Soil CO_2 Flux Measurements:

Comparisons Between the LI-COR LI-6400 and LI-8100

Madsen, R. A., Demetriades-Shah, T. H., Garcia, R. L., and McDermitt, D. K.
LI-COR Biosciences, P.O. Box 4425, Lincoln, NE 68504

Introduction

The basic design features of LI-COR soil CO_2 flux chambers were first published by Norman et. al., (1992), and the various factors known to influence the measurement of ground CO_2 flux were summarized in LI-COR Application Note #124 and Welles, et. al., (2001). One of these factors is the concentration of CO_2 in the chamber head space relative to the ambient atmospheric CO_2 concentration. CO_2 diffuses out of the soil in response to the concentration gradient between the soil pores and the chamber head space. If the chamber CO_2 concentration is allowed to rise above the ambient CO_2 concentration, then the CO_2 flux is suppressed to a level below the natural undisturbed value. For this reason, soil flux measurements made with the LI-6400 Portable Photosynthesis System (used with the 6400-09 Soil CO_2 Flux Chamber) are carried out near the ambient CO_2 concentration. This is equally important for measurements with the LI-8100 Automated Soil CO_2 Flux System, but we use a different approach to overcome it. In this application note, we outline the theory underlying the two systems and compare results obtained using them.

The protocol for determining soil CO_2 flux with the LI-6400 is to first lay the chamber on its side on top of the soil and measure the ambient atmospheric CO_2 concentration. The chamber is then placed on a soil collar and the chamber CO_2 concentration is scrubbed to a level just below the ambient atmospheric concentration. When the scrubber is turned off, CO_2 flux from the soil causes the chamber CO_2 concentration to rise until it reaches a set point that is just above the ambient atmospheric concentration, completing the measurement cycle. As the chamber CO_2 concentration rises, rates of change ($\partial C_c/\partial t$) are calculated every 2.5 seconds on about 10 points from the previous 7.5 seconds using linear regression. This produces a sequence of rates from which corresponding short-interval CO_2 fluxes are computed. The final estimate of soil CO_2 flux is calculated by performing a linear regression of the short-interval fluxes against the average chamber CO_2 concentration computed for each time interval, and using the slope and intercept of the regression to obtain the flux at the ambient CO_2 concentration. More details are presented on page 3-4 of the 6400-09 Soil CO_2 Flux Chamber Manual (2003).

The LI-6400 is designed for survey measurements, so using chemicals to scrub CO_2 works fine; however, the LI-8100 Automated Soil CO_2 Flux System is designed for long-term unattended operation where the use of chemicals is undesirable. Eliminating chemicals to scrub CO_2 has made it necessary to change the procedure for estimating the soil CO_2 flux rate at ambient CO_2 concentration. At the start of a measurement, the LI-8100 chamber is held open above the soil collar and the system measures the ambient CO_2 concentration ($C_c(0)$). When the chamber closes on the soil collar, the CO_2 concentration in the chamber ($C_c(t)$) begins to rise. Ignoring the dilution effect of water vapor, the rate of change in chamber CO_2 concentration with time ($\partial C_c/\partial t$) is given by:

$$\frac{\partial C_c(t)}{\partial t} = A\left(C_s - C_c(t)\right) \quad (1)$$

where C_s is the CO_2 concentration (µmol/mol) in the soil surface layers and A (s^{-1}) is a rate constant that is proportional to the CO_2 conductance at the soil surface and the surface-to-volume ratio of the chamber.

If A and C_s are constant, then integration with respect to time gives:

$$C_c(t) = C_s + \left(C_c(0) - C_s\right)e^{-At} \quad (2)$$

In the LI-8100 system, the chamber CO_2 concentration $C_c(t)$ versus time data are fitted with an exponential function of the form given in equation (2) yielding values for the parameters A and C_s. Soil CO_2 flux is then obtained by calculating the initial slope $\frac{\partial C_c(t)}{\partial t}$ from equation (1) at time zero when the chamber touches down and $C_c(0)$ = ambient. A complete description of the equations used in the LI-8100 system, including details of dilution corrections due to water vapor, is given in the LI-8100 Instruction Manual (2004).

