Thermal stability of soil organic matter pools and their $\delta^{13}C$ values after $C_3$–$C_4$ vegetation change

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Abstract

Carbon isotopic composition of soils subjected to $C_3$–$C_4$ vegetation change is a suitable tool for the estimation of C turnover in soil organic matter (SOM) pools. We hypothesized that the biological availability of SOM pools is inversely proportional to their thermal stability. Soil samples from a field plot with 10.5 years of cultivation of the $C_4$ plant Miscanthus × giganteus and from a reference plot under $C_3$ grassland vegetation were analysed by thermogravimetry coupled with differential scanning calorimetry (TG-DSC). According to differential weight losses (dTG) and energy release or consumption (DSC), five SOM pools with increasing thermal stability were distinguished: (I) $20–190^\circ C$, (II) $190–310^\circ C$, (III) $310–390^\circ C$, (IV) $390–480^\circ C$, and (V) $480–1000^\circ C$. Their $\delta^{13}C$ values were analysed by EA-IRMS. The weight losses in pool I were connected with water evaporation, since no significant C losses were measured and $\delta^{13}C$ values remained unchanged. The $\delta^{13}C$ of pools II and III in soil samples under Miscanthus were closer to the $\delta^{13}C$ of the Miscanthus plant tissues ($/C_0$ 11.8%) compared to the thermally stable SOM pool V ($/C_0$ 19.5%). The portion of the Miscanthus-derived $C_4$-C in total SOM in 0–5 cm reached 55.4% in the 10.5 years. The $C_4$-C contribution in pool II was 60% and decreased down to 6% in pool V. The mean residence times (MRT) of SOM pools II, III, and IV were similar (11.6, 12.2, and 15.4 years, respectively), while pool V had a MRT of 163 years. Therefore, we concluded that the biological availability of thermal labile SOM pools ($<480^\circ C$) was higher, than that of the thermal stable pool decomposed above 480 °C. However, the increase of SOM stability with rising temperature was not gradual. Therefore, the applicability of the TG-DSC for the separation of SOM pools with different biological availability is limited.

Keywords: $C_3$–$C_4$ vegetation change; Miscanthus × giganteus; Differential scanning calorimetry; Thermogravimetry; TG-DSC; Thermal stability; $\delta^{13}C$; Soil organic matter

1. Introduction

Carbon (C) isotopic composition of soil organic matter (SOM) after $C_3$–$C_4$ vegetation change (and vice versa) has been frequently used in the last decade to estimate C turnover rates in soil and the incorporation of new C in various SOM pools (Balesdent and Mariotti, 1987; Volkoff and Cerri, 1987; Ludwig et al., 2003; John et al., 2003, 2005; Kristiansen et al., 2005). This approach is based on the different stable isotope composition (represented as $\delta^{13}C$ value) of residues from plants with $C_3$ and $C_4$ photosynthesis (Farquhar et al., 1989; Ehleringer and Cerling, 2002). After $C_3$–$C_4$ vegetation change the $\delta^{13}C$ value of SOM starts to change slowly from the original $\delta^{13}C$ value, which is closer to that of $C_3$ vegetation, to a new steady-state $\delta^{13}C$ value, which is closer to that of $C_4$ vegetation. When the new steady state is not reached (as in most studies) and the period after vegetation change (the period after $C_3$–$C_4$ vegetation change is known, the contribution of the new $C_4$-derived C to the total SOM can be calculated. Based on this $C_4$-C contribution and the period after vegetation change, the SOM turnover rates can be roughly estimated (Balesdent and Mariotti, 1996).
Nearly all investigations using $^{13}$C natural abundance have been conducted with maize (Balesdent and Balabane, 1996; Ludwig et al., 2003; Kristiansen et al., 2005). In Europe another C$_4$ plants—*Miscanthus × giganteus* (Greef et Deu.)—is successfully cultivated as a bio-energy crop (Beuch, 2000). This perennial C$_4$ plant can be cultivated from 15 up to 25 years without replanting and is harvested yearly, often in the following spring to reduce ash contents. The first results of C turnover for *Miscanthus*, based on $^{13}$C natural abundance showed a higher contribution of *Miscanthus* C to the SOM than maize (Kao, 1997; Hansen et al., 2004).

