Quantifying CO_2 fluxes from soil surfaces to the atmosphere

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Abstract

Measurements of CO_2 fluxes from ground surface of the atmosphere (soil respiration) are needed to quantify biotic and abiotic reaction rates in unsaturated zones and to gain insight into the importance of these processes on global warming. The use of three techniques (dynamic closed chambers, static chambers, and gradient calculations) to determine soil respiration was assessed by measuring fluxes of microbially produced CO_2 from an unsaturated mesocosm (2.4 m dia. $\times$ 3.2 m thick) and two unsaturated minicosms (0.58 m dia. $\times$ 1.2 m thick), one maintained at 18–23 °C (HT) and the other at 5 °C (LT). By injecting known and constant CO_2 fluxes into the bottom of the HT minicosm and measuring the resulting fluxes, it was shown that the dynamic closed chamber (DCCS) technique yielded accurate measurements of fluxes over the range observed from natural unsaturated media. Over this same range, results showed that the concentration gradient method yielded reasonable estimates of fluxes but its accuracy was limited by uncertainties in both the concentration gradient and the gaseous diffusion coefficient in the soil atmosphere. The static chamber method underestimated the actual flux at higher CO_2 fluxes and when adsorption times of >24 h were used. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Accurate measurements of CO_2 fluxes from the soil to the atmosphere (soil respiration) are required to quantify biogeochemical reaction rates in unsaturated geologic media and soils (Hendry et al., 1993, 1999; Wood et al., 1993; Wood and Petraitis, 1984; Affek et al., 1998; Keller and Bacon, 1998; Hendry et al., 2000). In addition, accurate measurements of CO_2 fluxes can provide input needed for global warming models (Raich and Schlesinger, 1992; Bowden et al.,

1993; Hanson et al., 1993; Sundquist, 1993; Holland et al., 1995; Raich and Potter, 1995; Sellers et al., 1995; Thierron and Laudelout, 1996; Lavigne and Ryan, 1997; Wickland and Striegl, 1997; Buchmann and Schulze, 1999; Schlesinger and Andrews, 2000).

Soil respiration rates are determined using Fick's law (concentration gradient method), static flux chamber method, and more recently, using a dynamic chamber method. The accuracy of these methods has long been debated. Numerous field studies have compared methodologies (Edwards, 1982; Cropper et al., 1985; Freijer and Bouten, 1991; Norman et al., 1992; Rochette et al., 1992; Nakadai et al., 1993; Jensen et al., 1996; Norman et al., 1997; Rochette et al., 1997; Nay and Bormann, 2000; Janssens et al.,

1998, 2000, 2001). However, Rustad et al. (2000) noted that a contributing factor to our limited understanding of soil respiration is a lack of consensus on methods for measuring soil respiration rates. Rayment and Jarvis (1997), Norman et al. (1992) and Janssens et al. (2001) also noted that no standard appears to exist for establishing the accuracy of field measurements of soil respiration rates.

Studies show that the concentration gradient approach can yield a reasonable estimate of respiration rates (Jaynes and Rogowski, 1983; Leffelaar, 1987; Thorstenson and Pollock, 1989). However, this method is not necessarily accurate (de Jong and Schappert, 1972) and typically underestimates CO_2 fluxes (Freijer and Leffelaar, 1996) because it is an indirect estimate based on the use of moisture content measurements to calculate gas diffusion coefficients (Šimůnek and Saurez, 1993). Elberling et al. (1994) noted that the concentration gradient method cannot be applied to measuring fluxes under high water-saturated conditions because gas concentrations cannot be measured accurately. More complex numerical approaches based on the concentration gradient technique (Wood and Petraitis, 1984; Leffelaar, 1987; Ouyang and Boersma, 1992; Šimůnek and Saurez, 1993; Wood et al., 1993; Hendry et al., 1993, 1999, 2001; Freijer and Leffelaar, 1996) have been used to quantify soil respiration rates.

The use of the static chamber method to quantify soil respiration rates has been used for many years (cf. Lundegaardh, 1927). The CO_2 fluxes determined using the static chamber method consistently under-predict measurements using alternate methods (Edwards, 1982; Cropper et al., 1985; Ewel et al., 1987; Raich et al., 1990; Norman et al., 1992; Rochette et al., 1992; Nay et al., 1994; Hendry et al., 1999; Janssens et al., 2000). Jensen et al. (1996), however, concluded that static chambers overestimated soil respiration rates for fluxes <100 mg CO_2 m^2/h and underestimated respiration rates for fluxes >100 mg CO_2 m^2/h.

The dynamic closed chamber method has been used to determine soil respiration by several researchers. These include Cropper et al. (1985), Norman et al. (1990, 1992), Hall et al. (1990), Rochette et al. (1991), Jensen et al. (1996), McGinn et al. (1998), Striegl and Wickland (1998), Mielnick and Dugas (2000), and Janssens et al. (2000). A wide variety of

soil CO_2 evolution data compiled by Schlesinger (1977) indicates that the results obtained with static techniques are generally lower than those predicted by a regression equation relating latitude to soil CO_2 release, and that dynamic methods often produce values higher than those predicted by the regression equation.

Janssens et al. (2000) compared a dynamic closed-chamber infrared gas analysis system (DC1) with other systems for measuring soil CO_2 efflux: the soda lime technique, the eddy correlation technique, and another dynamic closed-chamber system (DC2). They concluded that among the four systems, the DC1 systematically gave the highest flux rates. They also concluded that the large and systematic differences in flux values among the four techniques highlight uncertainties in comparing fluxes from different sites obtained with different techniques. Rustad et al. (2000) also indicated that although several recent papers compared two or more of these techniques, a comprehensive study contrasting all techniques has not yet been reported making it difficult to compare data collected from different sites with different methods. Although the dynamic closed chamber method is a promising technique, its ability to accurately quantify soil respiration remains to be verified.

