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Title: “Technical Note: Isotopic fractionation corrections for the radiocarbon composition of CO_2 in the soil gas environment must include diffusion and diffusive mixing”
Authors: Jocelyn Egan et al.

Thanks to the editor and to the referees for their constructive comments. Based on the comments, we have reformatted the manuscript to be a Technical Note and believe that it has improved both its clarity and application. Referee and editor comments are listed below in bold, and our responses follow each. Our edited manuscript with tracked changes can be found after our responses.

Sincerely,
Jocelyn Egan (for all authors)

Associate Editor Comments to the Author:
This is a revised version with major revisions. I recommend another cycle of major revisions because the core of the paper, introducing a valid correction for interpretations of 14C in soil CO2 justifies publication. This is in spite of one reviewer being sufficiently frustrated with the revisions to indicate that another cycle is not justified (recommending rejection). And it seems the authors run the risk that our 2nd expert reviewer will respond the same way. I do concur with the main criticisms and the paper must sufficiently address it.

Generally, it seems everyone involved agree the paper raises a valid point regarding the need to introduce additional corrections when dealing with 14C in soil CO2. And as I think I pointed out upon submission, it would probably be most effective as an important short Method note (after considering the confusing parts such as noted by Ref 3). But it seems the author opted for more complicated options. This is apparent already in the Abstract, most of which focuses on "…assess the bias from using the conventional method… etc". And reach what is the real message of the work only at the last sentence: "…we propose a new correction for radiocarbon applications in soil gas that accounts for diffusion and mixing…" As a result, the paper is loaded with data while insisting it is not Experimental paper and just demonstrate the calculation, and so no need for details, and deferring various points to 'future work'. This does not seem to work well, raises more questions, provides unrealistic picture, and at the end fails to convince reviewers of the importance of the otherwise valid correction. If at all, a more effective demonstration would be to apply the corrections to a published work with soil profiles by others. (And in general, why focus on the 'size' of the correction rather than simply rest the case on the underlying 'correctness').

There are also some more minor issues that do not help in getting through these revisions. Just for example, the distinction between mass-dependent diffusion and mass-independent mixing is highlighted (correctly), but much effort is invested in insisting that these are more similar than not, using linguistic changes, such as changing 'mixing' to 'diffusive mixing' as a response, and using an odd definition of fractionation (which traditionally applies to reactant and product that are the same entity rather than a new one composed of the real product and any additional background). Or, the repeated cut and paste of the same response to different reviewers' comment (unpolite, to say it politely). BTW, comments on the relevance of carbonates is addressed with a single line saying CO2 interactions with carbonate is not mass-dependent, which seems odd.

I suggest to revise the paper with more attention to all comments, but consider changing the balance of the paper to further clarified theoretical part and reduced otherwise.

Thank you for the feedback. We agree that by focusing on the bias associated with using our proposed convention and the traditional convention that we were taking away from the main message of the paper. We have reformatted the manuscript into a Technical Note, and have removed the field data and the assessment of "how good" the different corrections were. Instead, we focus on the math and theory, and explain how based on this math, we must use our proposed correction in the case of soil gas work.

We also apologize for the confusion in describing the differences between mass-dependent diffusion and mass-independent mixing in the past round of edits. We have maintained the wording of "diffusive mixing" in the text so that it is understood that in the soil gas environment, this mixing is still occurring as a result of diffusion. We have made sure to go through the text and make this clear.

Referee #1

The authors made some efforts to correct the manuscript according to the reviewer's comments. However, it seems that some issues were only dealt with half-way.

For example, the text now refers to the right way to calculate the fractionation by diffusion of CO2 in air: "Binary Diffusion". But the same wrong equation still appears, and not that of binary diffusion.

For the request of soil profile description the authors added:

"There soils have sandy loam surfaces, with thin organic layers and soil layers that are poorly drained and have high clay content"

This leaves more questions than it answers. At what depth are these layers? Is there a clay layer in the middle of this profile? This has great implication for the model. And in the discussion the results are still discussed as if the soil is "clayey".

And where is the organic layer? As it is written, it appears to be not on the surface.

The authors also wrote in response for details on the field study:

"We thank the reviewer for this comment and agree that we have not been detailed enough explaining both the point of including the field data, and we have not been thorough enough in our description of the field site. In this paper we did not intend to use the field data as validation for the method, but as an example of how the new theory could be applied."

This is confusing. If the field data is important, than the site and methods should be described in detail. If not, this part should be removed.

Another main issue, that was raised by the reviewers before, is that diffusion is a mass-dependent processes, so the "standard method" will correct for it. It seems that the only addition here is including the effect of mixing. I was not convinced by the authors' response on this point.

