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Interactive comment on "Isotopic fractionation corrections for the radiocarbon composition of CO_2 in the soil gas environment must include diffusion and mixing" *by* Jocelyn E. Egan et al.

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Thanks to the referees and the editor for helpful comments that have led to a much-improved manuscript. Referee comments are listed below, and our responses follow each - line numbers refer to those in the revised version.

Sincerely, Jocelyn Egan (for all authors)

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Egan et al. correctly state that radiocarbon corrections based on 13C 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.

Response: Agreed, we 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 CO2 isotopic data requires the use of a model that includes transport and mixing processes.

Response: Agreed. However, we do not say that their approach is "wrong". In the abstract we state "We found that the conventional correction is inappropriate for interpreting the radio-isotopic composition of CO2 from biological production, because it does not account for diffusion and diffusive mixing." and we stand by this statement. 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. We have modified the text in the following places to highlight the important of interpretation as the referee suggests: line 16 on page 1, and lines 6-7 and 23 on page 2.

We also want it to be clear that in our proposed solution, a model is not required to interpret soil CO2 isotopic data. Here, we have used a model to illustrate the problem

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and solution, but with real data we suggest that people use $\Delta 14Cnew$ and $\Delta J14$ to report radiocarbon results measured in the soil gas environment (as shown in section 5.4).

Does anyone in the literature actually assume Method 1?

Response: We don't know the answer to this question. It's very hard to determine all the behind-the-scenes corrections that occur in complicated isotope papers. We have not found any treatment of diffusion and mixing in the literature similar to ours. 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.

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 13C of the source in equation 15 (which then might explain differences with Phillips2013?)

Response: The model used is a steady-state diffusion model, and it does not include advection or dispersion. 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.

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.

Response: We agree with the reviewer that this a direction for future research (Section 5.1). 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 $14CO_2$ user community can discuss, and push this work farther where sensible.

Added on page 16 lines 19-23: "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 authors are correct that a model such as the one they propose is required to deconvolve what is affecting observed gradients of $14CO_2$ and $13CO_2$ in soil pore space. However, it is worth pointing out that the authors have picked a rather extreme condition where the 14C 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 13C or [CO_2] were for these sites/dates).

Response: If the math and physics are correct when extreme boundary conditions are involved, then they are correct and should be dealt with in all cases.

The authors have assumed a case where both the production rate and the radiocar-

bon content of CO2 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?

Response: Our focus is not to represent every condition possible, but to highlight the problem. Hopefully others will investigate their own situations appropriately in the future.

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 14C 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 13C differences.

Response: 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 address this we have added the following on lines 19-28 of page 16: "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 δ13C 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 frac-

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tionation uncertainty (Egan et al., 2014) that may need to be evaluated. The real magnitude of error will be situationally specific, and sensitive to the soil conditions and sampling methodology."

Yes, the potential error is specific to our case ("there could be error of 100 permil") because we did need to use an example. To be clearer on this point, we have added to the text on lines 10-13 on page 16: "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 situationally specific as shown in Fig. 3 and 5.

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 CO2 and 13CO2 profiles) or removed from the paper, as it does not really fit with the rest.

Response: The field data was used in this manuscript as an example of the difference in using old and new reporting style. It was not meant to be an in depth field case.

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.

Response: The thought experiment model was also tested across the ranges described in section 3.1. The field data was not used in the model work. Figures 1,2 and 3 show the sensitivity of the model across a wide range of diffusivity and production rates. Figures 2 and 3 also demonstrate that our proposed solution, Method 2, is insensitive to soil parameters, as it worked across the ranges of parameters tested. We have added text on lines 1-2 of page 14 to make this clear in more than just a graphical sense as shown in the figures.

Lines 10-15 in the Introduction are somewhat misleading. The 'traditional' way to report

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14C values from CO2 in soil air would use the 13C signature of the CO2 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.

Response: As we noted above, mixing occurs by diffusion too.

