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Rate of Nitrogen Mineralized from Incorporated Crop Residues as Influenced by Temperature

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ABSTRACT

Methods are needed to predict seasonal mineralization of N when crop residues are added to soils in order to assess N availability to crops. The objective of this investigation was to evaluate and develop methods for predicting the effect of temperature on the rate of N mineralization (N_{min}) from crop-residue-amended soils maintained at near-optimum soil water content. Unamended and crop-residue-amended soils were incubated at temperatures between 5 and 35°C to obtain N_{min} rates for calculation of Q_{10} values, defined as the ratio of reaction rates at a temperature interval of 10°C. Measured Q_{10} depended on the C/N ratio of the residue and incubation time, indicating that for predictive purposes a single Q_{10} value is inadequate for describing the effect of temperature on crop-residue N_{min} . Temperature functions were developed from N_{min} data collected from unamended soils incubated at four temperatures under laboratory conditions. These functions were then tested in the MINIMO model (a subroutine of CERES-MAIZE) for residue-amended soils at four temperatures for up to 160 d. Model-predicted mineralizations was close to measured N_{min} for most crop-residue-soil mixtures tested. The use of the new temperature equations improved the precision of the model, reducing the residual sum of squares (RSS) from 9797 to 5286. However, the modified model was not able to accurately predict N_{min} for crop residues with a C/N ratio of 10 and 28. Inadequate prediction at these C/N ratios may be related to how the model allocates the pool sizes for soluble and insoluble plant N and the cellulose-hemicellulose pool size of the crop residues.

THE INFLUENCE OF TEMPERATURE on crop-residue decomposition and N_{min} rates has been described quantitatively with the temperature quotient Q_{10} . Values of Q_{10} for the N_{min} rate of native soil organic matter in the temperature range between 5 and 35°C have been reported to be approximately 2 (Stanford et al., 1973; Stanford and Epstein, 1974; Campbell et al., 1981; Cassman and Munns, 1980; Kladvko and Keeney, 1987). Campbell et al. (1984) reported that Q_{10} values may be higher in cool northern climates than in warmer tropical climates. They suggested that the increase in Q_{10} may be related to the relative resistance to degradation of the native soil organic matter in soils of the different climatic zones. The idea is that soils in cooler northern climates will tend to accumulate organic matter less resistant to decay relative to warmer southern soils. When brought into the lab under optimum conditions, the northern soils will tend to have a faster rate of decomposition of the soil organic matter than southern soils.

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Addiscott (1983) found that zero-order kinetics fit his experimental data better than first-order kinetics when describing temperature effects on N_{min} of three British soils. He measured Q_{10} values between 5 and 15°C that ranged from 2.3 to 3.2, while between 15 and 25°C they ranged from 1.8 to 2.6. Those findings agree with the findings of Campbell et al. (1981) and Hegarty (1973), which indicate that Q_{10} values tend to decrease with increasing temperatures. Ellert and Bettany (1992) analyzed different temperature response functions but were unable to identify a single best-fitting model that reliably described the time and temperature dependence of net N_{min} in a broad range of soils.

Although many studies have evaluated C mineralization (C_{min}) of decomposing crop residues as affected by temperature, few have been published on the effect temperature has on the N_{min} rate from decomposing crop residues. Pal et al. (1975) found that during the first 2 to 3 d of the decomposition of rice (*Oryza sativa* L.) straw, the Q_{10} for C_{min} was approximately 12 between the temperatures of 7.2 and 22°C. Clark and Gilmour (1983) reported Q_{10} values for C_{min} of approximately 2.7 in the temperature range between 14 and 30°C for sewage-sludge-amended soil. For decomposing tree leaves, Q_{10} values of 2.20 to 2.56 were reported for temperatures between 4 and 25°C (Howard and Howard, 1979). Stott et al. (1986) found that C_{min} of wheat (*Triticum aestivum* L.) was about 2 between 0 and 20°C in 4-wk incubations.

If N_{min} from crop residues is similar to C_{min} , then we might expect the initial Q_{10} for N_{min} of crop residues recently incorporated into soil to be >2. This would agree with ideas promoted by Campbell et al. (1984) that larger Q_{10} values are associated with soils that have organic materials less resistant to degradation.

Simulation models provide a means for predicting seasonal N_{min} because they account for the interacting factors of temperature, moisture, and soil and crop residue characteristics (de Willigen and Neetson, 1985; Vigil et al., 1991). Many of these models include a temperature function for adjusting N_{min} rate that approximates a Q_{10} of 2. However, these models are not generally used in a practical predictive mode for the adjustment of fertilizer recommendations. Their infrequent use for this purpose may be related to a lack of confidence in their predictive accuracy under field or laboratory conditions. These models need to be further evaluated and improved.

The N transformation subroutine MINIMO from CERES-MAIZE (Ritchie et al., 1985) uses TF to estimate the value of first order rate constants for temperatures

Abbreviations: N_{min} , nitrogen mineralization; C_{min} , carbon mineralization; TF, temperature factor; RSS, residual sum of squares; HUM, soil humus pool; FOM, fresh organic matter; ADF, acid detergent fiber; NDF, neutral detergent fiber; WFP, water-filled pore space; RMSE, root mean square error; RM, amount of N mineralized relative that mineralized at 35°C.

