

# Measured soil organic matter fractions can be related to pools in the RothC model

M. ZIMMERMANN<sup>a</sup>, J. LEIFELD<sup>a</sup>, M. W. I. SCHMIDT<sup>b</sup>, P. SMITH<sup>c</sup> & J. FUHRER<sup>a</sup>

<sup>a</sup>Agroscope ART Reckenholz-Tänikon, Swiss Federal Research Station for Agroecology and Agriculture, Air Pollution/Climate Group,

Reckenholzstrasse 191, CH-8046 Zürich, Switzerland, <sup>b</sup>Geographisches Institut der Universität Zürich, CH-8057 Zürich, Switzerland and

<sup>c</sup>Department of Plant and Soil Science, Cruickshank Building, Aberdeen University, St Machar Drive, Aberdeen AB24 3UU, UK

## Summary

Understanding the response of soil organic carbon (SOC) to environmental and management factors is necessary for estimating the potential of soils to sequester atmospheric carbon. Changes over time in the amount and distribution of SOC fractions with different turnover rates can be estimated by means of soil SOC models such as RothC, which typically consider two to five SOC pools. Ideally, these pools should correspond to measurable SOC fractions. The aim of this study was to test the relationship between SOC pools used in RothC and fractions separated through a fractionation procedure. A total of 123 topsoil samples from agricultural sites (arable land, grassland and alpine pasture) across Switzerland were used. A combination of physical and chemical methods resulted in two sensitive (particulate organic matter and dissolved organic carbon), two slow (carbon associated to clay and silt or stabilized in aggregates) and one passive (oxidation-resistant carbon) SOM fractions. These fractions were compared with the estimated equilibrium model pools when the corresponding soils were modelled with RothC. Analysis revealed strong correlations between SOC in measured fractions and modelled pools. Spearman's rank correlation coefficients varied between 0.82 for decomposable plant materials (DPM), 0.76 for resistant plant materials (RPM), 0.99 for humified organic matter (HUM) and biomass (BIO), and 0.73 for inert organic matter (IOM). The results show that the proposed fractionation procedure can be used with minor adaptations to identify measurable SOC fractions, which can be used to initialize and evaluate RothC for a wide range of site conditions.

## Introduction

Soil organic matter (SOM) turnover models are often used to predict changes in SOC in response to shifts in land use, management or climate. Such changes in SOC are associated with an altered CO<sub>2</sub> exchange between terrestrial ecosystems and the atmosphere, and they impact significantly on regional carbon budgets (Janssen *et al.*, 2003). A net carbon loss from soils adds to the increase in the atmospheric CO<sub>2</sub> concentration, probably leading to higher global temperatures (IPCC, 2001), which, in turn, could accelerate decomposition of SOM (Jones *et al.*, 2005), whereas net soil CO<sub>2</sub> sequestration could help to mitigate the greenhouse effect and to improve soil quality. Validation of model outputs is an important step for the reliable prediction of SOM. Apart from measuring total SOC and comparing it with modelled results, validation of conceptual

SOM subunits would enhance the confidence in using SOM models, and would allow for better characterization of interactions between site conditions and SOM. This has rarely been attempted (Smith *et al.*, 2002).

Most models are based on several conceptual SOM pools with different turnover rates. These pools can be ascribed to different organic constituents such as plant inputs, decomposers of the incoming organic material, and storage in various forms of SOM. Typically, the latter is divided into pools that differ from each other by decomposition rates and characteristic stabilization mechanisms, which are linked to rate modifiers. Changes in environmental conditions have different impacts on these pools. One feature most SOM models share is that they involve one to two labile and/or dynamic pools, two to three physically and chemically protected pools, and one passive or even inert pool (Christensen, 1996). Stabilized SOC is of special importance with respect to long-term CO<sub>2</sub> sequestration because it accounts for most of the SOC. Verification of the conceptual model pools can be accomplished through the

Correspondence: Michael Zimmermann. E-mail: Michael.Zimmermann@art.admin.ch

Received 23 February 2006; revised version accepted 25 May 2006

identification and measurement of soil fractions with corresponding turnover times.

Elliott & Paustian (1996) described an approach that isolated meaningful SOM fractions and allowed models to be built on the basis of measurable fractions. They concluded that only models that can be validated by measurements of individual pools are reliable enough to predict changes in SOM. By this approach, models predicting measurable fractions can only be used for sites in which variations in environmental and textural conditions are similar to the site for which the particular model was initialized. Therefore, these models would have to be adjusted to local climatic conditions, texture and land use. Skjemstad *et al.* (2004) proposed the use of measurable fractions to initialize SOC pools of the RothC model (Coleman & Jenkinson, 1999). They extracted a plant-derived particulate organic matter (POM) fraction and a charcoal fraction from Australian soils and calculated the other fraction by difference in order to initialize the model. However, the amount of charcoal and the nature of the mechanisms leading to stabilization of SOM in fire-prone Australian soils with a large char content differ greatly from those in agricultural soils in central Europe. Therefore, the aim of our study was to use an alternative approach to measure SOM fractions, and to test the relationship between these fractions and corresponding conceptual pools of RothC. This would have the advantage of allowing the model to be initialized at any point in a landscape, even if historical data are lacking.

