



**STATISTICAL EVALUATION OF DUPLICATE SAMPLES  
REGIONAL SEDIMENT SURVEYS,  
BRITISH COLUMBIA**

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**INTRODUCTION**

The ability to discriminate real trends related to geological and geochemical causes from those that result from spurious factors such as sampling and analytical errors is of paramount importance in the success of geochemical data interpretation. Since the estimate of reproducibility (precision) allows us to quantify the amount of variation due to sampling and laboratory analysis it is an integral part of the evaluation of geochemical data and should be conducted prior to carrying out any detailed interpretation.

As part of our continuing study of rapid but thorough evaluation procedures for multi-element stream-sediment data (for example, Matysek, *et al.*, 1981) we designed a systematic computer-oriented method of evaluating the quality of geochemical survey data based on field-site duplicates. It incorporates a bias test, an analysis of variance technique, and the Thompson and Howarth (1976) approach to quantifying precision.

This detailed procedure utilizes the type and quality of data incorporated in various regional geochemical programs undertaken by the British Columbia Ministry of Energy, Mines and Petroleum Resources (the Ministry), but can be adapted easily for other programs.

**GENERAL METHODOLOGY**

In brief, our general approach to evaluation of the quality of geochemical data sets involves the following steps:

- (1) Extraction of at least 50 independent, field-site duplicate pairs from a geochemical data set for use in subsequent data analysis.
- (2) Determination of the degree of systematic bias between duplicate pairs based upon the number of cases in which the first observation is greater than the duplicate.
- (3) Evaluation of the duplicated geochemical data set in terms of metal variability at the regional, between-sample site and at the local, within-sample site, sampling, and analytical levels by a two-factor analysis of variance technique.
- (4) Quantification of the within-sample site variability by estimating precision utilizing the Thompson and Howarth (1976) method.

**DATA**

Data obtained from the three most recent regional geochemical surveys undertaken by the Ministry (1981) were evaluated using this method. The base data consist of analyses of stream sediments and water samples collected at an average density of one sample per 17.3 square kilometres over NTS map-sheet areas 92H, 92I, and 92J. Silt samples were field dried and the minus 80-mesh (177 microns) fraction retained for subsequent analyses.

The samples were analyzed for zinc, copper, lead, nickel, cobalt, silver, manganese, iron, molybdenum, arsenic, and antimony by the atomic absorption method. Tungsten was determined colorimetrically, uranium in the water samples was determined by a fluorometric method, and fluoride in stream waters was determined using a specific ion electrode (Garrett, 1975).

Field-site duplicates were also collected to provide information on analytical precision over a range of concentrations and to give some impression of sample representivity or geologic variation. Altogether, 132 pairs of duplicate field-site samples were extracted from the data set. Individual duplicate samples were recorded as 'first' of field-site duplicate and 'second' of field-site duplicate in the publically available general information guide distributed by the Ministry. Duplicates were collected at a density of one per block of 20 samples. The location within the sample block was random so they could not be distinguished from other samples by the contracted commercial laboratory.

Sampling and analytical error associated with zinc, copper, nickel, cobalt, manganese, and iron distributions were investigated by this study. This particular suite of metals were selected for the following reasons:

- (1) The majority of their reported analytical values exceeded their published detection limits.
- (2) Their distributions exhibited a wide range of concentration values.

## BIAS TEST

A characteristic of numerical measurement is inconsistency in repeated measurements of the same quantity. Two types of error contribute to the unreliability of a measurement; random errors arising from the variations inherent to any sampling and measurement process, and non-random errors causing systematic negative or positive deviations from the true results. If these non-random systematic errors are significantly large, precision estimates determined by an analysis of variance or by the Howarth and Thompson method may be suspect, since they are meant to detect random error only.