The objective of this study was to ascertain which of the three methods (concentration gradient method, static flux chamber method, and dynamic chamber method) best approximates the CO_2 flux from soil surfaces in natural environments. This objective was attained by performing experiments in the laboratory in well-constrained minicosms and a mesocosm described by Richards (1998) and Hendry et al. (2001).

2. Materials and methods

2.1. Physical description of the minicosms and mesocosm

Two minicosms were used in this investigation. Each minicosm was constructed from a 0.58 m ID polyvinylchoride (PVC) tube, 1.3 m in height, fitted with removable airtight lids. The minicosms were filled with about 634 kg of sand excavated from an

unsaturated C-horizon (no A or B horizons) at a field site located 10 km south of Saskatoon, Saskatchewan, Canada (52.05 N Lat., 106.36 W Long.). The texture and chemistry of the C-horizon sand are described in Hendry et al. (1999, 2000). The methods of filling the minicosms and installation of the instrumentation are described in Richards (1998). On day 1 of the study (August 6, 1995), the water tables in the minicosms were lowered from ground surface to a depth of 0.95 m. One minicosm was maintained at room temperature (21–23 °C) (HT—high temperature) and the other minicosm at 5 ± 2 °C (LT—low temperature). The current investigation focused on the period of time from day 1324 to day 1646. For the duration of the study, distilled water was applied at surface at a rate of 1.82 l/week (6.88 mm/week).

The mesocosm used was a 2.4 m dia. × 4.6 m high cylinder filled with 65 t of C-horizon sand similar to that used to fill the minicosms. The methods of excavating the sand and filling the mesocosm as well as the installation of the instrumentation are described in Hendry et al. (2001). The water table in the mesocosm was lowered from ground surface to a depth of 3.2 m below surface on day 1 (December 28, 1992). The temperature of the mesocosm was held at room temperature (18–23 °C) from day 1. The current investigation focused on the period of time from day 2254 to day 2604. A uniform, controlled volume of distilled water was applied to the surface on a weekly basis (30 l/week, 6.63 mm/week) using a rain simulator system.

2.2. Moisture content

Gravimetric water content measurements from the mesocosm were made through a neutron access tube (0.05 m dia. Schedule 40 PVC pipe) installed in the center of the mesocosm to a depth of 3.7 m prior to lowering the water table (Hendry et al., 1999, 2001). Measurements were made monthly for the duration of the study at 0.15 m depth intervals between 0.10 and 3.25 m using a neutron moisture probe Model 3322 Troxler (Electronic Labs Inc., Research Triangle Park, NC). Gravimetric water contents were converted to volumetric water contents using dry density measurements and a calibration curve.

The methods of gravimetric water content measurements from the minicosms are described in Richards

(1998). The measurements were made using Troxler (Electronic Labs Inc., Research Triangle Park, North Carolina) gamma transmissivity equipment. Calibration of this method was by ASTM #D 2216-92 (1992) standard methodology for gravimetric water content. Water content measurements were taken at intervals of seven days starting on day 11 and less often after day 100 when moisture profiles approached steady-state (Richards, 1998). The moisture profiles in the minicosms were not measured during the period of interest.

2.3. Collection and analyses of gas samples

Minicosm gas samples were collected from gas sampling ports installed horizontally at depths of 0.02, 0.15, 0.30, 0.45, 0.60, 0.75 and 0.90 m, below surface, at least weekly for immediate analyses. Mesocosm gas samples were also collected at least weekly from duplicate bundles of gas ports (west and east profiles) installed at depths of 0.2, 0.47, 0.97, 1.47, 1.99 and 2.52 m below surface in the mesocosm.

All gas samples were analyzed for CO_2 within 1 h of sampling on a Carle Special Series S model 311 analytical gas chromatograph (GC) equipped with Porapack and molecular sieve columns and automatic valve switching. The GC was equipped with thermal conductivity and flame ionization detectors.

2.4. Dynamic closed chamber system

A series of Plexiglas collars (0.28 m dia. × 0.07 m high, and 0.005 m thick), was constructed. The collars were permanently inserted to a depth of 0.02–0.03 m into the soil in the HT and LT minicosms and the mesocosm, thus allowing for routine measurements of CO_2 fluxes without disturbing the soil surfaces. The chamber lids were attached to the collars with bolts and rubber O-rings provided seals between the collars and the lids. Perforated copper rings (0.40 m long) were fitted on the underside of the chamber lids to provide uniform air-dispersion in the chamber headspaces (0.5–1.0 l). Mixing in the chamber headspaces was achieved using an internal pump in the ADC 2250 differential infrared CO_2 gas analyzer (ADC BioScientific Ltd). The ADC 2250 CO_2 gas analyzer provided simultaneous absolute and differential gas measurements. Single bench (CO_2) peak-to-peak noise was typically <0.2 ppmV at 350 ppmV

CO_2. All CO_2 measurements were corrected for any pressure broadening and dilution effects caused by water vapor. The CO_2 fluxes from the sealed chambers were determined by circulating air continuously from the chambers through the CO_2 analyzer, and back into the chambers. The ADC analyzer allowed for scrubbing of the CO_2 using soda lime within the system for lower fluxes. When scrubbing could not be done internally, a larger soda lime scrubber was externally incorporated in the system. During the scrubbing mode, the air flow lines were re-routed to the larger scrubber by means of 3-way connector valves.

