

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/241326665>

Estimating RothC carbon pools from standard TOC combustion data only

Article · May 2010

CITATIONS

0

READS

182

3 authors, including:



[Lutz Weihermüller](#)

Forschungszentrum Jülich

163 PUBLICATIONS 5,846 CITATIONS

[SEE PROFILE](#)



[Harry Vereecken](#)

Forschungszentrum Jülich

1,278 PUBLICATIONS 40,026 CITATIONS

[SEE PROFILE](#)

Simple pedotransfer functions to initialize reactive carbon pools of the RothC model

L. WEIHERMÜLLER, A. GRAF, M. HERBST & H. VEREECKEN

IBG-3 Agrosphere Institute, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Summary

Modelling of carbon turnover is a widely used tool to estimate soil carbon stock changes as a response to climate and land-use change. Carbon turnover models are increasingly used not only at the point scale but also at regional and continental scales, and the Rothamsted carbon model (RothC) is a widely used model because of its simplicity and easy implementation. For the initialization of the RothC model, knowledge about the carbon pool sizes is essential. Pool size characterization can be either obtained from physical fractionation or equilibrium model runs, but both approaches are time consuming and tedious, especially for larger scale simulations. In our study, a pedotransfer function (PTF) for the estimation of all active carbon pools of the RothC model is presented. As independent variables, only total organic carbon (TOC) and clay content, which are easily available at most scales, are necessary. For validation of PTFs the resistant plant material (RPM) stock estimated from physical fractionation of soil of a wide range of types was predicted with a R^2 of 0.70. In a second step, associated errors induced by the use of PTFs were analysed by using simulation runs for a 100-year time period. Thereafter, the model was either initialized by the carbon pools extracted from physical fractionation or the PTF. Maximum relative deviations in TOC content were small (<9%) and declined to <4% after 100 years. Further, absolute errors were within the range of measurement error for soil organic carbon. Therefore, we propose that PTFs can be used to initialize the RothC model whenever physical fractionation is not feasible or equilibrium runs are considered too tedious.

Introduction

Soil organic carbon (SOC) dynamics play a key role in the global carbon (C) cycle. On a global scale, 68–98 PgC are annually emitted by the soil into the atmosphere, contributing to the second largest C flux between ecosystems and the atmosphere (Raich & Potter, 1995; Schimel *et al.*, 1996; Bond-Lamberty & Thomson, 2010). Therefore, even small changes in decomposition of SOC may directly affect the global atmospheric CO₂ content. Consequently, there is large scientific interest in the estimation of soil carbon stocks and their potential feedback to climate change (Davidson & Janssens, 2007). In order to predict SOC changes in response to climate change, especially to changes in the abiotic drivers of soil temperature and soil water content and also to land-use changes, various dynamic carbon turnover models have been developed. In general, the models are based on several conceptual carbon pools (with different turnover rates), which simplify the complex chemical, biological and physical characteristics of SOC (Smith *et al.*, 2002).

The Rothamsted Carbon Model (RothC) (Coleman & Jenkinson, 2005) has been widely used to simulate changes in SOC content and the release of CO₂ over a wide range of ecosystems, ranging from grassland and cropland to forest sites (Coleman *et al.*, 1997; Smith *et al.*, 1997; Ludwig *et al.*, 2003, 2007; Bauer *et al.*, 2012), and across scales from laboratory (Weihermüller *et al.*, 2009) and regional (Wang & Polglase, 1995; Falloon *et al.*, 1998b) to global (Post *et al.*, 1982; Jenkinson *et al.*, 1991; Jones *et al.*, 2005). Additionally, the RothC model can be used for different purposes to understand processes (Falloon *et al.*, 1998b, 2000; Weihermüller *et al.*, 2011; Xu *et al.*, 2011) or to predict the impact of climate and/or land-use change on carbon stocks without explicit examination of the carbon turnover dynamics and the changes in carbon quality itself (Tate *et al.*, 2000; Smith *et al.*, 2007).

Within the RothC model, SOC is partitioned into five conceptual pools, including two litter-driven compartments (decomposable plant material, DPM, and resistant plant material, RPM) and three other pools, namely microbial biomass (BIO), humified organic matter (HUM) and inert organic matter (IOM) (Coleman & Jenkinson, 2005). As the pools are purely conceptual, rather than defined by directly measurable properties, the question arises

Correspondence: L. Weihermüller. E-mail: l.weihermueller@fz-juelich.de

Received 17 January 2013; revised version accepted 17 January 2013

as to how to initialize the model. In general, three contrasting approaches are reported in the literature: (i) physico-chemical analysis of soil samples, (ii) running the model into equilibrium with present or historical climatic data and carbon inputs or (iii) the use of pedotransfer functions based on easily measureable state variables such as the total organic carbon (TOC) content.

For the physico-chemical approach, Skjemstad *et al.* (2004) introduced a fractionation scheme that can be used to initialize the RothC model based on ideas proposed by Elliott & Cambardella (1991). In this, SOC is separated into different fractions, depending on the particle size. A comparable method was also proposed by Zimmermann *et al.* (2007) for Swiss soils. Vance *et al.* (1987), on the other hand, proposed a fumigation-extraction method to estimate the BIO pool and Bornemann *et al.* (2008, 2010) proposed using mid-infrared spectroscopy (MIRS) for the rapid estimation of IOM and particulate organic carbon, which can be related to the RothC RPM pool. In addition to the soil carbon pools, the pool ratios from the incoming plant material (DPM:RPM) can be measured by using acid hydrolysis (Shirato & Yokozawa, 2006). Unfortunately, the physico-chemical analyses cannot be applied at larger scales because they are too expensive and tedious.

As an alternative, the model can be run into equilibrium matching a given TOC content at equilibrium (Herbst *et al.*, 2008; Ludwig *et al.*, 2010; Xu *et al.*, 2011). For this, historical climatic data and annual plant inputs will be looped to generate a sufficient time-series (about 10 000 years) for the equilibrium run. Unfortunately, there are two major drawbacks in the approach: first, the required assumption of equilibrium among pools, and second, unrealistic climatic data and plant input. The first problem can be substantial if land-use changed significantly within the last century or even over a shorter time-interval.

