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Abstract: A controlled field pilot has been developed in Bozeman, Montana, USA, to study near surface CO₂ transport and detection technologies. A slotted horizontal well divided into six zones was installed in the shallow subsurface. The scale and CO₂ release rates were chosen to be relevant to developing monitoring strategies for geological carbon storage. The field site was characterized before injection, and CO₂ transport and concentrations in saturated soil and the vadose zone were modeled. Controlled releases of CO₂ from the horizontal well were performed in the summers of 2007 and 2008, and collaborators from six national labs, three universities, and the U.S. Geological Survey investigated movement of CO₂ through the soil, water, plants, and air with a wide range of near surface detection techniques. An overview of these results will be presented.

Keywords: *Geological carbon sequestration; Controlled release of carbon dioxide; Transport models; Near surface monitoring; Eddy covariance; Hyperspectral imaging*

Introduction

One aspect of mitigating global climate change is the capture and storage of carbon in geologic formations. Technologies for assuring effectiveness of carbon capture and storage under deep injection conditions have already been implemented at pilot sites such as Weyburn (Whittaker 2004) and Frio (Hovorka et al. 2006).

Two other types of experiments have sought to address these issues and have yielded valuable information.

First, natural analog sites where geologically generated CO₂ rises to the surface such as Mammoth Mountain (Anderson and Farrar 2001; Lewicki et al. 2008) and the Lateral caldera in Italy (Annunziatellis et al. 2008) have been investigated using a variety of detection technologies which have determined soil gas concentrations and soil gas flux of CO₂ as well as impact on plant life. These sites have a long-established flux and an unknown source term which makes it difficult to establish detection limits for near surface monitoring technologies and hampers transport modeling because flow paths have been long established. Additionally, onset of environmental response such as plant stress and recovery rates after excess CO₂ exposure ceases cannot be studied at the natural analog sites. Both of these issues may be of interest in using plant response for leak detection in engineered storage sites.

Second, there has been a small scale experiment using ~2.5 x 2.5 m land plots each fed with a separate CO₂ line (West et al. 2009). This experiment is highly useful for its designed intent, understanding the biological response of various plant types at elevated CO₂ levels. The small spatial extent, however, makes it difficult to scale to potential seepage at a storage site and does not allow suitable testing of detection technologies that measure or survey larger areas.

Zero Emission Research and Technology Center (ZERT, a collaborative involving three universities and six DOE national laboratories) has developed a testing site with (1) controllable, shallow release of CO₂ to provide controlled flux, (2) the ability to start and stop flow to measure onset and recovery response times, and (3) a large enough spatial extent to permit testing of most relevant detection technologies.

A wide variety of detection methods have been implemented at the ZERT site with the goal of establishing detection limits for various methods, determining efficacy of monitoring strategies and understanding transport from the saturated zone to the vadose zone and ultimately to the atmosphere. Release rates were chosen to both challenge detection limits of near surface detection technologies and also mimic low-level seepages consistent with desired retention rates that would mitigate climate change as per the IPCC guidance (IPCC 2005). If a storage project

for a 500 MW power plant is envisioned, a total of ~200 Megatons of CO₂ will be emplaced over the power plant lifetime (~4 Mt/year times 50 years). A retention rate of 99.999% per year (99% retention over 1,000 years) would result in escape of approximately 20,000 t/year or 54 t/day. If this were to occur along a fault of dimensions 1 km long by 70 m wide, the ZERT facility would be 1% of this dimension. Thus, a flow of 0.54 t/day at the controlled site would yield the same surface flux (over a smaller area) that is realistic for desired retention rates. A rate was chosen that was a significant fraction of this value, 0.3 t/day.

Characterization of the field site

Soil and plants

The ZERT field site is located on a relatively flat 12 ha former agricultural plot at the western edge of the Montana State University-Bozeman campus in Bozeman, Montana, USA. It is at an elevation of 1,495 m. Vegetation on the site consists primarily of alfalfa, clover, dandelion, thistle, and a variety of grasses. Conditions underlying the field are typical of the Bozeman area with alluvial sandy gravel deposits (1,500–1,800 m thick) overlain by a few meters of silts and clays with a topsoil blanket (Mokwa R., “Subsurface exploration for the MSU CO₂ injection project-Phase I”, unpublished report, Montana State University, Civil Engineering Department, 2006). There is moderate variation in the thickness of the topsoil layer which manifests itself as gentle surface features such as swales and ridges on the field. Test pits and cores collected from several locations on the field consistently revealed two distinct soil horizons. The topsoil of organic silt and clay with some sand ranges in thickness from 0.2 to 1.2 m. Beneath this is a cohesionless deposit of sandy gravel extending to the deepest depths investigated (5 m).

To assess bulk soil properties that could influence CO₂ transport, several field measurements were performed. In October 2006 percolation tests were carried out to make estimates of hydraulic conductivity. These tests involved digging a hole 7 in. deep and repeatedly filling with 6 in. of water and measuring the time for the water level to drop 1 in. Resulting hydraulic conductivities were calculated in length/time units. The hydraulic conductivity measured in the upper soil (sandy silt) layer was ~0.76 and ~1.4 m/ day in the sand-gravel aquifer. In separate measurements the average bulk density of the topsoil layer was determined from core samples to be 1.4 g/cm³.

In July–October of 2007, 18 soil gas permeability measurements were taken using a compressed air-based permeameter developed by Iversen et al. (2003). The permeameter was used to measure the relative permeability to flowing air of the top 0.46 m of soil. Concurrent

measurements of soil moisture in the top 0.3 m of soil were made using Time Domain Reflectometry (e.g. Topp and Davis 1985). Soil moisture was expressed as percent saturation (i.e. percent of soil void space occupied by water) and air permeability was computed in Darcy units. Two observations were made: (1) under wet soil conditions (percent saturation ~95%) soil permeability to gas varied between 3.9 Darcy for soil with prairie grass growing in it and 9.5 Darcy for soil with alfalfa, and (2) for relatively dry soil conditions (percent saturation less than ~60%) soil gas permeability ranged between 106 and 437 Darcy with no correlation observed with plant species.

Groundwater

The depth of the water table at the ZERT field site varies seasonally but always remains quite close to the ground surface. Following heavy springtime precipitation events it has been observed to be essentially at the ground surface in lower lying areas of the field. Over the two and a half years the depth of the water table has been monitored at the site, a variation of about 1 m has been recorded. During summer months the depth of the water table averages about 1.5 m below ground surface at the southwest end of the horizontal well. From measurements made in 2006, the direction of the ground water gradient was estimated to be 17° west of north. Samples taken by the U.S. Geological Survey before the first CO₂ injection of 2008 showed the groundwater to have a pH of approximately 7 and a fresh water salinity of about 600 mg/L TDS. The dominant anion is HCO₃, and the dominant cations are Ca and Mg. There are relatively low concentrations of Cl and SO₄, and the concentrations of Fe, Mn, Zn, Pb and other trace metals are expectedly low, at ppb levels (see Kharaka et al., this issue for further details).