Prior to use in the DCCS, the accuracy of the CO_2 concentrations measured with the gas analyzer was tested by analyzing the CO_2 gas concentrations of a set of 14 gas samples collected from all gas ports in both HT and LT minicosms with the analyzer and the Carle GC. The CO_2 concentrations determined using the two methods agreed very well ($R^2 = 0.99$) over the range in CO_2 concentrations measured (0.04–0.21%) and showed that the ADC analyzer yields representative CO_2 concentrations.

Soil respiration from the HT minicosm was also measured over the entire surface area of the column (0.26 m^2). A Plexiglas lid (0.005 m thick) fitted with inlet and outlet fittings, and a rubber O-ring was fabricated in the manner similar to the smaller chamber lid described earlier. A perforated rubber tubing (1.20 m long) was fitted on the underside of the lid to provide uniform air-dispersion in the headspace. The lid was sealed to the column by clamps. The headspace volume between the soil surface and the lid was reduced from 13 to 1.8 l using foam materials fitted on the underside of the lid. Mixing in the headspace was supplemented using an external hand-operated vacuum pump NALGENE™ brand (Nalge Company, USA) incorporated in the line system connecting the analyzer and the lid fittings. The pump was fitted with a vacuum inlet and outlet, and a vacuum gauge. Air was exhausted at the rate of 36 cc/stroke (at atmospheric pressure). A soda lime CO_2 scrubber was connected in series with a hand-operated pump. This pump was used only during the CO_2 scrubbing mode from air from the chamber. In this mode, air was pumped through the soda lime CO_2 scrubber and back into the chamber using the hand-operated pump. The analyzer was in the meantime discon-

nected from the chamber via 3-way connector valves. The duration of the scrubbing and mixing using the hand-operated pump was dictated by the magnitude of the flux and the capacity of the soda lime CO_2 scrubber.

Prior to measuring fluxes, the ambient CO_2 concentrations (100% atmospheric CO_2 level) were measured at the collar. CO_2 was scrubbed from the air in the sealed chambers to lower the CO_2 concentration below ambient (approximately 99.5% ambient). In the measurement mode, the analyzer measured the CO_2 concentrations in the chambers, as the concentrations increased across the ambient CO_2 concentration, to higher concentrations (to approximately 100.5% ambient). The slopes were determined at the ambient concentrations. During this time-period, the CO_2 concentrations in the chambers were measured at intervals of 1 s and mean concentrations were recorded every 10 s. The flow rate through the chambers were maintained at approximately 39 l/h. The flux of CO_2 from the soil surface was calculated from the rate of change of CO_2 concentrations (ppmV) in the chambers using:

$$F = [\partial C / \partial t]^* h \qquad (1)$$

where F is the rate of CO_2 flux from the soil surface (mg/m^2/h), C the concentration in the chamber at ambient temperature and pressure, t the time, h the chamber height (m), and $\partial C / \partial t$ is the slope of the best fit of the time series as time approaches zero (Healy et al., 1996). The height, h, was selected based on the expected magnitude of the flux. The value of h was determined by measuring the variations in depth to soil surface from the top of the collars.

Fluxes were determined by averaging a series of between 6 and 10 measurement cycles. The time required to determine a series of flux measurements was about 2–15 min, depending on the magnitude of the flux. The sampling period was short, and therefore, changes in soil temperature and water content were negligible and buildup of CO_2 in the chamber was limited (Janssens et al., 2000).

Results of tests conducted to optimize soil respiration measurements using the DCCS (data not presented) showed that optimum fluxes were obtained when the headspace volume in the small chambers (0.062 m^2) was less than 0.6 l and the flushing rate (the ratio of the flow rate (l/min) over the volume of

the chamber (l)) was greater than unity. All reported DCCS measurements using the small chamber (0.062 m^2) were conducted within these limits. The use of the entire minicosm surface area (0.26 m^2) to measure CO_2 fluxes required a more rigorous (effective) mixing in the headspace to obtain a flushing rate greater than unity. A hand-operated pump was thus used to supplement the internal pump within the analyzer.

The optimization of DCCS procedure and measurements of CO_2 fluxes from minicosms using the small chamber and over the entire surface area was conducted over a 21-day period from day 1380 to day 1401 and day 1590 to day 1401, and from mesocosm over a 30-day period from day 2443 to day 2471 (also using the small chamber). Both the small chamber and the entire surface area of the minicosm were used in the assessment of the CO_2 fluxes measured by DCCS method in the HT minicosm over a 30-day period from day 1624 to day 1646.

2.5. Static chamber method

Soil respiration was determined using alkali traps (static chambers) by adsorbing the CO_2 effluxing from the soil into a sealed headspace chamber for a specific period of time using NaOH solutions. At the end of the adsorption period, the total mass of CO_2 in the alkali traps were determined by titrating the NaOH solutions from pH 8.3 to 3.7 with dilute 0.05N HCl for the minicosms and 0.1N HCl for the mesocosm, respectively.

For the static chamber measurements in the minicosms, 50 ml of 0.1N NaOH solutions were placed in beakers (0.057 m o.d.) on the surface of the minicosm and the entire surface area of each minicosm (0.26 m^2) was sealed using the air-tight lids. In the mesocosm, 100 ml of 0.5N NaOH solutions were placed in each of the two chambers. Each chamber covered an area of 0.025 m^2 (1.5 m apart in an east–west direction). These chambers were designed in the manner described by Garrett and Cox (1973) with a maximum chamber height of 0.2 m and a radius of 0.089 m pressed into the soil surface to a depth of 0.075 m. The areas of the beakers were 1 and 10% of the surface areas enclosed by the chambers in the minicosms and mesocosm, respectively.

