



Contribution of sorption, DOC transport and microbial interactions to the ^{14}C age of a soil organic carbon profile: Insights from a calibrated process model



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ABSTRACT

Profiles of soil organic carbon (SOC) are often characterized by a steep increase of ^{14}C age with depth, often leading to subsoil ^{14}C ages of more than 1000 years. These observations have generally been reproduced in SOC models by introducing a SOC pool that decomposes on the time-scale of millennia. The overemphasis of chemical recalcitrance as the major factor for the persistence of SOC was able to provide a mechanistic justification for these very low decomposition rates. The emerging view on SOC persistence, however, stresses that apart from molecular structure a multitude of mechanisms can lead to the long-term persistence of organic carbon in soils. These mechanisms, however, have not been incorporated into most models. Consequently, we developed the SOC profile model COMMISSION which simulates vertically resolved SOC concentrations based on representations of microbial interactions, sorption to minerals, and vertical transport. We calibrated COMMISSION using published concentrations of SOC, microbial biomass and mineral-associated OC (MOC), and in addition, ^{14}C contents of SOC and MOC of a Haplic Podzol profile in North-Eastern Bavaria, Germany. In order to elucidate the contribution of the implemented processes to the ^{14}C age in different parts of the profile, we performed model-experiments in which we switched off the limitation of SOC decomposition by microbes, sorptive stabilization on soil minerals, and dissolved OC (DOC) transport. By splitting all model pools into directly litter-derived carbon and microbe-derived organic carbon, we investigated the contribution of repeated microbial recycling to ^{14}C ages throughout the profile. The model-experiments for this site lead to the following implications: Without rejuvenation by DOC transport, SOC in the subsoil would be on average 1700 ^{14}C years older. Across the profile, SOC from microbial recycling is on average 1400 ^{14}C years older than litter-derived SOC. Without microbial limitation of depolymerization, SOC in the subsoil would be on average 610 ^{14}C years younger. Sorptive stabilization is responsible for relatively high ^{14}C ages in the topsoil. The model-experiments further indicate that the high SOC concentrations in the Bh horizon are caused by the interplay between sorptive stabilization and microbial dynamics. Overall, the model-experiments demonstrate that the high ^{14}C ages are not solely caused by slow turnover of a single pool, but that the increase of ^{14}C ages along a soil profile up to ages >1000 years is the result of different mechanisms contributing to the overall persistence of SOC. The dominant reasons for the persistence of SOC are stabilization processes, followed by repeated microbial processing of SOC.

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1. Introduction

Investigating soil profiles, i.e. studying the sequence of horizons, and the change of biological, chemical and physical properties with soil depth, is one of the cornerstones of soil science (Hartemink,

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2009). The vertical distribution of soil organic carbon (SOC) has long been an interest of soil scientists from plot to global scale (Jobbágy and Jackson, 2000). The size of global SOC stocks as the largest active terrestrial pool in the global carbon cycle is considered increasingly important due concerns about the potential feedback of SOC to climate change. Global SOC stocks are usually estimated down to 1 m depth (around 1500 Pg C) although there is 1.5–2 times more SOC if one considers a soil depth down to 3 m (Scharlemann et al., 2014).

Most SOC models, especially in Earth system models, are modeling SOC stocks without considering their vertical distribution. For most Earth system models it is unclear if they simulate SOC stocks throughout the full soil depth, the top 100 cm or top 30 cm (Todd-Brown et al., 2013; Carvalhais et al., 2014). This complicates the comparison of the modeled SOC stock with observations.

Models describing the complete SOC profile have been published since the late 1970s (Kaneyuki and Kichiro, 1978; Dörr and Münnich, 1989; Elzein and Balesdent, 1995), and recent years have witnessed a renewed interest (Baisden et al., 2002; Freier et al., 2010; Braakhekke et al., 2011; Guenet et al., 2013; Koven et al., 2013; Riley et al., 2014). These models are generally very well able to reproduce the SOC profile using representations of DOC transport, bioturbation, vertically distributed root litter input and microbial decomposition. In addition to the vertical distribution of SOC, its ^{14}C profile provides important information about the time-scale at which soil organic carbon is turning over.

The ^{14}C age of SOC generally increases strongly with soil depth up to ages of 1000–10,000 years (Rumpel et al., 2012). Vertical SOC profile models were generally successful at reproducing these millennial ^{14}C ages by introducing a SOC pool that decomposes according to first-order kinetics at the time-scale of millennia (e.g. Elzein and Balesdent, 1995; Baisden et al., 2002; Braakhekke et al., 2014) or by assuming a substantial slow-down of first-order decomposition rates with depth (e.g. Jenkinson and Coleman, 2008; Koven et al., 2013). This might have been well justified within what Schmidt et al. (2011) call the historical view on SOC cycling, namely that the molecular structure (chemical recalcitrance) was mainly responsible for the long-term persistence of organic carbon in soils. Schmidt et al. (2011), however, posed that, in addition to molecular structure, multiple processes are responsible for the long-term persistence of SOC. These can be distinguished between *stabilization processes* such as sorption of organic matter to mineral surfaces, energy limitation of the microbial decomposition, and mere *persistence processes* such as the repeated recycling of SOC through the microbial biomass (Gleixner, 2013) and the slow downward transport of soil organic matter, where sorption is a retardation factor (Braakhekke et al., 2011). For modeling the SOC profile, this implies that these different processes contribute to varying degrees to the apparent stability of soil organic carbon within the profile. In vertical profile models, however, these processes have rarely been explicitly incorporated. The models developed by Guenet et al. (2013) and Riley et al. (2014) are a recent effort to represent these mechanisms more explicitly.

Our objective for this study was to quantify the contribution of these different stabilization and persistence processes to the distribution of ^{14}C ages across an exemplary Haplic Podzol profile under a Norway spruce forest, using a mechanistic model. To this end we applied several well-established approaches such as the representation of transport from traditional SOC profile models, namely the SOMPROF model and its bioturbation and advection formulation (Braakhekke et al., 2011), the Schimel and Weintraub (2003) link between microbial dynamics and SOC

decomposition, and a Langmuir representation of sorptive SOC stabilization (Kaiser and Guggenberger, 2003; Mayes et al., 2012). We combined these different approaches to the COMMISSION model. The acronym **COMMISSION** highlights that this SOC model includes a **C**ontinuous representation of SOC in the organic layer and the mineral soil, **M**icrobial Interactions and **S**orptive **S**tabilization. By performing model-experiments with the calibrated COMMISSION model we want to answer the following questions:

1. What is the relative importance of DOC advection for the formation of the SOC and radiocarbon profile?
2. How much can microbes limit the depolymerization of SOC and what is their effect on the formation of the SOC and radiocarbon profile?
3. How important is sorptive stabilization of DOC on soil minerals for the formation of the SOC and radiocarbon profile?
4. How important are microbial products for the formation of the SOC and radiocarbon profile compared to plant-derived SOC?

2. Material and methods

2.1. The COMMISSION model

The COMMISSION model has all the typical elements of SOC profile models. The profile is discretized in several layers, in the current implementation 100, and the different layers receive organic carbon either as aboveground litter input on top, vertically distributed root litter input, or transport from other layers via advection with the water flux or bioturbation (Fig. 1). In order to represent the SOC profile continuously in the organic layer and the mineral soil, an additional advective term accounts for the upward shift of the soil surface during the buildup of an organic layer. Fig. 1 shows a conceptual overview of the COMMISSION model, while all constitutive equations of the COMMISSION model are listed with annotated terms in Table 1.

Two different model pools receive aboveground litter input and the vertically distributed root litter input. The readily leachable and soluble fraction of litter input enters a dissolved OC (DOC) pool (C_{DOC}), while the rest enters a residue pool (C_R) which represents polymeric, non-soluble SOC (Fig. 1, Table 1 – Eqs. (4) and (5)). The residue pool is depolymerized by extracellular enzymes produced by a microbial pool (C_B) to enter the C_{DOC} pool which represents SOC potentially available for assimilation by microbes. We assume that levels of extracellular enzymes scale with microbial biomass C_B , so that we do not model enzymes explicitly (Fig. 1, Table 1). Interactions of microbes with the C_R and C_{DOC} pool are modeled with traditional and reverse Michaelis–Menten kinetics (Eqs. (1) and (2)). This makes it possible to represent the priming effect, i.e. that SOC decomposition is accelerated by the amendment of substrate (Schmidt et al., 2011; Wutzler and Reichstein, 2013). In the COMMISSION model an additional input to the C_{DOC} pool can increase the microbial biomass (Eq. (7)) and thereby enhance the depolymerization of the C_R pool (Eq. (4)). By analogy, this approach is also able to represent the retardation of decomposition via energy limitation of microbes in the deep soil where substrate might be scarce. Here, the growth of microbial biomass can be limited due to lower inputs to the C_{DOC} pool (Eq. (7)) or a higher sorption of C_{DOC} on soil minerals. In turn, this slows down the depolymerization of the C_R pool (Eq. (4)). Overall, the representation of microbial decomposition is similar to the approaches of Schimel and Weintraub (2003) and Allison et al. (2010).

