



Modelling the long-term stabilization of carbon from maize in a silty soil

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Abstract

Soil organic carbon (SOC) models have been widely used to predict SOC change with changing environmental and management conditions, but the accuracy of the prediction is often open to question. Objectives were (i) to quantify the amounts of C derived from maize in soil particle size fractions and at various depths in a long-term field experiment using ¹³C/¹²C analysis, (ii) to model changes in the organic C, and (iii) to compare measured and modelled pools of C. Maize was cultivated for 24 years on a silty Luvisol which resulted in a stock of 1.9 kg maize-derived C m⁻² (36% of the total organic C) in the Ap horizon. The storage of maize-derived C in particle size fractions of the Ap horizon decreased in the order clay (0.65 kg C m⁻²) > fine and medium silt (0.43) > coarse silt (0.33) > fine sand (0.13) > medium sand (0.12) > coarse sand (0.06) and the turnover times of C₃-derived C ranged from 26 (fine sand) to 77 years (clay). The turnover times increased with increasing soil depth. We used the Rothamsted Carbon Model to model the C dynamics and tested two model approaches: model A did not have any adjustable parameters, but included the Falloon equation for the estimation of the amount of inert organic matter (IOM) and independent estimations of C inputs into the soil. The model predicted well the changes in C₃-derived C with time but overestimated the changes in maize-derived C 1.6-fold. In model B, the amounts of IOM and C inputs were optimized to match the measured C₃- and C₄-derived SOC stocks after 24 years of continuous maize. This model described the experimental data well, but the modelled annual maize C inputs (0.41 kg C m⁻² a⁻¹) were less than the independently estimated total input of maize litter C (0.63 kg C m⁻² a⁻¹) and even less than the annual straw C incorporated into the soil (0.46 kg C m⁻² a⁻¹). These results indicated that the prediction of the Rothamsted Carbon Model with independent parameterization served only as an approximation for this site. The total amount of organic C associated with the fraction 0–63 μm agreed well with the sum of the pools ‘microbial biomass’, ‘humified-organic matter’ and IOM of the model B. However, the amount of maize-derived C in this fraction (3.4 g kg⁻¹) agreed only satisfactorily with the sum of maize-derived C in the pools ‘microbial biomass’ and ‘humified organic matter’ (2.6 g kg⁻¹).

Introduction

Soil organic carbon (SOC) is a central element in the global carbon cycle. The turnover of carbon

during biomass formation and decomposition leads to the release or binding of the greenhouse gas CO₂. Type and intensity of land use have marked effects on the SOC storage and thus may affect global climate (Post and Kwon, 2000).

The storage of SOC depends on the C inputs (amount and quality of plant residues) and on

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the stabilization of organic carbon in soils. The stabilization of SOC is a function of the climate, the microbial activity and properties of the soil that protect the organic matter against microbial attack, in particular the amount and composition of clay minerals. Quantitative information about sizes of the various SOC pools and rates of turnover is needed to estimate the sequestration of C in the soil. Methods for the determination of the turnover of several SOC pools commonly include ^{14}C and/or ^{13}C measurements, whereby the natural abundance technique has been employed extensively for sites where a change from C_4 - to C_3 -plants (or vice versa) occurred (Balesdent et al., 1990; Collins et al., 1999; Ludwig et al., 2003; Puget et al., 1995).

Several models exist which calculate the C dynamics in soil. Most models need information about the C inputs into the soil and the amount of passive or inert organic matter (IOM) and they are able to estimate the C dynamics for decades or centuries for different management (Jenkinson and Rayner, 1977; Parton et al., 1987; Paustian et al., 1992; Smith et al., 1997). Reports about successful modelling exercises are common (Smith et al., 1997), whereas in some studies modifications (e.g. changes of the calculation of the amount of IOM (Ludwig et al., 2003) or changes in rate constants (Skjemstad et al., 2004)) were required or suggested (Smith et al., 1997). However, in some of the studies cited above, not all the important parameterization information is given. Additionally, the term "prediction" (use of independent measurements or estimations of the model parameters, e.g. C inputs) is sometimes used although the terms "description" or "calibration" (use of adjustable parameters) would be more appropriate. Successful descriptions or calibrations of the C dynamics are not surprising, since optimized C inputs or rate constants allow reproducing almost any time course of experimental C data.

The amount of IOM used in the Rothamsted Carbon Model largely affects the estimated C inputs into the soil (Falloon and Smith, 2000; Ludwig et al., 2003). Different approaches exist for its estimation (Falloon et al., 1998; Körschens et al., 1998; Rühlmann, 1999) but their applicability to different sites is open to question (Falloon et al., 1998; Ludwig et al., 2003). For instance, Ludwig et al. (2003) reported for the

continuous rye and maize experiments on a sandy Phaeozem at Halle, Germany, that only the approach by Körschens et al. (1998) gave a useful estimate for the IOM amount.

