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Alexander B. Mcbratney, Richard Webster, Ronald G. McLaren, Ronald B. Spiers. Regional variation of extractable copper and cobalt in the topsoil of south-east Scotland. *Agronomie*, 1982, 2 (10), pp.969-982. <hal-00884338>

HAL Id: hal-00884338

<https://hal.science/hal-00884338v1>

Submitted on 11 May 2020

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Regional variation of extractable copper and cobalt in the topsoil of south-east Scotland

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SUMMARY

*Copper,
Cobalt,
Topsoil,
Soil mapping,
Spatial analysis,
Kriging,
Scotland.*

The topsoil of more than 3 500 fields in the Border Region of Scotland had been sampled and copper and cobalt soluble in mild extractants measured to identify places where these metals are deficient for animals. The data have been analysed both by classical methods to assess the relationship between soil type as already mapped and metal concentration and by the newer geostatistical techniques of spatial analysis to provide local estimates and isarithmic ("contour") maps of the concentrations of the metals. Soil classification at association level accounts for 22 per cent of the variance in copper, representing the effect of parent material. Soil on the sedimentary rock of the Old Red Sandstone, especially that of the Mountboy and Hobkirk associations, contains less than 1.0 mg/kg of copper in many places and is regarded as deficient. Otherwise there is little relation between soil classes and metal concentration.

The sample semi-variograms for both copper and cobalt are isotropic and appear to combine three components of variation: a field-to-field or farm-to-farm component extending up to 3 km, a long range or geological component extending to 15 km and a non-spatial or "nugget" component, which accounted for 69 per cent of the variance in cobalt. Double spherical models were found to fit both semi-variograms better than any others, and these models were used to estimate the average metal concentrations of 1 km² square blocks optimally by kriging.

Isarithmic maps of the metal concentrations and their error variances were made by contouring a fine mesh of estimates. Several small areas of copper-deficient soil (containing less than 1 mg of soluble copper/kg) are shown, and are associated with the Old Red Sandstone sediments and Fluvio-Glacial sands. There are also small patches of land with large concentrations of copper, some near towns probably resulting from pollution, others associated with volcanic rocks. Much of the region has soluble cobalt concentrations less than 0.25 mg/kg, the deficiency threshold. The error maps show that precision is generally acceptable but identify a few parts of the region in which sampling is too sparse for confidence.

RÉSUMÉ

*Cuivre,
Cobalt,
Horizon supérieur,
Cartographie,
Analyse spatiale,
Krigage,
Ecosse.*

Variation régionale du cuivre et du cobalt de l'horizon supérieur du sol dans le sud-est de l'Ecosse

On a prélevé des échantillons de l'horizon supérieur de plus de 3 500 champs dans les régions frontalières de l'Ecosse et on a dosé leur teneur en cuivre et en cobalt solubles afin de repérer les lieux où ces métaux se trouvent en concentration insuffisante pour la nutrition des animaux. On a procédé à l'analyse des données par les méthodes classiques, afin d'établir les rapports entre les types de sol cartographiés et la concentration en métal, ainsi que par les plus récentes techniques géostatistiques de l'analyse spatiale pour fournir des estimations locales et des cartes des courbes de niveau (contour) de la concentration en métal. La classification des sols au niveau de l'association tient compte de 22 p. 100 des variations en cuivre, représentant l'influence de la roche mère. Les sols développés sur les roches sédimentaires du « Old Red Sandstone », surtout ceux des associations « Mountboy » et « Hobkirk », ont une teneur en cuivre de moins de 1,0 mg/kg dans plusieurs localités et sont considérés comme carencés. Autrement, il y a peu de rapports entre les classes de sol et la concentration en métal.

Les semi-variogrammes des échantillons sont isotropiques pour le cuivre et le cobalt et semblent réunir trois composantes de variance: une composante champ-à-champ ou exploitation-à-exploitation s'étendant jusqu'à 3 km, une composante « longue distance » ou géologique allant jusqu'à 15 km, et une composante non spatiale ou « nugget » qui tient compte de 69 pour 100 des variations en cobalt. Les modèles sphériques doubles s'ajustent le mieux aux deux variogrammes et on a utilisé ces modèles pour l'estimation optimale par le krigage de la moyenne des concentrations en métal dans des blocs de 1 km².

Des cartes des concentrations en métal et des écarts de variance ont été établies à partir d'un étroit réseau d'estimations. Elles démontrent que plusieurs régions de faible étendue présentent une carence en cuivre (avec une teneur soluble de moins de 1 mg/kg) et sont associées aux sédiments du vieux grès rouge et à des sables d'origine fluvio-glaciaire. On trouve aussi çà et là quelques terres riches en cuivre, certaines à proximité des villes à cause, sans doute, de la pollution urbaine et d'autres d'origine volcanique. Une grande partie de la région a une teneur en cobalt soluble de moins de 0,25 mg/kg, seuil critique de la carence. Les cartes des écarts montrent qu'en général la précision est acceptable, mais elles mettent en évidence certains endroits de la région où l'échantillonnage est trop faible pour que l'on puisse l'utiliser avec confiance.

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I. INTRODUCTION

Deficiencies of cobalt in sheep and of copper in both sheep and cattle are considerable problems in the Border counties of south-east Scotland. Severe cases of deficiency of these elements leading to the deaths of animals are uncommon nowadays, but sub-clinical deficiencies are thought to cause lack of thrift in live-stock. To what extent copper or cobalt deficiencies are the real causes of the latter is hard to say, however. Copper deficiency also occurs locally in cereals and PURVES & RAGG (1962) have studied its incidence in the region.

The East of Scotland College of Agriculture is responsible for advising farmers on animal health and on the nutrition of both animals and crops. It has analysed soil for many years to aid the diagnosis of trace element problems. In the course of advisory work, College staff have visited many farms and sampled soil, and sometimes herbage, to determine the concentrations of copper and cobalt. Staff have sampled the soil at many other sites also to give a reasonably even

coverage of the region so that places where there is deficiency, and also possibly toxicity, might be identified in addition to obtaining a general average. Since 1964, more than 3 500 fields have been sampled in this way and the soil analysed by the procedures described below. Figure 1 shows the extent of the region covered by the sampling and the soil associations recognized there, while figure 2 shows where the samples were taken.

In view of the coverage attained it seemed timely to produce maps of the region from the accumulated data delineating areas where the two metals were judged deficient or adequate. Such maps could be ideal for advisory purposes in helping to assess the likelihood of deficiency problems in particular cases. One possibility was to base the maps on existing soil survey maps and to show for each mapping unit the mean values for extractable copper and cobalt. PURVES & RAGG (1962) had shown that copper deficiency in cereals was related to a particular soil series in the area, while MACKENZIE (1974), in a preliminary analysis of data then available, found considerable differences

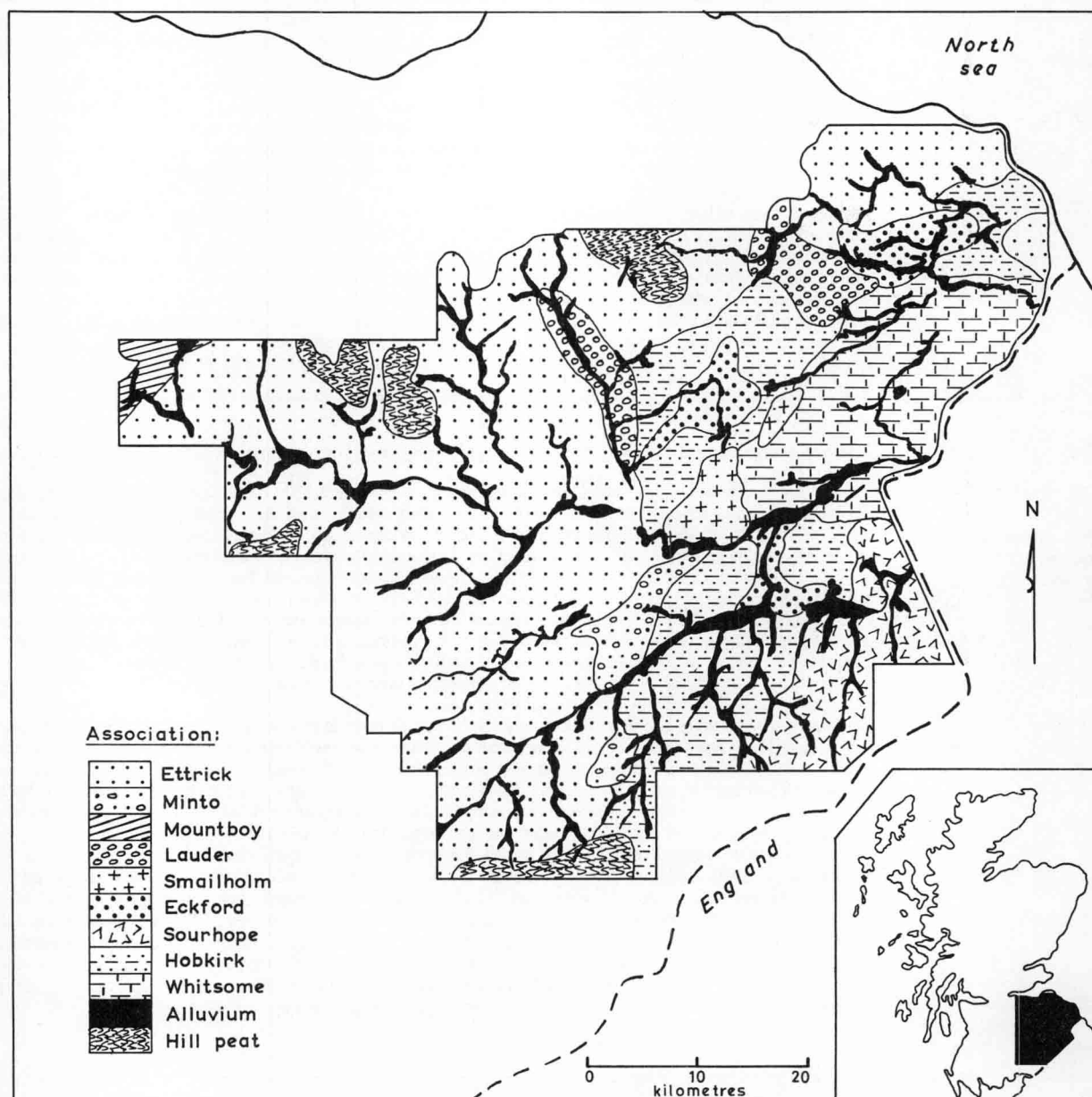


Figure 1

Map showing the extent of the region sampled and the more extensive soil associations recognized within it.

