

Surface Monitoring for Geologic Carbon Sequestration

Vol. 2: Monitoring Methods, Instrumentation, and Case Studies





Introduction

It is well known that carbon dioxide (CO₂) is a greenhouse gas that contributes to climate change. CO₂ is emitted into the atmosphere whenever fossil fuels are burned. The largest sources of man-made CO₂ emissions are coal- and gas-fired power plants and automotive transportation. Carbon Capture and Geologic Sequestration has been identified as a way to mitigate CO₂ emissions to the atmosphere.

Geologic formations suitable for underground CO₂ storage have been identified around the world. Typically, these formations are depleted oil and gas reservoirs, coal beds, and deep saline aquifers. The potential global capacity for geologic storage of CO₂ is large and could correspond to hundreds of years of anthropogenic CO₂ emissions. The ability of many of these reservoirs to store natural gas and naturally-occurring CO₂ over millions of years helps to prove the credibility of deep underground storage.

However leak-tight an underground storage formation may seem, it remains the responsibility of the project owner to prove no leakage of CO₂ is occurring. While ambient levels of CO₂ are harmless, concentrated CO₂ can be fatal to plants and animals, including humans. The public needs to be assured that no leaks exist that would endanger their health or negate the benefits of the carbon storage project. Surface monitoring above geologic storage formations is effective proof of storage formation integrity.

LI-COR® Biosciences published Volume 1 of Surface Monitoring for Geologic Carbon Sequestration in 2009; this updated edition briefly describes two methods for geologic sequestration surface monitoring, as well as the challenges associated with each method. Also described is instrumentation available from LI-COR Biosciences that has been used to effectively monitor for CO₂ leaks from geologic storage formations. At the end of this note we present two new case studies of surface monitoring projects already underway that use the LI-8100/LI-8100A Automated Soil CO₂ Flux System and/or LI-7500/A Open Path CO₂/H₂O Analyzer for Carbon Capture and Storage surface monitoring.

Instrumentation for Surface Monitoring

The LI-8100 was introduced in 2003 to address the need for a robust, dedicated system for measuring soil CO₂ flux over a wide variety of environmental conditions. Drawing upon more than a decade of experience in making soil CO₂ flux measurements, LI-COR designed a system that addresses both temporal and spatial variability with integrated survey and long-term chamber designs, as well as a multiplexer (LI-8150) that allows long-term measurements with as many as 16 chambers. For conducting measurements over a number of locations, 10 cm (8100-102) and 20 cm (8100-103) survey chambers allow rapid, repeatable measurements to obtain accurate determination of spatial variability. Long-term diel measurements can be automated at a single location for weeks or months at a time using the 8100-104 or 8100-104C long-term chambers, which, when combined with the LI-8150 Multiplexer, provides assessment of both temporal and spatial variability. Innovations like chamber drive mechanisms that automatically move the chamber away from the soil environment being measured, a pressure vent design that allows chamber pressure to track the ambient pressure under windy or calm conditions, perforated baseplates to minimize perturbations to the soil environment, and chambers that close automatically to eliminate variations caused by manual chamber placement ensure that soil CO₂ flux measurements are accurate and repeatable. In 2010, LI-COR released the LI-8100A, which expanded the LI-8100's capabilities by extending the CO₂ measurement range to 20,000 ppm, allowing for soil CO₂ flux measurements in high CO₂ environments. The LI-8100A also added Ethernet connectivity for two-way communication with networked computers, and remote setup, data collection, and diagnostics by simply logging onto any LI-8100A connected to a local network. Setup and operation are also possible with many Wi-Fi enabled devices using a Windows® Mobile application.

For measuring CO₂ fluxes above surfaces using micrometeorological methods such as Eddy Covariance, LI-COR offers the LI-7500A Open Path CO₂/H₂O Analyzer, which features the fast response times and low power requirements needed to make flux measurements between vegetation and the atmosphere, primarily on field station towers. In addition, a new Enclosed CO₂/H₂O Analyzer, the LI-7200, is also available, which combines the advantages of both open and closed path analyzers. The LI-7200 is based on the design of the LI-7500A, uses low power, and can be mounted in the same manner as the LI-7500A; however, the LI-7200 encloses the optical path by using a short intake tube, which eliminates CO₂ and H₂O losses during rain events.

Monitoring, Verification, and Accounting

The purpose of Monitoring, Verification, and Accounting (MVA) is to provide an accurate accounting of stored CO₂ and a high level of confidence that the CO₂ remains sequestered permanently. A successful effort enables sequestration project developers to ensure human health and safety and prevent damage to the host ecosystem. MVA requires an entire host of tools to effectively understand the CO₂ movement within the storage formation. One such tool is understanding and quantifying potential surface leakage sites. An active surface monitoring campaign helps to quantify natural ecosystem background fluxes, which makes understanding and quantifying leakage areas easier. Surface monitoring is also an effective way to convince the public that leaks are not occurring.

Surface Monitoring

Methods for soil CO₂ flux measurement

There are two primary methods to quantify the rate of CO₂ release from the ground to the atmosphere. One method is chamber-based, which includes an open-chamber and closed-chamber method. The other method is micrometeorological, which includes the Eddy Covariance method, Bowen-Ratio energy balance method and aerodynamic method (*Verma* [1]).

Chamber-based soil CO₂ flux measurement

The closed-chamber method is the most common approach used to estimate the fluxes of CO₂ (F_c , $\mu\text{mol m}^{-2}\text{s}^{-1}$) and other trace gases at the soil surface. It is widely used in carbon cycle research as well as other environmental research areas (*Norman et al.* [2]; *Davidson et al.* [3]). In this method, a small portion of air is circulated from a chamber to an infrared gas analyzer (IRGA) and then sent back to the chamber. F_c is estimated with Eq. 1 chamber volume, soil surface area, air temperature, atmospheric pressure, and the rate of CO₂ concentration increase inside the chamber (dC_c/dt , $\mu\text{mol mol}^{-1}\text{s}^{-1}$) which has been on the soil surface for a short period of time.

