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UNRELIABILITY OF ^{14}C DATES FROM ORGANIC MATTER OF SOILS

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ABSTRACT. Contamination by recent carbon and the turnover of organic matter make dating of ancient soils difficult. In order to isolate the oldest organic fraction of sediments, two main extraction methods were previously proposed: 1) alkaline solubilization of humus that separates humins, humic acids, and fulvic acids, and 2) successive hydrolyses that solubilize increasingly resisting products. Both preparation methods were tested on the same actual or fossil soils of different pedologic types from five geologic profiles on which other chronologic data are available.

Analytic results show that ^{14}C ages obtained from alkaline extraction products differ according to the duration of treatments and characteristics of soils: while hydrolysis should yield more homogeneous results and isolate oldest fractions. It seems likely that true ages of geologic formations were never obtained from their organic matter and that the oldest organic fraction, contemporaneous with the sediment formation, completely disappears. Thus, most ages from ^{14}C dating of organic matter of soils must be too recent.

INTRODUCTION

Radiocarbon dating of ancient soils is, in general, complicated by contamination with recent organic matter; the ages deduced from the ^{14}C activity of the total soil carbon are, therefore, too young. Contamination is mostly derived from plants growing on the soil surface, and must be removed if a true ^{14}C date is to be obtained. Unfortunately, the classic pretreatment with dilute alkali, which is quite efficient in removing recent material from specimens of charcoal or wood, is not adequate for eliminating such contamination from soil specimens. A fractionation technique, capable of separating the oldest components from the soil mixture, is needed. Dates so derived might then be considered representative of the age of soil formation. Such fractionations must first be applied to soil samples of different types and of known ages, in order to determine the reliability of the method.

Organic matter in soils

The accumulation of vegetal remains, wood, leaves, and roots, in the soil produces a continuous supply of fresh organic matter which then undergoes a series of chemical processes leading to the release of oses, proteins, and lignins. These organic components have different degradation cycles described by Paul (1970, fig 1). The oses and proteins are, for the most part, quickly mineralized, although a small quantity may remain fixed to the soil clays. Soon, only the lignin remains. Its longer decomposition cycle is due to polymerization of phenolic structures leading to fairly stable molecules known as "humic fraction". Therefore, the soil contains a series of components of differing ages, whether or not the supply of fresh organic matter is constant.

Fractionation procedures

Although the structures of these components are reasonably well known, single substances corresponding to a determined step in the biologic transformation are not isolated in the procedures used. Rather, groups of substances are separated according to their chemical characteristics.

Before the samples were fractionated, they were prepared by various pretreatments to eliminate most of the free organic matter. These included decarbonation, flotation, stirring and decantation, and sieving to separate samples of different grain sizes. The prepared samples were then fractionated by one of the following methods:

Alkaline solubilization. The solubilization of humus using sodium hydroxide (Perrin, Willis, and Hodge, 1964) or pyrophosphate (Tate, 1973)

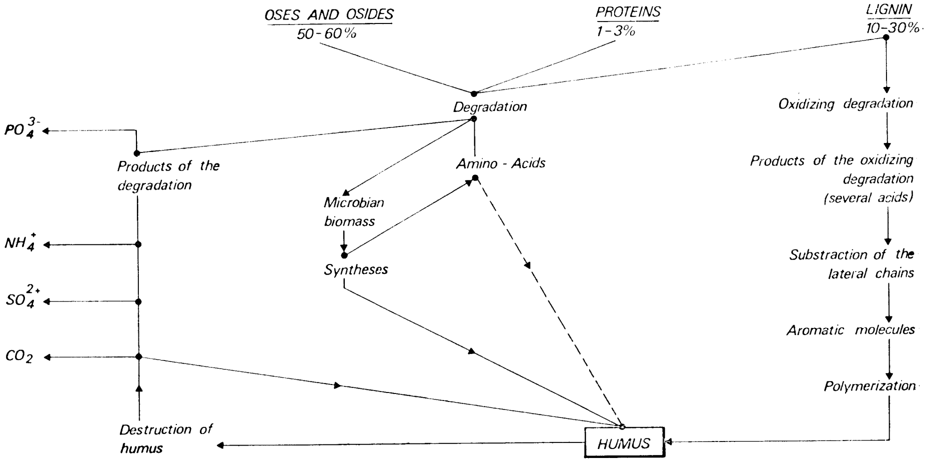

Fig 1. Degradation of the vegetal components and formation of the organic matter in soils (after Paul, 1970).

