EVALUATION OF SOIL ^{14}C DATA FOR ESTIMATING INERT ORGANIC MATTER IN THE RothC MODEL

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ABSTRACT. Changes in soil organic carbon stocks were simulated with the Rothamsted carbon (RothC) model. We evaluated the calculation of a major input variable, the amount of inert organic matter (IOM), using measurable data. Three different approaches for quantifying IOM were applied to soils with mainly recent organic matter and with carbon contribution from fossil fuels: 1) IOM estimation via total soil organic carbon (SOC); 2) through bulk soil radiocarbon and a mass balance; and 3) by quantifying the portion of black carbon via a specific marker. The results were highly variable in the soil containing lignite-derived carbon and ranged from 8% to 52% inert carbon of total SOC, while nearly similar amounts of 5% to 8% were determined in the soil with mainly recent organic matter. We simulated carbon dynamics in both soils using the 3 approaches for quantifying IOM in combination with carbon inputs derived from measured crop yields. In the soil with recent organic matter, all approaches gave a nearly similar good agreement between measured and modeled data, while in the soil with a fossil carbon admixture, only the ^{14}C approach was successful in matching the measured data. Although ^{14}C was useful for initializing RothC, care should be taken when interpreting SOC dynamics in soils containing carbon from fossil fuels, since these reflect the contribution from both natural and anthropogenic carbon sources.

INTRODUCTION

Soils are a major carbon reservoir in the global carbon cycle, exchanging large amounts of CO_2 with the atmosphere on relatively short timescales, and thus may act as a source as well as a sink of CO_2 (Trumbore et al. 1996; Schimel et al. 2001). Understanding the dynamics of soil organic carbon (SOC) is important for the prediction of the carbon sequestration potential of soils. The turnover of SOC can be simulated with the help of organic matter turnover models (Coleman and Jenkinson 1996; Parton 1996; Franko et al. 1997) that allow the prediction of changes in soil carbon stock arising from agricultural management practices or from rising temperatures due to climate change (Paul et al. 2004; Jones et al. 2005; Knorr et al. 2005).

Soil organic matter is a complex mixture of organic components, ranging from recent plant residues to complex products of transformation processes and including the microbial biomass (Stevenson 1994). To account for the large differences in degradability, SOC turnover models partition the organic matter into 2 or more pools, since a single homogeneous pool cannot reflect the different responses of fast and slow cycling organic components. The stable SOC pool is regarded as most important for long-term carbon sequestration (Swift 2001). Most models include at least several conceptual SOC pools, which cannot be measured directly because no generally applicable method for their separation exists. However, some models have been calibrated with measurable SOC fractions (e.g. Skjemstadt et al. 2004), and new models have been developed based on soil separation techniques (e.g. Sohi 2001). Nevertheless, most current models are quite successful in simulating changes in total SOC content as shown by a model comparison of Smith et al. (1997).

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The Rothamsted carbon (RothC) model 26.3 (Coleman and Jenkinson 1996) is a soil carbon turnover model tested with numerous long-term data sets and widely used for the prediction of SOC variations in different soils (Tate et al. 1993; Jenkinson and Coleman 1994; Coleman et al. 1997; Falloon and Smith 2002; Diels et al. 2004). In RothC, SOC is partitioned into 4 active pools decomposing within months to decades and 1 stable pool, called inert organic matter (IOM), turning over in >50,000 yr. Stable or passive carbon pools are included in numerous SOC models (Parton 1996; Franko et al. 1997; Falloon et al. 1998), although there is little evidence that organic components with mean residence times of several tens of thousands of years exist in natural soils (Gleixner et al. 2001). However, IOM may be considered as a mathematical construct, which is necessary to calculate rapid changes in SOC content and at the same time produce relatively low ^{14}C concentrations of bulk soil (Falloon et al. 2000). Since the amount of IOM has a major influence on the modeling results, its accurate estimation is essential (Jenkinson et al. 1991).

The amount of IOM in RothC is often determined i) by setting it to an arbitrary value (Coleman et al. 1997); ii) via total SOC; iii) through the ^{14}C concentration of the bulk soil; and iv) by using measurable soil fractions or components. The first approach should be avoided because it is the most imprecise method. The calculation via total organic carbon is derived from an empirical relationship between IOM and SOC (Falloon et al. 1998). The third option, the use of bulk soil ^{14}C data, preferably from pre- and post-bomb samples for the quantification of IOM, is based on a mass balance calculation and assuming soil organic matter being composed of 2 end-members: 1) plant-derived organic carbon, originally with atmospheric ^{14}C levels; 2) and fossil, ^{14}C-free carbon. Some studies used measurable soil fractions or components and assumed that these represent the stable organic carbon pool; for example, Skjemstadt et al. (2004) found charcoal-carbon to correspond with IOM in RothC. Black carbon, the residues of incomplete biomass and fossil fuel combustion (Goldberg 1985), may also be a significant component of stable or inert SOC since it is very resistant to degradation (Falloon and Smith 2000; Kiem et al. 2003). Soils may contain substantial portions of black carbon, mainly in areas with frequent vegetation fires (Poirier et al. 2002) and in urban or industrialized regions (Schmidt et al. 2002). The amount of the highly aromatic material can be quantified via the specific marker benzene polycarboxylic acids (BPCAs; Glaser et al. 1998; Brodowski et al. 2005).

