

Temporal and Spatial Patterns of Nitrate in a Claypan Soil

F. Ghidey* and E. E. Alberts

ABSTRACT

The temporal and spatial patterns of $\text{NO}_3\text{-N}$ were studied on a 35-ha field located in the claypan soil region of north-central Missouri. Soil samples were collected from the 0- to 5-, 5- to 10-, and 10- to 15-cm depths and were analyzed for $\text{NO}_3\text{-N}$ concentrations. Surface water samples from the field were collected for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ analysis during each surface runoff event. Groundwater samples were also taken from the field wells four times a year for 5 yr and analyzed for $\text{NO}_3\text{-N}$ concentrations. The effects of topography, depth to claypan, soil pH, organic matter (OM) content, cation exchange capacity (CEC), and soil water content on the spatial distribution of $\text{NO}_3\text{-N}$ concentration were also evaluated. Nitrate-N concentration in the 0- to 5-cm soil depth increased in the first few weeks following application, then decreased rapidly and was very low at harvest. During the study period, nitrate movement below the layer of fertilizer application was very low, and <5% of the total N applied in the soil was lost to surface runoff. Nitrate-N concentration in groundwater samples decreased by an average of $0.40 \text{ mg L}^{-1} \text{ yr}^{-1}$ from 1992 to 1996. The semivariograms did not exhibit strong spatial dependency except for the samples collected 1 and 4 wk after fertilizer applications in 1993 and 1995, respectively. Nitrate-N concentration was poorly correlated to soil water content and depth to claypan and relatively strongly correlated to elevation and soil pH.

CLAYPAN SOILS occupy about 4 million ha in Missouri and Illinois and are primarily found within Major Land Resource Area (MLRA) 113. Claypan soils have a unique hydrology characterized by the impedance of vertical soil matrix water flow by a restrictive clay layer (Jamison et al., 1968). Regions with claypan soils have been identified as potentially vulnerable areas for pesticide and nutrient contamination of surface water because runoff and soil losses from these regions are relatively high during the seedbed preparation period when agrichemicals are applied (Ghidey and Alberts, 1996). Previous studies indicate the application of herbicides and nutrients in Midwest claypan soils influence surface water quality more than groundwater quality (Burkhardt and Koplín, 1993; Blanchard et al., 1995). In the Midwest claypan soil, chemical loss to surface runoff was critical for the runoff events that occurred within 1-mo following application (Ghidey and Alberts, 1998).

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Determining the variability of agrichemicals and soil properties is important to efficiently manage crop inputs (particularly herbicides and fertilizer) and thus reduce the loss of excess chemicals to runoff and/or leaching. It encourages the use of site-specific crop management, which can improve production efficiency by adjusting crop treatments to the local conditions in the field (Birrell et al., 1993). A number of studies have been conducted to evaluate the spatial variability of soil properties (Sudduth et al., 1995; Cambardella et al., 1994; Lascano and Hatfield, 1992; Gajem et al., 1981) and pesticide distribution (Wood et al., 1987; Rao and Wagenet, 1985). Sudduth et al. (1995) reported considerable variability in water holding capacity, soil nutrients, soil pH, claypan characteristics, crop growth, and yield within fields and plots located in claypan soil areas. However, the spatial distribution of $\text{NO}_3\text{-N}$ and the effect of soil properties such as OM content, CEC, and soil pH on the variability of $\text{NO}_3\text{-N}$ within these fields and plots have not been studied.

Soil samples are usually studied by taking samples on some grid or other pattern with the assumption that properties measured at a point also represent the unsampled neighborhood. The extent to which this assumption is true depends on the degree of spatial dependence that exists among samples (Yost et al., 1982). Geostatistics, specifically the use of semivariograms and kriging, is a useful tool to quantify the spatial variability of soil properties (Burgess and Webster, 1980a,b; Vieira et al., 1981). Semivariograms are useful for analyzing spatial variability and are needed for kriging. Kriging is an optimal linear interpolation method used to predict values at unsampled locations by appropriately weighing the known values through the use of variograms (Tabor et al., 1984). This method of analysis can be used to prepare maps of predicted values along with variance estimates for each site.

The objectives of this study were to: (i) study the temporal and spatial variations in $\text{NO}_3\text{-N}$ concentration in a claypan soil; (ii) evaluate the correlation between topography, depth to claypan, soil pH, CEC, OM content, and soil water content with $\text{NO}_3\text{-N}$ concentration in the soil; and (iii) determine the loss of nitrates due to surface runoff.

Abbreviations: OM, organic matter; CEC, cation exchange capacity; MLRA, Major Land Resource Area; LOI, loss of weight on ignition; EM, electromagnetic induction; UAN, urea ammonium nitrate.

MATERIALS AND METHODS

The study was conducted on a 35-ha field-size watershed (Fig. 1) located in the Goodwater Creek Watershed, a 7250-ha agricultural area in north-central Missouri. Predominant soils are Udollic Ochraqualfs and Albaquic Hapludalfs of the Mexico and Adco series, respectively. Adco silt loam soil occupies about 70% of the study area. Claypan soils are considered poorly drained, partially because of an argillic claypan horizon located 10 to 120 cm below the surface. The clay content of the argillic horizon is generally >50% and is primarily montmorillonite.

The study area was farmed using a high chemical input minimum-till corn-soybean [*Zea mays* L.–*Glycine max* (L.) Merr.] rotation with the goals of maximizing grain yield and profit. During the 5-yr period (1992–1996), the area was cropped as soybean, corn, soybean, grain sorghum [*Sorghum bicolor* (L.) Moench], and soybean. In 1995, due to high rainfall during the planting period, it was not possible to plant corn. Instead, the study area was cropped to grain sorghum. Nitrogen (as UAN) was applied at the rate of 180 kg ha⁻¹ and 123 kg ha⁻¹ in 1993 and 1995, respectively. No N was applied during the years that soybean was grown. The fertilizer was broadcast and incorporated with a field cultivator before planting.

The area was divided into 36 (80 m by 120 m) equally spaced cells, and soil samples were collected from within each cell to a depth of 0- to 5-cm in 1993 and 0- to 5-, 5- to 10-, and 10- to 15-cm in 1995. Initial samples were collected before fertilizer application. Additional samples were collected 3 d, 1 wk, 2 wk, 4 wk, and 8 wk following application in 1993 and 1 wk, 4 wk, and 8 wk after application in 1995. Samples were also taken after harvest.

Soil samples (0- to 5-cm depth) were collected using a 2.5-cm diameter probe. Eight subsamples were taken from the ridges and furrows around each grid point (the distance between the subsamples was <10 cm) and were mixed and wrapped in aluminum foil. Samples were frozen before being sent to the USDA-ARS National Soil Tillage Laboratory at Ames, IA, for NO₃-N concentration and soil water content analysis. Soil samples were extracted with 2 M KCl and filtered for NO₃-N analysis. Nitrate was determined by reduction using copperized cadmium column and dioxidation of nitrite with *N*-(1-naphthyl) ethylenediamine dihydrochloride with a Lachat flow injection system (Lachat Instruments, WI¹).

