

FACTORS AFFECTING THE ACCURACY OF THE CARBON-DATING METHOD IN SOIL HUMUS STUDIES

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Factors affecting the accuracy of the carbon-dating method of analysis have been discussed by several workers (1, 3, 13, 14). Since, however, these workers were interested primarily in archeological and geological applications of carbon-dating, they were most concerned with the absolute age of a sample. All "young" materials, for example fulvates, were therefore extracted and discarded before a sample was dated.

In soil science it is not the absolute but the average age or mean residence time (m.r.t.) of the soil humus and soil humus components that is important. Thus the presence of younger fractions in a sample does not invalidate the results, and all organic fractions are dated.

Some of the factors which might affect the accuracy of this method as applied to soil science were mentioned briefly by Paul et al. (12). This paper presents data and discusses some of these factors more fully. The factors examined are: precision of analytical techniques, isotopic fractionation, incorporation of nuclear-bomb-produced C14 into humus, and contamination by re-use or soil-respired CO₂.

METHODS

Characterization of soils and fractions

The Melfort soil was sampled at the Canada Department of Agriculture Research Station, Melfort, Saskatchewan. The Waitvill and Oxbow samples were taken from sites about a mile apart approximately 100 miles west of Melfort. The Elstow and Regina samples were taken at Rosetown, Saskatchewan, about 90 miles south of the site from which the Oxbow was taken. The Melfort soil was fractionated into humic fractions (12); the humin and humic acids were further hydrolyzed with 6 N HCl (2). All soils and fractions were carbon-dated (12) and their apparent m.r.t.'s corrected for isotopic fractionation by normalization to a common C13/C12 (6).

Check on precision of analytical technique

The precision of the CO₂-generation process and the mass spectrometric analysis of CO₂-generation process and the mass spectrometric analysis of CO₂ was checked by comparing the $\delta C13^2$ (3 replicates measured on 3 different days) of the National Bureau of Standards (N.B.S.) oxalic acid standard for carbon-dating versus the N.B.S. Solenhofen limestone standard for mass spectrometric analysis of CO₂.

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² $\delta C13 = \left(\frac{C13/C12_{sample}}{C13/C12_{standard}} \right) - 1 \times 1000$; $\delta C13$ is expressed as per mil (per cent).

The precision of the humus fractionation techniques was checked by comparing $\delta^{13}\text{C}$ values for the same humic fractions obtained from separate fractionations. This comparison was done for 3 different humic fractions.

Effect of isotopic fractionation

The effect of isotopic fractionation as a source of error was assessed by comparing the $\delta^{13}\text{C}/\delta^{12}\text{C}$ of CO_2 gas generated from strontium carbonate formed from the carbon of the soil or humic fraction, with $\delta^{13}\text{C}/\delta^{12}\text{C}$ of CO_2 produced from the N.B.S. Solenhofen limestone.

Effect of incorporation of nuclear-bomb-produced ^{14}C into humus

The radiocarbon activity of wheat in Saskatchewan has doubled since 1955 (9). In time, incorporation of such plant residues into soil may increase the radiocarbon activity of humus, and thus tend to invalidate dates obtained for soil samples.

Two methods were used to investigate this phenomenon: (a) samples taken from the same plot at Melfort for 3 consecutive years during the nuclear-bomb testing period, and (b) samples taken at Rosetown from two different soil types before and after the advent of nuclear-bomb testing were carbon-dated.

Effect of contamination by re-use of soil-respired CO_2 .

This factor is discussed from a theoretical viewpoint with the aid of data from the literature.

RESULTS

Check on precision of analytical techniques

Comparison of $\delta^{13}\text{C}$ values for oxalic acid vs. Solenhofen limestone gave values of -15.6, -15.7, and -16.0 per mil for 3 replicate analyses. These results indicate high precision for both the mass spectrometric analysis and the CO_2 generation process.

Carbon-dating data previously reported (12) attested to the high precision of the carbon-dating and humus-fractionation techniques employed. The mass spectrometer was used as another check on the precision of the humus fractionation techniques; samples of a humic fraction, but from separate fractionations, gave $\delta^{13}\text{C}$ values with a range of 6 per mil, which is equivalent to an error of ± 50 years. In a similar check with two other fractions, the range was less than 2 per mil.

Effect of isotopic fractionation

As indicated by the $\delta^{13}\text{C}$ values (Table 1), isotopic fraction was fairly constant (the mean was -7.1 per mil and range -5.3 to -8.1 per mil) for all soils and fractions analyzed. This necessitated subtracting approximately 115 years from each apparent m.r.t. Relative to the Solenhofen standard, the $\delta^{13}\text{C}$ values ranged from -21.5 to -24 mil; these are similar to values reported by Broecker and Olson (4) for two similar humus fractions.