Meteorology

Meteorological data including barometric pressure, temperature, relative humidity, and wind speed and direction have been continuously monitored at the field site since September of 2006. This has been supplemented with precipitation data during and directly before and after CO₂ releases. Weather stations on the field record a fairly consistent diurnal pattern during summer months, with daytime winds tending to come from the W-NW and nighttime winds tending to come from the S-SE. This indicates the general pattern of air rising from the lower portions of the valley toward the higher elevations with daytime heating followed by nighttime downslope winds with valley cooling. In addition to weather data, local soil moisture levels in the upper 30 cm of soil were recorded by an array of 15 water content reflectometers in the summer of 2008.

Controlled release infrastructure

Horizontal well

The horizontal well was sited on the field 45° east off true north. This orientation was chosen to allow resolution of vector components perpendicular to the well of potential CO₂ transport both in groundwater and by wind. In order to minimize the disturbance to the formation, horizontal directional drilling was chosen as the method of installation over more aggressive, albeit easier and less costly methods such as trenching. The well casing is 98 m of 10.16 cm diameter Schedule 40, 304 L stainless steel pipe. Fifteen and twelve meters on the southwest and northeast ends, respectively, is solid casing. The remaining central 70 m is slotted with a 20-slot pattern and has an open area of 0.55%. Directed Technologies Drilling Inc. installed the well in early December of 2006. A biodegradable drilling fluid manufactured by Cetco called Cleandril that is composed largely of cornstarch, guar gum, and xanthan gum was used as a lubricant and later flushed with enzyme breaker in the well development stage. To preserve the connectivity with the surrounding formation use of bentonite as a drilling fluid was avoided. Although effective in the installation process, bentonite would have left an unacceptable impermeable annulus around the well casing.

Cobble in the gravel layer presented very difficult drilling conditions, and it was not possible to install the well screen without some deflection off of a level straight path. Vertical location (accuracy of ±5% of the absolute depth) of a sonde in the drilling head was done every 4.6 m along the length of the well during installation. Thus, depth below ground surface and the location on the surface directly above the well is known at intervals of 4.6 m. The average depth of the slotted section of the well is 1.8 m below the ground surface. For the 2007 and 2008 experiments this means that the CO₂ was injected into the sandy gravel layer and below the water table.

The CO₂ injected was food grade and originated from Alberta and Wyoming natural gas fields. The refrigerated liquid CO₂ stored on site was converted by a vaporizer to deliver gaseous CO₂ at roughly ambient temperature. An inline regulator stepped the pressure down to ~55 psig before it entered the mass flow controller system.

Mass flow controller and packer system

To improve the chances of getting an even distribution of CO₂ along the length of the slotted section of the pipe and to increase the flexibility of the system, the well was partitioned into six

zones (five 12 m long zones and one 9 m long zone) by a packer system designed by Lawrence Berkeley National Laboratory. The zones are isolated from each other by natural rubber packers inflated with compressed air. Because each zone is plumbed separately and has a dedicated mass flow controller, CO₂ flow to each zone can be controlled independently (Fig. 1). Line pressure, zone pressure, and flow rate to each zone is monitored and recorded as well as above ground ambient temperature and atmospheric pressure. The mass flow controller system delivered CO₂ to the well at injection pressures only slightly above atmosphere (0–6 psi). This was done to ensure the formation surrounding the well was not distorted by the injection.

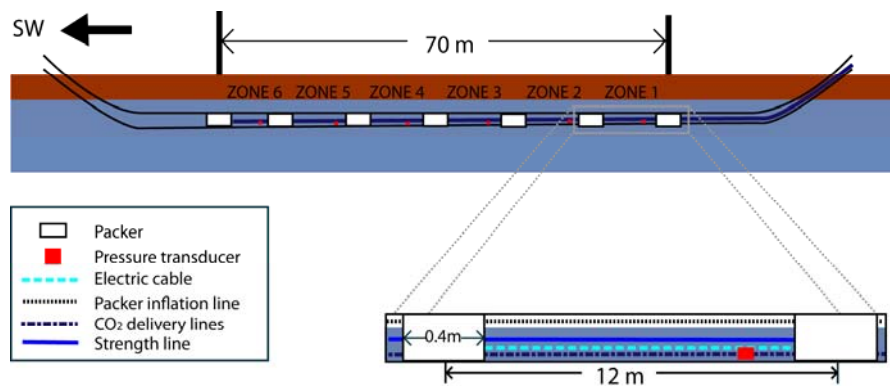


Fig. 1 Schematic of packer system installed in horizontal well. The 70 m slotted section of the well is partitioned by inflatable packers into six individually plumbed zones.

Reference grid

To provide a common reference system for researchers, a grid with 10 m spacing centered on the horizontal well was established with survey grade GPS equipment. The grid was defined to pass through the ends of the well. It extends 50 m off the line of the well to the northwest and southeast and 90 m southwest and northeast from the midpoint of the well.

Water monitoring wells

Changes in shallow ground water chemistry in response to CO₂ injection were investigated with five pairs of 5 cm diameter water monitoring wells (Fig. 2) installed at the southwestern end of the slotted section of the horizontal well (zone 6 in Fig. 9). The wells also permitted sampling of the head space gas. Each pair consists of one well that is 3 m deep and another well that is 1.5 m deep. The bottom 0.60 m of each well is screened. Four pairs are downgradient of the

horizontal well at distances from the horizontal well between 1 and 6 m, and one pair is 2 m upgradient. In December of 2008 three additional wells were installed. Well W6 is 4 m downgradient of the horizontal well. It is 2.6 m deep with the bottom 0.76 m screened. Wells W7 and W8 are approximately 12 m downgradient and upgradient, respectively, of W6 along the line of ground water flow. They are 3 m deep with the bottom 1.5 m of the well screened.

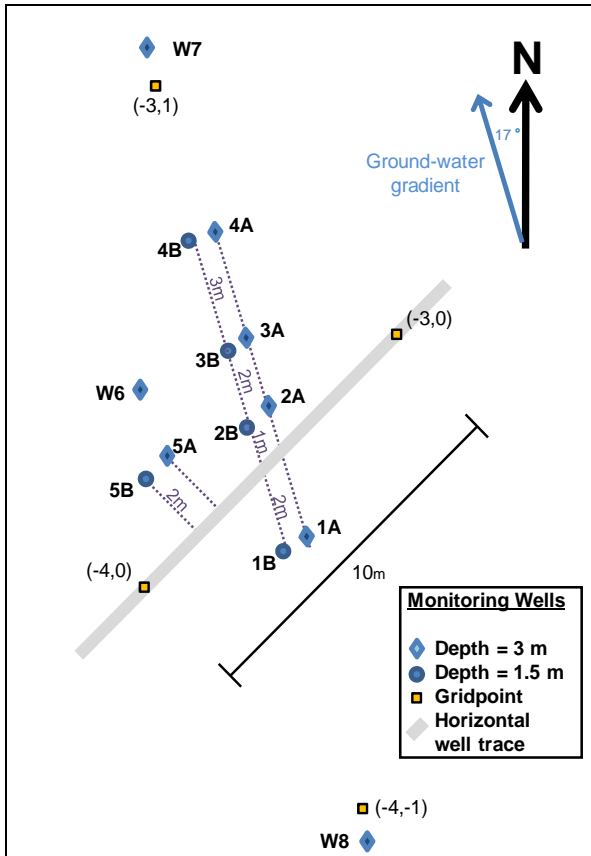


Fig. 2 Water monitoring well array. Ordered pairs refer to coordinates in the reference grid. The trace of the horizontal well on the ground surface is indicated in *gray*.

