

Increase in soil stable carbon isotope ratio relates to loss of organic carbon: results from five long-term bare fallow experiments

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Abstract Changes in the $^{12}\text{C}/^{13}\text{C}$ ratio (expressed as $\delta^{13}\text{C}$) of soil organic C (SOC) has been observed over long time scales and with depth in soil profiles. The changes are ascribed to the different reaction kinetics of ^{12}C and ^{13}C isotopes and the different isotopic composition of various SOC pool components. However, experimental verification of the subtle isotopic shifts associated with SOC turnover under field conditions is scarce. We determined $\delta^{13}\text{C}$ and SOC in soil sampled during 1929–2009 in the Ap-horizon of five European long-term bare fallow experiments kept without C inputs for 27–80 years and covering a latitudinal range of 11° . The bare fallow soils lost 33–65 % of their initial SOC content and showed a mean annual $\delta^{13}\text{C}$ increase of 0.008–0.024 ‰. The ^{13}C enrichment could be related empirically to SOC losses by a Rayleigh distillation equation. A more complex mechanistic relationship

was also examined. The overall estimate of the fractionation coefficient (ε) was -1.2 ± 0.3 ‰. This coefficient represents an important input to studies of long-term SOC dynamics in agricultural soils that are based on variations in ^{13}C natural abundance. The variance of ε may be ascribed to site characteristics not disclosed in our study, but the very similar kinetics measured across our five experimental sites suggest that overall site-specific factors (including climate) had a marginal influence and that it may be possible to isolate a general mechanism causing the enrichment, although pre-fallow land use may have some impact on isotope abundance and fractionation.

Keywords Stable carbon isotope ratio · Isotope fractionation · Rayleigh distillation · Natural abundance · Soil organic carbon

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Introduction

Soil organic C (SOC) is important in maintaining soil fertility and is a potential source/sink of atmospheric CO₂. Predicting changes in SOC turnover rates in response to changes in climate and land use is therefore of major importance (Lal 2004).

C isotope analysis is a powerful tool for the study of C turnover in the complex soil decomposer system. During recent decades, differences in the natural abundance of ¹³C in plants with different photosynthetic pathways have frequently been used to trace sources of SOC and of CO₂ from soil respiration (Balesdent and Mariotti 1996; Ekblad and Höglberg 2000; Bowling et al. 2008). Recent innovations have made mass spectrometers more abundant and precise, while the introduction of portable instruments to be used in the field (e.g. Bowling et al. 2003; Bahn et al. 2009; Subke et al. 2009; Epron et al. 2011; Menichetti et al. 2013) has contributed to more widespread use of stable C isotope techniques.

Studies of C turnover in soil often assume that the ¹²C/¹³C ratio ($\delta^{13}\text{C}$) of different SOC fractions does not change over time, although experimental verification of this assumption is meagre (Christensen et al. 2011). Balesdent and Mariotti (1996) found that the $\delta^{13}\text{C}$ value of SOC increased in the absence of inputs (soil under sustained bare fallow) while Clay et al. (2007) reported erroneous estimates of SOC losses from vegetation-free alleyways when effects of natural isotopic enrichment were neglected. Corrections for isotopic shifts may be superfluous when mixing sources (e.g. two C pools derived from plants with different photosynthetic pathways) are subject to similar and self-compensating isotopic shifts. But still there is little consensus regarding the quantitative significance and the generality of the longer-term isotopic shift observed under field conditions.

Processes leading to changes in ¹³C abundance are several, but are mainly ascribed to biological activity (Ehleringer et al. 2000). Isotopic fractionations occur within decomposer cells during their metabolism, where kinetic fractionation in metabolic branching points may lead to isotopically enriched and depleted products (Gleixner et al. 1993, 1998; Tu and Dawson 2005). Decomposer preferences for specific classes of organic compounds (for which $\delta^{13}\text{C}$ may differ by up to 10 ‰) also introduce changes in $\delta^{13}\text{C}$ of the residual SOC (Gleixner et al. 1998; Ehleringer et al. 2000; Bowling et al. 2008; Werth and Kuzyakov 2010). Vegetation and land use history can lead to a site-specific distribution of ¹³C across SOC fractions with different lability (e.g. Gerzabek et al. 2001; Schmidt and Gleixner 2005). Thus preferential decay of SOC fractions depleted in ¹³C will lead to a gradual increase in the $\delta^{13}\text{C}$ value of SOC left behind in the soil. One such example is

preferential retention in soil of ¹³C-enriched microbial biomass residues (e.g. Ehleringer et al. 2000; Boström et al. 2007; Clemmensen et al. 2013).

One possible source of $\delta^{13}\text{C}$ diversity in SOC is that the $\delta^{13}\text{C}$ value recorded for SOC at a given point in time reflects the isotopic composition of decomposition products cumulated from generations of plants that have experienced a gradual depletion in the ¹³C of atmospheric CO₂. This depletion, known as the Suess effect, relates to historical use of fossil energy and deforestation (Keeling 1979), which has decreased the atmospheric $\delta^{13}\text{C}$ from -6.3 ‰ in 1750 to around -8 ‰ today (Francey et al. 1999; Rubino et al. 2013). This change in the atmospheric $\delta^{13}\text{C}$ composition might have generated a $\delta^{13}\text{C}$ gradient in the SOC that has accumulated over decades to centuries. Preferential decomposition of SOC components, formed more recently and thus relatively depleted in ¹³C, adds to the ¹³C enrichment of the residual SOC. Preferential decomposition can also arise from physical or physico-chemical stabilisation of SOC fractions with different isotopic signatures. This process might be site specific, as suggested by Krull and Skjemstad (2003) in their study of $\delta^{13}\text{C}$ depth profiles in an Oxisol and a Vertisol, and by Wynn et al. (2005) in their study on the effect of soil texture on $\delta^{13}\text{C}$ in soil profiles under similar climate and vegetation.

