Geochemical Monitoring of Groundwater Impacts

Christina L. Lopano

NETL – Research & Innovation Center
FY2017 Research Team

- Hank Edenborn, NETL-RIC
- Angela Goodman, NETL-RIC
- Ale Hakala, NETL-RIC
- Christina Lopano, NETL-RIC
- Dustin McIntyre, NETL-RIC
- Paul Ohodnicki, NETL-RIC
- Rick Spaulding, NETL – RIC
- Chet Bhatt, ORISE - NETL
- Christian Goueguel, ORISE-NETL
- Mikey Hannon, ORISE - NETL
- Thai Phan, ORISE-NETL
- Mengling Stuckman, ORISE-NETL
- Jinesh Jain, AECOM – NETL
- Ki-Joong Kim, AECOM-NETL
- James Gardiner, AECOM-NETL
- R. Burt Thomas, AECOM – NETL
- Brian Stewart, Univ. Pitt
- Shikha Sharma, WVU

Technical approach employs a multidisciplinary team (chemists, geologists, materials engineers) to develop, demonstrate, and validate novel tools and techniques for geochemical MVA.
Task 8 (FY17): Geochemical Monitoring

• **Subtask 8.1: Geochemical Monitoring Tools and Protocols**
  – develop and demonstrate a suite of protocols and tools for new types of geochemically-based monitoring strategies in variable geological systems
  – 4 sub-subtasks: Geochemistry & Isotopes, Direct CO₂ Sensing, FO sensing, LIBS

• **Subtask 8.2: Geochemical MVA Field Validation**
  – validate tools and techniques developed for tracking the CO₂/brine interface and monitoring groundwater
  – Model and predict leaks in field conditions

• **Subtask 8.3: Perfluorocarbon Tracers for Monitoring Plume Migration**
  – Support analysis of PFC tracer samples acquired by the SW Partnership for the Farnsworth Field
Monitor Groundwater Impacts

Understand Natural Background Variability

- Develop & demonstrate a suite of geochemically-based monitoring strategies for groundwater systems.
- Statistical understanding of natural signals in CO₂ storage systems.
- Determine sensitivities of techniques in real world conditions.

Establish the Utility of Isotopes to Track Migration of a CO₂ Plume

Test and Validate the Use of CO₂ Monitoring Devices Under Field Conditions
Geochemical Monitoring: Scenarios

**Measurement of steady state conditions in groundwater leads to ▲ value in above plot**

**Measurement of steady state conditions in storage formation leads to ● value in above plot**

1. Leakage along well pathway to intermediate geologic formation; monitor changes in intermediate formation.
2. Leakage along well pathway to shallow groundwater aquifer; monitor changes in groundwater aquifer.
3. Leakage along other geologic conduit to intermediate formation.
4. Leakage along other geologic conduit to groundwater aquifer.
5. Leakage pathway directly from the well to the shallow aquifer (due to poor completion or other well failure).
Challenges to Current Practices

• Sparse monitoring wells may not constrain leakage pathways
• Baseline geochemistry varies with time
• Co-injected CO₂ tracers generally don’t provide evidence of the leakage source
• Laboratory-based analyses can be time consuming, have significant lag-time between sampling and analysis, and may be impractical for real-time monitoring of leaks

• This work improves on the current practices:
  – Geochemical fingerprints are left behind by specific fluid pathways
  – A diverse geochemical tracer toolkit covers leakage pathway blindspots.
  – New isotopic systems can distinguish natural baseline fluctuation from leakage signals.
  – Advancing the science-base for potential novel in-situ analysis techniques
Natural Geochemical Signals for MVA

Understand usual levels of change under “normal operations” versus a “leakage event”

- Sole use of common geochemical parameters (pH, alkalinity, total dissolved solids) can confuse sources of leaks
- Application of isotope geochemistry can identify:
  - Fluids from specific geologic units
  - Fluids/gas sourced from CO₂ storage reservoir
- Field and laboratory experiments build data resources needed to define the range of expected variations for a given geologic system, versus the outliers that identify a leak

Pfister et al, under review
## Natural Geochemical Signals for MVA

- **Outcome**: Definition of region-specific geochemical and isotopic targeted analytes for long-term monitoring of broad regions
- **Product**: Monitoring methodologies that can be applied at reduced cost with increased sensitivity and confidence, communicated through a best practices document.