The assessment of model pools by experimental measurements may result in more reliable models and may simplify the model calibration for different sites (Skjemstad et al., 2004; Smith et al., 2002). For instance, Balesdent (1996) used natural ^{13}C labelling to study the turnover of C in various separates from long-term field experiments on maize. He found that fractions coarser than $50\ \mu\text{m}$ had short lives, and he associated them with the plant structural compartment of the Rothamsted Carbon model. The other model pools IOM, 'humified organic matter' (HUM) and 'microbial biomass' (Cmic) were associated with the $0\text{--}50\ \mu\text{m}$ fraction (Balesdent, 1996). Similarly, Ludwig et al. (2003) reported that both the total organic C and the C derived from maize in the particle size fraction $0\text{--}63\ \mu\text{m}$ agreed well with the total and maize-derived sums of the model pools IOM, HUM and Cmic.

With the above findings in mind, we aimed (i) to determine the contribution of various particle size fractions to the total SOC stocks in different soil depths, (ii) to quantify the amounts of C derived from maize in particle size fractions after 24 years of continuous maize cropping using $^{13}\text{C}/^{12}\text{C}$ analysis, (iii) to model the C dynamics with the Rothamsted Carbon model and to compare measured and modelled pools of C, and (iv) to compare results for the inert C with approaches suggested by Falloon et al. (1998), Körschens et al. (1998) and Rühlmann (1999).

Materials and methods

Study sites

For our study we sampled soil from the long-term experiment of the 'Höhere Landbauschule' at Rotthalmünster, which is located in the 'tertiäres Hügelland' of the lower Rottal ($48^{\circ}21'47''\ \text{N}$, $13^{\circ}11'46''\ \text{E}$), Germany. The field trial is located 360 m above sea level. The mean annual precipitation and temperature are 886 mm and $8.7\ ^{\circ}\text{C}$, respectively. The soil type was a stagnic Luvisol derived from loess with the following horizons for the arable plots: Ap ($0\text{--}30\ \text{cm}$), E ($30\text{--}45\ \text{cm}$),

E/Bg (45–60 cm). At all experimental plots the texture was a silty loam with a nearly identical grain size distribution (mean \pm standard deviation) in the surface soils: (10.6 \pm 0.9)% sand, (73.1 \pm 1.7)% silt, and (16.4 \pm 1.2)% clay. The predominant minerals of the clay fraction in the A horizon decreased in the order illite > kaolinite > vermiculite (M. Kleber, personal communication).

Soil samples were taken from the three following sites which were located approximately within 150 m to each other and were originally on the same grassland: (i) A continuous maize plot (*Zea mays* L.), where only grains were harvested (stover plus roots were incorporated into the soil), established in 1979. Previous vegetation on the maize plot was a cultivated grassland which was established probably centuries ago until 1960, subsequently different C₃-crops were cultivated (1961–1970), followed by spring wheat and winter wheat (*Triticum aestivum* L.) (1971–1978). (ii) A cultivated grassland established in 1961. The vegetation of the grassland was dominated by the grass species *Trisetum flavescens* and *Alopecurus pratensis*. Previous vegetation of this plot was also grassland but there is no information about species composition of the former grassland; and (iii) a continuous wheat plot established in 1969 on former grassland; in most years mustard (*Sinapis alba* L.) was grown as an intercrop on the continuous wheat plot. The size of the plots were 45 m² (continuous maize plot), 32 m² (cultivated grassland) and 522 m² (continuous wheat plot).

At the wheat and maize fields, depth of tillage was 30 cm and the straw was returned to the field after harvest. Since 1998, conservation tillage with grubbing to a depth of 15 cm instead of ploughing was conducted at the wheat plot.

N fertilization was applied according to the estimated crop yield. The mean N application

rate was 180 kg N ha⁻¹ a⁻¹ for maize and 171 kg N ha⁻¹ a⁻¹ for wheat. Fertilization was achieved solely with mineral fertilizers (Schnellhammer and Sirch, 2001). The grassland was cut four times a year and the nitrogen fertilization rate was 160 kg N ha⁻¹ a⁻¹ using mineral fertilizers.

The mean amount of straw C (above ground) produced (and left on the field) was 0.46 kg m⁻² a⁻¹ for maize and 0.19 kg m⁻² a⁻¹ for wheat. The value for maize was obtained from an adjacent plot, where the total aboveground biomass was harvested. For wheat, the aboveground biomass was estimated from the grain yield and a ratio of straw to grain of 0.8:1. Assuming that the ratio (root biomass)/(aboveground yield of biomass and grains) was 0.2 (Balesdent and Balabane, 1992), the belowground C input from maize was 0.2 \times {0.46 kg C m⁻² a⁻¹ (straw) + 0.40 kg C m⁻² a⁻¹ (grain)}. Thus, the total annual input of maize litter C was 0.63 kg C m⁻² (0.46 kg C m⁻² straw C and 0.17 kg C m⁻² belowground C input). Assuming the same ratio for wheat, the total annual input of wheat litter C was 0.27 kg C m⁻² (0.19 kg C m⁻² straw C and 0.08 kg C m⁻² belowground C input) (rhizodeposition was not taken into account) (John et al., 2005).