It remains a challenge to link the outcome of short-term laboratory studies of specific fractionation processes and with specific substrates to the complex soil decomposer system with a multitude of substrates, in which several fractionation processes occur simultaneously and where most of the SOC turns over very slowly. Short-term laboratory studies are indispensable to reveal and quantify individual mechanisms that lead to $\delta^{13}\text{C}$ shifts, but fall short when results are extrapolated uncritically to field conditions and long-term scales (Lerch et al. 2011). The overall impact of C isotopic shifts associated with SOC turnover and its direction remains unsettled (Werth and Kuzyakov 2010).

Balesdent and Mariotti (1996) used the Rayleigh distillation function to link changes in $\delta^{13}\text{C}$ to losses of SOC in a long-term bare fallow experiment in Versailles (France). Here we extend this approach to soil samples from five European long-term bare fallow experiments that have been kept free of vegetation and organic inputs for 27–80 years. The experimental sites span 11° in latitude and 34° in longitude, with Versailles being the southernmost and Ultuna the northernmost site. The data set from the Versailles experiment used by Balesdent and Mariotti (1996) now includes a further 13 years of continuous bare fallow and data on soil particle size separates. Our objective when using the Rayleigh function was to examine whether a general relationship between SOC loss and increase in $\delta^{13}\text{C}$ could be established.

Table 1 Main characteristics of the five bare fallow experiments and years of the treatment covered in the present study

	Versailles	Grignon	Kursk	Askov	Ultuna
Longitude	48°48'N	48°51'N	51°34'N	55°28'N	59°49'N
Latitude	2°08E	1°55E	36°05E	9°07E	17°38E
Period	1928–2009	1959–2009	1947–2009	1956–1985	1956–2009
Pre-fallow history	Grassland	Grassland	Grassland	Arable	Arable
Plot size (m)	2 × 2.5	3.2 × 3.2	60 × 100	11.7 × 9.4	2 × 2
Soil sampling depth (cm)	0–25	0–25	0–~17.5	0–20	0–20
Clay/silt/sand (weight %)	17/57/26	30/54/16	30/65/5	10/13/77	36/41/23
Initial pH (H ₂ O)	6.4	8.2	6.5 ^a	6.0 ^b	6.5
Mean annual temperature (°C)	10.7	10.7	5.4	7.8	5.5
Mean annual precipitation (mm)	628	649	610	862	533
Initial SOC content (g C kg ⁻¹)	18.8 ± 0.5	13.9 ± 0.4	51.8 ± 0.2	15.1 ± 0.6	14.8 ± 0.2
Final SOC content (g C kg ⁻¹)	6.6 ± 0.2	8.3 ± 0.2	29.8 ± 0.1	10.1 ± 0.4	9.4 ± 0.2
Initial δ ¹³ C (‰)	-26.7 ± 0.3	-25.8 ± 0.1	-26.2 ± 0.1	-27.3 ± 0.1	-26.3 ± 0.4
Final δ ¹³ C (‰)	-24.7 ± 0.1	-25.2 ± 0.1	-25.6 ± 0.1	-27.0 ± 0.1	-25.7 ± 0.4

Errors are reported as SE

SOC Soil organic C, δ¹³C
¹²C/¹³C ratio

^a Measured in KCl extract

^b Maintained with lime

Materials and methods

Experimental sites

This study draws upon five differently sited experiments included in the European long-term bare fallow network (Barré et al. 2010). Each experiment fulfils the following criteria: (1) plots have been kept without vegetation and organic amendments for more than 25 years; (2) SOC in the Ap-horizon has been determined regularly; and (3) there is an associated soil archive, allowing for analyses of δ¹³C and SOC content after different periods of bare fallow. The five experimental sites are Versailles and Grignon (France), Kursk (Russia), Askov (Denmark) and Ultuna (Sweden).

Versailles

The Versailles fertilisation experiment (Table 1) was initiated in 1928 in the gardens of the Chateau of Versailles, situated at 48°N latitude in France. The area was covered by forest until the end of the sixteenth century and thereafter it is believed to have been mostly under unmanaged grassland until the start of the bare fallow experiment. The climate is the same as at Grignon (see below). The soil is classified as a Eutric Cambisol (IUSS Working Group 2007; Guenet et al. 2011), developed on the aeolian loess that characterises the Paris Basin (Barré et al. 2010). All plots are dug by hand twice a year to a depth of 25 cm, and kept almost free from vegetation by hand weeding and herbicide treatments. The site has ten plots receiving neither fertiliser nor organic amendments. All plots have been sampled regularly over the years and six plots were included in the present study.

The field received charcoal during World War II, probably due to nearby bombing, and the presence of charcoal has been substantiated recently by Vasilyeva et al. (in

review) using soil particle-size fractionation. The input of charcoal with a different C isotopic signature may compromise the δ¹³C value of the native SOC. Thus for the Versailles experiment, δ¹³C was determined for bulk soil and its clay and silt size fractions. These soil size fractions were observed to be devoid of visible charcoal. Data on the soil size fractions were taken from Vasilyeva et al. (in review).

Grignon

The Grignon site (Table 1) is a fertilisation experiment initiated in 1959 in the gardens of the Chateau of Grignon, situated at 48°N latitude in France. Before 1875, the area was mostly unmanaged grassland (Houot et al. 1989). The climate is classified as oceanic (Cfb) according to the Köppen classification (Peel et al. 2007). The mean annual temperature at the site is 11 °C, the mean for January–February is 3 °C and that for July–August is 25 °C. Mean annual precipitation is 649 mm. The soil is a silty loam classified as a Haplic Luvisol (Colbach et al. 2000; IUSS Working Group 2007), developed on colluvium carbonate deposits. All plots are dug by hand twice a year to a depth of 25 cm, and kept almost free from vegetation by hand weeding and herbicide treatments. The experiment includes six different treatments, including one reference treatment with no amendments which was considered in this study. Further details can be found in Morel et al. (1984).

