# Natural Analogs of Geologic $CO_2$ Sequestration: Some General Implications for Engineered Sequestration

Julianna E. Fessenden, Philip H. Stauffer, and Hari S. Viswanathan

*Los Alamos National Laboratory, Los Alamos, New Mexico*

Carbon dioxide emissions from geologic systems occur primarily from geothermal release of carbon in rock or subsurface biologic reservoirs. These systems can be very useful natural analogs for evaluating the impact of carbon dioxide leaks from engineered geologic storage reservoirs used to sequester $CO_2$. We describe three natural analog sites that illustrate very different leak scenarios that could occur at such engineered repositories. The Mammoth Mountain site, located in California, provides an example of diffuse $CO_2$ seepage. Crystal Geyser, Utah, is an example of a highly focused, episodic leakage geyser. Bravo Dome, NM is an example of a $CO_2$ reservoir where no leakage has been observed. We discuss monitoring techniques, technology placement, and modeling approaches that can be used at these natural analog sites to gain further insight into the viability of geologic $CO_2$ sequestration.

## 1. NATURAL ANALOGS AND LEAKAGE SCENARIOS

Carbon dioxide placement into geologic storage reservoirs is a novel approach that is being researched by the United States and other nations to reduce atmospheric $CO_2$ emissions. Pilot experiments are currently underway where $CO_2$ is being pumped underground in varying types of geologic reservoirs to understand the potential storage capacity, $CO_2$ movement, reservoir reactivity, and environmental impacts during geologic $CO_2$ storage. These pilot studies use monitoring technologies that detect $CO_2$ in the subsurface and surface regions; both direct and indirect methods of detection are being researched. These same monitoring technologies have been used to understand $CO_2$ movement, leakage, and impact in regions that naturally produce and trap $CO_2$. It is hypothesized that these natural analogs ($CO_2$-rich subsurface systems) can provide information on existing $CO_2$ storage scenarios and be applied to engineered geologic storage reservoirs.

Within the United States, the majority of natural analogs that produce and trap $CO_2$ are located at the base of or adjacent to mountain ranges and most are found in the Sierra Nevada and Rocky Mountain systems (*Chamberlain, et al.*, 2005; *Evans, et al.*, 2002; *Gilfillan, et al.*, 2006; *Kennedy-Bowdoin, et al.*, 2004; *McKenna and Blackwell*, 2003). $CO_2$ in most of these systems is produced through the interaction of fluid and rocks in geothermal reservoirs. The trapping efficiency of these systems is high, though can be compromised through natural or engineered impacts (e.g. faulting resulting from seismic events or puncturing caused by well placement) (*Bruno, et al.*, 2001; *D'Alessandro, et al.*, 2001; *Giggenbach, et al.*, 1993; *Goff and Janik*, 2002; *Hulston and Lupton*, 1996; *Kennedy, et al.*, 1987; *Lewicki, et al.*, 2007; *Sorey, et al.*, 1998b).

There are three types of leakage scenarios that are described in this manuscript, focused leakage, diffuse leakage, and no leakage. Focused leakage, either from a point source or along a line such as a fault, typically results from subsurface fractures that propagate to the surface where gas is released over a very limited surface area. Often, focused releases result in geysers or fumaroles. Diffuse leakage, also called seepage, occurs over large surface areas and can result from subsurface fractures or other high permeability pathways that do not propagate to the surface. In diffuse systems, $CO_2$ typically fills and then is released from the underlying fracture(s) then expands horizontally during migration towards the surface. As a result, a large surface footprint of $CO_2$ release (seepage) is observed. (*Allis*, 1982; *Bruno, et al.*, 2001; *Dalessandro, et al.*, 1997; *Kennedy and Truesdell*, 1996; *Lewicki, et al.*, 2007). Natural analogs of systems where no leakage occurs have reservoir seals that have not been compromised and/or whose fault systems have been cemented through mineral precipitation or displacement (re-sealing of a fault) (*Farrar, et al.*, 1995; *Hill, et al.*, 2002; *Kamenetsky and Clocchiatti*, 1996; *Moore, et al.*, 2005; *Pearce*, 2006). These natural accumulations of $CO_2$ with very good trapping mechanisms are often tapped to supply enhanced oil recovery operations where $CO_2$ is used to decrease oil viscosity. This often leads to increased total oil extraction fractions for a given field.

Natural analogs have been studied to understand the mechanisms of release and trapping of $CO_2$, the capacity and long-term production of $CO_2$, and the environmental impacts of released $CO_2$. The lessons learned from natural analog research can be directly applied to engineered geologic systems as both storage systems have similar mechanisms of leakage, $CO_2$ movement, and chemical reactivity in the reservoir and related groundwater systems (*Pearce*, 2006). The monitoring technologies used in natural analog systems can also be used in geologic storage sites.

Many natural analogs are in an equilibrium state, where the reservoir, overlying strata and groundwater have been exposed to $CO_2$ for hundreds to thousands of years. As a result, the chemistry and physical conditions of a natural $CO_2$ reservoir may have reached a steady state (*Lewicki, et* *al.*, 2007; *Pearce*, 2006). However, in engineered geologic systems, $CO_2$ will be introduced to a reservoir and the resulting chemical and physical changes due to this introduced $CO_2$ will be more dynamic in nature and time dependent changes of state will dominate the system and dictate ensuing modeling efforts. Because of the significant differences in equilibrium behavior, we have chosen two analog sites (focused release and diffuse release) that are clearly not in equilibrium in an attempt to locate sites that demonstrate some of the same effects that we might see in engineered systems. The case of 'no release' is more difficult to find a non-equilibrium example for because of the inherently long-lived nature of the sealing mechanisms that define such sites.

