[14]C MEASUREMENTS OF SOIL ORGANIC MATTER, SOIL CO_2 AND DISSOLVED ORGANIC CARBON (1987–1992)

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ABSTRACT. For several undisturbed sites in Germany, ^{14}C data are reported for soil organic matter (SOM) (4 sites), soil CO_2 (10 sites) and dissolved organic carbon (DOC) (1 site). With the assumption of a fast degradable component (lifetime *ca.* 1 yr) and a slow degradable component (lifetime *ca.* 100 yr), a range between 0.6 and 1.6 mm yr^{-1} has been determined for the downward migration rates of soil organic carbon at the sampling sites from the soil ^{14}C data. The soil CO_2 measurements show that in deciduous forests the fast degradable component is *ca.* 60% and the slow degradable component is *ca.* 40% of the SOM. In coniferous forests this ratio is reversed. The ^{14}C results for DOC could not be explained with the assumption of a first-order decay process. The removal of soil organic carbon by DOC is of minor importance for the estimation of carbon budgets for the investigated site.

INTRODUCTION

We report ^{14}C data for soil organic matter (SOM), soil CO_2 and dissolved organic carbon (DOC) in seepage water, all derived from undisturbed forest soil. The samples were collected to study the turnover mechanism of soil organic carbon, which was considered have two dynamic components: a slow degradable component with a lifetime (τ) of *ca.* 100 yr, and a fast degradable component with τ = 1 yr (Dörr and Münnich 1986). The ^{14}C content of soil CO_2 and of DOC from the seepage water should reflect the microbial degradation of the solid organic material in the soil profile and therefore give more detailed information about these degradation processes.

The sampled ^{14}C content of solid SOM was determined as a function of depth. The profile data reported here (M1, M4, W14C) were measured in 1987. Earlier soil profile data are reported in Dörr and Münnich (1986, 1989). The ^{14}C of soil CO_2 was measured at several sites (M1..4, SK1, RO1..3, RU, WQ) at different times of the year in 1990 and 1991. The DOC samples were collected at one site (M3) during 1989–1991 and processed in 1991–1992.

SAMPLING SITES

All sites are located in Germany: W14C is near Muenster (Westphalia) (51.6°N, 7.4°E). Sites M1, M2, and M3 are *ca.* 15 km south of Heidelberg in the upper Rhine River valley (49.2°N, 8.4°E). M1 is a mixed forest stand (75% beech, 25% spruce), with sandy soil (calcaric Regosol). Carbonate content in the topsoil is *ca.* 5%, and the soil pH is 7.7. It was previously a shifting sand dune and has been forested for 100 yr. M2 is a deciduous forest stand (beech, oak, maple) with a loamy soil layer (*ca.* 80 cm) over sandy sediments. The carbonate content in the topsoil is *ca.* 4%, and the soil pH is 8. Sited close to a former drainage ditch, this soil had been frequently flooded until the beginning of this century. M3 is a mixed forest stand (75% beech, 25% spruce) with no lower vegetation. The soil is sandy (podzolic brown earth); it contains no carbonates, and soil pH is 3.5. The site has been for-

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ested for *ca.* 300 yr; the humus layer is *ca.* 15 cm deep. M4 is *ca.* 25 km southeast of Heidelberg in the Odenwald hillside (49.2°N, 8.5°E). It is a coniferous forest stand (fir/Douglas fir) with loamy soil (calcaric Regosol). Carbonate content in the topsoil is <5% and soil pH is 5. The site has been forested for *ca.* 300 yr. SK1 is *ca.* 15 km northeast of Heidelberg in the Odenwald hillside (49.3°N, 8.6°E), in a coniferous forest stand (fir) with loamy soil. RO1, RO2 and RO3 are located 30 km southeast of Frankfurt and 90 km northeast of Heidelberg on a Main River terrace (49.6°N, 9.1°E). RO1 is a coniferous forest stand (60% spruce, 40% fir) with clay soil. RO2 is a coniferous forest stand (100% spruce) with sandy soil. RO3 is a mixed forest stand (70% deciduous (oak, birch, acacia), 30% spruce) with sandy soil. These sites have been uncultivated for at least the last 100 yr, with exception of RO3, which was cultivated until 40 yr ago.

RU is *ca.* 1 km north of Heidelberg (49.3°N, 8.4°E). It is cultivated, planted with a variety of vegetables. The soil is loamy. WQ is located in Sachsen, 40 km east of Hof and 50 km south of Plauen (50.1°N, 12.2°E). It is a lawn site over a gravelly soil.

