



# Soil organic carbon (SOC) now and in the future. Effect of soil characteristics and agricultural management on SOC and model initialisation methods using recent SOC data

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**Soil organic carbon (SOC) now and in the future- Effect of soil characteristics and agricultural management on SOC and model initialisation methods using recent SOC data**

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## **Soil Organic Carbon (SOC) now and in the future**

Effect of soil characteristics and agricultural management  
on SOC and model initialisation methods using recent SOC  
data

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## Abstract

Soil organic carbon (SOC) concentrations and greenhouse gas (GHG) emissions are not uniform across the landscape, but assemble in “hotspots” in specific areas. These differences are mainly driven by human-induced activities such as agricultural management. 40-50% of the Earth’s land surface is under agricultural land-use, for instance cropland, managed grassland and permanent crops including agro-forestry and bio-energy crops. Furthermore, 62% of the global soil C stock is SOC and the soil stores more than 3 times more C than the atmosphere. Thus, C sequestration in agricultural soil has a potentially important role in increasing SOC storage and GHG mitigation, and there is considerable interest in understanding the effects of agricultural management on SOC and GHG fluxes in both grasslands and croplands, in order to better assess the uncertainty and vulnerability of terrestrial SOC reservoirs.

For the sake of discovering the agricultural management practices relating to the effective and sustainable C sequestration in agricultural lands in Europe, simulating future terrestrial C stocks and GHG budgets under varied agricultural management systems in major European ecosystems is essential. Using models is a useful method with the purpose of this and abundant studies have carried out. However, many model results have not been validated with reliable observed long-term data, while other studies have reported a strong impact of model initialisation on model result. Nevertheless, predictions of annual to decadal variability in the European terrestrial C and GHG resources largely rely on model results. Consequently, finding the most appropriate and comprehensive model initialisation method for obtaining reliable model simulations became important, especially for process-based ecosystem models. In recent years, Zimmermann et al. (2007) have succeeded in initialising the Rothamsted Carbon model (RothC) using a physical and chemical soil fractionation method. For that reason, we hypothesised that measured detailed SOC data would be useful to initialise ecosystem models, and this hypothesis should be tested for different process-based models and agricultural land-use and management.

The objectives of this PhD thesis are: i) to evaluate how agricultural management influences SOC stocks using an experimental and a modelling approach and ii) to determine an effective model initialisation scheme. The PhD project involved : i) five European paired-sites, each comprising long term (i.e. 10 to 25yrs) contrasting agricultural management practices on mineral and organic soil (grassland : FR-Laqueuille, extensive vs. intensive grazing; CH-Oensingen, high vs. low nitrogen input and cut; NL-Reeuwijk, intensive vs. extensive cut and grazing; cropland: UK-Hertfordshire, inverted vs. non-inverted soil tillage; and IE-Carlow, conventional vs. reduced tillage), ii) a simple SOC model (RothC) and three processed-base ecosystem models (grassland PaSim and varied land-use DayCent and DNDC) and iii) different initialisation methods referring to the measured SOC pools values, to find an initialisation scheme which allows model simulation results to be close to measured values.

Firstly, in order to examine how agricultural management influences SOC, soil sampling campaigns were carried out, in winter 2011/2012, for the four European sites

(UK-Hertfordshire was sampled in November 2003 0-20 cm soil depth). Each site comprises a pair of contrasting agricultural managements. The sampled soil was analysed according to the soil fractionation method described by Zimmermann et al. (2007) for five soil depth layers (0-5, 5-10, 10-20, 20-40, 40-60 cm). Results show that, for a given depth and soil organic matter fraction, no significant differences were found in SOC stocks between contrasting practices concerning mineral soil. For mineral soils, the soil fractions derived from silt and clay exerted the greatest contribution to total SOC, especially in the topsoil (0-10 cm), compared to the deeper soil layers (> 10 cm depth). For organic soils (25 years under current management), the particulate organic matter (POM) had the greatest contribution to total SOC, and a significant difference in SOC distribution was observed between contrasting management practices. This shows that management practices influence SOC more rapidly in organic soils compared to mineral soils, which may be due to the larger quantity of POM in organic soils, being sensitive to land management change. Concerning the mineral soil sites (up to 10 years of contrasting management), it appeared that not enough time has elapsed since the onset management practices to detect statistically significant differences in SOC stocks.

With comparing RothC model spin-up run result, most of the site's current SOC were not at the equilibrium status except Oensingen (CH) site. Concerning the Oensingen (CH) site, plant residue C input which was used in this study was estimated value by another model in De Bruijn et al. (2012), and I assume this plant residue C input may already have been optimised for modelling. Furthermore, SOC in the extensive plot was closer to the equilibrium SOC than the intensive plot. Perhaps this is because only estimated plant input data was applied for the extensive plot while estimated plant input value and real manure application data were applied for the intensive plot in the equilibrium simulation. These results implied the difficulties for initialising models with spin-up run considering the current SOC is at the equilibrium status, especially with mineral soils.

Then we tested different initialisation methods using measured detailed SOC data with RothC regarding SOC model output and also with PaSim, DayCent and DNDC regarding model flux (GPP, NEE and Reco) results.

RothC model SOC results showed significant difference due to initialisation methods, and we found adjusting the total equilibrium SOC to the measured total SOC values during the spin-up run is the most user friendly and effective RothC model initialisation. In spite of the limited compatibility of Zimmermann et al. (2007)'s model SOC pools estimation from soil fraction data, other process-based ecosystem models such as PaSim, DayCent and DNDC did not show a significant difference in model flux results between spin-up run initialisation and initialisation methods using estimate Zimmermann et al. (2007) SOC pools data, suggesting model initialisation using SOC pools data largely affect SOC model output although not the model flux output.

### **Keywords**

Soil organic carbon (SOC), process-based models, paired-sites, carbon fluxes, model initialisation

## Résumé

La concentration de Carbone organique de sol (COS) et les émissions de gaz à effet de serre (GES) ne sont pas uniformes à travers l'espace, mais se regroupent en "hotspots" dans des endroits spécifiques. Ces différences s'expliquent principalement par les activités anthropiques telles que la gestion agricole. 40-50% de la surface de la Terre est utilisée par l'agriculture, par exemple les terres cultivées, les prairies gérées et cultures permanentes, y compris l'agro-foresterie et de bio-cultures énergétiques. En outre, 62% du carbone globale est COS, et le sol conserve plus que 3 fois plus de C que l'atmosphère. Ainsi, la séquestration du carbone dans les sols agricoles joue un rôle potentiellement important dans l'augmentation de stockage de COS et l'atténuation des GES, et il y a un intérêt considérable pour comprendre les effets de la gestion agricole sur le COS et les flux de GES aux prairies et terres cultivées, afin de mieux évaluer l'incertitude et la vulnérabilité des réservoirs de COS. Afin de découvrir les pratiques de gestion agricole qui contribuent à la séquestration efficace et durable du carbone aux terres agricoles en Europe, il est essentiel de simuler les stocks futurs de carbone terrestre et les budgets de GES par rapport aux systèmes de gestion agricole variées sur les grands écosystèmes européens. Dans ce contexte, la modélisation est une méthode utile, et la modélisation a déjà été utilisée dans beaucoup d'études. Cependant beaucoup de résultats de la modélisation n'ont pas encore été validés avec les données mesurées sur l'horizon long-terme, et d'ailleurs d'autres études ont constatés un fort impact de l'initialisation du modèle sur le résultat du modèle. Néanmoins, la variabilité des prévisions annuelles et décennales concernant le C et le GES en Europe dépendent des résultats du modèle. Par conséquent, il est important de trouver la meilleure méthode d'initialisation des modèles pour obtenir des résultats des modèles fiables, notamment pour les modèles d'écosystèmes dits "process-based." Au cours des dernières années, Zimmermann et al. (2007) a réussi à initialiser le modèle de Rothamsted carbone (RothC) en utilisant une méthode (physique et chimique) de fractionation des sols. Pour cette raison, j'ai fait l'hypothèse que les données COS détaillées seraient utiles pour initialiser des modèles d'écosystème, et que cette hypothèse doit être testée avec les modèles différents par rapport aux gestions agricoles différentes. Les buts de cette thèse sont les suivants: i) évaluation des influences des gestions agricoles sur le stockage de COS, en utilisant des approches expérimentales et des approches de modélisation; et ii) déterminer le meilleur méthode d'initialisation des modèles.

Le projet de thèse inclut: i) cinq sites jumelés en Europe en composant les gestions agricoles contraires à long terme (c'est-à-dire 10 à 25 ans) dans le sol minéral et le sol organique (prairies: FR-Laqueuille, pâturage intensif vs. extensif; CH-Oensingen, application d'azote et fauchage intensive vs. extensive ; NL-Reeuwijk, fauchage et pâturage intensif vs. extensif ; cultivation: UK-Hertfordshire, labour ('tillage') inversé vs. non-inversé; et IE-Carlow, labour ('tillage') conventionnel vs. réduit), ii) un modèle simple de COS (RothC) et trois modèles complexes d'écosystème (par exemple PaSim, DayCent et DNDC) et iii) méthodes d'initialisation des modèles concernant les données mesurées de bassins COS, pour trouver la meilleur méthode d'initialisation des modèles qui permet aux résultats des modèles d'être proches des valeurs mesurées. Tout d'abord, afin d'examiner comment la gestion agricole influence le COS, la campagne d'échantillonnage de sol a eu lieu en hiver 2011/2012 dans quatre sites européens

(Royaume-Uni-Hertfordshire a été échantillonnée en novembre 2003, avec 0-20cm de profondeur du sol). Chaque site a compris un paire de gestions agricoles contrastées. Les sols échantillonnés ont été analysés selon la méthode de fractionation des sols décrit par Zimmermann et al. (2007) concernant cinq profondeurs de sol (0-5, 5-10, 10-20, 20-40, et 40-60 cm). Les résultats montrent qu'aucune différence significative n'a été observée dans les stockages de COS entre les pratiques contrastées, à propos de chaque profondeur du sol et chaque fraction du sol concernant le sol minéral. En ce qui concerne le sol minéral, les fractions de sol provenant de limon et d'argile ont contribué largement au COS total, particulièrement dans la couche arable (0-10 cm), en comparant les couches plus profondes du sol (> 10 cm depth). En revanche, dans le sol organique, la matière organique particulaire (MOP) a contribué largement au COS total, si bien qu'une différence significative dans la distribution de COS a été observée entre les gestions contrastées. Ce résultat suggère que les gestions agricoles influent le COS plus rapidement dans le sol organique que dans le sol minéral, probablement parce que la plus grande quantité de MOP est incluse dans le sol organique, et le MOP est sensible aux changements de gestions agricoles. Dans les sites de sol minéraux (contrôlés depuis jusqu'à 10 ans de gestion contrastée), il semblerait qu'ils ont besoin de plus de temps (plus que 10 ans) pour détecter des différences significatives dans le COS. Lorsque l'on le met en comparaison avec les résultats de "spin-up run" obtenus par le modèle RothC, les COSs ne sont pas à l'équilibre (sauf le site Oensingen (CH)). Au site Oensingen (CH), on a utilisé les données de "plant residue C input" qui a été estimé par une autre étude (De Bruijn et al. (2012)). On suppose que ces données de "plant residue C input" ont probablement déjà été optimisées pour utiliser dans les modèles, ce qui implique que les résultats de modèles seront probablement proches des données mesurées. En outre, comparant les 'plots' extensifs et intensifs, le résultat de SOC à l'équilibre était plus proche au donnée mesurée dans le 'plot' extensif. Les données mesurées (concernant la quantité réelle du fumier) et les données estimées (concernant le "plant input") ont été utilisées pour obtenir le COS à l'équilibre intensif, tandis que la seule donnée estimée (concernant le "plant input") a été utilisée pour obtenir le COS à l'équilibre extensif (c'est-à-dire, il s'agit de la donnée mesurée, la quantité réelle du fumier, était la cause de cette déviation entre le résultat de modèle et la valeur observée). Ces résultats impliquent qu'il existe des difficultés d'initialiser les modèles par hypothèse que le COS présent est à l'équilibre, notamment avec le sol minéral. Ainsi, nous avons examiné les différentes méthodes d'initialisation utilisant les données détaillées de COS, en comparant le résultat de COS de RothC avec les résultats de flux de carbone (GPP, NEE et Reco) par PaSim, DayCent et DNDC. Les résultats de COS de RothC ont montré une différence significative par rapport aux méthodes d'initialisation, et la meilleure méthode d'initialiser les modèles est de régler la quantité d'entrée de carbone pendant le "spin-up run" jusqu'à ce que le total du COS à l'équilibre sera égale au total de COS observé. Malgré les difficultés de compatibilité de Zimmermann et al. (2007) avec les autres modèles, PaSim, DayCent et DNDC n'ont pas montré de différence significative par rapport aux méthodes d'initialisation des modèles en utilisant l'estimation des bassins COS. Ceci suggère que l'initialisation des modèles avec les données de COS influe largement les résultats de COS, mais pas les résultats de flux de carbone.

**Mots clés**

Carbone organique de sol (COS), modèles basés sur les processus, sites expérimentaux jumelés, flux de carbone, initialisation des modèles





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# Chapter 1

## Introduction





## 1.1 General Introduction

The world is facing a serious environmental, social and economic challenge: climate change. Anthropogenic greenhouse gas (GHG) emissions are exacerbating the natural “greenhouse effect.” Sequestration of carbon in agricultural soils has been recognised as a potentially important tool for mitigating climate change, as soil stores more than 75% of the Earth’s terrestrial organic carbon (C) and contains 4-5 times the amount of C in living vegetation (Lal (2004a); Breuning-Madsen et al. (2008)). 62% of the global soil C stock is soil organic carbon (SOC), and the soil stores more than 3 times more C than the atmosphere (Jobbágy and Jackson (2000); Lal (2002)).

Moreover, 40-50% of the Earth’s land surface is under agricultural land-use, such as cropland, managed grassland and permanent crops including agro-forestry and bio-energy crops (Smith et al. (2007a)). Thus, C sequestration in agricultural soil has a potentially important role in increasing SOC storage and GHG mitigation (around 90% contribution to the technical potential, Paustian et al. (1998); Foereid and Høgh-Jensen (2004); Smith et al. (2007a)). Furthermore, C sequestration in agricultural land may also contribute to increases in soil fertility (i.e. mineralisation of N), soil water retention and crop productivity (Drinkwater et al. (1998); Alvaro-Fuentes et al. (2009)). Realistic C sequestration of agricultural soils in Europe (EU-15) was estimated to be 16-19 Mt C/year during the period 2008-2012. This corresponds to 2% of European anthropogenic C emissions (Freibauer et al. (2004); Smith (2004a)), and agricultural management systems play an important role (Van Wesemael et al. (2010); Powlson et al. (2012)). Accordingly, there is considerable interest in understanding the effects of agricultural management on SOC and GHG fluxes in both grasslands and croplands, in order to better assess the uncertainty and vulnerability of terrestrial SOC reservoirs (Hassink (1994); De Bruijn et al. (2012); Schulp et al. (2008); Leifeld et al. (2009a); Xu et al. (2011); Zhao et al. (2013); Senapati et al. (2013); McSherry and Ritchie (2013)).

In Europe, grassland represents one of the dominant land uses, covering 22% of the EU-25 land area (EEA, 2005). Most grassland in Europe are managed for feeding domestic herbivores, either directly through grazing or through forage production which is stored as hay or silage. Thus, although grassland soils have a large potential as a terrestrial C reservoir, there are significant uncertainties regarding how management influences SOC stocks (McSherry and Ritchie (2013); Soussana et al. (2007)). For grasslands, the nature, frequency and intensity of disturbance plays a key role in the C balance, because SOC in these environments is mainly sequestered through the root system (e.g. rhizodeposition, root decomposition). Those management activities also influence plant litter and organic fertiliser inputs, which increase or reduce the natural capacity of soil to act as a C sink. Multi-decadal studies indicate that grassland practices can influence the rate of SOC sequestration for up to 20 years after conversion to grassland (De Bruijn et al. (2012); Poeplau et al. (2011)), with gains and losses of SOC mainly depending on the vertical distribution of C.

Cropland management activities (such as tillage, crop rotation and harvest) also have the potential to store terrestrial C by influencing soil C gain or loss. For example, tillage has been reported to increase the breakdown of organic residues, leading to soil erosion, losses of soil moisture and degradation of soil structure. Accordingly, conventional long-term tillage can reduce soil C stocks by as much as 20-50% (Murty et al. (2002); Ogle et al. (2003)). Conservation tillage reduces the negative impacts of tillage, preserves soil resources and can lead to an build-up soil C lost during tillage (Conant et al. (2007)).

The input of organic matter, whether as organic fertilisers or plant residues, may also enhance SOC stocks (Zhang et al. (2007); Chivenge et al. (2007); Van Groenigen et al. (2010a,b); Jagadamma and Lal (2010)). Some previous studies on organic fertiliser inputs suggest that organic systems may store more C in soil than conventional systems (Gattinger et al. (2012)).

However, others have suggested otherwise, showing no difference between the benefit of organic farming on SOC content and conventional management with manure and plant residue management (Leifeld et al. (2009a)). Consequently, detailed long-term land management data is needed to fully understand SOC changes in those managed systems (Van Wesemael et al. (2010)).

In addition to management and C inputs, land-use change (LUC) is considered as an important factor which influences SOC change (Post and Kwon (2008); Poeplau et al. (2011); Leifeld et al. (2011)). A review, using a number of LUC sites, showed that grassland conversion to cropland may attain the SOC equilibrium state 17 years after conversion (Poeplau et al. (2011)) and subsoil SOC changes are followed by changes observed in the topsoil. In contrast, after a conversion from cropland to grassland, no new equilibrium was reached within 120 years. However, these results have high uncertainty, due to limited sample size. In Europe, significant land-use change has occurred until now, and long-term agricultural sites with fixed land-use and management are rare (Smith et al. (2008, 2012)).

Thus, determining the agricultural management practices, which relate to an effective and sustainable C sequestration in agricultural lands in Europe, has become essential. Studies assessing the impact of a changing agricultural management are mainly undertaken to determine appropriate management strategies to optimise land use for production and C sequestration. However, climate also plays an important role for this purpose.

Using model approaches to assess the impact of natural and anthropogenic drivers on terrestrial C sequestration has become a useful method, and abundant studies have been carried out (Jenkinson and Rayner (1977); Jenkinson (1990); Parton and Rasmussen (1994); Parton et al. (1998); Del Grosso et al. (2000, 2001); Leifeld et al. (2009a); Senapati et al. (2013); Poeplau et al. (2013)). Nonetheless, these model results have not been validated against the large quantity of observational data, and they often struggle with considerable uncertainties and inconsistencies in the time horizons. Furthermore, many studies have reported that model initialisation methods have a large effect on the model simulation results.

Although many studies have been carried out recently, no common model initialisation method has been validated for process-based ecosystem models (Bruun and Jensen (2002); Smith et al. (2002a); Wutzler and Reichstein (2007); Carvalhais et al. (2008); Hashimoto et al. (2011); Xu et al. (2011)). In spite of this, the recent annual-to-decadal variability in the European terrestrial C and GHG resources largely relies on these model results.

Consequently, in order to determine the most effective agricultural management practices to sequester C, two major points became compelling areas of research: validating model results through long term data, and finding the most appropriate and comprehensive model initialisation method for obtaining reliable model simulation results.

## 1.2 Background

### Soil organic carbon (SOC) studies

Jenkinson (1965) pointed out the importance of the soil C decomposition with regard to agricultural management. In order to better understand SOC turnover, several methods have been considered.

Radio carbon dating is one method to understand soil carbon turnover (Jenkinson (1965, 1966); Martel and Paul (1974); Jenkinson and Ayanaba (1977); Jenkinson (1976); Jenkinson and Powlson (1976); Anderson and Paul (1984); Trumbore et al. (1989); Hsieh (1992); Wang et al. (1996); Paul et al. (1997); Trumbore (2000); Bruun et al. (2008); Leifeld and Fuhrer (2009)). Jenkinson (1965) used a  $^{14}\text{C}$  labelling method to determine plant material decomposition, and he found that the plant material decomposition rate was not influenced by small changes of plant

material input, and that plant material was decomposed quickly during the initial 6 months after carbon input, although large decomposition was not further observed after the initial 6 months. Jenkinson (1966) suggested that the size of soil biomass could be estimated by the size of CO<sub>2</sub> emission after CHCl<sub>3</sub> vapour treatment. He continued this study series until Jenkinson (1976), which studied how labelled <sup>14</sup>C and unlabelled C decompose for 10 years under plant residue input and field conditions (Jenkinson (1965, 1966, 1976); Jenkinson and Powlson (1976)). Radiocarbon dating in Jenkinson and Ayanaba (1977) showed that soil organic matter (SOM) contained fractions decomposed much more slowly than the slow pool in SOC models. Anderson and Paul (1984) discovered, using the radiocarbon dating method, that clay protects SOC, and this protection would be for the long-term (months, years or decades) rather than the short-term (days). Paul et al. (1997) reported that <sup>14</sup>C ages strongly influenced the total soil organic matter (SOM) content. Cultivation resulted in a lower amount of C in the soil, and the topsoil C age was 1200 years younger than that in the subsoil (Paul et al. (1997)). However, radiocarbon dating is expensive, so it is used sparingly by researchers.

The nuclear magnetic resonance (NMR) spectroscopy method is also used to investigate soil carbon turnover. This method is much less expensive than the radiocarbon dating method. The first experiment for understanding the structural characterisation of soil humic substances using NMR spectroscopy was published in Barton and Schnitzer (1963) (Preston (1996); Kögel-Knabner (1997)). At that time, <sup>13</sup>C NMR spectroscopy became a major method for studying soil organic matter structure as an improved method (Preston et al. (1994); Leifeld and Kögel-Knabner (2001); Golchin et al. (1994); Rumpel et al. (2002); Schöning and Kögel-Knabner (2006); Fontaine et al. (2007)), using <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>15</sup>N NMR on both solution and solid-state samples. This method increased our understanding of the characterisation of SOM and SOM turnover process, the effects of cultivation on SOM, characterisation of organic forms of N and P and interactions of SOM with other substances (Preston (1996)).

Due to the heterogeneous characteristics of soil, isolating biologically meaningful SOC compartments has been an active area of research (Sollins et al. (1999)). Chemical extraction and physical protection approaches have been considered for this purpose. The degree of physical protection of soil, soil particle size and soil particle density have been widely investigated. Chemical soil fractionation is based on the solubility in acid and base, providing humic acid, fulvic acid and humin fractions (Sollins et al. (1999)). For determining soil carbon vulnerability, Blair et al. (1995) used potassium permanganate (KMnO<sub>4</sub>) oxidation and Kleber et al. (2005) used NaOCl oxidation. Siregar et al. (2005) improved the chemical method, isolating stable soil organic matter by using NaOCl oxidation at pH 8. These methods provide a dissolved organic carbon (DOC) fraction, while chemical soil fractionation methods do not provide SOC compartments which differ in biological properties (Sollins et al. (1999)). Particle size soil fractionation was conducted in Preston et al. (1994), using ultrasonic dispersion ((Field and Minasny (1999); Amelung and Zech (1999); Zimmermann et al. (2007)), wet sieving (Six et al. (1998); Zimmermann et al. (2007); Alvaro-Fuentes et al. (2009)), centrifugation and gravity sedimentation (Sollins et al. (2006); Zimmermann et al. (2007); Alvaro-Fuentes et al. (2009)). Preston et al. (1994) analysed the carbon in these soil fractions using <sup>13</sup>C CPMAS (cross polarization and magic angle spinning) NMR.

Six et al. (1998) subsequently established an extensive and complex physical soil fractionation method, using aggregate separation and particle density separation (see Figure 1.1); this method has been cited by a large number of studies (e.g. Schlesinger and Andrews (2000); Paustian et al. (2000); Six et al. (2001); Christensen (2002); John et al. (2005); Lützow et al. (2006); Alvaro-Fuentes et al. (2009)). Bol et al. (2009) discovered the importance of particulate organic matter (POM) fractions in the SOC of arable soil. Nonetheless, the application of ultrasonic dispersion and particle size fractionation methods to soil was questioned, as some

soils contain considerable quantities of coal particles (Schmidt et al. (1999)). Skjemstad et al. (2004) proposed a method for matching measured soil fractions to each Rothamsted Carbon (RothC) model SOC pool. However, this method is specific to Australian soils which includes large proportions of charcoal carbon. Consequently, Zimmermann et al. (2007) proposed a soil fractionation method which produced measured fractions that were equivalent to the conceptual SOC pools in the RothC model, and this method has now been tested by several studies (Leifeld et al. (2009a); Leifeld and Fuhrer (2009); Dondini et al. (2009a); Senapati et al. (2013); Shirato et al. (2013); Poeplau et al. (2013)).

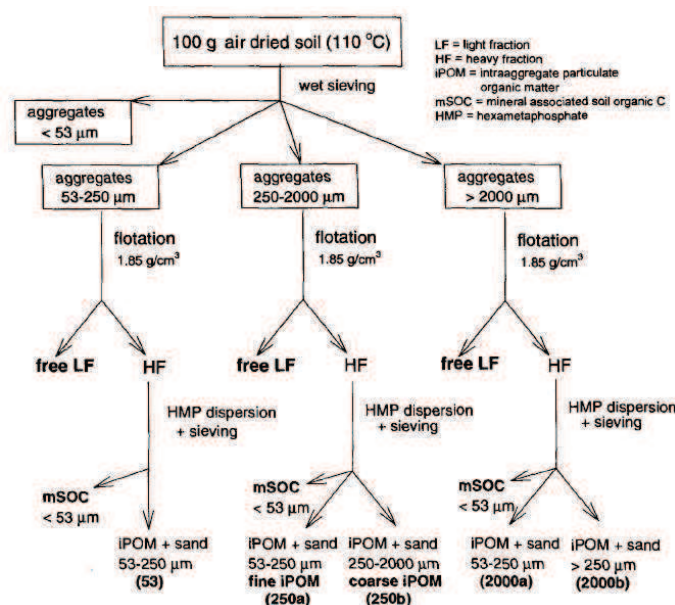


Figure 1.1: Physical soil fractionation scheme (Six et al. (1998))

## Climate Change studies

In an objective way, climate change and agriculture are inter-related processes, both of which take place on a global scale. On the one hand, global warming is projected to have significant impacts on conditions affecting agriculture, including temperature, carbon dioxide, precipitation and the interaction of these elements. On the other hand, agriculture has been shown to produce significant effects on climate change, primarily through the production and release of greenhouse gases such as carbon dioxide, methane, and nitrous oxide (Cole et al. (1997)). Also, land use change such as deforestation and desertification, together with the use of fossil fuels, are the major anthropogenic sources of carbon dioxide; which contribute to climate change.

To separate the effects of natural and anthropogenic origin on climate change, first studies have been reported in 1827 by Jean Baptiste Joseph Fourier (1768-1830), in “Mémoire sur les températures du globe terrestre et des espaces planétaires” (Fleming (1999)). Years later, Tyndall (1861) was the first researcher who showed the scientific evidence that absorption and radiation of heat by gases ( $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ) and water vapours could absorb heat. By quantifying the contribution of carbon dioxide (carbonic acid) to the greenhouse effect, Arrhenius (1896) first mentioned the high potential impact of fossil fuel combustion to climate. However, this theory aroused a large scientific discussion, and only in 1938 Callendar (1938) attempted to revitalise the greenhouse effect theory of Arrhenius (1896), by showing that world temperatures have increased at an average rate of  $0.005\text{ }^\circ\text{C}$  each year during the past half century (according to 200



meteorological stations in northern temperate regions, tropical regions and southern temperate regions).

The rising level of CO<sub>2</sub> in the atmosphere was demonstrated through a collection of multiple dry air CO<sub>2</sub> analyses (in Antarctica, Hawaii, California, South Pole, and North Pole), revealing non-equilibrated CO<sub>2</sub> emissions (i.e. combustion of fossil fuels) and absorption by the ocean Keeling (1960). In 1975, a first global circulation model was developed showing that the doubling the CO<sub>2</sub> concentration may affect the distribution of temperature in the atmosphere (Manabe and Wetherald (1975)). Furthermore, analysing global surface air temperature data (1880-1985) from a number of available meteorological stations indicated that the surface air temperature increased by 0.5-0.7 °C in the past century in both hemispheres (Hansen and Lebedeff (1987)).

In 1990, the IPCC First Assessment Report (FAR) brought attention to the human influence on climate change. The IPCC assessment reports have been published every 7 years since 1990. The IPCC Fourth Assessment Report (4AR) was published in 2007, underlining the doubtless existence of climate change, and the evidence that these changes are driven largely by human activities. The latest IPCC Fifth Assessment Report (5AR) was published by Working Group I in September 2013, mentioning that CO<sub>2</sub> concentrations have increased by 40% since the pre-industrial era, due to fossil fuel combustion and net land use change emissions.

In order to assess this critical point, climate reconstructions have been conducted and many studies have shown that the recent warming is doubtlessly larger than at any time during at least the past 500 years (Luterbacher et al. (2001, 2004)). Nevertheless, some researchers remain skeptical, suggesting that these changes are driven by natural forces with minimal influence of human activity (Chylek and Lesins (2008)).

#### **Climate Change and SOC studies in agricultural lands**

The positive feedback of the effect of global warming, and the decomposition of SOM releasing CO<sub>2</sub> to the atmosphere and enhancing the warming trend, was suggested by Jenkinson et al. (1991). Many researchers have presented evidence that increasing CO<sub>2</sub> emissions are mostly due to human-induced activities (Post et al. (1990); Jenkinson et al. (1991); Paustian et al. (2000); Smith (2008)).

The soil was recognised as one of the largest CO<sub>2</sub> sources in the global C cycle, and small soil respiration changes would greatly affect the CO<sub>2</sub> concentration in the atmosphere (Schlesinger and Andrews (2000)). Moreover, C storage in the soil is more than 3 times bigger than that of the atmosphere (Lal (2004a); Davidson et al. (2000); Davidson and Janssens (2006)). C sequestration transfers atmospheric CO<sub>2</sub> or other forms of C into long-lived SOC compartments, and removes C to pools, that are not diffused easily into the atmosphere, increasing SOC and soil inorganic carbon (SIC) stock by appropriate land use management (Smith et al. (1997); Lal (2004a)). The amount of the potential SOC sequestration of managed ecosystems is approximately equal to the amount of historical C loss (Lal (2004a,b)). Furthermore, 40-50% of the Earth's land surface is under agricultural land-use (Smith et al. (2007a)), and Smith et al. (2008) reported soil C sequestration could contribute about 90% of the total global agricultural mitigation potential by 2030. Thus, C sequestration in agricultural soil has a potentially important role in increasing SOC storage and GHG mitigation (Paustian et al. (1998); Foereid and Høgh-Jensen (2004); Lal (2004a,b); Smith et al. (2007a)).

In grasslands, management systems (i.e. fertilisation, grazing, mowing, conversion from other land-use, sowing legumes or grasses and irrigation) play an important role in sustainable production and SOC sequestration. Many studies have been conducted regarding the relationship between SOC and grassland management (Parton et al. (1987); Burke et al. (1989); Cambardella and Elliott (1992); Frank et al. (1995); Fearnside and Imbrozio Barbosa (1998); Conant et al.

(2001); Smith et al. (2008); Maia et al. (2009)). Burke et al. (1989) found that C losses due to land management were enhanced along with precipitation, while relative organic C losses were lower in clay soils, suggesting a close relationship between the management system, SOC stock, climate and soil texture. Frank et al. (1995) reported intensive grazing did not affect the SOC stock, although conversion from mixed species to single-species-dominant grassland reduced the SOC stock. Intensive grazing management effects relate closely to the soil moisture (Holechek et al. (1999)), and Conant et al. (2001) proposed that improved management systems, introduction of earthworms and irrigation resulted in considerable SOC accumulation. Conant et al. (2001) also mentioned that the intensity and timing of grazing management affect SOC accumulation by enhancing grass growth. Budge et al. (2011) discovered that Swiss alpine grasslands contain a large amount of labile SOC in the topsoil and stable SOC in the subsoil. Introducing grass species, which have high productivity or C allocation to deeper soil, could enhance SOC content (Smith et al. (2008)). Deep-rooted grasses could greatly increase SOC content (Smith et al. (2008)), and introducing legumes in grassland could enhance SOC amount by increasing N input to the soil (Soussana et al. (2004)). From grazed grassland, CH<sub>4</sub> emissions from ruminants and their dung are also significant (Smith et al. (2008)). Improving animal performance and vaccines against methanogenic bacteria are technologies that are currently under development to reduce CH<sub>4</sub> emissions.

Croplands management practices can be categorised as tillage (depth, timing), sowing, fertilisation, crop rotation, irrigation, harvesting, and use of fallow periods. The influence of cropland management on stable and active SOC pools, using radiocarbon dating at 0-20 cm, was studied in Hsieh (1992), finding that the stable SOC fraction is very resistant to biodegradation. Jenkinson et al. (2008) found that converting from conventional tillage to a non-tillage system could sequester C, but that the amount depended largely on crop rotation compared to monoculture. Alvaro-Fuentes et al. (2009) found that non tillage management with a long-fallowing period increased the amount of SOC and improved soil structure and aggregation. Appropriate levels of application of nitrogen and carbon by mineral fertilisers and manures, calculating the exact amount of nitrogen (N) and C required by the crop, is important to avoid unnecessary GHG emissions from agricultural lands (Cassman et al. (2003); Smith et al. (2008)). N and C input timing should also be considered carefully. However, Leifeld et al. (2009a) reported that there is no significant benefit of organic farming on SOC sequestration compared with management combining conventional mineral fertiliser and organic manure application, while Gattinger et al. (2012) show that SOC can be enhanced under organic systems.

Land-use change (LUC) is also considered to be an important factor which influences SOC change and CO<sub>2</sub> emissions to the atmosphere (Houghton et al. (1999); Caspersen et al. (2000); Conant et al. (2001); Guo and Gifford (2002); Post and Kwon (2008); Smith (2008); Poeplau et al. (2011); Leifeld et al. (2011); Smith et al. (2012)). 40-90 PgC are lost from the soil by cultivation and disturbance (Houghton et al. (1999); Smith (2008)). Most SOC loss occurs within the first few years following initial cultivation in Davidson and Ackerman (1993). Guo and Gifford (2002), in a meta-analysis, found that SOC decreases if land use changes from pasture to plantation (-10%), native forest to plantation or crop (-13% or -42% respectively), pasture to crop (-59%), although SOC increases if land use changes from native forest to pasture (+8%), crop to pasture or plantation (+19%, +18% respectively) and crop to secondary forest (+53%). C inputs are relatively small in croplands due to biomass removal in the harvested products and also due to tillage, which enhances SOC decomposition by disturbing soil aggregates (Smith (2008)). Poeplau et al. (2011) showed that grassland conversion to cropland may attain the SOC equilibrium state 17 years after conversion, and subsoil SOC changes are followed by changes observed in the topsoil. However, these results have high uncertainty, due to limited sample numbers. In Europe, significant land-use change has occurred over many centuries, and long-

term agricultural sites with fixed land-use and management are rare (Smith et al. (2008, 2012)). While many studies have been conducted regarding SOC changes due to managements and land-use changes, most researchers have used only topsoil samples (0-20 cm), and subsoil samples have rarely been studied until recently (Fontaine et al. (2007)).

### SOC and litter decomposition

Decomposition has been described as a key process in carbon and nutrient cycling, as litter decomposition is the major pathway of C release and inputs from and to soils, respectively. The most important controls over the rate of decomposition are climate, moisture and temperature, litter quality and soil microbial community composition (Melillo et al. (1982); Meentemeyer (1978)). Moreover, the chemical composition of decomposing material, such as C:N ratios and lignin content, are important for determining the decomposition rate (Melillo et al. (1982); Meentemeyer (1978)). In general, litter decomposition is negatively related to C:N ratios, lignin content and lignin:N ratios, and positively related to N concentrations (Melillo et al. (1989, 1982)). Some organic materials such as woods may take more time to decompose than others such as leaves (Melillo et al. (1982); Meentemeyer (1978)). The rapid plant residue decomposition rate by microbes and fungi mostly influences the SOM stability. Furthermore, some organic matter fractions consist of molecular aggregates of different degradation steps, which are hold together by organo-mineral interactions (Bol et al. (2009)). Such recalcitrant substances are a part of SOM, which made it necessary to apply chemical (alkaline/acid) extractions methods (e.g. Zimmermann et al. (2007)). The C turnover times largely depend on its form and geography. Some humus substances, covered with cellulose and lignin, are very stable, especially if lignin is complexed with amino acids (Schlesinger (1977)). According to Figure 1.2, non-living SOM is divided into at least three C pools: (1) the active pool with turnover rates of several years (root exudates, rapidly decomposed components of fresh plant litter); (2) the intermediate or slow pool with turnover rates of centuries; and (3) the passive pool with turnover rates of millennia (stabilized organic matter due to chemical or physical mechanisms) (Trumbore (1997)).

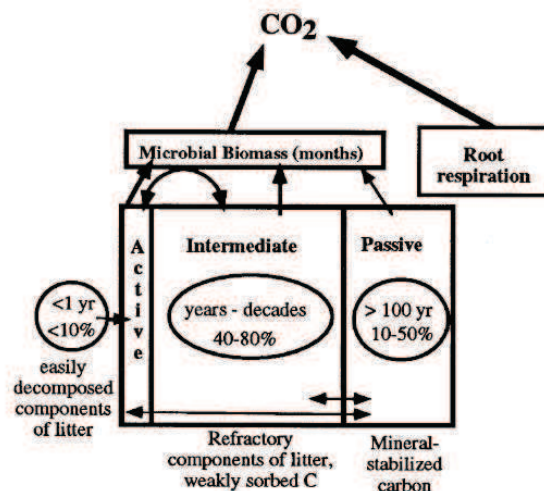


Figure 1.2: Conceptual model of SOM dynamics (Figure from Trumbore (1997), used with permission, Copyright (1997) National Academy of Sciences, U.S.A.)

### Modelling of SOC in agricultural lands

Whereas agriculture has a large greenhouse gas mitigation potential via SOC sequestration, the quantification of SOC stock changes from the regional to national scale has been shown to be

understudied (Van Wesemael et al. (2010)). For this purpose, biogeochemical models are very useful tools for finding the drivers of SOC distribution change (Van Wesemael et al. (2010)). There are a number of reasons for this. The carbon cycle is very complex and dispatched in many pools, which therefore make it very difficult to measure experimentally all of the components on temporal and spatial scales. For example, measuring changes in SOC stocks is extremely difficult due to the high spatial variability. Models are frequently used to estimate current and future stock changes. While models can be a substitute for measurements, they allow to integrate processes and advance our understanding of stock changes. In addition, once models are adequately calibrated, they can be used to investigate the effect of changes in management and climate. Several process-based ecosystem models have been considered since the 1900's. In this section, ecosystem models which are used in this thesis are introduced in order to review the relevant literature in relation to the existing models (RothC, DayCent, DNDC and PaSim), and to look back at the development of each model. For details on model structure and for a description of the submodels, see "Materials and methods".

#### *Rothamsted Carbon (RothC)-26.3 model*

The Rothamsted Carbon model (RothC) is a process-based model of carbon turnover in non-waterlogged soils depending on soil type. It was developed at Rothamsted Research in the UK using data from the Rothamsted long-term experiments (Jenkinson et al. (1987); Jenkinson (1990); Coleman and Jenkinson (1996)). It was originally developed for and parametrised to model the turnover of organic carbon in arable soils at the plot level, under a range of soil and climatic conditions. The model calculates total organic carbon ( $\text{t ha}^{-1}$ ) at a monthly frequency. The model calculates the SOC stock on an annual basis, from which the rate of change can be inferred. The current version is the Rothamsted Carbon (RothC)-26.3 model, which is accessible at <http://www.rothamsted.bbsrc.ac.uk/aen/carbon/rothc.htm>.

In the model, SOC ( $\text{t C ha}^{-1}$ ) is divided into decomposable plant material (DPM) and resistant plant material (RPM), both of which subsequently decompose into:  $\text{CO}_2$  which leaves the system; microbial biomass (BIO); humified organic matter (HUM); and chemically stabilised organic matter (COM). The COM compartment becomes the inert organic matter (IOM) compartment afterwards (Jenkinson (1990)). Incoming plant carbon is split between DPM and RPM, depending on the DPM/RPM ratio of the particular incoming plant material.

Jenkinson (1990) used the RothC-26.3 model to study the release of  $\text{CO}_2$  to the atmosphere due to SOC decomposition, which further enlarges the warming trend, due to global warming. The RothC model can simulate 0-23 cm as a bulk soil. Nitrogen and C dynamics in the soil are not intercorrelated in the RothC-26.3 model (McGill (1996)). The RothC-26.3 model can be used to calculate the organic C input rate for a specified stock of soil organic C and net primary production (McGill (1996); Jenkinson et al. (1999)). One advantage of the RothC-26.3 model is lower requirements for input data. RothC was originally developed for arable soils, but it has been extended to other site types and successfully applied to long-term, plot-level experiments across a range of soil and climatic conditions, including grassland, cropland and forest soils in the UK, Germany, England, USA, Czech Republic, China and Australia (Coleman et al. (1997); Guo et al. (2007); Yang et al. (2003)). RothC has also been successfully applied to the simulation of changes in SOC stocks due to land-use change. Romanya et al. (2000) used a chronosequence approach to study changes in SOC after afforestation of Mediterranean agricultural soils, and found that the changes in SOC were accurately simulated by RothC. Jenkinson and Coleman (2008) first published a model version (RothPC-1) allowing to simulate subsoil (0-23, 23-46, 46-69 and 69-92 cm).



### CENTURY model

CENTURY was developed to simulate long-term (decades to centuries) SOM dynamics, plant growth, nitrogen (N), phosphorus (P) and sulphur (S) for different plant-soil systems (McGill (1996)). The CENTURY model was originally developed for grassland soils (Parton et al. (1987)) but has since then been widely used for arable (e.g. Falloon and Smith (2002)) and forest soils (e.g. Kirschbaum and Paul (2002)). The model can simulate the dynamics of grassland systems (i.e. plant productivity and decomposition), agricultural crop systems, forest systems and savannah systems, by taking into account climate, human management and soil properties (Parton et al. (1987, 1993)). Similar to RothC, it operates on a monthly time step, and its major input variables are soil texture and weather data. Similar to other models of SOM dynamics, the soil organic matter submodel is based on multiple compartments for SOM (Jenkinson (1990); Jenkinson and Rayner (1977)): structural, metabolic, active, slow and passive SOC pools, assuming that the lignin-to-N ratio controls the split of plant residue into structural and metabolic material SOC pools. The nitrogen submodel has the same structure as the carbon submodel, estimating that most N is bonded to C (Parton et al. (1987)). Paustian et al. (1992) investigated the influence of the amount and quality of organic C and N fertiliser on C and N soil dynamics.

CENTURY has been successfully applied to long-term, plot-level experiments across a range of soil and climatic conditions including grassland, cropland and forest soils in the UK, Germany, Czech Republic (Kelly et al. (1997)), Denmark (Foereid and Høgh-Jensen (2004)), Australia (Kelly et al. (1997)), Brazil (Cerri et al. (2007)) and grassland soils in Germany. In order to improve phenological development of vegetation, nitrogen ( $\text{N}_2\text{O}$ ,  $\text{NO}_x$ ) and  $\text{CH}_4$  dynamics in varied grasslands, a daily version of CENTURY (DAYCENT) was developed in 1998 (Parton et al. (1998)). Since then, DAYCENT has been tested in many studies (Parton et al. (2001); Del Grosso et al. (2001, 2005); Li et al. (2006); Del Grosso et al. (2006); Stehfest et al. (2007); Del Grosso et al. (2009); Yeluripati et al. (2009)).

### Pasture Simulation Model (PaSim) model

Pasture Simulation Model (PaSim) is a process-based grassland biogeochemical model, simulating dry matter production, the  $\text{CO}_2$  fluxes, NEE (Net ecosystem exchange), GPP (Global primary production), Reco (Ecosystem respiration), SOC pools dynamics, soil  $\text{N}_2\text{O}$  emissions from nitrification and denitrification at grasslands, and  $\text{CH}_4$  emissions from grazing livestock and water in productive pastures (Riedo et al. (1998, 2000); Calanca et al. (2007); Vuichard et al. (2007a); Graux et al. (2012b,a)). The PaSim model was developed from the Hurley Pasture Model (HP-model) of Thornley (1998) by Riedo et al. (1998), who expanded the plant submodel for a reproductive developmental stage of a grass sward, allowing for dynamic effects in the fractional nitrogen content of plant structural dry matter, simulating leaf stomatal resistance, and altering the temperature dependence of processes which is linear in the HP-model. Further extensions to the model have been carried out by Schmid et al. (2001) in relation to the production and emission of  $\text{N}_2\text{O}$  from grassland, and by Riedo et al. (2000) in relation to the exchange of ammonia with the atmosphere. More recently, Vuichard et al. (2007a) have adapted the model in relation to water stress, senescence and the effects of diet quality on the emissions of  $\text{CH}_4$  from grazing animals, as well as the performance (i.e. milk and meat production) of grazing animals (Graux et al. (2012a,b)). The PaSim model operates on an hourly time step, and its major input variables are soil texture and weather data.

The model consists of five interacting modules: microclimate, soil, vegetation, herbivores and management. The soil module is based on the CENTURY soil decomposition approach, where litter decomposes over the total soil depth into structural and substrate components, supplying SOC into the structural and metabolic soil pools.

The model has been tested for a number of sites in Switzerland: Bern, Sion, Davos, Oberbuetschel and Kerzersmoos. Calanca et al. (2007) tested the PaSim model in various sites in Europe: Bugac-Puszt (Hungary), Easter-Bush (UK), Carlow (Ireland), Laqueuille (France) and Oensingen (Switzerland) (Riedo et al. (2000); Schmid et al. (2001); Vuichard et al. (2007a,b)), as well as climate-change impact studies (Graux et al. (2012a)), including an assessment of the contribution of forage-based systems on global warming (Graux et al. (2012b)).

#### DNDC model

The denitrification-decomposition (DNDC) model is a process-based computer simulation model of soil C and N biogeochemistry in agricultural ecosystems (Li et al. (1992, 1994)). This model predicts crop yield, soil carbon sequestration, nitrogen leaching, and trace gas emissions in agroecosystems, on a scale that ranges from site to region. The model operates at a daily time step and consists of two components. The first component consists of the soil climate, crop growth and decomposition submodels (e.g. soil temperature, moisture, pH, substrate concentration), which is driven by ecological drivers (e.g. climate, soil, vegetation and anthropogenic activity). The second component, consisting of the nitrification, denitrification and fermentation submodels, predicts NO, N<sub>2</sub>O, N<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub> fluxes based on the modelled soil environmental factors. Plant growth is modelled using a daily crop growth curve (specific to the plant type) to calculate the daily N-uptake, which was extracted from the available soil NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> pools down to the root depth (Giltrap et al. (2010)). Zhang et al. (2002) developed a more detailed physiological/phenological model of crop growth (crop-DNDC).

The SOC component is divided into four major pools: plant residue (i.e. litter), microbial biomass, humads (i.e. active humus) and passive humus. Each pool consists of two or three sub-pools with different specific decomposition rates. Daily decomposition rates for each sub-pool are determined by the pool size, the specific decomposition rate, soil clay content, N availability, soil temperature and soil moisture (Li et al. (1994, 1992); Li (2000)). During SOC decomposition, the decomposed carbon and nitrogen is allocated into other SOC pools and partially lost as CO<sub>2</sub>. Dissolved organic carbon (DOC) is produced as an intermediate during decomposition. However, DOC may be immediately consumed by the soil microbes.

Several modifications and improvements of DNDC have been carried out. Xu-Ri et al. (2003) improved the DNDC nitrification submodel with regards to the impact of soil frost and snow cover on N<sub>2</sub>O fluxes. Greenhouse gas fluxes from cropping lands in Japan, China and Thailand were used to validate DNDC performance in Cai et al. (2003). Pathak et al. (2005) modified DNDC crop physiological and phenological parameters for Indian rice fields. Sleutel et al. (2006) validated DNDC with detailed and large-scale data, and DNDC has been used in many studies so far (Smith et al. (2002b); Tang et al. (2006); Babu et al. (2006); Levy et al. (2007); Tonitto et al. (2007); Abdalla et al. (2009); Grote et al. (2009); Giltrap et al. (2010); Smith et al. (2010)) with field data from around the world.

Since then several relevant side-models have been developed such as Manure-DNDC (Li et al. (2012)), Forest-DNDC (Miehle et al. (2006); Lamers et al. (2007); Butterbach-Bahl et al. (2009)), ForestDNDC-tropica, PnET-N-DNDC (Photosynthesis and Evapotranspiration-Nitrification-DNDC, Stange et al. (2000); Li et al. (2000); Butterbach-Bahl et al. (2001); Kiese et al. (2005)), MoBiLE (Modular Biosphere Simulation Environment)-DNDC (Chirinda et al. (2011)), US Cropland Greenhouse Gas Calculator, etc.