A bias test was utilized to assess the degree of systematic non-random error between the determined metal contents of the first sample and its duplicate. The test is based upon the number of sample pairs in which concentration in the first sample is greater than that in the duplicate. If there is no bias this number ( $m$ ) should be close to half the total number of ( $n$ ) pairs and the frequency distribution of possible results should correspond with successive terms of the binomial expansion of:

$$[(1/2) + (1/2)]^n$$

The number of duplicate pairs exceeds 50, therefore, its frequency distribution approximates that of the normal distribution, having mean and a standard deviation of  $n/2$  and  $n/\sqrt{2}$  respectively. The observed incidence ( $m$ ) is then converted into the standardized normal deviate. The probability of obtaining a result of ( $m$ ) or greater can be obtained from the usual tables for the areas in the tails of the normal distribution.

## ANALYSIS OF VARIANCE

The second stage in our procedure is to evaluate the geochemical data set in terms of variability at regional (between-sample site) and local levels (within-sample site). Only if a significant proportion of the data variability is at the regional level can one be confident that differences in metal concentrations between-sample sites reflect a real trend related to geological and geochemical features, not merely a consequence of sampling and analytical error.

Significance of metal variability within-sample sites due to sampling and analytical errors versus dispersion between-sample sites can be determined by standard analysis of variance techniques. For our purposes, the significance of the various sources of variation can be determined from logarithmic values of duplicate samples using a two-factor analysis of variance. Theory and assumptions inherent in this method are described by Krumbain and Graybill (1965) and Koch and Link (1971). The formal design for the analysis of variance is given in Table 1.

TABLE 1. ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREE OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F
Error (sampling, sub-sampling, analysis)	$l - 1$	$m \sum_i (\bar{x}_i - \bar{x})^2$	$S_1^2 = \frac{m}{l-1} \sum_i (\bar{x}_i - \bar{x})^2$	$F_1 = S_1^2 / S_3^2$
Geochemical variation	$m - 1$	$l \sum_j (\bar{x}_j - \bar{x})^2$	$S_2^2 = \frac{1}{m-1} \sum_j (\bar{x}_j - \bar{x})^2$	$F_2 = S_2^2 / S_3^2$
Residual	$(l-1)(m-1)$	$\sum_{ij} (\bar{x}_{ij} - \bar{x}_i - \bar{x}_j + \bar{x})^2$	$S_3^2 = \frac{1}{(l-1)(m-1)} \sum_{ij} (\bar{x}_{ij} - \bar{x}_i - \bar{x}_j + \bar{x})^2$	
Total	$N - 1$	$\sum_{ij} (\bar{x}_{ij} - \bar{x})^2$	$S_4^2 = \frac{1}{N-1} \sum_{ij} (\bar{x}_{ij} - \bar{x})^2$	

$x_{ij}$  = result for the  $i$ th replicate from the  $j$ th site;  $i = 1, 2, \dots$  / $l$ th result ( $l$  is usually 2);  
 $j = 1, 2, \dots$   $m$ th result;  $N = lm$  = total number of results;  $\bar{x}_i$  = mean of  $i$ th replicate group;  
 $\bar{x}_j$  = mean of  $j$ th site group; and  $\bar{x}$  = overall mean.

The significance of metal variability between-sample sites (geochemical variation) and metal variability within-sample sites (sampling and analytical errors) is determined from the F-statistic. The value of F, which is significant, can be obtained from standard statistical tables; it is a function of the number of duplicates collected, the number of duplicates collected at each site, and the significance level selected for the investigation. Relative variance components have also been calculated as described by Garrett (1969, 1973) and correspond to the average percentage of variability explained by each source at a sample site.

### THOMPSON AND HOWARTH PRECISION METHOD

The final stage in our evaluation of the quality of geochemical data sets is to quantify the amount of variation due to sampling and analytical error. This variation can be expressed in terms of precision which, in geochemical practice, is specified as the per cent relative variation at the two standard deviation (95 per cent) confidence level:

$$Pc = 2 Sc/C * 100\% \quad (1)$$

where (Pc) is the precision in per cent at concentration (c) and (Sc) is an estimate of the analytical standard deviation (Oc) at that concentration.

Application of analysis of variation techniques can only determine an average precision value for a range of concentrations. In actual fact it has been shown (Thompson and Howarth, 1976) that where there is a wide range of concentrations in a set of samples, both the absolute and relative errors in analytical determinations can vary across the range. To overcome this failing, alternative methods of estimating precision using randomly selected duplicates have been considered by Thompson and Howarth (1973, 1976, 1978) and Howarth and Thompson (1976).

