# Modelling Organic Matter Mineralization and Exploring Options for Organic Matter Management in Arable Farming in Northern China

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| Promotor: | Dr. Ir. O. Oenema,<br>bijzonder hoogleraar in de Nutriëntenstromen en Bemesting |
| Co-promotor: | Dr. Ir. B.H. Janssen,<br>universitair hoofddocent bij de Vakgroep Bodemkunde en Plantevoeding |

# Modelling Organic Matter Mineralization and Exploring Options for Organic Matter Management in Arable Farming in Northern China

**H.S. Yang**

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## Propositions

1 Without organic matter the surface of the earth could hardly be correctly designated as soil.
C.E. Millar, L.M. Turk and H.D. Foth. 1958. *Fundamentals of Soil Science*. 3rd edition. p. 249. John Wiley & Sons Inc. New York.

2 We are only beginning to develop a truly quantitative understanding of the physical, chemical, and biological processes that go on in the soil. We need better and quantitative models of soil development, of changes effected by humans, and of the pedosphere-biosphere interactions in time and space.
D.H. Yaalon, 1996. Soil science in transition: soil awareness and soil care research strategies. *Soil Science*, 161, 3-8.

3 A major limitation of the current models (on SOM dynamics) is that the conceptual pools they contain do not correspond directly to the fractions of SOM that are measured by physical, chemical or biological methods.
European Commission, 1994. *Decomposition and Accumulation of Organic Matter in Terrestrial Ecosystems*. 1994 Ecosystem research report 12. Ed. P Buurman. pp. 9. ECSC-EC-EAEC, Brussels.Luxembourg

4 Development in modelling does not necessarily mean an increase in complexity of model structure or in number of parameters.

5 Reduction of model complexity can be achieved either by simplification or by integration. Only the latter has future.

6 Two parameters seem enough to describe the rate of C mineralization in soil: the relative mineralization rate in the beginning and the speed of its decrease over time.
This thesis

7 In general, the higher its initial value is, the more rapidly the relative C mineralization rate decreases over time.
This thesis

8 The effect of temperature on C mineralization in soil declines over time.
This thesis

9 Solving the 'water problem' (i.e. drought in spring and flood in summer) is a bigger challenge than improving fertility of soils in northern China.
Q. Zhao, 1989. Soil resources and their utilization in China. In: *Soils and Their Management - A Sino-European Perspective*. Eds. E. Maltby and T. Wollersen. pp 3-18. Elsevier Science

Publishers LTD, England.

10 There is no science without quantification.

11 Figures are the language of science, but they are not always telling the truth.

12 A road appears behind a hiker.

13 The tax of car should be levied according to the quotient of $milage^2/average\text{-}speed$.

14 Lacking food, animals can survive by sleeping; lacking funds, scientists can survive by modelling.

H.S. Yang
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Wageningen, 11 December 1996

# Abstract

Yang, H.S., 1996. Modelling organic matter mineralization and exploring options for organic matter management in arable farming in northern China. Doctoral thesis, Wageningen Agricultural University, The Netherlands. 159 pp, with English, Dutch and Chinese summaries.

The primary objectives of this thesis were to (i) to identify key factors in soil organic matter (SOM) dynamics in arable land of northern China, (ii) to predict long-term SOM dynamics under various scenarios, and (iii) to give suggestions for the most efficient use of the available organic resources. Modelling was chosen as a tool. Experimental data were collected from relevant sources, and used to test some C mineralization models, to develop and test a new model, to study various factors affecting mineralization, to compare efficiencies of various organic materials in SOM accumulation and to predict long-term SOM dynamics in northern China.

It was found that the average relative mineralization rate has a linear relationship with time in double logarithmic scales under constant environmental conditions. Based on this, several functions were derived for the description of the dynamics of SOM built from added substrate. This new model proved valid under diverse conditions for all types of substrates encountered in practice.

The model showed that differences in mineralization rates between different substrates fade away over time irrespective whether they are caused by different substrate properties or by different environmental conditions. Substrates mineralizing more quickly than others in the beginning may become more stable in the long run, and a positive effect of a raised temperature on C mineralization may disappear over time, or even become negative.

The model predicts that under the conditions of northern China, the efficiency of organic substrates in SOM accumulation decreases in the order: roots > straw > farmyard manure > green manure. Roots were identified as the key input of SOM in this region. SOM accumulated from different materials showed differences in quality. Roots and stubble can maintain SOM content at 10 g $kg^{-1}$ at the current level of grain yield. SOM content will rise with return of e.g. straw or farmyard manure (FYM). With increase in SOM content, the quality of SOM will improve, and the release of nutrients from SOM will rise. Increase in crop yield by e.g. use of chemical fertilizers, will bring about improvement of both content and quality of SOM in this region. For a sustainable soil fertility and grain production at high levels, the application of either straw or FYM to the soil should be increased. Long-term efforts are needed.

*Keywords*: arable farming, farmyard manure, mineralization, modelling, northern China, roots and stubble, soil organic matter, straw, temperature effect.

# Preface

I began this Ph.D study at the Department of Soil Science and Plant Nutrition, Wageningen Agricultural University in August 1993. The primary aim of the study was to use available experimental data and relevant information from northern China to quantitatively study soil organic matter dynamics in relation to soil fertility in arable land in this region. Upon finishing this study, I wish to express my sincere thanks to those without whose help I would not have completed this study.

First of all, I am deeply obliged to Dr. Ir. B.H. Janssen who is my supervisor and co-promotor. His understanding and encouragement, as well as logistic support led to the establishment of this study project. Throughout the three-year study, he provided luminous guidance to my day-to-day work. He was always ready to suggest ideas whenever I got stuck and felt perplexed. I benefited enormously from his wide and deep understanding in many subjects. He was so patient and enthusiastic in reading, discussing and rewording the manuscript of this thesis, and translating the English summary into Dutch. I will remember him forever, and I wish I could become a scientist like him in the future.

I am indebted to Prof. Dr. Ir. O. Oenema, my promotor, for critically and carefully examining the manuscript of the thesis. The comments and suggestions he made helped me effectively improve many parts of the thesis.

I am grateful to the staff of the Department of Soil Science and Plant Nutrition. Special thanks go to Dr. Ir. M.L. Van Beusichem, the Chairman of the Section Plant Nutrition, and Mr. K. Koenders, the Manager of the department for the financial and practical arrangement during my stay at the department.

I thank Mr. G. Gort of the Department of Mathematics for reading mathematical part of the thesis and for helpful discussions and suggestions.

I appreciate very much the help and encouragement from some of my colleagues in the Soils and Fertilizers Institute, Chinese Academy of Agricultural Sciences during my stay in Wageningen, as well as during the time I was there for collecting literature. I wish to thank particularly Prof. Z. Yao, Prof. Z. Chen, Prof. C. Li. and Prof. B. Lin (the former director of the institute).

The final words of thanks go to my dear wife, Ma Lan, and my lovely son, Luye. It is their understanding, support and patience that inspired me to concentrate on the study from the beginning to the end.

*This thesis is dedicated to my wife and my son*

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## Chapter 1

# Introduction

## 1.1 Current arable farming and soil fertility in northern China and emanating research objectives

### *1.1.1 Arable farming and fertilizing practices in northern China*

The area of arable land in northern China, mainly referring to Huang-Huai-Hai Plain in this thesis (Figure 1), currently is 25.3 million ha, and the population of this region is 258 million. It is the most important region for cereal production in China. In the 1980s, the production of wheat and maize in this region accounted for 48 and 40% of the national production, respectively (Chinese Academy of Agricultural Sciences, 1989; Liu and Mu, 1988). The cultivation of two crops per year, winter wheat followed by summer maize, is the dominating cropping system. The average annual grain yield of the two crops was around 7500 kg $ha^{-1}$ in the early 1990s (Ministry of Agriculture of China, 1992).

Until the early 1980s, soil fertility was traditionally maintained and improved mainly by organic fertilizers, such as farmyard manure (FYM), compost, green manure, straw and organic wastes. Since then, several changes have occurred in arable farming: (1) the scale of farming management has been reduced from production teams to individual farmers' households with on average 0.5 ha of arable land or less, while the ownership of the land has remained public; (2) chemical fertilizers, especially for nitrogen, have become widely available; (3) the increase in cropping index, i.e. the number of crops per year, has intensified farming activities; (4) labour costs have risen, and part of the labour forces have started to divert from agriculture to other economic sectors; and (5) economic returns are now playing a very important role in farmers' decision making. Notwithstanding this changes, proper farming machinery is still lacking, and hand-work is still dominating in the field.

As a result of these changes, the role of organic fertilizers as the main input of nutrients has largely been taken over by chemical fertilizers, in particular for N (Chen, et al., 1989; Portch and Jin, 1995; Zhou, 1989). Returning of straw into the soil and use of FYM are vanishing practices in many places. The planting area of green manure crops is shrinking, and other forms of organic fertilizers,

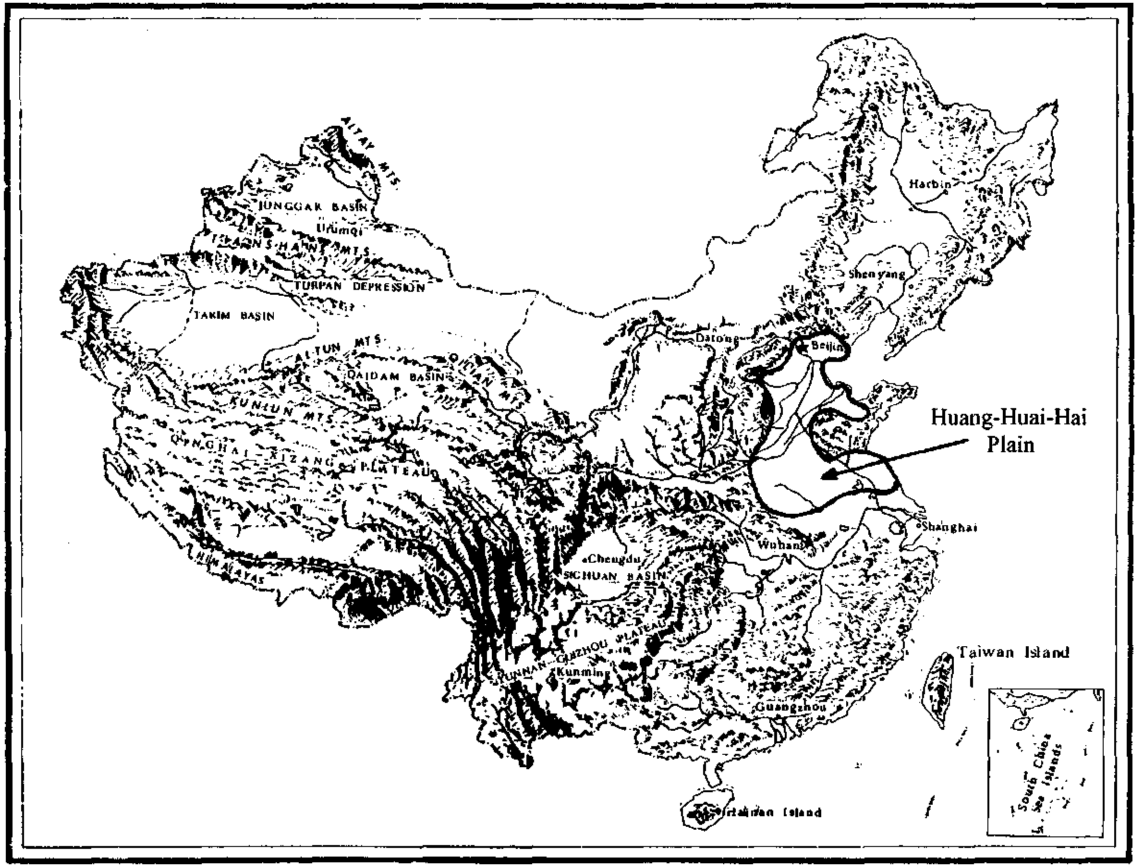

Figure 1 Sketch map of topography of China

such as municipal wastes, are becoming less attractive in arable farming (Portch and Jin, 1995; Yang, 1990; Zhou, 1989).

### *1.1.2 Soil organic matter and soil fertility in northern China*

This region is dominated by three types of soils: fluvo-aquic soils, alkaline soils and saline soils. They are derived from alluvial or fluvial deposits. The textural compositions of the soils vary from sandy soils to clay soils, depending on the sources of the deposits and topographic conditions (Du et al., 1990).
The fertility of arable soils depends mainly on soil organic matter (SOM) content. Therefore, SOM content of the soils in this region is a fundamental factor determining and influencing crop production. In this region, SOM content in arable land is commonly below or around 10 g $kg^{-1}$ (Cao et al., 1986; Wang et al., 1988; Zhao, 1989). Many experimental results have indicated that with the present often low SOM contents it is difficult to substantially increase yields (Cheng et al., 1991; Jiang et al., 1991; Yang et al., 1991; Zhou, 1991). At the same time, the demand for grain production is increasing, and that situation will continue in the future. To meet the grain requirements, SOM content should at least be maintained at the present levels or, better, raised.

On the other hand, the changed farming practices since the early 1980s make the dynamics of SOM in arable land uncertain, particularly in the long run. Controversial results or conclusions were obtained by different researchers under conditions of different SOM contents, crop yields, application rates of chemical fertilizers, etc. (Fu et al., 1992; Jiang et al., 1990; Wang et al., 1986; Zhou, 1991). Warnings were given on possible degradation of soil fertility, in particular SOM status, in this region. (Chen et al., 1991; Fu et al., 1992; Li et al., 1990; Yang, 1990). Moreover, the constraints in available land in this region strongly limit the potential production of organic materials, and hence the application of organic materials to soils used for food crops. Knowledge of the arable farming system and the long-term SOM dynamics are crucial for the design and evaluation of farming management strategies directed towards sustainable grain production. Therefore, reliable methods for the prediction of the dynamics of SOM are needed.

### *1.1.3 Primary objectives of this study*

The primary objectives of this study are to identify key factors in SOM dynamics in arable land of northern China, to predict long-term SOM dynamics under various scenarios, and to give suggestions for long-term strategies for high-efficiency use of available organic resources towards sustainable soil fertility and crop production.

These objectives require a systematic and quantitative study of available experimental data. Straight-forward comparison of experimental data, however, is not simple because many factors influence the results. For such purposes, modelling is a powerful tool.

In the following sub-chapters we discuss modelling as a tool in our research, the outline of the thesis, and the sources of data used for the various parts of our study.

## 1.2 Modelling mineralization of organic matter

### *1.2.1 General considerations on modelling*

Models have the potential of interpolating and extrapolating experimental results, of integrating and combining information from relevant sections in a system, of quantitatively evaluating their relationships, of testing and verifying current theories, and of providing wider, deeper and more comprehensive insights into the system under study. At the same time, misunderstandings of the system may be revealed, and fallacies in our knowledge may be corrected during modelling exercises (De Wit, 1986; De Wit and Keulen, 1987; Noij et al., 1993; Whisler, 1986).

Models are simplified representations of parts of reality. Because of the simplification and partiality models must be continuously subjected to testing in the real world before they can be applied in practice, and also thereafter during application testing remains necessary. This becomes more important and necessary in case that a model was developed on the basis of a few sets of data under specific conditions. Such a testing is necessary for the structure of a model as a whole, as well as for the formulations of specific relationships. This requires not only a good qualitative understanding of the system, but also a process-based interpretation of statistically analyzed experimental data. Computer-aided data handling, statistic analysis and data visualization are of great help in obtaining comprehensive, reliable and informative conclusions.

This thesis deals with an inventory and testing of some of the models on SOM dynamics, the development and testing of a new model, and applications of the newly developed model in studies of some general characteristics of mineralization of various types of organic substrates under different conditions, and in situations relevant for the sustainability of soil fertility in northern China.

### *1.2.2 Inventory of available models on mineralization*

Several models on dynamics of organic matter mineralization have been proposed by different authors (Janssen, 1984, 1986; Jenkinson and Ayanaba, 1977; Jenkinson et al., 1987, 1992; Kolenbrander, 1969, 1970; Martel and Paul, 1974; Parton et al., 1987; Van Veen and Paul, 1981). They differ in complexity and number of parameters required for their use (Chapter 2). They have so far been applied in some studies, and satisfactory results have been reported (Jenkinson et al., 1991, 1992; Noij et al., 1993; Parton et al., 1987).

### *1.2.3 Model development and applications*

In the process of model testing and evaluation, the understanding of the process of mineralization can significantly be improved. This may result in modifications of the models being tested, alternative approaches of modelling the system, or - in our case - the development of another model.

Once a model has proved to be valid under certain conditions, it can be used to extrapolate experimental observations for the prediction of long-term SOM dynamics, to compare various situations which can hardly or cannot be compared by experimental means, to reveal general phenomena of the process under different conditions, and to study functions of some single factors. For example, results obtained from different time scales can be generalized by means of the model, and the results can be integrated to study some common factors, e.g. temperature.

## 1.3 Outline of the thesis

After the introductory Chapter 1, Chapter 2 tests and evaluates several models on organic matter mineralization. Based on both statistical analysis and process-related considerations, it is concluded that for the purpose of the present study, none of these models is really satisfactory, because they are either too simple to give satisfactory results, or too complicated to be used. Therefore, a new mono-component model is proposed in Chapter 3 based on experimental data. The core of the model is the description of the dynamics of the relative mineralization rate in the equation of first-order kinetics. Equations describing the dynamics of both the quantity and the quality of a substrate undergoing mineralization are formulated. In Chapter 4, this model is tested with a large number of data, which cover several types of common substrates and diverse conditions.

Chapters 5 to 8 deal with the applications of the model.

In Chapter 5, the differences in short-term features and long-term features of mineralization are studied for different substrates under similar conditions, and for similar substrates under different conditions. It is attempted to link the effects that substrate properties and external conditions have on mineralization, and to show their changes over time.

The efficiency of various materials in long-term accumulation of soil organic matter, as was indicated by the model, and the implications for organic matter management in arable farming in northern China are discussed in Chapter 6. Several types of materials, including green manures, straw, roots, and farmyard manure, are compared under the conditions of northern China. The importance of roots in buildup and maintenance of SOM in arable farming is shown.

Chapter 7 presents the predictions by the model of the dynamics of SOM in arable land in northern China, in both quantitative and qualitative sense, taking into account the current farming practices and the possible development in the future. Present SOM levels, actual and potential yield levels and management scenarios are included, and possible strategies towards a sustainable soil fertility are suggested.

Chapter 8 deals with the effect of temperature on mineralization. Three methods commonly used in quantifying temperature effect, i.e. the Arrhenius function, the $Q_{10}$ concept and a time-scale-adjustment method, are tested with the model using the data collected from appropriate experiments. The results suggest that the temperature effect on mineralization is time-dependent.

The general discussion and conclusions are given in Chapter 9, together with recommendations for future research and the prospect of SOM status in northern China.

## 1.4 Collection and use of experimental data

### *1.4.1 Collection of experimental data*

Experimental data and observations are essential requirements for modelling exercises. Many field trials have been conducted in northern China on mineralization of both applied organic materials and existing SOM. In the beginning of my thesis study, I collected many mineralization data from publications as well as from internal reports in northern China. At the same time meteorological data and information on farming management of this region were gathered.

For the testing of potentially useful models, many experimental data from substrates other than those used in northern China and under different experimental conditions were derived from international scientific journals.

The thus obtained wide coverage of experimental materials and routines, soil types, environmental conditions, time spans and intensities in observations, provided a strong basis for model testing and development, and offered the opportunity to apply the new model for the uncovering of so far hidden relationships.

### *1.4.2 Use of experimental data*

The data used to test existing models represented a set of substrates ranging from glucose and cellulose to plant residues and farmyard manure (FYM), and a set of environmental conditions ranging from completely controlled situations in incubators in laboratories to the circumstances of field trials that were well managed, but subjected to changing weather conditions.

The same data were used for the development of the new model, but for the testing of the new model additional data were used covering wider ranges of substrates and environmental conditions. Still more data sets were included in the study of some general characteristics of organic matter mineralization

For the application of the new model to northern China, model input data were from that region only.

For the study of the influence of temperature on mineralization use was made only of data from experiments designed for that purpose.

## Chapter 2

# Test and evaluation of some selected models on dynamics of C mineralization

### Abstract

Two main approaches are followed in modelling the mineralization of organic matter, both based on the principle of first-order kinetics. One approach is to treat organic substrates or soil organic matter (SOM) as a whole with a characteristic relative mineralization rate (k), which is described either as a constant or as a time-dependent function (mono-component models). The other approach is to partition substrates and SOM into various components each with its own characteristic (constant) k (multi-component models). In these models, organic compounds are supposed to be transformed either into $CO_2$ only, or partly into $CO_2$ and partly into other organic compounds. The purpose of this chapter is to test and evaluate some selected models with experimental data collected from literature. The data cover various commonly used organic materials and different experimental conditions. Examination of the data revealed that k decreased over time, making mono-component models with a constant k inadequate for the description of mineralization. A two-component model with substrate transformations into $CO_2$ only yielded good fits to observations. The sizes and the k values of the two components proved to depend not only on the substrate itself but also on external conditions, and in the long run model outcomes showed increasing systematic deviations from experimental observations. This makes it difficult to apply two-component models under conditions different from those of the experiments used for the derivation of model parameters, and to make predictions for time spans longer than those of the experiments. Three multi-component models with substrate transformations into $CO_2$ and into other organic compounds were generally discussed, but not tested. They may have the potential of providing deeper and wider insights into the processes, but they are currently assembled on the basis of assumptions that need further confirmation, and require many input data which are difficult to obtain. Two of the five mono-component models found in literature with time-dependent relative mineralization rates, were tested. They gave poor fits to observations, mainly because the quantities of organic matter remaining after some years were substantially higher in the experiments cited in this chapter than in the experiments originally used for the formulation of the models. It was concluded that there is room for improving models with minimum requirements for input data and time-dependent relative mineralization rates. Existing experimental data are of value for that purpose, but at the same time more deliberate experiments are required to test assumptions and to derive values of parameters under diverse conditions.

## 2.1 Introduction

### 2.1.1 Basic concepts

In the last decades, modelling of organic matter mineralization has been an important subject in studies on soil fertility, soil erosion and environmental science that are related to soil organic matter (SOM) dynamics. It has been widely accepted as a tool to integrate current knowledge, to quantify processes of SOM turnover and the influences of environmental factors thereon, to predict SOM dynamics on the basis of available information, and to reveal areas which need further study. The temporal spans and spatial scales to which models have been applied, range from days to thousands of years, and from a specific site to global dimensions (Bouwman, 1989; Goto et al., 1994; Janssen, 1984; Jenkinson, 1990; Jenkinson et al., 1991, 1992; Motavalli et al., 1994; Newbould, 1982; Noij et al., 1993; Parton et al., 1987; Phillips et al., 1990; Post et al., 1992; Smith et al., 1992; Van der Linden et al., 1987; Van Veen and Paul 1981).

The principle of first-order kinetics has been widely adopted in modelling organic matter mineralization since it was proposed by Henin and Dupuis (1945). The change in the quantity of organic C is described as follows:

$$dY / dt = -k * Y \qquad (2.1)$$

in which t is time; Y is the quantity of organic C present at t; k ($\geq 0$) is the relative mineralization rate, or simply, the rate constant.

Integration of Equation 2.1 yields:

$$Y_t = Y_0 * \exp(-k * t) \qquad (2.2)$$

where $Y_0$ and $Y_t$ are the quantities of C at t=0 and t, respectively.

### 2.1.2 Terminology

The terms *transformation, gross decomposition, net decomposition* and *mineralization* are commonly used in studies on organic matter turnover. *Transformation* and *gross decomposition* refer to the process in which the organic compounds of a substrate are transformed partially into other organic compounds, and partially into gaseous $CO_2$. *Net decomposition* accounts for the production of gaseous $CO_2$ only, either from the original or from the transformed compounds. *Mineralization* means the process of conversion of organic C into gaseous $CO_2$, and therefore, it is fully identical to *net decomposition*. In this chapter only the terms *transformation* and *mineralization* are used.

### *2.1.3 Models for organic matter mineralization*

Based on the principle of first-order kinetics, two approaches have been adopted in modelling C mineralization in soil. In one approach a substrate is considered as a whole that has a characteristic relative mineralization rate which can be described either as a constant or as a dynamic function of time. The other approach is to partition incoming as well as existing organic matter into various components, each with its particular rate constant (k). The various components may be converted into $CO_2$ alone, or partially into $CO_2$ and partially into other organic compounds.

The two approaches result in four types of models:
1. mono-component models with a constant relative mineralization rate
2. multi-component models with transformation into $CO_2$ only
3. multi-component models with transformation into $CO_2$ and into other organic compounds
4. mono-component models with a time-dependent relative mineralization rate.

The first approach is adopted in the first type and the fourth type of models, and the second approach is employed in the other two types of models.

### *2.1.4 Objectives*

The purpose of this chapter is to test and evaluate some representatives of these models with experimental data collected from literature. The data cover various commonly used organic substrates and different experimental conditions. This test and evaluation forms the first step of the program of this study, as outlined in Chapter 1.

## 2.2 Model descriptions

### *2.2.1 Mono-component models with a constant relative mineralization rate*

In the mono-component models with a constant relative mineralization rate, the first-order equation (Equation 2.2) is applied to the entire quantity of organic matter. It has been used to describe *mineralization* of organic matter by many authors (Ajwa and Tabatabai, 1994; Andren et al., 1992, 1994; Henin and Dupuis, 1945; Hofman and Ruymbeke, 1980; Saggar et al., 1994; Tian et al., 1992).

The basic assumptions are that k in Equation 2.2 remains constant during the process of mineralization, and that the rate of mineralization is independent of the amount of organic matter that is added. The latter assumption proved valid, as was shown by e.g. Cheng (1987), Hao and Cheng (1983), Jenkinson (1977b), and Wang et al. (1989). The former assumption is tested in this chapter.

It was already realized by Henin and Dupuis (1945) that the relative decomposition rates of organic materials decrease strongly in the beginning. Therefore they assumed that organic materials became part of SOM at one year after addition to the soil. The ratio of the amount of organic material remaining after one year to the added amount was called 'humification coefficient' (indicated in our study by h.c.). In that case Equation 2.3 instead of Equation 2.2 should be applied:

$$Y_t = \text{h.c.} * Y_0 * \exp[-k * (t-1)] \tag{2.3}$$

in which t (in year) ≥ 1. Substitution of t = 1 gives:

$$\text{h.c.} = Y_1 / Y_0 \tag{2.4}$$

The use of 'humification coefficient' (h.c.) for the first year and of k for thereafter may represent a transition between mono-component and two-component models. Unfortunately, Equation 2.3 was not tested, because no data except those of Table 2.4 meet the requirement of having measurements at t=1 year and enough number of measurements thereafter.

### 2.2.2 *Multi-component models with transformation into $CO_2$ only*

Multi-component models have been developed because mono-component models were often found inadequate to give satisfactory results. They have had a big impact on modelling of organic matter dynamics (Breland, 1994; Gregorich et al., 1989; Jenkinson and Ayanaba, 1977; Jenkinson and Rayner, 1977; Ladd et al., 1981; Martel and Paul, 1974; Matus and Rodriguez, 1994; Sauerbeck, 1982; Sochtig and Sauerbeck, 1982; Voroney et al., 1989). They are based on two assumptions, that organic substrates can be partitioned into several components according to their resistance to mineralization, and that each component undergoes a first-order reaction with a characteristic rate constant (k) (Jenkinson, 1977a; Jenkinson and Ayanaba, 1977; Martel and Paul, 1974; Minderman, 1968). The general expression for such models is:

$$Y_t = y_1 * \exp(-k_1 * t) + y_2 * \exp(-k_2 * t) + ... + y_n * \exp(-k_n * t) \qquad (2.5)$$

where $Y_t$ is the total quantity of a substrate at t; $y_1$, $y_2$ and $y_n$ are the original quantities of components 1, 2 and n, and $k_1$, $k_2$ and $k_n$, the corresponding rate constants.

It is to be expected that multi-component models give a better fit to experimental data than mono-component models. The problem, however, is the experimental technique to measure the quantities of the individual substrate components with different resistance to mineralization. As a consequence, partitioning is commonly done mathematically, i.e. by fitting Equation 2.5 to a set of experimental data on $Y_t$ and t. The fitting refers to both the original quantities as well as the k values of the various components. The number of components cannot exceed half of the number of experimental observations, because at least one degree of freedom is required in regression analysis.

### *2.2.3 Multi-component models with transformation into $CO_2$ and into other organic compounds*

Multi-component models with transformation into $CO_2$ and other organic compounds have in common in the partitioning of incoming and existing organic materials into several components with the multi-component models with transformation into $CO_2$ only. The former differ from the later in that the former describe *transformations* of one organic component into others or into $CO_2$, and not just mineralization (Andren and Paustian, 1987; Ayanaba and Jenkinson, 1990; Bouwman, 1989; Hassink, 1995c; Jenkinson et al., 1987, 1992; Jenkinson and Rayner, 1977; Motavalli et al., 1994; Nicolardot and Molina, 1994; Nicolardot et al., 1994; Parton et al., 1987; Paustian et al., 1992; Van der Linden et al., 1987; Van Veen et al., 1985; Van Veen and Paul, 1981; Verberne and Hassink, 1990; Verberne et al., 1990). They have the potential of providing deeper and wider insights into the whole process (Newbould, 1982; Post et al., 1992; Smith et al., 1992; Verberne et al., 1990). They have so far been applied in time spans ranging from days to thousands of years, and in spatial scale from fields to

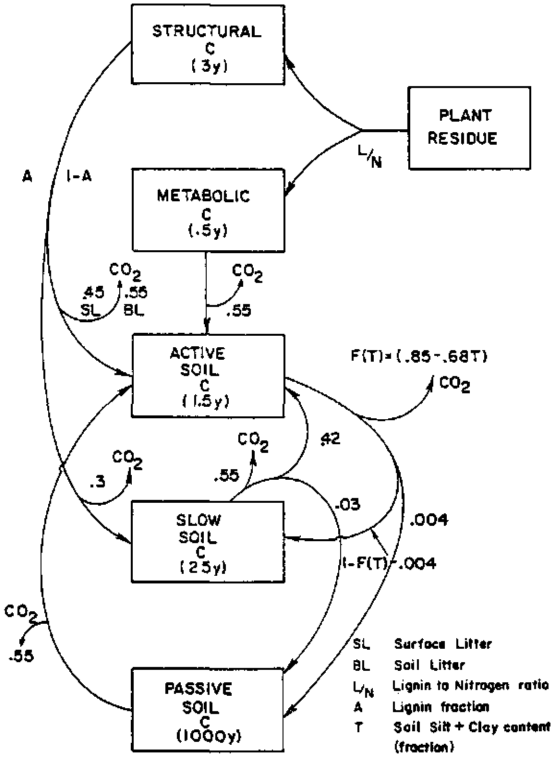

**Figure 2.1** Diagram of C flows in the Century model. Figures (in year) within boxes are the half-life times; figures or formulas beside arrows are the transformation coefficients. From Parton et al. (1987).

regions and even to global dimensions. The following three models may be considered as representative: Rothamsted model (Jenkinson et al., 1987, 1992), the model by Van Veen and Paul (1981) (see also Verberne et al., 1990), and the Century model (Parton et al., 1987). Figure 2.1 gives the schematic representation of Century model. The *transformation* of each component is described by first-order equations with individual rate constants (k). As said above, the products of the transformation consist of $CO_2$ and one or more organic compounds. The allocation to the various transformation reactions goes by transformation coefficients. Influences of external factors like soil texture, temperature, moisture, etc., are incorporated in the models by adjusting the k values, or the time scale, of the various first-order equations. Because of the transformations from one compound into others, this type of model requires many short time intervals (day or week); at the end of an interval the sizes of the various state variables are adjusted for the transformations that took place during the interval.

A major problem of such models is that rate constants (k) and transformation coefficients can be or have been derived only partly from experimental observations, and must therefore be based on assumptions or iterative runs of models themselves. For instance, the following assumptions are used in the Century model (Parton et al., 1987):

a. native SOM consists of three pools (active, slow and passive), and plant materials of two pools (metabolic and structural) distinguished after their lignin/N ratio;
b. a fixed proportion of the transformed material is lost as microbial respiration (55% for structural C, metabolic C, slow and passive SOM). The lignin in plant residues, which is entirely allocated to structural pool, is fully incorporated into slow soil-pool;
c. the rate constant (k) of plant structural pool is a function of its lignin content, and the k of slow SOM pool is equal to that of cellulose at the end of a 1500-day incubation;
d. soil texture determines the efficiency of stabilizing active SOM pool into slow SOM pool, and influences the decomposition rate of active SOM pool.

The use of so many assumptions will likely weaken the models as a tool to providing quantitative information on the processes laid out in these models (Motavalli et al., 1994). The number of parameters is big, ranging in the cited models from 8 to 29, and there may exist strong inter-correlations among them (Jenkinson et al., 1987; Parton et al., 1987; Smith, 1979; Van Veen and Paul, 1981; Verberne et al., 1990). Consequently, there is uncertainty about the performance of such models. The validation at component level requires far more information than current experiments can provide. Consequently, it will take a long time before these models can be applied in practice, either under controlled conditions or in the field. At present, such models are rather descriptive than explanatory (Verberne et al., 1990). The mentioned problems prevent them from being tested within the framework of our study.

### *2.2.4 Mono-component models with a time-dependent relative mineralization rate*

The characteristic for the mono-component models with a time-dependent relative mineralization rate is that a substrate is treated as a whole, and its relative mineralization rate is not constant but changes over time. Five such models were found in literature: Brunner and Focht (1984), Godshalk (1977), Janssen (1984, 1986), Kolenbrander (1969, 1970), and Middelburg (1989). They differ in the functions relating the relative mineralization rate to time. Only those of *Kolenbrander* and *Janssen* were tested in this study, because they were proposed for mineralization of common organic materials under agricultural conditions.

*Kolenbrander* (1969, 1970) is probably the first author who proposed this type of model (Van Dijk, 1982). Based on literature data on substrates like plant materials, manure and peat, he formulated the following equation:

$$Y_t / Y_0 = \exp\{-[n + p / (t + 1)] * t\} \qquad (2.6)$$

where **p** (dimensionless) and **n** (dimension $t^{-1}$) are two constant parameters. Comparison of Equation 2.6 with Equation 2.2 suggests:

$$K = n + p / (t + 1) \qquad (2.7)$$

where K is the average relative mineralization rate during the period between times 0 and t. K, the average relative mineralization rate, is not equal to the actual k at time t. The two will be equal only if k does not change over time.

*Janssen* (1984, 1986), working with the same data set as Kolenbrander, proposed another equation to relate the relative mineralization rate to time:

$$k = 2.82 * (a + f * t)^{-1.6} \qquad (2.8.a)$$

or,

$$\log(k) = 0.45 - 1.6 * \log(a + f * t) \qquad (2.8.b)$$

in which k is the actual relative mineralization rate at t; **a** is the so-called 'apparent initial age', an index for the resistance of a substrate to mineralization; **f** is a temperature correction factor (see also Noij et al., 1993).

Substitution of Equation 2.8 in Equation 2.1 and subsequent integration yield:

$$Y_t = Y_0 * \exp\{4.7 * [(a + f * t)^{-0.6} - a^{-0.6}]\} \qquad (2.9)$$

The essence of this model is the use of one general linear relationship between log(k) and log(t) for all organic materials. The difference in resistance is accounted for by assigning different 'apparent initial ages' (**a**) to different substrates. This model proved workable in some studies and was further adopted in researches conducted in other areas (Cheshire et al., 1988 and 1993; Middelburg, 1989; Noij et al., 1993).

It should be noticed that K in Equation 2.7 and k in Equation 2.8 are not the same. The (capital) K refers to the period between times 0 and t, whereas the (smaller letter) k refers to the point of time t exactly. As both decrease over time, the value of k is always smaller than that of K.

## 2.3 Data sets and statistical methods

For the present study four sets of data with 35 cases collected from literature were used (Tables 2.1, 2.2, 2.3 and 2.4). Some supplementary information on soil properties concerning these data are given in Table 2.5. All data are originally tabled values. The organic materials are commonly used in farming all over the world, with the exception of some materials in Table 2.1. Only experiments with materials that had been labelled with $^{14}C$ were included in order to get maximum resolutions of mineralization results. Because animal manure and farmyard manure are not labelled in conventional experiments, they are not considered in this chapter. During the experiments, lasting between 3 and 10 years, external conditions were kept constant in controlled experiments (Tables 2.1 and 2.2); in case of field trials (Tables 2.3 and 2.4) samples were taken in the same period of the year so that the external conditions among sampling were as much the same as possible. The materials were incorporated into the soils only once at the beginning of the experiments.

For testing the models described in Sections 2.2.1, 2.2.2 and 2.2.4, the data in Tables 2.1 to 2.4 were fitted to the models directly by nonlinear regression conducted in Statgraphics (STSC Inc., 1986). Adjusted $R^2$ was used for judging the fit between models and observations:

$$R^2 = 1 - \Sigma(y - y_{esti.})^2 / \Sigma(y - y_{mean})^2 \qquad (2.10)$$

$$\text{adj. } R^2 = 1 - n * (1 - R^2)/(n - p) \qquad (2.11)$$

where y = the observations, $y_{mean}$ = the arithmetic mean of y, $y_{esti.}$ = the model estimates, n = the number of observations, p = the number of independent variables in the model. For nonlinear regression it is possible that $\sum(y - y_{esti.})^2 > \sum(y - y_{mean})^2$. In that case, $R^2$ and adj. $R^2$ calculated by Equation 2.10 and 2.11, respectively, are negative, which indicates a total failure in fit of a model to observations (Kvålseth, 1985).

