geochemical baseline while the formation is undergoing varying oil extraction processes?
3) Does CO_2 injection have a persistent effect on the long-term geochemical baseline in producing formations?

System	Series	Central Basin Platform Group/Formation	Lithology	Average Depth (m) of Samples at field area	Hydrostratigraphic Unit
Quaternary		Alluvium	Silty sand		
Tertiary	Upper	Ogallala	Fluvial and lacustrine clastics	~45-55	Evaporite Confining System
Cretaceous	Albian	Fredericksburg	Limestone		
		Antler / Paluxy	Sandstone		
Triassic	Upper	Dockum Group / Santa Rosa Fm.	Fluvial-deltaic and lacustrine clastics	~460	
Permian	Ochoan	Dewey Lake	Halite, Anhydr., Sylvite		
		Rustler			
		Salado			
		Tansill	Sandstone and Anhydrite		
	Guadalupian	Yates			Deep Basin Aquifer System
		Seven Rivers			
		Queen			
		Grayburg			
		Upper San Andres	Dolomite	~1630	
		Lower San Andres			
	Leonardian	Holt	Limestone and Dolomite		
		Glorieta			
		Clear Fork Group			
		Wichita			
	Wolfcampian	Wolfcamp	Shale, carbonates		



Produced water variation under changing recovery methods

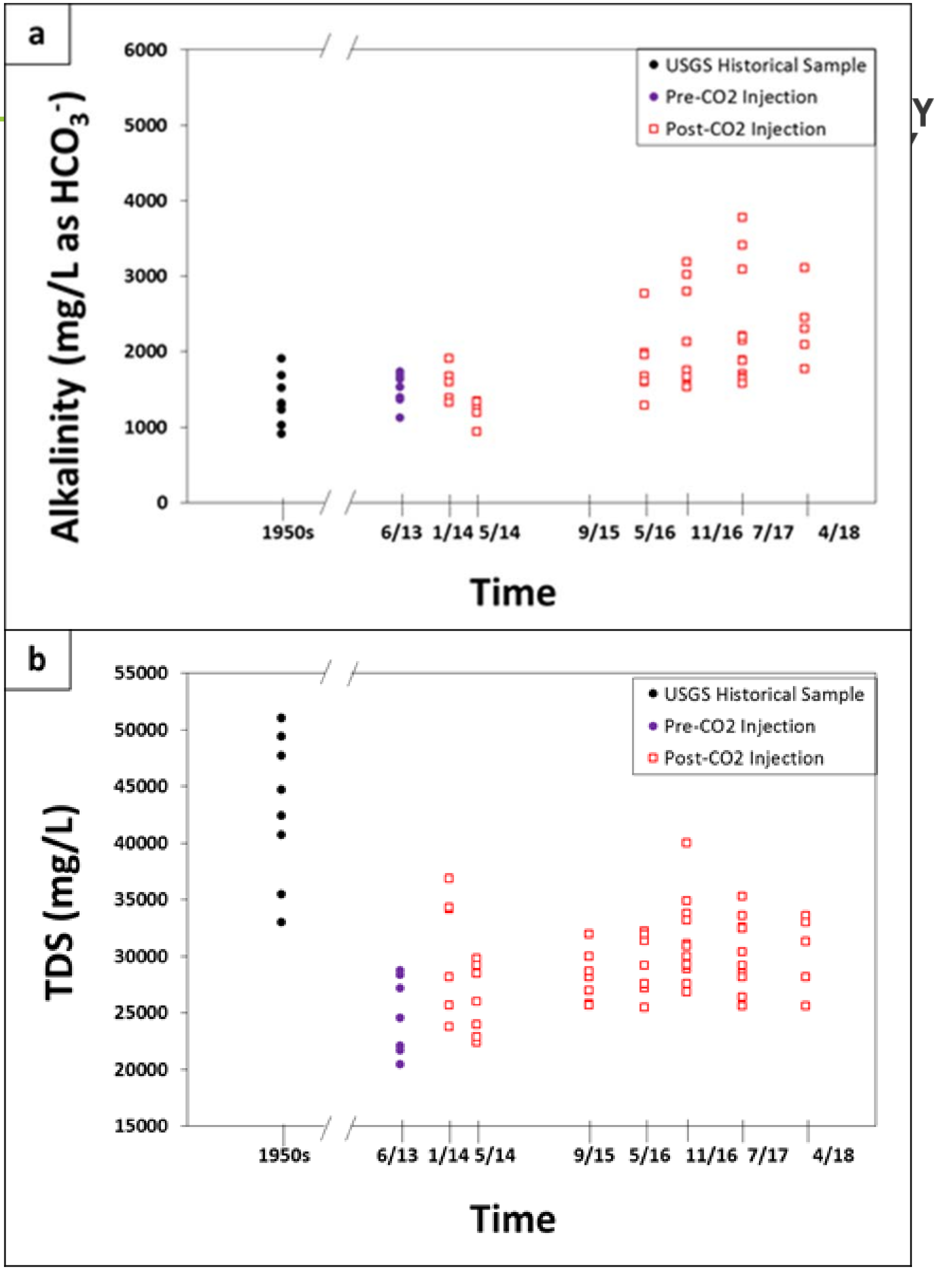
- Compared our dataset with historical values – USGS PWDB – criteria:
  - San Andres Formation
  - Gaines County
  - Adjacent Seminole field
  - Charge balance ≤10%
- **Result**
  - **Eight sampling events from five different wells, <20 km**
  - **Taken in 1950's, pre-waterflooding (Honarpour et al., 2010)**