As the estimation of the $\delta^{13}$C values of bulk SOM is not very informative, various fractionation techniques including density (Magid et al., 2002; John et al., 2005) and particle size fractionation (Jolivet et al., 2003; Ludwig et al., 2003), as well as sequential extractions (Ellerbrock and Kaiser, 2005) were combined with the $\delta^{13}$C analyses. One of the other methods suitable for SOM fractionation is based on thermal stability (Leinweber and Schulten, 1992; Siewert, 2001, 2004; Lopez-Capel et al., 2005; Plante et al., 2005). Thermal analysis by thermogravimetry coupled with differential scanning calorimetry (TG-DSC) involves a slow continuous temperature increase that leads to the progressive decomposition (mainly oxidation) of different organic compounds according to their thermal stability. Such a temperature increase coupled with the measuring of weight losses is termed thermogravimetry (TG). Energy released or consumed by the decomposition of organics is measured, simultaneous to the temperature increase, by differential scanning calorimetry (DSC).

Thermal analysis curves and heat fluxes provide important information on the structural composition of SOM (Provenzano and Senesi, 1999; Dell’Abate et al., 2002; Kuzyakov et al., 2006). The exothermic degradation of aliphatic and carboxyl groups at different temperatures was suggested to compare the proportions of labile and more stable components in SOM pools and whole soil (Brown, 1988; Siewert, 2001; Lopez-Capel et al., 2005).

The availability to microbial decomposition is an important characteristic of the SOM quality, which in turn allows to predict the transformation and turnover time of carbon in terrestrial ecosystems. Based on correlations between thermal stability of SOM pools in various temperature ranges and the CO$_2$ production by classical soil incubations, Siewert (2001) suggested that the thermal stability of SOM pools can be related to their biological degradability. It assumes that SOM pools decomposable at lower temperatures are more biologically accessible and utilizable compared to organics, which are decomposed at higher temperatures. However, the hypothesis of relation between the thermal stability of SOM pools and their availability to microbial mineralization was mainly supported by correlations between CO$_2$ evolution and thermogravimetical weight losses (Siewert, 2001) and, to the best of our knowledge, has never been tested by direct methods.

Thus, the aim of our study was to test the hypothesis of close connection between thermal degradability and biological stability by comparing $\delta^{13}$C values of SOM pools decomposed at increasing temperature in the soil after the vegetation changed from former C$_3$ grassland to C$_4$ plant *Miscanthus × giganteus*. If the hypothesis is true, then the thermally labile SOM pools would have $\delta^{13}$C values closer to the new vegetation compared to thermally stable SOM pools and the mean residence time (MRT) of labile pools would be shorter than those of stable ones.

The preliminary study testing this approach showed weak correlation between thermal and biological degradability when only three SOM pools were separated by TG-DSC (Kuzyakov et al., 2006). However, the preliminary study was insufficient for exact conclusions because of three reasons: (i) the absence of the reference soil developed solely under C$_3$ vegetation did not allow for estimation of the isotopic fractionation of C by thermal decomposition and by incorporation of C into pools with different thermal stability. So, in the absence of the reference soil the calculation of the MRT of the SOM pools was not possible; (ii) only three temperature ranges were separated; one of them was responsible for water evaporation and did not affect the $\delta^{13}$C values; (iii) the fast rate of temperature increase (5°C min$^{-1}$) during TG-DSC analysis in preliminary study led to some overlapping of pools with different thermal stability and therefore, did not allow their clear separation.

In the present study, the above-mentioned deficiencies were considered and therefore, the reference soil under grassland (solely C$_3$) was included into the experiment and the heating rate (2°C min$^{-1}$) was greatly reduced. This allowed for the better separation of the pools, especially those decomposed under high temperature. The inclusion of the reference soil in the experiment design allowed for the calculation of MRT.

2. Materials and methods

2.1. Soil samples

Soil samples were taken from the long-term experimental field located in Stuttgart-Hohenheim, Baden-Wuerttemberg, Germany (48°43’ north latitude, 9°13’ east longitude). The soil on the plot with *Miscanthus* and reference plot was a loamy Gleyic Cambisol (WRB, 1998) without carbonates (no reaction with HCl). The soil properties under *Miscanthus* were: pH 5.6, bulk density 1.1 g cm$^{-3}$, C$_{org}$ 2.13%, N$_{tot}$ 0.18%, C-to-N ratio 12.0. The properties of the reference soil were: pH 6.3, bulk density 1.3 g cm$^{-3}$, C$_{org}$ 1.62%, N$_{tot}$ 0.18%, C-to-N ratio 9.1. Mean annual temperature is 8.7°C and average rainfall 680 mm year$^{-1}$ (mean 1961–1990, meteorological station Stuttgart-Hohenheim).

