

## THE EFFECT OF FOSSIL FUEL AND BIOGENIC CO<sub>2</sub> ON THE <sup>13</sup>C AND <sup>14</sup>C CONTENT OF ATMOSPHERIC CARBON DIOXIDE

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ABSTRACT. The normalization of a measured  $\delta^{14}\text{C}$  value of atmospheric CO<sub>2</sub> to a  $\delta^{13}\text{C}$  value of  $-25\text{‰}$  does not take into account the presence of fossil fuel and biogenic CO<sub>2</sub>. In this paper, we try to assess these contaminations as well as the proper <sup>14</sup>C content of "clean air".

### INTRODUCTION

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

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

where  $\delta^{14}$  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  $\Delta^{14}$  thus obtained still refers to the <sup>14</sup>C content of the actual atmospheric CO<sub>2</sub>, including contamination by fossil fuel and biogenically derived CO<sub>2</sub>, the latter from humus decay and root respiration. Both may vary seasonally and locally. The <sup>13</sup>C correction should only take into account isotopic fractionation during sample treatment, *ie*, CO<sub>2</sub> 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 CO<sub>2</sub> (taken equal to the <sup>12</sup>C concentration) and <sup>13</sup>C, we can easily derive:

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

and

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

where  $f$  and  $b$  are the fractions of fossil fuel and biogenically derived CO<sub>2</sub>, and  $\delta$ ,  $\delta_o$ ,  $\delta_f$ , and  $\delta_b$ , respectively, refer to the actual sample, uncontaminated ("clean") air, fossil fuel, and biogenic CO<sub>2</sub>. If we denote the contamination CO<sub>2</sub> by  $a$  ( $=f + b$ ),  $f$  and  $b$  are then related to the  $\delta^{13}$  values by:

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

and

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

The <sup>14</sup>C concentration of the uncontaminated air CO<sub>2</sub> 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 <sup>14</sup>C content of the clean air CO<sub>2</sub> 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 <sup>14</sup>C values,  $\Delta^{14}$ , respectively,  $\Delta_o^{14}$ , under varying conditions. It is seen that during the period of high atmospheric <sup>14</sup>C content ( $\delta^{14} = +600\%$ ), relatively large errors in the assessment of  $\Delta_o^{14}$  may have been made in case the samples were collected from continental air (for instance, for  $\delta^{13} = -8.5\%$  due to fossil fuel CO<sub>2</sub>:  $\Delta^{14} - \Delta_o^{14} \cong -100\%$ !).

It is worthwhile to note that a biogenic CO<sub>2</sub> 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  $\Delta_o^{14}$ ; in that case  $\Delta^{14} = \Delta_o^{14}$ .

Unfortunately, many atmospheric CO<sub>2</sub> samples were collected by non-quantitative absorption in an alkaline solution. Because of the large

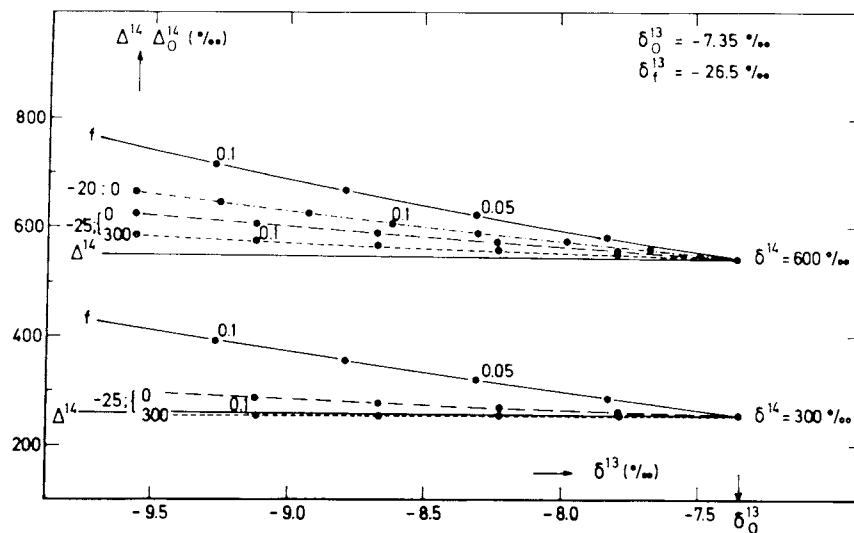


Fig 1. Comparison of the fractionation correction (equation 1) and the mixing correction (equation 8) and the effect of contamination of clean air carbon dioxide by varying amounts of CO<sub>2</sub> from fossil fuel combustion (*f*) or from biogenic origin (*b*). Starting from clean air CO<sub>2</sub> ( $\delta_o^{13} = -7.35\%$ ), two sets of lines are calculated, one for a measured  $\delta^{14}$  of 300‰, one for  $\delta^{14} = 600\%$ . The almost horizontal solid lines present the  $\Delta^{14}$  values (equation 1). The other lines refer to contamination by fossil fuel CO<sub>2</sub> (*f*), and to biogenically derived CO<sub>2</sub> (equation 8). The assumptions for the isotopic composition of the biogenic CO<sub>2</sub> are indicated in the graph as ( $\delta_b^{13}$ ;  $\delta_b^{14}$ , in ‰). The calculations are based on:

