

# Calibrating soil respiration measures with a dynamic flux apparatus using artificial soil media of varying porosity

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## Summary

Measurement of soil respiration to quantify ecosystem carbon cycling requires absolute, not relative, estimates of soil CO<sub>2</sub> efflux. We describe a novel, automated efflux apparatus that can be used to test the accuracy of chamber-based soil respiration measurements by generating known CO<sub>2</sub> fluxes. Artificial soil is supported above an air-filled footspace wherein the CO<sub>2</sub> concentration is manipulated by mass flow controllers. The footspace is not pressurized so that the diffusion gradient between it and the air at the soil surface drives CO<sub>2</sub> efflux. Chamber designs or measurement techniques can be affected by soil air volume, hence properties of the soil medium are critical. We characterized and utilized three artificial soils with diffusion coefficients ranging from  $2.7 \times 10^{-7}$  to  $11.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  and porosities of 0.26 to 0.46. Soil CO<sub>2</sub> efflux rates were measured using a commercial dynamic closed-chamber system (Li-Cor 6400 photosynthesis system equipped with a 6400-09 soil CO<sub>2</sub> flux chamber). On the least porous soil, small underestimates (< 5%) of CO<sub>2</sub> effluxes were observed, which increased as soil diffusivity and soil porosity increased, leading to underestimates as high as 25%. Differential measurement bias across media types illustrates the need for testing systems on several types of soil media.

## Introduction

Soil respiration is often measured in an effort to better understand and quantify carbon cycling in natural and managed ecosystems. Commercially produced measurement systems are readily available and use a variety of measurement techniques, and most researchers depend on these to assure that systems estimate CO<sub>2</sub> efflux accurately and precisely. Numerous studies have compared soil respiration techniques using field-based measurements (e.g. Rochette *et al.*, 1992, 1997; Norman *et al.*, 1997; Pongracic *et al.*, 1997; Le Dantec *et al.*, 1999; Janssens *et al.*, 2000, 2001; Nay & Bormann, 2000), but surprisingly, there have been few attempts to calibrate soil CO<sub>2</sub> efflux systems against known efflux rates (Nay *et al.*, 1994; Widen & Lindroth, 2003). Without knowing the true respiration rate, differences between measurement systems are relative and the process by which the methods differ cannot be fully understood. Consequently, normalization across measurement techniques may not hold under different soil conditions. There is no clear standard for calibrating soil respiration across measurement techniques or means to

test the accuracy of these methods (Norman *et al.*, 1997; Rayment & Jarvis, 1997; Janssens *et al.*, 2001). However, without accurate calibration, using measured soil CO<sub>2</sub> efflux rates to compare C budgets of different sites is problematic.

Nay *et al.* (1994) used a rigorous technique to create known effluxes from the surface of a simulated soil to elucidate measurement bias between dynamic and static (soda lime trap) methods. The most commonly used chamber methods employ either an open or a closed gas exchange principle. Previous studies have shown that closed systems can underestimate soil CO<sub>2</sub> efflux by as much as 34% (Hutchinson & Mosier, 1981; Nay *et al.*, 1994; Healy *et al.*, 1996; Conen & Smith, 2000; Rayment, 2000). The cause of the phenomenon is the subject of lively debate. Rayment (2000) reasoned that closed chambers underestimate soil CO<sub>2</sub> efflux because the effective chamber volume being measured is not only the volume of the chamber but also includes the volume of the air-filled spaces near the soil surface. The magnitude of the underestimation is largely determined by microsite factors that affect soil air volume, and variation in diffusivity can alter the relationship between measured and actual CO<sub>2</sub> efflux rates. An alternative approach is that placement of a closed chamber on the soil surface rapidly induces changes in gas concentration in the

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soil, thereby changing the diffusive gradient and altering surface flux, assuming constant gas concentration at some level in the profile (Hutchinson & Mosier, 1981; Healy *et al.*, 1996). Conen & Smith (2000) add the caveat of assuming constant gas production within the soil profile and that headspace accumulation of CO<sub>2</sub> in the chamber is linear. Both schools of thought agree that air-filled porosity will affect the degree of underestimation. Therefore, to create a laboratory apparatus that can generate CO<sub>2</sub> fluxes with the intent to calibrate or compare systems, it is necessary to employ a variety of soils or media with porosities and diffusivities typical of the soils to be measured *in situ*. Nay *et al.* (1994) employed a porous foam material that had 60% of the diffusivity of free air, while natural soils exhibit much greater resistance to gas diffusion (Lai *et al.*, 1976; Gliński & Stepniewski, 1985).

Native soils, or soils reconstructed in microcosms that have been allowed to settle, are difficult to use in a laboratory apparatus for physical and biological reasons. The interplay and variation of soil moisture, shrink–swell properties, cracks, voids, soil temperature, microbial activity and organic matter introduce too much physical heterogeneity in the system to create repeatable fluxes that are uniform across the soil surface. Despite these difficulties, Kabwe *et al.* (2002) succeeded in getting repeatable measurements with a dynamic closed chamber system by injecting concentrated CO<sub>2</sub> into a soil microcosm (0.58 m diameter × 1.2 m thick) of sandy soil. However, uncertainty was introduced because they had to subtract initial measurements of respiration to account for microbes and substrate native to the soil and it took 300 and 500 hours to achieve equilibrium at CO<sub>2</sub> injection rates of 400 and 800 mg CO<sub>2</sub> m<sup>-2</sup> hour<sup>-1</sup>, respectively. Widen & Lindroth (2003) also constructed a system that advanced chamber-based soil respiration measurement calibration and demonstrated important differences between an open and a closed measurement system using artificial soils of varying porosity through which CO<sub>2</sub>-enriched air was allowed to diffuse.