#### **Model initialisation**

In order to apply a model to the simulation of specific periods, initialisation is essential. To do so, most model initialisation techniques are based on the underlying assumption that the

observed carbon stocks represent equilibrium stocks, which allows to determine the initial state of a model for given constant average input and parameter set. To achieve this equilibrium state or steady state, the most common model initialisation method is to run the model over a few thousand years, repeatedly using recent management and weather data, until an equilibrium state is attained (spin-up-runs) (e.g. Smith et al. (2005)). However, observed soils might be far from equilibrium due to very long turnover times of stable compounds (i.e. passive pool) and disturbances such as fire, erosion, land management or land use change. Accordingly, the equilibrium assumption is only valid for steadily increasing carbon stocks of very old soils, which explains the reported mismatch between model simulation and observation data (Bruun and Jensen (2002); Pietsch and Hasenauer (2006); Wutzler and Reichstein (2007); Basso et al. (2010); Hashimoto et al. (2011)). Moreover, due to land management changes, the management and weather data that is used might not be representative for the purposes of setting the model to steady state conditions (Bruun and Jensen (2002)). Not surprisingly, model initialisation became an important research subject, as model simulation is largely affected by the initial SOC values, management and weather data.

Initialisation with measured SOC data, however, showed that model SOC pools cannot be initialised by a simple measurement (without soil fractionation or dividing soil depth into different strata etc), and using detailed pre-experimental data will improve model initialisation (Bruun and Jensen (2002); Smith et al. (2002a); Yeluripati et al. (2009)). However, reliable long-term management and weather data is difficult to collect. At the same time, Zimmermann et al. (2007); Skjemstad et al. (2004) succeed in initialising the Rothamsted carbon (RothC) model, using a complex physical and chemical soil fractionation method. Although RothC has also been applied with success in a number of studies, this method has not been tested for other soil models yet. Furthermore the fractionation method is quite labour intensive.

Assuming that the most useful initialisation method would include a precise estimate of carbon inputs (i.e. Bruun and Jensen (2002); Smith et al. (2002a)), a number of studies introduced “relaxed carbon cycle assumptions” to initialise given SOC pools (Wutzler and Reichstein (2007); Carvalhais et al. (2008); Hashimoto et al. (2011)).

For example, Wutzler and Reichstein (2007) assumed all pools are in equilibrium except the slowest pool. A transient correction method was applied during the spin up run, where the amount of the slowest SOC pool was reduced until the sum of total SOC (i.e. bulk soil) at the steady state would be equal to the observed SOC. However, this method was only applied to study sites which have not been disturbed for more than a century. As land use change is becoming a force of global importance and global croplands, pastures, plantations, and urban areas have expanded in recent decades (Foley et al. (2005); Yeluripati et al. (2009)), European land-use has also changed considerably in recent times. Thus, this assumption may not be realistic.

Carvalhais et al. (2008) used the “relaxed assumption” in a simple Net Ecosystem Production (NEP) prediction model comprising parameters, related to primary production and soil heterotrophic respiration (i.e. light use, temperature, water storage and C turnover rates). Carvalhais et al. (2008) results show that the use of relaxed assumptions on scaling soil carbon pools such as microbial and the slow turnover rates’ pools improve NEP efficiency by 21% and reduce the normalised average error in the model results by 92%. As a consequence, this initialisation method has been shown to be very useful, although uncertainty remains whether this method can be adapted to more complex process-based ecosystem models.

Further studies have adapted the Carvalhais et al. (2008) ‘relaxed assumption’ to the passive SOC pools of version 4 of the CENTURY model (Hashimoto et al. (2011)). In the adapted version, in addition to the relaxed assumption of the active and slow pools (Carvalhais et al. (2008)), Hashimoto et al. (2011) conducted three SOC scaling schemes (active+slow, slow+passive and

all SOC pools), to the adjusted microbial pool and the slowest C pool (that is, the pool with the slowest turnover rate). Results show that a more stable model prediction is obtained in the slow relaxed assumption scenario by either scaling slow+passive SOC pools, or else by scaling all SOC pools proportionally, compared to an initialisation that adjusts the active and slow SOC pools only (Hashimoto et al. (2011)). According to the SOC scaling schemes reported by (Hashimoto et al. (2011)), an initialisation of the slow and passive SOC pool improves model results considerably. However, it is uncertain whether these methods could apply to all of the ecosystem models and users (e.g. scaling several SOC pools simultaneously during the same spin-up run, beginning from the middle of the spin-up run, changing equations within the model program). Therefore, the objective in this study is to propose a simple and user friendly model initialisation method.

### 1.3 Objective and outline of the thesis

Though agricultural sector has a large potential for GHG mitigation by SOC sequestration, the accurate quantification of SOC stock changes from regional to national scale still remains a challenge (Van Wesemael et al. (2010)). For this reason, accurate model simulation results are essential. In past decades, the absence of long term data made it difficult to validate models with reliable observed long-term data. Nowadays, detailed weather data (e.g. wind speed, relative humidity, radiation) and land management data (mowing or grazing date, animal stocking rate, fertilisation dates and amount, sowing date, standing biomass, tillage depth and date), are available for a number of sites and years. Even though, information on different SOC fractions and soil properties (soil pH, bulk density, soil texture) regarding each soil depth are still scarce for verification and initialisation.

To overcome this problem, in this PhD study, I carried out a soil re-sampling in 2011/2012 and I conducted the detailed soil fractionation (Zimmermann et al. (2007)) in each soil profile. In order to separate anthropogenic agricultural management induced changes from those induced by natural forces on GHG emissions and SOC distribution, we chose five paired plot experimental sites which comprise adjacent contrasting agricultural management regimes (2 grasslands, 1 grassland with organic soil, 2 croplands). These sites possess detailed weather data (including wind speed, relative humidity, radiation) and land management data which are essential to run ecosystem models. These sites possess also C flux data (GPP, NEE and Reco) for a period of ~10 years, allowing to validate model simulations and to give sufficient confidence in model results for the future.

Model initialisation remains an issue, as detailed long term data on soil properties and SOC are still missing. This PhD thesis further aimed to assess different model initialisation methods, in order to determine the most appropriate initialisation method for process-based ecosystem models.

The PhD report is constructed in following structure. Chapter 1 introduces the main topic of the thesis: Section 1.1 contains the general introduction. Section 1.2 demonstrates the existing knowledge in the relationship among SOM, GHG emissions in agricultural lands (grassland and cropland), as well as the recent agricultural ecosystem process-based model initialisation studies, to provide background on the issue. The outline (main objectives) of the thesis is given in section 1.3. Chapter 2 (Material & Methods), provides a detailed description of the study sites, soil sampling method, soil fractionation method and process-based ecosystem models.

In Chapter 3 (1st manuscript), comprises an analysis of soil data with regard to SOC distribution changes due to land management systems, using the soil fractionation method (Zimmermann et al. (2007); Wurster et al. (2010)) for four different agricultural lands (grassland and

cropland) in Europe. Results of study sites involve SOC distribution in different soil fractions, regarding each soil profile for four contrasting management regimes. This study may suggest that management practices influence SOC more rapidly in organic soils compared to mineral soils, presumably due to a larger quantity of particulate organic matter (POM) in organic soils, being sensitive to land management change.

Chapter 4 (2nd manuscript), takes the results of Chapter 3 and analyses the current status of SOC whether they are at the steady state and how many years are required to attain the steady state, using the Rothamsted Carbon (RothC) model. This investigation was adopted to find a appropriate initialisation method for RothC model. After 10 years of continuous management, SOC was had not attained steady state at any site except Reeuwijk (NL) organic soil site, suggesting the common initialisation method of spin-up run (i.e. repeating recent management and meteo data) is not the appropriate model initialisation method in mineral soil sites. This study examined other initialisation schemes, whereby the total and SOC fractions (i.e. active, slow, inert, etc.) were adjusted to be equal to the measured total SOC and SOC fractions, by reducing or raising C input during spin-up run RothC model. Analyses reveal the adjusting the equilibrium total SOC to the measured total SOC value as the most appropriate method for RothC initialisation. As the total SOC includes all of the SOC pools data and total SOC data is available at many experimental sites, this initialisation method is accessible for more researchers.

The proposed model initialisation method for the RothC model (Chapter 4), were further tested for three process-based ecosystem models (Pasim, DNDC and DayCent) in order to analyse the impact of different model initialisations on model outputs; C fluxes such as GPP, NEE and Reco (Chapter 5, 3rd manuscript).

Chapter 6 synthesises, methods and findings of the thesis, and provides a critical analyses on lessons learned and general conclusions.









## **Chapter 2**

### **Material and Methods**





## 2.1 Site description

In this study, we chose five long-term (up to 10 years) European experimental sites from the CarboEurope Integrated Project (CEIP) ecosystem flux tower network, which have two adjacent contrasting management system plots (a paired-site): Laqueuille (Intensive/extensive grazing and high/no N input grassland, France) sampled in November 2008 and March 2011, Oensingen (high/low N&manure input and cut/no-cut grassland, Switzerland) sampled at the end of August 2012, Reeuwijk (Grazing peat grassland with fertilizer&manure input/ no-input, Netherlands) sampled in January 2011, Hertfordshire (ploughed/non-inverted and high/no N input cropland, United Kingdom) sampled in November 2003 and Carlow (Conventional & N input and reduced tillage & no N cropland, Ireland) sampled in January 2011. At these five sites, paired-plot experiments have been carried out for between 10 and 25 years. For reasonable sample sizes and statistical power, it may take >10 years for significant differences in SOC due to contrasting management to be observed (Smith, 2005).

### 2.1.1 Grassland

#### Laqueuille, France

Laqueuille (France) site is situated at 45° 38'N, 2° 44'E. Soil type is an Andosol (Klumpff et al. (2011)). Mean annual temperature is 7.68 °C, mean annual precipitation is 928.5 mm and elevation is 1040 m a.s.l. This grassland site is managed by INRA Clermont-Ferrand, UREP since 2002 until the present. Previously, this site was cultivated as a cropland from the beginning of 20th century to the 1950s. Sometime around 1950s, this site was converted to permanent grassland. This site was managed until 1980 by mowing, grazing, cattle manure and slurry application. Since the paired plot experiment started in 2002, the site was split into two contrasting management plots (intensive management and extensive management systems). These two management systems have been maintained until today. The intensive management system plot is grazed from spring until the summer by livestock (0.9-1.2 livestock unit (LSU)/ha). Ammonium nitrate was applied three times (191.5 kg N ha<sup>-1</sup>year<sup>-1</sup>) each year. The extensive plot is also grazed during the same period as the intensive plot by livestock (0.5-0.6 LSU/ha), though it has not been mown. No fertilizers were applied to the extensive plot. The mean soil pH was 5.13 (±0.23) for the intensive plot and 5.25 (±0.1) for the extensive plot in 2008, and 5.46 (±0.24) for intensive plot and 5.40 (±0.2) for extensive plot in 2011. For more detail, see Table 3.1 and Table 3.2 in Section 3.2.1 or Klumpff et al. (2011); Soussana et al. (2007); Allard et al. (2007).

#### Oensingen, Switzerland

The Oensingen site is situated in central Switzerland at 47°17' N, 7°44' E. The soil type is a Eutric-stagnic cambisol and the climate is temperate continental. The mean annual temperature is 9 °C, mean annual precipitation is 1100 mm and elevation is 450 m a.s.l. (Flechard et al. (2007)). This grassland is managed by Agroscope Reckenholz-Tänikon Research Station ART. The previous management of this site was a ley-arable rotation with an 8 year rotation (summer/winter wheat, rape, maize and bi-/tri-annual grass-clover mixture). Annual mean Nitrogen (N) input was 110 N ha<sup>-1</sup>year<sup>-1</sup>. The last ploughing took place in November 2000 and the grass was sown after ploughing. The site was split into two contrasting management plots in November 2000: intensive and extensive management. Until the present, the site is maintained as a paired plot experiment. The intensive management plot consists of 7 species of sown grassland (Ammann et al. (2009)) which is mown 4 times/year. No animal grazing is applied. The mean N

input over a 5 year period is  $230 \text{ kg N ha}^{-1} \text{ year}^{-1}$  divided into 2-3 applications each year. The mean carbon (C) input from 2002 to 2004 was  $47 \text{ g C m}^{-2} \text{ year}^{-1}$  dividing into 1-2 applications each year. The intensive plot was ploughed and the same 7 species were re-sown. The extensive management plot is a mixture of over 30 species of sown grassland and is mown 3 times each year (1st mowing is never before 1st June). There is no grazing by livestock and no fertiliser was applied. The mean soil pH is  $6.85 (\pm 0.49)$  for the intensive plot and  $5.81 (\pm 0.65)$  for the extensive plot. The soil contains carbonate. For more detail, see Table 3.1 and Table 3.2 in Section 3.2.1 or Ammann et al. (2007, 2009); Flechard et al. (2005); Leifeld et al. (2011); Flechard et al. (2007).

## Reeuwijk, Netherlands

Reeuwijk (Netherlands) site is situated at an altitude -1.7 to -1.6 m a.s.l.,  $52^\circ 2' \text{N}$  and  $4^\circ 47' \text{E}$  (intensive plot) and  $52^\circ 1' \text{N}$  and  $4^\circ 46' \text{E}$  (extensive plot). The soil type is a Fibric Eutric Histosol. The topsoil is peaty and clayey, and the subsoil is Eutrophic peat (Stolk et al. (2011)). The paired plots are located on the polder in the west of the Netherlands. Mean annual temperature is  $9.80^\circ \text{C}$  and mean annual precipitation is 800 mm (Jacobs et al. (2007); Veenendaal et al. (2007); Schrier-Uijl et al. (2008, 2010)). This site also has two contrasting management plots, though these plots are further apart than for the other sites (See Figure 2.1).

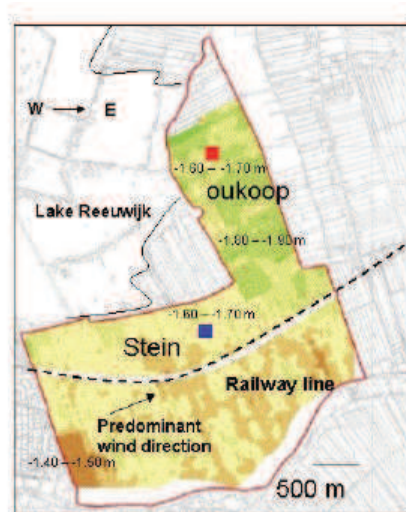


Figure 2.1: Reeuwijk INT (Oukoop) and EXT (Stein) sites (From Veenendaal et al. (2007))

This site was managed by University of Wageningen, Nature Conservation and the Plant Ecology Group, Wageningen, Netherlands between 2000 and 2004. The intensively managed site is called Oukoop and the extensively managed site is called Stein. Each management plot had an independent eddy-covariance tower. Both plots in Reeuwijk had been under intensive management (deep drainage, application of manure and fertiliser and grazing and harvesting of grass) for 30+ years before the start of the measurement period. About 25 years ago, the extensive plot was taken out of intensive management, and gradually became a meadow bird reserve which was established about 14 years ago (higher water table, no inputs of manure and fertiliser, low grazing, lower harvest rate of grass (see Veenendaal et al. (2007); Schrier-Uijl et al. (2008, 2010)). The paired plot experiment was started in the 1980's. The intensive management system was dairy farming and mowing, with grazing between the middle of May to the middle

of September each year. Mowing occurred 3 times per year, as did 2-3 short periods of grazing by livestock. The mean annual manure application level was  $1.67 \text{ kgC ha}^{-1}\text{year}^{-1}$  and  $309.67 \text{ kg N ha}^{-1}\text{year}^{-1}$ . The mean annual fertiliser application rate was  $88 \text{ kg ha}^{-1}\text{year}^{-1}$  divided into 2-3 applications per year. Manure and fertiliser were not applied in winter. Dominant grass species were rye grass and bluegrass and clover occupied less than 1% of the plot. The extensive management plot was a meadow bird reserve. This plot was mown twice after 15th June each year, with a short period of grazing by livestock on most of the plot, with a few areas grazed over the whole summer. This plot was gradually taken out of intensive grassland management after more than 20 years (Schrier-Uijl et al. (2008, 2010)). No manure and no fertilizer were applied to this plot. The mean soil pH is  $6.01 (\pm 0.08)$  for the intensive plot and  $5.34 (\pm 0.21)$  for the extensive plot. For more detail, see Table 3.1 and Table 3.2 in Section 3.2.1 or Jacobs et al. (2007); Veenendaal et al. (2007); Schrier-Uijl et al. (2008, 2010).

## 2.1.2 Cropland

### Hertfordshire, United Kingdom

Hertfordshire (UK) arable site is situated at an altitude 140 m a.s.l. and  $51^{\circ} 47' \text{N}$ ,  $0^{\circ} 28' \text{W}$ . The mean annual temperature is  $9.46^{\circ}\text{C}$  and the mean annual precipitation is 703.5 mm. Soil type is Chromic Luvisols and Orthic Acrisols (silt and clay loam) from FAO soil classification (Berthelin (1999)). The clay constitutes about 25% of the top soil and silt about 50%. Stones (flints) occupy about 10.8% of the top soil volume. The site is owned by W. Hill & Sons, Wood Farm in Hertfordshire UK. Soil sampling and eddy-covariance measurements were performed by the Department of Sustainable Soils and Grassland Systems, Rothamsted Research, Hertfordshire, UK in a research project funded by the UK Biotechnology and Biological Sciences Research Council, grant number D16053. This site is also a paired plot site. The experiment was conducted from 2001 to 2008. Dried soil samples were taken in November 2003. One management plot is ploughed and the other is minimum tillage. The site was grassland in the 1940s. Regarding the ploughed plot, the plot was grassland until the late 1960s, then it was converted to cropland (except 1972-1973 and 1976-1978, the plot was ley grassland). From 1980 to 1995, the mean average NPK input was  $217.71 \text{ kg ha}^{-1}\text{year}^{-1}$  (mostly N:P:K=5:24:24) and mean annual nitrogen fertiliser input was  $193 \text{ kg N ha}^{-1}\text{year}^{-1}$ . The mean annual yield was  $5.77 \text{ t ha}^{-1}\text{year}^{-1}$ . The crop rotation was around 4 years rotation with winter wheat, winter oilseed rape and spring peas. From 2003 to 2008, in the ploughed plot, the mean annual NPK input was  $49.27 \text{ kg ha}^{-1}\text{year}^{-1}$  and the  $\text{NH}_4^+$  input was  $152.79 \text{ kg ha}^{-1}\text{year}^{-1}$ . The crop rotation was around 5 years with winter wheat, winter oilseed rape and spring peas (as before). The mean annual yield (2003-2008) was  $5.9 \text{ t ha}^{-1}\text{year}^{-1}$ . Concerning to minimum tillage plot, 50% of the plot was converted to arable land. Early to late 1960, all of the plot was converted to arable land (except 1977-1979: ley grassland). From 1980 to 1995, the plot was ploughed and the mean annual NPK input was  $211.48 \text{ kg ha}^{-1}\text{year}^{-1}$  (mostly N:P:K=5:24:24 or 0:24:24) and the mean annual N fertiliser input was  $195.29 \text{ kg N ha}^{-1}\text{year}^{-1}$ . The Mean annual yield was  $5.89 \text{ t ha}^{-1}\text{year}^{-1}$ . In 1986, the plot was split into two and in 2000 the plot was set-a-side for a year. The crop rotation was around a 5 years rotation with the same crops as the ploughed plot. Minimum tillage management has started from 2001. Annual average (2003-2008) NPK input was  $43.50 \text{ kg ha}^{-1}\text{year}^{-1}$  and the  $\text{NH}_4^+$  input was  $57.63 \text{ kg ha}^{-1}\text{year}^{-1}$ . The crop rotation was the same as the ploughed plot. The mean annual yield (2003-2008) was  $6.28 \text{ t ha}^{-1}\text{year}^{-1}$ . This soil contains carbonate. Mean soil pH values are  $6.94 (\pm 0.23)$  for the intensive plot and  $6.56 (\pm 0.31)$  for the extensive plot. For more detail, see Table 4.1 and Table 4.2 in Section 4.2.1.

## **Carlow, Ireland**

Carlow (Ireland) site situates at altitude 57 m a.s.l., 52° 52'N and 6° 54'W. The mean annual temperature is 9.40 °C and the mean annual precipitation is 824 mm (Van Groenigen et al. (2010a,b); Walmsley et al. (2011)). Soil type is Eutric Cambisol (Osborne et al. (2010)). The site's land history is described in Van Groenigen et al. (2010a,b). Prior to 1847, the site was pasture, then from 1847 to 1977 the land was used as a school playing field under grassland. From 1977 to 1992, the site was mainly improved grassland with grazing and silage. In 1993, the site was converted to cropland with ploughing and crop rotation. From 2000, the site was cultivated mainly for spring barley for 3 consecutive years. From 2003, the paired plot experiment started. One management is the conventional tillage plot (20-25 cm depth ploughing) and the other is no-tillage plot. Since 2003, the site has been cultivated for spring barley. Regarding the conventional tillage plot, the plot is ploughed in March each year. After ploughing, spring barley was sown. The mean annual fertiliser input was 140 kg N ha<sup>-1</sup> year<sup>-1</sup>. The annual average grain harvest (2003-2010) was 6.34 t ha<sup>-1</sup> year<sup>-1</sup>. Regarding the no-tillage plot, harrowing (10-15 cm depth) was performed once per year in each August or September. Spring barley is sown in March each year. The mean annual fertilizer input is 140 kg ha<sup>-1</sup> year<sup>-1</sup>. The mean annual grain harvest (2003-2010) was 5.99 t ha<sup>-1</sup> year<sup>-1</sup>. Mean soil pH is 7.40 for the conventional tillage plot and 6.83 for no-tillage plot. For more detail, see Table 3.1 and Table 3.2 in Section 3.2.1 or Walmsley et al. (2011); Osborne et al. (2010); Davis et al. (2010).

## **2.2 Soil sampling and soil organic carbon (SOC) analysis method**

### **2.2.1 Soil sampling method**

In autumn/winter 2011/2012 soil sampling campaigns were carried out for the four agricultural paired-sites (8 plots in total). In each plot, 6 soil cores (60 cm depth for Laqueuille (FR) and Reeuwijk (NL) and 40cm depth for Oensingen (CH) and Carlow (IE)). At the intensive plot in Reeuwijk (NL), 4 soil cores were sampled at equal intervals (10m) along 60cm transect. Each soil core was separated into 0-5 cm, 5-10 cm, 10-20 cm, 20-40 cm and 40-60 cm depth layers that were air dried under laboratory conditions. Regarding Hertfordshire (UK), soil sampling (down to 20 cm soil depth, 8 soil cores each plot) was carried out in November 2003. UK site soil cores were not cut into any strata.

We have to mention that one of the limits of this experimental design using eddy covariance flux tower sites is the absence of replicates, thus a possible pseudo replication of soil samples (i.e. 6 soil cores per field). To overcome this problem, we have chosen a sampling design which covers foot-print area for comparing with flux measurement and model flux output (see Chapter 5). For sampling at Laqueuille (FR), Carlow (IE) and Reeuwijk (NL) sites, we followed to the sampling protocol (See Figure 2.2). For each adjacent field, soil within the footprint of the eddy-flux tower were sampled (i.e. about a soil core every 10m).

Sampled soils were immediately stored in a refrigerator at 4 °C. They processed this on the sampling date. They were thoroughly mixed. After weighing the wet soil weight, they placed soil samples into at 60 °C oven for 24 hours to dry.

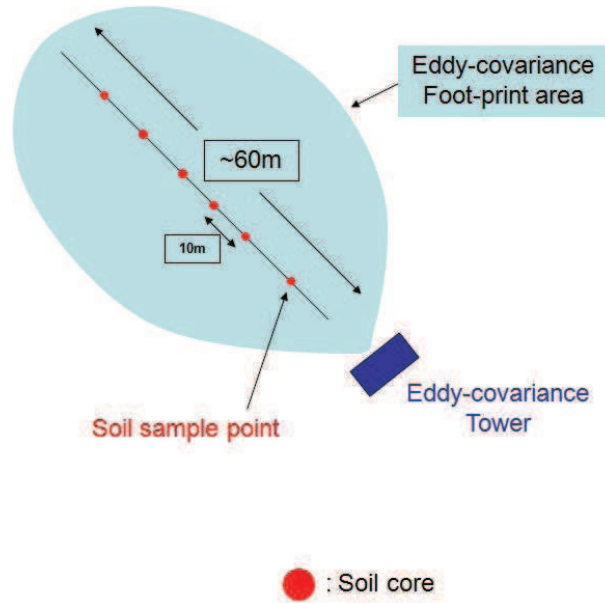


Figure 2.2: The soil sampling protocol

## 2.2.2 Soil pH measurement

We measured soil pH concerning Laqueuille (FR), Oensingen (CH), Reeuwijk (NL) and Carlow (IE) soil samples. Hertfordshire (UK) soil sample's soil pH have already measured at Department of Sustainable Soils and Grassland Systems, Rothamsted Research. For soil pH measurement, we followed to Soon and Hendershot (1993). We weighted 10g of air-dried mineral soil which was sieved at 2mm. Place them in a small beaker and added 20 mL of ultra pure water. Concerning organic soils (Reeuwijk, NL), we weighted 2g in 20 mL of ultra pure water. We stirred these samples for 1 hour, then we let them stand for 1 hour. We agitated the bottom of samples during this measurement. Hertfordshire (UK) soil sample's soil pH was measured in water with following to Jones Jr (1999).

## 2.2.3 Soil fractionation method

We used the method which was improved from Zimmermann et al. (2007) (See Figure2.3) soil fractionation method (Wurster et al. (2010)) concerning the step of separating heavy fraction (S+A) and light fraction (POM) from the  $>63\ \mu\text{m}$  soil fraction.

For separating S+A and POM, sodium ploytungstate (SPT) at  $\rho=1.85\text{g}/\text{cm}^3$  is used in Zimmermann et al. (2007) method, as SPT salt is non-toxic and can be mixed with deionised water (DI- $\text{H}_2\text{O}$ ). We took 30g dry soil for starting soil fractionation. Then, we disrupted the soil in 160mL DI- $\text{H}_2\text{O}$  with using ultrasonic probe (SONICS, vibracell, VCX500) at 34% amplitude and 22J/mL. After the disruption, wet sieving at  $63\ \mu\text{m}$  was done.

The fraction  $<63\ \mu\text{m}$  was centrifuged at 1800 rpm for 4 minutes, and the fraction between  $63\ \mu\text{m}$  and  $0.45\ \mu\text{m}$  was classified as silt and clay, and the  $<0.45\ \mu\text{m}$  fraction was classified as Dissolved Organic Carbon (DOC).

Silt and clay fraction was oxidised by Sodium Hypochlorite ( $\text{NaOCl}$ ), and the rest fraction after the oxidation is classified as resistant soil organic carbon (rSOC).

The fraction  $>63\ \mu\text{m}$  was dried in the oven then SPT was added from 20 to 30mL with



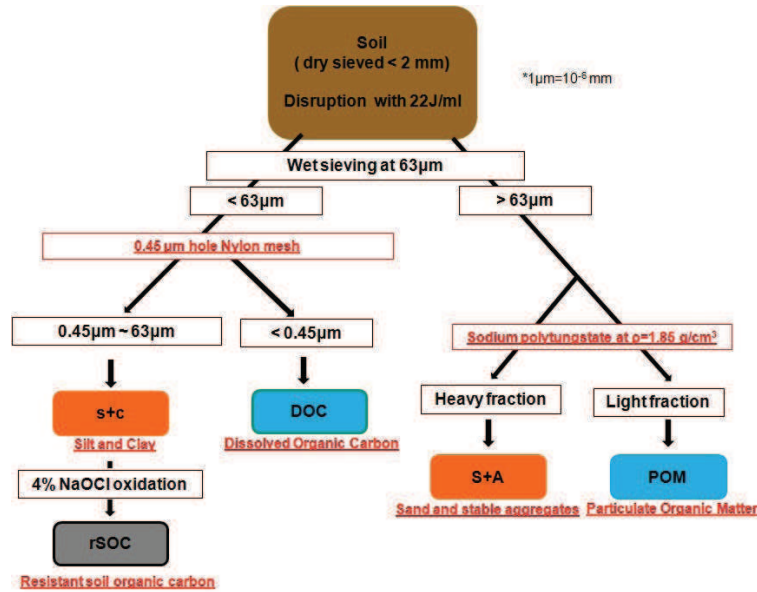


Figure 2.3: The Zimmermann Soil Fractionation method (based on Zimmermann et al. (2007))

using a wash bottle for each centrifuge tube in this study. The solution is mixed by turning the centrifuge tube slowly and gently from side to side, until well mixed with enough SPT solution and the  $>63 \mu\text{m}$  soil fraction. This process enables the organic material to float on the surface in a centrifuge tube. Separation usually takes place with using light centrifugation. In Zimmermann et al. (2007) method, the centrifugation was taken place at 1800 rpm for 15 minutes then they put the centrifuge tube at stable place for overnight. Then, usually floating light fraction (POM: Particulate Organic Matter) is either poured off or aspirated. However, it is difficult to separate POM and heavy fraction (S+A: Sand and Aggregates) with this method because POM tends to stick to the centrifuge tube walls. Furthermore, this method may remix the separated POM and S+A while pouring POM off or aspirating it (Wurster et al. (2010)). In Wurster et al. (2010), after separating process of  $>63 \mu\text{m}$  soil fraction into S+A and POM with SPT, the centrifuge tube was carefully placed in a freezer as upright position. The frozen sample was removed from the freezer and the surface material is immediately thawed off with using DI- $\text{H}_2\text{O}$  from a wash bottle and poured into a beaker. This process should be continued until seeing the frozen surface of S+A in the centrifuge tube. Frozen SPT solution and surface material can be readily recovered with washing off with DI- $\text{H}_2\text{O}$ . S+A was also thawed S+A off with using DI- $\text{H}_2\text{O}$  and washing off for removing SPT by DI- $\text{H}_2\text{O}$  with aspirating. In this study, we used SPT at  $\rho=1.85 \text{ g/cm}^3$ . At the end of this method, we got 5 fractions: Silt and Clay (s+c), Particulate Organic Matter (POM), Sand and aggregates (S+A), Dissolved Organic Carbon (DOC) and Resistant Soil Organic carbon (rSOC).

## 2.2.4 Carbon and Nitrogen analysis

SOC and nitrogen analysis have done in INRA Clermont-Ferrand with Thermo Electron Co-operation, NC analyser, Flash EA 1112 series, except total SOC and nitrogen of Oensingen site samples were analysed at Agroscope Reckenholz-Tänikon Research Station ART, Zürich, Switzerland.

Before the analysis, we did decarbonation regarding s+c, S+A, DOC and rSOC fractions

because we are interested in analysing soil organic carbon (SOC), and carbonates are inorganic carbon. With regard to soil pH in the Table 3.1 and 4.1, we had several sites' soil samples which contain carbonate. We also decarbonated to analyse total SOC and soil nitrogen amount. We did not decarbonate POM fraction for avoiding to damage plant materials which are contained a lot in POM fraction. Furthermore, SPT's density which we use in the soil fractionation is  $1.85 \text{ g cm}^{-3}$ . Carbonates, principally, consisted by  $\text{CaCO}_3$  (Calcite) and  $\text{CaMgCO}_3$  (Dolomite). These two carbonate minerals' (Calcite and Dolomite) densities are  $2.71 \text{ g cm}^{-3}$  and  $2.83 \text{ g cm}^{-3}$  respectively. Therefore, S+A, s+c, rSOC and DOC contain carbonates but not POM. They are not in the POM which is lighter than  $1.85 \text{ g cm}^{-3}$ . Decarbonate process have done by reference to Harris et al. (2001) but with some modification by ourselves. We placed soil fractions in Ag-foil capsules ( $8 \times 5 \text{ mm}$ ). The capsules were placed in the wells of a microtiter plate. We added  $40 \mu\text{L}$  ultra pure water for each capsule. Then we placed a small beaker with  $100 \text{ mL}$  of concentrated  $12\text{M}$  Hydrochloric acid (HCl) inside the vacuum  $5\text{L}$  desiccator. Then we placed the wells of a microtiter plate in the desiccator to expose to HCl vapour. Under the desiccator, we placed hot heater at  $40^\circ\text{C}$  to warm up the desiccator. We left these for 6 hours, then added  $25 \mu\text{L}$  ultra pure water each 2 hours during 4 hours. Then, dry the microtiter at  $60^\circ\text{C}$  for 48 hours<sup>1</sup>. All of the processes were done under hood. Agroscope Reckenholz-Tänikon Research Station ART treated with HCl in a desiccator to remove carbonate and by elemental analysis (combustion at  $1000^\circ\text{C}$ , released  $\text{CO}_2$  measured by GC-TCD). The difference between these two methods was between  $-0.27$  and  $1.14\%$ . So we can confirm that our HCl vapour method was correct enough to remove decarbonate and to analyse only SOC.

### 2.2.5 Eddy-covariance flux data

Briefly, Gross Primary Production (GPP) is C fixation by plants and Ecosystem respiration (Reco) is C flow due to respiration by plants, soil and animals. Net ecosystem exchange (NEE) is the difference between GPP and Reco, which includes plant, soil and animal influence on C flow. Each plot was equipped with a meteorological station and eddy covariance flux tower, registering half hourly data on meteorological variables (e.g. temperature, radiation, precipitation) and C fluxes. Fluxes data were processed according to EU guidelines (Aubinet et al. (2012)) to obtain NEE, where NEE was further partitioned according to European flux guidelines into GPP and Reco (Reichstein et al. (2005)).

## 2.3 Process-based models

We used four process-based models in this study: Rothamsted Carbon (RothC) model, Pasture Simulation Model (PaSim) and Denitrification / Decomposition Model (DNDC) and DailyCENTURY (DayCent).

The RothC model is the earliest and simplest SOC model for agricultural land. In this study, the Zimmermann et al. (2007) soil fractionation method was used, which has been tested as a compatible method for estimating model SOC pool sizes in several studies (Leifeld et al. (2009a); Dondini et al. (2009a); Senapati et al. (2013)). We tested several initialisation methods with the RothC model firstly, using our measured SOC fraction data. We then tested several initialisation methods with PaSim, DNDC and DayCent regarding flux outputs such as GPP, NEE and Reco.

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<sup>1</sup>HCl removing carbonates reaction is as following (Ramnarine et al. (2011)):  $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$  and  $\text{CaMg}(\text{CO}_3)_2 + 4\text{HCl} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$



PaSim model is a process-based grassland biogeochemical model which includes mowing and animal grazing modules specific to grassland management regimes. Since the RothC model was constructed as a process-based cropland model, verification with a process-based grassland model was necessary. PaSim was used for validating grassland simulation results. Furthermore, as RothC is a simple SOC model without any other submodels, validation with a more sophisticated process-based model containing several submodels was desirable, for its ability to simulate cropland and grasslands. The DayCent model's carbon and nitrogen submodels are the same as those of PaSim (both based on CENTURY) although DayCent can simulate grassland, cropland, forest and savannah systems. We also tested our initialisation methods using the DayCent model. We also ran the DNDC model due to its ability to simulate varied agricultural land uses. Table 2.1 shows the characteristics of each process-based model.

### 2.3.1 Rothamsted Carbon (RothC) -26.3 model

The RothC-26.3 model simulates agricultural topsoil processes (0-23 cm), and it does not contain a plant production submodel (Coleman and Jenkinson (1996, 1999); Coleman et al. (1997)). The model requires weather data (mean monthly air temperature (°C), monthly precipitation (mm) and monthly open pan evaporation (mm)). As site specific data, the model requires clay content of the soil (%), soil cover (vegetated or bare) and depth of soil layer sampled (cm). As site management data, it requires monthly plant residue input (tC/ha) and monthly farmyard manure input (tC/ha). The model is constructed with five SOC pools (Decomposable Plant Material (DPM), Resistant Plant Material (RPM), Microbial Biomass (BIO), Humified Organic Matter (HUM) and Inert Organic Matter (IOM)). In this model, SOC input is divided into two SOC pools: DPM and RPM. Then, from these two SOC pools, SOC flows to BIO, HUM and CO<sub>2</sub>. From these BIO and HUM SOC pools, SOC is further divided into BIO, HUM and CO<sub>2</sub> (see Figure 2.4). Each SOC pool's turnover time is DPM (0.165 years), RPM (2.31 years), BIO (1.69 years), HUM (49.5 years) and IOM (50,000 years)(Jenkinson and Rayner (1977); Coleman and Jenkinson (1999)). RothC model anticipate soil respiration as a flux output. For more detail of this model, see Coleman and Jenkinson (1999); Jenkinson and Coleman (2008).

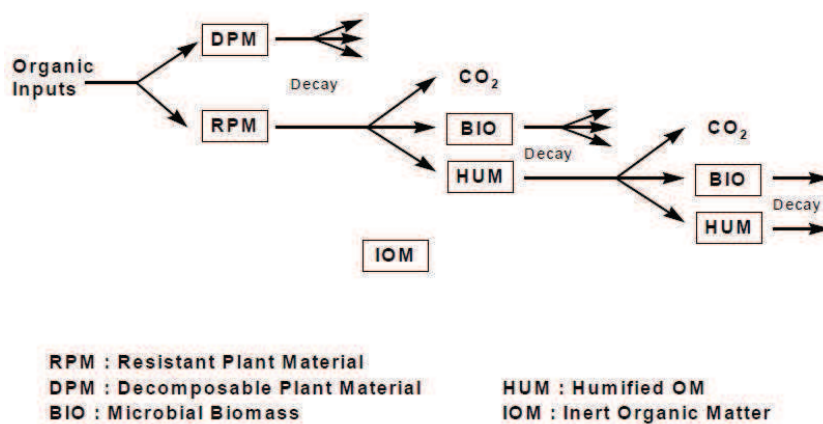


Table 2.1: Comparison among models in this study

	Model name			
	RothC	Pasim	DNDC	DayCent
Land-use type	Cropland	Grassland	Cropland	Cropland
	Grassland		Mois/Dry Grassland	Grassland
	Scrub	Deciduous/tropical woodland	Tree plantation	Savannah
			Rice paddy	Forest
			Wetland	
Submodel	Carbon	Soil physics (Soil C and N)	Carbon (Decomposition)	Soil Organic Matter
	Climate	Soil biology (soil water content, soil temperature)	Nitrogen (Denitrification, Nitrification)	Phosphorus
		Microclimate	Fermentation	Water flow
		Plant	Plant growth	Grass/Crop
		Animal	Soil climate	Tree growth
weather data	Monthly air temperature (°C)	Hourly air temperature (K)	Daily air temperature (°C)	Daily maximum air temperature (°C)
	Monthly precipitation (mm)	Daily precipitation (mm/day)	Daily precipitation (cm)	Daily minimum air temperature (°C)
	Evaporation (mm)	Hourly water vapour pressure (kPa)	* If available	Daily precipitation (cm)
		Hourly wind speed (m/s)	<i>Daily maximum air temperature</i>	*If available
		Hourly radiation (W/m <sup>2</sup> )	<i>Daily minimum air temperature</i>	<i>Solar radiation (langleys/day)</i>
		CO <sub>2</sub> concentration	<i>Daily precipitation (cm)</i>	<i>Relative humidity (%)</i>
		NH <sub>3</sub> concentration	<i>Daily Radiation (MJ/m<sup>2</sup>)</i>	<i>Wind speed (miles/h)</i>
			Daily wind speed (m/s)	
			Daily relative humidity (%)	]
Site data	% Clay	Latitude and longitude	Latitude and Longitude	Latitude and Longitude
	Depth soil sample was taken (cm)	Altitude	Soil texture (%)	%Sand, Clay, Silt, Rock
		Number of soil layers	Bulk density (g/cm <sup>3</sup> )	Bulk density (kg/L)
		%Sand, Clay and Silt	Soil pH	Wilting point
		Saturated soil water content (m <sup>3</sup> /m <sup>3</sup> )	Clay fraction (%)	Field capacity
		Soil pH	SOC at the surface (kgC/kg soil)	Soil pH
		Field capacity		SOC content (gC/m <sup>2</sup> )
		Saturated hydraulic conductivity (mm/d)		C/N, C/P, C/S ratio
Input		Main rooting depth (m)		Mineral N content (gN/m <sup>2</sup> )
		Relative root dry matter in different soil layers (%)		... <sup>b</sup>
		Bulk density (kg/L)		
		Air entry potential (mm)		
		... <sup>a</sup>		
Management data	Monthly plant residue (tC/ha)	Date of a cutting event (Day of the year)	Tillage date (day/month)	Crop type
	Farmyard (tC/ha)	Date of fertilisation event (Day of the year)	Tillage depth (cm)	Tillage date (Day of the year)
	Soil cover (bare or vegetated)	Amount of N-ammonium of mineral fertiliser (kgN/m <sup>2</sup> )	Planting/Harvest date (day/month)	Grazing, mowing, fire date
		Amount of N-nitrate of mineral fertiliser (kgN/m <sup>2</sup> )	N amount of mineral fertiliser (kg N/ha)	Amount of N,P,S to be added (gN/m <sup>2</sup> )
		Animal stocking rate (head/m <sup>2</sup> )	N fertiliser application depth (cm)	Fraction of N fertilizer that is NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> (0.0-1.0)
		Starting date of grazing (Day of the year)	C, N amount of manure (kgC/ha)	Fraction of live shoots removed by a grazing, mowing and fire event
		Amount of N of liquid manure (kgN/m <sup>2</sup> )	Irrigation date (day/month) and water depth (cm)	Amount of C of organic matter (gC/m <sup>2</sup> )
		Amount of N of slurry (kgN/m <sup>2</sup> )	Irrigation method	Lignin fraction content of organic matter
		Amount of solid manure (kgN/m <sup>2</sup> )	Plastic application date (day/month)	... <sup>b</sup>
		Live weight of young cows (kg/animal)	Grazing and mowing date (day/month)	
		Live weight of matured cows (kg/animal)	Animal stocking rate during grazing (head/ha)	
		Body condition score of young cows at the beginning of grazing	Mowing fraction (%)	
		Body condition score of mature cows at the beginning of grazing		
		... <sup>a</sup>		

<sup>a</sup>For more detail, please refer to Pasim User's guide<sup>b</sup>For more detail, please refer to CENTURY Tutorial

## 2.3.2 Denitrification / Decomposition Model (DNDC)

The DNDC model is a general model of C and N biogeochemistry in agricultural ecosystems (Li et al. (1994)). This model predicts crop yield, soil carbon sequestration, nitrogen leaching, and trace gas emissions in agro-ecosystems. DNDC, can run at site or regional scale. The model consists of two components (See Figure 2.5).

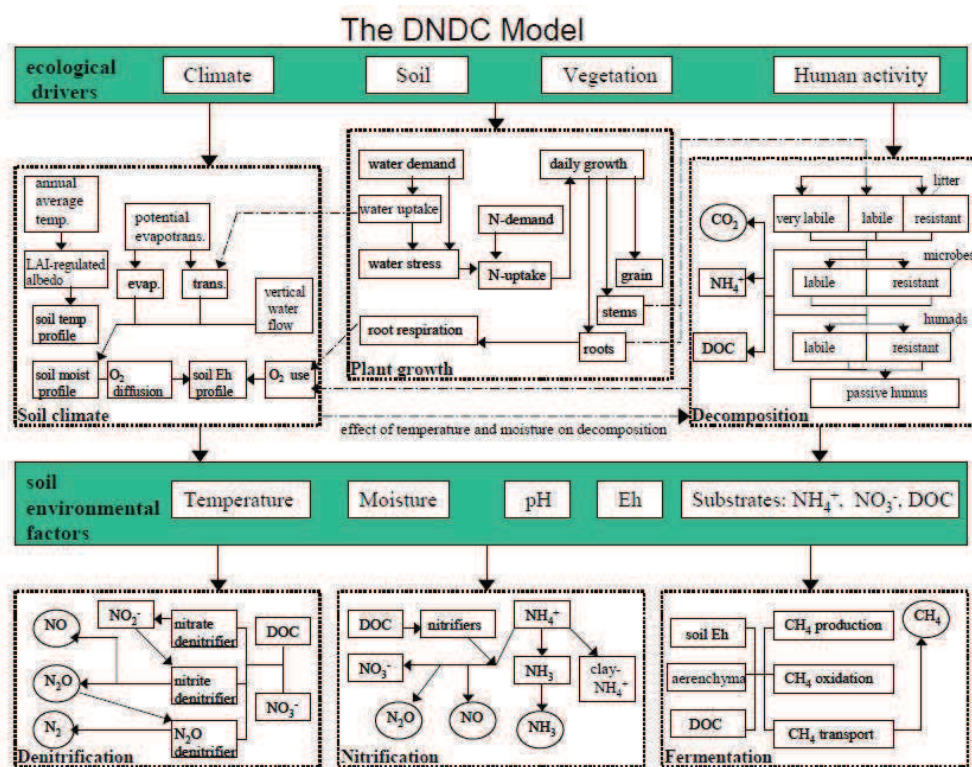


Figure 2.5: Description of DNDC

User's Guide for the DNDC Model Version 9.1 (Institute for the Study of Earth, Oceans and Space (2007))

The first component consists of the soil climate, crop growth and decomposition sub-models, predicting soil temperature, moisture, pH, redox potential (Eh) and substrate concentration profiles, driven by ecological drivers (e.g. climate, soil, vegetation and anthropogenic activity). The second component consists of the nitrification, denitrification and fermentation sub-models, predicting NO, nitrous oxide ( $\text{N}_2\text{O}$ ),  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{NH}_3$  fluxes based on the modelled soil environmental factors (User's Guide for the DNDC Model Version 9.1 Institute for the Study of Earth, Oceans and Space (2007)). The entire model is driven by four major ecological drivers: climate, soil physical properties, vegetation, and anthropogenic activities. Accurate input data will provide accurate simulation results at either site or regional scale (Li et al. (1994, 1992); Li (2000)). For more detail on this model, see Li et al. (1994, 1992); Li (2000).

In DNDC, SOC is divided into four major pools: plant residue (i.e. litter), microbial biomass, humads (i.e. active humus) and passive humus. Each pool consists of two or three sub-pools with different specific decomposition rates (Figure 2.5). The daily decomposition rate for each sub-pool is regulated by the pool size, the specific decomposition rate, soil clay content, N availability, soil temperature and soil moisture (Li et al. (1994, 1992); Li (2000)). If SOC decomposes, the decomposed C is partially allocated into other SOC pools and partially lost as

CO<sub>2</sub>. Dissolved organic carbon (DOC) is produced as an intermediate during decomposition. However, DOC may be immediately consumed by the soil microbes. During the processes of SOC decomposition, the decomposed organic nitrogen partially transfers to the next organic matter pool.

The organic nitrogen is also partially mineralised to ammonium (NH<sub>4</sub><sup>+</sup>), simulating nitrification (Li et al. (1994, 1992); Li (2000)). The ammonium concentration is controlled by clay-adsorbed NH<sub>4</sub><sup>+</sup> and dissolved ammonia (NH<sub>3</sub>) (Figure 2.5). NH<sub>3</sub> emission is controlled by NH<sub>3</sub> concentration in the soil water phase and soil environmental factors (e.g. temperature, moisture and pH)(User's Guide for the DNDC Model Version 9.1 Institute for the Study of Earth, Oceans and Space (2007)). The denitrification sub-model of DNDC calculates N<sub>2</sub>O and NO production, consumption and diffusion, during rainfall, irrigation and flooding events. DNDC simulates relative growth rates of nitrate, nitrite, NO, and N<sub>2</sub>O denitrificator based on soil heterotrophic respiration, and concentration of Dissolved Organic Carbon (DOC) and N oxides (Smith et al. (2007c)). DNDC predicts nitrification rates by tracking nitrification activity and NH<sub>4</sub><sup>+</sup> concentration. Growth and death rates of nitrifying bacteria are calculated as a function of DOC concentration, temperature and moisture, based on Blagodatsky and Richter (1998) and Blagodatsky et al. (1998) (Smith et al. (2007c)). DNDC calculates CH<sub>4</sub> production as a function of DOC concentration and temperature, under anaerobic conditions. In DNDC, CH<sub>4</sub> oxidation is calculated as a function of soil CH<sub>4</sub> and Eh (soil redo potential (mV)). CH<sub>4</sub> moves from anaerobic production zones to aerobic oxidation zones via diffusion, which is modelled using concentration gradients between soil layers, temperature and soil porosity (Li et al. (1994, 1992); Li (2000)). DNDC predicts NEE and Reco. Regarding GPP, we calculated using model NEE and Reco results.

