Isotopic corrections for the radiocarbon composition of CO$_2$ in the soil gas environment must account for diffusion and diffusive mixing

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Abstract. Earth system scientists working with radiocarbon in organic samples use a stable carbon isotope ($\delta^{13}$C) correction to account for mass-dependent fractionation. Although researchers apply this correction routinely, it has not been evaluated for the soil gas environment, where both diffusive gas transport and diffusive mixing are important. Towards this end we applied an analytical soil gas transport model across a range of soil diffusivities and biological CO$_2$ production rates, allowing us to control the radiocarbon ($\Delta^{14}$C) and stable isotope ($\delta^{13}$C) compositions of modeled soil CO$_2$ production and atmospheric CO$_2$. This approach allowed us to assess the bias that results from using the conventional correction method for estimating $\Delta^{14}$C of soil production. We found that the conventional correction is inappropriate for interpreting the radiocarbon-incorporated composition of CO$_2$ from biological production, because it does not account for both diffusive transport and diffusive mixing. The resultant $\Delta^{14}$C bias associated with the traditional correction is highest in soils with low biological production and/or high soil diffusion rates. We propose a new correction solution for radiocarbon applications in the soil gas environment that fully accounts for both diffusion and diffusive mixing.

1 Introduction

Understanding the age of soil-respired carbon is important for process-based carbon cycle studies in the face of climate change. By knowing the age of respired carbon, we can make predictions about the rate at which carbon stocks will be transformed under current and future climates. In the case of Arctic environments underlain by permafrost, this is especially important as “ancient” carbon sources previously stored may become available to decomposers as the permafrost thaws.

Radiocarbon allows us to measure the age of soil-respired CO$_2$ (CO$_2$ diffusing from the soil surface to the atmosphere, aka soil flux as in Cerling et al., 1991), but the traditional calculation and reporting convention for radiocarbon was not established for soil gas-phase sampling, but rather for solid (organic matter) sample analysis. The validity of this convention has never been explicitly tested for soil-respired CO$_2$.

The traditional radiocarbon reporting convention (Stuiver and Polach, 1977), uses a mass-dependent correction based on the
isotopic composition of wood. Its purpose is to correct for biochemical fractionation against the radiocarbon isotopologue ($^{14}$CO$_2$) abundance during photosynthesis, which is assumed to be twice as strong as for $^{13}$CO$_2$ based on their respective departures in molecular mass from $^{12}$CO$_2$. The classical reference describing these conventional calculations is Stuiver and Polach (1977).

In the soil gas environment, researchers have different implicit expectations for fractionation processes. They generally assume that $^{14}$C of CO$_2$ is not biochemically fractionated in the gas phase, between the points of CO$_2$ production (biological production of CO$_2$ by soil organisms and roots) and measurement (subsurface or flux chamber samples). This assumption is reasonable based on the short residence time of CO$_2$(minutes to days) in the soil profile before emission to the atmosphere. However, soil gas isotopic signatures depart in predictable ways from the signature of production because of physical fractionation. It has been recognized for decades that $\delta^{13}$C of CO$_2$ at any point in the soil profile will never equal the isotopic signature of production, because of transport fractionations that alter produced CO$_2$ before it is measured (Cerling et al., 1991). This theory extends readily to $^{14}$C. Overall, soil researchers have two implicit expectations, which is that physical fractionations are present, and that biochemical fractionations are absent. To date, no study has examined the conventional radiocarbon corrections with these implicit expectations in mind. We believe the traditional correction should be re-evaluated for soil gas studies.

The principal objective of this study is to determine a way to properly interpret measurements of radiocarbon from the soil gas environment. Using theory and physical modelling of soil gas transport we assess traditional techniques, propose and validate an alternative approach for specific use cases, and consider uncertainties that would result from the misapplication of traditional approaches.

2 Theory

To understand why the mass-dependent correction presented in Stuiver and Polach (1977) may be a poor fit for soil gas studies, we can look at our current understanding of the stable isotopic composition, $\delta^{13}$C, of soil CO$_2$ (pore space CO$_2$, mole fraction with respect to dry air). We use delta notation to present the stable isotopic composition of CO$_2$:

$$\delta^{13}\text{C} = \left(\frac{R_s}{R_{VPDB}} - 1\right) \times 1000,$$

where $\delta^{13}$C is the isotopic composition in ‰ (see Table 1 for a full list of abbreviations), $R_s$ is the $^{13}$C/$^{12}$C ratio of the sample, and $R_{VPDB}$ is the $^{13}$C/$^{12}$C ratio of the international standard, Vienna Pee Dee Belemnite.

From foundational work done by Cerling (1991) we know that the isotopic composition of soil CO$_2$ is different from that of soil-respired CO$_2$. Any change in $\delta^{13}$C of soil CO$_2$ with depth is influenced by 1) mixing of atmospheric and biological (or
biogeochemical) sources of isotopically-distinct CO₂, which may occur via diffusion (no bulk gas flow; referred to as diffusive mixing for the remainder of the paper) or advection (bulk gas flow) and 2) kinetic fractionation by diffusion. The effect of these is illustrated in Fig. 1. In panel (a) two depth profiles of δ¹³C of CO₂ were modelled in a steady-state environment are shown (the model will be described later). The profiles differ only in soil diffusivity; all other characteristics were held constant, including rates of production, and δ¹³C of CO₂ in the atmosphere (-8 ‰; circle) and biological production (-25 ‰; square with dashed line). In the resultant depth profile with higher soil diffusivity in panel (a), the δ¹³C of soil CO₂ ranges from -8 to -15.1 ‰. In the depth profile representing a soil with lower diffusivity, the δ¹³C of soil CO₂ ranges from -8 to -20.6 ‰. We stress again these two isotopic depth profiles differ only due to differences in transport as a result of their varying soil diffusivities. In the depth profile with lower soil diffusivity, atmospheric CO₂ does not penetrate downwards as readily, so the profile shape is much steeper near the soil-atmosphere boundary, and is more reflective of the production source composition, -25 ‰, at depth. In the depth profile with higher soil diffusivity, atmospheric air of -8 ‰ more readily mixes from the surface downward by diffusion, so the near surface isotopic composition will be more reflective of the atmosphere due to diffusive mixing of these end-members near the soil surface.

Importantly, the soil CO₂ never equals the δ¹³C of production (-25 ‰) at any depth, in either profile in Fig. 1(a). It is not possible to directly measure δ¹³C of production in situ, because diffusion and diffusive mixing alter the character of CO₂ immediately after its production. From the site of production in the soil, ¹²CO₂ diffuses somewhat faster through the soil than ¹³CO₂, because the former has lower mass. This diffusive difference leads to isotopic fractionation, and results in depth profiles of δ¹³C of soil CO₂ that are isotopically enriched (less negative) as compared to the source of production. Work by Cerling (1984) and later by Cerling et al. (1991), demonstrated that the mass differences between the two isotopologues led to a difference in diffusion rate of each in air, amounting to a fractionation of 4.4 ‰ (note that this applies only to binary diffusion of CO₂ in air and will differ if CO₂ diffuses in other gases). As a result, the δ¹³C of soil CO₂ measured at any depth will be enriched by a minimum of 4.4 ‰ relative to the biological production CO₂ source. However, the δ¹³C of soil-respired CO₂ can be considerably more enriched than 4.4 ‰ relative to production due to diffusive mixing with the atmosphere as shown in Fig. 1(a).

