

## Geostatistical Evaluation of Heavy Metals in Indo-Gangetic Alluvial Plains of North-west India

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**Abstract:** Spatial dependence of heavy metals like manganese (Mn), Nickel (Ni), Copper (Cu) and Cadmium (Cd) was measured using geostatistical technique in large land areas of Indo-Gangetic alluvial plains. Four hundred and seventy soil samples were drawn at 10 km x 10 km grid nodes throughout Haryana State. The coefficient of variation of Mn, Ni, Cu and Cd were 44.52, 57.94, 48.77 and 61.95%, respectively. The variability of these metals was expressed by Exponential (Mn and Cd), Gaussian (Ni) and Spherical (Cu) models. The estimates of mean by point kriging, block kriging and classical technique were more or less the same. The block kriging variances were 9.94 (Mn), 4.41 (Ni), 8.30 (Cu) and 6.67 (Cd) times less than the classical variances. The sample size by block kriging was very small compared to that in classical technique and point kriging methods.

**Key words:** Geostatistical technique, Spatial variability, Kriging, Indo-Gangetic plain, heavy metals.

The spatial distribution of heavy metals should be monitored for effective management of agricultural fields. Soil surveys may be carried out to obtain such information. Soil sampling and analysis are time and labor-consuming; thus, regular extensive and dense sampling is impossible. Geostatistics have proved useful in predicting the spatial distribution of heavy metals. The interpolation technique used is usually ordinary kriging. Application of geostatistical technique in most of the previous studies focused on data of relatively small spatial scale (McBratney *et al.*, 1982). So, this study was undertaken in the large area of Indo-Gangetic alluvial plains with the objectives of analyzing the extent of variation in Mn, Ni, Cu and Cd; determining the nature of spatial dependence; estimating, displaying and interpreting semivariograms as a measure of continuity; and designing optimum sampling strategy.

### Materials and Methods

Haryana state is a part of the Indo-Gangetic alluvial plains and extends between 27°39' and 30°55'N and 74°27'E and 77°36'E, with thickness of alluvium varying from few meters to 1200 m. The state has mostly a flat topography and a subtropical, semi-arid, continental monsoonal climate with an average precipitation of 300-1000 mm per year. The soils are light to medium in texture, dominated by illite and kaolinite clay minerals, alkaline in reaction, low in organic carbon and nitrogen, low to medium in phosphorus and high in potassium content. Soil samples from 470 locations at the nodes of a 10 x 10 km grid were collected. At each point five soil samples, each from 0-50 cm depth (effective root zone), were drawn randomly, mixed together to get a composite sample, and analyzed for

Table 1. Descriptive statistics of soil properties

Soil properties (mg kg <sup>-1</sup> )	Sample size	Mean	S.D.	CV (%)	Min.	Max.
Mn	470	8.50	3.78	44.52	1.00	28.30
Ni	232	1.49	0.87	57.94	0.08	4.80
Cu	470	1.36	0.66	48.77	0.40	4.40
Cd	423	0.23	0.14	61.95	0.04	0.92

DTPA-extractable heavy metals (Mn, Ni, Cu and Cd) by the methods of Lindsay and Norvell (1978) and determined on Atomic Absorption Spectrophotometer.

#### Classical analysis

Using classical statistical methods, mean ( $m$ ), variance ( $s^2$ ), standard deviation ( $s$ ) and coefficient of variation (CV) were computed. The number of observations required to obtain the mean value with a given degree of precision and confidence level was calculated (Dahiya *et al.*, 1984).

#### Geostatistical analysis

Variogram computation and statistical tests were performed on each variable. It may be recalled that variogram characterizes the variance of the increment of random function  $z$  between two locations separated by a distance  $h$ , and is defined under the hypothesis of first order as:

$$G(h) = 1/2 E\{[z(x+h)-z(x)]^2\} \quad \dots(1)$$

where,  $E$  stands for the expectation. Generally  $G(h)$  increases as  $h$  increases, which means that the influence of a measured value at location  $z$  is smaller and smaller away from  $x$ . In practice, several points are gathered in an arbitrary number of classes and  $G(h)$  is computed by discrete summation as:

$$G(h) = [\sum\{z(x_i+h)-z(x_i)\}^2]/2.N(h) \quad i=1-N \dots(2)$$

where,

$G(h)$  is the semivariance, and  $N(h)$  is the number of pairs of  $z(x_i)$  at a separate distance  $h$ . The sample semivariogram was then plotted with  $h$  on the abscissa and  $G(h)$  (semivariance) on the ordinate, and the resulting functions were fitted to exponential, gaussian and spherical models. Characteristics of the semivariogram such as nugget ( $Y$  intercept), sill (point of levelling off) and range (distance at which point becomes independent), can be useful in explaining the structure of spatial dependency in the field.