**Table 2.1** Remaining fractions (%) of single additions of various substrates, incubated at 20 °C. Soil moisture was maintained at 55% water-holding capacity (by weight). N was added in the form of $(NH_4)_2SO_4$ at a rate of 40 mg N per g C added. Data from Sorensen (1983)

| Substrate | Soil(b) | Case(c) | Days of incubation | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 10 | 30 | 90 | 365 | 730 | 1100 |
| glucose(a) | A | 1-1 | 28 | 22 | 17 | 10 | 10 | 7 |
| | L | 1-2 | 29 | 24 | 17 | 13 | 12 | 9 |
| | H | 1-3 | 34 | 29 | 20 | 18 | 16 | 12 |
| | R | 1-4 | 32 | 27 | 19 | 16 | 14 | 12 |
| hemicellulose(a) | A | 2-1 | 38 | 28 | 26 | 21 | 18 | 15 |
| | L | 2-2 | 40 | 27 | 24 | 19 | 18 | 15 |
| | H | 2-3 | 45 | 41 | 35 | 25 | 23 | 20 |
| | R | 2-4 | 59 | 51 | 39 | 29 | 25 | 23 |
| cellulose(a) | A | 3-1 | 55 | 41 | 32 | 26 | 23 | |
| | L | 3-2 | 56 | 38 | 28 | 22 | 19 | |
| | H | 3-3 | 52 | 43 | 28 | 20 | 17 | |
| | R | 3-4 | 66 | 44 | 34 | 23 | 22 | |
| maize straw | A | 4-1 | 62 | 50 | 42 | 28 | 24 | 22 |
| | L | 4-2 | 62 | 48 | 39 | 28 | 26 | 24 |
| | H | 4-3 | 60 | 48 | 38 | 27 | 22 | 21 |
| | R | 4-4 | 68 | 52 | 43 | 29 | 25 | 24 |
| barley straw | A | 5-1 | 74 | 71 | 57 | 32 | 22 | 18 |
| | L | 5-2 | 68 | 67 | 53 | 47 | 43 | 42 |
| | H | 5-3 | 63 | 51 | 39 | 32 | 27 | 24 |
| | R | 5-4 | 67 | 56 | 45 | 32 | 29 | 25 |

(a) Glucose, hemicellulose and cellulose were prepared from barley straw.
(b) The codes used for soils are explained in Table 2.5.
(c) The case-numbers are used in Table 2.6.

**Table 2.2** Remaining fractions[a] (%) of single additions of oat shoots with a C-N ratio of 57.9 in a light loamy sandy soil, incubated at 20 °C. The shoots were ground and sieved (<0.5 mm). Soil moisture was maintained at 60% matric potential (33 kPa). Data from Nowak and Nowak (1990)

| Fertilization[b] | Case[c] | Days of incubation | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 25 | 50 | 100 | 150 | 200 | 300 | 500 | 700 | 900 | 1200 | 1500 |
| Control | 6-1 | 57 | 46 | 41 | 40 | 39 | 38 | 36 | 35 | 33 | 32 | 31 | 31 |
| 1NPK | 6-2 | 56 | 44 | 40 | 38 | 37 | 36 | 34 | 33 | 31 | 30 | 29 | 29 |
| 3NPK | 6-3 | 55 | 42 | 37 | 36 | 35 | 33 | 31 | 30 | 29 | 28 | 27 | 27 |
| 3NPK+$CaCO_3$ | 6-4 | 50 | 37 | 32 | 30 | 29 | 28 | 25 | 24 | 22 | 21 | 21 | 21 |

[a] The remaining fraction was calculated from the sum of remaining fractions of bitumen, humic acid, fulvic acid and humine.

[b] Fertilizer rate (kg$^{-1}$ soil): control – no fertilizer; 1NPK – 166 mg N as $NH_4NO_3$, 133 mg $P_2O_5$ as $KH_2PO_4$ and 166 mg $K_2O$ as $K_2SO_4$; 3NPK – 3 times dose of 1 NPK; $CaCO_3$ – 1379 mg $CaCO_3$.

[c] The case codes are used in Table 2.6.

**Table 2.3** Remaining fractions (%) of single additions of mature wheat straw in six fields in Germany. Straw was coarsely ground. Cereals or root and tube crops were present at all sites. Data from Sauerbeck and Gonzalez (1977), and Sochtig and Sauerbeck (1982)

| Site | Case[a] | Years in field | | | |
|---|---|---|---|---|---|
| | | 2 | 4 | 6 | 8 |
| 1 | 7-1 | 24 | 18 | 16 | 14 |
| 2 | 7-2 | 24 | 19 | 17 | 15 |
| 3 | 7-3 | 24 | 21 | 19 | 17 |
| 4 | 7-4 | 28 | 22 | 21 | 20 |
| 5 | 7-5 | 31 | 25 | 23 | 19 |
| 6 | 7-5 | 30 | 25 | 22 | 20 |

[a] The case codes are used in Table 2.6.

**Table 2.4** Remaining fractions (%) of single additions of ground ryegrass (<0.5 mm) in the field in Rothamsted, England. The trial started in April 1962. Data from Jenkinson (1977a)

| Soil | Case[b] | Years in field | | | | |
|---|---|---|---|---|---|---|
| | | 0.5 | 1 | 2 | 5 | 10 |
| 1+2+3+5[a] | 8-1 | 32.7 | 31.6 | 25.0 | 18.6 | 12.4 |
| 6 | 8-2 | 45.8 | 42.5 | 30.1 | 20.2 | 13.6 |
| 7 | 8-3 | 28.1 | 26.8 | 21.5 | 15.1 | 9.8 |
| 8 | 8-4 | 41.5 | 35.9 | 25.9 | 16.9 | 12.8 |
| 4 | 8-5 | 31.8 | 27.9 | 24.4 | 18.4 | 12.3 |

[a] The data of Soils 1, 2, 3 and 5 have been averaged, because their remaining fractions at the same sampling time are almost the same.

[b] The case codes are used in Table 2.6.

**Table 2.5** Some properties of the soils referring to the data in Tables 2.1, 2.2, 2.3 and 2.4

| Table | Soil/Site | Clay % | pH | Total C g $kg^{-1}$ | Total N g $kg^{-1}$ |
|---|---|---|---|---|---|
| 2.1 | A | 6 | 6.2 | 8 | 0.7 |
| | L | 12 | 6.5 | 13 | 1.4 |
| | H | 16 | 7.2 | 20 | 2.4 |
| | R | 34 | 7.4 | 24 | 2.6 |
| 2.2 | loamy sand | n.d. | 5.6 | 10 | 0.9 |
| 2.3 | 1 | 16 | 5.4 | n.d. | n.d. |
| | 2 | 16 | 7.2 | n.d. | n.d. |
| | 3 | 4 | 6.7 | n.d. | n.d. |
| | 4 | 1 | 5.5 | n.d. | n.d. |
| | 5 | 5 | 4.6 | n.d. | n.d. |
| | 6 | 18 | 7.0 | n.d. | n.d. |
| 2.4 | 1+2+3+5 | 19 | 7.0 | n.d. | n.d. |
| | 6 | 21 | 3.7 | n.d. | n.d. |
| | 7 | 8 | 6.2 | n.d. | n.d. |
| | 8 | 5 | 3.7 | n.d. | n.d. |
| | 4 | 19 | 7.0 | n.d. | n.d. |

n.d.: no data given in sources.

## 2.4 Test and evaluation of models

### 2.4.1 Mono-component models with a constant relative mineralization rate

It is clear from the values of adjusted $R^2$ in Table 2.6 which are all negative except one, that the mono-component model in the form of Equation 2.2 is not suitable for describing mineralization. To examine whether k remained constant, the average k between two adjacent time points $t_1$ and $t_2$ ($k_{t1-t2}$) was calculated by Equation 2.12, and plotted against time (the middle between $t_1$ and $t_2$ was used) (Figure 2.2):

$$k_{t1\text{-}t2} = -\ln(Y_{t2}/Y_{t1})/(t_2 - t_1) \qquad (2.12)$$

where $Y_{t1}$ and $Y_{t2}$ are C quantities at times $t_1$ and $t_2$, respectively.

Figure 2.2 shows that k did not stay constant, but decreased over time, especially in the initial stage. As a consequence, the model is not suitable for describing the fate of added C, as has been pointed out by many authors (Cheshire et al., 1988; Faassen and Smilde, 1985; Gregorich et al., 1989; Janssen, 1984; Minderman, 1968; Ross, 1989; Van Dijk, 1982).

### 2.4.2 Multi-component models with transformation into $CO_2$ only

Equation 2.5 was applied using two components for various substrates, and the results are shown in Table 2.6. From the values of adjusted $R^2$ it can be concluded that the overall fit was very good with an average value of adjusted $R^2$ of 0.93. In one half of the 35 cases, the adjusted $R^2$ was 0.95 or higher, and only in one case the adjusted $R^2$ was as low as 0.72. It seems that two components are sufficient, surprisingly enough in view of the possible variability in experiments. The model estimates of C remaining over time are shown in Figure 2.3 for both the individual components and their sum, along with the observed total remaining quantities of C.

Table 2.6 and Figure 2.3 show that the first component mineralized much faster than the second. In most cases, the quantity of the first component became negligible after about 30 days, but for Case 7 (wheat straw) and Case 8 (ryegrass), it took about 2 and 1 year, respectively. After disappearance of the first component, the remaining substrate consisted of the second component only, as indicated by the overlap of the lines for Component 2 and Total in Figure 2.3.

**Table 2.6** Results of fitting the data in Tables 2.1, 2.2, 2.3 and 2.4 to four models

| Case | Mono-component constant k | | Two-component(b) | | | | Mono-component time-dependent K or k | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | *Kolenbrander* | | | *Janssen* | |
| | k(a) | adj. $R^2$ | Comp.1, % | $k_1$(a) | $k_2$(a) | adj. $R^2$ | n(a) | p | adj. $R^2$ | a, yr | adj. $R^2$ |
| 1-1 | 0.11 | (-) | 80 | 0.23 | 1.1E-3 | 0.89 | 1.1E-3 | 1.63 | 0.84 | 0.31 | (-) |
| 1-2 | 0.10 | (-) | 79 | 0.23 | 8.8E-4 | 0.86 | 8.3E-4 | 1.59 | 0.80 | 0.32 | (-) |
| 1-3 | 7.6E-2 | (-) | 75 | 0.21 | 7.1E-4 | 0.84 | 6.8E-4 | 1.40 | 0.76 | 0.38 | (-) |
| 1-4 | 8.5E-2 | (-) | 77 | 0.22 | 7.0E-4 | 0.84 | 6.9E-4 | 1.48 | 0.75 | 0.36 | (-) |
| 2-1 | 6.8E-2 | (-) | 73 | 0.19 | 5.8E-4 | 0.99 | 5.6E-4 | 1.32 | 0.98 | 0.42 | (-) |
| 2-2 | 6.6E-2 | (-) | 75 | 0.16 | 5.1E-4 | 0.97 | 5.0E-4 | 1.39 | 0.92 | 0.42 | (-) |
| 2-3 | 3.4E-2 | (-) | 62 | 0.22 | 7.1E-4 | 0.88 | 6.9E-4 | 0.98 | 0.86 | 0.65 | (-) |
| 2-4 | 1.7E-2 | (-) | 56 | 0.12 | 7.4E-4 | 0.87 | 7.8E-4 | 0.80 | 0.79 | 1.04 | (-) |
| 3-1 | 2.9E-2 | (-) | 64 | 0.12 | 7.2E-4 | 0.93 | 7.7E-4 | 0.99 | 0.77 | 0.71 | (-) |
| 3-2 | 3.3E-2 | (-) | 68 | 0.08 | 8.1E-4 | 0.96 | 9.5E-4 | 1.08 | 0.75 | 0.64 | (-) |
| 3-3 | 3.0E-2 | (-) | 63 | 0.13 | 1.3E-3 | 0.82 | 1.4E-3 | 0.97 | 0.70 | 0.66 | (-) |
| 3-4 | 2.1E-2 | (-) | 64 | 0.07 | 8.0E-4 | 0.97 | 1.1E-3 | 0.91 | 0.75 | 0.83 | 0.20 |
| 4-1 | 1.6E-2 | (-) | 55 | 0.11 | 8.2E-4 | 0.92 | 8.6E-4 | 0.77 | 0.85 | 1.08 | (-) |
| 4-2 | 1.8E-2 | (-) | 59 | 0.09 | 6.0E-4 | 0.92 | 6.7E-4 | 0.85 | 0.78 | 1.01 | (-) |
| 4-3 | 1.9E-2 | (-) | 58 | 0.11 | 8.0E-4 | 0.92 | 8.6E-4 | 0.84 | 0.83 | 0.96 | (-) |
| 4-4 | 1.4E-2 | (-) | 56 | 0.08 | 7.0E-4 | 0.94 | 8.2E-4 | 0.75 | 0.81 | 1.21 | (-) |
| 5-1 | 3.8E-3 | 0.48 | 31 | 0.14 | 1.6E-3 | 0.94 | 1.6E-3 | 0.38 | 0.93 | 1.73 | 0.81 |
| 5-2 | 1.4E-3 | (-) | 41 | 0.13 | 3.8E-4 | 0.72 | 3.9E-4 | 0.52 | 0.65 | 2.65 | (-) |
| 5-3 | 1.7E-2 | (-) | 57 | 0.09 | 6.1E-4 | 0.93 | 6.9E-4 | 0.79 | 0.82 | 1.12 | (-) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5-4 | 1.2E-2 | (-) | 52 | 0.09 | 7.0E-4 | 0.92 | 7.8E-4 | 0.68 | 0.82 | 1.41 | (-) |
| 6-1 | 7.8E-3 | (-) | 60 | 0.12 | 2.2E-4 | 0.95 | 2.4E-4 | 0.90 | 0.83 | 1.54 | (-) |
| 6-2 | 9.6E-3 | (-) | 62 | 0.12 | 2.5E-4 | 0.95 | 2.6E-4 | 0.94 | 0.84 | 1.40 | (-) |
| 6-3 | 1.2E-2 | (-) | 64 | 0.12 | 2.5E-4 | 0.95 | 2.6E-4 | 1.01 | 0.80 | 1.23 | (-) |
| 6-4 | 3.0E-2 | (-) | 70 | 0.12 | 3.5E-4 | 0.95 | 3.7E-4 | 1.17 | 0.81 | 0.87 | (-) |
| 7-1 | 0.53 | (-) | 77 | 1.50 | 6.0E-2 | 1.00 | 9.4E-3 | 2.10 | 0.99 | 1.70 | (-) |
| 7-2 | 0.51 | (-) | 76 | 1.66 | 5.8E-2 | 1.00 | -2.9E-3 | 2.12 | 0.97 | 1.74 | (-) |
| 7-3 | 0.48 | (-) | 74 | 2.37 | 5.3E-2 | 1.00 | -2.4E-2 | 2.15 | 0.77 | 1.82 | (-) |
| 7-4 | 0.42 | (-) | 77 | 1.32 | 1.9E-2 | 1.00 | -1.8E-2 | 1.97 | 0.99 | 1.97 | (-) |
| 7-5 | 0.37 | (-) | 67 | 1.74 | 6.6E-2 | 0.96 | 1.4E-2 | 1.69 | 0.93 | 2.09 | 0.16 |
| 7-6 | 0.38 | (-) | 69 | 1.70 | 5.5E-2 | 1.00 | 1.5E-3 | 1.77 | 0.96 | 2.07 | (-) |
| 8-1 | 1.41 | (-) | 67 | 7.74 | 0.11 | 0.95 | -5.2E-2 | 2.64 | 0.24 | 1.23 | (-) |
| 8-2 | 0.88 | (-) | 56 | 4.58 | 0.14 | 0.91 | 1.8E-2 | 1.88 | 0.86 | 1.59 | 0.66 |
| 8-3 | 1.76 | (-) | 71 | 8.40 | 0.12 | 0.96 | -7.0E-2 | 3.06 | 0.09 | 1.08 | (-) |
| 8-4 | 1.11 | (-) | 64 | 3.96 | 0.12 | 0.91 | -7.6E-3 | 2.24 | 0.87 | 1.39 | 0.59 |
| 8-5 | 1.55 | (-) | 70 | 6.05 | 9.2E-2 | 0.99 | -6.7E-2 | 2.81 | 0.12 | 1.18 | (-) |

(a) The unit of k and n is day$^{-1}$ (Case 1-1 to 6-4) and year$^{-1}$ (Case 7-1 to 8-5).

(b) Component 2 (%) = 100 − Component 1.

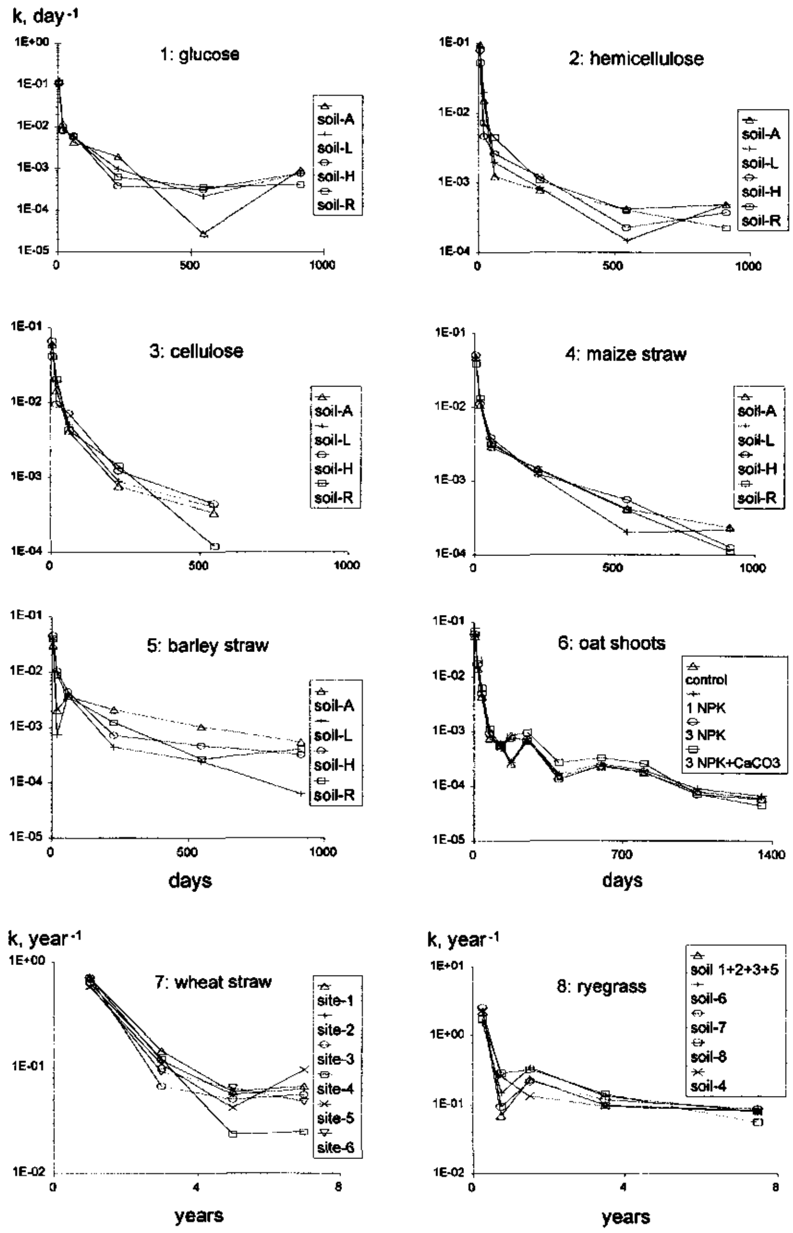

**Figure 2.2** Change of k (logarithmic scale) over time as calculated by Equation 2.12. The numbers refer to the cases in Table 2.6.

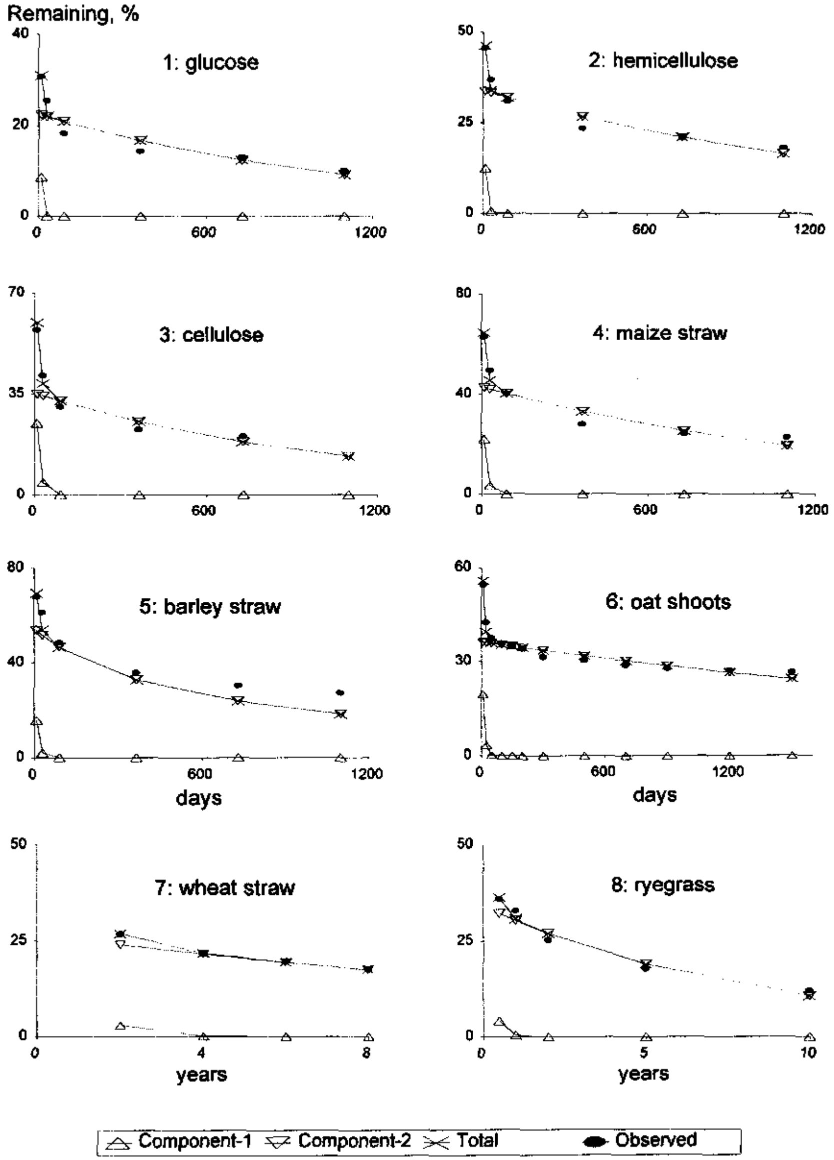

**Figure 2.3** Remaining components over time and their sums calculated by the two-component model. The numbers refer to the cases in Table 2.6.

The fact that even for glucose the initial quantity was not entirely allocated to the first component, means that the model considers a part of glucose as rather resistant. So, the homogenous compound is subdivided into two components. Moreover, it is seen in Table 2.6 that for a same substrate the size of the first component varied with treatments. Comparison of the size of the first component and the data in Tables 2.1 to 2.4 reveals that the less the remaining is - especially in the early stage, the larger the proportion is that is allocated to the first component. As external factors affect the part that is remaining, this suggests that the partitioning into two components is determined not only by substrate properties, but external conditions, as well.

Experimental results from Ladd et al. (1992), Saggar et al. (1994), and Van Veen et al. (1985) show that glucose added to soils entirely disappears within one to three days. The 20% to 25% of the total glucose allocated to the second component (Table 2.6) probably represents the secondary C-containing compounds derived from glucose during its transformation and present or not present in the microbial biomass. For more complex substrates, the second fraction consists partly of original substrate and partly of transformation products. In addition, the relatively small differences among the k values of the second components in Table 2.6 suggest either that the primary and secondary forms of C in this component are comparable in their resistance to mineralization, or that in all cases the second component mainly consists of secondary products with similar resistance to microbial attack. Further, it seems that the relative mineralization rate of the second component is less influenced by external factors than that of the first component.

According to Figure 2.3, the model tends to underestimate the quantities of remaining C in the later stage, and the underestimation will likely get relatively larger if the time span is extended. This systematic deviation suggests that the k value of the second component is not constant but decreases over time, though very slowly. Addition of a third component with a relative mineralization rate lower than Component 2, may improve the fit in the later stage.

### *2.4.3 Mono-component models with a time-dependent relative mineralization rate*

The average adjusted $R^2$ of the total 35 cases was 0.78±0.04 for the *'Kolenbrander-model'* (Table 2.6), indicating that the model did not sufficiently explain the observations. Furthermore, there were 7 cases with negative values of **n**, which makes the role of **n** in the model inconsistent in different cases.

Nevertheless, some of these cases had high values of adjusted $R^2$.

The model was further examined by comparing the values of K as calculated by Equation 2.7 using the values of **n** and **p** in Table 2.6 for the various points of time with the 'real' K which was calculated by Equations 2.2. The results in Figure 2.4 show that, except for wheat straw, Equation 2.7 did not correctly describe the decrease of K over time. The difference between the outcomes of Equations 2.2 and of 2.7 will likely become larger when time is extended. It can be concluded that the model by Kolenbrander is able to correctly describe mineralization under some but not under all conditions.

The *'Janssen-model'*, however, almost completely failed as indicated by adjusted $R^2$ in Table 2.6. The cause for the failure is suggested by Figure 2.5, in which the apparent initial age (**a**) of a substrate, as calculated by Equation 2.9 for the various points of time, was plotted versus time. It appears that the longer the time period, the larger the thus calculated value of **a** is. This suggests that a single parameter like **a** is not able to describe mineralization for a wide range of external conditions.

## 2.5 General discussion and conclusions

The models tested in this study all describe *mineralization*, i.e. the transformation of organic matter into $CO_2$, and not the *transformation into other organic compounds*. The performance of the models measured by adjusted $R^2$ differs considerably. The mono-component model with a constant relative mineralization rate totally failed. The mono-component model with a time-dependent relative mineralization rate that uses two model parameters (Kolenbrander) performed better than the one that uses only one parameter (Janssen). The two-component model without interrelations among components, gave the best results in this comparative study.

It is very obvious that the assumption of a constant k for a whole substrate is incorrect (Figure 2.2). Although this has been realized by many researchers, the first-order equation with a constant k is still used in some recently published researches.

The strategy of splitting an incoming substrate into two components with their characteristic k values, worked well, and hence has justly received much support.

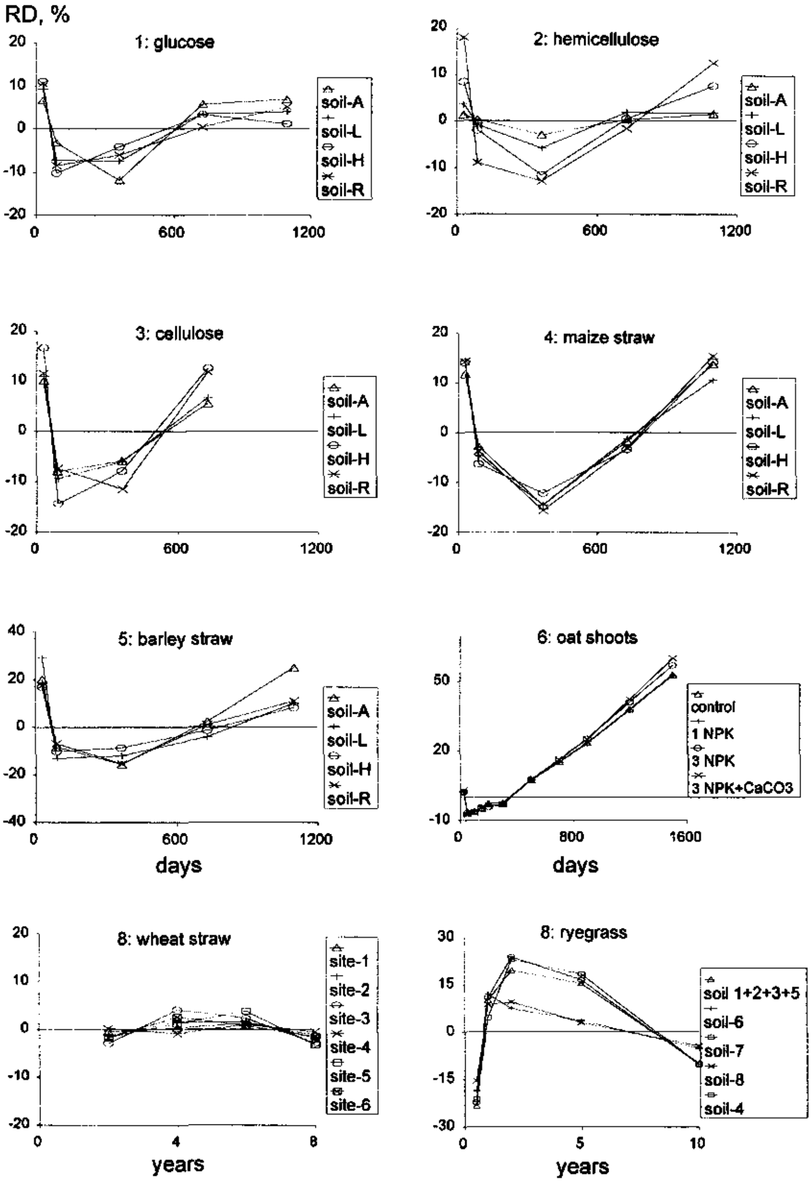

**Figure 2.4** Relative difference (RD, %) between K calculated by Equation 2.2 and K by Equation 2.7 with **n** and **p** from Table 2.6. $RD(\%) = 100 * (K_{Eq.2.7} - K_{Eq.2.2}) / K_{Eq.2.2}$. The numbers refer to the cases in Table 2.6.

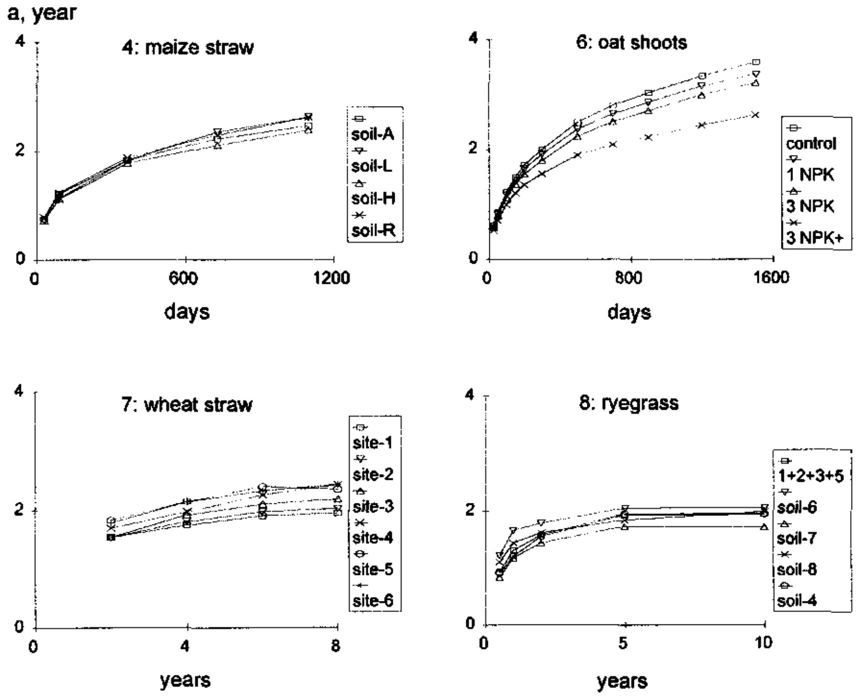

**Figure 2.5** Change of 'apparent initial age' (**a**) over time, as calculated by Equation 2.9. The numbers refer to the cases in Table 2.6.

The fact that even for substrates like glucose, two components were distinguished, gives an additional meaning to partitioning. Apparently around 20% to 25% of very easily mineralizable substrates are not comprised in the first component. This may be interpreted in the sense that not all C from glucose is released as $CO_2$. The variations in the proportion assigned to the first component by the model under different conditions, suggest that the partitioning into two fractions is determined not only by the properties of a substrate, but by external factors as well. This makes it difficult to allocate to substrates the values of model parameters that can be used under all circumstances, and limits the significance of such models in practical applications.

The results in Table 2.6 and Figure 2.3 may be interpreted in that the resistant component allocated by the two-component model includes both relatively resistant compounds in the original substrate and the compounds that have been transformed from the original substrate. Experimental evidences from Ladd et al. (1992), Saggar et al. (1994), and Van Veen et al. (1985) also support this suggestions. Table 2.6 also shows that the k value of the second component is not much affected by the nature of the substrate, and less by external factors like temperature than the k value of the first, easily mineralizable, component.

Notwithstanding the good fit of the two-component model, there is a trend that the model underestimates the total remaining quantities in the long run (Figure 2.3). This suggests that the model cannot be used for longer time spans than used for fitting. The remaining parts of the substrate would keep a constant k value and that is not in accordance with reality. Due to its weak points, the model was considered to oversimplify the real process of mineralization (Jenkinson, 1977a; Sierra, 1990; Voroney et al., 1989) and to be of more mathematical convenience than to reveal the biochemical processes (Cheshire et al., 1988).

The approach of treating an incoming substrate as a whole, and of dynamically describing the change of K or k over time, forms another main line in model development. It avoids the problem of unrealistic partitioning and is convenient in practice. Moreover, in agriculture the total quantity of SOM usually is of more concern than the composition. Both the *Kolenbrander* and the *Janssen* model performed much better, when fitted to the experimental data from which they had been derived (Table 2.7) than to those cited in the present paper. The disappointing performance is probably caused by the fact that the remaining fractions of organic matter were lower in the original sets of data than in the present ones. This is shown in Figure 2.6 comparing the average values of Tables 2.3 and 2.4 with the average data for green matter, straw and leaf litter collected by Kolenbrander (1969, 1970). That explains why the values of **a** increased when calculated from data referring to longer periods of mineralization, as was shown in Figure 2.5.

In the *Janssen* model the decrease over time of the relative mineralization rate (k) is fixed by the values 2.8 and 1.6 of the coefficients in Equation 2.8. The present study proves that to be too rigid. The model can be used in a more flexible way, when first the values of the coefficients are verified and adjusted when needed (Janssen, 1984). That procedure is followed in the following chapter, showing that the logarithms of the relative mineralization rate (k) and time are indeed linearly related, but that both the slope and intercept vary from case to case.

**Table 2.7** Values of the model parameters of *Kolenbrander* and of *Janssen*, and of the adjusted $R^2$ of models' fit to the data from Kolenbrander (1969, 1970) used in the model propositions.

| Substrate | Kolenbrander | | | Janssen | |
|---|---|---|---|---|---|
| | n | p | adj. $R^2$ | a | adj. $R^2$ |
| Green mass | 0.12 | 3.01 | 1.00 | 1.00 | 1.00 |
| Straw | 0.09 | 1.84 | 0.98 | 1.54 | 0.99 |
| Litter | 0.16 | 0.80 | 1.00 | 2.29 | 0.98 |
| FYM | 0.13 | 0.88 | 0.97 | 2.37 | 1.00 |
| Fir needle | 0.13 | 0.51 | 0.96 | 3.07 | 0.98 |
| Saw dust | 0.13 | 0.31 | 1.00 | 3.58 | 0.96 |
| Peat-4 | 0.12 | 0.30 | 1.00 | 3.89 | 1.00 |
| Peat-3 | 0.06 | 0.21 | 1.00 | 5.86 | 0.99 |
| Peat-2 | 0.05 | 0.10 | 1.00 | 7.74 | 1.00 |
| Peat-1 | 0.02 | 0.05 | 1.00 | 15.13 | 0.99 |

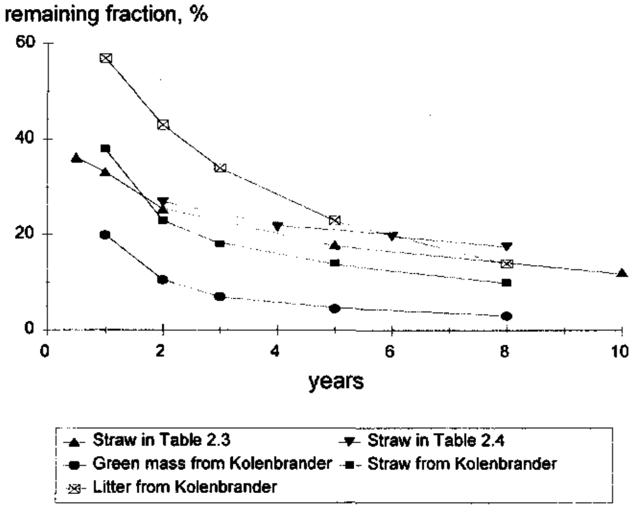

**Figure 2.6** Remaining fractions of straw (average values from Tables 2.3 and 2.4), and of green mass, straw and litter as found by Kolenbrander (1969, 1970).

For detailed studies of turnover of organic matter in soil, including possible reaction pathways, transformations from one organic compound into others, and changes of compositions of C pools during turnover, comprehensive multicomponent models may offer the best possibilities, because they explicitly take them into account. However, this type of models are not convenient for use in practice because i) they require quite a number of parameters (8 to 29) which cannot easily be provided; ii) the values of parameters are different under different conditions, and therefore need to be carefully tested with experimental data before they are used in a different situation; iii) the defining of processes with full and partial assumptions and their related quantitative descriptions need comprehensive examinations in studies with deliberate designs (Motavalli et al., 1994). Such models have been reported successful in some studies (Jenkinson et al., 1992; Nicolardot et al., 1994; Van der Linden et al., 1987). Nevertheless, such success cannot fully ensure that all routines in the models and the quantitative descriptions of processes are correct, because it is possible that positive and negative deviations within a model are counterbalanced so that the final overall results still fit observations. Such a counterbalance may get lost when environmental factors like temperature, moisture condition and soil properties change, and if this happens, the predictions by the model are wrong.

## Chapter 3

# A mono-component model for organic matter mineralization with time-dependent relative mineralization rates

### Abstract

A mono-component model is developed, treating a substrate as a whole that is characterized by a time-dependent relative mineralization rate. By examining data collected from literature, a linear relation was found between log(K), the average relative mineralization rate between time 0 and time t, and log(time) provided that prevailing soil conditions remained constant. It can be expressed as $\log(K) = \log(R) - S * \log(t)$, or $K = R * t^{S}$, in which R (dimension $t^{S-1}$) and S (dimensionless) are two regression constants. R represents the initial relative mineralization rate, or K between t=0 and t=1 unit, and S ($1 \geq S \geq 0$) is a measure of the speed at which K decreases, also called the speed of 'aging' of substrate. It was found that R and S are determined by the resistance of substrates to mineralization and external conditions. The substrate quantity remaining at t ($Y_t$) can be calculated by $Y_t = Y_0 * \exp(-R * t^{1-S})$, in which $Y_0$ is the substrate quantity in the beginning. The actual relative mineralization rate (k) is calculated by: $k = (1 - S) * R * t^{S}$, and hence $k = (1 - S) * K$. The influence of temperature is incorporated into the model by the introduction of **f**, a temperature correction factor that relates the experimental time to $t_9$, which is the time needed for a same mineralization at a temperature of 9 °C: $t_9 = f * t$. Equations were derived for the use of the temperature correction in simulation models with time steps differing in temperature. The developed model can be applied for both added organic materials and existing soil organic matter.

