Analysis of heterotrophic respiration response to soil temperature and moisture: experiments and modelling

Inaugural-Dissertation
zur
Erlangung des Grades

Doktor der Agrarwissenschaften
(Dr. agr.)

der
Hohen Landwirtschaftlichen Fakultät
der
Rheinischen Friedrich-Wilhelms-Universität
zu Bonn

vorgelegt im
März 2009
von
Jana Bauer
aus
Leisnig

Referent: Prof. Dr. H. Vereecken
Korreferent: Prof. Dr. H. Goldbach

Tag der mündlichen Prüfung: 03.07.2009
Gedruckt bei: Graphische Betriebe, Forschungszentrum Jülich
Erscheinungsjahr: 2009
Diese Dissertation ist auf dem Hochschulschriftenserver der ULB Bonn
http://hss.ulb.uni-bonn.de/diss online elektronisch publiziert.

Abstract

The temperature and moisture response of heterotrophic soil respiration are crucial for a reliable prediction of carbon dynamics with respect to climatic changes. However, despite numerous studies there are many controversies and open questions.

One objective of this thesis was to analyse the influence of different soil temperature and moisture response functions on the prediction of CO_2 production and effluxes. For this purpose, soil temperature and moisture reduction functions of six soil carbon decomposition models (CANDY, CENTURY, DAISY, PATCIS, RothC, and SOILCO2) were implemented in the SOILCO2/RothC model. As a test scenario, a respiration experiment on a silt loam in Columbia (USA) was chosen. The cumulative CO_2 fluxes simulated with different temperature reduction functions showed deviations up to 41% (1.77 t C ha^{-1}) for a six-month period in 1981. The influence of moisture reduction was smaller with deviations up to 2% (0.10 t C ha^{-1}). The functional sensitivity study showed that the choice of the soil temperature and soil moisture reduction function is a crucial factor for a reliable prediction of carbon turnover.

Most multi-pool models describe the temperature dependence of carbon decomposition by a response function which uniformly scales the decomposition constants of all carbon pools. However, it is not clear whether the temperature response does, indeed, conform to such a simple formulation. Therefore, a wheat decomposition experiment under six different temperatures (5°C, 9°C, 15°C, 25°C, 35°C, and 45°C) was performed and the cumulative CO_2 development over time was analyzed. Data were interpreted by assuming that litter could be sub-divided into two pools, a labile and a more recalcitrant one, that would each decay exponentially. The observed patterns of carbon loss were poorly described if the same relative temperature response functions for the decomposition of both pools was used and the same chemical recalcitrance (expressed as the ratio of labile and recalcitrant pool sizes) at all temperatures was assumed. Data prediction could be significantly improved by using different temperature response functions for the decomposition of the two different organic-matter fractions. Even better data prediction could be achieved by assuming that chemical recalcitrance varied with temperature. These findings thus suggest that the temperature dependence of organic matter decomposition cannot be fully described with the simple approaches usually employed in most laboratory experiments and modelling approaches, but that a more complicated interplay between the temperature dependence of decomposition rates and temperature effects on the chemical recalcitrance of different organic matter fractions exists.

The classical approach for the *in situ* determination of the temperature response (Q_{10} or activation energy) from a linear regression between log-transformed CO_2 fluxes and temperatures measured at predefined soil depths has been criticised for neglecting confounding factors as spatial and temporal changes in soil water content and soil organic matter quality and quantity. On the other hand, the derived temperature response is not unambiguous but depends on the depth of temperature measurement. To overcome both problems, we determined temperature and water content response equations of soil heterotrophic respiration by means of inverse parameter estimation using a 1-dimensional CO_2 transport and carbon turnover model. Analysis of different formulations of temperature response resulted in estimated response factors that hardly deviated over the entire range of soil water contents and for temperatures < 25°C. For higher temperatures the temperature response was highly uncertain due to the infrequent occurrence of soil temperatures > 25°C.

As an overall finding of all three studies, we can conclude that inverse parameter estimation using either conceptual or numerical models is a promising tool for a reliable determination of the temperature and water response of heterotrophic soil respiration.

Kurzfassung

Die Temperatur- und Feuchteabhängigkeit der heterotrophen Bodenrespiration sind wesentliche Kenngrößen für eine zuverlässige Vorhersage der Kohlenstoffdynamik unter verändernden Klimabedingungen. Trotz zahlreicher Studien bestehen jedoch immer noch viele Unstimmigkeiten und offene Fragen.

Ein Ziel dieser Arbeit bestand darin, den Einfluss verschiedener Temperatur- und Feuchteabhängigkeitsfunktionen auf die Modellvorhersage der CO_2-Bildung und der CO_2-Flüsse zu untersuchen. Dafür wurden Temperatur- und Feuchteabhängigkeitsfunktionen aus sechs Modellen für den Abbau von organischem Kohlenstoff im Boden in das SOILCO2/RothC-Modell implementiert. Als Testszenario wurden Daten eines Respirationsexperiments auf einem schluffigen Lehm in Columbia (USA) verwendet. Die modellierten kumulativen CO_2-Flüsse, die unter Verwendung verschiedener Temperaturabhängigkeitsfunktionen berechnet wurden, wichen für den sechsmonatigen Beobachtungszeitraum im Jahre 1981 um bis zu 41% (1.77 t C ha^{-1}) voneinander ab. Der Einfluss der Feuchteabhängigkeitsfunktionen ergab geringere Abweichungen bis zu 2% (0.10 t C ha^{-1}). Diese Ergebnisse zeigen, dass die Wahl der Temperatur- und Feuchteabhängigkeitsfunktionen sehr wichtig für eine zuverlässige Vorhersage des Kohlenstoffumsatzes im Boden ist.

In den meisten Multi-Pool-Modellen wird die Temperaturabhängigkeit des Kohlenstoffabbaus durch eine Abhängigkeitsfunktion beschrieben, die die Abbaukonstanten aller Kohlenstoff-Pools gemeinsam skaliert. Dabei ist es jedoch noch nicht eindeutig geklärt, ob die Temperaturabhängigkeit tatsächlich einen solch einfachen Zusammenhang widerspiegelt. In dieser Arbeit wurde daher ein Abbauexperiment mit Weizenrückständen durchgeführt und die zeitliche Entwicklung der CO_2-Flüsse unter sechs verschiedenen Temperaturenszenarien (5°C, 9°C, 15°C, 25°C, 35°C und 45°C) analysiert. Für die Datenanalyse wurde angenommen, dass sich die Weizenrückstände aus zwei Pools zusammensetzen, einem labilen und einem abbauresistenteren Pool, die beide einem exponentiellen Abbau unterliegen. Die beobachteten CO_2-Flüsse konnten jedoch nicht zufriedenstellend beschrieben werden, wenn die gleiche Temperaturabhängigkeit für den Abbau beider Pools und die gleiche chemische

Abbaubarkeit (konstantes Verhältnis des labilen und abbauresistenteren Pools) angenommen wurden. Durch die Verwendung verschiedener Temperaturabhängigkeiten für den Abbau beider Pools konnte die Vorhersage der Messwerte jedoch deutlich verbessert werden. Eine noch deutlichere Verbesserung wurde durch die Annahme erzielt, dass die chemische Abbaubarkeit ebenfalls temperaturabhängig ist. Die Ergebnisse zeigten, dass die Temperaturabhängigkeit des Abbaus der organischen Bodensubstanz nicht vollständig durch die einfachen Ansätze beschrieben werden kann, die üblicherweise in konzeptionellen oder numerischen Modellen verwendet werden, sondern dass es eine kompliziertere Wechselwirkung zwischen der Temperaturabhängigkeit der Abbauraten und Temperatureffekten auf die chemische Abbaubarkeit verschiedener Fraktionen der organischen Bodensubstanz gibt.

Der klassische Ansatz für die *in situ*-Bestimmung der Temperaturabhängigkeit (Q_{10}-Wert oder Aktivierungsenergie) anhand einer linearen Regression von log-transformierten CO_2-Flüssen und Temperaturmessungen in einer bestimmten Bodentiefe wurde in der Literatur bereits kritisiert, da dieses Vorgehen weitere Einflussgrößen wie z.B. die räumliche und zeitliche Veränderung des Bodenwasserhalts und der organischen Bodensubstanz nicht berücksichtigt. Außerdem ist die ermittelte Temperaturabhängigkeit nicht eindeutig, da sie von der gewählten Messtiefe der Bodentemperatur abhängig ist. Um beide genannten Probleme zu umgehen, wurden die Parameter der Temperatur- und Feuchteabhängigkeitsfunktionen der heterotrophen Bodenrespiration unter Verwendung eines 1-dimensionalen numerischen Modells für den CO_2-Transport und den Kohlenstoffabbau gemeinsam invers geschätzt. Die Verwendung verschiedener Temperaturabhängigkeitsfunktionen ergab Skalierungsfaktoren, die über den gesamten Feuchtebereich und für Temperaturen kleiner 25°C kaum Abweichungen aufwiesen. Für höhere Temperaturen war die Temperaturabhängigkeit sehr unsicher auf Grund des seltenen Auftretens von Bodentemperaturen oberhalb von 25°C. Die inverse Parameterschätzung unter Verwendung numerischer Modelle ist ein vielversprechendes Werkzeug für die zuverlässige Bestimmung der Temperatur- und Feuchteabhängigkeit der heterotrophen Bodenrespiration.

Contents

List of figures

List of tables

Abbreviations and symbols

Abbreviations

Abbreviation	Description
BC	Black carbon
BIO	Microbial biomass
DPM	Decomposable plant material
GPP	Gross primary production
HUM	Humified organic matter
IOM	Inert organic matter
IPCC	Intergovernmental channel on climate change
NEP	Net ecosystem production
NPP	Net primary production
PET	Potential evapotranspiration
POM	Particulate organic matter
ppm	Parts per million
PPT	Sum of stored water and precipitation
ppt	Parts per trillion
RPM	Resistant plant material
SOC	Soil organic carbon
SOM	Soil organic matter

Symbols

Symbol	Dimensions	Description
A	[M T^{-1}]	Addition rate
a	[L^{-1}]	Depth distribution parameter
a_1	[-]	Empirical parameter of temperature response equation according to O'Connell (1990)
a_2	[-]	Empirical parameter of temperature response equation according to Parton et al. (1987)
AIC		Akaike information criterion
AIC_c		Corrected Akaike information criterion
a_{PAT}	[-]	Parameter defining the maximal increase in the rate of soil decomposition with soil moisture
a_W	[-]	Empirical parameter of water response equation
a_x	[-]	Empirical constant of temperature response function for the initial pool ratio
b_1	[-]	Empirical parameter of temperature response equation according to O'Connell (1990)
B_1	[W L^{-1} K^{-1}]	Empirical constant of soil thermal conductivity function
b_2	[-]	Empirical parameter of temperature response equation according to Parton et al. (1987)
B_2	[W L^{-1} K^{-1}]	Empirical constant of soil thermal conductivity function
B_3	[W L^{-1} K^{-1}]	Empirical constant of soil thermal conductivity function
b_x	[-]	Empirical constant of temperature response function for the initial pool ratio
b_W	[-]	Empirical parameters of water response equation
C	[M T^{-2} L^{-1} K^{-1}]	Volumetric heat capacity of the porous medium
c_2	[-]	Empirical parameter of temperature response equation according to Parton et al. (1987)
c_a	[L^3 L^{-3}]	CO_2 content in the gas phase
c_p	[M C L^{-3}]	Pool concentration
c_{PAT}	[-]	Integration constant
c_{SC}	[M]	Amount of soil carbon

Symbol	Dimensions	Description
c_T	$[L^3\ L^{-3}]$	Total volumetric concentration of CO_2
C_w	$[M\ T^{-2}\ L^{-1}\ K^{-1}]$	Volumetric heat capacity of the liquid phase
c_w	$[L^3\ L^{-3}]$	CO_2 concentration in the liquid phase
c_x	[-]	Empirical constant of temperature response function for the initial pool ratio
d_2	[-]	Empirical parameter of temperature response equation according to Parton et al. (1987)
E	$[M\ L^2\ T^{-2}\ n^{-1}]$	Activation energy
e_2	[-]	Empirical parameter of temperature response equation according to Parton et al. (1987)
E_P	[L]	Potential evaporation
f_a	[-]	Response factor for aeration
f_m	[-]	Scaling factor for the decomposition constants
f_{MO}	[-]	Multiplicative factor
f_T	[-]	Response factor for soil temperature
f_W	[-]	Response factor for soil moisture
h	[L]	Water pressure head
h_2	[L]	Pressure head when CO_2 production is optimal
h_3	[L]	Pressure head when CO_2 production ceases
h_{50}	[L]	Pressure head at which the water extraction rate is reduced by 50%
i, j		Running indices
J_{ca}	$[L\ T^{-1}]$	CO_2 flux caused by convection in the gas phase
J_{cw}	$[L\ T^{-1}]$	CO_2 flux caused by convection in the dissolved phase
J_{da}	$[L\ T^{-1}]$	CO_2 flux caused by diffusion in the gas phase
J_{dw}	$[L\ T^{-1}]$	CO_2 flux caused by dispersion in the dissolved phase
J_w	$[L\ T^{-1}]$	Water flux density
K	$[L\ T^{-1}]$	Unsaturated hydraulic conductivity
K^*_M	$[L^3\ L^{-3}]$	Michaelis constant for the CO_2 content
K_s	$[L\ T^{-1}]$	Saturated hydraulic conductivity
l	$[M\ L\ T^{-3}\ K^{-1}]$	Thermal conductivity of the soil
L_{In}	$[M\ M^{-1}]$	Lignin concentration

Symbol	Dimensions	Description
m	[-]	Shape parameter of the Mualem van Genuchten equation
M	[-]	Number of fitted parameters
MAE		Mean absolute error
ME		Model efficiency
$MSSR$		Mean sum of squared residuals
n	[-]	Shape parameter of the Mualem van Genuchten equation
N	[-]	Number of measurements
N_{In}	[M M^{-1}]	Nitrogen concentration
P	[L]	Precipitation
PET	[L]	Potential evapotranspiration
p_{MO}	[-]	Relative size of the pool of micro-organisms
PPT	[L]	Sum of stored water and precipitation
PV	[L^3 L^{-3}]	Pore volume
Q	[L^3 L^{-3} T^{-1}]	Source/sink term
Q_{10}	[-]	Factor for which the decomposition rate increases for a temperature increment of 10 K
R	[M L^2 T^{-2} K^{-1} n^{-1}]	Universal gas constant (8.314 kg m^2 s^{-2} K^{-1} mol^{-1})
R^2		Coefficient of determination
S	[L^3 L^{-3} T^{-1}]	CO_2 production/sink term
s_1		Slope of the linear regression
S_e	[-]	Relative water saturation
SSR		Sum of squared residuals
t	[T]	Time
T	[K]	Temperature
T_{atm}	[K]	Atmospheric temperature
T_{opt}	[K]	Optimum temperature
T_{ref}	[K]	Reference temperature
$TSMD_{acc}$	[L^3 L^{-2}]	Accumulated topsoil moisture deficit
$TSMD_{max}$	[L^3 L^{-2}]	Maximum topsoil moisture deficit
T_{surf}	[K]	Surface temperatures
x_1	[M C M C^{-1}]	Initial proportion of the labile pool

Symbol	Dimensions	Description
x_{ML}	[-]	Partitioning factor between metabolic litter and structural litter
y_{obs}		Observed data
$\overline{y_{obs}}$		Mean value of the observed data
y_{sim}		Simulated data
$\overline{y_{sim}}$		Mean value of simulated data
z	[L]	Soil depth
Δt	[T]	Time step
α	$[L^{-1}]$	Inverse of the bubbling pressure
β	$[T^{-1}]$	Constant of the Arrhenius equation
γ_p	$[L^3 L^{-3} T^{-1}]$	CO_2 production by plant roots
γ_s	$[L^3 L^{-3} T^{-1}]$	CO_2 production by soil microbes
λ	$[T^{-1}]$	Decomposition rate
λ_0	$[T^{-1}]$	Decomposition constants, which are valid for optimal conditions of soil moisture and aeration and a reference temperature
θ	$[L^3 L^{-3}]$	Volumetric water content
θ_{opt}	$[L^3 L^{-3}]$	Optimal water content
θ_r	$[L^3 L^{-3}]$	Residual water content
θ_s	$[L^3 L^{-3}]$	Saturated water content

1 General introduction

1.1 Global climate change

Global climate protection is one of the most important and challenging tasks of the 21st century (e.g. Lackner, 2003; Pacala and Socolow, 2004). Human activities have markedly increased the global atmospheric concentrations of the greenhouse gases carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_20) since 1750 (IPCC, 2007a; WMO, 2008). The atmospheric concentration of CO_2 as the most important anthropogenic greenhouse gas has increased from the pre-industrial value of 280 ppm to 383 ppm in 2007 (WMO, 2008). This concentration is significantly higher than the atmospheric CO_2 concentrations of the last 650,000 years which have been determined from ice-cores and varied between 180 and 300 ppm (IPCC, 2007a).

The increase of greenhouse gases, especially of CO_2, strongly affects the earth climate and the various compartments of the earth system. During the 100 years from 1906-2005 the global surface temperatures increased by 0.56 to 0.92°C. Furthermore, changes of local precipitation amounts have been observed. For example, precipitation increased significantly in eastern parts of North and South America, northern Europe, and northern and central Asia. In contrast, precipitation decreased in the Sahel, the Mediterranean, southern Africa, and parts of southern Asia. Extreme weather events have likely changed in frequency and/or intensity, e.g. the frequency of heavy precipitation events increased over most areas (IPCC, 2007a).

In order to counteract global climate changes, the Kyoto protocol was passed at the third United Nations climate change conference in 1997. The participating states stipulated the reduction of relevant greenhouse gas emission within a given time frame, whereby the industrial countries committed to reduce the emission by 5% from 2008 to 2012 compared to 1990. To develop effective strategies for the reduction of greenhouse gas emissions the main sources and pathways of greenhouse gases must be determined. Therefore, exact knowledge about the global carbon cycling is necessary.

1.2 The global carbon cycle

The atmosphere contains ~800 Gt carbon, and is therefore, one of the smallest carbon reservoirs. In comparison, the oceans contain ~39,000 Gt C. Soils, vegetation, and detritus store ~2,000 Gt C (Figure 1.1) (Oelkers and Cole, 2008). The single carbon reservoirs exchange huge amounts of carbon, whereby the exchange rate between the atmosphere and the surface ocean is 90 Gt C y^{-1} and between atmosphere and vegetation is estimated to be 110 Gt C y^{-1} (Houghton, 2007). Nowadays, the increase of CO_2 in the atmosphere can be clearly related to anthropogenic emissions of CO_2 while fossil fuel burning, deforestation, and land use changes are the main sources. Present carbon fluxes from fossil fuel combustion and deforestation are estimated to account for 8.4 Gt C y^{-1} and ~ 1.5 Gt C y^{-1}, respectively (WMO, 2008). The rate of atmospheric CO_2 increase is less than the rate of CO_2 emissions since a part of the emitted CO_2 dissolves in the oceans or is taken up by terrestrial ecosystems.

Within the global carbon cycle soils are an important carbon reservoir. The top metre of the worlds soils contain twice as much carbon as currently present in the atmosphere (e.g. Adams et al., 1990; Anderson, 1992; Batjes, 1996; Jobbagy and Jackson, 2000). Due to the large amount of organic carbon stored in soils even small relative changes could significantly change the concentration of greenhouse gases in the atmosphere (Kirschbaum, 2000).

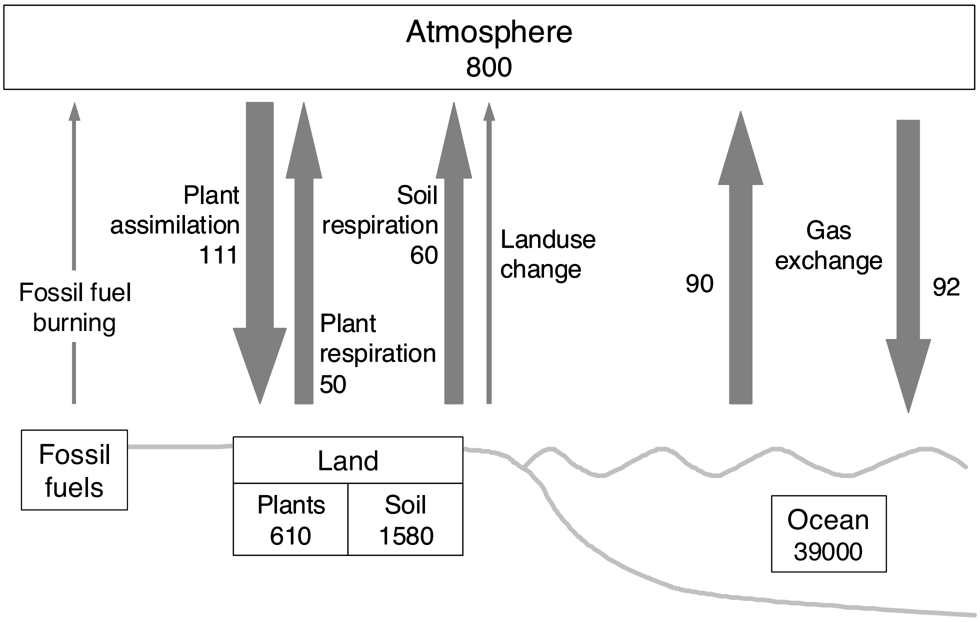

Figure 1.1: Simplistic schematic diagram of the global carbon cycle. Masses of the reservoirs are reported in [Gt C] and fluxes in [Gt C y^{-1}] (modified from Oelkers and Cole, 2008).

The terrestrial carbon cycle

Atmospheric carbon enters the biosphere by diffusion of CO_2 into plants where one part is converted to carbohydrates during photosynthesis (gross primary production, GPP, Figure 1.2). About half of this 'fixed' carbon is incorporated into new plant tissues and the other half is released back to the atmosphere by autotrophic respiration (net primary production, NPP). Finally, carbon is transferred to the soil by litter fall, root turn-over, or dead plants and animals. The fresh organic material entering the soil is the substrate for the formation of soil organic matter (SOM). To close the cycle soil carbon will return to the atmosphere as CO_2 or CH_4 by SOM decomposition referred to as heterotrophic respiration. In general, SOM consists of a great spectrum of organic substances. These compounds possess different mean turnover times due to different complexity. The decomposability of soil organic substances is furthermore determined by their bioavailability. Organic substances may be less available due to physical or chemical protection. While physical protection means e.g. the stabilization of organic substances in soil aggregates, organic substances are chemically protected by adsorption onto mineral surfaces (Oades, 1988).

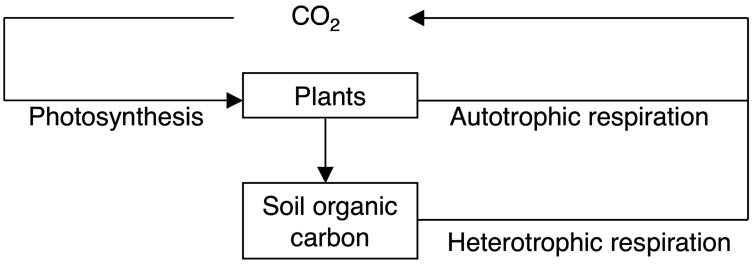

Figure 1.2: Terrestrial carbon processes.

Photosynthesis, as well as autotrophic and heterotrophic respiration are affected by solar radiation, temperature, and water availability. If soils will act as carbon sources or sinks therefore depends on the responses of SOM decomposition and NPP to climate change. Carbon is lost from the soil if decomposition is more enhanced than NPP and vice versa. As already noted, a decrease of soil organic carbon would constitute a positive feed back on global climate change. Besides climate atmospheric CO_2 concentration is another important factor. Increasing CO_2 concentrations enhance photosynthesis and water use efficiency (e.g. Garcia et al., 1998; Conley et al., 2001), and therefore, elevate NPP. Furthermore, net carbon loss or storage from soils is affected by land use changes and management practices (IPCC, 2001).

1.3 Carbon sequestration

Carbon sequestration refers to the transfer of atmospheric CO_2 into long-lived carbon reservoirs (Lal, 2008). Besides the idea of injection of CO_2 into geological formations (Holloway, 2001; Friedmann, 2007; Benson and Cole, 2008) and deep ocean layers (Adams and Caldeira, 2008) natural processes can be used to sequester CO_2 in biotic and pedologic pools. Historically, the conversion of large areas of native ecosystems to agricultural land resulted in a strong net loss of soil carbon (e.g. Paustian et al., 1997; Schlesinger, 1999), whereby these anthropogenic impacts can be traced back until the late stone age 8000 to 6000 years ago (Ruddiman, 2003). As a consequence of the strong carbon depletion, agricultural soils are a potential carbon sink, and are therefore, of special interest in the framework of climate protection. Even though the global mitigation potential of carbon sequestration in agricultural soils is limited to a period of 50 – 100 years and only accounts for 3-6% of total C-emissions from fossil fuels, it plays an important role within an overall mitigation concept of short-term atmospheric CO_2 increases (Paustian et al., 1997). Sequestration of carbon in agricultural soils requires appropriate management strategies. Sequestration strategies are e.g. reduced soil tillage, improved rotations, and conversion to grass and woodland (Lal, 2004; Smith, 2004). The efficiency of the single methods however depends on local climatic and soil conditions. To support which mitigation strategies are most effective for carbon sequestration under changing environmental conditions for the various local ecosystems model predictions are an important tool (e.g. Paustian et al., 1992; Lugato and Berti, 2008).

