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A GEOCHEMICAL SURVEY OF STREAM SEDIMENTS
OF THE PICEANCE CREEK BASIN, COLORADO

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by

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Geochemistry.

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ABSTRACT

A stream sediment survey was conducted in the Piceance Creek basin to study the spatial distribution of Zn, Mo, Hg, Cd and As for future baseline considerations. The pH and organic matter were also measured. From samples taken at the mouths (junctions) of most of the named creeks in the basin, it is concluded that none of the streams contained sediments with anomalous trace element concentrations with respect to the basin. But it is thought that Mo and possibly As could be potentially toxic because of their abundance and their mobility under the stream sediments' alkaline condition.

From a different sampling plan, designed to describe the background variance of five streams (Roan, Black Sulfur, Parachute, Yellow and Piceance Creeks), it was found that most of the variance occurred at distances from 0-10 m within 2 km stream segments 10 km apart for Mo, Hg, Zn, and organic matter. When the variance between the five streams was considered, it was found to dominate the variances of the other factors for Mo, Hg, and Zn. This variance between streams is actually thought to represent the variance between the major drainage system in the basin.

When comparison is made between the two sampling design results, it is thought that the trace element concentrations of stream junction samples represented the best range of expected values for the entire basin. The expected ranges

of the trace elements from the nested design are thought to be reasonable estimates of preliminary baselines for Parachute Creek, Roan Creek and Black Sulfur Creek within the restricted limits of the streams defined in the text.

From the experience gained in pursuing this study, it is thought that composite sampling should be considered, where feasible, to reduce the analytical load and to reduce the small scale variance.

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ACKNOWLEDGMENTS

Financial support for this work was derived in part from the Colorado Energy Research Institute and the Biomedical and Environmental Research Division of the Energy Research and Development Administration, contract number ERDA E(11-1)-4017.

It should be mentioned that the assistance from R. R. Tidball, J. McNeal, and A. T. Miesch of the U.S.G.S. more than compensated for their use of the thesis samples, as most of the sampling and statistical techniques utilized throughout this thesis have been extended from their work.

And finally I want to thank my thesis advisor, Prof. Ronald Klusman, for all the patience he had with me throughout this ordeal of learning something about sampling.

INTRODUCTION

The anticipation of an oil shale industry in Colorado, Utah and Wyoming has generated a strong interest in the environmental impact which would result from extracting hydrocarbons from the oil shale rock. In the area of regional geochemistry, ground work has already begun on the spatial distribution of elements and compounds in soils (Ringrose, et al., 1976), and in stream sediments (McNeal, et al., 1976). Preliminary baseline studies, such as the above referenced, must preclude studies dealing with the changes in distribution of elements and compounds resulting from energy developments.

This thesis also investigates the spatial distribution of trace elements in stream sediments. The similarity between the thesis and the study by McNeal, et al. (1976) is due to U.S. Geological Survey analyses of part of the samples collected in the early stages of this thesis. Thus the objectives of the two studies overlap somewhat, but as will be shown, the thesis work complements the McNeal, et al. (1976) study.

The objectives of the thesis are twofold: 1) to determine if any of the streams of the Piceance Creek Basin contain abnormally high trace element concentrations in their sediments, and 2) to determine the geochemical variation of the sediments from five streams (Roan, Black Sulfur, Para-

chute, Piceance, and Yellow Creeks) for the purpose of providing sampling interval information for future baseline studies. A knowledge of any streams containing anomalously high trace element concentrations will be important for making recommendations for any future oil shale plant sites. The possibility of anomalies were not considered in the McNeal, et al. (1976) study. The five selected streams are important because just about any future plant site drainages would eventually enter one of the stream systems included in this study. The McNeal, et al. (1976) study discussed only Roan and Black Sulfur Creeks.

GEOLOGICAL AND GEOCHEMICAL SETTING

The Piceance Creek basin is a major structural feature of the Colorado Plateau physiographic province. The basin is bordered on the north by the White River, on the east by the Grand Hogback and the Elk Mountains, on the south by the West Elk Mountains, on the southwest by the Uncompahgre Plateau, and on the west by the Douglas Creek Arch. The topographically high areas within the basin are the Roan Plateau, Battlement Mesa, and Grand Mesa. The extent of the study area is shown in Figure 1, which is a modification of Plate 48 (Donnell, 1961) with the Uinta formation replacing the Evacuation Creek member (Cashion, et al., 1974). The main watersheds are the Piceance and Yellow Creeks which drain into the White River, and Roan and Parachute Creeks which drain to the Colorado River.

