Novel Geochemical Signal Methodologies

FWP-1022403

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Carbon Management Research Project Review Meeting
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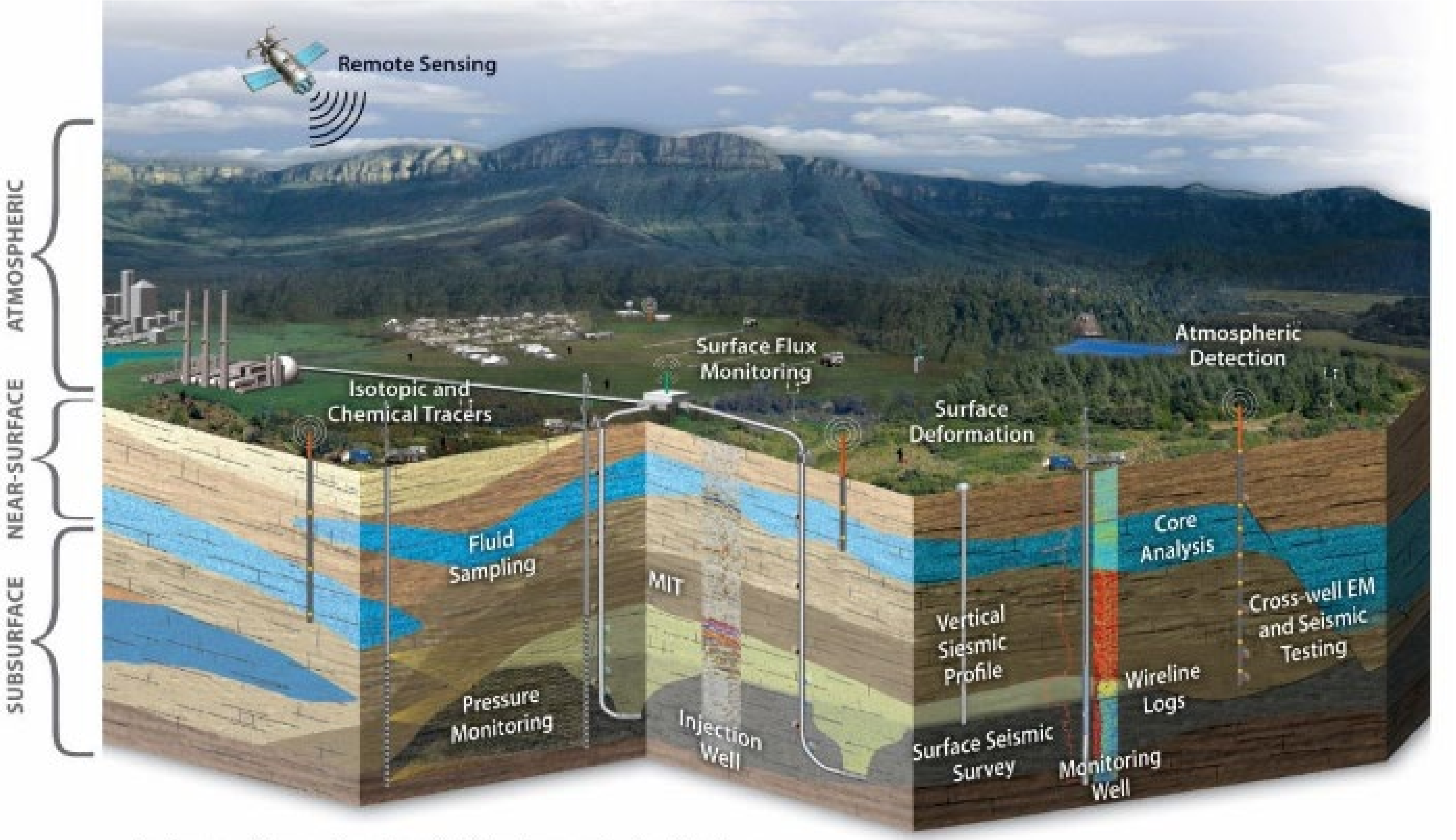
Need: Low-cost, easily implemented monitoring strategy for carbon storage reservoir leak detection

- Monitoring costs associated with CO_2 storage are projected to be **3 – 20%** of the operational costs of a geological carbon storage site.[1]
- **Injected chemical tracers** are demonstrated to provide a low-cost and reliable option for monitoring and quantifying migration of CO_2 from the primary storage reservoir.[2]
- **What if naturally-occurring chemical analytes could be used for low-cost, early detection of CO_2 and brine migration events?**



Background Image Courtesy of Schlumberger Carbon Services

[1]Calculated from values presented in Rubin et al., IJGHGC, 2015, 40, 378-400
[2]Roberts et al., IJGHGC, 2017, 65, 218-234

Image copied from: https://www.netl.doe.gov/coal/carbon-storage/advanced-storage-r-d/monitoring-verification-accounting-and-assessment

Geochemical Monitoring of Groundwater Impacts – Novel Geochemical Signal Methodologies Summary

NETL-RIC Advanced Storage (Task 21)

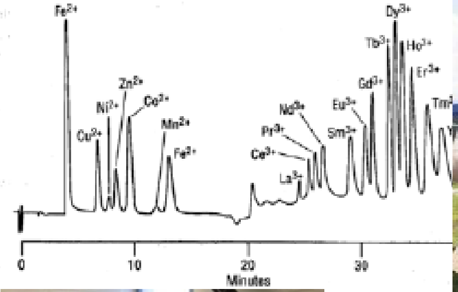
Prior Year Results (Tasks 20 & 21)

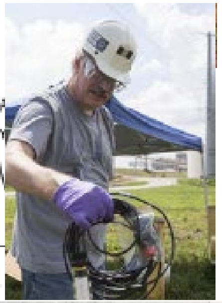
New Lab- and Field-Based Chemical Analysis
- Reduced analytical time and increased confidence in data from high-salinity bines = lower cost for monitoring
- Isotope techniques (Sr, Li, Ba, B)
- Metals by Ion Chromatography
- Direct field monitoring (CO_2, Fe, S)

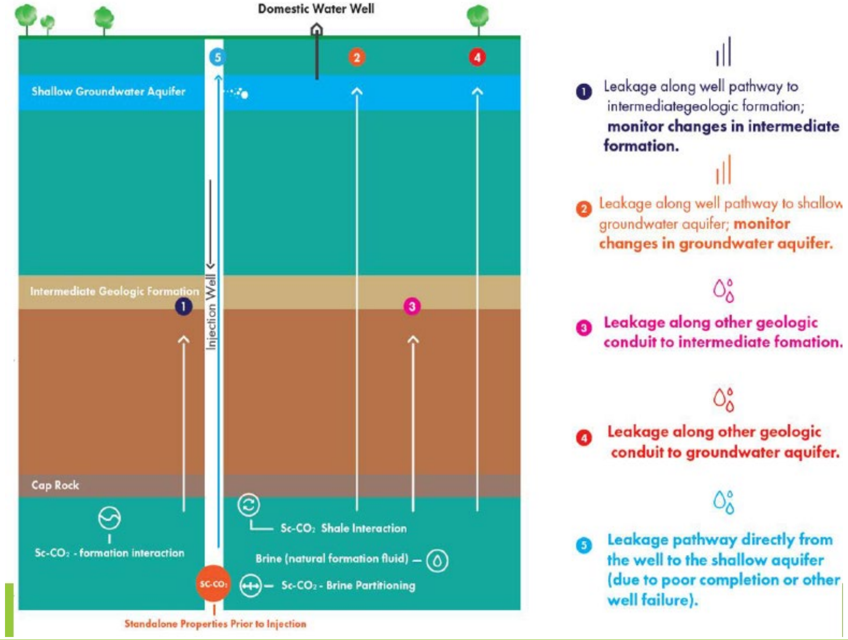
Robust Field Data Sets
- Two CO_2-EOR sites with multiple geologic formations monitored (3y)
- Comprehensive statistical analysis to identify mixing trends
- Identified of major geochemical signals that will indicate CO_2 migration into shallower formations

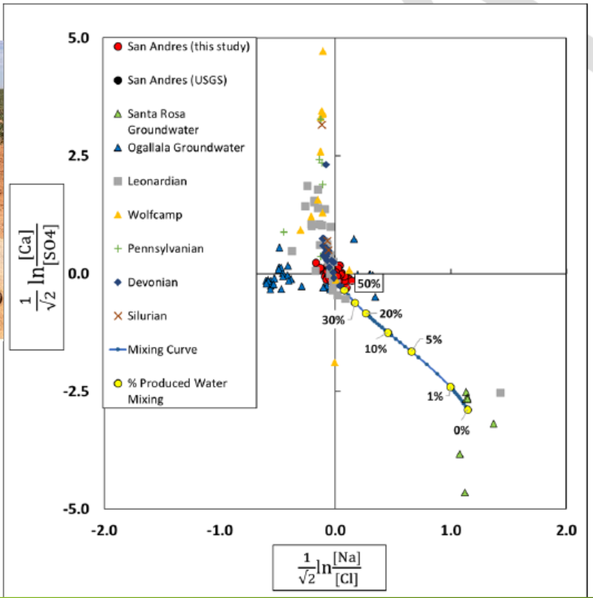
Task 21 EY20 – 21 Focus

<u>Final Product:</u> Predictive Model for Geochemistry-Based Early Leak Detection
- Merge key geochemical reactions identified with statistical approach
- Use to develop low-cost monitoring strategies *where chemistry can ID issues not detectable by other techniques*





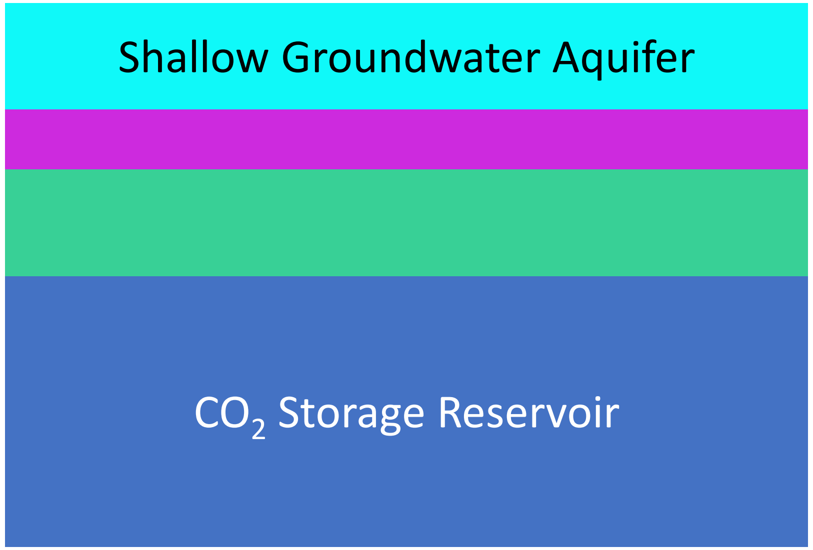




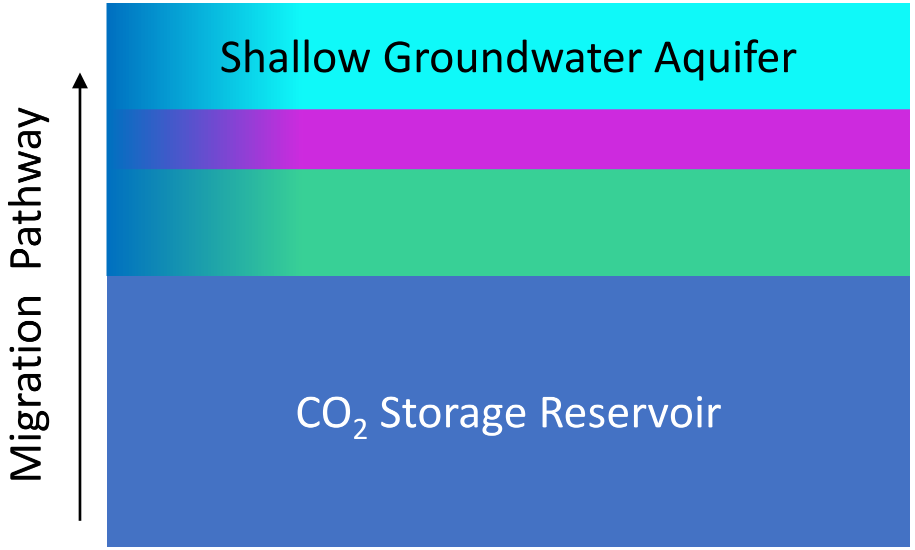
Opportunity 1: Leverage difference in chemistry between geologic formations to identify fluid mixing events

If chemical constituents from the storage reservoir are detected in an intermediate reservoir, or shallow groundwater aquifer, then a CO_2 or brine migration event may have occurred.