A convenient theoretical formulation for correcting δ¹³C for both diffusion fractionation and diffusive mixing was introduced by Davidson (1995), following on the work of Cerling (1984) and Cerling et al. (1991). This approach allows one to combine measurements of CO₂ and its isotopic composition within the soil and the air above it, to infer the isotopic composition of CO₂ produced in the soil. This only applies when transport within the soil is purely by diffusion (no bulk air movement). The Davidson (Davidson, 1995) solution uses the difference between the diffusion coefficients for ¹²C and ¹³C as follows:

\[
\delta_{j}^{13} = \frac{C_d(\delta^{13} - 4.4) - C_a(\delta^{13} - 4.4)}{1.0044(C_d - C_a)},
\]

(2)
where $\delta^{13}$ is the $\delta^{13}$C composition of CO$_2$ from soil production (biological respiration within the soil), $C_s$ and $\delta_s^{13}$ are the mole fraction and isotopic composition of soil CO$_2$, and $C_a$ and $\delta_a^{13}$ are the mole fraction and isotopic composition of CO$_2$ in the air just above the soil. In Fig. 2(a) the mole fraction and isotopic composition of soil CO$_2$ at a 40 cm depth and of the air just above the soil was “sampled” from model-generated soil depth profiles and the (unrounded) values were used to calculate the isotopic composition of production using Davidson’s equation ($C_s = 14780$ ppm, $\delta_s^{13} = -20.3832 \%$, $C_a = 380$ ppm and $\delta_a^{13} = -8 \%$). The resulting $\delta_a^{13}$ (e.g. Eq. (2)) at this depth equals the true isotopic composition of production (see inset box, 2(a)). However, because the Davidson approach accounts for diffusion and diffusive mixing, at any given soil depth, not just 40 cm, the modelled values of $C_s$ and $\delta_s^{13}$ in Fig. 1(a) and 2(a) will always yield (via Eq. (2)) the true isotopic composition of production, $\delta_i^{13} = -25 \%$ (dashed line). If $\delta^{13}$C of soil CO$_2$ were (erroneously) interpreted to represent the $\delta^{13}$C of soil-respired CO$_2$, the error could be as large as the absolute value of ($\delta_s - \delta_i^{13}$) $\approx 4.4 \%$. In Fig. 2(a), the error in interpreting $\delta^{13}$C of soil CO$_2$ at 40 cm depth ($\approx -20 \%$) as a value of production would be $\approx -5 \%$, and the error increases in magnitude at shallower depths. This Davidson (1995) $\delta_i^{13}$ approach has been shown to be robust when applied to field data from natural soils (Bowling et al., 2015; Breecker et al., 2012b; Liang et al., 2016).

While $^{14}$C is a radioactive isotope and thus decays with time, the half-life is sufficiently long so that $^{14}$CO$_2$ behaves similarly to stable isotopes on the timescales at which diffusion occurs in a soil gas system. The binary diffusion equation (rate of diffusion $\approx 1/\sqrt{\text{mass}}$) provides us with an expected difference in diffusion rate of isotopologues. In this way, $\delta^{13}$C diffusive fractionation theory can be applied to the radiocarbon isotopic composition, $\delta^{14}$C, so long as we account for the mass difference. The larger mass of $^{14}$C means that the diffusion fractionation factor is calculated to be $8.8 \%$ based on the atomic masses of $^{14}$CO$_2$, $^{12}$CO$_2$ and of bulk air (Southon, 2011).

We can show that $^{14}$CO$_2$ distribution in soils will be like that of $^{13}$CO$_2$, if we model its distribution through depth in the same synthetic soil gas environment. In Fig. 1(b) we present a modelled soil environment with defined atmospheric and production source CO$_2$ isotopic composition boundary conditions for $\delta^{14}$C, the $^{14}$C equivalent to $\delta^{13}$C:

$$\delta^{14}C = \left( \frac{A_s}{A_{abs}} - 1 \right) \times 1000, \tag{3}$$

where $\delta^{14}$C is the isotopic composition in $\%$, $A_s$ is the measured activity of the sample, and $A_{abs}$ is the activity of the oxalic acid standard (both unitless). As in Fig. 1(a), in panel (b) the profile with lower soil diffusivity, the downward penetration of atmospheric CO$_2$ into the soil profile is reduced, and as a consequence the isotopic depth profile more closely reflects (but does not equal) the composition of production ($\approx -50 \%$; dashed line). When the diffusion rate is high and transport is rapid, the atmospheric source is more readily able to penetrate the profile and mix with the production source. In both profiles, the measured value of soil CO$_2$ at a given depth will not equal the isotopic production value of -50 $\%$, because of diffusion and diffusive mixing. Similar profiles of $\delta^{14}$C of soil CO$_2$ with depth, highlighting the diffusive effects, have been presented by
Wang et al. (1994).

Since $\delta^{14}$C transport of soil CO$_2$ is like that of $\delta^{13}$C, it follows that we should apply corrections for $\delta^{14}$C like those in Eq. (2) in order to calculate the isotopic composition of production. The $\delta^{14}$C reformulation of Davidson’s $\delta^{13}$ equation is as follows:

$$
\delta_s^{14} = \frac{C_s(\delta_s^{14}-8.8)-C_a(\delta_a^{14}-8.8)}{1.088(C_s-C_a)},
$$

(4)

where $\delta_s^{14}$ is the $\delta^{14}$C composition of soil production, $C_s$ and $\delta_s^{14}$ are the mole fraction and $\delta^{14}$C composition of the soil CO$_2$, and $C_a$ and $\delta_a^{14}$ are the mole fraction and $\delta^{14}$C composition of CO$_2$ in the air just above the soil. This Davidson reformulation for $\delta^{14}$C, $\delta_s^{14}$, was applied to a model-generated profile of soil $\delta^{14}$C at a 40 cm depth in Fig. 2(b), like in panel (a) for $\delta^{13}$C ($C_s = 14780$ ppm, $\delta_s^{14} = -39.3989$‰, $C_a = 380$ ppm and $\delta_a^{14} = 45.5276$‰; see inset box, Fig. 2(b)). As was the case for $\delta^{13}$C in Fig. 2(a), the modelled values of $C_s$ and $\delta_s^{14}$ at any depth will yield the true isotopic composition of production, $-50$‰ (dashed line), because this approach accounts for diffusion and diffusive mixing.