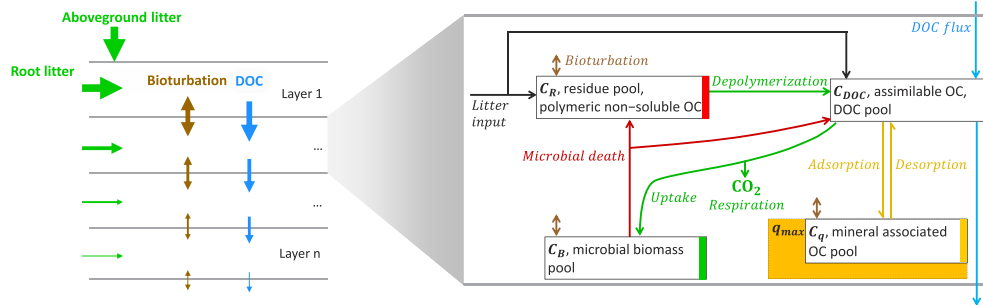


Fig. 1. Schematic representation of the COMMISSION model. Left: The soil profile is split in different soil layers ($n = 100$), aboveground litterfall is added on top of the profile; root litter input enters the different soil layers according to the root biomass profile. Bioturbation and DOC transport translocate carbon between the soil layers. Right: In each layer the non-leachable part of the litter input enters the C_R pool (polymeric non-soluble SOC, residue pool), while the leachable part of litter input directly enters the C_{DOC} pool (OC assimilable by microbes, DOC). The C_R pool is decomposed (depolymerization) with extracellular enzymes produced by the C_B pool (microbial biomass). Extracellular enzymes levels are assumed to be directly related to microbial biomass levels. Due to the depolymerization the carbon is now potentially available for assimilation as C_{DOC} . C_{DOC} can be either taken up by microbes, transported with the water flux through the profile, or sorbed to soil minerals until the sorption capacity q_{max} is filled. The sorbed OC in the C_q pool can also be desorbed again. All respiratory losses of the system are represented with a lumped parameter $1 - CUE$, where CUE describes the carbon use efficiency of microbes. Microbes die with the first-order rate π . A part p of the dying microbes enters the C_{DOC} pool. The insoluble part of dying microbes $1 - p$ (e.g. cell walls) enters the residue pool C_R . All pools except the C_{DOC} pool are transported via bioturbation and particle advection. Please note that this model structure resembles the models presented by Schimel and Weintraub (2003), Allison et al. (2010) and Todd-Brown et al. (2012) in terms of pool arrangement.

The adsorption and desorption of DOC to and from mineral surfaces controls the availability of carbon in the C_{DOC} pool for assimilatory uptake by microbes. The adsorption and desorption of DOC is modeled dynamically using Langmuir equations (Fig. 1, Eq. (3)). The C_{DOC} pool not only constitutes the substrate for the microbial pool, but is also transported via advection (Eq. (5)), and, after sorption, DOC forms the mineral-associated, stabilized C_q pool (Eq. (6)).

Soil organic carbon in COMMISSION is recycled within the soil profile through microbial processing – dead microbes (Fig. 1, Eq. (7)) either enter the C_{DOC} pool (e.g. the cytosol, Eq. (5)) or the C_R pool (e.g. cell envelopes, Eq. (4)), and might thereby also contribute to longer residence times with soil depth.

In the following three subsections we cover in-depth the three processes that form the acronym of the **COMMISSION** model – a **C**ontinuous SOC profile model with **M**icrobial **I**nteractions and **S**orptive **S**tabilization.

Microbial interactions

The spatial separation between microbes and SOC can potentially limit the decomposition of SOC (Schmidt et al., 2011). In the COMMISSION model we assume that this spatial separation limits two processes mediated by microbes. First, to overcome the spatial separation from the C_R pool microbes produce extracellular enzymes that diffuse through the soil matrix and depolymerize the C_R pool upon contact. Second, the produced substrate, C_{DOC} , has to diffuse back to the microbes. Similar to other studies (Vetter et al., 1998; Schimel and Weintraub, 2003; Rothman and Forney, 2007) we propose that the diffusing substance that overcomes the spatial separation limits the rate of the respective process.

Maximum depolymerization rates of C_R are attained at high microbial biomass levels, while low microbial biomass levels limit the depolymerization, assuming that extracellular enzyme levels scale with the microbial biomass C_B (Todd-Brown et al., 2012):

$$\text{Depolymerization} = \underbrace{V_{max,D} \cdot C_R}_{\text{maximum depolymerization}} \cdot \underbrace{\frac{C_B}{K_{m,B} + C_B}}_{\text{rate limitation by microbes}}, \quad (1)$$

where $V_{max,D}$ is the maximum specific depolymerization rate for C_R by extracellular enzymes excreted by C_B , and $K_{m,B}$ is the half-saturation constant for the depolymerization of C_R . This type of

microbial interactions is commonly called “reverse Michaelis–Menten” kinetics (Schimel and Weintraub, 2003) or biomass-saturated approach (Moorhead and Sinsabaugh, 2006).

Microbial uptake and growth is limited by the availability of the substrate (DOC), while at high DOC concentrations the ability of microbes to assimilate C_{DOC} is limiting microbial uptake of DOC:

$$\text{Uptake} = \underbrace{V_{max,U} \cdot C_B}_{\text{maximum DOC uptake}} \cdot \underbrace{\frac{C_{DOC}}{K_{m,U} + C_{DOC}}}_{\text{rate limitation by DOC}}, \quad (2)$$

where $V_{max,U}$ is the maximum specific assimilation rate of C_B by uptake of C_{DOC} , and $K_{m,U}$ is the half-saturation constant for the assimilation of C_{DOC} by C_B . We refer to this type of microbial interactions as “traditional Michaelis–Menten” kinetics or substrate-saturated approach (Moorhead and Sinsabaugh, 2006).

While both the traditional and reverse Michaelis–Menten kinetics have been used separately to represent microbial dynamics in different SOC decomposition models (Wutzler and Reichstein, 2008), we argue for a combination of both approaches in the COMMISSION model because the spatial separation of microbes and the C_R pool controls on the one hand the depolymerization of C_R by the availability of extracellular enzymes and on the other hand the microbial assimilation by the availability of DOC.

Sorptive stabilization

Using a dynamic Langmuir approach for representing mineral stabilization of SOC has the advantage that sorptive strength is dependent on the availability of sorption sites. Thereby more SOC is getting sorbed in horizons where most sorption sites are unoccupied compared to horizons where sorption sites are almost saturated:

$$\text{Adsorption} = \underbrace{k_{ads} \cdot C_{DOC}}_{\text{maximum adsorption}} \cdot \underbrace{\frac{(q_{max} - C_q)}{q_{max}}}_{\text{rate limitation by availability of sorption sites}}, \quad (3)$$

$$\text{Desorption} = k_{des} \cdot C_q.$$

Table 1

Governing equations of the COMMISSION model. All state variables are expressed in mass of C per volume bulk soil (kg C m⁻³).