Original Condition: Distinct chemical composition between geologic units



CO_2 or Brine Migration: Overlying geologic units show chemical signatures similar to primary storage reservoir that differ from the original condition.



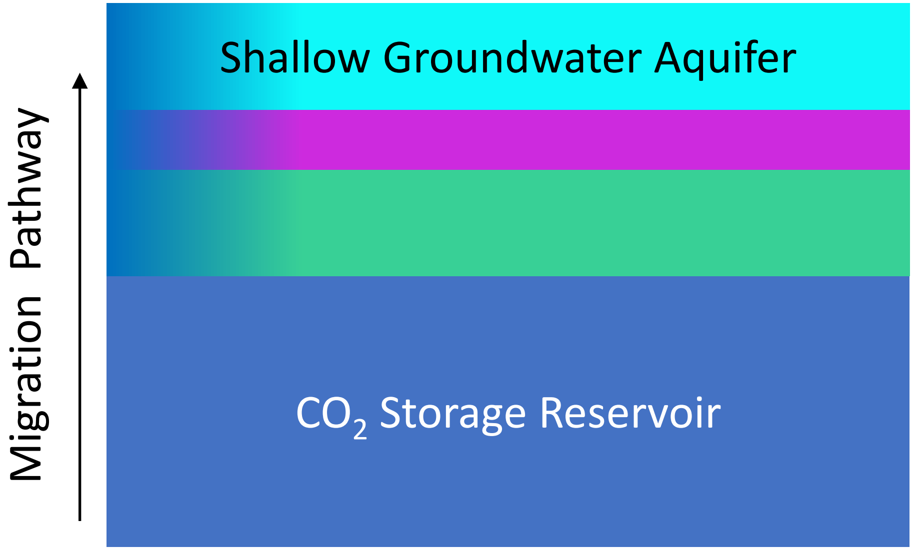
Challenge: What if the major aqueous chemical signatures between formations are similar or influenced by multiple processes?

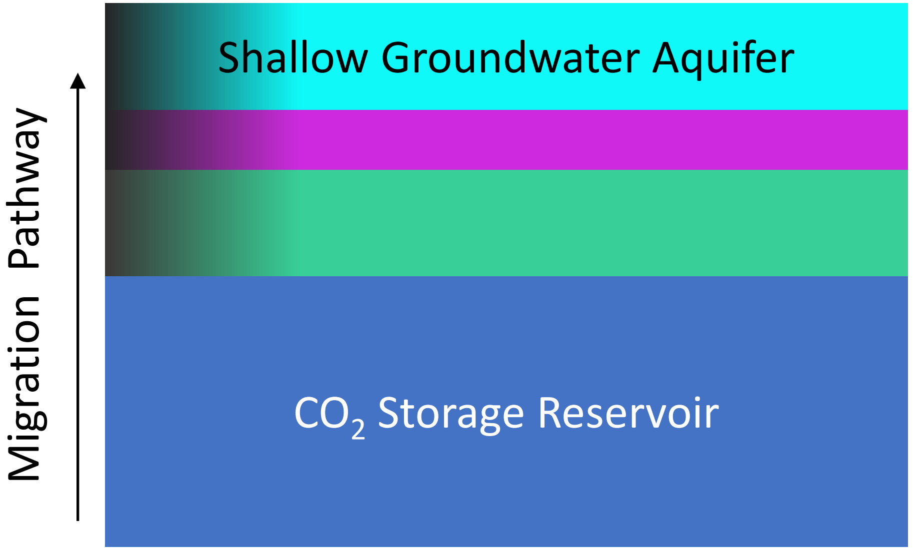
Opportunity 2: Leverage knowledge of CO_2-reservoir geochemical reactions to improve certainty of fluid source

If chemical signatures specific to CO_2-impacted reservoir fluids are detected in overlying formations, then there is likelihood that a migration occurred.

CO_2 Reservoir Origin: CO_2 and brine are expected to carry chemical signatures associated with the reservoir, that are transferred to the receptor geologic formation.

Other Origin: Sudden changes in chemical composition in overlying geologic units do not carry reservoir-specific chemical signatures.



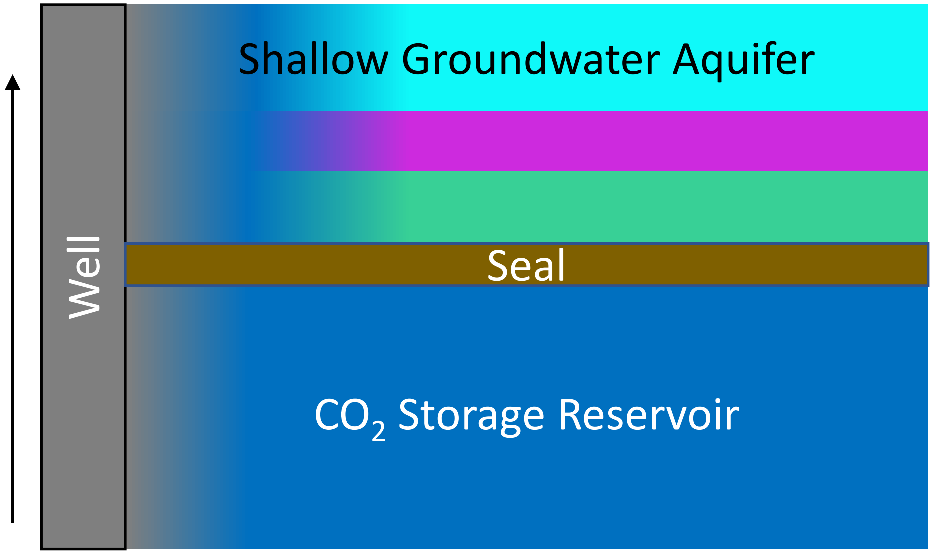


Challenge: Can we identify the migration pathway?

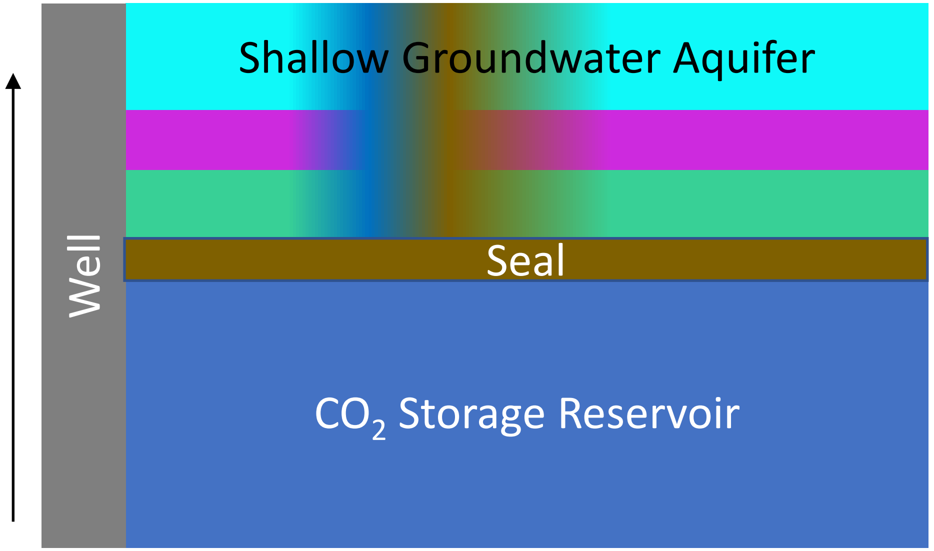
Opportunity 3: Leverage knowledge of geochemical reaction paths along different migration pathways to identify the source

If chemical signatures specific to certain migration pathways (e.g., along the well, or via fractures in the seal) are known, then mitigation techniques specific to those pathways may be developed to ensure long-term storage permanence and environmental sustainability.

Migration along well: CO_2 and brine are expected to carry chemical signatures associated with the **reservoir and well** that are transferred to the receptor geologic formation.



Migration across seal: CO_2 and brine are expected to carry chemical signatures associated with the **reservoir and seal** that are transferred to the receptor geologic formation.

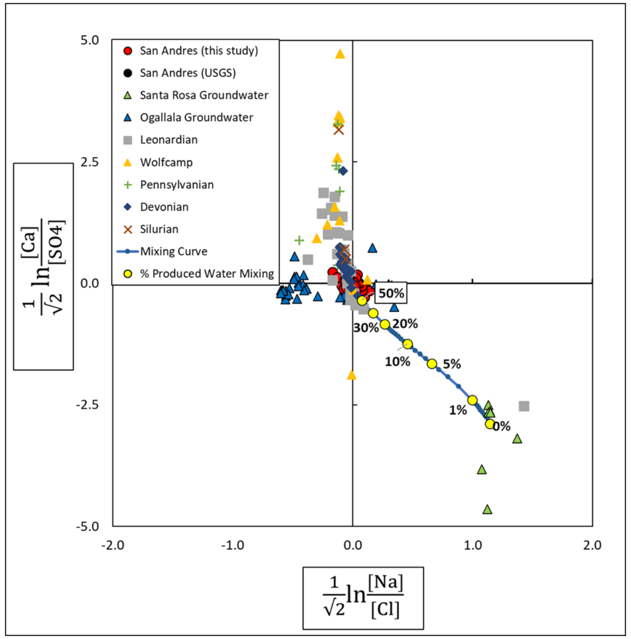


Challenge: Which signals indicate specific migration pathways for unique CS reservoirs?

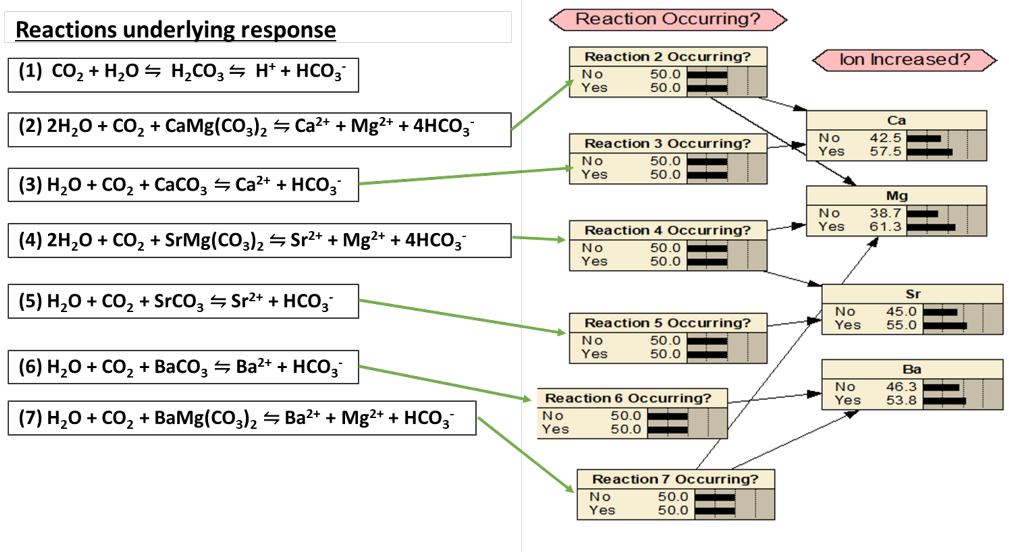
Early-stage geochemistry-based leak detection

Characterizing what a geochemical signal looks like under CO_2/brine leakage scenarios

1. Characterize expected signals of brine migration between geologic formations – mixing models developed with field data



2. Identify which combinations of chemical signatures indicate CO_2 migration – geochemical-statistical model to identify the probability that a leak occurred using common geochemical parameters

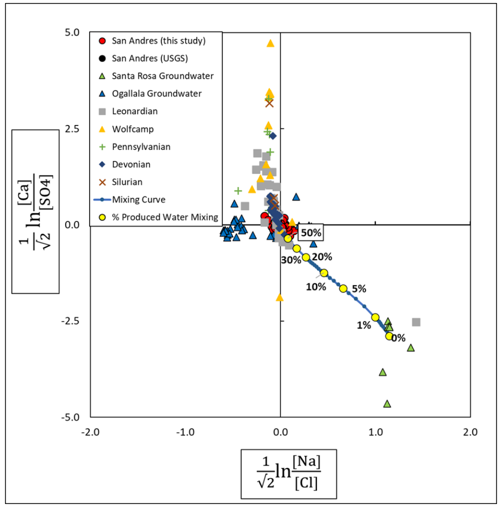


Approaches for geochemistry-based leak detection

- Identify which chemical tracers can: A) be reliably identified and measured in field samples with techniques of varied time and cost, and B) can be used to identify major processes that may occur during CO_2 and brine leakage

