

ASSESSING THE VARIABILITY OF SOIL NITROGEN  
MINERALIZATION

by

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B.S., Lake Superior State College, 1987  
M.S., Michigan State University, 1996

AN ABSTRACT OF A DISSERTATION

Submitted in partial fulfillment of the  
requirements for the degree

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Department of Agronomy  
College of Agriculture

KANSAS STATE UNIVERSITY  
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## ABSTRACT

Variable N fertilizer application recommendations would benefit from crediting the N that will be mineralized and available to the crop during the growing season. During the 1994 and 1995 growing season, the spatial and temporal pattern of N mineralization was assessed on two central Kansas corn fields. Net N mineralization was measured in the field using a buried bag and a resin core method. A 60 m sampling grid was established on the field and the N mineralization was measured at each grid point. The field N mineralization measured was then compared to three lab incubation (14 day anaerobic incubation, CO<sub>2</sub> evolved 1 day after rewetting, and N released on autoclaving) measurements to determine if the field N mineralization could be predicted by a laboratory test. Nitrogen mineralization in the field was highest in May and declined during the growing seasons. Patches of high N mineralization appeared and disappeared during the season, areas of high and low mineralization were not found in the same areas month after month. The semivariance of the laboratory incubations tended to be smoother near the origin than the field incubations, indicating that the field incubations were subject to more sources of variability (such as microclimatic variations) than the laboratory incubations.

Crop yields were not correlated with N mineralization in these fields. Soil moisture appeared to be more important to crop yields than the N contributed by mineralization. In these fields N mineralization does not need to be included in N fertilization recommendations unless the amount of fertilizer applied is much lower than in this study.

Finally, a method to estimate the initial  $\delta^{13}C$  content of a soil is proposed. This method can be used if a location can be found that has had a continuous  $C_3$ , a continuous  $C_4$  crop and a  $C_3 / C_4$  rotation treatment.

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## CHAPTER 1

### Literature Review

Nitrogen mineralization is a dynamic process that varies in space and time. This variability complicates spatial N fertilization recommendations. This dissertation attempted to characterize the spatial and temporal patterns of N mineralization in two central Kansas fields. Understanding N mineralization variability requires an understanding of both the N mineralization process and its geostatistical description.

#### 1. Geostatistics

It is frequently necessary to estimate the value of a property at an unsampled location. This problem can also be cast as that of estimating the shape and size of a volume from discrete sample points (Henley, 1981). It is well known that many properties of the environment behave more or less like continuous functions, so that the values of a given property can be expected to vary according to the distance separating adjacent sampling locations (Burgess and Webster, 1980). The initial development of the techniques collectively known as “geostatistics” was motivated by the desire of mining and petroleum engineers to estimate the volume and shape of ore and petroleum reserves. In contrast to conventional statistics, geostatistics makes use of spatial information, the location of the observations, and provides a way to describe the spatial continuity.

Geostatistics is concerned with several problems,

- (1) estimating the value of a parameter at an unsampled location or area,
- (2) describing and quantifying the spatial structure and the covariances among variables,
- (3) simulating the behavior of a parameter, and

(4) describing the likelihood that a parameter will exceed a threshold value.

Mapping the spatial distribution of a parameter was the goal of many of the early applications of geostatistics. More recent applications have focused on creating models of uncertainty (Deutsch and Journel, 1992; Bourgault et al., 1997), that is, creating probable realizations of the distribution of the parameter and then comparing the outcome of the process of interest given the realizations, although the procedure was described earlier by Journel and Huijbregts (1978).

**1.1. History.** Much of the early development of geostatistics was done by application engineers, who had to get results, rather than mathematicians who wanted correct results. While the underlying geostatistical theory had been developed in the 1950's and early 1960's (Deutsch and Journel, 1992; Journel and Huijbregts, 1978), widespread application in the earth sciences did not occur until sufficient computer power was available (Deutsch and Journel, 1992).

1.1.1. *Polygon/Triangulation Methods.* One of the simplest methods of estimating the area represented by a point sample is to define a “polygon of influence” and assign the value of that point to the polygon. The polygon of influence is that area that is closer to the sample point than to any other sample point. The polygonal model implies a discontinuity at the boundaries between each polygon, however continuous variables are also continuous at the boundaries, and so the polygon method can only approximate reality. Royle (1978) showed that this method produces biased estimates. However polygon methods can be useful for declustering to obtain averaging weights (Isaaks and Srivastava, 1989).

Although discontinuities in the values of properties sometimes do occur in nature, most properties vary in some continuous manner. Triangulation provides a more continuous description of the variable surface. Triangulation works by fitting a plane through the three closest points of measurement.

1.1.2. *Moving Average Methods.* Early methods of describing spatial variability focused on the idea of “moving window averages”. A rectangular or circular search region is passed over the sample area, and points within the window are averaged to produce the value of the parameter at the center point. All points receive the same weight of  $\frac{1}{m}$  where  $m$  is the number of points in the search region.

1.1.3. *Weighted Moving Average Methods.* Points that are “close” to the point to be estimated are assumed to be more similar to the point to be estimated than points that are farther away. So, various weighting methods have been proposed to improve the moving average method. Different methods in this section differ in the weighting function and/or in the search algorithm.

The inverse distance is a conventional method of computing the weighting factors. This method takes the weight assigned to a particular point as  $\frac{1}{d^c}$ , where  $c$  is a arbitrary number (not necessarily an integer) and  $d$  is the distance from the point to be estimated to the sample point. Common values of  $c$  are one (inverse distance) and two (inverse distance squared). The weighting function can be normalized by dividing each weighting factor by the sum of all the weighting factors used to estimate the point.

$$w_i = \frac{\frac{1}{d_i^c}}{\sum_{m=1}^n \frac{1}{d_m^c}} \quad (1)$$

Where  $w_i$  is the  $i$ 'th weighting factor and  $n$  is the number of weighting factors used. These weighting functions decrease the weighting as the distance from the point increases. The inverse distance method is sensitive to extreme data values and the spacing of the sample values. In an effort to make the method more robust, restrictions have been placed on the search method. For example, the search neighborhood can be divided into quadrants and a certain number of points considered from each quadrant. None of the moving average methods produce estimated values above the maximum or below the minimum data value. They lack a sound theoretical foundation (Burgess and Webster, 1980), but moving average methods especially the inverse

squared distance method (with the quadrant search) works well for general contouring and map making. Moving average techniques can be customized to take anisotropy into account and by choosing specific weighting functions they can produce maps that are nearly equivalent to those produced by kriging (Monmonier, 1982).

Some workers replaced the simple planes of the the polygonal and triangular methods with more complex polynomials (Student, 1914) or Fourier series. These methods work well for simple, smooth surfaces, but they are susceptible to noise and sensitive to the distribution of the data points (Henley, 1981). To represent complex surfaces the number of terms required quickly become unwieldy.

1.1.4. *Kriging.* While the various interpolation methods give good results for well behaved data sets (Burgess and Webster, 1980), and can be adapted to poorly behaved data sets (Monmonier, 1982), they lack a theoretical foundation (Burgess and Webster, 1980). A method with a theoretical statistical basis is known as kriging. The technique of kriging is credited to the South African mining engineer D. G. Krige, building of the statistical approach of H. S. Sichel (Krige et al., 1988). In the early 1950's Krige regressed the previously used log-normal estimates of the ore grades with the mean block ore grades and developed the first estimator that used information from outside the area to be estimated (Krige, 1951). Then in the early 1960's Mathéron (1963) formalized and extended some the ideas developed in South Africa into the theory of regionalized variables (Journel and Huijbregts, 1978; Krige et al., 1988). The simplest kriging estimator is aptly named simple kriging. It assumes a global mean  $\bar{Z}$ .

$$\hat{Z}(x) - \bar{Z} = \sum_{i=1}^{n(h)} \lambda_i(h_i)[Z(h_i) - \bar{Z}] \quad (2)$$

where  $\hat{Z}(x)$  is the estimated value of  $Z$  at location  $x$ ,  $\lambda_i(h)$  is the weight for the  $i$ 'th sample at lag distance  $h$  and the kriging system

$$\sum_{i=1}^n \lambda_i \gamma(x_i, x_j) = \gamma(x_i, X) \quad \forall j \in \{1, 2, \dots, n\} \quad (3)$$

where  $\gamma(x_i, X)$  is the semi-variance between each point and the average of all the points considered, and  $\gamma(x_i, x_j)$  is the semi-variance between each set of points. Simple kriging does not adapt to local trends, because the mean is assumed to be constant over the whole sample area. Therefore simple kriging is not used much for direct estimation of the value of variables at unknown locations.

Some of the deficiencies of the simple kriging estimator can be overcome by dropping the global mean and requiring that the weights sum to one. This method provides an optimal, unbiased estimator. The resulting estimator is called the ordinary kriging estimator.

$$\hat{Z}(x) = \sum_{i=1}^n \lambda_i Z_i(x) \quad (4)$$

where  $\hat{Z}(x)$  is the estimated value of  $Z$  at location  $x$ , and  $Z_i(x)$  is the measured value at location  $x$ . Solving the kriging system requires the insertion of a Lagrange parameter  $\psi$ .

$$\begin{cases} \sum_{i=1}^n \lambda_i \gamma(x_i, x_j) + \psi = \gamma(x_i, X) & \forall j \in \{1, 2, \dots, n\} \\ \sum_{i=1}^n \lambda_i = 1 \end{cases} \quad (5)$$

This method can be thought of as simple kriging with the average re-estimated for each location (Deutsch and Journel, 1992).

To handle larger trends than could be accommodated by ordinary kriging Matheron (Journel and Huijbregts, 1978) and Huijbregts and Matheron (1971) proposed the inclusion of a polynomial into the kriging equation. The underlying model was changed to  $Z(h) = a(h) + R(h)$ , where  $a(h)$  is the expectation of  $Z(h)$  and  $R(h)$  is a random residual with a zero mean.

Since some properties are generated by the same processes, they might be expected to vary in a similar manner. In these cases, the covariance between two variables can be used to improve kriging of either variable. Co-kriging is especially useful if one variable is much easier/cheaper to measure than the other variable.

1.1.5. *Non-linear Methods.* Non-linear kriging methods were developed to deal with the non-normality of the observed data. All non-linear methods are linear methods applied to non-linear transformations of the data. Since ore grades and other natural phenomena are often more or less log-normally distributed, Krige (1978) recommended transforming the data into a normal distribution with the following transformation.

$$y = \log(x + a) \quad (6)$$

where  $x$  is the original datum,  $y$  is the transformed datum, and  $a$  is a fitting parameter. Kriging these transformed values yields estimates of the logarithms of the variable. To recover the original value, the value of the estimate should be adjusted upward

$$\log \hat{y} = \log y + \frac{1}{2}\sigma^2 \quad (7)$$

where  $\log \hat{y}$  is the adjusted estimate, and  $\sigma$  is the variance. This is often nearly optimal, but the optimality is not guaranteed (Rivoirard, 1990). Log-normal kriging has been used in mining (Journel and Huijbregts, 1978; Rendu, 1979) as well as in soil science (Yost et al., 1982; Robertson et al., 1993). A generalization of the log-normal kriging is called multi-gaussian kriging (Journel and Huijbregts, 1978; Verly, 1983). Multi-gaussian kriging has the advantage that the back-transformation is a straight inverse.

Other non-linear transformations include indicator kriging and disjunctive kriging. In indicator kriging the aim is to estimate whether the value of the variable is below a certain cut-off point at the location to be estimated. In disjunctive kriging (Matheron, 1976) a polynomial transform of the data is chosen to make the data appear normal.

In a review by Krige et al. (1988) the major improvement in power of estimation was in the step from previous mining estimation techniques such as moving averages to simple kriging. Improvements in the power of estimating were much lower with increasingly complex kriging schemes. The law of diminishing returns strikes again.



1.1.6. *Non-parametric Methods.* The assumptions of normal distribution, additive combination, and stationarity are violated to some extent in all real situations. As an alternative to the more complex kriging methods introduced earlier, which try to relax these assumptions, a number of non-parametric techniques have been developed. The only assumption that is necessary for most non-parametric methods is that the samples are drawn from some continuous distribution. Henley (1981) proposed non-parametric methods that were a variant of the moving average methods, but using the median rather than the mean as the estimator.

**1.2. Concepts.** The following is a brief review of geostatistical concepts and assumptions. For a more in depth discussion, Isaaks and Srivastava (1989) provide a particularly easy to read non-mathematical introduction, although they leave out some topics. Other books/reviews include Journel and Huijbregts (1978), Webster (1985), Trangmar et al. (1985), Cressie (1993), and Bourgault et al. (1997).

1.2.1. *Random and Regionalized Variables.* The processes governing the variability of properties in space are often not understood well enough to allow deterministic predictions to be made, therefore the process is assumed to be the result of a random function with a certain probability law. A random variable is a variable whose values are randomly generated according to some probability law (Isaaks and Srivastava, 1989). The random variable can be characterized by the moments of its distribution, notably its mean and variance. A regionalized variable is a random variable whose value depends to some extent on its location (Journel and Huijbregts, 1978).

1.2.2. *Stationarity.* A random function is said to be first order stationary, if the expected value  $Z$  at any point  $x$  is the same  $m$  at all locations

$$E[Z(x)] = m, \quad \forall x \tag{8}$$

and the expected difference between the value of the function  $Z()$  at one point  $x$  and another point at some distance  $h$  from the first point is equal to 0 (Trangmar et al., 1985).

$$E[Z(x) - Z(x + h)] = 0, \quad \forall x \quad (9)$$

In other words the bivariate probability law of  $Z(x)$  and  $Z(x + h)$  does not depend on  $x$  but only on  $h$  (Isaaks and Srivastava, 1989).

Second order stationarity is defined as the existence of a covariance  $C()$  for a separation distance  $h$

$$C(h) = E[Z(x) - mZ(x + h) - m], \quad \forall x \quad (10)$$

and that  $C(h)$  approaches the variance of the random variable as  $h$  tends to zero (Henley, 1981; Journel and Huijbregts, 1978).

$$C(0) = Var[Z] = E[Z(x) \times Z(x + h)] - m^2 \quad (11)$$

The existence of second order stationarity implies the existence of first order stationarity. In addition it assumes an *a priori* variance (Journel and Huijbregts, 1978). Many physical phenomena do not have a finite variance, nor does a covariance have to exist (Journel and Huijbregts, 1978). In this case a weaker form of the second order stationarity, the intrinsic hypothesis, can be postulated. The intrinsic hypothesis requires first order stationarity and that all of the variance given a separation vector ( $h$ ) are both finite and does not depend on  $x$

$$2\gamma(h) = Var[Z(x) - Z(x + h)] = E[(Z(x) - Z(x + h))^2], \quad \forall x \quad (12)$$

where  $\gamma(h)$  is called the semi-variogram or variogram for short (David, 1977). Second order stationarity guarantees that the intrinsic hypothesis is satisfied, but the converse is not true (Journel and Huijbregts, 1978).

In some cases the continuing increase in variance can be modeled by a trend that is a function of the geographic position. In the case of a linear trend this could be expressed

$$Z(x) = Z_x + b_0 + b_1x + \epsilon \quad (13)$$

where  $Z_x$  is the “true” value of  $Z$  at  $x$ ,  $b_0$  and  $b_1$  are the coefficients, and  $\epsilon$  is the random error. If this trend can be removed, the dataset can sometimes be made stationary. Legendre (1993) pointed out that an apparent trend can also be produced by the spatial correlation of the variable:

$$Z(x) = Z_x + b_0 + \sum_{i=1}^n f(Z_i) + \epsilon \quad (14)$$

where  $f(Z_i)$  is some function of the sample points that influence the point  $Z(x)$ . If this is the case the semi-variance should be modeled without a sill. Of course differentiating a “true” trend from a “false” trend will require more information than just the data under consideration. For example it may require knowledge of the physics of the process or knowledge of other variables that covary with the variable of interest.

Even the intrinsic hypothesis can be relaxed if one considers that the variogram is only used for limited distances. In general the estimation neighborhood (“close points”) does not cover the whole study area. In this case it is acceptable to consider the data to be locally stationary or quasi-stationary within the local neighborhood. By moving the search area the whole area can be estimated (Journel and Huijbregts, 1978). This assumption holds if the variance changes slowly with location. Finally, variables have to be additive. That is, linear combination of the variable have to remain meaningful (Henley, 1981).

Heteroscedasticity is a statistical term for denoting that the variance is not uniform across the study area, i.e., some areas are more variable than others (Isaaks and Srivastava, 1989). The presence of heteroscedasticity causes problems with the

assumption that the variance is only dependent only on the separation distance and not on the location.

The degree of spatial continuity does not have to be constant in every direction (isotropic). An anisotropic pattern is quite common.

**1.3. Semi-variogram.** While properties which show second-order stationarity can be analyzed using autocorrelation functions (David, 1977), in general it is more convenient to assume the intrinsic hypothesis and use the semi-variogram to quantify spatial dependence (Trangmar et al., 1985). For one, the autocorrelation function needs to exhibit a finite variance to be meaningful, the semi-variogram does not have this restriction.

Since the number of points available to estimate the semi-variance is different at different lags the semi-variance is usually scaled by the number of points that make up the variance, so (12) becomes:

$$\gamma(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [Z(x) - Z(x+h)]^2 \quad (15)$$

where  $n(h)$  is the number of points that are used to estimate  $\gamma(h)$  for the separation vector  $h$ . In most practical applications, a certain amount of tolerance is given for the direction and the lag distance. This allows for the inclusion of a sufficient number of points to allow a stable estimation of  $\gamma(h)$  (Isaaks and Srivastava, 1989). This means that for a given separation vector ( $h$ ) and tolerance ( $\iota$ ), points which are between  $h - \iota$  and  $h + \iota$  are included in the semi-variogram calculation. In addition to the traditional way of calculating the semi-variogram, a number of other formulations have been employed that attempt to make the estimation more robust to non-normally distributed sample values. Two examples of these are the general relative semi-variogram, which is standardized by the squared mean of the data used,

$$\gamma_{gr}(h) = \frac{\gamma(h)}{\sum_{i=1}^{n(h)} \frac{Z(x_i) + Z(x_i+h)}{2}} \quad (16)$$

where  $\gamma_{gr}$  is the general relative semivariogram,  $n(h)$  is the number of points contributing to the lag distance  $h$  and  $Z_i(h)$  are the points that are used to calculate the semi-variance at the lag distance  $h$ . and the pairwise relative semi-variogram. In this variogram each pair is normalized by the average of the data values (Deutsch and Journel, 1992).

$$\gamma_{pr}(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} \left( \frac{Z(x_i) - Z(x_i + h)}{\frac{Z(x_i) + Z(x_i + h)}{2}} \right)^2 \quad (17)$$

where  $\gamma_{pr}(h)$  is the pairwise relative semi-variance,  $Z(x_i)$  is the data value at location  $x$ ,  $h$  is the separation distance and  $n(h)$  is the number of sample points that are considered when calculating the semivariance for the lag distance  $h$ .

1.3.1. *Semi-variogram models.* To guarantee that the kriging weights do not become negative, the semi-variogram model must be positive definite. That is, the function must never produce a negative kriging variance. It is difficult to prove that a function has this property. Furthermore, a function that is positive definite in one dimension, might not behave that way when extended to two or three dimensions. Fortunately, a number of functions that meet this criteria and follow the form of the experimental semi-variograms have been found. Some “safe” models are:

- (1) The spherical model has been found to fit a large number of situations in soil science (Vauclin et al., 1983; Trangmar et al., 1985; Robertson et al., 1993; Cambardella et al., 1994; Mahmondjafari et al., 1997) and ecology (Robertson, 1987)

$$\gamma(h) = \begin{cases} c \left( \frac{3}{2} \left( \frac{h}{a} \right) - \frac{1}{2} \left( \frac{h}{a} \right)^3 \right) & \text{if } 0 \leq h \leq a \\ c & \text{if } h > a \end{cases} \quad (18)$$

where  $c$  is the sill,  $a$  is the range, and  $h$  is the distance under consideration.

- (2) The power model:

$$\gamma(h) = c h^a \quad \text{if } h \geq 0 \quad (19)$$

where  $0 < a < 2$  and  $c > 0$ . In the case of  $a = 1$ , this is also known as the linear model. While it might be tempting to experiment with different exponents in this model, there is no guarantee that other exponents will keep the model positive definite.

- (3) The gaussian/exponential model is appropriate for smoothly varying processes (Isaaks and Srivastava, 1989).

$$\gamma(h) = c \left[ 1 - \exp\left(-3\frac{h}{a}\right)^b \right] \quad b \in \{1, 2\} \quad \text{if } h > 0 \quad (20)$$

where  $c$  is the sill,  $a$  is the range,  $h$  is the distance under consideration, and  $b$  is 1 for the exponential model and 2 for the gaussian model.

- (4) The hyperbolic model has not been widely used, but was used successfully by Vieira et al. (1981) to describe water infiltration.

$$\gamma(h) = \frac{h}{\alpha + \beta h} \quad \text{if } h > 0 \quad (21)$$

where  $\alpha$  and  $\beta$  are fitted parameters. This model was found to be positive definite at least for one and two dimensions (Webster, 1985).

- (5) The log-normal DeWijsian model has found application in geology (Krige, 1978).

$$\gamma(h) = c_0 + \log h + a \quad \text{if } h > 0 \quad (22)$$

$a$  is an empirically fitted constant added to make the sample distribution fit the log-normal distribution and  $c_0$  is the nugget variance. This model can also be expressed as a sum of several spherical models (Journel and Huijbregts, 1978).

The spherical, gaussian/exponential, and hyperbolic models are called sill models, since the variance reaches a finite value at some finite distance. The power model and the DeWijsian log model allows for the variance to increase with increasing distance. Adding a sill to these models can disrupt the positive definite condition. For example,

the linear model with a sill

$$\gamma(h) = \begin{cases} c h & \text{if } h \leq a \\ a & \text{if } h > a \end{cases} \quad (23)$$

is positive definite in one dimension, but not in two (Webster, 1985).

**1.4. Estimation.** Although a semi-variogram is useful by itself for comparing the spatial continuity of several variables, more commonly it is used to estimate the value of a parameter at unsampled locations. This might be used to interpolate the value of a parameter to make a contour map (point or punctual kriging), or to estimate the “best” average value of the parameter over a certain area (block kriging). Estimation of a point or area by kriging is a weighted local average. The process is called local because only sample points in the neighborhood of the estimated point are considered. So only a few points are considered when estimating each point saving considerable computing time. The weights are chosen to give an unbiased estimate and at the same time minimize the estimation variance in a manner similar to least squares curve fitting. Since it minimizes the estimation variance kriging is called *optimal estimation*.

