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A critical review of some approaches to modelling nitrogen mineralization

Abstract A number of approaches have been used to model and thus describe N mineralization kinetics in soils. In this paper, we review and present a comparative evaluation of some approaches to modelling adopted for this purpose. These may broadly be categorized as: (1) simple functional approaches to predict net N mineralization and, (2) mechanistic approaches that include a description of microbial biomass processes to predict long-term C and N turnover in soils. The following conclusions emerged. First, the simple functional models try to quantify one or more active fractions of organic matter with associated rate constants to predict net N mineralization. A minimum of two organic N fractions are considered essential to significantly contribute towards N mineralization. Second, the mechanistic models have the advantage that model algorithms represent the basic mechanisms believed to influence mineralization. The input parameters of the models could be obtained independently of the test data. However, it is difficult to validate the models as some of the presumed functional pools cannot be quantified by physical, chemical and biological techniques. Consequently, the models have to be calibrated by adjusting the rate coefficients and pool sizes (site-specific) to fit the measured data. Generally, the performance of a model depends on site-specific calibration. In future, a major challenge will be to free simulations from site-specific calibration and to devise experimental methods for providing initial values to run a model. The amount of N mineralized during laboratory incubation experiments and the parameter estimates for different models depend on methods used to pretreat the soil prior to incubation and their exposure to experimental conditions (such as temperature, soil moisture content) during the incubation. To obtain comparable values amongst studies it is, therefore, necessary to standardize methods of sample pretreatment as well as incubation conditions.

Introduction

Estimating an optimum dose of N fertilizers for crops is important from an economic as well as an environmental point of view. The application of amounts of fertilizer exceeding the optimum level leads to low N recoveries in crops, NO_3^- accumulation in the soil profile (Jolley and Pierre 1977; Benbi et al. 1991) and increased leaching of NO_3^- into streams or groundwater. Estimates of fertilizer rates depend on crop N requirements and the soil's ability to supply N, which is difficult to quantify. Problems stem partly from the fact that both the soil organic N and the microbes that mineralize N are poorly characterized. This situation is exacerbated by the fact that a number of soil and environmental conditions control the rates and products of mineralization in a poorly understood way (Seyfried and Rao 1988).

Mineralization is the process of conversion of organic forms of N to NH_3 or NH_4^+ and NO_3^-. The first step in the process, called ammonification, is an enzymatic process, and involves the conversion of organic N to NH_3. It is carried out exclusively by heterotrophic microorganisms that utilize C substances such as polysaccharides as an energy source and both C and N to build-up microbial biomass including microbial metabolites. The subsequent conversion of NH_3 to NO_3^-, termed nitrification, is mediated primarily through two groups of autotrophic bacteria (*Nitrosomonas* and *Nitrobacter*). Mineralization is always coupled with immobilization which operates in the reverse direction, with the soil microbial biomass assimilating inorganic N forms and transforming them into

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organic N constituents in their cells and tissues during the oxidation of suitable C substrates. However, immobilized N is likely to be available subsequently for mineralization due to the turnover of the microbial population. The continuous transfer of mineralized N into synthesized organic matter and the release of immobilized N back into inorganic forms is known as mineralization-immbolization turnover or MIT (Jansson and Persson 1982). Immobilized N is primarily derived from the NH_4^+ pool; however, small organic compounds such as amino acids may also be immobilized at a microsite scale (termed as Direct Hypothesis).

Total release of NH_4^+ through microbial activity, prior to any immobilization back into the organic forms, is termed gross mineralization. The difference between gross mineralization and immobilization constitutes net mineralization (or net immobilization). Since gross mineralization is difficult to measure, most often it is the net mineralization that is measured or estimated.

Modelling N mineralization kinetics in soil usually involves the prediction of an active fraction (Jansson 1963) of the total or organic N (termed as potentially mineralizable N) and a rate constant to predict the rate of mineralization. Approaches to modelling differ according to the level of detail at which the above processes are considered, and may be classified into the following two main groups:

1. Simple functional approaches to predict net N mineralization
2. Mechanistic approaches for simulating mineralization-immobilization turnover in soils.

In the present paper, we review some of the approaches used for modelling N mineralization kinetics.

Simple functional approaches

Simple functional approaches do not take into account the basic processes influencing mineralization. Models predict net N mineralization and do not consider the processes of ammonification and nitrification separately. The parameters for the models are obtained from laboratory incubation studies by fitting N mineralization data to the time of incubation.

Single-fraction approach

Stanford and Smith (1972) defined soil N mineralization potential as the quantity of soil organic N susceptible to mineralization at a rate of mineralization (k) according to first-order kinetics:

$$\frac{dN}{dt} = -kN \tag{1}$$

where N is the amount of mineralizable substrate (N), and t is time. Integration of this equation between time t_0 and t, yields:

$$N_t = N_0 \exp(-kt) \tag{2}$$

where, N_0 is the initial amount of substrate or the potentially mineralizable N and N_t is the amount of substrate at time t. The equation may be modified by substituting $N_t = (N_0 - N_m)$, where N_m is the N mineralized in time t, as:

$$N_m = N_0(1 - \exp(-kt)) \tag{3}$$

Using Eq. 3, Stanford and Smith (1972) found that the estimated values of N_0, at 35°C, for 39 soils from the USA ranged from 18 to 305 mg kg^{-1} soil. Values of k ranged from 0.035 to 0.095 week^{-1} with a weighted average of 0.054 week^{-1}. Similar average k values for soils from Chile (Oyanedel and Rodriguez 1977) and Queensland in Australia (Campbell et al. 1981) have been reported. However, widely varying k values have been reported for different soils (Table 1). This shows that soils differ not only in the amount of active organic N but also in their microbial turnover rate.

The first-order kinetic model has been used to describe N mineralization kinetics of soils under different land use, crop and climatic conditions (Griffin and Laine 1983; Campbell et al. 1984; Hadas et al. 1986; Carter and Macleod 1987; Cabrera and Kissel 1988a). In contrast, Lindemann and Cardenas (1984) found the first-order kinetic model to be inadequate for the description of N mineralization kinetics in soils treated with sewage sludge. In Chaparral soils (Marion et al. 1981), the fit to the data was improved by adding an exponent (b) to the time variable in the equation:

$$\log(N_0 - N_m) = \log N_0 - kt^b \tag{4}$$

A number of studies have demonstrated the inadequacy of the single pool first-order model to describe N miner-

Table 1 Range of parameter estimates for single-compartment first-order kinetic model as documented in different studies. N_0 Initial amount of substrate or potentially mineralizable N, k mineralization rate constant

Site/soil description	N_0 (mg kg^{-1})	k (week^{-1})	Reference
USA soils (39)	18–305[a]	0.035–0.095	Stanford and Smith (1972)
Chaparral, San Diego county	9.8–54[a]	0.042–0.073	Marion et al. (1981)
Red earth, black earth, prairie soil	67–256	0.058	Campbell et al. (1981)
Connecticut sewage sludge	145–438	0.024–0.081	Griffin and Laine (1983)
Dark grey, black and dark brown Chernozems	35–255	0.036–0.164	Juma et al. (1984)
Conestogo loam	67–106	0.121–0.139	Beauchamp et al. (1986)
Arctic tundra soils	121–1610	0.226–0.382	Marion and Black (1987)
Chaouia region, Morocco	120–241	0.060–0.274	El Gharous et al. (1990)
Thin black Chernozem	103–153	0.097–0.167	Campbell et al. (1991)

[a] Determined by a linear method

alization kinetics in soils (Molina et al. 1980; Nuske and Richter 1981; Deans et al. 1986; Diaz-Fierros et al. 1988; Matus and Rodriguez 1994). There were systematic deviations between first-order fitted curves and measured values. The model under-estimated mineralization at the beginning and end of the incubation period, and overestimated it at intermediate times (Bonde and Rosswall 1987; Seyfried and Rao 1988).