Finally, pedotransfer functions (PTF) have been proposed for specific carbon pools and regression used to determine almost constant ratios between certain pools. One of the most accepted PTFs was developed by Falloon *et al.* (1998a), who proposed that IOM had similar proportions in each soil, irrespective of the historical use or textural class, and could therefore be predicted from TOC data only. Zimmermann *et al.* (2007) suggested that the ratio between BIO and HUM could be estimated as 0.0272.

Physical fractionation is too time consuming and tedious (involving pretreatment, sieving, freeze drying and TOC analysis for bulk and sieved fractions) for large-scale modelling. Further, running the model into equilibrium needs additional data, such as historical climate data and uncertain information about the carbon input from plant residues and/or manure application. Thus an easier and faster alternative would be very useful, especially when applying the model on very large datasets, for instance those produced by combining climatic, land use and soil characteristics within a geographical information system, in order to compute long-term SOC stocks spatially (Bolker *et al.*, 1998; Martin *et al.*, 2007). Therefore, the aim of this study was to find an appropriate way to estimate the initial carbon pools at equilibrium directly from easily available data such as TOC and clay content.

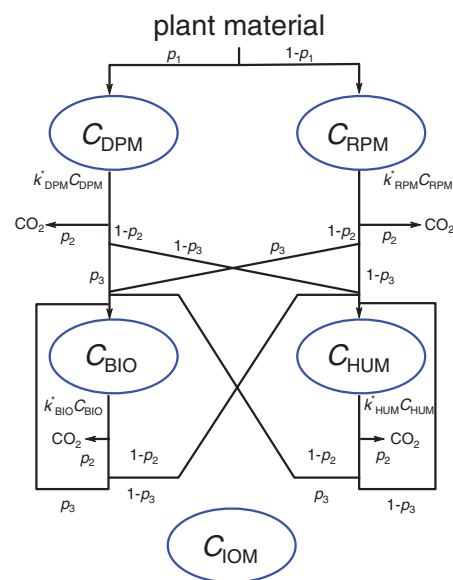


Figure 1 Flow chart of the RothC carbon model (Coleman & Jenkinson, 2005) taken from Scharnagl *et al.* (2010) with decomposition rates k_{DPM} , k_{RPM} , k_{BIO} and k_{HUM} and p_1 as portioning coefficients between decomposable plant material (DPM) and resistant plant material (RPM) from the incoming plant residues or farmyard manure. The proportion of carbon that is mineralized, p_2 , depends on clay content of soil, whereas a fixed ratio, p_3 , is used to partition carbon flux between microbial biomass (BIO) and humified organic matter (HUM) pools.

Materials and methods

The Rothamsted soil carbon model (RothC)

Within the Rothamsted soil carbon model (RothC), TOC is divided into the five carbon pools already noted: DPM, RPM, HUM, BIO and IOM (Coleman & Jenkinson, 2005) (see also Figure 1). The already decomposed plant material is regarded as HUM, whereas the total carbon mass of microbial organisms is represented by the BIO pool. All non-decomposable or inert material is defined as IOM (Coleman & Jenkinson, 2005). In general, all pools (except IOM) will decompose and form CO_2 , BIO and HUM (Figure 1). Decomposition is described by first-order kinetics at predefined rates (k) of 10, 0.3, 0.66 and 0.02 years^{-1} for DPM, RPM, BIO and HUM, respectively. The incoming plant material is generally separated into DPM and RPM with plant specific ratios such as 1.44 (59% RPM and 41% DPM) for wheat (Coleman & Jenkinson, 2005). Farmyard manure is divided to allocate 49% to each of DPM and RPM and the remaining 2% is assigned to HUM (Coleman & Jenkinson, 2005). Both plant material and farmyard manure decompose to CO_2 , BIO and HUM, which will be further decomposed (Figure 1). Additionally, partitioning among pools (RPM, BIO and HUM) depends on clay content, as indicated by p_2 in Figure 1. To account for abiotic factors, optimal decomposition rates are scaled by temperature and soil water content. Again, clay content triggers the soil moisture dependence.

For simulations, a 50-year time-series of climatic data from Bonn, Germany, was used with monthly aggregated precipitation and potential evaporation and monthly mean air temperature. Mean annual temperature was 10.1°C, with a minimum temperature of −4.3 and a maximum of 23°C. Annual precipitation was 643.2 mm (mean monthly precipitation = 53.6 mm), with maximum rainfall of 200 mm per month. Mean annual potential evaporation was 870.3 mm, with a mean monthly potential evaporation of 72.5 mm. This time-series was looped to sum up a final climatic dataset of 12 200 years for the equilibrium runs and 100 years for the error analysis. Additionally, the initial IOM pool was set to match the PTF proposed by Falloon *et al.* (1998a):

$$\text{IOM} = 0.049 \text{ TOC}^{1.139}, \quad (1)$$

where TOC is the total organic carbon content at equilibrium. In all simulations, the incoming plant material was equally distributed into the soil layer from 0 to 30 cm, with an assumed bulk density of 1.45 g cm^{−3}. Because partitioning among pools (RPM, BIO and HUM) depends on clay content, this was varied systematically from 0 to 100% in steps of 5% for smaller values (<40%) and steps of 10% for larger ones (>40%). Different carbon inputs were also assumed, whereby input was varied in time and amount but also in composition (plant residues only, farm yard manure and plant residues and crop rotation with farmyard manure). An overview of carbon inputs is given in Table 1. In total, 240 different combinations of carbon input and clay content were simulated. Finally, TOC data and pool sizes were averaged for the last year (year 12 200) to avoid any direct effect of the last carbon input. Using the TOC and clay content, a PTF was developed for the prediction of the RPM, BIO and HUM pools.