Description	Differential equation
C_R , polymeric non-soluble OC, residue pool	$\frac{\partial}{\partial t} C_R = \underbrace{(1-L) \cdot i}_{\text{non-leachable litter input}} + \underbrace{(1-p) \cdot \pi \cdot C_B}_{\text{non-soluble microbial remains}} - \underbrace{V_{\max,D} \cdot C_R \cdot \frac{C_B}{K_{m,B} + C_B}}_{\text{Depolymerization}} + \underbrace{\frac{\partial}{\partial z} \left(D_b \frac{\partial C_R}{\partial z} \right)}_{\text{Diffusion via Bioturbation}} - \underbrace{\frac{\partial(\omega \cdot C_R)}{\partial z}}_{\text{particle flux}} \quad (4)$
C_{DOC} , assimilable OC, DOC pool	$\begin{aligned} \frac{\partial}{\partial t} C_{DOC} = & \underbrace{L \cdot i}_{\text{DOC input from litter}} + \underbrace{p \cdot \pi \cdot C_B}_{\text{soluble microbial remains}} + \underbrace{V_{\max,D} \cdot C_R \cdot \frac{C_B}{K_{m,B} + C_B}}_{\text{Depolymerization}} - \underbrace{V_{\max,U} \cdot C_B \cdot \frac{C_{DOC}}{K_{m,U} + C_{DOC}}}_{\text{uptake of DOC by microbes}} \\ & - \underbrace{k_{ads} \cdot C_{DOC} \cdot (q_{\max} - C_q)}_{\text{adsorption}} + \underbrace{k_{des} \cdot C_q}_{\text{desorption}} - \underbrace{\frac{\partial(v \cdot C_{DOC})}{\partial z}}_{\text{DOC transport with water flux}} - \underbrace{\frac{\partial(\omega \cdot C_{DOC})}{\partial z}}_{\text{particle flux}} \end{aligned} \quad (5)$
C_q , mineral-associated OC pool	$\frac{\partial}{\partial t} C_q = \underbrace{k_{ads} \cdot C_{DOC} \cdot (q_{\max} - C_q)}_{\text{adsorption}} - \underbrace{k_{des} \cdot C_q}_{\text{desorption}} + \underbrace{\frac{\partial}{\partial z} \left(D_b \frac{\partial C_q}{\partial z} \right)}_{\text{Diffusion via Bioturbation}} - \underbrace{\frac{\partial(\omega \cdot C_q)}{\partial z}}_{\text{particle flux}} \quad (6)$
C_B , microbial biomass pool	$\frac{\partial}{\partial t} C_B = \underbrace{CUE \cdot V_{\max,U} \cdot C_B \cdot \frac{C_{DOC}}{K_{m,U} + C_{DOC}}}_{\text{uptake of DOC by microbes used for growth}} - \underbrace{\pi \cdot C_B}_{\text{microbial death}} + \underbrace{\frac{\partial}{\partial z} \left(D_b \frac{\partial C_B}{\partial z} \right)}_{\text{Diffusion via Bioturbation}} - \underbrace{\frac{\partial(\omega \cdot C_B)}{\partial z}}_{\text{particle flux}} \quad (7)$

where:

t	time (yr)
z	depth (m)
L	leachable fraction of litter input (-)
i	change in concentration due to litter input from roots or aboveground in depth z (kg C m ⁻³ yr ⁻¹)
p	soluble fraction of dead microbes (-)
π	mortality rate of C_B , first-order kinetics (yr ⁻¹)
$V_{\max,D}$	maximum specific depolymerization rate for C_R by extracellular enzymes excreted by C_B (yr ⁻¹)
$K_{m,B}$	half-saturation constant for the depolymerization of C_R (kg C m ⁻³)
D_b	bioturbation/biodiffusion coefficient (m ² yr ⁻¹)
ω	particle advection velocity due to particle displacement from litter input and SOM decomposition (m ³ m ⁻² yr ⁻¹)
$V_{\max,U}$	maximum specific assimilation rate of C_B by uptake of C_{DOC} (yr ⁻¹)
$K_{m,U}$	half-saturation constant for the assimilation of C_{DOC} by C_B (kg C m ⁻³)
k_{ads}	adsorption rate (m ³ (kg C) ⁻¹ yr ⁻¹)
q_{\max}	maximum sorption capacity (kg C m ⁻³)
k_{des}	desorption rate (yr ⁻¹)
v	average pore water velocity (m ³ m ⁻² yr ⁻¹)
CUE	carbon use efficiency of microbes C_B (-)

where C_q is the mineral-associated OC pool, k_{ads} is the maximum adsorption rate, when the surface is not occupied at all, q_{\max} is the maximum sorption capacity, and k_{des} is the desorption rate.

The Langmuir sorption approach also has the advantage that we can relate the total sorption capacity q_{\max} to soil properties, such as clay and silt content, or iron and aluminum oxides (Kothawala et al., 2009; Mayes et al., 2012) across different soils, but also within a soil profile.

Most SOC profile models have adopted a linear, equilibrium isotherm sorption approach. This simplification is likely unjustified under field conditions because the assumption of an instantaneous local equilibrium between adsorption and desorption is only reasonable if all the other processes (e.g. microbial uptake, depolymerization, microbial death, advective transport, diffusion) are several orders of magnitude slower. In batch sorption experiments, however, this is a valid assumption if microbial growth is suppressed through the addition of low quantities of HgCl₂ (Mikutta et al., 2007).

Continuous profile

Most SOC profile models do not account for the additional downward advective flux that stems from the accumulation of an organic layer on the soil surface due to litterfall and the counter-acting upward advective flux that stems from the loss of organic matter due to decomposition. One might regard this phenomenon as only relevant for modeling forest soils which are generally characterized by the presence of an organic layer. However, the absence or presence of an organic layer could be treated as an integral part of modeling when we explicitly account for this additional advective flow (Braakhekke and Ahrens, in prep.).

In marine ecology the problem of an additional advective flow due to sedimentation, when modeling reactive transport in sediments, has been extensively studied (Boudreau and Imboden, 1987; Mulsow et al., 1998; Meysman et al., 2005). In soils a similar approach has been adopted for modeling the effect of soil erosion on the soil carbon balance (Van Oost et al., 2005; Yoo et al., 2005). In both settings the deposition of sediments on top of the surface is

accounted for with an additional advective term which moves soil or sediment layers downwards according to the sedimentation velocity.

In the COMMISSION model we are able to simulate the SOC profile as a continuum by introducing the particle velocity ω that is driving an additional advective flux for all model pools (particle fluxes in Table 1). The particle velocity ω comprises two terms: an additional downward velocity due to aboveground and belowground litter inputs, and a counteracting upward advection velocity due to the loss of soil volume during litter decomposition, which effectively moves the reference frame for the soil profile upwards. More details on the continuous representation of the organic layer and the mineral soil can be found in the Supplementary Information.

The continuous profile approach also makes it possible to consistently model the advective transport of the DOC pool with an average pore water velocity, v , (Table 1, Eq. (5)) and bioturbation as a diffusive flux (Table 1, Eq. (4)–(7)) throughout the soil profile. Compared to the SOMPROF approach towards bioturbation (Braakhekke et al., 2011), we do not have to resort to an extra parameter that translates the bioturbation rate in the organic layer into a diffusion coefficient in the mineral soil.

2.2. Site description

The Coulissenhieb I site is a Norway spruce forest located in the Waldstein hillsides in the Fichtelgebirge Mountains in NE Bavaria (Germany). The site has been intensively studied and is referred to as Waldstein or Coulissenhieb (I) in the literature. The Waldstein hillsides have a continental temperate climate (Köppen classification), with high annual precipitation of 1163 mm and a mean annual temperature of 5.3 °C (Foken, 2003).

The soil was classified as a Haplic Podzol (FAO, 1998) with a sandy loam to loam texture and is overlain by a mor-like organic layer of 8.5 cm approximate thickness (Gerstberger et al., 2004). The soil developed on granitic bedrock and is characterized by low pH values throughout the soil profile.

The C/N ratio of the organic layer is rather low for a mor type (21–25) due to high levels of atmospheric nitrogen deposition. The soil receives a mean annual aboveground litterfall of 0.103 kg C m⁻² yr⁻¹ (Berg and Gerstberger, 2004). Belowground litter input from dead fine roots was estimated to be 0.21 kg C m⁻² yr⁻¹ using an estimate of fine-root turnover in the organic layer from sequential coring (Gaul et al., 2008a, 2008b) which was extrapolated down to 80 cm of the mineral soil using fine-root biomass stocks. The B horizons of the Haplic Podzol of the Coulissenhieb I site are characterized by high amounts of pedogenic oxides (Gerstberger et al., 2004).