The linearized form of Eq. 3 was applied to obtain values of N_0 giving the best linear fit for the regression of $\log(N_0 - N_m)$ on t (Stanford and Smith 1972; Oyanedel and Rodriguez 1977; Sinha et al. 1977; Herlihy 1979; Campbell et al. 1981). With the logarithmic transformation, undue weight is given to data from the end of incubation (Talpaz et al. 1981) and errors in the data are also log-transformed (Daniel and Wood 1971; Gold 1977). This makes it difficult to precisely evaluate the fit of the data to the model. The non-linear least square (NLLS) method provides more accurate estimates of N_0 and k relative to the linear least square (LLS) method (Smith et al. 1980; Reynolds and Beauchamp 1984). Recently, Benedetti and Sebastian (1996) reported that the NLLS method gave the best fit to the N mineralization data as compared to the maximum likelihood and LLS methods.

Multi-fraction approaches

Various authors (Molina et al. 1980; Juma and Paul 1981; Nuske and Richter 1981; Van Veen and Frissel 1981; Deans et al. 1986) have suggested that more than one fraction of soil organic N may be directly mineralized, each with its specific rate of decomposition. Models have been developed that describe net N mineralization by dividing the mineralizable soil organic N into different fractions, each of which is then assumed to mineralize according to first-order kinetics. This may be generalized as:

$$N_m = \sum_{i=1}^{n} N_{0_i} \left[1 - \exp(-k_i t) \right] \tag{5}$$

where i represents a specific N fraction, n is the total number of fractions, N_{0_i} is the potentially mineralizable N in the i-th fraction and k_i is the mineralization rate constant for the i-th fraction.

In the simplest form of the multi-fraction approach, two main fractions of organic N are assumed to mineralize at different rates (Nuske and Richter 1981; Nordmeyer and Richter 1985; Deans et al. 1986). One fraction consists of N compounds of easily decomposable plant material (DPM), e.g. residues mainly from the last crop, while the second fraction represents the more resistant or recalcitrant plant material (RPM), which accumulates within the soil. The DPM mineralizes at a faster rate than the RPM. This model may be described by a double exponential equation:

$$N_m = N_{DPM} \left[1 - \exp(-k_{DPM} t) \right] \\ + N_{RPM} \left[1 - \exp(-k_{RPM} t) \right] \tag{6}$$

where N_{DPM} and N_{RPM} represent potentially mineralizable N in the easily decomposable and resistant organic N fractions, respectively, and k_{DPM} and k_{RPM} are the corresponding rate constants. Various authors have confirmed that the double exponential model is superior to the single exponential model in describing N mineralization (Lindemann and Cardenas 1984; Deans et al. 1986; Cabrera and Kissel 1988a; Diaz-Fierros et al. 1988).

Beauchamp et al. (1986) argued that the apparent presence of a small extra pool of mineralizable N (that mineralizes relatively fast) may be an experimental artefact as a consequence of drying and rewetting the soil rather than due to N mineralization from a separate soil organic N fraction. This "artefact mineralization", could be accounted for by modifying the first-order kinetic model so that a fitted curve through the data points does not pass through the origin but intercepts the y-axis at N_e.

$$N_m = N_e + (N_0 - N_e)(1 - \exp(-kt)) \tag{7}$$

The model is based on the assumption that the killed microbial biomass N pool (N_e) is effectively used up by 7 days (usually the time by which the first measurement is made) and N mineralized subsequently originates entirely from the soil organic N pool. Beauchamp et al. (1986) argued that, since most of the N flush has already occurred by this time, there is little basis for selecting a kinetic model. However, it has been shown that drying and rewetting not only generates or enlarges an N pool that mineralizes rapidly according to first-order kinetics, but also increases the size of a more stable, slowly mineralizable N pool (Inubushi and Wada 1987; Cabrera 1993). The results of these studies support the hypothesis that drying-rewetting cycles are one of the mechanisms by which each soil N pool is replenished from successively more recalcitrant or physically protected N pools (Elliott 1986).

For dried soil samples, Richter et al. (1982) and Nordmeyer and Richter (1985) adopted a three-fraction approach, which accounted for dead biomass N, DPM and RPM. Ando et al. (1992) also observed that if a large amount of extractable C was detected in air-dried samples, the mineralization pattern was represented by three exponential equations. Evidence for more than two fractions contributing N had also been provided from tracer studies of Paul and Juma (1981).

Instead of the two-fraction double-exponential model (i.e. parallel first-order model) which describes N mineralization from two independent initial sources, Andrén and Paustian (1987) applied a consecutive first-order model (Eq. 8) to barley straw decomposition. The model is based on the assumption that the recalcitrant fraction is converted to a labile fraction (e.g. through solubilization of structural polymers) from which N mineralization occurs.

$$N_m = N_{RPM} \left(1 - e^{-k_{RPM} t} \right) + N_{RPM} \alpha \left(1 - e^{-k_{RPM} t} \right) \\ - N_{RPM} \alpha \left(1 - e^{-k_{DPM} t} \right) + N_{DPM} \left(1 - e^{-k_{DPM} t} \right) \tag{8}$$

in which, $\alpha = \frac{k_{RPM}}{k_{DPM}-k_{RPM}}$. This model is essentially a reparameterization of the double exponential model and would, therefore, yield the same values for the rate constants. However, the fractions of recalcitrant and labile material present at any given time will differ.

Mixed first- and zero-order kinetic approaches

Some researchers have suggested that, with the incubation methods, it may not be possible to quantify the N mineralization potential of soils because the slowly mineralizable N component may in fact follow zero-order kinetics (Bonde and Rosswall 1987; Bonde et al. 1988; Lindemann et al. 1988; Seyfried and Rao 1988). They advocated the use of a mixed first- and zero-order kinetic model (a "degenerate" form of the double exponential model):

$$N_m = N_l[1 - \exp(-k_l t)] + Kt \tag{9}$$

in which N_l represents the amount of mineralizable N in the easily decomposable pool at the start of incubation and k_l is the rate constant, and K is the zero-order rate constant. The first-order term of the model was interpreted as accounting for pretreatment effects (e.g. air-drying). Therefore, some authors have suggested that in the absence of air-drying, i.e. in field-moist soils, net N mineralization may be described by zero-order kinetics only, rather than by combined first- plus zero-order kinetics (Tabatabai and Al-Khafaji 1980; Addiscott 1983; Houot et al. 1989).

$$N_m = Kt \tag{10}$$

Addiscott (1983) found that N mineralization in Rothamsted soils kept moist prior to incubation could be adequately described by the zero-order kinetic model. The fit to the zero-order model in his studies may be due to a different experimental set up (non-leaching incubation) and the use of undried soils as opposed to dried soils used by other workers. However, other authors have documented the applicability of first-order kinetic models to net N mineralization in field-moist samples as well. Further, a closer look at the data of Tabatabai and Al-Khafaji (1980) shows that in some cases the cumulative N mineralized was not essentially linear with time. Recently, Mary et al. (1999) showed that the mineralization kinetics in situ are linear when a small fraction of organic N is mineralized and curvilinear when a larger fraction is mineralized.