Although detailed laboratory experiments were not conducted to optimize the design of the measurement procedure used with the CO_2 absorption method, a comparison of available literature with our experimental setup (see description earlier) indicated that the analytical conditions used to measure CO_2 fluxes from the minicosms and mesocosm with NaOH solutions were within an acceptable range. Research shows that different solution strengths, volumes, chamber sizes, absorption times, and absorption areas can affect the calculated flux using this technique (e.g. Kirita 1971; Gupta and Singh 1977). Gupta and Singh (1977) showed that increasing the normality of NaOH from 0.25 to 0.75N has no effect on CO_2 absorption capacity when sufficient volumes (>30 ml) of NaOH were used. They indicated that increasing the absorption area up to 19.9% of the total surface area of the ground enclosed had no effect on CO_2 absorption at 0.25 and 0.5N alkali concentrations. Minderman and Vulvo (1973) also show that additional increase in the volume of the NaOH volume beyond 30 ml had no effect on the measured rate of soil respiration at the concentrations tested (in the range of 0.5–2N).

The flux F was calculated using the total amount of CO_2 trapped over the adsorption period (t_{ads}):

$$F = (C_{trap} - C_{blank})/t_{ads}A \qquad (2)$$

where C_{trap} is the amount of CO_2 trapped in an enclosure and A is the area of the surface covered by the chambers. The use of a blank (C_{blank}) accounted for any bias related to the contamination of the alkali solution.

The NaOH solutions were sealed in the chambers for adsorption times ranging from 1 to 48 h and from 1 to 110 h for the minicosms and mesocosm, respectively. The NaOH solutions were titrated immediately after removal of the solutions from the sealed chambers. All measurements were done in duplicate. Alkali CO_2 fluxes were measured from day 1411 to day 1442 and day 2443 to day 2478 for the minicosm ($n = 2$) and mesocosm ($n = 2$), respectively.

2.6. Concentration gradient method

The concentration gradient method was used to calculate respiration rates in the mesocosm and minicosms. Using steady-state CO_2 concentrations at the shallowest depths between 0 and 0.64 m for the

mesocosm and between 0 and 0.02 m for the mini-cosms, the flux to the atmosphere was calculated using Fick's first law:

$$F = -D_e \frac{\partial C}{\partial z} \qquad (3)$$

where F is the flux of CO_2 gas (mg CO_2/m²/h), D_e the effective diffusion coefficient in soil (m²/h), C the concentration of gas (mg CO_2/m³) of air, and z is the depth (m).

The effective diffusion coefficient was calculated for the volumetric water content and total porosity using the relation given by Millington and Quirk (1959):

$$D_e = \frac{\theta_{air}^{10/3}}{\eta^2} D_g \qquad (4)$$

where θ_{air} is the volumetric gas content (m³_air/m³_soil), η the total porosity (m³_voids/m³_soil), and D_{air} is the CO_2 free-air diffusion coefficient (m²/h).

The volumetric gas content was determined by the following relationship:

$$\theta_{air} = \eta - \theta_w \qquad (5)$$

where θ_w is the volumetric water content.

Results of θ_w and η estimates on representative samples for the mesocosm and HT and LT minicosms were determined. Oven drying yielded values of porosities of 0.44 and 0.42 and dry density values of 1.58 and 1.54 for the sand in the mesocosm and mini-cosms, respectively. These data were used to approximate D_e values using Eq. (4).

The CO_2 gas diffusion corrected for temperature is given by the equation of Bird et al. (1960):

$$D_g = D_{g(uncorrected)} \left(\frac{T}{T^0} \right)^b \qquad (6)$$

where D_g is the gas diffusion coefficient, corrected for temperature (m²/h), $D_{g(uncorrected)}$ the gas diffusion coefficient, not corrected for temperature (m²/h), T the subsurface temperature (K), T^0 the reference temperature (298.15 K) and b is a constant.

Values of b range from 1.4707 to 2. Fuller et al. (1966) showed that a b value of 1.75 yields a reasonable agreement for most binary systems. Bird et al. (1960) and de Jong and Schappert (1972) used 1.823 and 2, respectively. The free-air diffusion coefficient for CO_2 was determined to be 5.47×10^{-2} m²/h at 20 °C using Fuller et al. (1966).

2.7. Testing of the CO_2 efflux techniques

The accuracy of the techniques to measure soil respiration rates were tested by injecting known constant flow rates of CO_2 gas into the HT minicosm through the gas port at 0.60 m depth. A gas with a known CO_2 concentration (8.16%, remainder nitrogen) was injected through the port using a MKS 1179A Mass-Flow Controller (MKS Instruments, Inc., Andover, MA) with a range of 50 standard cubic centimeter per minute interfaced to a MKS 246B Single Channel Readout (MKS Instruments, Inc., Andover, MA). The 1179A Flow Controller accurately controlled the mass flow rate of the gas according to given set points. In these tests, the control range of the MKC 246B ranged from 2 to 100% of full scale (FS) with an accuracy and resolution of ±1 and 0.1% of FS, respectively.

The gas was injected at a rate of 0.33 l/h (400 mg CO_2/m²/h) starting on day 1624. Once the CO_2 concentrations approached steady-state conditions at the gas ports (about day 1637), CO_2 flux from the surface of the minicosm to the atmosphere was determined using the DCCS, static chamber, and concentration gradient methods. For the DCCS testing, both the small chamber (0.062 m²) and the entire surface area of the minicosm (0.26 m²) were used. In contrast, static chamber measurements were only performed by completely sealing the surface of the minicosm with the lid. After these fluxes were measured, the gas flow injection rate was doubled (800 mg CO_2/m²/h) and the measurement procedure repeated. Once CO_2 concentrations at the gas ports approached steady-state conditions (about day 1645), CO_2 fluxes from the surface of the minicosm to the atmosphere were again measured using the DCCS, static chamber, and the concentration gradient methods. In the case of the DCCS testing, only the entire surface area of the column was used to measure the CO_2 fluxes from the surface of the minicosm to the atmosphere.