Soil and plant sampling

We collected undisturbed as well as mixed soil samples (four independent replicates each) from different depths (Table 1 shows the general characteristics of the maize plot) at all sites in September 2002. The undisturbed soil cores had a volume of 250 cm³ each and small pits were established to collect mixed soil samples from different horizons of the experimental plots. Plant residues were collected on the maize field (roots and aboveground biomass) and on the wheat field (straw).

Table 1. Bulk density, soil pH, N_{total} and organic C of the continuous maize plot with NPK fertilizer and C from maize

Depth (cm)	Bulk density (g cm ⁻³)	pH	Organic C		N _{total} (g N m ⁻²)	C from maize	
			(g kg ⁻¹)	(kg m ⁻²)		(g kg ⁻¹)	(kg m ⁻²)
0–30	1.38	6.9	12.9 (0.4)	5.35 (0.17)	558 (12)	4.6 (0.3)	1.91 (0.13)
30–45	1.53	6.5	6.7 (0.2)	1.55 (0.05)	178 (6)	1.0 (0.1)	0.24 (0.01)
45–60	1.52	6.6	4.1 (0.1)	0.93 (0.03)	126 (7)	0.4 (0.1)	0.09 (0.02)

Mean values and standard errors in brackets ($n = 4$).

Particle-size fractionation

Distilled water (150 ml) was mixed with 25 g of soil (<2 mm) and the suspension was sonicated at 60 J ml⁻¹ using a Branson sonifier 450-D. The coarse (630 µm–2 mm) and medium (200–630 µm) sand fractions including the particulate organic matter were obtained by wet-sieving. The remaining fraction was sonicated at 440 J ml⁻¹. The fractions fine sand (63–200 µm), coarse silt (20–63 µm), medium and fine silt (2–20 µm) and clay (0–2 µm) were obtained by sieving and sedimentation. We precipitated the clay fraction using AlCl₃ and HCl, and we discarded the supernatant. All fractions were dried at 40 °C and finely ground (Ludwig et al., 2003).

General soil analysis

The soil pH was determined in a 0.01 M CaCl₂ solution (soil:solution ratio 1:2.5). The total organic C and total N contents were determined by an automated C and N analyzer (Heraeus vario EL) after acidifying the ball-milled samples with 10% HCl. Soil bulk density was determined gravimetrically from undisturbed soil cores.

Carbon isotopic analysis

¹³C/¹²C isotope ratios of all samples were measured by an isotope ratio mass spectrometer (IRMS, Finnigan MAT, DELTA^{plus}, Bremen, Germany) connected to an elemental analyzer (NA 2500, Fisons, Milan, Italy). ¹³C/¹²C isotope ratios were expressed as δ¹³C values:

$$\delta^{13}\text{C}(\text{‰}) = [(\delta_{\text{sam}}/\delta_{\text{std}}) - 1] \times 10^3, \quad (1)$$

where δ_{sam} = ¹³C/¹²C ratio of the sample, and δ_{std} = ¹³C/¹²C ratio of the reference standard Pee Dee Belemite (PDB).

The proportion of C derived from maize in a sample was calculated according to Balesdent and Mariotti (1996). δ¹³C values (mean ± standard deviation) were (-12.7 ± 0.2)‰_{PDB} for maize and (-26.8 ± 0.1)‰_{PDB} for wheat, resulting in a difference of 14.1‰_{PDB}. The standard error SE of maize-derived proportions of *n* samples was calculated according to Ludwig et al. (2003).

Calculation of the apparent turnover time of of C₃-derived C

We calculated the apparent turnover time *T* of C₃-derived C in the SOC fractions of the maize site as:

$$T = 1/k = -(t - t_0)/\ln(C_t/C_{t_0}) \quad (2)$$

where *k* is the rate constant of the first-order decay equation, *t* gives the time of sampling (a), *t*₀ the time of vegetation change (a), *C*_{*t*} the proportion of remaining carbon labelled from C₃-derived C in the soil at the time of sampling (%), and *C*_{*t*0} the percentage of carbon labelled from C₃-plants at *t*₀(%). For our continuous maize cropping plot *t* was 2002, *t*₀ was 1979, *C*_{*t*0} was 100%, and *C*_{*t*} was calculated as 100%–(*f* × 100%).

Modelling the C dynamics with the Rothamsted carbon model

We used the Rothamsted Carbon Model (ROTHC26–3) (Coleman and Jenkinson, 1999; Jenkinson and Rayner, 1977) which included the pools decomposable plant material (DPM), resistant plant material (RPM), Cmic, HUM and IOM to calculate the amount of maize-derived C in the various pools of soil organic matter. This version had been tested by Smith et al. (1997). Figure 1 shows the structure of the model. The decay of the pools DPM, RPM, Cmic and HUM follows first-order kinetics and the decomposition rate constants (in a⁻¹) were set to 10.0 (DPM), 0.3 (RPM), 0.66 (Cmic) and 0.02 (HUM) as suggested by Coleman and Jenkinson (1999).

The model was run for the 0–30 cm horizon for the soil from site (i) which was converted from a cultivated grassland into a cultivation of different C₃-crops (1961–1970), followed by spring wheat and winter wheat (1971–1978) and then changed into a maize monoculture (1979–2002). The data requirements are given in Table 2.

