Nitrogen Mineralization from Soil Organic Matter: A Sequential Model

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A reliable method to predict N mineralization from soil organic matter (SOM) has proved difficult across a wide range of soils. Previous prediction models used discrete pool(s) of SOM that simultaneously decompose and mineralize organic N according to zero- or first-order kinetics, with each pool characterized for size and N mineralization rate. We propose a different approach: two N pools based on total N that decompose and mineralize organic N in sequence according to first-order kinetics. Data sets from four long-term studies were used to evaluate the sequential model. The 108 soils represented differing soil depths, tillage practices, organic amendments, and cropping systems. The rate constant for Pool I was correlated with N mineralization during the first week (k_{1wk}), calculated using long-term data. The percentage of total N in Pool I was estimated using the rate constant for Pool I. The rate constant for Pool II was related to the Pool I rate constant and the percentage of total N in Pool I. Because a long-term mineralization study to determine k_{1wk} is impractical as a routine test, k_{1wk} was correlated with total N, CO_2 evolution at 3 d, and clay content using data from one study (38 soils). The rate constant and size of Pool I and were also correlated with total N, CO_2 evolution at 3 d, and clay content. An equation describing the impact of temperature and water holding capacity on the rate constant for Pool I suggested that a single Q_{10} value is inappropriate for N mineralization from SOM.

Abbreviations: SOM, soil organic matter; WHC, water holding capacity.

Predicting N mineralization from SOM has been the goal of numerous laboratory studies (Benbi and Richter, 2002; Schomberg et al., 2009). While most studies have used optimum soil moisture, incubation times and temperatures have varied. The time course of N mineralization has been determined using a variety of approaches, including leaching and batch extraction methods. Most commonly, data have been analyzed using the single-exponential model:

$$N_t = N_0\left[1-\exp\left(-kt\right)\right] \qquad [1]$$

where N_t is cumulative N mineralized at time t, N_0 is the portion of total N undergoing N mineralization (potentially mineralizable N), k is the first-order rate constant (wk^{-1}), and t is time (wk). The double exponential model has also been used:

$$N_t = N_I\left[1-\exp\left(-k_I t\right)\right] + N_{II}\left[1-\exp\left(-k_{II} t\right)\right] \qquad [2]$$

where the subscripts represent N pools I and II; N_I and N_{II} have been referred to as the active (e.g., rapid) and slow pools, respectively, with regard to the N mineralization rate (Wang et al., 2004). Some studies have assigned biological meaning to these N pools using terms such as *decomposable plant material* and *recalcitrant plant material* (Benbi and Richter, 2002). Implicit in Eq. [2] is that N mineralization from both pools occurs simultaneously.

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It should be emphasized that Eq. [1] and [2] describe only net N mineralization and not replenishment of N_0, N_I, or N_{II} (Wang et al., 2004) or the feedback loops that occur as N is mineralized and immobilized by various N pools such as microbial biomass (Benbi and Richter, 2002; Cabrera et al., 2008). Also, these equations do not consider the influence of plant root systems on N mineralization (Dijkstra et al., 2009; Frank and Groffman, 2009). Each of these factors can alter the net N mineralized from SOM.

Incubation times have been too short in many studies to result in stable parameter estimates. Wang et al. (2003) showed that incubations at 35°C and optimum soil moisture for >30 wk resulted in stable estimates of N_0 and k in Eq. [1], while Cabrera and Kissel (1988) and Wang et al. (2004) reached a similar conclusion for N_I, k_I, N_{II}, and k_{II} in Eq. [2]. Where incubation times have been >30 wk, N_0 (Eq. [1]) has been correlated with soil properties. Hadas et al. (1986) found that N_0 was correlated with several soil N assays including total N. Schomberg et al. (2009) also found that N_0 was correlated with soil properties including total C, total N, and CO_2 production after 3 d (Franzluebbers et al., 2000). The parameters N_I and N_{II} have not been correlated with soil properties in long-term studies.

No correlations between k (Eq. [1]) and soil assays were reported by Hadas et al. (1986), Wang et al. (2003). or Schomberg et al. (2009). The parameters k_I and k_{II} have not been correlated with soil properties in long-term studies. Both Schomberg et al. (2009) and Wang et al. (2003) found that a constant value for k (0.054 wk^{-1}; Stanford and Smith, 1972) also described the time course of N mineralization. Similarly, Wang et al. (2004) found that constant values for k_I (0.693 wk^{-1}) and k_{II} (0.054 wk^{-1}) could be used in Eq. [2]. Wang et al. (2003) stated that the use of a constant k in Eq. [1] "allows comparison of N mineralization capacity among soils using the N_0 as an indicator." Wang et al. (2004) also suggested that the use of constant k_I and k_{II} in Eq. [2] would allow comparison of N_I and N_{II} among different soils.