The properties were interpolated at 5 km interval, both by point and block kriging. The kriged estimates,  $Z^*(x_0)$ , at a place  $x_0$  is a weighted local average of  $N$  measured values of  $z$  in the neighborhood at locations:

$$Z^*(x_0) = \sum\{W_i z(x_i)\} \quad i=1-N \quad \dots(3)$$

where,  $W_i$  are the weights attributed to the neighbors, subject to the restriction:

$$\sum W_i = 1 \quad i=1-N \quad \dots(4)$$

The variance of  $Z^*(x_0)$  is given by:

$$s^2_k = U + \sum\{W_i G(x_i, x_0)\} \quad i=1-N \quad \dots(5)$$

where,

$U$  is the Lagrange parameter.

The users of information are generally interested in blocks rather than point estimates, so block kriging is done by:

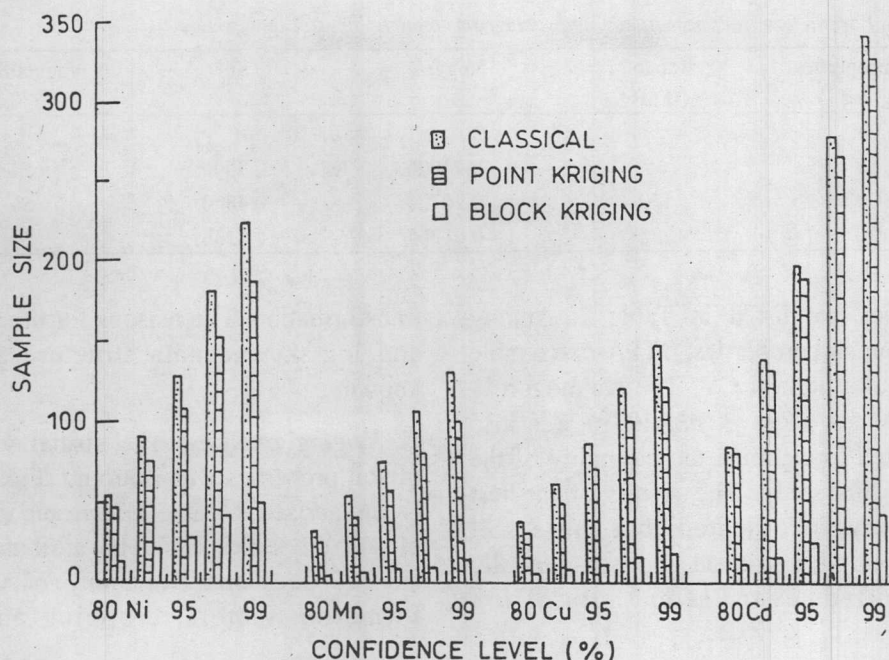


Fig. 1. Semi-variograms of Mn(A), Ni(B), Cu(C) and Cd(D).

$$Z^*V = \sum [W_i G(x_i, x_0)] \quad i=1-N \quad \dots(6)$$

The estimation variance,  $S^2_{kb}$ , is given by

$$S^2_{kb} = \sum_{i=1-N} W_i G(x_i, V) + UV - G(V, V) \quad \dots(7)$$

where,

$G(x_i, V)$  is the average semi-variance between the sample points  $x_i$  in the neighborhood and those in block  $V$ .  $G(V, V)$  is the average semivariance between all points within  $V$  (i.e., within block variance) and  $UV$  is the Lagrange parameter.