that are $<35^{\circ}\text{C}$ (35°C is assumed to be the optimum). This function is

$$\text{TF} = (\text{st} - 5)/30 \quad [1]$$

where TF is a relative temperature factor with values constrained between 0 and 1 and st is the average daily soil temperature ($^{\circ}\text{C}$) for any given soil depth or soil layer simulated. The average Q_{10} calculated using Eq. [1], beginning at the interval between 6 and 16°C up to 35°C , is 2.8 (the method employed in this calculation was to average 20 separate Q_{10} calculations uniformly covering the range of 6 through 35°C). Soil temperatures $>35^{\circ}\text{C}$ are constrained to a TF value of 1. The value of TF is 0 at daily average temperatures $\leq 5^{\circ}\text{C}$. The MINIMO model assumes there are four organic matter pools: a soil humus pool (HUM) and three pools associated with fresh organic matter (FOM) or crop residues. For simplicity, the mineralizable humus-N pool size is set equal to the value of total organic N of the soil layer simulated. The daily first-order decay rate constant for HUM is 0.000083. The FOM is partitioned into three pools as: 20% carbohydrate, 70% cellulose, and 10% lignin. The model includes an equation for N immobilization and a relative (0–1) soil moisture factor for adjusting the rate constant of mineralization when soil moisture contents are not optimal. Other aspects of MINIMO are described in detail in the publications by Ritchie et al. (1985), Godwin and Jones (1991), and recent suggested modifications described by Vigil et al. (1991).

The objectives of this investigation were to: (i) evaluate the temperature quotient for N_{min} of crop residues varying in C/N ratios when mixed with soil, and (ii) test and improve the TF factor for N_{min} as used in the MINIMO simulation model for predicting N_{min} from crop-residue-amended soils.

MATERIALS AND METHODS

Some chemical properties of the crop residues used are given in Table 1. Each residue sample was oven dried at 55°C for 3 d and ground to pass a 1-mm sieve. Total N was determined using a salicylic-sulfuric acid digestion (Bremner and Mulvaney, 1982), and N concentrations measured using a Technicon Autoanalyzer (Technicon Industrial Systems, 1977a,b). Total C was measured using a Leco carbon analyzer (Leco Corp., St. Joseph, MI) (Tabatabai and Bremner, 1970). Van Soest's fiber analysis procedure (Goering and Van Soest, 1970) was

Table 1. Selected chemical properties of the crop residues used in the lab incubations.

Residue	C/N	Total		Lignin	ADF†	NDF‡	Cellulose	Hemi-cellulose
		C	N					
g kg ⁻¹								
Sorghum leaves	38	410	11	43	290	506	219	216
Soybean stems	28	420	15	182	583	652	398	67
Sorghum leaves	20	420	21	56	332	568	244	234
Soybean leaves	10	440	44	48	201	284	141	83

† ADF is the acid detergent fiber concentration.

‡ NDF is the neutral detergent fiber concentration.

used to determine permanganate lignin, ADF, NDF, cellulose, and hemicellulose concentrations of the crop residues.

The soil samples used in the experiment were collected in August 1988 from the surface 10 cm of four soils mapped as Kahola silt loam (fine-silty, mixed, mesic Cumulic Hapludoll), Smolan silt loam (fine, montmorillonitic, mesic Pachic Argiustoll), Haynie fine sandy loam (coarse-silty, mixed (calcareous), mesic Mollic Udifluent), and Woodson silt loam (fine, montmorillonitic, thermic Abruptic Argiaquoll) (Table 2). The gravimetric water contents (kg water kg⁻¹ soil) of these soils at a matric soil water pressure of -33 kPa, are 0.13 for Haynie, 0.25 for Kahola, 0.24 for Woodson, and 0.21 for Smolan as determined using the pressure plate method described by Klute (1986). Each soil was mixed and sieved to pass 2 mm. Smolan, Kahola, and Woodson soils were wet to approximately 0.18 kg water kg⁻¹ soil and Haynie to 0.13 kg water kg⁻¹ soil. This was accomplished by spreading out the sieved soil in a 2-cm layer on a plastic sheet and using an aspirator bottle to slowly wet the soil to the desired moisture content. Soils were stored in an incubator at 35°C for 3 wk to equilibrate and avoid the mineralization flush that occurs when air-dried soils are sieved and rewetted. Two days prior to commencement of the experiment, moist soil, equivalent to 750 kg oven-dry weight, was leached without vacuum in porcelain buchner funnels attached to sidearm flasks. Approximately 20 pore volumes (7–8 L) of N-free nutrient solution (Cabrera and Kissel, 1988) were passed slowly through the soil. The soil was then gently evacuated and air dried until it reached 0.13 to 0.17 (kg kg⁻¹) water content and then mixed by hand on a plastic sheet. After removing plant litter, the soil was stored in 1-L, airtight tubs at 4°C until the following morning when the experiment was started.

Leaching Apparatus

The leaching-incubation tube consisted of a 60-mL syringe body with a filtering assembly at the bottom of the tube (Fig. 1). The filtering assembly was constructed by separating the rubber seal from the bottom of the syringe plunger and discarding the plunger handle. The rubber seal was trimmed of the first 3 mm of rubber, washed in hot, soapy water to remove a factory lubricant, and rinsed with deionized water. A 1.3-cm-diam. hole was made in the rubber seal to facilitate leaching. To eliminate the collection of leaching solution in the air space between the rubber seal and the walls of the syringe tube, silicone sealer was filled in the ridges on the outer perimeter of the rubber seal. The rubber seals were cured at 50°C for 24 h, then extracted with 2 mol L⁻¹ (2 h shaking time) to remove NH₃. No NH₄-N was found in the silicone sealer extract. The seals were acid washed and dried overnight at 55°C before assembly. Cured silicone was tested

Table 2. Selected physical and chemical properties of the four soils used in the laboratory incubations.

Soil	Textural class†	pH	First-order rate constant	Inorganic N	Total N	Total C
Haynie	vfsl	7.8	0.0009(4.39)‡	0.36	530	5.0
Kahola	sil	5.3	0.0006(3.25)	0.52	1220	16.2
Smolan	sil	6.4	0.0006(2.81)	0.22	1200	14.1
Woodson	sil	5.7	0.0005(3.69)	0.34	1150	16.5

† vfsl = very fine sandy loam; sil = silt loam.

