

Predicting Soil Nitrogen Mineralization Dynamics with a Modified Double Exponential Model

W. J. Wang,* C. J. Smith, and D. Chen

ABSTRACT

The double exponential model that separates mineralizable soil organic N into active (N_a) and slow (N_s) pools has been widely used to describe net N mineralization dynamics. However, the biological meanings of the model parameters and their relationships to soil properties and environmental conditions remain to be elucidated. In the present study, 18 soils were incubated at 35°C and 55% water-holding capacity (WHC) for 41 wk and two soils at 16 factorial combinations of temperature (5, 15, 25, or 35°C) and moisture (8, 11, 15, or 19%) for 29 wk. Although the model closely fitted the net N mineralization data, the model parameters often appeared to lack biological meanings and could vary with incubation time, temperature, and soil moisture in unpredictable manners. Thus, the conventional double exponential model was modified by (i) using defined mineralization rate constants for N_a and N_s under standard temperature (35°C) and moisture (approximately 55% WHC); and (ii) using soil-specific and fixed N_a and N_s values to estimate temperature- and moisture-dependent rate constants under non-standard conditions. This technique basically eliminated the time effect on the estimates of pool sizes and resulted in the rate constants with a consistent Q_{10} response to temperature and linear response to moisture changes. Predictions of soil net N mineralization dynamics under field conditions using the parameters estimated in laboratory agreed closely with the measured data. Multiple regression analysis indicated that the size of N_a is correlated with the initial water-soluble organic N and microbial biomass in soil, whereas N_s represents the combined effects of all the factors regulating long-term net N mineralization.

ACCURATE PREDICTION of the net N mineralization dynamics in soil is important for developing appropriate fertilization strategies, which maintain or increase productivity while minimizing adverse N impacts on the environment. Both complex mechanistic and simple kinetic models have been used for this purpose (De Willigen, 1991). The mechanistic models are process-based and generally require considerable input data. The kinetic models normally rely on laboratory incubations to obtain parameters and do not account for basic N turnover processes such as mineralization, immobilization, and nitrification. There is no proof that one approach is consistently better than the other for predicting net N mineralization during crop growing seasons (De Willigen, 1991; Benbi and Richter, 2002). Accurate but simple models that require less data input are preferred for practical use in making decisions on nutrient management.

Many kinetic models such as sigmoid, hyperbolic, and

single exponential plus linear models have been used to describe inorganic N production from soil or amended organic materials (Juma et al., 1984; Broadbent, 1986). However, few authors have fully explained the theoretical implications of the parameters in these mathematical equations (Ellert and Bettany, 1988). Consequently, first-order kinetic models including the single (Stanford and Smith, 1972) and the double (Molina et al., 1980) exponential models remain widely used.

The double exponential model separates the mineralizable organic N into active and slow pools and can be presented as:

$$N_t = N_a(1 - e^{-k_a t}) + N_s(1 - e^{-k_s t}) \quad [1]$$

where N_t is the cumulative amount of N mineralized at time t ; N_a and N_s are the sizes of the active and slow pools of mineralizable N, respectively; k_a and k_s are the corresponding mineralization rate constants for each pool. Equation [1] appears to be consistent with some mechanistic models that divide soil organic matter into active, slow, and resistant pools or other synonyms (Verberne et al., 1990; Hanssen et al., 1991; Parton, 1996). The resistant pool is not included in Eq. [1], assuming that it does not significantly contribute to N mineralization in a relatively short period. Several studies have confirmed that the double exponential model is better than the single exponential model for describing net N production in disturbed soils, wherein flushes of N mineralization usually occur during the early stages of incubation (Cabrera and Kissel, 1988c; Dou et al., 1996).

There have been appeals to link the conceptual pools in soil organic matter models to measurable fractions (Elliott et al., 1996). Mechanistic models usually allow for replenishment of the pools, whereas the kinetic model does not. To relate the kinetically determined pools to soil properties is of theoretical as well as practical interest. Nonetheless, there have been concerns that the estimated pool sizes and their rate constants in Eq. [1] could be affected by the incubation time (Cabrera and Kissel, 1988b; Dou et al., 1996). This led Sierra (1990) to comment, "the assumption of the existence of discrete size pools of mineralizable N is a faulty concept." Similarly, Dou et al. (1996) concluded that the model parameters are merely mathematically defined quantities and do not represent soil N mineralization potentials.

It is generally thought that the pool sizes of soil organic matter are soil specific, while their mineralization

W.J. Wang and D. Chen, School of Resource Management, the Univ. of Melbourne, Parkville 3052, Victoria, Australia; C.J. Smith, CSIRO Land and Water, GPO Box 1666, Canberra 2601, ACT, Australia. W.J. Wang, Present address: NR&M, 80 Meiers Rd, Indooroopilly, Brisbane, Qld. 4068, Australia. Received 12 Nov. 2003. *Corresponding author (weijin.wang@nrm.qld.gov.au).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: DOC, dissolved organic C; DON, dissolved organic N; k_a , mineralization rate constant for N_a ; k_s , mineralization rate constant for N_s ; LFC, light fraction organic C; LFN, light fraction organic N; MBC, microbial biomass C; MBN, microbial biomass N; N_a , active organic N pool; N_s , slow organic N pool; TON, total organic N; WHC, water-holding capacity.

rate constants vary with environmental conditions. Thus, net N production under field conditions can be predicted using the soil-specific pool sizes and their temperature- and moisture-dependent rate constants. If the above assumption is valid, one may expect that N_a or N_s estimated under different temperatures and moistures should be similar for a given soil. However, few studies, if any, have experimentally examined the impacts of temperature and moisture variations on the kinetically estimated N_a , N_s , k_a , and k_s , in spite of the fact that the incubation conditions used to obtain N mineralization data often differed considerably in different studies (Ellert and Bettany, 1988; Dendooven et al., 1997).

