Biogeochemistry (2008) 88:205–211
DOI 10.1007/s10533-008-9209-4

SYNTHESIS AND EMERGING IDEAS

Biased ^{14}C-derived organic carbon turnover estimates following black carbon input to soil: an exploration with RothC

Jens Leifeld

Received: 31 July 2007 / Accepted: 2 May 2008 / Published online: 28 May 2008

Abstract The radiocarbon signature of the atmosphere is frequently used as a tracer to derive and validate turnover estimates of soil organic carbon (SOC). Such models often rely on steady-state assumptions and presume a direct correspondence between the atmospheric signature of CO_2 and that of residues entering the soil with or without a time-lag. The input of combustion products either from recent (i.e. charcoal) or fossil sources (e.g. diesel soot) violates this premise on account of its non-continuous delivery over time, the lack of ^{14}C in fossil black carbon (BC) and its high inertness compared to plant residues. In this study, possible effects of BC inputs (0.6–5 t BC ha^{-1} of different ^{14}C age and supplied at different dates) on turnover calculations are discussed using hypothetical but realistic scenarios for two sites: cold grassland and temperate cropland. The carbon turnover model RothC 26.3 was used for the simulations. Turnover times may be over- or underestimated by up to 30%, depending on the underlying scenario. In the majority of cases, such effects are more pronounced and longer lasting at the colder site owing to its slower cycling. The models' inherent inert carbon pool improves the match of turnover times compared to runs where inert carbon is not accounted for. This is, however, achieved at the expense of mismatching the amount of BC when the latter is ^{14}C-young. The impact of BC on ^{14}C-based turnover calculations is disproportionate with respect to its amount, and an independent record of carbon fluxes and/or BC inputs and characteristics is suggested whenever BC is assumed to play a role in the ecosystem under investigation.

Keywords Black carbon · Charcoal · Radiocarbon · RothC · Modelling · Soot

J. Leifeld (✉)
Agroscope Reckenholz-Tänikon Research Station ART,
Reckenholzstrasse 191, 8046 Zurich, Switzerland
e-mail: jens.leifeld@art.admin.ch

Introduction

Spiking the atmosphere with ^{14}C from testing nuclear weapons during the late 1950s and early 1960s ('bomb ^{14}C') has introduced an artificial radiocarbon label to the biosphere that can be used to validate soil organic carbon (SOC) turnover models (e.g. Jenkinson and Coleman 1994; Trumbore 2000). The advantage of using bomb ^{14}C is its ubiquity, which makes turnover calculations largely independent of directed labelling experiments or studies relying on changes of vegetation with different photosynthetic pathways and thus isotopic signatures of the plant residues (C3–C4). Bomb ^{14}C turnover calculations are relatively straightforward under steady-state assumptions, i.e. when carbon inputs equal outputs of the soil system over the long-term and when annually fixed carbon has the same signature as the atmosphere of the same year. There is some uncertainty associated with time-

lags between assimilation and residue input, and this has been treated elsewhere (Hahn and Buchmann 2004). Non-steady-state conditions can also be tracked with ^{14}C, provided that both recent and archived soil samples are available (e.g. Trumbore et al. 1996; Bol et al. 2005); however, this is only rarely the case.

Ensuring that a simulation model not only matches measured SOC contents, but also ^{14}C leads to a more substantiated turnover estimate is of great importance for predicting future SOC levels. However, the above concept of ^{14}C turnover calculations based on annual inputs of plant residues as the major or even sole source of SOC becomes skewed under conditions of (i) occasional and thus non-steady-state input of organic materials with any bomb ^{14}C signature, and (ii) inputs with a radiocarbon signature that largely differs from that of the plant materials. In the first example, such a situation may derive from occasional inputs of black carbon (BC) from vegetation fires that enters the soil not annually, but only once or in decadal intervals. Vegetation fires are part of natural vegetation successions in many ecosystems and also play a role as man-made disturbances, for example, during slash-and-burn agriculture. Whereas the ^{14}C signature of the produced charcoal equals that of the biomass, fossil BC derived from incomplete combustion of fuels such as coal or diesel is ^{14}C-free and thus dilutes the bomb label (second example).

