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TWENTY-FIVE YEARS OF RADIOCARBON DATING SOILS: PARADIGM OF ERRING AND LEARNING

H. W. SCHARPENSEEL and PETER BECKER-HEIDMANN

Institute of Soil Science, Hamburg University, Allendeplatz 2, D-2000 Hamburg 13, Germany

ABSTRACT. Soil organic matter sequesters close to three times the carbon existing totally in the living biomass and nearly the same for the total carbon in the atmosphere. Models, such as Jenkinson's or Parton's Century model, help to define soil organic matter fractions of different functions, based on residence time/^{14}C age. Rejuvenation of soil carbon was felt to be the principal impediment to absolute soil dating, in addition to the ambiguity of the initiation point of soil formation and soil age. Recent studies, for example, of Becker-Heidmann (1989), indicate that a soil ^{14}C age of >1000 yr cannot have >0.1% rejuvenation in the total soil organic matter compartments/fractions to be possible and sustainable. Always problematic in earlier observations were age *vs.* depth increases, in ^{14}C profile curves showing an inflection of reduced age in the deepest samples, *i.e.*, from the rim of the organic matter containing epipedon. We attribute this phenomenon, in mollic horizons, to earthworm casts in the terminal part of the escape tube. Becker-Heidmann (1989) has shown, in thin layer soil profile dating, a highly significant correlation between the highest ^{14}C ages and the highest clay content. Thus, optimization of soil dating is, to a lesser degree, related to the applied extracting solvent system than to soil texture fractions. Such observations allow us to mitigate error ranges inherent in dating dynamic soil systems.

INTRODUCTION

Undoubtedly, the 40 to 50 ka covered by conventional radiocarbon dating exceed considerably the time required for predominant processes of pedogenesis. Thus, ^{14}C dating of soils could be acceptable, if it were not for some interference:

1. The pedosphere, comprising *ca.* 2 k Gt (2×10^{12} tons or 2×10^{18} g) of carbon as humus (close to 3 times the carbon pool sizes of ~720 Gt of carbon in the atmosphere and ~560 in the living biosphere), and, according to rough estimates (Yaalon 1990), nearly as much in calcretes of the subarid climate belt, about half of it being of biotic origin, receives annually ~50% of the 60 Gt of carbon from terrestrial photosynthesis. This input occurs in exchange with released CO_2 from respiration and soil organic matter (SOM) turnover, and rejuvenates the humus compartment of the topsoil. Soils with bicarbonate dynamics, *e.g.*, Mollisols and Vertisols, could also contain moderate amounts of lithogenic carbon in the humus fraction (Scharpenseel 1977) (Table 1).
2. Young, contemporary carbon is transported by percolation in highly acidic soils, *via* root growth, animal transport and through soil turbation processes, such as cryoturbation, bioturbation, downward peloturbation, inflecting also the subsoil to rejuvenation. Even in older, genetically rather stable Alfi- or Ultisols, ^{13}C enrichment in the argillic horizons indicates some percolation or partition transport of organic matter in the deeper profile, and possibly, in the phreatic groundwater zone.
3. In northern countries, especially in periglacial landscapes, only the last Stilfried II interstadial and the Holocene represent the soil-forming period at the dating levels, with clearly distinguishable soil profiles. In the (sub)tropics, most of the soils are truncated, eroded relics of very old Tertiary, even Mesozoic soil formations with young allochthonous, transported topsoil material.
4. The overriding problem for absolute dating of soils is that an exact numerical soil age is impossible. Was the origin of the pedogenesis the primordial formation of the first scanty bit of humus? Was it the beginning of taxonomic compliance with the model of an initial member of morphogenetic sequence of stages? Or is the real beginning of soil age the completion of pedogenesis to the level of the present species of the Great Soil Group, which we subject to dating (climax stage)?