We apologize that the referee was not satisfied with our responses and edits on the last round of revisions. We have checked to make sure the proper equation for binary diffusion is now included. Based on your feedback, as well as that from the other referees and editor, we have removed the field data from the manuscript. The manuscript has now been reformatted into a Technical Note, so that the focus is on the theory and math, and not on the field data, which we were trying to use as an example of how to apply our proposed correction with real data. We have included 1 new figure (Figure 3) to illustrate how our proposed correction works (which has an added correction for mixing) in comparison to the traditional one. We hope that by removing the field data and the assessment of how well the different methods worked, that we are now clearly demonstrating how our correction must be used in soil gas environment applications. We also hope that with this new format it is clear that our new correction includes the effect of mixing. We are sorry that you were not satisfied with how this was communicated in the past.

Referee #3
I fully agree with the editor's assessment that the authors run the risk of producing something that is mathematically correct but not clearly useful. It is for this reason that in the earlier review I asked for sensitivity studies and assumptions more likely to be found in real soils. As the authors have not seen fit to make these changes, I think they should either (1) be required to do so or (2) be required to remove the language that I still think overstates the importance of their correction for conditions likely to be found in real soils (up to 150 per mille, etc). I leave it up to the editor to decide which of these is more appropriate.

To me there are two main issues that remain.

First, the way the authors introduce the topic still adds unnecessary confusion to the already confusing nomenclature of the 14C.
At the end of the paragraph at the top of page 2, the authors still confuse the reporting conventions of 14C data with the interpretation of those data. As the authors need a soil-specific model to interpret soil gas data – and that model also contains assumptions, I would replace the last two sentences (page 2, lines 14-16) with a statement to the effect that "The reporting conventions using Fraction Modern or D14C for radiocarbon data implicitly assume mass-dependent fractionation based on observed 13C values accurately represent the processes contributing to observed 13C and 14C in the soil atmosphere – i.e. that the 14C is fractionated twice as much as 13C by biochemical and physical processes affecting both isotopes. We argue that this is not always the case in soil pore space, where mixing of air masses mean that this assumption no longer holds." In fact, there are other ways of reporting 14C that explicitly remove the 13C correction – this is the notation that the authors use starting in equation (3) and that was originally used by Wang et al (1994). However, the do not state that this notation is part of the reporting nomenclature suggested by Stuiver and Polach.

The authors could just avoid a lot of extra confusion and state at the outset that the small delta notation is preferred for reporting soil gas data over others like fraction Modern or "Delta" in cases where factors other than mass-dependent ones likely influence radiocarbon results.

We thank the referee for these useful comments. We have gone through the text to make sure it is clear that it is not the convention itself that has been wrong, but how it was applied for this specific environment. We have made edits as you suggested on page 2, lines 14-16 (now page 2 lines 5-7). We have also gone through to make it clear that the small delta 14C reporting convention is part of the nomenclature suggested by Stuiver and Polach.

Second, the assumptions built into the model demonstrably do not hold in real soils, and what the authors give as their main example is a case that is not likely to be observed in the real world. What they have added as 'sensitivity' tests do not really do much to inform the reader in my opinion, as they do not address the sensitivity to

this fundamental problem of how they have formulated their model. The results will clearly be highly sensitive to model formulation, and it is this sensitivity that is ignored in their discussion.
1) CO2 production rates drop exponentially with depth in most soils, because roots and most additions of new plant C are at concentrated at the surface. The authors argue in their response to previous comments that they wanted an equation they could solve analytically and use that to justify continuing to use this assumption. Do they really think this is the best way to interpret their own field data, or to represent production of CO2 with depth in soils? What is the sensitivity to this assumption? Analytical solutions for the case with constant diffusivity and exponentially declining respiration with depth exist (see for example the books by Crank or Carlslaw and Jaeger on diffusion and heat fluxes; or Cook (1995) Ecological Modelling 78: 277-283, though this is for oxygen consumption instead of CO2 production). Letting production change with depth would provide a much more realistic and useful case for the authors, as well as show how sensitive their results are to this important model assumption.
2) The assumption of a constant 14C signature of respired CO2 of -200 ‰ is also something I doubt was ever observed in a real soil. As stated in my previous review, observed values are mostly closer to the atmosphere 14CO2 value because of root respiration mixing with decomposition-derived CO2 – especially at the depths where most of the CO2 in soils is produced (at the surface). At the very least, it is worth seeing how important the correction is when the difference is 40 per mille instead of 300 per mille – again what is the sensitivity to the assumption?

I would therefore ask at a minimum that the authors include a case where they assume depth dependent CO2 productions rate (using published analytical solutions) and more realistic values for the radiocarbon signature of CO2 produced. It is also important to determine how important it is to vary diffusivity as they did in the paper.

Overall, my takeaway from this paper is that the authors are mathematically correct, and this approach should definitely be used. However, they have set up an artificial system to maximize how they state its importance and use this to imply that past attempts that did not use this approach have been subject to very large errors. Without more realistic scenarios, I remain unconvinced that applying these corrections in a more realistic scenario will lead to very important changes in how existing or future soil pore space data will be interpreted.

