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TECHNIQUES TO DETERMINE THE QUALITY OF GEOCHEMICAL DATA: EXAMPLES FROM REGIONAL LAKE SEDIMENT GEOCHEMICAL SURVEYS IN NEWFOUNDLAND

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ABSTRACT

The quality of geochemical data imposes limitations on how the data can be manipulated, displayed and interpreted. Geochemical data from the regional lake sediment survey of Newfoundland are used to illustrate a number of approaches to the evaluation of data quality, and to show the implications of such an evaluation on data presentation.

INTRODUCTION

Powerful software programs for statistical analysis and the display and enhancement of spatial patterns present in geochemical data are now available for microcomputers at reasonable cost. These new programs promise to be invaluable for the interpretation of exploration geochemical data, with their promise being limited only by the quality and consistency of the survey data. Indeed, because some techniques such as shaded relief plots can reveal subtle spatial features in geochemical data, it is important to ensure that these are not merely artifacts in the data due to errors. Furthermore, evaluation of data quality guides the proper choice of display and the interpretation of the geochemical results. For example, it provides an objective basis for deciding whether an element distribution should be contoured or presented as a discrete-symbol map, and, if contoured, on the choice of contours and implications for the resultant map's reliability. Provided that the system for monitoring data quality is designed appropriately, the relative contributions of analytical and sampling errors can be evaluated, so that if the reproducibility of an element is judged to be unsatisfactory, it can be determined whether laboratory or field procedures should be changed. Finally, where two multi-element analytical methods provide data for the same element, an objective assessment can be made of which method provides the better data.

The examples used here are from the regional lake sediment survey of Newfoundland. Quality is being carefully assessed for these data as part of a project to apply image analysis techniques to their interpretation. Most of the analytical data referred to was from a multi-element, instrumental neutron activation technique (INAA), which was discussed by Davenport (1988).

TECHNIQUES FOR DATA-QUALITY EVALUATION

The underlying assumption in geochemical surveys is that the spatial distribution of a particular element in the chosen sample medium reflects its distribution in the upper part of the earth's crust. Orientation studies are typically conducted to establish the appropriate sample medium, sample density, and analytical techniques. During the subsequent regional survey, it is most important to monitor the reproducibility or repeatability of the data to ensure that the survey specifications developed in the orientation study are met, and to be able to evaluate the overall reliability of the mapped element distributions. This is particularly important in large multi-year, multi-element surveys.

Two main aspects are generally considered in evaluating data quality: consistency of the analytical data throughout the survey, and the reproducibility of results in separate samples from the same site (e.g., the same lake). Both are important, although it is the variability shown by independent samples from the same site (i.e., the sum of both analytical variation and variation due to inhomogeneity in the sample medium) that controls the ultimate reliability of the element distribution map. In the lake sediment geochemical survey of Newfoundland, data quality is determined from the results of control reference materials and laboratory splits of single samples (analytical variance), and site duplicate samples (combined sampling and analytical variance). The identity of these three types of quality-control sample is concealed from the analyst, and each provides a unique perspective on data quality.

Analytical Variance

Techniques for, and the rationale behind, systematic monitoring of analytical quality have been reviewed by Thompson (1983). A total of 33 control reference materials, in conjunction with laboratory splits, were used to monitor analytical variance for the multi-element neutron activation analysis project.

Control reference samples. Ideally, control reference samples should be as close as possible in physical, mineralogical and chemical composition to the samples collected in the survey. The 33 control reference materials used are listed in Table 1, from which it can be seen that the majority (18) are lake sediment. Of the 708 individual determinations of control samples, over half were of internal lake sediment control materials used for routine analytical control in the Department of Mines and Energy laboratory (C-21 to C-31; Table 1). The Geological Survey of Canada (GSC) internal lake sediment controls, (CR-M, CR-P, CR-R) were included to allow a tie-in to the National Geochemical Reconnaissance (NGR) data in Labrador. The Canadian Centre for Mineral and Energy Technology (CANMET) materials MRG-1 and SY-2, and GSC/CANMET materials LKSD-1 to 4, STSD-1 to 4 and TILL 1 to 4 will allow comparison of the Newfoundland lake data with other NGR data sets, and will ultimately enable the accuracy of the data to be established. All these reference materials are useful in monitoring analytical precision and batch-to-batch consistency.

Method. The first step was to calculate a mean and standard deviation for each element in each control sample, and to identify outliers. Outliers were arbitrarily defined as values falling more than 2.5 standard deviations from the mean. This process was iterative, with the mean and standard deviation being recalculated after the identification and removal of outliers, until all remaining values fell within the ± 2.5 standard deviation range.

Variations in level from batch-to-batch, can be identified from plots of the values for each control, against the order in which they were analyzed. This can be done for each element from each control reference material but, with 33 different control samples and 28 elements to consider, the number of plots becomes unmanageable. The results can be conveniently summarized for each element by dividing the values for each control sample by the mean value, thus normalizing the data as shown for La in Figure 1. Values close to the overall mean, plot close to unity, whereas values significantly higher or lower than the mean, deviate markedly from unity. If the data are consistent throughout all the batches, the normalized values should cluster uniformly about a horizontal straight line. A noticeable slope indicates drift, e.g., for Br (Figure 2); a discontinuity, indicates a calibration change, e.g., for Lu (Figure 3). Smooth trends, such as for Br, where the regression of normalized value against order of analysis is significant ($r=0.34$, significance <0.0001), can be quantified by regression of the normalized values against analytical order.

The amount of scatter of element ratios is indicative of overall precision in the control samples. As is shown below, precision for most elements varies with absolute level, usually being highest near the analytical detection limit, and for many elements the control samples span a wide concentration range. Because the data are normalized, it is not possible to distinguish high- from low-absolute values in Figures 1 to 3, and the scatter makes trends hard to see for some elements.

Plotting precision against mean concentration in the control samples for each element illustrates the relationship between these parameters. Precision, p, is calculated in the usual manner in geochemistry (Thompson, 1983) at the 95 percent confidence level.