Geochemical Signals – E. Seminole

Interpreting geochemical datasets

- Produced water and groundwater from 8 sampling trips from June 2013-April 2018
- CO_2 flooding began in October 2013



Conclusions

(1) Waterflooding and CO_2 injection caused distinct shifts in produced water chemistry

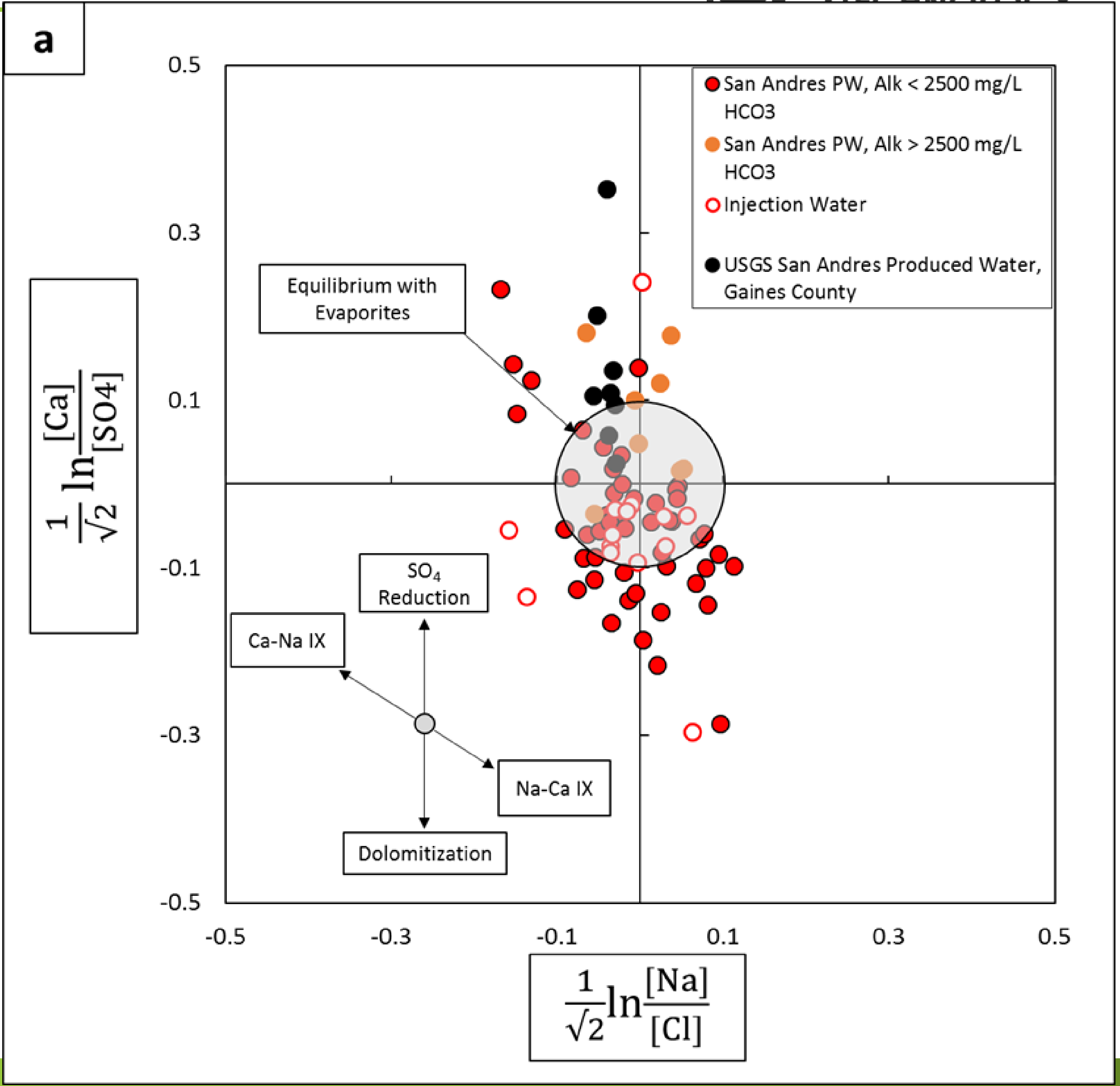
Utilization of produced water baseline as a groundwater monitoring tool at a CO_2-EOR site in the Permian Basin, Texas, USA (Manuscript in prep) James Gardiner, R. Burt Thomas, Thai Phan, Mengling Stuckman, Christina Lopano, J. Alexandra Hakala