1.4 Simulation of SOM turnover

Many different model approaches have been developed to describe SOM turnover. One of the first steps to interpret carbon turnover was introduced by the simple approach of Jenny (1941):

$$\frac{\partial c_{SC}}{\partial t} = -\lambda_0 c_{SC} + A \tag{1.1}$$

where c_{SC} is the amount of soil carbon [kg], t is time [d], λ_0 is the decomposition rate constant [d^{-1}], and A is the addition rate [kg d^{-1}]. One major limitation of this early approach is that the change in soil carbon quality caused by progressive decomposition was not taken into account, but carbon turnover was assumed to be constant with time neglecting changes in soil carbon stability and availability. To overcome these limitations, more complex model approaches were developed, e.g. additional components were introduced. So called multi-pool models are process-oriented models, which describe processes controlling the transformation of matter or energy movement and transformation (Paustian, 1994). Besides the process-oriented approaches, organism-oriented models have been also developed. Organism-oriented models are based on the flow of matter and energy through food-webs (Paustian, 1994). Nevertheless, multi-pool models are currently the most accepted approaches for the description of soil carbon turnover.

Multi-pool models

To describe the heterogeneity of the bulk SOM, several multi-pool models have been proposed, whereas the RothC (Jenkinson, 1990) and CENTURY (Parton et al., 1987) model are the most common ones. In general, all multi-pool models are conceptually very similar. Organic litter entering the soil is divided into fractions of different decomposability. During decomposition of the litter pools, several carbon pools of the mineral soil will be formed which differ in their turnover times. Decomposed soil carbon is either transferred into one or more pools or is released as CO_2. Decomposition of the carbon pools is typically described as a first-order kinetic process:

$$\frac{\partial c_p}{\partial t} = -\lambda_p c_p = -\lambda_0 \prod_i f_i c_p \tag{1.2}$$

where c_p is the pool concentration [kg C cm^{-3}]. The decomposition rates λ_p [d^{-1}] are determined by multiplication of the decomposition constants with various response factors f_i [-]. The decomposition constants of the pools are valid for optimal environmental conditions and a reference temperature. First-order kinetics implies that the amount of heterotrophic biomass does not directly affect the decomposition rate of organic matter pools and as a consequence soil microorganisms are simply treated as a fraction of SOM (Andrén and Paustian, 1987). Contrary to the approach of first-order kinetics, Monod kinetic approaches treat the decomposition rates as a function of the microbial biomass (McGill et al., 1981). An other possibility is the use of Michaelis-Menten kinetics (van Dam and van Breemen, 1995).

In general, multi-pool models have been developed and validated for specific environmental conditions. In a comparative study the applicability of nine different SOM turnover models was tested for the prediction of long-term carbon dynamics ranging over different ecosystems, climatic, and land-use conditions (Smith et al., 1997b). Six of nine models performed well across all data sets, among those the RothC (Jenkinson, 1990; Coleman and Jenkinson, 1996) and CENTURY (Parton et al., 1988; Parton, 1996) model. However, none of the models performed better than the others in each scenario. Nevertheless, for reliable predictions of SOM turnover at large scales and under future climate conditions models are needed that are able to accurately predict SOM dynamics without any site specific calibration (Smith et al., 1997a).

The SOILCO2/RothC model

In general, multi-pool models are zero-dimensional, i.e. decomposition of SOM and CO_2 release is simulated for a homogeneous surface soil layer. Both carbon pool sizes and the temperature and moisture response of carbon turnover will be averaged over this layer. As a consequence of this ‘bucket’ approach the produced CO_2 will be instantaneously released to the atmosphere.

In contrast, CO_2 transport models, often use very simplified approaches to simulate soil carbon turnover. For example, within the framework of the SOILCO2 model (Šimůnek and Suarez, 1993) microbial CO_2 release is described by an optimal CO_2 production rate which is exponentially distributed over the entire soil profile. Consequently, spatial and temporal changes of the quality and quantity of SOM will not be described.

In order to provide a more accurate description of the soil carbon cycling Herbst et al. (2008) integrated the RothC multi-carbon pool concept into the 1-dimensional physically-based water flow, heat, and CO_2 transport model SOILCO2 (Šimůnek and Suarez, 1993). By means of this coupled soil carbon turnover and CO_2 transport model (SOILCO2/RothC) quantitative and qualitative changes of SOM over the soil profile can be described in a high spatial resolution. For each soil depth (model node) the effective soil water contents and temperatures can be predicted which is essential for the accurate determination of the actual decomposition rates of the carbon pools. The moisture distribution is furthermore essential to describe the transport of CO_2 through the soil profile to the atmosphere.

1.5 Temperature and moisture response of SOM decomposition

Temperature has a strong influence on all biological and physicochemical processes in the soil. Hence, effects of the state variable temperature are most studied in the framework of SOM decomposition (Reichstein and Beer, 2008). However, controversial discussions within the scientific community show that the treatment of the temperature influence is still an unresolved problem. For example, Knorr et al. (2005) found a higher temperature sensitivity for more stable carbon fractions. In contrast to these findings, Fang et al. (2005) found no significant differences between the temperature sensitivity of labile and more stable soil carbon. Nevertheless, reliable prediction of the worlds soils role as carbon sinks or sources requires consensus on the decomposition sensitivity of SOM decomposition towards temperature (Davidson and Janssens, 2006).

The direct estimation of the temperature response of SOM decomposition will be complicated by several confounding factors (Kirschbaum, 2000; Davidson and Janssens, 2006; Kirschbaum, 2006; Reichstein and Beer, 2008). One of these confounding factors is the soil moisture content. In general, soil moisture content regulates different processes involved in SOM decomposition such as the accessibility of substrates and nutrients for the microorganisms and oxygen supply (Skopp et al., 1990). As a consequence, increasing water contents firstly encourage microbial activity but become repressive at a stage where a lack of oxygen occurs. The importance of soil moisture changes on soil organic carbon dynamics has been stressed out by Davidson and Janssens (2006) amongst others. Enormous carbon amounts may be released from wetlands and peatlands due to drying and the change from anaerobic to aerobic conditions. The estimation of the SOM decomposition response to temperature is furthermore biased by temporal and spatial changes in SOM quality and quantity due to inputs of fresh litter material or the alteration of SOM in the course of decomposition. Furthermore, besides heterotrophic respiration root respiration contributes to total soil respiration. It is unlikely that both processes have the same response towards changes in temperature. Finally, the attenuation and phase shift of the soil temperature amplitude vary with soil depth (Pavelka et al., 2007; Bahn et al., 2008; Reichstein and Beer, 2008). Consequently, different temperature responses will be found for different temperature measurement depths (e.g. Xu and Qi, 2001; Pavelka et al., 2007).

A reliable determination of SOM sensitivity on temperature therefore requires the consideration of these confounding factors in the data analysis (Reichstein and Beer, 2008). This has been clearly demonstrated by the study of Giardina and Ryan (2000) who did not consider differences in the relative abundances of the soil substrates in their analysis of soil samples from different latitudes and temperature regimes. Due to this insufficient assumption, they concluded that no correlation between temperature and soil carbon decomposition exists (Powlson, 2005). Since confounding factors can be better controlled in laboratory studies, Kirschbaum (2000; 2006) concluded that laboratory studies are more appropriate to determine the temperature response of SOM decomposition than field experiments. The reliability of response equations determined under laboratory conditions to field conditions, however, is questionable because laboratory conditions are always highly artificial.

Approaches for the temperature and moisture response of SOM decomposition

The correct determination of soil temperature and soil moisture response functions is crucial for a reliable prediction of SOM decomposition. No consensus has been found so far for a general formulation and parameterisation of temperature and soil moisture response functions. As a consequence, various equations for the temperature and moisture sensitivity of SOM decomposition can be found in literature. The most common expression for the temperature sensitivity is the Q_{10}- equation:

$$\lambda = \lambda_0 Q_{10}^{\left(T - T_{ref}\right)/10} \tag{1.3}$$

where λ_0 is the decomposition rate at the reference temperature T_{ref} [K] and Q_{10} [-] is the factor for which the decomposition rate increases for a temperature increment of 10 K. The Q_{10} approach is based on the observation that the reaction rate increases by a constant factor for a given temperature increment (Johnson and Thornley, 1985). In contrast to this empirical approach Arrhenius developed a theoretical based formulation for the temperature dependence of the decomposition rate:

$$\lambda = \beta \exp\left(\frac{E}{RT}\right) \tag{1.4}$$

Where β is a constant [d^{-1}], E is the activation energy [kJ mol^{-1}], and R is the universal gas constant (8.314 kg m^2 s^{-2} K^{-1} mol^{-1}). Besides the Q_{10} and Arrhenius relationships a great variety of formulations are in use (Kirschbaum, 2000; Tuomi et al., 2008) which will be discussed in Chapter 2.

In terms of SOM response to soil moisture a great inconsistency in the functional approaches (Rodrigo et al., 1997; Davidson et al., 2000) will be also found. Soil water content controls several processes involved in SOM decomposition such as substrate availability and oxygen supply for micro-organisms. Therefore, SOM decomposition will be enhanced by higher soil water contents as substrates and nutrients become increasingly available for the micro-organisms. On the other hand, high water contents are accompanied by an oxygen limitation which hampers SOM decomposition. The oxygen limitation effect may be implicitly included in the moisture response (e.g. Hansen et al., 1990) or in the form of a separate aeration response function, (e.g. Šimůnek and Suarez, 1993). Moisture response can be expressed in dependence on different state variables such as gravimetric or volumetric soil water content, soil matric potential, water holding capacity, water filled pore space, or precipitation indices (Davidson et al., 2000).

1.6 General objectives

This thesis is embedded in the general framework of global climate change research with a special focus on the temperature and moisture response of soil heterotrophic respiration. The objectives of this thesis are:

1. to analyse the influence of different temperature and moisture response functions on the simulated CO_2 efflux.
2. to investigate the suitability of widely accepted assumptions for the temperature response of carbon turnover in multi-carbon-pool concepts for the prediction of measured respiration data from the decomposition of ^{14}C-labelled wheat residues.
3. to determine the soil temperature and moisture response for a bare soil respiration experiment at the FLOWatch test-site Selhausen by the means of inverse parameter estimation.

1.7 Outline of this thesis

In general, this thesis is based on manuscripts published or submitted to international peer-reviewed journals (Chapter 2 to 4).

In Chapter 2 the effect of different combinations of temperature and moisture response functions from six well established carbon turnover models are investigated. Therefore, the SOILCO2/RothC model was validated first using measured CO_2 fluxes of a soil respiration experiment in Columbia (USA).

In Chapter 3 respiration data from laboratory wheat decomposition experiments were analysed using first-order two-pool models. In a first step, general assumptions of multi-pool models were used - constant initial pool ratio and the same temperature sensitivity of the decomposition rates of the active and recalcitrant pool. In a second step, it was tested if data prediction is significantly improved by assuming either a temperature dependent initial pool ratio or different temperature sensitivities of the pool decomposition rates. Finally, the applicability of the findings was tested using the RothC and CenW/CENTURY multi-pool models.

In Chapter 4 the temperature and moisture response of the heterotrophic soil respiration at the test site Selhausen were determined simultaneously using the SOILCO2/RothC model. In a first step, the model was calibrated on water content and temperature measurements at six different soil depths. In a second step, parameters of the soil moisture and temperature response functions were inversely estimated using the global optimisation algorithm Shuffled Complex Evolution (SCE). For the moisture response an exponential function expressed in dependence on the soil water content was used. The moisture response equation was combined with four different functional approaches of the temperature response from literature. Finally, the estimated temperature response was compared to the temperature response from a conventional linear regression method.

A general summary and further suggestions for future research are presented in Chapter 5.

2 Sensitivity of simulated soil heterotrophic respiration to temperature and moisture reduction functions[*]

2.1 Introduction

The atmospheric concentration of carbon dioxide as the most important greenhouse gas increased from the pre-industrial value of about 280 ppm to 379 ppm in 2005 (IPCC, 2007b). As stipulated by the Kyoto protocol, appropriate strategies must be developed to counteract the increase of atmospheric CO_2 concentrations. Besides the development of new technologies to reduce anthropogenic CO_2 emissions, changes in land use and land management play an important role (Lal, 2004) as soil respiration is one of the largest fluxes of CO_2 to the atmosphere (Schlesinger and Andrews, 2000). The main processes contributing to soil respiration are root and heterotrophic respiration. Heterotrophic respiration is not only determined by the total amount of soil organic matter (SOM) within the soil profile but also by the composition of SOM because of the high variability of biodegradability of different organic substances. To describe the heterogeneous character of SOM, several multi-pool models have been developed over the last decade, such as RothC (e.g.Coleman and Jenkinson, 2005), CANDY (Franko et al., 1995), and DAISY (Hansen et al., 1990). These models differ in the number of pools and the interactions between the single pools. Furthermore, multi-pool models are necessary to describe both short-term and long-term responses of soil carbon (Schimel et al., 1994; Trumbore, 2000). Most multi-pool models were developed and validated for specific sites and datasets and should not be used straightforward for simulation of carbon turnover at different sites. This has been clearly demonstrated by Smith et al.

---

[*] adapted from Bauer, J., Herbst, M., Huisman, J.A., Weihermüller, L., Vereecken, H., 2008a. Sensitivity of simulated soil heterotrophic respiration to temperature and moisture reduction functions. Geoderma 145, 17-27.

(1997b) using nine different soil carbon turnover models and twelve long-term datasets. The final results show that a number of models performed well for a range of datasets but none of the models was capable to satisfactorily simulate all scenarios. Nevertheless, prediction of SOM turnover at the global scale requires models that perform well under various environmental conditions.

Most SOM decomposition models are zero-dimensional without depth discretisation. Consequently, spatial variations in SOM concentration, soil temperature, moisture, and soil aeration cannot be considered. In contrast, physically-based models enable an accurate description of the transport of water, heat, and CO_2 in the soil profile, but often use very simplified approaches for calculation of SOM decomposition and are unable to describe carbon turnover dynamics. Recently, Herbst et al. (2008) integrated the multi-pool concept of the RothC model into the 1D physically-based water, heat, and CO_2 transport model SOILCO2 (Šimůnek and Suarez, 1993) to simulate depth-dependent SOM turnover. The RothC model has been widely used for various simulations of SOM decomposition processes (e.g. Coleman et al., 1997; Jenkinson et al., 1999; Cerri et al., 2003; Yang et al., 2003; Diels et al., 2004), and is therefore, well established. In RothC, SOM is separated into five pools. The first pool is inert organic matter (IOM), which is resistant to decomposition during the considered time period (≤ 100 y). The remaining four pools are decomposable plant material (DPM), resistant plant material (RPM), microbial biomass (BIO), and humified organic matter (HUM). In contrast to the original simple SOILCO2 approach for the CO_2 production by heterotrophic respiration, the RothC concept can describe quantitative changes of SOM due to plant input as well as qualitative SOM differences. Therefore, the coupling of SOILCO2 and RothC overcomes the weak points of both models.

Decomposition of the C-pools is usually described by first order kinetics with different decomposition rate constants. These constants are valid for optimal environmental conditions and a reference temperature and are transferred to the decomposition rates for the actual environmental conditions by reduction functions. The reduction concepts of the various SOM decomposition models include reduction functions using different dependencies and expressions. Soil temperature and moisture are considered as the most important variables for decomposition of SOM (Singh and Gupta, 1977). Moncrieff and Fang (1999) detected a two times higher sensitivity of CO_2 fluxes towards soil temperature than towards soil moisture after increasing the status variable values by 5%. Temperature dependence of SOM decomposition is often expressed as Q_{10}- or the related Arrhenius function, but other expressions are also in use (Kirschbaum, 2000). Temperature sensitivity of SOM decomposition is more complex than the pragmatic modelling approaches discussed here, as has been illustrated in the review of Davidson and Janssens (2006). Conflicting results (e.g. Fang et al., 2005; Knorr et al., 2005) indicate that this is an unresolved topic.

The expressions for soil moisture reduction functions are more diverse. For example, different models use different variables to describe the influence of soil moisture, such as volumetric water content (Fang and Moncrieff, 1999) or matric potential (Hansen et al., 1990; Šimůnek and Suarez, 1993). Another difference between the soil moisture reduction functions is that some models implicitly include the effects of soil aeration in the soil moisture reduction function (Hansen et al., 1990; Šimůnek and Suarez, 1993).

The diversity of reduction functions in models with similar structures can be attributed to different conditions of the test sites where the models were developed and validated (Heinen, 2006), and on the other hand, to different conceptual ideas. Rodrigo et al. (1997) illustrated the variation of temperature and moisture reduction factors between nine C-N models. They hypothesised that different reduction functions can lead to major differences in model outputs.

The aim of this study was to assess the influence of different soil temperature and moisture reduction functions on the simulation of SOM decomposition and CO_2 fluxes using a realistic scenario. In order to do so, we first validated the coupled SOILCO2/RothC model for the test scenario**.** In a next step, the sensitivity of soil CO_2 fluxes towards the reduction functions was quantified for the same test scenario.

2.2 Materials and methods

2.2.1 Modelling of SOM decomposition with the coupled SOILCO2/RothC model

In order to improve modelling of carbon dynamics in soils, the zero-dimensional RothC pool model (Coleman and Jenkinson, 2005) was integrated into the one-dimensional physically-based transport model SOILCO2 (Šimůnek and Suarez, 1993). A full description of the integration is given by Herbst et al. (2008). The water flow is calculated using the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} - 1\right)\right] - Q \tag{2.1}$$

where h is the water pressure head [cm], θ is the volumetric water content [cm^3 cm^{-3}], K is the unsaturated hydraulic conductivity [cm d^{-1}], t is time [d], z is the depth [cm], and Q is a source/sink term [cm^3 cm^{-3} d^{-1}]. The soil water retention $\theta(h)$ and hydraulic conductivity $K(h)$ functions are described by the Mualem-van Genuchten approach (van Genuchten, 1980):

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left(1 + |\alpha h|^n\right)^m} \tag{2.2a}$$

$$K(h) = K_s S_e^{0.5}\left[1 - \left(1 - S_e^{1/m}\right)^m\right]^2 \tag{2.2b}$$

$$\text{with} \quad S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \qquad m = 1 - 1/n \qquad n > 1 \tag{2.2c}$$

where θ_r and θ_s are the residual and saturated water contents [cm^3 cm^{-3}], α is the inverse of the bubbling pressure [cm^{-1}], K_s is the saturated hydraulic conductivity [cm h^{-1}], S_e is the relative saturation [-] and m and n are shape parameters [-].

Heat transport is calculated according to Sophocleous (1979) by:

$$C\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left[l(\theta)\frac{\partial T}{\partial z}\right] - C_w\frac{\partial J_w T}{\partial z} \tag{2.3}$$

where T is the soil temperature [°C], l is the thermal conductivity of the soil [kg cm d^{-3} $°C^{-1}$], C and C_w are the volumetric heat capacities [kg d^{-2} cm^{-1} $°C^{-1}$] of the porous medium and the liquid phase, respectively, and J_w is the water flux density [cm d^{-1}]. The first term on the right hand side of Eq. (2.3) represents the heat flow due to conduction and the second term the heat transported by water flow.

The transport of carbon dioxide is described by the following equation:

$$\frac{\partial c_T}{\partial t} = -\frac{\partial}{\partial z}\left(J_{da} + J_{dw} + J_{ca} + J_{cw}\right) - Qc_w + S \tag{2.4}$$

where J_{da} describes the CO_2 flux caused by diffusion in the gas phase [cm d^{-1}], J_{dw} the CO_2 flux caused by dispersion in the dissolved phase [cm d^{-1}], J_{ca} the CO_2 flux caused by convection in the gas phase [cm d^{-1}], and J_{cw} the CO_2 flux caused by convection in the dissolved phase [cm d^{-1}]. The total volumetric concentration of CO_2 is expressed by c_T [cm^3 cm^{-3}]. S is the CO_2 production/sink term [cm^3 cm^{-3} d^{-1}]. The term Qc_w is an expression for the dissolved CO_2 removed from the soil by root water uptake, where c_w is the CO_2 concentration in the liquid phase [cm^3 cm^{-3}] and Q is the root water uptake [cm^3 cm^{-3} d^{-1}].

The production of CO_2 is calculated as the sum of CO_2 production by soil microbes γ_s [cm^3 cm^{-3} d^{-1}] and CO_2 production by plant roots γ_p [cm^3 cm^{-3} d^{-1}]:

$$S = \gamma_s + \gamma_p \tag{2.5}$$

where γ_p is calculated using the original approach of the SOILCO2 model. The microbial CO_2 production γ_s is calculated from the sum of CO_2 formed during decomposition of the four active pools of the RothC model. Decomposition follows first order kinetics:

$$\frac{\partial c_p}{\partial t} = -\lambda_p c_p = -\lambda_{p,0}\prod_i f_i c_p \qquad \prod_i f_i = f_T f_W f_a \tag{2.6}$$

where the change of the concentration c [kg C cm^{-3}] of the different pools p over time is determined by the decomposition rate λ_p [d^{-1}]. To determine the actual decomposition rate the decomposition constants, which are valid for optimal conditions of soil moisture and aeration and a temperature of 9.25°C ($\lambda_{p,0}$) [d^{-1}], are scaled with various reduction factors f_i [-] for soil temperature (f_T), moisture (f_W), and aeration (f_a).

2.2.2 Integration of various reduction functions into the SOILCO2/RothC model

For the performance of the functional sensitivity analysis, soil temperature reduction functions and soil moisture reduction functions have been chosen from six well established models: CANDY (Franko et al., 1995), CENTURY (Parton et al., 2001), DAISY (Hansen et al., 1990), PATCIS (Fang and Moncrieff, 1999), RothC (Coleman and Jenkinson, 2005), and SOILCO2 (Šimůnek and Suarez, 1993). All temperature and moisture reduction functions are listed in Table A 1 and Table A 2, respectively (see Appendix).

We want to point out that temperature reduction factors generally do not vary between 0 and 1 but can also reach higher values. Only the CANDY model uses a function with a plateau for temperatures > 35°C expressing optimal decomposition conditions (see Appendix Table A 1). For all other models, decomposition increases steadily with temperature. Both the SOILCO2 and PATCIS model use a modified type of the Arrhenius equation (Johnson and Thornley, 1985) to describe the temperature dependence of the decomposition rate. However, there are differences in the reference temperature (20°C in the case of SOILCO2, 10°C for PATCIS) and in the parameterisation of the activation energy. The SOILCO2 model uses a fixed value for the activation energy over the entire temperature range, whereas PATCIS calculates the temperature reduction factor with activation energy values depending on soil temperature. For simulation of SOM decomposition with the coupled SOILCO2/RothC model, all soil temperature reduction functions were transformed to match 1 at 9.25°C as the decomposition rates of the RothC pools are valid for that temperature. The original temperature reduction functions $f(T)$ were therefore divided by the value of the original equation at the reference temperature (T_{ref} = 9.25°C) as expressed by the following equation:

$$f_T(T) = \frac{1}{f(T_{ref})} f(T) \tag{2.7}$$

The rescaled temperature reduction functions $f_T(T)$ are plotted in Figure 2.1. In general, the scaling factors of the models indicate considerable differences, particularly for high temperatures.

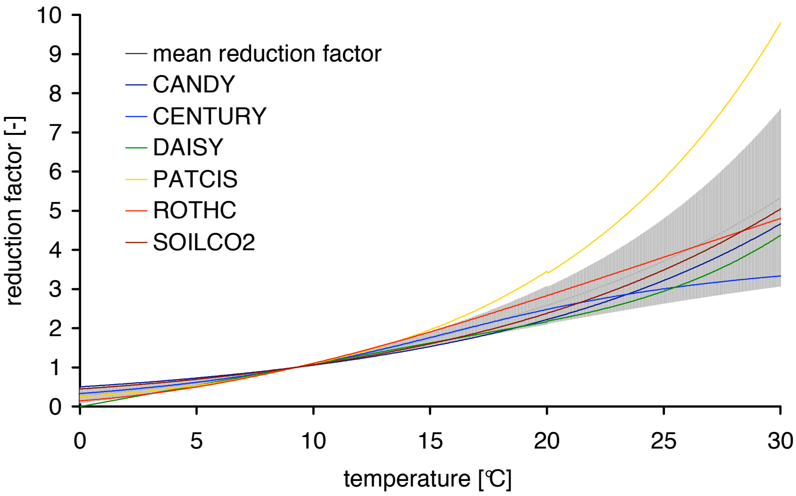

Figure 2.1: Soil temperature reduction functions of the six different carbon models transformed to the RothC reference temperature of 9.25°C. The grey area represents the standard deviation.

The soil moisture reduction functions from the six models use different variables (Appendix Table A 2). SOILCO2 and DAISY are based on pressure heads, whereas CANDY and PATCIS use the soil water content. The soil moisture reduction of the RothC model is calculated as a function of the soil clay content, precipitation, and evaporation rate. The soil moisture reduction function within the CENTURY model is calculated from the potential evapotranspiration *PET* and the sum of stored water and precipitation *PPT*.

To consider the soil moisture reduction functions of RothC and CENTURY for the integration into the SOILCO2/RothC model, modifications were required. For RothC, the accumulated topsoil moisture deficit was replaced by the difference between the water content at saturation and the actual water content, whereas the maximum soil moisture deficit was replaced by the difference between the water content at saturation and the residual water content. The ratio of *PPT* to *PET* of the CENTURY moisture reduction function can be interpreted as the water stress of the system. Therefore, we used the transpiration reduction function of SOILCO2 as a proxy for the moisture reduction function. We replaced the *PPT*/*PET* ratio by the ratio of the actual soil water content to the soil water content at the pressure head h_{50}. The h_{50} value defines the pressure head at which the water extraction rate is reduced by 50% and is included in the root water uptake equation of the SOILCO2 model introduced by van Genuchten (1987) which is based on the Feddes et al. (1978) approach. The moisture reduction factors of the different functions were plotted in dependence on the soil water content in Figure 2.2. The Mualem-van Genuchten approach (van Genuchten, 1980) was used to convert water content to pressure head. Therefore, the hydraulic parameters of the upper soil horizon of the test scenario were chosen (see next section). As shown in Figure 2.2 the soil moisture reduction functions implemented in the various models exhibit large differences. Nevertheless, all models show an increase of the reduction factor with higher soil water contents to the point of optimum moisture conditions. In contrast to the other concepts, the soil moisture reduction function of the DAISY model decreases again for higher water contents (Hansen et al., 1990). This behaviour is caused by the implicit consideration of reduced oxygen availability at higher water contents in the soil moisture reduction function of the DAISY model. For a meaningful comparability to the other moisture reduction functions the DAISY function was modified by neglecting the effect of soil aeration.

