

Capturing and processing soil GHG fluxes using the LI-8100A—Picarro

The LI-8100A Automated Soil CO₂ Flux System is designed to measure CO₂ efflux from soils using the closed non-steady state transient approach. While CO₂ is an important gas in many contexts, it is not the only gas of interest for many research applications. By exploiting some simple hooks in the system a third party analyzer capable of measuring other trace gases can be interfaced with the LI-8100A System and our data processing software (SoilFluxPro) can be used to compute fluxes for these additional gases. In this application note we describe considerations for selecting an appropriate third party analyzer, how to integrate it into the system and the procedure used to compute fluxes of additional gases in SoilFluxPro.

Flow, volume, and pressure considerations

There are three flow loops inside a multiplexed LI-8100A System: the primary *sampling loop* between the multiplexer and chamber, the *subsampling loop* between the LI-8100A and the multiplexer, and the *pressure regulation loop* inside the multiplexer. Each of these loops operates at a different flow rate. The nominal flow rate through the subsampling loop is between 1.5 and 1.7 SLPM at near atmospheric pressure.



Figure 1. Plumbing schemes for connecting an additional analyzer in to the LI-8100A System. Left hand panel: series configuration. Right hand panel: parallel configuration.

In a multiplexed configuration, the subsampling loop is where any additional analyzer should be placed, either in series with the air outlet from the LI-8100A or in parallel to it (Figure 1). Series placement is possible when the additional analyzer does not use its own internal pump and is capable of operating at the same flow rate and pressure as

the LI-8100A. Parallel placement is required when the additional analyzer operates at a different pressure or flow rate lower than the LI-8100A. In either configuration it is possible for the additional analyzer to cause a slight over-pressure on the LI-8100A's optical bench. Care should be taken to avoid creating flow restrictions in the subsampling loop and where these cannot be avoided it may be necessary to adjust the bias on the pressure regulation loop. To adjust the pressure regulation loop:

- 1 With all plumbing modifications and the additional analyzer in place, note the LI-8100A optical bench pressure when all flow pumps are off.
- 2 Open the LI-8150 multiplexer and remove the splash guard that covers the fuses.
- 3 Locate the blue **Pressure Adjust** potentiometer (up and to the left of the fuses, see Figure 2).
- 4 Turn on all flow pumps and look at the LI-8100A optical bench pressure.

If it is different from the pressure noted in step 1 use a small flat head screwdriver to adjust the **Pressure Adjust** potentiometer to minimize the pressure difference between when the pumps are on or off. Note that it may not be possible to bring the pressure difference to zero between when the flow pumps are on and off; within ± 0.5 kPa would be typical. If there is some offset, the calibration procedures outlined below should be followed to ensure that the LI-8100A performs as expected.



Figure 2. Pressure Adjust potentiometer.

When operating with a single chamber and standalone LI-8100A analyzer control unit, the third party analyzer should be placed on the AIR OUT line from the LI-8100A using one of the plumbing schemes described in Figure 1. The plumbing configuration follows the same guidelines when placing the additional analyzer in the subsampling loop of a multiplexed system. The flow rate between an LI-8100A and a single chamber, and the flow rate in the subsampling loop of a multiplexed system, are both nominally between 1.5 and 1.7 SLPM.

The volume of the additional analyzer will have at least two kinetic effects: 1) it brings additional air to the system, which dilutes trace gas entering the system from the soil surface and reduces the measured trace gas mole fraction rate of change (dC/dt); and 2) it creates a time delay in the onset of a monotonic concentration increase or decrease. Accurate fluxes can still be measured if the added volume is sufficiently small.

The quantitative impact of the added volume on dC/dt can be evaluated by considering the equation used to calculate flux F ($\text{mol m}^{-2}\text{s}^{-1}$, equation 1). This equation is derived based on the assumption of a single fixed volume V (m^3) with homogeneous air density ρ (mole m^{-3}). For simplicity in this discussion the effects of water corrections are neglected. This however, does not change the conclusions. Thus,

$$F = \frac{\rho V}{S} \frac{dC}{dt} \quad 1$$

where F is the flux of trace gas ($\text{mol m}^{-2}\text{s}^{-1}$), where ρ is air density (mol m^{-3}), dC/dt is the time rate of change in mole fraction of the gas being measured ($\text{mol mol}^{-1}\text{s}^{-1}$), and S (m^2) is the soil surface area over which the flux occurs. For a flux F , the trace gas mole fraction rate of change dC/dt is proportional to the total number of molecules in the system ρV .