The purpose of this manuscript is to describe three scenarios of $CO_2$ release from natural analogs (i.e. focused release, diffuse release, and no release). We discuss how the lessons learned from research conducted at these sites can be used to improve models of engineered $CO_2$ storage reservoirs. Specifically, monitoring technologies, placement of these technologies in varying network designs, and system model analyses of $CO_2$ movement and prediction of environmental impacts are discussed.

## 2. UTILITY OF NATURAL ANALOGS IN UNDERSTANDING ENGINEERED SYSTEMS-CASE STUDIES

### *2.1. Natural Analogs with Focused $CO_2$ Release, Crystal Geyser, UT*

Focused-release systems including geysers are being investigated as possible analogs to $CO_2$ release from fast pathways in engineered systems. Specifically, deteriorated wellbores in storage reservoirs are the analogous example of a geyser. The pathway of release, the impact on the conduit walls and interceding water layers, and the surface $CO_2$ plume are similar in both natural and engineered scenarios (*Carey, et al.*, 2007; *Lewicki, et al.*, 2007). Yet, the rate of chemical alteration, the release rate, and the time scales for impacts are different between engineered and natural focused-release scenarios. For example, some focused-flow natural analogs may have been exposed to $CO_2$ for thousands to tens of thousands of years (*Johnson, et al.*, 2003). Analysis of specific systems suggests that the surrounding rock has undergone chemical and physical changes and has probably reached a chemical equilibrium with the internal $CO_2$ and water (*Czernichowski-Lauriol, et al.*, 2006; *Hansen, et al.*, 2005; *Johnson, et al.*, 2003). The timing and flux of $CO_2$ release from geyser systems can be quite regular and the mechanisms of release are often uniform (e.g. near surface cavities that fill with water and gas and episodically release to the atmosphere depending upon chamber pressure and temperature (*Connor, et al.*, 1992; *Kennedy-Bowdoin, et al.*, 2004; *Rojstaczer, et al.*, 2003). As a result, $CO_2$ release from geyser systems can often be predicted and forecasted with only small changes occurring over decades to hundreds of years (e.g. Yellowstone Valley, (*Boomer, et al.*, 2000; *Hutchinson, et al.*, 1997)).

However, engineered systems are typically not in chemical or physical equilibrium. In engineered systems, rocks that have not been exposed to $CO_2$ are much more likely to experience strong disequilibrium processes, where non-linear rates of chemical precipitation and rapid changes in reservoir physical properties (e.g., temperature, pressure, porosity) are predicted to occur (*Pruess, et al.*, 2004). As a result, wellbores that are exposed to these conditions are expected to lose integrity when cement used to assist with casing emplacement or cement used for closure of old wellbores degrades in the presence of $CO_2$-rich fluids. Wellbore degradation may lead to $CO_2$ flow along fast pathways, either within open wellbore intervals above the reservoir, or along the damaged zone between the well casing and the country rock (*Chen, et al.*, 2003; *Pellegrini, et al.*, 2006; *Yu, et al.*, 2003). As $CO_2$ travels through a leaky wellbore, chemical reactions with the casing, the surrounding country rock, cement, and in situ water may lead to changes in permeability and porosity that will cause changes in the leakage rates of $CO_2$ with time(*May*, 2005; *Worden*, 2006). Additionally, phase changes associated with pressure drops along the upward flow path can lead to highly non-linear leak rates as supercritical $CO_2$ transitions to liquid, gas, and even solid $CO_2$ in special cases (*Pruess*, 2006; *Skinner*, 2003). The non-linear $CO_2$ flux and conduit chemical response that are likely to occur in engineered systems may be quite different than the fluxes found in natural focused-release systems that are thought to have reached quasi-equilibrium.

Crystal Geyser, Utah is an example of a geyser that is being studied to understand focused leakage release (*Allis*, 2005; *Gilfillan, et al.*, 2006; *Heath*, 2004; *Heath, et al.*, 2008) (). Crystal Geyser is located on the Colorado Plateau, on the east side of Utah, close to the Green River, 38.9ºN, 110.1ºW(*Heath, et al.*, 2008). This cold geyser was artificially created when a wellbore, drilled in 1935, intersected an artesian aquifer (the Navajo Sandstone) with water containing $CO_2$ (*Heath*, 2004; *Heath, et al.*, 2008; *Shipton, et al.*, 2004). As the $CO_2$ and water rise together in the wellbore, $CO_2$ degasses from the water and leads to changes in water/gas fractions in the borehole. Accumulation of gas in the borehole eventually leads to an explosive eruption. The irregular discharge seen at this site is related to the average rate of discharge of the aquifer into the borehole, the amount of $CO_2$ found in the water, the size and length of the borehole, and damage to the borehole as noted in Heath (2004) and Shipton et al. (2004). If any of these parameters were to change, the period and or magnitude of the geyser events would likely change. Although the geyser is a recent phenomenon, the borehole was sited in a travertine mound that is over 20 m thick, suggesting carbonate rich discharge at this site over the span of many years (*Gilfillan, et al.*, 2006; *Heath*, 2004; *Heath, et al.*, 2008; *Shipton, et al.*, 2004).