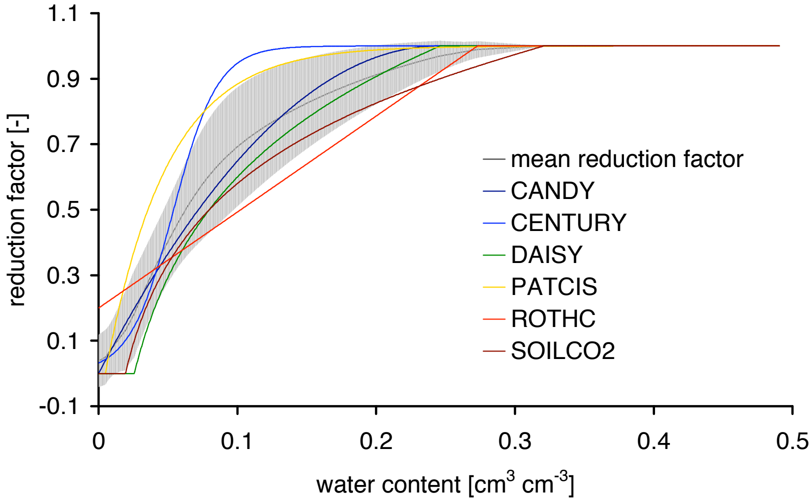

Figure 2.2: Soil moisture reduction functions of six different carbon models in dependence on the volumetric water content for the A horizon of the Missouri dataset with $\theta_s = 0.491$ cm^3 cm^{-3}, $\theta_r = 0.000$ cm^3 cm^{-3}, $n = 1.246$, $\alpha = 0.0512$ cm^{-1}, and $h_{50} = -1000$ cm. The grey area represents the standard variation.

In comparison, an additional reduction factor is included in the reduction term of the CANDY, PATCIS, and SOILCO2 model to consider oxygen shortage. Both PATCIS and SOILCO2 use the Michaelis-Menten equation, which is expressed in dependence on the oxygen concentration. Šimůnek and Suarez (1993) modified this function in the following manner:

$$f_{O_2}(c_a) = \frac{0.21 - c_a}{0.42 - c_a - K^*_M} \qquad \langle c_a < 0.21 \rangle$$
$$f_{O_2}(c_a) = 0.0 \qquad \langle c_a \geq 0.21 \rangle \tag{2.8}$$

where c_a is the CO_2 content in the gas phase [$cm^3\ cm^{-3}$], and K^*_M is the Michaelis constant for the CO_2 content [$cm^3\ cm^{-3}$]. A disadvantage of this expression is that the function is not equal to 1 for CO_2 contents $c_a = 0$. To improve this approach an additional term was added to the original function as suggested by Herbst et al. (2008):

$$f_{O_2,\mathrm{mod}}(c_a) = f_{O_2}(c_a) + \frac{0.21 - K^*_M}{0.42 - K^*_M} \qquad \langle c_a < 0.21 \rangle \tag{2.9}$$

2.2.3 Experimental dataset

In order to evaluate the influence of different soil temperature reduction functions and soil moisture reduction functions on the simulation of SOM decomposition and CO_2 fluxes a dataset from the Sanborn Field (Columbia, USA) respiration experiment (Buyanovsky and Wagner, 1983; Buyanovsky et al., 1986) was chosen. The data of the Missouri experiment were already used for validation of the original SOILCO2 (Suarez and Šimůnek, 1993) and the DNDC model (Li et al., 1994). Here, we only use the data for wheat cultivation since besides CO_2 concentrations also CO_2 fluxes were measured. During the experiment, wheat was planted on a Mexico silt loam in the middle of October and harvested by the beginning of July. CO_2 concentrations in the gaseous phase were measured *in situ* with disposable chromatographic tubes at intervals of two to three weeks. At intervals of usually two weeks CO_2 fluxes were determined by the alkali adsorption method during 24 h intervals. Besides CO_2 concentrations and CO_2 fluxes, soil moisture and temperature in the soil profile were measured using combined moisture-temperature cells. Data on average weekly air temperature, daily precipitation, and evaporation were obtained from a weather station located 5 km south of the study site.

2.2.4 Parameterisation and initialisation of the SOILCO2/RothC model

For the simulation of the transport of water, heat, and CO_2 the parameterisation, initial and boundary conditions (Table 2.1) were taken from Suarez and Šimůnek (1993). In addition, the coupled SOILCO2/RothC model requires the initial sizes of the RothC pools (see below). Furthermore, clay content is required for calculation of the proportions for the partitioning of decomposed carbon to the BIO and HUM pool (Coleman and Jenkinson, 2005). Therefore, the clay content of each layer was taken from Buyanovsky and Wagner (1983). Potential evapotranspiration was calculated by Suarez and Šimůnek (1993) from average weekly air temperatures using the Thornthwaite equation (de Marsily, 1986). The soil profile was divided into three horizons (A, B1, and B2) and the hydraulic properties were calculated from mean textural characteristics using a pedotransfer function (Suarez and Šimůnek, 1993). The parameters for the thermal conductivity of the clayey soil were taken from Chung and Horton (1987). Hydraulic properties, bulk density, organic matter, and clay content for each layer of the soil profile are listed in Table 2.2.

Table 2.1: Boundary and initial conditions for water, heat, and CO_2 transport.

	Lower boundary condition	Upper boundary Condition	Initial condition
water transport	free drainage at a depth of 1.7 m	Dirichlet (-15000 cm / 0 cm) / Cauchy (P-E_p)	constant pressure head of -1.0 m
heat transport	zero temperature gradient	Dirichlet (measured air temperature with a daily amplitude of 5°C)	constant temperature of 15°C for 1981 and 2°C for 1982
CO_2 transport	Cauchy (zero flux)	Dirichlet (0.033% CO_2)	CO_2 concentration 0.033% - 1.8% (1981), 0.033% - 1.5% (1982)

P: precipitation; E_P: potential evaporation.

Table 2.2: Hydraulic parameters according to the Mualem-van Genuchten approach (van Genuchten, 1980), bulk density ρ, organic matter OM, and clay content for the layers of the soil profile.

	θ_r [cm^3 cm^{-3}]	θ_s [cm^3 cm^{-3}]	α [cm^{-1}]	n [-]	K_s [cm d^{-1}]	Depth [cm]	ρ [g cm^{-3}]	OM [%]	Clay [g g^{-1}]
A	0.000	0.491	0.0512	1.246	100	0-13	1.37	2.9	0.22
						13-20	1.35	2.5	0.24
						20-28	1.33	1.7	0.24
B1	0.000	0.513	0.0508	1.199	100	28-36	1.29	1.1	0.31
B2	0.000	0.509	0.0488	1.142	100	36-51	1.29	1.2	0.53
						51-66	1.36	0.8	0.49
						67-170	1.36	0.1	0.49

θ_r: residual water content [cm^3 cm^{-3}], θ_s: saturated water content [cm^3 cm^{-3}], α: inverse of the bubbling pressure [cm^{-1}], n: shape parameter [-], K_s: saturated hydraulic conductivity [cm d^{-1}].

For the simulation of the rooting depth, using the root growth model of the SOILCO2 model, the initial root depth was set to 15 cm in 1981 and 5 cm in 1982. The heat units required for the plant to mature and roots to reach the maximum rooting depth [°C d] were calculated after Pirasteh and Welsh (1980) and resulted in 1275°C d. It was assumed that 65% of the roots were located in the top 10 cm expressed by a value of 10.5 m^{-1} for the parameter a [cm^{-1}] in the exponential depth reduction function (Suarez and Šimůnek, 1993).

2.2.5 Inverse estimation of the initial pool sizes

Since information on the composition of SOM was not available, the initial pool sizes had to be estimated. If no measurements are available, the *IOM* pool size [t C ha^{-1}] can be calculated according to Falloon et al. (1998) from the total soil organic carbon (*SOC*) content [t C ha^{-1}] by:

$$IOM = 0.049 SOC^{1.139} \tag{2.10}$$

where *SOC* [kg C kg^{-1}] was calculated from the organic matter contents [kg kg^{-1}] by dividing SOM with a factor of 1.724 and converted to t C ha^{-1} by multiplying with the bulk density [kg cm^{-3}] and horizon depth [cm].

The proportions of DPM, RPM, and BIO were determined inversely by minimising the sum of squared residuals (*SSR*) between measured and modelled CO_2 fluxes with a global optimisation algorithm (SCE-UA) as described by Duan et al. (1992). *HUM* [kg C kg^{-1}] was calculated as the remaining fraction of total *SOC* [*HUM*=*SOC*-(*DPM*+*RPM*+*BIO*+*IOM*)]. Additionally, it was assumed that the pool proportions do not vary with soil depth.

2.3 Results and Discussion

2.3.1 Simulation of soil temperature and soil moisture

Simulation of SOM decomposition requires exact predictions of soil temperature and soil water content. The modelling of soil temperature and water content was already validated by Suarez and Šimůnek (1993). Both soil temperature and soil water content in 20 cm soil depth could be predicted well by the model. In Figure 2.3e and 3f the simulated soil temperatures and soil water contents in the uppermost 50 cm of the soil profile are compared for the years

1981 and 1982. Due to the earlier start of the simulation period lower daily temperatures down to -2°C were measured in 1982. Slightly higher summer temperatures up to 27°C were recorded in 1981, compared to a maximum of 25°C in 1982. In both years, the soil water content varied between 0.10 to 0.51 cm^3 cm^{-3} indicating that even the soil surface was never completely dry.

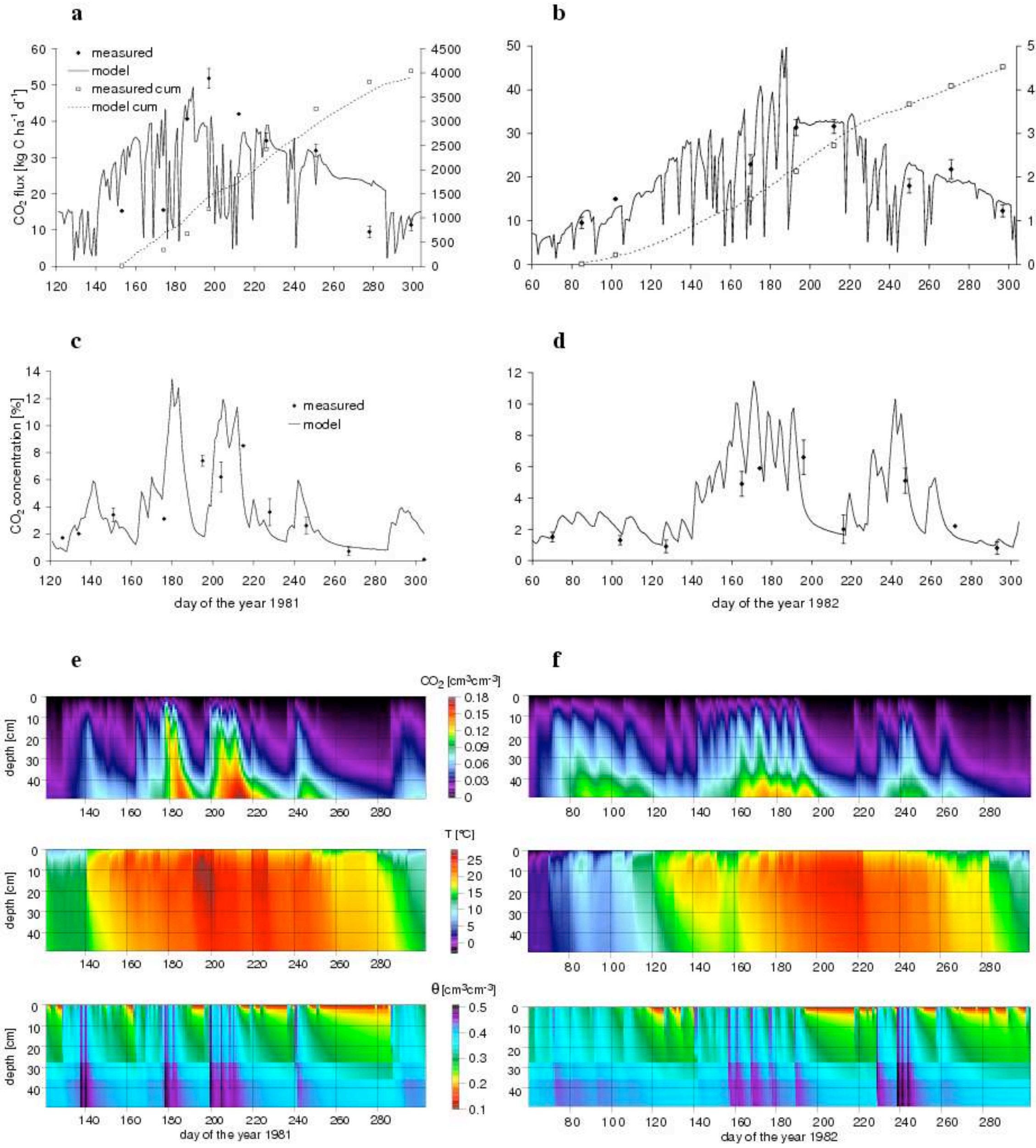

Figure 2.3: Measured and simulated CO_2 fluxes, cumulative CO_2 fluxes at the soil surface; CO_2 concentrations at 20 cm depth, and depth profiles of CO_2 concentration, soil temperature, and soil water content of the upper 50 cm (simulation results of the coupled SOILCO2/RothC model with SOILCO2 reduction functions) for the years 1981 and 1982.

2.3.2 Simulation of CO_2 concentrations and CO_2 fluxes

Due to the lack of information about SOM quality, the initial pool sizes were estimated. The IOM proportion was calculated from SOM content of each soil layer and set to the average value of 0.07 for the total soil profile. The proportions of the other pools were determined by calibration against measured CO_2 fluxes (Table 2.3). For both years, the calibrated proportion of DPM was very small. In 1981 a rather high content of RPM was calculated, while for the second year nearly no fresh organic matter was present. Consequently, both the proportions of the HUM and the BIO pool in 1982 are significantly higher than in the year before.

Table 2.3: Initial pool proportions determined by minimisation of *SSRflux* for the SOILCO2/RothC model and comparison to the original approach of Šimůnek and Suarez (1993).

		Pool proportion [-]					*SSRconc*	*SSRflux*
		DPM	RPM	BIO	HUM	IOM	[cm^6 cm^{-6}]	[cm^6 cm^{-4} d^{-2}]
1981	SOILCO2	exponential distribution*					0.0085	0.7072
	SOILCO2/RothC	0.0000	0.1594	0.0011	0.7695	0.0700	0.0148	0.9172
1982	SOILCO2	exponential distribution*					0.0027	0.1229
	SOILCO2/RothC	0.0010	0.0003	0.0759	0.8528	0.0700	0.0026	0.0970

*: In the SOILCO2 model CO_2 production γ_s [m^3 m^{-3} d^{-1}] is calculated from an optimal production rate $\gamma_{s,0}$ [m^3 m^{-2} d^{-1}] which is distributed over depth by an exponential function $f(z)$ [m^{-1}] and converted to the actual soil temperature T [°C] and pressure head h [m] according to the following equation: $\gamma_s = \gamma_{s,0} f(z) f_T(T) f_W(h)$ with $f(z) = a\exp(-az)$, where z is soil depth [m] and a is an empirical constant [m^{-1}].

As a measure of the quality of the model initialisation, the *SSR* of simulated and measured CO_2 concentrations was calculated for the SOILCO2/RothC model and the original SOILCO2 model (Table 2.3). In the original SOILCO2 approach, CO_2 production was calculated from an optimal microbial decomposition rate γ_0 (0.42 cm^3 cm^{-2} d^{-1}) which was distributed exponentially over depth. For that, the same approach as for the root depth distribution was used (Šimůnek and Suarez, 1993), where the depth distribution parameter a was set to 10.5 m^{-1}. In the RothC approach, CO_2 was produced by decomposition of the four active carbon pools. While the decomposition constants were set to the original values of the RothC model (λ_{DPM} = 10 y^{-1}, λ_{RPM} = 0.3 y^{-1}, λ_{BIO} = 0.66 y^{-1}, λ_{HUM} = 0.02 y^{-1}) the initial pool sizes of the DPM, RPM, HUM, and BIO pool were inversely estimated. The coupled SOILCO2/RothC model should provide a larger flexibility for predicting the measured CO_2

concentrations and fluxes due to the use of more parameters describing CO_2 production compared to the original SOILCO2 model. However, the deviations between measured and simulated CO_2 fluxes and concentrations were larger for the coupled SOILCO2/RothC model during the first year. Nevertheless, both measured CO_2 fluxes and CO_2 concentrations were simulated well (Figure 2.3a and 3c). For the year 1982 where the pools were again inversely estimated, both CO_2 fluxes and concentrations were reproduced very well (Figure 2.3b and 3d) with a smaller *SSR* for the coupled model compared to the original SOILCO2 model (Table 2.3).

Simulation results indicate that the contribution of plant roots to CO_2 production was very small (6% in 1981 and 9% in 1982). Root respiration contributed to soil respiration only during the vegetation period. During the subsequent fallow period, measured CO_2 fluxes can be exclusively attributed to heterotrophic respiration. Measured CO_2 fluxes were predicted well over the entire simulation period. Although root respiration was not separately measured, we conclude that the estimated proportion of root respiration is in the right order of magnitude. Consequently, the CO_2 production is clearly dominated by heterotrophic respiration for this experiment.

The CO_2 concentrations in the upper 50 cm of the soil profile for both simulation periods are shown in Figure 2.3e and 2.3f. Very high CO_2 concentrations up to 18% in 1981 and 14% in 1982 occurred during periods with high soil water content and soil temperature. Those conditions enhance SOM decomposition and CO_2 is retained in the soil due to limited gas transport through the saturated pore system. In the surface layer, CO_2 concentrations were very low at all times because of the close contact to the atmosphere. To summarise, CO_2 production and fluxes for both years were predicted in a reasonable way by the SOILCO2/RothC model. The model parameterisation is therefore appropriate for the performance of the functional sensitivity analysis.

2.3.3 Influence of the soil temperature and soil moisture reduction functions on SOM decomposition and CO_2 fluxes

To determine the influence of soil temperature and soil moisture reduction functions on the prediction of CO_2 fluxes, the SOILCO2/RothC model was run with the initialisation described above using different combinations of reduction functions. First, the influence of the soil temperature reduction function was studied. Therefore, the soil moisture reduction function of the SOILCO2 model (Appendix Table A 2) and the modified CO_2 reduction function (Eq. (2.9)) were combined with soil temperature reduction functions of all other models (Appendix Table A 1). In a second step, the sensitivity of the moisture reduction was assessed by using the different soil moisture reduction functions in combination with the soil temperature reduction function of the SOILCO2 model and the CO_2 reduction function as expressed by Eq. (2.9). Finally, soil temperature reduction functions and soil moisture reduction functions of each tested model were combined with the CO_2 reduction function in order to assess a potential interdependency of both functions. The simulated cumulative CO_2 fluxes from the soil surface in dependence on temperature reduction, moisture reduction, and a combination of both are compared in Figure 2.4. As a measure of sensitivity, the differences of the cumulative CO_2 fluxes during the simulation periods were calculated, where the cumulative CO_2 fluxes simulated with the reduction functions of the SOILCO2 model were taken as reference values. Furthermore, the mean absolute errors of the simulated CO_2 fluxes were calculated. The results are listed in Table 2.4. Deviations between the simulated CO_2 fluxes obviously depend on the course of soil temperatures and moisture, which explains the lower sensitivity towards the choice of different soil temperature and soil moisture reduction functions for the two months longer simulation period in 1982 compared to 1981. Hence, the influence of different reduction functions for soil temperature and soil moisture on the simulated CO_2 fluxes will be more or less pronounced for different climate conditions and soil characteristics.

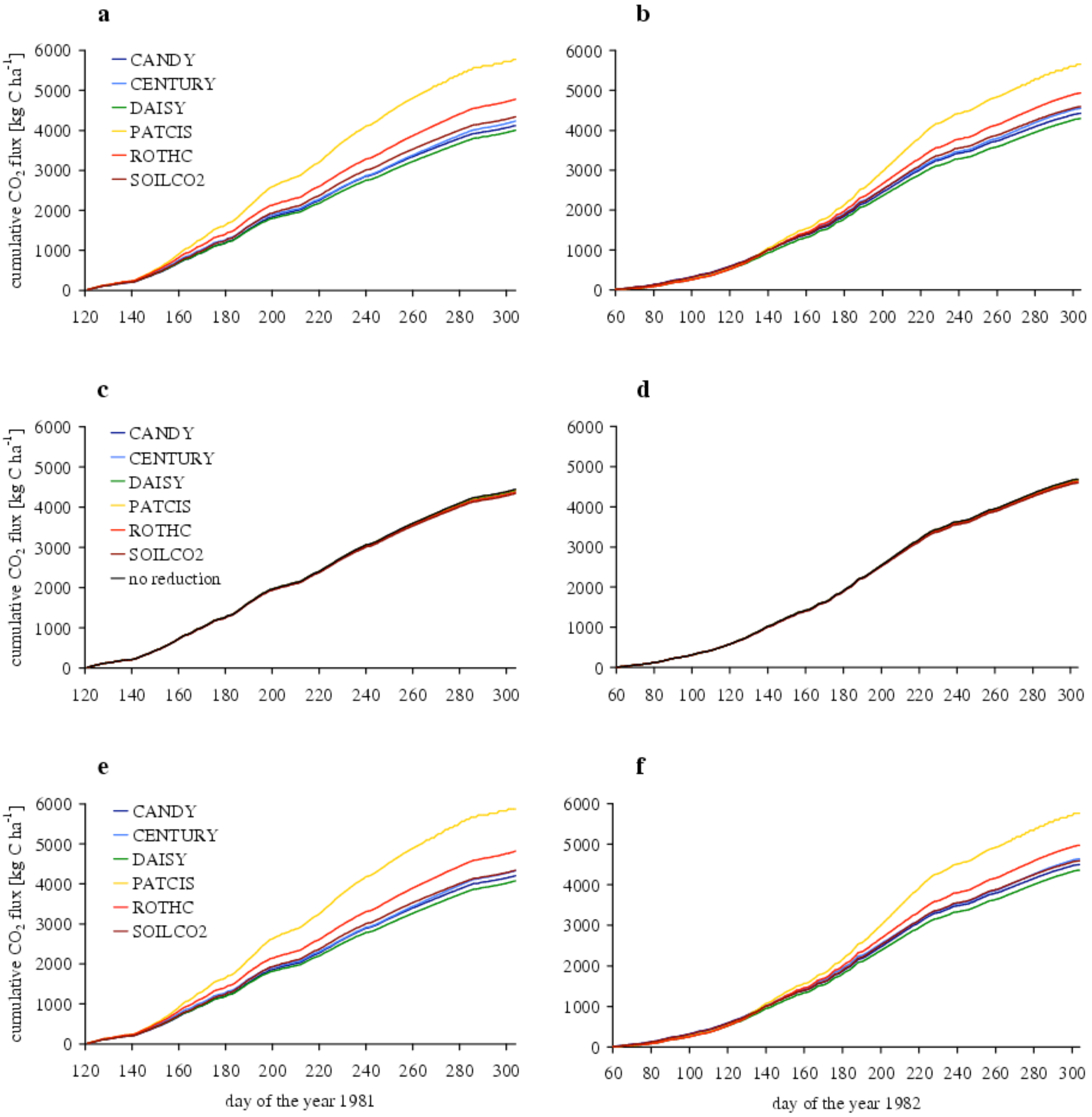

Figure 2.4: Cumulative CO_2 flux at the soil surface simulated with different soil temperature reduction functions (a and b), soil moisture reduction functions (c and d), and combined soil temperature reduction functions and soil moisture reduction functions (e and f) for the year 1981 and 1982, respectively.

Table 2.4: Deviation of cumulative CO_2 fluxes related to the cumulative CO_2 flux of SOILCO2 and mean absolute error (*MAE*) for variation of soil temperature, moisture, and temperature + moisture reduction.

	Variable function					
	Soil temperature		Soil moisture		Both	
	Cum. CO_2 flux [kg C ha^{-1}]	*MAE* [kg C ha^{-1} d^{-1}]	Cum. CO_2 flux [kg C ha^{-1}]	*MAE* [kg C ha^{-1} d^{-1}]	Cum. CO_2 flux [kg C ha^{-1}]	*MAE* [kg C ha^{-1} d^{-1}]
	1981					
CANDY	4120 (-5.1%)	228	4429 (2.0%)	95	4206 (-3.1%)	149
CENTURY	4235 (-2.5%)	304	4438 (2.2%)	105	4330 (-0.3%)	328
DAISY	4005 (-7.8%)	370	4416 (1.7%)	81	4077 (-6.1%)	313
PATCIS	5777 (33.0%)	1537	4434 (2.1%)	104	5877 (35.3%)	1676
RothC	4780 (10.1%)	438	4373 (0.7%)	35	4821 (11.0%)	475
SOILCO2	4342 (ref.)	ref.	4342 (ref.)	ref.	4342 (ref.)	ref.
no reduction	n. e.	n. e.	4443 (2.3%)	112	n. e.	n. e.
	1982					
CANDY	4426 (-3.6%)	197	4674 (1.8%)	94	4502 (-2.0%)	131
CENTURY	4553 (-0.9%)	263	4680 (1.9%)	104	4639 (1.0%)	273
DAISY	4296 (-6.5%)	322	4663 (1.5%)	81	4362 (-5.0%)	288
PATCIS	5657 (23.2%)	1239	4679 (1.9%)	102	5758 (25.4%)	1359
RothC	4935 (7.5%)	473	4628 (0.8%)	35	4971 (8.3%)	509
SOILCO2	4592 (ref.)	ref.	4592 (ref.)	ref.	4592 (ref.)	ref.
no reduction	n. e.	n. e.	4685 (2.0%)	110	n. e.	n. e.

ref.: reference; n. e.: not estimated.

