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**„Characterization of soil carbon stocks and site-specific sequestration potentials of agricultural soils’
Extended summary**

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Research Project

„Characterization of soil carbon stocks and site-specific sequestration potentials of agricultural soils“

(Charakterisierung der Kohlenstoffpools in landwirtschaftlichen Böden und Beurteilung des standortspezifischen Sequestrierungspotenzials)

Final Report

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Appendix: Spectroscopic quantification of soil organic carbon fractions that can be related to model pools. PhD-thesis Michael Zimmermann, 2006.

Summary

Reporting of changes in agricultural soil carbon stocks is an important element under the UNFCCC. Currently, Switzerland uses a Tier 1-2 approach with country-specific data for soil carbon stocks and corresponding rates of carbon losses and gains upon land conversion (NIR 2006). These estimates are based on a wide data base (Leifeld et al. 2003), but site-specific conditions and situations of non-equilibrium are not accounted for though both are known to affect the possible rate of change significantly. In this study, we aimed to develop a prognostic tool based on sophisticated measurements of bulk soil organic carbon and carbon in fractions representing different turnover times and thus different sensitivities to management or land-use. A further goal was the development of a fast method to quantify carbon in these fractions in order to avoid time-consuming sample preparations.

With the present report, we aimed to improve the methodological framework by using a novel combination of soil analysis and modelling that can be applied to many situations in agricultural soils of various soil textures. The approach is adjusted to Swiss conditions and allows for simulating soil carbon dynamics of mineral soils for:

- Land-use changes from arable rotation to grassland and vice versa
- Varying shares of leys in arable rotations
- Varying levels of organic fertilizers in arable or grassland systems

This goal was achieved by developing and combining a set of new tools that can be applied for the independent validation of current estimates for stock changes under several conditions:

- A fractionation procedure isolating soil carbon constituents that can be quantitatively related to a well-established soil organic carbon simulation model (RothC) in a way that the model run can be initialized without the assumption of a steady-state, i.e., for sites in transition from high to low carbon stocks or vice versa, and whose management or land-use history is unknown
- An infrared-based spectroscopic approach for the rapid quantification of carbon bound in differently stabilized soil fractions of various turnover times. This method is reliable to replace the time-consuming fractionation procedure that was necessary for its calibration
- A method that allows a relatively rapid screening of so-called black carbon as part of the very stable organic matter

- New insights into the contribution of labile, intermediate and resistant soil organic carbon for typical land-uses and management types across Switzerland

The analysis also provided country-specific data for C/N ratios of mineral soils for arable and grassland sites.

Insufficient performance of the above approach was observed for alpine soils higher than 1200 m elevation. The specific characteristics of alpine grassland systems need further evaluation before a model implementation will be feasible.

Not included in this approach are no-tillage practices and organic soils. The Swiss data base for no-till was deemed of being too small to be converted into a modelling approach, and results from other regions are partially contradictory with many studies showing no or depleting effects of no-till on SOC. Modelling the dynamic of organic soils is still at its beginning, and future Swiss efforts should above all concentrate on providing reliable emissions rates estimated from soil profiles and flux measurements.

The report provides an extended summary and an appendix consisting of the PhD-thesis of Michael Zimmermann with the manuscripts of the corresponding publications.

1 Aims and scope

The sensitivity of soil organic matter (SOM) storage to climatic or land-use change is still a matter of great debate. Globally, soils contain about twice the amount of carbon present in the atmosphere (Prentice, 2001). Most of it is in organic form and has turnover times ranging from months to millennia, with much of it around several years to a few decades (Trumbore et al. 1996). Under rising temperatures or shifts in land-use patterns, this large pool is likely to change and interact with climate change. The terrestrial biosphere is considered a strong CO₂ sink (Houghton 2003) and is projected to remain a net CO₂ absorber also during the next decades (King et al. 2006). However, the terrestrial sink is mainly attributed to assimilation by boreal vegetation (e.g. Schulze 2006), whereas land-use changes contribute by $1.6 \pm 0.8 \text{ Gt C a}^{-1}$ to the global carbon emission (Schimel et al. 2001). Based on the difference between pre-cultivated and current SOC stocks in cultivated soils, Paustian et al. (1997) estimated a global loss of 40-60 Gt C due to cultivation, from which the major part (approximately 80%) stems from aerated mineral soils and the remainder (approximately 11 Gt) from the drainage of “wetland soils” that is, Histosols and Gleysols. While the SOC loss estimated so far only accounts for a small fraction of the global SOC stock (2.5 to 6 percent), it contributes to one third of the estimated C loss of $156 \pm 55 \text{ Gt C}$ induced by land-use change since 1850 (Houghton 2003).

In view of the needs for reporting of soil carbon stock changes under the UNFCCC, the Air Pollution/Climate Group of ART was invited by the Federal Office for Environment (FOEN) to compile, evaluate and interpret data on carbon stocks in agricultural soils of Switzerland. Based on this project, a report (Leifeld et al. 2003) and a corresponding paper (Leifeld et al. 2005) has been published, where the estimate on carbon stocks of agricultural soils and their environmental drivers was discussed. This study relied on data on soil carbon stocks under different land-use types compiled from various soil surveys, and the corresponding stock estimates are currently used for the Swiss LULUCF reporting under UNFCCC (e.g., NIR 2006). The data in Leifeld et al. (2003) provide country-specific data on soil carbon stocks for arable land, temporary grassland (i.e., leys), and temperate and alpine permanent grasslands as well as an estimate of carbon stocks in organic soils. LULUCF-induced CO₂ fluxes in the agricultural sector are currently calculated by taking the absolute difference between two land-use types and dividing the stock difference by the number of years between two land-use inventories (currently 12). While this approach is in accordance to the GPG LULUCF (IPCC 2003), two drawbacks can be identified:

