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REGULAR ARTICLE

Effects of atmospheric CO_2 enrichment on $\delta^{13}C$, $\delta^{15}N$ values and turnover times of soil organic matter pools isolated by thermal techniques

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Abstract CO_2 applied for Free-Air CO_2 Enrichment (FACE) experiments is strongly depleted in ^{13}C and thus provides an opportunity to study C turnover in soil organic matter (SOM) based on its $\delta^{13}C$ value. Simultaneous use of ^{15}N labeled fertilizers allows N turnover to be studied. Various SOM fractionation approaches (fractionation by density, particle size, chemical extractability etc.) have been applied to estimate C and N turnover rates in SOM pools. The thermal stability of SOM coupled with C and N isotopic analyses has never been studied in experiments with FACE. We tested the hypothesis that the mean residence time (MRT) of SOM pools is inversely proportional to its thermal stability. Soil samples from FACE plots under ambient (380 ppm) and elevated CO_2 (540 ppm; for 3 years) treatments were analyzed by thermogravimetry coupled with differential scanning calorimetry (TG-DSC). Based on differential weight losses (TG) and energy release or consumption (DSC), five SOM pools were distinguished. Soil samples were heated up to the respective temperature and the remaining soil was analyzed for $\delta^{13}C$ and $\delta^{15}N$ by IRMS. Energy consumption and mass losses in the temperature range 20–200°C were mainly connected with water volatilization. The maximum weight losses occurred from 200–310°C. This pool contained the largest amount of carbon: 61% of the total soil organic carbon in soil under ambient treatment and 63% in soil under elevated CO_2, respectively. $\delta^{13}C$ values of SOM pools under elevated CO_2 treatment showed an increase from −34.3‰ of the pool decomposed between 20–200°C to −18.1‰ above 480°C. The incorporation of new C and N into SOM pools was not inversely proportional to its thermal stability. SOM pools that decomposed between 20–200 and 200–310°C contained 2 and 3% of the new C, with a MRT of 149 and 92 years, respectively. The pool decomposed between 310–400°C contained the largest proportion of new C (22%), with a MRT of 12 years. The amount of fertilizer-derived N after 2 years of application in ambient and elevated CO_2 treatments was not significantly different in SOM pools decomposed up

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to 480°C having MRT of about 60 years. In contrast, the pool decomposed above 480°C contained only 0.5% of new N, with a MRT of more than 400 years in soils under both treatments. Thus, the separation of SOM based on its thermal stability was not sufficient to reveal pools with contrasting turnover rates of C and N.

Keywords Thermal stability of SOM · Free air CO_2 enrichment · Delta ^{13}C · Delta ^{15}N · Thermogravimetry · Differential scanning calorimetry · TG-DSC · SOM turnover times · MRT

Introduction

Free-air CO_2 enrichment (FACE) experiments provide an opportunity to examine many aspects of elevated CO_2 effects on ecosystems, and to study the pathways of carbon (C) and nitrogen (N) in soil organic matter (SOM) under realistic field conditions (Leavitt et al. 2001; Miglietta et al. 2001; Kimball et al. 2002). FACE avoids most of the microenvironment effects imposed by the chamber technique and therefore more reliably reproduces soil processes under elevated CO_2 (Van Kessel et al. 2000b).

To study the fate of carbon (C) in soils under CO_2 enrichment, most FACE experiments use stable-C isotopic tracers (Hungate et al. 1997; Torbert et al. 1997; Van Kessel et al. 2000a, b; Leavitt et al. 2001; Niklaus et al. 2001; Hagedorn et al. 2003). The additional CO_2 is usually derived from fossil fuel, which is depleted in ^{13}C ($\delta^{13}C$ varies from −35‰ to −50‰) compared with atmospheric CO_2 (delta;^{13}C −8‰) (Hungate et al. 1996; Nitschelm et al. 1997; Van Kessel et al. 2000b; Jones and Donnelly 2004). The isotopic composition of CO_2 in the elevated CO_2 treatment is determined by the proportions of atmospheric and fossil fuel-derived CO_2, and provides a continuous C-isotope tracer. Plants grown in the elevated CO_2 atmosphere are depleted in $\delta^{13}C$ and, as the litter and rhizodeposits from these plants decompose and become incorporated into the SOM, the soil $\delta^{13}C$ will decrease. The contribution of the new FACE-derived C to total SOM can be calculated based on the $\delta^{13}C$ of the SOM under ambient conditions and the period after initiating CO_2 enrichment. This new C contribution and the CO_2 treatment duration then allow the SOM turnover rates to be estimated (Balesdent and Mariotti 1987). Beyond investigating the C pathways in SOM under elevated atmospheric CO_2, the study of N cycling provides insights into the transformation processes of these two elements in soil. Thus, the application of N fertilizers in FACE experiments was used to estimate N flows and plant uptake under elevated CO_2 (Hungate et al. 1997; Van Kessel et al. 2006; Zanetti et al. 1997). The use of N fertilizers labeled with ^{15}N provides an opportunity to study N turnover and to separate SOM N from the fertilizer N.

To track the new C and N in SOM pools, fractionation techniques including density (Magid et al. 2002; John et al. 2005) and particle size fractionation (Jolivet et al. 2003) as well as sequential extractions (Ellerbrock and Kaiser 2005) have been combined with $\delta^{13}C$ analyses. Another suitable approach for SOM partitioning is based on its thermal stability (Leinweber and Schulten 1992; Siewert 2001, 2004; Lopez-Capel et al. 2005a, 2005b; Plante et al. 2005; Kuzyakov et al. 2006). Thermogravimetry analysis coupled with differential scanning calorimetry involves a continuous, gradual temperature increase which decomposes (mainly oxidizes) different organic compounds according to their thermal stability. Such a temperature increase coupled with measuring of weight losses is termed thermogravimetry (TG). Simultaneously to temperature increase, energy released or consumed by decomposition of organics is measured by differential scanning calorimetry (DSC).