Briefly, their method involves dividing 50 or more duplicate samples into narrow concentration ranges and employing the medium of absolute differences between pairs of duplicate analyses ( $X_1, X_2$ ) as an estimator

of the standard deviation ( $O_c$ ). The group mean value of all the mean average values  $[(X_1 + X_2) / 2]$  is used as an estimator of the average concentration. If this procedure is repeated for a number of successive narrow concentration ranges a set of corresponding mean concentration and standard deviation estimates are obtained. The relationship between them can be found by simple linear regression. From the expression:

$$S_c = S_o + Kc \quad (2)$$

through substitution of (1) above  $P_c$  is given by:

$$P_c = 200 (S_o/c + K) \quad (3)$$

where ( $S_o$ ) is the standard deviation at zero concentration and ( $K$ ) is a constant.

This linear function has been determined in many practical cases to be a satisfactory model for the expression of the variation. In our case, where duplicates were independent samples collected in the field and analysed once each, the method will assess the overall error, which includes both sampling and laboratory error.

The following rapid procedure is suggested for estimation of precision from a minimum of 50 pairs of duplicate samples (Thompson and Howarth, 1976):

- (1) From the duplicate analyses obtain a list of the means and absolute difference.
- (2) Arrange the list in increasing order of concentration means.
- (3) From the first 11 results obtain the mean concentration and median difference from that group.
- (4) Repeat step (3) for each successive group of 11 results, ignoring any remainder less than 11.
- (5) Calculate or obtain graphically the linear regression of the median differences on the means and multiply the intercept and coefficient by 1.048 to obtain ( $S_o$ ) and ( $k$ ), respectively.

In order to assess the significance of the precision parameters obtained from the linear regression, the calculated slope and intercept were individually evaluated by a t-test. Significance of the resulting regression was also determined by an analysis of variance.

## RESULTS

Table 2 illustrates the results obtained from the bias test. From this table we observe:

- (1) Incidence of positive difference in metal content between duplicate pairs is greater than the number of negative differences for each of the metals analysed.
- (2) Metals nickel, cobalt, copper, and manganese exhibit appreciable, but minor, systematic bias.
- (3) A significant systematic bias for metals zinc and iron is indicated by the extremely low probability (<1 per cent) of obtaining such a high proportion of positive differences in metal contents between duplicate pairs.
- (4) The number of duplicate pairs exhibiting identical metal concentrations averages greater than 1 in 4.

TABLE 2. TEST FOR SYSTEMATIC BIAS

METAL	NO DIFFERENCES <i>No. (per cent)</i>	POSITIVE DIFFERENCES	NEGATIVE DIFFERENCES	PROBABILITY OF OBTAINING NO. OF POSITIVE DIFFERENCES <i>per cent</i>
Nickel	43 (32.6)	46	43	36
Arsenic	49 (37.1)	44	39	30
Cobalt	56 (42.4)	42	34	22
Copper	31 (28.5)	55	46	19
Manganese	14 (10.6)	64	54	17
Iron	31 (23.5)	64	37	<1
Zinc	23 (17.4)	68	41	<1

These results suggest that for the majority of metals no major systematic biases are present and application of techniques such as analysis of variance and Howarth and Thompson precision procedure should provide meaningful results. Results obtained for metals zinc, and iron, however, should be scrutinized carefully in light of their strong systematic bias. A high incidence of identical metal concentrations for individuals of a duplicate pair is also characteristic for all metals studied and intuitively appears unrealistically high considering: (1) that it occurs across the concentration ranges of each particular metal; and (2) the quoted sensitivity of the analytical method.

Results of the analysis of variance are presented in Table 3. As expected, the between-sample site variability is decidedly higher than the within-sample site dispersion for all of the metals studied. This feature is both encouraging and desirable because the purpose of these regional surveys is to define a regional trend related to geological and geochemical phenomena; the greater the variability in metal concentrations between-sample sites the greater the ease of defining such trends.