3. Results and discussion

3.1. Steady-state CO_2 concentration profiles in the minicosms and mesocosm

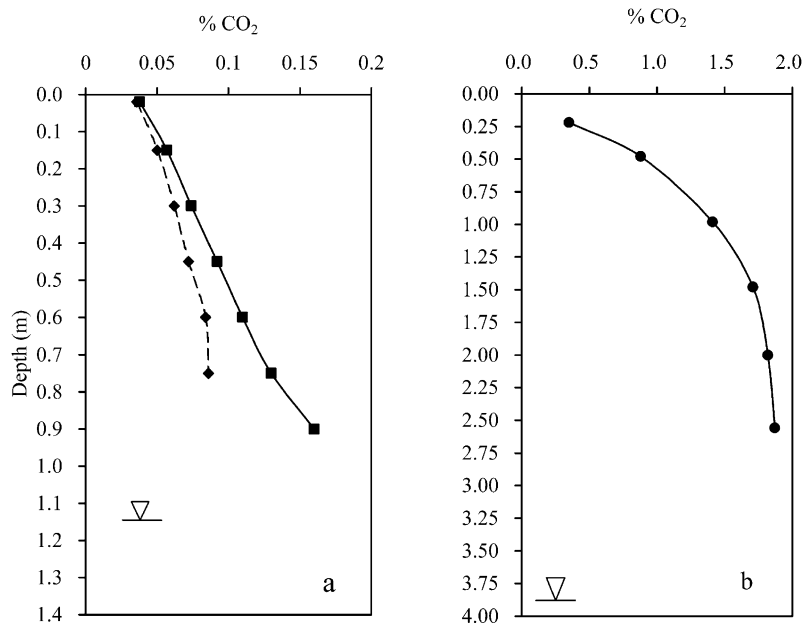The results of CO_2 gas analyses on samples from

Fig. 1. Average CO_2 concentration profiles in the (a) low temperature (5 °C) (♦) and high temperature (21–23 °C) (■) minicosms and (b) the nest of gas ports installed in the east side of the mesocosm (●). The water table is denoted by ▽.
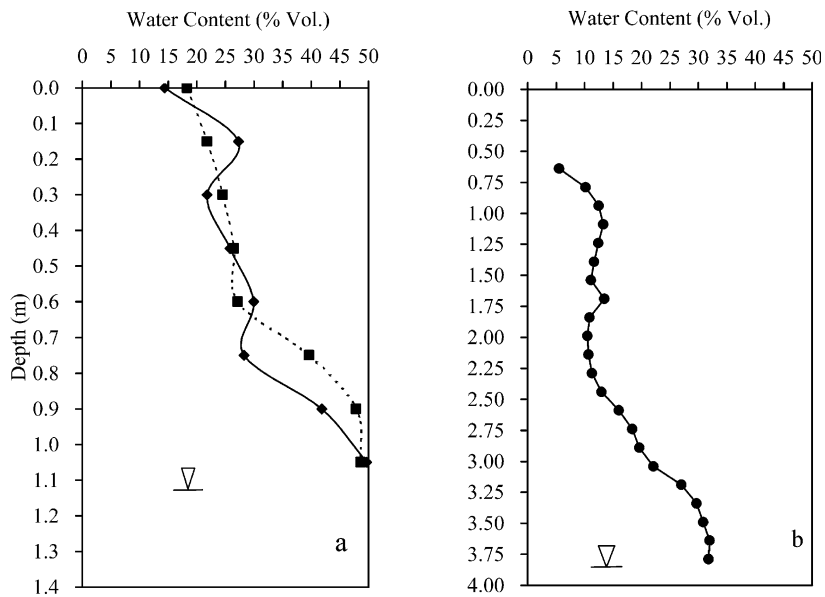

Fig. 2. Average volumetric water content profiles in the (a) low temperature (5 °C) (♦) and high temperature (21–23 °C) (■) minicosms and (b) mesocosm (●). The water table is denoted by ▽.

Table 1
Summary of CO_2 fluxes (mg $CO_2/m^2/h$) to the atmosphere determined in the minicosms and the mesocosm

Method	Minicosms		Mesocosm	HT	
	LT	HT		400 mg $CO_2/m^2/h$, injection A	800 mg $CO_2/m^2/h$, injection B
DCCS	85	107	296	504	897
Static chamber (1 h)	19.7	17.8	267	16	27
Static chamber (44–48 h)	3.7	6.8	41	19 (19 h)	66 (19 h)
Gradient	65	95	312	296	610

the gas ports from day 1324 to day 1600 in the minicosms and day 2254 to day 2600 in the mesocosm are presented in Fig. 1. The CO_2 concentrations increased with depth, reaching the greatest concentrations at the capillary fringe. The average CO_2 concentrations for the HT and LT minicosms ranged from 0.04 (0.02 m) to 0.13% (0.75 m) and from 0.04 (0.02 m) to 0.08% (0.75 m), respectively. Concentrations in the mesocosm ranged from 0.04 (0.22 m) to 2% (3 m). Statistical analysis of the CO_2 data ($n = 74$) from the duplicate sets of gas ports in the mesocosm (1.5 m apart in an east–west direction) showed that there was no lateral variability in CO_2 concentrations ($R^2 = 0.997$). This was in keeping with the findings of Hendry et al. (2001). As a result, only the east set of gas data are presented in Fig. 1. Standard deviations in CO_2 concentrations ranged from 0.004 to 0.017% and from 0.013 to 0.12% for the minicosms and mesocosm, respectively. The small standard deviations suggest that the CO_2 concentrations were at or very near steady-state conditions during the study period. The presence of CO_2 concentrations above atmospheric values (0.03%) in both the minicosms and mesocosm was attributed to microbial activity in the C-horizon sand (Richards, 1998; Hendry et al., 2001).