We tested two models A and B to calculate the SOC dynamics. Both models need an initial SOC amount in 1960. A reasonable assumption is that site (ii), the continuous cultivated grassland, is at a steady state and represents the initial conditions at the maize site in 1960 since both sites have the same long-term grassland history

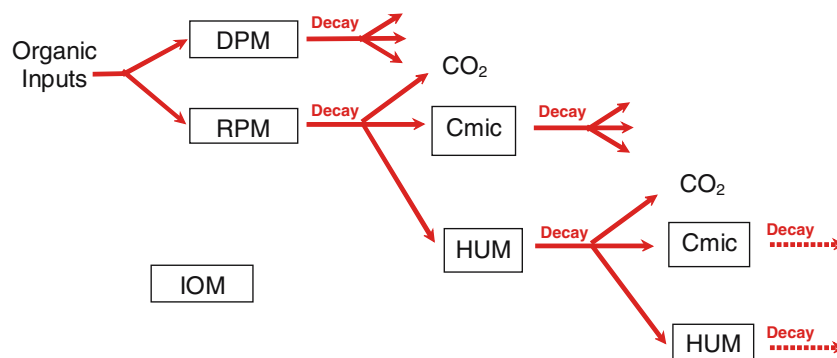


Figure 1. Structure of the Rothamsted Carbon Model (Coleman and Jenkinson, 1999).

Table 2. Data requirements for the Rothamsted carbon model

Variable	Data
Average monthly mean air temperature (°C) ^a	−2 (J), 0 (F), 3.9 (M), 8.1 (A), 12.7 (M), 15.8 (J), 17.9 (J), 17.5 (A), 13.6 (S), 8.8 (O), 2.9 (N), −0.2 (D)
Monthly precipitation (mm) ^a	57 (J), 54 (F), 60 (M), 63 (A), 83 (M), 108 (J), 112 (J), 110 (A), 65 (S), 59 (O), 56 (N), 66 (D)
Monthly evaporation (mm) ^a	0 (J), 0 (F), 19 (M), 46 (A), 87 (M), 110 (J), 123 (J), 105 (A), 70 (S), 39 (O), 12 (N), 0 (D)
Soil depth (cm)	30
Clay content of the soil (%)	17
DPM / RPM ratio ^b for wheat and maize ^c	1.44
Soil cover	Wheat crop production: covered from November until August. Maize crop production: covered from May until September.
Monthly input of plant residues	Unknown, obtained as described in the modelling section
Amount of inert organic matter	Unknown, obtained as described in the modelling section

^aThe weather data were taken from a nearby station.

^bRatio of decomposable plant material to resistant plant material.

^cThe value suggested by Coleman and Jenkinson (1999) was used.

until 1960. Site (iii), the wheat plot, was used to estimate the annual C inputs from wheat by using the grain yield as described above. The parameterization of the models A and B was as follows:

Model A (using the Falloon-equation and independent estimates of the C input)

1. The amount of inert organic C was estimated with the equation given by Falloon et al. (1998):

$$C_I = 0.049C_T^{1.139}, \quad (3)$$

where C_I is the amount of inert organic C, in t ha^{-1} , and C_T is the total organic C in the soil. The amount of inert C was 0.52 kg C m^{-2} .

2. Then, we used the model to calculate the average annual C input from the former grassland (until 1960) to match the measured values of SOC of 6.01 kg C m^{-2} in the depth from 0 to 30 cm at the continuous grassland site by assuming that a steady state was reached in 1960. We obtained a value of $0.39 \text{ kg C m}^{-2} \text{ a}^{-1}$.
3. The independently estimated C input (measured values of aboveground inputs plus estimated belowground inputs) for wheat of $0.27 \text{ kg C m}^{-2} \text{ a}^{-1}$ (1971–1978) was used for the years from 1961 to 1978. Then, the inde-

pendently estimated C input for maize (1979–2002) of $0.63 \text{ kg C m}^{-2} \text{ a}^{-1}$ was used for the following years.

Model B (using the additional information from the ^{13}C analysis)

1. We used this model to calculate the average annual maize-C-input (from 1979 onwards) that would be needed to match the measured value of maize-derived C in the maize plot in 2002 of $1.91 \text{ kg maize-derived C m}^{-2}$ in 0–30 cm (Table 1). We calculate that the average annual maize-C-input was 0.41 kg C m^{-2} .
2. Then, we used the model to calculate the average annual grass-C-input required and the amount of inert organic C needed (i) to match the measured value of soil organic C in the grassland plot of 6.01 kg C m^{-2} in 0–30 cm and (ii) to match the measured values of C_3 -derived C in the maize plot in 2002 of $3.44 \text{ kg C}_3\text{-derived C m}^{-2}$ (Table 1). Sensitivity analysis indicated that the annual wheat-C input in the range from 0 to 0.4 kg C m^{-2} from 1961 to 1978 had an insignificant effect on the C_3 -derived amount of SOC in 2002. Thus, we kept the estimated value of $0.27 \text{ kg C m}^{-2} \text{ a}^{-1}$ for the wheat-C input. We calculate that the annual grass-C inputs were 0.41 kg C m^{-2} until 1970. The calculated amount of inert organic C was 0.26 kg C m^{-2} .