The effects of soil temperature and soil moisture on the constant k in Eq. [1] and constants k_I and k_{II} in Eq. [2] have been described by Wang et al. (2003, 2004), respectively. For both equations, the effect of increasing soil moisture at a given temperature was linear, with the slope increasing with increasing temperature. Increasing soil temperature at a given soil moisture exhibited a curvilinear response with temperature.

In total, the single and double exponential models have been useful in characterizing N mineralization from SOM for individual soils and soils within a geographic area. Limited success in estimating the N pool size using soil properties has been reported. The estimation of rate constants from soil properties has been unsuccessful, leading to the use of constant values for comparing N pool sizes among soils and the impact of soil temperature and moisture. It is clear that an alternative approach that minimizes or eliminates these deficiencies and can be applied to a wide range of soils is needed.

One hypothesis that has not been tested is that SOM N mineralization kinetics can be defined by two N pools, where Pool I mineralizes and then Pool II mineralizes in sequence. Each N pool has a characteristic size and first-order rate constant. The sum of Pool I and Pool II is the total N. This approach has been used successfully for a number of substrates where sequential kinetics describing substrate decomposition were linked to N mineralization via the computer model DECOMPOSITION (Gilmour, 1998; Gilmour et al., 2003).

In order for the sequential model to apply to a wide variety of soils, three conditions must be met. First, rate constants and pool size must vary systematically with one or more measureable soil characteristics. Second, those soil characteristics must vary systematically with consistent and easily measured soil chemical, physical, or biological properties. And third, the time course of N mineralization must be related to the soil temperature and moisture status. The purpose of this study was to evaluate the potential of the sequential model for N mineralization from SOM and to determine if the three conditions can be met.

MATERIALS AND METHODS

Data were obtained from four long-term incubation studies by Schomberg et al. (2009), Wang et al. (2003), Hadas et al. (1986), and Griffin and Laine (1983). Each study was conducted at 35°C and optimum soil water holding capacity (WHC). Griffin and Laine (1983) used leaching to remove inorganic N from the soil; all other studies used batch extraction methods. The Schomberg et al. (2009) and Hadas et al. (1986) studies included surface soils and subsoils, while Wang et al. (2003) and Griffin and Laine (1983) used surface soils alone. The 108 soils represented a variety of soil management scenarios that included differing tillage practices, organic amendments, and cropping systems.

Each of the four studies used the single exponential model (Eq. [1]) to describe N mineralization. Schomberg et al. (2009) and Griffin and Laine (1983) did not include 0- to 2-wk N mineralization when estimating N_0 and k, while Griffin and Laine (1983) added the 0- to 2-wk N mineralization to the reported N_0. Using the published N_0 and k values, the cumulative total N mineralized at 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, and 40 wk was calculated using Eq. [1] for each soil in each study. These data were termed *observed N mineralization*.

Sequential Model Calculations

Nonlinear modeling was used to estimate the first-order rate constant of N Pool I, k_I, the percentage of total N in N Pool I, NP_I, and the first-order rate constant for N Pool II, k_{II}, as follows. The observed N mineralized from the four studies was converted to a percentage of the total N. The natural log of the total N remaining after N mineralization was the dependent variable (y, response). The independent variable (x, predictor equation) was the logical expression, shown as

$$\text{If } t \le \frac{b_I - b_{II}}{k_I - k_{II}},\ \text{then } -k_I t + b_I,\ \text{else } -k_{II} t + b_{II} \qquad [3]$$

where $-k_I t + b_I$ and $-k_{II} t + b_{II}$ are the linear segments of the plot of ln(N remaining) vs. time ($-k$ is the slope and b the intercept). The percentage of total N in Pool I was defined by the intersection of the two linear segments. The initial values for the parameters k_I, b_I k_{II}, and b_{II} were set before each model run. The values of k_I, NP_I, and k_{II} were then used to estimate the N mineralized for a given time increment $t_2 - t_1$:

Table 1. Locations, mean soil properties and mean first-order N mineralization rate constants (k) and potentially mineralizable N (N_0) contents and concentrations (Eq. [1]) for the four studies.

