

A laboratory comparison of two methods used to estimate the isotopic composition of soil $\delta^{13}\text{CO}_2$ efflux at steady state

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Received 27 February 2008; Revised 11 June 2008; Accepted 13 June 2008

The stable isotopic composition of soil $^{13}\text{CO}_2$ flux is important for monitoring soil biological and physical processes. While several methods exist to measure the isotopic composition of soil flux, we do not know how effective each method is at achieving this goal. To provide clear evidence of the accuracy of current measurement techniques we created a column filled with quartz sand through which a gas of known isotopic composition (-34.2‰) and concentration (3000 ppm) diffused for 7 h. We used a static chamber at equilibrium and a soil probe technique to test whether they could identify the isotopic signature of the known gas source. The static chamber is designed to identify the source gas isotopic composition when in equilibrium with the soil gas, and the soil probe method relies on a mixing model of samples withdrawn from three gas wells at different depths to identify the gas source. We sampled from ports installed along the side of the sand column to describe the isotopic and concentration gradient as well as to serve as a control for the soil probe. The soil probe produced similar isotopic and concentration values as the control ports, as well as Keeling intercepts. The static chamber at equilibrium did not identify the source gas but, when applied in a two end-member mixing model, did produce a similar Keeling intercept produced from the control ports. Neither of the methods was able to identify the source gas via the Keeling plot method probably because CO_2 profiles did not reach isotopic steady state. Our results showed that the static chamber at equilibrium should be used only with a Keeling plot approach and that the soil probe is able to provide estimates of uncertainty for the isotopic composition of soil gas as well as information pertinent to the soil profile. Copyright © 2008 John Wiley & Sons, Ltd.

Accurate measurements of the isotopic signature of soil-respired CO_2 are critical to understanding ecosystem metabolism^{1,2} and geologic processes.^{3,4} Yet, a clear technique to sample this flux has not emerged. Current methods include deploying static chambers to capture the $^{13}\text{CO}_2$ gradient evolved from the soil surface over time,^{5,6} deploying dynamic chambers connected to an infrared gas analyzer,⁷ or sampling a static chamber once the volume headspace is in equilibrium with the soil gas.⁸ An alternative to using surface chambers is collecting soil gas within wells that penetrate the soil surface and identifying the isotopic composition of respired CO_2 based on a two end-member mixing model.^{1,9} If we wish to evaluate estimates of soil-

respired $^{13}\text{CO}_2$ using different measurement approaches, the variability due to different measuring techniques needs to be minimized. One strategy to minimize differences between methods is to perform controlled experiments with a known CO_2 source, in the same way as has already been accomplished for soil flux chambers.¹⁰

Relatively few comparisons between measurement methods have been made in field conditions¹¹ and even fewer have been compared in a controlled laboratory experiment. The purpose of this study is to test current methods used to identify the isotopic composition of soil efflux in a well-controlled environment. Recent evidence suggests that data from samples of the CO_2 gradient over time within a static chamber may be prone to misinterpretation,¹² and the dynamic chamber is still in a state of development.⁷ The gas well method has been tested for reliability of soil $^{13}\text{CO}_2$ values¹³ and CO_2 flux,^{14,15} but a similar test for reliable estimates of the isotopic signature of the soil flux has not taken place. Thus, we chose to compare the static chamber at equilibrium⁸ with a series of stacked gas

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Contract/grant sponsor: National Science Foundation; contract/grant number: DEB 0132737, DEB 0416060.

Contract/grant sponsor: The Ecoinformatics IGERT at OSU.

wells, which we refer to as a soil probe, for this test. The selection of these two methods is reasonable given that (1) we gain both a belowground and aboveground perspective of soil-respired $^{13}\text{CO}_2$, (2) both methods are similar in measurement assumptions, and (3) they are both relatively straightforward in their implementation and analysis.