2.3. Data and calibration

For the calibration of COMMISSION we selected data from different studies conducted at the Coulissenhieb I site. The COMMISSION model was driven by the aforementioned above- and belowground litter inputs. Belowground litter input was distributed in the different layers according to the observed cumulative root biomass distribution using an exponential cumulative distribution function (Persson, 2000, e-folding depth 7.5 cm). Vertical profiles of five different variables were used together as constraints to estimate the parameters of COMMISSION:

- (1) Volumetric SOC concentrations (kg m⁻³) of the three organic layer horizons and six mineral soil horizons, calculated from measurements reported by Rumpel et al. (2002), were compared to the sum of the 4 different model pools ($C_R + C_{DOC} + C_q + C_B$).

- (2) The ¹⁴C content of SOC (in percent Modern, pM, according to Stuiver and Polach (1977)) in 5 mineral soil horizons (Rumpel et al., 2002) was compared with the combined ¹⁴C content of the 4 different model pools. The ¹⁴C module of COMMISSION was driven by atmospheric ¹⁴C contents as described in Ahrens et al. (2014). Radioactive decay of ¹⁴C was accounted for by an additional first-order decomposition rate $\lambda = 1/8267 \text{ yr}^{-1}$ that affects all pools of the ¹⁴C module of COMMISSION.
- (3) The C_q pool, representing mineral-associated organic carbon, was compared to the organic carbon content of the >1.6 g cm⁻³ density fraction as reported by Kaiser et al. (2002) for 6 mineral soil horizons. The >1.6 g cm⁻³ density fraction is thought to represent mineral-associated carbon, and is commonly referred to as the heavy fraction (HF) (Kögel-Knabner et al., 2008) or mineral-associated organic carbon (MOC) (Trumbore and Zheng, 1996). Throughout this study we will use the acronym MOC to refer to the >1.6 g cm⁻³ density fraction. The maximum sorption capacity q_{max} was prescribed based on findings by Guggenberger and Kaiser (2003). They performed DOC sorption experiments to estimate the available sorption capacity for 6 mineral horizons of the Haplic Podzol profile at Coulissenhieb. The available sorption capacity signifies organic carbon that can be sorbed in addition to what is already stabilized on minerals. Thus, following the considerations by Guggenberger and Kaiser (2003), we prescribe q_{max} (Fig. (S2)) as the sum of the available sorption capacity from the sorption experiments and the mineral-associated organic carbon fraction.
- (4) The ¹⁴C content of MOC (in percent Modern) of 6 mineral horizons as reported by Kögel-Knabner et al. (2008) was compared against the ¹⁴C content of the C_q pool of the COMMISSION model.
- (5) Hamer and Marschner (2005) estimated microbial biomass C contents for the Oa, EA and Bs horizon of the Coulissenhieb I profile with a fumigation-extraction method. We compared the measurements against the C_B pool of the COMMISSION model.

In total eleven model parameters (Table S1) were calibrated with the Differential Evolution algorithm for global optimization (Price et al., 2006; Ardia et al., 2013) by minimizing the total sum of squared residuals of all five observed variables (see Eq. (S5) for the definition of the multi-constraint cost function). The COMMISSION model was started from close to zero SOC and microbial biomass concentrations and run from 13,500 years BCE until present day, assuming a constant average pore water velocity, v , and constant litter inputs. As water flux we used the mean of modeled yearly water fluxes at Coulissenhieb I reported in Matzner et al. (2004a, 2004b). We further assumed that water fluxes decreased linearly with soil depth from throughfall at the soil surface to the modeled seepage flux in 90 cm soil depth.

2.4. Contribution of processes to SOC concentration and ¹⁴C age

To study how much the different processes in the COMMISSION model contribute to observed organic carbon and ¹⁴C profiles, we ran COMMISSION forward using the parameter set retrieved by the calibration and the same settings as in the calibration, while switching off processes that we want to study. This approach gives an indication of the relevance of a certain process in COMMISSION given the parameterization for the Haplic Podzol profile at Coulissenhieb I. Table 2 gives an overview on the different model-experiments.

Table 2Model-experiments to elucidate the effect of different mechanisms on ^{14}C age profiles.

Model-experiment	Description
No Advection	$v \stackrel{\text{def}}{=} 0$ in Eq. (5)
No depolymerization limitation by microbes	$\text{Depolymerization} = \underbrace{V_{\max,D} \cdot C_R}_{\text{maximum depolymerization}} \cdot \underbrace{\frac{C_B}{K_{m,B} + C_B}}_{\text{rate limitation by microbes}} \stackrel{\text{def}}{=} \underbrace{V_{\max,D} \cdot C_R}_{\text{maximum depolymerization}} \quad \text{in Eqs. (4) and (5)}$
No sorptive stabilization	$k_{\text{ads}} \stackrel{\text{def}}{=} 0$ and $k_{\text{des}} \stackrel{\text{def}}{=} 0$ in Eqs. (5) and (6)
Litter- vs microbe-derived OC	Recycling of microbial remains in separate pools

Furthermore, to quantify the importance of microbial recycling along the soil profile, we split the different carbon pools in directly litter-derived and microbe-derived carbon. For this purpose we set up a second set of the differential equations in Table 1. Contrary to the previous model-experiments we did not have to switch off any process to quantify the contribution of litter-derived against microbe-derived organic carbon along the SOC profile. Instead, the second set of pools just receives input in the form of microbial remains. The first set of pools on the other hand only receives litter input, but no organic carbon from microbial recycling. To assure that overall the same dynamics are achieved, the different rate-limiting terms (Eqs. (1–3)) are based on the sum of the respective litter- and microbe-derived carbon pools C_B , C_{DOC} and C_q .

In order to summarize and discuss the results of COMMISSION in different parts of the soil profile, we adopt the notation of topsoil and subsoil as used in the Harmonized World Soil Database (Nachtergaele et al., 2008). We refer to the top 30 cm of the mineral soil as topsoil. For the mineral soil below the top 30 cm we use the notation subsoil.

3. Results

3.1. Full COMMISSION model for a Haplic Podzol, COMMISSION_{Full}

After calibration the COMMISSION model is well able to represent the observations of the Haplic Podzol profile at the Coulissenhieb I site (Fig. 2A and C). The thickness of the organic layer is correctly represented, and it consists mainly of the C_R pool. The secondary maximum of OC concentrations in the Bh horizon is captured with the maximum of the C_q pool and a secondary peak of the C_R pool (Fig. 2A).

Also the modeled ^{14}C profiles represent the observed profiles well (Fig. 2C). From the organic layer down to the Bh horizon the ^{14}C profiles of the C_R , C_{DOC} , and C_B pool are characterized by the presence of modern “bomb-radiocarbon”, i.e. a ^{14}C value (% Modern) > 100. From the Bw horizon downward the ^{14}C signatures of the C_{DOC} and the C_B pool approach the ^{14}C signature of the C_q pool more and more. Of all model pools the C_R pool shows the steepest increase in apparent ^{14}C age with soil depth.

This calibration of the COMMISSION model with all processes included (COMMISSION_{Full}) serves as the reference point for the following model-experiments targeted at elucidating the importance of different processes for the formation of the SOC, MOC and microbial biomass profiles, and the ^{14}C age profiles of SOC and MOC. The parameters retrieved in the calibration can be found in the Supplementary Information in Table S1.