‡ Values in parentheses are the root mean square errors (RMSE) of the fitted rate constant when soils were incubated for 98 d at 35°C for daily mineralization. Rate constants were fit using the smallest RMSE in 15 iterations of the MINIMO model as criteria for best fit.

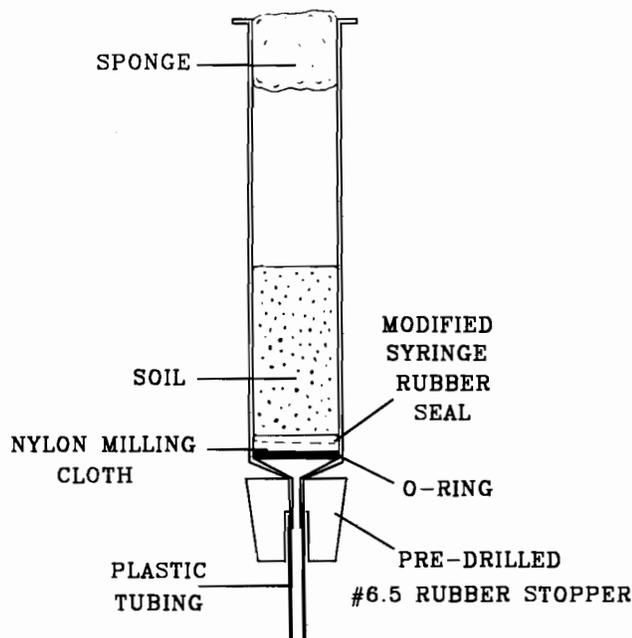


Fig. 1. Cross-sectional diagram of modified 60-mL syringe used as a leaching tube in experiment.

for its capability to release $\text{NH}_4\text{-N}$. No $\text{NH}_4\text{-N}$ immobilization or release was observed in a 1-wk incubation at 35°C .

The filtering assembly was constructed by placing a rubber O-ring (2.65-cm o.d.) at the bottom of the leaching tube. Nylon milling cloth (Nitex HC-3-46, H.R. Williams Milling Co., Kansas City, MO) was stretched over the perforated rubber seal and this was then pushed into the leaching tube, positioning the milling cloth between the O-ring and the rubber seal. The weight of each assembled leach tube was determined.

Leaching Apparatus Packing

On the day the experiment was started, the soil moisture content was determined gravimetrically. A subsample of each soil was dried at 45°C and analyzed for total N and C using the methods mentioned above. Soil pH (1:1 soil/water mixture) was measured. Inorganic N was extracted with 2 mol L^{-1} KCl and analyzed using the method of Cabrera and Kissel (1988).

Immediately after pH was determined, moist soil, equivalent to 15 g oven dried, was weighted into a 1-L plastic carton. Fifteen grams of oven-dried sand were mixed with the soil using the approach of Stanford and Smith (1972). Approximately 3 g of the soil-sand mixture was put into a separate beaker. The remaining soil-sand mixture was then mixed with 0.1714 g of the appropriate crop residue. This rate of 0.1714 g is equivalent to $8000\text{ kg crop residue ha}^{-1}$, assuming a bulk density of 1.4 Mg m^{-3} and a mixing depth of 10 cm. The residue-soil mixture was added to the syringe tube in three parts. Following each addition, the mixture was packed to an approximate bulk density of 1.1 Mg m^{-3} using a no. 4 rubber stopper attached to a 1.3-cm-diam. wooden dowel. The withheld 3 g of soil-sand mixture was then applied to the soil surface to reduce potential $\text{NH}_3(\text{g})$ volatilization loss. Ten milliliters of N-free nutrient solution was passed through each tube to further pack the soil to approximately 1.4 Mg m^{-3} and bring it to 55% WFP. The 55% WFP was achieved by measuring the volume of the soil core in the tube and then

calculating the desired moisture content and tube weight for 55% WFP, using equations developed by Linn and Doran (1984). The desired water content was achieved by placing the leach tube on a 250-mL sidearm flask and drawing off excess moisture using a vacuum (-20 to -30 kPa) until the desired weight was reached. Gravimetric moisture contents (kg water kg^{-1} soil) for these soils mixed with sand and maintained at 55% WFP were: 0.16 for Haynie, 0.17 for Kahola, 0.19 for Woodson, and 0.21 for Smolan. The gravimetric water contents of soil-sand mixtures at -10 kPa were 0.13 for Haynie-sand, 0.16 for Kahola-sand, 0.14 for Smolan-sand, and 0.16 for Woodson-sand.

To minimize soil water evaporation between leaching events, polyurethane foam (4-cm diam. by 3 cm long), moistened with distilled water, was inserted into the top of each leaching tube; about 7 to 8 cm^3 of head space was left above the soil.

Leaching tubes were placed in a humidity chamber (37.8-L glass aquarium with a 1.3-cm-thick plywood lid). About 2.5 L of distilled water were added to the chamber to provide a free water surface to maintain high humidity. Humidified air was passed through the chamber at 0.8 L min^{-1} to supply O_2 for soil respiration and to reduce accumulation of CO_2 inside the chamber. Four humidity chambers were prepared (one for each incubation temperature). Humidity chambers were placed inside Precision incubators (Model 815, Precision Scientific, Chicago, IL) with temperatures maintained at 5, 15, 25, or 35°C ($\pm 0.1^\circ\text{C}$).

At 35°C , all four soils were individually mixed with each of the four residue types, plus there was a check (soil without residue) for a total of 20 treatments prepared in duplicate. The leaching tubes containing Haynie and Smolan soil (20 tubes) were leached with 0.01 mol L^{-1} CaCl_2 , 7, 21, 35, 49, 86, and 98 d after setting up the experiment. The tubes containing Kahola and Woodson soils were leached after 7, 21, 34, 49, 88, and 100 d.

