I. GEOSTATISTICAL ANALYSIS OF FORMS OF SOIL NITROGEN IN A CONTINUOUSLY CROPPED WHEAT FIELD

II. GEOSTATISTICAL ANALYSIS OF SOIL PHOSPHORUS, POTASSIUM, ORGANIC CARBON AND pH IN A LONG-TERM WHEAT FIELD

III. CHANGES IN PHOSPHORUS, ALUMINUM AND MANGANESE IN THREE ACID-AFFECTED SOILS THAT HAVE BEEN AMENDED WITH PHOSPHORUS

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Submitted to the Faculty of the Graduate College of
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of the requirements for the Degree of
DOCTOR OF PHILOSOPHY
May, 1993

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NITROGEN IN A CONTINUOUSLY
CROPPED WHEAT FIELD

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ACKNOWLEDGEMENTS

I would like to thank the members of my committee (Dr. Brian Carter, Dr. Brett Carver, Dr. Larry Claypool and Dr. Andrew Sharpley) for the time and effort that they have spent directing my studies and research. Additionally, I would like to thank Dr. William Raun and Dr. Gordon Johnson for their revisions of my manuscripts, as well as all other types of useful advice and information. Finally, I would like to thank my major advisor, Dr. Robert Westerman, for his continued academic and financial support. The opportunity to study with him was an honor, and I have benefited greatly from the experience.

Support of all types has come from a varied and most enjoyable group of people. Encompassing everything from soil grinding to intellectual discussion, the following people are owed a debt of gratitude: Brian Unruh, Mohammed El Gharous, Randy Boman, John Sloan, Jackie Driver, Shannon Taylor, Steve Taylor, Keith Fletcher, Mickey Jojola, Maritza Sloan and Tara Herring.

The financial support for this degree has been generous and appreciated. I would like to thank Oklahoma State University for awarding me a Presidential Fellowship in Water Quality, and the Oklahoma State University Foundation for awarding me a University Fellowship. The support of The Department of Agronomy has also been appreciated, both in finances and facilities.

Thanks to Brian. Lastly, thanks to Mom, for always being there.

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INTRODUCTION

There are three parts in this dissertation, each discussing the results of research that was conducted for my doctoral degree. Each part is presented in a form suitable for publication in a professional journal.

CHAPTER I

GEOSTATISTICAL ANALYSIS OF FORMS OF SOIL NITROGEN IN A CONTINUOUSLY CROPPED WHEAT FIELD

ABSTRACT

A 3.0 ha agricultural field that had been cropped to continuous wheat since 1977 was sampled on a regularly spaced grid to a depth of 1.2 m. Each soil core was sectioned into six depths: 0-15, 15-30, 30-45, 45-60, 60-90, and 90-120 cm. Each sample was analyzed for soil NO_3-N and NH_4-N in 2M KCl extracts using a Lachat Flow Injection Analyzer. The 0-15 cm soil depths were also analyzed for total N using a Carlo Erba NA 1500 dry combustion furnace. Most semivariograms for soil NH_4-N were fit to a nugget model, indicating a random relationship between data values. Semivariograms for soil NO_3-N and total N were fit to spherical models, with average ranges of 80 and 90 m respectively. Total N was isotropic, as all the semivariograms behaved similarly regardless of direction. Block kriging and cross validation indicated that nested models were required to account for the anisotropic variability found in the soil NO_3-N data set. The direction of greatest spatial relationship changed with depth, moving from N at 0-15 cm to a general SW direction in deeper soil increments. Block kriging estimated regions of NO_3-N and total N with accuracy, matching the contours of the actual values. A geostatistical evaluation of soil N is a useful

tool for examining the spatial variability of soil NO_3-N and total N in an agricultural field, and is of particular use when the environmental concerns of soil NO_3-N are considered.

INTRODUCTION

Conventional soil sampling techniques employ a method of random selection in which the relationship between samples is not considered. Each sample removed from a field is independent of other samples, and the variability between that sample and neighboring samples is usually not examined. Samples are usually averaged, providing a mean for a field or region, a value that may not adequately describe the behavior of the nutrient across the area of interest, especially if spatial variability exists. By contrast, geostatistical techniques explore spatial relationships between samples, examining the continuity of sample values over both distance and, possibly, direction.

Relatively new methods for assessing spatial variability of soil characteristics are the geostatistical techniques of variogram construction, coupled with the estimation of values by kriging. Variogram construction provides an illustration of the behavior of soil characteristics across a field, while kriging estimates unknown values within, and possibly, beyond the site.

Variograms can be constructed from many types of data sets, and the technique is adaptable to different soil characteristics and sampling schemes.

The general equation for variogram calculation is:

$$(\gamma(h)) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2$$

where:

$N(h)$ = number of experimental pairs
$z(x_i)$ = experimental measures of the variable
h = distance between samples (lag distance)

(Journel and Huijbregts, 1978)

This equation may be modified (Cressie and Hawkins,1980; Cressie, 1985), but the basic procedure of squaring the difference between two values usually remains.

Variograms are usually shown as line diagrams, with the variogram value at a given lag ((h)), plotted against that lag distance, h. The 'one-half' term in the equation divides the symmetrical curve of the variogram in half, hence plotted information is more appropriately called a semivariogram. Variograms are created from available data points, and a model is fit to this experimental variogram. The model is often initially fit to an omnidirectional semivariogram, providing the best fit to a smooth 'average' semivariogram. Directional semivariograms are then used to indicate the presence of anisotropies, where spatial relationships differ over various directions. The presence of anisotropies can affect the accuracy of models fit to the semivariogram, which will, in turn, alter kriging estimates.

A modeled variogram provides several pieces of information about the sampled site. First, the model can supply an estimate of the nugget, that portion of the semivariogram attributable to pure random error. Second, some models will estimate the sill, where the semivariogram may level. Third, the distance at which samples are no longer spatially related to each other may be found. This distance is called the range.

The nugget, sill and range coefficients determined from the fitted model(s) are used in the estimation procedure of kriging. Kriging calculates estimates using weighted linear combinations of available data. Kriging is both an unbiased and best estimation method that attempts to have the mean error equal zero and the variance of these errors minimized (Isaaks and Srivastava, 1989).

Detailed and informative discussions about the theories and methodologies of semivariogram construction and kriging have been written by Isaaks and Srivastava (1989), Journel and Huijbregts (1978), Hamlett et al. (1986), and Warrick and Myers (1987), and Warrick et al. (1986). Additionally, a glossary of geostatistical terms may be found in the Appendix of this dissertation.

The use of geostatistics to examine the spatial variability of soil properties or characteristics is relatively new in soil science. Geostatistical techniques were first developed for estimating the depth and size of ore reserves, and the theories were not widely available until Matherons' (1963) publication. The methods then began to make their way from mining into other research areas, including soil science.

Semivariogram construction is often used to study the spatial variation of soil physical properties. Among these properties are sand content (Campbell, 1978; Tabor et al.,1985; Nash et al.,1988), infiltration rate (Vieira et al.,1981), soil-water pressure potential (Hamlett et al.,1986), clay content (Tabor et al.,1985; Nash et al.,1988; Ovalles and Collins,1988), soil temperature (Mulla,1988; Yates et al.,1988), and soil heat flux (Wolf and Rogowski, 1991).

Geostatistical examinations of soil chemical properties have centered upon properties such as pH (Campbell,1978; Tabor et al.,1985; Laslett and McBratney, 1990) and organic carbon content (Ovalles and Collins, 1988; West et al.,1989). Few studies have explored the spatial variability of nitrogen (Tabor et al.,1985; West et al.,1989). Forms of N that were examined varied, including total-N (West et al.,1989), soluble-NO_3 (Flaig et al.,1986), petiole-N and nitrate-N (Tabor et al.,1985).

As an estimation process, kriging of soil characteristics produced varying degrees of success (Nash et al., 1988; West et al., 1989). Point kriging of $CaCO_3$, clay and sand was suitable as an estimation method, but intense sampling was needed to lessen large nugget effects (Nash et al.,1988). In another paper, kriged values of total N from grazed pastures were used to indicate areas of enhanced total N near drinking water sources, illustrating the hypothesis that zones of nutrient enhancement that could be sampled separately for more effective fertilizer recommendations (West et al.,1989). Other work that examined water infiltration rates produced kriged values with mean estimation errors that were close to zero, and a low variance of the estimation errors (Vieira et al.,1981), indicators of reliable kriged estimates.

Block kriging is often found to provide more accurate estimates, when that procedure is compared to punctual kriging. Estimated sodium content from block kriging contained much lower estimation variances than sodium contents estimated by punctual kriging (Burgess and Webster,1980). Block kriging was used to estimate electrical conductivity (ECe) and soil NO_3-N (Tabor et al., 1985). It was found that soil NO_3-N was well correlated with ECe, exhibiting similar spatial structure over the sampled site.

The spatial variability of forms of soil N remains largely undocumented. The spatial variability of NO_3-N and NH_4-N might be large or small, depending on the balance between processes that add and remove NO_3-N and NH_4-N from soil. Total N is a function of these processes and the organic pool in the soil. The need for the spatial description and estimation of the forms of soil N is both economic and environmental. Identifying the degree and type of spatial relationships that exist for soil N may help increase the accuracy of soil sampling and testing, affecting the quantity and placement of fertilizer and lime applications. Additionally, the estimation of N values at unsampled regions may identify areas of the field with higher levels of NO_3-N, areas that contain the potential for nitrate leaching to occur. The objective of this research project was to describe the spatial variability of soil NO_3-N, NH_4-N and total N across a soil cropped to continuous wheat, examining spatial relationships as they change within a 1.2 m depth and 15 cm depth for soil NO_3-N and NH_4-N and total N, respectively. These spatial relationships were then used in the estimation procedure of block kriging, predicting soil N concentrations at unsampled regions within the field.

METHODS AND MATERIALS

A 3.0 ha field, measuring 200 m by 150 m, which had been cropped to continuous winter wheat (*Triticum aesivitum* L.) since 1979 was sampled across a regular grid pattern. The soil at this site was classified as a Pond Creek silt loam (Fine-silty, mixed, mesic Pachic Argiustoll). The site was uniformly level (slope < 2.0%), and had received annual applications of anhydrous ammonia

(112 kg/ha 82-0-0) since 1982. The field was last limed to a recommended pH of 6.5 in 1985. Additionally, 33 kg/ha P fertilizer was banded with the seed at planting. No K fertilizer was applied.

For sampling, a large scale grid covered the entire 3.0 ha site, and the soil was sampled, after wheat harvest, at 25 m intervals within this large grid. In order to lessen the random sampling variance a smaller 0.06 ha grid was located at the center of the large grid, and this smaller grid was sampled at 5 m intervals. A total of 99 samples were removed, with 63 and 36 removed from the large and small grids, respectively. Due to sampling errors, two sample cores that were located in the SW corner of the field were removed from the data set.

All samples were removed to a depth of 1.2 m, using a Giddings hydraulic soil probe. One soil core (4.5 cm i.d.) was removed at each sampling point, extruded into a plastic sleeve that was sealed and refrigerated until processing. At processing, each core was sectioned into six depths: 0-15, 15-30, 30-45, 45-60, 60-90, and 90-120 cm. All samples were air-dried and ground to pass a 2 mm sieve before further analysis.

Each sample was analyzed for soil NO_3-N and NH_4-N content. Additionally, the 0-15 cm depth was analyzed for total soil N. Soil NO_3-N and NH_4-N were determined from 2M KCl extracts (Keeney and Nelson,1982), using colorimetric analysis via a Lachat Flow injection analyzer. Total soil N was determined by dry combustion using a Carlo Erba NA 1500 furnace. All sample values were averages of duplicate determinations.

Statistical Analyses

All data were initially analyzed by standard statistical methods, providing estimates of the mean, minimum, maximum, standard deviation and skew for each variable. Geostatistical analyses were used to describe the spatial variability of soil NO_3-N, NH_4-N and total N content. All classical and geostatistical analyses were performed using the GEOEAS (v 1.1) geostatistical package (Englund and Sparks, 1988). Spatial relationships were described through the use of omnidirectional and directional semivariograms, employing actual data values.

Omnidirectional semivariograms were calculated from every pair of data points within one-half of the total sampled distance, considering every direction at each selected lag distance. Directional semivariograms were calculated over 4 directions: 0, 45, 90 and 135 degrees, each with an angular tolerance of 22.5 degrees. At a given lag distance all points located within 22.5 degrees of the selected direction were included in the semivariogram calculation, again limited to a final lag length of one-half the total sampled distance. In effect, the four directional semivariograms with an angular tolerance of 22.5 degrees divided the total area described by the omnidirectional semivariogram into four sections.

Directional semivariograms were used to determine if anisotropy existed within the data set. Anisotropies are said to occur if the semivariograms change over varying directions. The ranges of directional semivariograms were examined, and the major and minor axes of continuity were identified. A major axis of continuity was selected when a directional semivariogram contained a large range with a well-defined spatial structure. Minor axes of continuity existed when the semivariogram contained irregular spatial structure, usually coupled with a short range. Because several of the soil depths contained a region of similar spatial structure, some nested models were used in the kriging procedure, and these are expressed by two major axes of anisotropy.

Models fit to the experimental semivariograms were used in the estimation process of block kriging. Cross-validation was used to check the accuracy of the chosen model(s) intended for the block kriging procedure. Known values at each sampled location were estimated by kriging, and those estimated values were compared to actual values. Examination of the kriging error, mean of the estimation error, and variance of the estimation error were used to determine the accuracy of the chosen model.

Block kriging was used to estimate unknown values across the sampled site. A total of 150 blocks were estimated throughout the experimental area.

RESULTS AND DISCUSSION

Table 1 lists statistical summaries for total N at the 0-15 cm depth and soil NO_3-N and NH_4-N for all six soil increments. Large outliers in the soil NO_3-N data set contributed to high skew values in most of the depth increments, indicating variable data sets that could be difficult to model once semivariograms were created. Soil NH_4-N values were less variable, although the 90-120 cm depth was more variable than overlying soil increments. Soil NO_3-N declined rapidly with depth, with the mean NO_3-N value declining 21.1 mg kg^{-1} (83.4 % change) over the 120 cm sampling depth. In contrast, mean NH_4-N values declined by only 4.0 mg kg^{-1} (16.8 % change) over the first 90 cm, and increased at 90-120 cm. Surface total N measurements were relatively constant, and did not exhibit the large variations that were found in the NO_3-N and NH_4-N data sets.

The largest measured soil NO_3-N values were predominately located in the southeast corner of the sampled field, and this region of elevated soil NO_3-N values was found throughout the entire 1.2 m sampled depth, (Figure 1). There were no obvious drainage patterns or tillage practices that could explain the wide variation in soil NO_3-N values found within the sampled site. The region of high NO_3-N appeared to drift slightly southward as soil depth increased, possibly a result of NO_3-N leaching coupled with some lateral movement of this mobile chemical form of N.

Soil NH_4-N values (Figure 2) in the 0-15 cm depth were also higher in the southeast corner of the field. However, this region did not continue to show high values at deeper soil increments, and a zone of high ammonium values began to develop in the NW corner of the field. The 90-120 cm depth contained higher ammonium values than shallower soil, suggesting a change in some soil properties at around 90-120 cm.

Surface contours (0-15 cm) for total N were the least variable of the three studied nutrients. Shown in Figure 3, the total change in total N across the site was around 100 mg kg^{-1}. Regions that contained high levels of soil NO_3-N and NH_4-N also contained increased levels of total N.

Initial semivariogram constructions indicated that median polish techniques, logarithmic transforms or relative semivariograms did not affect the clarity of constructed semivariograms, nor the accuracy of models fit to the semivariograms. Because of this semivariograms were constructed and all kriging was performed on the original data values.

Constructed semivariograms provided information about the spatial variability of soil NO_3-N. For soil NO_3-N, omnidirectional semivariograms were moderately continuous, usually fitting a spherical model and rising to a well-defined range, as shown in Table 2 and Figure 4. As soil depth increased semivariograms for soil NO_3-N became more continuous, particularly at short lag distances. The directional semivariograms became less isotropic, and the N and NW directions contained the strongest spatial relationships, shown by the longer ranges in Table 2. These directional semivariograms were fit to Gaussian models, and it was thought that these models could be used in the kriging process. However, the cross-validation process for these models alone (not shown) was not as acceptable as those calculated from spherical models from the omnidirectional semivariograms.

In most cases, directional and omnidirectional semivariograms for soil NH_4-N content were fit to a nugget model, indicating random phenomena. The only directional semivariogram that consistently contained spatial structure was the northern direction. Both the 30-45 and 45-60 cm omnidirectional semivariograms contained slight spatial relationships within a short range, but directional semivariograms revealed these relationships were a function of a strong continuity in the northern direction only. Both omnidirectional and directional semivariograms at 90-120 cm were fit to linear models, and once past a range of 60 m the accuracy of the model fit declined rapidly.

Cross-validation and kriging were not performed on the soil NH_4-N data set, as the majority of the omnidirectional and directional semivariograms were fit to the nugget model. While there were some spatial relationships in the N direction these were not sufficient to provide accurate kriging estimates for the entire site.

The omnidirectional semivariogram for total N (Figure 6) was fit to a spherical model, as were all the directional semivariograms. This nutrient exhibited similar spatial relationships in all directions, as demonstrated by directional nuggets, sills and ranges that are almost equal. Linear models fit to these semivariograms (not shown) did not provide as accurate kriging estimators as the spherical models shown in Table 3.

The direction in which sample values were least related was (at all depths) SW (Table 4). The direction in which soil NO_3-N was most related changed with depth, moving from directly N at 0-15 cm to a general NW direction deeper in the soil. The direction of greatest relationship found at the soil surface could be developed, in part, from factors such as the direction of tillage and fertilizer-applicator travel. Natural landscape and soil factors such as direction of drainage and impeding layers within the soil profile would also be a consideration, and it may be that the varying anisotropic axes reflect such a changing soil profile.

The anisotropic ratio is the range of the major axis divided by the range of the minor; an anisotropic ratio of 1.0 signals an isotropic condition, and the spatial variability is the same in all directions. With the exception of the 45-60 cm depth the anisotropic ratio was close to 1.0, as there was not a large difference in the ranges of the directional semivariograms (shown in Table 2). The larger ranges found in the 60-120 cm depths indicate that soil NO_3-N is spatially related for a greater distance at that depth. This may be a function of: 1) less rooting volume to alter soil NO_3-N values, 2) limited impact from the surface, such as leached NO_3-N, or 3) beginning of a relatively continuous parent material.

Criteria used for the cross-validation procedure are summarized in Table 5.

Adequate model fits were indicated when the mean of the estimation errors were close to zero, and the variance of the errors is minimized and equal to the kriging variance. Additionally, the dimensionless mean square error (DMSE) should equal 1, while the mean normalized error (ME) should be close to zero. There can be other criteria for checking the accuracy of the cross-validation procedure, but these are four commonly used techniques (Samper and Neuman, 1989; Unlu et al.,1990). Although the variance of the estimation errors were equal to the kriging variance (Table 5) the variances for soil NO_3-N were not particularly small, a result of the wide variation in measured values found in the data sets.

Figures 7 and 8 indicate the results of the block kriging procedure for soil NO_3-N (all depths) and total N (0-15 cm depth). Each figure provides a contour plot of both the estimated soil NO_3-N values and the kriging standard deviation. Kriging standard deviations help pinpoint those areas that may contain less reliable estimates.

In general, kriged estimates produced reasonable maps of estimated soil NO_3-N content and total N. For both soil NO_3-N and total N the kriging standard deviation was smallest at the center of the sampled site, a function of the centered small sampling grid. Kriged estimates in this region came from a larger number of closely spaced samples, which lowered the kriging variance. For soil NO_3-N, the largest kriging standard deviations were found in the region of elevated soil NO_3-N values. These regions were most likely to contain a large NO_3-N value in close proximity to a small value, a situation which could create greater error in the estimation process.

Geostatistical methods have applications in exploring the spatial variability of some nutrients. Both the data and resultant semivariograms should be viewed with a knowledge of a fields' cultural treatments, particularly in the surface depth. This is especially true with plant nutrients applied to the soil. Field spatial variability as it is affected by reduced-tillage, erosion control structures such as terraces or irrigation could help explain the spatial variability of soil NO_3-N and other fertility nutrients.

A geostatistical analysis requires an adequate number of samples to describe spatial variability. It is likely that mobile nutrients such as soil NO_3-N may require a more intensive sampling scheme than soil physical properties. In this research project kriging variances were sensitive to regions that were less sampled and highly variable in soil NO_3-N content. Anisotropies and less continuous semivariograms existed for soil NO_3-N and NH_4-N, as compared to the relatively isotropic condition found with total N. Research will be needed on many sites and soils to determine the minimum number of samples required to accurately describe and predict a regions' spatial variability. Additionally, the spatial variability of soil NO_3-N might best be described through monthly or seasonal sampling. Determining if the spatial relationship of soil NO_3-N changes with season could be a useful tool for describing the long term spatial continuity of a mobile nutrient such as NO_3-N. Descriptions of spatial variability that consider seasonal changes could improve the accuracy of estimation procedures such as those used in block kriging. A spatial description and subsequent estimation of soil NO_3-N content within an agricultural field could be incorporated into the new computer-aided precision-fertilizer application technologies, eliminating over-fertilization and assisting in the protection of environmental quality.

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Table 1. Statistical summary for soil NO_3-N, NH_4-N and total soil N at varying depths.

	Soil NO_3-N					Soil NH_4-N				
Depth	Mean	Std Dv	Max	Min	skew	Mean	Var	Max	Min	skew
---cm---	mg/kg					mg/kg				
0-15	23.2	6.6	40.1	11.2	0.4	7.3	7.2	15.7	3.6	0.9
15-30	9.0	4.0	33.4	3.7	2.6	6.0	5.3	14.5	2.7	1.3
30-45	3.5	2.9	22.1	1.2	3.9	5.9	4.2	13.2	2.6	0.9
45-60	2.7	2.6	14.7	0.7	2.8	5.6	3.5	12.0	2.8	1.1
60-90	2.4	2.2	11.5	0.5	2.3	5.2	3.2	11.0	2.3	1.0
90-120	2.1	2.4	14.1	0.5	3.4	7.3	6.5	23.6	2.7	2.7
	Total Soil Nitrogen									
0-15	748.8	5025.6	950.0	599.5	0.4					

Table 2. Semivariogram parameters nugget, sill, range and model type for soil NO_3-N.