For a well-mixed system, when an additional volume V_{added} (m^3) that contains a gas of density ρ_{added} is inserted into the system, equation 1 becomes

$$F = \frac{(\rho_{\text{system}} V_{\text{system}} + \rho_{\text{added}} V_{\text{added}})}{S} \frac{dC}{dt} \quad 2$$

Assuming V_{system} (m^3) and V_{added} each operate at uniform temperature and pressure, $\rho_{\text{system}} = P_{\text{added}} / RT_{\text{added}}$ and $\rho_{\text{added}} = P_{\text{added}} / RT_{\text{added}}$, where R is the universal gas constant ($8.314 \text{ Pa m}^3\text{K}^{-1}\text{mol}^{-1}$), and T_{system} , P_{system} and T_{added} , P_{added} are the temperature (K) and pressure (Pa) in the system and additional volume respectively. Substituting these expressions and factoring gives,

$$F = \frac{\rho_{\text{system}} \left(V_{\text{system}} + V_{\text{added}} \frac{P_{\text{added}}}{P_{\text{system}}} \frac{T_{\text{system}}}{T_{\text{added}}} \right)}{S} \frac{dC}{dt} \quad 3$$

For data processing using SoilFluxPro, an effective volume $V_{\text{effective}}$ for the addition can be defined for the added analyzer and entered into the software.

$$V_{\text{effective}} = V_{\text{added}} \frac{P_{\text{added}}}{P_{\text{system}}} \frac{T_{\text{system}}}{T_{\text{added}}} \quad 4$$

Thus, the total volume used in equation 1 becomes simply $V_{\text{system}} + V_{\text{effective}}$ and the density is ρ_{system} . The system density is computed using P_{system} from the pressure measurement in the LI-8100A optical bench, and T_{system} from the chamber air temperature. There are inherently small variations in $V_{\text{effective}}$ due to changes in T_{system} and P_{system} , but these are generally small and subsequently neglected.

In cases where the volume of the addition operates at a non-uniform temperature and pressure or is not well known, $V_{\text{effective}}$ can be estimated experimentally by plumbing the third-party analyzer in a closed loop and injecting a known volume $V_{\text{injection}}$ (m^3) of pure CO_2 into the loop. The gas concentrations in the loop pre-injection C_1 (mol mol^{-1}) and post-injection C_2 (mol mol^{-1}) are defined as

$$C_1 = \frac{N_{\text{CO}_2}}{N_{\text{added}}} \quad 5$$

$$C_2 = \frac{N_{\text{CO}_2} + N_{\text{injection}}}{N_{\text{added}} + N_{\text{injection}}} \quad 6$$

where N_{CO_2} is the number of moles of CO_2 in the additional volume pre-injection, N_{added} is the total number of moles in the additional volume pre-injection, and $N_{\text{injection}}$ is the number of moles of CO_2 injected into the loop. Substituting equation 5 into 6 and rearranging to solve for N_{added} yields

$$N_{\text{added}} = \frac{N_{\text{injection}} (c_2 - 1)}{(c_1 - c_2)} \quad 7$$

where $N_{\text{added}} = \frac{P_{\text{added}} V_{\text{added}}}{RT_{\text{added}}}$ and $N_{\text{injection}} = \frac{P_{\text{injection}} V_{\text{injection}}}{RT_{\text{injection}}}$.

$T_{\text{injection}}$ (K) and $P_{\text{injection}}$ (Pa) are the temperature and pressure, respectively, of the gas injected into the closed loop. Substituting these into equation 7, and following from equation 4, yields

$$V_{\text{effective}} = \frac{P_{\text{injection}} T_{\text{system}} V_{\text{injection}} (c_2 - 1)}{P_{\text{system}} T_{\text{injection}} (c_1 - c_2)} \quad 8$$

In practice it is difficult to know $T_{\text{injection}}$ and $P_{\text{injection}}$ with great certainty. Making the assumption that $P_{\text{injection}} = P_{\text{system}}$ and $T_{\text{injection}} = T_{\text{system}}$ introduces some error in determining $V_{\text{effective}}$ experimentally, but it allows equation 8 to be simplified, eliminating the need to know temperature or pressure.

$$V_{\text{effective}} = \frac{V_{\text{injection}}(c_2 - 1)}{(c_1 - c_2)} \quad 9$$

In many cases, the impact of an added volume on flux calculations will be modest as $V_{\text{effective}}$ for many modern trace gas analyzers is small. For example, neglecting the additional volume of an analyzer with an internal volume of 325 cm³, operating at 18.75 kPa and 300.12 K would introduce an error of less than 1.5% for the nominal system volume of a multiplexed system.

By trapping air making its way around the measurement circuit, the volume of a third-party gas analyzer may also introduce an additional time delay and have other effects that can compromise the flux measurement. The magnitudes of these effects are related to the analyzer's volume V_{added} , its operating pressure and temperature, and the flow rate through it. We can qualitatively assess the kinetic consequences of adding the volume by defining a time constant for the effective volume of the added analyzer and comparing it empirically to tested cases. We define a time constant τ_{added} (s)

$$\tau_{\text{added}} = \frac{\rho_{\text{added}} V_{\text{added}}}{U_{\text{added}}} \quad 10$$

where U_{added} is the molar flow rate (moles s⁻¹) delivered to the analyzer, ρ_{added} is air density in the analyzer evaluated at the analyzer's internal temperature and pressure, and V_{added} is its actual volume.