Carte de la région de prélèvement, indiquant les plus importantes associations de sol relevées.

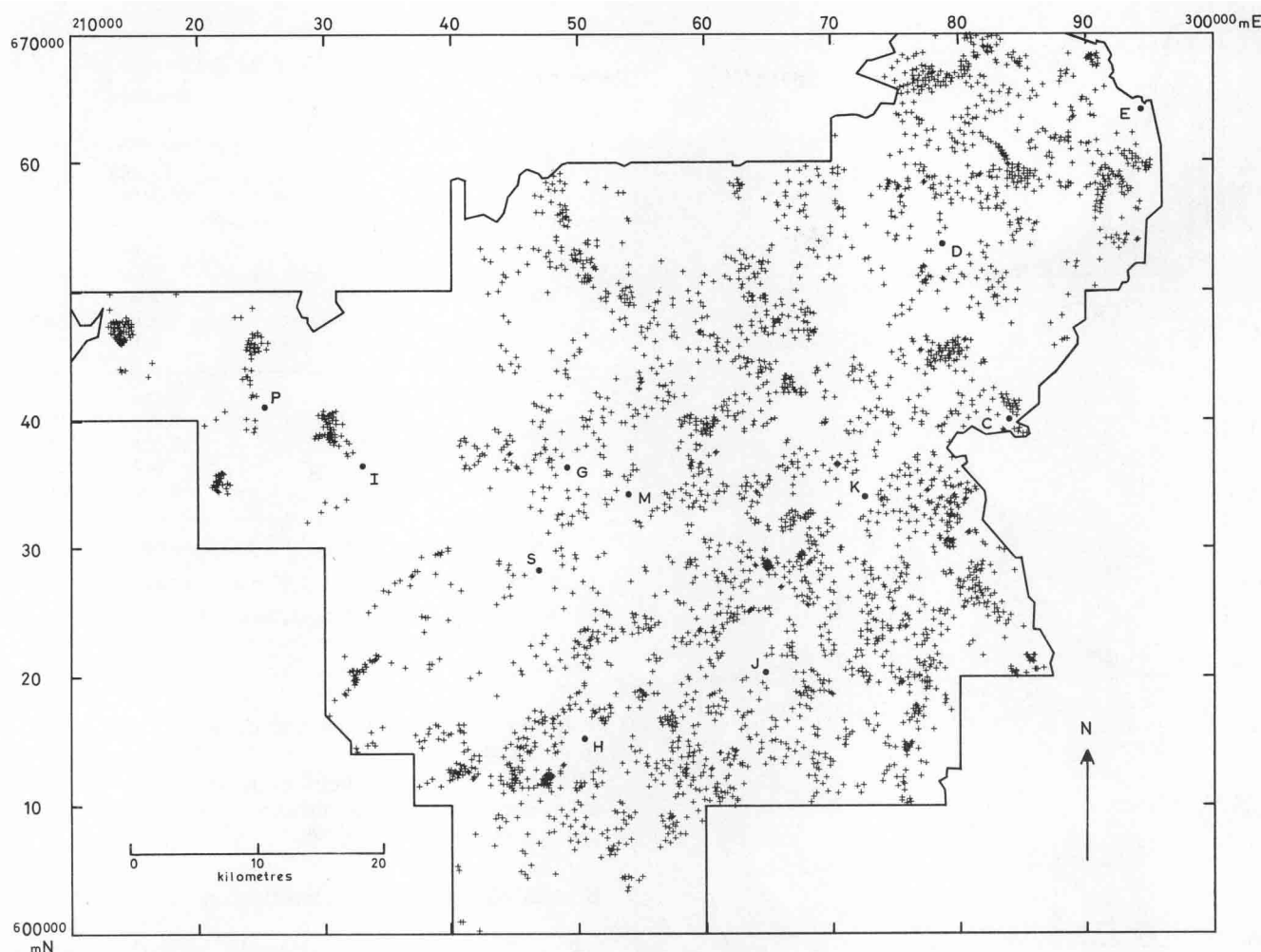


Figure 2

Map showing sites sampled for copper. Soil from almost all of these sites was analysed for cobalt and there were a few additional sites sampled for cobalt also. The principal towns are indicated on this map and in Figures 7, 8, 9 and 10 by their capital letters, below :

Carte indiquant les sites prélevés pour le cuivre. Les échantillons de presque tous ces sites ainsi que ceux de quelques sites supplémentaires, ont été analysés pour le cobalt. Les villes principales sont indiquées sur cette carte et dans les figures 7, 8, 9 et 10 par des lettres capitales :

C Coldstream	J Jedburgh
D Duns	K Kelso
E Eyemouth	M Melrose
G Galashiels	P Peebles
H Hawick	S Selkirk
I Innerleithen	

between soil series in the mean values for extractable copper and cobalt. The data have now been analysed both by classical statistical methods, in which quantities are related to particular classes of soil or rock, and by the newer methods of geostatistics that take account of spatial dependence. This paper presents the results.

II. SAMPLING AND CHEMICAL ANALYSIS

At each site the soil was sampled by screw auger to a depth of 20 cm. Some twenty cores were taken at random over an area of between 5 ha and 10 ha and bulked. The bulked samples, each weighing about 1 kg were air dried and ground to pass a 2 mm sieve.

Copper was extracted with 0.04 M ethylene diamine tetra acetic acid disodium salt at pH 4.5 (EDTA). 10 g of soil were shaken with 50 ml of EDTA reagent for one hour and then allowed to stand for a further hour. After filtering the copper was determined by atomic absorption spectrophotometry.

Cobalt was determined by extracting with 0.5 M acetic acid 20 g of soil were shaken overnight with 400 ml acetic acid solution and then filtered. The filtrate was evaporated to a small volume and the cobalt separated from interfering ions using 2-nitroso-1-naphtol before analysis by atomic absorption spectrophotometry.

III. RESULTS

A. Preliminary analysis and transformation

The data were first examined by computing the moments of the sample distributions. The results are summarized in table 1 and by histograms in figure 3. The most striking feature of the original data is their strongly skewed distributions. The smooth curves drawn on the a and c histograms are those of the lognormal distributions ; in each case the fit is good. The lower part of table 1 gives the moments of the data when transformed to their common logarithms. Both

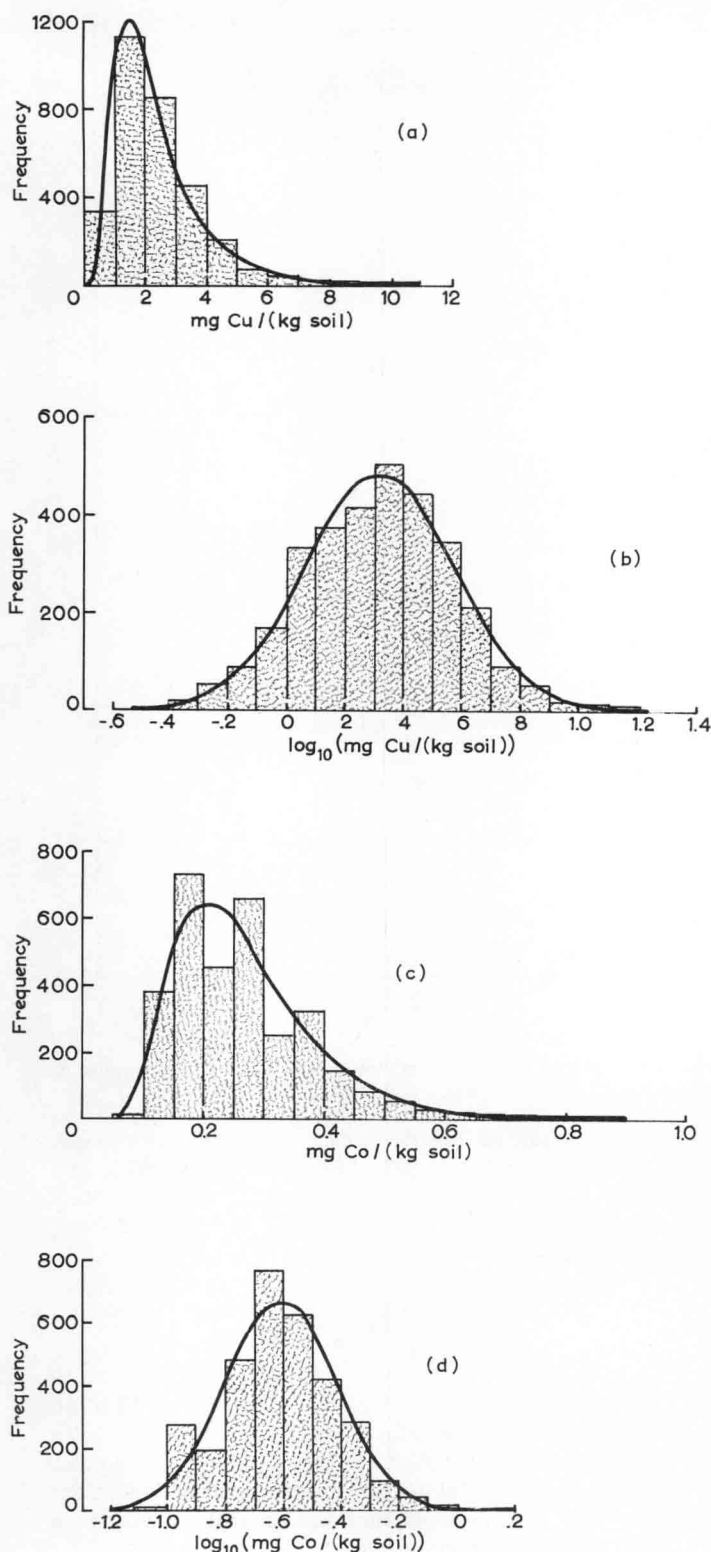


Figure 3

Histograms of copper (a) and cobalt (c) on the original measurement scale with lognormal curves fitted, and (b) and (d) on the scale transformed to common logarithms with the curves of the normal distribution fitted.