The LI-8100 and LI-6400 methods both rely on the assumption that the CO_2 diffusion rate is proportional to the CO_2 concentration gradient between the soil surface layers and the chamber atmosphere. The gradient between the soil and chamber decreases as CO_2 diffuses into the chamber, which causes the rate of change $(\frac{\partial C_c(t)}{\partial t}$ to decline linearly with chamber CO_2 concentration in accordance with equation (1), while the chamber CO_2 concentration increases exponentially in accordance with equation (2). The fundamental difference between the analyses used in the two systems is the equation used to calculate the flux rate. The LI-6400 uses equation (1) and calculates the flux at ambient CO_2 concentration by linear regression of the short-interval fluxes against average CO_2 concentration for each short interval. The LI-8100 uses non-linear regression to fit equation (2), which is the integrated form of equation (1), to $C_c(t)$ versus time. They both rely on the same theory and assumptions, and therefore, we expect them to give similar results.

The scrub-down protocol of the LI-6400 has been employed by researchers over many years and has been tested many times. It has also been verified by comparisons to known flux rates in test-beds such as those described by Pumpanen et. al (2004), Britta and Lindroth (2003), and Martin, et. al (2004), and against micrometeorological measurements (Norman et. al, 1997), where fluxes were determined without disturbing the ambient conditions. The purpose of this application note is to validate soil CO_2 flux measurements made with the LI-8100 system by comparing them to results obtained with the LI-6400 system under similar conditions.

Materials and Methods

Comparison tests between the LI-6400 and the LI-8100 were performed using two different methods. In the first method, we tested the LI-6400 with 6400-09 chamber and the LI-8100 with 8100-102 chamber on the test fixture shown in Figure 1. The fixture consisted of a soil collar attached to a 0.85 Liter chamber that had a sealed cap on the bottom and a polyethylene membrane on the top that was permeable to CO_2. The lower portion of the fixture was flushed with pure CO_2 from a liquid CO_2 cylinder and sealed at atmospheric pressure, which provided a constant CO_2 flux rate over several hours. A total of 9 paired measurements with the LI-6400 and LI-8100 were performed in sequence (Table 1) over a period of about one hour in the laboratory at 25°C .

Figure 1. Test fixture with a collar similar to those used for soil CO_2 flux measurements, attached to a 0.85 liter chamber with a sealed bottom and a polyethylene membrane permeable to CO_2. The chamber was flushed with pure CO_2 from a liquid CO_2 cylinder and then sealed at ambient pressure. This arrangement produced a CO_2 flux rate that was constant for several hours.

The second set of tests was performed in a tropical greenhouse with a soil floor that had very high organic matter content and high CO_2 flux rates. One soil collar was placed on soil that was watered daily, and a second collar was placed on a location that had not been watered for about one week. Soil moisture levels were not measured. The CO_2 concentration in the greenhouse was variable as people walked in and out, so we set target concentrations with the LI-6400 system that covered a wide range of CO_2 concentrations. This allowed us to generate curves showing how the CO_2 flux rate varied with chamber CO_2 concentrations for the collars on similar soils that were relatively dry or relatively moist. On each collar, measurements were taken with the LI-8100 before and after the LI-6400 concentration series was completed. Both sets of data were taken under non-windy conditions between 10:00 a.m. and 2:00 p.m. on 11 March 2004. Temperature ranged from 29°C to 32°C.

Results

Table 1 shows the results of measurements made with the LI-6400 and LI-8100 on the test fixture shown in Figure 1. Using this method, we found no significant difference between rates measured with the two systems. That is consistent with the hypothesis that the calculation approaches are consistent between the two instruments, and that the other measured values, such as system volumes, temperatures and pressures, are accurate.

Table 1. LI-6400 and LI-8100 comparison runs on a test fixture with a constant CO_2 flux.