Statistics

We applied a nonparametric test (Mann–Whitney U test) to identify significant differences ($P \leq 0.05$) of the yields, organic C content, maize-derived C and C/N ratios between the different particle size fractions.

Results and discussion

C stocks in the soils

SOC storage in the upper mineral soil (0–30 cm) was highest in the soil under grassland (6.0 kg C m^{-2}) followed by the soils under maize (5.4 kg C m^{-2}) and wheat (5.2 kg C m^{-2}). The percentage of maize-derived C decreased with depth from

35.7% (Ap horizon) to 15.4% (30–45 cm) and 10.2% (45–60 cm, Table 1) after 24 years of continuous maize cultivation. The accumulation of maize-derived C in the soil profile (Table 1) agreed well with observations from other sites. For instance, Gregorich et al. (1996) found for a clayey soil that after 32 years of maize cultivation 22 to 30% of soil C was maize-derived under NPK treatment. Collins et al. (1999) reported that of eight soils in the maize belt of the US with a texture range from silty clay to loam that had continuously grown maize for 8–35 years, the maize-derived C in the surface soils (0–20 cm) ranged from 23 to 60 % and from 9 to 32 % in the subsoils (25–50 cm).

Stabilization of total and maize-derived C in different particle size fractions

In all three depths of the maize site, the C storage in $\text{g C kg}^{-1} \text{ soil}^{-1}$ decreased in the order clay fraction > fine and medium silt > coarse silt > fine sand \approx medium sand \approx coarse sand (Table 3). The enrichment factors E (mass C per mass separate/mass C per mass soil) in the Ap horizon were 2.6 (clay fraction), 1.8 (medium sand), 1.2 (coarse sand), 0.9 (fine and medium silt), 0.6 (fine sand) and 0.3 (coarse silt). The increased enrichment factor of 2.6 for the clay fraction is in the range reported by Christensen (1996) (2 to 15) for the clay fractions of Danish arable soils and indicates that clay is generally more effective than silt and sand in sequestering OM. However, the low enrichment factor of 0.3 for the coarse silt is much less than reported by Christensen (1996) (1 to 5) and Ludwig et al. (2003) for other arable soils. This may be the result of the accumulation of small quartz grains (which are the main constituents of loess) in the coarse silt fractions of the loess-derived soil.

The stabilization of maize-derived C in the soil organic C depended on soil particle size. The storage of maize-derived C in the Ap horizon decreased in the order clay (1.6 g C kg^{-1}) > fine and medium silt (1.0) > coarse silt (0.8) > fine sand (0.3) and medium sand (0.3) > coarse sand (0.1) (Table 3) and emphasizes the importance of clay and silt particles in sequestering C (Six et al., 2002). In all three depths, the percentages

Table 3. Yields of the particle size fractions, organic C, C from maize and C/N ratios in particle-size fractions of the maize site (Ap horizon, 0–30 cm)

Particle size fraction	Yield (%)	Organic C (g C kg ⁻¹ soil)	Maize-derived C (% of the organic C)	Turnover time (years)	C/N
0–30 cm					
Coarse sand (630 μm –2 mm)	3.2 (0.3) ^a	0.47 (0.0) ^a	28.7 (2.3) ^a	71 (+7/–14)	26.3 (1.0) ^a
Medium sand (200–630 μm)	2.1 (0.1) ^b	0.46 (0.0) ^a	58.1 (1.4) ^b	28 (+1/–2)	19.2 (0.6) ^b
Fine sand (63–200 μm)	6.4 (0.2) ^c	0.48 (0.0) ^a	60.3 (1.8) ^b	26 (+1/–3)	18.1 (0.2) ^b
Coarse silt (20–63 μm)	40.5 (0.6) ^d	1.43 (0.1) ^b	57.2 (0.7) ^b	28 (+1/–1)	11.6 (0.2) ^c
Fine and medium silt (2–20 μm)	30.4 (0.7) ^c	3.37 (0.2) ^c	30.7 (1.4) ^a	65 (+4/–7)	9.6 (0.0) ^d
Clay (0–2 μm)	17.4 (0.4) ^f	5.76 (0.2) ^d	26.9 (0.8) ^a	77 (+3/–5)	8.5 (0.1) ^e
30–45 cm					
Coarse sand (630 μm –2 mm)	1.8 (0.1) ^a	0.21 (0.0) ^a	12.0 (2.4) ^a	188 (+50/–83)	40.4 (5.0) ^a
Medium sand (200–630 μm)	1.6 (0.0) ^a	0.18 (0.0) ^b	27.6 (4.3) ^{b,c}	74 (+16/–28)	27.7 (2.6) ^a
Fine sand (63–200 μm)	6.0 (0.3) ^b	0.25 (0.0) ^a	35.4 (2.0) ^c	55 (+4/–8)	17.4 (0.9) ^b
Coarse silt (20–63 μm)	38.8 (0.9) ^c	0.54 (0.1) ^c	32.9 (1.5) ^b	60 (+4/–7)	7.3 (0.3) ^c
Fine and medium silt (2–20 μm)	32.0 (0.8) ^d	1.52 (0.1) ^d	14.7 (1.1) ^a	151 (+13/–25)	8.0 (0.2) ^c
Clay (0–2 μm)	19.8 (0.2) ^e	3.55 (0.1) ^e	11.5 (1.1) ^a	196 (+22/–40)	8.1 (0.0) ^c
45–60 cm					
Coarse sand (630 μm –2 mm)	0.5 (0.1) ^a	0.08 (0.0) ^a	6.9 (1.1) ^a	336 (+66/–114)	76.6 (4.8) ^a
Medium sand (200–630 μm)	1.0 (0.1) ^b	0.14 (0.0) ^b	24.0 (2.8) ^b	87 (+13/–24)	28.0 (2.4) ^b
Fine sand (63–200 μm)	5.4 (0.3) ^c	0.17 (0.0) ^b	24.7 (5.0) ^{b,c}	85 (+25/–41)	14.1 (0.6) ^c
Coarse silt (20–63 μm)	37.2 (0.5) ^d	0.31 (0.0) ^c	26.8 (2.4) ^b	77 (+9/–16)	4.9 (0.3) ^d
Fine and medium silt (2–20 μm)	34.1 (0.5) ^e	0.90 (0.0) ^d	9.2 (2.4) ^{a,c}	249 (+92/–146)	6.3 (0.2) ^e
Clay (0–2 μm)	21.8 (0.3) ^f	2.24 (0.0) ^e	9.9 (2.9) ^a	230 (+100/–155)	7.3 (0.1) ^f

