Spatial Variability of Nitrogen Mineralization at the Field Scale

M. Mahmoudjafari, G. J. Kluitenberg,* J. L. Havlin, J. B. Sisson, and A. P. Schwab

ABSTRACT

Spatial variability of N mineralization represents a potential problem in predicting the quantity of N mineralized under field conditions. An understanding of mineralization variability is needed if prediction of potential mineralization is to be incorporated into fertilizer recommendation models. The objective of this study was to characterize spatial variability of N mineralization in a Kansas agricultural field. Intact undisturbed soil cores were collected at 108 locations within a 1.7-ha field following wheat (*Triticum aestivum* L.) harvest. The undisturbed cores were incubated aerobically, and NO_3^- was leached periodically as a measure of mineralization. Variability was characterized by examining the spatially distributed values of mineralization potential, N_0, and mineralization rate constant, *k*, parameters of the classical first-order mineralization rate model. Values of N_0 were distributed normally with low variability (coefficient of variation [CV] = 15%) and weak autocorrelation. Values of *k* also followed a normal distribution with low variability (CV = 14%) but were spatially independent. Both N_0 and *k* determined the spatial pattern of N_m, the quantity of N mineralized at a particular time. Variability in *k* controlled the spatial pattern of N_m earlier in the incubation period, and variability in N_0 controlled the spatial pattern late in the incubation period. The incubation approach used in this study allowed characterization of the spatial patterns in N_0, but the spatial variability of *k* observed in this study may not adequately represent field conditions because conditions of constant temperature and water content were used.

Nitrogen fertilization is an important factor for maximizing crop production. Improving the efficiency of N fertilization would improve the economics of crop production and decrease the risk of groundwater pollution. Correctly estimating the quantity of N needed by a crop requires an accurate assessment of the amount of organic N mineralized to NO_3^- and NH_4^+ during the growing season. The spatial variability in N mineralization, even within a small field, represents a potential problem in estimating the quantity of N mineralized under field conditions (Cabrera and Kissel, 1988). Denitrification rates and soil NO_3^- levels are highly variable and are characterized by highly skewed frequency distributions (Robertson et al., 1988; Parkin et al., 1988). Basic information on the variability of N mineralization is needed, if prediction of potential mineralization is to be used in fertilizer recommendation models. Few studies have been conducted to characterize the spatial variability of N mineralization for agricultural soils (Robertson et al., 1993; Goovaerts and Chiang, 1993; Cambardella et al., 1994). The need for this information is particularly urgent as a result of developments in technology for variable-rate fertilizer application. The opportunity to make spatial adjustments in fertilizer rate requires that we examine the importance of different sources of variability in fertilizer recommendation models. The objective of this study was to characterize the spatial variability of N mineralization in a Kansas agricultural field.

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Published in Soil Sci. Soc. Am. J. 61:1214–1221 (1997).

MATERIALS AND METHODS

Sample Collection

The spatial variability of N mineralization was evaluated in a 1.7-ha area (Fig. 1) mapped as Reading silt loam soil, 0 to 1% slopes (fine-silty, mixed, mesic Typic Arguidoll) at the Konza Prairie Research National Area near Manhattan, KS. The soil surface was bare at the time of sampling on 25 July 1987. Winter wheat (cv. Arkan) had been harvested on 1 July 1987, and all of the crop residue was incorporated into the soil with tillage. Soil was sampled after a rain to ensure that the soil was soft and that the probe would penetrate the soil with minimum compaction. Soil samples were collected at 100 locations that were selected by using the method of Warrick and Myers (1987). Eight additional samples were collected from one edge of the field that appeared undersampled.

The Stanford and Smith (1972) incubation method provides a useful approximation of mineralizable N in soil. The original procedure called for mixing sand and soil, incubating for preset time intervals, and leaching the mineralized NO_3–N and NH_4–N from the soil. Although dried and ground soil is frequently used, undisturbed cores provide a more realistic estimate of mineralization potential (Cabrera and Kissel, 1988). To obtain undisturbed cores that could be easily extracted with existing equipment, we developed a soil probe that places the undisturbed core directly into a plastic syringe that is routinely used in a mechanical vacuum extractor (Centurion International, Inc., Lincoln, NE). See Mahmoudjafari (1994) for a diagram of the probe. We have demonstrated that this technique is at least as precise as the original Stanford and Smith (1972) method and probably more accurate.

An intact soil core was collected at each sampling location directly in a 60-mL plastic syringe body that served as the incubation vessel and fit directly onto the vacuum extractor for leaching. The flange at the top of each syringe body was removed to allow placement into a soil probe. A glass wool pad was packed into the bottom of the syringe to retain soil during incubation and leaching. The syringe body was placed in the soil probe, the probe was manually driven into the soil to a depth of 10 cm, and the syringe containing the undisturbed soil core was removed from the probe. Another glass wool pad was then placed on the soil at the top of the syringe body to prevent mechanical disruption of the surface during leaching. With this approach, each undisturbed core was incubated and leached without ever having to remove the soil from the syringe. Samples were stored at 4°C until leaching and incubation were initiated.