1.4.1. *Punctual and Block Kriging.* Punctual kriging can be viewed as a special kind of block kriging, namely one in which the size, and thus the variance, of the block is zero. The variance of an area, called the dispersion variance is defined as the average semi-variance within a region. Technically, punctual kriging provides estimates for samples that are geometrically identical to the sample areas or volumes (i.e., the support). The estimate of a parameter  $Z$  ( $\hat{Z}$ ) at a location  $x_0$  is the sum.

$$\hat{Z}(x_0) = \lambda_1 Z(x_1) + \lambda_2 Z(x_2) + \lambda_3 Z(x_3) + \cdots + \lambda_n Z(x_n) \quad (24)$$

where  $\lambda$  are the weights associated with sample points  $(x_1, \dots, x_n)$  that are used to estimate the value at position  $x_0$ . If the weights sum to one:

$$\sum_{i=1}^n \lambda_i = 1 \quad (25)$$

then the estimate will be unbiased. The estimation variance is equal to the squared difference between the estimate and the “true” value (see equation 12).

$$\sigma_E^2(x) = E([Z(x) - \hat{Z}(x)]^2) \quad (26)$$

This can be expanded to:

$$\sigma_E^2(x) = 2 \sum_{i=1}^n \lambda_i \bar{\gamma}(x_i, X) - \sum_{i=1}^n \sum_{j=1}^n \lambda_i \lambda_j \gamma(x_i, x_j) - \bar{\gamma}(X, X) \quad (27)$$

where  $\bar{\gamma}(x_i, X)$  is the semi-variance between the estimated point and the average of all points considered,  $\gamma(x_i, x_j)$  is the semi-variance between each set of points, and  $\bar{\gamma}(X, X)$  is the average semi-variance for the area. In the case of point kriging the term  $\bar{\gamma}(X, X)$  is zero and the term  $\bar{\gamma}(x_i, X)$  becomes  $\gamma(x_i, x_0)$ , that is the semi-variance between the estimation point and each sample point.

To minimize the estimation variance, the partial derivatives with respect to each  $\lambda$  need to be found and a Lagrange parameter  $\psi$  added. Then the minimum variance is obtained when

$$\sum_{i=1}^n \lambda_i \gamma(x_i, x_j) + \psi = \bar{\gamma}(x_i, X) \quad \forall j \in \{1, 2, \dots, n\}. \quad (28)$$



This can be expressed in matrix notation as:

$$\begin{bmatrix} \gamma(x_1, x_1) & \gamma(x_2, x_1) & \dots & \gamma(x_n, x_1) & 1 \\ \gamma(x_1, x_2) & \gamma(x_2, x_2) & \dots & \gamma(x_n, x_2) & 1 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \gamma(x_1, x_n) & \gamma(x_2, x_n) & \dots & \gamma(x_n, x_n) & 1 \\ 1 & 1 & \dots & 1 & 0 \end{bmatrix} + \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_n \\ \psi \end{bmatrix} = \begin{bmatrix} \bar{\gamma}(x_1, X) \\ \bar{\gamma}(x_2, X) \\ \vdots \\ \bar{\gamma}(x_n, X) \\ 1 \end{bmatrix} \quad (29)$$

or more simply

$$\mathbf{A} + \begin{bmatrix} \lambda \\ \psi \end{bmatrix} = \mathbf{b} \quad (30)$$

so the weights can be calculated as:

$$\begin{bmatrix} \lambda \\ \psi \end{bmatrix} = \mathbf{A}^{-1} \mathbf{b}. \quad (31)$$

after the weights are calculated the kriging variance can be calculated as:

$$\sigma_E^2 = \mathbf{b}^T \begin{bmatrix} \lambda \\ \psi \end{bmatrix} - \bar{\gamma}(X, X). \quad (32)$$

1.4.2. *Co-Kriging*. If the same regionalized phenomena affect several variables, the variables might show a related spatial distribution. In this case knowledge of one variable can be used to estimate the value of another variable. This is especially useful if one variable is easier to measure than another variable. By using the covariance between the two variables the estimate of the hard to measure variable can be improved using information from the easy to measure variable (Trangmar et al., 1985). The cross semi-variogram between variable  $Z_1$  and  $Z_2$  can be written with

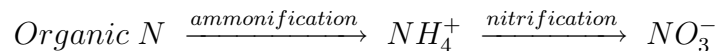
reference to (12) as:

$$\gamma_{1,2}(h) = \frac{1}{2N(h)} \sum_{i=1}^n [Z_1(x_i) - Z_1(x_i + h)][Z_2(x_i) - Z_2(x_i + h)]. \quad (33)$$

**1.5. Simulation.** Another purpose of defining a semivariogram is to use it in modeling the variability of the variable. Kriging, since it is an average, has the effect of smoothing the data. When such smoothing is undesirable knowledge of the semivariogram can be used to generate several equally likely realizations of the phenomena using simulation/relaxation techniques such as simulated annealing. This produces realizations of the random process that can be "rougher" than those produced by kriging.

## 2. Nitrogen Mineralization

**2.1. Overview.** Nitrogen mineralization is the microbial process of converting organic nitrogen to an inorganic form, usually ammonium ( $\text{NH}_4^+$ -N). Ammonium can then be further transformed into nitrate ( $\text{NO}_3^-$ -N). The first step in nitrogen mineralization is called ammonification and the second step nitrification. In most soils the ammonification rate is slower than the nitrification rate.

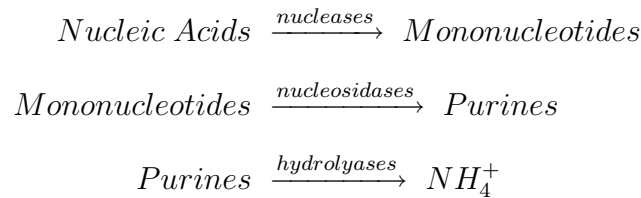


Ammonification is carried out by both aerobic and anaerobic microbes, while only aerobic microbes, mainly *Nitrosomonas* and *Nitrobacter*, are involved in nitrification.

When plants or animals die they contribute organic nitrogen to the soil. The major biological forms of this organic nitrogen are: proteins, cell wall constituents such as amino-sugars, and nucleic acids, such as DNA and RNA. A variety of enzymes (Ladd and Jackson, 1982) and microbes are involved in nitrogen mineralization. Proteins are macro-molecules consisting of long chains of amino acids. Proteins are broken down by proteinases and peptidases to amino acids. Then  $\text{NH}_3$  is released from the amino acids through dehydrogenases and oxidases (Stevenson, 1986).



Other compounds follow a similar enzyme mediated path from the intact macromolecule to  $\text{NH}_4^+$ . DNA and RNA are broken down rapidly by the action of nucleases to mono-nucleotides. Nucleotidases break down the mono-nucleotides to nucleosides and  $\text{PO}_4^{3-}$ . Other enzymes (nucleosidases) break these nucleosides down to purine and pyrimidine bases, which are in turn hydrolyzed to ammonium. Due to the phosphate ester bond, the energy content of nucleic acids are relatively high, and therefore they do not persist in soils (Paul and Clark, 1989).



The opposing processes to mineralization is called immobilization, which is the incorporation of inorganic N into organic forms. Since both immobilization and mineralization are occurring simultaneously, it is important to distinguish between *net* and *gross* mineralization rates. *Gross* mineralization is the total amount of organic N mineralized per unit time. *Net* mineralization is the difference between the *gross* mineralization rate and the immobilization rate. Unless isotope techniques are employed only the *net* mineralization rate can be measured. *Gross* mineralization can be occurring, even if the *net* mineralization rate is zero.

**2.2. Controls.** Nitrogen mineralization is influenced by a number of factors, mostly due to their influence on microbial activity. Some of the more important factors are soil water content (Myers et al., 1982), temperature (Myers, 1975; Marion and Black, 1987) and residue quality.

Soil water affects N mineralization rates. Low soil water will stress the microbes, reducing their activity, and reducing the mineralization rate. Too much soil water will reduce the oxygen content of the soil, again resulting in reduced microbial activity and a lower mineralization rate. Changes in soil water content can have a profound influence on the rate of N mineralization. Wetting a dry soil results in a flush of N mineralization (Birch, 1958). This flush of mineralization is generally short lived (Cabrera, 1993), and has been implicated in the lack of ability to predict N mineralization in the field (Campbell et al., 1988). This flush is thought to be due to mineralization of dead microbial biomass (Kieft et al., 1987). Reduced soil water levels decrease N mineralization. Pilbeam et al. (1993) reported a 74% reduction in ammonification when decreasing the matric potential from -0.063 to -0.42 MPa. Cassman and Munns (1980) reported maximum net mineralization when the matric potential was between -0.033 and -0.01 MPa. This translated to a water filled pore space of 80–90%.

Most microbes in temperate soils show maximum activity between 25°C and 37°C. Above that temperature the rate of mineralization is generally reduced. Below the maximum temperature, the rate of mineralization tends to decrease exponentially, until it stops close to 0°C. Temperature effects on mineralization rate is commonly modeled as a  $Q_{10}$  type relationship. That is, the rate of the reaction increases with increasing temperature. However  $Q_{10}$  values are not constant for all soils or even for all temperatures (Campbell et al., 1984). Honeycutt et al. (1988) proposed using thermal time to predict nitrogen mineralization and subsequently found good agreement with field data when water was non-limiting (Honeycutt and Potaro, 1990; Honeycutt et al., 1991).

Residue quality also controls net nitrogen mineralization rate. Residue quality can be expressed as C/N ratios, or ratios involving more specialized components of the total C and N fractions. This factor is basically a food limitation on the microbes.

TABLE 1. Variogram models of N mineralization.

Site	Model	Nugget (g m <sup>2</sup> ) <sup>2</sup>	Range – m –	sill (g m <sup>2</sup> ) <sup>2</sup>	Reference
Natural	spherical	0.056	10.7		Robertson et al. (1993)
Plowed	spherical	0.043	103.8		Robertson et al. (1993)
No-till	spherical	0.0065	65	0.038	Cambardella et al. (1994)
Plowed	spherical	68.6	38	119.5	Cambardella et al. (1994)
Plowed	spherical	56.8	63.3	94.3	Mahmondjafari et al. (1997)
Plowed	spherical	9.97	355	17.13	(Lengnick, 1997)
Plowed	spherical	0.03	7.2	0.04	Gross et al. (1995)
Old Field	spherical	0.2	5.4	0.45	Gross et al. (1995)
Mature Forest	spherical	0.22	9.8	0.31	Gross et al. (1995)
Plowed	spherical	55	310	62.8	Shahandeh et al. (2005)
Plowed	exponential	11	210	69	Shahandeh et al. (2005)

Lengnick (1997) used N uptake to study N availability and found that it was not necessarily related to soil N and C but was more influenced by soil moisture.

**2.3. Spatial Variability of Nitrogen Mineralization.** Some effort has been expended in the last couple of years to characterize the field-scale variability of biologically important soil parameters both in agricultural (Trangmar et al., 1985; Warwick et al., 1986) and non-agricultural (Robertson et al., 1988; Jackson and Caldwell, 1993b) sites. However, few studies have addressed the spatial and temporal variability of nitrogen mineralization in field soils. Robertson et al. (1988) measured N mineralization variability in an abandoned field, using a 10-day aerobic lab incubation. Mineralization was measured as the inorganic N produced during the incubation. They showed that samples beyond 30 m were uncorrelated. Nitrogen mineralization values were log-normally distributed.

Later Robertson et al. (1993) sampled 256 locations in a tilled field and 65 locations in an adjacent natural site. They used a stratified unaligned sampling strategy to select the sample locations (Webster and Oliver, 1990). While the mean and standard deviation of the N mineralization rate, and the nugget variance did not differ, the distance over which correlation was observed increased substantially from 10.7 m

in the natural site to 103.8 m in the cultivated site. Nitrogen mineralization rate in the natural site was characterized by small areas with high activity and large areas with low activity, while the cultivated site had more uniform N mineralization. This was assumed to be due to the homogenization effect of plowing and monoculture. More recently Gross et al. (1995) examined the N mineralization pattern in three successional communities, and found much shorter ranges of correlation ( $< 10$  m) than reported by Robertson et al. (1993). However, the distances between the samples were much smaller in the Gross et al. (1995) study than the study by Robertson et al. (1993). They showed that a substantial part of the variation in N mineralization occurs at scales of less than 1 meter. Starka et al. (2004) examined the spatial structure of microbial C and N as well as arginine ammonification, and observed no spatial structure at distances greater than 30 cm.

Goovaerts and Chiang (1993) measured N mineralization in a 0.16 ha field in the fall of one year and the spring of the following year. They took 73 samples, and determined potential N mineralization by using the anaerobic incubation technique of Keeney (1982). They observed that the spatial structure of the N mineralization pattern was stable over the winter months; however, they did not detect any strong spatial structure. Most of the variability was found at scales of less than 1 m. Jackson and Caldwell (1993a) reported that N mineralization around individual sagebush and bluebunch wheatgrass plants did not show any spatial correlation even though the smallest sample distance was only 12.5 cm. Stoyan et al. (2000) showed that a substantial part of the spatial structure in soil under poplar occurred at less than 25 cm.

Cambardella et al. (1994) reported much higher variability in N mineralization rates in a 36 ha field containing two potholes than in a uniform 96 ha field (Table 1). They sampled the pothole field on a 6.25 ha grid, while the other field was sampled on a 10 ha grid. The tighter sampling grid might have increased the apparent variance of the pothole field. Nitrogen mineralization estimates were based on a short term

anaerobic incubation (Keeney and Bremner, 1967). Nitrogen mineralization was non-normally distributed. A log-transformation failed to normalize the data. Nitrogen mineralization had a much higher variability in the pot-hole field ( $CV = 585\%$ ) than on the other field ( $CV = 24\%$ ).

Mahmondjafari et al. (1997) used long-term aerobic incubations to assess N mineralization in 1.7 ha field (a fine, mixed, Mesic Typic Argiudoll). They collected samples from 100 locations selected according to the procedure published by Warrick and Myers (1987), and incubated them with periodic leaching for 238 days. They demonstrated that both the amount of mineralizable N ( $N_0$ ) as well as the rate constant ( $k$ ) are spatially variable. Both  $N_0$  and  $k$  were normally distributed with low variability ( $CV = 14\text{--}15\%$ ). They found weak spatial correlation of  $N_0$ , but the rate constant was spatially independent.

Selles et al. (1997) characterized a field using a long-term aerobic incubation and a hot KCl extractable  $\text{NH}_4^+$ . They found only weak correlation between the long-term aerobic incubations and the hot KCl extractable  $\text{NH}_4^+$ . The spatial structure of the hot KCl extractable N was more closely related to total N, than to the N mineralized during a long term aerobic incubation.

Shahandeh et al. (2005) reported that short-term N mineralization estimates in a Texas corn field had a range of correlation of 310 m in 2002 and 210 m in 2003. However they fitted a spherical model in 2002 and an exponential model 2003. They reported that N mineralization correlated well to clay content and that the N mineralization pattern appeared to be stable for the two study years.

In Chapter 2 the spatial and temporal variability of N mineralization is explored using field estimates of N mineralization rates. In Chapter 3 the field N mineralization rates are correlated with lab estimates of mineralizable N, and finally in Chapter 4 a method is proposed to estimate the initial  $\delta^{13}\text{C}$  content of a soil, given a location that has had a continuous  $C_3$ , a continuous  $C_4$  and a  $C_3/C_4$  rotation treatment.

## CHAPTER 2

# Spatial Variability of Nitrogen Mineralization

### 1. Abstract

The availability of spatially variable N fertilization has created a need for spatially variable N fertilizer recommendations. Since N mineralization is one factor that can influence N fertilizer recommendation, it is important to quantify its spatial pattern. However, the spatial structure and temporal stability of N mineralization are not well known. Buried bag and resin absorption techniques were used to estimate the spatial variability of N mineralization in two central Kansas corn fields during the 1994 and 1995 field seasons. The average net N mineralization rate was  $44 \text{ kg N ha}^{-1} \text{ year}^{-1}$  and N mineralization rates were highly variable in space and in time. The majority of the N mineralization occurred in relatively small areas of the field. N mineralization was highest in May and then declined to a minimum in September. Due to different rainfall patterns, the spatial patterns of N mineralization differed between seasons, with some areas remaining high or low in N mineralization while other areas showed high N mineralization in one year and low N mineralization in the other year.

### 2. Introduction

Nitrogen mineralization as well as other biological processes such as denitrification (Parkin, 1987) are highly variable in space (Mahmoudjafari et al., 1990, 1991; Robertson et al., 1988, 1993) as well as in time (Zak and Pregitzer, 1990). Short range variability is common in soil properties that depend on biological processes, with much of that variability present in areas only a few square meters (Beckett and



Webster, 1971). This variability complicates N fertilizer recommendations. Predicting the amount of additional N fertilizer required by the crop, requires an estimate of N present in the soil and an estimate of the N that is likely to be mineralized during the season. Furthermore, the ability to spatially vary the application of N fertilizers has raised questions about how to incorporate spatial nitrogen mineralization variability into fertilizer recommendation models (Carr et al., 1992; van Noordwijk and Wadman, 1992). While information is available on estimating the N mineralization capacity of the soil (Allison, 1956; Bremner, 1965; Cornforth, 1968; Fox and Piekielek, 1978, 1984; Magdoff et al., 1984; Cabrera and Kissel, 1988; Aiman, 1992), very little information is available on the distribution and variability of N mineralization.

**2.1. Methods to Study Nitrogen Mineralization.** A number of methods have been used for estimating *in situ* net N mineralization rates. These methods include enclosing soil in polyethylene bags as pioneered by Eno (1960), using closed top soil cores to prevent N uptake by plant roots and leaching (Raison et al., 1987), sheltering an area of bare soil from direct rainfall (Rice et al., 1987), sampling a large portion of the soil profile (Cassman and Munns, 1980; Griffin and Lane, 1983) and using ion-exchange resins to absorb the nitrate and ammonium leaching out of a soil core (Schnabel, 1983; Binkley, 1984).

Buried polyethylene bag methods have been used to assess N mineralization in agricultural (Smith et al., 1977) and forest soils (Boone, 1992; Nadelhoffer et al., 1985). Enclosing the soil in a polyethylene bag prevents the exchange of water and nutrients with the environment, while it allows the exchange of gases and heat.

Other problems with the buried bag method center on plant root intrusion, and excavation by animals. If recognized it causes a loss of a data-point, if undetected it would cause an underestimation of the amount of N mineralized.

In the late 1950's, ion exchange resins were first used to assess the availability of potassium (Salomon and Smith, 1957) and phosphorus (Amer et al., 1955; Hislop and

Cooke, 1968). The techniques required fine grinding of the soil to separate the soil from the resin after the incubation. Sibbesen (1977) proposed enclosing the resin in a mesh bag to facilitate separation of the resin from the soil. Later, Yang et al. (1991) developed a resin capsule containing an anion and a cation resin and they derived a theoretical model of diffusion of ions from a saturated soil paste to the resin sphere.

Ion exchange bags were adapted for inorganic N determinations in the mid 1980's (Schnabel, 1983; Binkley, 1984; Carlyle and Malcolm, 1986). In field situations ion exchange bags absorb N from the soil solution passing thorough the bag rather than by creating a diffusion gradient (Binkley, 1984; Carlyle and Malcolm, 1986; Li et al., 1993). In order to better define the soil volume from which the N was mineralized, DiStefano and Gholz (1986) modified the closed top tube method of Adams and Attiwill (1986) by placing resin cores at the bottom of open topped tubes. Rouppet et al. (1994) showed that in a shortgrass ecosystem approximately 32 samples were necessary to reliably detect a statistically significant difference of  $1 \mu\text{g N g}^{-1}$  of soil using an alpha level of 5%.

The resin has often been treated with a biocide to inhibit bacterial growth during the incubation period, however N transformations in the resin seems to be minimal if the incubation time does not exceed 12 weeks (Schnabel, 1983; Binkley, 1984). Comparisons between ion-exchange and buried bag methods have produced similar results (Binkley et al., 1986; Zou et al., 1992).

Problems with the resin bag method include the loss of absorptive capacity when dried and the possibility of altering flow lines due to textural discontinuities between the soil and the resin. Since the resin particles are sand sized and the soil at the study sites is sandy, textural discontinuities should not be a problem. Drying of the resin might be counteracted by placing the resin deeper in the soil. Since the field was irrigated drying might be less of a concern. Li et al. (1993) did not report any deterioration of the resin with a 597.5 mm water deficit on a coarse mixed loamy Calciboroll.

A study on spatial application of fertilizers provided the opportunity to study the N mineralization of two central Kansas corn fields in conjunction with other soil and plant measurements.

The objective of this study was to describe and characterize the spatial and temporal variability of net N mineralization rates in two central Kansas fields. Secondary objectives included investigating how the net N mineralization rate variability compares to the variability of other soil and plant parameters, and the relationship between the N mineralization variability and the corn yield variability, and to test different methods of estimating soil N mineralization.

### 3. Methods

**3.1. Field Sites.** Two irrigated corn fields in central Kansas were used in this study. One of the fields was located in Barton Co. about 8 km south of Great Bend, KS (NE 1/4 of Section 27, T.20S, R13W) (Site 1). The other field was located in Stafford Co. about 40 km south of Great Bend, KS (W 1/2 of Section 16 T.23S, R12W.) (Site 2). Site 1 was 50 ha in size, while Site 2 contained 60 ha. The fields were sampled for N mineralization in 1994 and 1995. A square sampling grid (65 meter square) was established on each field. The center of the pivot was the center of the grid. The soil samples were taken at a grid point placed in the center of each square. In addition to the grid points an additional 40 points were located near the center of the field according to the procedure published by Warrick and Myers (1987). Briefly, it is an iterative procedure for adding sample points in such a way as to maximize the information content of the samples for the semivariogram estimation. The additional 40 Warrick and Myer (WM) points were only used in 1995. The terrain was flat to gently rolling, the maximum elevation difference was close to 10 m. Figures 1 and 2 show the elevations as measured from the center of the pivot. Site 1 shows a higher elevation on the west side and low elevations on the south-east and south-west sides. Site 2 shows an area of higher elevation in the center and the south and south-west

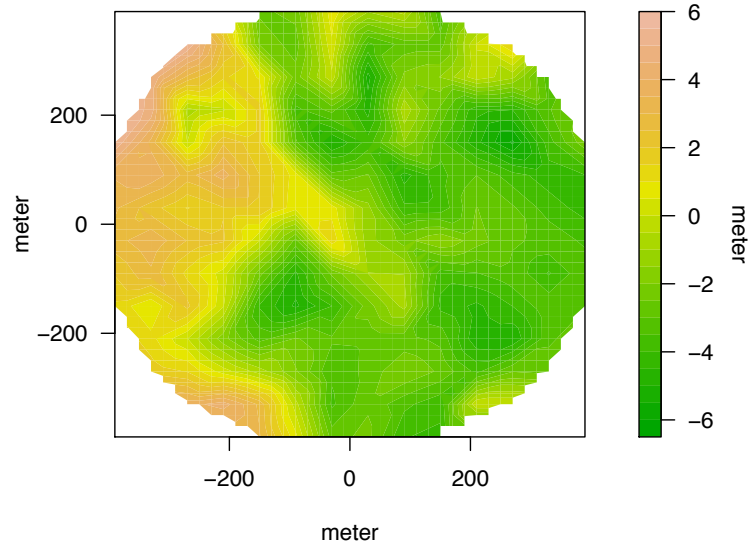


FIGURE 1. Elevation in meters of Site 1 relative to the center of the pivot.

sides of the field. Low areas were mainly in the eastern part of the field. Site 2 had been leveled to reduce the relief, so that the eastern central part of the field was much sandier than the rest of the field.

