

# MONITORING, VERIFICATION AND ACCOUNTING OF GROUNDWATER SYSTEMS ASSOCIATED WITH STORED CARBON DIOXIDE AT GEOLOGIC SEQUESTRATION SITES

## BACKGROUND

Safe and effective deployment of geologic carbon storage technology requires assurance that injected carbon dioxide (CO<sub>2</sub>) stays in the target storage formation and has no environmental impact on overlying groundwaters. Diverse methods devoted to monitoring, verification and accounting (MVA) activities associated with geologic sequestration are important for helping to protect human health and the environment, preserve sources of drinking water and monitor the integrity of CO<sub>2</sub> storage sites over time. Novel MVA approaches are needed to rapidly identify potential CO<sub>2</sub> and brine leaks at their inception, when mitigation strategies could limit impacts in overlying groundwaters. The methods deployed for use in MVA must be rapid, sensitive and inexpensive for widespread and effective use. A wide range of tools must be available to evaluate the viability of various techniques under changing geologic conditions.

R&D202, December 2023



## PROJECT DESCRIPTION

NETL conducts research on several novel and practical methods for the rapid detection of unintended CO<sub>2</sub> and brine migration into overlying groundwater at geologic CO<sub>2</sub> storage sites. These currently include the advanced geochemical and isotopic analysis of collected water samples; the development of predictive statistical models that identify priority parameters for carbon storage monitoring; and the determination of geochemical processes and measurable signals diagnostic of leakage pathways.



## PROJECT GOAL

This project develops and tests new tools and methods for the rapid detection of potential CO<sub>2</sub> and brine leaks into groundwater systems from CO<sub>2</sub> storage sites.

## OBJECTIVES

- Generate a suite of geochemical methods and analysis tools for novel groundwater monitoring strategies in geologic storage systems.
- Develop a statistical understanding of natural background variability in CO<sub>2</sub> storage sites.
- Demonstrate the accuracy and robustness of developed tools under field conditions at CO<sub>2</sub> storage and natural analog sites.

## CAPABILITIES

This project utilizes the following: state-of-the-art geochemical and isotopic analytical facilities; NETL scientists' expertise in aqueous geochemistry; field sampling; and geochemical and statistical modeling.

## BENEFITS

The development of rapid and effective methods to determine potential CO<sub>2</sub>/brine leakage from geologic CO<sub>2</sub> sequestration sites will help to build confidence in the safety of CO<sub>2</sub> storage and will be useful for operators demonstrating system conformance. The NETL technologies focus both on rapid screening in water and on more advanced isotopic tools that allow for understanding of chemical reactions signaling potential leakage sources and pathways, providing potentially actionable information to stakeholders.

## RECENT ACCOMPLISHMENTS

### Development of Novel High-Throughput Methods for Ion and Metal Isotope Measurements in Brines

The NETL research team successfully developed high-throughput and novel methods for accurately measuring ion and metal isotopes in brines affected by CO<sub>2</sub> injection. These brines have high total dissolved solid (TDS) concentrations, which make them challenging to accurately analyze. NETL has refined methods to rapidly analyze these high TDS field samples for ion concentrations that, when