Different temperature reduction functions provided significant differences of simulated CO_2 fluxes. The smallest temperature reduction was found for the PATCIS function with a cumulative CO_2 flux of 5777 kg C ha^{-1} in 1981 and 5657 kg C ha^{-1} in 1982. The reduction of the DAISY function was strongest resulting in cumulative CO_2 fluxes of 4005 kg C ha^{-1} in 1981 and 4296 kg C ha^{-1} in 1982. Both years showed long periods with soil temperatures above 20°C (Figure 2.3e and 3f). Because of the large range of temperature reduction factors at high temperatures (Figure 2.1), maximum deviations between the lowest and highest simulated CO_2 fluxes were up to 41% (Table 2.4). The different soil moisture reduction functions provide very similar CO_2 fluxes with maximum deviations of only ~ 2% (Table 2.4) and are only slightly lower than the CO_2 flux without moisture reduction which was 4443 kg C ha^{-1} in 1981 and 4685 kg C ha^{-1} in 1982. The reason can be found in the water contents, which never dropped below 0.1 cm^3 cm^{-3} (Figure 2.3e and 2.3f). Consequently, moisture reduction factors did not vary over the entire range but were always higher than 0.49

corresponding to the minimal reduction factor of the RothC soil moisture reduction function. For the reduction functions of the other models, minimum values were even higher e.g. the minimum moisture reduction value of the CENTURY model was 0.95. The variations of the moisture reduction factors are highest for soil water contents between 0.04 and 0.2 $cm^3 cm^{-3}$ (Figure 2.2). It can be concluded that deviations of the simulated CO_2 fluxes increase when dry soil moisture conditions occur. As shown in Figure 2.3, soil water contents between 0.1 and 0.2 $cm^3 cm^{-3}$ were only found in the top 5 cm during several relatively short time periods. As already mentioned above and illustrated by Table 2.4, different hydraulic properties and climatic conditions will likely result in higher deviations of simulated CO_2 fluxes due to the larger impact of soil moisture reduction functions at lower soil water contents. Especially in arid and semi-arid regions affected by longer drought periods, moisture reduction will have a stronger effect on the simulated CO_2 fluxes, as shown by Akinremi et al. (1999). The average mean absolute errors (Table 2.4) indicate a roughly 6 to 7 times higher sensitivity towards the temperature reduction function compared to the soil moisture reduction function confirming the results of the sensitivity analysis performed by Moncrieff and Fang (1999) for a mature slash pine plantation in Florida.

The actual decomposition rate is determined by multiplication of the decomposition constant with the product of the temperature, moisture, and aeration reduction factors. It can be argued that the single reduction functions are interdependent, and therefore, should always be used in their original combination. To investigate a potential interdependency between the soil temperature and soil moisture reduction functions derived from the same model, both reduction functions were varied simultaneously. The deviations of the simulated cumulative CO_2 fluxes (Table 2.4, Figure 2.4e and 4f) were reduced by combining the temperature reduction functions with the complementary moisture reduction functions in the case of CANDY, CENTURY, and DAISY. However, for PATCIS and RothC the deviations became higher. Thus, the magnitude of the deviations between the cumulative CO_2 fluxes can not be attributed to using just one factor of the various reduction functions.

The changes in the cumulative CO_2 fluxes due to the variation of the temperature reduction function found in this study are on average higher than the changes resulting from a 5% increase in the status variable value found by Moncrieff and Fang (1999). Thus, even a five percent error in the simulation or the measurement of soil temperature would be less relevant than the appropriate choice of the soil temperature reduction function.

2.4 Summary and conclusions

One objective of this study was the validation of the coupled SOILCO2/RothC model for the Missouri experiment. As already shown by Suarez and Šimůnek (1993) the temperatures and water contents within the soil profile were predicted well by the SOILCO2/RothC model. For the simulation of carbon turnover, the initial sizes of the RothC pools were estimated inversely. Inverse estimation of the initial RothC pool sizes is an appropriate tool if no additional information about SOM quantity and quality are available. Nevertheless, detailed studies concerning the inverse estimation of the C-pools with a comparison of measured C pool quantities would reduce uncertainty in the model predictions. The simulated CO_2 concentrations in 20 cm depth and CO_2 fluxes from the soil surfaces were in good agreement with the measured data of the Missouri experiment. To summarise, the dataset of the Missouri experiment was predicted well by the coupled SOILCO2/RothC model.

The validation of the SOILCO2/RothC model was the basis for the second objective of this study, which was to assess the influence of soil temperature and soil moisture reduction functions on the prediction of carbon turnover and CO_2 fluxes. For this purpose, soil temperature and soil moisture reduction functions from six well established carbon turnover models were integrated into the coupled SOILCO2/RothC model. For the conditions of the Missouri experiment the use of different soil temperature reduction functions had a strong effect on the simulation of CO_2 production and CO_2 fluxes. The maximum deviations of the simulated climate relevant cumulative CO_2 fluxes were 41% for the six month simulation period in 1981 and 30% for the eight month simulation period in 1982. In comparison, the effect of different soil moisture reduction functions was less strong with maximum deviations between CO_2 fluxes of 2% for 1981 and 1982. Simultaneous combination of soil temperature and soil moisture reduction functions resulted in higher deviations for the PATCIS and RothC model. For the CANDY, CENTURY, and DAISY model deviations were reduced. These contrary trends for the different models rebut a potential interdependency of soil temperature and moisture reduction functions. The functional sensitivity analysis revealed a roughly six times higher sensitivity of soil respiration towards the soil temperature reduction function than towards the soil moisture reduction function for the climatic and soil conditions of this experiment. This higher sensitivity is also effected by the reference temperature for rescaling of the temperature reduction functions. In our study, SOM decomposition was simulated with the RothC pool concept. Temperature reduction functions were therefore rescaled to the value of 1 at 9.25°C. The mean temperatures for the simulation periods in Missouri were clearly higher. As a consequence, the response to temperature was higher than the moisture response, where reduction functions did not have to be rescaled. For many applications, the choice of the temperature reduction function will be less influential. Usually, the fractions or the decomposition constants of the C-pools in a SOM model are calibrated for the experimental conditions. This procedure will remove some of the bias on the average respiration rates that arises from the choice of an inappropriate temperature reduction function.

Although multi-pool models differ in the number and interaction of C-pools the basic concept is the same. However, there is a great inconsistency in the approaches of temperature and moisture reduction functions for the calculation of the pool decomposition rates. We therefore think that the goodness of SOM turnover prediction is to a large extent determined by the formulation and parameterisation of the soil temperature and soil moisture reduction functions. In contrary, the model structure itself is of secondary importance. Hence, soil temperature and soil moisture reduction functions are a crucial factor for the application of carbon models at different field sites with conditions differing from those used to develop and validate a specific carbon turnover model. A reliable prediction of carbon turnover requires that the reduction functions of the model are valid for the environmental conditions of the simulation period, which is against the background of changing climatic conditions of high relevance.

3 Temperature response of wheat decomposition is more complex than the common approaches of most multi-pool models[*]

3.1 Introduction

The top metre of the world's soils contains twice as much carbon as the atmosphere (Eswaran et al., 1993). Soils are therefore an important component of the global carbon cycle, and any changes in stored soil carbon can significantly feed back onto atmospheric concentrations. For a reliable prediction of carbon dynamics under changing climatic conditions, the temperature sensitivity of soil organic matter (SOM) decomposition is highly relevant (Schlesinger and Andrews, 2000). Despite numerous studies that have been performed to determine the temperature sensitivity of SOM decomposition, there are still many open questions.

Well-established carbon turnover models, such as RothC (Coleman and Jenkinson, 2005), CENTURY (Parton et al., 2001), CenW (Kirschbaum and Paul, 2002), or DAISY (Hansen et al., 1990) express the temperature response of carbon turnover through a scaling factor that is applied uniformly to the decomposition rates of all pools. To describe the temperature response of SOM decomposition, different approaches are used. Besides the common Q_{10} and Arrhenius approaches, several other empirical formulations have been used by different authors (Kirschbaum, 2000). However, there have been discussions whether more resistant

---

[*] adapted from Bauer, J., Kirschbaum, M.U.F., Weihermüller, L., Huisman, J.A., Herbst, M., Vereecken, H., 2008b. Temperature response of wheat decomposition is more complex than the common approaches of most multi-pool models. Soil Biology and Biochemistry 40, 2780-2786.

fractions have a different temperature dependence than the more labile fractions (e.g. Coûteaux et al., 2001; Knorr et al., 2005). Other authors found that their datasets could be best explained by assuming that the degree of recalcitrance is itself a function of temperature (Zogg et al., 1997; Dalias et al., 2001b; 2001a). Possible explanations for that phenomenon could be shifts in the microbial community (Zogg et al., 1997) or biochemical pathways (Dalias et al., 2001a).

Numerous field and laboratory studies have been performed to investigate the temperature dependence of SOM decomposition. Due to numerous confounding factors, the determination of the temperature response from field experiments is challenging. Although laboratory experiments do not provide natural conditions, they are considered to be more appropriate for the determination of temperature responses than field experiments as confounding factors can be better controlled (Kirschbaum, 2000; 2006). A common approach for the interpretation of such respiration experiments is the use of a first-order two-pool model (Dalias et al., 2001a; Hyvonen et al., 2005; Rey and Jarvis, 2006; Braakhekke and de Bruijn, 2007).

In this study, we analysed respiration rates from the decomposition of wheat residues incubated at six different temperatures. The data were described by a first-order two-pool model, and we tested whether agreement between data and model could be improved by either using different temperature dependencies for the decomposition rates of the labile and recalcitrant carbon pool, or by assuming that the ratio of the initial pools also varied with temperature. Ultimately, our aim was to derive equations that could be used to describe the temperature response of wheat decomposition for use in simulating carbon turnover under field conditions.

3.2 Materials and methods

3.2.1 Soil and wheat characteristics

Soil was taken from the uppermost 25 cm from the lower part of the FLOWatch test site near Selhausen, Germany. A detailed description of the field site was provided by Weihermüller et al. (2007). In total, 59 soil samples were taken, which were mixed to obtain a single bulk sample. To provide identical initial conditions for each experiment, the bulk sample was homogenised by 2-mm sieving and mixing. The soil was stored at a temperature of 4°C in 2 l polyethylene flasks and adapted to the experimental temperature for three days before labelled wheat residues were added. The soil consisted of 14.4% sand, 68.9% silt, and 16.8% clay. Organic carbon, inorganic carbon, and nitrogen contents were 1.04, 0.106, and 0.13% (per unit mass), respectively. The soil contained 0.56 and 0.06% (per unit mass) of dithionite extractable Fe and Al, respectively, and the pH value was 6.8.

To follow the decomposition of fresh organic matter in the soil, growing spring wheat plants (Taifun) were labelled with ^{14}C. After harvest, the wheat residues, including roots, stems, and leaves, were airdried and finely ground to pieces smaller than 500 μm with an ultra centrifugal mill at 15000 RPM (Retsch, Germany). The wheat residues contained 39.5 ± 0.9% C and 1.34 ± 0.06% N. Specific activity was 0.134 kBq mg C^{-1}.

3.2.2 Experimental setup

Incubations for the assessment of the temperature dependence of soil respiration were carried out at six different temperatures (5°C, 9°C, 15°C, 25°C, 35°C, and 45°C) while the gravimetric water content of all samples was maintained at 16 ± 2% by regularly checking the weight of flasks and adding water as necessary. For samples incubated at 5°C, soil water content in the flasks had to be reduced by drying the air with silica gel before entering the sample flasks. During the initial phase of the 45°C experiment, the water content dropped to 9% before the problem was recognised and rectified. For each temperature, five replicates were examined. The experimental setup for the decomposition experiments is illustrated in Figure 3.1. For each replicate, 100 g of oven-dry soil was placed in a 250 ml glass flask and mixed with 0.5 g of ^{14}C labelled wheat straw residues. In order to guarantee a constant temperature, the reaction flasks were placed in temperature-controlled water baths. Temperature was maintained within ± 0.5°C. To avoid CO_2 enrichment within the microcosms, air was constantly pumped through the reaction system and any evolved CO_2 was trapped in a 0.5N - 1.0N NaOH solution (KMF, Germany). Samples were collected daily over the first 9 days of the experiment and with decreasing frequency over the later stages of the experiment. After each sample collection, NaOH flasks were exchanged with fresh ones.

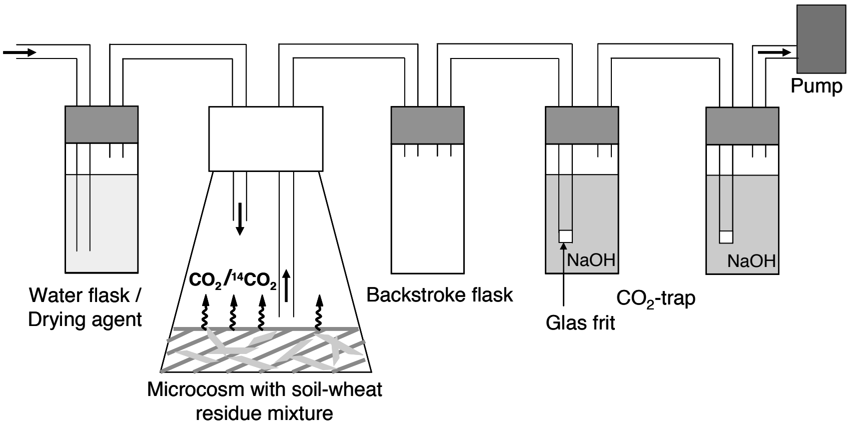

Figure 3.1: Schematic overview of the experimental setup for the decomposition experiment.

3.2.3 ^{14}C and elemental analysis

^{14}C concentrations in the wheat residues were determined from three aliquots using dry combustion (Tri-Carb sample Oxidizer 306, Canberra Packard, Groningen, The Netherlands). $^{14}CO_2$ was trapped in 15 ml Oxysolve (PerkinElmer, Boston, MA, USA) and quantified by liquid scintillation counting (LSC, Liquid Scintillation Analyzer 1500 Tri-Carb, Packard, Groningen, The Netherlands). ^{14}C concentrations in the NaOH solution were determined by LSC from three aliquots of 1 ml mixed with 10 ml Ultima-Gold (PerkinElmer, Boston, MA, USA). C, N, and H concentrations in the soil and wheat residue samples were determined using a Leco CHNS-932 analyser (St. Joseph, MI, USA) in the Central Division of Analytical Chemistry at the Forschungszentrum Jülich GmbH.

3.2.4 Interpretation of decomposition experiments

Data description by first-order two-pool models

We interpreted our respiration experiments by applying a first-order two-pool model. CO_2 production from first-order decay of two carbon pools was described by the following equation:

$$c_{CO2} = c_1\left(1 - e^{-\lambda_1 t}\right) + c_2\left(1 - e^{-\lambda_2 t}\right) \tag{3.1}$$

where c_1 and c_2 are the initial fractions [g C g C^{-1}] of a labile and a more recalcitrant pool, respectively, λ_1 and λ_2 [d^{-1}] are their decomposition rates, and t is time [d]. The initial phase of wheat decomposition was influenced by a lag-phase before maximal rates were observed. It is likely that the size of the initial microbial population was not sufficient to optimally utilise the large input of extra wheat straw, or that the population was not optimally adapted to the new litter material. In either case, there was evidence that there was a brief period when rates increased more or less exponentially which was indicative of the build-up of a microbial population of optimal size and composition. We included that effect by explicitly modelling the size of a microbial pool. The microbial growth rate was expressed by the depletion of the labile and recalcitrant pool. At the same time, the decomposition rates of both pools were limited by the relative size of the microbial pool. Within 10 days or less, depending on temperature, the microbial pool reached its optimal size and had no influence on the rate of decomposition processes subsequently. In order to describe the interdependence of the microbial growth and the decomposition of the carbon pools, equation (3.1) was expressed in a discrete form according to:

$$c_{CO2,i} = 1 - \left(c_{1,i} + c_{2,i}\right) \tag{3.2}$$

$$c_{p,i} = c_{p,i-1} \exp\left(-\lambda_p p_{MO,i-1} \Delta t\right) \tag{3.3}$$

where $c_{1,i}$ and $c_{2,i}$ are the concentrations of the labile and recalcitrant pools [g C g C^{-1}] at time i, respectively. The sum of the initial pool concentrations $c_{1,0}$ and $c_{2,0}$ [g C g C^{-1}] was equal to 1 by definition. Δt is the time step [d] which was set to 0.1 d. The decomposition rates λ_p [d] of the labile and recalcitrant pools were reduced by the relative size of the pool of micro-organisms p_{MO} [-] varying from 0 to 1 to indicate total inhibitory and non-limiting effects, respectively.

The microbial growth rate was controlled by the depletion of the labile and recalcitrant pool and a multiplicative factor f_{MO} [-].

$$p_{MO,i} = p_{MO,i-1} + p_{MO,i-1} f_{MO} \left(c_{1,i-1} - c_{1,i} + c_{2,i-1} - c_{2,i}\right)\left(1 - p_{MO,i-1}\right) \tag{3.4}$$

To determine a single parameter set that simultaneously described the measured CO_2 concentrations at all temperatures, the decomposition rates of the labile and recalcitrant pools were formulated as follows:

$$\lambda_p = \lambda_{0,p} f_T \tag{3.5}$$

where $\lambda_{0,p}$ [d] is the decomposition-rate constant of the labile or recalcitrant pool, which was multiplied by a scaling factor f_T as a function of temperature.

Data description by the RothC model and the SOM model of CenW/CENTURY

Respiration data were also interpreted by the well-established multi-pool-models RothC and CenW/CENTURY. The RothC model (Coleman and Jenkinson, 2005) consists of five carbon pools (Figure 3.2), four reactive ones and an inert pool (IOM). Plant inputs consist of decomposable plant material (DPM) and resistant plant material (RPM). The initial proportion of the DPM and RPM pool was inversely estimated. The DPM and RPM pools are decomposed to form microbial biomass (BIO), humified organic matter (HUM), and CO_2. As the BIO and HUM pools decompose, they form further BIO and HUM, with a proportion released as CO_2.

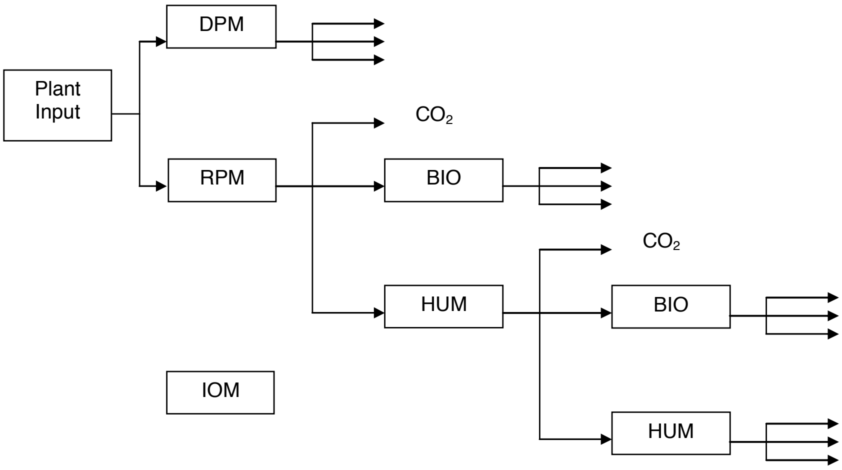

Figure 3.2: RothC pool concept (modified from Coleman and Jenkinson (2005)).

The CenW model (Kirschbaum, 1999; Kirschbaum and Paul, 2002) constitutes a coupling of the soil-organic matter component of the CENTURY model (Parton et al., 1987) with a more fully-developed and more detailed representation of above-ground plant- and ecosystem processes. For the present purpose, the CenW model is essentially the same as the CENTURY model of Parton et al. (1987). The SOM decomposition module of the CenW/CENTURY consists of five reactive carbon pools (Kirschbaum and Paul, 2002). Similar to the RothC model, plant input is partitioned between two pools, referred to as metabolic litter and structural litter. In CenW/CENTURY, the partitioning factor x_{ML} [-] is expressed in dependence on the lignin L_{In} [g g^{-1}] and nitrogen concentration N_{In} [g g^{-1}] of input material as:

$$x_{ML} = 0.85 - 0.018 L_{In} / N_{In} \tag{3.6}$$

Whereas the nitrogen concentration of the wheat residues was measured (see above), the lignin concentration was inversely estimated. The active, slow, and resistant SOM pools are charged from the decomposed fractions of the metabolic and structural litter pools and by each other. The carbon cycling between the single pools is illustrated in Figure 3.3.

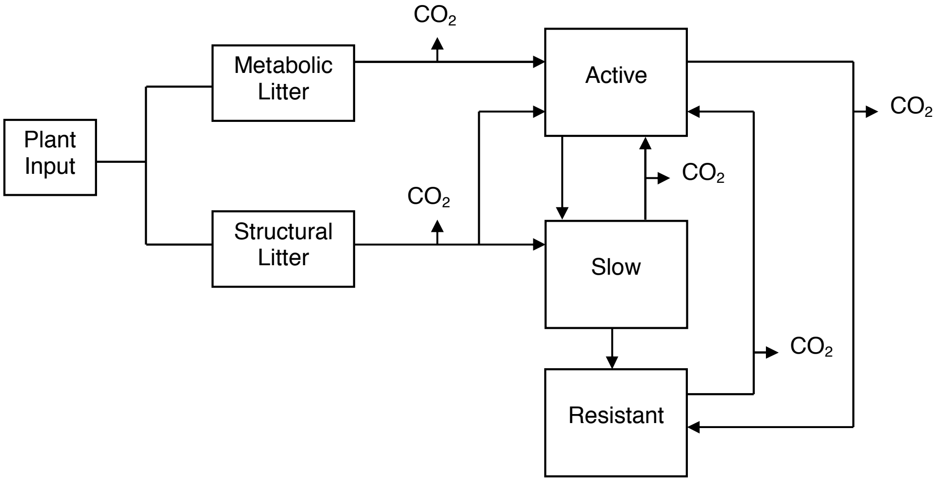

Figure 3.3: CenW/CENTURY pool concept (modified from Kirschbaum and Paul (2002)).

In both multi-pool models decomposition of all carbon pools follows first-order decay kinetics, where the decomposition rates of all pools are determined by scaling the decomposition rate constants with temperature and moisture reduction functions. The moisture reduction factor was the same for all temperature variants, as all experiments were conducted at the same water content.

Description of the relative temperature response

In order to describe the relative temperature response of wheat residue decomposition, the original formulation of the RothC model (Eq. ((3.7)), and for the CenW/CENTURY model, the equation derived by Kirschbaum (2000, Eq. (3.8)) was used.

$$f_T(T) = \frac{47.9}{1 + \exp\left(\frac{106}{T + 18.3}\right)} \tag{3.7}$$

$$f_T(T) = \exp(3.36(T - 40)/(T + 31.79)) \tag{3.8}$$

where T is the temperature [°C]. Furthermore, the common Q_{10} approach (van't Hoff, 1984) was chosen:

$$f_T(T) = Q_{10}^{(T - T_{ref})/10} \tag{3.9}$$

where T_{ref} is the reference temperature [°C].

3.2.5 Statistical analysis

The parameters providing the best prediction of the measured data were determined by the means of linear optimisation minimising the mean sum of squared residuals ($\Sigma MSSR$):

$$\Sigma MSSR = \sum_j \frac{1}{N_j} \sum_{i=1}^{N_j} \left(y_{obs,i} - y_{sim,i}\right)^2 \tag{3.10}$$

where y_{obs} are the observed data, y_{sim} are the simulated data, and N is the number of measurements of experiment j.

Akaike's information criterion (AIC) was calculated to decide which model described the decomposition experiment in the best way. The criterion, which was developed by Akaike (1973; 1974), describes the relationship between the Kullback-Leibler information (Kullback and Leibler, 1951) and likelihood theory and can be expressed as:

$$AIC = -2\log_e L_{Max} + 2M \tag{3.11}$$

where $\log_e L_{Max}$ is the maximised log-likelihood function and M is the number of model parameters. Within this manuscript, M is only the number of fitted parameters. For a least squares estimation with normally distributed errors, *AIC* can be calculated as:

$$AIC = N \log_e \left(\frac{\sum_{i=1}^{N} \left(y_{obs,i} - y_{sim,i} \right)^2}{N} \right) + 2(M+1) \qquad (3.12)$$

The equation uses M+1 instead of M because the variance needs to be estimated. Since the sample size was relatively small in the present work ($N/M < 40$ for the model with the largest M), the corrected Akaike information criterion (AIC_c) was used (Hurvich and Tsai, 1989; Burnham and Anderson, 2004):

$$AIC_c = AIC + \frac{2(M+1)(M+2)}{N-M-2} \qquad (3.13)$$

The best model is the one with the smallest *AIC* or AIC_c value.

A third performance measure considered in this study is the model efficiency (*ME*). This is an additional measure of model performance and is defined according to Nash and Sutcliffe (1970) as:

$$ME = 1 - \frac{\sum \left(y_{obs} - y_{sim} \right)^2}{\sum \left(y_{obs} - \overline{y_{obs}} \right)^2} \qquad (3.14)$$

where $\overline{y_{obs}}$ is the mean value of the observed data. *ME* values can vary between $-\infty$ and 1. High values close to 1 are obtained if observed and simulated data are closely related and without systematic bias. A negative *ME* indicates that the mean is a better predictor of the data than the applied model.