Based on these comments, as well as those from the other referee and editor, we have reformatted the manuscript into a Technical Note, so that the focus is no longer based on the bias resulting from either of the corrections (new or old), but rather on the math/theory and how based on it, we need to also correct for mixing. In this case, our steady-state model is only used to illustrate the theory using soil gas profiles, and nothing else. We do believe that in the future work in this field should include non-steady state models and field data, especially considering the lack of information known about the radiocarbon composition of soil-respired CO2 through different depths. We hope that the way we have reformatted the paper is a starting point and illustrates based on theory, why we must account for mixing. Based on your feedback from the last rounds of edits, the illustrative soil depth profiles were derived using a more realistic radiocarbon signature of production (- 50 permil).

Technical Note: 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, but it has not been evaluated for the soil gas environment, where both diffusive gas transport and diffusive mixing are important. Using theory and an analytical soil gas transport model, we demonstrate that the conventional correction is inappropriate for interpreting the radio-isotopic composition of CO_2 from biological production, because it does not account for important gas transport mechanisms. Based on theory used to interpret $\delta^{13}C$ of soil production from soil CO_2, we propose a new solution for radiocarbon applications in the soil gas environment that fully accounts for both mass-dependent diffusion and mass-independent diffusive mixing.

1 Introduction

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 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, $\Delta^{14}C$ (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

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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 readily extends to ^{14}C.

We argue here, that in the case of soil pore space ^{14}C where mixing of air masses occurs, that the assumption that mass-dependent fractionation is twice as large for ^{14}C as $\delta^{13}C$ by biochemical and physical processes no longer holds. Using theory and physical modelling of soil gas transport to illustrate the issue with the current reporting convention correction, we propose an alternative approach for specific use cases.

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2 Theory

To understand why the mass-dependent correction used in the Stuiver and Polach (1977) radiocarbon reporting convention 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:

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

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 CO_2, 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 using a simulated soil gas profile. In panel (a) two depth profiles of $\delta^{13}C$ of CO_2 that were modelled in a steady-state environment are shown (the model will be described in Section 3). The profiles differ only in soil diffusivity; all other characteristics were held constant, including rates of production, and $\delta^{13}C$ of CO_2 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 $\delta^{13}C$ of soil CO_2 ranges from -8 to -15.1 ‰. In the depth profile representing a soil with lower diffusivity, the $\delta^{13}C$ of soil CO_2 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 CO_2 does not penetrate downwards as readily, so the profile shape is much steeper near the soil-atmosphere

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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 CO_2 never equals the $\delta^{13}C$ of production (-25 ‰) at any depth, in either profile in Fig. 1(a). It is not possible to directly measure $\delta^{13}C$ of production *in situ*, because diffusion and diffusive mixing alter the character of CO_2 immediately after its production. From the site of production in the soil, $^{12}CO_2$ diffuses somewhat faster through the soil than $^{13}CO_2$, because the former has lower mass. This diffusive difference leads to isotopic fractionation, and results in depth profiles of $\delta^{13}C$ of soil CO_2 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 CO_2 in air and will differ if CO_2 diffuses in other gases). As a result, the $\delta^{13}C$ of soil CO_2 measured at any depth will be enriched by a minimum of 4.4 ‰ relative to the biological production CO_2 source. However, the $\delta^{13}C$ of soil-respired CO_2 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 $\delta^{13}C$ 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 CO_2 and its isotopic composition within the soil and the air above it, to infer the isotopic composition of CO_2 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 ^{12}C and ^{13}C as follows:

$$\delta_J^{13} = \frac{C_s(\delta_s^{13} - 4.4) - C_a(\delta_a^{13} - 4.4)}{1.0044(C_s - C_a)}, \qquad (2)$$

where δ_J^{13} is the $\delta^{13}C$ composition of CO_2 from soil production (biological respiration within the soil), C_s and δ_s^{13} are the mole fraction and isotopic composition of soil CO_2, and C_a and δ_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, δ_s^{13} = -20.3832 ‰, C_a = 380 ppm and δ_a^{13} = -8 ‰). The resulting δ_J^{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 δ_s^{13} in Fig. 1(a) and 2(a) will always yield (via Eq. (2)) the true isotopic composition of production, δ_J^{13} = -25 ‰ (dashed line). If $\delta^{13}C$ of soil CO_2 were (erroneously) interpreted to represent the

δ^{13}C of soil-respired CO$_2$, the error could be as large as the absolute value of (δ_a- δ_J^{13}) – 4.4 ‰. This Davidson (1995) δ_J^{13} approach has been shown to be robust when applied to field data from natural soils (Bowling et al., 2015; Breecker et al., 2012; 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. In this way, δ^{13}C diffusive fractionation theory can be applied to the radiocarbon isotopic composition, δ^{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 δ^{14}C, the ^{14}C equivalent to δ^{13}C (Stuiver and Polach, 1977):

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

where δ^{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 (-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 δ^{14}C of soil CO$_2$ with depth, highlighting the diffusive effects, have been presented by Wang et al. (1994).