3.2. Interaction between DOC transport, sorptive stabilization and microbes

Advection

Switching off DOC transport (Table 2, “No Advection”) influences the formation of the secondary OC maximum in the Bh horizon twofold: First, the Bh horizon receives less DOC input from upper soil layers and thereby is not able to fill the available sorption capacity (Fig. 3A). Second, the microbial pool C_B and the free sorption sites compete for DOC, and the overall lower DOC levels also lead to a smaller microbe density in the Bh horizon due to substrate scarcity (Fig. 3B). This slows down the depolymerization of the C_R pool in the Bh horizon, which is mediated by the microbial biomass C_B . Consequently, the secondary peak of the C_R pool is more pronounced compared to the COMMISSION_{Full} setup. Concurrently, the overall apparent ^{14}C ages in the Bh horizon would be

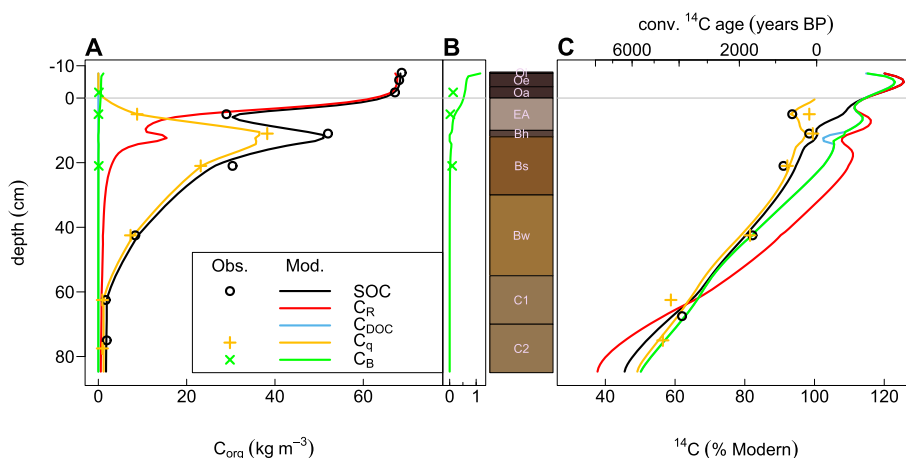


Fig. 2. Fit of the full COMMISSION model pools to different organic carbon fractions (A) and their respective ^{14}C profiles (C). Panel (B) shows the vertical distribution of the C_B pool in more detail. Lines show the model results, while circles, crosses and x's denote the measurements.

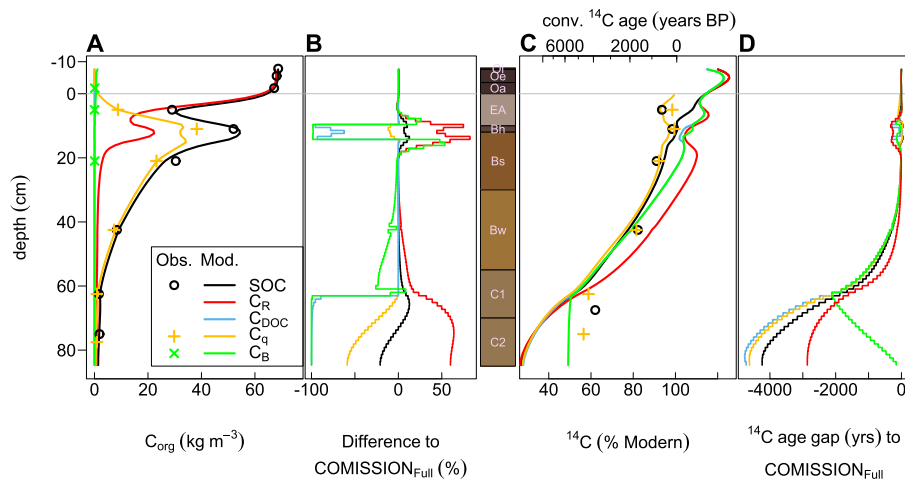


Fig. 3. Results of a COMMISSION simulation in which DOC advection is switched off – panel (A) shows organic carbon pools/fractions and panel (C) the respective ^{14}C signatures. Panel (B) shows the difference of COMMISSION without DOC advection to the full COMMISSION model in percent. Panel (D) compares the conventional ^{14}C ages of COMMISSION without advection to the full model.

slightly older with DOC transport switched off (Fig. 3D). Without DOC transport the apparent ^{14}C ages of SOC in the subsoil would be up to 4240 ^{14}C years higher (Fig. 3D). For the deep subsoil horizons, C1 and C2, DOC transport is also important for SOC stocks. Without the input of OC via advection into the subsoil horizons the overall SOC stocks would be up to 20% lower in these horizons (Fig. 3B).

Microbial depolymerization limitation

The most obvious change when switching off the rate limiting term for the depolymerization of the C_R pool (Table 2, “No depolymerization limitation by microbes”) is the disappearance of the secondary peak of the C_R pool in the Bh horizon (Fig. 4A). While the overall OC levels would still be well captured along the profile, the mismatch in the Bh horizon would be considerable (Fig. 4B). Nevertheless, switching off the rate limiting term for the depolymerization flux considerably affects OC dynamics throughout the soil profile (Fig. 4B). Especially, in the subsoil horizons the C_R pool would be so rapidly depolymerized that it is virtually absent (Fig. 4B). In the Bh horizon the lift of the depolymerization limitation leads to ample available DOC, alleviating the competition

between microbes and soil minerals for DOC, and thereby to a disproportionate growth of the microbial biomass (Fig. 4B). In $\text{COMMISSION}_{\text{Full}}$ the microbial biomass levels were very low because the competition for DOC with soil minerals via q_{max} was important.

Lifting the depolymerization limitation also has pronounced consequences for the apparent ^{14}C age profiles (Fig. 4C and D). Without depolymerization limitation the apparent ^{14}C age of SOC would be on average 610 years younger in subsoil horizons (Fig. 4D). The ^{14}C signature of the C_R pool would even reach modern levels down to the Bw horizon because the turnover of C_R would be so rapid that the root litter input essentially determines the ^{14}C signature (Fig. 4C). Depolymerization limitation is especially relevant in the C2 horizon where the C_R turnover is so fast – compared to the input to the layer – that C_R is almost absent (Fig. 4B). Overall, the depolymerization limitation contributes considerably to the apparent ^{14}C ages especially in subsoil horizons (Fig. 4D).

Sorptive stabilization

Switching off the sorptive stabilization of DOC on soil minerals (Table 2, “No sorptive stabilization”) obviously leads to the

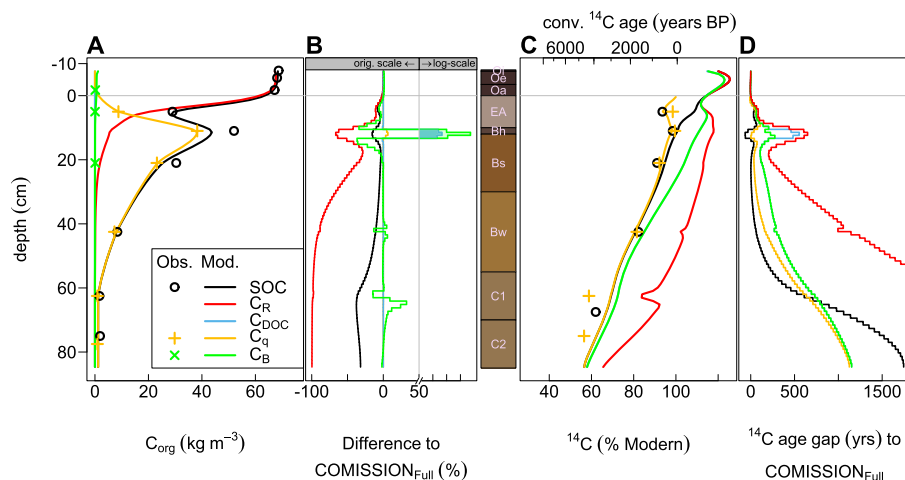


Fig. 4. Results of a COMMISSION simulation in which the limitation of depolymerization by microbial biomass is switched off – panel (A) shows organic carbon pools/fractions and panel (C) the respective ^{14}C signatures. Panel (B) shows the difference of COMMISSION without depolymerization limitation to the full COMMISSION model in percent. Panel (D) compares the conventional ^{14}C ages of COMMISSION without depolymerization limitation to the full model. The shading in panel (B) is intended to highlight the change to log-scale.

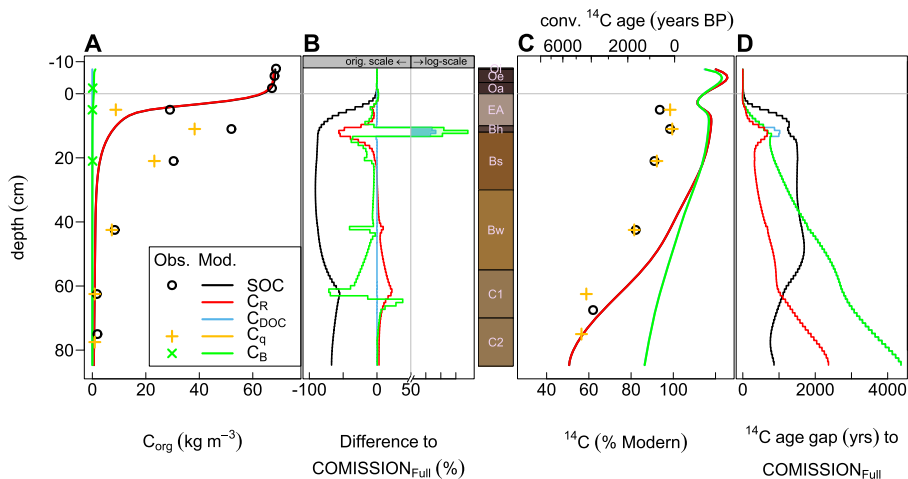


Fig. 5. Results of a COMMISSION simulation in which sorption is switched off – panel (A) shows organic carbon pools/fractions and panel (C) the respective ^{14}C signatures. Panel (B) shows the difference of COMMISSION without sorption to the full COMMISSION model in percent. Panel (D) compares the conventional ^{14}C ages of COMMISSION without sorption to the full model. The shading in panel (B) is intended to highlight the change to log-scale.

