Sampling variability of stream sediments in broad-scale regional geochemical reconnaissance

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Synopsis

The errors resulting from field sampling, sample preparation and analysis are investigated for drainage sediments derived from homogeneous sandstone, shale, limestone, basic igneous and granite lithologies as a background to a primary reconnaissance survey of England and Wales. Emission spectrographic analyses of approximately 350 samples for Al, Ca, Fe, K, Si, Ba, Co, Cr, Cu, Ga, Li, Mn, Ni, Pb, Sc, Sn, Sr and V and atomic absorption analyses for Cu, Ni, Mn, Co, Zn and Pb have been treated statistically. For routine broad-scale surveys analysis of the unground -80-mesh sediment fraction proves satisfactory. Sampling error between localities in a stream is shown to be less than spectrographic analytical error for many of the elements considered here, except where mineralization (contamination) occurs, but exceeds the atomic absorption analytical errors in most cases. Unless it it critical to reduce the amount of between-site variability (having regard to analytical errors) in the regional survey, there appears to be no advantage in the use of a more sophisticated sampling technique. The utility of moving-average maps in reducing the width of the confidence belt around the regional 'geochemical surface', and thus compensating to some extent for the sampling errors, is also demonstrated.

In this paper we are concerned with primary geochemical reconnaissance aimed at locating patterns in the distribution of the elements related to broad-scale features rather than the anomalous dispersion trains associated with individual deposits sought by conventional mineral exploration reconnaissance surveys. The material has been compiled as a background study for preliminary geochemical reconnaissance of England and Wales.

Primary regional geochemical reconnaissance of the type under discussion involves the compilation of maps based on the distribution of major and trace elements in active stream sediments sampled at spatial densities ranging from one sample per square mile to one sample per one hundred square miles. The *preliminary* broad-scale technique employed is aimed at locating, at minimum cost, areas suitable for more detailed investigation. Sampling procedure, sample density, analytical productivity and precision are chosen to obtain maximum cost-effectiveness.[23,24,25] The goal is the delineation of major geochemical features at scales related to the sampling density, and it may be neither economic in time nor cost-effective to obtain a high degree of confidence in the value of an individual sample point.

Chemical analysis of stream sediments appears to have been first attempted by Soviet geochemists in the 1930s.[11] The first regional-scale stream-sediment survey in the West was undertaken in 1954, and by 1966 the technique was generally accepted as an exploration tool.[4] This early phase was principally related to mineral exploration goals based on the criterion that the most suitable method is that which achieves reliable detection of 'adequate' anomalies by the cheapest means.[22] Regional surveys involving upwards of 10 000 samples for up to 30 elements are now being carried out, and the applications have been broadened to include geological, agricultural, medical and pollution studies.[24,25]

Since the mid-1950s the use of active stream sediments from tributary drainage has been based on its convenient approximation to a composite sample of the rock and soil upstream of the sample point, although the influence of secondary environment during weathering, soil formation, erosion, stream transport and deposition may have a modifying effect on this relationship. Sediment anomalies tend to be more stable with respect to seasonal changes than those of the associated stream waters, and, although similar trends are exhibited by rocks and soils on a regional scale, the stream-sediment patterns often tend to be less erratic.[24,25] Seasonal variations mainly affect the sediment type present and are principally related to climatic change, such as wet and dry seasons, and the precipitation of iron, manganese and associated metals.[2,3,8,17] The purpose of this paper is not, however, to discuss stream-sediment sampling in relation to other prospecting techniques but to evaluate the sampling errors inherent in the application of this method to broad-scale regional surveys.

The sampling pattern aims to achieve as homogeneous a spatial distribution of the data points as possible, having regard to (a) the scale of features which are to be detected (target size); (b) catchment basin areas; (c) the scale and complexity of the geology; (d) availability of suitable maps or air photographs; (e) access by road or track networks; and (f) the cost of transporting personnel to the sample sites.[1,3,6,7,11,14,17,21]

The active stream-sediment samples are commonly collected at two or more localities in the stream, care being taken to avoid sampling obvious sources of contamination or collapsed bank material. Sediment finer than coarse gravel grade is normally collected, dried and sieved. Duplicate samples taken from one stream locality are sometimes bulked prior to analysis.

During the mid-1950s the United States Geological Survey established that the -80 (U.S.) mesh fraction of the stream sediments gave satisfactory results for regional reconnaissance.[5,11] Subsequent work in various types of terrain and climatic regime[2,9,12,15,18,19,21,23,26] has shown that a 100-g stream-sediment sample will generally yield sufficient -80-mesh* material for subsequent analysis.[11] The -80-mesh fraction, in general, provides both comparable results for the

*Unless stated otherwise, -80 mesh as used in this paper refers to Schindler nylon bolting cloth with a nominal aperture size of 0·204 mm, corresponding to 82 threads per inch.

various rock types encountered in regional work and a reasonably satisfactory contrast of anomaly with the local background. In any investigation in which the enhancement of this contrast is of paramount importance (e.g. in some mineral exploration problems[2]), however, a field investigation of the optimum sediment size grade is desirable in the early stages of the exercise.