Direct measurements of IOM would greatly improve the predictive ability of the model. We thus tested the described methods ii–iv for determining the IOM pool size in soils at 2 different experimental sites. A further objective of this study was to assess the influence of anthropogenic, fossil carbon input on the amount of IOM calculated with the 3 quantification methods and on the ability of RothC to predict SOC dynamics. The sites chosen for these investigations were located in a highly industrialized area with significant contributions of fossil-fuel-derived carbon to soil organic matter and in a rural area with minor anthropogenic contamination. To identify the influence of the anthropogenic carbon admixture, we simulated the development of bulk SOC stocks (including carbon from fossil fuels) and of plant-derived SOC using RothC. The latter was done by predicting the accumulation of carbon from C_4 crops in a soil previously cultivated with C_3 plants and by comparing the result with measured data. The proportion of C_4-derived carbon in total SOC was determined by natural ^{13}C labeling (Balesdent et al. 1987), i.e. through the different stable isotopic composition of C_3 and C_4 plants. In all simulations, the annual carbon input was determined through the measured crop yields.

MATERIALS AND METHODS

Study Sites and Soil Sampling

Soil samples were taken from the plough horizon of 2 agricultural long-term study sites in Germany. The site at Halle (55°31′N, 11°60′E) is located in a region strongly influenced by open-cast lignite mining, using, and processing industries. The site is 110 m asl and the mean annual precipitation and temperature are 465 mm and 9.2 °C, respectively. The Halle soil is a Haplic Phaeozem derived from sandy loess consisting of about 70% sand, 20% silt, and 10% clay (Merbach et al. 1999). Soil samples were taken in 2000 from the plough horizon (0–25 cm) of 2 trials, one continuously cultivated with rye since 1878 and the other changed into maize cultivation in 1961. On both cultures, most of the straw was removed from the field after harvest and maize was used for silage, resulting in a relatively low carbon input. The trials investigated received mineral fertilizer (NPK) with annually about 40 kg nitrogen (N) per hectare (ha) until 1991, and 60 kg N ha^{-1} yr^{-1} in the following years. A soil sample analyzed for ^{14}C was collected on an unfertilized rye plot in 0–25 cm depth. $\delta^{13}C$ values were measured in archived soil samples collected in 1- to 2-yr intervals between 1961 and 1978 and from 1990 until 2000 (Ludwig et al. 2003).

The study site at Rotthalmünster (48°21′N, 13°11′E) is 362 m asl and located in a rural area with low pollution from anthropogenic sources. Mean annual precipitation and temperature are 886 mm and 8.7 °C, respectively. The soil is a Haplic Luvisol derived from loess consisting of 10% sand, 73% silt, and 17% clay. Soil samples from the Rotthalmünster site were taken from 0–30 cm depth in 2002. Two trials were sampled: 1) a continuous maize culture since 1979, formerly cultivated with grassland (until 1960) followed by different C$_3$ crops (1961–1970) and wheat (1971–1978); and 2) a continuous grassland. The maize culture received mineral NPK fertilizer with a mean annual nitrogen application between 1971 and 2001 of about 180 kg N ha^{-1} (Schnellhammer and Sirch 2002). On both cultures, most of the straw was left on the field after harvest.

Carbon Isotope Analysis

Soil samples were air-dried and sieved (<2 mm) and the fraction >2 mm was removed. For $\delta^{13}C$ analysis, samples were acidified with HCl and dried subsequently. ^{14}C measurements were done on untreated soil from Halle containing no carbonates, and on soil from Rotthalmünster treated with 1% HCl for 8 hr, which was removed by freeze-drying.