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

$$\delta_J^{14} = \frac{C_s(\delta_s^{14} - 8.8) - C_a(\delta_a^{14} - 8.8)}{1.0088(C_s - C_a)}, \tag{4}$$

where δ_J^{14} is the δ^{14}C composition of soil production, C$_s$ and δ_s^{14} are the mole fraction and δ^{14}C composition of the soil CO$_2$, and C$_a$ and δ_a^{14} are the mole fraction and δ^{14}C composition of CO$_2$ in the air just above the soil. This Davidson reformulation for δ^{14}C, δ_J^{14}, was applied to a model-generated profile of soil δ^{14}C at a 40 cm depth in Fig. 2(b), like in panel (a) for δ^{13}C

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(C_s = 14780 ppm, δ_s^{14} = -39.3989 ‰, C_a = 380 ppm and δ_a^{14} = 45.5276 ‰; see inset box, Fig. 2(b)). As was the case for δ^{13}C in Fig. 2(a), the modelled values of C_s and δ_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 typical approach that has been used for interpreting the ^{14}C composition of soil CO_2 and soil-respired CO_2 (e.g., Trumbore, 2000) differs from the δ^{14}C example above, because a δ^{13}C correction is applied to account for mass-dependent isotopic fractionation of biochemical origin, ultimately converting δ^{14}C to a variant called Δ^{14}C (Stuiver and Polach, 1977). 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 δ^{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:

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

$$= A_s \frac{\left[\left(1-\frac{25}{1000}\right) * R_{VPDB}\right]^2}{\left[\left(1+\frac{\delta^{13}C}{1000}\right) * R_{VPDB}\right]^2},$$

$$= A_s \frac{\left[\left(1-\frac{25}{1000}\right)\right]^2}{\left[\left(1+\frac{\delta^{13}C}{1000}\right)\right]^2}, \qquad (5)$$

where A_{SN} is the normalized sample activity, A_s is the sample activity, and δ^{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 Δ^{14}C, the δ^{13}C corrected variant of δ^{14}C, can then be created from Eq. (5) by substituting in delta notation for Δ^{14}C of $\Delta^{14}C = (A_{SN}/A_{abs} - 1)*1000$ as follows Stuiver and Robinson (1974):

$$\Delta^{14}C = \left[\left(1+\frac{\delta^{14}C}{1000}\right)\frac{\left(1-\frac{25}{1000}\right)^2}{\left(1+\frac{\delta^{13}C}{1000}\right)^2} - 1\right]1000. \qquad (6)$$

Combining Eqs. (3) and (6):

$$\Delta^{14}C_{old} = \left[\left(\frac{A_S}{A_{abs}}\right)\frac{\left(1-\frac{25}{1000}\right)^2}{\left(1+\frac{\delta^{13}C}{1000}\right)^2} - 1\right]1000. \qquad (7)$$

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 common approach used to date for soil gas applications - 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_{abs} in our notation is equivalent to A_O in Stuiver and Robinson (1974).

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Eq. 7 uses δ^{13}C as an input parameter to make a mass-dependent correction to obtain Δ^{14}C, but the profiles of δ^{13}C and δ^{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 δ^{13}C should actually be used in the place of the mass-dependent correction in the soil gas environment (δ^{13}C of the soil CO_2 is measured, but δ^{13}C of biological production is not) as diffusive mixing is not a mass-dependent process. When $\Delta^{14}C_{old}$ is modelled through depth like δ^{13}C and δ^{14}C in Figs. 1 and 2 it also varies with depth as shown in Fig. 2(c). However, using a Δ^{14}C variant of Davidson's δ_J (as for δ^{14}C in Fig. 2(b)) at the same 40 cm depth does not correctly reproduce the specified model value for the Δ^{14}C of production of -50 ‰, like it did for δ^{13}C and δ^{14}C (C_s = 14780 ppm, Δ_s= -48.4319 ‰, C_a = 380 ppm and Δ_a = 10 ‰; see inset box, 2(c)). We, therefore, adapted the mass-dependent correction in $\Delta^{14}C_{old}$ using Davidson's (1995) theory to demonstrate how and why it should be used for Δ^{14}C soil gas applications.