Pre-injection modeling

Modeling studies predicting pressures and migration patterns were carried out to assist in selecting CO₂ injection rates and designing a monitoring network. The goal was to choose an injection rate that produces (1) very small pressure increase around the well to minimize the possibility of fracturing the ground, (2) seepage flux and shallow concentrations that are large enough to be detectable while small enough to be challenging to detect, and (3) reasonable time between onset of injection and breakthrough at the ground surface so that personnel do not have

to wait a long time in the field for the seepage to begin. Two-dimensional simulations of CO₂ injection performed before the actual release gave information on what to expect for seepage flux, breakthrough time, subsurface spreading, and post-injection dissipation of injected CO₂.

The simulations were carried out using TOUGH2/EOS7CA (Oldenburg and Unger, 2003; 2004; Pruess et al., 1999), a research module of TOUGH2 that models subsurface flows of water, CO₂, and air. A two-dimensional grid transverse to the horizontal well with two layers, soil from 0 to 1.2 m depth, and cobble from 1.2 to 5 m depth (bottom of domain) as shown in Fig. 3 was used (The well is offset from the center line because simulations with flowing groundwater from left to right were also carried out although not presented here). Estimates of the soil properties were made from descriptions of the soil in test pit logs from the site. Further details of the transverse grid simulations can be found in Oldenburg et al. (2009), while only a brief summary is presented here. Simulations of the site using a three-dimensional model are presented by Oldenburg et al. (this issue).

The most important soil property for predicting flux and breakthrough times as a function of injection rate is permeability (Oldenburg and Unger 2003, 2004). For this property, a calibration was done based on CO₂ flux measurements made during a vertical injection well test. A ¾ in. Schedule 40 PVC vertical well was located 24 m northwest of the horizontal well and in similar soil conditions. It was installed to a depth of 3.5 m, and the bottom 0.6 m of the well was screened with a porous polyethylene well screen (SCHUMASOIL® manufactured by Johnson Screens). Carbon dioxide was injected at a rate of 4.1 kg/day. The calibration was done using a radial grid with the same layer thicknesses as shown in Fig. 3. Manually adjusting permeability of the two layers while keeping porosity constant at 0.35 for both layers resulted in a good fit for $k_{\text{soil}} = 5 \times 10^{-11} \text{ m}^2$, and $k_{\text{cobble}} = 3.2 \times 10^{-12} \text{ m}^2$. The good fit obtained with large permeability for the soil likely suggests the presence of macropores or root casts in the soil layer. Properties of the layers used in the simulations are provided in Table 1.

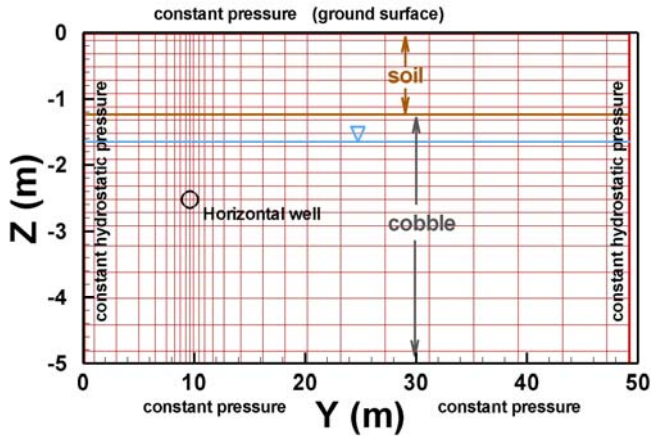


Fig. 3 Two-dimensional transverse grid model system showing cobble and soil layers, discretization, well location, and boundary conditions

Table 1 Properties of the two layers used in the model

	Soil	Cobble
Porosity	0.35	0.35
Permeability	$5 \times 10^{-11} \text{ m}^2$	$3.2 \times 10^{-12} \text{ m}^2$
Capillary Pressure	van Genuchten ¹ $\lambda = 0.291, S_{lr} = 0.15, \alpha = 2.04 \times 10^{-4} \text{ Pa}^{-1}, P_{max} = 5 \times 10^5 \text{ Pa}, S_{ls} = 1.$	van Genuchten ¹ $\lambda = 0.627, S_{lr} = 0.10, \alpha = 1.48 \times 10^{-3} \text{ Pa}^{-1}, P_{max} = 5 \times 10^5 \text{ Pa}, S_{ls} = 1.$
Relative permeability	Liquid: van Genuchten (1980); Gas: Corey (1954) $S_{lr} = 0.17, S_{gr} = 0.05$	Liquid: van Genuchten (1980); Gas: Corey (1954) $S_{lr} = 0.12, S_{gr} = 0.05$
Molec. diffusivity	Liquid: $10^{-10} \text{ m}^2 \text{ s}^{-1}$ Gas: $10^{-5} \text{ m}^2 \text{ s}^{-1}$	Liquid: $10^{-10} \text{ m}^2 \text{ s}^{-1}$ Gas: $10^{-5} \text{ m}^2 \text{ s}^{-1}$

¹Pruess et al., 1999.

The initial steady state gravity–capillary equilibrium with no infiltration is shown in Fig. 4. Note the capillary barrier produced by the soil–cobble interface that gives rise to higher liquid saturations in the soil than in the cobble below (blue above yellow). The less-saturated cobble below the capillary barrier is expected to have higher effective permeability to injected CO₂ than the more saturated soil above.

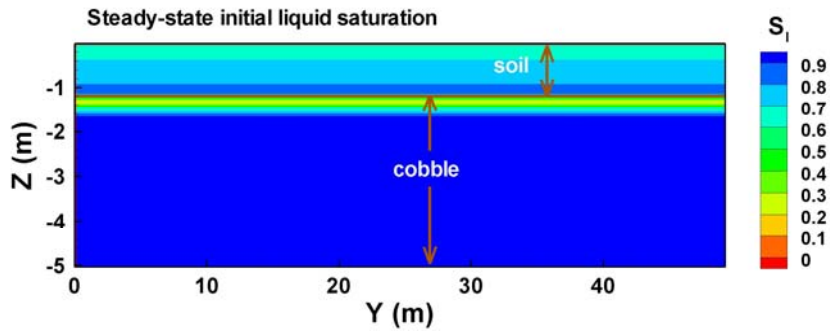


Fig. 4 Initial liquid saturation at gravity-capillary equilibrium with water table at a depth of 1.6 m

In Fig. 5 are shown examples of simulation results for a high injection rate (1,000 kg/day) and a low injection rate (100 kg/day) to compare breakthrough times and spreading patterns. As shown, the 1,000 kg/day injection rate is on its way to breakthrough after only 3 h and spreads over ten meters in width after 10 days. Note the preferential spreading in the unsaturated cobble. The low injection-rate case (Fig. 5c, d) shows breakthrough is just about to occur after 2 days, while after 10 days spreading at the surface is approximately 5 m. Surface flux and shallow-soil concentration as a function of a range of injection rates are shown in Fig. 6a, b. Note the maximum in surface flux that occurs at approximately 1 day for the 1,000 kg/day case as CO₂ strongly breaks through and then over a slightly longer time scale spreads in the subsurface thereby diminishing surface flux slightly.