**TABLE 3**  
**ANALYSIS OF VARIANCE OF RESULTS FOR**  
**132 DUPLICATE PAIRS OF STREAM SEDIMENTS**

METAL	GRAND MEAN (GEOMETRIC) <sup>1</sup>	BETWEEN	WITHIN	VARIANCE COMPONENTS	
		SITES	SITES	BETWEEN	WITHIN
		F <sub>1</sub>	F <sub>2</sub>	SITES	SITES
				%	%
Zinc	50	156.98 <sup>2</sup>	8.22 <sup>2</sup>	89	11
Copper	26	115.45 <sup>2</sup>	1.61 ns	97	3
Nickel	15	59.51 <sup>2</sup>	2.81 ns	91	9
Cobalt	8	40.70 <sup>2</sup>	0.20 ns	99	1
Manganese	292	276.88 <sup>2</sup>	0.26 ns	99	1
Iron	1.68	313.30 <sup>2</sup>	13.56 <sup>2</sup>	91	9

*The test depends on the following null hypothesis:*

- (a) Between sample sites — mean metal contents are equal at each site. Degrees of freedom are  $(m - 1, m - 1)$ , where  $m$  = number of sites = 132.
- (b) Within sample sites — mean of samples  $x_1$ , is equal to mean of duplicates  $x_2$ . Degrees of freedom are  $(1, m - 1)$ .

<sup>1</sup> All values are in ppm except for iron which is in per cent.

Probability ranges for accepting the null hypothesis:

<sup>2</sup> =  $0.01 > P$ ; <sup>3</sup> =  $0.05 > P > 0.01$ ; ns =  $P > 0.05$

From the F<sub>2</sub> ratios given in column 3 in Table 3, it is seen that for zinc and iron distributions there are also significant differences between the groups of the first field-site duplicate and the second field-site duplicate, probably reflecting the systematic bias discussed earlier. It is important to note that where there is a significant difference between the two groups, and the within-site variance component is large, the data may be of little value in prospecting, irrespective of the significance of the test for geochemical variation.

According to Bolviken and Sinding-Larsen (1970) where there is a significant difference between duplicate pairs of samples at individual sample sites and the within-site variance component is relatively small no large deviation can exist for many duplicates. Two possibilities exist: (1) there is a minor deviation between duplicates at many sample sites and considered not to seriously hamper prospecting potential; and (2) there is a major deviation between duplicates at a few sample sites and considered to be serious if is not detected by inspection of the data. In our case the significant F ratio and relatively low within-site variance component for metals zinc and iron is accounted for by the former possibility and, as a consequence, these metals can be used to define real geological and geochemical trends.

Comparable investigations by Bolviken and Sinding-Larsen (1970) and Chork (1972) using similar-type data and tests found that the variation within sites was about 10 to 25 per cent and the variation between sites was about 75 to 90 per cent. These results are considered typical for low-density stream-sediment surveys.