Table 1. Identity, nature, and source of control reference materials used to monitor analytical precision by INAA for Newfoundland lake sediment

ID	N
NDME internal lake sediment controls	
C-21	22
C-22	14
C-23	30
C-24	62
C-25	50
C-26	60
C-27	35
C-28	16
C-29	27
C-30	7
C-31	37
GSC internal lake sediment controls	
CR-M	17
CR-P	15
CR-R	17
NDME internal rock reference samples	
BS-1	11
GD-1	18
GD-2	15
RY-1	17
GSC/CANMET certified reference materials	
MRG-1	24
SY-2	28
GSC/CANMET reference materials to be certified	
LKSD-1	18
LKSD-2	21
LKSD-3	24
LKSD-4	35
STSD-1	13
STSD-2	24
STSD-3	9
STSD-4	11
TILL-1	6
TILL-2	8
TILL-3	7
TILL-4	10

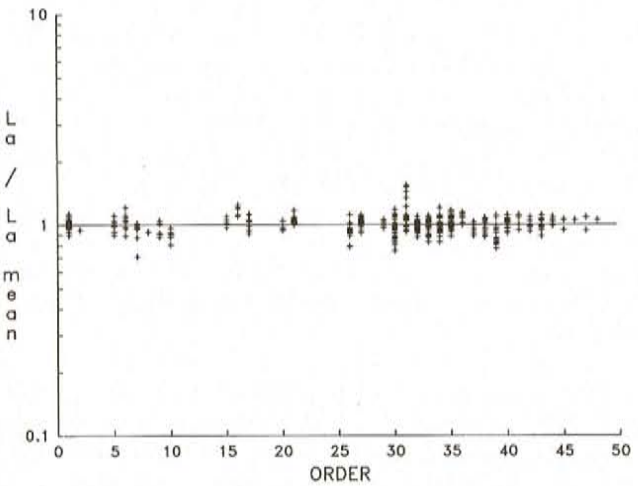

Figure 1. *Ratio of La to mean La in control reference samples plotted against order of analysis.*

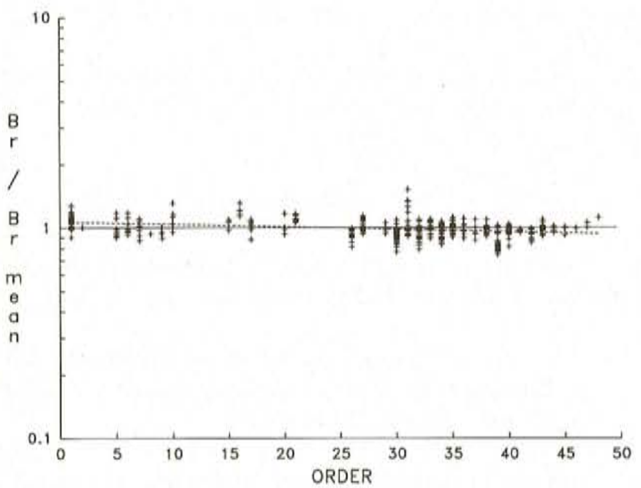

Figure 2. *Figure 2. Ratio of Br to mean Br in control reference samples plotted against order of analysis.*

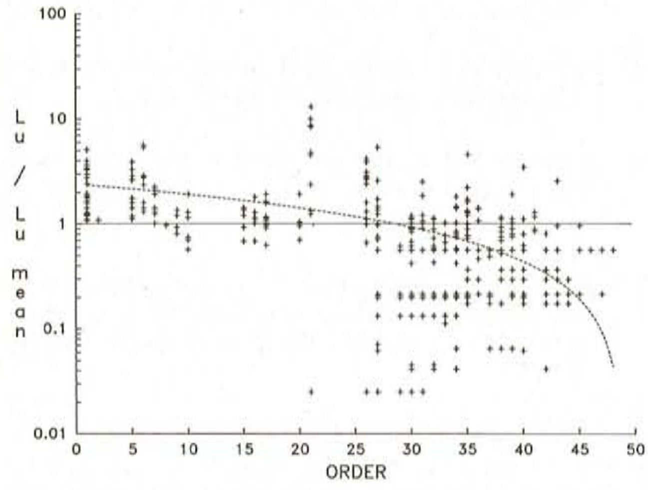

Figure 3. *Ratio of Lu to mean Lu in control reference samples plotted against order of analysis.*

$$p = (2s/X) \times 100\%$$

where s is the standard deviation of the values and X is the mean value.

An example is shown for Sb (Figure 4), which shows that precision in controls containing more than about 0.3 g/t is essentially constant and better than ± 25 percent, but below 0.3 g/t, it deteriorates rapidly to more than ± 100 percent. An estimate of the effective detection limit can be obtained using the criterion that it is the concentration at which precision reaches ± 100 percent (Fletcher, 1986); in the case of Sb, it is about 0.09 g/t. Other elements such as La (Figure 5) show precision to be almost constant at better than ± 25 percent throughout the concentration range shown by the control samples (i.e., all of the range is within the flat part of the Sb curve corresponding to Sb values > 0.3 g/t in Figure 4). Elements such as Au give rise to plots similar to the steep part of the Sb curve, where most of the samples have Au values below the detection limit.

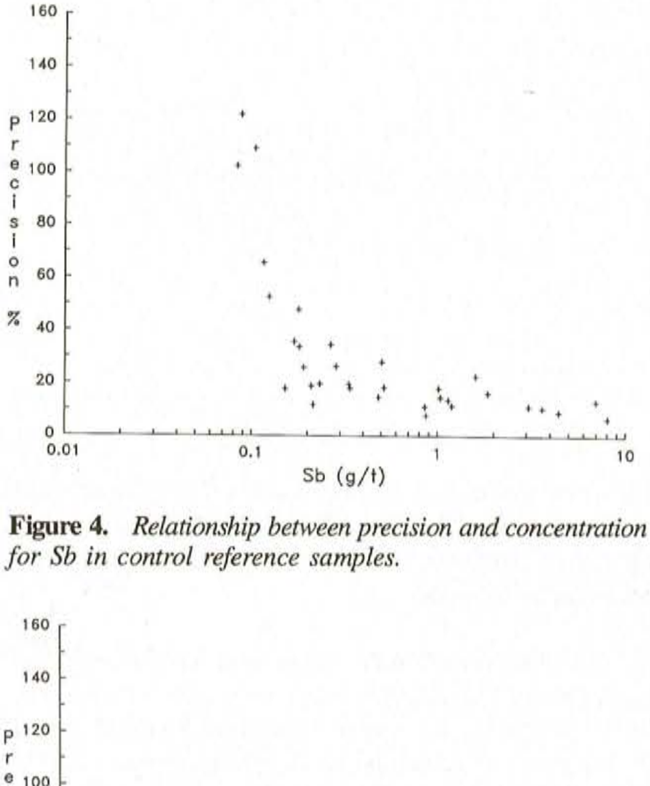

Figure 4. *Relationship between precision and concentration for Sb in control reference samples.*