<table>
<thead>
<tr>
<th>Isotope System</th>
<th>Analytical Method</th>
<th>Evaluation Approach</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}\text{C}/^{12}\text{C}$</td>
<td>Established methods (historical literature)</td>
<td>Field Monitoring</td>
<td>Identify fluids/gas from system with different source of inorganic carbon</td>
</tr>
<tr>
<td>$^{234}\text{U}/^{238}\text{U}$</td>
<td>Developed through prior Carbon Storage effort (FY 2012 – FY 2014)</td>
<td>Field Monitoring &amp; Laboratory Experimentation</td>
<td>Fluids sourced from different geologic formations; CO$_2$-water-rock reactions</td>
</tr>
<tr>
<td>$^{7}\text{Li}/^{6}\text{Li}$</td>
<td>Established methods, however improvements (Phan, 2016) underway (FY 2014 to FY 2017)</td>
<td>Field Monitoring</td>
<td>Clay-rich systems (e.g., fluid contact with cap rock)</td>
</tr>
<tr>
<td>$^{11}\text{B}/^{10}\text{B}$</td>
<td>Method under development (FY 2016 to FY 2019)</td>
<td>Field Monitoring &amp; Laboratory Experimentation</td>
<td>Identify whether leaked CO$_2$ contacted brine, or if it came directly from the sc-CO$_2$ plume</td>
</tr>
<tr>
<td>$^{81}\text{Br}/^{79}\text{Br}$</td>
<td>Method under development (FY 2017 to FY 2020)</td>
<td>Field Monitoring &amp; Laboratory Experimentation</td>
<td>Identify whether fluid is from storage reservoir or other formation</td>
</tr>
</tbody>
</table>
Isotope Separation Methods

• Important for measuring metal isotopes in complex matrices
• Methods developed will simplify the process of measuring these isotopes

NETL’s Thermo Scientific NEPTUNE PLUS MC-ICP-MS at University of Pittsburgh, Dept. of Geology & Environmental Science

• Br Separation (Ongoing)
  • Source of fluids
    ✓ Anion exchange resin AG 1-X4 100-200 mesh OH- (Bio-Rad)
    ✓ 4 step rinse (NaOH, MWQ, NH₄NO₃)

Sample matrix

Br isotopes

Not fully sep. from Mg
Boron Isotopes - Experimental

Boron Isotopic Fractionation Aqueous - CO$_2$ partition hypothesis:

Experiments Confirm

• CO$_2$ phase with distributions equivalent to 10-15% of B in the mobile CO$_2$ phase
• $\Delta^{11}$B$_{v-l}$ isotopic effect of approximately -3‰.
• Boron is a good candidate tracer for groundwater impacted by carbon dioxide.
• Rayleigh fractionation of B within a formation is a possible marker of CO$_2$ transit.

Thomas et al (2017) ACS Meeting
Geochemical Signals and Isotopes for MVAA: Field Study (EOR site in TX)

East Seminole & Emma Field

Six sampling trips over ~ 3.5 years, bracketing CO₂ injection

- Ogallala Fm. Groundwater
  - Depth: 150-180 ft.
  - Wells Sampled: 9

- Santa Rosa Fm. Groundwater
  - Depth: 1500 ft.
  - Wells Sampled: 1

- Upper San Andres Fm. Produced Water
  - Depth: ~5,500 to 5,700 ft.
  - Wells Sampled: 13

- Injection Waters
  - Depth: NA
  - Wells Sampled: 4
  - Mix of Santa Rosa Groundwater + San Andres Produced Water; strictly San Andres Fm. Produced Water after Oct/Nov 2015

Figure 12. Schematic of injection water mixing procedure at East Seminole oil field. Depths in figure represent the depth where representative formation samples were taken. For the Upper San Andres formation samples at the East Seminole oil field, downhole pressures were between 2200-3500 pounds per square inch (PSI) and the downhole temperatures were between 90-110°F. There is no scale intended for this image as it is just a schematic. Geologic patterns are from the USGS (2006).
Geochemical Signals and Isotopes for MVAA

End game - develop a multiple-component mixing plot that can be applied towards identifying normal operations vs- a leakage event with simple sampling and analytical protocols.

Bayesian isotopic mixing models predicting what the signals look like under different leakage scenarios at an EOR site.