TABLE 1. Soil Carbon Compartments

Compartment	Amount of carbon (Gt) Lithosphere	Atmosphere	Pedosphere
$CaCO_3$ in sediments	35,000,000		
$CaMg(CO_3)_2$ in sediments	25,000,000		
Organic sediments (kerogene)	15,000,000		
HCO_3 and CO_3, dissolved in the sea	40,000		
Fossil fuel, coal, gas, oil	5000		
Economically accessible fossil fuel C	1000		
Consumed fossil fuel C	250		
CO_2 in atmosphere		720	
Living biomass (microbes, plants, animals)			560
Dead soil biomass (humus)			1800
630.10^6 ha wetlands			500
Calcretes, caliches			1500
Terrestrial net-photosynthesis			60
Exchanged carbon in SOM by photosynthesis reaction			30
Carbon lost from plowing depth of epipedon in agroecosystems			50

Obviously, absolute age can be linked only to ^{14}C dating of safely buried paleosols, to charcoal or to a piece of wood. The former signals only the event, when, *e.g.*, the steppe burned, and the carbon became biologically and chemically inert; the latter reflects the age of the source of carbon at the time when the wood was burned, plus the time that lapsed afterward, until the present. All other ^{14}C dating of soils yields model age levels, expressed as Apparent Mean Residence Time (AMRT) of the dated organic carbon fraction (Table 2).

BENEFITS OF SOIL RADIOCARBON DATING

The many incalculable factors influencing soil development, turnover of organic parent material and neogenesis of soil humic substances introduce a strong element of deterministic chaos, particularly in the processes of oxidative and reductive, biotic, abiotic/protolytic and photochemical organic matter transformations, characterized by increasing entropy (Lorenz 1963; Grossmann & Thomae 1977; Haken 1988). However, some reliable principles of SOM dynamics enable us to interpret ^{14}C dates of soil.

In his exchange model, Becker-Heidmann (1989) demonstrated, on the basis of a sustained amount of SOM and a uniform substitution of all organic fractions of different ages by recent organic material, how the level of the AMRT reveals and scales the range of percentage of possible rejuvenation (at AMRT of 1 ka, <0.1%). This gives higher AMRT dates a fair amount of specificity regarding the range of rejuvenation (Fig. 1). A complication, not accounted for in the model, is the probable inertia of the clay organic complexes toward exchange with young/recent SOM species. Geyh, Benzler and Röschmann (1971) and Geyh (1970) were quite skeptical about ^{14}C dating soils in the 1970s, however, with maximized assessment of the rejuvenations to be expected. Other authors explored methods of isolating the least rejuvenated SOM fractions by chemical extraction, soil texture fractionation, particle size/mol weight gel chromatographic fractionation, repetitive 6 N HCl hydrolysis, coking, enzymatic treatment, *etc.* (Scharpenseel 1971, 1972, 1973, 1975a, b, 1977) (Table 3).

TABLE 2. Examples of True Age *vs.* AMRT (based on geological/historical evidence)

Sample origin	Approx. true age (ka BP)	AMRT (ka BP)	Depth (cm)	Geological/historical evidence
Germany				
Söllingen aquic Argiudoll	5.5–8	4.9–6.2	50–70	Climate optimum, 7–8 ka BP (Boreal-Atlantic of Holocene); oldest age in argillic horizon at level of highest clay content
Jerxheim aquic Haludoll	5.5–8	5.55	80–90	Climate optimum, 7–8 ka BP (Boreal-Atlantic of Holocene); oldest age at fringe of epipedon
Tunisia				
Cap Bon Xerochrept (3 paleosols)	0	0.72	Surface	Weak soil formation in erosive sand layer "Historique"
	1.4	1.3	120	50 cm below the "Historique" layer paleosol after *Quercus* deforestation upon Islamic conquest
	2.4	2.3	170	Paleosol below the transported material after deforestation during Carthage-Roman time
	4.5–8	4.23	190+	Paleosol indicating pedogenesis at climate optimum during Holocene/Rharbien
Wadi 18 km N of Tajerouine,	8	7.96	80	Paleosol below more sandy "Historique" from Holocene/Rharbien climate optimum
W of Le Kef Highway to Tajerouine	11–14	8.52	200	Paleosol, early Rharbien/Holocene or late Soltanien/Würmian

