

## ANNUAL VARIATIONS OF THE $^{14}\text{C}$ CONTENT OF SOIL $\text{CO}_2$

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**ABSTRACT.** A 6-year and a 2-year record of  $^{14}\text{C}$  measurements of soil  $\text{CO}_2$  in two soils are presented and discussed. The annual  $^{14}\text{C}$  variation of soil  $\text{CO}_2$  is controlled by the seasonally varying contribution of root respiration and of microbial decomposition of organic matter producing soil  $\text{CO}_2$ . The  $\Delta^{14}\text{C}$  soil  $\text{CO}_2$  difference between summer and winter is ca 50‰ in a soil where turnover of organic matter is fast ( $\tau = 2.5\text{a}$ ) and ca 100‰ in a soil of slow turnover ( $\tau = 60\text{a}$ ). A simple model describing the movement and turnover of organic matter is derived, giving the depth distributions of organic carbon and of  $^{14}\text{C}$ . The model needs a subdivision of the carbon reservoir into at least two reservoirs with residence times of  $\tau_1 = 1\text{a}$  and  $\tau_2 = 100\text{a}$ , respectively, and with a vertical transfer velocity in the order of 0.6mm/a.

### INTRODUCTION

Soil  $\text{CO}_2$  is produced by decomposition of organic matter and by root respiration. Along a concentration gradient soil  $\text{CO}_2$  diffuses into the atmosphere. The  $\text{CO}_2$  flux at the soil surface is called soil respiration. Depending on the residence time of organic material in the soil and on the relative contribution of root respiration to the total  $\text{CO}_2$  production, the  $^{14}\text{C}$  content of soil  $\text{CO}_2$  will be more or less different from the atmospheric  $^{14}\text{C}$  concentration. While root respiration  $\text{CO}_2$  can be assumed to be nearly identical with the atmospheric  $^{14}\text{C}$  level, the  $^{14}\text{C}$  content of decompositional  $\text{CO}_2$  may, depending on the carbon residence time in the soil, be depleted by radioactive decay or even enriched by the contribution of "bomb  $^{14}\text{C}$ ". Moreover, the  $^{14}\text{C}$  content of soil  $\text{CO}_2$  is an important parameter in modeling variations of atmospheric  $^{14}\text{C}$  content as well as for determining the initial value for  $^{14}\text{C}$  groundwater dating.

### EXPERIMENTAL METHODS

#### *Sampling*

Soil respiration  $\text{CO}_2$  samples are collected by Lundegardh's inverted cup method using 300ml 4N sodium hydroxide solution (Dörr & Münnich, 1980). Quantitative absorption is controlled by measuring the  $\text{CO}_2$  concentration under the inverted cup at the end of each sampling period. Even at times of high respiration rates, the  $\text{CO}_2$  concentration under the inverted cup did not exceed 250ppm to 350ppm. This "near atmospheric" concentration level ensures that the absorption of  $\text{CO}_2$  in the sodium hydroxide solution is sufficiently rapid, and that  $\text{CO}_2$  loss around the rim of the cup does not occur. A substantial gain of atmospheric  $\text{CO}_2$  is prevented by pressing the rim ca 5 to 10cm deep into the soil.

Soil cores are taken in metal cylinders 20cm long. The samples are subdivided and "cleaned" from living roots in the laboratory.

All  $^{14}\text{C}$  samples were processed and measured in this institute's  $^{14}\text{C}$  laboratory.

## Sites

The samples were taken in the Rhine Valley, ca 15km south of Heidelberg. The two sampling sites are in an uncultivated area with grass cover on a loamy soil (NU) and in a beech/spruce forest with a sandy soil (SA).

