

Estimates of Soil Nitrate Distributions Using Cokriging with Pseudo-Crossvariograms

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ABSTRACT

Nitrate (NO_3^-) is one of the major nonpoint source pollutants in the vadose zone. In this study, NO_3^- distributions were estimated in an 800 by 800 by 1.8 m soil volume using kriging and cokriging with nonsymmetric pseudo-crossvariograms. Cokriging with pseudo-crossvariograms maximized the use of available information at different soil depths. Cokriging allowed easily obtained information at shallow layers to be used to improve soil chemical estimations at deeper layers. Compared with kriging, cokriging significantly reduced the mean squared errors (MSEs) and mean kriging variances (MKVs) of the NO_3^- estimations in the soil. For the same estimation accuracy of kriging, cokriging with pseudo-crossvariograms used less than half the data; thus potentially it could reduce more than half the sampling cost than kriging estimation. Cokriging with pseudo-crossvariograms was shown to be a precise and an economic way for determining nonpoint source pollutant distributions in large fields.

THE QUALITY of our soil and groundwater is a nationwide concern for agricultural, public health, and environmental reasons. Mismanagement of chemicals has caused serious groundwater contamination in every state (Lau and Mink, 1987). For example, the U.S. Environmental Protection Agency (USEPA, 1990) surveyed 1300 wells throughout the country for 101 pesticides, 25 pesticide degradates, and NO_3^- . In over half the wells sampled, NO_3^- was the major pollutant. Nitrogen fertilizer and pesticide use in the USA has increased steadily, peaking in the early 1980s, and has resulted in chemicals being transported to groundwater systems through the vadose zone (USDA, 1990). This problem also affects Wyoming; groundwater contamination by NO_3^- was first observed in 1986 in Torrington. Nitrate levels dramatically increased in several wells by the spring of 1988, when concentrations in some wells exceeded the USEPA limit of $10 \text{ mg kg}^{-1} \text{ NO}_3^- \text{-N}$. By the end of 1988, all of the municipal wells were approaching the USEPA-recommended maximum concentrations.

Because of the high cost of sampling and analyzing NO_3^- concentrations in the field, there are only a limited number of field experiments. However, accurately estimating solute mass and distributions in the vadose zone and groundwater systems is critical in many environmental studies, such as designing best management practices of soil and water, protection of soil and water from nonpoint source pollution, and modeling chemical movement and fate in soils. With limited data, geostatistical analyses provide useful tools to characterize spatial distributions of soil chemicals and estimate solute mass in soils (Warrick et al., 1986).

Geostatistics can use interrelationships between two or more spatially-dependent variables to improve the

estimation of the variables. The interrelationships can be among different variables at the same space or among different depths for the same variable. Cokriging is an extension of the kriging method and incorporates both spatial and intervariable correlations into the estimation process. Cokriging has been applied to study various spatial variables. For example, Yates and Warrick (1987) estimated the soil water content using cokriging where the bare soil surface temperature and the sand content were used to supply additional information. Stein et al. (1988) used cokriging to increase computation precision in soil water content. Zhang et al. (1992b) improved the estimates of soil texture by including associated spectral properties in a cokriging procedure. Zhang et al. (1995) estimated concentrations of trace elements in soils and plants using kriging and cokriging.

An essential part of any geostatistical analysis using cokriging is the modeling of crossvariograms among the variables. A major disadvantage of standard approaches for modeling crossvariograms is that only values for the variables having common sample locations can be used to estimate the cross-correlation functions. Therefore, estimating crossvariograms requires a large number of locations where data are collected for each variable, a condition that is frequently not satisfied in practice. To alleviate this difficulty, Myers (1991) described a variation of cokriging that does not require measurements of variables at the same locations. The approach involves the development of pseudo-crossvariograms and their use in a cokriging algorithm. Zhang et al. (1992a) used cokriging with symmetric pseudo-crossvariograms to estimate spatial distributions of various soil chemicals. Zhang et al. (1997) applied nonsymmetric pseudo-crossvariograms in cokriging to improve estimates of soil solute concentrations.

To determine nonpoint source pollution in the vadose zone, it is necessary to measure soil chemicals at different locations and depths. However, the difficulty of measurement of soil chemicals increases dramatically with depth. To enhance estimation precision of chemical distributions at deeper layers using available data at shallower layers, cokriging is a logical choice by incorporating both spatial continuities and correlations of soil chemicals between layers into the estimation process. The purpose of this paper is to estimate NO_3^- distributions in a large soil volume using kriging and cokriging with pseudo-crossvariograms assuming only limited data are available at deeper layers.