Soil Incubation and Leaching

The soil in each syringe was wetted slowly with 45 mL of 0.01 *M* $CaCl_2$ after placement on the vacuum extractor. The syringes were allowed to equilibrate for 20 min to ensure slow wetting of the sample. Soil solution in the syringes was extracted during 12 h, followed by a 3-h extraction with another 45 mL of 0.01 M $CaCl_2$ to ensure rapid and complete leaching of mineral N. This method efficiently removed all of the NO_3^- from the soil. Subsequently, 25 mL of a N free nutrient solution (Cabrera and Kissel, 1988) was added to each syringe to replenish nutrients lost during leaching and to ensure continuous microbial activity. After allowing sufficient draining under vacuum, syringes were placed in an incubator at 35°C. The leachate was diluted to 100 mL in a volumetric flask by adding 0.01 M $CaCl_2$. Ammonium and NO_3^-–N concentration were determined by the colorimetric procedure using an autoanalyzer (Technicon Industrial Systems, 1977). All results are reported on an oven-dry soil weight basis. No significant amounts of NH_4–N were detected in leachates after initial extraction; therefore, only NO_3^-–N was determined in subsequent leachings. The leachings were repeated after 14, 28, 56, 91, 119, and 238 d of incubation.

Mineralization Assessment

Robertson et al. (1993) characterized the variability of N mineralization in their work by using a 10-d laboratory incubation. Mineralization was taken as the net amount of NH_4–N and NO_3–N produced during the incubation period. Goovaerts and Chiang (1993) characterized spatial patterns of potential mineralizable N using the technique of Keeney (1982), which involves estimation of NH_4–N produced under waterlogged conditions. Cambardella et al. (1994) also characterized spatial patterns in mineralizable N but used the method described by Keeney and Bremner (1967).

We characterized the spatial variability of N mineralization by examining the spatially distributed values of N_0 and k, parameters of the first-order rate model (Stanford and Smith, 1972)

$$N_m = N_0 (1 - e^{-kt}) \quad [1]$$

where N_m (mg kg^{-1}) is the mineralized N in time t (d), N_0 (mg kg^{-1}) is N mineralization potential, and k (d^{-1}) is the mineralization rate constant. The parameters N_0 and k were estimated by using a nonlinear least-squares method (Marquardt method; SAS Institute, 1990) to fit Eq. [1] to the N_m data for each sample. The nonlinear least squares procedure converged upon optimum N_0 and k values for each sample. Graphical analysis was used to confirm that the first-order rate model was appropriate for all samples.

First-Order Error Analysis

First-order error analysis is based on the theory of approximating statistical moments for random functions of independent random variables by using Taylor series expansions. The first-order Taylor series approximations for the mean and variance of an arbitrary function are given by Kempthorne and Allmaras (1986, p. 20). The first-order approximations for the mean and variance of Eq. [1] are

$$\mu_{N_m} \approx \mu_{N_0} (1 - e^{\mu_k t}) \quad [2]$$

$$\sigma^2_{N_m} \approx (1 - e^{-\mu_k t})^2 \sigma^2_{N_0} + (t\mu_{N_0} e^{-\mu_k t})^2 \sigma^2_k + 2\rho_{N_0,k}(1 - e^{-\mu_k t})(t\mu_{N_0} e^{-\mu_k t})\sigma_{N_0}\sigma_k \quad [3]$$

where, μ, σ^2, and ρ denote mean, variance, and the correlation between N_0 and k, respectively. These expressions yield the mean and variance of N_m, given the means and variances of N_0 and k, and the correlation between N_0 and k. Note that N_0 and k are treated as independent random variables in developing these relationships. Thus, the relationships ignore any spatial correlation that may exist between spatially distributed values of N_0 or k.

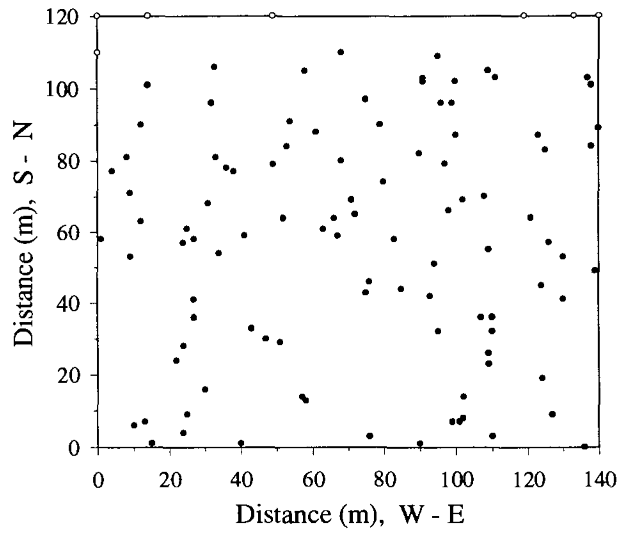

Fig. 1. Sampling locations for undisturbed cores. Dots represent the locations selected by the method of Warrick and Myers (1987). Open circles represent additional, arbitrarily chosen, sampling locations.

Geostatistical Analysis

Geostatistical analyses were performed with Geopack Version 1.0e. Geopack has a number of models that can be fitted to estimated semivariograms by using a nonlinear least squares procedure. The spherical model was used in this study:

$$\gamma(h) = \begin{cases} C_0 + C\left(\dfrac{3h}{2a} - \dfrac{h^3}{2a^3}\right); & 0 \le h \le a \\ C_0 + C; & h \ge a \end{cases} \quad [4]$$

where C_0 is the nugget variance, $C_0 + C$ is the sill, and a is the range of spatial correlation (Vauclin et al., 1983). It was selected over linear and exponential models based on more favorable weighted residual mean squares, jack-knifing results, and better visual fit to the data at short lags. Directional semivariograms were calculated for four principal directions (N–S, NE–SW, E–W, and SE–NW) with a direction tolerance of ±22.5° to investigate the presence of anisotropy (Trangmar et al., 1987).