More isotope systems provide more robust probability estimates of source proportions.
Direct Sensing: CO$_2$ in Shallow GW

- Non-Dispersive Infrared (NDIR)
  - Adapted from atmospheric sensors (Vaisala)
  - $< 1$ mg/L lower limit
  - NETL-adapted to sample pumped water
  - Sensor modified for field deployment
  - Commercial marine sensor being tested
Field testing and validation

Decatur IL ADM Plant, 2015-16

Brackenridge Field Site, Austin, TX 2016-2017

Central PA karst springs, 2017

Vaisala Sensor - Decatur Samples

Time of Equilibration (min)

Time

Well BFL01

CO2, mmol/L

CO2, mg/L

Vaisala Sensor - Decatur Samples

Well BFL01

CO2, mmol/L

Time

CO2, mg/L

January February March

WEAVER SPRINGHOUSE SMULLTON
Geochemical Monitoring: Nanomaterial Enabled Fiber Optic Chemical Sensors

NETL RIC Optical Fiber Sensor Efforts are Targeted at Distributed Chemical Sensing for Environmental Monitoring

Leverage In-House Capabilities in *Functional Materials, Optical Sensing* and *Geochemistry*

- Engineered Nanomaterials for Chemical Sensing Parameters of Interest
- Versatile and Can Be Applied to Any Environmental Parameters of Interest
- Examples: pH, CO$_2$, and CH$_4$

1 patent, 2 additional patents pending

*PI - Ohodnicki*
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

MOF integrated wave-guide CO$_2$ gas sensor

%T spectra to different CO$_2$ concentration

MOF-coated optical fibers

3 times

7 times
Geochemical Monitoring: Nanomaterial Enabled Fiber Optic Chemical Sensors

MOF integrated wave-guide CO$_2$ gas sensor

1) Clear selectivity to CO$_2$ relative to other gases.
2) Very fast (< 1 minute) response times and excellent reversibility.
3) Improved scientific understanding of the sensing mechanism for the optical fiber platform.

Future work now targets effects of water given the need for deployment in a wellbore environment.
Geochemical Monitoring: Laser Induced Breakdown Spectroscopy (LIBS)

- Measurement of multicomponent system
  - Chloride Solutions of Ba, Ca, Mg, Mn, Sr
  - Limits of Detection and Quantification vs. Pressure
  - Emission decay vs. pressure vs. element

- Laboratory experiments successfully demonstrate that low-ppm range concentrations of Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ and Mn$^{2+}$ can be accurately measured in CO$_2$-laden water at varied pressure conditions by using underwater LIBS.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>$S$</th>
<th>$R^2$</th>
<th>LOD (ppm)</th>
<th>LOQ (ppm)</th>
<th>CO$_2$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>0.0019 ± 2.93·10$^{-5}$</td>
<td>0.9993</td>
<td>31.68 ± 0.92</td>
<td>104.53 ± 1.06</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.0023 ± 3.56·10$^{-5}$</td>
<td>0.9996</td>
<td>31.12 ± 0.78</td>
<td>102.71 ± 2.54</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.0022 ± 1.87·10$^{-5}$</td>
<td>0.9998</td>
<td>30.83 ± 1.05</td>
<td>101.73 ± 3.74</td>
<td>400</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.0114 ± 1.16·10$^{-4}$</td>
<td>0.9996</td>
<td>2.48 ± 0.71</td>
<td>8.18 ± 0.20</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.0118 ± 3.85·10$^{-4}$</td>
<td>0.9958</td>
<td>2.45 ± 0.62</td>
<td>8.09 ± 0.09</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.0111 ± 2.46·10$^{-4}$</td>
<td>0.9980</td>
<td>2.67 ± 0.30</td>
<td>8.81 ± 1.01</td>
<td>400</td>
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<tr>
<td>Sr$^{2+}$</td>
<td>0.0076 ± 6.83·10$^{-5}$</td>
<td>0.9998</td>
<td>3.34 ± 0.11</td>
<td>11.02 ± 0.97</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.0080 ± 3.07·10$^{-4}$</td>
<td>0.9956</td>
<td>3.04 ± 0.13</td>
<td>10.04 ± 1.34</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.0080 ± 1.37·10$^{-4}$</td>
<td>0.9991</td>
<td>3.38 ± 0.31</td>
<td>11.15 ± 1.02</td>
<td>400</td>
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<tr>
<td>Ba$^{2+}$</td>
<td>0.0037 ± 3.53·10$^{-5}$</td>
<td>0.9997</td>
<td>4.38 ± 0.21</td>
<td>14.42 ± 2.03</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.0038 ± 2.13·10$^{-5}$</td>
<td>0.9998</td>
<td>4.86 ± 0.12</td>
<td>16.65 ± 1.09</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.0036 ± 5.06·10$^{-5}$</td>
<td>0.9994</td>
<td>3.91 ± 0.45</td>
<td>12.91 ± 3.23</td>
<td>400</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>0.0050 ± 7.94·10$^{-5}$</td>
<td>0.9989</td>
<td>10.47 ± 0.13</td>
<td>34.53 ± 1.05</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.0062 ± 1.76·10$^{-4}$</td>
<td>0.9968</td>
<td>7.42 ± 0.09</td>
<td>24.50 ± 1.00</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.0064 ± 1.06·10$^{-4}$</td>
<td>0.9989</td>
<td>5.24 ± 0.05</td>
<td>17.27 ± 0.55</td>
<td>400</td>
</tr>
</tbody>
</table>