Firstly, the current approach is static in a way that the measured carbon stocks for particular land-use types are considered being at steady-state, i.e., it is assumed that stock changes occur within the range given in Leifeld et al. (2003) and that the upper and lower limits of this range represent the end-member of possible transitional states. Because the carbon stocks for the different agricultural land-use and management types are mean values of samples drawn from a population where steady-state condi-

tions cannot be ascertained, this approach is potentially biased. Table 1 shows the current carbon stocks and their uncertainty for mineral soils in Switzerland with mean soil clay content (soil texture has been shown to be a major driver for carbon stocks in the temperate zone in Leifeld et al. [2003]) and an elevation below 600 m a.s.l. These values correspond to the stocks in the Swiss Greenhouse Gas Inventory. For the given clay content, the difference between mean stocks under permanent grassland and arable land in the temperate region of the Swiss Central Plateau is 8.6 tonnes carbon per hectare, but can be as small as 1.5 tonnes or as large as 16.3 tonnes when the upper and lower confidence limit of the distribution is taken, respectively. This comparison illustrates that the uncertainty is almost as high as the mean difference between arable and grassland stocks. The uncertainty derives from unknown, site-specific factors such as local climate, residue input into the soil, soil tillage or soil rotation that are not explicitly considered yet. Thus, a site-specific tool for the calculation of potential gains and losses under different land-use and management is needed.

Table 1. Carbon stocks (t C ha⁻¹ 0-30 cm) for arable and permanent grassland fields in Switzerland for a site below 600 m elevation with 24% clay (based on Leifeld et al., 2003).

	Mean stock	Upper limit ¹	Lower limit ¹
Arable	53.4	58.0	48.7
Grassland	62.0	74.6	48.2
Stock difference	8.6	8.6 (+7.7)	8.6 (-7.1)

¹ calculated by error propagation. Upper and lower confidence limits are different.

Secondly, there has been no independent validation yet of the method currently used under the LULUCLF-reporting. One possible way of validation is the use of simulation models. Dynamic soil organic matter turnover models are tools to simulate change in carbon stocks along with management or land-use changes (Smith et al. 1997), but need to be properly validated and adjusted to the site-specific conditions in order to be reliable. Many of these models are pool-based, i.e. they use discrete soil organic matter pools with specific decomposition rates that are modified by environmental variables such as temperature, moisture, or texture. Application of models often requires spinning-up runs to equilibrium conditions before effects of management or land-use change can be simulated. This equilibrium simulation is speculative in a way that former climatic or land-use histories are highly uncertain. Because changes in soil carbon stocks occur most rapidly in the so-called labile soil organic matter pools, a model-based approach with validation at the pool-level is desirable, because measured

pools rather than results from equilibrium runs could be used as starting conditions for any given site.

With the present project, we aimed to improve the methodological framework by using a novel combination of soil analysis and modelling that can be applied to many situations in agricultural soils. The approach is adjusted to Swiss conditions and allows for simulating soil carbon dynamics of mineral soils of various soil textures for:

- Land-use changes from arable rotation to grassland and vice versa
- Varying shares of leys in arable rotations
- Varying levels of organic fertilizers in arable or grassland systems

Not included in this approach are no-tillage practices and organic soils, and insufficient performance was observed for alpine soils above 1000 m elevation. The specific characteristics of alpine grassland systems need further evaluation before a model implementation will be feasible.

2 Carbon fractions of different turnover time in agricultural soils

2.1 Methodological approach

In a first phase of the project soil organic matter (SOM) fractions that respond to land-use and can be used as a proxy for the distribution of OM among model pools were defined and quantified. Based on the vast amount of literature on soil fractionation methods (e.g., Christensen 1996; Paul et al. 1997; Six et al. 2002; Leifeld & Kögel-Knabner 2005), we combined several techniques. The primary goal of such fractionation is to isolate SOM compounds of different turnover time that correspond to different stabilization 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 accessibility. 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 particulate organic matter (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 microaggregates or silt and clay particles. Eusterhues et al. (2003) found that soil organic carbon (SOC) resistant to oxidation is made up of very refractory and slowly cycling carbon with lower ^{14}C activities than total SOC. We extracted a non-oxidizable SOM fraction from the silt and clay fractions to isolate an old and stable SOC fraction.

The soil fractionation comprised isolation of five different fractions separated by physical-chemical procedures (Fig. 1 ovals; described in more detail in Zimmermann et al. 2007). This approach was applied to a range of agricultural soils across Switzerland including arable sites, temperate and alpine permanent grasslands.

2.2 Material

A) 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 +0.6 to -1.6°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 by 10 m, between 1985 and 1991. Soil samples from arable sites were taken as 0–20 cm cores.