METHODS

The ^{14}C content in each profile was determined from soil cores taken (including the litter layer) with metal cylinders 10 cm in diameter and 12 cm long. The samples were cleaned of living roots in the laboratory. Carbonates and the soluble organic fraction were then removed by washing in 0.1 N HCl and 0.1 N NaOH. Soil organic carbon contents were determined from the volume of CO_2 produced by combustion, or by the loss of weight after heating the sample to 800°C. Some of the samples were oxidized to CO_2 by combustion of the organic material in a closed system under an oxygen pressure of *ca.* 10 bar. This method is described in Dörr, Kromer and Münnich (1989).

For soil CO_2 measurements, soil gases were pumped through 300–400 ml 4 N NaOH solution for several hours to absorb the CO_2. *Ca.* 100–200 mMol CO_2 were recovered in each case, by sampling at 70 and 120 cm depth. Weber (1991) gives a detailed description of this sampling method.

We collected seepage water for DOC analysis using stainless-steel lysimeter plates that drained into plastic bottles. These were emptied weekly. Because of the low organic carbon concentrations, a minimum of 6 to 9 liters of water had to be collected over a sampling time of at least one year. We measured a "summer" (TDOC1) and a "winter" sample (TDOC4) from 5-cm depth, as well as samples from depths of 10 (TDOC2) and 50 cm (TDOC3). The samples were processed in two different ways: samples TDOC1 and TDOC4 were oxidized by UV radiation and the CO_2 produced was absorbed in 100 ml 4 N NaOH solution; samples TDOC2 and TDOC3 were dried and the residue was burned in O_2. A more detailed description of these procedures is given in Tegen (1992). All ^{14}C measurements were carried out in the ^{14}C Laboratory at the Institute for Environmental Physics, University of Heidelberg.

RESULTS AND DISCUSSION

The results for the measurements of soil profiles, soil CO_2, and DOC are listed in Tables 1 through 3, respectively. Carbon isotope enrichments are calculated and reported in accordance with the definitions of Stuiver and Polach (1977), *viz.*,

$$\Delta^{14}C = \delta^{14}C - (2\delta^{13}C + 50) \cdot \left(1 + \frac{\delta^{14}C}{1000}\right) \; (\text{‰}) \qquad (1)$$

where

$$\delta^{14}C = \left(\frac{\left(\frac{^{14}C}{^{12}C} \right)_{sample}}{0.95 \cdot \left(\frac{^{14}C}{^{12}C} \right)_{standard}} - 1 \right) \cdot 1000 \ (‰) \tag{2}$$

and

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C} \right)_{sample}}{\left(\frac{^{13}C}{^{12}C} \right)_{standard}} - 1 \right) \cdot 1000 \ (‰) \ . \tag{3}$$

$\delta^{14}C$ is the deviation in per mil from the NIST HOxII, $\delta^{14}C$ data are corrected in respect to a $\delta^{13}C$ standard value of $-25‰$ due to kinetic separation effects.

TABLE 1. Results of Soil Profile Measurements

Sampling site	Depth (cm)	Organic C (mMol cm^{-3})	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Date	Soil bulk density (g cm^{-3})
W14C	0–1	2.2	−30.5	236 ± 5	6/87	0.09
W14C	1–2	1.9	−28.4	262 ± 5	6/87	0.08
W14C	2–3	2.7	−28.5	275 ± 5	6/87	0.10
W14C	8–9	3.0	−27.5	59 ± 5	6/87	0.55
M1	0–1	1.9	−27.5	227 ± 6	7/87	0.2
M1	2–3	2.3	−27.4	218 ± 8	7/87	0.54
M1	3–4	2.1	−27.1	247 ± 6	7/87	0.57
M1	4–6	1.1	−26.8	174 ± 6	7/87	0.74
M1	6–8	0.65	−26.6	80 ± 6	7/87	0.9
M1	9–13	0.27	−26.8	40 ± 7	7/87	1.1
M4	0–0.5	2.4	−27.2	239 ± 7	7/87	0.20
M4	0.5–1	1.1	−27.8	215 ± 7	7/87	0.35
M4	1.5–3	1.2	−27.3	215 ± 7	7/87	0.82
M4	3–5	0.34	−26.6	206 ± 11	7/87	0.91
M4	5–7	1.0	−26.1	101 ± 5	7/87	0.95
M2	0–1	1.2	−27.0	143 ± 9	8/87	0.85
M2	1–2	1.2	−26.7	128 ± 9	8/87	0.87
M2	2–3	0.5	−27.1	159 ± 15	8/87	0.86
M2	3–4	1.7	−24.6	68 ± 6	8/87	0.86
M2	4–5	1.5	−24.2	55 ± 8	8/87	0.87