Time constants for different analyzers or model volumes inserted into the LI-8100A subsampling loop are shown in Table 1. We have tested the impact of adding volumes in both series and parallel configurations, and found that accurate fluxes were observed when a volume was added having a time constant of about 7 seconds, but not 17 seconds (Table 1). Based on these results, we expect that third-party analyzers added in series or parallel with time constants less than 5 to 7 seconds may work well. We recommend fluxes made with any other configuration not shown here be validated. Validation can be straightforward if the third-party analyzer measures CO₂ as well as other gases of interest.

Table 1. Time constants for different analyzers or volumes added to the LI-8100A subsampling loop. Temperatures and pressures pertain to conditions inside the added volumes or analyzers.

| Analyzer or added volume | Configuration | Volume (cm ³) | P (kPa) | T (K) | Flow rate (SLPM) | τ_{added} (s) | Flux OK? |
|--------------------------|---------------|---------------------------|---------|-------|------------------|---------------------------|----------|
| LI-8100A | Series | 14.5 | 98 | 323 | 1.7 | 0.5 | Yes |
| Test analyzer | Parallel | 325 | 18.75 | 300 | 0.8 | 4.6 | Yes |
| Test volume 1 | Series | 200 | 98 | 298 | 1.7 | 7.1 | Yes |
| Test volume 2 | Series | 500 | 98 | 298 | 1.7 | 17.7 | No |

The configurations reported in Table 1 all affect dC/dt and introduce time delays. But for systems with appropriate time constants, accurate fluxes can be obtained by entering the appropriate volumes, adjusting the dead band to accommodate delays, and computing fluxes using SoilFluxPro.

Calibration considerations

The calibration procedures outlined in the LI-8100A user manual are fine for normal operation of the instrument where optical bench pressure is not significantly altered from ambient. However, when plumbing additional volumes into the system, small pressure differences can cause offsets in the gas measurements when the standard calibration procedure is followed. These offsets tend to be small and may only be apparent when a CO₂ measurement is available at two different points in the system.

When operating with a third party analyzer plumbed into the system an alternative calibration routine can be used:

- 1 With the system plumbed for operation with the third party analyzer, turn on the flow pumps and note the optical bench pressure.
- 2 Disconnect the hose from the air inlet (AIR IN) and connect the calibration rig as described in Figure 3.
- 3 With the flow pumps on, adjust the flow rate through the rotometer such that bench pressure on the LI-8100A is as close as possible to what it was in step 1. A slight pressure difference (± 0.5 kPa) may be unavoidable and is okay. It is critical however, that flow through the rotometer exceeds the flow through the LI-8100A and that some small excess flow leaves the vent tube in the calibration rig. A flow rate of 2.0 to 2.5 LPM through the rotometer may be suitable to meet the demand of the LI-8100A pump and have a small flow out the vent.
- 4 When the gas concentration reading stabilizes, set the zero, span or span 2 using the LI-8100A interface software as described in the LI-8100A user manual.
- 5 Calibrating the third party analyzer following this same procedure may be wise as well. Check with its manufacturer for calibration details.

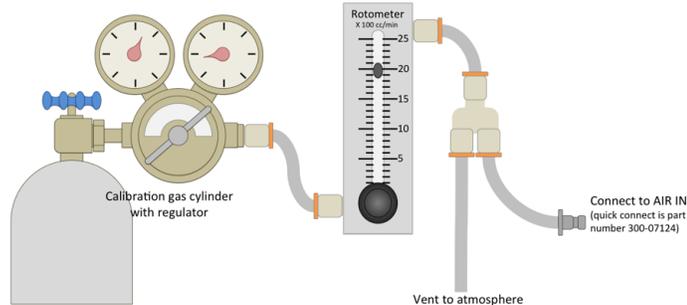


Figure 3. Calibration rig used to calibrate the LI-8100A at operating pressure.

Despite careful calibration some offsets may be seen between CO₂ and water vapor as measured by the LI-8100A and some third party analyzer plumbed in line with it. These offsets can appear due to a number of reasons, and are not necessarily important in the context of the flux measurement. For water vapor, differences during a given flux measurement may be expected due to interactions with surfaces at different points in the system that lead to a differential time response for water vapor for the two analyzers. For this reason it is important to record both the concentration of the gas of interest and water vapor from the additional analyzer, or where available, record the dry mole fraction for the gas of interest.

For CO₂, differences will occur due to an inherent time delay resulting from the additional analyzer being physically separated from the LI-8100A's analyzer; the magnitude of this delay is related to the volume, flow rate, operating pressure, and location of the additional analyzer. But differences may also occur due to drift of the LI-8100A over time or pressure induced calibration offsets as discussed previously. It should also be noted that the accuracy of the LI-8100A's analyzer is specified as 1.5% of reading.