The stable carbon isotopic composition was measured with a continuous-flow isotope ratio mass spectrometer (Delta^{PLUS}, Finnigan Mat, Bremen, Germany) coupled to an elemental analyzer (EA 1108 and NA 2500 from Fisons, Milan, Italy). $\delta^{13}C$ values of soil samples $(^{13}C/^{12}C)_{sample}$ were calculated relative to standard (VPDB) carbonate $(^{13}C/^{12}C)_{standard}$ as:

$$\delta^{13}C \text{ (‰ VPDB)} = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1] \times 1000 \qquad (1)$$

The proportion of C$_4$-derived carbon (f) in soil samples was determined from the difference in $\delta^{13}C$ between the soil collected in the maize trial (δ_{C4soil}) and a reference soil kept under the initial C$_3$ vegetation (δ_{C3soil}) relative to $\delta^{13}C$ values of C$_4$ ($\delta_{C4plant}$) and C$_3$ plants ($\delta_{C3plant}$). According to Balesdent and Mariotti (1996), the proportion of C$_4$-derived carbon (f) is:

$$f = (\delta_{C4soil} - \delta_{C3soil})/(\delta_{C4plant} - \delta_{C3plant}) \qquad (2)$$

[14]C was measured by accelerator mass spectrometry (AMS). Dried soil samples were combusted (900 °C, 4 hr) in sealed quartz tubes together with copper oxide and silver wool (Nadeau et al. 1998). The resulting CO_2 was reduced to graphite with a 10% excess of hydrogen (600 °C, 3 hr) over an iron catalyst (Nadeau et al. 1998). [14]C values were calculated from the measured ^{14}C/^{12}C ratios of the sample and the oxalic acid standard according to Stuiver and Polach (1977).

Structure of RothC and Input Variables

RothC 26.3 is described in detail by Coleman and Jenkinson (1999). The model consists of 4 active organic matter pools and 1 passive compartment. The active pools receive carbon from the crop residues added to the soil each year. The carbon input is partitioned between the decomposable plant material (DPM) and resistant plant material (RPM) by a predefined ratio depending on vegetation type. We used a DPM:RPM ratio of 1.44 as suggested by Coleman and Jenkinson (1999), which is valid for most crops and for grassland. DPM and RPM decompose by a first-order process at different rates to CO_2 and humified organic matter (HUM), and enter the microbial biomass carbon fraction (BIO). HUM and BIO decompose to produce CO_2 and to form more HUM and BIO. The inert organic matter (IOM) pool is set to a mean residence time of 50,000 yr and thus does not interact with the active pools. The decomposition rate constants of the active compartments (in yr^{-1}) are 10.0 (DPM), 0.3 (RPM), 0.66 (Cmic [microbial carbon]), and 0.02 (HUM) (Coleman and Jenkinson 1999). Decomposition rates are defined as functions of soil and climate conditions, namely soil cover, clay content, monthly air temperature, precipitation, and evaporation. Major input variables for RothC are summarized in Table 1.

Table 1 Input variables for RothC. Clay content, bulk density (BD), organic carbon (Corg), and ^{14}C content of the surface soil at Halle and Rotthalmünster.

Site	Culture	Soil cover	Depth (cm)	Clay (%)	BD (g cm^{-3})	Corg (kg m^{-2})	[14]C (‰)
Halle	Rye	Nov–Aug	25	10	1.44	5.36[a], 4.94[b]	–458.4 ± 4.5[c]
Halle	Maize	May–Sept	25	10	1.44	4.79[b]	—
Rotthalmünster	Wheat	Nov–Aug	30	17	1.38	5.20[d]	—
Rotthalmünster	Maize	May–Sept	30	17	1.38	5.35[d]	47.5 ± 3.1[e]
Rotthalmünster	Grass	Jan–Dec	30	17	1.41	6.01[d]	—

[a]Sampled in 1963–1967 (Merbach et al. 1999).
[b]Sampled in 1998 (Ludwig et al. 2003).
[c]Sampled in 2000.
[d]Sampled in 2002 (John 2003).
[e]Sampled in 2005 (0–20 cm depth).

Carbon Input Calculation via Crop Yields

The annual carbon input from plants was determined through the measured grain yields as follows. Following Flessa et al. (2000), we assumed the carbon content of grain to be 45%, the grain-straw ratio 1.0, the (stubble and roots):(aboveground yield) ratio 0.2 for maize (Balesdent and Balabane 1992), and 0.4 for rye and wheat (Skjemstadt et al. 2004). RothC requires the total amount of carbon added to the soil including carbon from rhizodepositions on a monthly or annual basis. The latter was considered by multiplying the carbon input from root residues with 0.3 for maize (J Augustin, personal communication) and 0.5 for rye and wheat (Kuzyakov and Domanski 2000). At the Halle site, we calculated a total carbon input of 0.12 kg C m^{-2} yr^{-1} from rye and 0.1 kg C m^{-2} yr^{-1} from maize. For the trial at Rotthalmünster, we used a carbon input from grass of 0.39 kg C m^{-2} yr^{-1} until

1960. Since no harvest yields were determined for the grassland, this value was determined by optimizing to the measured SOC contents (Ludwig et al. 2005). For the following cultivation with different C_3 crops (1961–1978), including wheat (1971–1978), we used 0.27 kg C m^{-2} yr^{-1} obtained from the estimation of Ludwig et al. (2005) plus carbon from root exudates calculated as described above and resulting in a total carbon input of 0.31 kg m^{-2} yr^{-1}.

