[Radiocarbon, Vol 25, No. 2, 1983, P 409-416]

THE UNRELIABILITY OF ^{14}C DATES OBTAINED FROM BURIED SANDY PODZOLS

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ABSTRACT. A test for the reliability of ^{14}C dating of soil was made at two sites with buried, autochthonous, and in parts, allochthonous sandy podzols, dated either litho- and pedostratigraphically or palynologically. The differences between the age ranges obtained and the apparent mean residence times (AMRT) calculated from the ^{14}C content of alkaline extracts from fossil soil layers and horizons lean in organic matter exceed 10,000 years, corresponding to a maximum contamination with recent carbon of up to 50 %. The use of correction factors for the apparent mean residence times of podzols is not valid, not even for climate zones, because these values have a broad scatter for the same profile.

INTRODUCTION: EXPERIENCES GATHERED IN SOIL ^{14}C DATING

Dating of soils is of general geoscientific interest because their formation depends upon climate, vegetation, lithologic environment, and topography. However, there is general agreement (Scharpenseel and Schiffmann, 1977) that ^{14}C dating of alkaline extracts of soils only yields apparent mean residence times (Geyh, Benzler, and Roeschmann, 1971; Scharpenseel, 1971). These are lower than the corresponding true ages, which start with the beginning of humus formation in the regolith. The best agreements have been obtained with the residue remaining after successive hydrolyses with 6N HCl (Scharpenseel, 1979; Gilet-Blein, Marien, and Evin, 1980). This residue may consist mainly of biologically inert carbon (Gerasimov, 1971; 1974), assuming such carbon exists in soils at all. It should be remembered that "soil dating" is a questionable attempt to date only a small part of the total humic matter of a soil horizon and to interpret the result as representative of the whole sample.

The discrepancy between ^{14}C soil dates and true ages results from the complexity of soil genesis, which is a continuous process of accumulation and decomposition of organic substances. Penetration of rootlets, bioturbation, and percolation of soluble humic substances (ie, chelates) cause rejuvenation, and the admixture of allochthonous plant residues (Schoute et al, 1981) may cause apparent aging. As a result, the organic matter in a soil is a mixture of an unknown number of compounds (Paul et al, 1964) of unknown chemical composition, concentration, and age. Therefore, the various classical humus extracts (fulvic acid, hymatomelanic acid, brown humic acid, gray humic acid, humin, humus coal) do not show the anticipated relationship of ^{14}C ages, carbon content, mean molecular weight, and the number of peripheral functional groups. Moreover, the ^{14}C/depth distribution cannot be deciphered in terms of a paleorecord of dynamic processes in a soil due to many factors that influence carbon transport in different soil profiles. The ^{14}C/depth gradients that have been postulated as characteristic for various soil types may not be usable without finer differentiation, eg, in primarily- and secondarily-formed podzols, as well as autochthonous and allochthonous podzol horizons and layers (Scharpenseel, 1972; Matthews, 1981).

Despite the now generally accepted discrepancy between AMRT and true ages, the deviation is often greater than assumed. Scharpenseel et al, (1980) believe they can determine rather reliable time marks for humid climatic periods with ^{14}C soil dates and carry out dendrochronologic corrections (Scharpenseel and Zakosek, 1979), which are theoretically unacceptable for such complex mixtures of old constituents. Matthews (1981) seeks reliable ^{14}C gradients in soil profiles in order to correct radiometric data, goals that conflict with the present uncertainty in ^{14}C soil dating.

CASE STUDIES

INVESTIGATION SITES. To estimate maximum rejuvenation and its scattering in a soil profile, two sites were chosen at which buried, sandy podzols of differing genesis occur. These podzols were dated roughly by geologic, paleopedologic, and geomorphologic field studies or by palynologic analyses. Podzols are formed in a relatively cool and moderately humid climate and show percolation of organic substances but little or no bioturbation.