The *Miscanthus × giganteus* (Greef et Deu) was planted on May 24, 1994 on a former grassland plot. The above-ground standing biomass of the *Miscanthus* has been
were carried out simultaneously using the NETZSCH STA analysis. 2.2. Thermogravimetry–differential scanning calorimetry and the soil was ball milled (MM2, Fa Retsch) for 15 s. and plant remains were carefully removed with tweezers size). After that, from a sub-sample of 5 g, all visible roots were air-dried at room temperature and sieved (2 mm mesh 0–5 cm layer of the Ah horizon was used. The soil samples diameter 6 cm) to a depth of 5 cm. So, only the upper 6 months. Soil samples were taken with a soil corer (inner cultivation period at the time of sampling was 10 years and the reference plot. The samples were taken from individual points with the distant of 5–10 m from each other. The the reference soil with continuous C3 vegetation; [d13C]b, [13C] is the amount of C in the bulk soil without combustion; [d13C]Cf, [13C]f, [13C]f2,…,[13C]f,n are the d13C values of the SOM pools after combustion up to the subsequent “threshold” temperature levels; Cf,1, Cf,2,…, Cf,n are the amounts of C in the SOM pools after combustion.

The portion of Miscanthus-derived C4-C in SOM (% C Miscanthus) was calculated according to Balesdent and Mariotti (1996) with the assumption of identical isotopic fractionation of the humification of C3 and C4 plant residues:

\[ \% C_{\text{Miscanthus}} = \frac{[d13C]_C - [d13C]_3}{[d13C]_4 - [d13C]_3} \times 100, \]  

where \([d13C]_C\) is the \(d13C\) value of the soil with Miscanthus; \([d13C]_3\) is the \(d13C\) value of the corresponding SOM fraction of the reference soil with continuous C3 vegetation; \([d13C]_4\) is the theoretical \(d13C\) value of a C4 soil developed solely under Miscanthus, calculated based on the \(d13C\) of the Miscanthus plant and corrected for isotopic fractionation during humification by the subtraction of the differences between \(d13C\) of C3 vegetation and \(d13C\) of the corresponding SOM fraction of the C3 soil. To calculate the annual contribution of new Miscanthus-derived C4-C in SOM and annual turnover rates (TR) of SOM, a simple exponential approach was selected (Balesdent and Mariotti, 1996):

\[ \text{TR} = -\frac{\ln (1 - (\% C_{\text{Miscanthus}}/100))}{\text{time}}, \]  

where time (years) is the cultivation period of Miscanthus and \(\% C_{\text{Miscanthus}}\) is the portion of C3-C that was replaced by C4-C derived from Miscanthus (Eq. (2)).

The MRT of Miscanthus-derived C4-C in bulk soil and in SOM pools was calculated as a reciprocal to the turnover rates (Gregorich et al., 1995).

The study was conducted with seven replications for Miscanthus soil samples and three replications for the reference soil. The significance of differences between \(d13C\), as well as the C content of different pools was examined using the two-way analysis of variance (ANOVA). The standard errors of means were presented on the figures and in the table as variability parameter.
3. Results

3.1. Thermal stability and differential scanning calorimetry analysis of the soil

The dTG clearly showed 3 maximums of weight losses at temperature increases (Fig. 1): (1) between 20 and 190 °C, (2) between 190 and 310 °C and (3) between 390 and 480 °C. The DSC traces were characterised by three temperature ranges, two with endothermic reactions: (1) from ambient temperature to 210 °C in soil under grassland and to 220 °C in soil under Miscanthus; (2) from 335 to 1000 °C in both reference soil and soil under Miscanthus; and one range with exothermic reactions between 210 or 220 and 335 °C (Fig. 1). The total weight losses of the soil under Miscanthus and the reference plot were 8.45% and 8.27%, respectively (Table 1). Assuming that the amount of SOM is 1.724 times higher than the C content (Post et al., 2001), then only 34.0% and 43.5% of the total weight losses at up to 1000 °C could be connected with the decomposition of SOM in the reference soil and soil under Miscanthus, respectively (Table 1).