Geopack was used to calculate drift for directional semivariograms. It uses a simple expression for drift in one-dimensional data that was presented by David (1977). Davidoff et al. (1986) argued that this is a poor drift estimator because the differencing of adjacent data couples eliminates all but several points from the beginning and end of the transect. This cancellation will occur to only a limited extent for directional semivariograms constructed from unequally spaced points (Fig. 1) that are differenced within a fixed tolerance angle.

The punctual kriging procedure in Geopack was used to obtain point estimates of soil properties at unsampled locations. Jack-knifing is one technique that can be used to check whether estimates produced by a system of kriging equations in fact are unbiased and have a minimum variance (Vauclin et al., 1983). Jack-knifing is a method of cross-validation in which a measurement from a single location is excluded from the data set and then the remaining points are used to make a kriged estimate at the same location. When repeated for all measurement locations, the mean and variance of the resulting pairs of measured and estimated values can be computed to check for unbiasedness and minimum variance. Vauclin et al. (1983) outlined a procedure for computing a mean reduced error ($\bar{R}_\epsilon$) and a reduced variance ($S^2_{R_\epsilon}$). The mean reduced error must be close to zero if the estimates are unbiased, and $S^2_{R_\epsilon}$ should be close to unity to satisfy the condition of minimum variance.

RESULTS AND DISCUSSION

Coefficients of variation for N_m ranged from 12 to 17% (Table 1). The range and standard deviation (SD) for N_m increased with time of incubation, but variability actually decreased as incubation progressed. Coefficients of variation decreased from 17 to 12% after 91 d of incubation and remained relatively constant thereafter. This variability is much lower than that reported by Robertson et al. (1993). They examined the spatial variability of net N mineralization in a 2.2-ha field by incubating 240 disturbed samples (mixed and sieved) at field water contents for a period of 10 d. They reported a CV of 58% for N_m at 10 d. We observed a CV of 17% at 14 d (Table 1). The large difference in variability is rather striking for two cultivated fields of similar size. Certainly, the different incubation methods used in the two studies could lead to differences in variability. Another possible cause for the difference is that our incubation procedure ensured relatively constant water contents in all undisturbed samples. The samples incubated by Robertson et al. (1993) varied in water content because they were incubated at field water contents. Water content is acknowledged to be a major factor influencing k (Stanford and Epstein, 1974; Cabrera and Kissel, 1988). Variations in water content, therefore, could increase the variability of N_m by introducing variability in k. If so, the low variability in N_m we observed in this study would be an artifact of the incubation method. In a later section, we will use Eq. [1] to examine how variability in k can influence variability in N_m. Soil temperature also is known to influence k. Therefore, incubation at constant temperature also could limit variability in k.

Fitted values of N_0 ranged from 86 to 187 mg N kg^{-1} soil with a mean of 138.7 mg N kg^{-1} soil; fitted values of k ranged from 0.004 to 0.0087 d^{-1} with a mean of 0.0062 d^{-1} (Table 1). These values are similar to those previously reported for incubation studies with undisturbed soil (Cabrera and Kissel, 1988; Myers, 1989; Rice and Garcia, 1994), but none of those researchers examined within-field variability of k and N_0. Variability in N_0 (CV = 15%) and k (CV = 14%) was similar to that observed for N_m.

Table 1. Mean, standard deviation (SD), and coefficient of variation (CV) of the fitted parameters N_0 and k and measured values of N_m at 14, 28, 56, 91, 119, and 238 d of incubation.

Variable†	Mean	SD	CV
	mg kg^{-1}		%
N_m, 14 d	11.5	2.0	17
N_m, 28 d	22.0	3.2	15
N_m, 56 d	32.2	4.2	13
N_m, 91 d	58.9	7.1	12
N_m, 119 d	77.5	9.4	12
N_m, 238 d	103.6	12.6	12
N_0	138.7	20.5	15
	d^{-1}		
k	6.2×10^{-3}	8.4×10^{-4}	14

† N_m = quantity of N mineralized at a particular time; N_0 = N mineralization potential; k = N mineralization rate constant.

The variability in N_0 is lower than that reported by others. Goovaerts and Chiang (1993) collected 73 samples across a 0.16-ha field on two occasions and reported 15.8 and 16.6 mg kg^{-1} as mean values of potentially mineralizable N. Coefficients of variation were found to be 36.4 and 29.5% for the two sampling dates, respectively. Cambardella et al. (1994) observed similar variability in a 10-ha field. Sampling at 72 locations yielded mean N mineralization of 44.2 mg kg^{-1} with a CV of 24%. However, they observed much greater variability in a 6.25-ha field containing two potholes. Mean mineralizable N was found to be 9.6 mg kg^{-1} with a CV of 585% (n = 241).

Histograms of N_0 and k (Fig. 2) approximate the normal distribution, although the k distribution exhibits a slight positive skew. Kolomogorov and Crammer-Von Mises statistics were computed following the methods outlined by Rao et al. (1979) so that distributional tests could be performed. Rao et al. (1979) also showed how the power ($1 - \beta$) of these tests can be approximated.

