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Uncertainties in static closed chamber measurements of the carbon isotopic ratio of soil-respired CO_2

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Abstract

The $\delta^{13}C$ of soil-respired CO_2 (δ_r) is frequently determined using static closed chamber methods. δ_r is obtained as the intercept of the least squares linear regression of δ vs $1/C^*$, where measured $\delta^{13}C$–CO_2 (δ) and volume fraction of CO_2 (C^*) values of chamber headspace samples are used. Theoretically, we show that the variance of the estimate of δ_r can be reduced by extending the $1/C^*$ interval of the regression towards (i) higher or (ii) lower values, or (iii) distributing the $1/C^*$ values optimally within the pre-selected headspace CO_2 sampling time period. Experimental applications of these approaches indicated that: (1) lowering the initial CO_2 level, thereby increasing $1/C^*$, yielded a positive bias to the δ_r result. (2) It was feasible to obtain lower variance in the δ_r estimate by lowering $1/C^*$ values through extended CO_2 sampling time. We also recommend that each chamber is sampled only once, mainly because this allows freedom to select the sampling times, in order to optimize the distribution of $1/C^*$ values.

Keywords: Soil respiration; Isotope ratio mass spectrometry; Keeling plot; Measurement uncertainty; Static chamber

The $\delta^{13}C$ value of soil-respired CO_2 (δ_r) is an important tool both for assessing the role of soils in the global CO_2 budget (Amundson et al., 1998; Flanagan and Ehleringer, 1998; Yakir and Sternberg, 2000), and for tracing local carbon fluxes in soil-plant-atmosphere systems (e.g. Högberg and Ekblad, 1996; Pataki et al., 2003). Despite the recognized importance of δ_r in this context, there are only few studies which discuss uncertainty estimates for δ_r (Cerling et al., 1991; Davidson, 1995; Buchmann and Ehleringer, 1998; Ekblad and Högberg, 2000; Pataki et al., 2003). In this work, we sought to estimate the uncertainty in the measurement of δ_r using a static closed chamber method. This method involves placement of a closed chamber (bottom cross section open) onto the ground to allow respired CO_2 to accumulate for a selected period of time (non-steady state operating conditions), during which the enclosed static (non-flow through) headspace air is sampled at intervals and then analysed (classification scheme given by Livingston and Hutchinson (1995)). The analytical results, volume fraction (C^*) and $\delta^{13}C$ (δ) of CO_2, sampled at a series of time points, are evaluated using a two-component mixing model:

$$\delta C^* = \delta_r C_r^* + \delta_0 C_0^*, \quad C^* = C_r^* + C_0^* \tag{1}$$

where superscript * refers to bulk CO_2 (^{12}C– and ^{13}C–CO_2), and subscripts r and 0 denote respired and initial chamber headspace CO_2, respectively. For evaluation of the δ_r value, rearrangement yields:

$$\delta = \delta_r + (\delta_0 - \delta_r)\frac{C_0^*}{C^*} \tag{2}$$

From Eq. (2) it follows that the δ_r value is determined by A, the estimate of the intercept α of the linear regression of δ ($=y$) against $1/C^*$ ($=x$) data, the so called Keeling plot (Keeling, 1958), defined by the model $y=\alpha+\beta x+\varepsilon$, where β is the slope, and ε the random deviations from the line representing variations in y in time and space

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(with variance σ^2). The aim of this work was to investigate various means to possibly reduce the uncertainty in the estimate of δ_r.

We used least squares regression (LSR), which presupposes that errors are present in the y variable only. Buchmann and Ehleringer (1998) advocate the use of geometrical mean regression (GMR) to account for errors in the x variable, which produce a bias in the LSR-estimate of δ_r. However, with errors in x, GMR yield also biased estimates of δ_r (Angleton and Bonham, 1995; Laws, 1997), and uncertainty estimates of regression parameters are available for LSR, but not for GMR. For these reasons, LSR was selected for this study. Moreover, Pataki et al. (2003) showed that, with $r^2>0.95$ in the Keeling plot, the A values obtained with LSR and GMR, respectively, are approximately equal. This makes the choice between the two methods of less importance. In addition, we performed Monte Carlo simulations of regressions on $y=5000x-24$ (‰, typically obtained here), with 2% relative standard deviation (SD) in x and $\sigma=0.5$‰ for the regression line. This yielded the intercept values of −23.98 and 24.06‰ for LSR and GMR, respectively.

The estimated variance of δ_r was measured by the estimated variance of A, i.e. $\hat{V}(\delta_r)=\hat{V}(A)$. The true variance $V(A)$ is expressed as (Draper and Smith, 1966, p. 21)

$$V(A)=\left(\frac{1}{n}+\frac{\bar{x}^2}{\sum(x_i-\bar{x})^2}\right)\sigma^2 \quad =\frac{\sigma^2}{n}\frac{\sum x_i^2}{\sum(x_i-\bar{x})^2}=\frac{\sigma^2}{n}Q \tag{3}$$