3 Methods – Model Description

We used an analytical gas transport model to simulate a range of natural soil profiles of $^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$ in order to present soil gas transport theory. The model is based on Fick's second law of diffusion:

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

where θ 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:

$$\frac{\partial Conc}{\partial t} = 0, \tag{9}$$

and both diffusion and production rates were constant with depth:

$$D(z) = D, \tag{10}$$

$$P(z) = P. \tag{11}$$

The following boundary conditions were used:

$$C(z = 0) = Conc_{atm}, \tag{12}$$

$$\frac{\partial C}{\partial z}\Big|_{z=L} = 0, \tag{13}$$

where $Conc_{atm}$ 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:

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

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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, 2009; 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 ($1x10^{-7}$, $1x10^{-6}$ and $1x10^{-5}$ m^2 s^{-1}), and soil production rates (0.5, 1, 2, and 4 µmol CO_2 m^{-3} s^{-1}). The specific soil diffusivity and production rates used to generate each profile are stated in the figure caption of that profile. We used a δ^{13}C of biological production (-25 ‰) and atmospheric CO_2 (δ_a; -8 ‰), and Δ^{14}C of biological production (-50 ‰) and atmospheric CO_2 (Δ_a; 10 ‰) to represent 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).

4 Results

4.1 Adapted Correction for Interpreting Radiocarbon Values of Soil and Soil-respired CO_2

Based on Davidson's (1995) theory and what we demonstrated with Fig. 2(c), rather than using the δ^{13}C soil pore space as a mass-dependent correction, we suggest instead using the value δ_J^{13} (Eq. (2)), the biological production of δ^{13}C, in its place in the denominator of Eq. (7) as follows:

$$\Delta^{14}C_{new} = \left[\left(\frac{A_S}{A_{abs}}\right)\frac{\left(1-\frac{25}{1000}\right)^2}{\left(1+\frac{\delta_J^{13}}{1000}\right)^2} - 1\right]1000. \qquad (15)$$

Values of $\Delta^{14}C_{new}$ through depth represent transport-fractionation-corrected soil CO_2 values of radiocarbon, and in comparison to $\Delta^{14}C_{old}$, they are corrected for mass-independent diffusive mixing.

A depth profile of $\Delta^{14}C_{new}$ is presented in Fig. 3 (dashed line). To generate this soil depth profile we used the numbers from the simulated profiles in Fig. 2 and inserted them into Eq. 2 to determine δ_J^{13} at each depth. These values were then used in Eq. 15 to obtain $\Delta^{14}C_{new}$ of soil CO_2 through depth. The $\Delta^{14}C_{new}$ profile (dashed line) is more isotopically enriched compared to the $\Delta^{14}C_{old}$ profile (solid line) in Fig. 3. Values "sampled" from the $\Delta^{14}C_{old}$ profile (the same as the one presented in Fig. 2 (c)) were not able to reproduce the specified model value for the Δ^{14}C of production of -50 ‰ using a Δ^{14}C variant of Davidson's δ_J. To demonstrate that $\Delta^{14}C_{new}$ does correct for gas-transport fractionations, it can be placed into Δ_J^{14}, a Δ^{14}C adaption of Davidson (1995) for ^{14}C (Eq. (4)) as follows:

$$\Delta_J^{14} = \frac{C_S(\Delta^{14}C_{new}-8.8)-C_a(\Delta_a^{14}-8.8)}{1.0088(C_S-C_a)}, \qquad (16)$$

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where Δ_J^{14} is the Δ^{14}C composition of soil production, C_s and $\Delta^{14}C_{new}$ are the mole fraction and Δ^{14}C composition of the soil CO_2, and C_a and Δ_a^{14} are the mole fraction and Δ^{14}C composition of CO_2 in the air just above the soil.

Unlike in the case of $\Delta^{14}C_{old}$ demonstrated in the inset box in Fig. 2 (c), using the same 40 cm depth from the $\Delta^{14}C_{new}$ profile, we were able to reproduce the specified model value for the Δ^{14}C of production of -50 ‰ (C_s = 14780 ppm, Δ_s = -39.3989 ‰, C_a = 380 ppm and Δ_a = 45.5276 ‰; see inset box, Fig. 3).

4.2 Workarounds and Establishing New Best Practice

In the soil gas environment, $\Delta^{14}C_{new}$ convention should be used to properly interpret soil-respired CO_2 from soil CO_2, as it corrects for all related transport fractionations. For researchers who have soil CO_2 data previously interpreted using $\Delta^{14}C_{old}$, the following steps will help correct for transport fractionations: 1) use δ_s^{13} and $\Delta^{14}C_{old}$ to back out the activity of the sample (A_s); 2) calculate the isotopic composition of production for δ^{13}C using Eq. (2), δ_J^{13}; 3) use δ_J^{13} and A_s in Eq. (7) to calculate $\Delta^{14}C_{new}$, and finally 4) determine the radiocarbon isotopic composition of production, using Eq. (16), Δ_J^{14}.

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), $\delta^{14}C$, the uncorrected radiocarbon variant, so that the first step above, i.e. use δ_s^{13} and $\Delta^{14}C_{old}$ 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 δ^{13} alongside Δ^{14}C, so that they are not dependent on the AMS measured δ^{13} for potential back-corrections.