Mean values with standard errors in brackets. Different characters within columns indicate significant differences ($P \leq 0.05$) between the particle size fractions of each depth. For the turnover times, however, the upper and lower values were calculated by using the standard errors of the maize-derived C.

of maize-derived C were much higher in the coarse silt, fine sand and medium sand fractions than in the other fractions (Table 3).

The turnover times of C₃-derived C in the Ap horizon were smaller in the fractions coarse silt, fine sand and medium sand (26–28 years) compared to the fine and medium silt fractions (65 years) and the clay fraction (77 years) (Table 3). Similar results were found for the subsoil horizons. However, the turnover times in the subsoils were considerable higher and varied from 55 to 87 years in the fractions coarse silt, fine sand, and medium sand, from 151 to

249 years in the fine and medium silt, and from 196 to 230 years in the clay fraction. Similarly Balesdent (1996) reported for eutric Cambisols under maize that the mean turnover times increased with decreasing particle size and were 18 (50–200 μm) and 63 years (0–50 μm) in the Ap horizons. However, the turnover times of C₃-derived C in the coarse sand fractions (71 (0–30 cm), 188 (30–45 cm) and 336 years (45–60 cm), Table 3) were exceptionally high in our study. This may be explained by a relatively increased content of black C in this fraction at low contents of total C and/or by the strong ¹³C

discrimination during the initial stage of litter decomposition. The $\delta^{13}\text{C}$ value of $\text{CO}_2\text{-C}$ evolved during decomposition of crop litter was shown to be about 3‰ lower than the $\delta^{13}\text{C}$ of the substrate (Kristiansen et al., 2004). This can bias the determination of turnover times especially in soil fractions containing mainly fresh plant residues.

The smallest C/N ratios were found in the clay fraction and fine and medium silt fraction (Ap horizon) and additionally in the coarse silt fraction (30–45 and 45–60 cm) (Table 3). The C/N ratios of 8.5 (0–30 cm), 8.1 (30–45 cm) and 7.3 (45–60 cm) for the clay fraction in our study compared well with the C/N ratio of 7.5 for the fine clay fraction of a Mollisol and ratios of 8–12 for the microbial biomass in soil (Baldock et al., 1992).

Modelling the C-dynamics

(a) Model A

In the model the amount of inert C was estimated using the equation of Falloon et al. (1998) and the wheat-C- and maize-C-inputs were taken as the sum of the aboveground residues incorporated into the soil and the independently estimated belowground C-inputs. The model predicted the changes in C_3 -derived SOC amounts well (Figure 2). However, the changes in maize-derived SOC were overestimated 1.6-fold in 2002 (Figure 2). These results indicated that the prediction of the Rothamsted Carbon Model with independent parameterization served only as an approximation for this site.

(b) Model B

Here we have used additional information from the ^{13}C analysis. For the 24 years of continuous maize cultivation, the model calculated that an average annual maize-C input of 0.41 kg m^{-2} was required to obtain a value of 1.91 kg m^{-2} maize-derived C in the Ap horizon. The input calculated is less than the independently estimated total input of maize litter C ($0.63 \text{ kg C m}^{-2} \text{ a}^{-1}$) and even less than the straw C incorporated into the soil ($0.46 \text{ kg C m}^{-2} \text{ a}^{-1}$).