Kursk

The Kursk site at 51°N latitude in Russia (Table 1) is located on a silty loam Haplic Luvisol (IUSS Working Group 2007) developed under grassland on loess deposits (Mikhailova and Post 2006). The area represents one of the last fragments of native Russian meadow steppe that has

been subjected only to haymaking and grazing for the last four centuries. The climate is classified as subarctic (Dfc) according to the Köppen classification (Peel et al. 2007). In 1935, the Central-Chernozem State Natural Biosphere Reserve was established. Part of the steppe at the site (the Streletzkaya Steppe) has been protected to restore its native vegetation, while another part has remained under annual haymaking. The bare fallow experiment was started in 1947 as a single 60-m × 100-m plot embedded in the annual haymaking area of the steppe. The mean annual precipitation is 610 mm and the mean temperature is -8.6 °C in January–February and 19.3 °C in July–August. The plot was tilled annually to a depth of 17–18 cm by horse-drawn implements until the mid-1970s and since then by tractor-drawn implements to a depth of 22–24 cm. Weeds are eliminated upon emergence by harrowing, which keeps the site almost free from vegetation. Soil was sampled with a hand-held probe in 1986 and 2008 and archived. In the absence of archive samples from time zero of the bare fallow, soil was sampled in 2008 from the adjacent Streletzkaya Steppe, which is under natural vegetation (Vasilyeva 2009).

Askov

Subsamples were retrieved from the soil archive of a field experiment with bare fallow initiated in 1956 and terminated in 1985 (Table 1). The experiment was situated next to the Lermarken B4 field of the Askov long-term field experiments on animal manure and mineral fertilizers (Denmark), located at 55° N latitude and with a oceanic (Cfb) climate according to the Köppen classification (Peel et al. 2007). The climate is characterised by mild winters, with a mean temperature in January–February of 0 °C, and cool summers, with a mean temperature in July–August of 15 °C. The mean annual precipitation is 862 mm. The soil is classified as a Haplic Luvisol (IUSS Working Group 2007), with 77 % sand, 13 % silt and 10 % clay developed from a morainic deposit. The dominant minerals in the clay-sized fraction are illite and smectite. The site came under arable use around 1800. Before that the area was mixed heath and grassland, with scattered deciduous scrubs. The experiment included four replicate plots kept almost free from vegetation by tractor-pulled implements and received a mineral fertilization corresponding to an average annual rate of 70 – 100 kg N ha $^{-1}$, 18 – 19 kg P ha $^{-1}$ and 66 – 87 kg K ha $^{-1}$. Every year, soil from 0- to 20-cm depth was retrieved from each replicate plot by bulking soil from nine to 11 random locations within the plot. The soil was dried and sieved before being stored in the soil archive. This study used soil sampled in 1956, 1962, 1968, 1976 and 1983 from the bare fallow treatment. Further details can be found elsewhere (Christensen and Johnston 1997; Christensen et al. 2011).

Ultuna

The Ultuna (Table 1) experiment was initiated in 1956 at a cool temperate site located at 59.5° N latitude in Uppsala (Sweden), with a humid continental (Dfb) climate according to the Köppen classification (Peel et al. 2007). The mean annual temperature is 6 °C, the mean temperature in January–February is -8 °C and that in July–August is 13 °C. The mean annual precipitation is 586 mm. The soil is a Eutric Cambisol (IUSS Working Group 2007) with 37 % clay and 41 % silt. The parent material is post-glacial clay dominated by illite (Gerzabek et al. 1997). The site has been in agricultural use for at least 300 years. Since the start of the experiment, all field work has been performed by hand to 20-cm depth and plots are kept almost free from vegetation by hand weeding. The experiment includes 15 treatments in a randomised block design, providing a total of 60 plots, each measuring 2 m × 2 m. Four plots are under bare fallow and are utilized in this study. Soil is sampled between 0- and 20-cm depth every second year with a soil corer at five random locations in each plot and a composite sample per plot is stored in the soil archive. Further details can be found in Kirchmann et al. (1994) and Kätterer et al. (2011). SOC was determined by the Walkley–Black method from 1956 to 1983 and thereafter by dry combustion.

Chemical analysis

The routine analyses data set (Table 1) for the sites has been retrieved from different sources applying different analytical procedures and equipment. For the Ultuna experiment, Kätterer et al. (2011) found a close relationship ($R^2 = 0.90$) between different SOC analyses performed in studies during the previous 50 years. The $\delta^{13}\text{C}$ values have also been analysed in different laboratories and times. The Ultuna series has partly been analysed at Örebro University Isotope Laboratory for the present study using an elemental analyser (EuroEA3024; Eurovector, Milan) coupled on-line to a continuous flow isotope-ratio mass spectrometer (IRMS) (Isoprime; GV Instruments, Manchester), and partly using an elemental analyser (NA 1500; Carlo Erba, Milan) coupled on-line with an IRMS (MAT 251, Finnigan, Bremen, Germany) (Gerzabek et al. 2001). The consistency of these two data sets has been confirmed by re-analyses of samples from the Ultuna soil archive at Örebro University. The analysis for Askov soils (Christensen et al. 2011) was based on a PDZ Europa ANCA-GSL elemental analyser interfaced to a PDZ Europa 20e20 IRMS (Sercon, Cheshire, UK). The Versailles, Grignon and Kursk soils were analysed in 2011 using a CHN NA 1500 (Carlo Erba) coupled with an IRMS (VG Sira 10). The elemental analysis and $\delta^{13}\text{C}$ values for the clay and silt particle size fractions from

Versailles are reported by Vasilyeva et al. (in review). In the present study, the changes in $\delta^{13}\text{C}$ at different sites were compared based on differences ($\Delta^{13}\text{C}$) between initial $\delta^{13}\text{C}$ values and the corresponding values at time t , eliminating any analytical biases in the determination of isotope ratios.

