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Title: Isotopic fractionation corrections for the radiocarbon composition of CO2 in the soil gas environment must include diffusion and mixing
Authors: Jocelyn Egan et al.

Thanks to the referees and the editor for their helpful comments. We apologize for previous insufficient responses. We appreciate all the comments and believe that they have now led to a much-improved manuscript. Referee comments are listed below in bold, and our responses follow each.

Sincerely,
Jocelyn Egan (for all authors)

Referee #1

The reviewed manuscript proposed new corrections for ^{14}C measurements in soil air, to account for diffusion and mixing. Experimental study, and modeling are used to illustrate the point, and recommendation for best practice are given. The logic of the authors is clear, and usually the manuscript is well written.

Thanks for the supportive comments.

The authors writes that the problem with the traditional method of ^{13}C based correction, is that it works only for biological process like photosynthesis and do not apply for example to fractionation in diffusion. This is not correct. The correction based on ^{13}C should work for any mass-dependent fractionation (i.e most fractionation processes). However, they are correct the traditional correction will not work for mixing. Because this is not a fractionating processes and no mass-dependent can be assumed. This error should be corrected in the text, abstract, and in the title (i.e. correction for mixing is not correction for fractionation).

Thank you to the reviewer for pointing this out. We agree, and think that we have not been clear with our terminology throughout the text. Although mixing might not be considered a traditional fractionating process, there are important isotopic effects associated with mixing. An isotopic fractionation is defined as a difference in the isotopic composition between a reactant and a product. For the application here with radiocarbon, the radiocarbon composition of biological respiration is the "reactant" and the soil gas is the "product". We must take into account all isotopic effects that influence the product in order to understand the true isotopic composition of the reactant. Therefore both diffusion and diffusive mixing need to be included and accounted for and that is the central message of our paper.

- In 22 instances in the text we have changed "mixing" to "diffusive mixing".
- We have also removed the word "fractionation" throughout the text when it was used in association with mixing.
- On Page 6, line 14 we also added the following highlighted text: "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 <u>both</u> 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."

Another point that can be mentioned in the text: In soils that contain carbonates,

isotopic exchange of CO_2 with the carbonates can introduce additional error which is not mass-dependent.

We thank the reviewer for this comment and we have added the following statement in the Discussion Section on page 12 to address this: "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)."

It is stated that: "Graham's law of effusion (rate of diffusion ~ 1/sqrt(mass)) provides us with an expected difference in diffusion rate of isotopologues." In fact, as it is written few lines before, this is a binary diffusion of CO_2 in air and hence binary diffusion equation (a one that invokes reduce-mass of CO_2 and air) should be used.

Thank you to the reviewer for pointing this out. We agree and have modified the text to say "binary diffusion equation" rather than "Graham's law of effusion" (see line 16 on page 4).

Minor comment: Please give a better description of the soil than just "clay".

Thank you for pointing out the vagueness of "clay" as a soil descriptor. The following detail has been added on page 8: "These sites were located in agricultural fields, with soils characterized as a combination of Estevan and Roughbark souls. There soils have sandy loam surfaces, with thin organic layers and soil layers that are poorly drained and have high clay content (SCSR, 1997)." In Table 2 and 3 we also included modeled examples of 3 potential soil types, including clay, based on general soil production and diffusion rates associated with those soils.

Referee #2

The paper proposes new corrections for the radiocarbon composition of CO_2 in the soil gas environment. The paper describes in detail how the authors have derived these new corrections to include diffusion and mixing in their approach. The paper should revive and encourage further discussions on this important but somewhat under explored topic. The topic therefore up to now has remained only partly resolved. Even the new corrections proposed by in the current papers have certain limitations, which the authors rightly highlight in the discussion of the paper.

Thanks for the positive comments.

Whereas, the isotope corrections are described in great detail, the field profile study is somewhat lacking in such details, especially the description of the site and soil used is rather scant. Please enhance this section.

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 fieldsite. 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.

We added the following details about the soil and field methods (page 8): "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. There soils have sandy loam surfaces, with thin organic layers and soil layers that are poorly drained and have high clay content (SCSR, 1997)."

We also added more detail about how we used the field data to apply our new proposed correction on page 9: "We used the $\Delta^{14}C$ values reported to us from the AMS laboratory along with $\delta^{13}C$ (presented in Risk. et al. 2013) to back-correct the values so that we could present the results using $\Delta^{14}C_{new}$ (Eq. 15) and then also calculate the radiocarbon composition of biological production using Δ_J^{14} (Eq.16)."

Furthermore, as the topic of the paper is rather specific, e.g. how and if the way the various formula's relate to each other is correct, some specific detailed isotope/radiocarbon expertise is needed to verify this.

We thank the reviewer for this comment and hope that the edits we have made based on the 3 referees' comments as well as the editor's comments will reinforce that the work we did is correct.

In a more general sense the paper can be published with minor revision also in light in the perception that it creates a focal point for further discussion around this paper on such isotope fractionation correction for radiocarbon (^{14}C) measurements.

Thanks, we would also like to see it published.

Referee #3

Egan et al. correctly state that radiocarbon corrections based on ^{13}C cannot be used to interpret radiocarbon data if there are processes involved that involve process that are not mass-dependent, like mixing. They use simple 1D models to show the potential biases in estimating the radiocarbon signature of source gases if gases in soil air space are interpreted without understanding that soil air both mixes and diffuses. The main advance here is that the authors use information on 13CO2 in pore space to estimate the mixing, which in turn allows a better way to estimate the 14C of CO2 sources.

Thank you for this supportive comment. We agree and feel this is an important advance.

In some sense, the authors have set up Stuiver and Polach (1977) as a target to shoot down in a way that is not entirely fair. Stuiver and Polach is a paper that sets out the conventions for reporting radiocarbon data – and only that. It is up to the investigator to interpret the radiocarbon data appropriately – including in the use of models such as those proposed in this paper. I would therefore not say that "their approach is wrong" as it was never their intention to tackle the interpretation of isotope profiles in soils. The authors need to be clear that the data should be correctly reported – i.e. according to Stuiver and Polach – but that to interpret soil CO_2 isotopic data requires the use of a model that includes transport and mixing processes.

We thank the reviewer for this comment. We agree that we were not clear enough. Our intention was not to target Stuiver and Polach (1977), but to highlight problems that have cropped up in the literature with regard to misinterpretation and misuse. We removed the word "convention" throughout the text, when what we really meant was that the mass-dependent correction did not account for diffusion and diffusive mixing in the soil gas environment (usually replaced with the word "correction"). We have also modified the text in the following places to highlight the importance of interpretation of the data as the referee suggests:

- One page 2 we removed the sentence that has a strike through it and added the following highlighted words: "Overall, soil researchers have two implicit expectations, which is that physical fractionations are present, and that biochemical fractionations are absent. ~~These expectations seem clearly out of step with the classical reporting conventions for ^{14}C that compensates only for biochemical fractionation~~. 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."
- On page 10 we added the highlighted word in the following: "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, $\Delta^{14}C_{old}$ (Eq. (7); solid line) and the second where the output was used to calculate $\Delta^{14}C_{new}$, our proposed convention for presenting radiocarbon soil CO_2 (dashed line)."