TG-DSC is extensively applied to various soil science studies. Leinweber and Schulten (1992); Leinweber et al. (1992) and Schulten and Leinweber (1999) used DSC to characterize organo-mineral complexes; Provenzano and Senesi (1999) have used DSC to study humic substances; Lopez-Capel et al. (2005a); Francioso et al. (2005), and Plante et al. (2005) applied the technique to evaluate the humification state of SOM. Studying correlations between thermal stability of SOM pools in various temperature ranges and CO_2 production by classical soil incubations, Siewert (2001) suggested the idea of a relationship between thermal stability of SOM pools and their biological degradability.

Thermogravimetry and differential scanning calorimetry could potentially provide a simple and rapid determination of gross changes in organic matter quality (Plante et al. 2005), but have apparently never

been used to examine the quality of SOM under altered environmental conditions such as elevated CO_2 concentration in the atmosphere. The objectives of this study were (1) to characterize the SOM quality in terms of thermal properties under ambient and elevated concentrations of atmospheric CO_2 in a 3-year Free Air Carbon dioxide Enrichment (FACE) experiment and (2) to test the hypothesis that the mean residence times (MRT) of SOM pools are inversely proportional to their thermal stability by comparing the $\delta^{13}C$ and $\delta^{15}N$ values of the SOM pools decomposed at low and high temperatures in both treatments.

Materials and methods

Soil samples were taken from the Free Air Carbon dioxide Enrichment facility located in Stuttgart-Hohenheim, Baden-Wuerttemberg, Germany (48°43′ north latitude, 9°13′ east longitude). The soil is a Gleyic Cambisol (WRB 1998) without carbonates (no reaction with HCl). Mean annual temperature is 8.7°C and average rainfall 680 mm a^{-1} (mean 1961–1990, meteorological station Stuttgart-Hohenheim). Properties of the soil under ambient and elevated CO_2 treatments were similar: pH 6.8, bulk density (0–10 cm) 1.4 g cm^{-3}, C_{org} 1.45%, N_{tot} 0.16%, C/N ratio 9.1.

The FACE experiment, starting in 2002, included plots with elevated atmospheric CO_2 level (540 ppm, $\delta^{13}C$ −19‰, because of using CO_2 at −48‰ for CO_2 addition), ambient plots (380 ppm, $\delta^{13}C$ −8‰), and control plots (ambient CO_2 level, no enclosures) (Erbs and Fangmeier 2006). Each treatment was replicated five times. To represent a typical agricultural ecosystem, spring wheat in combination with several weeds common for arable systems was annually planted on the plots since 2002. Average $\delta^{13}C$ value of plants grown under ambient CO_2 treatment was −27‰, under elevated CO_2 −39‰ (Erbs, personal communication). Soil was tilled in spring before wheat sowing. Beginning in 2003, inorganic NPK fertilizers including KNO_3 labeled with ^{15}N ($\delta^{15}N$ of the fertilizer was 333.75‰) were applied in equal amounts of 140 kg N ha^{-1}, 60 kg K ha^{-1}, 13 kg P ha^{-1} to each plot under ambient and elevated CO_2 treatments. No organic fertilizers were applied.

Soil samples for thermogravimetry and $\delta^{13}C/\delta^{15}N$ analysis were taken in October 2005 from 10 plots (five elevated treatments, five ambient treatments) from the depth of 0–10 cm using soil corers (inner diameters: 5 cm). The soil samples were air-dried at room temperature and sieved through 2 mm mesh. All visible roots and plant remains were carefully removed with tweezers from a subsample of 10 g and the soil was ball milled (MM2, Fa Retsch) for 15 s. Analogous procedure was done for soil sampled before the FACE experiment was started. These soil samples were used to obtain initial properties of soil important for calculation of fertilizer-derived N. No preliminary treatment was done to remove NO_3^- from soil samples prior to thermogravimetry analysis.

Thermogravimetry-differential scanning calorimetry analysis

Thermogravimetric analysis (TG) and differential scanning calorimetry analysis (DSC) were carried out simultaneously using the Netzsch STA 409EP device, regulated by the TASC 414/3 controller (Fa Netzsch). One hundred milligrams of soil sample was weighed out on an alumina crucible and then heated from 20 to 1000°C in air atmosphere (1.0 ml min^{-1}). The heating rate was 2.0°C min^{-1}. The weight of the soil sample (in mg), as well as the heat (in μV mg^{-1}) released or consumed by substance oxidation or water evaporation, was continuously scanned. Calcined kaolinite previously heated at 1250°C was used as the reference material. The obtained TG-DSC curves of soil samples from ambient and elevated treatments were used to determine "threshold" temperature levels. These levels were set as temperature values to heat soil samples in a muffle oven (Heraeus MR-260) for subsequent measurements of weight losses, C and N content, as well as $\delta^{13}C$ and $\delta^{15}N$ values of SOM pools. Four groups of soil samples were heated up to 200, 310, 400 and 480°C. No heating (20°C) corresponded to the bulk soil. Heating up to 200°C removed mainly water, but some organic and inorganic substances were decomposed between 20 and 200°C. Only the SOM pools remaining after 200°C were analysed for their C and N content, $\delta^{13}C$ and $\delta^{15}N$ values. The same approach was used to determine the SOM pools at other temperature thresholds. Then, considering the weight, C and N losses after heating up to the threshold temperatures, the corresponding values

(weight, C and N) were calculated for the intermediate SOM pools decomposed between 200 and 310, or 310 and 400, or 400 and 480°C (see below). The temperature range between 310 and 400°C was selected to better separate the pools decomposed below 310°C and above 400°C. The heating rate of the muffle furnace was the same as by TG-DSC analysis: 2.0°C min^{-1}.

$\delta^{13}C$ and $\delta^{15}N$ analyses

Ten to forty milligrams of soil samples remaining after heating in the muffle oven up to one of the threshold temperatures were weighed in tin capsules for $\delta^{13}C/\delta^{15}N$ analyses. The C and N isotopic composition was measured with a Delta Plus XP isotope ratio mass spectrometer (Thermo Finnigan, Bremen) coupled to the Euro EA C/N analyser (Eurovector Instruments and Software, Hekatech GmbH, Wegberg). Acetanilide was used as the internal standard for $\delta^{13}C$ and $\delta^{15}N$ analyses. The final isotopic composition is expressed as $\delta^{13}C$ units in relation to Pee Dee Belemnite ($^{13}C/^{12}C$=0.0112372) as the standard for C, and as $\delta^{15}N$ units in relation to atmospheric N_2 ($^{15}N/^{14}N$=0.0036765) as the standard for N.