Histogrammes du cuivre (a) et du cobalt (c) à l'échelle originale avec courbes logarithmiques normales ajustées, et (b) et (d) à l'échelle transformée en logarithmes décimaux avec courbes de la distribution normale ajustées.

skewness and kurtosis are negligible. It seems that both the extractable copper and cobalt in the soil of this region are distributed lognormally. They are examples of the type of distribution commonly observed in geochemistry but for

TABLE 1
Basic statistics of the sample.
Statistiques élémentaires de l'échantillon.

Sample size		Copper 3156	Cobalt 3220
Untransformed	Mean	2.467	0.271
	Standard deviation	1.663	0.134
	Skewness ⁽¹⁾	2.604	1.997
	Kurtosis ⁽¹⁾	12.148	7.840
	Geometric mean	2.061	0.244
Transformed to log ₁₀	Mean	0.314	-0.613
	Standard deviation	0.258	0.196
	Skewness ⁽¹⁾	0.051	0.126
	Kurtosis ⁽¹⁾	0.049	0.090
	Variance	0.066 56	0.038 42

⁽¹⁾ The coefficients of skew and kurtosis have been calculated as $\frac{1}{n} \sum (x - \hat{\mu})^3 / \hat{\sigma}^3$ and $\frac{1}{n} \sum (x - \hat{\mu})^4 / \hat{\sigma}^4 - 3$ respectively, where $\hat{\mu}$ and $\hat{\sigma}$ are the estimated mean and standard deviation respectively of n observations.

which no convincing explanation has so far been presented (see AHRENS, 1965, and SHAW, 1961, for discussion).

Because of their distributions the data were transformed to common logarithms to stabilize their variances for later analysis and interpolation.

B. Analysis by soil map classification

Soil classification has traditionally been the means by which observations of soil properties made at particular sites are used to infer values elsewhere. The underlying idea is that each class of soil is reasonably homogeneous with respect to the property of interest, and differs from at least some other classes. For a measured property the class mean becomes the expected value everywhere in that class. Soil is not usually classified and mapped to predict trace element concentration, but there have been local successes, notably in Somerset where teart (molybdenum-induced deficiency of copper in sheep) was associated with certain types of soil on the Lower Lias (AVERY, 1955; LE RICHE, 1959). Elsewhere in Britain trace element concentration has been linked to soil types already mapped for more general purposes (MINISTRY OF AGRICULTURE, 1976; THORNTON & WEBB, 1980). Of particular interest is the paper by PURVES & RAGG (1962), in which they record copper deficiency specifically in the Eckford series within the Border Region. In France, COPPENET & CALVEZ (1956, 1967) and COPPENET (1970) found that copper and cobalt deficiencies in a number of crops were associated with granite and certain quartz-rich sandstones in Brittany. The soil on these rocks contained substantially less of these two elements than that on other rocks of the region. With this background we sought to assess the value of soil classification as a means of predicting deficiencies.

The Soil Survey of Scotland had classified the soil and mapped most of the region at the 1:63 360 scale (MUIR, 1956; RAGG, 1960; RAGG & FUTTY, 1967; RAGG *et al.*, 1971). The principal mapping units are soil series. These, however, are essentially the intersection of two coarser subdivisions of the soil by parent material and by drainage status. The soil is divided first into 21 associations, distinguished mainly on parent material, but with four, alluvium,

basin peat, hill peat and a peat-alluvium complex, distinguished on other criteria. Each covers one or more substantial tracts of country (fig. 1). They are listed in table 3 (p. 974). The soils in the 17 associations on particular parent materials are further subdivided into series according to drainage, of which there are six groups. The structure of the classification is therefore as follows:

Alluvium and peat	4 classes
Parent material	17 classes
Drainage status	6 classes
Parent material \times drainage status	102 classes

This structure suggests an analysis of variance to determine the main effects of alluvium and peat, parent material and drainage status, and the interaction of parent material and drainage status. However, not all the combinations of parent material and drainage status exist, and not all of those that do occur were sampled. There is a serious lack of balance in the sample, and it is not possible therefore to perform such a neat analysis. So instead we analysed the data by regression techniques to estimate the within-groups variance for several combinations of classifying attributes (table 2).

The association and drainage class at each sampling site

TABLE 2

Summary of the analysis of variance for the Scottish soil classification. All values are for common logarithms.

Résumé de l'analyse de variance pour la classification écossaise du sol. Toutes les valeurs sont calculées pour des logarithmes décimaux.

	Degrees of freedom	Sum of squares	Mean square	Variance accounted for	Percentage accounted for
<i>Copper</i>					
Total	2 842	189.6	0.066 71		
Alluvium and Peat (AP)	2 838	180.9	0.063 74	0.002 97	4.4
AP + parent material	2 823	146.5	0.051 90	0.014 81	22.2
AP + drainage	2 833	172.8	0.061 00	0.005 71	8.5
AP + parent material + drainage	2 818	145.3	0.051 56	0.015 15	22.7
AP + parent material + drainage + interaction (soil series)	2 805	143.0	0.050 98	0.015 73	23.6
<i>Cobalt</i>					
Total	2 888	113.0	0.039 12		
Alluvium and Peat (AP)	2 884	112.4	0.038 97	0.000 15	0.4
AP + parent material	2 870	102.6	0.035 75	0.003 37	8.6
AP + drainage	2 879	107.6	0.037 37	0.001 75	4.5
AP + parent material + drainage	2 865	100.5	0.035 08	0.004 04	10.3
AP + parent material + drainage + interaction (soil series)	2 852	99.2	0.034 79	0.004 34	11.1

was determined as far as possible from the soil map. Sites in unmapped parts of the region and those where the identification in either grouping was uncertain were omitted. The analysis was then performed for copper and cobalt separately. Table 2 summarizes the results.

In table 2 the mean square is effectively the within-group variance, and the quantity headed « variance accounted for » is the difference between the within-groups variance and the total. The right hand column is simply this quantity expressed as a percentage of the total. The table shows that classification at the finest level using all the information (Alluvium and peat + parent material + drainage + interaction of parent material \times drainage) accounts for 23.6 p. cent of the variance of copper and 11.1 p. cent of that of cobalt. For both metals, however, it is little better than classification at association level (Alluvium and peat + parent material), which accounted for 22.2 and 8.6 p. cent respectively. Distinguishing the alluvium and peat classes only has little effect, as does distinguishing on drainage status only. The interaction is negligible.

Of the effects examined clearly only the soil associations are of any importance for copper and cobalt. The moderate success of classification by association represents the effect of the types of rock within the parent material of the soil. Table 3 lists the parent materials and gives the mean values for the soil on each. Note that the values given are the geometric means; i.e. the means of the logarithms transfor-

med back to the original scales of mg/kg. These effects might have been more marked had the subsoil been analysed. The properties of topsoil are more influenced by the addition of material such as loess and by farming activities — manuring and crop spraying. As a result the specific effects of identifiable rock types can be masked.

In general copper is least concentrated in soil formed in the Old Red Sandstone sediments and their derived drifts (Hobkirk, Lauder and Mountboy associations), and in soil developed in sandy fluvio-glacial drifts derived from them (Eckford association). Given the form of the distribution and taking 1 mg/kg of copper as an approximate minimum acceptable value (MACKENZIE, 1974) some 40 p. cent of the soil in the Mountboy association (mean 1.16 mg/kg) and about 30 p. cent in the Hobkirk association (mean 1.36 mg/kg) are likely to be deficient. The soil of most of the other associations has copper concentrations well above the 1 mg/kg threshold, and any deficiency is likely to be local only.

For cobalt the critical value for deficiency is taken to be 0.25 mg/kg (MACKENZIE, 1974). This is more than the mean of the sample as a whole, so that judged on this basis cobalt deficiency is widespread in this region. Only the soil of the Darleith Association and that of the Peat-Alluvium Complex contain substantially more on average than the critical amount. All others have concentrations near or much less than the critical value.

TABLE 3

*Extractable copper and cobalt contents of 21 soil associations.
Teneurs en cuivre et cobalt extractibles des 21 associations du sol.*

Association	Parent material	Copper		Cobalt	
		Sample size	Geometric Mean (mg/kg)	Sample size	Geometric Mean (mg/kg)
Alluvium		160	3.23	159	0.27
Basin peat		8	3.47	7	0.28
Bemersyde	Intrusive rhyolites and trachytes	9	2.19	9	0.14
Biel	Drifts from, Lower Carboniferous sediments and Upper Old Red Sandstone (O.R.S.) conglomerates and sandstones	3	3.77	3	0.20
Cairncross	Lower O.R.S. grits, ash beds and sandstones	35	3.08	37	0.22
Carter	Drifts from Lower Carboniferous sediments of the Calciferous Sandstone Series	1	3.45	1	0.26
Darleith	Lower Carboniferous basaltic intrusions and extrusions	16	1.89	16	0.33
Eckford	Fluvio-glacial sands	149	1.74	151	0.19
Ettrick	Drifts from Silurian greywackes and shales	1 030	2.35	1 115	0.26
Hill peat		4	1.36	4	0.21
Hobkirk	Drifts from sandstones and marls of Upper O.R.S. age	656	1.36	655	0.22
Innerwick	Fluvio-glacial sands derived mainly from Upper O.R.S. conglomerates	1	2.39	0	—
Lauder	Drifts from Upper O.R.S. conglomerates	119	1.74	129	0.23
Minto	Mixed till derived from Upper O.R.S., Silurian and Ordovician sediments	112	2.53	115	0.24
Mountboy	Drifts from Lower O.R.S. grits, sandstones and conglomerates with some basic and intermedite lavas	53	1.16	13	0.21
Peat-Alluvium complex		10	3.22	10	0.33
Priestlaw	Granodiorite and allied rocks	7	1.56	7	0.27
Smailholm	Upper O.R.S. sediments and Lower Carboniferous igneous rocks	58	2.40	56	0.29
Sourhope	Drifts from intermediate lavas of Lower O.R.S. age	281	1.73	284	0.18
Whitsome	Till derived from Lower Carboniferous sediments and basic lavas, Upper O.R.S. Silurian and Ordovician sediments	326	2.77	326	0.29
Yarrow	Fluvio-glacial gravels derived mainly from Ordovician and Silurian greywackes	71	3.57	71	0.29
General mean			2.061		0.244

Nevertheless, because classification by association accounts for only 8.8 p. cent of the variance in cobalt concentration, a better means of identifying regions of deficiency is desirable. In addition the error associated with prediction remains large, and it would be desirable to diminish this. A better means of representing regional variation in copper and for predicting local concentrations would also be valuable. In the next section we describe the alternative means provided by regionalized variable theory and present results.