Depth ---cm---	Direction	Nugget (mg/kg)^2	Sill (mg/kg)^2	Range --- m ---	Model
0-15	Omnidirect.	32.0	18.0	90.0	Spherical
	N	32.0	25.0	90.0	Spherical
	NW	13.0	35.0	90.0	Spherical
	W	20.0	45.0	90.0	Spherical
	SW	32.0	20.0	60.0	Spherical
15-30	Omnidirect.	7.0	14.0	90.0	Spherical
	N	7.0	14.0	90.0	Spherical
	NW	7.0	14.0	90.0	Spherical
	W	6.0	25.0	100.0	Spherical
	SW	5.0	10.0	80.0	Spherical
30-45	Omnidirect.	0.8	9.0	90.0	Spherical
	N	0.8	14.0	110.0	Spherical
	NW	0.5	5.0	90.0	Spherical
	W	0.5	15.0	120.0	Spherical
	SW	0.6	17.0	90.0	Spherical
45-60	Omnidirect.	0.4	7.0	60.0	Spherical
	N	0.4	11.0	90.0	Spherical
	NW	0.4	9.0	110.0	Gaussian
	W	0.4	9.0	80.0	Spherical
	SW				Nugget
60-90	Omnidirect.	0.6	5.5	90.0	Spherical
	N	0.6	7.0	120.0	Spherical
	NW	0.6	13.0	120.0	Gaussian
	W	0.8	7.5	120.0	Spherical
	SW				Nugget
90-120	Omnidirect.	0.7	6.0	100.0	Spherical
	N	0.7	10.0	120.0	Gaussian
	NW	0.7	13.0	120.0	Gaussian
	W	1.0	6.0	80.0	Spherical
	SW	0.1	5.5	80.0	Spherical

Table 3. Semivariogram parameters nugget,sill, range and model type for soil NH_4-N and total soil nitrogen.

Depth	Direction	Nugget	Sill	Range	Model
---cm---		(mg/kg)^2		---m---	
		Soil NH_4-N			
0-15	Omnidirect.				Nugget
	N	3.0	5.5	60.0	Spherical
	NW				Nugget
	W				Nugget
	SW				Nugget
15-30	Omnidirect.				Nugget
	N	2.0	6.0	60.0	Spherical
	NW				Nugget
	W				Nugget
	SW				Nugget
30-45	Omnidirect.	1.0	3.3	40	Spherical
	N	1.0	3.3	90	Spherical
	NW	1.5	3.5	80	Spherical
	W	2.8	1.9	60	Spherical
	SW				Nugget
45-60	Omnidirect.	2.0	2.0	34	Spherical
	N	0.5	2.0	45	Spherical
	NW	3.0			Nugget
	W	3.3			Nugget
	SW	3.3			Nugget
60-90	Omnidirect.				Nugget
	N	1.0	1.7	100.0	Spherical
	NW				Nugget
	W				Nugget
	SW				Nugget
90-120	Omnidirect.	2.0		60	Linear
	N	0.5		60	Linear
	NW	0.5		60	Linear
	W	1.0		60	Linear
	SW	1.0		60	Linear
		Total Soil Nitrogen			
0-15	Omnidirect.	1100	4000	90	Spherical
	N	1100	4000	90	Spherical
	NW	1100	4000	90	Spherical
	W	1100	4000	90	Spherical
	SW	1100	4000	90	Spherical

Table 4. Direction of anisotropy for soil NO_3-N and total soil nitrogen as determined by directional semivariograms.

Depth	Major Axis(es)	Minor Axis	Anisotropic Ratio
---cm---			
Soil NO_3-N			
0-15	N	SW	1.5
15-30	N and W	SW	1.1
30-45	N and W	SW	1.3
45-60	NW	SW	1.8
60-90	NW and N	SW	1.1
90-120	NW	SW	1.5
Total Soil Nitrogen			
0-15			1.0

Table 5. Cross-validation criteria for the best-fit models for total soil nitrogen and soil NO_3-N content.

Depth ---cm---	Mean Est. Errors †	Var. Est. Errors @	σ_K^2 @	DMSE *††	ME **†
			Soil NO_3-N		
0-15	0.006	46.2	42.3	1.11	-0.0003
15-30	0.04	16.0	16.5	0.95	0.009
30-45	0.06	8.2	8.2	0.99	0.02
45-60	-0.02	4.7	4.7	0.98	-0.007
60-90	-0.01	3.5	3.4	1.05	-0.005
90-120	-0.05	5.4	5.4	1.00	-0.02
			Total Soil Nitrogen		
0-15	0.05	3256.3	3329.0	0.99	0.0008

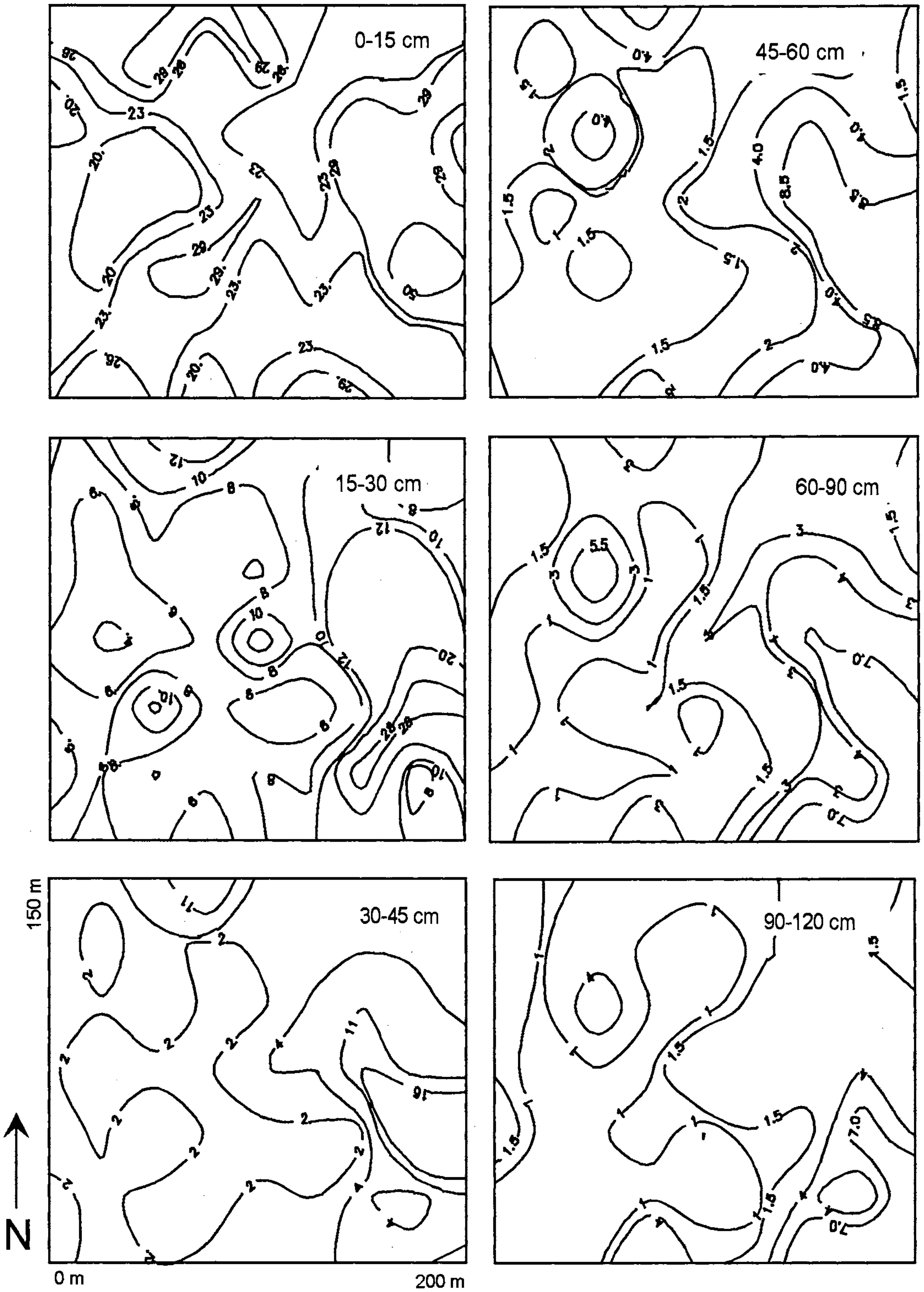
*Dimensionless Mean Square Error = $\left(\frac{1}{N}\ \frac{\sum(z^*_i - z_i)^2}{\sigma_K^2}\right)^{1/2}$

**Mean Normalized Error = $\left(\frac{1}{N}\ \sum\frac{z_i - z^*_i}{\sigma_K}\right)$

†,†† not significantly differently from 0,1 and 0, respectively, at α =0.01.

@ variances not signifcantly different at α = 0.10.

Figure 1. Contour plots of measured soil NO_3-N values (mg/kg).



0-15 cm

45-60 cm

15-30 cm

60-90 cm

30-45 cm

90-120 cm

Figure 2. Contour plots of measured soil NH4 -N values (mg/kg).

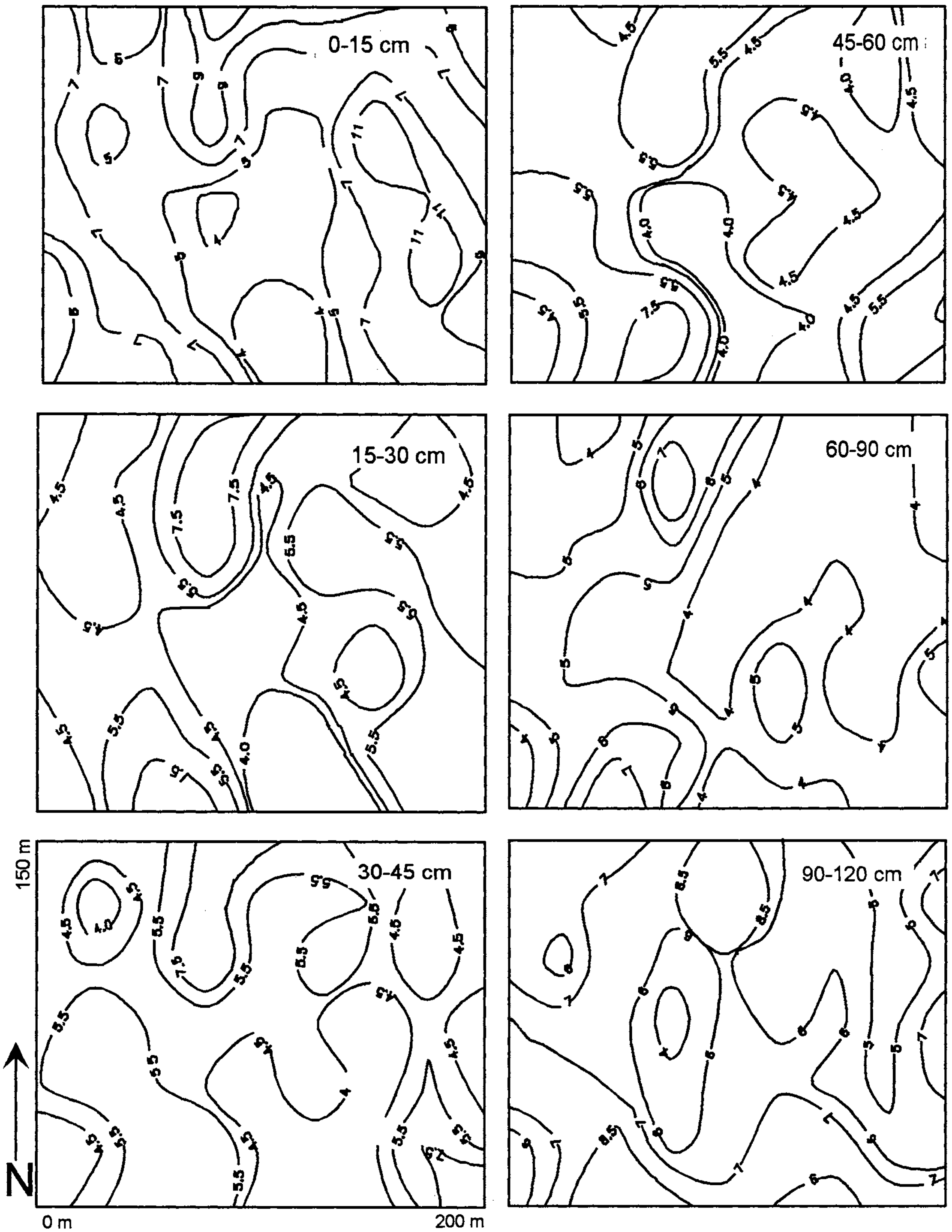


Figure 3. Contour plot of measured total soil nitrogen values (mg/kg).

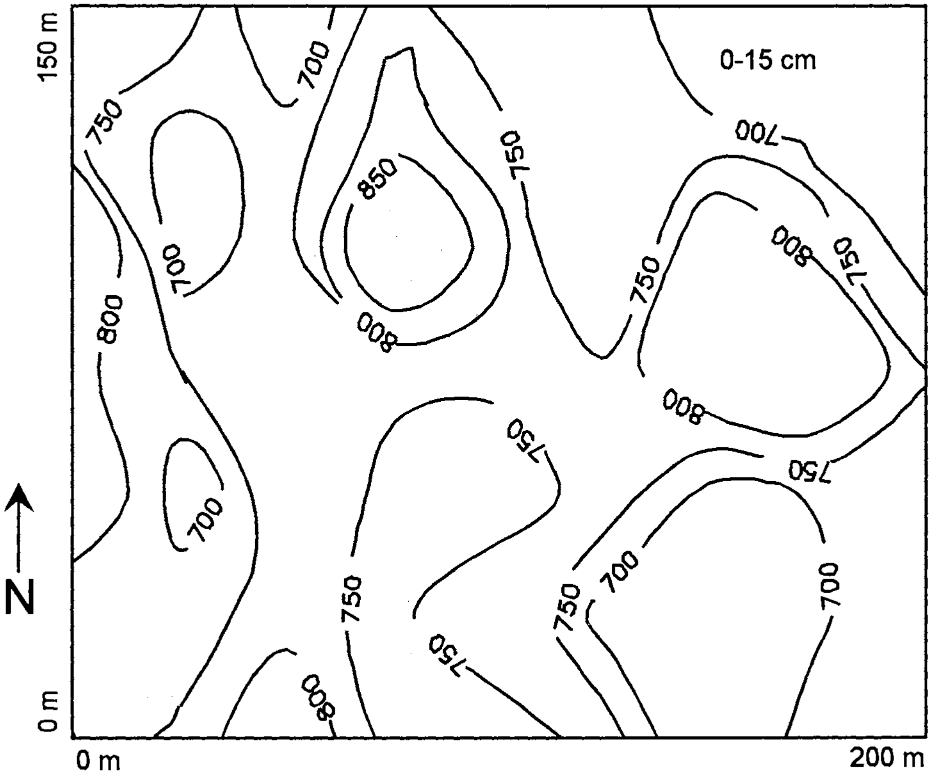


Figure 4. Omnidirectional semivariograms for soil NO_3-N content (mg/kg).

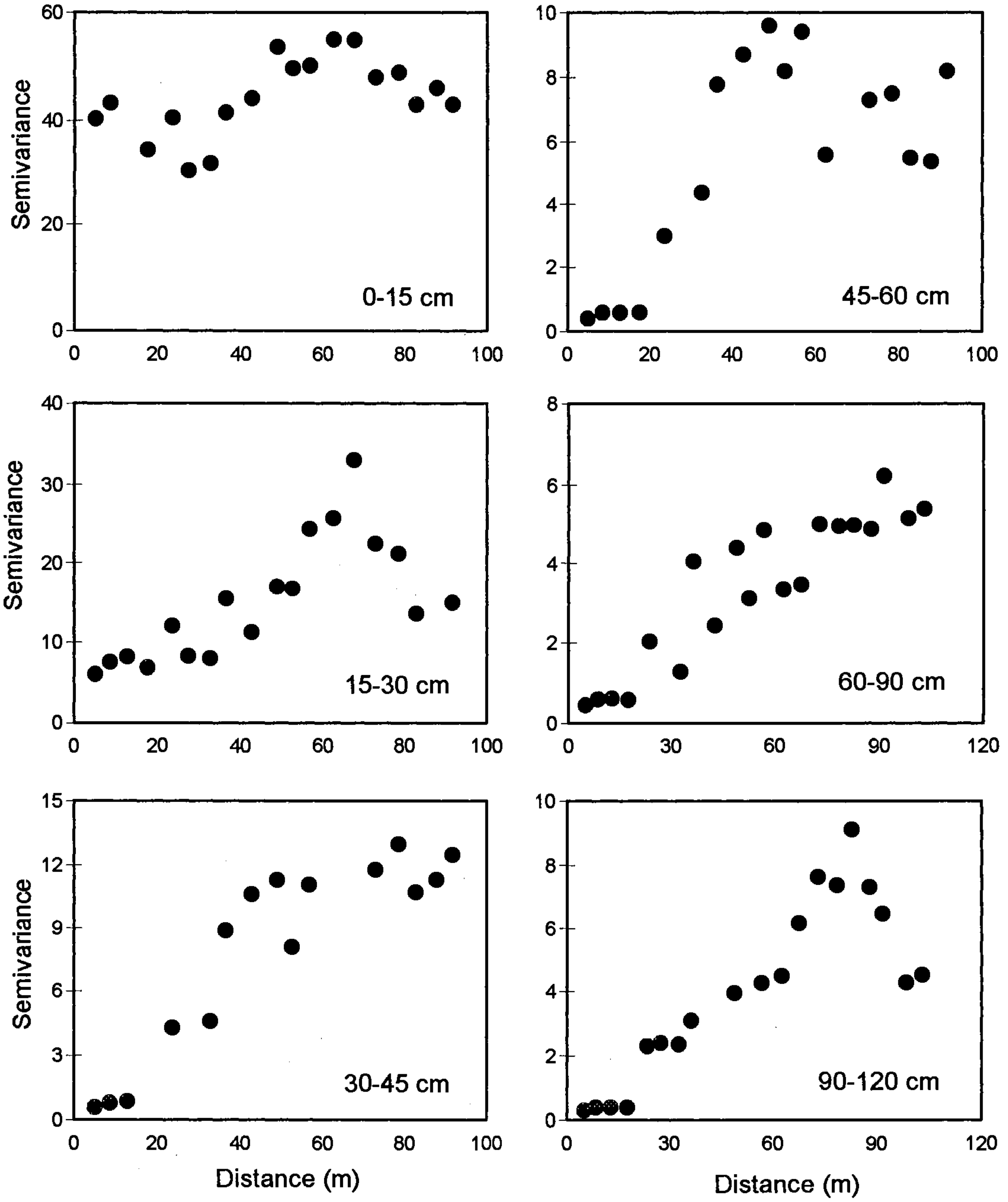


Figure 5. Omnidirectional semivariograms for soil NH_4-N content (mg/kg).

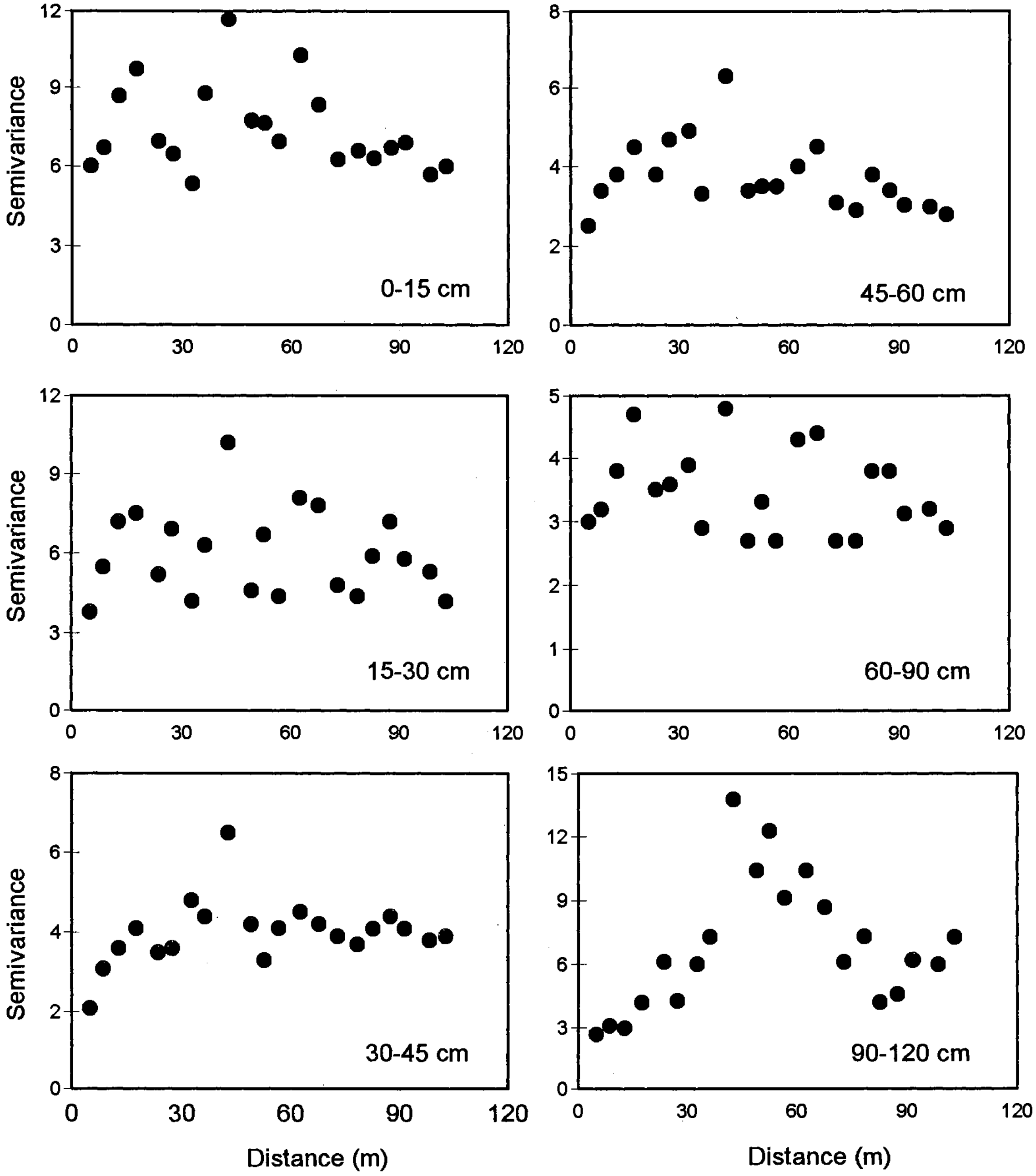


Figure 6. Omnidirectional semivariogram for total soil nitrogen (mg/kg).