The first site is 6 km northwest of Rotenburg/Wümme (53° 7'N, 9°0'W). As in another case study by Roeschmann (1975), 3 m of niveofluviatile stratified sands of Late Pleistocene age overlie a sandy fossil podzol profile from which four separate, allochthonous, redeposited A_h-horizon layers were dated. The originally autochthonous B horizon is disturbed by glacial cryoturbation. The soil profiles are several meters above the groundwater table (fig 1). A pine forest grows at the surface. Living roots penetrate all soil layers. Pollen grains are not preserved, but the ^{14}C ages were high enough to yield good estimates of maximum contamination. Depths of the sampling points below surface, relative carbon contents of the alkaline extract (mg/g of sample), and total quantity of carbon (g) used for dating are compiled in table 1.

https://doi.org/10.1017/S0033822200005695 Published online by Cambridge University Press

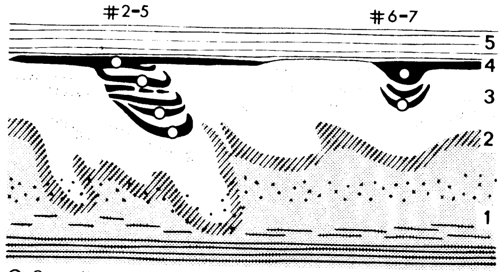

Fig 1. Fossil podzol from glacio-fluviatile sands of the Saale Glacial beneath niveo-fluviatile sands of the Weichsel Glacial in the Rotenburg sand pit in Lower Saxony. 1 = laminated. and in the upper parts. cryoturbated sands with gravel layers from the Saale Glacial. 2 = secondarily cryoturbated podzol B horizon. 3 = secondarily cryoturbated. bleached podzol horizon. in the upper part reworked by solifluction. 4 = reworked humus material. 5 = laminated niveo-fluviatile Weichselian sands.

Table 1. Results of the profile "Rotenburg"

No.	Profile	Depth m	C content mg/g	C content g	$\delta^{13}C$ ‰	Hv	Conventional ^{14}C age yr BP	q* %	q* ppm
1	IV 4	3.80	0.14	0.21	-26.8	8913	19,640 ± 1330	17.3	24
2	VI 10	2.80	0.91	1.54	-27.6	8901	27,415 ± 325	6.6	60
3	VI 10	2.90	0.86	1.69	-27.6	8903	41,200 ± 3160	1.2	10
4	VI 10	3.00	0.71	1.07	-24.2	8905	25,350 ± 450	8.5	60
5	VI 10	3.10	0.41	0.62	-26.0	8907	25,950 ± 980	7.9	32
6	VI 11	2.80	1.56	1.85	-27.5	8909	24,350 ± 395	9.7	151
7	VI 11	2.90	1.28	1.35	-26.8	8911	33,940 ± 1460	2.9	37
8	IX	7.80	1.68	2.70	-28.4	8915	39,500 ± 2150	1.5	25

* - contamination according to Eq 1

Along the eastern bank of the Dinkel river (52°23'N, 7° 0'W), samples were taken from several podzol horizons and peaty layers in four stratified profiles (fig 2). Roots from the forest were present in all of the samples. From previous pollen analyses (van der Hammen and Wijmstra, 1971) we know that soils were formed during late glacial and postglacial periods. The deepest, partly redeposited peaty layers and podzol horizons are probably seasonally inundated when the groundwater table rises in the springtime. The podzol horizons, classified according to Kuntze et al, (1981), depths below the surface, lithostratigraphically (S) or palynologically (P) estimated ages, relative carbon content of the alkaline extracts (‰), as well as the total quantity of carbon (g) used for dating are compiled in table 2.

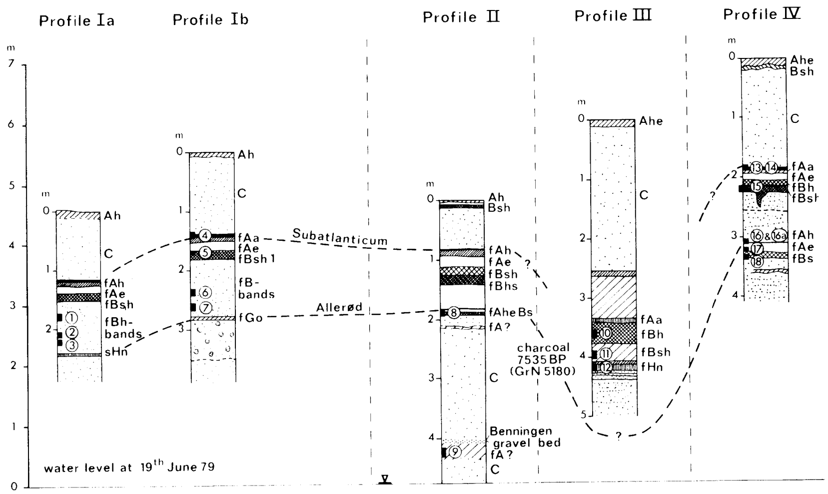

Fig 2. Five exposures with fossil soils in Weichselian sands at the Dinkel Valley near Denekamp. The Netherlands. Sampling sites are shown as circles with reference numbers. The symbols of the soil horizons follow the scheme given by Kuntze et al (1981).