Because heterogeneities may be present in the field that are not modeled, breakthrough in the field experiment is expected to be earlier rather than later than the model predictions. For this reason, and because the fluxes even at 100 kg/day are known to be readily measurable by some of the approaches deployed (e.g. the accumulation chamber), the 100 kg/day injection rate appeared to be reasonable as a starting point for the shallow-release experiment. The prediction of breakthrough at 2–3 days by the model agreed well with what was observed experimentally (Lewicki et al. 2007) in the first release of 2007 performed at an injection rate of 100 kg/day.

Space does not allow presentation of additional simulations carried out to predict the effects of the second release at 300 kg/day, nor of groundwater flow and transport simulations to predict effects of the test below the water table. However, modeling results describing the patchy emission seen in the 2007 and 2008 releases can be found in Oldenburg et al. (this issue).

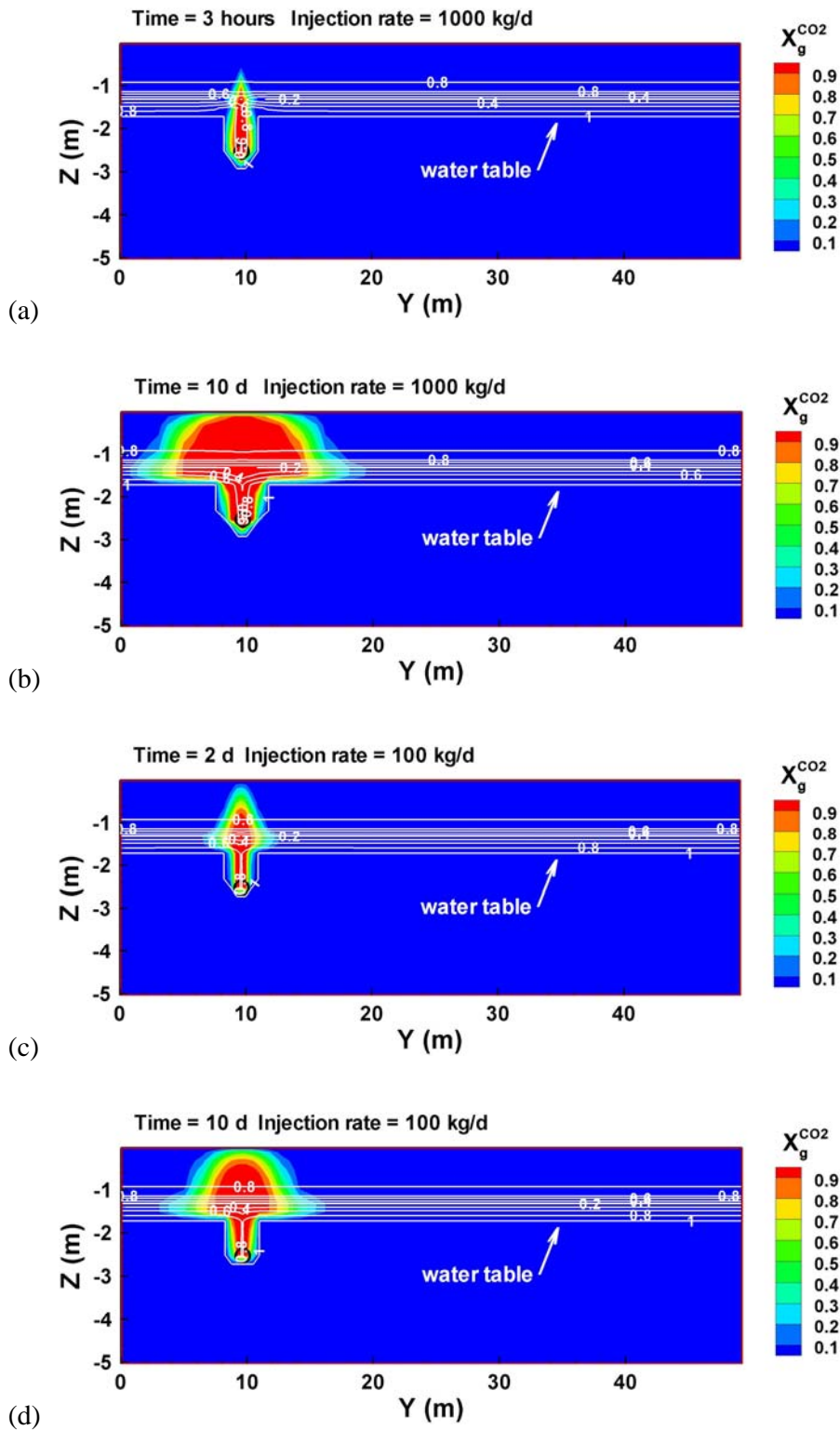


Fig. 5 Simulation results showing mass fraction of CO₂ in the gas phase (*color contours*) and contour lines (*white*) showing liquid saturation for **a** 1 t CO₂/day injection rate at $t = 3$ h, **b** 1 t CO₂/day at $t = 10$ days, **c** 100 kg CO₂/day at $t = 2$ days, and **d** 100 kg CO₂/day at $t = 10$ days

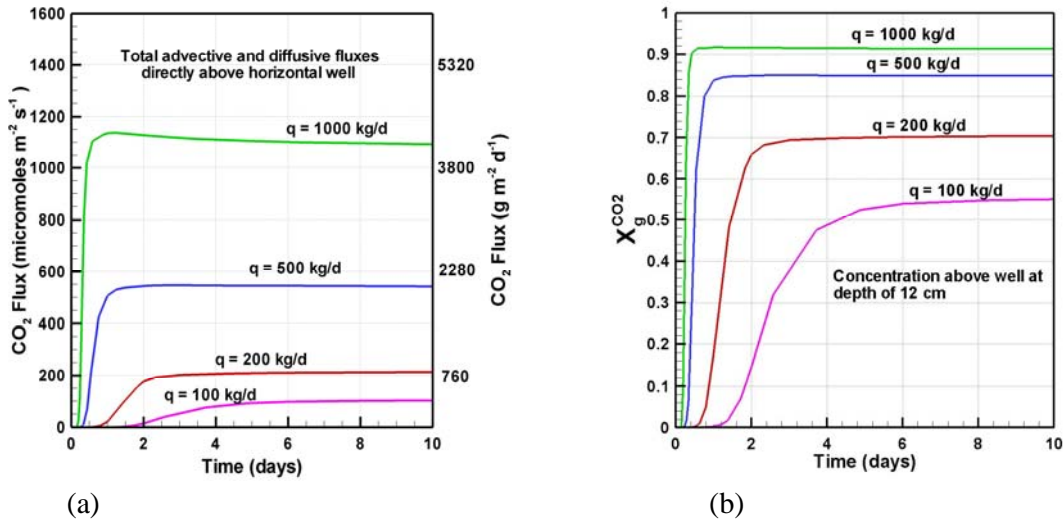


Fig. 6 Summary of **a** surface CO₂ flux and **b** shallow CO₂ concentration (mass fraction) for various injection rates as a function of time

Controlled CO₂ releases from the horizontal well

Two shallow subsurface releases of CO₂ were performed in the summer of 2007. The first was begun July 9 and lasted 10 days, ending on July 18. The total flow rate was 0.1 metric ton CO₂/day with flux into all six packer zones being equal. Additionally, 6.5 mL of a perfluorinated tracer (perfluoromethylcyclohexane) was injected into zone 4 during the first 48 h of CO₂ injection. A second release at a rate of 0.3 t CO₂/day with equal flux to all six zones was carried out from August 3 to August 10.

