

THIN LAYER $\delta^{13}\text{C}$ AND D^{14}C MONITORING OF “LESSIVE” SOIL PROFILES

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ABSTRACT. The natural ^{14}C and ^{13}C content of soil organic matter and their dependence on depth for two Alfisols are presented. This soil type which covers a large area of the earth's surface is characterized by clay migration processes (“Lessivé”). The samples were taken as successive horizontal layers of 2cm depth from an area of ca 1m² size as deep as the C content allows ^{14}C analysis. The minima of the D^{14}C distribution decrease with depth, while the maxima increase in the upper, leached horizon (A_1) due to bomb ^{14}C and decrease in the lower, clay illuviated (B_1). $\delta^{13}\text{C}$ indicates proceeding decomposition in A_1 and protection of carbon, probably due to the formation of clay humus complexes in B_1 . $\delta^{13}\text{C}$ values were also used for age correction of the ^{14}C data due to isotopic fractionation. The D^{14}C and $\delta^{13}\text{C}$ depth distributions are characterized by sharp peaks at the boundaries of the horizons, probably caused by the influence of textural changes on the transport of C with percolating water.

INTRODUCTION

Investigations on the global carbon cycle have become important since the predictions of the “greenhouse effect” caused by increasing CO_2 input to the atmosphere. Highly sophisticated global computer models already exist; however, precise data for certain compartments, such as soil humus are fragmentary. Estimates for the C reservoir of soil organic matter range from 1 to 3×10^{15} kg. The highest exchange rates are between the atmosphere and the biosphere and humus; therefore, small changes within the latter may have large effects on the other reservoirs. Several attempts have been made to examine the pathways of organic matter transformations and translocations within the soil. Numerous investigations deal with decomposition of organic matter by labeling the input with ^{14}C . Several attempts have been made to use ^{14}C dating of soil organic matter (*cf* Scharpenseel & Schiffmann, 1977; Stout, Goh & Rafter, 1981; Scharpenseel & Neue, 1984). Data on the distribution of ^{13}C in soil are rarely found in the literature. One of the problems of interpreting carbon isotope data in soils is in distinguishing between decomposition and transport-induced effects. Often only the uppermost soil horizon is used in studying and modeling organic matter decomposition, as in the 5–box model of Jenkinson and Rayner (1977). Goh *et al* (1976) and Goh, Stout and Rafter (1977) distinguished between topsoil and subsoil. Scharpenseel, Schiffmann and Hintze (1984) dated each horizon or even 5cm layers in special cases. In this study, we sampled layers for carbon isotope determination as thin as practically possible in order to get precise depth functions. We try to draw conclusions from the data regarding transformations and translocation of carbon. As the first soil type we chose a Parabraunerde, belonging to the order of Alfisols. These represent the greatest soil carbon reservoir (besides mountain soils) with 17.3% of total soil carbon, *ie*, 254.8×10^{12} kg (Buringh, 1984).

MATERIALS AND METHODS

The two soils are located north of Hamburg in the Wohldorf forest (53° 43' N, 10° 9' E) and south of Hannover in the Ohlendorf forest (52° 17'

N, 9° 42' E). Both are classified as Spodic Aquic Hapludalfs. Vegetation consists of ca 100-year-old copper beech trees without noteworthy undergrowth. The mean annual temperature is 8.5°C, the mean annual rainfall is 741mm and 582mm, respectively. A brief description of the soil properties is given in Table 1. Wohldorf forest soil developed in glacial sand overlying a terminal moraine of the Weichselian Ice age (II) with subsequent decalcification, clay eluviation (lessivage) from the top soil (A₁) with illuviation in subsoil (B₁) and formation of a clay pan (S_d) with impeded drainage (S_w). Recently a slight podzolization is observed (A_c—B_{hs}) due to industrial pollution. The Ohlendorf forest soil has developed in a 1.50m deep Würmian loess deposit with the same processes as the former.

Successive horizontal layers of 2cm depth were completely removed from ca 1m². Roots and stones were removed by hand and by sieving through a 2mm mesh. The soil was homogenized by mechanical stirring in distilled water for 1 hour, then dried at 105°C before analysis. As the samples were free of carbonate, they were combusted at 1000°C in an oxygen stream and the developed CO₂ was determined coulometrically in a Wösthoff apparatus. The nitrogen content was determined by the Kjeldahl method in a Büchi apparatus.