Stratigraphically the Piceance Creek basin consists of the sandy Uinta formation (Cashion, et al., 1974) overlying the Green River formation which contains the oil shale. Figure 2, which is a modified cross section from Plate 48 of Donnell (1961) with the Uinta formation replacing the Evacuation Creek member (Cashion, et al., 1974), illustrates the stratigraphic sequence of the various members and formations. The cross section of Roehler (1974) is in much greater detail. The Green River formation consists of the Douglas Creek and Garden Gulch members and the kerogen-rich

Figure 1. Simplified geological map of the study area.

Figure 2. Cross section of stratigraphic section in Piceance Creek basin.

Parachute Creek member. In the vicinity of Rifle, the Douglas Creek and Garden Gulch members are named the Anvil Points member. Below the Green River formation lie the varicolored mudstone and siltstone of the Wasatch formation (Donnell, 1961). The ages of the formations referred to above are considered to be Eocene.

The streams in the interior of the basin dissect the Uinta formation. The heads of the streams flowing easterly or westerly cut into the upper portion of the Parachute Creek member. This moderate dissection contrasts with the extreme dissection of streams cutting lithologies in the Roan Creek and Parachute Creek areas. It was interesting to note that most streams are carving deep stream channels within gulches and valleys throughout the basin. In the early spring months the higher order streams are normally bank-full from snow melting in the high plateau area.

When this study began, there were no geochemical data directly pertaining to the soils or stream sediments of the basin. Thus the decision of what constituents to analyze had to be based upon previous studies emphasizing the oil shales of the Parachute Creek member. These studies (Smith, 1974) concluded that the oil shale had been deposited under extreme alkaline conditions. Thus it was decided to look at potentially toxic elements such as F, B, Mo, As, and Se which become mobile as anions under alkaline conditions. Analytical results (Table 1) of rock outcrop samples selected

Table 1. X-ray fluorescence analysis of selected Piceance basin rock samples.

Crustal* Abundance	(ppm)	Parachute Cr. (n=8)			Uinta (n=5)		
		Min.	Mean	Max.	Min.	Mean	Max.
Mo	1.5	3	17	40	2	3	6
As	1.8	9	33	110	5	10	21
Se	0.05	2	2	2	2	2	3
Zn	70	29	47	95	19	39	52

*Krauskopf, 1967

mainly from the perimeter of the basin at the beginning of the study, indicated that some of these elements were elevated above crustal abundances, particularly in the Parachute Creek member. Thus it appeared that this was a reasonable choice of constituents to study.

Since this work began, the regional geochemistry of the soil and stream sediments of the basin has slowly started to evolve. A recent soils study (Ringrose, et al., 1976) concluded that surface soil from ridge tops and valley bottoms is chemically similar and that Be, Cu, Li and Zn showed a marked increase from north to south. The first part of a stream sediment study (McNeal, et al., 1976) concluded that nearly two-thirds of the elements analyzed exhibited significant differences between four streams (two from the Uinta Basin in Utah and two from the Piceance Creek Basin). The second part (McNeal, et al., 1976) concluded that Black

Sulfur and Roan Creeks in the Piceance basin showed little variation between streams; most of the variation was associated with sampling scales of 1-10 km and 0-10 m.

CHEMICAL ANALYSIS

When work initially started on this thesis, the plan was to have the Project Central Analytical Facility at the University of Colorado analyze for B, As, F, Mo, and Se. Due to delays in funding, the PCAF analyzed the stream sediments only for Mo. Because the Chemistry-Geochemistry Department at Colorado School of Mines was not equipped to analyze for B, F, and Se, the analysis for Cd, Zn, Hg and As was done instead as elements of secondary interest. The pH and organic matter were also determined at CSM as originally planned. The analysis of As was discontinued after the processing of approximately 35 samples because of analytical problems. Cadmium, Zn, Hg, and As were all analyzed directly by atomic absorption, or by indirect methods in the case of Hg. The analytical procedure for each constituent is discussed in detail in Appendix A.

SAMPLE DESIGNS

The sampling plan for determining which streams in the basin contain anomalous trace element concentrations in their sediments was to select two 200 g samples 10 meters apart at the mouths (junctions) of most of the named streams in the basin (fig. 3). To keep the analytical load at a feasible level only one of the two samples was analyzed. If a sample was thought to be abnormally high, the other sample was to be analyzed to substantiate the first high value.

The sampling design used to describe the background variation of the five major streams is considerably more complicated than the design for detecting anomalous creeks. As previously discussed, the objective is to try to describe as much of the geographic variability as possible. Once the variability is known, further sampling designs can be made to determine practical baselines for the area.

For the purpose of this study, a baseline is defined to be a reference that not only describes the mean and limits of concentration inherent in nature, but also accounts for the geographical scale of variability. The most effective way of expressing a baseline is with a geochemical map. But if the variability is local, it would require too many samples to develop a stable or reproducible geochemical map, thus an expected range would be the appropriate manner of expressing

Figure 3. Sampling distribution at stream junctions in study area.

the baseline.