Empirical approach

Empirically determined equations such as polynomials and parabolic functions have been proposed to describe net N mineralization in soils (Broadbent 1986; Marion and Black 1987). In Arctic tundra soils, a second-order polynomial equation with respect to both time and temperature best described N mineralization data (Marion and Black 1987). Broadbent (1986) observed that compared to the first-order kinetic model, a parabolic function ($Y=aX^b$) provided a better fit to the data obtained by various investigators in laboratory, greenhouse and field experiments.

Although empirically determined equations have been found to provide a better fit to the data compared to single-pool first-order kinetic model, no physical meaning can be attached to the regression coefficients. Further, the empirical relations have been compared against first-order single pool models, but their performance in comparison to multifraction models is not known.

Assessment of simple functional models

We made a critical assessment of a single-fraction first-order kinetic model (FOSF) (Eq. 3), a two-fraction first-order kinetic model (FOTF) (Eq. 6), a modified FOSF (MFO) (Eq. 7), and a mixed first-order plus zero-order model (FOZO) (Eq. 9) on previously published data from Griffin and Laine (1983), Lindemann and Cardenas (1984), Chae and Tabatabai (1986) and Richter et al. (1989). The description of soils and experimental conditions during the studies are given in Table 2. The models were assessed with respect to precision of parameter estimates and fit to the experimental data as indicated by the

Table 2 Experimental details of the published studies used for assessment of the models

Study	Soil/treatment description	Incubation temperature (°C)	Length of Incubation (weeks)
Griffin and Laine (1983)	Air-dried, sieved 2 mm, fine sandy loams, soil 7 previously amended with poultry manure, soil 14 unamended, soil 15 unamended	35	40
Lindemann and Cardenas (1984)	Air-dried, sieved 2 mm, coarse loamy Latene, fine silty Glendale, both amended with 15 and 30 g kg^{-1} sewage sludge	35	32
Richter et al. (1989)	Air-dried as well as field-moist treatments, Luvisols and Gleysols with deepened plough layers and ploughed grasslands	35	11.7
Chae and Tabatabai (1986)	Field-moist, sieved 2 mm, Harps soil: fine loamy Downs soil: fine silty	30	26

172

Table 3 Parameter estimates for models fitted to the published data of Griffin and Laine (1983), Lindemann and Cardenas (1984), Chae and Tabatabai (1986) and Richter et al. (1989). *FOSF* Single-fraction first-order kinetic model, *FOZO* mixed first-order plus zero-order model, *MFO* modified FOSF, *FOTF* two-fraction first-order kinetic model, *K* zero-order rate constant

Soil	FOSF (Eq. 3)		FOZO (Eq. 9)			MFO (Eq. 7)			FOTF (Eq. 6)			
	N_0 (mg kg^{-1})	k	N_1 (mg kg^{-1})	k (week^{-1})	K	N_0 (mg kg^{-1})	N_e (mg kg^{-1})	k (week^{-1})	N_1 (mg kg^{-1})	k_1 (week^{-1})	N_2 (mg kg^{-1})	k_2 (week^{-1})
Griffin and Laine (1983)												
7	241***	0.057***	81***	0.224**	3.69***	290***	27***	0.034***	36**	0.653*	276***	0.029**
14	289***	0.051***	77***	0.295***	4.72***	386***	34***	0.026***	50**	0.526*	437**	0.017*
15	198***	0.060***	78***	0.179**	2.77***	226***	20**	0.041***	28*	0.583NS	212***	0.034**
Lindemann and Cardenas (1984)												
Latene[a]	134***	0.106**	57**	0.362*	2.54**	154***	20***	0.059***	21***	2.784NS	135***	0.058***
Latene[b]	180***	0.111**	70***	0.511*	3.76***	216***	31**	0.055**	42**	1.095*	196***	0.041**
Glendale[a]	128***	0.155**	54***	1.030*	2.84***	174***	37***	0.043**	40***	2.270*	142***	0.038**
Glendale[b]	160***	0.241**	83***	1.211*	3.24***	204***	60***	0.054***	63***	2.804*	146***	0.050***
Richter et al. (1989)												
Arable (dry)	57***	0.473**	31***	1.928*	2.89***	69***	18***	0.176**	20**	5.110NS	51**	0.152*
Arable (moist)	52***	0.134***	16*	0.376NS	2.22**	58***	2NS	0.103**	14NS	0.408NS	173NS	0.015NS
Grassland (dry)	119***	0.662*	71***	2.634***	6.04***	161***	52***	0.135*	68***	2.845***	250NS	0.030NS
Grassland (moist)	117***	0.148***	26***	0.806**	6.28***	148***	9**	0.089***	10*	3.940NS	145**	0.080**
Chae and Tabatabai (1986)												
Harps	240**	0.024*	180NS	0.028NS	0.67NS	145***	−19***	0.057***	−34*	0.526*	164**	0.074**
Downs	313**	0.016**	10NS	0.242NS	3.74***	433NS	2NS	0.011NS	7NS	0.281NS	695NS	0.006NS

*$P<0.05$, **$P<0.01$, ***$P<0.001$, *NS* non-significant
[a] Amended with 15 g sewage sludge kg^{-1}
[b] Amended with 30 g sewage sludge kg^{-1}

residual mean squares. The statistical significance of differences in residuals between any two models was assessed by the *F*-test (Beck and Arnold 1977).

The parameter estimates produced by each model varied considerably (Table 3). For the data of Chae and Tabatabai (1986) on Harps soil, the coefficients for the FOZO and MFO models were statistically non-significant, as large SEs were associated with their estimates. The parameter estimates for this dataset varied greatly even with small changes in starting or initial values for iteration. In arable and grasslands (Richter et al. 1989), the FOTF model yielded inconsistent parameter estimates for the easily decomposable pool (N_1 *and* k_1). The double exponential model (FOTF) offered the best fit to the data as indicated by the minimum residuals (Table 4). However, the differences in residuals between MFO and FOTF models were significant ($P=0.05$) only in three out of 11 cases and the two models yielded statistically equivalent fits to different data. The FOSF model, invariably, provided poor fit to the data. Usually, there were systematic differences between the measured and the FOSF fitted curves (e.g. Fig. 1). Physically the MFO model may also be interpreted as a two-fraction model with mineralization potentials of N_e and N_0. But N_e is defined as the dead microbial biomass pool created due to
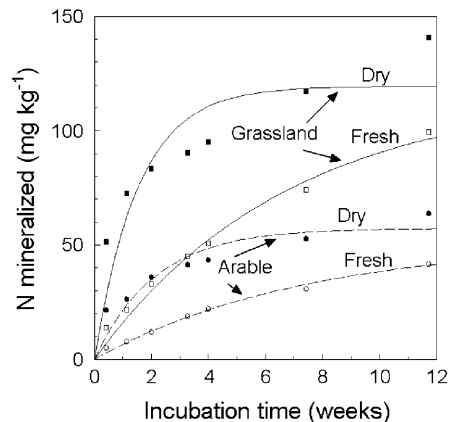

Fig. 1 Typical fit of a single-fraction first-order kinetic model to data from arable (*dashed line*) and grassland soils (*solid line*) [redrawn from the data of Richter et al. (1989)]

air-drying of soils prior to incubation, whereas the DPM fraction in the FOTF model is defined as easily decomposable plant material.