The Davidson (1995) δ_J method was the gradient approach we used in our study, but alternative gradient approaches such as those presented for δ^{13}C by Goffin et al. (2014) and Nickerson et al. (2014), and for Δ^{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 δ_J method.

6 Conclusions

This traditional Δ^{14}C solution, which uses δ^{13}C of soil CO_2 as a mass-dependent correction, is not appropriate for the soil gas environment, as it does not account for mass-independent mixing processes. We propose a new best practice for Δ^{14}C work in the soil gas environment that accounts for gas transport fractionations and produces true estimates of Δ^{14}C of production.

Author Contributions

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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.

Acknowledgements

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Table 1. List of symbols used. Note the isotope composition ratios are also unitless but traditionally expressed using permil (**‰**) notation.

Symbol	Description	Unit
A_s	sample activity	unitless
A_{SN}	normalized sample activity, relative to δ^{13}C of terrestrial wood	unitless
A_{abs}	age-corrected absolute international standard for activity	unitless
$Conc$	CO_2 concentration	µmol m^{-3}
$Conc_{atm}$	CO_2 concentration in air just above the soil	µmol m^{-3}
C_a	CO_2 mole fraction in air just above the soil	µmol mol^{-1}
CO_2	CO_2 mole fraction relative to dry air	µmol mol^{-1}
C_s	CO_2 mole fraction in soil pore space	µmol mol^{-1}
D	soil gas diffusivity	m^2 s^{-1}
$D(z,t)$	soil gas diffusivity at depth z and time t	m^3 s^{-1}
$\delta^{13}C$	stable (^{13}C/^{12}C) isotope composition (relative to VPDB)	‰
$\delta^{14}C$	radiocarbon (^{14}C/^{12}C) isotope composition (relative to A_{abs})	‰
$\Delta^{14}C_{old}$	radiocarbon (^{14}C/^{12}C) isotope composition with $\delta^{13}C$ correction	‰
$\Delta^{14}C_{new}$	radiocarbon (^{14}C/^{12}C) isotope composition with δ_J^{13}correction	‰
δ_a^{13}	δ^{13}C of CO_2 in air above the soil	‰
δ_a^{14}	δ^{14}C of CO_2 in air above the soil	‰
Δ_a	Δ^{14}C of CO_2 in air above the soil	‰
δ_J^{13}	δ^{13}C of CO_2 from soil production, calculated using Eq. (2)	‰
δ_J^{14}	δ^{14}C of CO_2 from soil production, calculated using Eq. (4)	‰
Δ_J^{14}	Δ^{14}C of CO_2 from soil production, calculated using Eq. (16)	‰
δ_s^{13}	δ^{13}C of CO_2 in soil pore space	‰
δ_s^{14}	δ^{14}C of CO_2 in soil pore space	‰
Δ_s	Δ^{14}C of CO_2 in soil pore space	‰
L	lower model depth boundary	m
$P(z,t)$	biological production rate at depth z and time t	µmol CO_2 m^{-3} s^{-1}
P	biological production rate	µmol CO_2 m^{-3} s^{-1}
R_s	isotopic ratio (heavy/light) of CO_2 sample	unitless
R_{VPDB}	isotopic ratio (heavy/light) of Vienna Pee Dee Belemnite standard	unitless
t	time	s
θ	air-filled porosity of soil	unitless
z	depth	m

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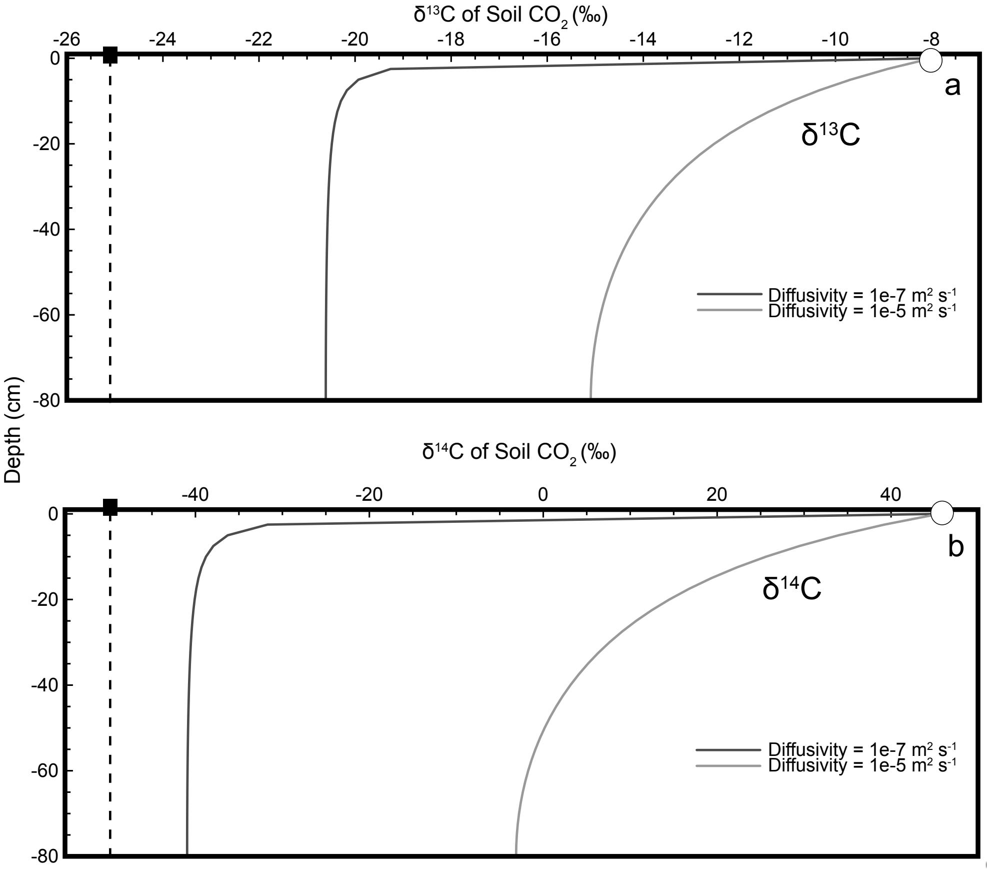