## 3.1 Introduction

According to the principle of first-order kinetics, the rate of change of a substrate under mineralization in soil, and its quantity can be described as follows:

$$dY/dt = -k * Y \qquad (2.1)$$

$$Y_t = Y_0 * \exp(-K * t) \qquad (2.2)$$

in which t is time; Y and $Y_t$ are the quantity of substrate at time t; k ($\geq 0$) is the actual relative mineralization rate at t; K is the average relative mineralization rate from times zero until t. The use of K instead of k in the integration form of

Equation 2.1, is because that k is not a constant, but decreases over time, as found in Chapter 2.

It was shown in Chapter 2 that it is not possible to correctly depict organic matter mineralization with mono-component models with a constant relative mineralization rate (k). Two other approaches offer better possibilities. One is to partition organic substrates into two or more components each with its particular k. The other approach is to treat a substrate as one component, and to describe the relative mineralization rate (K or k) as a time-dependent function. In Chapter 2 we concluded that for a number of reasons mono-component models with time-dependent relative mineralization rates have more perspectives than multi-component models, or at least they can be considered as interesting alternatives to sophisticated models which are very demanding for input data, especially in places where those requirements cannot be met. It is the low requirements for input data that make mono-component models attractive for application in the practice of research stations and extension services.

The aim of this paper is to develop a mono-component mineralization model directly from experimental data collected from literature. The focus is on the derivation of an expression relating the relative mineralization rates to time. Other equations that are relevant for applications in practice are derived as well. Furthermore, the influence of temperature is incorporated in the model.

## 3.2 Data sets and statistical analysis

The same sets of experimental data were used as in Chapter 2 (Tables 2.1, 2.2, 2.3, and 2.4), which comprise 35 cases. These data sets were used because: 1) they contain both complex materials, such as straw and grass, representing the common organic materials used in agriculture, and simple materials like glucose, hemicellulose and cellulose, representing the basic constituents of straw and grass; 2) all materials used in the experiments had been labelled with $^{14}C$, thus avoiding possible interference from other sources of C; 3) the experiments had lasted between 3 to 10 years, making their results suitable for the derivation of time-dependent relationships; 4) some experiments had been conducted under controlled laboratory or greenhouse conditions and others in the field, so that they represent various situations.

Both linear and nonlinear regression were conducted in Statgraphics Plus (STSC

Inc. 1986). Adjusted $R^2$ and probability levels were used for judging the goodness of linear regression, and in case of nonlinear regression, only adjusted $R^2$ was used.

## 3.3 Derivation of the model

### *3.3.1 Relation between average relative mineralization rate (K) and time*

The average relative mineralization rate (K) was calculated with Equation 2.2 for all the data in Tables 2.1 to 2.4. In Figure 3.1, K is plotted against time in X-Y logarithmic scales. It is obvious that K decreases over time according to a linear relationship between log(K) and log(t). The straight lines are more regular than those shown in Figure 2.2 in Chapter 2 between log('k') and log(time), where 'k' was calculated by Equation 2.12 for the successive time intervals. The reason is that K is calculated from time 0 to t, so that the total time intervals of the successive points have large overlaps and mask deviations of single intervals. However, in the early phase, the observed K which is calculated by Equation 2.2, is a little lower than expected (e.g. for cellulose, maize straw and oat shoots in Figure 3.1). For glucose the linearity starts at about 2 days after incorporation, and for the other substrates at about one month after incorporation. The linear relation between log(K) and log(t) is highly significant as appears from the values of adjusted $R^2$ and their corresponding probability levels. (Table 3). The relation of K to t can then be expressed as follows:

$$\log(K) = \log(R) - S * \log(t) \tag{3.1.a}$$

or,

$$K = R * t^{-S} \tag{3.1.b}$$

in which R (dimension $t^{S-1}$) and S (dimensionless) are regression constants.

From Equation 3.1 it follows that R = K at t = 1, implying that R represents the initial relative mineralization rate (K), or, to be exact, the K between t = 0 and t = 1. The slope of the line in Figure 3.1, S ($1 \geq S \geq 0$, see below), is a measure of the speed at which K decreases over time, or the speed of 'aging' of the substrate.

Since the value of K depends on the unit of time that is used, the value of R also depends on it. Let the values of t, K, R and S be presented by $t_a$, $K_a$, $R_a$ and $S_a$, and $t_b$, $K_b$, $R_b$ and $S_b$ in the cases the units of time are a and b, respectively, and let n = b/a, the conversion of the values of R is as follows:

$$R_b = R_a * (1/n)^{-Sa} * n^{-1}$$

$$= R_a * n^{Sa-1}$$

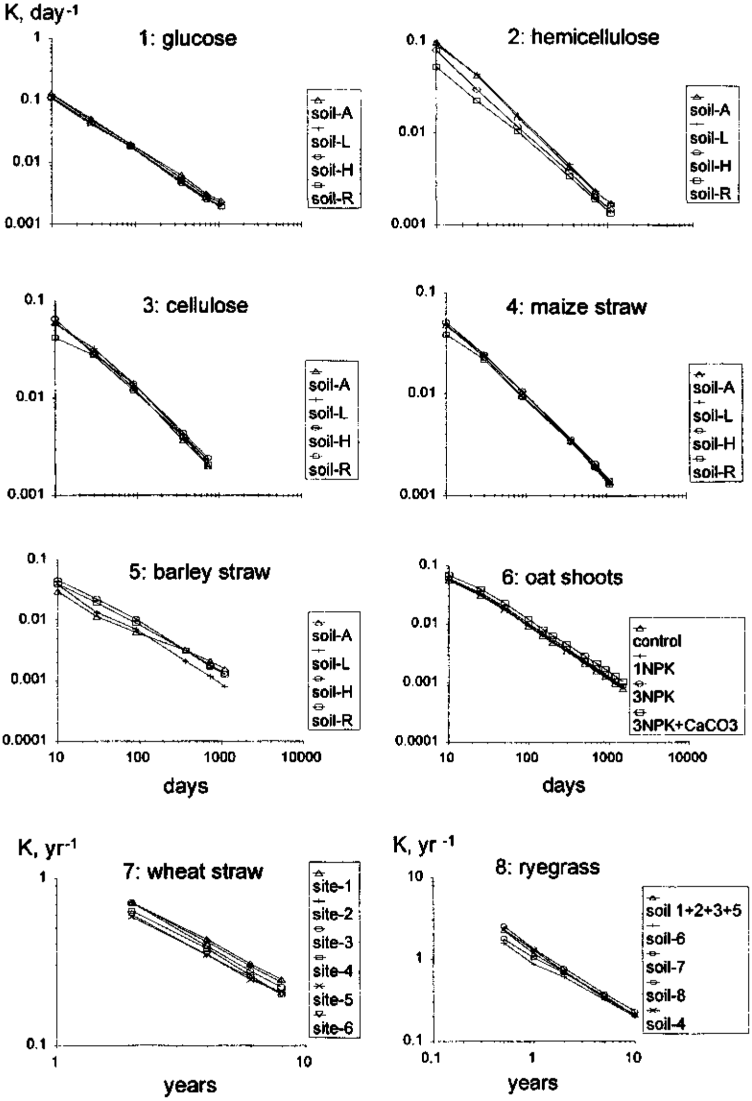

**Figure 3.1** Decrease of K over time in double logarithmic scales, as calculated by Equation 2.2

**Table 3** Results of linear regression of log(K) to log(t) by Equation 3.1.a, and of nonlinear regression of $Y_t$ to t by Equation 3.2(a)

| Case | linear regression | | nonlinear regression | | | | |
|---|---|---|---|---|---|---|---|
| | adj. $R^2$ | prob. level | R(b) | s.e.(c) | S | s.e.(c) | adj. $R^2$ |
| 1-1 | 1.00 | 0.000 | 0.91 | 0.06 | 0.85 | 0.01 | 0.97 |
| 1-2 | 1.00 | 0.000 | 0.94 | 0.07 | 0.87 | 0.01 | 0.96 |
| 1-3 | 1.00 | 0.000 | 0.84 | 0.10 | 0.87 | 0.02 | 0.88 |
| 1-4 | 1.00 | 0.000 | 0.89 | 0.08 | 0.88 | 0.02 | 0.94 |
| 2-1 | 1.00 | 0.000 | 0.86 | 0.06 | 0.90 | 0.01 | 0.94 |
| 2-2 | 1.00 | 0.000 | 0.93 | 0.04 | 0.90 | 0.01 | 0.97 |
| 2-3 | 1.00 | 0.000 | 0.51 | 0.02 | 0.84 | 0.01 | 0.99 |
| 2-4 | 1.00 | 0.000 | 0.34 | 0.03 | 0.79 | 0.02 | 0.98 |
| 3-1 | 1.00 | 0.000 | 0.55 | 0.05 | 0.85 | 0.02 | 0.96 |
| 3-2 | 1.00 | 0.000 | 0.57 | 0.06 | 0.83 | 0.02 | 0.95 |
| 3-3 | 0.99 | 0.002 | 0.41 | 0.08 | 0.77 | 0.04 | 0.93 |
| 3-4 | 1.00 | 0.001 | 0.43 | 0.05 | 0.80 | 0.02 | 0.96 |
| 4-1 | 1.00 | 0.000 | 0.32 | 0.02 | 0.77 | 0.01 | 0.99 |
| 4-2 | 1.00 | 0.000 | 0.40 | 0.03 | 0.81 | 0.01 | 0.98 |
| 4-3 | 1.00 | 0.000 | 0.36 | 0.02 | 0.79 | 0.01 | 0.99 |
| 4-4 | 1.00 | 0.000 | 0.31 | 0.03 | 0.77 | 0.02 | 0.98 |
| 5-1 | 1.00 | 0.000 | 0.07 | 0.01 | 0.54 | 0.02 | 1.00 |
| 5-2 | 0.99 | 0.000 | 0.24 | 0.05 | 0.81 | 0.03 | 0.90 |
| 5-3 | 1.00 | 0.000 | 0.36 | 0.04 | 0.80 | 0.02 | 0.97 |
| 5-4 | 1.00 | 0.000 | 0.27 | 0.02 | 0.76 | 0.02 | 0.99 |
| 6-1 | 1.00 | 0.000 | 0.58 | 0.01 | 0.90 | 0.00 | 0.98 |
| 6-2 | 1.00 | 0.000 | 0.60 | 0.01 | 0.90 | 0.00 | 0.98 |
| 6-3 | 1.00 | 0.000 | 0.65 | 0.02 | 0.90 | 0.00 | 0.98 |
| 6-4 | 1.00 | 0.000 | 0.72 | 0.02 | 0.89 | 0.01 | 0.98 |
| 7-1 | 1.00 | 0.000 | 1.22 | 0.03 | 0.77 | 0.01 | 0.99 |
| 7-2 | 1.00 | 0.000 | 1.24 | 0.02 | 0.80 | 0.01 | 1.00 |
| 7-3 | 1.00 | 0.000 | 1.28 | 0.02 | 0.85 | 0.01 | 0.98 |
| 7-4 | 1.00 | 0.001 | 1.15 | 0.06 | 0.83 | 0.03 | 0.91 |
| 7-5 | 1.00 | 0.001 | 0.99 | 0.04 | 0.76 | 0.03 | 0.97 |
| 7-6 | 1.00 | 0.000 | 1.04 | 0.00 | 0.79 | 0.00 | 1.00 |
| 8-1 | 1.00 | 0.001 | 1.22 | 0.04 | 0.79 | 0.03 | 0.95 |
| 8-2 | 0.99 | 0.004 | 0.93 | 0.03 | 0.67 | 0.03 | 0.98 |
| 8-3 | 1.00 | 0.001 | 1.38 | 0.04 | 0.80 | 0.03 | 0.95 |
| 8-4 | 1.00 | 0.001 | 1.07 | 0.02 | 0.70 | 0.02 | 0.99 |
| 8-5 | 1.00 | 0.000 | 1.28 | 0.03 | 0.81 | 0.02 | 0.97 |

(a) The data on the 10th day in Tables 2.1 and 2.2 were not included in the linear nor in the nonlinear regression analysis, see Section 3.3.1.

(b) The unit of R is day$^{S-1}$ from Cases 1-1 to 6-4 and is year$^{S-1}$ from Cases 7-1 to 8-5.

(c) standard error.

The value of S is independent of the unit of time, which is proved as follows:

$$S_b = \log(R_b / K_b) / \log(t_b)$$

$$= \log[R_a * n^{Sa - 1} / (K_a * n^{-1})] / \log(t_a * n)$$

$$= \log[R_a * n^{Sa} / (R_a * t_a^{-Sa})] / \log(t_a * n)$$

$$= S_a$$

### *3.3.2 Calculation of remaining organic matter*

Substitution of K in Equation 2.2 by Equation 3.1.b results in the following equation for the calculation of $Y_t$, the quantity of the substrate remaining at time t:

$$Y_t = Y_0 * \exp(-R * t^{1 - S}) \tag{3.2}$$

From Equations 3.1 and 3.2 it follows that $0 \leq S \leq 1$. If $S < 0$, K would increase with time, which has not been found so far under normal circumstances when conditions are kept constant, except sometimes in the very early stage of mineralization, e.g. within one month for normal plant materials. If $S = 0$, K becomes a constant and equal to R. If $S = 1$, $Y_t$ would not change over time. If S would be $> 1$, $Y_t$ would increase from 0 at $t \rightarrow 0$ to $Y_0$ at and $t \rightarrow \infty$, which is absurd.

The results of direct nonlinear regression by Equation 3.2 for the data in Tables 2.1 to 2.4 are also shown in Table 3, with resultant R, S and adjusted $R^2$. The average of adjusted $R^2$ is 0.97, suggesting that the model can almost fully explain the observations from various cases.

Using the values of R and S as given in Table 3, Equation 3.2 was applied to calculate $Y_t$, the quantities of remaining substrates at any t. The absolute differences between the calculated remaining fractions ($Y_t/Y_0$, %) and the observed (Tables 2.1 to 2.4) are shown in Figure 3.2. It can be seen from Figure 3.2 that the absolute differences in remaining fraction are all within the range of +3% to -3% over the time spans of the observations, and 97% of them are even within the range of +2% to -2%. This indicates that the model calculations agree very well with the observations.

When 'year' is used as the unit of time, Equation 3.2 yields the following relation between R and the humification coefficient (h.c.), which is the fraction remaining

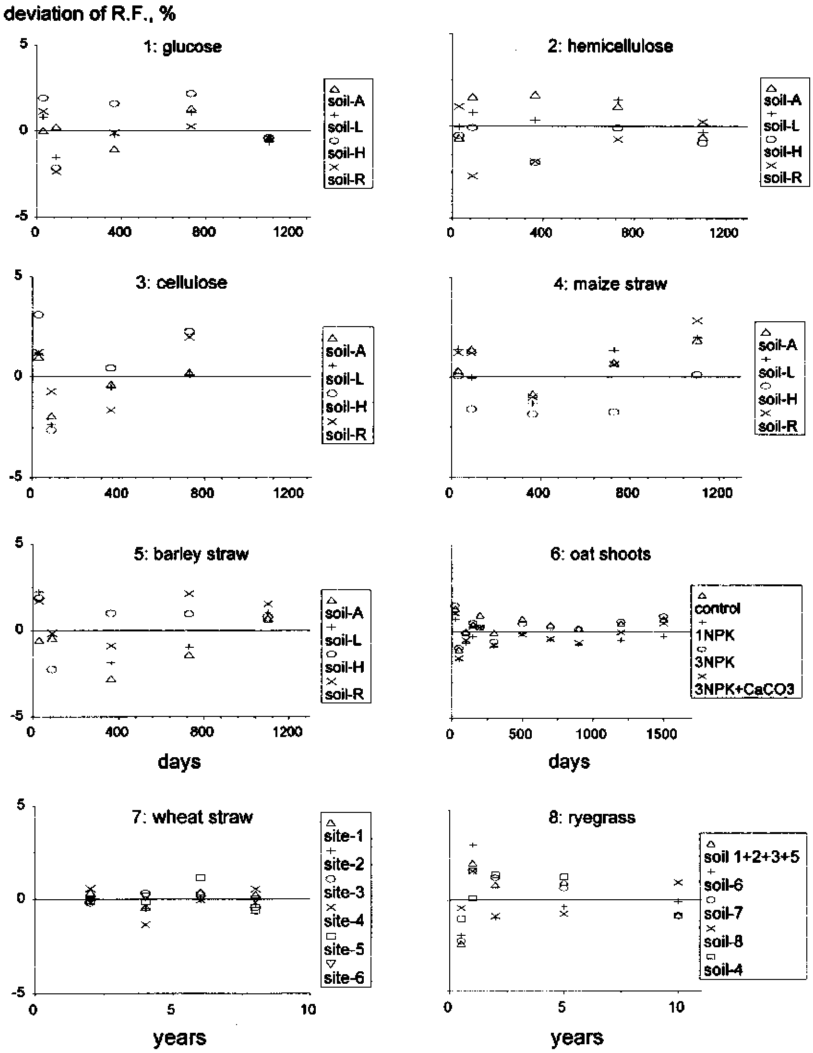

**Figure 3.2** Absolute deviation between observed and calculated remaining fractions (R.F.) by Equation 3.2.

at one year after addition of a substrate:

$$R = -\ln(h.c.) \tag{3.3}$$

### *3.3.3 Actual relative mineralization rate (k)*

K is the average relative mineralization rate between time 0 and time t, and it does not tell what the actual relative mineralization rate is at a specific moment t. Because dY/dt = -k * Y, by definition k can be found after differentiation of Equation 3.2:

$$dY/dt = Y_0 * \exp(-R * t^{1-S}) * [-R * (1 - S) * t^{-S}]$$

Substitution of $Y_0 * \exp(-R * t^{1-S})$ by $Y_t$ (Equation 3.2) yields:

$$dY/dt = -R * (1 - S) * t^{-S} * Y_t$$

At time t, it holds too:

$$dY / dt = -k * Y_t$$

and hence,

$$k = (1 - S) * R * t^{-S} \tag{3.4}$$

From the combination of Equations 3.1 and 3.4, it follows:

$$k = (1 - S) * K \tag{3.5}$$

Since $0 \leq S \leq 1$, thus k is always lower than K. Similar to K, log(k) has a linear relation to log(t). From Equations 3.1 and 3.4 it is derived:

$$\log(k) = \log[(1 - S) * R] - S * \log(t) \tag{3.6}$$

## 3.4 Incorporation of temperature effect in the model

### *3.4.1 Temperature correction factor f*

Temperature (T) is one of the most important factors influencing mineralization rate of organic matter. When using data sets from literature, one may face the problem that results of different experiments are difficult to compare because the temperatures during the various experiments may be different. These problems are circumvented by introducing a temperature correction in the model.

Results of field trials conducted in England and Nigeria (Jenkinson, 1977a; Jenkinson and Ayanaba, 1977) and Australia (Ladd et al., 1981) indicate that the relative mineralization rate of common plant materials was doubled per 9 °C rise in the mean annual temperature. In other words, one year of mineralization at 27 °C (in Nigeria) was equivalent to two years of mineralization at 18 °C (in Australia), or to four years of mineralization at 9 °C (in England). Hence, by changing the time scale, it is possible to incorporate the effect of temperature in the equations in a simple way. For that purpose a temperature correction factor (**f**) has been formulated, reading as follows (Janssen, 1986; Noij et al., 1993; Raijmakers and Janssen, 1995):

$$f = 2^{(T-9)/9} \qquad \text{for} \quad 9 < T \leq 27\ ^\circ\text{C} \qquad (3.7.a)$$

For temperatures below 9°C, the following relationships have been proposed by Janssen (1992):

$$f = 0.1 * (T + 1) \qquad -1 < T \leq 9\ ^\circ\text{C} \qquad (3.7.b)$$

$$f = 0 \qquad T \leq -1\ ^\circ\text{C} \qquad (3.7.c)$$

For temperatures between 27 and 35 °C, f=4 may be used, following the relationship as used by e.g. Van Veen and Paul (1981) and Parton et al. (1987).

Let $K_9$ = the average relative mineralization rate at a temperature of 9 °C being the temperature for which f=1, Equation 2.2 is transformed into:

$$K_9 = [-\ln(Y_t/Y_0)]/(f * t)$$

and because $K = [-\ln(Y_t/Y_0)]/t$, it holds:

$$K_9 = K/f \qquad (3.8)$$

where $f * t$ = the corrected period of time.

When log(K) is a linear function of log(t), there exists also a linear relation between $\log(K_9)$ and $\log(f*t)$, which is proven mathematically as follows.

Because $K_9 = K * f^{-1}$ (Equation 3.8), in Equation 3.1.b both sides are multiplied by $f^{-1}$; further $f^{-S}$ is introduced at the right side of Equation 3.1.b. This yields:

$$K * f^{-1} = R * f^{S} * f^{-1} * f^{-S} * t^{-S}$$

and hence,

$$K_9 = R * f^{S-1} * (f * t)^{-S} \tag{3.9.a}$$

or,

$$\log(K_9) = \log(R * f^{S-1}) - S * \log(f * t) \tag{3.9.b}$$

Because $R*f^{S-1}$ is a constant, $\log(K_9)$ is indeed linearly related to $\log(f*t)$.

In Equation 3.9.b, S is not affected by the introduction of **f**, in other words:

$$S_9 = S \tag{3.10}$$

Further $R_9$ is defined as the average relative mineralization rate (K) between times (t) of 0 and 1 unit at a temperature of 9 °C, or as the K between corrected times ($f*t$) of 0 and 1 unit. From Equation 3.9.a, it follows:

$$R_9 = R * f^{S-1} \tag{3.11}$$

so,

$$\log(K_9) = \log(R_9) - S * \log(f * t) \tag{3.9.c}$$

The correction for temperature makes it possible to calculate mineralization rates under varying temperatures, to translate the value of R obtained under a specific temperature into values to be expected at other temperatures, and thus to compare the results of mineralization studies carried out at different temperatures.

When $R_9$ and S are known, the values of K, k and $Y_t$ at any temperature can be calculated with the following equations:

$$K = R_9 * f * (f * t)^{-S} \tag{3.12}$$

$$k = (1 - S) * R_9 * f * (f * t)^{-S} \tag{3.13}$$

$$Y_t = Y_0 * \exp[-R_9 * (f * t)^{1-S}] \tag{3.14}$$

It is important to notice that **f** in above equations must refer to the entire period from times 0 to t. Because **f** is not proportional to temperature, and the formulations for the calculation of **f** differ in different temperature regimes (Equations 3.7.a, 3.7.b and 3.7.c), **f** calculated with an average T over an entire period of time may differ from the value obtained by averaging the **f** values calculated separately for all short sub-periods with different temperatures. The later method is the correct one.

### 3.4.2 *The use of f in simulation models*

In simulation models calculations are carried out per time step. If temperature varies from one time step to another, $Y_n$, standing for $Y_t$ at the end of time step n, cannot be calculated directly from the initial quantity ($Y_0$) with Equation 3.14, but has to be calculated from $Y_{n-1}$, which is Y at the end of the preceding time step $(n - 1)$. Also for K and **f**, their values referring to individual time steps have to be used. This requires some adaptations of the equations.

Suppose the following items are known: $R_9$, S, $Y_1$ (the quantity of a substrate remaining at time $t_1$), $\mathbf{f}_1$ (the average **f** from beginning till $t_1$, which can be calculated through $Y_1$ by means of Equation 3.14), $\mathbf{f}_{1\rightarrow2}$ (the **f** for the period from $t_1$ to $t_2$), the equations for calculating $Y_2$ (the quantity of a substrate remaining at $t_2$) are derived as follows:

For the time interval between $t_1$ and $t_2$, it follows from Equation 2.2:

$$Y_2 = Y_1 * \exp[-K_{1\rightarrow2} * (t_2 - t_1)]$$

where $K_{1\rightarrow2}$ is the average K from time $t_1$ to time $t_2$.

The value of $K_{1\rightarrow2}$ is obtained by integrating the actual relative mineralization rate (k) over the interval from $t_1$ to $t_2$, and dividing the integration result by the length of the time interval $(t_2 - t_1)$. Because the time must be corrected for temperature, $t_1$ and $t_2$ are corrected to $(f_t{*}t)_1$ and $(f_t{*}t)_2$, respectively, in which $\mathbf{f}_t$ is the average

**f** from t=0 to t. The time interval ($t_2 - t_1$) corrected for temperature is: $f_{1\to2} * (t_2 - t_1)$, where $\mathbf{f}_{1\to2}$ is the temperature correction factor for this time interval.

From Equation 3.13 it follows that $k_t$, the value of k at time t is:

$$k_t = (1 - S) * f_t * R_9 * (f_t*t)^{-S}$$

Integration of $k_t$ yields:

$$\int k = (1 - S) * f_t * R_9 * \int (f_t*t)^{-S}$$

$$= R_9 * f_t * (1 - S) * (f_t*t)^{1-S}/(1 - S)$$

$$= R_9 * f_t * (f_t*t)^{1-S}$$

From $(f_t*t)_1$ to $(f_t*t)_2$, in which $f = f_{1\to2}$, $(f_t*t)_1 = f_1*t_1$, and $(f_t*t)_2 = (f_t*t)_1 + (t_2 - t_1) * f_{1\to2}$, the integration is:

$$\int_{(f*t)_1}^{(f*t)_2} k = R_9 * f_{1\to2} * (f_t*t)_2^{1-S} - R_9 * f_{1\to2} * (f_t*t)_1^{1-S}$$

$$= R_9 * f_{1\to2} * [(f_t*t)_2^{1-S} - (f_t*t)_1^{1-S}]$$

Hence, the average K from $t_1$ to $t_2$ is:

$$K_{1\to2} = R_9 * f_{1\to2} * [(f_t*t)_2^{1-S} - (f_t*t)_1^{1-S}]/[f_{1\to2} * (t_2 - t_1)]$$

$$= R_9 * [(f_t*t)_2^{1-S} - (f_t*t)_1^{1-S}]/(t_2 - t_1)$$

Finally, substituting $K_{1\to2}$ in Equation 2.2 yields:

$$Y_2 = Y_1 * \exp\{\{-R_9 * [(f_t*t)_2^{1-S} - (f_t*t)_1^{1-S}]/(t_2 - t_1)\} * (t_2 - t_1)\}$$

hence,

$$Y_2 = Y_1 * \exp\{-R_9 * [(f_t*t)_2^{1-S} - (f_t*t)_1^{1-S}]\} \tag{3.15}$$

At the end of each time step, the **f** for the whole period from beginning can be calculated through $Y_t$ by means of Equation 3.14, in which **f** is the only unknown.

The resulting **f** will act as $\mathbf{f}_1$ for the calculation of Y at the end of next time step. In this way, calculations can be made in a simulation with steps differing in temperature.

## 3.5 Discussion and conclusions

The mono-component mineralization model developed in this chapter was derived directly from data that had been measured. There is no need for risky derivation of values that cannot directly be measured. Some of the experiments had been carried out under controlled conditions and others under varying conditions in the field, and the substrates used in the experiments varied from simple substances to complex compounds.

The pivot of the model is the decrease of the average relative mineralization rate (K) over time, as expressed by the linear relationship between log(K) and log(t). Some results (Cases 3, 4 and 6 in Figure 3.1) show, that the linearity between log(K) and log(t) did not start immediately after incorporation of a substrate. This phenomenon is discussed in next chapter.

As shown in Chapter 2, the attempts were already made by e.g. Kolenbrander (1969, 1970) and Janssen (1984, 1986), based on experimental data, to describe the decrease over time of K, the average relative mineralization rate (Kolenbrander), or k, the actual relative mineralization rate (Janssen):

$$K = n + p * (t + 1)^{-1} \tag{2.7}$$

$$k = 2.82 * (a + f*t)^{-1.6} \tag{2.8.a}$$

Equation 2.7 and 2.8.a resemble Equation 3.1 and 3.4, respectively, in that K or k is related to time in a nonlinear way. However, the results of Chapter 2 show that Equation 2.7 and 2.8.a are case sensitive: they fit very well the data from which they were proposed, but failed in some other cases. The main cause for this is that the values of exponential terms in both equations are fixed, making the functions too rigid to handle different situations. Nevertheless, Equation 3.6 proves that the intrinsic linear relationship between log(k) and log(t) shown by Equation 2.8.a does hold in various cases.

From the results in Table 3 it is obvious that both R, the average relative mineralization rate during the first time unit, and S, the speed at which K and k decrease, are determined not only by the inherent resistance of substrates, but also by soil properties and environmental factors. So far, temperature is the only environmental factor incorporated in the model. As shown in Section 3.4.1, the correction method for temperature was originally derived from a few data sets from experiments with only plant materials (ryegrass and legume plant material) and carried out at different locations (England, Nigeria and Australia). Therefore, it may not be simply applicable, when substrates or conditions or both differ significantly from those in the experiments used for the derivation of the correction factors. Some consequences for temperature effects are treated in Chapter 8.

Incorporation of other factors, like soil texture and pH, moisture condition and N availability, might also be achieved by correction of the time scale, as it is done for temperature, or by adjustments of S, or both, depending on the way the properties affect the mineralization process.

The two model parameters, R and S, can be obtained either by linear regression of log(K) and log(t) (Equation 3.1.a), or by direct non-linear regression of $Y_t$ and t (Equation 3.2). The results differ slightly from each other, because the (minimum) values of residual sum of square between estimated and observed values show different patterns for the linear regression of the logarithmic values and the non-linear regression of $Y_t$ and t. Because $Y_t$, the quantity of a substrate remaining at t, is the final criterion for the judgement of the goodness of fit between model calculations and observations, direct non-linear regression of $Y_t$ to t is considered the better procedure. Nevertheless, linear regression between log(K) and log(t) may be used when software programmes for non-linear regression are not available.

Chapter 4

# Test of a mono-component model for organic matter mineralization with time-dependent relative mineralization rates

## Abstract

The model presented in Chapter 3 of this study was tested with data collected from 30 articles and 2 internal reports. The experiments in these papers and reports were conducted in 14 countries all over the world and differed greatly in conditions and durations. They cover chemically simple substrates like glucose, hemicellulose and cellulose, and chemically and physically complex substrates such as plant material, animal manure, peat and native soil organic matter. In total there were 184 cases. Test criteria used were (1) adjusted $R^2$ and the probability levels of the linear regression of log(K) to log(t) under constant temperature, and to log(f*t) under changing temperatures (f = temperature correction factor); (2) adjusted $R^2$ of non-linear regression of remaining quantities of substrates ($Y_t$) to t; (3) the deviations between observed and model calculated remaining fractions of substrates ($Y_t/Y_0$). The results give rise to conclude that the model can accurately describe the dynamics of mineralization of C in soil in the time span from months to tens of years, provided that major environmental factors remain unchanged. The correction made for temperature was satisfactory. Some possible causes of deviations between model and experiments are discussed.

## 4.1 Introduction

In Chapter 3 it was found that the average relative mineralization rate from times zero to t (K) is not constant, but decreases over time. Under constant environmental conditions, it holds:

$$\log(K) = \log(R) - S * \log(t) \qquad (3.1.a)$$

and in case of varying temperatures:

$$\log(K_9) = \log(R_9) - S * \log(f * t) \qquad (3.9.c)$$

where R = the average relative mineralization rate during the first time unit; S = the speed at which K decreases over time, also called the speed of 'aging' of substrate. **f** = the temperature correction factor, $K_9$ and $R_9$ refer to K and R at a temperature of 9 °C.

There were some indications that in the very beginning of mineralization K was less than follows from the linear relationship between log(K) and log(t).

For the calculation of quantities of remaining substrate at time t ($Y_t$), the following equation was derived:

$$Y_t = Y_0 * \exp(-R * t^{1-S}) \qquad (3.2)$$

and in case of varying temperatures:

$$Y_t = Y_0 * \exp[-R_9 * (f * t)^{1-S}] \qquad (3.14)$$

where $Y_0$ is the quantity of substrate in the beginning. The temperature correction factor **f** is calculated by the following formulas:

$$f = 0 \quad \text{at:} \quad T \leq -1\ °C \qquad (3.7.a)$$
$$f = 0.1 * (T + 1) \quad -1 < T \leq 9\ °C \qquad (3.7.b)$$
$$f = 2^{(T-9)/9} \quad 9 < T \leq 27\ °C \qquad (3.7.c)$$

The purpose of this chapter is to test this mono-component model with data collected from 30 papers and 2 internal reports, issued in the past four decades. The described experiments were of different durations, covered many types of organic substrates and soils, and the external factors were controlled to divergent extent.

The testing consisted of three steps:
1. determination of the time at which the linearity between log(K) and log(t) starts;
2. assessment of the linearity;
3. assessment of the power of the model in predicting or explaining observations.

## 4.2 Data sets and test methods

Table 4.1 gives some details about the experiments described in the papers (including the four sets used in Chapters 2 and 3) and internal reports, all dealing with single additions of organic substrates only. They cover 29 different substrates which can be classified into four groups: (1) chemically simple compounds like glucose and cellulose; (2) plant materials including materials from both arable crops and trees; (3) animal manures, and (4) materials like peat, litter and native soil organic matter. The experiments were conducted in 14 countries in Europe, North America, East Asia, Africa and Australia, and in total 184 cases were included, including the 35 cases used in Chapters 2 and 3. In 102 cases, $^{14}C$-labelled materials were used. Environmental conditions, such as temperature and soil moisture content, had been kept constant in incubation experiments. In part of the field trials, sampling was carried out on an annual basis, which provides reasonably comparable external conditions for the successive inter-sampling periods. For the rest of the field trials, environmental conditions were subjected to change, but only the data for temperatures were available. Table 4.2 shows a summary of the cases in Table 4.1.

The goodness of linearity between log(K) and log(t), or between log($K_9$) and log(f*t), was measured by adjusted $R^2$ of linear regression and their corresponding probability levels. For judging the explanatory power of the model to observations, adjusted $R^2$ was used for nonlinear regression of $Y_t$ to t by Equation 3.2 (under constant temperatures), or by Equation 3.14 (under changing temperatures). The goodness of the nonlinear regression is considered the ultimate test and evaluation of the model, because it tells to what degree Equation 3.2 or 3.14 explains the changes in real observations. The goodness of the linearity between log(K) and log(t), or between log($K_9$) and log(f*t), gives the information on the correctness of the basic description of the decrease over time of K. Both linear and nonlinear regressions were conducted in Statgraphics (STSC Inc. 1986).

## 4.3 Results

### *4.3.1 Start of the linearity between log(K) and log(t)*

As examples, 5 sets of data were used to show at what time the linearity between log(K) and log(t) starts. They comprise 20 cases, and cover glucose, cellulose, holocellulose and plant materials, and all experiments were under constant temperatures. The values of K calculated by Equation 2.2 were plotted against t in double logarithmic scales in Figure 4.1.