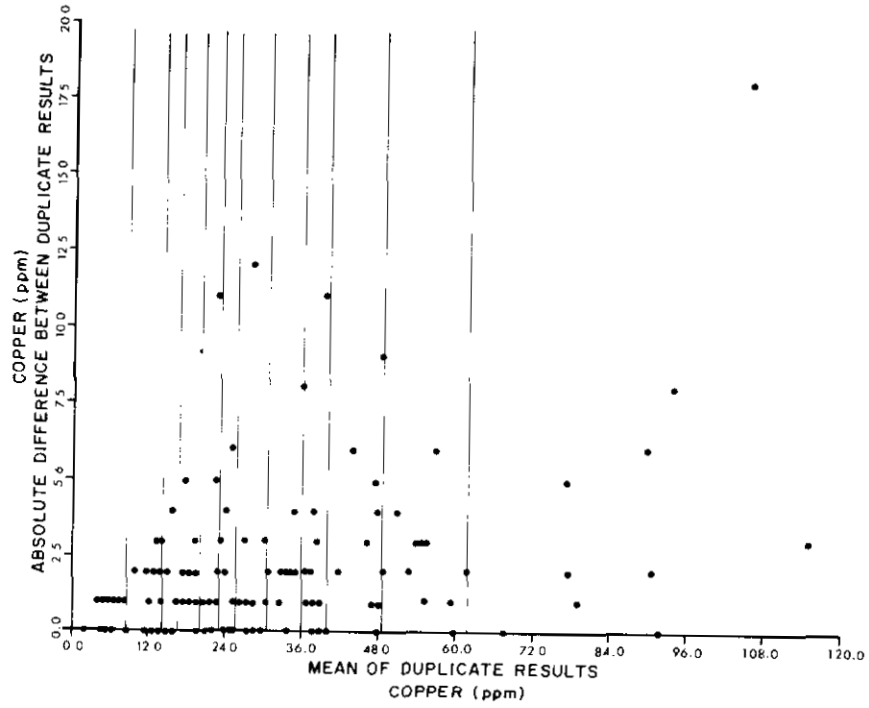


Figure 110. Absolute differences of paired data versus corresponding mean values of pairs, copper in stream sediments, British Columbia Regional Geochemical Survey.

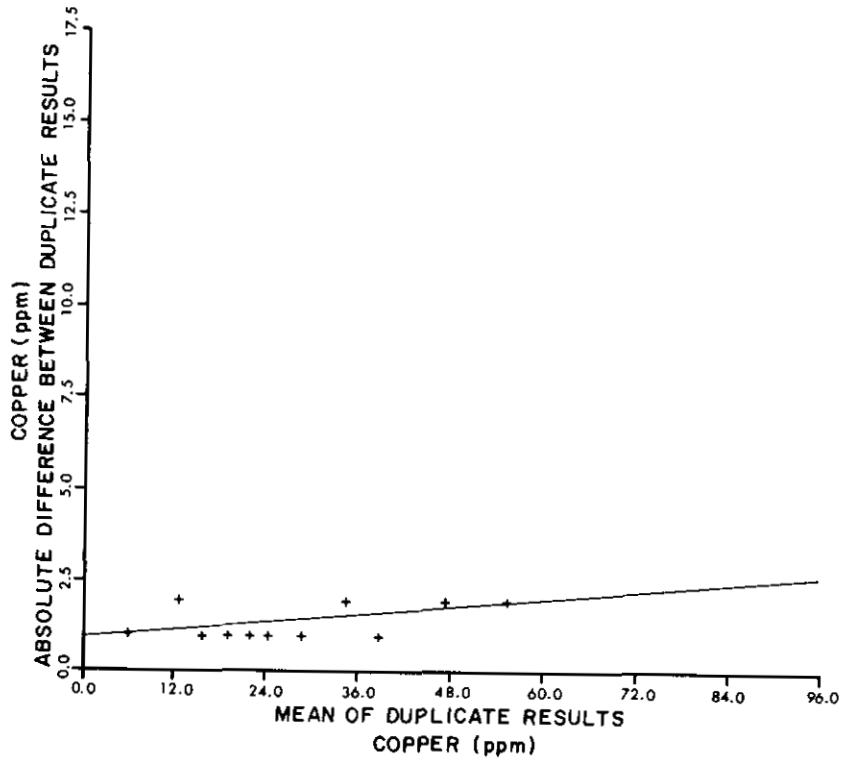


Figure 111. Linear model of average error as a function of concentration, copper in stream sediments, British Columbia Regional Geochemical Survey.

This is contrasted by results obtained from this study (Table 3) which exhibit surprisingly lower within-sample site variance, averaging less than 5 per cent of the total variability. The significance of these anomalous results is elaborated upon in a later section.

Results obtained from the Thompson and Howarth method are presented in Table 4 and illustrated graphically for copper on Figures 110 and 111. Although the regression of the median of absolute differences on the concentration means was only based on 12 points, analysis of variance proved significant at the 99 per cent confidence interval for all metals except cobalt (Table 4, column 6). A regression plot of copper illustrated on Figure 111, shows conclusively that simple linear regression more than adequately accounts for the relationship between the median of absolute differences and mean concentrations; thus it provides an excellent indicator of precision over the range.