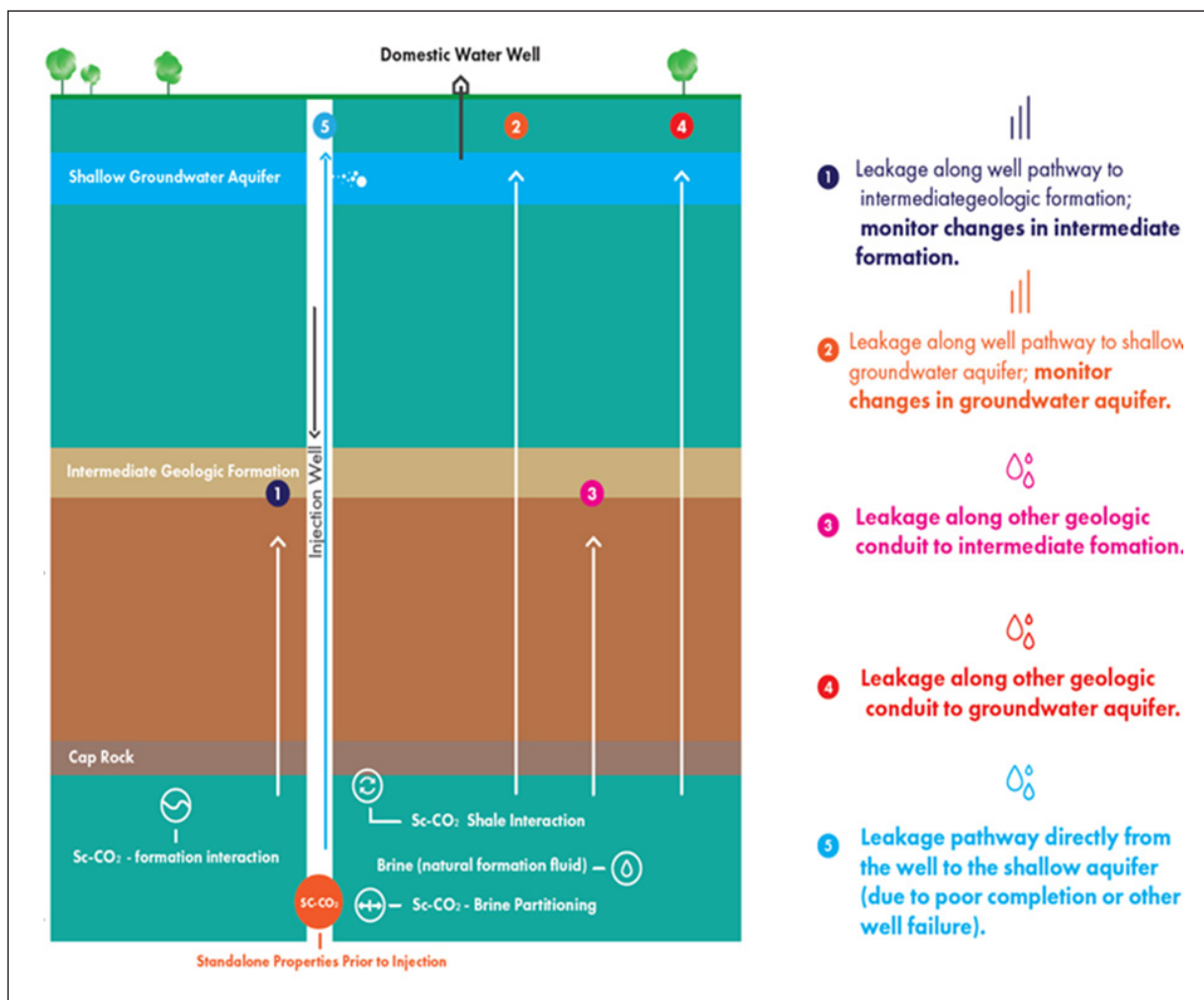


Figure 1. Schematic illustrating different CO<sub>2</sub> leakage pathways into overlying groundwaters.

analyzed, can suggest important CO<sub>2</sub>-water-rock interactions. Additionally, NETL has developed procedures for tracer analysis to include: strontium, lithium, uranium and boron isotope measurement in brine, groundwater and rocks using clean-lab chromatographic separation procedures, and NETL's multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

These methods are being applied to samples collected at NETL's field monitoring sites throughout the country. Aqueous geochemical and isotopic signals have been used to characterize pre- and post-injection brines and overlying groundwater at an active CO<sub>2</sub> injection site related to enhanced oil recovery (EOR). Fundamental controls on water chemistry in this system prior to and following CO<sub>2</sub> injection are being investigated. Published results indicate that there was no CO<sub>2</sub> induced brine leakage into overlying groundwaters, and that the integrity of the producing formation was maintained during five years of CO<sub>2</sub> injection. NETL researchers identified a suite of inexpensive and effective ion parameters that would indicate CO<sub>2</sub> induced brine leakage in the event of a hypothetical leak. None of these parameters displayed evidence of such leakage during the five-year monitoring study. NETL researchers additionally identified data transformation techniques that made these parameters more sensitive and transformed them into a source attribution tool that could aid in distinguishing between various groundwater salinization sources, such as CO<sub>2</sub>-EOR operations, agricultural activity or cross-formational flow.