**Table 4.1** Specifications of data

| substrate | duration | soil, condition, and others | Data source |
|---|---|---|---|
| glucose | 185 d | loamy soil, 1% $CaCO_3$, N%=0.1, incub. at 25°C, France | Mary et al., 1993 |
| glucose | 28 d | 2 sandy loams and 2 silt loams, pH=5.7 - 5.9, N%=0.46-0.94, $^{14}C$-labelled, incub. at 20 °C, New Zealand | Saggar et al., 1994 |
| glucose | 101 d | sandy loam and clay, pH>8.0$^{(a)}$, $^{14}C$-labelled, incub. at 25 °C, Australia | van Veen et al., 1985 |
| glucose | 140 d | silt clay loam, pH=7.3, N%=0.13, $^{14}C$-labelled, incub. at 4, 12, 20 and 28 °C, France | Nicolardot et al., 1994 |
| glucose | 3 yr | 3 sandy loams and 1 clay loam, pH=6.2-7.4, N%=0.07-0.26, $^{14}C$-labelled, incub. at 20 °C, Denmark | Sorensen 1983 |
| glucose | 7.3 yr | clay, N%=0.24, $^{14}C$-labelled, in field, Canada | Voroney et al., 1989 |
| hemicellulose | 3 yr | 3 sandy loams and 1 clay loam, pH=6.2-7.4, N%=0.07-0.26, $^{14}C$-labelled, incub. 20 °C, Denmark | Sorensen 1983 |
| holocellulose | 140 d | silt clay loam, pH=7.3, N%=0.13, $^{14}C$-labelled, incub. at 4, 12, 20 and 28 °C, France | Nicolardot et al., 1994 |
| cellulose | 90 d | 1 sand, 2 sandy loams and 1 clay loam, $^{14}C$-labelled, incub. at 10, 20 and 30 °C, Denmark | Sorensen 1981 |
| cellulose | 3 yr | 3 sandy loams and 1 clay loam, pH=6.2-7.4, N%=0.07-0.26, $^{14}C$-labelled, incub. at 20 °C, Denmark | Sorensen, 1983 |
| cellulose | 4.4 yr | 1 sand, 2 sandy loams and 1 clay loam, $^{14}C$-labelled, incub. at 20 °C, Denmark | Sorensen, 1981 |
| roots of maize | 185 d | 1 loam soil, 1% $CaCO_3$, N%=0.1, incub. at 25°C | Mary et al., 1993 |
| sesbania and rice straw | 12 wk | sandy loam, loam, silt clay and clay, pH =4.4-4.9, N%=0.10-0.12, incub. at 28 °C, India | Sarmah and Bordoloi, 1994 |
| straw and roots of winter wheat | 192 d | washed sand, incub., USA | Jawson and Elliott, 1986 |

| | | | |
|---|---|---|---|
| red-clover roots | 195 d | loam, pH=4.3, N%=0.13, incub. at 22 °C, Sweden | Berg et al., 1987 |
| sino milk-vetch | 218 d | red paddy soil, N%=0.11, $^{14}$C-labelled, incub. at 25 °C, China | Cai and Mao, 1980 |
| top and roots of 2 legume crops | 1 yr | average of 5 to 8 soils, pH=6.0-8.4, N%=0.03-0.18, $^{14}$C-labelled, in field, Australia | Amato et al., 1987 |
| maize stover, wheat straw (WS), semi--composted WS and *Vicia villosa* | 1 yr | fluvial sandy soil, pH=7.0(b), N%=0.05, in field, China | Zhang et al., 1986 |
| maize stover and rice straw | 1 yr | Brown Soil, pH=6.5(b), N%=0.08, incub. at 30 °C, China | Zhou et al., 1984 |
| maize stover | 2 yr | sandy loam, $^{14}$C-labelled, incub. at 22 °C, Germany | Haider and Martin, 1981 |
| sesbania, a fibre green manure, maize stover | 2 yr | loam(b), pH=7.0(b), N%=0.08, in field, China | Wang et al., 1984 |
| wheat straw | 2 yr | from 13 sites, pH=6.0-8.4, N%=0.03-0.18, in field, Australia | Amato et al., 1987 |
| ryegrass | 2 yr | loam(c), pH=6.7, N%=0.10, $^{14}$C-labelled, in field, Nigeria | Jenkinson and Ayanaba, 1977; Ayanaba and Jenkinson, 1990 |
| maize stover and barley straw | 3 yr | 3 sandy loams and 1 clay loam, pH=6.2-7.4, N%=0.07-0.26, $^{14}$C-labelled, incub. at 20 °C, Denmark | Sorensen, 1983 |
| legume residue | 4 yr | loam, pH=8.1(c), N%=0.14, $^{14}$C-labelled, in field, Australia | Ladd et al., 1983b |
| wheat straw, wheat root, maize stover, maize root, millet straw, millet root, sesbania straw | 4 yr | loam(b), pH=7.5(b), N%=0.09, in field, China | Wang et al., 1989 |
| legume residue | 4 yr | sand, loamy sandy, sandy loam and sandy clay, pH=8.2-8.6, N%=0.05-0.14, $^{14}$C-labelled, in field, Australia | Ladd et al., 1981 |
| oat-shoots under 4 treatments in sandy and loamy soil; oat-roots | 4.1 yr | loamy sand and clay loam, pH=5.6 and 4.7, $^{14}$C-labelled, incub. at 20 °C, Poland | Nowak and Nowak, 1990 |

| | | | |
|---|---|---|---|
| maize stover | 5 yr | loam(b), pH=7.0(b), N%=0.08, in field, China | Wang et al., 1989 |
| wheat straw | 7 yr | clay and loam, N%=0.24 and 0.21, $^{14}$C-labelled, in field, Canada | Voroney et al., 1989 |
| legume residues | 8 yr | loamy sand, pH=8.5, N%=0.94, $^{14}$C-labelled, in field, Australia | Ladd et al., 1985 |
| wheat straw | 8 yr | 3 sands and 3 sandy loams, pH=4.6-7.2, $^{14}$C-labelled, in field, Germany | Sochtig and Sauerbeck, 1982 |
| green mass, straw, litter, fir needle and saw dust | 8 yr | in compost pile, The Netherlands | Kolenbrander, 1969 and 1974 |
| wheat straw | 10 yr | clay and loam, N%=0.24 and 0.21, $^{14}$C-labelled, in field, Canada | Voroney et al., 1989 |
| maize stover, maize root, sweet-clover and soybean root | 10 yr | loam, pH=6.5(b), in field, China | Xu et al., 1993 |
| rice straw, green--duck-weed and rice root | 10 yr | paddy soil, pH=6.5(b), in field, China | Xu et al., 1993 |
| ryegrass | 10 yr | 2 sandy soils and 6 loamy soils, pH=3.7-8.1, N%=0.11-0.40, $^{14}$C-labelled, in field, England | Jenkinson, 1977a |
| barley straw, 1 | 20 yr | loamy sand, pH=6.0, N%=0.18, $^{14}$C-labelled, in field, Denmark | Sorensen, 1987 |
| fresh and stored manure | 84 d | 3 sandy soils, pH=8.0, N%=0.18, 0.09, 0.05, incub. at 20 °C, Sweden | Sorensen and Jensen, 1995 |
| FYM | 12 wk | sandy loam, loam, silt clay and clay, pH =4.4-4.9, N%=0.10-0.12, incub. at 28 °C, India | Sarmah and Bordoloi, 1994 |
| fresh and semi-composted pig manure | 1 yr | fluvial sandy soil, pH=7.0(b), N%=0.05, in field, China | Zhang et al., 1986 |
| FYM | 8 yr | in compost pile, The Netherlands | Kolenbrander, 1969 and 1974 |
| pig manure, cow manure and horse manure | 10 yr | 2 loams and 1 paddy soil, pH=6.5(b), in field, China | Xu et al., 1993 |
| peat | 1 yr | Brown Soil, pH=6.5(b), N%=0.08, incub. at 30 °C, China | Zhou et al., 1984 |

| | | | |
|---|---|---|---|
| 4 kinds of peat | 8 yr | in compost pile, The Netherlands | Kolenbrander, 1969 and 1974 |
| SOM | 10 yr | 3 loamy soils, pH=4.9, 7.0 and 7.1, N%=0.33, 0.38 and 0.40, in field, England | Jenkinson, 1977a |
| SOM | 12 yr | loamy sand, pH=6.0, N%=0.18, in field, Denmark | Sorensen, 1987 |
| SOM | 22 yr | in field, The Netherlands | Kortleven, 1963 |
| SOM | 100 yr | in field, England | Jenkinson and Rayner, 1977 |

(a) from Ladd et al., 1983a
(b) estimated
(c) from Ladd et al., 1985

**Table 4.2** Summary of the cases in Table 4.1

| Type of substrate | Total cases | No. of cases under specific conditions | | | |
|---|---|---|---|---|---|
| | | Use of $^{14}C$ | Constant temperature | Sampling on annual basis | f(b) involved |
| Simple material(a) | 51 | 50 | 50 | 1 | 0 |
| Plant material | 100 | 52 | 36 | 36 | 28 |
| Animal manure | 24 | 0 | 10 | 1 | 13 |
| Peat & SOM | 9 | 0 | 0 | 9 | 0 |

(a) including glucose, hemicellulose, cellulose and holocellulose
(b) temperature correction factor

For glucose, the linearity started after 1-2 days under normal conditions, and some days later under harsh conditions, such as a temperature of 4 °C in Figure 4.1-B. Examination of other references confirms that for glucose there is soon linearity, e.g. after 1 day (Saggar et al., 1994) and 3 days (Mary et al., 1993). In general, it may be assumed that the linear relationship between log(K) and log(t) starts after 2 days for glucose under normal conditions.

For cellulose, holocellulose, and shoots and roots of oat, the linearity started after approximately 1 month under favourable conditions (Figure 4.1-C and 4.1-E). In Figure 4.1-D, the linearity started after about 20 days at temperatures of 28 °C and 20 °C, whereas at 12 °C it did not appear until around 40 days. At a still lower temperature of 4 °C, the linearity did not show up in the whole period of

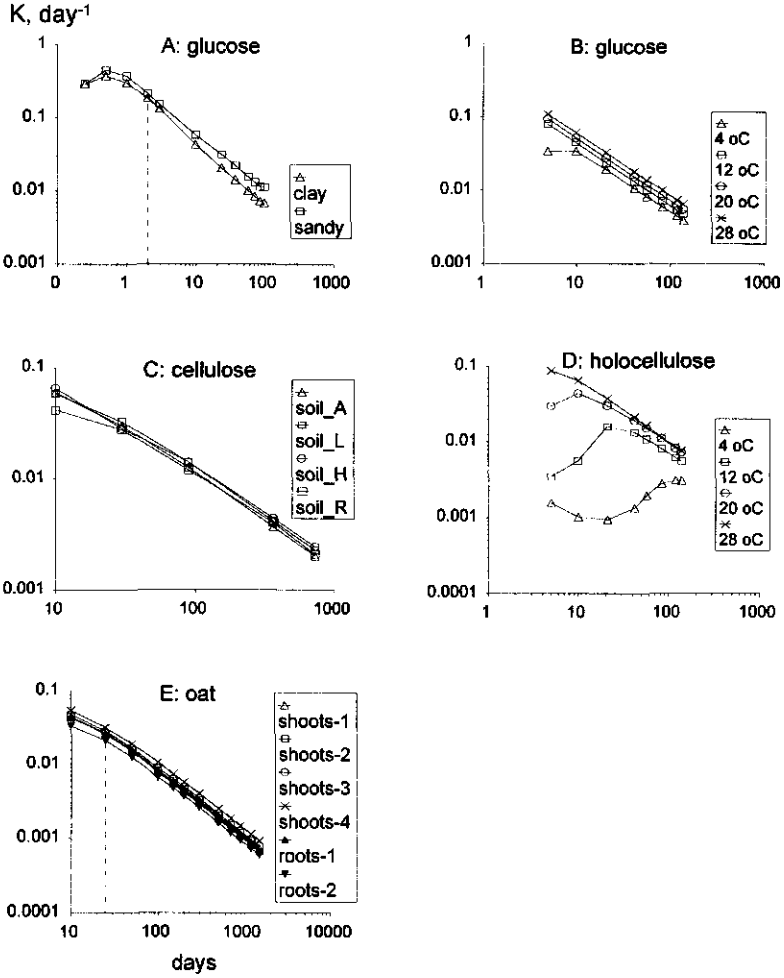

**Figure 4.1** Decrease over time of K calculated by Equation 2.2. The dashed vertical lines indicate the start of the linearity between log(K) and log(t). A: in clay and sandy soils at 25 °C (Van Veen et al., 1985); B & D: under four temperatures in a loamy soil (Nicolardot et al., 1994); C: in four soils at 20 °C (Sorensen, 1983) E: oat shoots in four treatments, and oat roots in two soils, at 20 °C (Nowak and Nowak, 1990)

140 days. It has been confirmed by other references in Table 4.1, for instance Berg et al. (1987), Cai and Mao (1980), Mary et al. (1993), Sorensen (1983), that the linearity normally starts after approximately one month for substrates like plant materials. Also for manure, litter or peat, one month could be taken as the starting time of the linear relationship between log(K) and log(t).

Based on these findings, it was decided to use for testing the model only the experimental data beyond the starting time of linearity, being roughly 0.1 year. In most cases all data were used as already the first sampling date was at time later than 0.1 year.

### *4.3.2 Goodness of the linearity between log(K) and log(t) or log(f*t)*

Figure 4.2 shows the frequency distribution of adjusted $R^2$ of the linear regression of log(K) to log(t) (under constant temperatures) or to log(f*t) (under changing temperatures), and that of the corresponding probability levels. For the 51 cases of simple materials, including glucose, hemicellulose, cellulose and holocellulose, no correction for temperature was needed, because 50 cases were from incubation experiments under constant temperatures, and the other one was from a field trial where sampling was done at the same time of the year. In 96% of the 51 cases, adjusted $R^2$ was $\geq 0.96$, and in 82% it was even $\geq 0.98$. The probability levels of adjusted $R^2$, were $\leq 0.04$ in 82%, and $\leq 0.02$ in 69% of the cases.

For plant materials, including five green manure crops, six cereal crops (straw and roots), four other plants and two woody materials, the adjusted $R^2$ was $\geq 0.96$ in 92%, and $\geq 0.98$ in 80% of the 100 cases in this group. The probability levels of adjusted $R^2$ were $\leq 0.04$ in 99% of the cases, and $\leq 0.02$ in 96%.

In the 24 cases of animal manure, covering FYM, horse manure, cow manure and pig manure, 87% of the adjusted $R^2$ reached values of $\geq 0.90$, and 67% of $\geq 0.96$, and 46 % of $\geq 0.98$. As to the probability levels of the adjusted $R^2$, they were $\leq$ 0.04 in 92%, and $\leq 0.02$ in 79% of the cases.

For peat and native SOM, 56% of the 9 cases reached adjusted $R^2$ values of $\geq$ 0.96, while the other 44% had values $< 0.90$. Probability levels of adjusted $R^2$ were $\leq 0.02$ in 89%, and $> 0.1$ in 11%.

Of the total 184 cases examined, 90% had adjusted $R^2 \geq 0.95$, and the probability levels of adjusted $R^2$ were $\leq 0.05$ in 93%, and $\leq 0.02$ in 85%.

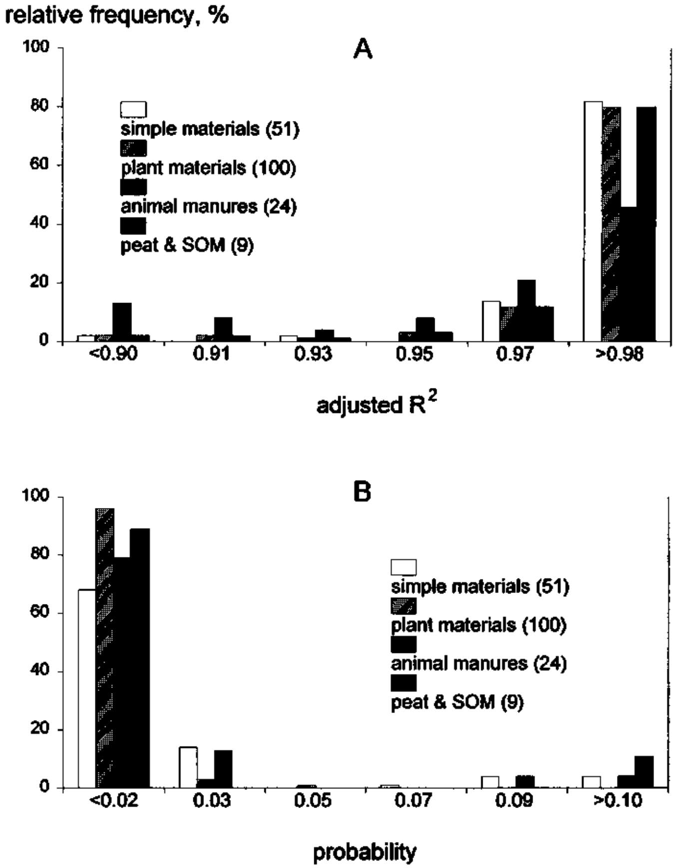

**Figure 4.2** Distribution of adjusted $R^2$ (A) and their corresponding probability levels (B) of linear regression of log(K) to log(t) (under constant temperature), or to log(f*t) (under changing temperature) for various types of substrates. The figures in legends refer to the numbers of cases for each type of substrate.

### *4.3.3 Explanatory power or goodness of fit of the model*

Figure 4.3 shows the results of adjusted $R^2$ for the non-linear regression of $Y_t$ to t by Equation 3.2 or 3.14. For the simple materials like glucose and cellulose, the adjusted $R^2$ was $\geq 0.90$ in 90% of the total 51 cases, and $\geq 0.95$ in 72%. For plant materials, 93% of the total 100 cases had adjusted $R^2$ values of $\geq 0.85$, 86% of $\geq 0.90$, and 68% of $\geq 0.95$. In 8 of the 14 cases with adjusted $R^2$ below 0.90, no $^{14}C$

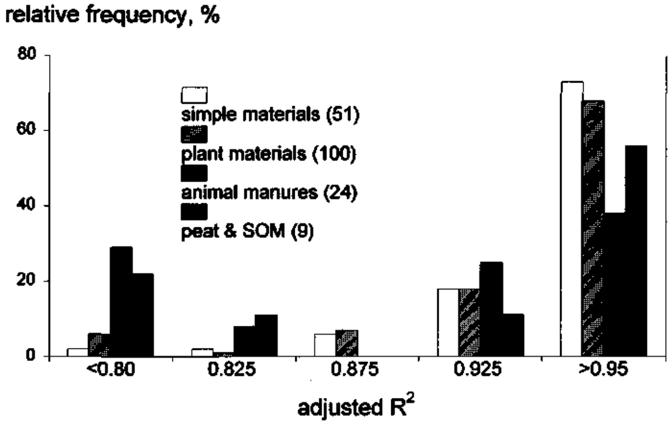

**Figure 4.3** Distribution of adjusted $R^2$ of nonlinear regression of observed remaining quantities of substrates to time by Equation 3.2 (under constant temperature) or Equation 3.14 (under varying temperatue).

labelling had been applied, or sampling had not been done at the same time in the year. In 71% and 63% of the total 24 cases of manures, the adjusted $R^2$ were $\geq$ 0.80 and $\geq$ 0.90, respectively. As to peat and native SOM, 78% of the 9 cases came out with adjusted $R^2$ of 0.80 or higher, and 67% with 0.90 or higher. Of the total of 184 cases, 82% yielded adjusted $R^2$ of $\geq$ 0.90, and 91% of $\geq$ 0.80.

Figure 4.4 shows the absolute deviations between observed remaining fractions (in %) and model calculations. For 93 percent of the total 1064 pairs of data, the deviation was less than ± 3%, and in 62 percent of the total it was less than ±1%. Figure 4.4 also indicates that the deviations are normally distributed in the whole range with 0 as the median, implying that the probabilities of positive and negative deviations are equal, and the model does not give systematic overestimation or underestimation.

## 4.4 Discussion and conclusions

When the principle of first-order kinetics is applied to mineralization of organic matter in soil, the description of the relative mineralization rates becomes the key issue. Under constant environmental conditions, K, the average relative

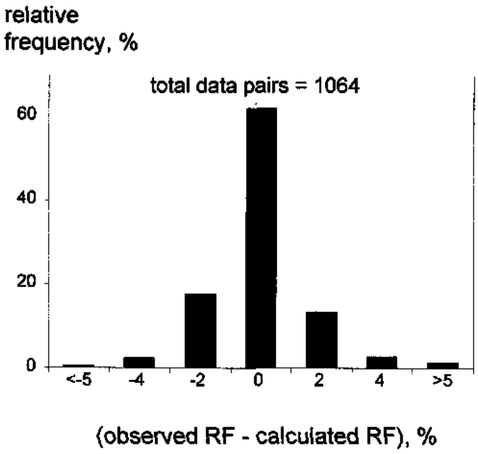

**Figure 4.4** Distribution of deviations between observed and model calculated remaining fractions (RF, %) of substrates. Mean=0.02; STD=1.67; median=0.

mineralization rate between t zero to t, proved to decrease over time according to a linear relationship between their logarithms (Figure 4.1) as described by Equation 3.1. Such a relationship was found for all the materials tested, ranging from chemically simple substrates, like glucose and cellulose, via chemically more complex materials, such as plant residues and animal manures, to old and stabilized SOM. For glucose, the linearity started after about 1-2 days in soils under normal conditions (Figure 4.1-A and 4.1-B), whereas for other types of substrates, like cellulose, plant residues, it begins to appear after approximately 1 month.

The results of the incubation experiments with glucose (Van Veen et al., 1985; Saggar et al., 1994), winter wheat straw (Jawson and Elliott, 1986), leaf litter (Chander et al., 1995), and of a field trial with wheat straw (Ocio et al., 1991), suggest that the linearity started at the moment when soil microbial biomass began to decline after having reached its maximum magnitude since the incorporation of the organic materials. This apparently implies that upon addition of fresh materials, it takes some time for soil microorganisms to build up their population, and only after that do soil microorganisms fully function (Alexander, 1977; Ross, 1989). It is suggested by Figure 4.1-B and 4.1-D that such a lag time gets longer under unfavourable conditions. This is probably due to the retardation of microbial growth in such situations. For manure and peat, the starting point could be set at 1 month in practice. For native SOM, however, there should not be such a lag time, because there is no fresh addition and hence no need to build up a microbial population.

The data collected and examined in this chapter (Table 4.1) cover different durations of experiments, and in all cases it seems that once the linearity between log(K) and log(t), or log($R_9$) and log(f*t), has started, it continues without bending off, provided major environmental factors remain unchanged.

The goodness of the linearity between log(K) and log(t), or between log($R_9$) and log(f*t), determines how well the model can describe C mineralization. The high values of adjusted $R^2$ (Figure 4.2-A) and the corresponding low probability levels (Figure 4.2-B) in the majority of the cases strongly indicate that mineralization is adequately characterized with such a relationship between log(K) and log(t), or between log($R_9$) and log(f*t). This is further confirmed by the results of the ultimate test of nonlinear regression by Equation 3.2 (under constant temperatures) or Equation 3.14 (under changing temperatures), as expressed either by adjusted $R^2$ (Figure 4.3), or by the deviation between observed and calculated remaining quantities of substrates (Figure 4.4). Considering the total number and the diversity of the data, in terms of types of substrates, soil properties, durations, procedures and locations of the experiments, it can be concluded that the model very well describes the dynamics of C mineralization.

In the cases where differences between model and reality were found, various factors may have contributed to the deviation. As far as the four groups of substrates are concerned, model results were the best for chemically simple compounds, followed by plant materials, and for both the results were better than for animal manures and native SOM. This must at least partly be related to the use or non use of $^{14}$C-labelled substrates, which can affect the resolution of the data. In 50 of the 51 cases of simple materials, $^{14}$C labelling had been applied, and for plant materials it was in 52 out of the 100 cases, but on the contrary in no case of manures and native SOM $^{14}$C had been used. Another possible cause for the differences in model performance among the various groups of substrates is that the duration of the experiments has different effects on these groups. For substrates resistant to mineralization, a longer experiment duration is required for getting reliable statistical tests of the model than for easily decomposable materials, because adjusted $R^2$ is sensitive to the absolute change in the remaining quantities of substrates, which are determined to a large degree by the duration of mineralization.

Another cause for deviations between calculated and observed data is that the requirement of constant environmental conditions could not always be met. For instance, no temperature correction was made for field experiments that lasted longer than one year and were sampled annually. For the other field trials and sampling frequencies corrections were made, but only for temperature and not for moisture conditions changing over the year.

Also the fact that there have probably been changes in the routines of chemical analysis during the tens of years during which long-term trials lasted, may have played a role in creating the deviation of model outcomes from observations.

## Chapter 5

# Short-term and long-term mineralization characteristics of various organic substrates under diverse conditions

### Abstract

Mineralization dynamics of both incorporated organic substrates and existing soil organic matter (SOM) were studied with the help of the model developed in Chapter 3. Experimental data were collected from 36 articles and reports, covering many types of substrates and environmental conditions. It was found that the initial relative mineralization rate (R) and the speed of 'aging' (S) of the remaining substrate during mineralization were affected by substrate characteristics as well as by environmental conditions. The 'aging' speed (S) proved positively related to the initial relative mineralization rate (R), and the lower the R, the stronger the sensitivity of S to changes of R. As a consequence the initially existing differences in relative mineralization rates gradually disappear, and it is even possible that the substrates mineralizing in the beginning more quickly than others become the more stable ones after a certain period of time. This implies that the differences in remaining quantities between substrates tend to fade away in the long run, and under certain circumstances the ranking order of remaining quantities may reverse. The observed trends were ascribed to (1) biochemical transformations of organic compounds; (2) concentration of relatively resistant components; (3) physical, chemical or physico-chemical protection of (transformed) organic compounds. The conclusions are thought to be valid irrespective of the causes of the differences in the initial relative mineralization rates lying in the chemical composition of substrates or in environmental conditions.

### 5.1 Introduction

Mineralization of organic materials is determined by both their chemical properties and external factors (Post et al., 1992). Amato et al. (1984, 1987) observed that different parts of plant mineralized at different rates. De Haan (1977), Dutil (1982), Gupta and Singh (1981), Herman et al. (1977), Janzen and Kucey (1988), and Tian et al. (1992) found that the rates of C mineralization were negatively correlated with C:N ratio and/or with the contents of highly resistant compounds such as lignin and polyphenols. It was suggested by Jawson and Elliott (1986), and Reinertsen et al. (1984) that the rates of C mineralization were positively related to the contents of water soluble C compounds. Differences in $CO_2$ production were observed by Martin et al. (1982) in each group of compounds with either chain or ring structures

External factors, such as soil pH, texture, moisture and temperature, influence C mineralization. Temperature and moisture were found to play an important role (Boddy, 1983; Clark and Gilmour, 1983; Donnelly et al., 1990; Gupta and Singh, 1981; Hanssen and Myhr, 1989; Jenkinson and Ayanaba, 1977; Kowalenko et al., 1978; Pal et al., 1975; Sorensen, 1981; Stott et al., 1986; Taylor and Parkinson, 1988). It has widely been observed that low pH and high contents of clay or amorphous Al cause a slackening of mineralization (Boudot et al., 1986; Hassink, 1994; Hopkins, et at., 1990; Jenkinson, 1977a; Johnston, 1982; Ladd et al., 1992; Martin et al., 1982; Nowak and Nowak, 1990; Sochtig and Sauerbeck, 1982; Sorensen, 1981; Van Veen and Kuikman, 1990). Also N availability influences the rate of C mineralization (Nowak and Nowak, 1990).

The above cited publications evince that many experimental data on mineralization rates are available. They cover many types of organic substrates and strongly diverse conditions, in terms of soil types, locations and durations of the experiments, and control of external factors. However, reports are scarce of studies that have systematically integrated the results from these experiments with the intention to deepen the insight in the short-term as well as in the long-term features of C mineralization. Such studies can be successful only if the data of individual experiments can be brought together in a assembly that facilitates comparison and generalization. Models may provide that possibility, and thus improve the understanding on the process of C mineralization, the identification of relevant properties of the substrates, and the quantification of the influence of external factors.

It was concluded in Chapter 4 that the relative mineralization rate starts to decrease ('aging') after a short period of time during which the microbial population is built up till its maximum magnitude. The speed of the 'aging' is expressed by S in Equation 3.1.a. The 'aging' is the results of three (combined) processes:

1. Biochemical transformations. It has been found in many experiments that chemical compounds that are mineralized very easily, like glucose, are very soon (within a few days) assimilated in the microbial biomass apart from the release of $CO_2$ (Amato and Ladd, 1992; Ladd et al., 1992; Saggar et al., 1994; Van Veen et al, 1985; Voroney et al, 1989). Microbiologically transformed products are far more resistant than the original compounds

(Martin et al., 1974).

2. Concentration of relatively resistant components. Substrates consisting of more than one component differing in resistance, first lose easily mineralizable components, and as a result, the proportion of resistant components in the remaining material increases over time (Berg et al., 1987; Summerell and Burgess, 1989; Wessen and Berg, 1986; Whitehead et al., 1979).
3. Protection or immobilization caused by mechanisms other than biochemical transformations. It is very likely that in soils all organic compounds undergoing mineralization or transformation are, to various degrees, protected or shielded chemically, physico-chemically or biochemically through association with some inorganic or organic constituents in soil (Kassim et al., 1982; Martin, 1971; Martin et al., 1974), and through physical or physico-chemical adsorption onto soil particles (Hassink, 1995a; Hassink et al., 1993; Sorensen, 1975).

## 5.2 Objectives

The purpose of this chapter is to study the short-term and long-term mineralization characteristics of different C substrates, as found in experiments carried out under different external conditions. This was done with the help of the model on C mineralization developed in Chapter 3. The study comprises three parts: (1) derivation of values of model parameters from the data collected; (2) examination of the relationships between the two model parameters; (3) exploration and discussion of the implications of the relationship found in (2) for the process of C mineralization.

## 5.3 Materials and methods

In total 290 cases of experimental data were collected from 36 publications and reports (Table 5). Among them, 184 cases are those used in Chapter 4, and the rest 106 cases are extra ones. The quality of part of the additional data, in terms of time spans of experiments and $R^2$ of the linear regression of log(K) to log(t), is somewhat lower than the first 184 cases, and that is why they have not been used for testing the model in Chapter 4.

**Table 5** Specifications of data

| Substrate | No. of cases | Data source, experiment location and condition |
|---|---|---|
| materials with simple structure: glucose, hemicellulose, cellulose, holocellulose, and polysaccharide | 68 | Martin et al., 1974 (California, USA(I)); Nicolardot et al., 1994 (France(I)); Pal et al., 1975 (California, USA(I)); Saggar et al., 1994 (New Zealand(I)); Sorensen, 1981, 1983 (Denmark(I)); van Veen et al., 1985 (South Australia(I)); Voroney et al., 1989 (Canada(F)); Zunino et al., 1982 (California, USA and Chile(I)) |
| materials with (poly)phenolic structures: catechol, ferulic acid and lignin | 29 | Haider and Martin 1981 (Germany(I)); Zunino et al., 1982 (California, USA and Chile(I)) |
| microbial cell | 36 | Martin et al., 1974 (California, USA(I)); Zunino et al., 1982 (California, USA and Chile(I)) |
| plant residues, including wheat straw and root, maize stalk and root, oat-shoots and roots, ryegrass, sino milk vetch, green manures, rice straw and roots, | 126 | Amato et al., 1987 (South Australia(F)); Ayanaba and Jenkinson, 1990 (England and Nigeria(F)); Berg et al., 1987 (Sweden(I)); Cai and Mao, 1980 (Nanjing China(I)); Haider and Martin, 1981 (Germany(I)); Jawson and Elliott, 1986 (Washington, USA(I)); Jenkinson, 1977 (England(F)); Jenkinson and Ayanaba, 1977 (England and Nigeria); Kolenbrander, 1969 and 1974 (The Netherlands(F)); Ladd et al., 1981, 1983, 1985 (South Australia(F)); Martin et al., 1974 (California, USA(I)); Nowak and Nowak, 1990 (Poland(I)); Pal et al., 1975 (California, USA(I)); Sarmah and Bordoloi, 1994 (India(I)); Sochtig and Sauerbeck, 1982 (Germany(F)); Sorensen, 1983, 1987 (Denmark(I)&(F)); Stott et al., 1986 (Washington, USA(I)); Voroney et al., 1989 (Canada(F)); Wang et al., 1984, 1989 (North China(F)); Xu et al., 1993 (North-East China(F)); Zhang et al., 1986 (Xuzhou China(F)); Zhou et al., 1984 (North-East China(I)); Zunino et al., 1982 (California, USA and Chile(I)) |
| FYM | 18 | Kolenbrander, 1969 and 1974 (The Netherlands(F)), Sorensen and Jensen, 1995 (Denmark(I)); Xu et al., 1993 (North-East China(F)); Zhang et al., 1986 (Xuzhou, China(F)) |

| | | |
|---|---|---|
| wood materials, peat and native SOM | 13 | Cai and Mao, 1980 (Nanjing, China(I)); Jenkinson, 1977 (England(I)); Jenkinson and Rayner, 1977 (England(F)); Kolenbrander, 1969 and 1974 (The Netherlands(F)); Kortleven, 1963 (The Netherlands(F)); Sorensen, 1987 (Denmark(F)); Zhou et al., 1984 (North-East China(I)) |

(I) incubation experiment under controlled conditions.
(F) field trial.

All the data concern C mineralization of substrates after single additions, or of existing SOM. Table 5 shows the types of substrates, locations and the degree of control of external conditions. The locations for these experiments may be indicative in a general way for soils used in the experiments and climatic conditions in case of field trials. Part of the data were found in tables in the cited sources and the rest were read from graphs.

For the data referring to constant temperatures or sampling on an annual basis the average relative mineralization rates (K) between time zero and the various points of time in the particular cases were first calculated with the following equation:

$$K = -[\ln(Y_t / Y_0)] / t \tag{2.2}$$

Next the values of the model parameters R and S were derived for each case by linear regression of log(K) to log(t), according to the model equation:

$$\log(K) = \log(R) - S * \log(t) \tag{3.1.a}$$

It was shown in Chapter 4 that for substrates used in farming practice, the linearity between log(K) and log(t) starts after about one month under normal field conditions. In this study, day was used as the unit of time. That makes the value of R a theoretical one because it represents the average relative mineralization rate (K) during the first day if linearity had started from the very beginning. This procedure, however, does not affect the results of the model and the conclusions of the study, as long as the first month after application of a substrate is left out of consideration.

In case that the average temperatures for the various time intervals of a case were not equal, the values of K and R could not be derived directly from the experimental data. First the length of an interval was multiplied with the appropriate value of the temperature correction factor **f**. Using the corrected time (f*t), the values of $K_9$ were assessed, and next $R_9$ was found with a modified version of the logarithmic equation:

$$\log(K_9) = \log(R_9) - S * \log(f*t) \qquad (3.14)$$

Finally R corresponding to the real temperature was calculated with:

$$R = R_9 / f_m^{(S-1)} \qquad (3.11)$$

where $\mathbf{f}_m$ is the mean **f** for the whole mineralization period. The ratio of the total calibrated time to the total true time of the mineralization experiment was used as ($f_m$). A full explanation of this procedure was given in Chapter 3.

For a restricted number of substrates also the actual relative mineralization rate at time t (k), and the fraction that is remaining over time ($Y_t$) were calculated, using the equations derived for those purposes in Chapter 3:

$$k = (1 - S) * R * t^{-S} \qquad (3.4)$$

$$Y_t = Y_0 * \exp[-R * t^{1-S}] \qquad (3.2)$$

where $Y_0$ is the quantity of substrate in the beginning.

## 5.4 Results

### *5.4.1 Linear regression of log(K) to log(t)*

Figure 5.1 shows the distribution of relative frequency of $R^2$ of the linear regressions of log(K) to log(t). In 72% of the total 290 cases, $R^2$ was $\geq 0.995$, and in 92% it was $\geq 0.975$. The remaining 8% have $R^2$ values ranging from 0.974 to 0.65. This high agreement between the model and the experimental data is confirmed by the low probability levels of the linear regression which are all below 0.01, except two cases with levels between 0.01 and 0.05. This indicates that the values of the two model parameters, R and S, derived from the data are reliable, and may be used for calculation of mineralization over longer period of time.

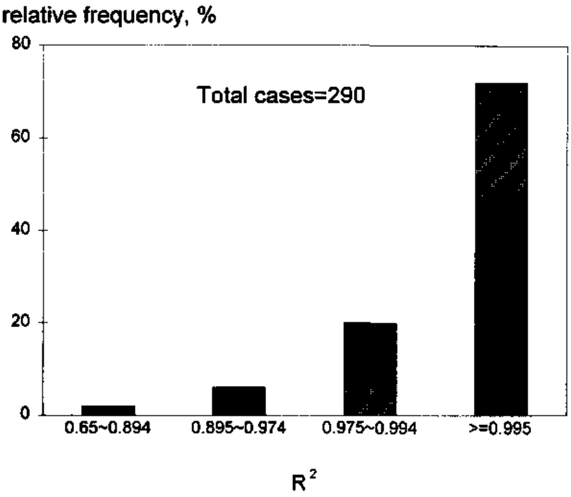

**Figure 5.1** Distribution of relative frequency of $R^2$ of linear regression of log(K) to log(t) or log($K_9$) to log(f*t) in all 290 cases.

### *5.4.2 Relationship between R and S*

For the six groups of substrates listed in Table 5, S was plotted against R (Figure 5.2). The materials in Figure 5.2-I, including glucose, hemicellulose, cellulose and holocellulose, which are known to mineralize relatively easily, show high values of both R and S. The substrates in Figure 5.2-II, consisting of dead microbial cells, have lower values of R and S than the substrates in group I, and the substrates in Figure 5.2-III, which include catechol, ferulic acid and lignin, have lower values of R and S. Those in Figure 5.2-IV, which comprises residues of grasses and common annual crops in agriculture, cover the widest range of R and S values. The lowest range of R and S values was found for the substrates in Figure 5.2-V, which are known as the most resistant organic compounds.

Plotting all data together in one graph (Figure 5.3) shows that the positive correlation between R and S is still present for different substrates and for similar substrates under different conditions. The change of S with R is most dramatic at low values of R (below $R \approx 0.2$ day$^{-1}$). At higher R the values of S are higher too, but the increase in S gets smaller and smaller. It implies that the relative mineralization rates decrease more quickly over time when the initial rate (R) is high than when it is low.

### 5.4.3 Actual relative mineralization rates

The consequences of the relationship between R and S become especially clear for the actual relative mineralization rate (k). For the comparison of differently

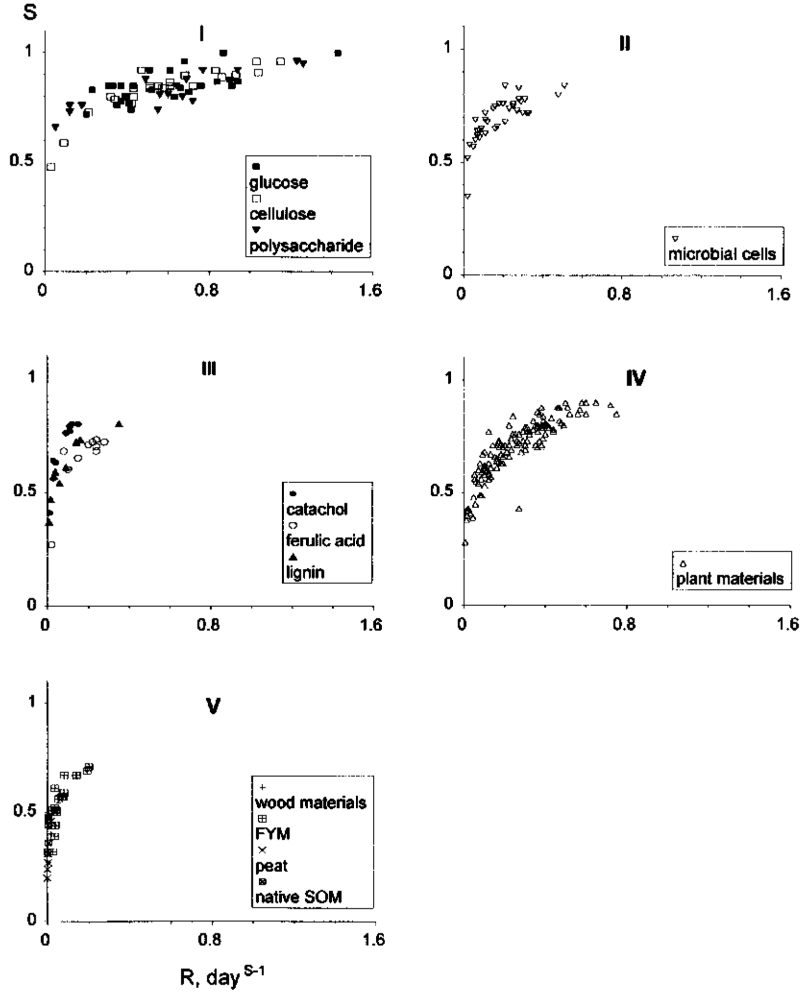

**Figure 5.2** Relationship of R and S of various types of substrates under diverse conditions.

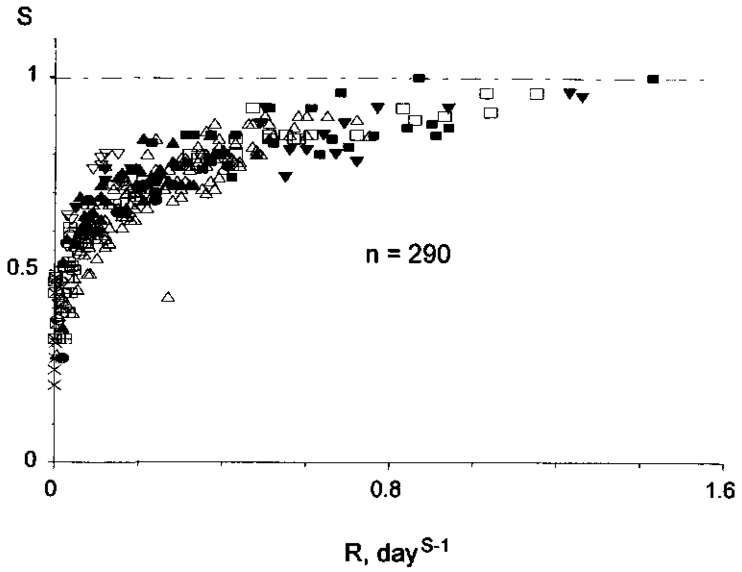

**Figure 5.3** Relationship of R and S for all 290 cases. The legend is the same as Figure 5.2.

mineralizable organic materials, five types of substrates were chosen: glucose, plant residues, microbial cells, (poly)phenolic compounds (including catechol, ferulic acid and lignin), and native SOM. The average value of R and S of the five types of substrates were substituted in Equation 3.4 for the calculation of k. In Figure 5.4, the relations of k and time are presented on a linear as well as on a logarithmic scale.