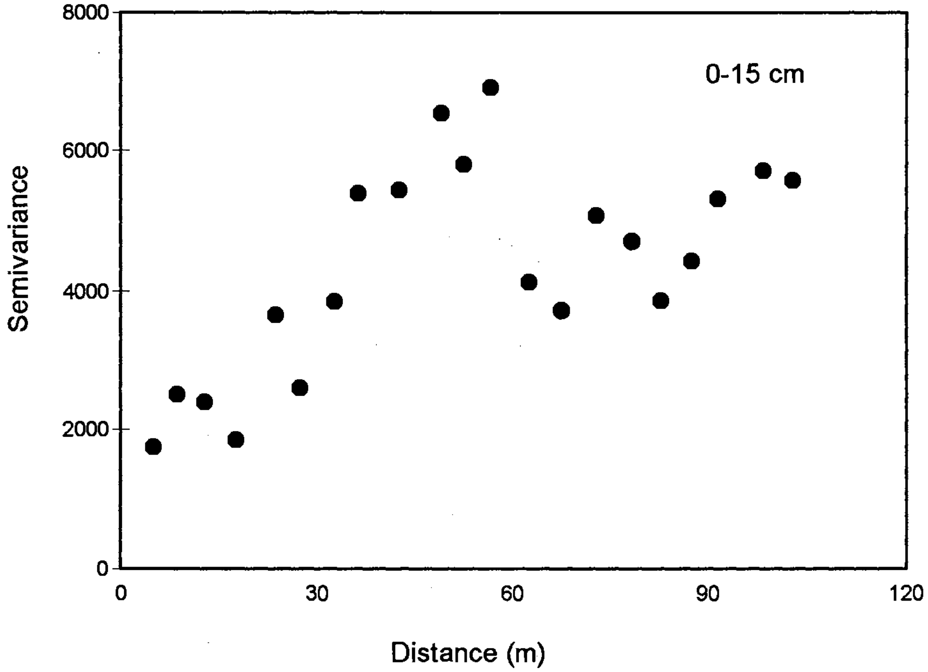


Figure 7. Kriged estimates and kriging standard deviations for soil NO_3-N (mg/kg)

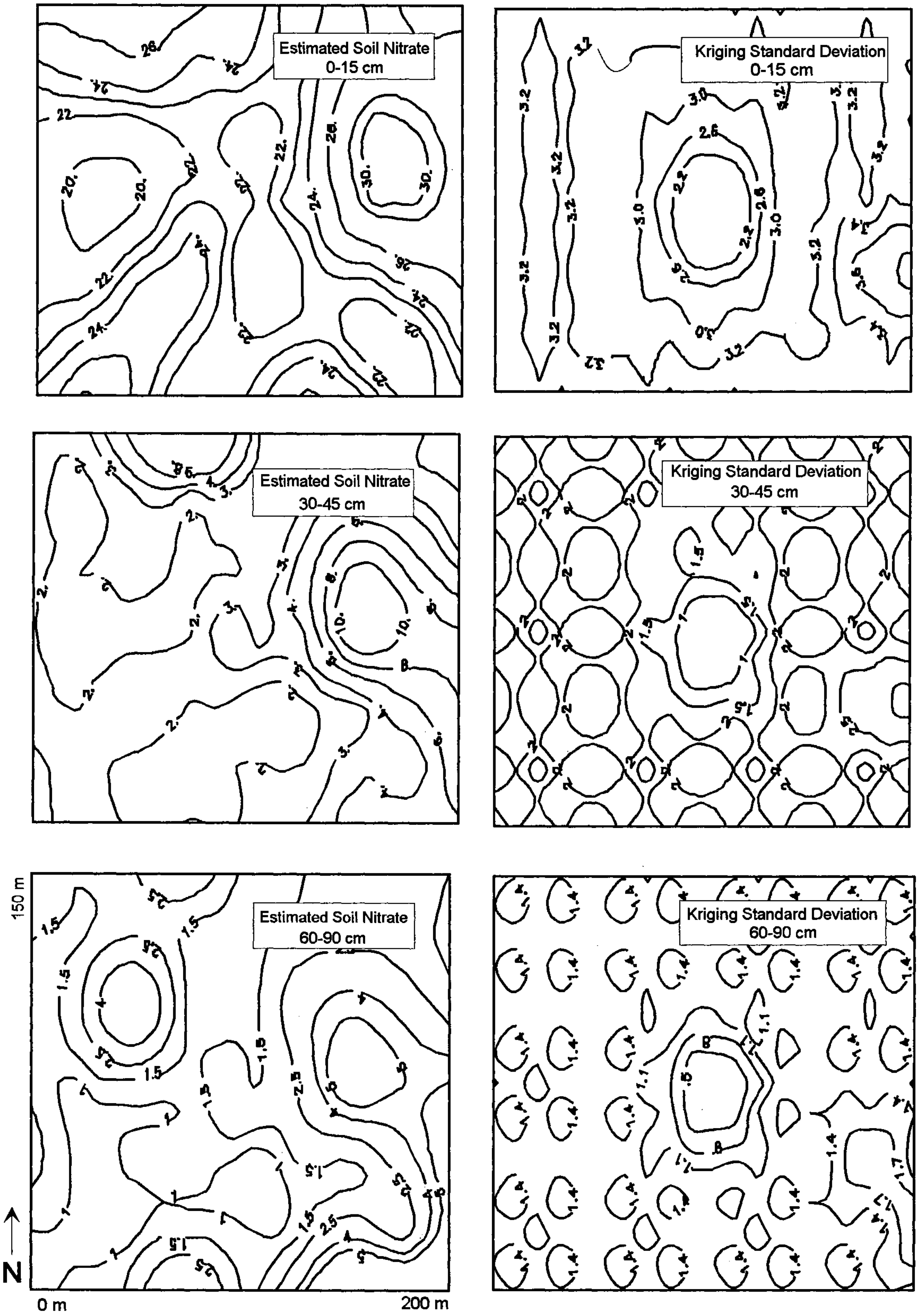
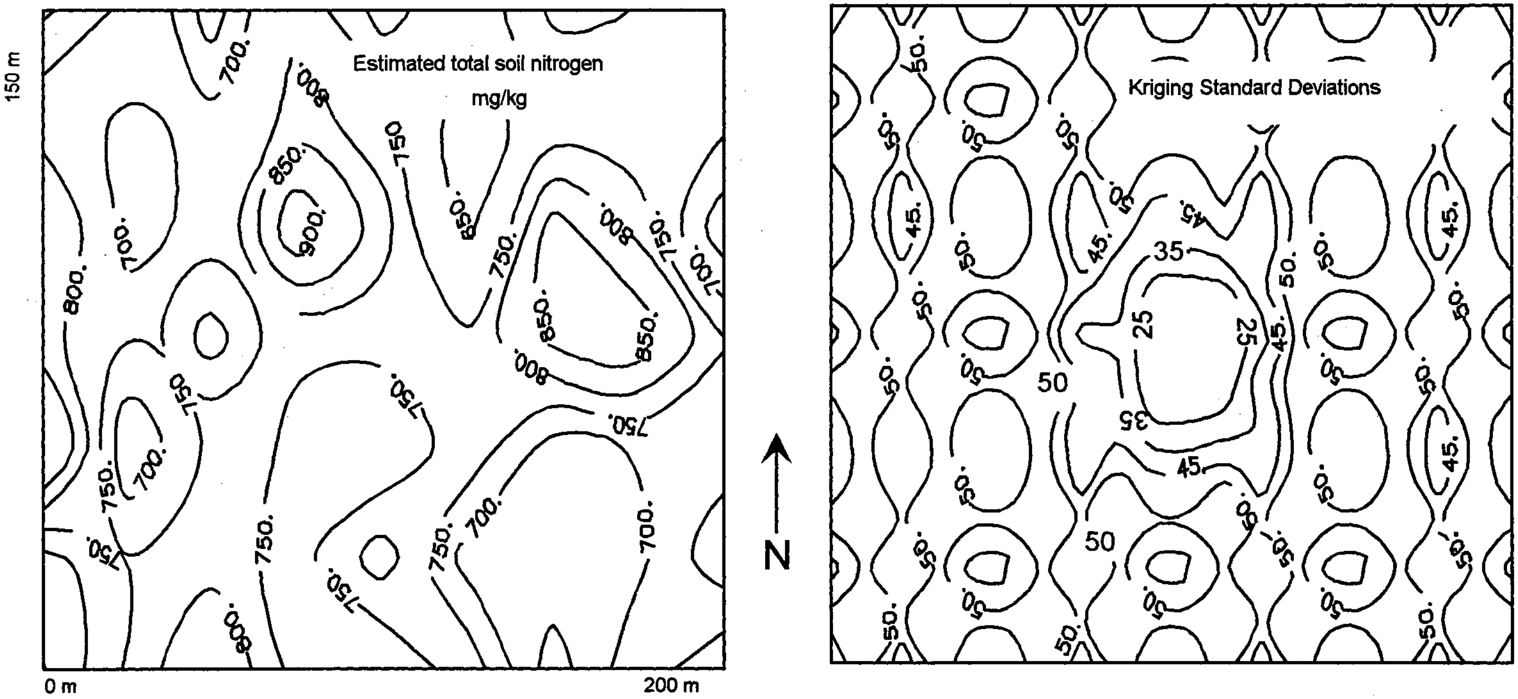


Figure 8. Kriged estimates and kriging standard deviations for total soil nitrogen (mg/kg).



CHAPTER II

GEOSTATISTICAL ANALYSIS OF SOIL PHOSPHORUS, POTASSIUM, ORGANIC CARBON AND pH IN A LONG-TERM WHEAT FIELD

ABSTRACT

An established agricultural field which had been cropped to continuous winter wheat since 1977 was sampled at regular intervals to a depth of 1.2 m. Each of the 99 soil cores was sectioned into six depth increments: 0-15, 15-30, 30-45, 45-60, 60-90, and 90-120 cm. Samples were analyzed for pH, organic carbon and Mehlich-III extractable P and K. The geostatistical techniques of semivariogram construction and block kriging were used to describe the spatial variability of these soil characteristics and estimate unknown values within the site. Constructed semivariograms revealed that both organic carbon and pH were spatially continuous, and spherical models with a defined range, nugget and sill could be fit to these semivariograms. Organic carbon was isotropic, as the semivariograms behaved similarly in all directions, with a range of 65 m. Semivariograms for pH exhibited a range of 60 m, regardless of the soil depth, and the proportion of the sill that was random (nugget) increased with increasing depth. Potassium semivariograms were less continuous, and nested models were necessary to obtain adequate cross-validation and kriging estimates. Soil phosphorus semivariograms were erratic, and all depths except

90-120 cm were fit to a nugget model, indicating a random phenomena. Block kriged estimates of soil K, pH and organic carbon were accurate, and adequately described the variability found in the actual data sets. It is likely that variable characteristics such as P and K are greatly affected by agricultural practices such as fertilization and cropping, and sampling distances may need to be adjusted so that close variability will not greatly influence the semivariograms. The use of cokriging and cross-semivariograms to estimate variable characteristics from more stable data sets is also recommended.

INTRODUCTION

The spatial variability of soil characteristics is a research topic that has received much attention in recent years. Like most natural phenomena, it is likely that soil characteristics contain some degree of spatial continuity, as variables are affected by their environment of deposition. Geostatistics is a method for describing this spatial variability; that is, a statistical procedure which considers the distance and, possibly, direction between samples. The description of the spatial variability of soil characteristics provides more than maximum and minimum values; it offers a picture of the continuity of a variable across a field or sampled area.

Initial studies of the spatial variability of soil characteristics examined physical soil properties. Such characteristics included sand and clay content and hydraulic properties, variables which are a relatively stable function of the soil itself when compared to the seasonal changes of characteristics such as soil P, K, or pH.

Of characteristics in soil fertility, soil pH is the variable that has been studied most extensively. Soil samples taken at 10 m intervals within a 7200 m^2 grid and analyzed for pH indicated that no spatial continuity existed, a behavior called the nugget effect (Campbell, 1978). Sampling within a small area (<150 m), researchers found that pH did exhibit spatial continuity, and a linear semivariogram was fit to the data (Tabor et al., 1985). Other research found that pH contained spatial continuity, with the distribution influenced by carbonaceous parent material, even in surface samples (Miller, et al, 1988). In addition to describing the spatial variability of soil pH, work by Laslett and McBratney (1990) examined the suitability of universal kriging for predicting values. The spatial variability of soil pH fit a spherical model with a fitted range of 55 m. It was concluded that geostatistical methods were superior to the other types of estimation methods for describing spatial variability and accurately calculating pH estimates.

The spatial variability of organic carbon has been fit to a spherical model, with a range of 500 m. The expressed variability of organic carbon in this study was isotropic, as the semivariograms behaved similarly over all directions (Miller, et al., 1988). By comparison, the organic carbon content from a 380 x 100-km sampling grid was found to be completely random, a function of the diverse factors which influence soil organic carbon content (Ovalles and Collins, 1988). The spatial continuity of organic carbon in a grazed pasture was approximated by a linear semivariogram (West, et al, 1989). In this study, estimated organic carbon contents were not as variable as P and K, particularly near the pastures water source.

The continuity and estimation of soil P and K is discussed in only a few studies. Soil P and K were also examined in the grazing study (West, et al.,

1989) and it was found that the semivariograms for these nutrients could be fit to a linear model. Kriging procedures highlighted areas of accumulated P and K, regions which could be sampled separately or avoided in order to obtain realistic fertilizer recommendations (West, et al, 1989). Potassium semivariograms in an irrigated cotton field were purely random, showing no spatial dependance for samples > 45 m apart, while the log transformation of phosphate data yielded semivariograms that were spatially related within a range of 80 meters (Tabor, et al, 1985).

Because the spatial variability of fertility constituents (pH, P, K, etc.) have not been widely documented, the objective of this paper was to examine the spatial continuity of soil characteristics that are important in agricultural systems. Among these are most certainly the added plant nutrients: N, P and K, and soil pH, which is an indicator of a soils' need for lime. Organic carbon content is a function of agricultural activities, including tillage, crop, and yield. Since the organic pool is a factor in N cycling, examination of its' spatial characteristics will help quantify variability of forms of N that have been discussed elsewhere (Guertal and Westerman, 1993, unpublished).

METHODS AND MATERIALS

A specific description of the sampling grid and sampling methodology can be found in Guertal and Westerman (1993, unpublished).

Once sectioned and air-dried, the samples were analyzed for Mehlich-III extractable P and K, and soil pH. Phosphorus content was measured colorimetrically, using the molybdate blue procedure (Murphy and Riley, 1962), and potassium was analyzed by atomic absorption. Only the 0-15 cm soil depth was analyzed for organic carbon content, employing dry combustion in a Carlo-Erba NA 1500 analyzer. Soil pH was recorded in a 1:1 soil:water solution, using a pH electrode. All reported values were averages of duplicate sample analyses.

Geostatistical analyses (semivariogram construction and kriging) and standard statistical analyses were performed using the geostatistical package GEOEAS (Englund and Sparks, 1988). Data employed in the calculations were untransformed, and no outlying values were removed from the data sets.

Semivariograms were created both directionally and omnidirectionally. The lag distance used in the calculations of the semivariograms was adjusted until a clear picture of spatial continuity emerged. Usually, this lag distance was 5 m for the omnidirectional semivariograms and 25 m for the directional semivariograms. These lag distances represented actual sampling distances for small and large grids, respectively. An angular tolerance of 22.5 degrees was used in the calculation of directional semivariograms. When this tolerance was used in connection with four directions (N, NW, W, SW) the spatial continuity for 180 degrees was described.

Models were visually fit to both omnidirectional and directional semivariograms. These models were employed in the estimation procedure of block kriging. In most cases the sill and nugget determined by the omnidirectional semivariogram model were employed in the block kriging procedure, and these coefficients were combined with the major and minor directions of anisotropy. Anisotropy existed if the directional semivariograms behaved differently across direction. If a directional semivariogram was fit to a nugget model then the omnidirectional model coefficients usually did not provide the best kriging estimate, and a nested model from directional semivariograms was employed.

The accuracy of models used in the kriging procedure were tested through a cross-validation procedure. Known values at each sample location were estimated by kriging, and those estimated values were compared to actual values. Adequate models were recorded when the mean of the estimation errors were close to zero and the variance of the errors was minimized and equal to the kriging variance. These indices of accurate models are hallmarks of the kriging procedure, which is a best, linear, unbiased estimation method (B.L.U.E.)(Issaks and Srivastava, 1989). Kriging is unbiased because the mean square error equals zero, and best because the variance of the errors is minimized.

Once cross-validation had confirmed the models accuracy, block kriging was performed. Block kriging produces an average estimated value for a region of interest, as compared to a single point value. Blocks with a 100 m^2 area were estimated, producing a total of 300 estimated areas within the sampled site. Both the estimated values and kriging standard deviations were illustrated through the use of contour plots, using a contouring program in the GEOEAS package.

Detailed discussions on the theories and methodologies of geostatistics may be found in Wolf and Rogowski (1991); Hamlett, et al., (1986), Mulla, D.J. (1988), Russo (1984), and Vieira, et al., (1981).

RESULTS AND DISCUSSION

Contour plots for organic carbon at the 0-15 cm depth and K, P and pH at six depth increments are illustrated in Figures 1-4, respectively. Summary statistics for these variables are listed in Table 1.

The contour plot of organic carbon content (Figure 1) illustrates the relatively constant organic carbon values found across the site. Deviations from the mean value were not particularly large (Table 1) and the skew was well below 1.0, indicating a data set that would produce stable semivariograms. The contour plot of organic carbon was similar to that found for total N (Guertal and Westerman, 1993, unpublished), a function of the close relationships that exist between this variable and total N.

Soil pH (Figure 4) also contained relatively low data variability, and none of the skews indicated data sets with large outliers. Surface pH values (0-15 cm) were acidic, reflecting the continuous removal of basic cations through cropping, nitrogen fertilizer application and lack of applied lime. Once past the 30 cm depth, mean pH values rose above 6.5, as cropping and nitrogen effects upon pH were limited. Generally, pH values declined as sampling moved eastward, but this trend decreased at the 60 cm soil depth. At 90-120 cm pH had stabilized to a mean value of 7.2 throughout the sampling area.

Variability of soil phosphorus changed both horizontally and vertically. Horizontally, skews were not particularly large at each soil depth, and the distribution of outlying values did not vary widely from one depth to another (Table 1). Vertically, regions of high P content were not contiguous from one depth to the next (Figure 3). For example, a region of high phosphorus at 15-30 cm was not found at 30-90 cm in that region. Mean P values decreased from 0-45 cm, but increased thereafter. This increase could be a function of: 1) less rooting volume at these lower depths to remove and redeposit P on the soil surface, or 2) an increase in soil P due to pedogenic processes.

Soil potassium demonstrated the largest variability of any of the measured soil characteristics. Skews were large, indicating the presence of outliers that could affect the quality of semivariogram construction. Despite the presence of outliers, mean potassium values were relatively stable over all depths (Table 1), and regions of higher K content remained constant over all depths (Figure 2).

Increased variability found in the P and K values reflects their labile nature, with a relatively small pool available to buffer the amounts of extractable P and K. In contrast, organic carbon contents are a function of a large, well-buffered pool of organic matter, and transformations of organic carbon over time are likely to proceed at a relatively slow and stable rate. This difference in variability is not a new phenomena, and has been previously recognized (West, et al., 1989).

Omnidirectional semivariograms for soil organic carbon, potassium, phosphorus and pH are provided in Figures 5 through 8. The presence of skews in the potassium data set is seen in the erratic shape of the semivariograms at each depth (Figure 6). Additionally, the proportion of variance that is purely random (the nugget) is large, further evidence of a variable data set. The semivariograms behave similarly at each depth, and all were fit to a general spherical model. Once past the surface, the range of the semivariograms dropped from 75 m (at 0-15 cm) to approximately 40 m. The increased range of spatial continuity found at the 0-15 cm depth is, in part, a function of fertilizer additions to the soil, as a large portion of extractable K would be residual from fertilizer applications.

Both the organic carbon and pH omnidirectional semivariograms were continuous, exhibiting the classical spherical shape with a defined nugget, range and sill (Figures 5 and 8). The range for organic carbon content was 65 m and the range for pH was 60 m. Samples taken farther apart than these distances were unrelated, and spatial statistics could not describe their behavior. Semivariograms of soil pH below the 0-15 cm depth were also fit to a linear model, but these models were less accurate than spherical models when evaluated through cross-validation. The 90-120 cm soil depth produced an omnidirectional semivariogram of pH that was close to a nugget effect, indicating that pH was almost a random occurrence at that depth.

With the exception of the 90-120 cm soil depth, soil phosphorus values exhibited a nugget effect. Regardless of the selected lag distance, semivariograms were erratic, with no discernable shape that could be modeled (Figure 7). Directional semivariograms for soil P are shown in Figure 11, further indicating the random nature of the data set. Phosphorus semivariograms show the extreme sensitivity of the semivariogram estimator at close lag distances. The largest semivariances occur at short lag distances, and the semivariograms become more stable at greater distances.

Because the majority of soil phosphorus semivariograms were fit to a nugget model, cross-validation and kriging were not performed on this data set.

Omnidirectional semivariograms (Figures 9,10,12) were used to determine if the data sets were isotropic or anisotropic. Anisotropy existed when the semivariograms varied by direction, indicating that the spatial continuity of the soil characteristic varied with direction. Major and minor axes of anisotropy and the degree to which the axes differed (anisotropic ratio) are provided in

Table 2.

Organic carbon semivariograms were found to be isotropic, with the same nugget and sill values fit to every directional semivariogram. The NW semivariogram contained the poorest spatial continuity, but the isotropic model still fit the direction relatively well. The isotropic ratio for organic carbon was 1.0, indicating that organic carbon behaved the same over all directions (Table 2). This isotropic condition was also found to exist for total N (Guertal and Westerman, 1993, unpublished). Since an isotropic case existed, the model used for cross-validation and kriging was the model fit to the omnidirectional semivariogram (Table 3).

Directional semivariograms for soil potassium and pH demonstrated the presence of anisotropy, as sills, nuggets and ranges varied by direction. These anisotropies are related to the variability found within these data sets: variabilities caused by tillage, fertility and cropping practices that may not affect organic carbon contents to the same extent. In general, sill, nugget and range values fit to directional pH semivariograms were less variable than those fit to potassium semivariograms, and coefficients fit to the omnidirectional semivariograms provided accurate cross-validation parameters (Tables 3 and 4). Potassium directional semivariograms were variable, and nested models that emphasized the major axis of anisotropy were necessary to obtain satisfactory cross-validation checks (Table 4).

Criteria used for the cross-validation procedure are summarized in Table 4. Adequate model fits were indicated when the mean of the estimation errors were close to zero, and the variance of the errors is minimized and equal to the kriging variance. Additionally, the dimensionless mean square error (DMSE) should equal 1, while the mean normalized error (ME) should equal zero. There can be other criteria for checking the accuracy of the cross-validation procedure, but these are four commonly used techniques (Samper and Neuman, 1989; Unlu, et al., 1990). All of the cross-validated models fit these criteria, although the mean of the estimation errors for soil K contained larger differences, and the variances, while minimized, were large. Again, this is a result of the large differences in semivariograms over direction and the variability of the potassium data itself.

