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SOIL NITROGEN MINERALIZATION DURING LABORATORY INCUBATION: DYNAMICS AND MODEL FITTING

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Summary-Soil nitrogen mineralization kinetics were studied for eight treatments of two soils in an aerobic long-term (30 wk) incubation experiment. Soil mineral-N (NH# and NO3) in the leachates was measured every week during the first 9 wk and every 2 or 3 wk thereafter. The NHt percentage of the mineral-N ranged between 85 and 99% for all treatments in the first week of incubation and remained high (>80%) in several treatments until the end of wk 4. Starting at wk 7, NHt concentrations were negligible in all treatments. The net N mineralization rate was 15-24 mg N kg⁻¹ wk⁻¹ during the first 4-6 wk and 2-5 mg N kg⁻¹ wk⁻¹ from wk 8 until the end of the incubation. Four models, (i) a one-component, first-order exponential model (the single model), (ii) a two-component, first-order exponential model (the double model), (iii) a one-component, first-order exponential model including a constant term (the special model), and (iv) a hyperbolic model, were fit to the cumulative mineral-N vs time data using a non-linear regression procedure. The goodness of fit of the four models depended on the duration of incubation. With 30 wk data, the double and special models were significantly better than the other two models; with the first 15 wk data, the four models had essentially the same goodness of fit for seven out of eight treatments. The values of the regression parameters derived from each model also depended on the incubation duration. Results from this study show that the pool size and mineralization rate parameters in the different models are merely mathematically-defined quantities obtained from the kinetic analysis of the net N mineralization and do not represent any rigorously-defined pool sizes of potentially-mineralizable N and their mineralization rate constants in the soils. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

In order to improve the efficiency of N fertilizer utilization and reduce the risks of polluting water resources, it is important to know the amount of N supplied to a growing crop from mineralization of soil organic matter. However, accurate methods for making such estimates are not presently available. Stanford and Smith (1972) developed a laboratory procedure to investigate soil N mineralization using a long-term (30 wk) aerobic incubation under optimum temperature and moisture conditions. A first-order exponential equation (referred to herein as the single model) was used to describe the data obtained when the mineral-N accumulation was analyzed as a function of time. From this equation, the authors introduced the concept of an N mineralization potential (N₀) that was believed to represent a pool of readily-mineralizable N in the soil

In the past two decades, the incubation procedure developed by Stanford and Smith has been employed with slight modification by many other researchers to further investigate soil N mineralization under controlled conditions in laboratories. Meanwhile, different mathematical models have been proposed to better analyze experimental cumulative mineral-N vs incubation time data. A model with two components (referred to as the double model) but with the same first-order exponential mathematical expression was proposed by Molina et al. (1980) in which the two components were assumed to represent two organic N pools, one active and the other resistant, decomposing independently and simultaneously with their corresponding rate constants. The double model has been further discussed by Deans et al. (1986) and used by several others (e.g. Hadas et al., 1983). Bonde and Rosswall (1987) modified the double model by replacing the resistant pool with a constant term multiplied by time (referred to as the special model). They believed that considering the relative shortness of incubation

with a mineralization rate constant (k₀) independent of soil type or management practices.

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compared to the half-life of the large resistant fraction of soil N, N mineralization from this resistant pool could appear to be linear rather than gradually declining. In addition, a hyperbolic equation (referred to as the hyperbolic model) was reported by Juma et al. (1984) to be as accurate as Stanford and Smith's single model in describing the kinetics of net N mineralization in their incubation study.

Despite the differences in the mathematical expressions, all the models except the special model have the same feature of including one or more components that supposedly represent a definable soil organic N pool with a corresponding mineralization rate constant. Estimated N_0 values have also been widely used as indices of soil organic N availability for determining the effects of various agricultural practices (such as tillage, crop rotation, and N fertilization management) on soil fertility. In addition, the N_0 value is an important input parameter required by several computer models simulating N cycling in soil-water-plant systems.

We conducted a laboratory incubation study following Stanford and Smith's procedure with the initial purpose of estimating N_0 values for two soils in order to facilitate the evaluation of computer simulation models. Our objectives were to: (i) record the observed mineralization and nitrification rate dynamics during a 30 wk incubation, (ii) compare the goodness of fit of four regression models using data from the 30 wk incubation or from only the first 15 wk of the incubation, and (iii) discuss the implications of the effect of incubation length on regression parameters and the limitations of using these parameters in computer simulation models.