Goueguel, C.L. et al “Quantitative determination of metal ions in high-pressure CO2-water solutions by underwater laser-induced breakdown spectroscopy” in prep
Task 8.3: Perfluorocarbon Tracers

Farnsworth, Texas
- Using CO₂ for enhanced oil recovery within the Farnsworth Unit
- 926 samples analyzed via
- Thermal desorption with cryogenic focusing gas chromatography/mass spectrometry (GC/MS) with chemical ionization (CI) and selected ion monitoring (SIM)
  - 2016: 629 samples
  - 2017: 297 samples to date
- Results of PFC tracer analyses coupled with modeling aid in distinguishing highly transmissive fault directing flow in the system.

Oak Ridge National Laboratory
- Planning a collaboration effort for 2017-Q4
- Will use different analytical methods to compare effects of hydrocarbon-rich sample matrices on PFT collection efficiency
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 materials – Communication across multi-disciplinary teams is key

– 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
• Novel isotopic separation techniques are being developed to increase efficacy of their use for monitoring – goal of identifying leakage sources

• Geochemical monitoring methods/tools are being field validated & baseline signals interpreted

• Information gained from knowledge of CO₂ storage systems is being used to inform development of novel in-situ chemical sensing tools
Next Steps – moving towards an “End game”

- Definition of region-specific geochemical and isotopic targeted analytes for long-term monitoring of broad regions
- Develop multiple-component mixing plots that can be applied towards identifying normal operations versus a leakage event with simple sampling and analytical protocols
- Identify and validate novel in-situ chemical monitoring tools
  - NDIR for CO₂ in shallow systems (natural analog in process)
  - LIBS – lab validated, moving towards field prototype
  - MOF coated FO lines for direct sensing lab validation in progress – field testing in upcoming 2 yrs
Synergy Opportunities

• Sample sharing – isotopic analyses for a wide range of geologic storage systems (sandstone-based, carbonate-based, different types of caprocks)

• Continued field-based collaboration to test new geochemical monitoring techniques and tools under different CO₂ storage conditions (e.g. FO coated sensors)

  • Natural analogs
  • Controlled release sites
  • EOR field systems

NETL researcher, Hank Edenborn (NETL) at the Brackenridge Field Site (Austin, TX)
FY2017 Task Accomplishments

• Task 8.1 - B isotope ($^{11}\text{B}/^{10}\text{B}$) partitioning autoclave laboratory experiments have been completed. The team plans to utilize B partitioning to help identify whether leaked CO$_2$ contacted brine, or if it came directly from the sc-CO$_2$ plume. The results of this work were presented at the Annual ACS meeting in April 2017, which fulfills milestone M1.17.8.A

• Task 8.1 – Successful integration of nanomaterials (ZIF-8 MOF) on FO platform
  – Strong pre preference for CO$_2$, with rapid read and refresh time
  – A linear relationship between optical response (transmittance) and CO$_2$ concentration

• Task 8.1 - Tin-doped indium oxide (ITO) nanocrystals were successfully synthesized by hot injection method, and a ligand exchanged ITO nanocrystal was successfully coated on the surface of HF-etched fiber optics for pH sensing under extreme conditions.

• Task 8.1 - Laboratory experiments successfully demonstrate that low-ppm range concentrations of Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ and Mn$^{2+}$ can be accurately measured in CO$_2$-laden water at varied pressure conditions by using underwater LIBS.
FY2017 Task Accomplishments

- Task 8.1 & 2: In-situ field measurements of CO₂ concentrations in karst streams using NDIR technology (C-Sense & Vaisala) are underway in north central PA. Data is collected and logged on an hourly basis in the stream systems. Results to-date have been good, and compare well to single point grab-samples collected in bottles in the field and measured with the lab-based Carbo-QC volumetric expansion method.