Because this geyser has both natural and anthropogenic components (i.e. natural $CO_2$ and a manmade wellbore), it is especially useful in understanding focused release from a wellbore. Typical $CO_2$ flux from this geyser is $1x10^{-3}$ tons/($m^2$ d) which is quite small compared to other geyser systems (45 $x10^3$ tons/($m^2$ d) Yellowstone volcanic fields) (*Allis*, 2005; *Werner and Brantley*, 2003). Research performed since 2002 includes surface analyses of $CO_2$ flux using soil chamber measurements, water chemistry analysis, and analysis of mineral precipitation on the walls of the well (*Allis*, 2005; *Evans, et al.*, 2002; *Moore, et al.*, 2005). Results have shown very little increased $CO_2$ flux away from the geyser with measurements returning to background values within a 10 m radius of the geyser. Measurements of well discharge show high bicarbonate and carbonate concentrations, high pH, high metal concentration, and large mineral deposits have been observed on the walls of the well (*Bruno, et al.*, 2001; *Giggenbach, et al.*, 1993; *Gilfillan, et al.*, 2006; *Heath*, 2004; *Heath, et al.*, 2008; *Heath, et al.*, 2002; *Rihs and Condomines*, 2002; *Shipton, et al.*, 2004; *Sorey, et al.*, 1998b; *Werner, et al.*, 2000).

Although the Crystal Geyser is only 65 years old, the regular release behavior is consistent with many of the mature geysers found in Yellowstone, implying that disequilibrium effects involving the wellbore, country rocks, and in situ waters are already at a quasi-equilibrium state. Further study of such hybrid natural/anthropogenic systems will be quite useful in determining likely behavior of leaking wellbores at $CO_2$ sequestration sites.

### *2.2. Natural Analogs with Diffuse $CO_2$ Release, Mammoth Mountain, CA*

Natural analogs that leak $CO_2$ and have a surface seepage release are being studied to understand the $CO_2$ migration and environmental impacts in caprock fracture scenarios in engineered reservoirs. When the caprock is fractured and $CO_2$ is released from the storage reservoir, deep in the subsurface, it will spread horizontally as it migrates to the surface (*Lewicki, et al.*, 2007; *Oldenburg and Unger*, 2005). This will cause the surface release to be more diffuse and spatially extensive. The $CO_2$ will impact a larger footprint of overlying rock, groundwater, and potentially vegetation (*Haszeldine, et al.*, 2005; *Lewicki, et al.*, 2007). As a result, quantifying the $CO_2$ plume will be more challenging.

The similarities between natural analogs and engineered $CO_2$ storage reservoirs expressing seepage release are the mechanisms of release (e.g. subsurface fault or fractures that release $CO_2$ and induce lateral spreading as the plume ascends) and the impacts to the surrounding rock and water layers. However, due to the difference in $CO_2$ exposure time between engineered and natural systems, natural systems may have more uniform $CO_2$ fluxes, near-equilibrium chemical states, and lower vegetation impacts than we expect to see in engineered systems.

One of the most famous diffuse $CO_2$ seepage natural analog sites within the United States is located in central California, at the base of Mammoth Mountain. Mammoth Mountain is located on the east side of the Sierra Nevada Mountain range, at 37.7ºN, 119.0ºW. Mammoth Mountain is currently releasing cold, diffuse $CO_2$ from a 6 km deep magma chamber (*Gerlach, et al.*, 2001; *Hill and Prejean*, 2005; *Sorey, et al.*, 1998a). The $CO_2$ escapes the chamber from fractured dikes and faults that opened in 1989 after a series of long-period seismic events (*Hill, et al.*, 2002). A clear indication that the near surface was not in equilibrium with the current $CO_2$ flux is the observation of massive tree-kills over the locations of increased $CO_2$ flux. The fact that the trees were unable to cope with the increased $CO_2$ flux implies that much lower fluxes were occurring until after the 1989 event. This site is of particular interest because of the obvious disequilibrium state of the system, making the Mammoth site more like a sequestration scenario than other analog sites that are closer to equilibrium.

At this site, $CO_2$ escapes through fractures and emerges in several 5 to 10 hectare regions around the base of the mountain (see Figure 1). The flux of $CO_2$ from these areas is calculated to be $7.5x10^{-3}$ tons/($m^2$ d). Extensive measurements at one of the tree-kill locations, Horseshoe Lake, range from $4.5x10^{-4}$ tons/($m^2$ d) to $1.33x10^{-3}$ tons/($m^2$ d) (*Evans, et al.*, 2001; *Farrar, et al.*, 1995; *Rahn, et al.*, 1996). Carbon dioxide concentrations of up to 90 % (by volume) have been measured in the soil gas. The high $CO_2$

concentrations have killed surface vegetation, changed the chemistry of the aquifer, and impacted the regional atmospheric concentrations of $CO_2$ (*Cook, et al.*, 2001; *Evans, et al.*, 2001; *Farrar, et al.*, 1995; *Sorey, et al.*, 1998b).