Satisfactory predictions of net N production in the field have been achieved using the kinetic models determined from laboratory incubation (Stanford et al., 1977; Marion et al., 1981; Campbell et al., 1984). However, overestimations have been occasionally reported by others (Verstraete and Voets, 1976; Cabrera and Kissel, 1988a). The overestimation could have been due to several causes including the crushing and air-drying of soil samples before incubation, removal of plant residues with high C/N ratios from incubated samples, plant debris or exudates inputs and/or possible N losses from soil under field conditions. Besides, the validity of using model parameters estimated from laboratory incubation could be affected by the fluctuations in temperature and moisture in field conditions (Sierra, 2002).

The objectives of this study were to (i) re-appraise the meaningfulness of the active and slow soil organic N pools and their mineralization rate constants obtained with the conventional double exponential model; (ii) examine the temperature and moisture dependence of the model parameters; (iii) modify the structure and fitting procedure of the model to estimate soil-specific pool sizes and temperature- and moisture-dependent mineralization rate constants; (iv) test the feasibility of using laboratory data to predict net N mineralization under field conditions; and (v) relate the kinetically estimated pool sizes to basic soil properties and several physical, chemical, and biological fractions of readily mineralizable organic N.

MATERIALS AND METHODS

Soils and Properties

Eighteen air-dried soil samples were used to provide a wide range in total organic C (TOC, 7–77 mg g⁻¹), total organic N (TON, 0.7–5.5 mg g⁻¹), clay content (30–760 mg g⁻¹), WHC (273–804 mg g⁻¹) and pH (4.6–8.6). Detailed description of the soils and their identification numbers have been presented in Wang et al. (2003b). Several physical or chemical techniques were used to separate the readily mineralizable organic C and/or N in soils before the incubation. As described by Wang et al. (2001), water soluble organic C (DOC) and N (DON) were determined by extracting soil with deionized water (1:2) for 15 min (Burford and Bremner, 1975), light fraction organic C (LFC) and N (LFN) by floating soil in 1.6 g cm⁻³ ZnBr₂ (Janzen, 1987), hot KCl-hydrolyzable organic N (KCl-N) by heating soil in 2 M KCl at 100°C for 4 h (Gianello and Bremner, 1986), HCl-hydrolyzable organic N (HCl-N) by boiling soil in 1 M HCl for 4 h (Xu et al., 1997), NaOH-hydrolyzable organic N (NaOH-N) by incubating soil in 1 M NaOH at 40°C for

24 h (Wang and Li, 1991), and microbial biomass C (MBC) and N (MBN) by the chloroform fumigation-extraction technique (Wang et al., 2003a). All results are expressed on an oven-dry basis.

Laboratory Incubation

The incubation procedures have been described in detail in Wang et al. (2003b). Briefly, triplicate soil samples equivalent to 200 g of oven-dry matter each were incubated in 2-L glass jars at the near optimum temperature (35°C, Stanford and Smith, 1972) and moisture (55–65% WHC) for 41 wk. The jars were normally closed but opened periodically to maintain an aerobic condition for the soils. Water loss in the jars was monitored by weight and replenished every time the jars were opened. No leaching was conducted during the course of incubation for reasons discussed in Wang et al. (2003b). The cumulative amount of inorganic N in soil was determined by sampling at 0, 1, 2, 4, 6, 9, 12, 16, 20, 24, 29, 35, and 41 wk. Net N mineralization during a period of time was calculated by subtracting inorganic N content at time zero from that at the time of sampling.

Soil 15 (Kandosol in Australian classification or Palexeralf in U.S. taxonomy, 220 g clay kg⁻¹, 14 mg TOC kg⁻¹, and 1.1 mg TON kg⁻¹) and Soil 17 (Chromosol in Australian classification or Rhodoxeralf in U.S. taxonomy, 120 g clay kg⁻¹, 21 mg TOC kg⁻¹, and 1.6 mg TON kg⁻¹) were incubated under four different temperatures (5, 15, 25, or 35°C) in factorial combination with four moisture levels (7, 11, 15, or 19% w/w) for 29 wk to study the effects of temperature and moisture on N production kinetics (Wang et al., 2003b). Net N mineralization in soil was determined by intermittent sampling as above.

Field Incubation

Soils 15 and 17 were used for this experiment. Air-dried sample equivalent to 100 g of oven-dry soil was weighed into twenty 200-mL polystyrene jars for each soil. The soils were then moistened to 55% WHC (19% w/w) with water. The jars of each soil were placed in a plastic box (40 × 30 × 25 cm³) that was then covered with a lid drilled with 15 evenly distributed holes (5 mm dia.) and half-buried into the ground in a birdcage. A wooden cover was placed about 30 cm above each box to shield from direct sunlight and rainfall. The temperature in each box was measured with six thermocouples randomly placed in soil at different locations within the box and recorded every 15 min with a data logger (Wesdata 692, Australia). Soil moisture was monitored by weight every 3 to 5 d, depending on the rate of moisture loss. The moisture in different jars was maintained at the same level by adding water, and controlled within the range of 8 to 19% (w/w) to avoid denitrification and drying-wetting effects on mineral N accumulation. At various time intervals, triplicate jars were destructively sampled for mineral N determination. This experiment was undertaken from 6 Sept. 1999 to 10 Jan. 2000 (the soils were incubated in the laboratory for the last 17 d during Christmas holiday).

Model Fitting and Statistical Analysis

Equation [1] was fitted with the Fit Curve procedures of SigmaPlot 7.1 (SPSS Inc., IL) that uses the Marquardt–Levenberg algorithm and an iterative process to find the parameter values that minimize the residual sum of squares. The resultant pool sizes and their mineralization rate constants, particularly k_a , could be sensitive to the initially assigned parameter values and the iteration step size. Generally, the auto-

matically estimated initial parameters resulted in acceptable parameter values. In some cases, manual adjustment of the initial parameter values and the step size was needed to obtain sensible results (e.g., k_a should not be greater than a few orders of magnitude; and the pool sizes should not be negative).