Kriged estimates and kriging standard deviations for oranic carbon, K and pH are found in Figures 13, 14 and 15. Estimated organic carbon contents accurately reflected the actual data values, only slightly overestimating regions of low organic carbon content. Kriging standard deviations were relatively constant throughout the site, and smallest at the center where the small sampling grid was located. As many as twenty-four closely spaced samples could be used to estimate values, and the number of closely spaced samples in this small grid region lowered the kriging standard deviation. The kriging standard deviations of both soil K and soil pH also demonstrated this impact of the small sampling grid, as standard deviations were smallest at the center of these plots.

Kriged estimates for soil pH agreed well with the actual data values, producing contour plots of estimated values that accurately described the increasing pH trend from E to W across the field. Kriged estimates and the kriging standard deviations from the 30-45 cm depth demonstrate the impact of the SW direction being fit to a nugget model (Table 2), as the NW direction is given increased weighting in the estimation process.

Estimated K contents were more variable than pH and organic carbon, and estimates were usually slightly larger than the actual values in the region. This can be partly explained by the block kriging procedure itself, which provides an average value for a region rather than a specific point. The positively-skewed values of the actual data could cause overestimation of the average block values within the site.

CONCLUSIONS

Geostatistical techniques of semivariogram construction and block kriging are useful for describing spatial continuity of some soil characteristics. The spatial variability of less alterable soil indices such as organic carbon and pH are continuous, and easily described by models with a defined nugget, range and sill. In comparison, soil P and K did not contain strong spatial relationships, and semivariograms were either a completely random model or anisotropic in nature.

Tillage, fertility and cropping practices can greatly affect the direction and degree of spatial continuity. This would most likely affect those nutrients which are applied for crop growth. The direction of greatest spatial continuity changed from SW to N and NW once past the 15 cm depth, a function of agricultural processes upon that 0-15 cm depth. For agricultural use, the sensitivity of semivariograms for close sampling distances may be avoided by spreading samples across more hectares at larger lag distances. The experimental sampling grid in this paper is useful for the initial validations of nutrient variability, but was too sensitive for actual fertilizer recommendation procedures. The spatial variability of changeable nutrients such as P and K may be better described over larger regions with increased sample spacing, particularly when environmental concerns are not the predominate reason for sampling. An alternative sampling scheme could use clustered samples, producing average values for smaller regions. These average values could then be used for semivariogram construction and kriging over larger areas.

It appears that the strong spatial continuity of soil characteristics such as organic carbon and pH could be useful tools in the estimation of variables that exhibit poorer spatial distributions. Using geostatistical procedures such as cross-semivariogram construction and cokriging, it could be possible to employ a variable such as organic carbon content in the estimation soil nitrogen content across a sampled site. Soil characteristics such as CEC may be used to estimate K contents, or pH as an estimator for soil nitrate content. These types of relationships deserve further study, and support the use of geostatistics for the description and estimation of soil characteristics.

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Table 1. Summary statistics for soil P, K, pH and organic carbon.

	Mehlich-III P					Mehlich-III K					pH				
Depth	Min	Max	Mean	Std Dv	Skew	Min	Max	Mean	Std Dv	Skew	Min	Max	Mean	Std Dv	Skew
--cm--	mg/kg					mg/kg					mg/kg				
0-15	49	135	88	23	0.2	129	707	271	80	2.2	4.1	6.0	5.0	0.4	0.3
15-30	16	105	45	20	1.1	127	371	200	47	1.5	4.4	6.4	5.5	0.4	-0.6
30-45	12	109	42	19	1.4	111	352	162	33	3.1	5.6	7.0	6.5	0.2	-1.0
45-60	14	122	58	22	0.8	109	406	154	33	4.9	6.2	7.4	6.9	0.2	-0.5
60-90	26	124	66	22	0.6	97	290	152	24	1.8	6.5	7.6	7.2	0.2	-0.5
90-120	31	163	81	29	0.4	112	362	197	34	0.7	6.2	7.7	7.2	0.3	-1.0
	Organic Carbon														
	mg/kg														
0-15	7158	10802	8527	614	0.6										

Table 2. Major and minor axes of anisotropy for soil potassium, pH and organic carbon.

	Potassium			pH			Organic Carbon		
Depth	Major Axis	Minor Axis	Anisotropic Ratio	Major Axis	Minor Axis	Anisotropic Ratio	Major Axis	Minor Axis	Anisotropic Ratio
0-15	SW	W	1.4	SW	NW	1.9			1.0
15-30	N	NW	1.7	NW	SW	1.5			
30-45	N	NW	1.2	NW	SW*	2.8			
45-60	N	NW*	3.0	NW	SW*	2.8			
60-90	N	NW*	3.2	NW	SW*	3.2			
90-120	N	NW	1.2	NW	N	1.2			

* Minor axis fit to a pure nugget model. Anisotropic ratio calculated by dividing the major axis range by sampling distance (25 m).

Table 3. Semivariogram model(s) used in the kriging procedure.

	Potassium				pH				Organic Carbon			
Depth	Model(s)	Nugget	Sill	Direction	Model(s)	Nugget	Sill	Direction	Model(s)	Nugget	Sill	Direction
0-15	Spherical	200	7000	SW	Spherical	0.05	0.08	SW	Spherical	150000	250000	isotropic
	Spherical	200	9000	N								
30-45	Spherical	300	1400	N	Spherical	0.02	0.04	NW				
90-120	Spherical	100	1500	N	Spherical	0.05	0.06	NW				
	Spherical	100	1200	SW								

Table 4. Cross-validation criteria for the best-fit models for soil potassium, pH and organic carbon.

Depth ---cm---	Mean Est. Errors †	Var. Est. Errors @	σ_K^2 @	DMSE* ††	ME** †
		Potassium			
0-15	-0.260	6889.5	6773.3	1.00	-0.003
30-45	-0.500	1095.6	803.7	1.11	-0.02
90-120	0.197	1056.3	1218.0	0.93	0.006
		pH			
0-15	-0.001	0.11	0.09	1.11	-0.002
30-45	0.001	0.05	0.05	1.01	0.006
90-120	0.003	0.10	0.09	1.07	0.009
		Organic Carbon			
0-15	-0.194	404496	409984	0.99	-0.003

* Dimensionless Mean Square Error = $\left(\frac{1}{N} \frac{\sum (z^*_i - z_i)^2}{\sigma_K^2}\right)^{1/2}$

** Mean Normalized Error = $\left(\frac{1}{N} \sum \frac{z_i - z^*_i}{\sigma_K}\right)$

†, †† not significantly differently from 0,1 and 0, respectively, at α =0.01.

@ variances not signifcantly different at α = 0.10.

Figure1. Contour plot of organic carbon content (mg/kg).
0-15 cm

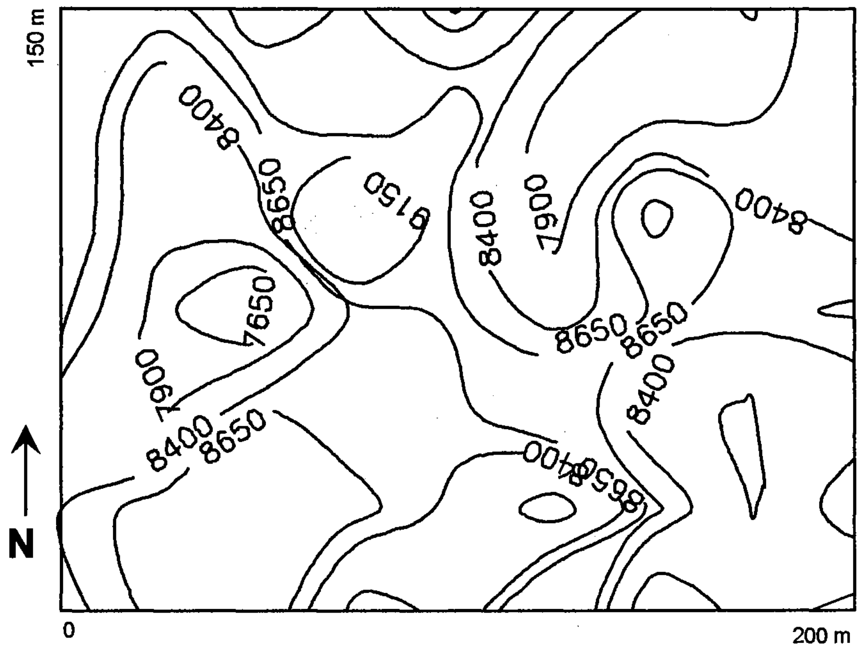


Figure 2. Contour plots of soil potassium content (mg/kg).

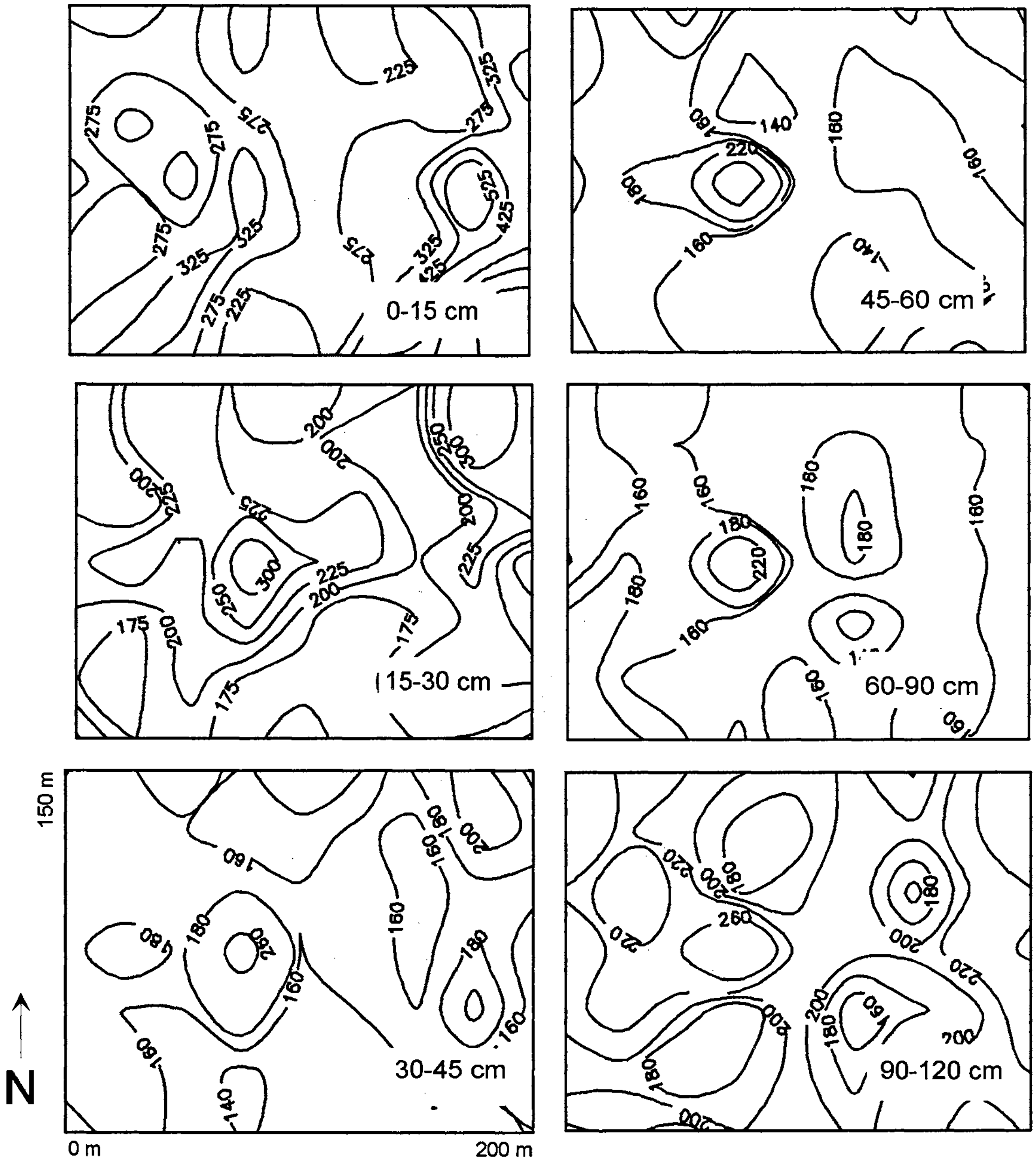


Figure 3. Contour plots of soil phosphorus values (mg/kg).

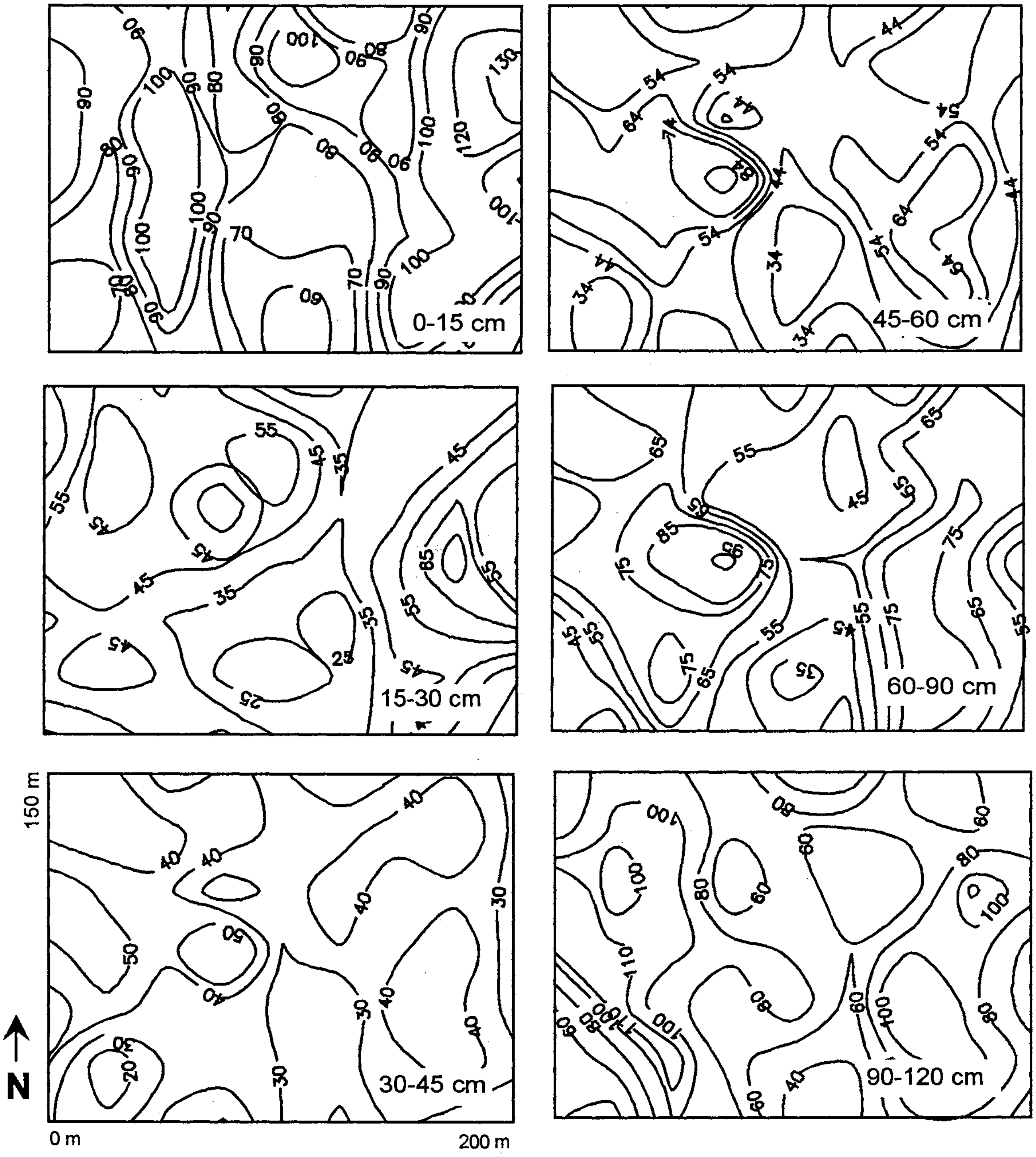


Figure 4. Contour plots of soil pH.

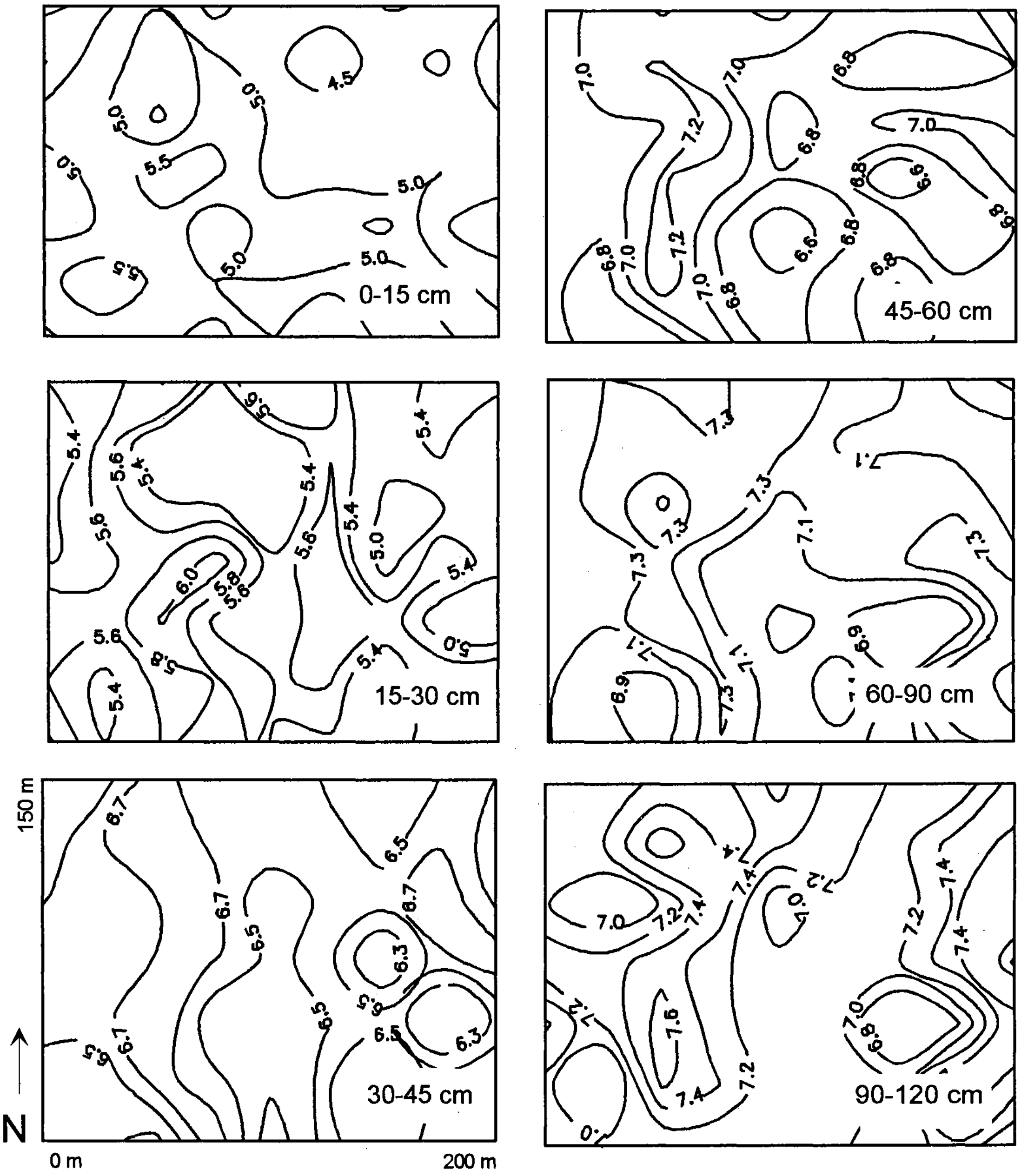


Figure 5. Omnidirectional semivariogram for organic carbon.

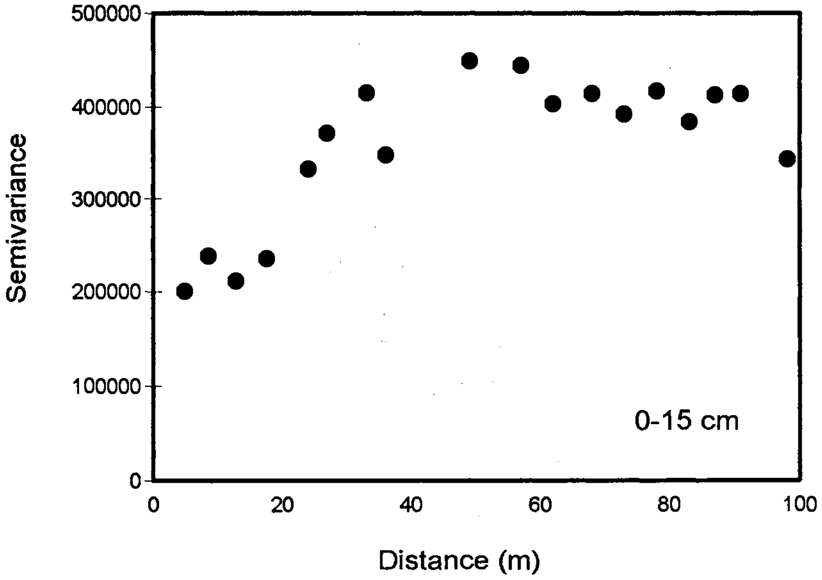


Figure 6. Omnidirectional semivariograms for soil potassium.

