8th INTERN. CONGRESS OF SOIL SCIENCE, BUCHAREST, ROMANIA, 1964

INVESTIGATIONS OF THE DYNAMICS OF SOIL HUMUS UTILIZING CARBON DATING TECHNIQUES

E. A. PAUL, C. A. CAMPBELL, D. A. RENNIE, K. J. MC. CALLUM [1]

The study of the dynamics, or turnover rates, of soil humic compounds has been hindered by the complexity of the system and by the length of time required for equilibrium. Since soil organic matter is an equilibrium product and normally in cultivated soils, there are nearly equal losses and additions of organic matter, a number of mathematical equations have been proposed to describe and evaluate the processes involved (Jenny, 1941; Bartholomew and Kirkham, 1960; Kononova, 1961). The mathematical descriptions are, however, presently greatly limited in their use due to the lack of information concerning the average age or mean residence time of the soil humus components.

Data concerning the residence time of soil organic matter can now be obtained by utilization of carbon dating techniques. This technique is regarded as a standard method for determining the age of carbonaceous materials for archeological and geological samples of recent origin. It hinges on the fact that although there is an equilibrium between assimilation and respiration of radioactive CO_2 ($C^{14}O_2$) in all living organisms, after death, assimilation ceases and decay of the C^{14} follows a first order reaction in that the rate of decay is proportional to the number of C^{14} atoms present. If the radio activity of C^{14} in a sample which incorporated CO_2 from the atmosphere during the last 50,000 years is determined by counting in a low background anti-coincidence counter, then from the known half-life of C^{14} it is possible to calculate the mean age of the sample (Libby, 1955).

This technique has been found to be reliable in determining the age of a wide cross-section of organic samples suchas materials from archaeological sites, tree rings, buried soil profiles and peats (Libby, 1955; Scholtes and Kirkhem, 1957; Radiocarbon, 1959—1963). The humus of the soil profile differs from other carbonaceous residues in that incorporation of radioactive C^{14} from the atmosphere via plant residues continues at all times. Thus, interpretation of the results concerning the residence time of humus is difficult. However, because of the importance of the carbon of soil humus in the interpretation of the geochemical carbon cycle, a few age determinations

[1] University of Saskatchewan, Saskatoon, Saskatchewan, CANADA.

have been conducted on soil humus. Tamm and Ostlund (1960) found a progressive decrease in radiocarbon with depth, the total organic matter in the *B* horizon of a soil in Sweden having a mean residence time of about 375 years. Broecker and Olson (1960) in investigating potential tracer applications of carbon 14 and to studies in soil science, suggested a mean life of humic acid between 50 and 250 years. The organic fractions remaining after humic acid extraction of this soil (Sol Brun Acide) from Palisades, New York had an age of 2,000 years. Simonson (1959) has quoted ages ranging from 100 to 400 years for some cultivated soils in the North Central U.S.A.

The natural C^{14} content of organic materials makes the use of this tracer over such a long period of time possible so that equilibrium of the organic constituents in the soil can be obtained. It has great potential for soil organic matter investigations both in the interpretation of problems in soil genesis, where effects of parent materials and different types of vegetation alter the content and stability of soil organic matter, and in soil fertility where the incorporation and turnover rate of organic matter differs under different cultural practices. It is obvious that such studies would be greatly facilitated by a knowledge of the mean residence time of the soil humus. This technique was therefore examined in detail to determine its applicability as a research tool for soil scientists.

Methods

The flow sheet (fig. 1) indicates the steps followed in the analysis of the radio activity of the carbon in a soil sample. Approximately 2 grams of soil carbon were required to obtain sufficient acetylene to fill the one litre counting chamber at atmospheric pressures.

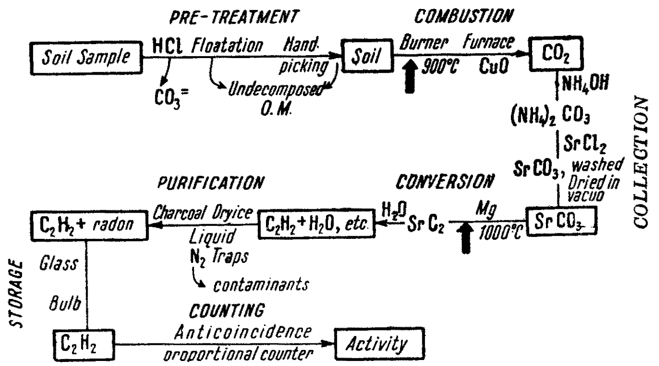

Fig. 1. Flow sheet showing preparation of sample, conversion to acetylene, and determination of C^{14} activity.