Effect of grinding on stream-sediment samples

It has been found that when wet-chemical methods of analysis are used there is little advantage to be gained from grinding the coarser fractions (20–80 mesh) prior to analysis. Kaewbaidhoon[13] found that grinding improved the precision of tin analyses, but remarked that it was not warranted for routine analyses as it resulted in a marked loss of productivity. Harden[9] found that for stream sediments from Zambia 'the results for nickel, zinc, cobalt and copper . . . indicate that there is little advantage to be gained'.

Garrett,[6] who used spectrographic analyses of stream sediments from Sierra Leone, found that the geometric means of −80-mesh fractions, both unground and ground to pass 120 mesh, were, in general, within 25 per cent for titanium, chromium, manganese, vanadium, nickel, cobalt, copper and lead. The grinding did reduce the variance at a site by a factor of about two, suggesting that the original high variance was caused by the inhomogeneous nature of the sample selected for analysis. As 'the number of samples revealing large variances at a single site is small', however, it was concluded that only marginal improvements were gained by grinding, and it was not undertaken on a routine basis.

A comparison has recently been undertaken of ground and unground −80-mesh fractions of bulk samples of stream sediments derived from homogeneous shale, basic igneous and granite bedrocks by use of an A.R.L. 29000B Quantometer (automatic emission spectrograph).

The samples were dried at about 60°C and sieved. The ground or unground −80-mesh fractions were ignited for 3 h at 450°C and were then mixed thoroughly with 1·5 parts of a buffer consisting of a mixture of sodium fluoride with 2 parts of carbon powder. The resulting mixture was arced at 10 A by use of a 3-mm electrode separation and a burn time of 90 sec. The electrodes were 6-mm carbon rods, the cathode being cut flat and the anode containing about 40 mg of the sample mixture in a conical cavity. Calibration was performed with various levels of trace elements in a synthetic base resembling an intermediate rock. Eight standard bulk samples of natural stream sediments and two synthetic rocks were repeatedly analysed during the course of a day to act as additional control on the analytical quality. Analytical precision* values for all elements in a variety of natural

drainage sediment types are given in Table 2 ; elements that occur in concentrations close to the detection limits (given in Table 2) will show poorer precisions compared with precisions that correspond to higher concentration levels.

In order to minimize the assumptions inherent in testing for significant differences between the ground and unground samples, a two-tail Kolmogorov–Smirnov test was used, based on ten replicate determinations of both the ground and unground −80-mesh fractions. This test makes no assumptions about the nature of the underlying frequency distributions, and is sensitive to any kind of difference in the distributions from which the two samples were drawn (e.g. differences in central tendency, dispersion and skewness). For this reason it was preferred to parametric tests. For small numbers of samples it is almost as powerful as the parametric t-test, and seems to be more powerful in all cases than the chi-square test.[20]

Table 1 Comparison of effect of grinding on −80-mesh sediments derived from shale, granite and basic igneous bedrocks by Kolmogorov–Smirnov test* (ppm, unless otherwise stated)

	Shale†	Granite‡	Basic igneous§
Al, %	—	—	—
Ca, %	—	***	—
Fe, %	—	***	—
K, %	—	—	—
Si, %	—	***	—
Ba	***	***	—
Co	—	***	—
Cr	—	—	—
Cu	—	—	—
Ga	—	—	—
Li	**	—	—
Mn	—	—	—
Ni	—	—	—
Pb	—	**	—
Sc	—	—	—
Sn	—	—	—
Sr	**	**	—
V	—	—	—

*Based on 10 ground and 10 unground samples. ***, Frequency distributions for ground and unground samples are different at 0·01 level of significance; **, different at 0·05 level of significance; —, not different at 0·05 level of significance.
†High metal shale, Onecote Grange, Derbyshire (Nat. Grid ref. 40473558).
‡High metal granite, Chagford, Devon (25640917).
§Basic igneous, Zoar, near Horndon, Devon (25270808).

The results for stream sediments derived from shale, granite and basic igneous rocks (Table 1) show that, as might be expected, significant differences between the unground and ground −80-mesh material are common *only* for the coarser-grained granite-derived sediment. Comparison of the precision values for the

*Precision (ϕ) is defined here as ±1·96σ/m per cent, where σ is the sample standard deviation and m is the arithmetic mean.
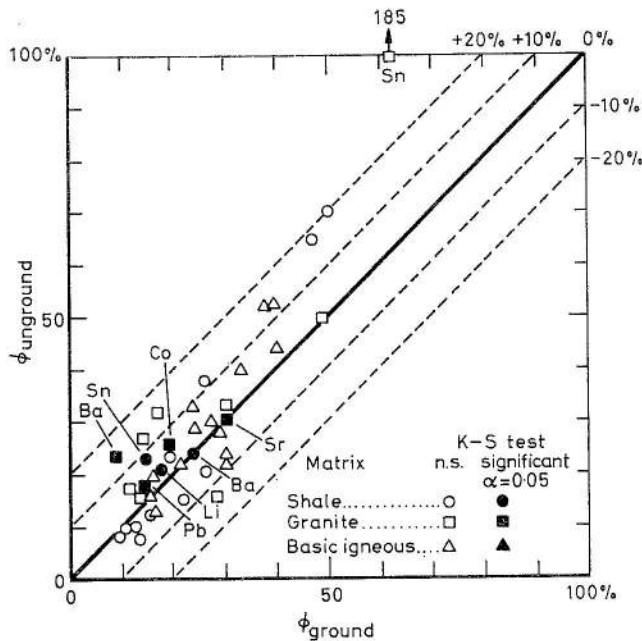
Fig. 1   Comparison of analytical precisions (ϕ per cent) for trace-element concentrations in ground and unground -80-mesh stream sediments. Open symbols, no significant difference at $0 \cdot 05$ level between the two populations on the basis of the Kolmogorov–Smirnov (K–S) test; solid symbols, two populations significantly different at $0 \cdot 05$ level on the basis of the K–S test. Sample size, $n_1 = n_2 = 10$