Calculations

Weight losses as well as C and N content of SOM pools decomposed between 20–200, 200–310, 310–400 and 400–480°C were calculated by subtraction of weights, C and N content of soil samples combusted up to the lower temperature threshold and higher temperature threshold:

$$M_{\mathrm{FR}}(x_n - x_{n+1}) = M_{\mathrm{R}}(x_n) - M_R(x_{n+1}), \quad (1)$$

where M_{FR} was weight losses, C or N content of a SOM fraction, M_R was weights, C or N content of SOM in residues combusted up to threshold temperatures, x_n was the lower threshold temperature, and x_{n+1} was the higher threshold temperature, respectively. Here, M_{FR} (x_1) = M_R (x_1) corresponding to weight, C and N of bulk soil, and M_{FR} (x_5) = M_R (x_5) corresponding to weight, C and N of SOM pool decomposed up to 480°C. For example, M_{FR} (200–310) was calculated by subtraction of M_R (200) and M_R (310).

The $\delta^{13}C$ and $\delta^{15}N$ values of four individual SOM pools of different thermal stability decomposed between 20–200, 200–310, 310–400 and 400–480°C were calculated based on the isotopic mass balance equation (Balesdent and Mariotti 1996):

$$\delta_{\mathrm{FR}}(x_n - x_{n+1}) = [M_{\mathrm{R}}(x_n)\cdot\delta_{\mathrm{R}}(x_n) - M_{\mathrm{R}}(x_{n+1})\cdot\delta_{\mathrm{R}}(x_{n+1})]/ M_{\mathrm{FR}}(x_n - x_{n+1}), \quad (2)$$

where δ_{FR} was $\delta^{13}C$ or $\delta^{15}N$ value of a SOM fraction, M_{FR} was the amount of C or N in a SOM fraction, M_R was C or N content of SOM in residues combusted up to threshold temperatures, δ_R was $\delta^{13}C$ or $\delta^{15}N$ value of SOM in residues combusted up to threshold temperatures, x_n was a lower threshold temperature, and x_{n+1} was a higher threshold temperature. Here, M_{FR} (x_1) and δ_{FR} (x_1) corresponded to M_R (x_1) and δ_R (x_1) of bulk soil, and M_{FR} (x_5) = M_R (x_5), δ_{FR} (x_5) = δ_R (x_5) in SOM pool decomposed up to 480°C.

The portion of FACE-derived C (C_{FACE}) in SOM was calculated for bulk soil and each temperature range according to Balesdent and Mariotti (1996) and adapted for FACE conditions:

$$C_{\mathrm{FACE}} = \left(\delta^{13}C_{\mathrm{elev}} - \delta^{13}C_{\mathrm{amb}}\right)/ \left(\delta^{13}C_{\mathrm{elev.theor.}} - \delta^{13}C_{\mathrm{amb}}\right)\cdot 100, \quad (3)$$

where $\delta^{13}C_{elev}$ was a $\delta^{13}C$ value of the SOM of bulk soil under elevated treatment and $\delta^{13}C$ of SOM pools under elevated treatment calculated according to Equation 2; $\delta^{13}C_{amb}$ was a $\delta^{13}C$ value of the SOM of bulk soil under ambient treatment and $\delta^{13}C$ of SOM pools under ambient treatment calculated according to Equation 2; $\delta^{13}C_{elev.theor.}$ was a theoretical $\delta^{13}C$ value of the bulk SOM and SOM pools decomposed at increasing temperatures developed under vegetation grown in continuously elevated CO_2 conditions. Isotopic signatures of theoretical SOM were calculated based on the difference between the $\delta^{13}C$ of the plants growing under elevated CO_2 and the $\delta^{13}C$ of bulk soil and SOM pools of different

thermal stability under ambient CO_2. The values were corrected for isotopic fractionation during humification by subtracting the differences between $\delta^{13}C$ of vegetation growing under ambient conditions and $\delta^{13}C$ of the corresponding SOM pool of the soil developed under ambient CO_2 treatment:

$$\delta^{13}C_{elev.theor.} = \delta^{13}C_{elev.plant} - \left(\delta^{13}C_{amb.plant} - \delta^{13}C_{amb}\right) \quad (4)$$

where $\delta^{13}C_{elev.plant}$ was $\delta^{13}C$ of the plants under elevated CO_2 treatment, $\delta^{13}C_{amb.plant}$ was $\delta^{13}C$ value of the plants under ambient CO_2 treatment, and $\delta^{13}C_{amb}$ was $\delta^{13}C$ of the bulk SOM and corresponding SOM pool of the soil developed under ambient CO_2 treatment.

Similar equation was used to calculate the portion of N derived from labelled fertilizers:

$$N_{fertil} = \left(\delta^{15}N_{soil\ actual} - \delta^{15}N_{soil\ initial}\right)/ \left(\delta^{15}N_{fertil} - \delta^{15}N_{soil\ initial}\right) \cdot 100, \quad (5)$$

where $\delta^{15}N_{soil\ actual}$ was a $\delta^{15}N$ value of the bulk SOM and SOM pools decomposed under increasing temperatures after fertilization during two years (Equation 2), $\delta^{15}N_{soil\ initial}$ was a $\delta^{15}N$ value of the bulk SOM and SOM pools decomposed under increasing temperatures before fertilization, and $\delta^{15}N_{fertil}$ was a $\delta^{15}N$ signature of N fertilizers.To calculate the contribution of new FACE-derived C and N from fertilizers in SOM for a particular period of the FACE experiment and annual turnover rates (TR) of SOM, a simple exponential approach was selected (Balesdent and Mariotti 1996):

$$TR = -\mathrm{In}(1 - M/100)/t, \quad (6)$$

where M was the portion of C_{FACE} or N_{fertil} (Eqs. 4 and 5) in bulk SOM and SOM pools decomposed under increasing temperatures, and t was the time of soil exposure to elevated CO_2 concentrations (3 years) and the period of N fertilization (2 years).