TABLE 1A
Profile description of Wohldorf Forest

Depth (cm)	Horizon	Description	% C	% N	pH
0–3	Ah	Mineral soil, loamy sand	3.5	.23	3.0
3–5	Ae	Bleached horizon	.7	.04	3.4
5–11	Bhs	Humus enriched	1.3	.1	3.7
11–23	Bv	Weathered horizon, sandy loam	.7	.05	4.0
23–40	IISwA1	Clay eluviated, sandy loam, impeded drainage	.5	.25	4.2
40–50	IISdBt1	Sandy loam, clay enriched, impeding drainage	.1	.02	4.0
50–63	IISdBt2	Loam	.1	.02	3.8
63–73	IISdBt3	Silt loam, maximum of clay illuviation	.1	.02	3.7
73–88	IISdBt4	Loam	.1	.01	3.7
88–100	IISdBt5	Same as above	.05	.005	3.6
100–110	IICv	Weathered unconsolidated horizon, loamy sand	.03	—	3.9

TABLE 1B
Profile description of Ohlendorf Forest

Depth (cm)	Horizon	Description	% C	% N	pH
0–2	Ah1	Substrate loess, silt	5.1	.30	3.4
2–4	Ah2	Silt loam	2.2	.14	3.6
4–8	Ae	Slightly bleached	.5	.04	3.5
8–15	Bhs	Humus enriched	1.0	.09	3.7
15–50	IIA1	Clay eluviated, silt loam	.2	.04	3.8
50–70	IISwBt	Clay illuviated, silt loam, impeded drainage dammed water	.1	.02	3.7
70–78	IISdBt	Clay illuviated, silty clay loam, impeding drainage	.05	.02	3.9

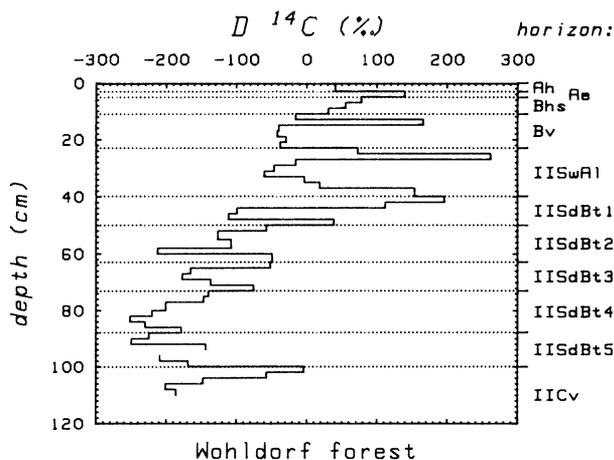


Fig 1. $D^{14}\text{C}$ distribution of the Wohldorf forest soil profile

Benzene for liquid scintillation counting of ^{14}C was prepared following the method described by Scharpenseel and Pietig (1968, 1970). The ^{14}C activity of the samples was measured for 2800 minutes in a Packard Tri Carb Model 3320 and a Berthold Betaszint BF 5000. The background of the measuring channel was 5.4cpm and 4.6cpm, respectively. Background and NBS standard were counted for 5000 minutes. The samples as well as standard and background samples were measured in the same special quartz vial to reduce the background. Counts were accumulated for periods of 20min and transmitted to a HP9845B desktop computer. The data were analyzed for Poisson distribution and trends and for quenching by the channels ratio method. The instruments were also checked by measuring a