MATERIALS AND METHODS

To study spatial distributions of NO_3^- , an extensive field experiment was conducted at an irrigation farm in the western part of Fresno County near the town of Mendota, CA. Soil

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Abbreviations: MSE, mean squared error; MKV, mean kriging variance; ICP, inductively coupled photometer; RMKV, relative mean kriging variance; RMSE, relative mean squared error.

samples were collected in an 800 by 800 m field at depths of 0.15, 0.30, 0.45, 0.60, 0.90, 1.20, 1.50, and 1.80 m. The number of samples varied at different depths, ranging from 108 data points at 0.15 m to 83 data points at 1.80 m (Table 1). The field site is a commercial farm that has a varying cropping history. Furrow irrigation using California Aqueduct water and well water was the primary irrigation practice. The soil type on the site was the Panoche silty clay loam (fine-loamy, mixed calcareous, thermic Typic Torriorthent). Soil samples were collected at the specified depths using a truck-mounted soil sampling machine. The soil collected from each depth increment was mixed as a homogenous soil for chemical analyses. The soil samples were extracted using a quantitative 1:1 soil/water extract procedure. Concentrations of NO₃⁻ (NO₃⁻, cmol_c L⁻¹) were measured using an inductively coupled photometer (ICP) and a flow injection analyzer. Other physical properties were also measured including gravimetric water content and bulk density.

In this study, cokriging is applied to estimate spatial distributions of NO₃⁻ using data from different depths by incorporating not only spatial correlations on the horizontal space but also the correlations of NO₃⁻ concentrations between depths. Let Z₁(x₁), ..., Z₁(x_m), ..., Z₁(x_n) denote NO₃⁻ concentration values measured at the sample locations x₁, ..., x_m, ..., x_n of depth 1 and Z₂(x₁), ..., Z₂(x_m) denote NO₃⁻ concentration values measured at the sample locations x₁, ..., x_m of depth 2 (depth 1 < depth 2 and n > m). The cokriging estimator of NO₃⁻ at x₀ of depth 2 can be written in the form (Myers, 1984):

$$Z_2^*(x_0) = \sum_{i=1}^{N_1} \lambda_{1i} Z_1(x_{1i}) + \sum_{j=1}^{N_2} \lambda_{2j} Z_2(x_{2j}) \quad [1]$$

where N₁ and N₂ are the number of neighboring values of Z₁ and Z₂, respectively. Accordingly, Z₂ at x₀ is estimated by a weighted average of the observations on the variable at the two depths and the spatial locations. The weighting factors λ₁ and λ₂ are determined based on the variograms of Z₁ and Z₂ as well as their crossvariogram. The problem is that the common m points at the two depths may not be enough to calculate a meaningful crossvariogram using traditional methods, whereas more data are available at depth 1.

To maximize the use of the available data, a pseudo-cross-variogram of Z₁ and Z₂ is defined as (Myers, 1991):

$$g_{12}(h) = g_{21}(-h) = 0.5Var[Z_1(x) - Z_2(x + h)] \quad [2]$$

It is assumed that this function depends only on the separation distance h. Note that it is not required that Z₁ and Z₂ are sampled at the same locations. The pseudo-crossvariogram is not necessarily symmetric. The sample pseudo-crossvariograms for the variable at depth 1 (Z₁) and depth 2 (Z₂) are computed as:

$$g_{12}^*(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z_1(x_i) - Z_2(x_i + h)]^2 \quad [3]$$

and

$$g_{21}^*(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z_2(x_i) - Z_1(x_i + h)]^2 \quad [4]$$

where N(h) is the number of sample pairs for lag h. If g₁₂^{*}(h) and g₂₁^{*}(h) are symmetrical, we may obtain a crossvariogram γ₁₂ from the pseudo-crossvariogram g₁₂ (Myers, 1991; Zhang et al., 1992a). If g₁₂^{*}(h) and g₂₁^{*}(h) are nonsymmetrical, and it is assumed in this study that they can be modeled by the common variogram functions (conditionally negative definite), such as exponential, spherical, and linear models. Parameters of the pseudo-crossvariogram are determined by cross validation. The cross validation procedure produces estimates corresponding to measured locations using the cokriging technique to be discussed below. In this procedure, every known

Table 1. Statistics of NO₃⁻ of the original data.