Modeling of Soil Carbon Dynamics with RothC

RothC was used for the simulation of changes in organic carbon stocks in the plough horizon at Halle (0–25 cm) and Rotthalmünster (0–30 cm). The model has been applied to these sites previously (Ludwig et al. 2003, 2005), although in these studies ^{14}C data and plant inputs including rhizodepositions were not considered as in our simulations described below.

At Halle, we simulated the buildup of plant-derived organic carbon from maize cultivation (C_4) started in 1961 on a former continuous rye culture (C_3), as well as changes in total organic carbon stocks between 1961 and 1998. For these calculations, RothC was initialized in 3 ways:

1. *Model A (IOM via SOC)*: The equation proposed by Falloon et al. (1998) was used to calculate the amount of IOM (C_I) from bulk SOC data (C_t).

$$C_I = 0.049C_t^{1.139} \tag{3}$$

   In the surface soil of the maize trial at Halle, 0.4 kg C m^{-2} of the total organic carbon (4.79 kg C m^{-2}) was inert. For modeling SOC dynamics, the IOM pool size in RothC was set to this value and initial sizes of the active pools at the start of the maize (C_4) experiment in 1961 were calculated by first running the model until equilibrium was reached. We assume steady-state conditions in the soil of the rye culture that was established in 1878. The buildup of carbon from maize cropping between 1961 and 1998 was then modeled by replacing the C_3 input with that from C_4 crops and setting the amount of carbon in the 4 active pools to 0—i.e. in 1961, SOC contains no C_4-derived carbon.

2. *Model B (IOM via BPCAs)*: IOM was set to the amount of black carbon—as an important fraction of resistant organic matter—that was quantified by BPCA analysis (Brodowski et al. 2005). The amount of black carbon/IOM in the Halle surface soil with maize cultivation was 0.69 kg C m^{-2}. Initial sizes of the active pools in RothC were calculated as in the description of Model A.

3. *Model C (IOM via ^{14}C)*: In this simulation, the amount of IOM was determined through the ^{14}C concentration of the bulk soil ($^{14}C_{measured}$), assuming SOC is a mixture of ^{14}C-free (X) and recent organic carbon ($^{14}C_{recent}$) by mass balance calculation:

$$X = [1 - (^{14}C_{measured} / {}^{14}C_{recent})] \times 100 \tag{4}$$

   The ^{14}C concentration of recent plant material in the soil ($^{14}C_{recent}$) had to be estimated because the plant material entering the soil each year is derived from atmospheric CO_2 of that year's growing season, which has changed drastically in ^{14}C level between 1954 and today due to the release of bomb-^{14}C, and also because the plant residues undergo decomposition. This correction was done using RothC, which includes the atmospheric ^{14}C record, and by running the decomposition model with similar input data as in the modeling of SOC dynamics. As no ^{14}C value was available for the fertilized maize culture, we used the concentration measured in the unfertilized rye soil of –458.4‰ (54.5 pMC) in 2000. This is a reasonable assumption because

the 2 trials are on the same field next to each other and they receive nearly similar carbon inputs from both crops. The model was run for the period from site establishment in 1878 until sample collection in 2000, using a short-term calculation and the bomb-^{14}C curve in RothC. A similar carbon input from rye as in the simulation of SOC dynamics was used. [14]C_{recent} thus determined was 132.7‰ (114 pMC). The amount of IOM determined with Equation 4 was 2.05 kg C m^{-2}.

We tested the models A to C at the second study site in the rural area of Rotthalmünster by predicting the decrease of "old" C_3-derived carbon in a continuous grassland soil, which was converted into maize (C_4) cultivation in 1979, as well as changes in total SOC in the same trial. Again, initial sizes of the active compartments in RothC were calculated by running the model until equilibrium and assuming steady-state conditions under permanent grassland (until 1960). The change into C_3 crops in 1961 was considered by a short-term calculation with 0.31 kg C m^{-2} yr^{-1} wheat input until 1978. Changes in C_3-derived carbon stocks after the conversion of this trial into C_4 (maize) cultivation were then simulated by setting the C_3 carbon input to 0. The amount of IOM used in Model A was 0.46 kg C m^{-2} (8.5% of SOC), determined via the SOC content (Equation 3), and 0.25 kg C m^{-2} (4.6% of SOC) in Model B, quantified by BPCA analysis. In Model C, IOM was determined via the ^{14}C concentration of 47.5‰ (105.4 pMC) measured in the surface soil under maize cultivation in 2005. [14]C contents of surface soil organic matter were not significantly influenced by soil cultivation as indicated by a previous study on soil fractions from this site (Rethemeyer et al. 2005), which justifies the use of this value instead of one for steady-state conditions under grassland. The average ^{14}C value ([14]C_{recent}, Equation 4) of the carbon input from different C_3 plants until 1978 (grass until 1960 followed by various C_3 crops including wheat) and from maize since 1979 (C_4) was calculated by running RothC using a sequence of short-term calculations including the bomb-^{14}C curve. The value of [14]C_{recent} thus determined was 104.1‰ (111 pMC), and the IOM determined with Equation 4 was 0.27 kg C m^{-2} of total SOC (5.33 kg C m^{-2}).

