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Decomposition and accumulation of organic matter in soil; comparison of some models

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ABSTRACT

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The goal of this report is to present an inventory of models on organic matter transformation as in use on the WUR institutes Alterra and Plant Research International and to compare the models with respect to their basic equations, response to environmental conditions and the dynamics of accumulation of organic matter. Effects on organic matter accumulation by changing temperature and supply of organic materials are discussed.

Keywords: Animo, Century, Cesar, Minip, Nucsam, Recafs, wheat straw, green manure, response to temperature, response to water content, mean residence time, mineralization rate.

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Contents

Preface 7

Summary 9

1 Introduction 11

2 Model description 13
  2.1 Introduction 13
  2.2 Mono-component models 14
    2.2.1 General description. 14
    2.2.2 MINIPa 14
    2.2.3 MINIPb 15
  2.3 Multicomponent models. 16
    2.3.1 General description 16
    2.3.2 CESAR 17
    2.3.3 The organic matter routine as used in RECAFS and CNGRAS. 19
    2.3.4 ANIMO 20
    2.3.5 NUCSAM 22
    2.3.6 CENTURY 23

3 Response to environmental conditions. 27
  3.1 Introduction 27
  3.2 Response as calculated by the different models 27
    3.2.1 MINIPa 27
    3.2.2 MINIPb 29
    3.2.3 CESAR 30
    3.2.4 RECAFS 30
    3.2.5 ANIMO 32
    3.2.6 NUCSAM 33
    3.2.7 CENTURY 33
  3.3 Comparison of response to environmental conditions 34

4 Quantitative comparison of the models. 37
  4.1 Introduction 37
  4.2 Parameter values 37
    4.2.1 MINIPa 37
    4.2.2 MINIPb 37
    4.2.3 CESAR 37
    4.2.4 RECAFS 37
    4.2.5 ANIMO 38
    4.2.6 NUCSAM 38
    4.2.7 CENTURY 39
  4.3 The time course of the overall mineralization coefficient. 39
  4.4 Equilibrium values for constant continuous supply of organic matter. 40

4.5 Mean residence time 42
4.6 Time course of organic matter in case of constant continuous supply under constant conditions 43
4.7 Change of organic matter supply 43
4.8 Change of temperature 44

5 Discussion and conclusions 47
5.1 Plausibility of the models 47
5.2 Mineralization rates and mean residence time 47
5.3 Current SOM content in arable land and calculated equilibrium SOM 50
5.4 Factors affecting SOM content and MRT 52
5.4.1 Land-use history 52
5.4.2 SOM and soil texture 54
5.5 Expected changes in SOM 55
5.6 Conclusions 57

Literature 59

Appendix 1 Application of the Laplace Transformation on a system of linear differential equations. 65
Appendix 2 Accumulation of carbon in the soil for constant continous application of one unit of C in fresh organic material. 67
Appendix 3 Accumulation of organic matter with time dependent supply. Calculations with CENTURY. 73

Preface

This report was written within the framework of the project “Carbon in soil” (project no. 5230985). The project deals with monitoring of the stock of carbon in the soil in the Netherlands. One of the goals of the project is to study the changes of soil organic matter content with the help of simulation models and making an inventory of simulation models available as done in this report is a first step to choose an appropriate model.

Thanks are due to Dr Caroline van de Salm, Dr. Luc Bonten and Dr. Marc van Wijk for their critical and helpful comments.

Summary

This report presents a comparison of seven models (MINIPa, MINIPb, CESAR, RECAFS, ANIMO, NUCSAM, and CENTURY) of transformation of organic matter added to the soil. The models discussed are all in use at Alterra and the Plant Research Institute. Except for the CENTURY model, all models were developed at WUR.

The models were classified in two groups: mono-component models and mult-component models.

The basic equations of the models are shown as well as the response to environmental conditions, particularly soil temperature and moisture content. The build up of soil organic matter (SOM) under constant conditions (temperature 9 ºC, and optimum moisture content) is presented for two types of organic material applied (wheat straw and green manure). The equilibrium values of SOM were calculated, except for the model MINIPa which does not reach an equilibrium. The ratio equilibrium value/annual supply ranged in case of wheat straw from 2.7 (ANIMO) to 15.1 (CENTURY), and in case of green manure from 1.7 (NUCSAM) to 13.2 (CENTURY). The half time to reach equilibrium from zero ranged from 7 (NUCSAM) to 64 years (RECAFS). The equilibrium value is proportional to the annual supply and to the reciprocal value of the relative decomposition rate. As the latter increases exponentially with temperature, the equilibrium value decreases exponentially with temperature.

The plausibility of the models is judged by comparing the model outcome with data on mean residence time (MRT) and SOM mentioned in literature. MRT as calculated by the models was much smaller than values mentioned in literature for five models,. Only CENTURY and MINIPb have the potential to reach a MRT of 1000 years. Some causes of the discrepancy between model and experimental results are discussed. The differences can mainly be ascribed to factors that have had an effect on the mineralization rates. The major factors are land-use, nutrient availability, pH, and drainage in the past, and soil texture. Sub-optimum levels of nutrients, pH, and drainage bring down the mineralization rate. Texture plays a dominant role in determining the build up of SOM. Clay offers protection of organic matter against decomposition and this probably is one of the most important causes of development of high SOM contents. In the Netherlands SOM may increase by about 1 g kg^{-1} per percent increase of clay. Two of the models (CENTURY and RECAFS) take effects of texture into account and CENTURY was able to reproduce the effect of texture quantitatively.

1 Introduction

Organic matter is an important soil quality indicator and affects biological, chemical and physical properties of the soil. Therefore, it may also strongly affect crop yield (Bauer & Black, 1994). Currently, there is a lot of attention for soil organic matter in agricultural and environmental policies in the Netherlands and European Union, such as the manure, climate and soil policies. These policies demand for predictions of changes in soil organic matter contents in the near future at different scenarios.

The Dutch manure policy (fertilizer act) aims at decreasing the inputs of nitrogen and phosphorus to soils via fertilizer and manure in order to comply with the targets of the Nitrates Directive (Directive 91/676/EEG) and Water Framework Directive (Directive 2000/60/EC) of the European Union (EU). A consequence of the decreasing inputs of fertilizer and manure is that the input of organic matter to agricultural soils also decreases. On the other hand, less input of nitrogen may result in smaller crop yields and thereby in less crop residues. Insight is required in the effect of the manure policy on the soil organic matter content (Velthof, 2005). Serious impact of the current manure policy may be expected on arable land on mineral soils, because organic matter contents of these soils are most vulnerable to changes in inputs of fertilizer and manure. Grasslands and peat soils have relatively high organic matter contents and are less vulnerable to decreasing inputs of organic matter. The time horizon for the manure policy is on a relatively short period of 5 to 10 years.

Soils are an important stock of carbon. Changes in the soil carbon stocks affect the emission of CO_2 to the atmosphere. Therefore, quantitative knowledge about changes in carbon stocks in soils is important for climate policy (http://unfccc.int Kuikman et al., 2002). Sequestration of carbon in soils has also been promoted as strategy to mitigate greenhouse gases emission in the atmosphere (Janzen, 2004). In contrast to the manure policy, in the climate policy the focus is not only on arable land, but also on grassland, peat soils and natural soils. The time horizon is longer than that of the manure policy (several decades). The reference year for the climate policy (Kyoto protocol) is the year 1990. Thus, changes in carbon stocks in soils must be related to the year 1990.

The European Union aims at the protection of soils. One of the topics of the Soil Thematic Strategy is the maintenance of soil organic matter (http://ec.europa.eu/environment/soil/index.htm). It is important to get insight in predicted trends of organic matter in the future at current policy and after implementation of a policy aiming at protecting or increasing soil organic matter contents.

Models that predict the effect of policy actions on organic matter contents are indispensable. The number of existing long-term field experiments is very limited (e.g. Jenkinson & Rayner, 1977; Wadman & De Haan, 1997). Setting up new experiments is costly and results can only be obtained after a long time (years to decades). Analyses of long-term data of soil analyses of practical farms (Reijneveld & Oenema, 2008) may also provide insight in changes in soil organic matter contents, but these data-sets are less useful for predictions for the future, especially if management in the future differs from that in the past.

A number of organic matter models are used in Wageningen University and Research Centre, including CESAR (Vleeshouwers & Verhagen 2001; Vleeshouwers & Verhagen 2002), MINIP a (Janssen, 1984; Janssen 1986), MINIP b (Yang, 1996; Yang & Janssen, 2000), ANIMO (Groenendijk et al., 2005), NUCSAM (Kros, 2002), and RECAFS (Conijn, 1995). All models are used for studies to underpin certain policies. However, it is not known if these models provide similar results and conclusions. The times scales of the models are not always the same. On the one hand there is the model RECAFS which is meant for one or a couple of growing seasons. On the other hand the model CESAR was developed to make predictions on the long run (several decades). The other models are supposed to be valid for periods of 5 to 50 years, and they may therefore be considered as most suited for the above mentioned time horizons of 5-10 years (manure policy) up to several decades (climate policy).

A study was conducted to describe and compare a few of commonly used organic matter models of WUR. The widely used CENTURY model was also tested, keeping in mind that this model is meant for longer periods of some centuries, as the name already indicates. The objectives of the study were (i) to provide a reference for those who are supposed to analyze and predict the possible consequences of EU environmental policies, and (ii) to explore model outcomes and to explain the differences among them, and (iii) to account for possible differences between model outcomes and reality.

2 Model description

2.1 Introduction

The models involved are in use at the institutes Alterra and PRI, as a reference we also included a well-known and much used US model CENTURY in the comparison.
Most of the models mentioned below consider not only C- and N-transformations. They are meant for calculations of crop growth, leaching and uptake of nutrients, acidification of forests soils etc. We will discuss here only the part of the models dealing with dynamics of organic matter. For convenience the name of the integral model will be used. The models involved are:

1) MINIP a (Janssen, 1984; Janssen 1986)
2) MINIP b (Yang, 1996; Yang & Janssen, 2000)
3) CESAR (Vleeshouwers & Verhagen 2001; Vleeshouwers & Verhagen 2002)
4) ANIMO (Groenendijk *et al.,* 2005)
5) NUCSAM (Kros, 2002)
6) RECAFS (Conijn, 1995)
7) CENTURY (Parton, 1996)

The first two can be considered as mono-component models, as they distinguish just one organic component. The next five are multi-component models, where organic matter is supposed to exist of different pools decomposing and transforming each in its own specific way.
Before starting the discussion it seems good to clarify some of the terms we will use frequently. We will employ the terminology given by Baldock(2007): "….*decomposition* refers to the removal of a given carbon substrate and is the sum of *mineralisation*, *assimilation* and *alteration*. *Mineralisation* is the release of carbon dioxide from biological respiration. *Assimilation* refers to the retention of substrate carbon by decomposer organisms as they synthesize cellular materials during growth. *Alteration* occurs when the chemical composition of an organic substrate is changed so that the remaining organic carbon is no longer identical to that present in the initial substrate." In this report assimilation and alteration usually are combined; we use the term adaptation for this combination. The decomposition rate coefficients will be denoted with only a numerical subscript, i.e. k_i for the i-th component. For mineralization and adaptation the subscripts M and A are used respectively, so $k_{M,i}$ and $k_{A,i}$ respectively.
In Sections 2.2 and 2.3 the course of C in organic materials is described upon a single application. Section 4.4 deals with the formation of soil organic carbon (SOC) upon continuous supply of organic materials.

2.2 Mono-component models

2.2.1 General description.

This type of models considers one pool consisting of the material applied and the humus/biomass generated from it. The mineralisation of the pool is given by

$$\frac{dC}{dt} = -k_M(t)C(t) \tag{1}$$

where C denotes the carbon in the single pool, and $k_M(t)$ the mineralisation coefficient, which generally is a function of time (t).
The solution of (1) with initial condition $t = 0,\ C = C_0$ reads:

$$C(t) = C_0 \exp\left[-\int_0^t k_M(x)dx\right] \tag{2}$$

Figure 1 present schematically the decomposition of the organic matter in these type of models.

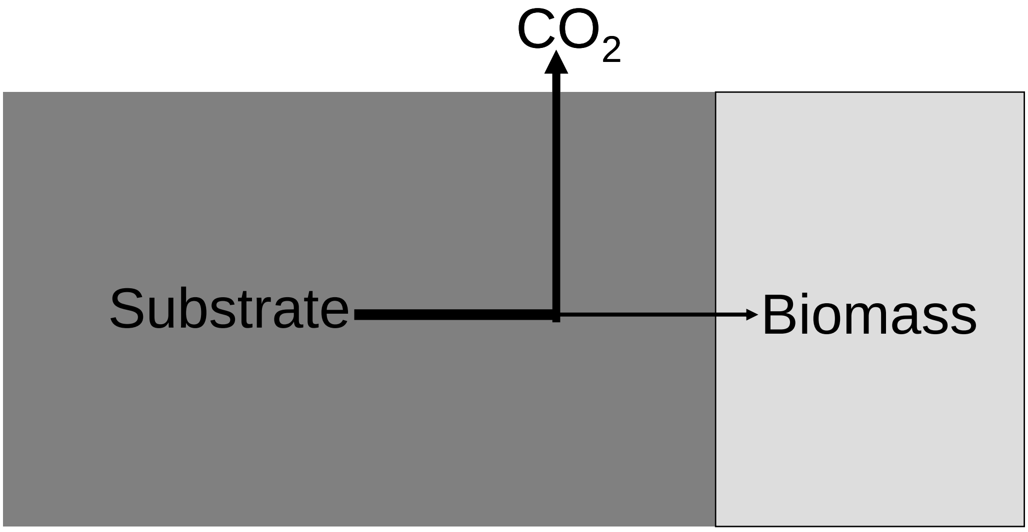

Figure 1 Scheme of transformations within the models MINIPa and MINIPb

2.2.2 MINIPa

The model MINIPa is based on the method developed by Janssen (1984, 1986), for the calculation of build up of "young" soil organic matter, where "young" means not more than 25 years. The attractiveness of the model is that it requires only one input parameter, a (the so-called apparent initial age) to characterize the organic material that is added to the soil. The time-dependent mineralisation coefficient $k_M(t)$ is described as follows:

$$k_M(t) = bm(a+t)^{-m-1} \tag{3}$$

where b and m are constants, with $b = 4.7\ y^m$, and $m = 0.6$[1], and a is the parameter dependent on type of organic matter. Substitution of (3) in (2) yields after evaluation of the integral:

$$C(t) = C_0 \exp\left[b(a+t)^{-m} - ba^{-m}\right] \tag{4}$$

Equation (4) describes the course of C in the applied material *and* that of the microbial biomass formed.

The initial age is in the range of 1-1.6 year for crop residues, for organic matter in manure it amounts to 2 - 2.5 year (Janssen, 1984, 1986), for compost to 4 year and for humus to 15 - 25 year (Janssen, 2002). Equation (4) implies a non-decomposable rest with size:

$$C_{rest} = C_0 \exp\left[-ba^{-m}\right] \tag{5}$$

In the range of a-values of 1 – 25 year this rest amounts to 1 – 50% of the initial value.

This also implies that for a constant annual application no equilibrium value will be reached. According to Janssen (2002), MINIPa is meant for periods of 40 to 50 years, maximally.

2.2.3 MINIPb

Yang (1996) showed that fixing $b = 4.7$, and $m = 0.6$ made MINIPa too rigid. Therefore he developed a more flexible equation for the mineralization of different materials and found it could be described quite well by:

$$C = C_0 \exp\left[-Rt^{1-S}\right] \tag{6}$$

where R (t^{S-1}) and S (dimensionless) denote parameters dependent on type of material and soil. There is a good relation between the two parameters; R increases with increasing S. It holds $0 \leq S \leq 1$. For $S = 0$ equation (6) becomes an exponential function (in form identical to CESAR), and for $S = 1$ C is constant. For $0 \leq S < 1$ there is no non-decomposable rest in contrast to MINIPa. So for constant applications and conditions eventually an equilibrium value for the carbon in soil is reached. From (6) follows the relative rate of mineralisation:

$$k_M(t) = R(1-S)t^{-S} \tag{7}$$

---

[1] Note that here we will give all parameters and constants positive values. Accordingly m is taken to be positive here.

MINIPb was calibrated for plant materials with data derived from experiments lasting between 3 months and 20 years. It could successfully be applied to analyze the result of farming practices in China over periods of some centuries (Yang, 1996; Yang and Janssen, 1997). The models MINIPa and MINIPb have in common that log($k_M(t)$) is linearly related to log(t), as follows from Equations (3) and (7).

2.3 Multicomponent models.

2.3.1 General description

Multicomponent models distribute added and/or organic matter in the soil over different components, each with its own specific decomposition rate. The models discussed here all assume first-order decomposition with a constant relative rate coefficient given constant environmental conditions. Products of decomposition are carbon dioxide and other components.