The ideal medium for generating artificial fluxes is inert to the gas being studied, is non-compressible, is composed of particles of uniform size and shape, and has air-filled spaces similar to those of natural soils. Complexities arising from microbe metabolism, soil chemistry, carbon substrate quality and fluctuating water content are avoided when an inorganic medium is utilized. In this study, we describe a dynamic flux apparatus that uses mass flow controllers, real-time feedback from CO<sub>2</sub> analysers, and logical routines to create virtually any soil CO<sub>2</sub> efflux rate. The apparatus is based on the principles of Nay *et al.* (1994), but uses soil media of greater complexity and air volumes that are representative of dry field soils. It differs from that of Widen & Lindroth (2003) in that a stable CO<sub>2</sub> concentration is maintained in the footspace below the soil, akin to variation present in natural soil profiles. We describe the diffusive properties of the three artificial soils and how we utilized each to assess flux

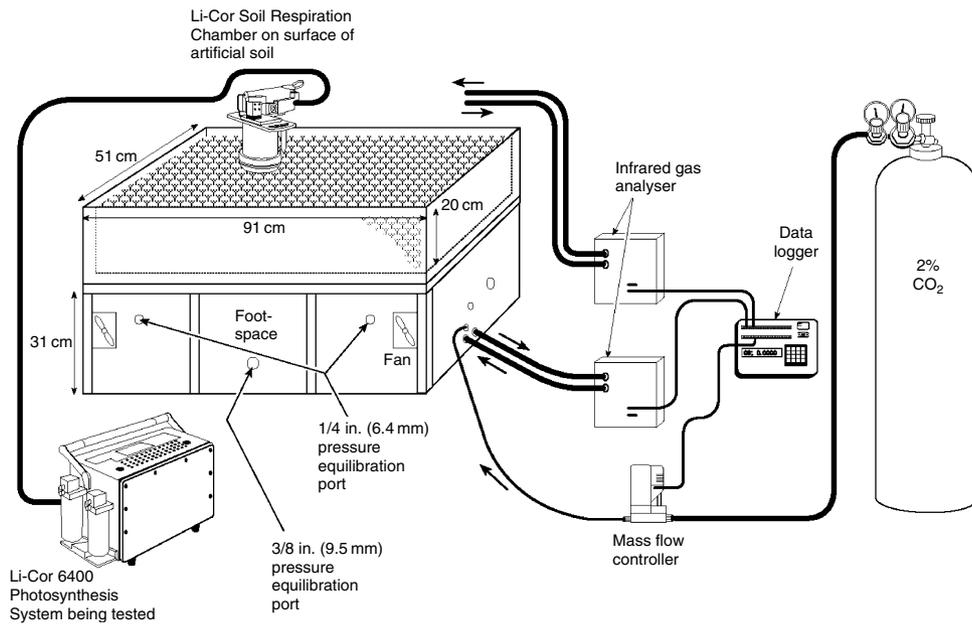
estimates using a commercial dynamic closed chamber system across a range of known CO<sub>2</sub> efflux rates.

## Methods

### Apparatus

The design of the dynamic soil efflux apparatus was based on that of Nay *et al.* (1994) and involves supporting an artificial soil above an air-filled footspace wherein the concentration of CO<sub>2</sub> in air can be manipulated. Our intent was not to pressurize the footspace in any way, so that only the diffusion gradient between the air in the footspace and the air at the soil surface drives the CO<sub>2</sub> efflux. The major changes, relative to Nay *et al.* (1994), include: controlled CO<sub>2</sub> injection via mass flow controllers, real-time monitoring of CO<sub>2</sub> concentration in the footspace and outside the apparatus, automated efflux generation and monitoring by a data logger, creation of a rugged frame to support more than 150 kg of soil medium, and use of media with similar CO<sub>2</sub> diffusivity and porosity as dry field soils.

The efflux tank was constructed using a rectangular Nalgene container (91 cm long × 51 cm wide × 51 cm high). To support the soil medium and create a footspace, an aluminium frame was constructed. On top of the frame, fibreglass netting was supported by thin wires and glued to the walls of the tank for extra support. A porous nylon air cleaner element was laid over the fibreglass mesh to prevent the medium from falling through. This construction (Figure 1) allowed the lower 31 cm of the tank to be a footspace (0.144 m<sup>3</sup>) and the upper 20 cm to be filled with a soil medium (0.093 m<sup>3</sup>). The footspace was equipped with: five small electric fans to mix the air (two shown), two windows constructed of Lexan<sup>TM</sup> (DuPont Corp., Wilmington, DE), two ports to monitor CO<sub>2</sub> concentration, one port to inject concentrated CO<sub>2</sub>, and six 1/4 inch (6.4 mm) ports (three shown) and four 3/8 inch (9.5 mm) ports (two shown) for pressure equilibration. During normal operation, two or three fans were used to achieve optimum mixing. Pressure in the footspace was monitored with a digital manometer (model MA2-005P, Modus Instruments Inc., Northboro, MA). All pressure equilibration ports were closed and then sequentially opened until the pressure differential with the atmosphere fell below detectable limits (+0.1 Pa), in order to select the minimum number of open ports needed to achieve equilibrium with atmospheric pressure. The CO<sub>2</sub> concentration in the footspace was monitored with an environmental gas monitor-2 (EGM-2) infrared gas analyser (IRGA) (PP Systems, Haverhill, MA) scaled 0 to 10 000 μmol CO<sub>2</sub> mol<sup>-1</sup>, configured to sample footspace air in a closed loop. The CO<sub>2</sub> concentration at the soil surface was monitored with an EGM-2 scaled 0 to 2000 μmol mol<sup>-1</sup>. A Campbell data logger Model 21 X (Campbell Scientific Inc., Logan, UT) was programmed to collect data from the two IRGAs, calculate real-time CO<sub>2</sub> efflux from the soil medium surface and maintain a preselected