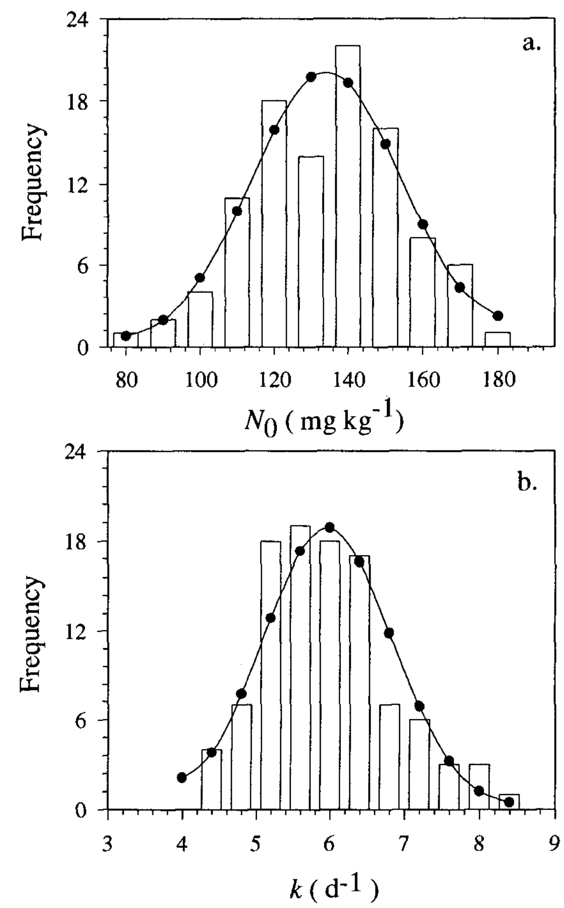

Fig. 2. Frequency distributions of (a) N mineralization potential, N_0 (mg kg^{-1}), and (b) the mineralization rate constant, k (d^{-1}). The histogram represents the measured frequency distribution, and the continuous solid line with points represents the normal frequency distribution.

The tests suggested that N_0 is distributed normally and k is distributed lognormally. However, extremely low power for the distributional tests rendered the test results meaningless. Testing N_0 for normality yielded a test power of $1 - \beta = 0.45$, when the lognormal distribution was specified as the alternative hypothesis. Testing k for lognormality yielded $1 - \beta = 0.20$ with an alternative hypothesis of a normal distribution. We have treated N_0 and k as normally distributed and have assumed that an incorrect distributional assumption will cause minimal error in additional analyses. In contrast, Robertson et al. (1993) found net N mineralization to be distributed lognormally. Mineralizable N also was found to be distributed lognormally in the two fields examined by Cambardella et al. (1994).

Spatial Pattern of Nitrogen Mineralization

The spherical model initially was fitted to the composite N_0 semivariogram (Fig. 3) by using the nonlinear least squares procedure. This was followed by cross validation. The model parameters after cross validation, $a = 63.3$ m, $C_0 = 252.7$ (mg kg^{-1})^2, and $C_0 + C = 419.9$ (mg kg^{-1})^2, were only slightly different from those obtained by nonlinear least squares fitting. The mean reduced error ($\overline{R}_\epsilon = -3.2 \times 10^{-2}$) and reduced variance ($S^2_{R_\epsilon} = 1.2$) remained unchanged as a result of cross validation. Although the spherical model accounts for the overall behavior of the semivariogram, it fails to account for the underlying cyclical pattern (Fig. 3). The composite k semivariogram exhibited pure nugget effect, indicating that the variance structure of k can be represented simply by the variance reported in Table 1, i.e., the variance structure is independent of sampling spacing for the lag distances used in this study.

The distribution of couple separation distances involved in the construction of the N_0 semivariogram is shown in Fig. 4a. The number of paired observations indicate that good estimates of the semivariogram were obtained for lag distances of 5 to 100 m. Employing the method of Warrick and Myers (1987) ensured this distribution of paired observations. Their method optimizes the selection of sample locations for variogram estimation with respect to a prespecified distance. The method provides a reasonable number of paired observations for variogram estimation both at short and long lags to enhance the reliability of the semivariogram as an estimator, while satisfying constraints on sample size. We employed a variant of the Warrick and Myers (1987) method in which sample locations were constrained to provide adequate coverage of the field. This permitted the results of a single sampling to be used for semivariogram estimation as well as mapping. Without the constraint of spatial coverage, a nearly uniform distribution of couples could have been achieved. In contrast to the distribution of couples obtained with the method of Warrick and Myers (1987), Fig. 4b shows the distribution of couples that would result from a 14 by 14 m sampling grid (110 points) imposed across the site shown in Fig. 1. This square grid gives uniform coverage of the field but fails to yield the couples at short lags that are so crucial to semivariogram estimation.

Anisotropy and drift were studied while evaluating directional semivariograms for N_0 and k in the four principal directions. Both anisotropy and drift were evident to some extent during this evaluation but were judged to be weak features of the data (Mahmoudjafari, 1994). The fact that the sill for the composite N_0 semivariogram (Fig. 3) was slightly below the sample variance provides additional evidence for the absence of significant drift or trend across the site (Trangmar et al., 1987).

The nugget variance represents the measurement er-

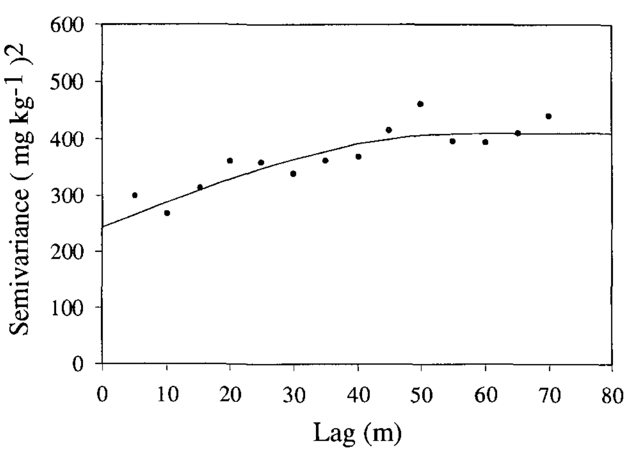

Fig. 3. Composite semivariogram for N mineralization potential, N_0. The solid line is the spherical model with range of spatial correlation, a = 63.3 m; nugget variance, C_0 = 252.7 (mg kg^{-1})^2; and sill, $C_0 + C$ = 419.9 (mg kg^{-1})^2.