In the present study, both forms of BC (charcoal and fossil BC) are considered as biochemically inert over the time horizon of the modelling experiment (i.e. between 34 and 100 years). The pathways of BC consumption in soil are still not fully understood, but turnover times of charcoal are considered to be small compared to non-pyrogenic organic matter (Glaser et al. 2002) and the assumption of relative 'inertness' over decades seems justified given that charcoal particles with an age of several millennia have been detected in topsoils (Carcaillet 2001). It has been shown, however, that BC is decomposed in soil (Cheng et al. 2006), and combined biological and chemical oxidation, delocation, or consumption by subsequent fires have been discussed as possible causes (Czimczik et al. 2003). Assuming a hypothetical oxidation rate of 0.01 a^{-1} (i.e. half of that of humified organic matter in the RothC 26.3 model; Coleman and Jenkinson 1999) and first-order decay, a BC reservoir would be reduced by 40% in 50 years.

The goal of this exercise is to quantify the systematic error in ^{14}C-based turnover calculations as a consequence of irregular inputs of (i) charcoal and (ii) fossil BC for situations in which the presence and age of BC is overlooked or unknown. This work is placed in the 'Synthesis and Emerging Ideas' section because it is a synthetic study querying the traditional kinetic pool thinking and its consequences for our understanding of soil carbon dynamics. This study uses a carbon turnover model to simulate two sites as examples: a cold grassland and a temperate cropland. The RothC 26.3 soil carbon model was selected for the simulations because it computes radiocarbon ages together with SOC dynamics, it considers a so-called inert carbon pool that is actually excluded from carbon cycling, and because it has been previously shown that the inert pool of the model could be parameterized using measured charcoal contents for a range of Australian soils (Skjemstad et al. 2004).

Sites and modelling

The cold grassland [mean annual temperature (MAT) 0.9 C, mean annual precipitation (MAP) 1,231 mm, 17% clay, 44.7 t SOC ha^{-1} 0–20 cm] is located in the canton of Valais, Switzerland. The temperate cropland is located in the Swiss Central Plateau (MAT 9.5°C, MAP 1,100 mm, 44% clay, 57.5 t SOC ha^{-1} 0–20 cm). Soil carbon stocks of both sites were measured in 2005 using replicated coring. For both sites, the atmospheric ^{14}C activity, expressed as percent modern carbon (pMC), was compiled using records from various sources: for 1511 to 1954 from Stuiver et al. (1998), for 1959 to 1983 (site 'Vermunt') from Levin et al. (1994), and for 1977 to 1997 (site 'Schauinsland') from Levin and Kromer (1997). The period between 1954 and 1959 was linearly interpolated. The exponential decrease in the ^{14}C activity at 'Schauinsland' was used to extrapolate the declining trend from 'Vermunt' to the year 2020. The Austrian site 'Vermunt' is geographically close to the two other sites. Because ^{14}C activities in the Northern hemisphere vary considerable from site to site and because the shape of the bomb peak is of uppermost importance for reliable turnover estimates (Bruun et al. 2005), the 'Vermunt' series represents the core of the atmospheric record used here. ^{14}C time-series are expressed as pMC and consist of ^{14}C measurements

referenced to the NBS oxalic acid standard and corrected for isotopic fractionation on the basis of $\delta^{13}C$ analysis (Stuiver and Polach 1977).

The above-mentioned site data were taken to simulate stocks and turnover times with the RothC 26.3 soil carbon model (Coleman and Jenkinson 1999). The ^{14}C series of the model was replaced by the time-series described above. One advantage of RothC is the simultaneous modelling of carbon dynamics and SOC ^{14}C signatures. The model consists of four kinetic and one so-called inert pool (IOM) that is uncoupled from the turnover and has a virtual ^{14}C age of 50,000 years. The IOM accounts for the very old soil carbon. In the first modelling experiment, the IOM pool was set to zero and the model was run in the inverse mode to simulate plant inputs and mean residence times (MRT) of the undisturbed SOC stocks, as measured in the field assuming equilibrium conditions, and for computing ^{14}C values for the year 2020. The latter was chosen arbitrarily to stress the hypothetical nature of the study. In the second modelling experiment, the size of the IOM pool was allowed to be adjusted by the model in order to match both the measured SOC stock and the radiocarbon age. This mode has been developed and applied by Jenkinson et al. (1992) and later by Ludwig et al. (2007) for the simulation of long-term experiments and the inverse calculation of plant inputs.