Stepwise multiple regression was performed using Sigma-Stat, Version 2.03 (SPSS Inc., Chicago, IL) to relate the model pool sizes with the physical, chemical, and biological properties of soil. Analysis of variance was performed using the procedure of GenStat 6th ed., Release 6.1 (Payne, 2002). The difference between treatment means was tested using the least significant difference (LSD) at levels of $P < 0.05$ and $P < 0.01$.

RESULTS AND DISCUSSION

Goodness of Curve-fitting and Vague Biological Meaning of Model Parameters

The dynamics of net N mineralization in some soils (e.g., Soils 8, 9, 10, 12, and 14) followed an evident two-phase pattern with a rapid N mineralization rate at the early stages of incubation (Fig. 1). The double exponential model (Eq. [1]) closely fitted the net N mineralization data from 0 to 41 wk ($R^2 = 0.984\text{--}0.998$; figures not shown). In comparison with the single exponential

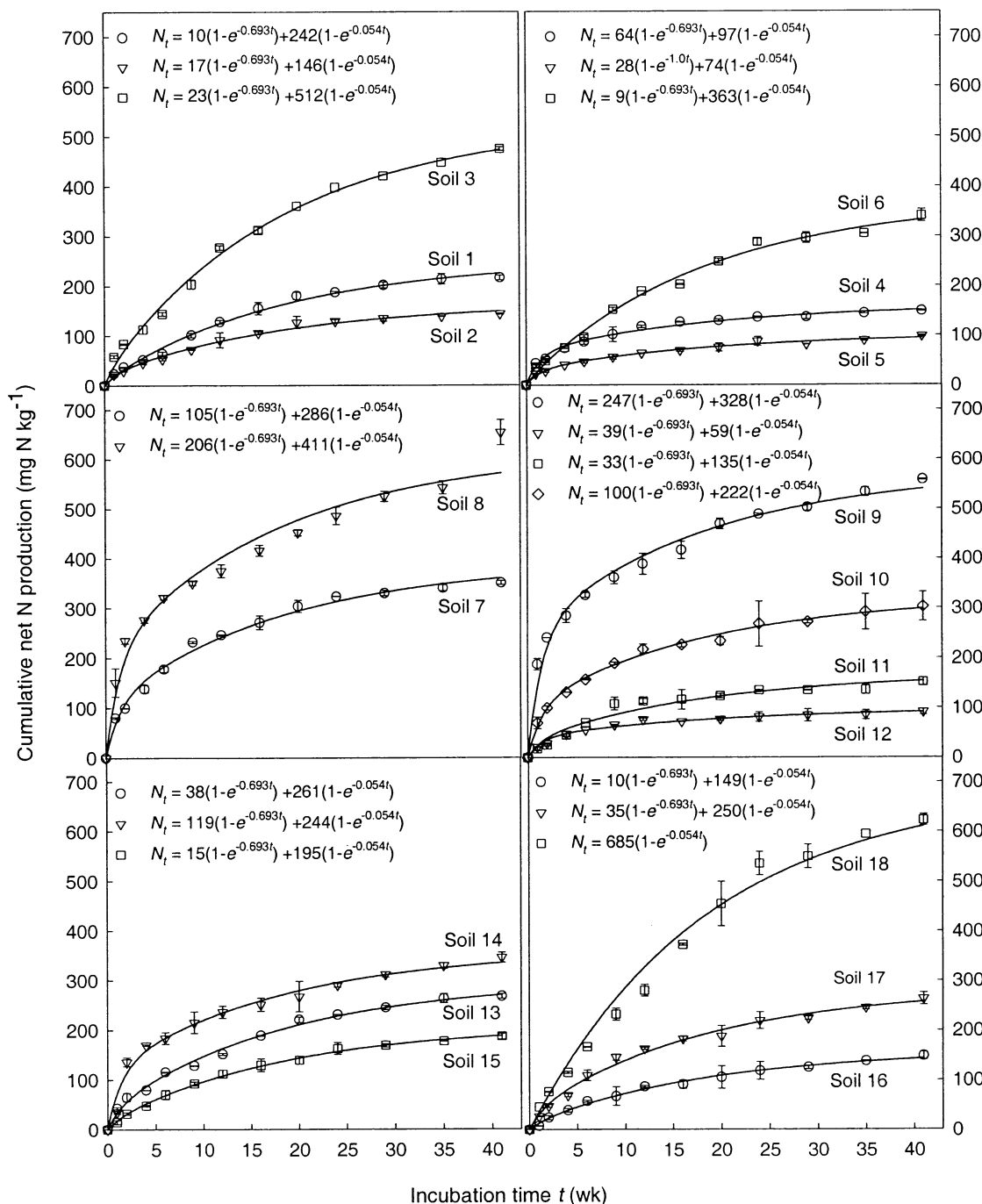


Fig. 1. Soil net N mineralization dynamics (35°C and 55% WHC) and the goodness of fit by the double exponential model with fixed mineralization rate constants. The vertical bars represent the standard deviation of triplicate measurements. $R^2 = 0.958\text{--}0.998$ (median 0.992) for the curves fitted.

model (Wang et al., 2003b), Eq. [1] more closely described N mineralization kinetics for the soils with large initial flushes without the need to exclude data in the first few weeks.

