A NEW $^{13}$C CORRECTION FOR RADIOCARBON SAMPLES FROM ELEVATED-CO$_2$ EXPERIMENTS

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ABSTRACT. Radiocarbon can be a valuable tracer of carbon cycling in elevated CO$_2$ experiments. However, the standard method of calculating $\Delta^{14}$C, which corrects sample $^{14}$C activity for isotopic fractionation by correcting the sample $\delta^{13}$C to $-25‰$, introduces significant errors to the reported $^{14}$C values. For elevated-CO$_2$ treatments the error arises because the $\delta^{13}$C of the sample is not an appropriate measure of isotopic fractionation to use when correcting sample $^{14}$C activity for isotopic fractionation. A suggested replacement approach, developed in this paper, is to use the $\delta^{13}$C of the same type of material (e.g. leaf, soil organic matter) from the control (ambient-CO$_2$) treatment in place of the sample $\delta^{13}$C in the correction.

INTRODUCTION

The fossil CO$_2$ used in elevated CO$_2$ experiments has an isotopic signature that can be used to track plant CO$_2$ exposure and ecosystem carbon cycling (e.g. Harrison et al. 1983; Torn et al. 1997; Table 1). However, radiocarbon labs need to modify the way that they correct $^{13}$C to $-25‰$ when calculating fraction modern or $\Delta^{14}$C for samples from elevated CO$_2$ experiments. This is because the normal assumption, that deviations from atmospheric $^{13}$CO$_2$ values are caused solely by isotopic fractionation, does not hold in these experiments. Thus the standard application of the Stuiver and Polach-type correction (Equation 3) using the sample $^{13}$C is inappropriate in these cases. Applying it can cause reported $\Delta^{14}$C values to be 5–20‰ too heavy. Either the $\Delta^{14}$C notation must be abandoned, and uncorrected (i.e. as-measured) isotopic ratios reported instead, or an alternative approach to the $^{13}$C correction must be adopted as described below. This revised correction scheme may be relevant also for studies of natural CO$_2$ springs, low level tracer additions, and areas with significant fossil inputs to plants, such as urban airsheds.

BACKGROUND: CORRECTING $^{14}$C MEASUREMENTS FOR THE $^{13}$C CONTENT

In calculating the fraction modern from raw accelerator mass spectrometry (AMS) or decay data, the sample activity is corrected for isotopic fractionation to $\delta^{13}$C = $-25‰$, where $\delta^{13}$C is the $^{13}$C/$^{12}$C ratio expressed as a per mil deviation from that of the PDB $^{13}$C standard. For a sample with measured specific activity ($A_s$) and measured $^{13}$C/$^{12}$C ratio ($\delta^{13}$C$_{sample}$), the fractionation-corrected specific $^{14}$C activity of a sample is:

$$ A_{S\text{[corrected to } \delta-25]} = A_s[\delta^{13}C_{\text{sample}}] \times \frac{(1 - 25/1000)^2}{(1 + \delta^{13}C_{\text{sample}}/1000)^2} $$

(1)

$$ \text{absolute fraction Modern} = \frac{A_{S[-25]}}{A_{\text{abs}}} $$

(2)

$$ \Delta^{14}C = 1000 \times [FM - 1] = 1000 \times \left[\frac{A_{S[-25]}}{A_{\text{abs}}} - 1\right] $$

(3)
where $A_{\text{abs}}$ is 0.95 times the activity of the oxalic acid standard in 1950, corrected to $\delta^{13}C = -19\%e$ (Stuiver and Polach 1977). For $^{14}C$ labs that measure $^{14}C/^{12}C$ ratios by AMS or specific activity by counting:

$$\Delta^{14}C = 1000 \times \frac{A_s \times (1 - 25/1000)^2}{(1 + \delta^{13}C_{\text{sample}}/1000)^2 - 1}.$$

(4)

The widespread use of the $\Delta^{14}C$ and Fraction Modern notations reflects their convenience, which arises precisely because these quantities are corrected for isotopic fractionation and can therefore be used in a very simple manner in mixing and carbon-cycle tracing calculations, without having to consider isotopic discrimination at each step. However, this can lead to significant errors in certain special cases as described below.