Two sorghum [*Sorghum bicolor* (L.) Moench] residues and soybean [*Glycine max.* (L.) Merr.] stems were also incubated in Haynie and Smolan soils at 5, 15, and 25°C . Leaching times at 25°C were 7, 35, 58, 86, and 106 d. Tubes incubated at 15°C were leached after 28, 86, 125, and 160 d. Tubes incubated at 5°C were leached after 49, 98, and 160 d.

Leaching Procedure

On the day of leaching, the tubes were removed from the humidity chamber and weighed after removing the sponge stopper and wiping away condensation. The volume of the soil-sand-residue mixture was then determined from a length measurement of the mixture (accuracy within 0.20 cm^3). The tube weights and soil volume measurement allowed us to calculate soil bulk density, gravimetric water content, and WFP of each tube before and after each leaching event.

Leaching was accomplished using 70 mL of 0.01 mol L^{-1} CaCl_2 in three 23-mL aliquots dribbled into the leach tubes while placed on 250-mL sidearm flasks. Each aliquot was allowed to leach by gravity for 1 h, after which vacuum was used to draw excess solution through the tube. After the last aliquot, 2 10-mL aliquots of N-free nutrient solution was leached by gravity for 30 min, after which vacuum was applied to remove excess solution. The volume and weight of each tube was measured. If the tube weight was greater than that calculated for 55% WFP, it was reattached to the vacuum system to remove additional soil solution. The leachates were

then brought up to 100-mL volume and analyzed for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ using an autoanalyzer.

Model Development and Q_{10} Calculations

Generally, incubations such as those conducted here result in curvilinear responses of cumulative net N_{min} vs. time. These can be represented by first-order kinetics (i.e., $N_{\text{min}} = N_0 e^{-kt}$), where k (the rate constant) is estimated by nonlinear regression and iteration techniques (Campbell et al., 1984). In our study (as shown below), the relationships for residue-amended soils, particularly at low temperatures, did not always fit the typical first-order model. Consequently, we calculated k as N_{min} divided by time (ΔN) for each temperature and treatment. We then used ΔN as a proxy for k in the normal linear form of the Arrhenius equation to calculate apparent Q_{10} values using an approach reported by Kladvik and Keeney (1987):

$$\ln k = \ln a - E_a/R(1/T) \quad [2]$$

where k is the rate constant, E_a is the activation energy, R is the gas constant, T is the absolute temperature, and a is a constant. This approach essentially assumes that N_{min} obeys zero-order kinetics for these treatments. The Q_{10} values were then calculated as the ratio of the rate constants k as predicted by the fitted Eq. [2] at 10°C temperature intervals.

Nitrogen immobilization tends to be the dominating process when fresh crop residues are first incorporated in soils. Because of this, we suspected that temperature effects on net N_{min}

just after residue addition might be different than later in the decomposition period. Therefore, separate calculations were made for the periods between 0 and 35 d, and between 35 and 98 d for each soil-residue treatment. In cases where the amounts of N mineralized by Days 35 and 98 were not measured, estimates were made by linear interpolation.

The amount of N_{min} in crop-residue-amended soils at different temperatures was also compared with that predicted by a modified version of MINIMO as described above (Vigil et al., 1991). The modified version of MINIMO was used in an iterative process to fit first-order rate constants for each of the four check soils without residue at 35°C . In all simulations, the fitted rate constants (Table 2) for each soil were substituted for the rate constant 0.000083 for HUM N. First-order rate constants were found using a bisecting algorithm (Burdon and Faires, 1985, p. 28-31), where the criteria for best fit was the smallest RMSE in 15 iterations of the model. The Smolan and Haynie check soils were used to develop two TFs based on the amount of N_{min} at 5, 15, and 25°C , relative to 35°C . The amount of N_{min} relative to that mineralized at 35°C will be referred to as RM. Two curves were fit through the RM data using nonlinear least squares and multiple linear regression. Nitrogen mineralization data collected from the four residue-amended soils at the different temperatures were then compared with predicted N_{min} using the modified MINIMO model with the new TF and fitted rate constant for each soil without crop residue. The residual sum of squares was calculated from N_{min} as predicted by MINIMO with the new TF equations and