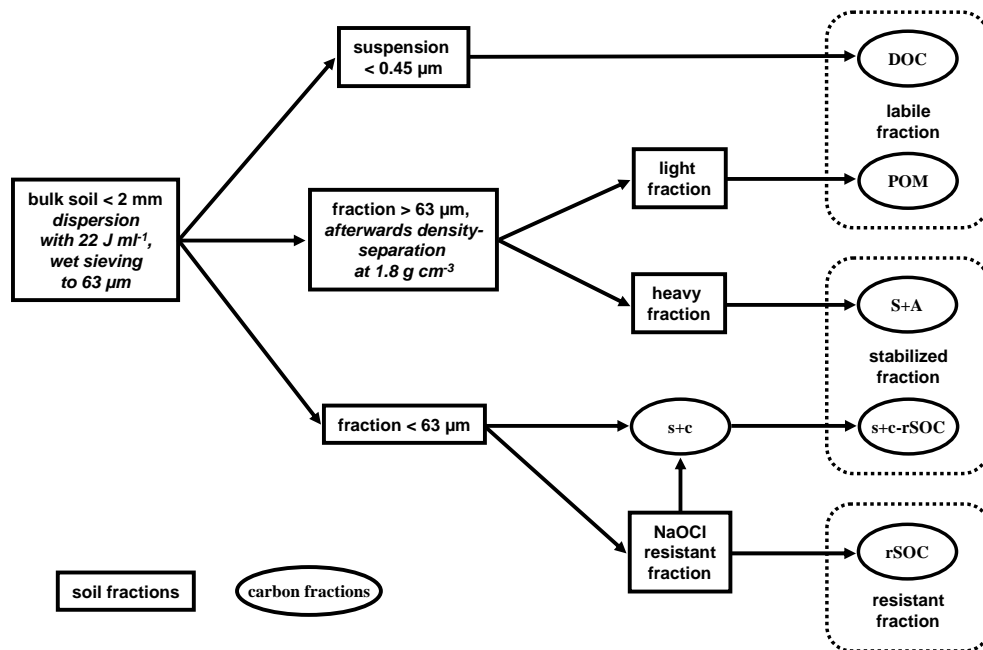


Fig. 1. Fractionation of soil samples according to Zimmermann et al. (2007). DOC dissolved organic carbon, POM particulate organic matter, S+A sand plus micro-aggregates, s+c silt plus clay fraction, rSOC oxidation-resistant fraction of s+c.

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 Desaules & Studer (1993). B) 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 et al. (2005). Each sample was a composite of 20 soil cores taken from the top 20 cm. All soil samples were carbonate-free with SOC contents of less than 8.7% (mineral soils).

2.3 Results

The distribution of the resulting fractions (Fig. 1) among arable sites, temperate grassland, and alpine grassland differed for some of the fractions (Fig. 2). Most of the SOC was stored in microaggregates and in the silt+clay fraction, while smaller amounts

were found in the labile fractions (POM and dissolved organic carbon [DOC]) and in the very stable fraction (oxidation-resistant carbon). Most pronounced differences between land-use types were found in the sand+microaggregate fraction (#5) accounting for 13% of the carbon in arable soils but for 55% in alpine pastures, and the silt+clay fraction (#6; 30% in arable soils opposed by 51% in temperate grasslands). The distribution of SOC among fractions reflects the importance of the different stabilization mechanisms responsible for SOM storage. It shows the SOC-fractions of POM and microaggregation to increase in the order arable land < temperate grassland < alpine grassland. In contrast, the relatively higher share of silt+clay-associated organic matter in arable soils results from the continuous disruption of aggregates due to soil tillage and the subsequent respiration of the released POM.

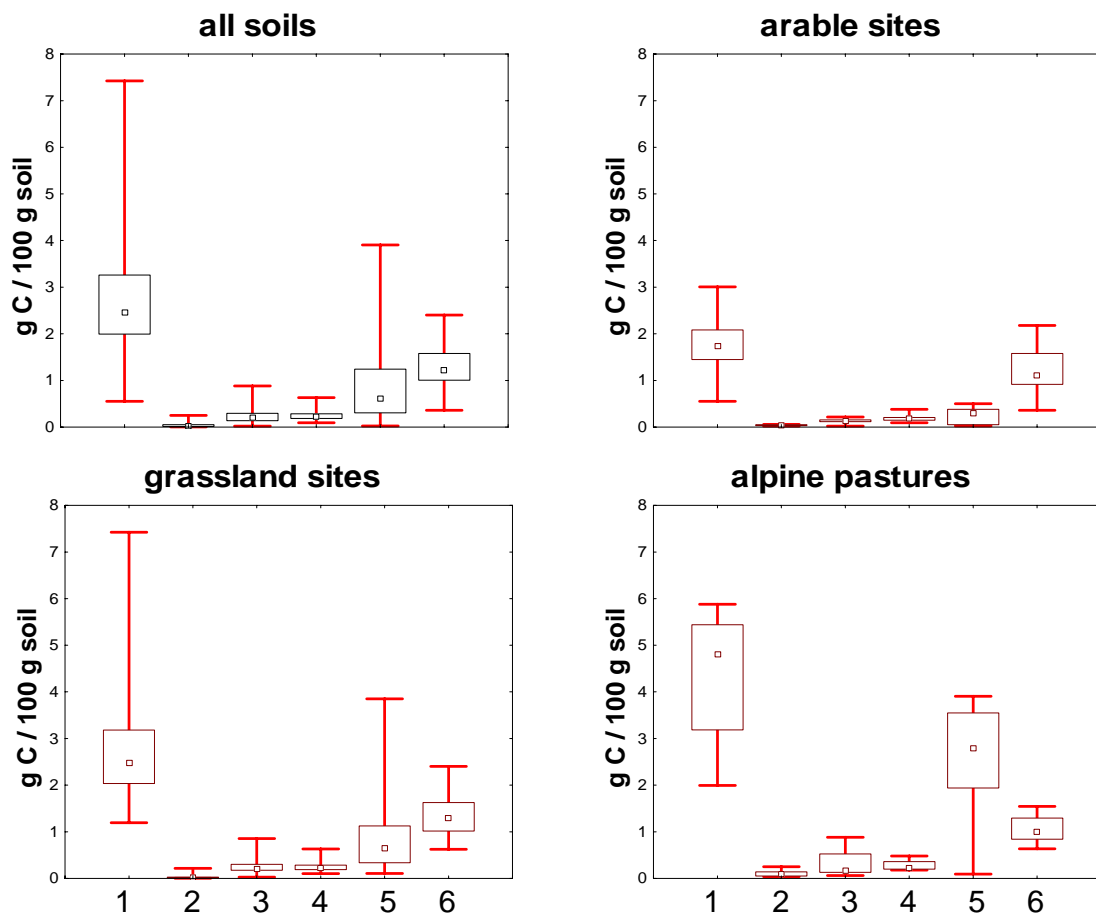


Fig. 2. Distribution of SOC among soil fractions for all soils (upper left panel) and classified according to land-use. Box plots show median, 25th and 75th percentile, and the non-outlier range. Numbers at X-axes correspond to 1 total SOC, 2 dissolved organic carbon DOC, 3 particulate organic carbon POM, 4 oxidation-resistant silt+clay fraction s+c, 5 sand + microaggregates S+A, 6 silt + clay minus oxidation resistant carbon s+c-rSOC.