3.2. Moisture content profiles

Soil moisture content data were used to calculate CO_2 fluxes with the concentration gradient method. The results of the mean moisture content data ($n = 10$) from day 2303 to day 2622 for the mesocosm are presented in Fig. 2(a). The mean moisture content varied from 4.15% at 0.64 m depth to 32.1% at 3.79 m depth. The water content in the mesocosm increased with increasing depth except from 1 to 2 m depth. In this zone, the water content remained

consistently high, which was attributed to heterogeneity introduced during filling (Hendry et al., 2001). Hendry et al. (2001) observed this same depth trend from day 30 to day 1492. The strong similarity between these data sets showed that the mesocosm was at steady state with respect to moisture content for over 2400 days. Although moisture content profiles were not measured in the minicosms during the period of interest, they did reach steady-state conditions after day 100 (Richards, 1998) (Fig. 2(a)).

3.3. CO_2 fluxes to the atmosphere under steady-state gas concentrations

Soil respiration rates from the minicosms and mesocosm under steady-state CO_2 gas concentrations (day 1324 to day 1646 and day 2254 to day 2604, respectively) were determined using the optimized DCCS, static chambers, and the gradient method. Results of these measurements and calculations (Table 1) yielded a wide range of fluxes for the minicosms and mesocosm. The DCCS technique yielded mean CO_2 fluxes in the HT minicosm of 104 mg $CO_2/m^2/h$ (sd = 7.7 mg $CO_2/m^2/h$; $n = 7$) and 112 mg $CO_2/m^2/h$ (sd = 13 mg $CO_2/m^2/h$; $n = 8$), using the small chamber and the entire surface area of the minicosm, respectively. Student's t-test analysis between the fluxes determined using the two chambers yielded a good correlation ($R^2 = 0.73$) and indicated that these two sets of data are from the same population and showed that sampling area did not influence the fluxes. As a result, these two data sets were combined to yield a mean flux of 107 mg $CO_2/m^2/h$ (sd = 15 mg $CO_2/m^2/h$; $n = 20$) for the HT minicosm using DCCS. The mean flux value from the LT minicosm was 85 mg $CO_2/m^2/h$ (sd = 5 mg $CO_2/m^2/h$; $n = 8$) using only the smaller chamber. The DCCS technique
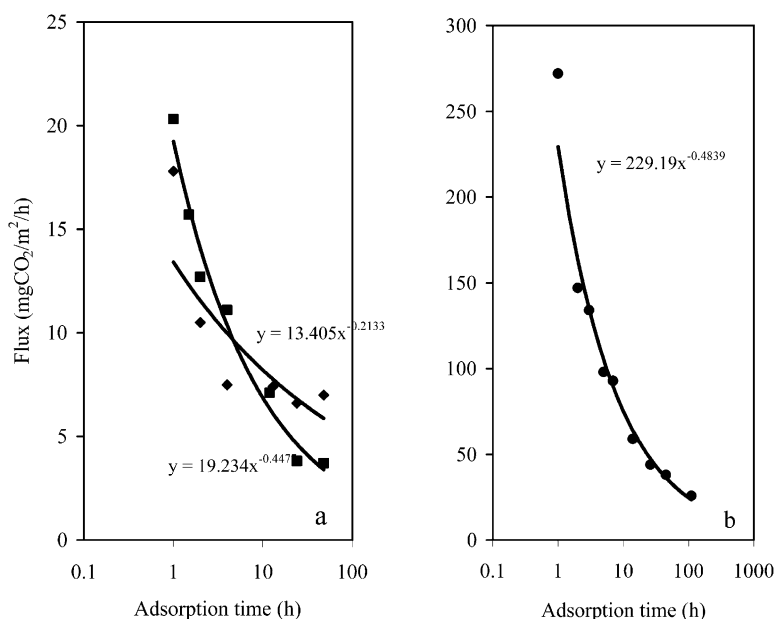
Fig. 3. Variations in CO_2 fluxes for various adsorption times measured with static chambers (alkali traps) for (a) the LT (◆) and HT (■) minicosms and (b) mesocosm (●).

yielded a mean flux of 296 mg $CO_2/m^2/h$ (sd = 20 mg $CO_2/m^2/h$; $n = 21$) from the mesocosm.

Duplicate CO_2 fluxes determined using static chambers installed in the mesocosm for a range in adsorption times yielded identical results ($R^2 = 0.999$; $n = 36$; data not presented). This indicated that the static chamber technique was reproducible. The CO_2 fluxes determined using static chambers installed in the minicosms and mesocosm were very sensitive to adsorption times, exhibiting a power decrease with time (Fig. 3). Fluxes from the minicosms decreased with increased adsorption time from 17.8 to 20.3 mg $CO_2/m^2/h$ for adsorption time of 1 h to minimum values of 7 and 3.7 mg $CO_2/m^2/h$ for an adsorption time of 48 h, for the HT and LT minicosms, respectively. Similarly, fluxes from the mesocosm decreased from 267 mg $CO_2/m^2/h$ for adsorption times of 1 h to minimum values of about 24 mg $CO_2/m^2/h$ for an adsorption time of 110 h. Alkali CO_2 flux values reported in the literature were mostly obtained under long adsorption times, typically over 24 h (cf. Edwards, 1982; Buyanovsky et al., 1986; Beyer, 1991; Norman et al., 1992; Rochette et al., 1992; Franzluebbers et al., 1995; Hendry et al., 2001). Rochette et al. (1997), however, noted that alkali

