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Corrected calculations for soil and ecosystem measurements of CO₂ flux using the LI-COR 6200 portable photosynthesis system

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Abstract The LI-COR 6200 portable photosynthesis system (LI-6200) is commonly used in combination with large chambers to measure ecosystem level CO₂ flux in ecosystems with small-statured canopies (agriculture, tundra, grasslands, forest understory, etc.). Two problems with the methodology lead to artifactually low estimates of rates of net ecosystem assimilation of CO₂ (or overestimates of ecosystem respiration). The first is that accuracy of the equations used by the LI-6200 to calculate photosynthesis depends on a constant vapor pressure in the chamber. This assumption is commonly violated with large ecosystem chambers when evapotranspiration rates are high. We provide equations that correct this problem and permit recalculation of the LI-COR fluxes. The second problem is that of boundary layer formation under still conditions, such as at night. As high concentrations of CO₂ close to the ground surface become mixed by chamber fans, exceptionally high values of net ecosystem respiration result. Substantial mixing time is necessary for rates to stabilize. As ecologists attempt to understand how global change might affect whole-ecosystem carbon balance, both of these technical problems must be addressed to get accurate results.

Keywords Assimilation · Band broadening · Boundary layer · Carbon balance · Soil respiration

Introduction

Measurements of net CO₂ flux of whole ecosystems are particularly important in understanding ecosystem feedbacks to changing climate. For example, studies in arctic tundra have suggested that this ecosystem may have switched from a sink for atmospheric CO₂ to a source before approaching equilibrium (Oechel et al. 1993, 1995, 2000). Many such studies rely on large chambers to cover the entire canopy and use the LI-COR 6200 portable photosynthesis system (LI-6200) for measuring net and gross ecosystem CO₂ assimilation and ecosystem respiration (e.g., Hobbie and Chapin 1998; Vourlitis et al. 1993). Two problems with the common methodology employed skew results toward lower net ecosystem CO₂ uptake. In many cases, the errors are sufficient to change actual net positive ecosystem assimilation into calculated net losses of CO₂ from the ecosystem to the atmosphere. (In this paper we will use the convention of net ecosystem uptake of CO₂ to be a positive flux and net ecosystem loss to be a negative flux, in accordance with the way it is described in the LI-COR manuals.) While LI-COR has a new portable open photosynthesis system on the market (the LI-6400) in which one of these problems is rectified, many LI-6200s are still in use. Operators need to be aware of the issues raised here to avoid biasing their results.

The first problem arises from a methodological requirement embedded in the equation used by the LI-6200 to calculate CO₂ assimilation rates (*A*). The equation includes the evapotranspiration term (*E*) as part of its calculation of CO₂ movement out of the chamber. However, accurate calculation of *A* in the LI-COR equations depends critically on keeping water vapor pressure (*e*) constant within the chamber by balancing any evapotranspiration with adjustable air flow through a magnesium perchlorate desiccant. Researchers investigating ecosystem-level fluxes frequently cannot achieve this balance; the relatively low flow rates through the desiccant, even at full flow (1–1.5 l min⁻¹), are insufficient to counteract the large amount of water vapor produced under large

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chambers (surface areas of 300–10,000 cm² with total volumes of 10–400 l). The requirement that e be constant cannot be met, and significant increases in chamber water vapor pressure over the course of the measurement ($de/dt \gg 0$) result in calculated values of net assimilation that are lower than actual fluxes. If gross photosynthesis just balances ecosystem respiration, and whole ecosystem CO₂ gain is only slightly positive (0–2 μmol CO₂ m⁻² s⁻¹), this effect can be sufficient to lead to the appearance of a net loss of CO₂ from the ecosystem to the atmosphere. The magnitude of the discrepancy between fluxes calculated by the LI-COR equations and alternative equations, outlined here, depends on rates of de/dt , chamber volume:surface area ratios, and the fraction of the air flow going through the desiccant.

The second problem occurs under still-air conditions, as at night, when a boundary layer with high CO₂ concentrations can form near the ground surface. In this case, when a chamber is placed over the ground and connected in a closed loop to the LI-6200, mixing by chamber fans of the high-CO₂ air close to the ground with lower CO₂ air higher up in the chamber can lead to the appearance of exceptionally high ecosystem respiration rates. These initial high rates are artifactual. If averaged with daytime fluxes over the course of a diel measurement cycle, these high respiration rates again bias results toward lower net ecosystem CO₂ assimilation. This paper describes these problems and their solutions (see also LI-COR Inc. 2001).

Assumptions of the CO₂ flux calculations

LI-COR equations

The LI-6200 uses a three-part equation for calculating CO₂ assimilation. We will refer to these three terms as A1, A2 and A3 in the discussion below. Equations from the LI-COR manual will be denoted by “L#”, where “#” is the equation number from the manual (LI-COR Inc. 1990). Other equations will be denoted by letters. See Appendix I for definitions of symbols.

$$A = \begin{matrix} A1 & A2 & A3 \\ A = [F_d * e * C / (100 * S * P)] - \{ [P * G * V_c / (8.314 * (T_a + 273) * S)] * dc/dt \} - [CEG] \end{matrix} \quad (\mu\text{mol m}^{-2} \text{s}^{-1})$$

Equation L 1.34 (above) is a combination of closed and compensating equations for CO₂ flux, where the first term (A1) relates to the flow of CO₂ into the chamber, the second (A2) to the change in CO₂ concentration (dc/dt) within the chamber and the third term (A3) to the flow of CO₂ out of the chamber. Such a combination of closed and compensating equations is also used by the LI-6200 for the water balance equation to calculate transpiration, because any flow through the desiccant removes water from the system. For CO₂, however, the system is essentially closed and the dc/dt term (A2) is presumed to predominate under normal conditions of use, which are defined as $de/dt=0$ (LI-COR Inc. 1990, p 1-4). Though users can often keep vapor pressure con-