Example: Applying isometric log-ratios (ilr)

East Seminole Field Geochemistry

- Isometric log-ratios (Blondes, 2015) are suitable for **high salinity waters**
- Plotted with relation to Ca/SO_4 [anhydrite] and Na/Cl [halite]
- San Andres PW from field area plot in a narrow range, near axes
- CO_2 injection did not affect likelihood of anhydrite or halite geochemical reactions

Gardiner et al (2019) Geological Society of America



Gardiner et al *In prep*

Conclusions

Bulk Geochemistry – East Seminole Field Site

(1) Waterflooding and CO_2 injection caused distinct shifts in produced water chemistry

- Waterflooding: increase in pH; decreases in TDS, Na+, Cl-, SO_4^{2-}, Ca^{2+}, Mg^{2+}
- CO_2 injection: increases in alkalinity, TDS, Na^+, Cl^-, SO_4^{2-}

(2) CO_2 injection did not spur significant dissolution-precipitation reactions

(3) Data transformation tool can establish produced water baseline

- Despite geochemical variations, isometric log-ratios display negligible variability

(4) Groundwater data shows no impact from CO_2-EOR operations

- Able to track mixing of San Andres produced water with overlying Santa Rosa groundwater

Gardiner et al *In prep*

Moving Forward

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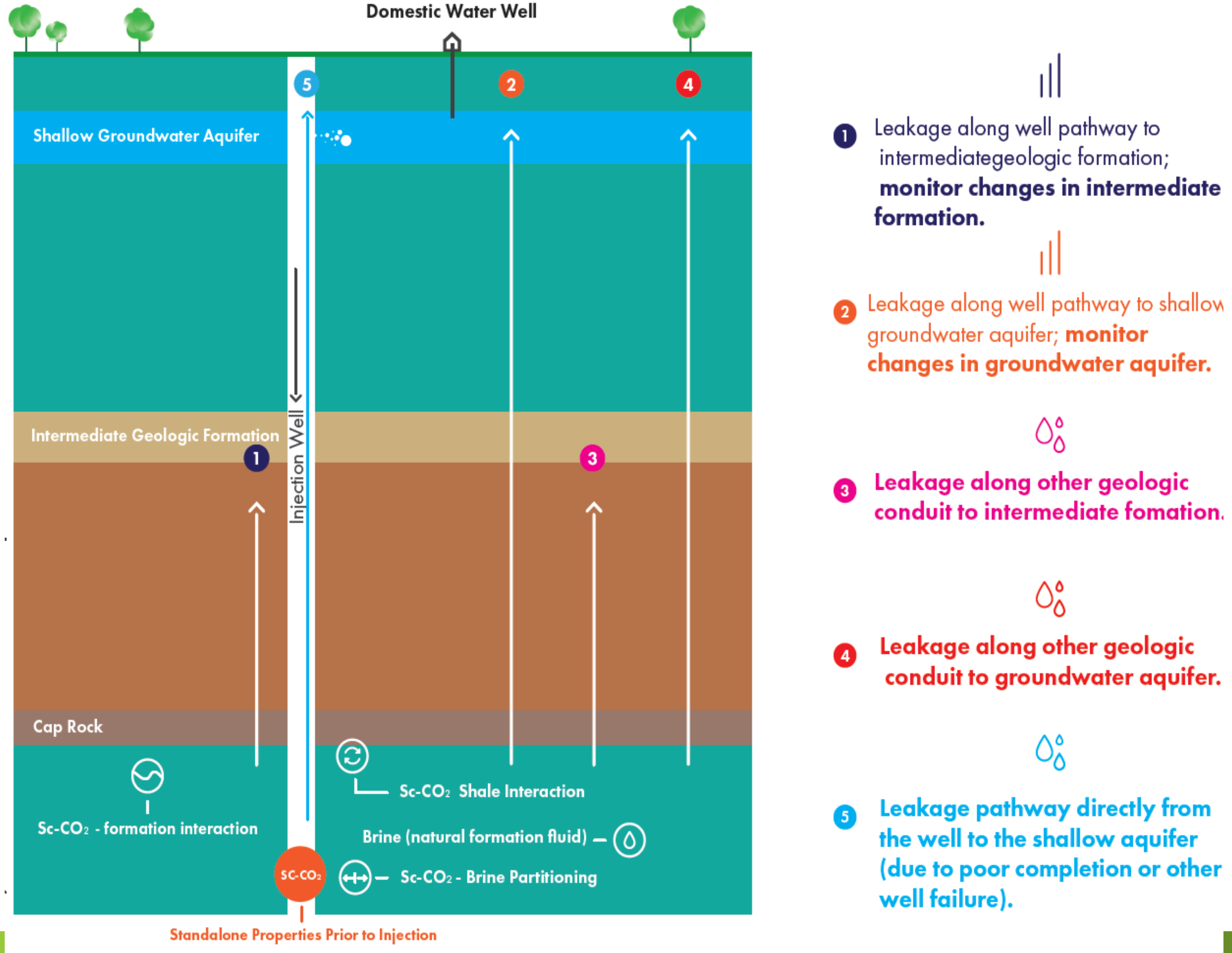
Determine statistical correlations between changes in chemistry to account for mixing under different flow scenarios/leakage pathways.

- ➢ Robust statistical analysis of potential geochemical signals (Mitch Small & CMU team)

Develop the process-based framework (w/ Katherine Romanak, UT-BEG)

- ➢ Utilize ilr of field data or historical data from different sites to aid in determining appropriate processes (& signals) for the different potential leakage pathways

What are the data gaps that require additional experimental or statistical analysis?



Synergy Opportunities

- Sample & data sharing – bulk geochemical and isotopic analyses (as available) for a wide range of geologic storage systems (sandstone-based, carbonate-based, different types of caprocks)