Location	Soils	Time	Total C	Total N	C/N ratio	k	N_0 content	N_0 conc.	Reference
	no.	wk	g kg^{-1}			wk^{-1}	mg kg^{-1}	%	
U.S. Southeast	38	41	12.0 b†	1.03 b	11.9 a	0.071 a	178 b	17.3 a	Schomberg et al. (2009)
Victoria, QLD, Australia	18	41	25.2 a	1.98 a	12.8 a	0.069 ab	258 ab	14.4 a	Wang et al. (2003)
Israel	35	32	6.1 b	0.59 b	10.4 b	0.065 ab	84 c	13.3 a	Hadas et al. (1986)
Connecticut	17	40	25.3 a	2.03 a	12.6 a	0.042 b	314 a	15.9 a	Griffin and Laine (1983)

† Means followed by the same letter are not significantly different.

$$\text{N mineralized} = (\text{total N remaining})\{1 - \exp[-k_\text{N}(t_2 - t_1)]\} \quad [4]$$

where $k_N = k_I$ until N mineralized > total N(NP_I/100), then $k_N = k_{II}$.

The observed mineralization of total N (N_{total}) for the first week of incubation (k_{1wk}) for the soils from the four studies was estimated by equating Eq. [1] [$N_0(1 - \exp(-k)$] with Eq. [4] for the first week {$N_{total}[1 - \exp(-k_{1wk})]$} and taking the natural logarithms. The result is

$$k_{1wk} = \ln(\text{N}_{total}) - \ln\{\text{N}_{total} - \text{N}_0[1 - \exp(-k)]\} \quad [5]$$

Equation [5] is relevant in that N mineralization across a geographically diverse group of soils may be related to the initial N mineralization rate.

Estimating Rate Constants for the First Week and Pool I and Total Nitrogen in Pool I from Soil Properties

Single and multiple regressions were used to determine if k_{1wk} (Eq. [5]), k_I (Eq. [4]), and NP_I (Eq. [4]) were correlated with total N; total C; the C/N ratio; the sand, silt, and clay contents; pH; KCl-extractable N (cold and hot); NaOH-distillable N; or 3-d CO_2 evolution for the 38 soils in the Schomberg et al. (2009) study.

Effects of Soil Temperature and Moisture

Wang et al. (2003) studied the impact of temperature and gravimetric water content on N mineralization for two soils. These data were used to estimate the effect of temperature and WHC on k_I for the 0- to 10-wk period where N mineralization occurred only from Pool I. Gravimetric water content was converted to WHC by using the relationship reported by Wang et al. (2003), where 19% gravimetric water content was 55% WHC.

The maximum values of k_I and the NP_I for the two soils were set to those values at 35°C and 55% WHC. The ratio of k_I at other soil temperatures and WHCs to the maximum value (k_{Imax}) was the dependent variable, while temperature and WHC were the independent variables in the multiple regression defining the impact of temperature and WHC on k_I.

Statistical Analyses

All statistics used SAS JMP Version 8.0 (SAS Institute, Cary, NC). Means and simple regressions were obtained using the Fit *Y* by *X* procedure. Multiple regressions were obtained using the Fit Model procedure, while nonlinear regressions utilized the Modeling, Non-Linear component of the Fit *Y* by *X* procedure.

RESULTS AND DISCUSSION

Summary information regarding the four studies used as input data is presented in Table 1. Incubation times ranged from 32 to 41 wk. Total C, total N, and the C/N ratio ranged from 6.1 to 25.3 g kg^{-1}, 0.59 to 2.03 g kg^{-1}, and 10.4 to 12.8, respectively. The values for k and N_0 in Eq. [1] ranged from 0.042 to 0.071 wk^{-1} and 84 to 314 mg kg^{-1}, respectively. There were statistical differences among mean k and N_0 values. The mean k value was 0.062 wk^{-1}, which was greater than the commonly used mean of 0.054 wk^{-1} based on a study by Stanford and Smith (1972). Future studies should consider using the mean reported here.