The inconsistent parameter estimates of the FOTF model for arable land and ploughed grasslands (Richter et al. 1989) was perhaps due to the nature of the samples

Table 4 Residual mean squares for models fitted to the published studies of Griffin and Laine (1983), Lindemann and Cardenas (1984), Chae and Tabatabai (1986) and Richter et al. (1989). Statistical ranks of a model [given by an *F*-test comparing residual mean squares (RMS) for a given treatment] shown by *a*, *b*, *c* and *d*. The RMS values followed by the *same letter* indicate models statistically equivalent for fitting. For abbreviations, see Table 3

Soil/treatment	Model			
	FOSF	FOZO	MFO	FOTF
Griffin and Laine (1983)				
Soil 7 (amended with poultry manure)	111 a	27.3 b	11.6 b	7.9 b
Soil 14 (unamended)	190 a	17.5 b	19.1 b	8.9 c
Soil 15 (unamended)	61 a	18.8 b	11.7 b	10.3 b
Lindemann and Cardenas (1984)				
Latene (+15 g sludge kg^{-1})	82 a	43.4 b	1.1 c	1.2 c
Latene (+30 g sludge kg^{-1})	206 a	45.2 b	25.1 b	7.8 d
Glendale (+15 g sludge kg^{-1})	245 a	24.9 b	5.1 c	4.7 b
Glendale (30 g sludge kg^{-1})	501 a	56.3 b	6.2 c	6.4 c
Richter et al. (1989)				
Arable (dry)	43 a	7.8 b	4.1 b	5.0 b
Arable (fresh)	1.7 a	1.3 a	1.2 a	1.7 a
Grassland (dry)	303 a	3.0 b	32.0 b	1.4 b
Grassland (fresh)	17.5 a	3.8 b	1.8 b	2.1 b
Chae and Tabatabai (1986)				
Harps	31.3 a	37.4 a	6.8 b	4.0 c
Downs	8.4 a	6.6 b	8.7 a	8.1 a

Table 5 Half-lives of soil organic N fractions, at 35°C, computed from laboratory incubation experiments (Nordmeyer and Richter 1985)

Organic N pool	Half-life (days)
Resistant plant material	100–140
Decomposable plant material	8–12
Microbiological organic material	1–4

(from deepened plough layers) and the relatively short incubation period (82 days). The decomposable organic N pool of soils consists of various organic components that are characterized by their half-lives (Table 5; Nordmeyer and Richter 1985). If the length of incubation is short compared to the half-life of the mineralizing organic N fraction, the N mineralization of soil N could appear to be linear, rather than gradually declining (Bonde and Rosswall 1987). Further, deepening of the ploughing depth causes mixing of organic matter pools of the topsoil and the deepened plough layers which have, probably, differing N mineralization kinetics. Until the plough layer soil attains (quasi) equilibrium, the DPM and RPM fractions may not be distinct. In that situation, the FOZO model may be a good approximation for the more complex FOTF model.

In situations where crop residues or organic manures of wider C:N ratios are added to soils, initially N immobilization may occur followed by net mineralization
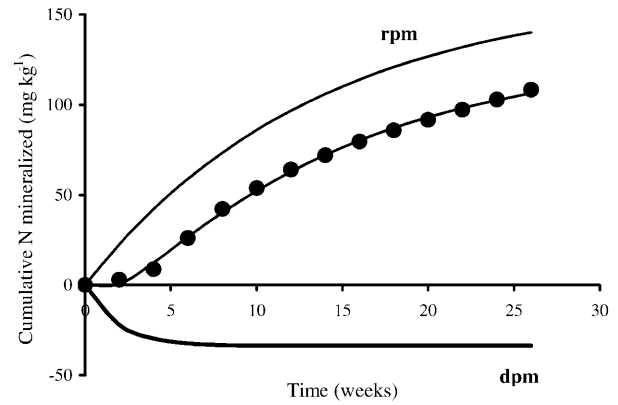

Fig. 2 A plot of a first-order two-compartment model (*lines*) fitted to the data (points) of Chae and Tabatabai (1986). *dpm* Decomposable plant material, *rpm* recalcitrant plant material

with the narrowing down of the C:N ratio. In the data of Chae and Tabatabai (1986) on Harps soils, this phenomenon was well described by the FOTF model as it yielded a negative N_1 value ($N_1 = -34$ mg kg^{-1}; Table 3). Presumably the negative N_1 value (N_{DPM}) corresponded to the N immobilization potential of the soil, which is perhaps related to the presence of fresh organic matter in the soil. A plot of the FOTF model for the data set shows the temporal occurrence of mineralization-immobilization processes during the course of the study (Fig. 2). Similarly, in the MFO model, a negative N_e value may be interpreted as corresponding to the immobilizing pool.

Bonde and Lindberg (1988) modified the FOTF and FOZO models to accommodate the initial immobilization to describe the data of Chae and Tabatabai (1986).

$$N_m = N_a \left[1 - \exp\left(-h_1 t - h_2 t^2/2\right)\right] + N_r \left[1 - \exp\left(-kt\right)\right] \tag{11}$$

$$N_m = N_0 \left[1 - \exp\left(-h_1 t - h_2 t^2/2\right)\right] + Kt \tag{12}$$

where, N_a and N_r are the amounts of mineralizable N initially present in the available and resistant fractions, respectively; h_1 and h_2 are rate constants for the mixed-order model, and other terms are as defined previously. This model (Eq. 12) is the same as the one presented by Brunner and Focht (1984) for microbial decomposition of C substrates, referred to as three-half-order (3/2 order), as it is suitable for substrate metabolism with (pseudo second order) or without (pseudo first order) growth. However, the immobilization phase cannot be described by equations (Eqs. 11 and 12), but it can be simulated with other simple exponential equations developed for crop residue decomposition (e.g. Nicolardot et al. 2001).

From the overview presented so far it may be concluded:

1. The FOSF generally provides a poor fit to the data and systematically deviates from the measured cumulative N mineralization.

2. In disturbed soil samples, a minimum of two pools of mineralizable N may be considered to significantly contribute towards N mineralization, as physical disturbance (e.g. during sampling, grinding, sieving, etc.) could lead to an extra pool of mineralizable N.

3. For precisely estimating potentially mineralizable N, the incubation needs to be continued until the mineralization rate appears to drop to a small relatively constant value. It appears that the longer the incubation, the more precise are the parameter estimates.

4. Large differences in N mineralization potentials and the rate of mineral N production could originate from differences in time of sampling (El-Haris et al. 1983; Nordmeyer and Richter 1985), probably due to seasonal variations in microbial biomass (Kaiser and Heinemeyer 1993; Joergensen et al. 1994) and the amount of undecomposed crop residues in the soil. Microorganisms may act both as a source (mineralization) and a sink (immobilization) for N during microbial biomass turnover. Therefore, models for N mineralization kinetics should, ideally, include a component for microbial biomass.