Table 2. Field data and analysis results from Dinkel profiles

No.	Profile	Pedol horizon	Depth m	Stratigraphic and palynologic age estimates yr BP		C content alkaline extract ‰	g	Hv	$\delta^{13}C$ PDB ‰	Conventional ^{14}C age yr BP	Contamination recent carbon %	ppm
1	I a	fBtBs	1.80	S-LD*	11500-10200	0.63	0.89	9783	-27.6	6325 ± 135	24-28	165-194
2	I a	fBt	2.10	S-LD*	11500-10200	0.36	0.39	9782	-28.1	6970 ± 175	19-24	70- 86
3	I a	fBht	2.25	S-LD*	11500-10200	0.42	0.63	9781	-28.4	7740 ± 225	14-19	60- 79
4	I b	fAa	1.30	P-Sa*	2500- 0	2.76	2.47	9787	-29.7	2145 ± 45	-	-
5	I b	fBsh1	1.60	P-Pb*	10200- 8900	1.63	1.48	9786	-28.8	3935 ± 110	42-46	687-752
6	I b	fBtBs	2.30	S-LD*	11500-10200	0.17	0.36	9784	-29.1	5230 ± 250	33-37	57- 63
7	I b	fBt	2.55	S-LD*	11500-10200	0.10	0.14	9785	-27.5	6145 ± 400	26-30	25- 29
8	II	AheBs	1.80	P-Al*	12000-11500	0.67	0.91	9789	-28.3	4125 ± 570	47-48	20
9	II	fA(?)	4.20	S-UP*	28000-13000	0.75	1.20	9788	-26.5	7580 ± 95	24-37	179-278
10	III	fBh	3.50	P-At*	7800- 5000	1.07	2.01	9791	-29.0	3060 ± 100	32-49	338-525
11	III	fBhs2	3.80	P-Bo*	8900- 7800	0.22	0.33	9792	-28.0	4245 ± 145	34-39	76- 87
12	III	peat	4.00	P-Pb*	10200- 8900	4.16	0.48	9790	-29.3	7850 ± 255	7-13	287-553
13	IV	charc	1.70	P-Sa*	2500- 0	220	2.74	9799	-24.9	8585 ± 110	?	?
14	IV	peat	1.70	P-Sa*	2500- 0	18	2.26	9800	-29.8	9205 ± 85	?	?
15	IV	fBsh	7.00	P-At*	7800- 5000	0.30	0.47	9797	-28.8	4225 ± 200	12-34	35-102
16	IV	fAh	2.95	S-Al*	12000-11500	0.13	0.25	9798	-27.2	5280 ± 510	37-38	47- 48
16a	IV	pom	2.95	S-Al*	12000-11500	0.57	0.16	11262	-25.8	1855 ± 235	73	415-418
17	IV	fAe	3.10	S-Al*	12000-11500	0.05	0.09	9795	-27.2	4800 ± 1560	41-42	22
18	IV	fBs	3.20	S-Al*	12000-11500	0.03	0.08	9794	-	6320 ± 1125	28-30	23- 24

* UP - upper pleniglacial; Al - Allerød; LD - Late Dryas; Pb - Preboreal; Bo - Boreal; At - Atlantic; Sa - Subatlantic; S - stratigraphic age; P - palynologic age; pom - NaOH-insolulable organic matter

SOIL SAMPLE PREPARATION FOR ^{14}C DATING

Recommended fractions for routine dating of soils are humic acids and humins extracted with hot sodium hydroxide solution (SCHARPENSEEL, 1971; 1972; 1979; Schoute et al, 1981) from organic complexes bound in clay if successive hy-

https://doi.org/10.1017/S0033822200005695 Published online by Cambridge University Press

drolyses with 6N HCl cannot be done due to a small carbon content (Gilet-Blein, Marien, and Evin, 1980). In our laboratory macroscopic, light-colored rootlets, as well as particulate organic matter were removed by course-sieving and flotation. Then, humic acids were dissolved in 2 % NaOH during 20 min of boiling and reprecipitated with concentrated HCl. The alkaline extract was washed until neutral, dried, burned, and transformed into acetylene, which serves as a counting gas in low-level proportional counters. With this treatment the bulk of extremely young organic substances (fulvic and hymatomelanic acids) is removed. The remaining humic acids are only a very small part of the total organic matter in the soil (table 2).