Where P is the atmospheric pressure (Pa), V (m^3) is the total system volume, including the volume of the chamber, the pump, and tubing in the measurement loop, R is the gas constant ($8.314 \text{ Pa m}^3 \text{ }^\circ\text{K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature ($^\circ\text{K}$), and S (m^2) is the soil area covered by the chamber.

$$F_c = \frac{PV}{RTS} \frac{dC_c}{dt} \quad (1)$$

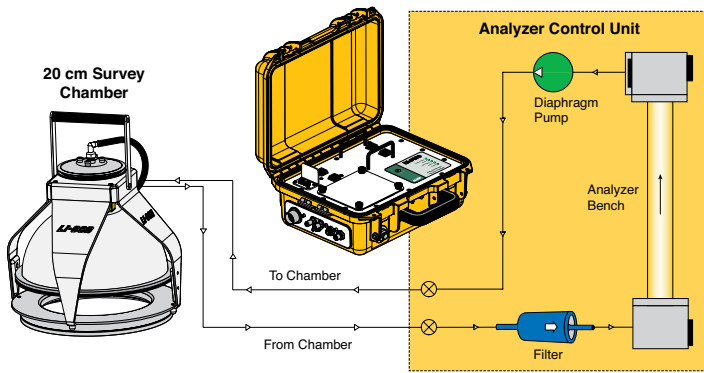


Figure 1. Schematic diagram of the measurement flow path for the Automated Soil CO₂ Flux System (LI-8100A, LI-COR Biosciences, Lincoln, NE). A 20-cm survey chamber is shown with the control unit. The system can also support measurements with a 10-cm survey chamber and 20-cm Long-term Chambers.

Many custom-made closed systems have been described in the literature (e.g. *Savage and Davidson* [4]; *Irvine and Law* [5]) and commercially available systems can also be used. Figure 1 presents a schematic diagram for the LI-8100A Automated Soil CO₂ Flux System showing the flow path, a 20-cm survey chamber and analyzer control unit, and optical bench. In addition to carbon cycle research, the closed chamber method has been used in agronomy, soil science, and ecological studies.

Instrumentation configuration

Soil CO₂ production depends strongly on many environmental (soil temperature, soil moisture, organic content) and biological factors (above ground canopy size, growth activity, etc). As a result, soil CO₂ flux often shows strong temporal and spatial variations, which means that the flux can change significantly over time and location at a research site. To address this issue, LI-COR Biosciences has developed survey chambers, long-term chambers, and a multiplexer for the LI-8100A System. Two survey chambers are available, 8100-102 (10 cm) and 8100-103 (20 cm). Both chambers operate with a unique pneumatic system that contracts and expands a bellows to raise and lower the chamber over the soil collar. This automation eliminates soil disturbances that would otherwise occur with mechanical installation and removal of the chamber from the collar between sampling repetitions. The pneumatic bellows system raises the chamber between repetitions to allow for equilibration with ambient CO₂ concentrations before gently lowering again to perform another repetition.

LI-COR offers two long-term chambers (8100-104, 8100-104C) to make long-term unattended measurements of soil CO₂ flux. The 8100-104/C chambers have a lift-and-rotate drive mechanism that rotates the chamber to six configurable open positions. During the non-measurement period, both long-term chambers 'park' away from the collar areas to ensure that disturbance to the soil environmental conditions inside the collar is kept to a minimum.

All four chambers close gently onto the collar to minimize pressure pulsations that can change the soil CO₂ concentration, which in turn affects the soil CO₂ flux measurement.

To satisfy both temporal and spatial resolution requirements for monitoring CO₂ flux, LI-COR Biosciences has developed the LI-8150 Multiplexer, which can allow up to 16 chambers to be connected to provide adequate spatial coverage. The system's automation enables long-term, unattended measurement of diurnal and seasonal flux at 16 different locations over an area with a diameter of 30 m.

Requirements for an accurate soil CO₂ flux measurement

The concept of chamber-based soil CO₂ flux measurements can at first seem quite simple. However, many considerations must be taken into account in the process of instrument design and making the measurements in order to have accurate flux data. As stated above, soil CO₂ production strongly depends on many environmental conditions. Also, soil CO₂ flux is a physical process driven primarily by the CO₂ concentration diffusion gradient between the upper soil layers and the atmosphere near the soil surface. The fundamental challenge for making accurate soil CO₂ flux measurements is that the deployment of chambers must minimize disturbance to environmental conditions that impact CO₂ production and transport inside the soil profile. The four most fundamental considerations for an accurate measurement are (1) maintain pressure equilibrium between inside a chamber and the ambient air, (2) ensure good mixing, (3) control altered CO₂ diffusion gradients, and (4) minimize the disturbances to environmental conditions. Below we will discuss the impact of each of these considerations on the measurement and how we carefully address them.

(1). Maintain pressure equilibrium between inside a chamber and the ambient air.

Pressure equilibrium between the inside of a soil CO₂ flux chamber and the surrounding air outside the chamber must be maintained during the measurement if measured flux is to accurately represent the rate occurring naturally outside the chamber. A simple open vent tube connecting to the chamber has often been used for the pressure equilibrium (e.g. *Hutchinson and Mosier* [6]; *Davidson et al.* [3]). This approach, however, is effective only under calm conditions. Under windy conditions, negative chamber pressure excursion will occur as wind blows over the vent tube's external open end, due to the Venturi effect. This excursion will cause a mass flow of CO₂-rich air from the soil into the chamber, leading to a significant overestimation of soil CO₂ flux. In fact, some researchers (e.g. *Conen and Smith* [7]) recommended eliminating the vent tube after recognizing the potential problem from the Venturi effect.

Scientists and engineers at LI-COR Biosciences have developed a patent-pending vent design for the chambers. The new vent has a tapered cross section as shown in Figure 2. Conservation of mass requires that the average air flow rate drops as the air enters the vent. According to Bernoulli's equation, as the air flow rate decreases, a major portion of dynamic pressure is converted to static pressure, raising the static pressure with which the chamber equilibrates. This design is radially symmetric to eliminate wind-direction sensitivity. Data from field experiments on differential pressure measurements between inside the chamber and the outside ambient air show that chambers equipped with our newly designed vent always have internal chamber pressure equal to outside the chamber under both calm and windy conditions. Our new vent virtually eliminates the Venturi effect. For more details, see our published journal paper (*Xu et al.* [8]).

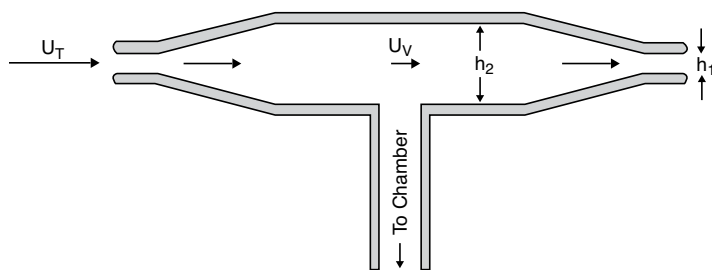


Figure 2. Cross-section view of the new vent design (patent pending). U_T is the wind speed at the height of the vent. U_V is the wind speed inside the vent near the vent tubing. h_1 and h_2 is the edge and the central distance between the upper- and the lower-half of the vent. U_V depends on the ratio of h_1 to h_2 .