- On page 13 we added the following text, where we wanted to emphasize interpreting the data incorrectly: "This isotopic difference is not large, but it still does not follow theory, so we also compared the difference between using $\Delta^{14}C_{new}$ and $\Delta^{14}C_{old}$ 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 $\Delta^{14}C_{old}$ 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."

Does anyone in the literature actually assume Method 1?

We do not think it is commonplace for researchers to assume Method 1, however we feel that it's important to get this issue out in the open so that people can consider it, and we have tried to present this as a way forward rather than targeting particular studies. We have added the following highlight text on page 9 to address this:

"Method 1 follows the traditional correction, where Eq. (7) was used to calculate $\Delta^{14}C_{old}$, and we interpret this value as the radiocarbon composition of CO_2 from biological production. Although this interpretation may not seem commonly used, as most people now understand the soil CO_2 and soil-respired CO_2 differ, we want to use it here as an example. If a researcher were to interpret a soil CO_2 radiocarbon measurement as old and representative of the end-member source it came from, as demonstrated in Section 2, this soil CO_2 sample will not necessarily be representative of the end-member production source because of gas transport mechanisms."

The abstract states that diffusion and mixing are both problematic. For pure molecular diffusion, the fractionation should be mass dependent (i.e. not problematic). Mixing, however, will not be mass-dependent and therefore cause problems. However, by lumping both into "diffusion" in their model, the authors are confounding things. I think what they are calling "D" in their model is really an "effective" diffusivity. This would effectively mean adding 4.4 per mille to the ^{13}C of the source in equation 15 (which then might explain differences with Phillips2013?)

We thank the reviewer for this comment as it has made it clear to us that we have not been clear enough with terminology throughout the paper. The model used is a steady-state diffusion model and it does not include advection or dispersion (or use "effective" diffusivity like that used in the following paper: D.R. Bowling and W.J. Massman, 2011, Pesistent wind-induced enhancement of diffusive CO_2 transport in a mountain forest snowpack, Journal of Geophysical Research, Vol. 116, G04006). However, mixing does of course occur via diffusion, and given boundary conditions of atmospheric CO_2 on one end and biologically-produced CO_2 on the other, with isotopic differences between them, the soil gas will be a diffusively-mixed environment. As pointed out by the referee 3 in the earlier comments above, it's the interpretation that is important. Our main point is to

highlight that interpreting the isotopic composition of soil CO_2 without appropriately accounting for the isotopic processes that affect it will lead to error.

As mentioned in our response to Referee #1, although mixing might not be considered a traditional fractionating process, there are important isotopic effects associated with mixing. An isotopic fractionation is defined as a difference in the isotopic composition between a reactant and a product. For the application here with radiocarbon, the radiocarbon composition of biological respiration is the "reactant" and the soil gas is the "product". We must take into account all isotopic effects that influence the product in order to understand the true isotopic composition of the reactant. Therefore both diffusion and diffusive mixing need to be included and accounted for and that is the central message of our paper. We have edited the text in 22 instances to say "diffusive mixing" rather than "mixing".

In very deep soils, one needs to worry about additional issues that the authors have not included, such as gravitational and thermal effects associated with non-steady state conditions. These issues are treated in Severinghaus et al. 1996 (Fractionation of soil gases by diffusion of water vapor, gravitational settling, and thermal diffusion, Geochim. Cosmochim. Acta, 60: 1005-1018). Any model that hopes to infer the isotopic signatures of sources from field data of CO_2 in pore space needs to include the possibility of non-steady state conditions, or at least demonstrate that steady state is a reasonable assumption.

We agree with the reviewer that this a direction for future research. For this paper, we decided to adhere to a readily understandable steady state model, so that it could be easily understood, solved analytically, and so that the soil $^{14}CO_2$ user community can discuss, and push this work farther where sensible.

We have added following text on page 12 to clearly address potential bias in ignoring non-steady state conditions: "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."

The authors are correct that a model such as the one they propose is required to deconvolve what is affecting observed gradients of $^{14}CO_2$ and $^{13}CO_2$ in soil pore space. However, it is worth pointing out that the authors have picked a rather extreme condition where the ^{14}C signature of decomposition derived CO_2 differs greatly (300 per mille) from the atmospheric value – in many soil profiles this is not the case as the sources of CO_2 are dominated by root respiration and decomposition of more labile soil organic matter rather than the decomposition of very old peat material, and the gradients in $14CO_2$ (and thus the biases) are much smaller. (This of course depends on fA, based on Figure 4 – though we do not know what ^{13}C or [CO_2] were for these sites/dates).

Thank you to the reviewer for pointing this out. We agree that the value of atmospheric $\Delta^{14}C$ is not common. We have changed the figures and text to address this.

The following text was added on pages 7 and 8 to reiterate that our proposed solution was tested under a range of values for $\Delta^{14}C$ of production:
"The analytical gas transport model was applied across a range of soil diffusivity ($1x10^{-7}$, $1x10^{-6}$ and $1x10^{-5}$ 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 (Δ_a; 10 ‰) and $\delta^{13}C$ of atmospheric CO_2 (δ_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)."

Based on your comments, for the updated Figures and Tables, we used a value of $\Delta^{14}C$ of atmospheric CO_2 of 10 ‰ and a $\Delta^{14}C$ of biological production of -50 ‰, so the range between the values is not as extreme. We agree that these values are more representative of soils primarily dominated by the decomposition of relatively young C sources.

The authors have assumed a case where both the production rate and the radiocarbon content of CO_2 produced by decomposition are constant with soil depth, whereas that is also not normally the case (production declines exponentially with depth, and radiocarbon tends to decline linearly). Why not test with a more realistic model?

We thank the reviewer for this comment. Our focus here was not to represent every condition possible, but to highlight the problem. Hopefully others will investigate their

own situations appropriately in the future. We added the following text on page 12 to highlight the limitation of our model: "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."

I do not accept the statement at the end of section 5.1 ("Our calculated error values are therefore conservative, as these non-equilibrium processes will only add error and uncertainty") without some demonstration of how sensitive the biases are to the assumptions. Also, I think the statements about the size of the potential error ("there could be error of 100 ‰") are a bit too specific to the case investigated. Certainly, there are biases, but perhaps these could be expressed as something a percentage of the difference between the ^{14}C of sources and that of overlying air (in the most extreme case here, 30 per cent, or 1/3 of (-200-100). As noted above, more realistic simulations would likely estimate smaller absolute values, but not necessarily percentages, as these are based on the ^{13}C differences.

Thank you for this comment. Our text could be improved here to add specificity. We were not intending to be overly definitive, but to communicate general learnings from previous studies, and useful examples so as to illustrate scale of effects.

To aid in demonstrating the sensitivity of our proposed correction method in Figure 3, we have remade Table 2. The Table demonstrates the range in bias in misinterpreting $\Delta^{14}C_{old}$ as both the value for soil CO_2 and soil production at two depths and over three different potential soil environments.