Soil samples (0- to 5-cm depth) were also taken from each cell to determine soil pH, cation exchange capacity (CEC), and organic matter (OM) content. Soil samples taken from the study area in 1993 (Birrell et al., 1993) and in 1995 (Drummond et al., 1995) did not display different spatial trends for the individual soil parameters. Hence, samples for pH, CEC, and OM content analysis were taken once from each cell 6 wk after planting in 1995. Soil OM content was determined by loss of weight on ignition (LOI) method (Brown and Rodriguez, 1983). Depth to claypan was estimated at the grid points using the electromagnetic induction (EM) method described by Doolittle et al. (1994). Detailed topographic data for the field were obtained using a total station surveying instrument and standard mapping procedure. Geostatistics (semivariogram and kriging) was applied to the topographic data to estimate elevations within 10-cm cell size. Descriptive statistics of the above soil parameters are presented in Table 1.

¹ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

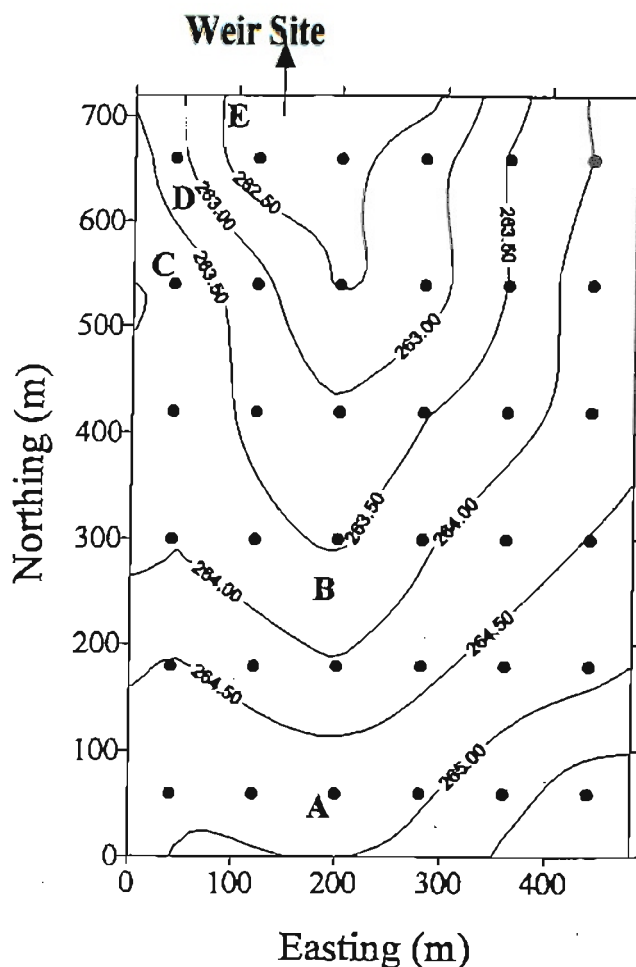


Fig. 1. Topographic map of the field. Soil sampling locations are superimposed on the contour map. Letters A, B, C, D, and E represent the locations of the groundwater Nests A through E. Contour elevation lines are shown in meters (drainage area = 35 ha).

The outlet of the area was instrumented with a concrete v-notch weir, water stage recorder, and a refrigerated pumping sampler to measure runoff and collect runoff samples for chemical analysis. The sampler automatically starts collecting when flow over the weir is significant and continues to sample until the end of the runoff period. The samples were stored in a refrigerated cabinet until transported back to the laboratory. Samples were filtered through 0.45-micron nylon filters within 48 h and analyzed for NO₃-N and NH₄-N using QuikChem method 10-107-04-1-A and 10-107-06-2-C, respectively, on a Lachat flow analyzer. Nitrate was measured colorimetrically by reduction to nitrite using Cd column and continuous flow autoanalyzer. The detection limit for the Cd reduction method was 0.05 N mg L⁻¹. The ammonia method was based on heating ammonia with salicylate and hypochlorite in an alkaline phosphate buffer to produce an emerald green color, which is proportional to the ammonia concentration.

The study area was also instrumented with five groundwater well nests with 3 to 4 wells in each nest (Fig. 1). The wells within each nest were within close proximity of each other with the total nest encompassing about 25 m². The wells within each nest were drilled and screened at different depths. Screened intervals were 1.2 m and ranged from the top of the glacial till (2.9 m) to the bottom of the glacial till (15.7 m). Water samples were collected quarterly (March, June, September, and December) and analyzed for NO₃ concentrations using the same procedure used for surface water samples.

Table 1. Descriptive statistics for parameters correlated with NO₃-N concentrations (0- to 5-cm depth). Values are mean of 36 samples.

Parameter	Minimum	Maximum	Mean	SD†	CV‡
Soil pH	5.40	7.20	6.68	0.08	7.62
CEC	6.00	18.40	7.63	0.18	14.42
OM	1.70	2.50	2.13	0.04	10.81
Elevation, m	262.1	265.8	263.9	0.14	0.32
Depth to claypan, cm	14.14	112.8	43.99	28.6	39.05
Soil water content, m m ⁻¹	14.8	20.6	18.0	1.43	8.1
1993 3 d	19.3	20.6	22.3	1.89	8.5
1 wk	13.0	19.5	16.1	1.82	11.3
4 wk	12.5	25.2	17.5	3.02	17.3
8 wk after harvest	19.3	25.2	22.2	1.39	6.3
1995 1 wk	12.5	20.2	16.5	1.84	11.2
4 wk	12.5	18.1	15.2	1.66	10.9
8 wk harvest	12.0	23.0	16.4	2.23	13.7
	16.9	22.6	19.4	1.23	11.0

† Standard deviation.

‡ Coefficient of variation.

Geostatistical Software (GS⁺, Gamma Design Software, St. Plainwell, MI) was used to quantify the spatial variability of NO₃-N concentrations in the soil profile. Data transformation before semivariogram calculation was not required because the frequency distribution of the soil NO₃-N concentrations data showed to have normal distribution. Semivariograms were constructed based on the semivariances obtained from the equation:

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

where γ is the semivariance, n is the number of sample pairs at each distance interval (h), and $Z(x)$ is the value for the variable at field location (x).

A nonlinear regression was used to obtain the best approximation semivariogram parameters (nugget, sill, and range). Linear, linear-sill, spherical, exponential, and gaussian models were examined, and the model with the lowest residual sum of squares and largest coefficient of determination (r^2) was chosen. Cambardella et al. (1994) used the nugget/sill ratio to define distinct classes of spatial dependence. If the ratio were $\leq 25\%$, the variable was considered strongly spatial dependent; if the ratio were between 25 and 50%, the variable was considered moderately spatially dependent; if the ratio were $> 75\%$, the variable was considered weakly spatially variable. This method of classification was used to determine the degree of spatial variability in NO₃-N concentration within the field during the sampling periods. Once the appropriate model was selected, the estimated semivariogram parameters were used to produce contour maps using blocked kriging. The kriged maps provide better visualization of the spatial distribution of NO₃-N and soil properties (soil pH, OM content, and CEC) within the field.

