SPATIAL VARIATION OF FLUORINE IN AN INDO-GANGETIC ALLUVIAL PLAIN OF INDIA

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SUMMARY: Spatial variability of water-soluble fluorine (F) in Haryana soils was studied geostatistically. Semivariogram based on 470 samples at a node of 10 x 10 km grid showed F to be correlated over space for a separating distance of 225 km between two observations. Fluorine was estimated by point and block kriging methods at unsampled sites (5 x 5 km grid). The means obtained by these three methods were almost the same, though the estimation variances calculated by point and block kriging were 1.19 and 8.76 times less than those obtained by the classical theory. However, block kriging variance was 7.34 times less than the point kriging variance, a good gain in efficiency. An isarithmic map of F drawn from the point kriged estimates was very spotty and discontinuous, whereas in the map prepared by block kriged estimates the spottiness disappeared to a greater extent, resulting in a better continuity. The estimated number of samples were 125 (classical), 104 (point kriging) at 99 per cent confidence level. However, the number of samples required at this precision were only 14 by block kriging, a good gain in precision.

Key words: Alluvial plains; Haryana, India; Spatial variability, Water-soluble soil fluorine.

Introduction

Fluorine is widely distributed in the environment and ranks 13th among the elements in order of abundance in the earth's crust. However, when absorbed in excessive amount fluorine may cause toxicity to plants\(^1\) and animals\(^2\). Plants tend to be more susceptible to fluorine injury from soil than from the atmosphere.\(^3\) The plant uptake of fluorine is governed by F concentration in equilibrium solution.\(^4\) Heavy textured soils absorb more fluorine than the light textured soils.\(^5\)

In view of the above facts, the present study had the following objectives: i) to quantify the spatial distribution of water-soluble fluorine by semivariogram analysis; ii) to use the spatial dependence for interpolation of values at unrecorded sites by the kriging technique; iii) to prepare an isarithmic map from the kriged and observed values; and iv) to estimate the optimum number of samples to be taken for a given precision level.

Materials and Methods

Haryana state extends between 27°39 and 30°55 N latitude and 74°27'8" to 77°36'5" E longitude with a total area of 44,222 km\(^2\). Of this total area, 12,840 km\(^2\) (29.03%) is arid, 26,880 km\(^2\) (60.78%) is semi-arid and 4,502 km\(^2\) (10.10%) is sub-humid. The soils are light to medium in texture and are derived from alluvium.

A grid map of the state at a node of 10 x 10 km was prepared for soil sampling. From each location, five soil samples, each from a depth of 0-50 cm (effective root

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zone), were taken randomly, composited, and the sub-sample was retained. In all, 470 samples were collected and analysed for water-soluble fluorine into 1:1 soil water extract and determined colorimetrically by the Zirconium Erichrome cyanin-R lake method. The resulting data have already been used to construct cumulative frequency plots and their spatial variation in different agroclimatic zones of the state.

Statistical Analysis

The kriging technique has been used for the estimation of fluorine, which varies geographically. The method has been in use for decades in South African goldfields. It is essentially a means of “weighted local averaging” in which the weights are chosen so as to give unbiased estimates while at the same time minimizing the estimation variance. Kriging is in this sense optimal.

Preliminary Analysis

Using classical statistical methods, mean (m), variance (s²), 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 significance level were calculated.

Spatial Analysis

This was carried out in the form of semivariance as per the procedure described. This function related the similarity of difference, expressed as semivariance, between values at different places to their separation distance. An average semivariance was defined by:

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

where \( G(h) \) is the semivariance; \( h \) is the modulus of interval; \( N \) is the number of pairs; \( z(x_i + h) \) and \( z(x_i) \) are values of soil property separated by a distance \( h \). A Gaussian Model was fitted to quantify the structural component of variation. Weights were assigned according to the number of pairs on which an estimate was based during fitting the least squares method. The values were interpolated at 5 km interval both by point and block kriging.

The measurement of value of a property at a number of places, \( x_i \), within a region to give values \( z(x_i) \), \( i = 1...N \); we wish to estimate the value of the property at some place \( x_0 \). The place might be a “point” i.e. an area of the same size and shape as those on which the measurements were made. Alternatively, it might be a larger area or block. The procedures for estimation in the two instances are known as point and block kriging, respectively.