The fundamental difference between the methods we chose is the location from which $^{13}\text{CO}_2$ is sampled: soil CO_2 is collected from the surface using the static chamber whereas the soil probe samples soil CO_2 at depth in the soil. The two methods are similar in that they assume soil CO_2 efflux is at steady state; when the isotopic signature of the CO_2 emitting from the soil surface is equal to the isotopic source of respired CO_2 .¹⁶ The static chamber at equilibrium is designed to measure the isotopic source of respiration, which is impossible to measure from the soil surface unless the isotopic source is at steady state. In the case of the soil probe, the estimate of the isotopic signature of the respiration source is systematically enriched in $^{13}\text{CO}_2$ as a result of soil gas sampled from within the soil matrix. The enriched soil gas is a function of the molecular rate of diffusion by $^{13}\text{CO}_2$, which is slower than that of $^{12}\text{CO}_2$, and results in a greater concentration of ^{13}C in the soil. When the soil CO_2 is at isotopic steady state, the soil probe estimate identifies the source of the isotopic signal of respiration when corrected for this increase in concentration of $^{13}\text{CO}_2$.

To test the static chamber at equilibrium and soil probe methods, we constructed a column filled with sand and plumbed a single CO_2 source of known isotopic value and concentration. We hypothesized that for CO_2 diffusing at steady state both methods will estimate the source gas isotopic composition.

EXPERIMENTAL

Soil probe

This method of sampling involves sampling gas for isotopic composition at different depths in the soil. The soil probe contains three isolated wells made from polyvinyl chloride (PVC). These wells are held at a fixed distance (5, 15 and 30 cm) by PVC tubing. Small diameter holes were drilled around the perimeter of each well which allows for equilibration with the soil gas at depth. A 0.635 cm diameter stainless steel tube was inserted into each well that extends to the soil surface where a stainless steel union was attached resulting in a total volume of 20 cm³ at the 5 cm depth, 23 cm³ at the 15 cm depth, and 27 cm³ at the 30 cm depth. A septum was inserted at the end of the union which allows for sampling with a syringe without atmospheric CO_2 entering the sampled well. The gas sample collected from each well was used in a Keeling plot analysis to identify the isotopic signature of the source gas.

The Keeling mixing model describes a sample of the air in a system as a mixture of two sources of $^{13}\text{CO}_2$, the background atmosphere, and the source of respiration.¹⁷ In field studies it is assumed that the soil source of respiration is a single, well-mixed gas of CO_2 production from microbial and root respiration. For our laboratory experiment, we used a single gas source to meet the assumptions of this model. The Keeling linear mixing model equation that relates the

observed ^{13}C to the observed $[\text{CO}_2]$ is given in Eqn. (1).

$$\delta_{\text{obs}} = \frac{C_{\text{bg}}}{C_{\text{obs}}} (\delta_{\text{bg}} - \delta_{\text{s}}) + \delta_{\text{s}} \quad (1)$$

where C is $[\text{CO}_2]$ and the subscripts obs, s, and bg refer to the observed, source and background values. In Eqn. (1), δ refers to the isotopic value of the component expressed in δ notation:

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000\text{‰} \quad (2)$$

where R is the molar ratio of heavy to light isotopes. The carbon isotope ratio ($\delta^{13}\text{C}$) is expressed relative to the standard Vienna Pee Dee belemnite. The Keeling plot method relies on the regression of the isotopic signature and the corresponding CO_2 concentration, the sample concentrations are inverted in order to apply a linear regression model, from a series of samples of a system. The intercept of the regression is the source of respiration. We used an ordinary least-squares regression model for the Keeling plot analysis; this combination has shown to provide accurate estimates of the isotopic signal of respiration.^{17,18} For estimates of intercept standard error, we bootstrapped the Keeling plot regression (10 000 iterations) using S-Plus (Insightful Corporation, Seattle, WA, USA).

For this application, the Keeling intercept identifies the isotopic source of CO_2 based on the samples that have been enriched in $^{13}\text{CO}_2$ due to kinetic fractionation associated with diffusion.¹⁹ We can correct for this diffusive enrichment by subtracting 4.4‰ from the Keeling intercept but we must also assume the system is at isotopic steady state. If the CO_2 is not at isotopic steady state, the concentration of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ could be less than the steady-state concentrations yielding erroneous isotopic ratios and Keeling intercepts.

Static chamber at equilibrium

We used a 10 cm diameter PVC chamber fitted with a 0.3 cm Swagelock and septum. The bottom of the chamber remained open to allow entry of soil gas when pushed into the sand surface (~1 cm). The static chamber at equilibrium technique assumes that, once in isotopic equilibrium, the isotopic signature of $^{13}\text{CO}_2$ in the chamber space is equal to the source of respired CO_2 .