Summarizing some recent findings for different sites (Lobe et al., 2005; Skjemstad et al., 2004; this study), the Rothamsted Carbon Model described the C dynamics well only when the assumed C inputs were very low (this study and Lobe et al., 2005) or a rate constant was modi-

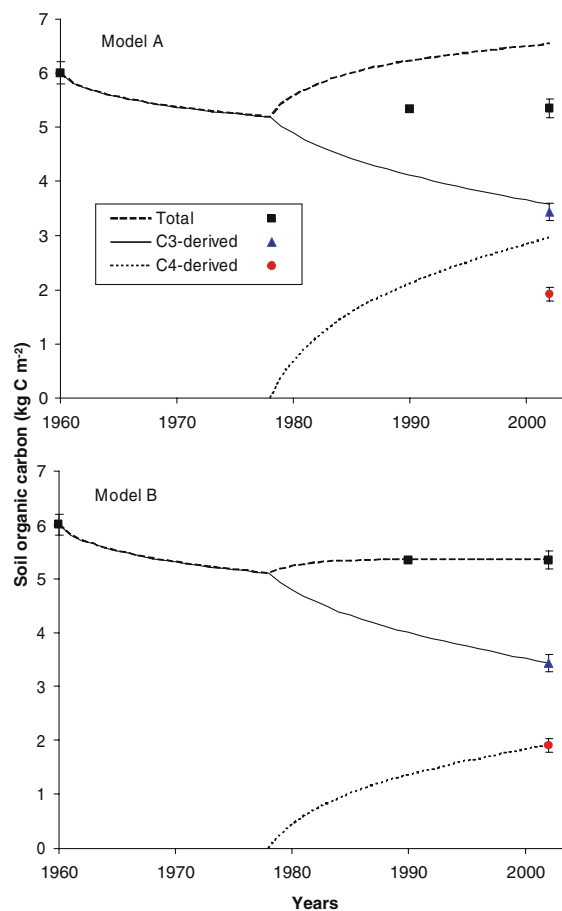


Figure 2. Amounts of soil organic carbon for the continuous grassland that was converted into a cultivation with C_3 crops (1961–1978) and then into a maize monoculture (1979–2002). The symbols show the measured quantities (mean values and standard errors, except for 1990, where only a single value was available), and the lines show the model results for model A and B.

fied (Skjemstad et al., 2004). A modification of a rate constant of one the four pools (Skjemstad et al., 2004) is likely to give improved model output when calibrated to the experimental data. However, it is unclear why for Australian agricultural sites different rate constants were used since the effect of climate on the C dynamics is already considered in the model with rate modifying factors for temperature and moisture. In contrast to changing rate constants, we believe that other modifications of the Rothamsted Carbon Model might enhance its applicability.

A modification could include the use of crop-specific DPM/RPM ratios. In the present version of ROTH-C, the suggested value for the DPM/

RPM ratio is 1.44 for agricultural crops although the composition differs widely for different crops as revealed by wet chemistry. Since maize contains less lignin than many other crops (Mueller et al., 1998), the use of crop-specific DPM/RPM ratios might be more accurate. However, preliminary sensitivity analysis for our site indicated that a DPM/RPM ratio of 2 results only in a slightly increased C input ($0.44 \text{ kg C m}^{-2} \text{ a}^{-1}$) to match the C_4 -SOC stock of 1.91 kg C m^{-2} . Thus, uncertainties in the DPM/RPM ratio are not the main cause for the deviations between measured and modelled C inputs of model B.

Other potential modifications which were not tested in our study might be (i) splitting the pool HUM into two pools with different rate constants, (ii) including a rate modifying constant for the biotic environment and (iii) including a rate modifying constant for soil cultivation.

Both model approaches A and B gave only small amounts of IOM (model A: 0.5 kg C m^{-2} , model B: 0.3 kg C m^{-2}). These values equal or are similar to the amount of black carbon at this site (0.3 kg C m^{-2} , S. Brodowski, personal communication), suggesting that black carbon is the main contributor of IOM at this site. In agreement with this, Skjemstad et al. (2004) reported for Australian soils that IOM was estimated using the amounts of black C. For the Halle site, Ludwig et al. (2003) found that IOM was much larger than the amounts of black C that was determined using the benzenepolycarboxylic acid method (Brodowski et al., 2001). However, Rethemeyer (2004) estimated black C at the Halle site as approximately 50% of total C using ^{14}C measurements. Thus, at present it is not entirely clear whether amounts of black C may generally be used as IOM in the model or not.

We tested the equations suggested by Rühlmann (1999):

$$C_{\text{fallow}} = 0.017a - 0.001 \exp(0.075a), \quad (4)$$

where C_{fallow} is the amount of soil organic C of long-term bare fallow soils, in %, and a is the percentage of soil particles $<20 \mu\text{m}$,

and by Körschens et al. (1998):

$$C_1 = 0.04a, \quad (5)$$

where C_1 is the amount of inert organic C, in %, and a is the percentage of soil particles $< 6.3 \mu\text{m}$.