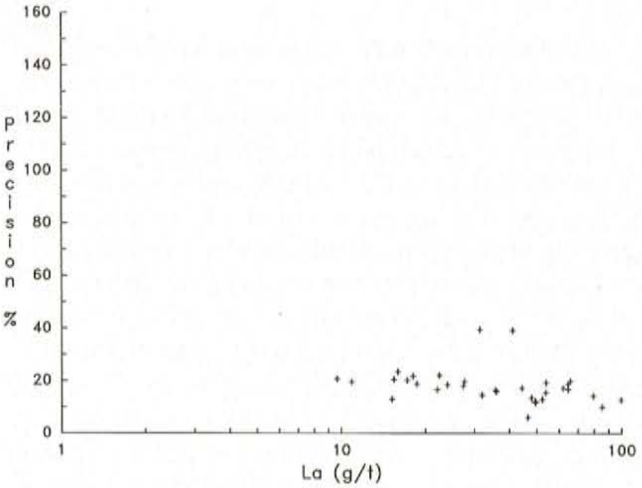

Figure 5. *Relationship between precision and concentration for La in control reference samples.*

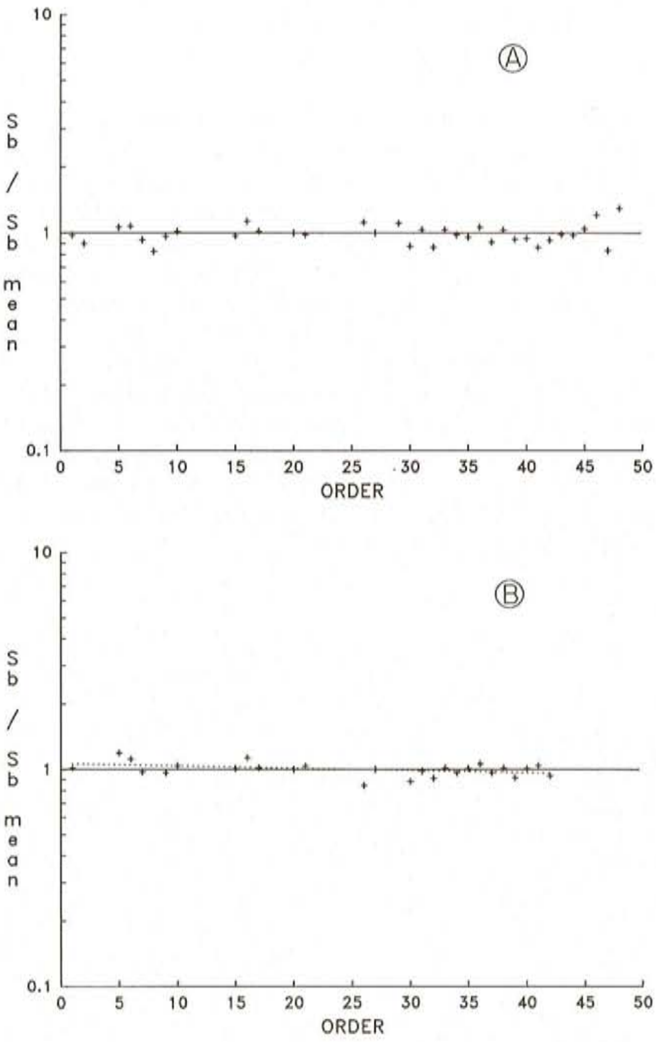

Figure 6. *Overall ratio of Sb to mean Sb for each analytical batch in control reference samples plotted against order of analysis: a) for mean Sb levels > 0.1 ppm; and b) for mean Sb levels > 0.5 ppm.*

Whereas batch to batch variation is fairly clear in the case of Br and Lu (Figures 2 and 3), in other cases where drift is subtle and the scatter is large, due to the inclusion of data from control samples at or near the detection limit, the identification of drift is difficult or impossible, either visually or through regression analysis. This scatter can be reduced by removing the control samples with mean element values near or below the detection limit. The effect of this is illustrated for Sb (Figure 6a). A statistically significant overall decrease in Sb level with analytical batch is noticeable when only controls having higher Sb values are considered (Figure 6b), but these trends are lost in the background noise in Figures 4 and 6a. From plots such as Figures 1, 2 and 6b, longer term drift can be better assessed, and, if statistically significant, a correction factor can be computed from the regression equation.

Laboratory splits. One in every set of 18 samples collected in the field, was divided into two subsamples after sieving. Each one of the pair was assigned a different, non-adjacent sample number and submitted for analysis in a way indistinguishable from the other samples. From the results of these laboratory duplicates, analytical precision may be estimated. The advantage of laboratory duplicates over control samples, is that when prepared and analyzed in this way throughout the analytical program, they constitute a subset truly representative in composition of the entire sample set. However, they do not give any indication of batch to batch variations.

The approach used to estimate precision was devised by Thompson and Howarth (1978), which is based on the assumption that the standard deviation of analytical error (S_c) varies as a linear function of concentration (c), thus

$S_c = S_o + kc$ ....(1)

where S_o is the hypothetical standard deviation of measurement at zero concentration and k is a constant.

Using a similar definition of analytical precision, Pc, at the 95 percent confidence level as employed for the control samples, where $P_c = 2\ S_c/c$,

then $P_c = 2\ S_o/c + 2k$......................(2)

The values of S_o and k may be estimated from the duplicates as follows (Thompson and Howarth, 1978):

1) calculate the means and absolute values of the differences of the pairs of duplicate analyses, $(X_1 + X_2)/2$ and $|X_1 - X_2|$ respectively;

2) sort the pairs of results, their differences and means in order of increasing mean value;

3) assign the sorted results to groups of eleven, ignoring the last group if it contains less then eleven results;

4) for each group obtain the overall mean of the mean concentrations and the median difference;

5) compute the regression equation for the median difference (dependent variable) against group mean (independent variable);

6) from the regression, the intercept is a measure of S_o and the slope a measure of k (strictly, these values should be multiplied by 1.048, Thompson and Howarth, 1978)

Equation (2) has the form of a hyperbola, a form of plot shown by most elements for the analytical duplicates (e.g., Sb in Figure 7). At higher values, where the curve is approximately horizontal, precision tends to a constant value, p ≈ 2k from equation (2). Using the practical definition of detection limit,