Depth	No. of data	Mean	Standard deviation	Skewness	Kurtosis
m		cmol _c L ⁻¹	cmol _c L ⁻¹	(cmol _c L ⁻¹) ³	(cmol _c L ⁻¹) ⁴
0.15	108	4.709	5.670	1.552	5.513
0.30	109	0.520	1.041	2.568	9.429
0.45	94	0.544	1.406	3.434	16.016
0.60	109	0.827	1.840	3.531	18.529
0.90	103	0.485	1.010	2.445	8.528
1.20	90	0.301	0.753	3.006	12.275
1.50	85	0.269	0.749	3.067	11.608
1.80	83	0.286	0.709	3.166	13.711

point is estimated by using neighboring observations, but not itself. Based on the statistical analysis of the estimates and measurements, an appropriate pseudo-crossvariogram can be chosen. Similar to the selections of variograms and crossvariograms through cross-validation (Yost et al., 1982a,b), the choice of a pseudo-crossvariogram should result in a near-zero value of mean error, and near unity for the reduced kriging variance.

In terms of the variograms and pseudo-crossvariograms of the random variable at two depths, Z₁(x) and Z₂(x), the cokriging equations are expressed in the form of

$$\begin{aligned} \sum_{i=1}^{N_1} \lambda_{1i} \gamma_1(x_{1i} - x_1) + \sum_{j=1}^{N_2} \lambda_{2j} g_{12}(x_{2j} - x_1) + \mu_1 &= \\ g_{12}(x_0 - x_1) \quad I = 1, 2, \dots, N_1 & \\ \sum_{i=1}^{N_1} \lambda_{1i} g_{21}(x_{1i} - x_j) + \sum_{j=1}^{N_2} \lambda_{2j} \gamma_2(x_{2j} - x_j) + \mu_2 &= \\ \gamma_2(x_0 - x_j) \quad J = 1, 2, \dots, N_2 & \\ \sum_{i=1}^{N_1} \lambda_{1i} = 0 \quad \sum_{j=1}^{N_2} \lambda_{2j} = 1 & \end{aligned} \quad [5]$$

Solving the system of linear equations, we can obtain the cokriging weights λ₁ and λ₂. It should be verified that the variograms and pseudo-crossvariograms in the equations satisfy the Schwarz's inequality given by (Myers, 1982)

$$\gamma_1(h)\gamma_2(h) > g_{12}(h)g_{21}(h) \quad [6]$$

This condition guarantees that the variance of the estimated variables is positive.

RESULTS AND DISCUSSION

In this study, we applied the kriging and cokriging techniques to estimate NO₃⁻ distributions in the three-dimensional field of 800 by 800 by 1.8 m. The use of cokriging can maximize the estimation precision by using limited data and other available information at different soil depths, which shows potential saving of sampling costs. In particular, we used nonsymmetric pseudo-crossvariograms that were computed using data sampled at the same and/or different horizontal locations at different depths.

Table 1 lists the descriptive statistics, including the mean, standard deviation, skewness, and kurtosis, of all NO₃⁻ data at the depths from 0.15 to 1.80 m. In general, the mean and standard deviation decrease with depth, which might be mainly attributable to the agriculture practices and transport processes. The vertical sample support sizes are 0.15 and 0.30 m, respectively, from 0.15 to 0.60 m and from 0.60 to 1.80 m. The smaller vertical support size at the shallow depths may also contribute to the larger values of standard deviation.

Table 2. Correlation (r) of NO_3^- concentration at different depths (68 common locations).

Depth	0.15	0.30	0.45	0.60	0.90	1.20	1.50	1.80
m								
0.15	1	0.121	0.010	0.200	0.060	0.171	0.349	0.184
0.30		1	0.483	0.256	0.295	0.564	0.666	0.629
0.45			1	0.518	0.611	0.591	0.552	0.757
0.60				1	0.526	0.459	0.407	0.477
0.90					1	0.802	0.603	0.698
1.20						1	0.831	0.778
1.50							1	0.826
1.80								1

Table 3. Linear variogram models for NO_3^- concentrations at different depths.

Depth	Intercept	Slope
m	($\text{cmol}_c \text{L}^{-1}$) ²	($\text{cmol}_c \text{L}^{-1}$) ²
0.15	28	0.015
0.30	0.73	0.0018
0.45	0	0.0042
0.60	1.8	0.004
0.90	0.45	0.0018
1.20	0.2	0.0015
1.50	0.3	0.001
1.80	0.2	0.00092

The correlations of NO_3^- concentrations at the depths are shown in Table 2. There are low correlations between data at 0.15 cm and other depths. The correlations between layers generally increase with depths.