Calculations

Data were analysed with the latest version of the R statistical software (R Development Core Team 2012). We adopted two different approaches to describe the observed results. The first approach considers the overall fractionation associated with SOC losses as CO_2 by using the Rayleigh distillation function (Mariotti et al. 1981; Rayleigh 1896). This function describes the development of $\delta^{13}\text{C}$ in a closed system:

$$\delta_r = \delta_i + \varepsilon \ln(f) \quad (1)$$

where δ_r is the $\delta^{13}\text{C}$ value of the residual SOC (f = the fraction of SOC remaining at time t), δ_i is the initial $\delta^{13}\text{C}$ value of the SOC and ε is the Rayleigh fractionation coefficient expressed as $\delta^{13}\text{C}$ ‰. The coefficient ε represents the slope of the enrichment, when the enrichment is linearly proportional to the natural logarithm of soil C losses. Equation 1 was used to calculate ε for each point of our data set. The subsequent estimation of the overall ε was performed according to Bayesian principles. This is advantageous since the combination of all sites may produce a relatively complex probability density space. We utilised a Metropolis–Hastings search algorithm running the model in R through the JAGS sampler (Plummer 2003), with a formal likelihood function built around the log-normal distribution. For ε we chose an uninformative a priori distribution, generated as a uniform distribution in the range 0 to -10 . The model was calibrated based on a chain of 100,000 runs for each site, and then on a chain of 300,000 runs to obtain the overall ε value. The error for each calibrated ε was considered as the SD of the population resulting from all runs. Conventionally, the Rayleigh function describes a distillation process occurring within a homogeneous substrate and applying the function to SOC in principle does not align with this assumption. Thus for our data set, the function merely describes an exponential change in the isotopic signature relative to the substrate left and should be considered a semi-empirical, aggregated function.

The second approach assumes the SOC to consist of one labile and one stable pool. The two SOC pools in the model were defined according to the exponential decay function:

$$\text{SOC}_t = \text{SOC}_{\text{stable}} + \text{SOC}_{\text{labile}} e^{(-kt)} \quad (2)$$

which describes total SOC at time t (SOC_t) as the sum of a stable SOC pool ($\text{SOC}_{\text{stable}}$) with no decay during the

period considered here and a labile SOC pool ($\text{SOC}_{\text{labile}}$) that decays at rate k . The k parameter in Eq. 2 was calibrated with a uniform distribution ranging between 0.001 and 0.2, and the $\text{SOC}_{\text{stable}}$ pool was calibrated considering a normal distribution in a range of ± 0.2 around the average value of the stable pools, estimated for the five experiments by Barré et al. (2010). Equation 2 has previously been identified as the best compromise between goodness of fit and complexity in describing total SOC decay in the bare fallow soils (Barré et al. 2010). The $\delta^{13}\text{C}$ of the total SOC was then examined by a weighted average between the $\delta^{13}\text{C}$ of the two pools according to the following equation:

$$\delta^{13}\text{C}_{\text{SOC}_{\text{total}}} = \frac{\delta^{13}\text{C}_{\text{SOC}_{\text{stable}}} \text{SOC}_{\text{stable}} + \delta^{13}\text{C}_{\text{SOC}_{\text{labile}}} \text{SOC}_{\text{labile}}}{\text{SOC}_{\text{stable}} + \text{SOC}_{\text{labile}}} \quad (3)$$

The complete model resulting from Eqs. 2 and 3 was calibrated by a Metropolis–Hastings search algorithm against the $\delta^{13}\text{C}$ of total SOC. This was to establish the theoretical difference in $\delta^{13}\text{C}$ between the two pools (defined by Eq. 2) that would fit the observed enrichment. The $\delta^{13}\text{C}$ of the two SOC pools in Eq. 3 was calibrated with a normal distribution centred on the mean $\delta^{13}\text{C}$ value of total SOC and with variance equal to 3 ‰. The error for each $\delta^{13}\text{C}$ difference was taken as the SD of the population resulting from the difference between the calibrated $\delta^{13}\text{C}$ of $\text{SOC}_{\text{stable}}$ and the calibrated $\delta^{13}\text{C}$ of $\text{SOC}_{\text{labile}}$ across all runs.

Results

The SOC concentrations decreased at all sites (Table 1; Fig. 1). At Versailles and Grignon, where the experiments were established on former grassland, SOC decreased from 18.8 to 6.6 g C kg⁻¹ dry soil (65 % in 80 years) and from 13.9 to 8.3 g C kg⁻¹ (40 % in 48 years), respectively. Both sites showed a steep initial decline. At Kursk, a former SOC-rich grass steppe, SOC decreased from 51.8 to 29.8 g C kg⁻¹ (42 % in 61 years). At Askov and Ultuna, where the experiments were established on former cultivated land, SOC decreased from 15.1 to 10.1 g C kg⁻¹ (33 % in 27 years) and 14.8 to 9.4 g C kg⁻¹ (36 % in 57 years), respectively, with a more constant decrease over time (Fig. 1).

The initial $\delta^{13}\text{C}$ differed somewhat between sites (Table 1), with -26.7 ‰ at Versailles, -25.8 ‰ at Grignon, -26.2 ‰ at Kursk, -27.3 ‰ at Askov and -26.3 ‰ at Ultuna. The increase in $\delta^{13}\text{C}$ over time was 2.0 ‰ at Versailles, 0.6 ‰ at Grignon, 0.6 ‰ at Kursk, 0.3 ‰ at Askov and 0.6 ‰ at Ultuna (Fig. 1). The mean annual increase in $\delta^{13}\text{C}$ ranged from 0.008 to 0.024 ‰.