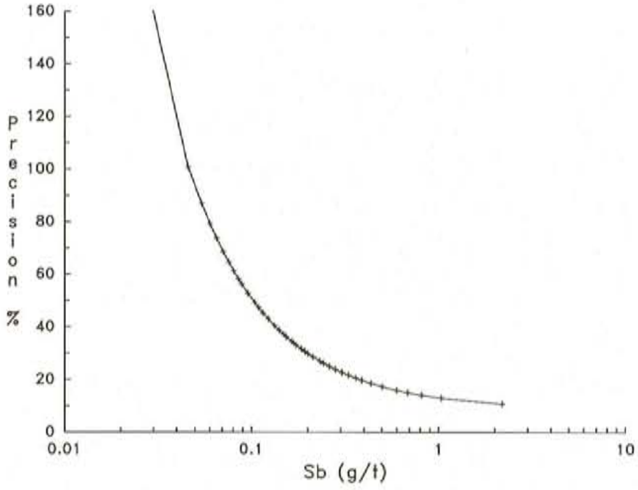

Figure 7. *Plot of precision against concentration for Sb in laboratory duplicates of lake sediment samples.*

Cd, when Pc = 1.0 (equivalent to 100 percent as discussed for the control samples), the value of Cd can be estimated from the curve in Figure 7, where it is 0.05 g/t. Alternatively, it may be estimated from the relationship:

$$C_d = 2\ S_0/(1-2k)$$

k=0.005, Cd = 0.05 g/t and S_0 = 0.0225 g/t.
where S_0 and k are derived from the regression equation as in step 6 above.

Of the 28 elements determined by INAA, the analytical duplicates of 22 of them (As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Mo, Na, Ni, Rb, Sb, Ta, Tb, Th, U, W, Yb and Zn) show a relationship between precision and accuracy similar to that shown in Figure 7, although in some cases all values were above the detection limit. Their conformity to this type of plot indicates that precision for these elements follows the form of equation (2), and that analytical errors for these elements are normally distributed (not log-normally). The elements Br, Sc and Sm show an increase in error with increasing concentration (e.g., Sc in Figure 8). For these elements, the initial assumption of equation (1) does not hold because the relationship of the standard deviation of analytical errors is not a linear function of concentration (it is lowest in the mid-range, increasing to both higher and lower concentrations).

In the case of Au and Se, precision is very poor, as their levels of abundance in most of the samples are below their detection limits. The approach of Thompson and Howarth (1978) as used for Sb cannot be applied. For Au, the nugget effect could also be contributing to the poor precision, because analytical errors may not be normally distributed (Thompson, 1983), unless the size of sample taken for analysis is very large.

The precision estimates from the control reference samples can be compared with estimates obtained from the laboratory splits using equation (2) to generalize, in a similar way, the relationship between precision and concentration for both controls and lab splits. The result is plotted in Figure 9 for Sb. Note the difference in concentration range covered by the control reference samples and the laboratory duplicates, the latter being representative of the actual lake sediment samples. The slightly poorer precision displayed by the control reference samples is probably due to the effects of batch to batch variation, on top of the within batch variation, which is reflected by the laboratory splits.

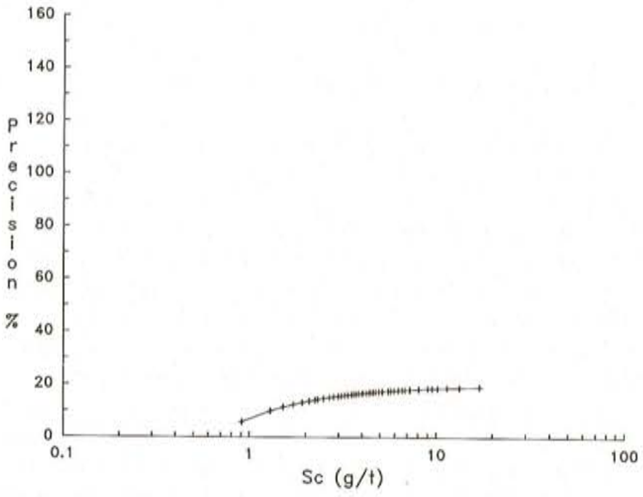

Figure 8. *Plot of precision against concentration for Sc in laboratory duplicates of lake sediment samples and in control reference samples.*

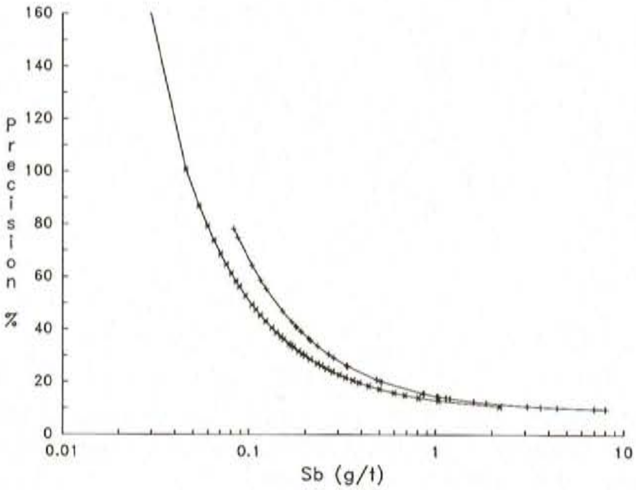

Figure 9. *Plots of precision against concentration for Sb in laboratory duplicates (asterisks) of lake sediment samples and in control reference samples (pluses).*

The estimates of detection limits determined from the analytical duplicates will be somewhat optimistic, as samples below the detection limit quoted by the laboratory are rounded to half that limit. Thompson and Howarth (1978) state that values should not be rounded, but this is usually impractical as most labs will not report negative analytical values that have only abstract meaning.

Combined Sampling and Analytical Errors

Throughout the survey, one lake in 18 was sampled in duplicate by taking two sediment cores at sites 5 to 20 m apart. The approach of Thompson and Howarth (1978), used above for the laboratory duplicates, can be applied as well to the data from site duplicate pairs, and in this case it provides information on the combination of analytical and sampling variations (at the 5- to 20-m scale). For most elements, the resulting plots are similar to Figure 7, implying that equation (1) is still valid, and that a new level of within-lake-variation can be calculated that is equivalent to analytical precision. Figure 10 shows, for Sb, the within-site variation (combined sampling and analytical errors), and the analytical variation both expressed as precision from site duplicates and laboratory duplicates respectively, against concentration. Both curves show the same form, but in detail it is clear that for any given concentration the within-site variance is always greater than the analytical variance. This indicates that for Sb, analytical errors are the main control on reproducibility, but that sample inhomogeneity within the lake makes a measurable contribution, contributing about ±10 percent to the combined sampling and analytical variance of ±20 percent at Sb values > 2 g/t. To improve the overall reproducibility of Sb, especially at lower concentrations, a more sensitive and precise analytical method is required.