(2). Ensure good mixing.

Because only a small portion of the chamber air is sent to the infrared gas analyzer (IRGA) to determine the increase rate of chamber CO_2 concentration (dC_c/dt), good mixing inside the chamber is essential. A mixing fan has been used in many custom-made soil CO_2 flux systems to achieve good mixing, but using a mixing fan inside a chamber can also cause disturbances in the pressure equilibrium. To eliminate any potential chamber pressure perturbation, a mixing fan is not used on LI-8100A chambers. Good mixing is achieved through both optimal chamber geometry (bowl shape for 8100-103 and -104 chambers) and a mixing manifold (8100-102 chamber).

(3). Control altered CO_2 diffusion gradients.

Soil CO_2 flux is driven primarily by the CO_2 diffusion gradient across the soil surface. With the closed-chamber technique for estimating flux, the chamber headspace CO_2 concentration (C_c) must be allowed to rise in order to obtain the rate of change in C_c (dC_c/dt). However, raising C_c will reduce the CO_2 diffusion gradient across the soil surface inside the chamber, leading to an underestimation of the flux. To overcome this, a

new exponential function is derived to fit the time series of C_c , taking the effect of water vapor dilution into account (Eq. 2). With the initial slope ($dC_c/dt|_{t=0}$) of the fitted function (Eq. 3), the flux is then estimated at the time of chamber closing, when C_c is close to the ambient level (Fig. 3).

$$C_c' = C_s' + [C_c'(0) - C_s']e^{-at} \quad (2)$$

$$\frac{dC_c'}{dt} = a[C_s' - C_c(0)']e^{-at} \quad (3)$$

where C_c' is the chamber CO_2 concentration corrected for water vapor dilution ($\mu\text{mol mol}^{-1}$), C_s' is the CO_2 concentration in the soil surface layer communicating with the chamber ($\mu\text{mol mol}^{-1}$), also corrected for water vapor dilution, and a is a rate constant (s^{-1}).

Comparison of F_c measurements between this new approach and an earlier draw-down method (*Norman, et al.* [2]; *Welles et al.* [9]) yielded an excellent agreement, suggesting that both approaches are effective in minimizing the impact of altered CO_2 diffusion gradients on the flux measurement. From the literature, a linear regression often has been used on the time series of chamber CO_2 data to determine F_c . Our experimental data show that the underestimation of F_c from the linear approach was systematic and significant, even though the linear regression sometimes gave a very high value for the regression coefficient (Fig. 3). Furthermore, the underestimation was greater for porous soils that had high conductance-to-gas transport. Therefore, we do not recommend using the linear regression on the time series of chamber CO_2 data to determine the dC_c/dt .

(4). Minimize the disturbances to environmental conditions.

For a long-term soil CO_2 flux measurement, it is critical to keep the environmental conditions inside the collar as close to the natural conditions as possible. The impact of installation of the long-term chamber on radiation balance, wind field, and precipitation interception should be minimized. This issue was addressed carefully when we designed the long-term chambers. Both chambers are parked away from the collar when they are not in the measurement mode. The baseplate of the two long-term chambers is also perforated to minimize perturbation to the soil environment around the collar.

All four chambers close and open automatically and slowly. This eliminates the possibility of pushing fresh ambient air into the soil or removing soil air during the chamber closing/opening. Temperature artifacts are minimized by careful consideration of chamber materials and coatings.

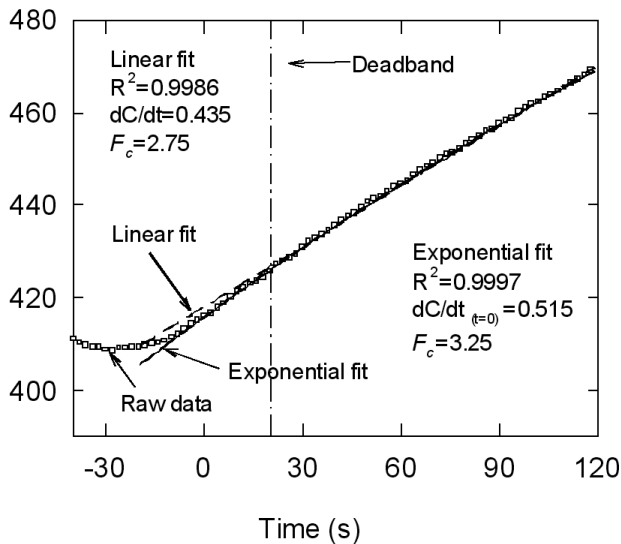


Figure 3. Illustration of the exponential approach implemented in LI-8100A Automated Soil CO₂ Flux System. An example of time series of chamber CO₂ concentration and a comparison of the slopes from the linear regression and the exponential regression. The chamber touched down at time $t = 0$. The observation length was 120 s and the deadband was set to 20 s. A deadband is required for the chamber to reach steady mixing. CO₂ data from 21 to 120 s were used to fit the linear equation and the exponential equation (Eq. 2).

Example of soil CO₂ flux measurement over a soybean field in Nebraska

Fig. 4 shows an example of diurnal soil CO₂ flux from a soybean field at the University of Nebraska-Lincoln Agricultural Experimental Station near Mead, NE. The dataset was obtained in the middle of the growing season (July 9 to 19, 2006). The flux value and soil temperature at 5 cm depth were averaged from 16 measurements at different locations with an LI-8100 multiplexed system. The soil CO₂ flux ranged from 2 to 7 $\mu\text{mol m}^{-2}\text{s}^{-1}$. The soil CO₂ flux shows a strong diurnal pattern and closely follows the soil temperature variations; this is because microbial respiration increases exponentially with temperature. This flux range of 2 to 7 $\mu\text{mol m}^{-2}\text{s}^{-1}$ was comparable with other soil CO₂ flux data published in the literature obtained from similar agricultural fields in the middle of the growing season. Normally, the soil CO₂ flux from natural ecosystems can vary from less than 1 $\mu\text{mol m}^{-2}\text{s}^{-1}$, to around 10 $\mu\text{mol m}^{-2}\text{s}^{-1}$, depending on the soil temperature, moisture, soil organic matter, plant canopy size, growing season, etc.