No significant C losses were measured in both soils at the temperature of up to 190 °C, but samples weight decreased by about 0.71% (Table 1). It means that the weight losses in the temperature area up to 190 °C were mainly connected with water evaporation. This was also clearly proven by the negative values of DSC that showed endothermic reactions by water evaporation (Fig. 1.). Starting from 190 °C, the weight losses increased simultaneously with strong DSC increases. This was a clear evidence of energy release by the thermal decomposition of organic substances. The maximum weight losses and energy release occurred between 190 and 310 °C,

![Fig. 1. Differential thermogravimetry (dTG, left Y-axis) and Differential Scanning Calorimetry (DSC, right Y-axis) of reference soil under grassland and soil under Miscanthus. Cumulative losses (TG) are scaled to 100% of the left Y-axis and total cumulative losses amounted to 8.27% and 8.45% for reference soil and soil under Miscanthus, respectively. Negative DSC values represent energy consumption (endothermic reactions) and positive DSC values represent energy release (exothenmic reactions). Arrows show the “threshold” temperature chosen for SOM fractionation.](image_url)

<table>
<thead>
<tr>
<th>Temperature fraction (°C)</th>
<th>Weight losses (%)</th>
<th>C content (%)</th>
<th>SOM on total losses (%)</th>
<th>δ13C (% PDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref</td>
<td>Misc</td>
<td>Ref</td>
<td>Misc</td>
</tr>
<tr>
<td>20–1000b</td>
<td>8.27</td>
<td>8.45</td>
<td>1.62 ± 0.13</td>
<td>2.13 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.72</td>
<td>0 ± 0.05</td>
<td>0 ± 0.09</td>
</tr>
<tr>
<td>190–310c</td>
<td>2.62</td>
<td>2.68</td>
<td>0.49 ± 0.04</td>
<td>0.81 ± 0.05</td>
</tr>
<tr>
<td>310–390c</td>
<td>2.26</td>
<td>2.31</td>
<td>0.90 ± 0.03</td>
<td>1.14 ± 0.06</td>
</tr>
<tr>
<td>390–480c</td>
<td>1.41</td>
<td>1.44</td>
<td>0.22 ± 0.02</td>
<td>0.21 ± 0.01</td>
</tr>
<tr>
<td>480–1000b</td>
<td>1.12</td>
<td>1.30</td>
<td>0.03 ± 0.002</td>
<td>0.02 ± 0.001</td>
</tr>
</tbody>
</table>

LSD0.05 = 0.42, 0.17, 1.14

aSOM (%) was determined as multiplication of the amount of C (%) by 1.724.
bMeasured.
cCalculated by isotopic mass balance equation.
dThe least significant differences (P < 0.05) were calculated for two-way ANOVA: soil x temperature.
amounting to 30% of total weight losses (8.27% and 8.45%) for both reference soil under grassland and soil under Miscanthus. The maximal DSC values of 0.07 and 0.10 μV mg⁻¹ were measured at 290 °C in reference soil and in soil under Miscanthus, respectively (Fig. 1). However, the maximum weight losses did not correspond to the maximum SOM losses. According to the C losses at individual temperature ranges, the maximum SOM decomposition was observed in the temperature range between 310 and 390 °C, where the soil under Miscanthus lost 85.3% of SOM from mass losses of fraction and the losses of organic matter from the reference soil amounted to 68.8% (Table 1). The third maximum of mass losses was related to the temperature fraction from 390 to 480 °C (Fig. 1). About 27.4% and 25.7% of total weight losses in this temperature range corresponded to SOM decomposition in soil under grassland and soil under Miscanthus, respectively (Table 1). The weight and SOM losses by further temperature increase to above 480 °C were much slower than at below this temperature. At up to 1000 °C, the reference soil and soil under Miscanthus lost only 1.12% and 1.30% of weight. SOM losses amounted to 4.7% and 3.3% of the weight losses within the last temperature range for soils under grassland and Miscanthus, respectively (Table 1). The DSC curve switched into negative values after the temperature increased to 340 °C and above showing energy consumption.