Fig. 2   Comparison of means (m ppm) for trace-element concentrations of ground and unground -80-mesh stream sediments. Symbols as for Fig. 1

ground and unground samples (Fig. 1) suggests that those elements which show significant differences between the two populations on the basis of the Kolmogorov–Smirnov test do not differ greatly in analytical precision. In any event the precisions of the majority of unground samples do not differ by more than 10 per cent compared with those of the corresponding ground sample. A similar plot for the means of the ground and unground samples (Fig. 2) suggests that differences in the means may be accounted for by shifts in the central tendency, and perhaps also the shape, of the distributions. The majority of trace elements that show a difference in the Kolmogorov–Smirnov test have means for the ground samples increased by up to 30 per cent over those of the unground samples.

Improvements in precision resulting from grinding are marginal in relation to sampling error, discussed below, and for most purposes in preliminary broad-scale reconnaissance grinding has not been found to markedly improve the *overall patterns* of trace-element distribution compared with those obtained from unground samples. In view of this, the additional time and cost of grinding the numbers of samples involved in major regional surveys may not be justified unless steps are taken to markedly reduce sampling variability. This would lead to a considerable increase in overall cost, which would be difficult to justify for most preliminary reconnaissance purposes.
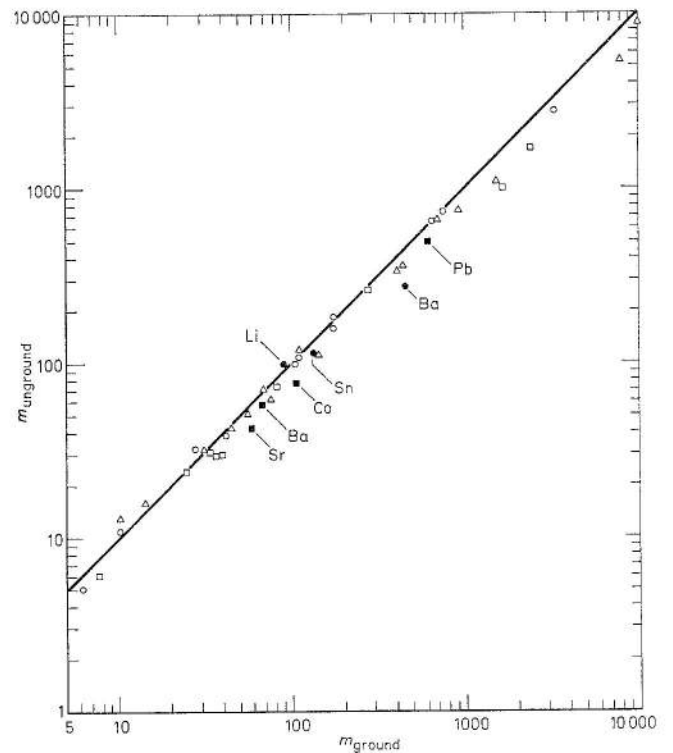
Sources of sampling error

The major sources of geochemical sampling error have been discussed at length by Miesch.[16] His ideas, with minor modifications for the stream-sediment regime, may be summarized as follows.

(a) *Overall bias* may be caused by a lack of exposure or accessibility of the parent rock bodies; inadequate surface drainage over particular lithologies (e.g. limestone); inaccessibility of the solid geology caused by drift cover; and personal bias on the part of the sampler, either in selection of sample sites or in obtaining the samples from the stream bed.

(b) *Variable bias* can arise through varying personal biases in the selection of the sediment samples by the different investigators (e.g. with regard to sample size, composition, contamination by bank material, etc., and locality within the stream bed); differences in the drainage channel characteristics from one locality to another; variation in the exposure of different lithologies; and variation in catchment size and the drainage density within it, causing variation in the proportions of rock types mixing together in the stream sediment in catchments overlying several lithologies.

(c) *Variable precision* may be caused by the effect of inhomogeneity of the sediment composition in a given stream, and variability of the trace-element concentration level, which Miesch[16] has suggested is proportional to the mean concentration.

The majority of these sources of sampling error are usually unavoidable, and the magnitudes of the

individual error components can rarely be determined. Carefully controlled objective sampling will serve to reduce operator-induced sampling bias and variable sampling precision. The effect of overall bias is only serious if the purpose of the investigation is to obtain highly accurate estimates of the geochemical abundance of a constituent. Variable bias or precision may render interpretation of the sampling results extremely difficult.

As Miesch[16] has remarked with regard to these sources of error, 'Despite the difficulties that can and do arise in the field and in the laboratory, sound geological judgment in designing a study and use of objective sampling plans can do much to reduce their effects. The many valid inferences made in geochemical studies attest to the fact that in many instances the errors are not great enough to invalidate the findings of the study'.