The traditional approach for interpreting the $^{14}$C composition of soil CO$_2$ and soil-respired CO$_2$ (e.g., Trumbore, 2000) differs from the $\delta^{14}$C example above, because a $\delta^{13}$C correction is applied to account for mass-dependent isotopic fractionation of biochemical origin (Stuiver and Polach, 1977), ultimately converting $\delta^{14}$C to a variant called $\Delta^{14}$C. The derivation of the mass-dependent correction is provided in Stuiver and Robinson (1974), where observations are normalized to an arbitrary baseline value of $-25$‰ for $\delta^{13}$C (a value for terrestrial wood), and the $^{13}$C fractionation factors are squared to account for the $^{14}$C/$^{12}$C fractionation factor as follows:

$$
A_{SN} = A_s \left[ \frac{P_a(-25)}{R_s} \right]^2,
$$

$$
= A_s \left[ \left( \frac{1}{1000} \delta_s^{13} \right)^{RVPDB} \right]^2, \nonumber
$$

$$
= A_s \left[ \left( \frac{1}{1000} \delta_s^{13} \right)^{RVPDB} \right]^2,
$$

(5)

where $A_{SN}$ is the normalized sample activity, $A_s$ is the sample activity, and $\delta^{13}$C is the isotopic composition of the sample (soil CO$_2$ in our case). As explained in Stuiver and Robinson (1974), the 0.975 term sometimes used in forms of $A_{SN}$ is equivalent to $\left( 1 - \frac{25}{1000} \right)$, which we will retain for clarity. The equation for $\Delta^{14}$C, the $\delta^{13}$C corrected variant of $\delta^{14}$C, can then be created from Eq. (5) by substituting in delta notation for $\Delta^{14}$C of $\Delta^{14}$C = $(A_{SN}/A_{abs} - 1)*1000$ as follows Stuiver and Robinson (1974):

5
\[ \Delta^{14}C = \left[ \left( 1 + \frac{\delta^{14}C}{1000} \right) \frac{(1 - \frac{25}{1000})^2}{(1 + \frac{\delta^{14}C}{1000})^2} - 1 \right] \times 1000. \]  

(6)

Combining Eqs. (3) and (6):

\[ \Delta^{14}C_{\text{old}} = \left[ \frac{A \delta}{A_{\text{abs}}} \left( \frac{(1 - \frac{25}{1000})^2}{(1 + \frac{\delta^{14}C}{1000})^2} - 1 \right) \right] \times 1000. \]  

(7)

For more information on the derivation of Eqs. (6) and (7) see Stuiver and Robinson (1974), page 88. In Eq. (7) we have added the subscript "old" to highlight that this is the traditional mass-dependent correction - we will introduce a "new" method with Eq. (15). The terms on the left-hand side of Eqs. (6) and (7) are identical. Note that \( A_{\text{abs}} \) in our notation is equivalent to \( A_0 \) in Stuiver and Robinson (1974).

This traditional approach uses \( \delta^{13}C \) as an input parameter to make a mass-dependent correction to obtain \( \Delta^{14}C \), but the profiles of \( \delta^{13}C \) and \( \delta^{14}C \) of soil \( CO_2 \) (Fig. 1) highlight that both vary within the soil because of diffusion and diffusive mixing. This makes it unclear what form of \( \delta^{13}C \) should actually be used in the correction in the soil gas environment (\( \delta^{13}C \) of the soil \( CO_2 \) is measured, but \( \delta^{13}C \) of biological production is not) as diffusive mixing is not a mass-dependent process. When \( \Delta^{14}C_{\text{old}} \) is modelled through depth like \( \delta^{13}C \) and \( \delta^{14}C \) in Figs. 1 and 2 it also varies with depth as shown in Fig. 2(c). However, using a \( \Delta^{14}C \) variant of Davidson’s \( \delta_j \) (as for \( \delta^{14}C \) in Fig. 2(b)) at the same 40 cm depth does not correctly reproduce the specified model value for the \( \Delta^{14}C \) of production of -50 \%, like it did for \( \delta^{13}C \) and \( \delta^{14}C \) (\( C_\delta = 14780 \) ppm, \( \Delta_\delta = -48.4319 \% \), \( C_a = 380 \) ppm and \( \Delta_a = 10 \% \); see inset box, 2(c)).

For soil studies, there is a discrepancy between conventions for expressing radiocarbon-\( CO_2 \), and our mathematical understanding of soil gas transport. Although theory presented above suggests that the Stuiver and Polach (1977) mass-dependent correction does not correct for soil gas transport processes, these examples do not consider the full possible range of natural soil conditions (diffusivities and production rates). For a more comprehensive exploration, and to test alternative proposed methodologies testing across a range of soil parameters, we used a model approach to simulate realistic natural soil depth profiles of \( ^{12}CO_2 \), \( ^{13}CO_2 \), and \( ^{14}CO_2 \). Once the simulated profiles were generated, we "sampled" from them as if we were making field measurements, and determined the radiocarbon isotopic composition of soil \( CO_2 \). Secondly, we adapted the traditional convention using Davidson’s (1995) theory and tested this new convention in the same way as the traditional one, by simulating soil profiles and “sampling” them to extract the isotopic composition at depth. We then used actual field observations, where natural soil depth profiles were sampled, to test the discrepancy between old and new correction methods used to report \( \Delta^{14}C \) with real data.
3 Methods

3.1 Testing the Traditional Approach

We used an analytical gas transport model to simulate a range of natural soil profiles of $^{12}$CO$_2$, $^{13}$CO$_2$ and $^{14}$CO$_2$. The model is based on Fick's second law of diffusion:

$$\theta \frac{\partial \text{Conc}}{\partial t} = \frac{\partial}{\partial z} \left( D(z, t) \frac{\partial \text{Conc}}{\partial z} \right) + P(z, t), \quad (8)$$

where $\theta$ is the soil air-filled pore space, Conc is the concentration, $t$ is time, $D(z, t)$ is the soil gas diffusion function, and $P(z, t)$ is the biological production function, with the latter two dependent on both depth $z$ and time $t$.

The model was run in steady-state:

$$\frac{\partial \text{Conc}}{\partial t} = 0, \quad (9)$$

and both diffusion and production rates were constant with depth:

$$D(z) = D, \quad (10)$$
$$P(z) = P. \quad (11)$$

The following boundary conditions were used:

$$C(z = 0) = \text{Conc}_{\text{atm}}, \quad (12)$$
$$\frac{\partial C}{\partial z} |_{z=L} = 0, \quad (13)$$

where Conc$_{\text{atm}}$ is the concentration of CO$_2$ in air just above the soil and $L$ is the model lower spatial boundary, the point below which no production or diffusion occurs. Eq. (8) is solved analytically to yield the following equation:

$$\text{Conc}(z) = \frac{P/L}{D} \left( L \times z - \frac{z^2}{2} \right) + \text{Conc}_{\text{atm}}. \quad (14)$$

In the model, isotopologues of CO$_2$ are treated as independent gases, with their own specific concentration gradients and diffusion rates (Cerling et al., 1991; Nickerson and Risk, 2009b; Risk and Kellman, 2008). We assume total CO$_2$ to be $^{12}$CO$_2$ because of its high abundance. The error associated with this assumption is less than 0.01% (Amundson et al., 1998). Eq. (14) is thus applied for $^{13}$CO$_2$ and $^{14}$CO$_2$. For the full derivation see Nickerson et al. (2014) Section 2.3.