Table 1

$\delta^{13}\text{C}$, $\delta^{14}\text{C}$ and Δ values of soils and humic fractions

Sample	$\delta^{14}\text{C}$ (‰)	$\delta^{13}\text{C}$ relative to N.B.S. oxalic acid standard (‰)	Δ (‰)	Normalized m.r.t. (years)
<i>Soils and year sampled</i>				
Waitville, 1962	-43.8 ± 7.6	-6.8	-30.8 ± 7.6	250 ± 60
Oxbow, 1962	-120.8 ± 7.5	-5.7	-110.5 ± 7.5	940 ± 60
Melfort				
1962	-115.5 ± 6.0	-7.3	-102.6 ± 6.0	870 ± 50
1963		-		790 ± 60
1964		-		860 ± 70
Regina				
1952		-		460 ± 70
1964		-		420 ± 60
Elstow, 1964		-		460 ± 70
<i>Humic fractions of Melfort soil</i>				
Humins	-146.0 ± 1.3	-8.1	-132.3 ± 6.3	1140 ± 50
Unhydrolyzed humins	-155.0 ± 7.1	-7.4	-142.5 ± 7.1	1230 ± 60
Humic acids	-154.8 ± 7.3	-7.8	-142.6 ± 7.3	1235 ± 60
Hydrolyzed humic acids	-13.3 ± 6.3	-5.3	-3.0 ± 6.3	25 ± 60
Unhydrolyzed humic acids	-171.2 ± 7.0	-6.8	-159.9 ± 7.0	1400 ± 60
Fulvic acids	-70.0 ± 11.5	-7.2	-56.6 ± 7.0	470 ± 90
1952 wheat grain	-	-4.2	-	-

* $\delta^{13}\text{C}$ for these samples was assumed to be -71 per mil.

Effect of nuclear-bomb-produced C^{14}

No difference was found between the m.r.t.'s of the 1952 and 1964 samples from Rosetown, nor between the 1962, 1963, and 1964 Melfort samples (Table 1). Therefore, both tests indicate that nuclear-bomb-produced C^{14} has had no discernible effect on the m.r.t. of soil humus.

DISCUSSION

The precision of the commonly used humus fractionation techniques and of the mass spectrometric analysis of humus carbon does not seem to be a serious limitation to the application of the carbon-dating method for soil humus studies.

Isotopic fractionation is a major contributor to the error in the m.r.t.'s of soils and humus fractions. As this error was fairly constant, corrections can be approximated with relative accuracy, and thus numerous and often expensive mass spectrometric determinations can be eliminated.

If it is assumed that the C13/C12 of the Solenhofen limestone represents the ratio of these atoms in the atmosphere, then the $\delta C13$ values (table 1) indicate that discrimination has taken place against the heavier carbon isotopes during their conversion from atmospheric to humus carbon. This discrimination might have occurred during either the physiological processes of the plant or the microbiological decomposition of plant materials to humus, or during both processes. The $\delta C13$ of 1952 wheat relative to Solenhofen limestone (-20 per mil) was no different from $\delta C13$ for samples of soil origin. [Craig (5) reported $\delta C13$ values for plant materials as -25 ± 5 per mil.] Discrimination due to the physiological processes of the plant could therefore account for all the isotopic discrimination observed in the soil samples, and suggests that discrimination against C14 by soil microorganisms is negligible.

Although the C14 concentration in plants has more than doubled since the pre-nuclear explosion period, the Melfort and Rosetown soils show no apparent increase in C14 activity. In all probability this is caused by one or all of three factors: the high carbon content of these soils, the rapid turnover rate of fresh organic residues in soils, and the relatively low m.r.t. of soil humus. These points can be demonstrated by calculating the apparent decrease in m.r.t. which would theoretically accompany the incorporation of an average wheat crop into two soils of contrasting organic carbon content and m.r.t.; for example, in the Melfort soil organic carbon = 5.6 per cent and m.r.t. = 1000 years, and in a Lethbridge soil³ organic carbon = 1.25 per cent, and m.r.t. = 2000 years.

Assuming a 30 bushel/acre wheat crop (that is, about 1500 pounds/acre carbon), 70 per cent decomposes in the first year (7), leaving 450 pounds/acre in the soil. Thus the fresh residual carbon in one year will constitute only a very small fraction of the total carbon: 0.4 and 1.8 per cent of the total carbon of the Melfort and Lethbridge soils, respectively.

Figure 1 was constructed from theoretical calculations. It shows the degree to which the true m.r.t. of a sample would be altered if it was contaminated by various percentages of either "contemporary"⁴ or "dead" carbon, and indicates that, as the per cent of "contemporary" carbon contamination increases, the m.r.t. decreases. Thus the higher the original carbon content of the soil the less likelihood of discerning the effects of nuclear-bombproduced C14 contamination.

Figure 1 shows also that the closer the ages of the sample and contaminant, the less significant will be the alteration in radiocarbon age. Because the contaminant is "young" material in this case, the effect will be less significant for the Melfort than for the Lethbridge soil.

The C14 activity of present-day plant material is about twice that of "contemporary" carbon, thus the contaminating effect of the wheat residues on the soil humus will be twice as great as where contamination is due to "contemporary" carbon. From figure 1 it is estimated that contamination of Melfort and Lethbridge soil humus by a year's wheat residues would result in a

³ This soil was described in a previous paper (12).