Effect of sampling error in broad-scale surveys

Work by Hawkes, Bloom and Riddell[10] in New Brunswick, Govett[8] in Zambia, James[12] in Sierra Leone and Band[2] in Norway, among others, suggested that the stream-sediment sampling error was small relative to the precision of the analytical methods used. Vertical profiles collected in the stream bed below the active stream sediments showed no significant variation in the exchangeable metal content of the −12-mesh fractions.[10] Khaleelee,[14] however, concluded from spectrographic analyses of stream sediments from the United Kingdom that sampling errors for a wide range of elements were 'usually at least equal in magnitude to the analytical errors', based on the relative error in replicate determinations of stream-sediment samples.

In an attempt to assess the sampling errors incurred during routine stream-sediment reconnaissance in England and Wales a carefully controlled sampling experiment was set up. A total of 350 stream sediments were collected (by P.L.L.) from a number of streams draining homogeneous bedrock. The rock types were chosen to yield a range of size grades and bulk compositions typical of those to be expected in the stream sediments collected during the regional reconnaissance.

In each stream several localities were sampled in duplicate, each of these duplicate samples itself consisting of a 100-g composite of two 'grabs' of active sediment, preferably of coarse sand to clay grade. Care was taken to exclude collapsed bank material when these samples were being collected. From 8 to 30 localities were sampled in this way in each stream, each locality being separated by at least 50 ft, where possible. In addition, bulk samples (ca 1 kg) were taken in duplicate from a number of localities in the two granite streams in order to assess the utility of bulk sample collection to reduce between-site sampling variability. It was suspected that the coarse-grained granite-derived sediments would give rise to the largest sampling error between localities.

The sampling method represented a deliberate attempt to reduce the between-site source of variation. The use of one sampling operator reduced the chance of overall bias, variable bias or precision arising from operator variation. Some overall bias and variable sampling precision may, however, remain—for the geological reasons outlined above.

It was also desirable to assess the relative importance of analytical error in comparison with the sampling error. Analyses of the unground −80-mesh fraction were carried out with the A.R.L. 29000B Quantometer (see earlier). The analytical variance was estimated from ten replicate analyses of fractions of a single bulk sample from each stream. Miesch[16] has discussed the application of parametric techniques to geochemical data. The assumptions required are that the errors must (1) have zero means; (2) be independent; (3) have a common variance; and (4) be normally distributed.

Following Miesch,[16] we observe that if overall bias is present, the assumption of zero means among the errors fails, but the analysis of variance may still be valid so long as criteria (2)–(4) remain true. For this to be so the following must be true: first, that the amount of one error is not significantly related to that of another error, e.g. that the errors do not tend to be distributed about different values at different localities; and, second, that variable bias does not occur among the localities, as this would destroy the property of additivity of variances upon which the method is based. The precision of sampling or analysis measured by the variance must not vary from one locality to the next, as this would mean that common variance among the errors is absent. The requirement of a normal distribution for the experimental errors does not affect the validity of the analysis of variance method for the estimation of the variance components, but it does affect the F-tests for significance of differences among the sampling locality means if the departure from a normal distribution is great.

Assuming that neither variable bias nor variable precision arising from causes outside the control of the sampling operator is of such magnitude that these criteria cannot be met, a parametric one-way analysis of variance may be carried out to test the null hypothesis that the population means at each site are equal for a given element. One may then determine whether there is a statistically significant between-site variance, and relate this to the magnitude of the analytical variance. Details of the method are given in Appendix 1.

The results obtained, based on the low-precision spectrographic data (typical of those obtained by our current broad-scale reconnaissance surveys), are summarized in Table 2 and the replicate sample grand means are given in Table 3. When the variance of the population means exceeds that of the analysis for a given element, and the null hypothesis that the within-site random error component is zero is rejected, there is a good case for concluding that the sampling error at a given site is high. The only element which appears to

Table 2 Comparison of population mean and analytical variance ratio (r) and precision (φ) for stream sediments based on low-precision spectrographic analyses