### 2.3.3 DayCent

CENTURY is available for monthly time step simulations, and DayCent is the daily time step version of CENTURY. CENTURY and DayCent were developed to deal with a wide range of cropping system rotations, tillage practices for systems analysis of the effects of management, global change on productivity and sustainability of agroecosystems. The daily time-step version of the CENTURY model, DayCent5, provides enhanced resolution of all the processes simulated by CENTURY5: plant production, decomposition, soil hydrology and temperature. Daily weather data is used in the DayCent, although monthly weather or the site parameter's statistical monthly weather can be used. The big difference between CENTURY and DayCent is, DayCent is driven by daily weather data which is better to predict N<sub>2</sub>O emission. The DayCent model structure is the same as that of CENTURY, although there are additional site parameters in DayCent 5: site parameters for Hydrology and Biophysical Controls and Soil Temperature (see Table 2.2). DayCent predicts only NEE (neither GPP nor Reco) as a C flux output.

DayCent comprises six different submodels: Carbon (C), Nitrogen (N), Phosphorus (P), Sulfur (S), soil water & temperature and plant production (Parton et al. (1987); Parton and Rasmussen (1994), CENTURY User's guide and References). The plant production submodel may be a grassland, cropland, forest and savannah systems. The grassland, cropland and forest system have different plant production submodels, linking to a common SOM submodel (Parton (1996)). Multiple agricultural management systems, including crop rotations, tillage practices, fertilisation, organic matter addition, irrigation, grazing and harvest methods, are simulated by DayCent.

Paustian et al. (1992) tested the CENTURY model with long-term SOM experiment data from Sweden. Parton et al. (1987) tested the CENTURY model with SOC and N plant production data from grassland soils in the United States Great Plains. Del Grosso et al. (2005, 2006)



Table 2.2: Additional input data in DayCent 5

Site parameters	Soil Temperature	Average Thermal Diffusivity of unfrozen soil <sup>a</sup> Average Thermal Diffusivity of frozen soil <sup>a</sup> Depth interval for soil temperature calculations (cm) <sup>b</sup> Time step correction factor for soil temperature model <sup>c</sup> Minimum soil temperature at bottom of soil profile for year (°C) Maximum soil temperature at bottom of soil profile for year (°C) Time lag from beginning of year to coldest time period (days) Initial soil temperature, each soil layer (°C) Saturated Hydraulic Conductivity for each soil layer (cm)
	Hydrology and Biophysical Controls	Minimum soil water content <sup>d</sup> for each soil layer Duration of rain event (hours) Multiplier on sublimation amount <sup>e</sup> Shortwave albedo of snow <sup>e</sup> Shortwave albedo of vegetation <sup>e</sup>

<sup>a</sup>:Valid Values = 0.001-0.005  
<sup>b</sup>:Valid Values = 1.0-5.0  
<sup>c</sup>:Valid Values = 0.001-0.009  
<sup>d</sup>:Fraction below wilting point  
<sup>e</sup>:Valid Values = 0-1

tested DayCent for GHG fluxes (nitrous oxide (N<sub>2</sub>O), CO<sub>2</sub> and CH<sub>4</sub>) for major crops in the USA. A simple description of the DayCent model (Parton and Rasmussen (1994)) is shown in the Figure 2.6 (Parton (1996)).

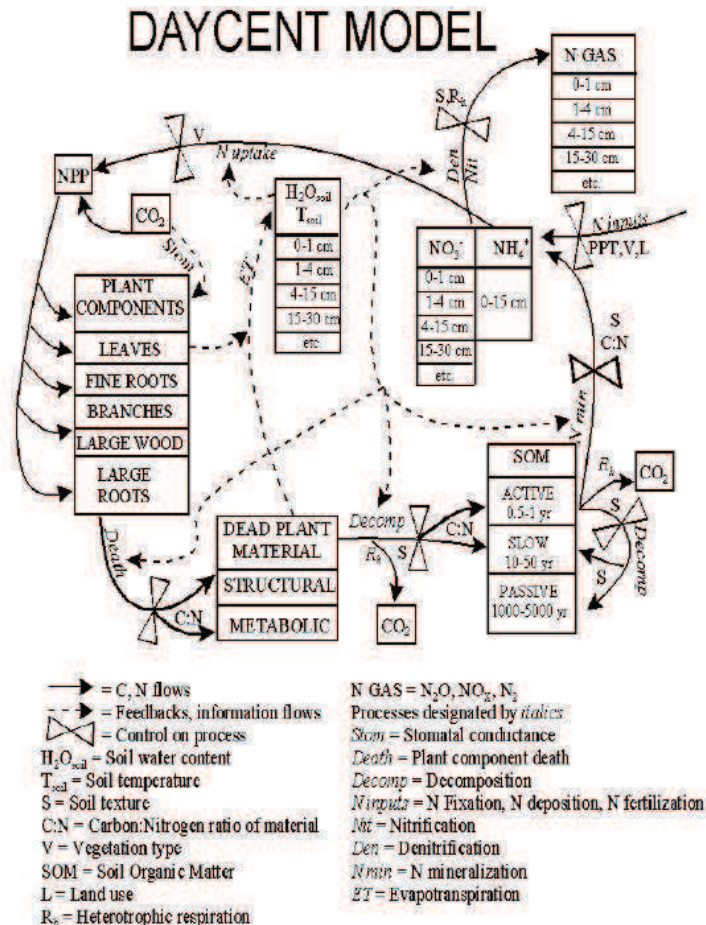


Figure 2.6: Simple description of DayCent model (Based on CENTURY tutorial)

DayCent 5 is the latest version of CENTURY, including a layered soil physical structure, and new erosion and deposition submodels.

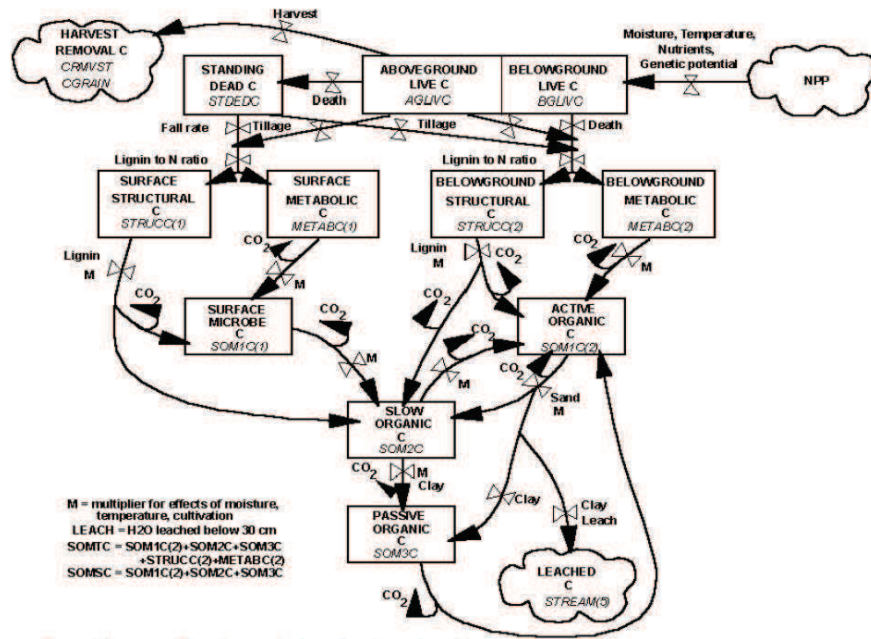


Figure 2.7: Carbon submodel in DayCent (CENTURY Tutorial)

In the model, all carbon decomposition is derived from microbial activity and microbial respiration, and is correlated with each carbon flow (Parton et al. (1987)). Figure 2.7 (CENTURY Tutorial) shows the detail of the carbon submodel in the latest version of DayCent 5. In the DayCent model, plant residue is divided into structural C pools (difficult to decompose) and metabolic C pool (readily decomposable), according to the lignin to N ratio (L/N) of the litter (more structural, higher L/N ratio). Aboveground and belowground C subpools are comprised in the structural and metabolic C pools. The structural C pool comprises cellulose, hemi-cellulose and lignin of plant material, although the metabolic C pool is easily decomposable. The active C pool includes live microbes and microbial products, sharing up to 2% of the total soil carbon with short turnover time period (1-3 months). The slow C pool, sharing 45-60% of total SOC, represents resistant plant materials originating from structural plant materials and physically protected soil microbial products, with turnover times of between 10 and 50 years, depending on the climate. The passive C pool (45-50% of total SOC) contains physically and chemically stabilised C, being resistant to decomposition (Parton et al. (1987); Parton and Rasmussen (1994)) and its turnover time is between 400 and 4000 years. In the CENTURY model, the turnover time of bulk SOC is as a function of turnover time in specific C pools, soil moisture and soil temperature. This factor is calculated multiplying the soil moisture factor (function of precipitation and stored soil water) and soil temperature factor (function of average monthly soil surface temperature) (Parton et al. (1987); Parton and Rasmussen (1994)). Regarding the active C pool's turnover time, the rate varies according to the soil texture: more rapid for sandy soil texture, while the stabilisation of the active C into slow C is a function of the silt and clay content. This means that higher stabilisation is derived from higher silt and clay content.

The basic N submodel structure is the same as that of the carbon submodel in DayCent (see Figure 2.8, Parton and Rasmussen (1994)). The N flow is calculated from the C/N ratio. The C/N ratio of the different N pools changes according to the soil mineral N. The detailed N flow in the model is explained in section 2.3.4 in the PaSim model. Turnover of active SOC creates most of the soil mineral N (Parton et al. (1987); Parton and Rasmussen (1994), see Figure 2.8).

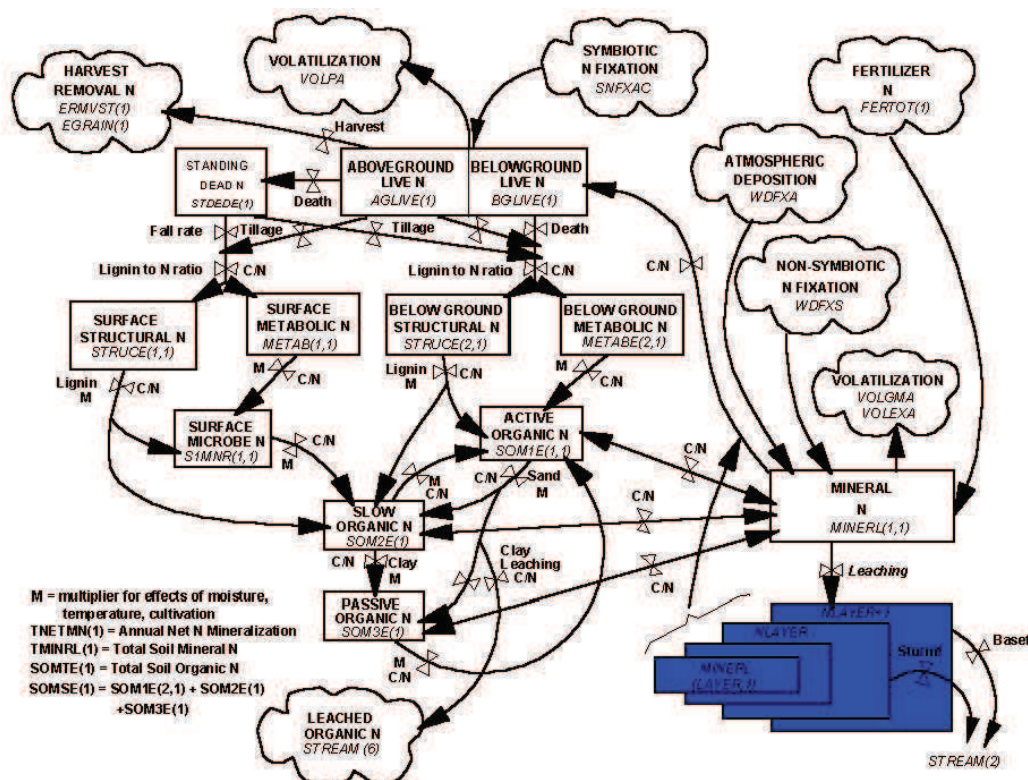


Figure 2.8: Flow diagram for the N submodel in CENTURY model version 5 (CENTURY User's guide and References)

For more detail of this model, see CENTURY tutorial or Parton et al. (1987); Paustian et al. (1992); Parton and Rasmussen (1994); Parton (1996); Del Grosso et al. (2000, 2001, 2002).

## 2.3.4 Pasture Simulation Model (PaSim)

The Pasture Simulation Model (PaSim) is a process-based grassland biogeochemical model, simulating dry matter production, CO<sub>2</sub> fluxes, NEE (Net ecosystem exchange), GPP (Global primary production), Reco (Ecosystem respiration), SOC pool dynamics, soil N<sub>2</sub>O emissions from nitrification and denitrification at grasslands, CH<sub>4</sub> emissions from grazing livestock and water in productive pastures (Riedo et al. (1998, 2000); Calanca et al. (2007); Vuichard et al. (2007a); Graux et al. (2012b,a)). The model is derived from the Hurley Pasture Model (HP-model) of Thornley (1998). Description of the Hurley Pasture Model is shown in Figure 2.9.

The vegetation submodel of the HP-model Thornley (1998) simulates the vegetative growth of grasses with depending on light, temperature and N, though reproductive growth is not considered (Riedo et al. (1998)). The HP submodel cannot, therefore, reproduce the asymmetric seasonal pattern of production, which is seen in infrequently cut swards. However, this seasonal production pattern relates with several physiological processes: photosynthesis and turnover of shoot/root to biomass. Hence, the HP-model needed to be modified to simulate both reproductive and vegetative growth in the course of a growing season (Riedo et al. (1998)). These developments were made by Riedo et al. (1998) when developing PaSim model from the HP-model by development of a new plant submodel (Figure 2.10). Riedo et al. (1998) expanded the plant submodel to (1) include the reproductive developmental stage of a grass sward, (2) allow



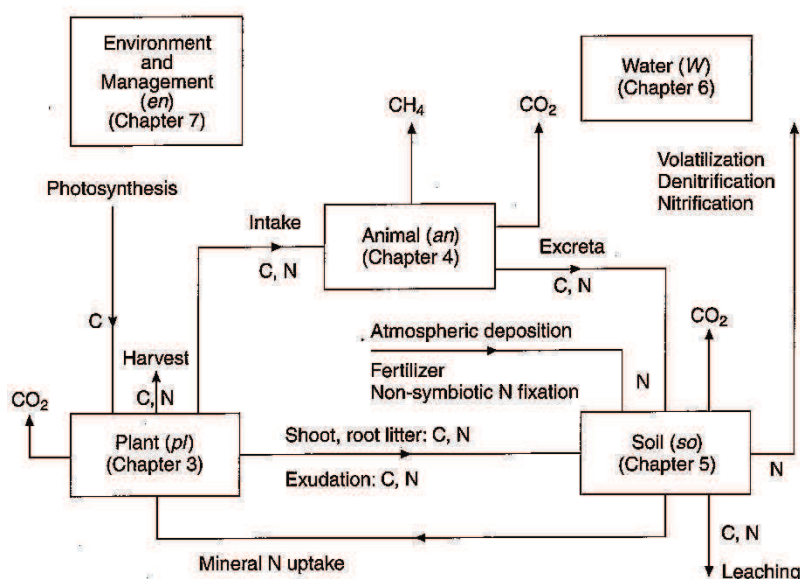


Figure 2.9: Description of the Hurley Pasture Model (Thornley (1998))

for a dynamic change in the fractional N content of plant structural dry matter, (3) simulate leaf stomatal resistance and (4) alter the temperature dependence of processes, which were linear in the HP-model.

PaSim is driven by hourly weather input data for radiation, temperature, vapour pressure, wind speed and precipitation (Riedo et al. (1998); Schmid et al. (2001)), simulating the annual production of plant biomass and the N balance, seasonal patterns of growth, seasonal latent, sensible and soil heat fluxes, C fluxes and water in permanent grassland ecosystems with a high time resolution (Riedo et al. (1998, 2000)). The original version of PaSim (Pasim ver. 1.0) is described in Riedo et al. (1998). The Pasim model comprises plant growth, microclimate, soil biology, soil biology and soil physic submodels (Riedo et al. (1998)). Site-specific model inputs include N input from mineral and/or organic fertilisers and atmospheric deposition, a constant fractional clover content of the grass/clover-mixture, the depth of the main rooting zone, and several soil physical parameters, including soil texture and bulk density. Schmid et al. (2001) has extended the PaSim 2.5 model to simulate N<sub>2</sub>O production from denitrification and nitrification, N<sub>2</sub>O concentration in the soil air and N<sub>2</sub>O emissions to the atmosphere from grassland caused by N inputs from different sources.

Riedo et al. (2000) and Schmid et al. (2001) tested the PaSim model with data from different sites in Switzerland: Bern, Sion, Davos, Oberbuetschel and Kerzersmoos. Calanca et al. (2007) tested the PaSim model in various sites in Europe: Bugac-Puszt (Hungary), Easter-Bush (UK), Carlow (Ireland), Laqueuille (France) and Oensingen (Switzerland).

Vuichard et al. (2007a,b) pointed out that a process-based modelling approach takes into account less socio-economic constraints on grassland management, suggesting process-based models cannot provide more realistic estimates of grasslands GHG emissions than empirical-based ones. Then, Vuichard et al. (2007a) investigated the impact of mowing vs. animal grazing practices on the GHG sources and sink function of grasslands, and tested whether European grasslands CO<sub>2</sub> sinks offset the sources of non-CO<sub>2</sub> gases in terms of greenhouse warming potential. Vuichard et al. (2007a,b) improved the calculation of aboveground vegetation dynamics for obtaining the realistic Leaf Area Index (LAI) decrease at the end of the growing season espe-

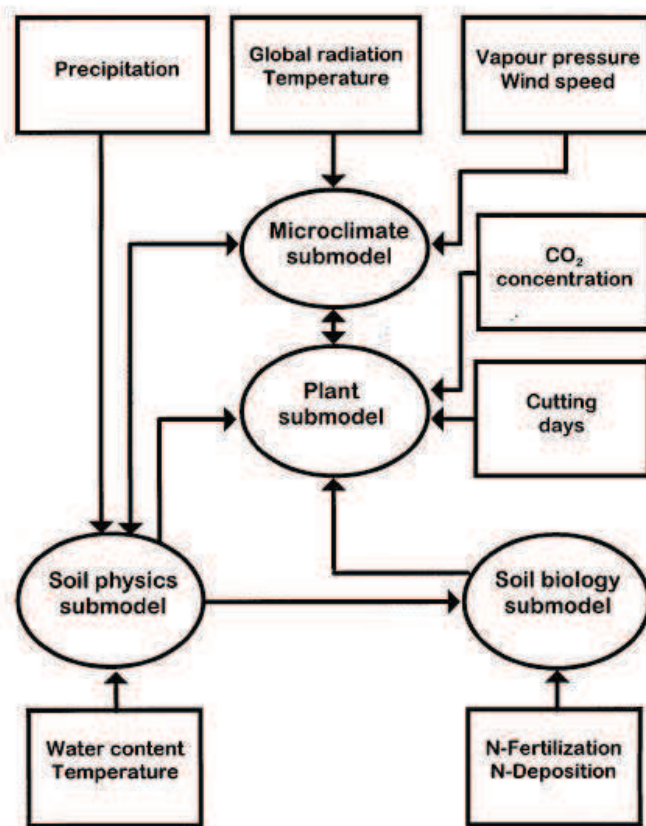


Figure 2.10: Description of the PaSim model (Riedo et al. (1998, 2000))

cially under conditions of water stress, senescence and the effects if diet quality on the emissions of CH<sub>4</sub> from grazing animals.

In previous version of the PaSim model, water stress was considered as limiting photosynthesis but not other plant processes (Calanca et al. (2007)). PaSim does not keep track of the plant-water status and defines water stress with respect to the soil water potential. Vuichard et al. (2007b) reduced shoot and root growth and enhanced shoot and root turnover in response to water stress. Graux et al. (2012a,b) have tested the PaSim model, using data from several sites in France. However, in order to make the simulation more realistic, it is necessary to construct management data for each major type of management in each region due to the diverse nature of European countries (Vuichard et al. (2007a)).

Carbon and nitrogen submodels in Pasim are based on those in the CENTURY model (Parton et al. (1988)). The carbon submodel is constructed with five SOC pools: structural, metabolic, active, slow and passive. In this model, plant residue (carbon input) is divided into two SOC pools: structural and metabolic. Structural and metabolic C pools do not interact. Then, from these SOC pools, SOC is divided into active, slow and CO<sub>2</sub>. From these active and slow C pools, SOC is divided into active, slow, passive C pools and CO<sub>2</sub> again (see Figure 2.11). Lignin to nitrogen ratio controls the split of plant residue into structural and metabolic pools, and all of the plant residual lignin flows into the structural compartment (Parton et al. (1987)). Structural and metabolic C pools do not interact, while active and passive interact with each other. Metabolic C is decomposed as active C or CO<sub>2</sub>. All carbon pools have access to the active pool. Parton et al.

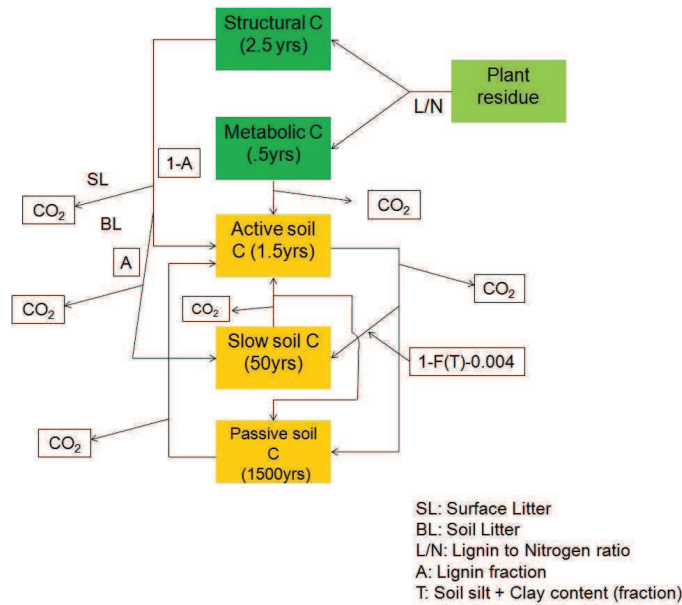


Figure 2.11: Carbon flow in soil biology submodel in PaSim model (Based on Parton et al. (1987); Riedo et al. (1998); Graux and Lardy (2010))

(1987) also assumed that the decay rate of structural material is a function of its lignin content and the lignin fraction is incorporated into the slow soil pool. The direct lignin flow into slow soil organic matter is based on data from laboratory incubation of labelled lignin-type material (Parton et al. (1987)). Only soil C and N in the main rooting zone is considered.

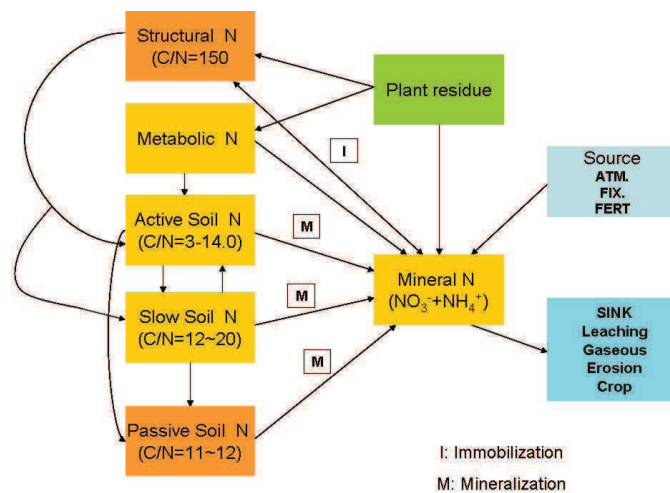


Figure 2.12: Nitrogen flow in soil biology submodel in PaSim model (Based on Parton et al. (1987); Riedo et al. (1998); Graux and Lardy (2010))

Figure 2.12 shows N flow in the soil biology submodel of PaSim (Parton et al. (1987); Riedo et al. (1998); Graux and Lardy (2010)). Minimum and maximum values of C/N ratio in active,

slow and passive SOC pool<sup>2</sup> are shown in Riedo et al. (1998). There is no limitation of C/N ratio in the metabolic plant residue pool (Riedo et al. (1998)). The nitrogen submodel is constructed with six SOC pools: structural, metabolic, active, slow, passive and mineral (see Figure 2.12). Plant residue is split into structural, metabolic and mineral pools. The mineral N pool is split into components for ammonium ( $N_{amm}$  (kgN/m<sup>2</sup>)) and nitrate ( $N_{nit}$  (kgN/m<sup>2</sup>)) and immobilised with the structural N pool. Metabolic N pool is split into mineral or active pools. Structural and metabolic N pools do not interact each other, while active and slow N pools interact between the two. Structural N is decomposed into active and slow N pools (see Figure 2.12). For more detail, see Riedo et al. (1998, 1999, 2000).

## 2.3.5 Model initialisation

### Applying measured SOC fractions to the model SOC pools

Each of the soil fractions which were derived from the Zimmermann et al. (2007) soil fractionation scheme were measured for organic carbon and nitrogen content. These data were converted to five different soil organic carbon pools: Decomposable Plant Material (DPM) and Resistant Plant Material (RPM), Microbial Biomass (BIO), Humified Organic Matter (HUM) and Inert Organic Matter (IOM), which correspond to RothC model SOC pools (Coleman and Jenkinson (1999)). Zimmermann et al. (2007)'s equation was applied to calculate the size of each model SOC pools from our measurements (see Figure 2.13). The equation which calculates DPM/RPM splitting ratio depends on land-use type, temperate grassland:  $y=0.048+0.011 \times MAT$  and arable land:  $y=0.035-0.003 \times MAT$ , where MAT is mean annual temperature. Regarding the BIO/HUM split ratio, we did a spin-up run of RothC, then took the BIO/HUM ratio at steady state. This BIO/HUM steady state ratio was used to split from (S+A)+(s+c) into BIO and HUM pools. The detail of the splitting ratios used are shown in Table 2.3.

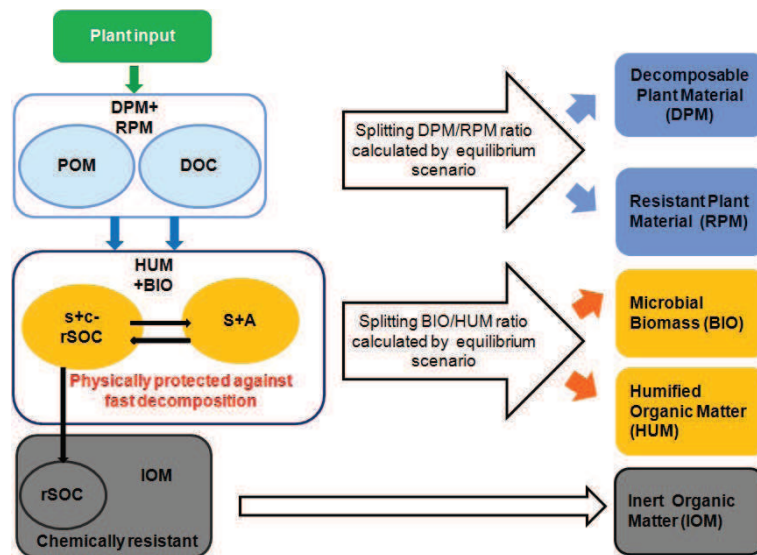


Figure 2.13: Calculation scheme from SOC fractions to SOC pools (Based on Zimmermann et al. (2007))

<sup>2</sup>Active: C/N 3.0 - 14.0 (kgC/kgN), Slow: C/N 12.0 - 20.0 (kgC/kgN), Passive: C/N 11.0 - 12.0 (kgC/kgN)



Table 2.3: Splitting ratio of measured fractions with Zimmermann et al. (2007) method

Site name	MAT (°C)	split ratio	
		DPM/RPM	BIO/HUM
Laqueille* (grass, FR)	7.68	0.132	0.027
Oensingen (grass, CH)	9	0.147	0.026
Reeuwijk (grass, NL)	9.8	0.156	0.026
Hertfordshire (crop, UK)	9.46	0.007	0.027
Carlow (crop, IE)	9.4	0.007	0.026

As shown in the Figure 2.11 (Carbon submodel in PaSim), in the Pasim model, carbon input is divided into two SOC pools: Structural C Pool (2.5 years) and Metabolic C Pool (0.5 years). Then, from these SOC pools, carbon is distributed into an Active C pool (1.5 years), a Slow C pool (50 years) and a Passive C Pool (1500 years). In the RothC model, SOC input is split into two SOC pools: DPM and RPM. Then, from these two SOC pools, SOC is split into BIO, HUM and CO<sub>2</sub>. From these BIO and HUM SOC pools, SOC is separate into BIO, HUM and CO<sub>2</sub> again. Each SOC pool's mean turnover time is DPM (0.165 years), RPM (2.31 years), BIO (1.69 years), HUM (49.5 years) and IOM (50,000 years)(Figure 2.4, Jenkinson and Rayner (1977)).

Table 2.4: SOC compartments included in earlier simulation models of SOM turnover (Christensen (1996))

Main module	Reference Nr	Compartment
Input	1	Decomposable&resistant
	2	Labile & resistant (above- & belowground; different depths)
	3	Decomposable, structural & ligniferous (above- & belowground)
	4	Residue
	5	Metabolic, structural & lignin
Decomposers	1	Microbial biomass
	2	Active & inactivedecomposers
	6	Protected & non-protected biomass
	7	Zymogenous & autochthonous biomass
	4	Labile & resistant
SOM	1	Physically & chemically stabilised
	3	Decomposable & recalcitrant (+/- physical protection)
	2	Humic material (different soil depths)
	4	Humads (labile & resistant) & stable humus
	6	Decomposable, recalcitrant, active protected & old
	7	Humified & Inert
	5	Active, slow and passive

1: Jenkinson and Rayner (1977), 2: Hunt (1977), 3: Veen and Paul (1981), 4: Molina et al. (1983), 5: Parton et al. (1987, 1988), 6: Van Veen et al. (1984), 7: Jenkinson et al. (1987)

Christensen (1996) compared earlier SOM turnover models with regard to the Carbon submodel. DNDC model's carbon submodel is based on the Molina et al. (1983) (reference number 4) and RothC model is reference number 1 or 7 in the Table 2.4

Christensen (1996) compared earlier SOM turnover models with regard to the Carbon submodel. DNDC model's carbon submodel is based on the Molina et al. (1983) (reference number

4) and RothC model is reference number 1 or 7 in the Table 2.4. Initialising different models SOC pools using detailed SOC measurement by Zimmermann et al. (2007) soil fractionation was one of the barricade in this study. Certainly, it is impossible to map conceptual SOC pools across from one model to another as all C submodel in different models have different pool sizes, turnover times, dependencies and inter-relationships. To overcome this problem, I learned each model's SOC pools turnover time and the C submodel construction referring to Christensen (1996). Considering all of the SOC pools difference in each models, I estimated there are certain SOC pools in each model which correspond to each certain RothC SOC pool, excluding DNDC litter C pool which correspond to the sum of DPM and RPM in RothC. I consider that these SOC data would give some idea for models regarding SOC distribution among SOC pools as the initial values. Estimated RothC DPM was applied to Metabolic SOC pool in (Pasim and DayCent), RPM was applied to Structural SOC pool (PaSim and DayCent). DPM+RPM were applied to Litter SOC pool in DNDC. BIO was applied to Active SOC pool (PaSim and DayCent) and Microbe SOC pool (DNDC). HUM was applied to Slow SOC pool (Pasim and DayCent) and Humads SOC pool (DNDC). IOM was applied to Passive SOC pool (Pasim and DayCent) and Passive Humus SOC pool (DNDC).

### **Model initialisation methods**

Prior to the model simulation, we applied roughly three different initialisation methods: (1) General spin-up initialisation (Control), (2) Adjusted spin-up initialisation reducing or increasing C input, during the spin-up run period (Ad) and (3) Initialisation with measured SOC data (ObSOC).

The monthly average weather data was calculated combining weather data from the CarboExtreme project (1901 to the year which the measured weather data is available) and more recent measured weather data.

**Spin-up run initialisation repeating average recent management data and 1901-2010 weather data (Control)** The model was run to the equilibrium status by repeating monthly average of recent (around 10 years) management regimes and weather data (1901-2010), except for the Pasim model which were repeated recent 20 year weather data was used. We compared our SOC measurement data with model equilibrium results. After the spin-up run, we continued the simulation with each site's recorded weather and management data for the available period (see Figure 2.14 (a)). The slowest SOC pool was calibrated (i.e. set to be the same as) the measured resistant soil organic carbon (rSOC) value.

**Spin-up initialisation reducing or increasing C input (plant litter and organic carbon manure input)** We adjusted the C input during the spin-up run period until the equilibrium SOC became equal to the measured SOC value. The slowest SOC pool was set up as the measured resistant soil organic carbon (rSOC) value. We call this spin-up run the adjusted spin-up run. We adjusted each equilibrium SOC pool to be equal to the each of the observed SOC pools, which was calculated from Zimmermann et al. (2007) soil fraction data, or the equilibrium total SOC to be equal to the total SOC value. Then, we continued simulation with each site's recorded weather and management data for each site's available period (see Figure 2.14 (b)).

**The observed SOC fraction data initialisation (ObSOC)** We initialised the model with our measured SOC pools value which was calculated from Zimmermann et al. (2007) soil frac-

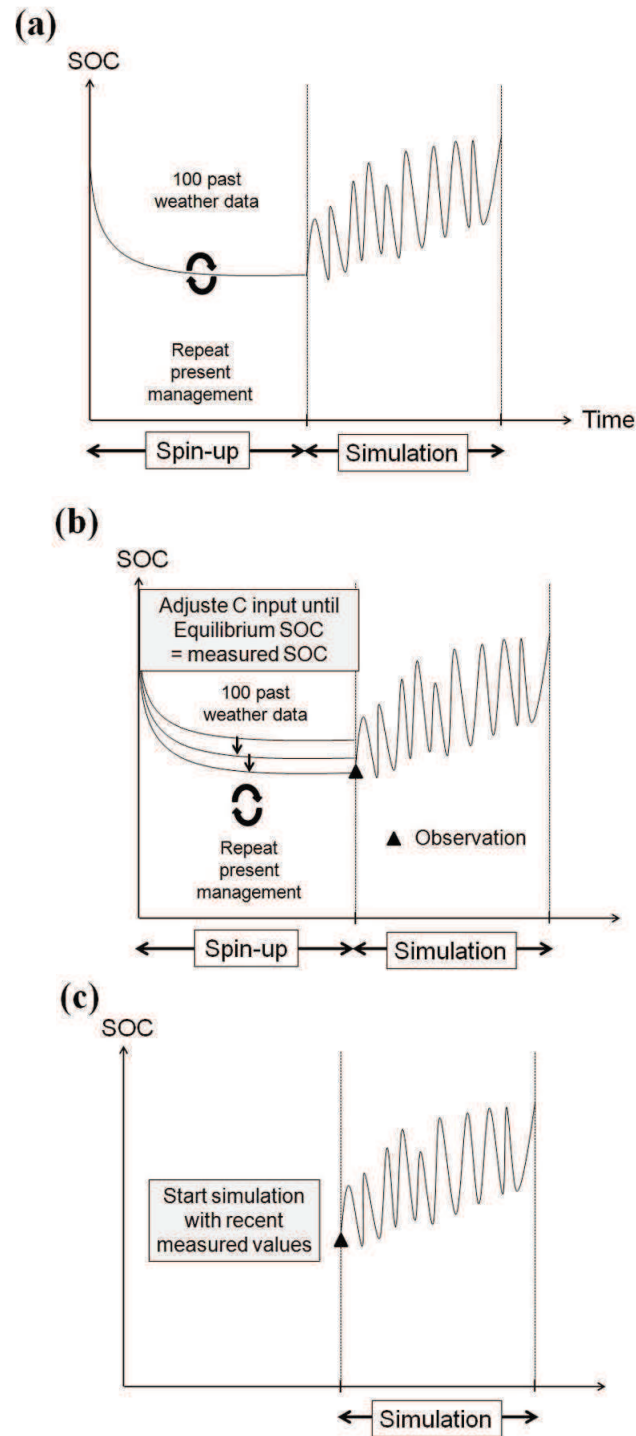


Figure 2.14: Different initialisation methods : (a) General spin-up initialisation, (b) Adjusted spin-up initialisation and (c) Initialisation with measured SOC data

tion data, then we immediately ran the model forward using recent data for available years with recorded management and weather data (see Figure 2.14 (c)).







# Chapter 3

## Effect of soil characteristics and agricultural management on Soil Organic Carbon (SOC) pools in European grasslands and cropland - soil profile and soil fractions

### Abstract

Soil organic carbon (SOC) concentrations and greenhouse gas (GHG) emission are not uniform across landscape with hotspots in specific areas. These differences are mainly driven by human-induced activities such as agricultural management. Hence, there is considerable interest in the effect of past and present agricultural management on SOC and GHG fluxes in different ecosystems. In this study, we examined how agricultural management influences SOC, using four European sites, each representing a pair of contrasting agricultural managements by soil sampling campaigns and analysis. The sampled soil was analysed according to the soil fractionation method described by Zimmermann et al. (2007) for four soil depth layers (0-5, 5-10, 10-20, 20-40 cm). For mineral soils, the soil fractions derived from silt and clay exerted the greatest contribution to total SOC, especially in the topsoil (0-10 cm), compared to the deeper soil layers (> 10 cm depth). For a given depth and fraction, no significant differences were found in SOC stocks between contrasting practices. For organic soils (Reeuwijk, NL, 25 years under current management), the particulate organic matter (POM) had the greatest contribution to total SOC, and a significant difference in SOC distribution was observed between contrasting management practices. This may suggest that management practices influence SOC more rapidly in organic soils compared to mineral soils, which may be due to the larger quantity of POM in organic soils, being sensitive to land management change. For the mineral soil sites, it appeared that not enough time has elapsed since the onset management practices to detect statistically significant differences in SOC stocks. However, more organic soil and volcanic soil (andosol) data are necessary to confirm these findings.

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### 3.1 Introduction

The soil stores more than 75 % of the Earth's terrestrial organic carbon (C) with more than 4-5 times the amount of C in living vegetation (Lal (2004a); Breuning-Madsen et al. (2008)) and > 3 times more C than the atmosphere (Jobbágy and Jackson (2000); Lal (2002)). Approximately 60 % of the global soil C is contained within SOC. Given that 40-50 % of the Earth's land surface is under agricultural land-use (Smith et al. (2007b)), C sequestration in agricultural soil has a potentially important role in increasing SOC storage and GHG mitigation (Paustian et al. (1998); Foereid and Høgh-Jensen (2004)). At the same time, C sequestration in agricultural land may also contribute to increase in soil fertility through increased nitrification and denitrification, soil N reservoirs, greater soil water retention and enhanced crop productivity (Drinkwater et al. (1998); Alvaro-Fuentes et al. (2009)). The rate of C sequestration of agricultural soils in Europe (EU-15) has been estimated to be 16-19 Mt C/year between 2008-2012 (Freibauer et al. (2004); Smith (2004a)). This corresponds to 2% of European anthropogenic C emissions (Freibauer et al. (2004); Smith (2004a)) with agricultural management practices having an important role in controlling sequestration rates (Van Wesemael et al. (2010); Powlson et al. (2012)). There is considerable interest in understanding the effects of agricultural management on SOC and GHG fluxes in both grasslands and croplands in order to better assess the uncertainty and vulnerability of terrestrial SOC reservoirs (Hassink (1994); De Bruijn et al. (2012); Schulp et al. (2008); Leifeld et al. (2009a); Zhao et al. (2013); McSherry and Ritchie (2013)). Although grassland soils are a large potential CO<sub>2</sub> reservoir, significant uncertainty exists concerning how management influences SOC stocks, including common practices such as grazing, mowing, organic or mineral fertilizer addition (McSherry and Ritchie (2013)). SOC in these environments are sequestered through the root system, as well as litter carbon and nitrogen inputs to the soil. The effects of management activities on root (e.g. rhizo-deposition, root decomposition), litter and organic fertilizer inputs can enhance or diminish the natural capacity of soil to act as a C sink (Bottner et al. (1999)). Data from multi-decadal studies indicate that grassland management practices can influence SOC sequestration rates for up to 20 years after conversion to grassland (De Bruijn et al. (2012)), with gains and losses of SOC mainly dependent on the vertical distribution of root senescence. Croplands also have the potential to store terrestrial C, with management activities such as tillage, crop rotation and harvesting influencing soil C gain or loss. Input of organic matter, whether as organic fertilisers or plant residues, may also enhance SOC stocks (Zhang et al. (2007); Chivenge et al. (2007); Van Groenigen et al. (2010a,b); Jagadamma and Lal (2010)). Accordingly, detailed long-term land management data is needed to fully understand SOC changes and the impact of different management practices in grassland and cropland (Van Wesemael et al. (2010)). SOC storage is also strongly influenced by soil texture, and it is uncertain to what extent this intrinsic soil property is affected by, or interacts with, human intervention to modulate the size of SOC stocks. Many studies have shown that the amount of SOC is texture-dependent and is highly correlated with the amount of fine particles, such as clay (Nichols (1984); Chivenge et al. (2007); Jagadamma and Lal (2010)). Chivenge et al. (2007) reported that tillage disturbance is an important factor reducing C stabilisation in a fine particle textured soil and Gosling et al. (2013) concluded that POM and light fraction organic matter (LFOM) are good variables which determinate long-term total SOC changes in both croplands and grasslands. Predicting changes in SOC stocks in response to management would, thus, need complete information on physical and chemical stabilisation of C; impacts of human activity on SOC at different soil depths; and the role of soil texture in controlling SOC fractions,



such as plant-derived POM (Zimmermann et al. (2007)). Soil physical and chemical fractionation is a useful method to investigate whether management practices influence SOC stocks, and which soil fractions are most sensitive to the influence of management practices (Gosling et al. (2013)). So far, only a few studies have investigated how contrasting management practices and variations in key soil properties (e.g. soil texture) influence SOC fractions and underlying C stabilisation mechanisms in Europe (Leifeld et al. (2009a); Dondini et al. (2009a); Senapati et al. (2013)). In this study, four European long-term grassland and cropland experiments, associated with contrasting management regimes, have been examined. The objective of this study was to evaluate the effect of agricultural management and key soil characteristics on SOC sequestration in European grasslands and croplands. Soil sampling campaigns were carried out in 2011/2012. The entire soil profile down to the bedrock was sampled where possible, and then sub-divided into specific layers (0-5, 5-10, 10-20, 20-40 cm). For deriving accurate data on different SOC fractions, the Zimmermann et al. (2007) soil fractionation method was used. This soil fractionation method has already been tested by several studies, and since the fractions have been shown to map onto model pools (Leifeld et al. (2009a); Dondini et al. (2009a); Senapati et al. (2013)), it allows the findings to be used in future model simulations.

## **3.2 Materials and Methods**

### **3.2.1 Site description**

In this study we chose four long-term (up to 10 years) European experimental sites from the CarboEurope Integrated Project (CEIP) ecosystem flux tower network. The sites are all located in the same bioclimatic region (the oceanic temperature climate zone (Lindner et al. (2010))) with mean annual temperatures ranging between 7.7 and 9.80 °C and mean annual precipitation ranging between 800 to 1100 mm (see Table 3.1). Each site comprised two adjacent plots of contrasting management: (1) Laqueuille (FR), intensively (high animal stocking rate and N fertiliser input) and extensively (low animal stocking rate and no fertiliser input) grazed grassland, (2) Oensingen (CH), intensively and extensively cut grassland with high and low N fertiliser input (intensive plot was ploughed and re-sown in 2008), (3) Reeuwijk (NL), a grazed peat-based grassland subject to field rate with high and no organic and mineral fertiliser input and (4) Carlow (IE), a spring barley cropping system subject to conventional and non-inversion tillage management and a cover crop on the non-inversion tillage plot during the fallow season. A summary of site detail can be found in Table 3.1 and 3.2.



Table 3.1: Site description and soil detail of sites in this study

Land-use	Site name, Country	Management	Depth (cm)	Clay (%)*	Silt (%)	Sand (%)	Soil pH	Bulk Density (g/cm3)	C (%)	MAT** (°C)	MAP*** (mm)	Elevation (m a.s.l.)	Latitude	Longitude	Soil type	
Grassland	Laqueuille <sup>d</sup> , FR	INT	0-5	26	55	19	5.09	0.46	14.48±0.74	7.68	857-1000	1040	45°38'N	2°44'E	Andosol	
			5-10	23	54	23	5.36	0.67	10.19±0.89							
			10-20	20	55	25	5.56	0.79	7.17±0.23							
			20-40	21	54.5	24.5	5.60	0.80	5.16±0.25							
		EXT	0-5	26	55	19	5.21	0.57	11.98±0.63							
			5-10	23	54	23	5.22	0.81	9.44±0.52							
			10-20	20	55	25	5.39	0.77	7.85±0.84							
			20-40	21	54.5	24.5	5.47	0.91	6.65±1.85							
	Oensingen <sup>a</sup> , CH	INT	0-5	42.45	32.35	25.2	6.38	0.98	3.32±0.1	9.00	1100	450	47° 17' N	07° 44' E	Eutri-Stagnic Cambisol (developed on clayey alluvial deposits)	
			5-10				6.79	1.12	2.97±0.1							
			10-20				6.77	1.10	3.09±0.12							
			20-40				7.56	1.12	2.12±0.08							
		EXT	0-5	44.05	38.1	17.85	6.73	0.64	4.16±0.27							
			5-10				5.28	1.04	3.31±0.19							
			10-20				5.42	1.20	2.80±0.09							
			20-40				5.79	1.22	1.87±0.07							
	Reeuwijk <sup>b</sup> , NL	INT	0-5	-	-	9	6.00	0.26	24.06±1.89	9.80	800	-1.60	52° 2' N	4° 46' E	Fibric Eutric Histosol Subsoil: Hydric Haplofibrist	
			5-10	-	-	10	5.93	0.31	21.01±0.37							
			10-20	-	-	15	6.00	0.38	18.63±0.01							
			20-40	-	-	14	6.15	0.31	16.84±0.18							
		EXT	0-5	31	40	29	5.22	0.42	16.06±1.56				52° 1' N	4° 46' E		
			5-10	31	40	29	5.18	0.63	10.92±1.15							
			10-20	33	37	30	5.39	0.50	8.35±0.54							
			20-40	46	50	4	5.55	0.43	8.63±0.81							
Cropland	Carlow <sup>c</sup> , IE	CON	0-5	17	26	56	7.06	0.64	2.36±0.13	9.40	824	57	52° 52' N	6° 54' W	Eutric Cambisol Topsoil: peaty clayey Subsoil: clay loam	
			5-10				7.45	0.81	2.11±0.24							
			10-20				7.46	0.93	2.31±0.11							
			20-40				7.64	1.00	1.46±0.27							
		NIT	0-5	17	25	58	6.67	0.71	2.26±0.05							
			5-10				6.66	0.75	1.94±0.06							
			10-20				6.85	0.98	1.79±0.06							
			20-40				7.15	1.06	1.00±0.11							

<sup>a</sup>: Ammann et al. (2009)<sup>b</sup>: Extensive: Stolk et al. (2011). Intensive: soil texture was estimated from this study. Weather data averaged over 11 years (Jacobs et al. (2006))<sup>c</sup>: Van Groenigen et al. (2010a,b); Osborne et al. (2010); Walmsley et al. (2011) and Davis et al. (2010), weather data averaged over 30 years<sup>d</sup>: Klumpp et al. (2011), Soussana et al. (2007) and Allard et al. (2007), weather data averaged over 22 years (1972–1984, 1995–2004)

\*: % of weight in minerals

\*\*: Mean annual temperature

\*\*\*: Mean annual precipitation

Table 3.2: Each site's present and past management information

Present land-use	Site, Country	Present Management	Experiment starting year	Present management (detail)	Previous land-use history
Grassland	Laqueuille <sup>d</sup> , FR	INT	Spring 2002	- Semi-natural grassland - No Mowing (except 2010, 3 times mowing) - Grazing: May- October, 0.9-1.2 (LUS), LW gain: 102.3 kg/animal - mean mineral N fertilizer input (6 years): 191.5 kg N/ha-year, - No manure input	- Beginning of 20th century: arable crop - Converted to permanent grassland since around 1950 - 1950-1980: Mowing, cattle grazing, cattle slurry and manure
		EXT		- Semi-natural grassland - No mowing - Grazing: May- October, 0.5-0.6 (LUS), LW gain: 106.3 kg/animal - No mineral N fertilizer and no manure input	
	Oensingen <sup>b</sup> , CH	INT	May 2001	- 7 species, sown grassland - Grass mowing: 4 times/year - No grazing - mean (7 years) mineral N fertiliser: 109.7 kg N ha <sup>-1</sup> year <sup>-1</sup> (3-4 times/year) - manure: 46.89 kg N ha <sup>-1</sup> year <sup>-1</sup> (2 times/year) - mean C input (2002-2004): 47 g C m <sup>-2</sup> year <sup>-1</sup> (1-2 times/year) - In 2008: Ploughed and the same 7 species were re-sown	- Ley-arable rotation management with 8 years period rotation* - N input mean: 110 kg N ha <sup>-1</sup> year <sup>-1</sup> - Nov 2000: Last ploughing
		EXT		- Mixture of over 30 grass, clover and herb species, sown grassland - Mowing: 3 times/year (1st mowing not before 1st Jun) - No grazing - No fertilization	
	Reeuwijk <sup>c</sup> , NL	INT	-	- intensive dairy farm - Mowing and grazing: mid-May to mid-Sep (×3 mowing, 2-3 period of grazing) - mean FYM: 1.67 tC ha <sup>-1</sup> year <sup>-1</sup> and 309.67 kg N ha <sup>-1</sup> year <sup>-1</sup> , Fertiliser: 88 kg N ha <sup>-1</sup> year <sup>-1</sup> (applied 2-3 times/year, not in winter) - Rye grass, bluegrass: dominant, clover: ≤1%	- Since 1970, Deep drainage, application of manure and fertilizer, grazing and mowing
		EXT		- Meadow bird reserve (Established about 14 years ago) - Mowing twice after 15th June - Short time period grazing by livestock/ few parcels whole summer - No fertilization/manure application	
	Carlow <sup>d</sup> , IE	CON	2003	- Conventional tillage (20-25cm depth ploughing) in March 1time/year - Spring barley (Sown in March) - mineral N fertiliser: 140 kg N ha <sup>-1</sup> year <sup>-1</sup> , No manure input - mean (2003-2010) grain harvest: 6.34 t ha <sup>-1</sup> year <sup>-1</sup> DM	- 1960-1989: Under rotations of sugar beet, spring barley, maize and oil seed rape - 1989-1990: A short period of pasture - 1990-2000: Under rotations of sugar beet, spring barley and oilseed rape
		NIT		- No ploughing - Harrowing (10-15 cm depth) in August/September 1 time/year - Spring barley (Sown in March) - mineral N fertiliser: 140 kg N ha <sup>-1</sup> year <sup>-1</sup> , No manure input - mean (2003-2010) grain harvest: 5.99 t ha <sup>-1</sup> year <sup>-1</sup> DM - a cover crop during the fallow period since September 2005 to the present	

\*: Summer- and winter wheat, rape, maize and bi- and tri-annual grass-clover mixture

\*\* : Winter wheat, Winter oilseed rape, Spring peas

<sup>a</sup>: From Klumpp et al. (2011), Soussana et al. (2007) and Allard et al. (2007)

<sup>b</sup>: From Ammann et al. (2007, 2009); Flechard et al. (2005); Leifeld et al. (2011) and Flechard et al. (2007)

<sup>c</sup>: From Stolk et al. (2011); Jacobs et al. (2007); Veenendaal et al. (2007); Schrier-Uijl et al. (2008) and Schrier-Uijl et al. (2010)

<sup>d</sup>: From Van Groenigen et al. (2010a,b); Osborne et al. (2010); Walmsley et al. (2011) and Davis et al. (2010)

### 3.2.2 Soil sampling and analysis method

In autumn/winter 2011/2012 soil sampling campaigns were carried out for the four agricultural paired-sites (8 plots in total). In each plot, 6 soil cores (40 cm depth) were sampled at equal intervals (10m) along 60 m transect. Each soil core was separated into 0-5 cm, 5-10 cm, 10-20 cm and 20-40 cm depth layers, that were air dried under laboratory conditions.