Differences in mean k (Eq. [1]) were not correlated with the means of total N, total C, or the C/N ratio, in agreement with the lack of predictability of k reported by Hadas et al. (1986), Wang et al. (2003), and Schomberg et al. (2009). There was no correlation between mean N_0 and total N, total C, or the C/N ratio, which suggested that the relationships reported by Hadas et al. (1986) and Schomberg et al. (2009) apply to soils from limited geographic areas. There were no statistical differences in the percentage of total N that was in the potentially mineralizable N pool (N_0) at 35°C and optimum soil moisture—the mean was 15%. This mean applies to a wide variety of soils from four different geographic areas, suggesting that potential N mineralization has a percentage limit that is probably related to experimental conditions and not SOM characteristics. In practice, soil temperatures are usually much less than 35°C and soil moistures are suboptimum, substantially limiting annual or growing season N mineralization to a few percentage of the SOM N pool.

Determination of Rate Constants for Pools I and II and Total Nitrogen in Pool I

Nonlinear regression using Eq. [3] provided a good fit to the observed data for the 108 soils in the four studies (data not shown). The relationship converged for each soil, resulting in specific values for k_I, k_{II}, and NP_I. Table 2 presents the mean k_{1wk}, k_I, k_{II}, and NP_I for the four studies. These parameters were not correlated with the means of total N, total C, or the C/N ratio. The values of k_{1wk}, k_I, and k_{II} for the Schomberg et al. (2009) study for soils from the U.S. Southeast were significantly greater than those of the Hadas et al. (1986) study for soils from Israel. Soils from Australia (Wang et al., 2003) and Connecticut (Griffin and Laine, 1983) were intermediate. Similar trends were apparent for NP_I: the mean was 8.2% or about half of the percentage of total N equal to N_0 (Eq. [1]). The mean k_I and NP_I in Table 2 did appear related to the mean k_{1wk}, the initial N mineralization rate, emphasizing the need to correlate k_{1wk} to soil properties such as total C, total N, or the C/N ratio. These relationships are discussed below.

Table 2. Mean values for sequential first-order rate constants for N mineralization during the first week (k_{1wk}) and for the active and slow N pools (k_I and k_{II}, respectively), and the total N in the active pool (NP_I) for the four studies (Eq. [3]).

Location	k_{1wk}	k_I	k_{II}	NP_I	Reference
	wk^{-1}			%	
U.S Southeast	0.0111 a†	0.0082 a	0.0022 a	10.2 a	Schomberg et al. (2009)
Victoria, QLD, Australia	0.0089 ab	0.0068 ab	0.0019 ab	8.6 a	Wang et al. (2003)
Israel	0.0056 c	0.0039 c	0.0013 b	6.1 b	Hadas et al. (1986)
Connecticut	0.0065 b	0.0050 bc	0.0021 ab	8.4 ab	Griffin and Laine (1983)

† Means followed by the same letter are not significantly different.

Individual soil k_I values (Eq. [4]) were compared with the corresponding k_{1wk} (Eq. [5]). The relationship is shown in Fig. 1. No significant differences in the parameter estimates among the four data sets were found for the quadratic equation for k_I vs. k_{1wk}. As noted above, the four studies were from different geographic areas that represented a variety of soil depths, tillage practices, organic amendments, and cropping systems. The k_I vs. k_{1wk} relationship in Fig. 1 suggested that