Sand column system

The sand column was constructed from 1.3 cm thick PVC pipe with a 30.5 cm diameter. The bottom of the pipe was inserted into a PVC cap and sealed with PVC cement. The column was filled with carbonless quartz sand to a depth of 60 cm. The sand has a bulk density of 3.22 g cm⁻³ and a diffusivity of 0.056 cm² s⁻¹. A PVC platform perforated with several 0.3 cm holes held up the column of sand which creates a sandless area approximately 25 cm deep at the bottom of the column. A thin layer of glass wool was laid between the platform and sand to prevent the sand from filling the reservoir. Swagelock bulkhead unions were installed into the sides of the sand column to create ports from which to measure the isotope and concentration profiles. The ports between 5 and 30 cm served as a control to the soil probe and we expected any effects due to the soil probe to materialize as differences in the concentration and

isotopic gradients between the soil probe and side ports. The source gas was plumbed into the reservoir with 0.635 cm diameter Teflon tubing. A Swagelock T connection, capped with a septum, was inserted between the regulator and a needle valve. This connection provided a point along the Teflon line to sample the source gas.

Test

We used the sand column to test the soil probe and static chamber methods in their ability to measure the isotopic composition of an isotopic source diffusing through the sand column. The source gas is a house standard of CO₂ mixed with N₂ yielding an isotopic value of -34.2‰ and CO₂ concentration of 3000 ppm ($\pm 2\%$). We hypothesized that for CO₂ diffusing at steady state both methods will estimate the source gas isotopic composition. At steady state we expected to observe the theoretical 4.4‰ offset between the source gas and the Keeling intercepts that we generated for the soil probe and control ports.

The experiment was run over a 7 h period during which the static chamber, soil probe and control ports were sampled at 2.5 h and 7 h. Source gas was sampled via an in-line T-connector near the tank regulator at 2.5 and 7 h. For each gas sample, a syringe needle was inserted into a septum and 12 mL of sand column gas was withdrawn. The syringe needle was left in the sampling port for at least 30 s to allow for equilibration. The gas samples were then injected into a pre-evacuated (100 mTorr) 12 mL Exetainer (Labco Exetainer[®], High Wycombe, UK). Two samples were withdrawn within 3 min of each other for each depth of the soil probe and control ports and headspace of the static chamber.

We took measures to make sure the gas transport was only diffusive through the sand column. If the transport mechanism was advective, mass flow due to a pressure gradient, then a higher concentration of ¹³CO₂ would be

present in the isotopic signal of the CO₂ emitting from the surface, violating the assumptions of the tested measurement techniques (i.e. the fractionation factor due to diffusion would be less than -4.4‰). To avoid advection from a pressure build-up in the sand column due to source gas flow, we plumbed a pressure release tube into the reservoir space that terminated into a flask of water. The pressure release tube ensured that the pressure in the reservoir was always close to atmospheric pressure.

Sample analysis

All gas samples were run at the Idaho Stable Isotopes Laboratory (ISIL). A gas autosampler (GC Pal, CTC Analytics, Zwingen, Switzerland) is used to sample CO₂ from the Exetainers and this was vented to an isotope ratio mass spectrometer (Delta+ XP, ThermoElectron Corp., Bremen, Germany) via a gas interface (Gas Bench II, ThermoElectron). Standardized CO₂ gases were analyzed every nine samples for assurance of stability, drift correction, and calculation of CO₂ concentration.

RESULTS AND DISCUSSION

In order to test the measurement techniques, CO₂ transport within the sand column was required to be diffusive and at steady state. The CO₂ concentration gradient was linear from the sand surface to the bottom reservoir of the sand column (Figs. 1(A) and 2(A)), as expected from a purely diffusive system,²⁰ and the concentrations predicted by a steady-state model for bulk soil²¹ were similar (Fig. 3), indicating that CO₂ transport was diffusive. To determine if the CO₂ flux was at isotopic steady state, we compared the gas samples from the control ports collected after 7 h with a steady-state isotopic model¹⁵ (Fig. 4). The isotopic values were depleted by at least 1.1‰ with reference to the predicted values, indicating that