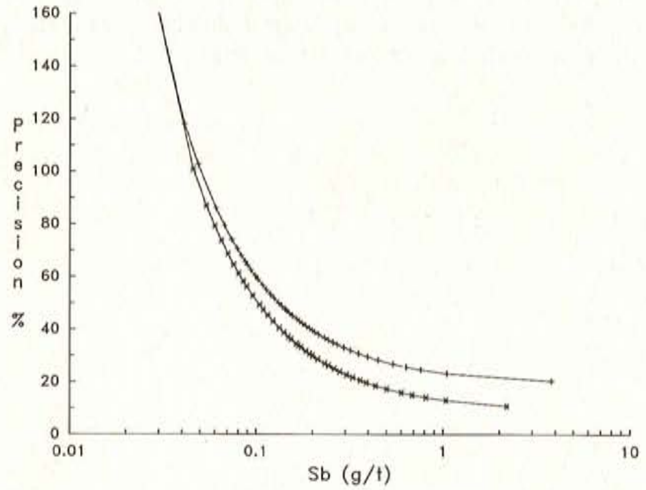

Figure 10. *Plots of precision against concentration for Sb in laboratory duplicates (asterisks) and in site duplicates (pluses) of lake sediment samples.*

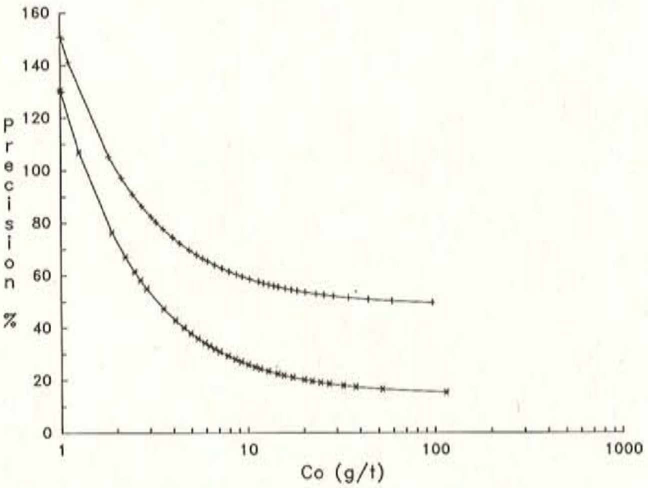

Figure 11. *Plots of precision against concentration for Co in laboratory duplicates (asterisks) and in site duplicates (pluses) of lake sediment samples.*

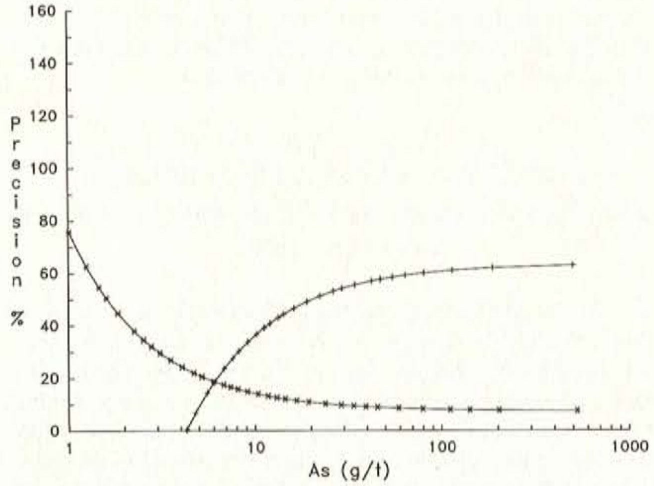

Figure 12. *Plots of precision against concentration for As in laboratory duplicates (asterisks) and in site duplicates (pluses) of lake sediment samples.*

The situation for Co (Figure 11) is somewhat different. Here, although analytical variation is significant at low concentrations, at higher levels (> 10 g/t), sample inhomogeneity contributes about 30 percent of the rather poor overall precision of ± 50 percent in the site duplicates. For As (Figure 12), the precision plot for the site duplicates shows a different form, implying the assumption of equation (2) is not valid in this case (although it is for the laboratory duplicates). For the site duplicates, the errors no longer vary linearly with concentration, as is illustrated in Figure 13, where the median difference in each group is plotted against concentration (on a log scale). The median difference, a measure of analytical errors, is relatively constant below about 10 g/t As, but increases rapidly at higher values. This type of curve yields a negative intercept when a regression line is fitted, and this results in the form of the curve for site duplicates in Figure 12.

An alternative approach is to log-transform all the data before analyzing the analytical and sample-site variance. The main disadvantage of doing this is the unfamiliarity for most people in dealing with log-transformed data, but this is outweighed by the fact that most trace-element data in geochemical surveys are closer to a log-normal distribution then a normal distribution.

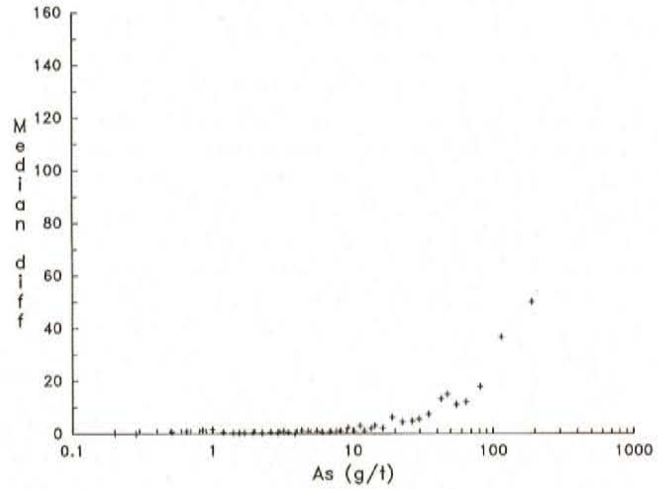

Figure 13. *Plot of the median differences (g/t) between pairs of site duplicates against their average concentration (on a log-scale) for As.*