Thus, interpolated values (point kriging) of the regionalised variables, \( Z^* \), at location \( x_0 \) is

\[ Z^*(x_0) = \sum_{i=1}^{N} w_i z(x_i) \]

where \( w_i \) is the weights attributed to the neighbours subject to the restriction that:

\[ w_i = 1 \quad \text{for } i = 1 \text{ to } N \]

* See page 175 for abstract
Kriging was done under the condition of unbiased and minimum variance in which it is an optimal interpolation technique.\textsuperscript{11} The kriging variance can be estimated by:

\[ S^2_k = w_i z(x_i, x_o) + U \]

where \( U \) is the lagrange multiplier with the minimisation of \( S^2_k \).

For interpolation of values by block kriging, a block size of 24 x 24 km was used, which gave the minimum estimation variance. The kriged value \( Z^* \) for any block \( V \) is the weighted average of the observed values \( x_i \) in the neighbourhood of the block, \textit{i.e.}

\[ Z^*_V = w_i z(x_i) \quad \text{for } i = 1 \text{ to } N \]

The estimation variance, \( S^2_{kb} \), is given by:

\[ S^2_{kb} = w_i G(x_i, V) + UV - G(V, V) \quad \text{for } i = 1 \text{ to } N \]

where \( G(x_i, V) \) is the average semivariance between the sample points \( x_i \) in the neighbourhood and those in the block \( V \). \( G(V,V) \) is the average semivariance between all points within \( V \) (\textit{i.e.} within block variance) and \( UV \) is the lagrange parameter associated with the minimisation.

Block kriging values relate to a different variable than the original point measurements. The averaging smooths out extremes values, producing a new variable with fewer and smaller fluctuations, thus making it easier to use for making predictions. Essential to success in kriging is the use of inherent spatial correlation in the sampling, which results in enhanced estimates, or, given a confidence level, one needs fewer observations to achieve a prescribed level of accuracy. Validation of the kriging procedure was done by the so-called Jack Knifing, or fictitious point method.\textsuperscript{12}

\textbf{Results and Discussion}

\textbf{Preliminary Analysis}

It is seen from Table 1 that the water-soluble F in Haryana soils ranged from 0.25 to 19.13 \( \mu g \text{ g}^{-1} \) with a mean of 4.19 \( \mu g \text{ g}^{-1} \). The coefficient of variation was 43\%, which indicates that this parameter had medium variation across the entire area studied.

\textbf{Spatial Analysis}

The bounded semivariogram of water-soluble F showed strong spatial dependence up to a lag distance of about 225 km and definite sill 4.2 (\( \mu g \text{ g}^{-1} \))^2, described by the Gaussian Model (Figure 1). The nugget variance (\( C_0 \)) was as high as 2.4 (\( \mu g \text{ g}^{-1} \))^2 \textit{i.e.} 72 per cent of the sample variance which corresponds to the variability that occurs within distances shorter than the sampling interval (10 km) and to experimental errors.

Practically, the semivariogram indicates that any two samples separated by a distance of 225 km would be mutually dependent. The samples collected with a separation distance of less than 255 km could not be used for determination of variance, standard deviation, and other sample statistics by classical statistical methods. In that case, the kriging interpolation technique would be most appropriate for this purpose. However, samples collected at a separating distance of more than 225 km would be spatially independent, \textit{i.e.} randomly distributed. Thus a
classical statistical approach is applicable beyond this distance. Available literature also indicates the presence of spatial dependence of fluorine.\textsuperscript{6,13,14}

\textbf{Mapping}

With the help of the fitted model of the semivariogram (Figure 1) and the observed values, additional values were kriged at the unsampled places both by point and block kriging. The kriged and original values were then used to prepare isarithms of fluorine. It is seen that the map prepared by point kriging (Figure 2) was extremely spotty due to high short range variation (Co). However, in the map prepared by block kriging (Figure 3), the spottiness disappeared to a great extent resulting in a smoother map. This was so, because block kriging smoothens the effect of short range variation to a great extent. For further interpretation of the results, the block kriging was used. A major part of the state (about 80\%) falls under the classes of 3.5-5.0 \( \mu g \ g^{-1} \) (57\% of total area) and 2.0-3.5 \( \mu g \ g^{-1} \) (23\%) (see Table 2).