In a closed system where fluxes are computed from a rate of change, measurement of absolute concentration may seem less important than ability of the analyzer to accurately measure a change in concentration. However, because the absorbance measured by the LI-8100A is a non-linear function of CO₂ (and water vapor) concentration over its calibration range, the absolute concentration and rate of change are interrelated, and offsets in the absolute concentration may have a small impact on the flux. In practice, this effect is small and arises because the slope of the calibration curve increases with increasing CO₂ concentration.

Data integration

Using analog signals

If available on the third party analyzer, its analog outputs can be used to integrate data on the LI-8100A resulting in a single .81x file containing the time series for multiple gas species that can be processed in SoilFluxPro. If the system includes a multiplexer these output channels can be fed into one or more of the three auxiliary inputs available for the 8100-104 or 8100-104C chambers. In software, the auxiliary inputs from a single chamber can be mapped to all ports, allowing the third party analyzer to be connected at only a single location (Figure 4). For single chamber systems, lacking a multiplexer, the outputs must be fed into one or more of the four auxiliary inputs available through the 8100-663 Auxiliary Sensor Interface regardless of the chamber used.

The auxiliary inputs available through either the chambers or the 8100-663 are measured in volts with 13 bit resolution over a 0 to 5V input range. The instrument software supports linear scaling (general purpose input), as well as a Steinhart-Hart conversion (Figure 4).

For integrating data in a multiplexed system an auxiliary input cable (part number 392-08577) is available that connects directly to the auxiliary inputs on the 8100-104 and 8100-104C chambers. This cable provides a weatherized connection at the chamber and bare leads to interface to the third party analyzer's analog outputs. One cable will be necessary for each channel in use, and due to the cable's length, the analyzer must be placed near the chamber it is connected to. A 2 m cable (392-07955) is also available that allows the additional analyzer to be attached directly to the LI-8150 in place of a chamber, allowing the LI-8150, LI-8100A and third-party analyzer to be collocated up to 15 m from the chambers. Only one of the 392-07955 cables is required to access all three of the auxiliary inputs. Pin outs for both cables are given in Table 2.

For connecting to the 8100-663 Auxiliary Sensor Interface a user supplied cable with a suitable connection to the third party analyzer on one end and bare leads on the other will be required. For details on how to connect to the auxiliary sensor interface see the LI-8100A user manual.

Using an external data file

Where analog signals are not available, it is possible to integrate a separate data file from a third party analyzer in post processing using the import feature in SoilFluxPro. This allows fluxes to be computed for data collected

remotely from the LI-8100A when analog outputs are not available from the additional analyzer. It is necessary that the data to be imported have time stamps that are reasonably synchronized with the LI-8100A; fixed offsets can be accounted for. The import routine will select or generate a data point from the import file for each record of the LI-8100A file. If there is not an exact match, it will pick the two closest values and interpolate. Thus, 1 Hz data is best, but is not required. The import routine supports native text file formats used by a number of gas analyzer manufactures, and can be configured to match a variety of other formats. For details on how to import external files see SoilFluxPro's user manual.

Time keeping and clock synchronization between the LI-8100A and other system clocks

Importing data from a third party analyzer into the LI-8100A's .81x files through SoilFluxPro Software is done by matching time stamps between the two data sets. This requires that the two devices keep time relatively consistently between each other. In cases where an offset exists in the timestamps, a fixed offset can be applied and accounted for in SoilFluxPro during importation. This requires, however, that the offset be constant over the entire data set being processed. On short time scales it may be reasonable to assume drift is minimal and that the offset is approximately constant, with any additional small deviations accounted for in the curve fitting process. Over longer time scales, the asynchronous nature of clock drift ensures that without some intervention the offset will not be a constant value.

There is no internal mechanism in the LI-8100A that allows the instrument clock to be synchronized to a standard, or for it to act as a standard for other connected devices. In its typical application, the LI-8100A system runs independently and relies on the user to manually set its clock through its interface software before collecting data.

For users wishing to automate clock synchronization there is hope however. The LI-8100A configuration grammar supports pushing a time and date stamp to the instrument through either its serial or Ethernet interfaces. This allows a computer or microcontroller connected to the instrument to serve as an external standard for the instrument's clock. In many cases the external standard can be the third-party analyzer (more details below).

Configuration grammar

When a measurement is not active the following command can be used to set the time and date:

```
<SR><CFG><CLOCK><TIME>{HHMMSS}</TIME> <DATE>
{YYYYMMDD}</DATE></CLOCK></CFG></SR>
```

In situations where automated clock synchronization would be desirable, it is unlikely that there will be open windows where a measurement is not active (e.g., continuous sampling with a multiplexed system). Thus, before sending the command to update the clock, it will be necessary to send the following command to end the active measurement:

```
<SR><CMD><MEAS>STOP</MEAS></CMD></SR>
```

To restart the measurement, send the following:

```
<SR><CMD><MEAS>START</MEAS></CMD></SR>
```

This will restart the measurement using the settings from the active configuration. To avoid file naming errors that will prevent the measurement from restarting, select append mode when configuring and starting the initial measurement through the interface software.