C. Regionalized variable theory

In the previous section we assumed that the classical analysis of variance was familiar enough and needed no explanation. The theory of regionalized variables is newer. It was developed to meet the needs of mining and mineral exploration largely by MATHERON (1965, 1971), and it has been applied mainly for ore reserve estimation (JOURNAL & HUIJBREGTS, 1978). Although there have been applications in other fields, for example, by MILLIER *et al.* (1972) to estimate forest resources, by DELHOMME (1976) in hydrogeology, and by CHILES (1976) in hydrology, bathymetry and meteorology, the theory and its practice are still largely unfamiliar to agricultural scientists. A brief account is therefore included.

In the classical model of variation the value of a soil property Z at any place i is given by

$$z_i = \mu + \epsilon_i, \quad (1)$$

where μ is the mean or expected value of Z and ϵ_i is a purely random term drawn from a population with a mean of zero and variance, σ^2 , and whose distribution is ideally normal. If regional variation is recognized then it is accommodated by creating a classification. In the simplest cases the classification can be represented in the model by an additional term, the deviation of the mean of the j th class from the general mean, α_j . In the example of the Scottish classification there are terms for the main effects and interactions. The classical analysis of variance, as performed above, estimates the effects of the class deviations and of the random component within classes.

In regionalized variable theory the random component at least is spatially dependent within some neighbourhood. The model becomes for the two dimensions of soil survey

$$z(\mathbf{x}) = \mu_V + \epsilon(\mathbf{x}) \quad (2)$$

where $\mathbf{x} = [x_1, x_2]$ is a place in the two dimensions, and μ_V is the mean within the neighbourhood V . The random spa-

tially dependent component, $\varepsilon(\mathbf{x})$ has a mean of zero and variance defined by

$$\text{var}[\varepsilon(\mathbf{x}) - \varepsilon(\mathbf{x} + \mathbf{h})] = E\{[\varepsilon(\mathbf{x}) - \varepsilon(\mathbf{x} + \mathbf{h})]^2\} = 2 \gamma(\mathbf{h}). \quad (3)$$

The vector \mathbf{h} , or *lag*, is the distance and direction separating two places. The function $\gamma(\mathbf{h})$ is the *semi-variogram*, and its particular form characterizes the spatial variation of a property that varies across the land surface. The value of the function at a particular lag is a semi-variance, and in the simplest cases it is equal to half the expected squared difference between values, thus

$$\gamma(\mathbf{h}) = 1/2 E\{[z(\mathbf{x}) - z(\mathbf{x} + \mathbf{h})]^2\}. \quad (4)$$

The expectation of the difference itself is zero :

$$E[z(\mathbf{x}) - z(\mathbf{x} + \mathbf{h})] = 0. \quad (5)$$

The semi-variogram of a soil property not only describes quantitatively the way in which the property varies but also contains essential information for interpolation and hence for mapping the regional distribution of the property.

1) Estimating the semi-variogram

In applying regionalized variable theory it is assumed that equation (4) applies everywhere ; i.e. that the value of γ depends only on \mathbf{h} , the separation between sites, and not on the actual positions of the sites. If the assumption holds then the semi-variogram for a region can be estimated readily from a single set of data. The semi-variance at a given lag, \mathbf{h} , is estimated simply as the average of the squared differences between all observations separated by that lag, thus

$$\hat{\gamma}(\mathbf{h}) = \frac{1}{2 n(\mathbf{h})} \sum_{i=1}^{n(\mathbf{h})} \{ z(\mathbf{x}_i) - z(\mathbf{x}_i + \mathbf{h}) \}^2, \quad (6)$$

where there are $n(\mathbf{h})$ pairs of observations.

In a survey such as this one where the sampling sites are irregularly scattered the actual lags are grouped by both distance and direction. The average semi-variance is then computed for each group for distances up to some desired maximum and for directions from 0 to 180°. A suitable mathematical model for the semi-variogram is then fitted to the estimated semi-variances by least squares approximation.

The spatial variation of copper and cobalt was analysed for eight directions from north-south in increments of 22.5° to north north-west to south south-east and each subtending an arc of 22.5°. We had little idea initially over what distances spatial dependence would extend and we therefore examined the dependence at two scales. For each direction we computed average semi-variances at 0.2 km intervals up to 8 km, and at 1 km intervals to 40 km, with data grouped into 0.2 km and 1 km segments respectively. The results for copper and cobalt were similar. First, there are no appreciable differences among the different directions : variation in both metals appears to be isotropic. We could therefore disregard the effects of direction, and so treat the lag, \mathbf{h} , as a scalar quantity, $h = |\mathbf{h}|$. Second, the semi-variograms computed to 8 km appeared to flatten at lags of 2 km (for copper) and 3 km (for cobalt), whereas those computed to 40 km flattened at around 15 km. This suggested that there is variation at two scales, and that the true semi-variograms are compound functions. We tried fitting several types of semi-variogram model to the sample

semi-variances by least squares approximation using Ross's maximum likelihood program, MLP (VILA, 1976 ; ROSS, 1980). In all instances each sample estimate was weighted by the number of pairs of comparisons that it comprised. For both copper and cobalt the model that was found to fit best, i.e. minimized the sum of squares of the residuals, was a double spherical model of the form :

$$\begin{aligned} \gamma(h) &= c_0 + c_1 \left\{ \frac{3h}{2a_1} - \frac{1}{2} \left(\frac{h}{a_1} \right)^3 \right\} + \\ &\quad + c_2 \left\{ \frac{3h}{2a_2} - \frac{1}{2} \left(\frac{h}{a_2} \right)^3 \right\} \quad \text{for } 0 < h < a_1 \\ \gamma(h) &= c_0 + c_1 + c_2 \left\{ \frac{3h}{2a_2} - \frac{1}{2} \left(\frac{h}{a_2} \right)^3 \right\} \\ &\quad \text{for } a_1 \leq h < a_2 \\ \gamma(h) &= c_0 + c_1 + c_2 \quad \text{for } h \geq a_2. \end{aligned} \quad (7)$$

In these equations c_1 and a_1 are the amplitude and range respectively of the local or short-range component, and c_2 and a_2 the amplitude and range of the longer-range component. The semi-variance at $h = 0$ is by definition zero, but c_0 , the nugget variance, is the value to which $\gamma(h)$ approaches as h approaches 0. Figure 4 shows the sampling semi-variances computed for all eight directions at 0.2 km intervals to 8 km and at 1 km intervals thereafter for copper. It also shows the fitted model (solid line) and, by dashed lines below, the nugget variance and the two spatial components. Figure 5 is a similar diagram for cobalt. Table 4 lists the parameter estimates for the two semi-variograms.

As above, the fitted models represent variation at two main scales one with a range of about 3 km ($a_1 = 2.26$ km for copper, 3.44 km for cobalt), and the other with a range of about 16 km ($a_2 = 15.46$ km and 16.26 km respectively for copper and cobalt). The smaller range may be an agricultural effect ; that is, it may arise from field-to-field and farm-to-farm differences. The longer-range variation is probably geological. The nugget variance, c_0 , accounting for 32 p. cent of the variance in copper and 63 p. cent of that for cobalt, is mainly due to variation within the shortest sampling interval, i.e. within 200 m. These percentages include any measurement or procedural error. Experience in the Edinburgh laboratory has shown that determinations of cobalt in soil from the same sampling are somewhat variable. They depend on the length of time and the way the soil is stored and on the analytical procedure itself. On the logarithmic scale used in this paper (see next section) variance among duplicates has been on average about 0.004, or some 10 to 15 p. cent of the total variance recorded over the region. This error will, of course, also be present in the estimated within-class variances of table 2, and will diminish the apparent usefulness of the classifications. For copper such error is less than 5 p. cent. For copper the short-range component, c_1 , makes the largest individual contribution, 39 p. cent, to the total variance, while for cobalt it is only 19 p. cent, approximately the same as for the long-range component. Thus, copper shows a greater degree of spatial dependence than cobalt in this region.