Decomposition, mineralization, alteration and assimilation can be generally described as follows (Heinen & De Willigen, 2001). If n components are considered then the following differential equation holds for the ith component:

$$\frac{dC_i}{dt} = \varepsilon_{1i}k_1C_1 + \varepsilon_{2i}k_2C_2 + ...(\varepsilon_{ii}-1)k_iC_i + ...\varepsilon_{ni}k_nC_n \qquad (8)$$

where $k_{,i}$ is the decomposition coefficient of C_i, and ε_{ji} the fraction of the decomposition of component *j* which is transferred to component *i*. The adaptation rate coefficient is thus given by: $k_{A,i} = k_i \sum_{j=1}^{n} \varepsilon_{ij}$ and the mineralization coefficient by

$$k_{M,i} = k_i - k_{A,i} = \left(1 - \sum_{j=1}^{n} \varepsilon_{ij}\right) k_i\,.$$

The system of equations can be most concisely written in matrix notation: $\frac{d\mathbf{C}}{dt} = \mathbf{k}\cdot\mathbf{C}$ (9)

Here **C** is the vector with n components and **k** the matrix of coefficients, e.g. for n=3:

$$\mathbf{k} = \begin{pmatrix} (\varepsilon_{11}-1)k_1 & \varepsilon_{21}k_2 & \varepsilon_{31}k_3 \\ \varepsilon_{12}k_1 & (\varepsilon_{22}-1)k_2 & \varepsilon_{32}k_3 \\ \varepsilon_{13}k_1 & \varepsilon_{23}k_2 & (\varepsilon_{33}-1)k_3 \end{pmatrix} \qquad (10)$$

As $k_{D,i}$ and ε_{ij} are only a function of environmental conditions, the differential equations in (10) are linear. These can be solved with the help of the Laplace transformation (Churchill, 1972). Details can be found in Appendix 1.

2.3.2 CESAR

This model (Vleeshouwers and Verhagen, 2001) is meant for calculations on the long run (several decades). It is essentially a two component model in which two types of organic matter are distinguished fresh organic material (C_1) and humus/biomass (C_2). For an application of a unit of fresh organic matter the time course is given by:

$$\frac{dC_1}{dt} = -k_1 C_1$$

$$\frac{dC_2}{dt} = k_{A,1} C_1 - k_{M,2} C_2 \qquad (11)$$

With initial conditions :

$$t = 0, C_1 = C_{1,0}, C_2 = C_{2,0}$$

where t is time in years, k_1 the decomposition rate constant of the fresh material, $k_{A,1}$ the adaptation rate constant of the fresh material and $k_{M,2}$ the mineralization rate constant of the humus. Figure 2 present schematically the decomposition of the organic matter in CESAR.

The solution of the system (11) is:

$$C_1 = C_{1,0} \exp(-k_1 t)$$

$$C_2 = \frac{k_{A,1} C_{1,0} \{\exp(-k_{M,2} t) - \exp(-k_1 t)\}}{k_1 - k_{M,2}} + C_{2,0} \exp(-k_{M,2} t) \qquad (12)$$

The fraction of fresh organic material which transforms into humus in one year is called the humification coefficient h_c, so:

$$k_{A,1} \int_0^1 \exp(-k_1 t) = h_c, \text{or}$$

$$k_{A,1} = \frac{h_c k_1}{1 - \exp(-k_1)} \qquad (13)$$

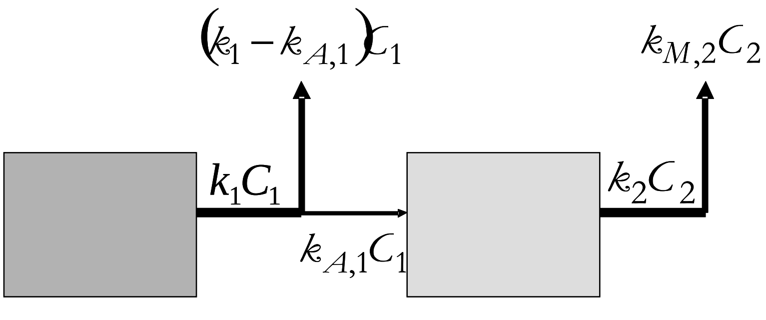

Figure 2 Scheme of decomposition of organic matter in CESAR. The component C_1 denotes fresh organic matter, C_2 the humus/biomass complex.

As it is assumed that the fresh organic material is converted in either carbon dioxide or in humus within one year, the value of the decomposition constant should be chosen such that (virtually) all fresh material has disappeared within one year, a value of e.g. $k_1 =$ 5 y^{-1} would do. The denominator $1-\exp(-k_1)$ in (13) then ≈ 1, and $k_{A,1} = h_c k_1 = 5h_c$. Figure 3 gives an illustration of the time course of the two components after an addition of one unit of fresh organic matter. It should be mentioned that the description of the model given here is not exactly the same as given by Vleeshouwers and Verhagen (2001), the equations are slightly changed so that these fit in the general equation system (8).

The mineralisation coefficient $k_{M,2}$ is estimated by fitting data pertaining to time course of organic matter content in fallow fields of three long-term experiments in the Netherlands (Kortleven,1963), England (Jenkinson, 1977) and Denmark (Dam Kofoed, 1982) to the model of Yang. The value of the mineralisation coefficient in the second year was considered to be representative for the course of mineralisation after the second year. To quote Vleeshouwers en Verhagen (2001):"In CESAR, organic material in the soil older than one year is considered soil organic matter. In the second year...... all age classes of soil organic matter are present without the decomposition rate being affected...... by the presence of easily decomposable crop residues, which remain in the soil shorter than one year. The value in the second year was considered most apt ....". The reference value was taken to be the average value of the fit of the three experiments, its value amounts to 0.029 y^{-1} (at 10 ° C).

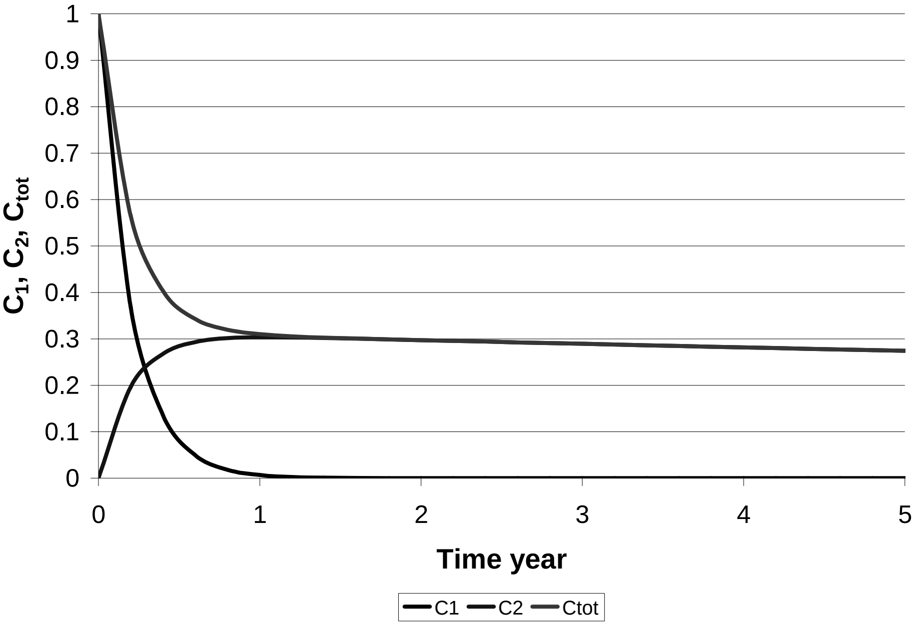

Figure 3 Time course of the fractions C_1, C_2 and C_{tot} according to CESAR. Parameters : $k_{,1}= 5\ y^{-1}$, $k_{A,2} = 1.56\ a^{-1}$, $C_{10} = 1$; $C_{20} = 0$, $k_{M,2} = 0.027\ y^{-1}$ (at 9°C) .

The values for the humification coefficient were taken from literature. For crop residues for instance these are in the range 0.21-0.33.

2.3.3 The organic matter routine as used in RECAFS and CNGRAS.

This sub-model is based on the theory and concepts as described by Berendse *et al.* (1987, 1989). Conijn (1995) implemented the module in RECAFS, a model meant to describe the nutrient cycle and competition for nutrients in agroforestry systems. More recently it is also a part of a grassland management model (CNGRAS, Conijn, 2005). We will for convenience address the module with the name RECAFS.

In the module the organic matter in soil is distributed over three components. Each component contains dead and living (microbial) biomass. There is no exchange of organic matter between the three components. Within a component there is conversion of dead organic material into microbial biomass and carbon dioxide only, analogous to the way MINIPa and MINIPb deal with transformation. So, the matrix of coefficients' reads:

$$\mathbf{k} = \begin{pmatrix} (\varepsilon_{11}-1)k_1 & 0 & 0 \\ 0 & (\varepsilon_{22}-1)k_2 & 0 \\ 0 & 0 & (\varepsilon_{33}-1)k_3 \end{pmatrix} \tag{14}$$

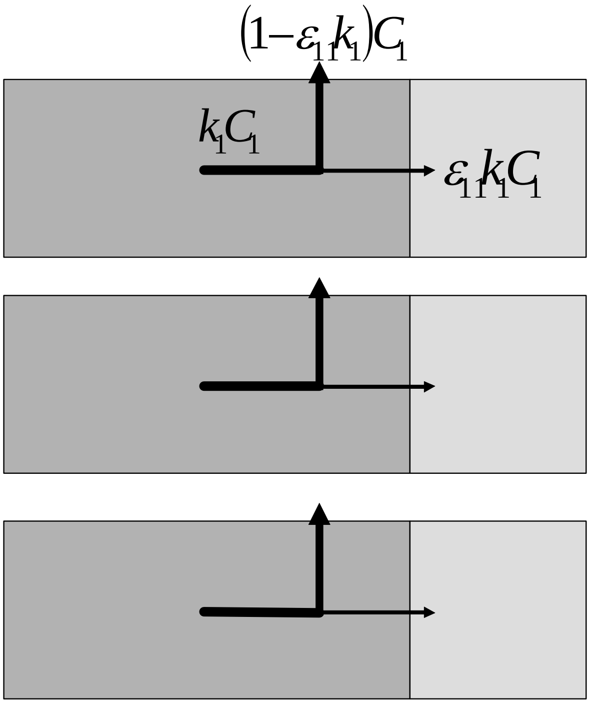

Figure 4 Decompostion scheme of organic matter in RECAFS.

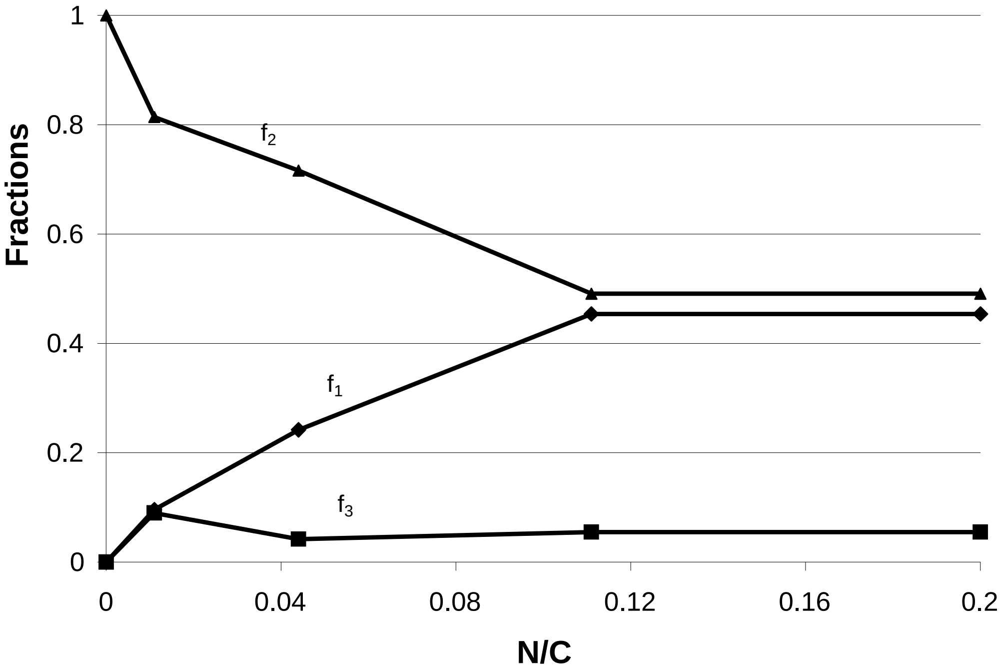

Figure 5 Distribution of added organic matter over the three fractions in RECAFS as a function of the N/C ratio of the material

At reference temperature (11 °C) and moisture status (water filled pore space is 0.6) the values of the coefficients k_1, k_2 and k_3 are 36.5, 2.99, and 0.031 y^{-1} respectively, and those of the efficiencies $\varepsilon_{11} = \varepsilon_{22} = 0.3$, en $\varepsilon_{33} = 0.35$.

Any addition of organic matter (e.g. plant residue, manure) is distributed over the three components on basis of their N/C ratio, as shown in Figure 5. For a given initial distribution and constant conditions the time course of component *i* is given by:

$$C_i = C_{i,0} \exp\left(\left(\varepsilon_{ii} - 1\right)k_i t\right) \tag{15}$$

and that of the total carbon by:

$$C_{tot} = \sum_{i=1}^{3} C_{i,0} \exp\left(\left(\varepsilon_{ii} - 1\right)k_i t\right) \tag{16}$$

2.3.4 ANIMO

ANIMO (Groenendijk *et al.*, 2005) as the majority of models discussed here is a model which deals with nutrient cycles in general, it accordingly contains modules on nutrient uptake, plant growth, soil chemistry and biology etc. We will discuss here only the organic matter module and denote it by the name ANIMO.

In ANIMO the organic matter added to the soil is assumed to consist of two fractions which partly change into carbon dioxide and partly into humus/biomass.

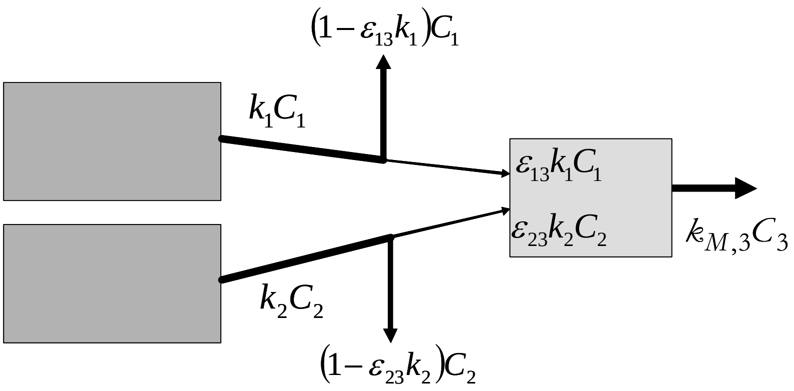

Figure 6 Decompostion scheme of organic matter in ANIMO.

The matrix of coefficients reads:

$$\mathbf{k} = \begin{pmatrix} -k_1 & 0 & 0 \\ 0 & -k_2 & 0 \\ \varepsilon_{13}k_1 & \varepsilon_{23}k_2 & -k_{M,3} \end{pmatrix} \tag{17}$$

and the corresponding decomposition scheme is found in Figure 6.
The values of the parameters are calculated with MINIPa. For a particular material, characterized by an apparent age *a*, a data set is produced by using equation(7) and by fitting the parameters of the relevant equation (equation (6.7) in Groenendijk *et al.*, 2005), and, in a slightly different form given in section 6.1) to this data set.
The values of the coefficients k_1, k_2, k_3 are fixed at 2, 0.2 en 0.02 y^{-1}, respectively, and it is assumed that $\varepsilon_{13} = \varepsilon_{23} = \varepsilon$, so it suffices to fit p (the fraction of the first component) and ε only. In doing so it was found that a good relation exists between p and ε and the apparent age a:

$$\begin{aligned} p &= -0.0105a^3 + 0.1394a^2 - 0.6904a + 1.4767 \\ \varepsilon &= -0.0066a^3 + 0.0673a^2 - 0.1096a + 0.0705 \end{aligned} \tag{18}$$

For a given initial distribution the time course of each fraction is found as:

$$\begin{aligned} C_1 &= C_{1,0}\exp(-k_1t) \\ C_2 &= C_{2,0}\exp(-k_2t) \\ C_3 &= C_{3,0}\exp(-k_{M,3}t) + \frac{k_1\varepsilon C_{1,0}\left(\exp(-k_1t) - \exp(-k_{M,3}t)\right)}{k_{M,3} - k_1} + \\ &\quad \frac{k_2\varepsilon C_{2,0}\left(\exp(-k_2t) - \exp(-k_{M,3}t)\right)}{k_{M,3} - k_2} \end{aligned} \tag{19}$$

2.3.5 NUCSAM

NUCSAM (Kros, 2002) is a mechanistic model meant for application on plot scale (e,g. 100 x100 m^2) for relative short time. The model was designed to calculate the nutrient cycle and soil acidification caused by nitrogen deposition in forests. The organic matter module is a small but important part of the model which is mainly aimed at a quantitative description of bio-geochemical processes.
The organic matter module distinguishes three fractions in soil: litter (L), fermented material (F) and humus (H). It is possible (Groenenberg *et al.*, 1998), contrary to the fractions postulated in the other multi-component models discussed, to determine the fractions experimentally. The litter fraction is decomposed into carbon dioxide and organic solutes, transformed into fermented material and replenished by dead leaves and roots. The fermented fraction is converted to carbon dioxide and humus. The last fraction is only mineralized into carbon dioxide. So where in ANIMO there are two parallel connected transformations in NUCSAM the transformations are connected in series.