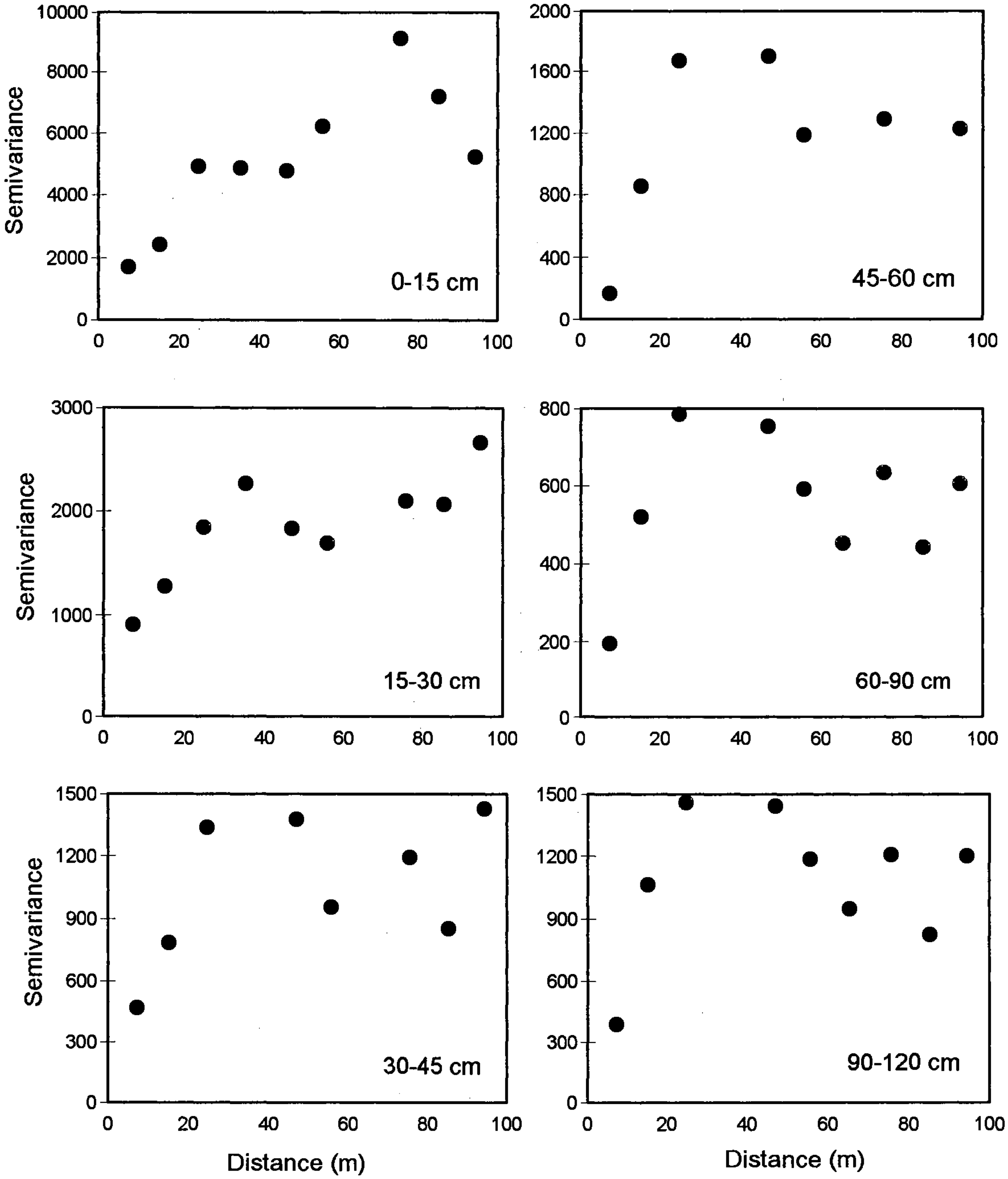


Figure 7. Omnidirectional semivariograms for soil phosphorus.

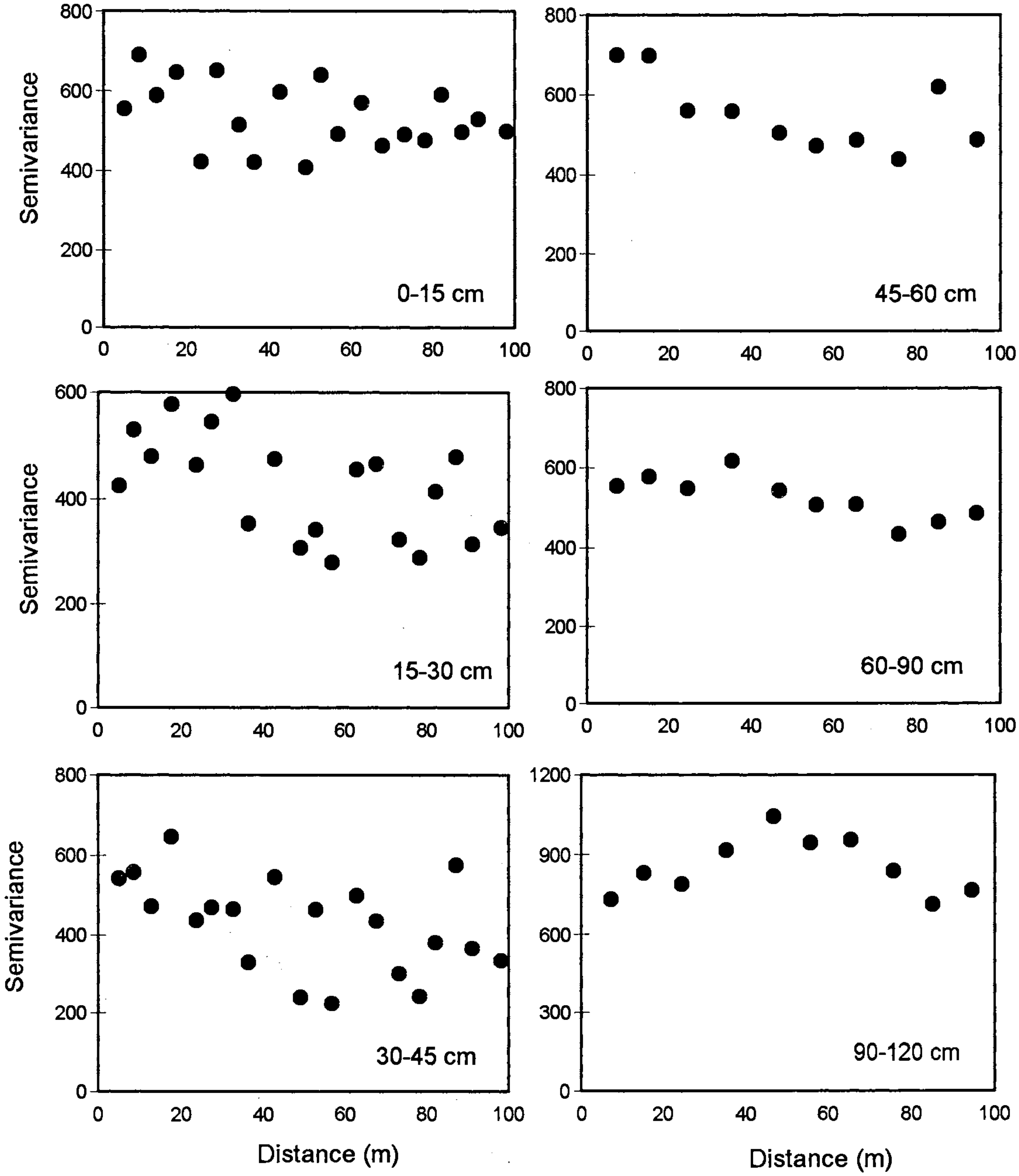


Figure 8. Omnidirectional semivariograms for soil pH.

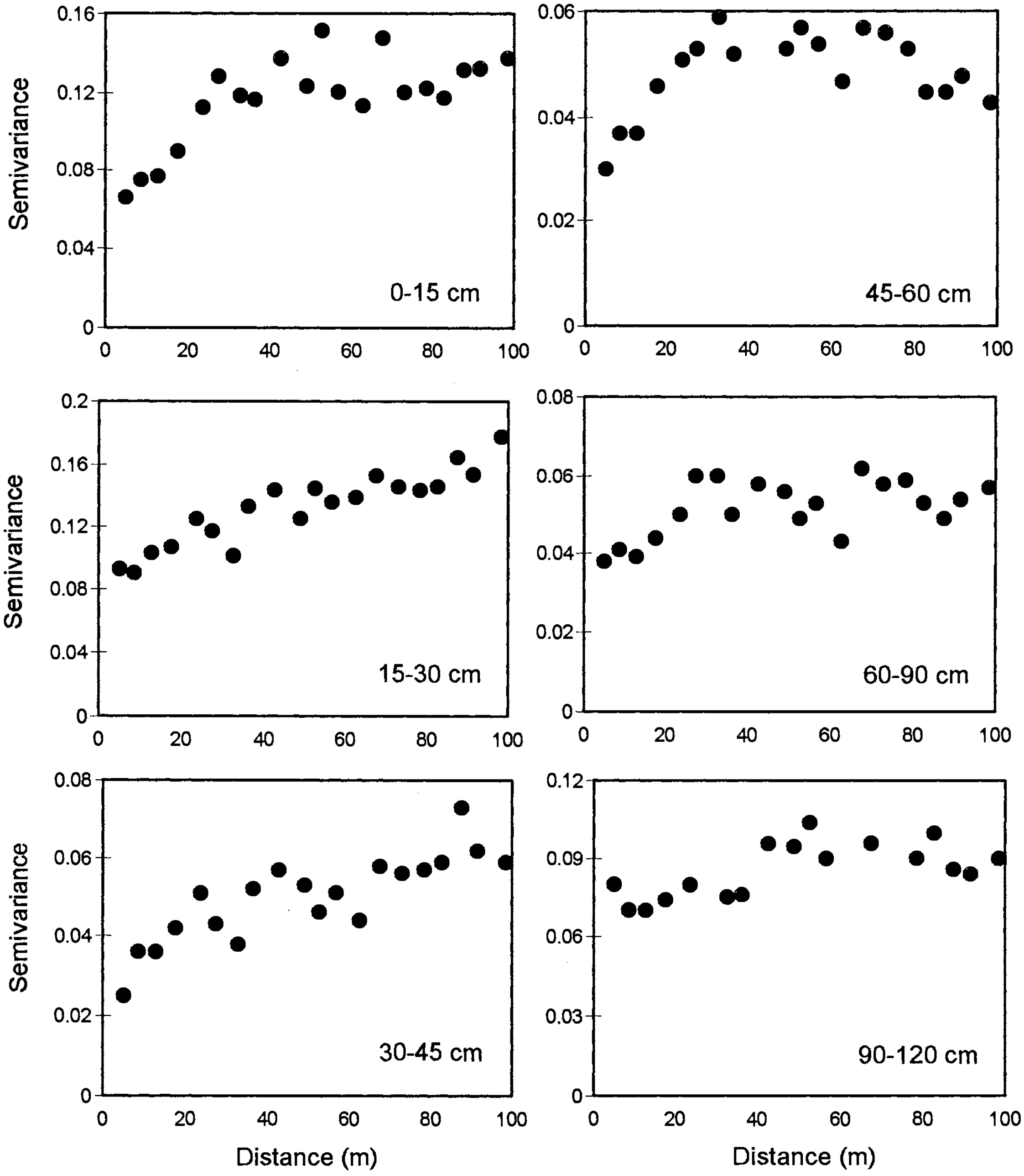


Figure 9. Directional semivariograms for organic carbon .
0-15 cm soil depth

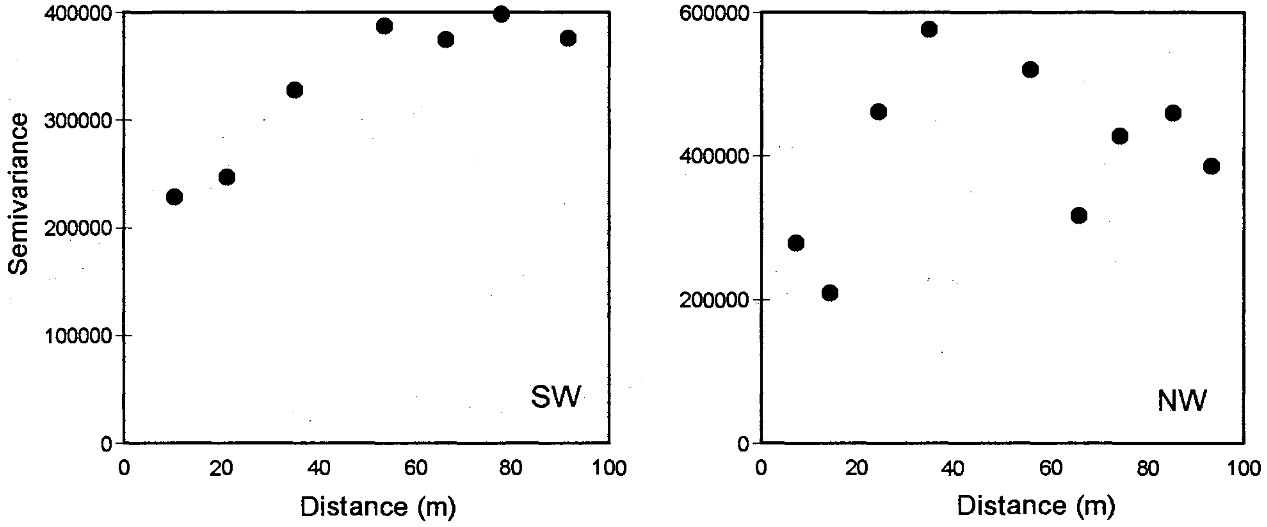


Figure10. Directional semivariograms for soil potassium.

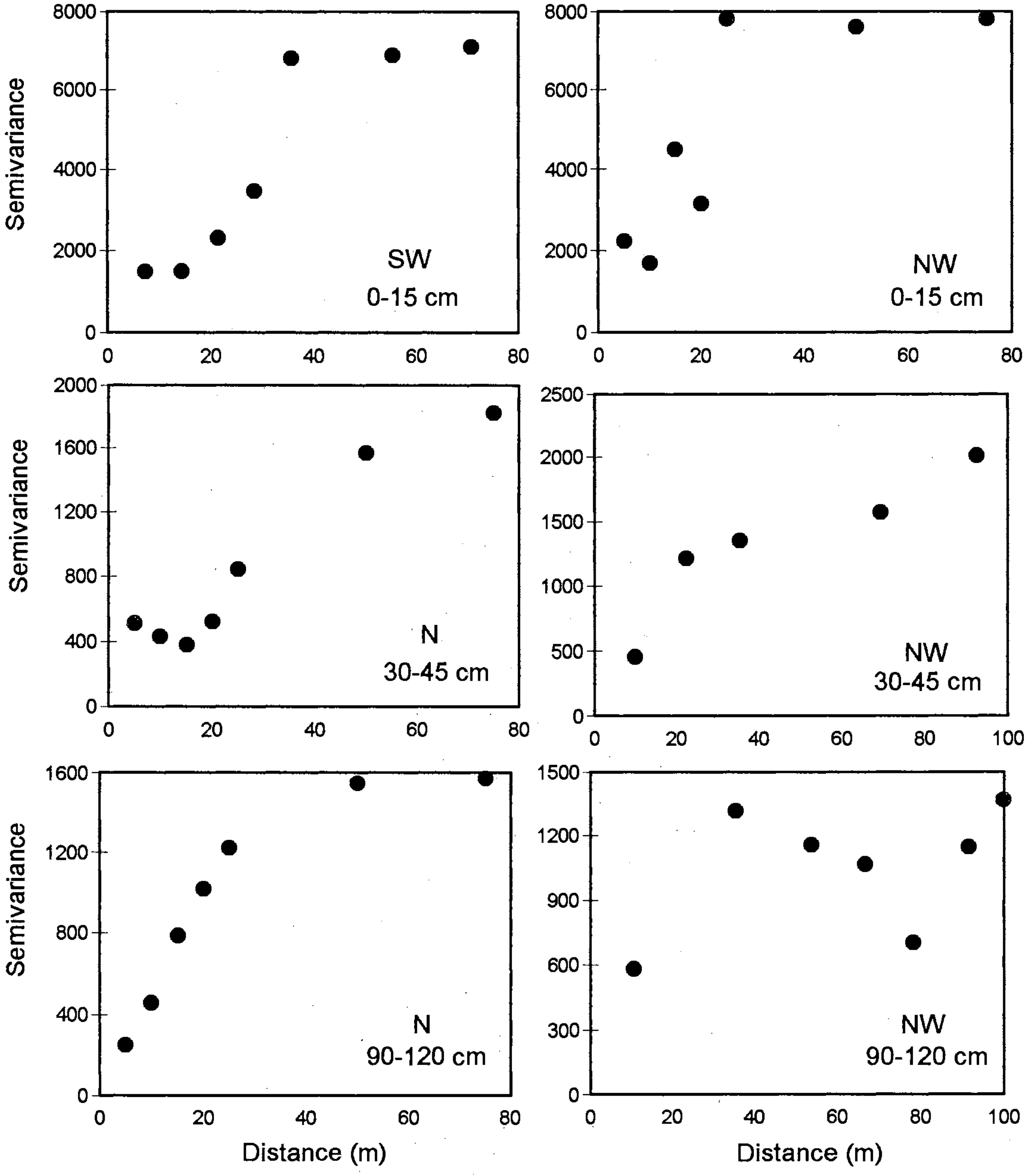


Figure 11. Directional semivariograms for soil phosphorus.

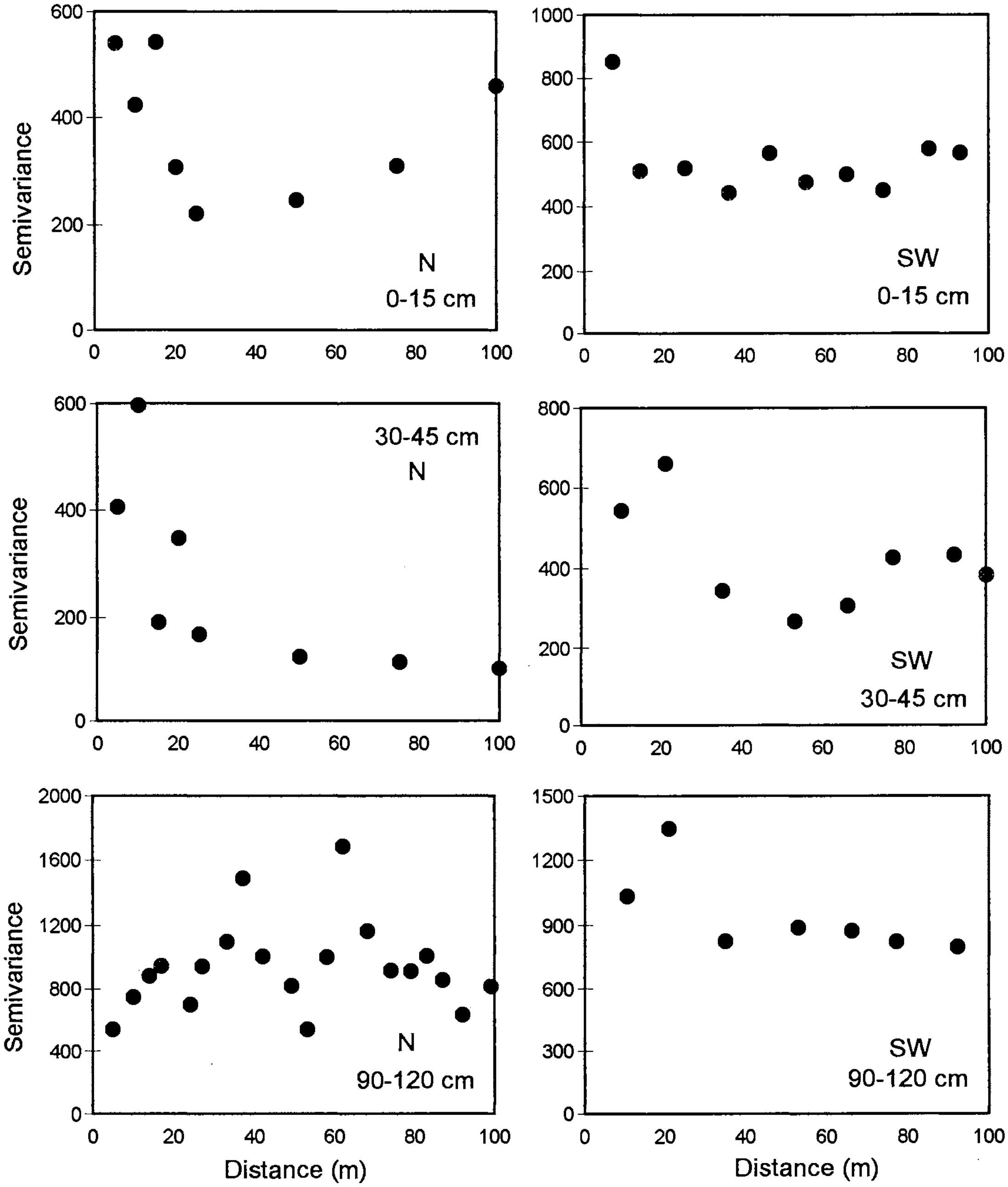


Figure 12. Directional semivariograms for soil pH.