MATERIALS AND METHODS

Experimental sites and soil sampling

The soil samples used in the incubation were collected from two experimental sites at the R. E. Larson Research Center in central Pennsylvania, U.S.A. Site one was an experiment on a Hagerstown silt loam (fine, mixed, mesic Typic Hapludalf) that was designed to measure nitrate leaching under corn (Zea mays L.) with different N sources. The field was planted to alfalfa (Medicago sativa L.) in 1984 and maintained through 1986. In 1987, alfalfa was ploughed down and corn was planted with only starter fertilizer (11 kg N ha -1) applied. When the N leaching experiment was initiated in April 1988, the soil in the plough layer (0-25 cm) had a pH of 6.5, 19 g organic matter kg⁻¹, 2.5 g total organic N kg⁻¹ and available P, K, and Mg contents in the optimum range for corn production. Corn was planted each year from 1988 to 1990 with a range of N fertilizer and manure treatments. In the N fertilizer system, five

rates of ammonium nitrate (0, 50, 100, 150 and 200 kg N ha - 1) were broadcast at planting. In the manure system, liquid dairy manure was applied at rates of 71 Mg ha⁻¹ (264 kg total N ha⁻¹, 116 kg NH₄+-N ha^{-1}) in 1988, 38.5 Mg ha^{-1} (132 kg total N ha^{-1} , 75 kg NH₄⁺-N ha⁻¹) in 1989, and 44.7 Mg ha⁻¹ (158 kg total N ha⁻¹, 63 kg NH₄⁺-N ha⁻¹) in 1990, respectively. Manure was applied prior to planting and incorporated by disking within 24 h in all three years. In spring 1991, alfalfa was planted into the plots where manure had been applied during 1988 through 1990. Soil samples included in the incubation study were taken from randomly-selected spots in the field in spring 1988 (referred to as the Initial treatment), in spring 1991 after 3 y continuous corn from the 0 and 200 kg N ha⁻¹ fertilizer treatments and the manure treatment (referred to as the Control, Fertilizer, and Manure treatments), and in spring 1993 from the alfalfa plots (referred to as the Alfalfa treatment). All samplings were conducted late March to early May, after the field surface had dried sufficiently to permit vehicle traffic. Three 4.3 cm dia cores were taken from each plot to a depth of 1.2 m. divided at depths corresponding to soil horizons and composited by depth. There were three replications. Additional experimental details were reported by Jemison and Fox (1994).

Site two was an experiment on a Murrill silt loam (fine-loamy, mixed, mesic Typic Hapludult) that was designed to study the N contribution from legume cover crops to succeeding corn crops. The field was in winter wheat (Triticum aestivum L.) in 1989-90. In 1990, red clover (Trifolium pratense L.) and hairy vetch (Vicia villosa Roth) were double-cropped with the winter wheat. Winter fallow after the wheat harvest was included as a comparison. The legumes were allowed to grow until 17 May 1991 when they were incorporated into the soil by ploughing and disking and corn was planted. At that time, the soil plough layer (0-25 cm) contained 26 g organic matter kg⁻¹ and had a pH of approximately 6.7 and available P, K, and Mg contents in the optimum range for corn production. Soil samples included in the incubation study were taken on 22 May 1991 from plots that were in winter fallow (referred to as the Fallow treatment) or cover crop of red clover (referred to as the Clover treatment) or hairy vetch (referred to as the Vetch treatment). Upon sampling, eight 2.5 cm dia cores were taken at random locations to a depth of 45 cm from each plot, divided into 0-25 cm and 25-45 cm and composited by depth. There were four replications. See Dou et al. (1994) for further details on the experiment.

All soil samples were dried in a forced-draft oven at 60-70°C and ground to 2 mm, then subsamples were taken and stored in sealed plastic bags at room temperature until the incubation study began in September 1993. Plough layer soils (0-25 cm) were selected to use in the incubation study. Soil samples from the three or four field replicates of the selected

treatments were composited, and three replicates of these composite samples were used in the incubation.

Soil drying and rewetting as well as other prior treatments (grinding, sieving, and storage) may alter the degradability of soil organic matter and change the community and proportion of microorganisms resulting in mineralization dynamics different from field conditions. However, dried soils were used in the incubation studies from which the four models used in this study were derived. Also, as the main scope of this paper was to present the results and discuss the implications of data fitting using the four models, the soil pretreatment method would not affect the conclusions we reached.