3.3 Results and Discussion

3.3.1 Description of carbon mineralization by two-pool-models

Previous studies have shown that carbon mineralization can be adequately described by models including two carbon pools decomposing simultaneously by first-order kinetics (Eq. (3.1)). In Figure 3.4 the observed decomposition of ^{14}C-labelled wheat residues at six different temperatures is compared. The decomposition pattern in the initial phase of incubation appeared to be considerably influenced by the adaptation of micro-organisms to the new substrate supply. Therefore, a further reduction factor for the scaling of the decomposition rates of the labile and recalcitrant pool was introduced. The omission of a description of this build-up lag-phase would have differentially affected the parameter estimation of the underlying temperature dependence.

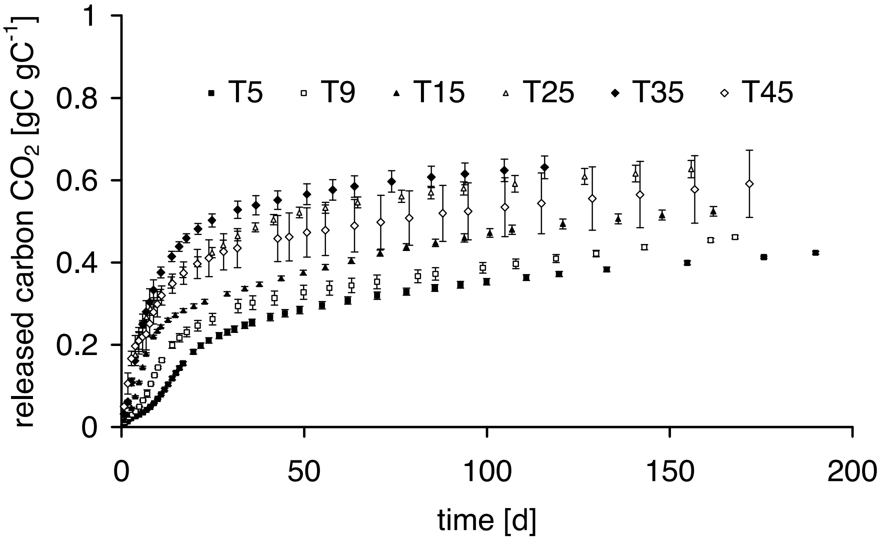

Figure 3.4: Measured cumulative carbon mineralization rates [g C g C^{-1}] from wheat residue decomposition at six temperatures. Data are illustrated as the mean values ± standard deviation from 5 replicates.

In Figure 3.5 the improvement of the prediction of measured initial CO_2 concentrations by first-order two-pool models by the inclusion of the lag-phase is illustrated. Firstly, measured data of the single experiments were predicted by a first-order two-pool model according to Eq. (3.1) as illustrated in Figure 3.5a. In this attempt, the lag-phase was omitted. In a second attempt, the microbial adaptation was included according to Eqs. (3.2) - (3.4). Thereby, data prediction was significantly improved (Figure 3.5b). Furthermore, during the first 7 days of incubation, the 45°C experiment was affected by a water loss of 7% which resulted in a temporary reduction of the decomposition rate. To describe the effect of the temporary water loss during the initial decomposition phase at 45°C, the calculated decomposition rate was reduced by an empirical factor over the few days of water shortage. It is not thought that this temporary water shortage would have caused any long-term effects on decomposition rate after it had been rectified.

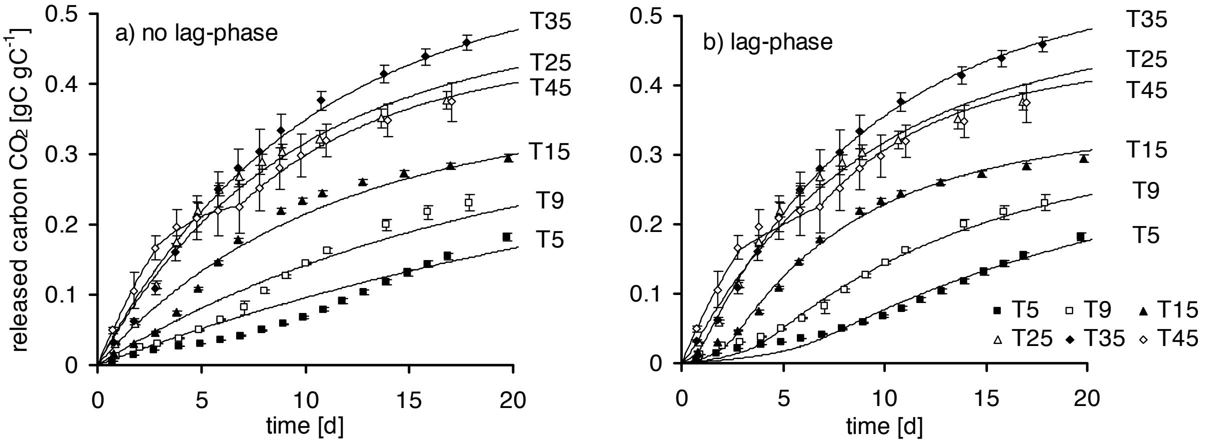

Figure 3.5: Initial phase of decomposition predicted by first-order two pool models, a) without consideration of microbial adaptation and b) with the introduction of a reduction factor to describe the adaptation of micro-organisms to substrate supply (lag-phase).

In Figure 3.6 we compare the state of decomposition after three and 110 days of incubation. The rate of carbon loss over the first three days provides a measure of the decomposition rate constant and the proportion of the labile carbon pool. After 110 days, the labile pool had been largely lost as CO_2 and the rate of carbon loss up to that point is therefore primarily determined by the recalcitrant pool. During the first three days, decomposition rates were highest at 45°C, whereas after 110 days, more carbon had been released from samples incubated at 35°C and 25°C than at 45°C. This observation indicates that more complex processes occur which cannot be described by simple two-pool models with the general expectation of a ratio of labile and recalcitrant pools that was invariant with temperature and the same temperature response functions for the decomposition of both labile and recalcitrant pools.

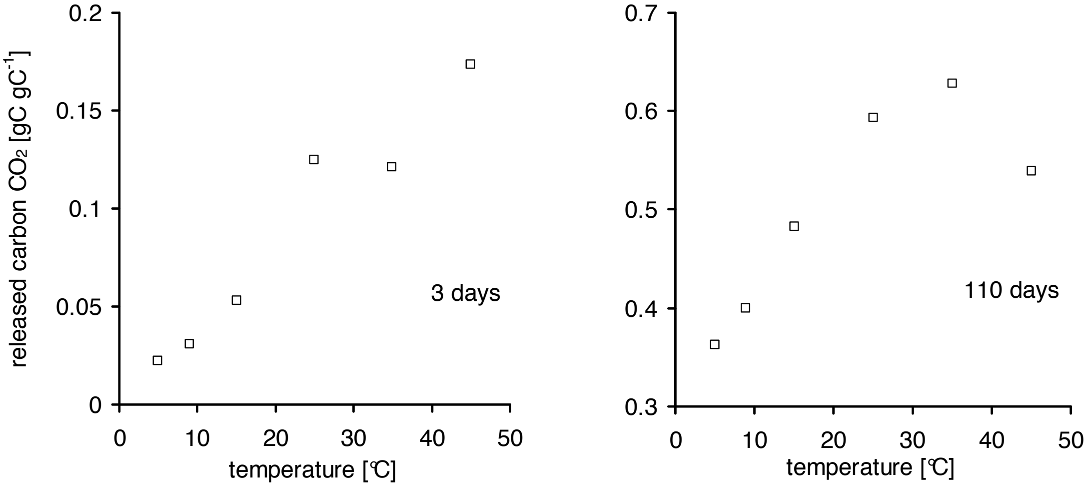

Figure 3.6: State of decomposition after 3 days and after 110 days of incubation.

For the interpretation of the measured CO_2 release by first-order two-pool models, we firstly assumed that the initial pool ratio was constant and determined the decomposition rates of the labile and recalcitrant pool assuming that both pools have the same underlying temperature dependence. Although the general course of CO_2 release at the six different temperatures was described by the model in an acceptable way over the time of incubation, carbon release rates tended to be under-estimated in the beginning and over-estimated in the later stages (Figure 3.7). We considered that the data description was not yet satisfactory and tested ways to improve the fit to the data.

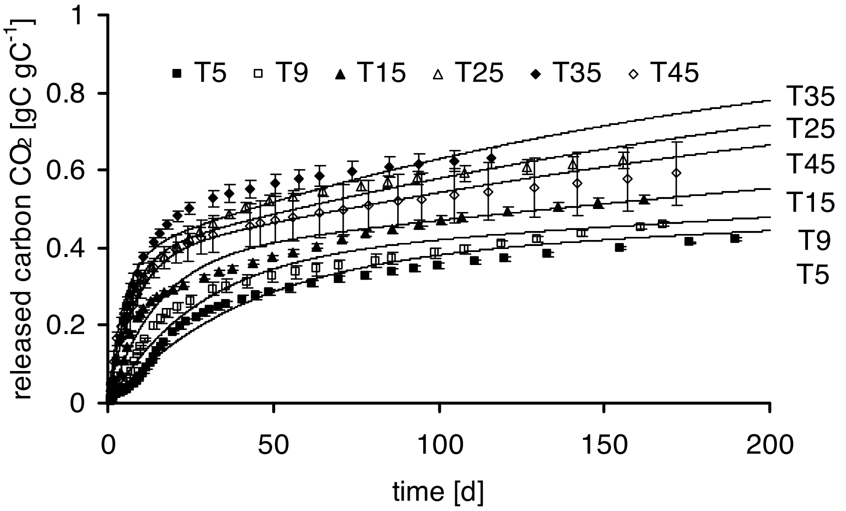

Figure 3.7: Prediction of CO_2 release from wheat residue decomposition at six temperatures by first-order two-pool models assuming a constant initial pool ratio and the same temperature dependence for the decomposition rates of the labile and recalcitrant pool.

To improve the data prediction, we tested two different hypothesises. Firstly, we assumed that the decomposition rates of the labile and recalcitrant pools had different temperature dependencies. Secondly, we assumed that the proportion of litter classified as labile or recalcitrant litter was itself a function of temperature. In other words, the underlying assumption was that the degree of chemical recalcitrance was in some way affected by temperature.

Both assumptions resulted in a significant improvement of data prediction expressed by smaller *MAE*s (Table 3.1), but the assumption of a temperature dependent initial pool ratio provided the strongest improvement. Not surprisingly, the more complex models provided better data prediction. However, models should also be as simple as possible. Hence, including additional processes into a model is only advisable if data prediction is significantly improved. Akaike's information criterion provides one objective measure of model quality by considering both the goodness of data prediction and model complexity. Applying that criterion to our possible models, we found that even though the two-pool model with a temperature dependent initial pool ratio had the highest number of parameters, it describes the data much better than two-pool models with a fixed initial pool ratio, and was therefore, judged to be the best of the three models. Measured CO_2 concentrations were predicted very well by this model as illustrated in Figure 3.8.

Table 3.1: Comparison of data prediction by first-order two-pool models with different assumptions for the initial pool ratio and the temperature response.

Scenario	Fitted parameters	*M*	*MAE* [-]	*AIC*$_c$ [-]	*ME* [-]
Same initial pool ratio / same temperature response	$c_1, p_{MO}, f_{MO}, f_W, k_1, k_2, f_T(T)$	12	0.0199	-1386	0.9797
Same initial pool ratio / different temperature responses	$c_1, p_{MO}, f_{MO}, f_W, \lambda_1(T), \lambda_2(T)$	16	0.0157	-1471	0.9877
Temperature dependent initial pool ratio / same temperature response	$c_1(T), p_{MO}, f_{MO}, f_W, \lambda_{0,1}, \lambda_{0,2}, f_T(T)$	17	0.0101	-1601	0.9938

Fitted parameters were the initial concentration of the labile pool (c_1), the initial ratio of micro-organisms (p_{MO}), the growth factor (f_{MO}), the moisture reduction factor (f_W), the decomposition constants of the labile ($\lambda_{0,1}$), the recalcitrant pool ($\lambda_{0,2}$), the temperature reduction factor (f_T), the decomposition rates of the labile (λ_1) and the recalcitrant pool (λ_2). If the parameter was assumed to be temperature dependent [(T)], a value was estimated for each incubation temperature. *M* is the number of fitted parameters, *MAE* is the mean absolute error, *AIC*$_c$ is the corrected Akaike information criterion, and *ME* is the model efficiency.

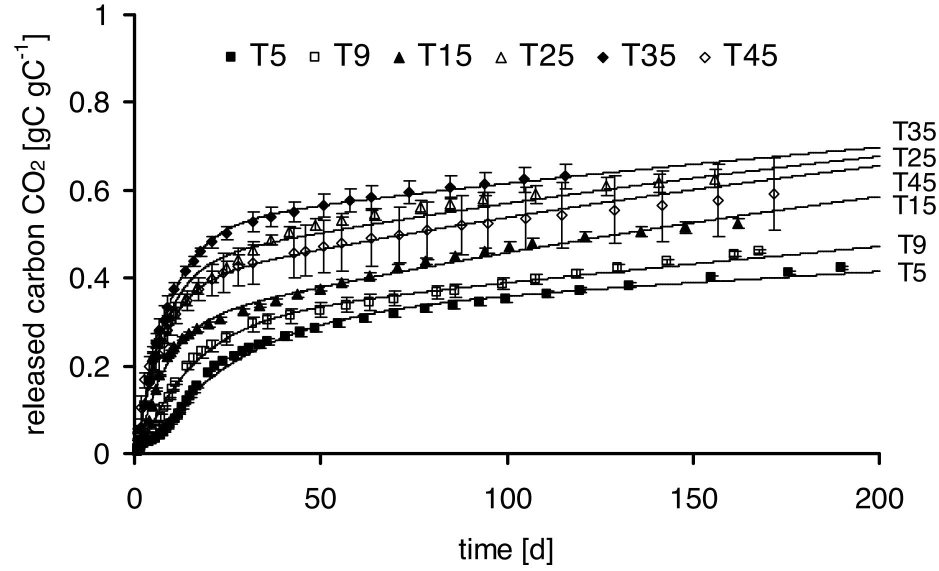

Figure 3.8: Prediction of CO_2 release from wheat residue decomposition at six temperatures by first-order two-pool models assuming a temperature dependent initial pool ratio and the same temperature dependence for the decomposition rates of the labile and recalcitrant pool.

3.3.2 Determination of temperature response functions

To determine the temperature response of the initial pool ratio, a Q_{10} equation was used to constrain the temperature course of the decomposition rate. By this preliminary fixing of the decomposition rates, a temperature course of the initial pool ratio emerged that was predicted well by an exponential equation according to:

$$x_1(T) = \exp\left(a_x + b_x T + c_x T^2\right) \tag{3.15}$$

where x_1 is the initial proportion of the labile pool [g C g C^{-1}]; a_x, b_x, and c_x are empirical constants [-]. The high value of the model efficiency shows that the formulation provides an unbiased estimation of the initial pool ratios. Using the two functional relationships presented in Figure 3.9, the *MAE* was 0.0133. The fitted Q_{10} value of 1.16 for the decomposition rate is quite low because much of the overall temperature response is expressed through an adjustment in the proportion of labile and recalcitrant pools. The decomposition rate constants at 20°C of the labile and recalcitrant pool were 0.1023 d^{-1} and 0.0022 d^{-1}, respectively.

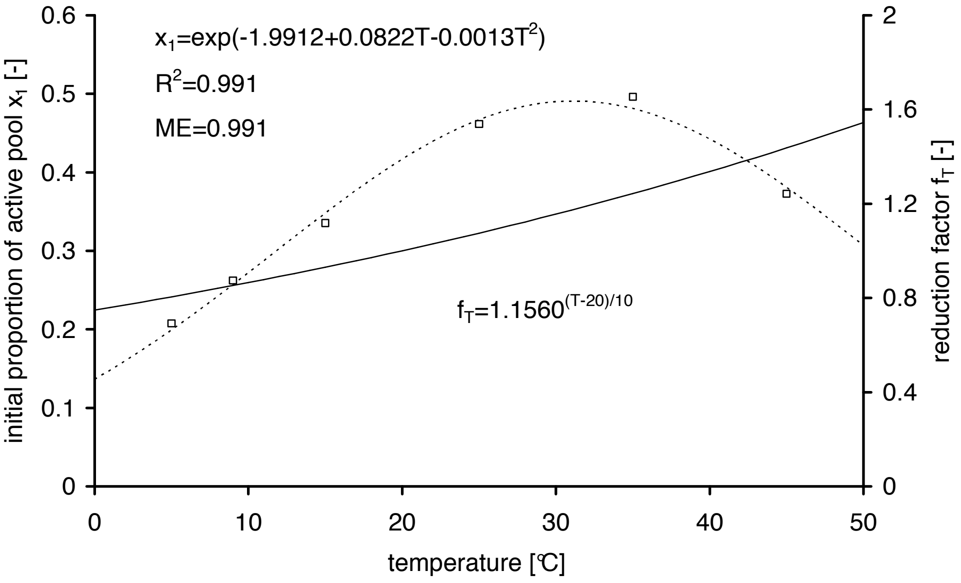

Figure 3.9: Temperature response for data prediction by a first-order two-pool model. The temperature dependence of the decomposition rates was predefined by a Q_{10} relationship (solid line). Fitted initial pool ratios for all temperatures (empty symbols) were described by an exponential function (dotted line).

3.3.3 Data description by multi-pool-models

The interpretation of short term laboratory experiments by two-pool models is a common approach. For the prediction of longer-term carbon turnover, however, more complex carbon pool models with a higher number of carbon pools are used. In the following, we assess the validity of our findings for the two multi-carbon-pool models, RothC and CenW/CENTURY. Therefore, the respiration data were fitted in a first step by both models retaining their original parameter settings and assumptions as described in the Section 3.2. With those original settings, the data were not well predicted by either multi-pool model as indicated by the high *MAE* values (Table 3.2). In a next step, we applied the temperature response concept that we developed for the two-pool model to the multi-pool models. According to this, the fresh litter pool ratio was defined by an exponential equation (Eq. (3.15)) and the relative temperature response by a Q_{10} relationship (Eq. (3.9)). Data prediction was significantly improved when we applied the temperature response functions derived in the upper section to the multi-pool models. Sufficient data prediction by either multi-pool model was only provided when temperature sensitivity was extended to the initial partitioning of fresh litter material (results not shown).

Table 3.2: Comparison of data prediction by the RothC and CenW/CENTURY model with different assumptions for the pool ratio of the fresh litter pools and the relative temperature response.

Scenario	Fitted parameters	M	MAE [-]	AIC_c [-]	ME [-]
RothC					
Original model assumptions[1]	$c_{DPM}, p_{MO}, f_{MO}, f_W, f_m$	5	0.0335	-1180	0.9353
Modified assumptions[2]	$a, b, c, p_{MO}, f_{MO}, f_W, f_m, Q_{10}$	8	0.0153	-1488	0.9875
CenW/CENTURY					
Original model assumptions[1]	$c_{Lig}, p_{MO}, f_{MO}, f_W, f_m$	5	0.0458	-1081	0.8912
Modified assumptions[2]	$c_{Lig}, a, b, c, p_{MO}, f_{MO}, f_W, f_m, Q_{10}$	9	0.0143	-1514	0.9892

[1]: Original model assumptions were the same initial pool ratio and the same relative temperature response defined by Eq. (3.7) for the RothC model and Eq. (3.8) for the CenW/CENTURY model.

[2]: Modified assumptions were a temperature dependent initial pool ratio described by Eq. (3.15) and the same relative temperature response defined by a Q_{10} relationship (Eq. (3.9)).

Fitted parameters were the initial concentration of DPM (c_{DPM}), the initial ratio of micro-organisms (p_{MO}), the growth factor (f_{MO}), the moisture reduction factor (f_W), a scaling factor for the decomposition constants (f_m), the initial lignin concentration (c_{Lig}), the Q_{10} value and the empirical parameters of the exponential response function (a, b and c). M is the number of fitted parameters, MAE is the mean absolute error, AIC_c is the corrected Akaike information criterion, and ME is the model efficiency.

3.4 General discussion and conclusions

In our work we set out to obtain simple temperature scaling factors for use in organic-matter turn-over models. However, the observed pattern of carbon loss could not be well described by application of simple scaling factors. Instead, our findings illustrate that the temperature response of SOM decomposition is more complicated than the pragmatic approaches used in most organic matter turnover models. This confirms the findings of other studies which have discussed the complexity of temperature sensitivity in a more theoretical way (Thornley and Cannell, 2001; Davidson and Janssens, 2006; Ågren and Wetterstedt, 2007). Other studies have used empirical approaches to identify differences in temperature dependence of decomposition by the different fractions (Coûteaux et al., 2001; Bååth and Wallander, 2003; Bol et al., 2003) but work to date has been inconclusive, and no real and consistent differences have been identified.

Coûteaux et al. (2002) investigated the decomposition of ^{14}C labelled wheat straw which was incubated *in situ* at six sites along a transect in the Venezuelan Andes. Similar to our findings, Coûteaux et al. (2002) found that the chemical recalcitrance of SOM was altered by temperature. Braakhekke and de Bruijn (2007), however, re-analysed the dataset of Coûteaux et al. (2002) by first-order two-pool models with a constant initial pool ratio and found that the data were predicted almost equally well as the more complex model chosen by Coûteaux et al. (2002). A weak point of the dataset was that the labile pool had been almost depleted by the time of the first measurement, and therefore, a reliable estimation of the decomposition rate of the labile pool was not possible. Due to the high number of observations, the dataset analysed in our study provides sufficient information for a more reliable estimation of the decomposition rates of the labile and recalcitrant pools.

For long-term dynamics of organic matter in soils, stabilisation of soil organic matter through interactions with the soil matrix is an important process (e.g. van Veen and Kuikman, 1990). It is less clear, however, what quantitative role it plays over the shorter term of incubation experiments. We performed a number of model test runs to assess the effect of stabilisation on the decomposition patterns with constraints by parameter sets of realistic turn-over times and pool sizes of the stabilised soil organic matter in natural soils. With such constraints, we found that SOM stabilisation had very little effect on the model results and hardly modified any trends we observed (data not shown). Therefore, we did not consider this process in our models any further.

Our work indicates that either the decomposition of differently labile materials responds differently to temperature or that there is an even more complex interaction between temperature and the degree of chemical recalcitrance. Our results gave the greatest possible improvement if we assumed that chemical recalcitrance changed with temperature. A question may be asked how chemical recalcitrance could change with temperature, but it is possible, for example, that some fatty acids may be liquefied at higher temperature and readily decomposable, whereas become solidified and much more recalcitrant at lower temperature.

The existence of such more complex temperature interactions, if it can be confirmed through further work, considerably complicates the use of organic matter turn-over models. While it might, in principle, be possible to add temperature as an extra variable in defining the categorization of litter into different fractions, this becomes significantly more difficult when temperature changes continuously with time and would require a continuous adjustment of litter fractions with any change in temperature. Nonetheless, models need to attempt to describe reality as it is understood, and if experimental data suggest that temperature interactions are more complex than currently implemented in existing models, then it makes a case for modification of these models in order to capture reality.

4 Inverse determination of soil heterotrophic respiration response to temperature and water content under field conditions*

4.1 Introduction

Soil respiration is an important flux of CO_2 to the atmosphere (Schlesinger and Andrews, 2000). Against the background of global climate change, reliable model predictions of soil respiration are highly relevant. Amongst other factors, accurate knowledge of the response of soil carbon decomposition to changes in soil temperature and water content is essential for reliable predictions (Singh and Gupta, 1977; Howard and Howard, 1993; Davidson and Janssens, 2006). In the past, both laboratory and field experiments have been used to determine the response of soil heterotrophic respiration to changes in soil temperature and water content. Thereby, it is assumed that laboratory studies provide more reliable estimates of these temperature and water responses than field experiments (Kirschbaum, 2000; 2006). However, laboratory incubation experiments are typically performed under highly artificial conditions. For example, the natural soil structure is commonly destroyed by sieving and homogenisation. Therefore, the transferability of response equations determined in the laboratory to real field situations is ambiguous.

---

* adapted from Bauer, J., Weihermüller, L., Huisman, J. A., Herbst, M., Graf, A., Séquaris, J. M., Vereecken, H., 2009. Inverse determination of soil heterotrophic respiration response to temperature and water content under field conditions. Biogeochemistry. Submitted.

The direct estimation of temperature and water responses from *in situ* measurements is complicated and often biased by confounding factors. For example, soil temperature and water content are highly interdependent because high temperatures are often accompanied by low water contents and vice versa (Davidson et al., 1998). Such a strong interdependency makes it difficult to separate the effects of temperature and water on soil respiration. Furthermore, changes in soil organic matter (SOM) quantity and quality during the course of a field experiment (e.g. fresh litter input, depletion of labile compounds) could strongly influence the direct estimation of response functions. A third confounding factor is that soil respiration originates from two processes: i) the decomposition of soil organic matter (heterotrophic respiration) and ii) root respiration. It is unlikely that both processes have the same response towards changes in temperature and water content. A fourth and final confounding factor is related to the choice of measurement depth/volume to relate soil temperature, soil water, and soil respiration. For example, the attenuation and phase shift of the soil temperature amplitude vary with soil depth (Pavelka et al., 2007; Bahn et al., 2008; Reichstein and Beer, 2008), which means that different temperature responses will be found for different temperature measurement depths (e.g. Xu and Qi, 2001; Pavelka et al., 2007). Recently, Graf et al. (2008) provided recommendations to obtain more reliable approximations of the temperature response from field measurements.