RESULTS AND DISCUSSION

Rainfall Characteristics

Daily precipitation and runoff measured from the study area during the 1993 and 1995 growing seasons are presented in Fig. 2. Annual precipitation in 1993 and 1995 for the study area was 1343 and 1150 mm, respectively. The 53-yr mean annual precipitation measured near the field at Centralia, MO, is 900 mm. Annual surface runoff accounted for 40 and 33% of the annual precipitation in 1993 and 1995, respectively. The amount of runoff that occurred during the 2-mo period following fertilizer application was 12 and 29% of the annual

runoff in 1993 and 1995, respectively. This period is considered to be critical for chemical loss to surface runoff.

Nitrate-Nitrogen and Ammonium-Nitrogen Concentrations in Surface Runoff

Nitrate-N and NH₄-N concentrations in surface runoff during the study period are shown in Table 2. For the runoff events before fertilizer application in 1993 and 1995, NO₃-N and NH₄-N concentrations in runoff were very low or nondetectable. In 1993, 3 d after fertilizer application, about 32.3 mm of rain and 1.8 mm of runoff were measured from the area, and the concentration in runoff was very high (36.9 mg L⁻¹ for NO₃-N and 19.4 mg L⁻¹ for NH₄-N). Three weeks later about 38.4 mm of rain and 13.6 mm of runoff were measured; and NO₃-N concentrations were still high (27.1 mg L⁻¹), but NH₄-N concentration was very low (< 2.5 mg L⁻¹). Nitrate-N and NH₄-N concentrations in surface runoff were very low or nondetectable within 8 and 6 wk after fertilizer application, respectively. Throughout the growing season, about 5711 g ha⁻¹ (4036 g ha⁻¹ NO₃-N and 675 g ha⁻¹ NH₄-N) of total N was lost to runoff, representing 3.2% of that applied as fertilizer. More than 85% of the total loss occurred within the first 3 wk of application. In 1993, NO₃-N concentration in surface runoff water exceeded the current drinking water standards (10 mg L⁻¹) for all the events that occurred within 3 wk of fertilizer application.

In 1995, approximately 40, 3, 18, and 8 mm of runoff were measured from the drainage area after 10, 11, 12, and 13 d of fertilizer application, respectively (Table 2). During these events, NO₃-N and NH₄-N concentrations in runoff were low (< 8 mg L⁻¹ for NO₃-N and < 3 mg L⁻¹ for NH₄-N). The next runoff event occurred 7 wk after chemical application. Nitrate-N concentration was similar to those measured from the previous runoff events (6 mg L⁻¹), and NH₄-N concentration was nondetectable. Throughout the growing season, about 6827 g ha⁻¹ (5534 g ha⁻¹ NO₃-N and 1293 g ha⁻¹ NH₄-N) of total N was lost to runoff, representing 5.6% of that applied as fertilizer. In 1995, because of the large rainfall events that occurred within 2 wk after fertilizer application, NO₃-N concentration in all the runoff events did

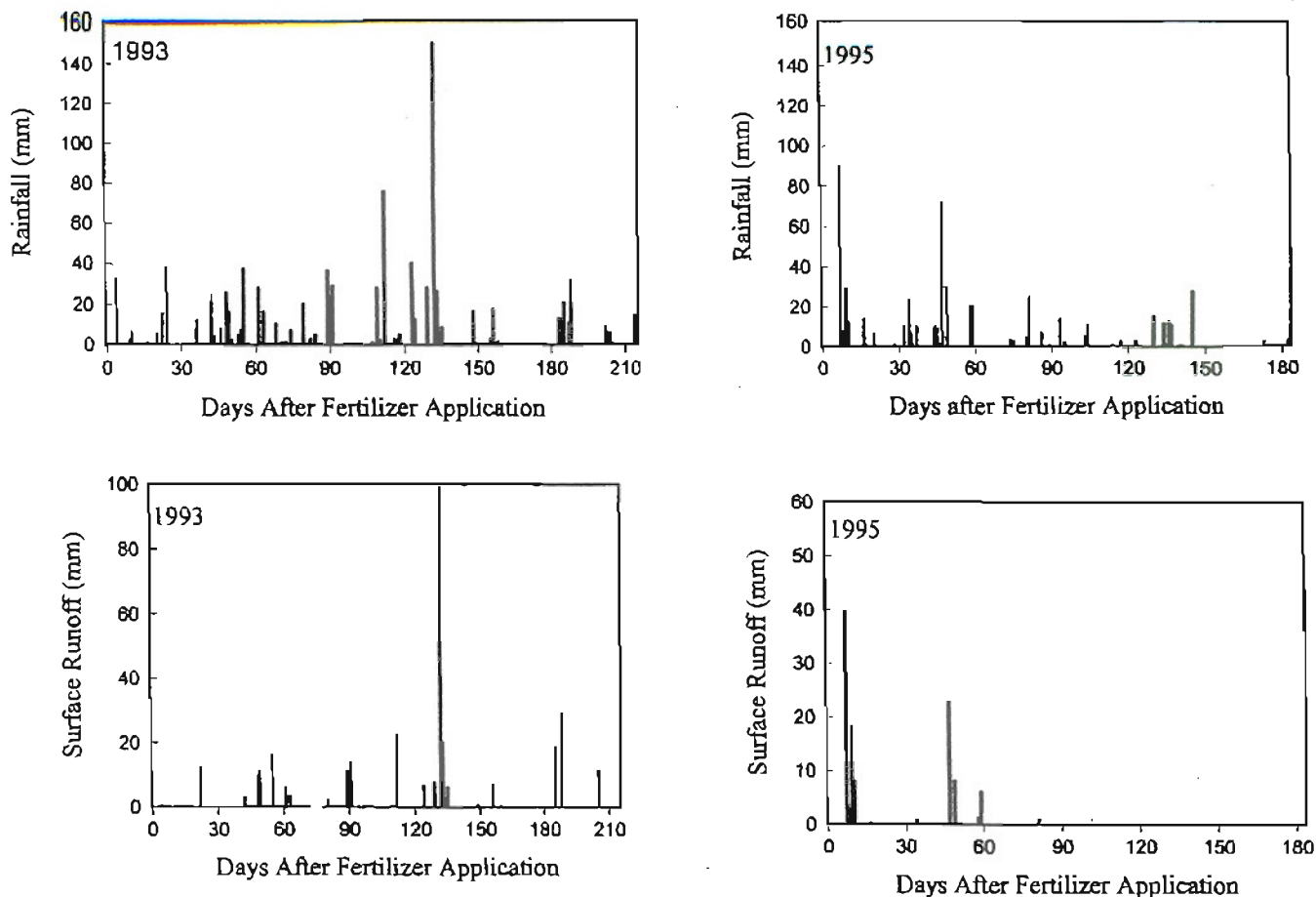


Fig. 2. Daily rainfall and runoff measured during the 1993 and 1995 growing seasons.

not exceed the current drinking water standard (10 mg L^{-1}).