- Work towards identifying signals/processes for different leakage pathway scenarios
- Continued field-based collaboration to test new geochemical monitoring techniques, signals, and tools under different CO_2 storage conditions
  - Natural analogs
  - Controlled release sites
  - EOR field systems

NETL researcher, Hank Edenborn (NETL) at the Brackenridge Field Site (Austin, TX)

Accomplishments to Date

- B isotope da collected to develop insights on applicability of B isotopes for monitoring CO_2 migration, and on developing laboratory-based rapid-screening analyses for dissolved solutes in high-TDS brines
- Researchers incorporated April 2018 sampling trip data (Figure 21-1) into Seminole data set (rounding out the 5-year sampling). This data will be included in the manuscript to be submitted to *Applied Geochemistry* (in preparation).
- Completed all analysis and interpretation of oxygen, hydrogen, and carbon isotope data from East Seminole.
- Gardiner, J., Thomas, R.B., Phan, T., Stuckman, M., Spaulding, R., Lopano, C., and Hakala, J.A., "Geochemical Variation of Produced Waters and Overlying Groundwaters at an Active CO_2 Enhanced Oil Recovery Field in the Permian Basin Central Platform," TRS Report, submitted to Rights in Data on March 29, 2019 and approval received on April 4, 2019.
  - The TRS Report will be publicly released after peer reviewed manuscript released

Accomplishments to Date

- FY19 work focused on evaluating “What is a Baseline?”
- This work entailed processing and compilation of years of background, injection, and post-injection geochemical signals from an EOR site in East Seminole, Texas, to develop a promising evaluation of what a “baseline” is in a producing formation (Permian Basin, Texas).
- Based on the results from this study, produced water intrusion into overlying groundwaters would be identifiable using certain general geochemical parameters (Alkalinity, TDS, Na^+, Ca^{2+}, K^+, Cl). The large differences between the produced water and overlying groundwaters is expected, but these parameters are discretionary geochemical signals that can indicate produced water intrusion.