Element	Sandstone[a]		Sandstone[b]		Shale[c]		Shale[d]		Limestone[e]		Basic igneous[f]		Basic igneous[g]		Granite[h]			Granite[i]			Detection limits[j]
	r	φ	r	φ	r	φ	r	φ	r	φ	r	φ	r	φ	r[k]	r	φ	r[k]	r	φ	
Al	—	29	(2·0)	26	—	30	—	30	—	22	—	39	10	39	—	—	30	—	3·1	18	0·15%
Ca	—	101	—	38	—	38	—	109	(2·9)	45	(1·5)	49	—	49	—	—	109	—	—	164	0·2%
Fe	—	44	(1·7)	20	(1·2)	17	—	48	—	21	—	35	—	35	—	—	48	—	32	36	0·1%
K	—	24	(1·7)	14	(2·0)	12	(1·5)	27	—	14	—	58	3·9	58	(2·3)	3·9	27	(1·1)	7·2	30	0·01%
Si	—	35	—	15	—	15	—	40	—	11	—	20	—	20	—	—	40	—	—	26	0·5%
Ba	—	32	4·5	40	2·0	23	—	28	—	31	—	38	—	38	—	—	28	—	—	66	10
Co	—	75	—	21	5·0	10	—	51	n.d.	n.d.	—	47	—	47	—	20	51	20	279	20	3
Cr	—	246	—	62	—	67	—	85	—	73	—	43	—	43	n.d.	n.d.	85	n.d.	n.d.	n.d.	10
Cu	—	32	(2·0)	27	—	120	—	44	n.d.	n.d.	631	63	(2·6)	63	—	16	44	—	76	16	3
Ga	—	46	—	47	—	30	—	40	n.d.	n.d.	—	32	2·0	32	(2·0)	—	40	—	6·0	40	1
Li	—	38	—	45	—	32	—	80	—	39	—	86	—	86	—	—	80	—	2·3	27	5
Mn	(3·9)	42	(1·3)	25	2·0	34	—	56	6·0	17	—	56	—	56	—	35	56	n.d.	35	17	5
Ni	—	88	—	61	2·3	17	(1·7)	50	n.d.	n.d.	—	24	n.d.	24	n.d.	—	n.d.	n.d.	n.d.	n.d.	5
Pb	—	68	—	22	2·5	17	—	30	n.d.	n.d.	19	52	—	52	—	10	30	n.d.	30	21	3
Sc	—	8	—	29	—	48	—	72	—	24	(1·2)	53	1·8	53	—	—	70	—	—	57	2
Sn	65	641	186	299	26	652	n.d.	n.d.	228	140	1·8	151	120	151	158	—	1540	—	—	224	5
Sr	—	46	(2·2)	37	—	32	1·5	50	—	33	—	35	(1·4)	35	—	30	50	—	—	49	6
V	n.d.	n.d.	—	48	—	39	—	71	n.d.	n.d.	—	52	—	52	—	n.d.	71	n.d.	n.d.	n.d.	10
n		20		20		18		21		21		8		12			8			10	5

r, Ratio of population mean/analytical variance : —, r is less than 1.; 3, r when within-site random error component differs from zero at 0·05 level of significance : (3.), r when within-site random error component is not different from zero at the 0·05 level of significance : φ, analytical precision (± φ per cent), based on 10 replicate analyses : n.d., population mean below detection limit : n, number of localities sampled in duplicate.

[a] Permo–Triassic sandstone. Copplestone, Devon (Nat. Grid ref. 27621019).
[b] New Red Sandstone, Osmaston, Derbyshire (41913434).
[c] Shale, Upper Cotton, Staffordshire (40583475).
[d] Shale (known to have high trace-element values). Onecote Grange, Derbyshire (40473558).
[e] Limestone, South Cadbury, Somerset (36311248).
[f] Basic igneous, Cudlipptown, Devon (25210788).
[g] Basic igneous (with possible contamination from adjacent mine dumps), Zoar, near Horndon, Devon (25270808).
[h] Granite, Devon (25640917).
[i] Granite (with trace-element enhancement caused by secondary environment controlled manganese–iron precipitation), northwest Dartmoor, Devon (26080891).
[j] Detection limits after Dr. M. Thompson (personal communication, 1971) ; values in ppm unless stated otherwise.
[k] Bulk samples.

Table 3   Replicate sample grand means (ppm, unless otherwise stated)

	Sandstone[a]	Sandstone[b]	Shale[c]	Shale[d]	Limestone[e]	Basic igneous[f]	Basic igneous[g]	Granite[h]	Granite[i]
n	20	20	18	21	21	8	12	30	10
Al, %	3·44	3·92	2·79	4·05	3·30	7·63	10·00	8·37	4·79
Ca, %	0·34	0·58	0·47	3·04	2·37	2·98	1·42	1·15	0·31
Fe, %	2·78	1·98	1·68	5·54	1·88	5·48	5·88	1·88	10·17
Fe, % *	1·36	1·89	1·19	4·73	0·91	5·15	—	0·87	10·08
K, %	0·82	0·83	0·39	0·68	1·05	0·83	1·06	3·14	2·12
Si, %	40·05	36·47	34·38	35·03	39·79	30·62	26·78	29·84	25·65
Ba	163	341	152	387	272	167	195	173	15
Co	5	9	11	23	n.d.	46	75	6	63
Co *	8	14	8	25	8	55	—	n.d.	103
Cr	27	37	47	77	68	130	187	11	n.d.
Cu	7	11	15	368	n.d.	73	105	9	52
Cu *	6	11	14	361	5	107	—	12	66
Ga	4	5	3	5	n.d.	15	20	19	18
Li	97	28	26	45	12	109	188	65	172
Mn	365	359	266	657	228	2263	1760	289	9083
Mn *	418	420	261	807	231	1930	—	183	8750
Ni	9	17	18	68	n.d.	123	127	5	n.d.
Ni *	20	20	15	84	14	139	—	n.d.	13
Pb	5	175	22	100	n.d.	47	66	33	540
Pb *	n.d.	282	n.d.	137	n.d.	85	—	36	647
Sc	5	7	6	4	3	29	26	10	5
Sn	13	12	9	n.d.	8	199	330	730	2682
Sr	49	41	23	90	55	71	70	82	9
V	n.d.	26	15	131	4	151	149	24	n.d.
Zn	—	—	—	—	—	—	—	—	—
Zn *	42	124	79	757	37	229	—	39	56

*Indicates atomic absorption determinations (Table 7); others by direct reading spectrograph.
Other symbols as for Table 2.

have a consistently high sampling error is tin. The high population mean variability of copper, lead and tin in the sediments derived from the Zoar basic igneous rocks (g in Table 2) is probably associated with contamination from nearby mining activity. The relatively more frequent instances of sampling error exceeding analytical error in the case of the two granite-derived sediments would be consistent with their greater inhomogeneity.

