

THE EFFECT OF FOSSIL FUEL AND BIOGENIC CO₂ ON THE ¹³C AND ¹⁴C CONTENT OF ATMOSPHERIC CARBON DIOXIDE

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ABSTRACT. The normalization of a measured $\delta^{14}\text{C}$ value of atmospheric CO₂ to a $\delta^{13}\text{C}$ value of -25‰ does not take into account the presence of fossil fuel and biogenic CO₂. In this paper, we try to assess these contaminations as well as the proper ¹⁴C content of "clean air".

INTRODUCTION

It is a common practice to correct the results of ¹⁴C measurements on atmospheric carbon dioxide for isotopic fractionation. By international agreement (Broecker and Olson, 1959), the ¹⁴C correction is related to the deviation of the measured δ^{13} from a standard value (δ_s^{13}) of -25‰ (vs PDB) (in the following equations δ values are not necessarily in ‰):

$$\Delta^{14} = \delta^{14} - 2 (\delta^{13} - \delta_s^{13}) (1 + \delta^{14}) / (1 + \delta^{13}) \quad (1)$$

where δ^{14} is defined by:

$$\delta^{14} = (A_s^{14}/A_{\text{ON}}^{14} - 1) \quad (\times 10^3 \text{‰}) \quad (2)$$

(cf Stuiver and Polach, 1977).

One complication might be overlooked in this correction. The Δ^{14} thus obtained still refers to the ¹⁴C content of the actual atmospheric CO₂, including contamination by fossil fuel and biogenically derived CO₂, the latter from humus decay and root respiration. Both may vary seasonally and locally. The ¹³C correction should only take into account isotopic fractionation during sample treatment, *ie*, CO₂ extraction from the atmosphere and further laboratory preparation of the actual sample to be counted. By using equation 1, however, mixing effects are interpreted as fractionation.

From the mass balances for both total CO₂ (taken equal to the ¹²C concentration) and ¹³C, we can easily derive:

$$\delta^{13} = (1 - f - b) \delta_o^{13} + f \delta_r^{13} + b \delta_b^{13} \quad (3)$$

and

$$\delta^{14} = (1 - f - b) \delta_o^{14} + f \delta_r^{14} + b \delta_b^{14} \quad (4)$$

where f and b are the fractions of fossil fuel and biogenically derived CO₂, and δ , δ_o , δ_r , and δ_b , respectively, refer to the actual sample, uncontaminated ("clean") air, fossil fuel, and biogenic CO₂. If we denote the contamination CO₂ by a ($=f + b$), f and b are then related to the δ^{13} values by:

$$f = \frac{\delta^{13} - \delta_o^{13} + a (\delta_o^{13} - \delta_b^{13})}{\delta_r^{13} - \delta_b^{13}} \quad (5)$$

and

$$b = \frac{\delta^{13} - \delta_o^{13} + a (\delta_o^{13} - \delta_r^{13})}{\delta_b^{13} - \delta_r^{13}} \quad (6)$$

The ¹⁴C concentration of the uncontaminated air CO₂ follows from equation 4:

$$\delta_o^{14} = [\delta^{14} - f \delta_f^{14} - b \delta_b^{14}] / (1 - a) \quad (7)$$

After the conventional correction for isotopic fractionation, the normalized ¹⁴C content of the clean air CO₂ is:

$$\Delta_o^{14} = \delta_o^{14} - 2 (\delta_o^{13} - \delta_s^{13}) (1 + \delta_o^{14}) / (1 + \delta_o^{13}) \quad (8)$$

where $\delta_s^{13} = -25\%$. Figure 1 shows the erroneous and proper ¹⁴C values, Δ^{14} , respectively, Δ_o^{14} , under varying conditions. It is seen that during the period of high atmospheric ¹⁴C content ($\delta^{14} = +600\%$), relatively large errors in the assessment of Δ_o^{14} may have been made in case the samples were collected from continental air (for instance, for $\delta^{13} = -8.5\%$ due to fossil fuel CO₂: $\Delta^{14} - \Delta_o^{14} \cong -100\%$!).

It is worthwhile to note that a biogenic CO₂ content in the atmosphere having an isotopic composition of $\delta_b^{13} = \delta_s^{13} = -25\%$ and $\Delta_b^{14} = \Delta_o^{14}$, does not affect the calculation of Δ_o^{14} ; in that case $\Delta^{14} = \Delta_o^{14}$.