Research on $CO_2$ flux, regional water chemistry, associated trace gas emissions, stable and radiogenic isotope signatures, and vegetative and microbial response has been conducted at this site since 1993. More than 10 years of data are available on monitoring technologies and environmental response to $CO_2$ emission at this natural analog location. These data from Mammoth can provide constraints on diffuse $CO_2$ seepage that may be analogous to leakage from geologic $CO_2$ storage reservoirs.

### *2.3. Natural Analogs with No $CO_2$ Release, Bravo Dome, NM*

Naturally occurring accumulations of $CO_2$ that currently show undetectable surface $CO_2$ leakage or seepage are also being studied to understand characteristics that promote effective engineered $CO_2$ storage reservoirs. Effective $CO_2$ traps are important storage reservoirs that provide examples of geologic systems that are impermeable to $CO_2$ leakage. These systems are also important in understanding reservoir rock and water chemistry changes as well as pressure change impacts on seal integrity as $CO_2$ is mined out of the reservoir system (e.g. McElmo Dome, Bravo Dome). Within these $CO_2$ traps, it is often more difficult to use direct measurements to look at $CO_2$ impacts to the rock and water chemistry because drilling and core extraction is required. Drilling may severely impact the integrity of the seal and therefore indirect (seismic) imaging is often used to understand these 'no leakage' subsurface systems (*Roberts and Godfrey*, 1994).

The extent of reaction and the $CO_2$ impact on the water and rock chemistry will be dynamic, and therefore difficult to evaluate, in engineered systems due to the timing of exposure to $CO_2$. It is hypothesized that these systems will eventually reach equilibrium and, if the seal is never compromised, will behave in a similar fashion to natural $CO_2$ traps after thousands to tens of thousands of years (*Czernichowski-Lauriol, et al.*, 2006; *Hansen, et al.*, 2005; *Haszeldine, et al.*, 2005; *Johnson, et al.*, 2003; *Pearce*, 2006; *Worden*, 2006).

Bravo Dome, NM (39.8 ºN, 111.8 ºW)) is being studied as an effective $CO_2$ trap. Bravo Dome is one of the world's largest natural $CO_2$ fields and is actively being mined for enhanced oil recovery markets (*Wash*, 1984). The $CO_2$ is trapped in a sandstone reservoir (Tubb Sand) with a shale caprock (Devonian Shale) (*Broadhead*, 1991). The reservoir is between 500 to 700 m deep and is being dynamically filled (*Baines and Worden*, 2000). Seismic research has shown small stratigraphic anomalies and fairly uniform caprock structure (*Roberts and Godfrey*, 1994). Soil $CO_2$ flux measurements and groundwater chemistry measurements have shown no anomalous $CO_2$ flux or change in water chemistry due to the underlying $CO_2$ reservoir (*Baines and Worden*, 2000). Therefore, it is concluded that this reservoir is an effective $CO_2$ trap.

## 3. DATA COLLECTION AND ANALYSIS

### *3.1. Monitoring Technologies Used at Analog Sites*

There are both direct and indirect monitoring technologies that have been used at natural analog sites. These technologies are being adapted for engineered storage sites. However uncertainties in the resolution of these technologies are constraining the efficacy of monitoring $CO_2$ storage in engineered systems. As a result, an adaptive tool set, applicable to the engineered storage reservoir type, is required for effective measurement, monitoring and verification (MMV) of $CO_2$ in engineered systems.

The most common direct monitoring technologies that have been used at natural analog sites are $CO_2$ flux measurements (from chamber, tower, or aircraft platforms), trace gas and isotopic tracers, water chemistry analyses, and mineralogy analyses on various rock surfaces. The most common indirect monitoring technologies used at natural analog sites are seismic imaging. Additionally, recent work in acoustic, electric, and gravimetric imaging appears promising. Each of these technologies will be described in detail below with the exception to the novel indirect methods which will be reserved for another manuscript.

Measurement of carbon dioxide flux is a dominant monitoring technology that has been used at Mammoth Mountain, Crystal Geyser, and Bravo Dome to quantify $CO_2$ release and heterogeneity (temporal and spatial) of the $CO_2$ flux at the surface (*Allis*, 2005; *Anderson and Farrar*, 2001; *Martini*, *et al.*, 2000). This technology relies on monitoring the $CO_2$ concentration change with time at varying spatial scales from point locations (chamber), to local scales (tower), to regional scales (aircraft). An infrared gas analyzer (IRGA) or a laser system is used to measure the absorption of $CO_2$ (*Martini, et al.*, 2004; *Martini, et al.*, 2000). Specific results of these technologies used at Mammoth Mountain have shown concentrations of $CO_2$ as high as 10, 000 ppm at 600 m and as high as 100,000 ppm at 2 m in the atmospheric column above areas of severe tree kill (*Martini, et al.,* 2004; *Martini, et al.,* 2000).