The effect of bulk sample collection was investigated over the two granite areas. 1-kg samples were collected from a number of localities in these two streams, and the resulting population mean variances are compared with those from 'normal' samples in Table 4. In those cases in which the within-site random error component (σ_e^2) is not significantly different from zero, the population mean can be evaluated with σ_e^2 considered to be zero (Appendix 1). The bulk sample variances in these cases are consistently smaller than those of the normal samples (where $\hat{\sigma}_\mu^2 > 0$), with the exception of calcium and silicon in the high metal granite. It must also be borne in mind that the number of samples of both types from the high metal granite is relatively small, and may account for the greater sampling variance/analytical variance ratios (Table 2) compared to the low

metal granite. The magnitude of these variance reductions does not, however, appear to be very great. Comparison of the element concentrations in the normal and bulk samples by use of the two-tail Kolmogorov–Smirnov test showed differences at the 0·05 level of significance between the distributions of aluminium, potassium, silicon, barium, strontium and lithium for the low metal granite; and for iron for the high metal granite.

We may therefore conclude that the sampling error is generally less than the low-precision spectrographic analytical error for all the elements considered here, and only in a few cases, such as the occurrence of mineralization (or contamination), does the ratio of sampling to analytical variance exceed a factor of about three. It would appear that for primary multi-element reconnaissance there is little advantage in taking bulk stream-sediment samples, even over coarse-grained rocks, such as granites. Variability of elements that occur as discrete heavy mineral grains (e.g. cassiterite or wolframite) may be caused by variation in hydrodynamic sedimentation conditions, and markedly improved results would therefore not be expected to result from the use of bulk samples, unless these were very large.

Table 4 Comparison of normal and bulk sample population mean variance for low and high metal granites based on low-precision spectrographic analyses

Element	Low metal granite[h] Normal	Bulk	High metal granite[i] Normal	Bulk
Al, %	***	***	***	1·32
Ca, %	0·05	0	0	0·03
Fe, %	0·02	0	0	***
K, %	***	0·03	0·19	**
Si, %	0	0	13	20
Ba, ppm	44	0	0	0
Co	0	0	**	***
Cr	0	0	***	0
Cu	18	2	***	***
Ga	***	2	16	**
Li	0	0	2428	**
Mn	3481	0	3×10^4	**
Ni	9	5	10	0
Pb	1239	0	***	**
Sc	***	**	0	0
Sn	***	***	0	***
Sr	69	0	2	0
V	14	11	9	0
Zn	227	0	**	0
n	30	8	10	5

Tabulated values are of variance $\hat{\sigma}_{\mu}^2$; per cent² for major elements; ppm² for trace elements (Appendix 1).

, within-site random error component σ_e^2 not equal to zero at 0·05 level of significance; *, within-site random error component σ_e^2 not equal to zero at 0·01 level of significance. Other symbols as for Table 2.

Treatment of reconnaissance data by moving-average mapping

As was previously stated, the prime purpose of low-density regional geochemical reconnaissance is to delineate the overall *patterns* of element distribution. In this context the relative values of adjoining groups of samples are more important than knowledge of the precise value at any specific location. Smoothing of the raw data by use of a spatial moving-average technique is therefore desirable. This low-pass filtering removes 'noise' produced by sampling and analytical errors and local small-scale features, and enhances the spatial trends or geochemical 'patterns' present over the area of interest.

A square window of fixed dimensions is moved across the map, all data points falling within the window are averaged and that value is taken to represent the mean height of the 'geochemical surface' for the current window position, or 'cell'. The parameters of window size and the degree of overlap between adjacent positions of the window are fixed by the investigator prior to the smoothing of the data.

If we now consider the spatial distribution of data points over a map in terms of the number of points per cell of a fixed size (e.g. 10-km squares), a typical distribution may be Poissonian in form (see Table 5). Then, by use of a Monte Carlo simulation based on this, we empirically derive the frequency distribution for the number of points per cell by employing a window size of 3 cells with a 1 cell overlap. That is, each window position will average all points lying within 9 adjacent cells in the original map. In this case the frequency distribution obtained for the total number of points averaged per window position was as shown in Table 6.

If the precision of the individual determination (ϕ) (this figure may include allowance for sampling plus
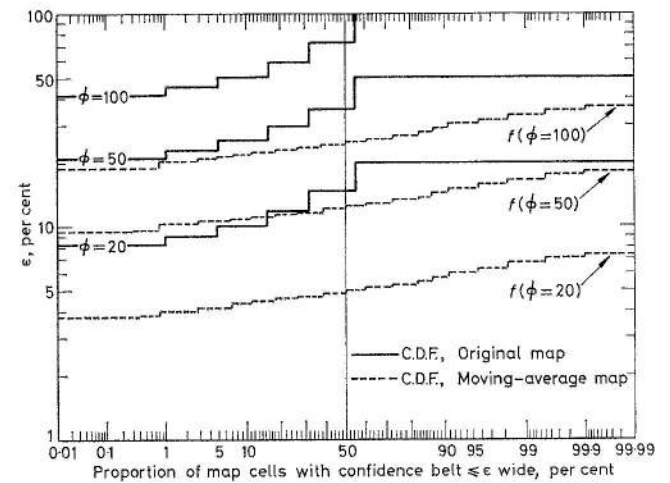