Instrument	Mean Flux ($\mu mol\ m^{-2}\ s^{-2}$)	SE	Significance (n=9)
LI-6400	4.53	0.025	p=0.13
LI-8100	4.46	0.039	ns*

* not significant

Figure 2 shows comparisons of measurements made on the soil floor of a tropical greenhouse under both dry (Figure 2a) and well-watered (Figure 2b) conditions. People walking in and out of the greenhouse caused the ambient CO_2 concentration to vary over a wide range. To compensate for this, we used the LI-6400 to measure CO_2 flux over a range of chamber CO_2 concentration set points, which produced a response curve showing how CO_2 varied with chamber CO_2 concentration. With the LI-8100, it is not possible to establish an arbitrary set point. Instead, the measurement is performed at the ambient concentration that holds when the chamber actually closes. The response curve generated by the LI-6400 allowed us to make valid comparison measurements even when the ambient concentration varied.

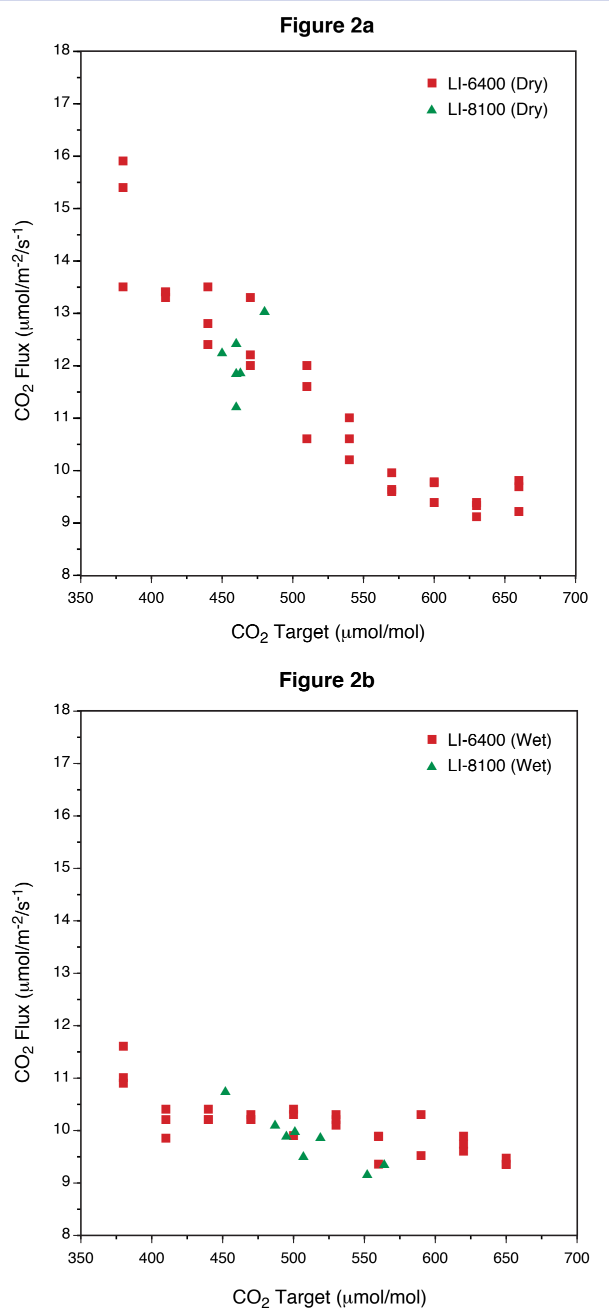

Figure 2. Flux of CO_2 from a highly fertile soil in a tropical greenhouse from which a) water was withheld for one week and b) was irrigated daily. This soil was not in pots, but formed a seed bed on the floor of the greenhouse. See text for details.

It is clear from Figure 2 that the LI-6400 and LI-8100 gave very similar rates when chamber concentrations were the same. This is as we expect, since both systems rest on the same theory and assumptions. The LI-6400 is well suited for detailed measurements and survey measurements, but is not suitable for continuous long-term measurements. By contrast, the LI-8100 was designed specifically for long-term, unattended measurements over weeks, or longer, as well as for survey measurements, but does not support generation of CO_2 response curves.