Soil samples

Soil samples were taken from the long-term soil monitoring programme (Bodendauerbeobachtung, BDF) of the State Authority for Mining, Energy and Geology, Geological Survey of Lower Saxony, Hannover (Landesamt für Bergbau, Energie und Geologie, LBEG). Within this study we used 39 topsoil samples (0–20 cm depth) from various locations within Lower Saxony (Germany), all originating from agricultural crop land. All samples were taken during spring 2009 by the LBEG. Overall, the samples covered a wide range of typical soils (including sea marsh, pseudogley and luvisols) developed on various geological units (including wetlands and till). The various sampling locations also ensured that more or less all different agricultural practices (no manure application, high manure application, input of different amounts of crop residues, as well as conventional and reduced tillage) were represented within the sample survey. As a consequence of the different geological, pedological and agricultural conditions, the samples differed widely in soil texture as well as in soil chemical properties (Table 2). Sand content was determined by wet sieving and silt and clay by the pipette method. Figure 2 shows the particle size distribution of all soil samples in a ternary

Table 1 Carbon inputs (t ha^{−1}) for RothC equilibrium model runs

Run	FYM / t ha ^{−1}	PR / t ha ^{−1}	C-input / t ha ^{−1}	Month											
				1	2	3	4	5	6	7	8	9	10	11	12
1	1.00	1.00	1	0.2	0.2	0.2	0.2	0.2	0.2	0.4					
2	2.00	2.00	2	0.4	0.4	0.4	0.4	0.4	0.4	0.8					
3	5.00	5.00	5	1.0	1.0	1.0	1.0	1.0	1.0	2.0					
4	6.00	6.00	6	1.2	1.2	1.2	1.2	1.2	1.2	2.4					
5	0.50	0.50	1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	(0.5)				
6	1.00	1.00	2	0.2	0.2	0.2	0.2	0.2	0.2	0.4	(1.0)				
7	1.50	1.50	3	0.3	0.3	0.3	0.3	0.3	0.3	0.6	(1.5)				
8	2.00	2.00	4	0.4	0.4	0.4	0.4	0.4	0.4	0.8	(2.0)				
9	2.50	2.50	5	0.5	0.5	0.5	0.5	0.5	0.5	1.0	(2.5)				
10	3.00	3.00	6	0.6	0.6	0.6	0.6	0.6	0.6	1.2	(3.0)				
11	1.80	0.98	2.78	0.164	0.164	0.164	0.164	0.164	0.164	0.49	0.115	(1.8)			
12	0.18	0.70	0.88	0.171	0.171	0.171	0.171	0.171	0.171	0.51	0.115	0.115	0.35 (0.18)		
13	—	1.02	1.02	0.15	0.15	0.15	0.15	0.15	0.15	0.45			(1.8)		
14	1.80	0.90	2.70												
15	1.80	0.30	2.10												
16	4.85	2.79	7.64												
				Crop rotation with plant residues and FYM											
											0.009	0.009	0.27	(1.8)	

FYM is farmyard manure and PR is plant residues. All FYM applications are in parentheses.

Table 2 Physicochemical characteristics of the 39 soil samples used for physical fractionation

	pH	TOC / mass %	Total N / mass %	Bulk density / g cm ⁻³	Porosity / vol. %	Elevation asl. / m
Mean	5.94	1.54	0.13	1.40	43.5	81.0
SD	0.99	0.78	0.05	0.12	4.2	65.0
Min	3.90	0.63	0.06	1.14	32.0	-0.50
Max	7.90	4.55	0.30	1.76	52.0	310

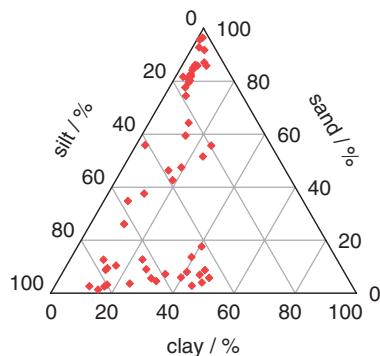
**Figure 2** Particle grain size distribution of the 39 soil samples used in the pedotransfer function (PDF) for the prediction of equilibrium pool size distribution.

diagram. Soils covered a broad spectrum of soil textural classes, but the sand and silt fraction predominates in most soils. The clay fraction varied between 0 and 50%.

Physical fractionation

Several physical fractionation methods have been used, but the advantage of the scheme introduced by Skjemstad *et al.* (2004) is that it can be used to initialize the RothC carbon pool model directly; we therefore applied this method in our study. Soil samples were air-dried and sieved to <2 mm. Ten grams of soil were then dispersed with 10 ml 5.2 g l⁻¹ concentrated sodium polyphosphate solution and shaken overnight. The suspension was passed through two sieves with 200 and 53 µm mesh, and rinsed with deionized water until the effluent was clear. The material remaining on the sieves was transferred into bottles and freeze-dried. Samples were weighed and homogenized by grinding before TOC analysis with a LECO RC-412 (LECO Inc., St Joseph, MI, USA) carbon analyser. The smallest fraction (<53 µm) was discarded and calculated from the mass balance (Skjemstad *et al.*, 2004). For all samples, three replicates were fractionated and the arithmetic means as well as the standard deviations were calculated. The RPM content (t ha⁻¹) was calculated as the sum of the carbon content of the two sieved fractions (200 and 53 µm). Inert OM was assigned by the use of Equation (1) and the remaining TOC was partitioned to BIO and HUM fractions using the linear partitioning of 0.0272 as proposed by Zimmermann *et al.* (2007). It has to be noted that this fractionation scheme does not allow the separation of RPM and DPM in the sieved

fraction (200 and 53 µm), and therefore any DPM still available within the sample will be allocated to the RPM fraction.

Error analysis

Error propagation induced by the use of the PTF in the RothC model runs was performed for a time-series of 100 years. For this, the 50 years of climatic data from Bonn were looped twice to obtain a data series of 100 years. Carbon inputs from the crop rotation listed in Table 1 were 7.64 t ha⁻¹ (4.85 t ha⁻¹ farmyard manure (FYM) and 2.79 t ha⁻¹ plant residues (PR)). Again, incoming PR and FYM were assumed to be mixed homogeneously into the 0–30 cm of soil and the bulk density was set to 1.45 g cm⁻³.

Testing against the reference condition, we used the data simulated with the initialization from physical fractionation with the RPM pool sizes listed in Table 3 (RPM-1 wet sieving). The IOM content was again estimated with Equation (1) and TOC content. Additionally, the remaining BIO and HUM were portioned according to the ratio of 0.0272, as suggested by Zimmermann *et al.* (2007). Carbon pools were predicted by Equations (2)–(4) (see next section) using TOC and clay content for the same samples. Finally, the mismatch between both model runs was calculated as a relative deviation, whereby 0% relative deviation indicated perfect agreement between model results obtained from physical fractionation and PTF. Negative agreement indicated an under-estimation and positive an over-estimation of TOC simulated by the model runs initialized by the PTF.