Table 2. Bias from interpreting the radiocarbon isotopic composition of soil CO_2 and biological production using $\Delta^{14}C_{old}$. The depth profiles used to calculate the bias 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 m^2 s^{-1}: P = 0.5 µmol m^{-3} s^{-1}), loam (D = 1e-6 m^2 s^{-1}: P = 4 µmol m^{-3} s^{-1}), and sand (D = 1e-5 m^2 s^{-1}: P = 2 µmol m^{-3} s^{-1}). All bias values are absolute.

Soil Type	Depth (cm)	$\Delta^{14}C_{old}$ (‰)	Δ_J^{14} from $\Delta^{14}C_{old}$ (‰)	$\Delta^{14}C_{new}$ (‰)	Δ_J^{14} from $\Delta^{14}C_{new}$ (‰)	$\Delta^{14}C_{old}$ - $\Delta^{14}C_{new}$ (‰)	-50 - Δ_J^{14} from $\Delta^{14}C_{old}$ (‰)
Clay	2.5	-43.0	-58.1	-31.7	-50.0	11.3	8.1
D = 1e-7 m^2 s^{-1}							
P = 0.5 µmol m^{-3} s^{-1}	50	-49.5	-58.3	-40.8	-50.0	8.6	8.3
Loam	2.5	-41.5	-58.1	-29.6	-50.0	11.9	8.1
D = 1e-6 m^2 s^{-1}							
P = 4 µmol m^{-3} s^{-1}	50	-49.3	-58.3	-40.6	-50.0	8.7	8.3
Sand	2.5	-3.9	-57.0	24.9	-50.0	28.8	7.0
D = 1e-5 m^2 s^{-1}							
P = 2 µmol m^{-3} s^{-1}	50	-38.5	-58.0	-25.3	-50.0	13.2	8.0

The "field experiment" and the use of models to interpret these data are not well enough described for the reader to understand. Were the same assumptions (constant production and 'effective' diffusion with depth) applied for interpreting these results? Either this needs to be more thoroughly described (for example by including the CO_2 and $13CO_2$ profiles) or removed from the paper, as it does not really fit with the rest.

We are sorry that we were not more specific. We have added the following text on page 9 to explain how we used the field results to give an example of how to apply our solution: "We used the $\Delta^{14}C$ values reported to us from the AMS laboratory along with $\delta^{13}C$ (presented in Risk. et al. 2013) to back-correct the values so that we could present the results using $\Delta^{14}C_{new}$ (Eq. 15) and then also calculate the radiocarbon composition of biological production using Δ_J^{14} (Eq.16)."

Overall, the authors need to do more sensitivity tests with their 'thought experiment" models; if they use the field data it needs to be much better described.

We apologize for not explaining our sensitivity analysis better.

We have added text to the following paragraph on pages 7 and 8 to show the ranges of parameters that our solution was tested across:

"The analytical gas transport model was applied across a range of soil diffusivity ($1x10^{-7}$, $1x10^{-6}$ and $1x10^{-5}$ 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 (Δ_a; 10 ‰) and $\delta^{13}C$ of atmospheric CO_2 (δ_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). "

We have also remade Table 2, as mentioned in a response above, and created Table 3 to also demonstrate the sensitivity of the δ_J^{13} value used in $\Delta^{14}C_{new}$ and Δ_J^{14} calculations.

Table 3. Sensitivity of the δ_J^{13} value in $\Delta^{14}C_{new}$ and Δ_J^{14} calculations. The depth profiles used to calculate the bias from using the wrong δ_J^{13} 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 m^2 s^{-1}: P = 0.5 µmol m^{-3} s^{-1}), loam (D = 1e-6 m^2 s^{-1}: P = 4 µmol m^{-3} s^{-1}), and sand (D = 1e-5 m^2 s^{-1}: P = 2 µmol m^{-3} s^{-1}). All bias values are absolute.

Soil Type	Depth (cm)	Deviation in δ_J^{13} (‰)	Bias using wrong δ_J^{13} in $\Delta^{14}C_{new}$ (‰)	Bias using $\Delta^{14}C_{new}$ with wrong δ_J^{13} to calculate Δ_J^{14} (‰)
Clay	2.5 cm	-0.5	1.0	1.0
D = 1e-7 m^2 s^{-1}		+0.5	1.0	1.0
P = 0.5 µmol m^{-3} s^{-1}		-1	2.0	2.0
		+1	1.9	1.9
		-5	10.0	9.8
		+5	9.9	9.7
	50 cm	-0.5	1.0	1.0
		+0.5	1.0	1.0
		-1	2.0	2.0
		+1	2.0	1.9
		-5	9.9	9.8
		+5	9.8	9.7
Loam	2.5 cm	-0.5	1.0	1.0
D = 1e-6 m^2 s^{-1}		+0.5	1.0	1.0
P = 4 µmol m^{-3} s^{-1}		-1	2.0	2.0
		+1	2.0	1.9
		-5	10.0	9.8
		+5	9.9	9.7
	50 cm	-0.5	1.0	1.0
		+0.5	1.0	1.0
		-1	2.0	2.0
		+1	2.0	1.9
		-5	9.9	9.8
		+5	9.8	9.7
Sand	2.5 cm	-0.5	1.1	1.0
D = 1e-5 m^2 s^{-1}		+0.5	1.1	1.0
P = 2 µmol m^{-3} s^{-1}		-1	2.1	2.0
		+1	2.1	1.9
		-5	10.6	9.8
		+5	10.4	9.7
	50 cm	-0.5	1.0	1.0
		+0.5	1.0	1.0

		-1	2.0	2.0
		+1	2.0	1.9
		-5	10.1	9.8
		+5	9.9	9.7

We have also added the following text on page 14 to address the sensitivity of the δ^{13} value: "The back-correcting solution does, however, assume that the researcher has measured a value of δ_s^{13} independent from $\Delta^{14}C_{old}$, as the AMS measured δ^{13} is not comparable to Isotope-Ratio Mass Spectrometry (IRMS) measured δ^{13}. To assess the sensitivity of the δ_J^{13} value in calculating $\Delta^{14}C_{new}$ and Δ_J^{14} for back corrections, in Table 3 we present the error in using a δ_J^{13} value that is wrong by ± 0.5, 1, and 5 ‰. If rounded to the nearest ‰ value, the bias associated with using a δ_J^{13} ± 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 $\delta^{13}C$ measurements independently, although we recommend against using this back correction method for new data ."

Lines 10-15 in the Introduction are somewhat misleading. The 'traditional' way to report ^{14}C values from CO_2 in soil air would use the ^{13}C signature of the CO_2 that was sampled. This value is important as it by definition would include both the biochemical and physical (diffusion) effects in a system where mixing is not important. As noted above, the reporting of the data should not be confounded with the interpretation of the data.

Thank you to the reviewer for pointing this out. We agree, and think that we have not been clear with our terminology throughout the text. Although mixing might not be considered a traditional fractionating process, there are important isotopic effects associated with mixing. An isotopic fractionation is defined as a difference in the isotopic composition between a reactant and a product. For the application here with radiocarbon, the radiocarbon composition of biological respiration is the "reactant" and the soil gas is the "product". We must take into account all isotopic effects that influence the product in order to understand the true isotopic composition of the reactant. Therefore both diffusion and diffusive mixing need to be included and accounted for and that is the central message of our paper.