Over the 2008 field season CO₂ was released at a flow rate of 0.3 t/day from July 9 to August 7. Again, flux into all six packer zones was equal. Perfluorotrimethylcyclohexane tracer (16.5 mL) was released into zone 4 over 5 ½ days starting at 17:30 on July 9. From August 27 to September 9 CO₂ was injected into only zone 3 at a total flow rate of 0.05 t/day.

During the 2007 releases the depth of the water table measured at the water monitoring well array in zone 6 averaged 1.6 m below ground surface. For the summer 2008 experiments the water level was measured to be about 1.5 m below the ground surface.

Weather conditions during horizontal release experiments

The weather conditions during the 2007 releases were generally above-average temperatures with below-average precipitation, while during the 2008 releases below-average temperatures

and above-average precipitation prevailed. During the first 2007 release (July 9–18) the measured air temperature at the experiment site exceeded the average high (27–29°C) for the Gallatin Field National Weather Service site every day except one, usually by several degrees centigrade. The extreme difference occurred on July 15 when the measured temperature was 35°C, 7°C warmer than the average. Similarly, the measured daily low temperatures were nearly all 2–7°C warmer than average (8–9°C). During the second 2007 release (August 3–10), the measured temperatures were near and even slightly below average, with the highs generally running approximately 26–28°C, compared to 29°C average, and the lows staying near the average of 9°C.

The 2008 releases occurred during a generally much cooler and wetter summer season. During the first 2008 release (July 9–August 7) the measured high temperatures stayed near the average (~28–29°C), actually falling below by 5°C or more on at least 8 days. The measured low temperatures also stayed generally at or below the average values. The second 2008 release (August 27–September 9) encompassed an unusually cool period, with nine of the 14 days experiencing high temperatures that were 7°C or more below average (26–28°C). The extreme difference occurred on September 1, when the measured high temperature (7°C) barely exceeded the average low (5°C). It should be noted that the average temperatures cited here are for the Gallatin Field Airport, approximately 15 km northwest of the ZERT field site and approximately 100 m lower elevation, so these averages should be used only as general guidelines.

Figure 7 shows time-series plots of daily precipitation for the time period encompassing the 2007 (Fig. 7a) and 2008 (Fig. 7b) release periods. Note the large difference in vertical scale for the 2 years. During the first 2007 release there was no measurable precipitation until the afternoon of the last day, while during the second 2007 release there were several light rains, comparable with seasonal daily precipitation ≤ 0.1 cm, and one relatively heavy rainfall of approximately 0.6 cm. The 2008 releases occurred during a period of significantly higher precipitation, with the first release experiencing several extremely heavy rain events accompanied by short but intense periods of hail of diameters reaching approximately 3 cm. The precipitation during the second 2008 release was comparable to the daily average of 0.1–0.13 cm.

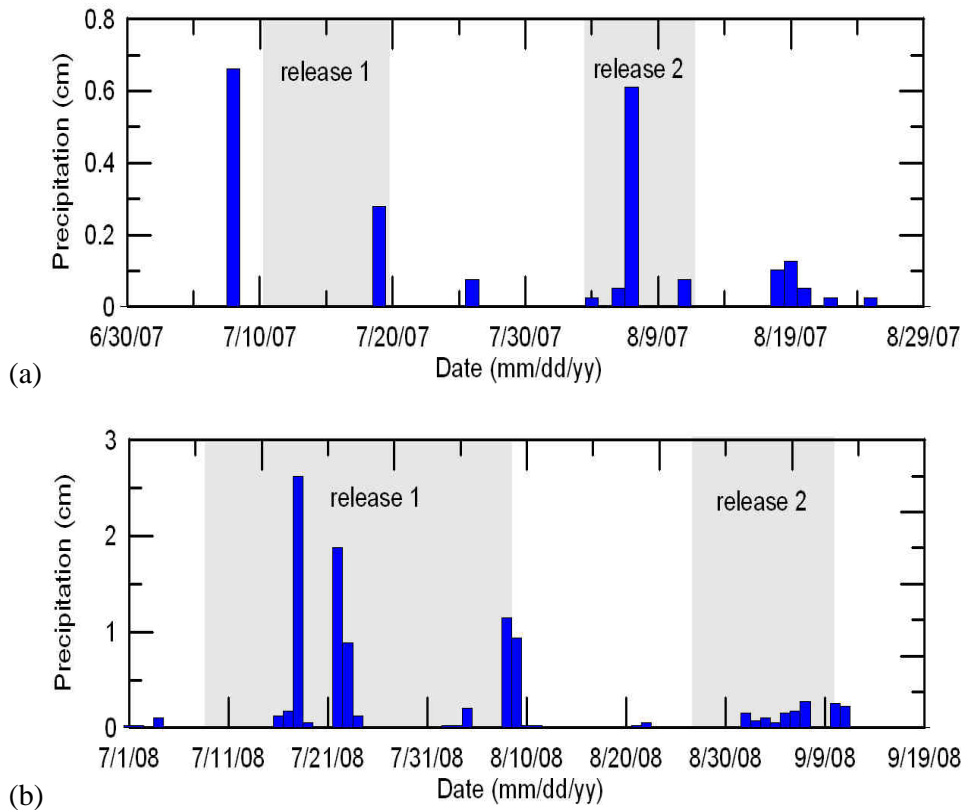


Fig. 7 Time-series plots of daily precipitation during the **a** 2007 and **b** 2008 field seasons. *Gray areas* indicate timing of CO₂ releases

An array of 15 water content reflectometers (Campbell Scientific CS616) was installed on the southwestern edge of zone 4 in mid-summer of 2008. They measured volumetric water content averaged over the top 30 cm of soil. Figure 8 shows a time-series plot of the volumetric water content measured by one of these probes which was located on the pipeline on the northeast edge of the plant strip near grid coordinate (-1.55, 0). The significance of spatial variations among the array of soil moisture probes is currently being studied, but this timeseries plot is typical. The general drying trend that occurs in the soil during Montana summers was altered very significantly by the unusually heavy precipitation events that occurred during the first 2008 release (Fig. 7b). An interesting and meaningful consequence of the heavy precipitation events that occurred early in the first 2008 release experiment is that the soil moisture was slightly higher at the end of the first release than it appears to have been at the start of the release. Following the fairly heavy precipitation events of August 8 and August 9 (2008), the soil moisture decreased to a fairly constant late-summer level that extended into the start of the second 2008 release. During this second release there were seasonal precipitation events that caused the soil moisture to rise slightly.