\textbf{Figure 1.} Semivariogram of water soluble soil fluorine

\begin{center}
\includegraphics[width=\textwidth]{image1.png}
\end{center}
Figure 2. Isarithmic map of F based on point kriging
Figure 3. Isarithmic map of F based on block kriging
The means and their dispersion statistics obtained by point and block kriging are compared with those obtained by the classical approach (Table 1). The estimates of the means by the three methods are more or less the same. The estimation variances obtained by classical and point kriging approaches differed by a factor of 1.19 without showing any substantial gain in the apparent precision by the kriging method over the classical method. However, those obtained by classical and block kriging approaches differed significantly by a factor of 8.76. This represents very substantial gain in the apparent precision by the block kriging method over the classical method. It means that the classical method greatly overestimated the variance assuming that the block kriging variance is close to the true value. Practically, it means that if a parameter is spatially dependent, the estimation variance by classical method is not a reliable parameter for the interpretation of the data. Overestimation of the variance of the spatially dependent data of different properties by the classical approach has been reported by several workers.9,11,15

**TABLE 1. Summary of sample and kriging statistics**

<table>
<thead>
<tr>
<th>Statistical Parameter</th>
<th>Classical</th>
<th>Point kriging</th>
<th>Block kriging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (μg g⁻¹)</td>
<td>4.19</td>
<td>4.16</td>
<td>4.16</td>
</tr>
<tr>
<td>Range (μg g⁻¹)</td>
<td>0.25-19.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Variance*(μg g⁻¹)²</td>
<td>3.33</td>
<td>2.79</td>
<td>0.38</td>
</tr>
<tr>
<td>Standard deviation(μg g⁻¹)</td>
<td>1.82</td>
<td>1.67</td>
<td>0.62</td>
</tr>
<tr>
<td>Coefficient of variation (%)</td>
<td>43</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Ratio of classical and point kriging variance = 1.19
Ratio of classical and block kriging variance = 8.76
Ratio of point kriging and block kriging variance = 7.34

**TABLE 2. Distribution of water-soluble fluorine in Haryana soils**

<table>
<thead>
<tr>
<th>Fluorine (μg g⁻¹)</th>
<th>Area (cm²)</th>
<th>*Percentage of total area of State</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 2.0</td>
<td>10.0</td>
<td>5.68</td>
</tr>
<tr>
<td>2.0 - 3.5</td>
<td>40.2</td>
<td>22.81</td>
</tr>
<tr>
<td>3.5 - 5.0</td>
<td>100.0</td>
<td>56.75</td>
</tr>
<tr>
<td>5.0 - 6.5</td>
<td>20.0</td>
<td>11.35</td>
</tr>
<tr>
<td>&gt; 6.5</td>
<td>6.0</td>
<td>3.41</td>
</tr>
<tr>
<td>Total</td>
<td>176.2</td>
<td>100.00</td>
</tr>
</tbody>
</table>

* Computed from Figure 3, where 1(cm)² = 250.976(km)² on ground
It is further seen from the ratio of the point and block kriging variances that the block kriging variance was 7.34 times smaller than that obtained by point kriging (Table 1). Similar improvement in estimation precision has been achieved using block kriging compared to point kriging\textsuperscript{10,11,15,16}

**Designing Optimum Sampling Strategy**

The results of geostatistical analysis can further be used to design the optimal sampling scheme of the given parameter\textsuperscript{2}. The standard deviation of the kriged data was determined, and the number of observations required to get the precision with ±10\% error at different probability levels (80, 90, 95, 98 and 99\%) were calculated and compared with those obtained by the classical method. Block kriging reduced the sample size by 8.93 and 7.43 times compared to classical and point kriging methods, respectively (Figure 4), indicating that only 14 solid samples would be sufficient instead of 470 samples to get the same precision at the 99\% confidence level for the parameter studied. Thus block kriging reduced the sampling effort and cost considerably compared to other methods.

**Figure 4.** Sample size of F by classical, point and block kriging methods at different confidence levels

![Diagram](image-url)
References