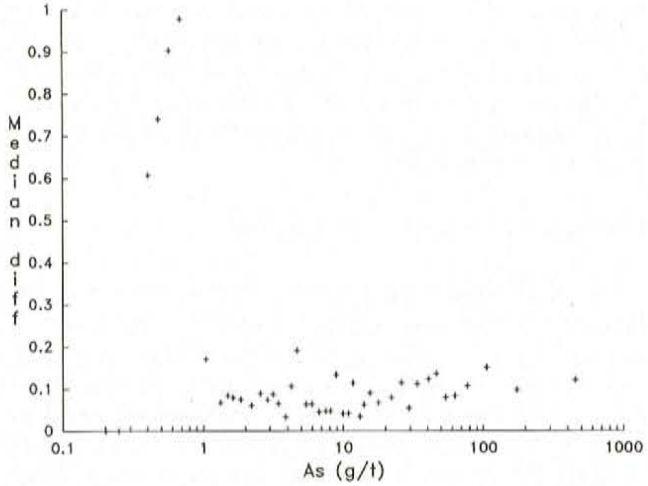

Figure 14. *Plot of the median differences between site-duplicate pairs against their average concentration for log-transformed data for As.*

Figure 14 shows a plot of the median difference of pairs of site duplicates plotted against their mean concentration for log-transformed As data. The median difference gives a measure of the combined sampling and analytical variance. Although the data show some scatter, above about 1.0 g/t, the median difference, is essentially constant at about 0.1 log units; below 1.0 g/t median difference values increase sharply, indicating that this value is the effective detection limit. This detection limit compares well with those estimated for As from the laboratory duplicates and control reference materials. Clearly, there is no simple, linear relationship between the median difference and concentration for the duplicate pairs in the log-transformed data, so it would be inappropriate to regress the median difference against mean concentration as was done for the untransformed As data, hence an estimate of standard deviation as a function of concentration cannot be obtained from equation (1). Instead, the standard deviation of the duplicates over the range of concentrations was determined as follows, using an approach modified from Garrett (1973);

1) calculate the means $(X_1 + X_2)/2$ and the squares of the differences $(X-X_2)^2$ of the log-transformed data;

2) sort the pairs of results, their squared differences and means in order of increasing mean value;

3) assign the sorted results to groups of 30, ignoring the last group if it contains less than 30;

4) for each group calculate the mean of the means, and the standard deviation of the variation between paired values from the relationship

$$S_{SA} = 1/2N \sqrt{\Sigma(X_1-X_2)^2} \quad . \; . \; . \; . \; . \; (3)$$

where N is the number of pairs (in this case 30).

The group size of 30 is chosen to obtain a fairly reliable estimate of the standard deviation (following Garrett, 1973), so a fairly large, total number of duplicate pairs is required to cover a reasonable concentration range. The result for As in site duplicate pairs is shown in Figure 15. Combined sampling errors are lowest in the 2 to 8 g/t As range (better than 0.10), increasing to 0.15 at higher As levels, and increasing rapidly to more than 0.30 below 1 g/t. Using a two-standard deviation margin of error, a standard deviation of 0.15 translates to a error factor of antilog (2 x 0.15) = 2. Applied to an As value of 100 g/t, this would give a margin of error from 50 to 200 g/t. Error margins larger than this indicate data that are semi-quantitive at best, so a standard deviation of 0.15 for the combined sampling and analytical error for log-transformed data is a limit comparable to the ± 100 percent precision limit, commonly used to define analytical detection limit.

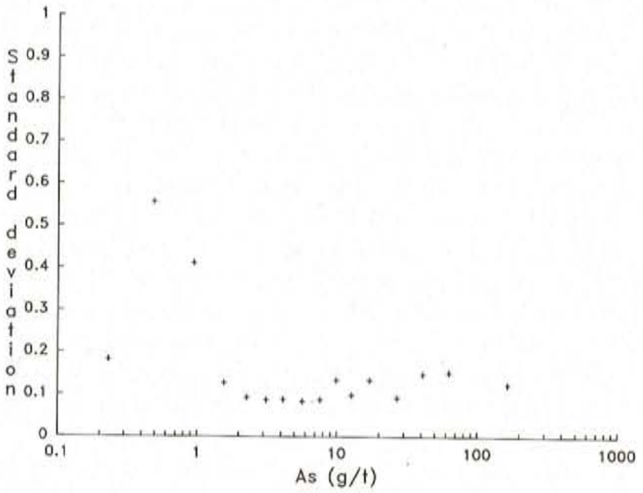

Figure 15. *Plot of the standard deviation from site-duplicate pairs against their average concentration for log-transformed data for As.*

The results from analytical duplicates can be treated in the same way, and the results for As are plotted in Figure 16. As expected, the standard deviation is smaller than for the site duplicates, averaging about 0.05 above 3 g/t. Below 1 g/t, the standard deviation of analytical error increases rapidly to more than 0.30, indicating again, a 1 g/t detection limit for As.

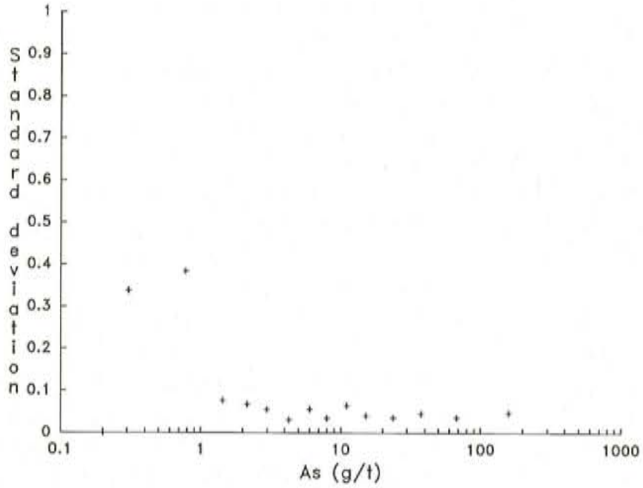

Figure 16. *Plot of the standard deviation from laboratory-duplicate pairs against their average concentration for log-transformed data for As.*

PRACTICAL APPLICATIONS

Very commonly, the results from geochemical surveys are reviewed cursorily, the obvious anomalies identified, often in an *ad hoc* manner, and these alone form the basis for further exploration. In the early years of geochemical surveys, anomaly detection was the main purpose of the survey and often their design, particularly their analytical methods, limited them to this goal. Today, quantitative multi-element geochemical analysis is the norm, and when sampling design is appropriate, to merely focus on obvious anomalies is to ignore a great deal of subtle information that is relevant to mineral exploration. Models have been developed for a large number of different mineral deposit types that predict variations in the geochemical background around deposits in elements other than the ore metals. In many cases, these associated patterns, which may be due to enrichments, depletions or a characteristic spatial redistribution (e.g., zoning), are substantially larger than the primary dispersion patterns of the ore-elements themselves. The integration of these models with the interpretation of geochemical survey data can greatly aid in mineral exploration programs. In many cases, the patterns characteristic of mineralizing processes sought in the geochemical data are within the mid-concentration range of the data, or even at their lower end. Also, spatial patterns commonly reflect geological structure, which are manifest as local contrasts in level of the data, not patterns of extreme enrichment (or depletion), and therefore not anomalies in the classical sense.

