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# COPPER AND COBALT DEFICIENCY IN SOIL: A STUDY USING DISJUNCTIVE KRIGING

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**ABSTRACT.** Grazing cattle and sheep obtain essential copper and cobalt in the herbage they eat, which in turn takes it up from the soil. In some regions the soil contains too little of these elements, and the animals suffer from deficiency locally. The concentrations of the elements can be measured in the soil, and farmers are advised to treat their soil or their livestock where estimated concentrations are less than critical thresholds.

In south east Scotland the soil is judged to be deficient in copper if the concentration is less than 1.0 mg per kg of topsoil and in cobalt if its concentration is less than 0.25 mg/kg. Measurements from nearly 2000 fields in a 1600 km$^2$ portion of the region have been analysed. The average concentrations of copper and cobalt have been estimated over 1 km x 1 km blocks by disjunctive kriging, as have the values of the indicators $\mathbf{1}$[Cu<1.0] and $\mathbf{1}$[Co<0.25], which estimate the probabilities of deficiency. The results are presented as maps showing where there appear to be deficiencies and where farmers should know the risks of deficiency even though the estimates exceed the critical thresholds.

## CONTENTS

## INTRODUCTION

All mammals need copper and cobalt. In the normal way grazing cattle and sheep obtain these from the grass and other herbs they eat, which in turn take it up from the soil. Plants do not need cobalt, and so it is possible for them to grow well on soil that contains none. Animals introduced into such an environment will inevitably sicken and die prematurely for want of the element. Plants do need copper. Nevertheless, they too may take up less than grazing animals need. Most soil contains some of both copper and cobalt, but not necessarily enough to support a thriving population of cattle or sheep, and deficiencies are serious in some parts of the world.

Deficiency is common is south east Scotland. At one time cattle and sheep suffered severely locally, and deaths were common. Severe deficiency is rare nowadays, but subclinical deficiency is thought still to cause lack of thrift. To identify causes of sickness and poor growth of livestock, and if possible to forestall them, the local agricultural advisory service, the East of Scotland College of Agriculture, analyses topsoil for farmers and advises corrective treatment if the soil seems deficient. This may involve spraying the land with salts of copper or cobalt, or more usually adding them as salt licks to the diet of the stock.

The chemistry of both copper and cobalt in the soil is complex, and only small proportions of the elements can be taken up by plants at any one time. These fractions are known as the available portions of the elements. They can be extracted from the soil with a dilute solution of some mild acid and measured, and this measurement is the basis of any recommendation. The East of Scotland College uses ethylene diamine tetra acetic acid for copper and 0.5 M acetic acid for cobalt. Its research has shown that if the available copper measured in this way exceeds 1.0 mg/kg of soil (on an air-dry basis) and the concentration of cobalt exceeds 0.25 mg/kg then there should be enough in the herbage for cattle and sheep grazing it. If on the other hand the concentrations of either element are less than the above thresholds then graziers should be aware, check their animals for deficiency, and take corrective action if necessary.

The available copper and cobalt are measured on small samples of soil. In practice these represent the topsoil of whole fields (see below). There are many more fields that are not sampled, and the farmer or his advisor might wish to predict values in other fields, unsampled ones, from the data. However, a cow or sheep does not spend its whole life in one field. The farmer moves his stock over the whole of his farm or a hill side. Each animal performs a kind of integration over the farm or hill, and so it might not suffer as a result of copper or cobalt deficiency in the soil of any one field if there is enough elsewhere. In this case it is a whole farm or hillside that is of interest, not individual fields. And so the farmer wants to know whether the soil contains enough copper and cobalt, i.e. whether the thresholds are exceeded on average, for such blocks of land. He can never be certain, and he must be satisfied with an estimate, which may be regarded as a probability that his soil is deficient on average: it gives him an idea of the risk he runs if he does nothing.

The particular problem was first explored by McBratney *et al.* (1982) in their original study using ordinary kriging. However, it is precisely of the kind for which Matheron (1976a, b) derived disjunctive kriging, even though his solution was for mining, and Webster & Oliver (1989a,b) and Webster (1991) analysed the situation afresh using disjunctive kriging. We have since taken the analysis a little further, and here we summarize the results. The mathematics of the technique can be found in Matheron's original papers and in Rivoirard's (1990) new introduction, and it has not seemed necessary to repeat all of the theory here.

## DATA

### The Survey

Since 1964 the East of Scotland College has analysed topsoil from several thousand fields in south east Scotland. In each field, of area 5 to 10 ha, some 20 cores of topsoil (0 to 20 cm depth) were taken at random and then bulked and thoroughly mixed for chemical analysis. Larger fields were divided, and each part was sampled and analysed separately. The support of the sample was thus the top 20 cm of soil over approximately 5 to 10 ha.

By 1980 there were records for more than 3500 fields, giving an average intensity of about 1 sampled field per square kilometre. In the west of the region sampling was very uneven, and not all records were kept. In the east coverage was fairly even and records were complete. We have therefore restricted this study to the eastern portion, and specifically to the east of the British National Grid line 360 to 1 km resolution. Fig. 1 shows the region, which extends over approximately 1600 km$^2$ between Edinburgh and the English border. Within it there are almost 2000 sampled fields for nearly all of which there are values of both available copper and cobalt in the soil and whose grid coordinates are known to the nearest 100 m. These constitute the data, and their positions are marked by points in the Figure.

Although there are many data, each value refers to a support of only 5 to 10 ha, i.e. a single field. As above, the stock farmer is likely to be more concerned to know the average value over his farm, and so the problem is to use the data to decide whether the concentrations are enough over supports larger than the sample — say 1 km x 1 km blocks.

### Statistical Summary

Table 1 summarizes the statistics from the survey. Values of copper range from 0.3 mg/kg (deficient) to 16.0 mg/kg (abundant) with a mean of 2.22 mg/kg. Cobalt's concentrations vary from 0.05 mg/kg (very deficient) to 1.0 mg/kg (ample). Their mean is 0.254 mg/kg, which is only slightly more than the critical threshold for deficiency. The data for both elements are strongly positively skewed (the skewness coefficients are 2.52 for copper and 1.61 for cobalt). The histograms, Fig. 2, display the distributions.