2) Interpolation and mapping

The semi-variograms found above were then used for interpolation and mapping by kriging. MATHERON (1965,

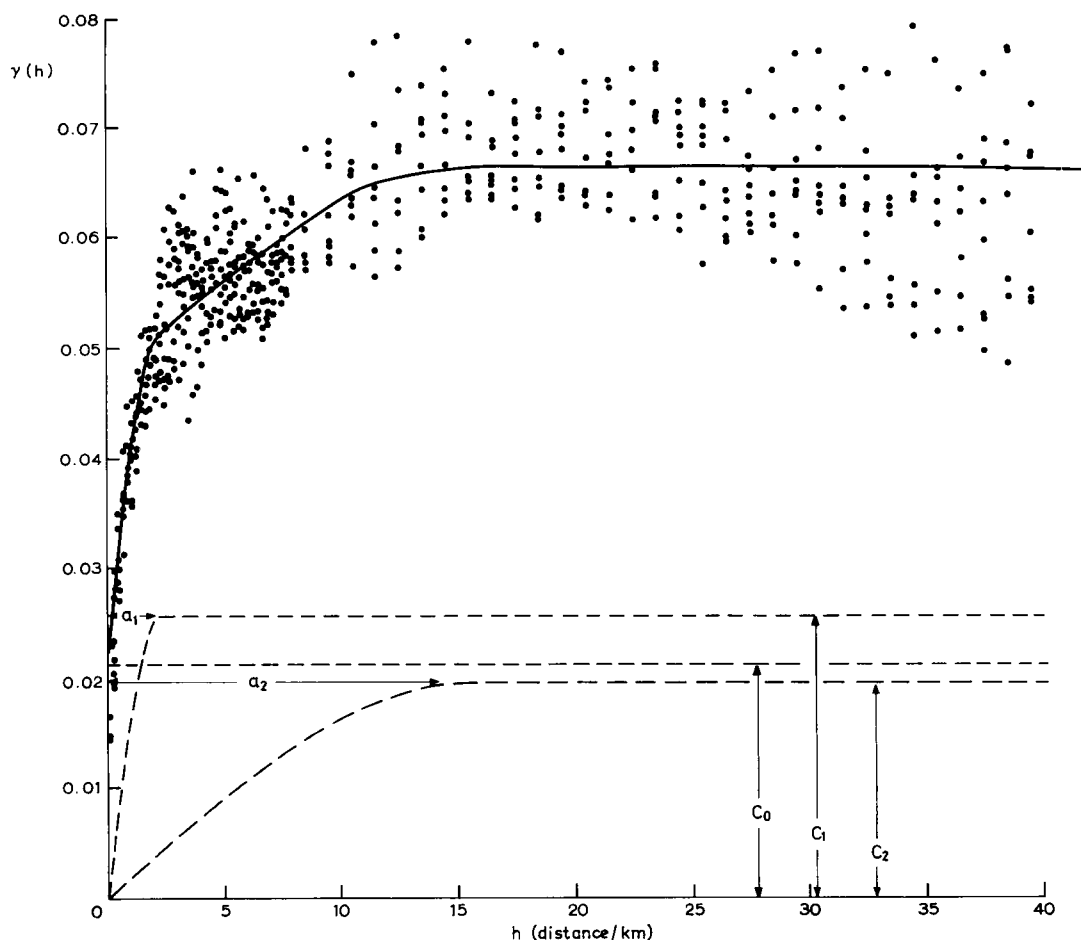


Figure 4

Semi-variogram for copper. Symbols show the estimated semi-variances and the solid line is the graph of the fitted model. The dashed lines show the three components of the model.

Semi-variogramme pour le cuivre. Les symboles montrent les semi-variances estimées et la ligne continue est la courbe du modèle ajusté. Les lignes discontinues indiquent les trois composantes du modèle.

TABLE 4

*Parameter estimates for the double spherical semi-variogram model.
Estimations des paramètres pour le semi-variogramme sphérique double.*

	log ₁₀ copper	log ₁₀ cobalt
Parameter	Parameter estimate	Parameter estimates
c ₀ (variance)	0.021 3	0.024 1
c ₁ (variance)	0.025 7	0.007 3
c ₂ (variance)	0.019 6	0.006 8
a ₁ (km)	2.261	3.441
a ₂ (km)	15.46	16.26

1971) provides a full account of the method and its underlying theory, while those details necessary for its application to soil survey are given by BURGESS & WEBSTER (1980a, b). Here we indicate the essential features of the procedure.

Kriging is a means of local estimation in which each estimate is a weighted average of the observed values in its neighbourhood. Thus, the interpolated value of Z at a place \mathbf{x}_0 is

$$\hat{z}(\mathbf{x}_0) = \sum_{i=1}^k \lambda_i z(\mathbf{x}_i). \quad (8)$$

The weights, λ_i , are chosen so that $\hat{z}(\mathbf{x}_0)$ is an unbiased

estimate of $z(\mathbf{x}_0)$, the true value, and that the estimation variance is a minimum. The weights therefore sum to 1, and with this constraint the minimum variance is obtained when

$$\sum_{j=1}^k \lambda_j \gamma(\mathbf{x}_i, \mathbf{x}_j) + \psi = \gamma(\mathbf{x}_i, \mathbf{x}_0) \quad \text{for all } i. \quad (9)$$

The quantities $\gamma(\mathbf{x}_i, \mathbf{x}_j)$ and $\gamma(\mathbf{x}_i, \mathbf{x}_0)$ are the semi-variances of Z between the observed places \mathbf{x}_i and \mathbf{x}_j and between the observed \mathbf{x}_i and the interpolated place \mathbf{x}_0 respectively, and are obtained from the semi-variogram. The quantity ψ is the Lagrange multiplier associated with the minimization. Solution of the kriging equation (9) gives the weights and, as a by-product, provides an estimate of the estimation variance. The interpolated value is thus the best, in the sense of most precise, possible from the data and one that can be used with known confidence. For mapping interpolation is carried out at many sites. This is usually done on a fine grid to produce a regular figure field, and the results displayed by drawing isarithms ("contours") through the grid of values.

Apart from its optimality, kriging has a further advantage over other means of interpolation in that the area over which the estimate is made can be varied. Equation (9) refers to estimates for volumes of soil the same size and shape as those on which the original measurements were made (punctual kriging). In the present case this means the topsoil of fields some 5-10 ha in extent. Optimal estimates can be obtained, however, for larger areas (block kriging). This involves replacing the right hand sides of the kriging equations by the average semi-variances between the obser-

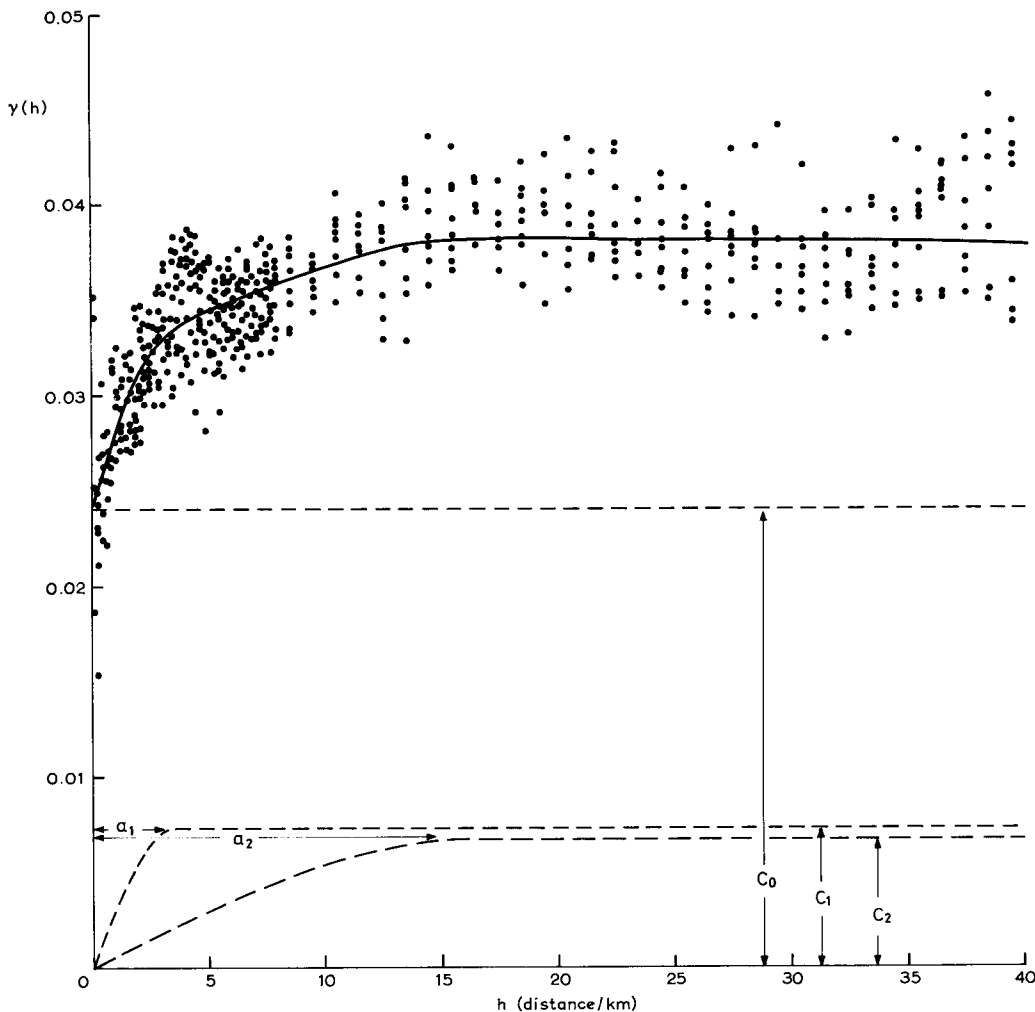


Figure 5

Semi-variogram for cobalt. Symbols show the estimated semi-variances and the solid line is the graph of the fitted model. The dashed lines show the three components of the model.

Semi-variogramme pour le cobalt. Les symboles montrent les semi-variances estimées et la ligne continue est la courbe du modèle ajusté. Les lignes discontinues indiquent les trois composantes du modèle.

vation points and the block whose average value is to be estimated. For this the semi-variogram must be integrated for the area concerned.

Using the double spherical semi-variograms with coefficients given in table 4 we carried out trials by interpolating a number of fine grids of values from the data of both copper and cobalt in a 100 km² square for different block sizes and grid values. We then drew contour maps from them.

The maps made with block size equal to zero, i.e. by punctual kriging, were very intricate where grid nodes coincided with sampling points. This arose because punctual kriging is an exact interpolator, and the large nugget variances in this study caused discontinuities at the sampling points. As discussed elsewhere (BURGESS & WEBSTER, 1980b) such maps undoubtedly represented the data as faithfully as is possible. They are not entirely desirable for soil mapping, however. The local detail can obscure broader regional differences in the soil, and the position of the detail is itself a sampling effect since it depends on the particular places at which sampling was carried out. Further, in regional mapping, estimates are likely to be needed for areas larger than fields. We therefore preferred block kriging. There is no intricate detail: the kriged surfaces are smoothly varying, as are those of the estimation variances. The latter are also much smaller for the larger areas.