Incubation and chemical analysis

The leaching-incubation procedure followed that of Stanford and Smith (1972) using triplicate soil samples. However, instead of using a 15 g soil plus 15 g sand mixture, we used 10 g soil and 2 g of sieved (between 0.64 and 1.27 mm) horticultural grade perlite. We found that the speed of leaching in our preliminary trials using sand or vermiculite was very slow. Triplicate samples of perlite alone (no soil) were included as blanks and mineral-N concentrations in the leachates from these blanks were negligible throughout the incubation. Before incubation, the soil-perlite mixture was leached with 100 ml 10 mM CaCl₂ in 10 ml increments, followed by 25 ml N-free nutrient solution. After leaching was completed, a vacuum (60 cm Hg) was applied to adjust the moisture content of the samples (Stanford and Smith, 1972). The soils were kept at 35°C and leached weekly for the first 9 wk of incubation and following wk 11, 13, 15, 18, 21, 24, 27 and 30 using the same procedure as for the pre-incubation leaching described above. During incubation, the tubes were covered with parafilm, which allowed air exchange but retarded moisture loss. Loss of water through the openings at the bottom of the tube ranged from 1 to 2 g per tube during the 3 wk interval, which was about 2-5% of the water held by the contents of the leaching tube at the beginning of the interval. Leachates were analyzed for NO3-(cadmium reduction method) and NH4+ (phenate method) as described by Keeney and Nelson (1982), using an automated analyzer.

The models

The four models used in this study are defined by the following equations:

The single model (Stanford and Smith, 1972):

$$N_{t} = N_{0}(1 - e^{-k_{0}t}) \tag{1}$$

where N_t is the cumulative mineral-N (mg N kg⁻¹ of soil) at time t (wk). N_0 is defined as the potentially mineralizable N and k_0 as the mineralization rate constant.

The double model (Molina et al., 1980):

$$N_t = N_1(1 - e^{-k_1 t}) + N_2(1 - e^{-k_2 t})$$
 (2)

where N_1 and N_2 represent the active and resistant pools decomposing at specific rates k_1 and k_2 . The sum of N_1 and N_2 has the same physical meaning as the N_0 in Eq. 1 (Deans *et al.*, 1986).

The special model (Bonde and Rosswall, 1987):

$$N_t = N_a(1 - e^{-k_a t}) + Ct$$
 (3)

where N_a and k_a have the same meanings of N_1 and k_1 as in Eq. (2) and C is a constant, identified by the authors as the product of a large resistant N pool mineralizing at a low, constant rate. The authors proposed the special model as an approximation to the double model when the incubation length was short compared to the half-life of the large resistant pool.

The hyperbolic model (Juma et al., 1984):

$$N_{t} = N_{0}^{h}t/(bN_{0}^{h} + t)$$
 (4)

where N_0^h is the potentially mineralizable N and b is a constant [wk (mg N kg⁻¹ soil)⁻¹].

Statistical analysis

The four models were fit to the observed N_t vs t data set using the non-linear regression (NLIN) procedure with the Marquardt iterative method in SAS (SAS Institute, 1990). Significance of difference between any two of the four models was detected by the F-test described by Robinson (1985). In addition, analysis of variance using the SAS general linear models procedure (SAS Institute, 1990) was run on the data of total cumulative mineral-N at the end of incubation and least significant differences (LSD) were computed to detect differences in N_t (t = 30) among the treatments.

RESULTS AND DISCUSSION

Ammonium proportion

The mineral-N content of leachate after the first week of incubation was dominated by NH4 in all treatments, with 85-99% of the mineral-N extracted being NH₄⁺. During the following few weeks, NH₄⁺ as the percentage of total mineral-N extracted exhibited different trends among the treatments of the two soils. In the control, fertilizer and manure treatments of the Hagerstown soil, the proportions of NH₄⁺ decreased steadily in the following 3 wk and reached 5% by the end of wk 4 (see manure treatment as an example in Fig. 1, square symbol). In the initial treatment of the Hagerstown soil and the fallow, clover and vetch treatments of the Murrill soil, the proportions of NH₄⁺ remained high (> 80%) until the end of wk 4, then dropped considerably and reached less than 5% by the end of wk 6 (see the initial and fallow treatments in Fig. 1). The alfalfa treatment had trends between the two contrasting

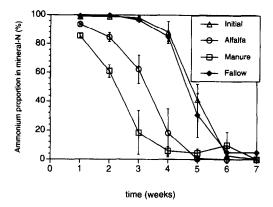


Fig. 1. The proportions of NH₄⁺ in the mineral-N extracted, expressed as percentage, during the first 7 wk of incubation: —(△)— for the initial treatment of the Hagerstown soil, —(○)— and —(□)— for the alfalfa and manure treatments of the Hagerstown soil, and —(♠)— for the fallow treatment of the Murrill soil. Error bars indicate two standard errors of the mean of the observed data.

groups (Fig. 1). After the first 7 wk, NH₄+ concentrations and their proportion of the mineral-N were minimal in all treatments until the end of incubation.