The soils were mapped as Pratt loamy fine sands on Site 1 and Pratt-Trivoli loamy fine sands on the Site 2 site (Typic Ustipsammets and Psammentic Haplustalfs). Soils were more than 90% sand with distinct clay lenses located from 25 cm to more than 1 m below the surface. The depth to clay was mapped during the profile nitrate sampling and with an “electro-inductive” remote sensing system. Some of the soil parameters are summarized in Table 1.

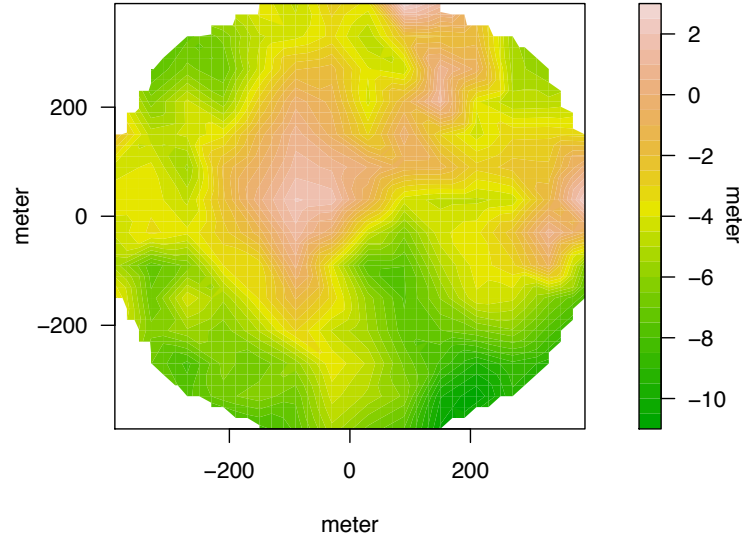


FIGURE 2. Elevation of Site 2 relative to the center of the pivot.

TABLE 1. Soil parameters in the surface (0–30 cm) soils at the grid points

Parameter	Site 1			Site 2			
	Min.	Avg.	Max.	Min.	Avg.	Max.	
pH	5.03	6.51	7.20	4.93	6.07	7.35	
O.M.	g C kg <sup>-1</sup>	2.7	7.9	22.6	1.8	7.3	21.6
P	ppm	9.0	44.6	148	11.0	30.5	92.0
Sand	%	58.5	85.3	96.2	74.5	92.7	98.6
Silt	%	0.17	7.39	25.7	0	2.84	15.7
Clay	%	0.47	7.24	16.9	0	4.46	12.3
Elevation <sup>†</sup>	m	-6.11	-1.24	5.55	-10.9	-4.08	2.96

<sup>†</sup> Elevation is measured from the center of the pivot.

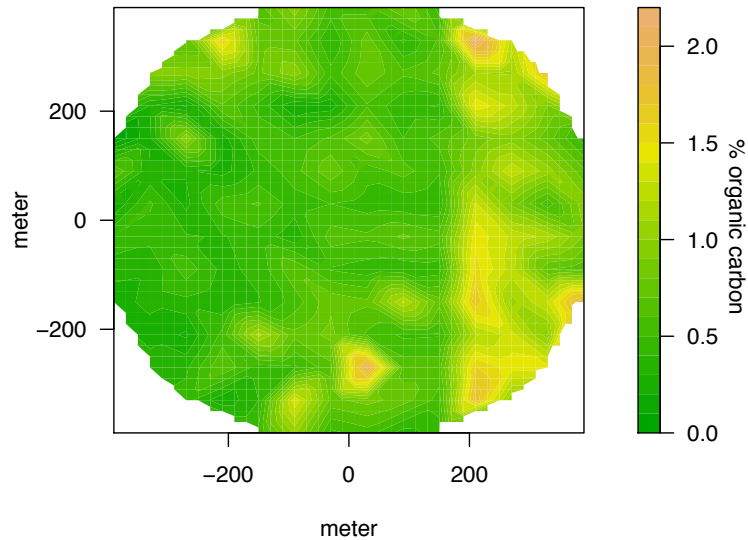


FIGURE 3. Percent Organic Carbon in the top 30 cm at Site 2.

Both fields were low in organic matter, although the soil organic matter ranged from 2.7 to 22.6 g C kg<sup>-1</sup>, the average was only 7 g C kg<sup>-1</sup>. In Site 1 the high organic C samples came primarily from the west end of the field, while on the Site 2 field they came from the south side.

Site 1 was higher in clay (7.4%) than Site 2 (4.5%) (Redulla, 1998). At Site 1 the clayey areas were around the outside of the field (Figure 5), while in Site 2 they were both in the southern and northern end of the field (Figure 6). The clayey areas were depressions and tended to collect water during rainy periods. The north-eastern quadrant of Site 2 was under water during May and June 1995. In addition to the clay in the surface soil, the soil was characterized by clay lenses in the subsoil. These clay lenses were located within the first meter of soil in some locations, and may be present in the rest of the field at deeper depths.

Both fields were fertilized in 60 meter squares. Fertilizer recommendations were computed for each grid cell. The field was divided into strips, half of the strips

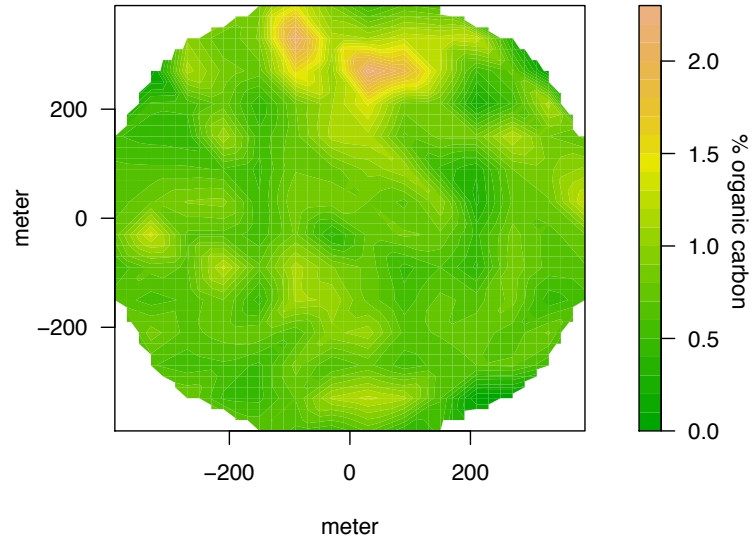


FIGURE 4. Percent Organic Carbon in the top 30 cm at Site 1

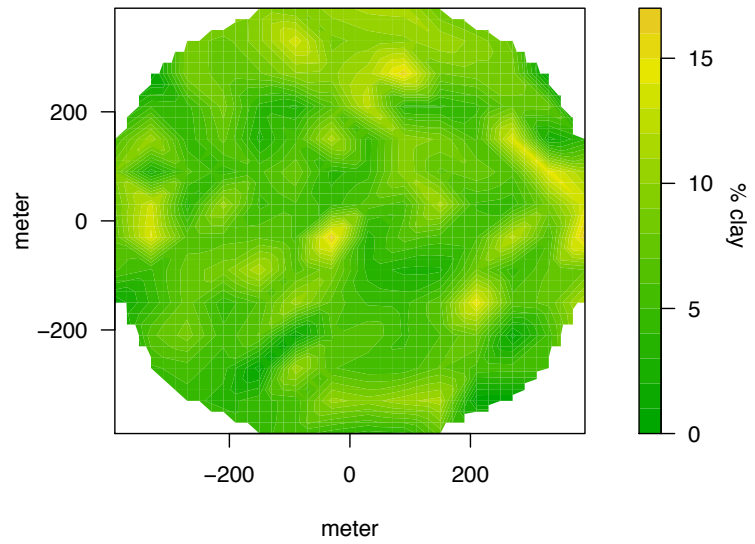


FIGURE 5. Percent clay in the top 30 cm of Site 1.

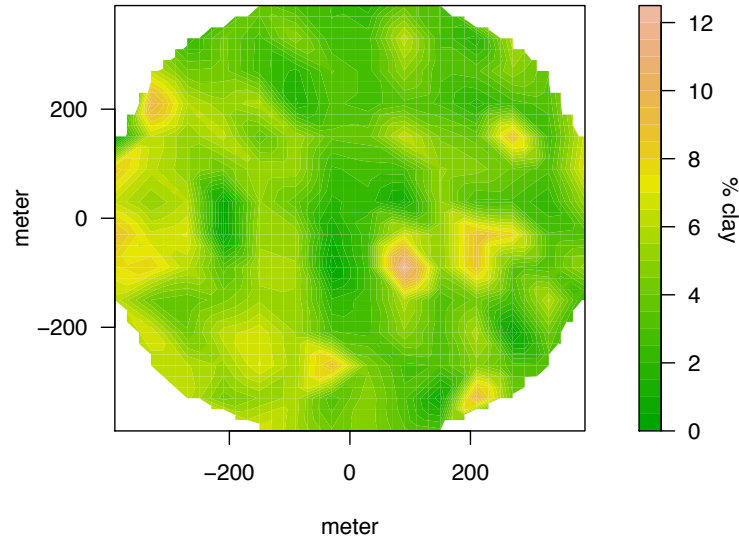


FIGURE 6. Percent clay in the top 30 cm of Site 2.

TABLE 2. Fertilizer application schedule

Application	Form	Amount kg N/ha
Preplant	Ammonium Phosphate	10
Preplant	Urea Ammonium Nitrate	10
Preplant	Uniform Urea	110
Preplant	Variable Urea	0 – 170
Starter	Urea Ammonium Nitrate	10
Sidedress	Anhydrous Ammonia	90
Fertigation	Urea Ammonium Nitrate	20

cells were fertilized at a uniform rate, the other half was fertilized according to the variable rate recommendations generated from the previous fall nitrate concentration in the soil. Both fields received that same fertilizer except for the Uniform or Variable Urea treatment. Fertilizer amounts were essentially the same in both years. Table 2 summarizes the nitrogen fertilizer additions. Details on the fertilizer applications are summarized in Redulla (1998)



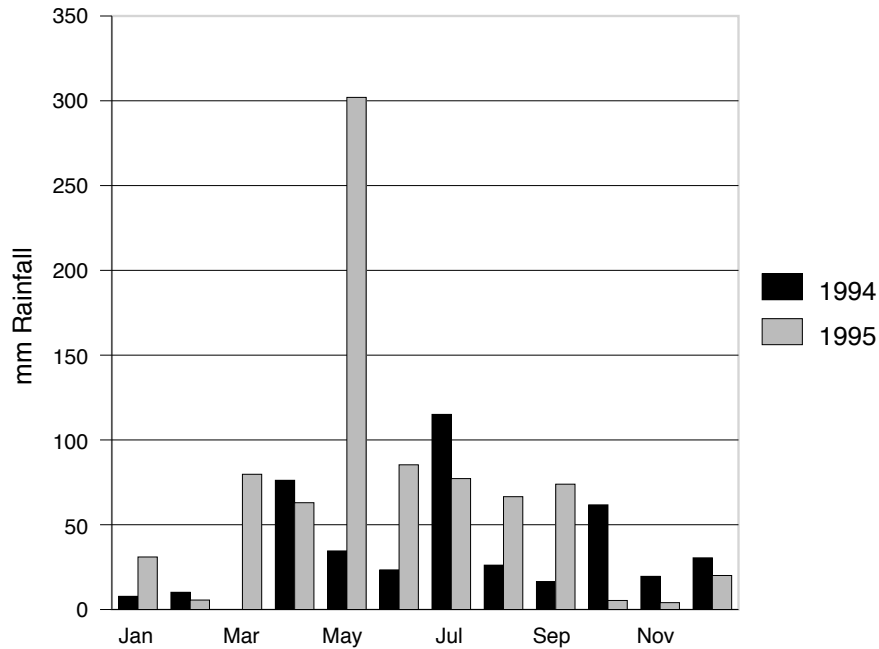


FIGURE 7. Monthly rainfall totals for 1994–1995 at Site 2.

**3.2. Weather.** The monthly rainfall, at Site 2, during 1994–1995 is shown in Figure 7. Rainfall in 1994 was lower and more evenly distributed than in 1995. In 1994, April, July, and October were the wettest months. While 1995 had a wet summer and a very wet spring that caused flooding in parts of the fields, resulting in poor stands in low lying areas. Since the fields were irrigated, lack of water was easy to deal with, while excess water can not be as easily managed. Total rainfall was 421 mm in 1994 and 813 mm in 1995. In 1995 wet soils, caused by the large amount of rain in May, required a re-planting of Site 1.

The average annual temperature is 14.8°C. A trace of the 1994 temperature at Hudson KS, which is located close to Site 2, is shown in Figure 8. Temperatures in 1995 and at Site 1 were similar.

**3.3. Plant Analysis.** Two one meter sections of row were hand harvested at each of the grid points. No harvesting was done on the 40 Warrick and Meyer points.

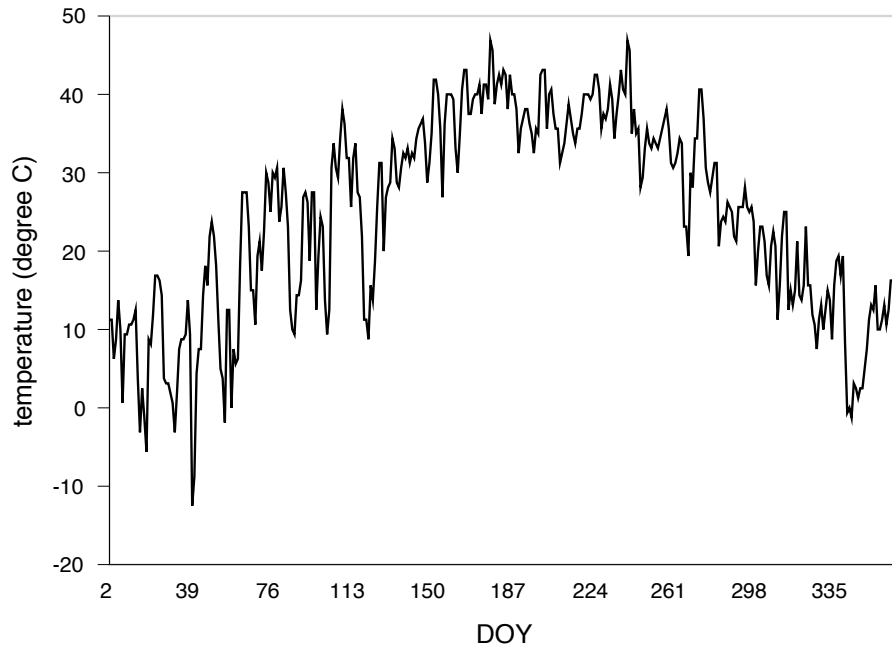


FIGURE 8. Temperature in 1994 at Site 2

Grain and stover was separated, and the grain and stover was dried at 60°C. Stover was ground in a Wiley mill followed by further grinding in a centrifugal mill. The grain was shelled and ground in a centrifugal mill. Cobs were ground in a Wiley mill followed by further grinding in a centrifugal mill. Nitrogen and carbon content were determined by direct combustion on a C/N-analyzer (Carlo Erba, Strumentazione, Milan, Italy).

The rest of the fields were harvested with a 6 row (International Harvester) Combine equipped with a yield monitor and a global positioning system (Trimble GPS) unit. Readings of grain yield were taken every second. The readings were then averaged for 7.3 m<sup>2</sup>. Other measurements included soil texture, soil profile nitrate in the spring and fall described in detail in (Redulla, 1998), and a fertilizer rate study.

**3.4. Nitrogen balance.** An N balance was calculated by subtracting the N removed in the grain and the N remaining in the soil profile in the fall from the N

in the soil profile in the spring and the N added as fertilizer. Since the stover was returned to the field, the N removed in the stover was also returned to the field, some of the N will leach into the soil over the winter and may be represented in the following spring soil sample. Some of the N from the stover will be released during the following growing season. Because of the uncertainty in the amount of stover N that would be available during the following year this N was not added to the spring N stock the following year. An alternate approach would be to estimate the amount of N that remains in the stover in the spring of the following year and add it to the spring N stock. The N balance will give a lower estimate of N mineralized since leaching, denitrification and some of the stover N were not included,

$$N_{springsoil} + N_{fertilizer} - N_{grain} - N_{stover} - N_{fallsoil} = N_{balance} \quad (34)$$

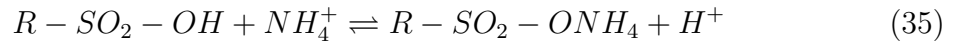
**3.5. Buried Bag Experiment.** Three soil cores were taken with an Oakfield sampler (2.54 cm diameter  $\times$  30 cm long). The soil was placed in 12.7 cm<sup>2</sup> polyethylene bags. The bags were closed by tying a “twist-tie” around the neck and buried 10 cm below the surface. The top of the bag was allowed to protrude above the soil surface to facilitate retrieval of the bags. A second composite sample (three cores) was taken for analysis of the initial nitrate and ammonium. After about three weeks the bags were retrieved from the field, and taken back to the laboratory for nitrate and ammonium analysis as discussed later. A new bag was prepared in the manner described previously.

**3.6. Resin Core Experiment.** At each grid point in the field, one 30 cm PVC core (5 cm diameter) was pushed into the soil. The core was then removed from the soil, and the bottom 5 cm of soil removed and the two resin bags (anion and cation) inserted. The anion bag was placed above the cation bag. Soil was used below the bags to hold them in place during re-insertion. The core was then re-inserted into the same hole, marked with a flag and left in the field. After two months the cores were

removed and the resin bags were recovered from the core or the hole. New resin bags were then placed into the cores and the cores were reinserted into the soil. At the end of the season, the cores and resin bags were removed and returned to the laboratory for analysis.

Ion exchange resin bags were produced by enclosing a teaspoon of resin ( $\approx 10$  g) in a nylon tube (panty hose). Both ends were secured by folding a large staple around the opening. Dowex Amberlite IRN-77 was used as the cation exchange resin, while Amberlite IRN-78 was used as the anion exchange resin. The active sites on the Amberlite IRN-77 resin consist of sulfonyl groups saturated with  $H^+$ . The cation exchange capacity for the resin was reported to be 5 meq/gram. If all of the exchange sites were occupied by  $NH_4^+$  one g of the resin should sorb approximately 90 mg of ammonium.

The reactions for the sorption of  $NH_4^+$



and for desorption of  $NH_4^+$  with KCl.



The reactions with the anion exchange resins proceed analogously.

**3.7. Laboratory Analysis.** Approximately 5 g of field moist soil was weighed into a 250 mL polyethylene centrifuge bottle and 50 mL of 1 M KCl solution added. The bottle was shaken at 250 RPM for 1 h and then centrifuged at 16,000 g for 10 min. The supernatant was collected through a fiberglass cloth. The supernatant was analyzed for  $NO_3^-$  and  $NH_4^+$  on a Lachat Flow analyzer (Hach Company, Loveland, CO). Nitrate was determined using the modified Griess-Ilosvay procedure after reduction to  $NO_2^-$  in a Zn reduction column (Keeney and Nelson, 1976). Ammonium

was determined using the indophenol blue method described by Keeney and Nelson (1976).

To determine the soil moisture 10 g of field moist soil was weighed into a tin, and dried for 24 hours at 105°C. The soil moisture was used to calculate the N content on a dry weight basis.

The ion-exchange resins were extracted by placing both anion and cation bags into a 250 mL polyethylene centrifuge bottle and 100 mL of 2M KCl added. The bottle was shaken at 250 RPM for 1 h , and the supernatant collected and analyzed for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  as described previously. Initial experiments indicated that 1 M KCl was insufficient to remove the  $\text{NH}_4^+$  from the resin, but 2 M KCl was adequate.

**3.8. Geostatistical Analysis.** Univariate statistics and distributions were calculated using SAS (SAS Institute, 1982) and R (R Development Core Team, 2007). Geostatistical analysis was performed using the software package gslib (Deutsch and Journel, 1992). Semivariogram parameters were estimated from the experimental semivariograms using  $r^2$  as the criterion. Block kriging was used to obtain maps of the parameters.

## 4. Results

### 4.1. Nitrogen Balance.

4.1.1. *Univariate Statistics.* Grain and silage yields are summarized in Table 3. Grain yields at Site 1 decreased from 12.7 Mg/ha in 1994 to 7.9 Mg/ha in 1995, mainly due to the wet spring in 1995 that forced a late planting. The wet spring also contributed to the increased variability in the silage yields (Table 3 and Figure 10). At Site 2 the corn was planted early and did not suffer as much from the wet soil conditions. Yields at Site 2 were lower than at Site 1 in both years. Nitrogen uptake in the silage increased at Site 1 due to the larger amount of silage at harvest. This might also be due to the additional fertilization at replanting that the field received in 1995. At Site 2 no additional fertilizer was applied and the N uptake at harvest

TABLE 3. Corn grain and silage yields and N uptake at Site 1 and Site 2.

Year	Grain	SD	Silage	SD	Grain N	SD	Silage N	SD
	Mg/ha				kg/ha			
	<i>Site 1</i>							
1994	12.7	1.6	14.8	1.7	153	19	179	35
1995	7.9	1.7	23.8	4.0	113	27	273	75
	<i>Site 2</i>							
1994	9.9	2.0	8.2	1.3	118	24	92	26
1995	7.8	1.8	6.1	1.3	98	28	75	22

declined in 1995 along with the yields. The grain and silage yields were distributed somewhat normally (Figure 9, 10); therefore, no transformation was performed on the data.

By combining the N uptake values with spring and fall profile nitrate a minimum estimate of the N mineralization can be made. This estimate is a conservative estimate since denitrification and leaching are not included.