traps provide an integrated estimate of the flux over an extended period, typically 4–24 h. The short period of time (<24 h) available for adsorption reduced the errors associated with the distortion of the concentration gradient (Rochette et al., 1997; Healy et al., 1996). Long adsorption times (>48 h), however, make it difficult to prevent any disturbance of the natural conditions and to avoid the risk of serious bias on the flux measurement by the alkali traps (Ewel et al., 1987; Rochette et al., 1992; Norman et al., 1992; Nay et al., 1994; Rochette et al., 1997). The CO_2 flux values obtained using the static chamber method for adsorption times longer than 24 h compared well with reported data for the mesocosm (Hendry et al., 2001).

Soil respiration rates determined using the concentration gradient method were 312 mg $CO_2/m^2/h$ for the mesocosm and 95 and 65 mg $CO_2/m^2/h$, for the HT and LT minicosms using a b value of 1.75 (Fuller et al., 1966). Steady-state CO_2 concentrations and the soil moisture content at the shallowest depths between 0 and 0.022 m for the minicosms and 0 and 0.20 m for the mesocosm were used to calculate CO_2 fluxes by the gradient method. The shallowest depth for soil moisture measurements in the mesocosm, however,
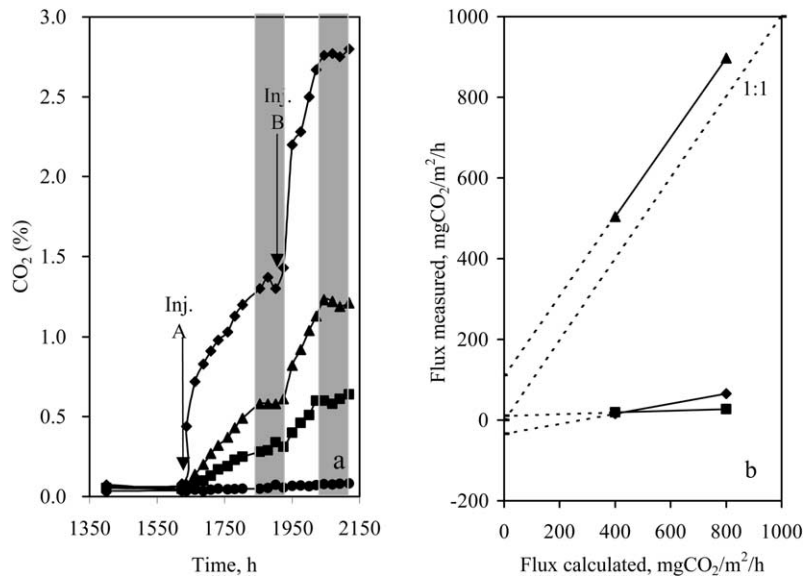
Fig. 4. Results of injections of known fluxes of CO_2 gas at a depth of 0.6 m below surface in the high temperature minicosm (a) measured CO_2 gas concentrations vs. time (at depths of ● 0.02 m, ■ 0.15 m, ▲ 0.30 m, ◆ 0.45 m) and (b) measured CO_2 fluxes vs. injected CO_2 fluxes (▲ DCCS, ■ Alk(1 h), ◆ Alk(19 h)). In (a), Inj. A and Inj. B denote the start of the injection of known fluxes of CO_2 into the minicosm and the highlighted areas define regions of near steady-state CO_2 concentrations after each injection.

was at 0.98 m depth. It was desirable to use values of soil moisture content and CO_2 concentrations measured at exactly the same depth, since the effective diffusion coefficient of CO_2 is sensitive to moisture content. This could have affected the flux values.

In summary, the DCCS and concentration gradient methods yielded comparable CO_2 fluxes of 296 and 312 mg $CO_2/m^2/h$ for the mesocosm. However, the DCCS method, yielded CO_2 flux values that were 1.4 and 1.2 times greater than those obtained using the gradient method for the HT and LT minicosms, respectively. In contrast, the static chamber method yielded CO_2 fluxes that were more than 7 and 20 times lower than those measured by DCCS and concentration gradient methods for the mesocosm and minicosms, respectively for adsorption times >24 h. However, the static chamber yielded a relatively high flux value of 269 mg $CO_2/m^2/h$ for an adsorption time of 1 h for the mesocosm. This value is similar to than those obtained with the other two methods. These findings are supported by Rochette et al. (1997) who reported some agreement between dynamic closed chambers and alkali traps for short adsorption times (<24 h).

The variability in flux measurements prohibited an

assessment of which, if any, of the three flux methods best approximated the actual soil respiration rate. However, coupling these measurements with additional measurements made under conditions of adding known fluxes of CO_2 near the base of the HT minicosm to the natural flux allowed us to assess the flux measurement techniques over a range in CO_2 fluxes observed in natural environments.