Both in 1993 and 1995, the total N loss to runoff water was $<6\%$ of that applied as fertilizer. Although $\text{NO}_3\text{-N}$ concentration in runoff exceeded current drinking water standards in the first few events following fertilizer application, in this study surface runoff was not an important process to explain the temporal decrease in $\text{NO}_3\text{-N}$ concentration in the top soil layer.

Temporal Variability and Distribution of Nitrate-Nitrogen in the Soil Profile

Soil $\text{NO}_3\text{-N}$ concentrations measured in the top 5 cm during the 1993 growing season are presented in Fig. 3. For samples taken 1 wk before fertilizer application, $\text{NO}_3\text{-N}$ was found in all 36 samples with concentrations ranging from 0.8 to 5.2 mg kg^{-1} . The next soil samples were taken 3 d after fertilizer application, and the mean $\text{NO}_3\text{-N}$ concentration was 36.73 mg kg^{-1} . The concentration increased until 4 wk after application mainly due to conversion of $\text{NH}_4\text{-N}$ into $\text{NO}_3\text{-N}$ at a higher rate than that lost to runoff, leaching, or plant uptake. After Week 4, $\text{NO}_3\text{-N}$ started to decrease dramatically, probably from N uptake by the corn plants. Nitrate-N concentrations measured 8 wk after application were 27 mg kg^{-1} as compared with 72 mg kg^{-1} measured at 4 wk. After harvest, only 1.67 mg kg^{-1} of $\text{NO}_3\text{-N}$ was detected in the top 5-cm of the soil.

In 1995, soil $\text{NO}_3\text{-N}$ concentrations were measured in the 0- to 5-, 5- to 10-, and 10- to 15-cm depth increments (Fig. 4). For soil samples taken 1 wk before fertilizer application, $\text{NO}_3\text{-N}$ was found in all the samples, and the concentrations ranged from 1.8 to 15.0 mg kg^{-1} . There were no significant ($p < 0.05$) differences in the mean $\text{NO}_3\text{-N}$ concentrations measured among the three layers. The second set of soil samples was taken 1 wk after fertilizer application, and the mean concentration in the 0- to 5-cm depth was 64.2 mg kg^{-1} . The mean $\text{NO}_3\text{-N}$ concentrations at the 5- to 10- and 10- to 15-cm depths were 9.2 and 4.7%, respectively, of that measured in the top layer. For the soil samples collected 4 wk after fertilizer application, $\text{NO}_3\text{-N}$ concentrations in the top layer slightly increased. Nitrate-N concentrations also slightly increased in the subsoil layers compared with the previous sampling period; however, concentration in the subsoil was still much lower than the concentration in the top layer. For the samples collected 8 wk after application, $\text{NO}_3\text{-N}$ concentration in the top layer was 9 mg kg^{-1} as compared with 70 mg kg^{-1} measured at 4 wk. Concentrations in the 5- to 10- and 10- to 15-cm soil depths were lower than those measured in the previous sampling period and were still appreciably lower than the concentrations measured from the top layer.

Nitrate-N concentrations in the soil below 15-cm depth were not measured in this study; however, soil

Table 2. Nitrate-N and $\text{NH}_4\text{-N}$ concentrations and loading in surface runoff.

Date	Days after applic.	Rainfall		Runoff		$\text{NO}_3\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{NH}_4\text{-N}$
		mm				mg L^{-1}	g ha^{-1}	mg L^{-1}	g ha^{-1}
10 May 1993	-4	23.9	7.0	0.4	28.0	0.0	0.0		
17 May 1993	3	32.3	1.8	36.9	665.2	19.4	349.7		
6 June 1993	23	38.4	13.6	27.1	3691.0	2.3	313.3		
24 June 1993	41	29.2	3.0	8.3	249.4	0.4	12.0		
7 July 1993	54	38.4	18.0	1.7	306.5	0.0	0.0		
13 July 1993	60	28.5	6.7	1.0	67.1	0.0	0.0		
10 Aug. 1993	88	36.8	12.4	0.2	28.4	0.0	0.0		
2 Sept. 1993	111	50.6	25.1	0.0	0.0	0.0	0.0		
17 May 1995	-29	67.1	52.3	0.0	0.0	0.0	0.0		
25 June 1995	10	89.9	39.8	6.0	2391.5	2.2	876.9		
26 June 1995	11	7.8	3.0	7.7	231.3	2.2	66.1		
27 June 1998	12	29.2	18.4	6.5	1197.8	1.9	350.1		
28 June 1995	13	12.7	8.1	4.0	324.5	0.0	0.0		
4 Aug. 1995	50	72.0	22.8	6.0	1370.0	0.0	0.0		
17 Aug. 1995	60	20.3	6.2	0.3	18.6	0.0	0.0		

cores were taken from plots near the field after harvest in 1994, and $\text{NO}_3\text{-N}$ concentrations in the 0- to 30- and 30- to 60-cm depth intervals were measured. Mean $\text{NO}_3\text{-N}$ concentrations from plots under a farming system similar to the field study (fertilizer was applied at the rate of 180 kg ha^{-1}) were 15.5 and 5.7 mg kg^{-1} , for the 0- to 30- and 30- to 60-cm depth intervals, respectively. Similar results were also observed from plots where fertilizer was applied at the rates of 134 and 224 kg ha^{-1} . In general, concentrations in the top 30-cm of soil were almost three times higher than in the lower 30 cm.

Because claypan soils are characterized by preferential flow paths, $\text{NO}_3\text{-N}$ movement through the rootzone area could be much higher than that observed in the soil samples. Kitchen et al. (1998) measured water and chemical movement through the root zone using lysimeters from plots located near the study area. They found that leaching losses of $\text{NO}_3\text{-N}$ (1992–1996) from plots under a farming system similar to our field study were $<10\%$ of the fertilizer applied. The extent of leaching, however, varied greatly between plots under the same farming system, which was probably due to variability in preferential flow paths.

Water samples collected from 1992 through 1996 from

wells located in the field showed only small changes in $\text{NO}_3\text{-N}$ concentrations (Kitchen et al., 1997). Nitrate-N concentrations in groundwater measured from the top glacial till (2.9 m depth) of the nested wells (Fig. 1) from 1992 through 1996 are presented in Fig. 5. The mean (average of four quarterly samples) $\text{NO}_3\text{-N}$ concentrations in 1992 were 9.66 , 3.42 , 4.94 , 3.04 , and 2.82 mg L^{-1} for nests A, B, C, D, and E, respectively. The reason for higher $\text{NO}_3\text{-N}$ concentration in Nest A was unclear. The mean $\text{NO}_3\text{-N}$ concentration in 1996 (after 5 yr under corn-soybean rotation) were 6.76 , 1.90 , 3.08 , 3.94 , and 3.74 mg L^{-1} for Nests A, B, C, D, and E, respectively. Compared with the initial (1992) values, concentrations in Nests A, B, and C decreased by 30, 44, and 38%, whereas concentrations in Nests D and E increased by 30 and 33%, respectively. Averaged over wells and years, NO_3 concentration was 4.46 mg L^{-1} . Relative annual changes in concentrations during the 1993 to 1996 period with respect to the initial (1992) concentration are presented in Fig. 6. Averaged over wells, relative annual changes in $\text{NO}_3\text{-N}$ concentrations were $+0.28$, -0.29 , -0.70 , and -0.90 mg L^{-1} in 1993, 1994, 1995, and 1996, respectively. Averaged over years and wells, $\text{NO}_3\text{-N}$ concentration in the groundwater de-