Considering the lower sampling cost at shallower layers and correlations of the chemical concentrations among the layers, we chose the available 103 data at 0.90 m and different reduced data sets at each layer below 0.90 m. Sample variograms at the layers were computed using all the data. The sample variograms are characterized with linear models and their slopes decrease with depths from 0.015 to 0.00092 (Table 3). Figures 1A and B show the sample variograms and models for NO_3^- concentrations at the depths 0.90 and 1.20 m, respectively. The pseudo-crossvariograms of NO_3^- concentrations between the depths 0.90 and 1.20 are presented in Fig. 2. As shown in Table 4, both g_{12} and g_{21} of NO_3^- between the depths of 0.90 and 1.20 m, 0.90 and 1.50 m, and 0.90 and 1.20 m are linear models; however, the slope of g_{21} is about two to three times that of g_{12} . The variograms and pseudo-crossvariograms in the tables satisfied the Schwarz's inequality given in Eq. [6] among the depths. For example, between the depths 0.90 and 1.20 m, we have

$$\gamma_1(h)\gamma_2(h) = (0.45 + 0.0018h)(0.2 + 0.0015h) \quad [7]$$

$$g_{12}(h)g_{21}(h) = (0.12 + 0.00216h)(0.12 + 0.001h) \quad [8]$$

Thus,

$$\gamma_1(h)\gamma_2(h) - g_{12}(h)g_{21}(h) =$$

$$0.076 + 6.56 \times 10^{-4} h + 6 \times 10^{-7} h^2 > 0 \quad [9]$$

Using the variograms and pseudo-crossvariograms in Tables 3 and 4 and cross-validation, we estimated NO_3^- concentration at the sample locations at the depths of 1.20, 1.50, and 1.80 m with kriging and cokriging techniques.

The following criteria were used to compare kriging

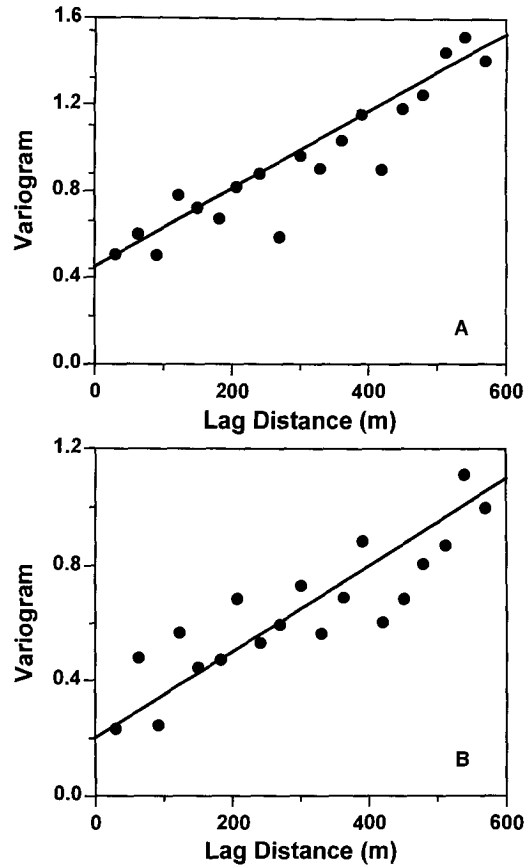


Fig. 1. Sample variograms (circles) and models (solid lines) of NO_3^- at the depths of (A) 0.9 and (B) 1.20 m.

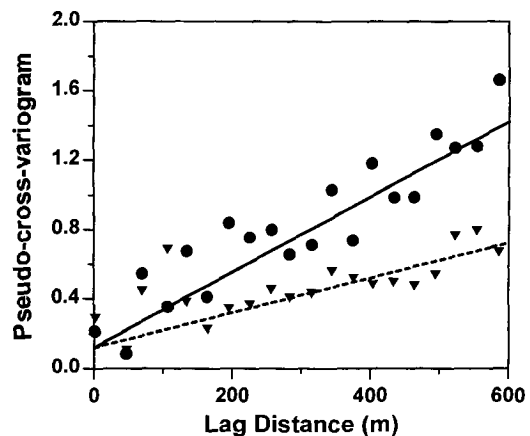


Fig. 2. Pseudo-crossvariograms of NO_3^- , g_{12} , and g_{21} , between the depths of 0.90 and 1.20 m. The circles and triangles represent the sample pseudo-crossvariograms, g_{12}^s and g_{21}^s , respectively, whereas the solid and dashed lines represent the fitted pseudo-crossvariograms.

and cokriging estimates. The MSE is calculated with

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n [Z(x_i) - Z^*(x_i)]^2 \quad [10]$$

where $Z(x_i)$ and $Z^*(x_i)$ are the measured and estimated values at x_i , respectively. Relative improvement, or relative reduction of MSE, is defined by

$$\text{RMSE} = 100\%(\text{MSE}_k - \text{MSE}_{\text{ck}})/\text{MSE}_k \quad [11]$$

Table 4. Pseudo-crossvariogram models for NO₃⁻ concentrations between depths.