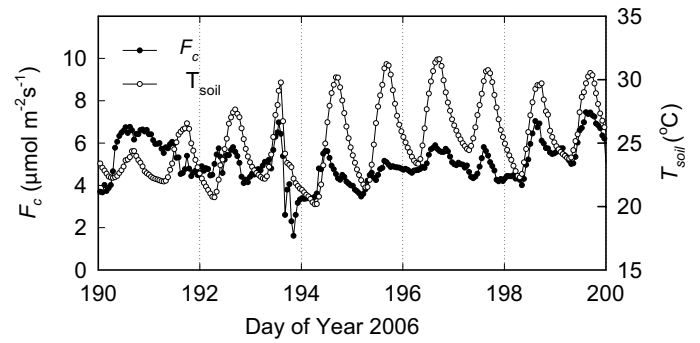


Figure 4. Example of diurnal soil CO₂ flux (F_c) measured with an LI-8100 sixteen chamber multiplexed soil CO₂ flux system from a soybean field at University of Nebraska Lincoln Agricultural Experimental Station at Mead, Nebraska. Soil temperature at a depth of 5 cm (T_{soil}) is also shown.

Micrometeorology-based Flux Measurements

Perhaps the most direct method available for measuring CO₂ fluxes above a surface is the Eddy Covariance method, which was first proposed by *Swinbank* [10]. This method relies on measurements of the deviation (or so-called perturbation) of vertical wind velocity (w') and of an associated scalar from their mean values. Taking CO₂ flux (F_c) measurement as an example, vertical wind velocity perturbation (w') and air CO₂ density (CO_2') can be calculated from high frequency (usually 10 Hz) measurements of vertical wind velocity and air density according to:

$$w' = w - \bar{w} \quad (4)$$

$$CO_2' = CO_2 - \overline{CO_2} \quad (5)$$

The over bar denotes time averaged values. F_c over a surface can be determined as:

$$F_c = -\overline{w'CO_2'} \quad (6)$$

This method relies on measurements of the fluctuating components of vertical wind and CO₂ density in the constant flux region of the surface-boundary layer (*Monteith and Unsworth* [11]).

Although it was proposed in the early 1950s (*Swinbank* [10]), this method was used over crop fields and other natural ecosystems only after development of fast-response sensors and computer data-acquisition equipment (*Baldocchi et al.* [12]). Most recently, this method has been widely used for the measurement of CO₂ flux between natural vegetation and the atmosphere in the network of field stations for the research of global carbon budget, including AmeriFlux, CarboEurope, AsiaFlux, and the Canadian Carbon Program (*Baldocchi et al.* [13]; *Verma et al.* [14]).



Figure 5. An example of the instrumentation setup for an Eddy Covariance flux measurement. Picture shows a 3-D sonic anemometer (Gill Windmaster™, Gill Instruments Ltd., Lymington, England) and an Open Path CO₂/H₂O analyzer (LI-7500A, LI-COR Biosciences, Lincoln, NE).

Sensors for Eddy Covariance measurement are normally mounted on a tower. The response time for sonic and gas analyzers must be 10 Hz or faster because spectrum analysis shows that the turbulent transport of any scalar in the surface boundary layer from eddy sizes range from 0.001 to 10 Hz. This method measures the average CO₂ flux over an integrated area as seen by the sonic anemometer and the gas analyzer. As a rule of thumb, this integrated area extends to a distance about 100 times the height of the sensors to the up-wind direction.

The requirements for making an Eddy Covariance CO₂ flux measurement are (1) fast response of both the sonic anemometer and gas analyzer; (2) density correction arising from the fluxes of sensible heat and latent heat flux (*Webb-Pearman-Leuning correction* [15]), and (3) a relatively large, flat field site. For more information on how to make the Eddy Covariance CO₂ flux measurement, printed and/or electronic copies of a handbook entitled 'A Brief Practical Guide to Eddy Covariance Flux Measurements', authored by LI-COR scientists, is available at: www.licor.com/ec-analyzers

LI-COR also offers an introductory course with hands-on training on site in Lincoln, NE. More information and registration forms are available here: <http://www.licor.com/ec-training>.

Designed by LI-COR scientists, the course provides information on the general principles, requirements, applications, and processing steps of the Eddy Covariance method.

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Carbon Capture and Storage Projects

In terms of Carbon Capture and Storage, a universal regulatory framework needs to be in place that requires uniformity in all aspects of pre-injection, injection, and post-injection activities such as Surface Monitoring to ensure the CO₂ stays in place. Currently there are numerous studies and pilot projects underway that are helping to determine the best methods for monitoring CO₂ release from the surface both pre- and post-injection.

LI-COR Biosciences has specialized in ambient CO₂ monitoring for the last 25 years. Our open and closed path CO₂ analyzers are used worldwide in many different applications. In terms of CCS technology, the LI-8100A Automated Soil CO₂ Flux System can be used to monitor surface leaks and natural background fluxes in multiple locations. LI-COR also offers the LI-7500A Open Path CO₂/H₂O Analyzer that is commonly used in Eddy Covariance measurements to determine the vertical CO₂ flux over a relatively large area. The Eddy Covariance method is an effective way to monitor large areas where CO₂ may escape from the subsurface. Below we will discuss two of the many surface monitoring projects already underway that involve using the LI-8100A and/or LI-7500A for Carbon Capture and Storage.

Case Study 1:

Midwest Geological Sequestration Consortium Illinois Basin – Decatur Project

The Midwest Geological Sequestration Consortium (MGSC), in cooperation with Archer Daniels Midland (ADM) Company, is conducting a large-scale carbon sequestration demonstration project in Decatur, Illinois. In 2011, the Illinois Basin - Decatur Project (IBDP) will begin injecting 1,000 tonnes/day of carbon dioxide for three years into the Mount Simon Sandstone at a depth of approximately 2,100 meters. The project seeks to demonstrate the ability of a deep saline formation to safely store one million tonnes of CO₂ in the Illinois Basin, a 155,000 square-kilometer subsurface geologic feature which occurs in Illinois, southwestern Indiana, and western Kentucky.

MGSC is conducting an extensive monitoring, verification and accounting program in the deep subsurface and near-surface environments. Near-surface monitoring equipment includes the LI-COR LI-7500 Open Path CO₂/H₂O analyzer, a portable LI-COR LI-8100 Automated Soil CO₂ Flux System, and a multiplexed LI-8100/LI-8150 System. This instrumentation is being used to collect baseline data to characterize net CO₂ fluxes and soil CO₂ fluxes and will be used throughout the project to monitor for potential CO₂ leakage signals.



Figure 1. Measuring soil CO₂ fluxes at the IBDP site using the LI-COR LI-8100.

A network of 118 soil flux rings has been developed at the project site. Soil CO₂ fluxes have been monitored weekly since June 2009 using a single-chamber LI-8100 (Figure 1) to assess spatial and temporal variability and to develop a long-term baseline record.

A unique approach has been taken at the IBDP site to evaluate multiple types of ring installations and determine which type would be the most effective in monitoring for potential CO₂ leakage. The three installation techniques being evaluated are: 1) bare-shallow, 2) bare-deep, and 3) natural-shallow rings. Natural-shallow rings are minimally maintained with the natural grassy vegetation left undisturbed (Figure 2).