The counting procedures were essentially those of Suess (1954). Each sample was counted for at least two 20-hour periods. The standard for modern carbon was taken as 0.950 times the activity of the National Bureau of Standards (Washington) Oxalic acid standard for radiocarbon measurements.

The Melfort soil was fractionated into humic acids, "mobile" humic acids, fulvic acids and humin based on the relative solubility of these fractions in dilute acid and base in a scheme similar to that proposed by Tyurin (Kononova, 1961). The fractions obtained were dried by rotary evaporation under reduced pressure at 15—20°C. The dried samples were then converted to $SrCO_3$, then subsequently to acetylene and counted as shown (fig. 1). Total carbon was determined quantitatively by the dry combustion method.

Results

The mean residence time of the total organic matter of the two Black Orthic Chernozemic soils (Melfort and Oxbow) is approximately 1,000 years (table 1). Since the soil was obtained from cultivated fields which contained

Table 1

Effect of vegetation and type of surface deposit (P.M.) on mean residence time of soil organic matter of podzolic and chernozemic soils

Soil	P.M.	Organic Matter %	Apparent Meant Residence Time Years
Grey Wooded Podzolic	Glacial Till	3.36	360±60
Black Chernozemic	Glacial Till	7.81	1030±70
Black Chernozemic	Glacial Lacustrine		
0—6″		9.65	990±60
6—10″		10.10	1130±70

recent crop residues with a high specific activity, either the majority of the carbon fractions must be very stable to yield such a high figure, or very little of the recently incorporated carbon has become a part of the soil humus. The two Chernozemic soils, although on different parent materials, showed a markedly similar age. The mean residence time of the organic matter of the two glacial till soils (Oxbow and Waitville), located within less than two km. distances but on different topographical positions, was strikingly different.

The difference in age can presumably be attributed to factors such as : quality of the organic residues, the nature of the microbial population, and the physio-chemical properties of the humic constituents. The results obtained confirm speculation by other workers (Kononova, 1961) regarding the lower persistence of residues in Podzolic in comparison to that of Chernozem's soils.

The results, in table 2, show the effect of cultural practices on the mean residence time of soil organic matter of a Dark Brown Chernozemic soil (Chestnut). The soil samples dated were obtained from two, three-year rotational plots at the Canada Department of Agriculture Research Station, Lethbridge, Alberta. They differed in that for 30 years a soil improving crop—sweet clover

Table 2

Effect of cultural practices on the mean residence time of soil organic matter of a dark broun chernozemic soil

Plot No.	Crop Rotation	Yield bu/ac	Organic Matter %	Apparent Mean Residence Time Years
13	Wheat	23.1		
	Wheat	15.6	2.22	2250 ± 90
	Summerfallow	—		
	Wheat	22.7		
20	Wheat and Sweet Clover	16.6	2.48	1680 ± 80
	Hay-Summerfallow			

— was included in the rotation on Plot No. 20, while only wheat straw residues were incorporated on Plot No. 13. Both plots were in fallow at time of sampling.

The inclusion of sweet clover in the rotation maintained the soil organic matter at a level 10 per cent higher than the wheat- wheatsummerfallow rotation, but the mean residence time of the soil organic matter was thirty per cent lower.

The organic matter of both samples was much older than that of the three soils taken from central Saskatchewan (table 1). Further work will have to be conducted to ascertain whether this can be attributed to : 1) the differing soil-forming factors under the drier climatic condition in S. E. Alberta ; 2) the greater geological age of the samples ; the Pleistocine glaciation receded much earlier from the Alberta site than from the Saskatchewan sites studied.

The organic matter of one of the Black Chernozemic soils (Melfort) was fractionated into the humin, humic and fulvic acids ; these fractions constituted 31, 40 and 29 per cent respectively of the total carbon. The mean residence time of the carbon of each fraction was determined (table 3). Within the error of measurement, the age of the humic acid and humin fractions could not be differentiated, but that of the fulvic acid fraction was much younger. The 'mobile' humic acids were intermediate in apparent age between the humic and fulvic acids.