The values of k for all five types of substrates decrease much sharper in the beginning than later, which is most pronounced for easily mineralizable substrates like glucose. In line with the relationship between R and S shown in Figures 5.2 and 5.3, the value of k for easily mineralizable substrates decreases more quickly over time than that of more resistant substrates, and after a while the lines of the various substrates intersect each other. Thereafter the order of substrates when ranked by resistance changes: the initially quickly mineralizing ones finally become the most resistant ones. Examples are the line of glucose that crosses those of plant materials, polyphenols and microbial cells already within the first 0.1 year, and the lines of polyphenols and microbial cells crossing each other at

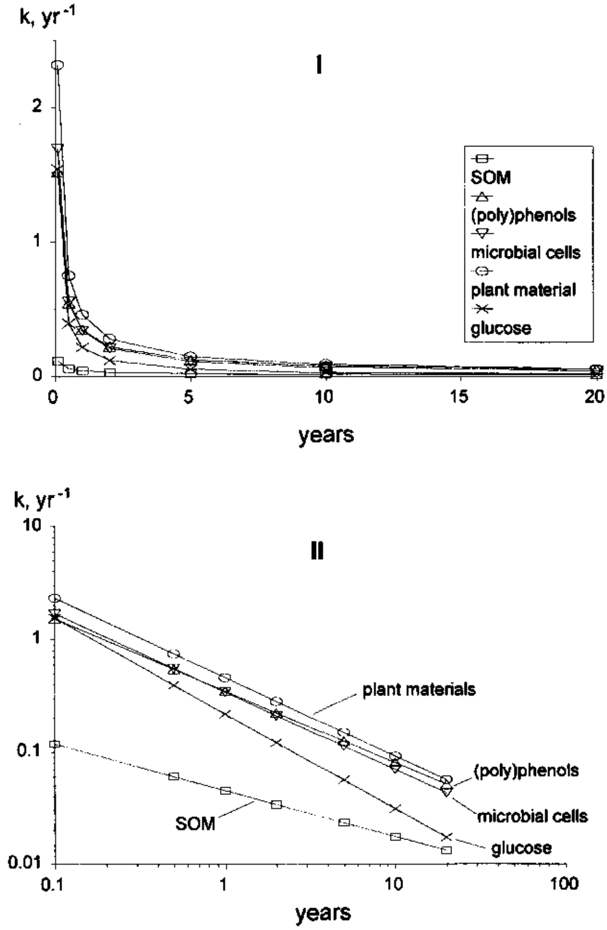

**Figure 5.4** Decrease of actual relative mineralization rate (k) over time. I: in X-Y linear scales; II: in X-Y logarithmic scales.

around 1 year.

### *5.4.4 Remaining quantities of added substrates*

The change in the resistance of substrates has important consequences for the quantities of the substrates that will remain in the soil in course of time. For the five types of organic matter, these quantities, expressed as the remaining fractions (in %) of the originally applied amounts, were calculated with Equation 3.2, and plotted against time in Figure 5.5.

In the first half year glucose has the smallest quantity of remaining substrate, followed by plant materials, microbial cells, (poly)phenolic substances, and native SOM. After several years, however, the remaining fraction of glucose becomes higher than those of plant materials, microbial cells and (poly)phenolic substances, but is of course still much lower than that of native SOM. From 0.5 to 20 years, the remaining fraction is the lowest for plant materials. The initial difference in remaining fractions between microbial cells and (poly)phenolic substances has almost disappeared after twenty years.

## 5.5 Discussion and conclusions

### *5.5.1 Causes of different relative mineralization rates*

The values of R, the initial relative mineralization rate (Figures 5.2 and 5.3) differ among different substrates, but may also vary among similar substrates. The causes of the variations are different for the next two situations.

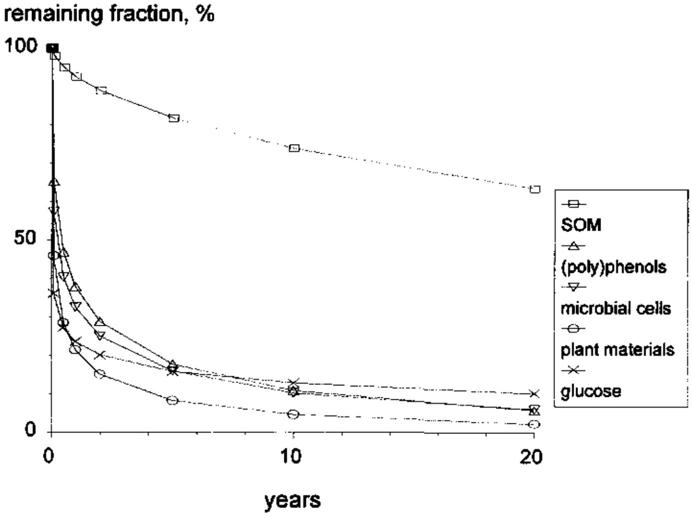

**Figure 5.5** Decrease over time of remaining fractions of various types of substrates in soils.

For different substrates the variation is explained by the difference in the chemical composition. Chemically simple substances like glucose and cellulose, are easily mineralized, but (poly)phenolic compounds, such as lignin and ferulic acid, have chemically stable structures and are highly resistant to microbial attack. SOM has gone through a humification process, resulting in compounds that are highly resistant to microbial degradation and physically protected. Materials like microbial cells, plant residues and animal manures are in fact composed of components differing in chemical properties, and thus have a wide and medium range of decomposability.

For similar substrates, the variation in the values of R must be ascribed to differences in the external conditions, such as clay content, pH, temperature, moisture and nitrogen availability. Because mineralization is mainly a result of microbial activities, any changes in external conditions that influence microbial activity will also affect mineralization rate.

### *5.5.2 Causes of different speeds of 'aging'*

As shown in Figures 5.2 and 5.3, S increases with R, especially in the range of low R values. This is explained by the fact that any factors leading to a high initial relative mineralization rate - for example, higher temperatures or better moisture conditions - inevitably increases the rate of biochemical transformations and the rate of loss of easily mineralizable compounds, and stimulates the reshaping of the remaining organic compounds into forms suited for physico-chemical protection, thus promoting the 'aging.'

Within a rather short time the composition of substrates added to soils becomes a mixture of resistant components that are still in their original forms, and transformed or protected compounds (Voroney et al., 1989), and then the measured relative mineralization rate does not refer any more to the originally added substrate. In this context, it is understandable that substrates like glucose can become even more resistant than materials as plant materials, as was found by Voroney et al. (1989).

### *5.5.3 Quantity and quality of remaining substrates*

Once the residue of glucose becomes more resistant, the remaining quantity diminishes less rapidly than that of plant materials, and the difference in remaining quantities of glucose and plant materials will become smaller and smaller. Under certain circumstances, the remaining quantity of the glucose residues can become even higher than that of the plant residues, as was observed by Ayanaba and Jenkinson (1990), Bremer et al. (1991), Broder and Wagner (1988), Hassink (1995b), Jenkinson (1977a), Ladd et al. (1995), Smith and Jackson (1987), and Voroney et al. (1989).

The practical significance of these trends depends strongly on the time that is required to nullify the initial differences, and on the absolute value of the quantities remaining at the time when the original differences have disappeared. Using the data from Sorensen (1983), it was calculated that it would take, at a temperature of 20 °C, almost 200 years for the transformed residue of glucose to become equally resistant as the transformed residue of maize stover. By that time only 2% of the initial quantity of both materials would still be in the soil.

### *5.5.4 Role of external factors*

The results in Figures 5.2, 5.3 and 5.4 may have important consequences for the prediction of changes in mineralization rates induced by external factors like global warming or the 'greenhouse effect'. Under favourable conditions, mineralization initially goes quickly. Accordingly, a high 'aging' speed (S) is to be expected, which means that the mineralization rate decreases more rapidly than under less favourable conditions. As a result, the enhancement of mineralization rate under favourable conditions rapidly becomes weaker, eventually disappears and may even turn into a negative effect. From Figure 5.3 it can be expected that such a 'counteraction' in C mineralization upon changes in external conditions, would be more obvious for more resistant substrates than less resistant ones.

For materials like crop residues which mineralize rather easily, the change in 'aging' speed upon changes of external conditions may not be significant, because their initial mineralization rates are rather high. Moreover, in many practical situations, more external factors than one can change simultaneously. Therefore, the changes both in R and S are in fact the net effect from these changes. Consequently, it is possible that R and S do not change accordingly. This can be seen from the results and conclusions from Jenkinson (1977a), and Jenkinson and Ayanaba (1977), in which the same ryegrass differed only in R, but not in S when it mineralized in England (mean value of eight different soils) and in Nigeria (mean value of two treatments).

It should be noted that the lines of Figures 5.4 and 5.5 are mainly meant to indicate trends that are revealed by the data. The positions of the substrates with respect to each other may not be realistic, because most of the data were from separate experiments, with different soil properties and other conditions.

Moreover, the influences of types of substrates, soil properties and external conditions have not been separated, and all must have played a role in this study and affected the values of R and S. In Chapter 8 the effect of temperature will be treated for cases where the other factors could be kept constant. Unfortunately the available data were not sufficient, neither quantitatively nor qualitatively, to study individually the effects of other variables in a statistically reliable way.

### *5.5.5 Conclusions*

To sum up, for C mineralization in soils, the 'aging' speed (S) is positively related to the initial relative mineralization rate (R), and the lower the R, the stronger the sensitivity of S to changes in R. As a consequence, the initially existing differences in relative mineralization rates gradually disappear, and it is even possible that the substrates mineralizing in the beginning more quickly than others become the more stable ones after a certain period of time. As a consequence, the differences in remaining quantities between substrates tend to fade away in the long run, and under certain circumstances the ranking order of remaining quantities may reverse. This conclusion is thought valid for similar substrates under different conditions, as well as different substrates but under similar conditions.

## Chapter 6

# Differences among various organic materials in long-term accumulation of soil organic matter and implications for farming practices in northern China

### Abstract

The purpose of this chapter is to compare the efficiency of various organic materials, including roots, straw, farmyard manure (FYM) and green manure, in accumulation and maintenance of soil organic matter (SOM) in the long run. The parameters of the earlier proposed model on mineralization are calibrated to data collected from northern China, and next the accumulation efficiency of the various organic materials are calculated. It is predicted that under conditions of northern China, SOM accumulation at steady state is 6.8 times the annual input of organic materials when only roots form that input. Roots are 3, 5 and 7 times as efficient as straw, FYM and green manure, respectively. The relative annual mineralization rate of steady-state SOM varies from 5.8% to 25.6 %, depending on the type of materials from which SOM has been built up. From comparisons of model calculations with experimental data, it is concluded that roots play a predominant role in SOM balance in arable farming in northern China. To maintain SOM content at its present level of 10 g kg$^{-1}$, C additions are essentially constant for roots, but increase for green manure, straw and FYM. This increase is due to the replacement of existing SOM by SOM from these materials. When the composition of SOM changes while its content is maintained, the mineralization rate of the SOM changes, leading to the change in the rate of nutrients release from SOM. In northern China, green manure can best be used as animal fodder, straw be used as fodder or composted. The high efficiency of roots in SOM accumulation makes it possible to improve SOM balance by the use of chemical fertilizers and irrigation, since that results in an increase of root production.

## 6.1 Introduction

Soil organic matter (SOM) is the pivot of soil fertility. Maintenance or improvement of SOM content is a fundamental requirement for sustainable soil fertility, in particular for soils of which organic matter content is low. In arable farming, loss of SOM by mineralization is often balanced out through supply of crop roots and stubble, and additions of organic materials such as straw, farmyard manure (FYM) and green manure. For a good farming management, it is very important to understand the efficiency of different materials in accumulating SOM under given environmental conditions, and the long-term consequences of various management options for SOM accumulation.

In Huang-Huai-Hai Plain of northern China (Figure 1), SOM content in arable soils is commonly below or around 10 g $kg^{-1}$, (Cao et al., 1986; Wang et al., 1988; Zhao, 1989). The growing demand for grain production in this region requires that SOM contents at least be maintained, but better be increased. On the other hand, the resources of organic material, consisting mainly of plant materials, are very limited. The biomass of crops, both below-ground and above-ground, is the primary source for domestic fuel, animal fodder and organic amendments for soil. The main forms of organic input into soil are the portion of straw that is not used as domestic fuel and fodder, FYM and green manure, along with roots and stubble left in field. After the need for use as fuel has been satisfied, 30 to 60% of the straw is left for other purposes, such as fodder and organic fertilizers (Liu and Mu, 1988). The scale of green manuring has become very limited (Soil and Fertilizer Institute, 1986; Chen et al., 1989). Therefore, the efficiency of the use of available organic materials becomes a crucial item in the search for strategies directed towards maintaining and improving SOM content in arable fields in northern China.

The aim of this chapter is to study the efficiency of various materials, including roots, straw, FYM and green manure in accumulating and maintenance of SOM, and to predict the consequences in the long run. The results are further used to develop alternatives of farming management which lead to an optimum use of these materials with respect to the maintenance or rise of SOM content.

## 6.2 Data, model and calculation schemes

To be able to assess the efficiency of individual materials in accumulating organic matter in the soil, experimental data on mineralization of straw and roots of wheat and maize, FYM, green manures and existing soil organic matter were collected. In total there are 47 cases with 296 observations. Sources were Green Manuring Group (1985), Jenkinson (1977a), Jenkinson and Rayner (1977), Kortleven (1963), Wang et al. (1984), Wang et al. (1989), Wang et al. (1989), Xiong et al. (1987), Xu et al., (1993), and Zhang et al. (1986).

Most information is from northern China. Because only two sets of data on SOM mineralization were available from this region, also two sets of data from England (Jenkinson, 1977a; Jenkinson and Rayner, 1977) and one from The Netherlands (Kortleven, 1963), were used to derive the average values of model parameters for SOM mineralization.

The data were analyzed with the model developed in Chapter 3. The two main model parameters $R_9$ and S (Table 6.1) were derived by nonlinear regression, conducted in Statgraphics (STSC Inc., 1986), of the equation:

$$Y_t = Y_0 * \exp[-R_9 * (f * t)^{1-S}] \qquad (3.14)$$

The temperature correction (**f**) was applied wherever needed, according to the procedure outlined in Chapter 3. The annual mean temperature in northern China ranges from 12 °C (in Beijing) to 14 °C (in Zhengzhou) (Liu and Mu, 1988; Meteorological Institute of CAAS, 1994). The values of **f** corresponding to the two temperatures were found by calculating and averaging the monthly values of **f** in the way suggested in Chapter 3, and proved to be 1.6 and 1.8, respectively. Therefore, **f** of 1.7 is used as an average in the main calculations.

The time unit was year, and hence the values of $R_9$ represent the average relative mineralization rates during the first year, if the annual temperature would be 9 °C. With $R_9$ the humification coefficients (h.c.) for the situation of annual temperature of 9° C can be calculated as:

$$\text{h.c.} = \exp(-R_9) \qquad (3.3)$$

Added organic materials were considered to become part of SOM at one year after application (Henin and Dupuis, 1945; Kortleven, 1963). SOM accumulation was calculated by simply adding the remaining quantities of the various years. After n additions, each equal to $Y_0$:

$$SOM_n = Y_1 + Y_2 + Y_3 + .... + Y_n \qquad (6.1)$$

This expression cannot be integrated and it is therefore not possible to calculate steady-state SOM content. $SOM_n$ may virtually have reached an equilibrium after 1000 years of annual additions. Therefore, an operational 'equilibrium' or 'apparent steady state', was defined in this study as: the steady state ($SOM_{ss}$) has been reached when SOM equals 99% of SOM in year 1000. The $SOM_n$ at this steady state is indicated by $SOM_{ss}$, hence,

$$SOM_{ss} = 0.99 * SOM_{1000} = Y_1 + Y_2 + Y_3 + .... + Y_{ss} \tag{6.2}$$

Related to $SOM_{ss}$ are the following concepts of $AF_{ss}$, $FM_{ss}$, $R_{9,\,ss}$ and $S_{ss}$.

The accumulation factor, $AF_{ss}$, is defined as the ratio of SOM or C accumulation at the 'apparent steady state' to the annual addition ($Y_0$):

$$AF_{ss} = SOM_{ss} / Y_0 \tag{6.3}$$

At the 'apparent steady state' SOM mineralization equals the first-year remaining quantity ($Y_1$) of the annual addition ($Y_0$). The fraction of $SOM_{ss}$ that is mineralized per year ($FM_{ss}$) is thus defined as:

$$FM_{ss} = Y_1 / SOM_{ss} \tag{6.4}$$

Let $R_{9,\,ss}$ and $S_{ss}$ refer to $R_9$ and S in Equation 3.14 at the 'apparent steady state', respectively. They were derived by nonlinear regression of Equation 3.14 with $f$=1.7, in which for $Y_0$ is substituted by the quantity of accumulated C at the 'apparent steady state' ($SOM_{ss}$), and for $Y_t$ the C remaining from it after 50 years of mineralization without new additions of $Y_0$. Hence, $Y_t = SOM_{ss+50} - SOM_{50}$.

After calibration to the experimental data, the model was used to assess the accumulation efficiencies of individual organic materials, and to predict the required application rates to maintain SOM at a level 10 g kg$^{-1}$ which is seen as the common value in northern China. Since the required applications are proportional to SOM contents, the results for the SOM content of 10 g kg$^{-1}$ can simply be translated into the required rates for other SOM contents.

## 6.3 Results

### *6.3.1 Mineralization and steady-state characterization*

The values of the model parameters $R_9$ and S, as were derived from the pooled data by nonlinear regression, are presented in Table 6.1. The table also gives the values of the humification coefficients (h.c.) calculated by Equation 3.3; they are quite similar to the data of Kolenbrander (1969, 1974).

Figure 6.1 shows the theoretic SOM accumulation that would be obtained in northern China with a fixed annual input for each material. The curves, as well as the calculations for year 1000 (not shown), indicate that after 1000 years of annual additions, the increase of SOM has virtually ceased. Table 6.2 shows the time required for each material to reach the 'apparent steady state' ($SOM_{ss}$, defined as 99% of SOM after 1000 year) and some other characteristics of the 'apparent steady-state SOM'.

Figure 6.1 and Table 6.2 show that the quantities of SOM accumulated until the 'apparent steady state' differ considerably among the four materials, in particular, between roots and the other three. SOM accumulation from roots additions proceeds for 540 years until reaching the 'apparent steady state', and $SOM_{ss}$ is 680 units. The accumulation factor ($AF_{ss}$), which is calculated as the ratio of the $SOM_{ss}$ to the annual addition ($Y_0$), is thus 680/100 = 6.8 for roots. Second in efficiency after roots is straw with accumulation factor of 2.1. FYM and green manure, on the other hand, have accumulation factors of only 1.3 and 0.9, respectively.

The SOM accumulated from different sources tends to mineralize at different rates at the 'apparent steady state' as shown in Table 6.2. Among the four materials, the SOM originated from roots mineralizes most slowly with a fraction mineralized annually ($FM_{ss}$) of 5.8%, whereas FYM and green manure show such a $FM_{ss}$ of over 20%, and the $FM_{ss}$ for straw falls in between with a value of 12.1%. In general it holds that the longer the time needed to reach the 'apparent steady state', the lower the $FM_{ss}$ is.

The pattern of the difference as found for the fraction mineralized annually is also

**Table 6.1** $R_9$ and S derived by non-linear regression of Equation 3.14 and humification coefficient (h.c.) calculated by Equation 3.3.

| | $R_9$ $yr^{S-1}$ | s.e.^(a)^ | S | s.e.^(a)^ | adj. $R^2$ | No. observa. | h.c. |
|---|---|---|---|---|---|---|---|
| Green manure | 1.39 | 0.04 | 0.64 | 0.02 | 0.80 | 76 | 0.25 |
| Straw | 1.11 | 0.02 | 0.66 | 0.02 | 0.84 | 100 | 0.33 |
| Roots | 0.80 | 0.03 | 0.67 | 0.02 | 0.89 | 36 | 0.45 |
| FYM | 0.82 | 0.02 | 0.49 | 0.03 | 0.90 | 62 | 0.44 |
| SOM | 0.057 | 0.008 | 0.46 | 0.04 | 0.91 | 22 | |

(a) standard error

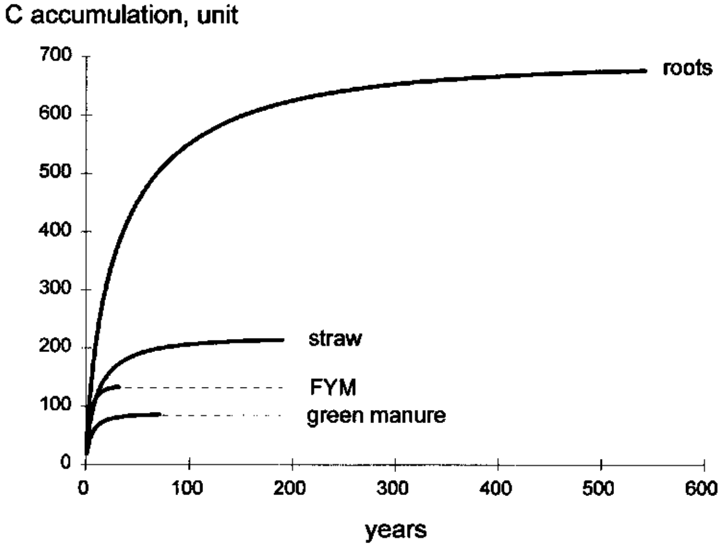

**Figure 6.1** C accumulation in soil by individual materials at the annual addition of 100 units of organic C in northern China. The solid lines cease when the C accumulation reaches 99% of that at year-1000.

**Table 6.2** Time required to reach the 'apparent steady state' of SOM ($SOM_{ss}$, expressed by C) with some organic materials in northern China, and some related properties of $SOM_{ss}$. The annual organic C addition is 100 units.

| | Time, year | $SOM_{ss}$, unit | $AF_{ss}$ | $FM_{ss}$, % | $R_{9,\ ss}$ $year^{S-1}$ | $S_{ss}$ |
|---|---|---|---|---|---|---|
| Green manure | 70 | 90 | 0.9 | 22.1 | 0.20 | 0.34 |
| Straw | 190 | 210 | 2.1 | 12.1 | 0.12 | 0.34 |
| FYM | 30 | 130 | 1.3 | 25.6 | 0.22 | 0.23 |
| Roots | 540 | 680 | 6.8 | 5.8 | 0.054 | 0.32 |

found for the values of $R_{9,\ ss}$, which were derived by nonlinear regression of Equation 3.14 with $Y_0$ being $SOM_{ss}$, $Y_t$ being ($SOM_{ss+50}$ − $SOM_{50}$), and with f=1.7. In all four cases, the adjusted $R^2$ of the nonlinear regression was over 0.998. The values of $S_{ss}$ for roots, straw and green manure are similar, and they are higher than that for FYM, like it was for the values of S after a single application (Table 6.1).

### *6.3.2 Requirements for SOM maintenance and consequences*

The annual requirement of C from each material to maintain SOM content at 10 g $kg^{-1}$ in northern China was calculated and shown in Figure 6.2. Since it was found that the requirements are overestimated for the first two years, the results of the first two years were not shown in Figures 6.2, 6.3 and 6.4.

Figure 6.2 shows that except for roots, the requirements are increasing over time, and that the increase is stronger as materials mineralize more easily. Initially, the annual increment in C requirement increases, but thereafter it decreases over time, as shown in Figure 6.3. In the example of FYM, it is around 90 kg $ha^{-1}$ in the initial ten years, and it goes down to about 40 kg $ha^{-1}$ in the last years of the 50-year period. Finally it will approach zero, when 'equilibrium' has been reached. For roots, however, the annual C requirement is much more constant; in the beginning there is a decrease in the requirement and after ten years there is practically an 'equilibrium' (Figure 6.3).

The four materials also differ in the quality of SOM they produce. Figure 6.4 shows that the annual mineralization rates of SOM increase, in particular, for FYM and green manure. For roots, a decrease occurs in the initial years, and a stable stage is reached thereafter.

## 6.4 Discussion

The difference in efficiency of accumulation or maintenance of SOM among the four materials must primarily be attributed to the difference in their chemical compositions. Results from Bloomfield et al. (1993), Jawson and Elliott (1985), and Tian et al. (1992) show that roots normally contain larger proportions of components, such as lignin, which are highly resistant to mineralization, than above-ground plant parts like straw and leaves. As a result, roots are less easily mineralized. Green manure, on the contrary, has high protein contents and low contents of resistant components. Being the product of animal digestion from fodder, (pure) FYM should be more resistant to microbial attack than feedstuffs among which straw is important, and its $R_9$ is indeed lower (Table 6.1). The value of S is, however, higher for straw than for FYM, and hence in the long run straw is more efficient in SOM accumulation according to the calculations. Since

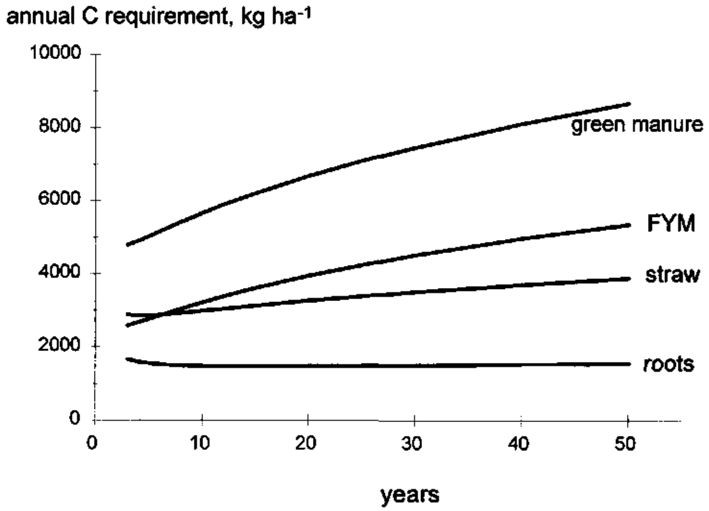

**Figure 6.2** Annual C requirement for individual materials to maintain SOM content at 10 g C kg$^{-1}$ in northern China.

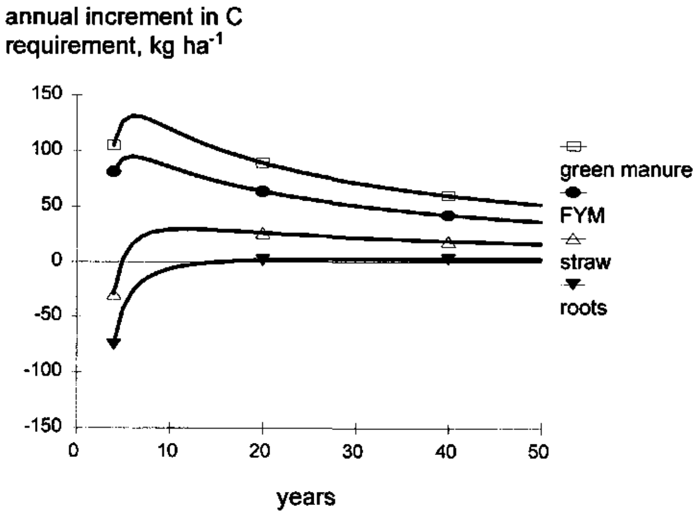

**Figure 6.3** Annual increment in C requirement for individual materials to maintain SOM content at 10 g C kg$^{-1}$ in northern China.

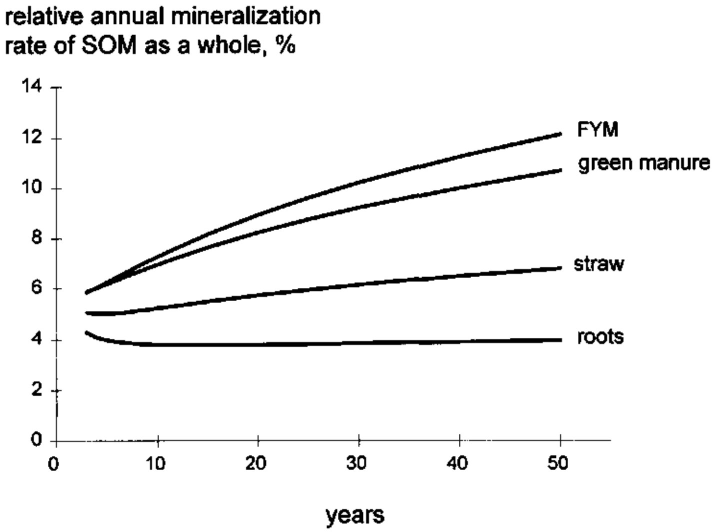

**Figure 6.4** Relative annual mineralization rate of SOM as a whole when from time zero onwards the indicated materials form the only addition of organic matter in northern China.

FYM produced in northern China normally contains a large proportion of undigested bedding materials, its properties may fall between pure FYM and feedstuffs. These outcomes also heavily depend on the rightness of the assumption that the relation between log(K) and log(t) remains unchanged after the periods of the relevant experiments.

The data of SOM used in this study refer to soils used for arable farming, dominantly for cereal production. Therefore, apart from the grain, most of the straw has been removed from the field and used for other purposes, like domestic fuel and fodder. Consequently, the organic input to soil has been dominated by roots and stubble for a long time. This proposition can be confirmed by the results in Figure 6.1 and Table 6.2. With roots as the sole organic input in northern China, the SOM at the 'apparent steady state' ($SOM_{ss}$) has a relative annual mineralization rate ($FM_{ss}$) of 5.8%. This is close to the range of 2 ~ 5% found in this region by Wang et al. (1988). This proposition can further be confirmed by the closeness between $R_{9,\ ss}$ of 0.054 $year^{-1}$ for SOM accumulated from roots (Table 6.2), and $R_9$ of 0.057 $year^{-1}$ derived from the experimental data (Table 6.1). In addition, the calculated value of S for the SOM built up from roots (Table 6.2) is closer to the value of S of real SOM (Table 6.1) than the value of S calculated for SOM accumulated from FYM.

The reason that the C requirement for maintaining SOM content by roots is substantially constant, while it increases for other three materials, is a consequence of gradual replacement of existing SOM by materials which differ, to various extent, from SOM in mineralization characteristics. Since the existing SOM is presumably mainly derived from root-C in the farming history, a substantially constant quantity of C from roots is required for its continuous maintenance. The replacement of existing SOM by SOM from the other three materials will change the composition of SOM as a whole. Because the other materials have higher mineralization rates that roots, the mineralization rate of SOM rises, as shown in Figure 6.4. With the continuous rise of the mineralization rate of SOM as a whole over the 50 years, the annual C requirements from these materials also increase, but the annual increments in C requirement get gradually reduced (Figure 6.3).

In practice it is more likely that one or more materials, along with roots, form the organic inputs to soil. The results in Figure 6.4 indicate that the mineralization rate of SOM as a whole will change and increase when the composition of inputs shifts, i.e. from roots to roots+straw, or roots+FYM. This will lead to a higher rate of nutrients release from SOM, as observed by Chen and Wang (1987) and Huang (1984).

Since the current SOM contents in arable land of northern China must be maintained, or better, further raised by means of the limited organic resources, the understanding of the difference in efficiency and of the consequences of different materials for the accumulation or maintenance of SOM becomes very important in the consideration of long-term farming management towards a high-efficiency use of the resources.

The role of green manure in maintenance of SOM content should be replaced by those such as straw or FYM because of its low efficiency in this regard (Figure 6.1 and 6.2). Alternatively, green manure, as a good fodder, can first be fed to animals, and the FYM can then be returned to soil. This way of using green manure is more profitable, not only economically, but socially as well, as suggested by many people (Chen et al., 1993; Li et al., 1981; Shi, 1983; Wu and Shi, 1993).

As straw is the main source of domestic fuel and fodder in rural area of this region, only a small portion of it can be used for composting, or be directly incorporated into soil (Liu and Mu, 1988). In view of the ongoing development in animal production, more straw will be used as fodder. Meanwhile, because of the lack of proper machinery, direct return of straw to soil after each harvest is not always feasible, particularly in summer when maize must be sown after the harvest of wheat as quickly as possible. Therefore, it is more realistic to first compost the available straw, and to apply the compost at appropriate times.

FYM has long been used as an organic fertilizer in arable farming in this region. Though its efficiency is lower than that of straw (Figure 6.2 and 6.3), its production will increase in the future. But a problem lies in the quality of FYM in this region. As reported by Cao et al. (1986), Wu and Shi (1993), and Zeng et al. (1992), the organic C content in most FYM used in arable farming is only about 20 to 30 g per kg of dry FYM. As a consequence, a large quantity of 'gross' FYM is needed, and this raises the cost of transporting and casting considerably, while costs are now a very important consideration in farmer's management. Therefore, the quality of FYM must be significantly improved, e.g. by reducing the proportion of soil in compost, in order to make it economically and operationally more attractive.

The high efficiency of roots in accumulation and maintenance of SOM, as shown by Figure 6.2 and 6.3, confirms the conclusions from Li and Xu (1987), and Zhang and Wang (1984) that roots play a very important role in maintaining SOM content in arable farming in northern China. Therefore, the increase in biomass production of roots, such as with increase of grain yield, will benefit the balance of SOM. In this light, the farming practices, such as use of chemical fertilizers and irrigation, will likely promote and improve the status of SOM in arable farming, as suggested by many people in last ten years (Cao et al., 1986; Liu and Mu, 1988; Zeng et al., 1992; Zhou, 1989).

## Chapter 7

# Analysis of impact of current farming practices on dynamics of soil organic matter in northern China

### Abstract

The objectives of this chapter are to predict the long-term SOM dynamics in arable land under changed farming situations in northern China, and to suggest measures to be taken for the maintenance and improvement of SOM content. Relevant SOM data collected in this region were analyzed with the newly developed model on organic matter mineralization. After calibration, the model was applied to calculate the course of SOM content and SOM quality over a time span of 50 years. Two levels of annual grain yields were considered: 'mean yields' of 7500 kg ha$^{-1}$ and 'high yields' of 15000 kg ha$^{-1}$, and three scenarios for organic inputs into the soil: (1) only roots and stubble; (2) as (1) plus the direct return of one third of the straw that is produced; (3) as (2) plus the application of FYM made with another one third of the straw that is produced. It was found that under the three scenarios SOM contents can be maintained at 10, 13 and 15 g kg$^{-1}$ in the case of the mean yield level, and at 15, 19 and 21 g kg$^{-1}$ in the case of the high yield level. The present SOM contents are often below 10 g kg$^{-1}$. Depending on whether the SOM contents at present are below or above these 'steady-state' levels, they will increase or decrease. The absolute annual change in SOM content is related to the difference between the present and the final SOM content, and it will become smaller over time, sharply diminishing in the beginning and slowly at a later stage. As a measure of SOM quality, the fraction that is mineralized per year (FM) was taken. According to the calculations, the quality of SOM improves (increasing FM) with the magnitudes of annual organic inputs. Hence, in most arable fields in northern China, both the quantity and the quality of SOM will rise upon an increase in annual crop production, e.g. as a result of the use of chemical fertilizers. Similar positive effects on SOM will be brought about by returning (a part of) the straw, either directly by leaving it in the field or indirectly by applying it as FYM. Theoretically, the direct return is more efficient for improvement of both SOM content and SOM quality than the indirect application, but it may be less attractive for farmers because it takes away the use of straw as fodder.

## 7.1 Introduction

Northern China, mainly referring to Huang-Huai-Hai Plain (Figure 1) in this study, is the most important area for grain production (mainly wheat and maize) in China (see Chapter 1). Before 1980s, soil fertility was maintained and improved mainly by the use of organic fertilizers or amendments, such as farmyard manure (FYM), compost, green manure, straw and organic wastes. At present, more than half of the arable land has a medium to low soil fertility, and soil organic matter (SOM) content is below 10 g $kg^{-1}$ in most soils. Straw is used for several purposes; the top priority among them is the use as domestic fuel, followed by animal fodder, and the least priority has the use as organic fertilizer (Cao et al., 1986; Portch and Jin, 1995; Wang et al., 1988; Zhao, 1989).

As a result of economic reforms starting from the beginning of 1980s discussed in Chapter 1, the practices of organic manuring, such as use of FYM and municipal wastes, green manuring, and return of straw, has declined, and largely been replaced by the use of inorganic fertilizers, especially for N (Chen et al., 1989; Portch and Jin, 1995; Yang, 1990; Zhou, 1989).

The effects of these changes in inputs of organic materials on the dynamics of SOM are difficult to predict, particularly in the long run. In field trials contrasting results have been reported. SOM contents could decrease, increase, or remain constant. The changes depended on initial SOM contents and annual crop yields in fields not receiving any organic inputs apart from roots and stubble (Cheng, 1987; Jiang et al., 1990; Kong et al., 1987; Ma, 1989; Wang et al., 1986; Zeng et al., 1992; Zhang et al., 1985; Zhao et al., 1987; Zhou, 1991; Zhou et al., 1990).