Figure 2. Natural (left) and bare (right) soil rings used to determine soil CO₂ fluxes at the IBDP site.

These rings are used to determine the ‘natural’ soil CO₂ flux. In contrast, a 60-cm diameter ‘dead zone’ in and around each bare-shallow and bare-deep ring location is maintained by the periodic application of herbicide and manual removal of plant debris to minimize plant and root respiration in and near the rings (Figure 2). Natural-shallow and bare-shallow rings were driven about 8 cm into the ground. Bare-deep rings were driven about 46 cm into the ground and are intended to minimize shallow root zone influences on flux measurements. As expected, the CO₂ fluxes were greatest in the natural shallow rings and fluxes in the bare-deep and shallow were similar (Figure 3). The decline of fluxes from the bare-deep rings until October 2010 is likely due to surficial vegetation dying after initial ring installation (Figure 3).

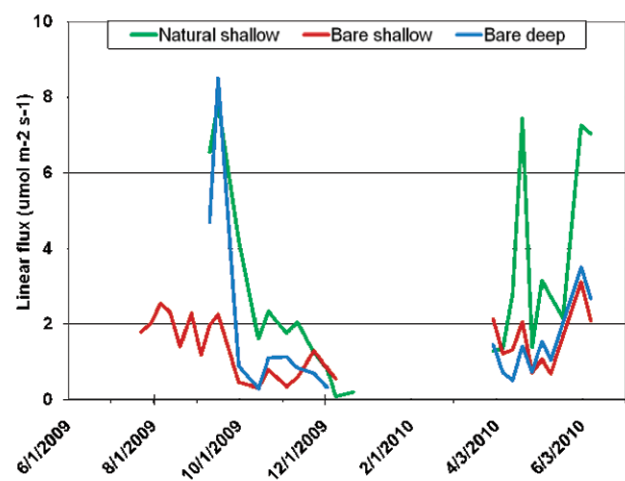


Figure 3. Soil CO₂ fluxes measured for three types of soil ring installations at the IBDP site.

An LI-8100/LI-8150 Multiplexed System was recently deployed to provide a better temporal understanding of soil fluxes at the project site. Ports are being monitored at 30-minute intervals to evaluate soil CO₂ flux from bare-shallow rings and natural-shallow rings. These data will be used to enhance interpretation of the atmospheric CO₂ flux data collected by an Eddy Covariance system.

An Eddy Covariance (EC) system was deployed at the IBDP site and used a LI-COR LI-7500 Open Path CO₂/H₂O Analyzer mounted on top of a 10-meter tall tower to measure CO₂ and water vapor densities at a frequency of 10 Hz. Atmospheric CO₂ flux (F_c) measured from July 2009 to May 2010 varied, as expected, based on season (Figure 4). F_c values typically ranged from -20 to 10 $\mu\text{mol m}^{-2}\text{s}^{-1}$ in July-August 2009, declined to -10 to 5 $\mu\text{mol m}^{-2}\text{s}^{-1}$ in September 2009, and then were about 0 $\mu\text{mol m}^{-2}\text{s}^{-1}$ in November 2009-May 2010. F_c values remained low through spring (May), prior to significant plant re-growth. When winds were blowing from about 140 to 220 degrees, (1) relatively high positive and negative F_c were measured, and (2) a relatively large number of F_c data were lost due to filtering according to quality control criteria (Figure 4). Poor F_c quality associated with these wind directions was likely due in part to disturbances in airflow caused by the large waste water treatment structures located southeast of the EC tower.

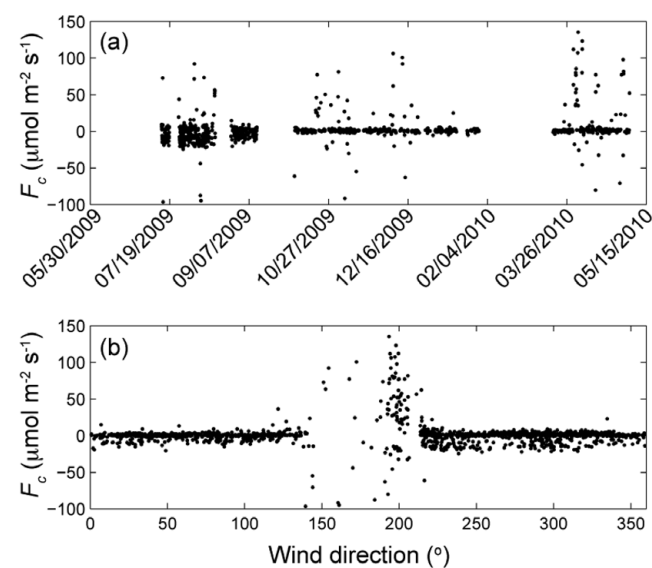


Figure 4. Atmospheric CO₂ flux (F_c) in relation to time and mean horizontal wind direction measured by the Eddy Covariance tower at the IBDP site.

For additional information see:

Locke, R.A. II, I.G. Krapac, J.L. Lewicki, and E. Curtis-Robinson, 2010, Characterizing near-surface CO₂ conditions before injection – Perspectives from a CCS project in the Illinois Basin, USA: Proceedings of the 10th International Conference on Greenhouse Gas Technologies, September 19-23, 2010, Amsterdam, The Netherlands: Energy Procedia, (in press).

Case Study 2:

SECARB Black Warrior Injection Test, Tuscaloosa County, Alabama

The Black Warrior Basin has produced a large quantity of coalbed methane and has the potential for considerable enhanced coalbed methane production. Additionally, as bituminous coal can adsorb approximately twice as much CO₂ as methane at reservoir pressure, the basin has significant potential for CO₂ sequestration. A field test is being conducted and has been designed to test reservoir conditions in the three primary target coal zones.* A number of monitoring activities are planned for the site, including reservoir pressure monitoring in deep observation wells, fluid and pH monitoring in each coal bed, shallow groundwater quality monitoring, soil gas composition, conservative tracers, and soil CO₂ flux monitoring. A set of soil gas samples was collected and soil flux monitoring was performed at a control site located in Deerlick Creek to provide additional background information on near surface conditions in the region. Preliminary results indicate that a significant volume of CO₂ is found in the soil profile and carbon isotopic data suggests that the CO₂ is of bacterial origin. Soil CO₂ flux data was collected for nine months and indicated a high variability among individual sites and through time. The data show significant seasonal variations, with high flux rates during the warm months associated with high soil activity and low flux rates during the winter months.

*Author's Note: As of the time of printing, this study was recently completed.