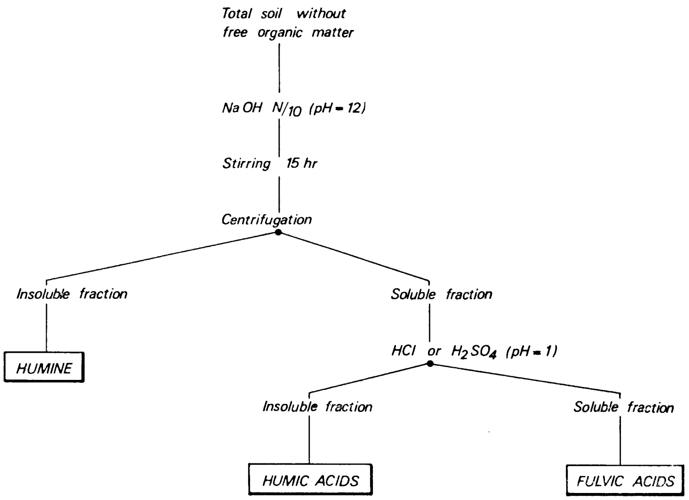

Fig 2. Extraction of organic matters from soils by *Alkaline Solubilization* for ^{14}C datings.

is the oldest and most widely used method. The sample was stirred for 15hr in 0.1N NaOH at room temperature. The remaining insoluble fraction bound to the clay is called humin. The soluble fraction is treated with acid (HCl or H_2SO_4) which causes precipitation of the humic acids, while the fulvic acid fraction remains in solution. The most resistant material, humin, is generally presumed to be the oldest (fig 2).

Successive hydrolyses. This method, introduced by Jansson and Persson (1968), uses progressively more concentrated acid solutions (HCl or H_2SO_4) in 15hr steps under reflux. The resulting solutions are designated by the normality of the acid used and the letter H+ (eg, H+.5N or H+ 6N) for the hydrolysates obtained with 0.5N or 6N acids. The residue after the last hydrolysis is then treated with sodium hydroxide (0.5N) producing a basic extract and leaving a final residue (fig 3). Again, the most resistant fraction (final residue) is generally assumed to be the oldest.

Measurement of ^{14}C activities

Liquid scintillation was used for measurements, generally, made on 3ml of benzene. For very low activities, it was necessary to synthesize larger quantities (10ml). In other cases, the amount of carbonaceous material extracted was insufficient to provide the 3ml of benzene required, and inactive benzene was added to make up the quantity. The precision of such measurements is naturally reduced.

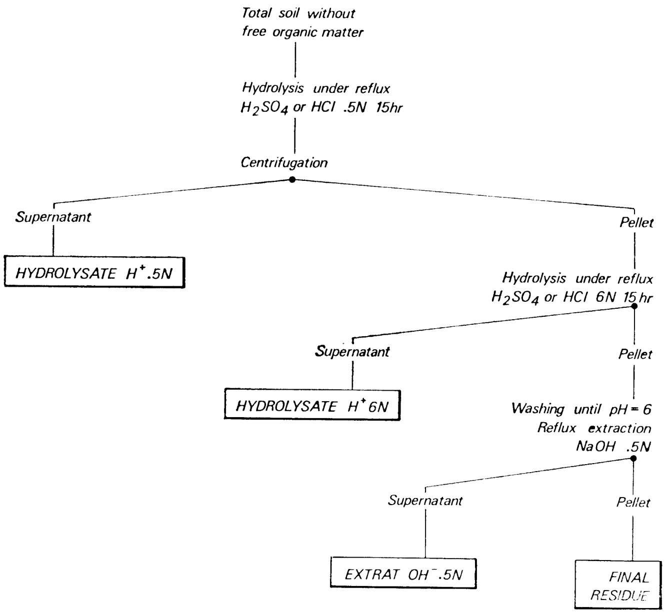

Fig 3. Extraction of organic matters from soils by *Successive Hydrolyses* for ^{14}C datings.