All commands sent to the LI-8100A need to be followed with a line feed (ASCII 10) for the instrument to recognize them. The instrument sends an acknowledgment after receiving a valid command.

8100sync

In cases where the third-party analyzer runs a Windows operating system, clock synchronization can be done using a simple application, 8100sync, and the Windows Task Scheduler.

You can download 8100sync at:

<https://www.licor.com/documents/7sz6ddmimlskqez39wistcx1qwj56zpxsync>

8100Sync is a tool used to manipulate the clock on an LI-8100A running embedded software 4.0 or above, and includes some basic file management functionality. It is intended to be run from the Windows Task Scheduler at some regular interval to synchronize the LI-8100A clock to PC time. 8100Sync has been tested on Windows Vista, 7 and 10, and may be compatible other versions of Windows.

It consists of two separate executable files: 8100Sync2.0.exe and comscript.exe, and a simple configuration file. 8100Sync2.0.exe provides a graphical interface for comscript.exe with real-time status updates and an editor for the configuration file. Comscript.exe handles communication with the LI-8100A and can be run independent of 8100Sync2.0.exe. When run independently

comscript.exe provides no user feedback, but will trigger a save-only version of the configuration editor if problems are found with the configuration file. 8100Sync2.0.exe is dependent on comscript.exe and the application will automatically exit when comscript.exe is done executing; this allows either application to be used in the Task Scheduler. When the configuration editor is opened from either application, comscript.exe stops and will restart when the editor is closed.

Full details on how to use 8100Sync and how to configure the Task Scheduler can be found in the documentation included with the application.

Table 2. Pin out of cables that can be used to integrate analog signals into the LI-8100A System.

| 392-08577 | | | 392-07955 | |
|-----------|--|--------|-------------------------------|--------|
| Pin | Description | Color | Description | Color |
| 1 | Analog input (+) | Brown | Ground | White |
| 2 | 4 mA limited, 5 VDC regulated reference output | Pink | Chamber temp. signal (+) | Brown |
| 3 | 100 mA limited, 5 VDC supply | Blue | Analog ground | Green |
| 4 | Not used | Grey | Auxiliary input V4+ | Yellow |
| 5 | 50 mA limited unregulated output | Red | Chamber stop signal | Grey |
| 6 | 30 mA limited, switched 5 VDC supply | Yellow | Auxiliary input V3+ | Pink |
| 7 | Analog input (-) | Green | Chamber open and close signal | Blue |
| 8 | Ground | White | Auxiliary input V2+ | Red |
| 9 | N/A | N/A | Switch 5V supply control | Orange |
| 10 | N/A | N/A | Voltage supply to chamber | Tan |

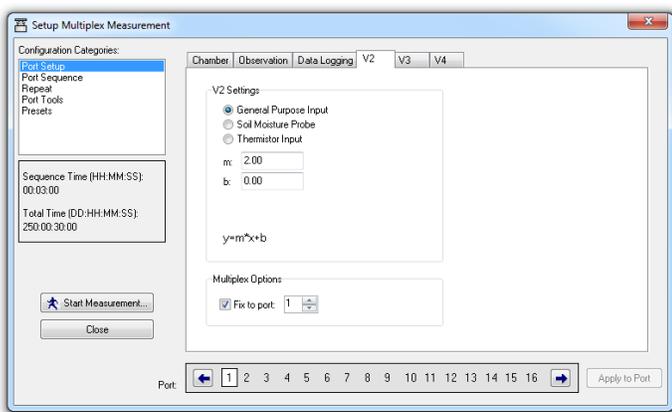


Figure 4. Analog input settings. For a linear voltage input select General Purpose Input and use the m and b coefficients to scale the raw voltage to meaningful engineering units: recorded value = $mV_{in} + b$. In multiplexed configuration use **Fix to port:** to route the analog inputs from one chamber to all the other chambers. This will ensure that the third party analyzer’s data is recorded in the correct location in the data file.

Curve fitting and computing fluxes using SoilFluxPro

To compute fluxes for additional variables included in the .81x file access the recompute dialog; This can be done for all records in a file using the **Recompute** icon at the top of the SoilFluxPro window, or for a single record by double clicking the record in the summary view and going to the **Recompute** tab in that record’s observation view. Figure 5 shows the recompute window for a single record.