where x_i, $i=1,\ldots,n$ are the values of the independent variable for the n observations, $\bar{x}$ their mean value, and $Q=\sum_{i=1}^{n}x_i^2/\sum_{i=1}^{n}(x_i-\bar{x})^2$. $\hat{V}(A)$ is obtained by exchanging σ for its estimate $\hat{\sigma}$. From Eq. (3), it is seen that $V(A)$ is reduced by the following changes in the experimental design conditions: (i) the number n of observations is increased, (ii) the standard deviation σ is decreased (not feasible because the main contributor to σ is the variation in space and time of the soil respiratory process itself), and (iii) Q is minimized by an optimal selection of the x_i's, which lie within the closed interval $[x_{\min}, x_{\max}]$, where $0<x_{\min}<x_{\max}$. Q is minimized by selecting m_0 of the x_i equal to $x_{\min}$ and the remaining x_i equal to $x_{\max}$, where m_0 is either the integer part of $nx_{\max}/(x_{\min}+x_{\max})$, or this number + 1. Note that this selection of x_i's is recommended only if it is known that the regression function is linear in the interval $[x_{\min}, x_{\max}]$, which should be confirmed experimentally. (iv) Q is minimized also when $x_{\min}$ and $x_{\max}$ is chosen as small and large as possible, respectively.

The proof of the third and fourth statement above is as follows: Q can be written as $Q=1/(1-P/n)$, where $P=\left(\sum_{i=1}^{n}x_i\right)^2/\sum_{i=1}^{n}x_i^2$. To minimize Q is equivalent to minimize P. Consider the modified P equal to $P^0=\left(a+\sum_{\Omega}x_i\right)^2/\left(b+\sum_{\Omega}x_i^2\right)$, where Ω denotes a subset of $i=1,\ldots,n$, and a and b are constants >0. By equating to zero, the partial derivatives of P^0 with respect to the variables in Ω, it is seen that the only solution is $x_k=\left(b+\sum_{\Omega}x_i^2\right)/\left(a+\sum_{\Omega}x_i\right)$ for all i in Ω. This solution yields a maximum of P^0, and thus there is no local minimum of P^0. At the global minimum (on the boundary), at least one of the x_i's with i in Ω is either equal to $x_{\min}$ or $x_{\max}$. Starting with $P_1=P^0(a=b=0)$, we see that at least one of the x_i's (x_1) equals $x_{\min}$ or $x_{\max}$ (at minimum). Inserting this value, we get a function $P_2=P^0(a=x_1,\quad b=x_1^2)$, and by repeating the steps above we obtain the value of x_2 as again either equal to $x_{\min}$ or $x_{\max}$. Consequently, it is seen that the global minimum is obtained by choosing one set of x_i's equal to $x_{\min}$ and the rest equal to $x_{\max}$. If m of the x_i's are chosen equal to $x_{\min}$ (and $n-m$ equal to $x_{\max}$), the value of P equals $P_m=(mx_{\min}+(n-m)x_{\max})^2/(mx_{\min}^2+(n-m)x_{\max}^2)$. Treating m as a continuous variable, $\partial P_m/\partial m=0$ at optimum, which leads to the result that $m=nx_{\max}/(x_{\min}+x_{\max})$. The fourth statement above follows from a derivation of P_m with respect to $x_{\min}$ and $x_{\max}$. This directly shows that P_m (and thus also Q), for every m, is reduced by increasing $x_{\max}$ or decreasing $x_{\min}$.

In the Keeling plot, the $x_{\max}$ value (maximum $1/C^*$ value) could potentially be increased by reducing the initial amount of atmospheric CO_2 within the chamber headspace, e.g. by flushing with CO_2-free air. The $x_{\min}$ value (minimum $1/C^*$ value) could be decreased by allowing the respired CO_2 to accumulate for longer period of time within the chamber. We performed two field experiments to investigate the feasibility of these two approaches for reduction of the uncertainty in δ_r. The site was a Norway spruce (*Picea abies* (L.) Karst.) dominated stand in Umeå, Sweden (63°50′N, 20°20′E), with understorey characterised by *Vaccinium myrtillus* (L.) and *Oxalis acetosella* (L.), and the soil classified as an Orthic Podzol with a mor layer of about 10 cm thickness. The chambers were placed onto the ground with a chamber spacing of >2 m. Chamber size and construction, CO_2 sampling technique and ^{13}C isotopic analysis is described in Högberg and Ekblad (1996). The precision was ≈0.2‰ (SD) for δ, and ≈2% (relative SD) for C^* for analysis of a single gas sample. In the first experiment (see Fig. 1 legend for more experimental details), where the chamber was initially flushed using synthetic air (Linde gas, Sweden; CO_2 mole fraction measured to be ≈9 μl l^{-1}, with $\delta^{13}C\approx-22$‰), the chamber was removed about 1 m from the measurement spot, the chamber basal cross section covered, using a plastic sheet held tightly against the chamber bottom frame. After flushing (at 0.1 l s^{-1} for 3 min), the chamber was positioned at the ground measurement spot, and within 15 s from the repositioning, the plastic sheet was quickly pulled away, thereby exposing the chamber headspace to the soil surface for CO_2 accumulation. In the second experiment (see Fig. 2 legend for more experimental details), the accumulation time was further extended, and it was demonstrated that a limited number (n) of x_i values can be distributed freely within the sampling time interval, if each chamber is sampled only once.