RESULTS AND DISCUSSION

Quantification of Inert Organic Matter

Figure 1 shows the amount of inert organic matter and black carbon, respectively, in the plough horizon of the experimental sites at Halle and Rotthalmünster. IOM estimation through bulk SOC content as suggested by Falloon et al. (1998) gave nearly similar quantities of 8.4% and 8.5% (0.4 and 0.46 kg inert C m^{-2}), respectively for Halle and Rotthalmünster, since both soils have comparable organic carbon contents (Table 1). The small portion of IOM determined for the Halle soil is in opposition to the very low ^{14}C concentration of –458.4‰, which equals a ^{14}C age of 4880 yr. It reflects either extremely large amounts of stabilized SOC—unrealistic for agricultural surface soils—or the contribution of fossil-fuel-derived carbon to soil organic matter. Previous studies revealed high inputs of fossil carbon from lignite mining and from surrounding industries and power plants at this and nearby sites (Schmidt et al. 1996; Rethemeyer et al. 2004). The Falloon equation thus seems limited in its applicability for estimating IOM in soils containing fossil carbon, which is confirmed by the modeling result discussed below.

The IOM pool size quantified by the ^{14}C concentration of bulk soil organic matter reflects that 52.2% (2.05 kg C m^{-2}) of total organic carbon in the Halle soil is of fossil origin. This is very high but realistic because of the site's location in a highly industrialized area. Schmidt et al. (1996) reported even higher amounts of 51% to 97% coal-derived carbon in particle-size fractions from a surface soil in this region. At Rotthalmünster, a small portion of 5.2% (0.28 kg C m^{-2}) carbon of total SOC is inert or ^{14}C-free. However, the nearly modern ^{14}C concentration of the plough horizon
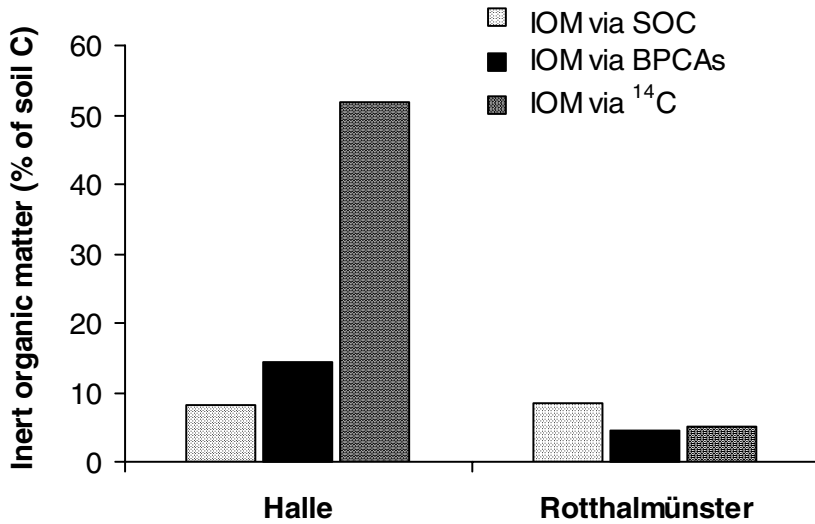
Figure 1 Percentage of inert organic matter (IOM) and black carbon in soils with maize cultivation at Halle (0–25 cm) and Rotthalmünster (0–30 cm). IOM was quantified via total soil organic carbon (SOC; Equation 3), by analysis of benzene polycarboxylic acids (BPCAs) as an indicator for black carbon, and by mass balance calculation via bulk soil ^{14}C (Equation 4).

and the location of the site in a rural area question the contribution of carbon from fossil fuels to the soil at this rural site.