TABLE 1

^{14}C activities of soil fractions from Le Pilat

Fractions	Level A.1, actual			Level A.1, fossil			Level A.2, fossil			Level Bh, fossil		
	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP
Total soil size < 2mm	Ly-1318	102.6 ± 1.7	post-bomb	Ly-1315	98.7 ± 1.6	modern	Ly-1317	95.5 ± 1.6	370 ± 130	Ly-1316	87.6 ± 1.4	1060 ± 120
Humine	Ly-1413	94.4 ± 1.4	460 ± 120	Ly-1415	97.0 ± 1.5	240 ± 120	Ly-1417	91.3 ± 1.4	730 ± 120	Ly-1419	80.8 ± 2.3	1710 ± 220
Humic acids	Ly-1412	101.7 ± 1.5	post-bomb	Ly-1414	99.6 ± 1.5	modern	Ly-1416	91.0 ± 2.5	760 ± 120	Ly-1418	89.4 ± 2.6	900 ± 230
Hydrolysate H$^+$ .5N	—	—	—	Ly-1371	102.2 ± 1.4	post-bomb	—	—	—	Ly-1375	100.2 ± 1.5	modern
Hydrolysate H$^+$ 6N	—	—	—	Ly-1372	96.8 ± 2.8	260 ± 230	—	—	—	Ly-1376	91.3 ± 2.7	730 ± 240
Extract OH$^-$ .5N	—	—	—	Ly-1373	96.4 ± 1.4	250 ± 110	—	—	—	Ly-1377	93.2 ± 1.4	560 ± 120
Final residue	—	—	—	Ly-1374	92.5 ± 1.2	630 ± 110	—	—	—	Ly-1378	82.5 ± 2.3	1550 ± 230
Charcoal	—	—	—	Ly-1314	100.0 ± 1.5	modern	—	—	—	Ly-1497	70.8 ± 1.1	2770 ± 120

TABLE 2

^{14}C activities of soil fractions from Chambolle

Fractions	Level 0, actual			Level 1, actual			Level 8, fossil			Level 14, fossil		
	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP
Total soil	Ly-1161	105.3 ± 1.5	modern	Ly-1162	94.1 ± 1.5	790 ± 130	Ly-1020	2.7 ± 0.4	28,900 ± 1000	Ly-1022	1.2	35,600
Total soil 100 < size < 250 mu	—	—	—	Ly-1226	95.3 ± 1.5	380 ± 130	—	—	—	—	—	—
Total soil 100 mμ	—	—	—	Ly-1163	100.8 ± 1.5	modern	Ly-1167	4.24 ± 0.14	25,400 ± 250	—	—	—
Humin	—	—	—	Ly-1165	103.6 ± 1.5	post-bomb	Ly-1169	4.85 ± 0.17	24,320 ± 280	—	—	—
Humic acids	—	—	—	Ly-1166	99.3 ± 1.4	modern	Ly-1170	4.04 ± 0.17	25,790 ± 270	—	—	—
Hydrolysate H^+ 66N	—	—	—	Ly-1164	90.3 ± 1.5	820 ± 130	Ly-1168	2.75 ± 0.14	28,880 ± 410	—	—	—

Soils

Sites for soil sampling were chosen by the availability of: 1) large samples with good organic content from several levels in the same section, from well-stratified rich fossil soils, 2) chronologic, palynologic, malacologic or geologic documentation, 3) accessibility.