## RESULTS AND DISCUSSION

*Organic Matter Decomposition*

Figure 1 shows the annual variation of the  $^{14}\text{C}$  content of respiration  $\text{CO}_2$  from a grass-covered and forested area. The straight lines indicate the

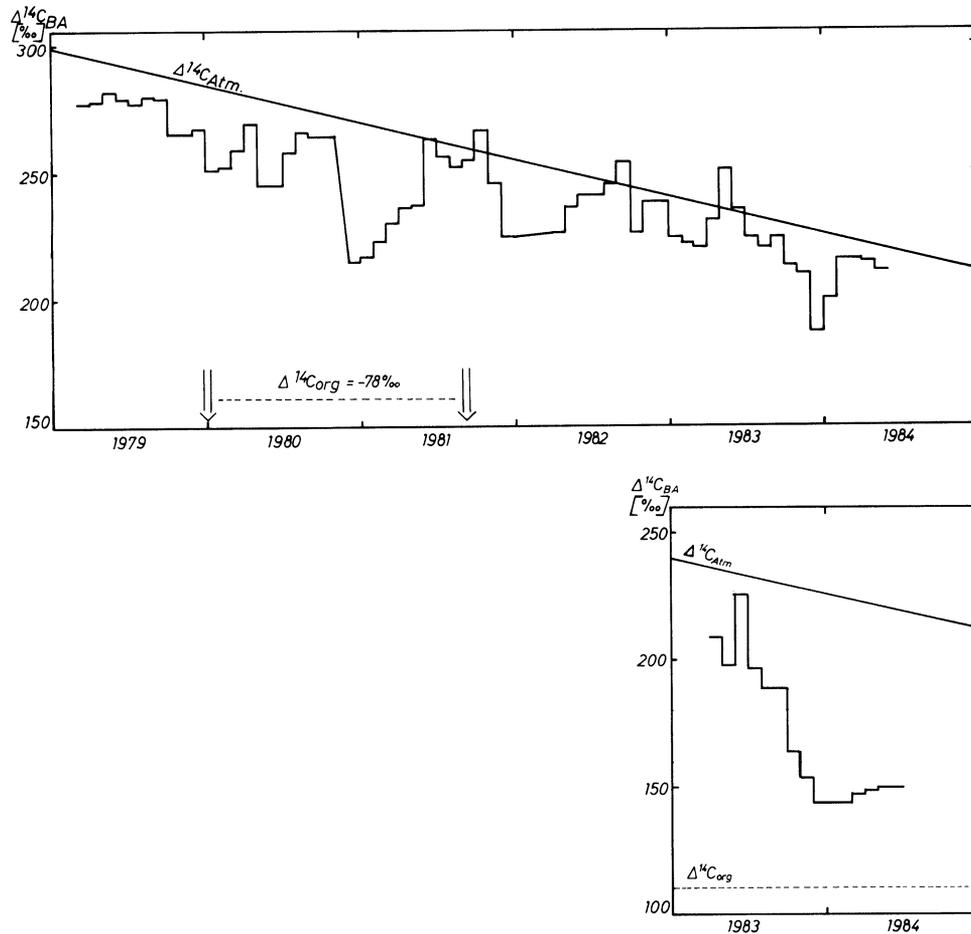


Fig 1. Annual variation of the  $^{14}\text{C}$  content of soil respiration  $\text{CO}_2$  on an uncultivated grass-covered area (upper curve, NU) and in a beech/spruce forest (righthand curve, SA). The straight lines indicate the atmospheric  $^{14}\text{C}$  level, the dotted line represents the mean  $^{14}\text{C}$  content of soil organic matter.