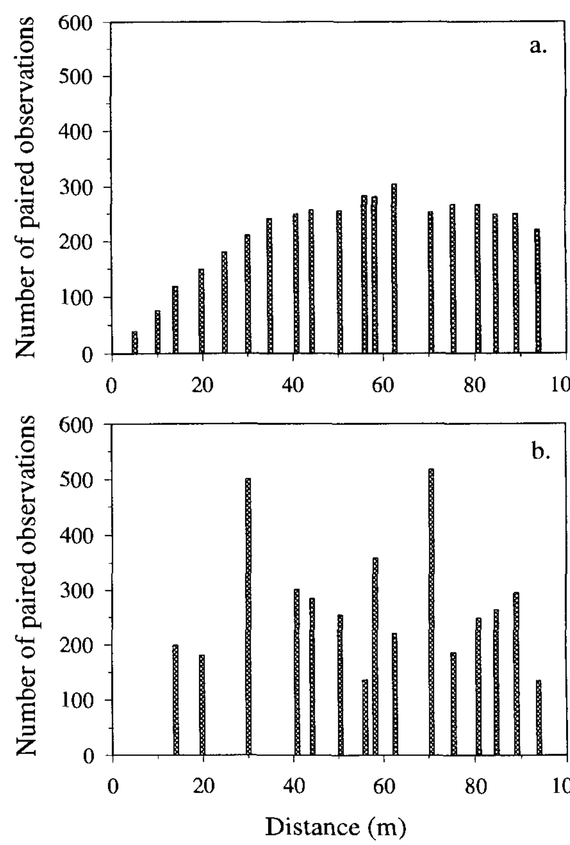

Fig. 4. Distribution of couple separation distances for (a) the sampling scheme portrayed in Fig. 1, and (b) 110 points on a 14 by 14 m grid.

ror or autocorrelation present at a distance shorter than the smallest lag. Nitrogen mineralization potential has a relatively large nugget variance that is ≈60% of the sill. The accuracy of N_0 estimates obtained from incubation of undisturbed soil cores is unknown. Thus, we are unable to partition the nugget variance into measurement error and autocorrelation at distances <5 m, the smallest mean lag spacing.

Nitrogen mineralization potential was point-kriged on a 3.5 by 4 m grid (1271 locations) by using the 10 nearest neighboring points within a search radius of 25 m (Fig. 5). The range of kriged N_0 values was 112 to 162 mg kg^{-1}, somewhat narrower than the range of the measured N_0 values (86–187 mg N kg^{-1}). Kriging, like all methods of spatial estimation, generally yields estimates that are smoother than the original measurements. In fact, kriged estimates will exactly match measurements at locations where measurements were made, but the grid used for point kriging coincides with only two of the measurement locations shown in Fig. 1. A contour map (Fig. 6) shows the spatial pattern of rate coefficients. Kriging could not be used for spatial estimation of k, because k values exhibited no spatial correlation.

The spatial patterns of N_m at 14, 28, 56, 91, 119, and 238 d also were examined, but only the results for N_m at 56 d, $N_m(56)$, are presented. The spatial correlation exhibited by $N_m(56)$ was weaker than that observed for N_0; the nugget variance for the $N_m(56)$ semivariogram was 72% of the sill value. A point-kriged map of $N_m(56)$ was constructed using the same 1271-point grid that was used to krige N_0 (Fig. 7). The 56-d mineralization results exhibit a spatial pattern notably different from the spatial patterns of k (Fig. 6) and N_0 (Fig. 5). Comparison of Fig. 5, 6, and 7 shows that high mineralization (Fig. 7) coincides with portions of the field having both high mineralization potential (Fig. 5) and high rate constant (Fig. 6). Low rate constants caused reduced mineralization in some portions of the field with high mineralization potential. Likewise, low mineralization potential

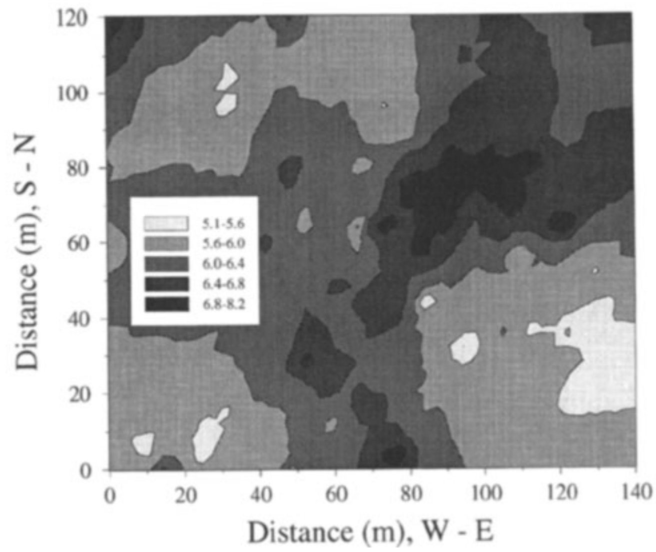

Fig. 6. Contour map of $10^3 \times k$ (d^{-1}), the mineralization rate constant.

caused reduced mineralization in some portions of the field with high rate constants. Both k and N_0 appear to be important in determining $N_m(56)$. This result is not surprising, inasmuch as the mineralization data were modeled well by the first-order rate model, and we know from the model that the amount of N mineralized will be controlled by the parameters k and N_0. Simply examining the model, however, does not reveal the relative importance of the spatial variation of k and N_0 in controlling the spatial variation in mineralized N.