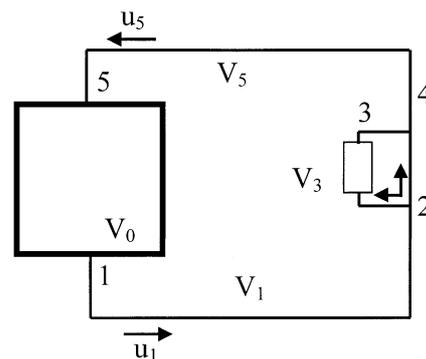


Fig. 1 Schematic of the LI-6200 chamber and IRGA (redrawn from the LI-6200 Technical Reference (LI-COR Inc. 1990). V_0 is volume of the chamber, V_1 is the volume of the lines leading to the desiccant, V_3 is the volume of the desiccant, and V_5 is the volume of the lines leading from the desiccant to the chamber. Relative humidity and temperature are measured in the chamber. Air leaving the chamber, at location 1 at a flow rate of u_1 , is assumed to have the same properties as air in the chamber (LI-COR Inc. 1990). Air entering the chamber at location 5, at a flow rate of u_5 , differs in water vapor pressure from air leaving the chamber, depending on what fraction of the flow goes through the desiccant at location 2. Air entering and leaving may also differ if vapor pressure in the chamber is changing because of the time it takes for the air leaving the chamber to travel through the IRGA and back to the chamber. Flow rate is measured at location 3; CO₂ concentration is measured at location 4

stant in smaller leaf chambers, it is often impossible to keep vapor pressure constant in the large chambers used for ecosystem measurements. According to the LI-6200 manual (LI-COR Inc. 1990, p 1-6), the flow terms serve mainly to account for changes in CO₂ concentration as a result of transpiration during the time it takes for a parcel of air to travel from the chamber to the infrared gas analyzer (IRGA) and back again. When the change in water vapor pressure in the chamber is large, however, the influence of the evapotranspiration term, E , on A3 can dominate the calculation of CO₂ assimilation, leading to inaccuracy of the CO₂ flux measurement. Significant discrepancies in net ecosystem CO₂ balance result where chambers are large and it is not possible to zero de/dt .

The crux of the problem

The problems with the original LI-6200 calculations arise from an incorrect calculation of the amount of CO₂ leaving the chamber and going to the IRGA relative to the amount re-entering the chamber from the IRGA. In this section, we describe how that incorrect flow calculation leads to discrepancies with alternative methods of flow calculation.

The transpiration term, E , enters the photosynthesis equation in term A3 as a way to estimate how much CO₂ is leaving the chamber. This comes from the assumption that the air flow out of the chamber (u_1 , mol s⁻¹) is equal

to the flow in (u_5 , mol s⁻¹) plus the amount of water produced per second by transpiration (Fig. 1):

$$u_1 = u_5 + sE$$

where s is the surface area in m² and E is the transpiration rate (mol H₂O m⁻² s⁻¹).

This equation (L 1.2) is correct only when the water vapor removed by the desiccant balances the water vapor produced by evapotranspiration (i.e., $de/dt=0$). Translated into LI-COR notation, Ball (1987) and Field et al. (1989) give the equation for the increase in flow going out of a chamber due to inputs of gas (e.g. water vapor) into the chamber as

$$u_1 = u_5(1 - w_5)/(1 - w_1) \quad (a)$$

where, u_1 = flow rate (mol s⁻¹) out of the chamber, u_5 = flow rate (mol s⁻¹) into the chamber, w_1 = mole fraction of water vapor (mol H₂O mol⁻¹ total gas) leaving the chamber, w_5 = mole fraction of water vapor entering the chamber.

This is equivalent to $u_1 = u_5/(1 - fw_1)$, as derived in LI-COR Inc. (2001). For convenience, we will refer to Eq. (a) as the Ball/Field equation in the rest of this paper.

When de/dt equals zero

If $de/dt=0$, then the LI-COR and Ball/Field methods reduce to the following (see Appendix II):

$$u_{1L} = F_x(1 - w_1 + f * w_1) / [10^6 * (1 - w_1)] \quad (b)$$

$$u_{1B} = F_x/10^6(1 - fw_1) \quad (c)$$

where $F_x/10^6$ is the measured maximum air flow in mol s⁻¹ and f is the fraction of the flow through the desiccant.

If, in addition, $f=0$, then the LI-COR and Ball/Field methods are the same: $u_1 = u_5 = F_x/10^6$. This makes sense: with no changes in vapor pressure and no flow through the desiccant, the flow out of the chamber equals the flow in. (Because concentrations of CO₂ are so low compared with water vapor, changes in CO₂ concentration can be ignored for flow calculations). If all the flow goes through the desiccant and $f=1$, then again the LI-COR and Ball/Field methods are equivalent: $u_1 = F_x/[10^6(1 - w_1)]$. With $f=1$, dry air is entering the chamber so the flow out is greater than the flow in in proportion to the water vapor mole fraction in the chamber. Under common conditions when P (atmospheric pressure) = 1,013 mb, T_a (air temperature) = 20°C, and relative humidity = 75%, $w_1=0.017$, so u_1 is greater than u_5 by about 1.7%. Even at 40°C and 100% humidity, $w_1=0.072$, leading to only about a 7% increase of u_1 over u_5 under these extreme conditions.

When de/dt is greater than zero

When de/dt does not equal 0, the calculated flow out by the LI-6200 (u_{1L}) and Ball/Field (u_{1B}) methods give different results (see Appendix II for derivations).

If $f=0$,

$$u_{1L} = F_x/10^6 + (K_{abs} * V_t * de/dt) / [R * T_K * (1 - w_1)] \quad (d)$$

$$u_{1B} = F_x * (1 - w_1 + \Delta w) / [10^6 * (1 - w_1)] \quad (e)$$

If $f=1$,

$$u_{1L} = F_x / [10^6 * (1 - w_1)] + (K_{abs} * V_0 * de/dt) / [R * T_K * (1 - w_1)] \quad (f)$$

$$u_{1B} = F_x / [10^6 * (1 - w_1)] \quad (g)$$

where K_{abs} is a constant (usually 1.1–1.5) used by the LI-6200 to estimate water adsorption by the chamber and lines, V_t and V_0 are total volume and chamber volume, respectively, R (universal gas constant) = 8.314×10⁴ mb ml mol⁻¹ K⁻¹, and T_K (degrees Kelvin) = $T_a + 273$ (see Appendices I and II).

The change in the mole fraction of water vapor in the chamber (Δw) is included in u_{1B} because of de/dt during the time it takes a parcel of air to travel from the chamber, through the IRGA and back to the chamber. This correction is necessary because the relative humidity sensor is in the chamber but the flow measurement occurs at the desiccant before air re-enters the chamber (Fig. 1; Appendix II). Here the Ball/Field calculation predicts that, with no flow through the desiccant, no water vapor is removed from the system, and the flow out of the chamber is greater than the flow in only by the increase in water vapor that has occurred since the inflowing air left the chamber several seconds earlier (Appendix II). Even at high values of de/dt (e.g., 0.3 mb s⁻¹), Δw is quite small: approximately 0.002 mol water mol⁻¹ air (at $T_a=20^\circ\text{C}$, $P=1013$ mb, and $F_x=1,200$ μmol s⁻¹) (Appendix II). So if $f=0$, and relative humidity = 75% at 20°C, the increase in flow out of the chamber relative to flow in is only about 2%. If $f=1$ (all flow through the desiccant), the Ball/Field method indicates that the flow out of the chamber is independent of de/dt . In contrast, the results from the LI-COR calculations suggest that the flow out of the chamber is greater than the flow in by values that are roughly proportional to de/dt and the volume of the chamber. When both are large (e.g., $de/dt=0.3$ mb s⁻¹, $V_0=100,000$ ml), the deviation from the true flux out can be greater than 100%, and LI-COR equation 1.34 overestimates the flux of CO₂ leaving the chamber relative to the flux entering. Since the chamber/IRGA system is essentially closed with respect to CO₂, there should be almost no difference in the total moles of CO₂ exiting and entering the chamber.