At Site 2 in 1994 an average of 117 kg N ha<sup>-1</sup> was removed in the grain and 92 kg N ha<sup>-1</sup> was taken up by the stover. The soil profile contained 31 kg of N ha<sup>-1</sup> in the spring and 55 kg N ha<sup>-1</sup> in the fall, 234 kg N ha<sup>-1</sup> were applied as fertilizer. This produced an average gain from the field of 1 kg N ha<sup>-1</sup>. By the spring of 1995 the average profile N content was 27 kg N ha<sup>-1</sup> with 344 kg N ha<sup>-1</sup> of fertilizer applied. At the end of the season 91 kg N ha<sup>-1</sup> was in the corn grain while 32 kg N ha<sup>-1</sup> was in the soil profile and 75 kg N ha<sup>-1</sup> was in the stover. This produced an average loss of 173 kg N ha<sup>-1</sup> during the growing season.

At the Site 1 in 1994 an average of 152 kg N ha<sup>-1</sup> was removed in the grain and 177 kg N ha<sup>-1</sup> was taken up by the stover. The soil profile contained 30 kg N ha<sup>-1</sup> in the spring and 39 kg N ha<sup>-1</sup> in the fall. Adding 248 kg N ha<sup>-1</sup> produced an average gain of 90 kg N ha<sup>-1</sup>. By the spring of 1995 only 31 kg N ha<sup>-1</sup> remained in the soil profile. In 1995 an average of 113 kg N ha<sup>-1</sup> was removed by the grain, 273 kg N ha<sup>-1</sup> was taken up by the stover and 56 kg N ha<sup>-1</sup> remained in the soil profile in the fall.

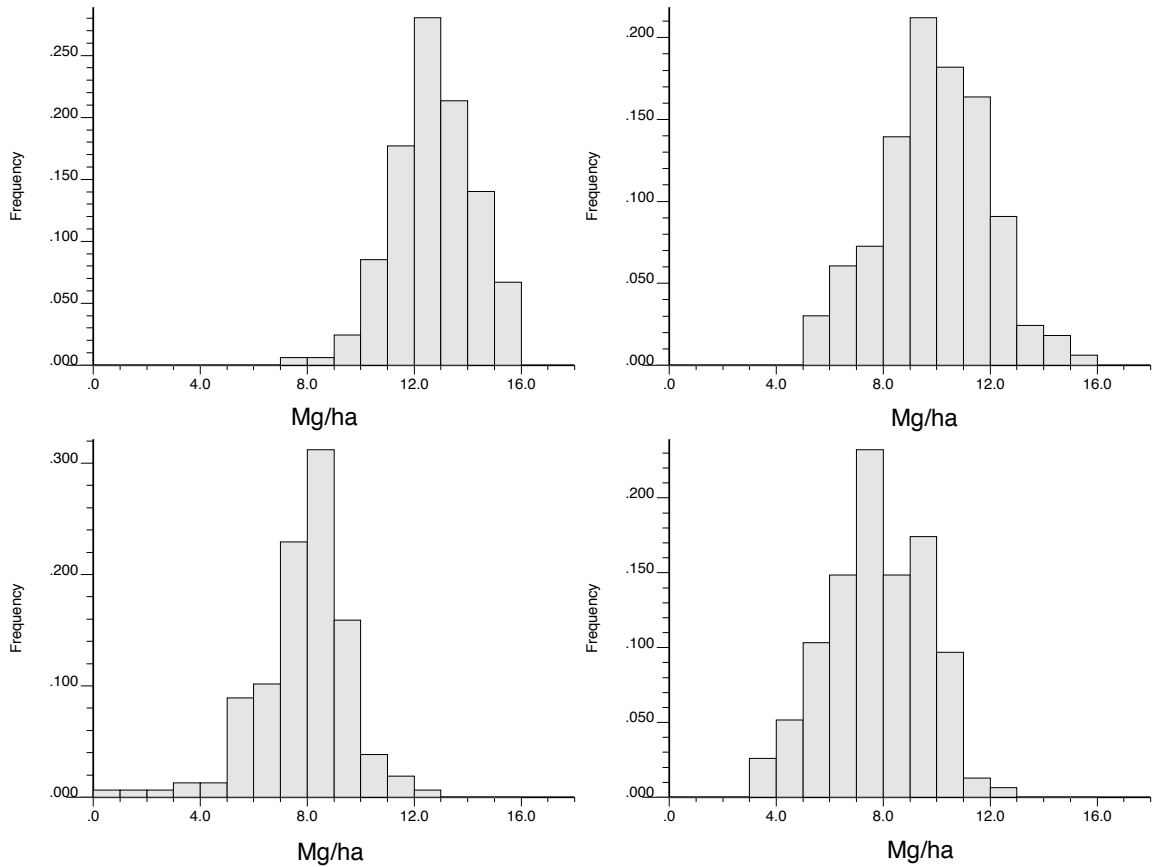


FIGURE 9. Distribution of the corn grain yields (Mg/ha) at Site 1 (left) and Site 2 (right) in 1994 (top) and 1995 (bottom)

With an average of  $345 \text{ kg N ha}^{-1}$  applied as fertilizer an average of at least  $66 \text{ kg N ha}^{-1}$  was mineralized during the year. The net N balance decreased with increasing fertilization (Figure 11), possibly due to increased leaching or denitification as a lower percentage of the total N was captured by the plants. In 1994 the N balance with respect to fertilizer input was similar on Site 1 and Site 2. In 1995 more N was lost on Site 2 than on Site 1 .

4.1.2. *Geostatistical Analysis.* The N losses were not distributed uniformly. At the Site 1 in 1994 there was a small area near the center of the field that had more

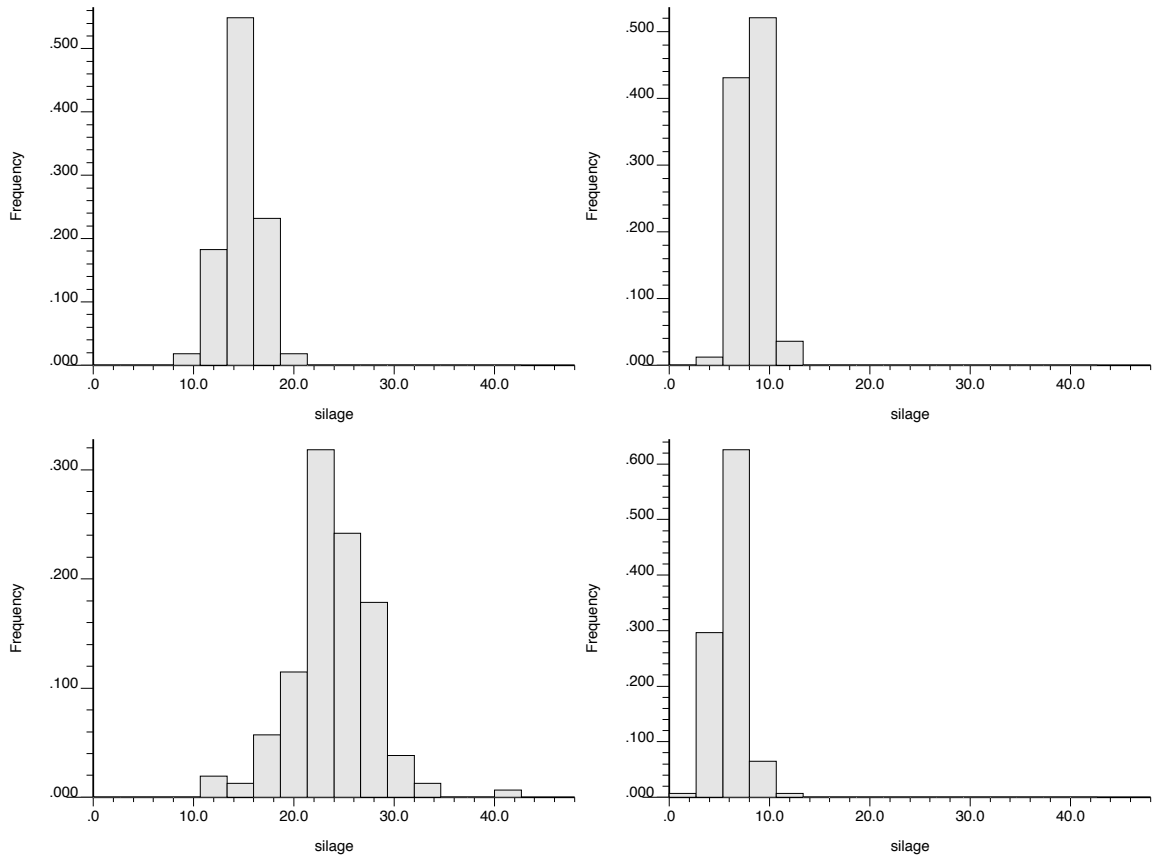


FIGURE 10. Distribution of the corn silage yields (Mg/ha) at Site 1 (left) and Site 2 (right) Site 1 in 1994 (top) and 1995 (bottom)

nitrogen in the surface soil in the fall than in the spring (Figure 12). In 1995 there was no area that had more nitrogen in the fall than what was measured in the spring and applied during the season. Lower N loss occurred on the more clayey soils at the western edge of the field (Figure 13). The spring rains in 1995 may have leached most of the initially applied nitrogen.

At Site 2 the N balance was more uniform in 1994 than 1995. In both years a higher N balance was detected near the western edge of the field. In 1995 more N was observed in the western central sector (Figure 15).



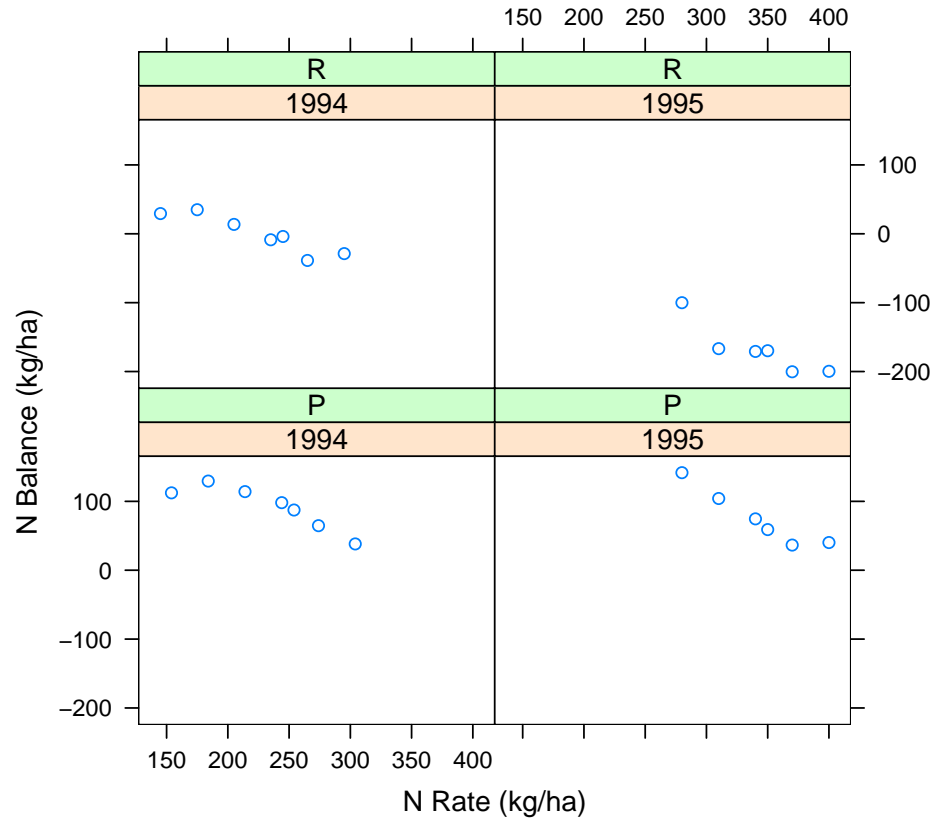


FIGURE 11. N balance as a function of fertilization at Site 1 and Site 2.

4.1.3. *Summary.* The N balance calculation revealed that over most of the field there was some N loss due to either leaching or denitrification. A minimum of 10 kg N ha<sup>-1</sup> was produced during 1994.

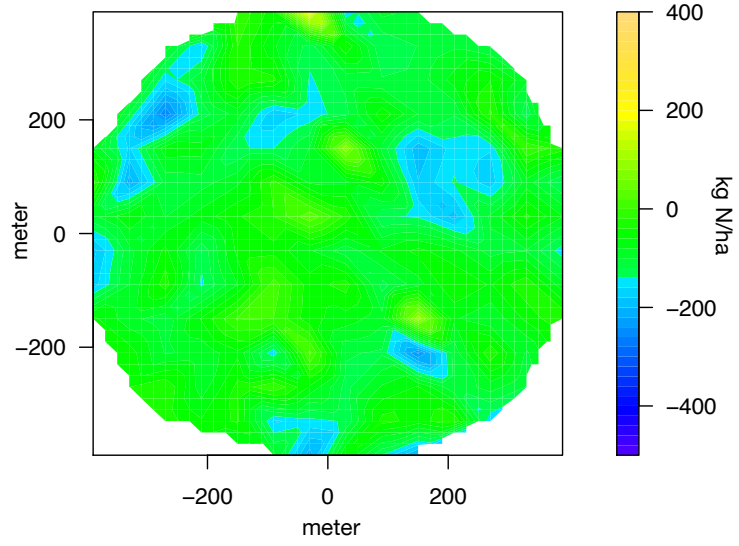


FIGURE 12. N Balance (kg N/ha) on Site 1 during 1994

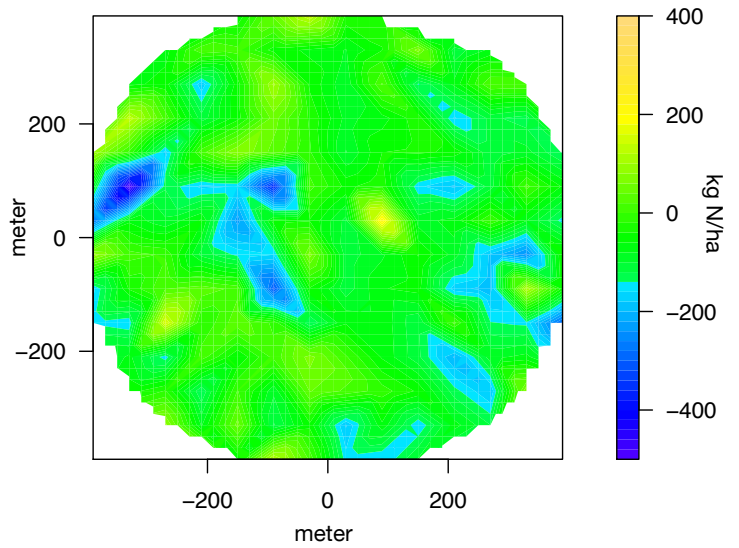


FIGURE 13. N Balance (kg N/ha) on Site 1 during 1995

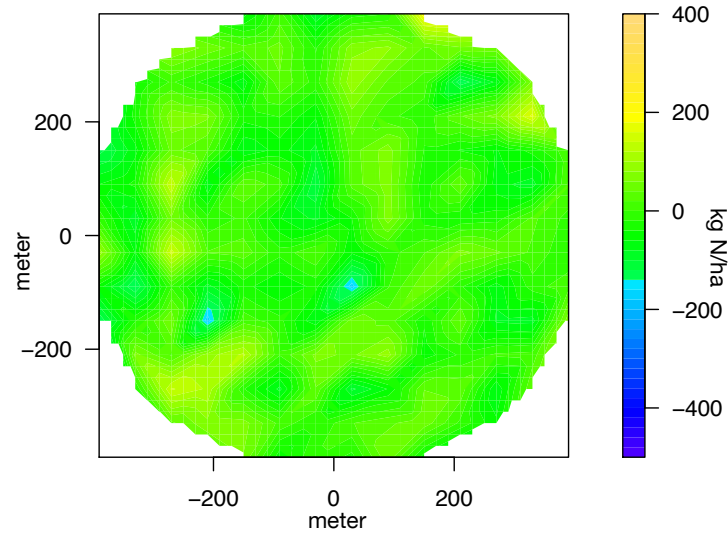


FIGURE 14. N Balance (kg N/ha) on Site 2 during 1994

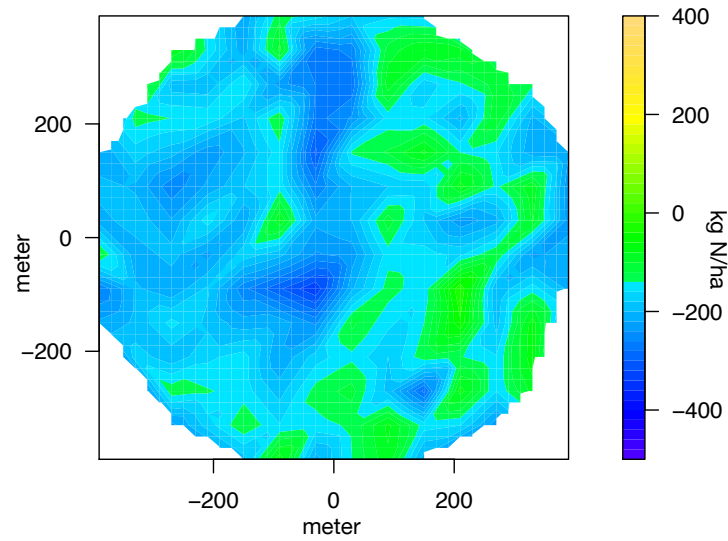


FIGURE 15. N Balance (kg N/ha) on Site 2 during 1995

## 4.2. Buried Bag Experiment.

4.2.1. *Univariate Statistics.* The data are summarized in Table 4. Means were always higher than the medians and standard deviations were about as high as the means. The large standard deviations may be partially explained by the non-normal distribution, but mineralization was probably variable. Mineralization at Site 2 was reduced from 13 mg kg<sup>-1</sup> month<sup>-1</sup> in May to 5.1 mg N kg<sup>-1</sup> month<sup>-1</sup> in September. At Site 1 the mineralization rate was higher with a median of 18 mg N kg<sup>-1</sup> month<sup>-1</sup> and declined in August and September to 8 and 4 mg N kg<sup>-1</sup> month<sup>-1</sup> as the field was allowed to dry in preparation for harvest. During June and July, the actively growing corn crop resulted in a large number of bags lost due to root penetration. Since N mineralization is a micro-site phenomena with most sites having low activity and a few sites having high activity, the distribution of the measured N mineralization values was highly skewed in both fields (Figures 16 – 17). Log transformation was used to normalize the data.

TABLE 4. Univariate description of the Bag N mineralization parameters based on the buried bag technique at Site 1 and Site 2

Month	number of samples	Mean	Median	SD
		–mg/(kg month) –		
		<i>Site 2</i>		
May	119	15.9	13.5	12.5
June	107	13.2	10.3	12.0
July	96	15.5	10.8	16.9
August	130	13.7	10.2	13.2
September	139	6.1	5.1	5.8
Total (mg/kg)		64	50	
		<i>Site 1</i>		
May	135	21.6	18.4	17.2
June	87	13.8	10.4	12.7
July	68	19.4	16.3	16.3
August	111	9.3	8.4	7.8
September	140	4.7	4.2	3.0
Total (mg/kg)		64	58	