The steps of data-quality evaluation outlined above are more than exercises. Significant batch to batch variation can give rise to spurious spatial patterns when the data are plotted together, and therefore, data-levelling using the results of control reference materials is essential. To bring out patterns in the high-, intermediate- and low-element concentration ranges, requires subdividing the data in a manner consistent with their quality: too few subdivisions may mask real but subtle features; too many will produce a cluttered plot where these features may also be hidden. The site duplicate data provide information on appropriate contour intervals, and, together with the laboratory duplicates, on realistic detection limits.

Data-quality evaluation can also provide the basis for determining which analytical method provides the better data for an element determined by two methods—an increasingly common situation with multi-element analytical methods. Finally, for elements for which the combined sampling and analytical errors are deemed too large to allow expected subtle features to be discerned in the data, the relative contributions of analytical and sampling errors may be compared, and the necessary remedial measures identified. These measures would include seeking a more sensitive and precise analytical technique (a fairly low-cost prospect if sample material has been archived) or, if the sampling strategy is inadequate, initiating a new survey.

Data Correction and Data Selection

Data levelling. If the results of control reference materials indicate a smooth trend in concentration level with order of analysis (Figure 7), levelling of the data should be considered, because where results from an earlier batch plot next to results from a much later batch, a discernible boundary discontinuity is likely. If the trend is smooth and linear, the regression equation can be used to calculate consistent values. When the GSC/CANMET control reference materials are standardized, it should be possible to adjust the data to correspond to the recommended values.

For elements that show an abrupt break or breaks in level, it may also be possible to level the data in some cases, but for Lu (Figure 3), the data are rather noisy and the change is so large that many of the later analyses fall below the detection limit, so the data are therefore of little use.

Comparison of different analytical techniques. Low-cost, multi-element analytical methods are becoming commonplace, and there is usually some overlap in the element suites offered. Assuming that two methods provide comparable data (e.g., both provide total-element values, not a partial extraction), an objective way to determine which method provides the better data is useful. Plotting the variation of precision with concentration for the laboratory duplicates provides a rapid visual method. Figure 17 shows that the Co data by atomic absorption are more precise over the whole concentration range than the results by INAA.

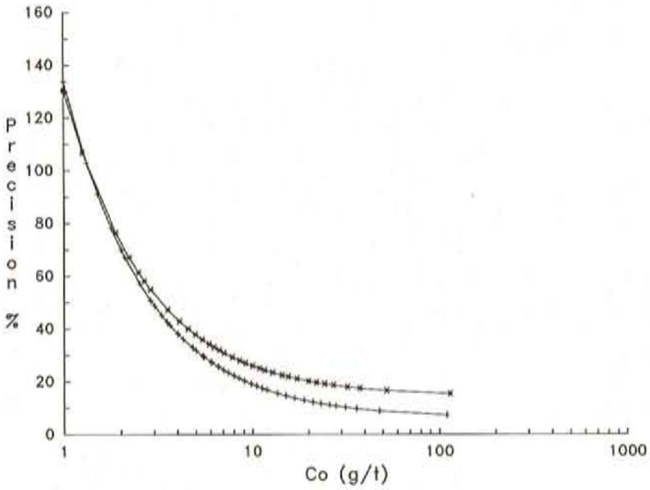

Figure 17. *Plot of precision against concentration in laboratory-duplicate pairs for Co by AAS (pluses) and INAA (asterisks).*

Data Presentation

Although sometimes regarded as cosmetic, proper presentation of geochemical survey results is as important as proper sampling and analysis. There are two main considerations: the relationship of the frequency distribution of the data and its components to spatial, geological features, and the limitations imposed by the quality of the data itself. Both of these considerations must serve the overall objectives of the survey. For discussions of the analysis of frequency distributions in exploration geochemistry, the reader is referred to Sinclair (1976, 1983) and Stanley (1987). The constraints imposed by data quality can be determined from an analysis of the analytical and site duplicate data, which can determine whether the data may be usefully contoured, and if so, provide a realistic detection limit and minimum interval for the contours.

Table 2. Comparison of total variance to combined sampling and analytical variance from site duplicates for element data by INAA for Newfoundland lake sediment samples; all data were log-transformed

Element	Variance		F-Ratio
	Total Data S^2_D	Site Duplicate S^2_{SA}	$F = S^2_D/S^2_{SA}$
As	0.6839	0.04721	14.5
Au	0.0433	0.03160	1.4
Ba	0.1482	0.04004	3.7
Br	0.1190	0.01241	9.6
Ce	0.1600	0.01218	13.1
Co	0.3341	0.04455	7.5
Cr	0.1369	0.03157	4.3
Cs	0.1681	0.01928	8.7
Eu	0.1211	0.06033	2.0
Fe	0.2294	0.01468	15.6
Hf	0.2777	0.07906	3.5
La	0.1197	0.00500	23.9
Mo	0.1376	0.01219	11.3
Na	0.1858	0.01149	16.2
Ni	0.1197	0.03080	3.9
Rb	0.2333	0.04221	5.3
Sb	0.1980	0.03900	5.1
Sc	0.0795	0.00520	15.2
Se	0.0266	0.02000	1.3
Sm	0.1459	0.00887	16.5
Ta	0.1303	0.03172	4.1
Tb	0.1063	0.00866	12.3
Th	0.1332	0.00420	31.5
U	0.3770	0.01918	24.6
W	0.0900	0.01969	4.6
Yb	0.1892	0.04095	4.6
Zn	0.1142	0.02493	4.6

Contour maps or symbol maps. Contour maps are the most widely used format for presenting data that vary continuously over the earth's surface. They have been commonly used in displaying geochemical data, although symbol plots are preferred by some (e.g., the Geochemical Atlas of Fennoscandia, Bolviken *et al.*, 1986). Garrett (1969, 1973) addressed the problem of testing the relationship of the combined sampling and analytical variance (within-site variance from site duplicates) to the total variance of the data. The between-site variance should be substantially greater than the within-site variance, if the data are likely to show clear spatial patterns, and be suitable for contouring. Values of the variance ratio for the INAA data for Newfoundland lake sediments are listed in Table 2. The F-ratios may be compared to the initial value of Fisher's F (for 519 pairs of site duplicates critical F is 1.25 at the 99 percent confidence level). All elements have an F-ratio substantially greater than 1.25, except for Au and Se, and thus may be usefully contoured. For Au and Se, symbol plot maps may be more appropriate, although this is not to imply these data will show no real spatial patterns at all. Indeed, Au in lake sediment in Newfoundland is a very useful exploration guide (Davenport, 1989; Davenport and McConnell, 1988). Such spatial patterns in noisy data are due to autocorrelation between neighbouring samples, (*see* Stanley and Smee, 1988, 1989).