**Figure 1** Diagram of the dynamic flux apparatus.

or pre-programmed rate of efflux by injecting 2% by volume CO<sub>2</sub> in air into the footspace via a Sierra 'sidetrak' mass flow controller Model 840 L (Sierra Instruments, Inc., Monterey, CA) as needed.

#### Efflux theory and application

The concept of the dynamic flux apparatus requires the footspace to be maintained at a specific CO<sub>2</sub> concentration, allowing CO<sub>2</sub> to move through the soil medium via gas diffusion. The CO<sub>2</sub> efflux can be calculated using Fick's law:

$$F/At = f = -D_p(dc/dx), \quad (1)$$

where  $F$  is grams of gas,  $A$  is area (m<sup>2</sup>),  $t$  is time (s),  $f$  is gas flux density (g gas m<sup>-2</sup> soil s<sup>-1</sup>),  $D_p$  is soil gas diffusivity (m<sup>3</sup> soil air m<sup>-1</sup> soil s<sup>-1</sup>),  $c$  is the concentration of CO<sub>2</sub> in the gaseous phase (g gas m<sup>-3</sup> soil air), and  $x$  is the thickness of the medium (m).

To create a known CO<sub>2</sub> efflux using artificial soil, it is necessary to understand the diffusive properties of the material. Soil gas diffusivity ( $D_p$ ) and soil aeration are the major physical factors controlling the diffusion of gas through soil (Kruse *et al.*, 1996; Moldrup *et al.*, 2000). Under native soil conditions, soil air content varies through displacement by soil water. For the purposes of this work, we focus on the diffusion of CO<sub>2</sub> through non-organic, dry soils to eliminate any confounding processes. The most difficult part of creating a steady-state flux apparatus is the accurate determination of  $D_p$ , which we calculate empirically. A laboratory diffusion apparatus was built and operated according to the design originally described for argon and nitrogen gas

movement in soil (Evans, 1965; Rolston, 1986). Diffusivity was calculated using Rolston (1986):

$$\ln[(C - C_s)/(C_o - C_s)] = -D_p(At/Vl), \quad (2)$$

where  $C_s$  is the ambient CO<sub>2</sub> concentration (μmol mol<sup>-1</sup>),  $C_o$  is the initial CO<sub>2</sub> concentration (μmol mol<sup>-1</sup>),  $C$  is the observed CO<sub>2</sub> concentration (μmol mol<sup>-1</sup>),  $V$  is volume of the diffusion chamber (m<sup>3</sup>) and  $l$  is the length of the chamber (m).

These calculations of  $D_p$  did not account for the additional resistance to diffusion created by the rugged materials that support the medium in the dynamic flux apparatus (Figure 1), or for the settling of medium particles over time. Therefore efflux tanks themselves were also used to derive empirically  $\ln[(C - C_s)/(C_o - C_s)]$ . This allowed the additional resistance to diffusion of the materials supporting the medium in the efflux tank to be accounted for in the calculation of  $D_p$ . The ratio of chamber air to soil air in the Evans (1965) type apparatus was sufficiently large to minimize dilution errors, which are similar to closed chamber errors described by Rayment (2000), but the footspace volume in our apparatus was not large enough to avoid these errors and could result in detectable error. Rolston (1986) provides a correction equation, which we applied to our values of  $D_p$ . The two methods compared favourably, but as expected the  $D_p$  values of the dynamic flux apparatus remained somewhat smaller (6–14%). For the purposes of the experiment, corrected values, determined from the efflux apparatus, were used since these data accounted for structural material supporting the medium and any potential leaks in the tanks, fittings or tubes. The value of  $D_p$  was determined for three different artificial soils: coarse landscaping pebbles, fine sand and a 50:50 mixture of fine sand and landscaping pebbles

(mixed soil). Once  $D_p$  was determined for each artificial soil, efflux was calculated by measuring the  $\text{CO}_2$  concentration within the footspace and at the soil surface (Equation (1)).

### Measurement of surface fluxes

To demonstrate the utility of this technique, a Li-Cor 6400 photosynthesis system (Li-Cor Inc., Lincoln, NE) equipped with a 6400-09 soil  $\text{CO}_2$  flux chamber was used to measure surface fluxes generated by the apparatus. This measurement device utilizes a dynamic closed-chamber system (DCCS) that uses a non-steady state gas-exchange principle across a soil surface area of  $0.00716 \text{ m}^2$ . The 6400-09 allows the user to determine the insertion depth, thus varying the system volume, which at zero insertion depth is  $0.000991 \text{ m}^3$ . We used an insertion depth of  $0.02 \text{ m}$  resulting in a volume of  $0.000848 \text{ m}^3$ . The 6400-09 operates by drawing down the headspace  $\text{CO}_2$  concentration within the chamber (near-ambient concentration) and then shifts into measurement mode whereby  $\text{CO}_2$  accumulates to a preselected concentration at which point the rate of increase is closely monitored and flux is calculated. A series of flux rates was generated through each of the artificial media to test the DCCS. The maximum flux rate obtainable was limited by the range limit of the IRGA and the value of  $D_p$ . It usually took 60–120 minutes to ensure system equilibrium after a  $1 \mu\text{mol m}^{-2} \text{ s}^{-1}$  change in efflux. The  $\text{CO}_2$  concentration in the footspace was held constant during each measurement interval. We measured as many rates as possible in a 2–3-day period for each medium.