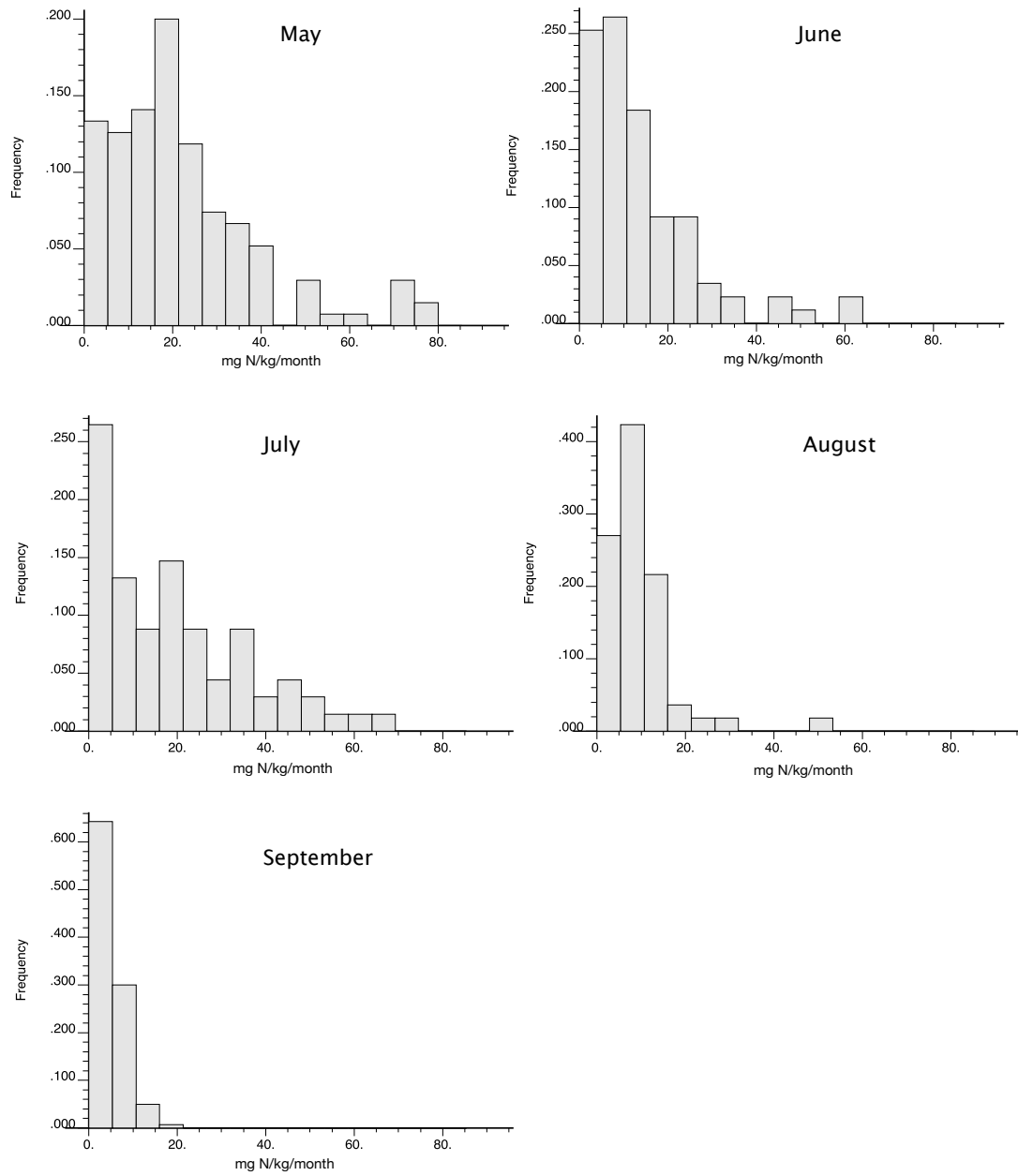


FIGURE 16. Distribution of the N mineralization rates at Site 1

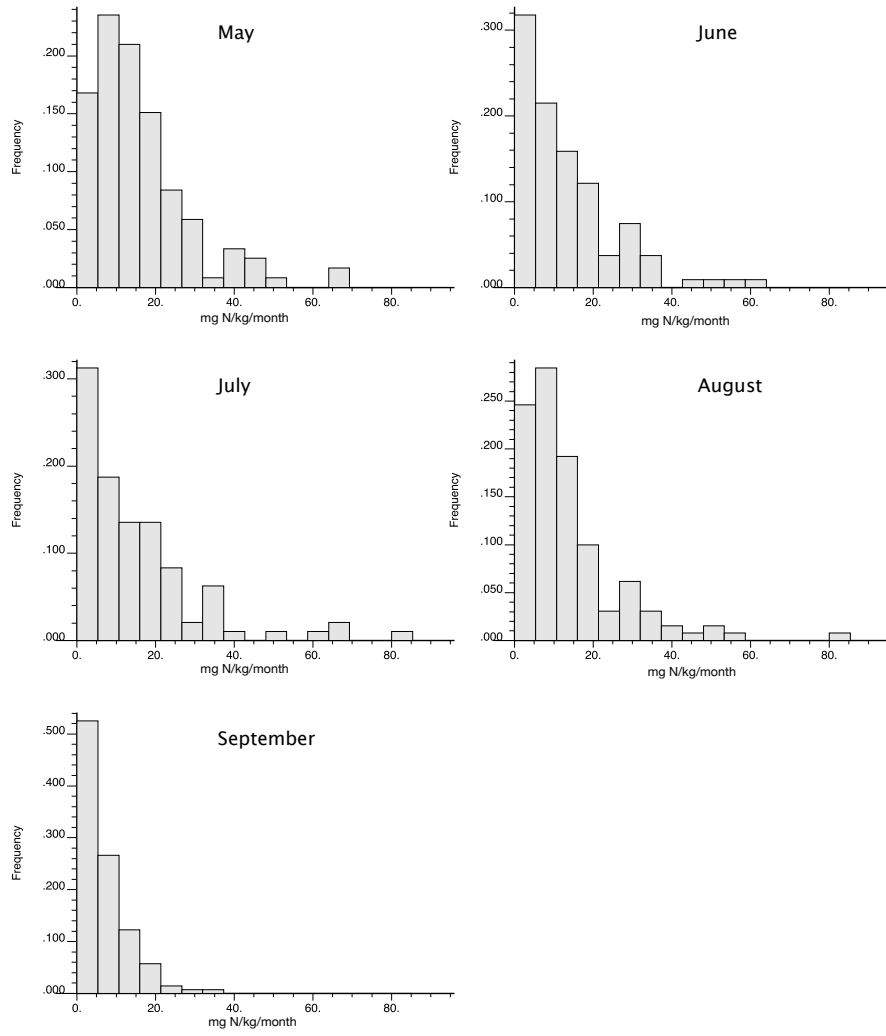


FIGURE 17. Distribution of the N mineralization rates at Site 2

4.2.2. *Geostatistical Analysis.* Since log transformation of the data yielded normal distributions, the experimental variogram were computed for the original and log transformed data. The experimental semivariograms of the log transformed data are shown in Figures 18 and 19. Little spatial structure could be determined in either the original or the log transformed data. Trimming the data by removing “high” N mineralization values did not result in improved semi-variograms. During July and August some spatial structure was evident at both sites. The range of spatial correlation was around 300 m at Site 1 and 350 m at Site 2.

The lack of spatial correlation at the scales studied indicates that N mineralization was not autocorrelated at scales larger than 60 m. However, there might be correlation at shorter distances.

Maps were estimated by kriging on a 30 m grid, followed by a backtransformation ( $e^z+1$ ). During May the N mineralization was highest in the northwestern quadrant of the field. This area was where cattle, grazing on the corn stubble in the winter, where fed and watered. Lower N mineralization rates were recorded in the southwestern

TABLE 5. Fitted variogram models for the buried bag experiment after  $\ln(z+1)$  transformation (maximum lag distance = 662 meters).

	Model	Nugget ( mg N g <sup>-1</sup> ) <sup>2</sup>	Sill	Range meter	r <sup>2</sup>
Site 1					
May	Linear	0.795	0.937	662	0.313
June	Linear	0.817	0.817	662	0.056
July	Exponential	0.682	1.184	302	0.576
August	Spherical	0.339	0.469	314	0.872
September	Linear	0.297	0.316	662	0.257
Site 2					
May	Linear	0.570	0.581	662	0.017
June	Linear	0.808	0.863	662	0.143
July	Spherical	0.680	0.926	339	0.461
August	Spherical	0.470	0.669	387	0.565
September	Linear	0.531	0.531	662	0.124

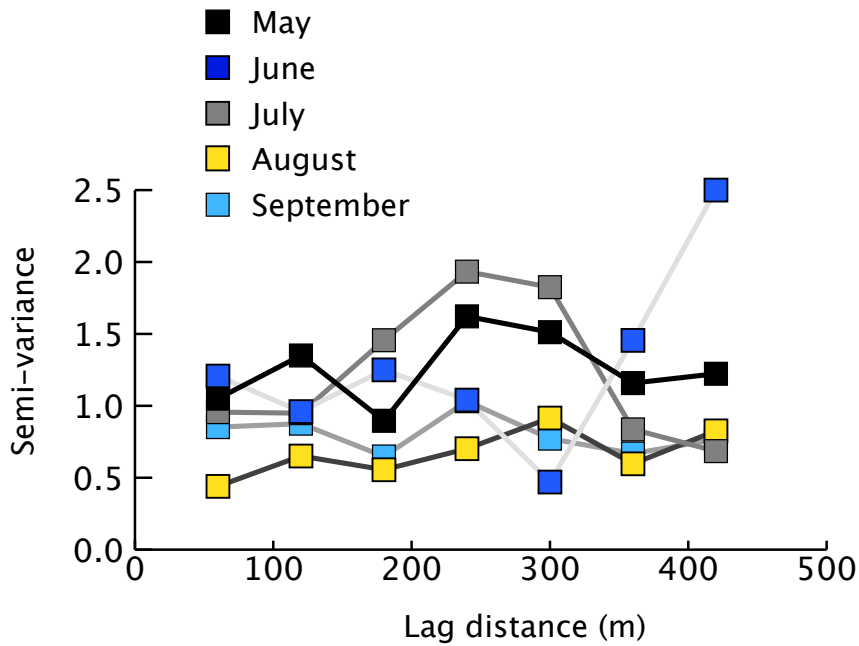


FIGURE 18. Standardized variograms of the logarithms of the N mineralization values as determined by the buried bag method for May through September on Site 1.

and southeastern section (Figure 20). The areas of low N mineralization roughly correspond to the low elevations. Nitrogen mineralization could have been depressed in those areas due to low soil temperatures or high water levels. During June there were no samples that showed high N mineralization (Figure 21). The location with high N mineralization rates evident in the May sample did not produce as much during the following month. The highest N mineralization rates during June occurred in the northeastern quadrant. An area in the southwest that is low in elevation had slightly increased in N mineralization rates. During July a band of N mineralization stretching from the northeast to the southwest was the most prominent pattern in the field (Figure 22). Nitrogen mineralization continued in the northwestern quadrant and increased in southeastern quadrant. During August N mineralization activity declined (Figure 23). Most of the field showed N mineralization of  $< 20 \text{ mg N g}^{-1} \text{ month}^{-1}$ .



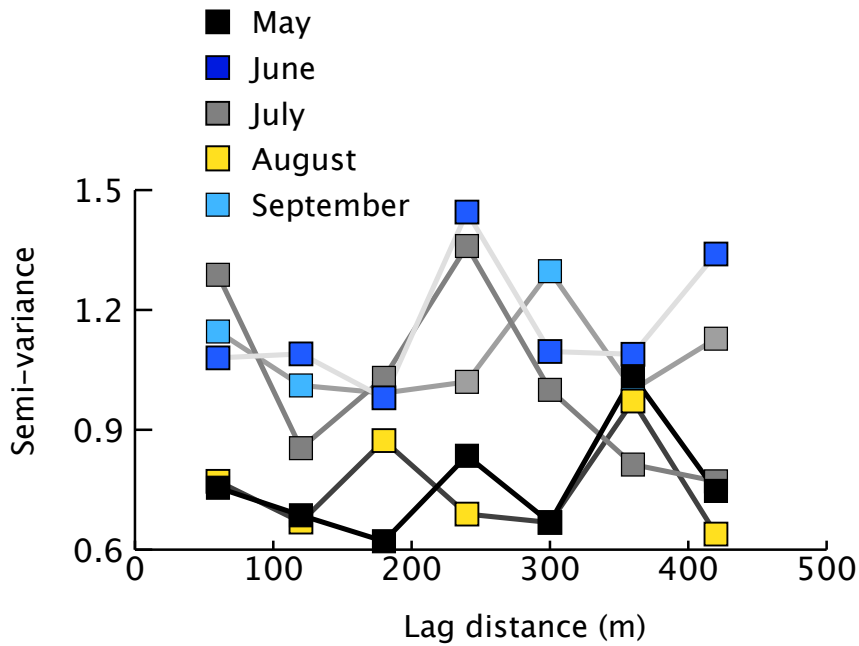


FIGURE 19. Standardized variograms of the logarithms of the N mineralization values as determined by the buried bag method for May through September on Site 2.

The band of higher N mineralization activity was no longer detected, except for a slight remnant in the center of the field. Nitrogen mineralization may have declined because of the reduced water input towards the end of the month or because of substrate depletion. During September N mineralization declined further  $< 10 \text{ mg N g}^{-1} \text{ month}^{-1}$  (Figure 24). This decline was probably due to low moisture conditions after the irrigation was stopped to allow the corn to dry.

At Site 2 N mineralization rates during May were below  $10 \text{ mg N g}^{-1} \text{ soil}$ , except for the southwestern and southeastern edge where N mineralization rates were  $15 - 20 \text{ mg N g}^{-1} \text{ of soil month}^{-1}$  (Figure 25). As expected the area that had been leveled in the westcentral part of the field had low N mineralization activity. As with the Site 1 N mineralization activity did not increase significantly during June (Figure 26). More N mineralization was detected in the northeastern, and southeastern quadrant and

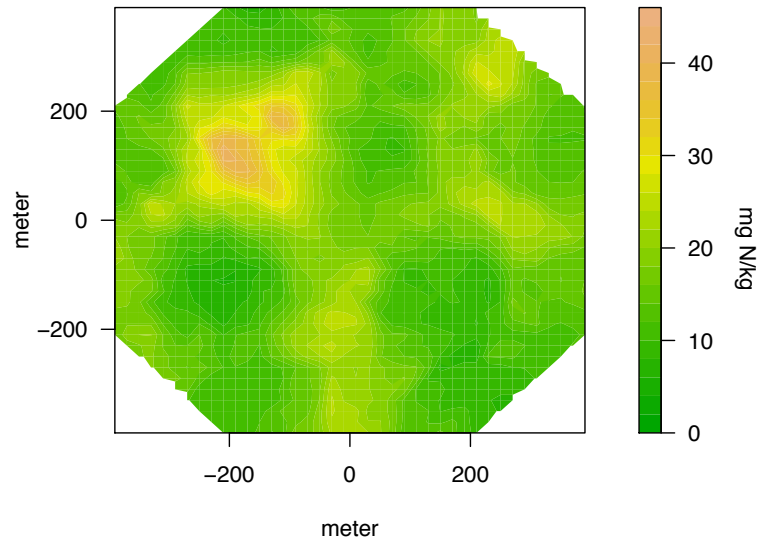


FIGURE 20. Nitrogen mineralization (mg N/kg/month) estimates during May 1994 at Site 1 as determined by the buried bag method

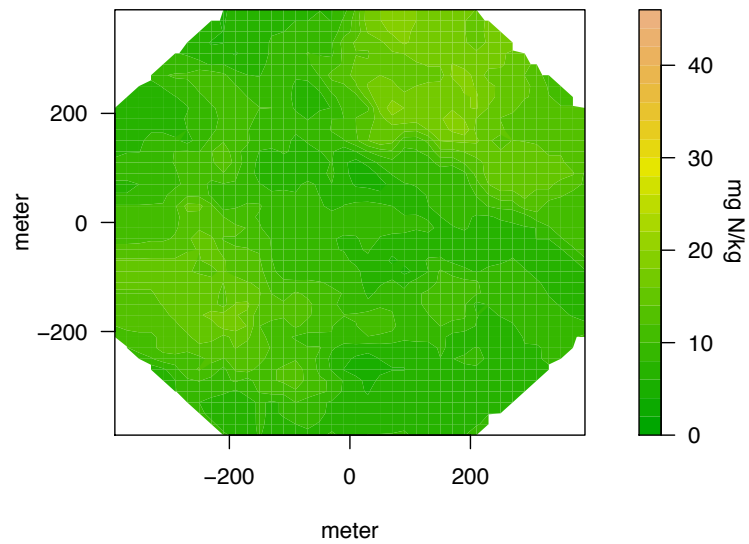


FIGURE 21. Nitrogen mineralization (mg N/kg/month) estimates during June 1994 at Site 1 as determined by the buried bag method

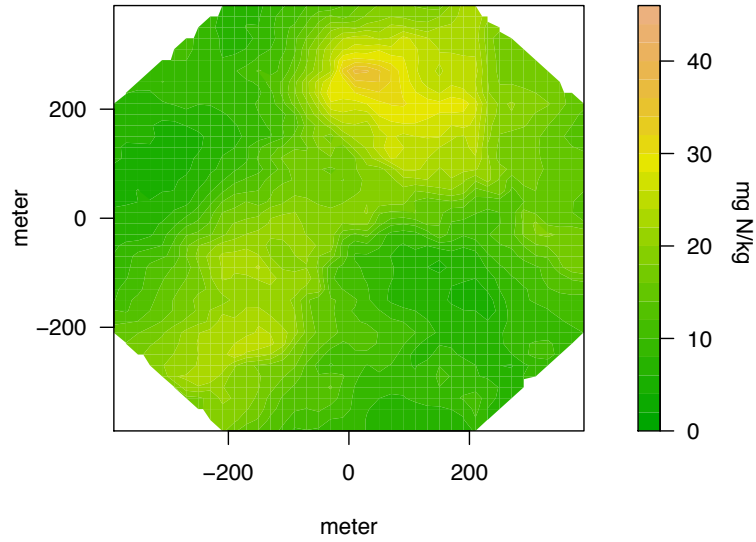


FIGURE 22. Nitrogen mineralization (mg N/kg/month) estimates during July 1994 at Site 1 as determined by the buried bag method

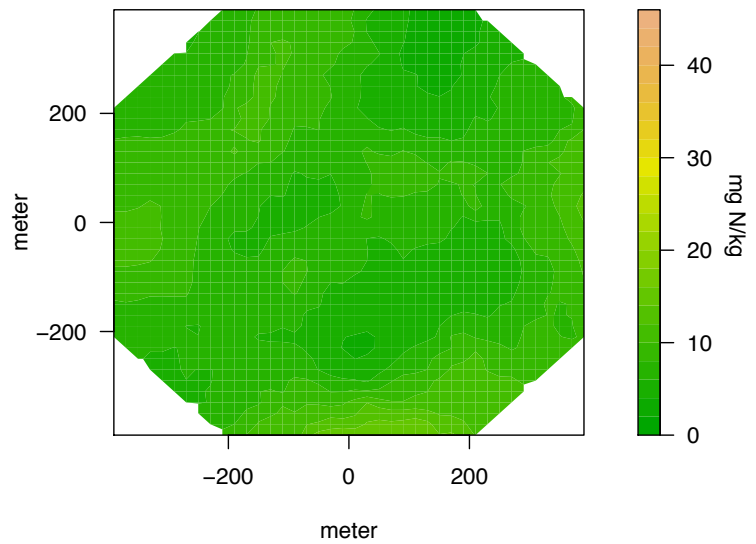


FIGURE 23. Nitrogen mineralization (mg N/kg/month) estimates during August 1994 at Site 1 as determined by the buried bag method

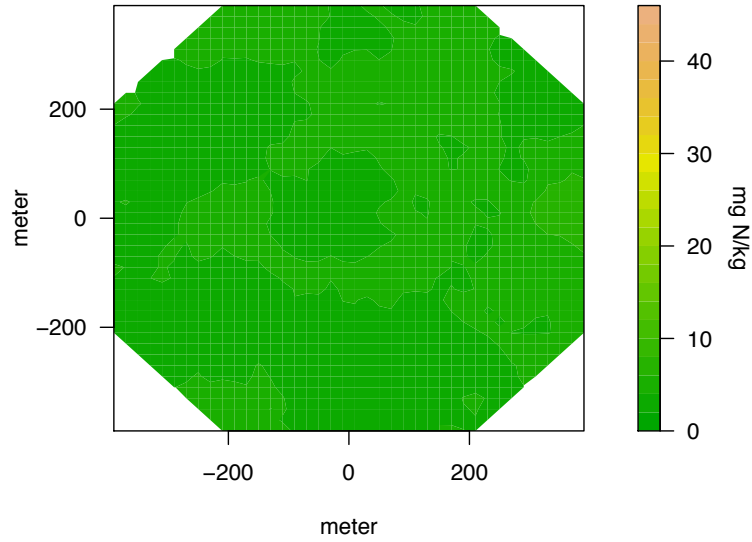


FIGURE 24. Nitrogen mineralization (mg N/kg/month) estimates during September 1994 at Site 1 as determined by the buried bag method

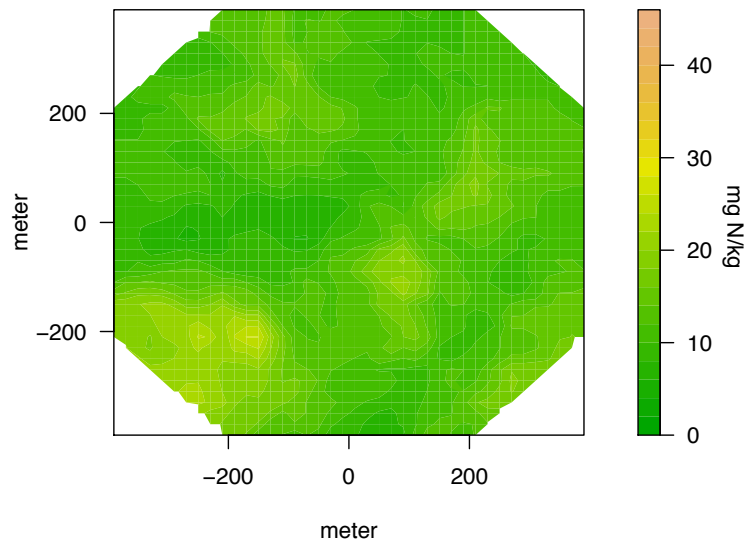


FIGURE 25. Nitrogen mineralization (mg N/kg/month) estimates during May 1994 at Site 2 as determined by the buried bag method

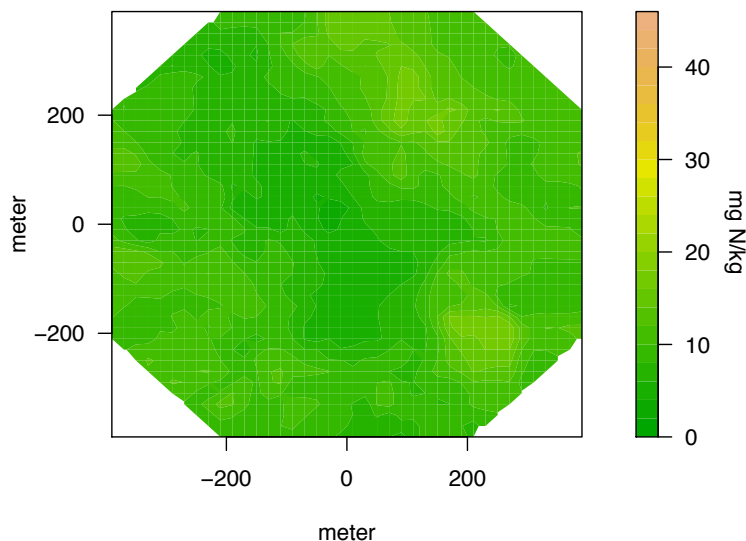


FIGURE 26. Nitrogen mineralization (mg N/kg/month) estimates during June 1994 at Site 2 as determined by the buried bag method

the N mineralization was reduced in the southwestern part of the field. In July an N mineralization “hot spot” appeared in the eastern part of the field (Figure 27). As much as  $30 \text{ mg N g}^{-1}$  soil was mineralized in that area. The rest of the field remained below  $10 \text{ mg N g}^{-1}$  soil. The area of high N mineralization corresponds loosely to a broad valley, that did not have a particularly high organic matter content. The areas of high organic matter were mostly to the east of the N mineralization activity. During August the extent of the N mineralization “hot spot” appears to decrease (Figure 28), but the intensity increased a little. The area of higher activity also moved a little bit to the south towards the soil that was higher in organic matter. In September the N mineralization activity was much reduced, similar to Site 1. Again this was probably a reflection of the reduced moisture inputs as the irrigation was stopped. Most of the field produced  $< 5 \text{ mg N g}^{-1}$  soil month<sup>-1</sup> during the sample period.