The approach was based on the separation of soil samples from Swiss agricultural sites into fractions that correspond to different physical and chemical stabilizing mechanisms. A crucial factor for the decomposition of organic material is its accessibility to microbes; plant debris not physically protected is attacked first. Physical protection can be achieved through aggregation and adsorption of SOM on mineral surfaces, which strongly reduces its decomposability. Aggregates are vulnerable to changes in land use and management (Baldock & Skjemstad, 2000) and therefore they can lose physical protection. A smaller part of SOM is chemically resistant to microbial degradation (Krull *et al.*, 2003). Here, we dispersed labile aggregates in the soil samples by use of a weak ultrasonic treatment and density separation to obtain a light POM fraction. This POM fraction is predominantly plant derived, has a turnover time of 10–50 years (Six *et al.*, 2000) and is expected to be sensitive to land use and management. Furthermore, we isolated two fractions from the soil samples, which consisted of either stable micro-aggregates or silt and clay particles. Eusterhues *et al.* (2003) found that SOC resistant to oxidation is made up of very refractory and slowly cycling carbon with less  $^{14}\text{C}$  activity than total SOC. We extracted a non-oxidizable SOM fraction from the silt and clay fractions to isolate an old and stable SOC fraction.

To test whether these measured fractions correspond to calculated pools of a SOM model, we modelled sites, assuming them to be in equilibrium, with RothC Ver. 26.3 (Coleman &

Jenkinson, 1999). This model has been applied to sites with diverse agricultural management worldwide (Smith *et al.*, 1997). The advantage of RothC is the small number of parameters needed to initialize the model. The specific questions of this study were: (i) Can measured SOM fractions be related to RothC modelled pools for soils under equilibrium conditions? (ii) Is it useful to initialize RothC with measured SOM fractions?

## Materials and methods

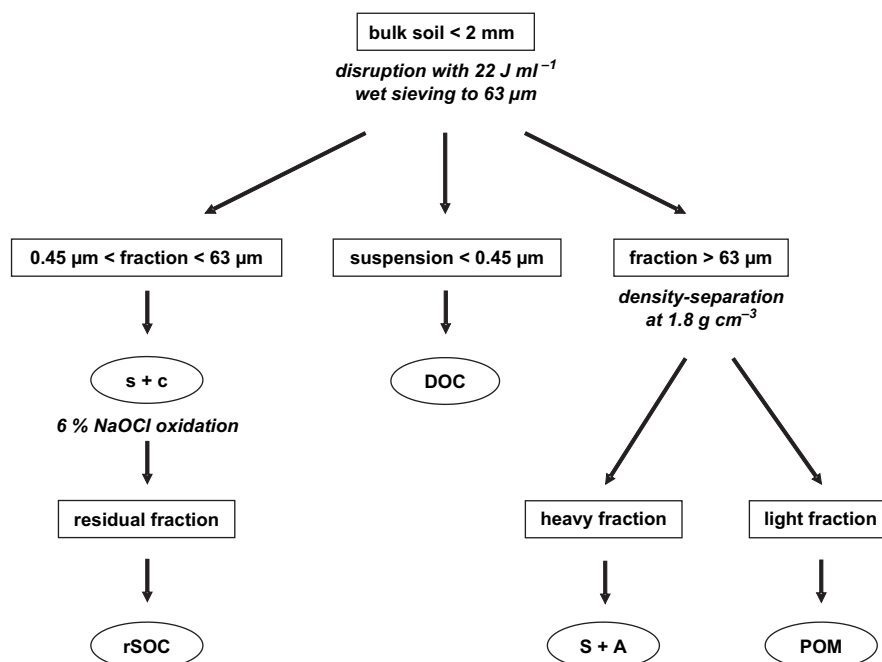
### Soil samples

We analysed 123 soil samples from two different research projects in Switzerland. From the Swiss national soil survey archive, we took 48 soil samples, which originated from agricultural (arable, temperate grassland, or alpine pasture) sites at altitudes ranging from 265 to 2400 m above sea level (a.s.l.). Thus, the sites represented a gradient in mean annual temperature (MAT) from +10.6 to  $-1.6^{\circ}\text{C}$ , and in mean annual precipitation from 722 to 2327 mm. Composite soil samples from all sites were taken from 50 cores (3 cm diameter) within a plot of  $10 \times 10$  m, between 1985 and 1991. Soil samples from arable sites were taken as 0–20 cm cores. Undisturbed topsoils from temperate grasslands and alpine pastures were either divided into horizons of 0–5 cm, 5–10 cm and 10–20 cm or, in some cases, also taken as 0–20 cm cores. A detailed description of sampling technique together with site characteristics (climate, geology and land use) can be found in Desautels & Studer (1993). The second set of samples was taken from a biodiversity study in extensively managed meadows on the Swiss Central Plateau. The set consisted of 75 soil samples. These soil samples were collected at three different regions at altitudes between 420 and 670 m a.s.l., with annual precipitation between 964 and 1333 mm. Management intensity of these grassland sites varied considerably. Sampling sites and agricultural management are described in detail by Buholzer & Jeanneret (2005). Each sample was a composite of 20 soil cores taken from the top 20 cm.

All soil samples are carbonate-free with SOC contents of less than 8.7% (mineral soils). The soil samples were dried at  $40^{\circ}\text{C}$ , crushed, and particles  $> 2$  mm were removed. Silt and clay contents were determined by the pipette method and sand contents calculated by difference.

### Fractionation procedure

Soil samples were fractionated by means of physical and chemical procedures, as shown in Figure 1. Thirty grams of the soil ( $< 2$  mm) were added to 150 ml water and dispersed using a calibrated ultrasonic probe-type (Bandelin, Berlin, Germany) with an output-energy of  $22 \text{ J ml}^{-1}$ . Application of more energy may disrupt coarse sand-sized SOM (Amelung & Zech, 1999). This dispersed suspension was then wet sieved over a  $63\text{-}\mu\text{m}$  aperture sieve till the rinsing water was clear. The fraction  $> 63 \mu\text{m}$ , containing the sand fraction and stable aggregates (S + A)



**Figure 1** Diagram of the fractionation procedure; s + c = silt and clay, rSOC = resistant soil organic carbon, DOC = dissolved organic carbon, S + A = sand and stable aggregates, and POM = particulate organic matter.

together with POM, was dried at 40°C and weighed. The suspension < 63 μm was filtered through a 0.45-μm aperture nylon mesh and the material > 0.45 μm was dried at 40°C and weighed. An aliquot of the filtrate was frozen to measure the amount of dissolved SOC (DOC).