Some authors suggest that the initial N mineralization flush represents the artifact of soil disturbance and thus can be excluded from model fitting (Stanford and Smith, 1972; Groot and Houba, 1995). Others believed that the pattern of N mineralization during the first few weeks of incubation might be critical for understanding the N availability status of soils (Bundy and Meisinger, 1994). Similarly, there has been an on-going debate about conducting incubations with field-moist vs. air-dried soils (Drinkwater et al., 1996). Drying and wetting cycles in most soils and mechanical disturbance in tilled agricultural soils are regular occurrences, particularly for surface soils where organic matter content is normally high. In some cases, crop response has been found to be better correlated with estimates of available N obtained from laboratory incubations of air-dry than field-moist soils (Keeney and Bremner, 1966). Like most other studies where the double exponential model was found useful to describe N mineralization dynamics, the goal of our study was to predict N mineralization in soils that may be subjected to routine physical disturbance. It is recognized, however, that initial N mineralization flushes and thus the active pools might not be significant in constantly moist and intact soils.

The sum of $N_a + N_s$ initially given by the non-linear regression procedure exceeded the TON for Soils 6, 8, 10, 11, and 17 (data not shown), which was similar to the findings of Dendooven et al. (1997). When a constraint of $N_a + N_s \leq \text{TON}$ was applied in the curve-fitting procedure, the values of R^2 and residue mean square (RMS) were not significantly affected. The standard error for a parameter could be multiples of the parameter value per se, suggesting that the model parameters obtained from the non-linear regression were not necessarily unique for a data set. Furthermore, the mineralization rate constants varied widely across soils ($k_a = 0.065\text{--}37 \text{ wk}^{-1}$; $k_s = 0.0007\text{--}0.108 \text{ wk}^{-1}$). At times, k_s for one soil was greater than k_a for another. Therefore the active or slow pool as mathematically estimated by the regression process had different meanings for

different soils, and no single parameter can be used as an indicator of soil N mineralization capacity.

Furthermore, the magnitudes of N_a , N_s , k_a , and k_s varied considerably with incubation time for most soils. Cabrera and Kissel (1988b) found that the pool sizes increased, whereas their rate constants decreased as the incubation time increased. Nonetheless, the opposite results were also obtained for some soils in the present study (e.g., Soils 2 and 3; Table 1). For several soils (e.g., Soils 5, 6, 8, 16, and 18), changes in the magnitudes of N_a , N_s , k_a , and k_s with time had no consistent trend, although close fitting to N mineralization data was always achieved ($R^2 > 0.99$ in most cases).

It has been suggested that a strategy to obtain stable model parameters would be to continue the incubation until the mineralization rate declines to a small and constant level (Bonde and Lindberg, 1988; Benbi and Richter, 2002). This was achieved for some of our soils (e.g., Soils 1, 2, 3, 5, 13, and 15; partially shown in Table 1), but not for others (e.g., Soils 6, 8, 14, 16, and 18) where further incubation from 29 to 41 wk did not result in constant pool sizes. Extension of the incubation time over 41 wk could become practically unacceptable and less meaningful.

Influences of Temperature and Moisture on Model Parameters

The dynamics of net N mineralization for Soils 15 and 17 at different temperature and moisture combinations were given in Wang et al. (2003b). The cumulative net N mineralization increased consistently with increasing temperature and moisture within the tested ranges. The double exponential model closely fitted the experimental data from 0 to 29 wk under all the temperature-moisture combinations for both soils ($R^2 = 0.945\text{--}0.999$; median 0.995). Unlike the cumulative net N mineralization, however, changes in N_a and N_s with temperature and moisture were largely inconsistent and unpredictable. Poor trends were also observed for the values of k_a and k_s (data not presented).

Changes in the kinetically determined pool sizes, and inconsistent or little changes in the rate constants with temperature and soil moisture contradicted the general

Table 1. Examples of the active (N_a) or slow (N_s) organic N pool sizes for soils after various lengths of incubation (wk), as estimated using the double exponential model with four variable parameters and a modified version with fixed mineralization rate constants ($k_a = 0.693$ and $k_s = 0.054 \text{ wk}^{-1}$).

Time	Soil ID													
	Conventional model with four variables							The modified model with fixed rate constants						
	2	3	5	6	8	16	18	2	3	5	6	8	16	18
	$N_a \text{ (mg kg}^{-1}\text{)}$													
0–20	17	34	17	15	249	79	26	14	24	30	13	249	13	0
0–24	14	32	29	18	250	57	662	14	21	28	7	241	12	0
0–29	12	28	19	15	249	65	502	16	23	29	8	232	13	0
0–35	11	25	21	164	236	61	426	18	24	29	11	227	12	0
0–41	10	25	19	291	265	57	0	20	23	28	9	206	10	0
	$N_s \text{ (mg kg}^{-1}\text{)}$													
0–20	292	696	67	393	758	1087†	2257†	163	502	69	349	288	141	641
0–24	181	622	113	481	791	1109†	662	161	511	76	368	314	143	670
0–29	156	543	73	400	780	1111†	440	156	507	71	366	341	143	676
0–35	147	515	74	191	488	305	406	150	504	72	357	354	145	682
0–41	144	513	80	2157†	5298†	223	781	146	505	74	363	411	149	685

† A constraint of $N_a + N_s \leq \text{TON}$ was applied in model fitting.

assumption in modeling that the sizes of soil organic matter pools should be unaffected by, whereas their mineralization rate constants should be a function of the environmental factors (Stanford et al., 1977; Parton et al., 1987; Jenkinson, 1990; Goncalves and Carlyle, 1994). The temperature dependence of the kinetically estimated pool size rather than the rate constant was interpreted by Zogg et al. (1997) as the result of alternation in microbial composition, wherein dominant populations at higher temperatures have the ability to mineralize substrates that are not used by microbes at lower temperatures. Similarly, Dalias et al. (2003) concluded that the substrate pools should be defined not only by their chemical quality but also by the temperature under which decomposition takes place.