The magnitude of the problem

Discrepancies between the original LI-6200 calculations (A_1) and corrected calculations depend on three factors: rates of change in vapor pressure (de/dt), chamber volume to surface area ratio ($V:S$), and the fraction of flow through the desiccant (f) (see also LI-COR Inc. 2001). The greatest discrepancies occur when de/dt is high, when chamber $V:S$ is high, and when $f=1$.

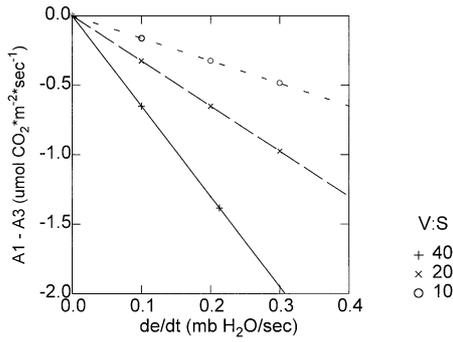


Fig. 2 Difference in CO₂ inflow (A1) and outflow (A3) terms as a function of de/dt and chamber volume:surface area ratio ($V:S$) using LI-COR equation 1.34. Negative flux means net CO₂ loss from ecosystem to atmosphere. Term A2, the calculated flux resulting from a change in CO₂ concentration within the chamber, is set at zero. A1–A3 is therefore the net CO₂ flux recorded by the LI-6200 even in the absence of any change in CO₂ concentration. Parameters used in the calculations: P (air pressure) = 1,013 mb; V_g (IRGA volume) = 154 ml; F_x (maximum flow) = 1,200 $\mu\text{mol s}^{-1}$; $K_{\text{abs}} = 1.1$; measurement time = 21.5 s; T_a (air temperature) = 20°C; C (average ambient CO₂ concentration) = 360 $\mu\text{l l}^{-1}$; e (average ambient water vapor pressure) = 20 mb; dc/dt (change in CO₂ concentration in the chamber) = 0 $\mu\text{l l}^{-1} \text{s}^{-1}$; S (chamber base surface area) = 1,600 cm²

The problem increases as a linear function of both de/dt and $V:S$. As either de/dt or $V:S$ doubles, so does the discrepancy between A1, the flow of CO₂ into the chamber, and A3, the flow of CO₂ out of the chamber (Fig. 2). In most soil or ecosystem measurements, the surface area is the basal area of the chamber, so chamber height is equivalent to $V:S$. Total chamber volume is not the issue; whether a chamber is 1 m×1 m or 0.2 m×0.2 m does not matter, but in either case, as chamber height doubles, A1–A3 doubles (for a given value of de/dt). The difference is attributable to the effects of the calculated value of E in equation L 1.16 (Appendix I) on the calculation of A3, the CO₂ flux out of the chamber. In equation L 1.16, the chamber volume (or total volume, depending on f) is divided by S , so for any given volume, the same de/dt coming from a smaller surface area means greater E . Under standard conditions, for a chamber height of 40 cm, and $de/dt=0.10 \text{ mb s}^{-1}$, the resulting calculated flux is approximately $-0.66 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$. Any increase in either de/dt or $V:S$ leads to a proportional increase in calculated flux (Fig. 2). In actual measurements, de/dt depends on $V:S$, because with lower $V:S$, the more rapid will be the build-up of water vapor in the chamber. In this sense, the two parameters can offset each other. It is worth noting the effects of $V:S$ on flux calculations, however, to alert researchers to potential problems with past data. Where the dc/dt term A2 is small (e.g., gross photosynthesis just balances ecosystem respiration), the difference between A1 and A3 can dominate the net photosynthesis calculation. At higher values of de/dt and chamber height, a large A3 term can lead to the appearance of a net negative flux (loss of CO₂ from ecosystem to atmosphere), even when the change in CO₂ concentration in the chamber indicates net ecosystem CO₂ uptake.

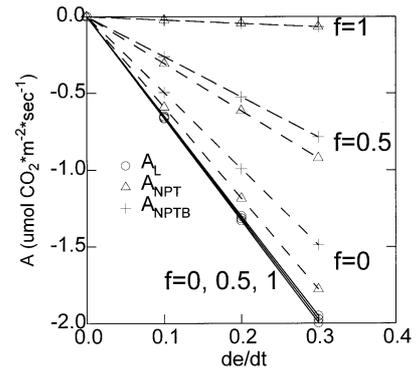


Fig. 3 The effect of varying f (the fraction of the flow through the desiccant) and de/dt (mb H₂O s⁻¹) on the correspondence between calculated values of assimilation using LI-COR equation 1.34 (“A_L”, solid lines) and our alternative, Eq. 13 (“A_{NPTB}”, dashed lines). Values are also shown for our alternative equation without the band-broadening correction (“A_{NPT}”, dashed lines). Parameters for calculations are the same as for Figure 2, except chamber height ($V:S$) is set at 40 cm. A_L values for different levels of f all lie quite close together

Any solution to the problem of violating the assumptions of the LI-6200 equations must account for changes in water vapor pressure for two reasons: (1) its effects on measurement of CO₂ in the LI-6200 IRGA and (2) its effect on pressure within the chamber. The LI-6200 has no band broadening or vapor pressure correction within the IRGA (as does the LI-6262, for example) (LI-COR Inc. 1996). Therefore, the measured concentration of CO₂ will change because of changes in water vapor mole fraction, whether or not any CO₂ is produced or consumed by the ecosystem being measured. At high rates of evapotranspiration, the changes in pressure caused by water vapor can also lead to significant effects on calculations of CO₂ flux, particularly if the chamber is well sealed to the ground and not vented to equilibrate pressure (Norman 1992). Therefore, ignoring relative humidity and water vapor during measurements or calculations is not a good solution.

Because of the effects of water vapor on CO₂ flux estimates, the fraction of the flow through the desiccant (f) can have a large effect on results. If de/dt is positive, the LI-6200 equations calculate a net release of CO₂ from ecosystem to atmosphere, even in the absence of changing CO₂ concentration in the chamber ($dc/dt=0$), for the reasons outlined previously. In this situation, f has only a small effect on the calculation of assimilation by the LI-6200 (A_L) (about 2% as f varies from 0 to 1) (Fig. 3, solid lines). In our alternative method of calculation of net photosynthesis (abbreviated A_{NPTB}, outlined in the next section), f necessarily corrects CO₂ concentration as measured at the IRGA for dilution by water vapor (see Appendix III).