The rate equations read in their original form:

$$\begin{aligned}
\frac{dL}{dt} &= -k_{mi,L}L - k_{tr,L}L \\
\frac{dF}{dt} &= k_{tr,L}L - k_{mi,F}F - k_{tr,F}F \\
\frac{dH}{dt} &= k_{tr,F}F - k_{mi,H}H
\end{aligned} \tag{20}$$

where k_{tr} en k_{mi} are alteration and mineralisation constants in the notation of Kros (2002). The decomposition constants read in the notation of (8):

$$\begin{aligned}
k_1 &= k_{mi,lt} + k_{tr,lt} \\
k_2 &= k_{mi,fm} + k_{tr,fm} \\
k_3 &= k_{M,3} = k_{mi,hu}
\end{aligned}$$

where subscripts lt, fm and hu refer to litter, fermented material and humus, respectively

Thus $\varepsilon_{ii} = 0$, $\varepsilon_{12} = \dfrac{k_{tr,lt}}{k_{tr,lt} + k_{mi,lt}}$, and $\varepsilon_{23} = \dfrac{k_{tr,fm}}{k_{tr,fm} + k_{mi,fm}}$

The matrix of coefficients for NUCSAM accordingly is:

$$\mathbf{k} = \begin{pmatrix} -k_1 & 0 & 0 \\ \varepsilon_{12}k_1 & -k_2 & 0 \\ 0 & \varepsilon_{23}k_2 & -k_3 \end{pmatrix} \tag{21}$$

The decomposition scheme is depicted in Figure 7.

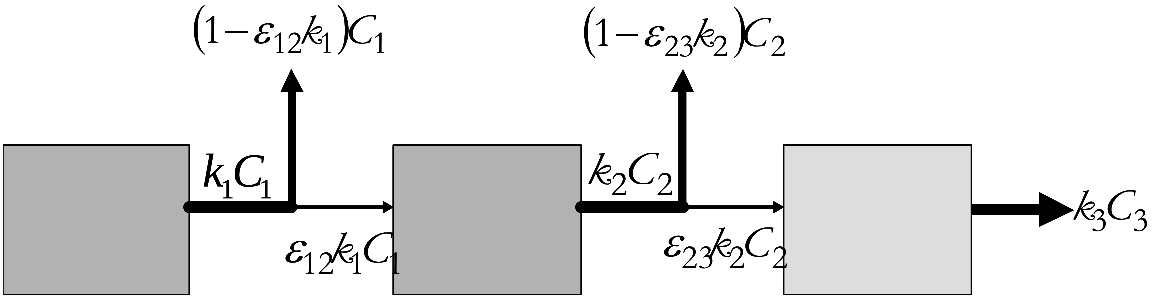

Figure 7 Decomposition scheme of organic matter in NUCSAM

Kros (2002) found the following values of the parameters by calibration of the total model on data: $k_{mi,L}$ = 0.29 y^{-1}, $k_{tr,L}$ = 0.37 y^{-1}, $k_{mi,F}$ = 0.046 y^{-1}, $k_{tr,F}$ = 0.013 y^{-1}, $k_{mi,H}$ = 0.005 y^{-1}. It follows that k_1 = 0.66 y^{-1}, k_2 = 0.059 y^{-1}, k_3 = 0.005 y^{-1}, ε_{12} = 0.56, ε_{23} = 0.22. The values for the mineralisation coefficients apply to a temperature of 10° C, a pH of 6, and optimum moisture status.

For a given initial distribution the time course of each fraction is found as:

$$\begin{aligned}
C_1 &= C_{1,0}\exp(-k_1t) \\
C_2 &= C_{2,0}\exp(-k_2t) + \frac{k_1\varepsilon_{12}C_{1,0}\left(\exp(-k_1t) - \exp(-k_2t)\right)}{k_2-k_1} \\
C_3 &= C_{3,0}\exp(-k_3t) + \frac{k_2\varepsilon_{23}C_{2,0}\left(\exp(-k_2t) - \exp(-k_3t)\right)}{k_3-k_2} + \\
&\quad k_1\varepsilon_{12}k_2\varepsilon_{23}C_{1,0}\left(\frac{\exp(-k_1t)}{(k_1-k_2)(k_1-k_3)} + \frac{\exp(-k_2t)}{(k_2-k_1)(k_2-k_3)} + \frac{\exp(-k_3t)}{(k_3-k_1)(k_3-k_2)}\right)
\end{aligned} \tag{22}$$

2.3.6 CENTURY

CENTURY is a model for simulation of organic matter in soil (Parton *et al.*, 1987). It simulates the dynamics of C, N, P, and S on a time scale of centuries to millennia. Soil organic matter is distributed over three components: active (A), slow (S) and passive (P). Fresh organic matter (plant residue, manure) is added to the surface and/or below ground and consists of a structural and a metabolic fraction. The size of the metabolic fraction is a function of the lignin/nitrogen content of the material:

$$f_M = 0.85 - 0.018 * L/N \tag{23}$$

where f_M is the fraction metabolic , and L/N the lignin/nitrogen ratio.

Table 1 Components of organic matter in CENTURY

Plant residue	Structural	
	Lignin	C_1
	Rest	C_2
	Metabolic	C_3
Soil Organic matter	Active	C_4
	Slow	C_5
	Passive	C_6

In total there are seven components (surface structural, surface metabolic, below ground structural, below ground metabolic, and active, slow and passive soil organic matter) and thus seven conversion coefficients. In our discussion we will leave out the organic matter in the surface layer as in the other models such a distinction has not been made. This reduces the system to five components and five conversion coefficients. The component 'structural' consists of two fractions, lignin and rest. Both are decomposed with the same relative rate, but the lignin is transferred to the slow pool and the rest to the active pool. For convenience we will consider lignin and the rest as two different components, so "structural" is not a component as such and there are six components in total. Table 1 gives a survey.

The matrix of coefficients reads:

$$\begin{pmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & -k_3 & 0 & 0 & 0 \\ 0 & k_2\varepsilon_{24} & k_3\varepsilon_{34} & -k_4 & k_5\varepsilon_{54} & k_6\varepsilon_{64} \\ k_1\varepsilon_{15} & 0 & 0 & k_4\varepsilon_{45} & -k_5 & 0 \\ 0 & 0 & 0 & k_4\varepsilon_{46} & k_5\varepsilon_{56} & -k_6 \end{pmatrix} \tag{24}$$

The actual values of the coefficients k_1 and k_2 depend on the fraction lignin in the structural material:

$$k_1 = k_{1,ref}\exp(-3L_s) \tag{25}$$

where k_1 is the actual value and L_S is the fraction lignin in the structural material. The correction of k_2 is done in an identical way. The flow of C in the model is shown in Figure 8.

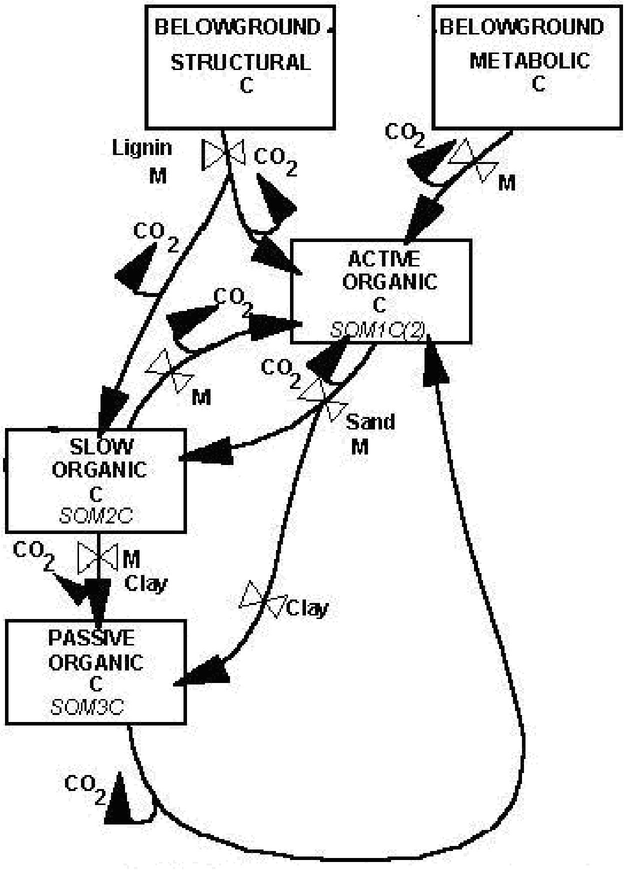

Figure 8 Flow of C in Century. For explanation see text sections 2.3.6 and 4.2.7

3 Response to environmental conditions.

3.1 Introduction

All microbial activities are influenced by environmental conditions. Of these, temperature and moisture content play the most important role, but also other factors e.g. oxygen availability, soil texture, influence the rates of conversion. In the models discussed here the relative rate coefficients are multiplied by dimensionless variables each of which is a function of a certain environmental variable. Interaction between factors is assumed to be multiplicative. So in general a relative rate coefficient is related to its value at reference conditions by:

$$k_{act} = k_{ref} \prod_{i=1}^{n} e_i \tag{26}$$

All of the models consider temperature and moisture response, we will therefore focus on temperature and moisture effects, but also will give attention to effect of soil texture where it is taken into account, in the case of RECAFS and CENTURY.

3.2 Response as calculated by the different models

3.2.1 MINIPa

In MINIPa, the rate coefficient k_M decreases over time, this has consequences for the ratio of the rates at different temperatures. Janssen (1986, 1996) proposed to correct the time with a factor f_T depending on temperature:

$$C = C_0 \exp\left(b((a + f_T t)^{-m} - a^{-m})\right) \tag{27}$$

In this way care is taken that the amount of mineralization at time t at the reference temperature (where f_T is 1) is also obtained at time t/f_T for other temperatures. It follows that the rate coefficient $k_M(t)$ at any temperature is given by:

$$k_M(t) = bmf_T(a + f_T t)^{-(m+1)} \tag{28}$$

Or

$$e_T = \frac{k_M(t)}{k_{M,ref}(t)} = \frac{f_T(a + f_T t)^{-(m+1)}}{(a + t)^{-(m+1)}} = \frac{(a + t)^{(m+1)}}{(a + f_T t)^{(m+1)}} f_T \tag{29}$$

where $k_{Mref}(t)$ is the rate coefficient when e_T is 1, i.e. at the reference temperature of 9 ºC. So the ratio between the rate coefficient at any temperature and that at reference temperature depends on time and via the parameter a on the type of material.

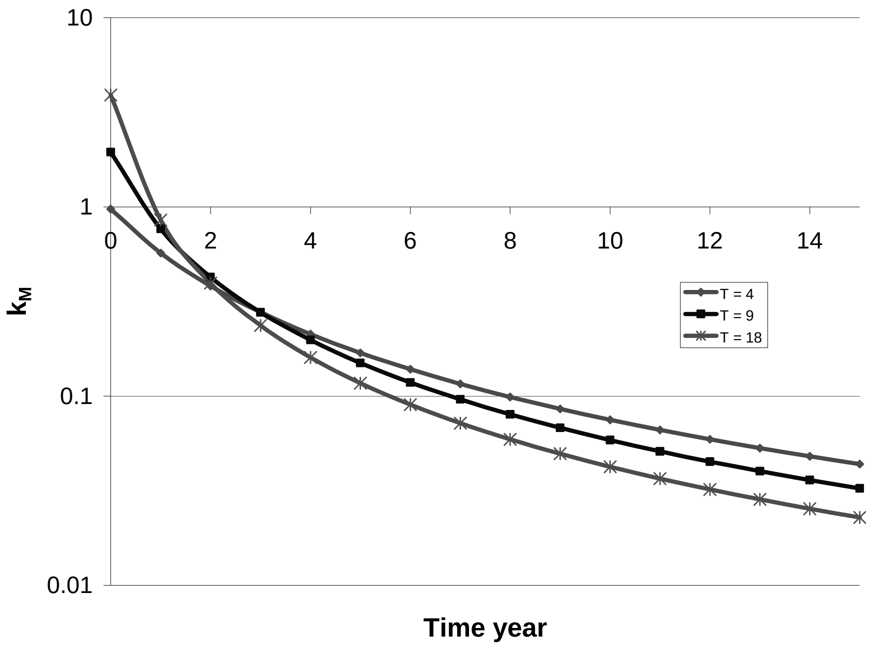

Figure 9 Time course of K_M at three temperatures. Note the ordinate has logarithmic scale to better show the differences between the curves.

Equation (28) is graphically presented in Figure 9. It shows that $k_M(t)$ decreases faster with time at high than at low temperature. As a consequence e_T increases over time at low temperature and decreases over time at high temperature.

The relation between the correction factor (f_T) and temperature is given by (Yang, 1996):

$$f_T = \begin{cases} 0 & T \le -1\ ^0\mathrm{C} \\ \dfrac{T+1}{10} & -1\ ^0\mathrm{C} < T \le 9\ ^0\mathrm{C} \\ 2^{\frac{T-9}{9}} & 9\ ^0\mathrm{C} < T \le 27\ ^0\mathrm{C} \\ 4 & 27\ ^0\mathrm{C} < T \end{cases} \tag{31}$$

The function for f_T between 9 and 27^{0}C was derived from decomposition experiments with ryegrass, carried out in England as well as in Nigeria (Jenkinson and Ayanaba, 1977). The period considered was 2.5 years in Nigeria and 10 years in England. The decomposition constant in Nigeria (26.1 ^{0}C) was four times as high as the decomposition constant in England (8.9^{0}C).

So e_T for MINIPa would be simply equal to f_T if $k_M(t)$ measured over a period of (f_T times t) would be compared with $k_{M,ref}$ measured over a period t. From Jenkinson and Ayanabe (1977) it follows that at those points in (mineralization) time, the remaining substrates have a same composition and an equal resistance to decomposition at both temperatures.

Because e_T of MINIPa depends on time, it is not useful to compare this e_T with e_T values of other models.

The correction factor for moisture content e_W has the form (B.H. Janssen, pers. comm.)

$$e_w = \begin{cases} \dfrac{WFPS}{WFPS_{wp}} 0.05 & WFPS \leq WFPS_{wp} \\ 0.05 + \dfrac{WFPS - WFPS_{wp}}{0.5 - WFPS_{wp}}(1 - 0.05) & WFPS_{wp} < WFPS < 0.5 \\ 1 & 0.5 \leq WFPS \leq 0.7 \\ 1 + \dfrac{WFPS - 0.7}{1 - 0.7}(0.1 - 1) & 0.7 < WFPS \end{cases} \tag{32}$$

WFPS denotes the "water filled pore space", the ratio between actual and saturated moisture content:

$$WFPS = \frac{\theta}{\theta_{sat}} \tag{33}$$

The values of e_W as given above are derived from Alexander (1961), but these have never been put to the test. In case the values of both, e_w and e_T, deviate from 1, the best option likely is to multiply the two, but again no experimental evidence is available (B.H. Janssen, pers. comm.).

3.2.2 MINIPb

Here the time is corrected in a similar way as in MINIPa, viz. by multiplication by a temperature dependent factor.

$$C = C_0 \exp\left[-R(f_T t)^{1-S}\right] \tag{34}$$

The relation between the correction factor (f_T) and temperature is the same as shown for MINIPa. The rate coefficient now is:

$$k_M(t) = f_T(1-S)Rf_T^{-S}t^{-S} \tag{35}$$

or

$$e_T = \frac{k_M(t)}{k_{M,ref}(t)} = f_T^{1-S} \tag{35}$$

So, contrary to the situation in MINIPa, the ratio is independent of time, but still a function (via S) of the material. The correction for moisture content is dealt with in the same way as in MINIPa.

3.2.3 CESAR

Here only the influence of temperature and moisture content are taken into account

$$k_{act} = k_{ref}\, e_T\, e_m \qquad (36)$$

where the temperature response e_T increases or decreases by a factor two with a temperature change of 10 degrees with respect to the reference temperature (10 °C):

$$e_T = 2^{\left[\frac{T - T_{ref}}{10}\right]} \qquad (37)$$

The response to moisture content is given by:

$$\begin{aligned} e_w &= 1, && \theta > \theta_{cr} \\ e_w &= \frac{\theta - \theta_{wp}}{\theta_{cr} - \theta_{wp}} && \theta_{wp} < \theta \le \theta_{cr} \\ \theta_{cr} &= \frac{\theta_{wp} + \theta_{fc}}{2} \end{aligned} \qquad (38)$$

where θ is the moisture content, θ_{wp} the moisture content at wilting point and θ_{fc} the moisture content at field capacity.

3.2.4 RECAFS

As in the preceding models the rate coefficients are a function of temperature and moisture content.