In addition to the distribution among soil fractions, SOC age of selected samples was determined by ^{14}C dating in order to verify the assignment of carbon into fractions of different turnover time (Fig. 3). Silt+clay fractions comprised most of the total SOC and thus had ^{14}C values similar to that of the bulk soil. The oxidation-resistant carbon was distinctly older than s+c, providing evidence that the isolation of an old fraction was successful.

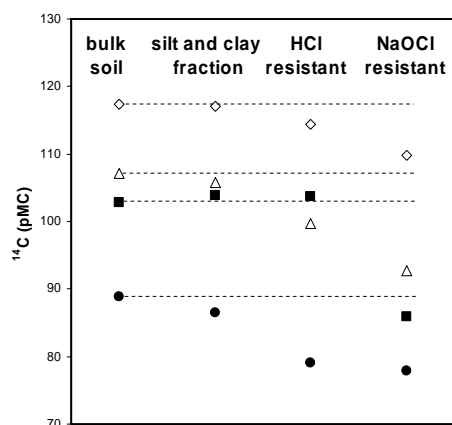


Fig. 3. ^{14}C activities as percent modern carbon of bulk soils and fractions (dotted lines are referred to bulk soil values; ◇ = temperate meadow 0-5 cm, △ = arable site 0-20 cm, ■ = temperate meadow 10-20 cm and ● = alpine pasture 7-18 cm). Percent modern carbon values higher than 100% are strongly influenced by inputs of so-called ‘bomb’ ^{14}C ; values much below 100% refer to very old carbon.

An additional benefit of the analysis of many different soils derives from the measured C/N ratios in bulk soils under arable and grassland use, which can be used for the current Swiss LULUCF reporting (Table 2).

Table 2. C/N ratios (0-20 cm or sub-stratified) for mineral agricultural soils in the Switzerland based on samples analyzed by Zimmermann et al. (2006a) and Leifeld et al. (2003). Values in brackets are one standard deviation.

	C/N ratio	N
Arable	9.4 (2.0)	26
Grassland	9.8 (2.2)	106
Alpine grassland (> 1000 m)	10.4 (1.5)	16

The C/N ratio of arable sites is close to the IPCC-defaults (IPCC 2006, Vol 4; page 11.16; arable land: C/N = 10, range 8-15) but much smaller than the default for both, temperate and alpine grasslands (IPCC grassland: C/N = 15, range 10-30). The

smaller difference in C/N ratios between arable land and grassland for Switzerland is likely to be caused by i) the high share of leys in arable rotations and ii) the comparable intensive use of permanent grasslands with regularly application of mineral and organic N-fertilizers. From the data in Table 2 it can be inferred that the amount of N₂O emitted through the conversion of grassland to cropland is higher per unit SOC mineralized as it would be based on the IPCC default values.

3 Rapid quantification of differently stabilized soil organic matter fractions

3.1. Methodological approach

The second phase of the project aimed at applying a spectroscopy-based statistical tool for the rapid quantification of the fractions above. While the fractionation resulted in meaningful fractions with respect to their sensitivity to land-use and turnover time, the procedure is very time-demanding. Based on previous studies that attempted to quantify soil properties by means of infrared spectroscopy in combination with partial-least squares regression (e.g., Janik & Skjemstad 1995; McCarthy et al. 2002; Leifeld 2006a), we applied this combined method to quantify carbon in fractions by measuring diffuse reflectance infrared spectra (DRIFT) of the bulk soil (Zimmermann et al. 2007). The latter is clearly much faster than soil fractionation (scanning of an infrared-spectra takes about 3 minutes plus 10 minutes sample preparation in the lab as compared to several days to fractionate a handful of soil samples), but had not been applied so far for soil fractions. Partial least squares (PLS) regression is a statistical approach where the y-variable (e.g., C-content) is regressed against the x-variable (i.e., the infrared spectra) to obtain so-called latent variables (LV) or PLS-factors. It is similar to principal component regression but takes advantage of the variability of the y-variable during calibration and of multiple information in the infrared spectra. A calibrated model is usually tested against unknown samples that were not part of the calibration in order to check the models' reliability. The appropriateness of the chemometric prediction method was evaluated by the residual prediction deviation (RPD), which is the ratio between the standard deviation (s.d.) of the validation sample set and the standard error of prediction (SEP, Williams & Norris, 1987):

$$RPD = \frac{s.d.}{SEP}$$

In agricultural applications, RPD values >3 are considered satisfactory, whereas prediction models with RPD values <3 should only be used as screening methods (Malley et al., 2000).

3.2. Results

The DRIFT-PLS method was applied to 111 out of the 123 samples used for fractionation. Hundred samples were taken for calibration, and the PLS model for any particular soil property was checked against the remaining eleven samples. More detailed information is provided in Zimmermann et al. (2007).