If $f=0$, $de/dt>0$, and $dc/dt=0$, the A_{NPTB} equation calculates a net negative flux because if CO₂ concentration as measured at the IRGA is not changing, despite the increasing mole fraction of water vapor, then the ecosys-

tem must be producing CO_2 to keep $dc/dt=0$ in the face of the increasing water vapor concentration. In this situation, the original LI-6200 equations, corrected LI-6200 equations (LI-COR Inc. 2001), and our alternative calculations without any band-broadening correction give similar results (Fig. 3). At $f=0$, however, the band-broadening correction is maximal, with greatest influence at high values of de/dt . Incorporation of the band-broadening correction reduces the calculated efflux from the ecosystem (Fig. 3, A_{NPT} vs A_{NPTB}).

On the other hand, when $f=1$, water vapor is removed before CO_2 concentration is measured at the IRGA. Results are only minimally affected by changing water vapor concentration due to changes in total pressure in the system, and there is no need for band-broadening corrections. If $dc/dt=0$, as assumed in Fig. 3, the A_{NPTB} equation (and the corrected LI-COR calculations; LI-COR Inc. 2001; data not shown) indicate close to zero net flux, as expected (Fig. 3). With $f=1$, however, we see the greatest discrepancy with the original LI-COR equations (Fig. 3, solid lines).

Solutions

Operational recommendations

Fraction of flow through the desiccant

If measurements have not yet been made, LI-COR Inc. (2001) recommends keeping $f=0$ to avoid the calculation problems entirely. Under these conditions the original LI-COR equations and more recent alternatives [see below and LI-COR Inc. (2001)] give similar results (Fig. 3). In practice, however, two problems can keep the $f=0$ solution from being effective. First, keeping $f=0$ and allowing unrestricted increase in vapor pressure increases the risk of condensation on chamber walls and tubing. Condensation in the chamber can significantly affect light levels reaching the plants and condensation in the tubing can absorb CO_2 . Second, at $f=0$, a band-broadening correction has its greatest effect and must still be applied if $de/dt > 0$ (Burch et al. 1962; LI-COR Inc. 1999) (Fig. 3). LI-COR Inc. (2001) does not include this correction.

Several operational possibilities exist. First, if using the LI-6200 in conditions where condensation is not a problem and de/dt is minimal, then setting $f=0$ is a reasonable alternative. Of course, when de/dt is minimal, the original LI-COR equations work anyway. If de/dt is not minimal with $f=0$, at least a band-broadening correction will be necessary. Second, if flow through the desiccant can minimize de/dt , then using $f=1$ could be effective, especially since this obviates the need for a band-broadening correction. If $f=1$ and de/dt is not very low, then recalculation will be necessary, either by the revised LI-6200 equations (LI-COR Inc. 2001), or by the alternatives we present below.

Chamber dimensions

We emphasize the effects of chamber height on calculation deviations to alert researchers to potential problems with past data. If results indicate high de/dt and the chamber used was tall, the resulting calculations will be more biased than for a shorter chamber at the same de/dt , and researchers will likely need to recalculate fluxes. Because increased V:S ratios lead to greater discrepancies between the original and corrected LI-6200 calculations, it is tempting to suggest using a relatively low chamber for future measurements. However, there are important tradeoffs in chamber design that caution against that simplistic recommendation. First, chambers for measuring ecosystem carbon balance clearly need to be tall enough to fit over whatever vegetation is relevant. Second, chamber volume and de/dt are linked: smaller chamber volumes (i.e., lower chamber heights for a given surface area) will lead to a more rapid build-up of water vapor pressure. Third, diffusion models indicate that build-up of CO_2 or other trace gases in the headspace of static chambers can perturb the concentration gradients that in part determine flux rates from soils (Healy et al. 1996; Hutchinson and Mosier 1981; Hutchinson et al. 2000). Taller chambers help reduce this effect. A balance must be struck between low enough V:S ratios to allow measurable changes in CO_2 (or other trace gas) concentration under the conditions of measurement (e.g., soil flux rates, measurement period) and minimal disturbance to ambient conditions such as soil-atmosphere concentration gradients. Chamber dimensions should be a function of these constraints, since we recommend recalculation of flux rates under most conditions.

Calculations solutions

Problems caused by the LI-COR calculation of photosynthesis will likely require recalculation whenever de/dt is substantial ($\sim 0.05 \text{ mb s}^{-1}$, though perhaps less depending on other parameters). If $f=0$, the only correction necessary is for band broadening. If $f > 0$, then additional corrections are also warranted. There are two options for recalculation. LI-COR Inc. (2001) presents revised equations that can be used to correct previous measurements with relatively minimal data requirements (f , average CO_2 concentration, de/dt , air temperature, and chamber volume and surface area), as well as equations that can be used to directly calculate CO_2 fluxes with some additional parameters. Their approach does not include band-broadening corrections, however, and so is most appropriate when $f=1$ (provided, of course, that the desiccant is fresh and indeed removing all water vapor).

Below, we present a second option for recalculation, in which we model the entire chamber/IRGA system as a closed system with respect to CO_2 , based on the equation of Field et al. (1989). This approach has the advantages of: (1) simplicity, because it starts with the basic premises of the ideal gas law and conservation of mass in a

closed system, and (2) inclusion of band-broadening corrections. Without the band-broadening correction, the results are essentially the same as the LI-COR revised equations (LI-COR Inc. 2001), though our equations are in finite difference form and theirs are in continuous differential form. We describe our approach below and in Appendix III, and abbreviate it as A_{NPTB} : Assimilation corrected for number of moles (N , i.e., dilution by water vapor), pressure changes (P), temperature changes (T), and band-broadening (B). These equations use data stored by the LI-6200 in each page of output and can, therefore, be used in a spreadsheet in combination with a downloaded and formatted LI-COR file after measurements have been done. These equations reproduce the original LI-COR calculations under conditions where de/dt is minimal, but provide a more accurate estimate of CO_2 flux as de/dt increases (Fig. 3).