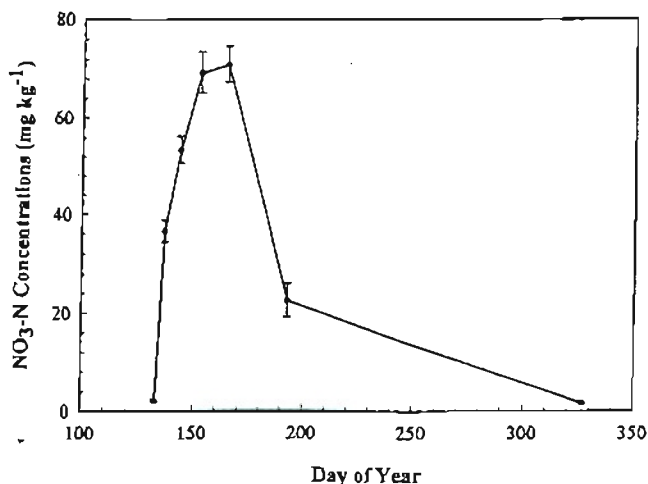


Fig. 3. Nitrate-N concentration in the 0- to 5-cm soil depth measured in 1993. Each point is a mean of 36 samples. The vertical bars are standard errors.

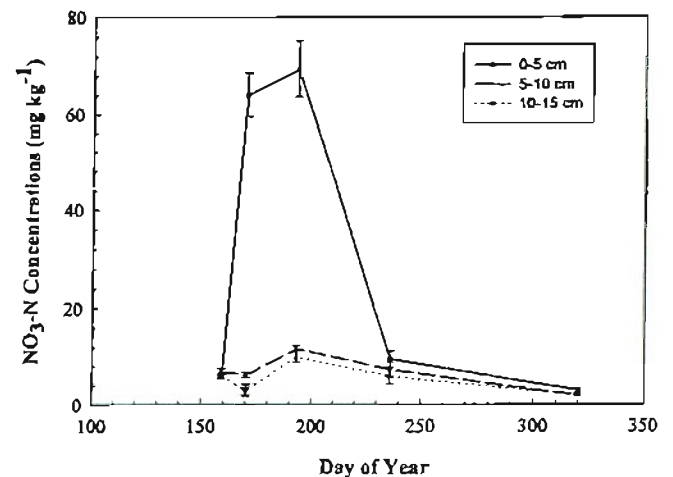


Fig. 4. Nitrate-N concentration in the 0- to 5-, 5- to 10-, and 10- to 15-cm soil depths measured in 1995. Each point is a mean of 36 samples. The vertical bars are standard errors.

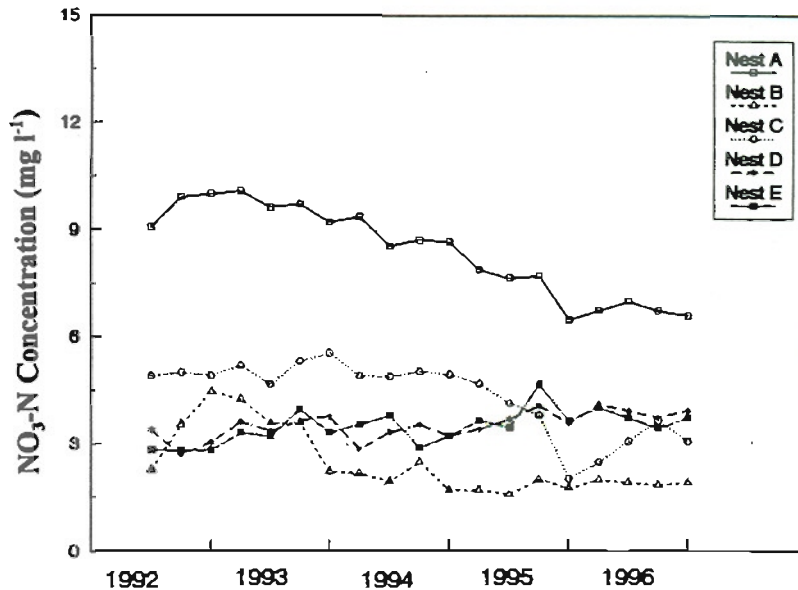


Fig. 5. Nitrate-N concentrations in the top glacial-fill groundwater (2.9 m depth) measured quarterly from 1992 to 1996.

creased by an average of $-0.40 \text{ mg L}^{-1} \text{ yr}^{-1}$. Similar results were also observed in the water samples collected from the deeper wells (Kitchen et al., 1997). Overall, the above results showed that $\text{NO}_3\text{-N}$ losses below the area of application were small compared with the total loss from the field.

SPATIAL VARIABILITY OF NITRATE-NITROGEN IN THE SOIL SURFACE

The spatial variability of $\text{NO}_3\text{-N}$ concentration for the samples collected from the top soil layer (0- to 5-cm soil depth) was analyzed using Geostatistics. The semivariograms for soil $\text{NO}_3\text{-N}$ concentrations measured in 1993 and 1995 are shown in Fig. 7 and Table 3. In all cases, isotropic models for the semivariogram were fitted using nonlinear least square regression analysis. Except for the samples collected 1 wk after applica-

tion, the semivariograms in 1993 showed weak spatial dependency as evidenced by high nugget variance (Table 3 and Fig. 7). The semivariogram constructed for the samples collected immediately (3 d) after fertilizer application in 1993 exhibited pure nugget effect. This could mean that the range of spatial dependence was less than the 80-m sampling interval or that $\text{NO}_3\text{-N}$ concentrations were not spatially dependent. The semivariogram for the samples taken 1 wk after application in 1993 showed a strong spatial dependency and was defined by a spherical model with a range of influence of 215 m. The semivariograms for the samples collected 4 wk, 8 wk, and after harvest exhibited weak spatial dependency (Table 3 and Fig. 7). In 1995, all the semivariograms, except for the samples collected 4 wk after application, were defined by linear models and exhibited moderate spatial dependency. The semivariogram for the samples collected 4 wk after application in 1995

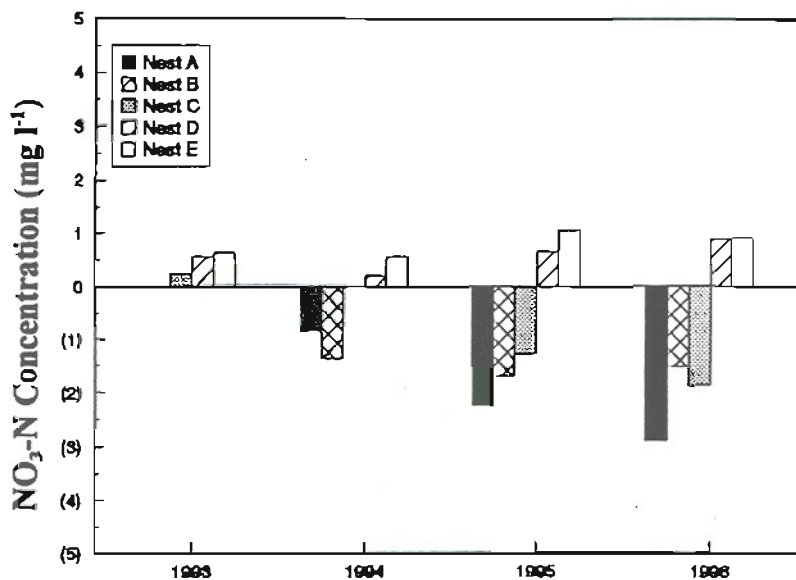


Fig. 6. Average annual change in groundwater $\text{NO}_3\text{-N}$ concentration over 5-yr period.