The analytical gas transport model was applied across a range of soil diffusivity ($1 \times 10^{-7}$, $1 \times 10^{-6}$ and $1 \times 10^{-5}$ m$^2$ s$^{-1}$), soil production rates (0.5, 1, 2, and 4 µmol CO$_2$ m$^{-3}$ s$^{-1}$), $\delta^{13}$C of biological production (-30 ‰, -20 ‰, -15 ‰), and $\Delta^{14}$C of biological production (-500 ‰, -200 ‰, -1 ‰, 1 ‰, 200 ‰, 500 ‰). In addition it used $\Delta^{14}$C of atmospheric CO$_2$ ($\Delta_a$; 10 ‰) and $\delta^{13}$C of atmospheric CO$_2$ ($\delta_a$; -8 ‰), representing realistic conditions found in nature. The other model boundary
conditions were as follows: \( L = 0.8 \) m, \( z = 0.025 \) m, and \( Conc_{atm} = 15833 \) µmol m\(^{-3}\) (~380 ppm). The output of the model under these applied conditions were profiles of \(^{12}\)CO\(_2\), \(^{13}\)CO\(_2\), and \(^{14}\)CO\(_2\) for each depth (z) down to the bottom boundary (L).

### 3.2 Testing the Traditional and Alternative Corrections

The model-generated soil pore space values of \(^{12}\)CO\(_2\), \(^{13}\)CO\(_2\), and \(^{14}\)CO\(_2\) at each depth were then used to produce soil depth profiles of \(\delta^{13}\)C, \(\delta^{14}\)C, and \(\Delta^{14}\)C of CO\(_2\) as demonstrated earlier in Figs. 1 and 2. To simulate the traditional correction for radiocarbon (referred to as \(\Delta^{14}\)C\(_{\text{old}}\) here), we input the soil pore space values into Eq. (7) to calculate the \(\Delta^{14}\)C depth profiles.

Our proposed new approach is based on Davidson’s (1995) theory. Rather than using the \(\delta^{13}\)C soil pore space as a mass-dependent correction in Fig. 2, we suggest instead using the value \(\delta^j\)\(^{13}\)C (Eq. (2)), the biological production of \(\delta^{13}\)C, in its place in the denominator of Eq. (7) as follows:

\[
\Delta^{14}\text{C}_{\text{new}} = \left( \frac{\Delta \delta^{13}\text{C}}{\Delta \delta^{13}\text{C}} \right) \left( \frac{1 - \frac{1}{1000} \left( \frac{\delta^{13}\text{C}}{1000} \right) z}{1 + \frac{1}{1000} \left( \frac{\delta^{13}\text{C}}{1000} \right) z} \right) - 1 \times 1000. \tag{15}
\]

The model-generated soil pore space isotope values were input into Eq. (15) to produce depth profiles of \(\Delta^{14}\text{C}_{\text{new}}\). Values of \(\Delta^{14}\text{C}_{\text{new}}\) through depth represent transport-fractionation-corrected soil CO\(_2\) values of radiocarbon. For our simulated data, we assume the measurement year is present day, as we do not use the oxalic acid (\(A_{\text{abs}}\)) in Eq. 15. Then to calculate the radiocarbon composition of production, \(\Delta^j\)\(^{14}\)C, the \(\Delta^{14}\)C composition of the soil CO\(_2\), \(\Delta^{14}\text{C}_{\text{new}}\), can be placed into our adaption of Davidson (1995) for \(^{14}\)C (Eq. (4)) as follows:

\[
\Delta^j\)^{14}\text{C} = \frac{C_s(\Delta^{14}\text{C}_{\text{new}} - 0.8) - C_a(\Delta^s\)^{14}\text{C} - 0.8)}{1.088(C_s - C_a)}. \tag{16}
\]

where \(\Delta^j\)\(^{14}\)C is the \(\Delta^{14}\)C composition of soil production, \(C_s\) and \(\Delta^{14}\text{C}_{\text{new}}\) are the mole fraction and \(\Delta^{14}\)C composition of the soil CO\(_2\), and \(C_a\) and \(\Delta^s\)\(^{14}\)C are the mole fraction and \(\Delta^{14}\)C composition of CO\(_2\) in the air just above the soil.

### 3.3 Field Soil Profiles

To demonstrate our new approach with real data, we used \(\Delta^{14}\)C values collected in the field. We collected samples of soil CO\(_2\) at 3 depths from the soil profile and from the air just above the soil, from 3 sites in Weyburn, Saskatchewan, for both stable and radio-isotope analysis. These sites were located in agricultural fields, with soils characterized as a combination of Estevan and Roughbark souls. These soils have sandy loam surfaces, with thin organic layers and soil layers that are poorly drained and have high clay content (SCSR, 1997).
To collect samples, we installed horizontal polyvinyl chloride (PVC) soil gas wells, 60 cm long, with 3-ply Gore-tex™ membranes covering 2 cm holes drilled every 10 cm along the length of PVC, at soil depths of 5 cm, 10 cm, 20 cm, 50 cm and 75 cm. Details on the soil gas well design and sampling disturbance prevention are described in detail in Risk et al. (2013). We withdrew a minimum of two samples (one shallow and one deep) and one air sample at each of the three sites 6 times (approximately every 2 months) between August 2011 and May 2012 as described in Risk et al. (2013), by connecting a N2-purged and evacuated 1 L stainless steel canister (Lab Commerce) to the well and allowing it to equilibrate for 15 mins. The samples were sent to the University of Florida for cryogenic purification and then to the University of California Irvine Keck Accelerator Mass Spectrometer (AMS) facility to be graphitized and analyzed for Δ14C.

As described in Risk et al. (2013), on each visit triplicate samples were also collected in 10 ml N2-purged and evacuated Exetainers vials (Labco, UK) at each depth as well as from the air above the soil. The triplicate samples were analyzed for bulk CO2 and δ13C within 2 weeks of sampling using a GV Isoprime CF-IRMS and Multiflow gas bench (Isoprime, UK).

We used the Δ14C values reported to us from the AMS laboratory along with δ13C (presented in Risk. et al. 2013) to back-correct the values so that we could present the results using Δ14C_{new} (Eq. 15) and then also calculate the radiocarbon composition of biological production using Δ_{f}^{14} (Eq.16).