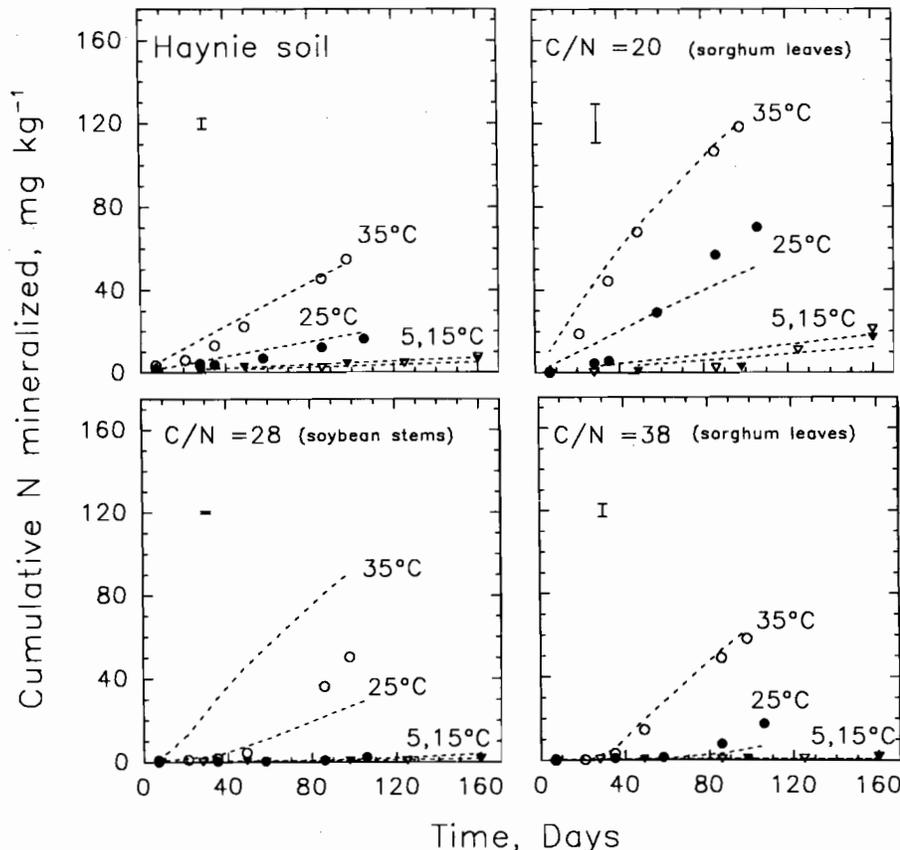


Fig. 2. Influence of temperature and C/N ratio of residues on N mineralized in crop-residue-amended Haynie soil. The error bar is the largest standard error of the mean of N mineralized for all residues calculated on any day. The symbols are measured values, the dashed line is predicted by MINIMO with the new temperature function Eq. [3].

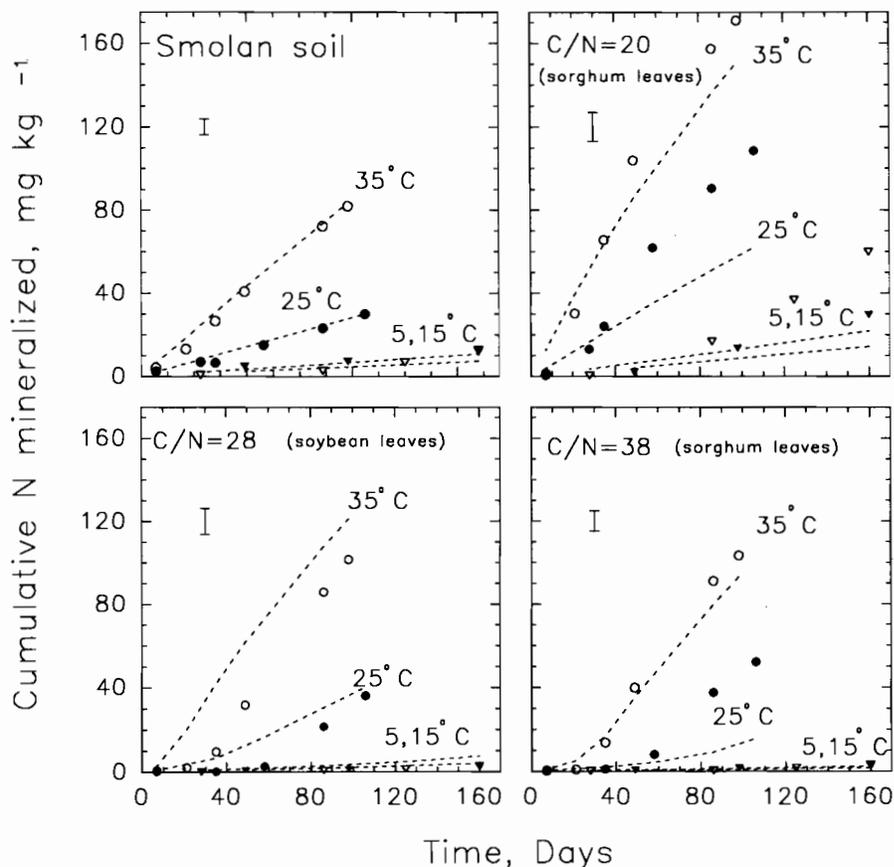


Fig. 3. Influence of temperature and C/N ratio of residues on N mineralized in crop-residue-amended Smolan soil. The error bar is the largest standard error of the mean of N mineralized for all residues calculated on any day. The symbols are measured values, the dashed line is predicted by MINIMO with the new temperature function Eq. [3].

Eq. [1], and from the measured amount of N_{\min} accumulated between each leaching event.

RESULTS AND DISCUSSION

The N_{\min} rate for Haynie soil was directly proportional to temperature (Fig. 2). Cumulative N_{\min} for the soil with residue (C/N ratio of 28) was 50 mg kg^{-1} at 35°C , but $<20 \text{ mg kg}^{-1}$ for all other temperatures (Fig. 2). Similar trends with temperature occurred for the Smolan soil (Fig. 3). The N mineralized from residue-amended and unamended soils at 5 and 15°C was nearly the same, and much less than that accumulated at 25 or 35°C (Fig. 2 and 3). This was the typical relationship measured for all residue-treated soils. For Haynie and Smolan soils and all residue treatments, there was a lag (probably due to immobilization) in the amount of N_{\min} with time at 5 and 15°C (Fig. 2 and 3). At 25°C , there was also a lag, but of shorter duration. The greater lag at the lower temperatures may reflect slowing of the biochemical processes involved with N mineralization-immobilization-turnover. The lag may also reflect a small active resident population of microbes capable of metabolizing crop residues at low temperatures. A longer time is probably required for microbial colonization of the incorporated residues at low temperatures. Typically, greater

cumulative N_{\min} was measured with decreasing C/N ratio (Fig. 4).

Using the data in Fig. 2, 3, and 4, an estimate of the time duration of N immobilization by a soil-residue mixture can be determined by subtracting the amount of N_{\min} in unamended soil from the amount mineralized in residue-amended soil. This subtraction also provides an estimate of the net N mineralized from the added crop residues only. For soils treated with sorghum leaves (C/N 38) and soybean stems (C/N 28), net immobilization was observed up to 49 d after residue addition at 35°C (Fig. 2, 3, and 4). At 25°C , immobilization was observed for residues with C/N of 38 and 28, 106 d after residue addition in Haynie soil, and 86 d in Smolan soil (Fig. 2 and 3). This immobilization period precluded the use of the typical first-order kinetic model for quantifying the estimated net N_{\min} from the crop residues only.