Based on the BPCA method (Brodowski et al. 2005), the proportions of black carbon in the topsoil at Halle and Rotthalmünster were estimated at 14.8% and 4.5% (0.69 and 0.25 kg C m^{-2}), respectively (Brodowski et al. 2007). For the Halle soil, the amount of black carbon determined via BPCA analysis was considerably smaller than the proportion of fossil carbon estimated via ^{14}C. We attribute this discrepancy between both IOM estimates to differences between the 2 approaches. The BPCA method relies on the assumption that only the highly condensed aromatic carbon of charred organic material, which can be converted to BPCAs, contributes to IOM. In contrast to the ^{14}C-based estimation, non-charred organic substances that do not yield BPCAs (Glaser et al. 1998) are not considered. This is indicated by the low black carbon/IOM estimate for the Halle soil, suggesting that a relatively small proportion of coal-derived fossil carbon is highly aromatic, charred material and a considerable portion are non-combusted lignite particles. Furthermore, an arbitrary conversion factor is used to estimate the amount of black carbon in these soils by multiplying the BPCA yield by 2.27 as suggested by Glaser et al. (1998). Since this conversion factor varies between different black carbon types, the true black carbon content might be slightly higher (Brodowski et al. 2005). At Rotthalmünster, ^{14}C and BPCA analyses gave nearly similar small IOM values. At this rural site, the contribution of carbon from fossil fuels is considered negligible, which is indicated by the nearly modern ^{14}C concentration of bulk soil organic matter (47.5‰). This result suggests that the major source of old, refractory organic carbon in this soil is ancient, charcoal-derived black carbon, which was also suggested by Brodowski et al. (2007) comparing BPCA patterns in Halle and Rotthalmünster soils.

Simulation of Plant-Derived and Total Organic Carbon Dynamics in Halle Soil

- *Model A (IOM via SOC)*: The small amount of 0.4 kg C m^{-2} IOM (8.4% of total SOC) used in this model, which was determined with Equation 4 proposed by Falloon et al. (1998), resulted

in a rapid increase and a considerable overestimation of C_4-derived carbon from maize cultivation started in 1961. In 1998, 25.2% of total SOC originated from C_4 crops compared to the measured value of 15.4% (Figure 2). Similarly, the predicted total SOC stocks shown in Figure 3 obtained with this approach were about 0.7× smaller than measured carbon contents. The small IOM estimate calculated with the Falloon equation disagrees with the low ^{14}C concentration of the Halle soil that mainly results from a high admixture of fossil carbon to soil organic matter (Rethemeyer et al. 2004; Wiesenberg et al. 2004). This result shows that the Falloon equation cannot be applied if soils contain large amounts of fossil carbon.

- *Model B (IOM via BPCAs)*: In Halle, the amount of highly aromatic black carbon as measurable refractory carbon pool was only little higher than the IOM value used in Model A. Hence, the simulated buildup of C_4-derived carbon from maize cultivation is almost similar to the curve of Model A, with 22.8% carbon from C_4 crops in 1998, and does not agree with the measured data. Because the BPCA method only detects highly aromatic compounds, it is of limited applicability in soils with large portions of non-aromatic, presumably refractory carbon from uncharred fossil fuels.

- *Model C (IOM via ^{14}C)*: The amount of IOM in the Halle soil (2.05 kg C m^{-2}) quantified via bulk soil ^{14}C and a mass balance (Equation 4) is about 5× higher than in Model A. The simulation with RothC gave an amount of organic carbon from maize (C_4) cultivation of 16.5%, which is close to the measured value of 15.4% (both in 1998). Figure 3 shows a good agreement of modeled and measured total SOC stocks using ^{14}C for the calculation of IOM. The variability of the measured SOC contents is mainly caused by anthropogenic influences. A decrease in SOC between 1965 and 1976 results from a change in ploughing depth from 20 to 25 cm around 1970, and the following variation between 1985 and 1995 can mainly be attributed to variability in lignite usage (Merbach et al. 2000).
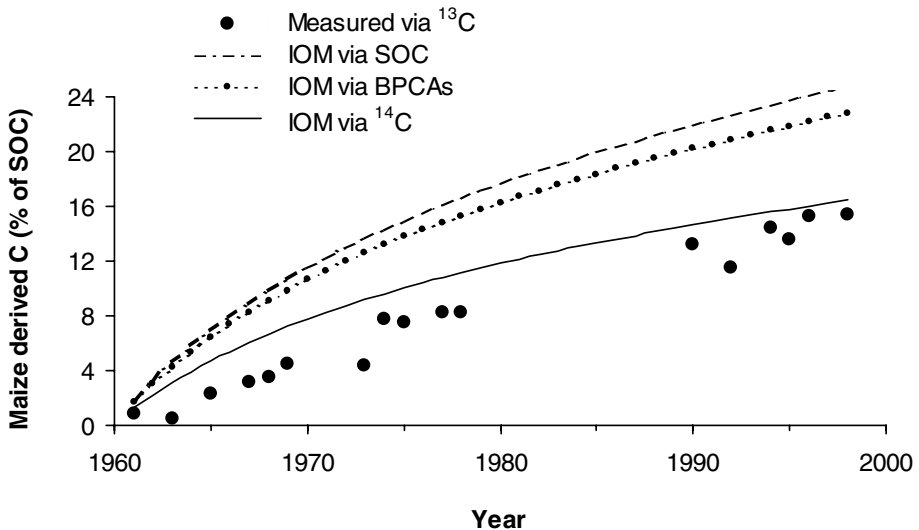

Figure 2 Accumulation of maize (C_4)-derived carbon in Halle soil, calculated from ^{13}C values (circles, Equation 2), and modeled with RothC (lines). Annual carbon inputs were determined via the crop yields and IOM via total soil organic carbon (SOC, Model A), benzene polycarboxylic acids (BPCAs, Model B), and ^{14}C of SOC (Model C).