Figure 1: Modelled steady-state diffusive vertical depth profiles for δ^{13}C and δ^{14}C of soil CO_2. In the top panel the δ^{13}C of atmospheric CO_2 (circle) is -8 ‰ and CO_2 from biological production (square with dashed line; δ_J) is -25 ‰. In the bottom panel the δ^{14}C of atmospheric CO_2 (circle) 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.

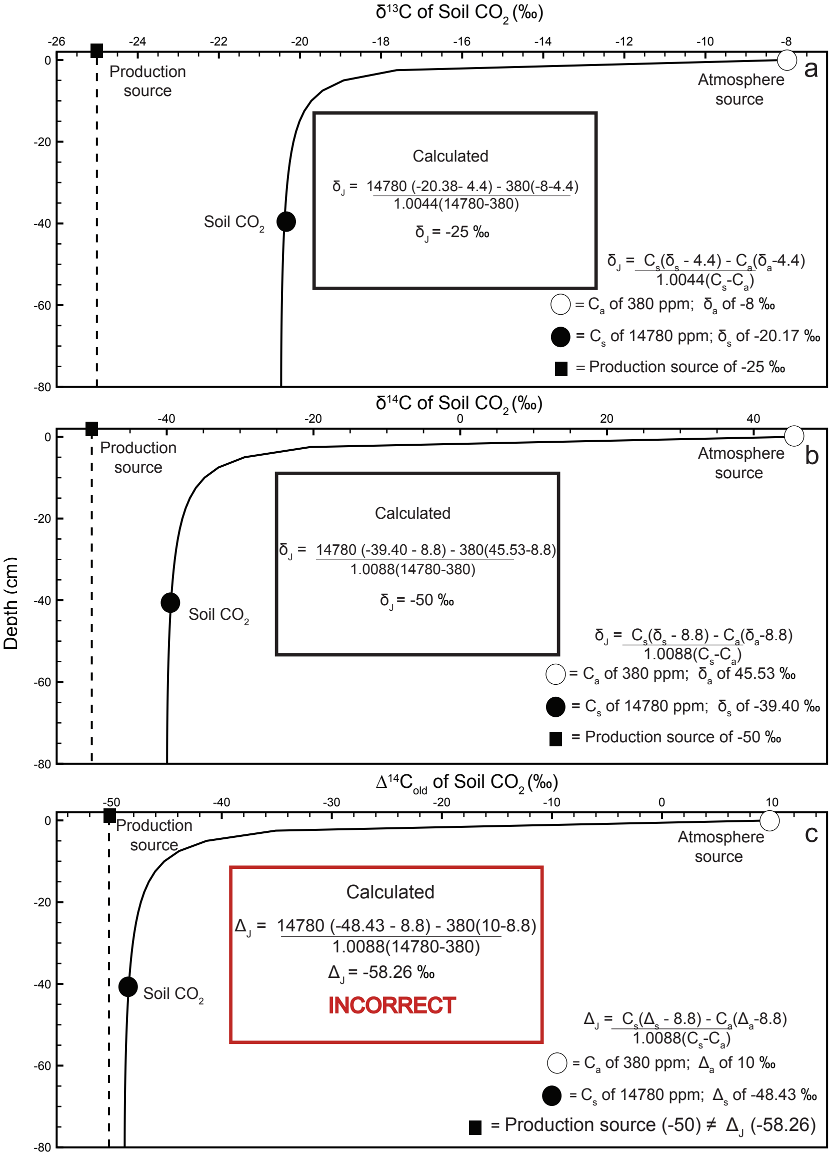
$\delta^{13}C$ of Soil CO_2 (‰)
-26
-24
-22
-20
-18
-16
-14
-12
-10
-8
0
-20
-40
-60
-80
Production source
Atmosphere source
a
Soil CO_2
Calculated
$\delta_J = \frac{14780\,(-20.38 - 4.4) - 380(-8-4.4)}{1.0044(14780-380)}$
δ_J = -25 ‰
$\delta_J = \frac{C_s(\delta_s - 4.4) - C_a(\delta_a - 4.4)}{1.0044(C_s - C_a)}$
○ = C_a of 380 ppm; δ_a of -8 ‰
● = C_s of 14780 ppm; δ_s of -20.17 ‰
■ = Production source of -25 ‰
$\delta^{14}C$ of Soil CO_2 (‰)
-40
-20
0
20
40
0
-20
-40
-60
-80
Depth (cm)
Production source
Atmosphere source
b
Soil CO_2
Calculated
$\delta_J = \frac{14780\,(-39.40 - 8.8) - 380(45.53-8.8)}{1.0088(14780-380)}$
δ_J = -50 ‰
$\delta_J = \frac{C_s(\delta_s - 8.8) - C_a(\delta_a - 8.8)}{1.0088(C_s - C_a)}$
○ = C_a of 380 ppm; δ_a of 45.53 ‰
● = C_s of 14780 ppm; δ_s of -39.40 ‰
■ = Production source of -50 ‰
$\Delta^{14}C_{old}$ of Soil CO_2 (‰)
-50
-40
-30
-20
-10
0
10
0
-20
-40
-60
-80
Production source
Atmosphere source
c
Soil CO_2
Calculated
$\Delta_J = \frac{14780\,(-48.43 - 8.8) - 380(10-8.8)}{1.0088(14780-380)}$
Δ_J = -58.26 ‰
INCORRECT
$\Delta_J = \frac{C_s(\Delta_s - 8.8) - C_a(\Delta_a - 8.8)}{1.0088(C_s - C_a)}$
○ = C_a of 380 ppm; Δ_a of 10 ‰
● = C_s of 14780 ppm; Δ_s of -48.43 ‰
■ = Production source (-50) ≠ Δ_J (-58.26)