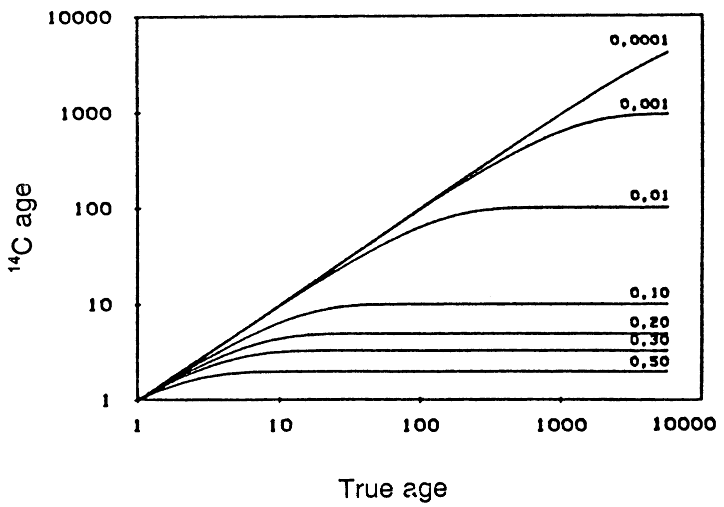


Fig. 1. ^{14}C age as result of a sustained homogeneous annual exchange of organic carbon (according to Becker-Heidmann 1989)

TABLE 3A. Fraction Dates from Hydrolysis Replications (see Scharpenseel 1977)

Treatment	Asel soil (yr BP)	Argiudoll (pMC)	Landshut soil (yr BP)	Argiudoll (pMC)
O_2 combustion		>100	4640 ± 90	56
N_2 coking + O_2 combustion		>100	4570 ± 110	56.6
1st hydrolysis step		>100	5610 ± 80	49
2nd hydrolysis step	2530 ± 80	73	5820 ± 110	48.5
3rd hydrolysis step	2410 ± 70	74	5700 ± 100	49.2
4th hydrolysis step	2340 ± 80	74.7	5540 ± 110	50.1
5th hydrolysis step	2770 ± 80	70.8	6110 ± 90	46.8
6th hydrolysis step	2560 ± 90	72.8	5790 ± 90	46.8
7th hydrolysis step	2960 ± 80	69.2		
8th hydrolysis step	3260 ± 100	67.2		

TABLE 3B. Radiocarbon Dates from Soil Extracts and Fractions

Treatment (extractant)	Udortent Mendig (yr BP)	Koiselhof Terric Medihemist (yr BP)
Petroleum benzene		3290 ± 320
Benzene	4130 ± 100	6630 ± 130
Methanol		6380 ± 90
Fulvic acids	1140 ± 200	6860 ± 250
Fulvic acids (dialyzed)		7060 ± 110
Total humic acids	6970 ± 210	8810 ± 120
H. A. sephadex 1 (percolate)	6110 ± 100	7590 ± 120
H. A. sephadex 2 (retained)	6830 ± 130	7820 ± 120
Humin	10,320 ± 140	7110 ± 110
Humic coal	9940 ± 140	7230 ± 110
Soil hydrolyzate	2510 ± 100	
Hydrolysis residue	11,360 ± 150	9730 ± 170
Whole soil	10,600 ± 120	7200 ± 110

We found no breakthrough to standardize sample preparation for absolute dating. Also, possibilities for correcting the rejuvenated results, including various models were not too rewarding, except by geological analogy, based on samples of known geological age (Scharpenseel & Schiffman 1977a, b). Only after systematic ^{14}C dating of thin-layer sections of soil profiles (Scharpenseel *et al.* 1989) did we find that, in a soil profile, the highest ^{14}C age is always linked to the zone of highest clay content (Becker-Heidmann 1989, 1990). This was a generally valuable confirmation of the hypothesis that clay organic complexes, once formed, do not easily exchange the organic component with infiltrated younger humus components (Fig. 2).