Completed

Application of Field Data from Permian Basin CO_2-EOR Sites to Quantify Operational Baseline and Fluid Mixing



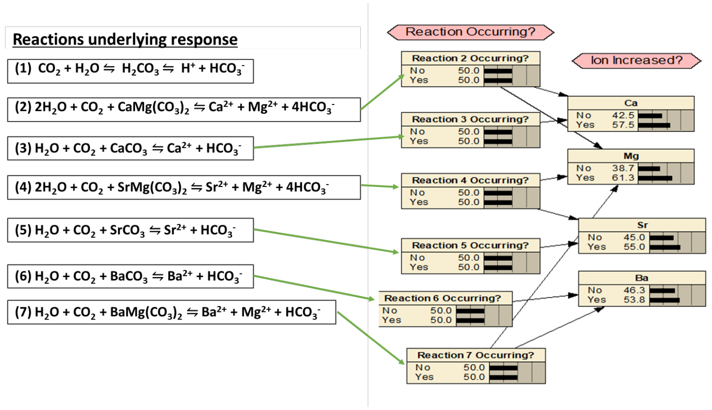
Completed

Development of Reaction Matrix for Testing with Bayesian Belief Network Statistical Modeling

	A	B	C	D	E	F
	Reaction Pathways	**Base Case Brine**	**Base Case Brine + CO_2**	**Mechanisms Underlying Responses**	**Parameters related to Leakage Pathway**	**Confidence in Detecting Change**
1	Dolomite (1° res.) → Wellbore migration	Equilibrium with formation	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Cement dissolution	·Dissolved ions [Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}] ·Barium and strontium isotopes	·TBD using Bayesian Belief Network
2	Dolomite (1° res.) → Shale (seal) → Overlying Units	Box B1 + Shale Rxns	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Shale dissolution	·Dissolved ions [Ca^{2+}, Mg^{2+}, Sr^{2+}] ·Strontium isotopes	·TBD using Bayesian Belief Network
3	Sandstone (1° res.) → Wellbore migration	Equilibrium with formation	CO_2 Induced Water-Rock Rxns	·Silica dissolution ·Cement dissolution	·Dissolved ions [Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}] ·Barium strontium isotopes	·TBD using Bayesian Belief Network
4	Sandstone (1° res.) → Shale (seal) → Overlying Units	Box B3 + Shale Rxns	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Shale dissolution	·Dissolved ions [Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}] ·Strontium isotopes	·TBD using Bayesian Belief Network

In Progress

Development of Bayesian Belief Network Statistical Model for Expected Signals from Migration Event



Monitoring geochemical changes at a CO_2-EOR site in West Texas, USA

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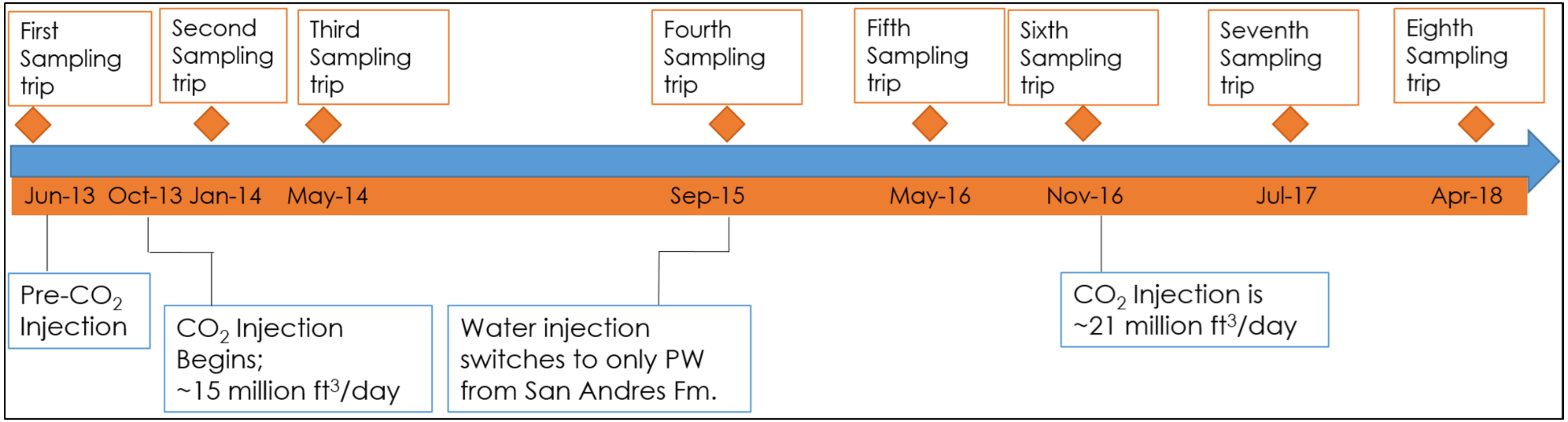
East Seminole Field Data



Opportunity to:

(1) Observe CO_2 induced changes in produced water
(2) Monitor overlying groundwaters for produced water intrusion

Potential Implications/Impact

(1) Understand CO_2 water-rock-interactions
(2) Develop applications of geochemical tools for monitoring, measurement, and verification

Gardiner et al., 2020, *App. Geochem.*

Major sampling zones for East Seminole field sampling

Target CO_2-EOR reservoir, Intermediate Formation, and Groundwater

System	Series	Central Basin Platform Group/Formation	Lithology	Average Depth (m) of Samples at field area	Hydrostratigraphic Unit
Quaternary		Alluvium	Silty sand		Evaporite Confining System
Tertiary	Upper	Ogallala	Fluvial and lacustrine clastics	~45-55	
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			
		San Andres	Dolomite	~1630	
	Leonardian	Holt	Limestone and Dolomite		
		Glorieta			
		Clear Fork Group			
		Wichita			
	Wolfcampian	Wolfcamp	Shelf limestones, minor shale		
Pennsylvanian		Cisco "Cline"			
		Canyon			
		Strawn			
		Atoka	Shale		
Mississippian		Barnett			
		Mississippian	Limestone		

Approach for identifying brine migration demonstrated through application of data transformation techniques to Permian Basin CO_2-EOR field results

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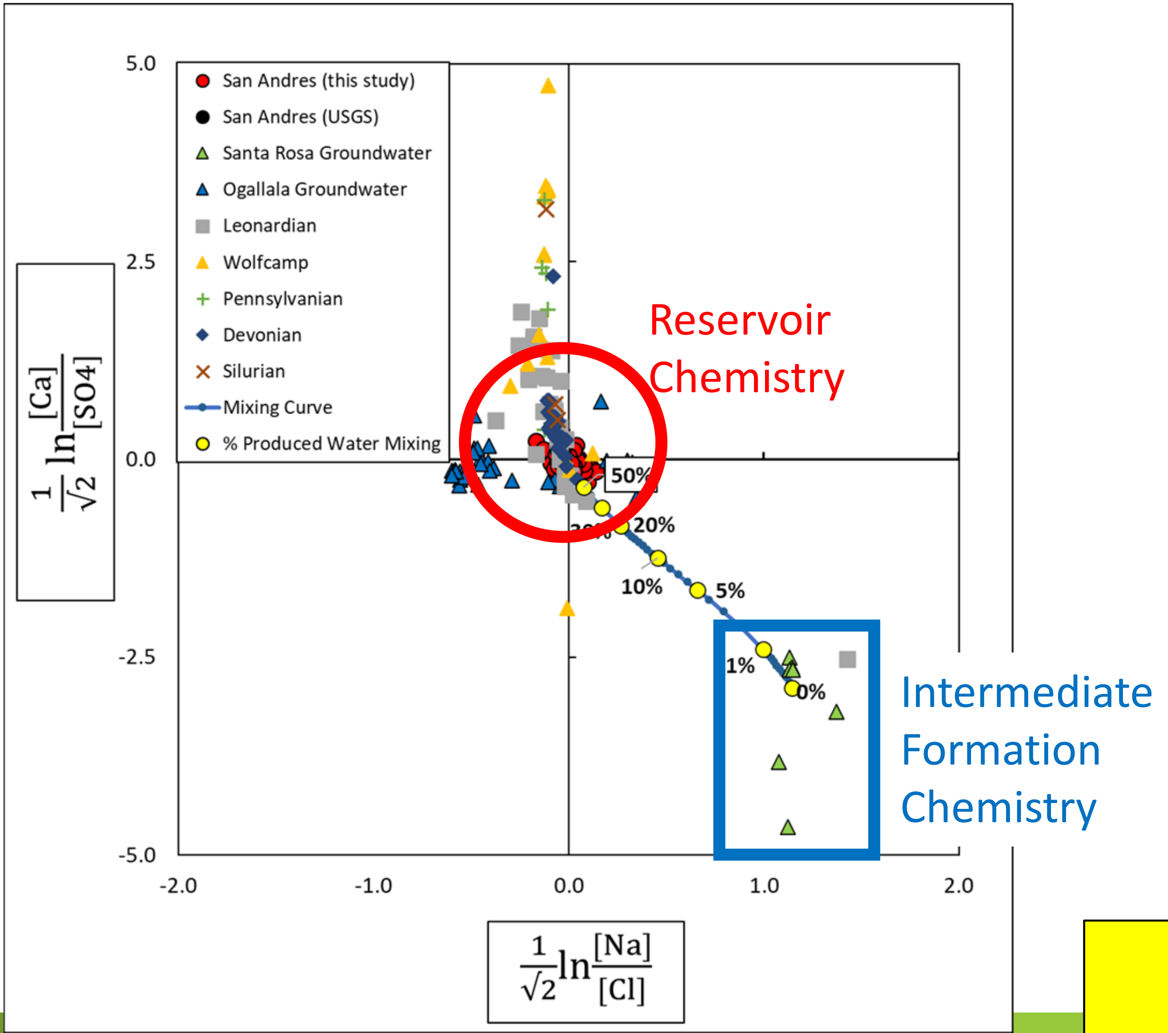


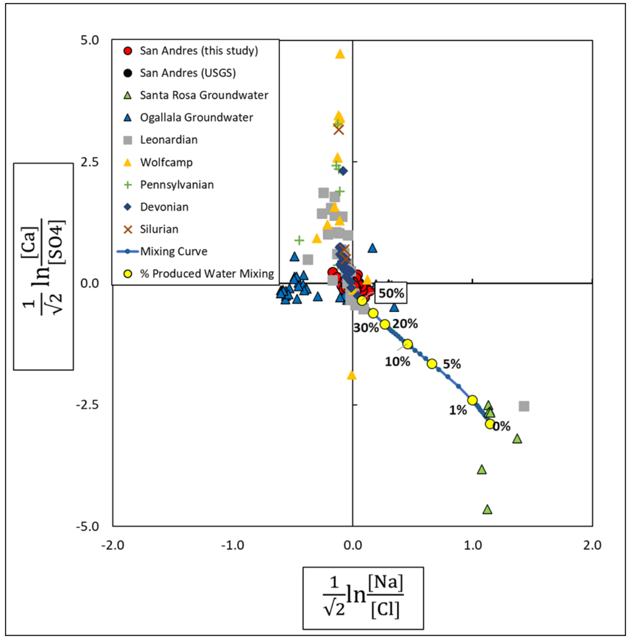
- **Low-cost analytical techniques leveraged to monitor chemical composition of water samples: Na^+, Ca^{2+}, K^+, Cl^-, alkalinity, and TDS**
- **Leakage into groundwaters could be detected using these parameters, however competing inputs of these ions from agriculture complicate signal interpretation**
- **Solution: Focus on an intermediate geologic formation, that already contains installed wells, for monitoring**
- ***Applying isometric-log ratios (ilr), a data transformation technique, provides a more robust source attribution tool***
  - Produced water (PW) ilr are consistent during CO_2 injection → stable tracer
  - PW ilr distinct from Santa Rosa groundwater

Small amount (5%) of reservoir mixing with overlying formation water would result in significant chemical shift