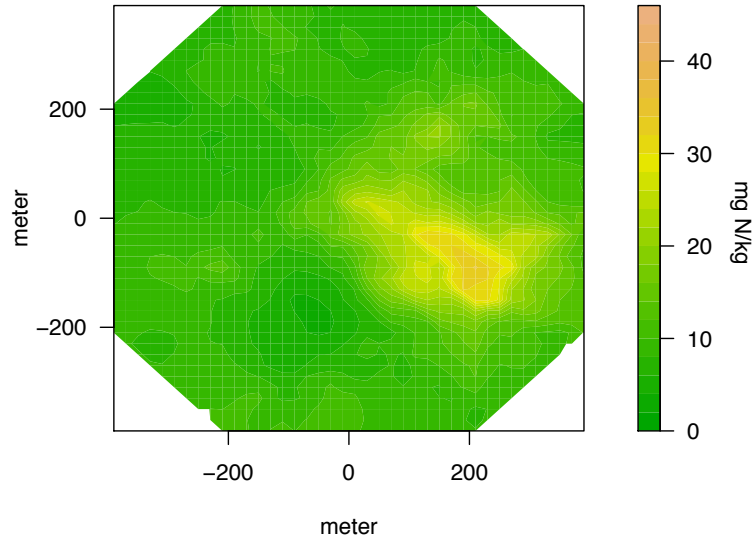


FIGURE 27. Nitrogen mineralization (mg N/kg/month) estimates during July 1994 at Site 2 as determined by the buried bag method

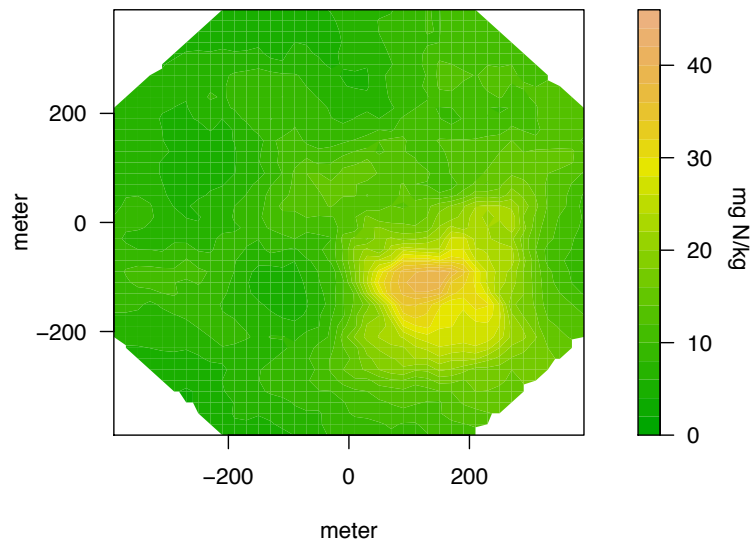


FIGURE 28. Nitrogen mineralization (mg N/kg/month) estimates during August 1994 at Site 2 as determined by the buried bag method

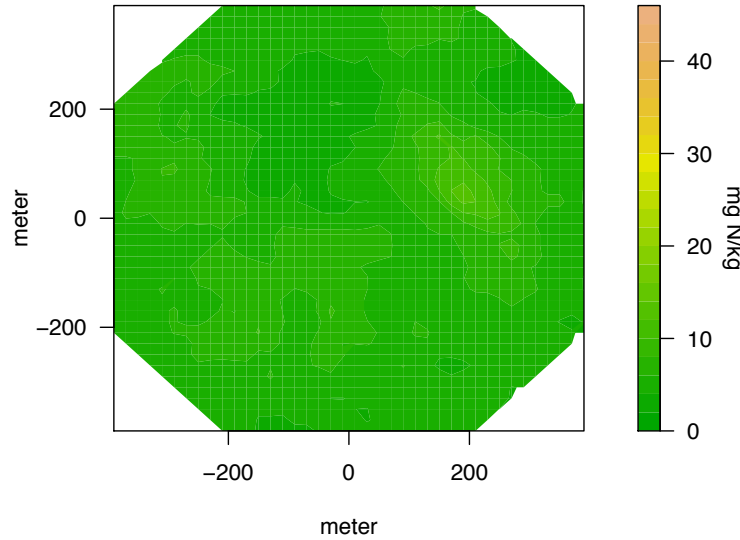


FIGURE 29. Nitrogen mineralization (mg N/kg/month) estimates during September 1994 at Site 2 as determined by the buried bag method

4.2.3. *Summary.* The buried bag method revealed high spatial and temporal variability of net N mineralization in these corn fields. Net N mineralization peaked in May and declined throughout the rest of the season. The decline in the net N mineralization rates in August and September can be attributed to the reduced soil moisture levels in those months as the irrigation was reduced in preparation for harvesting. The buried bag method proved to be an unsatisfactory method for measuring the nitrogen mineralization in a production field, since cultivation forced the placement of the bags in the rows. This made it more likely that the bags would be penetrated by roots due to the close plant proximity. If the between row sites had been available, fewer sample points might have been lost.

### 4.3. Resin Core Experiment.

4.3.1. *Univariate Statistics.* During 1994 an average of  $38 \text{ mg N kg}^{-1}$  was measured at Site 1, while an average of  $55 \text{ mg N kg}^{-1}$  was measured at Site 2. In 1995

TABLE 6. Univariate descriptions for the resin bag incubations. (Numbers in parenthesis have 3 high data points removed)

Year	number of samples	Mean	SD	Skewness	Kurtosis
mg N/kg					
Site 1					
1994	159	38.13	85.58	2.47	11.1
		(14.43)	(7.82)	(0.427)	(-0.414)
1995	147	127.4	52.8	-0.313	-0.827
Site 2					
1994	149	55.5	55.3	1.68	3.38
1995	125	122	56.5	-0.264	-0.964

TABLE 7. Semivariogram model parameters computed for the resin bag incubation

Year	number of samples	Model	Nugget	Sill	Range	r <sup>2</sup>
– mg N/kg – meter						
Site 1						
1994	159	Linear	1728	3913	662	0.913
1995	147	Spherical	2656	3155	130	0.053
Site 2						
1994	143	Linear	61	61	662	
1995	125	Linear	2753	2753	662	

the estimates doubled and tripled (Table 6). This might have been due to additional fertilizer applied, after the wet spring. The numbers were corrected by subtracting 337 kg of N ha<sup>-1</sup> from each of the estimates. Eliminating the three highest data-points at Site 1 during 1994 reduced the variability and non-normality significantly.

4.3.2. *Geostatistical Analysis.* As with the buried bag method, measurements using the resin bags were only weakly correlated at the scales studied. At Site 2 the variograms were essentially flat, indicating that no correlation was detected. At Site 1 the 1994 variogram was linear, while in 1995 a spherical variogram provided the best fit (Table 7). The range of 130 m was less than the ranges estimated from from the buried bag methods. In both years the nugget was a high percentage of the sills. Indicating that variability was occurring at distances of < 60 m.



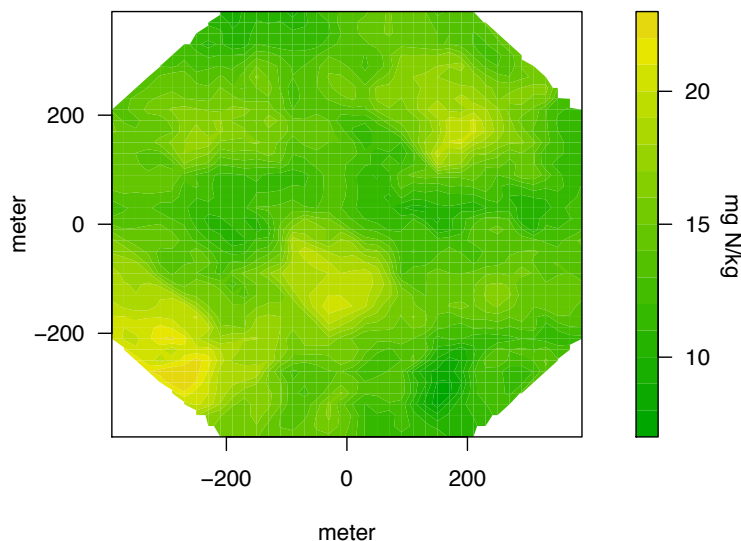


FIGURE 30. Nitrogen mineralization (mg N/kg/season) estimates during 1994 at Site 1 as determined by the resin bag method

The kriged maps of the N mineralization as measured by the resin bag method are shown in Figures 30 – 33. At both sites, N mineralization rates in 1995 were higher than in 1994. In 1994 the N mineralization at Site 2 was predominantly detected in the southeastern section of the field (Figure 32). This area roughly corresponds to the area showing high mineralization in the buried bag experiment (Figure 27 – 28).

4.3.3. *Summary.* Nitrogen mineralization as measured by the resin core method showed that mineralization was highest in some of the same area where high mineralization was observed in the buried bag method. The PVC cores were more effective at excluding corn roots from the sample volume. The pattern of N mineralization changed between the two years.

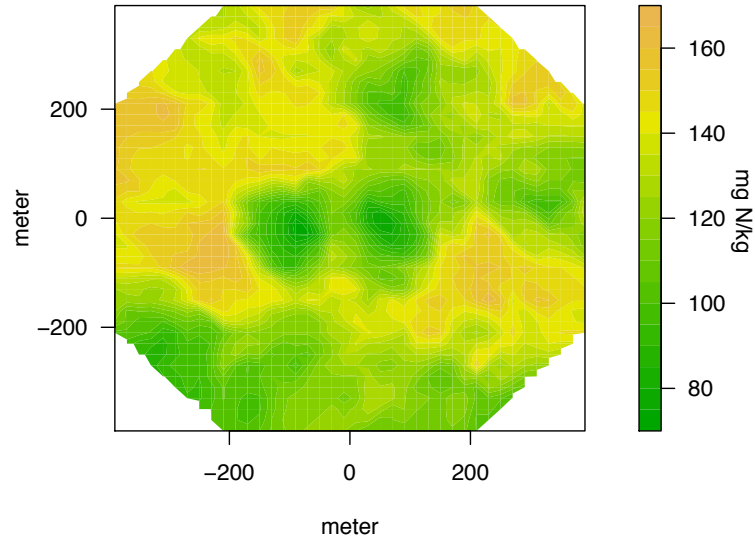


FIGURE 31. Nitrogen mineralization (mg N/kg) estimates during 1995 at Site 1 as determined by the resin bag method

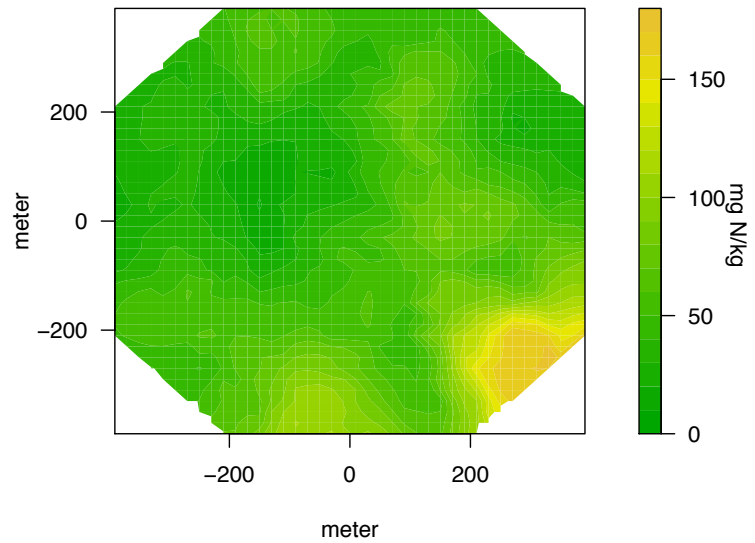


FIGURE 32. Nitrogen mineralization (mg N/kg) estimates during 1994 at Site 2 as determined by the resin bag method

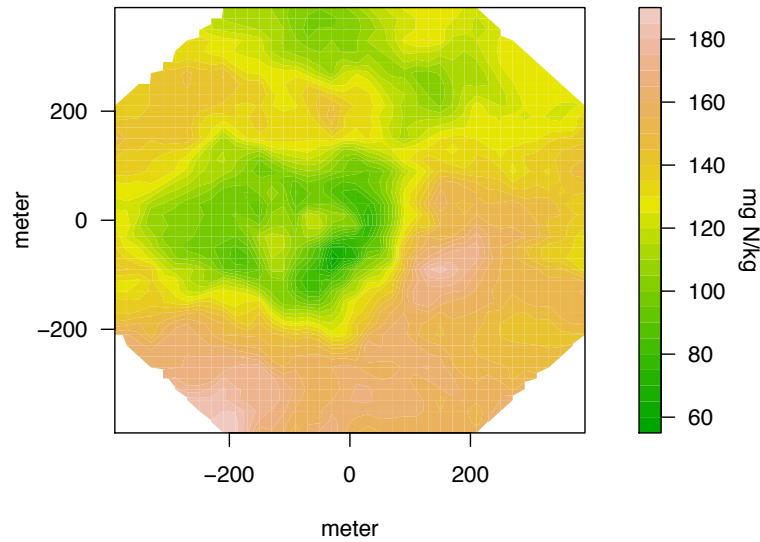


FIGURE 33. Nitrogen mineralization (mg N/kg) estimates during 1995 at Site 2 as determined by the resin bag method

## 5. Discussion

Both the buried bag method and the resin core method measure the net N mineralization rate in a small closed volume of soil. The activity in the test volumes might not mirror exactly the activity in the soil. In particular the free exchange of nutrients and water is reduced creating a microclimate that might be higher in moisture and inorganic nutrients than the surrounding soil.

The resin bag method avoids some of the limitations of the buried bag method, but adds some of its own. Soil moisture is allowed to fluctuate as it does in the rest of the soil and free nitrate is leached onto the resin and may be protected against denitrification. Nitrogen may be lost due to ion competition and microbial growth on the resin (Schnabel, 1983). Nitrogen may not be captured due to bypass flow or resin saturation (Hanselman et al., 2004).

The N-balance method only provides a lower limit on the amount of N mineralized during the season, since losses to the groundwater and denitrification are not measured. If the losses are distributed uniformly, the N-Balance method should show the same pattern as the other two methods. While there was some correspondence between the high mineralization areas as determined by the N-balance method with the other two methods, the correspondence was not strong.

Average N mineralization during the season was at least  $10 \text{ kg N ha}^{-1}$  as measured by the N balance method. The buried bag method estimated approximately  $43 \text{ kg N ha}^{-1}$  mineralized during the 1994 growing season. The average was  $44 \text{ kg N ha}^{-1}$  when estimated by the resin core method. Compared to the total N input of about  $300 \text{ kg N ha}^{-1}$  the contribution of N mineralization at these sites was minimal. In addition the N-balance method revealed that for a large part of the field the N balance was negative, meaning that N was lost either by denitrification or by leaching. This suggests that the application of N could be better tailored to the needs of the plant. Nitrogen mineralization was not spatially structured at the scales studied. Field estimates of N mineralization are few. In Colorado Hook and Burke (2000) used a resin core technique and reported that N mineralization in the shortgrass steppe showed weak spatial correlation despite soil N and C pools showing strong correlation with topography and soil texture. They speculated that N mineralization might be tied to particulate organic carbon (POM) which may be distributed differently than total C and N pools. Paschke et al. (2000) were unable to detect differences in nitrogen mineralization in the short-grass steppe when carbon contents were manipulated, although plant available N as measured by resin absorption was reduced at higher C additions.

The field estimates of N mineralization should be similar to estimates of soil respiration, since both are the product of microbial activity. The reported range of autocorrelation for soil respiration has varied between 12 cm and 5 m (Robertson et al., 1988), depending on the size and spacing of the samples. Stoyan et al. (2000)

reported that most of the spatial variability occurred at less than 10 cm. The sample spacing of 60 m was much larger than that, so it would not be surprising to find little autocorrelation present at these scales. From the maps, it appears that that some of the areas that registered high N mineralization rates in the buried bag method also showed high N mineralization in the resin method; however, since areas that had high N mineralization rates in one method did not consistently show high N mineralization rates in the other method, the overall correlation between the buried bag and the resin core method was low (Table 8). Nitrogen mineralization was only slightly correlated with organic matter, clay content, and elevation. This suggests that micro-scale factors such as the availability of food, oxygen, and moisture control the mineralization.

TABLE 8. Correlations between Field Indices of N mineralization

	Organic Matter					
	Resin '95	Resin '94	Buried Bag	Clay	Silt	Elevation
	Site 2					
Resin '95	1.00	-0.0854	0.115	0.0243	0.0465	-0.0333
Resin '94		1.00	0.002	0.0138	0.109	0.178*
Buried Bag			1.00	0.131*	-0.103	-0.121*
Organic Matter				0.0611	0.547*	-0.209*
Clay				1.00	0.0895	-0.211*
Silt					1.00	-0.322*
Elevation						1.00
	Site 1					
Resin '95	1.00	-0.226	-0.064	-0.041	-0.103	0.118
Resin '94		1.00	-0.117	0.263*	0.32	-0.082
Buried Bag			1.00	-0.045	0.012	0.0945
Organic Matter				0.96	0.037	-0.157
Clay				1.00	0.602*	-0.162*
Silt					1.00	-0.257*
Elevation						1.00

\* significant at the 5 percent level

## 6. Summary

Nitrogen mineralization during the season was at least  $10 \text{ kg N ha}^{-1}$  as measured by the N balance method. The buried bag method estimated that approximately  $43 \text{ kg N ha}^{-1}$  were released during the 1994 growing season. The resin bag method yielded estimates of 37 and  $55 \text{ kg N ha}^{-1}$  mineralized during the 1994 season for Site 1 and Site 2 respectively. In 1995 the resin bag method estimated that 127 and  $122 \text{ kg N ha}^{-1}$  was mineralized on Site 1 and Site 2 respectively.

In these fields soil moisture was much more important than nitrogen mineralization for crop growth. In 1994 the contribution from the N mineralization is low compared to the fertilizer inputs, so differences in the mineralization would not have a large effect on the yields. In 1995 there was a greater contribution of N mineralization, but because of the high soil moisture levels in the spring it is likely that the N was leached before it could be taken up by the corn. The weak spatial structure of N mineralization, as compared to organic carbon and elevation, suggest that N mineralization either is influenced by a sub pool of N or C such as POM (Hook and Burke, 2000) or that micro-climatic factors play a large role.

## CHAPTER 3

# Estimating nitrogen mineralization for Variable Rate N Fertilization

### 1. Abstract

Spatially variable N fertilization techniques require spatially variable N fertilizer recommendations. Accurate tests for N mineralization tend to take a long time to perform, while quick tests tend to be less accurate. It may be possible to use a quick test to predict net N mineralization variability, if not the level of N mineralization. Three laboratory N tests (waterlogged incubation, autoclaving, CO<sub>2</sub> released on rewetting a dried soil) as well as a chlorophyll field test were used to estimate N mineralization in two central Kansas corn fields. None of the estimates provided good correlation with measured field N mineralizations, nor were they consistently successful in identifying areas in the field that experienced high or low N mineralization. The laboratory tests showed higher correlations with organic C and silt, than with measured N mineralization. The laboratory mineralizations were much more continuous (i.e. they had a smaller nugget variance and longer ranges) than the field estimates, suggesting that there are other source of variation, such as soil moisture patterns and microclimatic differences that influence field N mineralization.

### 2. Introduction

If N mineralization is to be used for fertilizer prediction, N mineralization must be predicted quickly and cheaply. Field mineralization methods are too cumbersome and expensive for routine work. Therefore, lab methods or quick field tests have been sought to determine the N mineralization. A number of lab methods have been



proposed to measure nitrogen mineralization. Most of these methods work by treating the soil in some way to release some of the organic N. The increase in inorganic nitrogen is measured after the treatment.

Waring and Bremner (1964) first proposed using the increase in ammonium during a water logged incubation as an index of nitrogen mineralization. This approach was subsequently refined by Bremner (1965) and Keeney (1982). Nitrogen released in this procedure is thought to come mostly from the living biomass, and is more representative of the microbial biomass than the N supplying capacity. Methods to oxidize a portion of the organic matter have also been used to estimate the nitrogen mineralization potential. Oxidizing agents include potassium permanganate, peroxidases, and heat. One of the heat based methods involves autoclaving a soil/suspension for 16 hours. Since N mineralization is closely tied to carbon mineralization, Franzlubber et al. (1996) proposed a test of N mineralization based on the amount of CO<sub>2</sub> evolved one day after rewetting an air-dry soil. They found close correspondence between the amount of CO<sub>2</sub> evolved in one day after rewetting an air-dry soil and the N mineralization during a 21 day laboratory incubation performed according to a modification of the procedure of Stanford and Smith (1972). Jalil et al. (1996) proposed a test based on the ammonium increase after boiling a soil sample in 1 M KCl at 100°C for 4 hours, followed by analysis of the released N using steam distillation. They found a close relationship between this test and the N mineralization determined using the traditional Stanford and Smith (1972) procedure. They reported r<sup>2</sup> values close to 0.8 for a number of Saskatchewan soils. However, the variograms developed with the hot KCl test were much more continuous at the origin than those developed using long incubation N mineralization (Selles et al., 1997).

Field indicators of N mineralization can use measurements of the crop to indicate the nutritional status of the crop. Chlorophyll content is related to the N status of the plant. Chlorophyll content of a leaf can be measured by determining the attenuation of green light as it passes through a leaf. Minolta (Ramsey, NJ) is selling

an instrument (Spad meter) which clamps onto the leaf, and measures the attenuation of a green light beam. The attenuation depends on the place that the reading is taken, i.e., the leaf structure under consideration, the age of the leaf, and dust on the leaf. Multiple readings can be averaged to reduce the effect of these variables. Chlorophyll measurements have been used to fine-tune side-dress fertilizer application. Although chlorophyll measurements are variety specific, they can be used to indicate areas of the field which are under-fertilized with respect to the rest of the field, or in comparison to a fertilizer trial.

### 3. Objective

To find a laboratory or quick field method that could predict the spatial variability in the field mineralization. If patches of high or low N mineralization can be identified, fertilizer recommendations can be adjusted accordingly. If a pattern of N mineralization can be identified it could be used to determine if the field would benefit from spatially varying nitrogen applications.

### 4. Methods

**4.1. Anaerobic Incubation.** Ten grams of field moist soil collected in the spring 1995 was placed into a 25 ml serum bottle, 10 ml water added, the vial capped, and placed in a 40°C incubator for 7 days. The nitrate and ammonium produced were measured by steam distillation followed by titration of the distillate. (Keeney, 1982). The initial nitrate and ammonium were determined by extraction of 5 grams of soil in 100 ml 1M KCl for one hour, followed by centrifugation, decanting through a glass-fiber cloth, and analysis on a Lachat Autoanalyser (Hach Company, Loveland, CO).

**4.2.  $\text{NH}_4^+$  released by Autoclaving.** Ten grams of field moist soil collected in the spring of 1995 was weighed into a 25 ml serum bottle and 10 ml of 0.1 M  $\text{CaCl}_2$  added. The bottle was capped and autoclaved at 121°C for 16 hours. The

$\text{NH}_4^+$  released was determined by steam distillation followed by titration of the distillate. Initial  $\text{NH}_4^+$  content of the soil was obtained from a previous KCl extraction and measured using a continuous flow method (Lachat Instruments, WI, now Hach Company, Loveland, CO).