The mean residence time of FACE-derived C and N from fertilization in bulk soil and in SOM pools was calculated as a reciprocal to the turnover rates (Gregorich et al. 1995):

$$MRT = 1/TR \quad (7)$$

Amounts of C_{FACE} and $N_{fertil.}$ in kg ha^{-1} were calculated using soil bulk density of 1.4 g cm^{-3} and the layer of 10 cm. The study was conducted with five and four replicates under elevated and ambient CO_2 treatments, respectively, both for TG-DSC and isotopic analysis. The initial soil for no-^{15}N control was replicated three times. The significance of differences between $\delta^{13}C$, $\delta^{15}N$, as well as the C and N content of different pools under ambient and elevated CO_2 treatments was examined using one-way analysis of variance (ANOVA). The standard errors of means are presented on the figures and in the tables as the variability parameter.

Results

TG-DSC analysis of soil samples

Thermal analysis of soil samples provided two data sets: mass losses due to thermal decomposition of soil organic and inorganic constituents, and heat flow defined by exothermic or endothermic reactions while decomposing these constituents. Data for thermogravimetry analysis were represented by two curves: cumulative weight losses (TG, %) and differential weight losses (dTG, %°C^{-1}) (Fig. 1). The dTG curve showed three well-defined peaks of differential weight losses from soil samples under elevated and ambient CO_2 treatments during the heating from 20 to 1,000°C: 1) between 20 and 200°C (temperature range A), 2) between 200 and 310°C (temperature range B) and 3) between 400 and 480°C (temperature range D). Minimal weight losses occurred from 310 to 400°C (temperature range C) and from 480 to 1,000°C (temperature range E) (Fig. 1). The most intensive losses were observed in the temperature range A, with the maximum of 0.035 percent weight loss per degree (% °C^{-1}) at 50°C. The subsequent maxima of differential weight losses were smaller: 0.023% °C^{-1} in soil under elevated treatment, 0.024% °C^{-1} in soil under ambient treatment, both at 285°C in temperature range B, and 0.015% °C^{-1} at 460°C in temperature

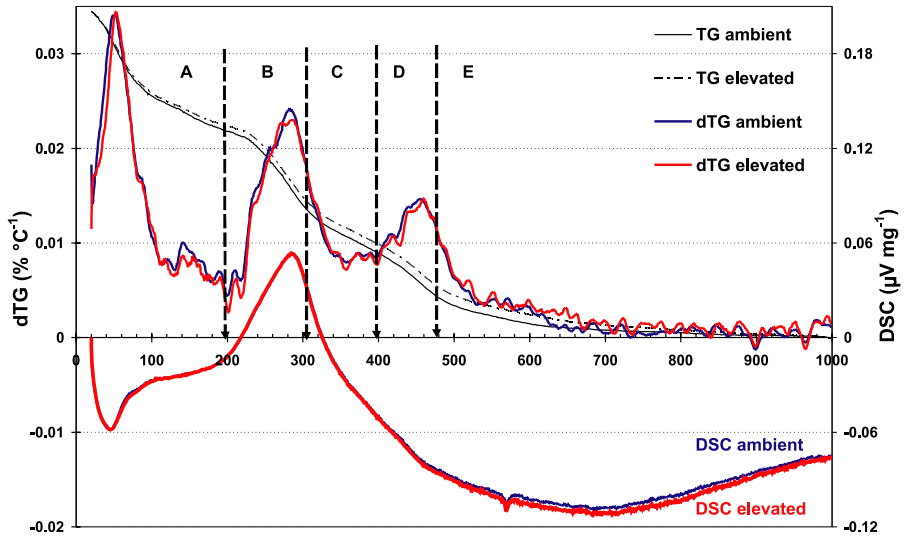

Fig. 1 Differential thermogravimetry (dTG, *left Y axis*) and Differential Scanning Calorimetry (DSC, *right Y axis*) of soil under ambient and elevated CO_2 treatments. Cumulative losses (TG) are scaled to 100% of the *left Y axis* and totalled 6.44% of sample weight for soil under ambient treatment and 6.71% for soil under elevated CO_2 treatment. Negative DSC values represent energy consumption (endothermic reactions), positive DSC values – energy release (exothermic reactions). *Arrows* show the "threshold" temperature chosen for SOM fractionation

range D for both treatments (Fig. 1). The loss minima were less clearly defined. Within temperature range A the minima were from 0.01 to 0.002%°C^{-1}, in temperature range C from 0.009 to 0.007% °C^{-1}; values in the last temperature range approached zero.

The DSC traces of the samples under both treatments were characterised by three temperature ranges, two with endothermic reaction: (1) 20–220°C, (2) 325–1000°C, and one exothermic reaction between 220 and 325°C. The first endothermic reaction, occurring within temperature range A, had a maximum energy consumption of −0.06 µV per milligram of a sample weight (µV mg^{-1}) at around 50°C, corresponding to the maximal weight losses in the same temperature range. Starting from 220°C the energy release due to decomposition processes of organics (see Discussion) switched the DSC curve to positive values. Maximal energy release of 0.052 µV mg^{-1} occurred at 285°C, corresponding to the peak of differential mass losses within temperature range B (Fig. 1). From 325°C and up to 1,000°C the heat flow of the soils samples showed a maximum energy consumption of −0.112 µV mg^{-1} between 680 and 715°C. The distinctive feature of the DSC curves of the soils under both treatments was a small negative peak at 570°C (Fig. 1).

Neither differential weight losses from soil samples nor DSC data showed significant differences between ambient and elevated CO_2 treatments; this allowed similar temperature levels to be chosen for thermal fractionation of SOM in soil samples under both treatments.

Weight losses, C and N contents of SOM pools

To fractionate the SOM into individual pools with different thermal stability, the losses of mass for soil samples during heating were chosen as the main criteria. Since the mass losses and energy release are related to various organic and inorganic components, the DSC values cannot be directly linked to the individual substances. Thus, the DSC traces were used here to confirm the temperature thresholds estimated by mass losses.