- In 22 instances in the text we have changed "mixing" to "diffusive mixing".
- We have also removed the word "fractionation" throughout the text when it was used in association with mixing.
- On Page 6, line 14 we also added the following highlighted text: "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 <u>both</u> 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."

Page 4, line 16 – the estimation of the isotopic effect is based on comparing the reduced masses of the ^{12}C-air, ^{13}C-air, or ^{14}C-air system, not just the square root of the masses of the isotopic species of CO_2 alone (air has a 'mass' of 28). This is unclear from what is written.

We agree. We have added a citation on page 3 for Cerling et al. 1991 who describes in detail with appropriate references.

Most radiocarbon is measured directly these days as isotope ratios, rather than activities as presented in equation (5). Perhaps this nomenclature could be updated.

We agree, and we do use isotope ratio further on, but we wanted to present the math as it was originally, to show how we get to the isotope ratios from there.

While $\Delta^{14}C$ is the $\delta^{13}C$-corrected version of $\delta^{14}C$ as stated in line 24 on page 5, both of these include an additional correction for the decay of the standard since 1950 . (This is actually correct in the formula stated by the authors, which uses $A_a$bs , but could be really confusing for the reader who does not know what A_{abs} is and how it differs from the equations (5) that refer only to the activity of oxalic acid. This correction is not negligible, the oxalic acid standard has decreased by about 10 ‰ since 1950. (The same is not true for Fraction Modern or $D^{14}C$, which are not expressed relative to A_{abs} , because the standard and sample are presumed to decay at the same rate). Because of this, the authors should really state the assumed year of sampling/measurement in their simulations (as noted above, $\Delta^{14}C$ and $\delta^{14}C$ will differ slightly depending on the year of measurement/sampling).

We thank the reviewer for this comment. We found that while reading the foundational papers on radiocarbon reporting, the description of terms and equations lacked detail, and we were at times unclear on all the different terms. We believe that as we build a new foundation for interpreting radiocarbon of the soil gas environment, it is important that we're very clear on nomenclature. When we use our proposed solution we assume that year is present day, because there is no oxalic acid correction in our form of $\Delta^{14}C$ (added this on page 8).

The current $\Delta^{14}C$ of atmospheric CO_2 is closer to 10 ‰ than 100 ‰.

Thank you for pointing this out. As mentioned above, we have updated the text as well as all the figures and tables to include modeled profiles using a value of 10 ‰.

One problem with the "new" approach is that one must assume that they know the $\delta^{13}C$ signature of the CO_2 being produced – what is the sensitivity to getting that value incorrect by 1-2 ‰?

We agree that this could be problematic for back-correcting older data, but moving forward if researchers are going to measure the radiocarbon signature of soil CO_2 at different depths to infer production, they should also measure $\delta^{13}C$. We added the following text on page 14 to address this: "We also suggest that researchers measure δ^{13} alongside $\Delta^{14}C$, so that they are not dependent on the AMS measured δ^{13} for potential back-corrections, to prevent potential error ranging from 1-10 ‰ (Table 3)."

We also performed some sensitivity analysis of the δ_j^{13} value in calculating $\Delta^{14}C_{new}$ and Δ_j^{14} as mentioned above, which can be found in Table 3.

Table 2 compares with "Phillips et al 2013" but that is first mentioned in the Discussion – it should be explained in the methods or the introduction if used.

We updated Table 2 and removed this reference, and to instead just use a general example of the bias associated with using $\Delta^{14}C_{old}$ to calculate the radiocarbon composition of production using any gradient method.

Page 12, line 20. Presumably the authors are pointing out that the movement of air in dynamic chambers could cause some kind of enhanced exchange with soil pore space air – where does the 200 ‰ number come from? – is there a reference for this? Wouldn't mixing also mean that in this case the 'standard' ^{13}C correction would not be appropriate for interpreting the ^{14}C of the measured flux?

The value for 200 ‰ is referenced as coming from the Egan et al. 2014 study. We have removed the Discussion Section addressing all the different potential additional bias associated with all different methods, thanks to this comment as well as a comment from the Editor. We did however, leave in the section about the flux chambers in the following text on page 12: "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."

We left this section as we think it is important that the readers understand why the old interpretation correction will still work with this method.

Page 12, line 32. "Changes in oxygen availability will also affect fractionations related to the rate of production. " This statement needs a reference. What the authors mean here is that the source of C might change as might any fractionation associated with respiration under low O2. However, the isotopic signatures of CO_2 that accumulate in the chamber will still represent that source without need for additional corrections.

As mentioned above, this whole section is now removed from the paper as it was disjointed and did not help.

Page 14, lines 5-10. AMS laboratories measure all three isotopes, but the ^{13}C they measure includes fractionation processes in the sample preparation and measurement (all of which are correctable using mass-dependent assumptions). However, the AMS- measured $\delta^{13}C$ is not a good measure compared to the ^{13}C of the CO_2 that is measured with an IRMS. Therefore, the labs cannot easily report the $\Delta^{14}C$ as the authors propose unless the user has independently supplied the $\delta^{13}C$ values for their samples. Instead I would advise people to 'uncorrect' the reported data themselves (and give them the formula). The current guidelines are to use Fraction Modern and report the year of collection and the year of measurement so that other ways of expressing ^{14}C can be calculated. Also, AMS labs do not measure activity, they measure isotope ratios.

We agree with this. In Section 5.1 we give the formula for how people can "uncorrect" their already reported data: "…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 $\delta^{13}C$ 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}." This is what we did with our already reported data in Fig. 4 and Section 4.2.

Isotopic ~~fractionation~~ 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 radio-isotopic 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.

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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. ~~These expectations seem clearly out of step with the classical reporting conventions for ^{14}C that compensates only for biochemical fractionation~~. 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:

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

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.

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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. In panel (a) two depth profiles of $\delta^{13}C$ of CO_2 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 $\delta^{13}C$ 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 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.

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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:

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

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 $\delta^{13}C$ of soil-respired CO_2, the error could be as large as the absolute value of (δ_a- δ_J^{13}) – 4.4 ‰. In Fig. 2(a), the error in interpreting $\delta^{13}C$ of soil CO_2 at 40 cm depth (~ -20 ‰) as a value of production would be ~5 ‰, and the error increases in magnitude at shallower depths. 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., 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 ~ $1/\sqrt{\text{mass}}$) 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 $\delta^{13}C$:

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

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 (-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

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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 δ_J^{13} equation is as follows:

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

where δ_J^{14} is the $\delta^{14}C$ composition of soil production, C_s and δ_s^{14} are the mole fraction and $\delta^{14}C$ composition of the soil CO_2, and C_a and δ_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 $\delta^{14}C$, δ_J^{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, 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 $\delta^{13}C$ 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 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:

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

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

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

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

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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):

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

Combining Eqs. (3) and (6):

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

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_{abs} in our notation is equivalent to A_O 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 $\Delta^{14}C_{old}$ 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 δ_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_s = 14780 ppm, Δ_s= -48.4319 ‰, C_a = 380 ppm and Δ_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:

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

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:

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

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

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:

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

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 ($1x10^{-7}$, $1x10^{-6}$ and $1x10^{-5}$ 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 (Δ_a; 10 ‰) and $\delta^{13}C$ of atmospheric CO_2 (δ_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 $\Delta^{14}C_{old}$ 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 δ_J^{13} (Eq. (2)), the biological production of $\delta^{13}C$, in its place in the denominator of Eq. (7) as follows:

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

The model-generated soil pore space isotope values were input into Eq. (15) to produce depth profiles of $\Delta^{14}C_{new}$. Values of $\Delta^{14}C_{new}$ 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_{abs}) in Eq. 15. Then to calculate the radiocarbon composition of production, Δ_J^{14}, the $\Delta^{14}C$ composition of the soil CO_2, $\Delta^{14}C_{new}$, can be placed into our adaption of Davidson (1995) for ^{14}C (Eq. (4)) as follows:

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

where Δ_J^{14} is the $\Delta^{14}C$ composition of soil production, C_s and $\Delta^{14}C_{new}$ are the mole fraction and $\Delta^{14}C$ composition of the soil CO_2, and C_a and Δ_a^{14} 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. There soils have sandy loam surfaces, with thin organic layers and soil layers that are poorly drained and have high clay content (SCSR, 1997).

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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 N_2-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 $\Delta^{14}C$.

As described in Risk et al. (2013), on each visit triplicate samples were also collected in 10 ml N_2-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 CO_2 and $\delta^{13}C$ within 2 weeks of sampling using a GV Isoprime CF-IRMS and Multiflow gas bench (Isoprime, UK).

We used the $\Delta^{14}C$ values reported to us from the AMS laboratory along with $\delta^{13}C$ (presented in Risk. et al. 2013) to back-correct the values so that we could present the results using $\Delta^{14}C_{new}$ (Eq. 15) and then also calculate the radiocarbon composition of biological production using Δ_J^{14} (Eq.16).

3.4 Interpreting Soil Profiles

Our primary goal was to correctly extract the isotopic composition of CO_2, produced by biological production. We applied two methods to extract this signal from the model-generated soil CO_2 profiles as well as soil CO_2 profiles from the field:

Method 1 follows the traditional correction, where Eq. (7) was used to calculate $\Delta^{14}C_{old}$, and we interpret this value as the radiocarbon composition of CO_2 from biological production. Although this interpretation may not seem commonly used, as most people now understand the soil CO_2 and soil-respired CO_2 differ, we want to use it here as an example. If a researcher were to interpret a soil CO_2 radiocarbon measurement as old and representative of the end-member source it came from, as demonstrated in Section 2, this soil CO_2 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 CO_2 from biological production in two steps, as described in Section 3.2. First, the transport corrected radiocarbon composition of soil CO_2, is calculated using Eq. (15) ($\Delta^{14}C_{new}$). Then this properly interpreted soil CO_2 value can be used in Eq. (16) to calculate the radiocarbon composition of production, Δ_J^{14}.

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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, $\Delta^{14}C_{old}$ (Eq. (7); solid line) and the second where the output was used to calculate $\Delta^{14}C_{new}$, our proposed convention for presenting radiocarbon soil CO_2 (dashed line). All of the $\Delta^{14}C_{old}$ depth profiles in Fig. 3 had slightly (~ 10 ‰) more depleted $\Delta^{14}C$ soil CO_2 values than the $\Delta^{14}C_{new}$ depth profiles. When the radiocarbon composition of CO_2 from biological production, Δ_J^{14}, was calculated using $\Delta^{14}C_{new}$ (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 $\Delta^{14}C_{old}$ soil CO_2 to be the radiocarbon composition of CO_2 from biological production, the $\Delta^{14}C_{old}$ 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, $\Delta^{14}C_{old}$, 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 (Δ_J^{14}), where the reported radiocarbon values were back-corrected using our new approach, $\Delta^{14}C_{new}$, and then input into Eq. (16) (Method 2). When considering age, the radiocarbon compositions of production (Δ_J^{14}), 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.

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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 $\delta^{13}C$ (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 $\Delta^{14}C$ calculation on the same equations, this is what we expected, where values of $\Delta^{14}C$ of soil CO_2 differed in the soil profile (shown in Fig. 3) were intermediate between the two mixing sources (CO_2 in the air just above the soil and soil biological production). These effects of diffusion and diffusive mixing demonstrate that Method 1 (which assumes $\Delta^{14}C_{old}$ of soil CO_2 = $\Delta^{14}C$ of soil production) is inappropriate for the soil gas application because it does not describe the radiocarbon composition of CO_2 as produced, and before alteration by gas transport processes. In contrast, Method 2 (where the $\Delta^{14}C$ isotopic signature of production, Δ_J^{14}, is calculated from $\Delta^{14}C_{new}$) 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 $\Delta^{14}C_{old}$. 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 ^{14}C 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 CO_2 (f_a) 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 CO_2 in the soil compared to the total CO_2. These scenarios have a much higher f_a 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 CO_2 present compared to the total amount of CO_2, and therefore the isotopic depth profile more closely resembles a mass-mixing profile. These soil CO_2 depth profiles have lower f_a 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_a 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.

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Aside from our proposed correction, a few other analytical alternatives might be appropriate for correcting ^{14}C in soil CO_2. The Davidson (1995) δ_J 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 δ_J method. However, if a researcher chooses to use an alternate gradient approach, they should still use $\Delta^{14}C_{new}$ rather than $\Delta^{14}C_{old}$ to calculate soil CO_2 first, as $\Delta^{14}C_{old}$ does not account for transport fractionations. To demonstrate the bias associated with using $\Delta^{14}C_{old}$ 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 $\Delta^{14}C_{old}$ 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 $\Delta^{14}C_{new}$ and $\Delta^{14}C_{old}$ 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 $\Delta^{14}C_{old}$ 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 $\Delta^{14}C_{old}$ 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 $\Delta^{14}C_{old}$ 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