The C^{14} activity of each fraction multiplied by the fraction of the total organic matter it represents, yields the net activity. The balance sheet of the C^{14} activities of the individual fractions of the soil humus, together with the corresponding apparent mean residence times (table 3), indicates that the sum of the C^{14} activities of the humin and fulvic and humic acid fractions (12.72 ± 0.38) is within the experimental error of that obtained for the composite soil (13.09 ± 0.10). This attests to the validity of the techniques employed and suggests that the mean residence time of one of the fractions of a soil can be estimated by difference, if the activities of the C^{14} of the rest of the fractions and of the whole soil are known. This would be especially useful for the soluble fraction such as the fulvic acids where up to 70 l. of extracting solution had to be dried *in vacuo* before dating procedures could be employed.

Table 3

"Balance sheet" of C^{14} activities of fractions of soil organic matter together with corresponding apparent mean residence times

	Humin	Humic Acids (+)	Fulvic Acids (I & II)	Composite Soil
(a) Mean activity of C^{14}	12.53±.10	12.42±.07	13.50±.14	13.09±.10
(b) Fraction of total organic C	0.3083±.011	0.4020±.023	0.2860±0.015	
Net activity* of C^{14} (a · b)	3.863±.14	4.993±.29	3.861±.21	
Apparent Mean Residence Time	1.240± 60	1.308± 64	630± 60	990± 60

The "mobile" Humic acids included in the humic acid data above constituted 0 . 250 of total organic C and dated 875 ± 57 years.

* Sum of the net specific activity of the fractions = 12 . 72 ± 0.38.

DISCUSSION

The data shown in the tables indicate some of the possible applications of the carbon dating technique in the study of the dynamics of soil organic matter. The word "apparent" has been used in listing the mean residence times, because there are a number of factors affecting the calculations which transform the C^{14} activity data obtained into mean residence times in years. Some of these factors which still require further research are discussed below.

The C^{14} content of the atmosphere is not uniformly distributed over the earth's surface and the pattern in homogeneity may have been different in the past (de Vries, 1958). Individual carbon dating laboratories must therefore have carefully calibrated control samples, especially if the radiocarbon dates are to be accurate within less than 100 years. The possibility of isotopic exchange between the carbon molecules in the humus and the inorganic carbonates of the soil solution is unlikely, because of the high stability of the covalent bond of organic materials (Libby, 1955).

The isotopic composition of an element such as carbon (C^{12}, C^{13} and C^{14}) can be changed during chemical and biological transformations. However, since the stable isotope C^{13} is affected in addition to C^{12} and C^{14}, determination of the C^{13}/C^{12} ratio using a mass spectrometer makes a correction of the measured C^{14}/C^{12} ratio determined in the dating procedure possible (Libby, 1955).

Mass spectrometric measurements of the C^{13}/C^{12} ratio of the soil organic samples discussed in table 3 were conducted. The δ C^{13} relative to the solenhofen NBS limestone standard was found to be 21 to $26^0/_{00}$. There thus appears to be very little discrimination during soil humus formation, the largest percentage of the discrimination occuring during the photosynthesis process. Correction of the mean residence times shown in the tables would reduce all the values by approximately 100 years.

The per cent error in measurement of the mean residence time of the younger organic matter in the Podzolic soil (table 1) was much larger than that for the Chernozemic soils. Broecker and Olson (1960), presented data that explains the reason for the relative insensitivity of the C^{14} dating technique to measure mean residence times of 200 years or less. This lack of sensitivity stems, in part, from the post-1900 decrease in atmospheric C^{14}/C^{12} ratios (Suess, 1955). These authors suggest that the sensitivity of the C^{14} dating technique for relatively young organic materials should improve significantly as a result of bomb-produced C^{14}, presently in the atmosphere. Careful measurements and interpretation of the factors affecting the radiocarbon measurements in the soil system can therefore be used not only to overcome the variables involved, but to increase the applicability of this tool. The C^{14} dating of the Ap horizons of a Podzol, two Black and one Dark Brown Chernozemic soil can be used to illustrate the application of radiocarbon measurements in soil genesis studies. The organic matter of the Chernozemic soils is apparently much more resistant than that of the Podzolic. It was suggested above, that the greater geologic age of the Dark Brown soil may explain the relatively old age of carbon contained in the Ap horizon. However, the Podzolic and Black Chernozemic soils can be assumed to be of the same geologic age; these data, therefore, indicate the instability of organic residues under the podzolization process as compared to the relatively high stability of at least a portion of the incorporated grass residues in the Chernozemic soils.