### 3.4 Interpreting Soil Profiles

Our primary goal was to correctly extract the isotopic composition of CO2, produced by biological production. We applied two methods to extract this signal from the model-generated soil CO2 profiles as well as soil CO2 profiles from the field:

Method 1 follows the traditional correction, where Eq. (7) was used to calculate Δ14C_{old}, and we interpret this value as the radiocarbon composition of CO2 from biological production. Although this interpretation may not seem commonly used, as most people now understand the soil CO2 and soil-respired CO2 differ, we want to use it here as an example. If a researcher were to interpret a soil CO2 radiocarbon measurement as old and representative of the end-member source it came from, as demonstrated in Section 2, this soil CO2 sample will not necessarily be representative of the end-member production source because of gas transport mechanisms.

Method 2, our proposed solution, instead determines the radiocarbon composition of CO2 from biological production in two steps, as described in Section 3.2. First, the transport corrected radiocarbon composition of soil CO2, is calculated using Eq. (15) (Δ14C_{new}). Then this properly interpreted soil CO2 value can be used in Eq. (16) to calculate the radiocarbon composition of production, Δ_{f}^{14}.
4 Results

4.1 Testing the Traditional Approach

In Fig. 3 we present the results from model scenarios that simulated natural soil diffusive mixing profiles between sources that are intended to represent a realistic range of values as a function of depth and soil properties. All the scenarios presented had the same prescribed $\Delta^{14}C$ source values (CO$_2$ in the air just above the soil and soil biological production), and only soil diffusivities and production rates differed. Like the $\delta^{13}C$ and $\delta^{14}C$ soil CO$_2$ depth profiles in Fig. 1, the $\Delta^{14}C$ soil CO$_2$ profiles varied as a function of soil diffusivities and production rates. In the model scenarios in Fig. 3(a), the depth profiles with higher soil diffusivities had more enriched $\Delta^{14}C$ soil CO$_2$ (20-60 ‰ more enriched, depending on depth) than the scenarios with lower soil diffusion rates. In Fig. 3(b), the depth profiles with lower production rates had more enriched $\Delta^{14}C$ of soil CO$_2$ (5-10 ‰ more enriched) than scenarios with higher production rates. In the profiles with steeper diffusive gradients near the surface, soil CO$_2$ through depth was more representative of the production source, as we would expect from theory.

In Fig. 3 two depth profiles are plotted for each model iteration, one where the model output was used to calculate the conventional representation of radiocarbon, $\Delta^{14}C_{\text{old}}$ (Eq. (7); solid line) and the second where the output was used to calculate $\Delta^{14}C_{\text{new}}$, our proposed convention for presenting radiocarbon soil CO$_2$ (dashed line). All of the $\Delta^{14}C_{\text{old}}$ depth profiles in Fig. 3 had slightly (~ 10 ‰) more depleted $\Delta^{14}C$ soil CO$_2$ values than the $\Delta^{14}C_{\text{new}}$ depth profiles. When the radiocarbon composition of CO$_2$ from biological production, $\Delta_f^{14}C$, was calculated using $\Delta^{14}C_{\text{new}}$ (Eq. (16); Method 2), the result was equal to the radiocarbon value of production input into the model (-50 ‰) through the entire soil CO$_2$ depth profile under all soil scenarios. In contrast, when Method 1 was applied, we would (incorrectly) interpret $\Delta^{14}C_{\text{old}}$ soil CO$_2$ to be the radiocarbon composition of CO$_2$ from biological production, the $\Delta^{14}C_{\text{old}}$ values through depth never equalled the $\Delta^{14}C$ value of soil production input into the model (-50 ‰).

4.2 Field Experiment

The radiocarbon values for two of the sampling dates where soil CO$_2$ samples were collected from a field site in Weyburn, Saskatchewan, Canada, are presented in Fig. 4. The traditional $\Delta^{14}C$ convention, $\Delta^{14}C_{\text{old}}$, reported to us by the laboratory where the samples were analysed are plotted with solid lines. If Method 1 was used, we would (incorrectly) interpret these values as the values of biological production, but instead they represent soil CO$_2$ values. The dotted lines are the radiocarbon compositions of production ($\Delta_f^{14}C$), where the reported radiocarbon values were back-corrected using our new approach, $\Delta^{14}C_{\text{new}}$, and then input into Eq. (16) (Method 2). When considering age, the radiocarbon compositions of production ($\Delta_f^{14}C$), calculated using Method 2, were older in the springtime than those calculated using Method 1, despite the fact that Method 2 values lie on either sides of Method 1 values (more deplete at the surface and more enriched at depth). Although the values are more enriched at depth, in terms of age, they are still older C. This is because both Method 1 and 2 values fall within the post 1950s $^{14}C$ bomb spike period (Trumbore, 2000), but the more enriched values are still slightly older in terms of age.
5 Discussion

5.1 Correction Bias and Limitations

Diffusion- and production-controlled soil gas profiles, similar to those presented in Fig. 3, have been shown in other papers for δ¹³C (e.g., Bowling et al., 2015; Breecker et al., 2012a; Cerling, 1984; Cerling et al., 1991; Davidson, 1995; Nickerson and Risk, 2009b). Given that we based our gas transport corrected Δ¹⁴C calculation on the same equations, this is what we expected, where values of Δ¹⁴C of soil CO₂ differed in the soil profile (shown in Fig. 3) were intermediate between the two mixing sources (CO₂ in the air just above the soil and soil biological production). These effects of diffusion and diffusive mixing demonstrate that Method 1 (which assumes Δ¹⁴C old of soil CO₂ = Δ¹⁴C of soil production) is inappropriate for the soil gas application because it does not describe the radiocarbon composition of CO₂ as produced, and before alteration by gas transport processes. In contrast, Method 2 (where the Δ¹⁴C isotopic signature of production, Δ¹⁴C new, is calculated from Δ¹⁴C new) does not have any error because this method is able to calculate the true isotopic composition of soil production along the entire soil profile diffusive mixing gradient, no matter how steep or shallow the gradient.

The degree of error for Method 1 will depend on a given soil environment, where soil diffusivity and production rates will either amplify or decrease the error. When we “sampled” model-produced depth profiles using Method 1, we were unable to correctly extract the specified isotopic compositions of biological production that were input in the model, under any scenario. Method 1 error can be quantified as the absolute difference between the model’s prescribed isotopic value of production, and Δ¹⁴C old. In the specific scenarios shown in Fig. 3, the smallest Method 1 error (0.3 ‰) was in model scenarios with high production rates or low diffusivities, and the largest error (18 ‰) was in scenarios with higher soil diffusivities. Based on the rate of decline of atmospheric bomb ¹⁴C of 4 to 5.5 ‰ yr⁻¹ (Graven et al., 2012), a 18 ‰ error would equate to a 3.3 to 5 year age error.