The ^{14}C data from equilibrium runs of the undisturbed SOC stocks above (hereinafter referred to as the control) were modified with (i) single pulses of charcoal of 1, 2 and 5 t ha^{-1} in the year 1986 and (ii) 5 t in 1954. The input years were selected to represent (i) maximum effects of a single spike with a ^{14}C signature of 115.9 pMC (equivalent to the signature of 70-year-old wood in 1986) and (ii) the effect of a single pulse of charcoal in 1954 (70-year-old wood, pMC 98.2), i.e. before the bomb peak. Radiocarbon signatures of the wood were calculated assuming a linear tree growth rate and using the ^{14}C model of Harkness et al. (1986). Input rates are within the range of single fire events, as discussed by Preston and Schmidt (2006). A second virtual experiment represents an annual input of 0.01 t fossil BC (e.g. soot; pMC = 0; representing diffuse pollution) over 60 years from 1921 to 1980, leading to an additional input of 0.6 t C ha^{-1} over this period. For the resulting SOC stocks and their corresponding ^{14}C ages, the model was again run in the inverse mode to equilibrium to match both the ^{14}C values of the BC scenarios and their corresponding SOC stocks either with or without an IOM pool. In any case, the BC does not enter a specific pool of the model (which would need a priori knowledge), but is described by changes in the amount and radiocarbon signature of the bulk SOC. Effects of BC on turnover calculations were obtained by comparing the control run (i.e. that representing the dynamics of each site without BC) with the runs in which BC was added to soil. No reduction of plant residue input after char incorporation (i.e. after a fire event) is considered in the simulations. Previous runs (not shown) indicated that this effect is negligible if a full recovery of primary productivity of grassland or cropland in the following 1–2 years is assumed.

Results and discussion

Figures 1 and 2 show the SOC radiocarbon signature of both sites (bulk soil 0–20 cm) for the different BC inputs and the control run without BC. From approximately 1960 onwards, the radiocarbon increase mimics the atmospheric increase but is buffered by the large amount of SOC with subatmospheric ^{14}C concentrations present in the soil relative to the small amount of carbon with atmospheric ^{14}C levels. For comparison, atmospheric radiocarbon values in the time-series peak in 1964 at 183.5 pMC. The cold site

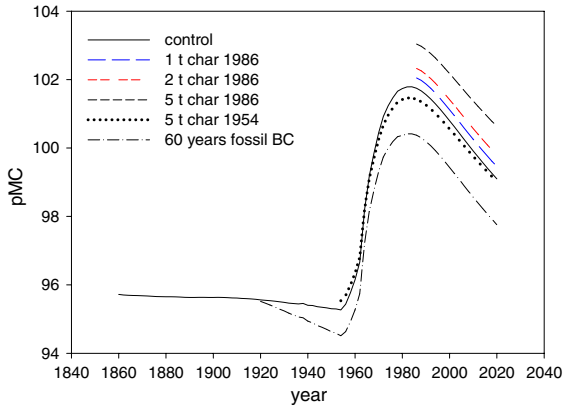

Fig. 1 ^{14}C activity (percent modern carbon, pMC) of soil carbon in cold grassland over a period of 80 years without black carbon (BC) addition (control) and for different BC treatments (see text). BC inputs are in t ha^{-1}. ^{14}C activities of charcoal are 98.2 (year 1954) and 115.9 (year 1986) pMC. Total added amount of fossil BC (^{14}C-free) is 0.6 t ha^{-1}