Results and discussion

C-pool distribution at equilibrium

To analyse the carbon pool distribution at equilibrium for the 240 different combinations of carbon inputs (Table 1) and clay content (0–100%), the averaged carbon pool sizes from the last year of the equilibrium model run were taken and the results were plotted as three-dimensional surface plots in Figure 3. As expected, a clear dependency between equilibrium TOC content and pool fractions (RPM, HUM and BIO) was seen at a given clay content. On the other hand, a non-linear correlation between changes in clay and the equilibrium TOC for the same plant input was observed, with a stronger non-linearity for HUM and BIO pools than with the RPM pool. This non-linearity was a consequence of the model structure, where the partitioning between pools depended on clay

Table 3 Organic carbon (TOC), clay content and resistant plant material (RPM) from physical fractionation (RPM-1), as well as inert organic matter (IOM), RPM, microbial biomass (BIO) and humified organic matter (HUM) estimated from Equations (1) to (4) (see text) and based on measured TOC and clay content

Sample	TOC / t ha ⁻¹	Clay / mass %	RPM-1 wet sieving / t ha ⁻¹	IOM (Equation 1) / t ha ⁻¹	RPM (Equation 2) / t ha ⁻¹	BIO (Equation 3) / t ha ⁻¹	HUM (Equation 4) / t ha ⁻¹	TOC error / t ha ⁻¹	TOC error / %
BDF001	51.11	13.9	9.75	4.33	7.00	0.86	38.89	0.03	0.0
BDF002	62.64	16.9	13.57	5.46	8.38	1.06	47.71	0.03	0.0
BDF003	52.42	5.2	8.50	4.45	7.92	0.86	39.19	-0.01	0.0
BDF004	49.16	14.9	8.58	4.14	6.69	0.83	37.47	0.02	0.0
BDF005	43.96	16.2	4.70	3.64	5.94	0.75	33.62	0.01	0.0
BDF006	38.56	14.4	4.85	3.14	5.29	0.65	29.49	-0.02	0.0
BDF007	43.65	11.0	4.84	3.62	6.15	0.73	33.16	0.00	0.0
BDF010	93.53	5.0	16.21	8.61	14.09	1.53	69.46	-0.17	-0.2
BDF012	60.25	23.7	6.09	5.22	7.77	1.04	46.19	0.03	0.0
BDF014	40.00	11.8	5.46	3.27	5.60	0.67	30.46	-0.01	0.0
BDF016	53.94	4.5	12.03	4.60	8.26	0.88	40.21	-0.01	0.0
BDF017	42.83	4.6	6.08	3.54	6.57	0.70	32.05	-0.03	-0.1
BDF019	98.96	7.0	22.51	9.18	14.44	1.63	73.90	-0.18	-0.2
BDF021	86.13	4.4	19.20	7.84	13.14	1.40	63.87	-0.12	-0.1
BDF022	52.85	15.4	7.75	4.50	7.16	0.90	40.27	0.03	0.1
BDF026	57.20	0.9	14.09	4.92	9.80	0.92	41.56	0.01	0.0
BDF027	66.99	7.9	12.30	5.89	9.69	1.11	50.30	0.00	0.0
BDF031	132.24	18.6	20.50	12.78	17.39	2.24	100.31	-0.47	-0.4
BDF032	105.92	2.5	23.35	9.92	16.90	1.71	77.70	-0.31	-0.3
BDF033	53.29	2.2	16.08	4.54	8.67	0.86	39.25	-0.03	-0.1
BDF036	42.87	5.4	10.61	3.54	6.48	0.71	32.17	-0.02	-0.1
BDF043	48.50	16.3	6.21	4.08	6.54	0.82	37.04	0.02	0.0
BDF045	41.35	3.0	6.56	3.40	6.59	0.67	30.73	-0.05	-0.1
BDF046	58.29	19.0	6.87	5.03	7.71	0.99	44.53	0.03	0.1
BDF047	44.50	11.4	6.40	3.70	6.24	0.75	33.81	0.01	0.0
BDF049	54.59	8.0	8.52	4.66	7.91	0.91	41.10	0.01	0.0
BDF050	52.42	4.2	7.45	4.45	8.08	0.86	39.04	-0.02	0.0
BDF051	82.00	46.1	14.00	7.41	9.79	1.45	63.44	-0.09	-0.1
BDF052	67.43	11.0	8.29	5.93	9.43	1.13	50.92	0.01	0.0
BDF056	54.59	1.5	9.17	4.66	9.10	0.88	39.97	-0.02	0.0
BDF057	122.67	5.4	12.08	11.73	18.31	2.01	91.07	-0.44	-0.4
BDF058	50.46	13.6	7.40	4.26	6.93	0.85	38.39	0.02	0.0
BDF059	47.96	13.0	6.82	4.02	6.62	0.81	36.48	0.02	0.0
BDF063	82.87	32.3	10.23	7.50	10.29	1.44	63.69	-0.06	-0.1
BDF064	33.19	4.2	8.05	2.65	5.16	0.55	24.91	-0.08	-0.2
BDF065	142.68	33.9	26.49	13.93	17.55	2.48	109.37	-0.65	-0.5
BDF067	47.42	5.1	7.87	3.97	7.19	0.78	35.49	-0.01	0.0
BDF069	74.39	24.1	7.61	6.63	9.55	1.28	56.92	-0.01	0.0
BDF070	82.22	26.8	8.44	7.44	10.43	1.42	62.98	-0.04	-0.1

TOC errors calculated from the mismatch between TOC measurements and the sum of all predicted pools.

content. As a consequence of these changes in partitioning, carbon pools with different turnover rates would be stabilized differently.

The surface plots also indicate that single pools can be predicted using TOC and clay content simultaneously. Therefore, we developed a combination of a linear and non-linear regression within one expression to account for the linear dependency of the pools on TOC and a second expression to account for the non-linear dependency of the pools on clay content. To fit the

data we used the global optimization routine Shuffled Complex Evolution developed at the University of Arizona (SCE-UA) as described by Duan *et al.* (1992, 1994). This optimization routine has been already successfully used in a wide range of applications in hydrology (Mertens *et al.*, 2005; Mboh *et al.*, 2011) but also for the estimation of parameters in non-linear carbon models (Weihermüller *et al.*, 2009; Bauer *et al.*, 2012).