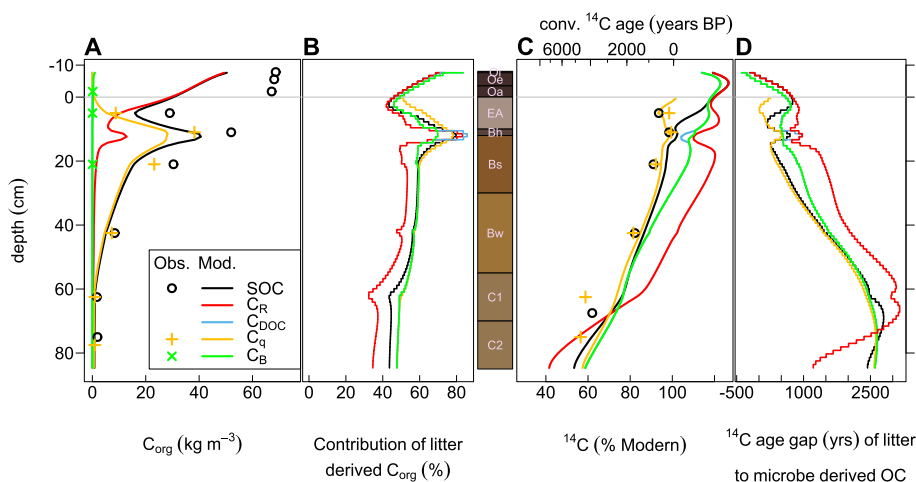


Fig. 6. Contribution of plant litter along the SOC profile. COMMISSION model forward run showing only litter-derived organic carbon – panel (A) shows organic carbon pools/fractions and panel (C) the respective ^{14}C signatures. Panel (B) shows the contribution of plant-litter-derived OC to overall OC of COMMISSION in percent. Panel (D) compares the conventional ^{14}C ages of litter-derived carbon to microbially recycled OC.

disappearance of the C_q pool (Fig. 5A). While the organic layer is not affected by the omission of sorption, the topsoil and subsoil mineral horizons show considerable differences to *COMMISSION*_{Full}. First, the secondary peak of the C_R pool disappears due to the missing interactions between q_{max} and microbes. Apparently, the overall high sorption capacity of the Bh horizon was responsible for the development of a secondary peak of the C_R pool (together with the depolymerization limitation). Apart from the decrease of the C_R pool in the Bh horizon, without sorption the C_R pool becomes more prominent in deeper parts of the soil profile compared to *COMMISSION*_{Full} (Fig. 5B). This is because without sorption more DOC is translocated or leaving the soil in the subsoil horizons; thereby less substrate is available for microbial growth and ultimately depolymerization of the C_R pool (Fig. 5B). This means that sorption has a dual role: It can suppress microbes by removing substrate, but also may stimulate them by retaining substrates (preventing loss by advection) and gradually releasing them.

In the *COMMISSION*_{Full} model run sorptive stabilization is responsible for ^{14}C ages of around 600 years in the topsoil horizons (Fig. 2C). Without sorption the apparent ^{14}C ages would be much

younger in the topsoil (Fig. 5C and D). In the subsoil horizons the ^{14}C signature of the C_R pool diverges from that of the C_{DOC} and C_B pools. Without adsorption and desorption DOC is transported without retardation to deeper soil layers and is dominated by the ^{14}C signature of litter inputs (Fig. 5C). Due to the strong coupling of microbes and DOC, microbes follow the ^{14}C signature of DOC throughout the soil profile (Fig. 5C). With faster decomposition and lower SOC stocks in the absence of sorptive stabilization, the C_R pool and the overall SOC stocks show modern ^{14}C signatures down to the Bw horizon (Fig. 5C). Below the Bw horizon the C_R pool consists mainly of microbial remains (cf. Fig. 7B), which is reflected in the high apparent ^{14}C ages in deeper subsoil horizons for the COMMISSION model without sorption.

3.3. Contribution of litter-derived vs microbe-derived organic carbon

In order to quantify the contribution of litter and microbe-derived organic carbon we split the model pools into a set that only receives input in form of microbial remains and a set that only

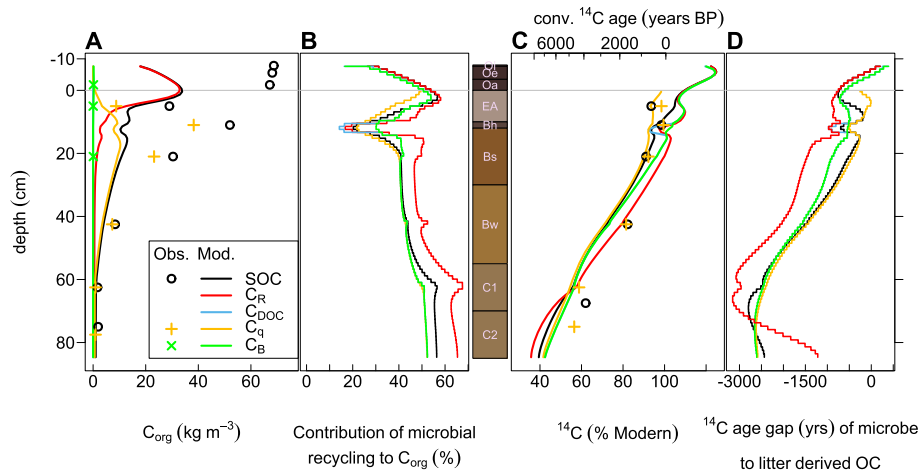


Fig. 7. Contribution of microbial recycling along the SOC profile. COMMISSION model forward run showing only microbially recycled organic carbon – panel (A) shows organic carbon pools/fractions and panel (C) the respective ^{14}C signatures. Panel (B) shows the contribution of microbially recycled OC to overall OC of COMMISSION in percent. Panel (D) compares the conventional ^{14}C ages of microbially recycled carbon to litter-derived OC.

receives input from litter (cf. Section 2.3, Table 2, “Litter- vs microbe-derived OC”). In the Oi horizon litter-derived OC makes up more than 70% of the total SOC stocks (Fig. 6B). In the organic layer the contribution of litter-derived carbon is, however, already decreasing to about 50% at the boundary between the organic layer and the mineral soil. This is in line with the concept that the Oa horizon of the organic layer represents more “humified” material (i.e. processed by the soil food web) (Fig. 7A,B). With the transition to the mineral soil sorptive stabilization comes into play and the depolymerization of root litter input is impeded because of lower microbial growth due to the competition of sorption capacity and microbes for DOC. Overall, this leads to a higher depolymerization limitation in the topsoil horizons than in the organic layer. This is reflected in a higher contribution of litter-derived carbon in the first mineral horizon (EA horizon) compared to the last organic horizon (Oa horizon) (Fig. 6B). The split in litter-derived and microbe-derived organic carbon also reveals that the secondary peak of the C_R pool in the Bh horizon is derived from root litter input and not microbial recycling (Fig. 6A,B and Fig. 7A,B).

Starting from the Bw horizon the importance of microbe-derived OC is increasing up to contributions of around 60% in the C1 and C2 horizons (Fig. 7B). This is partially explained by the fact that root litter is not the dominant form of carbon input there (Fig. 6B), but also because continued microbial recycling is getting more important with soil depth.