Against the background of possible global warming caused by rising atmospheric CO_2, it is important to estimate the carbon fluxes between the atmosphere and the soil. Organic carbon is added to the soil by litter and removed by microbial decomposition of the SOM into both CO_2 and DOC. The global soil organic carbon reservoir is estimated at 1400 Gt. *Ca.* 60 Gt yr^{-1} are added to the soil by litter and 60 Gt yr^{-1} are removed as CO_2 (Macdonald and Sertorio 1989). Our investigations showed that the removal of organic carbon as DOC is only *ca.* 1% of that removed as CO_2 at our sampling site (Tegen 1992). Thus, we conclude that, for the soils investigated, the DOC flux is of minor importance for the

estimation of carbon budgets. However, the ^{14}C data of DOC can help to describe the microbial processes in the soil that lead to the production of DOC. It cannot be determined whether removal of soil organic carbon by DOC production would be significant at other locations or on a global scale.

Given a scenario of global warming, the carbon fluxes between atmosphere and biosphere are no longer in steady state. Not only is vegetation likely to respond with enhanced litter production and therefore more production of SOM, the rate of degradation of soil organic material could be accelerated by enhanced microbial activity. In this context, it is important to investigate the time constants (τ) of this microbial degradation, which can be determined by comparing ^{14}C measurements of soil organic carbon and soil CO_2.

Table 1 lists the results from the soil profile measurements. SOM is not homogenous but consists of at least two components (Dörr and Münnich 1986): a fast degradable component with a lifetime (τ) of ~1 yr and a slow degradable component with τ ~100 yr. The ^{14}C depth profiles show that organic material is younger at the top of the soil than at the bottom. From these ^{14}C data, Dörr and Münnich (1989) determined for the downward migration rates of organic material a range between 0.6 and 1.6 mm yr^{-1} at the sampling sites M1–M4.

Table 2 lists the ^{14}C data of soil CO_2. Included here are CO_2 concentrations, $\delta^{13}C$, and $\Delta^{14}C$ or soil CO_2 and for atmospheric CO_2. With these $\Delta^{14}C$ data, the $\Delta^{14}C$ of soil respiration ($\Delta^{14}C_{\text{soil respiration}}$) are calculated to reflect the actual CO_2 emissions out of the soil, using

$$\Delta^{14}C_{\text{soil respiration}} = \frac{CO_{2\,\text{soil}} \cdot \Delta^{14}C_{\text{soil air}} - CO_{2\,\text{air}} \cdot \Delta^{14}C_{\text{air}}}{CO_{2\,\text{soil}} - CO_{2\,\text{air}}} - 8\text{‰} . \tag{4}$$

The 8‰ has to be subtracted because of the kinetic separation due to molecular diffusion in the soil. These values range between −46 and 251‰. The microbial degradation of SOM into CO_2 is assumed to be a first-order process. Using this assumption, Weber (1991) calculated the ratio of the fast and slow decomposable organic fraction with the $\Delta^{14}C$ data listed in Table 2 in the analyzed soils. In deciduous forest soils, Weber (1991) found the short-lived fraction of organic matter to be 63 ± 17% and the long-lived fraction to be 37 ± 17%. In coniferous forest soils, the short-lived fraction of organic matter is 37 ± 24% and the long-lived fraction is 63 ± 24%.