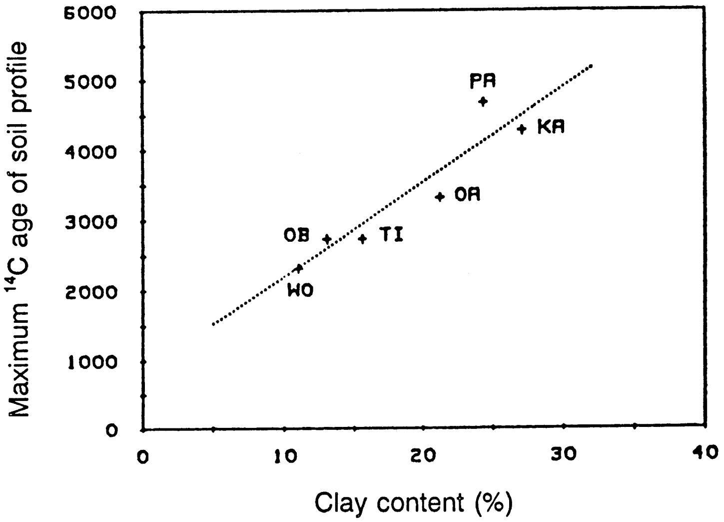


Fig. 2. Relation between maximum ^{14}C age and clay content (according to Becker-Heidmann 1989). WO, OB TI, OR, PA, KA = different Alfisol profiles

Genuine benefits of soil ^{14}C dating with δ^{13}C measurement, which is receiving a growing appreciation, arise from the elucidation of soil dynamic processes. These involve SOM and landscape developments/changes, as well as characterizing functional SOM compartments and modeling SOM dynamics.

By scanning the ^{14}C data of thin-layer Mollisol and Vertisol profiles, *e.g.*, we can interpret age *versus* depth-gradient conclusions on the soil zone, which has undergone bioturbation or peloturbation, or age/argilluviation (Scharpenseel *et al.* 1986a, b; Martel & Paul 1974; Becker-Heidmann, Liu & Scharpenseel 1988; Stephan *et al.* 1983; Blackburn, Sleeman & Scharpenseel 1979; Becker-Heidmann 1989; Becker-Heidmann & Scharpenseel 1986).

^{14}C dating and δ^{13}C measurements in soils are increasingly rewarding in studies of landscape development. Aside from residence times of ^{14}C , stable isotope measurements also reveal landscape-historical changes, *e.g.*, from tropical rainforest/gallery forest with C_3 photosynthesis to savannah with mainly C_4 grass vegetation (Martin *et al.* 1990). Similarly, we observe landscape successions from coconut groves or other ecologies with oxidative biodegradation, δ^{13}C of *ca.* −25‰, to rice land with reducing biodegradation, and a δ^{13}C-enriched carbon remainder due to emission of very light methane carbon with δ^{13}C of *ca.* −45 to −55‰ (Neue, Becker-Heidmann & Scharpenseel 1990; Nakamura, Takai & Wada 1990) (Fig. 3).

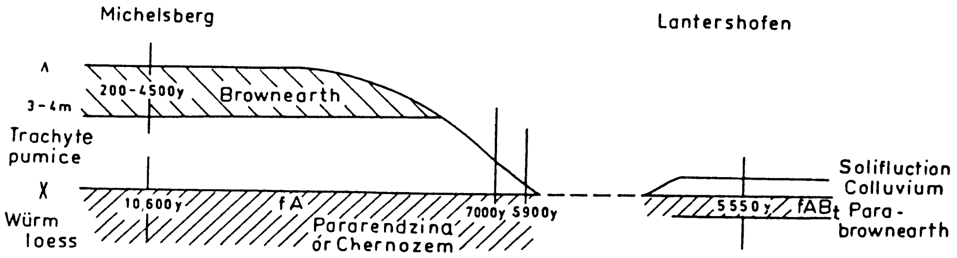
Extensive studies on isotope shifts in Pseudogleys (Aqualfs) (Schleser, Pohling & Kerpen 1981), in Spodosols (Bertram & Schleser 1982) and in calcareous crusts (calcretes/caliches) (Schleser, Bertram & Scharpenseel 1983; Freytag 1985), based mainly on the stable isotopes, ^{13}C and ^{18}O, with but a few ^{14}C dates for orientation of identity of sedimentation and migration, were highly successful in describing mechanisms of pedogenesis and zonal, geographic specificity.