As a result of these trials we mapped the copper and cobalt in the whole region by kriging values for 1 km square

blocks at intervals of 400 m to produce figure fields of both estimated values and associated estimation variances. These were then contoured using the program Surface II (SAMPSON, 1978). The results are shown in figures 7, 8, 9 and 10.

3) Discussion of the maps

First an explanation of two of the features of figures 7 and 8 is required. The variance of 1 km square blocks sampled over the area will of course be smaller than the variance of point samples. Krige's relation (JOURNEL & HUIJBREGTS, 1978),

$$\sigma^2(a/A) = \sigma^2(0/A) - \sigma^2(0/a) \quad \text{if } 0 < a < A, \quad (10)$$

describes this. The symbol 0 represents points, i.e. zero area, a represents 1 km square blocks, and A the whole area studied. The variance of 1 km square blocks in the whole area is denoted by $\sigma^2(a/A)$, and can be estimated for copper and cobalt as follows. The variance of the point samples within the area, $\sigma^2(0/A)$, is estimated by the variance of the data. The variance of point samples within 1 km square blocks, $\sigma^2(0/a)$, can be estimated from the point semi-variogram as:

$$\sigma^2(0/a) = \gamma(a, a) = \frac{1}{a^2} \int a \int a \gamma(\mathbf{x} - \mathbf{x}') d\mathbf{x} d\mathbf{x}', \quad (11)$$

and denotes the mean value of the function $\gamma(\mathbf{h})$ when one extremity, \mathbf{x} , of the vector \mathbf{h} , equal to $\mathbf{x}-\mathbf{x}'$, describes the area a and the other extremity, \mathbf{x}' , independently describes the same area. Equation (11) can be solved by numerical integration. The values of $\sigma^2(0/a)$ are 0.03084 for copper and 0.02605 for cobalt, which in turn give estimates for $\sigma^2(a/A)$ of 0.03572 and 0.01237 respectively. The effect of this variance reduction is shown in figure 6. When estimates are based on point samples 11 p. cent of the area can be expected to have soil containing less copper than the critical deficiency value of 1 mg/kg, whereas for 1 km square blocks this expectation is reduced to 5 p. cent. For cobalt, whose mean value is less than the critical deficiency, 52 p. cent of point samples can be expected to contain less than the critical deficiency value of 0.25 mg/kg, whereas for 1 km square blocks the expectation increases only slightly to 54 p. cent. There is nevertheless a dramatic reduction in the variability.

Figure 7 shows considerable variation in the concentration of copper. The largest concentrations are close to the towns Hawick, Melrose, Galashiels and Peebles, and probably arise from pollution. Around grid reference NT8762 there are weathered volcanic ashes close to the surface. RAGG & FUTTY (1967) distinguished a soil series, the Ferney series, on them. These ashes are likely to have contributed to the large quantity of copper in the soil there. Similarly weathering of the basalt intrusion has probably caused the large concentration around NT6141. The parts of the region where copper appears to be deficient (less than

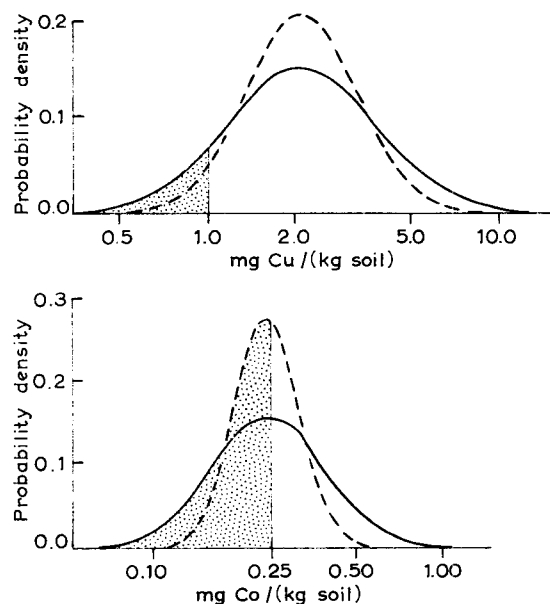


Figure 6

Probability density functions (pdf) for copper top and cobalt bottom showing the deficiency cut-off. For each element the broken curve shows the estimated pdf for samples averaged over 1 km square blocks and the continuous curve the pdf for point samples (fields).
Densité de probabilité (pdf) pour le cuivre en haut et le cobalt en bas indiquant le seuil de carence. Pour chaque élément la courbe en traits discontinus indique la densité estimée pour la moyenne des échantillons sur blocs carrés de 1 km et la ligne continue la densité des échantillons individuels (les champs).

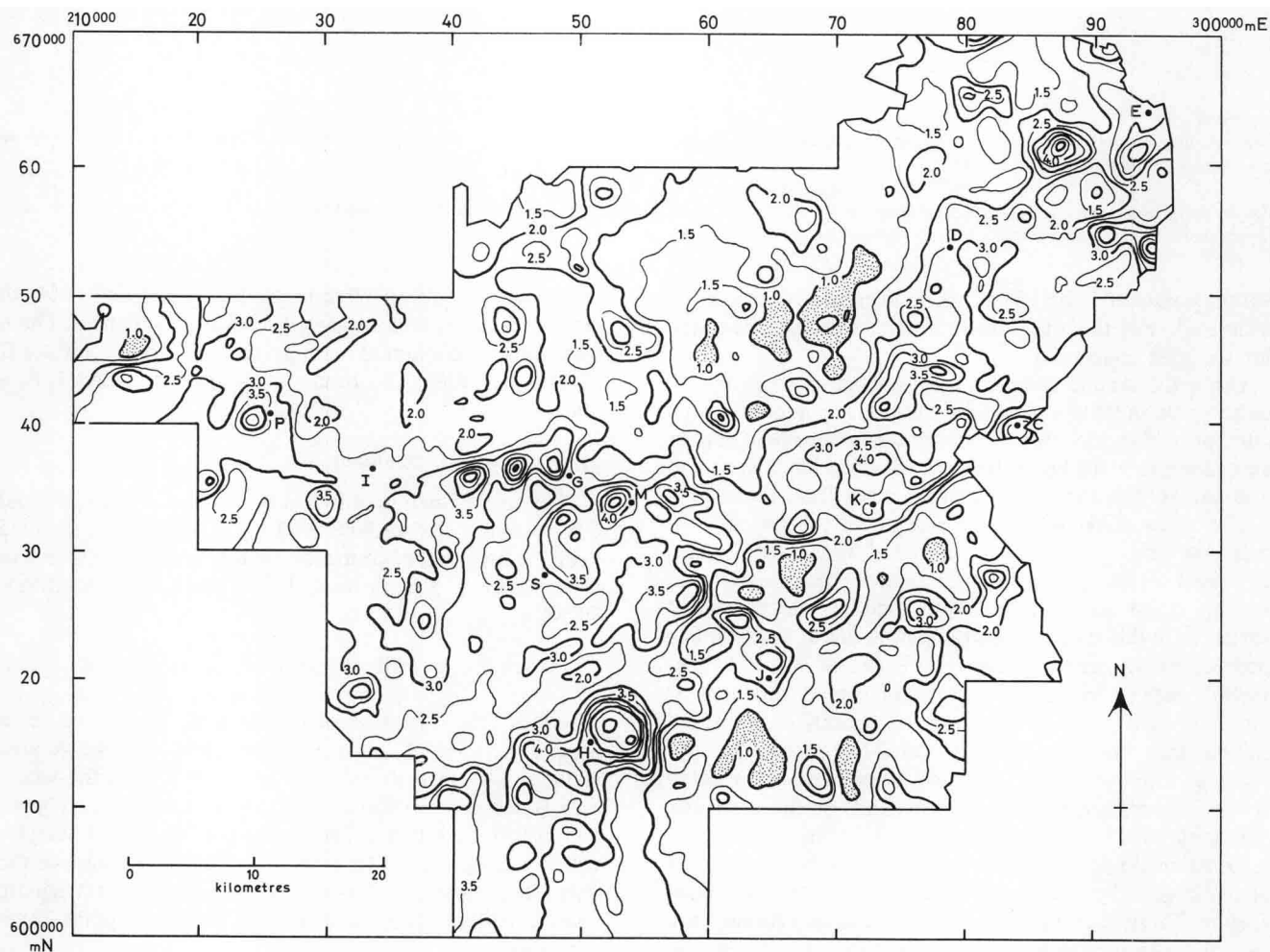


Figure 7

Map of copper in the soil estimated over 1 km² blocks and contoured from figure field with 400 m interval.
Carte de la teneur en cuivre estimée sur blocs de 1 km² à 400 m d'intervalle.

1.0 mg/kg) are south west of Duns, which includes the district around Gordon where PURVES & RAGG (1962) found widespread deficiency, to the south east and south west of Kelso, to the south of Jedburgh, and a small patch of country in the extreme west. The occurrences around NT6628 and NT7730 are in exceptionally sandy soil of the Hobkirk series, and those around NT6414 and NT7214 in strongly leached podzols, of the Hobkirk association.

Cobalt (fig. 8), for reasons explained above, appears less variable than copper (fig. 7). Only around Jedburgh are there any substantial concentrations of the metal, some of which are associated with intrusion of basalt. There are, however, large parts of the region with apparent deficiency.