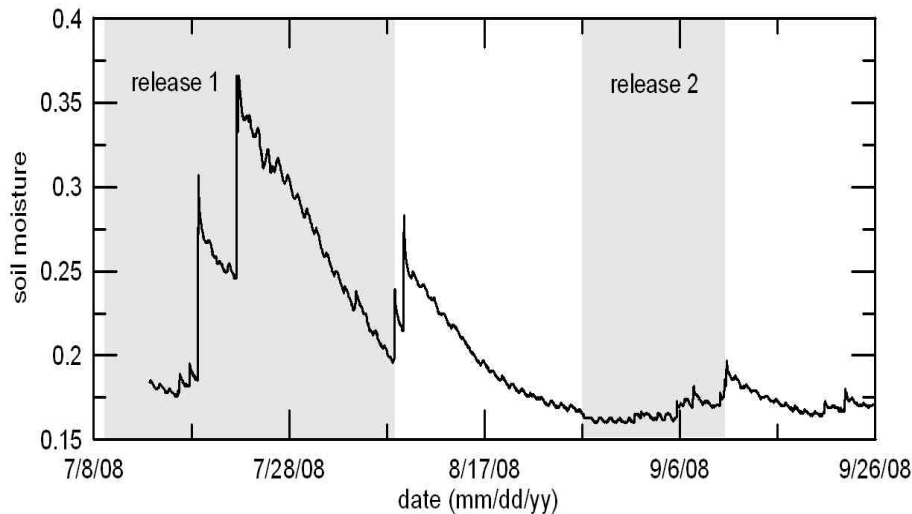


Fig. 8 Representative volumetric water content measured in the top 30 cm of soil

Layout of experimental techniques

Transport of CO₂ through the soil, water, plants, and air was investigated with near surface detection techniques deployed by collaborators from Lawrence Berkeley National Lab (LBNL), the National Energy Technology Lab (NETL), Los Alamos National Lab (LANL), Pacific Northwest National Lab (PNNL), Lawrence Livermore National Lab (LLNL), Brookhaven National Lab (BNL), U.S. Geological Survey (USGS), Montana State University, Bozeman (MSU), University of California, Santa Cruz (UCSC), and West Virginia University (WVU). Techniques included soil flux chambers, eddy covariance, soil gas measurements, perfluorocarbon tracer studies, laserbased differential absorption measurements (both free space atmospheric and below surface soil gas), stable isotope studies, multispectral and hyperspectral imaging for plant stress detection, water sampling, and soil elemental analysis using gamma-ray spectroscopy induced by inelastic neutron scattering. Figure 9 shows a schematic of the layout of experimental techniques for the 2007 and 2008 field seasons.

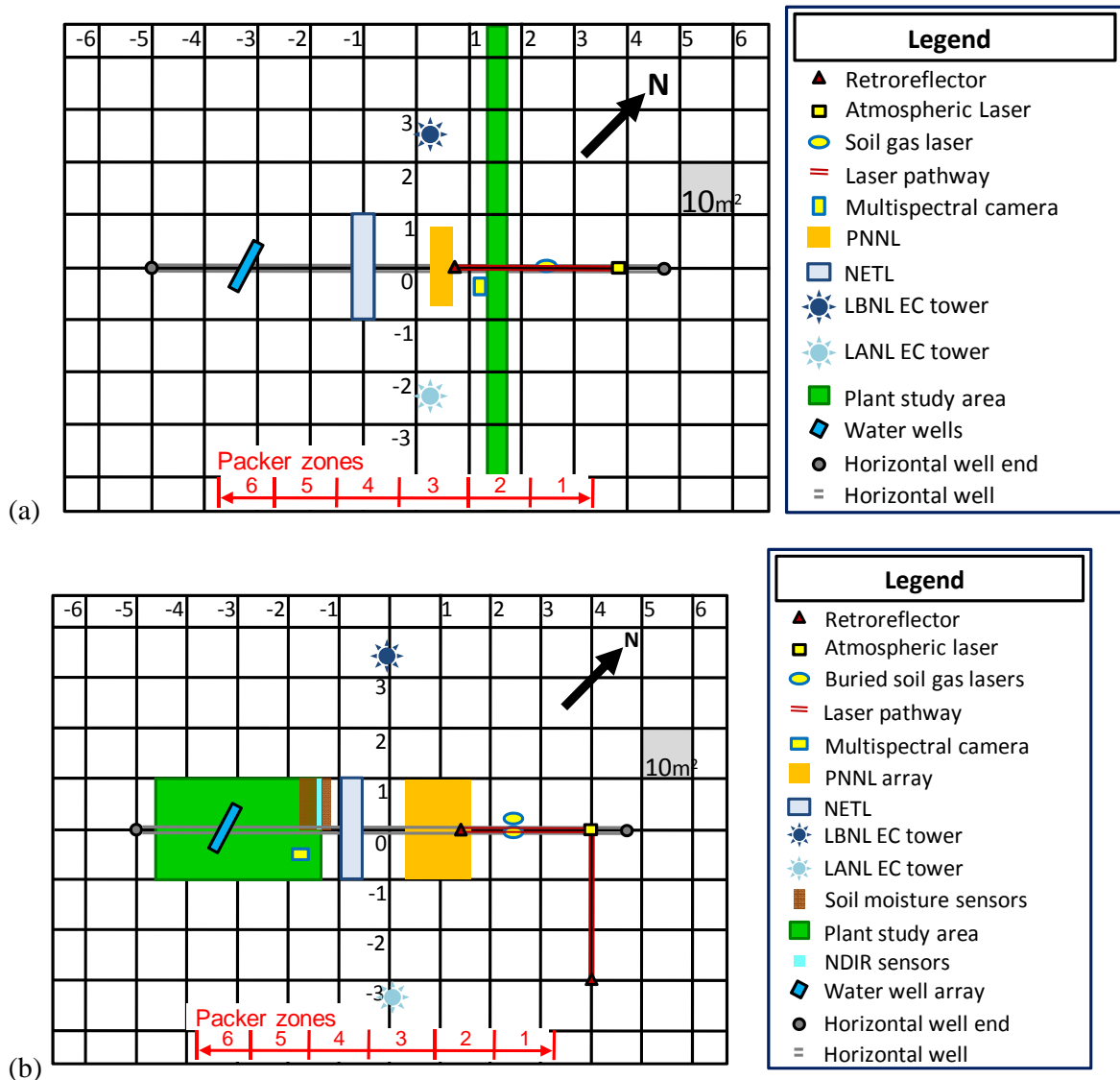


Fig. 9 Layout of experimental techniques for **a** 2007 and **b** 2008 field seasons. Well ends (*gray circles*) show extent of the horizontal well. Perfluorocarbon tracer detection and soil flux measurements were performed in the area labeled NETL. The area labeled PNNL housed an array of steady-state soil CO₂ flux chambers. Stars represent the locations of eddy covariance stations. Non-dispersive infrared sensors measured gaseous CO₂ in the soil and atmosphere along the strip labeled NDIR sensors.

Soil

Soil CO₂ flux

Accumulation chamber measurements

Evolution of the CO₂ leakage signal was followed in space and time by soil CO₂ flux measurements. Measurements using a WEST Systems Fluxmeter (WEST Systems, Pisa, Italy)

based on the accumulation chamber method (e.g. Chiodini et al. 1998) were made on a daily basis by LBNL on a grid surrounding the horizontal well for both releases of 2007 and the first release of 2008. Figure 10 shows a map of soil CO₂ flux measured on July 30, 2008 (day 22 of the first release of 2008). Six concentrated areas of CO₂ flux, or “hot spots,” can be seen on the surface along the length of the well. There was little lateral spread off the well trace (<5 m). These hot spots were likely due to flow of CO₂ injected into a zone to the highest elevation within the zone followed by vertical migration to the ground surface. Detailed results including time to breakthrough and establishment of steady state flow as well as comparison to pre-injection modeling for the 2007 release can be found in Lewicki et al. (2007). Discussion of soil CO₂ flux accumulation chamber measurements for Release 1 of 2008 can be found in Lewicki et al. (this issue).