The persistence of a high concentration and proportion of ammonium during the early stages of incubation has rarely been reported in the literature. Bonde and Rosswall (1987) reported NH₄⁺-N concentrations ranging from 1 to 4 mg kg⁻¹ wk⁻¹. Cassman and Munns (1980) found negligible amounts of NH₄⁺ in their 13-wk incubations. Both studies used air-dried, sieved soil samples collected from agronomic research sites. In most other soil N mineralization laboratory studies, the authors reported only mineral-N without mentioning the relative proportions of NH₄⁺ vs NO₃⁻.

The predominance of NH4+ during the early stage of the incubation suggested that nitrification processes were inhibited in the micro-environment of the soil-perlite mixture during that period. A possible explanation was a delayed buildup of the nitrifier community (Schmidt, 1982). The nitrifier community in natural soils is low due to limited substrate (NH₄⁺) supply. The processes of soil sample preparation, especially the drying, might have further reduced its size since this community of microbes was found to be less tolerant of water stress than ammonifiers (Paul and Clark, 1989), and is generally sensitive to other environmental conditions such as temperature, chemicals, etc. We do not know what caused the differences in the rates of apparent buildup of the nitrifier communities among the different soils.

One of the essential factors affecting the transformation of NH₄⁺ into NO₃⁻ is oxygen supply. It is unlikely that there was an oxygen shortage in the leaching-incubation tubes because the procedure used to adjust moisture conditions after each leaching was the same as used by Stanford and Smith (1972)

and many others. More importantly, NH4+ dropped to fairly low concentrations after the first few weeks while the mineralization rate was still high. By the end of wk 5, for example, the NH4+ percentages in the fallow, clover and vetch treatments of the Murrill soil were reduced to about one-third of that in wk 1 (see the fallow treatment in Fig. 1) while the magnitude of the average mineralization rate was similar to that in wk 1 (Fig. 2). The high NH4+ concentration was not due to the perlite because NH4+ was essentially non-detectable in the blank samples. The NH₄⁺ proportions and dynamics in soil-sand or soil-vermiculite mixture samples included in the incubation for comparison purposes were similar to those in the soil-perlite mixture (data not presented).

Acidity is another important factor affecting nitrification. The soil samples in the incubation had initial pH values of 5.6–6.1 (1:1 soil:H₂O ratio), which were sufficiently high for nitrification to occur (Schmidt, 1982). Although pH changes during the incubation were not measured in our study, Stanford and Smith (1972) found little change in pH over the course of their incubation. Moreover, the initial pH values of the soil samples in the first group (the control, fertilizer and manure treatments) that decreased rapidly in NH₄+ percentage after the first wk were not different from the initial pH values of the other soil samples in which the high proportion of NH₄+ in the leachate was prolonged.

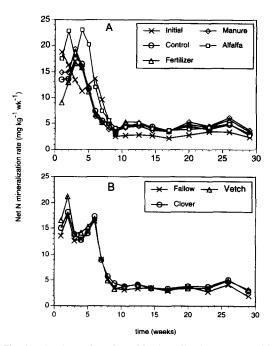


Fig. 2. The dynamics of net N mineralization rate (mg N kg⁻¹ soil wk⁻¹) during a 30 wk incubation for soil samples from five treatments of a Hagerstown soil (A) and three treatments of a Murrill soil (B). Two standard errors of the mean of the observed data ranged from 0.22 to 5.28 at wk 1 and 0.02 to 1.04 at wk 30.