At the cutting edge of MVA method development, NETL researchers have used several naturally occurring stable isotopes as tools to identify complicated geologic interactions in CO<sub>2</sub> storage related environments. Lithium isotope results, for example, indicate that these measurements would show early indication of potential brine migration into deep groundwater.

### Natural Analogue Sites

NETL researchers have also applied isotopic geochemical tools at natural analogue sites, which are locations where upwelling CO<sub>2</sub> affects groundwaters. Using strontium, uranium, and carbon isotope data, NETL researchers were able to identify groundwaters affected by two CO<sub>2</sub> transport mechanisms: (1) gas phase CO<sub>2</sub> and (2) CO<sub>2</sub> dissolved in brine. These CO<sub>2</sub> transport mechanisms had different impacts on local groundwater, and identifying the transport mechanism could help mitigation efforts in the case of a leakage event.

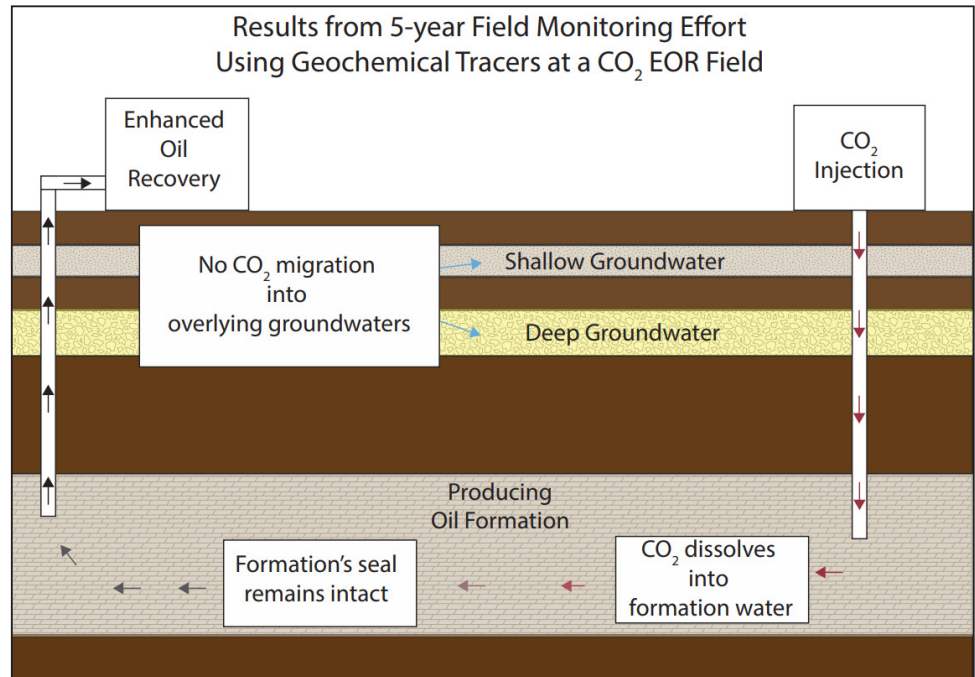


Figure 2. Graphic abstract that illustrates primary conclusions from geochemical tracer work at CO<sub>2</sub> EOR field over five-year monitoring effort.

### Using Geochemical and Statistical Models To Predict Leakage Signals and Understand Leakage Detectability

Based on field monitoring work, researchers have developed geochemical and statistical tools that demonstrate the processes and signals involved in hypothetical leakage scenarios. These models demonstrate how to monitor for leakage events using the most sensitive geochemical tools depending on the aquifer and fluid characteristics. Using these geochemical model results, the statistical model captures the causal relationship between upstream nodes (CO<sub>2</sub> concentration, geologic formation, aqueous chemistry) and downstream nodes (groundwater parameter changes). This statistical model identifies priority parameters using this probabilistic approach to predict the chance of CO<sub>2</sub> leakage in a storage site.