Page 4, line 16 – the estimation of the isotopic effect is based on comparing the reduced masses of the 12C-air, 13C-air, or 14C-air system, not just the square root of the masses of the isotopic species of CO2 alone (air has a 'mass' of 28). This is unclear from what is written. Response: We agree. We have added a citation on Page 5 lines 21-22 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. While Δ14C is the δ13C-corrected version of δ14C 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 Aabs , but could be really confusing for the reader who does not know what Aabs 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 D14C, which are not expressed relative to Aabs , 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, Δ14C and δ14C will differ slightly depending on the year of measurement/sampling).

Response: 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 sufficient 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 Δ14C (added this on line 8-9 page 11).

The current Δ14C of atmospheric CO2 is closer to 10 ‰ than 100 ‰

Response: Thank you for pointing this out. The model works with any atmospheric value for Δ14C.

One problem with the "new" approach is that one must assume that they know the δ13C signature of the CO2 being produced – what is the sensitivity to getting that value incorrect by 1-2 ‰

Response: 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 CO2 at different depths to infer production, they should also measure δ13C (added text on lines 2-5 of page 20 to address this.) There is a high sensitivity to the δ13C signature of production. As shown in Fig. 2 and Section 2, where we had to include all decimal places for δ13Cs and δ14Cs from the model to input into the Davidson (1995) δJ, in order to get the true value of production. We've added text on line 5 and page 20 to address this. However, if δJ is used to calculate the δ13C signature of the CO2 being produced, using δ13C of soil CO2 from any depth, it should still yield the true radiocarbon composition of production, as in shown in Fig. 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.

Response: On Page 13 line 4-6 we added the following: In Section 5.2 we compare these two Methods to that used in Phillips et al. (2013), which we will call the Phillips2013 Method. Phillips et al. (2013) use a different gradient approach (not Eq. 16; Δ_J^14) along with Δ14Cold to calculate the radiocarbon composition of produc-

tion.

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' 13C correction would not be appropriate for interpreting the 14C of the measured flux?

Response: The value for 200 ‰ is referenced as coming from the Egan et al. 2014 study. As mentioned on page 17 lines 9-14 the 'standard' 13C correction actually works in the case of chamber-based measurements for flux ("...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).").

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.

Response: We agree with the reviewer, so we have removed the following statement from the top of page 18: "Changes in oxygen availability will also affect fractionations related to the rate of production."

Page 14, lines 5-10. AMS laboratories measure all three isotopes, but the 13C they measure includes fractionation processes in the sample preparation and measurement (all of which are correctable using mass-dependent assumptions). However, the AMS-measured $\delta 13C$ is not a good measure compared to the 13C of the CO_2 that is measured with an IRMS. Therefore, the labs cannot easily report the $\Delta 14C$ as the authors propose unless the user has independently supplied the $\delta 13C$ values for their sam-

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ples. 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 14C can be calculated. Also, AMS labs do not measure activity, they measure isotope ratios.

Response: We agree with this. On lines 20-23 of page 19 we give the formula for how people can "uncorrect" their already reported data: "...1) use $\delta 13s$ and $\Delta 14Cold$ to back out the activity of the sample (As); 2) calculate the isotopic composition of production for $\delta 13C$ using Eq. (2), $\delta J13$; 3) use $\delta J13$ and As in Eq. (7) to calculate $\Delta 14Cnew$, and finally 4) determine the radiocarbon isotopic composition of production, using Eq. (16), $\Delta J14$." This is what we did with our already reported data in Fig. 4 and Section 4.2. We also added the following text on lines 23-25 of page 19: This solution assumes that the researcher has measured a value of $\delta 13s$ independent from $\Delta 14Cold$, as the AMS measured $\delta 13$ is not comparable to Isotope-Ratio Mass Spectrometry (IRMS) measured $\delta 13$.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-451/bg-2018-451-AC3-supplement.pdf

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-451, 2018.