Lessons Learned

- Research Gaps/Challenges: Natural Variability
- Field operators make changes on their time-table
  - Key = Talk to that site manager in the pick-up truck while you are sampling to pick up the anecdotal nuances of the EOR activities
- Real-world field-based scenarios can provide important insights for those developing and testing novel techniques or materials
- Challenges: Taking technologies from lab concept to field ready is a time-consuming, costly, and technically challenging process
- Work on synergistic opportunities to aid in making the leap

Appendix

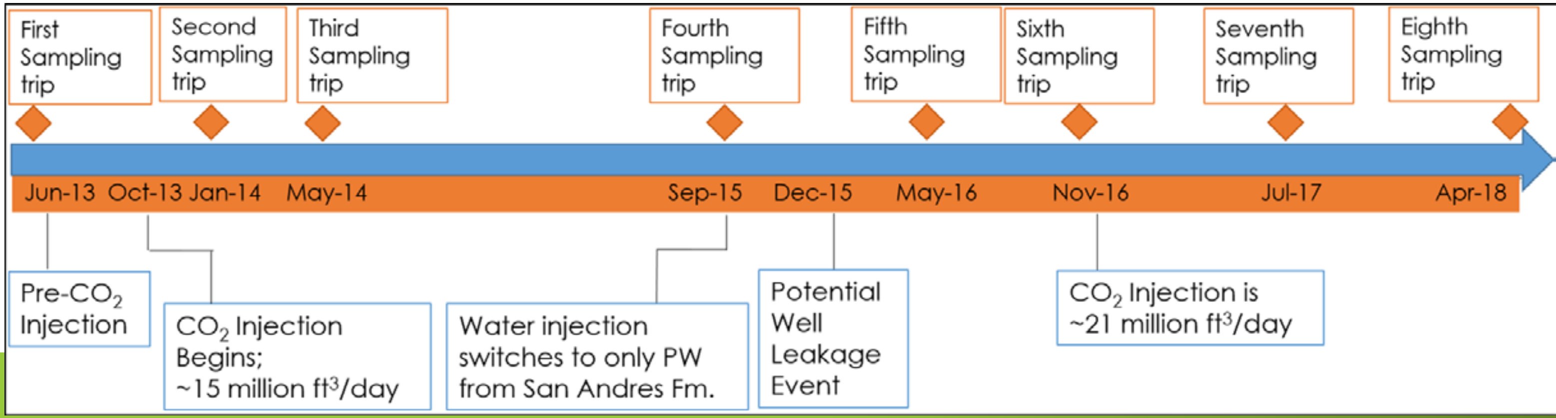
- These slides will not be discussed during the presentation, but are mandatory.

E. Seminole Site Background

Sampling trips (June 2013 – April 2018)

- CO_2 flooding began in October 2013
- Samples within 16 km^2
  - **San Andres** (~1630 m) PW; 12 wells, sampled 64 times
  - **Santa Rosa** (~460 m) GW; 1 well, sampled 7 times
  - **Ogallala** (~50 m) GW; 10 wells, sampled 45 times