POM was separated by stirring the fraction > 63 μm with sodium polytungstate (Sometu, Berlin, Germany) at a density of 1.8 g cm<sup>-3</sup> (Sohi *et al.*, 2001). The mixture was centrifuged at 1000 g for 15 minutes and the light fraction was decanted. Both fractions were washed with deionised water to remove all sodium polytungstate, dried at 40°C and weighed.

A chemically resistant carbon fraction (rSOC) was extracted from the fraction < 63 μm (s + c) by NaOCl oxidation. Oxidation was done with 6% (60 g litre<sup>-1</sup>) NaOCl at room temperature after a modified method of Kaiser & Guggenberger (2003). One gram of s + c was oxidized for 18 hours at 25°C with 50 ml of 6% NaOCl adjusted to pH 8 with concentrated HCl. The oxidation residue was centrifuged at 1000 g for 15 minutes, decanted, washed with deionised water and centrifuged again. This oxidation step was repeated twice.

Carbon and nitrogen contents of solid fractions were measured by combustion with an elemental analyser (Vario EL Elemental, Hanau, Germany) and of liquid samples by thermal oxidation with a liquid analyser (Dimatoc 2000, Dimatec, Essen, Germany).

#### Application of RothC Vers. 26.3

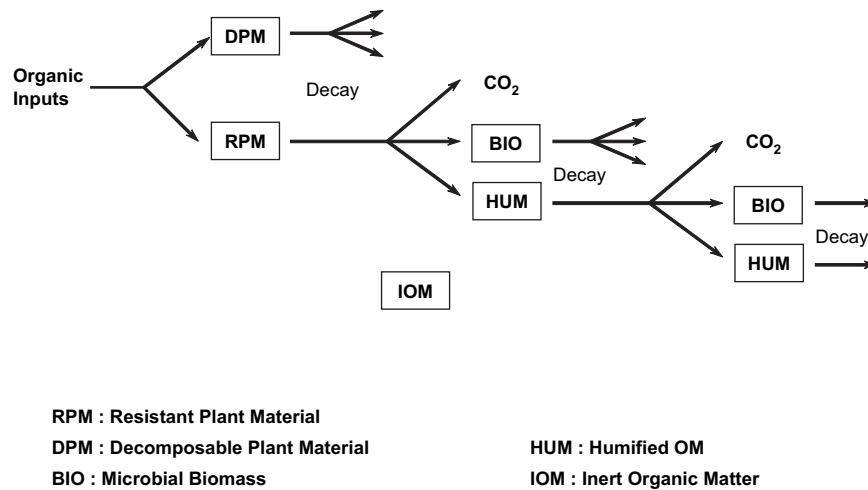
RothC is a model for the turnover of SOM and was developed to simulate changes in SOC stocks in arable topsoils from the

Rothamsted Long-term Field Experiments in the UK. It was then extended to model SOM turnover in grassland and woodland soils in different climatic regions worldwide (Smith *et al.*, 1997; Coleman & Jenkinson, 1999;). The model can be used in two modes: (i) forward mode to simulate SOM under changed agricultural management and input of plant materials; and (ii) inverse mode to calculate required plant inputs to reach the measured SOC content for equilibrium conditions with known land-use history.

In this model, SOM is partitioned into five pools (Figure 2). IOM is defined as inert organic matter with a nominal radiocarbon age of 50 000 years. Incoming plant material is separated into decomposable (DPM) and resistant (RPM) plant material with an empirically validated DPM:RPM ratio of 1.44 for arable and grassland soils. The plant material decomposes to form CO<sub>2</sub>, biomass (BIO) and humified organic matter (HUM), depending on clay content, and BIO and HUM are further decomposed to form more CO<sub>2</sub>, BIO and HUM. All pools except IOM decompose by first-order decay at rates (year<sup>-1</sup>) of 10 for DPM, 0.3 for RPM, 0.66 for BIO and 0.02 for HUM. Decomposition rates are modified by temperature, moisture and the degree of soil cover.

We used the model to calculate the partitioning of SOC into pools. For this purpose, we assumed that the sites are in equilibrium with respect to SOC, given that management had remained constant for at least the previous 30 years. We calculated the annual return of carbon to soil from known total carbon content, clay content, climatic conditions (monthly rainfall, temperature and evaporation) and land use. The model approximated

### Structure of the Rothamsted Carbon Model



**Figure 2** SOC pools as defined by RothC (after Coleman & Jenkinson, 1999).

IOM with the equation proposed by Falloon *et al.* (1998). With the estimated plant inputs required to match the present SOC content, the model also partitions the SOC into pools that arise at equilibrium (nominally after 10 000 years). We assumed a bulk soil density of  $1.48 \text{ t m}^{-3}$  for all sites, for RothC, as well as for the different fractions, which is a typical value for mineral soils in Switzerland (Desaules & Studer, 1993). Measured carbon contents of the fractions were converted to  $\text{t C ha}^{-1}$ , which is the same unit as output by RothC.