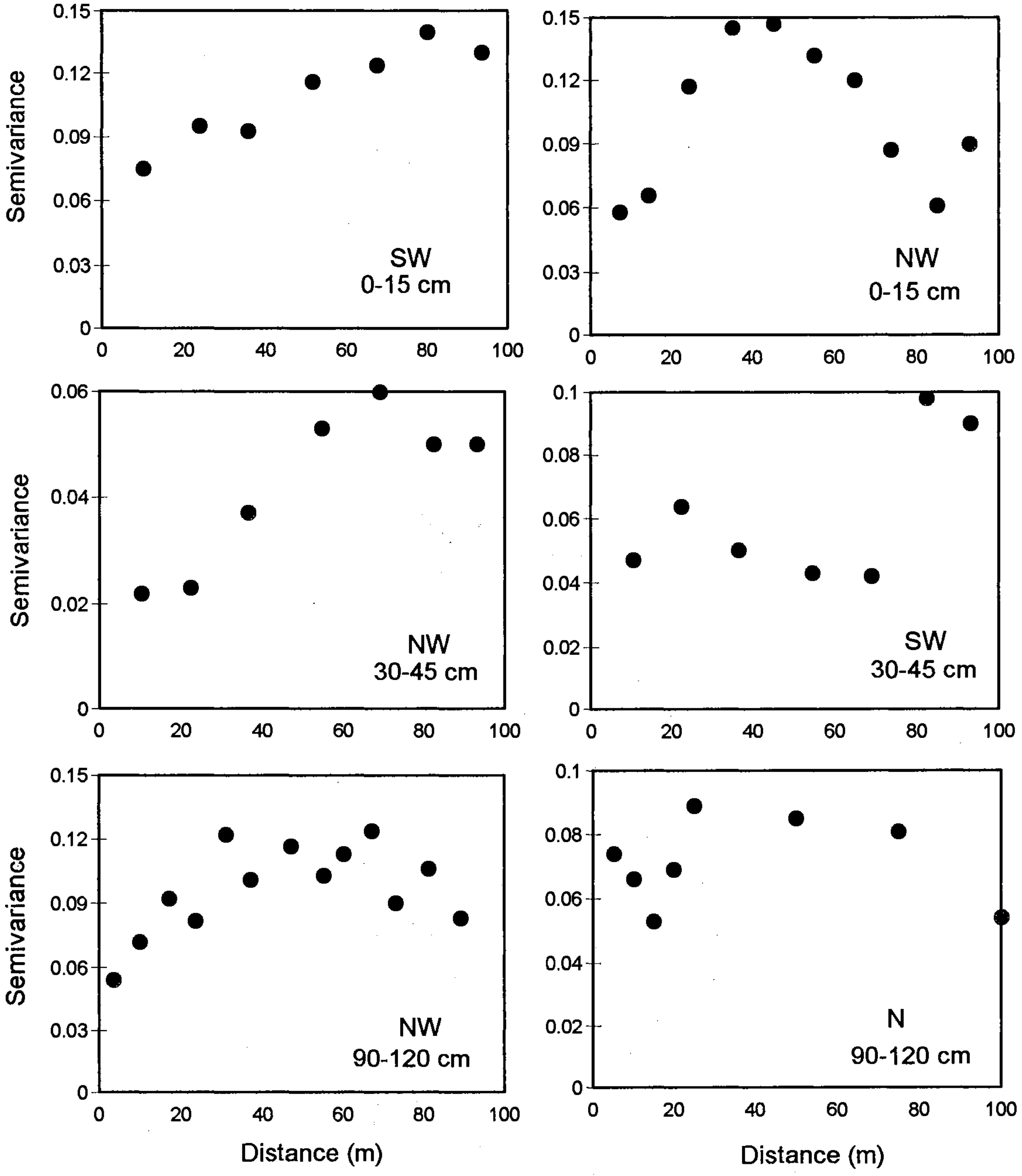


Figure 13. Estimated soil organic carbon content and kriging standard deviations.
0-15 cm soil depth

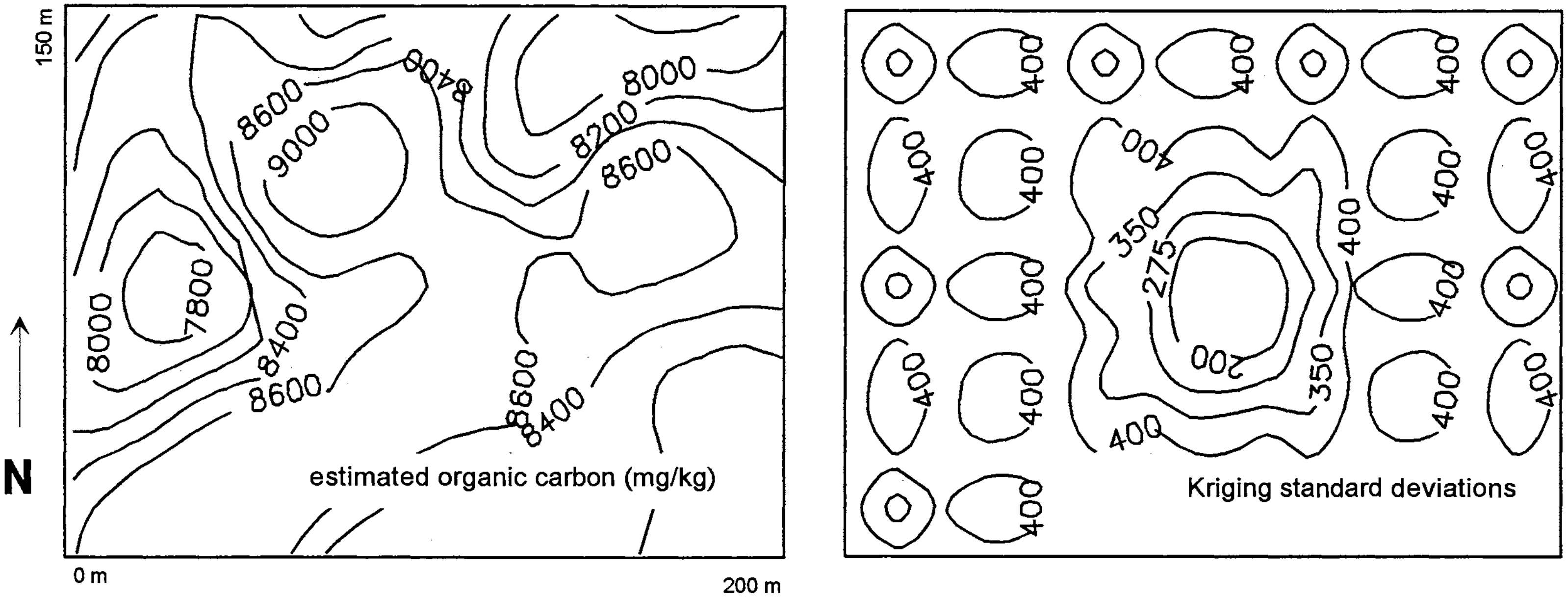


Figure 14. Kriged estimates and kriging standard deviations for soil potassium.

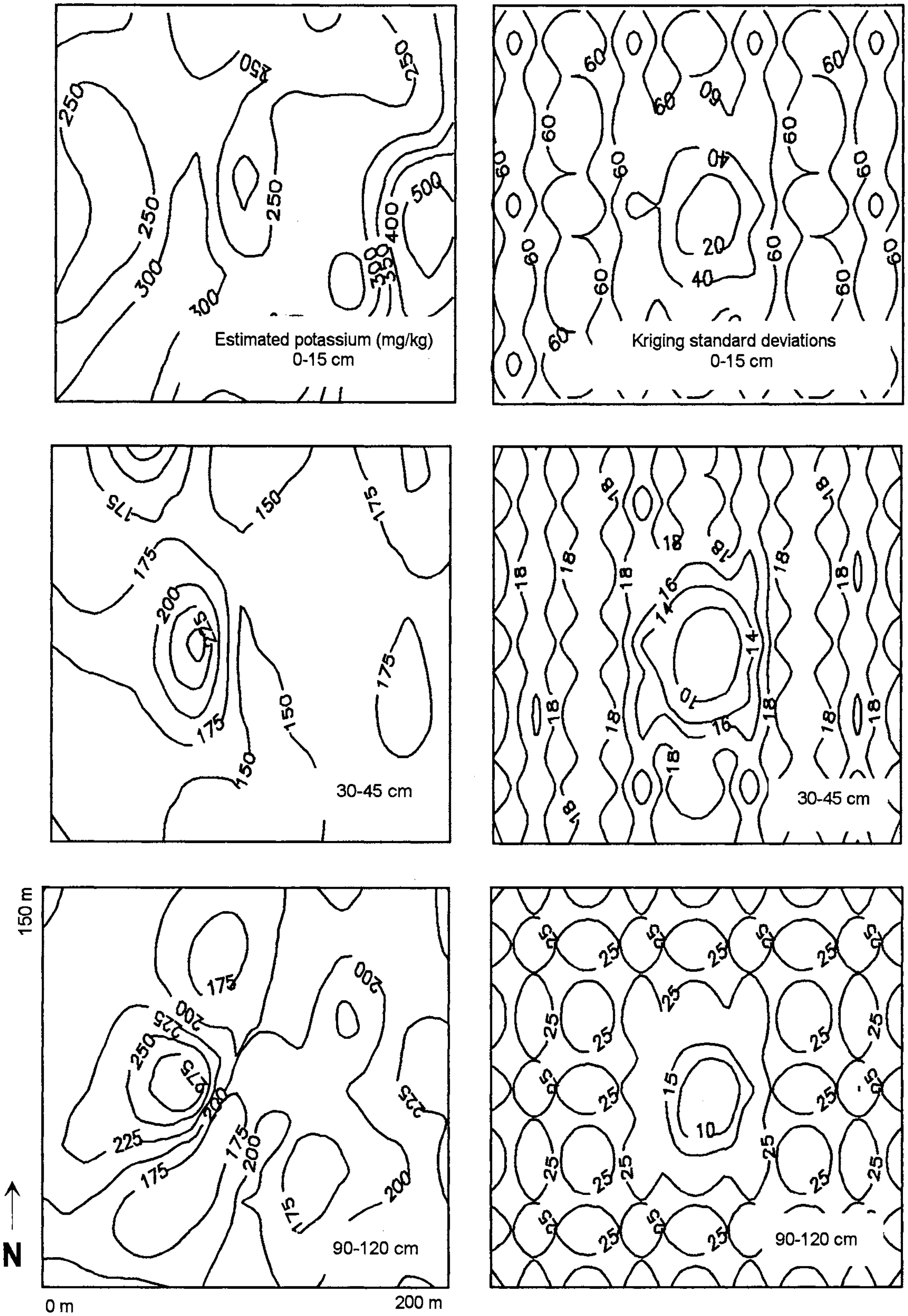
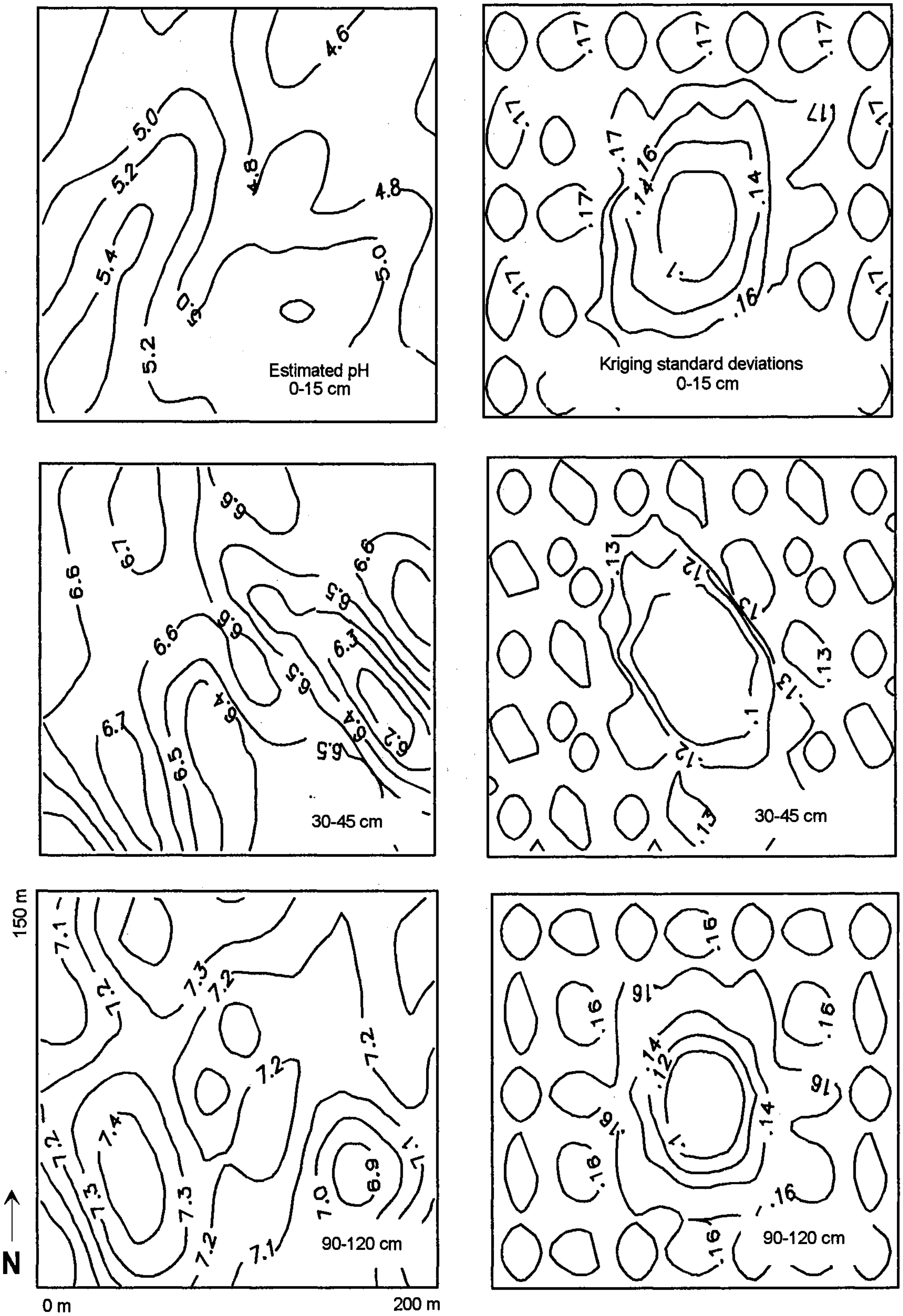


Figure 15. Kriged estimates and kriging standard deviations for soil pH.



CHAPTER III

CHANGES IN PHOSPHORUS, ALUMINUM AND MANGANESE IN THREE ACID-AFFECTED SOILS THAT HAVE BEEN AMENDED WITH PHOSPHORUS

ABSTRACT

Many soils in the southern Great Plains region that have been extensively cropped without additions of lime have developed an acidic surface layer, which may hinder wheat germination and growth. Field remediation of this problem is the application of banded P fertilizer, which is thought to alleviate Al toxicity for a limited period of time. Both a yield and forage response to banded P was observed, even though these soils contain sufficient amounts of residual P for crop growth and yield. The objective of this research was to examine the effect of added P on the behavior of Al, Mn and P in both . solution and extracted acidic soil. Soils were equilibrated with 0,1,3,5,7,10 mg P/L solutions for shaking times of 1,6,12 and 24 h, and the supernatant analyzed for P, Al and Mn content. The remaining soil was then extracted with either 2M KCl or Mehlich-III, and the resulting solutions were analyzed for Al and Mn or P, respectively. Phosphorus concentrations increased with P added, both in the supernatant and Mehlich-III solutions, and amounts of P in the solution decreased over time, at all levels of added P. Concentrations of Al decreased with added P, both in the solution and 2M KCl extractant. Concentrations of

Mn in both the solution and extractant did not decrease with added P, and in some cases the measured level of Mn increased over time. Addition of P to these acid soils appears to decrease both solution Al and extractable Al, but not Mn.

INTRODUCTION

Many soils located in the southern Great Plains are intensively cropped, and often planted to continuous winter wheat. Continued additions of nitrogen fertilizer and the removal of basic elements have slowly acidified the soils' plow layer, creating a zone of acid soil which hinders wheat seedling growth. The common remediation for this condition is the addition of lime, a remediation which is not economically viable in many rural areas.

Both aluminum and manganese become more available in acid soils. Aluminum toxicity limits root branching and rooting depth, severely inhibiting plant growth (Alam and Adams, 1976; Foy, 1984), while toxic levels of Mn appear to affect plant tops rather than roots (Foy, 1973). Aluminum reduces nutrient uptake, binding P on root surfaces and inhibiting the uptake of P (Ohki, 1985; Clarkson, 1966). The uptake of Ca, K, and Mg may also be altered when toxic levels of Al (Foy, 1984) or Mn (Ohki, 1984) are present.

The exact form of Al that damages growing wheat seedlings is uncertain, and conflicting research exists as to the specific nature of the rhizotoxic Al species. It is generally believed that the monomeric forms of aluminum are toxic (Wright, et al., 1987; Alva et al., 1986), forms which include Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$. Recently, research has demonstrated the phytotoxicity of polynuclear hydroxy-Al complexes in wheat (Parker, et al., 1988; Parker, et al., 1989). These hydroxy-Al polymers were generalized as the "Al_{13}" polymer (triskaidekaaluminum), a polynuclear Al species that is 10 times more rhizotoxic than Al^{3+} (Kinraide, 1991; Parker et al., 1989). However, the contribution of this phytotoxic polynuclear species in acidic soil conditions is still unknown (Parker, et al., 1989).

In acid soils ($pH < 5.5$) $\{Al^{3+}\}$ increases, and the activities of all other Al species decline. The predominate species include Al^{3+} and the mononuclear hydroxy-Al species $AlOH^{2+}$ and $Al(OH)_2^+$ (Kinraide, 1991). Because these species are commonly believed to be phytotoxic, the ferron colorimetric method is appropriate for Al analyses. Other Al colorimetric methods have been considered, but the ferron method is well suited for determining toxic Al (Al^{3+} + $AlOH^{2+}$ + $Al(OH)_2^+$) relatively rapidly and easily (Hodges, 1987).

The addition of phosphorus to acidic soil leads to the formation of Fe, Al and Mn phosphates. Commonly, some form of the Al-phosphate variscite ($AlPO_4.2H_2O$) will control P solubility (Wright and Peech, 1960; Lindsay, 1979; Pierzynski et al., 1990), although other Al phosphates such as K-taranakite ($H_6K_3Al_5(PO_4).18H_2O$) have been found to control the solubility of P (Sloan et al., 1993, unpublished; Lindsay, 1979). The presence of K-taranakite as a reaction product is a function of fertilization: the presence of K^+ in fertilizers temporarily depresses the solubility of taranakite, making it more stable than variscite for a period of time (Lindsay, 1979). Added P will also precipitate manganese phosphates ($MnPO_4.1.5\ H_2O$), and the production of these reaction products will limit Mn toxicity (Boyle and Lindsay, 1986).

Recent research indicates that liming is not the only method that may be used to reduce Al toxicity in acid affected soils. A new technique for temporarily alleviating soil acidity employs the use of banded P and its ability to form insoluble Al-P and Mn-P complexes (Boman et al.,1992). The addition of P fertilizer does not change the soil pH, but it does limit Al toxicity sufficiently to allow seed germination and growth. A yield (forage and grain) response to banded P is observed even in soils that test high in phosphorus.

The effects of banded P on acid-affected soil have only been quantified by these observed increases in forage and grain. The individual behavior of Al and Mn was not examined, and the soil was not frequently sampled to allow observation of changes in soil Al, P and Mn. To date, no laboratory studies have explored the chemical behavior of these acid-affected soils when P is added. The objective of this research was to evaluate the behavior of Al, Mn and P in a controlled laboratory setting, studying equilibrium solution and exchangeable Al, Mn and P when P had been added to three strongly acid surface soils.

METHODS AND MATERIALS

Three soils that exhibited an acidic plow layer (0-15 cm) were selected for this study. The soils were: 1) Pond Creek silt loam (Fine-silty, mixed, thermic Pachic Argiustoll), 2) Bethany silt loam (Fine-silty, mixed, thermic Pachic Paleustoll), and 3) Taloka silt loam (Fine, mixed, thermic Mollic Albaqualf). The 0-15 cm soil depth of each soil was sampled, and samples were air-dried and ground before further analysis. Mean 1M KCl extractable Al and Mn, Mehlich-III (Mehlich, 1984) extractable P and 1:1 soil/water pH values for the three soils are listed in Table 1.

One gram of each soil was weighed into separate 50 ml plastic centrifuge tubes, and 30 ml of P solution was added. The P solution contained either 0,1,3,5,7 or 10 mg P/L (as 0.03 NaH_2PO_4) in 0.05M $Ca(NO_3)_2$. Each soil/P solution concentration was replicated four times, resulting in a total of 24 soil/solution P tubes for each specific shaking time. A set of 24 tubes was shaken on a side-to-side shaker at room temperature (25° C) for either 1, 6, 12 or 24 hours.

After shaking the appropriate time, the tubes were centrifuged (15,000 rpm for 15 min), and the supernatant decanted. The pH of the supernatant was recorded using a pH electrode, and the supernatant was then refrigerated (5° C) until further analysis. Thirty ml of deionized water was added to the soil in the centrifuge tube, and it was shaken for 30 seconds. The purpose of this water 'rinse' was to dilute and remove the remaining P solution that may not have been decanted from the soil. The tubes were then centrifuged, and the water rinse decanted and refrigerated until later analysis.

Each group of four tubes (one P rate) was split into pairs. The soil in two tubes was extracted with 2M KCl (1 h shaking time), while the soil in the remaining two tubes was extracted with Mehlich-III extracting solution (5 min shaking time)(Mehlich, 1984). All soil extracts were filtered through Whatmann-2 filter paper, and the resulting solutions were stored under refrigeration until further analysis.

All of the solutions (P solution and water rinse) and extracted solutions were analyzed for P, Al and Mn. Amounts of P, Al and Mn measured in the water rinse were small (usually < 20.0 ug/g), and these values were added to the much larger readings found in the P solutions. Phosphorus was analyzed colorimetrically, using the standard molybdate blue procedure (Murphy and Riley, 1962). Manganese was measured by atomic absorption, and Al was determined colorimetrically using the ferron procedure (Jardine and Zelazny, 1986). The ferron procedure is a kinetic procedure, and readings within 1min are considered to reflect {Al^{3+}} in the system. Readings did not change after 1min, evidence that most of the Al in these soils was present as mononuclear forms.

Statistical analyses were performed using a complete randomized block design, using SAS (SAS, 1988). Additionally, solubilities of the formed Al-P constituents were evaluated using solubility diagrams and double function parameter plots (Lindsay, 1979).

RESULTS AND DISCUSSION

Plots of solution P, Al and Mn concentrations as a function of P addition are illustrated in Figures 1, 2 and 3, while Figure 4 shows the change in solution pH at the six rates of added P. Steady state or equilibrium conditions are reached only when the calculated ion activity products are constant over time. This condition is unlikely to have been achieved, even in the 24 h sampling. Nevertheless, the use of the term 'solution' identifies an isotonic solution that is, to some degree, approaching steady state, and it separates this solution from the soil solution itself, or a soil extractant.

The analysis of variance for solution P (Table 2) indicates that the addition of P was significant, at all rates of added P, and that this P was less available over time. Phosphorus added to the soil is rapidly sorbed to the surface of clays or oxides, and precipitation of relatively insoluble forms of P eventually occurs. This observed decrease in solution P is well-documented (Barrow and Shaw, 1975; van Riemsdijk et al., 1984; Kunishi and Vickers, 1980).

The addition of phosphorus decreased solution Al at all shaking times. The dissolved Al found in the solution may result from a combination of: 1) $Ca(NO_3)_2$ displacement of adsorbed aluminum, and 2) initial formation of some type of aluminum-phosphate complex or precipitate. The apparent $Ca(NO_3)_2$ displacement of Al is most obvious at 6 h in the Bethany soil. The Bethany soil did not demonstrate a displacement effect at h 1, and it may be that the high indigenous levels of Al and larger Al/P ratio (Table 1) in this soil buffered against the desorbing action of the added 0.05M $Ca(NO_3)_2$ for a longer period of time.

In general, the addition of P did not decrease solution Mn in any of the soils (Figure 3). Only the Bethany soil exhibited a decrease in solution Mn with the addition of phosphorus. There were significant P rate x hour interactions for all three soils (Table 2), and comparisons within hours revealed that, in all cases, P rate was linearly significant. The Taloka soil contained significant P rate x hour interactions, both linear and quadratic. It is likely that the significant quadratic term results from the 0 mg P addition at h 1 (Figure 3).

The addition of P caused the solution pH in both the Pond Creek and Bethany soils to decline between hours 6 and 12. Displaced Al from the addition of 0.05 M $Ca(NO_3)_2$ may have formed initial amorphous gibbsite-like precipitates, removing OH^- from the solution. All the soils contained a significant P rate x hour interaction for solution pH, and none of the soils demonstrated a clear incremental decrease in soil pH with increasing rates of P. Generally, (for Bethany and Pond Creek) the highest rates of P addition created solutions with the lowest pHs. The explanation for this occurrence is unknown. While the addition of Ca could remove OH^- from the system and displace H^+ into the solution, this would be a constant effect, since the amount of Ca added to each centrifuged tube was from a 0.05M background solution. The decline in pH is partly a product of P additions, a short-term (<24 h) phenomena which deserves further exploration.