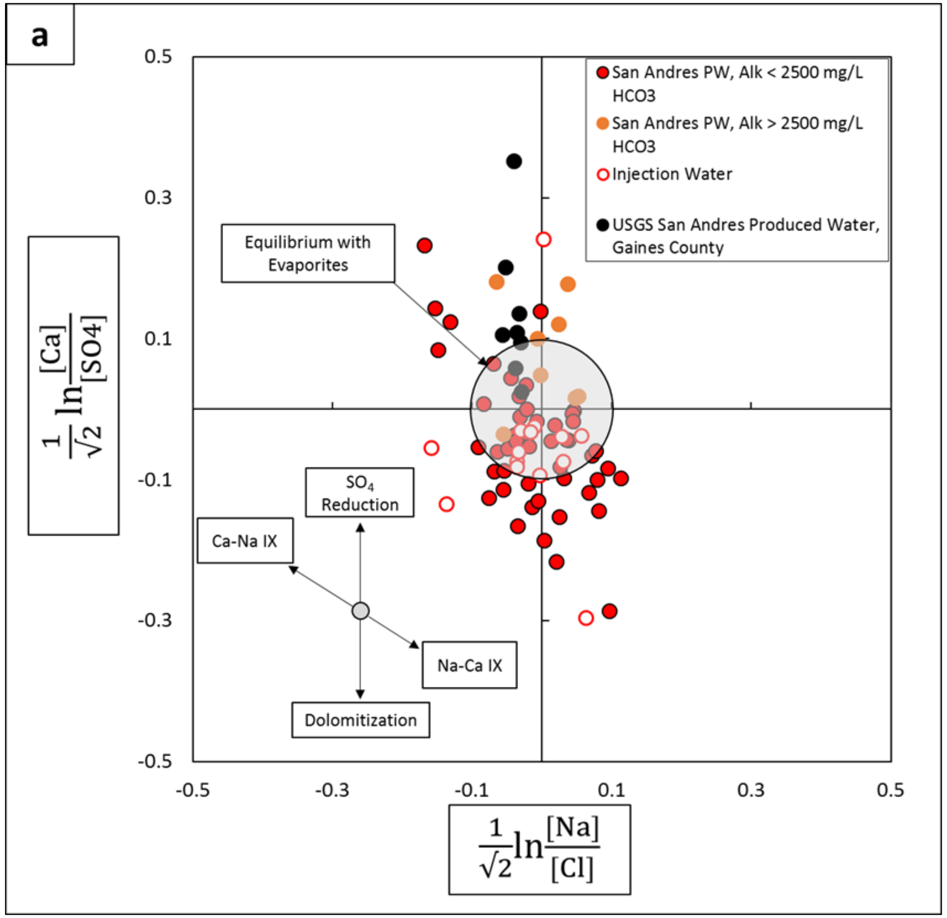
System	Series	Central Basin Platform Group/Formation	Lithology	Average Depth (m) of Samples at field area	Hydrostratigraphic Unit
Quaternary		Alluvium	Silty sand		
Tertiary	Upper	Ogallala	Fluvial and lacustrine clastics	~45-55	Evaporite Confining System
Cretaceous	Albian	Fredericksburg	Limestone		
		Antler / Paluxy	Sandstone		
Triassic	Upper	Dockum Group / Santa Rosa Fm.	Fluvial-deltaic and lacustrine clastics	~460	
Permian	Ochoan	Dewey Lake	Halite, Anhydr., Sylvite		
		Rustler			
		Salado			
		Tansill			
	Guadalupian	Yates	Sandstone and Anhydrite		Deep Basin Aquifer System
		Seven Rivers			
		Queen			
		Grayburg			
		Upper San Andres	Dolomite	~1630	
		Lower San Andres			
	Leonardian	Holt	Limestone and Dolomite		
		Glorieta			
		Clear Fork Group			
		Wichita			
	Wolfcampian	Wolfcamp	Shale, carbonates		



Challenge: Signals? What signals?

Results of CO_2 incursions or variable field operations

- How to "normalize" for variable operator procedures in the field?
  - Water, gas flooding over time
  - Case study – East Seminole site
  - Compare to historical data
- It's all salty....what are real correlations?
  - Utilize isometric log ratios (ilr) (Blondes et al 2015) – adjust for correlation errors induced by fluid mixing between fluids of differing ionic strength.
    - a type of Compositional Data Analysis (CoDA) that addresses geochemical inaccuracies in high salinity waters (Blondes et al., 2015)
    - Use the ilr to aid in distinguishing statistically pertinent "Processes"



Benefit to Program

Goals & Benefits

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.*

Project Overview

Goals & Objectives

- The objectives of this project are to develop reliable approaches for measuring geochemical tracers in brines (and other solutions with elevated total dissolved solids [TDS] content), and to develop approaches for verifying whether field-measured geochemical tracers indicate a specific type of leak from carbon storage reservoirs into shallow formations. The goal is to develop a rapid screening and analysis approach for determining if a CO_2 or brine leak has occurred, and the cause of the leak (breach in the caprock; leakage along a wellbore; etc.).
- The products of this work are: analytical chemistry-based methods for measuring geochemical tracers in solutions high in TDS and CO_2; laboratory-based verification of new geochemical tracers for monitoring carbon storage sites; field sampling; matrix of key aqueous geochemical signals that provide expected multiproxy “fingerprints” of geological carbon storage (GCS) that assure permanent carbon storage in a wide range of storage formations and conditions.

