A NEW ^{13}C CORRECTION FOR RADIOCARBON SAMPLES FROM ELEVATED-CO_2 EXPERIMENTS

Margaret S Torn

Earth Science Division, Lawrence Berkeley National Laboratory, MS 90-1116, Berkeley, California 94720, USA.
Email: mstorn@lbl.gov.

John Southon

Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California 94550, USA

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:

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

$$\text{absolute fraction Modern} = \frac{A_{s[-25]}}{A_{abs}} \tag{2}$$

$$\Delta^{14}C = 1000 \times [FM-1] = 1000 \times \left[\frac{A_{s[-25]}}{A_{abs}} - 1\right] \tag{3}$$

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

$$\Delta^{14}C = 1000 \times \left[\frac{A_s}{A_{abs}} \times \frac{(1 - 25/1000)^2}{(1 + \delta^{13}C_{sample}/1000)^2} - 1 \right]. \quad (4)$$

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 every 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 $\delta^{13}C_{sample}$ 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 $-21.5‰$ and $\Delta^{14}C$ should be $-450‰$. However, using $^{13}C_{sample}$ in Equation (1) implies a 13.5‰ 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‰ (see Table 1). In the same manner, the ^{13}C content of photosynthate also suggests more discrimination than actually occurred and leads to an error of almost 25‰ in the reported $\Delta^{14}C$ value. This "false discrimination" in ^{13}C of $-13.5‰$ will be propagated through photosynthate, soil organic matter and soil respiration if $^{13}C_{sample}$ 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

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in correcting the measured sample activity is to substitute the $\delta^{13}C_{control\ sample}$ into the equations (e.g. Equation 1–4), in place of $\delta^{13}C_{sample}$ 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 $\delta^{13}C_{control}$ or $\delta^{13}C_{sample}$, 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).

Carbon source	$\delta^{13}C$ (‰) sample	$\Delta^{14}C$ (‰) corrected using actual discrimination (correct method)	$\Delta^{14}C$ (‰) corrected using ^{13}C sample (current method)
Ambient CO_2 (in 1997)	–8	100	100
Fossil fuel CO_2	–35	–1000	–1000
Elevated CO_2 chambers (50% fossil fuel, 50% ambient)	–21.5	–450	–435
Plant material, control Isotopic discrimination = –20‰	–28	100	100
Plant material, 2 × CO_2 Isotopic discrimination = –20‰	–41.5	–450	–434
Soil organic matter in 2 × CO_2 plot (measured after 6 yr of treatment)	–32.7	–93	–84

Plant Material

$A_s / A_{abs} = 0.546621$

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

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

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

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

Soil Organic Matter

$A_s / A_{abs} = 0.901589$

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

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

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

$$\Delta^{14}C = 1000 \times [\ A_s / A_{abs} \times (1 - 25/1000\ )^2 / (1 + \mathbf{-28}/1000)^2 - 1] = -92.9‰$$

DISCUSSION AND CAVEATS

There are of course some errors in using the control plots as a proxy for isotopic discrimination in the elevated CO_2 plots. For one, elevated CO_2 levels can affect isotopic discrimination by decreasing stomatal conductance and thus altering the leaf CO_2 gradient that governs discrimination of photosynthesis. The ^{13}C discrimination by plants in the control treatments will be slightly lower (typically 0.1–1.0‰ lower) than that in the elevated CO_2 environment. If sufficient data are collected to measure the treatment effect on isotopic photosynthetic discrimination, this effect should be linearly added to the $\delta^{13}C_{control}$ so that all isotopic discrimination is taken into account. Second, different plant tissue can have differences in $\delta^{13}C$ of 0.1–0.5‰, likewise organic matter at different soil depths can have differences in $\delta^{13}C$ 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 CO_2 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 ^{13}C of the altered atmosphere. This means the $\delta^{13}C = -25$‰ value (–8‰ *current* atmosphere plus average plant discrimination of –17‰) is replaced by $\delta^{13}C_{\textit{new}\ \text{atmosphere}}$ plus plant discrimination. This method is appropriate only (1) for samples derived entirely from the new CO_2 source (e.g. new plant growth), and (2) where the $^{13}CO_2$ of the experiment atmosphere can be determined (e.g. by frequent measurements or by analysis of ^{13}C in C_3 and C_4 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 ^{13}C value. The approach of using the control $\delta^{13}C$ should offer a relatively simple solution to the problem posed by samples—for example in elevated CO_2 experiments—for which the $\delta^{13}C$ has been altered by more than isotopic fractionation alone.

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