Initially, two sites, one with acidic and the other with basic soil, that met these criteria, were studied. Later, samples of three different soil layers were also included, one from a shallow position in an ancient cemetery and two others embedded under a deep series of sand or loess (fig 4).

Acid soil profile from Le Pilat. This profile lies beside a forest road in Le Pilat massif, about 50km southwest of Lyon (45° 20′ N, 4° 31′ E). It consists of an evolved pozzolic soil, 55cm thick, above a granitic substratum (fig 5). Organic matter was extracted from 4 pedologic horizons. ^{14}C measurements were obtained on all the organic fractions from 2 horizons, and some measurements from the other 2 levels (table 1). The pollen diagram indicates formation has probably been continuous since the beginning of the Sub-Atlantic period.

Calcareous soil profile from Chambolle. This profile is the working-face of an ancient quarry in a landslip at the foot of a cliff beside a small valley near Chambolle in the Burgundy region, about 20km south of Dijon (47° 11′ N, 4° 56′ E). The total profile is 7m thick and is divided into 16 levels (fig 6). The present soil is a rendzine similar to the fossil soils found at levels 8, 13, and 14. By the malacologic diagram (Puissegur, ms), the soil at level 8 may be attributed to an interstadial phase of the

Fig 4. Selected French sites for ^{14}C datings of soil fractions.

Early Würm (perhaps Brörupt). Therefore, we made measurements only on this material and discarded the other from the deeper level as obviously too old for ^{14}C dating (it is attributed to the Riss-Würm interglacial). We were unable to obtain sufficient carbon from hydrolysis fractions for the total profile, and could only measure the activities of the final residues (table 2).

Archaeologic filling at Crotenay. These samples were taken from the ancient cemetery of Crotenay village in the Jura mountains, about 25km east of Lons le Saunier (46° 45′ N, 5° 49′ E). Merovingian (Early Middle ages) graves were dug in fluvioglacial formations, but black earth, rich in organic matter and derived from ancient soil, was used to cover the wooden coffins. Our samples consisted of human bone from one of the burials and organic matter from the overlying black earth presumably older than the grave (table 3).

Geologic horizon at Beylongue. This sample was obtained from a single organic layer embedded under some 10m of sand at Beylongue in the Landes region, about 30km west of Mont de Marsan (43° 55′ N, 0° 49′ W). Studies on this organic layer made at neighboring sites (Latouche, Legigan, and Thibault, 1974) suggest attribution to before or during the Würmian III stadial (table 3).

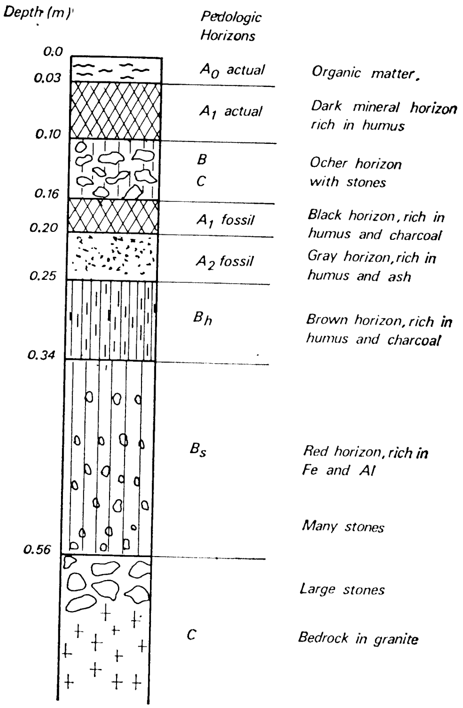

Fig 5. Profile of Chambolle site.