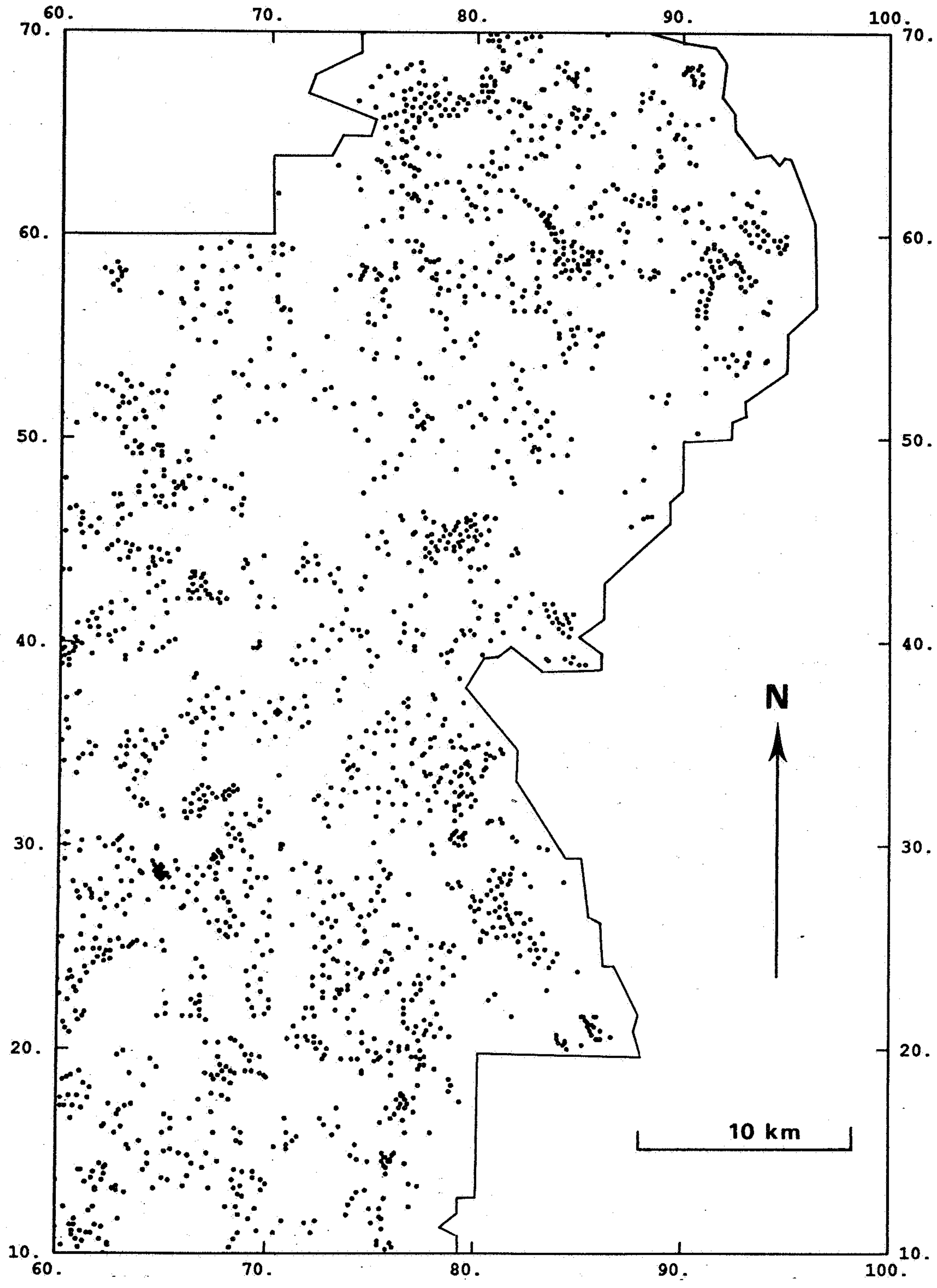


Fig. 1. Region of study with fields sampled marked by points.

Table 1. Summary statistics of copper and cobalt. Original measurements in mg/kg of soil

| | Copper | Cobalt |
|---|---|---|
| Number of observations | 1949 | 1981 |
| Minimum | 0.30 | 0.05 |
| Maximum | 15.70 | 1.00 |
| Mean | 2.22 | 0.254 |
| Standard deviation | 1.46 | 0.123 |
| Variance | 2.1346 | 0.01507 |
| Skew | 2.52 | 1.61 |
| Deficiency threshold | 1.0 | 0.25 |

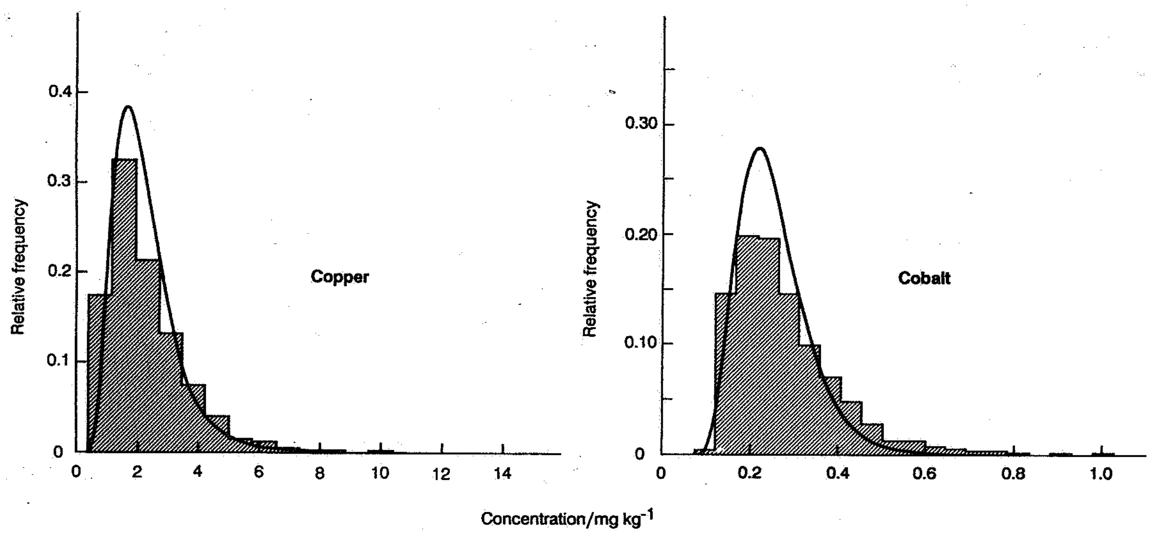


Fig. 2. Histograms with curves of the block distributions.

## GEOSTATISTICAL ANALYSIS

### The Variograms

The sample variograms have been calculated at intervals of 0.5 km to 25 km using the usual computing formula:

$$\hat{\gamma}(\mathbf{h}) = \frac{1}{2M(\mathbf{h})} \sum_{i=1}^{M(\mathbf{h})} \{z(\mathbf{x}_i) - z(\mathbf{x}_i + \mathbf{h})\}^2,$$

where $\hat{\gamma}(\mathbf{h})$ is the average semivariance of the regionalized variable, $Z(\mathbf{x})$, at lag $\mathbf{h}$, $z(\mathbf{x}_i)$ and $z(\mathbf{x}_i + \mathbf{h})$ are observed values of $Z$ at places $\mathbf{x}_i$ and $\mathbf{x}_i + \mathbf{h}$ separated by $\mathbf{h}$, and $M(\mathbf{h})$ is the number of paired comparisons at that lag. The variation is isotropic, and the computed values are averages over all directions. The sample values are plotted as points in Fig. 3, on which the fitted models (the continuous curves passing through the points) are also drawn. In both cases the models are double spherical with nugget:

$$\gamma(h) = c_0 + c_1 \left\{ \frac{3h}{2a_1} - \frac{1}{2}\left(\frac{h}{a_1}\right)^3 \right\} + c_2 \left\{ \frac{3h}{2a_2} - \frac{1}{2}\left(\frac{h}{a_2}\right)^3 \right\} \text{ for } 0 < h \leq a_1,$$

$$\gamma(h) = c_0 + c_1 + c_2 \left\{ \frac{3h}{2a_2} - \frac{1}{2}\left(\frac{h}{a_2}\right)^3 \right\} \text{ for } a_1 < h \leq a_2,$$

$$\gamma(h) = c_0 + c_1 + c_2 \text{ for } h > a_2.$$

The coefficients of the models are given in Table 2.