The importance of continued microbial recycling is even more evident from the ^{14}C age difference between litter-derived carbon and microbe-derived carbon along the soil profile (Figs. 6D and 7D). The apparent ^{14}C age of the litter-derived SOC is on average more than 1400 years younger than the ^{14}C age of microbe-derived SOC. More importantly, the ^{14}C age gap between litter-derived and microbe-derived carbon is increasing with depth due to the continued recycling of SOC through microbes (Figs. 6D and 7D). The ^{14}C age difference of the litter-derived C_R pool to the microbe-derived C_R pool is even more positive (Fig. 6D) because, “modern” root litter input is dominating the litter-derived C_R and because microbe-derived C_R is getting older while being processed again and again. The ^{14}C signature of the litter-derived C_R , however, would not be “modern” throughout the soil profile (Fig. 6D). Due to the small amount of root litter input in the subsoil and the interaction of stabilization mechanisms (depolymerization limitation and sorption), the ^{14}C signature of litter-derived C_R would still show apparent ^{14}C ages of more than 2000 years in the deep subsoil.

4. Discussion

4.1. Contribution of different model processes to the observed SOC and ^{14}C profiles

The goal of our study is to explain observed ^{14}C ages of more than 1000 years using a more mechanistic representation of soil carbon cycling than the models typically applied. Riley et al. (2014) showed recently that the formerly used decomposition rates on millennial time scales for “stable” pools are not necessary to explain observed ^{14}C age trends with depth. The insights gained with the calibration of the COMMISSION model and the model-experiments support and extend these findings.

In particular with the factorial model-experiment in which processes were switched off, we were able to shed light on the relative importance of the different processes implemented in COMMISSION. Based on their conceptual model of dissolved organic matter cycling along the soil profile, Kaiser and Kalbitz (2012) suggested that the transport of microbially recycled DOC is responsible for millennial ^{14}C ages in the subsoil. Due to an increasing energy limitation of microbes, especially in the C1 and C2 horizons, which are dependent on DOC transport for SOC input, our model-experiment suggests that without DOC transport ^{14}C ages in the subsoil would be much older (Fig. 3D). Nevertheless, as microbe-derived DOC makes up around 50–60% of DOC in the subsoil (Fig. 7B), microbially recycled DOC contributes considerably to ^{14}C ages in the subsoil.

Switching off depolymerization limitation and sorption showed how different stabilization mechanisms act in different parts of the soil profile. In the topsoil the ^{14}C age is quite high, mainly due to stabilization on mineral surfaces. In the subsoil both the depolymerization limitation of microbes (Fig. 4D) and sorptive stabilization explain (Fig. 5D) a large portion of the observed ^{14}C ages (1280 and 610 ^{14}C years on average in subsoil SOC) according to our model-experiments. Depolymerization limitation can be regarded as one of the processes that were “unresolved” in other modeling studies (Jenkinson and Coleman, 2008; Koven et al., 2013) and inspired the use of an “arbitrary” depth-dependence of decomposition rates (Riley et al., 2014). Although other first-order SOC profile models did not use this depth-dependence of decomposition (Elzein and Balesdent, 1995; Baisden et al., 2002; Braakhekke et al., 2014), in these models a pool with a millennial turnover time was needed to explain observed ^{14}C profiles. In these studies

this “stable” or “slow” pool is present throughout the soil profile, but it is unclear if this pool is meant to represent SOC that is chemically recalcitrant or stabilized on minerals.

Overall, this means that the value of the information contained in ^{14}C data has been overestimated with SOC profile models that lacked a mechanistic description of processes that could lead to the long-term persistence of SOC. By attempting to explain the ^{14}C profile with these models, one had to either introduce a depth-dependence of decomposition rates (Jenkinson and Coleman, 2008) or include a pool with a millennial turnover time (Braakhekke et al., 2014). At the same time these models underutilized the ^{14}C data because the steep increase of ^{14}C ages with depth has in essence not been used to constrain any of the mechanisms that could lead to a long-term persistence of SOC.

Riley et al. (2014) showed with their BAMS1 model that relatively fast decomposition rates can be reconciled with the observed ^{14}C age profile if stabilization mechanisms, similar to those implemented in COMMISSION, are explicitly considered. In addition, we highlight the importance of continued microbial recycling (Gleixner, 2013) for the ^{14}C age profile (Fig. 7D). It is noteworthy that this process cannot be necessarily subsumed under the term “stabilization process”, but is merely a process that leads to long-term persistence of plant litter inputs in the soil profile. This persistence is so pronounced that radioactive decay is relevant for the radiocarbon signal of this part of SOC. Especially the increasing contribution of microbe-derived OC along soil profiles (Fig. 7B) contributes substantially to the observed apparent ^{14}C age trends (Fig. 7C). Therefore, it is crucial that SOC profile models not only consider explicit stabilization processes such as depolymerization limitation or sorptive stabilization, but also processes such as continued microbial recycling that just lead to a long-term persistence of SOC in the soil.

4.2. Key features of COMMISSION

DOC links microbial interactions and sorptive stabilization

From our model-experiments it is evident that the C_{DOC} pool is a crucial component for models that include both microbial interactions and sorptive stabilization. In the COMMISSION model soil minerals and the microbial biomass essentially compete for DOC throughout the profile in the mineral soil. The representation of sorption using the Langmuir equations made it possible to fit the secondary peak of the C_R pool in the Bh horizon which is mainly made up of root litter-derived OC (Fig. 6B). In the Bh horizon, where the sorption capacity, q_{max} , is at its maximum, the adsorption strength is strongest and reduces the microbial uptake of DOC in the Bh horizon. As we assumed traditional Michaelis–Menten kinetics for the microbial uptake of DOC (Eq. (2)), DOC concentrations limit the rate of microbial uptake and growth (Fig. 4B).

Although the COMMISSION model is not designed to represent the process of podsolization, our link between microbial interactions and sorption in COMMISSION is able to amend theories of podzolization. Buurman and Jongmans (2005) noted that traditional theories of podzolization cannot explain the dominance of silt- and sand-sized pellets of particulate organic matter in Podzol-B horizons. Although our Bh horizon is not dominated by this material, we still observe a secondary peak of the light fraction/ C_R pool in the Bh horizon. The competition between soil minerals and microbial biomass offers a mechanistic explanation as to why root residues might be more abundant in Podzol-B horizons.

SOC decomposition models with explicit microbial interactions and explicit DOC pools often overlook the effect of “competition” for DOC by processes other than microbial uptake (e.g. Schimel and Weintraub, 2003; Allison et al., 2010; Moorhead et al., 2012)

because these models are neither accounting for the sorptive stabilization of DOC, nor for DOC leaching into deeper soil layers. If this seeming competition for DOC is not taken explicitly taken into account, soil mineralogy would have no direct influence on the ability of soil microbes to take up substrate and thereby to decompose SOM. Other SOC models with explicit representations of microbial biomass and DOC have started to take sinks for DOC other than microbial uptake into account (Wang et al., 2013; Riley et al., 2014), while Sulman et al. (2014) have already addressed possible effects of interactions between microbial decomposition and protection on soil minerals with the CORPSE model. This model, however, does not have an explicit DOC pool.

In order to be able to model the response of SOC to increased ecosystem productivity under elevated CO_2 , it is essential to consider interactions between microbial decomposition and protection on soil minerals (Sulman et al., 2014). Plants could allocate more carbon to root exudates to enhance nutrient uptake or the mineralization of SOM in order to meet their increased nutrient demands under CO_2 fertilization (Norby et al., 2010). The input of root exudates may lift a potential depolymerization limitation of microbes and hence prime the decomposition of SOM or the elevated litter inputs. The modeling results of Sulman et al. (2014) with the CORPSE model at two FACE sites indicated that stabilization on soil minerals can attenuate the priming effect induced by increased root exudates. In the COMMISSION model the carbon loss via priming may also be reduced if the available sorption sites are competing with microbes for the root exudates. With the COMMISSION model we are able to address the question of whether increased carbon allocation to the subsoil is leading to an increase or decrease of subsoil SOC stocks due to sorptive stabilization and increased litter inputs or exudate priming. Compared to the model of Sulman et al. (2014), in which sorptive stabilization is represented with linear sorption kinetics, the response to increased root exudates may vary depending on soil depth if an upper limit of SOC storage on soil minerals is defined via the q_{max} parameter. q_{max} might be saturated in the topsoil and would thereby not be able to alleviate the priming effect induced by root exudates, while in the subsoil root exudates can still be stabilized on minerals, depriving the microbial pool of a potential energy source.