The total weight losses of the five SOM pools in both ambient and elevated treatments were not significantly different. Losses of weight from soil samples under ambient CO_2 treatment amounted to 6.44±0.18% of the total mass of samples and 6.71±0.21% – for soil samples under elevated CO_2 treatment (Table 1). Peak weight losses occurred in the SOM pool decomposed between 200 and 310°C: 2.65±0.02% of the initial sample mass was lost in soil under ambient CO_2 treatment, and 2.61±0.03% in soil under elevated CO_2 treatment. The least weight losses were observed at 20–200°C, where the soil under ambient treatment lost 0.68±0.04% and the soil

under elevated CO_2 treatment lost 0.69±0.02% of total mass losses (Fig. 1).

The maximum C and N losses corresponded to maximal weight losses in SOM pools decomposed at 200–310°C. The lowest C and N contents were measured in SOM decomposed above 480°C (Table 1).

C and N isotopic composition

Due to the available analytical facilities the $\delta^{13}C$ values were measured in soil residues decomposed up to the threshold temperatures rather than directly in the CO_2 released by decomposition at certain temperatures as done by Lopez-Capel et al. (2005a). Then, considering C and N losses, and based on the isotopic mass balance equation (Equation 1), the $\delta^{13}C$ and $\delta^{15}N$ values of intermediate SOM pools decomposed from 200–310, 310–400, and 400–480°C were calculated (Tables 2 and 3).

Fumigation with elevated CO_2 for three years significantly depleted the $\delta^{13}C$ signature of bulk soil (Table 1). In SOM pools decomposed in temperature ranges 310–400°C and 480–1000°C the $\delta^{13}C$ values under elevated CO_2 treatment were significantly lower than in the ambient CO_2. However, there were no significant decrease of the $\delta^{13}C$ in temperature ranges 20–200, 200–310 and 400–480°C the depletion of $\delta^{13}C$ signatures was insignificant (Table 2). The largest ^{13}C depletion occurred at 20–200°C: the soil under ambient treatment had a $\delta^{13}C$ value of −32.32±2.15‰, whereas the soil under elevated treatment had $\delta^{13}C$ of −34.32±1.85‰. However, this difference was not statistically significant (Table 2). Large standard errors in the SOM pools decomposed at 20–200°C compared to other pools were connected with high weight losses by water evaporation which were not accompanied by the respective C and N losses. Therefore, very small changes of total C and N by heating from 20 to 200°C led to small changes of their $\delta^{13}C$ and $\delta^{15}N$ values resulting in high estimation error. The rise of the $\delta^{13}C$ values under both treatments (Tables 1 and 2) was occurred due to the slow combustion process, when the lighter ^{12}C decomposed faster than the heavier ^{13}C, leading to accumulation of the latter in the residual SOM pools (Lopez-Capel et al. 2005a).

Statistical analysis showed no significant difference in $\delta^{15}N$ values of bulk soil and SOM pools with different thermal stability between ambient and elevated CO_2 treatments (Table 3). The bulk soil and SOM pools decomposed at 20–200, 200–310

Table 1 Measured weight losses, amount of C, N, and $\delta^{13}C$ and $\delta^{15}N$ values in soil under ambient and elevated CO_2 treatments in residue samples after heating up to threshold temperatures

Temperature threshold (°C)	Treatment	Weight losses (%)	C content (%)	N content (%)	$\delta^{13}C$ (‰ PDB)	$\delta^{15}N$ (‰ air N_2)
200						
	Ambient	0.68±0.04	1.287±0.016	0.146±0.0015	−26.19±0.25	18.25±1.12
	Elevated	0.69±0.02	1.327±0.018	0.150±0.0016	−27.14±0.18*	19.06±0.68
310						
	Ambient	3.33±0.02	0.394±0.015	0.078±0.0018	−23.37±0.35	19.43±0.70
	Elevated	3.30±0.03	0.406±0.017	0.082±0.0029	−25.58±0.25**	20.26±0.58
400						
	Ambient	4.48±0.06	0.110±0.010	0.028±0.0009	−20.79±0.69	15.43±0.81
	Elevated	4.38±0.04	0.100±0.002	0.029±0.0006	−21.85±0.24	15.82±0.67
480						
	Ambient	5.56±0.02	0.039±0.003	0.0082±0.0001	−16.86±0.20	8.91±0.37
	Elevated	5.61±0.08	0.035±0.001	0.0085±0.0002	−18.07±0.35*	9.37±0.57
Bulk soil[a]						
	Ambient	6.44±0.18	1.451±0.016	0.159±0.0013	−26.90±0.04	18.10±0.93
	Elevated	6.71±0.21	1.461±0.017	0.160±0.0016	−27.78±0.11**	19.02±0.67

Values are means of four replicates in ambient CO_2 treatment and five replicates in elevated CO_2 treatment ± SE

[a] Bulk soil represents not heated soil samples

* $P<0.05$ and ** $P<0.01$ represent the significance of differences between ambient and elevated CO_2 treatments

and 400–480°C had similar $\delta^{15}N$ values, averaging 18.00‰. Higher $\delta^{15}N$ values were observed in the SOM pool decomposed between 310–400°C: 22.15‰ on average, and the lowest values – 9.37‰ on average – were obtained at 480–1000°C (Table 3).

The portion of FACE-derived C and fertilizer-derived N in SOM pools with different thermal stability

During three years of CO_2 fumigation the amount of the new C reached 7.3% of total C in the upper layer of bulk soil (Fig. 2) – equivalent to 1524±68 kg ha^{-1} (Table 2). This amount of FACE-derived C was distributed among SOM pools as follows: 38±39 kg ha^{-1} at 20–200°C, 419±168 kg ha^{-1} at 200–310°C, 941±62 kg ha^{-1} at 310–400°C, 75±8 kg ha^{-1} at 400–480°C and 51±8 kg ha^{-1} at 480–1000°C (Table 2). The calculated turnover rates and MRT of SOM pools showed no relation between the MRT values and temperature increase. Thus, the SOM pools decomposed between 20–200°C had 2.0% of the new C and between 200–310°C 3.2%. Their MRT values were 149±150 and 92±49 years, respectively. The corresponding values at 310–400°C were 21.6% FACE-derived C (MRT 12 years), at 400–480°C 8.2% (35 years),and at 480–1000°C 10.1% (28 years) (Fig. 2, Table 2).