In the present study, the patterns of mineral N accumulation appeared linear at lower temperatures, but curvilinear at higher temperatures (Wang et al., 2003b). This is probably because demand for the readily mineralizable organic N by microbes was so small at lower temperatures that substrate supply was not the primary limiting factor for their activity throughout the period of incubation; while at higher temperatures the readily mineralizable organic matter was consumed faster and N mineralization gradually slowed down due to the limit of substrate availability. The values of the model parameters are affected by net N mineralization patterns and by errors in the experimental data. However, we hypothesize that the meaninglessness of the estimated model parameters and their inconsistent changes with time, temperature and moisture were largely because Eq. [1] has too many (four) unknown parameters to be derived by the iterative curve-fitting procedure and these parameters (particularly N_a vs. k_a and N_s vs. k_s) are interdependent.

Model Modification

The conventional double exponential model (Eq. [1]) was modified following the approach of Christensen and Olesen (Christensen and Olesen, 1998). Based on the k_a values given by Eq. [1] and visual inspection of the mineral N accumulation dynamics (Fig. 1), a half-life ($t_{1/2}$) of 1 wk was used to define the turnover rate of N_a that was responsible for the initial net N mineralization flush. As $1/2N_a = N_a e^{-k_a t_{1/2}}$, the mineralization rate constant for N_a would therefore be $\bar{k}_a = \ln 2/t_{1/2} = 0.693 \text{ wk}^{-1}$. The mineralization rate constant for N_s was defined as $\bar{k}_s = 0.054 \text{ wk}^{-1}$, an average value obtained by Stanford and Smith (1972) after removal of the first two weeks' data. So the conventional double exponential model (Eq. [1]) was modified into a model with two unknown parameters (N_a and N_s), each with a standard mineralization rate constant:

$$N_t = N_a(1 - e^{-0.693t}) + N_s(1 - e^{-0.054t}) \quad [2]$$

Moderate variation in the empirically defined k_a and k_s values would not significantly affect the goodness of fit to data; a higher rate constant would normally result in a lower pool size, and vice versa. The k_a and k_s values defined in this study are considered appropriate for the

incubation conditions (at 35°C for 41 wk). Indeed, there have been no universally agreed values for the empirically defined active and slow pools. The rate constants for a namely synonymous pool in different mechanistic models could differ by many folds (Molina and Smith, 1998), mainly depending on the time scale of prediction. If an incubation is conducted for a period much longer than in the present study, the rate constant for the slow pool may need to be adjusted, or a resistant pool with a lower rate constant can be added in the model.

Equation [2] fitted the net N mineralization data from 0 to 41 wk very well (Fig. 1); the R^2 values were in the range of 0.958 to 0.998, which were identical to or only slightly lower (mostly in the third decimal) than those for Eq. [1]. In contrast to the model with four unknown parameters (Eq. [1]), use of fixed \bar{k}_a and \bar{k}_s in fitting Eq. [2] resulted in N_a or N_s values that were remarkably similar at different lengths of incubation after 20 wk (partly shown in Table 1). Therefore, the modified double exponential model successfully solved the problem of time-dependence in N_a and N_s values that has been a concern to many researchers (Cabrera and Kissel, 1988b; Sierra, 1990; Dou et al., 1996; Dendooven et al., 1997).

Equation [2] also eliminated the confounding effect of the otherwise variable rate constants on pool size estimates. This allowed soil N mineralization capacity to be expressed explicitly with pool sizes. A high N_a value should indicate a large initial N mineralization flush, and a high N_s value should suggest a large long-term N mineralization rate. The use of fixed \bar{k}_a and \bar{k}_s values provides a basis toward a more standardized concept of active or slow pool, that is, N_a or N_s for different soils in different studies would be comparable, providing the incubation conditions are standardized or corrected (e.g., 35°C and approximately 55% WHC or field capacity).

Temperature and Moisture Effects on Rate Constants of the Modified Model

Because the pool sizes in Eq. [2] were insensitive to the length of incubation after 20 wk, the N_a ($\bar{k}_a = 0.693 \text{ wk}^{-1}$) and N_s ($\bar{k}_s = 0.054 \text{ wk}^{-1}$) were estimated for Soils 15 and 17 using the N mineralization data under 35°C and 55% WHC (19% w/w for both soils) from 0 to 29 wk, a duration close to that used by Stanford and Smith (1972) and many others. Assuming that N_a (14 mg kg⁻¹ for Soil 15 and 36 mg kg⁻¹ for Soil 17) and N_s (199 mg kg⁻¹ for Soil 15 and 247 mg kg⁻¹ for Soil 17) do not change with temperature and moisture, Eq. [1] was modified to fit the data of net N mineralization under other temperature and moisture treatments by using fixed pool sizes and variable rate constants as below:

$$\text{Soil 15: } N_t = 14(1 - e^{-k_a t}) + 199(1 - e^{-k_s t}) \quad [3]$$

$$\text{Soil 17: } N_t = 36(1 - e^{-k_a t}) + 247(1 - e^{-k_s t}) \quad [4]$$

Equations [3] and [4] closely described net N mineralization dynamics under different temperature and moisture conditions ($R^2 = 0.915\text{--}0.998$ and median = 0.985 for Soil 15; $R^2 = 0.881\text{--}0.998$ and median = 0.994 for

Soil 17). Compared with the single exponential model with a fixed N_0 and an unknown k (Wang et al., 2003b), better fittings to the experimental data were achieved in many cases with Eq. [3] and [4], as indicated by higher R^2 and lower RMS values (data for RMS not presented).

In contrast to the results obtained with Eq. [1], the mineralization rate constants of the slow pool for Soil 15, and of both the active and slow pools for Soil 17, showed clear trends of linear increases with increasing moisture (Fig. 2). The lack of consistent relation between k_a and soil moisture for Soil 15 was probably because the size of N_a (14 mg kg⁻¹) was so small that the moisture effect was obscured by experimental errors. The moisture effect on both k_a and k_s was insignificant for the treatments at 5°C for both soils ($P > 0.05$).