Combination of traditional and reverse Michaelis–Menten kinetics

A novel feature in the structure of the decomposition equations of COMMISSION is the combination of traditional and reverse Michaelis–Menten kinetics. Wutzler and Reichstein (2008) and later Wang et al. (2014) showed that the traditional Michaelis–Menten kinetics have the undesired effect that the steady-state of the main SOC pools is completely independent of litter inputs. For reverse Michaelis–Menten kinetics on the other hand the main SOC pools scale with litter inputs (Wutzler and Reichstein, 2008). For COMMISSION we mechanistically argued that the decomposition of litter inputs and microbial remains in the C_R pool would be limited by the diffusion of extracellular enzymes and thereby by the amount of microbes C_B , while the microbial uptake of DOC would be limited by the diffusion of the substrate (DOC) to the microbes and thereby by the amount of DOC available. This combination of reverse (for C_R) and traditional Michaelis–Menten kinetics (for C_{DOC}) leads to the desired feature that the steady state of the main carbon pool (C_R) scales with litter inputs (Eq. (S6)). However, without sorption the steady state of the C_{DOC} pool would be independent of litter inputs (Eq. (S7)). We believe that this more mechanistically justified use of either the reverse or traditional Michaelis–Menten equation warrants further investigation, especially whether the Michaelis–Menten uptake of DOC has desired properties for a DOC pool.

Langmuir sorption – making the heavy fraction modelable

Representing mineral stabilization with Langmuir sorption has been of interest in several modeling studies. Riley et al. (2014) noted that they aim to represent sorption as Langmuir sorption in future versions of their model. Wang et al. (2013) included Langmuir sorption in their MEND model. Overall, these and our approaches can be seen as a scheme to represent mineral stabilization more mechanistically in models. Representing mineral sorption as Langmuir adsorption has the advantage of being able to represent an upper limit of mineral-associated OC storage in soils (q_{max}) which is widely assumed to exist (Wiesmeier et al., 2014). Hassink (1997) and Hassink and Whitmore (1997) were the first to define such a maximum mineral sorption capacity both for field studies and model applications. While the empirical approach of Hassink (1997) has found widespread use in experimental studies (Feng et al., 2013; Beare et al., 2014; Wiesmeier et al., 2014), the use of the empirical q_{max} in its modelling counterpart – the Langmuir equation – is limited.

Our approach with the COMMISSION model showed that Langmuir sorptive stabilization is very helpful to be able to model what is perceived as the “mineral-associated fraction” obtained from various physical SOM fractionation methods (von Lützow et al., 2007). The concept of mineral-associated SOC implies that the size of this pool is limited by the amount of mineral surfaces available (Hassink et al., 1997). Also if one adopts the view of a zonal model of organo-mineral interactions as by Kleber et al. (2007) with intermediate and outer zones based on organo–organo interactions, the amount of OC in these zones would still depend on the amount of mineral surfaces being in immediate contact with the first layer of organic molecules. There is ample evidence from different studies that organo-mineral associations do not form monolayer equivalents that cover the complete mineral surface area (e.g. Ransom et al., 1997; Mayer, 1999; Kaiser and Guggenberger, 2003), but that OC attaches preferentially on the rough surfaces of minerals (Vogel et al., 2014). Nevertheless the amount of these rough surfaces should also scale with the amount of total mineral surfaces available, regardless whether they are suited for organo-mineral interactions or not.

4.3. Model limitations and future directions

Stabilization by aggregation

The stabilization of SOM by occlusion within aggregates (Six et al., 2004; Conant et al., 2011) is not explicitly modeled in COMMISSION. In principle one could model the effect of aggregation similar to the q_{max} approach with dynamic Langmuir equations, where q_{max} would here be the capacity of a soil horizon to occlude SOM within aggregates. To a certain extent this capacity would also be dependent on the clay and oxide content of a soil horizon (Six et al., 2004). Compared to the q_{max} for sorptive stabilization, however, the capacity to occlude SOM within aggregates would be much more dynamic as the formation and turnover of aggregates also depend on soil physical conditions such as freezing and thawing, and drying and rewetting (Six et al., 2004). Furthermore, the capacity to occlude SOM within aggregates would depend on the size and turnover time of the microbial pool as aggregate formation is enhanced by microbial extracellular polysaccharides (Wagai et al., 2009).

Multi-profile calibration and application to global scale models

In order to apply and calibrate COMMISSION within an ecosystem model it is necessary to represent the temperature and moisture sensitivity of the different processes. In this study we purposefully did not do this as within COMMISSION soil temperature and moisture are not modeled. This is especially important for disentangling the

contributions of the root biomass profile, soil texture changes, and soil temperature and moisture profiles to between-site differences in depth trends of ^{14}C ages.

The depolymerization of the C_R pool and the microbial uptake of C_{DOC} are assumed to be limited by diffusion of enzymes and DOC. Based on the considerations of Davidson et al. (2012) for their DAMM model, the concentrations of enzymes and DOC at the respective reaction sites (C_R and C_B) could constitute the respective rate-limiting resource in Eqs. (1) and (2). These concentrations at the reaction site are dependent on how well enzymes and DOC can diffuse through the soil water film. Davidson et al. (2012) argue that diffusion is higher in thick soil water films. Geometrical considerations imply that the thickness of the soil water film is related to the cube of the volumetric soil water content. Similarly, to account for oxygen limitation in wet soils one can introduce another Michaelis–Menten term where oxygen constitutes the rate-limiting resource (Davidson et al., 2012). The oxygen concentration can then be calculated as a function of volumetric soil moisture and porosity (Davidson et al., 2012; Sulman et al., 2014). Here, one could include a dependence on soil aggregation as also aggregates limit oxygen diffusion (Six et al., 2013).

Little is known about the temperature sensitivities of the half-saturation constants and adsorption and desorption rates. However, several authors have already provided useful descriptions and parameterizations for the temperature sensitivity of the maximum depolymerization and uptake rate, $V_{max,D}$ and $V_{max,U}$ (Allison et al., 2010; Todd-Brown et al., 2012; Wang et al., 2012). Regarding the sensitivity of CUE to temperature several scenarios and strategies have been proposed (Allison et al., 2010; Manzoni et al., 2012; Todd-Brown et al., 2012), but the uncertainty is high (Wieder et al., 2013).

The application of COMMISSION in an Earth system model requires a global map of q_{max} . Using the Harmonized World Soil Database, q_{max} could be derived globally from quantile regressions of MOC data against the clay + silt content (Feng et al., 2013; Beare et al., 2014), or hydrological properties that can be related to the surface area of soil minerals. This would lead to quite similar q_{max} estimates in the top- and subsoil, while based on our current definition of q_{max} , the MOC profile closely follows the prescribed q_{max} because the available sorption capacity from the batch sorption experiments is relatively low in subsoil horizons. In future work we aim to study the effect of different q_{max} definitions, especially if other stabilization mechanisms apart from DOC sorption might be relevant for these alternative definitions.

5. Conclusions

We showed with the COMMISSION model that an explicit consideration of stabilization and persistence processes renders millennial turnover times unnecessary. Our model results suggest that in the topsoil sorptive stabilization is responsible for relatively high apparent ^{14}C ages, while in the subsoil the combination of depolymerization limitation and sorption is responsible for a large part of the observed ^{14}C ages. However, apart from processes that can be clearly characterized as stabilization processes, observed ^{14}C age trends along a soil profile could be traced back with the COMMISSION model to the continued microbial recycling of SOM. Together with microbial interactions the transport of DOC along the profile leads to lower ^{14}C ages in the subsoil compared to a hypothetical situation without advection.

Overall, our results lead us to conclude that a more detailed description of stabilization and persistence processes give a more realistic explanation of apparent ^{14}C ages in soil profiles of more than 1000 years. Apart from explaining ^{14}C age trends, the explicit

representation of SOC profiles in Earth system models is essential to assess the feedbacks between climate change, changing atmospheric deposition and SOC, and to make the SOC module of Earth system models comparable with observations. The interaction of microbial processes and sorptive stabilization is especially relevant for studying the response of SOC to potentially higher belowground C allocation under elevated CO₂ concentrations. Sorption may reduce potential SOC losses due to priming by root exudates, especially in the subsoil where the sorption capacity may be far from saturation. This once again highlights the importance of a vertically explicit representation of different stabilization processes in SOC models.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.soilbio.2015.06.008>.

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