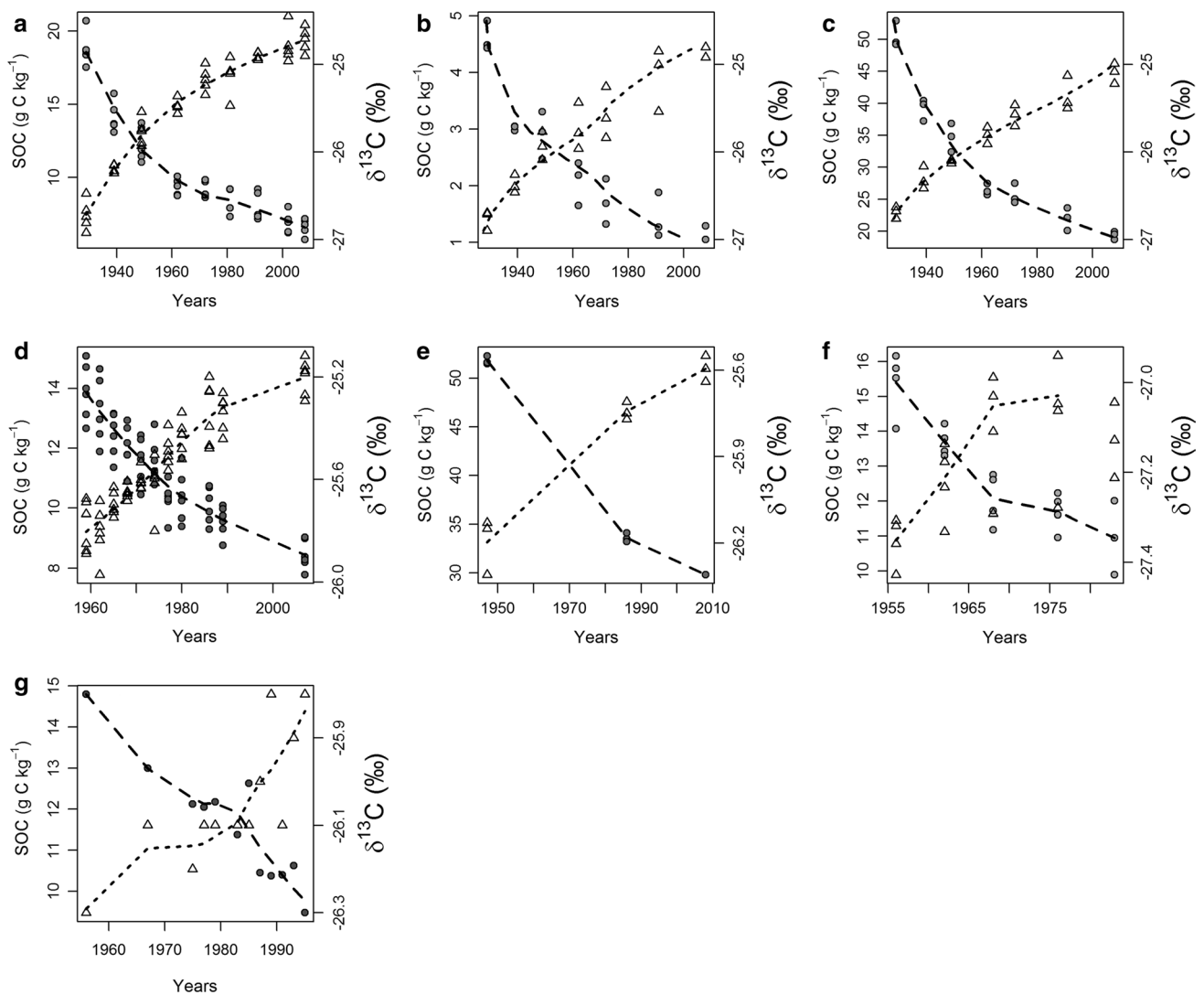


Fig. 1 Changes in soil organic C (SOC; circles) and $^{12}\text{C}/^{13}\text{C}$ ratio ($\delta^{13}\text{C}$; triangles) for Versailles bulk soil (a), Versailles silt fraction (b), Versailles clay fraction (c), Grignon (d), Kursk (e), Askov (f) and Ultuna (g). Trends highlighted by lines represent non-parametric local regressions

The initial $\delta^{13}\text{C}$ value for the Versailles clay and silt fractions was -26.7 and -26.8 ‰, respectively. The $\delta^{13}\text{C}$ showed an increase of 1.6 ‰ in the clay and 1.9 ‰ in the silt size fraction (Vasilyeva et al., in review). The annual increase in $\delta^{13}\text{C}$ was 0.020 ‰ in the clay and 0.024 ‰ in the silt fraction.

Relating shifts in $\delta^{13}\text{C}$ to loss of total SOC

The $\delta^{13}\text{C}$ increase (reported as $\Delta^{13}\text{C}$) was proportional to the natural logarithm of SOC loss (Fig. 2). The relationship was not systematically affected by soil type or climate, but site history seemed to play a role in one case. At Versailles, $\Delta^{13}\text{C}$ was slightly higher than at the other sites and the logarithmic relationship steeper (Fig. 4). This is most likely attributable to the charcoal, which has a $\delta^{13}\text{C}$ about

3 ‰ higher than that of the native SOC (Vasilyeva et al., in review). The Versailles clay and silt fractions, devoid of visible charcoal, showed a relationship between a $\delta^{13}\text{C}$ increase and SOC loss that was in accordance with that observed for bulk soils from the other bare fallow sites (Fig. 3). At Versailles, the site-specific enrichment coefficients (ε) were -1.9 ± 0.1 , -1.6 ± 0.2 and -1.3 ± 0.3 ‰ for bulk soil, clay and silt, respectively. At the other sites, the coefficient ε was -1.1 ± 0.2 ‰ at Grignon, -1.1 ± 0.3 ‰ at Kursk, -0.9 ± 0.4 ‰ at Askov and -1.0 ± 0.5 ‰ at Ultuna. When Versailles bulk soil was replaced with clay and silt fractions, the overall ε value across all sites was -1.2 ± 0.3 ‰. An ANOVA performed on the population of ε calibrated for each replicate plot gave no significant differences [confidence interval (CI) 95 %] between sites, except when using bulk soil values for Versailles.