**THE PROBLEM IN ELEVATED CO$_2$ EXPERIMENTS: FACTORS OTHER THAN ISOTOPIC DISCRIMINATION**

The atmosphere in an elevated CO$_2$ treatment is produced by the physical mixing of two gases: ambient air and fossil fuel-derived CO$_2$. The reduction of $^{13}C$ abundance in the elevated-CO$_2$ atmosphere is not due to isotopic fractionation but rather to the mixing-in of the $^{13}C$ signature of the added CO$_2$. Plants grown in the treated atmosphere will be depleted in $^{13}C$ relative to ambient CO$_2$ due to both plant discrimination and to the depletion caused by the mixing of the two CO$_2$ sources. The $\delta^{13}C_{\text{sample}}$ is not a good indicator of isotopic discrimination for samples from these experiments. The problem pertains for labs that measure either $^{14}C/^{12}C$ or $^{14}C/^{13}C$ ratios, but the magnitude of the error is 50% smaller for AMS labs that measure $^{14}C/^{13}C$ ratios, because their correction for $^{13}C$ is not squared as it is in the equations above (e.g., see Equation 16 in Donahue et al. 1990). Note that in some respects this problem is similar to that introduced by post-depositional carbonate dissolution-driven changes in groundwater $\delta^{13}C$, as discussed by Wigley and Muller (1981).

**Example of the Problem**

Consider a Double-CO$_2$ atmosphere created with equal contributions of ambient and fossil CO$_2$, with isotopic values shown in Table 1. In the Double CO$_2$ atmosphere, $\delta^{13}C$ will be $-21.5\%e$ and $\Delta^{14}C$ should be $-450\%e$. However, using $\delta^{13}C_{\text{sample}}$ in Equation (1) implies a $13.5\%e$ isotopic discrimination whereas no actual isotopic discrimination occurred (only mass mixing of two gases occurred), which leads to overestimating the $^{14}C$ content by $15\%e$ (see Table 1). In the same manner, the $^{13}C$ content of photosynthesize also suggests more discrimination than actually occurred and leads to an error of almost $25\%e$ in the reported $\Delta^{14}C$ value. This “false discrimination” in $^{13}C$ of $-13.5\%e$ will be propagated through photosynthesize, soil organic matter and soil respiration if $\delta^{13}C_{\text{sample}}$ is used as a measure of isotopic fractionation.

**A Practical Solution**

What is needed is a more appropriate $^{13}C$ value to use in the correction; one that is based on a measure of the isotopic fractionation. It is generally not possible to directly measure the $^{13}C$ isotopic discrimination at each stage in the C cycle under an elevated CO$_2$ treatment (for example, the $^{13}C$ content of plants and soil will be controlled by the mixing of material fixed before and after the labeling treatment began). Fortunately, carbon cycling through the control and elevated CO$_2$ plots follows the same bio-geochemical pathways. We suggest that $^{13}C$ from the control treatment can be used as a proxy for the relevant isotopic fractionation. The control treatment means plots that are the same as the elevated CO$_2$ plots except that atmospheric CO$_2$ has not been manipulated. The way to use this
in correcting the measured sample activity is to substitute the $\delta^{13}C_{\text{sample}}$ into the equations (e.g. Equation 1–4), in place of $\delta^{13}C_{\text{sample}}$ for comparable material. See examples below. This solution is recommended for air, plant, or soil samples, for AMS and counting labs, regardless of whether $^{14}C/^{12}C$ or $^{14}C/^{13}C$ activity is measured.

**Examples of Solution**

In each case below, the measured sample activity is $^{13}C$-corrected by using either $\delta^{13}C_{\text{control}}$ or $\delta^{13}C_{\text{sample}}$, for comparable material, with the former case being the recommended approach. The $\delta^{13}C$ of sample or control is in boldface type. These examples use Equation 4 and input data from Table 1.

Table 1 The $^{13}C$ and $^{14}C$ content of CO$_2$, plants, and soil organic matter in an elevated CO$_2$ experiment, based on observations at the Jasper Ridge open top chamber experiment (Town et al. 1997). The $\Delta^{14}C$ values include a $^{13}C$ correction as shown in Equation 4 (i.e., for labs that measure $^{14}C/^{12}C$ ratios, with either the $\delta^{13}C$ of the control (correct method) or the $\delta^{13}C$ of the elevated CO$_2$ sample (current method).