- Task 8.2: Geochemical data of rock samples from San Andres formation were collected, together with water chemistry, to aid in understanding of CO₂-water-rock interactions in the subsurface throughout a lifespan of oil wells.

- Task 8.2: To date, Sr isotope signature in freshwater wells near the EOR site remain constant, suggesting that there is no external source of water contributing to freshwater aquifers (no brine leakage detected) associated with the nearby CO₂-flooding EOR.

- Task 8.3: All PFC tracer analyses have been completed for samples received to date (907 Samples over a 14 month time period) for the SW Regional Partnership monitoring of plume migration in the Farnsworth field.
Appendix

– These slides will not be discussed during the presentation, but are mandatory.
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.
Project Overview: Goals and Objectives

Monitoring Groundwater Impacts – What suite of measurements and/or tools can used in groundwater to detect CO$_2$ and/or brine leakage and to evaluate the impact?

- Develop and apply metal isotope tracers for QMVA and to potentially track plume migration
- Better understand physical-chemical-biological parameters impacting signals for geochemical tracers
- Develop & test novel materials and sensors for in-situ monitoring
- Test and validate the use of CO$_2$ monitoring devices under field conditions
- Understand natural variability in background

Monitoring of underground sources of drinking water (USDW) is crucial to the successful implementation of geologic carbon storage. Protection of groundwater resources is the main focus of regulations that dictate the requirements for permitting of CO$_2$ storage sites. It is also critical to the program goal ensuring 99% storage permanence to be able to quantify leakage of CO$_2$ to the near surface.
Organization Chart

• Hank Edenborn, NETL-RIC  (PI - Task 8.1.2, 8.2.2)
• Angela Goodman, NETL-RIC  (PI - Task 8.3.1)
• Ale Hakala, NETL-RIC  (PI - Tasks 8.1.1, 8.2.1)
• Christina Lopano, NETL-RIC  (TTC Task 8, PI Task 8.2.3)
• Dustin McIntyre, NETL-RIC  (PI Task 8.1.3)
• Paul Ohodnicki, NETL-RIC  (PI Task 8.1.4)
• Rick Spaulding, NETL – RIC  (Task 8.2.1)
• Chet Bhatt, ORISE – NETL  (Task 8.1.3)
• Christian Goueguel, ORISE-NETL  (Task 8.1.3)
• Mikey Hannon, ORISE – NETL  (Task 8.2.3)
• Thai Phan, ORISE-NETL  (Tasks 8.1.1, 8.2.1, 8.2.3)
• Mengling Stuckman, ORISE-NETL  (Task 8.2.1)
• Jinesh Jain, AECOM – NETL  (Task 8.1.3)
• Ki-Joong Kim, AECOM-NETL  (Task 8.1.4)
• James Gardiner, AECOM-NETL  (Tasks 8.1.1., 8.2.1)
• R. Burt Thomas, AECOM – NETL  (Tasks 8.1.1., 8.2.1)
• Brian Stewart, Univ. Pitt   (Tasks 8.1.1., 8.2.1)
• Shikha Sharma, WVU     (Task 8.2.1)
### 8.1.1 Natural Geochemical Tracers in Groundwater (FY16)

This activity will develop and demonstrate a protocol for the use of a combination of natural geochemical tracers (e.g., isotopic, trace elements, etc.) to monitor groundwater systems. Halogen isotopes (e.g., Br) will be investigated as complementary tracers for augmenting current capabilities with B, Sr and Li isotopes established in prior years. Experimental studies validating isotope signals under various aquifer conditions will also be explored.

**Hakala, Phan, Stewart (Pitt), Thomas, Gardiner**

### 8.1.2 Continuous CO₂ Monitoring Devices (FY16)

This activity will understand the response and limitations of CO₂ monitoring devices (volumetric expansion and NDIR) relative to CO₂ detection, including in the context of potential interference by other constituents (e.g., H₂S). Novel metal carbonate-hydrogel CO₂ sensors will be developed and tested.

**Edenborn, Jain**

### 8.1.3 Development and Assessment of LIBS for Measurement of CO₂ Impacts in Groundwater (FY16)

Develop and demonstrate LIBS as a tool to monitor chemical signals to groundwater that reflect potential impacts to groundwater resulting from the introduction of CO₂ and/or brine.

**McIntyre, Jain, Bhatt, Goueguel**

### 8.1.4 Fiber-Optic Technology for Downhole Measurement of Potential Groundwater Impacts (FY16)

Develop novel materials for and demonstrate FO-based tool(s) to monitor the introduction of CO₂ and/or brine into groundwater systems either by direct measurement of CO₂ or by other geochemical indicators such as pH.