Mechanistic approaches for simulating mineralization-immobilization turnover

While simple functional models are designed to predict net N mineralization, mechanistic models attempt to simulate gross mineralization and associated immobilization (viz. mineralization-immobilization turnover). These are process-based models which try to include the best possible description of the processes involved. Based on our current understanding of organic matter decomposition in soil, hypotheses and assumptions about various processes are made that are used to develop mathematical formulae for the decay process. Existing models differ considerably in complexity and conceptual treatment of the turnover processes.

Non-compartment models

The model of Bosatta and Ågren (1985) and Ågren and Bosatta (1987) considers the decomposition of soil organic matter (SOM) as a continuum. Upon decay, the organic matter is assumed to move down a quality scale. The fresh, easily decomposable organic matter is assumed to have a high quality (=1) while the most resistant material in the system is considered of zero quality. Though this approach has obvious advantages over the pool approach, its mathematics are complex and have not found favour with modellers. Another non-compartment model that describes the process of humification of various organic substances in the first stage of soil humus formation was presented by Ionenko et al. (1986). The degree of humification (γ), defined as the ratio of mass of substance transformed at time t (S_t) to initial

mass of the substance (S_0), viz. S_t/S_0, was described in the form of a first-order autocatalysed process.

$$\gamma = \frac{1}{1 - \exp k\,(\tau_{1/2} - t)} \tag{13}$$

The change in degree of humification with time was expressed as:

$$\frac{d\gamma}{dt} = \frac{k \exp k\,(\tau_{1/2} - t)}{\left[1 - \exp k\,(\tau_{1/2} - t)\right]^2} \tag{14}$$

where $\tau_{1/2}$ is the half-life of the reaction. Ionenko et al. (1986) showed that the proposed model could accurately predict decomposition of lupin material under natural conditions. The model-predicted decomposition rates calculated from CO_2 evolution matched with the measured rates. However, the model needs to be validated against long runs of data from agricultural soils.

Multicompartment models

The decomposition of organic matter is simulated by defining different fractions of organic matter as functional pools, each with its specific quality as substrate for soil biota. Generally, small pools with high turnover rates (referred to as "decomposable" or "labile" or "active") and larger pools with slower turnover rates (referred to as "recalcitrant" or "resistant" or "slow") are distinguished (Jenkinson and Rayner 1977; Van Veen and Frissel 1981; Molina et al. 1983; Jenkinson et al. 1987; Parton et al. 1987; Jenkinson 1990; Hansen et al. 1991; Rijtema and Kroes 1991; Bradbury et al. 1993). In each of these pools the turnover rates are simulated by first-order kinetics and the rate coefficients are modified by superimposing the effects of abiotic factors such as temperature, soil moisture and clay content using empirical relations. The pools in different models vary greatly in number, N and C content and turnover rates (Table 6). These functional pools are defined on the basis of their presumed chemical characteristics and location in the soil (Van Veen and Kuikman 1990). But the question arises as to the reasons for different assumptions in distributing organic matter into different pools, and how the pool numbers, sizes and their behaviour over time have been parameterized by the authors or the users. Some models consider microbial biomass as one of the defined pools (e.g. Jenkinson 1990; Hansen et al. 1991; Whitmore et al. 1991) while others do not include a biomass pool and model it as part of the stable organic matter/humus pool (Rijtema and Kroes 1991). Even models with a distinct biomass pool do not consider microbial growth and maintenance explicitly. These are only represented by parameter values of the C and N reservoirs.

While the fractionation of SOM into functional pools is important for developing a better understanding of SOM dynamics, there is no proof that these models give better results for N mineralization than the simpler (functional) ones (De Willigen 1991). Increasing the

Table 6 Functional pools of soil and added organic matter, their C/N ratios, turnover times and first-order rate coefficients (*k*) as considered in different models. *SOM* Soil organic matter, *AOM* added organic matter, *OM* organic matter, *DPM* Decomposable plant material, *RPM* recalcitrant plant material

Functional pool	C/N	k (week^{-1})	Half-life	Turnover time (years)
Parton et al. (1987): Century model				
Active SOM	8	0.14 at 35°C	–	1–5
Slow SOM	11	0.0038	–	20–40
Passive SOM	11	0.00013	–	200–1500
Structural AOM	150	0.094	–	1–5
Metabolic	10–25	0.35	–	0.1–1
Jenkinson (1990): Rothamsted model				
DPM	–	0.192 at 9.3°C	–	0.1
RPM	–	0.0058	–	3.3
Microbial biomass	–	0.0127	–	1.5
Humified OM	–	3.85×10^{-4}	–	50
Inert OM	–	–	–	–
De Ruiter and Van Faassen (1994)				
DPM	17	0.081 at 10°C	–	–
RPM	80	0.035	–	–
Physically protected SOM	12	0.0012	–	–
Microbial biomass	4	0.035	–	–
Hansen et al. (1991): DAISY				
Biomass pool 1	6	0.007 at 15°C	693 days	–
Biomass pool 2	10	0.098	49.5 days	–
SOM pool 1	11	2.6 ± 10^{-5}	515 years	–
SOM pool 2	11	0.0013	10 years	–
AOM 1	100	0.074	66 days	–
AOM 2	–	0.735	6.6 days	–
Rijtema and Kroes (1991): ANIMO				
Humus	16	2.7 ± 10^{-4} at 15°C	50 years	–
Fraction 2	12	0.063	77 days	–
Fraction 3	58	0.0044	3 years	–
Fraction 4	76	0.037	130 days	–
Fraction 5	76	0.133	37 days	–
Fraction 6	24	0.075	65 days	–
Fraction 7	24	0.0082	590 days	–
Vereecken et al. (1991): SWATNIT				
Litter	8	0.007 at 15°C	693 days	–
Manure	10	0.007	693 days	–
Humus	12	7 ± 10^{-5}	189 days	–

number of pools does not necessarily increase model predictability, instead it increases the number of input parameters required (Diekkrüger et al. 1995). Further, it is difficult to validate these models, as most of the functional pools cannot be quantified by physical, chemical and/or biological techniques. Attempts have been made to establish linkages between the model pool definitions and measurable quantities either by devising advanced laboratory fractionation procedures to match measurable organic matter fractions with model pool definitions or by revising model pool definitions to coincide with measurable quantities (Christensen 1996). Elliott et al. (1996) coined the phrase "modeling the measurable or measuring the modelable" to represent the two approaches.