Trace gas and isotopic tracers have been used to determine the origin of the $CO_2$ observed in both the atmosphere and groundwater systems. This technology has been used extensively at Mammoth Mountain, Crystal Geyser, and tested at Bravo Dome (*Allis*, 2005; *Cook, et al.*, 2001; *Evans, et al.*, 2002; *Farrar, et al.*, 1995; *Gerlach, et al.*, 2001; *McGee, et al.*, 2000; *Moore, et al.*, 2005; *Rahn, et al.*, 1996; *Rihs and Condomines*, 2002; *Sorey, et al.*, 1998a). The trace gases that have been associated with subsurface $CO_2$ reservoirs are typically sulfur-containing gases ($H_2S$, $SO_2$), methane rich gas, and high concentrations of radon (*Bruno, et al.*, 2001; *D'Alessandro and Vita*, 2003; *Rihs and Condomines*, 2002; *Sorey, et al.*, 1998a). Isotopic tracers used to verify subsurface $CO_2$ origin have been the stable and radiogenic isotopes of carbon in the $CO_2$ ($^{14}C/^{12}C$, $^{13}C/^{12}C$), and the $^3He/^4He$ ratios associated with the $CO_2$ plume (*Allis*, 2005; *Cook, et al.*, 2001; *Evans, et al.*, 2002; *Farrar, et al.*, 1995; *Gerlach, et al.*, 2001; *Heath*, 2004; *Heath, et al.*, 2008; *McGee, et al.*, 2000; *Moore, et al.*, 2005; *Rahn, et al.*, 1996; *Rihs and Condomines*, 2002; *Sorey, et al.*, 1998a). Typically, measurements of trace gasses and isotopic ratios are made in the laboratory on gas chromatographs and mass spectrometers (*Farley and Neroda*, 1998; *Kennedy, et al.*, 1985; *Ramsey and Hedges*, 1997).

Water chemistry data including pH, alkalinity, isotopes, trace gases, major and minor ions, and trace elements are used to monitor and analyse $CO_2$ impacts on local and regional aquifers (*Aiuppa, et al.*, 2000; *McGee and Gerlach*, 1998; *Sasamoto, et al.*, 2007; *Stephens and Hering*, 2004). Water and gas chemistry of aquifers associated with $CO_2$ releases have been measured at Mammoth, Crystal Geyser, and Bravo Dome to determine the impact of degassing (*Aiuppa, et al.*, 2000; *Allis*, 2005; *Evans, et al.*, 2002). Results from water chemistry analyses can be a first indication of $CO_2$ seepage or leakage from underground systems. As the parent rock begins to weather, the metals and trace elements contained in the soluble components of the rocks can be mobilized. Inductively coupled plasma mass spectrometers (ICP-MS) are used to measure trace metal concentrations, with a precision of ± 0.01 ppb for most elements. Ion chromatographs are used to measure major and minor ions (precision of ± one ppb), and titration systems are used to measure pH.

Changes in the mineral volume fractions of calcite, aragonite, dolomite, or siderite are used as indicators of $CO_2$ impact on regional parent rock (*Chamberlain, et al.*, 2005;

*Czernichowski-Lauriol, et al.*, 2006; *Emberley, et al.*, 2002; *May*, 2005; *Worden*, 2006). These changes can either increase or decrease permeability and porosity, leading to changes in the rate of leakage through the subsurface (*Czernichowski-Lauriol, et al.*, 2006; *Kamenetsky and Clocchiatti*, 1996; *May*, 2005; *Moore, et al.*, 2005; *Worden*, 2006). Calcite precipitation has been observed at Crystal Geyser, Utah, where precipitation rates of one mm per month have been measured in the near surface walls of the geyser spout (*Gilfillan, et al.*, 2006; *Heath*, 2004; *Heath, et al.*, 2008). Rock precipitation and dissolution have not yet been documented at Mammoth Mountain. Although Bravo Dome is thought to be at a quasi-equilibrium with respect to fluid/rock interactions, the processes involved in depressurization during $CO_2$ extraction could change the thermodynamic state and allow changes in mineral precipitation and dissolution in regions near the extraction wells.

Seismic reflections can be used in geologic $CO_2$ sequestration reservoirs to delineate the location of injected $CO_2$, storage capacity, fractures, and stratigraphy. Data from geophone arrays are used in complex algorithms to generate 3D images of the strata, fractures, and liquids located in the subsurface. The imaging process can be repeated to provide a temporal component yielding information on changes in fractures, $CO_2$ or liquid movement, and capacity estimates (*Reasnor and Jenner*, 2003; *Yamamoto, et al.*, 2004). There are three seismic methods that use boreholes to get finer resolution measurements of strata, liquids, and fractures. Vertical Seismic Profiling (VSP) is a method that uses geophones installed down a borehole with the source remaining on the surface (*Korneev, et al.*, 2004; *Newrick and Lawton*, 2003); cross well tomography uses geophones and sources placed in two separate boreholes (*Gritto, et al.*, 2004); and passive seismic imaging uses geophones in one borehole with natural seismic events as the source (*Pullammanappallil, et al.*, 2004). All three of these methods increase the resolution of the seismic profiling between the source and receiver.

### *3.2. Technology Placement: Spatial and Temporal Constraints*

In the natural analogs presented, limited resources and spatial/temporal uncertainties constrain the experimental designs used for the technologies mentioned above. These technologies have limited ranges of resolution and result in uncertainty and monitoring gaps at a given research site. As a result, verification and quantification of $CO_2$ plumes in the subsurface (a requirement in engineered $CO_2$ reservoirs) becomes problematic if not impossible. Therefore, there is a need to increase the range of monitoring (both spatially and temporally) of existing technologies or to find new technologies that can fill the gaps.