^{14}C dating of soils could prove that the SOM turnover, expressed as a simple exponential function

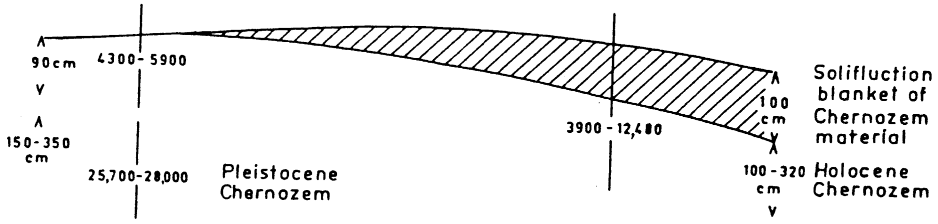
$$(C = C_e + (C_o - C_e)e^{-rt})$$

where C = SOM content; C_e = equilibrium SOM content; C_0 = initial SOM content; r = fraction of carbon decomposed per year; t = time in years, is oversimplified, as Jenkinson (1981) also emphasizes. Obviously, different SOM fractions have different characteristics of decomposition, whereas in the equation, we assume that all organic matter of carbon behaves identically in a decomposition pattern. Thus, ^{14}C dating leads to soil carbon ages of >1 ka instead of 0.1 ka, as one would expect as a result of pure exponential decomposition.

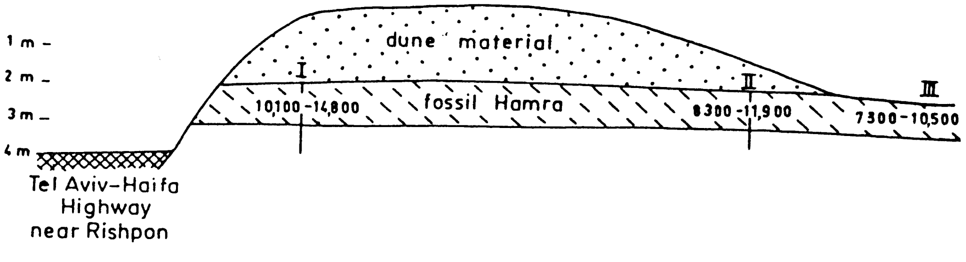
Fig. 3A–E. Examples of ^{14}C dating and ^{13}C measurements of soils used to describe landscape changes



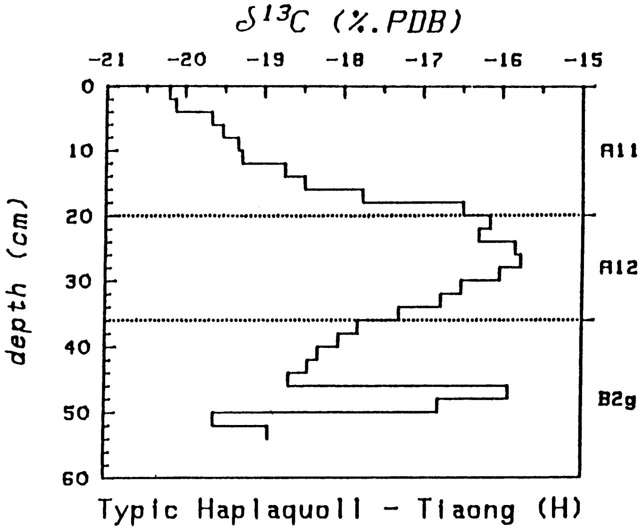
3A. Schematic section of Allerød trachyte pumice covering Würm loess, Michelsberg, Lantershofen, FRG. Soil ^{14}C age in different geomorphological positions (Scharpenseel 1971)