RESULTS

ROTENBURG PROFILES. Table 1 lists results of the isotope analyses and the estimated maximum contamination. Only alkaline extracts were analyzed since none of the samples contained sufficient NaOH-insoluble organic matter for dating. The conventional ^{14}C ages exceed 20,000 yr BP (table 1). ^{14}C results for stratigraphically co-eval samples, eg, #2 and #6, as well as #3 and #7, do not agree within the range of their standard deviations. Moreover, there is no trend in the ^{14}C ages with depth. The pedologic explanation is that the organic matter of the humic layers probably stems from redeposited A_h horizons of adjacent soils. However, the soils might also have been contaminated during the Holocene and the actual soil ages may exceed the maximum conventional ^{14}C age of 41,000 yr BP obtained. In order to estimate the maximum degree of carbon contamination we assumed that the alkaline extract of soil with a ^{14}C content A_a is contaminated with q % organic matter of a ^{14}C content A_c. Then, the measured ^{14}C content A_m of this sample is given by

$$A_m = q / 100 * (A_c - A_a) + A_a \qquad (1)$$

The ^{14}C content A can be calculated from the conventional ^{14}C age T by

$$A = 100 * e^{-T/8033} \qquad (2)$$

In the Rotenburg case, the ^{14}C content of the admixed Holocene organic matter is assumed to be 50 %. Then, the maximum degree of contamination q amounts to ≤17 % according to Eq 1, or ≤125 μg of ca 5000-yr-old carbon per gram sample (ppm). Contamination of this amount could have easily occurred and it is obvious that the use of "age correction factors" (Scharpenseel, 1971) for at least such sites would be incorrect.

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DINKEL PROFILES. The results of the pollen and isotope analyses, as well as of their interpretation as a measure of contamination, are compiled in table 2. The relative carbon content of the alkaline extracts of the samples (‰), and the carbon quantities (g) used for dating are in the same range as those from the Rotenburg profiles. However, the conventional ^{14}C ages are much lower (≤ 9200 yr BP) although litho-, pedostratigraphic, and palynologic age estimates range up to 28,000 yr BP. Thus, contamination with very young carbon must have occurred (A_c is assumed to be 100 %).

For samples containing little organic matter, the relative and absolute contamination with recent carbon ranges from 15 - 55 % (Eq 1) or 20 to 750 ppm, respectively. Rapid decrease in contamination and carbon content with depth is obvious. This is due to blocking of the fine pores in the fossil soil by organic matter during podzolization, thus reducing carbon transport with increasing depth. Rejuvenation of the organic matter may be even so great that samples older than 20,000 yr BP appear younger than 10,000 yr BP.

Three exceptional results must be interpreted separately: the NaOH-insoluble fraction of sample #16a contained sufficient carbon for dating. The low age and the relatively large carbon content are explained by the presence of rootlets, the ^{14}C dates of peat and charcoal samples #13 and #14 from profile IV are very much greater then the pollen ages. Geomorphologically, the samples may be redeposited organic sediments. The results emphasize the fact that the interpretation of ^{14}C soil dates must consider not only the soil profiles, but also the paleorelief. Only in this way can autochthonous and allochthonous soil horizons and sediments be distinguished and the primary origin of the organic matter at the time of soil formation (ie, before any contamination with younger material) be reliably recognized.

CONCLUSIONS

The results of our study show that, 1) ^{14}C dating of fossil podzol horizons yield AMRT values which may differ from the true ages by 10,000 years and even more. Therefore, Pleistocene and Holocene soils cannot always be distinguished, 2) the degree of particularly contemporaneous contamination (rootlets, humic acids) may cover at least one order of magnitude in the same podzol profile and does not justify the use of "age correction factors" for humid areas, 3) conventional ^{14}C data obtained from fossil podzol soils of different profiles will not be comparable as time marks in any case, even if they were obtained from the same laboratory, and 4) soil dating demands a detailed description of the soil with primary and secondary soil types as well as autochthonous and allochthonous soil features dependent on the paleorelief (Roeschmann, 1971).

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