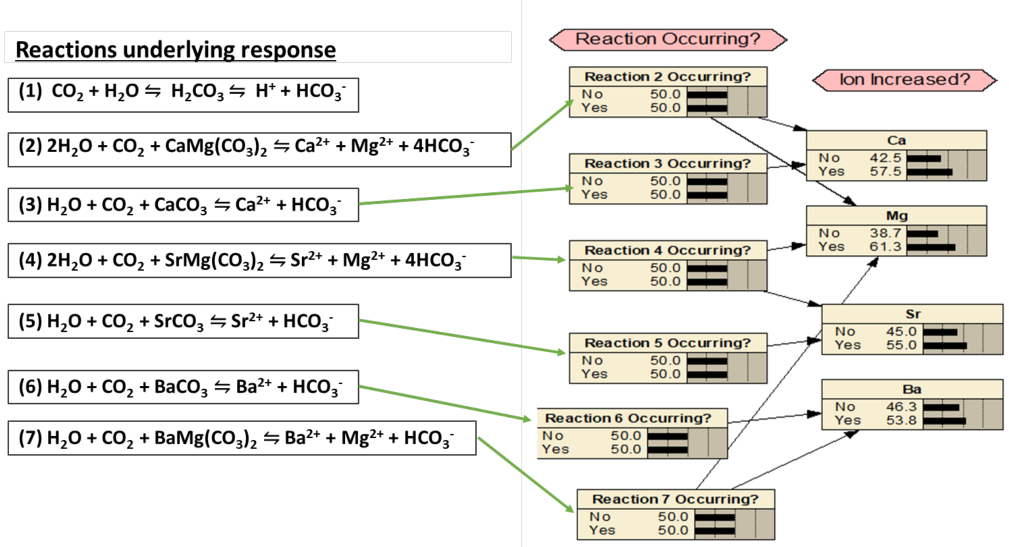
Early-stage geochemistry-based leak detection

Characterizing what a geochemical signal looks like under CO_2/brine leakage scenarios

1. Characterize expected signals of brine migration between geologic formations – mixing models developed with field data



2. Identify which combinations of chemical signatures indicate CO_2 migration – geochemical-statistical model to identify the probability that a leak occurred using common geochemical parameters



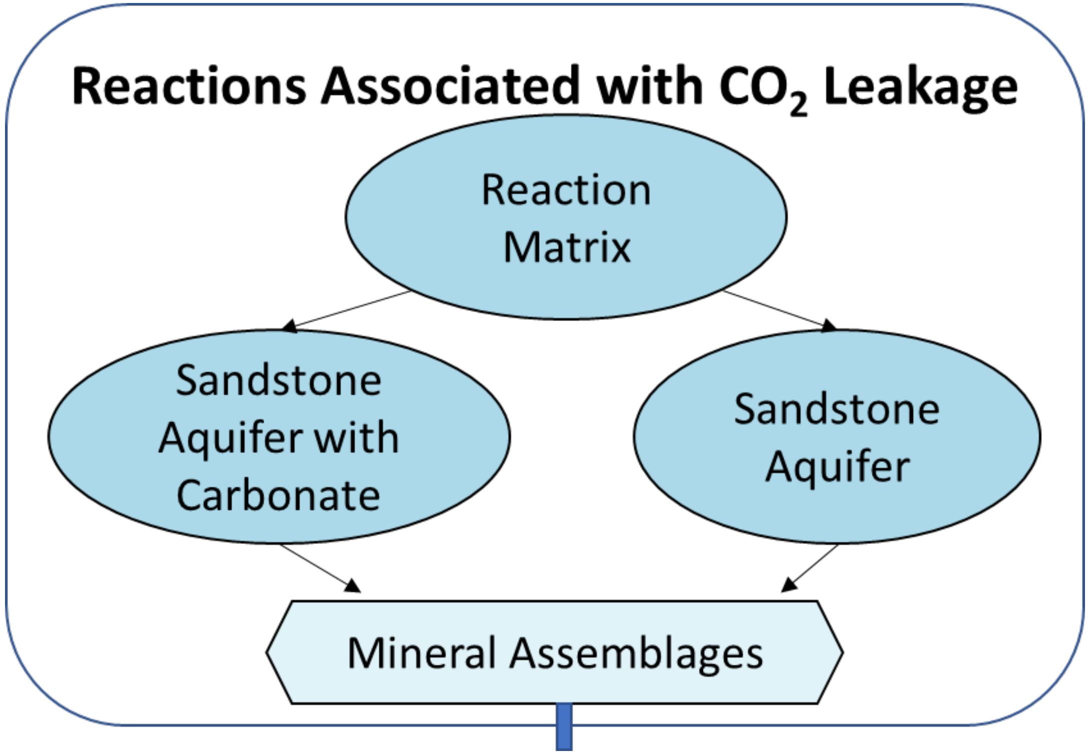
What does a leak look like (geochemically) and when do we need to do something about it?

Applying predicted geochemical reactions towards the statistical model

Identify which combinations of chemical signatures indicate CO_2 migration – geochemical-statistical model to identify the probability that a leak occurred using common geochemical parameters

Reactions Associated with CO_2 Leakage → **Leakage Event Simulation: Geochemical Reaction Path Model** → **Identifying CO_2 Leakage: Bayesian Belief Network**

Identified reaction matrix to represent dominant CO_2-sandstone aquifer reactions



- Reaction matrix identifies relevant CO_2-rock reactions
- Mineral assemblages emphasize abundant minerals
  - Geochemical parameters are sensitive to these reactions

Developing Predictive Model Based on Field Observations

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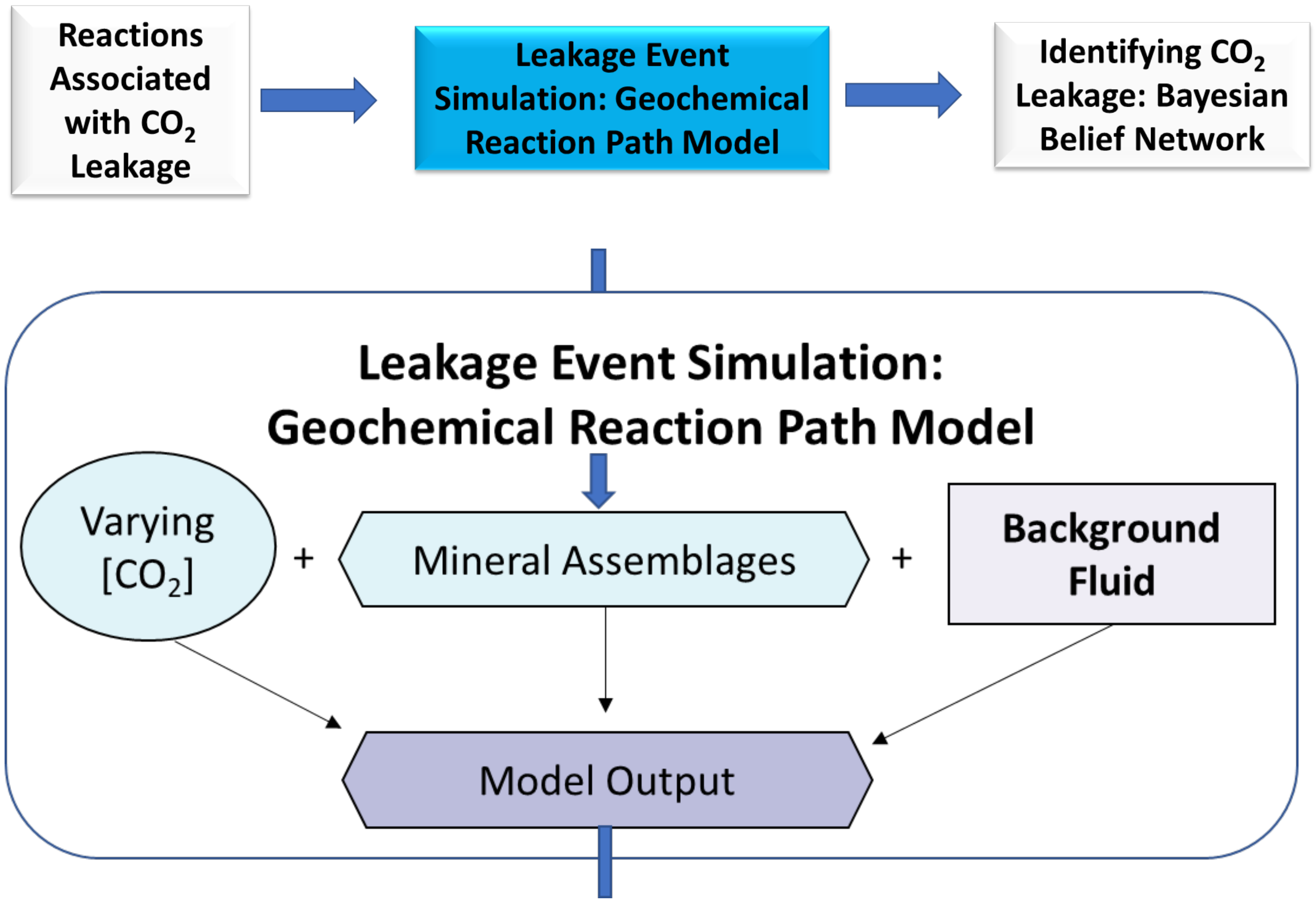
Step 1. Generating Reaction Matrix and Model based on Previous Research

	A	B	C	D	E	F
	Reaction Pathways	**Base Case Brine**	**Base Case Brine + CO_2**	**Mechanisms Underlying Responses**	**Parameters related to Leakage Pathway**	**Confidence in Detecting Change**
1	Dolomite (1° res.) → Wellbore migration	Equilibrium with formation	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Cement dissolution	·Dissolved ions [Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}] ·Barium and strontium isotopes	·TBD using Bayesian Belief Network
2	Dolomite (1° res.) → Shale (seal) → Overlying Units	Box B1 + Shale Rxns	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Shale dissolution	·Dissolved ions [Ca^{2+}, Mg^{2+}, Sr^{2+}] ·Strontium isotopes	·TBD using Bayesian Belief Network
3	Sandstone (1° res.) → Wellbore migration	Equilibrium with formation	CO_2 Induced Water-Rock Rxns	·Silica dissolution ·Cement dissolution	·Dissolved ions [Na^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}] ·Barium strontium isotopes	·TBD using Bayesian Belief Network
4	Sandstone (1° res.) → Shale (seal) → Overlying Units	Box B3 + Shale Rxns	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Shale dissolution	·Dissolved ions [Na^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}] ·Strontium isotopes	·TBD using Bayesian Belief Network

Calculated changes in water chemical signals based on CO_2 reaction with the defined reaction matrix



- 18 mineral assemblages tested, involving different amounts of:
  - carbonate (calcite), feldspar (albite and anorthite), mica (annite and phlogopite), and chlorite (ripidolite)
- Quartz and kaolinite included in all reactions as the major sandstone phases
- Each mineral assemblage first equilibrated with Santa Rosa groundwater average fluid data, then reacted with different concentrations of dissolved CO_2

Application of statistical model to identify when dissolved ion combinations could relate to CO_2 leak