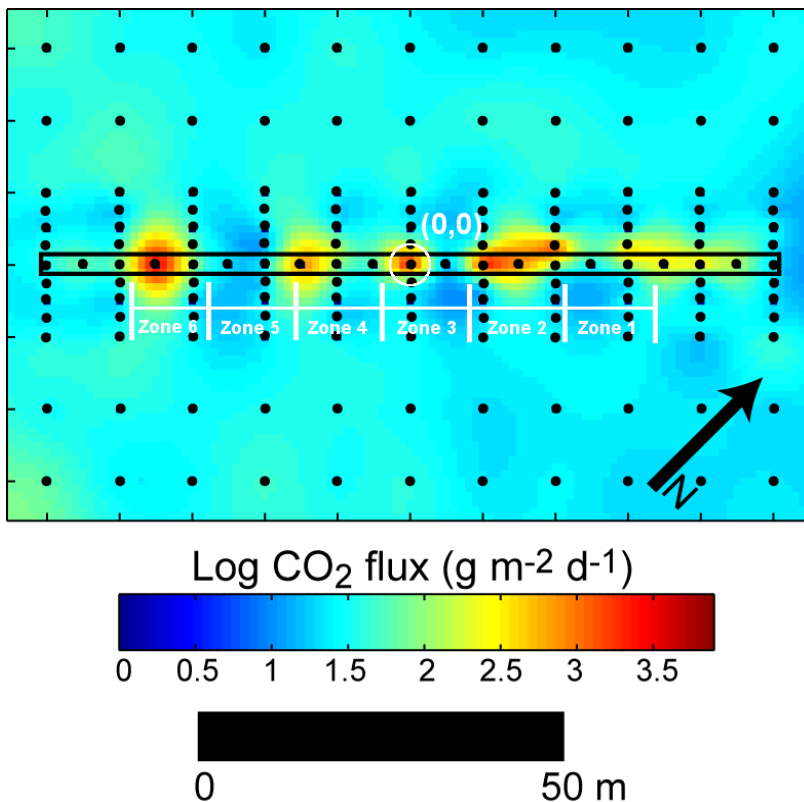


Fig. 10 Map of log soil CO₂ flux measured on 7/30/2008 using the accumulation chamber method. Point (0,0) indicates the location of the reference grid origin. The *black box* in the center of the grid points shows the approximate location of the trace of the horizontal well on the ground surface.

Non-steady state CO₂ soil flux measurements were also made by NETL during the first releases of both 2007 and 2008. A LI-COR 6400 photosynthesis chamber with the soil CO₂ flux

chamber (6400-09) was used to map out one of the two surface flux anomalies in zone 4 on a finer spaced grid (Strazisar et al. 2009). These results and those of the 2008 experiment are detailed in Wells et al. (this issue).

Pacific Northwest National Laboratory deployed a 3 x 5 array of 15 surface flux chambers to make steady state measurements of soil CO₂ fluxes during the first release of 2007. The chambers covered a 4-m x 8-m area centered over the horizontal CO₂ injection well in zone 3 with an additional reference chamber placed 10 m from the well. This array was expanded for the second release of 2008 to 24 chambers covering a 10 m x 5 m area in packer zones 2 and 3 and three additional reference chambers located more than 10 m from the well. The multi-channel analysis system dilutes samples automatically prior to determination of CO₂ concentrations by a LICOR LI-7000 analyzer, collects concentration/flux data continuously with minimal maintenance, and can be controlled remotely by a cellular modem link. In 2008, Montana State University placed five LI-COR LI-8100-104 Long-Term Chambers (for non-steady state measurements of CO₂ flux) within the PNNL array for comparison. For these results and a description of the PNNL 2007 and 2008 findings (see Amonette et al., this issue).

Soil gas concentration

Perfluorocarbon tracers

For part of the first releases of 2007 and 2008, a perfluorocarbon tracer was injected along with the CO₂ into zone 4. Each injection contained a unique tracer so that tracer identity could be clearly distinguished. NETL researchers installed an array of sorption tubes at a depth of 1 m below ground surface to monitor for the appearance of this tracer. Soil gas CO₂ depth profiles were also taken. For further details see Strazisar et al. (2009) and Wells et al. (this issue).

Differential absorption measurements using laser based instruments

A differential absorption instrument based on a continuous wave temperature tunable distributed feedback (DFB) laser (Repasky et al. 2006; Humphries et al. 2008) was deployed in zone 1 by MSU to measure real time underground CO₂ soil gas concentrations. Light from the laser is delivered by fiber optic to sensors buried underground in waterproof cases. These cases are fitted with gas permeable membranes to allow soil gas to diffuse into the sensors. In 2007, a 1 m long absorption cell was buried approximately 0.75 m below the ground surface directly above the horizontal well. Results of these experiments can be found in Humphries et al. 2008. In 2008, the case with the 1 m long absorption cell was buried approximately 0.75 m below the ground surface 1 m northwest off the horizontal well. A second case with a 0.3 m absorption cell and a sensor using a photonic band gap fiber was buried directly above the horizontal well at a

depth of ~0.75 m. In both the 2007 and 2008 experiments elevated CO₂ levels from the release were clearly measurable above natural variability in the soil CO₂ concentration. Typical background CO₂ soil gas concentrations of 4,000 ppm were measured. During the 0.3 t/day release of 2008, 30,000 ppm CO₂ was regularly seen. The results for the 2008 experiment can be found in Barr et al. (2009).

Non-dispersive infra-red sensors

In 2008 an array of non-dispersive infrared (NDIR) sensors for the measurement of gaseous carbon dioxide were installed at the southwest edge of zone 4 (Fig. 9b). Sensors installed at 30 cm depth in the soil at 0, 2.5, 5, 7.5, and 10 m on a line going northwest off the well and at 4 cm above the ground surface at 0 and 5 m northwest of the well continuously measured soil and atmospheric CO₂ concentrations. A discussion of soil and atmospheric CO₂ concentration data and their relationship to meteorological and soil parameter variations during the first release of 2008 can be found in Lewicki et al. (this issue).

Total carbon in soil

Inelastic neutron scattering

Brookhaven National Laboratory tested Inelastic Neutron Scattering (INS) at the field site to see if it could detect CO₂ seepage from the controlled release. The INS system, based on gamma-ray spectroscopy induced by fast neutrons, offers two distinct advantages: it is a non-destructive method, and it also provides multi-elemental analysis in situ. This system consisting of an electrical neutron generator, an array of detectors, and a power supply is mounted on a cart hovering about 30 cm above the ground. Its high-energy neutrons and gamma rays interrogate uniquely large soil volumes of about 0.3 m³ to an effective depth of 30 cm and over an approximate footprint of 1.5 m². The data for multi-elemental analysis is acquired during operation either in static or scanning modes, thus covering arbitrarily large areas. Wielopolski et al. (2008) gives a detailed description of the system. To look for changes in the soil during the first release of 2008, an INS system was placed above a point on the horizontal well with known high soil CO₂ flux in zone 3. The results collected at that point were compared with background measurements taken at several places adjacent to the horizontal well. From among the elements measured by the INS system only a difference in carbon was observed, as reported in Wielopolski and Mitra (this issue).