As a first step in addressing this issue, we computed simple linear correlation coefficients (r) between the parameters N_0 and k and the measured values of N_m at 14, 28, 56, 91, 119, and 238 d (Table 2). At 56 d, N_m appears to be related more strongly to N_0 (r = 0.58) than k (r = 0.25). However, the correlation coefficients for different times reveal that the relative contributions by N_0 and k to total variation are not constant with time. The correlation between N_m and N_0 increases with time,

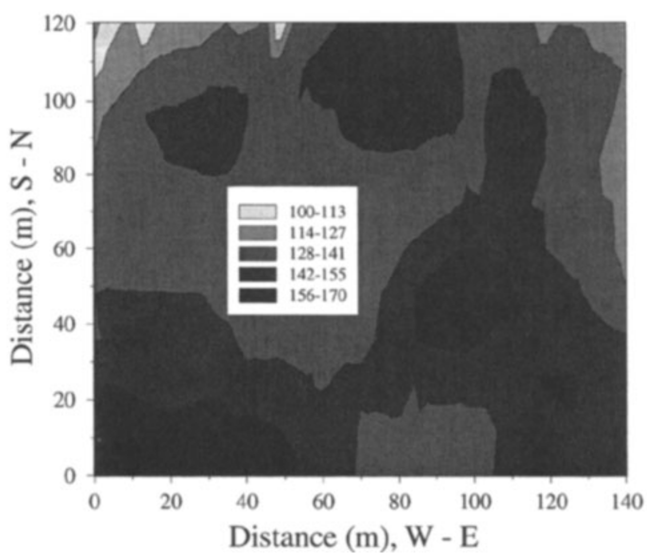

Fig. 5. Punctual kriged map of N_0 (mg kg^{-1}), the N mineralization potential.

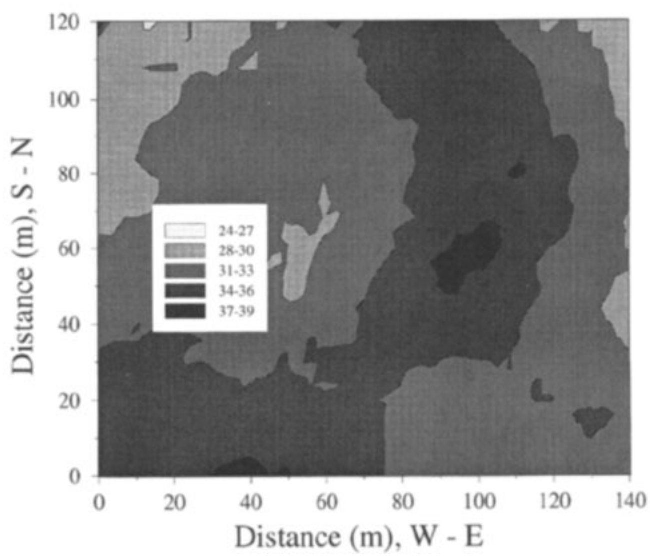

Fig. 7. Punctual kriged map of mineralized N, N_m, (mg kg^{-1}) after 56 d of incubation.

Table 2. Simple linear correlation coefficients (r) between the parameters N_0 and k and measured values of N_m at 14, 28, 56, 91, 119, and 238 d of incubation.

Variable†	r	
	N_0†	k†
N_m, 14 d	0.32	0.46
N_m, 28 d	0.48	0.34
N_m, 56 d	0.58	0.25
N_m, 91 d	0.68	0.17
N_m, 119 d	0.79	0.01
N_m, 238 d	0.91	−0.22

† N_m = quantity of N mineralized at a particular time; N_0 = N mineralization potential; k = N mineralization rate constant.

whereas the correlation between N_m and k decreases. This indicates that spatial variation in mineralization was controlled predominantly by spatial variation in k earlier in the incubation period and predominantly by N_0 later in the incubation period. This result is consistent with the behavior of Eq. [1]. A graph of Eq. [1], N_m plotted vs. time, is characterized by a steep (exponential) initial rise that eventually levels off and approaches the asymptotic value N_0. The steepness of the initial rise is controlled predominantly by the value of k; thus, variability in N_m will be dictated by variability in k. Later in the incubation period, variability in N_m will be dictated by variability in N_0, because it is the asymptotic value of N_0 that controls curve shape at late times. First-order error analysis is used in the next section to formalize these observations regarding the relative importance of variability in k and N_0.