Physical fractionation procedures based on differential densities and sizes that separate coarse (light) fractions from fine (heavy) fractions have been used to provide relationships between density or the size of the fractions and their decomposability (Balesdent et al. 1988; Martin et al. 1990; Hassink 1994). It has been suggested that fractions that are 53–2,000 μm may provide an estimate of the slow pool, while those finer than 53 μm may provide an estimate of the passive pool (Cambardella and Elliott 1992). Alternatively, fractions of various densities may be recovered by densitometer techniques, but they cause considerable problems, e.g. high potential toxicity of the liquids used can substantially modify the biological characteristics of the fractions (Christensen 1992). It is, therefore, imperative that biologically meaningful pools which can be measured, such as CO_2, mineral N, microbial biomass C and N, organic materials defined on the basis of function and substrate availability, are considered. This will lead to redefinition of the structure of current models and the factors that regulate the material fluxes between compartments. Christensen (1996) presented a revised model structure based on soluble and insoluble input fractions and separate above-

and below-ground input routes. Gaunt et al. (2001) presented an alternative approach using analytically defined pools and measurement of ^{13}C and ^{15}N stable isotope tracers to derive model parameters. But introduction of these proposed pools in model structures has yet not been accomplished. Sallih and Pansu (1993) presented a five compartment (labile and stable plant material, microbial biomass and labile and stable organic matter) model constructed from the measurements of ^{14}C in the assumed pools under controlled conditions. The model which is an updated version of an earlier more simple model (Pansu and Sidi 1987) has one equation to describe the C dynamics in each compartment:

$$\frac{dC_m}{dt} = -k_m C_m + P_m \sum_{i=1}^{5} k_i C_i \qquad (15)$$

where, C_m, C_i represent C contents of compartments with associated rate constants of k_m and k_i, respectively. P_m is the proportion of C input into compartment m. Recently, the above model has been adopted for modelling N mineralization by using a constant multiplying factor for N kinetic constants and including two additional compartments viz. exchangeable NH_4^+-N and NO_3^--N.

While the models presented in the preceding paragraphs do not simulate microbial growth explicitly, the models presented by Parnas (1975), Smith (1979), McGill et al. (1981), Knapp et al. (1983), and Grant et al. (1993) explicitly use biomass kinetics to simulate C and N cycling during organic matter decomposition. Availability of organic C mainly controls microbial growth, which in turn controls N immobilization and mineralization. Models (Smith 1979; McGill et al. 1981; Van Veen and Frissel 1981; Simkins et al. 1986) employing microbial biomass explicitly, use Monod (1942) kinetics to predict the decomposition rate (ξ_i) of the organic pool i:

$$\xi_i = \frac{\mu_{max} \cdot S_i}{K_S + S_i} B \qquad (16)$$

where, S_i is the substrate concentration in pool i, B is the size of the microbial biomass, μ_{max} is the maximum specific growth rate and K_s is the half saturation constant for growth.

While several identical features are included in this kind of models, they differ considerably in the treatment of many processes. For example, most of the models treat biomass turnover or microbial death explicitly in relation to substrate/energy availability (Parnas 1975; McGill et al. 1981; Van Veen and Frissel 1981; Kersebaum and Richter 1994). However, the Phoenix model (McGill et al. 1981) additionally includes a function to describe microbial death through predation and density-dependent death of microorganisms, and a floating C:N ratio of microbes. Van Veen et al. (1984) simulated labile and protected parts of biomass. Other authors distinguish cell walls and cytoplasm (Paustian and Schnürer 1987) or labile cell C and assimilated live biomass (Knapp et al. 1983). However, none of the models
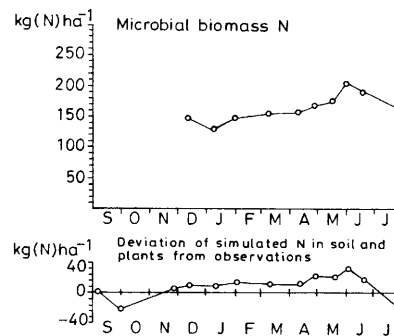

Fig. 3 Deviation of the model from observed N in plants and soil for a loess soil in western Germany and corresponding microbial biomass N determined by the fumigation-extraction method [adapted from Kersebaum and Richter (1991)]

describe the transition rates between different parts of biomass.

A crucial point for soil microbial biomass modelling is simulation of the composition of soil microbiota. The common approach is separation of the biomass pool into two or more components such as fungi and bacteria (Smith 1979) or fungi, bacteria and actinomycetes (McGill et al. 1981). Distribution of microbial biomass into fungi and bacteria is an important consideration as the two populations vary in their efficiency for substrate C use. Their ratio would regulate the relationship between CO_2 evolution and the size of the microbial biomass (Sakamoto and Oba 1994).

Following the original idea of Winogradsky (1949), Kersebaum and Richter (1994) divided microbial biomass into two pools – zymogenous and autochthonous – and used non-linear death or decline rate involving logistic growth on both biomass pools. Although the model provided a good description of the data of Smith et al. (1986) from a steady state incubation experiment, the model is overparameterized and needs to be further tested on long-term field data.

Depending on substrate availability, the microbes in the soil are at different states of physiological activity (Anderson and Domsch 1985). Therefore, it may be hypothesized that in late spring or early summer, part of the biomass may enter a dormant state because of N limitation. As soon as fertilizer N is added, the dormant biomass is activated and mineral N is immediately immobilized in the microbial biomass. Then the immobilized N can be mineralized. This may (partly) explain the temporary disappearance of mineral N shortly after the application of fertilizer N in late spring and early summer as reported in a number of studies (Neeteson et al. 1986; Nielsen and Jensen 1986; De Willigen 1991; Groot and Verberne 1991). The results of Kersebaum and Richter (1991) support this hypothesis. They showed that for a loess soil in Germany there was an increase of about 80 kg N ha^{-1} in the microbial biomass, especially during May and June, indicating possible immobilization, which was comparable to their model-simulated deviations in mineral N (Fig. 3).

While the models incorporating biomass explicitly are valuable for understanding the processes involved in organic matter turnover in soil, usually too large a number of input parameters are required to apply the models. They require data on the rates of uptake of organic compounds by soil organisms, the efficiency of substrate use for biosynthesis and energy supply, and on the nature and rates of release of organic products from the soil microbial biomass. Some parameters are difficult to obtain under field conditions. Use of information extrapolated from laboratory studies may not be very precise as the behaviour of the biomass differs considerably in the soil and solution cultures. Independent tests of the biomass-based models other than those undertaken by the authors have not been encountered. With the increased use of models for regional, national and global applications, evaluation of models to determine their generality (or lack thereof) becomes crucial (Paustian 2001). A major difficulty in validating SOM models is the inability to quantify some of the functional pools, particularly the slow pool consisting of as yet unknown physical properties and chemical composition. Consequently, the model has to be calibrated by adjusting the rate coefficients and pool sizes (site-specific) to fit the measured data. Generally, the performance of SOM models depends on site-specific calibration (Smith et al. 1997). Therefore, in future a major challenge in SOM modelling will be to free simulations from the calibration process and to devise experimental methods that will provide initial values relevant to the dynamic requirements of the model (Molina et al. 1997).

Food web models

Another class of models has been developed in which C and N fluxes in the soil are related to the abundance and activity of soil organisms, constituting the soil food web (Hunt et al. 1987; De Ruiter et al. 1993). In these models, organisms are classified as functional groups according to food choice and life history parameters (Moore et al. 1988). Consumption rates among the groups of organisms are calculated based on biomass and turnover rates. N mineralization rates are computed from consumption rates using information on energy conversion efficiencies and C:N ratios of the organisms. De Ruiter and Van Faassen (1994) compared a multicompartment model [modified form of Jenkinson and Rayner's (1977)] with a food web model to simulate N mineralization dynamics in an arable system. Both models simulated annual N mineralization rates close to the observed ones, but failed to predict N immobilization.