## Results

Physical properties affecting gas diffusion were assessed for each of the three dry artificial soils (Table 1). The combination of sand and pebbles (mixed soil; 50:50 by volume) produced a medium that had greater bulk density than its constituent materials (Table 1), the result of the pebble pore volume being packed with sand. Since only dry materials were used, total porosity and air-filled porosity are the same and are referred to as porosity throughout. The porosity of the mixed soil was almost half that of pebbles alone. Using pebbles, sand and the mixed soil, we were able to achieve a range of

porosities and  $D_p$  values (Tables 1 and 2). The pebbles exhibited a diffusion coefficient more than four times that of the mixed soil. The relationship between air content of soil, bulk density, tortuosity and  $D_p$  is illustrated in Figure 2. Bulk density and tortuosity increase, as  $D_p$  declines, while greater soil porosity results in larger  $D_p$  values. The interaction between  $D_p$  and porosity is frequently presented as a non-linear relationship (e.g. Moldrup *et al.*, 2000); however, with only three points fitted, non-linear equations could lead to biased interpretation, therefore a linear model was applied (Figure 2).

The  $\text{CO}_2$  concentration of air in the footspace of the flux apparatus could be manipulated from near ambient ( $370 \mu\text{mol mol}^{-1}$ ) to  $10\,000 \mu\text{mol mol}^{-1}$   $\text{CO}_2$  in air (limitation of the gas analyser). Based on the diffusivity of each soil medium, the maximum efflux for mixed, sand and pebble media was approximately 6, 12 and  $24 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ , respectively. The relationship between  $\text{CO}_2$  efflux generated by the apparatus and the flux measured by the DCCS was linear for all soil types (Figure 3). Observed efflux versus expected efflux was virtually inseparable for the mixed soil, but deviated in sand and pebbles (Figure 3). Since the maximum obtainable  $\text{CO}_2$  efflux rate is different for each soil type, direct comparisons between the soils can be made only at the low end of the range (Figure 4). The deviation from expected efflux increased with efflux rate, but stabilized rapidly in the mixed and sand media to a constant level (Figure 5). The generated efflux correlates exceptionally well with the DCCS measures on mixed soil medium (Figure 5) – the difference is less than 5%. Measurements with the DCCS underestimated (10–15%) the generated flux through sand, but were rather consistent across a range of effluxes (Figure 5). Efflux measured on the pebble medium was greater than expected at low efflux rates ( $< 2 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) before stabilizing to a more consistent underestimate that was as high as 25% (Figure 5).

## Discussion

The soil characteristics of  $D_p$ , porosity, bulk density and tortuosity are clearly co-related and their mutual relationships (Figure 2) illustrate the physical properties that control  $\text{CO}_2$

**Table 1** Physical properties of three non-organic, dry, artificial soils utilized with the dynamic flux apparatus

Medium	Bulk density /Mg $\text{m}^{-3}$	Porosity (dry)	Particle density /Mg $\text{m}^{-3}$	Diffusion coefficient of $\text{CO}_2^a$ / $\text{m}^2 \text{ s}^{-1}$	Tortuosity <sup>b</sup>
Mixed (sand and pebbles)	1.87	0.26	2.54	$2.72 \times 10^{-7}$	2.396
Sand	1.64	0.38	2.66	$5.83 \times 10^{-7}$	1.997
Pebbles	1.40	0.46	2.61	$12.78 \times 10^{-7}$	1.805

<sup>a</sup>Data averaged over entire profile.

<sup>b</sup>(Dimensionless) ratio of average capillary tube length to the length of the porous medium, along the diffusion axis, in a sinuous capillary tube of uniform diameter (Moldrup *et al.*, 2001).

**Table 2** Comparison of gas diffusion coefficients of CO<sub>2</sub> measured with the dynamic soil efflux apparatus with published values