### Indicator variograms

The variables in this case study are $\mathbf{1}[\text{Cu}<1.0]$ for copper and $\mathbf{1}[\text{Co}<0.25]$ for cobalt. These are the indicators of deficiency that are to be estimated in addition to the concentrations themselves.

To justify the normal model for disjunctive kriging the auto and cross variograms of several indicators in the range of the data were computed and examined. For copper the cutting values were chosen at 1.0, 3.0, and 5.0 mg/kg, giving classes containing respectively 13, 65, 17 and 5 percent of the values. For cobalt we chose 0.15, 0.25 and 0.40 mg/kg as cut-offs, which gave four classes 12, 40, 42, and 6 percent of the values in them. The corresponding indicators are $\mathbf{1}[\text{Cu}\geq 1.0]$, $\mathbf{1}[\text{Cu}\geq 3.0]$, and $\mathbf{1}[\text{Cu}\geq 5.0]$ for copper, and $\mathbf{1}[\text{Co}\geq 0.15]$, $\mathbf{1}[\text{Co}\geq 0.25]$, and $\mathbf{1}[\text{Co}\geq 0.4]$ for cobalt. Figs 4 and 5 show the auto and cross variograms for the two elements. The cross variograms are clearly more structured, i.e. they show stronger spatial dependence, than the auto variograms. This suggests that a diffusion model may represent the spatial processes and that we may use a Gaussian model for the disjunctive kriging (Rivoirard, 1989, 1990).

Table 2. Coefficients of double spherical models of the variograms and statistics of the regularization. Variances, $c_0, c_1$, and $c_2$, of the raw variograms and block variances are in $(\mathrm{mg/kg})^2$, and all distances for $a_1$ and $a_2$ are in km.

| | copper | cobalt |
|---|---|---|
| *Raw variogram* | | |
| $c_0$ | 0.75 | 0.008 |
| $c_1$ | 0.97 | 0.0042 |
| $c_2$ | 0.53 | 0.0036 |
| $a_1$ | 2.4 | 3.7 |
| $a_2$ | 20.0 | 16.0 |
| *Regularization* | | |
| Block variance | 1.1764 | 0.006762 |
| Change-of-support coefficient | 0.776 | 0.692 |
| *Normalized block variogram* | | |
| $c_1$ | 0.51 | 0.44 |
| $c_2$ | 0.49 | 0.56 |
| $a_1$ | 2.8 | 3.7 |
| $a_2$ | 20.0 | 16.0 |

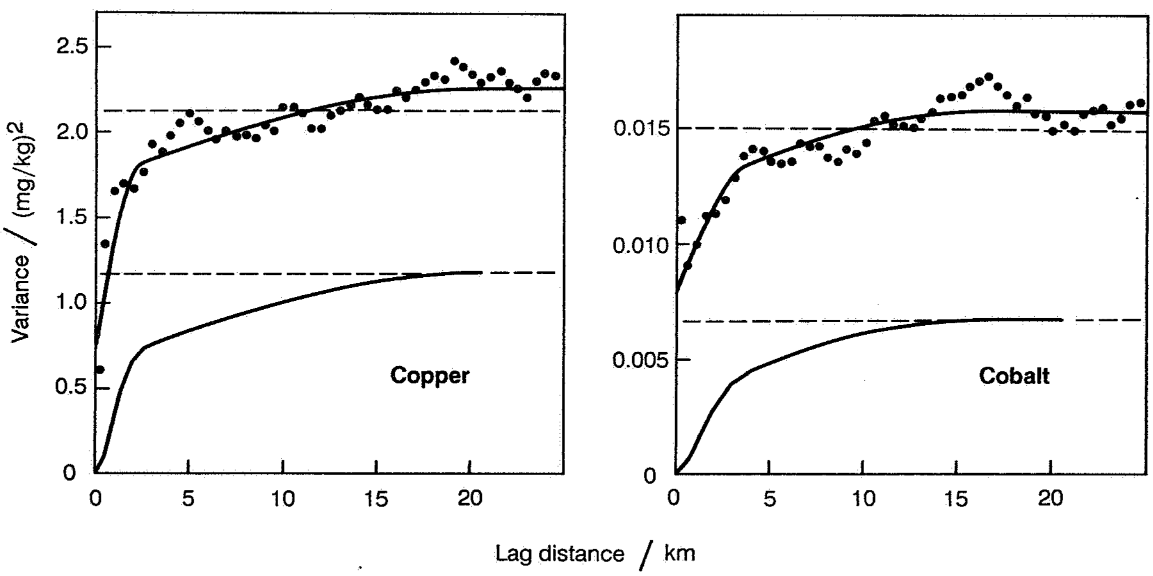


Fig. 3. Variograms. Plotted points are the sample variograms with fitted models shown as the curves though them. The lower curves are the regularized variograms.