Dried soil samples were then passed through a 2 mm sieve to remove larger particles and debris. A sub-sample was dried for 48h at 60 °C to determine residual humidity, bulk density and total C and N content. soil pH was measured following the method of Soon and Hendershot (1993).

#### Soil fractionation

Zimmermann et al. (2007) fractionation method was used to separate SOC into five different fractions: Sand and Aggregate (S+A), POM, silt and clay (s+c), Dissolved Organic Carbon (DOC) and Resistant SOC (rSOC). Soil fractionation was undertaken using a 30 g sample of dry 2mm sieved soil. Briefly, soil fractionation is achieved through ultrasonic dispersion, wet sieving (63 $\mu$ m), density separation and NaOCl (6%) oxidation. To separate the heavy fraction (S+A) and POM from > 63 $\mu$ m soil fraction, the fraction was mixed with sodium polytungstate (SPT) and frozen over night (see Wurster et al. (2010)). This freezing method avoids mixing up heavy and POM fractions physically when we extract these fractions. For extracting the light fraction, we used distilled water to thaw the frozen POM. For more detail, see Zimmermann et al. (2007) and Wurster et al. (2010).

#### Carbon and Nitrogen analysis

Soil fractions and 2 mm sieved bulk soil was analysed for C and N content using NC analyser (Thermo Electron Cooperation, Flash EA 1112 series). Prior to analysis, all fraction (s+c, S+A, DOC and bulk soil), except the POM fraction (which contain certain amount of plant-derived carbon that could be degraded by HCl), were decarbonated following the methodology of Harris et al. (2001); Dondini et al. (2009a).

### 3.2.3 Statistical analysis

Linear regression models with 95 % confidence intervals were used to analyse differences between managements and soil layers. Differences were further tested with a Tukey HSD (honestly significant difference) test in conjunction with an ANOVA to find means. For analysing the influence of soil properties and land management on SOC (tC/ha), we applied a stepwise regression procedure investigating the following explanatory variables, soil texture (sand, silt and clay), soil pH, bulk density, mineral nitrogen fertiliser amount (kg N ha<sup>-1</sup>year<sup>-1</sup>), manure carbon input (kgC ha<sup>-1</sup>year<sup>-1</sup>), manure nitrogen input (kg N ha<sup>-1</sup>year<sup>-1</sup>) and their interactions with using the R system for statistical computing R 2.14.2. We tested 5 linear regression models: (1) SOC content =  $f_1(\text{silt} + \text{sand} + \text{clay}) + \epsilon_1$ , (2) SOC content =  $f_2(\text{silt} + \text{sand} + \text{clay} + \text{soil pH}) + \epsilon_2$ , (3) SOC content =  $f_3(\text{silt} + \text{sand} + \text{clay} + \text{soil pH} + \text{Bulk density}) + \epsilon_3$ , (4) SOC content =  $f_4(\text{Mineral nitrogen fertiliser (kg N ha}^{-1}\text{year}^{-1}) + \text{Manure applied (kg N ha}^{-1}\text{year}^{-1}) + \text{Manure applied (kgC ha}^{-1}\text{year}^{-1}) + \text{tillage depth (cm)}) + \epsilon_4$ , (5) SOC content =  $f_5(\text{Mineral nitrogen fertiliser (kg N ha}^{-1}\text{year}^{-1}) + \text{Manure applied (kg N ha}^{-1}\text{year}^{-1}) + \text{Manure applied (kgC ha}^{-1}\text{year}^{-1}) + \text{tillage depth (cm)}) + \epsilon_5$ .

kgC ha<sup>-1</sup>year<sup>-1</sup>) + tillage depth (cm) + silt + sand + clay + soil pH + bulk density) +  $\epsilon_5$ . Before all statistical analysis, Shapiro-Wilk's test of normality was undertaken to confirm normal distribution (true in all cases).

### 3.3 Results

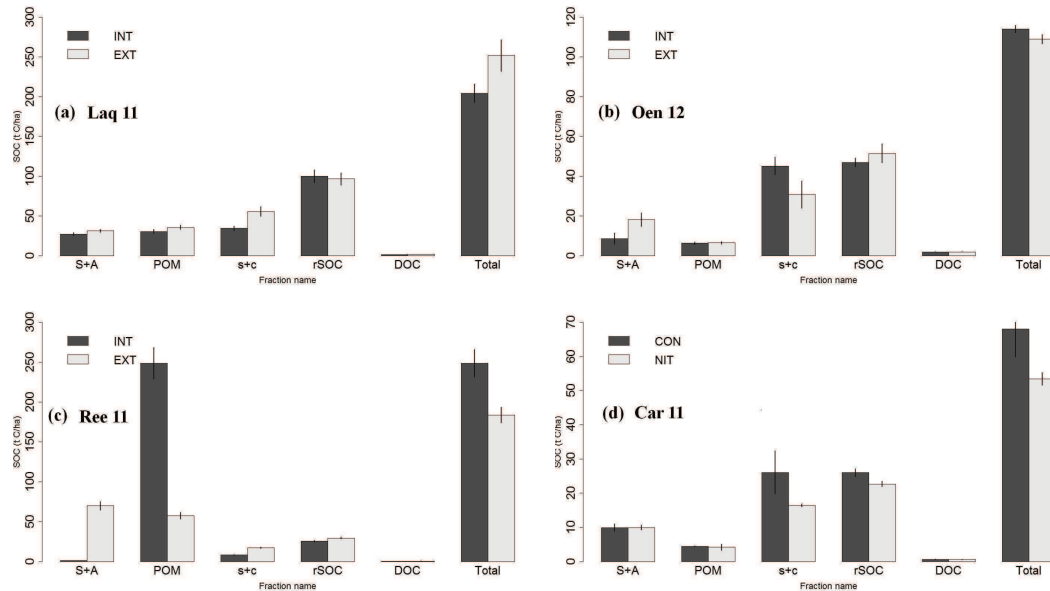


Figure 3.1: Comparison of the sum of SOC fractions (tC/ha) 0-40 cm between contrasting managements: a-d here: (a) Laqueuille (grassland, FR) 2011, (b) Oensingen (grassland, CH) 2012, (c) Reeuwijk (grassland, peat soil, NL) 2011, (d) Carlow (cropland, IE) 2011

Table 3.3: Test of significant difference between management with regard to a bulk SOC (tC/ha) 0-40 cm:  $\frac{\text{Estimates (t value)}}{R^2}$  showing for significant difference

Site name	Fraction					
Country	S+A	POM	s+c	rSOC	DOC	Total
Laq2011	-6.73 (-1.55)	-5.56 (-1.63)	-4.64 (-0.97)	-17.46 (-2.08)	-0.47 (-3.19)	-3.82 (0.25)
FR	<b>0.15</b>	<b>0.13</b>	<b>0.35</b>	<b>0.07</b>	<b>0.01</b>	<b>0.81</b>
Oen2012	-5.52 (-2.09)	-0.73 (-0.65)	19.16 (3.56)	-5.46 (-0.92)	0.07 (0.43)	17.11 (2.14)
CH	<b>0.30</b>	<b>0.04</b>	<b>0.56</b>	<b>0.08</b>	<b>0.02</b>	<b>0.31</b>
Ree2011	-68.63 (-6.05)***	206.64 (8.33)***	-8.01 (-3.39)**	-3.56 (-0.91)	-0.14 (-3.65)**	68.54 (4.16)**
NL	<b>0.82</b>	<b>0.9</b>	<b>0.59</b>	<b>0.09</b>	<b>0.63</b>	<b>0.68</b>
Car2011	0.04 (0.03)	-0.22 (-0.23)	-9.64 (-1.53)	-3.28 (-2.26)	-0.06 (-0.61)	-14.68 (-1.74)
IE	<b>0.00</b>	<b>0.01</b>	<b>0.19</b>	<b>0.34</b>	<b>0.04</b>	<b>0.23</b>

Key to significance stars: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1

The result of the soil organic carbon fractions for the entire soil profile (0-40 cm depth) for each of the sites and management treatments are shown in Figure 3.1. The statistical analysis of differences between management regimes are shown in Table 3.3. For the sum of total SOC across the whole soil profile sampled, only the Reeuwijk (NL) site showed a significant difference between management practices, where total SOC for the intensive and extensive treatments were found for all fractions, with the exception of rSOC. For all other sites (i.e. mineral soil



sites), there were only small differences in SOC (Figure 3.1 and Table 3.3) due to management, however, slight but not significant differences were observed in the s+c fraction.

Table 3.4: Test of significant difference between management with regard to total SOC ( $\text{tC ha}^{-1}\text{cm}^{-1}$ ) for each depth:  $\frac{\text{Estimates (t value)}}{R^2}$  showing for significant difference

Land-use	Site name Country	Total SOC ( $\text{tC ha}^{-1}\text{cm}^{-1}$ )			
		0-5 cm	5-10 cm	10-20 cm	20-40 cm
Grassland	Laq	-0.3(-0.4)	-0.84(-1.41)	-0.3(-0.66)	-1.93(-1.02)
	FR	<b>0.02</b>	<b>0.17</b>	<b>0.04</b>	<b>0.09</b>
	Oen	0.6(1.75)	-0.06 (-0.25)	0.04 (0.21)	0.1 (0.82)
	CH	<b>0.23</b>	<b>0.01</b>	<b>0</b>	<b>0.06</b>
	Ree	0.75 (-0.93)	1.52 (1.93)	2.94 (4.71)	1.58 (2.12)
	NL	<b>0.1</b>	<b>0.32</b>	<b>0.73</b>	<b>0.36</b>
Cropland	Car	0.09 (0.46)	-0.31(-1.09)	-0.36 (-2.73)*	-0.5 (-1.13)
	IE	<b>0.02</b>	<b>0.11</b>	<b>0.43</b>	<b>0.11</b>

Key to significance stars: 0 \*\*\*\* 0.001 \*\*\* 0.01 \*\* 0.05 \* 0.1

When examining each soil depth separately, we found no significant difference due to management practices in total SOC concentration ( $\text{tC ha}^{-1}\text{cm}^{-1}$ ) (Table 3.4). Total SOC concentration ( $\text{tC ha}^{-1}\text{cm}^{-1}$ ) decreased below 20 cm soil depth except for the Laqueuille (FR) extensive plot (Figure 3.2 (b)). Total SOC concentration among all of the soil depths was similar in Laqueuille (FR) extensive plot (Figure 3.2 (b)), although the Laqueuille (FR) intensive plot showed a gradual decrease in total SOC concentration down the soil profile, with a similar trend seen in the Reeuwijk (NL) intensive plot (Figure 3.2(a) and (e)). In the Oensingen (CH) intensive grassland plot, total SOC was similar across the shallow soil depth up to 20 cm depth, probably indicating the influence of ploughing and re-sowing in the upper 20 cm layers (Figure 3.2 (c)). The Oensingen (CH) extensive plot shows that the very top soil layer (0-5cm) has lost SOC (Figure 3.2 (d)). The result for the Carlow conventional tillage plot reflects the influence of ploughing depth and soil aggregate disturbance on SOC, showing homogenised total SOC concentration among all of the soil depths layers (Figure 3.2 (g)). For the non inversion treatment (Carlow, IE), the total SOC concentration in the 20-40 cm layer was significantly different from the other soil layers (Figure 3.2 (h)). For the extensive grassland plot in Reeuwijk (NL), the SOC concentration changed significantly, up to 2  $\text{tC ha}^{-1}\text{cm}^{-1}$ , in the 10-20 cm soil depth (Figure 3.2 (f)). The Reeuwijk (NL) intensive grassland plot shows a gradual loss of SOC down the soil profile at depths below 5 cm (Figure 3.2 (e)).

To better understand which of the soil fractions had the greatest influence on total SOC, we analysed the difference in SOC content for each soil fraction at each sample depth for each study site (Figure 3.3). For the mineral soil sites (i.e. all sites except Reeuwijk (NL) site), the soluble organic C (DOC fraction) did not have a major influence on total SOC (Figure 3.3 and 3.4 (a)-(d), (g)-(h)). Our analysis indicated that the s+c and rSOC fractions (i.e. those fractions derived from finer-textured silt and clay sized particles) contained more SOC than any of the other fractions across all the soil profiles as a whole, with the greatest contribution to total SOC storage in the upper 10 cm of soil (Figure 3.3 and 3.4 (a)-(d), (g)-(h)). This implies that soil texture exerted a strong influence on total SOC. For individual depth increments (e.g. 0-5 cm, 5-10 cm etc), the relative proportion of total SOC stored in each fraction varied among sites and management regimes (Figure 3.3). The overall trend for mineral soils was for POM to account for a significantly larger proportion of total SOC in the upper most 0-5 cm depth than elsewhere in each soil profile; in some cases equal to the SOC stored in the s+c and rSOC fractions (Figure 3.3 (a)-(d) and (g)-(h)). At other depths, finer-textured fractions (i.e. s+c and rSOC) accounted

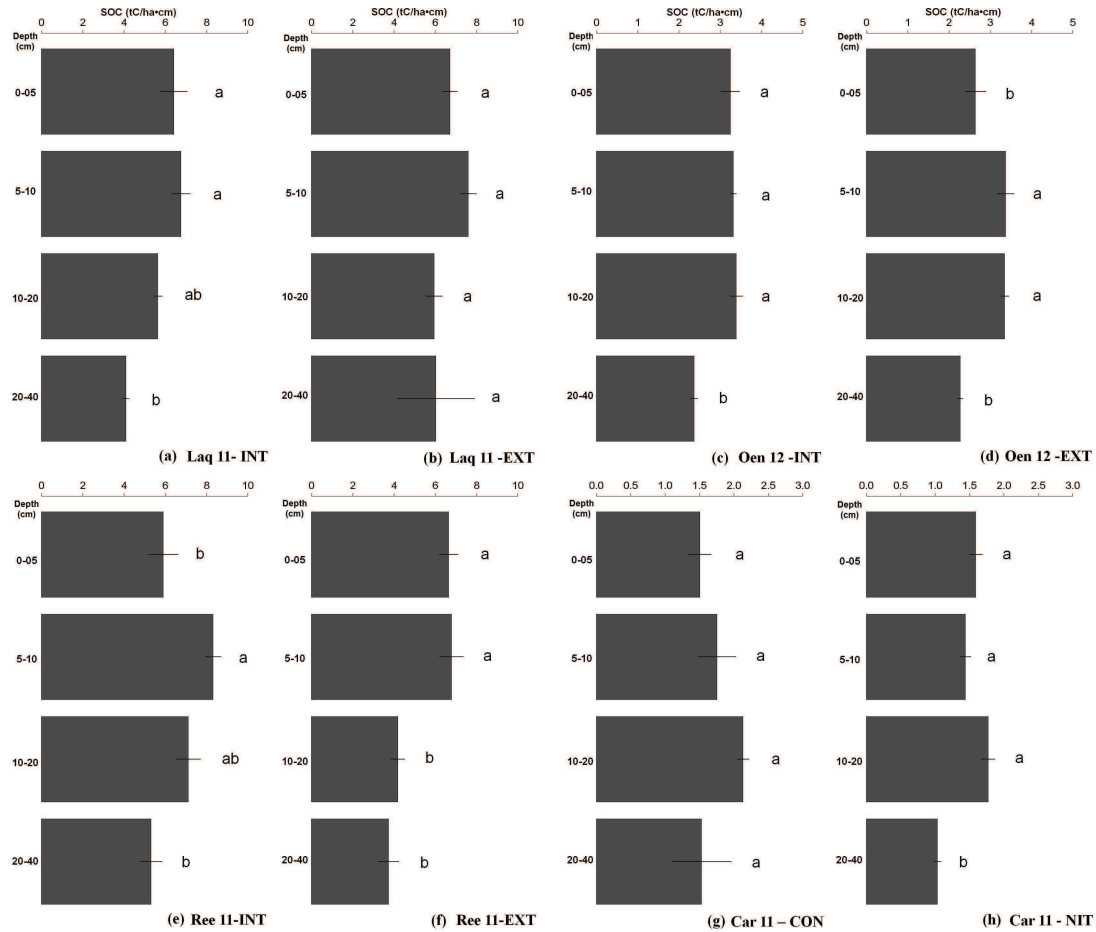


Figure 3.2: Total SOC (tC ha<sup>-1</sup> cm<sup>-1</sup>) comparison among each soil depth: a-h here (a) Laqueuille (grassland, FR) 2011 INT, (b) Laqueuille (grassland, FR) 2011 EXT, (c) Oensingen (grassland, CH) 2011 INT, (d) Oensingen (grassland, CH) 2011 EXT, (e) Reeuwijk (grassland, peatland, NL) 2011 INT, (f) Reeuwijk (grassland, peatland, NL) 2011 EXT, (g) Carlow (cropland, IE) 2011 Conventional Tillage, (h) Carlow (cropland, IE) 2011 Non inversion. Data was normalized to the same thickness, accordingly stock was expressed in tC ha<sup>-1</sup> cm<sup>-1</sup>. The same letter, in the same site and management, represents that there is no significant differences between soil strata.

for the bulk of total SOC storage in mineral soils (e.g. at deeper than 10 cm depth, Laqueuille (FR): 73.84 ~ 78.21 %; Oensingen (CH): 79.67 ~ 84.88 %; Carlow (IE): 75.94 ~ 78.12 %). For the organic soils (Reeuwijk (NL)), the POM fraction made the greatest contribution to total SOC. rSOC shows a similar contribution at all soil profile depths (Figure 3.3 (e) and (f)). However, apparent differences were found due to management: the POM fraction contributed 81.48 ~ 89.85 % to SOC in the intensive plot, while the extensive plot, POM dominated the total SOC, with 43.77 % in the top 0-5 cm and 23.25 ~ 35 % in the > 5 cm soil depths (Figure 3.3 (e) and (f)). Extensive plot in Reeuwijk (NL), the S+A fraction accounted for a large part of the total SOC in all of the soil depth profiles (Figure 3.3 (f)).

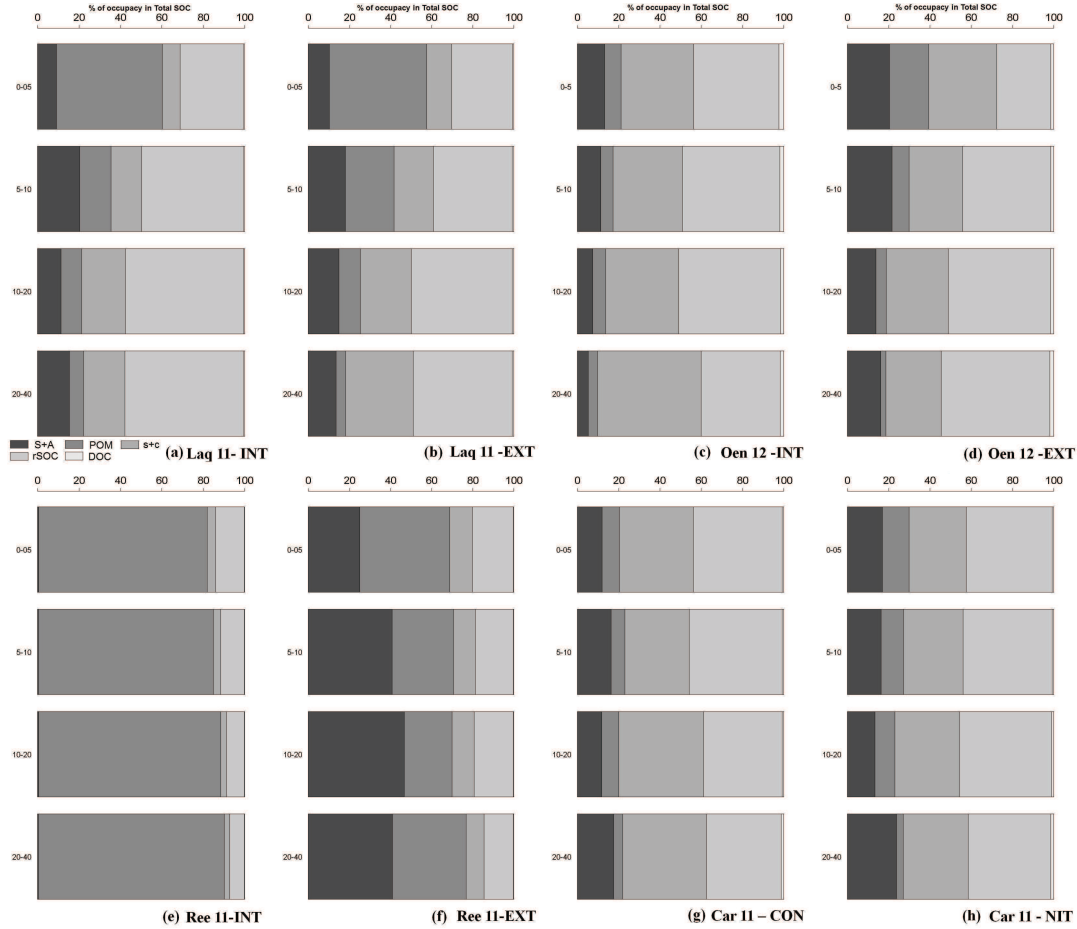


Figure 3.3: Each fraction SOC (tC/ha) occupancies in Total SOC: a-h here (a) Laqueuille (grassland, FR) 2011 INT, (b) Laqueuille (grassland, FR) 2011 EXT, (c) Oensingen (grassland, CH) 2011 INT, (d) Oensingen (grassland, CH) 2011 EXT, (e) Reeuwijk (grassland, peatland, NL) 2011 INT, (f) Reeuwijk (grassland, peatland, NL) 2011 EXT, (g) Carlow (cropland, IE) 2011 Conventional Tillage, (h) Carlow (cropland, IE) 2011 Non inversion.

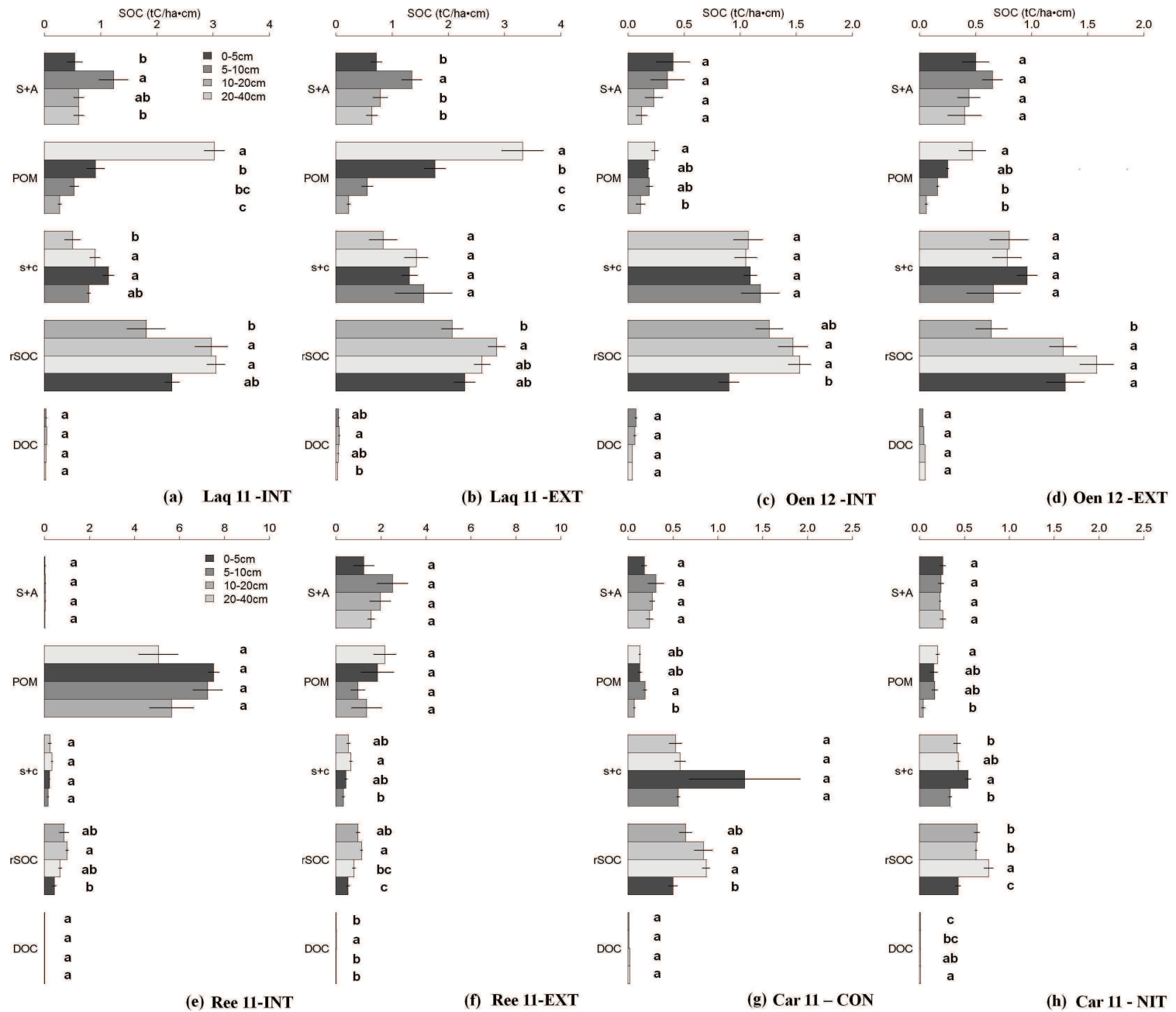


Figure 3.4: SOC (tC ha<sup>-1</sup> cm<sup>-1</sup>) for each fraction and each depth: a-h here (a) Laqueuille (grassland, FR) 2011 INT, (b) Laqueuille (grassland, FR) 2011 EXT, (c) Oensingen (grassland, CH) 2011 INT, (d) Oensingen (grassland, CH) 2011 EXT, (e) Reeuwijk (grassland, peatland, NL) 2011 EXT, (f) Reeuwijk (grassland, peatland, NL) 2011 EXT, (g) Carlow (cropland, IE) 2011 Conventional Tillage, (h) Carlow (cropland, IE) 2011 Non inversion. Data was normalized to the same thickness, accordingly stock was expressed in tC ha<sup>-1</sup> cm<sup>-1</sup>. The same letter, in the same site and management, represents that there is no significant differences between soil strata.



For mineral soils, significant differences were found in SOC content for different study sites and also among different depth increments in each study sites (Figure 3.4 (a)-(d) and (g)-(h)). Both bivariate linear regression and multivariate stepwise linear regression indicates that management practices did not have a significant impact on SOC (Table 3.5 and Table 3.6). Instead we found that stepwise models that included only soil characteristics (e.g. soil texture, soil pH and bulk density; see models 1-3 in Table 3.6) better predicted SOC content than a separate model that only included management (model 4 in Table 3.6). In terms of soil characteristics, the estimate of each variables was in general, in the order bulk density > soil pH > soil texture. Average changes in bulk density and soil pH between contrasting managements were 0 ~ 0.44 and 0 ~ 0.25 respectively (Table 3.1), then these variables did not dramatically influence SOC concentration. On the other hand, soil texture differences between contrasting management were more than 1 for each soil texture (Table 3.1), and had a greater influence on SOC were than bulk density or soil pH. A model incorporating both soil characteristics and management best predicted SOC (model 5 in Table 3.6); although the effect of management were small relative to inherent soil characteristics (p-values: management 0.034 ~ 0.87, soil characteristics 2.00E-16 ~ 0.36). Of all soil characteristics, soil texture was the most important factor determining total SOC storage, both for the soil profile as a whole and for each individual depth increment. This influence is supported by earlier analysis, indicating that s+c and rSOC fractions (derived from silt and clay content) exert the greatest influence on total SOC storage (Figure 3.3 and Figure 3.4), with a higher contribution in the topsoil (0-10cm) compared to the deeper soil layers (>10 cm depth). Tillage depth does not influence SOC distribution in our mineral soil sites. In organic soils, SOC did not vary significantly with depth when under the same management regime. However, SOC did vary significantly between the two plots, suggesting that management may have altered total SOC and SOC in each fraction (Figure 3.4 (e) and (f)). The exception to this pattern was the rSOC fraction, which did not vary between management regimes. Because of differences in underlying soil characteristics between the two Reeuwijk (NL) sites (Table 3.1), we used a multivariate stepwise linear regression to assess the relative influence of management and intrinsic soil characteristics on SOC storage. Soil texture (sand, silt and clay content), soil pH, bulk density, N supply ( $\text{kg N ha}^{-1}\text{year}^{-1}$ ), C supply ( $\text{kgC ha}^{-1}\text{year}^{-1}$ ) and tillage depth (cm) (See Table 3.7) were regressed against total SOC. We also found that bulk density was weakly correlated with SOC storage in topsoil (0-10 cm), while bulk density sand mineral nitrogen fertiliser application strongly influenced SOC in the deeper soil layers (deeper than 10 cm depth) (Table 3.7).

### 3.4 Discussion

After 10 years of contrasting management regimes, the results of this study show no significant difference in total SOC concentration due to management practices in mineral soils. In study of Torn et al. (1997), soil mineralogy was found to be the main determinate of the quantity of SOC and SOC turn over with time. Qian et al. (2003) also found soil type exerts a significant impact on the dynamics of SOC. We have to mention that one of the limits of this experimental design using eddy covariance flux tower sites is the absence of replicates and thus a possible pseudo replication of soil samples (i.e. 6 soil cores per field). To overcome this problem we have chosen a sampling design which covers foot-print area for comparing with flux measurement and model flux output (see Chapter 5). However, performing soil fractionation at different depth soil

Table 3.5: Tests of significant differences between land management systems:  $\frac{\text{Estimate (t value)}}{R^2}$  with highlight for significant difference

Site name	Depth (cm)	Fraction					
		S+A	POM	s+c	rSOC	DOC	Total
Laq2011	0-05	<b>-0.8972 (-1.062)</b> 0.101	<b>-1.497 (-0.734)</b> 0.051	<b>-1.698 (-1.197)</b> 0.125	<b>-1.34 (-0.687)</b> 0.045	<b>-0.06973 (-1.317)</b> 0.148	<b>-1.504 (-0.402)</b> 0.016
	05-10	<b>-0.577 (-0.367)</b> 0.013	<b>-4.2619 (-3.41)**</b> 0.538	<b>-2.6357 (-2.317)*</b> 0.349	<b>0.5402 (0.329)</b> 0.011	<b>-0.12136 (-3.343)**</b> 0.528	<b>-4.204 (-1.41)</b> 0.166
	10-20	<b>-1.796 (-1.149)</b> 0.117	<b>-0.2467 (-0.191)</b> 0.004	<b>-1.699 (-1.003)</b> 0.091	<b>4.536 (2.108).</b> 0.308	<b>-0.1179 (-2.236)*</b> 0.333	<b>-3.024 (-0.657)</b> 0.041
	20-40	<b>-0.660 (-0.252)</b> 0.006	<b>0.904 (1.12)</b> 0.111	<b>-15.41 (-1.514)</b> 0.186	<b>-0.4225 (-0.093)</b> 0.001	<b>-0.16352 (-2.991)*</b> 0.472	<b>-38.68 (-1.023)</b> 0.095
Oen2012	0-05	<b>-0.491 (-0.511)</b> 0.025	<b>-1.117 (-1.826).</b> 0.25	<b>1.3093 (1.233)</b> 0.132	<b>3.0755 (3.388)**</b> 0.534	<b>0.169 (2.346)*</b> 0.355	<b>3.010 (1.748)</b> 0.234
	05-10	<b>-1.490 (-1.699)</b> 0.224	<b>-0.333 (-3.70)**</b> 0.578	<b>1.347 (1.685)</b> 0.221	<b>0.933 (1.043)</b> 0.098	<b>0.073 (1.845).</b> 0.254	<b>-0.275 (-0.253)</b> 0.006
	10-20	<b>-2.129 (-1.64)</b> 0.212	<b>0.333 (1.042)</b> 0.098	<b>1.284 (1.156)</b> 0.118	<b>4.536 (2.108).</b> 0.01	<b>-0.034 (-0.743)</b> 0.052	<b>0.388 (0.208)</b> 0.004
	20-40	<b>-5.501 (-1.698)</b> 0.224	<b>0.945 (1.269)</b> 0.139	<b>10.4 (1.737)</b> 0.232	<b>-7.945 (-2.064)</b> 0.299	<b>-0.14109 (-1.701)</b> 0.224	<b>1.94 (0.822)</b> 0.063
Ree2011	0-05	<b>-6.039 (-2.07).</b> 0.349	<b>14.516 (3.117)*</b> 0.548	<b>-1.5346 (-2.585)*</b> 0.455	<b>-0.5576 (-0.548)</b> 0.036	<b>-0.021239 (-3.671)**</b> 0.627	<b>-3.763 (-0.934)</b> 0.098
	05-10	<b>-12.418 (-2.904)*</b> 0.513	<b>28.375 (6.074)***</b> 0.822	<b>-1.6655 (-4.013)**</b> 0.668	<b>-0.647 (-1.624)</b> 0.248	<b>-0.0363 (-2.743)*</b> 0.485	<b>7.611 (1.93).</b> 0.318
	10-20	<b>-19.266 (-3.298)*</b> 0.576	<b>62.788 (9.628)***</b> 0.921	<b>-2.2502 (-3.126)*</b> 0.55	<b>-0.978 (-0.962)</b> 0.104	<b>-0.0134 (-1.038)</b> 0.119	<b>29.364 (4.706)**</b> 0.735
	20-40	<b>-30.909 (-8.504)***</b> 0.9	<b>85.47 (3.748)**</b> 0.637	<b>-3.345 (-2.574)*</b> 0.453	<b>-2.017 (-0.816)</b> 0.077	<b>-0.0680 (-2.227).</b> 0.383	<b>31.59 (2.116).</b> 0.359
Car2011	0-05	<b>0.411 (2.206).</b> 0.3273	<b>0.374 (2.773)*</b> 0.4346	<b>-0.524 (-1.310)</b> 0.1465	<b>0.009 (0.025)</b> 0.0001	<b>0.007 (0.843)</b> 0.0663	<b>0.440 (0.458)</b> 0.0206
	05-10	<b>-0.324 (-0.688)</b> 0.045	<b>0.167 (0.741)</b> 0.052	<b>-0.782 (-2.7)*</b> 0.422	<b>-1.044 (-2.176).</b> 0.321	<b>-0.007 (-0.809)</b> 0.062	<b>-1.562 (-1.088)</b> 0.106
	10-20	<b>-0.371 (-1.071)</b> 0.103	<b>-0.243 (-0.642)</b> 0.04	<b>-7.613 (-1.364)</b> 0.171	<b>-0.965 (-1.646)</b> 0.213	<b>-0.011(-1.003)</b> 0.091	<b>-3.63 (-2.728)*</b> 0.427
	20-40	<b>0.324 (0.334)</b> 0.011	<b>-0.618 (-1.24)</b> 0.161	<b>-4.383 (-7.057)**</b> 0.833	<b>-1.283 (-1.07)</b> 0.103	<b>-0.048 (-0.548)</b> 0.029	<b>-9.932 (-1.131)</b> 0.113

Key to significance stars: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1

Table 3.6: Mineral soils: stepwise linear model results regarding soil texture, soil characteristics and management systems for total SOC:  $\frac{\text{Estimate (t value)}}{R^2}$

Depth (cm)	Fraction	Variables	Model name				
			(1)	(2)	(3)	(4)	(5)
			Soil texture	Soil texture Soil pH	Soil texture Soil pH Bulk Density	Management	Management Soil texture Soil pH Bulk Density
0-5	Total	Clay	-0.12 (-2.19)*	0.22 (0.68)	-0.48 (-1.73)		-0.33 (-5.26)***
		Silt	0.7 (17.04)***	0.79 (8.26)***	0.677 (9.2)***		0.67 (15.77)***
		Sand	-0.14 (-5.06)***	0.18 (0.58)	-0.38 (-1.49)		-0.31 (-6.08)***
		Soil pH		-3.87 (-1.04)	1.28 (0.44)		NA
		Bulk Density			16.71 (5.31)***		20.04 (5.49)***
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>				0.13 (4.47)***	0.004 (0.42)
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>				0.09 (0.57)	-0.09 (-1.63)
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>				NA	NA
		Tillage depth (cm)				-0.42 (-1.33)	-0.02 (-0.28)
		R <sup>2</sup> (DF*)	0.97 (33)	0.97 (32)	0.98 (31)	0.45 (33)	0.98 (29)
5-10	Total	Clay	-0.12 (-2.81)**	-0.11 (-1.21)	-0.29 (-2.78)**		-0.33 (-3.44)**
		Silt	0.79 (23.25)***	0.8 (15.67)***	0.79 (16.92)***		0.79 (17.16)***
		Sand	-0.18 (-7.11)***	-0.16 (-1.5)	-0.18 (-1.83)		-0.21 (-3.85)***
		Soil pH		-0.19 (-0.17)	-0.89 (-0.81)		NA
		Bulk Density			12.07 (2.73)*		9.85 (2.08)*
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>				0.13 (4.06)***	-0.01 (-1.4)
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>				0.08 (0.47)	0.01 (0.24)
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>				NA	NA
		Tillage depth (cm)				-0.39 (-1.09)	-0.01 (-0.17)
		R <sup>2</sup> (DF*)	0.98 (33)	0.98 (32)	0.98 (31)	0.40 (33)	0.98 (29)
10-20	Total	Clay	-0.04 (-0.69)	-0.06 (-0.42)	-0.43 (-1.7)		-0.53 (-2.58)*
		Silt	1.21 (32.27)***	1.2 (14.6)***	1.09 (10.84)***		1.17 (21.98)***
		Sand	-0.19 (-4.78)***	-0.22 (-1.12)	-0.46 (-1.99)		-0.35 (-3.47)**
		Soil pH		0.31 (0.15)	1.33 (0.63)		NA
		Bulk Density			16.59 (1.78)		21.46 (2.33)*
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>				0.27 (5.6)***	-0.03 (-2.20)*
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>				0.16 (0.48)	0.1 (1.34)
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>				NA	NA
		Tillage depth (cm)				-0.66 (-1.02)	0.12 (0.98)
		R <sup>2</sup> (DF*)	0.99 (45)	0.99 (44)	0.99 (43)	0.46 (45)	0.99 (41)
20-40	Total	Clay	-0.22 (-0.58)	-0.26 (-0.26)	-0.72 (-0.57)		-0.78 (-0.93)
		Silt	1.96 (7.87)***	1.95 (4.83)***	1.81 (3.9)***		2.17 (6.1)***
		Sand	-0.36 (-1.46)	-0.4 (-0.38)	-0.74 (-0.62)		-0.24 (-0.42)
		Soil pH		0.42 (0.04)	1.69 (0.15)		NA
		Bulk Density			20.43 (0.6)		10.78 (0.31)
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>				0.36 (3.99)***	-0.13 (-1.64)
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>				0.25 (0.40)	0.33 (0.68)
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>				NA	NA
		Tillage depth (cm)				-0.81 (-0.67)	0.32 (0.39)
		R <sup>2</sup> (DF*)	0.81 (45)	0.8 (44)	0.81 (43)	0.31 (45)	0.82 (41)

Key to significance stars: 0 \*\*\*\* 0.001 \*\*\* 0.01 \*\* 0.05 \*

<sup>a</sup>: DF=Degree of freedom

<sup>b</sup>: NA=lack of the number of data to get accurate statistical result

samples and analysing SOC is labour intensive and it is not feasible for a large number of soil samples. Other studies have reported lower number of sampling: four and six soil cores from a 15×30m and 14×21 m sampling area at 0-15 and 15-30 cm and down to a depth of 80 cm soil depth (Dondini et al. (2009b); Poeplau and Don (2013b)). In this study, we sampled 6 to 8 soil cores from around along a representative transect of the soil inventory and foot-print area. The soil sampling areas were covered with eddy-covariance measurement, then it is scientifically attractive to compare SOC distribution among SOC fraction and flux measurement such as GPP, NEE and Reco which are affected by plant growth and soil respiration mechanisms. Another limit of the experimental design in this study is most of the experimental sites might not have enough time to arrive at the SOC equilibrium after the land-use change. Laqueuille (FR) site was converted from cropland to grassland around 1950. Reeuwijk (NL) grassland has been a permanent grassland. Carlow (IE) site has been cropland since at least 1960 and Hertfordshire (UK) cropland was converted from grassland in 1960. Oensingen (CH) was converted from cropland to grassland in 2000. Poeplau et al. (2011) have reported using a number of LUC sites that grassland conversion to cropland may arrive the SOC equilibrium after 17 years. On the other hand, a conversion from cropland to grassland took around 120 years. We agree that 50-40 years after conversion may not be enough to arrive at the SOC equilibrium due to land-use.

Table 3.7: Organic soils: stepwise linear model results regarding soil texture, soil characteristics and management systems for total SOC:  $\frac{\text{Estimate (t value)}}{R^2}$

Depth (cm)	Fraction	Variables	Model name				
			(1)	(2)	(3)	(4)	(5)
			Soil texture	Soil texture Soil pH	Soil texture Soil pH Bulk Density	Management	Management Soil texture Soil pH Bulk Density
0-5	Total	Silt+Clay	0.28 (5.56)***		0.21 (3.69)**		0.23 (1.74)
		Sand	0.47 (2.82)*		0.05 (0.18)		NA
		Soil pH			NA		NA
		Bulk Density			40.6 (1.92).		40.6 (1.92).
		Mineral kgN/ha-year					-0.01 (-0.18)
		Manure kgN/ha-year					NA
		Manure kgC/ha-year					NA
		R2 (DF*)	0.97 (8)		0.98 (7)		0.98 (7)
5-10	Total	Silt+Clay	0.46 (9.41)***		0.53 (3.64)**		0.72 (1.62)
		Sand	0.06 (0.34)		0.47 (0.60)		NA
		Soil pH			NA		NA
		Bulk Density			-27.3 (-0.55)		-27.3 (-0.55)
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>					-0.14 (-0.6)
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>					NA
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>					NA
		R2 (DF*)	0.98 (8)		0.98 (7)		0.98 (7)
10-20	Total	Silt+Clay	1.01 (9.64)***		0.71 (6.3)***		-0.20 (-0.82)
		Sand	-0.95 (-3.00)*		-2.14 (-5.1)**		NA
		Soil pH			NA		NA
		Bulk Density			111.62 (3.29)*		111.62 (3.29)*
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>					0.52 (5.1)**
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>					NA
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>					NA
		R2 (DF*)	0.98 (8)		0.99 (7)		0.99 (7)
20-40	Total	Silt+Clay	0.62 (4.43)**		-0.60 (-1.9).		-0.38 (-1.27)
		Sand	3.78 (2.75)*		5.45 (5.96)***		NA
		Soil pH			NA		NA
		Bulk Density			259.84 (3.98)**		259.84 (3.98)**
		Mineral kgN ha <sup>-1</sup> year <sup>-1</sup>					0.65 (5.96)***
		Manure kgN ha <sup>-1</sup> year <sup>-1</sup>					NA
		Manure kgC ha <sup>-1</sup> year <sup>-1</sup>					NA
		R2 (DF*)	0.95 (8)		0.98 (7)		0.98 (7)

Key to significance stars: 0 \*\*\*\* 0.001 \*\*\* 0.01 \*\* 0.05 \*

a: DF=Degree of freedom

b: NA=lack of the number of data to get accurate statistical result

However, several studies have also found SOC distribution difference in different SOC fractions due to management regimes even after land-use conversion at 1950s-1970s (Conant et al. (2003); Leifeld et al. (2009a)). Additionally, Poeplau et al. (2011) mentioned that these number of years are uncertain due to inadequate number of samples for the study. Furthermore, in this study, we excluded several natural induced impacts such as soil texture, climate and geographical conditions so we hypothesised SOC distribution difference due to management regimes might allow detection of changes in detailed SOC fractions over shorter periods (Smith (2004b)). We also choose varied contrasting agricultural lands: two croplands in UK and Ireland and one permanent grazing grassland with Nitrogen fertiliser application (France), mowing grassland with mineral soil converted from cropland with Nitrogen and manure application (Switzerland) and mowing and manure applying grassland with organic soil (Netherlands). As each sampling sites possess adjacent contrasting management regimes, this let us to compare the absolute management impact on SOC distribution. Hence, we sampled 6-8 soil cores from our five paired-sites which possess two adjacent contrasting management regimes and eddy-covariance flux measurement towers for each management regimes. Our analysis also indicates, in mineral soils, the s+c and rSOC fractions, which were derived from silt and clay, contributed the greatest amount to total SOC (Figure 3.3 and Figure 3.4 (a)-(d) and (g)-(h)), especially in the topsoil (0-10cm). For the organic soil, POM contributed the greatest amount to total SOC (Figure 3.3 and Figure 3.4 (e) and (f)). Accordingly, the organic soil results were not easily compared to the mineral soils examined here, as very different fractions dominated in these soils compared to the mineral ones. Notably, our data suggest that applying a density-based soil fractionation (Zimmermann



et al. (2007)) to organic grassland soils improved our understanding of soil composition. The analyses confirmed that the soil fractionation scheme seems to be effective for organic soils which contain up to 16% of OC. The soil characteristics of the Reeuwijk (NL) site were different to all other sites, and even between contrasting plots within Reeuwijk (NL) site (See Table 3.1). Contrasting management did not have a significant impact on total SOC across each of the soil fractions and sample depths within the soil profile, except at the Reeuwijk (NL) site (Table 3.3). However, it was unclear whether the significant differences were due to management or different soil characteristics between the plots. Soil composition data (Table 3.1) indicates the possibility that two contrasting plots in Reeuwijk (NL) have already significant difference in soil types at the beginning of the experiment and this may cause the significant difference in SOC between two contrasting plots in Reeuwijk (NL). In mineral soils, soil texture is especially influential in determining the total SOC for all soil depths (Table 3.6), supporting our proposal that the s+c and rSOC fractions, which were derived from silt and clay (soil texture), exerted the greatest contribution to total SOC (Figure 3.3 and Figure 3.4), with a higher contribution in the topsoil (0-10cm) compared to the deeper soil layers (deeper than 10 cm depth). This could be because less disturbance in deeper soil layers helps to produce aggregates comprising silt and clay, while this mechanism can be easily disturbed in the topsoil. Tillage depth does not influence SOC distribution in our mineral soil sites, which in contrast to other studies (Six et al. (2000); Van Groenigen et al. (2010a,b)), although we might need more time to detect significant influence of tillage on SOC. In organic soils, bulk density slightly influences topsoil (0-10cm) SOC stock (Table 3.7). However, bulk density and the amount of mineral nitrogen fertilizer applied ( $\text{Nkg ha}^{-1}\text{year}^{-1}$ ) had a stronger influence in deeper soil layers (>10 cm depth). Perhaps this is because mineral soil is more compacted than organic soil, then changes in bulk density being proportional to soil depths may influence SOC more significantly than mineral soil. Organic soil bulk density is much smaller than that of mineral soil, then deeper soil layers in organic soil may receive easily the effect of mineral nitrogen fertiliser. Furthermore, inflexibility in mineral soil requires longer times before detection can occur than in organic soil (e.g. C decomposition, nitrification, microbial activities). This suggests that management practices could exert easily more of a contribution to total SOC in organic soils than in mineral soils (Table 3.3). POM and light fraction organic matter (LFOM) are good indicators of long-term total SOC change in both cropland and grasslands (Gosling et al. (2013)) and low-density fractions are more sensitive to alterations in management practice (Zhang et al. (2007)). Figure 3.3 (e) and (f) (organic soil result) show that POM in the organic soils contribute the greatest amount to total SOC, and the significant difference due to management practices were found in only organic soils (Table 3.3), suggesting that management practices influence total SOC *via* their impact on POM. Smith (2004b) found that the time required to detect a significant change in SOC pools due to management in agricultural systems is dependent on both soil characteristics and the rate of change in C input to the soil, but could take many years. Many studies have already found that tillage practices disturb soil aggregates and reduce SOC stocks (Six et al. (2000); Chan et al. (2002); Van Groenigen et al. (2010a,b)), suggesting that we need longer term studies (more than 10 years) in mineral soils for assessing these changes. Furthermore, Chevallier et al. (2008) reported C correlated positively to the allophanic clay amount and C decomposition is lower if soil contain more allophanic clay. Andosol contains significant allophanic clay and this effect should be considered in French soil data result.