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

The fractional concentrations (0.025, 0.05, etc) of the contaminants are indicated along the lines. It is evident that by interpreting variations in  $\delta^{13}$  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  $\text{CO}_2$  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  $^{13}\text{C}$  and  $^{14}\text{C}$  concentration of clean air  $\text{CO}_2$  ( $O$  in fig 2), the additional biogenic  $\text{CO}_2$  (arbitrarily presented by  $B$ ) causes the isotopic composition to shift proportionally to  $b$  towards  $B$ . Similarly, additional fossil fuel  $\text{CO}_2$  ( $F$ ) 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  $\text{CO}_2$  fraction, in excess of the uncontaminated atmospheric  $\text{CO}_2$  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  $-7.24\text{‰}$  (by 1-1-1978), decreasing by about  $0.025\text{‰}$  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  $\text{CO}_2$  content and averaged over one year. The average  $\delta_0^{14}\text{C}$  at present is probably about  $+400\text{‰}$ . The  $\delta_1^{13}\text{C}$

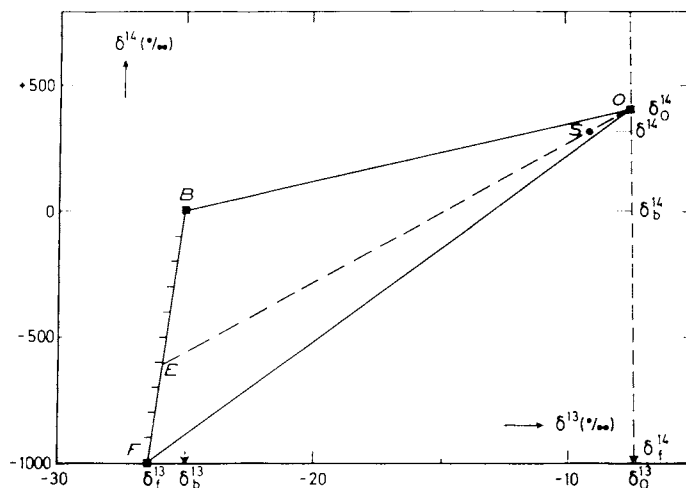


Fig 2. Relation between  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$  of clean air  $\text{CO}_2$  ( $O$ ), biogenic  $\text{CO}_2$  ( $B$ ) and fossil fuel  $\text{CO}_2$  ( $F$ ).  $S$  refers to an arbitrary atmospheric  $\text{CO}_2$  sample. The fraction of contaminating  $\text{CO}_2$  ( $f + b$ ) is presented by  $OS/OE$ , while  $f/b = BE/FE$ . The isotopic compositions of  $B$  and  $F$  are arbitrarily chosen.

and  $\delta_f^{14}$  values are, respectively,  $-26.5\%$  (Keeling, Mook, and Tans, 1979) and  $-1000\%$ . The first value might show regional variations. Isotopic compositions of the biogenic CO<sub>2</sub> component are the most uncertain:  $\delta_b^{13}$  probably ranges between  $-20$  and  $-25\%$  depending on the kind of vegetation,  $\delta_b^{14}$  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 CO<sub>2</sub> 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 CO<sub>2</sub>.

*Assessment of the <sup>14</sup>C content of clean air CO<sub>2</sub> in a continental environment*

In continental environments, the atmosphere is always contaminated by fossil fuel and/or biogenically derived CO<sub>2</sub>. Therefore, direct and accurate measurement of  $\delta_o^{14}$ , as in the case of oceanic air, is not possible. In this section, we will investigate to what degree of accuracy  $\delta^{14}$  measurements do provide the true  $\delta_o^{14}$  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 CO<sub>2</sub> concentration), the  $\delta^{13}$  analysis of the sam-