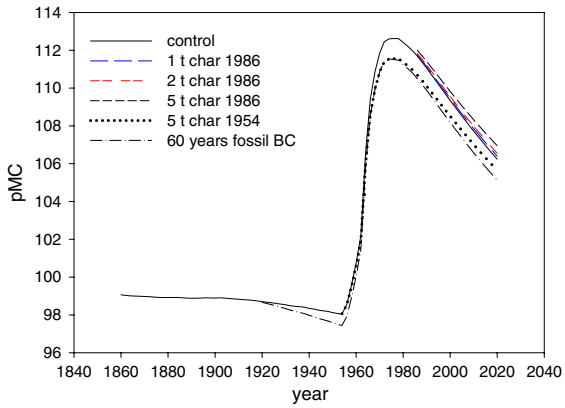

Fig. 2 ^{14}C activity (percent modern carbon, pMC) of soil carbon in temperate cropland over a period of 80 years without black carbon (BC) addition (control) and for different BC treatments (see text). BC inputs are in t ha^{-1}. ^{14}C activities of charcoal are 98.2 (year 1954) and 115.9 (year 1986) pMC. Total added amount of fossil BC (^{14}C-free) is 0.6 t ha^{-1}

has a lower radiocarbon level than the temperate soil because of its much smaller productivity and thus residue inputs and a longer mean residence time of carbon. At both sites, charcoal inputs in 1986 with bomb ^{14}C concentration of 115.9 pMC shift the ^{14}C signature towards higher values compared to undisturbed soil, while pre-bomb injection of charcoal with 98.2 pMC and of fossil BC with 0 pMC leads to a lower modelled ^{14}C curve. The BC effects are larger at the cold site for most treatments with respect to calculated MRT or pMC in 2020 (Table 1).

A soil survey in 2020 would yield the predicted carbon stocks and corresponding radiocarbon values in Table 1.

Under the premise that the BC history of the sites is not known, SOC stocks would be simulated by matching the measured SOC and ^{14}C values for the given site conditions (climate, soil, etc.) by changing the input rate of plant residues (i.e. as proposed by Jenkinson et al. 1992). For model computations without an inert carbon pool, these simulations would result in MRT and steady-state inputs of carbon given in the 'A' columns of Table 1. Compared to the control site (in bold), MRT at the cold site are underestimated by up to 19.1 years (+5 t char ha^{-1} in 1986) and overestimated by a maximum of 17.3 years (0.6 t fossil BC ha^{-1}). The effect of adding 5 t char in 1954 is negligible owing to the similar signature of added BC and pre-bomb SOC and the slow replacement of pre-bomb material by bomb carbon. The bias is smaller for the warmer site, where BC effects are blurred by a faster turnover. An exception to this is the addition of 5 t char ha^{-1} in 1954, which leads to a MRT that is 2.1 years longer than the control compared to only +0.2 years for the cold site. This example underpins the need to quantify site-specific effects. It is notable that for a particular site—given the

Table 1 Soil carbon stocks, ^{14}C activity (percent modern carbon, pMC) for the year 2020 and corresponding mean residence times (MRT) and steady-state residue inputs of a cold grassland and a temperate cropland for different BC treatments

Scenario	SOC 2020 (t C ha^{-1})	pMC 2020 (%)	MRT A (years)	Input A (t C ha^{-1} a^{-1})	MRT B (years)	Input B (t C ha^{-1} a^{-1})
Cold grassland control (a, b)	44.7	99.1	**65.7**	**0.68**	55.6	0.80
+1 t ha^{-1} charcoal 1986 (c)	45.7	99.5	60.2	0.76	55.4	0.83
+2 t ha^{-1} charcoal 1986 (d)	46.7	99.8	56.4	0.83	55.4	0.84
+5 t ha^{-1} charcoal 1986 (e)	49.7	100.6	46.6	1.07	55.4	0.90
+5 t ha^{-1} charcoal 1954 (f)	49.7	99.0	65.9	0.75	55.6	0.89
+0.6 t ha^{-1} fossil BC over 60 years (g)	45.3	97.8	83.0	0.55	56.3	0.80
Temperate cropland control (a, b)	57.5	106.2	**14.9**	**3.87**	14.9	3.87
+1 t ha^{-1} charcoal 1986 (c)	58.5	106.4	14.2	4.11	14.9	3.94
+2 t ha^{-1} charcoal 1986 (d)	59.5	106.6	13.7	4.34	14.9	4.00
+5 t ha^{-1} charcoal 1986 (e)	62.5	107.0	12.2	5.10	14.9	4.21
+5 t ha^{-1} charcoal 1954 (f)	62.5	105.7	17.0	3.68	14.9	4.19
+0.6 t ha^{-1} fossil BC over 60 years (g)	58.1	105.1	19.0	3.05	15.0	3.87