### 3.5 Conclusion

Our study indicates that management impacts on SOC in mineral soils cannot be detected for any soil profile depth (0-40 cm) after 10 years if consistent land management. Furthermore, we found that the fine particle size soil fraction (s+c and rSOC:  $\leq 63 \mu\text{m}$ ) makes an important contribution to the total SOC distribution at soil depths greater than 10 cm in mineral soils. In organic soils (16 ~ 24% OC), management apparently drove significant changes in SOC for all of the soil profile depths examined, soil in which POM, which is known to be more sensitive to management change than high density fractions, dominates. The linear regression results indicate that the amount of mineral fertiliser applied influences total SOC in organic soils. However, two contrasting plots' soil types in Reeuwijk (NL) may have been different significantly at the beginning of the experiment (which is difficult to examine). This may cause the significant difference in the SOC between two contrasting plots in Reeuwijk (NL). As we found no significant difference due to management in the mineral soils, our findings suggest that we need longer term studies than those utilised in this study (more than 10 years) to detect the impacts of land management practice on SOC pools in mineral soils. Furthermore, more research is required to better understand the role of land management and soil characteristics on SOC changes within organic soil and andosol systems. Physical and chemical soil fractionation was applied to organic grassland soils for the first time in this study, confirming its utility for use in organic rich soils (8-16% OC).



## Chapter 4

# Soil organic carbon (SOC) equilibrium and model initialisation methods for the Rothamsted Carbon (RothC) model -26.3

### Abstract

Improved initialisation of process-based ecosystem models is required in order to provide accurate assessments of soil organic carbon (SOC) in agricultural management research. The most common initialisation approach is to run the model until equilibrium, when the pools of SOC stabilise. However, this method does not always produce results that are consistent with measured values, either because the SOC is not in equilibrium or because of inaccuracies in the description of model processes. At our experimental sites, which include contrasting adjacent managements, SOC was not at equilibrium after 10 years of continuous management, suggesting that the commonly used spin-up initialisation method, using repeated recent management data, is not the most appropriate approach to use. In this study we propose another spin-up initialisation scheme that involves adjusting the total equilibrium SOC to match the measured SOC by reducing or raising C input during the entire spin-up run period using the RothC model. The root mean square error (RMSE) showed that the model outputs, using the adjusting the equilibrium total SOC to the measured value method, swerved mostly less in the all of the SOC pools and total SOC comparing the other initialisation methods. Furthermore, as total SOC includes all of the SOC pool data, and because the total SOC data is more readily available at most experimental sites than soil fraction data, we conclude that model initialisation using the total SOC content is the most appropriate of those tested for RothC model initialisation .

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## 4.1 Introduction

The terrestrial C stock is more than 3 times of that in the atmosphere and Smith et al. (2007a) report that 40-50% of the Earth's land surface is occupied by agricultural lands (e.g. cropland, managed grassland and agro-forestry). Furthermore, anthropogenic greenhouse gas (GHG) emissions are enhancing the natural "greenhouse effect" (Intergovernmental Panel on Climate Change (IPCC) (2007); Alexander et al. (2013)). In 2005, 10-12% of total global anthropogenic emissions of GHG were due to agricultural activities (Smith et al. (2007a)). Hence, the contribution of modifications to current agricultural management practices has significant potential to mitigate climate change through a reduction in GHG emissions.

There are several ways to mitigate GHG emissions in agriculture, and one of the most effective options is to increase SOC sequestration (Smith et al. (2007a)). Process-based ecosystem models, such as the CENTURY model, the DNDC model and the RothC model, represent useful tools to evaluate the mitigation impacts of appropriate agricultural management practices, as it is often difficult to conduct appropriate field trials. Moreover, these models allow us to project the impacts of future climatic variability on the interaction between the terrestrial and atmospheric carbon cycle, which is difficult to achieve through experimentation alone (Hashimoto et al. (2011)). The results of model simulations are greatly influenced by initial parameter/variable values and management regimes (Bruun and Jensen (2002)), therefore initialisation is critical for accurate ecosystem modelling. However, the most common model initialisation method (i.e. running a model until the equilibrium is achieved using recent management and weather conditions) often fails to replicate observed values (Bruun and Jensen (2002); Pietsch and Hasenauer (2006); Wutzler and Reichstein (2007); Basso et al. (2010); Hashimoto et al. (2011)). This is because the observed SOC may not be at steady state, given that even old soils (more than a century old) can still accumulate SOC and also because many agricultural ecosystems may be in disequilibrium due to frequent management interventions (Wutzler and Reichstein (2007); Basso et al. (2010); Hashimoto et al. (2011)).

Furthermore, a number of studies have mentioned that theoretical SOC pools do not correspond well with the measured fractions, and these theoretical SOC pools cannot be initialised easily based on experimental measurements (Bruun and Jensen (2002); Smith et al. (2002a)). Although, Zimmermann et al. (2007) have succeeded in initialising the Rothamsted Carbon model (RothC) using a physical and chemical soil fractionation method. Accordingly, we hypothesised that although measured SOC data can be useful for initialising ecosystem models, simple SOC measurements may not correspond to model derived SOC pools.

Bruun and Jensen (2002) concluded that the only appropriate SOC initialisation method is to correctly simulate the pre-experimental period. However, the lack of long-term management and weather information is often a limitation to this type of model initialisation. Thus, it is necessary to find an initialisation scheme that enables model simulation results to match measured values. Assuming that the most useful initialisation method should include estimates of plant litter and manure inputs, which should be varied depending on the management system (e.g. intensively or extensively applying organic manure or nitrogen fertiliser, grazing, mowing), the equilibrium assumptions, reducing or increasing plant litter or manure input to the terrestrial system during the spin-up run period, have been proposed (Bruun and Jensen (2002); Pietsch and Hasenauer (2006); Wutzler and Reichstein (2007); Basso et al. (2010); Hashimoto et al. (2011)). The slowest SOM pool continues to accumulate C over a long time and a small amount of C accumulation could cause a significant change in the theoretical equilibrium C state (Wutzler and Reichstein

(2007)). To overcome this problem, SOC distribution in the slowest SOC pool can be analysed by means of  $^{13}\text{C}$  and  $^{14}\text{C}$  analysis (Bruun and Jensen (2002); Wutzler and Reichstein (2007)), although this may not be accessible for many experimental studies.

Wutzler and Reichstein (2007) proposed the relaxed equilibrium assumption, which assumes that all SOC pools are in equilibrium, with the exception of the slowest pool, and a transient correction method was applied that reduced decomposition rate in the slowest C pool until the sum of SOC at equilibrium matches an independently observed sum of SOC. However, this method could not be applied to study sites that have not been disturbed for more than a century. As land use change can result in significant soil derived carbon losses, changing land cover is becoming a topic of global importance, in particular as the global extent of croplands, pastures, plantations and urban areas which have expanded in recent decades (Foley et al. (2005)). Based on such patterns of land use change, it is difficult to find an experimental site that has not been disturbed in recent times (<100 years), suggesting that the model initialisation approach as suggested by Wutzler and Reichstein (2007) is not widely applicable.

Carvalhais et al. (2008) also used a relaxed assumption approach with regard to several different parameters including light use efficiency, temperature, water storage, soil pools and turnover rates of SOC in soil pools in a simple Net Ecosystem Production (NEP) prediction Carnegie Ames Stanford Approach (CASA) model. All of these parameters are included in the model, which relate directly to net primary production (NPP) or soil heterotrophic respiration submodels, that act to determine the net carbon gain or loss from an ecosystem. During the spin-up run to initialise the model, optimisation was firstly applied to alternative parameters for scaling soil carbon pools parameter individually. Then, they removed one of the alternative parameters at the time as well for seeing the impact of each parameter to the model outputs. By applying the relaxed assumption method on a parameter scaling soil carbon pools (microbial and the slow turnover rates' pools) before the model simulation starts, Carvalhais et al. (2008) improved the NEP model output accuracy by 21%, and reduced the normalised average error by 92%, in their model results. While this initialisation method may be useful, there is still uncertainty whether this method works even in complex process-based ecosystem models where several sub-models interact. Carvalhais et al. (2008) applied a relaxed assumption on a scaling soil carbon parameter at the initial point of model prediction, scaling the microbial and the slow SOC pools turnover rates in the model, which correspond to the active and slow SOC pools in the CENTURY model.

Based on the work of Carvalhais et al. (2008), Hashimoto et al. (2011) have tested the slow-scaling-SOC-pools approach to initialise the CENTURY model (version 4) from 600 to 1999 years, where the total spin-up run was set for 2000 years.

Several SOC pools within the main SOC pools of the CENTURY model (the active, slow and passive pools) were adjusted during the spin-up period in the work of Hashimoto et al. (2011). Hashimoto et al. (2011) conducted three SOC scaling schemes: the active + slow, slow + passive and all SOC pools. More stable model predictions were obtained with the slow relaxed assumption and adjusting only active and slow SOC pools were less stable than other scaling schemes Hashimoto et al. (2011). However, it is uncertain whether the scaling of several SOC pools simultaneously from middle of spin-up run period (e.g. from 600 to 1999 years, where the total spin-up run was set to 2000 years (Hashimoto et al. (2011)) or modifying equations within the model program (Wutzler and Reichstein (2007); Carvalhais et al. (2008)) are applicable for all process-based ecosystem models.

In light of these uncertainties and knowledge gaps, we developed a simple and accessible

initialisation approach that could be applied to different process-based models for accurately predicting SOC stocks in agro-ecosystems. In order to do this, we firstly tested the effect of reducing or increasing C input during the spin-up simulation, using the RothC model, in order to achieve comparable modelled and measured SOC stocks. The RothC model initialisation procedure was tested using three different methods: (1) A spin-up run using monthly average 100 year weather data and recent 10 year management data (Control), (2) As spin-up initialisation where C input was increased or reduced (through varying plant litter and manure input) during the spin-up run period to adjust the equilibrium SOC (one SOC pool at a time individually, or the total SOC) and (3) An initialisation with the measured SOC pool data.

The input of C through plant litter, and organic manure-derived carbon is largely influenced by the management system (e.g. intensive or extensive mowing, grazing, organic manure or nitrogen fertilizer application to enhance plant growth). In this study, as we focused on finding an appropriate model initialisation method by changing the C input during the spin-up run, and repeating recent monthly averaged management and weather data, we tested these initialisation method with varied management systems. Furthermore, we also explored the influence of management system on SOC stock changes for each SOC pool and for the total SOC.

For this study we used SOC fraction data from four European long-term (up to 10 years) grassland and cropland experiments, with associated contrasting management regimes to determine an effective model initialisation scheme and, ultimately, to test the performance of the RothC model. In order to derive accurate data on different modelled SOC pools, the Zimmermann et al. (2007) soil fractionation method was used. This soil fractionation method has already been tested in several studies, and since the fractions have been applied to RothC model pools (Leifeld et al. (2009a); Dondini et al. (2009a); Senapati et al. (2013); Shirato et al. (2013)), it allows the findings to be used in future RothC model simulations.

## **4.2 Materials and Methods**

### **4.2.1 Site description**

In this study, four long-term (up to 10 years) experimental sites from the CarboEurope Integrated Project (CEIP) ecosystem flux tower network were selected. The sites are all located in the temperate oceanic climatic zone (Lindner et al. (2010)) with mean annual temperatures ranging between 7.7 and 9.80 °C and mean annual precipitation ranging between 703 to 1100 mm (see Table 4.1). At each site contrasting management were applied: (1) Laqueuille (FR), intensively (high animal stocking rate and N fertiliser input) and extensively (low animal stocking rate and no fertiliser input) grazed grassland, (2) Oensingen (CH), intensively and extensively cut grassland with high and low N fertiliser input (intensive plot was ploughed and re-sown in 2008), (3) Carlow (IE), a spring barley cropping system subject to conventional and non-inversion tillage management with residue incorporation and a cover crop on the non-inversion tillage plot during the fallow season and (4) Hertfordshire (UK), a rotating cropping system subject to conventional and reduced tillage management. A summary of all management related site details can be found in Table 4.2. These sites, which contain two adjacent and contrasting management systems, were chosen to investigate SOC changes in individual SOC pools and in the total SOC pool due to management.

Table 4.1: Site description and soil detail of sites in this study

Land-use	Site name, Country	Management	Depth (cm)	Clay (%)*	Silt (%)	Sand (%)	Soil pH	Bulk Density (g/cm <sup>3</sup> )	C (%)	MAT** (°C)	MAP*** (mm)	Elevation (m a.s.l.)	Latitude	Longitude	Soil type
Grassland	Laqueuille <sup>c</sup> , FR	INT	0-5	26	55	19	5.09	0.46	14.48±0.74	7.68	857-1000	1040	45°38'N	2°44'E	Andosol
			5-10	23	54	23	5.36	0.67	10.19±0.89						
			10-20	20	55	25	5.56	0.79	7.17±0.23						
		EXT	0-5	26	55	19	5.21	0.57	11.98±0.63						
			5-10	23	54	23	5.22	0.81	9.44±0.52						
			10-20	20	55	25	5.39	0.77	7.85±0.84						
	Oensingen <sup>d</sup> , CH	INT	0-5	42.45	32.35	25.2	6.38	0.98	3.32±0.1	9.00	1100	450	47° 17' N	07° 44' E	Eutri-Stagnic Cambisol (developed on clayey alluvial deposits)
			5-10				6.79	1.12	2.97±0.1						
			10-20				6.77	1.10	3.09±0.12						
		EXT	0-5	44.05	38.1	17.85	6.73	0.64	4.16±0.27						
			5-10				5.28	1.04	3.31±0.19						
			10-20				5.42	1.20	2.80±0.09						
Cropland	Carlow <sup>b</sup> , IE	CON	0-5	17	26	56	7.06	0.64	2.36±0.13	9.40	824	57	52° 52' N	6° 54' W	Eutric Cambisol Topsoil: peaty clayey Subsoil: clay loam
			5-10				7.45	0.81	2.11±0.24						
			10-20				7.46	0.93	2.31±0.11						
		NIT	0-5	17	25	58	6.67	0.71	2.26±0.05						
			5-10				6.66	0.75	1.94±0.06						
			10-20				6.85	0.98	1.79±0.06						
	Hertfordshire <sup>d</sup> , UK	CON	0-20	25	50	25	7.04	1.04	1.83±0.023	9.46	703.5	142	51° 47' N	0° 28' W	Chromic Luvisols & Orthic Acrisols (silty clay loam)
			0-20				6.66	1.13	1.92±0.061						

<sup>a</sup>: Ammann et al. (2009)<sup>b</sup>: Van Groenigen et al. (2010a,b); Osborne et al. (2010); Walmsley et al. (2011) and Davis et al. (2010), weather data averaged over 30 years<sup>c</sup>: Klumpp et al. (2011), Soussana et al. (2007) and Allard et al. (2007), weather data averaged over 22 years (1972–1984, 1995–2004)<sup>d</sup>: Hertfordshire pH were measured at Rothamsted Institute by KCl method, , weather data averaged over recent 4 years (2003-2006)

\*: % of weight in minerals

\*\*: Mean annual temperature

\*\*\*: Mean annual precipitation



Table 4.2: Each site's present and past management information

Present land-use	Site, Country	Present Management	Experiment starting year	Present management (detail)	Previous land-use history
Grassland	Laqueuille <sup>a</sup> , FR	INT	Spring 2002	- Semi-natural grassland - No Mowing (except 2010, 3 times mowing) - Grazing: May- October, 0.9-1.2 (LUS), LW gain: 102.3 kg/animal - mean mineral N fertilizer input (6 years): 191.5 kgN ha <sup>-1</sup> year <sup>-1</sup> , - No manure input	- Beginning of 20th century: arable crop - Converted to permanent grassland since around 1950 - 1950-1980: Mowing, cattle grazing, cattle slurry and manure
		EXT		- Semi-natural grassland - No mowing - Grazing: May- October, 0.5-0.6 (LUS), LW gain: 106.3 kg/animal - No mineral N fertilizer and no manure input	
	Oensingen <sup>b</sup> , CH	INT	May 2001	- 7 species, sown grassland - Grass mowing: 4 times/year - No grazing - mean (7 years) mineral N fertiliser: 109.7 kg N ha <sup>-1</sup> year <sup>-1</sup> (3-4 times/year) - manure: 46.89 kgN ha <sup>-1</sup> year <sup>-1</sup> (2 times/year) - mean C input (2002-2004): 47 g C m <sup>-2</sup> year <sup>-1</sup> (1-2 times/ year) - In 2008: Ploughed and the same 7 species were re-sown	- Ley-arable rotation management with 8 years period rotation* - N input mean: 110 kg N ha <sup>-1</sup> year <sup>-1</sup> - Nov 2000: Last ploughing
		EXT		- Mixture of over 30 grass, clover and herb species, sown grassland - Mowing: 3 times/year (1st mowing not before 1st Jun) - No grazing - No fertilization	
Cropland	Hertfordshire, UK	Plough	1980	- Ploughed - mean (2003-2008): NO <sub>3</sub> 49.27 kg ha <sup>-1</sup> year <sup>-1</sup> , NH <sub>4</sub> 152.79 kg ha <sup>-1</sup> year <sup>-1</sup> - Crop rotation: around 5 years rotation** - mean yield 5.9 t ha <sup>-1</sup> year <sup>-1</sup>	- 1940 to 1960's: Grassland - Late 1960: Converted to cropland (Except 1972-1973, 1976-1978: grass Ley) - 1980-1995: annual mean NPK: 217.71 kg ha <sup>-1</sup> year <sup>-1</sup> (N:P:K=5:24:24)+ 193 kg N ha <sup>-1</sup> year <sup>-1</sup> , Yield mean 5.776 t ha <sup>-1</sup> year <sup>-1</sup> - Crop rotation: around 4 years rotation**
		Min Till	2001	- Minimum tillage - mean (2003-2008): NO <sub>3</sub> 43.50 kg ha <sup>-1</sup> year <sup>-1</sup> , NH <sub>4</sub> 57.63 kg ha <sup>-1</sup> year <sup>-1</sup> - Crop rotation: around 5 years rotation** - mean yield 6.28 t ha <sup>-1</sup> year <sup>-1</sup>	- 1940 to late 1940: Grassland - 1940: 50% converted to arable - Early to Late 1960 : 100% converted to arable (Except 1977-1978: grass Ley) - 1980-1985: Ploughed/ Discd and Direct Drilled/McConnel Shakerator - 1980-1995: Ploughed, mean fertilisation: NPK:211.48 kg ha <sup>-1</sup> year <sup>-1</sup> (N:P:K=5:24:24 or 0:24:24)+195.29 kg N ha <sup>-1</sup> year <sup>-1</sup> , 2times FYM 24.71 kg ha <sup>-1</sup> year <sup>-1</sup> , Yield: 5.89 t ha <sup>-1</sup> year <sup>-1</sup> - The field was split into two in 1986 and the plot was set-a side in 2000. - Crop rotation: around 5 years rotation**
	Carlow <sup>c</sup> , IE	CON	2003	- Conventional tillage (20-25cm depth ploughing) in March 1time/year - Spring barley (Sown in March) - minral N fertiliser: 140 kg N ha <sup>-1</sup> year <sup>-1</sup> , No manure input - mean (2003-2010) grain harvest: 6.34 t ha <sup>-1</sup> year <sup>-1</sup> DM	- 1960-1989: Under rotations of sugar beet, spring barley, maize and oil seed rape - 1989-1990: A short period of pasture - 1990-2000: Under rotations of sugar beet, spring barley and oilseed rape
		NIT		- No ploughing - Harrowing (10-15 cm depth) in August/September 1 time/year - Spring barley (Sown in March) - mineral N fertiliser: 140 kg N ha <sup>-1</sup> year <sup>-1</sup> , No manure input - mean (2003-2010) grain harvest: 5.99 t ha <sup>-1</sup> year <sup>-1</sup> DM - a cover crop during the fallow period since September 2005 to the present	

\*: Summer- and winter wheat, rape, maize and bi- and tri-annual grass-clover mixture

\*\*: Winter wheat, Winter oilseed rape, Spring peas

<sup>a</sup>: From Klumpp et al. (2011),Soussana et al. (2007) and Allard et al. (2007)

<sup>b</sup>: From Ammann et al. (2007, 2009); Flechard et al. (2005); Leifeld et al. (2011) and Flechard et al. (2007)

<sup>c</sup>: From Van Groenigen et al. (2010a,b); Osborne et al. (2010); Walmsley et al. (2011) and Davis et al. (2010)

## 4.2.2 Soil sampling and analysis method

The soil sampling campaigns at the Laqueuille (FR), Oensingen (CH) and Carlow (IE) sites were carried out in the autumn/winter of 2011/2012, when each of the paired treatment plots was sampled. In each plot, 6 soil cores (40 cm depth) were sampled at 10 metre intervals along a 60 metre transect. Each soil core was separated into 0-5 cm, 5-10 cm, and 10-20 cm depth layers. At the Hertfordshire (UK) site, the soil was sampled in November of 2003 where 8 soil cores of up to 20 cm in depth were sampled from each plot. The cores taken from the Hertfordshire site were not separated into different soil depths after sampling and the soil analysed from this site were from homogenised samples. At all sites, the soil samples were air dried under laboratory conditions and then passed through a 2 mm sieve to remove larger particles and debris. A sub-sample was dried for 48h at 60 °C to determine residual humidity, bulk density and total C and N content. Soil pH was measured following the method of Soon and Hendershot (1993).

**Soil fractionation** The Zimmermann et al. (2007) fractionation method was used to separate SOC into five different fractions: Sand and Aggregate (S+A), Particulate Organic Matter (POM), silt and clay (s+c), Dissolved Organic Carbon (DOC) and Resistant SOC (rSOC). Soil fractionation was undertaken using a 30 g sample of dry <2mm sieved soil. Briefly, soil fractionation is achieved through ultrasonic dispersion, wet sieving (63  $\mu\text{m}$ ), density separation and NaOCl (6 %) oxidation techniques. In order to separate the heavy fraction (S+A) and POM, the fraction > 63  $\mu\text{m}$  was fractionated by density separation using sodium polytungstate (SPT) and frozen over night based on the methodology of Wurster et al. (2010). By freezing the samples the heavy and POM fractions can be easily extracted with lower risk of contamination. The light fraction was extracted from the frozen samples using distilled water to thaw the frozen POM. Further details on the fractionation and sampling techniques can be found in Zimmermann et al. (2007) and Wurster et al. (2010).

**Carbon and Nitrogen analysis** Soil fractions and <2 mm sieved bulk soil were analysed for C and N concentration using an CN analyser (Thermo Electron Cooperation, Flash EA 1112 series). Prior to analysis, all fractions (S+C, S+A, DOC and bulk soil), except the POM fraction (which contains a certain amount of plant-derived carbon that could be degraded by HCl), were decarbonated following the methodology of Harris et al. (2001) as proposed by Dondini et al. (2009a).

## 4.2.3 Measurement data application to model

The RothC-26.3 model (Jenkinson and Rayner (1977); Coleman and Jenkinson (1999)) was used to estimate SOC pool distribution under equilibrium conditions. This model was developed to simulate the carbon cycle processes that occur in the upper layers of agricultural soils (0-23 cm), but it does not contain a plant productivity sub-model (Coleman and Jenkinson (1999); Coleman et al. (1997)). The model requires particular input data, including weather data (mean monthly air temperature (°C), monthly precipitation (mm) and monthly open pan evaporation (mm)), as well as site specific data, including clay content (%), soil cover (vegetated or bare) and depth of soil layer sampled (cm). The site management data requirements include monthly plant residue input (tC/ha) and monthly inputs of organic manure (tC/ha). SOC is partitioned into 5 pools: Decomposable Plant Material (DPM), Resistant Plant Material (RPM), Microbial

Biomass (BIO), Humified Organic Matter (HUM) and Inert Organic Matter (IOM). In this model, the monthly carbon input is divided into two SOC pools: DPM and RPM, and from these pools SOC is further decomposed into BIO, HUM and the emission of CO<sub>2</sub> to the atmosphere. From the BIO and HUM SOC pools, SOC was further divided into BIO, HUM and CO<sub>2</sub>. For further details on this model and its application, see Jenkinson and Rayner (1977); Coleman and Jenkinson (1999).

**Soil Organic Carbon Pools calculation** For each soil fraction the organic carbon and nitrogen content (0-20 cm depth) was determined. These estimates were converted into five different soil organic carbon pools: Decomposable Plant Material (DPM) and Resistant Plant Material (RPM), Microbial Biomass (BIO), Humified Organic Matter (HUM) and Inert Organic Matter (IOM) which corresponding to the RothC model SOC pools (Coleman and Jenkinson (1999)). The value for each model SOC pool was determined from the measured fractions using the methodology of Zimmermann et al. (2007). The equation that was used to calculate the DPM/RPM splitting ratio depends on land-use type. For temperate grassland,  $y=0.048+0.011 \times \text{MAT}$  and arable land:  $y=0.035-0.003 \times \text{MAT}$ , where MAT is mean annual temperature. The BIO/HUM split ratio was estimated by performing a spin-up with RothC, then taking the BIO/HUM ratio at equilibrium. This equilibrium BIO/HUM ratio was used to split  $S+A+(s+c)$  into BIO and HUM pools. The details of the splitting ratios used are shown in Table 4.3.

Table 4.3: Splitting ratio of measured fractions with Zimmermann et al. (2007) method

Site name	MAT (°C)	split ratio (Unitless)	
		DPM/RPM	BIO/HUM
Laqueuille* (grass, FR)	7.68	0.132	0.027
Oensingen (grass, CH)	9	0.147	0.026
Hertfordshire (crop, UK)	9.46	0.007	0.027
Carlow (crop, IE)	9.4	0.007	0.026

**RothC-26.3 model input data preparation** The RothC model was used to estimate the equilibrium SOC value at each site. Only limited data on plant residue input (tC/ha) was available, and so this was estimated from harvest or standing biomass (tC/ha) data and also the observation date. For the Laqueuille (FR) site, above-ground litter data were available for each plot from April to September, 2003-2010. Plant residue at the Oensingen (CH) site was estimated by De Bruijn et al. (2012) to be: 527 DW g m<sup>-2</sup> y<sup>-1</sup> for the intensive plot and 585 DW g m<sup>-2</sup> y<sup>-1</sup> for the extensive plot. For the distribution of grass litter during the year at the Oensingen (CH) site, we used the same grass litter distribution ratio as Laqueuille (FR) site. The C concentration of grass residue was assumed to be 40 % for grasslands (Van Groenigen et al. (2010a, 2011)). For the Carlow (IE) site, we used grain harvest data to estimate plant litter inputs. To estimate plant residue from grain harvest, we followed the estimates of Van Groenigen et al. (2011) using the DNDC model defaults for C partitioning in crops (Li et al. (1994)). The carbon partition for barley was estimated as 40 % grain, 47 % root and 23 % shoot. For the Hertfordshire site, we used dead plant weight data to estimate plant residues for the RothC model. We used a 110 year (1901-2010) average for the monthly weather data, which was taken from the CARBO Extreme

project database for spin-up runs at all sites. Potential evapotranspiration was calculated following Mdaghri-Alaoui and Eugster (2001). Management data (i.e. fertiliser application date, applied fertiliser amount) were available at Laqueuille (FR) from 2003 to 2011, Oensingen (CH) from 2002 to 2008, Carlow (IE) from 2004 to 2007, and Hertfordshire (UK) from 2003 to 2006. We took monthly mean values for management data during these periods for each site for the spin-up run.

### RothC-26.3 model run

Prior to the model simulation, we applied three different initialisation methods: (1) Spin-up run initialisation repeating average recent management data and 1901-2010 weather data (Control), (2) Spin-up initialisation involving reducing or increasing C input (plant litter and organic carbon manure input) to adjust the equilibrium SOC (individual SOC pools or total SOC) to the measured values and (3) initialisation with measured SOC data. The RothC spin-up consists of an initialisation run equivalent of 10,000 years, to attain the SOC equilibrium state, repeating monthly average management regimes (plant residues, manure and vegetation) and weather data (temperature, precipitation and evapotranspiration). The monthly average weather data was calculated by combining CARBO Extreme weather data from 1901 to the year where the measured weather data was available, and to the recent weather data from each site.

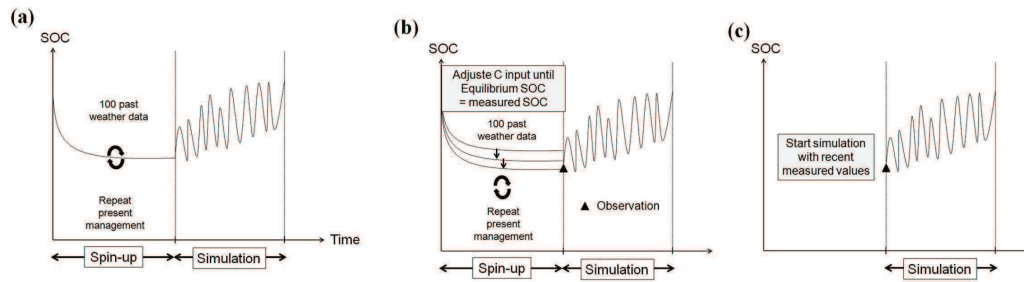


Figure 4.1: Different initialisation methods : (a) Control, (b) Adjusted spin-up initialisation and (c) Initialisation with measured SOC data

**Spin-up run initialisation using the recent management and 1901-2010 weather data (Control)** The model was run to equilibrium by repeating an average monthly management regime (around 10 years) and monthly average weather data (1901-2010). After this spin-up run initialisation period, we simulated SOC using each site's recorded weather and management data for the available periods (see Figure 4.1 (a)). The IOM was set as the value obtained from the Zimmerman fractionation. This model initialisation method is quite common and we set up this method as the control for comparing the model outputs with those derived by other initialisation methods.

**Spin-up initialisation involving a reduction or an increase in C input (plant litter and organic carbon manure input)** We reduced or increased C input until the equilibrium SOC amount of total SOC, DPM, RPM, BIO or HUM pools individually one at the time matched each measured SOC amount during the spin-up run. The IOM was set as the value obtained from



the Zimmerman fractionation. We call this spin-up run “the adjusted spin-up run initialisation”. After this “adjusted spin-up run initialisation”, we simulated SOC using the weather and management data for each site for the available periods (see Figure 4.1 (b)). Adjusting DPM pool to the measured value during the spin-up run is called as AdDPM. The same as AdDPM, the other adjusting spin-up run initialisation methods are called AdRPM, AdBIO, AdHUM and AdTot depending on which SOC was adjusted during the spin-up run.

**The observed SOC fraction data initialisation (ObSOC)** We initialised the model with the measured SOC fraction data, and then simulated values for SOC using the recorded weather and management data for each site (see Figure 4.1 (c)). This initialisation method is called ObSOC in this study.

#### 4.2.4 Statistical analysis

Linear regression models with 95 % confidence intervals were used to analyse differences between management practices and soil layers, using the R system for statistical computing R 2.14.2. For comparing the model output results and the experimental data, we analysed the root mean square error (RMSE). Differences were further tested with Tukey HSD (honestly significant difference) test in conjunction with ANOVA to find means. Before all statistical analysis, Shapiro-Wilk’s test of normality was undertaken to confirm the normal distribution of the data (true in all cases).

### 4.3 Result

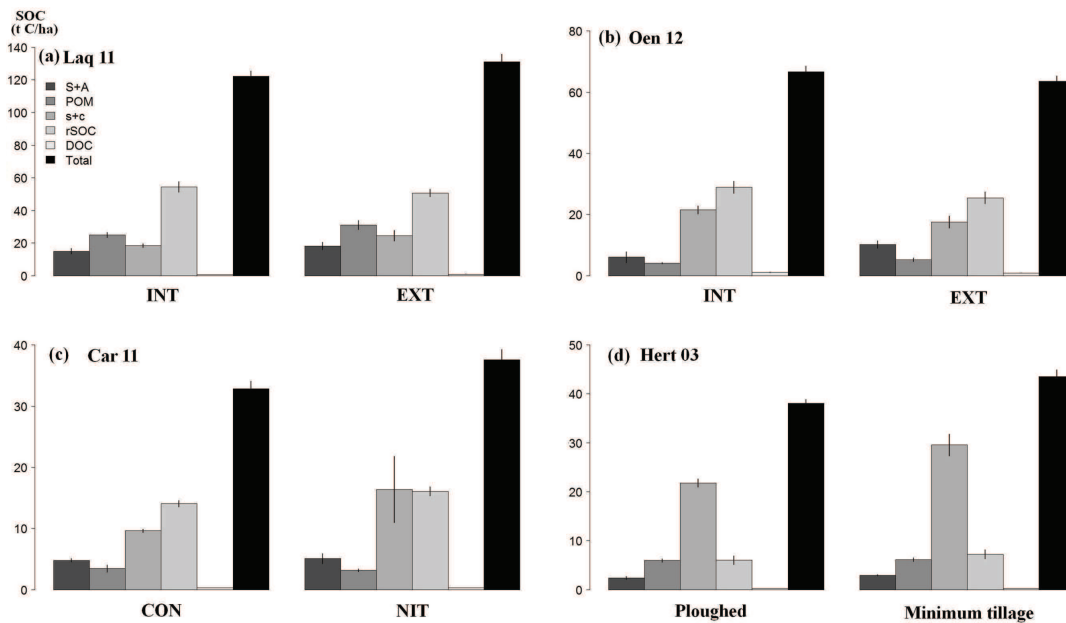


Figure 4.2: SOC (tC/ha) for each fraction 0-20 cm: a-d here (a) Laqueuille (grassland, FR) 2011, (b) Oensingen (grassland, CH) 2011, (c) Carlow (cropland, IE) 2011 and (d) Carlow (cropland, IE) 2011

Table 4.4: Test of significant difference between management with regard to each SOC fraction and total SOC (tC/ha) 0-20 cm:  $\frac{\text{Estimates (t value)}}{R^2}$  showing for significant difference

Site	POM	S+A	s+c	rSOC	DOC	Total
Laq 2011	-6.01 (1.82) <b>0.25</b>	-3.27 (-1.11) <b>0.11</b>	-6.03 (-1.71) <b>0.23</b>	3.74 (0.94) <b>0.08</b>	-0.31 (-2.86) <b>0.45</b>	-8.73 (-1.52) <b>0.19</b>
Oen 2011	-1.12 (-1.7) <b>0.22</b>	-4.11 (-1.89) <b>0.26</b>	3.94 (1.65) <b>0.21</b>	3.44 (1.24) <b>0.13</b>	0.21 (2.1) <b>0.31</b>	3.12 (1.24) <b>0.13</b>
Car 2011	0.3 (0.46) <b>0.02</b>	-0.28 (0.32) <b>0.01</b>	-6.75 (-1.24) <b>0.13</b>	-2 (-2.2) <b>0.33</b>	-0.01 (-0.73) <b>0.05</b>	-4.75 (-2.26)* <b>0.34</b>
Hert 2003	-0.2 (-0.39) <b>0.01</b>	-0.58 (-1.73) <b>0.18</b>	-7.79 (-3.27)** <b>0.43</b>	-1.2 (-0.92) <b>0.06</b>	0 (-0.23) <b>0</b>	-5.46 (-3.45)** <b>0.46</b>

Key to significance stars: 0 '\*\*\*\*' 0.001 '\*\*\*' 0.01 '\*\*' 0.05 '.' 0.1

The result of the soil organic carbon fractions and the total SOC across the 0-20 cm layer for each of the sites and management regimes, and statistical analysis of differences between management, are shown in Figure 4.2 and Table 4.4. Laqueuille (FR) showed a very similar SOC distribution among SOC fractions (Figure 4.2 (a)), and the management system did not influence the SOC distribution (Table 4.4). At the Oensingen (CH) site, the extensive plot tended to show slightly more SOC in the S+A fraction and less SOC in the s+c fraction than the intensive plot (Figure 4.2 (b)), but this difference was not statistically significant (Table 4.4). All of the other fractions and the total SOC across the 0-20 cm layers were not significantly different between contrasting management regimes (Figure 4.2 (b) and Table 4.4). The Carlow (IE) conventional tillage plot showed significant differences due to management regimes in the total SOC 0-20 cm soil depth (Table 4.4) and the s+c fraction in the non-inversion-tilled plot, which contained more SOC than the conventional tillage plot (Figure 4.2 (c)), although these were not significant (Table 4.4). For the Hertfordshire (UK) site, significant differences due to management among the four experimental sites were found (Table 4.4). These differences were specific to the s+c fraction of SOC and the total SOC (0-20 cm) between contrasting managements (Figure 4.2 (d) and Table 4.4).

In general, the equilibrium SOC pools and total SOC by spin-up repeating an average monthly management regime (around 10 years) and monthly average weather data (1901-2010), which is called Control in this study, showed a distinct difference between contrasting managements at each site (Figure 4.3). The equilibrium total SOC was significantly different between contrasting management plots within each site (Figure 4.3). For both plots at Laqueuille (FR), the SOC distribution in each SOC compartment and the total SOC across the 0-20 cm soil profile were far from the equilibrium point (Figure 4.3 (a) and (b)). The SOC in the intensive plot at Oensingen (CH) was further from the equilibrium SOC value than the extensive plot (Figure 4.3 (c) and (d)). The same pattern was found in Carlow (IE) comparing the conventional tillage and non-inversion plots (Figure 4.3 (e) and (f)). At the Hertfordshire (UK) site, SOC for both plots was different to the estimated equilibrium SOC point estimated by the RothC model (Figure 4.3 (g) and (h)).

Depending on management regime, soil organic C pools required different time spans to achieve equilibrium, as would be expected from their differing turnover rates, with pools with longer turnover times taking longer to equilibrate. Decomposable plant material (DPM) arrived very quickly at the equilibrium point (1-9 years). Resistant plant material (RPM) required 20-40 years, except for the conventional tillage plot in Carlow (IE) that required 200 years to reach the equilibrium point (Figure 4.4). With regard to microbial biomass (BIO), in the permanent grassland at Laqueuille (FR), both plots required 30 years, while for the sown grassland at Oensingen

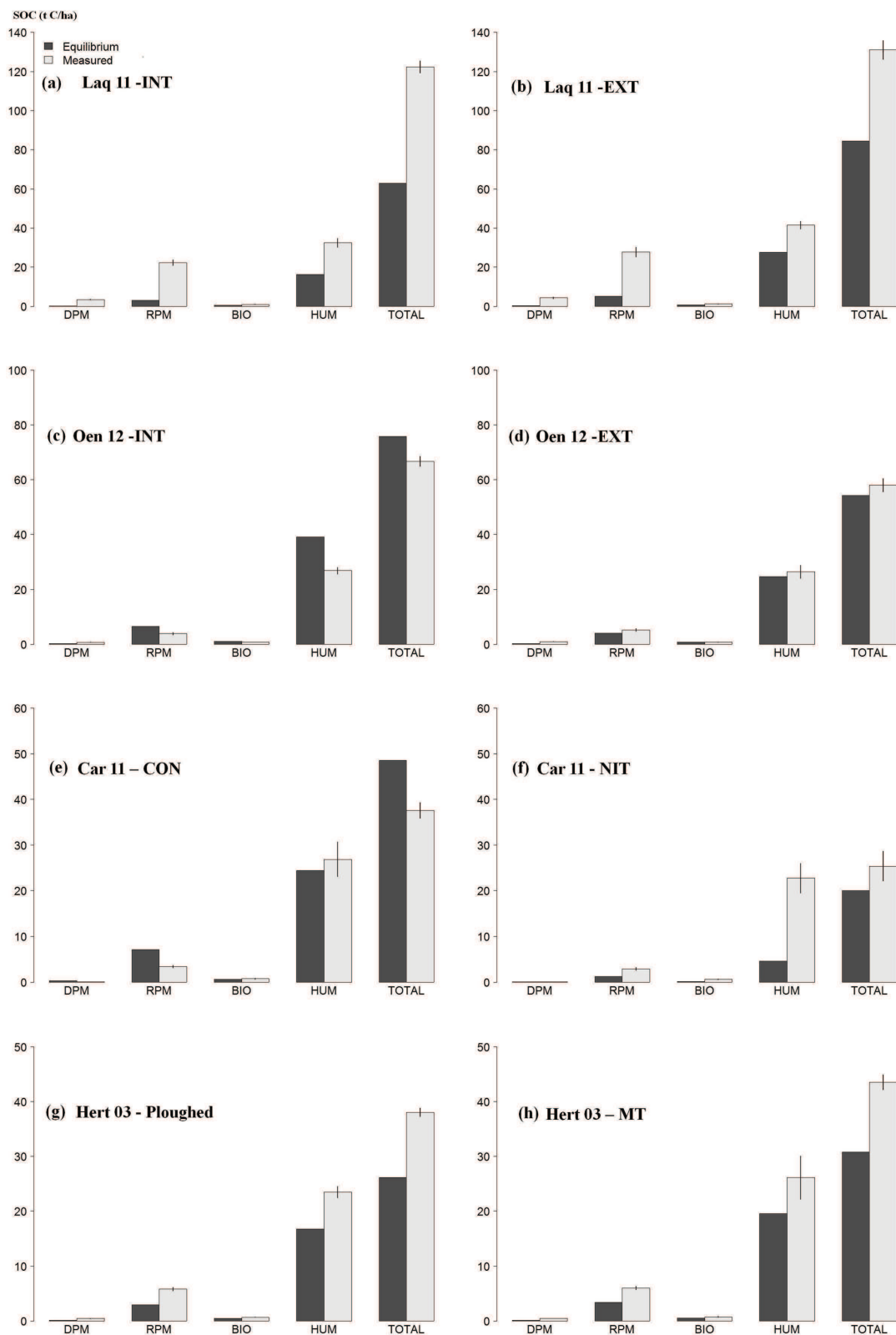


Figure 4.3: Measured SOC (tC/ha) for each fraction 0-20 cm and Equilibrium SOC by spin-up run with average recent management/weather data: a-h here (a) Laqueuille (grassland, FR) 2011 INT, (b) Laqueuille (grassland, FR) 2011 EXT, (c) Oensingen (grassland, CH) 2011 INT, (d) Oensingen (grassland, CH) 2011 EXT, (e) Carlow (cropland, IE) 2011 Conventional Tillage, (f) Carlow (cropland, IE) 2011 Non inversion, (g) Hertfordshire (cropland, UK) 2003 Plough and (h) Hertfordshire (cropland, UK) 2003 Minimum Tillage.

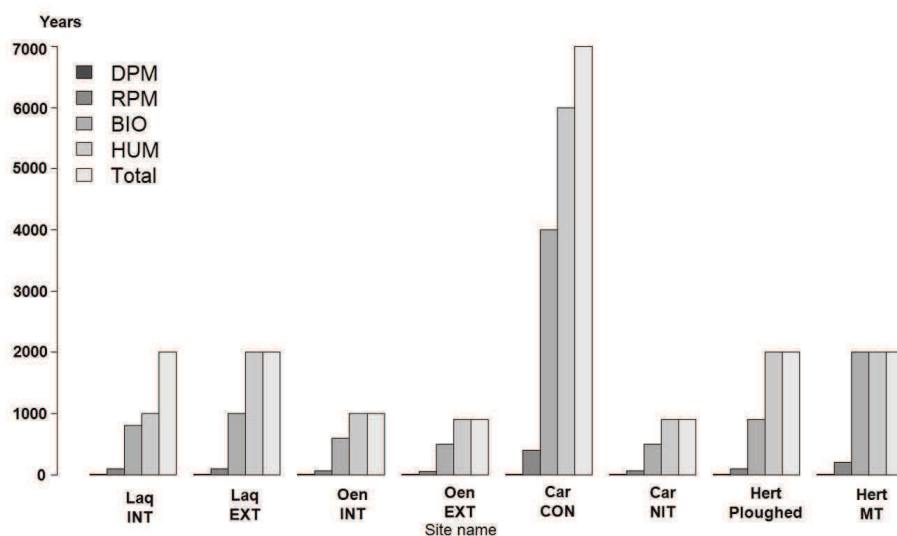


Figure 4.4: Required number of years to attain the equilibrium state with average recent management/weather data for each site. Equilibrium point is SOC changes become  $<0.0001$  tC/ha.

(CH) the extensive plot needed only 8 years, compared to 60 years in the intensive plot. The Carlow (IE) non-inversion cropland plot needed 8 years, but the conventional tillage plot required 70 years. The Hertfordshire (UK) ploughed plot did not reach equilibrium for 300 years, while the minimum tillage plot required 20 years at this site. Humified organic matter (HUM), which is the largest SOC compartment, required 300-700 years to arrive at the equilibrium state (Figure 4.4). As the HUM is the largest SOC compartment in the RothC model, when HUM reaches the equilibrium, the total SOC across the 0-20 cm layer also reached its equilibrium state. The total SOC across the 0-20 cm layer reached the equilibrium point after 300-900 years (Figure 4.4). Except for the Carlow (IE) site, the required time span to reach equilibrium was not significantly different between contrasting management regimes (Figure 4.4).

As shown by the RothC model results, 10 years of continuous land management is not sufficient to attain the equilibrium state of SOC as there was no significant SOC stock difference between two adjacent contrasting management systems in the same site (Figure 4.3 and Figure 4.4). Accordingly, model initialisation, which assumes the actual SOC is at the equilibrium state, could lead to model outputs that do not correspond with measured values. We tested different spin-up run methods to initialise the RothC model in order to analyse the initialisation that was the most suitable. We have run the RothC model for 10,000 years reducing or raising monthly plant residue input, until the equilibrium SOC fits the observed values (see Figure 4.5).