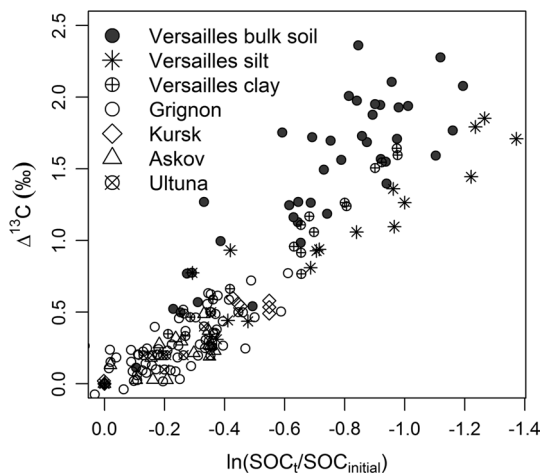


Fig. 2 Changes in $\delta^{13}\text{C}$ signatures in all individual plots at the five sites plotted against the natural logarithm of the fraction of C remaining

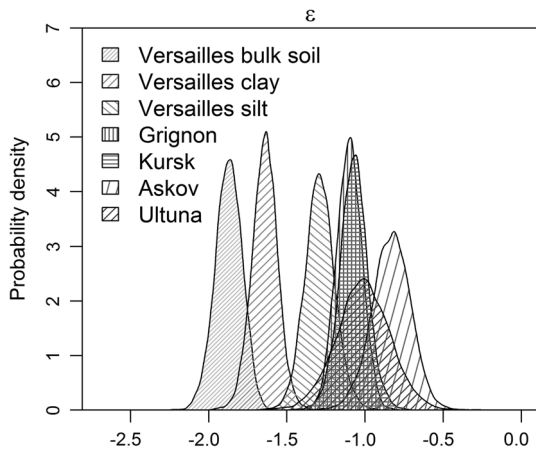


Fig. 3 Probability density distributions of the enrichment coefficient (ϵ) estimated by a Raleigh distillation function for the five sites

Shifts in $\delta^{13}\text{C}$ with a two-pool SOC model

On applying the model with a stable and a labile SOC pool (Barré et al. 2010) and using Eq. 3 to estimate the

$\delta^{13}\text{C}$ of the two pools that would fit the observed changes in $\delta^{13}\text{C}$ (Fig. 1), we found the differences between the pools to be $3.4 \pm 0.2 \text{ ‰}$ at Versailles, $2.0 \pm 0.3 \text{ ‰}$ at Grignon, $1.8 \pm 0.3 \text{ ‰}$ at Kursk, $1.1 \pm 0.5 \text{ ‰}$ at Askov and $1.7 \pm 0.6 \text{ ‰}$ at Ultuna (Table 2). Although the estimates depend on the calibration procedures and on the prior assumptions, the use of a two-pool SOC decay model represents a more mechanistic approach to analyse the observed enrichment in ^{13}C . Given the decay model and the prior assumptions, the Bayesian framework allows the uncertainty of the estimates to be analysed. After being calibrated by minimising the error in predictions of $\delta^{13}\text{C}$, the model resulting from Eqs. 2 and 3 presented smaller errors than the Rayleigh equation in the case of Versailles and Grignon (former grassland sites), whereas no big differences were found for the other three sites (Table 3).

Discussion

The main objective of this study was to describe changes in ^{13}C abundance as a function of SOC decay and test whether one general relationship would fit data from all five sites. The natural logarithm of the fraction of SOC remaining accounted for most of the recorded $\Delta^{13}\text{C}$ at all five sites studied (Fig. 2), substantiating that the Rayleigh model provides a satisfactory fit (Table 3; Fig. 4). ϵ for the Versailles bulk soil was slightly higher than that reported by Balesdent and Mariotti (1996), probably because more than 10 years of data were added to their time series. Because of the longer time frame considered here, a higher ϵ is consistent with a relatively larger influence of a recalcitrant C pool with time (see the discussion below on using a two-pool model). All ϵ values were substantially smaller than the average values of 3.45 and 6.96 ‰ reported by Clay et al. (2007) for a sandy loam and loamy sand, respectively. However, the history of their experimental set up was less consistent than the long-term continuous bare fallow experiments involved in our study.

The site-specific ϵ values did not differ significantly, except that the Versailles bulk soil had a somewhat larger ϵ according to the Bayesian calibration (Fig. 3) and the

Table 2 Calibration results for the two-pool model in which we estimated what differences in isotopic signatures of a labile pool and a stable pool are needed in order to explain the observed changes in $\delta^{13}\text{C}$ in the bare fallow experiments

	Versailles	Grignon	Kursk	Askov	Ultuna
$\delta^{13}\text{C}$ stable pool (‰)	-23.6 ± 0.1	-24.8 ± 0.2	-24.8 ± 0.2	-26.4 ± 0.4	-25.1 ± 0.4
$\delta^{13}\text{C}$ labile pool (‰)	-27.1 ± 0.1	-26.8 ± 0.2	-26.6 ± 0.1	-27.6 ± 0.1	-26.8 ± 0.2
$\delta^{13}\text{C}$ difference (‰)	3.4 ± 0.2	2.0 ± 0.32	1.8 ± 0.3	1.1 ± 0.5	1.7 ± 0.6
Stable pool proportion ^a	0.17 ± 0.02	0.51 ± 0.07	0.25 ± 0.03	0.26 ± 0.07	0.32 ± 0.09

Errors are reported as SE

^a The proportion of C in the stable pool was from data in Barré et al. (2010)