The temperature effects on the mineralization rate constants of both active and slow pools were significant ($P < 0.05$) and more evident than the moisture effects (Fig. 2). The Q_{10} function described the relationships between mineralization rate constants and temperature very well. The temperature and moisture effects on k_a and k_s were positively interactive ($P < 0.01$) and could be described using correction factors for moisture θ (% w/w) and temperature T (°C) as below:

Soil 15: $k_a = 0.693 f_\theta \times f_T$

$$= 0.693 \left(0.73 + 0.25 \times \frac{\theta}{\theta_{\max}} \right) \times 2.75^{(T-35)/10},$$

$$R^2 = 0.834 \quad [5]$$

$$k_s = 0.054 f_\theta \times f_T$$

$$= 0.054 \left(-0.27 + 1.23 \times \frac{\theta}{\theta_{\max}} \right) \times 3.11^{(T-35)/10},$$

$$R^2 = 0.982 \quad [6]$$

Soil 17: $k_a = 0.693 f_\theta \times f_T$

$$= 0.693 \left(0.19 + 0.44 \times \frac{\theta}{\theta_{\max}} \right) \times 2.08^{(T-35)/10},$$

$$R^2 = 0.943 \quad [7]$$

$$k_s = 0.054 f_\theta \times f_T$$

$$= 0.054 \left(-0.02 + 1.07 \times \frac{\theta}{\theta_{\max}} \right) \times 3.28^{(T-35)/10},$$

$$R^2 = 0.993 \quad [8]$$

where f_θ and f_T are moisture and temperature correction factors, respectively; θ_{\max} is the optimum soil moisture for net N mineralization.

Prediction of Net Nitrogen Mineralization under Controlled Field Conditions

The temperature during the 126-d field incubation of Soils 15 and 17 fluctuated considerably (2.5–35.8°C; Fig. 3a,d). The soil moisture was operationally controlled within a range of >8% (w/w) to avoid the drying-rewetting effect and <55% WHC to avoid N loss from denitrification (Fig. 3b,e).

The fluctuating field conditions contrasted with the constant temperature and moisture used in the laboratory incubations. Therefore, this experiment would provide a robust test for the usefulness of the laboratory results to predict in situ net N mineralization, without the complications often encountered in field studies such as changes in the labile organic C and N pools due to inputs from plant root exudates and debris, leaching of soluble organic matter by rain water, drying-wetting cycles, or N loss via leaching and denitrification. Indeed, such complications are realities under natural conditions; but it is unrealistic to expect an empirical net N mineralization model to capture all the affecting factors. The effects of other than mineralization/immobilization processes should be dealt with separately.

To predict net N mineralization under fluctuating temperature and moisture using the model parameters estimated under constant conditions, k_a and k_s were adjusted using Eq. [5] and [6] for Soil 15 and using Eq. [7] and [8] for Soil 17 in both hourly and daily time intervals. The temperature during each time interval was calculated as the arithmetic mean of the measurements, and the moisture was estimated by linear interpolation between two sequential measurements. The amount of N mineralized from N_a during the first time interval (N_{t1}) was calculated as below:

$$N_{t1} = N_a(1 - e^{-k_{a1}t}) \quad [9]$$

where N_a was 14 mg kg⁻¹ for Soil 15 and 36 mg kg⁻¹ for Soil 17; k_{a1} was the rate constants for the first time interval calculated using Eq. [5] for Soil 15 and using Eq. [7] for Soil 17; $t = 1/(7 \times 24)$ wk when hourly time interval was used and $t = 1/7$ wk when daily time interval was used. The predicted cumulative amount of mineral N produced from N_a by the end of the second time interval was calculated as:

$$N_{t2} = N_{t1} + (N_a - N_{t1})(1 - e^{-k_{a2}t}) \quad [10]$$

and so on for the following time intervals.

The cumulative amounts of N mineralized from N_s were calculated using the same algorithm. The sum of the predicted net N mineralization from both N_a and N_s was used as the prediction of the amount of N mineralized from the soil.

The predicted dynamics of mineral N in the soils during the 126-d field incubation agreed satisfactorily with the measured data (Fig. 3c,f). The results predicted with daily mean temperature were lower than those with hourly mean temperature and the measured data for Soil 15 ($P < 0.01$). The underestimation obtained with daily mean temperature was primarily because of the non-linear response of mineralization rate constants to temperature (Fig. 2), which should increase with the increase in the Q_{10} coefficient and the amplitude of the temperature fluctuation (Das et al., 1995). However, the error associated with the use of daily mean temperature was minor for Soil 17 (Fig. 3f). Sierra (2002) found that use of daily mean temperature induced considerable underestimation of net N mineralization from an Oxisol that had a Q_{10} of 4. The results of this study confirmed that in situ N mineralization dynamics could