Validation of the kriging procedure was done by the so-called Jackknifing or fictitious-point method (Tabios and Salas, 1985). The criteria for validation were: (i) comparison of means of experimental and kriged values; (ii) the coefficient of

efficiency (ratio of the variance of kriged values to the variance of experimental values); (iii) set of errors ( $e$ ) found by subtracting the observed values from the kriged values; (iv) zero mean estimation error ( $e'$ ), the unbiased condition (paired t-test); and (v) standard deviation ( $s_e$ ) of the estimation errors and the percentage of errors lying within  $\pm 2s_e$  of the mean estimation error that was calculated for low variance conditions of the kriging estimation (Journal and Huijbregts, 1978).

## Results and Discussion

### Descriptive statistics

The mean, standard deviation, coefficient of variation (CV %), and the minimum and maximum values of the tested soil

Table 2. Parameters for best-fitted semivariogram models of soil properties

Soil properties (mg kg <sup>-1</sup> )	Range (km)	Nugget	Sill	Nugget/Sill (%)
Mn		$r = 0.958$		
Ni	65	0.43000	0.8000	54
Cu	150	0.26700	0.4800	56
Cd	225	0.01265	0.0236	54

properties are listed in Table 1. Among these four soil properties, DTPA-extractable Cd had the highest CV. The Kolmogorov-Smirnov test (Rao *et al.*, 1979) was also conducted to examine the normality of the data in this study. The results of the test (not shown) indicated that these soil properties were skewed and non-normally distributed even after natural-log

transformation. The reasons for the skewed and log-skewed data structure are not known.

*Kriging analysis:* The spatial variation of soil properties was isotropic (Fig. 1) and is summarized in Table 2. Isotropic variation of soil properties could be attributed to a lack of directional variability of the soil formation factors, cropping and soil

Table 3. Comparison of statistical parameters using different approaches

Statistical parameter	Mn	Ni	Cu	Cd
<b>Classical Technique</b>				
Mean (m)	8.50	1.49	1.36	0.23
Variance (s <sup>2</sup> )	14.32	0.75	0.44	0.02
Standard deviations (s)	3.78	0.87	0.66	0.14
<b>Point Kriging</b>				
Mean (m <sub>k</sub> )	8.40	1.46	1.36	0.23
Variance (s <sup>2</sup> )	10.57	0.64	0.36	0.02
S.D. (s <sub>k</sub> )	3.25	0.80	0.60	0.14
<b>Block Kriging</b>				
Mean (m <sub>kb</sub> )	8.39	1.46	1.36	0.23
Variance (S <sup>2</sup> <sub>kb</sub> )	1.44	0.17	0.05	0.03
S.D. (S <sub>kb</sub> )	1.19	0.41	0.23	0.05
<b>Ratio</b>				
S <sup>2</sup> /S <sup>2</sup> <sub>k</sub>	1.35	1.17	1.22	1.00
S <sup>2</sup> /S <sup>2</sup> <sub>kb</sub>	9.94	4.41	8.30	6.67
S <sup>2</sup> <sub>b</sub> /S <sup>2</sup> <sub>kb</sub>	7.34	3.76	6.79	6.67

where,

$S^2/S^2_k$  is ratio of sample variance vs. point kriging variance

$S^2/S^2_{kb}$  is ratio of sample variance vs. block kriging variance

$S^2_b/S^2_{kb}$  is ratio of point kriging variance vs. block kriging variance.

Table 4. Statistical parameters for testing the zero mean estimation error

Soil properties	$\hat{\epsilon}$	$Se^2$	Se	t	Percentage of observed estimation errors contained with $e^{\circ} \pm 2 Se$
Mn	0.260	10.950	3.31	0.4598	95.1
Ni	-0.0011	0.567	0.75	0.0711	96.1
Cu	0.002	0.354	0.59	0.1328	95.5
Cd	0.001	0.017	0.13	0.0615	96.5

$t_{0.05} = 2.093$

$\hat{\epsilon}$  = mean estimation error;  $Se^2$  = variance of errors; Se = standard deviation of errors.

management practices in the alluvial plain (Grewal *et al.*, 1977). The semivariograms were best described by Exponential model (Mn and Cd), Gaussian model (Ni) and Spherical model (Cu). The range of spatial correlation for these soil properties varied from 65 km (Ni) to 225 km (Cd).