Figures 9 and 10 are contour maps of the kriging variance. They are essentially reliability maps for the survey in which the contour values depend very largely on the sampling density. The locally-intensive sampling around Peebles and Innerleithen shows especially in very small variances. By contrast the immediately adjacent parts of the region were sparsely sampled and so kriging variances are largest there. Indeed, the values may be regarded as unacceptably large and further sampling desirable to diminish the error there. The variances are, of course, in units of $(\log_{10} \text{concentration})^2$ so that it is not easy to judge immediately whether the map is precise enough. Nevertheless, consider as an example a place some 10 km north of Innerleithen with an estimated copper concentration of 2.0 mg/kg and estimation variance 0.05. This is equivalent to a \log_{10} concentration of

$0.301 \pm \text{an error of } 0.223$. The 90 p. cent symmetrical confidence limits are 0.301 ± 0.366 , or on the untransformed scale, effectively 0 to 4.64 mg/kg. This does not seem acceptable. As resources become available further sampling should be carried out in that part of the region. In contrast, a kriging variance of 0.01 seems fairly typical in the remainder of the region. There the 90 p. cent symmetrical confidence limits about an estimated value of 2 mg/kg are 1.37 and 2.91 respectively. This does seem reasonable.

IV. CONCLUSIONS

The results are summarised under three headings :

Soil classification. Soil classification at association level accounts for a modest proportion (22 per cent) of the variance in copper concentration in the soil. By the definition of associations this is an effect of parent material. Soil on the sedimentary rocks of the Old Red Sandstone, especially that of the Mountboy and Hobkirk associations, is deficient in copper. Otherwise the value of soil classification was disappointing.

Spatial analysis. There are two components of spatial variation for both copper and cobalt. The one has a range of some 2 to 3 km, and probably arises from differences in the treatment of soil and crops from farm to farm. The other extends to about 15 km. In view of the results of the analysis of variance by associations (table 2), the way in which many

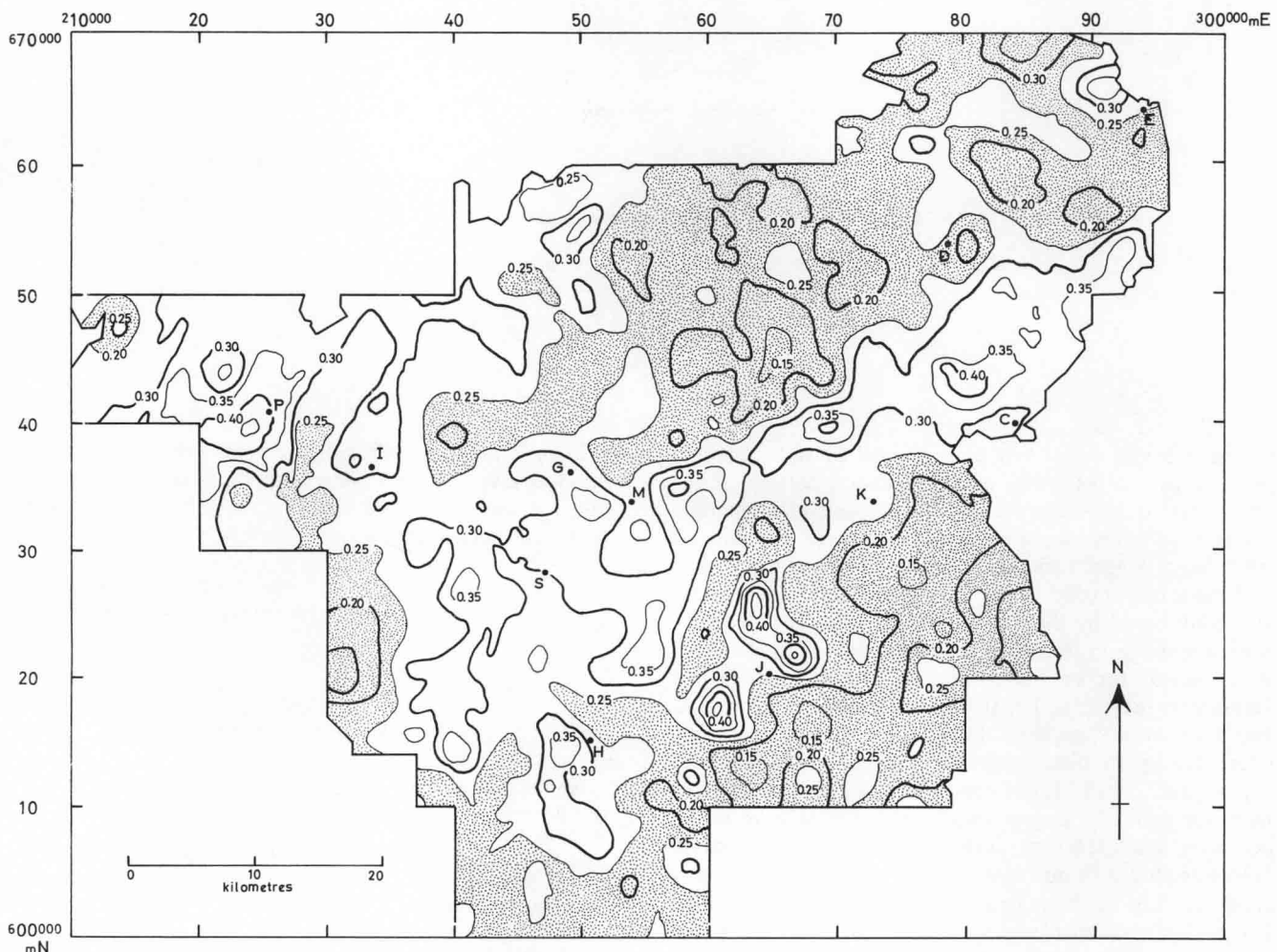


Figure 8

Map of cobalt in the soil estimated over 1 km² blocks and contoured from figure field with 400 m interval.

Carte de la teneur en cobalt estimée sur blocs de 1 km² à 400 m d'intervalle.

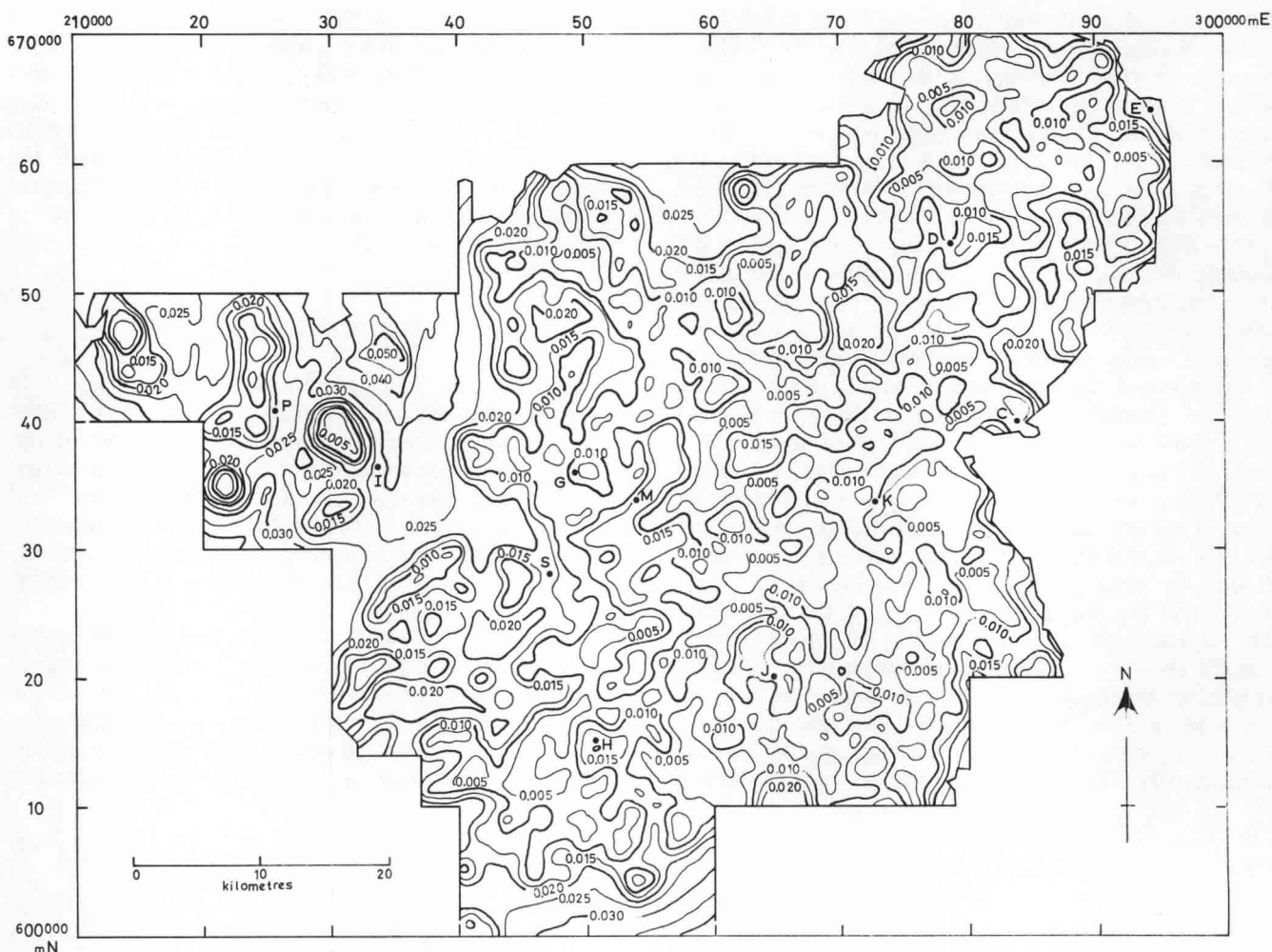


Figure 9

Map of kriging variance for copper associated with figure 7.

Carte de la variance du krigeage pour le cuivre en association avec la figure 7.

of the extreme values can be explained by occurrence of peculiar parent materials, and the general pattern of the parent material distribution (fig. 1), this second component is almost certainly caused by geological change. Both metals have large nugget variances. For cobalt it was more than half the total, to which some 15 p. cent of the total variance was contributed by the handling and analytical procedure. This large nugget effect partly explains why so little variance is accounted for by the earlier soil survey: the nugget variance is present within the mapping units at all levels. *Interpolation and mapping.* Isarithm maps made by kriging over 1 km square blocks show the regional variation of both copper and cobalt. Local concentrations of copper occur near some of the larger towns, probably as a result of pollution, and a few other small areas of large concentration are associated with outcrops of volcanic rocks. Three fairly small portions of the region are deficient (having less than 1.0 mg/kg of available copper), and these occur on the strongly leached and sandier soil of the Hobkirk and Eckford associations on Old Red Sandstone sediments and fluvio-glacial drift. Large parts of the region have cobalt concentrations less than the generally accepted threshold of

0.25 mg/kg. The precision of the maps displayed as corresponding maps of the kriging variance, is generally acceptable, but more intensive sampling is needed in those parts that have been sampled only sparsely.