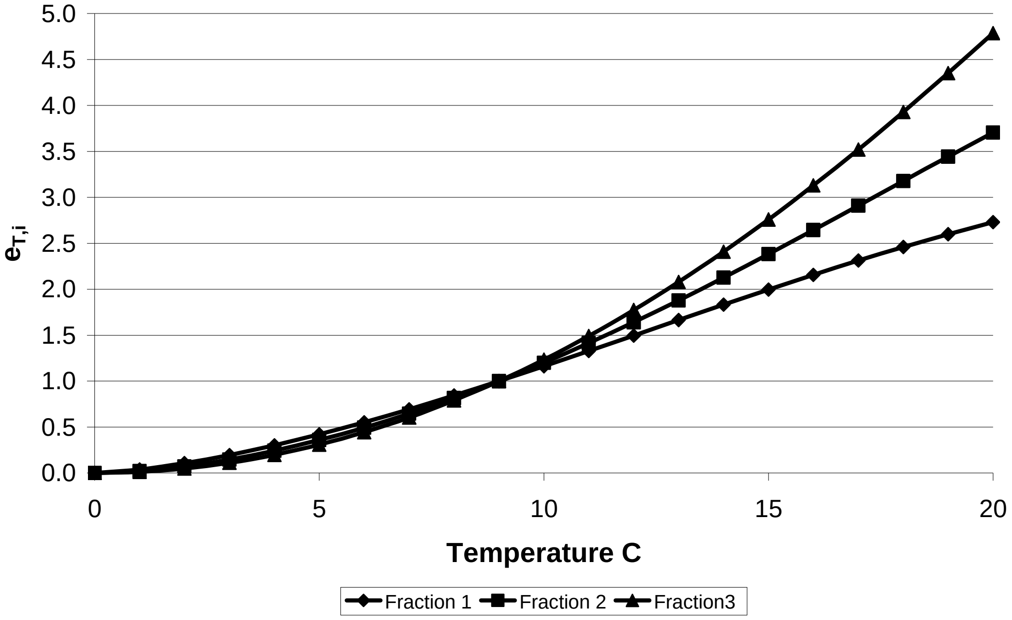

Figure 10 Temperature response for the three fractions distinguished in RECAFS

The temperature response is of the form (Bril *et al.*, 1994):

$$e_T = \frac{a_1 T^{a_2}}{1 + a_3 T^{a_4}} \tag{39}$$

The parameters a_i have different values for the three fractions distinguished. Figure 10 shows the response for the three fractions. The responses are quite similar up to a temperature of 15 °C.

The reaction to the moisture/aeration status is governed by the water filled pore space and is in contrast to the temperature response identical for the three fractions. RECAFS takes the influence of texture into account, the parameters k_2 and k_3 decrease with increasing clay content as depicted in Figure 11.

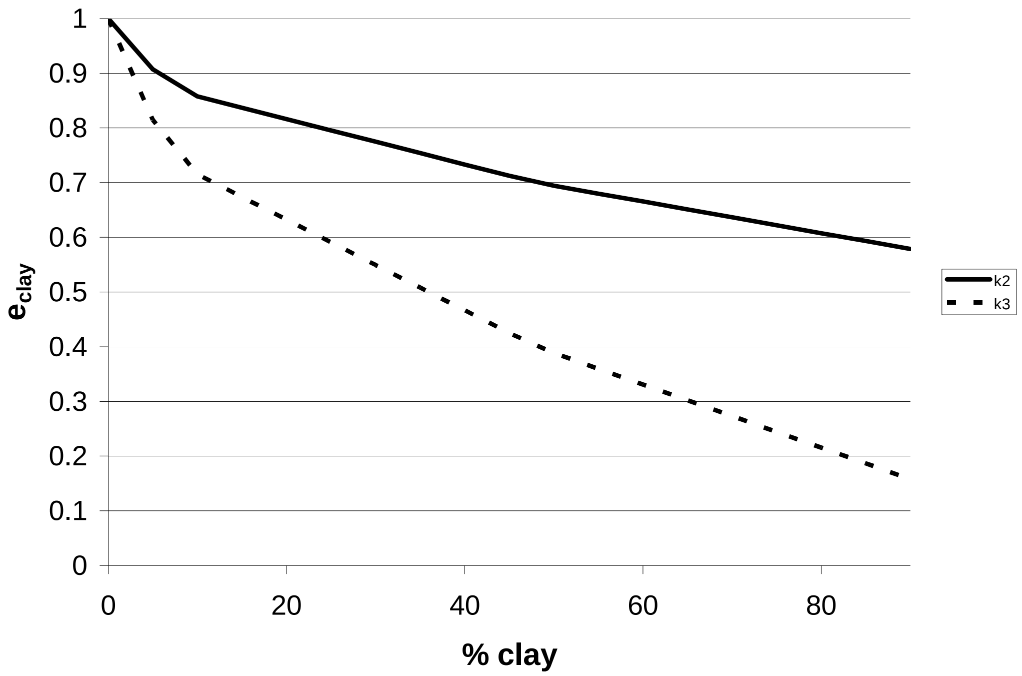

Figure 11 Influence of clay content on the rate constants of RECAFS.

3.2.5 ANIMO

In this model the rate coefficients are corrected for a series of environmental factors reflecting the effect of aeration (e_{ae}), moisture content (e_θ), temperature (e_T) and pH (e_{pH}), and in case of humus also a factor which depends on depth (e_Z).

$$k = e_{ae} e_T e_\theta e_{pH} (e_Z) k_{ref} \tag{40}$$

There are two options to calculate the aeration factor. The first (original) is quite complicated and will not be considered here. Details can be found in Groenendijk *et al.* (2005), page 75-82. The second uses the water filled pore space to calculate e_{ae} in the following fashion:

$$\begin{aligned} e_{ae} &= \frac{6WFPS^2}{1+9WFPS^4}, \qquad WFPS < WFPS_{crit} \\ &= a_0 + a_1 WFPS + a_2 WFPS^2 \quad WFPS \geq WFPS_{crit} \end{aligned} \tag{41}$$

where $WFPS_{\mathrm{crit}}$ is a critical value. The parameters $a_0 - a_2$ are calculated by requiring that e_{ae} and its derivative with respect to $WFPS$ are continuous for $WFPS = WFPS_{\mathrm{crit.}}$ A third condition is the requirement that at the point $WFPS = 1$ (water saturated soil) e_{ae} equals the relative decomposition rate of organic matter at saturation (k_{anae}):

$$a_0 + a_1 + a_2 = k_{anae} \tag{42}$$

The value of k_{anae} is in the range 0.001 – 0.1 (Groenendijk pers. Comm..)

The temperature response is described with an Arrhenius equation:

$$e_T = \exp\left[-9000\left(\frac{1}{T+273} - \frac{1}{T_{ref}+273}\right)\right] \tag{43}$$

3.2.6 NUCSAM

The rate coefficients are corrected for temperature, moisture, and pH effect. The temperature response is:

$$e_T = Q_{10}^{\frac{T-T_{ref}}{10}} \tag{44}$$

where Q_{10} (value 1.6)is the relative increase at a temperature rise of 10 degrees, and T_{ref} a reference temperature (10 °C). Effect of moisture availability is given as a function of the mean ground water table in spring (MSW in m):

$$e_w = \begin{cases} 0.25 & MSW \le 0.25 \\ \log(4MSW) & 0.45 < MSW < 2.5 \\ 1 & MSW \ge 2.5 \end{cases} \tag{45}$$

3.2.7 CENTURY

Here only temperature and moisture effects are dealt with. The calculation of the temperature response depends on the time step considered. When the calculation is done for a time step of one day then:

$$\begin{aligned} e_T &= \frac{g(T)}{g(30)} \\ g(T) &= 11.75 + \frac{29.7}{\pi}\arctan[0.031\pi(T-15.4)] \end{aligned} \tag{46}$$

For a time step of one month:

$$e_T = 0.125\exp[0.07T] \tag{47}$$

The relative moisture content determines the response to moisture status. It is defined as:

$$r_w = \frac{\theta - \theta_{WP}}{\theta_{FC} - \theta_{WP}} \tag{48}$$

where θ is the actual moisture content, θ_{WP} that at wilting point and θ_{FC} that at field capacity. The moisture response is given by:

$$e_w = \frac{1}{1 + 4\exp(-6r_w)} \tag{49}$$

3.3 Comparison of response to environmental conditions

As all models consider a temperature and a moisture content response, these can be compared. Figure 12 gives the comparison of the response to temperature of the models. As said before, the MINIPa response of temperature (e_T) depends on time (Section 3.2.1). Hence, it only makes sense to compare it with the e_T of the other models at equal mineralized fractions. The form of the curves is more or less similar but the actual values differ considerably as Table 2 shows. The responses of Cesar and Century almost coincide. This can be explained by rewriting the response of Cesar and remembering that T_{ref} is 10 C:

$$e_T = 2^{\left[\frac{T-T_{ref}}{10}\right]} = \exp\left(\frac{T - T_{ref}}{10}\ln(2)\right) = \frac{\exp\left(\frac{T}{10}\ln(2)\right)}{\exp(\ln(2))} = \frac{\exp(0.069T)}{2}$$

Comparing this expression with (29) one sees that both are almost identical when the response is divided by that at a temperature of 9 C as then the constant factor (1/2 and 0.125 respectively) cancels in both equations.

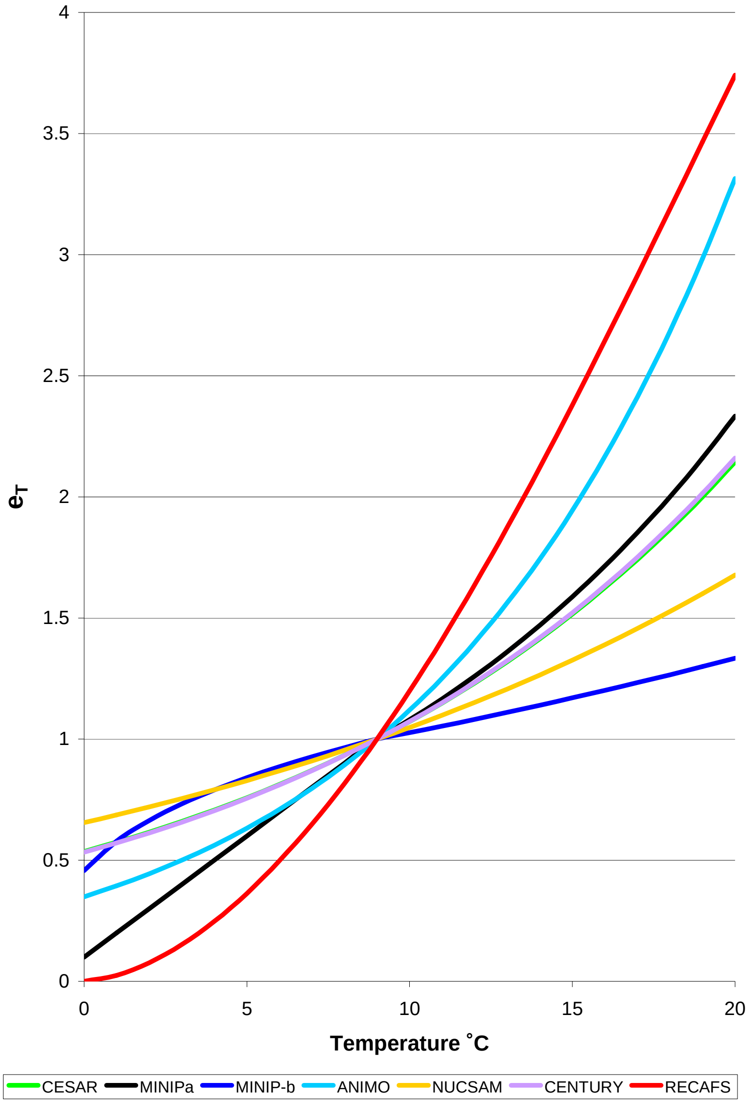

Figure 12 Temperature response of the different models. The results for MINIPa are obtained for equal mineralized fractions)

Table 2 Values of the temperature response for three temperatures. The results for MINIPa and MINIPb pertain to wheat straw.

	MINIPa [1]	**MINIPb**	**CESAR**	**RECAFS**	**ANIMO**	**NUCSAM**	**CENTURY**
T=5ºC	0.6	0.84	0.756	0.36	0.63	0.83	0.756
T=10ºC	1.08	1.03	1.07	1.20	1.12	1.05	1.07
T=15ºC	1.59	1.17	1.52	2.38	1.94	1.33	1.52

[1] At equal mineralized fractions (Section 3.2.1)

Figure 13 compares the response to soil moisture content, the model NUCSAM is an exception as it calculates the response from the mean ground water table depth in spring (see Eq. 49), so its response is absent from Figure 13. The value of the relative decomposition rate at saturation (k_{anae}) in the figure is 0.1. The calculations of Figure 13 pertain to a sandy soil (Sand B1) from the Staring series (Wösten *et al.*, 2001). Field capacity was taken as the water content at a pressure head -100 cm and wilting point that at -16000 cm. The corresponding values for the water content were 0.255 and 0.03 respectively. Table 3 gives the response for three values of water content.

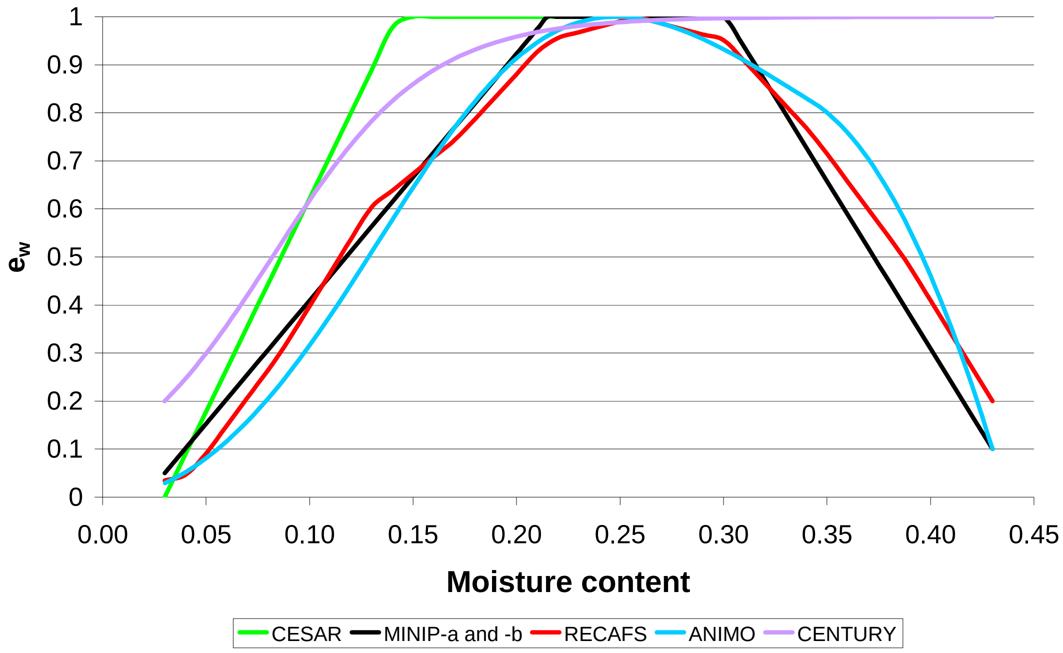

Figure 13 Response to moisture content for the different models.

Table 3 Values of the moisture content response for three moisture contents.

	MINIP a,b	**CESAR**	**RECAFS**	**ANIMO**	**CENTURY**
$\theta = 0.05$	0.153	0.18	0.091	0.08	0.300
$\theta = 0.1$	0.409	0.62	0.398	0.316	0.618
$\theta = 0.15$	0.666	1.00	0.673	0.644	0.86

At high water content decomposition of organic substrates is not limited by lack of water but by lack of aeration. The models MINIPa and b, RECAFS, and ANIMO take this into account implicitly, i.e. the moisture response decreases with water content after an optimum value (see Eq. 36 and figure 3). For ANIMO $WFPS_{crit}$ was given the value 0.8 (Piet Groenendijk pers. comm.), and k_{anae} the value 0.20.

4 Quantitative comparison of the models.

4.1 Introduction

We will discuss here different aspects of the development of organic matter in soil according to the different models. In doing so we restrict ourselves to two types of plant residue viz. wheat straw and green manure. The conditions are constant, temperature is 9 ºC, and other environmental parameters are at their optimum value. The calculations pertain to a soil, with texture sand 42%, silt 50% and clay 8%. A soil with this texture is in the Dutch system of soil classification positioned on the boundary between sandy and loamy soils. We will use here the term "sandy soil".

The model MINIPa is not included in the comparison sections 4.4, 4.5 and 4.6 as the emphasis here is on equilibrium, which is not reached by MINIPa. Moreover long term development will be discussed and MINIPa is should not be used when for when the term (a + t) > 25 year.

4.2 Parameter values

4.2.1 MINIPa

This model has only one parameter, the apparent age a, see Equation (5). According to Velthof (pers. comm.) a of straw amounts to 1.26 y, and of green manure 1.13 y.

4.2.2 MINIPb

This model has two parameters R and S. According to Yang (1996, Table 6.1) for straw $R = 1.11\ y^{-0.34}$, $S = 0.66$, and for green manure $R = 1.39\ y^{-0.36}$, $S = 0.64$.

4.2.3 CESAR

Vleeshouwers & Verhagen (2001) assume one value for $k_{M,2}$ independent of type of material: $k_{M,2}\ (T=9\,^{\circ}C)$ = 0.027 y^1 The coefficient of humification in case of straw amounts to 0.31. They do not mention a value for green manure, here it is assumed that the coefficient of humification of green manure equals that of vegetables: 0.23.