Table 3 Goodness of fit for the two models evaluated

	Rayleigh distillation function					Model with two SOC pools				
	Versailles (bulk)	Grignon	Kursk	Askov	Ultuna	Versailles (bulk)	Grignon	Kursk	Askov	Ultuna
RMSE	0.25	0.11	0.05	0.08	0.09	0.13	0.07	0.05	0.08	0.09
NSE	0.85	0.71	0.96	0.69	0.59	0.96	0.86	0.96	0.67	0.54
<i>D</i>	0.96	0.91	0.99	0.91	0.87	0.99	0.96	0.99	0.9	0.84
<i>R</i>	0.93	0.85	0.98	0.84	0.77	0.98	0.93	0.98	0.82	0.74
<i>R</i> ²	0.87	0.71	0.96	0.70	0.60	0.96	0.86	0.96	0.67	0.54

RMSE Root mean squared error, NSE Nash–Sutcliffe efficiency, *d* index of agreement, *r* Pearson's correlation coefficient, *R*² coefficient of determination

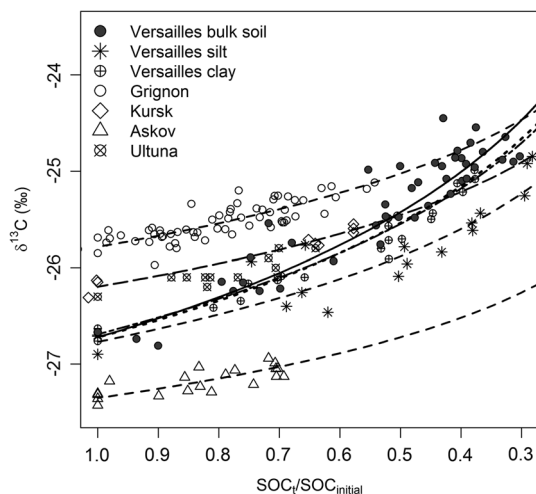


Fig. 4 The $\delta^{13}\text{C}$ for SOC vs. the proportion of C remaining. Lines indicate the Rayleigh function calibrated for each site. The black solid line represents the ϵ calibrated in this paper for Versailles, while the black dotted line represents ϵ calibrated by Balesdent and Mariotti (1996). Root mean squared error = 0.21 for Versailles silt, 0.10 for Versailles clay, 0.25 for Versailles bulk soil, 0.10 for Grignon, 0.05 for Kursk, 0.09 for Askov and 0.08 for Ultuna

ANOVA performed on the calibrated parameters. The ϵ coefficient averaged over all sites was associated with an error of just 0.09 ‰ δ units, lower than with Rayleigh equations calibrated for the individual sites. Thus it was possible to extract a general description of the enrichment across the five sites, although the variance of ϵ indicates some site-specific differences.

Difference in the continuous probabilities (Fig. 3) may be examined also beyond the 95 % CI (Webster 2007). It has been indicated that edaphic factors could play a role in the fractionation process. Wynn et al. (2005) suggested that texture might affect enrichment kinetics. For coarse-textured soils, they observed a linear rather than an exponential trend and suggested that physical mixing between pools with different isotopic signatures may be important. The more sandy soil at Askov showed probability distributions of the ϵ value toward the lower end of the recorded ϵ range,

while at Versailles SOC associated with clay was slightly more enriched in ^{13}C than SOC in silt. However, the only significant difference (95 % CI) was found for Versailles bulk soil, which had a higher ϵ than the other soils, probably due to the presence of ^{13}C -enriched charcoal. Charcoal can be considered as inert SOC within the time frame considered here, and its relatively high $\delta^{13}\text{C}$ (−23.6 ‰; Vasilyeva et al., in review) may influence the observed kinetics of the enrichment, providing one example of isotopic shifts due to preferential decomposition or preferential stabilisation of specific SOC components. The charcoal in the Versailles soil may represent a mixed pool of relatively young origin (from vegetation burning) as well as fossil origin (Lichtfouse et al. 1997).

Possible mechanisms leading to ^{13}C enrichment of SOC

The consistent increase in $\delta^{13}\text{C}$ observed in our experiments clearly demonstrates that the C lost from the SOC pool must have been depleted in ^{13}C . The loss of SOC may in principle take two directions, either upwards as gas emissions or downwards as dissolved inorganic C (DIC) and dissolved organic C (DOC). Annual losses of DOC may account for up to 10–20 % of total C losses (Bergkvist et al. 2003; Worrall et al. 2012) and losses of DIC for 10–20 % (Kindler et al. 2011). However, DIC (Skidmore et al. 2004) and DOC (Werth and Kuzyakov 2010; Blagodatskaya et al. 2011) appear to be enriched in ^{13}C relative to SOC, and losses of dissolved C would therefore tend to deplete rather than enrich the residual SOC in ^{13}C . Relevant CH_4 emissions from agricultural mineral soils, dominated by aerobic conditions, are unlikely (Powlson et al. 1997). CH_4 from any micro-sites capable of supporting methanogenesis remains negligible in the total C budget at the scale considered here. We are confident that the dominant loss of C from our permanent bare fallow soils has occurred as ^{13}C -depleted CO_2 .

Incubation studies report depletion (Šantrůčková et al. 2000; Kristiansen et al. 2004), no difference or enrichment (Ekblad and Höglberg 2000; Ekblad et al. 2002; Boström

et al. 2007; Werth and Kuzyakov 2009; Blagodatskaya et al. 2011) or enrichment followed by depletion (Lerch et al. 2011) of the ^{13}C in respired CO_2 relative to the substrate involved. The observed increase in $\delta^{13}\text{C}$ of the SOC over the bare fallow period clearly indicates that the net result of these processes must have been a release of CO_2 depleted in ^{13}C compared with the bulk SOC. Discrepancies in the literature might be caused by pre-incubation soil treatments, by the initial mineralisation of ^{13}C -enriched dead microbial biomass (Šantručková et al. 2000) or by the analytical approach used (Cheng 1996).