The PLS prediction accuracy for OC differed considerably between fractions (Table 3). Correlation coefficient for measured vs. predicted OC in the DOC fraction was 0.90, but the RPD value was 2.0. As discussed by Malley et al. (2000), prediction models with such low RPD values should only be used for screening and not be accepted as measurements. The relative SEP was 51% and the slope of the regression was 0.738, which indicates that the PLS model predicted DOC inaccurately. One reason for the inaccuracy could be the small amount of DOC compared to the total mass; on average, DOC accounted for only 0.04% of the total mass. Conversely, PLS prediction for OC in the POM fraction was excellent ($r=0.97$, slope of the regression = 0.993), and the RPD value of 3.4 also indicated a high reliability of the prediction model, although relative SEP was 22%. The prediction model for OC in the S+A fraction was less accurate. The PLS model did not overestimate the amount of OC in S+A (slope = 1.025) and r was 0.93, but relative SEP of 36% was high, and the RPD of 2.6 was low. The same situation applied to the prediction of OC in the s+c without rSOC. For this fraction, the RPD value of 2.8 was also low, but with a relative SEP of 12%, a regression slope of 0.975 and $r = 0.94$, the PLS prediction model still yielded acceptable results for the quantification of OC stabilized in this fraction. The correlation coefficient between measured and predicted OC in the fraction rSOC was 0.89 and the relative SEP 16%. However, the RPD value of 2.0 was very low. But with a slope of the regression of 0.991, the PLS prediction did not lead to systematic over- or under-estimations.

Table 3 Correlations between measured and PLS-predicted values for the calibration and validation (n=11) sample sets with number of latent variables (LV) used for calibration, Pearson's correlation coefficients (r), regression equations through zero, relative standard errors of predictions (rel SEP), and residual prediction deviations (RPD). Predicted values were abbreviated as C_{tot} = total organic carbon, N_{tot} = total nitrogen, C_{DOC} = dissolved organic carbon, C_{POM} = particulate organic carbon, $C_{\text{S+A}}$ = carbon in sand and stable aggregates, $C_{\text{s+c-rSOC}}$ = carbon in silt and clay fraction without resistant soil organic carbon (rSOC), $C_{\text{labile fractions}}$ = carbon in C_{DOC} plus C_{POM} , and $C_{\text{stable fractions}}$ = carbon in $C_{\text{S+A}}$ plus $C_{\text{s+c-rSOC}}$.

Property	calibration			Validation			
	LV	r	n	regression equation	r	rel SEP %	RPD
Clay	4	0.96	91	$y = 1.013x$	0.97	10	3.5
C_{tot}	12	0.99	90	$y = 1.021x$	0.97	10	4.1
N_{tot}	7	0.96	93	$y = 0.976x$	0.96	9	4.0
C_{DOC}	5	0.90	90	$y = 0.738x$	0.90	51	2.0
C_{POM}	9	0.91	92	$y = 0.993x$	0.97	22	3.4
$C_{\text{S+A}}$	6	0.93	94	$y = 1.025x$	0.93	36	2.6
$C_{\text{s+c-rSOC}}$	7	0.89	94	$y = 0.975x$	0.94	12	2.8
C_{rSOC}	8	0.85	93	$y = 0.991x$	0.89	16	2.0
$C_{\text{labile fractions}}$	12	0.96	92	$y = 0.965x$	0.98	16	4.1
$C_{\text{stable fractions}}$	11	0.99	92	$y = 0.954x$	0.98	11	4.1

Overall, the results of these statistical analyses suggest that OC of all fractions except DOC could be estimated with PLS using their bulk soil infrared spectra, but that relative SEP and RPD were not always convincing. One reason for the latter could be the low OC concentrations of the different fractions.

To improve prediction models, we tested the predictive capability to quantify OC contents of combined labile and combined stabilized fractions (see Figure 1). PLS models for these combined fractions were computed using the same methods as before. By relating measured to PLS-predicted OC values, we obtained an r-value of 0.98 for both fractions. Also RPD values for both prediction models were excellent (4.1). The PLS model for the stabilized fraction had a relative SEP of 11% and for the labile fraction of 16%. Both prediction models only slightly underestimated OC contents. The slope of the regression for the combined labile fractions was 0.965 and for stabilized fractions it was 0.954. The improvement in the predictions for these combined fractions relative to the results for the separate fractions could be explained by the higher amount of soil components that is correlated to the spectra. Attained relative SEP were comparable to standard errors of OC in repeated fractionation steps. Leifeld & Kögel-Knabner (2005) obtained standard errors of OC in POM and sand-sized fractions of 9 – 21%, and Six et al. (2000) obtained standard errors of OC in size classes and density fractions in macroaggregates of 11%.

3.3 Black carbon

Black carbon consists of residues from incomplete combustion and mainly occurs in soil as soot and as charcoal. Because of its relative biochemical stability, it takes part in the SOM turnover only at very small annual rates. However, quantification of stable organic matter is needed for smart modelling because its pool size determines in addition to other recalcitrant compounds the ‘baseline’ of soil organic carbon that is hardly affected by land-use or management. For the current project, we developed a new and rapid approach to detect and quantify black carbon in soil by means of differential scanning calorimetry (DSC). Briefly, this method relies on the different thermal stability of charcoal and soot relative to biogenic derived organic matter compounds under oxidative conditions. The method has been shown to work quantitatively and adds to the rSOC-approach described above for sites that are high in black carbon and are probably not well reflected in the current calibration. Details of the method are described by Leifeld (2006b).

4 Comparison of measured fractions with modelled pools

4.1. Model description

In the third part of the study, we tested whether the measured soil carbon fractions correspond to calculated pools of a SOM model by modelling all of the 123 sites, assuming them to be in equilibrium, with the model 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?