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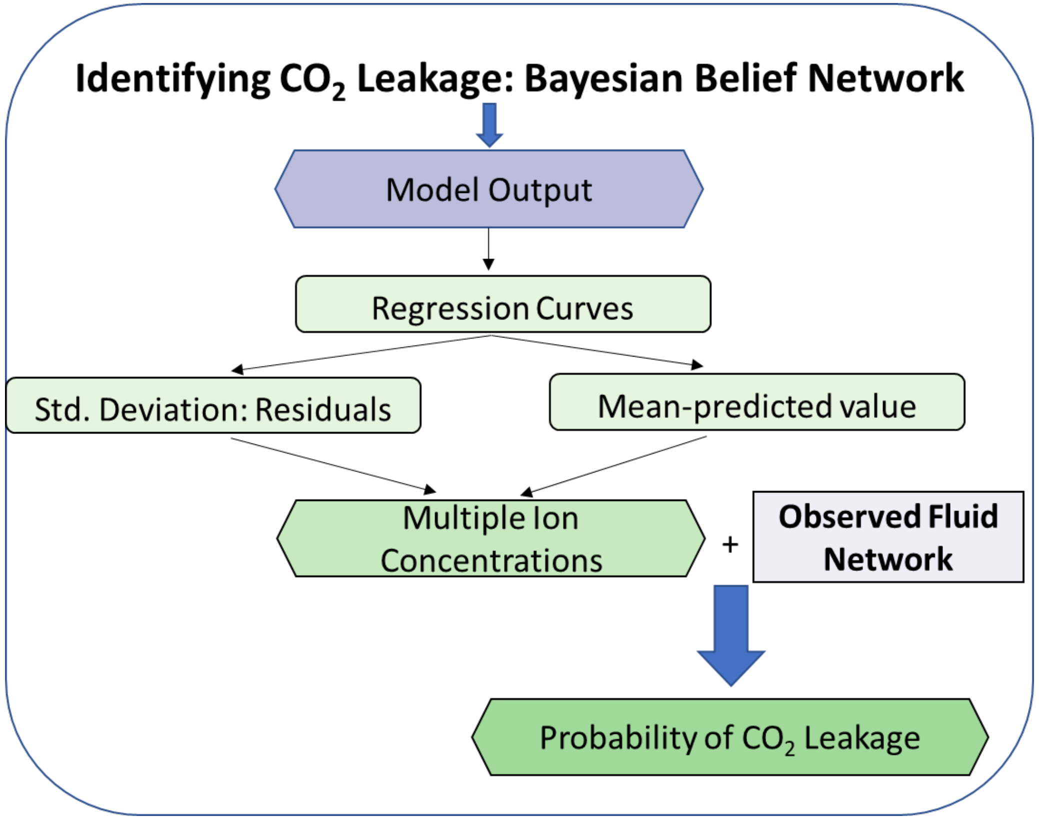
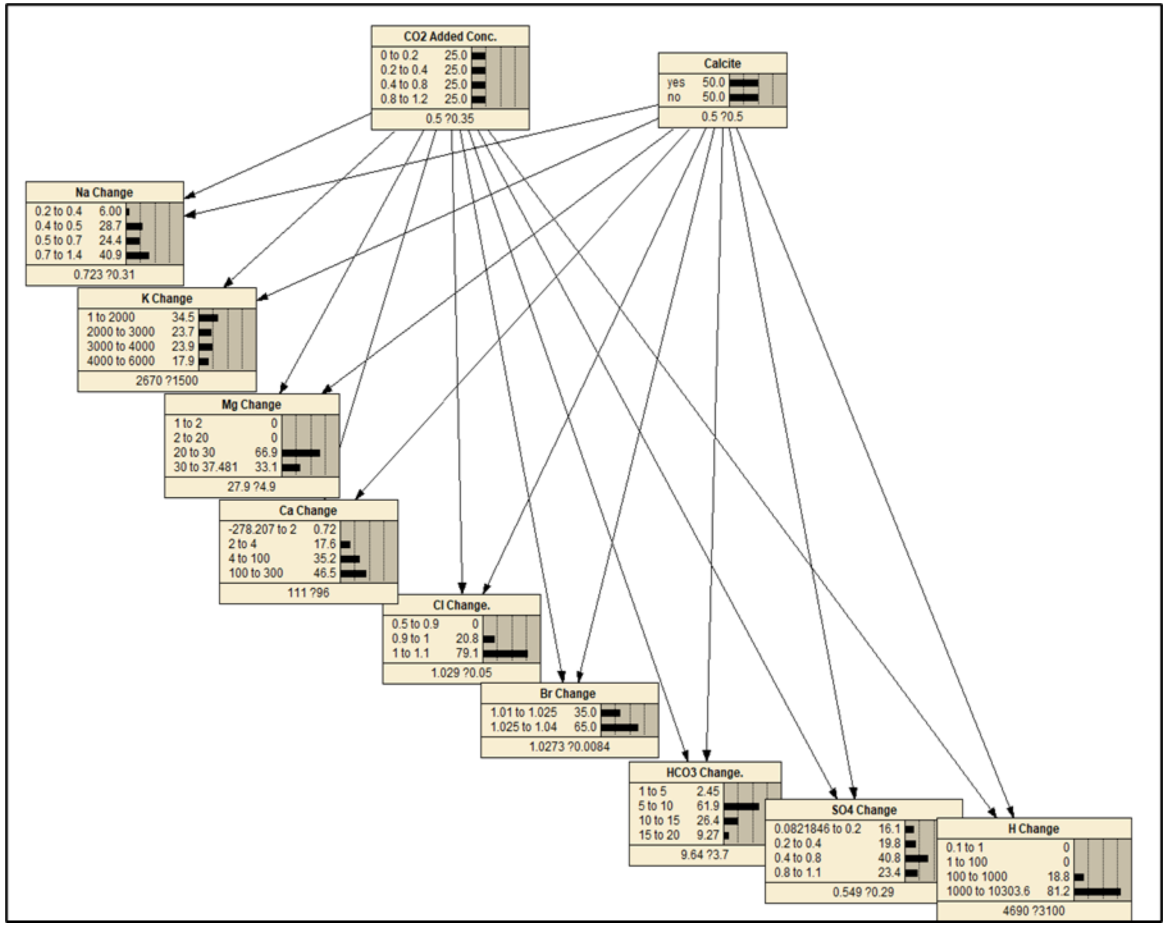
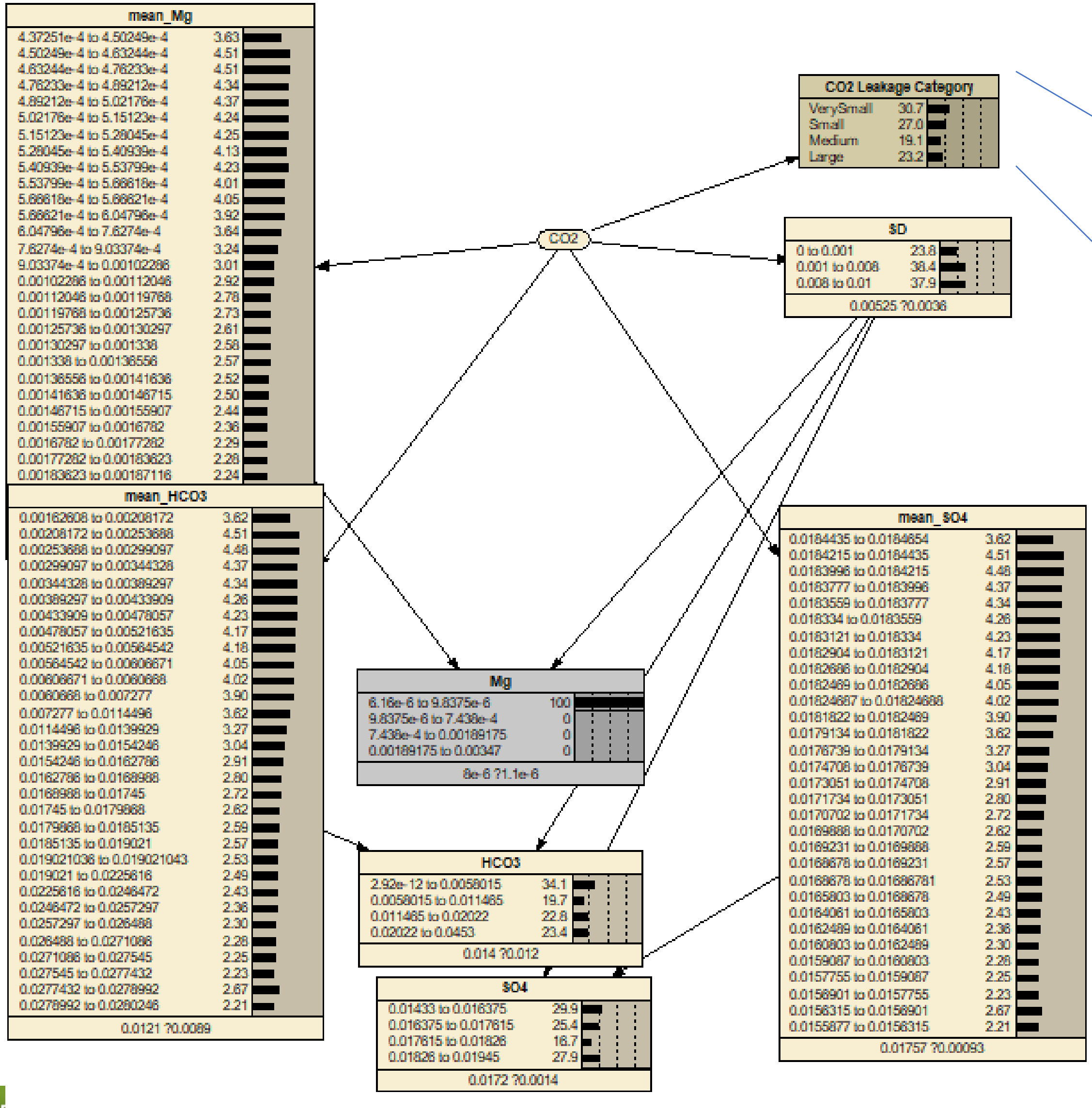
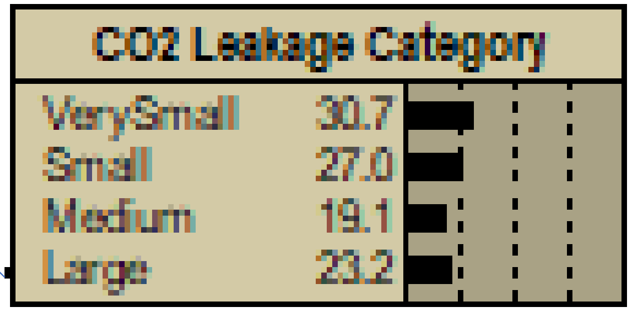
Reactions Associated with CO_2 Leakage → **Leakage Event Simulation: Geochemical Reaction Path Model** → **Identifying CO_2 Leakage: Bayesian Belief Network**





Using the Geochemical-Statistical model to identify priority parameters for monitoring – 1 Parameter Example