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production. Previously reported data using the traditional Stuiver and Polach (1977) reporting convention, can be back-corrected using our solution. The back-correcting solution does, however, assume that the researcher has measured a value of δ_s^{13} independent from $\Delta^{14}C_{old}$, as the AMS measured δ^{13} is not comparable to Isotope-Ratio Mass Spectrometry (IRMS) measured δ^{13}. To assess the sensitivity of the δ_J^{13} value in calculating $\Delta^{14}C_{new}$ and Δ_J^{14} for back corrections, in Table 3 we present the error in using a δ_J^{13} value that is wrong by ± 0.5, 1, and 5 ‰. If rounded to the nearest ‰ value, the bias associated with using a δ_J^{13} ± 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 $\delta^{13}C$ 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 $\Delta^{14}C_{old}$ calculation, 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 $\delta^{13}C$ 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 $\Delta^{14}C$, so that they are not dependent on the AMS measured δ^{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 $\Delta^{14}C$ 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 $\Delta^{14}C$ solution, which uses a $\delta^{13}C$ correction, is not appropriate for the soil gas environment. We propose a new best practice for $\Delta^{14}C$ work in the soil gas environment that accounts for gas transport fractionations and produces true estimates of $\Delta^{14}C$ 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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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 $\delta^{13}C$ 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}	$\delta^{13}C$ of CO_2 in air above the soil	‰
δ_a^{14}	$\delta^{14}C$ of CO_2 in air above the soil	‰
Δ_a	$\Delta^{14}C$ of CO_2 in air above the soil	‰
δ_J^{13}	$\delta^{13}C$ of CO_2 from soil production, calculated using Eq. (2)	‰
δ_J^{14}	$\delta^{14}C$ of CO_2 from soil production, calculated using Eq. (4)	‰
Δ_J^{14}	$\Delta^{14}C$ of CO_2 from soil production, calculated using Eq. (17)	‰
δ_s^{13}	$\delta^{13}C$ of CO_2 in soil pore space	‰
δ_s^{14}	$\delta^{14}C$ of CO_2 in soil pore space	‰
Δ_s	$\Delta^{14}C$ of CO_2 in soil pore space	‰
f_a	fraction of C_a in soil relative to total CO_2 in soil pore space	unitless
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

Table 2. Bias from interpreting the radiocarbon isotopic composition of soil CO_2 and biological production using $\Delta^{14}C_{old}$. The depth profiles used to calculate the bias 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 m^2 s^{-1}: P = 0.5 µmol m^{-3} s^{-1}), loam (D = 1e-6 m^2 s^{-1}: P = 4 µmol m^{-3} s^{-1}), and sand (D = 1e-5 m^2 s^{-1}: P = 2 µmol m^{-3} s^{-1}). All bias values are absolute.

Soil Type	Depth (cm)	$\Delta^{14}C_{old}$ (‰)	Δ_i^{14} from $\Delta^{14}C_{old}$ (‰)	$\Delta^{14}C_{new}$ (‰)	Δ_i^{14} from $\Delta^{14}C_{new}$ (‰)	$\Delta^{14}C_{old}$ - $\Delta^{14}C_{new}$ (‰)	-50 - Δ_i^{14} from $\Delta^{14}C_{old}$ (‰)
Clay	2.5	-43.0	-58.1	-31.7	-50.0	11.3	8.1
D = 1e-7 m^2 s^{-1}							
P = 0.5 µmol m^{-3} s^{-1}	50	-49.5	-58.3	-40.8	-50.0	8.6	8.3
Loam	2.5	-41.5	-58.1	-29.6	-50.0	11.9	8.1
D = 1e-6 m^2 s^{-1}							
P = 4 µmol m^{-3} s^{-1}	50	-49.3	-58.3	-40.6	-50.0	8.7	8.3
Sand	2.5	-3.9	-57.0	24.9	-50.0	28.8	7.0
D = 1e-5 m^2 s^{-1}							
P = 2 µmol m^{-3} s^{-1}	50	-38.5	-58.0	-25.3	-50.0	13.2	8.0

Table 3. Sensitivity of the δ_J^{13} value in $\Delta^{14}C_{new}$ and Δ_J^{14} calculations. The depth profiles used to calculate the bias from using the wrong δ_J^{13} 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 $m^2 s^{-1}$: P = 0.5 µmol $m^{-3} s^{-1}$), loam (D = 1e-6 $m^2 s^{-1}$: P = 4 µmol $m^{-3} s^{-1}$), and sand (D = 1e-5 $m^2 s^{-1}$: P = 2 µmol $m^{-3} s^{-1}$). All bias values are absolute.

Soil Type	Depth (cm)	Deviation in δ_J^{13} (‰)	Bias using wrong δ_J^{13} in $\Delta^{14}C_{new}$ (‰)	Bias using $\Delta^{14}C_{new}$ with wrong δ_J^{13} to calculate Δ_J^{14} (‰)
Clay	2.5 cm	-0.5	1.0	1.0
D = 1e-7 $m^2 s^{-1}$		+0.5	1.0	1.0
P = 0.5 µmol $m^{-3} s^{-1}$		-1	2.0	2.0
		+1	1.9	1.9
		-5	10.0	9.8
		+5	9.9	9.7
	50 cm	-0.5	1.0	1.0
		+0.5	1.0	1.0
		-1	2.0	2.0
		+1	2.0	1.9
		-5	9.9	9.8
		+5	9.8	9.7
Loam	2.5 cm	-0.5	1.0	1.0
D = 1e-6 $m^2 s^{-1}$		+0.5	1.0	1.0
P = 4 µmol $m^{-3} s^{-1}$		-1	2.0	2.0
		+1	2.0	1.9
		-5	10.0	9.8
		+5	9.9	9.7
	50 cm	-0.5	1.0	1.0
		+0.5	1.0	1.0
		-1	2.0	2.0
		+1	2.0	1.9
		-5	9.9	9.8
		+5	9.8	9.7
Sand	2.5 cm	-0.5	1.1	1.0
D = 1e-5 $m^2 s^{-1}$		+0.5	1.1	1.0
P = 2 µmol $m^{-3} s^{-1}$		-1	2.1	2.0
		+1	2.1	1.9
		-5	10.6	9.8
		+5	10.4	9.7
	50 cm	-0.5	1.0	1.0
		+0.5	1.0	1.0
		-1	2.0	2.0
		+1	2.0	1.9
		-5	10.1	9.8
		+5	9.9	9.7