A: RothC with IOM = 0; B: IOM simulated

Values of controls in bold

uncertainty of carbon stock measurements—large differences in MRT may occur for SOC stocks that are virtually identical.

Whereas inverse modelling with kinetic pools alone is close to the inherent assumption of other common pool-based models, RothC should give better results for the scenarios when the IOM pool is included because this pool resembles the inertness of BC. When the model is allowed to adjust its IOM pool size to the SOC stocks and ^{14}C ages of the year 2020, the match between the MRT of the control, given as 'control A', and the simulations is improved ('B' column in Table 1) and the spread of the MRT between the different scenarios becomes small. The root mean square error (RMSE) relative to the control MRT is 19.0% and 16.6% for simulations without IOM and 15.4% and 0.4% for those with IOM for the alpine and temperate site, respectively. However, the model systematically underestimates the turnover time at the alpine site by approximately 10 years whereas it matches the control value at the temperate site almost perfectly.

The improved match of turnover times in the scenarios including IOM is accomplished through a flexible size of the models' IOM pool. That is, the amount of virtually inert carbon is adjusted according to the combined constraint of preset radiocarbon value (pMC 2020 in Table 1) and site-specific decomposition rate constants. What are the consequences of this adjustment for the comparison of scenario BC contents and the models' IOM pool size? Despite an improved match between control and simulated turnover calculations of the bulk SOC at the temperate site, the model strongly underestimates the BC content for any of the charcoal treatments at both sites (Fig. 3, scenarios c–f), because this char has a young radiocarbon signature in contrast to the models' IOM pool. BC amounts are reasonably computed by RothC for the case of fossil BC addition (scenario 'g') because this material has the same ^{14}C age as the IOM pool. For a scenario without BC addition, the model computes negligible IOM pools of <0.2 t C ha^{-1} (and thus close to the control of zero) in order to match the ^{14}C content in the bulk soil.

Computed steady-state inputs change inversely to the turnover time, but at a relatively higher rate (Table 1). The effect is again more pronounced at the colder site. For example, input rates without IOM for the scenario +5 t ha^{-1} char in 1986 are higher by 57%