Figures 5, 6 and 7 illustrate the behavior of extractable soil P, Al and Mn, respectively. Similar to solution P, the addition of P significantly increased the amount of P that was extracted by the Mehlich-III extractant (Figure 5). There was a significant P rate x hour interaction for Mehlich-III P, and P rate was significant in all three soils at all hours (Table 3). In the Taloka silt loam moderate rates of P addition (5 and 7 mg P/L) at hours 12 and 24 provided levels of extractable P equal to the 10 mg P/L rate (Figure 5). By h 24 the three highest rates of P addition all provided the same amount of Mehlich-III extractable P. This could be related to the low levels of native P in the Taloka soil, as any added P was rapidly converted to highly unavailable forms.

The addition of P significantly affected the amount of 2M KCl extractable Al in the soil, an effect measured in all three soils. Generally, at all shaking times, the addition of P decreased levels of extractable aluminum. Extractable Al exhibited a significant linear P rate x hour interaction, and the Bethany and Pond Creek soils also exhibited a significant quadratic interaction (Table 3).

As with solution Mn, the addition of P usually did not decrease 2M KCl extractable Mn. Only the Bethany silt loam contained a significant P rate x hour interaction, but this interaction was not a direct result of P addition. There was no defined decline in extractable Mn as P rate increased, and the interaction results from variation in the data at all rates of added P and sampling times.

Solubility equilibria diagrams are illustrated in Figures 8, 9 and 10. While these diagrams do not prove the existence of a phase or mineral, they do provide evidence for the potential of a mineral to form (Lindsay, 1979). Figure 8 is a double function plot which uses H_2PO_4, H^+ and Al^{3+} to examine solubilities in the solutions. In general, the Bethany and Pond Creek soils are most likely supersaturated with respect to variscite, as most of the plotted points lie above that line. The Taloka data plotted directly on top of the Bethany points, and are not included in the solubility diagram. Each clustered set of markers represents a P rate at hours 1,6, 12 and 24, indicating that equilibrium has not yet been reached in this solubility diagram. Although the soils are likely to be supersaturated with respect to variscite, the vertical plotting of the data points indicates that the points could also be undersaturated with respect to gibbsite and oversaturated with respect to kaolinite. The addition of P to the soil increased phosphorus by more than two log units, indicating that the initial reaction products from the addition of P were more soluble than variscite, and may have been some type of amorphous aluminum phosphate (Lindsay, 1979; Pierzynski, et al., 1990).

Figures 9 and 10 both strengthen this hypothesis of an amorphous Al-phosphate or amorphous variscite form precipitating in the solution. Almost all of the plotted points in Figure 9 lie above the variscite line and below the K-taranakite line, indicating that the solubility is most likely controlled by some variscite-like product. Figure 10 indicates that pH was not the controlling factor in these reactions, as the solubility relationships between $H_2PO_4^-$ and Al^{3+} with respect to variscite at a constant pH are similar to those found in the other solubility diagrams.

Prior studies have demonstrated that some form of amorphous variscite is a likely product from P fertilization (Lindsay, 1962; Pierzynski et al., 1990). Regardless of the specific solubility product, it seems unlikely that adsorption processes are a dominate or long-term contributor to Al-phosphorus behavior in these soils.

CONCLUSIONS

When phosphorus was added to acidic soils the measurable forms of aluminum, both in the solution and soil extracts, were lowered. While this research did not attempt to differentiate between forms of Al, it was likely that most of the Al removed from the soil solution was toxic, and the removal of that Al allows seedling growth and development. Acidic soils that contain sufficient levels of P for crop growth and development (Pond Creek, Bethany) could certainly benefit by the banding of fertilizer P to alleviate Al toxicity. The likely mechanism for this alleviation appears to be the formation of some type of amorphous variscite precipitate.

The addition of phosphorus did not affect, to any considerable degree, the levels of manganese found in either the solution or the soil extracts. This manganese was measured as exchangeable Mn (Table 1), and, in general, all of this exchangeable Mn was measured in the solution. For example, in the Pond Creek soil, the indigenous exchangeable Mn concentration was 112 mg Mn/kg soil, and an average of 115 mg Mn/kg soil was recovered in the h 1 solution. In the Bethany soil an average of 47 mg Mn/kg soil (h 1) was recovered, compared to a 1M KCl extractable Mn concentration of 41 mg Mn/kg soil. It appears that most of the measurable exchangeable Mn is rapidly (within 1 h) desorbed or removed into the solution, and the of addition P does not greatly reduce the quantity of measured Mn. It is likely that the Mn measured in the 2M KCl extracts represents residual exchangeable Mn.

The banding of phosphorus fertilizer appears to be an effective, affordable and timely means for limiting Al toxicity in wheat fields that have developed acidic surface layers. However, the procedure is not a long-term substitute for liming. Banded P will not change the soil pH, and continued cropping and fertilizer additions will continue to lower the soil pH, allowing more Al and Mn to come into solution.

Continued research is needed to assess the impact of this banded P upon Al and Mn contents in field situations. Additionally, the yield increases found with banded P have only been demonstrated on two soils, and laboratory work has only been performed on the three soils presented in this paper. Soils with a wide range of P, Al and Mn contents should be examined, both in the lab and field. Lastly, the effect of eventual liming upon these residual bands of P should be studied. Excess phosphorus is being banded when there is no need to apply P as a plant food or nutrient, and P will accumulate in the soil. The eventual addition of lime may greatly alter the availability of this accumulated P, and the speed and longevity with which these transformations occur should be examined.

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Table 1. 1M KCl Exchangeable Al, Mn, Mehlich-III Extractable P, and soil pH for Bethany silt loam, Taloka silt loam and Pond Creek silt loam.

Soil	Mehlich-III P	1M KCl Exch. Al	1M KCl Exch. Mn	pH	Al/P
	----------mg kg^{-1}----------				
Bethany	33.3	95.9	41.0	4.00	2.88
Taloka	6.8	39.5	53.0	3.96	1.40
Pond Creek	60.8	73.1	112.0	3.99	1.20

Table 2. Analysis of variance and comparisons for equilibrium solution variables.

Source of variation	df	Pond Creek sil	Bethany sil	Taloka sil
		----------mean squares-equilibrium solution P----------		
P rate	5	63768.7**	29247.7**	63758.8**
P rate_linear	1	**	**	**
P rate_quadratic	1	**	**	**
P rate x hour	15	285.7**	219.2**	593.4**
P rate_lin x hour	3	**	**	**
P rate_quad x hour	3	**	**	**
		----------mean squares-equilibrium solution Al----------		
P rate	5	239.7**	414.0**	608.9**
P rate_linear	1	**	**	**
P rate_quadratic	1	**	**	**
P rate x hour	15	21.8**	6.4**	90.0**
P rate_lin x hour	3	**	**	**
P rate_quad x hour	3	**	*	**
		----------mean squares-equilibrium solution Mn----------		
P rate	5	34.5*	54.3**	130.8**
P rate_linear	1	*	**	**
P rate_quadratic	1	ns	ns	*
P rate x hour	15	50.7**	3.8*	33.2**
P rate_lin x hour	3	**	*	**
P rate_quad x hour	3	ns	ns	**
		----------mean squares-equilibrium solution pH----------		
P rate	5	0.03**	0.02**	0.03**
P rate_linear	1	**	**	**
P rate_quadratic	1	@	ns	@
P rate x hour	15	0.002**	0.003**	0.03**
P rate_lin x hour	3	*	**	**
P rate_quad x hour	3	ns	ns	**

@,*,** significant at 0.10,0.01 and 0.001 probability levels, respectively.

Table 3. Analysis of variance and comparisons for soil extracts.

Source of variation	df	Pond Creek sil	Bethany sil	Taloka sil
		---------mean squares-Mehlich-III extractable P---------		
P rate	5	792.9**	2856.9**	689.0**
P rate_linear	1	**	**	**
P rate_quadratic	1	**	ns	ns
P rate x hour	15	14.4**	17.2**	21.1**
P rate_lin x hour	3	**	**	**
P rate_quad x hour	3	**	**	**
		----------mean squares-2M KCl extractable Al----------		
P rate	5	38.0**	81.3**	183.3**
P rate_linear	1	**	**	**
P rate_quadratic	1	*	**	**
P rate x hour	15	3.6**	5.0**	29.4**
P rate_lin x hour	3	**	**	**
P rate_quad x hour	3	@	*	**
		----------mean squares-2M KCl extractable Mn----------		
P rate	5	1.2@	0.6@	0.3
P rate_linear	1	ns	**	**
P rate_quadratic	1	ns	ns	ns
P rate x hour	15	0.9	0.2	1.1**
P rate_lin x hour	3	ns	ns	**
P rate_quad x hour	3	ns	ns	ns

@,*,** significant at 0.10,0.01 and 0.001 probability levels, respectively.

Figure 1. Solution phosphorus.

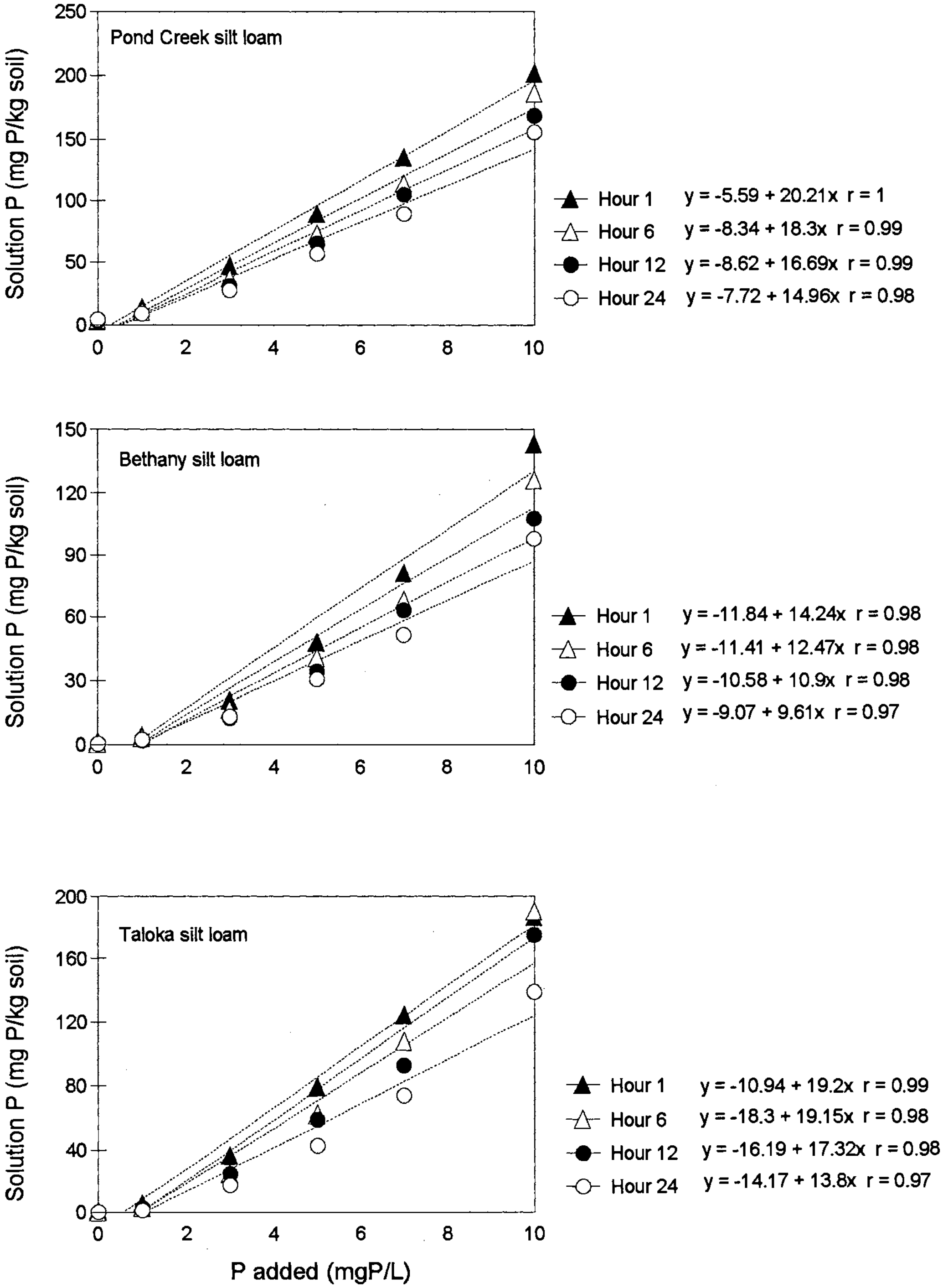


Figure 2. Solution aluminum.

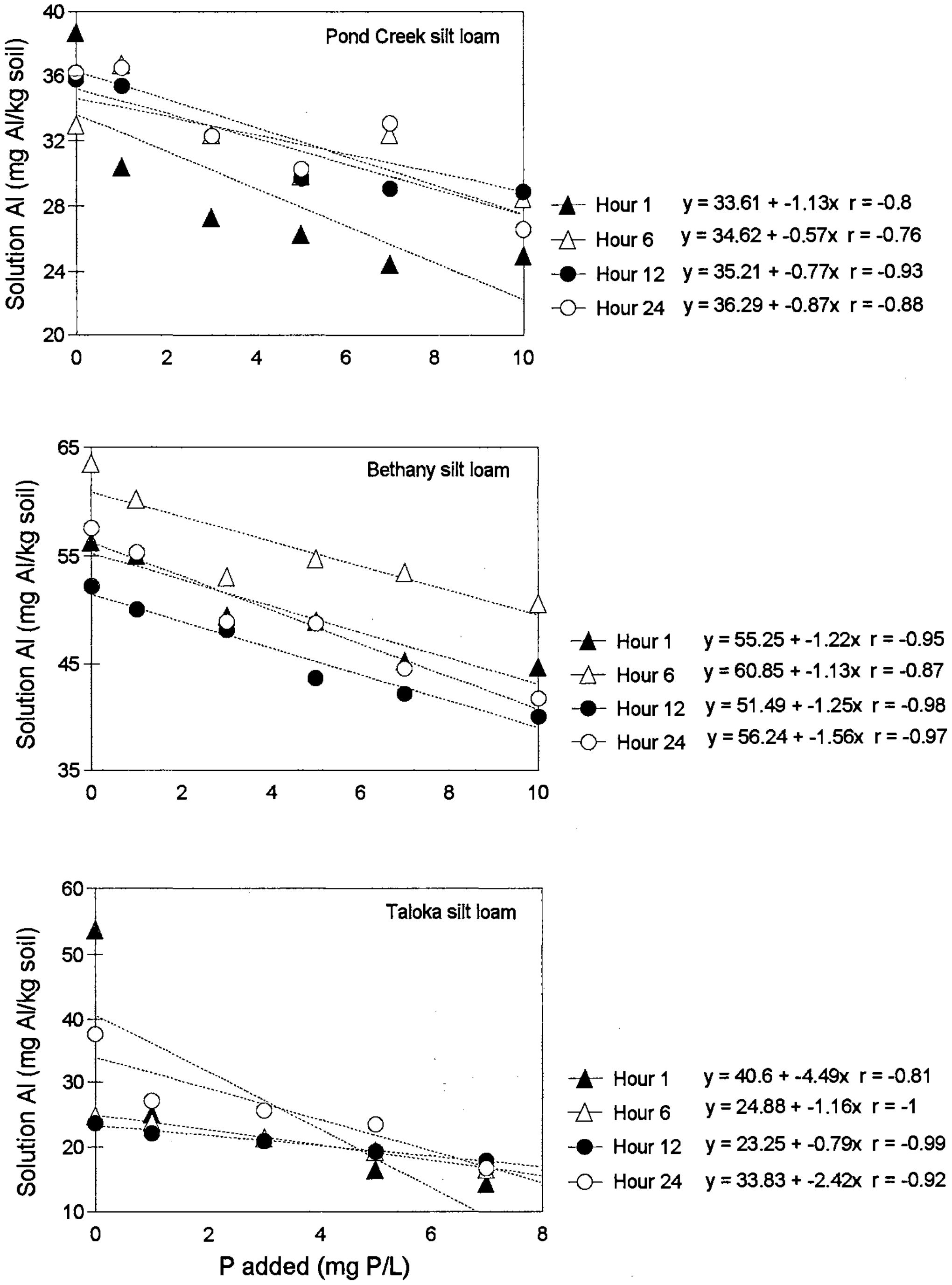


Figure 3. Solution manganese.

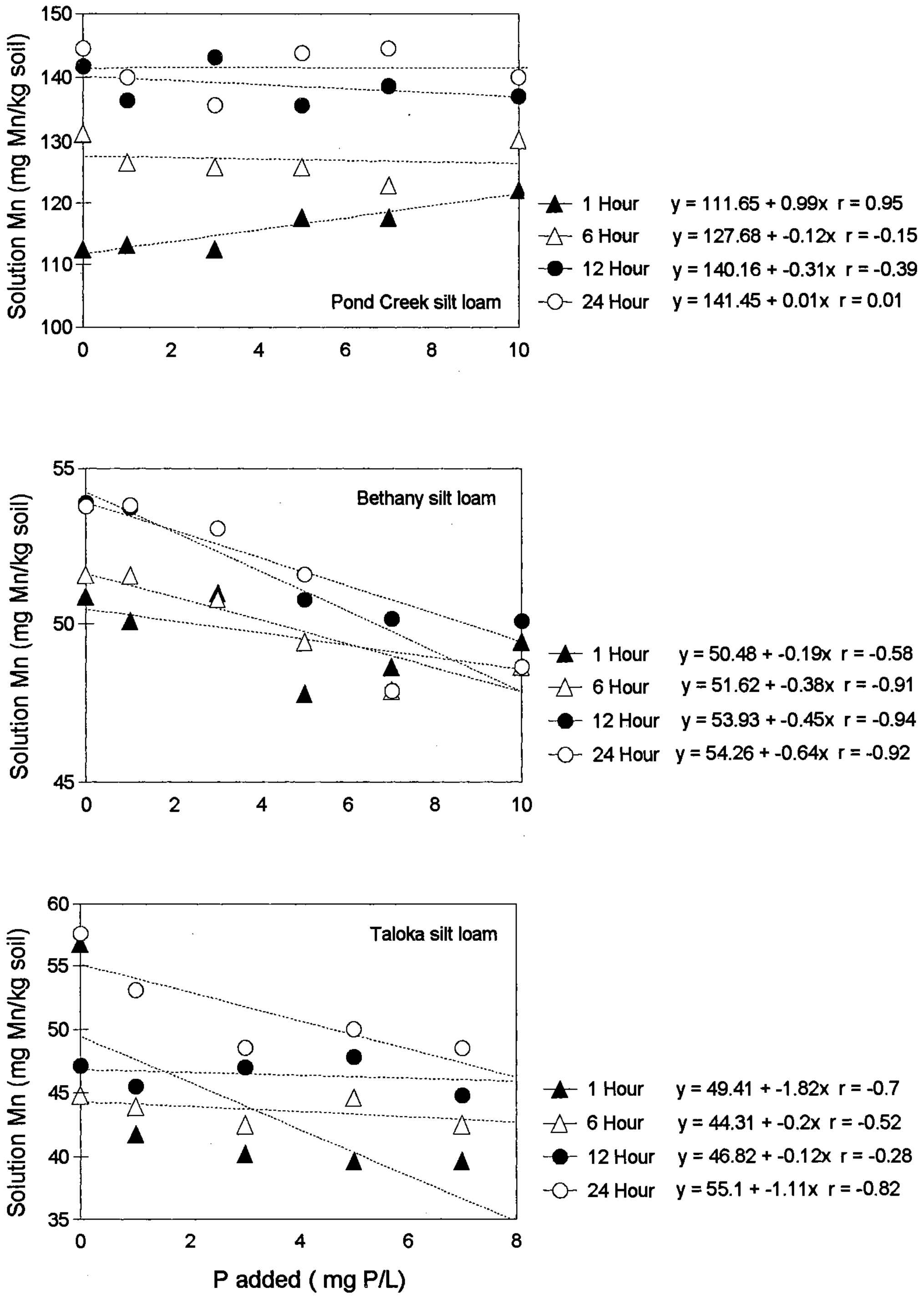


Figure 4. Solution pH.

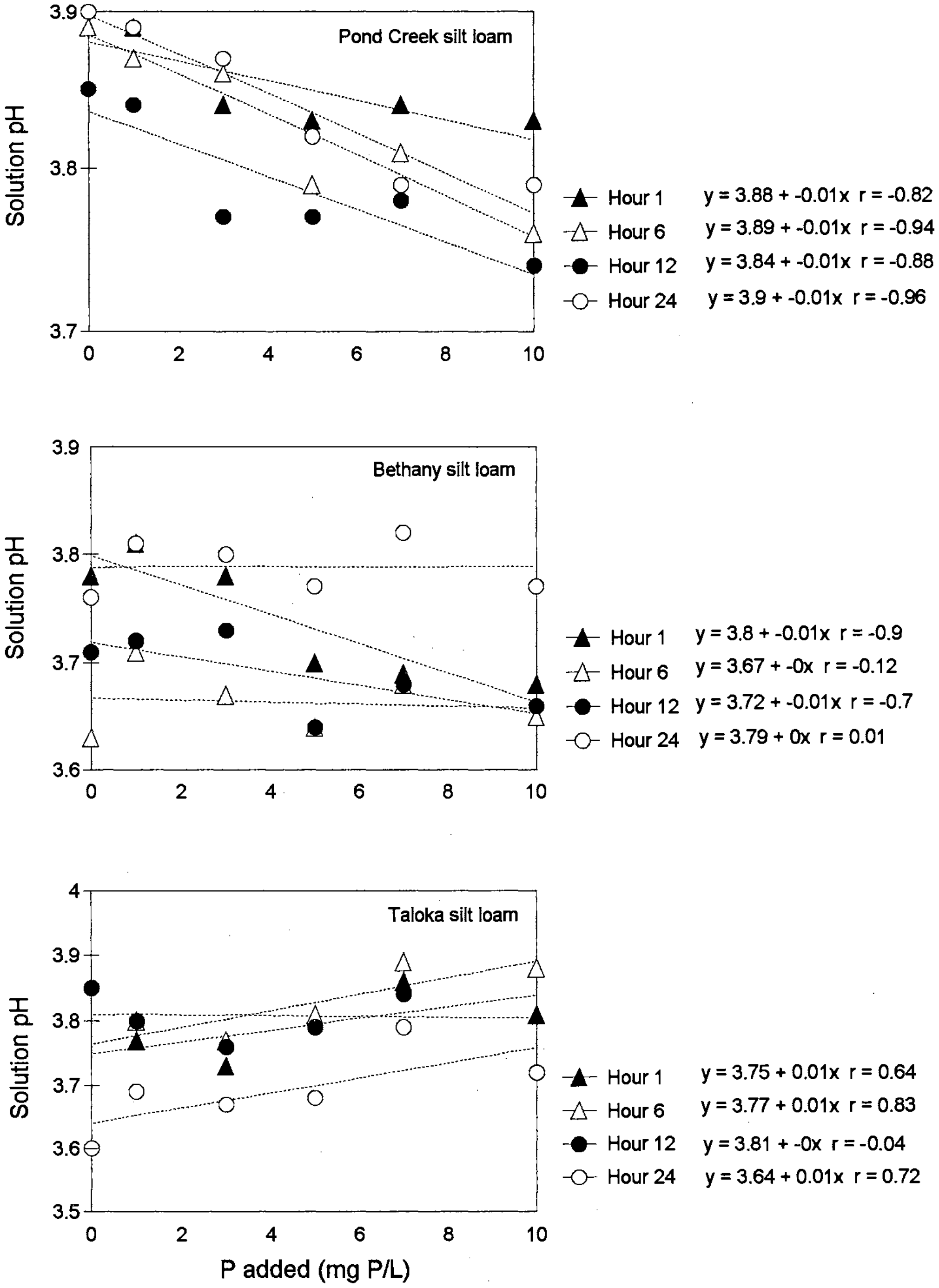


Figure 5. Mehlich-III extractable phosphorus.