Source	Medium	Depth /cm	Diffusion coefficient of CO <sub>2</sub> <sup>a</sup> /m <sup>2</sup> s <sup>-1</sup>
Our apparatus	Mixed (sand and pebbles)	0–20	$2.72 \times 10^{-7}$
Our apparatus	Sand	0–20	$5.83 \times 10^{-7}$
Our apparatus	Aquarium gravel <sup>b</sup>	0–20	$1.19 \times 10^{-6}$
Our apparatus	Pebbles	0–20	$1.28 \times 10^{-6}$
Lai <i>et al.</i> (1976)	Moist lawn soil <sup>c</sup>	0–23	$5.83 \times 10^{-7}$
Lai <i>et al.</i> (1976)	Dry lawn soil <sup>c</sup>	0–23	$1.17 \times 10^{-6}$
Lai <i>et al.</i> (1976)	Cultivated soil, with dry cracked surface <sup>c</sup>	0–23	$9.44 \times 10^{-7}$
Lai <i>et al.</i> (1976)	Soil irrigated for 7 days, surface water-logged <sup>d</sup>	0–23	$3.06 \times 10^{-7}$
Lai <i>et al.</i> (1976)	Water-logged soil after 5 days of drying <sup>d</sup>	0–23	$7.50 \times 10^{-7}$
Nay <i>et al.</i> (1994)	Polyurethane foam	0–18	$9.89 \times 10^{-6}$
Gliński & Stepniewski (1985)	Expected range on various dry soils		$8.10 \times 10^{-6}$ to $3.20 \times 10^{-7}$
Gliński & Stepniewski (1985)	Expected range on various saturated soils		$8.80 \times 10^{-10}$ to $3.50 \times 10^{-11}$
Bakker & Hidding (1970)	Non-puddled topsoils, air-filled porosity 0.04–0.4 <sup>e</sup>		$2.16 \times 10^{-6}$ to $2.16 \times 10^{-8}$
Gradwell (1961)	Silt loam topsoils, air-filled porosity 0.02–0.4 <sup>e</sup>		$1.97 \times 10^{-6}$ to $2.20 \times 10^{-8}$
Gliński & Stepniewski (1985)	CO <sub>2</sub> in free air at 20°C		$1.59 \times 10^{-5}$
Gliński & Stepniewski (1985)	CO <sub>2</sub> in H <sub>2</sub> O at 20°C		$1.77 \times 10^{-9}$

<sup>a</sup>Data averaged over entire profile.

<sup>b</sup>Tested with diffusion apparatus (Evans, 1965), but not used with our flux apparatus.

<sup>c</sup>Sandy loam measured *in situ*.

<sup>d</sup>Loamy sand measured *in situ*.

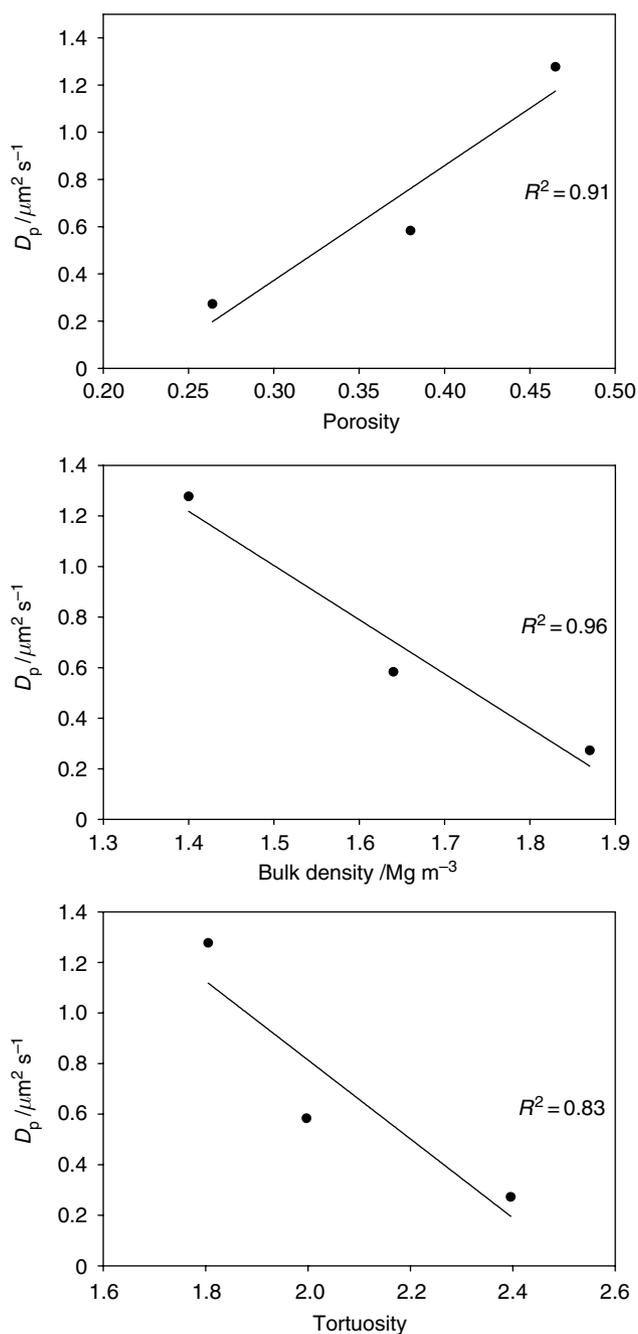
<sup>e</sup>Calculated from model describing the relationship of  $D_p$  soil/ $D_p$  air as a function of air-filled porosity at 20°C (Gliński & Stepniewski, 1985).

efflux across soil media in our apparatus. As bulk density and tortuosity increase,  $D_p$  decreases. Conversely, as porosity increases,  $D_p$  increases. Our values of  $D_p$  are at the low end of the range expected for dry soils (Table 2; Gliński & Stepniewski, 1985). It seems likely that the structure of the efflux tank induced some additional resistance to diffusion, possibly from the compaction of the air-cleaner element. The diffusivities we created were still one tenth that of the polyurethane used by Nay *et al.* (1994). The value of  $D_p$  in water is  $10^{-4}$  that of  $D_p$  in free air, hence wet or saturated soils exhibit substantially lower  $D_p$  than the media used in our study (Table 2). Our  $D_p$  values were similar to those measured by Lai *et al.* (1976) in a variety of soils under field conditions, but when compared with Bakker & Hidding (1970) and Gradwell (1961) these values would be at the high end of the range encountered in the field (Table 2). Porosities achieved with the media (0.26 to 0.46) used in the study fall within the range commonly observed in the field (0.15 to 0.60), but do not get as small as those found in very wet soils (Gliński & Stepniewski, 1985).