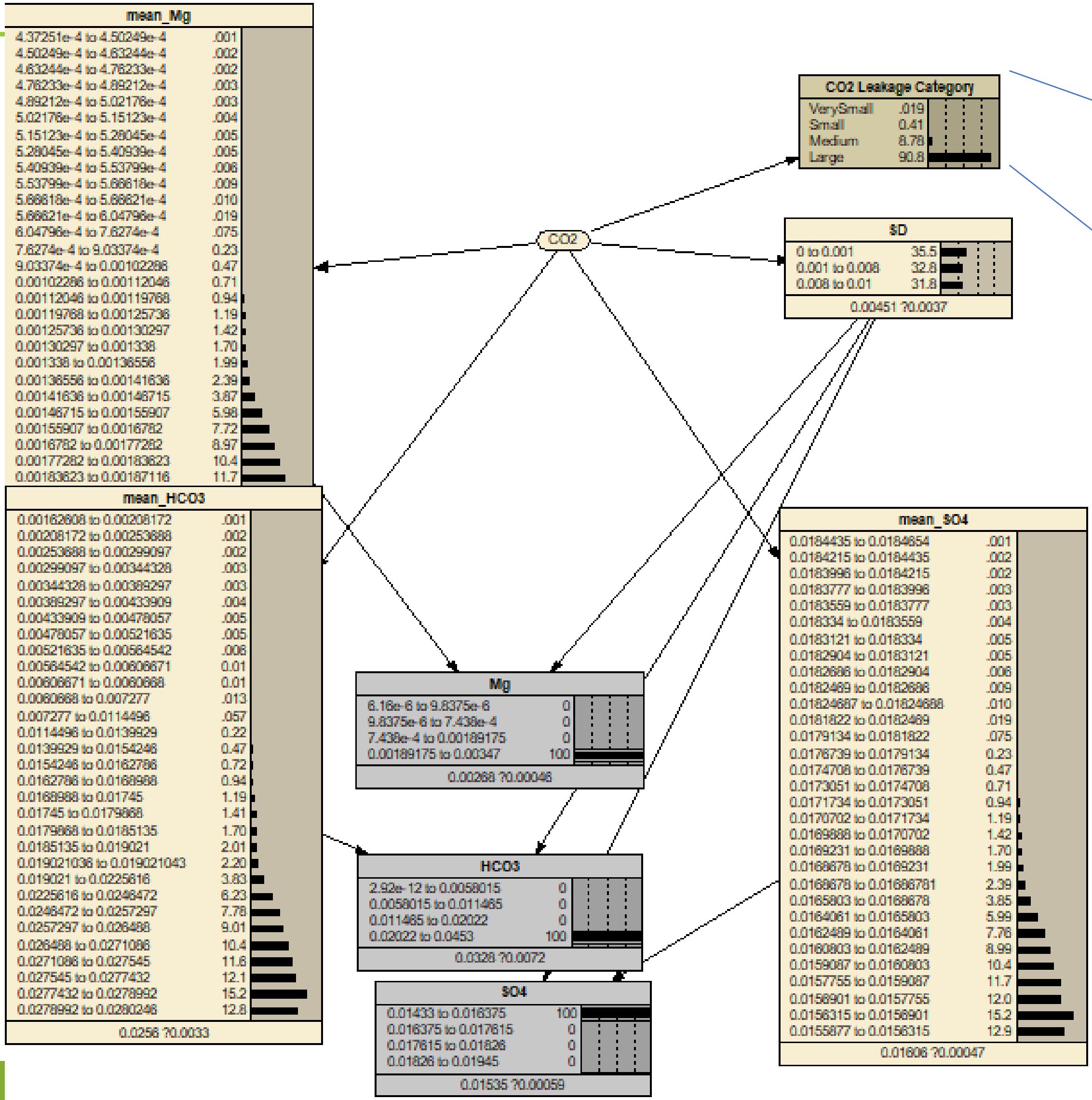


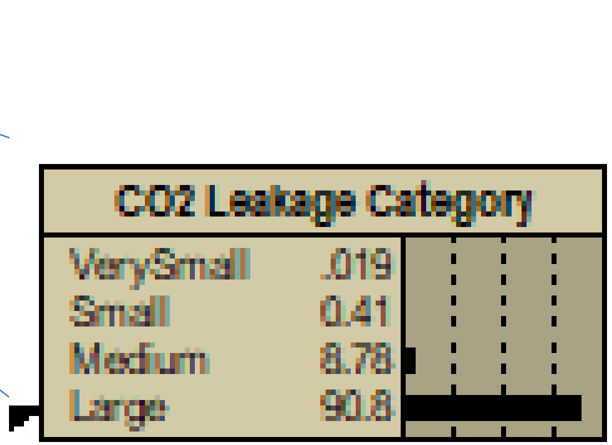


Example: Mg data input (only) from field data → inconclusive results

Bayesian Belief Network (BBN) model for leak inference with low magnesium concentrations.

Using the Geochemical-Statistical model to identify priority parameters for monitoring – 3 Parameter Example





Example: Mg^{2+}, HCO_3^-, and SO_4^{2-} data input (only) from field data → likely occurrence of large CO_2 leak

Lessons Learned & Synergy Opportunities

- **Lessons Learned**
  - CO_2 concentration alone may not provide information on "early leaks"
  - Simple geochemical parameters can provide a first-pass check on whether fluid communication or CO_2 leakage occurred
  - More advanced geochemical analytical techniques can be used to better pinpoint the cause for unwanted migration

- **Synergy Opportunities**
  - Apply isometric log ratio and the geochemical-statistical model at field demonstration sites
  - Interface with NRAP IAM

Develop Process-Based Statistical Models using Geochemistry-Based Tools

- Identify which chemical tracers can: A) be reliably identified and measured in field samples with techniques of varied time and cost, and B) can be used to identify major processes that may occur during CO_2 and brine leakage

Refine the Reaction Matrix for Testing with Bayesian Belief Network Statistical Modeling - incorporate ***isotope-based tracers*** as part of the decision tree of key aqueous species for identifying migration pathway

	A	B	C	D	E	F
	Reaction Pathways	**Base Case Brine**	**Base Case Brine + CO_2**	**Mechanisms Underlying Responses**	**Parameters related to Leakage Pathway**	**Confidence in Detecting Change**
1	Dolomite (1° res.) → Wellbore migration	Equilibrium with formation	CO_2 Induced Water-Rock Rxns	·Carbonate dissolution ·Cement dissolution	·Dissolved ions [Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}] ·Barium and strontium isotopes	·TBD using Bayesian Belief Network
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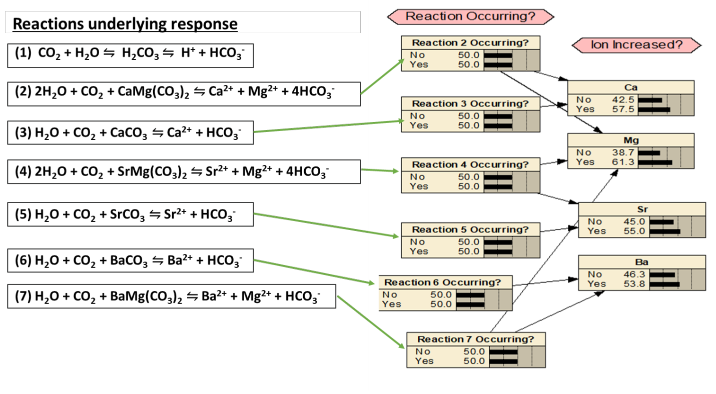
Demonstrate Application of Bayesian Belief Network Statistical Model for Expected Signals of a Migration Event



Key Products:

- 2020: Develop decision tree of key aqueous geochemical signals for identifying potential leakage points from carbon storage reservoirs to groundwater. (Completed)
- 2021: Demonstrate application of process-based model towards identifying the signals most important for monitoring leakage in a geologic system of interest. (Expected EY21-Q4)

Questions?

Thank you!

Contact: Alexandra.Hakala@netl.doe.gov

Acknowledgement: Research support from the Office of Clean Coal, Tabula Rasa Energy (field site access), private well owners for site access

Appendix 1

Products from CS Geochemistry-Based Monitoring R&D

Geochemical Monitoring of Groundwater Impacts – Novel Geochemical Signal Methodologies

Advanced Storage Task 21 Project – Total Project Value $ k

Products:

- 2020: Demonstrate hypothetical processes and signals in a carbonate system if migration occurs in a CO_2-EOR reservoir (Completed EY20-Q2)
- 2020: Develop decision tree of key aqueous geochemical signals for identifying potential leakage points from carbon storage reservoirs to groundwater. (Completed EY20-Q4)
- 2021: Demonstrate application of process-based model towards identifying the signals most important for monitoring leakage in a geologic system of interest. (Expected EY21-Q4)

Direct Sensing Chemical Analysis for CS Monitoring

Developed/Verified through CS Geochemistry-Based Monitoring Projects (2011 – 2017) & Task 20 (2017 – 2019)

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Geochemical Tracer	What it Shows	Evaluation Approach		Field Deployment Status	Technology Transfer	
Direct Monitoring Field-Based Techniques					**Published**	**In Progress**
Direct CO_2 Measurement in Shallow Wells	• Amount of dissolved CO_2 in groundwater via direct measurement	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR and natural analog sites	Field-tested		
Field-Based Electrochemical Sensors	• Presence and concentrations of dissolved iron and reduced sulfur species – identifies intrusion of fluids that impact local reservoir chemical conditions	Laboratory	Verified analytical techniques and applied to measuring iron and sulfur in samples collected at a natural analog site	Deployable (shallow monitoring); NETL-modified technique		• TRS report with details on electrode construction and field deployment
CarboQC for Direct CO_2 measurement	• Direct measurement of dissolved CO_2 through PVT technique	Laboratory + Field Assessment	Verified analytical techniques and tested in emergent groundwaters	Deployable; NETL-modified technique	Vesper and Edenborn, J. of Hydrol., 2012, 438-439	

Laboratory-Based Chemical Analysis of Field Samples for CS Monitoring

Developed/Verified through CS Geochemistry-Based Monitoring Projects (2011 – 2017) & Task 20 (2017 – 2019), Slide 1 of 5

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Geochemical Tracer	What it Shows	Evaluation Approach		Field Deployment Status	Technology Transfer	
Ion Chromatography-Based Techniques					**Published**	**In Progress**
Cations Li^+, Na^+, NH_4^+, K^+, Mg^+, Ca^+, Sr^{2+}, Ba^{2+}	• Screen major cations for large field sample sets within a few days – indicator of water source and whether additional tracers need to be analyzed for prediction/interpretation	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR and natural analog sites	Deployable; NETL-modified technique	• Gardiner et al. Applied Geochemistry (2020)	• NETL TRS describing use of ion chromatography to screen high-TDS field samples
Anions fluoride, chloride, nitrite, nitrate, bromide, bromate, phosphate, chromate, iodide, sulfate, thiosulfate, sulfite	• Screen major anions for large field sample sets within a few days – indicator of water source and whether additional tracers need to be analyzed for prediction/interpretation	Laboratory + Field Assessment	Verified analytical techniques and applied to field samples from CO_2-EOR site	Deployable; NETL-modified technique	• Gardiner et al. Applied Geochemistry (2020)	• NETL TRS describing use of ion chromatography to screen high-TDS field samples
Organic Acids acetate, lactate, formate, butyrate, propionate, pyruvate, succinate, oxalate, citrate	• Screen organic acids in for large field sample sets – indicators of biological activity	Laboratory + Field Assessment	Verified analytical techniques and applied to field samples from CO_2-EOR site	Deployable; NETL-modified technique	• Gardiner et al. Applied Geochemistry (2020)	• NETL TRS describing use of ion chromatography to screen high-TDS field samples

Laboratory-Based Chemical Analysis of Field Samples for CS Monitoring

Developed/Verified through CS Geochemistry-Based Monitoring Projects (2011 – 2017) & Task 20 (2017 – 2019), Slide 2 of 5

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Geochemical Tracer	What it Shows	Evaluation Approach		Field Deployment Status	Technology Transfer	
Ion Chromatography-Based Techniques					**Published**	**In Progress**
Transition Metals Fe^{3+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}	• Screen large field sample sets for metals within a few days – identify whether more detailed ICP-based techniques are needed to characterize water source • Identify redox changes that may indicate fluid migration	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR sites	Deployable; NETL-modified technique		• NETL TRS describing use of ion chromatography to screen high-TDS field samples
Rare earths La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	• Screen large field sample sets for REEs within a few days – identify whether more detailed ICP-based techniques are needed to characterize water source	Laboratory + Field Assessment	Verified analytical techniques and applied to field samples from CO_2-EOR site	Deployable; NETL-modified technique		• NETL TRS describing use of ion chromatography to screen high-TDS field samples
Sulfides sulfide, cyanide	• Complement field-based electrochemical monitoring techniques • Identify redox changes that may indicate fluid migration	Laboratory + Field Assessment	Verified analytical techniques and applied to field samples from CO_2-EOR site	Deployable; NETL-modified technique		• NETL TRS describing use of ion chromatography to screen high-TDS field samples

Laboratory-Based Chemical Analysis of Field Samples for CS Monitoring

Developed/Verified through CS Geochemistry-Based Monitoring Projects (2011 – 2017) & Task 20 (2017 – 2019), Slide 3 of 5

Geochemical Tracer	What it Shows	Evaluation Approach		Field Deployment Status	Technology Transfer	
Isotope-Based Techniques					**Published**	**In Progress**
Strontium $^{87}Sr/^{86}Sr$	• As stable isotope indicator of the sources of geologic brines and reservoir CO_2-fluid-rock reactions • Used to define mixing curves for expected values in receptor formations	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR and natural analog sites	Deployable; May be location-specific (NETL-developed technique)	• Wall et al. JAAS (2013) • Wall et al. TRS report • Phan et al. App Geochem (2018 • Gardiner et al. IJGHGC (2020)	• Multi-isotopic monitoring of CO_2-EOR site in Permian Basin
Carbon $^{13}C/^{12}C$	• C indicates source of CO_2 detected • Used to identify whether CO_2 is from the storage reservoir	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR and natural analog sites	Deployable (established techniques)	• Gardiner et al. IJGHGC (2020)	• Multi-isotopic monitoring of CO_2-EOR site in Permian Basin
Oxygen $^{18}O/^{16}O$	• Indicates geologic versus atmospheric contributions to water • Used to identify whether high TDS fluid is from deep reservoirs	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR and natural analog sites	Deployable (established techniques)	• Gardiner et al. IJGHGC (2020)	• Multi-isotopic monitoring of CO_2-EOR site in Permian Basin

Laboratory-Based Chemical Analysis of Field Samples for CS Monitoring

Developed/Verified through CS Geochemistry-Based Monitoring Projects (2011 – 2017) & Task 20 (2017 – 2019), Slide 4 of 5