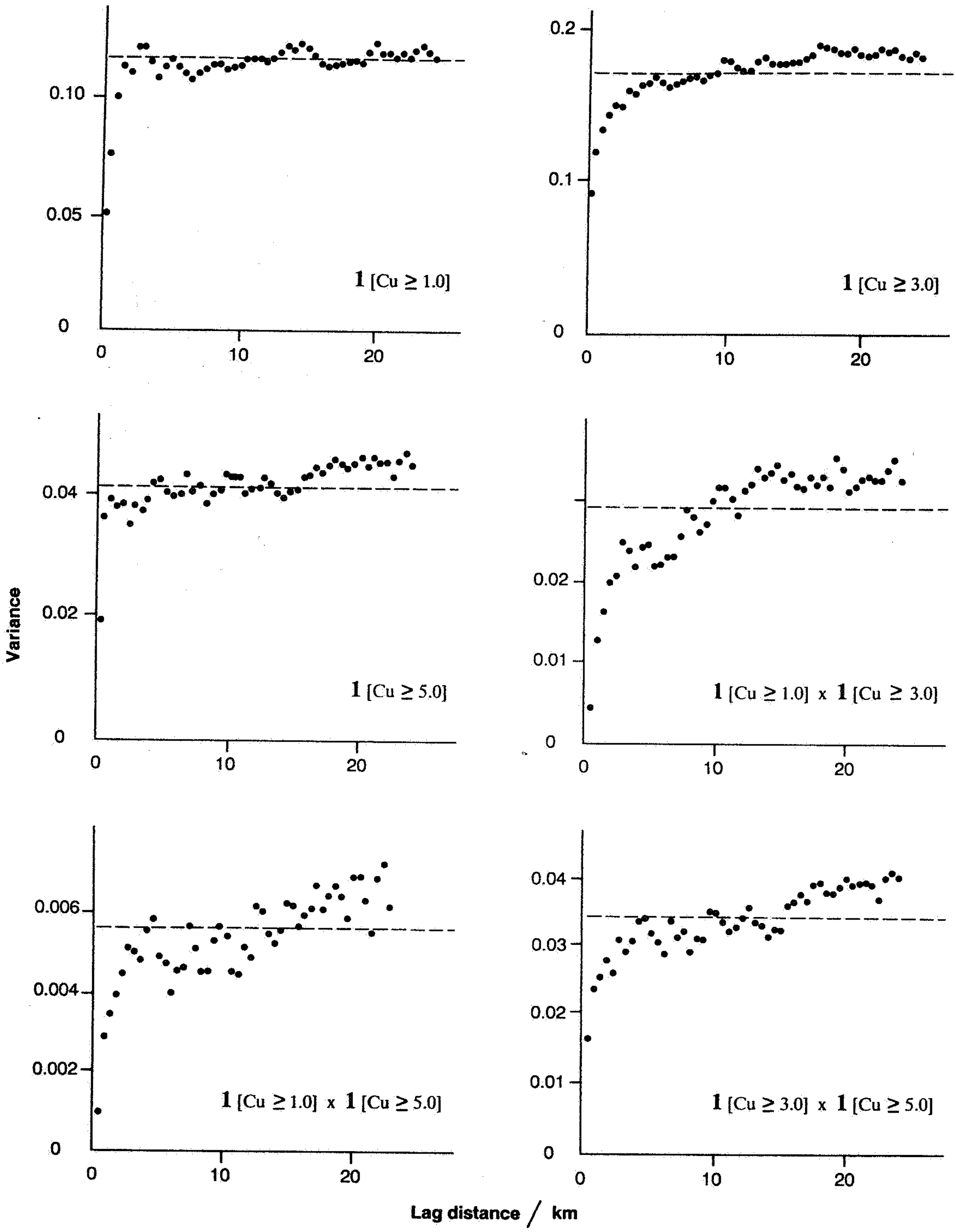


Fig. 4. Auto and cross variograms of the indicators for copper.

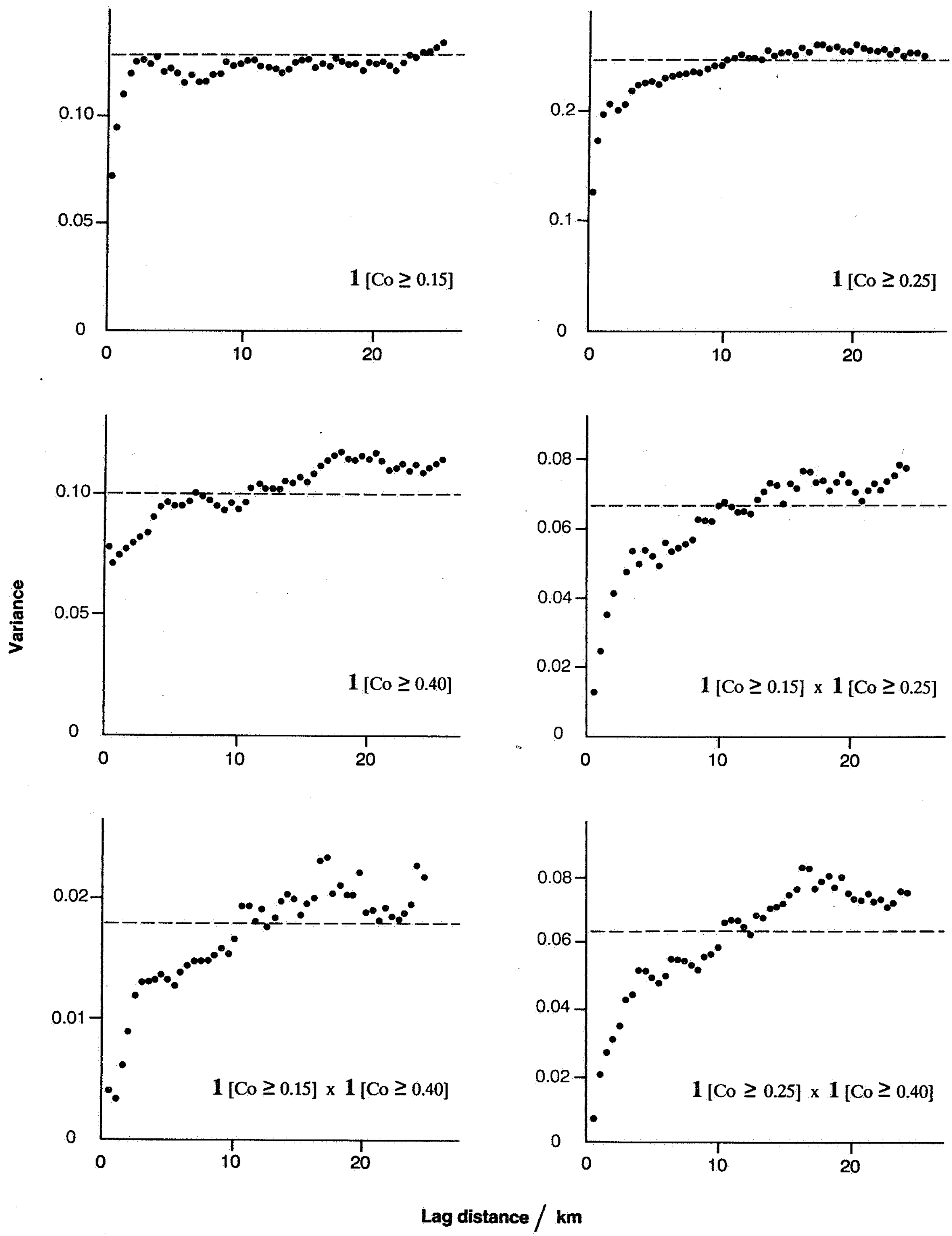


Fig. 5. Auto and cross variograms of the indicators for cobalt.

## Transformation and regularization

To use the Gaussian model we need to transform the data, which as Fig. 2 shows, are far from normal to standard normal form. This is done using Hermite polynomials. Here 30 of them were computed, and Fig. 6 shows the transformation curves. Both are strongly concave upwards, which is to be expected given the strong positive skew in the data.

