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BIASES OF CHAMBER METHODS FOR MEASURING SOIL CO_2 EFFLUX DEMONSTRATED WITH A LABORATORY APPARATUS

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Investigators have historically measured soil CO_2 efflux as an indicator of soil microbial and root activity and more recently in calculations of carbon budgets. The most common methods estimate CO_2 efflux by placing a chamber over the soil surface and quantifying the amount of CO_2 entering the chamber per unit area of soil per unit time. Schlesinger (1977), Anderson (1982), Rolston (1986*a*), Raich and Nadelhoffer (1989), and Nakayama (1990) have reviewed various chamber methods. No single method is established as a standard (Anderson 1982, Nakayama 1990, Norman et al. 1992), partly because methods are not compared to known effluxes (Nakayama 1990). Past comparisons have only shown a method to be higher or lower than another method.

This study compared the responses of two commonly used chamber methods to known effluxes from the surface of a simulated soil. Our known effluxes are based on calculations using Fick's law of diffusion. The two methods we tested were a static-chamber method with soda lime as a CO_2 absorbent and a dynamic-chamber method consisting of an infrared gas analyzer in a closed air-circulation loop. Because the absorption rate of alkali materials used in static chambers is thought to be a source of bias (Freijer and Bouten 1991, Nakadai et al. 1993), we were also interested in how the soda-lime absorbent affected the headspace CO_2 concentration of the static chambers.

Methods

The apparatus for testing the two methods (Fig. 1) consisted of a CO_2 generator, a diffusion box, and a diaphragm pump to circulate air between the two. Carbon dioxide was generated in a flask of 0.5 mol/L HCl solution by continuous additions of 0.3 mol/L $NaHCO_3$ solution at a controlled rate ranging from 0 to 30 mL/h. The diffusion box, constructed of 0.5-cm-thick Plexiglas, had inside dimensions of 75 × 75 × 40 cm. Air with CO_2 from the generator was introduced into the bottom half of the box (footspace) through a plenum and mixed with two fans. Above the footspace, an 18-cm-thick layer of polyurethane foam provided a porous medium through which the CO_2 diffused. We used a water manometer to test for overpressure of the footspace; none was detected. Laboratory air temperatures ranged from 21° to 29°C and relative humidity ranged from 21 to 55%.

Four different CO_2 efflux rates ranging from 0 to 0.77 $g \cdot m^{-2} \cdot h^{-1}$ were achieved in trials lasting 24 h. This range of effluxes is similar to those reported for soils globally (Raich and Schlesinger 1992). The efflux of CO_2 (*J*) from the surface of the foam was calculated based on Fick's law of diffusion:

$$J = -D\frac{dC}{dz},$$

where *D* is the diffusivity of CO_2 in the foam and dC/dz is the CO_2 concentration gradient through the foam. The diffusivity of the foam was determined at 25°C to be 0.099 ± 0.002 cm^2/s (mean ± 1 SE, $n = 3$), using methods described by Rolston (1986*b*). The CO_2 gradient was calculated as the difference in CO_2 concentration between the top and bottom surfaces of the foam divided by the foam thickness. *D* was corrected for minor variations in air temperature by using the equation: $D = 0.083(T/273K)^2$, where 0.083 cm^2/s is the foam diffusivity adjusted to 273K and *T* is air temperature in kelvins.

Air samples were collected with a 0.5-mL syringe at the top foam surface and through a septum in the footspace, and the CO_2 concentrations were determined by gas chromatography (GC-8A fitted with a Porapak Q column and a thermal conductivity detector [Shimadzu, Kyoto, Japan]). These samples were taken at ≈30- to 60-min intervals. Throughout the trials, the footspace CO_2 concentration was regulated by minor adjustments to the flow rate of $NaHCO_3$ solution.