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 UK. It was then extended to model SOM turnover in grassland and woodland soils in different climatic regions worldwide (Coleman & Jenkinson 1999; Smith et al. 1997). The model can be used in two modes: i) forward mode to simulate SOM under changed agricultural management and input of plant materials, 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 4). 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 CO₂, biomass (BIO) and humified organic matter (HUM), depending on clay content, whereas BIO and HUM are further decomposed to form more CO₂, BIO and HUM. All pools except IOM decompose by first order decay at rates (year⁻¹) 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.

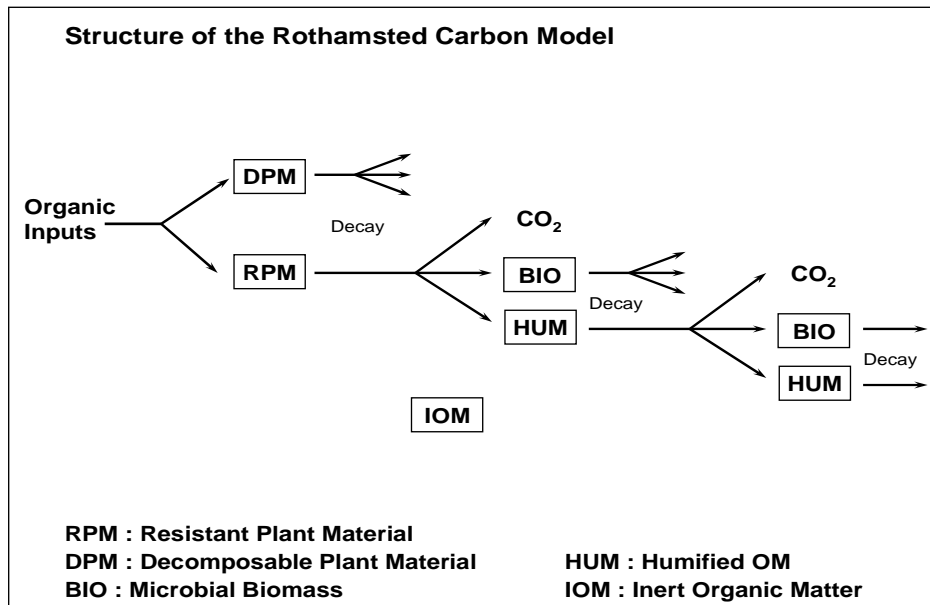


Fig. 4. SOC pools as defined by RothC (after Coleman and Jenkinson 1999). DPM decomposable plant material, RPM resistant plant material, HUM humified organic matter, BIO microbial biomass, IOM inert organic matter.

4.2. Methodological approach

We used the model to calculate the partitioning of SOC into pools. For this purpose, we assumed that the 123 sites are in equilibrium with respect to SOC, given that management had remained constant for at least the previous 30 years, and for more than 100 years in many cases. 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 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 t m^{-3} for all sites, for RothC, as well as for the different fractions which is a typically value for mineral soils in Switzerland (Desaules & Studer 1993). Measured carbon contents of the fractions were converted to t C ha^{-1} , which is the same unit output by RothC, and carbon in soil fractions was related to modelled RothC pools according to Fig. 5.

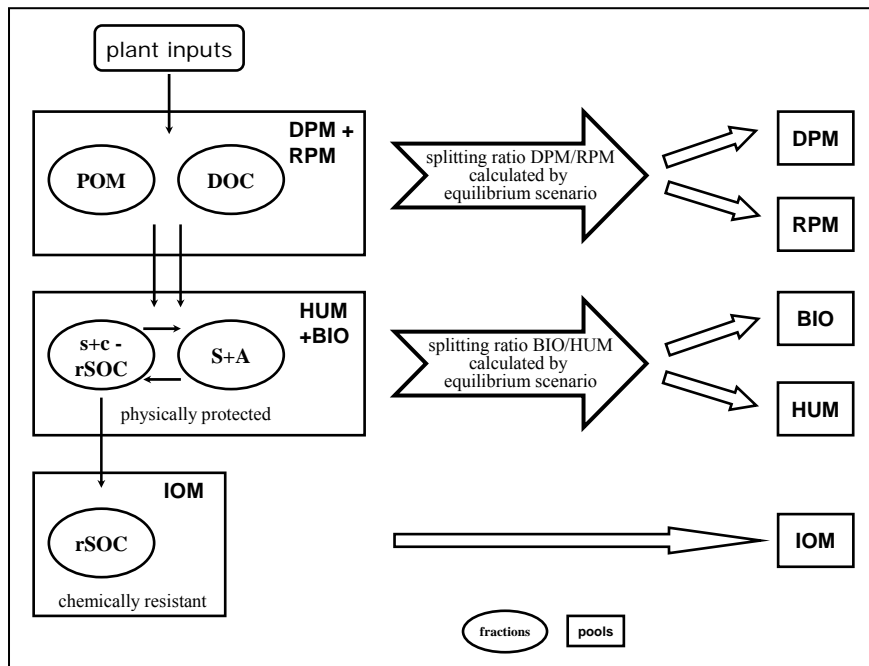


Fig. 5. Assignment of measured fractions to modelled pools for equilibrium conditions. For details, see Zimmermann et al. (2006).

4.3 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 ± 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).

4.4. Results

4.4.1 Correlation of measured with modelled data

Results of Spearman's rank order, R , correlations are given in Table 4. 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 (Fahrmeier et al. 2004). Strongest correlations were obtained for BIO and HUM with an R of 0.99, but also most other correlations were modest to strong, except for RPM in the case of alpine pasture sites ($P > 0.05$, $R = 0.57$). 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 since the 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.

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 slightly larger in the model than obtained by measurements. Changing the density of sodium polytungstate to $2.0 - 2.2 \text{ g cm}^{-3}$ 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 since 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 to 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.