In all sites, DPM was not affected by the different initialisation methods, showing only small differences in root mean square error (RMSE), 0-0.02, between modelled and measured SOC. Regarding the RPM pool, adjusting the equilibrium DPM to the measured DPM initialisation method showed mostly swerving model output from the observation values in Oensingen (CH) and Hertfordshire (UK) among different initialisation methods, RMSE 2.76-4.37 and 4.73-5.27 respectively (Figure 4.6 (c)-(d), (g)-(h)). In the Laqueuille (FR) site and in the conventional tillage plot in the Carlow (IE) site, Control initialisation method resulted in the most deviated model output in the RPM pool, RMSE 19.43-23.22 and 1.33 respectively (Figure 4.6 (a)-(b) and (e)). Only the Carlow (IE) non-inverted plot showed the most variable model output (RMSE:



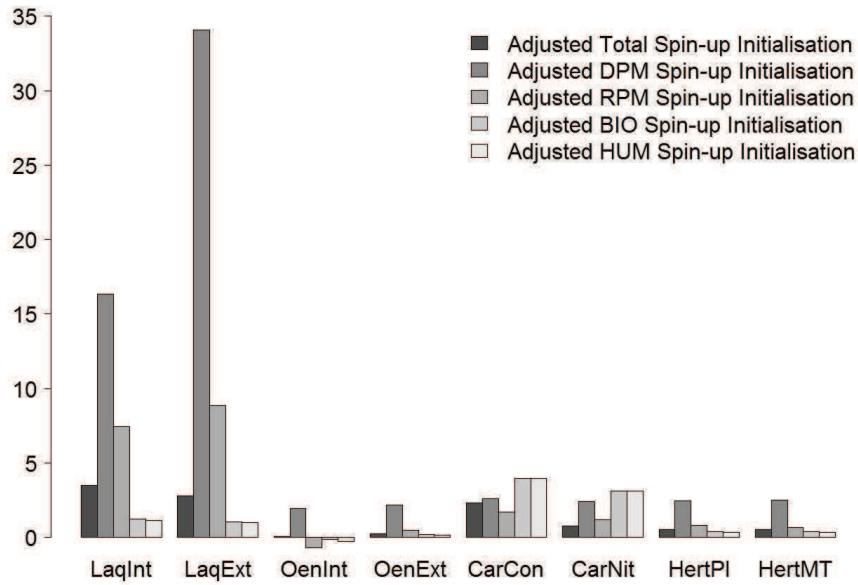


Figure 4.5: Changes in C input (tC/ha) according to initialisation method

1.46) by AdBIO or AdHUM (Figure 4.6 (f)). For the BIO pool, the RMSE between the simulated SOC and the measured SOC was in the range of 0.08-0.95, except for the intensive and extensive plots at the Laqueuille (FR) site, where these were 0.14-1.79, and 0.15-6.97, respectively, because AdDPM initialisation estimated large deviation in Laqueuille (FR) site (Figure 4.6 (a)-(b)). Using the initialisation method where AdDPM resulted in large deviations from the observed values in the HUM and total SOC pools in all of the sites except Carlow (IE) site (Figure 4.6 (a)-(d), (g)-(h)). In the Carlow (IE) site, the method adjusting the equilibrium BIO or HUM to the observed values estimated mostly deviated from the measured values, RMSE: 23.31-28.27 (Figure 4.6 (e)-(f)). In a comparison of the different initialisation methods all sites together (Figure 4.7 (a)-(g)), while the initialisation method involved AdDPM and AdRPM resulted in large deviations, especially in the HUM and total SOC pools. All initialisation methods regarding each SOC pools were tested with Tukey HSD test (Figure 4.6 (a)-(g)). Significant difference in the model result accuracy due to initialisation methods were not found regarding DPM RPM, HUM pools and total SOC. Significant difference regarding model result accuracy was found in BIO pool, showing the initialisation method that involved AdTot (Figure 4.7 (b)) gave the closest model output to the measured values in all of the SOC pools and the total SOC compared the other initialisation methods (Figure 4.7 (a)-(g)). For contrasting management plots in the same site, the RMSE variability was quite similar.

## 4.4 Discussion

In general, there was no significant difference due to management systems in Table 4. However, total SOC in Carlow (IE) and s+c and total SOC in Hertfordshire (UK) showed significant differences (Table 4.4). At both sites, these differences were apparently due to soil texture SOC

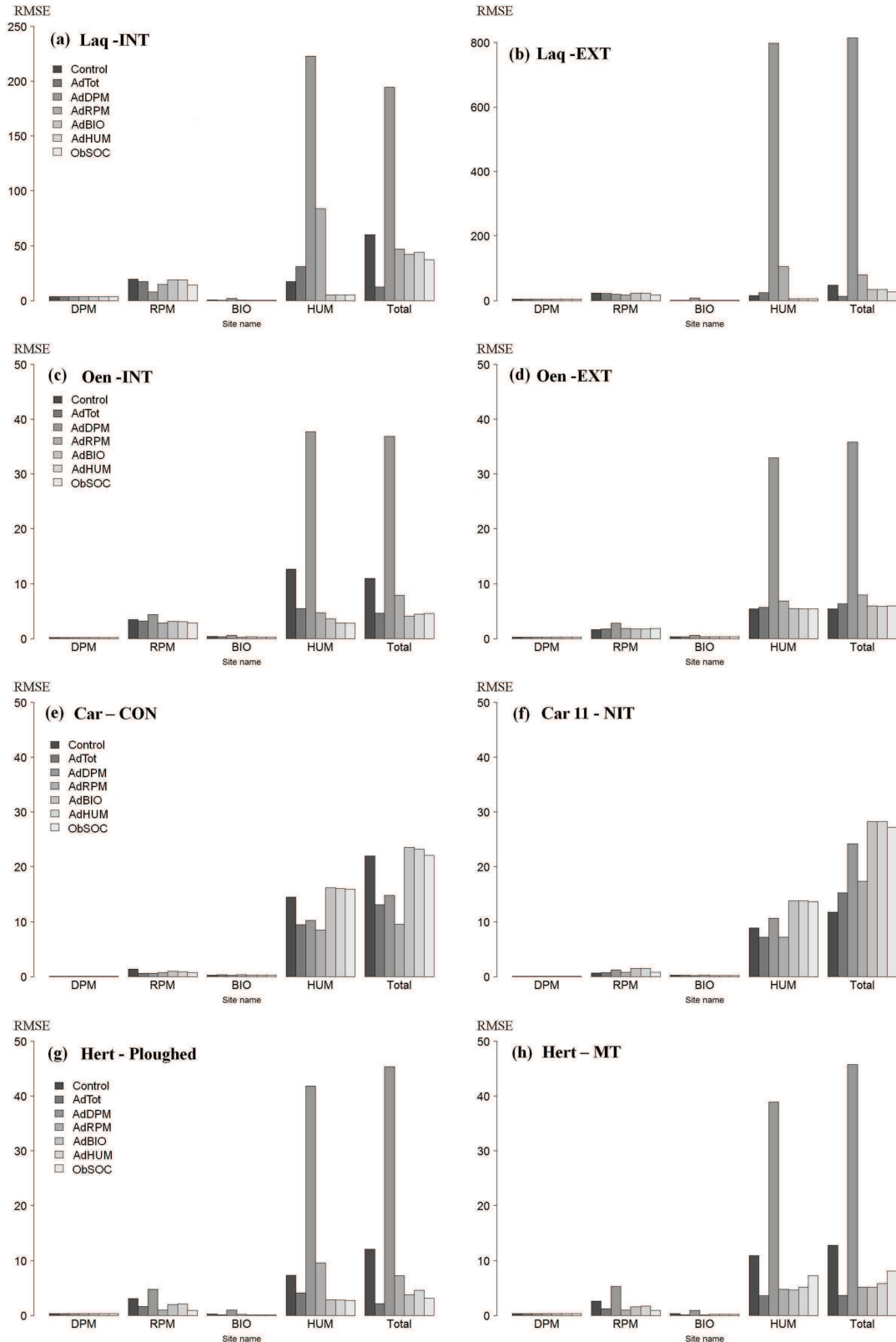


Figure 4.6: Root mean square error (RMSE) for observation (individual samples) and simulation results derived by each initialisation methods: a-h here (a) Laqueuille (grassland, FR) INT, (b) Laqueuille (grassland, FR) EXT, (c) Oensingen (grassland, CH) INT, (d) Oensingen (grassland, CH) EXT, (e) Carlow (cropland, IE) Conventional Tillage, (f) Carlow (cropland, IE) Non inversion, (g) Hertfordshire (cropland, UK) Plough and (h) Hertfordshire (cropland, UK) Minimum Tillage.

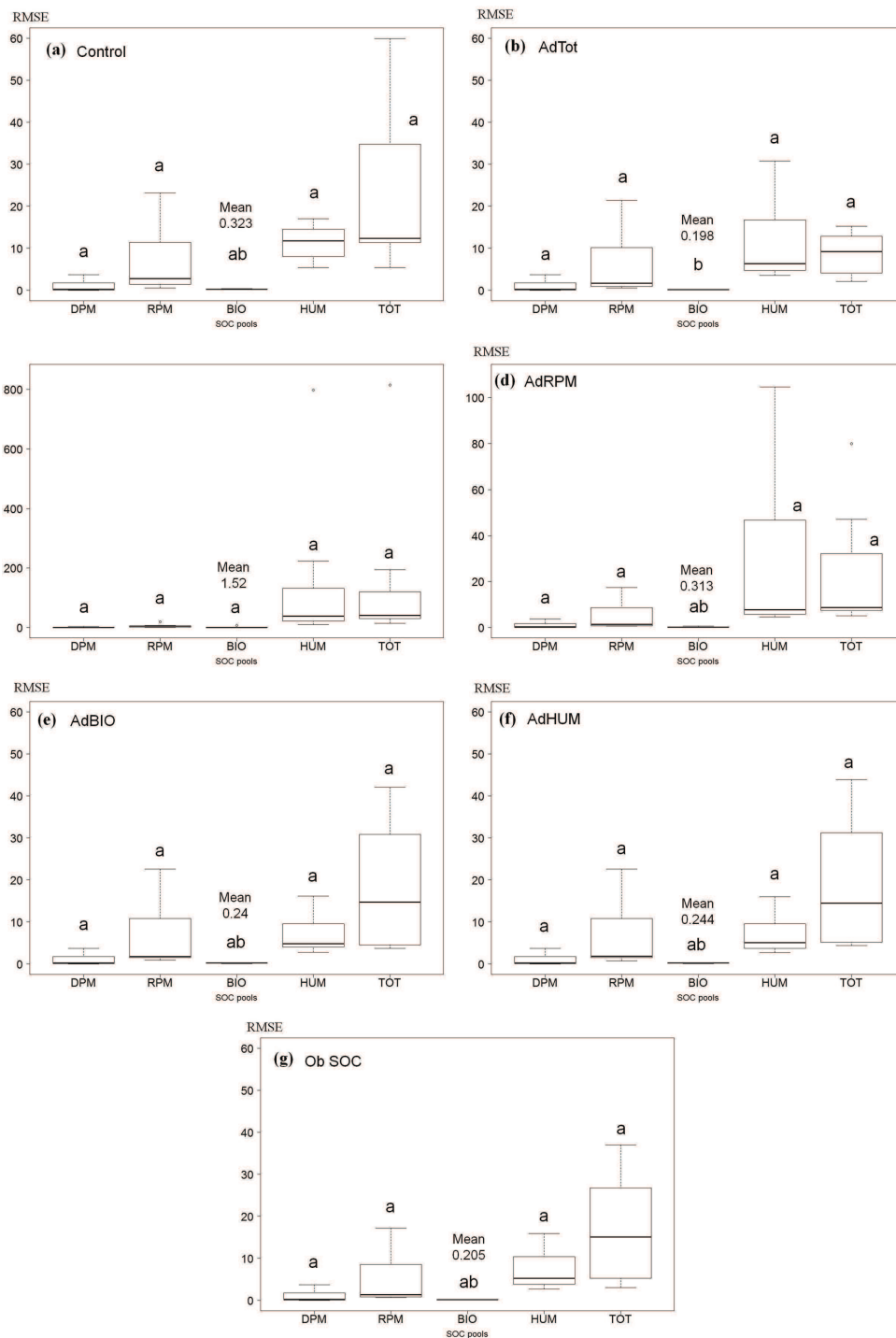


Figure 4.7: All site together Root mean square error (RMSE) for observation (individual samples) and simulation results derived by each initialisation methods regarding each SOC pools and total SOC: a-g here (a) Control initialisation (b) Adjusting the equilibrium Total SOC to the measured values (AdTot), (c) Adjusting the equilibrium DPM to the measured values (AdDPM), (d) Adjusting the equilibrium RPM to the measured values (AdRPM), (e) Adjusting the equilibrium BIO to the measured values (AdBIO), (f) Adjusting the equilibrium HUM to the measured values (AdHUM), (g) Measured SOC initialisation (ObSOC)

(s+c), as this fraction forms the largest component of these soils (Figure 4.2). Soil mineralogy determines the quantity of SOC and SOC turn over time (Torn et al. (1997); Qian et al. (2003); Hassink et al. (1997); Hassink and Whitmore (1997)) and the required time span to detect SOC changes due to management largely depend on soil type and land use type (Smith (2004b)). Poeplau et al. (2011) showed that grassland conversion to cropland may attain the SOC equilibrium state 17 years after conversion, and subsoil SOC changes are followed by changes observed in the topsoil. Since Carlow (IE) and Hertfordshire (UK) are croplands (the other sites are grasslands), SOC might more rapidly reaches an equilibrium state under croplands than grasslands.

The comparison between modelled SOC at equilibrium and measured SOC showed that most of the mineral soils at the study sites have not reached an equilibrium state (Figure 4.3 (a)-(b), (e)-(h)), suggesting that a potential “minimal time” of 10 years is not sufficient for steady state conditions (Smith (2004b)). Additionally, the equilibrium total SOC were significantly different between contrasting management plots, indicating SOC sequestration difference management difference would appear after longer term (more than 10 years) continuous experiment (Figure 4.3). On the other hand, at the Oensingen (CH) site, the current SOC content of both plots was close to the equilibrium state (Figure 4.3 (c) and (d)). This outcome could be explained by the amount of plant input. In fact, the estimated plant residue in Oensingen (CH) were referred to the model estimating aboveground biomass in (De Bruijn et al. (2012)) and these values may not be realistic (De Bruijn et al. (2012)) and supposedly calibrated to the SOC equilibrium would be close to the measured SOC value. The extensive plot in Oensingen (CH) showed larger deviation between model output and measured value than the intensive one, perhaps because the extensive plot received only estimated plant input data while the intensive plot was parameterised with estimated plant input data and also measured input manure data. There are also several limitations in RothC model. For instance, RothC model does not require mowing, grazing, tillage, harvesting, nitrogen fertiliser data. All of these management data should be taken into account as plant input data, although it is difficult to find appropriate data on this issue. On the other hand, RothC model has been tested widely and several studies reported that RothC model is an appropriate tool for estimating SOC (Senapati et al. (2013); Poeplau et al. (2013)). In this study, we take into account the RothC’s limitations although we still use RothC SOC equilibrium assumption as reliable result. The required number of years to attain the SOC equilibrium state (Figure 4.4) was 900-2000 years, while the DPM pool reached the equilibrium state very quickly (1-9 years). This also suggests that more than 10 years of continuous management are required to observe significant changes in SOC distribution in the DPM pool. At Carlow (IE) the conventional tillage plot required a much longer time to attain equilibrium compared to the other sites, which might suggest that the plant residue estimation was incorrect as we estimated this from the harvested grain record (Figure 4.4). In addition, our results suggest that the equilibrium assumption may not be appropriate for disturbed agricultural sites, explaining the difficulties of model initialisation using a general spin-up run methodology as reported elsewhere (Pietsch and Hasenauer (2006); Wutzler and Reichstein (2007); Carvalhais et al. (2008)).

Indeed, in this study, the comparison of the general spin-up run and the measured SOC data showed significant differences in the estimation of SOC equilibrium. This may be because the slowest SOM pool continues to accumulate C over a long time and a small amount of C accumulation could result in a significant change in the theoretical equilibrium C state (Wutzler and Reichstein (2007)). Initialising models by accurately simulating the pre-experimental period using detailed information, especially long-term land use management history of the site may be a useful method (Bruun and Jensen (2002)). However, site history data for pre-experimental peri-



ods is often difficult to acquire and long term studies (greater than 20 years) providing detailed and reliable management and weather (i.e. wind speed, relative humidity) data are insufficient. An alternative option is to identify a site that has not been disturbed for over a century to initialise models using spin-up run assumptions (Wutzler and Reichstein (2007)), although this is not very realistic due to the fact that few sites are truly undisturbed. Scaling several SOC pools simultaneously during the spin-up run and changing the equations within the model is another option, though this method may not be easy to achieve for all model users and for all ecosystem models (Hashimoto et al. (2011)). However, it is feasible that a detailed 10 year dataset of reliable management and weather data could be available at many sites. Therefore, we hypothesised that, where this data is available, the most realistic and appropriate model initialisation method would be to initialise the total SOC content as close as possible to the current total SOC content, as the soil C stock will not change greatly over such a relatively short time period. We initialised the model by increasing or decreasing C input until the equilibrium SOC matched the measured SOC during the whole of the spin-up run repeating monthly average recent management and weather data, and analysed which C pools were most important for accurately initialising the RothC model (see Figure 4.5 and Figure 4.6). The measured SOC used for comparison with model results was measured independently with a removing soil inorganic carbon process. The fraction of total SOC held within the POM fraction was measured without the removing soil inorganic carbon process due to the sensitivity of plant residue to HCl. Moreover, there were slight SOC losses during soil fractionation process. We expect these may have caused a slight difference between the measured total SOC independently and the sum of all of the SOC fractions in Figure 4.6.

Initialising the equilibrium SOC to the measured SOC values with quick turning SOC pools such as DPM and RPM resulted in large over/under estimations (Figure 4.6). The DPM and RPM pools have been shown to have a fast turnover time of between 0.165 years and 2.31 years respectively (Jenkinson and Rayner (1977)) and the potential stock rate is relatively smaller than the HUM pool. Accordingly, adjusting the DPM or RPM either through a large increase or decrease in the amount the amount of carbon in the HUM pool resulted in total SOC contents that were significantly different to the observed values. Therefore, this method is not expected to be the ideal model initialisation method. AdBIO (adjusting equilibrium BIO pool which had a turnover time of 1.69 years) did not have a major impact on the other SOC pools in the same way as the DPM and RPM adjustment methods. However, we observed significant over and under-estimations of total SOC compared to the measurement values (Figure 4.6 (a)-(h)). Except for the Carlow (IE) site, the same tendency for under/over estimation was found in comparisons with the total SOC. In the Carlow (IE) site, RPM, BIO and HUM were under estimated, although the total SOC was over estimated in both plots. This may be because the measured total SOC data is not the sum of each SOC fraction but measured independently after decarbonation. In the Carlow site, we expect these differences were more evident than in the other sites. For contrasting management plots in the same site there was a similar tendency (Figure 4.4, 4.5 and 4.6), suggesting appearing the SOC changes due to the management regimes may need the same time span after starting the new management system. The required time span to show significant SOC change due to management largely depends on the soil characteristics such as soil texture, soil pH etc. Since HUM and the sum of SOC showed large variations due to different initialisation methods, the best initialisation method should reproduce HUM and the sum of SOC accurately. AdHUM led the HUM simulation result certainly close from the actual HUM SOC value (Figure 4.6 (a)-(d), (g)-(h), RMSE: 2.75-16.03). However, this initialisation method over-

as well as under-estimated the sum of SOC. For example RMSE was 43.84 in the Laqueuille (FR) intensive plot (Figure 4.6 (a)-(h)). By AdTot, we found much less deviation between model results and observation for each SOC pool especially in BIO pool (RMSE: RPM 0.58-21.42, BIO 0.08-0.3, HUM 3.55-30.78) and the total SOC pool (RMSE: 2.11-15.23) compared to the other methods (Figure 4.7 (a)-(g)). Furthermore Tukey HSD test showed that AdTot initialisation method show the most accurate model fit among different methods. (Figure 4.7 (a)-(g)) Hence, the spin-up initialisation involving adjustments in the total SOC was the best initialisation method when using the RothC model. In particular, the SOC adjustment method showed a good match with observations even in agricultural lands that have been disturbed in the recent past.

## 4.5 Conclusion

This study indicates that soil texture largely governs total SOC and that 10 years of continuous land management is not sufficient to bring SOC to an equilibrium state. The time span for significant SOC changes due to a particular management regime largely depends on soil characteristics. Assessment of three modified spin-up initialisation methods showed that repeating recent management and weather data is not the best method to use and the most effective effective using the RothC model was the adjusting total SOC initialisation method both over and under-estimated the sum of SOC in European crop and grass study sites. We also confirm that plant inputs are a key variable in the RothC model and these need to be assessed with particular accuracy.



## Chapter 5

# Impact of the initialisation method on the simulation of grassland carbon fluxes using detailed soil organic carbon data and alternative models - a case study

### Abstract

Model initialisation can greatly influence the outputs of process-based ecosystem models. Application of detailed SOC data may help models to be better initialised to estimate more precisely C fluxes and changes in SOC. However, a universally applicable SOC fractionation scheme for all ecosystem models does not exist, and this makes it more difficult to initialise models accurately. In this study, we used the Zimmermann et al. (2007) soil fractionation method to derive fractions which were used to initialise the distribution of SOC in the pools of different models. We wanted to test if the use of measured fractions could be used to initialise different SOC models, even if model theoretical SOC model pools are not precisely compatible to each measured fraction. We compared the measured C fluxes such as GPP (Global Primary Production), NEE (Net ecosystem exchange) and Reco (Ecosystem respiration) with modelled flux estimates using five different initialisation methods: (1) Spin-up run using recent up to 100 years weather data and recent 10 years management data initialisation (Control), (2) initialisation of model pools with measured SOC fraction data (ObSOC), (3) Spin-up initialisation while reducing or increasing C input (plant litter and organic carbon manure input) during the spin-up run to adjust the slowest SOC pool to be equal to the measured IOM SOC fraction (AdIOM), (4) As for 3, except adjust the largest SOC pool to be equal to the measured HUM SOC fraction (AdHUM) and (5) As for 3, except adjust the total SOC to be equal to the measured total SOC (AdTot). The results showed that model initialisation with detailed SOC fraction data does not significantly improve model flux results.

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## **5.1 Introduction**

Process-based ecosystem models represent a useful tool to evaluate the mitigation potentials of agricultural management practices, allowing us to overcome financial, time and land constraints (which are often difficult to study in field trials). Moreover, model simulations allow the impacts of future climatic variability on interactions between the terrestrial and atmospheric carbon cycle to be analysed, which is difficult to achieve through experimentation. The output/results of model simulations can be greatly influenced by initial parameter/variable values and management regimes (Bruun and Jensen (2002)); therefore, model initialisation is critical for accurate ecosystem modelling. However, the most common model initialisation method (spin-up run), whereby the models runs for many years with repeated recent management and weather data until the total soil organic carbon (SOC) content reaches equilibrium, often cannot replicate current observed values of SOC (Bruun and Jensen (2002); Pietsch and Hasenauer (2006); Wutzler and Reichstein (2007); Hashimoto et al. (2011)). Many agricultural ecosystems may not be in equilibrium due to frequent management interventions (Wutzler and Reichstein (2007); Basso et al. (2010); Hashimoto et al. (2011)). Furthermore, a number of studies have shown that modelled SOC pools often do not correspond closely to the measured fractions, and these model SOC pools often cannot be initialised easily from experimental measurements (Bruun and Jensen (2002); Smith et al. (2002a)). Bruun and Jensen (2002) concluded that the only appropriate SOC initialisation method is to correctly simulate the pre-experimental period, although the lack of long-term management and weather information is often a limitation to this type of model initialisation. Methods for initialisation of models using SOC fractions were proposed and tested by Zimmermann et al. (2007) and Skjemstad et al. (2004), who both succeeded in initialising the Rothamsted Carbon model (RothC), using a combined physico-chemical soil fractionation method. Other researchers have proposed equilibrium assumptions scaling the size of SOC pools during the spin-up run, assuming that the most useful initialisation method should include a precise estimate of plant litter and organic manure inputs to soil, which should be varied depending on the management type (Wutzler and Reichstein, 2007; Carvalhais et al., 2008; Hashimoto et al., 2011). However, these tests have only been carried out with a specific model and not with several different models, as we do here.

## **5.2 Materials and Methods**

In this study, Pasture Simulation (PaSim), Daily Century (DayCent) and Denitrification / Decomposition (DNDC) models were used due to their additional sub-models, simulating aspects of ecosystem functioning other than soils (RothC is a soil only model). For example, the PaSim grassland model contains detailed animal sub-models compared to the DayCent model. The DNDC model is constructed using very different soil sub-models compared to the Pasim and DayCent models, but it is able to simulate various agricultural land uses. Due to individual model constraints, the Pasim model was initialised for SOC pools for a depth of 0-60cm, while DNDC and DayCent were initialised for the 0-10 cm and 0-20 cm soil depths respectively. Two long-term (up to 10 years) European grassland sites from the CarboEurope Integrated Project



(CEIP) ecosystem flux tower network were analysed in this study. The sites are all located in the same bioclimatic region (the oceanic temperature climate zone (Lindner et al. (2010)), with mean annual temperatures ranging between 7.7 and 9.0 °C and mean annual precipitation ranging between 857 and 1100 mm. Each site comprised two adjacent plots with contrasting management types: (1) Laqueuille (FR), intensively (high animal stocking rate and N fertiliser input) and extensively (low animal stocking rate and no fertiliser input) grazed grassland, and (2) Oensingen (CH), intensively and extensively cut grassland with high and low N fertiliser input (intensive plot was ploughed and re-sown in 2008). A summary of site details can be found in Chapter 3, Tables 3.1 and 3.2. In autumn/winter 2011/2012, soil sampling campaigns were carried out for the two grassland paired-sites (4 plots in total) within the measured area of the eddy-covariance flux tower (foot-print). In each plot, 6 soil cores (60 cm depth in Laqueuille and 40 cm depth in Oensingen) were sampled at equal intervals (10m) along a 60m transect. Each soil core was separated into 0-5 cm, 5-10 cm, 10-20 cm, 20-40 cm and 40-60 cm depth layers. At all sites, all of the soil samples were air dried under laboratory conditions. Dried soil samples were then passed through a 2 mm sieve to remove larger particles and debris. A sub-sample was dried for 48h at 60 °C to determine residual humidity, bulk density and total C and N content. The Zimmermann et al. (2007) fractionation method was used to separate SOC into five different fractions: Sand and Aggregate (S+A), POM, silt and clay (s+c), Dissolved Organic Carbon (DOC) and Resistant SOC (rSOC). Soil fractionation was undertaken using a 30g sample of dry <2mm sieved soil. Briefly, soil fractionation is achieved through ultrasonic dispersion, wet sieving (63  $\mu$ m), density separation and NaOCl (6%) oxidation. To separate the heavy fraction (S+A) and POM from the > 63  $\mu$ m soil fraction, the fraction was mixed with sodium polytungstate (SPT) and frozen overnight (see Wurster et al. (2010)). This freezing method avoids mixing up heavy and light fractions. For extracting the light fraction, we used distilled water to thaw the frozen sample. For more details, see Zimmermann et al. (2007) and Wurster et al. (2010). After fractionation, soil fractions and <2 mm sieved bulk soil were analysed for C and N content using the NC analyser (Thermo Electron Cooperation, Flash EA 1112 series). Prior to analysis, all fractions (s+c, S+A, DOC and bulk soil), except the POM fraction (which contains a certain amount of plant-derived carbon that could be degraded by HCl), were decarbonated following the methodology of Harris et al. (2001). (For more details regarding the soil sampling and soil analysis, please refer to Chapter 2 Section 2.2.) Soil fractionation results were converted to five different soil organic carbon pools: Decomposable Plant Material (DPM) and Resistant Plant Material (RPM), Microbial Biomass (BIO), Humified Organic Matter (HUM) and Inert Organic Matter (IOM), according to the RothC model (Coleman and Jenkinson, 1999). To separate (S+A)+(s+c) into a microbial pool (BIO) and humus (HUM) a splitting ratio was estimated by RothC spin-up. For further details of the splitting ratios used, see Chapter 2, Section 2.3.5. Each plot was equipped with a meteorological station and an eddy covariance flux tower, registering half-hourly data of meteorological variables (e.g. temperature, radiation, precipitation) and C fluxes. Flux data were processed according to CarboEurope-IP guidelines (Aubinet et al. (2012)) to obtain NEE. NEE was further partitioned according to CarboEurope-IP guidelines into Gross Primary Productivity (GPP) and Ecosystem Respiration (Reco) (see Reichstein et al. (2005)). We aimed to examine the use of estimated RothC pools (DPM (0.165 year, turnover time), RPM (2.31 year), BIO (1.69 year), HUM (49.5 year) and IOM (50.000 year)) from the Zimmermann et al. (2007) SOC fractions to test whether this simple and accessible model initialisation approach could be created to be applied across different process-based models, to allow them to accurately predict GPP, NEE and Reco in agro-ecosystems. The Zimmermann

et al. (2007) soil fractionation method was developed specifically to match RothC model pools. We know that the theoretical SOC model pools are not precisely compatible to each measured fraction and estimated SOC pool from the Zimmermann et al. (2007) method. However, we use it to assess its utility for estimating SOC distribution among SOC pools as the initial point of model runs for the Pasture Simulation (PaSim), Daily Century (DayCent) and Denitrification / Decomposition (DNDC) models. According to Christensen (1996), estimated RothC DPM was used to set the Metabolic SOC pool in (PaSim and DayCent), and estimated RothC RPM was used to set the Structural SOC pool (PaSim and DayCent). Estimated RothC DPM+RPM was used to set the Litter SOC pool in DNDC. Estimated RothC BIO was used to set the Active SOC pool (PaSim and DayCent) and the Microbe SOC pool (DNDC). Estimated RothC HUM was used to set the Slow SOC pool (PaSim and DayCent) and the Humads SOC pool (DNDC). Estimated RothC IOM was used to set the Passive SOC pool (PaSim and DayCent) and the Passive Humus SOC pool (DNDC). Effects of model initialisation on C fluxes were tested by applying five model initialisation methods: (1) Spin-up run using up to 100 years of recent weather data and 10 years recent management data initialisation (Control); (2) initialisation of model pools with measured SOC fraction data (ObsSOC); (3) Spin-up initialisation while reducing or increasing C input (plant litter and organic carbon manure input) during the spin-up run to adjust the slowest SOC pool to be equal to the measured IOM SOC fraction (AdIOM); (4) The same as 3, except the largest SOC pool was adjusted to be equal to the measured HUM SOC fraction (AdHUM); and (5) The same as 3, except the total SOC was adjusted to be equal to the measured total SOC (AdTot). For analysing model fit, we focused on Model Efficiency (ME) and Relative root mean square error (RRMSE) (Bennett et al. (2012); Carvalhais et al. (2010); Jørgensen et al. (1986)).

## 5.3 Results

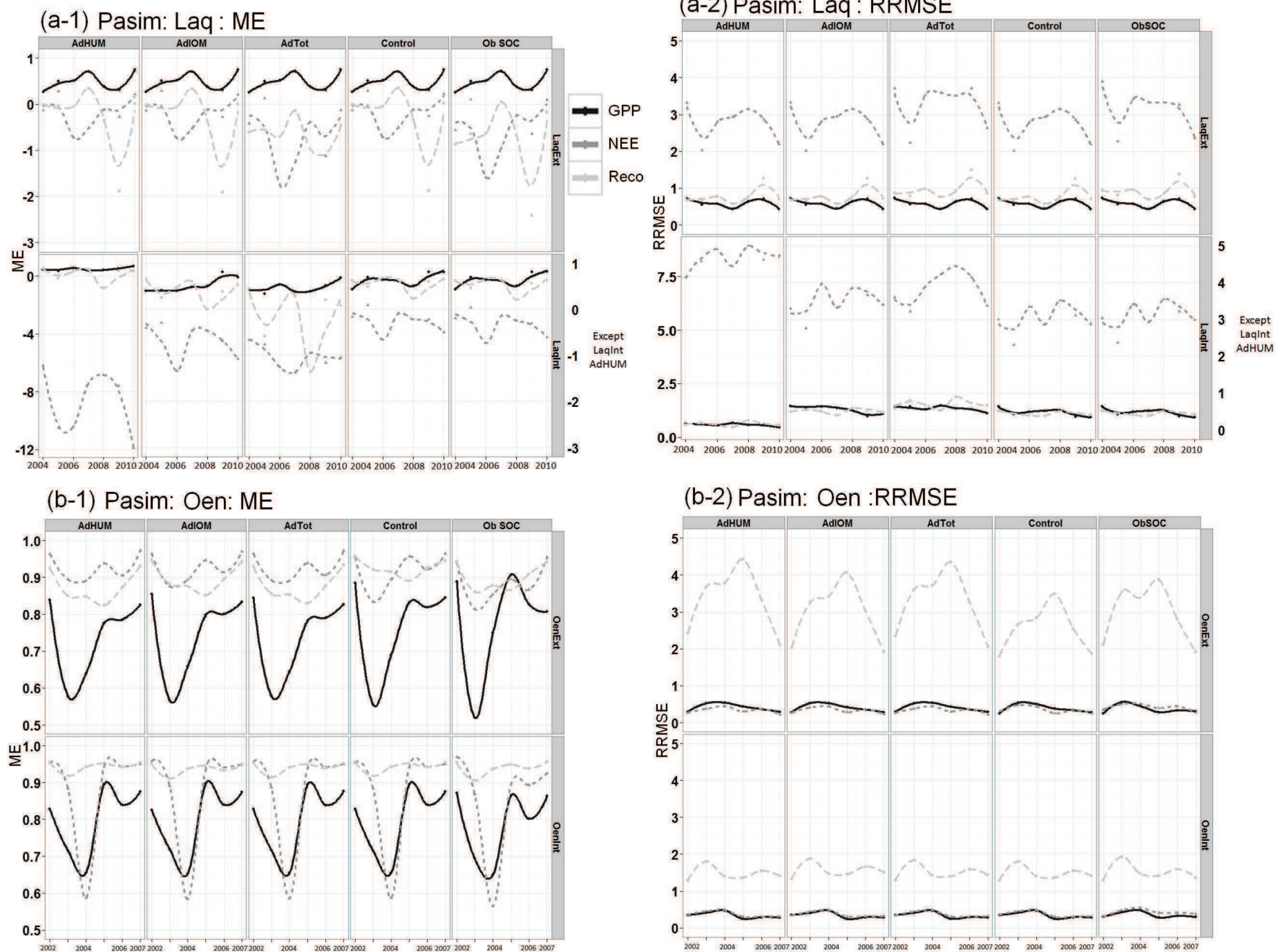


Figure 5.1: Each year's Model efficiency (ME) and Relative Root mean square error (RRMSE) for Pasim. Here: (a-1) ME Laqueuille (FR) intensive and extensive plots, (a-2) RRMSE Laqueuille (FR) intensive and extensive plots, (b-1) ME Oensingen (CH) intensive and extensive plots and (b-2) RRMSE Oensingen (CH) intensive and extensive plots. The y axis of AdHUM in Laqueuille (FR) extensive plot is different from the others.



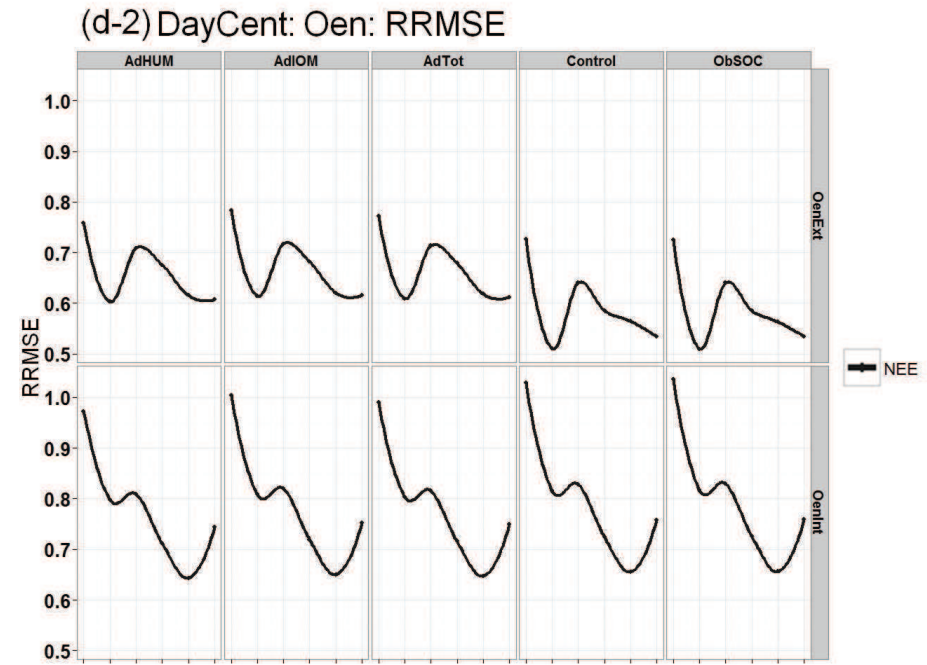
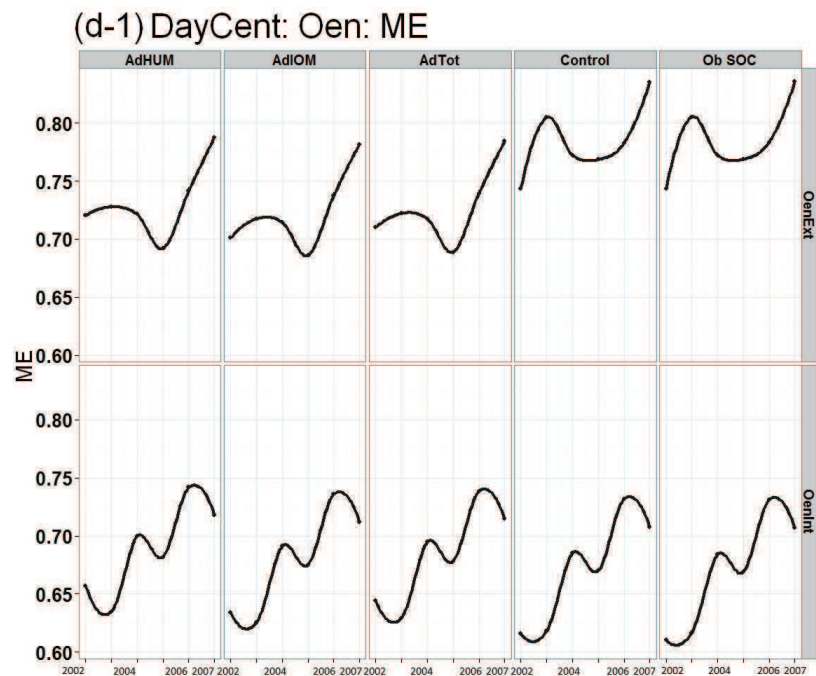
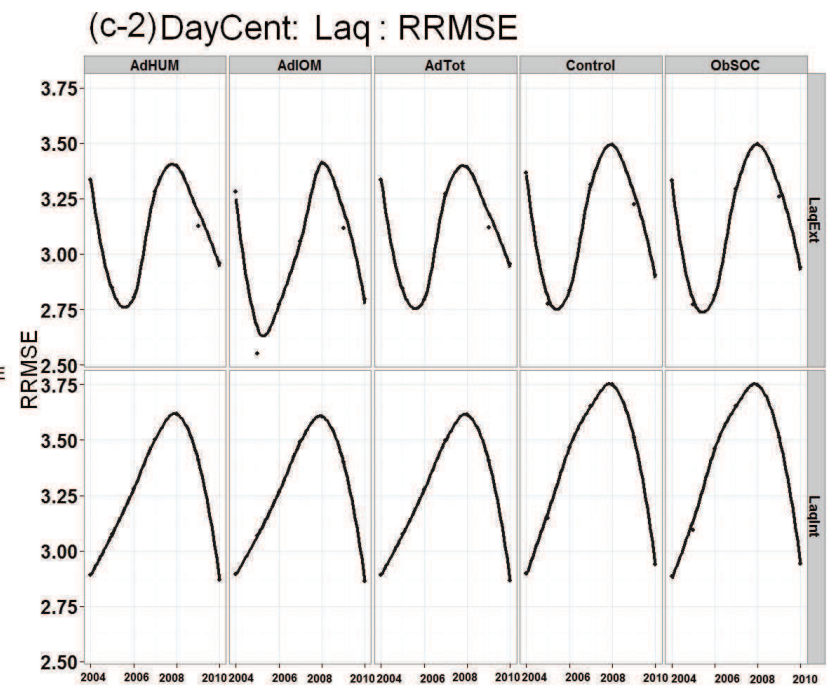
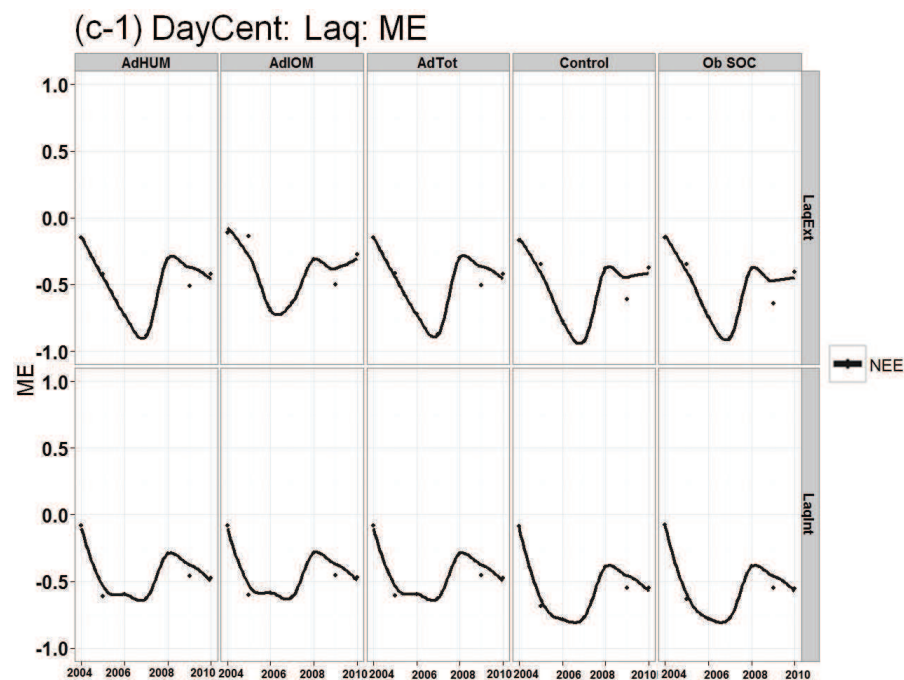


Figure 5.2: Each year's Model efficiency (ME) and Relative Root mean square error (RRMSE) for DayCent. Here: (c-1) ME Laqueuille (FR) intensive and extensive plots, (c-2) RRMSE Laqueuille (FR) intensive and extensive plots, (d-1) ME Oensingen (CH) intensive and extensive plots and (d-2) RRMSE Oensingen (CH) intensive and extensive plots.

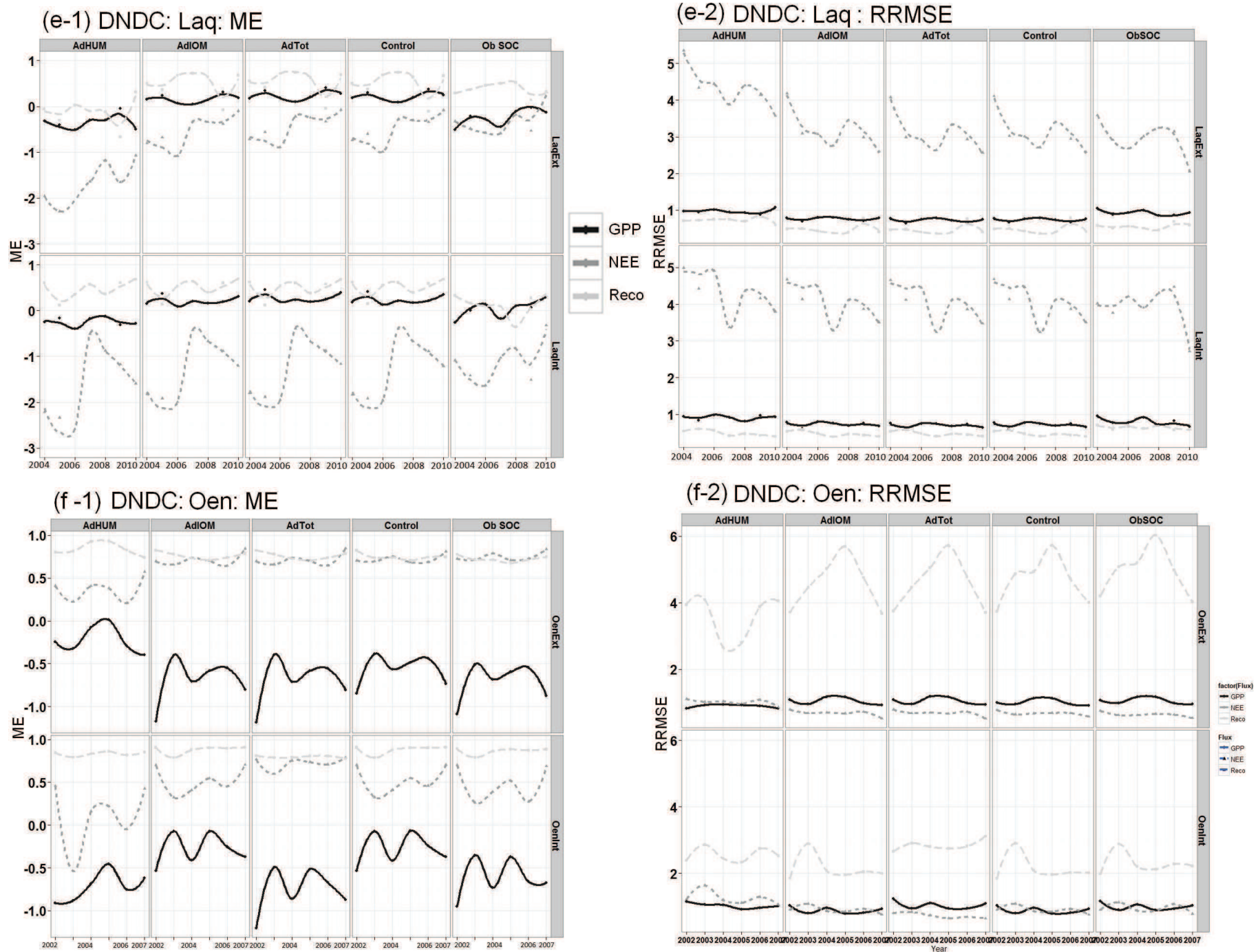


Figure 5.3: Each year's Model efficiency (ME) and Relative Root mean square error (RRMSE) for DNDC. Here: (e-1) ME Laqueuille (FR) intensive and extensive plots, (e-2) RRMSE Laqueuille (FR) intensive and extensive plots, (f-1) ME Oensingen (CH) intensive and extensive plots and (f-2) RRMSE Oensingen (CH) intensive and extensive plots.