Mineralization rate and total N mineralized

The net N mineralization rate, calculated as the measured amount of mineral-N in each leachate sample divided by the amount of soil and the span of weeks from the last leaching, showed two distinct phases in all treatments: a rapid phase with the mineralization rate ranging from 15 to 24 mg N kg⁻¹ wk⁻¹ in the first 3-6 wk, and a slow-steady phase with a rate of 2–5 mg N kg $^{-1}$ wk $^{-1}$ extending to the end of the incubation (Fig. 2). The transition period between the two phases lasted 2-3 wk with an abrupt decrease in mineralization rates in all treatments (Fig. 2). The two-phase pattern could be interpreted as the result of both substrate availability and microbial characteristics: first, the rapid degradation by the "zymogeneous" microbes of readily available organic material originating in the soil, released during soil drying-rewetting, and microbial cells lysed during soil sample preparation; then the slow-steady degradation of more resistant organic matter by the "autochthonous" group of microbes (Paul and Clark, 1989).

The measured cumulative mineral-N at the end of 30 wk ranged from 162 to 216 mg N kg⁻¹ (Table 1), accounting for about 5-10% of the Kjeldahl-N in the soil samples. Although we did not measure the amount of organic N in the leachate it was determined to be a relatively small proportion of total leachate N by other researchers (Beauchamp et al., 1986; Smith, 1987). If we consider the cumulative mineral-N values as a relative measure of the soil's organic N availability, analysis of variance and LSD tests revealed enhanced organic N availability in the two legume treatments of the Murrill soil compared to that in the fallow treatment. For the Hagerstown soil, the alfalfa treatment had the greatest and the initial treatment the least N availability. No significant differences in cumulative mineral-N were detected among the control, fertilizer or manure treatments (all sampled in March 1991). This was not expected because soil N availability in continuous corn receiving no non-starter N has been shown to decrease in experiments similar to the one reported here (Fox and Piekielek, 1983). One possibility is that different amounts of N from the different treatments might have been released in the field prior to soil samplings since samples were not taken immediately following spring thaw.

Model fitting

For model fitting, an initiation value of 250 was used for N_0 , N_0^h , and N_a for the single, hyperbolic and special models, and 25 and 250 were used for N_1 and N_2 in the double model. The default value of the criterion for convergence ($c = 10^{-8}$) in the NLIN iteration had to be increased when the double model was used in order to obtain convergence.

Based on the Mean Square Error (MSE) for the equations describing mineralization kinetics for the 30 wk incubation, the double and special models were significantly better than the other two models for all treatments (Table 1). Although the special model had slightly smaller MSE values than the double model in all cases, there were no significant differences between the two. Also, the curves of predicted cumulative mineral-N vs t by these two models essentially overlapped for all treatments. Two examples, the manure treatment of the Hagerstown soil and the vetch treatment of the Murrill soil, are displayed in Fig. 3 in which the predictions by the double and special models coincide. The hyperbolic model produced lower error terms than the single model (Table 1). Comparisons of observed vs predicted cumulative mineral-N by the different models indicate that the double and special models produced generally good predictions for all treatments throughout the incubation. The single and hyperbolic models overpredicted N mineralization during wk 9-21 and underpredicted N mineralization towards the end of the incubation for all treatments. In addition, the single and hyperbolic models underpredicted N mineralization during wk 3-8 for the control, fertilizer and manure treatments.

That the double and special models fit the data better is to be expected considering the two-phase microbial activity pattern that develops during the decomposition of substrates. Since soil organic

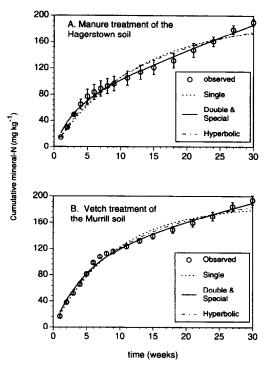


Fig. 3. Comparisons of observed (open circles) vs predicted (lines) cumulative mineral-N (NH\$\tau\$ plus NO\$\tilde{\ta}\$) for the manure treatment of the Hagerstown soil (A) and the vetch treatment of the Murrill soil (B) during a 30 wk incubation. Predictions were by the single (...), the double and special (--), and hyperbolic (--) models. Error bars indicate two standard errors of the mean of the observed data.