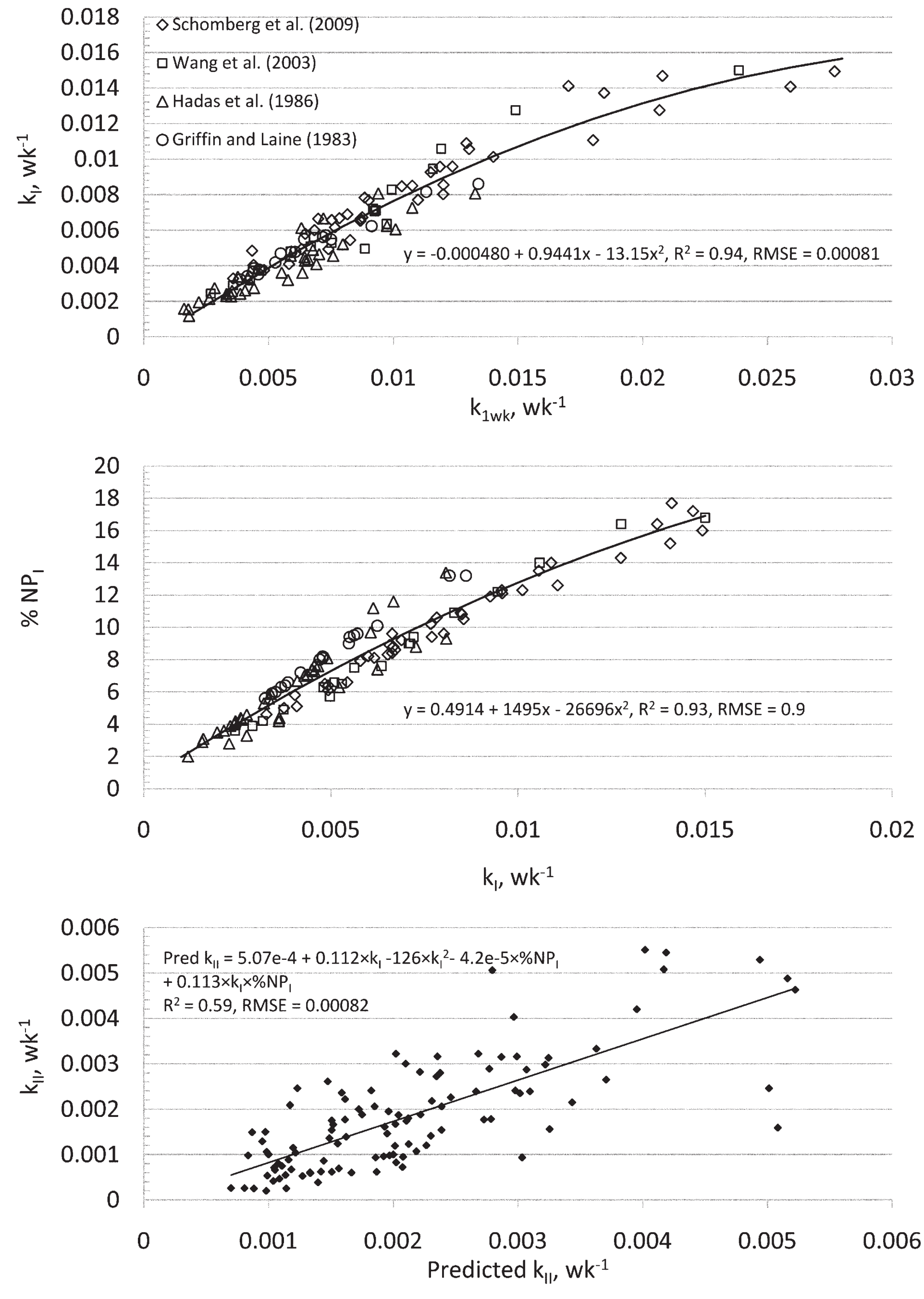

Fig. 1. Relationships used to calculate Sequential Model k_I(N Pool I rate constant), $\%NP_I$ (Percentage of total N in N Pool I), and k_{II} (N Pool II rate constant.

the time course of SOM N mineralization when N Pool I is undergoing decomposition is directly related to N mineralization during the first week of incubation excluding the flush of N mineralization that is due to rewetting a dried, disturbed soil. The emphasis on using long-term data to estimate k_{1wk} is important because the flush of N mineralization that usually accompanies rewetting of dried, disturbed soil (Cabrera, 1993; Benbi and Richter, 2002) precludes the use of a short-term incubation to estimate k_{1wk}.

The total N in Pool I (Eq. [4]) was compared with k_{1wk} and k_I. Second-order polynomial equations where k_{1wk} or k_I were independent variables were good predictors of NP_I. The NP_I vs. k_I resulted in the most significant relationship (Fig. 1). No significant differences in the parameter estimates among the four data sets were found for the quadratic equation for NP_I vs. k_I. These results suggested that the size of the more labile N pool (N Pool I) increased as the rate of N mineralization of that N pool (k_I) increased irrespective of soil location, depth, tillage practice, organic amendment, and cropping system. A similar relationship was not found for N_0 vs. k in the single exponential model (Eq. [1]) when data from the four studies were considered together. Griffin and Laine (1983) and Wang et al. (2003) presented data where N_0 declined as k increased ($r^2 = 0.4$), while no relationship was found for the data of Hadas et al. (1986) and Schomberg et al. (2009) (data not shown).

No correlation was obtained for k_{II} (Eq. [4]) and single variables such as k_{1wk}, k_I or NP_I; however, a multiple regression where k_I and NP_I were independent variables did describe the variability in k_{II} (Fig. 1). A single k_{II} value representing this more stable N pool may be as useful as a calculated value in a practical application of these results. The mean value of k_{II} in Table 2 ($0.0019\ wk^{-1}$) is suggested in this regard.