Introduction

The Black Warrior Basin has produced more than 2 Tcf of coalbed methane and the basin is conservatively estimated to have the potential to store 5.9 Tcf of CO₂ in mature reservoirs. Based on this estimate, sequestration of CO₂ would enhance coalbed methane recovery, increasing reserves by more than 20 percent [1]. A field verification test program of carbon sequestration in coal is being conducted in the Black Warrior Basin under the auspices of the U.S. Department of Energy's Southeastern Regional Carbon Sequestration Partnership (SECARB [2]). The test is a small-scale, short-term test in an area where technical feasibility and commercial applicability are considered to be high. Part of this project is to begin to develop and demonstrate technology to ensure the safe and permanent storage of CO₂ in coal seams.

Project Design

The project focuses on the injection of about 1,000 tons of CO₂ into a mature coalbed methane well and a series of buildup and falloff tests that will be monitored in the injection well and

a series of remote observation wells. Before the injection test, one shallow water observation well and three deep observation wells will be drilled (Figures 1 and 2), and the injection well's mechanical integrity will be tested to ensure that the test can be conducted safely. Coal samples from cores in the deep wells will be sent off to have adsorption isotherms for CH₄ and CO₂ run, for remaining gas in place analysis, and for proximate, ultimate, and petrographic analysis.

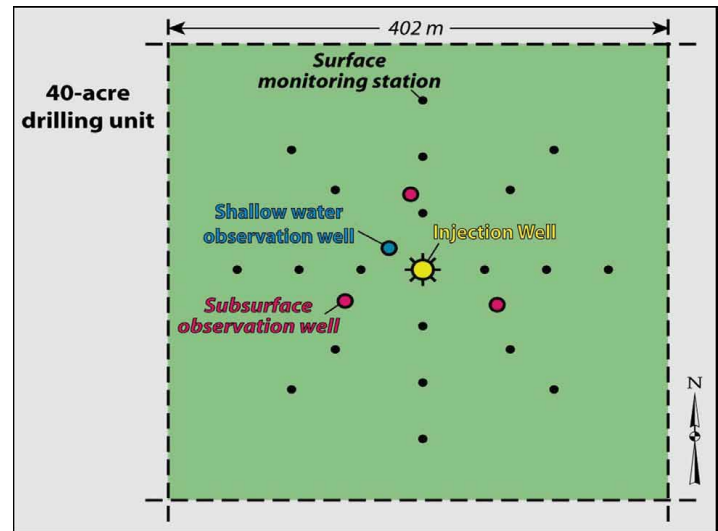


Figure 1. Schematic of planned locations for wells and surface monitoring stations.

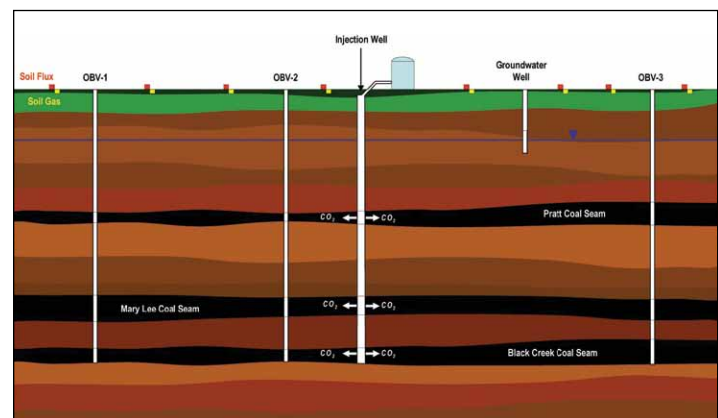
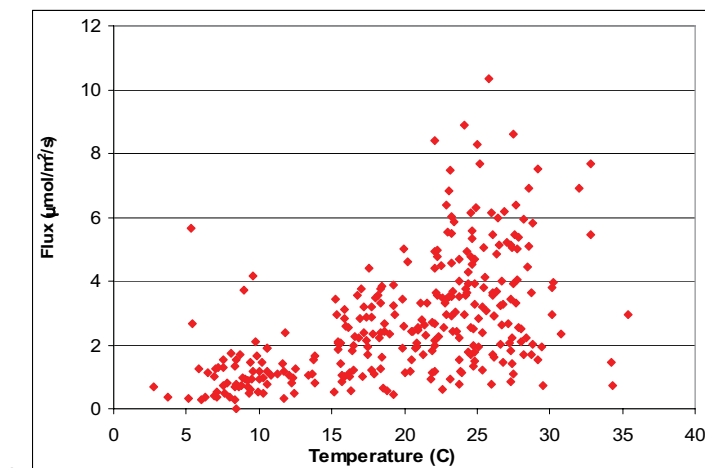


Figure 2. Schematic cross-section showing injection well and observation wells.

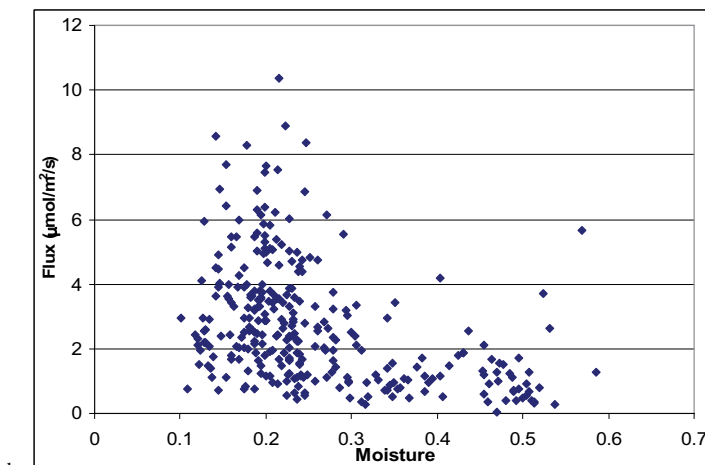
The injection test will begin with a pressure build-up test to determine the time required for pressure stabilization of the well and shut-in pressure. The injection of the CO₂ will occur in two stages at each of the three coal zones. The first stage of the injection consists of a 40-ton slug of CO₂ injected to test the injectivity and help estimate the pressure and rate to inject a larger amount of CO₂. After pressure stabilizes in the coal, 280 tons of CO₂ will be injected to test longer term changes in injectivity and pressure response. Once pressure stabilizes in the Black Creek coal zone, the test will be repeated in the Mary Lee coal zone and then the Pratt coal zone [2, 8].