In this study, we evaluate an alternative inverse modelling approach to determine the temperature and water response of soil heterotrophic respiration. Recently, Weihermüller et al. (2009) presented a laboratory experiment to determine the soil water response function of soil respiration using inverse modelling. However, inverse modelling has not yet been used to determine both temperature and water responses from field data. Since the inverse modelling approach can account for many of the confounding factors discussed above, it could provide a more reliable quantification of the response of soil respiration to changes in soil temperature and water content. To this end, we analyse a dataset of bare soil respiration using the SOILCO2/RothC-model for the simulation of the 1-dimensional water flux, heat and CO_2 transport, and CO_2 production (Herbst et al., 2008). The parameters of different functional approaches to describe the temperature and water response are determined using inverse modelling. Finally, we compare the temperature response functions obtained with inverse modelling with those obtained from a classical regression method.

4.2 Materials and methods

4.2.1 Model description

We used the 1-dimensional numerical model SOILCO2/RothC to predict soil water content, soil temperature, CO_2 production, and CO_2 transport. A brief model description is provided in Chapter 2. For detailed information, we refer to Šimůnek and Suarez (1993) and Herbst et al. (2008).

4.2.2 Response functions

The availability of water is essential for soil microbial activity. Increasing soil water content enhances substrate diffusion. However, the supply of oxygen is reduced when water content is high (Skopp et al. 1990). As a consequence, increasing water content first enhances microbial activity, but becomes repressive for water contents higher than some optimum. We used an exponential relationship to describe the water response f_W:

$$f_W(\theta) = \frac{\exp\left(a_W\theta + b_W\theta^2\right)}{\exp\left(\frac{-a_W^{\;2}}{4b_W}\right)} \tag{4.1}$$

where θ is the volumetric water content [$cm^3\ cm^{-3}$], and a_W and b_W are empirical parameters. The denominator is a normalisation factor used to obtain a maximum value of 1 at the optimal water content, θ_{opt} [$cm^3\ cm^{-3}$], which is located at:

$$\theta_{opt} = -\frac{a_W}{2b_W} \tag{4.2}$$

For the temperature response, we used several common approaches from literature. First, we used the temperature reduction function of the RothC pool concept:

$$f_{T,orig} = \frac{47.9}{1+\exp\left(\frac{106}{T+18.3}\right)} \tag{4.3}$$

where T is the temperature [°C].

The original RothC equation is equal to 1 at a reference temperature T_{ref} of 9.25°C. This formulation can be rescaled by dividing the original formulation by the value of the original equation at the reference temperature as expressed by the following equation:

$$f_T = \frac{1}{f_{T,orig}\left(T_{ref}\right)} f_{T,orig} \tag{4.4}$$

Second, we used a modified form of the Arrhenius relationship (e.g. Šimůnek and Suarez, 1993; Fang and Moncrieff, 1999):

$$f_T = \exp\left(\frac{E*\left(T - T_{ref}\right)}{R*\left(273.15 + T\right)*\left(273.15 + T_{ref}\right)}\right) \tag{4.5}$$

where E is the activation energy of the reaction [kg cm^2 d^{-2} mol^{-1}] and R is the universal gas constant [kg cm^2 d^{-2} °C^{-1} mol^{-1}] (R=8.314 kg m^2 s^{-2} K^{-1} mol^{-1}). Both the RothC and the Arrhenius approach show an increase in microbial decomposition with increasing temperature. Additionally, we analysed relationships with an optimal temperature. The first one is an exponential equation according to O'Connell (1990):

$$f_T = \exp\left(a_1 + b_1 T\left(1 - 0.5T/T_{opt}\right)\right) \tag{4.6}$$

where a_1 and b_1 are empirical parameters and T_{opt} is the optimum temperature. The second relationship was introduced by Parton et al. (1987):

$$f_T = a_2 + b_2 T^{d_2} - \left(T/c_2\right)^{e_2} \tag{4.7}$$

where a_2, b_2, c_2, d_2, and e_2 are empirical parameters. Negative response factors were set to 0.

4.2.3 Determination of the activation energy from linear regression analysis

Conventionally, the activation energy of soil respiration is derived from a linear regression analysis based on the Arrhenius formulation (Johnson and Thornley, 1985) according to:

$$\lambda = \beta \exp\left(\frac{E}{R(T+273.15)}\right) \tag{4.8}$$

where β [h^{-1}] is a constant. This formulation can be linearised using a log-transform:

$$\log_e \lambda = \log_e \beta - \frac{E}{R(T+273.15)} \tag{4.9}$$

The activation energy can then be calculated from the slope s_1 of the linear regression equation according to:

$$E = -s_1 R \tag{4.10}$$

4.2.4 Field measurements

All measurements were perfomed at the FLOWatch test site which is located in the river Rur catchment. The soil was classified as an Orthic Luvisol according to USDA classification and consists of three horizons ranging from 0 to 33 cm, 33 to 57 cm, and 57 to 130+ cm. The soil texture is a silt loam. A detailed description of the test site is given by Weihermüller et al. (2007). Our investigation covered the time period from October 2006 until October 2007. CO_2 flux measurements were only available until September 2007. During this period, weeds were continuously removed manually and/or by herbicide (glyphosate) application. In April 2007, the soil was power harrowed. In June 2007, a larger amount of weed was removed manually.

Soil temperature was measured at 0.5, 3, 5, and 10 cm depth by type T thermocouples and at 15, 30, 45, 60, 90, and 120 cm depth by pF-meters (Ecotech, Bonn, Germany). Soil water content was measured at 15, 30, 45, 60, 90, and 120 cm depth from April to October 2007 by custom made 3 rod TDR probes with a rod length of 20 cm. All TDR probes were connected to a Campbell multiplexing and data logging system (Campbell Scientific, Logan, Utah, USA). The raw waveforms were stored and analysed semi-automatically using the Matlab routine TDRAna developed in the Forschungszentrum Jülich GmbH. Matric potentials were recorded at 120 cm by pF-meters (Ecotech, Bonn, Germany). Climatic data were provided from the meteorological tower of the Forschungszentrum Jülich GmbH (5.4 km NW from the test site).

CO_2 fluxes were measured by automated soil CO_2 flux chambers (Li-8100, Li-Cor Inc., Lincoln, Nebraska, USA) operated with the Li8100 multiplexer system. From October 2006 to April 2007, CO_2 fluxes were measured twice an hour using a single chamber. In April 2007, we installed a three chamber multiplexer system that measured 4 times per hour. All chambers were placed on a soil collar with a diameter of 20 cm and a height of 7 cm, of which 5 cm were belowground. Each chamber was closed for two minutes and the rise in CO_2 concentration was measured with an infrared gas analyser. To estimate the CO_2 flux, a linear regression was fitted to the measured CO_2 concentrations. Finally, hourly mean CO_2 fluxes and standard deviations were calculated. In order to remove outliers, we did not consider fluxes with a standard deviation larger than 5 times the mean standard deviation.

To characterise the organic carbon within the Ap-horizon, samples were taken with a spate from 3 depths (0-10, 10-20, and 20-30 cm) in October 2006. Additionally, mixed soil samples from 3 locations were taken from deeper depths (30-40, 40-50, 50-60, 60-100 cm) in June 2007. The organic carbon content of the soil samples was analysed using a Leco CHNS-932 analyser (St. Joseph, MI, USA). The particulate organic matter (POM) content was determined according to Skjemstad et al. (2004) as the physical carbon fraction from 53 to 2000 μm. Black carbon was determined using mid infrared spectroscopy (Bornemann et al. 2008), and was taken as an equivalent for the inert organic carbon (IOM) content.

4.2.5 Model parameterisation and initialisation

Since measured data were not available at the beginning of the simulation, the initial soil water profile was derived from measurements for a comparable period in 2007. An atmospheric boundary condition was used to describe the upper boundary. The reference potential evapotranspiration was estimated according to the FAO guidelines (Allen et al., 1998) from measured atmospheric temperature, precipitation, wind speed, atmospheric pressure, relative humidity, and actual duration of sunshine. The potential evaporation of a bare soil was calculated from the reference potential evapotranspiration by multiplication with a factor of 1.15 (Allen et al., 1998). The lower boundary was described by measured matric potentials. Figure 4.1 shows the precipitation and potential evaporation for the study period. The total precipitation was 831 mm and the total potential evaporation was 757 mm.

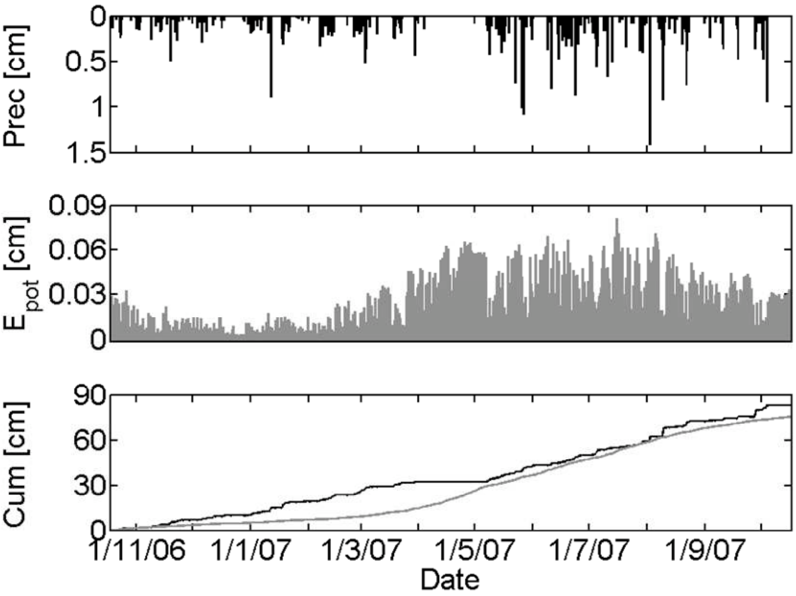

Figure 4.1: Precipitation (Prec), potential evaporation (E_{pot}), cumulative precipitation (black), and potential evaporation (grey) between October 2006 and October 2007.

The initial conditions and the upper and lower boundary conditions for heat transport were derived from measured soil temperatures. Missing surface temperatures (T_{surf}) were estimated from atmospheric temperatures (T_{atm}) using a linear regression function ($T_{surf} = 1.1173 T_{atm} - 0.9057$; $R^2 = 0.88$). Missing temperatures in 120 cm soil depth were estimated by linear interpolation. The parameters for the thermal conductivity of a loamy soil were taken from Chung and Horton (1987, Table 4.1) and are summarised in Table 4.1.

Initial CO_2 concentrations within the soil profile were taken from a forward model run from a comparable period in 2007. CO_2 concentration at the soil surface was set to the atmospheric concentration of 0.038%. The lower boundary was defined as a zero flux boundary. All additional CO_2 transport parameters are summarised in Table 4.1.

Table 4.1: Heat (Chung and Horton, 1987) and CO_2 transport parameters (Patwardhan et al., 1988) used in the numerical simulation.

Parameter	Value	Unit
Heat transport		
Thermal dispersivity	1.5	cm
Empirical constant B_1 of soil thermal conductivity function	1.134E+12	kg cm^{-1} h^{-3} $°C^{-1}$
Empirical constant B_2 of soil thermal conductivity function	1.834E+12	kg cm^{-1} h^{-3} $°C^{-1}$
Empirical constant B_3 of soil thermal conductivity function	7.157E+12	kg cm^{-1} h^{-3} $°C^{-1}$
CO_2 transport		
Molecular diffusion coefficient of CO_2 in air at 20°C	572.4	cm^2 h^{-1}
Molecular diffusion coefficient of CO_2 in water at 20°C	0.0637	cm^2 h^{-1}
Longitudinal dispersivity of CO_2 in water	1.5	cm

The initial carbon pool sizes were determined using the physical fractionation scheme of Skjemstad et al. (2004). The size of the IOM pool was set to the measured black carbon fraction. We assumed that the soil did not contain any DPM at the beginning of the simulation. The RPM fraction c_{RPM} was defined by the measured POM fraction. The fraction of HUM and BIO was calculated as the remaining fraction from the total organic carbon [$c_{HUM} + c_{BIO} = c_{org} - (c_{DPM} + c_{RPM} + c_{IOM})$]. The proportion between BIO and HUM was 0.0272 according to Zimmermann et al. (2007). Since no information about SOM composition for soil layers deeper than 30 cm was available at the beginning of the simulation period, we used the SOM characteristics determined 8 months later and assumed that SOM was not significantly altered in the deeper soil horizons. This assumption was later confirmed by our simulations, which indicate that the mean carbon loss from the RPM pool was only 4% in the 30 to 60 cm depth range for the entire study period. Carbon pool concentrations were linearly distributed between the mean measurement depths. In Table 4.2 the measured concentration of SOM, POM, and black carbon are summarised.

Table 4.2: Measured carbon concentration of soil organic matter (SOM), particulate organic matter (POM), and black carbon (BC) in the soil profile. In brackets the percentages of POM and BC from SOM are given.

Depth [cm]	SOM [mg C cm^{-3}]	POM [mg C cm^{-3}]	BC [mg C cm^{-3}]
0-10	18.54	3.30 (17.8%)	2.12 (11.4%)
10-20	17.87	2.50 (14.0%)	2.43 (13.6%)
20-30	17.21	2.50 (14.5%)	2.52 (14.6%)
30-40	7.92	0.51 (6.4%)	1.93 (24.4%)
40-50	5.62	0.29 (5.2%)	1.71 (30.4%)
50-60	4.72	0.23 (4.9%)	1.42 (30.1%)
60-100	4.26	0.21 (4.9%)	1.35 (31.7%)

Fresh weed material was added to the upper 15 cm of the soil after soil tillage in April 2007. For different crop stands, crop rotations, and fertilization rates various authors proposed annual carbon inputs via roots and crop residuals ranging from 1.5 to more than 3.8 t C ha^{-1} (Jenkinson and Coleman, 1994; Coleman and Jenkinson, 1996; Coleman et al., 1997; Falloon et al., 1998). In general, largest C inputs were reported for grasslands and lower ones for different crop rotations. In all cases, large proportions of the plant material will be removed by harvesting. In our case, larger amounts of fresh plant material were incorporated into the soil, and therefore, we assumed a total input of 3 t C ha^{-1}.

4.2.6 Inverse parameter estimation

To find the set of model parameters that best describe the measurements, the global optimisation algorithm SCE-UA was used (Duan et al., 1992). This algorithm searches the parameter space to find the minimum of used-defined objective function. In this study, we used the sum of squared residuals (*SSR*):

$$SSR = \sum_{i=1}^{N} \left(y_{obs,i} - y_{sim,i} \right)^2 \qquad (1)$$

where y_{obs} and y_{sim} are the observed and simulated data, respectively and N is the number of data pairs available to compare observation and simulation. The SCE algorithm has been shown to be a powerful tool for calibration of hydrological models (Madsen et al., 2002) and has been successfully applied in other application areas (e.g. Bauer et al., 2008; Peters and Durner, 2008).

For a reliable prediction of the water transport, the hydraulic parameters of four soil layers were inversely estimated. To reduce the number of estimated parameters, we assumed that the saturated and residual water contents were constant over the entire soil profile. This assumption is in good agreement with laboratory results for the same location, where the mean saturated water content is 0.390 cm^3 cm^{-3} with a standard deviation of only 0.03 cm^3 cm^{-3}. In total, we estimated 14 hydraulic parameters (one θ_s and θ_r for the entire profile and α, n, and K_s for each layer). Additionally, we imposed a decrease of K_s with depth. We used 3899 water content measurements at 15, 30, 45, 60, and 90 cm and 2247 measurements at 120 cm depth in the inversion. In a second step, we inversely estimated the parameters of the temperature and water content response equations from 6269 CO_2 flux measurements. For both optimization runs, SCE-UA was stopped when the change of the objective function was less than 0.1% in 10 consecutive loops.

4.2.7 Statistical criteria of model quality

Two criteria were used to judge the quality of the model simulations. First, we calculated the coefficient of determination (R^2):

$$R^2 = \left(\frac{\sum_{i=1}^{N} \left(y_{obs,i} - \overline{y_{obs}}\right)\left(y_{sim,i} - \overline{y_{sim}}\right)}{\sqrt{\sum_{i=1}^{N} \left(y_{obs,i} - \overline{y_{obs}}\right)^2 \sum_{i=1}^{N} \left(y_{sim,i} - \overline{y_{sim}}\right)^2}} \right)^2 \tag{4.11}$$

where $\overline{y_{obs}}$ and $\overline{y_{sim}}$ are the arithmetic means of the observed and simulated data, respectively. The model efficiency *ME* (Nash and Sutcliffe, 1970) was used as a second criterion:

$$ME = 1 - \frac{\sum_{i=1}^{N} \left(y_{obs,i} - y_{sim,i}\right)^2}{\sum_{i=1}^{N} \left(y_{obs,i} - \overline{y_{obs}}\right)^2} \tag{4.12}$$

A model efficiency close to 1 indicates that observed and simulated data are closely related and without systematic bias. A model efficiency lower than 0 means that the mean is a better predictor of the data than the applied model.

4.3 Results and discussion

4.3.1 Simulation of soil water contents and soil temperatures

In order to predict the water flow, the hydraulic parameters were inversely estimated. The measured soil water content could not be sufficiently described by the model with one set of hydraulic parameters for the plough horizon Ap (upper 33 cm). Corresponding to the findings of Abbaspour et al. (2000), the Ap horizon had to be divided into two separate layers with different hydraulic properties to provide a good prediction of the measured soil water content (Figure 4.2). The Ap horizon was divided at a depth of 20 cm, which is the penetration depth of the power harrow. The hydraulic properties yielding the best prediction of measured soil water content are summarised in Table 4.3. The resulting high n value ($n = 1.97$) of the upper soil layer is not representative for a silt loam soil, which might be due to the large coarse fraction (10 - 15 mass% > 2 mm). In addition, the soil structure of this upper layer was changed due to tillage. However, the water flow of the upper soil layer was predicted well and 87% of the variation in soil water content measured at 15 cm depth was explained.

Table 4.3: Estimated hydraulic parameters according to the Mualem-van Genuchten approach (van Genuchten, 1980) of the soil layers. Note that θ_r and θ_s were assumed to be constant with depth to reduce number of parameters for the estimation.

Layer	Depth [cm]	θ_r [cm^3 cm^{-3}]	θ_s [cm^3 cm^{-3}]	α [cm^{-1}]	n [-]	K_s [cm h^{-1}]
1	0-20	0.008	0.389	0.012	1.97	3.82
2	20-33	0.008	0.389	0.023	1.23	2.64
3	33-57	0.008	0.389	0.011	1.30	2.12
4	57-120	0.008	0.389	0.007	1.22	0.28

θ_r: residual water content, θ_s: saturated water content, α: inverse of the bubbling pressure, n: parameter, K_s: saturated hydraulic conductivity.

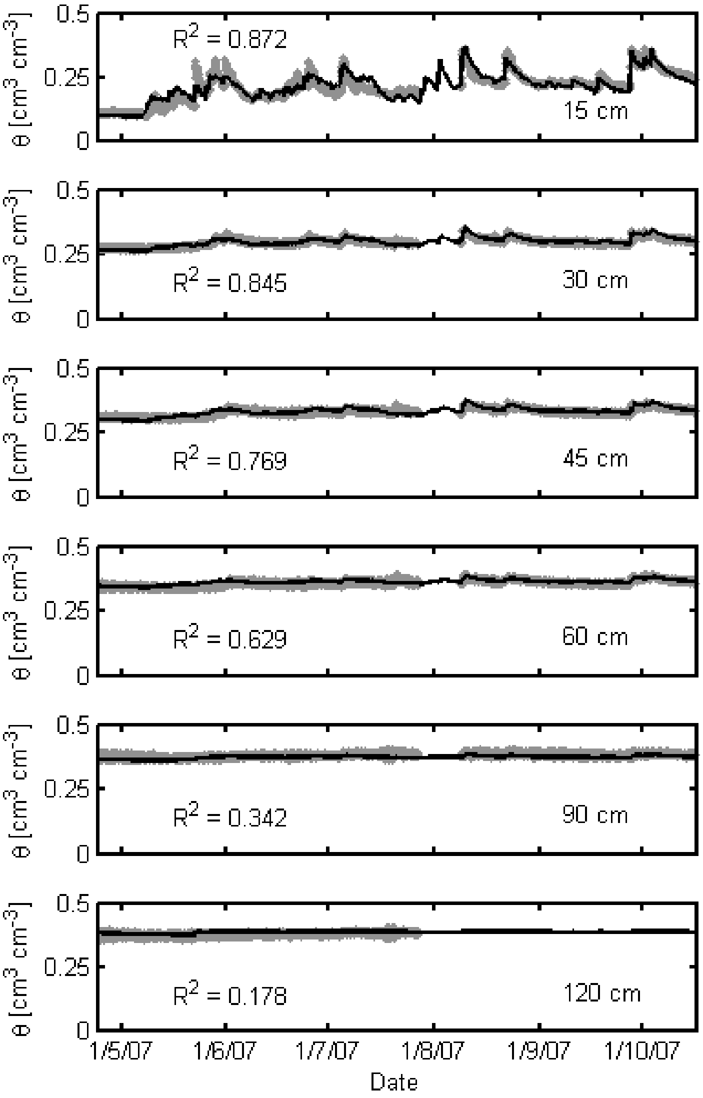

Figure 4.2: Measured (grey symbols) and simulated (black lines) water contents at different soil depths.

Measured soil temperatures were predicted well by the model (Figure 4.3) with the parameter settings described in Section 4.2. However, soil temperature was overestimated by up to 3°C for the first soil layers from mid-November to early January. In this period, only a few surface temperature measurements were available, and therefore, surface temperatures were estimated from atmospheric temperatures.

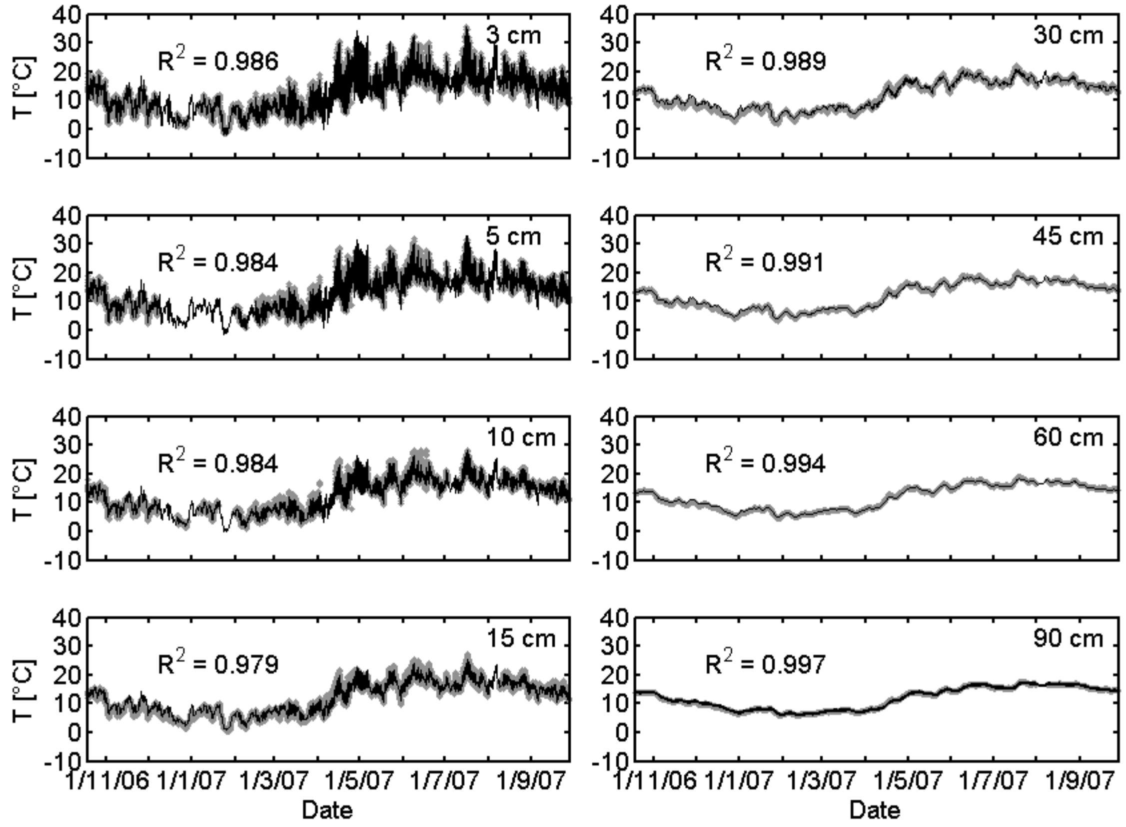

Figure 4.3: Measured (grey) and simulated (black) temperature in different soil depths.

4.3.2 Simulation of CO_2 fluxes

To determine the temperature and water response equations which are most appropriate to describe the measured CO_2 fluxes, the parameters of an exponential water content response function and four different temperature response functions were inversely estimated. The results are summarised in Table 4.4. Data prediction was worst when the original RothC temperature response equation was used. Prediction of measured CO_2 fluxes was significantly improved when the RothC temperature response equation was scaled to another optimised reference temperature (Sum of Squared Residuals, *SSR,* decreased from 812 to 632 (kg C ha^{-1} $h^{-1})^2$). Best data prediction was provided by the approach of Parton et al. (1987) with a *SSR* value of 538 (kg C ha^{-1} $h^{-1})^2$. However, the Arrhenius and O'Connell (1990) equations produced only slightly larger errors (*SSR* of 542 and 547 (kg C ha^{-1} $h^{-1})^2$, respectively). The mean measured CO_2 flux was 0.398 kg C ha^{-1} h^{-1}. The temperature response equation of O'Connell (1990) provided the highest agreement between measured and simulated mean CO_2 flux ($\overline{y_{sim}}$ = 0.399 kg C ha^{-1} h^{-1}, Table 4.4). We therefore consider the equation of O'Connell (1990) as the most appropriate formulation to describe the temperature response for our field dataset.

Table 4.4: Prediction of measured CO_2 fluxes using different approaches for the temperature response.