4.2.4 RECAFS

The values of the coefficients of decomposition k_1, k_2 en k_3 at a temperature of 9 °C amount to 39.3, 3.02, and 0.0214 y^1, respectively. The clay content of 8 % leads to a

e_{clay} of 0.877 for k_2 and 0.755 for k_3. The final values are thus found as 39.3, 2.65, and 0.0162.

The distribution of the added carbon over the three fractions postulated in this model depends on the N/C ratio (see Figure 2). For straw with a C/N ratio of 47 and hence a N/C of 0.022 (Velthof pers. comm.) the fractional distribution is 0.141, 0.784, 0.075, and for green manure (C/N = 11, N/C = 0.091) 0.390, 0.558, 0.0511. The efficiencies are independent of the type of material $\varepsilon_{11} = \varepsilon_{22} = 0.3$, en $\varepsilon_{33} = 0.35$.

4.2.5 ANIMO

As mentioned before the values of the coefficients k_1, k_2, k_3, are fixed at 2, 0.2 en 0.02 y^1, respectively. Moreover, the two efficiencies are assumed to be identical. The added material consists of two components. The fraction assigned to the first component and the efficiency are both functions of the apparent age of the material as used in MINIPa (see paragraph 4.2.2). Substitution of the two values 1.26 (straw) and 1.13 (green manure) in Equation (21) yields $p = 0.807$, and $\varepsilon = 0.026$ for straw, and $p = 0.859$, and $\varepsilon = 0.023$ for green manure.

4.2.6 NUCSAM

This model is designed for forest soils, and the parameter values hold for these soils. So the values cannot be applied as such for the materials (straw and green manure) used here. We therefore constructed a data set of time course of the decomposition of straw and green manure with MINIPb and fitted Equation (25). MINIPb was used for this purpose because its parameter values for straw and green manure had been derived from a great number of observations (Yang, 1996, Table 6.1). The parameters obtained for NUCSAM are found in Table 4.

Table 4 Fitted values for the parameters of the NUCSAM model

Parameter	Value	Dimension
STRAW		
k_1	4.89	y^{-1}
k_2	0.492	y^{-1}
k_3	0.0680	y^{-1}
ε_{12}	0.406	-
ε_{23}	0.360	-
GREEN MANURE		
k_1	5.40	y^{-1}
k_2	0.603	y^{-1}
k_3	0.103	y^{-1}
ε_{12}	0.338	-
ε_{23}	0.282	-

4.2.7 CENTURY

According to Paustian et al. (1992) the lignin content (p_1) of wheat straw is 0.15 and its N-content 0.012, so the ratio L/N = 12.5. According to (26) the fraction metabolic (p_3) is 0.625, and the fraction rest (p_2) is 1 – 0.15 – 0.625 = 0.225. To calculate the effect of lignin on the rate coefficient (k_1) of structural material the lignin content with respect to structural material should be used, this ratio is 0.15/(1 – 0.625) = 0.4. The rate coefficient should thus be corrected with a factor exp(-3.0*0.4) = 0.3. For green manure the lignin content is 0.06 and the nitrogen content 0.036, so by a similar calculation as above one finds p_2 = 0.12 and p_3 = 0.82, whereas the lignin content of the structural material is found as 0.06/(1 – 0.82) = 0.33 which leads to a correction factor of 0.368. Some of the parameters (k_4, ε_{45}, ε_{46}, ε_{54}, ε_{56}) depend on the sand and clay content of the soil (see Heesmans and de Willigen for more details).

The parameter values are found in Table 5. As a reference the standard values are also given, these pertain to a temperature of 9 ° C and a soil consisting of pure sand.

Table 5 Parameter values of CENTURY for straw and green manure

Parameter	Straw	Green manure	Standard values	Dimension
k_1	0.346	0.423	1.15	y^{-1}
k_3	4.34	4.34	4.34	y^{-1}
k_4	0.968	0.968	1.71	y^{-1}
k_5	0.0470	0.0470	0.0469	y^{-1}
k_6	0.00106	0.00106	0.00106	y^{-1}
ε_{15}	0.7	0.7		-
ε_{24}	0.45	0.45	0.45	-
ε_{34}	0.45	0.45	0.45	-
ε_{45}	0.539	0.539	0.147	-
ε_{46}	0.0056	0.0056	0.003	-
ε_{54}	0.45	0.45	0.45	-
ε_{56}	0.003	0.003	0.003	-
ε_{64}	0.45	0.45	0.45	-
p_1	0.150	0.06		
p_2	0.225	0.12		
p_3	0.625	0.82		

4.3 The time course of the overall mineralization coefficient.

Organic matter consists of a continuum of materials each with its own resistance against microbial attack (Jenkinson and Rayner, 1977). To approximate the overall mineralisation rate one approach is to assume that the mineralisation coefficient is changing (decreasing) with time as done in the models MINIPa and MINIPb. A more common approach is to assume that the material consists of various components each decomposing with a constant relative decomposition rate. The overall rate then changes because the composition of the material changes.

The relative rate is for a material with *n* components calculated as:

$$\bar{k}_M = \frac{1}{\sum_{i=1}^{n} C_i} \frac{d}{dt} \sum_{i=1}^{n} C_i \tag{50}$$

In Figure 14 the time course of the overall relative mineralization rate of wheat straw at 9°C is shown.

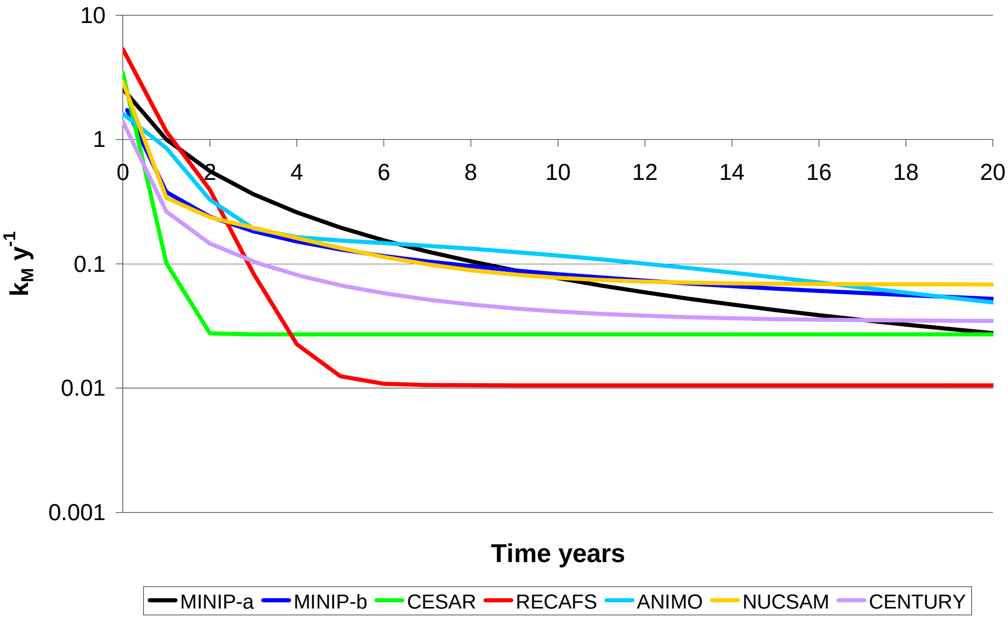

Figure 14 The time course of relative mineralization rate of total organic C (wheat straw) for the different models. Note the logarithmic ordinate.

4.4 Equilibrium values for constant continuous supply of organic matter.

Equilibrium values (C_E) of accumulated organic carbon for a continuous supply of wheat straw and green manure have been calculated for the considered models, with the formulas given in Appendix 2 and the parameters mentioned in section 4.2. In all cases the temperature was set at at 9°C. The results are given in Table 6. The values are expressed with respect to the annual input, e.g. in case of the model CESAR the ultimate value of carbon in the soil is 11.8 times the annual input of wheat straw and 8.8 times that of green manure (Table 6).

It may be questioned whether the models can be used for the calculation of C_E. Only the models CESAR and CENTURY have been developed for longer periods (Section 1). The parameters of the other models have been calibrated over periods of not more than 25 years. The consequence likely is that the values of C_E in Table 6 are too low. This point is further discussed in Section 5.3

Table 6 Equilibrium values (C_E) (with respect to annual supply) found with the models, the soil texture was 42% sand, 8 % clay and 50% silt (only relevant for CENTURY and RECAFS). The meaning of C(1), SOC$_{1a}$, $k_{M,1a}$, and MRT$_{1a}$ are explained in Section 5.2

Model	Material	Fraction	C_E	*C(1)*	SOC$_{1a}$	$k_{M,1a}$	MRT$_{1a}$
MINIPa			n.a				
MINIP-b	Straw		**4.10**	**0.448**	**3.65**	**0.122**	**8.16**
	Green Manure		**1.83**	**0.375**	**1.45**	**0.258**	**3.88**
CESAR	Straw		**11.8**	**0.446**	**11.31**	**0.039**	**25**
	Green Manure		**8.77**	**0.382**	**8.394**	**0.045**	**22**
RECAFS	Straw	1	0.005				
		2	0.37				
		3	5.39				
		Total	**7.55**	**0.442**	**7.11**	**0.062**	**16.1**
	Green Manure	1	0.014				
		2	0.263				
		3	3.67				
		Total	**5.17**	**0.323**	**4.85**	**0.067**	**15.0**
ANIMO	Straw	1	0.404				
		2	0.964				
		3	1.30				
		Total	**2.67**	**0.536**	**2.13**	**0.251**	**3.98**
	Green Manure	1	0.430				
		2	0.703				
		3	1.153				
		Total	**2.29**	**0.510**	**1.78**	**0.287**	**3.48**
NUCSAM	Straw	1	0.204				
		2	0.825				
		3	2.15				
		Total	**3.18**	**0.488**	**2.69**	**0.181**	**5.51**
	Green Manure	1	0.560				
		2	0.928				
		3	0.185				
		Total	**1.67**	**0.416**	**1.26**	**0.331**	**3.02**
CENTURY	Straw	1	0.55				
		2	0.60				
		3	0.158				
		4	0.589				
		5	8.78				
		6	4.45				
		Total	**15.1**	**0.656**	**14.5**	**0.045**	**22.1**
	Green Manure	1	0.149				
		2	0.277				
		3	0.191				
		4	0.605				
		5	7.62				
		6	4.35				
		Total	**13.2**	**0.591**	**12.6**	**0.046**	**21.3**

4.5 Mean residence time

In Section 5.2, the mean residence time (MRT) as measured in soil samples is compared with the C_E values calculated in Table 6. Mean residence time (MRT) is defined as the time to replace the equilibrium amount of soil C (C_E) by the (annual) supply (A). So if A is expressed in g m^{-2} y^{-1} and C_E is expressed in g m^{-2}, the residence time is given by: MRT = C_E/A expressed in a (years). Because in Table 6 the equilibrium value C_E is given with respect to unit supply rate, MRT is numerically equal to this C_E value.

One can also express MRT in terms of the overall k value corresponding to the equilibrium value. According to (50):

$$\frac{d}{dt}\sum_{i=1}^{n} C_i = \bar{k}_M \sum_{i=1}^{n} C_i$$

So that at equilibrium:

$$\bar{k}_M \sum_{i=1}^{n} C_{i,E} = \bar{k}_M C_E = A, \text{or } C_E = \frac{A}{\bar{k}_M}$$, which leads to:

MRT = $1/\bar{k}_M$

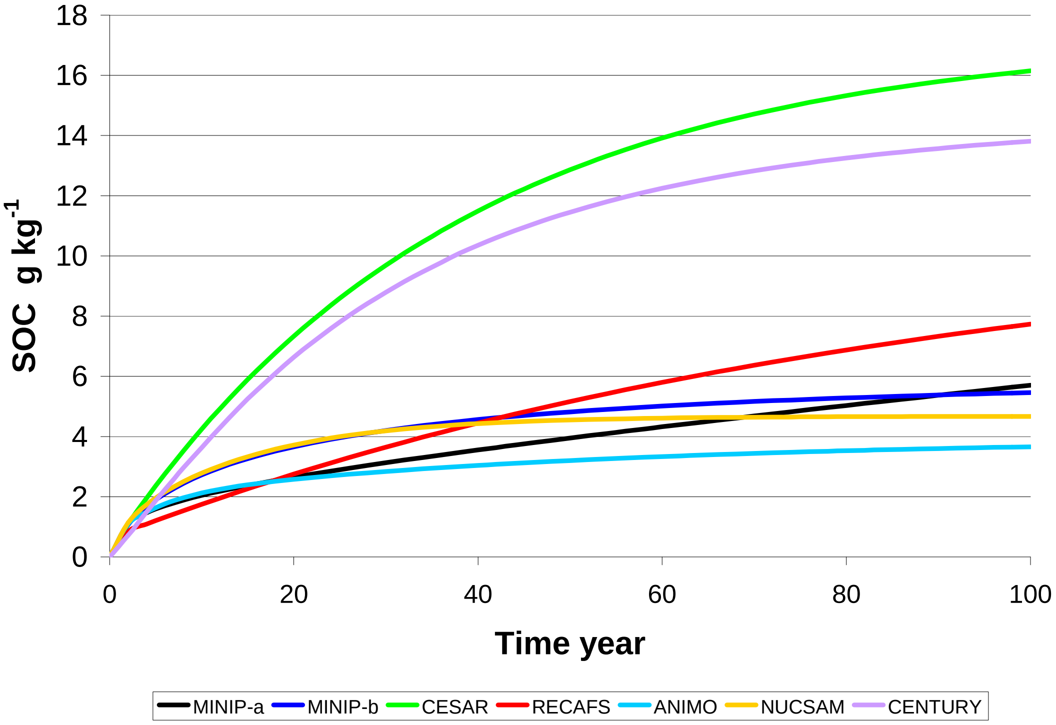

Figure 15 Time course of soil organic C (SOC) for a continuous supply of 1.47 g kg-1 y^1 of C in wheat straw. Temperature 9°C, texture 42% sand, 8 % clay, 50% silt

4.6 Time course of organic matter in case of constant continuous supply under constant conditions

In appendix 2 the solutions for this case are given. The time course of organic C is given in Figure 15. Initial value of organic C-components were set at zero. The supply is 8500 kg ha^{-1} y^{-1} of dry organic matter, i.e. the residues of a winter wheat crop (Velthof pers. Comm.). With a plow layer of 20 cm and a bulk density of 1300 kg m^{-3}, this means a supply rate of 3.27 g kg^{-1} y^{-1}. Given a C fraction of 0.45 in straw organic matte, the supply rate of wheat C is 1.47 g kg^{-1} y^{-}1. If this value is multiplied by the value for total in Table 6 one obtains the absolute values in g C per kg soil. For clarity these are given in Table 7. There appears considerable difference between the models, reflecting the differences in the overall relative decomposition coefficient discussed in section 4.3 and shown in Figure 9. The time course can be characterized by a half-value time, i.e. the time required to reach half of the equilibrium value. These are given in Table 7.

Table 7 Values of half time and E_C of the models. Wheat straw is annually supplied at a rate of 8500 kg ha^{-1}. Temperature is 9°C, texture 42% sand, 8 % clay, 50% silt

Model	Half time (year)	Equilibrium g C per kg soil
MINIP-b	12	6.03
CESAR	26	17.4
RECAFS	64	12.1
ANIMO	8	3.92
NUCSAM	7	4.68
CENTURY	46	22.2

Figure 14 shows that *k* of total C decreases much sharper in Recafs than in the other models, which explains why the half life time of RECAFS has such an extreme position in Table 7.

4.7 Change of organic matter supply

When the supply of organic C is changed the equilibrium value changes proportional to the new supply, i.e. if the supply is halved the new equilibrium value is half the old value. Figure 1 shows the time course of soil organic matter (SOM) in the soil for the situation that there is no more supply of organic matter after the equilibrium value has been reached for MINIPb and CENTURY. The three fractions of soil organic matter of the latter model decrease as governed by their decomposition constants. So the active fraction (almost) disappears first followed by the slow fraction whereas the passive fraction decreases very slowly. The time to reach half of the initial value of the total C ($t_{1/2}$) is (Table 7) 46 year, $t_{1/4}$ is 185 years, and $t_{1/8}$ more than 500 years. The half time for the passive fraction is –ln(0.5)/0.001 = 690 years. The half time of the total C will tend to this value in due course. So, the alarming initial rapid decrease of soil organic matter is followed by a much slower decline thereafter. For MINIPb the half time is 12 years, $t_{1/4}$ is 40 years, $t_{1/8}$ 50 – 60 years, so organic matter is disappearing in a relatively much faster rate. The absolute losses of SOC (in g kg^{-1}), however, as calculated by CENTURY are greater than as calculated by MINIPb.