The fraction of atmosphere-sourced CO₂ (fₐ) present in the soil profile caused by diffusive mixing scenarios typically associated with different types of soils can be a predictor for Method 1 error, as illustrated conceptually in Fig. 5. Soil environments that typically have higher soil diffusivities and lower production rates will have smaller soil-diffusive gradients, and there is a larger amount of atmospheric CO₂ in the soil compared to the total CO₂. These scenarios have a much higher fₐ value. In these scenarios, diffusive mixing dominates, which amplifies Method 1 error. In contrast, in soils with larger soil-diffusive gradients, there is a much smaller amount of atmospheric CO₂ present compared to the total amount of CO₂, and therefore the isotopic depth profile more closely resembles a mass-mixing profile. These soil CO₂ depth profiles have lower fₐ values and thus Method 1 will be less erroneous in these scenarios, because diffusive mixing is not as prominent.
Using our field study as an example (profiles shown in Fig. 4), the high clay content of its soil (SCSR, 1997) likely has relatively low soil diffusivity, and is most like the lower soil diffusivity scenarios in Fig. 3. In Fig. 5, this soil is like the intermediate scenario, with an intermediate \( f_c \) value, and diffusive mixing gradient. The use of Method 1 in this type of soil environment would be less erroneous than, for example, a dry desert soil environment with a high soil diffusion rate. Based on our model simulations, we can assume that Method 2 is producing the true \( \Delta^{14} \)C value of production, so Method 1 error can be calculated as the difference between Method 1 and 2 for this real data. In our case here, we observed Method 1 error to be as low as 10 \( \% \) (2 to 2.5 year age error) in February and up to 100 \( \% \) (18-25 year age error) at depth in May, although the magnitude of expected error is variable and is dependent on diffusivity and production rates as shown in Fig. 3 and 5.

This analysis does, however, have limitations. The synthetic soil environment is simplified in our approach, and in reality soil diffusion and production rates are not constant through depth. The model is necessarily simplified so that it can be easily solved analytically, but in reality soils are typically not in steady state (van Asperen et al., 2017; Bowling et al., 2009; Bowling and Massman, 2011; Goffin et al., 2014; Maier et al., 2010; Moyes et al., 2010; Nickerson and Risk, 2009b; Risk and Kellman, 2008). For example, gravitational settling and thermal diffusion can impact the diffusive non-steady state in deep soils (Severinghause et al., 1996) and diurnal temperature cycles (Nickerson and Risk, 2009b; Phillips et al., 2010; Risk and Kellman, 2008) and wind advection (Bowling and Massman, 2011) can be of impact non-steady state in near surface soils. The error values presented here are therefore likely conservative, since previous \( \delta^{13} \)C studies have shown that these non-equilibrium processes generally add fractionation uncertainty (Nickerson and Risk, 2009b; Phillips et al., 2010; Risk and Kellman, 2008). Additionally, sampling methods may impose an additional layer of non-equilibrium fractionation uncertainty (Egan et al., 2014) that may need to be evaluated. The real magnitude of error will depend on the given soil environment and will be sensitive to the soil conditions and sampling methodology. Additionally, carbonate soils could introduce more error, as the isotopic exchange between soil gas and carbonates is not mass-dependent (Breecker et al., 2009).

Surface flux chambers are commonly used sampling methodology used for measuring the radiocarbon composition of production, and were not addressed in our analysis. However, Method 1 is actually acceptable for use in the case of surface flux chambers, because unlike soil CO\(_2\) which will always differ from soil production soil-respired CO\(_2\), conservation of mass dictates that isotopic values of flux must represent soil production so long as the soil is in steady-state (Cerling et al., 1991). While radiocarbon surface flux data need no correction for transport fractionation, researchers should be cautious when using surface flux chambers because they can cause isotopic dis-equilibrium (Albanito et al., 2012; Egan et al., 2014; Midwood and Millard, 2011; Nickerson and Risk, 2009a). As shown in the Egan et al. (2014) study, static chamber methods (i.e. Hahn et al., 2006) and the proposed forced-diffusion chamber technique were the least erroneous for radiocarbon measurements, whereas dynamic chamber sampling techniques (i.e. Gaudinski et al., 2000; Schuur and Trumbore, 2006) could cause up to 200 \( \% \) bias under certain soil diffusion and production scenarios.
Aside from our proposed correction, a few other analytical alternatives might be appropriate for correcting $^{14}$C in soil CO$_2$. The Davidson (1995) $\delta$ method was the only gradient approach we tested for Method 2 in our study, but alternative approaches such as those presented for $\delta^{13}$C by Goffin et al. (2014) and Nickerson et al. (2014), and for $\Delta^{14}$C by Phillips et al. (2013) would likely be similarly successful in producing depth-dependent compositions of production. They are, however, not quite as straightforward as the $\delta$ method. However, if a researcher chooses to use an alternate gradient approach, they should still use $\Delta^{14}$C$_{\text{new}}$ rather than $\Delta^{14}$C$_{\text{old}}$ to calculate soil CO$_2$ first, as $\Delta^{14}$C$_{\text{old}}$ does not account for transport fractionations. To demonstrate the bias associated with using $\Delta^{14}$C$_{\text{old}}$ with another gradient approach, we calculated error values for three soil environments with given transport parameters in Table 2. As expected, across all three soil environments and depths, Method 2 had no error. If a researcher were to use $\Delta^{14}$C$_{\text{old}}$ with another gradient approach, the bias would be between 7 and 8 ‰ depending on the soil type and depth. This isotopic difference is not large, but it still does not follow theory, so we also compared the difference between using $\Delta^{14}$C$_{\text{new}}$ and $\Delta^{14}$C$_{\text{old}}$ to interpret the isotopic composition of soil CO$_2$ in these same soil environments in Table 2. In the three soil types modelling, the bias in using $\Delta^{14}$C$_{\text{old}}$ to interpret soil CO$_2$ was always larger near the surface, and was largest in sandy type soils with mid-range production rates and high soil diffusion rates.

In at least one other specialized instance, researchers have recognized that the normal Stuiver and Polach (1977) reporting convention was not applicable under the circumstances of an experiment and chose to reformulate it for their application. The Torn and Southon (2001) study evaluated the use of $\Delta^{14}$C$_{\text{old}}$ when radiocarbon is used as a tracer in C cycling field experiments with elevated atmospheric CO$_2$ concentrations. Torn and Southon (2001) proposed that in these experiments, the $\delta^{13}$C correction used in $\Delta^{14}$C$_{\text{old}}$ was invalid because differences in $^{13}$C abundance associated with elevated atmospheric CO$_2$ was associated with diffusive mixing of different atmospheric masses, and not isotopic fractionation. They instead used a $\delta^{13}$C value from an adjacent control plot (non-elevated CO$_2$ concentrations) to accurately estimate $\Delta^{14}$C, because the control plot followed the same fractionation pathways, but without the elevated atmosphere.

Both the Torn and Southon (2001) study and ours highlight the importance of reassessing old isotopic approaches for new application environments. To date, only three known studies (Egan et al., 2014; Phillips et al., 2013; Wang et al., 1994) have accounted for $^{14}$C diffusion-transport, though ours is the first to propose a straightforward and theoretically-robust correction that replaces the Stuiver and Polach (1977) solution for the soil gas environment (Method 2).