The values of k and N_0 in the single exponential model (Eq. [1]) were also evaluated (data not shown). No significant relationships for k vs. k_{1wk}, N_0 vs. k_{1wk}, or N_0 vs. k were found.

Estimating Rate Constants for the First Week and Pool I and Total Nitrogen in Pool I from Soil Properties

Previous studies have identified soil properties that are correlated with N mineralization. Total N (Schomberg et al., 2009; Hadas et al., 1986) and CO_2 evolution at 3 d (Schomberg et al., 2009; Picone et al., 2002; Franzluebbers et al., 2000) were the best predictors of the size of the mineralizable N pool, N_0, and the total N mineralized during a specified time period. Gordillo and Cabrera (1997) found that sand, silt, and clay contents were correlated with potentially mineralizable N for broiler litter. While Picone et al. (2002) and Schomberg et al. (2009) reported clay content, they did not test for a relationship between N mineralization from SOM and clay content. Data from the latter studies were evaluated in this study—no correlation between N mineralization from SOM at 24 d and clay content was found (data not shown).

The values of k_{1wk}, k_I, and NP_I could be predicted from total N, 3-d CO_2, and clay content, however, using the Schomberg et al. (2009) data, as shown in Fig. 2, 3, and 4, while k_{II} could not. Estimates of k_I (Eq. [4]) from k_{1wk} (Fig. 1) were essentially the same as those estimated from total N, 3-d CO_2, and clay content (Fig. 3). The equation that described this relationship was linear, with a slope near unity and an intercept not significantly different from zero ($y = 0.0004 + 0.94x$, $R^2 = 0.94$, RMSE = 0.00064). Estimates of NP_I (Eq. [4]) from k_I (Fig. 1) were also related to those estimated from total N, 3-d CO_2, and clay content (Fig. 4). The equation was a second-order polynomial ($y = -18.5 + 4.2x - 0.0109x^2$, $R^2 = 0.92$, RMSE = 1.6). These relationships show that either k_{1wk} or soil properties (e.g., total N, 3-d CO_2, clay content) could be used to determine parameter estimates in the sequential model (Eq. [4]). Total N, 3-d CO_2 and clay content serve as inputs irrespective of the approach.

Future research should focus on improving the relationships shown in Fig. 2, 3, and 4, with emphasis on methods that might be used in routine soil testing. Picone et al. (2002) reported that the gas evolved after soil treatment with $Ca(ClO)_2$ and NH_4^+

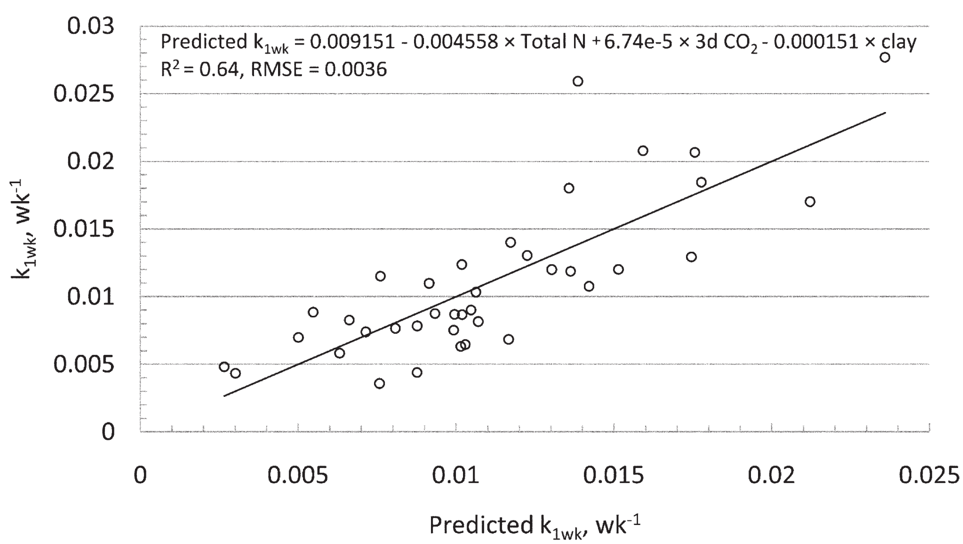

Fig. 2. Observed versus predicted k_{1wk} (mineralization of total N during Week 1) where predicted values were based on total N, CO_2 evolution at 3 d (3d CO_2) and %clay from Schomberg et al. (2009).