The food web models require information on physiological parameters such as assimilation efficiency, production efficiency, death rate, etc. for different functional groups of soil biota. As these values are not constant throughout the year/season, such models can calculate N mineralization kinetics only during a period under observation and are thus of descriptive value.

Effects of methodology on N mineralization kinetics

The amount of N mineralized during laboratory incubation experiments and the parameter estimates for different models depend on methods used in pretreating the soil prior to incubation and experimental conditions (such as temperature, soil moisture content) during the incubation.

Soil pretreatment

N mineralization in soils has frequently been studied in air-dried samples that are rewetted prior to the initiation of incubation. Air drying of soils alters the subsequent N mineralization. A greater mineralization flush is observed during the initial periods of incubation (Birch 1958; Eagle and Matthews 1958; Munro and MacKay 1964; Storrier 1966; Ross et al. 1979; Seneviratne and Wild 1985). Several factors may contribute to the N flush. Presumably, there exists an N fraction with a high decomposition rate in air dried-rewetted samples (Nordmeyer and Richter 1985). Drying the soils causes changes in soluble organic matter. Some of the solubilized organic compounds may come from the microbial biomass, which is killed by drying the soil samples. On rewetting, the dead biomass becomes mineralized rapidly (Marumoto et al. 1977; Nordmeyer and Richter 1985; Kieft et al. 1987; Van Gestel et al. 1991).

The implication of the N flush that follows rewetting the air-dried soil may be that another pool of N has to be added to the N mineralization models (e.g. Nordmeyer and Richter 1985; Beauchamp et al. 1986; Cabrera 1993). Stanford and Smith (1972) proposed that the amount of N mineralized during the first 2 weeks of incubation should not be included in the cumulative N mineralized for computing N mineralization potential (N_0). They suggested that the amount be added subsequently to the N_0 values computed from a first-order kinetic model. Contrarily, Beauchamp et al. (1986) argued that because the N flush occurs due to the drying and rewetting of soil samples, it may be considered as an experimental artefact rather than a part of true N_0 and, therefore, should be modelled separately. However, the short duration of the N flush emphasizes the need to make several measurements within the first few days after rewetting to obtain data for the selection of a kinetic model (Cabrera 1993).

Not only air-drying but also other physical disturbance to the soil samples (such as grinding and sieving) can increase the potentially mineralizable N in the soil. While a first-order model described the N mineralization in undisturbed samples, a double exponential model was required to describe N mineralization in disturbed samples to account for the flush of N release (Cabrera and Kissel 1988a). The higher amount of N released in disturbed samples compared to undisturbed samples was attributed to the breaking down of micro-aggregates during soil sampling and sample preparation. It has been

shown that disruption of soil aggregates can increase organic N mineralization (Craswell and Waring 1972; Hiura et al. 1976) by exposing the organic matter which was protected from microbial attack (Cabrera and Kissel 1988a). This physically protected organic matter has a lower C:N ratio than the rest of the SOM (Hassink 1992) and is thus rapidly mineralizable.

Although there is no direct evidence for the existence of the physical protection of organic matter, indirect evidence such as an increase in net N mineralization after fine sieving (Hassink 1992) and rapid mineralization in sandy soils in comparison to clay soils (Hassink et al. 1990; Verberne et al. 1990) support the hypothesis. The lower net mineralization in clay soils is assumed to be due to greater physical protection of SOM from microbial attack (Verberne et al. 1990) as a larger proportion of readily mineralizable organic N is entrapped in small aggregates than in larger aggregates (Craswell et al. 1970; Cameron and Posner 1979), and due to the relatively complex chemical structure of organic matter in small aggregates as it bonds with mineral particles (Buyanovsky et al. 1994). Clays facilitate the formation of micro-aggregates containing organic material physically inaccessible to microorganisms (Edwards and Bremner 1967; Tisdall and Oades 1982; Elliott and Coleman 1988).

Experimental conditions during incubation

In addition to sample pretreatment, incubation method and experimental conditions such as incubation temperature (Stanford et al. 1973; Tabatabai and Al-Khafaji 1980; Addiscott 1983; Campbell et al. 1981; Nordmeyer and Richter 1985; Marion and Black 1987; Ellert and Bettany 1992; Howard and Howard 1993), soil moisture content (Stanford and Epstein 1974; Cassman and Munns 1980; Myers et al. 1982; Campbell et al. 1984), volume of leaching solution used (Smith et al. 1980; Deans et al. 1986), organic N measurements in the leachate (Smith et al. 1980; Beauchamp et al. 1986; Robertson et al. 1988), length of incubation (Cabrera and Kissel 1988b) etc. affect N_0 and the shape of the N mineralization curve.

The temperature dependence of the N mineralization rate constant, k, has usually been described by an Arrhenius function (Stanford et al. 1973; Addiscott 1983; Campbell et al. 1981; Nordmeyer and Richter 1985), $k=Ae^{-B/T}$, in which k is the mineralization rate constant, T is the absolute temperature and A and B are regression coefficients. There are considerable differences in the coefficients reported for Arrhenius functions by various researchers. To make a comparison between the studies, we normalized the Arrhenius functions reported in different studies to 1.0 at 5°C (Fig. 4). Stanford et al. (1973) and Campbell et al. (1981) conducted their studies between 5°C and 40°C, Nordmeyer and Richter (1985) between 10°C and 35°C and Addiscott (1983) between 5°C and 25°C. As can be seen there are large dif-
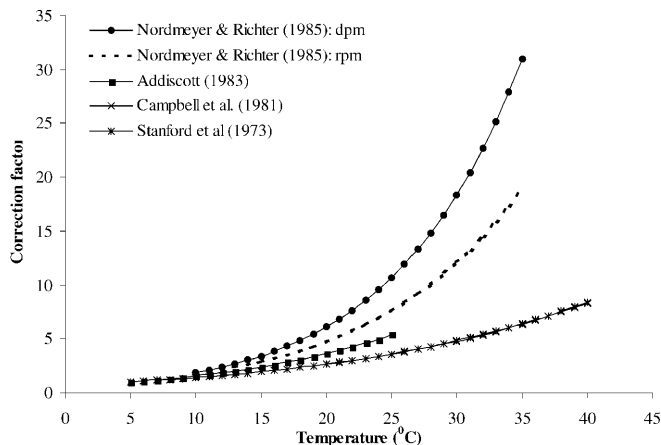

Fig. 4 Temperature functions for correcting mineralization rate constants reported in different studies. All functions normalised to 1.0 at 5°C

ferences in the temperature-adjustment factor reported in different studies (Fig. 4). Nordmeyer and Richter (1985) found that the turnover of the rapidly decomposable fraction of added plant residues was affected much more by temperature than turnover of the more resistant fraction of the added plant residues. This suggests that the temperature effect on the turnover rate is related to the nature of the organic matter in the soil.

In the kinetic models, the effect of temperature is generally incorporated by adjusting the rate coefficient and assuming the pool size to be constant at all temperatures, which is estimated solely from the N mineralization pattern at the highest temperature. Ellert and Bettany (1992) proposed simultaneous fitting of the kinetic model and temperature response function to the N mineralization data. Recently, MacDonald et al. (1995) showed that it is the mineralizable N pool (N_0) rather than the rate constant (k), which is temperature dependent. MacDonald et al. (1995) observed an increase in the mineralizable N pool with an increase in temperature from 5°C to 25°C. They argued that this may be due to a shift in the microbial community, changes in biochemical composition of the fraction mineralized, or changes in transport processes such as diffusion with temperature. In view of these results, the temperature dependence of N mineralization kinetics needs to be further investigated.