Arrhenius plots of the ΔN between Days 0 and 35 and Days 35 and 98 are presented in Fig. 5. Although the relationships were not as linear as we would have hoped, we used simple linear fits of Eq. [2] to assess the data between 5 and 35°C and between 15 and 35°C . The simple linear fitted equations were used to estimate rate constants (k values) for 5, 15, 25, and 35°C . Linear fits between 5 and 35°C had R^2 values that ranged between 0.36 and 0.93. Linear fits between 15 and 35°C had R^2 values that ranged between 0.73 and 0.99. Values

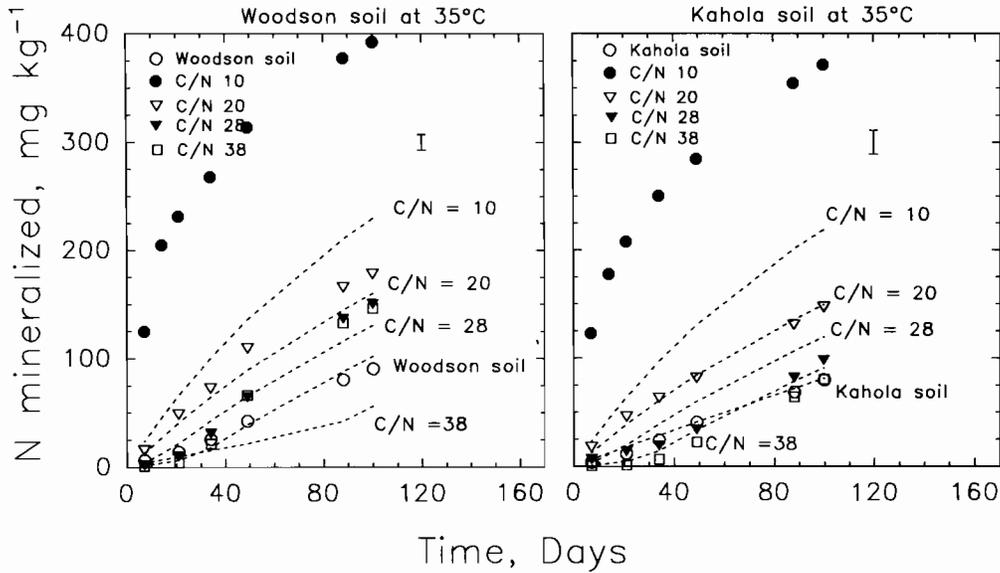


Fig. 4. Influence of temperature and C/N ratio of residues on N mineralized in crop-residue-amended Woodson and Kahola soils. The error bar is the largest standard error of the mean of N mineralized for all residues calculated on any day. The symbols are measured values, the dashed line is predicted by MINIMO with the new temperature function Eq. [3].

of apparent Q_{10} calculated as the ratio of the predicted rate constants (k values) for the temperature ranges cited above generally were inversely related to C/N ratio of the residue during the 0- to 35-d period (Table 3). Because of the steeper slope for equations fitted between 15 and

35°C compared with those fitted between 5 and 35°C, the Q_{10} values calculated between 15 and 35°C were larger than those calculated for 5 to 35°C.

The steeper slopes for the equations fit between 15 and 35°C correspond to only a small increase in the

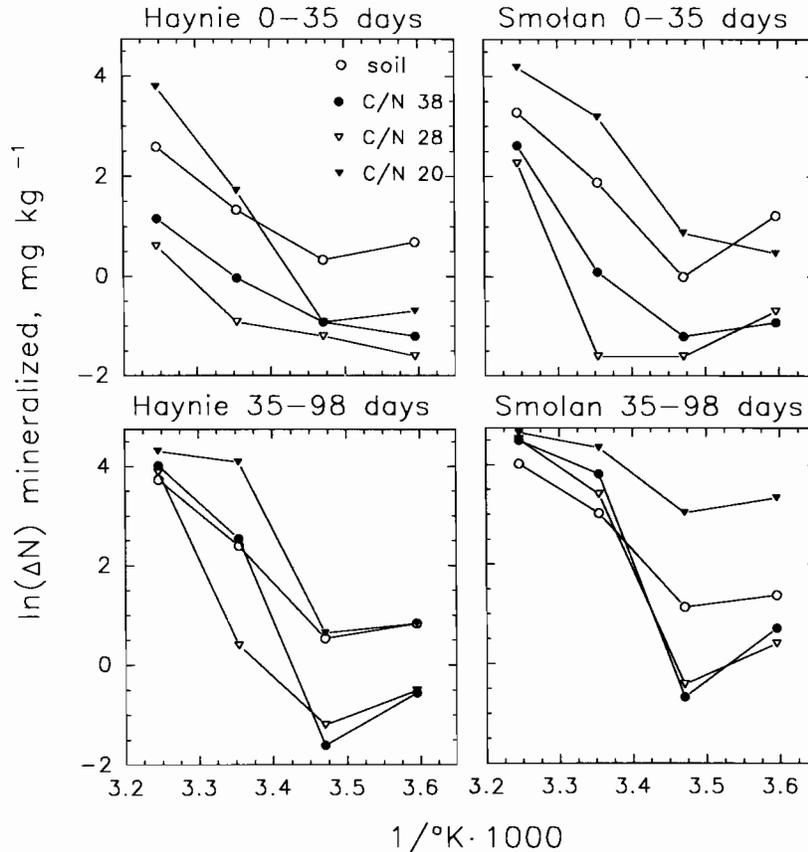


Fig. 5. Arrhenius and plots for Haynie and Smolan soils for the change in N mineralized between 0 and 35 d and between 35 and 98 d (assuming zero-order kinetics applies and that $\Delta N = k$).