Depths	Pseudo-crossvariogram
m	(cmol _c L ⁻¹) ²
0.90 and 1.20	$g_{12}(h) = 0.12 + 0.00216h$ $g_{21}(h) = 0.12 + 0.001h$
0.90 and 1.50	$g_{12}(h) = 0.1 + 0.00167h$ $g_{21}(h) = 0.1 + 0.0005h$
0.90 and 1.80	$g_{12}(h) = 0.1 + 0.0015h$ $g_{21}(h) = 0.1 + 0.0005h$

where MSE_k and MSE_{ck} are the mean squared errors for kriging and cokriging, respectively. Similarly, relative reduction of the kriging variance is defined by

$$RMKV = 100\%(MKV_k - MKV_{ck})/MKV_k \quad [12]$$

where MKV_k and MKV_{ck} are the mean kriging variances of kriging and cokriging, respectively. The correlation coefficient (*r*) between measurements and estimates was also used for the comparison.

The original data sets and various reduced data sets at the depths were used for cross-validation, that is, the available 103 data at 0.90 m and the common 60, 40, and 20 data points at each depth below 0.90 m. At each of the data points, the concentration was estimated by using neighboring observations, but not itself. The results are summarized in Table 5. Compared with kriging, cokriging reduced the MSEs from 23 to 58% and the MKVs from 24 to 47%. For all the cases, the correlation coefficients between the measurements and cokriging estimates are significantly higher than those between the measurements and kriging estimates. Note that cokriging provided more negative estimated values than kriging at the locations with zero concentrations. Nevertheless, physically the negative values can be set as zeros. As shown in Table 5, the correlation coefficients between the measurements and cokriging estimates by setting the negative estimated values as zeros were very close to (slightly higher than) those between the measurements and the original cokriging estimates. The total 210 kriging and cokriging estimates at the depth 1.20 m and 203 kriging and cokriging estimates at the depth 1.80 m are compared with the corresponding measure-

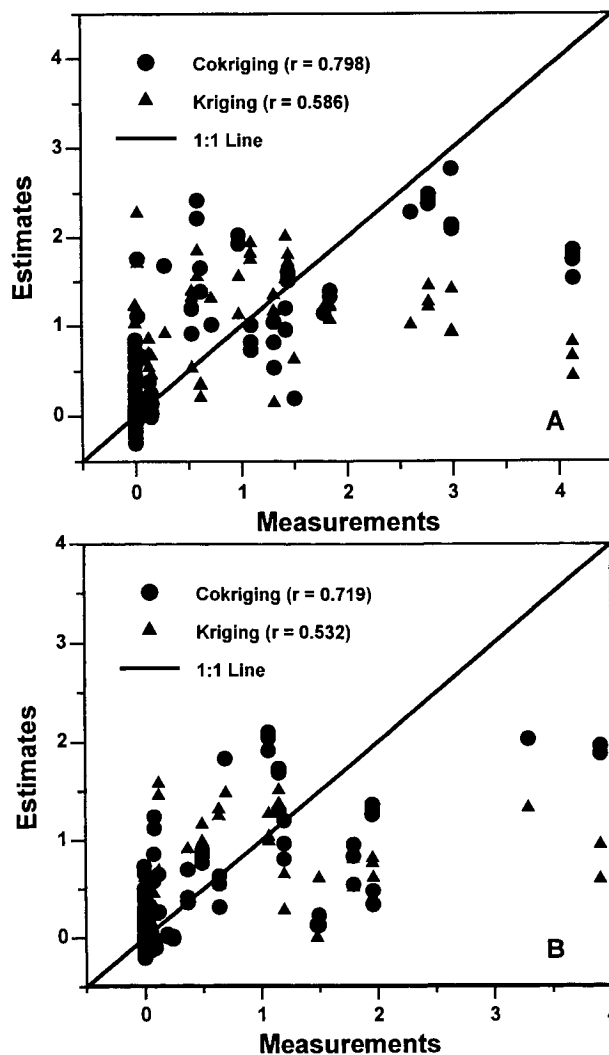


Fig. 3. Comparison of kriging and cokriging estimates vs. measurements at the depths of (A) 1.20 and (B) 1.80 m.

ments in Fig. 3A and B, respectively. Again the correlation coefficients (*r*) between the measurements and cokriging estimates are much higher than those between measurements and kriging estimates.