Table 1. Cumulative mineral-N at the end of 30 week incubation (N_{1,30)} and the mean square error (MSE) produced by the single, double, special and hyperbolic model fittings using 30 wk data or the first 15 wk data. Soil samples in the incubation were from two experiments with different N management strategies and soils, a Hagerstown soil and a Murrill soil

	Treatment										
	Hagerstown Soil						Murrill Soil				
Model	Initial	Control	Fertilizer	Manure	Alfalfa	Fallow	Clover	Vetch			
	Cumulative mineral-N, mg N kg-1†										
$N_{1(30)}$	162 e	181 cd	181 cd	190 bc	216 a	173 de	191 bc	194 b			
			MSEt.	30 wk incubatio	n (n = 17)						
Single	44 a	57 a	53 a	105 a	84 a	42 a	53 a	61 a			
Double	19 c	17 c	21 c	28 c	37 c	26 bc	25 c	26 c			
Special	15 c	13 c	16 c	21 c	33 c	23 c	22 c	22 c			
Hyperbolic	25 b	36 b	39 b	73 b	51 b	29 b	34 b	37 b			
	MSE \ddagger , 15 wk incubation (n = 12)										
Single	10 b	13 a	15 a	14 a	30 a	21 a	16 a	17 a			
Double	13 b	14 a	15 a	17 a	33 a	24 a	16 a	19 a			
Special	11 b	14 a	17 a	15 a	33 a	24 a	18 a	19 a			
Hyperbolic	18 a	15 a	17 a	17 a	44 a	30 a	24 a	26 a			

[†]The mineral-N values in the same row with the same letter are not significantly different at the 95% confidence level.

matter has heterogeneous components with varying degrees of degradability, any model having multiple pools should be more accurate than a single pool model in describing soil N mineralization.

Based on 30 wk incubation data, the N mineralization potential and corresponding rate constant derived from the different models vary greatly (Table 2). The single model gave No values very close to or even smaller than the measured cumulative mineral-N (Table 2). This illustrates another weakness of the single model since, in concept, No is supposedly the upper limit of potentially mineralizable N, and therefore it should be greater than the observed cumulative mineral-N at t = 30. Undoubtedly, more mineral-N would have been released if the incubation was carried out longer than 30 wk. The hyperbolic model produced N₀^h values that were 1.2-1.6 times greater than the measured cumulative mineral-N (Table 2). However, it is not feasible to make a direct comparison between the N_0^h value from the hyperbolic model and the N_0 value from the single model because the rate constants in these two models have different values

and units. The k_0 in the single model has a unit of wk⁻¹ that was referred to as the percentage of the remaining mineralizable N that is mineralized per wk (Stanford and Smith, 1972) while the b in the hyperbolic model has a unit of [wk (mg N kg⁻¹ soil)⁻¹]. The double model produced N mineralization potential values, calculated as N₁ plus N₂, from 268 to 556 mg N kg⁻¹ with 10–30% of the total in the N₁ pool (Table 2). With the special model, it is not possible to estimate N mineralization potential values, although the model does contain a component representing an active N pool. Our data suggest that the so-called N mineralization potential and mineralization rate constant have only relative values depending on specific models used to generate them.

When the data from the first 15 wk of incubation were analyzed using the same non-linear regression procedure, the goodness of fit by the four models ranked differently from that with the 30 wk data. The single, double and special models had essentially the same goodness of fit based on the MSE results (Table 1). The hyperbolic model produced MSE values that were slightly but not significantly greater

Table 2. Estimates of parameters using the single, double, special and hyperbolic models based on 30 weeks incubation

Model		Treatment								
	Parameter	Hagerstown Soil						Murrill Soil		
		Initial	Control	Fertilizer	Manure	Alfalfa	Fallow	Clover	Vetch	
	Observed (N ₁₃₀)	162	181	181	190	216	173	191	194	
Single	$N_0^{(250)}$ ‡	153	186	199	191	208	171	189	187	
	k o ^(0.1)	0.123	0.082	0.065	0.081	0.112	0.103	0.095	0.107	
Double	$N_1 + N_2$	268	353	384	494	556	373	524	546	
	N ₁ ⁽²⁵⁾	82	55	4 2	54	108	90	87	95	
	$\mathbf{k}_{i}^{(i)}$	0.246	0.292	0.291	0.359	0.235	0.197	0.211	0.226	
	$N_2^{(250)}$	186	298	34 2	440	448	283	437	451	
	k ₂ (0.05)	0.017	0.018	0.017	0.012	0.0089	0.0112	0.0087	0.0079	
Special	N _a (250)	91	69	57	62	115	98	94	101	
	k _s (0.1)	0.231	0.250	0.243	0.327	0.226	0.186	0.203	0.218	
	$\mathbf{C}_{(1)}$	2.275	3.718	4.099	4.175	3.301	2.467	3.149	3.000	
Hyperbolic	Noh (250)	199	258	288	263	274	230	258	249	
	b _(0.02)	0.044	0.058	0.071	0.057	0.036	0.049	0.049	0.042	

[†]Units are mg N kg⁻¹ soil for the N pool parameters (N₀, N₁, N₂, N_n and N₀); week⁻¹ for the mineralization rate constants of k₀, k₁, k₂ and k_n and [week (mg N kg⁻¹ soil)⁻¹] for parameter b in the hyperbolic model. ‡Values in parentheses are the initiation values used in the SAS program.