summer mean value of atmospheric  $^{14}\text{C}$  concentration (Levin *et al.*, 1985). The notion of depletion of atmospheric  $\text{CO}_2$  in winter by fossil fuel burning can be dismissed, since plant assimilation occurs in spring and summer only. The data show that in summer at high respiration rates,  $^{14}\text{C}$  soil  $\text{CO}_2$  nearly reaches the atmospheric level while in winter soil  $\text{CO}_2$  is depleted in  $\Delta^{14}\text{C}$ . This depletion results from a decreasing influence of root respiration in winter and a relatively increasing contribution of microbial decomposition of soil organic matter. The difference in  $\Delta^{14}\text{C}$  between summer and winter is ca 50‰ at NU and ca 100‰ at SA. Further, we find a higher respiration rate ( $j = 6.6\text{mmol}/(\text{m}^2\text{h})$ ) and a lower standing crop of soil organic matter ( $I = 2.2\text{kg}/\text{m}^2$ ) at the grass-covered area at NU if compared to the forested area SA ( $j = 4.2\text{mmol}/(\text{m}^2\text{h})$ ;  $I = 16\text{kg}/\text{m}^2$ ). A small difference in  $\Delta^{14}\text{C}$  between summer and winter means a larger fraction of root respiration and fast decomposition, and thus, a lower accumulation rate of soil organic matter. As the  $^{14}\text{C}$  content of soil  $\text{CO}_2$  comes closer to the atmospheric level, the remaining organic material is more depleted in  $^{14}\text{C}$  ( $\Delta^{14}\text{C}_{\text{NU,org}} = -78\text{‰}$ ;  $\Delta^{14}\text{C}_{\text{SA,org}} = 110\text{‰}$ ).

With the simplified assumption that soil  $\text{CO}_2$  is primarily produced by fast decomposition of organic material and by root respiration both with practically no difference in  $^{14}\text{C}$  from atmospheric  $\text{CO}_2$ , and by decomposition of a long-living soil organic matter component. The relative contribution of these two reservoirs to the total soil respiration flux can be calculated with a two-component mixing model following the equation

$$^{14}\text{C}_{\text{sr}} = ^{14}\text{C}_{\text{atm}}C_1 + ^{14}\text{C}_{\text{org}}C_2$$

with

- $^{14}\text{C}_{\text{sr}}$ :  $^{14}\text{C}$  content of soil respiration  $\text{CO}_2$
- $^{14}\text{C}_{\text{atm}}$ :  $^{14}\text{C}$  content of atmospheric  $\text{CO}_2$
- $^{14}\text{C}_{\text{org}}$ :  $^{14}\text{C}$  content of soil organic matter
- $C_1, C_2$ : relative contribution of fast and slow components,  $C_1 + C_2 = 1$ .

At the sampling station NU the contribution of the slow carbon reservoir ranges between 0 and 2% in summer and between 15 and 20% in winter, while at location SA the contribution of the slow reservoir is ca 25% in summer and 75% in winter. Figure 2 shows the annual cycle of the contribution of the slow and fast reservoir to the total soil respiration at site SA, calculated with  $\Delta^{14}\text{C}_{\text{org}} = 110\text{‰}$ , which is the weighted mean  $^{14}\text{C}$  content of soil organic matter. The relative fractions,  $C_1$  and  $C_2$  are multiplied with the measured monthly average  $\text{CO}_2$  flux at the soil surface (Dörr, 1984) to obtain the *fluxes* of the fast and the slow carbon reservoir.

In June, July, and August 1983 soil respiration is reduced as a consequence of an extremely low soil moisture content (Dörr, 1985). Figure 2 shows that this moisture effect on soil respiration mainly influences the "slow reservoir". The yearly average soil respiration rate at this site is  $4.2\text{mmol}/(\text{m}^2\text{h})$ . On the yearly average the slow reservoir contributes 60% and the fast reservoir contributes 40% to the total  $\text{CO}_2$  production. The

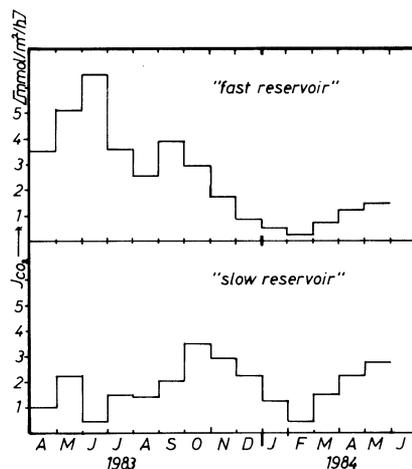


Fig 2. Annual cycle of the contribution of the "slow" and "fast" carbon reservoir to the total soil respiration at site SA. The curves are calculated with  $\Delta^{14}\text{C}_{\text{org}} = 110\text{‰}$  and the contemporary atmospheric  $^{14}\text{C}$  level.

amplitude of the annual cycle of  $^{14}\text{C}$  content of total soil respiration  $\text{CO}_2$  thus depends on the fraction and the  $^{14}\text{C}$  content of the slowly decomposing soil organic carbon reservoir.