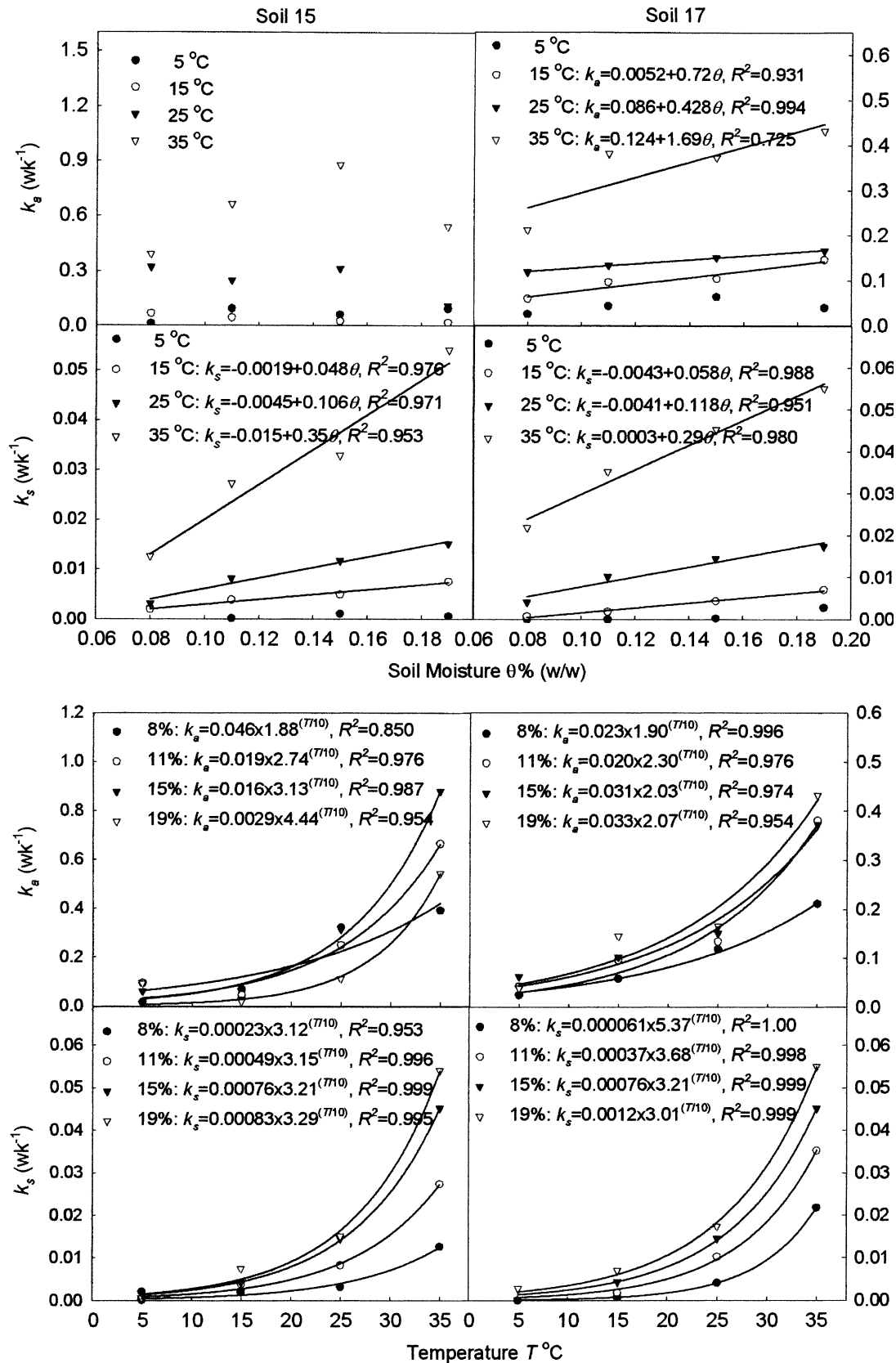


Fig. 2. Temperature and moisture responses of the mineralization rate constants of the active (k_a) and slow (k_s) organic N pools. k_a and k_s were estimated by the double exponential model with fixed pool sizes that were obtained with the data at 35°C and 55% WHC using standard k_a (0.693) and k_s (0.054). The equations for insignificant moisture responses were not shown.

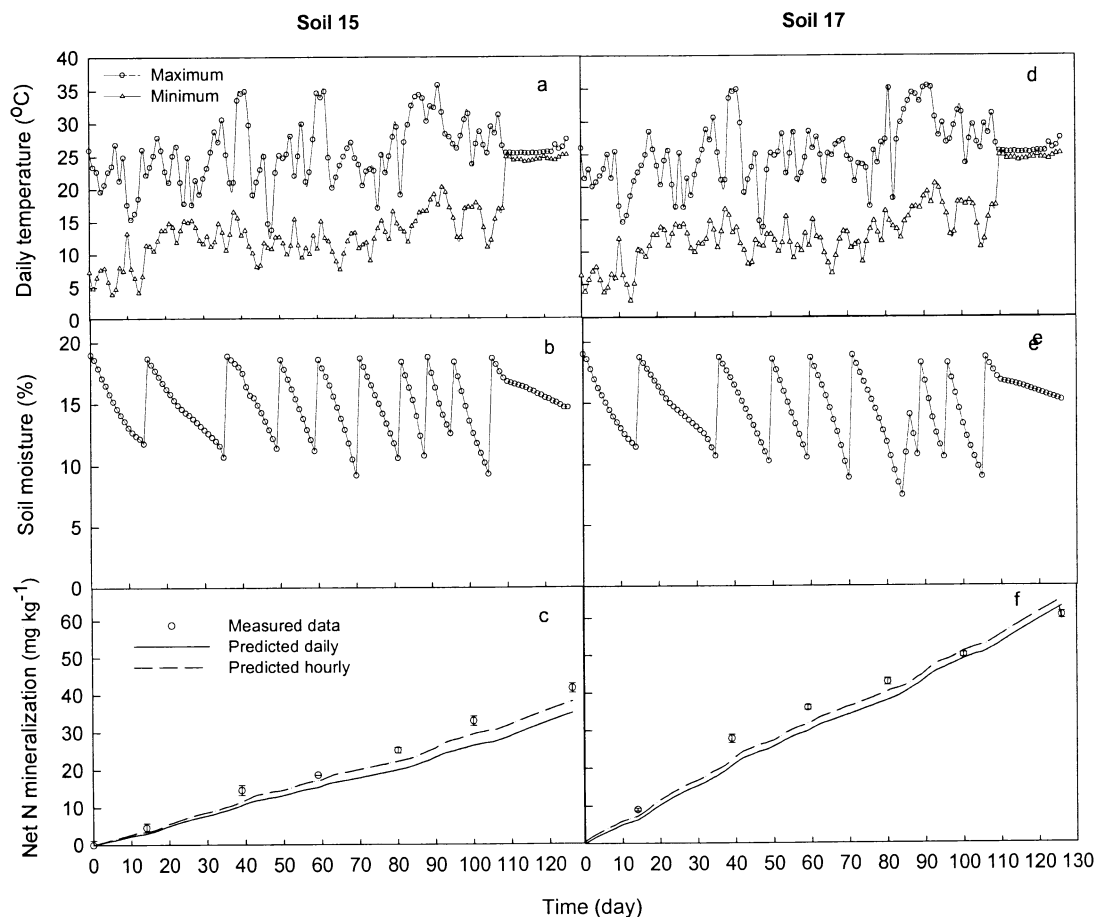


Fig. 3. The measured and predicted net N mineralization for Soils 15 and 17 during a 126-d field incubation under fluctuating temperature and moisture conditions.

be satisfactorily predicted with the parameters determined in the laboratory.

