

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

## BACKGROUND

Deep geologic sequestration of carbon dioxide (CO<sub>2</sub>) that comes from coal-burning power plants and industrial manufacturing processes is being investigated as an effective way to lessen global atmospheric warming. 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. MVA approaches are needed to rapidly identify potential CO<sub>2</sub> and brine leaks that could occur in overlying groundwater of geologic storage sites. The methods deployed for use in the field 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. In addition, variation of CO<sub>2</sub> concentrations in natural groundwaters must be well understood to quantify potential leaks from geologic sequestration sites.

# NETL

NATIONAL ENERGY TECHNOLOGY LABORATORY

## PROJECT DESCRIPTION

The National Energy Technology Laboratory (NETL) conducts research on several novel and practical methods for the rapid detection of CO<sub>2</sub> and brine 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 direct determination of CO<sub>2</sub> by volumetric expansion and non-dispersive infrared sensors; and the development of emerging in-situ sensing technologies such as novel nanocoatings to enhance fiber optic-based sensors and the rapid detection of ions associated with CO<sub>2</sub>-rock interactions using laser-induced breakdown spectroscopy (LIBS). NETL has also developed and deployed various perfluorocarbon tracers (PFT) to aid in tracking CO<sub>2</sub> releases in shallow systems.

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## PROJECT GOAL

The primary goal of this project is to develop and test 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

This project aims to achieve the following objectives:

- Develop a suite of protocols and tools for new types of geochemically based monitoring strategies for groundwater systems
- Develop a statistical understanding of natural groundwater 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 system sites or analogous sites that mimic conditions expected in the field

## CAPABILITIES

This project will utilize NETL scientists' expertise in aqueous geochemistry, materials science and sensor development, laser technology and field sampling.

## 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 ensure the effectiveness of this storage approach and protect the environment. The NETL technologies focus both on rapid screening in water and on more advanced isotopic analyses that allow for understanding of chemical reactions signaling potential leakage sources and pathways.

## ACCOMPLISHMENTS

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

The NETL research team has successfully developed high-throughput and novel methods for 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).



Figure 1. NETL's MC-ICP-MS housed at the University of Pittsburgh.

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These methods are being applied to samples collected at NETL's field monitoring sites throughout the country. Aqueous geochemical signals and natural metal isotopes have been used to characterize brines containing introduced CO<sub>2</sub> and natural groundwaters overlying an enhanced oil recovery (EOR) site. Fundamental controls on water chemistry in this system prior to and following CO<sub>2</sub> injection are being investigated. Preliminary results showed that deep groundwater and brine maintain distinct isotopic signatures that can provide an early indication of potential brine migration.



Figure 2. NETL researchers collecting brine samples at a Texas EOR site.

## 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: Direct analysis of CO<sub>2</sub> using the volumetric expansion method.

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

NETL analysis is being conducted to support field CO<sub>2</sub> injection projects. In these studies, various PFTs are added to the CO<sub>2</sub> injection stream at the wellhead.

Concurrently, novel gas-permeable glass tubes filled with Ambersorb® adsorbent are deployed in the soils near the surface and monitored to track if CO<sub>2</sub> leakage has occurred. The tubes are 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.



Figure 4. Glass tubes filled with Ambersorb® carbonaceous polymer adsorbent (pen for scale).

## Emerging In-Situ Sensing Technologies

NETL researchers are working to develop a series of novel in-situ analysis tools for detection of CO<sub>2</sub>, pH and bulk water chemistry for future down-hole sensing. These include the development of miniaturized laser-induced breakdown spectroscopy (LIBS) sensing devices that will allow for in-situ real-time analysis of changes in water chemistry, and novel nano-material 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).

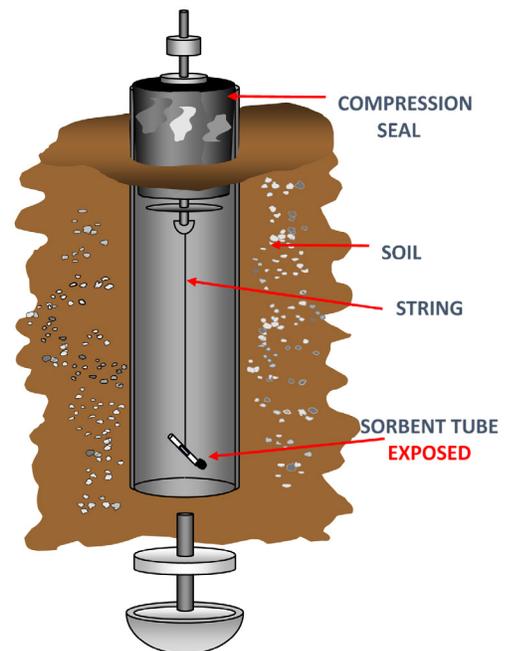


Figure 5. Schematic of the detachable head penetrometer used for deploying sorbent tubes in the field for collecting PFT gas samples.

### Partners

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