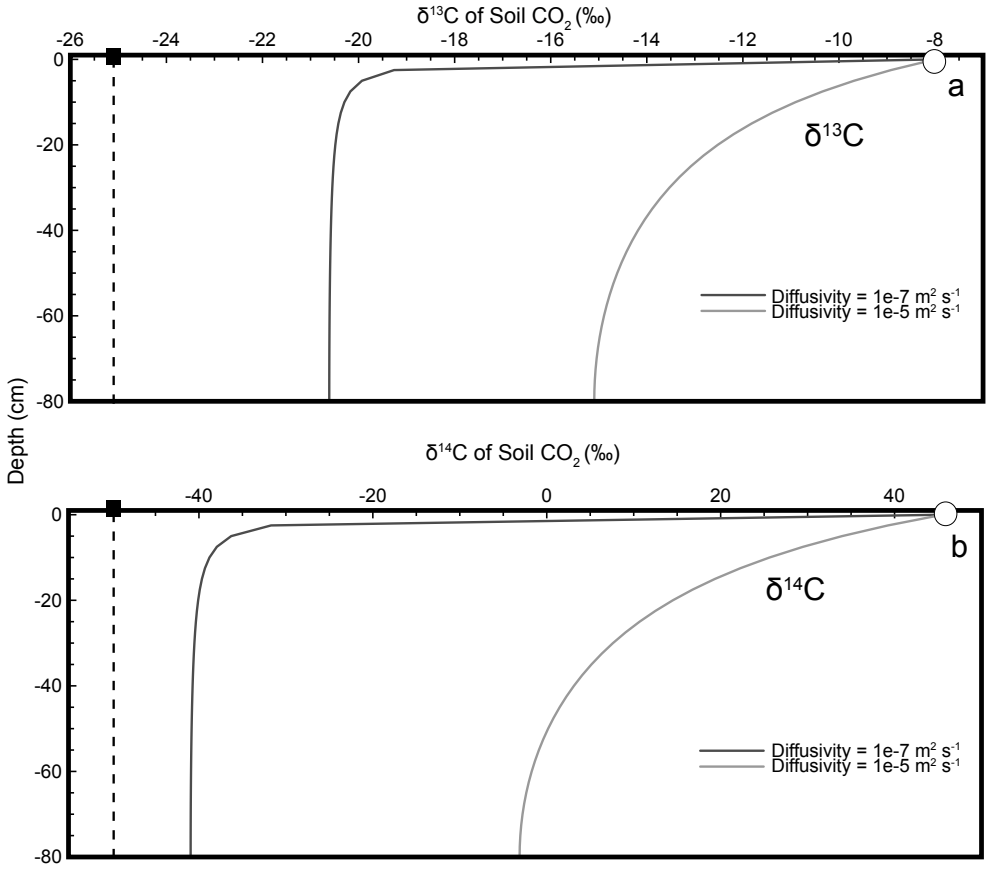

Figure 1: Modelled steady-state diffusive vertical depth profiles for $\delta^{13}C$ and $\delta^{14}C$ of soil CO_2. In the top panel the $\delta^{13}C$ of atmospheric CO_2 (circle) is -8 ‰ and CO_2 from biological production (square with dashed line; δ_J) is -25 ‰. In the bottom panel the $\delta^{14}C$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

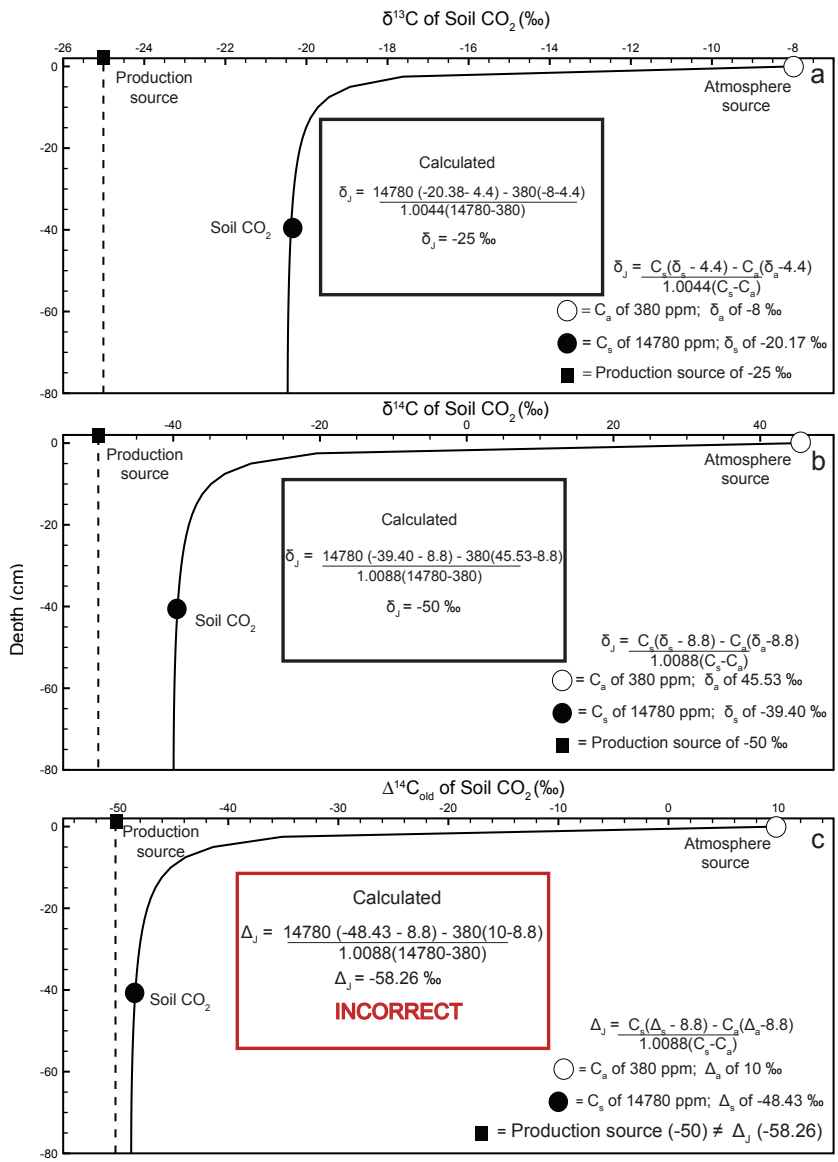
δ13C of Soil CO2 (‰)
Production source
Atmosphere source
a
Calculated
δJ = 14780 (-20.38- 4.4) - 380(-8-4.4) / 1.0044(14780-380)
δJ = -25 ‰
Soil CO2
δJ = Cs(δs - 4.4) - Ca(δa-4.4) / 1.0044(Cs-Ca)
= Ca of 380 ppm; δa of -8 ‰
= Cs of 14780 ppm; δs of -20.17 ‰
= Production source of -25 ‰
δ14C of Soil CO2 (‰)
Production source
Atmosphere source
b
Calculated
δJ = 14780 (-39.40 - 8.8) - 380(45.53-8.8) / 1.0088(14780-380)
δJ = -50 ‰
Soil CO2
δJ = Cs(δs - 8.8) - Ca(δa-8.8) / 1.0088(Cs-Ca)
= Ca of 380 ppm; δa of 45.53 ‰
= Cs of 14780 ppm; δs of -39.40 ‰
= Production source of -50 ‰
Depth (cm)
Δ14Cold of Soil CO2 (‰)
Production source
Atmosphere source
c
Calculated
ΔJ = 14780 (-48.43 - 8.8) - 380(10-8.8) / 1.0088(14780-380)
ΔJ = -58.26 ‰
INCORRECT
Soil CO2
ΔJ = Cs(Δs - 8.8) - Ca(Δa-8.8) / 1.0088(Cs-Ca)
= Ca of 380 ppm; Δa of 10 ‰
= Cs of 14780 ppm; Δs of -48.43 ‰
= Production source (-50) ≠ ΔJ (-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 ($1e^{-6}$ 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.