The fossil carbon contribution to the Halle soil reveals difficulties in the different approaches for estimating the amount of IOM and errors in the SOC dynamics simulated with RothC. A problem of ^{14}C as an indicator for IOM (Model C) is that variable ^{14}C concentrations of bulk soil over time will give different amounts of IOM, and thus different predictions of SOC stocks. The errors mainly result from the fact that soil organic matter at Halle is a mixture of natural, plant-derived plus anthropogenic, fossil-fuel-derived organic carbon. Consequently, RothC, which was designed for natural systems, considerably underestimates the turnover of natural, plant-derived organic carbon because of the large amount of IOM derived from low soil ^{14}C values. To eliminate the fossil carbon from the simulation, while accounting for natural aging of SOC and natural IOM, ^{14}C concentrations of archived soil samples collected before the beginning of the extensive lignite combustion are required for the calculation of IOM using Equation 4. Unfortunately, such samples were not available at the Halle site. The lignite admixture in the Halle soil is either not (Method A) or only partly (Laskov et al. 2002; Method B) accounted for in the IOM estimation. As a result of the smaller IOM estimates, the simulated development of total SOC stocks are much lower than the measured data (Figure 3). Natural ^{13}C abundance was used to quantify the accumulation of plant-derived carbon from C_4 crops that were grown on a former C_3 culture (Equation 2). We believe that the results are strongly influenced by the continuous (until about 1990) addition of C_3 carbon from lignite diluting the δ^{13}C signal of the C_4 vegetation. Thus, the enrichment of C_4-derived carbon within 40 yr since vegetation change in Halle is considerably underestimated. These findings suggest that results of natural ^{13}C labeling can only be used as validation data in uncontaminated soils.
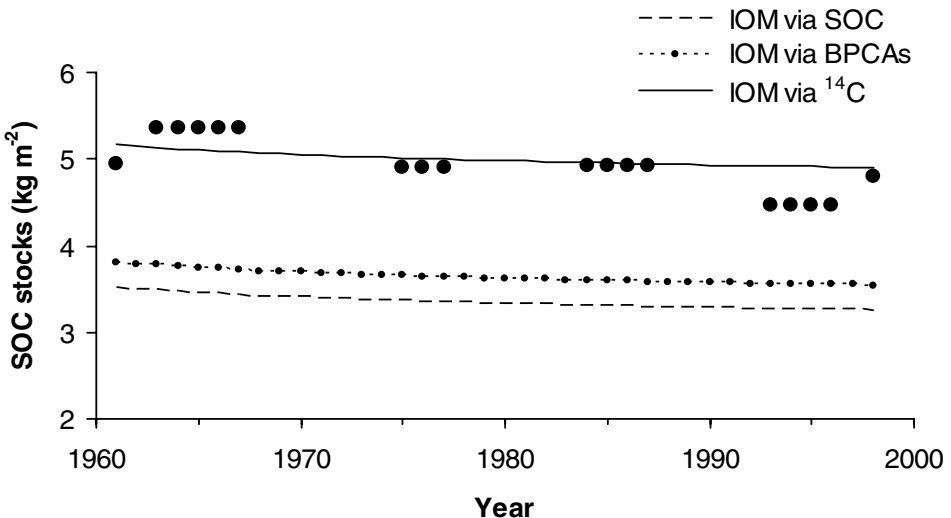

Figure 3 Measured (circles; Merbach et al. 1999; Ludwig et al. 2003) and modeled (lines) changes in soil organic carbon (SOC) stocks in the maize cultivated Halle soil (0–25 cm). Three different simulations were applied, including annual carbon input estimates from measured grain yields and IOM determined via SOC (Model A), by BPCA analysis (Model B), and through bulk soil ^{14}C (Model C). The large differences in SOC stocks at the start of the maize trial in 1961 result from the different IOM pool sizes used for the calculation of steady-state conditions until 1960.

Prediction of C_3-Derived and Total Carbon Turnover in Rotthalmünster Soil

We applied models A, B, and C for estimating the amount of IOM at our second study site in Rotthalmünster, which is located in a rural area far from industry and traffic. At this site, the decline of

C_3-derived carbon in a soil that has been changed into C_4 cultivation was simulated (Figure 4). Since no archived soil samples were available at Rotthalmünster, we assumed the SOC content of 6.01 kg C m^{-2} of the adjacent grassland (C_3) to represent the initial steady-state conditions at the start of the maize (C_4) trial in 1979, because previous long-term cultivation was grassland. Similar to the Halle site, the initial size of the active pools was determined by running RothC until equilibrium. All models were quite successful in matching the measured amount of organic carbon in 2002 (3.44 kg C m^{-2}) because the IOM estimated via SOC (0.46 kg m^{-2}), BPCAs (0.25 kg m^{-2}), and ^{14}C (0.27 kg m^{-2}) was not very different.