The *static-chamber method,* based on Edwards (1982), estimated CO_2 entering the chamber by the mass increase of the soda-lime absorbent. Three polyvinyl chloride (PVC) chambers 21 cm in diameter by 20 cm in height were used in each trial. Soda lime (60 g, 1.7–3.4 mm granules) was contained in tins 8 cm in diameter by 5 cm in height and set directly on the foam surface inside a collar. Five-centimetre-tall collars made of the same PVC material as the chambers were inserted into the foam to a depth of 2.5 cm. Static chambers were affixed to the collars and sealed with duct tape. We used three blanks in each trial to account for

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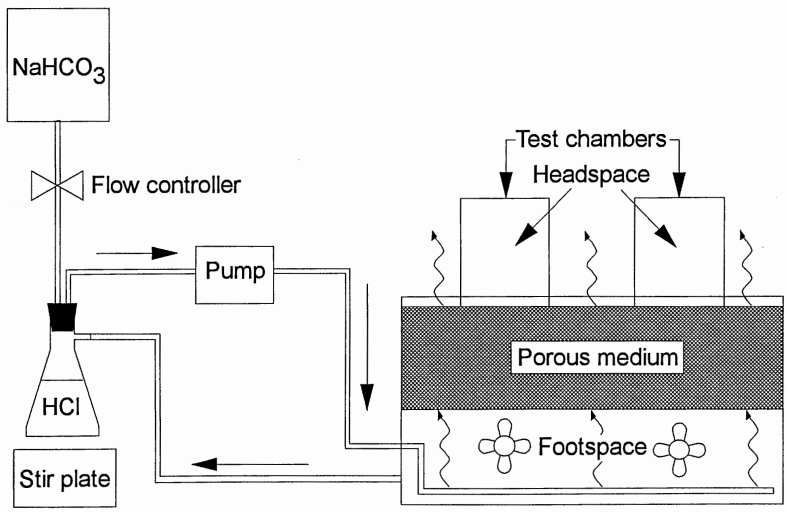

FIG. 1. Laboratory apparatus for testing chamber methods to measure soil CO_2 efflux.

mass change from handling of the soda lime. The headspace concentrations of CO_2 in the static chambers were also monitored during a trial by taking 5–8 syringe samples through a rubber septum in the top of each of the chambers.

The *dynamic-chamber method,* based on Norman et al. (1992), used an infrared gas analyzer (LI-6200, LI-COR, Lincoln, Nebraska, USA) to monitor changes in the CO_2 concentration of air circulating to and from the dynamic chamber. Our dynamic chamber was of the same dimensions and materials as our static chambers. Before each sampling the chamber was allowed to equilibrate with the ambient air by resting on its side. After equilibration the chamber was affixed to a collar, also the same as the static chambers, and sealed with a closed-cell foam-rubber gasket. The rate of CO_2 concentration buildup was then measured for 78 s. Three locations on the foam surface were sampled $\approx$8 times over the course of each trial except during the highest efflux when two locations were sampled.

Results and Discussion

Both the static- and dynamic-chamber methods exhibited biases when compared to the calculated efflux based on Fick's law of diffusion. The static-chamber method greatly overestimated the zero efflux, overestimated the two intermediate CO_2 effluxes of 0.12 and 0.24 $g \cdot m^{-2} \cdot h^{-1}$ by $\approx$25%, and underestimated the highest CO_2 efflux of 0.77 $g \cdot m^{-2} \cdot h^{-1}$ by 57%. The dynamic-chamber method consistently underestimated all effluxes above zero by 15% (Fig. 2).

The average headspace CO_2 concentrations of the static chambers differed from the ambient air by −180, −60, +15, and +450 μmol/mol during the CO_2 efflux trials of 0, 0.12, 0.24, and 0.77 $g \cdot m^{-2} \cdot h^{-1}$, respectively. The three greatest differences were statistically significant (ANOVA, $\alpha = 0.05$). No significant differences were found among headspace concentrations within a trial. The headspace CO_2 concentration of the dynamic chamber changed on average from the ambient air by +36 μmol/mol in the 0.77 $g \cdot m^{-2} \cdot h^{-1}$ CO_2 efflux trial and was proportionally less for the other trials.