A certain minimum SOM content is a basic requirement for sustainable production of high crop yields. According to Pieri (1989), there is a serious risk of physical soil degradation in the Saharan zone of Africa when SOM content is less than 0.05(clay+silt), expressed in mass fractions. Many experimental results from northern China have indicated that with the present often low SOM contents it is difficult to substantially increase grain yields (Cheng et al., 1991; Jiang et al., 1991; Yang et al., 1991; Zhou, 1991). This implies that in the major part of the arable land, SOM contents should be improved rather than maintained if the growing demands for grain production are to be met. Therefore, analysis and prediction of long-term changes in SOM quantity and quality are crucial for the design and evaluation of farming strategies directed to sustainable grain production.

## 7.2 Objectives and design

The objectives of this chapter are to predict the long-term SOM dynamics under the new circumstances and to suggest measures to be taken for the maintenance and improvement of SOM content. In Chapter 6, an analysis was made of literature dealing with changes in SOM content and with trials studying the effects of application of organic materials. For that purpose relevant experimental data had been collected from this region, and analyzed with the model proposed in Chapter 3 on dynamics of organic matter mineralization. In the present chapter, the model was applied, with parameter values calibrated to the conditions of northern China, to predict the course of SOM content and SOM quality over a time span of 50 years.

Three management scenarios for organic inputs into the soil were formulated: (1) only roots and stubble; (2) as (1) plus the direct return of one third of the straw that is produced; (3) as (2) plus the application of FYM made with another one third of the straw that is produced. Scenario 1 represents the most common practice in this region; Scenario 2 is derived from the estimates by Liu and Mu (1988) that the quantity of straw that can be made available, is about one third of the present straw production; Scenario 3 represents the situation of maximum organic inputs in arable fields, assuming that one third of straw is needed as fuel in households.

Two levels of annual grain yields, which are the summed yields of two crops, wheat and maize, are considered: 'mean yields' of 7500 kg $ha^{-1}$ and 'high yields' of 15000 kg $ha^{-1}$. The former level is the average yields in this region in the early 1990s (Ministry of Agriculture of China, 1992), and the latter represents the current maximum yields that have been realized in some areas (Chinese Academy of Agricultural Sciences, 1989). Three initial SOM contents are regarded, namely 5, 10 and 20 g $kg^{-1}$, representing low, medium to high, and very high levels in this region (Cao et al., 1986; Liu and Mu, 1988; Soil and Fertilizer Institute of CAAS, 1986; Wang et al., 1988; Zhao, 1989).

## 7.3 Methods

The equation proposed in Chapter 3, was applied in this study:

$$Y_t = Y_0 * \exp[-R_9 * (f * t)^{1-S}] \qquad (3.14)$$

in which t is time; $Y_0$ and $Y_t$ are the substrate C quantities at t=0 and t, respectively; f is the temperature correction factor; $R_9$ is the average relative mineralization rate between t=0 and t=1 at the temperature of 9 °C; and S denotes the speed of 'aging' of substrate.

In Chapter 4 this equation proved valid under diverse environmental conditions and for existing SOM, as well as for various types of organic materials that are commonly applied in arable farming, such as plant materials and animal manure.

The same data sets as in Chapter 6 were used. One extra case for FYM from Western Europe (Kolenbrander, 1969, 1974) was also used because it refers to the situation existing before the present intensive animal production in West Europe, and hence may be comparable to the FYM produced in traditional farmers' households in northern China.

The values of derived model parameters $R_9$ and S in Table 6.1 (Chapter 6) were reused in this study, except those for FYM. The addition of the extra case from Kolenbrander (1969, 1974) slightly changed the value of $R_9$ from 0.82 to 0.81, and S from 0.49 to 0.50.

The data on organic inputs from roots, stubble and straw were derived from grain yields. Experimental results from Anderson (1988) and Tong et al. (1988) indicate that roots, straw and grain at harvest respond approximately in the same way to changes in growing conditions in the case of wheat, but not in the case of maize. Consequently, the average mass ratios of Grain:Straw:Roots (in the top 20 cm) for maize should be adjusted for different crop yields. For annual grain yields (wheat plus maize) of 7500 kg $ha^{-1}$, the average ratios are 1:1.22:0.37 (Li et al., 1990; Wang et al., 1986; Zhang and Wang, 1984). Interpolation and extrapolation of experimental results from Tong et al. (1988) indicate that the annual biomass production of straw and roots rise by only 46% and 32%, respectively, when the summed annual grain yields of maize and wheat increase from 7500 to 15000 kg $ha^{-1}$.

At both yield levels, a part of the total production of straw was allocated to stubble. According to the data by Wang et al. (1988), annually 2250 kg $ha^{-1}$ of stubble remains in the field, when the grain yield of wheat plus maize is 7500 kg $ha^{-1}$. This means that straw is subdivided into stubble and mown straw in the ratio of 1:3. The quantities of organic matter and carbon in various parts of the crops at the two yield levels are given in Table 7.1. For stubble and mown straw added to the soil, the same values of $R_9$ and S were taken.

**Table 7.1** Dry matter quantities (kg ha$^{-1}$) of various crop parts at mean and high yield levels.

| Yield level | Grain | Straw | | | Roots |
|---|---|---|---|---|---|
| | | total | mown | stubble | |
| mean | 7500 | 9150 | 6900 | 2250 | 2780 |
| high | 15000 | 13360 | 10020 | 3240 | 3660 |

Within our knowledge there are no generally used criteria for SOM quality. Frequently used index is cation exchange capacity per unit of SOM, another is the relative mineralization rate. Instead of the later, usually the fraction that is mineralized per year (FM) is taken. In view of the available data, we decided to use FM as a measure of SOM quality.

All calculations were confined to the top 20 cm of soil. Soil bulk density was set at 1.3 g cm$^{-3}$, C content of root, stubble and straw at 450 g kg$^{-1}$ (Lawlor, 1991) and that of SOM at 580 g kg$^{-1}$. Following the suggestion by Zhang et al. (1985), it was assumed that after the conversion of straw into FYM, still 56% is recovered in FYM of the C present in the straw that is supplied to animals as fodder and bedding.

## 7.4 Results

As shown in Chapter 6, the annual mean temperature ranges from 12 °C to 14 °C in this region. The corresponding values of **f** in Equation 3.14 are 1.6 and 1.8, respectively. Because the curves of remaining SOM are hardly affected by this difference (Figure 7.1), all showing that around 45% of the presently existing SOM will have disappeared after 50 years, it was justified to use 1.7 as value for **f** in northern China.

The graph in Figure 7.1 refer to situations where no new organic material is added to the soil. In such cases the relative mineralization rate of the existing SOM slows down over time. The fraction that is mineralized per year is on average 3.5% during the first five years, 1.6% during the second five years, and 0.7% during the last five years of the 50-year period. The value of 3.5% for the first five years falls well within the range of 2-5% found by Wang et al. (1988) in the same region.

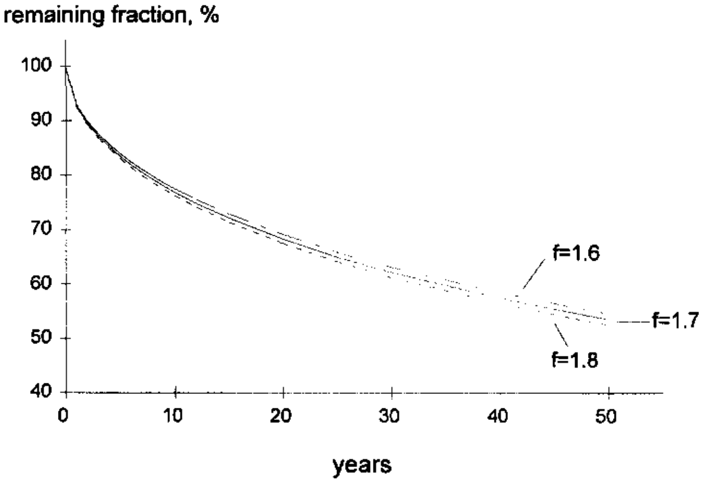

**Figure 7.1** Remaining fraction of SOM over time when no organic materials are added, calculated for mean annual temperatures of 12, 13 and 14 °C which correspond to f values of 1.6, 1.7 and 1.8. Values of $R_9$ and S were set at 0.057 $\text{year}^{-1}$ and 0.46, respectively.

The data in Figure 7.2, 7.4, 7.5 and 7.6 refer to the situation where new organic materials (roots, stubble, straw, FYM) are added to the soil. In our calculations, these materials, i.e. the remaining parts of them, were allocated to SOM one year after application. As a result of such additions, the relative mineralization rate of SOM may increase or decrease over time.

The predicted changes in SOM content under each of the three scenarios are shown in Figure 7.2 for the three initial SOM contents and the two yield levels. Irrespective of initial SOM contents, finally a steady-state SOM content will be reached for each scenario-yield combination (Table 7.2). In the first scenario, in which roots and stubble are the only organic inputs, SOM content can be maintained at 10 and 15 g $\text{kg}^{-1}$ in the mean-yield and high-yield situations, respectively. These are about two thirds of the values obtained in the third scenario, in which FYM and straw are applied. For Scenario-3, no comparison with the real world could be made since no relevant experimental results were available. For Scenarios 1 and 2, the model predictions on changes of SOM contents agree reasonably well with the experimental results from Cheng (1987, two-year trial), Jiang et al. (1990, five-year trial), Zhao et al. (1987, five-year trial), and Zhou (1991, twelve-year trial). As an example, Figure 7.3 shows the

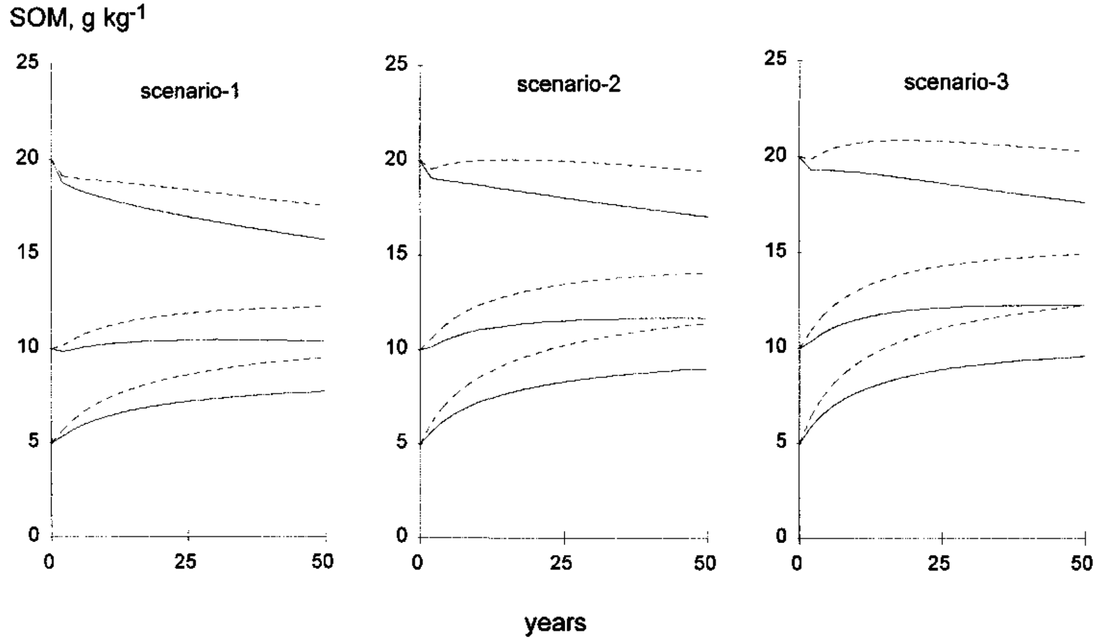

**Figure 7.2** Dynamics of SOM in three scenarios. Initial SOM contents are 5, 10 and 20 g $kg^{-1}$. Annual grain yields are 7500 kg $ha^{-1}$ (——) and 15000 kg $ha^{-1}$ (- - -).

**Table 7.2** Steady-state SOM contents (SOM, g kg$^{-1}$) and the corresponding fractions of SOM that are mineralized annually (FM, %) for mean and high levels, and three scenarios of organic-matter management.

| Yield level | Scenario-1 | | Scenario-2 | | Scenario-3 | |
|---|---|---|---|---|---|---|
| | SOM | FM | SOM | FM | SOM | FM |
| Mean | 10 | 4.8 | 13 | 5.2 | 15 | 5.6 |
| High | 15 | 4.8 | 19 | 5.2 | 21 | 5.6 |

observed and calculated SOM contents over a period of twelve years for the trial by Zhou (1991).

It is obvious from Figure 7.2 that SOM contents may approach the steady-state levels either by increasing or by reducing SOM content, depending on whether the initial contents are below or above the steady-state levels. The absolute annual change in SOM content is related to the difference between the present and the final SOM content, and hence it will become smaller over time, sharply diminishing in the beginning and slowly at a later stage, as shown in Figure 7.4.

As explained before, the fraction of SOM that is mineralized per year (FM) was used as a measure of SOM quality. Newly formed SOM has a higher relative mineralization rate than existing (old) SOM, and hence the quality of SOM improves with increasing proportions of newly formed SOM in total SOM. Such situations are created by increasing the annual organic inputs, and hence the quality increases in the order of Scenario-1 < Scenario-2 < Scenario-3 and it is

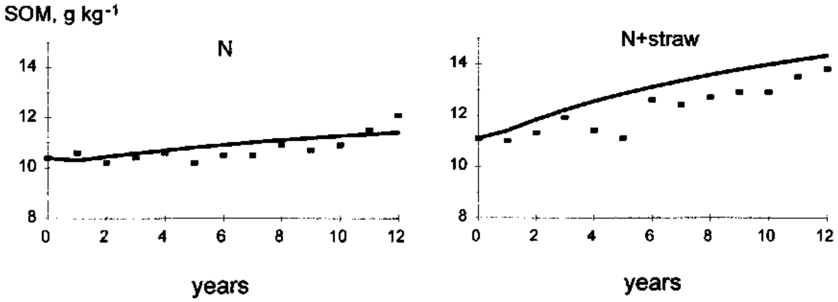

**Figure 7.3** Observed (points) and model calculated (lines) SOM contents for a field trial from Zhou (1991). N is the treatment with use of N fertilizer, and N+straw is with N fertilizer plus returns of straw.

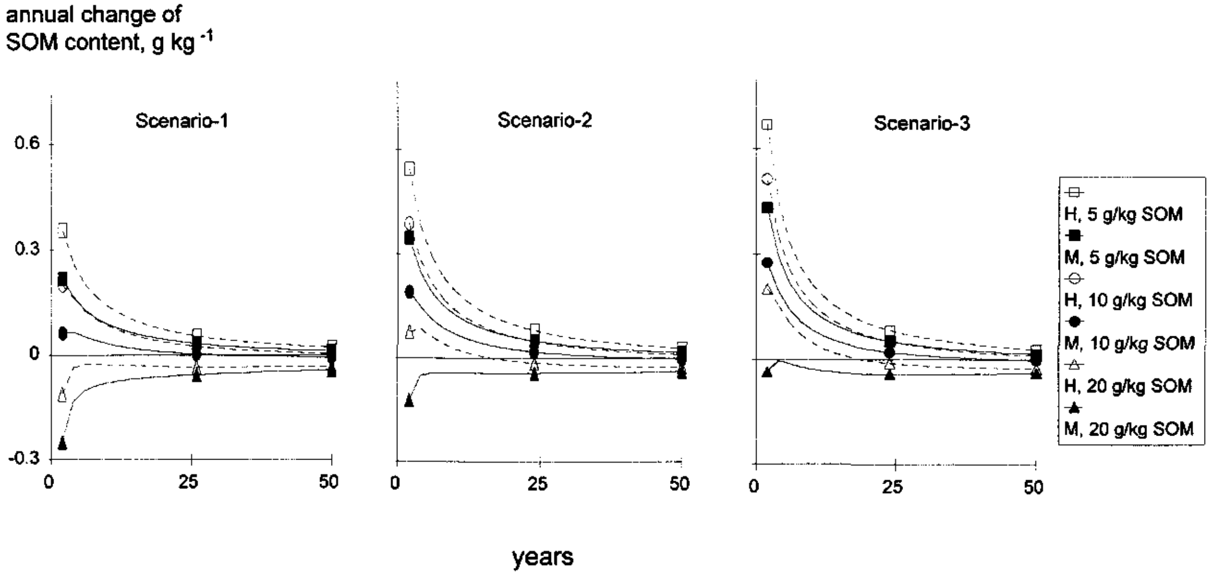

**Figure 7.4** Annual change of SOM content in three scenarios with three initial SOM contents and two annual grain yields in northern China. M = mean yield (7500 kg ha$^{-1}$), H = high yield (15000 kg ha$^{-1}$).

higher for high yield than in the case of mean yield. For a given scenario-yield combination, the lower the initial SOM content is, the higher the annually mineralized fraction is (Figure 7.5). The absolute quantity of annually mineralized SOM is, however, lower at a lower initial SOM content (Figure 7.4).

Figure 7.5 also shows that the annually mineralized fraction of SOM may change over time. Three patterns of change can be distinguished. The first pattern is an increase of the mineralized fraction followed by a decrease; it is found when SOM content increases over time (compare Figure 7.2). The second one is that the fraction that is mineralized annually tends to remain constant; it is found when SOM content remains unchanged over time. The third pattern is a decrease of the mineralized fraction followed by an increase; it is found when SOM content decreases over time (compare Figure 7.2). Since the six variants of organic inputs approach specific steady-state SOM contents, the fractions of SOM that are mineralized annually should also approach certain specific steady-state levels which are independent of the initial SOM contents. The trends can be seen clearly in Figure 7.5, and the values of the fractions mineralized that will finally be obtained, are given in Table 7.2. They differ among the three scenarios, indicating the variation in input compositions, since roots, stubble and FYM have different values of $R_9$ and S, but they hardly differ for the yield levels because the distribution of organic matter inputs is practically the same for both yield levels.

## 7.5 Discussion and conclusions

The outcomes of the foregoing calculations help to understand experimental data, and to reconcile seemingly contradictory results. They also indicate how much and at what pace SOM content may change under various management scenarios.

The amount of organic matter in the soil is the resultant of input and output. The output is difficult to manage, as the relative mineralization rate of SOM is largely determined by environmental factors, such as temperature, soil pH and soil texture. The inputs, on the contrary, are partly controllable like those by FYM or straw, and partly difficult to control like those by roots and stubble. The base steady-state SOM content is dependent on the annual returns of roots and stubble. The quantity of stubble is affected by the height at which crops are mown, and further it is closely related to crop yield (Tong et al. 1988). The quantity of roots too is closely related to crop yields, and it is therefore not better manageable than yield itself. Once the yield level has been determined, the quantity of roots is

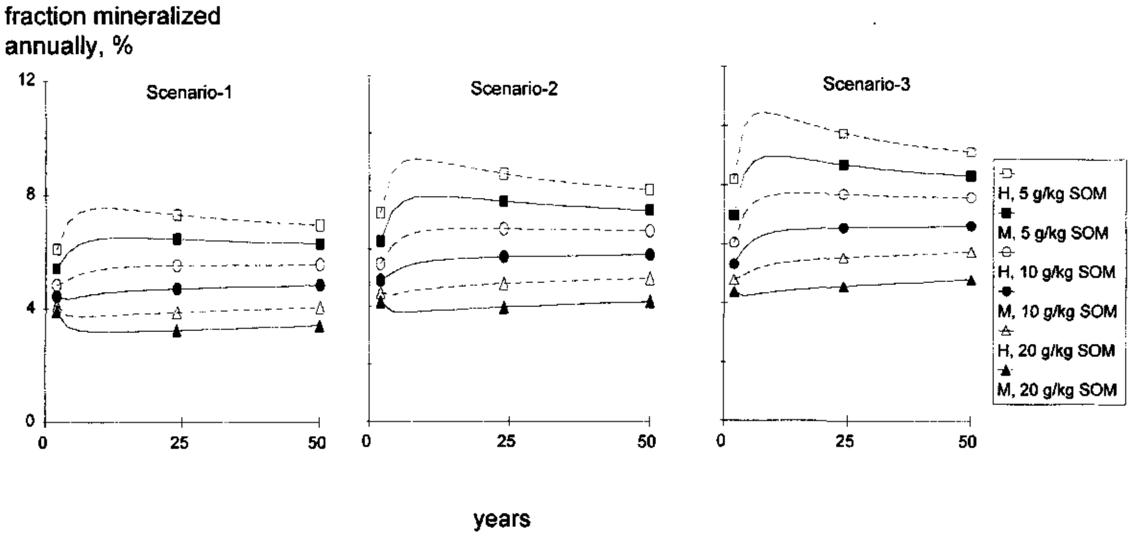

**Figure 7.5** Fraction of SOM mineralized per year in three scenarios with three initial SOM contents and two annual grain yields in northern China. M = mean yield (7500 kg $ha^{-1}$), H = high yield (15000 kg $ha^{-1}$).

fixed.

The results in Table 7.2 and Figure 7.2 show that the base SOM content is about 10 g $kg^{-1}$, when the yields of wheat plus maize are 7500 kg $ha^{-1}$, reflecting the current situation in northern China. This figure would rise to 15 g $kg^{-1}$ when grain yields would be doubled. With only roots and stubble as organic inputs, a decrease or an increase in SOM content is to be expected, depending on whether the present SOM content is higher or lower than 10 (or 15) g $kg^{-1}$. This may explain why decreasing, increasing, or constant SOM contents have been observed in the field trials mentioned earlier.

As shown in Figure 7.4, the annual change in SOM content becomes smaller and smaller over time, and new steady-state SOM contents (Table 7.2) will be established only in the long run. This implies that linear extrapolation of changes in SOM content found in trials lasting only a few years, inevitably results in an overestimation of the real changes (Chen and Wang, 1987).

It does not make sense to recommend additions of organic materials that in practice cannot be realised. The realistic Scenario 2 would eventually result in SOM contents of 13 and 19 g $kg^{-1}$ at the current average yields and at potential yields, respectively. The values of 15 and 21 g $kg^{-1}$ corresponding with mean and high yields found in our third scenario, may be seen as the upper limits of SOM content in arable fields in this region in the long run.

Direct application of straw is more effective than indirect application in the shape of FYM. Scenarios 2 and 3 may be considered as two examples of all possible combinations of direct and indirect use of straw. Theoretically higher SOM contents than 15 and 21 g $kg^{-1}$ for the two yield levels may be obtained, when more than two thirds of the straw is used, as is shown in the map of isolines for steady-state SOM contents (Figure 7.6). That would take away the use of straw as fodder or fuel, which is not a realistic scenario at present.

A sufficiently high SOM content is needed for high and sustainable soil productivity, and conversely, high yields are needed to improve SOM content. Although Scenarios 2 and 3 are not pointless, in many practical situations only a small contribution is to be expected from FYM and straw. In the past it has not been different. As suggested in Chapter 6, roots must always have been the most important source for SOM in northern China. Increasing the biomass of roots and stubble by increasing yields can be achieved by, among others, the use of

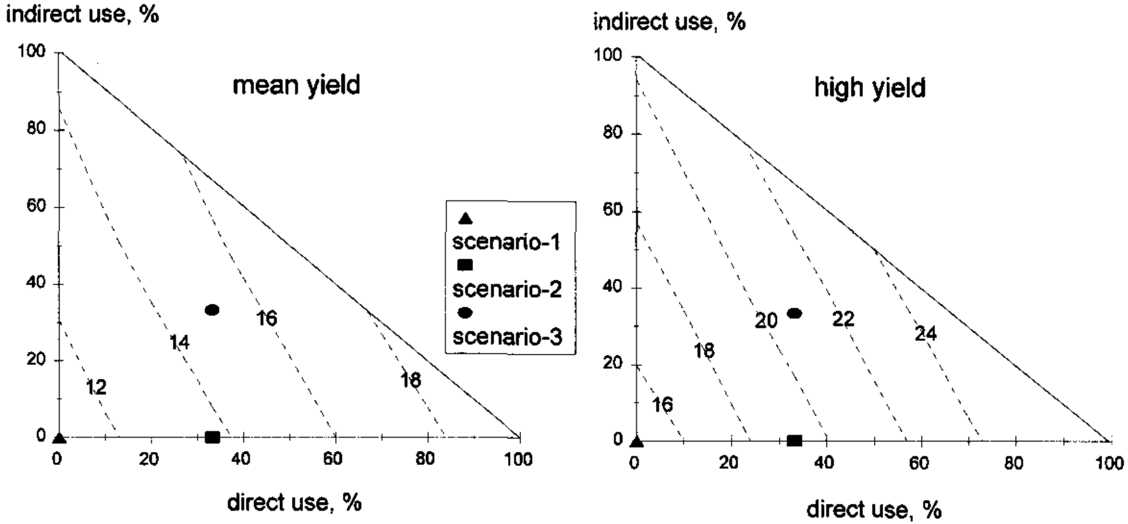

**Figure 7.6** Isolines of steady-state SOM content (g $kg^{-1}$) indicated by the figures, at mean yield and high yield with different combinations of direct use of straw and indirect use of straw via FYM. The sum of the two rates is ≤ 100%.

chemical fertilizers. The strategy of improving SOM content by means of chemical fertilizers, the so-called 'obtaining SOM by chemical means' approach, has been suggested by several scientists in the last ten years (Cao et al., 1986; Liu and Mu, 1988; Zeng et al., 1992; Zhou, 1989).

Farmers should be stimulated to keep the above-ground crop residues, and to return them to the soil, directly or indirectly in other forms, in order to increase SOM contents above the base levels defined by roots and stubble. On the other hand, it should be realized that significant improvements will always require long-term efforts. At the same time, farmers should improve the quality of FYM by increasing its organic matter content, which in practice means less soil should be mixed into FYM. Such an improvement of FYM would effectively reduce the costs of transport and spreading in the field.

Changes in SOM contents (Figure 7.2) bring about changes in SOM quality, in terms of the fraction mineralized annually (Figure 7.5), due to the change in the general composition of SOM. As newly formed 'young' SOM mineralizes more quickly than 'old' SOM, and the higher the proportion of newly formed SOM, the higher the relative mineralization rate of SOM as a whole is. This has been demonstrated by a.o. Janssen (1984), van Dijk, (1981), and Verveda (1983). So, with an increase in SOM content, the release of nutrients may increase relatively as well as absolutely.

The reliability of the above predictions depends strongly on the quality of the basic data, in particular of the data from long-term field experiments which were used to deduce the values of the model parameters. Also, the reality is more complicated than what has been considered in this paper. Thus, the predictions can surely be improved when more data of high-quality become available, and the practical situations for which the model should be applicable are described in more details.

Summarizing, in most arable fields in northern China, both the quantity and the quality of SOM will rise upon an increase in annual crop production, e.g. as a result of the use of chemical fertilizers. Similar positive effects on SOM will be brought about by returning (a part of) the straw, either directly by leaving it in the field or indirectly by applying it as FYM. Theoretically, the direct return is more efficient for SOM content and quality, but it may be less attractive for farmers because it takes away the use of straw as fodder.

## Chapter 8

# Temporal changes in the effect of temperature on mineralization rates of organic matter in soils

### Abstract

The objective of this chapter is to examine the changes over time of the effect of temperature on organic matter mineralization. The temperature effect was expressed by the Arrhenius equation, and two temperature correction factors commonly used in simulation models, namely $\mathbf{Q_{10}}$ and $\mathbf{f_{10}}$. The model developed in Chapter 3 of this thesis was applied to calculate the change in the relative mineralization rate of various organic substrates used in incubation experiments at different temperatures. A good fit of experimental data collected from literature to model calculations was obtained. The results indicate that the Arrhenius equation holds for glucose, but not for other materials such as cellulose, plant materials and soil organic matter, because of the continuous decrease of the temperature effect on relative mineralization rates. Mathematical expressions were formulated to relate $\mathbf{Q_{10}}$ and $\mathbf{f_{10}}$ to the initial average relative mineralization rate (R) and the speed of 'aging' (S), which are the main model parameters, and used to examine the dynamics of $\mathbf{Q_{10}}$ and $\mathbf{f_{10}}$. It was found that both $\mathbf{Q_{10}}$ and $\mathbf{f_{10}}$ decrease over time for cellulose, plant materials and existing soil organic matter, but not for glucose. The decrease in the effect of temperature on mineralization is more remarkable in the beginning than later. In some situations, the effect of temperature on mineralization rate was positive initially, but became negative in the long run.

## 8.1 Introduction

Temperature is one of the most important environmental factors influencing the rate of mineralization of organic matter in soils. Many studies have shown that within the common range of temperatures in the field (roughly 5-35°C), higher temperatures lead to higher mineralization rates. The quantitative interpretation of experimental data requires mathematic descriptions of the temperature effect. For that purpose, several functions and indices have been proposed and applied. One of them is *Arrhenius* equation (Addiscott, 1983; Clark and Gilmour, 1983; Ellert and Bettany, 1992; Nyhan, 1976; Stanford et al., 1973; Stone and Morgan, 1990):

$$\ln(K) = A - B/T_a \tag{8.1}$$

where K is the rate constant of first-order kinetics, $T_a$ is the absolute temperature, A and B are constants.

Another way of describing the effect of temperature is by the use of $\mathbf{Q_{10}}$, being the ratio of the rate constants at two temperatures differing by 10 °C (Ellert and Bettany, 1992; Kirschbaum, 1995; Stanford et al., 1973). If two temperatures differ by values other than 10 °C, $\mathbf{Q_{10}}$ is calculated by:

$$Q_{10} = (K_2 / K_1)^{10/(T2-T1)} \tag{8.2}$$

where $T_1$ and $T_2$ are the temperatures, and $K_1$ and $K_2$ are the rate constants found at $T_1$ and $T_2$, respectively. If $\mathbf{Q_{10}}$ is 1, there is no effect of a raised temperature. Above and below 1, positive and negative effects of temperature on mineralization rate are expected, respectively.

In his review, Kirschbaum (1995) showed that the values of $\mathbf{Q_{10}}$ for commonly used organic materials could vary from 1.5 to 8 within the temperature range of 0 to 35 °C. In addition, some attempts were made by, e.g. Douglas and Rickman (1992), Nicolardot et al. (1994), Nyhan (1976), O'Connell (1990), and Stott et al. (1986), to describe the effect of temperature by statistical or empirical approaches. For instance, Douglas and Rickman (1992) used 'cumulative degrees days' to allow for the effect of temperature on mineralization of crop residues, whereas Nicolardot et al. (1994) adopted a polynomial regression equation with either T (in °C) alone or T and $T^2$, as independent variables.

Some models on soil organic matter dynamics in soils use the strategy of adjusting the time scale in the equations when accounting for the effect of temperature (Chapter 3 of this thesis; Jenkinson et al., 1987; Noij et al., 1993; Parton et al., 1987; Van Veen and Paul, 1981). Generally it goes as follows:

$$t_{T1} = f * t_{T2} \tag{8.3}$$

where **f** denotes the temperature correction factor, and $t_{T1}$ and $t_{T2}$ denote the time periods corresponding to $T_1$ and $T_2$ ($T_2 > T_1$), respectively. It means that the period needed for a certain mineralization is **f** times as long at $T_1$ as at $T_2$, or the relative mineralization rate at $T_2$ is **f** times as high as at $T_1$.

In none of these methods (Arrhenius, $\mathbf{Q_{10}}$, **f**), it is taken into account that the temperature effect on mineralization rate may change over time. Experimental results from Pal et al. (1975), Sorensen (1981), and Chapter 5 of this thesis, suggest that the effects of external conditions, such as temperature and soil texture, on mineralization tend to decline over time. The answer to the question whether the effect of temperature changes over time may assist in understanding the mechanisms of the temperature effect on mineralization, and in analyzing and predicting the long-term effects of changing temperatures (e.g. global warming) on consequences of mineralization like the increase of $CO_2$ concentration in the atmosphere.

The purpose of this chapter is to examine the changes over time of the effect of temperature on mineralization rate in soils. Results of conventional experiment data, such as the quantities of remaining organic matter over time, form the starting point of this study, but it is difficult to see through the data as such the changes of the temperature effect. Use of experimental results by means of a relevant model offers better possibilities, because the model can reproduce and summarize the experimental results in a manageable way, thus facilitating comparison of results of different studies and conceiving of general characteristics and rules of the processes. In this chapter, the model proposed in Chapter 3 was applied to experimental data collected from three publications. Only data sets from controlled experiments with temperature as the sole treatment were used to avoid confounding with other factors, such as moisture.

## 8.2 Theoretical considerations

### *8.2.1 Basic equations*

In Chapter 3 the following equations were proposed to describe mineralization and to calculate the quantity of remaining substrate C under constant environmental conditions like temperature and moisture:

$$K = R * t^{-S} \tag{3.1.b}$$

$$k = (1 - S) * R * t^{-S} \tag{3.4}$$

$$Y_t = Y_0 * \exp(-R * t^{1-S}) \tag{3.2}$$

in which t is time; R ($t^{S-1}$) is the average relative mineralization rate between t=0 and t=1; S denotes the speed of 'aging' or decrease of decomposability of the substrate; K ($t^{-1}$) is the average relative mineralization rate between time zero and t, k ($t^{-1}$) is the actual relative mineralization rate at t; $Y_0$ and $Y_t$ are the quantities of substrate at times zero and t, respectively.

The essence of this model is that the relative mineralization rates (K and k) are treated not to be constant, even not under constant conditions, but to decrease over time. A linear relationship between log(K) or log(k) to log(t) was found, described by the parameters R and S, which are constant under constant environmental conditions. In Chapter 4 this model proved valid in diverse environmental situations, for existing SOM as well as for simple organic compounds and for various types of plant materials that are commonly applied.

### *8.2.2 Calculation of $Q_{10}$*

For the study of the effect of temperature the model parameters receive subscripts. If subscript 1 refers to the lower temperature ($T_1$), and subscript 2 to the higher temperature ($T_2$), the relationship for $\mathbf{Q_{10}}$ (Equation 8.2) can be found as the quotient of $K_2$ and $K_1$, each described with Equation 3.1.b:

$$K_1 = R_1 * t^{-S1}$$

$$K_2 = R_2 * t^{-S2}$$

$$K_2 / K_1 = (R_2 * t^{-S2}) / (R_1 * t^{-S1})$$

$$= (R_2 / R_1) * t^{S1-S2}$$

Substitution in Equation 8.2 yields:

$$Q_{10} = (R_2 / R_1)^{10/(T2-T1)} * t^{10(S1-S2)/(T2-T1)} \tag{8.4}$$

For convenience, we assume that $T_2 - T_1 = 10$ °C, and simplify Equation 8.4 into:

$$Q_{10} = (R_2 / R_1) * t^{S1-S2} \tag{8.5}$$

Equations 8.4 and 8.5 show that $\mathbf{Q_{10}}$ is a function of t. The first-order and the second-order derivatives of $\mathbf{Q_{10}}$ in Equation 8.5 indicate its dynamics over t:

$$dQ_{10} / dt = (R_2 / R_1)(S_1 - S_2) * t^{S1-S2-1}$$

$$d^2Q_{10} / dt^2 = (R_2 / R_1)(S_1 - S_2)(S_1 - S_2 - 1) * t^{S1-S2-2}$$

The value of **$Q_{10}$** will not change over time if dQ/dt=0, which requires that $S_1$ be equal to $S_2$. If $S_1 < S_2$, $(dQ_{10}/dt) < 0$, thus **$Q_{10}$** will decrease over time, and the decrease is sharper in the earlier stage than in later stage because $(d^2Q_{10}/dt^2) > 0$. In the hypothetical case that $S_1 > S_2$, **$Q_{10}$** would increase over time. Usually $S_1 < S_2$, therefore, **$Q_{10}$** will decrease over time.

The time required for **$Q_{10}$** to reach the value of 1 is denoted by $t_{Q10=1}$. From Equation 8.4 it is derived:

$$t_{Q10=1} = (R_2 / R_1)^{1/(S2-S1)} \tag{8.6}$$

*8.2.3 Calculation of f*

By definition, **f** is the ratio of the time periods, which are needed at $T_1$ and $T_2$ for a same mineralization (see Equation 8.3). If the time at $T_2$ is set as t, the time at $T_1$ should be f*t. So,

$$Y_{T1} = Y_0 \exp[-R_1 * (f * t)^{1-S1}]$$

$$Y_{T2} = Y_0 \exp[-R_2 * t^{1-S2}]$$

Because $Y_{T1} = Y_{T2}$, it holds:

$$-R_1 * (f * t)^{1-S1} = -R_2 * t^{1-S2}$$

and hence,

$$f = (R_2 / R_1)^{1/(1-S1)} * t^{(S1-S2)/(1-S1)} \tag{8.7}$$

The first-order and the second-order derivatives indicate the dynamics of **f**:

$$df / dt = (R_2 / R_1)^{1/(1-S1)} * [(S_1 - S_2) / (1 - S_1)] * t^{[(S1-S2)/(1-S1)] - 1}$$

$$\begin{aligned} d^2f / dt^2 = (R_2 / R_1)^{1/(1-S1)} * [(S_1 - S_2) / [(1 - S_1)] \\ * [(S1 - S2) / (1 - S1) - 1] * t^{[(S1-S2)/(1-S1)] - 2} \end{aligned}$$

Like $\mathbf{Q_{10}}$, **f** is dependent on time. It remains constant only if $S_1 = S_2$. If $S_1 < S_2$ (the most common situation), **f** decreases since $(df/dt) < 0$, and the decrease is quicker in the beginning than later as $(d^2f/dt^2) > 0$. **f** increases in the unlikely case that $S_1 > S_2$.

So far, **f** was used for any temperature interval $(T_2 - T_1)$. For a correct comparison of **f** with $\mathbf{Q_{10}}$, the temperature interval across which **f** is calculated should be 10 °C. Using the symbol $\mathbf{f_{10}}$ for such an **f** value, it follows:

$$f_{10} = (t_{T1} / t_{T2})^{10/(T2-T1)} = f^{10/(T2-T1)} \tag{8.8}$$

Thus,

$$f_{10} = (R_2 / R_1)^{10/[(1-S1)(T2-T1)]} * t^{10(S1-S2)/[(1-S1)(T2-T1)]} \tag{8.9}$$

Since $(S_1 - S_2)$ is negative and $(1 - S_1)$ is $< 1$, the value of the exponent of t in Equation of 8.9 is more negative than the value of the exponent of t in Equation of 8.4, and hence the time effect on **f** decreases more rapidly with time than the time effect on $\mathbf{Q_{10}}$.