TABLE 3

	CROTENAY			BEYLONGUE		
Fractions	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP
Total soil or bones	Ly-1411	85.0 ± 2.5	1380 ± 240	—	—	—
Hydrolysate H^+ 6N	Ly-1368	86.2 ± 2.6	1190 ± 240	Ly-1537	17.6 ± 0.8	13,960 ± 360
Extract OH^- .5N	Ly-1369	83.2 ± 2.2	1480 ± 200	—	—	—
Final residue	Ly-1370	82.4 ± 2.6	1550 ± 280	Ly-1538	12.4 ± 0.7	16,760 ± 440
Humic and fulvic acids	—	—	—	—	—	—
Humin	—	—	—	—	—	—

Loess horizons at Sergines. These samples were taken at three levels in a loess profile at Sergines in the west Burgundy region, about 20m north of Sens (48° 20′ N, 3° 15′ E). The three organic layers were embedded under loess formations attributed to Late Würmian stadial (Lautridou, 1973) (table 3).

RESULTS

Comparison between true ages and ^{14}C ages deduced from ^{14}C activities of the organic fractions from soils

Figure 7 summarizes ^{14}C dates obtained from the different fractions compared with the chronologic position of the sediments as determined by independent dating methods. It can readily be seen that the ^{14}C dates are always too young by one or several millennia; this corresponds to about 5 percent modern activity. This is true even for the oldest of the separated fractions. The only material yielding a date corresponding to the true age is charcoal, which is also the only material that can be completely freed of contamination during pretreatment.

This study cannot differentiate between two possible mechanisms for recent contamination in all fractions: either the original organic material in the sediment disappears and is replaced by more recent material, or, rather, there is a continuous contamination by recent organic material of all fractions whatever their state of polymerization.

Comparison between the ^{14}C activities of different fractions from the studied samples

It must be emphasized that the different fractions do not correspond to biologic criteria, but only to physico-chemical characteristics by which

^{14}C activities of soil fractions from various sites

SERGINES								
Level 1			Level 2			Level 3		
Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP	Lab no.	^{14}C % mod	Ages BP
—	—	—	—	—	—	Ly-809	2.4 ± 0.4	30,100 + 1600 − 1300
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
Ly-805	6.9 ± 0.7	21,500 ± 700	Ly-807	4.5 ± 0.5	25,000 ± 850	Ly-811	3.6 ± 0.6	27,300 + 1700 − 1200
Ly-806	6.3 ± 0.4	22,300 ± 500	Ly-808	4.3 ± 0.4	25,400 ± 700	Ly-810	5.2 ± 0.6	23,800 ± 500

they were separated. Theoretically, they might be of any age. The results obtained from fractions prepared by two techniques from three profiles are shown in figure 8.

Relative apparant ages of the fractions obtained by alkaline extraction seem to depend on soil type: humine fraction is "older" than humic acid in acid soils from Le Pilat, whereas the reverse is observed in fractions from the basic soils from Chambolle and sometimes at Sergines. The total soil extract may date between these fractions (Le Pilat) or may give the oldest apparent date (Sergines, level 3). Without adequate acid hydrolysis fractions from Chambolle soils, we are unable to compare this method for different soil fractions. We can only suggest that the more resistant to acid hydrolysis, the older the apparent date of the fraction. In three cases, the oldest dates were obtained on the final residue, which may be considered the least unreliable of these fractions whatever the pedologic soil type.

CONCLUSION

Our results suggest that most fossil soils cannot be dated by ^{14}C measurements of components of their organic matter obtained by our fractionation techniques. Except for truly fossilized soil underlying an impermeable layer, a continuous process of organic turnover occurs in soils although often very slowly. Recent carbon is continuously incorporated into the organic matter and is found in any separated fraction, as was previously shown by Scharpenseel, Ronzani, and Pietig (1968). As there is no physcial or chemical treatment to eliminate this recent fraction, or to isolate the original material contemporaneous with the sedi-