#### *Transport of Soil Organic Matter*

To investigate the movement and turnover of soil organic matter a depth profile of the  $^{14}\text{C}$  content of soil organic matter was measured. Figure 3 shows the depth distribution of  $\text{C}_{\text{org}}$  and of  $\Delta^{14}\text{C}_{\text{org}}$  in a forest soil at location SA. The decrease in  $\Delta^{14}\text{C}$  from ca  $300\text{‰}$  in the first 2cm of the soil to ca  $-60\text{‰}$  in 8cm depth indicates a young component (influenced by "bomb  $^{14}\text{C}$ ") in the top layer and predominance of an older component (decreased by radioactive decay) in the lower part of the profile. The soil organic matter has a constant  $\delta^{13}\text{C}$  value over the whole profile of  $\delta^{13}\text{C}_{\text{org}} = -28.2 \pm 0.3\text{‰}$ . This indicates a rather uniform decomposition process. Different animal and plant metabolism should lead to different isotopic fractionations in the remaining organic material (Schleser, 1981).

It is evident from Figure 3 that soil organic matter is not a well-mixed reservoir (no significant bioturbation by earthworms or soil fauna). Thus, the system is not fully characterized by just the total turnover time  $\tau = I/j$  (Bolin & Rodhe, 1972) which is calculated from the total standing crop  $I = 16\text{kg/m}^2$  and the annual carbon input  $j = 250\text{g}/(\text{m}^2 \text{ a})$ . Rather, the carbon reservoir in the soil should be subdivided into two reservoirs at least, a fast and a slow one. If we simply assume, that the yearly litter fall itself consists of a more and of a less resistant component, this subdivision will be found in the soil organic material as well. From direct analysis of the yearly litter fall it is found that ca 60% may be attributed to the slow reservoir (leaf

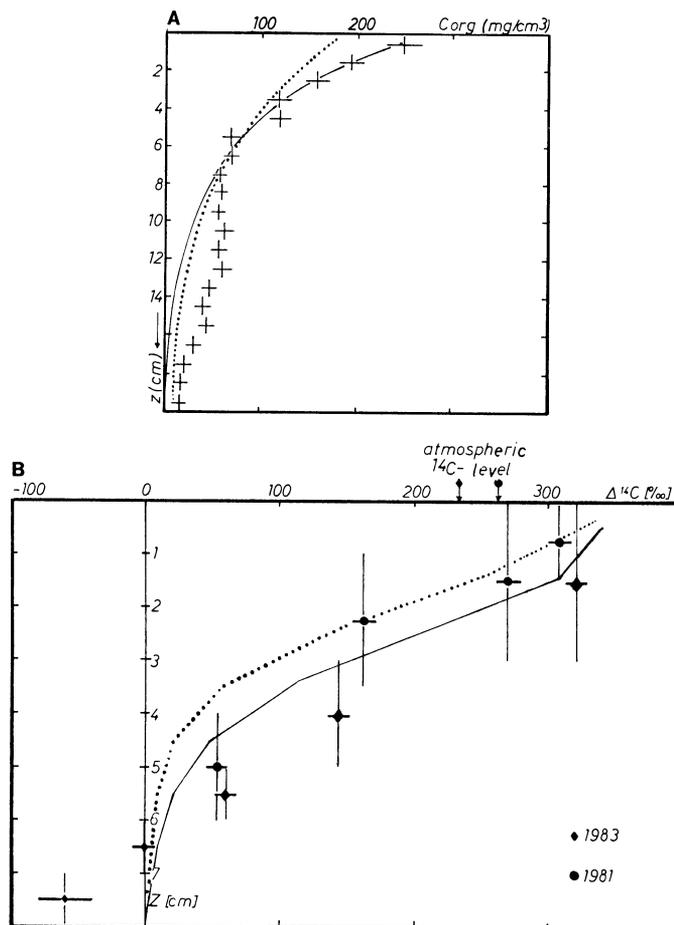


Fig 3A. Depth distribution of soil organic carbon at site SA. The plotted curves are calculated with  $H = 1\text{cm}$ ,  $\tau = 100\text{a}$ ,  $j_0 = 150\text{g}/(\text{m}^2 \text{a})$ , and  $w = 0.4\text{mm}/\text{a}$ ,  $w = 0.6\text{mm}/\text{a}$  (dotted), respectively.