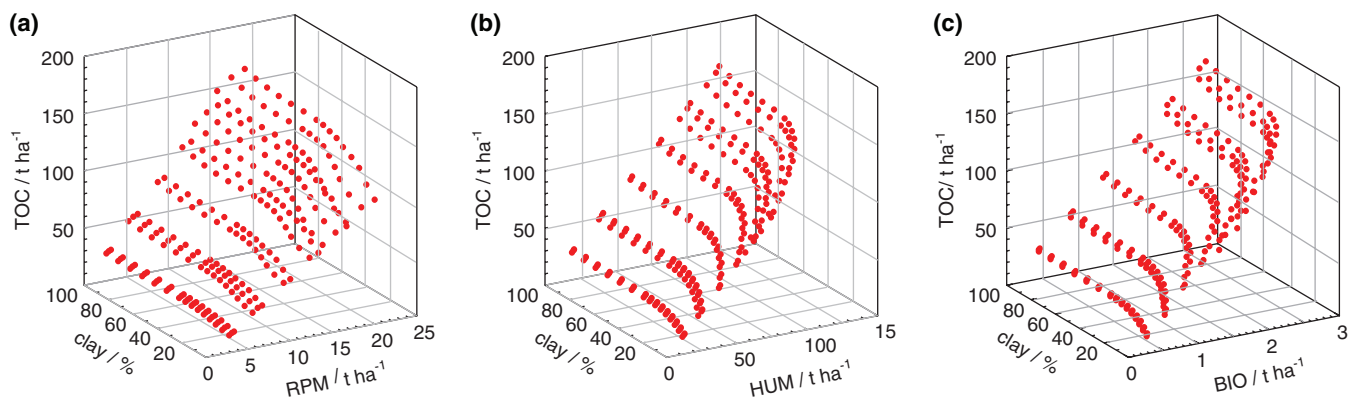


Figure 3 Total organic carbon (TOC) and clay content plotted against (a) equilibrium resistant plant material (RPM) content, (b) equilibrium humified organic matter (HUM) content and (c) equilibrium microbial biomass (BIO) content for the different carbon input scenarios listed in Table 1. Note that TOC, RPM, HUM and BIO were averaged over the last 12 months of each consecutive model run.

We minimized the mismatch between predicted and measured pool sizes (here measurements equal the simulation outputs) using the co-variables of TOC and clay content in the least square sense. The final regressions for the three carbon pools are shown in the following equations:

$$RPM = (0.1847 TOC + 0.1555) (clay + 1.2750)^{-0.1158}, \quad (2)$$

$$HUM = (0.7148 TOC + 0.5069) (clay + 0.3421)^{0.0184}, \quad (3)$$

$$BIO = (0.0140 TOC + 0.0075) (clay + 8.8473)^{0.0567}, \quad (4)$$

where TOC is expressed in t ha^{-1} and clay in % mass.

The statistics of the fitted model are listed in Table 4. The large R^2 value of 0.99 indicates an almost perfect match for all combinations. Correlations between predicted and reference pool sizes are plotted in Figure 4(a–c) for the RPM, HUM and BIO pool to visualize the goodness of fit. Again it becomes clear that the regressions are able to predict equilibrium pool distribution with a large degree of accuracy, which is not only because of the large R^2 but also because the points scatter only slightly along the 1:1 line. Root mean square error (RMSE) is fairly small, with 0.53, 0.72 and 0.05 t ha^{-1} for the RPM, HUM and BIO pools, respectively. Assuming a relative analytical error in carbon determination in the laboratory of about 0.1%, this results in a mean error for all TOC contents analysed of 0.82 t ha^{-1} , which would be larger than the largest RMSE found for the HUM pool (0.72 t ha^{-1}).

Now it can be questioned whether the derived PTF can be also applied in regions with different climates to that used in this study. The model structure means that different climates would only change the rate-modifying factors for the temperature and soil moisture for each simulation time-step t_n , but not the partitioning between the pools itself. To prove this, we calculated the carbon pool and TOC sizes for some randomly selected equilibrium model runs and predicted the pool sizes from resulting equilibrium TOC and clay content. For this, we changed the standard climatic scenario described earlier by changing monthly temperature by

Table 4 Regression statistics for the different carbon pools of resistant plant material (RPM), humified organic matter (HUM) and microbial biomass (BIO), estimated by total organic carbon (TOC) and clay content

C-pool	R^2	ME / t ha^{-1}	RMSE / t ha^{-1}
RPM	0.99	0.280	0.529
HUM	0.99	0.517	0.719
BIO	0.99	0.003	0.054

ME = mean error and RMSE = root mean squared error in t ha^{-1} .

$\pm 2^\circ\text{C}$ as well as the total monthly precipitation sum by $\pm 20\%$. Each run was performed for different clay contents of 0, 50 and 100%. Plant input was also varied. Scenarios 1, 10 and 19 (Table 1) were used for 0% clay. Scenarios 5, 9 and 14 were used for 50% clay and scenarios 6, 12 and 16 were used for 100% clay inputs. This combination resulted in a total of 36 additional model runs. Finally, the R^2 values between equilibrium carbon pools and predicted carbon pools using the PTF (Equations (2)–(4)) were calculated. As expected from theory, the R^2 value exceeded 0.99 for all predictions.

Comparison of measured and predicted C pools

We compared the RPM carbon pool estimated from physical fractionation with that predicted by Equation (2), taking into account the measured clay and TOC contents of the soil samples. The direct comparison between predicted and measured RPM pool size is plotted in Figure 5. The regression was reasonable, with a R^2 of 0.70. However, a systematic shift occurred when slightly larger RPM contents were measured, resulting in a RMSE of 3.47 t ha^{-1} . Reasons for the mismatch between measured (fractionated) and estimated RPM are manifold. As can be seen in Figure 5, variability in estimated RPM was large for some samples, which can be attributed to (i) problems in sample splitting for the replicates, (ii) sample pretreatment, especially in the removal of large macroscopic plant residues before fractionation