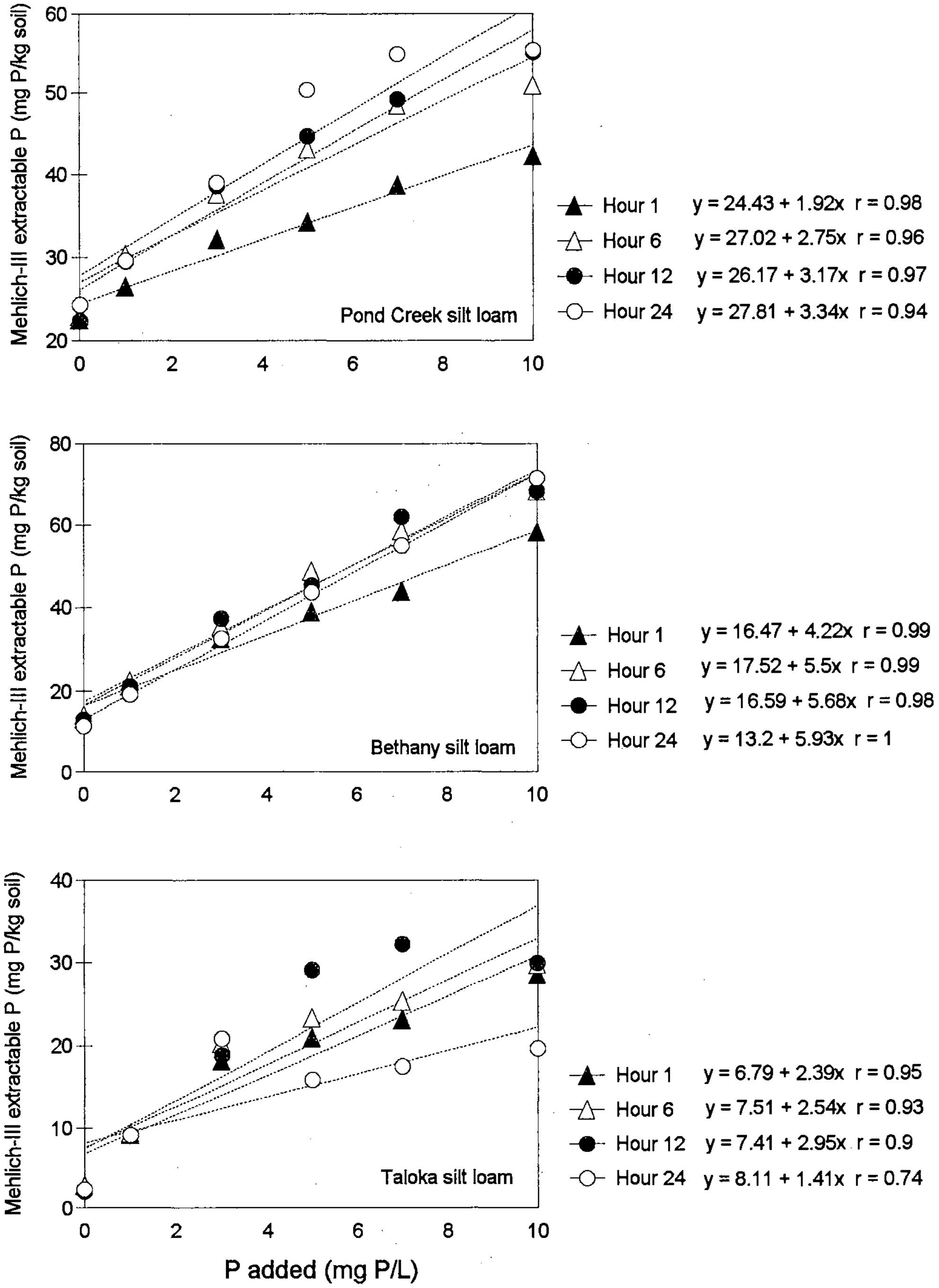


Figure 6. 2M KCl extractable aluminum.

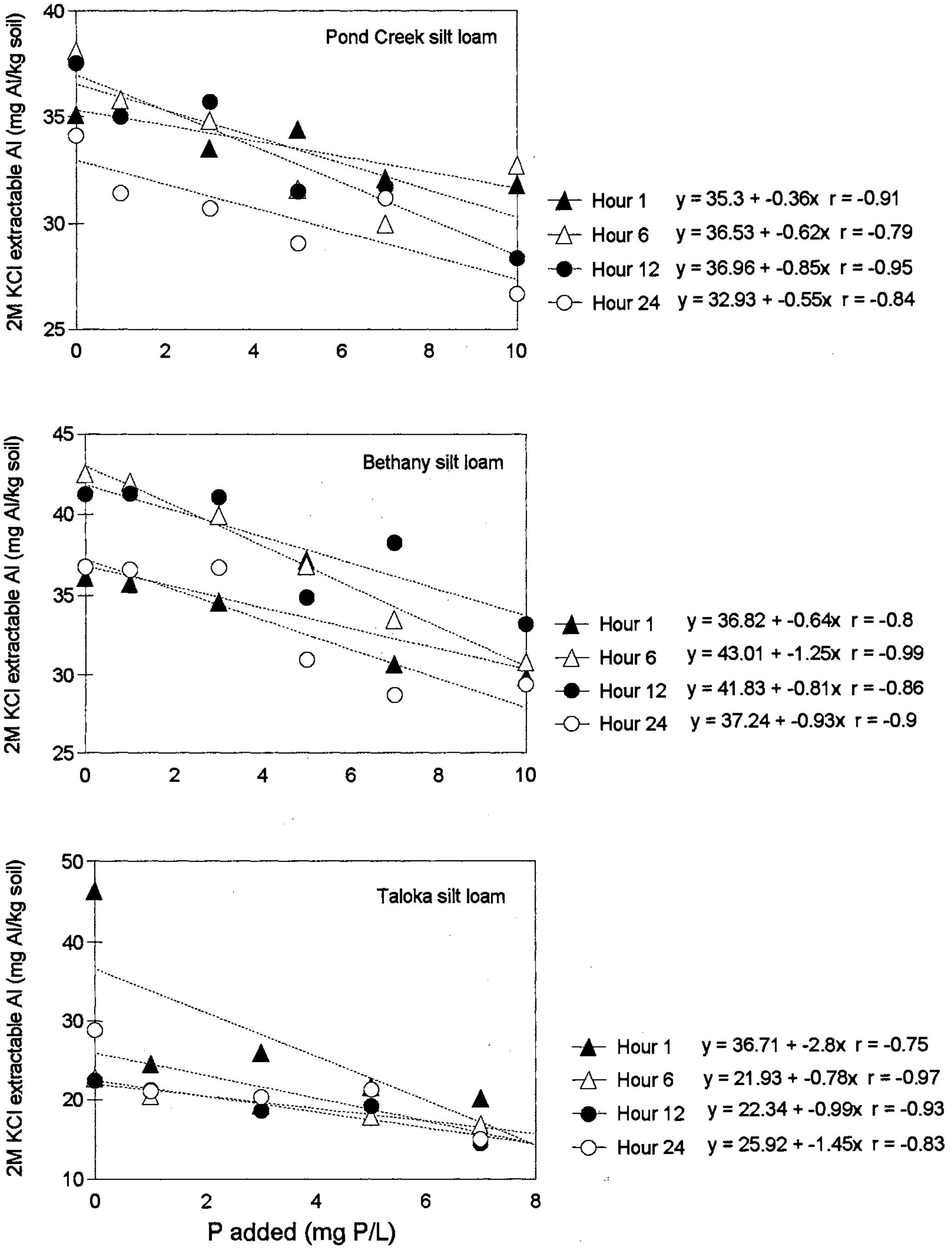


Figure 7. 2M KCl extractable manganese.

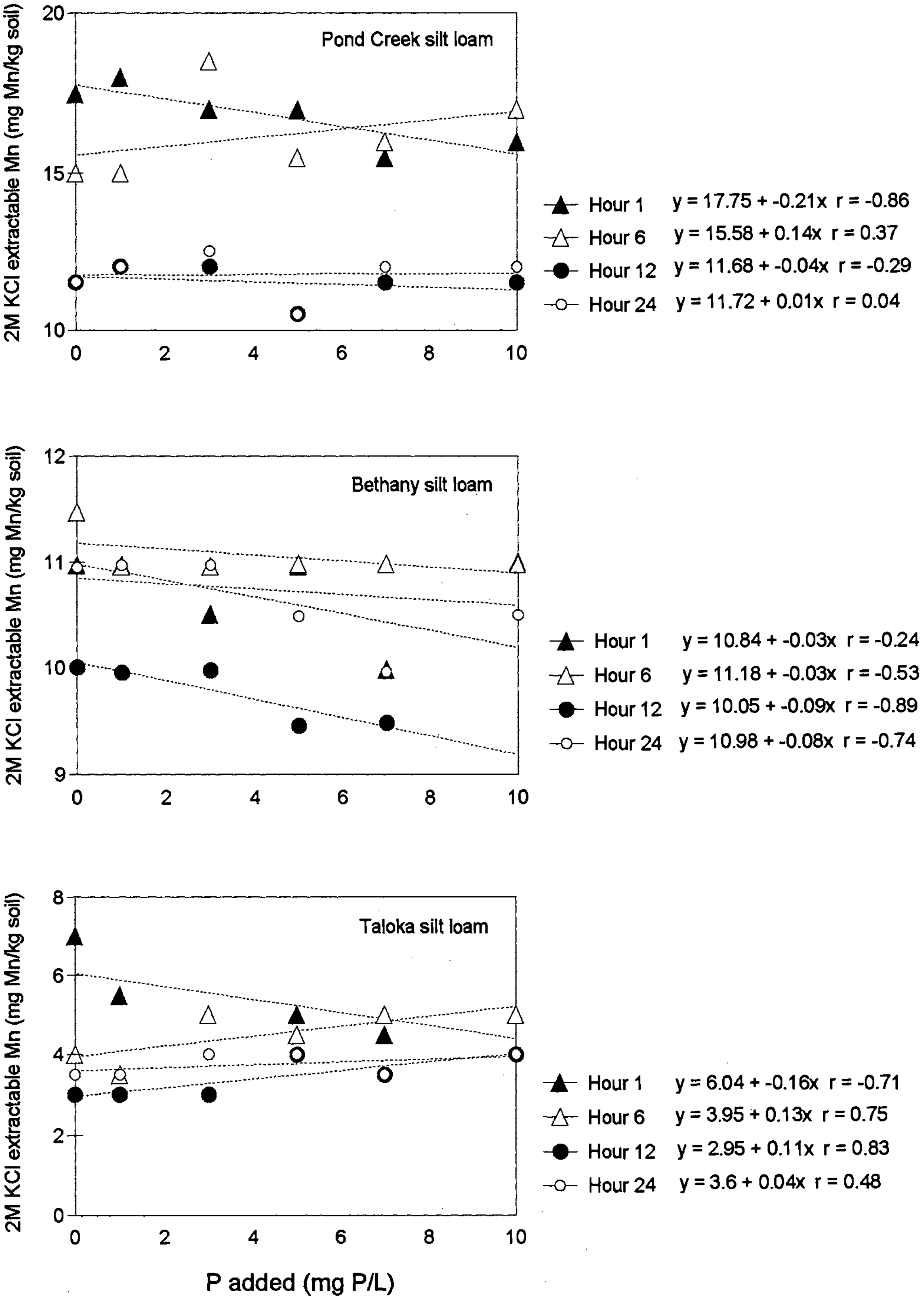
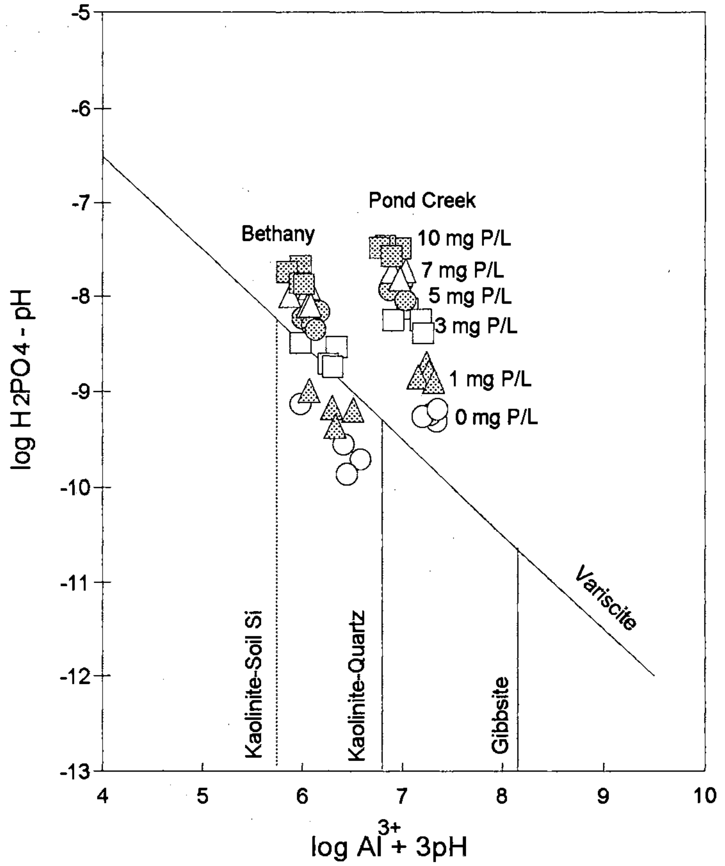
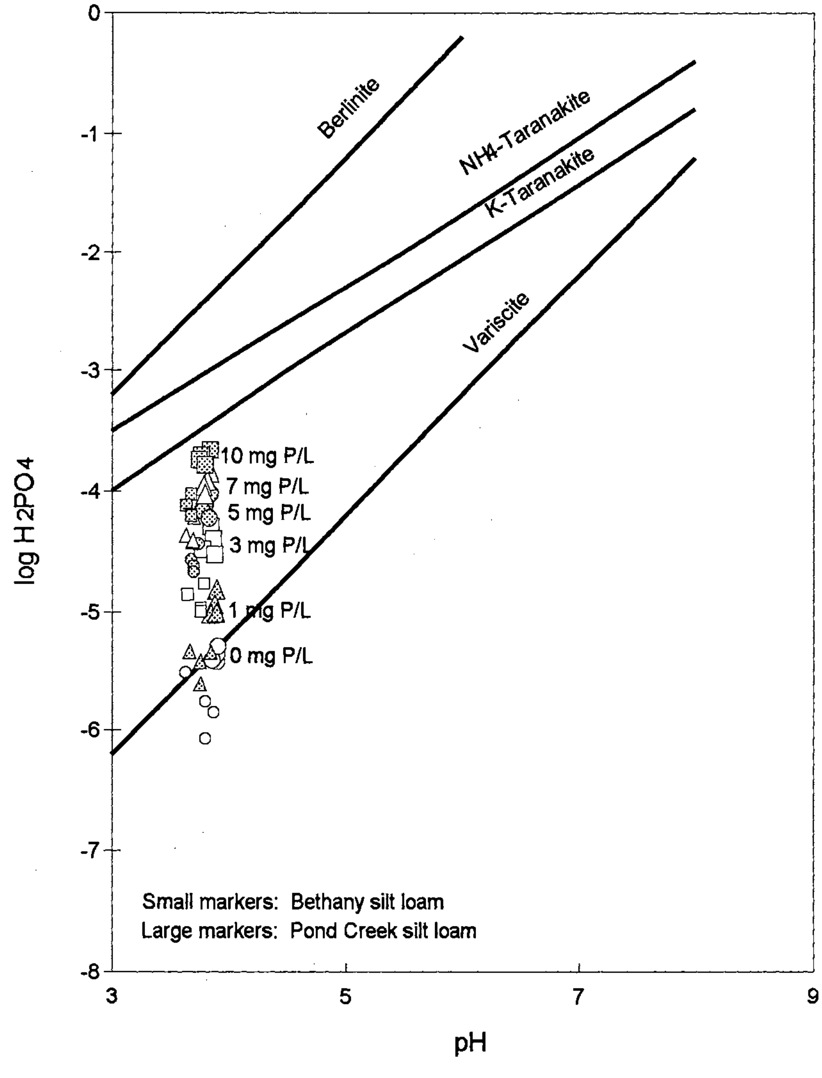


Figure 8. Changes in the solubility of the solutions after addition of P.



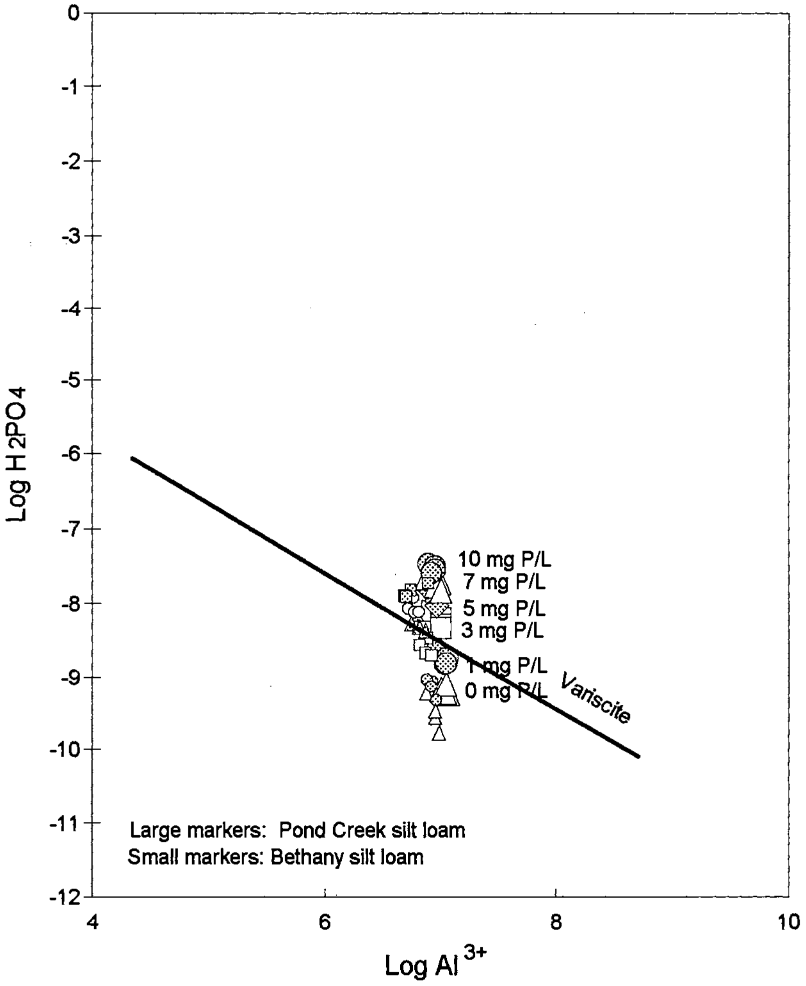
Adapted from Lindsay, 1979

Figure 9. Solubility of solution phosphates.



Adapted from Lindsay, 1979

Figure 10. Solubility of solution phosphates at a constant pH of 3.8.



APPENDIX

GLOSSARY OF GEOSTATISTICAL TERMS

Anisotropy:	The situation where samples are more alike in one direction, exhibiting smoother spatial continuity than some other direction.
Anisotropic ratio:	The longest range (direction with best spatial continuity) divided by the shortest range (direction with worst spatial continuity). If an isotropic condition exists than the isotropic ratio will be 1.0.
Block kriging:	A kriging method which provides an average estimated value for a region of interest.
Cross-validation:	A technique for testing the validity of a variogram model by kriging each sampled location with all of the other samples in the search neighborhood, and comparing the estimates with the true sample values (Englund and Sparks, 1988).
Directional semivariograms:	Semivariograms that are calculated over specific directions, providing a picture of changing spatial continuity with direction.
Gaussian model:	A positive definite model that is often fit to experimental semivariograms, often indicating relatively continuous data.
Geostatistics:	A statistical method for analyzing spatially correlated data.
Isotropy:	When semivariograms exhibit similar spatial behavior in all directions.
Kriging:	A weighted-moving-average interpolation method for estimating unknown values. The method is a best, linear, unbiased estimation method, so that kriging weights sum to 1.0, the kriging variance is minimized and the estimation errors are close to zero.
Lag:	The distance between samples, used in the calculation of semivariograms.

Nested semivariogram model:	A model fit to a semivariogram which is a combination of two or more models.
Nugget model:	A model indicating a completely random phenomena. Often used in combination with other models.
Omnidirectional semivariogram:	A semivariogram that is calculated by considering all possible directions in the sampling site. Often, omnidirectional semivariograms provide an overall view of spatial continuity within the sampling site.
Range:	The distance at which samples are no longer spatially related. The linear model does not contain a range, but the spherical and gaussian models do. Once lag distances exceed the range geostatistical techniques are not longer applicable.
Search neighborhood:	An area centered upon the point or area being kriged. Only samples used within the ellipse or circle are used for kriging.
Semivariogram:	Mathematically, the variogram term divided by two. In practical use, the terms semivariogram and variogram are often used interchangeably.
Sill:	The upper limit of a semivariogram model, where the semivariogram 'levels off' at the range. This value is also an indicator of the variance of the data set.
Spherical model:	Often considered to be the 'classical' semivariogram model, used to describe the spatial variability of the data. This model, like the gaussian, is often used in conjunction with the nugget model.
Tolerance:	As used in GEO-EAS, the angular tolerance that is allowed when a semivariogram value is calculated. Usually, an angular tolerance of 22.5 degrees is considered, so that all samples within 22.5 degrees of the search direction are considered.
Variogram:	A plot of the variance (one-half the mean squared difference) of paired sample measurements as a function of the distance (and optionally of the direction) between samples (Englund and Sparks, 1988).

VITA

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III. CHANGES IN PHOSPHORUS, ALUMINUM AND MANGANESE IN THREE ACID-AFFECTED SOILS THAT HAVE BEEN AMENDED WITH PHOSPHORUS.

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