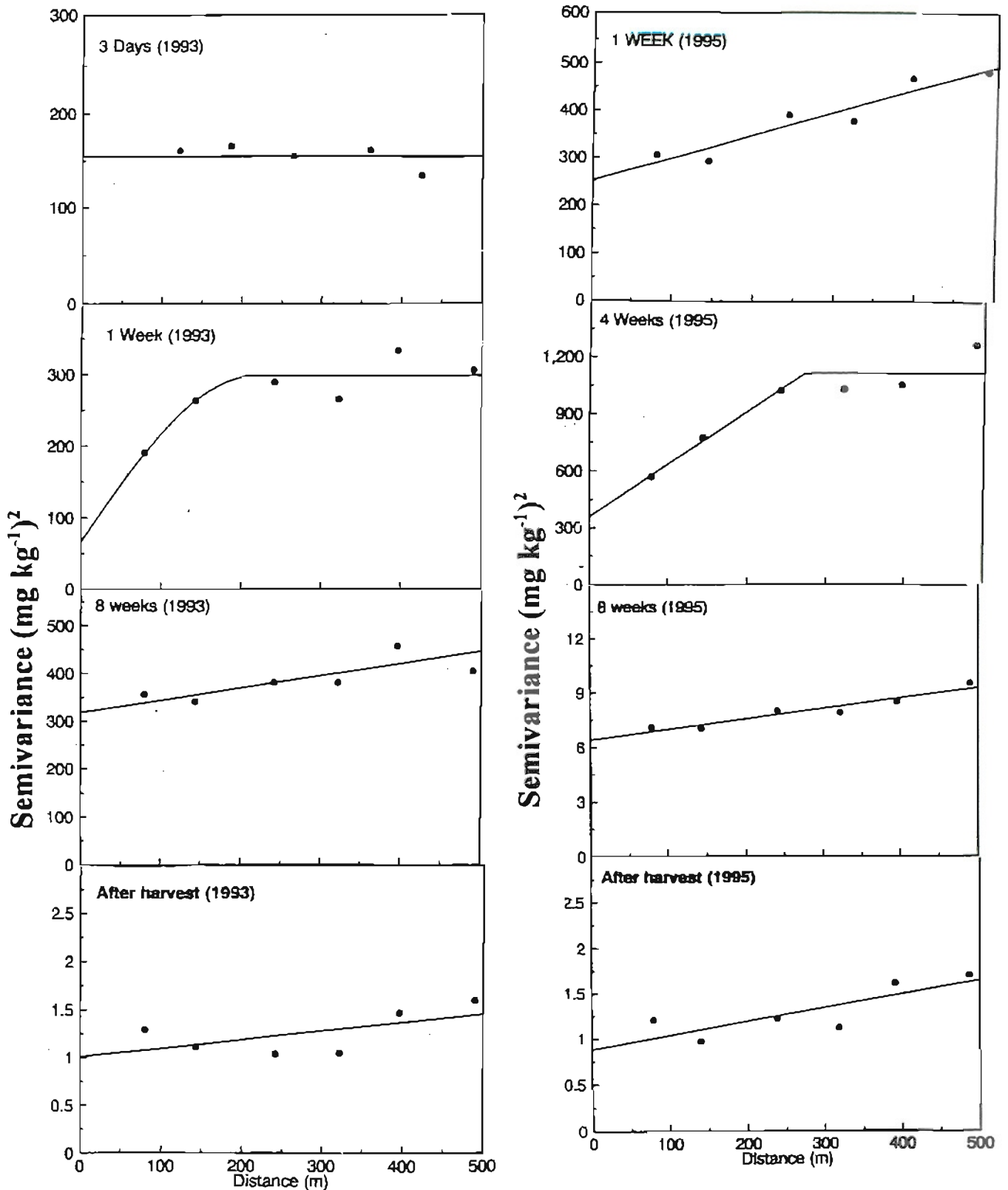


Fig. 7. Semivariograms of $\text{NO}_3\text{-N}$ concentrations (0- to 5-cm depth) measured in 1993 and 1995.

was defined by a linear-sill model with range of influence of 272 m, and its spatial dependency was moderately stronger than the other sampling periods.

The correlation of rainfall, soil water content, elevation, depth to claypan, soil pH, CEC, and OM with

$\text{NO}_3\text{-N}$ concentration in the soil (0- to 5-cm depth) was also evaluated in this study (Table 4). Nitrate-N concentrations were relatively highly correlated to elevation, particularly in 1993. Higher $\text{NO}_3\text{-N}$ concentrations were measured in the southern portion of the field (Fig. 8),

Table 3. Parameters for the semivariogram models.

Time after applic.	Model	Nugget	Sill	% of sill	Range, m	r^2	Spatial class
1993							
3 d	linear	156.5	156.5	100.0	>500	0.40	W
1 wk	spherical	61.0	303.2	20.0	215	0.81	S
4 wk	linear	359.6	372.6	97.0	>500	0.08	W
8 wk	linear	333.3	430.0	75.0	>500	0.60	W
After harvest	linear	1.02	1.40	70.0	>500	0.34	W
1995							
1 wk	linear	252.7	492.7	51.3	>500	0.90	M
4 wk	linear/sill	359.0	1111.0	32.3	272	0.89	M
8 wk	linear	6.41	9.24	69.4	>500	0.91	M
After harvest	linear	0.88	1.65	53.5	>500	0.66	M

which is an area of higher elevation and relatively lower slope, probably due to slower removal of nitrates by surface runoff. In 1995, concentrations were significantly ($p < 0.10$) negatively correlated to elevation for the samples collected 4 and 8 wk after fertilizer application. During these periods, higher concentrations were measured in the northern portion of the field (Fig. 8), which is an area of deposition. Between the periods 1 and 4 wk after fertilizer application in 1995, about 51 mm of runoff was measured from the field that may have resulted in moving nitrates from the relatively higher portions of the field and depositing them in the lower portion. The study did not show significant ($p < 0.10$) correlation between NO_3 concentration and depth to claypan.