Table 3. Means of Q_{10} † values for selected residue-amended treatments averaged across Haynie and Smolan soils for different incubation periods, assessed for 5 to 35°C, and 15 to 35°C.

Residues	C/N ratio	0-35 d incubation		35-98 d incubation	
		5-35°C	15-35°C	5-35°C	15-35°C
Check		2.1	4.3	2.7	4.9
Sorghum leaves	38	2.7	5.0	5.3	16.6
Soybean stems	28	2.2	4.9	4.6	13.4
Sorghum leaves	20	4.4	8.5	2.8	4.6
LSD (0.05)		0.7	4.0	1.0	2.0

† Values of Q_{10} determined from the ratio of rate constants predicted from a fitted linear regression of the Arrhenius equation: $\ln(\Delta N) = \ln a - E_a/R(1/T)$, where ΔN is the change in N mineralized during a given time period, which is substituted for the rate constant k ; E_a is the activation energy, R is the gas constant, $1/T$ is the inverse of temperature in degrees Kelvin.

amount of N mineralized between 5 and 15°C, whereas between 15 and 25°C and between 25 and 35°C, a larger increase in the amount of N mineralized was measured (Fig. 2 and 3). It is interesting that the average Q_{10} between 5 and 35°C for the 0- to 35-day period for the two soils is about 2 (Table 3), similar to the findings of Stanford et al. (1973). The large Q_{10} of 4.35 for sorghum leaves with the narrow C/N ratio of 20 is similar to the findings of Pal et al. (1975), who found that the addition of a readily usable C source increased the rate of C decomposition 12-fold early in the incubation period; that is much more than a Q_{10} of 2 would predict for a 10°C increase in temperature.

The Q_{10} values determined for the soils amended with residue of C/N ratio 20, during the 35- to 98-d period, were less than Q_{10} values determined between 0 and 35 d (2.83 vs. 4.35; Table 3). During the 35- to 98-day period, this residue treatment was beyond the initial rapid phase of N_{\min} observed between 0 and 35 d. During the 35-

to 98-d period, greater N_{\min} was observed at the higher temperatures but the effect was not as great as that observed during the 0- to 35-d period. At 98 d, the immobilization period observed for the soybean stems (C/N of 28), and the sorghum leaves (C/N of 38) was over. For those residues a large increase in the amount of N produced was observed with increasing temperature, raising the calculated Q_{10} value to 16.64 for the residue with a C/N of 38 and to 13.35 for a C/N of 28 (Table 3).

These widely variable results indicate that a general Q_{10} for N_{\min} of crop-residue-treated soils may not be easily used to predict temperature effects on N_{\min} rate. For residues with narrow C/N ratios, the effect of temperature will be greatest early in the decomposition period. For residues with wide C/N ratios, the effect of temperature on the N_{\min} rate constant is most apparent when those residue-amended soils just begin to show net N_{\min} , which may be 40 to 60 d after residue addition.

Simulation models allow us to account for such interacting factors as C/N ratio, soil temperature, soil moisture, and duration of the decomposition period. The TF currently used to modify first order decomposition rates in the MINIMO model is a relative (0-1) factor given by Eq. [1] (Fig. 6). This function maximizes decomposition and N_{\min} rate at 35°C. When Eq. [1] was used, MINIMO predicted more N_{\min} from the soil tested than we measured (Fig. 7). Most of the overprediction occurred between 5 and 25°C. Because of overprediction at these temperatures, we developed the following TF equations from N mineralized in unamended soil for use in MINIMO:

$$TF = -0.010 + 0.039(st) - 0.014(st)^{1.5} + 0.00036(st)^{2.5} \quad [3]$$

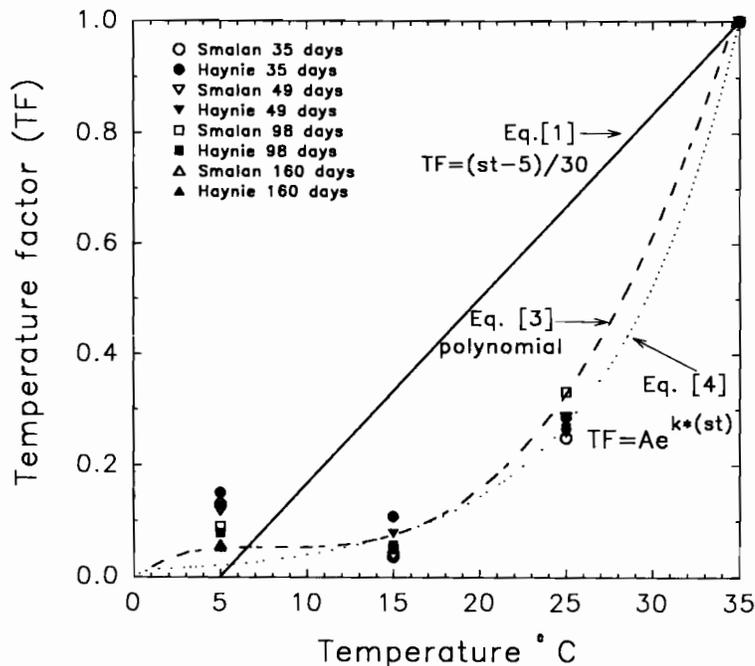


Fig. 6. The relative temperature factor (TF) for adjusting first-order N-mineralization rate constants for less-than-optimum daily average soil temperatures (st) between 0 and 35°C. Equation [1] is currently used in MINIMO. Equations [3] and [4] are new functions fitted to measured N_{\min} data obtained at temperatures that are less than optimum relative to the optimum at 35°C for unamended Haynie and Smolan soils.