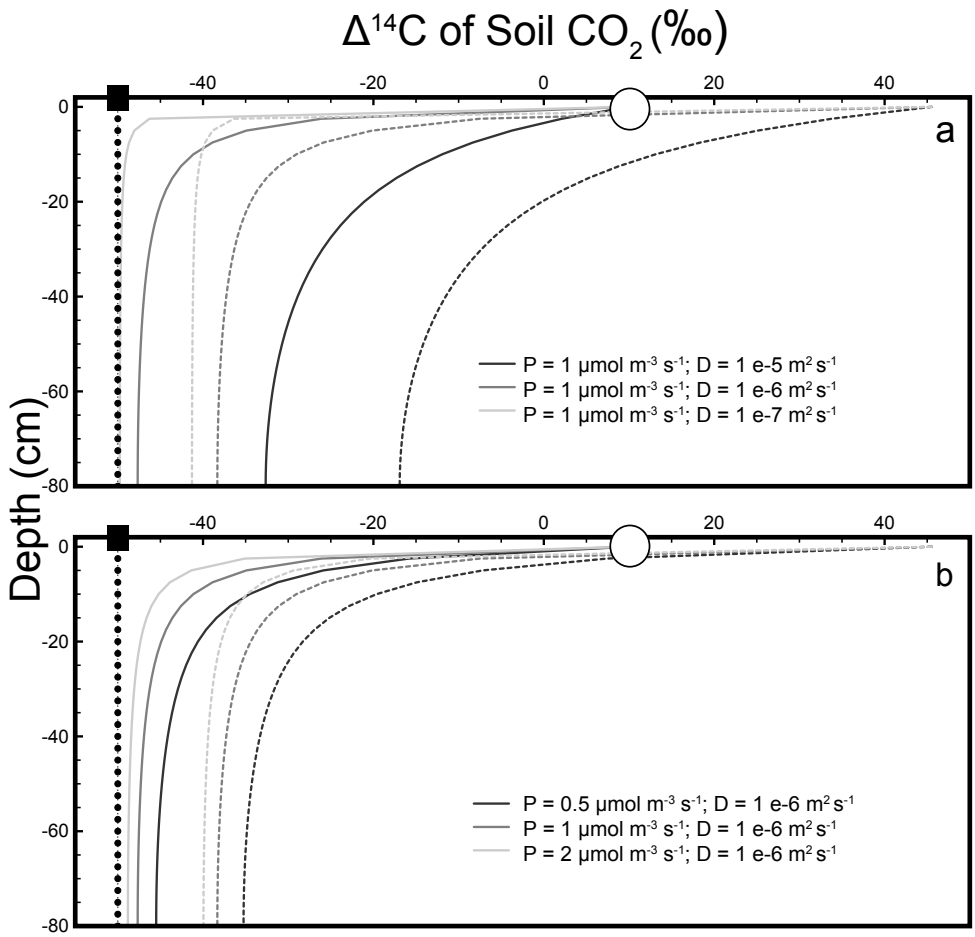

Figure 3: Modelled steady-state vertical depth profiles for $\Delta^{14}C$ of soil CO_2. In panel A the model scenarios have the same rates of production (P), but differing diffusivities (D) (solid lines are Method 1, $\Delta^{14}C_{old}$; dashed lined are Method 2, $\Delta^{14}C_{new}$). In panel B the model scenarios have the same diffusivities but differing production rates. The model input for $\Delta^{14}C$ of production was -50 ‰ in all cases (Δ_J^{14}; black dashed line) and $\Delta^{14}C$ of the atmospheric source was 10 ‰ (white circle).

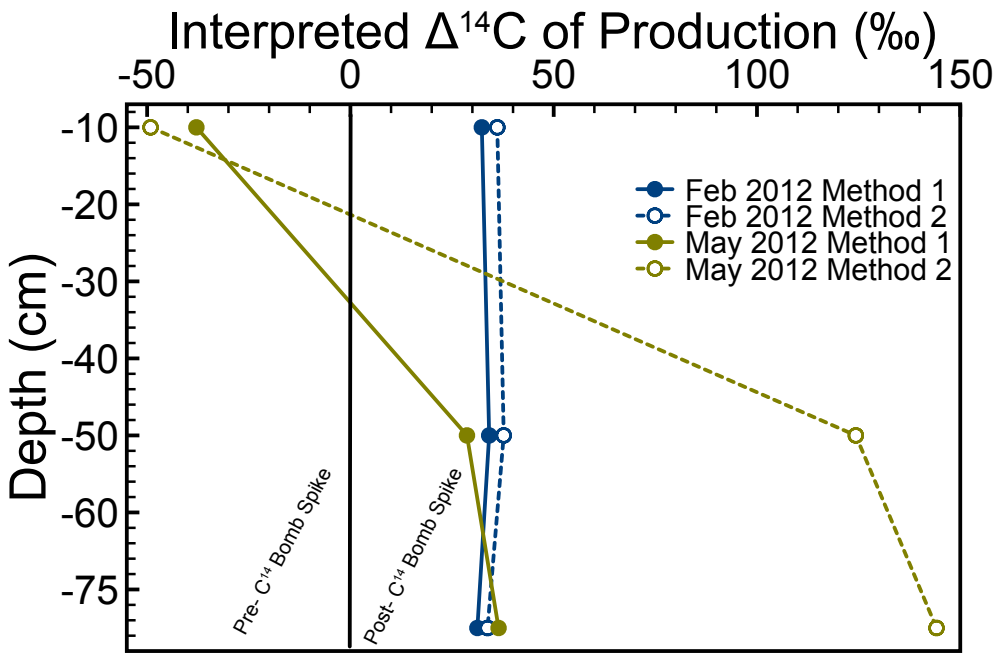

Figure 4: Field results for interpreted $\Delta^{14}C$ of production calculated from soil CO_2 gas samples collected at 10 cm, 50 cm, and 75 cm depths from soil gas wells in February and May 2012 from a site in Saskatchewan, Canada. Solid lines are $\Delta^{14}C$ calculated using Method 1 and the dashed lines are calculated using Method 2.

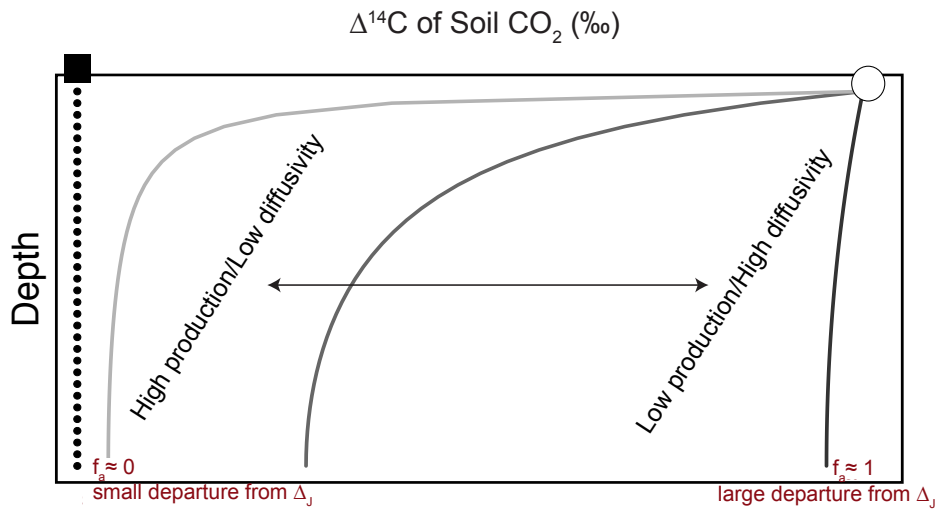

Figure 5: Method 1 error can be estimated using f_a, the fraction of soil CO_2 that originated from the atmosphere that has mixed downward into the soil gas profile. The radiocarbon composition of biological production is presented with a black square, and the atmospheric source of CO_2 is presented as a white circle.