Monitoring Plan

A number of different methods are planned to monitor the injection and ensure the safety and effectiveness of this program. Surface soil monitoring activities consist of analysis of soil gas composition and the measurement of soil gas flux. The twenty-one monitoring stations (Figure 1) are arranged in a radial array at 50 m, 100 m, and 150 m from the well. Soil gas samples were taken in February 2007 at the control site and samples will be taken at the test site about three months before and after injection. Samples are taken at a depth of 0, 0.3, 0.6, and 1.0 meters at each station and analyzed for gas composition (N_2 , O_2 , CO_2 , CH_4 , and light hydrocarbon concentrations) and isotopic composition of CO_2 . Soil CO_2 flux monitoring at the control site began in May 2007 and continued through February 2008. Flux was measured at each of the 21 monitoring stations once a month and weekly measurements were made at two stations. Flux monitoring will begin at the test site at least three months before injection and continue until site closure. Shallow ground water and surface monitoring will provide important baseline and post-injection information to be used to evaluate the environmental safety of carbon sequestration and ECBM in the Black Warrior Basin [8].



a.



b.

Figure 3. Soil temperature, soil moisture levels, and flux rate. a) Flux vs. soil temperature, and b) Flux vs. soil moisture.

Surface Monitoring - Soil CO_2 Flux

Soil CO_2 flux was measured using a LI-COR Biosciences LI-8100 Automated Soil CO_2 Flux System. Raw data were collected in the field, and flux rates were calculated using the software provided with the LI-8100. Two stations were sampled weekly; all 21 stations were sampled monthly. Soil temperature and moisture were also measured at each station.

Soil flux is highly variable between stations and over time. Differences of $7.77 \mu\text{mol}/\text{m}^2/\text{s}$ between two sites on the same day have been measured and a difference of $5.13 \mu\text{mol}/\text{m}^2/\text{s}$ from one week to the next at one site. While some stations are consistently below or above average, average flux rates vary wildly. There appears to be little correlation between soil temperature or soil moisture and flux rates (Figure 3); however, there does appear to be a seasonal fluctuation (Figure 4). Seasonal variations are to be expected as there is more soil microbial activity in the warm months than in the winter months. The results of soil flux monitoring demonstrate that significant CO_2 is issuing from the soil profile at the control site, and comparison of pre- and post-injection data at the test site will provide critical information on soil gas emissions and the potential effects of commercial sequestration and ECBM operations.

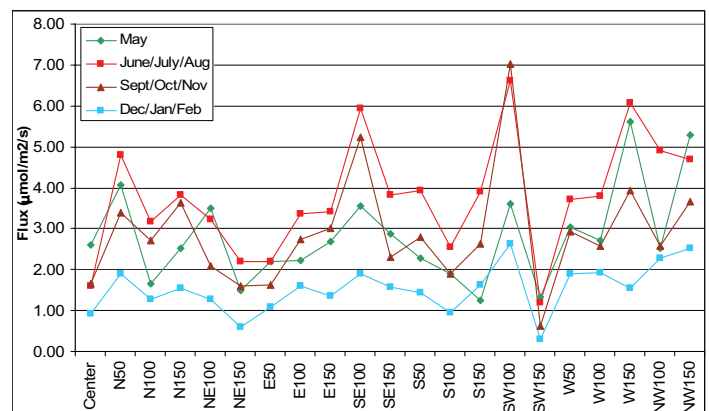


Figure 4. Graph of seasonal averages at each station.

Conclusions

A field test is being conducted in the Black Warrior Basin that is designed to test reservoir conditions in three Pottsville coal zones. A number of monitoring activities are planned for the site including reservoir pressure monitoring in deep observation wells, fluid and pH monitoring in each coal bed, shallow groundwater quality monitoring, soil gas composition, conservative tracers, and soil CO_2 flux monitoring. A significant quantity of CO_2 is found in the soil naturally, and concentrations tend to increase with depth as the CO_2 becomes depleted in ^{13}C ; this is consistent with bacterial activity in the soil profile. Less than one percent of the soil gas is light hydrocarbons and methane and ethane dominate. The hydrocarbon fraction has a dryness index of about 0.98 and is wetter than the gas

produced in the adjacent well; the lower dryness of the soil-gas hydrocarbons suggests that they are locally derived from the soil profile and not the reservoir coal beds. There is a net movement of CO₂ out of the soil year round at the control site between 0.2 μmol/m²/s and 10.35 μmol/m²/s. Flux rate exhibits a seasonal variation, with higher rates in the summer and lower rates in the winter.

Acknowledgements

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Research Experience in Carbon Sequestration (RECS)

Carbon Capture and Sequestration (CCS) technologies have significant potential to reduce atmospheric CO₂ emissions by permanently storing CO₂ in underground geologic formations. As recently as 2004, however, there were few educational programs that focused on implementing and managing CCS programs. This left people who were interested in climate change solutions with few opportunities to learn about CCS technologies.

Pamela Tomski recognized this deficit and responded by starting the Research Experience in Carbon Sequestration (RECS) program. RECS provides training and education for early-career professionals and students through a combination of classroom instruction and field activities, which typically include visits to a geologic CO₂ storage site, power plant, and natural CO₂ reservoir. Participants learn about CCS topics that encompass energy studies, geology, climate science, and related fields.

Tomski organized the first RECS program in 2004 with support from the U.S. Department of Energy and other private organizations. The RECS program has been popular since its inception – and has seen a steady increase in interest. In 2010 RECS selected 30 participants out of several hundred applicants. In the future Tomski hopes to expand the program and hold two training sessions each year.

As part of the program, these up-and-coming professionals are introduced to instruments used for CCS monitoring, including the LI-8100A Automated Soil CO₂ Flux System and the LI-7500A Open Path CO₂/H₂O Analyzer. Both instruments are designed for outdoor deployment and are useful for meeting Monitoring, Verification, and Assurance requirements within the CCS framework. LI-COR instruments and technologies offer simple, powerful solutions for monitoring geological carbon storage sites, and are included in the RECS program to provide participants with hands-on experience using CCS monitoring technologies.

Ongoing research into CCS technology will resolve technical challenges and validate its value for limiting carbon emissions, while RECS will give professionals and students a head start by providing them with the diverse skill set required to implement effective CCS programs.



A RECS participant makes soil CO₂ flux measurements with the LI-8100 in New Mexico.

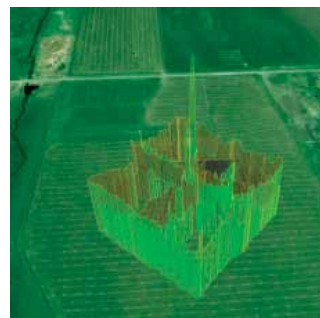


LI-COR at ZERT

The ZERT Center graciously provided access to their research site so that LI-COR scientists could get firsthand experience at an injection site, using the LI-8100A Automated Soil CO₂ Flux System to measure CO₂ effluxes with the enhanced 20,000 ppm concentration range of the LI-8100A. In addition, LI-COR was able to test soil chamber collar adapters that increase the volume:area ratio for 20 cm chambers (below).