Similar to $\mathbf{Q_{10}}$, also $\mathbf{f_{10}}$ can reach a value of 1 and less, and the time (t) at which $\mathbf{f_{10}}$=1 is derived from Equation 8.9 as:

$$t_{f10=1} = (R_2 / R_1)^{1/(S2-S1)} \tag{8.10}$$

Apparently,

$$t_{Q10=1} = t_{f10=1}$$

## 8.3 Materials and methods

In total 27 sets of experimental data were collected from three publications, as summarized in Table 8.1. With the exception of existing SOM in the paper by Pal et al. (1975), all substrates had been labelled, either with $^{14}C$ or with $^{13}C$, and been incorporated in soils. The moisture content of soils was kept constant throughout the experiments. The C mineralization was determined by measuring $CO_2$ evolution over time and the original data were presented either in a table (Sorensen, 1981), or in graphs (the other two sources).

**Table 8.1** Summary of the data sets.

| Case | Substrate | Soil | Temperature | Period, day | Source |
|---|---|---|---|---|---|
| 1-a | glucose | silty clay loam, pH=7.3 | 4, 12, 20, 28 | 10 - 140 | Figure 1 of Nicolardot et al., 1994[a] |
| 1-b | holocellulose | as above | 12, 20, 28 | 42 - 140 | |
| 2-a | cellulose | sandy loam, pH=6.6 | 10, 20, 30 | 30 - 90 | Table 2 of Sorensen, 1981[b] |
| 2-b | as above | loam, pH=7.7 | as above | as above | |
| 2-c | as above | clay loam, pH=7.1 | 10, 20 | as above | |
| 3-a | rice straw | clay-1, pH=5.7 | 7.2, 22, 37 | 30 - 120 | Figure 1 and 3 of Pal et al., 1975[c] |
| 3-b | as above | clay-2, pH=6.3 | as above | as above | |
| 3-c | SOM | clay-1, pH=5.7 | as above | as above | |
| 3-d | as above | clay-2, pH=6.3 | as above | as above | |

[a] For Case 1-b the data before 42 days were not included.

[b] Only those with addition of 2 g cellulose. The observation on 10-day were not included. For Case 2-c the data at 30 °C were not included.

[c] The data before 30 days were not included. Each set of data for Case 4-c and 4-d is the mean of two treatments with and without addition of rice straw.

The first step of this study was to examine the goodness of the fit, as indicated by adjusted $R^2$ of nonlinear regression, of Equation 3.2 to the data of the experiments of Table 8.1, and values of R and S were derived. Then, by using these values of R and S, the effect of temperature on mineralization over time was studied with regard to the remaining quantities of C (Equation 3.2), relative mineralization rates (K in Equation 3.1.b, or k in Equation 3.4), Arrhenius equation (Equation 8.1), $\mathbf{Q_{10}}$ (Equation 8.4), and $\mathbf{f_{10}}$ (Equation 8.9).

## 8.4 Results

### *8.4.1 Calculation of R, S and $K_{0.1y}$*

Table 8.2 shows the results of fitting the data to Equation 3.2 by nonlinear regression. Among the 27 data sets, 26 had adjusted $R^2$ of 0.95 or higher, and 15 had 0.99 or above. This indicates that Equation 3.2 can accurately describe the mineralization of substrates in soils under different temperatures, and that the values of the key parameters, R and S (Table 8.2), can be reliably used to study the temperature effect.

Because a lag time of usually one month was found in the beginning of mineralization of substrates like plant materials (see Chapter 4), some data obtained in the starting times of the incubations have been excluded, and the regression analysis refers to the period thereafter, as mentioned in Table 8.1. The values of R are therefore overestimates of K at Day 1. For a more realistic comparison, it is better to consider the values of K at 0.1 year ($K_{0.1y}$), which were calculated with Equation 3.1.b. They are also given in Table 8.2, and plotted versus temperature in Figure 8.1.

Table 8.2 shows that R increases with temperature, and S too, except in the case of glucose where S kept the same value from 12 to 28 °C. The usually higher value of S at higher temperature implies that the decomposability, expressed in the relative mineralization rate (K or k) of the substrate decreases more quickly at higher temperatures. Figure 8.2 shows this for some cases of Table 8.2. Only glucose has parallel lines for the different temperatures, in the other cases the lines become closer to each other and sometimes intersect already within the first year. It would be difficult to arrive at such conclusions from 'elementary' graphs of remaining organic material plotted against time (Figure 8.3). The elementary graphs are suited to show that higher temperatures result in higher rates of mineralization, but not to demonstrate differences in the rate of decrease of K over time; hence with such graphs the essential information on characteristic features of the processes is missed.

### *8.4.2 Arrhenius equation*

Because K, the average relative mineralization rate, decreases over time, the values of regression parameters A and B of the Arrhenius relationship (Equation 8.1) must also change with time. The values of K were calculated for each temperature at 0.1, 0.3, 0.5, 0.7 and 1.0 year, and ln(K) was plotted against the reciprocal of absolute temperature ($T_a$) in Figure 8.4. It shows that the relationship between ln(K) and $1/T_a$ was linear for glucose, and was curvilinear for other substrates. In course of time, the sign of the slope of the lines could change corresponding to the change in values of **f** from >1 into <1.

### *8.4.3 Changes of $Q_{10}$ over time*

**Table 8.2** Results of fitting the data from sources in Table 8.1 to Equation 3.2 by nonlinear regression, and $t_{Q10=1}$ and $t_{f=1}$ calculated by Equation 8.6.

| Case | T °C | R $day^{S-1}$ | S | adj. $R^2$ | $K_{0.1y}$ | $t_{Q10=1}$ & $t_{f10=1}$, year(a) |
|---|---|---|---|---|---|---|
| 1-a | 4 | 0.23 | 0.83 | 0.99 | 1.2E-2 | |
| | 12 | 0.32 | 0.85 | 1.00 | 1.5E-2 | ∞(b) |
| | 20 | 0.36 | 0.85 | 1.00 | 1.7E-2 | ∞ |
| | 28 | 0.43 | 0.85 | 1.00 | 2.0E-2 | ∞ |
| 1-b | 12 | 0.21 | 0.73 | 1.00 | 1.5E-2 | |
| | 20 | 0.39 | 0.80 | 0.99 | 2.2E-2 | 15.6 |
| | 28 | 0.52 | 0.85 | 0.97 | 2.4E-2 | 0.7 |
| 2-a | 10 | 0.09 | 0.45 | 0.98 | 1.7E-2 | |
| | 20 | 0.14 | 0.52 | 0.97 | 2.3E-2 | 5.4 |
| | 30 | 0.57 | 0.79 | 0.97 | 3.4E-2 | 0.4 |
| 2-b | 10 | 0.10 | 0.44 | 1.00 | 2.0E-2 | |
| | 20 | 0.25 | 0.65 | 1.00 | 2.4E-2 | 0.2 |
| | 30 | 0.59 | 0.83 | 0.89 | 2.9E-2 | 0.3 |
| 2-c | 10 | 0.06 | 0.41 | 1.00 | 1.5E-2 | |
| | 20 | 0.34 | 0.79 | 0.96 | 2.0E-2 | 0.2 |
| 3-a | 7.2 | 0.11 | 0.74 | 0.99 | 7.4E-3 | |
| | 22 | 0.24 | 0.81 | 1.00 | 1.3E-2 | ∞ |
| | 37 | 0.39 | 0.87 | 0.97 | 1.7E-2 | 12.6 |
| 3-b | 7.2 | 0.08 | 0.66 | 0.95 | 7.8E-3 | |
| | 22 | 0.26 | 0.74 | 0.95 | 1.8E-2 | ∞ |
| | 37 | 0.47 | 0.93 | 0.97 | 1.7E-2 | 0.1 |
| 3-c | 7.2 | 0.0028 | 0.61 | 0.95 | 3.1E-4 | |
| | 22 | 0.0073 | 0.67 | 0.96 | 6.6E-4 | ∞ |
| | 37 | 0.0156 | 0.78 | 0.98 | 9.4E-4 | 2.7 |
| 3-d | 7.2 | 0.0043 | 0.62 | 0.98 | 4.6E-4 | |
| | 22 | 0.0097 | 0.68 | 0.98 | 8.3E-4 | ∞ |
| | 37 | 0.0232 | 0.85 | 0.99 | 1.1E-3 | 0.5 |

(a) Each value is for the temperature range from itself to the one above.

(b) > 700 years.

Values of R and S for two adjacent temperatures in Table 8.2 were substituted in Equation 8.4 to calculate $Q_{10}$. Figure 8.5 shows the phenomena that were discussed above in the theoretical considerations: $Q_{10}$ remained unchanged if S had the same value at different temperatures (glucose), and $Q_{10}$ decreased over time if S increased with increasing temperature (all other substrates). As predicted with Equation 8.5, the decline over time was more remarkable in the beginning than later. The values of $Q_{10}$ may become even lower than 1 after some time, which means that the mineralization rate is lower at the higher temperature than that at the lower temperature.

### 8.4.4 *Changes of $f_{10}$ over time*

Figure 8.6 shows the changes of $f_{10}$ over time as calculated by Equation 8.9. For glucose, there is no change of $f_{10}$ over time from 12 to 20 °C and from 20 to 28 °C, but $f_{10}$ decreases over time from 4 to 12 °C. For other substrates, $f_{10}$ obviously decreases over time in the various ranges of temperature, and the decrease is more outspoken in the beginning than later. As indicated before, the temperature correction factor $f_{10}$ is similar to $Q_{10}$ in that it decreases over time if S increases

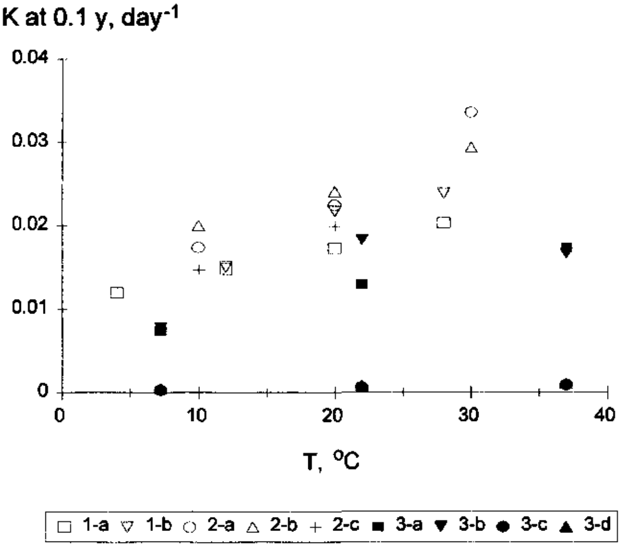

**Figure 8.1** Relationship between K at 0.1 year and temperature for the substrates in Table 8.1.

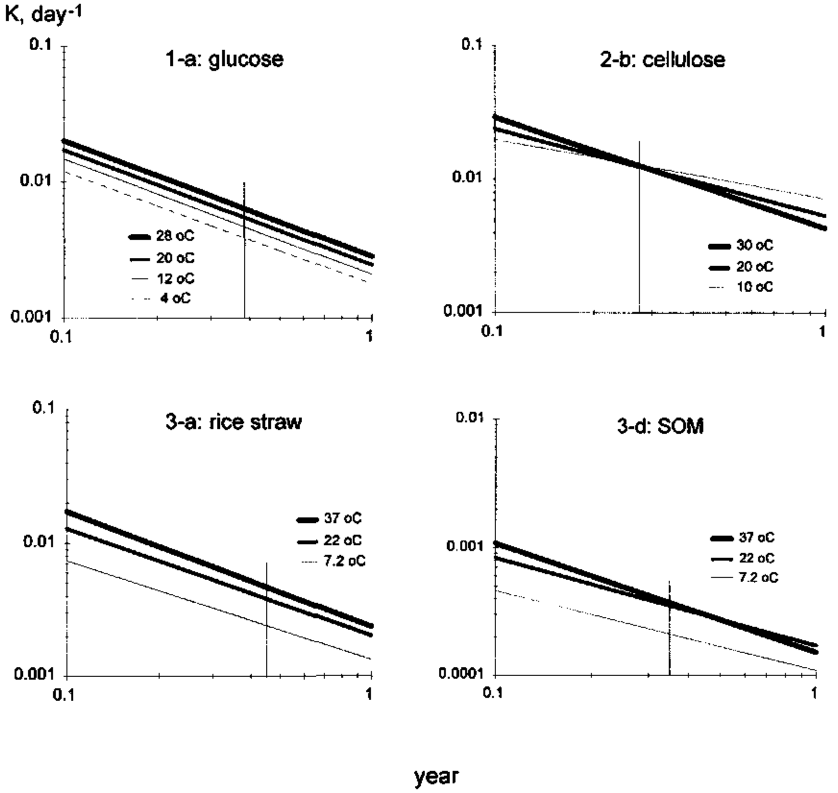

**Figure 8.2** Relationship between log(K) and log(t) for some cases in Table 8.2. The vertical lines indicate the ending of experiments.

with an increase of temperature, and it remains unchanged if S does not change with temperature. The changes of $\mathbf{f_{10}}$ over time, however, are sharper than the changes of $\mathbf{Q_{10}}$, which is in agreement with the difference between Equations 8.5 and 8.9, as discussed before.

Similar to $\mathbf{Q_{10}}$ in Figure 8.5, the continuous decrease of $\mathbf{f_{10}}$ over time reflects situations where the temperature effect declines from positive to zero, e.g., the range of 20 to 28 °C in Case 1-b, or even becomes negative (f<1) like in Case 2-a between 20 and 30 °C.

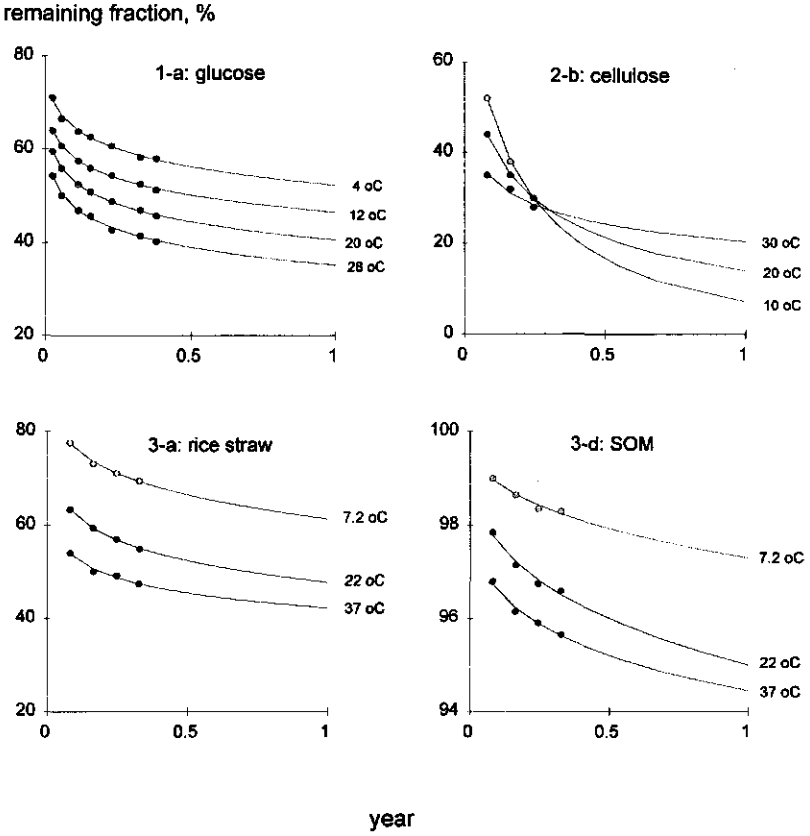

**Figure 8.3** Decrease of remaining quantity of organic materials over time for some cases of Table 8.2. Points are observations and lines are model calculations.

## *8.4.5 Temperature effects on substrate decomposability at equal quantity*

So far, the temperature effect on mineralization rate was studied by comparing the mineralization at different temperatures during a certain period of time. During that period the decomposability of the substrate decreases and this decrease is stronger at a high than at low temperature. After a period of time, the substrates mineralizing at different temperatures differ in their decomposability. In fact this means that they are not suitable any more for a fair assessment of the temperature effect.

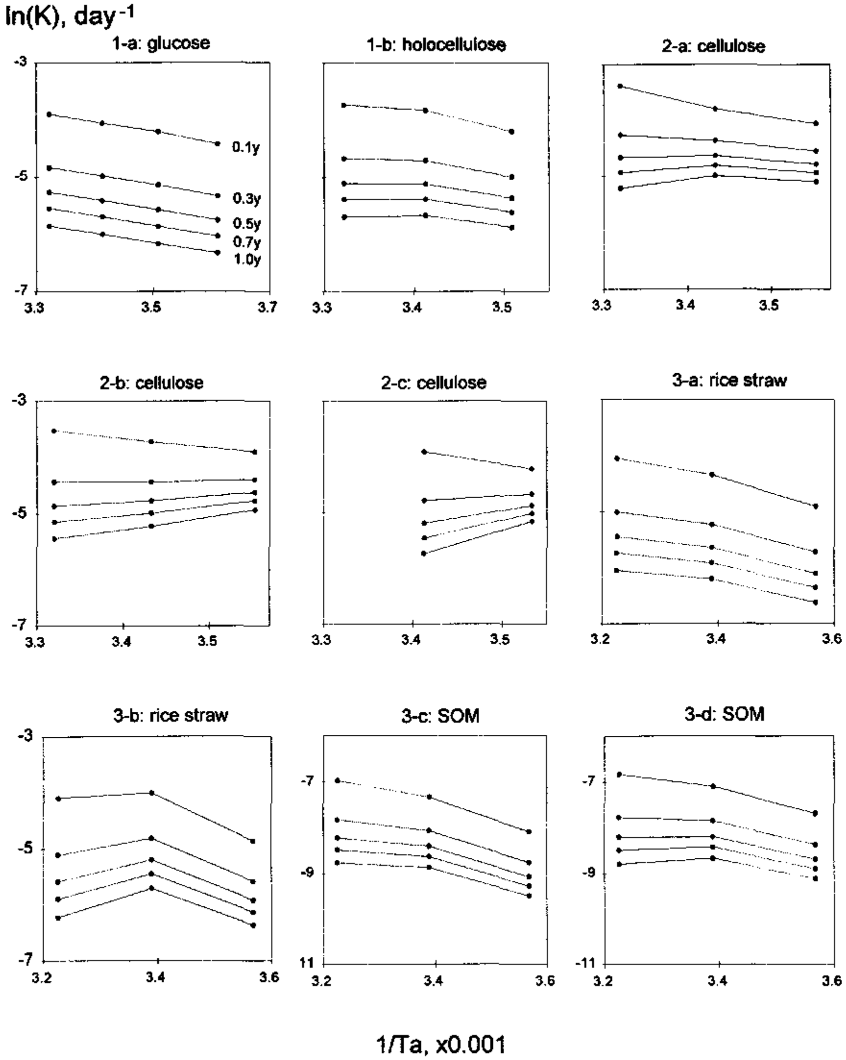

**Figure 8.4** Relationship between ln(K) and 1/Ta (Arrhenius equation). The figures in 1-a indicate the time (in year).

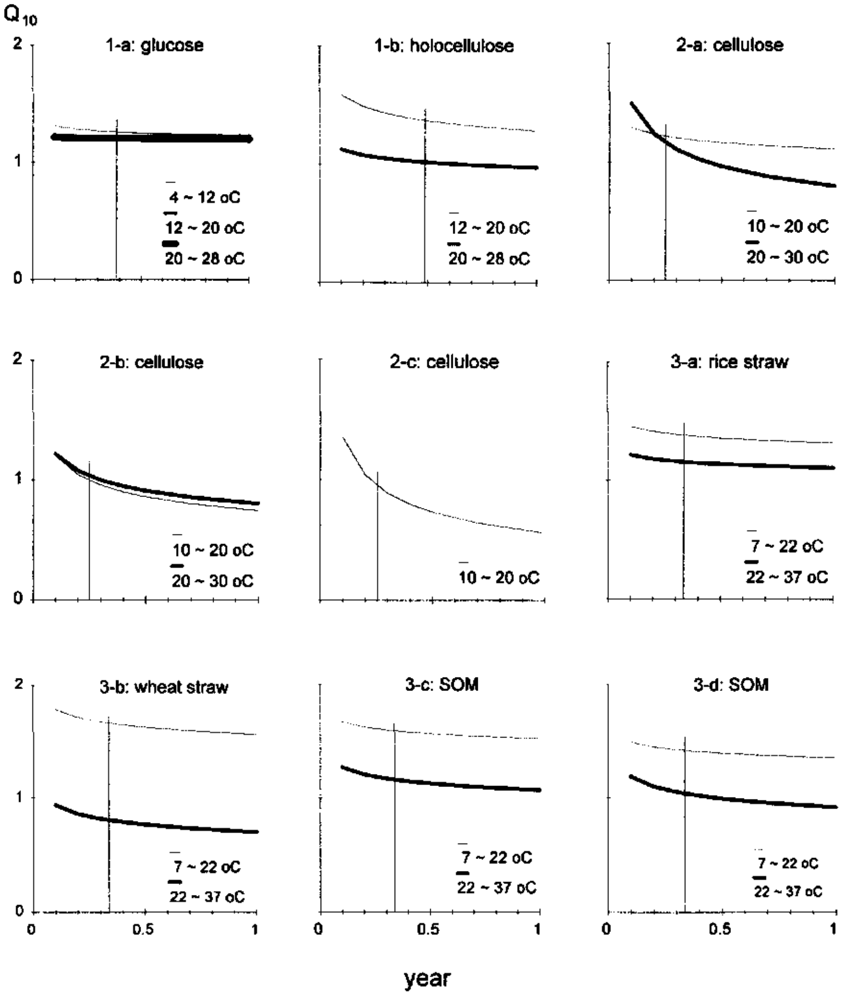

**Figure 8.5** Change of $Q_{10}$ over time. The vertical lines indicate the ending of experiments.

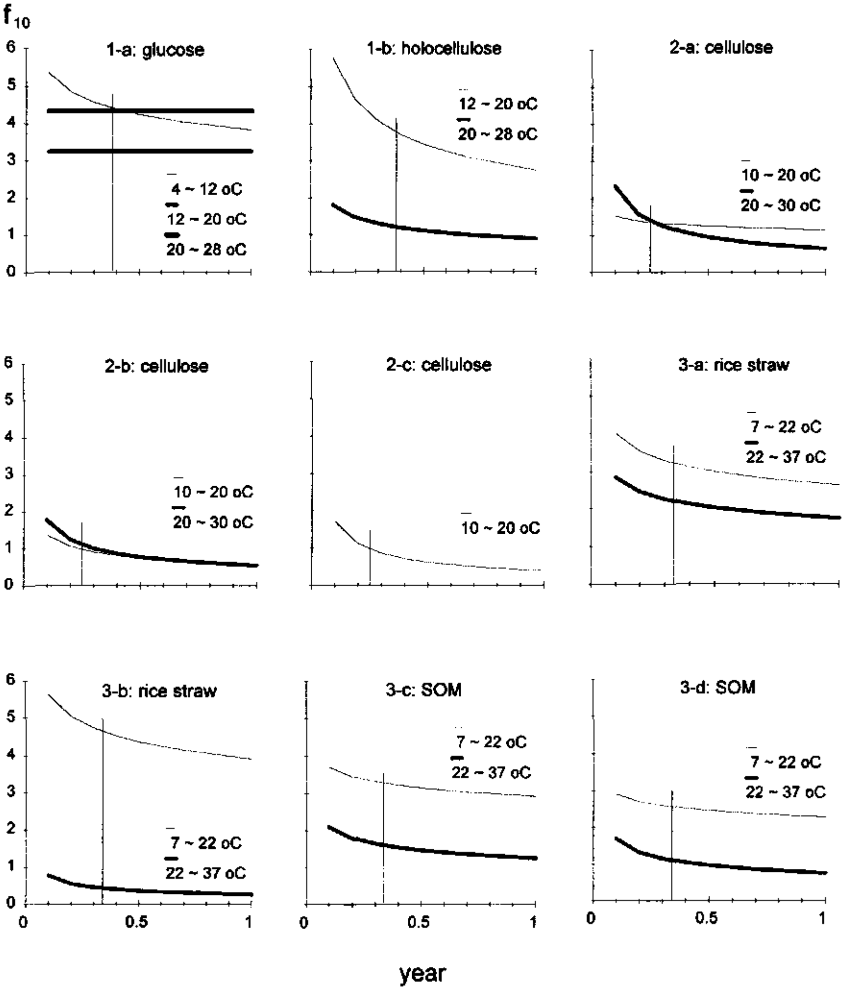

**Figure 8.6** Change of $f_{10}$ over time. The vertical lines indicate the ending of experiments.

As a first approximation, it is justified to assume that the remainders of a same substrate mineralizing at different temperatures are equally decomposable when they are compared at the points of the time when the remaining quantities are equal. To verify this, the actual relative mineralization rates (k) have been plotted in Figure 8.7 against the fraction of remaining C for some cases of Table 8.2.

In Case 1-b, for example, k is higher at 28 °C than at 20 and 12 °C, when the remaining fraction is 60%, but when the remaining fraction is less than 40 or 30%, k is lower at 28 °C than at 20 and 12 °C, respectively. This suggests that when compared at a stage of equal remaining fractions, being 40% or less in this case, the remaining residue is more stable at 28 °C than at the lower temperatures. This points to differences in chemical composition or in degree of protection. At present it is difficult to give an explanation, as no experimental data seem available to verify the hypothesis.

## 8.5 Discussion and conclusions

### *8.5.1 Use of model calculations*

The changes over time of the effect of temperature on C mineralization rate have not been examined and even not been registered in the publications we reviewed in the present study. This may have been caused by the lack of appropriate theoretical models which are needed for such a purpose. As was discussed with Figure 8.3, graphs showing data on C loss against time, or data on remaining fraction of applied organic matter as derived from conventional experiments against time, cannot easily produce the information on changes in the temperature effects on mineralization rate. For example, in Case 3-d of Figure 8.3, the difference between the remaining C at 7.2 °C and that at 22 °C still increases within the experimental time span, and the gap between the remaining quantities of C at 22 °C and at 37 °C remains the same, while according to the model there is a decreasing effect of temperature over that period.

It is obvious from the present study that a mathematical model calibrated to such experimental data provides the tool to study such changes. The high values of adjusted $R^2$ in Table 8.2 give the confidence to the equations used in this chapter. Predictions based on the values of the parameters R and S derived with Equation 3.2, may therefore be considered as reliable, especially for periods that are within the experimental time spans.

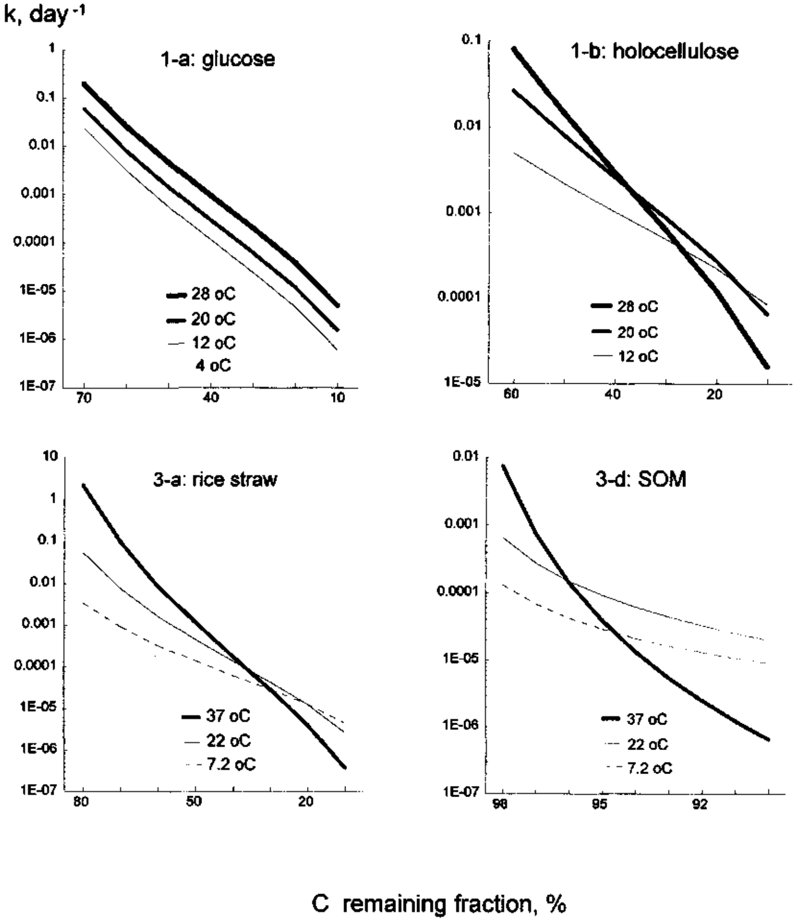

**Figure 8.7** Relationship between actual relative mineralization rate (k, in logarithmic scale) and fraction of remaining C for some cases of Table 8.2.

### *8.5.2 Arrhenius equation*

The finding that in most cases the Arrhenius plots for the description of the temperature effect on mineralization in soils were not perfect (Figure 8.3), may be due to the fact that such a relationship was originally proposed for elementary chemical reactions (Stone and Morgan, 1990). This type of reactions concerns only one step of product formation and follows the principle of first-order kinetics. In contrast, mineralization in soils involves far more than one step, and does not follow simple first-order kinetics with a single rate constant, as concluded in Chapters 1 and 2. Deviations from the Arrhenius relationship have also been observed in experiments on N and S mineralization by Ellert and Bettany (1988), and Nicolardot et al. (1994).

### *8.5.3 Diminishing temperature effects over time*

The model calculations indicate that the effect of temperature on mineralization rate in the soil of materials such as cellulose, plant residues and existing SOM, in other words, of all materials that are not as simple as glucose, declines over time, and that the decline is more remarkable in the beginning than later (Figures 8.5 and 8.6). In principle, the temperature effect may even become negative in the long run. This has indeed been observed in some experiments. For example, Sorensen (1981, Case 2 in Table 8.2) found that the remaining quantities of added cellulose at 10 and 20 °C were still different after 30 days (52 and 44%, respectively), but they were the same after 90 days (Case 2-b in Figure 8.3). In another soil from the same experiment (Case 2-c in Table 8.2), 62 and 50% remained after 30 days at 10 and 20 °C, respectively, while after 90 days 40% was found at 10 °C and 42% at 20 °C. Pal et al. (1975, Case 3 in Table 8.2) observed remaining fractions of rice straw of 54% at 22 °C and of 55% at 37 °C after 30 days, and of 41% at 22 °C and 51% at 37 °C after 120 days (Case 3-b in Table 8.2). In a recent publication De Neve et al (1996) reported that the remaining quantity of leaf-blades of cauliflower in an incubation trial was higher at 5.5 °C than at 16 °C during the initial 4-5 weeks, but the difference disappeared after 5 weeks, and thereafter the substrate remained less at 5.5 °C than at 16 °C.

Such phenomena can also be seen from the reduced gap or reversed order in decomposability of substrates at equal quantity in course of mineralization (Figure 8.7). Furthermore, the trend of vanishing and even reversed temperature effects appears also from the values of $t_{Q10=1}$ or $t_{f10=1}$ (Table 8.2), although the predictions are surely prone to variation. The most important and meaningful conclusion is that the temperature effect on mineralization is not lasting.

The decline of the temperature effect on mineralization must be the result of the processes underlying mineralization, involving chemical, physical, and, probably the most important, microbially mediated biochemical reactions (Ross, 1989), which so far are not understood very well (Buurman, 1994). The processes include a sequence of breakdown of primary structures of substrates and complex organic molecules, conversion of organic molecules into $CO_2$, microbial products, and other organic compounds, association of organic molecules with the inorganic soil matrix, etc. Consequently, the remaining substrate consists of a mixture of primary and secondary components, that undergo different processes. Temperature may affect the various processes in different degrees, and hence the speed at which the resistance of the remaining organic material increases over time is different for $T_2$ and $T_1$. At $T_2$, the substrate may soon become more resistant than at $T_1$, and the difference in decomposability increases over time. As a consequence, the substrates that are compared in the calculation of $\mathbf{Q_{10}}$ are not identical.

For glucose, the processes and steps involved in mineralization may be simpler than for the other substrates. Experimental results from Ladd et al. (1992), Saggar et al. (1994), and Van Veen et al. (1985), suggest that all original glucose has been converted after a very short period (1-3 days under normal conditions). Such a period may be too short to create divergent situations, and it is that uniformity that may make the temperature effect more constant than in the case of complex materials like plant residues.

### *8.5.4 Consequences and validity of the presented results*

Because of the decline over time of the temperature effect on C mineralization in soils, the concepts of $\mathbf{Q_{10}}$ and $\mathbf{f}$ (or $\mathbf{f_{10}}$) result in systematic errors (overestimation) of predicted mineralization in soils at a raised temperature, if the trials from which the values of $\mathbf{Q_{10}}$ or $\mathbf{f}$ are derived lasted much shorter than the time span of predictions. This awareness may improve the understanding of long-term consequences of the green-house effect on soil organic-matter dynamics.

In this chapter only temperature variations in the same soils were examined and discussed. If temperature effects of geologically different locations are compared, the effects of soil properties and environmental conditions may be confounded with temperature effects. For instance, Jenkinson and Ayanaba (1977) compared ryegrass mineralization data of a ten-year field trial in England (mean annual temperature of 9 °C) with those of a two-year field trial in Nigeria (mean annual temperature of 27 °C). They found that the effect of the different temperatures, as expressed by **f**, was constant. The persistence of the temperature effect may be related to different soil properties and external conditions such as moisture at the two sites, and that may have interfered with the temperature effect.

Since the effect of temperature on C mineralization is process-related, confirmation of the model predictions and identification of responsible processes by experiments are absolutely needed. In this respect, long-term experiments under controlled conditions would be very valuable.

## Chapter 9

# General discussion and conclusions

## 9.1 Modelling as a tool in soil organic matter research

Models are simplified representations of parts of reality. The simplification may be done in various ways and to different degrees, depending on the purposes of modelling, the types and resolutions of available data, the limits set by theoretical knowledge and by the feasibility of the implementations in practice. This may explain the fact that, in regard to organic matter mineralization, several types of models have been proposed so far, as was shown in Chapters 2 and 3. They differ in the treatment of incoming and existing organic matter, in the demarcation of components and processes, in the inclusion of external factors influencing mineralization, and in the mathematical descriptions of relevant processes.

Such differences determine the processes and state variables that are included in models, and the conditions, in terms of the types of substrates, time scales, ranges of external conditions, etc. For instance, for the purpose of making prediction of the future of SOM content in behalf of extension services, a model will be regarded as acceptable as long as it is able to do that job no matter how it works.

The task of scientific research is, by using available evidences and information, to deepen the insight in the systems under study, to find answers to questions, and to widen the scope for solving new problems. This implies that models should not only be able to fit existing evidence and to produce acceptable predictions, but also, more importantly, to provide additional information which is not directly 'visible' in the existing data and information, and to extend the available evidences beyond the current reach (e.g. extrapolations over time). In this sense, models for scientific research should be 'creative'. Models should therefore be able to provide unbiased quantitative information.

However, the use of models in scientific research can not exceed the boundaries set by the simplifications in the models. In other words, the 'black boxes' made up of simplifications can not be penetrated by their corresponding models. In this sense, models are not creative. Moreover, the reliability of results and conclusions from model studies depends strongly on the correctness of simplifications for specific situations. This is because models are often applied into situations different from those in which they were developed. With respect to organic matter mineralization, the difference can refer to types of substrates and soils, environmental conditions, and time spans. Detection of deviations of model outputs from reality will in turn help to improve the applicability of models.

## 9.2 Experimentation and modelling

Experimental observations, like all the data used in this thesis, provide first-hand evidence on the behaviour of the system under study. Individual experiments, however, do not usually provide a continuous flow of data, and the supplied information is confined within the boundaries of experiment designs with regard to time spans and relevant conditions. Comparisons of data from different sources are difficult. By contrast, modelling studies are able to reproduce the results of individual experiments, and more importantly, to extend the significance of experiments beyond their domains. Models may generalize the meaning of individual experiments, and after that the integrated results can be used in further studies. This can effectively widen the scope of processes being examined, and guide designs of new experiments. For instance, the decline over time of the temperature effect on C mineralization in soils, cannot easily be derived from the experimental data used in Chapter 8 without help of the model. Chapter 5 can be seen as an example of the integration of observations from different sources.

New insights and understandings that are obtained from the extension and integration of experimental observations by modelling, require confirmation. New experiments can be designed for this purpose. By this, models can be further tested, modified and developed. By such an interactive and iterative procedure of experimenting and modelling, the reality may increasingly be better understood.

## 9.3 The use of published experimental data in modelling

Organic matter mineralization is a process which is affected by substrate properties, soil properties, and environmental conditions. When these factors differ from case to case, the rate of mineralization varies. To assess the effects of substrate, soil and environment, many experiments on organic matter mineralization have been conducted.

These experiments have proved their values as is manifested by the fact that some of the results and data have repeatedly been cited to confirm or explain the evidence from later studies. They have also been of great value in the modelling studies of this thesis. The diversity in factors and conditions represented by the data, provided excellent opportunities for testing available models, finding their limitations, and proposing and testing the new model. Moreover, it was possible to detect some general trends and phenomena in these data, and to study by generalization and integration of the data the functions of single factors. It was the diversity in the data that helped to find general clues and to draw general conclusions.

## 9.4 The models evaluated in this study

The four models tested with data in this study (Chapter 2) represent the mathematical formulations of C mineralization that have had the widest influence. The recognition of the inadequacy of mono-component models with constant k resulted in the proposition of multi-component models and of mono-component dynamic-k models with a dynamic k.

The 'excellent' goodness of fit to measurements of multi-component models with only two components, as found in many reports, has strongly contributed to their wide adoption. However, the test in Chapter 2 indicates that such an approach may convey confusing messages, such as different sizes of components under varying conditions, and systematic deviations from measured data in long-lasting experiments. This is mainly caused by the fact that k is regarded as constant for each component, which proved incorrect in Chapter 3. Nevertheless, two-component models can be used for predictions within limited time spans.

The proposal by Kolenbrander and Janssen to describe K or k in the first-order equation as a function of time, proved to be a promising approach in modelling and understanding of the processes of mineralization, though the test showed unsatisfactory results with the relationship between K or k and time they had formulated. Their basic ideas pointed to the direction of the relationship of K to t that was found in Chapter 3.