Our results demonstrate that soil physical properties can affect how accurately a dynamic closed-chamber system (DCCS) estimates soil respiration. On the soil medium with the lowest porosity (mixed), there was minimal deviation between observed and expected flux rates (Figure 5). On the other soil media with higher porosities, the DCCS markedly underestimated calculated flux (Figures 3 and 4). Underestimation by DCCS has been reported by others (Hutchinson &

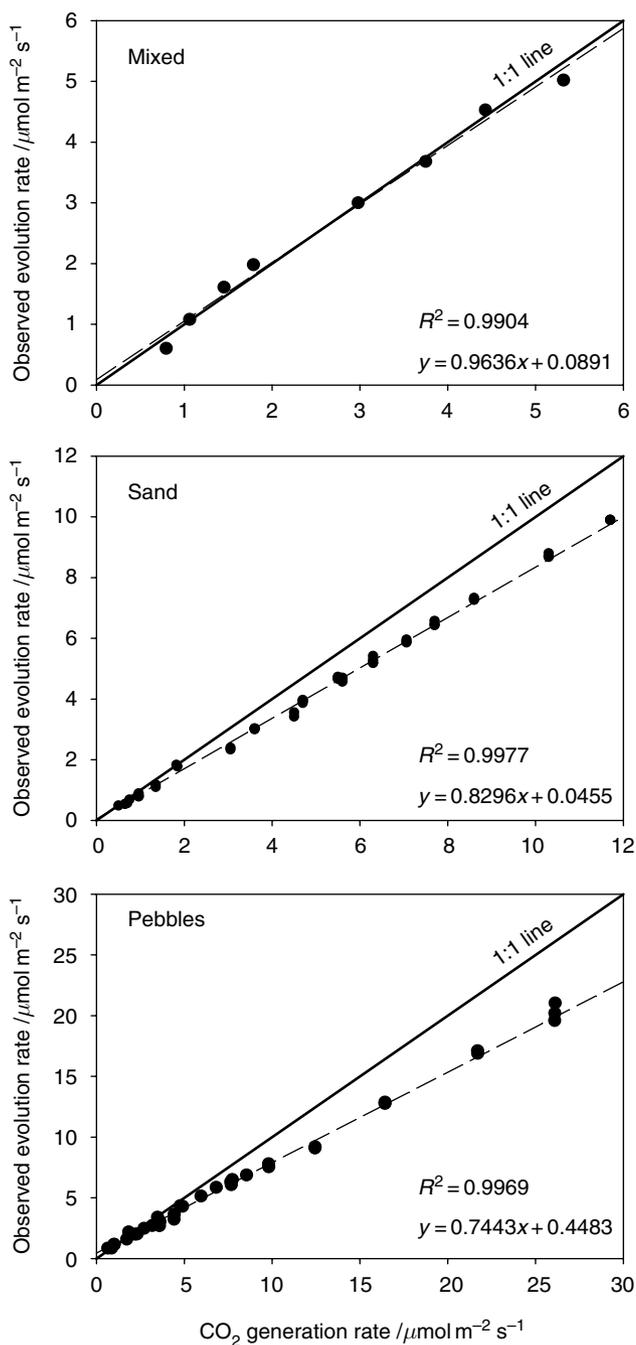
Mosier, 1981; Healy *et al.*, 1996; Conen & Smith, 2000; Rayment, 2000; Widen & Lindroth, 2003). Conen & Smith (2000) presented a model that predicts the underestimation of fluxes from closed chambers using total soil air volume and chamber volume. Our results are in close agreement on the sand and pebble substrates, though the flux underestimate was lower than predicted on the mixed soil (Figure 6). Conen & Smith's (2000) model could be used to convert results for particular soils; however, fluctuations in soil moisture confound the determination of soil air volume and make retrospective analysis or corrections difficult. The best means of preventing or reducing underestimation of gas flux by closed chambers is increasing chamber height (Matthias *et al.*, 1978; Healy *et al.*, 1996; Conen & Smith, 2000).

Using a laboratory apparatus to create CO<sub>2</sub> fluxes, Nay *et al.* (1994) found a near-constant 15% underestimate of CO<sub>2</sub> flux with a DCCS. We generally observed constant underestimation except at the lowest flux rates (Figures 4 and 5). At rates less than  $2 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  our DCCS overestimated flux on the pebble and mixed media. This deviation is relatively small when compared with the complete range of fluxes that were created (Figure 3). It could be that the gas mixing or circulation in the measurement chamber may be dislodging or disturbing soil air and this was detectable only at low flux rates. Widen & Lindroth (2003) demonstrated a linear relationship between measured and reference CO<sub>2</sub> fluxes using a Li-Cor



**Figure 2** Effects of soil physical properties on the diffusion coefficient of  $\text{CO}_2$  ( $D_p$ ) in soil air. Curves are fitted with linear equations.