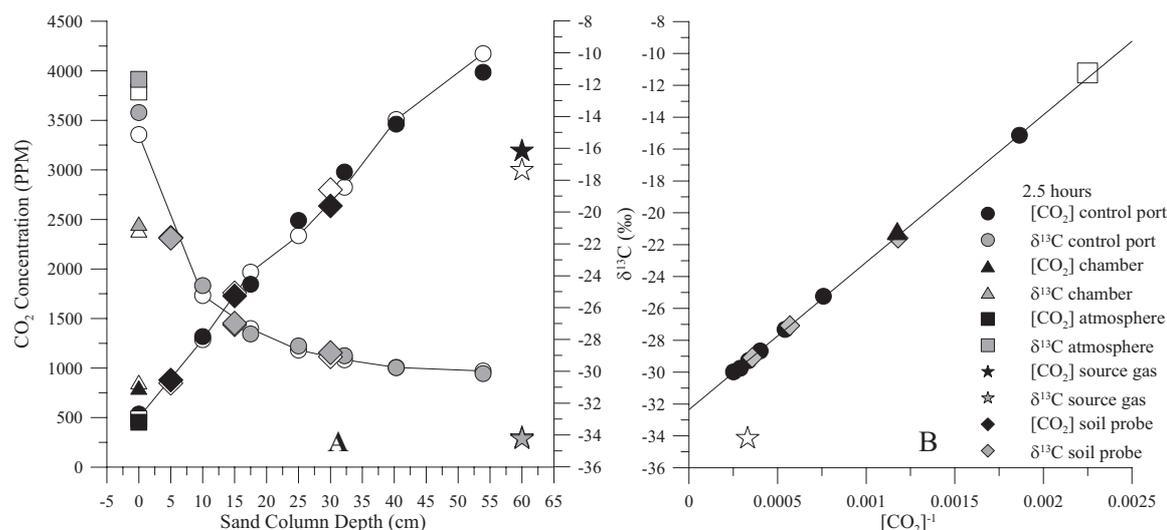


Figure 1. (A) Concentration (black) and ¹³C (grey) gradients after 2.5 h of diffusion of a known gas source through a 60 cm column of quartz sand. The trend line refers to the control port samples. Each depth was sampled twice successively, the solid symbol is the first sample and the open symbol is the second. (B) Keeling plot of the gas samples from the control ports. Samples from the soil probe, static chamber and atmosphere were not included in generating the Keeling plot mixing line.

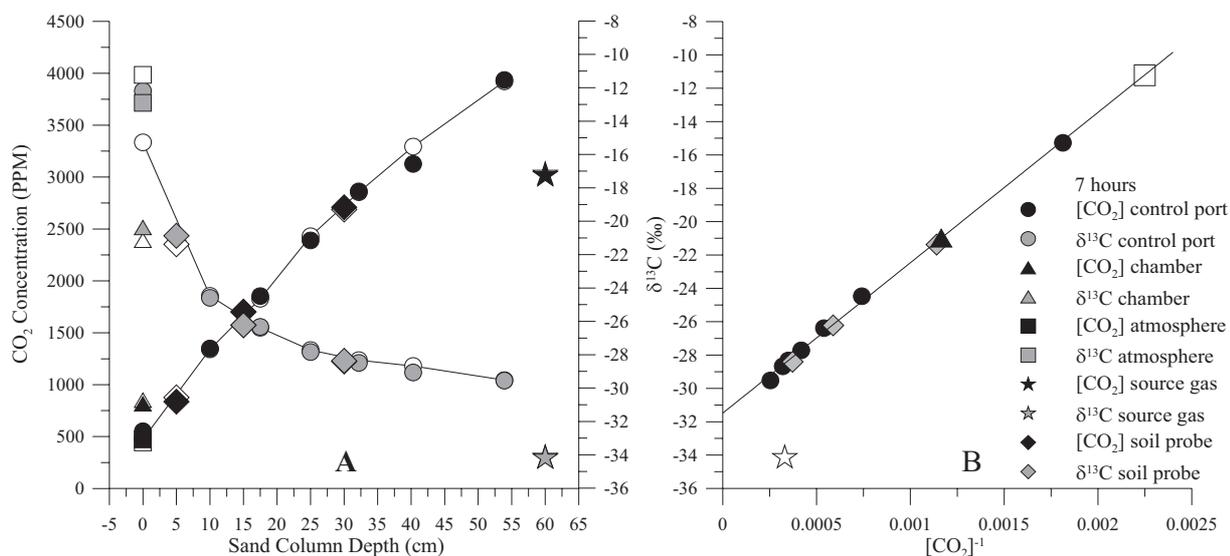


Figure 2. (A) Concentration (black) and ¹³C (grey) gradients after 7 h of diffusion of a known gas source through a 60 cm column of quartz sand. The trend line refers to the control port samples. Each depth was sampled twice successively, the solid symbol is the first sample and the open symbol is the second. (B) Keeling plot of the gas samples from the control ports. Samples from the soil probe, static chamber and atmosphere were not included in generating the Keeling plot mixing line.