### 3.2. C isotopic composition of SOM pools with different thermal stability

According to the thermal stability of the SOM, five temperature ranges were chosen for soil heating in the muffle oven for the subsequent isotopic analyses: (1) no heating (20 °C) corresponds to the bulk soil, (2) heating up to 190 °C, (3) heating up to 310 °C, (4) heating up to 390 °C, and (5) heating up to 480 °C (Fig. 1). Four SOM pools with increasing thermal stability were obtained after the combustion up to the “threshold” temperatures: pools with peaks between 190 and 310 °C, and between 390 and 480 °C; intermediate pool between 310 and 390 °C; all SOM remaining after 480 °C. The heating up to 310 °C removed the SOM pool with the “threshold” temperatures of between 190 and 310 °C, so only the SOM remaining after 310 °C was analysed. The same approach was used to determine other SOM pools. The temperature range between 310 and 390 °C (intermediate fraction) was selected for better separation of the fractions decomposed below 310 °C and above 390 °C. The analysis of C isotopic composition showed that the heating up to 190 °C does not change δ¹³C values of reference soil or soil under Miscanthus (Fig. 2). This is in agreement with the absence of total C losses for temperatures up to 190 °C (Table 1). Further heating up to 310 °C increased δ¹³C values by 0.99% in reference soil, and by 0.64% in soil under Miscanthus (Fig. 2). The δ¹³C value of SOM pool remaining after combustion of up to 390 °C showed a significant difference only in the reference soil, where it increased by 1.12‰, compared to δ¹³C in the SOM decomposed up to 310 °C. The largest shift in δ¹³C value occurred in the SOM remaining after heating up to 480 °C: the δ¹³C in the soil under Miscanthus decreased by 2.2‰ which implied, that C in the thermal stable SOM pools remained closer to the previous C₃ vegetation (δ¹³C = -28.0‰) compared to the C of less stable SOM pools, that decomposed at temperatures of up to 190, 310, and 390 °C. In contrast to the soil under Miscanthus, the value of δ¹³C in the reference soil in the same fraction (>-480 °C) showed an increase of up to 3.55‰ in comparison with the δ¹³C value in the SOM fraction decomposed up to 390 °C. The observed ¹³C enrichment in the SOM pools with increasing thermal stability of the reference soil is mainly connected with isotopic discrimination of ¹³C by decomposition during slow temperature increase.

### 3.3. Portion of Miscanthus-derived C₄-C and mean residence time of the SOM pools

The portion of Miscanthus-derived C₄-C in the SOM was calculated according to the approach by Balesdent and Mariotti (1996) (Fig. 2). During 10.5 years of Miscanthus cultivation, the amount of new C₄-C in the SOM of bulk soil reached 55.4% (Table 2). However, the C₄-C contribution in the 190–310 °C pool was 60.4% and decreased down to 6.4% in the pool decomposed above 480 °C. Based on this C₄-C contribution and the period after vegetation change (10.5 years), the SOM turnover rates were calculated (Table 2). The C turnover in the pools decomposed at lower temperatures was much faster than that in the pools decomposed at higher temperatures. The MRT, calculated as the reciprocal to the turnover rates (Gregorich et al., 1995) of SOM pools 190–310, 310–390, and 390–480 °C were similar: 11.6, 12.2, and 15.4 years, respectively. The pool above 480 °C had a much longer MRT of 162.6 years (Table 2). However, the amount of C₄-C incorporated in the last pool as well as the total amount of Corg in this pool was much lower than in the pools decomposed below 480 °C. Therefore, the pool decomposed above 480 °C is of minor ecological importance.

### 4. Discussion

#### 4.1. Thermal stability

In contrast to our previous study (Kuzyakov et al., 2006), the temperature increase in this study was 2.5 times slower and TG-DSC was used to separate the SOM pools with different thermal stability. Slower temperature increases allowed for much better resolution of individual maximums of mass losses, especially of the maximum above 390 °C. According to the dTG curve, five temperature ranges were grouped (Fig. 1). The first interval up to
190 °C was connected with the losses of hygroscopic water, since no C was lost and no changes of isotopic composition were observed. The consumption of energy by water volatilization was clearly confirmed by negative DSC values up to 210 or 220 °C in reference soil and soil under Miscanthus, respectively. The endothermic reactions measured by DSC up to 120–150 °C by TG-DSC studies of SOM were observed by many authors (Dell’Abate et al., 2002;Francioso et al., 2005; Plante et al., 2005). This bound water mainly consisted of water absorbed from air moisture and hygroscopic water of salts (Gaál et al., 1994).