For a closed system with $de/dt > 0$, the equations must account for several changes: (1) changes in CO_2 concentration because of changes in water vapor pressure resulting from both evapotranspiration and flow through the desiccant; (2) changes in pressure of the total system due to the same; (3) band broadening in the IRGA due to the same; and (4) changes in air temperature. The equations developed here correct for all of these factors. It is important to note that many chambers for both soil and ecosystem measurements are vented to prevent build-up of pressure (Norman 1992). In other cases, such as placement of unvented chambers on porous surfaces (e.g., relatively dry moss mats), it may be difficult to determine the degree to which the chamber is tightly sealed versus leaky and able to equilibrate pressure. As it turns out, the same equations are applicable independent of the degree of leakiness (within reason), if one makes the assumption that the amount of CO_2 lost from the system through pressure equilibration in a vented system is proportional to the change in water vapor pressure times the average CO_2 concentration. Similarly, the revised LI-6200 equations are applicable across the normal range of leakiness as well (LI-COR Inc. 2001). This is not to say that operators shouldn't be concerned about tightly sealing the chamber to the ground or chamber base, because other disruptions (e.g., wind-blown mixing or high CO_2 air from breath) could also adversely affect the accuracy of measurements.

While pressure and temperature changes are generally small, they can significantly affect flux calculations when dc/dt is low (low CO_2 flux rates). If temperature increases in the chamber by $1.5^\circ C$ during the course of a 20-s measurement, the ideal gas law (and the A_{NPTB} equation) indicates a net flux of about $1 \mu mol CO_2 m^{-2} s^{-1}$ because of the effect of temperature on the density of air. Small changes in pressure (5–6 mb over the course of a 20-s measurement for a relatively large de/dt of $0.3 mb s^{-1}$) can have equally large effects on flux calculations. If the chamber is totally sealed, $de/dt > 0$, and no flow is going through the desiccant, the pressure must increase because the total amount of gas in the system has increased by the amount of water vapor. If $dc/dt = 0$ also, then there must be additional moles of CO_2 to keep

that mole fraction equal. Our corrected calculations show net respiration, as is appropriate.

Part of the reason for the surprisingly significant effects of relatively small changes in temperature and pressure on the calculated values of A_{NPT} is the fact that dc/dt values are often quite low, on the order of $0-5 \mu l l^{-1}$ for a 20-s measurement. This means that a change on the order of $1/300$ in temperature or pressure ($1 K/300 K$ or $6 mb/1,000 mb$) leads to a corresponding calculated change in CO_2 concentration of about $1 \mu l l^{-1}$, very significant for the range of dc/dt in many ecosystems (Chris Field, personal communication). A smaller chamber height (volume:surface area ratio) would help with the temperature effect, since larger values of dc/dt would result; however, water vapor pressure would presumably increase more quickly in a smaller volume as well, and greater perturbations to soil/atmosphere concentration gradients are likely (Healy et al. 1996).

Another issue to consider when using the A_{NPTB} equation is the proportion of the flow that goes through the desiccant, as discussed above. If moisture conditions warrant that a substantial fraction of the flow needs to go through the desiccant, the desiccant can eventually clog and reduce total flow through the system. Because F_x is an entered parameter, not a measured one, this could make it appear as though f , the fraction of flow through the desiccant, is decreasing, when in fact it is always 1. To make accurate measurements in this way, the fraction of the flow through the desiccant can be set to 1 permanently by going to Function E3, scrolling to "Channel 22 – fract" (fraction of flow through desiccant), hitting return at the "label" prompt and entering "C1" at the "Code" prompt. This makes "fract" a constant (1) instead of dividing F_d by F_x (Code = 16A565) (Jon Welles, LI-COR Technical Support, personal communication). If this approach is used, care must be taken to ensure that the desiccant stays fresh enough to adequately scrub out all water vapor; if flows drop substantially because of wet desiccant, then the data should be questioned.

The A_{NPTB} equations assume a linear increase in CO_2 concentrations within the chamber. However, such an assumption is not always valid. Measurements and modeling of static chamber fluxes indicate that build-up of trace gases within the chamber can lead to a non-linear (logarithmic) change in concentrations over time (Healy et al. 1996; Hutchinson and Mosier 1981; Hutchinson et al. 2000; Matthias et al. 1978). Nonlinearity can be minimized by larger chamber $V:S$ ratios and short measurement times, and can be tested by saving and plotting the individual CO_2 measurements from the LI-6200 versus time. If linearity is a problem, alternative calculation techniques may be warranted (e.g., Pedersen 2000; Pedersen et al. 2001). Before using these alternative calculations, the individual CO_2 measurements should first be corrected for the effects of changes in water vapor concentration (dilution, band-broadening), following the approach in Appendix III.

In summary, the A_{NPTB} equations provided here, in conjunction with knowledge about a few key parameters

affecting chamber performance, can be used to substantially increase the accuracy of soil or ecosystem flux measurements, even after measurements have already been taken. The corrections are large enough to affect the sign (net photosynthesis vs. net respiration) as well as the absolute magnitude of calculated fluxes under conditions that are commonly encountered in both soil and whole ecosystem measurements.

Boundary layer problems

At night, accumulation of CO₂ near the ground surface under conditions of low wind and low atmospheric mixing can result in high and unstable estimates of ecosystem respiration. As the boundary layer becomes mixed by chamber fans, pulses of high CO₂-air lead to very high ecosystem respiration rates as measured by the LI-6200. There may be additional pulses of high CO₂-air that have built up in the upper soil layers as a result of the high boundary layer CO₂ concentrations at the soil surface. The initially high rates of flux then decrease until the pulses of high CO₂-air have mixed throughout the chamber and soil CO₂ concentrations re-equilibrate with atmospheric CO₂ (Fig. 4).

When measuring ecosystem assimilation or respiration with the LI-6200, most researchers take multiple short observations within each measurement and average these observations to get an estimate of net CO₂ flux (LI-COR Inc. 1990; Vourlitis et al. 1993). For example, in our work in Alaskan tundra, we used an initial stabilization period with the chamber in place (about 1 min), followed by three 20-s observations. These observations were then averaged to get one estimate of net assimilation. In our work in interior Alaska, we used a stabilization period of up to 10 s, followed by a 75-s measurement period (though the first 15 s of the measurement period were often excluded from the individual flux calculations). Short stabilization and measurement times are preferable to avoid departures from ambient conditions (e.g., chamber heating or CO₂ drawdown or build-up). To obtain daily CO₂ budgets, measurements are often taken through the night as well as during the day, with methodology kept constant throughout – presumably good scientific practice. However, night-time measurements may require substantially longer equilibration times before rates stabilize, particularly when CO₂ gradients form within the plant canopy or litter layer under cool, still conditions. This phenomenon has been observed in eddy covariance measurements also, where flux rates are quite low throughout the night as CO₂ gathers in the boundary layer, then a burp of high-CO₂ air is released in the morning as atmospheric warming breaks up this layer. In these eddy flux measurements, instantaneous rates for soil CO₂ flux are not accurate and must be averaged over the entire night-time measurement period (Fan et al. 1995).