TABLE 4  
RELATIVE PRECISION ESTIMATES, THOMPSON-HOWARTH METHOD  
BRITISH COLUMBIA REGIONAL GEOCHEMICAL DATA  
(92H, 92I, and 92J)

METAL	DETECTION LIMIT <sup>1</sup>	MAXIMUM VALUE	SLOPE	INTERCEPT	REGRESSION F-VALUE	PRECISION ESTIMATES AT SELECTED PERCENTILES		
						90th %	95th %	99th %
Zinc	2	210	0.027 <sup>3</sup>	0.892 ns	7.19 <sup>4</sup>	7.0	6.8	6.5
Copper	2	720	0.018 <sup>2</sup>	0.945 <sup>2</sup>	16.60 <sup>2</sup>	6.7	5.9	5.1
Nickel	2	1300	0.012 <sup>2</sup>	0.629 <sup>2</sup>	55.44 <sup>2</sup>	4.0	3.2	2.5
Cobalt	2	96	0.029 <sup>4</sup>	0.212 ns	3.14 <sup>4</sup>	8.0	7.4	6.7
Manganese	5	3700	0.036 <sup>2</sup>	2.785 ns	40.72 <sup>2</sup>	7.8	7.7	7.6
Iron	0.02	5.70	0.011 <sup>2</sup>	0.051 <sup>4</sup>	2.57 <sup>4</sup>	5.0	4.7	4.1

<sup>1</sup> All values are in ppm except iron which is in per cent.

Probability ranges for accepting t-tests on the slope and intercept and F-test on the regression:

<sup>2</sup> = 0.01 > P; <sup>3</sup> = 0.05 > P > 0.01; <sup>4</sup> = 0.10 > P > 0.05; ns = P > 0.10

Estimates of the slope also proved significantly different from zero at the 99 per cent confidence level (Table 4, column 4) for all metals except cobalt. However, only copper and nickel intercepts were found to be significantly different than zero (Table 4, column 5). This implies first, that the slope is major influence on the precision estimate of a given metal and second, that the magnitude of the slope reflects the relative precision. Examination of Table 4, column 4 reveals that nickel possesses the relatively lowest slope (0.012) whereas manganese is the highest (0.036). The intercept for most of the metals is not significantly different from zero and the magnitude of the slopes is extremely small, therefore, the precision is incredibly low.

For example, Figures 110 and 111 illustrate for the metal copper: (1) the plot of absolute differences against means of duplicate pairs with the concentration range divided into equal frequency intervals; and (2) a plot of the regression of the median absolute difference against mean concentration of copper. To determine the precision as an absolute value obtain graphically the median absolute difference corresponding to a selected concentration value on the regression line and multiply by 2. Thus, for copper at the:

50th percentile (26 ppm) absolute precision = 2.8 ppm

95th percentile (59 ppm) absolute precision = 3.9 ppm

99th percentile (80 ppm) absolute precision = 4.7 ppm

## DISCUSSION OF RESULTS

In general, all data collected in stream sediment surveys contain errors that are acquired through sampling, laboratory analysis, and data handling. Taking the existence of sampling errors into account, a precision of

10 to 15 per cent at the 95 per cent confidence level is generally regarded as acceptable for laboratory variability in most exploration programs (Fletcher, 1981). Studies tailored to the evaluation of error in drainage surveys, such as Plant (1971), Howarth and Larsen (1971), Bolviken and Sinding-Larsen (1973), Plant, *et al.* (1975), and Chork (1977) generally concluded:

- (1) Variable bias and variable precision introduced by secondary environment effects obscure the primary regional geochemical variation. The factors involved are complex and related to several variables in the primary and secondary environments investigated.
- (2) Metal dispersion within-sample sites depends on such factors as:
  - (a) concentration of the metal under investigation;
  - (b) concentration of other metals (for example, iron);
  - (c) homogeneity of sediment composition;
  - (d) catchment size at sample site.
- (3) The combined variability due to local variation and sampling error ranged from 10 to 25 per cent.
- (4) Sampling errors tended to exceed analytical errors when precise analytical techniques such as atomic absorption spectrometry are used.

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