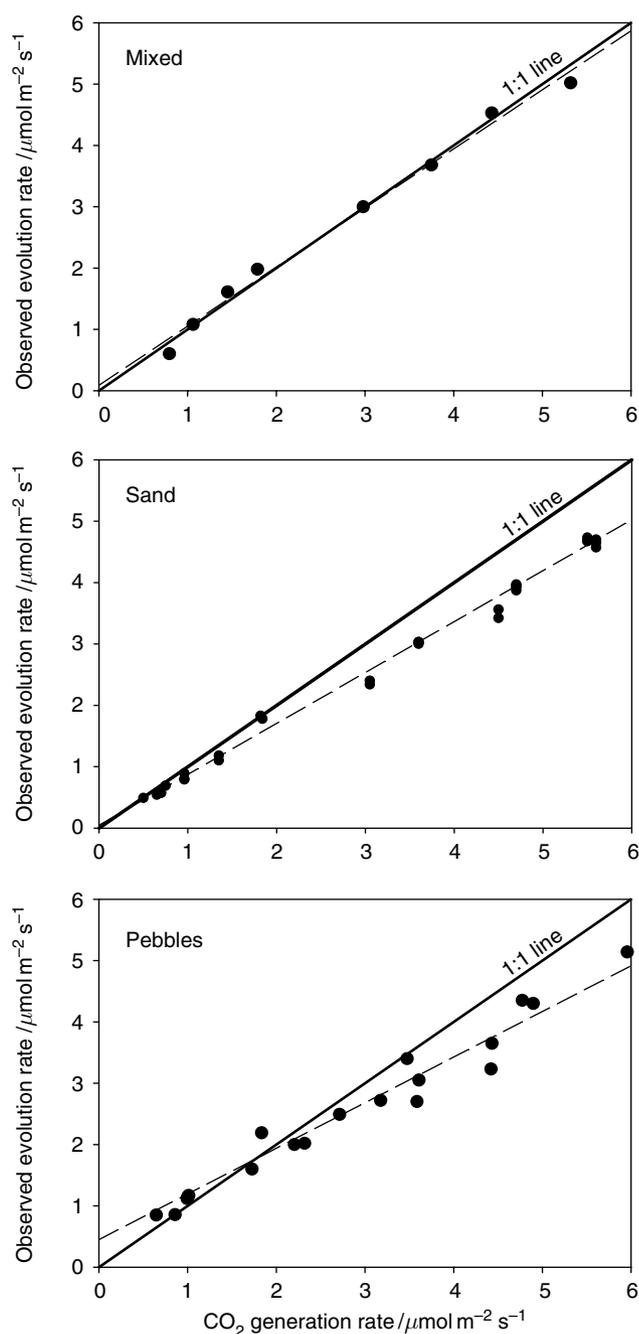
6200-09 soil respiration system. They generated fluxes through three sandy soils of varying porosity (0.60, 0.34 and 0.34 with water added) and found that the DCCS underestimated on the most porous sand (0.60), was in agreement with generated flux on the dry sand (0.34) and overestimated generated flux on the wetted sand ( $< 0.34$ ). While differences exist between our results and those of Widen & Lindroth (2003),



**Figure 3** Comparison of  $\text{CO}_2$  evolution generated by the dynamic flux apparatus and  $\text{CO}_2$  evolution measured by the DCCS. Data are presented across the full range of fluxes generated on each medium.

the trend with respect to the effect of porosity on measured flux is similar.

We believe that the dynamic flux apparatus presented here, when used with a variety of soil media, represents an improvement over other means of generating precisely known  $\text{CO}_2$  gas



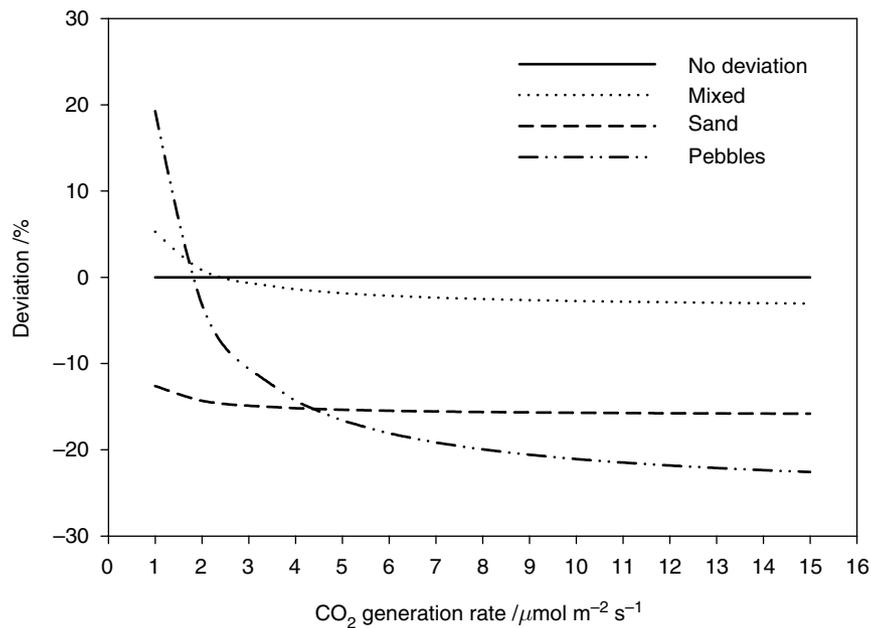
**Figure 4** Comparison of CO<sub>2</sub> evolution generated by the dynamic flux apparatus and CO<sub>2</sub> evolution measured by the DCCS. Data are scaled from 0 to 6  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  to facilitate direct comparison across soil medium.