After two years of fertilization, 72.5±6.5 kg ha^{-1} of the new N were incorporated in bulk soil under ambient CO_2 treatment and 79.5±4.7 kg ha^{-1} – under elevated CO_2 treatment, corresponding on average to 28% of applied mineral N (140 kg ha^{-1} annually) (Table 3). The SOM pools decomposed between 310 and 400°C had the largest amounts of the fertilizer-derived N: 30.3±1.0 kg ha^{-1} for soil under ambient CO_2 treatment and 34.7±0.9 kg ha^{-1} for soil under elevated treatment. The lowest quantity (around 1 kg ha^{-1}) was observed in SOM pools decomposed at 480–1000°C (Table 3). Similar MRT values of approximately 65 years were recorded for the new N of the bulk soil and SOM pools decomposed at 20–200, 200–310 and 400–480°C. The longest MRT

Table 2 Amount of C, $\delta^{13}C$ values, amount of FACE-derived C and the mean residence time (MRT) of C in bulk soil and SOM pools isolated in five temperature ranges for soils exposed for 3 years to elevated and ambient CO_2 concentrations

Temperature interval (°C)	Treatment	C content (%)	$\delta^{13}C$ (‰ PDB)	C_{FACE} (kg ha^{-1})[a]	MRT (years)[a]
20–200					
	Ambient	0.164±0.016	−32.32±2.15		
	Elevated	0.134±0.018	−34.32±1.85	37.9±38.82	149±150
200–310					
	Ambient	0.893±0.015	−27.45±0.18		
	Elevated	0.921±0.017	−27.82±0.11	419.5±167.9	92±49
310–400					
	Ambient	0.284±0.010	−24.28±0.19		
	Elevated	0.306±0.002*	−26.81±0.09**	940.5±62.3	12±1
400–480					
	Ambient	0.071±0.003	−22.97±0.09		
	Elevated	0.065±0.001	−23.94±0.24	75.2±8.2	35±6
480–1000					
	Ambient	0.039±0.003	−16.86±0.20		
	Elevated	0.035±0.001	−18.07±0.35*	50.8±8.2	28±5
Bulk soil					
	Ambient	1.451±0.016	–26.90±0.04		
	Elevated	1.461±0.017	−27.78±0.11**	1523.9±67.6	39±2

Values are means of four replicates in ambient CO_2 treatment and five replicates in elevated CO_2 treatment ± SE

[a] FACE-derived C and MRT could only be assessed at the elevated CO_2 treatment. Therefore, the effect of CO_2 was not included for these variables.

* $P < 0.05$ and ** $P < 0.01$ represent the significance of differences between ambient and elevated CO_2 treatments

(433±53 and 337±104 years) was observed in the SOM pool decomposed between 480–1000°C in the ambient and elevated treatments, respectively.

Discussion

Thermal properties of SOM under ambient and elevated CO_2 conditions

Unequal weight losses during gradual heating justified a separation into five temperature intervals (Fig. 1). The first interval A (up to 200°C) reflected losses of bound water and volatile organic substances. As stated earlier (Siewert 2001; Kuzyakov et al. 2006), weight losses between 20 and 200°C mainly corresponded to the evaporation of bound water: water absorbed from air moisture, crystalline lattice water and hygroscopic water of salts (Gaál et al. 1994; Zimmermann et al. 1987). Negative DSC values up to 220°C (Fig. 1) confirmed the energy consumption by water volatilization. The endothermic reactions measured by DSC up to 120–150°C were observed by many authors in TG-DSC studies of SOM (Dell'Abate et al. 2003; Francioso et al. 2005; Plante et al. 2005).

Not only water, however, but also organics were decomposed up to 200°C. According to studies by Johnson (1977); Kristensen (1990) and Zimmermann et al. (1987), these organics are volatile low molecular compounds such as free amino and carboxylic acids, which decomposed at relatively low temperatures (i.e. below 150°C).

The temperature ranges B (200–310°C) and C (310–400°C) yielded the largest losses of C and N (Tables 2 and 3). As observed by Kristensen (1990) the organic substances decomposed up to 310°C comprise plant material such as cellulose. Herrera et al. (1986) used dTG to determine that the major percentage weight loss of hemicelluloses and celluloses occur at the low temperature range between 200 and 350°C.

The DSC traces of soil samples under both ambient and elevated CO_2 treatments showed intensive energy release due to decomposition of organic compounds, whereby the maximum at 285°C exactly coincided with the maximum weight losses (Fig. 1). Nearly the same temperature (~300°C) corresponded to the

Table 3 Amount of N, $\delta^{15}N$ values, amount of fertilizer-derived N including the percentage from total amount of N in a pool and the mean residence time (MRT) of N after 2 years of fertilization in bulk soil and SOM pools isolated in five temperature ranges for soils under ambient and elevated CO_2 treatments

Temperature interval (°C)	Treatment	N content (%)	$\delta^{15}N$ (‰ air N_2)	N_{fertil} (kg ha^{-1})	(% from N content)	MRT (years)
20–200						
	Ambient	0.0135±0.0015	16.41±1.12	5.2±7.1	(2.69)	73±36
	Elevated	0.0107±0.0016	18.50±0.68	5.1±4.4	(3.33)	59±43
200–310						
	Ambient	0.0681±0.0018	16.83±0.86	27.5±2.4	(2.84)	69±7
	Elevated	0.0676±0.0029	17.53±0.69	29.3±2.1	(3.05)	65±5
310–400						
	Ambient	0.0493±0.0009	21.69±0.43	30.3±1.0	(4.31)	45±2
	Elevated	0.0529±0.0006*	22.69±0.30	34.7±0.9	(4.62)*	42±1
400–480						
	Ambient	0.0201±0.0001	17.99±0.07	9.1±0.1	(3.17)	62±1
	Elevated	0.0207±0.0002*	18.41±0.21	9.7±0.1	(3.29)**	60±1
480–1000						
	Ambient	0.0082±0.0001	9.16±0.19	0.53±0.07	(0.46)	433±53
	Elevated	0.0085±0.0002	9.57±0.41	0.72±0.15	(0.59)	337±104
Bulk soil						
	Ambient	0.159±0.0013	18.10±0.93	72.5±6.5	(3.20)	61±6
	Elevated	0.160±0.0016	19.02±0.67	79.5±4.7	(3.49)	56±4