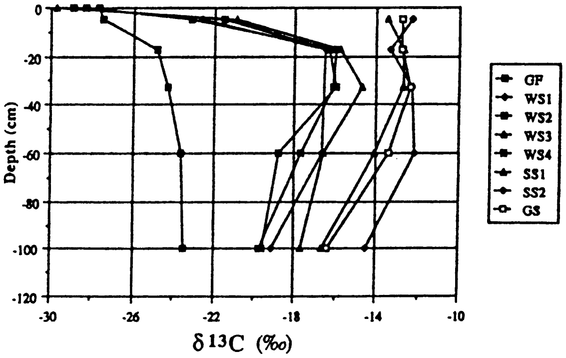
3B. Schematic section of Chernozem soils covered by solifluction material, Sedlec, Czechoslovakia. ^{14}C age of recent and buried paleosols in Würmian loess (Scharpenseel 1971)



3C. Schematic section of Hamra (Rhodoxeralf) soil, partly covered by dune sand, Rishpon, near Tel Aviv, Israel. ^{14}C ages of the same soil formation, exposed as well as buried, 1 m and 2 m deep (Scharpenseel 1971)



3D. ^{13}C enrichment in remaining SOM of rice paddy due to methane release



3E. δ^{13}C profiles of SOM under the four types of vegetation at Lamto (Ivory Coast): GF–gallery forest; WS–savanna protected from fire for 25 yr (4 profiles); SS–shrub savanna (2 profiles); GS–grass savanna (Martin *et al.* 1990)

Models, checked by (long-term) field experiments, require an observation of several SOM fractions of different functions. Both major models in use distinguish five functional SOM compartments:

The Jenkinson model (Jenkinson 1981; Jenkinson & Rayner 1977) leans on a long, continual annual input of 1.2 t C × ha^{-1} in Rothamsted, England. The SOM compartments are:

DPM	readily decomposable plant material	MRT 0.2 yr
RPM	resistant plant material	MRT 3.3 yr
BIO	microbial biomass	MRT 2.4 yr
POM	physically protected organic matter	MRT 71 yr
COM	chemically stabilized organic matter	MRT 2900 yr

The Century model (Parton *et al.* 1987, 1989) originates from the Great Plains (USA) grassland. The compartments are:

Structural carbon	MRT 3 yr
Metabolic carbon	MRT 0.5 yr
Active carbon	MRT 0.25 yr

Slow carbon	MRT 5 yr
Passive carbon	MRT 1000 yr

The residence time of carbon is the major distinctive criterion for the separate functional fractions, where ^{14}C dating, at least for the larger, older fractions, becomes imperative, if the philosophical model approach is to be translated into field evidence and quantifying compartmental rates.

CONCLUSIONS

In soil ^{14}C dating, "soil age" is definable and applicable for absolute dating in a limited way, only in the case of well-protected paleosols, charcoal or wood relics. Soil ^{14}C dating, along with $\delta^{13}C$ and $\delta^{18}O$ measurements, has great potential for exploring soil properties and soil dynamic processes, such as in, *e.g.,* cryo-, bio-, peloturbation in mollic, vertic, spodic and argillic horizons. Such measurements are also of value for learning about organic matter oxidation as fuel for the reduction of iron and sulfur compounds, as in acid sulfate soils or in ferrolysis, and also processes of pedolith, *e.g.,* calcrete, formation. The value of these measurements also extends to the exploration of processes of landscape formation/change, concomitant with C_3, C_4 and CAM plant changes or alterations of soil hydrology, leading to a transition from oxidative (CO_2 has $\delta^{13}C$ of *ca.* −25‰) to reductive biotransformation (CH_4 has $\delta^{13}C$ of *ca.* −45 to −55‰).

Further, the need for ^{14}C dating of SOM fractions is steadily growing with the modeling programs of functional carbon (SOM) compartments. Thin-layer sampling of soil profiles reveals that the samples with the highest clay content best mitigate the rejuvenation of the ^{14}C age. Dating of clay organic complex fractions appears optimal.

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