To estimate NO₃⁻ distributions in the 800 by 800 by

Table 5. Summary statistics of concentration estimation using cokriging and kriging.

Depth	No. of estimates	Cokriging			Kriging			RMKV	RMSE
		MSE†	MKV	<i>r</i>	MSE	MKV	<i>r</i>		
m		(cmol _c L ⁻¹) ²			(cmol _c L ⁻¹) ²			%	
1.20	90	0.2124	0.1789	0.791 (0.794)‡	0.3460	0.3332	0.624	46	39
	60	0.2358	0.1893	0.801 (0.807)	0.3993	0.3551	0.625	47	41
	40	0.3040	0.2066	0.811 (0.815)	0.7161	0.3875	0.476	47	58
	20	0.0641	0.2611	0.616 (0.613)	0.0838	0.4625	0.316	44	41
1.50	85	0.3324	0.3093	0.638 (0.640)	0.4395	0.4154	0.468	26	24
	60	0.4604	0.3201	0.622 (0.623)	0.6238	0.4327	0.426	26	26
	40	0.3381	0.3349	0.648 (0.649)	0.4562	0.4547	0.527	26	26
	20	0.7961	0.3859	0.650 (0.651)	1.1086	0.5091	0.461	24	28
1.80	83	0.2238	0.2054	0.741 (0.744)	0.3236	0.2966	0.591	31	31
	60	0.1897	0.2139	0.727 (0.731)	0.3154	0.3113	0.474	31	40
	40	0.1475	0.2260	0.515 (0.518)	0.1906	0.3277	0.270	31	23
	20	0.1777	0.2744	0.739 (0.739)	0.2660	0.3921	0.551	30	33

† MSE = mean squared error; MKV = mean kriging variance; RMKV = relative reduction of mean kriging variance; RMSE = relative reduction of mean squared error.

‡ Correlation coefficients between the measurements and cokriging estimates by setting the negative estimated values as zeros.

1.8 m soil volume, kriging and cokriging were applied to estimate 1681 values of the NO_3^- concentration on a grid of 20 by 20 m at each layer. For soil layers above 0.90 m, all data and kriging were used for the concentration estimation. Three schemes were applied to estimate NO_3^- concentrations below 0.90 m: (i) kriging with all data at each layer; (ii) kriging using the common 40 data points at each layer; (iii) cokriging with the same 40 data at each layer and the 103 data at 0.90 m. In terms of sampling cost, cokriging with the pseudo-cross-variograms (scheme 3) used less than half the data than scheme 1. In terms of estimation precision, cokriging produced better results than kriging using all of the data. Cokriging produced much more precise results than kriging using the same 40 data points at the depths. The kriging variances are more than two times the cokriging variance at the estimated points.

SUMMARY

It is critical to estimate chemical distributions in soils for many agricultural and environmental problems, such as nonpoint source pollution. A large-scale field experiment was conducted to measure NO_3^- concentration at depths of 0.15, 0.30, 0.45, 0.60, 0.90, 1.20, 1.50, and 1.80 m in an area of 800 by 800 m. Geostatistical methods, kriging, and cokriging were applied for studying sampling and estimation strategies. Especially, cokriging with pseudo-crossvariograms was used to maximize the use of data at different depths and improve estimation of NO_3^- spatial distributions at deeper layers. The pseudo-crossvariograms were nonsymmetric for all depths and were modeled with linear variograms.

It was shown that cokriging can be used to increase estimation precision and reduce sampling requirements. Through cokriging, much more easily sampled information at shallow layers was used to improve estimations at deeper soil layers. Compared with kriging, cokriging reduced the MSEs and the MKVs up to 60 and 50%. Cokriging with the nonsymmetric pseudo-crossvari-

grams used less than half data for the estimation of NO_3^- distributions, thus it potentially could reduce more than half the sampling cost than kriging estimation. Therefore, cokriging with pseudo-crossvariograms is an economic yet precise method for estimating distributions of nonpoint source pollutants in large fields.

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