Flux measurements taken from chamber systems resolve about areas up to one $m^2$ at the soil surface, while eddy covariance systems resolve areas in the range of 10 $m^2$, and aircraft flux measurements can resolve areas up to one $km^2$, above the soil and vegetative biomass (see Figure 2). Isotopic and trace gas analyses can resolve areas up to 10 $m^2$ and as deep as 100 m below ground surface, depending upon aquifer and fumarole depth (*Sorey, et al.*, 1998a). Water chemistry can resolve areas up to one $km^2$ depths to 60 m depending upon the aquifer geometry, well depth, and well placement (*Blanford, et al.*, 2005). Seismic imaging can resolve up to one $km^2$ and 10 km depth depending upon the placement of geophones (*Korneev, et al.*, 2004; *Newrick and Lawton*, 2003; *Reasnor and Jenner*, 2003). Depending upon infrastructure available for monitoring (e.g. wells), there is a gap of resolvable imaging or monitoring located between the $CO_2$ storage reservoir and the ground surface (e.g., the "intermediate zone" described by McPherson and Sundquist, 2008, the final chapter of this volume). If $CO_2$ escapes above the reservoir of interest there is limited technology that can observe and quantify $CO_2$ migration in the region between the caprock and the shallow subsurface. Sequestration sites are likely to be on the order of one km or deeper. Therefore, there is a significant need for more research exploring technologies that can better resolve this gap region, especially those using novel imaging technologies (e.g., indirect methods).

There has been some interesting research at the natural analogs sites (Mammoth, Crystal Geyser, Bravo Dome) exploring the placement of technologies to maximize resolution windows. For example, at Mammoth Mountain, flux chamber placement has ranged from point locations to regular grids across the tree-kill areas. Surprisingly little difference has been observed at the regional scale using these varying designs (see (*Evans, et al.*, 2001; *Gerlach, et al.*, 1999; *Rahn, et al.*, 1996)), though differences have been observed at the local scale (*Rogie, et al.*, 2001). At Crystal Geyser, flux chamber measurements have been made on transects across geologic features such as fractures and geysers (*Allis*, 2005; *Gilfillan, et al.*, 2006). High flux of $CO_2$ has been observed within a 2 m radius from the geyser, returning to natural background values by 10 m ((*Allis*, 2005; *Gilfillan, et al.*, 2006). From these examples it is clear that care must be made when interpreting results from varying technologies.

In addition to spatial heterogeneity, temporal variations of signals exist at a given research site (both micro- and macro-scales). Significant temporal changes have been observed in the results of some of the technologies listed above. The temporal changes are typically caused by meteorological and biological activity. For example, at Mammoth Mountain, $CO_2$ flux was measured at a single location over time and showed a change by a factor of two, from 2500 g/(m$^2$ d) to 5000 g/(m$^2$ d) within 24 hours depending upon atmospheric pressure (*Rogie, et al.*, 2001), or as much as a factor of 20, from 300 g/(m$^2$ d) to 6000 g/(m$^2$ d), depending on the interaction between flux chamber placement, local atmospheric conditions, and topography (*Rogie, et al.*, 2001). Also, significant seasonal impacts on water chemistry and tracer signatures have been observed at Mammoth and Crystal Geyser (*Allis*, 2005; *Rogie, et al.*, 2001). Therefore, care must be made when interpreting the results from the varying technologies. To minimize errors associated with temporal oscillations, both diurnal and seasonal analyses should be performed on any monitoring technology of interest to determine how a given method is affected over these time scales at a given site.

## 4 Using Natural Analogs to Predict Long Term Fate of $CO_2$ in Engineered Natural Systems

In addition to monitoring techniques, models need to be developed to assess geologic $CO_2$ sequestration sites. These models will need to predict sequestration behavior over long time scales (on the order of 1000 years) and over large areas (100s of km$^2$). Measurements that target long-term behavior of natural analog sites can be used to gather data these large spatial and temporal scales. These data can be used to verify the ability of the models to simulate general system behavior of the natural analog sites. Positive outcomes from such modeling will increase confidence in the capability of the models to simulate long-term sequestration behavior. Sites such as Mammoth can be used to explore diffuse leak scenarios whereas sites such as Crystal geyser can be used to examine focused releases. In addition, characterization of natural analogs is one of the most straightforward methods for obtaining information about the long term fate of $CO_2$ in a natural system. In this section, we describe the necessary components for a realistic system model and how natural analogs could help evaluate portions of the model.

Storage of $CO_2$ over long periods of time will rely on three aspects or processes in an engineered natural system: efficacy of impermeable seals, dissolution of $CO_2$ into brines, and mineralization through water-rock- $CO_2$ interactions. The first of these will likely be the primary mode for $CO_2$ containment in the short term, so predicting the flux through these seals and the long-term performance of these seals are of critical importance. Large-scale implementation of geologic storage in the U.S. will require reservoir seals with a cumulative area amounting to hundreds of square kilometers per year and will require a large number of storage sites. These factors highlight the need for a robust and reliable method for evaluating the suitability of specific sites to ensure that they will perform to required goals. Any evaluation method must address fundamental physics and chemistry over a large range in scale and must address uncertainties both in these phenomena and in the properties of the reservoir. In addition, the method must link these fundamental scientific inputs to decisions based on a required goal (e.g. <0.01% of $CO_2$ released per year).

