Biogeosciences

Discussions

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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.

Anonymous Referee #3

Received and published: 3 December 2018

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 $^{13}CO_2$ in pore space to estimate the mixing, which in turn allows a better way to estimate the ^{14}C of CO_2 sources.

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. Does anyone in the literature actually assume Method 1?

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?)

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.

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 ^{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).

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? 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.

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.

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.

Other points:

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.

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.

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 Δ^{14}C is the δ^{13}C-corrected version of δ^{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_abs , 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, Δ^{14}C and δ^{14}C will differ slightly depending on the year of measurement/sampling).

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

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

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.

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?

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.

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 δ^{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 Δ^{14}C as the authors propose unless the user has independently supplied the δ^{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.