The data in Figure 2 provides other interesting insights into CO_2 flux from the soil. First, we note that the initial slope of the flux versus CO_2 concentration curve is much steeper for the drier soil in Figure 2a than for the moist soil in Figure 2b. Equation (1) shows that this slope should be negative and proportional to A, which in turn, is proportional to conductance. Thus, the steeper slope obtained from the drier soil suggests that the CO_2 conductance from the soil to the atmosphere is higher for the drier soil than for the moist soil, which is not surprising, since the air filled porosity will be greater in the drier soil.

Also, we observe in Figure 2a that there is a nearly linear relationship between flux and chamber CO_2 concentration from about 370 ppm up to about 550 ppm, but then the curve levels off. The nearly linear portion of the curve is consistent with the prediction of equation (1) ***and implies that C_s changed but little while the chamber CO_2 concentration was increased up to approximately 550 ppm.*** The leveling off that we observe suggests that by the time the higher chamber CO_2 concentrations were reached, C_s had increased significantly, evidently by trapping CO_2 in the soil under the chamber. Elevated C_s will cause a larger gradient and, therefore, a higher flux than would be predicted under the assumption of constant C_s, as we observe. We do not see such a dramatic leveling off in Figure 2b where conductance is lower. Evidently, the chamber atmosphere and soil atmosphere are not as tightly coupled in less porous soils. In any case, we see that the impact of the chamber on the measured flux is likely to differ with different soil porosities.

Finally, we note that the soils on which these collars were placed were both similar and highly fertile. The main difference was the moisture content. In this case, the maximum rate was higher for the drier soil (Figure 2a) than for the moist soil (Figure 2b); however, it may be unwise to conclude from these point-in-time measurements that CO_2 production was greater in the drier soil than in the moist soil. The reduced flux could also be due to reduced conductance, or to a combination of factors.

Conclusions

It is clear from the data in Table 1 and Figure 2 that the LI-6400 and LI-8100 gave substantially similar results under the conditions tested, thus validating results with the LI-8100. These results are encouraging, but they represent a limited number of trials under calm conditions. Other field comparisons have led to similar conclusions, although they were compromised somewhat by the effects of wind on measurements made by both systems. Since these results were obtained, we have designed a vent that substantially eliminates the effects of wind in the LI-8100. We will continue to perform field tests comparing results from the LI-8100 and the LI-6400 and report the results as they become available.

References

Britta, W. and Lindroth, A. (2003). A Calibration System for Soil Carbon Dioxide-Flux Measurement Chambers: Description and Application. *Soil Sci. Soc. Am. J.* 67:327-334.

LI-COR Biosciences, Application Note 124 (1998). Considerations for measuring ground CO_2 fluxes with chambers. LI-COR Biosciences, Lincoln, NE, USA 68504.

Martin, J. G., Bolstad, P. V., and Norman, J. M. (2004). A carbon dioxide flux generator for testing infrared gas analyzer-based soil respiration systems. *Soil Sci. Soc. Am. J.* 68:514-518.

Norman, J. M., Garcia, R. and Verma, S. B. (1992). Soil surface CO_2 fluxes and the carbon budget of a grassland. *J. Geophys. Res.* 97(D17):18845-18853.

Norman, J. M., Kucharik, C. J., Gower, S. T., Baldocchi, D. D., Crill, P. M., Rayment, M., Savage, K., and Striegl, R. G. (1997). A comparison of six methods for measuring soil-surface carbon dioxide fluxes. *J. Geophys. Res.* 102(D24):28771-28777.

Pumpanen, J., Kolari, P., Ilvesniemi, H., Minkkinen, K., Vesala, T,. Niinistö, S., Lohila, A., Larmola, T., Morero, M., Pihlatie, M., Janssens, I., Yuste, J. C., Grünzweig, J. M., Reth, S., Subke, J.-A., Savage, K., Kutsch, W., Østreng, G., Ziegler, W,. Anthoni, P., Lindroth, A., Hari, P. (2004). Comparison of different chamber techniques for measuring soil CO_2 flux. *Agric. and For. Meteorol.* 123:159-176.

Welles, J. M., Demetriades-Shah, T. H., and McDermitt, D. K. (2001). Considerations for measuring ground CO_2 fluxes with chambers. *Chem. Geol.* 177:3-13.

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