This result, in comparison with findings for the Halle soil, suggests that IOM can only be determined from organic carbon contents and by BPCA analysis (models A and B) in soils containing no fossil-fuel-derived carbon. The ^{14}C approach (Model C) seems useful for soils with different properties including those with fossil carbon contributions and a consequently larger IOM pool. This, however, leads to an incorrect prediction of plant-derived SOC stocks and turnover rates.
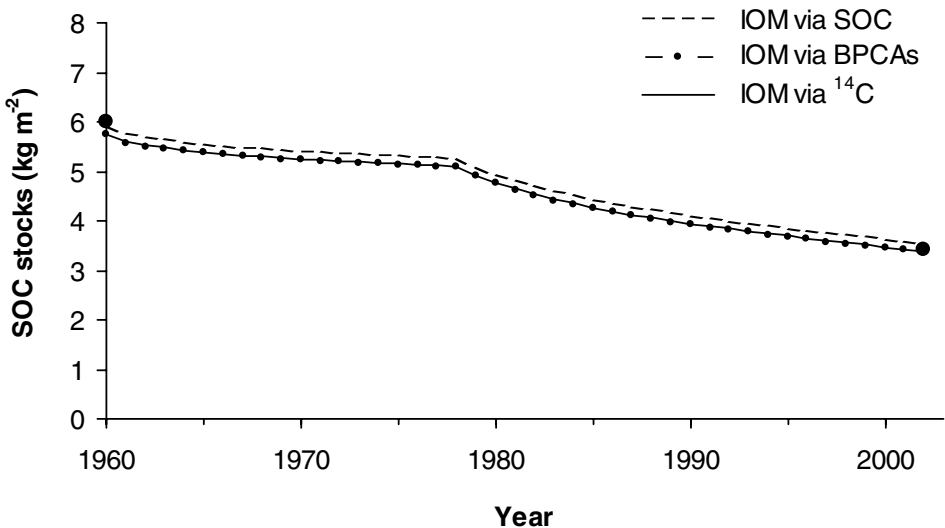

Figure 4 Measured (symbols) and modeled (lines) decline of soil organic carbon (SOC) from C_3 crops (grass and wheat) in Rotthalmünster soil (0–30 cm), after conversion into C_4 cultivation (maize). IOM was determined with models A (via SOC), B (via BPCAs), and C (via ^{14}C).

CONCLUSIONS

We used RothC for the simulation of organic carbon dynamics in soils comprising mainly recent organic matter and containing a high portion of carbon from fossil fuels. The amount of IOM required for initializing the model was determined via 3 different approaches, and the carbon input from plants was calculated from the measured crop yields. A comparison of simulated and measured SOC stocks in both soils showed that IOM assessment via SOC cannot be applied if soils contain large amounts of fossil carbon. The anthropogenic admixture of presumably recalcitrant carbon is not included in the IOM estimate, resulting in a considerable underestimation of SOC stocks by RothC. Similarly, black carbon determined by BPCA analysis can only be used as an indicator for IOM in soils with a low input of non-aromatic organic compound from fossil fuels, such as non-charred coal dust. In contrast, the estimation of IOM via the ^{14}C concentration of bulk soil organic matter and using a mass balance calculation was successful for both soils, and predicted SOC con-

tents nearly matched the measured data. Although ^{14}C data of bulk soil seem useful for initializing RothC irrespective of soil properties, the results obtained for soils with high admixtures of fossil carbon may be misinterpreted, since SOC stocks reflect the mixture of natural and anthropogenic carbon sources.

The dynamic of natural, plant-derived carbon was investigated by natural ^{13}C labeling. The comparison of the measured and modeled accumulation of carbon from C$_4$ crops in the lignite-contaminated soil revealed both data sets were influenced by the anthropogenic carbon source. Because of the continuous addition of C$_3$ carbon from lignite, the amount of carbon from C$_4$ crops was considerably underestimated by the natural ^{13}C abundance method. Only 15% of total SOC was derived from C$_4$ crops 40 yr after the vegetation change from C$_3$ into C$_4$ cultivation. When subtracting the amount of fossil carbon quantified through the ^{14}C concentration of bulk SOC, a much higher value of 27% carbon from C$_4$ crops is obtained, which corresponds well with data for the uncontaminated site. We thus conclude that natural ^{13}C labeling can only be used as validation data or for quantifying active C pools in RothC in soils not contaminated with carbon from fossil fuels.

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