Organization Chart

Describe project team, organization, and participants.

- Link organizations, if more than one, to general project efforts (i.e., materials development, pilot unit operation, management, cost analysis, etc.).

Please limit company specific information to that relevant to achieving project goals and objectives.

Table of Personnel

Tasks 20 and 21, Carbon Storage Portfolio

Team Member	Organization	Expertise	Contribution	Task/Subtask (per timeline)
Alexandra Hakala	NETL-RIC Pgh	Aqueous, Redox, and Organic Geochemistry	PI Task 20, Team member Task 21,RP for Brine Chem Lab and Redox Geochem Lab, Geochemist providing project direction and interpretation of data for tasks listed in next column	20.1.1 (Isotope Lab Methods), 20.1.2 (Electrochemical Signals), 20.1.4 (Rapid Screening Tool), 20.2.1 (Boron Experiments, 20.3.1 (E. Seminole and Emma); Task 21
Christina Lopano	NETL-RIC Pgh	Mineralogy, Inorganic Chemistry	PI Task 21, Team Member Task 20, Geochemist providing project direction and interpretation of data for tasks listed in next column	20.2.1 (Boron Experiments), 20.3.1 (E.Seminole and Emma); Task 21
James Gardiner	LRST (NETL-RIC Pgh)	Isotope and Inorganic Geochemistry, Geology	Team Member Tasks 20 and 21. Field trip coordination, data compilation and analysis, reporting (conferences and journal articles); Coordinating data to be modeled in Task 21	20.3 (All subtasks); Task 21
Burt Thomas	AECOM (NETL-RIC Alb)	Organic/inorganic Biogeochemistry and Geology; Former USGS with experience in CS	Team Member Tasks 20 and 21. Field trip coordination, data compilation and analysis, reporting (conferences and journal articles); Coordinating data	20.2.1 (Boron experiments), 20.3 (All subtasks); Task 21

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Tasks 20 and 21, Carbon Storage Portfolio

Team Member	Organization	Expertise	Contribution	Task/Subtask (per timeline)
Mengling Stuckman	AECOM (NETL-RIC Pgh)	Environmental Geochemistry and Microbiology	Team Member Task 20. coordinates analyses for IC and TOC; field sampling coordination and logistics	20.1.4 (Rapid Screening), 20.3.1 (E. Seminole and Emma)
Brandon McAdams	ORISE (NETL-RIC Pgh)	Environmental Redox Geochemistry and Geology	Team Member Task 20. Developing electrochemistry-based tools for monitoring Fe and S species in field samples	20.1.2 (Electrochemical tools), 20.3 (Field sites as appropriate)
Rosemary Capo	University of Pittsburgh/LRST Sub-contractor	Isotope and Carbonate Geochemistry; MC-ICP-MS	Analysis of isotopes by MC-ICP-MS and instrument capability maintenance	20.1.1 (Isotope methods); 20.3 (Field samples)
Brian Stewart	University of Pittsburgh/LRST Sub-contractor	Isotope and Petrology Geochemistry; MC-ICP-MS	Analysis of isotopes by MC-ICP-MS and instrument capability maintenance	20.1.1 (Isotope methods); 20.3 (Field samples)
Robert Thompson	LRST (NETL-RIC Pgh)	Analytical Chemistry; HR-MS; MC-ICP-MS; ICP-MS	Inorganic fluid chemistry analysis by HR-MS & ICP-MS; isotope analysis by MC-ICP-MS	20.1.1 (Isotope methods); 20.3 (Field samples)

Table of Personnel

Tasks 20 and 21, Carbon Storage Portfolio

Team Member	Organization	Expertise	Contribution	Task/Subtask (per timeline)
Mitchell Small	Carnegie Mellon University/LRST Sub-contractor	Statistical analysis	Coordinate statistical analysis methods with NETL field data and researchers	Task 21
Jiaan Wang	Carnegie Mellon University/LRST Sub-contractor	Statistical analysis	Conduct statistical analyses on field data	Task 21
Katherine Romanak	UTBEG / LRST Sub-contractor	Geochemist	Expertise in the Permian Basin; Process-Based approach application to carbon storage systems	Task 21
Bob Dilmore	NETL-RIC Pgh	Environmental Engineering and NRAP Modeling Toolset	Application towards NRAP, developing risk assessment models using field data; input on process-based approach	Task 21