And finally, LI-COR scientists tested a prototype intake tube connected to the LI-8100A Analyzer Control Unit, fitted with a GPS unit, to test the feasibility of using the LI-8100A to detect and map leaks at CO₂ injection sites (below). Several transects along the injection pipe were made, and were used to generate a 3-D model of CO₂ efflux at the test site.



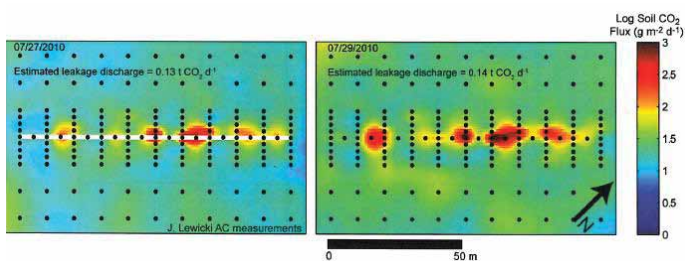
The plot to the left shows CO₂ concentration on July 22, 2010, three days after CO₂ was injected through the pipe. CO₂ values ranged from 360 ppm (base level) to a peak of 506 ppm in the center of the plot.

Zero Emission Research and Technology (ZERT) Center

The Zero Emission Research and Technology (ZERT) Center is a research group focused on understanding the basic science of underground (geologic) CO₂ storage and for developing tools to ensure safety and reliability. ZERT is a collaboration involving several private corporations, DOE laboratories (Los Alamos National Lab, Lawrence Berkeley National Lab, National Energy Technology Lab, Lawrence Livermore National Lab, and Pacific Northwest National Lab), as well as Montana State and West Virginia University.

In order to understand the possible fates of injected CO₂, ZERT is performing laboratory experiments to understand CO₂ physical and chemical interaction with geologic formation minerals and fluids. ZERT is also developing monitoring and verification techniques to determine the behavior of the underground CO₂ and underground storage capacity for different geologic formations.

As part of the initial experiments, a 100 meter length of perforated pipe was installed at a depth of approximately 2.5 meters below the surface. Controlled release of CO₂ into the pipe began in the summer of 2007. Various groups at the site perform measurements to characterize leakage at the surface, as well as other biological measurements, including leaf spectral measurements, ground water and below ground CO₂ monitoring, and Eddy Covariance flux measurements.



The chart above shows soil CO₂ effluxes measured by Jennifer Lewicki of Lawrence Berkeley National Laboratory in 2009 and 2010.

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Sequestration Partnership (SECARB) and the Midwest Geological Sequestration Consortium (MGSC) for their input and contribution to this document.

Ordering Information

LI-8100A Analyzer Control Unit.

Includes Auxiliary Sensor Interface, Serial Cable Interface, RS-232 Serial Cable, RS-232 to USB Adapter, Spares Kit, Compact Flash Memory Card, PC Card Adapter, Shoulder Strap Kit, Software CD (Windows®, Windows® Mobile, and Palm® Interface plus Data Analysis Software) and Instruction Manual (Chamber, Battery, and Battery Charger not Included)

Chambers

8100-102 Survey Chamber, 10 cm

Includes 8100-201 soil temperature probe, gasket kit, spares kit, and six soil collars

8100-103 Survey Chamber, 20 cm

Includes 8100-201 soil temperature probe, gasket kit, spares kit, and six soil collars

8100-104 Long-Term Chamber

Includes gasket kit, spares kit, and two soil collars

8100-104C Clear Long-Term Chamber

Includes gasket kit, spares kit, and two soil collars

LI-8100-M1 Four Chamber Multiplexed Package

Includes LI-8100A Analyzer Control Unit, LI-8150-8 Multiplexer, four 8100-104 Long-Term Chambers and four 8150-705 Cable/Hose Assemblies. Requires AC or DC power (DC power cable included). Auxiliary sensors sold separately.

LI-8100-M2 Four Chamber Multiplexed Package

Includes LI-8100A Analyzer Control Unit, LI-8150-16 Multiplexer, four 8100-104 Long-Term Chambers and four 8150-705 Cable/Hose Assemblies. Requires AC or DC power (DC power cable included). Auxiliary sensors sold separately.

LI-8100-P8 Eight Chamber Multiplexed Package

Includes LI-8100A Analyzer Control Unit, LI-8150-8 Multiplexer, eight 8100-104 Long-Term Chambers, eight 8150-705 Cable/Hose Assemblies, 8150-706 DC power cable, eight 8150-203 soil temperature thermistor,s and two year extended warranties for the LI-8100A and LI-8150-8.

LI-8100-P16 Eight Chamber Multiplexed Package

Includes LI-8100A Analyzer Control Unit, LI-8150-16 Multiplexer, sixteen 8100-104 Long-Term Chambers, sixteen 8150-705 Cable/Hose Assemblies, 8150-706 DC power cable, sixteen 8150-203 soil temperature thermistors, and two year extended warranties for the LI-8100A and LI-8150-16.

Greenhouse Gas Systems (GHG)*

GHG-1

LI-7700 Open Path CH₄ Analyzer, 5m power and Ethernet cables, calibration fixture, washer assembly, mounting hardware, radiation shield, spares kit, carrying case, Windows® software CD, and instruction manual.

LI-7500A Open Path CO₂/H₂O Analyzer, LI-7550 Analyzer Control Unit, 5m IRGA cable, USB-to-serial adapter, 5m data cables (RS-232, Ethernet, DAC), calibration fixture, Windows® software CD, and instruction manual.

7550-101 Auxiliary Sensor Interface for analog inputs.

GHG-2

LI-7700 Open Path CH₄ Analyzer, 5m power and Ethernet cables, calibration fixture, washer assembly, mounting hardware, radiation shield, spares kit, carrying case, Windows® software CD, and instruction manual.

LI-7200 Enclosed CO₂/H₂O Analyzer, LI-7550 Analyzer Control Unit, 7200-101 Flow Module, 1m intake tube with insect screen, 5m IRGA cable, USB-to-serial adapter, 5m data cables (RS-232, Ethernet, DAC), calibration fixture, Windows® software CD, and instruction manual.

7550-101 Auxiliary Sensor Interface for analog inputs.

* The Greenhouse Gas Systems include the LI-7700 Open Path CH₄ Analyzer, for those users interested in adding simultaneous eddy flux measurements of *in situ* methane, as well as carbon dioxide and water vapor.

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“Trust in the LORD with all your heart and do not lean on your own understanding. In all your ways acknowledge Him, and He will make your paths straight.”

—Proverbs 3:5,6