In addition to temperature, soil moisture is an important factor that dictates N mineralization rates in soils. Water potentials between –0.01 MPa and –0.03 MPa and a temperature around 35°C are considered optimum for N mineralization from SOM. However, the two have been shown to interact and the effect of moisture on microbial activity is enhanced at higher temperatures (Quemada and Cabrera 1997).

Garau et al. (1986) compared leaching and non-leaching methods for studying N mineralization kinetics in soils. They found that the cumulative mineralized N given by the leaching method and the potentially mineralizable N exceeded that obtained for the non-leaching one.

The addition of minus N nutrient solution at each leaching, as is usually done with Stanford and Smith's incubation method, significantly increased the cumulative amount of N mineralized and its effect was maximal after about 45 days of incubation (Seyfried and Rao 1988). The amount of mineralized N leached is dependent upon the volume of leaching solution used. As the volume of leaching solution increased, the value of N_0 decreased and that of the rate constant for the easily decomposable fraction increased (Deans et al. 1986), probably because the larger volume of the extract leached higher amounts of soluble mineralizable organic N (Smith et al. 1980). Several workers found considerable amounts of organic N in the leachates. The values reported varied from 13% to 163% (Smith et al. 1980), 9–12% (Beauchamp et al. 1986), and 30% (Robertson et al. 1988) of total mineralized N. Smith et al. (1980) indicated that the leached organic N probably represented an easily mineralizable fraction and, therefore, should be included in the cumulative mineralized N when determining the parameters for the first-order models. On the other hand, Smith (1987) observed that the soluble organic N losses in the leachates were not a major factor associated with the recovery of mineralized N as major losses of organic N occurred during the initial leaching prior to incubation.

Length of incubation

Length of incubation is the single most important factor that varies widely amongst studies. N mineralization parameters for first-order kinetic models have been computed from incubation studies ranging from 6 weeks (Beauchamp et al. 1986) to as long as 47 weeks (Carter and Macleod 1987). Depending on the length of incubation, the shape of the curve of cumulative N mineralization vs. time may change. This may lead to either improper model selection or imprecise parameter estimates. Cabrera and Kissel (1988b) found that extending the incubation time increased the estimated potentially mineralizable N in the two pools (N_1 and N_2), and decreased the associated rate constants k_1 and k_2 for the two-compartment first-order kinetic model. As an illustration here, we used the data from the previously published study of Juma et al. (1984). The effect of length of incubation on parameter estimates of a first-order single-compartment model is presented in Table 7. In general, by successively minimizing the incubation time from the maximum (25 weeks) used in the study, the value of N_0 increased and that of k decreased. However, irrespective of the length of incubation the product $N_0 \times k$ remained almost constant, suggesting thereby that different splitting of parameter estimates will result when variable lengths of incubation data are used for fitting the model. Many workers have emphasized the importance of the product of $N_0 \times k$ as a better indicator of N availability in soil than N_0 alone (Griffin and Laine 1983; Nordmeyer and Richter 1985; Campbell et al. 1991; Serna and Pomares 1992).

Table 7 Effect of length of incubation time on parameter estimates of a FOSF model [data from Juma et al. (1984)]. For abbreviations, see Table 1

Soil/ treatment	Length of incubation	No. of measurements	N_0 (mg kg^{-1})	k (week^{-1})	$N_0 \times k$
Rotation R	25	14	163	0.066	10.78
	22	13	171	0.061	10.46
	19	12	189	0.054	10.19
	15	11	198	0.051	10.11
Rotation C	25	14	160	0.055	8.78
	22	13	170	0.051	8.69
	19	12	191	0.044	8.40
	15	11	329	0.023	7.57

The dependence of the parameter estimates of the first-order kinetic models on length of incubation may present problems for comparing parameters from studies with different incubation times. Therefore, results from different studies should be compared with caution. Further, for a shorter duration of incubation, the models may be overparameterized due to the small number of observations recorded during the incubation period.

Relationship of N_0 with some soil characteristics

A number of studies have documented significant relationship between N_0 and soil C (Campbell et al. 1981; Griffin and Laine 1983) and total N (Marion et al. 1981; Campbell et al. 1981; Griffin and Laine 1983; Hadas et al. 1986; Campbell et al. 1991). In contrast, Carter and Macleod (1987) obtained a poor relationship between N_0 and SOM for eight Prince Edward Island soils. They obtained a close relationship between N_0 and the amount of C ($r=0.98$) and N ($r=0.97$) within the microbial biomass. Other studies on a range of soils of various texture and organic C levels have also shown a similar but less close ($r=0.76$) relationship (Carter and Rennie 1982). Soil clay content has been shown to be an important factor affecting mineralizable N from the resistant (RPM) N fraction (Nordmeyer and Richter 1985). With increasing clay content the product of $N_{RPM} \times k_{RPM}$ increased linearly. Similarly, Cabrera and Kissel (1988a) found that for very fine sandy loam to silty clay loam soils in Kansas the value of $N_0 \times k$ of the one-pool exponential model for undisturbed soil samples could be predicted from total N and clay contents of the soil.

Conclusions

We have discussed different approaches to modelling N mineralization kinetics in soils. There are doubtless more models that have been used to describe organic matter turnover and N mineralization in soils, but based on the approaches presented here, the following conclusions may be drawn:

1. Among the simple functional approaches, we regard fitting data to the curves described by two-compartment models as useful for the purpose of obtaining parameters needed for modelling N dynamics in soils or to allow data to be tabulated in comparable forms. In view of the complexity of the system and interdependence of a number of biotic and abiotic factors, one should not try to infer the mechanism of the reaction from a good fit between experimental data and a particular mathematical form alone. Though the partitioning of organic matter into two or more fractions each with a distinct N_0 and k is a gross simplification of the turnover process, it is easier to parameterize and is, therefore, in accordance with the principle of parsimony.

2. Multicompartment mechanistic models based on three or more organic N pools are difficult to parameterize. Some of these models are difficult to validate on independent data as the presumed functional pools cannot be quantified by physical, chemical and biological techniques.

3. The models based on microbial biomass kinetics explicitly represent basic mechanisms believed to influence mineralization, and the model parameters could be established independently of the test and calibration data. But these models have not been validated against reliable data, especially that obtained in the field. Therefore, experiments coupled with simulation studies are needed for the adequate description of N turnover in soil.

4. The cumulative amount of N mineralized during incubation and, therefore, the estimated N release parameters depend on methods used in pretreating the soil before incubation and experimental conditions during incubation. Any disturbance introduced by soil sampling and soil preparation has a strong influence on subsequent N mineralization. Sieving the soil, better air circulation as well as optimal availability of nutrients causes extra mineralization. So our N mineralization parameters are actually, in part, an expression of these arbitrary treatments in the laboratory. To obtain values which are comparable amongst studies it is, therefore, necessary to standardize methods of sample pretreatment as well as incubation conditions.

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