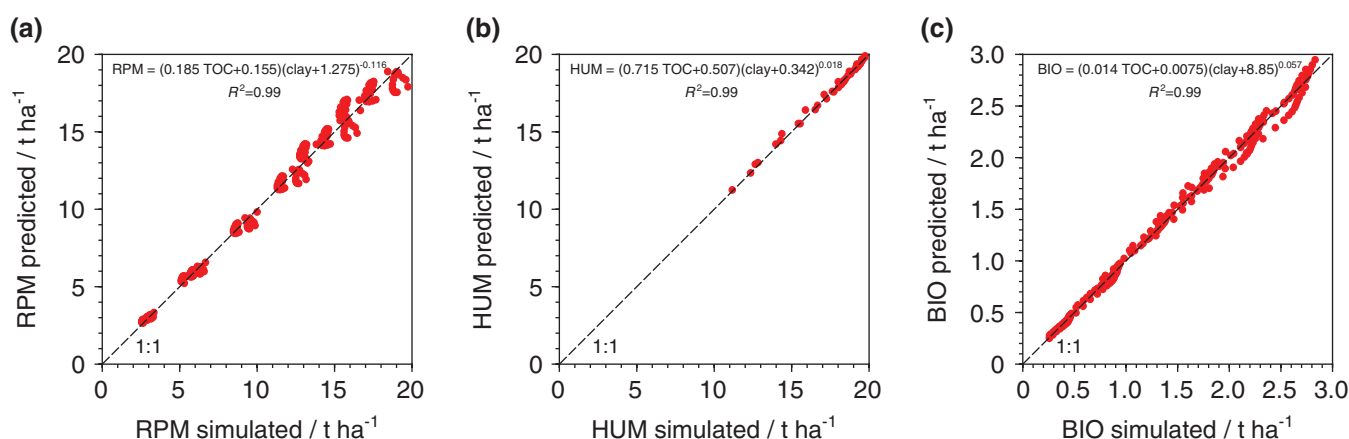


Figure 4 (a) Simulated plotted against predicted resistant plant material (RPM), (b) simulated against predicted humified organic matter (HUM) and (c) simulated against predicted microbial biomass (BIO) for all runs listed in Table 1 with varying clay contents ranging from 0 to 100%.

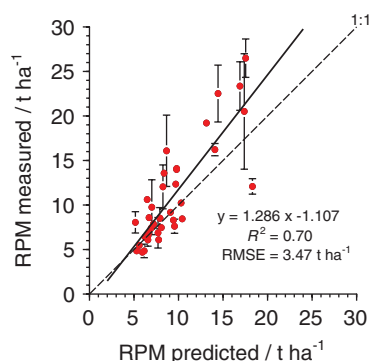


Figure 5 Predicted (based on Equation (2)) plotted against measured resistant plant material (RPM) concentration.

and (iii) the fractionation procedure itself. The latter includes subjective steps, whereby laboratory staff decide when the rinsate is clear. Second, the mismatch can be partly explained by the assumption that the carbon pools are in equilibrium (which is the underlying assumption for the PTF). Carbon contents in most agricultural fields are not in equilibrium, and this especially matters if samples are taken at only one time during the season because there may be periodic residue or manure inputs or changes in land management (crop rotation or transformation from grassland to arable land). Finally, some uncertainty in the RPM prediction might be caused by the variability in TOC and clay content, which directly influence the predicted RPM. Nevertheless, even taking all these error sources into account, the prediction seems appropriate for large-scale modelling purposes.

Error analysis

To assess the errors associated with the carbon pool estimation based either on the derived PTF or physical fractionation, RothC simulations were performed for a 100-year time-series using either the fractionated RPM pools or the predicted pools from Equations

(2)–(4). Individual clay and TOC contents for each of the 39 samples were taken from measurements for the prediction of pools. The relative deviation of the simulated TOC is plotted in Figure 6. PTF (Equations (2)–(4)) were not able to predict the TOC contents exactly in the first phase of the simulation, resulting in an increase of difference with a general maximum deviation of <9% around 180 months after the start of the model. Error was systematically reduced beyond this point and was <5% at the end of the simulation period, indicating that a false initialization would be compensated for by yearly carbon input reaching a new equilibrium after a few decades. Calculating the mean difference for all model runs yielded a maximum deviation of 1.6%, with a mean standard deviation of 2.5%. Considering outliers in Figure 6, a maximum difference of 8.3% occurred for the model run BDF-033, where the difference between fractionated RPM (16.08 t ha^{-1}) and predicted RPM (8.67 t ha^{-1}) was largest. On the other hand, BDF043 was nearly perfectly predicted by the PTF, with a deviation of $\pm 0.1\%$, even when the predicted RPM deviated by >5% from the fractionated (Table 3). Looking at the extreme cases, but using the absolute TOC contents at the end of the model runs as an indicator for the mismatch, model run BDF033 over-estimated TOC by 3.1 t ha^{-1} (86.8 and 89.9 t ha^{-1} TOC for the fractionated and predicted model runs, respectively). We further analysed the mean TOC error for all model runs, which was 0.88 t ha^{-1} (or 0.02% by mass) only, and therefore, close to the noise level of TOC by the analytical method (1% error in TOC measurements = 0.82 t ha^{-1} for all samples). Additionally, TOC content is known to be highly variable in space (Herbst *et al.*, 2010), which therefore introduces an additional error source.

The same behaviour of increasing difference at short times and a convergence at longer times between the two initialization methods has been already observed by Xu *et al.* (2011), who stated that these large differences in the early years mainly stem from the false initialization of the RPM pool with its fast turnover and not from false initialization of the much larger but slower HUM pool. Additionally, Xu *et al.* (2011) proposed that the difference caused

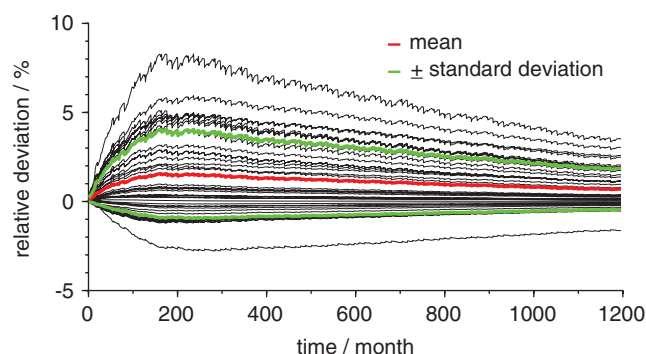


Figure 6 Relative deviation of total organic carbon (TOC) of the 100-year simulation run initialized according to Table 3, whereby relative error was calculated as the mismatch between fractionation and pedotransfer function (PTF) from Equations (1) to (4).

by the initialization should be $<1\%$, which was in the overall range of difference we found when averaging all model runs.