the sand column was at near-steady state. The isotopic gradient in the sand column had a curvilinear pattern, as we would expect from a two CO₂ sources mixing,²² and the average change in isotopic value over a 5 h period was less than 0.60‰. The isotopic values of CO₂ at lower depths in the sand column were more depleted than the predicted values and became more enriched over time. This pattern, as predicted by simulations of CO₂ transport,¹⁶ is explained by ¹²CO₂ arriving at steady state before ¹³CO₂. Overall, the sand column system did not interfere with the analysis and

successfully reproduced a purely diffusive system allowing for future comparisons of measurement techniques.

To evaluate any effects that the soil probe might have on the composition of CO₂, we compared samples from the soil probe and from the control ports. The isotopic composition and concentrations of CO₂ from the three depths of the soil probe fell on the same concentration and mixing lines (Figs. 1(B) and 2(B)) as the control ports, and therefore reflected the same δ¹³CO₂ signature derived from the Keeling plot (Table 1). The soil probe did not alter the isotopic

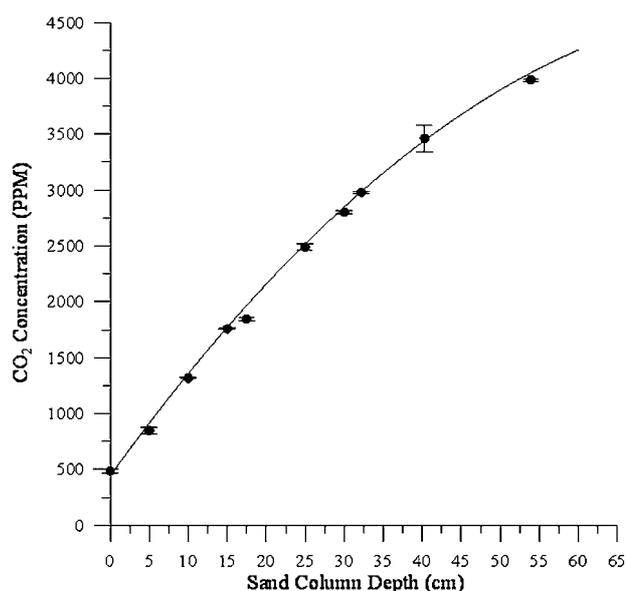


Figure 3. Measured sand column CO₂ concentration values versus concentration values predicted by the steady-state model of Cerling *et al.*²¹ for a rate of production of $2.5 \times 10^{-12} \text{ mol m}^{-3} \text{ s}^{-1}$ and lower flux boundary of 85 cm.

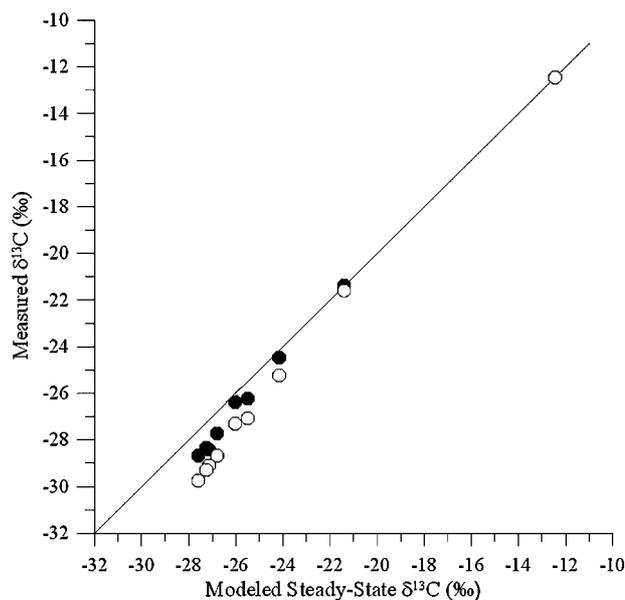


Figure 4. Measured sand column ¹³CO₂ values versus isotopic values predicted by the steady-state model of Amundson *et al.*¹⁶ for a rate of production of $2.5 \times 10^{-12} \text{ mol m}^{-3} \text{ s}^{-1}$ and lower flux boundary of 85 cm.