**4.3.  $\text{CO}_2$  released on rewetting.** Five grams of soil was weighed into a 25 ml serum bottle. The bottle was left open to the atmosphere and the soil was allowed to dry out at lab temperature ( $\approx 24^\circ\text{C}$ ) for three days, 1 ml of water was added and the serum bottle capped with a red rubber stopper secured with a metal clasp. After 24 hours the concentration of  $\text{CO}_2$  in the bottle was measured by removing 0.5 ml of headspace gas and injecting it into a gas chromatograph (GC) (Shimadzu Inc.). The GC had a thermal conductivity detector (TCD) and a 1 meter Porepak 40 column operated at  $65^\circ\text{C}$ . Helium was used as the carrier gas.

**4.4. Chlorophyll content at 10th leaf.** In 1994, plant heights were measured to get an index of corn growth. In 1994 and 1995 chlorophyll measurements were taken using a Minolta Spad Chlorophyll meter (Minolta, Ramsey, NY) at each grid point when the corn was at the 10th leaf stage. Five readings on three to four plants were averaged.

Chlorophyll content was measured with a Minolta Spad Chlorophyll meter. Ten leaves were measured and averaged by the instrument at each sample point. Several “fences” i.e., closely spaced transects, were also measured to obtain information at shorter lag distances. The “Waring & Meyer” points were not measured. To calibrate the sensor leaves on fertilizer trials conducted on the same field were measured.

## 5. Results

**5.1. Laboratory Experiments.** The indicator tests have been summarized in Table 1. There were no significant correlations between the field estimates of mineralization and any of the indicators.

TABLE 1. Univariate Statistics for the laboratory indicators

Test	Units	N	Mean	Stdev	Skewness
Site 1					
Autoclavable	g N kg <sup>-1</sup>	207	22.8	15.6	-0.054
Anaerobic	g N kg <sup>-1</sup>	207	127.4	52.8	-0.313
CO <sub>2</sub>	nmol C g <sup>-1</sup>	194	528.8	182.3	0.656
Chlorophyll 1994		163	56.8	8.95	-4.74
Chlorophyll 1995		163	56.2	12.5	-3.85
Site 2					
Autoclavable	g N kg <sup>-1</sup>	198	32.9	14.6	1.96
Anaerobic	g N kg <sup>-1</sup>	207	4.92	4.25	1.23
CO <sub>2</sub>	nmol C g <sup>-1</sup>	208	552.8	187.7	-0.473
Chlorophyll 1994		162	51.3	6.24	-0.387
Chlorophyll 1995		164	49.2	7.02	-4.27

5.1.1. *Univariate Statistics.* The standard deviation was much higher for the CO<sub>2</sub> treatment than for the other treatments. In the “Site 1” samples the anaerobic incubation released more N than the autoclave procedure, while in the “Site 2” samples the autoclave procedure resulted in a higher average N release.

The autoclave procedure was weakly correlated to the anaerobic incubation and correlated to the one day CO<sub>2</sub> procedure. The anaerobic incubation did not correlate with the CO<sub>2</sub> procedure. It was surprising to find only weak correlations between the autoclavable N and the organic matter as well as between the anaerobic incubation and the organic matter. This might be explained by the low level of organic matter in these soils. At Site 2 the autoclavable N correlated slightly with the N mineralization as measured by the resin N in 1994.

5.1.2. *Geostatistical Analysis.* Lab measurements showed much more continuity at the origin (ie. a lower nugget effect) than the field measurements (Table 3). This probably reflects the reduction in variability due to the more controlled and uniform conditions in the laboratory. Conversely it also reflects the failure of the laboratory test to accurately model field N mineralization. Nugget variances ranged from 20 to 80% of the sill variances. Nugget variances were higher for the one day CO<sub>2</sub> test than

TABLE 2. Correlations between the laboratory and field Indications of N mineralization

	Anaerobic	CO <sub>2</sub>	Resin '95	Resin '94	Buried		Organic	Matter	Clay	Silt	Elevation	
					Bag	Autoclave						
	Site 1											
Anaerobic	1.00	-0.079	-0.0048	-0.044	0.0	-0.117	0.062	0.209	0.3263	0.224		
CO <sub>2</sub>		1.00	-0.024	-0.063	-0.041	0.164	-0.135	-0.101	-0.041	-0.056		
Resin '95			1.00	-0.085	0.115	0.104	-0.051	0.0243	0.0465	-0.0333		
Resin '94				1.00	0.002	0.114	0.233*	0.0138	0.109	0.178*		
Buried Bag					1.00	0.023	0.126	0.131*	-0.103	-0.121*		
Autoclave						1.00	-0.101	-0.165	-0.123	-0.205		
Organic Matter							1.00	0.0611	0.547*	-0.209*		
Clay								1.00	0.0895	-0.211		
Silt									1.00	0.322*		
Elevation										1.00		
	Site 2											
Anaerobic	1.00	0.0749	-0.0582	0.225*	-0.107	0.351*	0.0604	-0.0989	-0.0191	0.145*		
CO <sub>2</sub>		1.00	0.0061	-0.178*	-0.055	0.313*	-0.172*	-0.0433	-0.281*	0.0353		
Resin '95			1.00	-0.0854	-0.104	0.0585	-0.0510	0.0243	0.0465	-0.0333		
Resin '94				1.00	0.018	0.258*	0.233*	0.0138	0.109	0.178*		
Buried Bag					1.00	-0.0719	0.1259	0.132	-0.104	-0.121		
Autoclave						1.00	-0.151*	0.0452	-0.248*	0.268*		
Organic Matter							1.00	0.0611	0.547*	-0.209*		
Clay								1.00	0.0895	-0.211*		
Silt									1.00	-0.322*		
Elevation										1.00		

\* significant at the 5 percent level

TABLE 3. Semivariogram model parameters fitted to the laboratory indicators

Test	Model	Nugget	Sill	Range	$r^2$
Site 1					
Autoclavable	Spherical	214	247	123	0.163
Anaerobic	Exponential	76.2	124	142	0.694
CO <sub>2</sub>	Exponential	28800	33710	78.3	0.686
Chlorophyll 1994	Linear	33.3	103.8	662	0.940
Chlorophyll 1995	Linear	155.4	162.7	662	0.170
Site 2					
Autoclavable	Spherical	31.7	187.4	252	0.946
Anaerobic	Spherical	3.19	20.48	404	0.966
CO <sub>2</sub>	Linear	35600	35603	662	0.044
Chlorophyll 1994	Linear	2.95	64.2	662	0.977
Chlorophyll 1995	Spherical	36.2	48.8	210	0.232

for the other tests. The nugget variances for the chlorophyll tests were higher in 1995 than in 1994.

At Site 1, the autoclavable N test indicated high N mineralization in the center and on the southeastern edge of the field. The southeastern edge showed higher mineralization activity in 1995, while the center portion did not seem active in either year (Figure 1). The anaerobic N test showed a different picture. The anaerobic test detected the high organic matter in the eastern part of the field. It is harder to explain the high values in the the southern part of the field, as well as the absence of high values on the eastern side of the field. Both autoclavable N and the anaerobic N tests indicated some higher areas in the southern part of the field. The area of high mineralization in the center of the field that was detected in the autoclavable N test was absent in the anaerobic N test (Figure 2). The one day CO<sub>2</sub> test showed higher values in the center to north western part of the field, as well as the north eastern edge (Figure 3). Neither area correspond to high field N mineralization areas as indicated by the field tests. The CO<sub>2</sub> test did not seem to measure the same parameters as the anaerobic and autoclavable N, since the pattern of high values did not overlap with those tests.

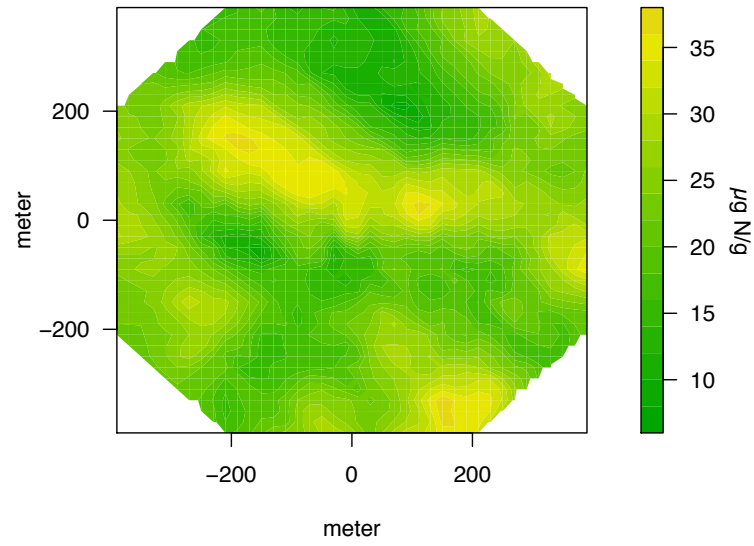


FIGURE 1. Autoclavable N at Site 1

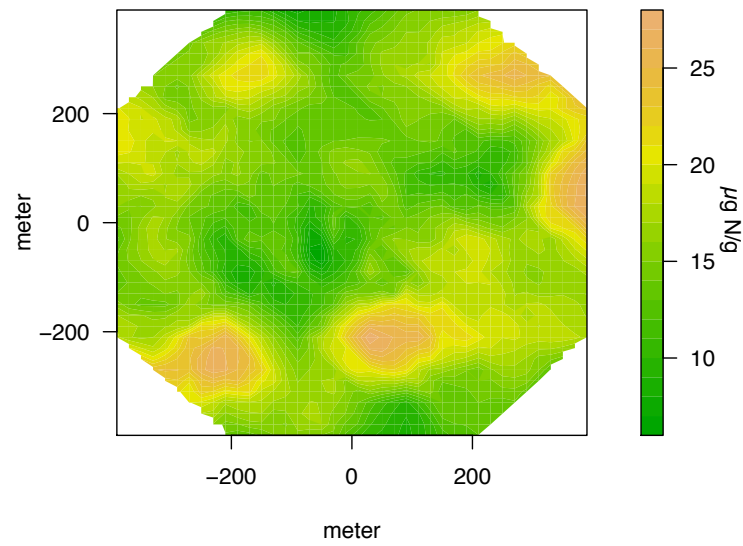
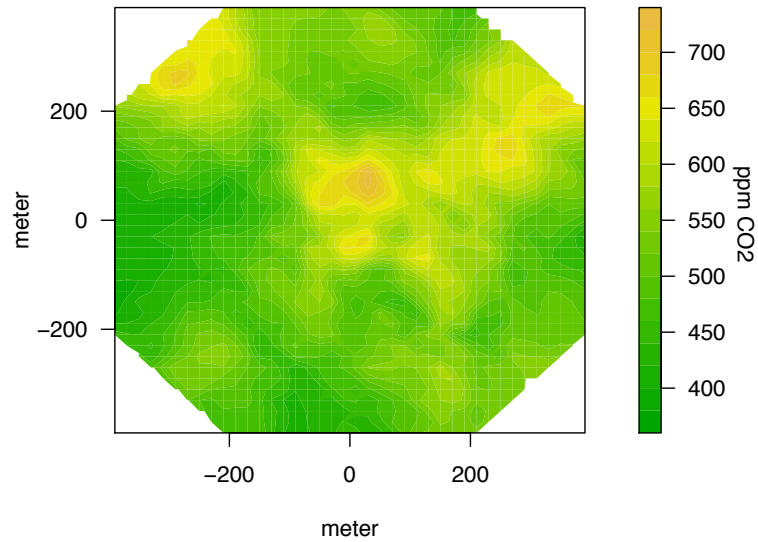


FIGURE 2. Anaerobic N at Site 1

FIGURE 3. One Day CO<sub>2</sub> at Site 1

At Site 2, the autoclavable N test (Figure 4) correctly predicted the area of low mineralization on the western part of the field, where the field had been leveled as well as showing the high mineralization area in the southeastern part of the field.

The anaerobic N test (Figure 5) also detected the leveled part of the field. It correctly indicated higher mineralization in the southeastern part of the field, however it also indicated higher mineralization in the northeastern part of the field. That did not show up in the field tests. The one day CO<sub>2</sub> test (Figure 6) did not indicate the leveled part of the field. It indicated higher mineralization potentials in the eastern part of the field, but the area indicated was further north than the ones indicated by the other two lab tests.

The chlorophyll measurements on the microplots indicated that the corn received an adequate N supply when fertilized with 100 kg N/ha. Fertilization with 50 kg N/ha produced a significant decrease in the chlorophyll content of the leaves, as well



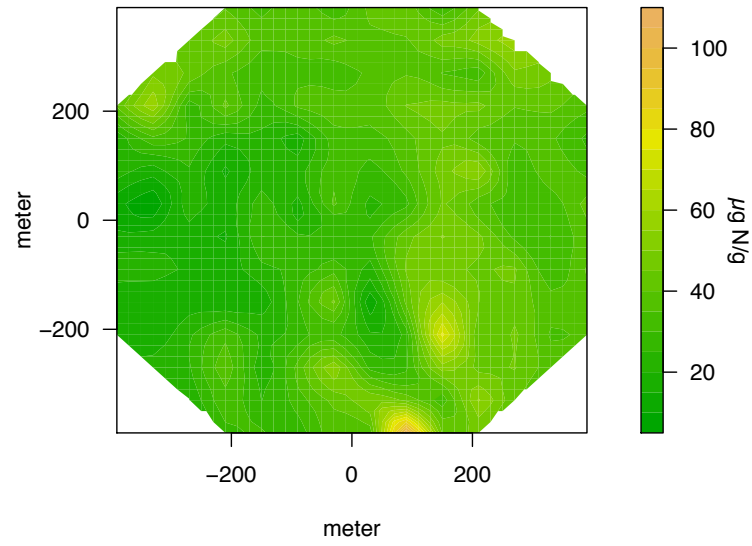


FIGURE 4. Autoclavable N at Site 2

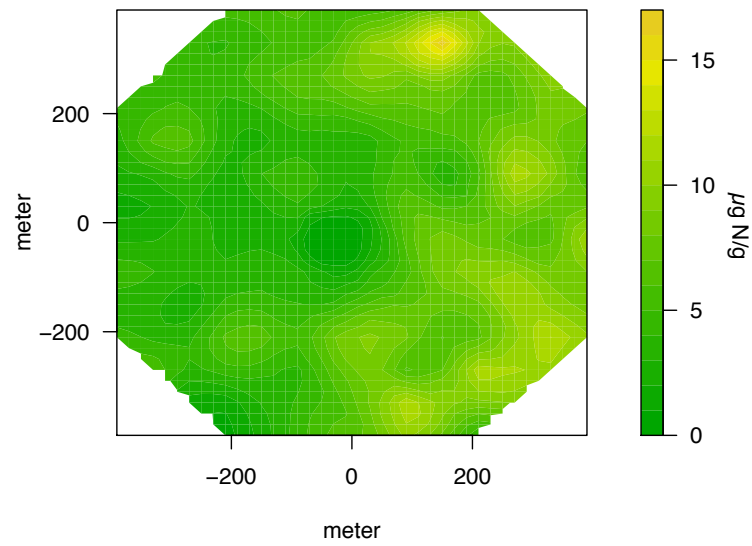


FIGURE 5. Anaerobic N at Site 2

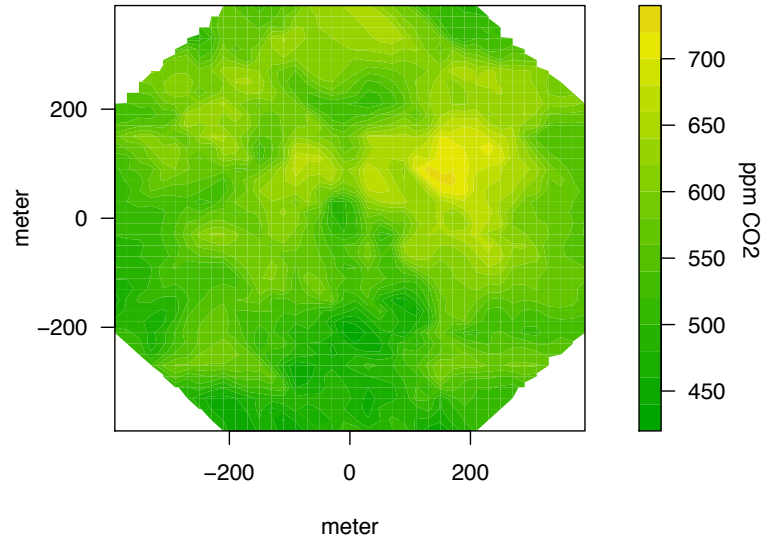
FIGURE 6. One Day CO<sub>2</sub> at Site 2

TABLE 4. Chlorophyll measurements on the Microplots

Field	Year	Treatment	Spad Meter Value	LSD
Site 2	1995	250	53.0	A
		200	53.5	A
		150	51.97	A
		100	52.0	A
		50	49.5	B
		0	47.1	C
Site 1	1995	250	59.2	AB
		200	60.1	A
		150	60.1	A
		100	58.4	AB
		50	57.5	B
		0	58.7	AB

as a small decrease in grain yields. Since the whole field received at least 260 kg N/ha, there were no parts of the fields that were N deficient.

## 6. Summary

Laboratory incubations were unsuccessful in predicting the pattern of field N mineralization. While some methods were able to match some features of the spatial distribution of N some of the time, they were unsuccessful at consistently predicting areas of active mineralization. They were more closely related to the soil organic matter than to the actual N mineralization. If the laboratory mineralization estimates reflect N mineralization potentials, this study illustrates that large differences exist between potential and actual rates. Franzlubber et al. (1996) reported that the CO<sub>2</sub> evolved during the 1st day after rewetting was a good indicator of potential N mineralization. Later Franzluebbbers et al. (2000) reported that the relationship between the 1 day CO<sub>2</sub> release and potential N mineralization was strong only when samples representing a large geographical area were pooled, but weakened when soils from the same region was considered. The predictive power of the 1 day CO<sub>2</sub> incubation may not be large enough to separate out different areas in a single field.

Curtin and McCallum (2004) tested the ability of a hot KCl extraction, anaerobic incubations and aerobic incubations to estimate the N mineralization of Australian pasture soils. Their reference method was growing oats without added N and subtracting soil mineral N at the beginning of the growing period from the soil mineral N plus plant N at the end of the growing period. They found the neither the anaerobic nor the hot KCl method was correlated with the N-mineralization as measured by the oat plant uptake. The aerobic incubation was the best predictor ( $r^2=0.79$ ), but the correlation between the CO<sub>2</sub> evolved during the incubation and the N mineralized was variable.

At Site 2 the anaerobic incubation and the N released on autoclaving were somewhat correlated. Both methods are a measure of microbial biomass, with the autoclave releasing a greater percentage of the biomass than the anaerobic incubation. The autoclavable N was also weakly correlated to the CO<sub>2</sub> released on rewetting.

Again the CO<sub>2</sub> released on rewetting measures the percentage of the microbial community that dies after a step change in environmental conditions. The CO<sub>2</sub> released on wetting was also negatively correlated to the amount of silt in the soil and with organic matter content. In 1994 mineralization as measured by the resin bag method was correlated to the lab measurements of mineralization, but that correlation disappeared in 1995.

None of the methods yielded variability patterns that was similar to the field N mineralization. They were more similar to the levels of organic matter, and as a whole were more continuous than the field mineralization. This may reflect the weak spatial pattern in N mineralization which is not necessarily correlated to total C and N pools (Hook and Burke, 2000).

In these fields elevation seems to be as predictive of nitrogen mineralization as the laboratory tests. Elevation in these fields is correlated with soil moisture and clay content. The presence of clay lenses further complicates the picture as plants are able to explore these higher nutrient areas if they are close to the surface.

In these fields N mineralization does not need to be taken into account when making fertilizer recommendations, unless the amount of N fertilizer is much lower than in the current study. The amount of N mineralized in most of the field was just a small fraction of the total N fertilizer applied and as the chlorophyll meter measurements showed, no area of the field was deficient in nitrogen.

## CHAPTER 4

# Estimating carbon turnover from long term crop rotation experiments

### 1. Abstract

Changes in the carbon-13 ( $\delta^{13}C$ ) values due to changes in vegetation can be used to estimate the carbon turnover. Past approaches have required an independent estimate of the initial  $\delta^{13}C$  of the soil. A method which does not require an independent initial  $\delta^{13}C$  estimate is proposed. This method requires data from crop rotation experiments, including a  $C_3$  plant, a  $C_4$  plant, and a rotation treatment. By simultaneously solving three simple mixing models, representing the three treatments, and two ancillary equations, estimating the  $\delta^{13}C$  value of the residue and the proportion of “new” carbon of the rotation treatment from the  $C_3$  and  $C_4$  treatments, an estimate of the initial  $\delta^{13}C$  of the soil can be found. The estimate is very sensitive to the amounts of residue added to the soil.

### 2. Introduction

Carbon turnover by  $^{13}C$  tracer has been estimated on sites that have experienced a shift from  $C_3$  to  $C_4$  vegetation or vice versa (Gregorich et al., 1995; Wedin et al., 1995; Balesdent et al., 1987). Assuming that mineralization and humus formation do not cause carbon isotope fractionation, a simple mixing model is used to calculate the proportion of carbon in the soil that is derived from the plant residue added since the vegetation change. This can be written as:

$$\delta_f = (1 - x)\delta_i + x\delta_p \tag{37}$$

where  $\delta_f$  is the  $\delta^{13}C$  value of the soil at present,  $\delta_i$  is the  $\delta^{13}C$  value of the soil before the vegetation change, and  $\delta_p$  is the  $\delta^{13}C$  value of the new vegetation. If the total carbon added to the soil since the change in vegetation can be estimated, then the percentage of the total carbon added that is still in the soil can be obtained. Fitting a first order exponential decay model allows the calculation of the half-life of the “new” carbon. If the change in the soil organic matter is known the half-life of the “old” carbon can also be estimated. The problem is that if the exact history of the site is unknown, estimates of the initial  $\delta^{13}C$  content have to be based on nearby sites that have not had the vegetation change (Gregorich et al., 1995; Balesdent et al., 1987).

Balesdent et al. (1988) argued that, since carbon is added to the surface and then translocated downward the change in  $\delta^{13}C$  values down the soil profile should be proportional to the inverse of the carbon content at the same depths.

$$\delta^{13}C \propto \frac{1}{C} \quad (38)$$

As  $\frac{1}{C} \rightarrow 0$  the  $\delta^{13}C$  value should approach that of the vegetation residue. Estimating the initial  $\delta^{13}C$  value of a soil is possible if a soil can be found that has had a continuous  $C_3$  and a continuous  $C_4$  vegetation. The vegetation must be present long enough to allow the carbon signatures to penetrate into the subsoil. Then two lines are estimated, representing the  $\delta^{13}C$  value with respect to depth, one from each of the two vegetation types. The  $\delta^{13}C$  value at the intersection on the lines is the initial  $\delta^{13}C$ . Hsieh (1996) proposed a combined  $\delta^{13}C$ ,  $\delta^{14}C$  method to estimate carbon turnover from a single plot.