In the recompute dialog, click the + under **Flux Computations** to add an additional variable for which fluxes are to be computed. Under **Gas column label:** select the variable. In the example here methane mole fraction was logged as umol/mol through auxiliary input V2. Check the box for **Curve Fit** and select start and stop times for the curve fit. These may need to be adjusted later. Under **Dilution correct with** select the channel where water vapor was recorded from the additional analyzer and use the scalar below it to scale the value to mol/mol. In the example, water vapor was logged on V4 as mmol/mol, so it needs to be multiplied by 0.001 to convert to mol/mol. If the third party analyzer reports dry mole fraction, then no additional dilution correction is needed. Under **Vext** input the effective volume determined following the guidelines presented under *Flow, volume, and pressure considerations*. In this case the additional analyzer has an actual volume of approximately 325 cm³ and operates at 18.75 kPa and 300.12 K. At a chamber pressure of 100 kPa and temperature of 298.5 K the effective volume was 60.62 cm³.

It should be noted that in the example presented here effective volume is treated as a constant. But in practice chamber temperature and pressure are typically not constant, leading to an effective volume that may be different for each measurement. However, when the effective volume is small relative to the total system volume, the error associated with treating it as a constant may not be important. For the example presented here, changing the chamber temperature by 25 °C affects the total volume by less than 0.1% and for a 5 kPa change in chamber pressure, the effect is less than 0.04%.

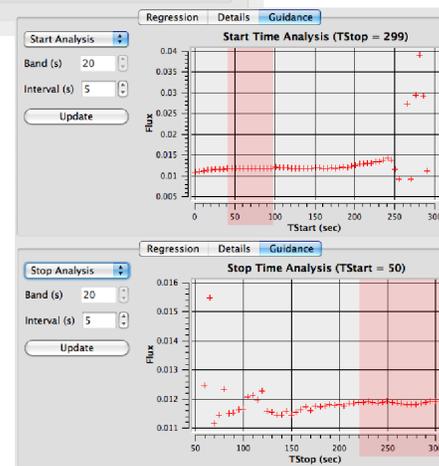
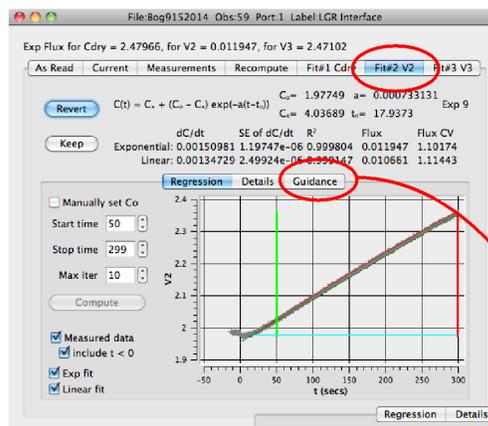
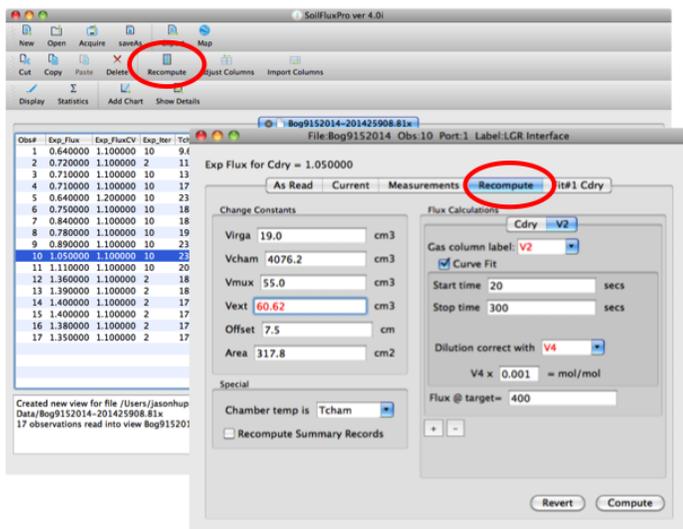


Figure 5. The recompute dialog.

Open the observation view for a record and go to the tab for the additional flux computation. In the example shown here, the tab is labeled **Fit#2 V2** (Figure 6). Use the **Guidance** tab to determine appropriate start and stop times for the curve fitting. In the example dataset, a start time between 40 and 100 seconds and a stop time of greater than 220 seconds would work (shaded areas in Figure 6). For the start time look for the initial plateau and select a time in that window. For stop time, select a time after the values level off. If the **Stop Time Analysis** curve does not level off or is very noisy, it is possible that the measurement length was too short. Once appropriate start and stop times have been determined it will be necessary to go back and recompute the data set if these times differ from the times used in the initial flux computation.

Note that for gas species with large fluxes and low resistance to diffusion in the soil, long measurement periods may lead to underestimations of the final flux due to buildup of the gas in the soil air space during the measurement. For gas species with low fluxes, such as methane, long measurement periods may be required to get enough data for a good curve fit. This means when measuring methane and carbon dioxide together, it will often be necessary to use different stop times for the two gases in the flux computation, with the stop time for carbon dioxide occurring much before that of methane.