Establishing a realistic detection limit. For most trace elements, the analytical techniques used in exploration geochemistry cannot adequately determine the lowest abundance levels encountered in the materials sampled. The uncertainty of measurement typically increases at very low levels to the point where the reliability of the data can no longer be assessed. This lower limit is the practical detection limit, and is usually taken as the concentration level at which the margin of error about this level is equal to the level itself. This is usually determined from the analytical duplicates as already described, although in many cases this value increases when sampling errors are considered, and a more realistic limit for contouring may be determined from the site duplicates.

Contour levels and map reliability. A common approach to selecting contour intervals is to choose an interval equal to twice the standard deviation of the measurement errors (Sharp, 1987). In the case of geochemical surveys, this would be twice the combined sampling and analytical errors, so that if a site were resampled using the same method employed in the original survey, the result should lie within one contour level of the original value, 19 times out of 20.

Repeatability of survey data was discussed by Garrett (1983), who developed the concept of a reliability factor, (RF) given by the expression

$$RF = \text{antilog}\ (k \sqrt{S^2_{SA}}):$$

where k is a constant dependent on the number of duplicates (it is approximately 2 if the number of duplicates exceeds 30, and the 95 percent confidence level is used). The variance term S^2_{SA} is calculated from the entire subset of site duplicates, reflecting the range of concentration found in the whole sample set. As discussed above, for most elements, the combined sampling and analytical variance changes with concentration, implying that contour intervals should be wider at lower values, and may be decreased while keeping the same level of repeatability at high values. A few elements (e.g., As, Figure 15) show lowest S^2_{SA} values at intermediate levels, with higher values both near the detection limit and at the highest concentration levels, due to sample inhomogeneity. Again, other elements show more or less constant values for S^2_{SA} over the entire concentration range, implying that contours may be based on equal log-intervals throughout the range.

The minimum contour intervals and lower detection limit determined from plots of standard deviation against concentration for the log-transformed data may then be applied to cumulative frequency plots of the data to determine the final contour intervals (Figure 18). The maximum number of intervals is determined by the ratio of the data range (above detection limit) to minimum contour interval. In some cases, the contour interval chosen may be greater than the minimum interval to keep the number of contours to a reasonable total.

Evaluation of analytical and sampling errors. From plots such as Figures 10 and 11, which show the relative contributions of sampling and analytical errors as a function of element concentration, the effectiveness of sampling strategy and analytical methods can be evaluated. The analytical precision for Co by INAA is quite good compared with other elements, but it is even better by AAS (Figure 17), so that the combined sampling and analytical error for the AAS data is substantially smaller at all concentrations than the INAA data. The main part of the variance for Co is, nonetheless, due to sample-site variability (Figure 11), suggesting that if combined sampling and analytical errors are to be reduced, it must be by a reduction in sample variability: i.e., the sampling technique must be inproved or another sample medium chosen.

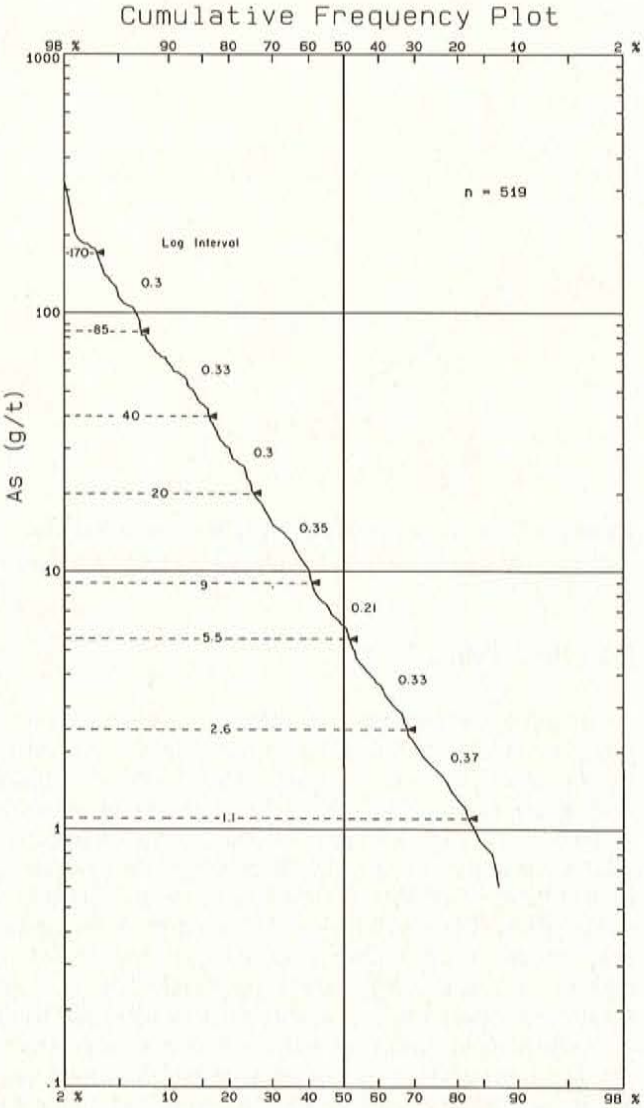

Figure 18. *Subdivisions of As in lake sediment based on cumulative frequency plot using intervals and detection limit from site-duplicate data.*

CONCLUSIONS

The potential of new digital, image-analysis technology to allow a full interpretation of geochemical data is limited fundamentally by data quality. By evaluating the results of control reference samples, laboratory duplicates and site duplicates, this data quality can be assessed. In some cases, batch-to-batch variations in concentration level can be corrected, and from the site-duplicate data realistic methods of data presentation can be selected objectively. Finally, analysis of the results from laboratory and site duplicates permits a retrospective analysis of survey design that can be used to guide both further analytical programs on archived sample material, and the design of further, improved surveys.

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