Fig 3B. Depth distribution of  $\Delta^{14}\text{C}$  in soil organic carbon at site SA from two soil cores sampled 1981 (circles) and 1983 (rhombic). The plotted curves are calculated with  $H = 1\text{cm}$ ,  $\tau = 100\text{a}$ ,  $j_0 = 150\text{g}/(\text{m}^2 \text{a})$ , the contemporary atmospheric  $^{14}\text{C}$  content (since 1958) and  $w = 0.8\text{mm}/\text{a}$ , respectively,  $w = 0.6\text{mm}/\text{a}$  (dotted).

veins, branches) and ca 40% to the fast reservoir. Together with the results from the  $^{14}\text{C}$  measurements of respiration  $\text{CO}_2$  it can be concluded that root respiration is only a small fraction of the total  $\text{CO}_2$  production at this sampling site.

The contribution of root respiration to the fast carbon reservoir can be obtained from  $\text{CO}_2$  concentration measurements in the soil air (Dörr, 1984). A steep gradient between 0 and 20cm depth indicates that the  $\text{CO}_2$  production zone is localized primarily in the uppermost 20cm of the soil. Root respiration (tree roots reach a depth of 1 to 3m) obviously causes only

a slight increase of the  $\text{CO}_2$  concentration between 50cm and 350cm depth (see Fig 4). Calculation of the  $\text{CO}_2$  source strength from concentration profiles gives only ca 1% contribution to the total  $\text{CO}_2$  production from the deeper soil layers.

Thus, we subdivide the total annual carbon input to the soil into a  $100\text{g}/(\text{m}^2 \text{ a})$  fast component and  $150\text{g}/(\text{m}^2 \text{ a})$  slowly decomposable organic material.

With an assumed residence time of  $\tau_1 = 1\text{ a}$ , the fast reservoir gives no contribution to the total standing crop ( $I_1 = \tau_1 j_1 = 100\text{g}/\text{m}^2$ ). The residence time  $\tau_2$  of the slow carbon reservoir can then be calculated from  $\tau_2 = I_2/j_2$  with  $I_2 = I = 16\text{kg}/\text{m}^2$  and  $j_2 = 150\text{g}/(\text{m}^2 \text{ a})$  to be  $\tau_2 = 100\text{ a}$ . Further information can be drawn from the penetration of "bomb  $^{14}\text{C}$ " in the soil and from the  $^{14}\text{C}$  depletion by radioactive decay of "natural"  $^{14}\text{C}$ . The movement of soil organic matter can be described by a chromatographic HETP model (Keulemans, 1959; Thoma *et al.*, 1979) with the two parameters  $H$  (box height, describing statistical fluctuations in the downward movement) and  $w$  (transfer velocity), following the continuity equation

$$\text{div } j + Q - \lambda c = dc/dt$$

where  $j = wc$  is the flux density,  $Q$  the annual input at  $z = 0$  and  $c$  the tracer concentration (either organic carbon or  $^{14}\text{C}$  concentration at each depth). With a transfer velocity between  $w = 0.4\text{mm}/\text{a}$  and  $w = 0.8\text{mm}/\text{a}$ ,  $H = 1\text{ cm}$  and  $\tau = 1/\lambda = 100\text{ a}$  the depth distribution of  $C_{\text{org}}$  and  $^{14}\text{C}$  can satisfyingly be reproduced using the known annual carbon input and the contemporary  $^{14}\text{C}$  content of the atmosphere. The calculated profiles of  $C_{\text{org}}$  and  $\Delta^{14}\text{C}$  are plotted in Figure 3. Comparison of model calculations and measured  $C_{\text{org}}$