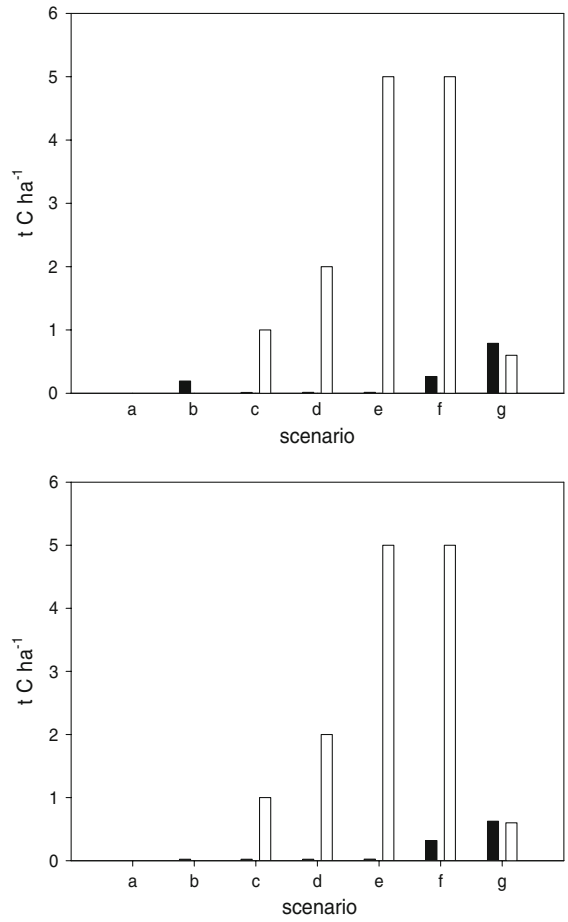

Fig. 3 Size of the inert pool modelled by RothC (black bars) compared to the size of the black carbon pool in the scenarios (white bars), where a = IOM and BC of the control sites (i.e. zero); b = control but with calculation of IOM by the model; c = +1 t charcoal 1986; d = +2 t charcoal 1986, e = +5 t charcoal 1986; f = 5 t charcoal 1954; g = 0.6 t fossil BC over 60 years. Upper panel: alpine site, lower panel: temperate site

compared to the control run, whereas C stocks differ by only 11%. Without independent measurements of input rates using methods other than ^{14}C dating and SOC turnover modelling, the picture of carbon fluxes through the soil could become alarmingly biased. In case BC is degraded in soil, but more slowly than plant residues, the model would still deviate from the control but at a smaller value, depending on the BC decomposition rate, which is probably a function of BC type and climate.

The above scenarios discuss systematic errors or biases that occur independently of random variation (e.g. spatial heterogeneity, sampling or analytical

errors). The latter, however, typically determine the actual measurability of effects in practice. For both model applications, either with or without IOM, the differences in radiocarbon content amongst the scenarios must be seen in view of these errors. For example, the analytical error of the ^{14}C measurement by AMS is approximately 0.7 pMC (1σ, Bol et al. 2005). Without replicated measurements, an addition of 1 and 2 t charcoal in 1986 or of 5 t in 1954 would not be analytically distinguishable from the control at both sites, and only the high charcoal input in 1986 and the fossil BC scenario would significantly affect the ^{14}C contents in 2020.

The scenarios demonstrate the need for independent measurements other than stocks or 'bomb' radiocarbon values to estimate the kinetics of SOC. This can be achieved by a separate quantification of fluxes or historical records of BC inputs. However, once incorporated into the soil architecture, the isolation, quantification and dating of BC is challenging. Skjemstad et al. (2004) successfully initialized RothC for long-term experiments from two Australian sites by measuring charcoal to size the IOM pool of the model. Despite this evidence, it remains unknown whether this match in pool size also reflects a match in age because no radiocarbon datings were used in their study. Given the high age of IOM in the RothC model, any assignment of radiocarbon younger than 50,000 years to this pool will inevitably result in a faster cycling of carbon in the kinetic pools if measured soil radiocarbon values are to be matched (see Table 1 cold grassland control MRT 'A' versus 'B'). This is the case for char from vegetation fires, which has a recent radiocarbon signature, in contrast to fossil fuel-derived soot or coal. If the actual date of charcoal origin is known, the models' IOM age could be accordingly adopted and the turnover estimate would become more realistic at the same time.

Some long-term agricultural experiments in Europe indicated a comparatively low radiocarbon activity (Rethemeyer et al. 2005; Helfrich et al. 2007; Ludwig et al. 2007; Jenkinson et al. 2008), and it has been hypothesized that possible contamination by fossil BC or coal may have contributed to this (Schmidt et al. 1996; Leifeld et al. 2006; Jenkinson et al. 2008). This study supports the view of a need for a more rigorous examination of the role of BC for reliable calculations of soil carbon dynamics.

References

Bol R, Eriksen J, Smith P, Garnett MH, Coleman K, Christensen BT (2005) The natural abundance of C-13, N-15, S-34 and C-14 in archived (1923–2000) plant and soil samples from the Askov long-term experiments on animal manure and mineral fertilizer. Rapid Commun Mass Spectrom 19: 3216–3226

Bruun S, Six J, Jensen LS, Paustian K (2005) Estimating turnover of soil organic carbon fractions based on radiocarbon measurements. Radiocarbon 47:99–113

Carcaillet C (2001) Are Holocene wood-charcoal fragments stratified in alpine and subalpine soils? Evidence from the Alps based on AMS 14C dates. Holocene 11:231–242

Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH (2006) Oxidation of black carbon by biotic and abiotic processes. Org Geochem 37:1477–1488

Coleman K, Jenkinson DS (1999) RothC-26.3. A model for the turnover of carbon in soils. Herts, IACR—Rothamsted, 45 pp

Czimczik CI, Preston CM, Schmidt MWI, Schulze ED (2003) How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: stocks, molecular structure, and conversion to black carbon (Charcoal). Global Biogeochem Cycles 17. doi:10.1029/2002GB001556

Glaser B, Lehmann J, Zech W (2002) Ameliorating physical and chemical properties of highly weathered soils in the Tropics with charcoal—a review. Biol Fertil Soils 35:219–230

Hahn V, Buchmann N (2004) A new model for soil organic carbon turnover using bomb carbon. Global Biogeochem Cycles 18: Art No GB1019

Harkness DD, Harrison AF, Bacon PJ (1986) The temporal distribution of bomb C-14 in a forest soil. Radiocarbon 28:328–337

Helfrich M, Flessa H, Mikutta R, Dreves A, Ludwig B (2007) Comparison of chemical fractionation methods for isolating stable soil organic carbon pools. Eur J Soil Sci 58:1316–1329

Jenkinson DS, Coleman K (1994) Calculating the annual input of organic matter to soil from measurements of total organic carbon and radiocarbon. Eur J Soil Sci 45:167–174

Jenkinson DS, Harkness DD, Vance ED, Adams DE, Harrison AF (1992) Calculating net primary production and annual input of organic matter to soil from the amount and radiocarbon content of soil organic matter. Soil Biol Biochem 24:295–308

Jenkinson DS, Poulton PR, Bryant C (2008) The turnover of organic carbon in subsoils. Part 1. Natural and bomb radiocarbon in soil profiles from the Rothamsted long-term field experiment. Eur J Soil Sci 59:391–399

Leifeld J, Franko U, Schulz E (2006) Thermal stability responses of soil organic matter to long-term fertilization practices. Biogeosciences 3:371–374

Levin I, Kromer B (1997) δ14CO2 records from Schauinsland. In Trends: a compendium of data on global change. Carbon dioxide information analysis center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., USA

Levin I, Kromer B, Schoch-Fischer H, Bruns M, Münnich M, Berdau D, Vogel JC, Münnich KO (1994) δ14CO2 record

from Vermunt. In Trends: a compendium of data on global change. Carbon dioxide information analysis center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., USA

Ludwig B, Schulz E, Rethemeyer J, Merbach I, Flessa H (2007) Predictive modelling of C dynamics in the long-term fertilization experiment at Bad Lauchstädt with the Rothamsted carbon model. Eur J Soil Sci 58:1155–1163

Preston CM, Schmidt MWI (2006) Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeosciences 3: 397–420

Rethemeyer J, Kramer C, Gleixner G, John B, Yamashita T, Flessa H, Andersen N, Nadeau MJ, Grootes PM (2005) Transformation of organic matter in agricultural soils: radiocarbon concentration versus soil depth. Geoderma 128:94–105

Schmidt MWI, Knicker H, Hatcher PG, Kögel-Knabner I (1996) Impact of brown coal dust on the organic matter in particle—size fractions of a Mollisol. Org Geochem 25:29–39

Skjemstad JO, Spouncer LR, Cowie B, Swift RS (2004) Calibration of the Rothamsted organic carbon turnover model (Rothc Ver. 26.3) using measurable soil organic carbon pools. Aust J Soil Res 42:79–88

Stuiver M., Polach HA (1977) Discussion: reporting of C-14 data. Radiocarbon 19:355–363

Stuiver M, Reimer PJ, Braziunas TF (1998) High-precision radiocarbon age calibration for terrestrial and marine samples. Radiocarbon 40:1127–1151

Trumbore S (2000) Age of soil organic matter and soil respiration: radiocarbon constraints on belowground C dynamics. Ecol Appl 10:399–411

Trumbore SE, Chadwick OA, Amundson R (1996) Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change. Science 272: 393–396