**Ohodnicki, Kim, Zhang (OSU), Chong (OSU)**
<table>
<thead>
<tr>
<th>Task ID</th>
<th>Task Description</th>
<th>Details</th>
<th>Participants</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.2.1</td>
<td>Comprehensive Groundwater Field Testing</td>
<td>This task serves to coordinate and perform field sampling efforts for established collaborations with industry and university partners. It encompasses planning and coordination between other subtasks for the collection of produced water samples in addition to overlying well water and/or groundwater samples.</td>
<td>Hakala, Lopano, Gardiner, Thomas, Phan, Stuckman, Spaulding, Sharma (WVU), Stewart (Pitt)</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Field Validation of Groundwater Sensors</td>
<td>This element will implement the various monitoring tools that have been developed for evaluating groundwater impacts in field settings ranging from natural analog to various CO2 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.</td>
<td>Edenborn, Jain, Herman (Bucknell)</td>
</tr>
<tr>
<td>8.2.3</td>
<td>Geochemical Modeling and Statistical Evaluation of Field Data</td>
<td>This element will document baseline variability for key monitoring signals in groundwater for aquifers prior to and during CO2 injection. Statistical analysis on chemistry results will be performed to document baselines in potential source terms from the CO2 reservoir. This element will also conduct forward geochemical modeling of what a leak to groundwater aquifers would look like under various field conditions (utilizing field data to guide model parameters)</td>
<td>Lopano, Hannon, Phan, Gardiner</td>
</tr>
<tr>
<td>8.3.1</td>
<td>Perfluorocarbon Tracer Analysis</td>
<td>This element will continue to provide analytical support for the SW Partnership Farnsworth Field project to detect perfluorocarbon tracers (PFT) co-injected with CO2</td>
<td>Goodman, Sanguinito</td>
</tr>
</tbody>
</table>
### Task 8.0 Geochemical Monitoring of Groundwater Impacts

#### 8.1 Geochemical Monitoring Tools and Protocols for Groundwater Systems

- **Milestone** – Obtain Br isotope standards and test sample preparation and measurement via MC-ICP-MS.

- **M1 Milestone (M1.17.8.A)** – Complete B isotope laboratory validation experiments and analysis of implications for B isotope signals.

- **Milestone** – Complete testing of at least one sensor material formulation for CO$_2$ sensing in aqueous conditions.

- **Milestone** – Explore impacts of commercially available membranes on H$_2$O interference with CO$_2$ sensing.

#### 8.2 Geochemical MVA Field Activities

- **Milestone** – Conduct post-CO$_2$ injection and well-blow out groundwater sampling at EOR Site in Texas.

- **Milestone** – Measure and monitor CO$_2$ concentrations in shallow groundwater wells during real-time CO$_2$ releases and compare data with FO sensor CO$_2$ sensing system with collaborators at the University of Texas – Austin.

- **Milestone** – Process and analyze data associated with FY17 field effort.

- **Milestone** – Deploy NDIR-based CO$_2$ sensors in karst aquifer systems for assessment of long-term monitoring capabilities and collect hourly groundwater CO$_2$ baseline concentrations over 6 months, in collaboration with Bucknell and Temple universities.

#### 8.3 Perfluorocarbon Tracers for Monitoring Plume Migration

- **Milestone** – Complete analysis of existing sorbent tubes from the Farnsworth Field Site (270 samples).

- **Milestone** – Provide analysis of sorbent tubes for future tracer tests associated with the Farnsworth Field Site.

- **Milestone** – Initiate exchange of sorbent tube samples between ORNL and NETL researchers to compare the effects of hydrocarbon-rich sample matrices on PFT collection efficiency on a standard sorbent and assess desorption/quantification efficiency using GC-ECD and GC-MS methods.
Bibliography

• Publications:

  • Pfister, S., Capo, R.C., Stewart, B.W., Macpherson, G.L., Phan, T.T., Gardiner, J.B., Diehl, J.R., Lopano, C.L., and Hakala, J.A. “Geochemical and lithium isotope tracking of dissolved solid sources in Permian Basin carbonate reservoir and overlying aquifer waters at an enhanced oil recovery site, northwest Texas, USA. Submitted to Applied Geochemistry.
  • Phan, T.T., Hakala, J.A., Bain, D.J, Sharma, S. Colloidal controls on the natural geochemical tracers of groundwater and produced waters from oil and gas wells (manuscript in prep)
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