NATIONAL ENERGY TECHNOLOGY LABORATORY

Geochemical Tracer	What it Shows	Evaluation Approach		Field Deployment Status	Technology Transfer	
Isotope-Based Techniques					**Published**	**In Progress**
Lithium $^7Li/^6Li$	• Identifies whether reservoir brine contacted the seal layer or organic-rich zones • Identifies whether migrated brine originates from the carbon storage reservoir	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR site	Deployable; May be location-specific (NETL-developed technique)	• Pfister et al. (2017) • Phan et al. App Geochem (2018)	• NETL TRS report on application of Li isotopes as geochemical tracers for carbon storage
Boron $^{11}B/^{10}B$	• Identifies whether leaked CO_2 contacted brine, or if it came directly from the sc-CO_2 plume	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR site	Deployable; May be location-specific (NETL-modified technique)	• Phan et al. COGEL (2020)	• NETL TRS report on application of B isotopes as geochemical tracers for carbon storage

Laboratory-Based Chemical Analysis of Field Samples for CS Monitoring

Developed/Verified through CS Geochemistry-Based Monitoring Projects (2011 – 2017) & Task 20 (2017 – 2019), Slide 5 of 5

Geochemical Tracer	What it Shows	Evaluation Approach		Field Deployment Status	Technology Transfer	
Isotope-Based Techniques					**Published**	**In Progress**
Uranium $^{234}U/^{238}U$	• Relevant for regions with elevated uranium present in subsurface reservoirs • Identifies fluid migration and oxidation-reduction processes	Laboratory + Field Assessment	Verified analytical techniques and applied to field sampling at CO_2-EOR and natural analog sites	Location-specific (need detectable concentrations of U; established techniques)	• Phan et al. GCA (2019) • Gardiner et al. IJGHGC (2020)	
Barium $^{138}Ba/^{134}Ba$	• Relevant for regions with elevated Ba • Indicates fluid mixing between the CS reservoir and overlying geologic units	Laboratory + Field Assessment	Verified analytical techniques and applied to field samples from CO_2-EOR site	Technique developed in 2018-2019 for onshore gas (NETL-developed technique); Modified for carbon storage in 2019-2020		• Multi-isotopic monitoring of CO_2-EOR site in Permian Basin • NETL TRS on application of Ba isotopes as geochemical tracers for carbon storage

Appendix 2

Additional information on Permian Basin CO_2-EOR geochemical monitoring

Milestone: Model what a leak would look like in the geochemical signals at different leakage points in a CO_2-EOR system.

E. Seminole Field Data

- CO_2-EOR field initiating CO_2 flood **(Fig. 1)**

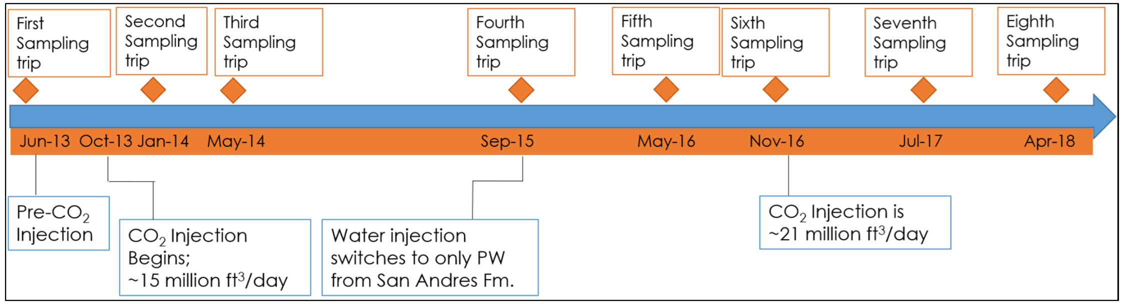


Figure 1. Timeline of sampling history at field site, with dates of sampling trips and major field events below.

Opportunity to:

(1) Observe CO_2 induced changes in produced water

(2) Monitor overlying groundwaters for produced water intrusion

Potential Implications/Impact

(1) Understand CO_2 water-rock-interactions

(2) Develop applications of geochemical tools for monitoring, measurement, and verification

- Sampled produced waters and groundwaters **(Fig. 2)**

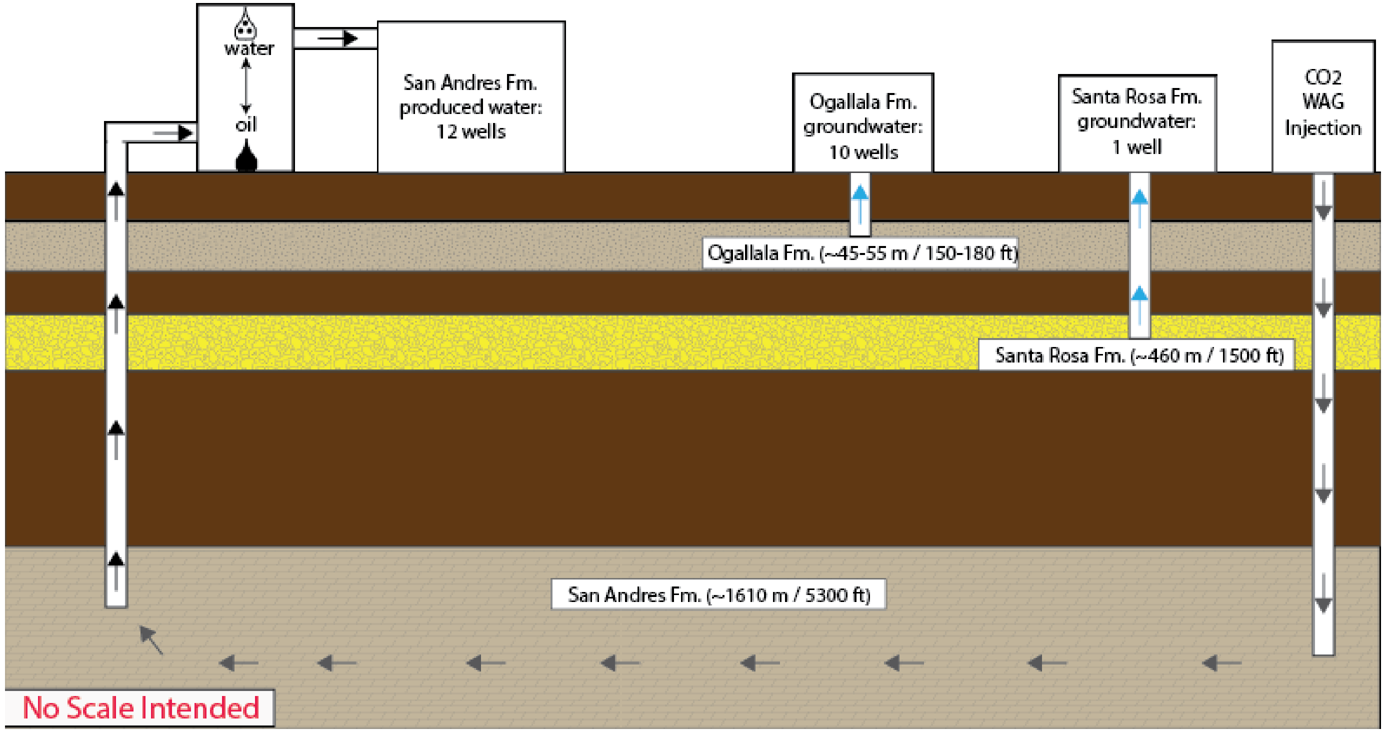
System	Series	Central Basin Platform Group/Formation	Lithology	Average Depth (m) of Samples at field area	Hydrostratigraphic Unit
Quaternary		Alluvium	Silty sand		
Tertiary	Upper	Ogallala	Fluvial and lacustrine clastics	~45-55	Evaporite Confining System
Cretaceous	Albian	Fredericksburg	Limestone		
		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			
		San Andres	Dolomite	~1630	
	Leonardian	Holt	Limestone and Dolomite		
		Glorieta			
		Clear Fork Group			
		Wichita			
	Wolfcampian	Wolfcamp	Shelf limestones, minor shale		
Pennsylvanian		Cisco "Cline"			
		Canyon			
		Strawn			
		Atoka	Shale		
Mississippian		Barnett			
		Mississippian	Limestone		

Figure 2. Simplified stratigraphic column[1] of the Central Basin Platform; highlighted formations were sampled at E. Seminole field.

[1]Figure B based on previous editions from Stueber et al. (1998), Engle et al. (2016) and Pfister et al. (2017).

Geochemical changes: Producing Formation

San Andres Fm. Produced Waters



- Statistically significant ($p < 0.5$) increases in dissolved inorganic constituents [alkalinity, TDS, Na^+, Cl^-, SO_4^{2-}] in produced waters
- Alkalinity increases due to dissolution of CO_2 into formation water
- Sulfate increase likely due to sulfur-mineral oxidation
- Na^+, Cl^-, and TDS increases due to enhanced mixing with denser formation water below oil-water contact
- No increase in Ca^{2+} or Mg^{2+}, suggesting negligible carbonate reservoir dissolution
  - Indicates geologic leakage out of producing formation unlikely at this time

Geochemical changes: Producing Formation

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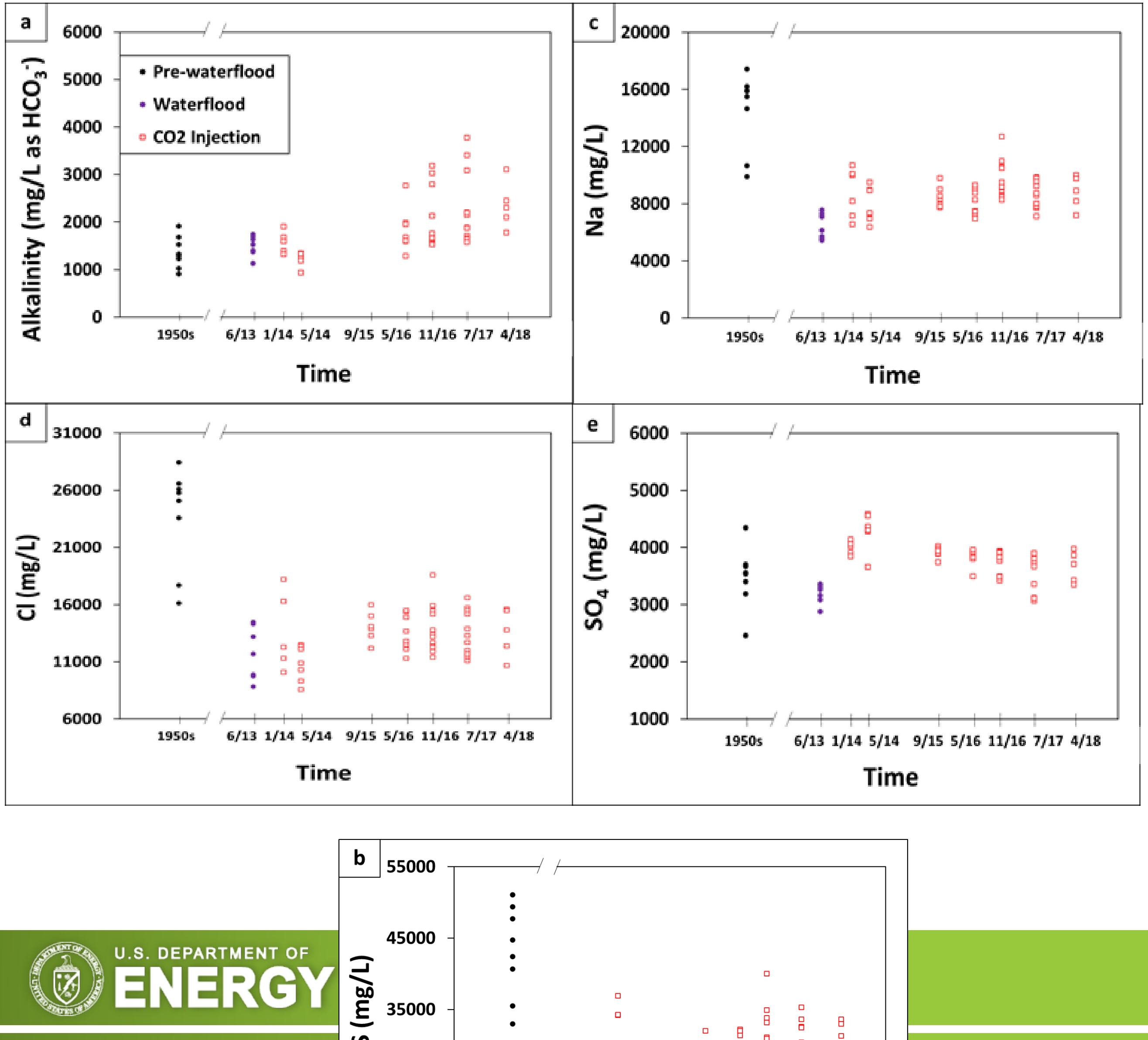
San Andres Fm. Produced Waters