Two additional factors can exacerbate this flux pattern, particularly in an ecosystem with a porous surface

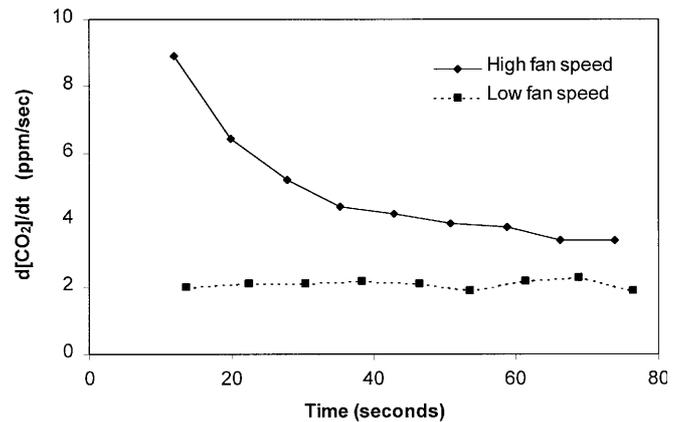


Fig. 4 Symptoms of a boundary layer mixing problem and the effect of fan speed on rate of change of CO₂ concentration in an ecosystem chamber measurement. Measurements were made in a feathermoss (*Pleurozium schreberi*) understory of a black spruce forest at 0700 hours under conditions of low surface wind speed that allow CO₂ buildup within the moss layer

organic mat, such as mosses. First, firm placement of the chamber, movement of the collar base, or foot traffic near the chamber during measurements will release CO₂ from the soil into the bottom of the chamber, resulting in a flux of CO₂ that can greatly exceed ambient values. Second, excessive fan speed within the chamber can increase near-surface winds substantially above ambient conditions, resulting in a scrubbing of CO₂ from porous organic surfaces (Kimball and Lemon 1971). Although mixing is necessary, researchers need to achieve a fan speed that balances relatively rapid equilibration times with the need to reduce artificial scrubbing of surface soil layers (Fig. 4). Some modelling studies show that atmospheric conditions within the chamber should match as closely as possible those conditions prior to deployment. This means that under conditions of low boundary conductance, mixing by fans should be reduced to a minimum or eliminated altogether, though fan speeds should be higher when winds cause turbulent mixing (Hutchinson et al. 2000). These precautions are important whether measurements are being made during the day or at night.

The symptoms of boundary layer and related mixing problems are fluxes that decrease continuously through the observations within a measurement, as well as through subsequent repeated measurements (Fig. 4). Only after several repeated measurement cycles might rates eventually stabilize at much lower values than originally recorded. The magnitude of this problem varies greatly with weather conditions and surface type, but decreases in respiration rates to less than half of the first measurement are not unusual. The problem is most pronounced in ecosystems with a porous surface layer (e.g., moss canopy or a surface organic layer) that traps high concentrations of CO₂ (Hutchinson et al. 2000; Kimball and Lemon 1971). There are several potential solutions to this problem, best used together: (1) reduce fan speed within the chamber so that CO₂ is not blown out of the plant canopy and surface litter; (2) place the chamber carefully and minimize foot

traffic around the chamber during measurements; (3) repeat measurements until the chamber air is well-mixed and flux rates stabilize. We recommend making 5–10 observations within each measurement and accepting only those observations where consecutive flux estimates show no upward or downward trend with time. If the chamber remains in place for extended periods while multiple measurements are made, it will be necessary to check for linearity of concentration changes, as discussed above (Calculations solutions). Unfortunately the problem of unstable fluxes is most pronounced at times when darkness and user fatigue makes patience less likely. Finally, during the data-analysis phase, it is important to remove any observations within a measurement where flux rates are not constant, i.e., where CO₂ concentration does not increase or decrease linearly with time.

Conclusions

Both of the problems with using the LI-6200 with large chambers for ecosystem measurements of CO₂ flux lead to underestimates of daily net carbon assimilation. While both only occur under certain environmental conditions (high rates of evapotranspiration for the calculation problem, still air or temperature inversions for the chamber-mixing problems), these conditions are common enough to occur frequently throughout a season-long research

project. In many cases, the errors are sufficient to lead to apparent net ecosystem loss of CO₂ to the atmosphere, either because of lower apparent photosynthesis rates or higher apparent respiration rates, even though net ecosystem assimilation may actually be positive. The recalculation solutions outlined here, or, under some conditions, the alternatives in the LI-COR technical reference (LI-COR Inc. 2001) provide a relatively easy method of correction for the assimilation equation problems for the LI-6200. The corrections can be applied even after measurements have been made. For the boundary layer problem, no post-measurement solution exists. Therefore, care and patience are critical, especially when making measurements under cool, still conditions. The extent to which such errors have influenced previously reported measurements is unknown, but researchers in the future should guard carefully against such biases.

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Appendix I. LI-COR equations

The LI-COR manual uses a combination of closed and compensating equations for CO₂, stating that the flow terms, unlike in the case for transpiration, should be relatively minor with respect to the dc/dt term. They serve mainly to account for the time lag for a parcel of air to travel from the chamber to the IRGA and back again. They also assume a constant value of ρ , the density of air, for simplicity. In the following discussion, equations from the LI-6200 manual (LI-COR Inc. 1990) will be denoted by "L#", where "#" is the equation number from the manual. Other equations will be denoted by letters. The mass balance equation for photosynthesis given by LI-COR (L 1.22) is as follows (see Figure 1):

$$-sA = V_0 * \rho * dc/dt + c_1 u_1 - c_5 u_5,$$

where s = surface area (m²), V_0 = chamber volume (ml), ρ = density of air [= $P/(T^*R)$], where P = pressure in mb, T = temperature in degrees Kelvin (K), and R = universal gas constant = 8.314×10^4 mb ml mol⁻¹ K⁻¹, $\rho \approx 4.16 \times 10^{-5}$ mol ml⁻¹ at atmospheric pressure and 20°C, dc/dt = change in CO₂ concentration [μ mol mol⁻¹s⁻¹], c_1 , c_5 = concentrations of CO₂ [μ mol mol⁻¹] leaving and entering the chamber, respectively, u_1 , u_5 = flow rates [mol s⁻¹] leaving and entering the chamber, respectively.