⁴ "Contemporary" carbon refers to 95 per cent of the radiocarbon activity of the N .B.S. oxalic acid standard for carbon-dating and not to truly contemporary organic material. The latter will be referred to as present-day plant material.

decrease of about 5 and 60 years, respectively. Thus, it is not surprising that no apparent increase in C14 activity of soils has been observed to result from nuclear-bomb-produced C14.

The possibility exists that direct assimilation of soil CO₂ by plants might be a source of error for carbon-dating studies of soils. Data from the literature tend to indicate that this source of error will probably be negligible. For example, the amount of soil CO₂ absorbed via plant roots is only about 2 per cent of the total CO₂ assimilated by the plant (11). Musgrave and Moss (10) reported that soil-respired CO₂ is fixed by plants during the photosynthetic process, but that most of the CO₂ is respired by the soil during periods when plants are using little CO₂. and thus enough time is allowed for thorough mixing of soil-respired and atmospheric CO₂. Furthermore, the C14 activity of the CO₂ evolved from soils is only slightly lower than that of the previous year's plant materials (4). Thus it can be assumed that the potential error from this source will be negligible.

It is concluded that the principal sources of error leading to inaccuracies will be imperfect precision of analytical methods and isotopic fractionation. The bomb-carbon effect and that of the re-use of soil-respired CO₂ by plants will be of lesser significance. When unhumified organic residues are removed before dating and normal precautions are observed (8), this technique should be accurate enough to permit its use in soil science studies.

SUMMARY

The effect of isotopic fractionation, nuclear-bomb-produced C14, and precision of analytical techniques employed in studying soil humus, on the accuracy of the carbon-dating method as applied to soil science was investigated. The effect of re-use of soil CO₂ by plants is discussed.

C14 fractionation, calculated from C13/C12, was constant for several soils and humic fractions, and necessitated subtracting about 115 years from each measured mean residence time (m.r.t.).

No apparent error has so far resulted from the increased incorporation of nuclear-bomb-produced C14 by plants.

The possible error arising from lack of precision of the analytical techniques employed in carbon-dating studies of soil humus was relatively small, and was not considered a limiting factor to this type of study.

Comparison of $\delta^{13}\text{C}$ data from plant material, soil humus, and Solenhofen limestone indicated that microorganisms do not discriminate between carbon isotopes during decomposition of organic matter.

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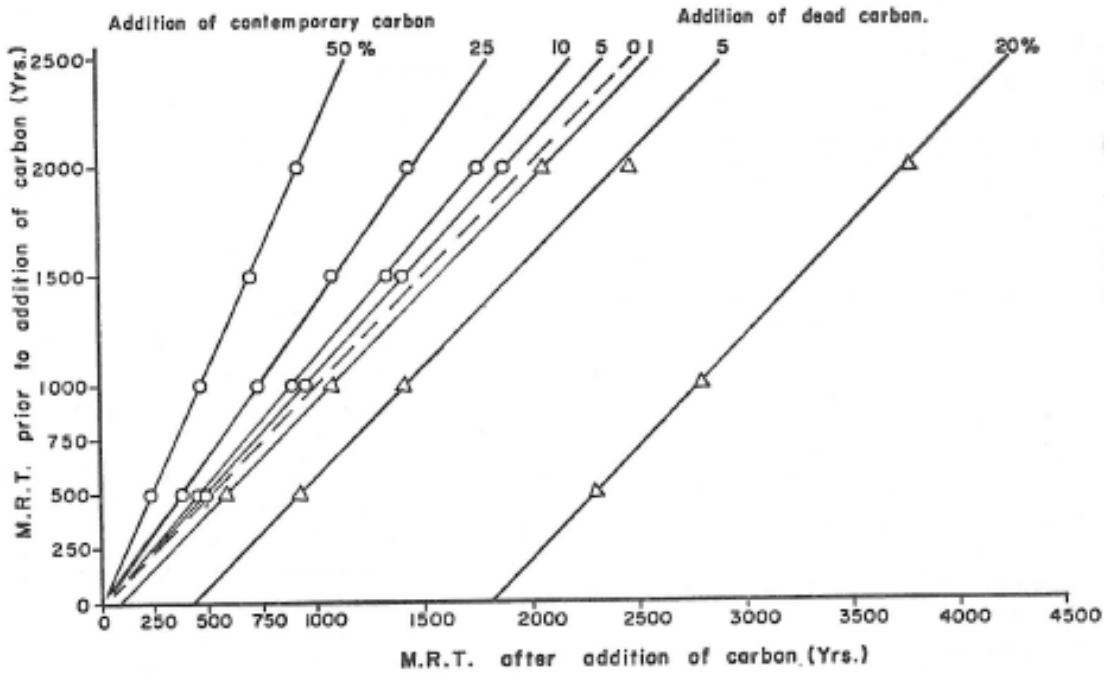


Fig. 1. Effect of added carbon on the "true" m.r.t. of a sample.