#### Conceptual pooling of measured fractions

To quantify fractions, comparable with RothC pools, measured fractions were conceptually summarized and split as shown in Figure 3. Plant material in RothC is subdivided into DPM and RPM, whereas plant debris in soils is found in the POM fraction and in mostly decomposed form as DOC. We combined the SOC in POM and DOC and compared these values with the SOC values of the DPM and RPM pools for each individual site. Stabilized SOM in RothC is referred to as HUM and is decomposed by the microbial biomass. These two pools can be found in the measured  $s + c$  and  $S + A$  fractions, which are physically protected against fast decomposition. Again, we combined the  $S + A$  and the  $s + c$  fractions without the  $r\text{SOC}$  fraction, and we compared these SOC values with those of both the HUM and BIO pools, assuming that most of BIO is in the fraction  $< 63 \mu\text{m}$ . The  $r\text{SOC}$  fraction, as part of  $s + c$ , is not further decomposed by microbes and corresponds directly to the IOM pool. The sum of SOC in POM and DOC can then be split according to the ratio of the DPM and RPM pools obtained by RothC for equilibrium conditions. This ratio refers to the pool sizes after 10 000 years and not to the separating ratio of the incoming plant materials. The same procedure is used to

separate the  $s + c$  and  $S + A$  fractions into BIO and HUM pools. Fractions combined and split by this procedure are later referred to as 'quantified' fractions.

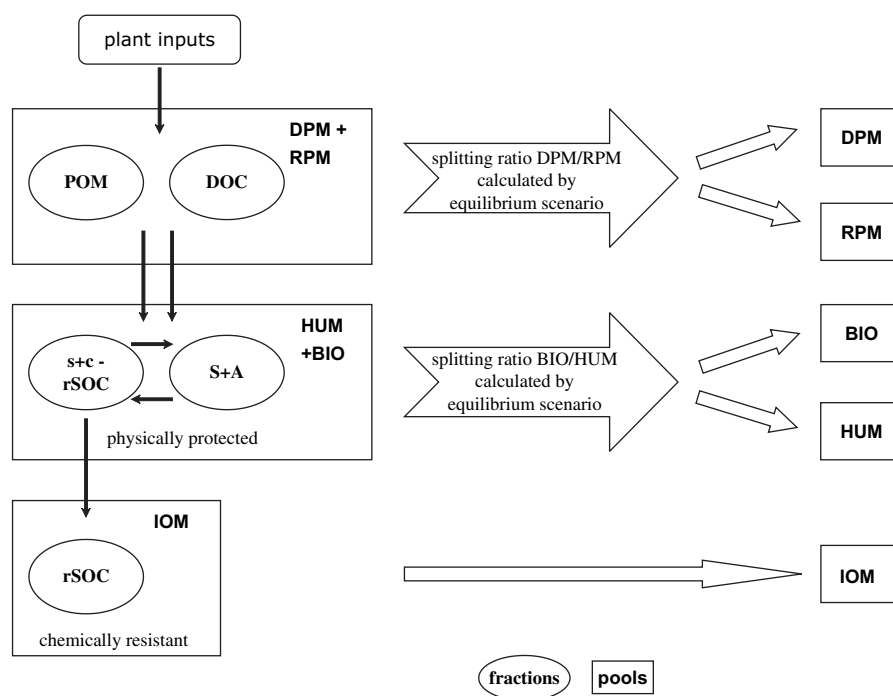
#### Statistical analysis

Data for SOC in the modelled pools and quantified fractions were tested for normality using Shapiro-Wilk's  $W$ -test with a critical level of  $P < 0.05$  in order to select the appropriate statistical methods to determine outliers, correlations and significant differences. Sites were distinguished between arable, grassland and alpine pasture and tested for outliers by Grubb's test for normally distributed groups. When groups were not normally distributed, values outside a range of  $\pm 2$  standard deviations from the median were rejected. Correlations between quantified and modelled values in non-normally distributed groups were determined by Spearman's rank order,  $R$ . The Kolmogorov-Smirnov test was used to test whether differences between non-normally distributed means of modelled pools and quantified fractions were significant. Correlations between dependent variables were expressed as linear regressions with coefficients of determination ( $R^2$ ).

### Results

#### Test for normality and outliers

The Shapiro-Wilk's  $W$ -test revealed that only the data for the  $r\text{SOC}$  fraction and RPM pool were normally distributed. Therefore, correlations and comparisons of modelled pools and quantified fractions in all further analyses were based on non-parametric methods. Based on an outliers test, data from 12 sites had to be excluded from the following analysis.



**Figure 3** Concept of summarizing and splitting SOC fractions and pools.

#### Partitioning of SOC into fractions

The partitioning of total SOC into different measured fractions is shown in the top part of Figure 4. The major part of SOC was in the s + c and S + A fractions. Together, these two fractions contained about 75% of total SOC. Soil samples containing little SOC in S + A had more SOC in s + c, and *vice versa*. POM and rSOC contributed about 10% and DOC about 4% to total SOC.

#### Partitioning of SOC into RothC pools

The box plots at the bottom of Figure 4 depict the distribution of SOC among the pools modelled with RothC. Under equilibrium conditions, the largest part of SOC appeared in HUM pools. RPM pools contained about 14% and IOM pools about 9% of total SOC. Smallest pools were DPM and BIO, each with about 2% of total SOC.

To make comparisons with modelled pools, SOC contents in the measured fractions were summarized and split as explained above. An overview of the splitting ratios of DPM to RPM pools and BIO to HUM pools is given in Table 1. According to land use, the ratios were grouped in temperate grassland, arable land and alpine pastures. Ratios of DPM to RPM pools were greatest for sites with temperate grassland and smallest for sites with arable land, whereas ratios for BIO to HUM pools varied little among sites.