To better understand the viability of $CO_2$ sequestration, process-level models (e.g. FEHM (Finite Element Heat and Mass Transfer) (*Tenma, et al.*, 2003; *Viswanathan and Valocchi*, 2004) or TOUGHREACT OR TOUGH2 (*Talman, et al.*, 2004; *Xu, et al.*, 2006) or FLOTRAN (*Holder, et al.*, 2000; *Lichtner, et al.*, 2001)) calibrated with field data and laboratory experiments are required to represent accurately the fundamental scientific processes over a wide variety of scales. However, we also need to assess the behavior of the overall system which requires abstracting complex process-level models into more simple forms and coupling them together into a system level model. The latter task is underway with the development of $CO_2$-PENS (Predicting Engineered Natural Systems)(*Stauffer, et al.*, 2006).

We have created $CO_2$-PENS, a system model that simulates many aspects of geologic $CO_2$ sequestration including: capture, transport to the injection site, storage, possible leakage pathways, fate in the reservoir and the affect of leaks on the atmospheric concentration. In addition, the model includes economic factors that can be used to assess the cost-benefit ratio of monitoring schemes described in preceding sections of this chapter. The eventual purpose of the model is to assess the viability of sequestering $CO_2$ at various sites.

One of the major challenges in modeling such a complex system is determination of model efficacy. Laboratory experiments take place over small time and length scales and their results need to be carefully interpreted for evaluating large sequestration sites that need to store $CO_2$ for 100s to 1000s of years. Field experiments and pilot sequestration sites can address the length scale problem but not the time scale issue. Natural analogs can greatly help in this area since they provide information about the long term fate of $CO_2$ in a natural system. Using the model to simulate a natural analog scenario would provide at least a partial evaluation of whether the model correctly predicts the long term fate of $CO_2$ in a natural system.

The Mammoth mountain site provides an example of a diffuse leak of $CO_2$ in an area where topography and atmospheric conditions are a challenge to simulate. Mammoth also is a site that is far from equilibrium and may yield clues to what long-term changes we should expect to see in rocks overlying a failed seal at a storage site. Crystal geyser provides an example of a focused leak from a well that can be used to validate wellbore release scenarios. Bravo dome can be used to investigate the stratigraphy of a location that has successfully sequestered $CO_2$ over geologic time.

The measurements obtained from the methods discussed in previous sections can be used to calibrate and evaluate efficacy of portions of a system model. Specifically, groundwater chemistry measurements can be used to detect the location of the $CO_2$ plume in the subsurface and can be compared to results from reactive transport models to check that the reactive transport processes occurring in the subsurface are being simulated meaningfully. As new data from these sites become available, the conceptual and numerical models of flow and transport must be constantly checked and updated (improved) as our understanding of the different systems expands. Seismic methods can be used to gain information about the geologic stratigraphy and fluid movement in the subsurface. These measurements can be compared against reservoir models. At the surface, flux chambers, flux towers and aircraft can be used to detect $CO_2$ concentration over a range of scales. Flux chamber measurements can be used to measure focused $CO_2$ emissions and can be compared to atmospheric simulation models for focused release scenarios. Measurements from flux towers and aircraft provide average concentration over a given area. These could be compared to atmospheric simulations of diffuse leak scenarios.

Comparing model results against natural analogs is a key step in evaluating their use for choosing engineered natural system sites for $CO_2$ sequestration. As models advance and more data become available, natural analogs need to play a role in improving models.

## 5. SUMMARY AND CONCLUSIONS

Data from natural analogs sites can be used in combination with system and process models to understand and predict the fate of $CO_2$ in engineered storage reservoirs. Data of $CO_2$ emission rates, water chemistry, and chemical precipitation-dissolution rates from these natural analogs can provide estimates for seepage, reservoir impacts, and aquifer chemistry for engineered geologic $CO_2$ storage reservoirs.

Comparison of scenarios of $CO_2$ release from diffuse and focused source natural analogs shows that these release scenarios behave differently and require different monitoring schemes. For example, the required spatial and temporal density of monitoring instruments as well as the instrument sensitivity for monitoring networks are quite different. Detection of diffuse systems requires more sensitive instruments with high spatial resolution, while focused leaks require high resolution temporal monitoring but can be detected with lower sensitivity instruments. With a high-resolution model, different monitoring schemes can be evaluated. The model could then be used to determine the optimum placement of measurement devices. In addition, a cost-benefit analysis could be performed to select the appropriate monitoring scheme.

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Dr. Julianna Fessenden, Earth and Environmental Sciences, Los Alamos National Laboratory, MS D462, Los Alamos, NM 87545.

Dr. Philip Stauffer, Earth and Environmental Sciences, Los Alamos National Laboratory, MS D462, Los Alamos, NM 87545.

Dr. Hari Viswanathan, Earth and Environmental Sciences, Los Alamos National Laboratory, MS D462, Los Alamos, NM 87545.