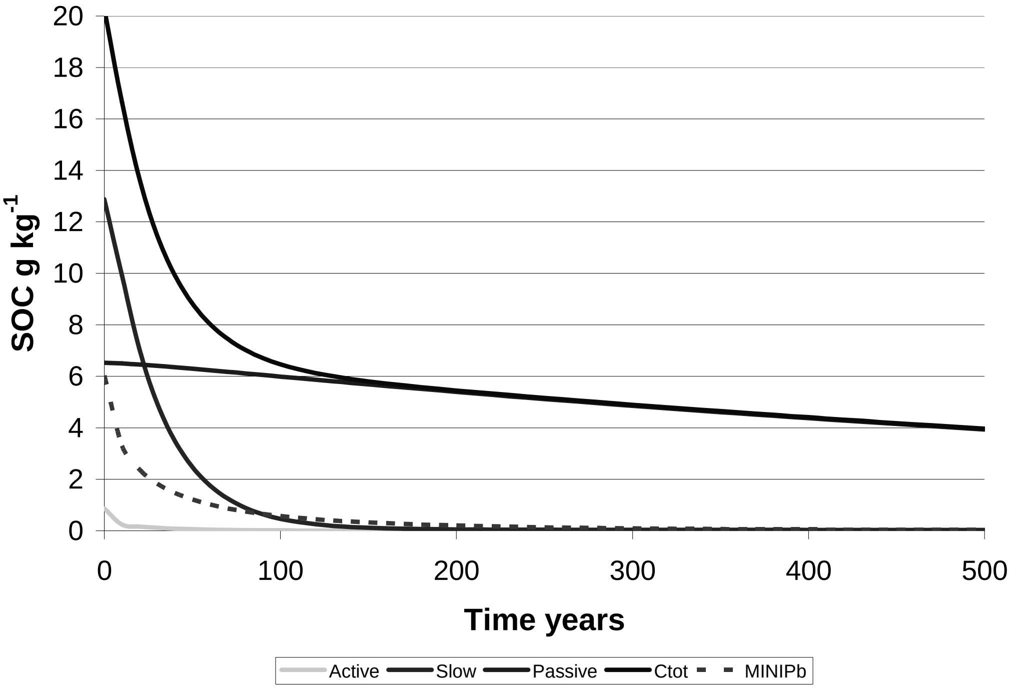

Figure 16 Decrease of SOC of the three components of CENTURY and the single component of MINIPb when after reaching equilibrium input of carbon is zero. Temperature is 9°C, texture 42% sand, 8 % clay, 50% silt

4.8 Change of temperature

In chapter 3 the response to environmental conditions has been discussed. In general, at least within the temperature range considered here, the values of the decomposition rate coefficients change in an exponential fashion with increase of temperature (Figure 12). This obviously has consequences for the time dynamics of the development of organic C in the soil as well as for the equilibrium values. To start with the latter, for the multi-component models the equilibrium values are proportional to the reciprocal values of the decomposition coefficients (e.g. see Equation (A2-19 a-f) so they decrease with temperature in an exponential fashion. For MINIPb the effect of temperature on equilibrium value can be found as:

$$C_E = A\left(f_T^{1-S}R\right)^{\frac{1}{S-1}}\frac{\Gamma\left(\frac{1}{1-S}\right)}{1-S} = \frac{AR^{\frac{1}{S-1}}}{f_T}\frac{\Gamma\left(\frac{1}{1-S}\right)}{1-S}$$

So it appears that in the case of MINIPb, equilibrium is also proportional to the reciprocal value of the temperature response.

When the supply is halved the half time to reach the new equilibrium value decreases with higher temperature. In case of CENTURY for instance this time amounts to 40 years at a temperature of 11 ºC compared to 46 years (Table 7) at 9 ºC.

5 Discussion and conclusions

5.1 Plausibility of the models

There are obviously several ways to compare models. One way is to run the models for a given data set and compare their performance with respect to the estimation of the experimental output data. This has been done by e.g. De Willigen and Neeteson 1985 (six models), De Willigen 1991 (fourteen models), Diekkrüger et al. 1995 (nineteen models), Kersebaum et al. 2005 (eighteen models).

Here we decided to focus on comparison of the way the models describe quantitatively the fate of organic carbon added to the soil. The comparison was based on the prediction of the model outcomes under constant conditions and their relation to organic carbon measured in agricultural soils, rather than on comparison with detailed data from field experiments. Nevertheless it is possible to make some comments on the plausibility of the models.

In Section 5.2 the model outcomes are compared with measured Mean Residence times (MRTs). In Section 5.3 it is calculated how much organic materials must have been applied to get the measured actual SOC levels. Section 5.4 discusses factors that may help to understand the causes of the discrepancy between reality and model calculations. In Section 5.5 the possible effects of lower applications of organic matter and climate change are considered. Finally, in Section 5.6, the major conclusions are presented of this study on decomposition an accumulation of organic matter in soil.

5.2 Mineralization rates and mean residence time

Of the seven models discussed in this report, the model MINIPa is considered to be unsuitable for long-term predictions of changes in carbon content. As explained in Section 2.2.2, the model implies a non-mineralizable rest. That makes it impossible to calculate equilibrium levels (C_E). The model was meant for periods not longer than 40-50 years (Janssen, 2002), but in view of the results in this report it is recommended to limit the use of MINIPa to even shorter periods, say not more than 25 years, about equal to the period of calibration.

Figure 15 and Table 6 show that the calculated SOC levels decrease in the order CENTURY > CESAR > RECAFS > MINIPb> NUCSAM > ANIMO. The high C_E levels found with CESAR are a result of the assumption that applied organic matter behaves after one year as soil organic matter with a constant k_M of 0.027 y^{-1}. Vleeshouwers and Verhagen (2002) based this assumption on three long-term experiments in which soil organic matter was measured at regular times. These experiments, however, do not refer to recently applied organic material, but to soil organic matter. The assumptions they made are similar to those of Kortleven (1963) which have been shown to be invalid. Since that time, a tremendous amount of evidence has been obtained (compiled by e.g. Kolenbrander, 1974, Yang, 1995), showing that the mineralization rate constants of applied organic materials are still strongly affected after one year by the characteristics of the original materials, and for all materials much higher than the mineralization rate constant of SOM.

The high SOC values obtained with CENTURY can be understood by allocation of a part of organic matter to the slow and passive pool. The reciprocals of the equilibrium values (C_E) of Table 6, represent the mean relative mineralization rates (k_M y^{-1}) of soil organic matter; they vary from 0.084 (CESAR) to 0.375 (ANIMO) for straw, and from 0.114(CESAR) to 0.599 (NUCSAM) for green manure in case the total quantity of organic material is considered.

Because A was set at 1, the equilibrium values of Table 6 are equal to the mean residence times of C_E including the C from newly added organic materials. These newly added organic materials decompose very easily and hence have a small MRT. Measured MRTs as given in literature, however, refer to SOM without newly added organic materials, as these materials are removed from the soil sample before the chemical analysis is done. It is difficult to indicate at what time after its application added organic material can be considered as soil organic matter. In the Netherlands, the boundary was set at 1 year (Kortleven, 1963). Taking into account that farmers applied animal manure once a year in springtime, it had also practical advantages to assume that after one year added organic material was "humified". Crop residues are also added to the soil once a year. Most important, however, is that soil samples are taken just before and not just after the addition of animal manure. Hence the analyzed SOC represents SOC$_{1a}$ rather than C_E as calculated in the models. For the comparison of model outcomes to measured SOC data it is therefore better to consider SOC$_{1a}$ than C_E.. The equilibrium values of soil organic carbon that is at least for one year in the soil (henceforth denoted by SOC$_{1a}$), can be found as:

$$\mathrm{SOC}_{1\mathrm{a}} = C_E - C(1) \tag{56}$$

where $C(1)$ is soil carbon built up at the end of Year 1. $C(1)$ also represents the annual addition to SOC$_{1a}$. Hence, in equilibrium it holds (see section 4.5):

$\mathrm{SOC}_{1\mathrm{a}} = \dfrac{C(1)}{k_{M,1a}}$, and the overall mineralization rate of SOC$_{1a}$ can be found as

$$k_{M,1a} = \frac{C(1)}{\mathrm{SOC}_{1\mathrm{a}}} \tag{57}$$

The mean residence times of SOC$_{1a}$ denoted by MRT$_{1a}$ would then be $1/k_{M,1a}$. In Table 6 the values for $C(1)$, SOC$_{1a}$, $k_{M,1a}$ and MRT$_{1a}$ are shown. In BOX 1 the mean residence time of organic matter which is more than 1 year in the soil is calculated. The values of MRT$_{1a}$ in Table 6 vary from 3 to 25 years and are far below MRT measured with ^{14}C, varying from hundreds to thousands of years (Wattel-Koekkoek et al., 2003; Buurman and Jongmans, 2005). Buurman (personal communication) has some data on ^{14}C age (which is MRT) in podzols in The Netherlands. In well drained soils he found ^{14}C ages of 1290-2390 and of 2370-2590 years in the horizons Bh1 and Bh2, respectively. In hydromorphic soils these values were 2170-3650 and 3860 (only one sample) years, respectively. Buurman (personal communication) ascribes these high values to low pH and low chemical soil fertility of the examined podzols (see also Section 5.4).

It may be questioned whether surface soils do contain such old organic matter. O'Brien and Stout (1978) arrived at the conclusion that 16% of SOC in a grassland soil was very old (7000 years) and distributed over the whole profile, the remaining part was ‘modern’ and less than 100 years old. On average, SOC till a depth of 94 cm was 1490 years old. Also they conclude that part of SOC must already have been in the soil before the present form of land-use started.

In the Netherlands, Römkens et al. (1998) found MRT values of SOM in surface soils (0-30 cm) of arable land of 42 years and of grassland of 444 years; in sub-soils (60-80 cm) these values were 1625 and 2456 years, respectively. Depending on the SOM fraction analyzed, MRT varied between 2 and 2000 years in the surface soil and between 2 and 3500 years in the sub-soil. The very high MRT values were of SOM connected to fine soil particles. The half times for the mineralization of topsoil SOM varied between 7 and 39 years (Römkens et al.,1999) which is in agreement with our data in Table 7.

In conclusion, most of the calculated mineralization rates cannot explain the measured longevity of SOM. The relative mineralization rate of the most resistant pool of ANIMO is 0.02 y^{-1}, that of RECAFS (calculated as $(1-\varepsilon)k$) amounts to 0.01134, and the corresponding MRTs are 50 and 88 years. CENTURY has 0.001 for k and 0.00058 for k_M for the passive pool in the soil, corresponding to a MRT of 1720 years. According to MINIPb, it takes 8021 and 16507 years before k_M of the oldest portions of continuously applied straw and green manure, respectively, have reached the value of 0.001. So, under optimum mineralization conditions only MINIPb and CENTURY have the potential to reach a MRT of 1000 years. Under sub-optimal conditions, however, mineralization rates may be considerably lower than assumed in the model calculations, and as a result the corresponding MRT values may be considerably higher. On the other hand, the contents of SOM would have been much higher than they are (see Section 5.3), if MRTs were that high and applications of organic materials were as assumed below. The explanation why SOM is not so high is that most of the very old SOM is found somewhere in the soil profile where mineralization is retarded and new addition of organic material does not or hardly occur. The difference between measured and calculated MRT must therefore mainly be ascribed to factors that have had an effect on the mineralization rates. The major factors are land-use, nutrient availability, pH, and drainage in the past, and soil texture (See Section 5.4).

BOX 1

Equilibrium values of SOC of MINIP-b and CENTURY for application of various type of organic materials

Considering annual applications of 1700, 2000 and 750 kg C per ha with respectively 3800 kg green manure, 6350 kg wheat organic residue and straw, and 10 tons of FYM as realistic, the expected equilibrium SOC would be according to MINIPb:

$1.83 * 1700 + 4.1 * 2000 + 8.1 * 750 = 17386$ kg ha^{-1} or 6.68 g kg^{-1} C. This is about 11 g kg^{-1} SOM. The corresponding average k_M of total SOM would then be $(1700+2000+750)/17386 = 0.256$.

For CENTURY the equilibrium is calculated as:

$13.2 * 1700 + 15.1 * 2000 + 18.3 * 750 = 66365$ kg ha^{-1} or 22 g kg^{-1} C, corresponding to 38 g kg^{-1} SOM

5.3 Current SOM content in arable land and calculated equilibrium SOM

According to data of the former Stichting voor Bodemkartering, cited by Janssen et al. (1990), SOM may vary from less than 10 g kg^{-1} (drifting sands) to more than 900 g kg^{-1} (peaty soils) in the Netherlands. In mineral surface soils of arable land the variation is from 20 to 60 g kg^{-1}.
In the calculations below we set the fraction of carbon in SOM at 0.58, and that in plant residue at 0.45. The mass of the topsoil is 2.6 million kg per ha (see Section 4.6), and hence, 20 g kg^{-1} SOM corresponds to 20*0.58*2600 = 30160, say 30 ton C per ha. The amounts of straw or green manure required to maintain SOM at 20 g kg^{-1}, can be calculated using the equilibrium values (C_E) in Table 6. We take the greatest C_E that was calculated, i.e. 15 by CENTURY for a sandy soil with 42 % sand, 50% silt and 8% lutum. This requires annual additions of 30/15 or 2 tons C in straw or (rounded) 4.4 tons of straw organic matter per ha per year. The organic residue of winter-wheat is about 5200 kg ha^{-1} and 8500 kg ha^{-1} if straw is included (Ministerie van Landbouw en Visserij, 1980). This is considerably more than the required supply of 4.4 tons to maintain a SOM content of 20 g kg^{-1}. The amount of residue mentioned corresponds to the yields obtained in the last decennia of the 20th century. According to FAOstat the yield of winter-wheat increased from an average of 4000 kg ha^{-1} in 1961 to 8900 kg ha^{-1} in 2004, a doubling time of 40 years (see also Figure 17). If we assume that the same doubling time applies to the period before 1961 and that the harvest index did not change, this implies the amount of organic residue including straw added annually to the soil around the year 1920 would have been 2125 kg ha^{-1} which corresponds to an annual addition of 0.37 g C per kg. The equilibrium value for this addition is (Table 6) 15 times as high or 5.6 g C per kg.

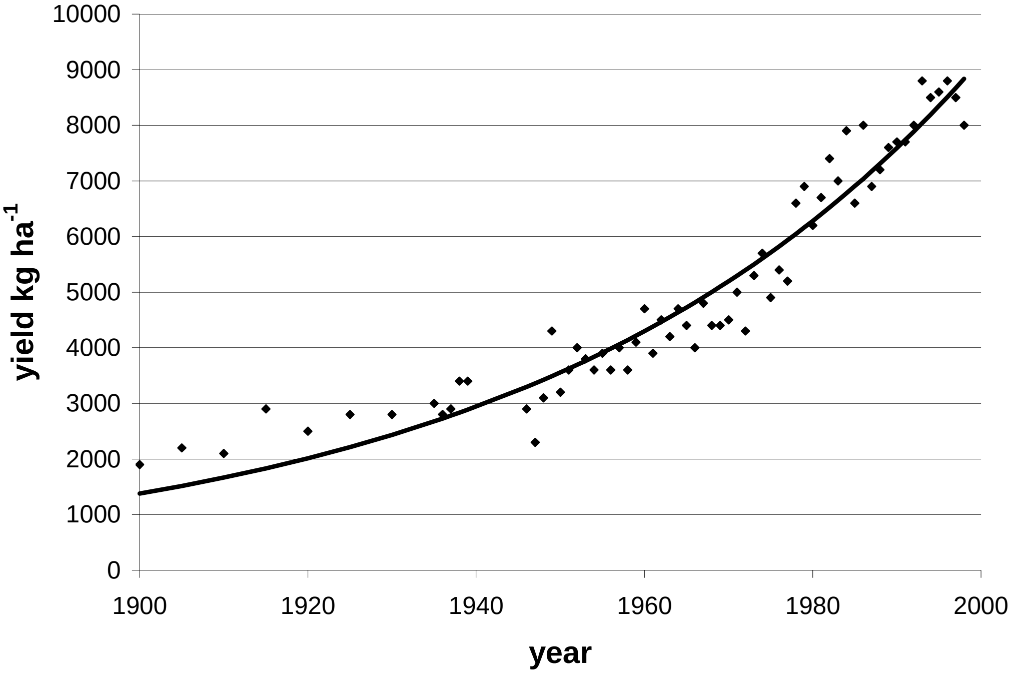

Figure 17 Development of wheat grain yields in the Netherlands Data collected by Oenema (Pers. comm.)

If we assume that the yield increase (and the concomitant increase in residue left) after 1920 proceeds in an exponential fashion with a doubling time of 40 years, the annual addition is time dependent: $A = A_0\exp(at)$, where $a = \ln(2)/40 = 0.0173\ y^{-1}$, and A_0, the addition in 1920, is 0.37 g C per kg, it can be calculated (according to the procedure given in Appendix 3) that after 80 years, i.e. in 2000, SOC has increased to 12.6 g C per kg or about 22 g SOM per kg. This value is within the range found for arable land.

An often applied organic material that decomposes more slowly than straw is farmyard manure (FYM). Using the Model MINIPb, equation A2-6, and taking 0.7059 and 0.6023 as values for the R and S parameters for FYM (Ten Berge et al., 2007), the equilibrium SOC or C_E is calculated as 8.1. This comes down to annual additions of 30160/8.1 or 3723 kg C per ha to maintain SOM at 20 g/kg. FYM contains 75 kg C per ton, so the required annual additions of animal manure are around 50 tons per ha to keep SOM at 20 g/kg. It is unlikely the farmers have supplied such quantities during 5000 years.

Calculations with CENTURY setting the lignin content of FYM at 0.25 and the N-content at 0.023, yielded an equilibrium value of 18.3, about 2.3 times that calculated with MINIP-b. So, the required annual addition of FYM to keep SOM at 20 g/kg would be 30160/18.3 or 1648 kg C, corresponding to 22 ton per ha. Such an addition is quite realistic if it takes place once in a rotation of say 4 years, but it is still not realistic to assume that farmers could annually apply these quantities during several centuries.