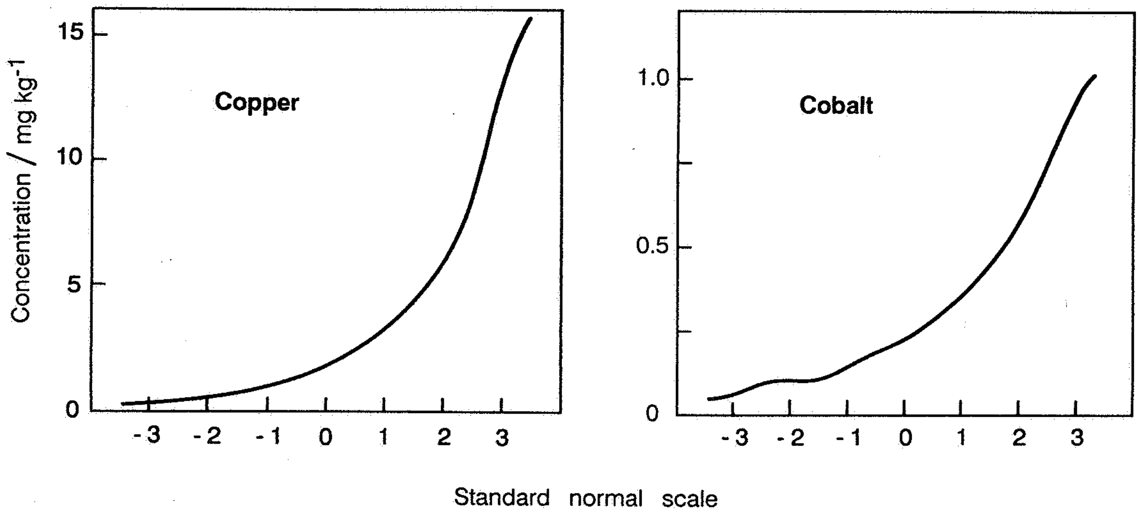


Fig. 6. Graphs of the transformation functions.

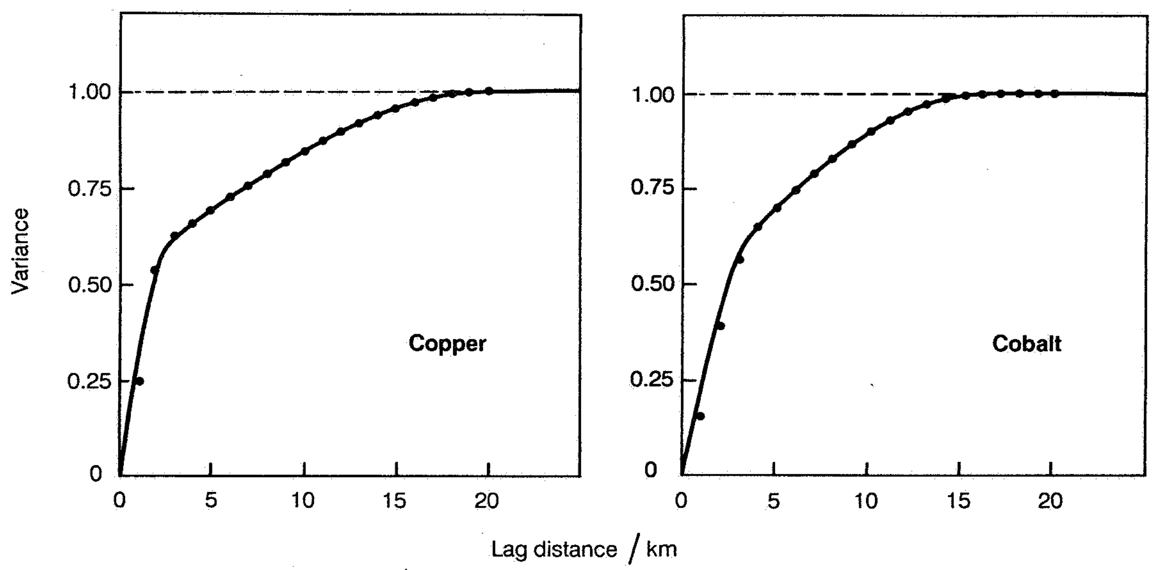


Fig. 7. Variograms of the transformed block variables with the estimated values plotted as points and the fitted models as the curves.

We also wish to change the support of the estimates from that of the points, in this case fields of 5 to 10 ha, to larger areas, 1 km x 1 km squares. The variograms have therefore been regularized to this support, with the results shown as the lower curves in Fig. 3. Their forms are very similar to the models fitted to the observed semivariances. The variances are much less, of course, mainly because the large nugget variance disappears: it is contained in the within-block variance. The sill variances are given in Table 2. The change-of-support coefficients, also given in Table 2, are 0.776 for copper and 0.692 for cobalt. The smaller variances of the block averages show in the distribution functions, which are superimposed on the raw histograms in Fig. 2. They are more strongly peaked than the original distributions and are lighter in the tails.

The final preliminary to the disjunctive kriging is to compute and model the variograms of the Gaussian variable on the block support. The results of this stage are shown in Fig. 7 with the discrete estimates plotted as points and the fitted models as continuous lines. The models for both copper and cobalt are again double spherical, though without nugget components. The coefficients are listed in Table 2.

## RESULTS

### Disjunctive Kriging

Using the regularized variograms and the other relations for the discrete Gaussian model the concentrations of copper and cobalt were estimated for 1 km x 1 km blocks, using for each block the data in the block plus those in the eight neighbouring blocks. In addition the indicators $\mathbf{1}[\mathrm{Cu}<1.0]$ and $\mathbf{1}[\mathrm{Co}<0.25]$ were estimated for each block. Their values estimate the probabilities, given the data, that the true average values are less than the thresholds.

The principal results are presented as maps. Fig. 8 shows the estimated concentration of copper. For most of the region there is much more than the threshold, and only locally in a few fairly small patches does the soil appear to be deficient. The map of the indicator $\mathbf{1}[\mathrm{Cu}<1.0]$, Fig. 9, is complementary and confirms the picture.

The map of cobalt concentration, Fig. 10, shows deficiency to be widespread. Only in the central belt running through the region from south west to north east does there there appear to be sufficient. Even within that belt the probability of deficiency is not negligible, as Fig. 11 shows.

### Relations

The maps of estimated concentrations and probabilities present complementary views from the analysis. The relations between the estimates can be seen to advantage in scatter diagrams. That for cobalt is displayed in Fig. 12. The relation is close and effectively linear with a correlation coefficient of -0.965. We can see from the graph more clearly than from the maps that the probabilities of deficiency are substantial where the estimated concentrations are only a little more than the threshold, 0.25 mg/kg. We can also see at approximately what concentration the grazier might risk doing nothing. Intuitively it looks to be about 0.35 mg/kg.

To some extent the close relation in Fig. 12 is to be expected because the concentration and the indicator are estimated by the same procedure, and the cutting value is near the mean of the data.