Much has been said about the influence of soil improving crops on soil productivity. The C^{14} dating technique should provide a sound basis on which to measure the persistence of both the indigenous humus and the added organic matter in the soil under specific cultural and cropping practices. The mean residence times given in table 2 suggested that the inclusion of sweet clover in a three-year grain rotation significantly reduced the average age of the organic matter in the soil. Further verification of this trend is under way. Bomb-produced C^{14} may prove a valuable tracer in the short-term period (four- to five-year equilibrium period), providing samples of crop residues incorporated into the soil are available.

Mathematical descriptions of the biological decay sequences and turnover rates of added crop residues and the more stable soil humus have been described for soils in long-term experimental plots (Bartholomew and Kirkham, 1960). These have, however, been severely limited by the fact that no knowledge of the residence time or age of the organic components was known. The data obtained from carbon dating measurements, especially that utilizing the increased level of tracer carbon in the atmosphere at present, should be particularly useful in this regard.

The C^{14} dating technique also provides a potentially useful tool to measure the significance of isolated humus constituents. To date, numerous authors have reported the results of short-term studies where tagged organic residues were added to soils (Jansson, 1960; Simonart and Mayaudon, 1958). While studies of this type provide a basic understanding of the fate of recent carbon additions to soils, they shed little light on the indigenous carbon fractions which accumulated in the soil under an environment entirely different from the laboratory or growth chamber, and much longer periods of time. On the basis of the limited data presented in table 3 it is possible that the humin and humic acids could be portions of the same organic fractions, since their age was approximately the same; however, the fact that the "mobile" humic acids were considerably younger refutes this contention. Further investigations of the significance of the C^{14} dating technique in the field of soil biochemistry should yield needed information on the significance of the soil humic substances and also of the chemically definable components such as carbohydrates, amino acids, and phenolic residues.

Acnowledgments

The authors wish to thank Mr. J. Wittenberg who operated the carbon dating equipment, and the Saskatchewan Research Council for financial assistance.

REFERENCES

Bartholomew, W. V., Kirkham, D., 1960, *Mathematical Descriptions and Interpretations of Culture Induced Soil Nitrogen Changes.* Trans, 7th Intern. Congress of S. Sci. Madison, Wisc. U.S.A., 3, 471—477.

Broecker, W. S., Olson, E. A., 1960, *Radiocarbon from Nuclear Tests, II. Future concentrations predicated for this isotope in the earth's carbon cycle suggest its use in tracer studies,* Science, 132, 712—718.

Jansson, S. K., 1960, *On the Establishment and Use of Tagged Microbial Tissue in Soil Organic Matter Research.* Trans. of 7th Intern. Congress of S. Sci. Madison, Wisc. U.S.A., 3, 635—642.

— 1963, *Balance Sheet and Residual Effects of Fertilizer Nitrogen in a 6-year Study of N 15,* Soil Sci., 95, 31—37.

Jenny, H., 1941, *Factors of Soil Formation,* McGraw-Hill Book Co.

Kononova, M. M., 1961, *Soil Organic Matter,* Pergamon Press, New York.

Libby, W. F., 1955, *Radiocarbon Dating,* 2nd Edition, University of Chicago Press.

Radiocarbon, Vols. I to V, 1959—1963, Published by American Journal of Science.

Scholtes, W. H., Kirkham, D. 1957, *The Use of Radiocarbon for Dating Soil Strata,* Pedologie, VII, 316—323.

Simonart, P., Mayaudon, J., 1958, *Study of the Decomposition of the Organic Matter in the Soil by means of Radioactive Carbon,* Plant and Soil, 9, 367—384.

Simonson, R. W., 1959, *Outline of a Generalized Theory of Soil Genesis,* S. S. Soc. Amer. Proc., 23, 152—156.

Suess, H. E., 1954. *The Natural Radiocarbon Measurements by Acetylene Counting,* Science 120, 5—7.

— 1955, *Radiocarbon Concentration in Modern Wood,* Science, 122, 415—417.