The temperature ranges between 190–310 and 310–390 °C were characterized by the most intensive weight and SOM losses (Table 1). Moreover, the portion of SOM contributing to weight losses in the temperature range 310–390 °C amounted to 85% in soil under Miscanthus. The decomposition of organic compounds in these temperature ranges led to strong energy release with maximum at 290 °C. Nearly the same temperature (~300 °C) corresponded to the exothermic maximum observed by decomposition of humic acids extracted from different peats, lignites and leonardites (Francioso et al., 2005). This exothermic reactions reflected thermal decomposition of polysaccharides, decarboxylation of acidic groups and dehydration of hydroxylate aliphatic structures (Dell’Abate et al., 2002).

The third maximum of mass losses was related to the temperature fraction of 390 to 480 °C (Fig. 1). About 26% of the mass losses that occurred in this fraction were from SOM decomposition for both reference soil under grassland and soil under Miscanthus (Table 1). The decomposed organics could be referred to as stable constituents with aromatic compounds, such as lignin dimers (Leinweber and Schulten, 1992; Siewert, 2004; Lopez-Capel et al., 2005), although the mass losses were not supported by the DSC curve, which showed endothermic reactions from 317 and up to 1000 °C. As suggested by Plante et al. (2005), the energy consumption within this temperature range occurred due to the dehydroxylation of the clay minerals, prevailing the decomposition of organics.

In the last temperature range (>480 °C), 1.12% and 1.30% of mass were lost in the reference soil and soil under Miscanthus, respectively, whereas only 5.4% and 4.2% of these losses were connected with SOM decomposition in both soils, respectively. The other 95% were referred to the O, S, P, and H losses through mineral changes at temperatures between 480 and 1000 °C (Schultze, 1969). One of such changes could be seen as a small endothermic peak on the DSC curve at 570 °C that indicated the release of constitutional water and the collapse of the lattice of such clay minerals as kaolinite and halloysite (Schultze 1969, p. 204).

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**Table 2**
The portion of C4-C, turnover rates, and mean residence time (MRT) of SOM (+SD) accumulated in 10.5 years of Miscanthus cultivation

<table>
<thead>
<tr>
<th>Temperature fraction (°C)</th>
<th>Miscanthus-derived C4-C (%)</th>
<th>Turnover rates (year⁻¹)</th>
<th>MRT (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20–1000</td>
<td>55.4±2.3</td>
<td>0.077±0.005</td>
<td>13.1±0.8</td>
</tr>
<tr>
<td>20–190</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>190–310</td>
<td>60.4±5.2</td>
<td>0.090±0.013</td>
<td>11.6±1.6</td>
</tr>
<tr>
<td>310–390</td>
<td>57.9±3.1</td>
<td>0.083±0.007</td>
<td>12.2±1.0</td>
</tr>
<tr>
<td>390–480</td>
<td>49.6±2.1</td>
<td>0.065±0.004</td>
<td>15.4±0.9</td>
</tr>
<tr>
<td>480–1000</td>
<td>6.4±0.7</td>
<td>0.006±0.001</td>
<td>163±18</td>
</tr>
</tbody>
</table>

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**Fig. 2.** $\delta^{13}$C values of bulk reference soil under grassland and soil under Miscanthus and four SOM pools remaining after heating up to 190 °C (>190 °C), up to 310 °C (>310 °C), up to 390 °C (>390 °C), and up to 480 °C (>480 °C). The calculated theoretical $\delta^{13}$C values of C4 soil developed solely under C4 vegetation (pure C4 soil) were used to estimate the portion of C4-C in the SOM. Whiskers present standard error (±SE). LSD0.05 of means amounting for 1.14% shows significant differences between the two soils and temperature ranges.
4.2. Carbon isotopic composition and the portion of the Miscanthus-derived C4-C in SOM