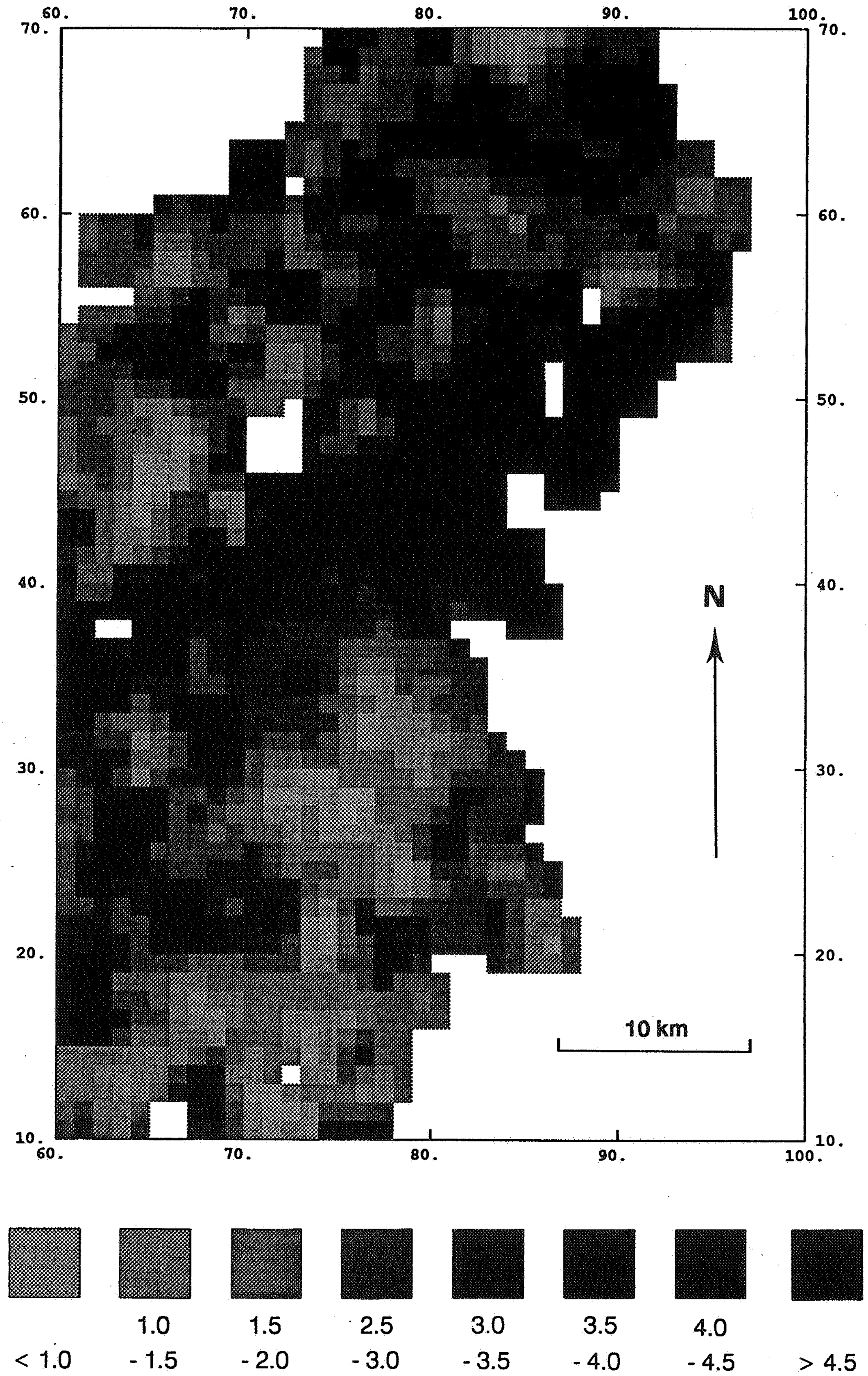


Fig. 8. Map of estimated concentration of copper in mg/kg.

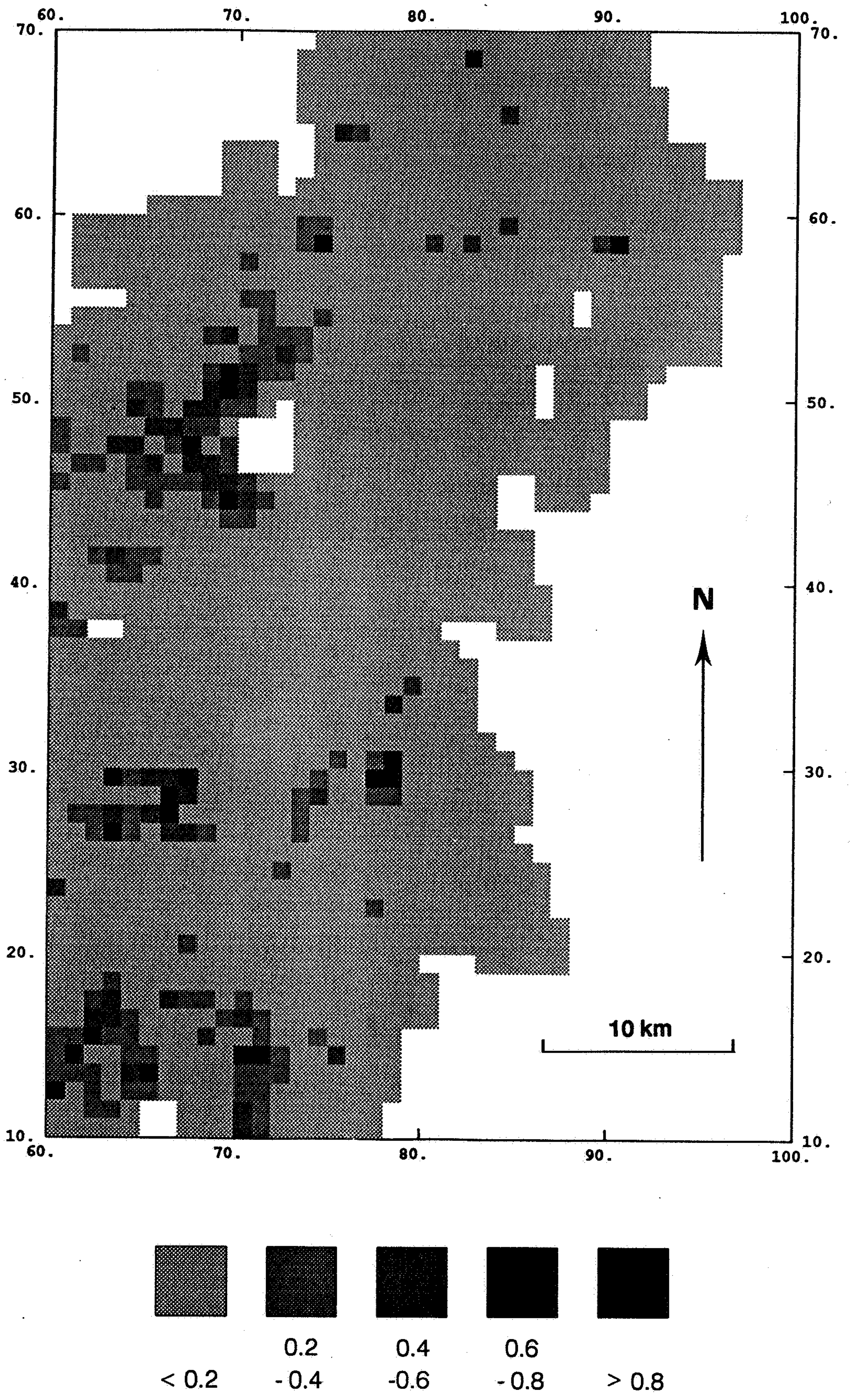


Fig. 9. Map of estimated probability of copper deficiency.