Relationships of the Kinetically Estimated Pools to Chemical, Physical, and Microbial Organic Nitrogen Fractions

The use of defined rate constants for different soils made it possible to explicitly assess the relationships between N_a or N_s and measurable soil organic matter fractions and other soil properties without the confounding effect of k_a or k_s . Stepwise multiple linear regression was conducted to relate N_a and N_s to clay content, TON, C/N ratio, LFC, LFN, KCl-N, NaOH-N, HCl-N, DOC, DON, MBC, and MBN at time zero (MBC_0 and MBN_0), MBC and MBN at the end of the first-week incubation (MBC_7 and MBN_7), microbial biomass C after 42-d incubation (MBC_{42}), net N mineralization during the first 14 d (N_{0-14}), and net N mineralization from Day 14 to 28 (N_{14-28}). The results suggested that N_a could be estimated by:

$$N_a = -36 + 2.5 \text{ DON} + 0.13 \text{ MBC}_0 \quad [11]$$

$$R^2 = 0.91, n = 18$$

where N_a , DON and MBC_0 were expressed as mg kg⁻¹. Dissolved organic N contributed more to the prediction of N_a than did MBC_0 as indicated by the incremental F

value for each independent variable (86 and 11, respectively), suggesting that the size of N_a is primarily determined by the amount of available substrate in soil before incubation.

Substantial increases in the amount of soluble organic matter after air-drying and flushes of C or N mineralization during subsequent incubation of rewetted dry soils have been observed in many studies (Davidson et al., 1987; Lundquist et al., 1999; Franzluebbers, 1999). In the present study, the size of N_a was greater than the amount of DON for most soils, particularly those with $N_a > 30 \text{ mg kg}^{-1}$. Thus, DON should not be regarded as a direct measure of N_a ; its value is affected by the extraction procedures such as temperature, vigor and time of shaking, and filter pore size.

N_s was not correlated with any single organic C and/or N fraction described above, but could be approximately estimated by the following equation:

$$N_s = -21.9 - 0.16 \text{ LFC} + 3.7 \text{ LFN} + 0.82 \text{ MBC}_7 - 9.7 \text{ MBN}_7 + 14.3 \text{ } N_{14-28} \quad [12]$$

$$R^2 = 0.78 (P < 0.05), n = 18$$

where N_{14-28} had a much higher contribution to the prediction of N_s (incremental $F = 25$) than other variables (incremental $F < 5$).

The use of fixed rate constants is not meant to suggest

that the quality of soil organic matter in N_a or N_s be identical in different soils. Also, N_a and N_s estimated with fixed mineralization rate constants do not represent the absolute amounts of mineralizable organic N in each pool, but rather indicate the N mineralization ability of soil in different time scales, which is interactively determined by soil physical, chemical, and biological properties. The N_a indicates the magnitude of N mineralization flush during the early stages of incubation, and is mainly determined by the readily mineralizable organic N content in the original soil (Eq. [11]). The N_s pool is largely affected by the magnitude of net N mineralization after the initial flush, which is determined by the long-term capacity of soil to replenish bio-available substrate. The process of replenishment can be interactively regulated by substrate quantity and quality, and soil biological and physical properties in complicated manners. The amount of N mineralized from Day 14 to 28 (N_{14-28}) integrated the impacts of all regulating factors, hence provides better estimation for N_s than any other single index tested.

Equations [11] and [12] are not only useful for depicting the nature of N_a and N_s , but also shed light on the possibility of estimating the organic N pools and thus predicting in situ net N mineralization with relatively less time-consuming techniques. Further evaluation of these equations with results from field studies would be worthwhile. However, attention should be paid to the fact that mineral N accumulation in the field is subject to possible influences from several N-consuming processes in addition to N mineralization/immobilization. Such processes should be quantified to properly assess the performance of the empirical model.

CONCLUSIONS

The double exponential model provided good descriptions of the net N mineralization dynamics in disturbed soils incubated under constant temperature and moisture, without the need to exclude data in the first few weeks. However, when the conventional model with four unknown parameters was used, the output parameters varied significantly with duration of incubation, temperature, and moisture without consistent trends. Using empirically defined values for k_a and k_s in fitting the model to data obtained under near optimal temperature and moisture conditions (35°C and 55% WHC) resulted in the estimates of model parameters that were basically independent of incubation length from 20 to 40 wk. The pool sizes estimated with this technique provide unambiguous measures of soil N-supplying ability through mineralization/immobilization and can be directly related to soil properties without interference from the variations in rate constants. The k_a and k_s values under different temperature and moisture conditions became more predictable when constant pool sizes for a specific soil were used in model fitting. The model parameters estimated from laboratory incubation predicted mineral N dynamics under field conditions very well. Hourly mean temperature may be better than daily mean temperature for estimating k_a and k_s if the temper-

ature fluctuation and Q_{10} coefficient were large. The active organic N pool, N_a , was related to the initial DON and MBN contents in soil, but the slow pool, N_s , represents the integration of a number of soil properties. Further evaluation of the empirical model with more field data is required.

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