Once satisfied with the curve fitting and summary values, the **Export** icon at the top of the main SoilFluxPro window can be used to export the summary values. For additional details on computing additional fluxes and exporting data see the SoilFluxPro manual accessed under **Help** in the software.

Figure 6. Viewing the curve fit for additional flux computations and using **Guidance** to select appropriate start and stop times. Windows with appropriate start and stop times are shaded in red.

Example measurements using the Picarro G2508 analyzer



Figure 7. A multiplexed LI-8100A System deployed with the Picarro G2508.

A five-species gas analyzer (model G2508) from Picarro, Inc. was integrated into a multiplexed LI-8100A System (Figure 7) using a parallel plumbing configuration. Data from the G2508 were logged to the analyzer's hard disk and merged with the LI-8100A's data in post processing using SoilFluxPro's import utility. 8100Sync was run on the G2508 from the Windows Task Scheduler, and used to synchronize the LI-8100A's clock to the clock of the G2508 every day at midnight. Clock synchronization was done over Ethernet using a direct connection between the LAN ports on the two instruments.

Flow through the G2508 was provided by the analyzer's vacuum pump and additional external plumbing was required to connect the two devices. While the G2508 optical bench has a specified volume of approximately 35 cm³, the additional external plumbing and pump represented a significant fraction of the total additional volume the analyzer added to the system. This complicated the computation of $V_{effective}$ as temperature and pressure were not uniform through the total volume and were only known in the optical bench. As such, $V_{effective}$ was determined for the G2508 experimentally as described in Flow, volume, and pressure considerations. Results are presented in Table 3.

Table 3. Effective volume as determined by injecting pure CO₂ into the G2508. Values are shown as mean plus or minus one standard error for n=3. The effective volume used for flux calculations was the mean of that determined for the three injection volumes; 62.13 cm³.

| Injection Volume (μl) | Change in CO ₂ concentration (μmol mol ⁻¹) | V _{effective} (cm ³) |
|-----------------------|---|---|
| 10 | 161.3 ± 3.97 | 62.02 ± 1.55 |
| 20 | 311.6 ± 3.14 | 64.10 ± 0.65 |
| 40 | 662.8 ± 12.65 | 60.28 ± 1.13 |

The system was deployed on a mowed lawn and an artificial peat bog in Lincoln, NE to measure fluxes of carbon dioxide and methane. During deployment at the lawn site the two analyzers were cross calibrated by passing dry standard gases through them to ensure they were functioning correctly.

At both sites methane fluxes were relatively small and consistent with expectations based on soil conditions (Figure 8). At the lawn site predominately small negative fluxes were observed (mean of -1.8×10^{-4} μmol m⁻² s⁻¹) and were attributed to methane oxidation in the soil. Accumulation curves for methane at this site showed an oscillation in concentration across the curve (Figure 9). While similar oscillations have been observed in accumulation curves due to pressure perturbations or poor mixing in the chamber, in this case the oscillations appear to be due to the asynchronous nature of the G2508's measurements and concentration changes approaching the instrument's limit of precision (<10 ppb + 0.05% of reading, precision for raw signal). Methane was measured approximately every eight seconds by the G2508 and was up-sampled by the instrument to generate an approximately one sample per second times series. At the bog site, where fluxes were higher (mean of 1.2×10^{-2} μmol m⁻² s⁻¹) and larger changes in methane concentration were observed, similar oscillations were not evident in the accumulation curves.

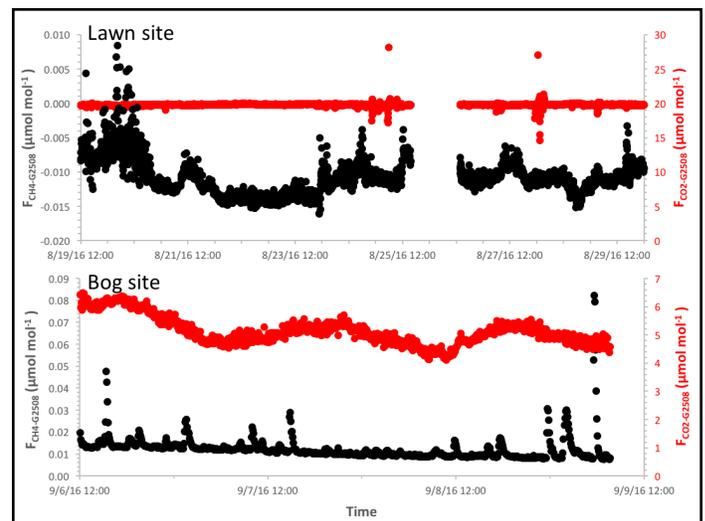


Figure 8. Methane and carbon dioxide fluxes from the lawn and bog sites as measured by the G2508. The gap on 8/26/16 was a period when other tests were being done with the system.