The complex multi-component models with transformations of C from one organic compound into others can be seen as the most complete integrations of the current knowledge on C mineralization and transformations. The correctness of such models relies heavily on the way the models define mathematically described individual processes and their mutual relations. It may take a long time before these models will fully have been validated, and only after that they can reliably be applied in practice.

## 9.5 Characteristics of the model developed in this study and its applications

The major characteristics of the model developed in this study (Chapter 3) are:

1) The model is based on the principle of first-order kinetics. A substrate is treated as a whole, and no assumptions are needed on the composition of the substrates.

2) The pivot of the model is the linear relationship between log(K) (the average relative mineralization rate between t=0 and t) and log(t). The process of mineralization is characterized by R (the average relative mineralization rate during the first time unit) and S (the speed of decrease of K over time).

3) All other relevant model equations are derived mathematically, and do not require any assumptions. They include k (the actual relative mineralization rate), $Y_t$ (the remaining quantity of substrate), and the incorporation of **f** (temperature correction factor).

4) The calibration of the model parameters R and S requires data on the quantities of the substrate that are remaining in the course of time. It is not necessary that the experiments are carried out under constant environmental conditions. If field experiments are used sampling should be at the same time of the year. For common organic materials such as straw, the effect of varying temperatures under field conditions can be incorporated in the calculation procedure.

5) The model can handle practically all substrates ranging from chemically simple ones like glucose and cellulose, via plant materials like straw and roots, to SOM, and it can be applied under controlled as well as under field conditions. In principle, the model can be used in all soils and climates.

Chapter 3 shows that the model is simple in its basic expressions (Equations 3.1 and 3.2). It is shown in Chapter 4 that it can easily be tested with data from conventional experiments, thus facilitating a reliable application.

Once the model parameters R and S have been assessed, the model can be used to study the changes of both quantity ($Y_t$) and quality (K or k) of a substrate undergoing mineralization for extended time spans. For example, the dynamics of SOM can be predicted following periodic additions of different materials, and the consequences of different scenarios can be compared (Chapters 6 and 7).

The results in Chapter 8 indicate the high potential the model has for studies of the effects on mineralization of single factors, such as temperature, soil texture and pH. The model can be of great help in detecting phenomena which are not directly visible in the experimental data.

Because organic matter mineralization is fully characterized by the two parameters, R and S, the model is a handy tool to compare experimental data from different sources, in terms of types of substrates, soils, external conditions, and durations of experiments. On the basis of such comparisons, data can be extrapolated, as was done in Chapter 5. That capability makes the model very suited to study, by (re)interpretation of available data, the effects of e.g. clay content, pH, dry season, etc.

Since the processes of N, P and S mineralization follow C mineralization, the model may be extended to included these processes, e.g. in the way it was done by Janssen and Noij (1996), and Noij et al. (1993). This model is not suited to provide information on C transformation from one organic compound into others.

## 9.6 The general phenomena on organic matter mineralization found in this study

It is found in Chapter 5 that the difference in mineralization rates among substrates differing in initial decomposability or among similar substrates but under different conditions, declines over time. The initial ranking of different substrates by mineralization rates may even reverse in the long run. The same holds for the ranking of the conditions that influence mineralization.

It was found in Chapter 6 that under the conditions of northern China, roots are the most effective material in accumulation of SOM, followed by straw, FYM and green manure. Using the annual rate of mineralization as a quality index of SOM that a high rate indicates a high quality, it may be expected that green manure forms SOM of the highest quality, followed by FYM, straw and roots.

It was found in Chapter 8 that the effect of temperature on C mineralization declines over time. In the long run the difference in mineralization rates at different temperatures may disappear, and under some conditions, the long-term mineralization rate at a low temperature may exceed that at a high temperature. Recently published experimental evidence confirms this (De Neve et al., 1996). It was found that Arrhenius equation only holds for glucose, and not for substrates like plant materials and SOM. Both $\mathbf{Q_{10}}$ and $\mathbf{f_{10}}$ are not constant, but decrease over time.

The common feature of these findings is that they are all time-related. They can improve our understandings on the process of mineralization, and rectify some of our long-term expectations, such as the enhanced green-house effect, which are based on short-term evidences.

## 9.7 The prospects of SOM status in northern China

In view of the limited and still shrinking arable land resources, and the still growing population, increasing the per ha grain production is and will be the top priority of arable farming in China. For that task, maintenance and further improvement of SOM status in northern China is one of the fundamental requirements.

Intervention in SOM dynamics is possible at the input side. In this region roots and stubble left in the field have probably been the key input factor contributing to the buildup and maintenance of SOM, in particular in places where SOM contents are low (Chapters 6 and 7). Such awareness is important, because the inputs in the form of roots and stubble are closely related to grain yield levels, and little influenced by farming management. Moreover, they determine the basic SOM content when no extra inputs are given. Therefore, it is meaningful to try to improve SOM content by methods that increase crop yield, such as the use of chemical fertilizers in fields where nutrient availability limits crop yields.

In northern China, it is very important to use the available organic resources, like green manure, straw and FYM, as efficiently as possible. Because of the low efficiency of green manure in accumulating SOM, direct return of green manure into the field should be replaced by indirect use via animals. On the other hand, straw should directly be returned wherever and whenever possible, but if that is not feasible, it can be returned after having been composted or used as fodder. Improvement in the quality of FYM in terms of organic matter content, e.g. by reducing the use of soil for bedding and in compost piles, will make their use more attractive and profitable. Removing straw from fields by burning should not be promoted, because it is a great waste of organic resources, but may be inevitable under some conditions.

In the current system of land-use and land-ownership, the management of individual farmers is heavily driven by short-term economical considerations. As a result, the long-term consequence of the currently reduced use of organic fertilizers on SOM status can easily be ignored. On the other hand, any suggestions or advices given by scientists to increase the use of organic manure for the long-term benefit of soil fertility and productivity, must first comply to the practical considerations of individual farmers, because it is the farmers who have to make their day-to-day life out of the land. In this sense, the knowledge and awareness from both scientists and farmers is only one part of the entire solution to the maintenance and further improvement of SOM status in arable land in this region. The others are social, economical and political factors, because these factors determine whether or not, and to what extent the recommended management derived from such knowledge and awareness can be realized in practice. Meanwhile, it should be kept in mind that a long-term effort is needed for a successful improvement of SOM content.

China needs a cropping system that is high-yielding and sustainable. Further improvement of SOM content is one of the fundamental prerequisites. Soil scientists should be the pioneers in understanding the consequences of different management strategies, and in exploring feasible solutions. Farmers should be encouraged by social, economical and political means to pay more attention to long-term soil fertility, to the benefit of both farmers and the entire society.

# Summary

Northern China, mainly referring to Huang-Huai-Hai Plain in this thesis, is the most important region for cereal production in China. The dominant cropping system consists of two crops, winter wheat followed by summer maize. The average annual grain yield of the two crops was around 7500 kg $ha^{-1}$ in the early 1990s. This yield level has to be raised to meet the demands for food by the increasing population. Soil fertility was traditionally maintained and improved mainly by various types of organic fertilizers. The soil organic matter (SOM) content in arable land is commonly below 10 g $kg^{-1}$, which is considered insufficient for sustaining grain production at a high level.

Since the early 1980s, organic fertilizers as the main input of nutrients have been replaced by chemical fertilizers. Organic manuring has become a vanishing practice. Quantitative predictions of the consequences, i.e. the changes in SOM content in the long run, are needed for designing farming managements directed towards a sustainable soil fertility and a high grain production.

The primary objectives of this study are (i) to identify key factors in SOM dynamics in arable land of northern China, (ii) to predict long-term SOM dynamics under various scenarios, and (iii) to give suggestions for the most efficient use of the available organic resources.

Relevant experimental data and other information were collected from the region. Modelling was chosen as a tool for the required systematic and quantitative study of the data.

Models have to be tested before they are applied in situations differing from those from which the models were proposed. Therefore, more data from international journals were collected. The experimental data were used to test a number of existing models (Chapter 2), to derive and test a new model (Chapters 3 and 4), to study general characteristics of organic matter mineralization (Chapters 5, 6 and 8), and to analyze the impact of current farming practises on SOM dynamics in northern China (Chapter 7).

In Chapter 2 four types of existing models were examined. The results showed that simple mono-component models with a constant relative mineralization rate are inadequate, because the relative mineralization rate is not constant, but decreases over time. In the literature several mathematical functions have been proposed to describe the decrease of the relative mineralization rate. Two of them were tested. They proved to give no good agreement with experimental results of other sources than the ones that had been used for the derivation of the two functions.

Next a model was tested in which it is assumed that organic materials consist of two components. Both components were assumed to mineralize into $CO_2$, but at different rates. The two-component model performed very well, but a weak point was that external conditions proved to affect the partitioning of a substrate, as calculated by the model from the experimental data. As a consequence the same substrate was partitioned into components in different ways under different conditions. Moreover the model was not suitable for extended time spans.

Finally multi-component models were discussed. In these models organic compounds may be transformed into others compounds as well as into $CO_2$. It was concluded that such models require many input data and therefore cannot yet easily be applied in practice at present. They have not been tested in this study.

In Chapter 3 the average relative mineralization rate (K) from time zero to time t was calculated for a substrate as a whole, applying the principle of first-order kinetics. It was found that log(K) is a linear function of log(t) under constant environmental conditions: $\log(K) = \log(R) - S * \log(t)$, or $K = R * t^{-S}$. In this expression R (dimension $t^{S-1}$) represents the relative mineralization rate during the first unit of time, and S (dimensionless and $1 \geq S \geq 0$) is the speed at which K decreases over time. Hence, S denotes the speed of 'aging' of the substrate. The quantity of a substrate ($Y_t$) that is remaining at a certain time t can be calculated by: $Y_t = Y_0 * \exp(-R * t^{1-S})$, in which $Y_0$ is the substrate quantity in the beginning ($t = 0$). The actual relative mineralization rate at time t (k), proved related to K according to: $k = (1 - S) * K$. In case of varying temperatures, the mineralization time (t) is multiplied by a temperature correction factor (f).

This model proved to be valid for substrates ranging from chemically simple ones, like glucose and cellulose, via plant materials like straw and roots to SOM. It can be applied under controlled as well as under field conditions (Chapter 4).

With the help of the model developed in Chapter 3, the mineralization dynamics of both incorporated organic substrates and existing soil organic matter (SOM) were studied (Chapter 5). Experimental data collected from 36 articles and reports covered many types of substrates and environmental conditions, and for each set of data R and S were calculated. The results indicated that both R and S were affected by substrate characteristics as well as by environmental conditions. The values of S proved positively related to those of R. As a consequence, initially existing differences in relative mineralization rates gradually disappear, and it is even possible that the substrates mineralizing most quickly in the beginning become the most stable ones after a certain period of time. This implies that the differences in remaining quantities tend to fade away in the long run. The observed trends were ascribed to (1) biochemical transformations of organic compounds; (2) concentration of relatively resistant components; (3) physical, chemical or physico-chemical protection of (transformed) organic compounds. The conclusions are thought to be valid irrespective the differences in the initial K are caused by differences in the chemical composition of the substrates or by different environmental conditions.

The efficiencies of various organic materials, including roots, straw, farmyard manure (FYM) and green manure, in accumulating and maintaining soil organic matter (SOM) in the long run were compared in Chapter 6. The parameters of the newly proposed model were calibrated to the data collected from northern China. It was predicted that when only roots form that input, SOM accumulation at steady state is 6.8 times the annual input of organic matter. Under the conditions of northern China, roots are 3, 5 and 7 times as efficient as straw, FYM and green manure, respectively. The calculated fraction of steady-state SOM that is annually mineralized varies from 5.8% to 25.6 %, depending on the type of materials from which SOM has been built up. It was further concluded that roots play a key role in the SOM budgets of arable land in northern China.

The required input necessary to maintain SOM content at a given level in this region, remains essentially constant if the input consists of roots, but it increases if the input consists of green manure, straw and FYM. This is due to the replacement of existing SOM by SOM from these materials. When SOM changes in composition, it changes in mineralization rate too, leading to a change in the rate of nutrients release from SOM. From the calculations it can be derived that it is better to use green manure crops as fodder and after that as FYM than to plough them in directly. On the other hand, straw can best be ploughed in directly, but if that is not possible it may be used as fodder or be composted. The high efficiency of roots in SOM accumulation makes it possible to increase SOM content by increasing the yield and related root production by the use of chemical fertilizers and irrigation.

In Chapter 7, the model was applied to predict the long-term dynamics of both quantity and quality of SOM in arable land in northern China. Two yield levels were considered, the current mean yield of 7500 kg $ha^{-1}$ for maize plus wheat, and the potential yield of 15000 kg $ha^{-1}$. Three scenarios for organic inputs into the soil were formulated: (1) only roots and stubble; (2) as (1) plus the direct return of one third of the straw that is produced; (3) as (2) plus the application of FYM made with another one third of the straw that is produced.

It was found that under the three scenarios SOM contents can be maintained at 10, 13 and 15 g $kg^{-1}$ in the case of the mean yield level, and at 15, 19 and 21 g $kg^{-1}$ in the case of the potential yield level. Depending on whether the present SOM contents are below or above these 'steady-state' levels, they will increase or decrease. The absolute annual change in SOM content is related to the difference between the present and the final SOM content, and it will become smaller over time, sharply diminishing in the beginning and slowly at a later stage.

As a measure of SOM quality, the fraction that is mineralized per year was taken. Calculations show that the quality of SOM improves with the magnitudes of the annual organic inputs. Hence, in most arable fields in northern China, both the quantity and the quality of SOM may rise upon an increase in annual crop production, e.g. as a result of the use of chemical fertilizers. Similar positive effects on SOM will be brought about by returning (a part of) the straw, either directly by leaving it in the field or indirectly by applying it as FYM. Theoretically, the direct return of straw is more efficient for improvement of both SOM content and SOM quality than the indirect application, but it may be less attractive for the farmer because it takes away the use of straw as fodder.

In Chapter 8 the developed model was applied, using relevant experimental data, to examine the changes over time of the effect of temperature on organic matter mineralization. The effects were described by the Arrhenius equation, by $\mathbf{Q_{10}}$ being the increase in K per 10 °C, and by $\mathbf{f_{10}}$ being the ratio of the time periods needed for a certain mineralization at temperatures differing by 10 °C. The results indicate that the temperature effect on relative mineralization rates continuously decreases. The Arrhenius equation held for glucose, but not for other materials such as cellulose, plant materials and soil organic matter. Both $\mathbf{Q_{10}}$ and $f_{10}$ were found to decrease over time for cellulose, plant materials and existing soil organic matter, but not for glucose. The decrease in the effect of temperature on mineralization was more remarkable in the beginning than later. In some situations, the effect of temperature on mineralization rate was positive initially, but became negative in the long run. The results may help to improve the understanding of the processes affected by an increase in temperature as a consequence of an enhanced green-house effect, and to possibly rectify the long-term expectations of organic C dynamics in soil.

Chapter 9 discusses the qualities of models as a tool in scientific research, and the great value of published experimental data in modelling studies. Emphasis is put on integrating data from different sources, and uncovering information which is not directly 'visible' from the experimental evidence. The maintenance and improvement of SOM content in northern China require long-term efforts. Soil scientists should be the pioneers in understanding the consequences of different management strategies, and in exploring feasible solutions. Farmers should be encouraged by social, economical and political means to pay more attention to long-term soil fertility. This will be to the benefit of both farmers and the entire society.

# Samenvatting

Noord China, waaronder in dit proefschrift vooral de Huang-Huai-Hai vlakte wordt verstaan, is het belangrijkste gebied voor graanproductie in China. Het overheersende teeltsysteem bestaat uit twee gewassen, namelijk wintertarwe gevolgd door zomermais. De gemiddelde jaarlijkse korrelopbrengst van de twee granen lag rond 7500 kg $ha^{-1}$ in het begin van de negentiger jaren. De opbrengsten zullen hoger moeten worden om aan de vraag naar voedsel van de groeiende bevolking te kunnen voldoen. De bodemvruchtbaarheid werd traditioneel onderhouden en verbeterd door voornamelijk verschillende typen organische meststoffen. Het gehalte aan organische stof in bouwland is gewoonlijk minder dan 10 g $kg^{-1}$ en dat wordt beschouwd als onvoldoende voor een duurzame graanproductie op een hoog niveau.

Sinds begin jaren tachtig zijn organische meststoffen vervangen door kunstmest als voornaamste aanvoer van nutriënten. De praktijk van organische bemesting is aan het verdwijnen. Kwantitatieve voorspellingen over de consequenties daarvan, i.e. over veranderingen in het gehalte aan organische stof op de lange termijn, zijn nodig om maatregelen te kunnen treffen die leiden naar een duurzame bodemvruchtbaarheid en hoge graanprodukties.

De primaire doelstellingen van deze studie zijn (i) de sleutelfactoren te identificeren van de organische-stofdynamiek in het bouwland van Noord China, (ii) de lange-termijn organische-stofdynamiek onder verschillende scenario's te voorspellen, en (iii) suggesties te doen over het meest efficiënte gebruik van de beschikbare organische materialen.

Relevante experimentele gegevens en andere informatie uit het gebied werden verzameld. Voor de noodzakelijke systematische en kwantitatieve bestudering van de gegevens werd gebruik gemaakt van modellen.

Modellen moeten worden getoetst voordat ze kunnen worden toegepast in situaties die anders zijn dan de omstandigheden waarin ze werden ontwikkeld. Daarom werden ook gegevens uit internationale tijdschriften verzameld. De experimentele gegevens werden gebruikt om een aantal bestaande modellen te toetsen (Hoofdstuk 2), om een nieuw model uit af te leiden en te valideren (Hoofdstukken 3 and 4), om algemene karakteristieken van de mineralisatie van organische stof te bestuderen (Hoofdstukken 5, 6 and 8), en om de invloed van de huidige landbouwpraktijk op de organische-stofhuishouding in Noord China te analyseren (Hoofdstuk 7).

In Hoofdstuk 2 werden vier typen bestaande modellen onderzocht. De resultaten toonden aan dat eenvoudige mono-component modellen met een constante relatieve mineralisatiesnelheid niet geschikt zijn om de mineralisatie te beschrijven, omdat k niet constant is maar afneemt met verloop van tijd. Om de afname van de relatieve mineralisatiesnelheid in de tijd te beschrijven zijn in de literatuur verschillende wiskundige functies voorgesteld. Twee daarvan werden getoetst. Ze bleken geen goede overeenstemming te geven met de experimentele resultaten van andere proeven dan die gebruikt waren voor de afleiding van de functies.

Vervolgens werd een model getoeststst waarin wordt aangenomen dat organische materialen uit twee componenten zijn opgebouwd. Beide componenten werden verondersteld te mineraliseren tot $CO_2$, maar met verschillende snelheden. Het twee-componentenmodel voldeed uitstekend, maar een zwak punt was dat de externe proefomstandigheden van invloed bleken te zijn op de door het model uit de experimentele gegevens berekende verdeling van de componenten in het substraat. Dat leidde er toe dat hetzelfde substraat bij bijvoorbeeld verschillende condities op verschillende wijzen in componenten werd verdeeld. Bovendien was het model niet geschikt voor perioden van meer dan 10 jaren.

Als laatste werden multi-component modellen besproken. In deze modellen kunnen de organische bestanddelen zowel in andere organische bestanddelen als in $CO_2$ worden omgezet. Er werd geconcludeerd dat zulke modellen zeer veel invoergegevens vragen en daarom thans nog niet gemakkelijk in de praktijk kunnen worden toegepast. Ze werden in dit onderzoek niet getoetst.

In Hoofdstuk 3 werd de gemiddelde relatieve mineralisatiesnelheid (K) tussen de tijdstippen nul en t berekend voor een substraat in zijn geheel, gebruik makend van de principes van eerste-order kinetiek. Er werd gevonden dat log(K) een lineaire functie is van log(t) onder constante proefomstandigheden: $\log(K) = \log(R) - S * \log(t)$, ofwel: $K = R * t^{-S}$. Hierin is R (dimensie $t^{S-1}$) de initiële relatieve mineralisatiesnelheid, d.w.z. de relatieve mineralisatiesnelheid gedurende de eerste tijdseenheid, en is S (dimensieloos en $1 \geq S \geq 0$) de snelheid waarmee K afneemt in de tijd., S geeft dus de snelheid van 'veroudering' van het substraat aan. De hoeveelheid substraat ($Y_t$) die overblijft op zekere tijd t kan worden berekend met: $Y_t = Y_0 * \exp(-R * t^{1-S})$, waarin $Y_0$ de hoeveelheid substraat is aan het begin ($t = 0$). Tussen K en de actuele relatieve mineralisatiesnelheid ten tijde t (k), werd mathematisch het volgende verband gevonden: $k = (1 - S) * K$. In geval van variërende temperaturen wordt de mineralisatietijd (t) vermenigvuldigd met een correctiefactor (f) voor de temperatuur.

Dit model bleek geldig voor substraten uiteenlopend van chemisch eenvoudige verbindingen zoals glucose en cellulose, via plantaardige materialen zoals stro en wortels tot organische stof in de bodem. Het kan zowel onder gecontroleerde als onder veldomstandigheden worden toegepast (Hoofdstuk 4).

Met behulp van het model zoals ontwikkeld in Hoofdstuk 3 werd de mineralisatie-dynamiek van zowel ondergewerkte organische substraten als de bestaande organische stof in de bodem bestudeerd (Hoofdstuk 5). Experimentele gegevens afkomstig van 36 artikelen en rapporten bestreken veel typen substraten en proefomstandigheden, en voor iedere serie gegevens werden R en S berekend. De resultaten lieten zien dat beide, R en S, zowel van de eigenschappen van het substraat als van de proefomstandigheden afhingen. De waarden van S bleken positief gerelateerd te zijn aan die van R. Ten gevolge hiervan verdwenen initieel bestaande verschillen in relatieve mineralisatiesnelheid geleidelijk. Het was zelfs mogelijk dat de substraten die in het begin van de mineralisatie het snelst gemineraliseerd werden na een zekere tijd het meest stabiel waren. Dit heeft tot gevolg dat de verschillen in overblijvende hoeveelheden substraat op den duur wegebben. De gevonden tendenzen werden toegeschreven aan (1) biochemische transformaties van organische bestanddelen; (2) "indikken" van relatief resistente componenten; (3) fysische, chemische en fysisch-chemische bescherming van (getransformeerde) organische bestanddelen. De conclusies worden geacht te gelden onafhankelijk van de vraag of de beginverschillen in K veroorzaakt worden door verschillen in de chemische samenstelling van de substraten, of door verschillen in de proefomstandigheden.

In Hoofdstuk 6 werd voor een aantal organische materialen, te weten wortels, stro, stalmest en groenbemesters, de doelmatigheid vergeleken waarmee ze op lange termijn de organische stof in de bodem kunnen opbouwen en onderhouden. De parameters van het nieuwe model werden gecalibreerd met de gegevens die in Noord China waren verzameld. Voorspeld werd dat wanneer de jaarlijkse aanvoer van organisch materiaal uitsluitend uit gewaswortels bestaat het gehalte aan organische stof in de bodem in een stationaire toestand 6.8 keer zo groot is als die aanvoer. Onder de omstandigheden van Noord China zijn wortels respectievelijk 3, 5 en 7 keer zo efficiënt als stro, stalmest en groenbemesters in het opbouwen van organische stof in de bodem. De berekende fractie van de organische stof in de bodem die in stationaire toestand jaarlijks gemineraliseerd wordt, loopt uiteen van 5.8% to 25.6 %, afhankelijk van het type materiaal waaruit de organische stof in de bodem wordt opgebouwd. Voorts werd geconcludeerd dat gewaswortels een sleutelrol vervullen in de organische-stofbalans van bouwland in Noord China.

De hoeveelheid organisch materiaal die aangevoerd moet worden om het gehalte aan organische stof in de bodem op een zeker niveau te houden in dit gebied, blijft volgens de berekeningen vrijwel constant indien de aanvoer uit wortels bestaat, maar neemt toe als de aanvoer bestaat uit groenbemesters, stro of stalmest. Dit is een gevolg van de vervanging van de bestaande organische stof in de bodem door organische stof opgebouwd uit deze materialen. Wanneer de organische stof van samenstelling verandert, verandert de mineralisatiesnelheid ervan ook, en dat leidt weer tot een verandering van de snelheid waarmee nutriënten eruit vrijkomen. Uit de rekenresultaten kan worden afgeleid dat het beter is groenbemesters als veevoer en vervolgens als stalmest te gebruiken dan ze direct onder te ploegen. Stro daarentegen kan het best direkt worden ondergeploegd, maar mocht dat niet mogelijk zijn dan kan het worden gebruikt als veevoer of het kan worden gecomposteerd. De goede eigenschappen van wortels m.b.t. de opbouw van organische stof in de bodem maken het mogelijk het gehalte aan organische stof te doen toenemen door de gewasopbrengst en daarmee verbonden de wortelproduktie te verhogen door toepassing van kunstmest en irrigatie.

In Hoofdstuk 7 werd met behulp van het model de lange-termijn dynamiek van de hoeveelheid en de kwaliteit van organische stof in bouwland in Noord China voorspeld. Twee opbrengstniveaus werden vergeleken: de huidige gemiddelde opbrengst van 7500 kg ha$^{-1}$ voor mais plus tarwe, en een potentiële opbrengst van 15000 kg ha$^{-1}$. Drie scenario's voor organische-stofaanvoer werden geformuleerd: (1) alleen wortels en stoppelresten; (2) als (1) plus direkt onderwerken van een derde van het stro dat wordt geproduceerd; (3) als (2) plus toediening van de stalmest die geproduceerd kan worden wanneer een derde van het stro aan de dieren wordt gevoerd. Er werd gevonden dat onder de drie scenario's het gehalte aan organische stof in de bodem kan worden gehandhaafd op 10, 13 en 15 g kg$^{-1}$ bij het gemiddelde opbrengstniveau, en op 15, 19 en 21 g kg$^{-1}$ in het geval van het potentiële opbrengstniveau. Afhankelijk van de vraag of ze nu lager of hoger dan deze 'stationaire-toestand' niveaus zijn, zullen de gehalten aan organische stof in de bodem stijgen of dalen. De absolute jaarlijkse verandering in het gehalte houdt verband met het verschil tussen het huidige en uiteindelijke gehalte. Die verandering zal eerst snel zijn en later langzaam kleiner worden.

De fractie die jaarlijks wordt gemineraliseerd werd gebruikt als een maat voor de kwaliteit van de organische stof in de bodem. De berekeningen leerden dat de kwaliteit toeneemt met de grootte van de jaarlijkse aanvoer van organisch materiaal. Daarom zal in het merendeel van het bouwland in Noord China zowel de hoeveelheid als de kwaliteit van de organische stof toenemen, als de graanproduktie stijgt t.g.v. bij voorbeeld het gebruik van kunstmest. Soortgelijke positieve effecten kunnen teweeggebracht worden door (een deel van) het stro aan de grond toe te voegen, hetzij direct door het in het veld achter te laten of indirect door het als stalmest aan te wenden. Theoretisch is voor de verbetering van de hoeveelheid en de kwaliteit van de organische stof in de bodem, de directe toepassing efficiënter dan de indirecte toepassing, maar voor de boer is de directe toepassing minder aantrekkelijk omdat die hem de mogelijkheid ontneemt het stro als voer voor het vee te gebruiken.

In Hoofdstuk 8 werd het ontwikkelde model toegepast om, met gebruik van relevante experimentele gegevens, de verandering in de tijd van het effect van de temperatuur op de mineralisatie van organische stof na te gaan. De effecten werden beschreven met de Arrhenius-vergelijking, met $Q_{10}$ die de toename van K per 10 °C aangeeft, en met $f_{10}$ die gedefinieerd is als de verhouding van de tijdsduren die bij twee temperaturen met een verschil van 10 °C nodig zijn om eenzelfde mineralisatie te doen plaats vinden. De resultaten wezen uit dat het temperatuureffect op de relatieve mineralisatiesnelheid met verloop van tijd voortdurend daalt. De Arrhenius-vergelijking ging wel op voor glucose, maar niet voor andere materialen zoals cellulose, plantaardig materiaal en organische stof in de bodem. Ook $Q_{10}$ en $f_{10}$ bleken af te nemen in de tijd voor cellulose, plant materiaal en organische stof in de bodem, maar niet voor glucose. De vermindering van het effect van de temperatuur op de mineralisatie was in het begin meer uitgesproken dan later. In sommige situaties was het effect van de temperatuur op de mineralisatie aanvankelijk positief, maar werd het negatief op de lange termijn. De resultaten kunnen bijdragen tot een beter begrip van de processen die beïnvloed worden door een temperatuurstijging als gevolg van een versneld broeikaseffect en tot een mogelijke bijstelling van de lange-termijn verwachtingen over de organische-stofdynamiek in de grond.

Hoofdstuk 9 gaat in op de bruikbaarheid van modellen als instrument in wetenschappelijk onderzoek, en op de grote waarde van gepubliceerde proefresultaten voor modellenstudies. De nadruk wordt gelegd op de integratie van gegevens van verschillende bronnen, en op het 'ontsluieren' van informatie die niet direct 'zichtbaar' is in de proefresultaten. Het handhaven en verbeteren van het gehalte aan organische stof in Noord China vraagt lange-termijn inspanningen. Bodemkundigen dienen als eersten de consequenties van verschillende beheersmaatregelen te begrijpen, en haalbare oplossingen te verkennen. Boeren moeten met sociale, economische en politieke middelen worden aangemoedigd meer aandacht te besteden aan de bodemvruchtbaarheid op lange termijn. Dat zal zowel de boeren zelf als de gehele maatschappij ten goede komen.

# 有机质矿化的模型研究及中国北方农田有机质管理对策

## 摘要

位于中国北方的黄淮海地区是中国最重要的商品粮基地．冬小麦-玉米一年两作是目前主要的种植方式．九十年代初的平均年产量为 7500kg/ha．为满足日益增长的人口对粮食的需求，这一产量需进一步提高．在传统的耕作制度中土壤肥力的维持主要依靠各种有机肥料．目前大部分地区耕地土壤有机质含量不足 10g/kg，不足以维持作物的高产．八十年代以来土壤养分的补给以已有机肥转变为化肥，有机肥的施用已显著减少．为规划长远的高产粮食生产战略，土壤有机质的动态需要进行定量预测．

本论文的目的为：(1)确定中国北方(黄淮海地区)农田土壤有机质动态中的关键因子 (2)预测不同管理措施下土壤有机质的长期动态；(3)提出高效率利用现有有机物料的建议．有关的试验数据及资料均来自于这一地区．为进行这一系统的定量研究，模型研究为主要的研究方法．

当用于新的条件下时，模型首先需要进行检验．为此从国际刊物中收集了有关的试验数据．利用相关的数据检验了几个目前常用的模型 (第二章)，提出并检验了一个新的数学模型(第三，四章)，研究了有机物在土壤中分解的一般特点(第五，六，八章)，分析和预测了中国北方农田土壤有机质质量和含量的长期动态(第七章)．

第二章对四类有机质分解的数学模型进行了检验．结果表明简单的单组分常数相对分解速率模型不能描述相应的试验数据，因为试验数据表明相对分解速率不是常数，而随时间而降低．在文献中不同作者提出了几种不同的数学方程用于描述相对分解速率随时间的降低，其中的两个被检验．结果表明这两个模型都不能很好地拟合不同来源的试验数据．

第二章也检验了二组分模型．此类模型假定两个组分以不同的相对分解速率降解为二氧化碳．检验结果表明这一模型能很好地拟合试验数据．但其缺点是外界条件影响这两个组分的分组．所以，同一材料在不同条件下两个组分的大小不同．另外，此模型不适用于时间上的外延．另外，第二章对多组分模型进行了讨论．在这类模型中，有机化合物既转变为别的有机化合物，同时降解为二氧化碳．作者认为这类模型需要的参数量太多，因此目前难以在实际中应用．

在第三章应用一级反应动力学原理计算了有机物整体从零到某一时刻 (t) 的平均相对分组速率 (K)．作者发现在不变的环境条件下，log(K)和log(t)为一直线关系，即：$\log(K)=\log(R)-S*\log(t)$，或：$K=R*t$ ，其中 R (单位 $t^{S-1}$ )为第一个单位时间内的平

均相对分解速率；S（无单位）为 K 随时间的递减速度，或称为有机物的老化速度. 由此推倒出在任一时刻（t）有机物的残留量（$Y_t$）的计算方程：$Y_t = Y_0 * \exp(-R * t^{1-S})$，其中 $Y_0$ 为材料的加入量，并且进一步证明在任一时刻有机物的实际相对分解速率（k）与从零开始的平均相对分解速率（K）的关系为：$k = (1-S) * K$. 当温度变化时，其效应可通过一温度校正系数来调整时间.

第四章证明这一模型适用于各种有机物，包括化学结构简单的（如葡萄糖，纤维素），及复杂的（如植物材料和土壤有机质），既能用于控制的试验条件，也能用于田间条件.

在第五章应用这一新的模型对多种有机物料及土壤有机质的分解特性进行了探索. 试验数据来自从三十六篇文献，涉及多种有机物料及环境条件，对每组数据均计算出模型参数 R 和 S. 结果显示 R 和 S 既决定于有机物的性质，也决定于环境条件，并且发现 R 与 S 呈正相关关系. 因此，在分解初期表现出的相对分解速率上的差异将随时间而逐渐消失，甚至一定时间后在初始阶段分解较快的有机物反而变得较为稳定. 因此，从长远看初始阶段分解速度的差异将会消失. 导致这一现象的原因可能为：(1)有机化合物的转化；(2)相对难分解的组分的浓缩；(3)各种物理的，化学的，和物理-化学的保护作用. 作者认为这一结论既适用于不同的有机物料之间，同时也适用于相同的物料但不同的环境条件下.

第六章对几种农业中常用的有机物料在土壤中积累和维持有机质的效率进行了比较，包括作物根，秸秆，农家肥和绿肥. 从中国北方收集的数据中计算出模型的参数值. 预测表明当达到平衡态时，根可积累六倍于年投入量（以炭计）的土壤有机质. 在这一地区，根积累土壤有机质的效率是秸秆的三倍，农家肥的五倍，绿肥的七倍（均以炭计）. 计算结果表明，由不同物料积累的土壤有机质的年相对分解率变动于 5.8% 到 25.6% 之间. 作者进一步推断残留于田间的作物根茬是中国北方地区农田有机质最重要的物质来源.

在这一地区当用根茬来维持土壤有机质时，其需要量基本不变；但如用绿肥，秸秆或农家肥时，其用量则每年增加（均以炭计）. 其原因是现存土壤有机质被新积累的有机质所替代. 当土壤有机质的组成发生变化时，其分解速率也相应改变，从而导致养分从土壤有机质中释放速度的改变. 结果显示绿肥用作牲畜饲料进而转化成农家肥的效率高于直接还田；而秸秆可直接还田，或用作饲料，或用于堆肥. 由于根茬在土壤有机质积累上的高效率，通过提高作物产量如施用化肥和灌溉来改善土壤有机质是可行的.

在第七章用这一新的模型对中国北方农田土壤有机质的质量及含量的长期动态（50年）进行了预测. 作物的年产量水平包括目前这一地区的平均产量 7500kg/ha 和目前的高

产水平 15000kg/ha．有机物的投入量为 (1)只有根茬留田 (2)根茬加上三分之一的秸秆 (3)根茬加上三分之一的秸秆再加上由三分之一的秸秆转化的农家肥．结果表明在目前平均年产量下 (7500kg/ha)，三种有机物料投入量可使土壤有机质分别平衡在 10，13 和 15g/kg．在高产下土壤有机质水平可分别达到 15，19 和 21g/kg．目前土壤有机质含量是否继续提高或降低决定于当前的水平是否低于或高于相应的平衡态水平．此外，土壤有机质含量的年变化率决定于当前的含量与平衡态间的差距，并且年变化率随时间而逐渐变小．

土壤有机质的年分解率可用来衡量其质量．计算表明土壤有机质的质量随有机物的年投入量的不同而变．据此，在这一地区随作物产量的提高(如施用化肥)土壤有机质的质量和数量都会有所改善，秸秆还田和施用农家肥会有同样的效果．理论上秸秆直接还田比经牲畜转化为农家肥更有利于土壤有机质的积累，但在实际中由于对饲料的需求农民可能更愿意采纳后者．

在第八章应用这一模型探讨了温度在有机物分解上的效应随时间的变化．通常温度的效应用以下方式来表达：(1)Arrhenius方程 (2) $Q_{10}$ (温度相差10度相对分解速率的比率) (3) $f_{10}$ (温度相差10度达到同一分解量所用时间的比率)．结果表明温度对有机物分解的影响随时间而减弱．Arrhenius方程只适用于葡萄糖，但不能用于其它物料如纤维素，植物材料和土壤有机质．除葡萄糖外，在其它物料上 $Q_{10}$ 和 $f_{10}$ 均随时间而降低，并且在初始阶段降低得比后期要快．在某些情况下初始阶段的高温下的正效应会随时间而变为负效应．这一发现将有助于加深对温度在有机物分解上效应的认识，以及正确预测温室效应的长期后果和土壤有机质的长期动态．

第九章讨论了模型在科学研究中的作用和现有试验数据的更广泛的应用．重点讨论了不同来源的试验数据的综合及对数据中不可见信息的开发．作者认为中国北方农田土壤有机质的维持和进一步提高需要长期的努力．土壤科学工作者应该成为探索不同管理措施的效果和可能的方法的先锋．社会各方面应以各种方式支持农民着眼未来，维持和不断改善土壤肥力，利国利民．

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## Curriculum vitae

Yang Haishun was born on April 11, 1963 in Tianjin, China. From 1980 until 1984, he studied at the Agricultural University of China (the former Beijing Agricultural University). He got a BSc degree with a specialization in soil science and plant nutrition. Upon graduation until 1991, he worked at the Soils and Fertilizers Institute, Chinese Academy of Agricultural Sciences (CAAS). From 1984 until 1986, he worked in the group of Soil Survey, and was mainly involved in the field work at several sites. After that, he moved to the group of Soil Fertility, and was mainly engaged in the national network of soil fertility research. He was promoted by the institute to lecturer in 1990. From 1991 until 1993, he followed the 'MSc Program Soil and Water' of Wageningen Agricultural University (WAU), The Netherlands, and made his thesis research entitled 'Study of interactions and their reversibility between aluminium and oxalate in aqueous solution' at the Department of Soil Science and Geology. After that he started his Ph.D study at the Department of Soil Since and Plant Nutrition, WAU.