[‡]The MSE values in the same column with the same incubation duration followed by the same letter are not significantly different at the 95% confidence level according to the F-test suggested by Robinson (1985).

Table 3. Estimates of parameters using the single, double, special, and hyperbolic models based on 15 weeks incubation

Model	Parameter	Treatment								
			Murrill Soil							
		Initial	Control	Fertilizer	Manure	Alfalfa	Fallow	Clover	Vetch	
Single	N ₀ (250)‡	132	137	138	130	173	146	157	15 7	
•	k ₀ (0.1)	0.164	0.139	0.116	0.162	0.158	0.136	0.132	0.148	
Double	$N_1^{(25)}$	70	76	60	9 7	70	57	58	65	
	$\mathbf{k}_{1}^{(1)}$	0.191	0.142	0.116	0.182	0.158	0.154	0.132	0.173	
	$N_2^{(250)}$	64	61	78	36	103	90	99	94	
	k ₂ (0.05)	0.131	0.135	0.116	0.0975	0.158	0.122	0.132	0.128	
Special	$N_a^{(250)}$	132	133	138	119	173	146	157	157	
	k _a (0.1)	0.164	0.141	0.116	0.174	0.158	0.136	0.132	0.148	
	C ₍₁₎	0	0.161	0	0.576	0	0	0	0	
Hyperbolic	Noh(250)	188	200	209	185	249	218	23 4	228	
	b _(0.02)	0.041	0.048	0.059	0.043	0.033	0.047	0.045	0.039	

†Units are mg N kg⁻¹ soil for the N pool parameters (N₀, N₁, N₂, N₃ and N₀); week⁻¹ for the mineralization rate constants of k₀, k₁, k₂ and k₃ and [week (mg N kg⁻¹ soil)⁻¹] for parameter b in the hyperbolic model.

‡Values in parentheses are the initiation values used in the SAS program.

than those from the other three models except in one case (the initial treatment, Table 1). The model parameter values also differed from those based on the 30 weeks data (Table 2). The magnitudes of N_0 and N_0^h from the single and hyperbolic models were slightly reduced. The N₁ plus N₂ in the double model was equal or close to the N_0 from the single model with the k_1 , k_2 , and k_0 values all similar. With the special model, initial iterative computing using the first 15 wk data produced negative C values for six of eight treatments. Since C cannot be negative as it is given the physical meaning of resistant organic N pool multiplied by its mineralization rate constant (Bonde and Rosswall, 1987), C was constrained in the NLIN program to be ≥ 0. With this constraint, the special model produced N mineralization potential and the corresponding rate constant values that were identical to the results from the single model for six of the eight treatments (Table 3).

The dependence of goodness of fit and the magnitudes of parameters on specific models and incubation time as shown by our study suggest that the parameters derived from models do not represent N mineralization potentials for a given soil, if such potentials do exist for the soil sample under given conditions. They are merely mathematically-defined quantities obtained by non-linear regression analysis as concluded by Paustian and Bonde (1987). The results of our study also support the findings of Juma et al. (1984), Cabrera and Kissel (1988), Sierra (1990) and Dendooven et al. (1990).

Nevertheless, models and their corresponding parameters are essential to mathematically describe soil N mineralization kinetics as well as other N transformation processes. Many computer models simulating the N cycle in biological systems utilize such mathematical models in one way or another, and their potential users are often obliged to provide or search for the corresponding parameters. Under this situation, the number of components to be considered (single, double or whatever) would depend on the purpose of the modeling, the accuracy

desired, and the performance of other model components such as the simulation of water dynamics. From the practical view of evaluating or using one or more simulation models that contain fixed N mineralization submodels, caution must be taken if one has no measured input parameters (N₀, k₀, etc.) available for the target soils and has to use literature values. If values are taken from the literature, factors such as duration of incubation, specific model used, and management and field history must be considered. In addition, we suggest that, if possible, the "N pool size" and "mineralization rate constant" is taken from the same source because these two parameters have a reciprocal relationship and the "mineralization rate constant" is not a true constant. For the same reason, it would be helpful if both "pool size" and "rate constant" are dealt with as input parameters by model developers and included in the input file so that potential users can have access to both.