Unfortunately, many atmospheric CO₂ samples were collected by non-quantitative absorption in an alkaline solution. Because of the large

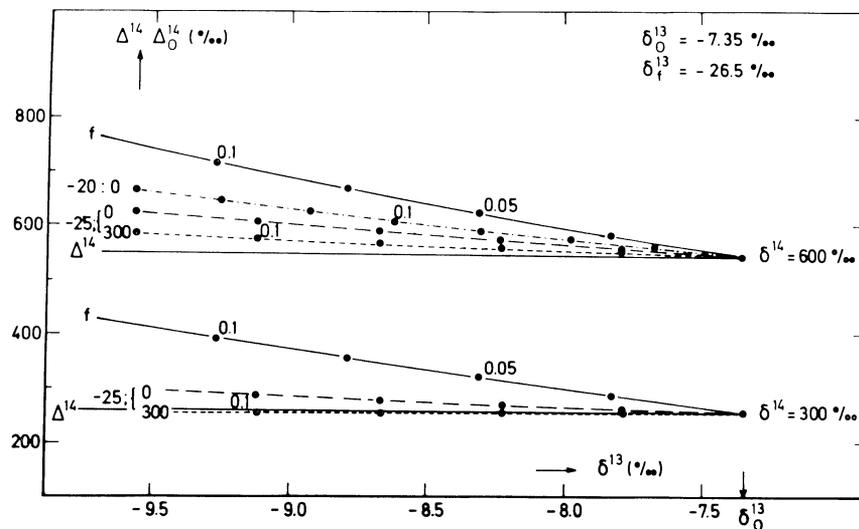


Fig 1. Comparison of the fractionation correction (equation 1) and the mixing correction (equation 8) and the effect of contamination of clean air carbon dioxide by varying amounts of CO₂ from fossil fuel combustion (*f*) or from biogenic origin (*b*). Starting from clean air CO₂ ($\delta_o^{13} = -7.35\%$), two sets of lines are calculated, one for a measured δ^{14} of 300% , one for $\delta^{14} = 600\%$. The almost horizontal solid lines present the Δ^{14} values (equation 1). The other lines refer to contamination by fossil fuel CO₂ (*f*), and to biogenically derived CO₂ (equation 8). The assumptions for the isotopic composition of the biogenic CO₂ are indicated in the graph as (δ_b^{13} ; δ_b^{14} , in $\%$). The calculations are based on:

$$\delta_o^{13} = -7.35\%, \delta_f^{13} = -26.5\% \text{ and } \delta_r^{14} = -1000\%.$$

The fractional concentrations (0.025, 0.05, etc) of the contaminants are indicated along the lines. It is evident that by interpreting variations in δ^{13} as fractionation effects, severe errors arise.

and unknown isotopic fractionation involved in this technique, the assessment of the actual $\delta^{13}\text{C}$ values of those samples is not possible.

From the above, it is obvious that it is essential that atmospheric CO_2 is collected by a quantitative and non-fractionating absorption method. This is easily realized by pumping the air at a slow rate through a 40cm column or a series of columns containing an alkaline solution, or by the procedure described by Levin, Munnich, and Weiss (1980).

Assessment of the fossil fuel and biogenic contamination

Starting from a supposed ^{13}C and ^{14}C concentration of clean air CO_2 (O in fig 2), the additional biogenic CO_2 (arbitrarily presented by B) causes the isotopic composition to shift proportionally to b towards B . Similarly, additional fossil fuel CO_2 (F) causes a proportional (to f) shift towards F . The fractional concentrations, f and b , in an actual sample (S) can be determined from:

$$BE/FE = f/b \text{ and } OS/OE = f + b \quad (9)$$

or the measured CO_2 fraction, in excess of the uncontaminated atmospheric CO_2 concentration ($a = f + b$) (Keeling, Mook, and Tans, 1979). This supposes, however, that the isotopic compositions of O , B and F are known. Keeling, Mook, and Tans (1979) recently reported a $\delta_0^{13}\text{C}$ value of -7.24‰ (by 1-1-1978), decreasing by about 0.025‰ per year. According to the present calibration $\delta_0^{13}\text{C} = -7.35\text{‰}$ might be a better value. By using this value "clean air" is defined as the air which shows a minimal seasonal variation in the CO_2 content and averaged over one year. The average $\delta_0^{14}\text{C}$ at present is probably about $+400\text{‰}$. The $\delta_t^{13}\text{C}$