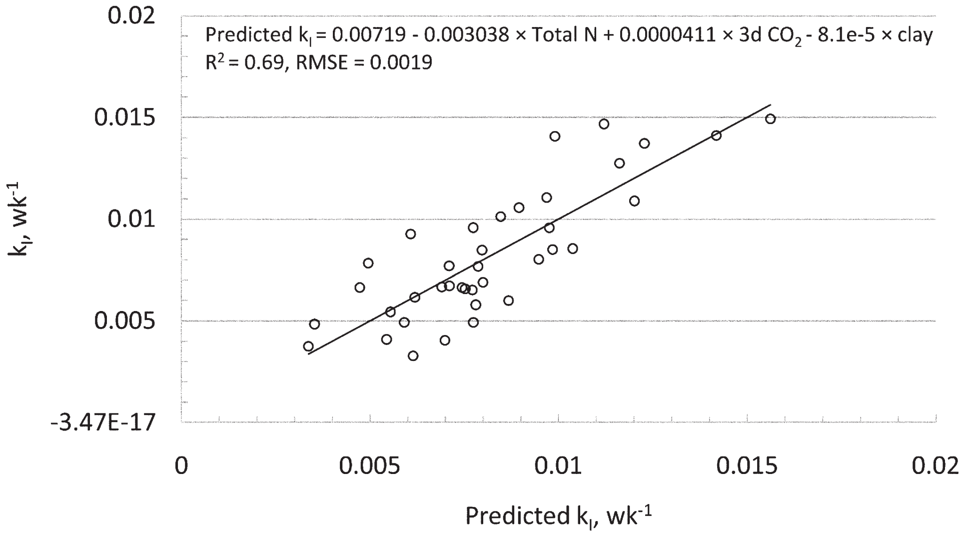

Fig. 3. Observed versus predicted k_I (N Pool I rate constant) where predicted values were based on total N, CO_2 evolution at 3 d (3d CO_2) and %clay from Schomberg et al. (2009).

extracted with hot KCl were correlated with N mineralization after 24 d. Schomberg et al. (2009) reported the same correlations and added NaOH-distillable N to the list. Each method is suitable for routine soil testing. The $Ca(ClO)_2$, hot KCl, and NaOH data from Schomberg et al. (2009) were tested as replacements for 3-d CO_2 in the multiple regression shown in Fig. 2. None of the replacement methods improved the prediction of k_{1wk}. Each of the methods was correlated with total N. These results suggest that new methods that better predict early decomposition of SOM are needed.

Effects of Soil Temperature and Moisture

Adjusting k_I and k_{II} to suboptimum soil temperature and moisture was the final step in assessing the sequential model approach. Wang et al. (2003) studied N mineralization for two soils at 35, 25, 15, and 5°C and 55, 43, 32, and 23% WHC in all combinations. The ratio k_I/k_{Imax} as a function of soil temperature and moisture was described by

$$\frac{k_I}{k_{Imax}} = 0.240 - 0.0310T - 0.00241\mathrm{WHC} + 0.000862T^2 + 0.000459T(\mathrm{WHC}) \quad [6]$$

The square of the correlation coefficient was 0.96, while the RMSE was 0.064. At 5°C, the WHC had no effect on the ratio. At higher temperatures, the effect of the WHC was linear with slope, increasing as temperature increased. While the overall change in k for a 10°C change in temperature (Q_{10}) was 2.0, the range was 2.9 (25–15°C and 25% WHC) to 0.8 (15–5°C and 25% WHC). These results suggest that the use of a single Q_{10} or moisture correction to correct k_I is inappropriate.

Figure 5 presents k_I/k_{Imax} vs. temperature for the two soils. Good agreement between the calculated and observed values ($y = 0.2 + 1.0x$, $R^2 = 0.96$, RMSE = 0.062) supported the approach taken here.