The ratio of nugget variance to sill expressed in percentage can be regarded as a criterion to classify the spatial dependence of soil properties (Table 2). There is generally moderate spatial dependence among soil parameters (Cambardella *et al.*, 1994). The pattern of moderate spatial dependence was also found for soil properties at this sampling scale in this study area. The ratio of nugget variance to sill for each soil property was 54 to 56%, indicating that most of the soil properties were moderately spatial-dependent.

#### *Spatial distribution estimated by kriging:*

The additional values of Mn, Ni, Cu and Cd were generated at unrecorded sites by point and block kriging, using semivariograms of these properties. A block size of 24 x 24 km was used for interpolation because it gave the minimum estimation variance, compared to other block sizes. The estimates of the means by kriging (point

and block) and classical techniques were almost the same for all the properties (Table 3). The estimated variances obtained by block kriging were 4.41-9.94 times less than the sample variances, showing improvement in estimation precision over the classical techniques. It could, therefore, be inferred that kriging could explain most of the variation in the original data. This means that if a variable is spatially dependent, the estimation of variance by the classical method is not a reliable parameter for the interpretation of the data. Further, the ratio of the point and the block kriged variance exhibited 3.76 to 7.34-fold differences for these properties (Table 3). Similar efforts were also made by other workers (Grewal *et al.*, 1977; Trangmar *et al.*, 1986; Webster, 1985; Wopereis *et al.*, 1988).

By comparing mean, variance and Student's t-values, we validated kriging for all the spatially dependent parameters. Validation could also be done from a mean estimation error ( $\hat{\epsilon}$ ), a variance of errors ( $Se^2$ ) and from standard errors (Se). The kriged values (point and block) were tested and validation was found to be better for block kriged estimates because of their lower standard errors (Table 4).

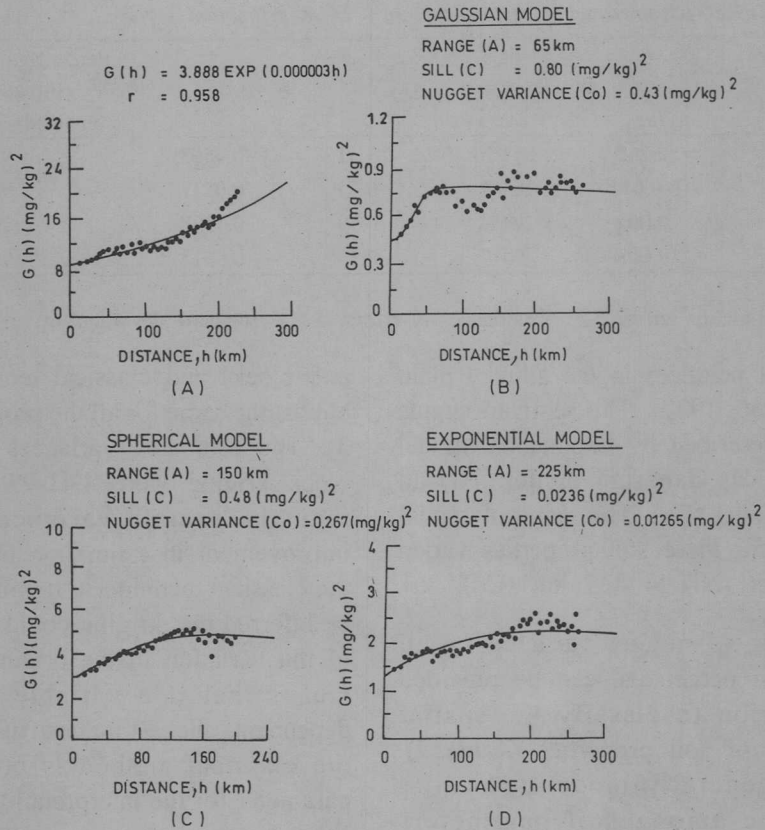


Fig. 2. Number of observations to be recorded within  $\pm 10\%$  of the true mean at different confidence levels.

### Designing optimal sample size

The standard deviations of observed and kriged estimates were used for calculating the number of samples required to improve precision within  $\pm 10\%$  of the true mean at different confidence levels. Block kriging reduced the sample size by 4-10 and 3-8 times compared to classical and point kriging methods, respectively (Fig. 2), within  $\pm 10\%$  of the true mean at 95% confidence level for the parameters studied. This would considerably reduce the sampling effort and cost.

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