We looked for the main parameters controlling the DPM to RPM pool ratios and calculated multiple regression models for

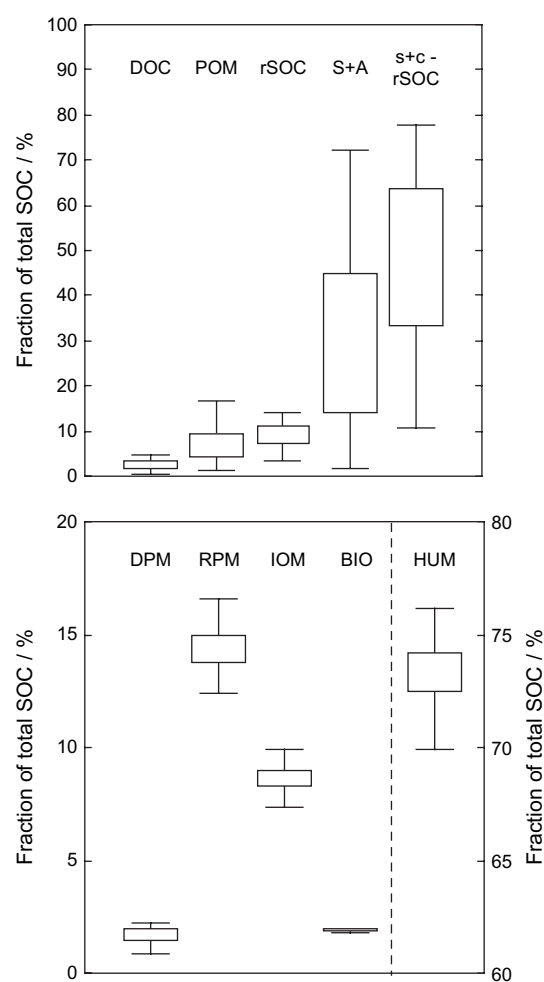
prediction. Parameters tested were mean annual temperature (MAT), mean annual precipitation, mean annual evaporation, moisture surplus and clay content. The only significant parameter was MAT, and so we calculated linear regressions between DPM to RPM pool ratios and temperature for all sites (Table 2). Coefficients of determination ( $R^2$ ) are about 0.77.

#### Correlation of measured with modelled data

Results of Spearman's rank order,  $R$ , correlations are given in Table 3. Data are presented for all sites and separately for different land uses.  $R$  values above 0.8 indicated a strong correlation, those between 0.5 and 0.8 a modest correlation, and  $R$  values smaller than 0.5 only a weak correlation (Fahrmeir *et al.*, 2004). Strongest correlations were obtained for BIO and HUM with an  $R$  of 0.99, but most other correlations were modest to strong, except for RPM in the case of alpine pasture sites ( $P > 0.05$ ,  $R = 0.57$ ). Scatter plots revealed the strong relationships between modelled and measured data for different SOC pools (Figure 5).

#### Comparison of modelled pools and quantified fractions

Table 3 summarizes the main parameters of the Kolmogorov-Smirnov tests. For BIO, HUM and IOM, modelled and quantified fractions could not be distinguished as being from separate populations. This finding applied to all three types of land use. No parameters are given for RPM of alpine pasture sites as the



**Figure 4** Box plots for the partitioning of total SOC into measured fractions (top) and RothC modelled pools (bottom). Note the different scale for modelled HUM pools.

correlation between measurement and model output was not significant. Conversely, quantified fractions and modelled pools of DPM for alpine pasture sites were not different, but differences between means for DPM and RPM in soils from temperate grassland and arable sites were significant. Modelled values of DPM and RPM were slightly larger than quantified ones.

## Discussion

### Comparison of fractions and pools

Process-based soil carbon models such as RothC are important tools for projecting likely changes in soil carbon over long time periods, and for studying historic and future changes in SOC under variable climatic and management conditions (e.g. Smith *et al.*, 2005). Typically, these models separate SOC into pools characterized by different turnover times. When these model pools were conceived, they were conceptual in nature and

**Table 1** Splitting ratios for DPM to RPM pools and BIO to HUM pools under equilibrium conditions

	Minimum <sup>a</sup>	Maximum <sup>b</sup>	Mean	SD <sup>c</sup>	n
Ratios of DPM pools to RPM pools					
All sites	0.0075	0.1419	0.1119	0.0382	111
Temperate grassland	0.0946	0.1419	0.1271	0.0108	92
Arable	0.0075	0.0107	0.0102	0.0015	11
Alpine pasture	0.0682	0.1027	0.0967	0.0410	8
Ratios of BIO pools to HUM pools					
All sites	0.0258	0.0274	0.0260	0.0004	111
Temperate grassland	0.0258	0.0260	0.0259	0.0001	92
Arable	0.0271	0.0274	0.0272	0.0007	11
Alpine pasture	0.0259	0.0271	0.0261	0.0005	8

<sup>a</sup>Minimal value.

<sup>b</sup>Maximal value.