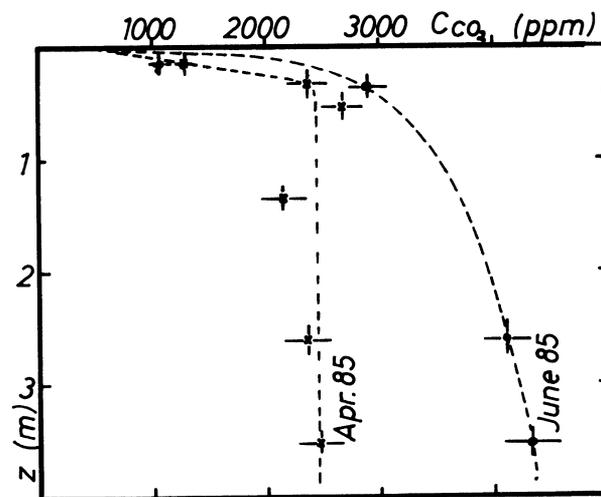


Fig 4.  $\text{CO}_2$  concentration profiles in soil air at site SA. The profile from April 1985 shows a steep gradient between 0 and 20cm and constant concentrations at greater depth, while in June 1985, the steep gradient in the top layer is followed by a slight increase of  $\text{CO}_2$  concentration up to 3.5m deep.

and  $^{14}\text{C}$  concentrations in greater depth indicates that a further, very slowly decomposing organic reservoir should be considered. At 7 to 8cm depth the  $^{14}\text{C}$  concentration is  $\Delta^{14}\text{C} = -60 \pm 20\%$ . Based on radioactive decay the turnover time of the very slow reservoir can be estimated from this value to be  $\text{ca } \tau_3 = 500\text{a}$ .

On this simplified basis the following model concept for the transport of organic matter in a sandy soil matrix without bioturbation can be constructed:

After deposition at the soil surface, the annual litter fall is reduced to small pieces by the action of micro-organisms and by weathering. At a given size the organic particles percolate with infiltration water into the soil. The downward movement, therefore, is combined with an aging of soil organic matter, because only sufficiently small and, thus, old particles can penetrate into deeper layers.

Note that we have approximated here the real soil organic reservoir by a set of only two reservoirs each "well mixed" (exponential), *ie*, described by a single time constant, and thus, the mean age of material stored in the reservoir is identical with the mean age ( $^{14}\text{C}$  content) of the respiration  $\text{CO}_2$  leaving it.

#### CONCLUSIONS

The data presented show that the annual variations of the  $^{14}\text{C}$  content of soil  $\text{CO}_2$  depend on the fraction of root respiration and the turnover of soil organic matter. A high contribution of root respiration and fast turnover of organic material results in a "near atmospheric"  $^{14}\text{C}$  level of soil  $\text{CO}_2$ . The  $^{14}\text{C}$  depletion of respiration  $\text{CO}_2$  in winter depends on the amount and turnover of the slow decomposable carbon reservoir in the soil.

The atmospheric  $^{14}\text{C}$  level is not influenced by soil respiration in summer, while in winter a depletion of atmospheric  $^{14}\text{C}$  by burning of fossil fuel can partly be due to low soil respiration  $^{14}\text{C}$ . In the industrial area around Heidelberg, for example, minimum soil respiration in winter is  $\text{ca } 5\% - 10\%$  of the  $\text{CO}_2$  production from burning of fossil fuel. The total  $\text{CO}_2$  input to the atmosphere (anthropogenic + soil respiration) will, thus, have a  $^{14}\text{C}$  content of  $\text{ca } 10\text{pmC}$  resulting from a mixture of  $10\% \text{CO}_2$  with  $110 - 120\text{pmC}$  and  $90\%$  with zero  $^{14}\text{C}$  content.

The initial  $^{14}\text{C}$  content used in groundwater dating also depends on the turnover of the slow carbon reservoir in the soil, because groundwater recharge occurs mainly in winter, when root respiration and fast decomposition of organic material is reduced.

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