Table 1. Keeling intercept values (‰) for the soil probe, static chamber and control ports. The standard errors calculated from bootstrapping the Keeling plot (10 000 iterations) are in parentheses. The Keeling intercepts are uncorrected since the sand column was at near steady state. Fractionation factors (‰) represent the difference between the source gas and the Keeling intercept. The static chamber Keeling intercept was calculated with two samples which did not allow for an estimate of intercept error

Sampling method	Keeling intercept 2.5 h (‰)	Δ (‰)	Keeling intercept 7 h (‰)	Δ (‰)
Control ports	-32.5 (0.13)	-1.7	-31.6 (0.12)	-2.6
Soil probe	-32.4 (0.05)	-1.8	-31.6 (0.14)	-2.6
Static chamber	-32.2 NA	-2.0	-32.0 NA	-2.2

composition or concentration of soil gas. There was very little variation between the first and second samples taken at each depth (Figs. 1(A) and 2(B)) for the soil probe and control ports. This suggests that the probe can equilibrate with the surrounding soil gas within 5 min and may therefore capture diurnal variation in field studies.

The static chamber at equilibrium estimate of the source gas was enriched by 13‰ in our experiment. The concentration and isotopic signature of the CO_2 in the chamber at the 2.5 and 7 h sampling resembled values of the soil probe at 5 cm (Figs. 1(A) and 2(A)). The results from this study agree with those from Mora and Raich⁸ who found that the isotopic composition in the static chamber headspace reached equilibrium after an extended period of time; however, the isotopic composition of the gas in the static chamber did not accurately reflect that of the source gas. As depicted by the isotopic and concentration profile, the signal in the static chamber at equilibrium is more likely to be from soil gas at the depth to which the chamber was inserted. In a similar test of a dynamic chamber method on a sand column,⁸ the same conclusions were drawn concerning the insertion depth of the chamber. While the chamber value did not equal the isotopic source in our experiment, the chamber value did fall on the same mixing line (Figs. 1(B) and 2(B)) derived from the control port samples, indicating that the chamber could be used in a Keeling plot with the addition of a sample of the atmosphere (Table 1).

For all sampling methods, the Keeling intercepts were enriched with reference to the source gas, but the fractionation factors after 7 h were $-2.6 \pm 0.1\%$, about half the theoretical value of -4.4% (Table 1). Figure 5 depicts a hypothetical steady-state mixing line that would be approached at steady state if the theoretical diffusive fraction factor of -4.4% is applied. We can estimate the time to achieve isotopic steady state for the sand column, based on our existing data, and the assumption that the approach to equilibrium follows an exponential function:

$$\Delta_{\delta^{13}\text{C}} = 4.4e^{-\left(\frac{t}{\tau}\right)} - 4.4 \quad (3)$$

where τ is the exponential time constant of the system, and T is the time since the beginning of the experiment. A good fit to the data in Table 1 is obtained for $\tau = 8$ h, implying that an approach to steady state would only occur after ~ 48 h. Given the well-known temporal variability in soil flux rates over a diurnal cycle,^{23,24} it is unlikely that typical real-world soil systems ever reach a true isotopic steady state with respect to