Both in 1993 and 1995, $\text{NO}_3\text{-N}$ concentrations were positively correlated to soil pH for the samples collected 1 wk after application and negatively correlated for the remaining sampling periods. The correlation, however, was not significant ($p < 0.10$) in 1993. There was no significant ($p < 0.10$) correlation between $\text{NO}_3\text{-N}$ concentration and CEC in 1993; however, there was significant ($p < 0.10$) positive correlation in 1995, particularly for the samples collected 4 and 8 wk after application and after harvest. There was no significant ($p < 0.10$) correlation between $\text{NO}_3\text{-N}$ concentration and OM content except for the 4 wk period in 1993 and 8 wk period in 1995. In general, lower $\text{NO}_3\text{-N}$ concentrations were measured in areas of higher pH and lower CEC and OM content (Fig. 8 and 9).

Although soil pH showed relatively stronger correlation than CEC or OM, it is difficult to evaluate the

influence of each parameter on the spatial variability of $\text{NO}_3\text{-N}$ concentration within the field, because there were significant correlations among pH, CEC, and OM content. Soil pH was significantly ($p < 0.05$) negatively correlated with CEC ($r = -0.56$) and OM content ($r = -0.39$); and CEC was significantly ($p < 0.05$) positively correlated with OM content ($r = 0.43$).

Nitrate-N concentrations were not significantly ($p < 0.10$) correlated to soil water content, except for the samples collected 4 wk after fertilizer application in 1993 and after harvest in 1995. Previous studies indicated that soil moisture influences denitrification rate (Pennock et al., 1992). Christensen et al. (1990) stated that denitrification rate increases when the soil is at field capacity or higher. However, in this study, because samples were collected when the soil was relatively dry, the mean soil moisture content for each sampling period (Table 1) was much lower than the moisture content at field capacity for a Mexico silt loam soil ($\theta_{fc} = 0.30 \text{ m m}^{-3}$). The correlation between soil moisture content and $\text{NO}_3\text{-N}$ concentration probably could have been much higher if soil samples were collected when the soil was wet.

Previous studies have shown that <50% of fertilizer input is accounted for in harvested crop material (Pratt and Adriano, 1973; Legg and Meisinger, 1982). Other than crop harvest, N outputs from row crop fields occur as a result of denitrification, volatilization, seepage and drainage, and surface runoff. In this study, N loss to runoff and leaching was about 15% of that applied (total N loss to seepage was obtained from the plots under the same farming system located near the field). Assuming about 50% of the total N applied was used by the plants,

Table 4. Coefficient of correlation (r) between soil characteristics and $\text{NO}_3\text{-N}$ concentrations in the soil (0- to 5-cm depth).

Time after applic.	Soil water content	Elevation	Depth to claypan	pH	CEC	OM
1993						
3 d	0.24	0.41**	-0.17	0.20	-0.21	0.04
1 wk	0.26	0.34**	-0.20	0.17	0.05	0.12
4 wk	-0.39**	0.21	-0.05	-0.13	-0.10	-0.34**
8 wk	0.13	0.30*	-0.21	-0.22	-0.08	0.16
After harvest	0.08	0.39**	-0.26	-0.07	0.07	0.30*
1995						
1 wk	-0.10	0.18	-0.05	0.41**	-0.03	0.05
4 wk	0.02	-0.35**	0.41	-0.64***	0.41**	0.05
8 wk	0.20	-0.31*	0.11	-0.32*	0.42**	0.22
After harvest	0.33**	0.21	0.01	-0.20	0.26	0.48**

*, **, *** $p < 0.10$, $p < 0.05$, and $p < 0.01$, respectively.

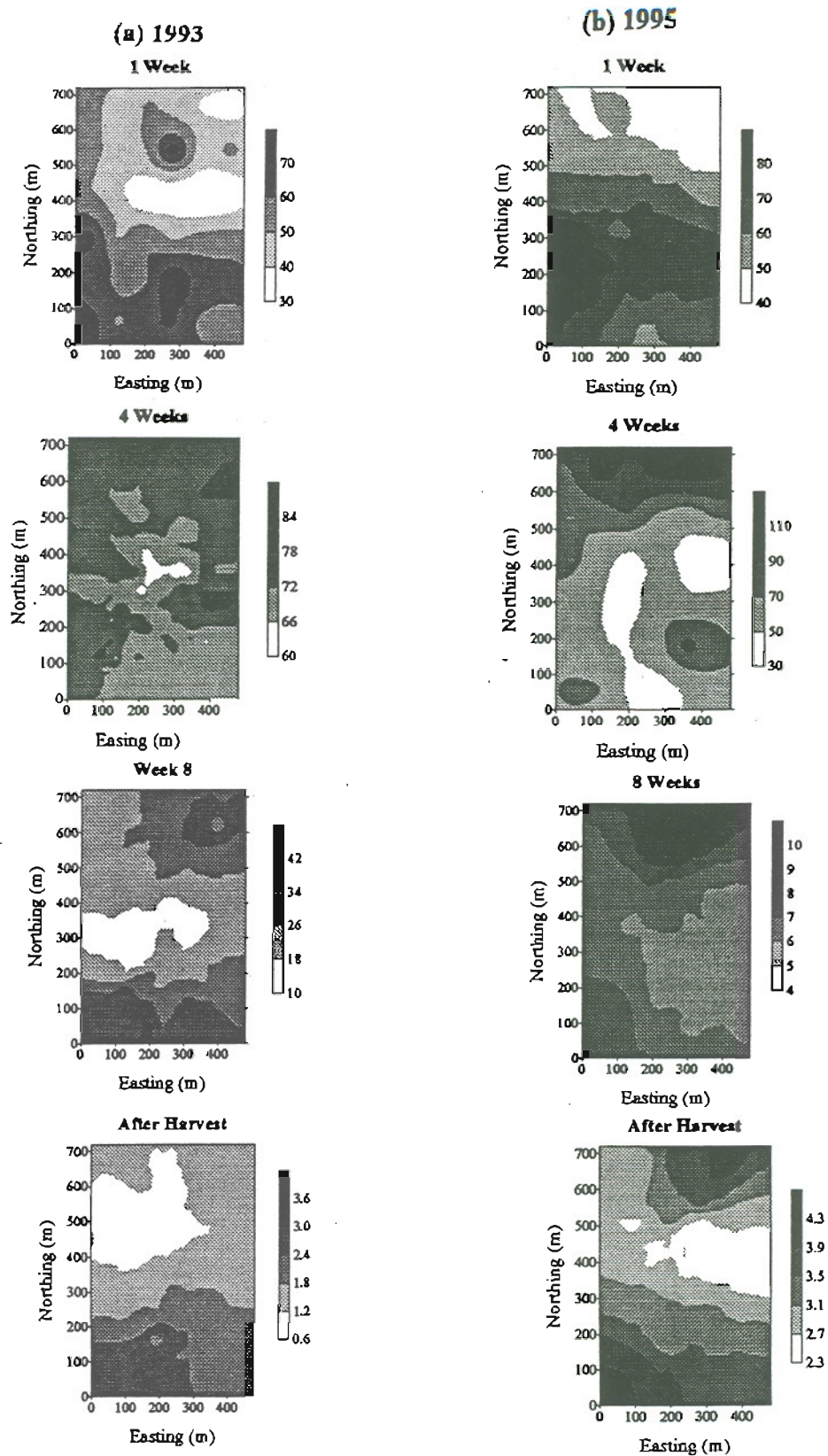


Fig. 8. Kriged $\text{NO}_3\text{-N}$ concentrations (mg kg^{-1}) measured 1 wk, 4 wk, 8 wk, and after harvest in 1993 and 1995. Samples were collected from 0- to 5-cm depth.