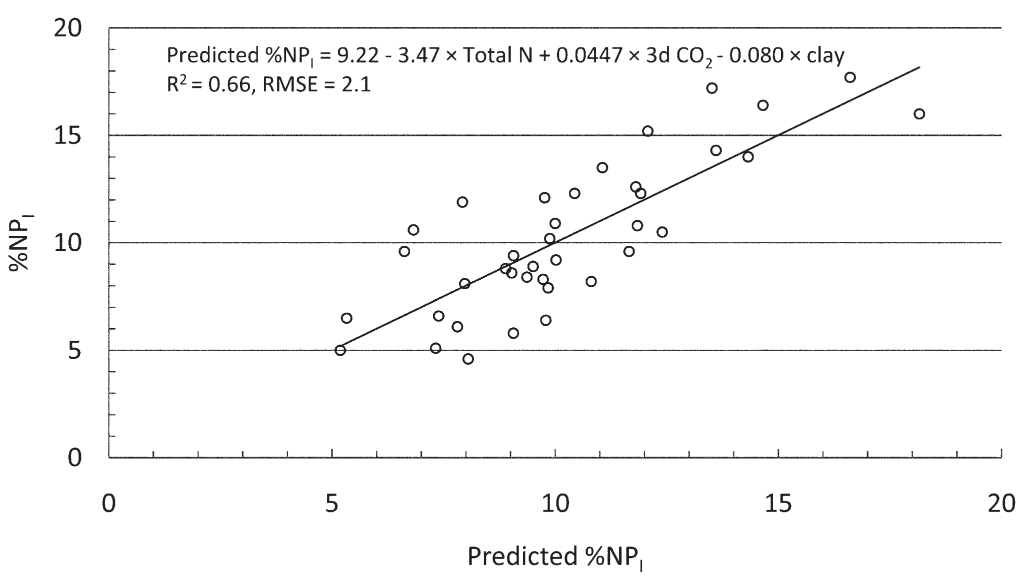

Fig. 4. Observed and predicted %NP_I (percentage of total N in N Pool I) where predicted values were based on total N, CO_2 evolution at 3 d (3d CO_2) and %clay from Schomberg et al. (2009).

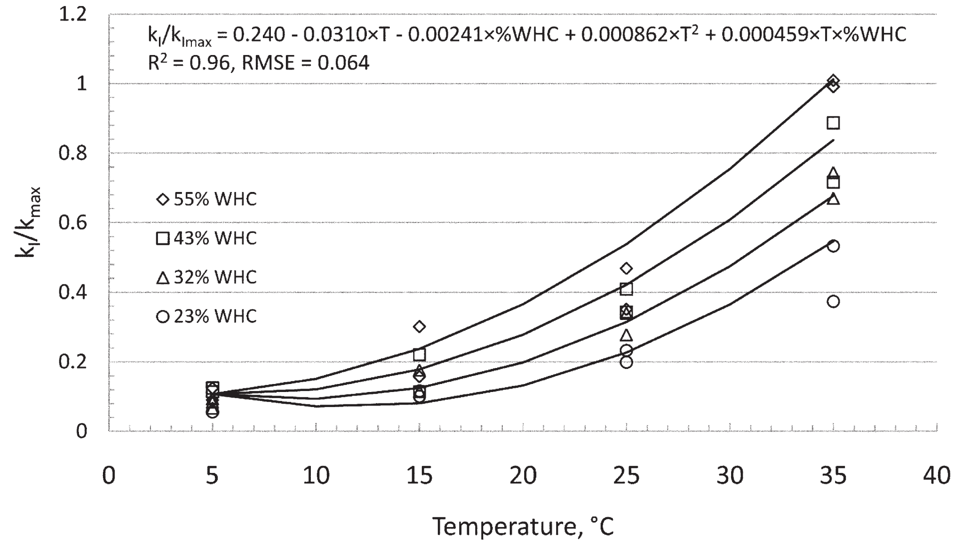

Fig. 5. Observed k_I/k_{Imax} using data from Wang et al. (1986). Data points represent k_I/k_{Imax} for two soils at 35, 25, 15 and 5°C and 23, 32, 43 and 55% WHC. Solid lines were calculated using Eq. 6.

SUMMARY

The sequential model for total N mineralization described the process well for a wide variety of soils. The parameters of the sequential equation (k_I, k_{II}, and NP_I) were correlated with k_{1wk}, the N mineralization during the first week estimated from long-term data. The parameters of the single exponential model (k and N_0) were not related to k_{1wk}, while k_{1wk}, k_I, and NP_I could be calculated from total N, CO_2 evolution at 3 d, and clay content for individual soils. The time course of N mineralization was related to soil temperature and moisture status, thus only total N, CO_2 evolution at 3 d, clay content, and soil temperature and moisture status with time were needed to estimate SOM N mineralization using the sequential model.

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