Fig. 3 Log-probability plot for cumulative distribution functions of precision (ϵ per cent) associated with each map cell for unsmoothed and smoothed (with a window of 1 cell effective radius) data for an original analytical precision (ϕ) of 20, 50, and 100 per cent

Table 5

Number of points per cell	0	1	2	3	4	5	6	7
Relative frequency, per cent	14·0	27·0	27·0	18·0	8·0	4·0	1·5	0·5

Table 6

Points per cell	≤7	8	9	10	11	12	13	14	15	16	17	18
Relative frequency, per cent	0	0·4	1·3	2·6	4·7	4·3	3·8	9·8	12·8	9·8	11·6	11·6
Points per cell	19	20	21	22	23	24	25	26	27	28	≥29	
Relative frequency, per cent	8·5	7·2	4·3	2·6	1·7	2·1	0	0	0·4	0·4	0	

analytical error) is known, the error in the moving-average surface (ϵ) may be calculated on the basis of the number of points per cell (n) (Appendix 2). Fig. 3 shows the cumulative frequency distributions for the proportions of cells in the original and smoothed maps which could be expected to have an error (ϵ) better (lower) than a given value for original precisions of $\phi = 100$, 50 and 20 per cent. It will be seen that the error in the smoothed map is reduced by a factor in excess of 3 in more than 95 per cent of the cells compared with the original map. Use of larger windows would further reduce the width of the confidence interval, but would also broaden the scale of the features in the map as the spatial frequency passed by the filter is lowered.

Unless individual data-point truth is required (which is not generally the aim of a low-density primary regional survey), moving-average mapping is advocated for routine presentation of the results.

Discussion

We have shown that treatment of low-precision broad-scale reconnaissance data by moving-average techniques will achieve the stated aim of locating patterns in the distribution of the elements related to broad-scale features. In other types of survey, however, the aim may be to locate a more specific target, such as

pling error is now greatly in excess of the analytical error in most cases. The variance of iron and manganese is pronounced over all rock types, and the effects of heterogeneity of the granites and possible contamination around the Zoar basic igneous rocks is very marked.

It is clear that in any investigation in which accurate concentration levels at individual sample sites are of paramount importance carefully designed sampling experiments should be carried out prior to the survey to enable the magnitude of the sampling variability effects to be determined.

For example, the sampling and analytical variance between replicate samples at one locality, between localities in one stream, between streams draining one rock type, between rock types, and so on, could be determined. Such a nested or hierarchical sampling design could then be analysed by an analysis of variance. This would enable the sampling (or analytical) level at which error is most important to be located and, hence, the design of subsequent collection methods to reduce this error to be optimized. Sample variability will probably be determined to a great extent by variation at a relatively localized level, say, within a stream. In order to obtain the best estimate of the mean element concentration at a given locality it may prove to be more efficient to obtain several samples from scattered sites and average these individual results

Table 7 Comparison of population mean and analytical variance ratio (r) and precision (ϕ) for stream sediments based on atomic absorption analyses

Element	Sandstone[a]		Sandstone[b]		Shale[c]		Shale[d]		Limestone[e]		Basic igneous[g]		Granite[h]		Granite[i]		Detection limits[j]
	r	ϕ	r	ϕ	r	ϕ	r	ϕ	r	ϕ	r	ϕ	r	ϕ	r	ϕ	
Cu	6·8	5	13	5	6·7	16	3·5	9	39	17	6995	14	1875	11	639	4	2
Ni	7·1	8	(3·5)	14	3·5	12	6·0	5	8·2	14	—	6	n.d.	n.d.	85	14	10
Mn	92	14	7·9	12	22	7	17	6	34	7	5434	5	(8)	16	1214	3	3
Fe	49	4	33	3	15	5	2711	3	14	5	120	5	33	6	127	4	5
Co	(2·2)	18	—	13	(2·1)	17	(1·5)	9	143	0	18	11	n.d.	n.d.	233	5	5
Zn	37	6	16	4	51	4	5·4	3	21	5	10633	5	421	7	267	4	1
Pb	n.d.	n.d.	7·4	5	n.d.	n.d.	2·0	6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	187	5	18
n	20		20		18		21		21		12		30		10		

For explanation of symbols see Table 2.

the occurrence of individual mineral deposits, and operational criteria may dictate the use of a more precise analytical technique, making the sampling error relatively more important. In order to investigate the magnitude of this effect the replicate samples discussed above were reanalysed with greater precision by atomic absorption spectrophotometry for copper, nickel, manganese, iron, cobalt, zinc and lead. A nitric–perchloric acid sample attack was employed, and analysis was carried out by use of a Perkin-Elmer 403 instrument with an air–acetylene flame under standard operating conditions. The results obtained (Table 7) clearly show that with analytical precisions under 20 per cent the sam-

rather than to collect a single bulk sample from one site.

The magnitude of the sampling problem will depend on the element being determined and the objectives of the survey. Cost-effectiveness should be the criterion used in the final decision-making about the type of sampling plan to be adopted, it being borne in mind that the sample collection is likely to be the most expensive part of the operation.