then a significant amount of N was probably lost by denitrification and volatilization. Denitrification rates increase with increasing soil pH (Bremner and Shaw, 1958; Cleemput and Patrick, 1974) and soil water con-

centration (Pennock et al., 1992). Nitrogen losses from UAN solutions through volatilization are influenced by soil pH, texture, temperature, moisture, and exchangeable cations (Ferguson and Kissel, 1986; Fenn and Hossner,

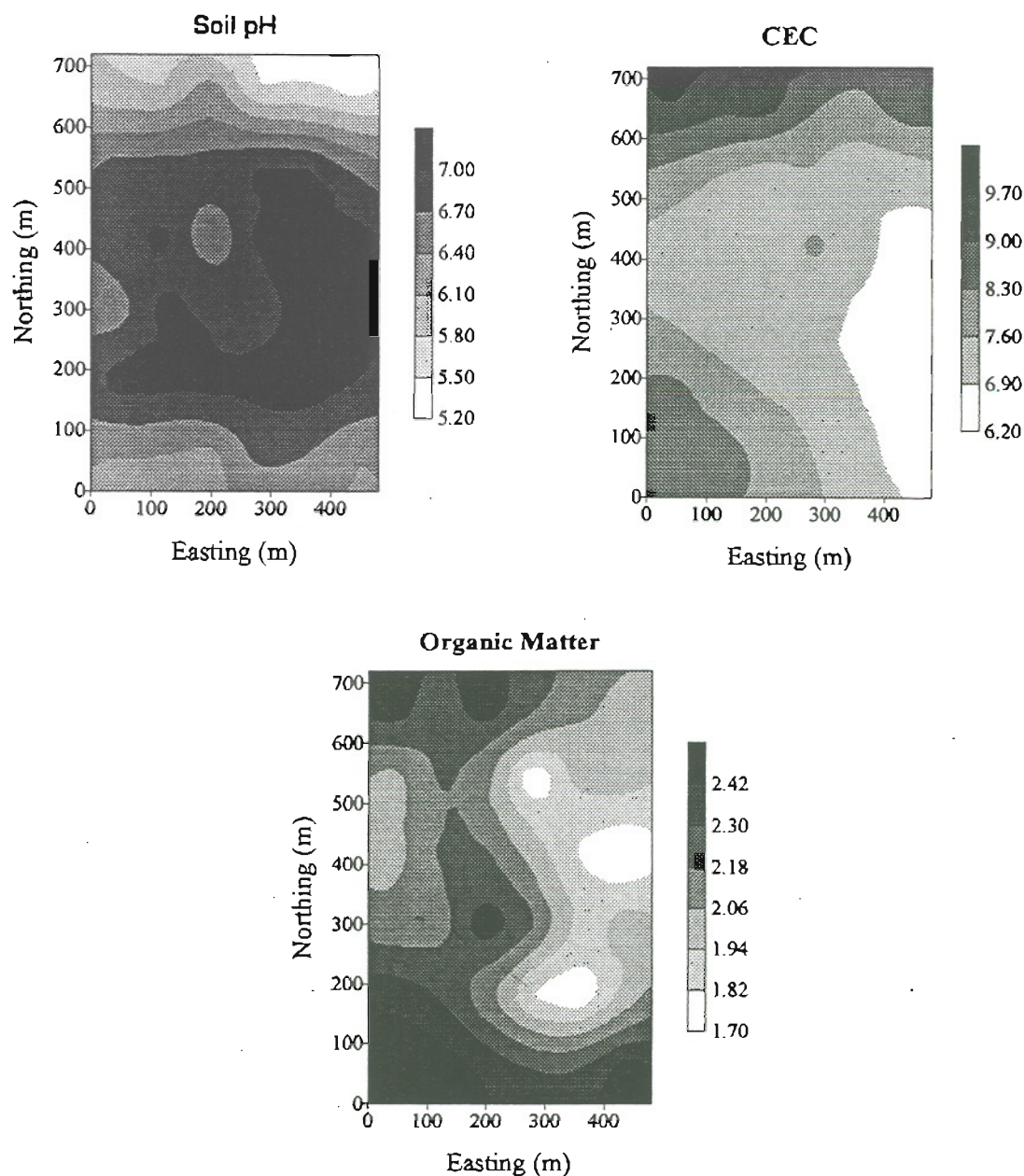


Fig. 9. Kriged soil pH, CEC, and OM content in the 0- to 5-cm soil depth.

1985; Verma and Sarkar, 1974). Although denitrification and volatilization were not measured in this study, it is believed that they significantly contributed to the spatial and temporal variability of $\text{NO}_3\text{-N}$ concentration in the top soil layer. Because denitrification and volatilization are partly controlled by soil properties, particularly soil pH, the reason for lower $\text{NO}_3\text{-N}$ concentrations in areas of higher soil pH and lower CEC and OM content (Fig. 9) could then be due to higher N losses by these processes, particularly in 1995.

SUMMARY AND CONCLUSION

Nitrate-N concentration in the top layer (0- to 5-cm depth) increased for the first few weeks after fertilizer application, then decreased dramatically and was very low ($<2 \text{ mg kg}^{-1}$) at harvest. Throughout the sampling periods, $\text{NO}_3\text{-N}$ concentrations in the 5- to 10- and 10-

to 15-cm soil depths were $<10\%$ of those measured from the 0- to 5-cm depth. Total N loss to surface runoff was $<5\%$ of the fertilizer N applied in the soil. Thus, loss to surface runoff was not a significant cause of the temporal decrease in $\text{NO}_3\text{-N}$ concentrations. Surface water contamination by runoff, however, was serious for the events that occurred within 1 to 3 wk following application, particularly in 1993.

The semivariograms constructed for soil $\text{NO}_3\text{-N}$ concentrations for each sampling period did not exhibit strong spatial dependency, except for the samples collected 1 and 4 wk after fertilizer applications in 1993 and 1995, respectively. Nitrate-N concentration in the top soil profile was poorly correlated to soil water content and depth to claypan and relatively strongly correlated to elevation and soil pH. In general, higher $\text{NO}_3\text{-N}$ concentrations were observed in areas of lower slopes, lower soil pH, higher CEC, and higher OM content.

Overall, understanding the processes controlling spatial and temporal variability of nitrates at field scale is important to improving fertilizer management in row crop settings. The results of our study, in combination with crop yield information, could serve as the basis for variable rate fertilizer application.

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