5.4 Workarounds and Establishing New Best Practice

More research groups are starting to use soil gas wells/soil CO$_2$ in conjunction with gradient techniques because of the known isotopic effects caused by many chamber techniques (Albanito et al., 2012; Egan et al., 2014; Midwood and Millard, 2011; Nickerson and Risk, 2009a). Gradient approaches also allow researchers to determine depth-dependent values of
production. Previously reported data using the traditional Stuiver and Polach (1977) reporting convention, can be backcorrected using our solution. The back-correcting solution does, however, assume that the researcher has measured a value of $\delta^{13}_o$ independent from $\Delta^{14}\text{C}_{\text{old}}$, as the AMS measured $\delta^{13}$ is not comparable to Isotope-Ratio Mass Spectrometry (IRMS) measured $\delta^{13}$. To assess the sensitivity of the $\delta^{13}_f$ value in calculating $\Delta^{14}\text{C}_{\text{new}}$ and $\Delta^{14}_f$ for back corrections, in Table 3 we present the error in using a $\delta^{13}_f$ value that is wrong by ± 0.5, 1, and 5 ‰. If rounded to the nearest ‰ value, the bias associated with using a $\delta^{13}_f$ ± 0.5, 1 and 5 ‰ across the three soil types and depths modelled is always 1, 2, and 10 ‰, respectively. The back correction solution can therefore work if a researcher collected $\delta^{13}\text{C}$ measurements independently, although we recommend against using this back correction method for new data.

For researchers who have soil CO$_2$ data previously interpreted using the $\Delta^{14}\text{C}_{\text{old}}$ calculation, the following steps will help correct for transport fractionations: 1) use $\delta^{13}_s$ and $\Delta^{14}\text{C}_{\text{old}}$ to back out the activity of the sample ($A_s$); 2) calculate the isotopic composition of production for $\delta^{13}\text{C}$ using Eq. (2), $\delta^{13}_f$; 3) use $\delta^{13}_f$ and $A_s$ in Eq. (7) to calculate $\Delta^{14}\text{C}_{\text{new}}$, and finally 4) determine the radiocarbon isotopic composition of production, using Eq. (16), $\Delta^{14}_f$.

Going forward, several changes to best practice are recommended. On a lab level, for new soil CO$_2$ data, we propose that AMS laboratories report radiocarbon using Eq. (3), $\delta^{14}\text{C}$, the uncorrected radiocarbon variant, so that the first step above, i.e. use $\delta^{13}_s$ and $\Delta^{14}\text{C}_{\text{old}}$ to back out the activity of the sample ($A_s$), can be avoided, and researchers can proceed with steps 2-4. We also suggest that researchers measure $\delta^{13}$ alongside $\Delta^{14}\text{C}$, so that they are not dependent on the AMS measured $\delta^{13}$ for potential back-corrections, to prevent potential error ranging from 1-10 ‰ (Table 3).

The Stuiver and Polach solution is, however, appropriate for solid sample analysis in the soil environment, and for determining the radiocarbon composition of atmospheric CO$_2$ samples.

6 Conclusions

As our fieldwork and analysis has shown, there could be error of 100 ‰ for researchers using the traditional $\Delta^{14}\text{C}$ reporting convention, where soil CO$_2$ is used to interpret sources and ages of production. In cases where we are trying to predict the turnover rate and ages of sources of CO$_2$ in future climate scenarios, an error this large is unacceptable. This traditional $\Delta^{14}\text{C}$ solution, which uses a $\delta^{13}\text{C}$ correction, is not appropriate for the soil gas environment. We propose a new best practice for $\Delta^{14}\text{C}$ work in the soil gas environment that accounts for gas transport fractionations and produces true estimates of $\Delta^{14}\text{C}$ of production.

Author Contributions
JE, DB and DR conceptualized the theory and method for proving the new solution for radiocarbon applications in the soil gas environment. JE carried out the modeling, validation, visualization and writing of the original draft. DB, DR and JE reviewed and edited the draft.