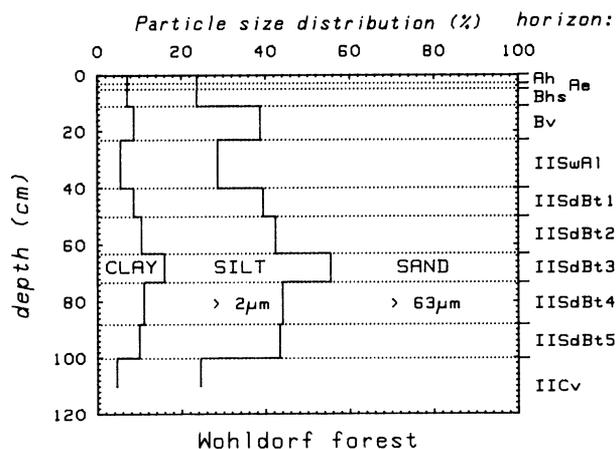


Fig 2. Particle size distribution of the Wohldorf forest soil profile

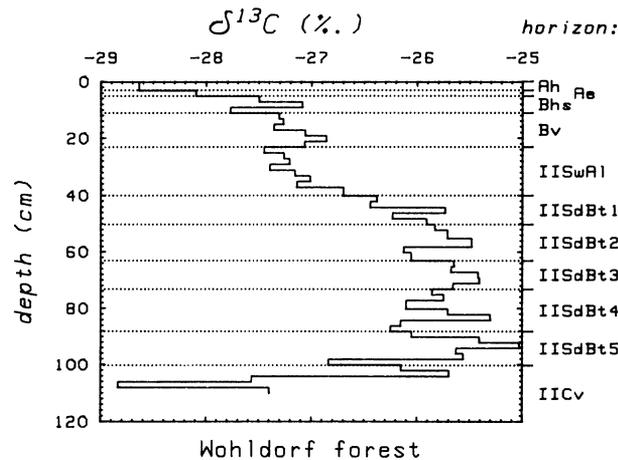


Fig. 3. $\delta^{13}\text{C}$ distribution of the Wohldorf forest soil profile

high-activity standard in a flame-sealed ampule before and after each age determination.

For ^{13}C analysis the samples were ground and then combusted at 1000°C in an oxygen stream. The developed CO_2 was purified from SO_2 and halogenides and transferred to a high vacuum line. The water was retained in a trap at -70°C and the CO_2 condensed in a trap at -150°C . NO_x was reduced to N_2 by repeated cycling of the sample gas through a CuO containing oven at 650°C . The N_2 was removed by the vacuum pump while the purified CO_2 was trapped in a finger kept at liquid nitrogen temperature. The samples were measured in a Finnigan MAT 250 mass spec-

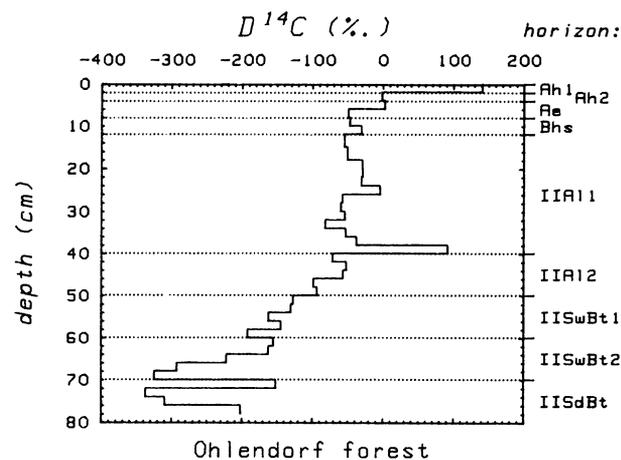


Fig. 4. D^{14}C distribution of the Ohlendorf forest soil profile

trometer. Our laboratory standard is tank CO_2 , which was calibrated against PDB. The complete procedure and equipment are checked regularly with a charcoal standard (Merck No. 2204), which gives a standard deviation for $\delta^{13}\text{C}$ of 0.1‰. The measuring process and calculation of the ^{13}C results from the acquired data for masses 44, 45, 46 was controlled by a HP9815 computer using the correction procedures according to Craig (1957) and Mook and Grootes (1973). Further details were presented elsewhere (Becker-Heidmann, ms).

RESULTS AND DISCUSSION

The results of ^{14}C measurements are reported as $D^{14}\text{C}$ following the recommendations of Stuiver and Polach (1977). Figure 1 shows the distribution of $D^{14}\text{C}$ in relation to depth in the Wohldorf forest profile. Although the variation between successive layers are considerable, there is a general tendency of decreasing ^{14}C concentration with depth as found in previous investigations (Scharpenseel, 1972). A regression line through the minima yields $D^{14}\text{C}_{\text{min}} = 32.85 - 3.19 \times \text{depth}$, where $D^{14}\text{C}$ is expressed in per mil and depth in cm. The maxima increase with depth down to the bottom of A_1 horizon and decline in B_t representing the depth distribution of "bomb ^{14}C " in the soil. Both minima and maxima increase in C_v . It is striking that the maxima of $D^{14}\text{C}$ coincide exactly with the boundaries of the horizons. This is probably due to differences in particle size distribution (see Fig 2) and consequently in pore volume at the horizon boundaries. This results in a locally decreased water permeability and increased moisture status which cause exchange rates between the already present "old" and the "young" carbon. This "young" carbon is mostly supplied by percolating water; in the upper horizons there might also be a contribution by the roots. The exchange is probably impeded in the B_t horizon, because the