Common practice is to apply various types of organic matter, *e.g.* green manure, straw and FYM,. For realistic application rates of green manure, wheat straw and farmyard manure equilibrium values for MINIPb and CENTURY are found as 11 and 38 g kg^{-1} SOM respectively (see BOX 2 for explanation of the calculation). The equilibrium value found with MINIPb is about half of the lowest value of the mentioned range of 20-60 g kg^{-1}, that of CENTURY on the other hand is well within the range for arable soils.

In conclusion: the equilibrium SOM contents as calculated by most models are much lower than the present SOM levels in arable soils. Only results by CENTURY are in the same range as the measured SOM contents. This outcome is not a surprise as only CENTURY and CESAR were developed for the calculation of equilibrium SOM. The other models are more appropriate to calculate how much SOM can be built in say 25 years. Figure 15 shows a great difference between the models CESAR and CENTURY on the one hand and MINIP, RECAFS, ANIMO and NUCSAM on the other hand. In view of methods applied for parameter calibration, MINIPb and RECAFS likely are most reliable for the short run, and CENTURY for the long run.

BOX 2

SOC_{1a} values and corresponding MRT

To find the content of SOC_{1a}, standing for SOC that is at least one year in the soil Section 5.2.1), the organic carbon that is built up during the first year after application ($C(1)$ in Table 6) has to be subtracted from equilibrium SOC (C_E), as shown in Equation 56. For MINIPb in case of FYM, $C(1)$ is estimated at 0.61.The expected equilibrium of SOC_{1a}, would be according to MINIPb:
$(1.83- 0.375) \cdot 1700 + (4.1-0.448) \cdot 2000 + (8.1- 0.61) \cdot 750 = 15331$ kg ha^{-1} or 5.90 g kg^{-1} C, which corresponds to SOM_{1a} of about 10.2 g kg^{-1}. These calculations indicate that 'normal' use of arable land on sandy loams would result in 1% SOM_{1a} according to MINIPb, and about thrice as much or 3% according to CENTURY after at least 500 years. SOM_{1a} would be around 0.8% according to the models ANIMO and NUCSAM, and between 1 and 3 % according to CESAR and RECAFS.

In equilibrium, the annual decomposition of SOC_{1a} is equal to the annual addition ($C(1)$), being $0.375 \cdot 1700 + 0.448 \cdot 2000 + 0.61 \cdot 750$ or 1991 kg C ha^{-1} y^{-1}, and the corresponding MINIPb k_M is $1991/15331 = 0.13$ y^{-1}. The corresponding MRT is 7.7 years, much lower than those mentioned in Section 5.2.1.

According to CENTURY C_E values are about thrice the values found with MINIPb; and k would be $0.13/3 = 0.043$, and the corresponding MRT 23 years, still far below the measured MRTs.

5.4 Factors affecting SOM content and MRT

5.4.1 Land-use history

In general, SOM contents decrease in the order: grassland (steppe) > forest> arable land. Under steppe the organic material annually added to the soil is 2-4 times as high as under forest (Kononova, 1975). Although the steppe material decomposes more easily than the forest material, the overall effect is that steppe soils have higher SOM contents than forest soils. In the Netherlands, climate is and was too wet for steppes, but natural or permanent grasslands behave at least partly similar as steppe vegetation. The low SOM in arable land is caused by the removal of the major part of organic materials produced above-ground, and the stimulation of decomposition by tillage. Van Hove (1969) gave the following average SOM contents in topsoils (0-30 cm) in Belgium: grassland 46, forest 42, arable land 27 g/kg. A similar pattern was found by Velthof (2003) on löss soils, but not or not always on sandy soils. Velthof ascribes this to the biased distribution in his study of arable land to deep man-made soils.

Apart from the inappropriateness of most models, several other reasons may be put forward to explain why the actual SOM contents are higher than those calculated in 5.1.3. A special situation is found in man-made soils, 'eerdgrond (NL)/ plaggen epipedon (soil taxonomy)'. These have been formed by additions of farmyard manure from deep litter houses. A rough proxy is that the ratio of the area of arable land to the area of non-arable land (heat and grassland) was 1 : 10 (Edelman, 1960).

Every year heather was brought to the deep litter houses, where it got mixed with animal droppings. In spring the mixture was used as manure for the arable land. This process has been continued for centuries. On average, the thickness of the thus formed soil with high SOM contents (50 -100 g/kg) increased 10 cm per century (Edelman, 1960, page 23) Especially man-made soils may contain charcoal which decomposes slowly (see van Minnen, 2008) and thus contributes to high SOM and MRT values.

Another type of difference in land-use between the past and the present situation in the Netherlands is found in former sea and lake bottoms. Here a subdivision of SOM in two parts can be made: the remainders of the original SOM in the sediments and the newly formed SOM. A well-known example is the situation in the in the Noordoostpolder. The polder was reclaimed in 1944. In 1951 three experimental farms were established with three different organic matter management scenarios (Grootenhuis, 1976). In 1976, SOM in the topsoil consisted of 72 tons of old SOM and (depending on the organic matter scenario) 6-15 tons of SOM formed in 25 years of agricultural land-use (Janssen 1984 , Janssen and Van Reuler 1986). The values of k_M were calculated to be 0.007 and 0.12 for the old and the newly formed SOM, corresponding to MRTs of 143 and 8 years, respectively.

Also in other reclaimed lake bottoms a distinction into old and new SOM proved the key to understand the present mineralization characteristics of SOM (Janssen, personal communication).

In a similar way, SOM in former peaty land, such as in the "Veenkoloniën", can be subdivided into two parts: the remainders of the original peaty material and the newly formed SOM. Poor drainage in the past has resulted in the formation of peat, a poor quality SOM as reflected in high C:N, low CEC and low mineralization rate. The newly formed SOM has a "normal" C:N around 10-12 and a "normal" mineralization rate (Van Dijk, 1968; Janssen, 2002). Once drainage has been improved, mineralization rate sharply increases. Buurman (2008) found higher MRT-values in hydromorphic soils than in well-drained soils.

In natural ecosystems, being the historic land-use of most soils, lack of N and sometimes lack of P have retarded the decomposition of added organics. This is reflected in high C:N and high C:P ratios of SOM. Van Hove (1969) found C:N to be higher in sandy than in clayey soils. In soils with 50% sand, C:N was 22 under pine forest, 16 under deciduous forest and 11 in agricultural land. The higher SOM under forest than in agricultural land, mentioned above is probably at least partly caused by N deficiency suffered by the decomposing microorganisms.

In a study by Van Dijk (1968), C:N varied from 24 in soils with 170 g SOM kg^{-1} to 11 in soils with 33 g SOM kg^{-1}, again suggesting that N deficiency was a partial cause of slow decomposition. Podzols and some man-made soils ("zwarte enkeerd- and gooreerdgronden") have C:N between 17 and 23 (Janssen et al., 1990; Velthof, 2003), reflecting the origin of heather and the possible presence of charcoal. They point to poor N supply and hence slow mineralization in the past, thus contributing to still rather high SOM levels.

Related to lack of nutrients is low pH. In general SOM is higher at high pH than at low pH, which is ascribed to higher plant production at high pH. Rates of decomposition, however, are also higher at high pH with an optimum at pH 7-8. The relation between SOM and pH may therefore show a minimum.

The MRT studies by Buurman (2008) refer to natural ecosystems. He has observed that levels of SOM with a high MRT may decrease once the soil receives lime and fertilizers facilitating the decomposition of SOM.

5.4.2 SOM and soil texture

Protection of organic material against decomposition on clayey soils probably is one of the most important causes of high SOM contents. SOM may increase by 0.7 to 1.1 g/kg per % increase in clay, as can be derived from Kortleven (1963), Janssen et al. (1990), Hassink (1995). In his studies, Hassink introduced the concept of saturation of the protective capacity of a soil, and he found that the protective capacity could be described by: $Y = 4.07 + 0.37\ x$, where $y = C$ (g/kg) in fraction < 20 mu and $x =$ particles (%) < 20 mu. Soils with a 'saturation deficit' have lower decomposition rates than soils saturated with organic matter. Once soils have become saturated by organic matter addition in the past, newly added organic material cannot be protected anymore. The high decomposition rates calculated with the models used in the present report refer to situations of non-protected organic matter, as found in sandy soils and in clayey soils without a saturation deficit. Only CENTURY and RECAFS take soil texture into account. Figure 18 shows results of a calculation with CENTURY of the role of clay content in accumulation of carbon. In this calculation annually 382 C per m^2 (corresponding to 8500 kg wheat straw per ha) was applied. The equilibrium values are expressed in g C per kg by using the soil bulk densities as calculated by CENTURY, where soil bulk density is a function of clay content. The increase of SOM (roughly 2 times the value of SOC shown in the figure) per % increase in clay is about 1.5 g kg^{-1}. As equilibrium values are proportional to annual supply, a supply of 2/3 of 382 g m^{-2} would lead to a slope of 1 g (kg %clay)$^{-1}$.

Wattel et al. (2003) assessed MRT's of organic matter in the clay-size fractions; average values were 357 and 1089 years in case the clay mineral was kaolinite and smectite, respectively. For soils in the Netherlands, where illite is the main clay mineral, MRT may be estimated to be around 700 years. The corresponding *k* is 0.0014.

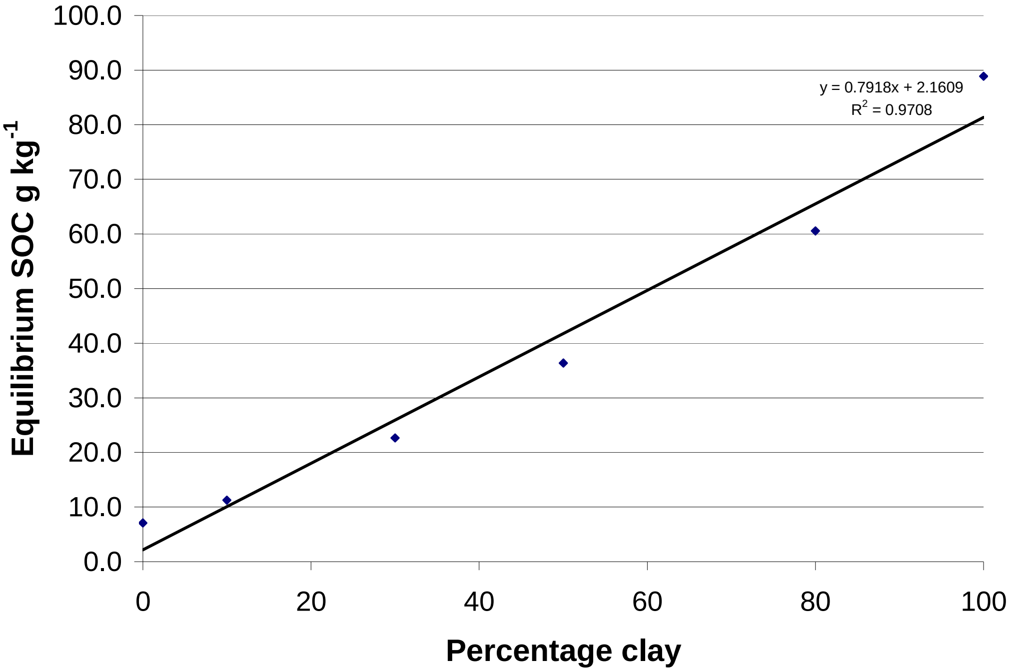

Figure 18 Equilibrium values of soil organic C (SOC) as a function of clay content according to CENTURY. Annual supply rate 382 g m-2.

5.5 Expected changes in SOM

The fact that the current SOM content only partially reflects the present land-use, poses a major problem to understand and predict the behavior of SOM as a response to a reduction of FYM according to European regulations or as a response to climate change.

According to the tested models (Section 5.3), present land-use on arable soils would result in SOM_{1a} levels between 8 and 30 g kg^{-1} in sandy soils. The rest of SOM is a heritage of the past and related to clay and fine-silt particles. Poor drainage and low nutrient status may have retarded the decomposition of organic matter, resulting in higher levels of SOM and MRT than are found in limed and fertilized arable land. In some cases high SOM contents have been created on manmade soils (eerdgronden, soils with a plaggen epipedon), where during centuries large quantities of organic materials have been applied.

Reducing the present application levels of organic materials by 50% may lead to losses of 4 and 15 g kg^{-1} of SOM at infinity. The half life times (Table 7; Section 4.7) vary from 7 to 45 years, implying SOM losses of 2 to 8 g kg^{-1} during such periods. Figure 16 shows the expected course according to CENTURY and MINIPb. The figure refers to situations where the present SOM has been formed by the present land-use and where nutritional, drainage or draught conditions are not limitating to decomposition of SOM and no protection by clay particles are found.

Some questions are still to be answered:

- How can we find the portion of SOM that is not related to the present land-use?
- How can we find the portion of SOM that is related to clay and silt particles?
- How does a change in annual additions of organic matter affect the decomposition of SOM that is not related to the present land-use?
- How does a change in annual additions of organic matter affect the decomposition of SOM that is related to clay and silt particles?

For the first two questions no suitable methods of chemical analysis do exist, and some "tricks" are needed. The answer to the first question may be found making use of the fact that SOM formed under the present conditions of highly fertile arable land must have a C:N ratio of 8 to 10, while SOM formed under poor conditions has a C:N considerably higher than 10. The study by Van Dijk (1968) followed this line for reclaimed peat soils (Veenkoloniale gronden). For instance: a soil contained 6% SOM with a C:N ratio of 17. Indicating the content of SOM formed under the present landuse by X, and assuming that peat remainders have C:N of 25, it follows from $X \cdot 10 + (6 – X) \cdot 25 = 6 \cdot 17$, and that $X = 3.2$. So the 6% of SOM could be split in 3.2 % formed recently and 2.8 % from former peat particles. Of course the outcome heavily depends on the assumed C:N. The assumption of a C:N of 20 of SOM formed in the past under poor conditions would result in $X = 1.8$, in that case 4.2% SOM would be remnants from the past. Circumstantial information may help to assign a correct C:N to old SOM.
A similar approach can be followed to find the portion of SOM connected with the fine soil particles. SOM connected with these particles usually has C:N of 10 (*e.g.* Chichester, 1969). Further, the relations developed by Hassink (1995) for C and N associated with the fraction of particles < 20 mu may be used:
$C\ (g\ kg^{-1}) = 4.09 + 0.37 \cdot \%$ particles< 20 mu, and
$N\ (g\ kg^{-1}) = 0.40 + 0.037 \cdot \%$ particles< 20 mu
These relations also point to C:N of 10 in the fine particles.

The questions how changes in annual applications of organic matter influence SOM that is not related to the present land-use and SOM that is connected with clay and silt particles are even more difficult to answer. SOM with a high MRT decomposed slowly in the past, but perhaps decomposes at similar rates as 'modern' SOM once the external conditions of pH and nutrient supply have been improved. From incubation experiments in the study by Van Dijk (1968) with reclaimed peat soils, it is derived, however, that 'modern' SOM mineralized two to four times as fast as SOM from former peat.
From field trials it was estimated that the relative mineralization rate of 'modern' SOM (25 years in this study) was about 18 times the relative mineralization rate of old SOM from the former sea bottom (Janssen, 1984). Ten Berge et al. (2007, Bijlage 3), applying model MINIPb, arrived at the conclusion that k_M of soil organic matter built up during 25 years by green manure, straw, FYM or compost is 9 to 16 times the k_M of original SOM that did not receive any new organic material during those 25 years, and 2 to 3 times as high the k_M of original SOM that continuously received

new organic material. As a practical first proxy k_M of "old" SOM may be set at one tenth of k_M of SOM developed recently, *i.e.* under the present land-use during at least 25 years.

According to literature (Chichester, 1969; Hassink, 1995), conflicting results have also been obtained as far as it concerns decomposition rates of organic C and N associated with fine particles. This is certainly true for N mineralization. Possible retardation of C mineralization compared to C mineralization of not-protected SOM does not necessarily result in retarded N mineralization, because SOM connected with fine particles has a lower C:N and therefore more N mineralized per unit of C mineralized. Again formulating a practical first proxy, k_M of "protected" SOM may be set at half the k_M of not-protected SOM.

It is obvious that the here suggested proxies require more experimental evidence. Unfortunately, long-term field experiments have low priority among research-funding agencies these days.

Given the supposed differences in k_M of modern and old SOM, a change in temperature would mainly affect SOM developed during the last decades. An increase of 1°C speeds up decomposition by a factor of 1.03 to 1.20 (Table 2). The equilibrium SOM would decrease by the reciprocal values, so at infinity SOM would be 0.97 to 0.83 times the present value. See also Section 4.7.