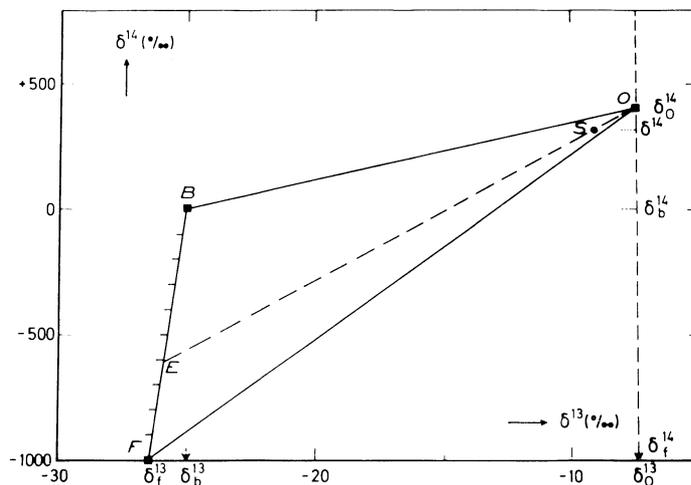


Fig 2. Relation between $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$ of clean air CO_2 (O), biogenic CO_2 (B) and fossil fuel CO_2 (F). S refers to an arbitrary atmospheric CO_2 sample. The fraction of contaminating CO_2 ($f + b$) is presented by OS/OE , while $f/b = BE/FE$. The isotopic compositions of B and F are arbitrarily chosen.

and δ_f^{14} values are, respectively, -26.5% (Keeling, Mook, and Tans, 1979) and -1000% . The first value might show regional variations. Isotopic compositions of the biogenic CO₂ component are the most uncertain: δ_b^{13} probably ranges between -20 and -25% depending on the kind of vegetation, δ_b^{14} between zero and a few hundred per mil. The most reliable procedure is to analyze, both for concentration and for isotopes, a series of atmospheric CO₂ samples with varying biogenic contributions. This series of samples should be collected in a restricted and rural area, in order to avoid varying contributions of fossil fuel CO₂.

Assessment of the ¹⁴C content of clean air CO₂ in a continental environment

In continental environments, the atmosphere is always contaminated by fossil fuel and/or biogenically derived CO₂. Therefore, direct and accurate measurement of δ_o^{14} , as in the case of oceanic air, is not possible. In this section, we will investigate to what degree of accuracy δ^{14} measurements do provide the true δ_o^{14} values. In order to be able to find an answer to this question, we have to assume that the isotopic compositions of the contaminants (*B* and *F* in fig 2) are known.

If the value of *a* is known from a concentration measurement (fraction above the clean air CO₂ concentration), the δ^{13} analysis of the sam-