FIGURE CAPTIONS

**Figure 1a.** Map of the Mammoth Mountain area. Dark gray zones indicate tree kills or measured high soil $CO_2$ concentrations and are identified as Horseshoe Lake (HSL), Horseshoe Lake Fumarole (HSLF), Red's Lake (RL), Red's Creek (RC), Chair 12 (CH12), Lodge East (LE), and Lodge South (LS). Numbered black squares indicate the location of stations occupied for tree collection in August, 1995**. 1b.** Aerial photograph of south side of Mammoth Mountain highlighting the Horseshoe Lake tree kill, with Horseshoe Lake in the foreground.

**Figure 2.** Spatial resolution of monitoring technologies given in 2D surface scales (left panel) and depth scales (right panel). Solid lines delineate length scale and gray text indicates technologies that are applicable within the length scale.

NATURAL ANALOG APPLICATION TO $CO_2$ STORAGE

FESSENDEN, STAUFFER, VISWANATHAN

# Natural Analogs of Geologic $CO_2$ Sequestration: Some General Implications for Engineered Sequestration

Julianna E. Fessenden[1], Philip H. Stauffer[1], and Hari S. Viswanathan[1]

*Los Alamos National Laboratory, Los Alamos, New Mexico*

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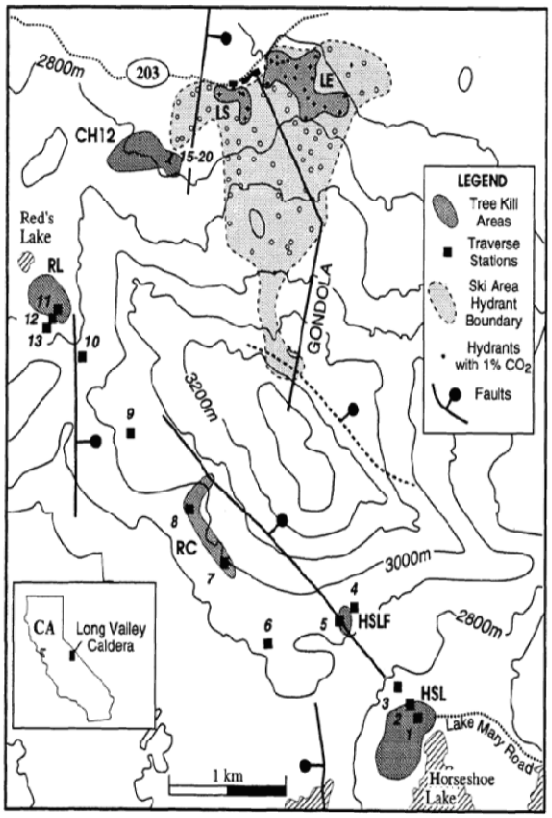
[1] Earth and Environmental Sciences, Los Alamos National Laboratory, MS D462, Los Alamos, NM 87545


2800m
203
LE
LS
CH12
15-20
LEGEND
Tree Kill Areas
Traverse Stations
Ski Area Hydrant Boundary
Hydrants with 1% CO2
Faults
Red's Lake
RL
11
12
13
10
9
3200m
GONDOLA
8
RC
7
3000m
4
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HSLF
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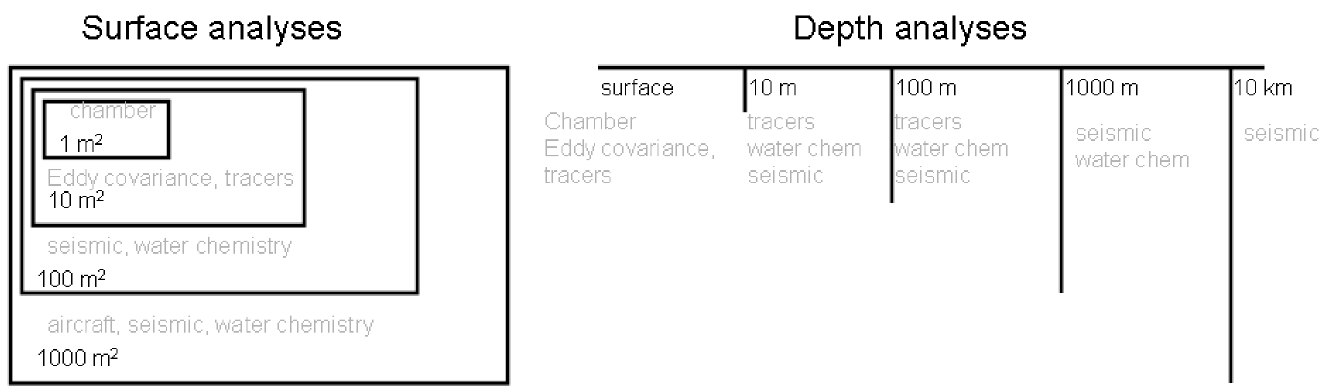
2800m
3
HSL
2
1
Lake Mary Road
Horseshoe Lake
1 km
CA
Long Valley Caldera

**Figure 1**


Surface analyses
chamber
1 m²
Eddy covariance, tracers
10 m²
seismic, water chemistry
100 m²
aircraft, seismic, water chemistry
1000 m²
Depth analyses
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10 km
Chamber
Eddy covariance,
tracers
tracers
water chem
seismic
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water chem
seismic
seismic
water chem
seismic

**Figure 2**