3.4. Assessment of the CO_2 flux measurement methods

CO_2 flux of 400 and 800 mg $CO_2/m^2/h$ were introduced into the HT minicosm to approximate the range of CO_2 fluxes commonly reported under field conditions. For example, Jensen et al. (1996) reported forest and pasture rates by the dynamic method ranging between 30 and 300 mg $CO_2/m^2/h$. These rates were similar to those reported for other temperate systems (Cropper et al., 1985; Ewel et al., 1987; Beyer, 1991; Norman et al., 1992). In arable lands, rates obtained by the static method ranged from 0 to ca. 300 mg $CO_2/m^2/h$ and by the dynamic method from 0 to ca. 2500 mg $CO_2/m^2/h$ (Jensen et al., 1996). De Jong and Schappert (1972) reported the average respiration of about 1090 mg $CO_2/m^2/h$ in summer in native

prairie grassland by the concentration gradient method. Striegl and Wickland (1998) and Clark and Kemper (1967) reported fluxes measured on bare soils ranging from 94 to 300 mg $CO_2/m^2/h$.

The evolution of the CO_2 concentration profiles in the HT minicosm from the onset of the injection of known fluxes of CO_2 gas (day 1626) are presented in Fig. 4(a). A near steady-state CO_2 concentration profile was attained within 300 h of the start of injecting CO_2 (400 mg $CO_2/m^2/h$). At these near steady state, the CO_2 concentrations, the CO_2 concentration profiles ranged from 1.4% at 0.45 m to 0.03% near the soil surface. After 300 h, the CO_2 injection rate was increased to 800 mg $CO_2/m^2/h$. Near steady-state conditions were attained with respect to the CO_2 concentrations within about 500 h. Under this flux, near steady-state CO_2 concentration profiles ranged from 2.8% at 0.45 m to 0.082% near the soil surface.

The CO_2 fluxes from the surface of the minicosm to the atmosphere were determined using the DCCS, static chamber, and concentration gradient methods at each of the two injection conditions. Results are presented in Table 1. For an injection of 400 mg $CO_2/m^2/h$, the results of applying the DCCS technique using the small chamber (0.062 m^2) and the entire minicosm surface area (0.26 m^2) produced very similar mean flux values of 505 ± 20 mg/m^2/h ($n = 7$) and 504 ± 20 mg/m^2/h ($n = 8$) for the small chamber and the entire minicosm surface area, respectively. The mean flux from the minicosms to the atmosphere under an injection rate of 800 mg $CO_2/m^2/h$ was measured as 897 ± 20 mg $CO_2/m^2/h$ ($n = 8$) using the DCCS technique and the entire minicosm surface area.

A linear regression of the DCCS fluxes vs. the associated injected fluxes ($n = 2$) yielded an intercept of 111 mg $CO_2/m^2/h$ (Fig. 4(b)). Although the regression is based on only two data points, the intercept is within 4% of the DCCS measured CO_2 flux (107 mg $CO_2/m^2/h$). This suggested that the application of the DCCS technique can provide accurate estimates of CO_2 fluxes from soil surface to the atmosphere. This finding was supported by the research conducted by Witkamp (1969), Kucera and Kirkham (1971), Edwards and Sollins (1973), Jensen et al. (1996) and Janssens et al. (2000). Their results also demonstrated that the dynamic method provided accurate estimates of surface CO_2 flux.

In contrast to the DCCS technique, the static chamber method underestimated the fluxes by a factor of more than 15 fold for both injection rates. For the 400 mg $CO_2/m^2/h$ injection rate, the static chambers yielded values of 16 and 19 mg $CO_2/m^2/h$ for adsorption times of 1 and 19 h, respectively. For the 800 mg $CO_2/m^2/h$ injection rate, the static chambers yielded values of 66 and 27 mg $CO_2/m^2/h$ for adsorption times of 1 and 19 h, respectively. This confirmed the observations made by Janssens et al. (2001), Jassens and Ceulemans (1998), Norman et al. (1992) Edwards (1982), Edwards and Sollins (1973) and Kucera and Kirkham (1971), that the alkali trap method grossly underestimates fluxes, especially for higher CO_2 fluxes. It is noted that the NaOH solution strengths used in these static chambers were not increased although higher flux rates were expected after injection of known CO_2 gas into the bottom of the HT minicosm. This may explain, in part, the poor results of the alkali trap technique when applied to the minicosms.

The concentration gradient method underestimated the fluxes by a factor of more than 1.5 for both injection rates. This method yielded values of 296 and 610 mg $CO_2/m^2/h$ for the 400 and 800 mg $CO_2/m^2/h$ injection rate. This finding confirmed the observations made by Freijer and Leffelaar (1996) that the concentration gradient method typically underestimates CO_2 fluxes and that the magnitude of the errors made by the application of Fick's law to model gas transport associated with soil respiration depend strongly on the variables that are compared, and the way Fick's law is implemented.

4. Conclusions

The results of this study showed that the DCCS technique can yield reliable measurements of CO_2 fluxes to the atmosphere over the wide range of fluxes observed in natural environments. The results of this study also confirmed that the alkali trap method, as used, underestimates fluxes, especially when using long adsorption times (>24 h). The quality of measurements of CO_2 flux using the alkali traps may however be improved by optimizing the chamber dimensions, volumes and strength of solutions, and using short adsorption times (<4 h). In addition,

results showed that although the concentration gradient method yielded reasonable estimates of fluxes in many cases, representative properties for the soils at the shallowest depth must be accurately determined to apply this method since the effective diffusion coefficient of CO_2 is very sensitive to moisture content. The dynamic closed chamber method has distinct advantages over the other methods in terms of accuracy, speed, and repeatability. The method can be used to measure the CO_2 fluxes in situ at the same locations using the same chambers with minimal disturbance of the soil. Based on the tests conducted in this study, the DCCS method is suitable for research to characterize the temporal and spatial dynamics of soil CO_2 fluxes and, as a result, is being used to quantify the spatial and temporal distribution of surface CO_2 fluxes from thick unsaturated waste-rock piles. These fluxes will provided needed upper boundary conditions for mathematical modeling of CO_2 gas production and redistribution in the piles.

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