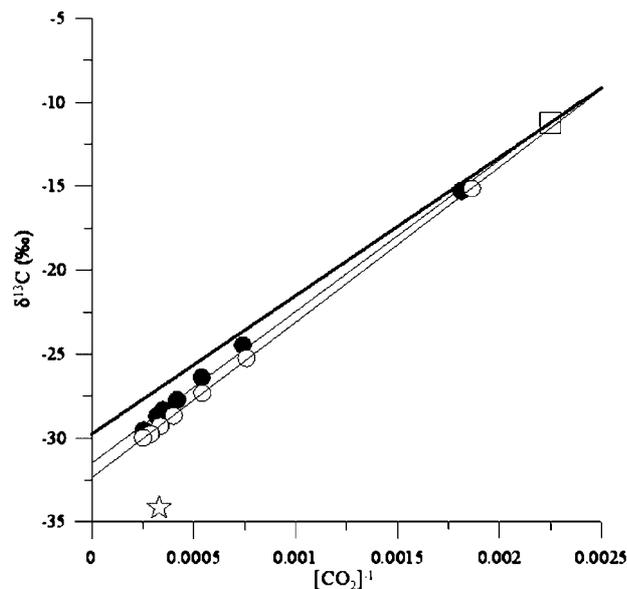


Figure 5. Keeling mixing lines of control port samples after 2.5 h (open symbols) and 7 h (filled symbols) of diffusion of a known gas source in a 60 cm column of quartz sand. The square symbol is the atmospheric value and the bold line is the theoretical mixing line that is needed to achieve a 4.4‰ offset from the source gas (star).

diffusion. This means that field studies that employ isotopic methods to fingerprint sources of CO_2 from soils relative to vegetation must consider non-steady-state effects.

Although our system never reached isotopic steady state, the overall experiment was still able to demonstrate the feasibility of both the static chamber and the soil probe techniques. We have shown that the static chamber can be applied when in equilibrium with the soil gas although only through a Keeling plot approach. However, implementing only two points in a regression for a Keeling plot does not provide enough degrees of freedom for the evaluation of uncertainty in the Keeling intercept. The soil probe that we used in this experiment has three wells, but has the potential for multiple wells, to draw samples from within the soil. This will allow for error estimates of the intercept at the cost of increased mass spectrometer time and labor.

The soil probe has the added benefit of providing samples of soil gas that describe the soil profile. The CO_2 soil profile has been shown to be useful in describing advective and

diffusive boundaries,^{3,19} soil flux,^{25,26} and the effects of meteorological fluctuations on soil gas transport.^{13,27,28} Davidson *et al.*²⁹ used the soil CO₂ profile to determine productivity at different soil depths and thus to discern different contributions to soil respiration. The soil probe could be applied in the same manner to evaluate the isotopic composition of each depth within the soil to provide information regarding isotopic partitioning of soil respiration. For example, in a separate experiment we injected 60 mL of ambient air into the chamber at 30 cm depth and implemented samples accumulated over a 25 min period to identify the isotopic composition at that depth using a Keeling plot. This approach measures the isotopic composition of production at a certain depth. To clarify, the isotopic signal measured here contributes to the isotopic signal of the well-mixed source of the entire soil column which is identified via a Keeling plot as the isotopic signal of soil respiration. In this initial test, the difference between the Keeling intercept and control port value was less than 1% (−36.0‰ calculated value vs. −35.3‰ control port value at 30 cm), indicating that, with further refinement and replication, this technique could be a viable method towards soil component partitioning.

CONCLUSIONS

Using both the static chamber and the soil probe sampling technique we calculated the same Keeling intercept as the control ports. The soil probe provides additional information through CO₂ soil profiles and estimates of uncertainty for the Keeling intercept. After 7 h of diffusive gas transport, CO₂ in the sand column was not at isotopic steady state, and as a result the apparent fractionation with diffusive transport was not fully expressed. Based on the samplings at 2.5 and 7 h after initiating the experiment, we calculate an exponential time constant equilibration of about 8 h suggesting that the approach to isotopic steady state with respect to diffusion would take about 48 h. If our sand column experiment is representative of soil gas diffusion in more complex real-world situations with diurnal cycles of temperature and CO₂ production, our study implies that it is unlikely that these soil systems ever reach isotopic steady state with respect to diffusion. This means that field studies that use carbon isotope signatures to fingerprint CO₂ sources on timescales of less than a few days will have to consider the dynamics of carbon fluxes in diffusive systems.

The inferences drawn from the experiment are limited to the imposed conditions of a carbonless sand medium of homogenous physical properties, no moisture content, a single gas source, and a single concentration gradient. However, the soil matrix is complex in physical and biological properties rendering simple laboratory exercises, such as the experiment presented here, a requisite to identifying the optimal method of sampling.

Acknowledgements

Funding for this research was provided by the National Science Foundation (grants DEB 0132737, DEB 0416060) and the Ecoinformatics IGERT at OSU. We thank Renee Brooks, Claire Phillips and two anonymous reviewers for helpful comments on the manuscript. We also thank Benjamin Miller of ISIL and Andrew Ross of the COAS mass spectrometry lab for their assistance in running samples.

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