Model results were clearly sensitive to initialization. However, average trends can be predicted fairly well using TOC and clay contents for the prediction of the steady-state initial pool distribution. Additionally, Foereid *et al.* (2012) stated that the predicted differences between climate scenarios were less sensitive to the initialization method than to the initial soil carbon content, which points to the applicability of the proposed PTF.

Conclusions and outlook

The RothC model is one of the most commonly used models to predict carbon stock changes over decades for analysis of climate change feedbacks on terrestrial carbon stocks. Unfortunately, the model has to be initialized with carbon pools, which are nearly impossible to quantify on larger regional to continental scales. To overcome this problem, the model must be run into equilibrium, which is time consuming and tedious. We developed a set of pedotransfer functions (PTFs) based on easily available total organic carbon (TOC) and clay content data to predict all active carbon pools of the RothC model. From multiple regressions, equilibrium pool sizes were predicted with a R^2 of 0.99, whereby remaining uncertainty can be associated with periodic carbon input into the system, and hence with deviations from ideal equilibrium.

Additionally, we analysed the difference between the RPM pool size obtained from physical fractionation and PTF predictions. Measured RPM pools could be fairly well predicted with a R^2 of 0.7 using TOC and clay content data only. Finally, we analysed the absolute and relative deviations of model runs either initialized based on physical fractionation or estimates from the PTFs. Maximum relative errors were $\pm 9\%$ and declined to $\pm 5\%$ after 100 years of simulation. Absolute maximum error was $<3.1 \text{ t ha}^{-1}$ and on average only $<0.8 \text{ t ha}^{-1}$ for all model runs, which is within the range of analytical error for TOC, sub-sampling variability, and/or inter-field TOC variability. In conclusion, we present a PTF that is applicable for large-scale modelling of carbon turnover using the RothC model. Our

findings also indicate future research needs as follows. First, laboratory-derived relationships between RPM and TOC should be further tested for more samples from different climates and ecosystems all over the globe. Second, the somewhat surprising reliability of pool partitioning according to both the fractionation and the equilibriumrun methods raises an important question: do these widespread methods fail to relate to meaningful C-pools in nature, or are the latter stable functions of TOC?

Acknowledgements

We acknowledge J. Backhausen from the central division of chemical analysis (ZCH) from the Forschungszentrum Jülich GmbH for TOC measurements. Many thanks also to S. Deitelhoff and H. Lee for physical fractionation of soil samples. Soil material and basic soil parameters were provided by the Soil Monitoring Programme of Lower Saxony, State Authority for Mining, Energy, and Geology, Geological Survey of Lower Saxony, Hannover, Germany.

References

- Bauer, J., Weihermüller, L., Huisman, J.A., Herbst, M., Graf, A., Sequisar, J.M., *et al.* 2012. Inverse determination of heterotrophic soil respiration response to temperature and water content under field conditions. *Biogeochemistry*, **108**, 119–134.
- Bolker, B.M., Pacala, S.W. & Parton, W.J. 1998. Linear analysis of soil decomposition: insight from the CENTURY model. *Ecological Applications*, **8**, 425–439.
- Bond-Lamberty, B. & Thomson, A. 2010. Temperature-associated increases in the global soil respiration record. *Nature*, **464**, 499–500.
- Bornemann, L., Welp, G., Brodowski, S., Radionov, A. & Amelung, W. 2008. Rapid assessment of black carbon in soil organic matter using mid-infrared spectroscopy. *Organic Geochemistry*, **39**, 1537–1544.
- Bornemann, L., Welp, G. & Amelung, W. 2010. Particulate organic matter at field scale – rapid acquisition using mid-infrared spectroscopy. *Soil Science Society of America Journal*, **74**, 1147–1156.
- Coleman, K. & Jenkinson, D.S. 2005. *ROTHC-26.3. A Model for the Turnover of Carbon in Soil. Model Description and Windows Users Guide*. IACR - Rothamsted, Harpenden.
- Coleman, K., Jenkinson, D.S., Crocker, G.J., Grace, P.R., Klir, J., Korschens, M., *et al.* 1997. Simulating trends in soil organic carbon in long-term experiments using RothC-26.3. *Geoderma*, **81**, 29–44.
- Davidson, E.A. & Janssens, I.A. 2007. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, **440**, 165–173.
- Duan, Q.Y., Gupta, V.K. & Sorooshian, S. 1992. Effective and efficient global minimization for conceptual rainfall–runoff models. *Water Resources Research*, **82**, 1015–1031.
- Duan, Q.Y., Sorooshian, S. & Gupta, V.K. 1994. Optimal use of the SCE-UA global optimization method for calibrating watershed models. *Journal of Hydrology*, **158**, 265–284.
- Elliott, E.T. & Cambardella, C.A. 1991. Physical separation of soil organic matter. *Agriculture, Ecosystems & Environment*, **34**, 407–419.
- Falloon, P.D., Smith, P., Coleman, K. & Marshall, S. 1998a. Estimating the size of the inert organic matter pool from total soil organic carbon content for use in the Rothamsted carbon model. *Soil Biology & Biochemistry*, **30**, 1207–1211.