First-Order Analysis

The following two examples show how first-order error analysis can be used to examine the relative importance of variability in k and N_0. In the first example, the measured quantities σ_{N0}, σ_k, μ_{N0}, μ_k (Table 1), and $\rho_{N0,k} = -0.58$ were substituted into Eq. [2] and [3]. These equations then were solved for t = 14, 28, 56, 91, 119, and 238 d to compare the calculated μ_{N_m} and σ_{N_m} values (Table 3, Columns 2 and 3) with the measured values (Table 1, Columns 2 and 3). The calculated and measured values of μ_{N_m} and σ_{N_m} agree closely and suggest that the first-order error analysis is appropriate. The fourth, fifth, and sixth columns in Table 3 contain the actual values of the three terms in Eq. [3]. For each time, these three terms are summed to give the predicted standard deviation, σ_{N_m}. A comparison of the three terms shows that the contribution of the second term relative to the others diminishes with time. The second term represents the direct contribution of variability in k and shows that variability in k contributes significantly to variability in mineralized N early in the incubation period. Later, the variability in N_0 begins to dominate. These results agree with what we concluded earlier by simply considering a graph of Eq. [1]. The utility of the analysis presented here is the ability to actually quantify the effect that variability in k has on variability in N_m. We will take advantage of this in the next example calculation.

Earlier, we discussed the possibility that incubation at constant water content and temperature limited the spatial variability of rate coefficients measured in this study. Water content and temperature in the 0- to 10-cm soil layer are known to vary spatially and temporally in the field, and both are known to affect k. Thus, we might expect to observe greater spatial and temporal variations in rate constants if incubation took place at field water contents and temperatures. We also suggested earlier that increased variability in k would lead to increased variability in N_m. First-order error analysis provides a means of exploring how increased variability in k influences variability in N_m.

Table 4 shows the results of the second example in which all the inputs except σ_k were held at the same levels as used in the first example. The standard deviation of k was increased arbitrarily fivefold to $\sigma_k = 0.0042$ d^{-1} (CV = 68%) without altering $\rho_{N0,k}$, and the computations were carried out to 500 d. Note the magnitude of the second term at early times, relative to the other terms, and the effect it has on σ_{N_m}, the variability of N_m. Because μ_{N_m} was unaffected by the increase in σ_{N_m}, increases in σ_{N_m} caused corresponding increases in the N_m CV (Table 4, Column 6). The larger variability in k caused a significant increase in the variability of N_m, and the increased variability persisted for some time. This exercise clearly demonstrates that increased variability in k will indeed result in increased variability of N_m, if mineralization proceeds as we have assumed in Eq. [1].

The first-order error analysis that we have presented requires the existence of σ_{N0} and σ_k. Although σ_{N0} and σ_k are given in Table 1, the intrinsic hypothesis that forms the basis for kriging does not require the existence of σ_{N0} and σ_k. A finite variance exists only when second-

Table 3. Mean (μ_{N_m}), standard deviation (σ_{N_m}), and coefficient of variation (CV) of N_m as computed by first-order analysis. Measured values of σ_{N0}, σ_k, μ_{N0}, μ_k, and $\rho_{N0,k}$ were used in the calculations.†

Time	μ_{Nm}‡	σ_{Nm}§	Term 1¶	Term 2¶	Term 3¶	CV
d	mg kg^{-1}		(mg kg^{-1})^2			%
14	11.6	1.5	2.8	2.2	−2.9	12.9
28	22.2	2.8	10.4	7.6	−10.3	12.6
56	40.8	5.0	35.2	21.3	−31.8	12.3
91	59.9	7.2	76.0	36.5	−61.1	12.0
119	72.5	8.6	111.3	44.1	−81.3	11.9
238	107.2	13.0	243.2	40.3	−114.9	12.1

† N_m = quantity of N mineralized at a particular time; N_0 = N mineralization potential; k = N mineralization rate constant.
‡ Computed with Eq. [2].
§ Computed as the square root of Eq. [3].
¶ Computed from individual terms of Eq. [3].

Table 4. Mean (μ_{N_m}), standard deviation (σ_{N_m}), and coefficient of variation (CV) of N_m as computed by first-order analysis. Calculations were performed with the same values of σ_{N_0}, μ_{N_0}, μ_k, and $\rho_{N_0,k}$, that were used to generate Table 3, with the exception that σ_k was arbitrarily increased fivefold to 0.0042 d^{-1}.†

Time	μ_{N_m}‡	σ_{N_m}§	Term 1¶	Term 2¶	Term 3¶	CV
d	mg kg^{-1}		(mg kg^{-1})^2			%
14	11.6	6.3	2.8	50.9	−13.9	54.3
28	22.2	11.5	10.4	171.3	−48.9	51.8
56	40.8	19.2	35.2	484.1	−151.4	47.1
91	59.9	24.8	76.0	828.3	−291.0	41.4
119	72.5	26.9	111.3	1000.9	−387.2	37.1
238	107.2	24.7	243.2	915.4	−547.3	23.0
500	132.7	15.8	372.7	156.8	−280.5	11.9

† N_m = quantity of N mineralized at a particular time; N_0 = N mineralization potential; k = N mineralization rate constant.
‡ Computed with Eq. [2].
§ Compnted as the square root of Eq. [3].
¶ Computed from individual terms of Eq. [3].

order stationarity holds. The geostatistical analysis in the previous section shows that both k and N_0 appear to exhibit stationarity of order two over the spatial domain considered in this study. Thus, we assumed the existence of σ_{N_0} and σ_k for the purpose of making the example calculations.