By using a long-term rotation study the initial  $\delta^{13}C$  content of the soil does not have to be known. It does not require sampling with depth as the approach of Balesdent et al. (1988), nor the determination of  $\delta^{14}C$ . It requires a continuous  $C_3$  treatment, a continuous  $C_4$  treatment and a  $C_3/C_4$  rotation, as well as an estimate of the residue amounts added to the soil. This would enlarge the pool of possible

study sites. This paper illustrates the technique by using data from a long-term crop-rotation study at the Ashland Experimental Station (Manhattan KS).

### 3. Model

For a rotation treatment ( $C_r$ ) of alternating  $C_3$  and  $C_4$  species (i.e. Soybean/Sorghum), a  $C_3$  treatment (i.e. continuous soybean), and a  $C_4$  treatment (i.e. continuous sorghum) a simple mixing model can be used to estimate the proportion of carbon in the soil of each treatment that is due to the crop:

$$\delta_{f_{C_4}} = (1 - x_1)\delta_i + x_1\delta_{p_{C_4}}, \quad (39)$$

$$\delta_{f_{C_3}} = (1 - x_2)\delta_i + x_2\delta_{p_{C_3}}, \quad (40)$$

$$\delta_{f_{C_r}} = (1 - x_3)\delta_i + x_3\delta_{p_{C_r}} \quad (41)$$

where  $\delta_{f_n}$  is the final (measured)  $\delta^{13}C$  value of the soil from the treatment,  $\delta_i$  is the initial (unknown)  $\delta^{13}C$  value of the soil prior to the start of the study, and  $\delta_{p_n}$  is the  $\delta^{13}C$  value of the residue added to the soil. Since the study started at some point, it is assumed that the initial  $\delta^{13}C$  content was the same for all treatments.  $x_n$  is the percentage of carbon derived from each plant material respectively.

Assume that in the rotation treatment the residue from two years was added every two years, so that:

$$\delta_{p_{C_r}} = \frac{m_3\delta_{p_{C_3}} + m_4\delta_{p_{C_4}}}{m_3 + m_4} \quad (42)$$

where  $m_n$  is the mass of the respective residue. Let  $z$  be the fraction of residue carbon of the  $\delta_{C_4}$  treatment.

$$z = \frac{m_4}{m_4 + m_3} \quad (43)$$

Then equation 42 can be expressed as:

$$\delta_{p_{C_r}} = z\delta_{p_{C_4}} + (1 - z)\delta_{p_{C_3}} \quad (44)$$

Assuming that the breakdown of each residue is independent of the other  $x_3$  can be expressed as:

$$x_3 = \frac{m_4 x_1 + m_3 x_2}{m_3 + m_4} \quad (45)$$

or using the  $z$  factor as above:

$$x_3 = z x_1 + (1 - z) x_2 \quad (46)$$

Equation 41 can be rearranged to isolate  $x_3$

$$\delta_{f_{C_r}} = \delta_i + (\delta_{p_{C_r}} - \delta_i) x_3 \quad (47)$$

Substituting equation 46 into equation 47

$$\delta_{f_{C_r}} = \delta_i + (\delta_{p_{C_r}} - \delta_i)(z x_1 + (1 - z) x_2) \quad (48)$$

results in three equations (40, 39, 48 with three unknowns  $x_1$ ,  $x_2$ , and  $\delta_i$ .

Rearranging equations 39 and 40 to isolate  $x_1$  and  $x_2$  respectively

$$x_1 = \frac{\delta_{f_{C_4}} - \delta_i}{\delta_{f_{P_4}} - \delta_i} \quad (49)$$

and

$$x_2 = \frac{\delta_{f_{C_3}} - \delta_i}{\delta_{f_{P_3}} - \delta_i} \quad (50)$$

Furthermore, since  $x_1$ ,  $x_2$ , and  $x_3$  are fractions:

$$0 \leq x_1 \leq 1 \wedge 0 \leq x_2 \leq 1 \wedge 0 \leq x_3 \leq 1 \quad (51)$$

this can provide a check for the results of the calculations.

By substituting equations 49, 50 and 44 into equation 48,  $\delta_i$  becomes the only unknown.

$$\delta_{f_{C_r}} = \delta_i + (z \delta_{p_{C_4}} + (1 - z) \delta_{p_{C_3}} - \delta_i) \left( z \frac{\delta_{f_{C_4}} - \delta_i}{\delta_{f_{P_4}} - \delta_i} + (1 - z) \frac{\delta_{f_{C_3}} - \delta_i}{\delta_{f_{P_3}} - \delta_i} \right) \quad (52)$$



TABLE 1. Crop rotation effects on the  $\delta^{13}C$  values in an eastern no-till Kansas Soil.

Depth cm	Soybean	Sorghum	Soybean
	Sorghum	Sorghum	Soybean
	$\delta^{13}C$		
0–5	-15.14	-14.75	-19.03
5–15	-14.68	-14.61	-16.25
15–30	-14.40	-14.66	-14.54
30–60	-14.28	-13.64	-14.49

Solving this for  $\delta_i$  yields a solution in the quadratic form:

$$\delta_i = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (53)$$

where

$$a = \delta_{f_{C_r}} + \delta_{f_{C_3}}(z - 1) - \delta_{f_{C_4}}z \quad (54)$$

$$\begin{aligned} b = & -\delta_{f_{C_r}}(\delta_{p_{C_3}} + \delta_{p_{C_4}}) + \delta_{f_{C_3}}(\delta_{p_{C_3}}(z - 1)^2 - \delta_{p_{C_4}}z^2 + \delta_{p_{C_4}}) \\ & + z(\delta_{f_{C_4}}(\delta_{p_{C_4}}z - \delta_{p_{C_3}}(z - 2)) - (\delta_{p_{C_3}} - \delta_{p_{C_4}})^2(z - 1)) \end{aligned} \quad (55)$$

$$\begin{aligned} c = & \delta_{f_{C_3}}\delta_{p_{C_4}}(z - 1)(-z\delta_{p_{C_3}} + \delta_{p_{C_3}} + \delta_{p_{C_4}}z) \\ & + \delta_{p_{C_3}}(\delta_{f_{C_r}}\delta_{p_{C_4}} + \delta_{f_{C_4}}z(\delta_{p_{C_3}}(z - 1) - \delta_{p_{C_4}}z)) \end{aligned} \quad (56)$$

After calculating a value of  $\delta_i$ , the values for  $x_1$ ,  $x_2$  and  $x_3$  can be determined from equations 39, 40, and 41 and checked against equation 51. It appears that it is the positive version of equation 53 is the one that provides realistic estimates of  $\delta_i$ . Figure 1 shows the effect of changing the final  $\delta^{13}C$  value on  $\delta_i$ . All of the other parameters have the same value as in the next example.

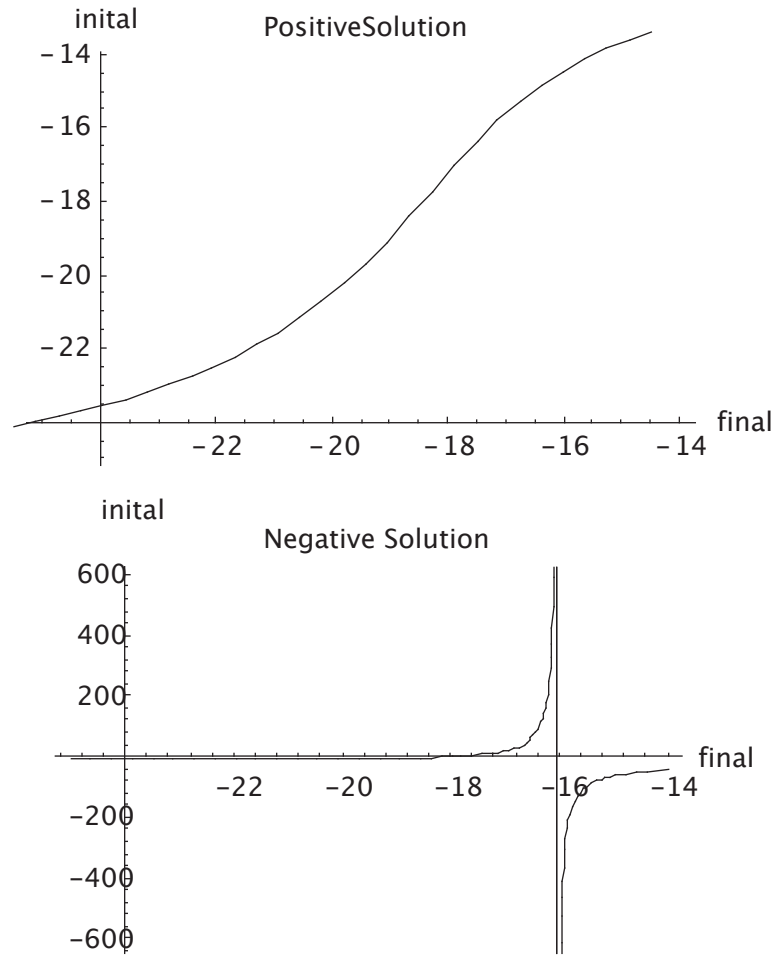


FIGURE 1. Effect of the final  $\delta^{13}C$  value on the calculated initial  $\delta^{13}C$  value.

TABLE 2. Values of the model coefficients estimated from an eastern Kansas soil.

Depth (cm)	$x_3$	$x_2$	$x_1$	$\delta_i$	$\delta_{p_{C_r}}$
0-5	0.11	0.32	0.018	-14.7	-18.2
5-15		No solution			-18.2
15-30		No solution			-18.2
30-60	0.16	0.065	0.19	-13.5	-18.2

To illustrate the procedure  $\delta^{13}C$  are set to values of the surface layer (0-5 cm) sampled (from Table 1). The average residue inputs were 2.4 Mg ha<sup>-1</sup> for the soybean, and 5.8 Mg ha<sup>-1</sup> for the sorghum (Peterson, 1983). If we assume that the sorghum had an average  $\delta^{13}C$  value of -14 and the soybean is -28 (O'Leary, 1988; Smith and Epstein, 1971).

$$\begin{array}{lll}
 z = 0.7 & \delta_{f_{C_4}} = -14.75 & \delta_{f_{C_3}} = -19.03 \\
 \delta_{f_{C_r}} = -15.14 & \delta_{p_{C_4}} = -14 & \delta_{p_{C_3}} = -28
 \end{array}$$

Ignoring equation 51 the solutions are:

the "positive" solution

$$x_3 = 0.11 \quad x_2 = 0.32 \quad x_1 = 0.018 \quad \delta_i = -14.8 \quad \delta_{p_{C_r}} = -18.2$$

and the "negative" solution

$$x_3 = 1.07 \quad x_2 = 1.28 \quad x_1 = 0.98 \quad \delta_i = -59.2 \quad \delta_{p_{C_r}} = -18.2$$

Applying equation 51 shows that the "positive" solution is the desired one. Table 2 shows the estimated values for the remaining depth using the values from Table 1.

TABLE 3. Sensitivity of the model to changes in the parameters

Parameter	positive solution	negative solution
$\delta_{fC_4}$	0.271547	-22.0116
$\delta_{fC_3}$	-0.0309746	-13.9842
$\delta_{fC_r}$	0.908158	34.847
$\delta_{pC_4}$	-0.117466	-4.45435
$\delta_{pC_3}$	-0.0312644	6.60308
z	-2.34045	-89.8057

Table 3 shows the sensitivity of solution (1) to changes in the parameters when the input parameters are the ones given earlier. They were obtained by taking the first derivative of the model with respect to the parameter. It is obvious that the “negative solution” is much more sensitive than the “positive solution”. It also shows that the equation is most sensitive to the estimate of z, that is the relative proportion of the residue inputs. Without good harvest records this number would be difficult to estimate accurately.

#### 4. Methods

Soil from a long-term tillage/crop rotation experiment was used for this study. The study site was located on the Ashland Experimental station in Riley county (in north-eastern Kansas). The site was established in 1975. Site characteristics and management have been described previously (Havlin et al., 1990). In brief, grain sorghum [*Sorghum bicolor* (L.) Moench] and soybean [*Glycine max* (L.) Merr.] were grown continuously and in rotation on a Muir silt (fine-silty, mixed, mesic Cumulic Haplustoll). The experiment was a split-plot design with four replications. Main plots were crop rotation and sub-plots were tillage.

Soil cores were taken with a hand-held Oakfield sampler on June 12, 1996. Surface residue was removed before sampling. No attempt was made to remove plant residue after the soil was sampled. Soil cores were separated into 0–5 cm (20 cores), 5–15 cm (15 cores), 15–30 cm (10 cores), and 30–60 cm (5 cores) increments. The samples

were dried at 40°C and ground in a roller bar mill. Soil from the no-till plots was used for the isotope analysis, while soil from all of the plots were used for total carbon and nitrogen analysis. The carbon isotope ratio was determined by combustion, chromatographic separation and analysis in a single inlet mass-spectrometer (Europa Scientific, Crewe, UK). Total carbon and nitrogen was determined by combustion, chromatographic separation and analysis on a automated CN-analyzer (Carlo-Erba, Milan, Italy). Since the soil pH was  $< 7$  (Havlin et al., 1990), it was assumed that the carbon measured was organic carbon.

TABLE 4. Crop rotation and tillage effect on soil organic C and N content in an eastern Kansas soil.

Tillage	Depth cm	Organic N				Organic C			
		Soybean Sorghum	Soybean Sorghum	Soybean Sorghum	Soybean Sorghum	Soybean Sorghum	Soybean Sorghum	Soybean Sorghum	Soybean Sorghum
		$\text{g kg}^{-1}$							
CT	0-5	1.57	1.52	1.25	15.35	16.13	10.46		
	5-15	1.24	1.24	1.12	12.00	11.78	10.31		
	15-30	1.19	1.17	1.00	12.06	10.93	10.04		
	30-60	0.99	1.14	1.02	9.35	10.31	9.50		
NT	0-5	1.84	1.96	1.54	18.77	20.16	14.06		
	5-15	1.26	1.28	1.14	12.33	12.30	10.92		
	15-30	1.16	1.14	1.13	11.17	10.74	10.24		
	30-60	1.02	1.12	1.06	9.83	10.41	9.56		

## 5. Discussion

Using the method of plotting the  $\delta^{13}C$  value against the reciprocal of the carbon content (Balesdent et al., 1988) with the soybean and sorghum data an initial  $\delta^{13}C$  value of -15.1 was calculated (Figure 2). This value is lower than that obtained by the proposed method. However the range of organic carbon is smaller in these samples, than in the samples used by Balesdent et al. (1988), resulting in a larger uncertainty in estimating the slopes of the lines and consequently the intersection. Moreover, since the  $\delta^{13}C$  value of the residue is much different from the  $\frac{1}{C}$  values, the estimate of the  $\delta^{13}C$  value of the residue has a large effect on the slope of the line and the estimate of the initial soil  $\delta^{13}C$  value. Since only the surface soil shows a significant shift in the  $\delta^{13}C$  value, little additional information is gained from the lower depths.

Table 2 shows the estimated values of the model parameters for the different depths of the no-till plots at the study site. Estimated  $\delta_i$  values ranged from -13.5 to -14.7. Since the  $\delta^{13}C$  value for the rotation in the 15–30 cm depths was higher than the corresponding value from the  $C_4$  treatment no solution satisfying equation 51 could be found, in the 5–15 cm depth the  $\delta^{13}C$  values decrease in the order Soybean/soybean ; Soybean/Sorghum ; Sorghum/Sorghum, yet unless the  $\delta^{13}C$  difference between Soybean/Sorghum and Sorghum/Sorghum is at least 0.15 a negative value will be calculated for the carbon fraction derived from the sorghum. One assumption that could cause this effect is that  $z$  was held constant with depth. It may be that the proportion of  $C_3$  and  $C_4$  carbon added to the surface was different from the proportion of  $C_3$  and  $C_4$  carbon added in the lower layers of the soil, possibly due to differences in the rooting structures of the plants. Changing  $z$  from 0.7 to 0.8 resulted in  $x_n$  fractions that satisfied equations 51. Since the soil is mostly  $C_4$  carbon the equation 39 is not applicable since the mixing model can only distinguish  $C_3$  from  $C_4$  carbon and not old  $C_4$  carbon and new  $C_4$  carbon.

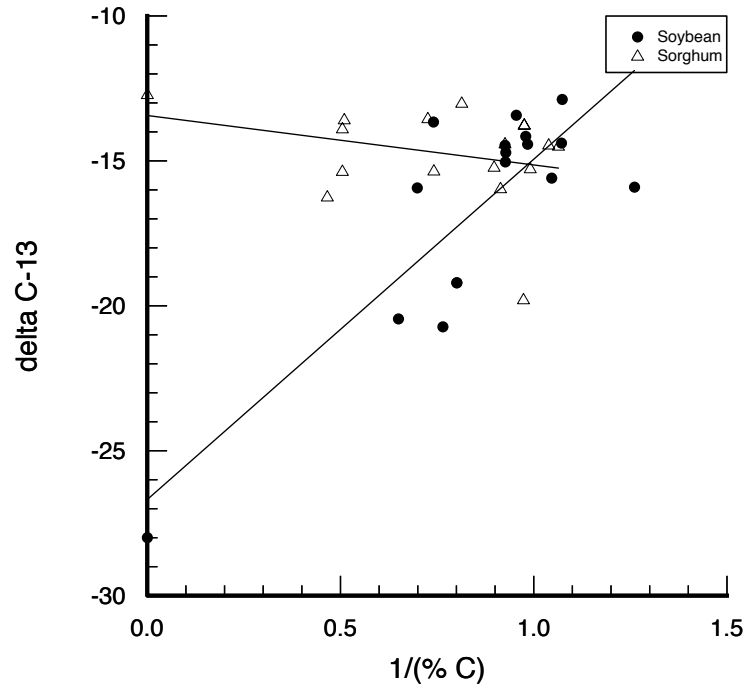


FIGURE 2. Relationship between  $\delta^{13}C$  and the reciprocal of the carbon content in the soils from the continuous soybean and the continuous sorghum treatment.



Table 1 shows the  $\delta^{13}C$  values from the no-till plots at the study site. It shows the increase in  $\delta^{13}C$  values in the  $C_3$  treatment as opposed to the  $C_4$  treatment. It also shows the decrease in  $\delta^{13}C$  values with depth. Since the plots are no-till new carbon is added mainly at the surface, while less carbon is incorporated in the deeper layers. The calculated initial  $\delta^{13}C$  value of -13.5 – -14.7 is similar to the  $\delta^{13}C$  values at the 30–60 cm depth.

Since the initial  $\delta^{13}C$  value  $\delta_i$  indicates that the soil carbon is composed mostly of  $C_4$  carbon only 40 can be used to estimate the amount of carbon contributed by the soybean. It is not possible to distinguish old  $C_4$  carbon from new  $C_4$  carbon. The estimated fraction of  $C_3$  plant carbon in the soil ranges from 32% at the surface to 6% in the 30–60 cm depth. This means that in the surface layer, 32% of the carbon in the soybean treatment was deposited since 1975. Taking the values for the no-till surface from Table 4 this would work out to about 4.5 Mg ha<sup>-1</sup> of new carbon in the soybean treatment,. For the soybean treatment about 48 Mg ha<sup>-1</sup> of residue has been deposited in the last 20 years. Only 4.5 Mg ha<sup>-1</sup> is currently left in the soil. So about 90% of the added residue has been lost as CO<sub>2</sub>, and 10% is incorporated into the soil organic matter.

Twenty years of cropping increased the carbon and nitrogen content of the soil planted to continuous sorghum compared to soil planted to continuous soybean. The average carbon content was 12.8 g kg<sup>-1</sup> in the continuous sorghum, 12.6 g kg<sup>-1</sup> in the rotation, and 10.6 g kg<sup>-1</sup> in the soybean treatment. The average nitrogen content was 1.32, 1.28 and 1.15 kg kg<sup>-1</sup> respectively.

Havlin et al. (1990) sampled the same fields in 1986, but they sampled in different increments (0-2.5 cm, 2.5-7.5 cm, 7.5-15 cm and 15-30 cm). To compare the results, the top three depths were averaged and compared to the average of the top two depths of the current study using the bulk densities reported by McVay et al. (2006). The comparison shows that in the 0-15 cm layer in conventional tillage treatment, the carbon content of the continuous soybean plot decreased 1.5 Mg ha<sup>-1</sup> from 20.3 to

TABLE 5. Analysis of variance of the crop rotation and tillage effects on soil organic C and N in and eastern Kansas soil.

ANOVA	df	Organic N	Organic C
		$P > F$	$P > F$
Depth	3	0.0001	0.0001
Rotation	2	0.0001	0.0001
Rotation(Tillage)	3	0.0034	0.0696
Rotation * Depth	6	0.0105	0.0012
Rotation(Tillage) * Depth	9	0.0028	0.0609

18.8 Mg ha<sup>-1</sup> between 1986 and 1996, while the carbon content of the continuous sorghum plots increased slightly (0.1 Mg ha<sup>-1</sup> from 23.9 g to 34 Mg ha<sup>-1</sup>). In the 15-30 cm layer the continuous soybean treatment gained 0.8 Mg C ha<sup>-1</sup> while the continuous sorghum treatment lost 0.1 Mg C ha<sup>-1</sup>

In the 0-15 cm layer of the no-till plots, the carbon content increased by 0.6 Mg ha<sup>-1</sup> from 22.9 to 23.5 Mg ha<sup>-1</sup> on the continuous soybean plots, and 3.2 Mg ha<sup>-1</sup> from 26.1 to 29.3 Mg ha<sup>-1</sup> on the continuous sorghum plots. In the 15-30 cm layer the no-till plots gained 0.5 Mg C ha<sup>-1</sup> on the continuous soybean treatment and 0.3 Mg C ha<sup>-1</sup> on the continuous sorghum treatment.

Higher soil organic carbon and nitrogen in rotation with sorghum is related to the higher residue input on the sorghum treatment (Havlin et al., 1990). However the correlation coefficient was reduced from 0.99 in 1986 to about 0.85 in 1996.

The proposed method works best when the difference between the initial  $\delta^{13}C$  and the final  $\delta^{13}C$  are fairly large. In our case the estimate of the initial  $\delta^{13}C$  appears to be reasonable, but there is no way to confirm it.

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