Values are means of four replicates in ambient treatment and five replicates in elevated CO_2 treatment ± SE

* $P<0.05$ and ** $P<0.01$ represent the significance of differences between ambient and elevated CO_2 treatments

exothermic maximum observed by decomposition of humic acids extracted from different peats, lignites and leonardites (Francioso et al. 2005). These exothermic reactions reflected thermal decomposition of polysaccharides, decarboxylation of acidic groups and dehydration of hydroxylate aliphatic structures (Dell'Abate et al. 2002)

C losses in the temperature range D (390 to 480°C) amounted to 4.5–5% of total C and were lower than the percent N losses (12.5–13%) under both elevated and ambient treatments. Larger losses of N-containing versus C-containing compounds within this temperature range were reported by Schulten and Leinweber (1999). The decomposed organics comprise stable constituents with aromatic compounds such as lignin, humic substances and kerogens (Kristensen 1990; Leinweber et al. 1992; Siewert 2004; Lopez-Capel et al. 2005a).

In the last temperature range E (480–1000°C) the losses of organic matter were very small (Table 1). Most mass losses here reflect clay mineral decomposition (Schultze 1969). The DSC traces showed strong energy consumption and a small endothermic peak at 570°C, indicating quartz lattice collapse (Schultze 1969).

C isotopic composition and the portion of new FACE-derived C

Three years of elevated CO_2 treatment significantly altered the C isotopic composition of bulk soil, showing the inputs of new C to SOM. However, the C content of the bulk soils under ambient and elevated CO_2 did not differ significantly (Table 1). The lack of total C change under elevated CO_2 was expected because SOM formation and decomposition processes are not strongly affected by elevated CO_2 (Leavitt et al. 2001) and 3 years are insufficient to obtain significant changes in bulk amount. The significant difference in the isotopic signature of the bulk soil under the two treatments was mainly because of the SOM pools decomposed at medium and high temperatures (310 to 1000°C). The $\delta^{13}C$ of SOM pools decomposed at 20–200 and 200–310°C was not significantly altered by elevated CO_2 (Table 2).

The isotopic signatures of the carbon in bulk soils and SOM pools under ambient and elevated CO_2 allowed the amount of new FACE-derived C incorporated into SOM pools over three years to be calculated. After 3 years of CO_2 fumigation, this

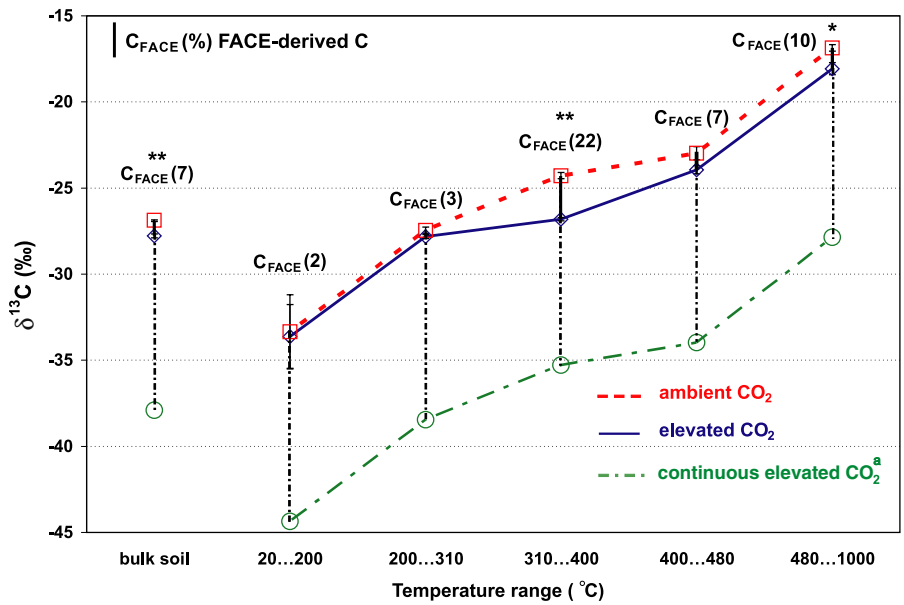

Fig. 2 $\delta^{13}C$ values of bulk soil and five SOM pools with different thermal stability under ambient and elevated CO_2 treatments. The calculated theoretical $\delta^{13}C$ values of soil developed under continuous elevated CO_2 conditions were used to estimate the portion of FACE-derived C (C_{FACE}) in the SOM (*vertical bold lines* and *numbers in brackets*). *Whiskers* present standard error (±SE). $^{*}P<0.05$ and $^{**}P<0.01$ represent the significance of differences between ambient and elevated CO_2 treatments. [a]Theoretical $\delta^{13}C$ values under continuous elevated CO_2 were calculated based on Equation 3: $\delta^{13}C_{elev.theor.} = \delta^{13}C_{elev.plant} - \left(\delta^{13}C_{amb.plant} - \delta^{13}C_{amb}\right)$

value in bulk soil under the elevated treatment reached 7.3% (Fig. 2). This agrees with the C inputs by spring wheat in a 2-year enrichment with CO_2 reported by Leavitt et al. (2001). They found the new carbon fraction to be 6.3% in the upper 15 cm of soil. Studies with cotton showed that the average amount of new C ranged from 6 to 12% after three years of elevated CO_2 (Leavitt et al. 1994). Van Kessel et al. (2006) reported higher C inputs of 22–26% under a grassland consisting of *Lolium perenne* and *Trifolium repens* in a FACE experiment after three years of CO_2 enrichment. These larger new C inputs, however, mainly reflect grassland plant species and the absence of tillage (Van Kessel et al. 2006).