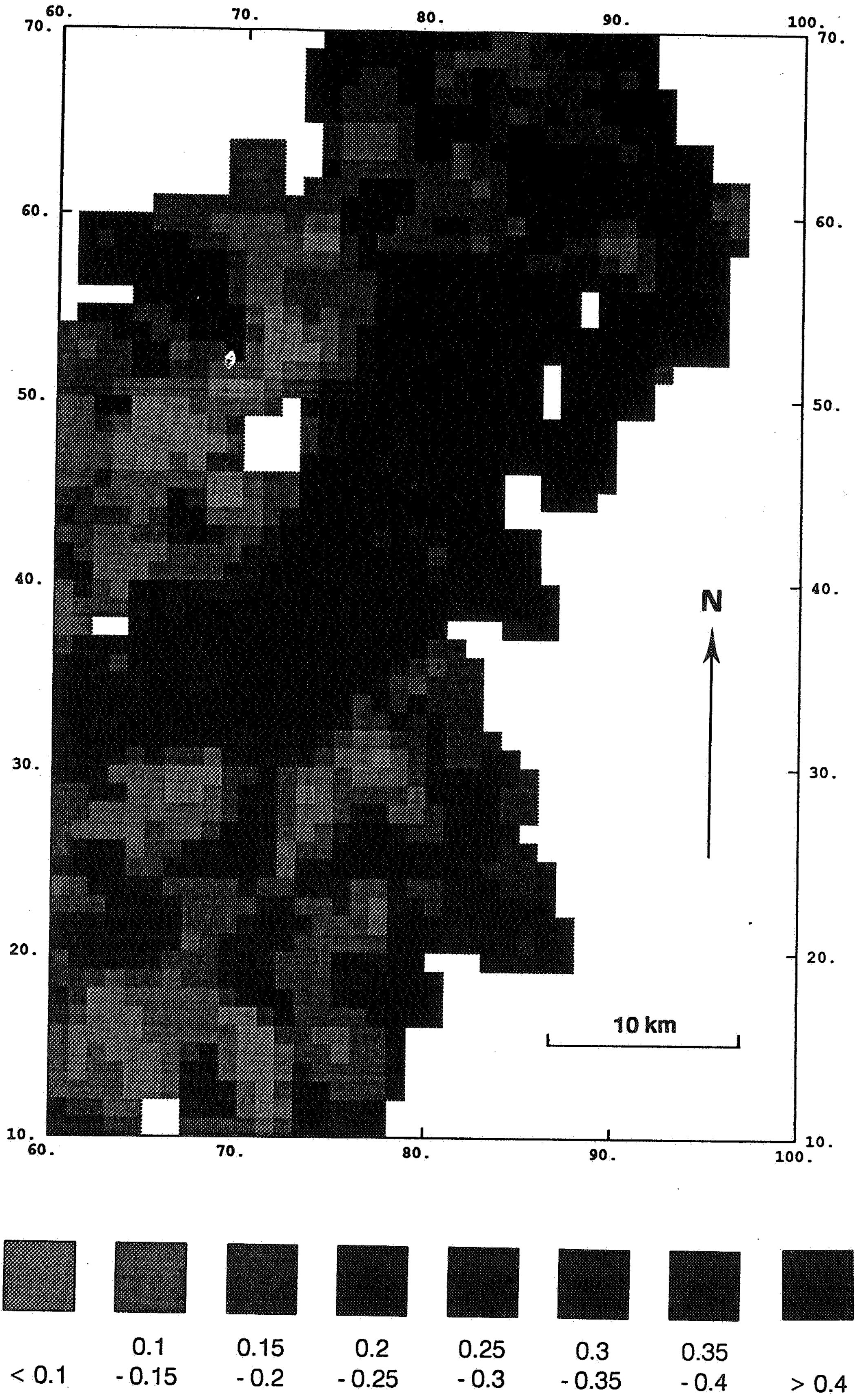


Fig. 10. Map of estimated concentration of cobalt in mg/kg.

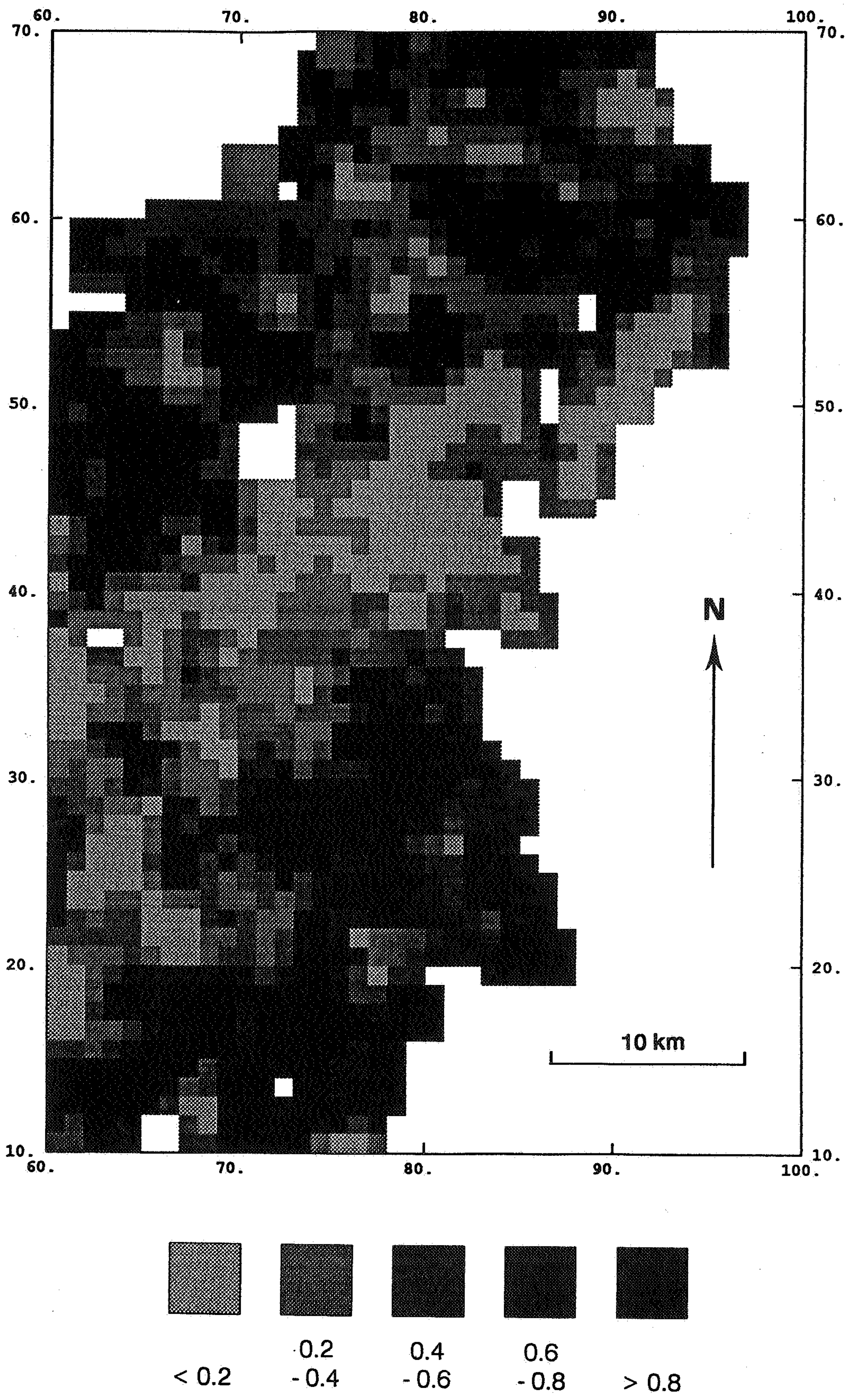


Fig. 11. Map of estimated probability of cobalt deficiency.