This converts to the following (equation L 1.34), using the parameters that the LI-6200 measures or has as inputs (see LI-COR manual for full derivation):

$$A = [F_d * e * C / (100 * S * P)] - \left[\frac{P * G * V_t}{(8.314 * (T_a + 273) * S)} \right] * dc/dt - [CEG] \quad (\mu\text{mol m}^{-2} \text{ s}^{-1})$$

where F_d = flow through desiccant [μ mol s⁻¹], e = water vapor pressure in the chamber [mb], C = [CO₂] in μ l l⁻¹ (same as μ mol mol⁻¹), S = leaf area (or ground area) in cm²; $S/10,000$ gives area in m² so that in the final equation, the 10^4 factor in R and the 10,000 divisor for S cancel out; P = atmospheric pressure [mb], $G = 1 - f w_1$, where $f = F_d / F_x$, i.e., the fraction of the flow through the desiccant; F_x = maximum flow rate through the desiccant in μ mol s⁻¹, and w_1 = mole fraction of water vapor leaving the chamber [mol H₂O mol⁻¹ air]; $w_1 = e/P$, V_t = total system volume [= chamber volume (V_0) plus IRGA volume (V_g)] [ml], dc/dt = rate of change of CO₂ concentration in μ l l⁻¹ s⁻¹, negative so that a decrease in [CO₂] (uptake from the atmosphere) constitutes positive net photosynthesis; $8.314 = R$, universal gas constant (8.314×10^4 mb ml mol⁻¹ K⁻¹), T_a = air temperature in °C ($K = 273.16 + T_a$), E = transpiration rate of leaf [mol H₂O m⁻² s⁻¹].

$$E = \left[F_d * e / (100 * P) + \left\{ K_{\text{abs}} / (8.314 * (273 + T_a)) \right\} * (V_t - V_g * F_d / F_x) \right] * de/dt / [S * (1 - e/P)]$$

(equation L 1.16), where K_{abs} = empirical constant accounting for water absorbed by the system, which LI-COR says should be in the realm of 1.1; de/dt = rate of change of water vapor pressure, mb s⁻¹.

Appendix II. Flow calculations using LI-COR method and Ball/Field method

LI-COR method

According to LI-COR, the flow out of the chamber (u_1) is equal to the flow in (u_5) plus the amount of water produced per second by transpiration (L 1.2):

$$u_1 = u_5 + sE$$

where s is the surface area in m^2 and E is the transpiration rate in $\text{mol H}_2\text{O m}^{-2} \text{s}^{-1}$. From equation L 1.2, where $u_5 = F_x * 10^{-6}$ (the factor of 10^{-6} is to bring units into mol s^{-1}), f (the fraction of the flow through the desiccant) = F_d/F_x , w is the mole fraction of water vapor: $w = e/P$, and u_{IL} stands for the flow out of the chamber by LI-COR calculations, then

$$u_{\text{IL}} = F_x * 10^{-6} + s[(F_d * e / (100 * P)) + (K_{\text{abs}} * (V_t - V_g * f) * de/dt) / (8.314 * (273 + T_a))] / [S * (1 - w_1)] \quad (1)$$

After canceling out the surface area terms, we get

$$u_{\text{IL}} = F_x * 10^{-6} + [(F_d * w_1 / 100) + (K_{\text{abs}} * (V_t - V_g * f) * de/dt) / (8.314 * (273 + T_a))] / [10^4 * (1 - w_1)] \quad (2)$$

Because the surface area, S , in the denominator of E is in cm^2 , canceling s (m^2) and S (cm^2) puts a factor of 10^4 in the denominator of the E term.

If $de/dt=0$, then Eq. 2 further reduces to

$$u_{\text{IL}} = F_x * 10^{-6} + [(F_d * w_1 / 100)] / [10^4 * (1 - w_1)] \quad (3)$$

$$u_{\text{IL}} = F_x (1 - w_1 + f * w_1) / [10^6 * (1 - w_1)] \quad (4)$$

If, in addition to $de/dt=0$, $f=0$ also, then $u_{\text{IL}}=u_5=F_x/10^6$. If all the flow goes through the desiccant, then $f=1$ and $u_{\text{IL}}=F_x/[10^6 (1-w_1)]$.

When de/dt does not equal 0, Eq. 2 rearranges to

$$u_{\text{IL}} = F_x (1 - w_1 + f * w_1) / [10^6 * (1 - w_1)] + [K_{\text{abs}} * (V_t - (f * V_g)) * de/dt] / [8.314 * 10^4 * (T_a + 273) * (1 - w_1)] \quad (5)$$

If $f=0$, and using $R=8.314 \times 10^4$ and $T_K=T_a+273$,

$$u_{\text{IL}} = F_x / 10^6 + (K_{\text{abs}} * V_t * de/dt) / [R * T_K * (1 - w_1)] \quad (6)$$

If $f=1$,

$$u_{\text{IL}} = F_x / [10^6 * (1 - w_1)] + (K_{\text{abs}} * V_0 * de/dt) / [R * T_K * (1 - w_1)] \quad (7)$$

Ball/Field method

$$u_{\text{IB}} = u_5 (1 - w_5) / (1 - w_1) \quad (8)$$

where u_1 = flow rate (mol s^{-1}) out of the chamber, u_5 = flow rate (mol s^{-1}) into the chamber, w_1 = mole fraction of water vapor leaving the chamber, ($\text{mol H}_2\text{O mol}^{-1}$ to-

tal gas); $w = e/P$, w_5 = mole fraction of water vapor entering the chamber.

Relative humidity is measured in the chamber and flow rate is measured after the desiccant (Fig. 1), so we know w_1 and u_5 . w_5 differs from w_1 at any given moment, depending on how much air flows through the desiccant and the extent to which vapor pressure is changing inside the chamber. Even with no flow through the desiccant, if vapor pressure is increasing in the chamber, then w_5 will be less than w_1 because the parcel of air entering the chamber left the chamber several seconds previously when w_1 was lower. So,

$$w_5 = (1 - f) (w_1 - \Delta w) / (1 - f * w_1) \quad (9)$$

where Δw is the change in the mole fraction of water vapor in the chamber because of changing water vapor pressure during the time it takes a parcel of air to travel from the chamber, through the IRGA and back to the chamber.

$$\Delta w = (de/dt * t_5) / P \quad (10)$$

where $t_5 = V_g \rho / F_x$, the time it takes for a parcel of air to pass through the IRGA from point 1 to point 5. F_x is the measured total maximum flow rate ($\mu\text{mol s}^{-1}$) through the IRGA, V_g is the volume of the IRGA (ml), and ρ is the density of air ($\rho \approx 4.16 \times 10^{-5} \text{ mol ml}^{-1}$ at atmospheric pressure and 20°C). If $F_x = 1,000 \mu\text{mol s}^{-1}$ and $V_g = 154 \text{ ml}$, t_5 is about 6.9 s at STP. Therefore, u_1 calculated by the Ball/Field method, will be

$$u_{\text{IB}} = F_x * (1 - w_1 + \Delta w - f * \Delta w) / [10^6 (1 - w_1) (1 - f * w_1)] \quad (11)$$

If $f=0$, $u_{\text{IB}} = F_x (1 - w_1 + \Delta w) / [10^6 (1 - w_1)]$.

If, in addition, $de/dt=0$, then $\Delta w=0$ and $u_{\text{IB}} = F_x / 10^6$.