5.6 Conclusions

The models discussed in our study are – at least originally - meant for predictions at different time scales. CESAR, MINIPa and MINIPb were used for forecasts over several decennia. RECAFS and ANIMO are designed for use for a couple of growing seasons, though ANIMO now is part of the chain of models called STONE (Schoumans *et al.*, 2002) which is used to explore the effects of different scenarios on leaching and eutrofication for a period of 30-50 years. NUCSAM, as applied here, is also meant to be used for short periods, but it has been scaled up to models which could be used for larger time and spatial scales. CENTURY is specifically meant for use on large time scales (indeed for centuries), which explains that its results are especially for this scale more in agreement with empirical data of SOM content than the outcomes of the other models. The predictions of SOM content by CENTURY are in the range expected for arable soils. The distribution over the components, however, is such that the resulting MRT of SOM developed in pure sand is far too low. The fraction of SOM in the component "slow" is about twice of that in the component "passive", this leads to a MRT of about 20 years, and to a loss of 2/3 of the SOM within 100 years, as shown in Figure 16.

A major problem encountered when comparing model outcomes and actual SOM contents is that actual SOM contents are only partly the result of the present conditions. Former land-use, poor drainage, the absence of fertilizer use and liming practices must have retarded the decomposition rate of SOM in the past, say before 1900, and by that caused accumulation of organic matter. On the other hand, crop yields, and hence quantities of crop residues that could be worked into the soil, were lower than at present, resulting in lower SOM levels than expected on the basis of the present applications of organic matter. Another complication is the effect of the fine soil particles. Generally accepted rules of thumb to take soil texture into account are not at hand.

Despite the uncertainties in the assumptions and thus in the predictions, it is estimated that halving the applications rates of organic materials may lead to absolute SOM losses of 2 to 8 g per kg within about 20 years. This comes down to changes in SOM contents from 20 to 18 g kg^{-1} or from 60 to 52 g kg^{-1}. An increase in temperature of 1ºC would render SOM contents 0.97 to 0.83 times the values at present temperature.

It may be questioned whether such a decrease would harm soil structure and effect yields. The lowest level of 18 g kg^{-1} is still above threshold values of 6 to 10 g kg^{-1} mentioned in literature (Loveland and Webb, 2003; Janssen and De Willigen, 2006). According to Pieri (1989), there is little risk of physical degradation if SOM is at least 0.07 times (clay + silt). In extremely heavy soils, containing no sand fraction at all, 70 g kg^{-1} of SOM would be required, but in light soils with less than 100 g kg^{-1} of (clay + silt), 7 g kg^{-1} of SOM would suffice. Droeven et al. (1982) have shown in a 20-years field experiment dealing with different organic manure treatments that yields kept increasing although soil structure decreased over time. Hoogerkamp (1973) clearly demonstrated that the effect of SOM on yield merely was an effect of N. In his experiments lasting 9 years, none so-called "additional" effects could be found, and fertilizer N could compensate for yield reduction on soils with lower SOM contents.
So the risk of yield reduction and severe damage to soil structure is considered very small, but the mentioned decrease in SOM of 2 to 8 g kg^{-1} may result in a decrease in N mineralization, which is estimated at of 30 to 50 kg N per ha per year. In principle, yields remain at the same level provided extra fertilizer N additions compensate for the lower mineralization.
After the first 20 years it will take some hundreds of years to lose another 2 to 8 g SOM per kg soil. That loss likely has less effect on N mineralization than the SOM lost in the first 20 years because the lost SOM after 20 years has a lower relative mineralization rate.
For calculations about expected changes in 5 to 25 years, probably models as MINIPb and RECAFS are more suited than the others.

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Appendix 1 Application of the Laplace Transformation on a system of linear differential equations.

The system of equations in matrix form was in gievn in the main tezt Equation (12)

$$\frac{d\mathbf{C}}{dt} = \mathbf{k} \cdot \mathbf{C} \tag{A2-1}$$

If the vector of initial values is denoted by $\mathbf{C}_0$ the Laplace transformed version of (A2-1) reads:

$$s\mathbf{I} \cdot \mathbf{U} - \mathbf{C_0} = \mathbf{k} \cdot \mathbf{U} \tag{A2-2}$$

where s is the Laplace parameter, **I** the identity matrix, and **U** the Laplace transformed **C**-vector. So that:

$$\mathbf{U} = \left(s\mathbf{I} - \mathbf{k}\right)^{-1} \cdot \mathbf{C}_0 \tag{A2-3}$$

Then **U** can be transformed back into **C**, by well-known technmiques or as is done here with the help of a formula-manipulation program like Mathematica.

Appendix 2 Accumulation of carbon in the soil for constant continous application of one unit of C in fresh organic material.

MINIP-a and -b

For the mono component models MINIP-a and –b, is is not possible to solve the rate equation as each addition has to be followed in time. The solution can be given , however, as an integral:

$$C(t) = A\int_0^t f(x)dx \tag{A2-1}$$

MINIP-a

Substitution of *f*(*x*) = $\exp\left[b(a+x)^{-m} - ba^{-m}\right]$ into (A2-1) does not lead to a solution in terms of known functions, the integral has to be evaluated numerically.

MINIP-b

The substitution of *f*(*x*) = $\exp\left[-Rt^{1-S}\right]$ into (A2-4) and integration leads to:

$$C(t) = A\int_0^t \exp\left[-Rx^{1-S}\right]dx = AR^{\frac{1}{S-1}}\frac{\Gamma\left(\frac{1}{1-S}, Rt^{1-S}\right) - \Gamma\left(\frac{1}{1-S}\right)}{S-1} \tag{A2-2}$$

where the incomplete gamma function is defined as $\Gamma(a,z) = \int_z^\infty t^{a-1}e^{-t}dt$ and the complete gamma function as $\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}$. By taking the limit as $t \rightarrow \infty$ of (A2-2) the equilibrium value is found as:

$$C_E = A\frac{R^{\frac{1}{S-1}}\Gamma\left(\frac{1}{1-S}\right)}{1-S} \tag{A2-3}$$

CESAR

When there is a continous supply of *A* (for instance in g m^{-2} a^{-1}) the rate equation reads:

$$\begin{aligned} \frac{dC_1}{dt} &= -k_{D,1}C_1 + A \\ \frac{dC_2}{dt} &= h_c k_{D,1}C_1 - k_{M,2}C_2 \end{aligned} \tag{A2-4}$$

With initial conditions $t = 0,\ C_1 = C_{1,0}, C_2 = C_{2,0}$ the solution of (A2-4) is:

$$C_1 = \frac{A(\exp(-k_{D,1}t)-1)+k_{D,1}C_{1,0}\exp(-k_{D,1}t)}{k_{D,1}}$$

$$C_2 = \frac{1}{k_{m,2}(k_{D,1}-k_{M,2})}\begin{bmatrix}-h_c k_{D,1}k_{M,2}C_{1,0}\exp(-k_{D,1}t)+(h_c k_{D,1}C_{1,0}\exp(-k_{M,2}t)+k_{m,2}(k_{D,1}-k_{M,2})C_{2,0})+ \\ h_c A(-k_{D,1}\exp(-k_{M,2}t)+k_{D,1}-k_{M,2}+k_{M,2}\exp(-k_{D,1}t)\end{bmatrix}$$

(A2-5)

The equilibrium value can be obtained by either taking the limit as $t \rightarrow \infty$ of (A2-5) or by setting $dC/dt = 0$ in (A2-4). One finds:

$$C_E = \frac{h_c A}{k} \qquad \text{(A2-6)}$$

RECAFS

For this model the rate equations and solutions are analogous to that for CESAR, for the ith component the rate equation is:

$$\frac{dC_i}{dt} = (\varepsilon_{ii}-1)k_i C_i + p_i A \qquad \text{(A2-7)}$$

The solution is:

$$C_i(t) = \frac{p_i A}{(1-\varepsilon_{ii})k_i}(1-\exp(-(1-\varepsilon_{ii})k_i t)) + C_{0,i}\exp(-(1-\varepsilon_{ii})k_i t) \qquad \text{(A2-8)}$$

And the total amount of carbon is thus:

$$Y(t) = \sum_{i=1}^{3} C_i(t) = \sum_{i=1}^{3} \frac{p_i A}{(1-\varepsilon_{ii})k_i}(1-\exp(-k_i t)) + C_{0,i}\exp(-k_i t) \qquad \text{(A2-9)}$$

Equilibriumvalues are found from (A2-7) for the ith component:

$$C_{i,E} = \frac{p_i A}{(1-\varepsilon_{ii})k_i} \qquad \text{(A2-10)}$$

ANIMO

The rate equation for the two fractions of the added organic matter is again analogous to that given for CESAR, but that for humus differs:

$$\frac{dC_1}{dt} = -k_1 C_1 + pA \qquad (a)$$

$$\frac{dC_2}{dt} = -k_2 C_2 + (1-p)A \qquad (b) \qquad \text{(A2-11)}$$

$$\frac{dC_3}{dt} = \varepsilon k_1 C_1 + \varepsilon k_2 C_2 - k_3 C_3 \qquad (c)$$

The solution for C_1 and C_2 is similar to that given in (A2-2), that for C_3(t) is in symbolics quite long for convenience we write:

$$u_1 = \exp(-k_1 t); u_2 = \exp(-k_2 t);\ u_3 = \exp(-k_3 t)$$

It is found

$$
\begin{aligned}
&C_1(t) = \frac{pA}{k_1}(1-u_1) + C_{1,0}u_1 && (a)\\
&C_2(t) = \frac{(1-p)A}{k_2}(1-u_2) + C_{2,0}u_2 && (b)\\
&C_3(t) = \frac{A\varepsilon}{k_3} + \frac{pA\varepsilon - k_1\varepsilon C_{1,0}}{k_1-k_3}u_1 + \frac{A\varepsilon(1-p) - k_2\varepsilon C_{2,0}}{k_2-k_3}u_2 + && (c)\\
&\left[C_{0,3} + \frac{A\varepsilon\left(k_2(k_3-k_1) + pk_3(k_1-k_2)\right) + k_1\varepsilon C_{1,0}\left(k_3(k_2-k_3)\right) + k_2\varepsilon C_{2,0}\left(k_3(k_1-k_3)\right)}{k_3(k_1-k_3)(k_2-k_3)}\right]u_3
\end{aligned}
\qquad \text{(A2-12)}
$$

Equilibrium values for the first two components are found from (A2-11a-b):

$$
\begin{aligned}
&C_{1,E} = \frac{pA}{k_1} && (a)\\
&C_{2,E} = \frac{(1-p)A}{k_2} && (b)
\end{aligned}
\qquad \text{(A2-13)}
$$

and for the last component from (A2-12)c, bearing in mind that $\lim_{t\to\infty} u_1 = \lim_{t\to\infty} u_2 = \lim_{t\to\infty} u_3 = 0$, is

$$
C_{3,E} = \frac{A\varepsilon}{k_3} \qquad \text{(A2-13 c)}
$$

NUCSAM

The rate equations are now:

$$
\begin{aligned}
&\frac{dC_1}{dt} = -k_1C_1 + A && (a)\\
&\frac{dC_2}{dt} = \varepsilon_{12}k_1C_1 - k_2C_2 && (b)\\
&\frac{dC_3}{dt} = \varepsilon_{23}k_2C_2 - k_3C_3 && (c)
\end{aligned}
\qquad \text{(A2-14)}
$$

with solutions, using the notation given above:

$$
\begin{aligned}
&C_1(t) = C_{10}u_1 + \frac{A(1-u_1)}{k_1} && (a)\\
&C_2(t) = C_{20}u_2 - \frac{\varepsilon_{12}\left\{k_1k_2C_{10}(u_2-u_1) + A\left(k_2(u_1-1) - k_1(u_2-1)\right)\right\}}{k_2(k_2-k_1)} && (b)\\
&C_3(t) = C_{30}u_3 + k_2\varepsilon_{23}\left\{\begin{array}{l}\dfrac{A\varepsilon_{12}\varepsilon_{23}}{k_2k_3} - \dfrac{\varepsilon_{12}(A-k_2C_{10})}{(k_1-k_2)(k_1-k_3)}u_1 - \\ \dfrac{k_2C_{20}(k_2-k_1) + \varepsilon_{12}k_1(A-k_2C_{10})}{k_2(k_2-k_1)(k_2-k_3)}u_2 - \\ \dfrac{k_3C_{20}(k_3-k_1) + \varepsilon_{12}k_1(A-k_3C_{10})}{k_3(k_3-k_1)(k_3-k_2)}u_3\end{array}\right\} && (c)
\end{aligned}
\qquad \text{(A2-15)}
$$

The equilibrium value of the first component is found from (A2-14a):

$$C_{1,E} = \frac{A}{k_1} \qquad \text{(A2-16a)}$$

Substituting this result in the right hand side of (A2-14b) and equating the result to zero gives:

$$C_{2,E} = \frac{\varepsilon_{12} A}{k_2} \qquad \text{(A2-16b)}$$

Finally doing like wise with (A2-16b) and (A2-14c) it is found:

$$C_{3,E} = \frac{\varepsilon_{12}\varepsilon_{23} A}{k_3} \qquad \text{(A22-16c)}$$

CENTURY

The rate equations are:

$$\begin{aligned}
\frac{dC_1}{dt} &= -k_1 C_1 + p_1 A && (a)\\
\frac{dC_2}{dt} &= -k_2 C_2 + p_2 A && (b)\\
\frac{dC_3}{dt} &= -k_3 C_3 + p_3 A && (c)\\
\frac{dC_4}{dt} &= k_2 C_2 \varepsilon_{24} + k_3 C_3 \varepsilon_{34} - k_4 C_4 + k_5 C_5 \varepsilon_{54} + k_6 C_6 \varepsilon_{64} && (d)\\
\frac{dC_5}{dt} &= k_1 C_1 \varepsilon_{15} + k_4 C_4 \varepsilon_{45} - k_5 C_5 && (e)\\
\frac{dC_6}{dt} &= k_4 C_4 \varepsilon_{46} + k_5 C_5 \varepsilon_{56} - k_6 C_6 && (f)
\end{aligned} \qquad \text{(A2-17)}$$

The solutions for the (A2-12 a-c) are similar to that for CESAR:

$$\begin{aligned}
C_1 &= C_{1,0} u_1 + \frac{p_1 A}{k_1}(1 - u_1) && (a)\\
C_2 &= C_{2,0} u_2 + \frac{p_2 A}{k_2}(1 - u_2) && (b)\\
C_1 &= C_{3,0} u_3 + \frac{p_3 A}{k_3}(1 - u_3) && (c)
\end{aligned} \qquad \text{(A2-18)}$$

These solutions can be substituted in (A2-12 d-f) and the resulting equations are in principle solvable, the solutions, however, are very long and complicated. It was chosen to first substitue the values of the parameters and then solving the equations. Equilibrium values for the three components of the residue are found as before with results:

$$C_{1,E} = \frac{p_1 A}{k_1} \qquad (a)$$

$$C_{2,E} = \frac{p_2 A}{k_2} \qquad (b) \qquad \text{(A2-19)}$$

$$C_{3,E} = \frac{p_3 A}{k_3} \qquad (c)$$

Substitution of (A2-19a-c) into (A2-17e-f) together with the requirement of zero change yields three linear equations in the three unknowns C4, C5, and C6. These can be solved with known techniques, we used the routine Solve from Mathematica, obtaining:

$$C_{4,E} = \frac{p_2\varepsilon_{24} + p_3\varepsilon_{34} + p_1\varepsilon_{15}\left(\varepsilon_{56}\varepsilon_{64} + \varepsilon_{54}\right)}{\left(1 - \varepsilon_{46}\varepsilon_{64} - \varepsilon_{45}\left(\varepsilon_{56}\varepsilon_{64} + \varepsilon_{54}\right)\right)} \frac{A}{k_4} \qquad (d)$$

$$C_{5,E} = \frac{\left(p_2\varepsilon_{24} + p_3\varepsilon_{34}\right)\varepsilon_{45} - p_1\varepsilon_{15}\left(\varepsilon_{46}\varepsilon_{64} - 1\right)}{\left(1 - \varepsilon_{46}\varepsilon_{64} - \varepsilon_{45}\left(\varepsilon_{56}\varepsilon_{64} + \varepsilon_{54}\right)\right)} \frac{A}{k_5} \qquad (e) \quad \text{(A2-19)}$$

$$C_{6,E} = \frac{p_1\varepsilon_{15}\left(\varepsilon_{46}\varepsilon_{54} + \varepsilon_{56}\right) + p_2\varepsilon_{24}\left(\varepsilon_{45}\varepsilon_{56} + \varepsilon_{46}\right) + p_3\varepsilon_{34}\left(\varepsilon_{45}\varepsilon_{56} + \varepsilon_{46}\right)}{\left(1 - \varepsilon_{46}\varepsilon_{64} - \varepsilon_{45}\left(\varepsilon_{56}\varepsilon_{64} + \varepsilon_{54}\right)\right)} \frac{A}{k_6} (f)$$

Appendix 3 Accumulation of organic matter with time dependent supply. Calculations with CENTURY.

The rate equations for the components of added organic matter are:

$$\frac{dC_i}{dt} = -k_i C_i + p_i A(t) = -k_i C_i + p_i A_0 \exp(\alpha t) \tag{A3-1}$$

for $i = 1,2,.3$.

For the components of soil organic matter they are the same as given in (A3-17 d-f).

The solution of (A3-1) with initial condition $t = 0\ C_i = C_{i,0}$ is:

$$C_i = C_{i,0} \exp(-k_i t) + \frac{p_i A_0 (\exp(\alpha t) - 1)}{k_i + \alpha} \tag{A3-2}$$

Like before the equations (A3-2-) are substituted in (A3-17 d-f), and the resulting system is solved with the help of the Laplace transformation.