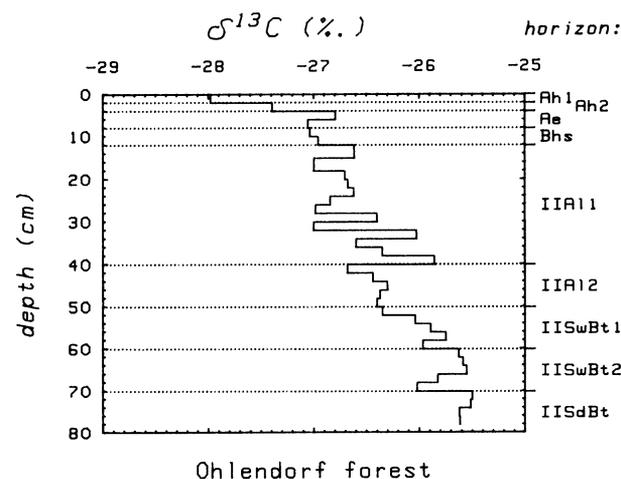


Fig 5. $\delta^{13}\text{C}$ distribution of the Ohlendorf forest soil profile

old C is strongly adsorbed in clay interdomain spaces, so that the young carbon will mostly percolate down to the C_v horizon (Theng & Scharpenseel, 1975). The protection of humus by clay-humus-complexation has been postulated already by Gerasimov and Chichagova (1971) and Paul and Van Veen (1978). Anderson and Paul (1984) recently found that the coarse clay-associated humus was the oldest fraction of a clayey Haploboroll. We obtained similar results in two German Mollisols with middle clay fraction (0.2 to $0.6\mu\text{m}$) (Scharpenseel *et al.*, ms). The developed hypothesis is supported by the depth distribution of $\delta^{13}\text{C}$ (Fig 3). The $\delta^{13}\text{C}$ in the A_h is close to the initial value of the organic matter input $\delta^{13}\text{C} = -28.6\text{‰}$, which agrees with Craig (1953), who found $\delta^{13}\text{C} = -27\text{‰}$ for leaves of various species of trees. Schleser and Bertram (1981) reported $\delta^{13}\text{C} = -28\text{‰}$ for the uppermost layer of a German forest soil and $\delta^{13}\text{C} = -28$ to -30‰ in the A horizon of a Podzol (Bertram & Schleser, 1982), and Balabane (1983) found $\delta^{13}\text{C} = -28.3$ to -25.1‰ in humus layers of different Podzols. $\delta^{13}\text{C}$ increases with depth down to B_t in the soils we analyzed. The isotope effect in chemical reactions as well as in bacterial decomposition processes results in a higher $\delta^{13}\text{C}$ of the residues (Rosenfeld & Silverman, 1959; Kaplan & Rittenberg, 1964). Based on this observation, O'Brien and Stout (1978) computed a linear increase of ^{13}C with depth. We found the decomposed, ^{13}C enriched, material mainly in the B_t , fixed to clay either by adsorption or complexation. This material is concentrated in the central layers of the horizons.

The Ohlendorf forest profile shows the same tendencies in $D^{14}\text{C}$ and $\delta^{13}\text{C}$ as Wohldorf (see Figs 4 & 5); however, they are less pronounced. This fact is probably due to the smaller differences in texture between the horizons (see Fig 6). There is no linear relationship between $D^{14}\text{C}$ and depth as in the Wohldorf profile, which can be attributed to transport of old carbon

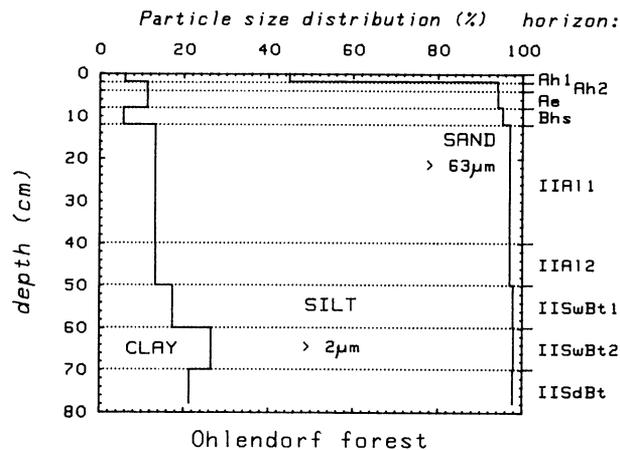


Fig 6. Particle size distribution of the Ohlendorf forest soil profile

from A_1 to B_t . According to von Buch (1981) lessivage of clay is still proceeding in this profile.

CONCLUSIONS

D^{14}C as well as $\delta^{13}\text{C}$ results support the general tendency of decreasing D^{14}C with depth and the protection of old carbon by complexation with clay, as reported by several investigators.

The advantage of the thin layer method is the high resolution of the depth functions which enables the distinction between old and modern carbon within the individual horizons. The young and undecomposed material is mostly concentrated at horizon boundaries, as indicated by both D^{14}C and $\delta^{13}\text{C}$.

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