<sup>c</sup>Standard deviation.

could not be directly related to measurable fractions. The results of this study demonstrate that it is possible to identify SOC fractions, which are quantitatively related to SOC pools used in RothC. The size of the different fractions obtained here is strongly correlated with the modelled pools. Thus, as modelled pools and quantified fractions of BIO, HUM and IOM are from the same populations, model and laboratory fractionation separate SOC into equal parts with respect to turnover times. Strong correlation coefficients demonstrate the same partitioning of SOC for quantified fractions and modelled pools under the various site-specific conditions. RothC requires only few input parameters to partition total SOC into its five model pools, including temperature, ratio of decomposable to resistant incoming plant material, soil moisture deficit, and agricultural land use. In contrast, partitioning into physical and chemical fractions depends on site-specific conditions. These results have implications both for models and for measurement as follows: (i) the proposed fractionation procedure is suitable to measure pools as modelled with RothC; and (ii) RothC predicts the partitioning of SOC into pools well, as confirmed by the measurements. If the aim is to find a fractionation procedure, which yields fractions as similar as possible to RothC pools, then the proposed method can be used with minimal adaptation. The values for DPM and RPM are

**Table 2** Linear regression models to predict DPM to RPM pool ratios dependent on mean annual temperatures (MAT) for different management sites

Site	Equation	R <sup>2</sup>	n	Mean	SE <sup>a</sup>
Temperate grassland	$y = 0.048 + 0.011 \times \text{MAT}$	0.77	92	0.1271	0.0108
Arable	$y = 0.035 - 0.003 \times \text{MAT}$	0.78	11	0.0102	0.0015
Alpine pasture	$y = 0.068 + 0.007 \times \text{MAT}$	0.76	8	0.0875	0.0108

<sup>a</sup>Standard error.

**Table 3** Spearman's rank order correlations, R, and statistical parameters of Kolmogorov-Smirnov analysis of modelled and quantified pools

		Kolmogorov-Smirnov test				<i>n</i>	<i>P</i> -level	
		Spearman's R	Mean mod. <sup>a</sup>	Mean quant. <sup>b</sup>	Std. dev. mod. <sup>c</sup>			Std. dev. quant. <sup>d</sup>
			/t C ha <sup>-1</sup>					
All sites								
DPM	0.82	1.05	0.67	0.54	0.41	111	< 0.001	
RPM	0.76	9.22	5.93	3.56	2.86	111	< 0.001	
BIO	0.99	1.23	1.32	0.49	0.55	111	> 0.1	
HUM	0.99	47.22	50.72	18.79	21.43	111	> 0.1	
IOM	0.73	5.71	5.79	2.58	2.27	111	> 0.1	
Temperate grassland								
DPM	0.74	1.2	0.77	0.43	0.36	92	< 0.001	
RPM	0.78	9.51	6.14	3.47	2.96	92	< 0.001	
BIO	0.99	1.24	1.34	0.47	0.53	92	> 0.1	
HUM	0.99	48.03	51.62	18.14	20.36	92	> 0.1	
IOM	0.70	5.84	5.95	2.48	2.24	92	> 0.1	
Arable								
DPM	0.68	0.08	0.05	0.03	0.02	11	< 0.001	
RPM	0.77	7.48	5.02	2.51	1.79	11	< 0.025	
BIO	0.99	1.09	1.14	0.41	0.44	11	> 0.1	
HUM	0.99	40.14	41.71	15.12	16.36	11	> 0.1	
IOM	0.65	4.64	5.62	1.89	2.35	11	> 0.1	
Alpine pasture								
DPM	0.76	0.64	0.37	0.51	0.26	8	> 0.1	
RPM	0.57	ND <sup>e</sup>	ND <sup>e</sup>	ND <sup>e</sup>	ND <sup>e</sup>	8	ND <sup>e</sup>	
BIO	0.93	1.24	1.38	0.76	0.94	8	> 0.1	
HUM	0.93	47.62	52.84	29.32	36.13	8	> 0.1	
IOM	0.76	5.65	4.11	4.14	2.16	8	> 0.1	

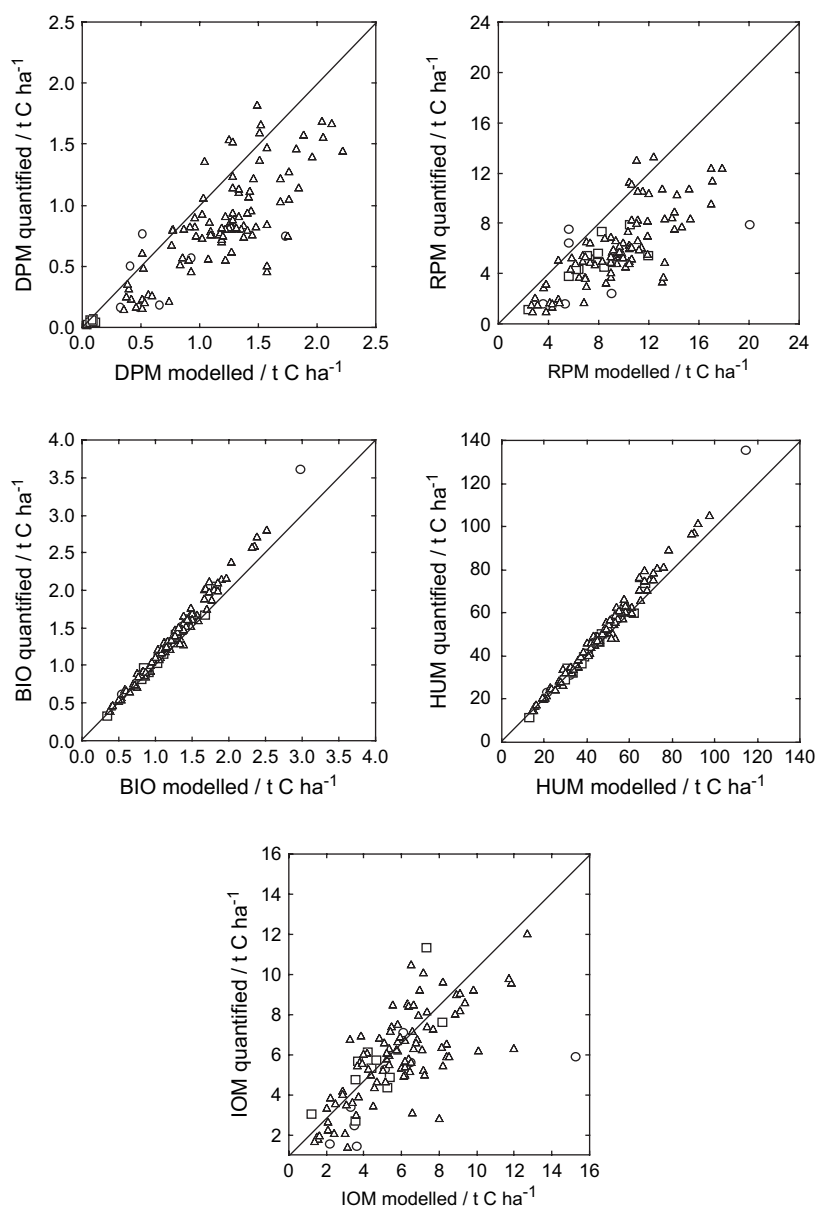
<sup>a</sup>Modelled mean.<sup>b</sup>Quantified mean.<sup>c</sup>Standard deviation of modelled mean.<sup>d</sup>Standard deviation of quantified mean.<sup>e</sup>Not determined.