Calculating the FACE-derived C in SOM pools with different thermal stability as a kg C ha^{-1} provided detailed information on the quantity of the new carbon in a pool. Surprisingly, the SOM pool decomposed at 200–310°C had the largest C content but accumulated 2.3 times less new C than that decomposed in the next temperature range (310–400°C) (Table 2). This is indicated by the small differences in $\delta^{13}C$ values between soil samples under ambient and elevated CO_2 decomposed from 200 to 310°C.

The turnover rate of the FACE-derived C in the bulk soil corresponded to the MRT of 39±2 years. The MRTs of the SOM pools decomposed at various temperatures ranged from 12±1 years (310–400°C) to 149±150 years (20–200°C) (Table 2). Results on the MRTs of pools decomposed at 20–200 and 200–310°C have to be interpreted with care due to the large standard errors appearing from small isotopic differences in corresponding SOM pools between CO_2 treatments. The MRTs of the thermally stable SOM pools showed lower values of 35±6 (400–480°C) and 28±5 (480–1,000°C) years compared to thermally labile SOM pools (Table 2). Balesdent (1996) found that chemical separations of SOM failed to isolate the SOM pools of different turnover time. Thus, the SOM pools isolated by acid hydrolysis or wet oxidation and thermal decomposition were poorly correlated with soil C age. In contrast, physical separation of soil into particle-size fractions showed good correlation between the turnover time of SOM and its association with a particle size fraction – the turnover rates decreased with decreasing particle size (Balesdent 1996). Studies using density fractionation as another kind of physical separation of SOM showed that light fractions including recent, partially decomposed plant residues have faster turnover rates of C compared to heavy fractions (organo–mineral complexes) (Pendall et al. 2004; Sleutel et al. 2006; Six et al. 2001). The absence of correlation between the thermally isolated SOM pools and their MRTs in our study suggests that thermal oxidation is more closely analogous to chemical, rather than physical, fractionation of SOM.

It is important to note that the hypothesis of correlation between the thermally isolated SOM pools and their MRTs is complicated by two factors. Firstly, different biochemical plant components (cellulose, lignin) are decomposed in a wide temperature range (Lopez-Capel et al. 2005b). It means that individual components of plant residues may be directly incorporated into or even mixed with the thermal stable SOM fraction and so will mask the low turnover rates of this fraction. Secondly, individual plant compounds such as cellulose and lignin have different isotopic composition (Hobbie and Werner 2004; Lopez-Capel et al. 2005a). By our hypothesis we assumed that the new C from wheat grown under elevated CO_2 has uniform isotopic compositions. Hence, specific $\delta^{13}C$ values of plant residue compounds decomposed up to threshold temperatures could change the calculated MRTs of SOM pools of different thermal stability and need to be studied in further experiments. However, if we assume that the average difference of $\delta^{13}C$ values between cellulose and lignin is about 4‰ (Hobbie and Werner 2004), and incorporation of these compounds amounts less than 10% of C of a SOM pool, then the error produced by unequal isotopic composition of plant residues is less than 5% of the calculated contributions of new C. Furthermore, this is the maximal error connected with unequal isotopic composition because the plant residues and rhizodeposits of wheat contain little lignin and because individual compounds are not incorporated into only one specific SOM pool.

The portion of new fertilizer-derived N

The statistical analysis of $\delta^{15}N$ values performed for the bulk soils and SOM pools decomposed at different temperatures showed no effect of elevated CO_2 treatment on N cycling (Table 3). Other studies yielded contrasting results on N turnover under the elevated CO_2 concentrations. Dijkstra et al. (2005)

and Van Kessel et al. (2006) reported results similar to ours, showing no significant influence of atmospheric CO_2 on N dynamics. Daepp et al. (2000); Hartwig et al. (2002) and Zanetti et al. (1997) showed lower N turnover under elevated CO_2. Accelerated N turnover under elevated CO_2 was observed for N_2-fixing legumes (Hartwig et al. 2002; Nitschelm et al. 1997; Zanetti et al. 1997).

SOM pools decomposed from 310 to 400°C under both ambient and elevated CO_2 treatments showed the largest enrichment in ^{15}N. $\delta^{15}N$ values of the latter SOM pools (21.69±0.43‰ under ambient treatment and 22.69±0.30‰ under elevated CO_2 treatment) were closer to the signature of fertilizers compared to other SOM pools (Table 3). In the most thermally stable SOM pools (480–1000°C), the $\delta^{15}N$ values (9.16±0.19‰ under ambient treatment and 9.57± 0.41‰ under elevated CO_2 treatment) were similar to that of bulk soil before applying ^{15}N labeled fertilizers (7.2‰). Distribution of the new fertilizer-derived N among the SOM pools of different thermal stability under both treatments showed two pools with the largest amount of N_{fertil}, those decomposed at 200–310 and 310–400°C. However, MRTs of the pools decomposed in the wide temperature range of 20–480°C indicated similar values averaging to 60 years (Table 3). Only the most thermally stable SOM pool (480–1000°C) having the smallest amount of N_{fertil} had MRT of hundred of years indicating very slow N incorporation.

A study conducted by Van Groenigen et al. (2002, 2003) on N turnover in SOM pools in grassland by means of density and aggregates size fractionation under elevated CO_2 and N fertilization showed gradual decrease in the N_{fertil}. The largest amount of fertilizer-derived N was detected in free light fraction of SOM, an intermediate amount – in intra-aggregate particular OM, and the lowest amount in mineral associated OM. On the one hand, low incorporation of N_{fertil} into the most thermally stable SOM pool in our experiment coincides with the lowest amount of fertilizer-derived N in mSOM found by Van Groenigen et al. (2002, 2003). However, in contrast to the findings of Van Groenigen et al. (2002, 2003) our results indicated non-gradual distribution of N_{fertil} among SOM pools with very contrasting values of MRT.

We conclude that differential thermal analysis of soil under three years of elevated CO_2 was not sufficient for clear separation of SOM pools with contrasting turnover rates. However, direct measurements of isotopic signature of CO_2 released by respective temperature may improve the applicability of the approach.

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