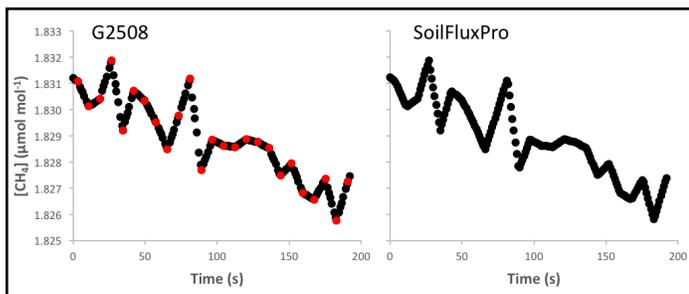


Figure 9. Example of methane concentration time series from a representative chamber measurement at the lawn site. The left panel shows measured (red) and interpolated (black) values from the G2508's output file. The right panel shows the same measurements after being imported through SoilFluxPro.

At both sites carbon dioxide fluxes were of a relatively similar magnitude; mean of $8.8 \mu\text{mol m}^{-2} \text{s}^{-1}$ at the lawn site and $5.0 \mu\text{mol m}^{-2} \text{s}^{-1}$ at the bog site as measured by the LI-8100A. A cross comparison was made between the flux of carbon dioxide computed from the LI-8100A's data and that of the G2508 (Figure 10). After careful optimization of the measurement start times, a small residual difference was observed in the fluxes computed from carbon dioxide dry mixing ratio, with fluxes computed from the G2508's data on average 2.7% larger than those computed from the LI-8100A. This offset was consistent across data from both deployments and did not appear to be due to a calibration offset between the two instruments, as they reported expected values when sampling dry standard gases during the initial cross calibration. Fluxes computed using a traditional dilution correction applied to the G2508's wet mole fraction data to get dry mixing ratio (Hupp 2011), were more similar to the LI-8100A fluxes (mean difference of 0.27% across both sites). The dilution correction used to compute dry mixing ratios on board the G2508 includes an additional spectroscopic correction not included in a traditional dilution correction (Rella 2010).

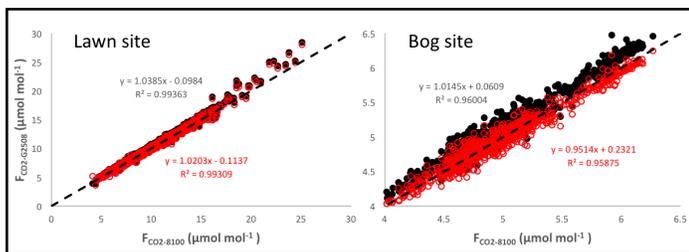


Figure 10. Comparison of exponential fluxes for carbon dioxide from the lawn and bog sites for the G2508 ($F_{\text{CO}_2\text{-G2508}}$) and the LI-8100A ($F_{\text{CO}_2\text{-8100}}$). At the lawn site start times were 50 seconds and 60 seconds for the LI-8100A and G2508 respectively. At the bog site start times were 30 seconds and 50 seconds. At both sites stop times

were 180 seconds. Data in red were computed using wet mole fractions from the G2508 and a traditional dilution correction. Data in black were computed using the dry mixing ratio as reported by the G2508. Dashed lines represent a 1:1 relationship.

References:

- Hupp, J.R. 2011. The Importance of Water Vapor Measurements and Corrections. LI-COR, Inc., Application Note 129.
- Rella, C.W. 2010. Accurate Greenhouse Gas Measurements in Humid Gas Streams Using the Picarro G1301 Carbon Dioxide/Methane/Water Vapor Gas Analyzer. Picarro, Inc., White Paper.

Useful Part Numbers

| LI-COR Part Number | Description |
|--------------------|---|
| 8150-250 | Bev-a-line tubing (15m roll) |
| 300-07385 | ¼" Quick-connect "T" fitting |
| 300-03367 | ¼" Quick-connect "Y" fitting |
| 300-03123 | ¼" Quick-connect straight union |
| 300-07124 | Male stainless steel quick-connect (connects to LI-8100A AIR IN) |
| 300-07125 | Female stainless steel quick-connect (connects to LI-8100A AIR OUT) |
| 294-03334 | 0-2.5 LPM flow meter (rotometer) |
| 300-08118 | 1/8" NPT to ¼" Quick-connect right angle fitting (two used with rotometer) |
| 392-08577 | Auxiliary sensor input cable for 8100-104 or 8100-104C chambers |
| 392-07955 | Turck to bare leads cable, 2 m long |
| 314-03430 | Male DB-9 connector with shielded housing (used to access Ultra-Portable GGA's analog outputs) |
| 9981-188 | Pre-assembled Turck to DB-9 cable for connecting the Ultra-Portable GGA to the LI-8150. |
| 9981-189 | Pre-assembled hose assembly for plumbing additional analyzers in parallel to the LI-8100A subsampling loop. |



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