4.4.2 Combining and splitting of measured fractions

Ratios of BIO to HUM pools under equilibrium conditions are relatively constant (Zimmermann et al. 2006). 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 rather they 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 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⁻¹. 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. 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 which correspond to pools used in RothC, independent of any values taken from RothC model runs.

Table 4 Spearman's rank order correlations, *R*, and statistical parameters of Kolmogorov-Smirnov analysis of modelled and quantified pools.

	Spearman's R	Kolmogorov-Smirnov test				<i>n</i>	<i>P</i> -level
		Mean mod. ^a	Mean quant. ^b	Std. dev. mod. ^c	Std. dev. quant. ^d		
		/ tC ha ⁻¹					
All sites:							
DPM	0.82	1.05	0.67	0.54	0.41	111	<i>P</i> < 0.001
RPM	0.76	9.22	5.93	3.56	2.86	111	<i>P</i> < 0.001
BIO	0.99	1.23	1.32	0.49	0.55	111	<i>P</i> > 0.1
HUM	0.99	47.22	50.72	18.79	21.43	111	<i>P</i> > 0.1
IOM	0.73	5.71	5.79	2.58	2.27	111	<i>P</i> > 0.1
Temperate grassland:							
DPM	0.74	1.2	0.77	0.43	0.36	92	<i>P</i> < 0.001
RPM	0.78	9.51	6.14	3.47	2.96	92	<i>P</i> < 0.001
BIO	0.99	1.24	1.34	0.47	0.53	92	<i>P</i> > 0.1
HUM	0.99	48.03	51.62	18.14	20.36	92	<i>P</i> > 0.1
IOM	0.70	5.84	5.95	2.48	2.24	92	<i>P</i> > 0.1
Arable:							
DPM	0.68	0.08	0.05	0.03	0.02	11	<i>P</i> < 0.001
RPM	0.77	7.48	5.02	2.51	1.79	11	<i>P</i> < 0.025
BIO	0.99	1.09	1.14	0.41	0.44	11	<i>P</i> > 0.1
HUM	0.99	40.14	41.71	15.12	16.36	11	<i>P</i> > 0.1
IOM	0.65	4.64	5.62	1.89	2.35	11	<i>P</i> > 0.1
Alpine pasture:							
DPM	0.76	0.64	0.37	0.51	0.26	8	<i>P</i> > 0.1
RPM	0.57	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e	8	n.d. ^e
BIO	0.93	1.24	1.38	0.76	0.94	8	<i>P</i> > 0.1
HUM	0.93	47.62	52.84	29.32	36.13	8	<i>P</i> > 0.1
IOM	0.76	5.65	4.11	4.14	2.16	8	<i>P</i> > 0.1

^a modelled mean

^b quantified mean

^c standard deviation of modelled mean

^d standard deviation of quantified mean

^e not determined

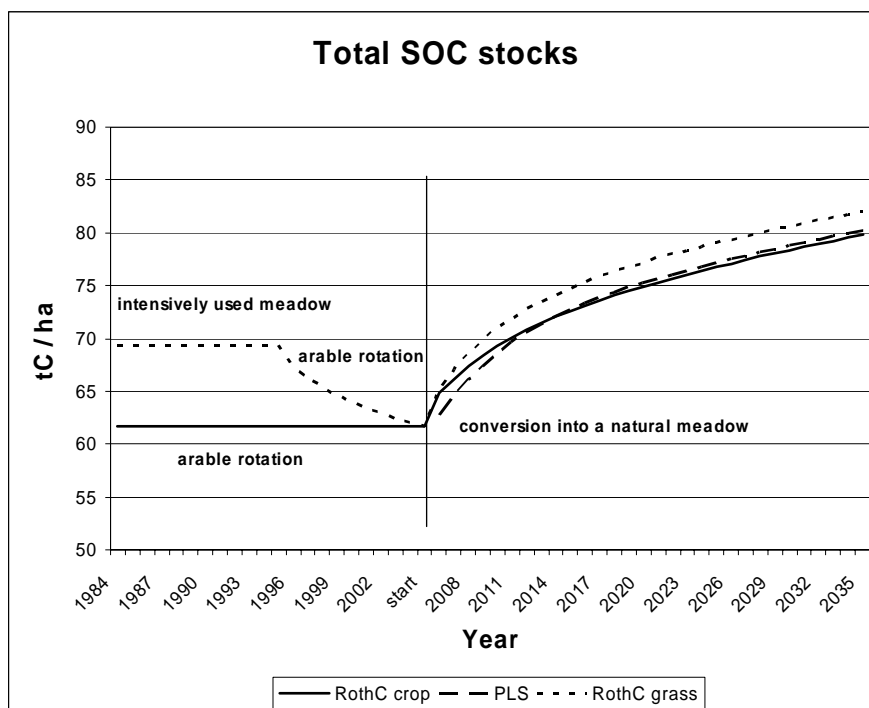
5 Application of the carbon model to non steady-state conditions

To initialise 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 were constant during that period. Compared to these highly unlikely assumptions, the use of measured fractions to initialize RothC has the advantage that processes which 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 initialise RothC at any point of the landscape even with a lack of historical data. For sites with comparable climatic conditions, splitting ratios for DPM to RPM pools and BIO to HUM pools can be adopted.