slightly larger in the model than obtained by measurements. Changing the density of sodium polytungstate to 2.0–2.2 g cm<sup>-3</sup> can increase the amount of OC in the POM fraction. Simultaneously, this will result in smaller amounts of SOC in S + A and s + c fractions. This reduction would not lead to a significant change as these two pools account for the major part of SOC.

The correlations between modelled pools and quantified fractions for alpine pasture sites are less satisfying. Modelled pool sizes of DPM and RPM differed substantially from the measured amounts of accumulated plant debris. One possible explanation is the low MAT of about 1.6°C. Plant decomposition decreases at low temperatures, and RothC was not developed to simulate SOC turnover under these cold climatic conditions. This disagreement could also be due to the difference in the amount of plant inputs under low MAT as compared with more temperate conditions, and also the ratio of DPM to RPM in the incoming plant material, which could differ from the empirical value of 1.44.

#### Summarizing and splitting of measured fractions

Ratios of BIO to HUM pools under equilibrium conditions are relatively constant (Table 1). Thus, the means of these empirical values for temperate grassland, arable and alpine pasture could be extrapolated to sites with unknown land-use history. However, DPM to RPM pool ratios are not constant, but vary within sites. As no topsoil moisture deficit was observed at any site, ratios of DPM to RPM pools appear to be controlled primarily by temperature. The strong coefficients of determination allow reasonable predictions of ratios for DPM to RPM pools. This leads to the conclusion that splitting ratios for all fractions can be determined independently of RothC by using these empirical linear equations. On the other hand, the amount of DPM may vary considerably during the year, as the decay rate of DPM is 10 year<sup>-1</sup>. Also, the amount of POM and DOC in soils may depend on what time during the year the soil samples were collected. This is not taken into account by the modelled equilibrium conditions but is reflected in the soil samples.



**Figure 5** Scatter plots of modelled vs. measured SOC values for the different pools in soils from temperate grassland ( $\Delta$ ), arable ( $\square$ ) and alpine pasture ( $\circ$ ) sites. The solid line is the 1:1 line.

Nonetheless, we can predict the DPM to RPM pool ratios as all the soil samples were taken in spring. When we use the predicted ratios of DPM to RPM pools to split the summarized POM and DOC fractions and then compare the quantified fractions with the modelled pools, Spearman's rank correlations are 0.83 for DPM and 0.76 for RPM when using data from all sites. Differences in means are significant for both groups, as revealed by Kolmogorov-Smirnov tests, whereas modelled pools are slightly larger than quantified fractions, similar to the splitting ratios obtained from RothC. We used constant BIO to HUM pool ratios (0.0259 for temperate grassland, 0.0272 for arable and 0.0261 for alpine sites) and

found strong correlations ( $R = 0.99$ ) between quantified fractions and modelled pools with no significant differences between these groups. It can thus be concluded that for any site with climatic conditions similar to those prevailing in Switzerland, SOC can be separated and converted into fractions that correspond to pools used in RothC, independent of any values taken from RothC model runs.

#### *Estimating the inert organic matter pool*

The amount of IOM in RothC can be calculated either by radiocarbon data or by estimating the size of this pool with



the empirical equation proposed by Falloon *et al.* (1998). This equation is often used to avoid the large costs of radiocarbon dating. Falloon *et al.* (1998) used data from several studies in which radiocarbon data were measured in chemically resistant soil fractions. These fractions were obtained by removing plant residues from the bulk soil samples, followed by treatment with hydrochloric acid. Here, we measured IOM in the s + c fraction by NaOCl oxidation. This fraction is free of plant residues, POM and aggregates. NaOCl oxidation at room temperature does not affect inorganic soil constituents (Siregar *et al.*, 2004) and is not expected to produce stable, melanoidin-like artefacts, such as happens with hot acid hydrolysis (Allard *et al.*, 1998). Although these two methods determine the amount of IOM by completely different approaches, both methods resulted in the same pool sizes.

#### Initializing RothC with measured values

To initialize RothC for modelling long-term changes in SOC contents and turnover, the partitioning of SOC into the different model pools is necessary. In the model, this partitioning can be achieved by backward calculation of the necessary plant inputs for 10 000 years, while assuming that climatic conditions and agricultural management are constant during that period. Compared with these highly unlikely assumptions, the use of measured fractions to initialize RothC has the advantage that processes that are ignored in the model, but which influence SOC, are taken into account in SOC partitioning. Thus, measured fractions reflect better than any model the conditions under which SOC is accumulated. Moreover, measured fractions are determined independently of the model. The fractionation procedure presented here, with the adaptation in the density separation, can be used to initialize RothC at any point in the landscape, even with a lack of historical data, and for sites with comparable climatic conditions, splitting ratios for DPM to RPM pools and BIO to HUM pools can be adopted.