Table 5.1: The percentage of time for which ME was greater than 0.5 during the simulation period (for example, if a five year simulation had three years for which ME was greater than 0.5, then this corresponds to 60% of the time)

Site	Management	Model	Method	ME		
				GPP	NEE	Reco
Laq (FR)	INT	Pasim	AdHum	—	---	--
			AdIOM	—	---	—
			AdTot	—	---	---
			Control	+++	---	++
			ObSOC	+++	---	++
	EXT		AdHum	+	---	---
			AdIOM	+	---	---
			AdTot	+	---	---
			Control	+	---	---
			ObSOC	—	---	---
Oen(CH)	INT		AdHum	+++	+++	+++
			AdIOM	+++	+++	+++
			AdTot	+++	+++	+++
			Control	+++	+++	+++
			ObSOC	+++	+++	+++
	EXT		AdHum	+++	+++	+++
			AdIOM	+++	+++	+++
			AdTot	+++	+++	+++
			Control	+++	+++	+++
			ObSOC	+++	+++	+++
Laq (FR)	INT	DayCent	AdHum		---	
			AdIOM		---	
			AdTot		---	
			Control		---	
			ObSOC		---	
	EXT		AdHum		---	
			AdIOM		---	
			AdTot		---	
			Control		---	
			ObSOC		---	
Oen(CH)	INT		AdHum		+++	
			AdIOM		+++	
			AdTot		+++	
			Control		+++	
			ObSOC		+++	
	EXT		AdHum		+++	
			AdIOM		+++	
			AdTot		+++	
			Control		+++	
			ObSOC		+++	
Laq (FR)	INT	DNDC	AdHum	---	---	+
			AdIOM	---	---	++
			AdTot	---	---	++
			Control	---	---	++
			ObSOC	---	---	---
	EXT		AdHum	---	---	---
			AdIOM	---	---	+
			AdTot	---	---	++
			Control	---	---	++
			ObSOC	---	---	--
Oen(CH)	INT		AdHum	---	---	+++
			AdIOM	---	+	+++
			AdTot	---	+++	+++
			Control	---	+	+++
			ObSOC	---	+	+++
	EXT		AdHum	---	--	+++
			AdIOM	---	+++	+++
			AdTot	---	+++	+++
			Control	---	+++	+++
			ObSOC	---	+++	+++

Indicators show the percentage of ME higher than 0.5 (moderate correlation Hinkle et al. (2003)): 0-10%:(---), 10-30%(--), 30-50% (-), 50-70% (+), 70-80% (++), 80-100%(+++)

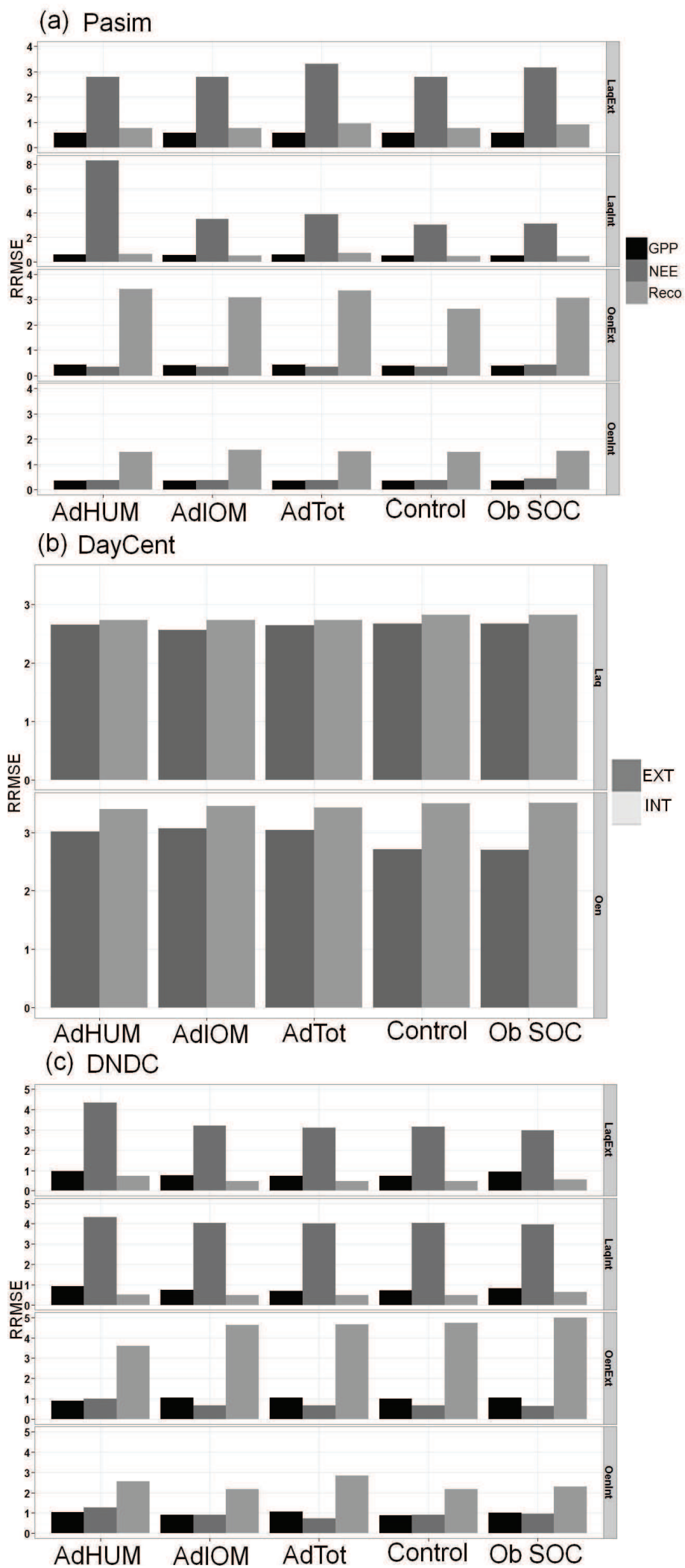


Figure 5.4: Relative Root Mean Square Error (RRMSE) for each model taking together all year. Here: (a) Pasim, (b) DayCent and (c) DNDC

### ***PaSim model***

For the grazed Laqueuille site, independent of initialisation method, the model performed poorly in estimating the annual variations and flux fluctuations of NEE (i.e. RRMSE, normalized deviation between individual model result and observation), while this was accurate for Reco and GPP (Figure 5.1 (a-2)). The efficiency of model estimation (ME, simulation vs observation with respect to annual mean) was satisfactory concerning GPP for both treatments, while NEE was poorly estimated (Figure 5.1 (a-1)). Reco was adequately predicted in the intensively grazed plot except for the AdHUM initialisation method. In the extensive grazing plot, Reco was poorly estimated (Figure 5.1 (a-1)). For the mown Oensingen site, independent of initialisation method, a high inter-annual variability was observed (i.e. RRMSE) in the Reco model simulation compared to GPP and NEE (Figure 5.1 (b-2)). This was more obvious for the extensive than the intensive mowing. PaSim anticipated fairly accurately all fluxes (ME>0.5) in Oensingen (Figure 5.1 (b-1)), though a high inter annual variability was observed for GPP and NEE of the intensively mown treatment. Across years, independent of initialisation methods, PaSim simulated well GPP for both sites and treatments respectively (RRMSE, Figure 5.4 (a)). Predicted Reco fitted well with observed values for the Laqueuille site compared to the Oensingen site, and vice versa for the NEE. Independent of initialisation methods, PaSim reproduces all fluxes efficiently for the mown Oensingen site, while for the grazed grassland (Laqueuille) only GPP was well represented (i.e. ME, Figure 5.5 (a)). Notably, differences have been found between the two grazing intensities (see also Table 5.1). Compared to the control group, no noticeable difference was observed among initialisation methods for Oensingen. Model initialisation methods slightly affect the Laqueuille extensive plot. Compared to Control, Adtot and ObsOC resulted in negative model efficiency in NEE and Reco (Figure 5.5 (a)), and seemed to increase the discrepancy between simulated and observed data. In the Laqueuille (FR) intensive plot, the AdHUM method could not estimate NEE correctly. PaSim performed an efficient simulation of C fluxes in the following order: NEE > GPP > Reco (in mowing grassland) and GPP > Reco > NEE (in grazing grassland), referring to Figure 4 and 5 (a). Taking all sites and years together, the ability of PaSim to estimate well takes the following order: GPP > Reco > NEE (Figure 5.6 and 5.7 (a)). Pasim does not show an outstanding difference in model simulations due to model initialisation methods.

### ***DayCent***

The daily version of Century, DayCent only offers the possibility to simulate net ecosystem exchange (NEE). Comparison of model simulation with observed values shows a high inter annual variability for the Laqueuille site, where especially 2008 shows the most difficulties in both plots for simulating the fluctuation of fluxes (RRMSE, Figure 5.2 (c-2)). In the extensive plot, DayCent could predict well in 2005 although poorly in 2008. However, this difference should not be significant (see Appendix A). Model efficiency confirms both grazing managements are not correctly predicted (Figure 5.2 (c-1) and Table 5.1). Compared to the Laqueuille site, DayCent showed better (smaller RRMSE) model results for the Oensingen site, whereas the extensive mowing plot was estimated more precisely than the intensive plot (Figure 5.2 (d-2)). This was confirmed by model efficiency, showing higher ME values for the extensive than for the intensive plot (Figure 5.2 (d-1)). DayCent predicted accurately NEE in the intensive plot independent to different methods. For the extensive plot, AdIOM, AdHUM and AdTot were less precise than the Control. Only ObsOC predicted NEE in the same manner of Control. Across years, independent of initialisation methods, DayCent simulated well NEE in Oensingen both plots. Extensive plot tended to be predicted better (i.e. lower RRMSE) than the intensive

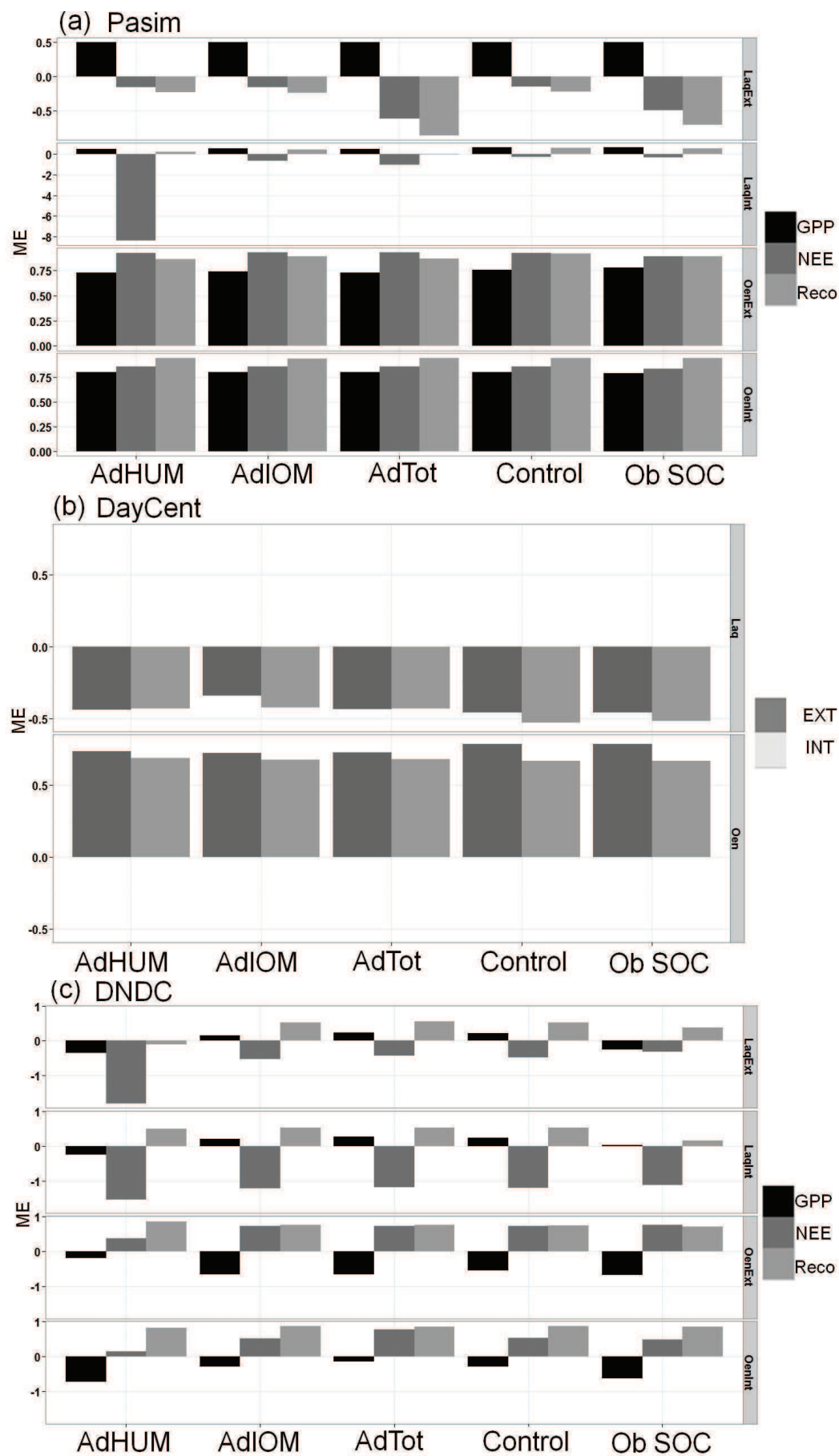


Figure 5.5: Model Efficiency (ME) for each model taking together all year. Here: (a) Pasim, (b) DayCent and (c) DNDC

management (Figure 5.4 (b)). However, ME shows that DayCent predicts less efficiently (negative ME: difference between observed and measured data is higher than inter-annual variability of observed data) in grazing grassland (Laqueuille site) compared to the mown Oensingen site (Figure 5.5 (b)). This result is distinct in the Table 5.1. Taking together all sites and years, DayCent does not show an outstanding difference in model simulations due to model initialisation methods (Figure 5.6 (b) and Figure 5.7 (b)).

### ***DNDC***

In the Laqueuille site, NEE showed high inter annual variability although DNDC could not estimate precisely enough NEE in both management regimes with all initialisation methods (Figure 5.3 (e-2)). GPP and Reco fluctuation were accurately predicted with DNDC. There is no significant difference of model result accuracy among initialisation methods (Figure 5.3 (e-2)). ME shows in both management regimes, Reco was well predicted with DNDC except the intensive plot with AdHUM method (Figure 5.3 (e-1)). GPP was not accurately predicted especially in AdHUM and ObSOC in both managements. DNDC could not estimate NEE correctly in intensive and extensive regimes. In the Oensingen site, the fluctuation of GPP and NEE was adequately predicted in both managements (Figure 5.3 (f-2)). In the intensive plot, Reco was better estimated than in the extensive plot. In the extensive plot, Reco was poorly estimated. Model efficiency (ME) showed that AdHUM tended to exacerbate model result in the extensive plot among initialisation methods (Table 5.1). Taking together all years, independent of initialisation methods, DNDC simulated well GPP for both sites and treatments (RRMSE, Figure 5.4 (c)), where for other fluxes, Reco was well fitted for the Laqueuille site (grazing grassland) compared to the Oensingen site (mowing grassland), and vice versa for the NEE. DNDC simulated C fluxes in the following order (better to worse): NEE > GPP > Reco in mowing grassland and Reco > GPP > NEE in grazing grassland. Model initialisation seemed not to affect model simulation at that level. Taking all sites and years together, DNDC predicted C fluxes efficiently in the following order: GPP > Reco > NEE (RRMSE, Figure 5.6 and 5.7(c)). However, this was not confirmed by model efficiency, which revealed a better prediction of Reco than for GPP (i.e. Reco > GPP > NEE) (Figure 5.7 (c)). Compared to control, initialisation with AdHUM reduced model efficiency for GPP and NEE, so did the initialisation with Ob SOC for GPP (Figure 5.7 (c)).



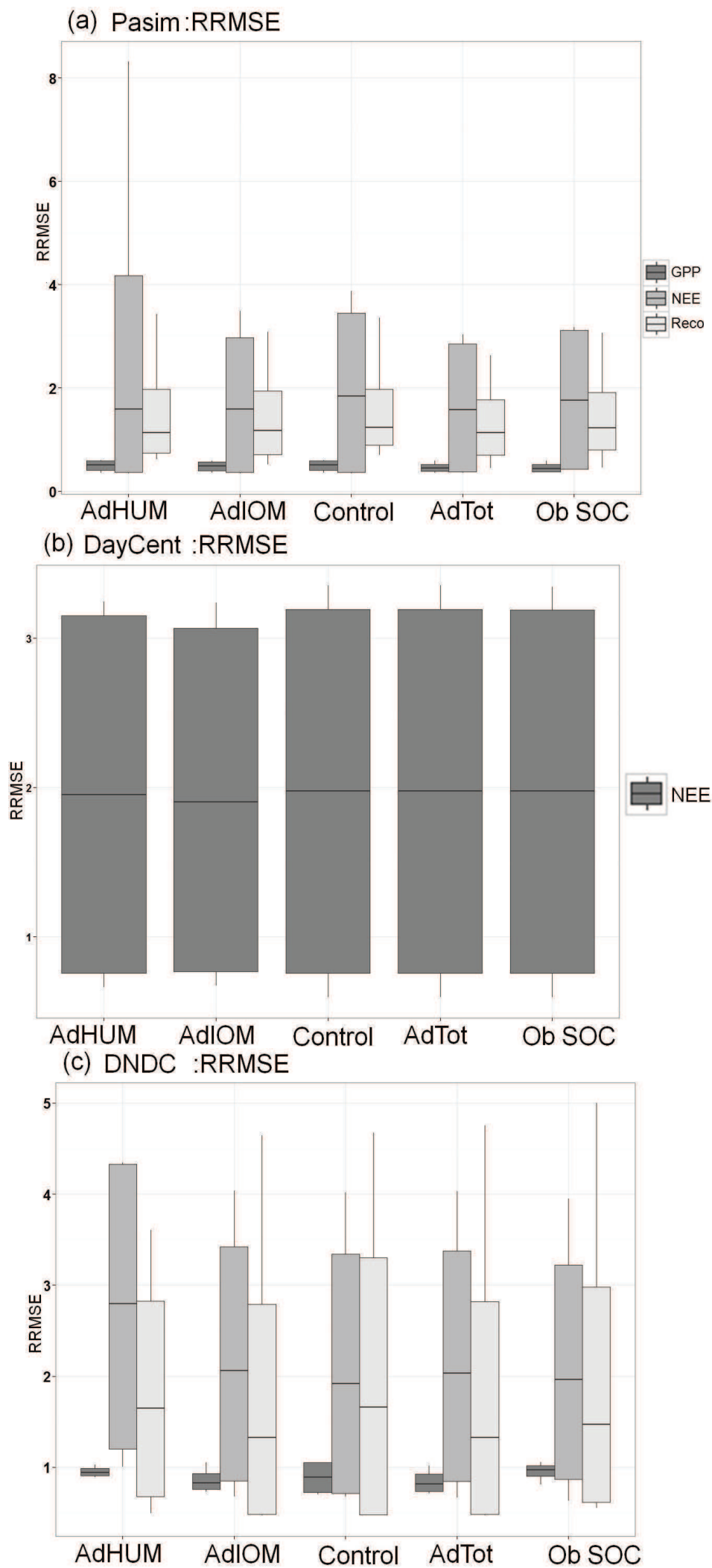


Figure 5.6: Relative Root Mean Square Error (RRMSE) for each model taking together all year and all sites. Here: (a) Pasim, (b) DayCent and (c) DNDC

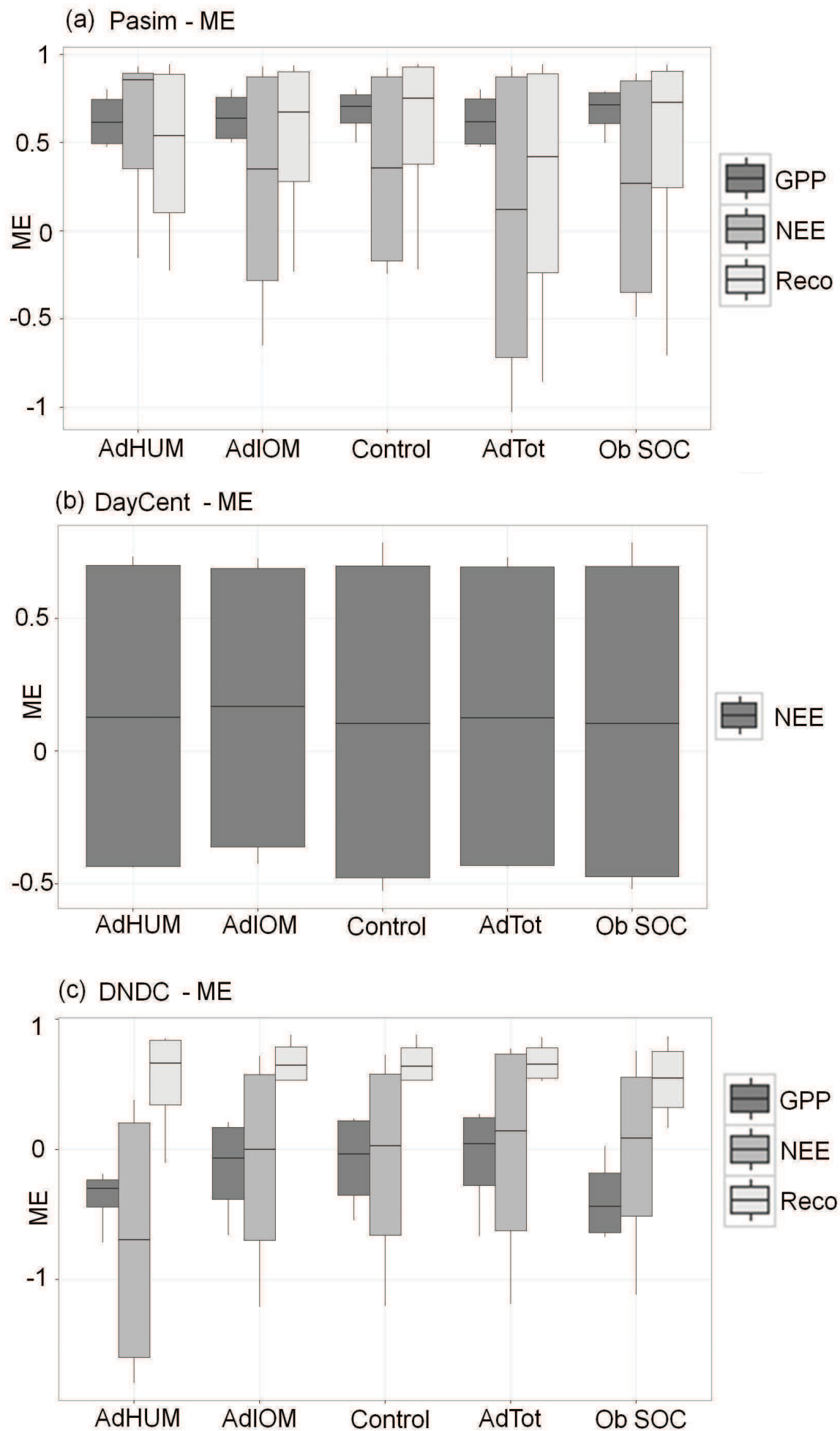


Figure 5.7: Model Efficiency (ME) for each model taking together all year and all sites. Here: (a) Pasim, (b) DayCent and (c) DNDC

### ***Model comparison***

RRMSE shows PaSim and DNDC can predict well GPP independent of initialisation methods. DNDC model seemed to have more difficulties to predict the fluctuation of Reco. From RRMSE results, independent of initialisation methods, the fluctuation of GPP and Reco was predicted well in the following order: PaSim > DNDC (Figure 5.6 (a) and (c)). ME results provided evidence that GPP was correctly estimated in the following order: Pasim > DNDC, where Reco was predicted better with DNDC (Figure 5.7 (a) and (c)). NEE prediction accuracy was similar among all of the models independent of initialisation methods except AdHUM method with DNDC (Figure 5.6 (a)-(c)). NEE in grazing grassland was the most difficult flux to estimate in all of three ecosystem models in this study (Figure 5.6 and 5.7). Except AdTot method, Pasim generally predicted better NEE than DNDC and DayCent. DayCent estimated NEE similarly to DNDC except AdHUM method (Figure 5.7 (b) and (c)). The accuracy of NEE prediction was similar in PaSim and DNDC (Figure 5.6 (a) and (c)). The impact of initialisation methods on NEE anticipation is small in DayCent.

## **5.4 Discussion and conclusion**

Compared to DNDC, PaSim and DayCent are the models which contain the detailed plant growth submodel. PaSim considers the variables light, temperature, nitrogen, dead shoot/root materials, leaf photosynthesis, stomatal conductance, leaf temperature and canopy development, as taken from Riedo et al. (1998, 2000)). The DayCent model considers information relating to plant canopy, leafy and root compartments, dead plant residues, plant type, etc. The DNDC model is the ecosystem model which developed from the soil carbon decomposition and denitrification model (Li et al. (1992)). DNDC started out as cropland model although in this study we also applied the DNDC model to the grassland ecosystems, which led to some difficulties. DNDC accurately predicted Reco flux tendency (ME), which relates largely to soil respiration, although GPP related to plant growth. DNDC model tightly couples plant growth with soil biogeochemical and climatic components, and simulates C, N and water cycles in agroecosystems (Zhang et al. (2002)). In Oensingen (mowing grassland), DNDC could correctly predict (RRMSE) the GPP inter annual variations and flux fluctuation, while Reco ones were much more difficult to be predicted (Figure 5.6 (c)). This may be because DNDC could estimate detailed soil data on the basis of soil texture, bulk density and total SOC data. This detailed soil estimation would be useful for predicting the general flux fluctuation tendency (Figure 5.7 (c)) although this may not be enough to accurately estimate flux data (Figure 5.6 (c)).

PaSim, was originally developed to estimate mowing grassland, which explains the fact that PaSim produced more accurately C fluxes of the Oensingen (CH) site compared to the Laqueuille (FR) site. DayCent, does not provide the possibility to adjust the number of grazing cows, compared to Pasim which comprises a highly developed animal submodel requiring type of grazing ruminant (i.e. suckling cow, heifers, sheep etc), animal stocking rate and live weight. We consider due to these differences more efficient model fit was observed with Pasim than with DayCent regarding grazing grassland (Laqueuille).

These three process-based models (PaSim, DNDC, DayCent) are quite representative of existing process-based models (Manzoni and Porporato (2009)). Very few models include nitrogen inhabitation and carbon over flow mechanisms, although these are included in DNDC which is based on NCSOIL model (Manzoni and Porporato (2009)). This may indicate that the other

process-based models would show similar results which I found in this study, as Manzoni and Porporato (2009) reported a few concepts are behind large number of different process-based models.

We conclude that over all, model initialisation using SOC data does not have a large effect on the prediction of C fluxes. Among the different methods, AdHUM method does not offer an improved model fit. For most of the model fit is due to model estimating capability regarding flux but not due to the initialisation of SOC pools. On the other hand, we need to test whether model initialisation adjusting model results to the measured flux data would improve model fit, as we found SOC initialisation methods greatly affect SOC model fit in Chapter 4. Furthermore, we need to consider theoretical SOC pools calculation for each ecosystem models using detailed soil organic matter data. Also, combining other model calibration methods such as Bayesian calibration (Yeluripati et al. (2009); Ben Touhami et al. (2013)) may improve model fit regarding flux outputs.

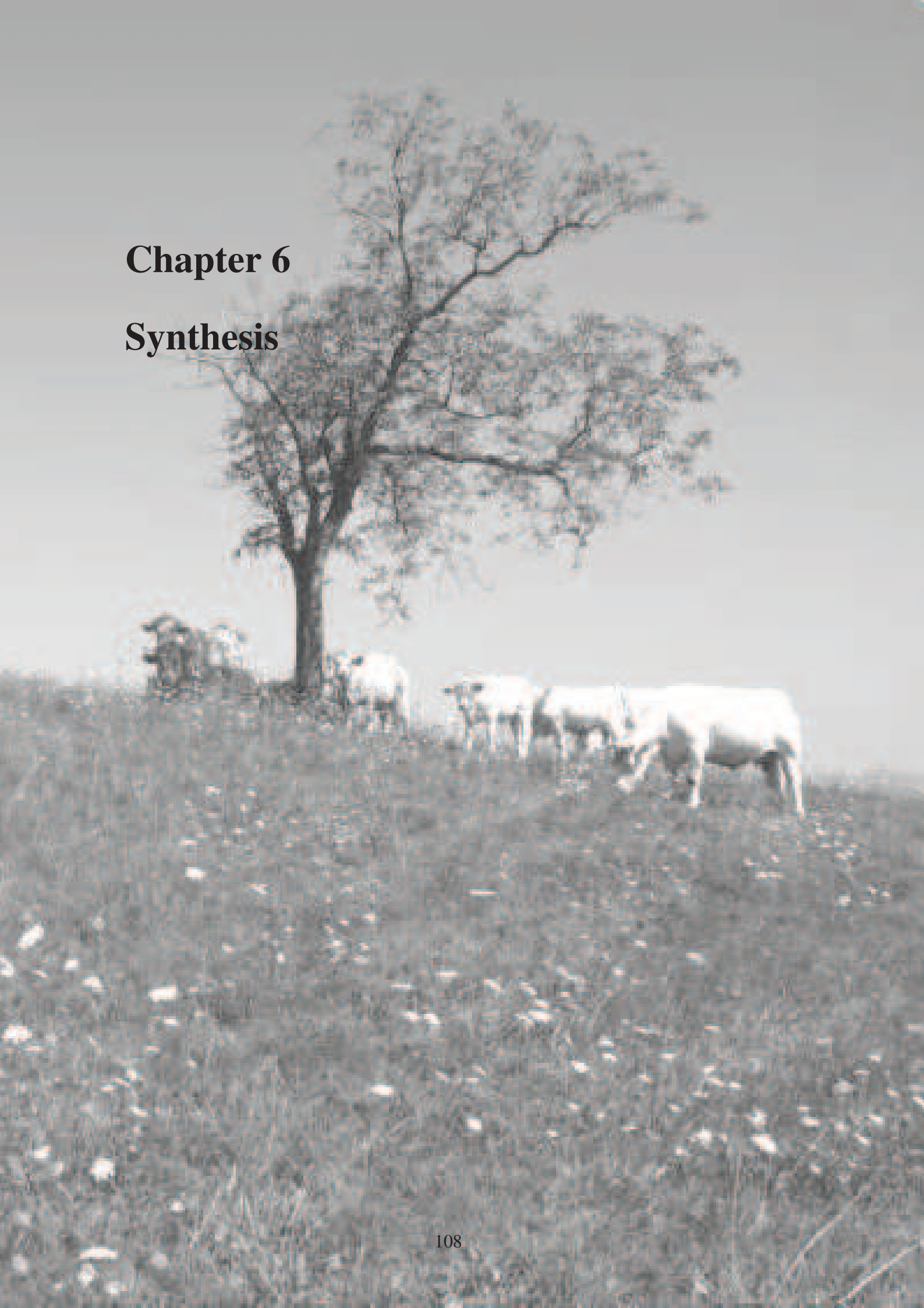






# **Chapter 6**

## **Synthesis**



Projected changes in the global climate system are likely to have significant implications for agriculture. Agricultural land covers almost half of the Earth's land surface and globally contribute between 14-24% to atmospheric concentrations of key greenhouse gases (GHG) such as methane, nitrous oxide and emissions/sequestration of carbon dioxide. Regarding C sequestration, the terrestrial biosphere currently acts as a net C sink, absorbing about 30% of anthropogenic CO<sub>2</sub> emissions in the past decade (Canadell et al. (2007)). Globally 62 % of C is stored as SOC, where the soil stores more than 3 times more C than the atmosphere (Smith et al. (2007a); Jobbágy and Jackson (2000); Lal (2002)). Studying the SOC stock in agricultural lands and measuring fluxes from these areas help to understand which agricultural management systems and practices release less GHG and sequester more C. Over the last 40 years, impacts of singular land management (apart from natural induced drivers such as soil texture, climate, geographical conditions) on SOC stock and C cycling have largely been studied by soil inventories, litter decomposition experiments and GHG chamber measurements. However, due to individual site conditions, those studies often consist of different soil types and climates, allowing few general conclusions on management and climate impacts to be drawn (Lal (2002); Franzluebbers (2005, 2010)).

Nowadays, the eddy covariance technique offers a useful tool to analyse detailed multi-site time-series of C fluxes (Kutsch et al. (2010); Soussana et al. (2007)). However, for assessing management impacts under comparable climate and soil conditions, adjacent contrasting management systems with two individual eddy-covariance flux measurement towers (paired-plots) have been shown to be very useful (Klumpp et al. (2011); Ammann et al. (2007); Jacobs et al. (2007)). In spite of this, these paired-plot sites do not exist in great numbers and only a small number of studies have been conducted regarding exclusive land management impacts on SOC stock and fluxes in agricultural lands. The other way of analysing effects of management regimes on fluxes and the amount of C sequestration is the use of process-based ecosystem models, and numerous studies have shown that modelling is useful for this purpose. However, numerous studies have shown that model predictions can be greatly affected by model initialisation. Recently, a number of model initialisation methods have been suggested (for details see Introduction "Model initialisation": Bruun and Jensen (2002); Hashimoto et al. (2011); Wutzler and Reichstein (2007); Yeluripati et al. (2009); Carvalhais et al. (2008)). Though, a common and easily accessible model initialisation method has not been found.

In view of this, the objectives of this PhD thesis were to analyse SOC pools and C fluxes of long term paired-plot agricultural sites in order to assess the most appropriate and compatible initialisation method for process-based ecosystem models. To assess if model initialisation using detailed SOC data (e.g. SOC fractions and SOC pools) would improve model results, I analysed the SOC distribution among different SOC fractions in each of the management regimes (Chapter 3) for five long term (10 years) paired-plot sites.

Each of this five paired-plot sites possesses two plots of adjacent contrasting management regimes and an individual eddy-covariance flux measurement system to follow C fluxes for each regime. The studied paired-plot -sites involve two cropland and three grassland sites, where one of the grasslands was composed of organic soil. Within the eddy covariance tower measuring area (foot-print area), I sampled 6 to 8 soil cores (0-5cm, 5-10cm, 10-20cm, 20-40cm and 40-60cm) per management plot and performed the Zimmermann et al. (2007) soil fractionation, to determine distinct SOC pools for initialising process-based ecosystem model SOC pools. I have applied Zimmermann et al. (2007) soil fractionation to organic soil which include 16-24 % organic carbon and I found organic soil which contain 8-16 % carbon can be applied this

soil fractionation. However, I agree that we cannot apply this fractionation method for all of the organic soils. One of the limitations of this experimental design of using eddy covariance flux tower sites is the absence of replicates, and thus a possibility of pseudo replication of soil samples (i.e., 6 soil cores per field). To overcome this problem, I have chosen a sampling design which covers foot-print area for comparing with flux measurement and model flux output (see Chapter 5). Performing soil fractionation at different soil depths and analysing SOC is labour intensive and is not feasible for a large number of soil samples. Besides, other studies have used a lower number of replicates to provide evidence of SOC changes after land use change: four and six soil cores from a 15×30m and 14×21 m sampling area at 0-15 and 15-30 cm and down to a depth of 80 cm soil depth respectively (Dondini et al. (2009b); Poeplau and Don (2013b)). In this study, we sampled 6 to 8 soil cores from a representative transect of the soil inventory and foot-print area. Since the soil sampling areas were covered by eddy-covariance measurements, it is scientifically attractive to compare SOC distribution among SOC fractions and flux measurements such as GPP, NEE and Reco, which are affected by plant growth and soil respiration mechanisms. Another limitation of the experimental design in this study is that most of the experimental sites are relatively young and might not have had enough time to arrive at the SOC equilibrium after the land-use change. The Laqueuille (FR) site was converted from cropland to grassland around 1950 and was under constant management from over 10 years ago. The Dutch Reeuwijk (NL) grassland has been a permanent grassland for many years and was drained about 20 years ago. The Carlow (IE) site has been a cropland since at least 1960 and Hertfordshire (UK) cropland was converted from grassland in 1960. The Oensingen (CH) was converted from cropland to grassland in 2000. Analysing a number of LUC sites where grassland were converted to cropland, Poeplau et al. (2011) showed that a new SOC equilibrium can be attained after 17 years. On the other hand, a LUC site converted from cropland to grassland will take around 120 years for SOC changes appear. However, other studies have reported a difference in SOC distribution in different SOC fractions due to management regimes, even after land-use conversion during the 1950s-1970s (Conant et al. (2003); Leifeld et al. (2009a)). In this study, due to the paired-plot site design, we may exclude other natural induced impacts on SOC equilibrium such as soil texture, climate and geographical conditions, which allows us to isolate the cause of any observed differences in SOC pools to differences in management regime. Results of soil fractionation demonstrated that the soil fractionation method could be used for organic soil containing 8-16% organic carbon. Compared to organic soils, mineral soils showed no significant difference regarding SOC distribution among different SOC fractions due to contrasting management. Moreover, in the organic soil, we observed marked differences between topsoil and subsoil, indicating that topsoil SOC acquires more impact from management systems, while subsoil SOC seemed to reflect the effect of soil texture. This effect has already been reported by several studies (Poeplau et al. (2011)). We conclude that not enough time may have elapsed since the onset of current management practices to generate statistically significant differences in SOC stocks in the mineral soils given the sampling intensity. Results also provide evidence that soils containing more particulate organic matter (POM) may react faster management changes than the soil containing less POM. Budge et al. (2011) mentioned that the high proportion of labile C may be more sensitive to external changes than the other fractions. For mineral soils, the absence of differences between management regime, indicated that those soils need a longer time to arrive at the equilibrium point after management systems have changed, and that 10 years of continuous land management is not sufficient to reach this state even if land use conversion has taken place 50-60 years ago.

To test the current SOC status at each site, I compared the measured SOC with SOC at equilibrium using RothC model. To do so, I carried out different initialisation methods using detailed measured SOC data with the RothC model (see Chapter 4): (1) General spin-up run: repeating the average monthly weather data 1901-2010, and using the average monthly recent 10 years management data (control), (2) Adjusting the SOC spin-up by increasing or decreasing C input during the spin-up run until the individual SOC pools or total SOC arrive at the equilibrium point and (3) Initialising with measured SOC fraction data. Assessment of different initialisation methods by comparing measured SOC and different SOC pools and total SOC model results, confirmed that a general spin-up run is not suitable for sites where soils are not in the equilibrium. Other initialisation methods involving adjustments of C inputs until a given SOC pool size reached the measured SOC values, showed that initialising with quickly turning-over SOC pools, such as DPM and RPM, largely over/under estimation total SOC compared to measurements. This was also true for the passive SOC pool (HUM), and only adjustment of total SOC revealed a good agreement with measured values, so this method was shown to be the best initialisation method for the RothC model under these circumstances.

To further investigate a common model initialisation method, four model initialisation methods were tested for three ecosystem models based on other SOC pools than RothC: CENTURY (Pasim, DayCent), and N driven decomposition (DNDC) (see Chapter 5). Though soil fractionation was done thoroughly, this approach is important as the Zimmermann et al. (2007) soil fractionation method has only been tested with the RothC model, but not other ecosystem models. To overcome this problem, referring to Christensen (1996), I examined C submodel construction and turnover time of SOC pools of each model and considering all particularities of the different SOC pools in each models, indicated that that certain SOC pools may corresponded well to some of those used by the RothC model (see Material and Method). Accordingly, I assessed initialisation methods for models other than RothC, though comparing the modelled SOC pools with measured SOC fractions determined by Zimmermann et al. (2007) fractionation proved difficult, but it was important to test its feasibility. (see Appendices B \*omitted DayCent result as PaSim has the same C submodel). Another way to compare efficiency of initialisation methods in other models is to compare model flux outputs with measured flux data. I compared predicted carbon flux data (GPP, NEE and Reco) with C fluxes measured by the eddy-covariance flux towers. Through analysing two grassland sites (Laqueuille (FR) and Oensingen (CH)), results did not indicate a significant pattern concerning model outputs and model initialisation methods. With regard to general spin up runs (control), DNDC (Li et al. (1992)) predicted Reco better than it predicted GPP at both sites (see Chapter 5, Figure 5.3 (e-1) and (f-1)), where Reco relates largely to the soil respiration and GPP to plant growth. Pasim and DayCent are models that contain detailed plant growth submodels and provided a better fit for GPP in Laqueuille (FR), which relates to plant growth, than for NEE and Reco, which are partly affected by soil respiration. Notably, at the Oensingen (CH) site, all fluxes (GPP, NEE and Reco) were predicted accurately. Compared to PaSim, DayCent does not require the number and weight of grazing cows to simulate grazed grasslands, which might be the reason that a more efficient model fit was observed with Pasim than with DayCent at the Laqueuille (FR) site. Relating to other initialisation methods, except “adjusting with HUM”, which resulted C fluxes far from observations, the three ecosystem models seem relatively insensitive to initialisation compared to regular spin up run (control). Contrary to expectation, results suggested the model initialisation using SOC data has small effects on the prediction of C fluxes, while other initialisation methods, which improve the plant component have shown contrary findings (i.e. Bayesian calibration). This may be ex-



plained by the fact that model outputs are relatively insensitive to initial soil conditions; rather they are more sensitive to management and meteorological data. Accordingly, initial conditions have their greatest influence on C fluxes during the first years of simulation. On the other hand, we need to test whether model initialisation using flux data would improve model fit, as I found SOC initialisation methods could influence SOC model fit in Chapter 4.

I have learned much during the course of this PhD and have reflected on how I might do things differently next time, or additional measures I would take if I were to be advising another PhD student following me doing similar work.

Below, I summarise some of these reflections:

1. Taking >4 soil cores within contrasting management plots, but outside of EC foot print in parallel for showing whether soils are homogeneous inside of plots. However this would increase the number of soil samples to take and the soil fractionation and CN analysis. This requires more time for analysis. If I focused on model initialisation, I could take more soil samples but only to a depth of 30 cm, as some models did not require subsoil information.
2. Choosing several organic soil sites which possess adjacent contrasting management regimes. In this study, we had just only one organic soil site and this made firm conclusions difficult.
3. Radio carbon analysis. This is expensive although this would provide a better understanding of SOC decomposition processes due to management.
4. Time series analysis. Numerous soil samples and frequent sampling is essential in the SOC studies. SOC fraction data taken in different years would help us to understand SOC distribution changes among different soil fractions over time.
5. Nitrogen (N) relates closely to C. Therefore analysing C and N distribution in different soil organic fractions, and analysing whether N is closer to equilibrium compared to C would be interesting.
6. For confirming whether organic soil is easy to be influenced by management changes, it would be interesting to convert a part of Reeuwijk (NL) intensive plot to an extensive one, and a part of the extensive plot to an intensive one. Then analysis of soil fractions in 2 years (DPM arrived at the equilibrium by RothC spin-up run), 5 years and 10 years (BIO arrived at the equilibrium in some sites by RothC spin-up run).
7. Improve the soil fractionation method for organic soils, as organic soils contain abundant humus which was easy to loose during the soil fractionation process. However this might not change the results significantly, as the total SOC without soil fractionation and the sum of all of the fractions' SOC were not greatly different.
8. Combine other model calibration methods such as Bayesian (Yeluripati et al. (2009); Ben Touhami et al. (2013)) calibration. One of the limits of the Bayesian model calibration method is the necessity for precise and detailed data for best model fit. However, detailed, precise and abundant data are difficult to come by. As modelling is useful to predict future conditions and understand observed data where detailed data is missing, we need to improve this method. Combining my modified model initialisation spin-up run (adjusting equilibrium total SOC to be equal to the measured total SOC during the spin-up run each site) and Bayesian model calibration may significantly improve model fit.

Despite identifying things I would do differently with hindsight (which is part of the research process), I have discovered new things about SOC and SOC modelling. To summarise, I have

shown that 10 years of a continuous management system is not long enough to show significant difference in SOC distribution among SOC pools with the given sampling regime, due to management even if grassland conversion has taken place 50-60 years ago. This questions the use of general spin up runs for model initialisation and provides a reason to initialise with SOC data. However, so far there is not a common soil fractionation method which could estimate correctly SOC distribution among SOC pools for different ecosystem models, indicating another difficulty for model initialisation. For the RothC model, where a soil fractionation method was developed by Zimmermann et al. (2007), adjusting the total SOC equilibrium to the measured total SOC has been shown to be the most useful model initialisation method, although this method did not show significant efficiency in the flux estimation. The model initialisation using SOC data does not greatly affect model flux results if the model predicts fluxes accurately in several different ecosystem models. Model accuracy is more important than SOC pool initialisation for predicting fluxes.









# Appendices





# Appendix A

## Supplementary figures

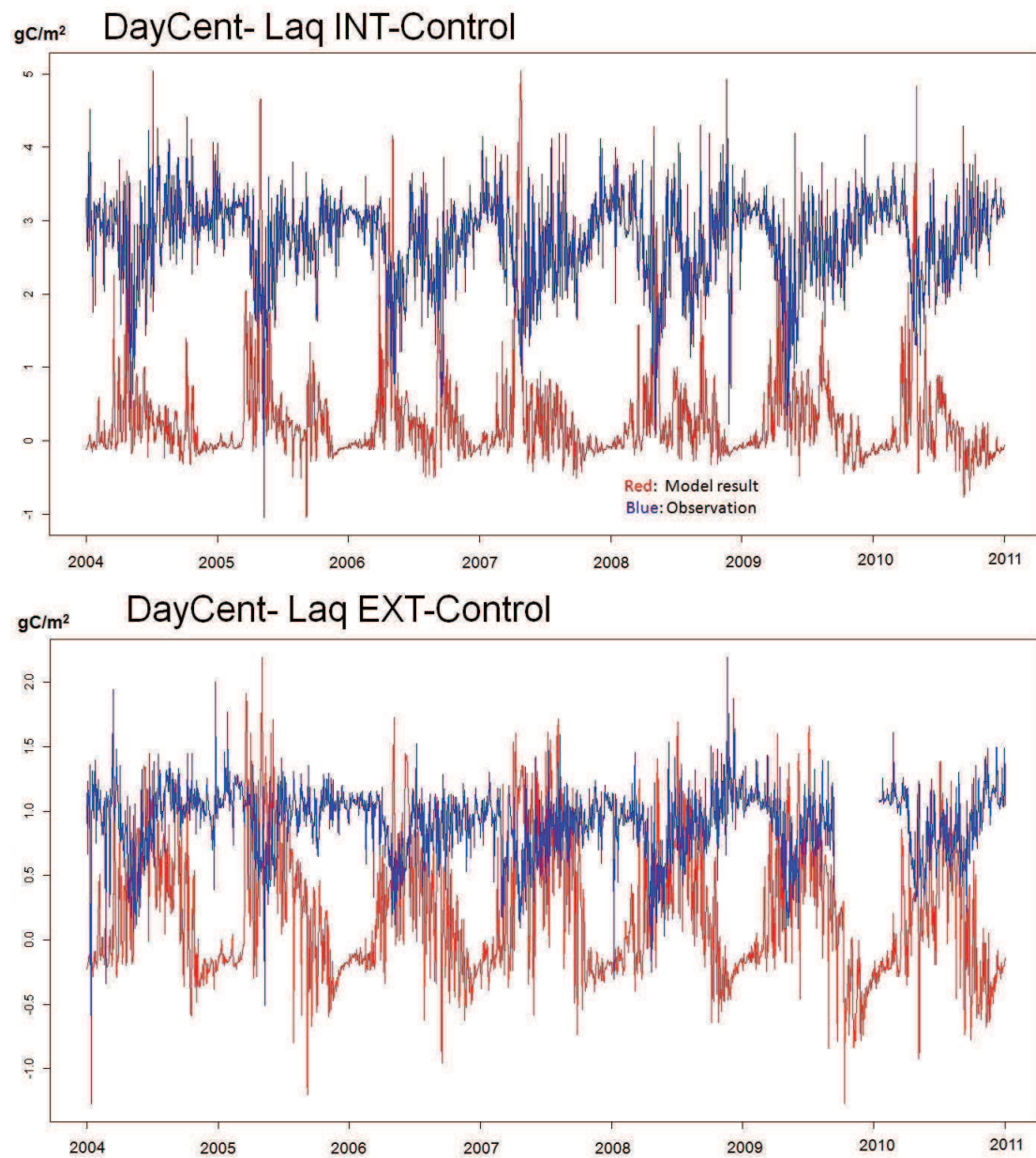


Figure A.1: DayCent output and observation of NEE in Laqueuille (FR)

# Appendix B

## Supplementary information for the summary

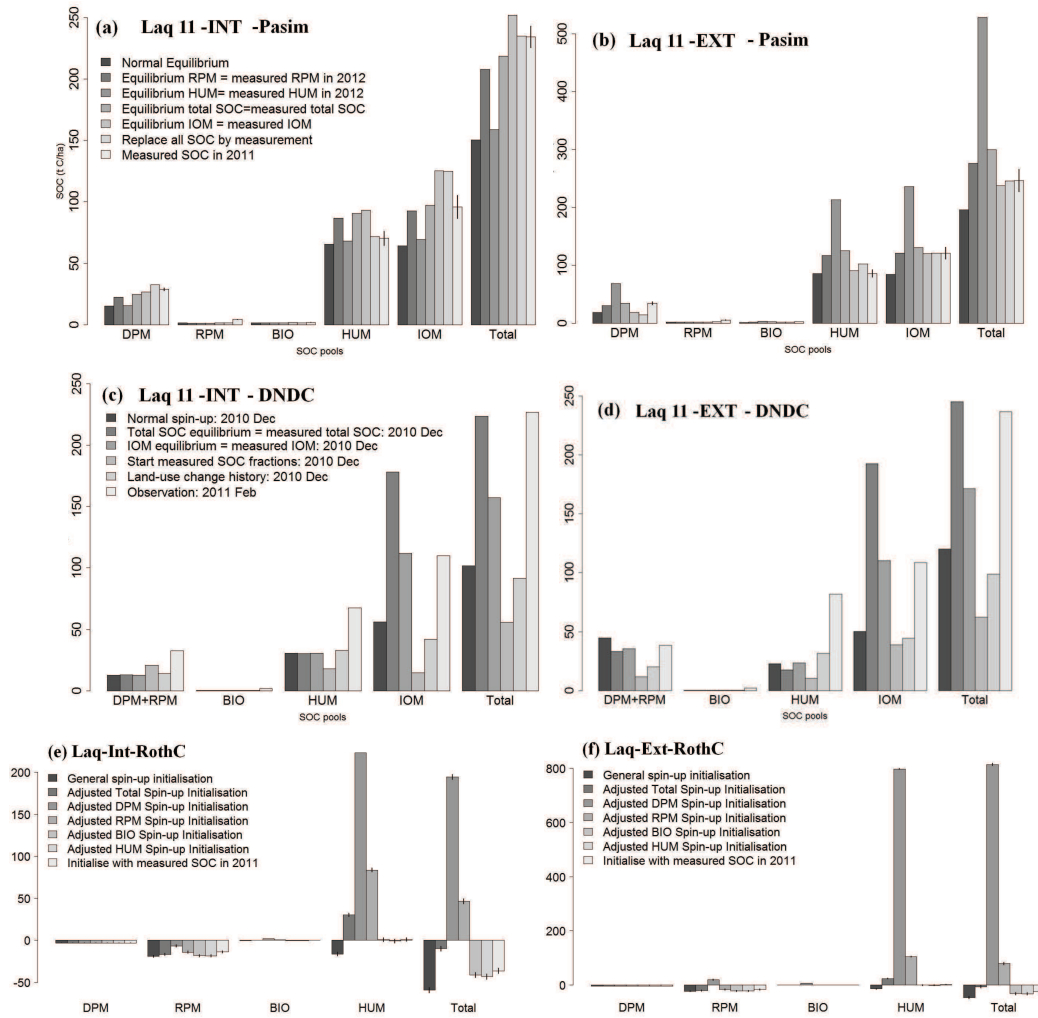


Figure B.1: Equilibrium SOC by different model initialisation and measured SOC



# Appendix C

## Reproducibility of a soil organic carbon fractionation method to derive RothC carbon pools

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### Abstract

Fractionation of soil is performed to isolate organic carbon with distinct functional properties, such as stability and turnover times. Soil organic carbon (SOC) fractionation helps to better understand the response of SOC to changes in land use, management or climate. However, fractionation procedures are often poorly defined and there is little information available on its reproducibility in different laboratories. In a ring trial, the fractionation method introduced by Zimmermann et al. (2007) is assessed regarding its reproducibility. The isolated fractions can be linked to the model pools of the Rothamsted carbon model (RothC). We found significant differences between six laboratories for all five fractions in three different soils with coefficients of variation ranging from 14 to 138%. During ultrasonic dispersion, the output power (energy per time) has been identified as an important factor controlling the distribution of SOC in the five fractions, while only the output energy has been standardized. The amount of water to flush the sample during wet sieving significantly influenced the amount of extracted dissolved organic carbon (DOC). We therefore suggest using a fixed amount of power for ultrasonic dispersion (20 W) in addition to the total amount of energy as well as a minimum amount of water for wet sieving (2000 ml). RothC pools were derived from the measured fractions and compared with RothC equilibrium pool size distributions. Under a virtual bare fallow model simulation, soil carbon stocks derived from model initialization with measured fractions were found to be more stable than those derived from the pool size distribution of RothC equilibrium runs. To increase the amount of isolated particulate organic matter (POM) as a labile carbon fraction, we suggest increasing the density of polytungstate to  $2.0 \text{ g cm}^{-3}$ . The modified fractionation procedure introduced as a result of this ring trial aims to increase the reproducibility across different laboratories and to gain a better match with the RothC pools.