Equations (4) and (5) gave considerably larger amounts of inert organic C for both treatments (3.2 and 4.1 kg C m^{-2} , respectively) than equation (3). This indicates that SOC in long-term bare fallow plots consists of SOC pools with rate constants which are not negligible plus stabilized pools (e.g. charcoal) with only very low rate constants. No meaningful model results were obtained when the results of equations (4) or (5) were used as amounts of IOM in the model: amounts of C_3 -derived SOC in 2002 were overestimated by 1.5 (equation 4) or 2.0 kg C m^{-2} (equation 5).

Comparison of the model results for the Halle site where maize was grown for 39 years (Ludwig et al., 2003) and the Rothalmünster site

The approaches by Falloon et al. (1998) and Rühlmann (1999) were not suitable as IOM pool for the sandy haplic Phaeozem at Halle (Ludwig et al., 2003), whereas for the Rothalmünster site, the approaches by Körschens et al. (1998) and Rühlmann (1999) were not suitable. Thus, none of the three approaches which either estimate the amount of inert organic matter (Falloon et al., 1998) or of organic C in soil under long-term bare fallow (Körschens et al., 1998; Rühlmann, 1999) are generally suitable for use as IOM pool in the Rothamsted Carbon Model.

In both studies, the use of stable isotopes helped to improve the parameterization and to find erroneous assumptions. For the Halle site, we showed that equation (3) by Falloon et al. (1998) could not be used as IOM pool and for this site, stable isotopes indicated that the use of independently estimated maize C inputs in the model can result in a large overestimation of the maize-C stabilization in soil with time.

For the Halle site, modelling by using the information of stable isotopes was considered as successful, because independently estimated maize-C inputs and optimized maize-C inputs differed only by 11% (0.079 vs. $0.089 \text{ kg C m}^{-2} \text{ a}^{-1}$) (Ludwig et al., 2003). For this site, however, deviations between them were large (0.63 vs. $0.41 \text{ kg C m}^{-2} \text{ a}^{-1}$). A simple explanation could be that the Rothamsted Carbon Model becomes inaccurate for sites with large C inputs. However, for the Hoosfield experiment in

Table 4. Model B: model results for the amounts of C₃-derived and maize-derived C (g C kg⁻¹ soil) after 24 years of continuous maize cropping

	DPM ^a	RPM ^a	Cmic ^a	HUM ^a	IOM ^a
C ₃ -derived C	0.00 (0%)	0.01 (0.3%)	0.03 (10.1%)	7.64 (76.7%)	0.63 (100.0%)
Maize-derived C	0.14 (100.0%)	1.92 (99.7%)	0.24 (89.9%)	2.32 (23.3%)	0.00 (0%)

Values in parentheses are the percentages of the amount in each pool.

^aDPM: decomposable plant material; RPM: resistant plant material; Cmic: microbial biomass; HUM: humified organic matter; IOM: inert organic matter.

the UK, SOC amounts were predicted well also for a variant with annual addition of farmyard manure (Coleman and Jenkinson, 1999). Thus, a modification of the model structure of the Rothamsted Carbon Model as suggested above might be required to get more accurate results of the SOC dynamics.

Comparison of analytical SOC fractions and model SOC pools

Balesdent (1996) suggested that the organic C in the fraction 0–50 μm represents the sum of the pools Cmic, HUM and IOM of the ROTH-C model. We found the measured fraction 0–63 μm of the total (C₃- and maize-derived) organic C to be 10.6 g C kg⁻¹ soil (Table 3). This agreed well with the sum of C₃- and maize-derived C from the pools Cmic, HUM and IOM of the model B (10.9 g C kg⁻¹ soil, Table 4). However, the C from maize in the 0–63 μm fraction (3.4 g C kg⁻¹ soil) was higher than the sum of maize-derived C in the pools Cmic and HUM of the model (2.6 g C kg⁻¹ soil). Accordingly, the maize-derived C in the fraction >63 μm was less than the maize-derived C in the RPM pool. These differences were probably due to a better decomposability of maize residues compared to other crops and a higher ratio of DPM to RPM might be more appropriate.

Density fraction of the soil from this site showed that the yield of C decreased in the order mineral-associated C (86.8% of the total C) > occluded particulate organic matter (9.1%) > free particulate organic matter (4.1%) (John et al., 2005). The percentage of mineral-associated C compares well with the percentage of the sum the pools HUM and IOM (81.9% of the total C, Table 4). However, the percentage of maize-derived C was 21.9% for these two pools (Table 4) compared to a maize-derived C of

31.4% for the mineral-associated C (John et al., 2005).

Conclusions

The Rothamsted Carbon model was employed to predict (model A: using independent parameterization) or describe (model B: using optimized C inputs) the long-term C dynamics in a silty soil. However, the results of model A indicated a 1.6-fold overestimation of the maize-derived C. In contrast, model B with optimized C inputs described the SOC data well, but the modelled maize-C inputs were less than the independently estimated total input of maize litter C and even less than the straw C inputs in the experiment. These results indicated that the prediction of the Rothamsted Carbon Model with independent parameterization served only as an approximation for this site.

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