Water

Water chemistry

During the 2007 and 2008 field seasons several water chemistry parameters were sampled at the water monitoring well array in zone 6 before, during, and after CO₂ injection. For details on the change in water chemistry due to the injection of CO₂ during the 2007 field season. In 2008 the USGS measured water level, pH, alkalinity, electrical conductance, and dissolved oxygen in the field. Major, minor and trace inorganic compounds, dissolved organic carbon (DOC), and a selection of organic compounds as well as some isotopes were analyzed in the laboratory. Results show rapid systematic and significant to major changes in most of the chemical parameters determined following CO₂ injection (for results of the July–August release of 2008 see Kharaka et al., this issue).

Plants

Plant health

Hyperspectral and multispectral imaging

The response of plant health to the injection of CO₂ in the shallow subsurface was monitored by UCSC and MSU. A high wavelength resolution portable field spectrometer (ASD Inc.), a portable hyperspectral imaging system (Resonon Inc.), and one stationary multispectral imager followed the changes in the visible and near infrared reflectance spectra of plants located varying distances from the horizontal well in both the 2007 and 2008 experiments. The Resonon hyperspectral imager was also flown over the field site 27 days after the beginning of the first release of 2008.

The portable field spectrometer measured reflectance spectra from the same 68 plants almost daily before, during, and after the first 2008 release. The spectral signatures clearly showed stressed vegetation over the hot spots mapped by Lewicki et al. (this issue) (see also Fig. 10). The effects on the plants of CO₂ from the injection were detectable above natural seasonal variations. The level of plant response to the injected CO₂ was dependent on plant species and began when soil CO₂ concentrations reached 4–8%, which was two to three times greater than background levels. Plants up to 2.5 m off hot spots along the horizontal well showed deterioration in health. Further description of the daily spectral measurements and the hyperspectral overflight image are given in Male et al. (this issue).

The hyperspectral (Keith et al. 2009) and multispectral (Rouse 2008) imaging techniques also detected compromised plant health at the 0.3 t CO₂/day release rate in 2007 and 2008. The ability of the multispectral imager to obtain calibrated reflectance images during cloudy and clear conditions showed the feasibility of deploying a system longterm to collect a continuous data record. Statistically significant signal changes that are correlated with CO₂ injection patterns in space and time were observable in both field seasons. For a description of the stationary multispectral imaging experiments (see Shaw et al., this issue).

Air

Net CO₂ flux

Eddy Covariance measurements

An eddy covariance station from LBNL positioned approximately 30–35 m northwest of the horizontal well measured net flux of CO₂ continuously during the summers of 2006, 2007, and 2008 (Lewicki et al. 2009a, b). The method is based on measuring the temporal covariance of vertical wind velocity and CO₂ density at a fixed height above the ground (e.g. Baldocchi et al. 1988; Foken and Wichura 1996; Aubinet et al. 2000; Baldocchi 2003). Changes in eddy covariance CO₂ fluxes were difficult to discriminate from background variations during the first 2007 release at 0.1 t CO₂/day. A clear surface leakage signal, however, was discernable during the 0.3 t CO₂/day release of that year. A second eddy covariance station from LANL was placed approximately 30 m southeast of the horizontal well in 2007 and 2008.

CO₂ concentration

Differential absorption measurements using laser based instruments

A second differential absorption instrument was deployed near the northeast end of the horizontal well to measure atmospheric concentration of CO₂ above the horizontal well. It is also based on a continuous wave temperature tunable DFB laser developed at MSU (Repasky et al. 2006). The laser is directed at a retroreflector which sends the light back to a detector measuring the amount of absorption by CO₂ over the path length the laser light travels. From this information atmospheric CO₂ concentration can be calculated. The laser was placed near the northeast end of the slotted section of the horizontal well (see Fig. 9). In 2007, the retroreflector was positioned on the well trace 43 m to the southwest for a total path length of 86 m. Estimation of the background atmospheric CO₂ concentration was made by moving the entire

laser system to a location ~120 m away from the horizontal well where contributions from injected CO₂ were expected to be negligible. For details of the system design and results of the 2007 release (see Humphries et al. 2008). In 2008, the retroreflector was placed above the horizontal well 29 m southwest of the laser system. Estimates of background CO₂ concentrations were made by using a flip mirror in the laser housing to direct the beam to a second retroreflector located 90° off the well trace. For the release rates of 2007 and 2008 atmospheric CO₂ concentration levels above the natural diurnal cycles were easily measurable by this system. The results for the 2008 experiment can be found in Barr et al. (2009).

Mapping the atmospheric CO₂ plume

Perfluorocarbon tracers

For the first release of 2008 NETL deployed an array of sorption tubes above the soil surface at a height of 1.2 m in order to detect and characterize the atmospheric plume of CO₂ by looking for perfluorinated tracer co-injected with the CO₂ in zone 4. A clear plume was detected with tracer concentrations more than five orders of magnitude greater than background downwind of the release point. In addition, a plume of residual tracer from the 2007 release was also detected, likely due to long residence time in the soil. Details are given in Wells et al. (this issue).

Stable isotopes of CO₂ in atmospheric, vegetation, soil, and groundwater reservoirs

Stable isotopes of CO₂ can be a useful marker for identifying leakage of injected CO₂. The carbon dioxide injected in the ZERT field experiments originated from a natural gas field and thus has a carbon isotope signature ($\delta^{13}\text{C}$ measured to be -52‰) distinct from the natural background produced by organic respiration and photosynthesis.

The stable isotopes of carbon were measured on soil cores (from 0 to 70 cm below the surface), on dissolved inorganic carbon (DIC) in groundwater, dominant plants, and in the local CO₂ (using Keeling plots from chamber CO₂) and regional CO₂ (using Keeling plots on CO₂ collected at an eddy covariance tower—2 m height). The light stable isotopes were measured in these reservoirs prior to and during the first releases of 2007 and 2008. A signature from the injected tank CO₂ was seen in the groundwater, plants, chamber and regional CO₂ after the release. This experiment showed that $\delta^{13}\text{C}$ in carbon reservoirs is a useful tool to detect CO₂ seepage either within days or weeks of release, depending upon the reservoir and also distance from the source. For a detailed description of the stable isotope studies (see Fessenden et al., this issue).

Conclusions

A facility has been constructed to perform controlled shallow releases of CO₂ at flow rates that challenge near surface detection techniques and can be scalable to desired retention rates of large scale CO₂ storage projects. Preinjection measurements were made to determine background conditions and characterize natural variability at the site. Modeling of CO₂ transport and concentration in saturated soil and the vadose zone was also performed to inform decisions about CO₂ release rates and sampling strategies.

Four releases of CO₂ were carried out over the summer field seasons of 2007 and 2008. Transport of CO₂ through soil, water, plants, and air was studied using near surface detection techniques. Soil CO₂ flux, soil gas concentration, total carbon in soil, water chemistry, plant health, net CO₂ flux, atmospheric CO₂ concentration, movement of tracers, and stable isotope ratios were among the quantities measured. Even at relatively low fluxes, most techniques were able to detect elevated levels of CO₂ in the soil, atmosphere, or water. Plant stress induced by CO₂ was detectable above natural seasonal variations.

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