Temperature response	Estimated temperature parameters	Estimated water parameters	SSR [(kg C ha^{-1})^2]	R^2 [-]	ME [-]	$\overline{y_{sim}}$ [kg C ha^{-1}]
RothC$_{orig}$ (Eq. (4.3))	-	$a_W = 157.81$ $b_W = -360.44$	812	0.63	0.60	0.457
RothC$_{scale}$ (Eq. (4.3), (4.4))	$T_{ref} = 14.3°C$	$a_W = 58.16$ $b_W = -126.30$	632	0.70	0.69	0.421
Arrhenius (Eq. (4.5))	$T_{ref} = 15.5°C$ $E = 98$ kJ mol^{-1}	$a_W = 64.91$ $b_W = -136.39$	547	0.73	0.73	0.409
O'Connell (Eq. (4.6))	$a_1 = -3.3416$ $b_1 = 0.2611$ $T_{opt} = 42.64$	$a_W = 60.90$ $b_W = -127.55$	542	0.73	0.73	0.399
Parton (Eq. (4.7))	$a_2 = 0.2073$ $b_2 = 0.0001$ $c_2 = 31.52$ $d_2 = 3.254$ $e_2 = 75.69$	$a_W = 61.44$ $b_W = -128.50$	538	0.73	0.73	0.405

SSR: sum of squared residuals, R^2: coefficient of determination, ME: model efficiency, $\overline{y_{sim}}$: arithmetic mean of simulated respiration.

In Figure 4.4 the measured and simulated CO_2 flux is shown for the temperature response equation according to O'Connell (1990). Furthermore, the distribution of CO_2 released during decomposition, soil water content, and soil temperature in the upper soil horizon (0-33 cm) are illustrated. In general, the course of measured CO_2 fluxes was well described by the model. In January 2007, soil surface temperatures dropped below 0°C. This freezing period was followed by a strong CO_2 release up to 1.4 kg C ha^{-1} h^{-1}. A possible explanation for the observed CO_2 flush is the death of microbial biomass due to the low temperature and the subsequent decomposition of this new carbon source with increasing soil temperatures and reactivated microbial activity (e.g. Matzner and Borken, 2008). Since this process can not be described by the model, the measurements of this period were not considered to avoid bias in the inverse parameter estimation procedure. The simulations indicate that most CO_2 was produced in the upper 15 cm of the soil profile in May and June 2007. In the last half of April and the first half of May 2007, the soil surface layer was almost dry. The low water content obviously hampered SOM decomposition since CO_2 fluxes were significantly lower than in the following period despite high temperatures and fresh carbon input in April 2007 due to tillage. High measured CO_2 fluxes were systematically underestimated during the first half of June 2007. The higher uncertainty in the measured CO_2 fluxes during this period expressed by the high standard deviations of up to 1.5 kg C ha^{-1} can not completely explain the observed mismatch. Probably, additional CO_2 was released by decomposing plant roots which remained in the soil after manual weed removal. The period of highest soil temperatures in July 2007 was not accompanied by highest CO_2 fluxes despite moderate soil water contents. This can be explained by the decrease of the fresh litter input quantity and quality during the course of decomposition.

Figure 4.5 presents the four temperature response functions obtained using inverse modelling. The RothC function clearly deviates from the other three functions. This can be explained by the limited flexibility of the RothC function where only the reference temperature was variable and the curvature was fixed. The other three functions are very similar for temperatures < 25°C. For temperatures above 25°C, the three functions highly diverge. Despite this divergence, the prediction of measured CO_2 fluxes is similar good. The reasons for the uncertainty in the course of the temperature response function for high temperatures are twofold. First, temperatures ≥ 25°C only occurred up to a maximum depth of 18 cm. Second, simulated temperature exceeds 25°C only 1.6% of the time. Overall, the good agreement between these three temperature response equations despite their different functional forms is a good indicator for the reliability of the inverse modelling approach.

The optimized water responses are also shown in Figure 4.5. The curvatures of the water response equations combined with the temperature response function of Arrhenius, O'Connell (1990), and Parton et al. (1987) are almost identical (Figure 4.5). The calculated optimal water content was 0.24 cm^3 cm^{-3}, which corresponds to a water filled pore space of 62%. This value is in good agreement with many other studies that found optimal aerobic microbial activity between 50 and 80% water filled pore space (e.g. Greaves and Carter, 1920; Rovira, 1953; Rixon and Bridge, 1968; Pal and Broadbent, 1975; Weihermüller et al., 2009).

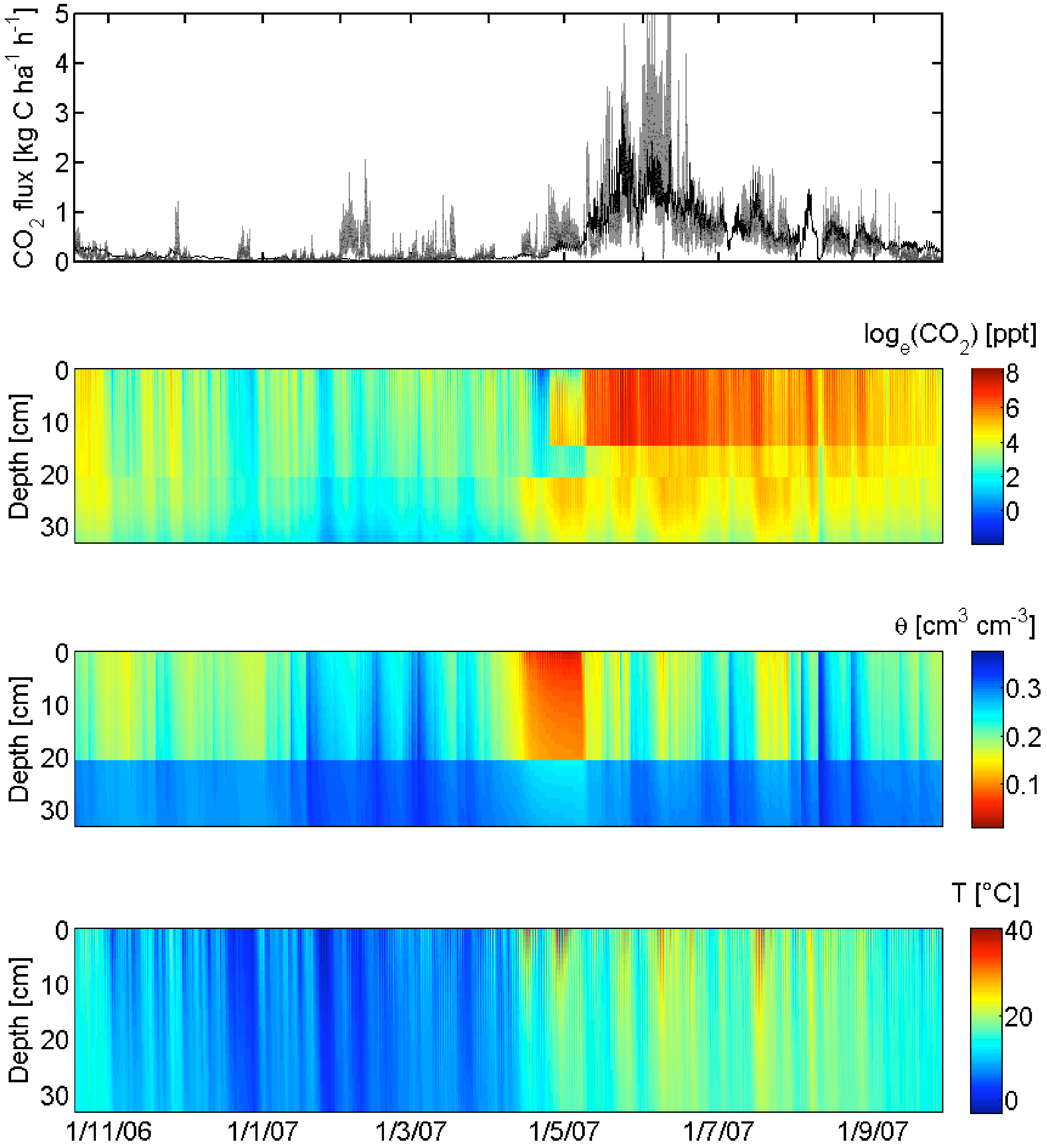

Figure 4.4: Measured and modelled CO_2 flux using an exponential water response equation and the temperature response equation according to O'Connell (1990). Measured CO_2 fluxes are shown as mean values with standard deviation (grey). Simulated CO_2 fluxes are illustrated as black line. Simulated CO_2 concentration, water content, and temperature are plotted for the plough horizon (upper 33 cm). CO_2 concentration is plotted as natural logarithmic values in parts per trillion (ppt = 10^{-12} cm^3 cm^{-3}).

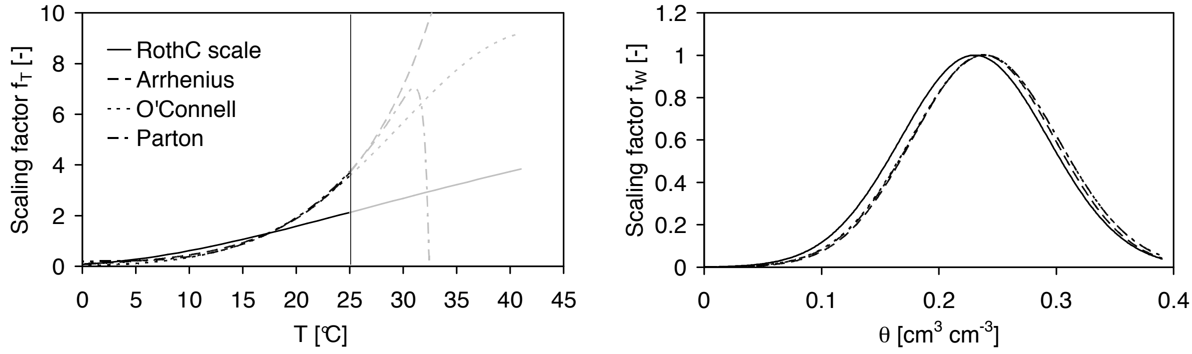

Figure 4.5: Optimized temperature and water response functions. Parameters for all functions are listed in Table 4.4

4.3.3 Comparison to conventionally determined temperature responses

Typically, the temperature response of soil respiration in field studies is quantified by fitting a regression between fluxes measured at the surface and temperatures measured in a certain soil depth (or occasionally air temperature). This practice has been criticised because confounding factors such as correlations with water (Davidson et al., 1998), or the effect of temperature measurement depth (Graf et al., 2008) might strongly affect the temperature sensitivity. It is therefore insightful to compare the temperature sensitivity determined by our model study, which takes into account water effects and heat transfer in the soil, to the one that would have been determined by the conventional way. For reasons of comparability between the two different methods of data analysis, we used simulated instead of measured soil temperatures. This is justified by the excellent model predictions for soil temperature (Figure 4.3). As has been shown before, temperature response derived from the traditional regression analysis highly depends on the depth of the temperature measurement with apparently stronger temperature responses with increasing depth (Pavelka et al., 2007; Graf et al., 2008). The linear regression analysis provided an activation energy of 92 kJ mol^{-1} for temperature measurements at the soil surface and a much higher value of 126 kJ mol^{-1} for a depth of 10 cm, illustrating the ambiguity of the classical regression method. The inversely estimated activation energy was 98 kJ mol^{-1}, which is in between the activation energy estimates for soil surface temperature and the temperature measured at 10 cm depth (Figure 4.6). Assuming that water sensitivity, and temporal and spatial distribution of substrate supply are determined correctly, this value represents an estimate of the intrinsic temperature sensitivity. Unlike the regression-based estimates which depend on the set-up and scale of the study, it provides the best estimate for use in any process-based forward model, fulfilling the criteria given by Reichstein and Beer (2008).

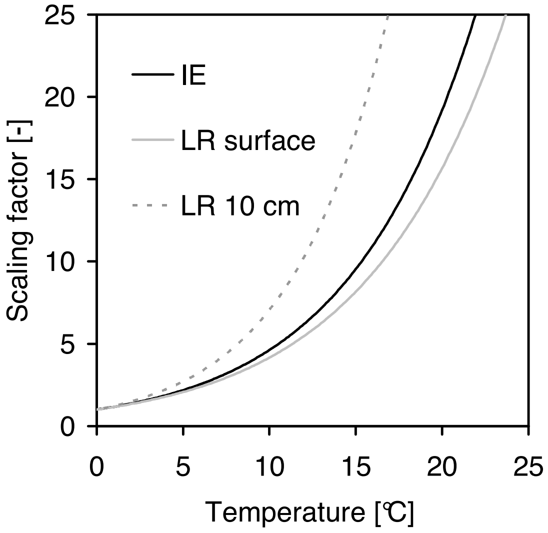

Figure 4.6: Comparison of temperature response determined by inverse parameter estimation (IE) and the conventional linear regression method (LR) for different soil depths.

4.4 Summary and conclusions

The temperature and water response of soil heterotrophic respiration are crucial for a reliable prediction of soil carbon dynamics. In this study, we determined the temperature and water response of soil heterotrophic respiration from an agricultural soil at the test site Selhausen by the means of inverse parameter estimation using the SOILCO2/RothC model. Due to the implementation of the RothC multi-pool carbon concept into the physically based transport model SOILCO2, temporal changes of temperature, water content, and the concentration and composition of SOM can be described in a high spatial resolution over the entire soil profile.

The inverse parameter estimation approach considered four widely used temperature response functions. The best prediction of measured CO_2 fluxes was obtained by an exponential water response function with an optimum at 62% water filled pore space and a temperature response equation according to the formulation of O'Connell (1990). However, the commonly used Arrhenius equation provided similarly good results. The divergence of the fitted temperature response functions for temperatures > 25°C indicates that the fitted functions might not be reliable in this range. The excellent agreement between the temperature response functions for temperatures below 25°C is encouraging.

The direct determination of the temperature and water response from field measurements is complicated by the interdependency of soil temperature and water, the quantitative and qualitative change of SOM, and the contribution of root respiration to measured soil respiration. Apparent response equations derived from relating measured CO_2 flux to temperature or water indicators (e.g. matric potential, water content, precipitation and evapotranspiration) determined in specific soil depths may significantly differ from the intrinsic response. The activation energy determined using the conventional regression method varied between 92 kJ mol^{-1} and 126 kJ mol^{-1} for the upper 10 cm of the soil profile, whereas the intrinsic response was equal to 98 kJ mol^{-1}. The activation energy of the Arrhenius equation determined by inverse modelling was nicely bracketed by those determined using the conventional regression approach. In conclusion, the inversely estimated temperature and water response equations provide an unbiased and reasonable prediction of measured CO_2 fluxes. Determination of response equations from *in situ* measurements by the means of inverse parameter estimation is a promising method for a more reliable prediction of soil carbon turnover for areas with different soil and climate conditions.

5 Synthesis

5.1 Summary

This thesis focused on the investigation of the temperature and moisture response of soil heterotrophic respiration either in numerical models, or laboratory and field experiments.

The general motivation of the work was the ongoing discussion about appropriate formulations for the temperature and moisture response of heterotrophic soil respiration. Therefore, we started up to analyse the influence of the choice of different temperature and moisture response functions from six well-established carbon turnover models on the prediction of heterotrophic respiration using a realistic case scenario (Chapter 2). In a second step, we performed laboratory microcosm experiments to study the decomposition process of ^{14}C labelled wheat residues at variable ambient temperatures (Chapter 3). Finally, we determined the temperature and moisture response equations from *in situ* measurements by the means of inverse parameter estimation (Chapter 4).

As already stated, the aim of the first study was the assessment of the influence of different soil temperature and moisture reduction functions on the simulation of SOM decomposition and CO_2 fluxes (Chapter 2). In order to do so, we first validated the coupled SOILCO2/RothC model for the chosen test scenario**.** In a next step, the sensitivity of soil CO_2 fluxes towards the reduction functions taken from six different well established carbon turnover models was quantified. As a overall finding we calculated deviations of up to 41% in the predicted cumulative CO_2 efflux between different model scenarios based on the choice of the temperature response equation. The influence of the different moisture response equations was lower with deviations between the simulated CO_2 fluxes up to 2%. These results lead to the conclusion that much of model uncertainty may be reduced by using temperature and moisture response equations that have been determined from experiments at the investigated field sites.

As a consequence, we performed a decomposition experiment of fresh organic matter incubated at six ambient temperatures (Chapter 3). The background to do so was the assumption that laboratory experiments are considered to be more appropriate to determine the temperature and moisture response of soil heterotrophic respiration compared to field trials, since confounding factors such as spatial and temporal changes in soil water content and soil organic matter can be better controlled. To clearly identify the decomposition process we used ^{14}C-labelled wheat residues. Respiration data were interpreted by first-order two-pool models. The overall findings showed that measured respiration could not be sufficiently described by the general assumptions of i) a constant initial pool ratio and ii) the same temperature response of the decomposition rates of all pools. Nevertheless, we significantly improved data prediction by the assumption that different temperature responses of the labile and recalcitrant pool exist. However, the integration of a temperature dependent chemical recalcitrance provided even higher improvement in data prediction. The findings of this study indicate that the temperature dependence of organic matter decomposition cannot be fully described with the simple approaches that are usually employed.

Although confounding factors can be better controlled in laboratory experiments, they are performed under highly artificial conditions and the transferability of the derived temperature and moisture responses to field conditions is therefore questionable. To overcome this restrictions temperature and moisture response equations were determined from *in situ* measurements by the means of inverse parameter estimation (Chapter 4). In contrast to the classical method for the *in situ* determination of the temperature response (Q_{10} or activation energy) from a linear regression between log-transformed CO_2 fluxes and temperatures measured in a definite soil depth, the inverse modelling approach considers all confounding factors included in the model. Furthermore, the derived temperature response is univocal and provides a more realistic estimate of the intrinsic temperature response. Measured CO_2 fluxes were best predicted by an exponential water content response equation with an optimum at 62% water filled pore space and a temperature response equation according to the formulation of O'Connell (1990). Although different approaches for the temperature response were tested, the estimated response factors showed a high agreement over the entire range of soil water contents and for temperatures < 25°C.

5.2 Conclusions and perspectives

Several processes are involved in SOM turnover such as stabilisation processes, the supply of substrates, nutrients, and oxygen. Most of these processes are affected by temperature and/or soil moisture content. A reliable prediction of soil carbon turnover under changing environmental conditions requires models which describe the involved processes in a realistic way. On the other hand, models should be as simple as possible to keep them manageable. Multi-pool models are currently the most accepted approach for the simulation of soil carbon turnover. Although progress has been made in relating conceptual pools of multi-pool models to measureable soil carbon fractions, carbon pools remain largely simplified modelling constructs (Davidson and Janssens, 2006). A central question is whether this simplified model approaches are appropriate to represent soil carbon dynamics in a reliable way or if additional process understanding is needed and should be included. In this work some of the open questions could be solved. The key for all work presented was the use of carbon turnover modelling in combination with parameter estimation.

Nevertheless, several processes need to be further investigated. Among these, the influence of the soil microbial community on SOM decomposition is considered to be very important (Reichstein and Beer, 2008). Furthermore, processes changing soil structure need to be further investigated since carbon pool sizes are often related to physical soil fractions. Processes which change the soil structure include i) aggregate formation, e.g. by microbial cementing agents and root exudates and ii) aggregate destruction, e.g. by tillage practises, wetting and drying events, or freezing and thawing (Paustian, 1994). Although temperature and moisture are the most important abiotic factors controlling SOM decomposition, the influence of other factors such as soil acidity, oxygen and nutrient availability should be investigated in more detail (Reichstein and Beer, 2008).

Bibliography

Abbaspour, K., Kasteel, R., Schulin, R., 2000. Inverse parameter estimation in a layered unsaturated field soil, Soil Science, pp. 109-123.

Adams, E.E., Caldeira, K., 2008. Ocean storage of CO_2. Elements 4, 319-324.

Adams, J.M., Faure, H., Fauredenard, L., McGlade, J.M., Woodward, F.I., 1990. Increases in terrestrial carbon storage from the last glacial maximum to the present. Nature 348, 711-714.

Ågren, G.I., Wetterstedt, J.Å.M., 2007. What determines the temperature response of soil organic matter decomposition? Soil Biology and Biochemistry 39, 1794-1798.

Akaike, H., 1973. Information theory as an extension of the likelihood principle. In: B.N. Petrov, F. Csaki (Eds.), International Symposium on Information Theory. Akademiai Kiado, Budapest, pp. 267-281.

Akaike, H., 1974. A new look at the statistical model identification. IEEE Transactions on Automatic Control 19, 716–723.

Akinremi, O.O., McGinn, S.M., McLean, H.D.J., 1999. Effects of soil temperature and moisture on soil respiration in barley and fallow plots. Canadian Journal of Soil Science 79, 5-13.

Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop evapotranspiration - guidelines for computing crop water requirements - FAO irrigation and drainage paper 56, FAO - Food and Agriculture Organization of the United Nations, Rome, Italy.

Anderson, J.M., 1992. Responses of soils to climate-change. Advances in Ecological Research 22, 163-210.

Andrén, O., Paustian, K., 1987. Barley straw decomposition in the field - a comparison of models. Ecology 68, 1190-1200.

Bååth, E., Wallander, H., 2003. Soil and rhizosphere microorganisms have the same Q(10) for respiration in a model system. Global Change Biology 9, 1788-1791.

Bahn, M., Rodeghiero, M., Anderson-Dunn, M., Dore, S., Gimeno, C., Drösler, M., Williams, M., Ammann, C., Berninger, F., Flechard, C., Jones, S., Balzarolo, M., Kumar, S., Newesely, C., Priwitzer, T., Raschi, A., Siegwolf, R., Susiluoto, S., Tenhunen, J., Wohlfahrt, G., Cernusca, A., 2008. Soil respiration in European grasslands in relation to climate and assimilate supply. Ecosystems 11, 1352 - 1367.

Batjes, N.H., 1996. Total carbon and nitrogen in the soils of the world. European Journal of Soil Science 47, 151-163.

Bauer, J., Herbst, M., Huisman, J.A., Weihermüller, L., Vereecken, H., 2008. Sensitivity of simulated soil heterotrophic respiration to temperature and moisture reduction functions. Geoderma 145, 17-27.

Benson, S.M., Cole, D.R., 2008. CO_2 sequestration in deep sedimentary formations. Elements 4, 325-331.

Bol, R., Bolger, T., Cully, R., Little, D., 2003. Recalcitrant soil organic materials mineralize more efficienctly at higher temperatures. Journal of Plant Nutrition and Soil Science 166, 300-307.

Braakhekke, W.G., de Bruijn, A.M.G., 2007. Modelling decomposition of standard plant material along an altitudinal gradient: A re-analysis of data of Couteaux et al. (2002). Soil Biology and Biochemistry 39, 99-105.

Burnham, K.P., Anderson, D.R., 2004. Multimodel inference - understanding AIC and BIC in model selection. Sociological Methods and Research 33, 261-304.

Buyanovsky, G.A., Wagner, G.H., 1983. Annual cycles of carbon dioxide level in soil air. Soil Science Society of America Journal 47, 1139-1145.

Buyanovsky, G.A., Wagner, G.H., Gantzer, C.J., 1986. Soil respiration in a winter wheat ecosystem. Soil Science Society of America Journal 50, 338-344.

Cerri, C.E.P., Coleman, K., Jenkinson, D.S., Bernoux, M., Victoria, R., Cerri, C.C., 2003. Modeling soil carbon from forest and pasture ecosystems of Amazon, Brazil. Soil Science Society of America Journal 67, 1879-1887.

Chung, S.O., Horton, R., 1987. Soil heat and water flow with a partial surface mulch. Water Resources Research 23, 2175-2186.

Coleman, K., Jenkinson, D.S., 1996. RothC-26.3 - A model for the turnover of carbon in soil. In: D.S. Powlson, P. Smith, J.U. Smith (Eds.), Evaluation of Soil Organic Matter Models Using Existing Long-Term Datasets. NATO ASI Series I. Springer-Verlag, Heidelberg, pp. 237-246.

Coleman, K., Jenkinson, D.S., Crocker, G.J., Grace, P.R., Klir, J., Korschens, M., Poulton, P.R., Richter, D.D., 1997. Simulating trends in soil organic carbon in long-term experiments using RothC-26.3. Geoderma 81, 29-44.

Coleman, K., Jenkinson, D.S., 2005. ROTHC-26.3. A Model for the Turnover of Carbon in Soil. Model Description and Windows Users Guide, Harpenden, 45 pp.

Conley, M.M., Kimball, B.A., Brooks, T.J., Pinter, P.J., Hunsaker, D.J., Wall, G.W., Adam, N.R., LaMorte, R.L., Matthias, A.D., Thompson, T.L., Leavitt, S.W., Ottman, M.J., Cousins, A.B., Triggs, J.M., 2001. CO_2 enrichment increases water-use efficiency in sorghum. New Phytologist 151, 407-412.

Couteaux, M.M., Sarmiento, L., Bottner, P., Acevedo, D., Thiery, J.M., 2002. Decomposition of standard plant material along an altitudinal transect (65-3968 m) in the tropical Andes. Soil Biology and Biochemistry 34, 69-78.

Coûteaux, M.M., Bottner, P., Anderson, J.M., Berg, B., Bolger, T., Casals, P., Romanyà, J., Thiéry, J.M., Vallejo, V.R., 2001. Decomposition of ^{13}C-labelled standard plant material in a latitudinal transect of European coniferous forests: Differential impact of climate on the decomposition of soil organic matter compartments. Biogeochemistry 54, 147-170.

Dalias, P., Anderson, J.M., Bottner, P., Couteaux, M.M., 2001a. Long-term effects of temperature on carbon mineralisation processes. Soil Biology and Biochemistry 33, 1049-1057.