Figure 2: Modelled steady-state diffusive vertical depth profiles for $\delta^{13}C$ (top panel; a), $\delta^{14}C$ (middle panel; b), and $\Delta^{14}C_{old}$ (bottom panel; c) of soil CO_2. The three soil profiles were generated using the same soil production and diffusivity rates (2 µmol m^{-3} s^{-1} and $1e^{-6}$ m^2 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.

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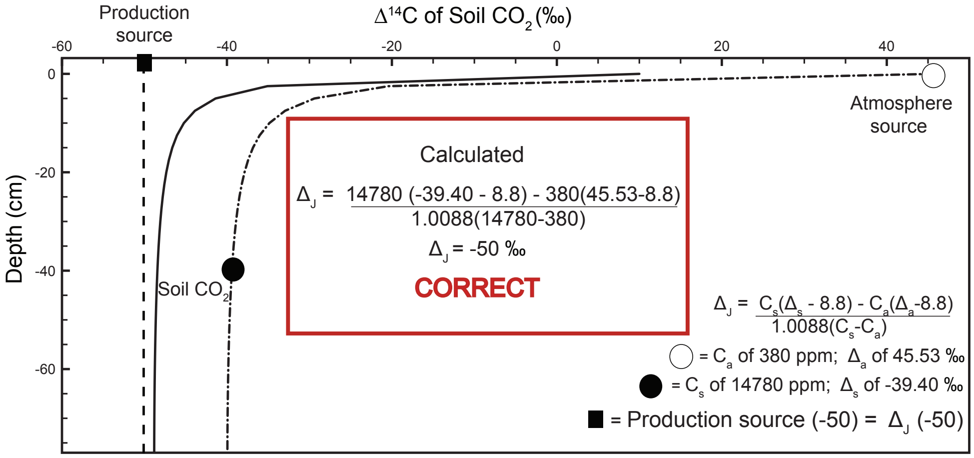

Figure 3: Modelled steady-state diffusive vertical depth profiles for $\Delta^{14}C_{old}$ (solid line; same profile as in Fig. 2 (c)) and $\Delta^{14}C_{new}$ (dashed line) of soil CO_2. The $\Delta^{14}C_{new}$ soil profile was calculated from the profiles in Fig. 2 (soil production and diffusivity rates of 2 µmol m^{-3} $s^{-}1$ and $1e^{-6}$ m^{2} s^{-1}, respectively). The inset "Calculated" panels show how, using input data read directly from the depth profile of $\Delta^{14}C_{new}$, a user would arrive at the correct 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 and atmosphere are rounded for ease of reading, but are actually -39.3989 ‰ and 45.5276 ‰, respectively. These values are drawn from the curve at a depth of 40 cm.