for which the R^2 , RMSE, and F of regression were 0.99, 0.0237, and 2386, respectively, and:

$$TF = 0.0106[e^{0.12979(st)}] \quad [4]$$

In this equation the nonlinear R^2 and RMSE were 0.99 and 1.802. Equations [3] and [4] fit the measured N_{min} at temperatures $<35^\circ\text{C}$ relative to N_{min} at 35°C (RM data) much better than Eq. [1] (Fig. 6). The use of Eq. [3] as a TF in MINIMO substantially improved the agreement between measured and predicted N_{min} for unamended Haynie and Smolan soils (Fig. 2 and 3). Because Eq. [4] has a shape similar to Eq. [3] (Fig. 6), it provided a similar prediction. Simulation of N_{min} for the other residue-soil mixtures were then made to evaluate the ability of the new modified model to predict the amount of N_{min} in the residue-amended treatments. In general, the agreement between measured and predicted N_{min} was close (Fig. 2 and 3). These two equations decreased the RSS from 9798 for the old TF Eq. [1] to 5286 for Eq. [3] and 5566 for Eq. [4]. The fitted regressions between measured N_{min} and predicted N_{min} using Eq. [4] and [3] in the MINIMO model have slopes and intercepts not significantly different from one and zero, respectively (t -test at the 0.05 level of probability), indicating a close fit (Fig. 7). Both the slope and intercept using Eq. [1] were significantly different from one and zero, indicating a poor prediction for the MINIMO model using Eq. [1].

The model did not accurately predict the amount of N_{min} in soils amended with soybean leaves (C/N of 10) (Fig. 4). In all four soils the model underpredicted the N_{min} in soils amended with soybean leaves. Several changes in the rate constants for carbohydrate-like and cellulose-like pools in MINIMO were made in an attempt to improve the prediction. These adjustments of rate

constants did not improve model accuracy. The largest discrepancies were underprediction in the first 14 d after residue addition. We suspect that the pool size for soluble carbohydrates and N and for cellulose-like plant tissue in combination with the rate constant may be part of the explanation for poor predictability with some residue-soil mixtures. For simplicity, the MINIMO model now partitions crop residue into three residue-organic matter pools: carbohydrate-like, cellulose-like, and lignin-like. These pools are automatically set by the model at reasonable values of 20% carbohydrate, 70% cellulose, and 10% lignin. Soybean leaves have a greater proportion of nonstructural carbohydrate and soluble N components than the MINIMO model allows. We have a different carbohydrate pool size for soybean leaves than for the other, more typical, residues. The amount of nonstructural carbohydrate (the soluble carbohydrate fraction) can be estimated by subtracting the NDF fraction from 1000 (Goering and Van Soest, 1970). For soybean leaves, we calculated a soluble fraction of 716 g kg^{-1} (Table 1), which is larger than for the other residues.

The model was also not able to satisfactorily predict the amount of N_{min} in soil amended with soybean stems (C/N of 28) (Fig. 2 and 3). This residue had the largest NDF concentration and the smallest soluble carbohydrate fraction of 348 g kg^{-1} . From a survey of 60 different crop residues (our unpublished data, 1993), we suspect that a rough prediction of the partitioning of fiber for a given residue could be made based on the N concentration of the residue. In any event we believe our new TF equations are an improvement but should be tested for their predictive ability using other data sets.

In summary, the use of a single Q_{10} may not be appropriate for predicting changes in the N_{min} rate of crop-residue-amended soils as affected by temperature. Two new TF equations were developed from unamended soil incubated at four temperatures between 5 and 35°C . The use of the new TF equations improved the ability of MINIMO to predict N_{min} from soils amended with residues and incubated for several weeks in the laboratory under optimal soil moisture conditions. In particular, the new equations were more effective in predicting the considerably lower rates of N_{min} at temperatures below 25°C . Even with these improvements, the MINIMO model has some difficulty with prediction of N_{min} for residues with narrow C/N ratios or those that have atypical amounts of fiber. For these four surface soils from the midwestern USA, the difference in the amount of N_{min} at 5 and 15°C was small even after 160 d of incubation. This data also showed the inadequacy of using a simple first-order model to describe N_{min} of soils that have recently been amended with crop residues.

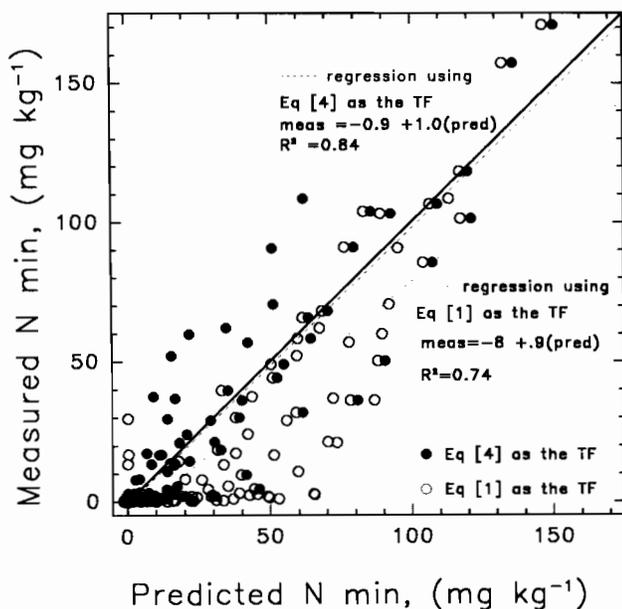


Fig. 7. Measured (meas) vs. predicted (pred) accumulated N mineralized (N_{min}) for crop-residue-amended Haynie and Smolan soils at four temperatures. The solid line is the 1:1 line.

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