SUMMARY AND CONCLUSIONS

In this study, the spatial variability of N mineralization was characterized by examining spatially distributed values of N_0 and k, parameters of the first-order rate model of Stanford and Smith (1972). The values of N_0 were found to be distributed normally with low variability (CV = 15%) and weak autocorrelation (nugget variance ≈60% of semivariogram sill). The mineralization rate coefficient also followed a normal frequency distribution with low spatial variability (CV = 14%) but was shown to be spatially independent. The spatial variability of k observed in this study may not adequately represent field conditions, inasmuch as the incubation was carried out under conditions of constant temperature and water content. Soil temperature and water content affect the rate of mineralization, and both vary spatially. Thus, the incubation approach used in this study apparently allowed characterization of the spatial patterns in N mineralization potential but not mineralization rate.

Ultimately, we are interested in describing spatial patterns of mineralized N not the parameters N_0 and k. However, the results presented here clearly show that both N_0 and k play critical roles in determining the spatial patterns of N_m. Variability in k controlled the spatial pattern of N_m early in the incubation period, and the variability in N_0 controlled the spatial pattern of N_m later. Furthermore, the first-order error analysis showed that increasing variability in k caused increased variability in N_m. Therefore, if we underestimated the spatial variability of k by using an incubation procedure with constant water content and temperature, then we probably also underestimated the spatial variability in mineralized N. These observations bring us to the conclusion that prediction of spatial patterns in N_m will require spatial characterizations of both N_0 and k, not just N_0, especially at relatively early incubation times. Even if accurate spatial characterizations of N_0 and k are available and are used to predict a spatial pattern of N_m, correlations with field estimates of the contribution of N_m to total crop N uptake will be necessary to make practical use of N_m patterns in spatially variable crop N management.

REFERENCES

Cabrera, M.L., and D.E. Kissel. 1988. Mineralizable nitrogen in disturbed and undisturbed soil samples. Soil Sci. Soc. Am. J. 52: 1010–1015.

Cambardella, C.A., T.B. Moorman, J.M. Novak, T.B. Parkin, D.L. Karlen, R.F. Turco, and A.E. Konopka. 1994. Field-scale variability of soil properties in central Iowa soils. Soil Sci. Soc. Am. J. 58:1501–1511.

David, M. 1977. Geostatistical ore reserve estimation. Elsevier Scientific Publ. Co., Amsterdam.

Davidoff, B., J.W. Lewis, and H.M. Selim. 1986. A method to verify the presence of a trend in studying spatial variability of soil temperature. Soil Sci. Soc. Am. J. 50:1122–1127.

Goovaerts, P., and C.N. Chiang. 1993. Temporal persistence of spatial patterns for mineralizable nitrogen and selected soil properties. Soil Sci. Soc. Am. J. 57:372–381.

Keeney, D.R. 1982. Nitrogen — Availability indices. p. 711–733. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Keeney, D.R., and J.M. Bremner. 1967. Determination of isotope-ratio analysis of different forms of nitrogen in soils: VI. Mineralizable nitrogen. Soil Sci. Soc. Am. Proc. 31:34–39.

Kempthorne, O., and R.R. Allmaras. 1986. Errors and variability of observations. p. 1–31. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Mahmoudjafari, M. 1994. Spatial variability of nitrogen minerlization in soil. Ph.D. diss. Kansas State Univ., Manhattan (Diss. Abstr. 95–17475).

Myers, R.G. 1989. Estimation of nitrogen mineralization from soil organic matter. M.S. thesis. Kansas State University, Manhattan.

Parkin, T.B., J.J. Meisinger, S.T. Chester, J.L. Starr, and J.A. Robinson. 1988. Evaluation of statistical estimation methods for lognormally distributed variables. Soil Sci. Soc. Am. J. 52:323–329.

Rao, P.V., P.S.C. Rao, J.M. Davidson, and H.C. Hammond. 1979. Use of goodness-of-fit tests for characterizing the spatial variability of soil properties. Soil Sci. Soc. Am. J. 43:274–278.

Rice, C.W., and F.O. Garcia. 1994. Biologically active pools of carbon and nitrogen in tallgrass prairie soil. p. 201–208. *In* J.W. Doran et al. (ed.) Defining soil quality for a sustainable environment. SSSA Spec. Publ. 35. SSSA and ASA, Madison, WI.

Robertson, G.P., J.R. Crum, and B.G. Ellis. 1993. The spatial variability of soil resources following long-term disturbance. Oecologia 96:451–456.

Robertson, G.P., M.A. Huston, F.C. Evans, and J.M. Tiedje. 1988. Spatial variability in a successional plant community: Patterns of nitrogen availability. Ecology 69:1517–1524.

SAS Institute. 1990. SAS procedure guide, release 6.03 ed. SAS Inst., Inc., Cary, NC.

Stanford, G., and E. Epstein. 1974. Nitrogen mineralization — Water relations in soils. Soil Sci. Soc. Am. Proc. 38:103–107.

Stanford, G., and S.J. Smith. 1972. Nitrogen mineralization potentials of soils. Soil Sci. Soc. Am. Proc. 36:645–672.

Technicon Industrial Systems. 1977. Nitrate and nitrite in soil extracts. Industrial Method no. 487–77 A. Technicon Industrial Systems, Tarrytown, NY.

Trangmar, B.B., R.S. Yost, M.K. Wade, G. Uehara, and M. Sudjadi. 1987. Spatial variation of soil properties and rice yield on recently cleared land. Soil Sci. Soc. Am. J. 51:668–674.

Vauclin, M., S.R. Vieira, G. Vachaud, and D.R. Nielsen. 1983. The use of cokriging with limited field soil observations. Soil Sci. Soc. Am. J. 47:175–184.

Warrick, A.W., and D.E. Myers. 1987. Optimization of sampling locations for variogram calculations. Water Resour. Res. 23:496–500.