Conclusions

The aim of preliminary geochemical reconnaissance at the regional level is to locate patterns in the distribution of elements related to broad-scale features (e.g. mineral

districts as distinct from individual mineral deposits). Low-precision emission spectrographic analysis of the unground −80-mesh fraction of the stream sediment, followed by moving-average smoothing, gives a satisfactory approximation to the regional geochemical surface at minimum cost. The sampling error, however, becomes of relatively great importance when more precise analytical techniques are used, and when individual sample-site truth is required. The potential value of carefully controlled hierarchical analysis of variance should be investigated as a means of isolating the main variance components before a decision is taken on the final sampling and analytical techniques to be adopted.

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Appendix 1

One-way analysis of variance method used

Taking duplicate samples at each site, let $Y_{ij} = j$th observation from the ith site, where $i = 1, 2, \ldots, k$ and $j = 1, 2$
Then let

$$\bar{Y}_{i\cdot} = \frac{Y_{i1} + Y_{i2}}{2}$$

and

$$\bar{Y}_{\cdot\cdot} = \frac{\sum_k (\bar{Y}_{i\cdot})}{k}$$

We may then derive the analysis of variance table of Table 1.

Table 1   One-way analysis of variance model

Source of variation	df	Sum of squares	MS	E(MS)
Among sites	$(k-1)$	$\sum_i \left(\bar{Y}_{i\cdot} - \bar{Y}_{\cdot\cdot}\right)^2 = S_t^2$	$\dfrac{S_t^2}{(k-1)} = A$	$\sigma^2 - 2\sigma_\mu^2$
Among samples within sites	k	$\sum_i \sum_j \left(\bar{Y}_{ij} - \bar{Y}_{i\cdot}\right)^2 = S_s^2$	$\dfrac{S_s^2}{k} = B$	σ^2

df, degrees of freedom; MS, mean square; E(MS), expected mean square.

An initial estimate of the variance of the population means (σ_μ^2) is given by $(A - B)/2$, since there are two samples per site. We may, however, write the residual variance (σ^2) as

$$\sigma^2 = \sigma_a^2 + \sigma_e^2$$

where σ_a^2 is the analytical determination variance for the element in question, and σ_e^2 is a random error component. We may then determine if the mean element values at the sites are equal by testing if $\sigma_\mu^2 = 0$, by taking the ratio (A/B) and referring to F-tables on $((k-1), k)$ degrees of freedom at, say, the 95 per cent confidence $(0 \cdot 05$ significance) level. Let the observed analytical variance (C) be used as an estimate of σ_a^2. It is now possible to test whether the within-site random error component $\sigma_e^2 = 0$ by taking the ratio B/C and referring to F-tables on $(k, 10)$ degrees of freedom. If σ_e^2 can be considered to be zero either *a priori* or otherwise, then we can allow for the analytical variance C in estimating σ_μ^2. The new estimate of σ^2 (which will no longer contain a σ_e^2 component) will be $(B + C)/2$, and, hence, the final estimate of the variance of the population means will be

$$\hat{\sigma}_\mu^2 = \left(\frac{A - \dfrac{B + C}{2}}{2}\right)$$

(If this result is negative, it is customary to set it to zero.)

Appendix 2

Moving-average map error in terms of analytical precision

The sample size n needed to obtain an estimate m of the mean μ_x of the universe, in this case the data-point values, with a probability P that the amount of sampling error in m is not more than k units in absolute magnitude is obtained by solving for n the equation

$$\frac{t \cdot S_x}{(n-1)^{\frac{1}{2}}} = k \qquad . \qquad . \qquad . \quad (1)$$

where S_x is the observed standard deviation. Then

$$n = 1 + \left(\frac{t \cdot S_x}{k}\right)^2 \qquad . \qquad . \qquad . \quad (2)$$

and at the 95 per cent confidence level (two-tail test)

$$n = 1 + (1 \cdot 96 \, S_x/k)^2 \qquad . \qquad . \qquad . \quad (3)$$

Hence, the confidence belt on μ_x when σ_x for the universe is unknown is

$$m_x - \frac{1 \cdot 96 \, S_x}{(n-1)^{\frac{1}{2}}} < \mu_x < m_x + \frac{1 \cdot 96 \, S_x}{(n-1)^{\frac{1}{2}}} \qquad . \qquad . \quad (4)$$

Defining the analytical precision at the 95 per cent confidence level for the element being mapped as

$$\phi = \frac{1 \cdot 96 \, S_x}{m_x} \times 100 \qquad . \qquad . \qquad . \quad (5)$$

Let the error in determination of the mean be

$$\epsilon = \frac{k}{m} \times 100 \qquad . \qquad . \qquad . \quad (6)$$

Rearranging equations 5 and 6 in terms of S_x and k, and substituting in equation 3, we obtain

$$n = 1 + \left(\left(\frac{m\phi}{100}\right) \Big/ \left(\frac{m\epsilon}{100}\right)\right)^2 = 1 + \left(\frac{\phi}{\epsilon}\right)^2 \qquad . \qquad . \quad (7)$$

Hence, the error in the moving-average surface (ϵ) as a function of analytical precision (ϕ) and number of points per cell n is given by

$$\epsilon = (\phi^2/(n-1))^{\frac{1}{2}} \text{ per cent} \qquad . \qquad . \quad (8)$$