- Falloon, P., Smith, P., Smith, J.U., Szabó, J., Coleman, K. & Marshall, S. 1998b. Regional estimates of carbon sequestration potential: linking the Rothamsted carbon model to GIS database. *Biology & Fertility of Soils*, **27**, 236–241.
- Falloon, P., Smith, P., Coleman, K. & Marshall, S. 2000. How important is inert organic matter for predictive soil carbon modelling using the Rothamsted Carbon model? *Soil Biology & Biochemistry*, **32**, 433–436.
- Foereid, B., Bellamy, P.H., Holden, A. & Kirk, G.J.D. 2012. On the initialization of soil carbon models and its effects on model predictions for England and Wales. *European Journal of Soil Science*, **28**, 32–41.
- Herbst, M., Hellebrand, H.J., Bauer, J., Huisman, J.A., Šimůnek, J., Weihermüller, L., *et al.* 2008. Multiyear heterotrophic soil respiration: evaluation of a coupled CO₂ transport and carbon turnover model. *Ecological Modelling*, **214**, 271–283.
- Herbst, H., Prolingheuer, N., Graf, A., Huisman, J.A., Weihermüller, L., Vanderborght, J., *et al.* 2010. Multivariate conditional stochastic simulation of soil heterotrophic respiration at plot scale. *Geoderma*, **160**, 74–82.
- Jenkinson, D.S., Adams, D.E. & Wild, A. 1991. Model estimates of CO₂ emission from soil in response to global warming. *Nature*, **351**, 304–306.
- Jones, C., McConnell, C., Coleman, K., Cox, P., Falloon, P., Jenkinson, D., *et al.* 2005. Global climate change and soil carbon stocks; predictions from two contrasting models for the turnover of organic carbon in soil. *Global Change Biology*, **11**, 154–166. doi: 10.1111/j.1365-2486.2004.00885.x.
- Ludwig, B., John, B., Ellerbrock, R., Kaiser, M. & Flessa, H. 2003. Stabilization of carbon from maize in a sandy soil in a long-term experiment. *European Journal of Soil Science*, **54**, 117–126.
- Ludwig, B., Schulze, E., Rethmeyer, J., Marbach, I. & Flessa, H. 2007. Predictive modelling of C dynamics in the long-term fertilization experiment at Bad Lauchstädt with the Rothamsted carbon model. *European Journal of Soil Science*, **58**, 1155–1163.
- Ludwig, B., Hu, K., Niu, L. & Liu, X. 2010. Modelling the dynamics of organic carbon in fertilization and tillage experiments in the North China Plain using the Rothamsted carbon model-initialization and calculation of C inputs. *Plant & Soil*, **332**, 193–206.
- Martin, M.P., Cordier, S., Balesdent, J. & Arrouays, D. 2007. Periodic solutions for soil carbon dynamics equilibria with time-varying forcing variables. *Ecological Modelling*, **204**, 523–530.
- Mboh, C.M., Huisman, J.A. & Vereecken, H. 2011. Feasibility of sequential and coupled inversion of time domain reflectometry data to infer soil hydraulic parameters under falling head infiltration. *Soil Science Society of America Journal*, **75**, 775–786.
- Mertens, J., Madsen, H., Kristensen, K., Jaques, D. & Feyen, J. 2005. Sensitivity of soil parameters in unsaturated zone modelling and the relation between effective, laboratory and in situ estimates. *Hydrological Processes*, **19**, 1611–1633.
- Post, W.M., Emanuel, W.R., Zinke, P.J. & Stangenberger, A.G. 1982. Soil carbon pools and world life zones. *Nature*, **289**, 156–159.
- Raich, J.W. & Potter, C.S. 1995. Global patterns of carbon dioxide emissions from soils. *Global Biogeochemical Cycles*, **9**, 23–36.
- Scharnagl, B., Vrugt, J.A., Vereecken, H. & Herbst, M. 2010. Information content of incubation experiments for inverse estimation of pools in the Rothamsted carbon model: a Bayesian perspective. *Biogeosciences*, **7**, 763–776.
- Schimel, D., Alves, D., Enting, I., Heiman, M., Joos, F., Raynaud, D., *et al.* 1996. CO₂ and the carbon cycle. In: *Climate Change 1995: The Science of Climate Change. Contribution of Working Group I to the Second Assessment Report of the IPCC* (eds. Houghton, J.T., Meira Filho, L.G., Callander, B.A., Harris, N., Kattenberg, A. & Maskell, K.), pp. 65–86. Cambridge University Press, Cambridge, UK.
- Shirato, Y. & Yokozawa, M. 2006. Acid hydrolysis to partition plant material into decomposable and resistant fractions for use in the Rothamsted carbon model. *Soil Biology and Biochemistry*, **38**, 812–816.
- Skjemstad, J.O., Spouncer, L.R., Cowie, B. & Swift, R.S. 2004. Calibration of the Rothamsted organic carbon turnover model (RothC Ver. 26.3), using measurable soil organic carbon pools. *Australian Journal of Soil Research*, **42**, 79–88.
- Smith, J.U., Smith, P., Monaghan, M. & MacDonald, A.J. 2002. When is a measured soil organic matter fraction equivalent to a model pool? *European Journal of Soil Science*, **53**, 405–416.
- Smith, P., Smith, J.U., Powlson, D.S., McGill, W.B., Arah, J.R.M., Chertov, O.G., *et al.* 1997. A comparison of the performance of nine soil organic matter models using datasets from seven long-term experiments. *Geoderma*, **81**, 153–225.
- Smith, P., Smith, J.U., Franko, U., Kuka, K., Romanenkov, V.A., Shevtsova, L.K., *et al.* 2007. Changes in mineral soil organic carbon stocks in the croplands of European Russia and the Ukraine, 1990–2070; comparison of three models and implications for climate mitigation. *Regional Environmental Change*, **7**, 105–119.
- Tate, K.R., Scott, N.A., Parshotam, A., Brown, L., Wilde, R.H., Giltrap, D.J., *et al.* 2000. A multi-scale analysis of a terrestrial carbon budget – is New Zealand a source or sink of carbon? *Agriculture, Ecosystems & Environment*, **82**, 229–246.
- Vance, E.D., Brookes, P.C. & Jenkinson, D.D. 1987. An extraction method for measuring soil microbial biomass C. *Soil Biology & Biochemistry*, **19**, 703–707.
- Wang, Y.P. & Polglase, P.J. 1995. Carbon balance in the tundra, boreal forest and humid tropical forest during climate change – scaling-up from leaf physiology and soil carbon dynamics. *Plant, Cell & Environment*, **18**, 1226–1244.
- Weihermüller, L., Huisman, J.A., Graf, A., Herbst, M. & Sequis, J.-M. 2009. Multistep outflow experiments for the simultaneous determination of soil physical and CO₂ production parameters. *Vadose Zone Journal*, **8**, 772–782.
- Weihermüller, L., Huisman, J.A., Graf, A., Herbst, M. & Vereecken, H. 2011. Errors in modelling carbon turnover induced by temporal temperature aggregation. *Vadose Zone Journal*, **10**, 195–205.
- Xu, X., Liu, W. & Kiely, G. 2011. Modeling the changes in soil organic carbon of grassland in response to climate change: effects of measured versus modelled carbon pool for initializing the Rothamsted Carbon model. *Agriculture, Ecosystems & Environment*, **140**, 372–381.
- Zimmermann, M., Leifeld, J., Schmidt, M.W.I., Smith, P. & Fuhrer, J. 2007. Measured soil organic matter fractions can be related to pools in the RothC model. *European Journal of Soil Science*, **58**, 658–667.