#### Acknowledgements

This study was supported by the Swiss Agency for the Environment, Forests and Landscape, and by a grant for a short visit to the University of Aberdeen from the European Science Foundation programme 'The role of soils in the terrestrial carbon cycle'. We would like to thank the Swiss National Soil Survey (NABO) and H.-R. Oberholzer for providing soil samples, and the staff of the Plant and Soil Science Section at the University of Aberdeen for help with RothC. The study contributes to the COST Action 627.

#### References

Allard, B., Templier, J. & Largeau, C. 1998. An improved method for the isolation of artifact-free algaenans from microalgae. *Organic Geochemistry*, **28**, 543–548.

Amelung, W. & Zech, W. 1999. Minimisation of organic matter disruption during particle-size fractionation of grassland epipedons. *Geoderma*, **92**, 73–85.

Baldock, J.A. & Skjemstad, J.O. 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. *Organic Geochemistry*, **31**, 697–710.

Buholzer, S. & Jeanneret, P. 2005. Evaluation der Oekomassnahmen – Bereich Biodiversität. *Schriftenreihe der FAL*, **56**, in press.

Christensen, B.T. 1996. Matching measurable soil organic matter fractions with conceptual pools in simulation models of carbon turnover. In: *Evaluation of Soil Organic Matter Models Using Long-Term Datasets* (eds D.S. Powlson, P. Smith & J.U. Smith), pp. 143–159. NATO ASI Series 1: Global Environmental Change, 38. Springer-Verlag, Heidelberg.

Coleman, K. & Jenkinson, D. 1999. *RothC-26.3. A Model for the Turnover of Carbon in Soils. Model Description and Windows Users Guide*. IACR – Rothamsted, Harpenden.

Desaules, A. & Studer, K. 1993. *Nationales Bodenbeobachtungsnetz Messresultate 1985–91*. Schriftenreihe für Umwelt, 200. Bundesamt für Umwelt, Wald und Landschaft, Bern.

Elliott, E.T. & Paustian, T.K. 1996. Modelling the measurable or measuring the modelable: a hierarchical approach to isolating meaningful soil organic matter fractionations. In: *Evaluation of Soil Organic Matter Models Using Long-Term Datasets* (eds D.S. Powlson, P. Smith & J.U. Smith), pp. 161–179. NATO ASI Series 1: Global Environmental Change, 38. Springer-Verlag, Heidelberg.

Eusterhues, K., Rumpel, C., Kleber, M. & Koegel-Knabner, I. 2003. Stabilisation of soil organic matter by interactions with minerals as revealed by mineral dissolution and oxidative degradation. *Organic Geochemistry*, **34**, 1591–1600.

Fahrmeir, L., Künstler, R., Pigeot, I. & Tutz, G. 2004. *Statistik – der Weg Zur Datenanalyse*. Springer Verlag, Berlin.

Falloon, P., Smith, P., Coleman, K. & Marshall, S. 1998. Estimating the size of the inert organic matter pool from total soil organic carbon content for use in the Rothamsted carbon model. *Soil Biology and Biochemistry*, **30**, 1207–1211.

IPCC 2001. *Climate Change 2001. The Scientific Basis* (eds J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden & D. Xiaosu). Cambridge University Press, Cambridge. URL: <http://www.ipcc.ch>

Janssens, I.A., Freibauer, A., Ciais, P., Smith, P., Nabuurs, G.-J., Folberth, G. *et al.* 2003. Europe's terrestrial biosphere absorbs 7–12% of European anthropogenic CO<sub>2</sub> emissions. *Science*, **300**, 1538–1542.

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.

Kaiser, K. & Guggenberger, G. 2003. Mineral surfaces and soil organic matter. *European Journal of Soil Science*, **54**, 219–236.

Krull, E.S., Baldock, J.A. & Skjemstad, J.O. 2003. Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover. *Functional Plant Biology*, **30**, 207–222.

Siregar, A., Kleber, M., Mikutta, R. & Jahn, R. 2004. Sodium hypochlorite oxidation reduces soil organic matter concentrations without affecting inorganic soil constituents. *European Journal of Soil Science*, **56**, 481–490.

Six, J., Merckx, R., Kimpe, K., Paustian, K. & Elliott, E.T. 2000. A re-evaluation of the enriched labile soil organic matter fraction. *European Journal of Soil Science*, **51**, 283–293.

- Skjemstad, J.O., Spouncer, L.R., Cowie, B. & Swift, R.S. 2004. Calibration of the Rothamsted Organic Carbon Turnover Model (Rothc, Version 26.3), using measurable soil organic carbon pools. *Australian Journal of Soil Research*, **42**, 79–88.
- Smith, J.U., Smith, P., Monaghan, R. & Macdonald, R.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, J.U., Smith, P., Wattenbach, M., Zaehle, S., Hinderer, R., Jones, R.J.A. *et al.* 2005. Projected changes in mineral soil carbon of European croplands and grasslands, 1990–2080. *Global Change Biology*, **11**, 2141–2152.
- Sohi, S.P., Mahieu, N., Arah, J.R.M., Powlson, D.S., Madari, B. & Gaunt, J.L. 2001. A procedure for isolating soil organic matter fractions suitable for modeling. *Soil Science Society of America Journal*, **65**, 1121–1128.