Dalias, P., Anderson, J.M., Bottner, P., Couteaux, M.M., 2001b. Temperature responses of carbon mineralization in conifer forest soils from different regional climates incubated under standard laboratory conditions. Global Change Biology 7, 181-192.

Davidson, E.A., Belk, E., Boone, R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. Global Change Biology 4, 217-227.

Davidson, E.A., Verchot, L.V., Cattanio, J.H., Ackerman, I.L., Carvalho, J.E.M., 2000. Effects of soil water content on soil respiration in forests and cattle pastures of eastern Amazonia. Biogeochemistry 48, 53-69.

Davidson, E.A., Janssens, I.A., 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 440, 165-173.

de Marsily, G., 1986. Quantitative hydrology - Groundwater hydrology for engineers. Academic, San Diego, Calif., 440 pp.

Diels, J., Vanlauwe, B., Van der Meersch, M.K., Sanginga, N., Merckx, R., 2004. Long-term soil organic carbon dynamics in a subhumid tropical climate: C-13 data in mixed C-3/C-4 cropping and modeling with ROTHC. Soil Biology and Biochemistry 36, 1739-1750.

Duan, Q.Y., Sorooshian, S., Gupta, V., 1992. Effective and efficient global optimization for conceptual rainfall-runoff models. Water Resources Research 28, 1015-1031.

Eswaran, H., Vandenberg, E., Reich, P., 1993. Organic-carbon in soils of the world. Soil Science Society of America Journal 57, 192-194.

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

Fang, C., Moncrieff, J.B., 1999. A model for soil CO_2 production and transport 1: Model development. Agricultural and Forest Meteorology 95, 225-236.

Fang, C.M., Smith, P., Moncrieff, J.B., Smith, J.U., 2005. Similar response of labile and resistant soil organic matter pools to changes in temperature. Nature 433, 57-59.

Feddes, R.A., Kowalik, P.J., Zaradny, H., 1978. Simulation of field water use and crop yield. John Wiley, New York, 188 pp.

Franko, U., Oelschlägel, B., Schenk, S., 1995. Modellierung von Bodenprozessen in Agrarlandschaften zur Untersuchung der Auswirkungen möglicher Klimaveränderungen. UFZ-Bericht 3/1995, UFZ-Umweltforschungszentrum Leipzig-Halle GmbH, Leipzig.

Friedmann, S.J., 2007. Geological carbon dioxide sequestration. Elements 3, 179-184.

Garcia, R.L., Long, S.P., Wall, G.W., Osborne, C.P., Kimball, B.A., Nie, G.Y., Pinter, P.J., Lamorte, R.L., Wechsung, F., 1998. Photosynthesis and conductance of spring-wheat leaves: field response to continuous free-air atmospheric CO_2 enrichment. Plant Cell and Environment 21, 659-669.

Giardina, C.P., Ryan, M.G., 2000. Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature. Nature 404, 858-861.

Graf, A., Weihermüller, L., Huisman, J.A., Herbst, M., Bauer, J., Vereecken, H., 2008. Measurement depth effects on the apparent temperature sensitivity of soil respiration in field studies. Biogeosciences 5, 1175-1188.

Greaves, J.E., Carter, E.G., 1920. Influence of moisture on the bacterial activities of the soil. Soil Science 10, 361-387.

Hansen, S., Jensen, H.E., Nielsen, N.E., Svendsen, H., 1990. DAISY - Soil Plant Atmosphere System Model. NPO Report No. A 10. NPo-forskning fra Miljostyrelsen. The National Agency for Environmental Protection, Copenhagen, 272 pp.

Heinen, M., 2006. Simplified denitrification models: Overview and properties. Geoderma 133, 444-463.

Herbst, M., Hellebrand, H.J., Bauer, J., Huisman, J.A., Šimůnek, J., Weihermuller, L., Graf, A., Vanderborght, J., Vereecken, H., 2008. Multiyear heterotrophic soil respiration: Evaluation of a coupled CO_2 transport and carbon turnover model. Ecological Modelling 214, 271-283.

Holloway, S., 2001. Storage of fossil fuel-derived carbon dioxide beneath the surface of the earth. Annual Review of Energy and the Environment 26, 145-166.

Houghton, R.A., 2007. Balancing the global carbon budget. Annual Review of Earth and Planetary Sciences 35, 313-347.

Howard, D.M., Howard, P.J.A., 1993. Relationships between CO_2 evolution, moisture-content and temperature for a range of soil types. Soil Biology and Biochemistry 25, 1537-1546.

Hurvich, C.M., Tsai, C.L., 1989. Regression and time-series model selection in small samples. Biometrika 76, 297-307.

Hyvonen, R., Agren, G.I., Dalias, P., 2005. Analysing temperature response of decomposition of organic matter. Global Change Biology 11, 770-778.

IPCC, 2001. Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change In: J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, C.A. Johnson (Eds.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 881.

IPCC, 2007a. Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change In: C.W. Team, R.K. Pachauri, A. Reisinger (Eds.). IPCC, Geneva, Swizerland, pp. 104.

IPCC, 2007b. Climate change 2007: The physical science basis. Summary for policymakers.

Jenkinson, D.S., 1990. The turnover of organic-carbon and nitrogen in soil. Philosophical Transactions of the Royal Society of London Series B-Biological Sciences 329, 361-368.

Jenkinson, D.S., Coleman, K., 1994. Calculating the annual input of organic-matter to soil from measurements of total organic-carbon and radiocarbon. European Journal of Soil Science 45, 167-174.

Jenkinson, D.S., Harris, H.C., Ryan, J., McNeill, A.M., Pilbeam, C.J., Coleman, K., 1999. Organic matter turnover in a calcareous clay soil from Syria under a two-course cereal rotation. Soil Biology and Biochemistry 31, 687-693.

Jenny, H., 1941. Factors of Soil Formation. McGraw-Hill, New York.

Jobbagy, E.G., Jackson, R.B., 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecological Applications 10, 423-436.

Johnson, I.R., Thornley, J.H.M., 1985. Temperature dependence of plant and crop processes. Annals of Botany 55, 1-24.

Kirschbaum, M.U.F., 1999. CenW, a forest growth model with linked carbon, energy, nutrient and water cycles. Ecological Modelling 118, 17-59.

Kirschbaum, M.U.F., 2000. Will changes in soil organic carbon act as a positive or negative feedback on global warming? Biogeochemistry 48, 21-51.

Kirschbaum, M.U.F., Paul, K.I., 2002. Modelling C and N dynamics in forest soils with a modified version of the CENTURY model. Soil Biology and Biochemistry 34, 341-354.

Kirschbaum, M.U.F., 2006. The temperature dependence of organic-matter decomposition - still a topic of debate. Soil Biology and Biochemistry 38, 2510-2518.

Knorr, W., Prentice, I.C., House, J.I., Holland, E.A., 2005. Long-term sensitivity of soil carbon turnover to warming. Nature 433, 298-301.

Lackner, K.S., 2003. Issues of carbon sequestration - Response. Science 301, 1326-1327.

Lal, R., 2004. Soil carbon sequestration to mitigate climate change. Geoderma 123, 1-22.

Lal, R., 2008. Soil carbon stocks under present and future climate with specific reference to European ecoregions. Nutrient Cycling in Agroecosystems 81, 113-127.

Lugato, E., Berti, A., 2008. Potential carbon sequestration in a cultivated soil under different climate change scenarios: A modelling approach for evaluating promising management practices in north-east Italy. Agriculture Ecosystems and Environment 128, 97-103.

Madsen, H., Wilson, G., Ammentorp, H.C., 2002. Comparison of different automated strategies for calibration of rainfall-runoff models. Journal of Hydrology 261, 48-59.

Matzner, E., Borken, W., 2008. Do freeze-thaw events enhance C and N losses from soils of different ecosystems? A review. European Journal of Soil Science 59, 274-284.

McGill, W.B., Hunt, H.W., Woodmansee, R.G., Reuss, J.O., 1981. PHOENIX: A model of the dynamics of carbon and nitrogen in grassland soil. In: F.E. Clark, T. Rosswall (Eds.), Terrestrial Nitrogen Cycles, Processes, Ecosystem Strategies and Management Impacts. Ecological Bulletins, Stockholm, pp. 49-115.

Moncrieff, J.B., Fang, C., 1999. A model for soil CO_2 production and transport 2: Application to a Florida Pinus elliotte plantation. Agricultural and Forest Meteorology 95, 237-256.

Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models part I -- A discussion of principles. Journal of Hydrology 10, 282-290.

O'Connell, A.M., 1990. Microbial decomposition (respiration) of litter in eucalypt forests of south-western Australia - an empirical-model based on laboratory incubations. Soil Biology and Biochemistry 22, 153-160.

Oades, J.M., 1988. The retention of organic-matter in soils. Biogeochemistry 5, 35-70.

Oelkers, E.H., Cole, D.R., 2008. Carbon dioxide sequestration: A solution to a global problem. Elements 4, 305-310.

Pacala, S., Socolow, R., 2004. Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. Science 305, 968-972.

Pal, D., Broadbent, F.E., 1975. Influence of moisture on rice straw decomposition in soils. Soil Science Society of America Journal 39, 59-63.

Parton, B., 1996. The CENTURY model. In: D.S. Powlson, P. Smith, J.U. Smith (Eds.), Evaluation of Soil Organic Matter Models Using Existing Long-Term Datasets. NATO ASI Series I. Springer-Verlag, Heidelberg, pp. 283-293.

Parton, B., Ojima, D., Del Grosso, S., Keough, C., 2001. CENTURY Tutorial. Supplement to CENTURY User's Manual.

Parton, W.J., Schimel, D.S., Cole, C.V., Ojima, D.S., 1987. Analysis of factors controlling soil organic matter levels in great-plains grasslands. Soil Science Society of America Journal 51, 1173-1179.

Parton, W.J., Stewart, J.W.B., Cole, C.V., 1988. Dynamics of C, N, P and S in grassland soils - a model. Biogeochemistry 5, 109-131.

Patwardhan, A.S., Nieber, J.L., Moore, I.D., 1988. Oxygen, carbon-dioxide, and water transfer in soils - Mechanisms and crop response. Transactions of the Asae 31, 1383-1395.

Paustian, K., Parton, W.J., Persson, J., 1992. Modeling soil organic-matter in organic-amended and nitrogen-fertilized long-term plots. Soil Science Society of America Journal 56, 476-488.

Paustian, K., 1994. Modelling soil biology and biochemical processes for sustainable agriculture research. In: Z.E. Pankhurst, B.M. Doube, V.V.S.R. Gupta, P.R. Grace (Eds.), Soil biota management in sustainable farming systems. CSIRO Information Services, Melbourne, pp. 182-193.

Paustian, K., Andren, O., Janzen, H.H., Lal, R., Smith, P., Tian, G., Tiessen, H., Van Noordwijk, M., Woomer, P.L., 1997. Agricultural soils as a sink to mitigate CO2 emissions. Soil Use and Management 13, 230-244.

Pavelka, M., Acosta, M., Marek, M.V., Kutsch, W., Janous, D., 2007. Dependence of the Q(10) values on the depth of the soil temperature measuring point. Plant and Soil 292, 171-179.

Peters, A., Durner, W., 2008. Simplified evaporation method for determining soil hydraulic properties. Journal of Hydrology 356, 147-162.

Pirasteh, B., Welsh, J.R., 1980. Effect of temperature on the heading date of wheat cultivars under a lengthening photoperiod. Crop Science 20, 453-456.

Powlson, D., 2005. Climatology - Will soil amplify climate change? Nature 433, 204-205.

Reichstein, M., Beer, C., 2008. Soil respiration across scales: The importance of a model-data integration framework for data interpretation. Journal of Plant Nutrition and Soil Science - Zeitschrift für Pflanzenernährung und Bodenkunde 171, 344-354.

Rey, A., Jarvis, P., 2006. Modelling the effect of temperature on carbon mineralization rates across a network of European forest sites (FORCAST). Global Change Biology 12, 1894-1908.

Rixon, A.J., Bridge, B.J., 1968. Respiratory quotient arising from microbial activity in relation to matric suction and air filled pore space of soil. Nature 218, 961-962.

Rodrigo, A., Recous, S., Neel, C., Mary, B., 1997. Modelling temperature and moisture effects on C-N transformations in soils: comparison of nine models. Ecological Modelling 102, 325-339.

Rovira, A.D., 1953. Use of the Warburg apparatus in soil metabolism studies. Nature 172, 29-30.

Ruddiman, W.F., 2003. The anthropogenic greenhouse era began thousands of years ago. Climatic Change 61, 261-293.

Schimel, D.S., Braswell, B.H., Holland, E.A., Mckeown, R., Ojima, D.S., Painter, T.H., Parton, W.J., Townsend, A.R., 1994. Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils. Global Biogeochemical Cycles 8, 279-293.

Schlesinger, W.H., 1999. Carbon Sequestration in soils. Science, 2095.

Schlesinger, W.H., Andrews, J.A., 2000. Soil respiration and the global carbon cycle. Biogeochemistry 48, 7-20.

Šimůnek, J., Suarez, D.L., 1993. Modeling of carbon dioxide transport and production in soil: 1. Model development. Water Resources Research 29, 487-497.

Šimůnek, J., Suarez, D.L., Sejna, M., 1996. The UNSATCHEM software package for simulating the one-dimensional variably saturated water flow, heat transport, carbon dioxide production and transport, and multicomponent solute transport with major ion equilibrium and kinetic chemistry. Version 2.0. 141, Riverside.

Singh, J.S., Gupta, S.R., 1977. Plant decomposition and soil respiration in terrestrial ecosystems. Botanical Review 43, 499-528.

Skjemstad, J.O., Spouncer, L.R., Cowie, B., Swift, R.S., 2004. Calibration of the Rothamsted organic carbon turnover model (RothC ver. 26.3), using measurable soil organic carbon pools. Australian Journal of Soil Research 42, 79-88.

Skopp, J., Jawson, M.D., Doran, J.W., 1990. Steady-state aerobic microbial activity as a function of soil-water content. Soil Science Society of America Journal 54, 1619-1625.

Smith, P., Powlson, D.S., Smith, J.U., Elliott, E.T., Editors, G., 1997a. Preface. Geoderma 81, 1-3.

Smith, P., Smith, J.U., Powlson, D.S., McGill, W.B., Arah, J.R.M., Chertov, O.G., Coleman, K., Franko, U., Frolking, S., Jenkinson, D.S., Jensen, L.S., Kelly, R.H., Klein-Gunnewiek, H., Komarov, A.S., Li, C., Molina, J.A.E., Mueller, T., Parton, W.J., Thornley, J.H.M., Whitmore, A.P., 1997b. A comparison of the performance of nine soil organic matter models using datasets from seven long-term experiments. Geoderma 81, 153-225.

Smith, P., 2004. Carbon sequestration in croplands: the potential in Europe and the global context. European Journal of Agronomy 20, 229-236.

Sophocleous, M., 1979. Analysis of water and heat flow in unsaturated-saturated porous media. Water Resources Research 15, 1195-1206.

Suarez, D.L., Šimůnek, J., 1993. Modeling of carbon dioxide transport and production in soil: 2. Parameter selection, sensitivity analysis, and comparison of model predictions to field data. Water Resources Research 29, 499-513.

Thornley, J.H.M., Cannell, M.G.R., 2001. Soil carbon storage response to temperature: an hypothesis. Annals of Botany 87, 591-598.

Trumbore, S., 2000. Age of soil organic matter and soil respiration: Radiocarbon constraints on belowground C dynamics. Ecological Applications 10, 399-411.

Tuomi, M., Vanhala, P., Karhu, K., Fritze, H., Liski, J., 2008. Heterotrophic soil respiration--comparison of different models describing its temperature dependence. Ecological Modelling 211, 182-190.

van't Hoff, J.H., 1984. Etudes de Dynamique Chemique, Amsterdam.

van Dam, D., van Breemen, N., 1995. NICCE: a model for cycling of nitrogen and carbon isotopes in coniferous forest ecosystems. Ecological Modelling 79, 255-275.

van Genuchten, M.T., 1980. A closed form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal 44, 892-898.

van Genuchten, M.T., 1987. A numerical model for water and solute movement in and below the root zone. Research report, U.S. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Riverside, Calif.

van Veen, J.A., Kuikman, P.J., 1990. Soil structural aspects of decomposition of organic-matter by microorganisms. Biogeochemistry 11, 213-233.

Weihermüller, L., Huisman, J.A., Lambot, S., Herbst, M., Vereecken, H., 2007. Mapping the spatial variation of soil water content at the field scale with different ground penetrating radar techniques. Journal of Hydrology 340, 205-216.

Weihermüller, L., Huisman, J.A., Graf, A., Herbst, M., Sequaris, J.-M., 2009. Multistep outflow experiments for the simultaneous determination of soil physical and CO_2 production parameters. Vadose Zone Journal, In press.

WMO, 2008. Greenhouse gas bulletin: The state of greenhouse gases in the atmosphere using global observations through 2007. 4.

Xu, M., Qi, Y., 2001. Spatial and seasonal variations of Q(10) determined by soil respiration measurements at a Sierra Nevadan forest. Global Biogeochemical Cycles 15, 687-696.

Yang, X.M., Zhang, X.P., Fang, H.J., Zhu, P., Ren, J., Wang, L.C., 2003. Long-term effects of fertilization on soil organic carbon changes in continuous corn of northeast China: RothC model simulations. Environmental Management 32, 459-465.

Zimmermann, M., Leifeld, J., Schmidt, M.W.I., Smith, P., Fuhrer, J., 2007. Measured soil organic matter fractions can be related to pools in the RothC model. European Journal of Soil Science 58, 658-667.

Zogg, G.P., Zak, D.R., Ringelberg, D.B., MacDonald, N.W., Pregitzer, K.S., White, D.C., 1997. Compositional and functional shifts in microbial communities due to soil warming. Soil Science Society of America Journal 61, 475-481.

Appendix

Table A 1: Scaling factors for the dependence of decomposition on soil temperature.

Model	Equation	T_{ref} [°C]	References
CANDY	$f(T) = Q_{10}^{(T-35)/10} \quad \langle T \le 35 \rangle$ $f(T) = 1 \quad \langle T > 35 \rangle$ $Q_{10} = 2.1$	35	(Franko et al., 1995)
CENTURY	$f(T) = 0.56 + 0.465 \arctan(0.097(T - 15.7))$	30	(Parton et al., 2001)
DAISY	$f(T) = 0.0 \quad \langle T \le 0 \rangle$ $f(T) = 0.1T \quad \langle 0 < T \le 20 \rangle$ $f(T) = \exp(0.47 - 0.027T + 0.00193T^2) \quad \langle T > 20 \rangle$	10	(Hansen et al., 1990)
PATCIS	$f(T) = \exp\left(\frac{E*(T - T_{10})}{R*(273.15 + T)*(273.15 + T_{10})}\right)$ $\mathrm{E} = 78.2\,\mathrm{kJ\,mol^{-1}} \quad \langle \mathrm{T} > 20°\mathrm{C} \rangle$ $\mathrm{E} = 79.3\,\mathrm{kJ\,mol^{-1}} \quad \langle 10°\mathrm{C} < \mathrm{T} \le 20°\mathrm{C} \rangle$ $\mathrm{E} = 94.9\,\mathrm{kJ\,mol^{-1}} \quad \langle \mathrm{T} \le 10°\mathrm{C} \rangle$ $T_{10} = 10°C$	10	(Fang and Moncrieff, 1999; Moncrieff and Fang, 1999)
RothC	$f(T) = \frac{47.9}{1 + \exp\left(\frac{106}{T + 18.3}\right)}$	9.25	(Coleman and Jenkinson, 2005)
SOILCO2	$f(T) = \exp\left(\frac{E*(T - T_{20})}{R*(273.15 + T)*(273.15 + T_{20})}\right)$ $\mathrm{E} = 55.5\,\mathrm{kJ\,mol^{-1}} \quad T_{20} = 20°C$	20	(Šimůnek and Suarez, 1993; Suarez and Šimůnek, 1993)

E: activation energy of the reaction [J $\mathrm{mol^{-1}}$]; Q_{10}: van't Hoff constant [-]; *R*: universal gas constant [kg $\mathrm{cm^2\,d^{-2}\,°C^{-1}\,mol^{-1}}$] (R=8.314 J $\mathrm{K^{-1}\,mol^{-1}}$); *T*: soil temperature [°C]; T_{ref}: reference temperature where $f(T) = 1$.

Table A 2: Scaling factors for the dependence of decomposition on soil water content.

Model	Equation	References
CANDY	$f_W(\theta)=4\theta/PV(1-\theta/PV)$ $\langle\theta/PV\le 0.5\rangle$ $f_W(\theta)=1.0$ $\langle\theta/PV>0.5\rangle$ assumption: $PV=\theta_s$	(Franko et al., 1995)
CENTURY	$f_W(\theta)=(1+30*\exp(-8.5PPT/PET))^{-1}$ assumption: $PPT/PET=\theta/\theta(h_{50})$ $h_{50}=-10^3 cm$	(Suarez and Šimůnek, 1993; Parton et al., 2001)
DAISY	$f_W(h)=1.0$ $\langle h\ge -10^{0.5}\rangle$ $f_W(h)=1.625-0.25\log(-100h)$ $\langle -10^{0.5}>h\ge -10^{4.5}\rangle$ $f_W(h)=0.0$ $\langle -10^{4.5}>h\rangle$	(Hansen et al., 1990)
PATCIS	$f_W(\theta)=0.0$ $\langle\theta<c_{PAT}/a_{PAT}\rangle$ $f_W(\theta)=1-\exp(-a_{PAT}\theta+c_{PAT})$ $\langle\theta\ge c_{PAT}/a_{PAT}\rangle$ mineral soil: $a_{PAT}=22.6$ $c_{PAT}=0.11$	(Fang and Moncrieff, 1999; Moncrieff and Fang, 1999)
RothC	$f_W(\theta)=1.0$ $\langle TSMD_{acc}<0.444\ TSMD_{\max}\rangle$ $f_W(\theta)=0.2+0.8*\frac{(TSMD_{\max}-TSMD_{acc})}{(0.556*TSMD_{\max})}$ $\langle TSMD_{acc}\ge 0.444\,TSMD_{\max}\rangle$ assumptions: $TSMD_{acc}=\theta_s-\theta$ $TSMD_{\max}=\theta_s-\theta_r$	(Coleman and Jenkinson, 2005)
SOILCO2	$f_W(h)=1.0$ $\langle h_2\le h\le +\infty\rangle$ $f_W(h)=\frac{\log\lvert h\rvert-\log\lvert h_3\rvert}{\log\lvert h_2\rvert-\log\lvert h_3\rvert}$ $\langle h_3\le h<h_2\rangle$ $f_W(h)=0.0$ $\langle -\infty\le h<h_3\rangle$ $h_2=-10^2 cm$ $h_3=-10^7 cm$	(Suarez and Šimůnek, 1993; Šimůnek et al., 1996)

a_{PAT}: parameter defining the maximal increase in the rate of soil decomposition with soil moisture [-]; c_{PAT}: integration constant [-]; h: pressure head [cm]; h_2: pressure head when CO_2 production is optimal [cm]; h_3: pressure head when CO_2 production ceases [cm]; h_{50}: pressure head at which the water extraction rate is reduced by 50% [cm]; PET: potential evapotranspiration [cm]; PPT: sum of stored water and precipitation [cm]; PV: pore volume [cm^3 cm^{-3}]; $TSMD_{max}$: maximum topsoil moisture deficit [cm^3 cm^{-2}]; $TSMD_{acc}$: accumulated topsoil moisture deficit [cm^3 cm^{-2}]; α: van Genuchten parameter; θ: soil water content [cm^3 cm^{-3}]; θ_s: saturated water content [cm^3 cm^{-3}].

Acknowledgements

This thesis was developed with the assistance of many people.

First, I want to thank my referee Prof. Dr. Harry Vereecken, head of the Institute of Chemistry and Dynamics of the Geosphere - Agrosphere, ICG-4 at the Forschungszentrum Jülich, GmbH, and Dr. Thomas Pütz, head of the core research unit “Matter fluxes in agroecosystems” for giving me the opportunity to conduct my studies at the ICG-4 institute. I also want to thank Prof. Dr. Heiner Goldbach for the evaluation of this thesis.

For numerous helpful ideas, discussions and corrections of my manuscripts I gratefully acknowledge Michael Herbst, Lutz Weihermüller, Sander Huisman, and Alexander Graf.

I am indepted to Miko U. F. Kirschbaum for the fruitful discussions and his intensive, helpful corrections during my stay at Landcare Research and afterwards. Furthermore, I am grateful to the colleagues at Landcare Research for the convenient working atmosphere and for providing me insight into the Kiwi-world.

I am very grateful to Anne Berns for her expertise in radioactive working. I thank Lutz Weihermüller for his support and advices concerning the experimental set-up of the decomposition experiments. For their assistance during the performance of laboratory experiments I am very grateful to Stefan Masjosthusmann and Simon Kordowich. Special thanks to Ansgar Weuthen and Jürgen Höltkemeier for their technical advices and support. Furthermore, I am thankful to Joseph Noel, Armin Arnecke, Rainer Harms, Stephan Köppchen, Martina Krause, Ulrike Langen, Werner Mittelstädt and Claudia Walraff for their advices and help in the laboratory.

I thank Sander Huisman for his great support in the inverse parameter estimation. I also thank Peter Bauer-Gottwein for his patience in explaining basics of soil physics to me and for introducing me into Matlab.

I also want to thank John Köstel, Christoph Oberdörster, and Benedikt Scharnagl for their help with different kind of workaday problems.

I owe a special thanks to Horst Hardelauf for introducing numerous new input parameters into the model code. Jens Heidbüchel and Thomas Schuster always quickly resolved all computer problems. Many thanks for that!

I want to thank all colleagues of the ICG-4 for the nice working atmosphere, especially my officemates Myriam, Anne, and Katrin.

Finally, I thank my dear parents, family, and friends for their great encouragement and I thank Tom for believing in me and balancing my mind.