The average shoot and root δ13C values of Miscanthus growing on the soils were −11.8‰ and of grassland plants previously grown on this plot were −28.0‰. Considering the increase of the δ13C value of the soil under Miscanthus up to 8.8‰% comparing to the δ13C value of bulk soil under continuous C3 vegetation (−26.47‰%) and the isotopic discrimination of 1.0‰ by humification (Agren et al., 1996; Ehlieringer and Cerling, 2002), the amount of C exchanged in the total SOM during the last 10.5 years was 55.4% (Table 2). This is much higher than the contribution of new C within 10 years, observed in most studies done on maize (Flessa et al., 2000; Ludwig et al., 2003). This higher contribution of Miscanthus-derived C was reflected in its much greater above and below-ground biomass and annual mulching of part of the above-ground plant residues in comparison to maize. The large amount of Miscanthus-derived C in our study contradicted the findings of the study by Foereid et al. (2004), which was conducted with Miscanthus, where the portion of new C4-C reached only 18% after 11 years. The difference is probably connected to the fact that various soil layers had been investigated in their study. In our study, only the upper 0–5 cm was used, where the C turnover is faster compared to the soil depths of 0–10, 0–20 or even 0–30 cm, which were used in other studies (Gregorich et al., 1995; Flessa et al., 2000; Foereid et al., 2004).

The turnover rates (TR) corresponding to the MRT of 13.1 years for bulk soil and of 11.6, 12.2, and 15.4 years for pools decomposed between 190–310, 310–390 and 390–480 °C, respectively, were faster than the MRTs in the most of other studies with maize (Huggins et al., 1998; Collins et al., 1999). However, Gregorich et al. (1995) obtained a similar MRT of 15 years for soil under maize. These fast turnover rates and short MRT were connected to the very high input of Miscanthus C in the upper 0–5 cm soil layer and the labile compounds that were accumulated in the SOM during the period of Miscanthus cultivation (10.5 years). Foereid et al. (2004) showed that the stability of Miscanthus-derived SOM was correlated to the time of Miscanthus cultivation. The Miscanthus-derived C in the 11-year old Miscanthus field had a MRT not much longer than the fresh residues (1 year), while the MRT of the older field (18-year old) was longer (3.5 years).

The MRT of C4-C in SOM pool decomposed above 480 °C was more than 160 years (Table 2). So due to very low incorporation of Miscanthus-derived C into this SOM pool (6.4%), this pool could be considered as an inert or recalcitrant one. Many other studies had looked for appropriate methods to separate the recalcitrant fraction of the SOM and considered this pool by modelling (reviewed by Ludwig et al., 2003). Most methods failed in the experimental estimation of the inert fraction because the recalcitrance may be connected with various chemical, physical, and biological properties (Six et al., 2001; Ludwig et al., 2003; Plante et al., 2005). Foereid et al. (2004) hypothesized that the recalcitrance of SOM under Miscanthus cropping was connected to the formation of insoluble carbon in the SOM, which increased its stability upon microbial attack.

The slow turnover rate of the pool with the highest thermal stability suggested its recalcitrance. However, the amount of this fraction (14% of SOM) in our study was lower than the results of other studies, where the inert SOM amounted to 30–40% of the total C (John et al., 2005; Kristiansen et al., 2005).

The experimental data showed that the differences in δ13C values between SOM pools 190–310, 310–390, 390–480 °C were small and therefore, the portion of new Miscanthus-derived C was very similar (Tables 1 and 2). Consequently, the portion of C subjected to a short-time turnover with rates of years and decades was nearly similar in all SOM pools decomposed up to 480 °C. Only small amounts of C (<1% of Corg) in the SOM pool decomposed above 480 °C could be referred to as a stable C with MRT of about 160 years.

5. Conclusions

Thermogravimetry coupled with differential scanning calorimetry (TG-DSC) was suitable to separate soil organic matter (SOM) pools based on their stability to thermal decomposition. Despite clear separation of SOM pools of different thermal stability by TG-DSC, the isotopic analyses showed that the accordance between thermal and biological degradability was not gradual. All SOM pools with low and medium thermal stability decomposed below 480 °C had faster turnover rates than the pool, decomposed above 480 °C. Microbial availability of all pools decomposed below 480 °C was similar (MRT of 12–15 years) suggesting no clear correlation between thermal and microbial decomposability. A long MRT of 160 years was measured for the thermally stable pool decomposed above 480 °C. However, the ecological significance of this pool is of minor importance because of very low C amounts in the pool. Due to the very poor correlation between δ13C values and thermal stability of SOM pools we conclude that the applicability of the TG-DSC for the separation of SOM pools with different biological availability is limited.

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References