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Geochemical changes: Producing Formation

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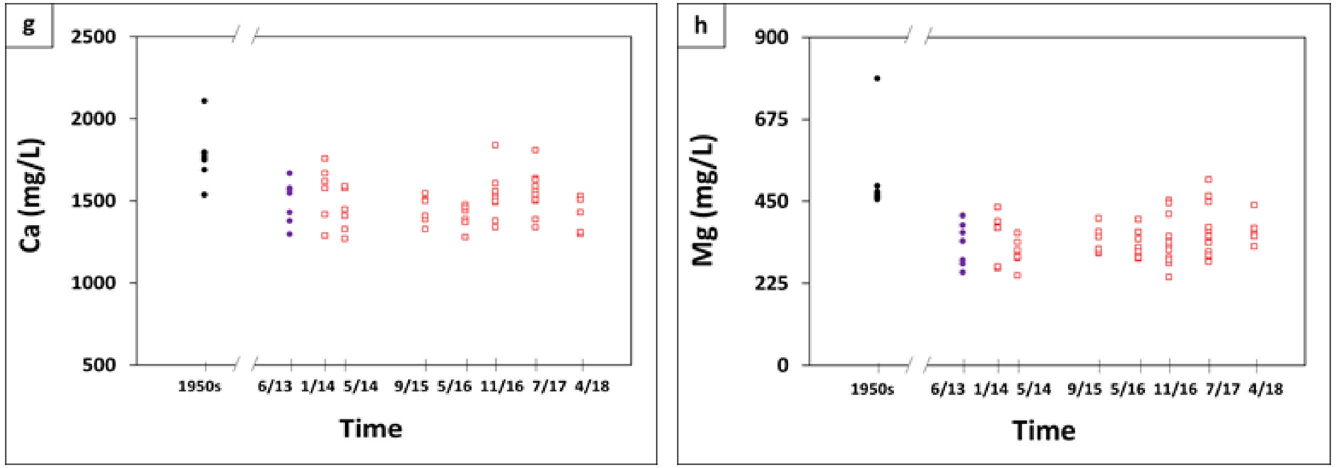

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Milestone: Model what a leak would look like in the geochemical signals at different leakage points in a CO_2-EOR system.

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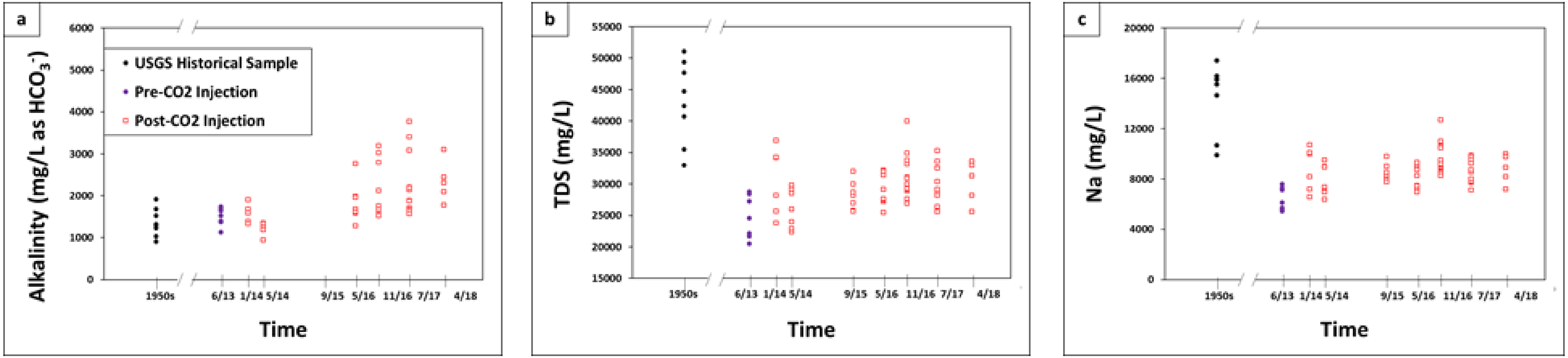
E. Seminole Field Data

- ***Produced Water Results***
  - After CO_2 injection, significant shifts in certain analytes [alkalinity, TDS, Na^+, Cl^-, SO_4^{2-}]
  - No significant shifts in others [Ca^{2+}, Mg^{2+}]



- ***Interpretation***
  - Injected CO_2 is dissolved in water [solubility trapping] and not likely causing carbonate dissolution → ***Reservoir integrity preserved***
  - Produced water geochemistry reflects CO_2 injection → ***Track CO_2 plume in reservoir***

Milestone: Model what a leak would look like in the geochemical signals at different leakage points in a CO2-EOR system.

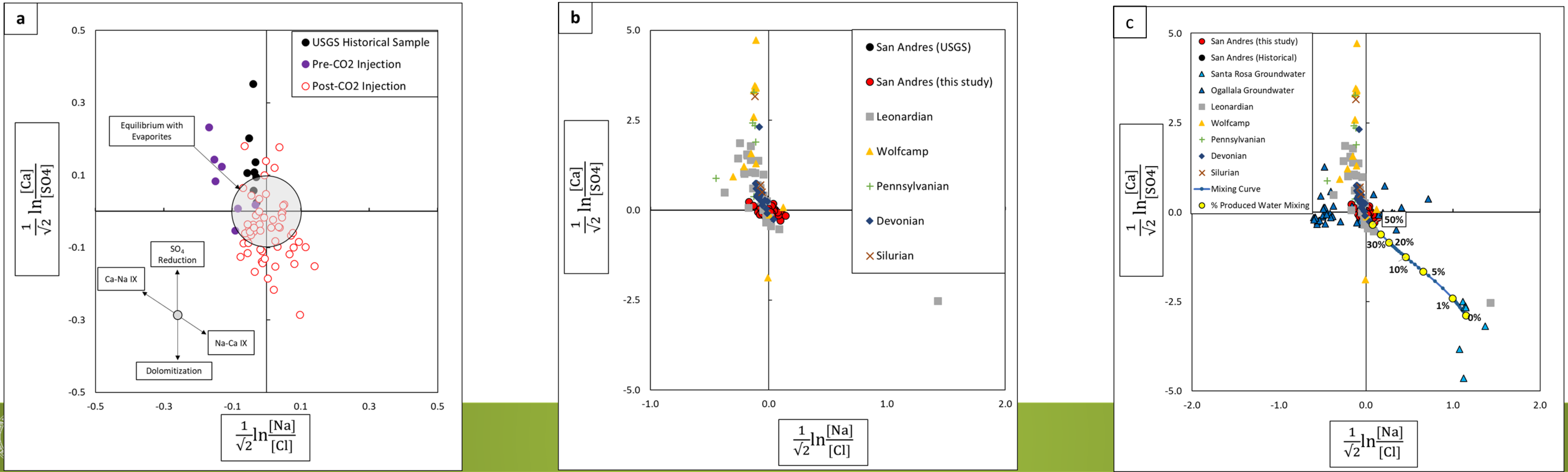
E. Seminole Field Data

· *Distinctive geochemistry*

- Applied data transformation tool (isometric log-ratios) to produced water
- Despite shifts following CO_2 injection, E. Seminole produced water still occupies a small, distinctive range **(Fig. A)**

· *Groundwater Results: Detecting Leakage*

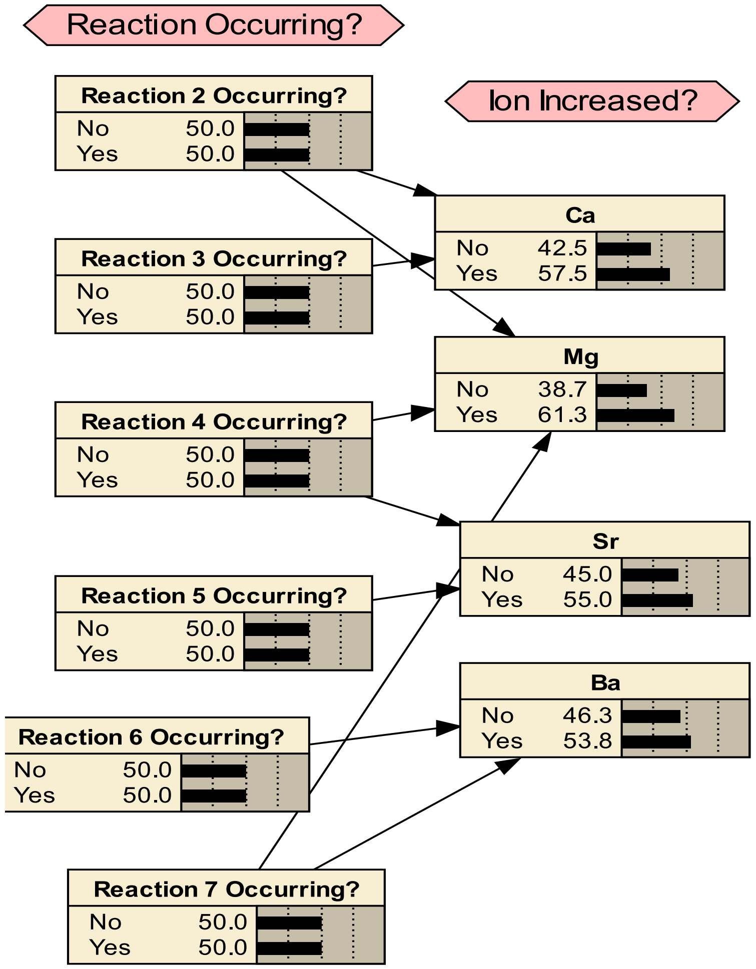
- E. Seminole produced water occupies small range relative to local produced waters **(Fig. B)**
- Mixing model demonstrates ***hypothetical*** detection of leakage from producing formation into overlying, intermediate groundwater **(Fig. C)**



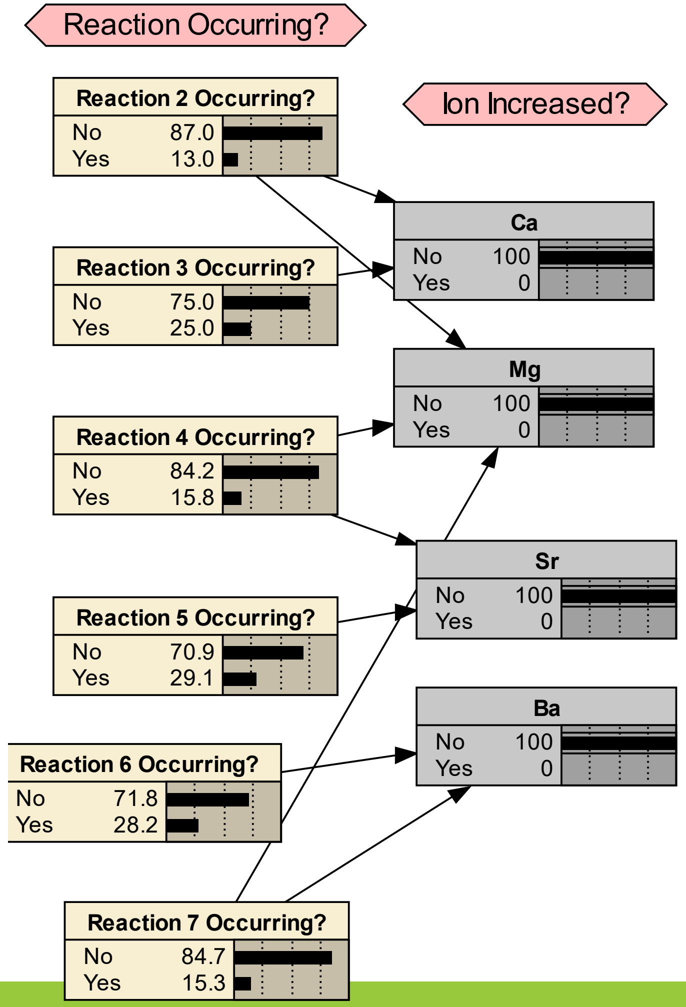
Bayesian Belief Network: Incorporating Reaction Matrix

Dolomite reservoir

Prior Network (no measurements)



Nothing found in measurements



Mg, Sr, and Ba found in measurements