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**Keywords:** C dynamics, C pool, carbon cycling, carbon modelling, carbon stabilization.



## C.1 Introduction

Soil organic carbon (SOC) consists of several components, which differ in their physicochemical properties and hence their degree of stabilization and turnover time (Bol et al. (2009)). Active SOC fractions are considered to respond relatively fast to changes in land use, climate or management (Purakayastha et al. (2007)), while other fractions are hypothesized to be more stable or even inert (Krull and Skjemstad (2003)). The distinct turnover times range from less than one year to thousands of years. The composition of SOC with its individual fraction size distribution thus determines its sensitivity towards any kind of disturbance (Conant et al. (2003)). Modelling of SOC dynamics plays a key role for large scale estimates and predictions of SOC stock changes by accounting for the variability of soils, climate and land-use (Paustian (2001)). Starting in the late 1970s, several multi-compartment models have been developed (Jenkinson and Rayner (1977)). The majority of these models are based on the partition of SOC in different functional pools with distinct first-order kinetics and climatic and edaphic rate modifiers (Paustian (2001)). Since almost two decades many attempts have been made to develop SOC fractionation methods to correlate laboratory derived carbon fractions with functional model pools in order to initialize the models or to validate the model outputs (Motavalli et al. (1994)). Elliott et al. (1996) stated that only models that can be validated by measurements are reliable enough to predict SOC changes. However, it is challenging to achieve a good match of operationally defined SOC fractions with the conceptional model pools, since the turnover of a specific fraction depends on its chemical and physical properties. Smith et al. (2002a) state that a measured fraction is only equivalent to a model pool if its unique and does not contain “sub-fractions” with contrasting properties. Existing fractionation methods can be divided into two major groups: physical and chemical fractionation, which are based on different scopes regarding the mechanisms of SOC stabilisation. Physical fractionation is based on the assumption that the association to soil particles and in aggregates plays the key role in SOC stabilization and thus different SOC fractions are isolated by different degrees of disaggregation, dispersion, density fractionation and particle size separation (Amelung and Zech (1999); Christensen (2002); Elliott and Cambardella (1991); Six et al. (2001)). In contrast, chemical fractionation methods are based on the assumption that the chemical composition of each fraction determines its stability and thus its turnover time (Blair et al. (1995); Helfrich et al. (2007); Lefroy et al. (1995)). Chemical fractions are obtained by the extraction of SOC in different solutions, the hydrolysability of SOC with water or acid and the resistance to oxidation. In several studies a combination of physical and chemical fractionation has been used (Kaiser and Ellerbrock (2005); Leifeld and Kögel-Knabner (2001); Mikutta et al. (2005); Trumbore et al. (1989)). The idea is to separate rather fresh SOC from mineral bound SOC by density or particle size fractionation and these physical fractions are chemically treated to further separate fractions of different stabilization degree and turnover times. However, the use of loose terms, such as ‘recalcitrance’ or the vague definitions for fractions such as particulate organic matter (POM) or mineral associated organic matter (MOM) confused the discussion and hampered direct comparisons of obtained results (Schmidt et al. (2011)). Additionally, fractionation procedures are often poorly defined and there is little information available on their reproducibility in different laboratories. Therefore, there is a need for more standardized methods. A new attempt to combine physical and chemical fractionation has been made by Zimmermann et al. (2007). They isolated fractions which were related to the modelled pools of the Rothamsted carbon model (RothC) (Jenkinson and Rayner (1977)). Two active, two slowly cycling and one passive fraction are isolated. Meanwhile the method has been

used in different studies and has a potential to become a new widely used fractionation method due to its simplicity and its good match with the RothC pools when applied to low elevation agricultural and grassland soils (Dondini et al. (2009a); Leifeld et al. (2009b); Poeplau and Don (2013a,b); Xu et al. (2011)). However, not all steps of the fractionation procedure are described in detail (Zimmermann et al. (2007)). It is therefore likely that each laboratory thus finds its own set up and optimization, which might in turn lead to significantly different results. Therefore, we set up a ring trial to compare the measured SOC fractions of six different laboratories among each other and relate them to the RothC modelled carbon pools. Primarily, the aim of this work is to identify the most bias-sensitive work steps. As a second step we aim to suggest a more standardized fractionation protocol for this method.

## C.2 Materials and methods

### C.2.1 Soils, sample preparation and experimental setting

Three different cropland soils (0-20 cm) with contrasting properties have been selected for a ring trial. Soil “A” is a loamy clay from the experimental farm Kungsängen (University of Uppsala, Sweden), soil “B” a loamy sand from the agricultural research station Reckenholz (ART, Switzerland) and soil “C” a coarse sand from the experimental farm Jyndevad (University of Aarhus, Denmark) (Table C.1).

Table C.1: Characteristics of the three soils and site characteristics at the sampling sites, C<sub>org</sub> concentration, SOC stock (0-20 cm depth), pH (KCl), and clay, silt and sand contents

Soil	Site	Country	C <sub>org</sub> /%	Bulk Density / g cm <sup>-3</sup>	SOC stock /Mg ha <sup>-1</sup>	pH (KCl)	Clay %	Silt %	Sand %
A	Kungsängen	Sweden	2.9	1.01	58.3	4.4	38.1	54.4	7.6
B	Reckenholz	Germany	0.95	1.32	25	4.6	14.9	35.7	49.5
C	Jyndevad	Denmark	1.19	1.27	30.3	5.6	4.7	5.7	89.6

A further description of the sites can be found in Poeplau and Don (2013a). The soils have been under permanent crop cultivation since more than 100 years (Soils A and C) and 60 years (site B). The main crops in Kungsängen (site A) were spring barley, spring wheat, winter wheat, ley and oats in Reckenholz (site B) were winter wheat, maize, potatoes, spring barley and ley and in Jyndevad (site C) spring barley, winter barley, winter rye and oats. Only in Kungsängen the field received farmyard manure with an average carbon input of 0.4 Mg C ha<sup>-1</sup> yr<sup>-1</sup>. All three soils were free of carbonate. The soils were dried at 40 °C, sieved to 2 mm and cleared from visually detectable fine roots. Soil sampling, sample preparation and SOC stock calculation are described in detail in (Poeplau and Don (2013a)). To obtain homogenized and reproducible subsamples of 30 grams, which is the required amount for the fractionation, we used a sample splitter (RT, Retsch, Haan, Germany). The reproducibility was tested on five randomly selected subsamples for each soil. For soils A and B the coefficient of variation (CV) of the carbon content accounted for 2 and 3% among the subsamples. For site C, which is characterized by a high content of particulate organic matter (POM), but a relatively low content of total SOC (1.2%) we only achieved a CV of 5%, which was however considered sufficient. Three randomly selected subsamples of each soil (total n=9) were sent to each of the participants of the ring trial. A total of six laboratories joined the ring trial, situated at the following institutes: Thünen Institute of

Climate Smart Agriculture (Germany), Agroscope Reckenholz (Switzerland), INRA Clermont-Ferrand (France) in cooperation with University of St Andrews (United Kingdom), Technical University Munich (Germany), University of New England (Australia), and University of Aberdeen in cooperation with the Centre for Ecology and Hydrology (CEH) (United Kingdom). The participants were asked to conduct the fractionation as described in Zimmermann et al. (2007) and to document every fractionation step in detail. The participating institutes have been made anonymous by randomly numbering (1-6). To avoid an additional instrumental-bias, the participants were asked to send the dried fractionated samples back to the Thünen Institute where all solid fraction samples were analysed for total carbon and nitrogen via dry combustion in an elemental analyser (LECO TruMac, Michigan, USA). Only the dissolved organic carbon fraction (DOC) was analysed by each laboratory due to the difficulties of sending frozen soil extracts.

### C.2.2 SOC fractionation

The fractionation (Zimmermann et al. (2007)) comprised the following steps: (i) ultrasonic dispersion with  $22 \text{ J mL}^{-1}$  to disperse labile macroaggregates, (ii) wet-sieving over a  $63 \mu\text{m}$  sieve to separate the coarse, the fine and the dissolved fraction, (iii) density fractionation with a sodium polytungstate solution with a density of  $1.8 \text{ g cm}^{-3}$  to separate a light and a heavy fraction within the coarse fraction; and (iv) a sodium hypochlorite ( $\text{NaOCl}$ ) oxidation with a 1-g subsample of the fine fraction to simulate aggressive decomposition. The method isolates the following five fractions: particulate organic matter (POM), dissolved organic carbon (DOC) (both considered to be active C pools), SOC attached to sand grains and in stable aggregates (S+A), SOC attached to silt and clay particles without being chemically resistant (both considered to be slow cycling) and a chemically resistant fraction (rSOC) (Figure C.1)

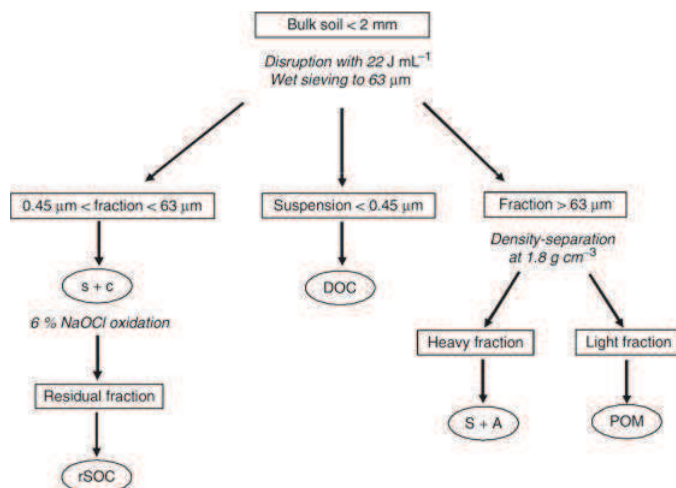


Figure C.1: Soil carbon fractionation scheme after Zimmermann et al. (2007).

### C.2.3 Modelling the pool sizes with RothC and converting fractions to pools

To estimate the SOC pool size distributions for the three soils with RothC, we used the model's inverse approach, which calculates the plant carbon input to achieve the measured total SOC stock at equilibrium. The required input data were thus reduced to the following: precipitation, temperature, open-pan evaporation and plant cover on a monthly basis, clay content and amount and time of organic manure application. From these data the monthly C input was estimated with RothC and the pool of inert organic matter (IOM) was calculated by the model and using the equation proposed by Falloon et al. (1998). Both sets of information are required to initialize an equilibrium run, which we subsequently conducted. The assumption that all three soils were in an approximate equilibrium at the time of sampling could be made because they have been under cultivation without major management changes for 60 (site B) or more than 100 (sites A and C) years. To compare the effect of pool size distribution, either derived from the equilibrium runs or from soil fractionation, on the long-term fate of simulated SOC we converted the measured SOC fractions into pools according to the procedure described by Zimmermann et al. (2007) (Figure C.2). The splitting ratios for decomposable plant material (DPM) and resistant plant material (RPM) (DPM/RPM) as well as microbial biomass (BIO) and humified organic matter (HUM) (BIO/HUM) were derived from the modelled equilibrium situation at each site, in which the size of each pool was predicted. We also used the measured pools from the six laboratories and the RothC modelled pools to initialize a short model run in RothC to predict the effect of the individual pool size distributions on relative SOC stock depletion. The sensitivity of the total SOC stock, as determined by the different pool size distributions, is thus assessed. To do so, an unrealistic scenario of 40 years bare fallow without any C input was assumed. In the following this modelling exercise will be referred to as the 'bare fallow simulation'.

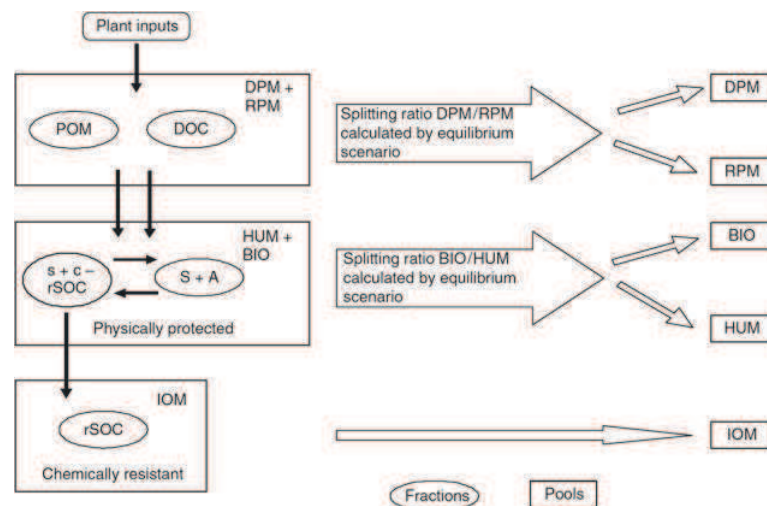


Figure C.2: Concept of converting measured carbon fractions to RothC pools Zimmermann et al. (2007).



## C.2.4 A posteriori fractionation experiments

We found a large variability in quantified fractions among laboratories, as well as systematic deviations from the RothC modelled pool size distributions, and therefore we conducted several a posteriori fractionation experiments in order to improve the protocol and to verify identified sources of laboratory bias.

**Wet sieving and density fractionation** As the amount of extracted DOC was correlated with the amount of water used for wet sieving with a saturation occurring at 2000-3000 ml, we a posteriori conducted the wet sieving for all three soils with 3000 ml water. Zimmermann et al. (2007) isolated only small amounts of DOC and POM, which resulted in a misfit with the RPM+DPM pools. They proposed that the density of sodium polytungstate (SPT) solution used for density fractionation should be increased to 2.0-2.2. We tested the effect of this increase by conducting additional density fractionation with an SPT solution density of 2.0-2.2. To calculate the amount of POM needed to match the modelled RPM and DPM pools, we used the amount of DOC that was a posteriori isolated with 3000 ml water and subtracted this amount from the RPM and DPM pools. We also checked whether the amount of isolated DOC could be increased by hot-water extraction of the suspension after ultrasonic dispersion. After a pretest, in which a sample was extracted for 5, 10, 15, 30 and 60 minutes, we decided to extract the samples for 60 minutes in a water bath.

**NaOCl oxidation.** Chlorine in NaOCl solution is easily lost, so we varied the concentrations of NaOCl to test this as a potential source of bias and used 3, 4, 5, 6 and 7% NaOCl solutions.

## C.2.5 Statistical analysis

To assess whether the size of each fraction is significantly influenced by the laboratory that conducted the analysis and to quantify differences regarding the inter-laboratory variability between the three soils, we conducted linear mixed effect model analyses with crossed random effects. There were obvious differences in carbon content between the three soils, which were therefore accounted for by a fixed site effect. The six laboratories were considered as a random selection of a larger number of possible laboratories and therefore treated as random effects. Similarly, the analysed soil samples constituted a random selection of all possible soil samples. As they were split before sending them to the different laboratories, the samples themselves had to be treated as a random effect in the statistical analysis. Two modifications of this basic model were made: first, the differences in carbon content between the different soils were associated with differences in the within-laboratory variability (variance heterogeneity). The residual variance was therefore chosen to be sample-type specific. Second, we had to assume that the differences between laboratories were sample-type specific, demanding an additional random laboratory x sample interaction to be included in the model. Variance components in this model were estimated with the restricted maximum likelihood method as implemented in the nlme-package of the statistical environment R. Model selection was made by using the Akaike Information Criterion (AIC). The level of significance was set to  $P = 0.05$ . To quantify in which soil and fraction the laboratory effect was most evident, we calculated the coefficient of variation (CV) for each soil and fraction, as well as a ratio of this CV and the residual error (standard deviation) as revealed by the model, which was recalculated into a 'residual CV' (intra-laboratory variability).

The larger this ratio, the larger was the difference between laboratories. A ratio  $<1$  thus indicates that the intra-laboratory variability exceeded the inter-laboratory variability. In addition to the five fractions, we conducted this analysis for the ratio of carbon in the fine fraction ( $<63 \mu\text{m}$ ) (s+c, DOC) and carbon in the coarse fraction ( $>63 \mu\text{m}$ ) (POM, S+A).

### C.3 Results and discussion

**Inter-laboratory variability of SOC fractions** We found a significant difference between laboratories for all fractions and the  $\text{C}(<63 \mu\text{m}):\text{C}(>63 \mu\text{m})$  ratio (Figure C.3).

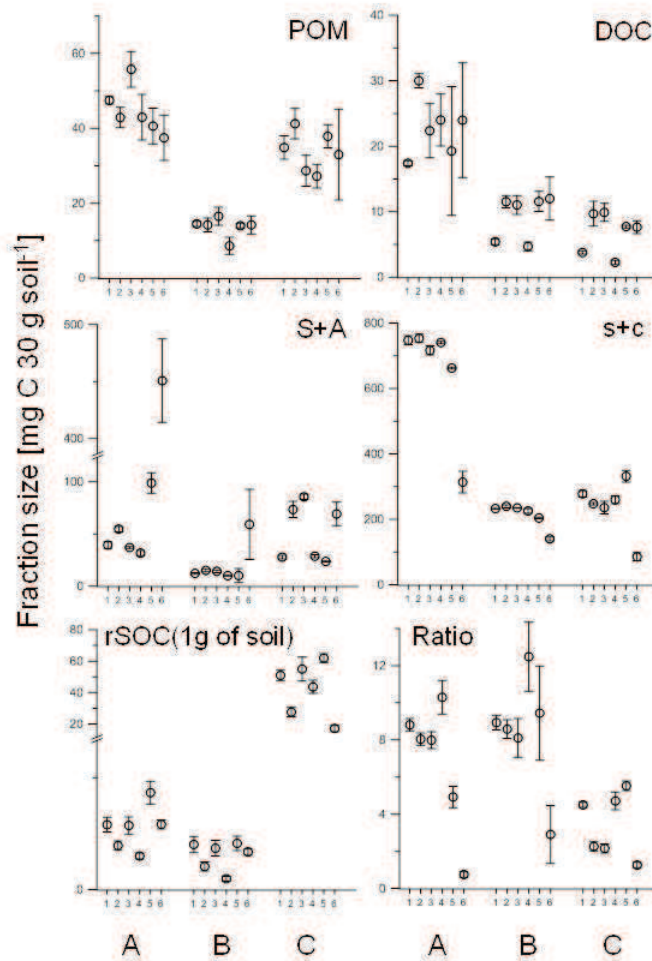


Figure C.3: Isolated carbon in each measured fraction and the ratio  $\text{C}(<63 \mu\text{m}):\text{C}(>63 \mu\text{m})$  with standard deviations for sites A, B and C and laboratories 1-6.

The POM fraction had the least variability between laboratories and thus the best reproducibility with a CV of 12.9% for site A, 17.6% for site B and 13.1% for site C (Table C.2).

Density fractionation, which isolates the POM fraction, can thus be classified as the most robust fractionation step regarding the reproducibility between laboratories. The residual CV of the POM fraction was of the same order of magnitude as the CV between laboratories. For site

C it was even larger, resulting in a CV:residual CV ratio of 0.7. This was surprising because we expected the POM fraction to be variably distributed in the different soil samples. However, the largest variability between laboratories was observed for the S+A fraction, with a CV of 126.7% for site A, 86% for site B and 58.3% for site C, which is reflected by the large variability of the C(<63  $\mu\text{m}$ ):C(>63  $\mu\text{m}$ ) ratio and indicates that the first fractionation steps (ultrasonic dispersion and wet sieving) were very sensitive to a laboratory bias (Figure C.3, Table C.2).

Table C.2: Coefficients of variation (%) (inter-laboratory error), residual coefficients of variation (%) (intra-laboratory error after fractionating three replicate samples) and their ratio for the fractionation results of all sites and the fractions particulate organic matter (POM), dissolved organic carbon (DOC), organic carbon in sand and stable aggregates (S+A), organic carbon in silt and clay (s+c) and resistant soil organic carbon (rSOC) plus the ratio of carbon in the fine fraction (<63  $\mu\text{m}$ ) and carbon in the coarse fraction (>63  $\mu\text{m}$ )

fractions	CV (inter-laboratory error)			Residual CV (inter-laboratory error)			CV: residual CV		
	A	B	C	A	B	C	A	B	C
F POM	12.9	17.6	13.1	10.4	13.7	17.5	1.2	1.3	0.7
DOC	17.2	33.7	44.9	25.7	14.5	19.7	0.7	2.3	2.3
S+A	126.7	86	58.3	13.1	69.7	11.2	9.6	1.2	5.2
s+c	21.2	17.7	15.8	2.5	2.1	5.7	8.4	8.3	2.8
rSOC 1 g	29.1	41.5	31.1	11	10.8	37.6	2.6	3.8	0.8
C(<63 $\mu\text{m}$ ):C(>63 $\mu\text{m}$ )	48.1	29.4	53.9	7.6	18	8	6.4	1.6	6.8

The largest reproducibility within laboratories was found for the s+c fraction, with a residual CV of 2.5 for site A, 2.1 for site B and 5.7 for site C. This can be explained by the fact that this fraction contains the largest proportion of the total SOC and is thus more robust against losses during fractionation than smaller fractions. Even at site C, which contained only 10.4% clay and silt, 69 $\pm$ 17% of the total SOC was found in the s+c fraction (data not shown). Laboratories 1-5 isolated an s+c fraction of similar size (mg C), whilst laboratory 6 found a significantly smaller s+c fraction for all three soils (Figure C.3). This was different for the rSOC fraction, which was obtained by NaOCl oxidation of 1 g of the s+c fraction. The variability between laboratories was much larger for the rSOC than for the s+c fraction, which indicates that the NaOCl oxidation was more sensitive to bias.

**Modelled and measured SOC pools** The variability of the SOC pool size distributions among the six laboratories and the deviations from the corresponding modelled SOC pool size distribution were large for all three soils (Tables C.3, C.4).

Table C.3: Coefficients of variations (%) among the six laboratories for each pool and site after the mean fractionation results of each laboratory have been converted into RothC pools

Pool	Site A	Site B	Site C
RPM+DPM	10.4	23.5	17.8
HUM+BIO	13.4	14.4	24.2
IOM	48.6	54.7	59.7
Total C	2.6	8.5	21.8

The soil with the smallest variability in the total determined SOC stock with a coefficient of variation of 2.6% was the fine textured, carbon-rich soil from Kungsängen (A). Three of the six

Table C.4: Deviation of each laboratory from the bare fallow simulation initialized with the RothC equilibrium pools for all three soils (% SOC change RothC - % SOC change measured pool) and the residual sum of squares (RSS) for each laboratory and soil

Laboratory	Site A	Site B	Site C	RSS (laboratoires)
1	-6.8	-9.4	-13.7	322
2	-3.9	-4.8	-5.2	65
3	-9.2	-9.3	-21.8	646
4	-3.1	-4.5	-13.7	218
5	-10.4	-9.1	-6.8	472
6	-1.3	-5.1	1.3	29
RSS (soils)	264	327	1163	-

laboratories (2, 4 and 6) measured a similar pool size distribution to that modelled by RothC for site A (Figure C.4a, Table C.4), which is reflected in the bare fallow simulation (Figure C.4b).

Site A lost 40.6% SOC in 40 years with the RothC equilibrium pool size distribution and 36.7, 37.6 and 39.4% SOC using the measured SOC pool size distribution from laboratories 2, 4 and 6. In contrast, with the fractionation data from laboratories 1, 3 and 5, SOC depletions of only 33.8, 31.4 and 30.2% were computed. The greatest variability in the total measured SOC stock among laboratories (21.8%) was observed in the sandy soil at site C (Table C.3). The results of the bare fallow simulation ranged from relative SOC losses of 27.5-50.7%. The average deviation from the bare fallow simulation with the RothC equilibrium pools was also greatest for site C, as revealed by the residual sum of squares, which increased from site A (264) to site B (327) to site C (1163) (Table C.4). The loamy sand (site B) had an intermediate variability in pool size distribution and SOC stock depletion after the bare fallow simulation (Figure C.4, Table C.3). The IOM pool had the largest variability among all pools and in all soils with coefficients of variation of 48.6% (site A), 54.7% (site B) and 59.7% (site C) (Table C.3). Laboratories 1, 3 and 5 measured an up to four times larger IOM pool than predicted by RothC; laboratories 3 and 5 quantified an up to seven times larger IOM pool than predicted by RothC. However, laboratories 2, 4 and 6 were able to match the IOM pool at least for sites A and B (Figure C.4). Laboratory 4 isolated only half of the RothC predicted IOM pool for site B. A systematic deviation from the RothC-predicted pool sizes was found in the RPM and DPM pools, for which all laboratories found smaller pool sizes in all three soils (Figure 4), with laboratory 6 being an exception with site C. This might be explained by the fact that laboratory 6 had a recovery rate of only 57% and that not all fractions were equally affected by C loss. On average, the quantified RPM+DPM pools together were 37% (site A), 45% (site B) and 35% (site C) smaller than the RothC equilibrium pools. This indicates that insufficient POM or DOC was isolated with the existing procedure in order to match the RPM and DPM pools as predicted by RothC (Figure C.4). As a result, all measured pool size distributions, with the exception of laboratory 6 for site C, led to smaller SOC losses with the simulated 40 years of bare fallow than the RothC-derived equilibrium pool size distribution. This was because the amounts of isolated POM or DOC (RPM, DPM) were too small and, the rSOC fraction was mostly too large (IOM). Laboratory 6 was able to match the RothC pools most closely but had a poor carbon recovery rate during the fractionation procedure and in particular for site C (64±9%). Poor recovery rates are indicators of C losses during the fractionation that may lead to strong biases in the results.



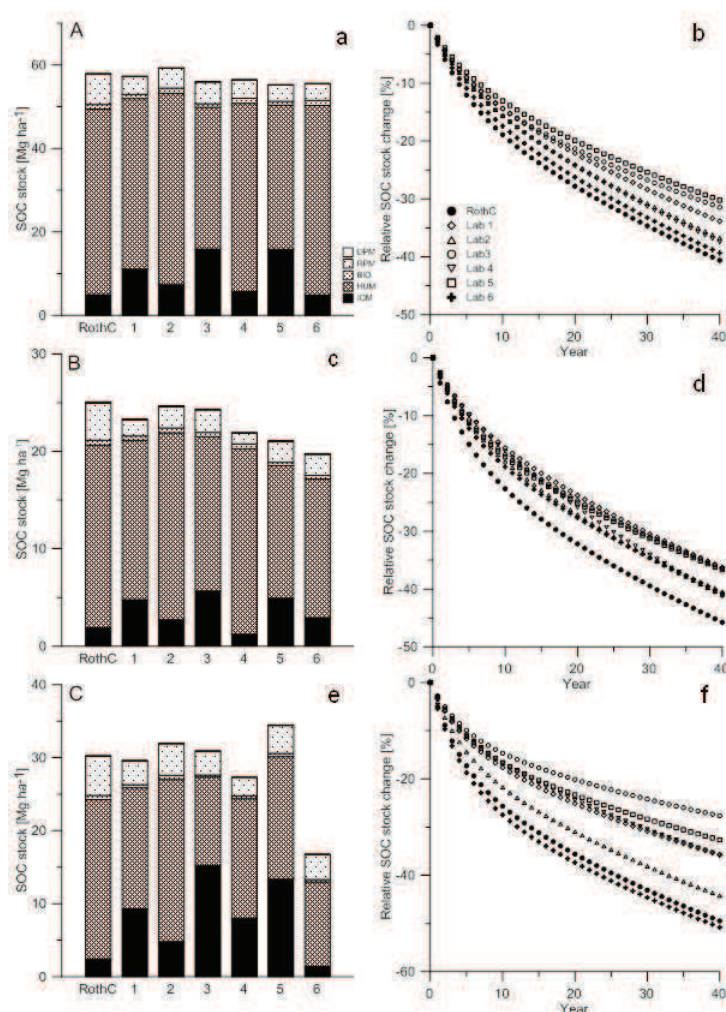


Figure C.4: Modelled and measured pool sizes (a, c, e) and relative SOC stock change after using each pool size distribution to initialize the 40-year bare fallow simulation in RothC (b, d, f) for sites A, B and C.

The mean carbon recovery rate for all laboratories was  $94 \pm 10\%$  and ranged from 93.9 to 102.7% for site A, from 81.3 to 97.4% for site B and from 54.3 to 113.1% for site C.

### Critical work steps *Ultrasonic dispersion.*

Ultrasonic dispersion and wet sieving are the first steps in the fractionation procedure and have thus a major influence on the overall SOC fraction distribution. The ultrasonic dispersion determines the amount of destroyed macroaggregates and thus the quantity of carbon washed into the  $<63 \mu\text{m}$  fractions. The ratio between the quantified s+c and DOC fractions ( $<63 \mu\text{m}$ ) and the S+A and POM fraction together ( $>63 \mu\text{m}$ ) describes the effect of ultrasonic dispersion and wet sieving. We found significant differences in  $C(<63 \mu\text{m}):C(>63 \mu\text{m})$  between laboratories for all three soils (Figure C.3), which identifies the first fractionation steps as being bias-sensitive. The amount of applied ultrasonic power (energy per unit time) varied considerably among laboratories and ranged from 22 to 90W. In the current fractionation protocol, only the amount of

energy was standardized, which allowed each laboratory to modify the amount of power and time. We found significant exponential relationships between the ratio  $C(<63\ \mu\text{m}):C(>63\ \mu\text{m})$  and the amount of ultrasonic power used for all three soils ( $R^2 = 0.43$ ,  $R^2 = 0.61$  and  $R^2 = 0.74$  for soils A, B and C, respectively). The  $<63\ \mu\text{m}$  fractions increased with increasing ultrasonic power (Figure C.5).

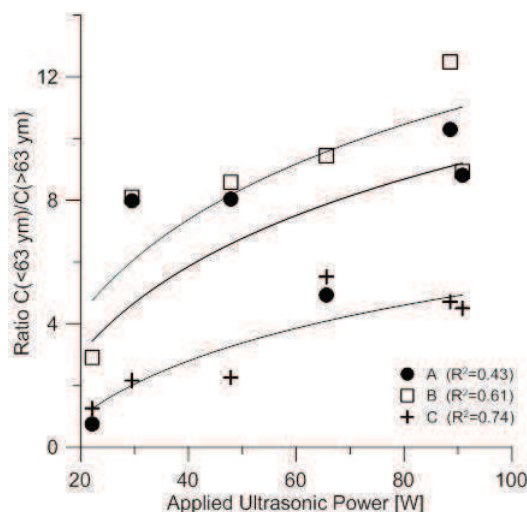


Figure C.5: Ratio of  $C(<63\ \mu\text{m}):C(>63\ \mu\text{m})$  as a function of applied ultrasonic power with exponential fits and  $R^2$  values for each soil.

This was surprising because standardization of ultrasonic dispersion in almost all SOC fractionation protocols is done by means of the applied energy with little attention being paid to the power of the ultrasonic dispenser. However, the importance of the power used is in line with the findings of Raine and So (1997), who quantified significantly more dispersion when greater power was applied but the output energy was kept constant. Aggregate breakdown during ultrasonic dispersion is mainly driven by the stresses caused by cavitation of the fluid (Mayer et al. (2002)). The main factor driving cavitation during ultrasonic dispersion is the acoustic pressure of the ultrasound, which depends on the density of the fluid, the sound velocity in the fluid and the sound vibration velocity amplitude (Kuttruff (1988)). As the amount of water and soil were the same in each laboratory, the acoustic pressure varied as a function of the sound vibration velocity amplitude, which is proportional to the applied power (Mayer et al. (2002)). We suggest that a standardized amount of power should be specified in the protocol to achieve more comparable results. As the laboratory which used the smallest amount of power achieved the best overall fit with the RothC pools (laboratory 6: 22W), we propose that 20W should be used. To obtain the output energy of  $22\ \text{J ml}^{-1}$ , the dispersion time would be 177 s for a volume of 161 ml (150 ml water and 30 g of soil with an assumed density of  $2.65\ \text{g cm}^{-3}$ ).

#### *Wet sieving.*

In the original protocol, Zimmermann et al. (2007) proposed that the samples should be flushed during wet sieving until the rinse water is clear. This, however, led to very different amounts of water that were used in our ring trial, ranging from 533 to 8500 ml to flush the same sample. The amount of water used was exponentially correlated with the size of the DOC fraction, with the greatest increase occurring at less than 2000 ml (Figure C.6).

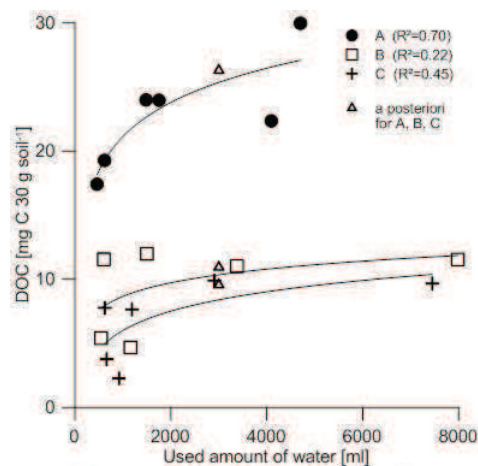


Figure C.6: Mean amount of DOC extracted as a function of the amount of water used during wet sieving.

The a posteriori test, which was conducted with 3000 ml of water, confirmed that the fitted exponential model is a valid predictor of the amount of DOC. When more than 2000 ml of water was used to flush the samples no significant influence of the amount of water on the amount of DOC could be observed. To exclude this source of variation, we therefore suggest using 2000 ml as a minimum amount of water to flush the sample. Zimmermann et al. (2007) filtered the suspension through a  $0.45 \mu\text{m}$  membrane filter to obtain the DOC fraction. We observed that filtering the suspension is, however, very time consuming, which led to the widespread use of centrifuging and decanting of the liquid before filtering. When 3000 ml of water was used for wet sieving, 10 minutes of centrifugation at 2000 g apparently sufficed to separate the solid and the liquid phase.

#### *Density fractionation.*

The comparison of modelled and laboratory-derived pool size distributions revealed that the RPM and DPM pools, which are calculated from the DOC and POM fractions, were underestimated by all laboratories (Figure C.4). This is in line with the finding of Zimmermann et al. (2007), who found the quantified pools to be systematically smaller than the modelled ones. They proposed that the density of SPT be increased to  $2.0\text{--}2.2 \text{ g cm}^{-3}$ ; however, this is not yet in widespread practice. To our best knowledge in both published (Dondini et al. (2009a); Leifeld et al. (2009a); Xu et al. (2011); Poeplau and Don (2013a)) and unpublished work, the density of  $1.8 \text{ g cm}^{-3}$  has been used. Additionally, Xu et al. (2011) could not confirm this systematic deviation, but found a large scatter of modelled compared with measured DPM and RPM pools. We therefore decided to maintain this density for the ring trial. However, a posteriori we tested whether an increased density of the SPT solution would lead to a better match of modelled and laboratory-determined RPM and DPM pools. Even with a density of  $2.2 \text{ g cm}^{-3}$  we isolated only 15% (A), 49% (B) and 20% (C) more POM than with a density of  $1.8 \text{ g cm}^{-3}$ ; an increase of 84% (A), 144% (B) and 69% (C) would have been needed to match the labile modelled pools (Figure C.7).

We therefore tested whether the amount of DOC could be increased by hot water extraction (Landgraf et al. (2006)) of the suspended sample before wet sieving: this increased the amount of DOC by a factor of 1.6, 1.8 and 1.9 for soils A, B and C, respectively. Summing the increased

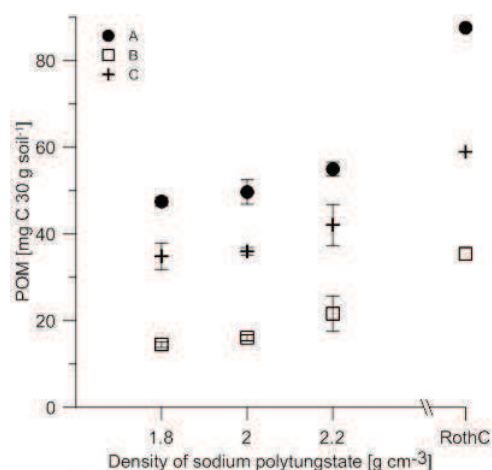


Figure C.7: Size of the POM fraction obtained using different densities of sodium polytungstate compared with the fraction size, which should be obtained to match the RPM and DPM pools estimated by RothC.

amount of POM achieved with an SPT density of  $2.2 \text{ g cm}^{-3}$  and the hot-water extracted amount of DOC, leads to a total proportion of 88% (A), 85% (B) and 90% (C) of the modelled RPM and DPM pools. It is likely that the hot water extraction would have decreased the amount of isolated POM if both steps had been conducted on the same set of samples. Therefore, we do not see a possibility of adjusting the protocol in order to match the RPM and DPM pools with POM and DOC. Moreover, Shaymukhametov et al. (1984) characterized the SOC in different density fractions and found that the SOC (density below  $1.8\text{--}2.0 \text{ g cm}^{-3}$ ) consisted of slightly decomposed macro-organic matter of plant and animal origins with little mineral content, the SOC (density between  $2.0$  and  $2.4 \text{ g cm}^{-3}$ ) consisted of organo-clay complexes and the heavy fraction (density  $<2.4 \text{ g cm}^{-3}$ ) consisted of sand grains coated with SOC. Sollins et al. (2006) determined a mean residence time of 210 years for SOC separated with a density of  $2.0\text{--}2.28 \text{ g cm}^{-3}$  in a forest soil. Thus, even though an increased density does increase the amount of isolated POM and therefore comes empirically closer to the RPM and DPM pools of RothC, it is doubtful whether a fraction obtained with a density of  $2.2 \text{ g cm}^{-3}$  or greater would resemble the functional role of the labile RPM and DPM pools. We suggest that a density of  $2.0 \text{ g cm}^{-3}$  should be used and that the sample should not be hot-water extracted.

#### *NaOCl oxidation.*

The IOM pool had the largest variability between laboratories among all quantified pools and only three out of six laboratories were able to isolate a fraction size that was comparable to the RothC-predicted pool (Figure C.4, Table C.3). As chloride in the NaOCl solution is volatile, the oxidation efficiency decreases with time and is dependent on temperature during storage. We therefore recommend that fresh NaOCl solution in which the Cl concentration is known is used or that the Cl concentration is determined immediately before the solution is used for oxidation. We tested a posteriori whether the differences between laboratories could be explained by different concentrations of Cl in the NaOCl solution (Figure C.8). All three soils had a relatively smaller sensitivity to different Cl concentrations than the variability between laboratories, indicating that differences in Cl can only partly explain the observed variability. Moreover, we found a significant positive correlation between the  $C(<63 \mu\text{m}):C(>63 \mu\text{m})$  ratio and the proportion of



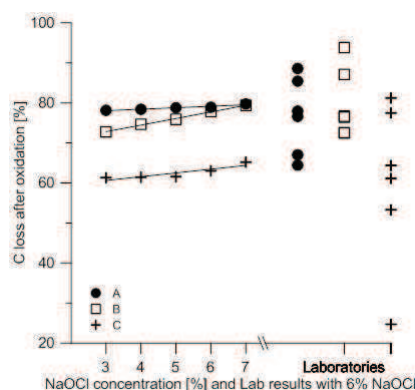


Figure C.8: Carbon loss after oxidation as a function of NaOCl concentration and the results from the laboratories using a NaOCl concentration at 6% as a comparison.

oxidizable carbon in the s+c fraction ( $r=0.43$ , data not shown). This indicates that quality and quantity of SOC in the s+c fraction is again determined by ultrasonic dispersion through the breakdown of macroaggregates and thus the release of occluded carbon. The better the dispersion efficiency of the ultrasonic dispersion, the more potentially labile SOC is found in the s+c fraction and thus the more oxidizing agent is needed to isolate the same amount of rSOC. This hypothesis is in line with the findings of Siregar et al. (2005), who treated 12 different soils with NaOCl and determined an oxidation efficiency range from 12 to 72%, which was negatively correlated with the clay content of the soils ( $r = 0.45$ ). Similarly, Kleber et al. (2005) explain the same results with either a varying degree of recalcitrance of SOM or a different degree of protection exerted by the soil matrix. Thus, the oxidation efficiency is strongly dependent on the quality of the organic matter present. Furthermore, the differences among laboratories in the size of the s+c fraction, which is again determined by ultrasonic dispersion, potentially contribute to explaining the variability in the size of the rSOC fraction. The oxidation is conducted with 1 g of the sample but the fraction size is determined by multiplying the resistant C in 1 g with the total amount (g) of s+c. The variability of the total amount of s+c material thus contributed about one-third of the coefficient of variation for the rSOC fraction. This stresses the need for an improved standardized ultrasonic procedure. Another possible source of the large laboratory bias could be the different intensities of shaking the sample after the addition of fresh NaOCl. To ensure a complete oxidation of the oxidizable C in the soil sample, the sedimented soil a posteriori in the vessel must be brought fully in suspension; ideally, a vortex mixer should be used. We did not test this in the current study.

#### *The role of the S+A fraction.*

The SOC in the S+A fraction is probably the most heterogeneous SOC fraction in terms of composition and stability. It comprises POM  $>0.63 \mu\text{m}$ , which is visually detectable, occluded POM in aggregates with different cohesive strength, and also SOC in clay-sized organo-mineral particles within these aggregates and as coatings on sand grains (which might have a long turnover time) (Shaymukhametov et al. (1984)). This, however, contradicts the perception that SOC fractions should ideally be unique and non-composite in order to match model pools (Smith et al. (2002a)). Zimmermann et al. (2007) considered the S+A fraction to be physically stabilized and thus slower cycling than the labile fractions of DOC and POM. However, recent work has shown that the S+A fraction had a larger or only slightly smaller sensitivity to land-use change

than DOC (Poeplau and Don (2013a)). Dondini et al. (2009a) observed a larger proportion of C4-derived carbon in the S+A fraction than in the POM fraction 14 years after a C3-C4 vegetation change. This indicates that this fraction would contain a larger proportion of ‘fresh’ SOC than of stabilized SOC. In contrast, Leifeld and Fuhrer (2009) calculated mean residence times (MRTs) of >100 years for the S+A fraction, while the POM fraction was not older than 5 and 7 years in the upper 4 cm of a subalpine pasture and meadow, respectively. This, however, does not exclude the possibility that the S+A fraction consists of old SOC, but also a substantial amount of fresh SOC. We therefore calculated the RPM and DPM pools by adding S+A to the POM and DOC fractions to test this. Thirteen of 18 recalculated measurements (six laboratories and three soils) achieved a better match with the RPM and DPM pools than with the proposed calculation with only POM and DOC (Table C.5).

Table C.5: Mean deviations of the quantified POM+DOC and POM+DOC+S+A fractions from the RothC equilibrium RPM+DPM pools ( $\text{MgC ha}^{-1}$ ) for all three soils

Laboratory	A		B		C	
	POM+ DOC	POM+ DOC+ S+A	POM+ DOC	POM+ DOC+ S+A	POM+ DOC	POM+ DOC+ S+A
1	-2.98	-0.35	-2.05	0.32	-2.04	-0.97
2	-2.44	1.2	-1.01	5.24	-1.53	-0.21
3	-2.09	0.38	-2.06	5.22	-1.37	-0.14
4	-2.83	-0.72	-2.83	-0.39	-2.61	-1.73
5	-3.31	3.28	-1.45	0.56	-1.55	-0.67
6	-3.2	27	-1.94	5.5	-1.68	2

Eight of these 13 recalculated measurements with POM, DOC and S+A were still less than the RPM and DPM pools from RothC. Laboratory 6, which used the smallest amount of ultrasonic power and thus isolated the largest S+A fraction, would over-estimate the RPM+DPM fractions when S+A is included. In contrast, laboratory 1, which used the greatest amount of ultrasonic power, would achieve a better match with the RPM+DPM pools for all three soils if the S+A fraction was included (Table C.5). To maintain the current concept of the fractionation method, we therefore suggest that a small amount of ultrasonic power (20W) is used. However, to identify the functional role of the S+A fraction, as well as that of all other fractions, the mean residence time (MRT) of each fraction should be investigated by using repeated  $^{14}\text{C}$  measurements (Baisden et al. (2012)). Only this information would permit us to validate a mechanistic framework for the existing fractionation procedure, which is currently based only on conceptual considerations and empirical relations of measured fraction sizes and the modelled pools. Even so, a perfect fit of fractions and conceptual pools will not be achievable because the nature of SOC is a continuum rather than consisting of distinct pools. In the specific case of RothC this is especially true for the IOM pool, which is estimated using the Falloon equation (Falloon et al. (1998)), while the actual size of IOM in a specific soil or even the existence of such a pool remains very uncertain. Fractionation, as well as modelling with different functional pools, will thus remain an approximation.

## C.4 Conclusion

The conducted ring trial revealed that the fraction procedure described by Zimmermann et al. (2007) was not described precisely enough and led to individual laboratory-specific adjustments and thus significantly different results for three different soils and all fractions. The amount of applied ultrasonic power during ultrasonic dispersion as the first step of the fractionation

scheme strongly drives the disruption of aggregates and thus influences the quality and size of all fractions. We thus suggest standardizing not only the ultrasonic energy, but also the ultrasonic power (20W). The amount of isolated DOC is a function of the amount of water used for wet sieving, which demands a minimum amount of water (2000 mL) to be used. Calculating the distribution of SOC over pools of the RothC biogeochemical model led systematically to a stronger allocation of SOC to stable model pools than with the RothC model's equilibrium pool size distributions. Neither increasing the density of the SPT solution for density fractionation, nor increasing the concentration of NaOCl for isolating the rSOC fraction, could solve this entirely. Moreover, a substantial part of the S+A fraction might be young and fast cycling material, contrary to the original concept that this fraction coincides with a relatively stable SOM pool. This hypothesis needs to be further tested and possibly an additional fractionation step would be required to split the S+A fraction into a young component, which adds to the RPM and DPM pools in the RothC model, and an old part, which would actually relate to the turnover of the HUM pool. However, to achieve more comparable results between laboratories and to achieve a better fit with RothC-predicted pools by maintaining the current conceptual framework of this soil carbon fractionation method, we suggest an improved fraction protocol (see File S1).

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