## PRIOR ACCOMPLISHMENTS

### Direct CO<sub>2</sub> Measurement Tools Applied in the Field

A volumetric expansion method used by the carbonated beverage industry and non-dispersive infrared (NDIR) CO<sub>2</sub> sensors adapted for use in water were tested extensively in NETL laboratories. These methods have been used successfully in the field to detect and directly measure CO<sub>2</sub> concentrations in groundwater pumped to the surface at a storage site in Illinois and at an EOR site in Texas.

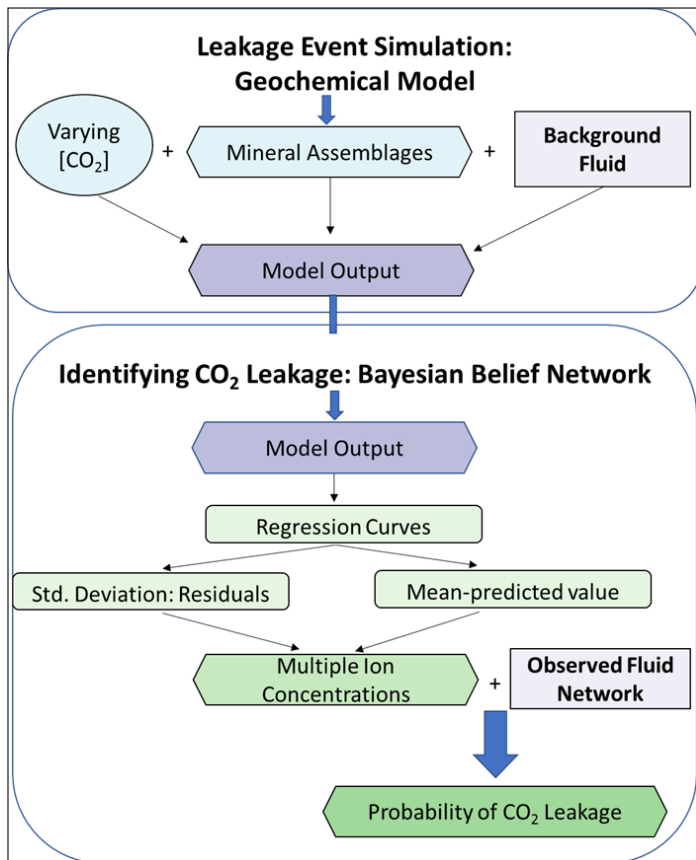


Figure 3. Model framework that displays integration of geochemical model output with statistical modeling of sensitive parameters.

### NETL-Developed Sorbent Tubes for Novel PFT for Soil Gas Monitoring

NETL analysis was conducted to support field CO<sub>2</sub> injection projects. In these studies, various perfluorocarbon tracers (PFTs) were added to the CO<sub>2</sub> injection stream at the wellhead. Concurrently, novel gas-permeable glass tubes filled with Ambersorb® adsorbent were deployed in the soils near the surface and monitored to track if CO<sub>2</sub> leakage occurred. The tubes were then retrieved for analysis using NETL's thermal desorption with cryogenic focusing gas chromatography/mass spectrometry with chemical ionization and selected ion monitoring. PFTs can be measured down to 200 parts per quadrillion.

### In-Situ Sensing Technologies

NETL researchers developed a series of novel in-situ analysis tools for detection of CO<sub>2</sub>, pH and bulk water chemistry for future downhole sensing. These include the development of miniaturized laser-induced breakdown spectroscopy sensing devices that will allow for in-situ, real-time analysis of changes in water chemistry, and novel nanomaterial coatings for fiber optic downhole lines that are engineered to detect CO<sub>2</sub> and/or pH fluctuations at harsh field conditions (elevated temperature and pressure).

NETL is a U.S. Department of Energy (DOE) national laboratory dedicated to advancing the nation's energy future by creating innovative solutions that strengthen the security, affordability and reliability of energy systems and natural resources. With laboratories and computational capabilities at research facilities in Albany, Oregon; Morgantown, West Virginia; and Pittsburgh, Pennsylvania, NETL addresses energy challenges through implementing DOE programs across the nation and advancing energy technologies related to fossil fuels. By fostering collaborations and conducting world-class research, NETL strives to strengthen national energy security through energy technology development.

### Partners

Leidos Research Support Team (LRST) | University of Pittsburgh | Oak Ridge Institute for Science and Education (ORISE) |

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