If $f=1$, $u_{\text{IB}} = F_x / [10^6 (1 - w_1)]$, and is independent of Δw and de/dt .

Appendix III

Alternative calculations – modeling the LI-6200 as a closed system for CO_2

Field et al. (1989) give the basic equation for assimilation in a closed system (Eq. 11.31, p 248) as

$$A = [C_b (P_b / T_b) - C_f (P_f / T_f)] * V / [t * s * (P_v / T_v)] [\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}] \quad (12)$$

where C_b , $C_f = [\text{CO}_2]$ at beginning and end of measuring period, respectively [$\text{mol CO}_2 \text{ mol}^{-1} \text{ air}$], P_b , P_f = atmospheric pressure at beginning and end of measuring period, respectively [they use Pa, LI-6200 uses mb], T_b , T_f = temperature (K) at beginning and end of measuring period, respectively, V = volume of system, in moles of air, t = elapsed time, seconds, s = surface area, m^2 , P_v , T_v = pressure and temperature at time of measuring chamber volume.

We use this equation and the LI-6200 output for dc/dt , de/dt , e , T_a and CO_2 concentration to calculate actual

concentrations of CO₂ in the chamber at the beginning and end of the measurements (C_b and C_f , respectively, in Eq. 8). We add corrections to the flux calculation for temperature, pressure, and water vapor changes during the measurement. We refer to this as the A_{NPTB} equation – Assimilation corrected for moles (N), pressure (P), temperature (T), and band broadening (B).

In the equations below, the subscript meanings are as follows: o = value measured in, or calculated to be in, the chamber; i = value measured in or calculated to be in the IRGA; b = at the beginning of the measuring period; f = at the end of the measuring period. For example, e_{ob} = vapor pressure of air in the chamber at the beginning of the measurement, e_{if} = vapor pressure of air in IRGA at the end of the measurement.

The calculations assume some flow through the desiccant, which occurs before air reaches the IRGA in the LI-6200. Therefore, the first step is to calculate the vapor pressure and mole fractions of water at the IRGA (e_{ib} and w_{ib}) because e_{air} is calculated from relative humidity and air temperature in the chamber. This calculation assumes good mixing in the chamber and that the volume of air in the loop from the desiccant to the chamber is very small relative to the total system volume. We then calculate CO₂ concentration at the IRGA, depending on the average CO₂ concentration and the rate of change of CO₂. The CO₂ concentration at the IRGA is next corrected for band-broadening caused by water vapor in the air (Burch et al. 1962; LI-COR Inc. 1999). The LI-6200 does not automatically correct for this band broadening, and no correction is necessary if all flow goes through the desiccant. If $f < 1$, however, and if water vapor content changes through time, the band-broadening correction becomes important. Finally, from the corrected CO₂ concentration at the IRGA and the mole fractions of water at the IRGA and in the chamber, we calculate CO₂ concentration in the chamber. These calculations are done for the beginning and end of the measurement period.

Beginning

$$e_{ob} = e_{air} - (t/2 * de/dt)$$

$$w_{ob} = e_{ob}/P_b$$

$$w_{ib} = w_{ob} (1 - f)$$

$$f = F_d/F_x$$

$$C'_{ib} = [CO_2] - (t/2 * dc/dt)$$

$$C_{ib} = (1 + 0.5w_{ib}) * C'_{ib} * [1 - 0.5w_{ib}Y_c(C'_{ib})]$$

[band – broadening correction]

$$C_{ob} = C_{ib} * (1 + w_{ib}) / (1 + w_{ob})$$

$$T_b = T_a - (T_{air,range}/2)$$

For the band-broadening correction, C_{ib} is the corrected CO₂ concentration, C'_{ib} is the original measurement without the band-broadening correction, and the function $Y_c(C'_{ib})$ is defined as:

$$Y_c(C'_{ib}) = [a + b * (C'_{ib})^{1.5}] / [a + (C'_{ib})^{1.5}] + C'_{ib} * x$$

Here $a=6606.6$, $b=1.4306$, and $x=2.2464 \times 10^{-4}$. LI-COR notes that this equation is very consistent among IRGAs (LI-COR Inc. 1999). A similar set of corrections occurs for the final CO₂ concentration.

Final

$$e_{of} = e_{air} + (t/2 * de/dt)$$

$$w_{of} = e_{of}/P_f$$

$$P_f = P_b + (t * de/dt)$$

since the increase in H₂O is the only source of increased pressure;

$$w_{if} = w_{of} (1 - f)$$

$$C'_{if} = [CO_2] + (t/2 * dc/dt)$$

$$C_{if} = (1 + 0.5w_{if}) * C'_{if} * (1 - 0.5w_{if}Y_c(C'_{if}))$$

[band – broadening correction]

$$C_{of} = C_{if} * (1 + w_{if}) / (1 + w_{of})$$

$$T_f = T_a + (T_{air,range}/2)$$

So, if we correct net ecosystem assimilation for dilution, pressure, temperature, and band broadening all at once, we get the following (in $\mu\text{mol m}^{-2} \text{s}^{-1}$):

$$A_{NPTB} = - [C_{of} * P_f / (273.16 + T_f) - C_{ob} * P_b / (273.16 + T_b)] * V_i / (t * 8.314 * S) \quad (13)$$

This equation should hold for both tight and leaky chambers because losses of air, and therefore CO₂, through any chamber vent will be proportional to the average CO₂ concentration in the chamber and the change in pressure created by evapotranspiration.

Symbols:

- RH, T_a : relative humidity and temperature (°C) in the chamber, used by LI-COR to calculate e_{air}
- e_{air} : vapor pressure of air as given by LI-6200, which is the mean for the span of the measurement [mb]
- de/dt : change of e_{air} with time [mb s^{-1}]; calculated by the slope of e_{air} versus time by the LI-6200
- dc/dt : change in CO₂ concentration with time [$\mu\text{l l}^{-1} \text{s}^{-1}$]; calculated by the slope of [CO₂] vs time by the LI-6200
- t : time of measurement [s]
- e : vapor pressure of air [mb]
- P : atmospheric pressure [mb] as entered by the user into LI-6200 for a given site
- w : mole fraction of water [$\text{mol H}_2\text{O mol}^{-1}$ total gas]; $w=e/P$
- C : CO₂ concentration [$\mu\text{l l}^{-1} = \mu\text{mol mol}^{-1}$]
- T_a : air temperature (°C) as recorded by LI-COR, mean from duration of measurement
- $T_{air,range}$: difference between min and max T_a ; this equation assumes T_a is always increasing during the span of measurement
- V_i : total volume of the system, chamber (V_o) plus IRGA (V_g) [ml]
- S : surface area (or chamber base area) [cm^2]

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