<table>
<thead>
<tr>
<th>Carbon source</th>
<th>$\delta^{13}C$ (%) sample</th>
<th>$\Delta^{14}C$ (%) corrected using actual discrimination (correct method)</th>
<th>$\Delta^{14}C$ (%) corrected using $^{13}C$ sample (current method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient CO$_2$ (in 1997)</td>
<td>−8</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Fossil fuel CO$_2$</td>
<td>−35</td>
<td>−1000</td>
<td>−1000</td>
</tr>
<tr>
<td>Elevated CO$_2$ chambers (50% fossil fuel, 50% ambient)</td>
<td>−21.5</td>
<td>−450</td>
<td>−435</td>
</tr>
<tr>
<td>Plant material, control Isotopic discrimination = $−20%$</td>
<td>−28</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Plant material, $2 \times$ CO$_2$ Isotopic discrimination = $−20%$</td>
<td>−41.5</td>
<td>−450</td>
<td>−434</td>
</tr>
<tr>
<td>Soil organic matter in $2 \times$ CO$_2$ plot (measured after 6 yr of treatment)</td>
<td>−32.7</td>
<td>−93</td>
<td>−84</td>
</tr>
</tbody>
</table>

**Plant Material**

$A_s / A_{\text{abs}} = 0.546621$

1. Standard Approach, using $\delta^{13}C_{\text{sample}}$

$$\Delta^{14}C = 1000 \times [A_s / A_{\text{abs}} \times (1 - 25/1000)^2/(1 + -41.5/1000)^2 - 1] = -434\%$$

2. Recommended Approach, using $\delta^{13}C_{\text{control}}$

$$\Delta^{14}C = 1000 \times [A_s / A_{\text{abs}} \times (1 - 25/1000)^2/(1 + -28/1000)^2 - 1] = -450\%$$

**Soil Organic Matter**

$A_s / A_{\text{abs}} = 0.901589$

1. Standard Approach, using $\delta^{13}C_{\text{sample}}$

$$\Delta^{14}C = 1000 \times [A_s / A_{\text{abs}} \times (1 - 25/1000)^2/(1 + -32.7/1000)^2 - 1] = -84\%$$

2. Recommended Approach, using $\delta^{13}C_{\text{control}}$

$$\Delta^{14}C = 1000 \times [A_s / A_{\text{abs}} \times (1 - 25/1000)^2/(1 + -28/1000)^2 - 1] = -92.9\%$$
DISCUSSION AND CAVEATS

There are of course some errors in using the control plots as a proxy for isotopic discrimination in the elevated CO₂ plots. For one, elevated CO₂ levels can affect isotopic discrimination by decreasing stomatal conductance and thus altering the leaf CO₂ gradient that governs discrimination of photosynthesis. The ¹³C discrimination by plants in the control treatments will be slightly lower (typically 0.1–1.0‰ lower) than that in the elevated CO₂ environment. If sufficient data are collected to measure the treatment effect on isotopic photosynthetic discrimination, this effect should be linearly added to the δ¹³C_control so that all isotopic discrimination is taken into account. Second, different plant tissue can have differences in δ¹³C of 0.1–0.5‰, likewise organic matter at different soil depths can have differences in δ¹³C of 0.2–3‰. As a practical matter, this should not be a big problem if care is taken to use similar types of plant or soil material from the control and the elevated CO₂ treatments.

There is an alternative that can be used in some cases, and that offers an approach when there is no control sample value (D Yakir, personal communication 2000). In this alternative, the numerator in Equations 1–4 is changed so that it normalizes samples relative to the ¹³C of the altered atmosphere. This means the δ¹³C = −25‰ value (−8‰ current atmosphere plus average plant discrimination of −17‰) is replaced by δ¹³C_new atmosphere plus plant discrimination. This method is appropriate only (1) for samples derived entirely from the new CO₂ source (e.g. new plant growth), and (2) where the ¹³CO₂ of the experiment atmosphere can be determined (e.g. by frequent measurements or by analysis of ¹³C in C₃ and C₄ plants). Unlike the solution shown in the example calculations above, this alternative is not appropriate for soil organic matter, woody biomass, or other material derived from a mixture of pre-experiment and experiment carbon sources.

There may be other possible approaches as well. However, the solution developed in this paper can be applied to all kinds of samples and experiments, providing there is some proxy for a control ¹³C value. The approach of using the control δ¹³C should offer a relatively simple solution to the problem posed by samples—for example in elevated CO₂ experiments—for which the δ¹³C has been altered by more than isotopic fractionation alone.

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REFERENCES

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