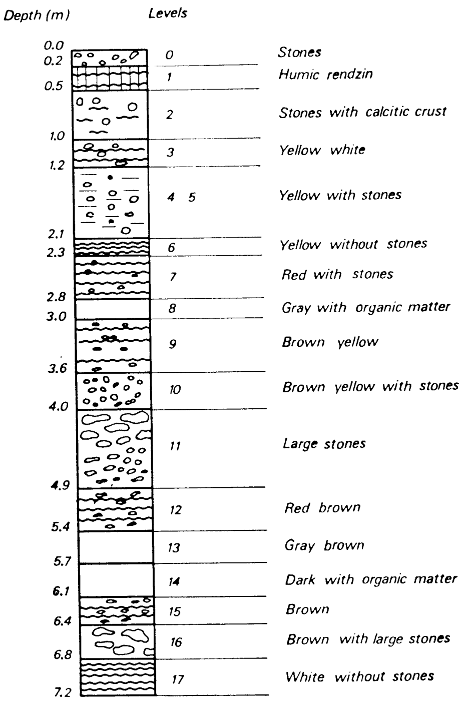

Fig 6. Pedologic profile of Le Pilat site.

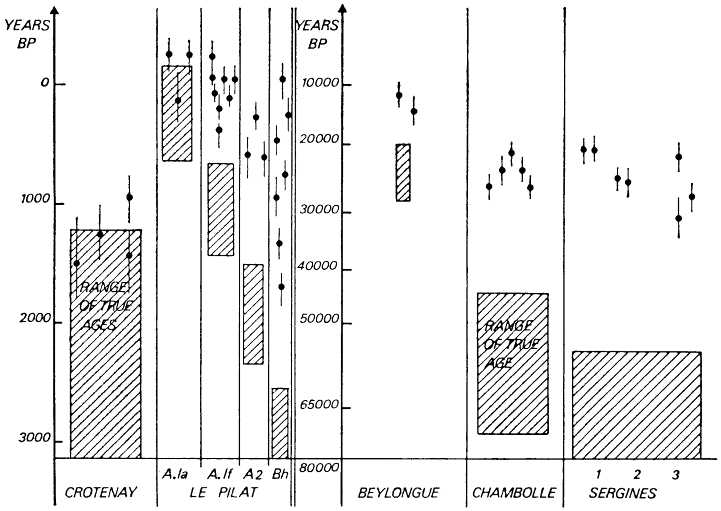

Fig 7. Comparison between ^{14}C apparent ages of soils and the presumed true ages of the sediments.

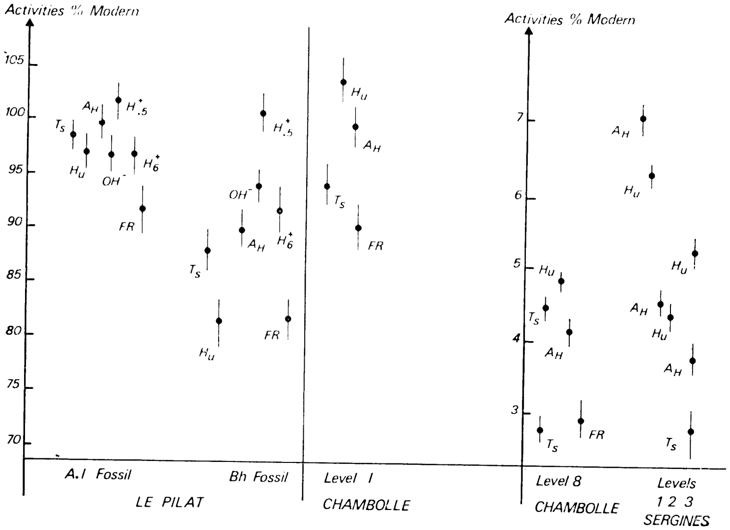

Fig 8. Comparison between ^{14}C activities of different organic fractions of soils.

ment, most ages from ^{14}C dating of organic matter from soils must be too recent. These ages should only be considered as minimal.

Measurements on the different humic fractions are of considerable interest for the information they provide on the processes of humification, and the resident time of organic matter in different soils (Gilet, 1978).

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