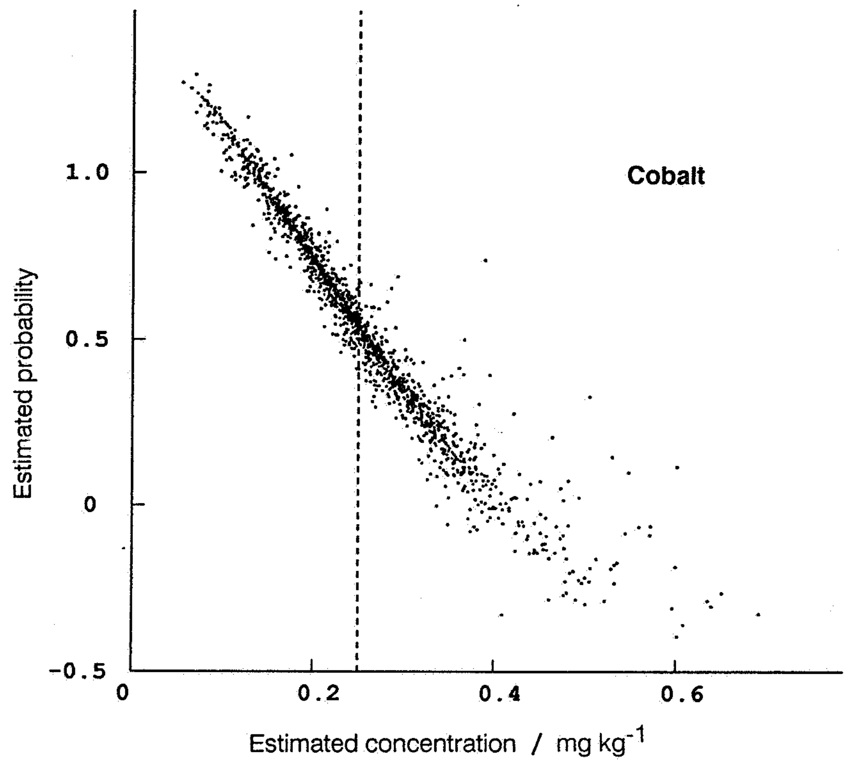


Fig. 12. Scatter diagram of estimated probability of cobalt deficiency against estimated concentration.

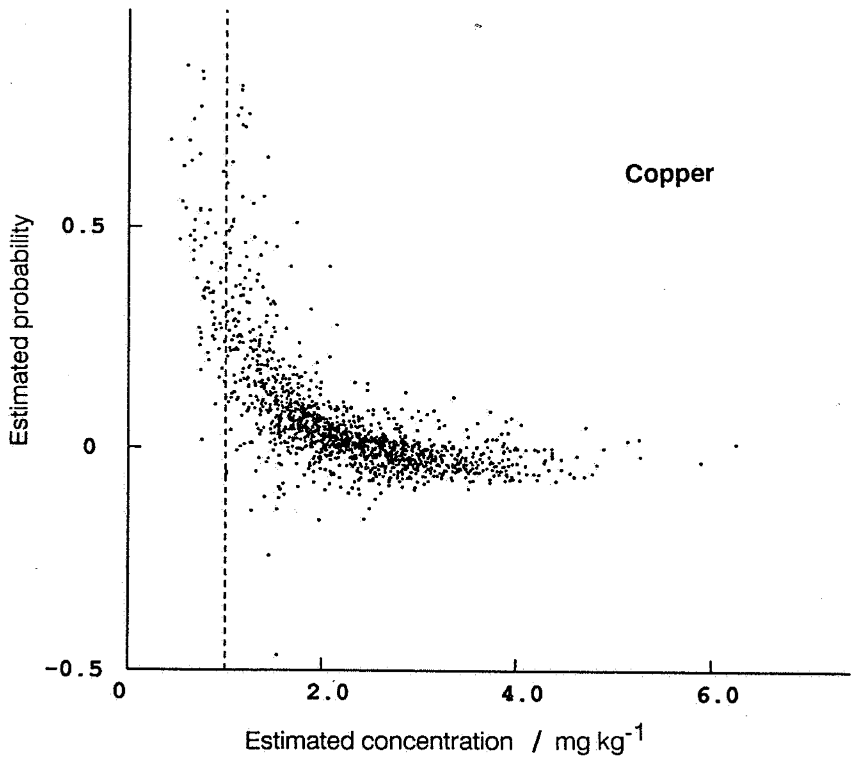


Fig. 13. Scatter diagram of estimated probability of copper deficiency against estimated concentration.

For copper, however, the relations are very different, Fig. 13. The deficiency threshold, 1.0 mg/kg, is near the minimum of the observed range and well away from the mean. Most estimates far exceed the threshold, and the estimates of $\mathbf{1}[\mathrm{Cu}<1.0]$ are near 0 for almost all estimated concentrations exceeding 2.0 mg/kg. Clearly, if the estimated concentration for a farm is less than 1.0 mg/kg then the grazier should do act, regardless of the estimated probability of deficiency. At concentrations between 1.0 and 2.0 mg/kg he cannot rely on any general relation between the two, and he should base his decisions on the computed probabilities. [1]

## CONCLUSIONS

Deficiencies of nutrients and excesses of toxic substances and pollutants are widespread in soil. Agricultural advisors have to decide whether to act to correct them from estimates that are more or less in error, and for this they should know the probabilities of deficiency or excess and the risks they incur if they do nothing. Given the nature of most soil data disjunctive kriging seems admirably suited for their purpose. This case study of copper and cobalt deficiency in south east Scotland illustrates the technique well, providing both estimates and the probabilities of deficiency on which a manager can make his decisions.

## ACKNOWLEDGEMENTS

This set of data from the East of Scotland College of Agriculture has once again proved very valuable for studying the application of geostatistics to agriculture, and we are grateful to the College and its staff, Mr H. M. Gray, Dr R. G. McLaren and Mr R. B. Spiers, for the data.

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[1] The disjunctive kriging estimates of an indicator are not probabilities in a strict mathematical sense, and so values outside the range [0,1] can be found.

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