The possible causes for the observed enrichment fall into two main categories, one representing microbial metabolism and the other substrate effects. For substrate effects, enrichment may arise from preferential decay of SOC pools with different lability and different $\delta^{13}\text{C}$ values. The gradual depletion of atmospheric CO_2 - ^{13}C that has taken place since the start of the industrial revolution (the Suess effect) may have contributed to the $\delta^{13}\text{C}$ increase in SOC. Plants grown on the soil before the start of the bare fallow period were exposed to CO_2 that gradually declined in ^{13}C , whereby an age-dependent isotopic gradient was formed in the SOC pool. Thereby older SOC components would have higher $\delta^{13}\text{C}$ values than younger SOC components. The faster disappearance of the younger and more labile SOC would then introduce an isotopic enrichment in the remaining SOC. However, the magnitude of the Suess effect seems to be too small to explain the observed enrichment. Comparing the $\delta^{13}\text{C}$ values in archived samples of wheat grown during 1845 and 1997 in unfertilised plots of the Rothamsted Broadbalk continuous wheat experiment, Zhao et al. (2001) observed a decrease of 2.5–2.8 ‰ in the $\delta^{13}\text{C}$ of grain and of straw over 153 years. But most of this decrease occurred after the 1960s and was partly ascribable to changes in wheat cultivars. The overall change in $\delta^{13}\text{C}$ was less than 0.5 ‰ during the period 1845–1950. Since our soils were converted to bare fallow before 1959, we conclude that the pre-fallow Suess effect has played only a marginal role in the observed ^{13}C enrichment. Another potential cause for differences in the $\delta^{13}\text{C}$ of SOC pools is the different isotopic signature of the biochemical compounds that entered the soil before the fallow period. Plant compounds considered to be chemically recalcitrant during the initial phases of litter decomposition are usually depleted in ^{13}C (Bowling et al. 2008), while labile components are generally enriched in ^{13}C (e.g. Gerzabek et al. 2001; Schmidt and Gleixner 2005; Jagadamma and Lal 2010). This suggests that in a longer time perspective, CO_2 derived from SOC compounds with more negative $\delta^{13}\text{C}$ may prevail when organic inputs cease.

Historical differences between sites in vegetation, climate (Ghosh and Brand 2003), land use, and different origins of soil parent material can potentially cause isotopic differences in SOC pools. For example at Ultuna the parent

material includes material that was formed in the sediments of the former Littorina Sea. Such sediments contain not only organic C of marine origin but also recalcitrant organic C of terrestrial origin that can be thousands of years older than the sediment per se (Miltner et al. 2005; Kortekaas et al. 2007). The Ultuna soil may still contain SOC that originates from these postglacial sediments. The two-pool model was conceptually based on isotopically different SOC pools with different turnover rates, and provided a good simulation of the observed changes in ^{13}C that in some cases reduced the unexplained variance compared to the simpler Rayleigh model. The estimated difference between the $\delta^{13}\text{C}$ of the two SOC pools (ranging from 1.14 ‰ at Askov to 3.45 ‰ at Versailles) falls within the range of $\delta^{13}\text{C}$ observed for different experimentally defined SOC fractions (e.g. Jagadamma and Lal 2010). Thus the two-pool model seems compatible with observations. But the discrepancy between the stable pool size estimated by our model and that of Barré et al. (2010) for Versailles suggests that a two-pool model, although better representing the general kinetics, still misses some of the involved processes. The Versailles site seems already to have approached a steady state level for the SOC but not for the isotopic composition of the SOC.

Another category of processes promoting isotopic differences in SOC relates to microbial activity and metabolism. Changes in the $\delta^{13}\text{C}$ of SOC can arise from preferential stabilisation of ^{13}C -enriched microbial C. One process that contributes to ^{13}C enrichment of the microbial biomass is anaplerotic re-fixation of CO_2 by carboxylase. Ehleringer et al. (2000) estimated that a 5 ‰ contribution of re-fixed soil CO_2 (enriched by 4.4 ‰ relative to CO_2 in the soil gas phase) would lead to a 1–1.5 ‰ higher $\delta^{13}\text{C}$ value in the microbial biomass. Preferential use of ^{13}C -enriched SOC components by microbial decomposers (Šantručková et al. 2000) and, in the case of mycorrhizal fungi, of ^{13}C -enriched carbohydrates from the host plant (Hobbie and Colpaert 2004; Boström 2008) may also enrich the microbial biomass in ^{13}C . Isotopic fractionation in metabolic branch points may also affect the microbial $\delta^{13}\text{C}$ (e.g. Blair et al. 1985). A recent study by Yang et al. (2014) suggested that an increase in the complexity of the microbial community structure lead to an increased isotopic discrimination and that the microorganism life cycle could play a role in the enrichment. However, our study does not involve the level of resolution that allows a precise determination of a specific mechanism, but only an identification of the kinetic of the process.

Conclusion

The soil archives of our network of five European long-term bare fallow experiments provided a unique research platform

for the experimental verification of the subtle isotopic shifts associated with medium- to long-term SOC turnover. The bare fallow soils, kept without vegetation and organic inputs for 27–80 years and having lost 33–65 % of their initial SOC content, showed a distinct increase in $\delta^{13}\text{C}$. This increase in $\delta^{13}\text{C}$ was successfully related to SOC loss with a Rayleigh distillation function, providing an overall ε of -1.2 ± 0.3 ‰. Estimated site-specific ε were similar across gradients of soil texture and climate settings. Although the data did not allow specific mechanisms to be identified, two mechanisms, alone or in combination, most likely dominate the ^{13}C increase with loss of SOC: preferential decomposition of a labile SOC pool depleted in ^{13}C relative to a stable SOC pool, and preferential stabilisation of ^{13}C -enriched microbial biomass and metabolites. Our observation of an overall ε of -1.2 ± 0.3 ‰ identifies a common process behind the enrichment observed in several sites, and represents an important input to studies of SOC dynamics in agricultural mineral soils based on differences in the natural abundance of ^{13}C .

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