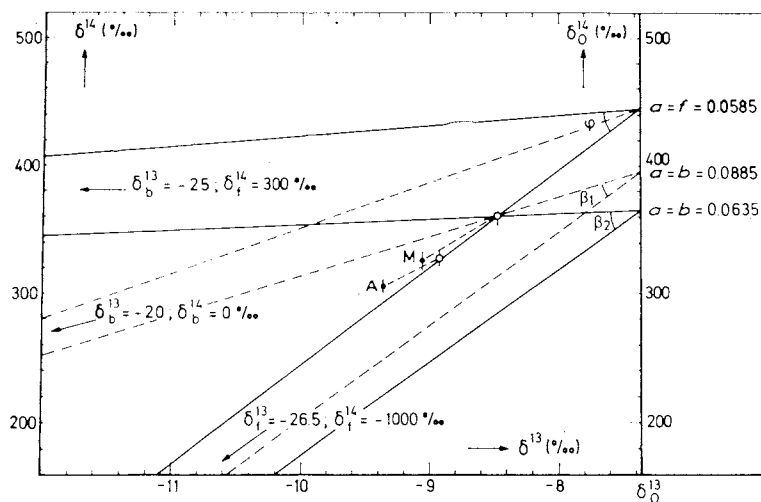


Fig. 3.  $\delta^{13}$  and  $\delta^{14}$  results of monthly atmospheric CO<sub>2</sub> samples from April (A) and May (M) 1979, collected in the city of Groningen (solid points) and in the rural environment of Smilde on top of a TV station (open points). From the Smilde result of May three sets of lines similar to figure 2 are constructed, indicating the extrapolated  $\delta_o^{14}$  values of clean air. The set  $\varphi$  is based on the assumption that  $\delta^{13}$  deviates from  $\delta_o^{13}$  only because of a contamination by fossil fuel CO<sub>2</sub>. Sets  $\beta_1$  and  $\beta_2$  refer to a purely biogenic CO<sub>2</sub> contamination with two extreme  $\delta_b^{13}$  and  $\delta_b^{14}$  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 <sup>14</sup>C 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  $\delta_o^{14}$  is calculated from equation 7.

If the  $\text{CO}_2$  concentration cannot be measured,  $\delta^{13}$  poses certain limits to the values of  $f$  and  $b$ . As an illustration, we choose a few results on atmospheric  $\text{CO}_2$ , 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  $\varphi$  is based on the assumption that the contamination is only due to fossil fuel  $\text{CO}_2$ . 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  $\delta_o^{14}$ . 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,  $\beta_1$  and  $\beta_2$ . Here it is assumed that the deviation of  $\delta^{13}$  from  $-7.35\text{‰}$  is only caused by biogenic  $\text{CO}_2$  with the extreme isotopic compositions of  $(-20; 0)$  and  $(-25; 300)$ , respectively. From both extrapolated  $\delta_o^{14}$  values, the "fossil fuel lines" ( $OF$ ) are drawn.

It is apparent that all analytical data on atmospheric  $\text{CO}_2$  derived from clean air  $\text{CO}_2$  having a certain isotopic composition ( $\delta_o^{13}, \delta_o^{14}$ ) should fall within the area of the graph covered by, for instance,  $\varphi, \beta_1$  or  $\beta_2$ .

The position of the data (neglecting the standard deviations in the  $\delta^{14}$  values) would point to varying amounts (above  $f = 0.058$ ) of fossil fuel  $\text{CO}_2$  in the sample, in the (almost complete) absence of biogenic  $\text{CO}_2$ . The resulting  $\delta_o^{14}$  value is relatively high ( $\Delta_o^{14} = 445\text{‰}$ ). On the other hand, considering the data within  $\beta_1$  and  $\beta_2$ , we would conclude to an almost constant biogenic  $\text{CO}_2$  level ( $b$  between 0.088 ( $\beta_1$ ) and 0.063 ( $\beta_2$ )) with, again, varying degrees of contamination with fossil fuel  $\text{CO}_2$ . In this case, the resulting  $\Delta_o^{14}$  is between 395 and 366‰, depending on the isotopic composition assumed for the biogenic  $\text{CO}_2$ . 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  $\delta_b^{14}$  and  $\delta_b^{13}$  (less important) and preferably about the atmospheric  $\text{CO}_2$  concentration, in order to be able to conclude to  $\Delta_o^{14}$  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  $\Delta_o^{14}$ .

#### REFERENCES

- Broecker, W S and Olson, E A, 1959, Lamont radiocarbon measurements VI: Radiocarbon Supp, Am Jour Sci, v 1, p 111-132.  
 Keeling, C D, Mook, W G, and Tans, P P, 1979, Recent trends in the  $^{13}\text{C}/^{12}\text{C}$  ratio of atmospheric carbon dioxide: Nature, v 277, p 121-123.

- Levin, Inge, Münnich, K O, and Weiss, Wolfgang, 1980, The effect of anthropogenic CO<sub>2</sub> and <sup>14</sup>C sources on the distribution of <sup>14</sup>C in the atmosphere, *in* Stuiver, Minze and Kra, Renee, eds, Internatl radiocarbon conf, 10th, Proc: Radiocarbon, v 22, no. 2, p 379-391.
- Stuiver, Minze and Polach, H A, 1977, Discussion: Reporting of <sup>14</sup>C data: Radiocarbon, v 19, p 355-363.

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 CO<sub>2</sub>, which makes  $\delta_0^{14}\text{C}$  larger than  $\delta^{14}\text{C}$ .