Our study demonstrates that both overestimates and underestimates of CO_2 efflux result from the use of a

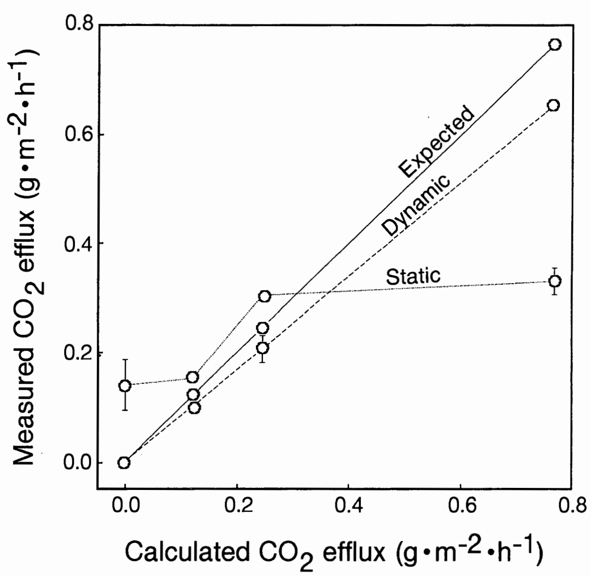

FIG. 2. CO_2 efflux measured by chamber method compared with CO_2 efflux calculated by Fick's law, with ± 1 SE for chamber method estimates (some SES obscured by data points).

static-chamber method with soda-lime absorbent. The corresponding increase in the headspace CO_2 concentration in our highest efflux trial likely also reduced the CO_2 gradient in the foam directly below the chamber and altered a portion of the diffusion path of CO_2 away from the chamber. In the two lowest efflux trials, the reduced concentration in the headspace had an opposite effect. The CO_2 gradient was increased, thus enhancing the diffusion of CO_2 from the foam and surrounding air into the static chamber. The underestimate by the dynamic chamber may be a result of our using a linear rather than a nonlinear model to estimate efflux from the rate of change in the headspace CO_2 concentration (Hutchinson and Livingston 1993).

The bias for the static method observed in this study may be more pronounced than the bias in field studies because of differences in diffusivities between the foam and natural soils. The diffusivity of our foam was 60% of the diffusivity of free air, whereas the diffusivities of soils typically range from 2 to 50% of free air (Gliński and Stępniewski 1985). Given two soils with the same CO_2 efflux, the soil with the higher diffusivity will have a lower CO_2 gradient. With a lower gradient, changes in headspace CO_2 concentrations will have a larger effect on the gradient and consequently on the measured efflux. In field studies (Cropper et al. 1985, Ewel et al. 1987, Norman et al. 1992, Rochette et al. 1992) comparing static to dynamic methods of measuring CO_2 efflux, when the dynamic-method measures exceed $0.2\ g \cdot m^{-2} \cdot h^{-1}$, the static-method estimates diverge from the dynamic estimates. This point of divergence is similar to what we observed by using foam.

Our results should raise a certain degree of caution about using any chamber methods that have not been calibrated against known effluxes, especially in calculating carbon budgets where accurate measurements are essential. Any use of the static-chamber method ought to be particularly scrutinized. Although disagreement exists about the accuracy of static-chamber methods with alkali absorbents, these techniques—if applied carefully—are believed to allow accurate relative comparisons of in situ soils (Anderson 1982). This assumption may not be valid. Depending on the range of effluxes, true differences in soil CO_2 efflux could be nearly impossible to detect with the static-chamber method. For this technique to be effective for relative comparisons, the sensitivity range must be wide enough to capture the true range of effluxes being measured. At a minimum, the air in the static-chamber headspace should be sampled to determine if the CO_2 concentration has been significantly altered from ambient conditions.

The apparatus we introduce in this study is a much simplified model of a natural soil. Future work should proceed from this point to incorporate more of the complexity of a natural system. Our approach has the advantages of providing a known CO_2 efflux, not being limited to the existing conditions of field studies, and isolating confounding factors of the environment and chamber design that influence results.

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