The advantage of applying DRIFT-PLS predicted SOC fractions in the RothC model is shown in the following example (Figure 6), which is based on differently used agricultural sites in the Swiss Central Plateau. The field site to be modelled is an arable site in Koppigen (BE) with a mean annual temperature (MAT) of 8.5° C, mean annual precipitation (MAP) of 1266 mm, and a clay content of 21 %. This site has a known land-use history with at least a 30 year-long period of arable rotation. The measured carbon stock in 2005 was 61.62 t C ha⁻¹ for the 0-20 cm horizon. The equilibrium conditions for RothC and the annual carbon input can be calculated inversely by the model itself to obtain the starting conditions of the different SOC pools for simulating a change in agricultural management. In our scenario, this site will be converted to a natural meadow in 2006. To obtain the annual carbon input under these new conditions, we calculated the annual carbon input of a natural meadow with a measured carbon stock of 122.37 t C ha⁻¹ in Russwil (LU) with very similar climatic and textural site conditions (MAT = 7.8° C, MAP = 1333 mm, clay content = 20%) to that of Koppigen. The so calculated annual carbon input of 6.81 t C ha⁻¹ for the natural meadow was used in RothC to simulate the SOC changes in Koppigen after conversion to meadow for the next 30 years, assuming no climatic changes at this site ('RothC crop' in Figure 6). But how reliable is this simulation, if the land-use history was not constant during the model-assumed last 10 000 years, but the site in Koppigen was used as arable rotation site only for e.g. the last 10 years? This question was addressed by simulating a scenario, in which the site in Koppigen was used as intensive meadow for decades, and has been converted into an arable rotation site in 1995 ('RothC grass' in Figure 6). To simulate the conditions before 1995, we took SOC values of an intensively used meadow with a carbon stock of 69.35 t C ha⁻¹ in Russwil again to have similar site conditions. The annual carbon inputs from 1995 to 2005 were then fitted in RothC to match the measured SOC stock in 2005, and the

calculated SOC pools of 2005 was used as the starting condition for the conversion of the arable site into a natural meadow with the annual carbon input of 6.81 t C ha^{-1} as above. So both start conditions before the conversion of the arable site to a natural meadow were calculated by the model itself. They had the same total SOC stock, but a different distribution of organic carbon among pools. To have a model-independent SOC distribution into the different pools in 2005, we quantified the pools in the Koppingen soil by DRIFT-PLS as introduced above. The pool sizes as predicted by PLS were used as initial conditions in RothC, and the expected annual carbon input of 6.81 t C ha^{-1} for a natural meadow applied as before (PLS in Figure 6) for the duration of 30 years.

Figure 6 Changes in the SOC stock of an arable site after conversion into a natural meadow considering different starting condition in 2005 ('RothC crop': starting conditions calculated from equilibrium runs, 'RothC grass': starting conditions calculated from non steady-state conditions, 'PLS': starting conditions quantified by DRIFT-PLS).



The results show that the prediction of SOC stock-changes depends on the SOC distribution among RothC pools at the beginning of the simulation and thus on land-use history. For a site with known land-use history, the simulated SOC stock changes are very similar for starting conditions defined either by equilibrium runs or by pool prediction with DRIFT-PLS ('RothC crop' and 'PLS'). But if the starting conditions are not known exactly, i.e. the site can not be assumed to be in equilibrium ('RothC

grass'), the inverse modelling lead to an inaccurate simulation of the SOC stocks. In our example, the biased initialization for 'RothC grass' overestimates the accumulation of SOC along the conversion from arable cropping to meadow by around 3 t ha^{-1} . This overestimation is mainly caused by the amount of inert SOM, which is a function of the total SOC stock in RothC. By quantifying the site-specific pool sizes independently from the model through DRIFT-PLS, simulation results become more reliable.

6 Conclusion: Current perspectives and future research needs

With the results of this project, significant progress has been made in order to enable validation of some of the soil CO_2 fluxes induced by land-use change as calculated in the Swiss Greenhouse Gas Inventory. As mentioned in the introduction, the coordinated approach using soil fractionation, IR-based quantification and initialization of model runs without assuming equilibrium conditions is currently applicable to land-use change from arable land to grassland and vice versa, for leys in arable rotations and for organic fertilization. It thus includes major drivers of SOM dynamics in Swiss agriculture. The IR-based quantification is likewise applicable to no-till conditions, but the current version of the RothC-model does not take into account no-till management. Though no-till is an important task to be handled within future CO_2 emission and sequestration estimates, it is currently not possible to predict the carbon storage of a soil under no-till over time with sufficient certainty, mainly because experimental results on the effect of no-till on SOM storage is contradictory and some processes are not well understood. The same applies for the dynamic of alpine grasslands under changing climatic conditions. For some high-elevation sites, accumulation of labile plant residues exceeds those in temperate soils by a factor 2-3 even if the low temperature of these sites is considered in the simulation. Further research on the driving factors is thus necessary in order to proceed with the prediction of SOC dynamics in alpine grasslands. Modelling the dynamic of organic soils is still at its beginning, and future Swiss efforts should above all concentrate on providing reliable emissions rates estimated from soil profiles and flux measurements.

**7 List of own publications at ART that are in total or partially funded by FOEN
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1. Zimmermann, M., Leifeld, J., Fuhrer, J. 2007. Quantifying soil organic carbon fractions by infrared spectroscopy. *Soil Biology & Biochemistry* 39, 224-231.
2. Zimmermann, M., Leifeld, J., Schmidt, M.W.I., Smith, P. and Fuhrer, J. 2006. Measured soil organic matter fractions can be related to pools in the RothC model. *European Journal of Soil Science*, doi: 10.1111/j.1365-2389.2006.00855.x.
3. Leifeld, J. and Zimmermann, M. 2006. Thermal analysis of mineral soils before and after oxidation with sodium hypochlorite. *Journal of Thermal Analysis and Calorimetry*, doi: 10.1007/s10973-006-7695-y.
4. Leifeld, J., Franko, U. and Schulz, E. 2006. Thermal stability responses of soil organic matter to long-term fertilization practices. *Biogeosciences* 3, 371-374.
5. Leifeld, J. 2006. Application of diffuse reflectance FT-IR spectroscopy and partial least squares to predict NMR properties of soil organic matter. *European Journal of Soil Science* 57, 846-857.

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