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REFERENCES

Beauchamp E. G., Reynolds W. D., Brasche-Villeneuve D. and Kirby K. (1986) Nitrogen mineralization kinetics with different soil pretreatments and cropping histories. Soil Science Society of America Journal 50, 1478-1483.

Bonde T. A. and Rosswall T. (1987) Seasonal variation of potentially mineralizable nitrogen in four cropping systems. Soil Science Society of America Journal 51, 1508-1514.

Cabrera M. L. and Kissel D. E. (1988) Length of incubation time affects the parameter values of the double exponential model of nitrogen mineralization. Soil Science Society of America Journal 52, 1186-1187.

Cassman K. G. and Munns D. N. (1980) Nitrogen mineralization as affected by soil moisture, temperature, and depth. Soil Science Society of America Journal 44, 1233-1237.

Deans J. R., Molina J. A. E. and Clapp C. E. (1986) Models for predicting potentially mineralizable nitrogen and decomposition rate constants. Soil Science Society of America Journal 50, 323-326.

- Dendooven L., Verstraeten L. and Vlassak K. (1990) The N-mineralization potential: an undefinable parameter. In *Fertilization and the Environment* (R. Merckx, H. Vereecken and K. Vlassak, Eds), pp. 170-181. Leuven University Press, Louvain.
- Dou Z., Fox R. H. and Toth J. D. (1994) Tillage effect on seasonal nitrogen availability in corn supplied with legume green manures. *Plant and Soil* 162, 203-210
- Fox R. H. and Piekielek W. P. (1983) Response of corn to nitrogen fertilizer and the prediction of soil nitrogen availability with chemical tests in Pennsylvania. Bulletin 843. The Pennsylvania State University, College of Agriculture, Agricultural Station, University Park, PA.
- Hadas A., Bar-Yosef B., Davidov S. and Sofer M. (1983) Effect of pelleting, temperature, and soil type on mineral nitrogen release from poultry and dairy manures. Soil Science Society of America Journal 47, 1129-1133.
- Jemison J. M., Jr and Fox R. H. (1994) Nitrate leaching from N fertilized and manured corn managed with zero-tension lysimeters. *Journal of Environmental Quality* 23, 337-343.
- Juma N. G., Paul E. A. and Mary B. (1984) Kinetic analysis of net nitrogen mineralization in soil. Soil Science Society of America Journal 48, 753-757.
- Keeney D. R. and Nelson D. W. (1982) Nitrogen-inorganic forms. In Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties (A. L. Page, R. H. Miller and

- D. R. Keeney, Eds), pp. 643-698. American Society of Agronomy, Madison, WI.
- Molina J. A. E., Clapp C. E. and Larson W. E. (1980) Potentially mineralizable nitrogen in soil: The simple exponential model does not apply for the first 12 weeks of incubation. Soil Science Society of America Journal 44, 442-443.
- Paul E. A. and Clark F. E. (1989) Soil Microbiology and Biochemistry. Academic Press, San Diego, CA.
- Paustian K. and Bonde T. A. (1987) Interpreting incubation data on nitrogen mineralization from soil organic matter.
 In Soil Organic Matter Dynamics and Soil Productivity.
 Proceedings INTECOL Workshop, INTECOL Bulletin (J. H. Cooley, Ed.), 15, pp. 101-112. International Association for Ecology, Athens, GA.
- Robinson J. A. (1985) Determining microbial kinetic parameters using nonlinear regression analysis. *Advances in Microbial Ecology* 8, 61-114.
- SAS Institute. (1990) SAS User's Guide: Statistics. 5th ed. SAS Institute, Cary, NC.
- Schmidt E. L. (1982) Nitrification in soil. In Nitrogen in Agricultural Soils (F. J. Stevenson, Ed.), pp. 253-288. American Society of Agronomy, Madison, WI.
- Sierra J. (1990) Analysis of soil nitrogen mineralization as estimated by exponential models. Soil Biology & Biochemistry 22, 1151-1153.
- Smith S. J. (1987) Soluble organic nitrogen losses associated with recovery of mineralized nitrogen. Soil Science Society of America Journal 51, 1191-1194.
- Stanford G. and Smith S. J. (1972) Nitrogen mineralization potentials of soils. Soil Science Society of America Proceedings 36, 465-472.