Tamm, C. O., Ostlund, H. G., 1960, *Radiocarbon Dating of Soil Humus,* Nature, 185, 706—707.

de Vries, H. I., 1958, *Variation in Concentration of Radiocarbon with Time and Location on Earth,* Proc. K. Ned. Akad. Wetesch. B, 61, 1—9.

SUMMARY

The radioactivity of naturally occurring C^{14} in soil humus when compared to the C^{14} activity of a standard of recent origin (carbon dating) can be used to estimate the mean residence time of the soil humus in studying problems in soil genesis, fertility and biochemistry.

The apparent mean residence time of humus from a Black Chernozemic soil was approximately 1,000 years. The C^{14} activity of "Humin" and "Humic Acids" isolated from this soil was lower than that obtained from the whole soil. The fulvic acids, however, had a substantially higher activity and a corresponding lower mean residence time.

A Grey Wooded Podzolic soil sample, developed under different vegetation than the chernozemic, had mean residence time approximately 1/3 that of the chernozemic soil.

Carbon dating techniques can also be used to study the dynamics of soil organic matter under diffeing cultural techniques and in soil biochemistry investigations. When integrating these data, factors such as isotopic discrimination and variations in the C^{14} content of the atmosphere must however be taken into consideration in all studies using this technique.

RÉSUMÉ

La radioactivité du C^{14} existant naturellement dans l'humus du sol, comparée à l'activité d'un étalon d'origine récente (détermination par carbone), peut être utilisée pour esti mer l'âge moyen de séjour (mean residence time) de l'humus du sol dans l'étude des pro blèmes de genèse, de fertilité et de biochimie du sol.

Le temps moyen apparent du séjour de l'humus d'un sol noir chernozémique était approximativement de 1 000 ans. L'activité de l'„Humine" et des „Acides Humiques" isolés de ce sol a été plus réduite que celle obtenue pour le sol entier. Toutefois les acides fulviques ont eu une activité bien plus élevée et un temps de séjour moyen correspondant plus réduit.

Un échantillon de sol podzolique gris de forêt, développé dans des conditions de végétation différentes de celles du sol chernozémique a eu un temps moyen de séjour d'approximativement 1/3 de celui du sol chernozémique.

Les techniques de détermination de l'âge à l'aide du carbone peuvent donc être employées aussi à l'étude de la dynamique de la matière organique du sol sous différentes techniques culturales ainsi que dans les recherches de biochimie du sol. Dans l'interprétation de ces données, des facteurs tels que la séparation à l'aide des isotopes et les variations en teneur du C^{14} de l'atmosphère doivent être pris en considération dans toutes les études utilisant cette technique.

ZUSAMMENFASSUNG

Die Radioaktivität des im Bodenhumus in natürlicher Weise vorkommenden C^{14}, kann, wenn mit der Aktivität eines Standards neuerer Herkunft verglichen (Zeitbestimmung durch Kohlenstoff), zur Einschätzung der mittleren Verweilzeit des Bodenhumus beim Studium von Bodengenese-, Fruchtbarkeits- und Biochemieproblemen eingesetzt werden.

Die anscheinende durchschnittliche Verweilzeit des Humus eines schwarzen tschernosemartigen Bodens betrug ungefähr 1 000 Jahre. Die Aktivität des aus diesem Boden ausgeschiedenen „Humins" und der „Huminsäure" war geringer als jene, die im gesamten Boden erzielt wurde.

Die Fulvosäuren wiesen jedoch eine wesentlich höhere Aktivität und eine entsprechend kürzere durchschnittliche Verweilzeit auf.

Eine Probe aus einem grauen podsolierten Waldboden, der unter einer unterschiedlichen Vegetation als jene des tschernosemartigen Bodens entstand, wies ungefähr 1/3 der mittleren Verweilzeit des letzteren auf.

Das Zeitbestimmungsverfahren mittels Kohlenstoff kann ebenfalls zum Studium der Dynamik des organischen Bodenstoffes unter verschiedenen Bodenarbeitungsverfahren sowie bei biochemischen Bodenuntersuchungen angewendet werden. Bei der Verwertung dieser Angaben müssen jedoch bei allen, diese Technik benützenden Unterschungen, Faktoren wie isotopische Trennung und Variationen im C^{14}-Gehalt der Atmosphäre, in Betracht gezogen werden.