fluxes from porous, soil-like material (Nay *et al.*, 1994; Bekku *et al.*, 1997; Kabwe *et al.*, 2002; Widen & Lindroth, 2003). Natural soils will probably have several layers or regions of varying porosity and lower values of  $D_p$ . The potential for leaf litter to induce air volume based errors may be even more

dramatic and complex. Respiration chambers are often placed on litter and organic material on forested sites. Not only are these materials potential sources of CO<sub>2</sub>, but their complex aeration can be difficult to account for and may pose problems for closed chambers. Newly fallen litter may exhibit much greater air volume than the soils below or in some cases become a barrier to diffusion (Maier & Kress, 2000). This could be problematic on sites with deep litter layers. Our dynamic flux apparatus allows chamber systems to be tested with soils of varying porosity under ideal circumstances, which will identify areas of concern with the chamber technique. This experiment did not consider the effects of soil water, changes in barometric pressure, air turbulence or mass flow, which can alter soil respiration via processes other than diffusion. In contrast to systems described by Nay *et al.* (1994) and Bekku *et al.* (1997), we used soil media that exhibited porosity and  $D_p$  values similar to dry field soils and demonstrated the impact of varying soil properties on flux determination by a DCCS. By using artificial media it was not necessary to consider the effects of soil microbes and moisture, as done by previous workers (e.g. Bekku *et al.*, 1997; Kabwe *et al.*, 2002). Kabwe *et al.* (2002) used microcosms, which afforded great stability of the media, but required weeks to come into equilibrium; thus, sufficient sampling across a range in efflux rates would take a prohibitively long time. The system described by Widen & Lindroth (2003) is an excellent means of testing or calibrating respiration chambers, but there are some notable differences with our dynamic or steady-state calibration system. Our dynamic flux apparatus uses deeper soil (20 cm versus 5 cm) providing more resistance to surface eddies that could dislodge air parcels from deep within the apparatus. The dynamic flux apparatus creates a steady-state condition allowing a constant flux of CO<sub>2</sub> from the medium, much like CO<sub>2</sub> efflux from natural soil. Since steady flux rates can be generated, the apparatus can be used to test static measurement techniques (soda lime or alkali trap). This system is also programmable, so that it can perform automated tests (on open design systems) that can run without disturbing the measurement chamber.

A drawback of our method is the need to measure  $D_p$  precisely through the soil medium (including the apparatus structure), which can be time-consuming. In addition, the apparatus needs to be checked for leaks and whether its components have the capacity to adsorb or desorb CO<sub>2</sub> during the empirical determination of  $D_p$ . The parameters must be verified before a calibration exercise because any settling or layering of particles has the potential to alter  $D_p$  over time.

Chamber-less methods of measuring or calculating CO<sub>2</sub> efflux from soils are becoming more prevalent, yet chamber measurements remain essential to the study of carbon cycling in a multitude of ecosystems. Chambers are applied to check assumptions used to estimate soil fluxes from net ecosystem exchange values and test forest carbon exchange models (Lai

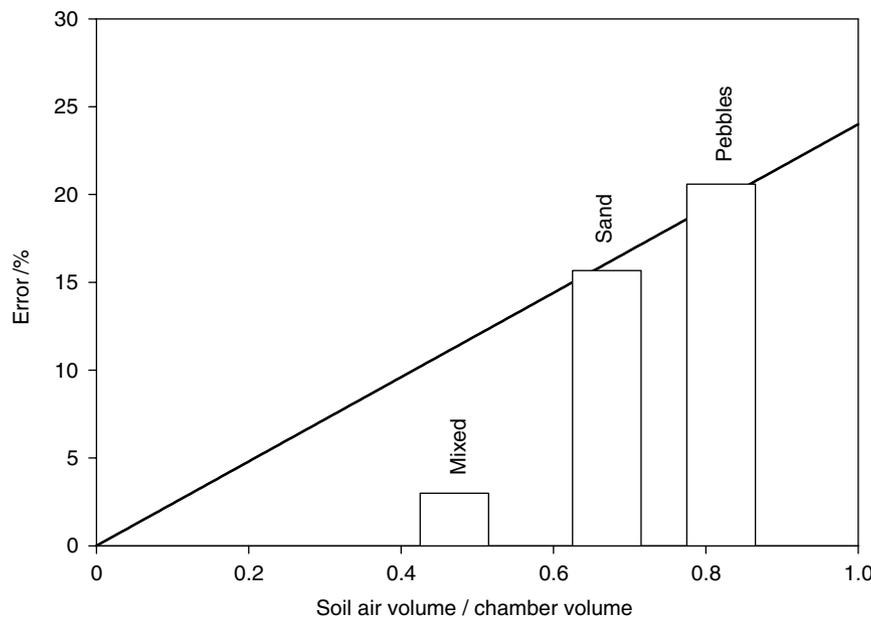


**Figure 5** Deviation of CO<sub>2</sub> efflux measured with the DCCS compared with the CO<sub>2</sub> generated through soil medium.

*et al.*, 2002a,b). Chamber-based soil respiration sampling also allows analysis of microsite variability and closely spaced treatments or plots. Rigorous testing and calibration are necessary to ensure the accuracy of chamber-based soil respiration measurements so that their use in quantifying absolute C fluxes is tenable.

The purpose of this study was not to examine the functionality of a popular commercial respiration system, but to illus-

trate the need for a calibration system that uses media of varying porosities. In fact, our work demonstrates that although measurement bias differed among the soil media used, the relationship between generated and measured flux rates was always linear. In addition, although the DCCS used may not always be accurate under all soil porosities, it was precise on a given soil medium. Such qualities greatly simplify the construction of calibration curves.



**Figure 6** Comparison of flux underestimation (% error) by the DCCS technique and the ratio of soil air to chamber volume at the point where the error becomes stable (see Figure 5). The solid line represents the relationship predicted by Conen & Smith (2000).

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