TABLE 2. Results of Soil CO_2 Measurements

Site	Sampling date	$CO_{2\,soil}$ (ppm)	$CO_{2\,air}$ (ppm)	$\delta^{13}C_{soil}$ (‰)	$\delta^{13}C_{air}$ (‰)	$\Delta^{14}C_{air}$ (‰)	$\Delta^{14}C_{soil\,air}$ (‰)	$\Delta^{14}C_{soil\,respiration}$ (‰)
M3	4/90	2663 ± 39	436 ± 65	−26.55 ± 0.05	−11 ± 2	137 ± 4	154 ± 8	150 ± 10
M2	4/90	6473 ± 165	436 ± 65	−23.13 ± 0.05	−11 ± 2	137 ± 4	143 ± 6	135 ± 6
M4	4/90	5324 ± 103	436 ± 65	−22.05 ± 0.05	−11 ± 2	137 ± 4	145 ± 6	137 ± 7
M1	5/90	3233 ± 33	436 ± 65	−21.4 ± 0.05	−11 ± 2	137 ± 4	168 ± 5	165 ± 6
M2	7/90	9930 ± 53	436 ± 65	−23.45 ± 0.05	−11 ± 2	137 ± 4	156 ± 6	149 ± 6
SK1	7/90	13,442 ± 4	436 ± 65	−26.71 ± 0.05	−11 ± 2	137 ± 4	164 ± 6	157 ± 6
M1	7/90	4271 ± 71	436 ± 65	−21.26 ± 0.05	−11 ± 2	137 ± 4	180 ± 6	176 ± 7
M3	7/90	5354 ± 432	436 ± 65	−21.35 ± 0.05	−11 ± 2	137 ± 4	158 ± 6	152 ± 7
M4	7/90	9758 ± 164	436 ± 65	−22.04 ± 0.05	−11 ± 2	102 ± 4	144 ± 6	136 ± 6
M4	1/91	4037 ± 376	436 ± 65	−23.99 ± 0.05	−11 ± 2	102 ± 4	134 ± 6	130 ± 7
M2	1/91	3831 ± 76	436 ± 65	−22.29 ± 0.05	−11 ± 2	102 ± 4	158 ± 7	157 ± 8
M1	1/91	1884 ± 37	436 ± 65	−20.82 ± 0.05	−11 ± 2	102 ± 4	162 ± 6	172 ± 9
M3	1/91	2171 ± 40	436 ± 65	−20.12 ± 0.05	−11 ± 2	102 ± 4	115 ± 5	111 ± 7
RO3	3/91	1378 ± 29	436 ± 65	−20.45 ± 0.05	−11 ± 2	102 ± 4	209 ± 6	251 ± 15
RO1	3/91	1315 ± 42	436 ± 65	−19.33 ± 0.05	−11 ± 2	102 ± 4	149 ± 6	165 ± 12
RO2	3/91	1222 ± 97	436 ± 65	−18.97 ± 0.05	−11 ± 2	102 ± 4	152 ± 6	172 ± 13
RU	4/91	10,078 ± 376	423 ± 32	−24.13 ± 0.05	−9 ± 2	120 ± 4	−32 ± 6	−46 ± 6
WQ	5/91	13,337 ± 667	411 ± 15	−23.32 ± 0.05	−9 ± 2	120 ± 4	32 ± 3	22 ± 3

Table 3 lists the $\Delta^{14}C$ data for DOC which range between 29 and 105‰. Because of the long time interval between the sampling date and the date of analysis, the easily degradable component of DOC is probably removed from the samples and the data describe the slowly degradable component of DOC. Unlike the soil CO_2, the $\Delta^{14}C$ data of DOC could *not* be described by a model that assumes DOC to be produced from the solid organic matter by a first-order decay process. The data could be explained by assuming that SOM is not degraded into DOC earlier than 20–30 yr after deposition (Tegen 1992).

TABLE 3. Results of DOC Measurements

Sample	Sampling date	DOC (mg liter^{-1})	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Date of analysis
TDOC1	6/89–10/89 5/90–10/90	80	−29.2	29 ± 27	6/91
TDOC4	10/89–5/90 10/90–5/91	30	−29.9	88 ± 25	12/91
TDOC2	6/89–7/90	40	−28.3	93 ± 11	9/91
TDOC3	6/89–7/90	50	−27.6	105 ± 8	4/92

CONCLUSION

In undisturbed soils, ^{14}C measurements can be used to determine turnover rates for soil organic carbon. Knowledge of such turnover rates is necessary to investigate the role of SOM in the global carbon budget and the impact of changing climatic conditions on soil organic carbon fluxes. Our results indicate that the type of vegetation cover affects the turnover rates of the carbon reservoirs, as coniferous forests appear to produce 50% more slow than fast degradable SOM, whereas deciduous forests produce 50% more fast than slow degradable SOM. These results need to be compared to results for different ecosystems. Unlike the soil CO_2 $\Delta^{14}C$ data, the DOC $\Delta^{14}C$ results cannot be explained by a first-order decay process but seem to indicate a time lag of several years between litter fall and production of non-volatile DOC. Although at our sampling site the contribution of DOC to the carbon budget seemed to be of minor importance, it remains to be investigated whether this holds true for other sites, specifically sites with different climatic conditions.

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