Reçu le 24 décembre 1981.

Accepté le 12 juillet 1982.

ACKNOWLEDGEMENTS

We are most grateful to Mr. J. M. RAGG for discussing our paper and for much of the explanation of the distribution of the metals. We also thank the staff of the Trace Element Department of the East of Scotland College of Agriculture for the chemical analyses, Mr. H. M. GRAY who was responsible for most of the sampling and recording the map references, Mrs. Joyce W. MUNDEN for preparing the diagrams and help with computing, and Mr. P. G. N. DIGBY and Mr. R. W. PAYNE for suggesting and analysing the variance for the classification model. Finally, we thank the Department of Agriculture and Fisheries for Scotland for awarding a Post-Graduate Agricultural Studentship to A. B. McBRATNEY tenable in the Department of Soil Science at the University of Aberdeen.

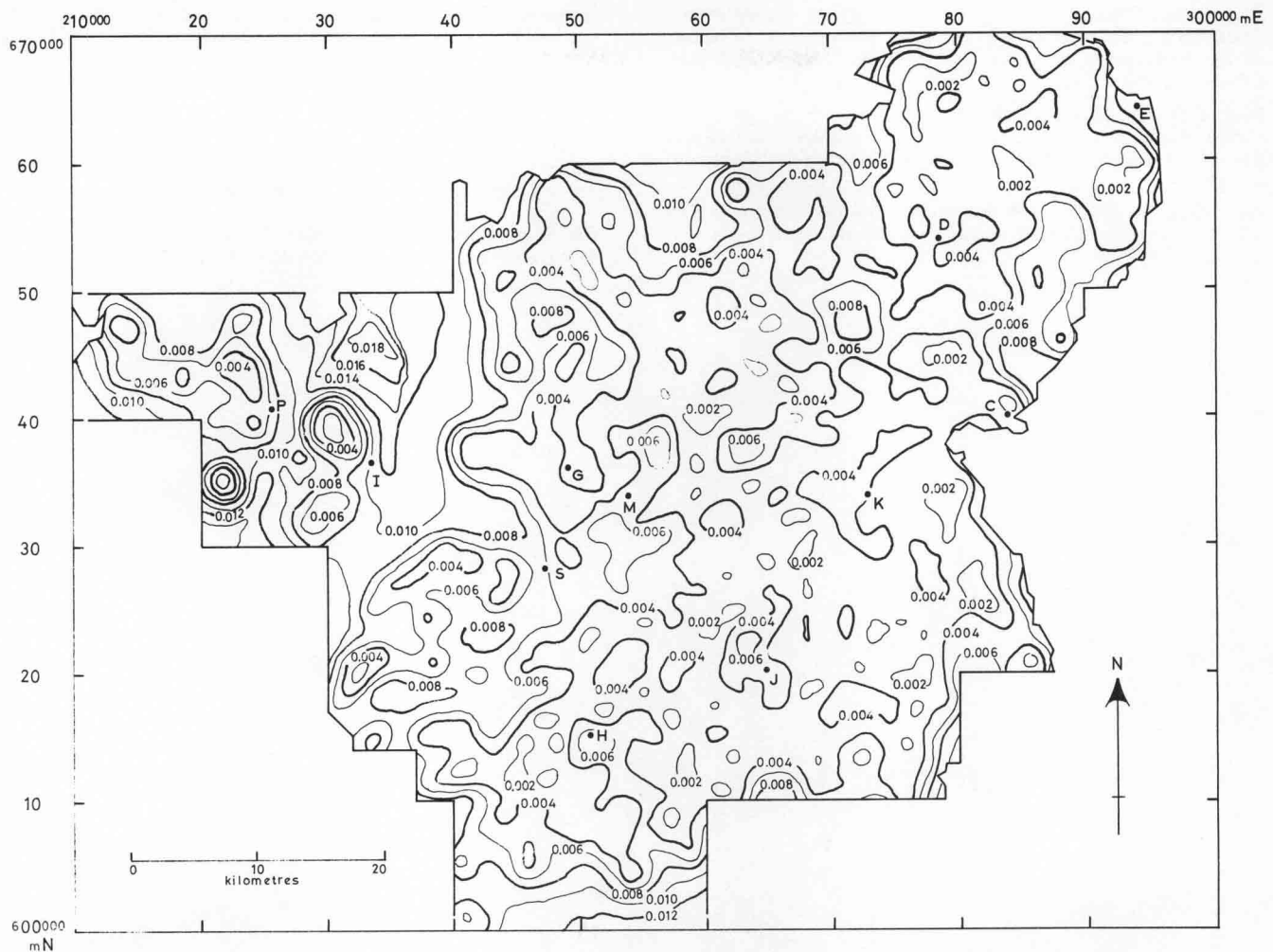


Figure 10

Map of kriging variance for cobalt associated with figure 8.

Carte de la variance du krigeage pour le cobalt en association avec la figure 8.

REFERENCES

- Ahrens L. H., 1965. *Distribution of elements in our planet*. McGraw Hill, New York, 110 p.
- Avery B. W., 1955. *The soils of the Glastonbury District of Somerset (Sheet 296)*. Memoirs of the Soil Survey of Great Britain. H. M. Stationery Office, London, 131 p.
- Burgess T. M., Webster R., 1980a. Optimal interpolation and isarithmic mapping of soil properties. I. The semi-variogram and punctual kriging. *J. Soil Sci.*, **31**, 315-331.
- Burgess T. M., Webster R., 1980b. Optimal interpolation and isarithmic mapping of soil properties. II. Block kriging. *J. Soil Sci.*, **31**, 333-341.
- Chilès J. P., 1976. How to adapt kriging to non-classical problems: three case studies. In: Guarascio M., David M., and Huijbregts C. (Editors). *Advanced geostatistics in the mining industry*. Reidel, Dordrecht, 69-89.
- Coppinet M., 1970. Exemples de problèmes régionaux. I. Le massif Armoricaïn. *Ann. agron.*, **21**, 587-601.
- Coppinet M., Calvez J., 1956. Sur l'origine des carences en cuivre. *Rap. 6^e Cong. Intern. Sci. Sol*, **13**, 493-497.
- Coppinet M., Calvez J., 1967. Les oligo-éléments et en particulier le cobalt dans les sols et les fourrages du Finistère. *C.R. Acad. Agric. Fr.*, **53**, 939-947.
- Delhomme J. P., 1976. *Applications de la théorie des variables régionalisées dans les sciences de l'eau*. Thèse de Docteur-Ingénieur. Université Pierre et Marie Curie, Paris.
- Journel A. G., Huijbregts C. J., 1978. *Mining geostatistics*. Academic Press, London. 600 p.
- Le Riche H. H., 1959. Molybdenum in the Lower Lias of England and Wales in relation to the incidence of teart. *J. Soil Sci.*, **10**, 133-136.
- Mackenzie E. J., 1974. *Extractable copper and cobalt in soils*. Technical Note No. 67 A/C, East of Scotland College and Agriculture, Edinburgh. 7 p.
- Matheron G., 1965. *Les variables régionalisées et leur estimation*. Masson, Paris. 305 p.
- Matheron G., 1971. *The theory of regionalized variables and its applications*. Cahiers du Centre de Morphologie Mathématique 5, Fontainebleau, 211 p.
- Millier C., Poissonet M., Serra J., 1972. *Morphologie mathématique et sylviculture*. In: 3^e Conférence du Groupe Consultatif des Statisticiens Forestiers, Jouy-en-Josas, 7-11 septembre 1970. I.N.R.A. Publ. 72-3, 287-307.
- Ministry of Agriculture, 1976. *Trace element deficiencies in crops*. ADAS Advisory Paper No. 17. Ministry of Agriculture, Fisheries and Food, London. 34 p.
- Muir J. W., 1956. *The soils of the country round Jedburgh and Morebattle (sheets 17 and 18)*. Memoirs of the Soil Survey of Great Britain. H. M. Stationery Office, Edinburgh. 178 p.
- Purves D., Ragg J. M., 1962. Copper-deficient soils in south-east Scotland. *J. Soil Sci.*, **13**, 241-246.
- Ragg J. M., 1960. *The soils of the country round Kelso and Lauder (sheets 25 and 26)*. Memoirs of the Soil Survey of Great Britain. H. M. Stationery Office, Edinburgh. 201 p.

Ragg J. M., Futton D. W., 1967. *The soils of the country round Haddington and Eyemouth (sheets 33, 34 and part of 41).* Memoirs of the Soil Survey of Great Britain. H. M. Stationery Office, Edinburgh. 310 p.

Ragg J. M., Bibby J. S., Orbell G. A., Duncan N. A., 1971. Soil survey of Scotland, systematic soil survey : Peebles, sheet 24 and part of Edinburgh sheet 32. Macaulay Institute for Soil Research, Aberdeen.

Ross G. J. S., 1980. *MLP Maximum likelihood program.* The Statistics Department, Rothamsted Experimental Station, Harpenden.

Sampson R. J., 1978. *Surface II graphics system (Revision one).* Kansas Geological Survey, Lawrence. 240 p.

Shaw D. M., 1961. Element distribution laws in geochemistry. *Geochim. Cosmochim. Acta*, **23**, 116-134.

Thornton I., Webb J. S., 1980. Regional distribution of trace element problems in Great Britain. In: B. E. Davies, editor, *Applied soil trace elements*. Chichester, Wiley, 381-439.

Vila J. P., 1976. *MLP, Maximum likelihood program.* Présentation. Utilisation. Ronéo 76-20, I.N.R.A. Biométrie, Jouy-en-Josas.