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References


### Table 1. List of symbols used.

Note the isotope composition ratios are also unitless but traditionally expressed using permil (‰) notation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s$</td>
<td>sample activity</td>
<td>unitless</td>
</tr>
<tr>
<td>$A_{SN}$</td>
<td>normalized sample activity, relative to $\delta^{13}C$ of terrestrial wood</td>
<td>unitless</td>
</tr>
<tr>
<td>$A_{abs}$</td>
<td>age-corrected absolute international standard for activity</td>
<td>unitless</td>
</tr>
<tr>
<td>$Conc$</td>
<td>CO$_2$ concentration</td>
<td>μmol m$^{-3}$</td>
</tr>
<tr>
<td>$Conc_{atm}$</td>
<td>CO$_2$ concentration in air just above the soil</td>
<td>μmol m$^{-3}$</td>
</tr>
<tr>
<td>$C_a$</td>
<td>CO$_2$ mole fraction in air just above the soil</td>
<td>μmol mol$^{-1}$</td>
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<tr>
<td>$CO_2$</td>
<td>CO$_2$ mole fraction relative to dry air</td>
<td>μmol mol$^{-1}$</td>
</tr>
<tr>
<td>$C_a$</td>
<td>CO$_2$ mole fraction in soil pore space</td>
<td>μmol mol$^{-1}$</td>
</tr>
<tr>
<td>$D$</td>
<td>soil gas diffusivity</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D(z,t)$</td>
<td>soil gas diffusivity at depth $z$ and time $t$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
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<td>stable ($^{13}C/^{12}C$) isotope composition (relative to VPDB)</td>
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<tr>
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<td>$\delta^{13}C$ of CO$_2$ in air above the soil</td>
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<tr>
<td>$\delta^{14}_a$</td>
<td>$\delta^{14}C$ of CO$_2$ in air above the soil</td>
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<tr>
<td>$\Delta_a$</td>
<td>$\Delta^{14}C$ of CO$_2$ in air above the soil</td>
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<td>$P$</td>
<td>biological production rate</td>
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<td>isotopic ratio (heavy/light) of Vienna Pee Dee Belemnite standard</td>
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<td>$t$</td>
<td>time</td>
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<tr>
<td>$z$</td>
<td>depth</td>
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Table 2. Bias from interpreting the radiocarbon isotopic composition of soil CO₂ and biological production using Δ¹⁴C old. The depth profiles used to calculate the bias was generated from a model with a Δ¹⁴C of production of -50 ‰ and combinations of diffusion and production rates to represent three different general soil types: clay (D = 1e-7 m² s⁻¹; P = 0.5 µmol m⁻³ s⁻¹), loam (D = 1e-6 m² s⁻¹; P = 4 µmol m⁻³ s⁻¹), and sand (D = 1e-5 m² s⁻¹; P = 2 µmol m⁻³ s⁻¹). All bias values are absolute.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Depth (cm)</th>
<th>Δ¹⁴C old (‰)</th>
<th>Δ¹⁴ from Δ¹⁴C old (%)</th>
<th>Δ¹⁴C new (‰)</th>
<th>Δ¹⁴C old - Δ¹⁴C new (‰)</th>
<th>-50 - Δ¹⁴ from Δ¹⁴C old (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>2.5</td>
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<td>-58.1</td>
<td>-31.7</td>
<td>-50.0</td>
<td>11.3</td>
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<td></td>
<td>50</td>
<td>-49.5</td>
<td>-58.3</td>
<td>-40.8</td>
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<tr>
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Table 3. Sensitivity of the $\delta^{13}_j$ value in $\Delta^{14}C_{\text{new}}$ and $\Delta^{14}_j$ calculations. The depth profiles used to calculate the bias from using the wrong $\delta^{13}_j$ value was generated from a model with a $\Delta^{14}C$ of production of -50 ‰ and combinations of diffusion and production rates to represent three different general soil types: clay ($D = 1e^{-7} \text{ m}^2 \text{s}^{-1}$; $P = 0.5 \mu\text{mol m}^{-3} \text{s}^{-1}$), loam ($D = 1e^{-6} \text{ m}^2 \text{s}^{-1}$; $P = 4 \mu\text{mol m}^{-3} \text{s}^{-1}$), and sand ($D = 1e^{-5} \text{ m}^2 \text{s}^{-1}$; $P = 2 \mu\text{mol m}^{-3} \text{s}^{-1}$). All bias values are absolute.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Depth (cm)</th>
<th>Deviation in $\delta^{13}_j$ (%)</th>
<th>Bias using wrong $\delta^{13}<em>j$ in $\Delta^{14}C</em>{\text{new}}$ (%)</th>
<th>Bias using $\Delta^{14}C_{\text{new}}$ with wrong $\delta^{13}_j$ to calculate $\Delta^{14}_j$ (%)</th>
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<tr>
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<td>-1</td>
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Figure 1: Modelled steady-state diffusive vertical depth profiles for $\delta^{13}$C and $\delta^{14}$C of soil CO$_2$. In the top panel the $\delta^{13}$C of atmospheric CO$_2$ (circle) is -8 ‰ and CO$_2$ from biological production (square with dashed line; $\delta_{13}$) is -25 ‰. In the bottom panel the $\delta^{14}$C of atmospheric CO$_2$ (circle) is 45.5 ‰ and CO$_2$ from biological production (square with dashed line) is -50 ‰. Both profiles in each of the panels have the same biological production rates and isotopic composition of biological production, but each profile has a different soil diffusivity as indicated.
\[ \delta^{13}\text{C} \text{ of Soil CO}_2 (‰) \]

**Diagram a**
- Production source
- Calculated
  \[ \delta_j = 14780 \times (-20.38 - 4.4) - 380 \times (-8 - 4.4) \]
  \[ \delta_j = 25 \% \]
- \( \delta_j = C_s (\delta - 4.4) - C_a (\delta_a - 4.4) \times 100 \%
- C_s of 380 ppm; \( \delta_s \) of -8 \%
- C_a of 14780 ppm; \( \delta_a \) of -20.17 \%
- Production source of -25 \%

**Diagram b**
- Production source
- Calculated
  \[ \delta_j = 14780 \times (-39.40 - 8.8) - 380 \times (45.53 - 8.8) \]
  \[ \delta_j = -50 \% \]
- \( \delta_j = C_s (\delta - 8.8) - C_a (\delta_a - 8.8) \times 100 \%
- C_s of 380 ppm; \( \delta_s \) of 45.53 \%
- C_a of 14780 ppm; \( \delta_a \) of -39.40 \%
- Production source of -50 \%

**Diagram c**
- Production source
- Calculated
  \[ \Delta_j = 14780 \times (-48.43 - 8.8) - 380 \times (10 - 8.8) \]
  \[ \Delta_j = 58.26 \% \]
- \( \Delta_j = C_s (\Delta_s - 8.8) - C_a (\Delta_a - 8.8) \times 100 \%
- C_s of 380 ppm; \( \Delta_s \) of 10 \%
- C_a of 14780 ppm; \( \Delta_a \) of -48.43 \%
- Production source (-50) \neq \Delta_j (-58.26)

**Incorrect**
Figure 2: Modelled steady-state diffusive vertical depth profiles for $\delta^{13}$C (top panel; a), $\delta^{14}$C (middle panel; b), and $\Delta^{14}$C$_{\text{old}}$ (bottom panel; c) of soil CO$_2$. The three soil profiles were generated using the same soil production and diffusivity rates ($1 \times 10^{-6}$ m$^2$ s$^{-1}$ and 2 µmol m$^{-3}$ s$^{-1}$, respectively). Panels 2(a) and 2(b) were prepared using $\delta^{13}$C and $\delta^{14}$C as noted. Panel 2(c) shows an approach consistent with present day, where the $\Delta^{14}$C profile generated by the model incorporates the traditional Stuiver and Polach (1974) correction for biochemical fractionation. Inset “Calculated” panels show how, using input data read directly from each depth profile, a user would arrive at either the correct, or incorrect isotopic value of production using a Davidson approach to adjust for in-soil gas transport. The atmospheric source (Ca) composition is presented as a white circle, the soil CO$_2$ composition ($C_s$) is a black circle, and the isotopic composition of production is a black square. Note that values for the isotopic composition of soil in the three panels are rounded for ease of reading, but are actually -20.3832‰, -39.3989‰, and -48.4319‰ respectively for panels (a), (b), and (c). These values are drawn from the curve at a depth of 40 cm.
Figure 3: Modelled steady-state vertical depth profiles for Δ^{14}C of soil CO₂. In panel A the model scenarios have the same rates of production (P), but differing diffusivities (D) (solid lines are Method 1, Δ^{14}C_{old}; dashed lined are Method 2, Δ^{14}C_{new}). In panel B the model scenarios have the same diffusivities but differing production rates. The model input for Δ^{14}C of production was -50 ‰ in all cases (Δ^{14}C; black dashed line) and Δ^{14}C of the atmospheric source was 10 ‰ (white circle).
Figure 4: Field results for interpreted $\Delta^{14}C$ of production calculated from soil CO$_2$ gas samples collected at 10 cm, 50 cm, and 75 cm depths from soil gas wells in February and May 2012 from a site in Saskatchewan, Canada. Solid lines are $\Delta^{14}C$ calculated using Method 1 and the dashed lines are calculated using Method 2.
Figure 5: Method 1 error can be estimated using $f_a$, the fraction of soil CO$_2$ that originated from the atmosphere that has mixed downward into the soil gas profile. The radiocarbon composition of biological production is presented with a black square, and the atmospheric source of CO$_2$ is presented as a white circle.