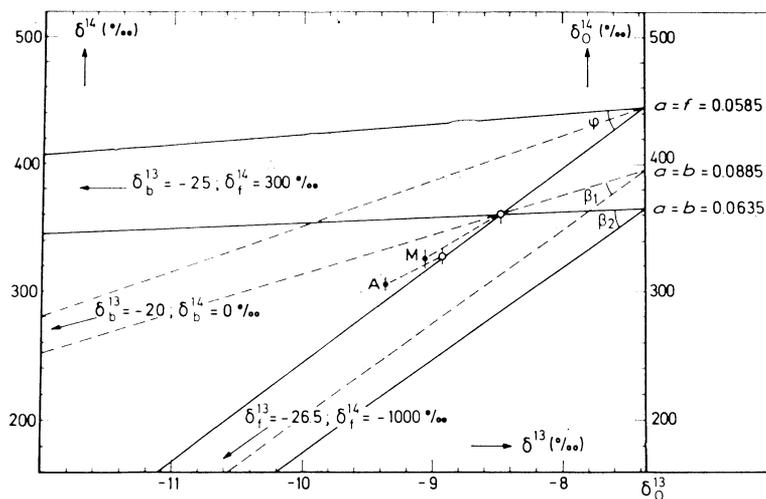


Fig. 3. δ^{13} and δ^{14} results of monthly atmospheric CO₂ samples from April (A) and May (M) 1979, collected in the city of Groningen (solid points) and in the rural environment of Smilde on top of a TV station (open points). From the Smilde result of May three sets of lines similar to figure 2 are constructed, indicating the extrapolated δ_o^{14} values of clean air. The set φ is based on the assumption that δ^{13} deviates from δ_o^{13} only because of a contamination by fossil fuel CO₂. Sets β_1 and β_2 refer to a purely biogenic CO₂ contamination with two extreme δ_b^{13} and δ_b^{14} values: $\delta_b^{13} = -25\%$ for moderate climatic regions (C-3 plants, $= -20\%$ for mixed C-3 and C-4 vegetations; $\delta_b^{14} = +300\%$ equal to the present-day ¹⁴C content of growing plants, $= 0\%$ for plant material grown prior to the nuclear testing period. The resulting fractional contaminations are indicated in the upper right-hand corner of the graph.

ple provides f and b , using equations 5 and 6. Then δ_o^{14} is calculated from equation 7.

If the CO_2 concentration cannot be measured, δ^{13} poses certain limits to the values of f and b . As an illustration, we choose a few results on atmospheric CO_2 , which we collected in two locations: inside the city of Groningen and on top of the TV transmitting station of Smilde, at a distance of about 40km from Groningen and a height of 100m above ground level in a rural environment. Figure 3 shows the results for two sets of samples collected during April (A) and May (M) 1979. The solid points refer to the Groningen samples.

Starting from the Smilde result of May, three sets of lines have been constructed according to figure 2 (OB and OF). The set marked φ is based on the assumption that the contamination is only due to fossil fuel CO_2 . Extrapolation from $\delta_f^{13} = -26.5\text{‰}$ and $\delta_f^{14} = -1000\text{‰}$ to $\delta_o^{13} = -7.35\text{‰}$ gives the value of δ_o^{14} . From this value two different "biogenic lines" (OB) are drawn, one towards $(\delta_b^{13}, \delta_b^{14}) = (-20; 0)$, the other towards $(-25; 300)$.

A similar procedure is followed in constructing the sets, β_1 and β_2 . Here it is assumed that the deviation of δ^{13} from -7.35‰ is only caused by biogenic CO_2 with the extreme isotopic compositions of $(-20; 0)$ and $(-25; 300)$, respectively. From both extrapolated δ_o^{14} values, the "fossil fuel lines" (OF) are drawn.

It is apparent that all analytical data on atmospheric CO_2 derived from clean air CO_2 having a certain isotopic composition ($\delta_o^{13}, \delta_o^{14}$) should fall within the area of the graph covered by, for instance, φ , β_1 or β_2 .

The position of the data (neglecting the standard deviations in the δ^{14} values) would point to varying amounts (above $f = 0.058$) of fossil fuel CO_2 in the sample, in the (almost complete) absence of biogenic CO_2 . The resulting δ_o^{14} value is relatively high ($\Delta_o^{14} = 445\text{‰}$). On the other hand, considering the data within β_1 and β_2 , we would conclude to an almost constant biogenic CO_2 level (b between 0.088 (β_1) and 0.063 (β_2)) with, again, varying degrees of contamination with fossil fuel CO_2 . In this case, the resulting Δ_o^{14} is between 395 and 366‰, depending on the isotopic composition assumed for the biogenic CO_2 . It seems evident that the lower values at Groningen during both months are due to fossil fuel contamination.

From the foregoing, it is evident that we need more pertinent knowledge about δ_b^{14} and δ_b^{13} (less important) and preferably about the atmospheric CO_2 concentration, in order to be able to conclude to Δ_o^{14} value to within an accuracy of 10‰ or better. Apart from this, also a more extensive series of data from different locations during the same period will restrict the inaccuracy in Δ_o^{14} .

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DISCUSSION

Cain: Why was corrected $\Delta^{14}\text{C}$ lighter? Didn't you correct to $\delta^{13}\text{C}$ of -7 per mil?

Mook: Compared to the $\delta^{14}\text{C}$ values, the $\Delta^{14}\text{C}$ values are smaller because they include the isotope fractionation correction down to -25% . The $\Delta_0^{14}\text{C}$ values are less small, because the $\delta^{14}\text{C}$ is first corrected to $\delta_0^{14}\text{C}$ for the presence of fossil fuel CO₂, which makes $\delta_0^{14}\text{C}$ larger than $\delta^{14}\text{C}$.