To obtain an estimate of natural variability in the five major streams, a hierarchical or nested sampling design was used. The U.S.G.S. (Miesch, et al., 1976a, p. 45) has made extensive use of this type of sampling because of its efficiency in describing geochemical variability on a regional basis. The dashed lines across the streams in Figure 4 show the predefined limits of this type of sampling for each stream. The dashed boxes indicate the length of channel expressed by the nested sampling on each stream. The position of each of the nested sampling groups was chosen at random. The detailed breakdown of each of the nested sampling groups is shown in Figure 5 or expressed in another manner by Figure 6.

Figure 5 illustrates the various sampling factors (2 km, 200m, 20m, and samples) which partition the total variance. Briefly, two 2-km segments were chosen 10 km apart. Within each of these 2-km segments, two 200 meter segments were chosen at random, one within each 1 km segment. Then within each 200 meter segment, two 20 meter segments were chosen at random, one within each 100 meter segment. And finally within each 20 meter segment, 2 samples were chosen, one within each 10 meter segment.

Figure 4. Boundaries of the nested model.

Figure 5. Detailed breakdown of nested sample design.

Figure 6. Diagram of nested model for each individual stream.

INTERPRETATION OF NESTED SAMPLE DESIGN

Definition of Models and Variables

The same definition of sampling locality will apply here as defined in various papers by Miesch (1976b,p.3). For the design as shown in Fig. 6, there are four factors -- 2 km segments, 200 m segments, 20 m segments, and samples. Two 200 m segments were chosen at random within each 1 km segment of the 2 km segments. This choice was made as a way of assuring that the average distance between segments would be 1 km. The other factors were done in like manner so that the average distances between 20 m segments and samples would be 100 m and 10 m, respectively.

The model used for this design is

$$X_{ijklm} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijkl} + \varepsilon_{ijklm} \quad , \quad (1)$$

where α represents the localities (2 km segments), β , γ and δ represent sublocalities (200 m segments, 20 m segments, samples), and ε represents the analysis. More specifically, X_{ijklm} represents the m^{th} analytical determination on the l^{th} sample from the k^{th} sublocality of the j^{th} sublocality of the i^{th} locality. α_i is the difference between the grand mean and the mean for the i^{th} locality; β_{ij} is the difference between the mean of j^{th} sublocality taken from the i^{th} locality and the mean for the i^{th} locality ($\mu + \alpha_i$). The rest of variables are defined in a similar manner. The total variance among the analytical determinations will be separated

into the following components:

$$\sigma_x^2 = \sigma_\alpha^2 + \sigma_\beta^2 + \sigma_\gamma^2 + \sigma_\delta^2 + \sigma_\epsilon^2 . \quad (2)$$

The nested model will estimate these components as

$$s_x^2 = s_\alpha^2 + s_\beta^2 + s_\gamma^2 + s_\delta^2 + s_\epsilon^2 . \quad (3)$$

Although the frequency distribution of the data was not examined, a log to the base 10 transformation of the data was made. It is well known that trace element distributions in natural systems are generally lognormal. Since the U.S.G.S. has taken this approach, any comparisons of results from this study and their studies are more likely to be meaningful. Also, assuming that the samples did come from a lognormal distribution, the likelihood of variable bias will have been reduced and tests for the significance of the five variance components will be more valid by making the transformation.

The interpretation of the variance components is explained in various papers (Miesch, 1976b, Krumbein, et al., 1956). As previously stated, the sampling was designed such that the average distance between samples was 10 m, the average distance between 20 m segments was 100 m, etc. Thus, the variance component s_δ^2 is taken as a measure of all variation in the stream channel that is on a scale of 10 m or less. Following the same reasoning s_γ^2 , the next variance component, is taken to represent the natural variance from 10 m to 100 m. The other variance components are defined in like manner and are listed in Table 2.

Table 2. Geographic scales of variance components.

s_{δ}^2	0 - 10 m
s_{γ}^2	10 - 100 m
s_{β}^2	100m- 1 km
s_{α}^2	1 - 10 km
s_B^2	variance between the five selected streams

If a comparison is made between streams, a new component of variance (B_i) is created in the model:

$$x_{ijklmn} = \mu + B_i + \alpha_{ij} + \beta_{ijk} + \gamma_{ijkl} + \delta_{ijklm} + \epsilon_{ijklmn} \quad (4)$$

The estimate of the variance between streams, s_B^2 , would be interpreted as representing just the variance between the five selected streams. The variance due to processing and analyzing the samples (Miesch, 1976b) is s_{ϵ}^2 .

Interpretation of the Nested Samples

The analysis of variance of the nested design for the major streams in the Piceance basin is summarized in Table 3. The part of the table listed as "Analysis of Logarithmic Variance" indicates that all data were transformed to log base 10 before computing the analysis of variance (Keith, et al., 1974). Under "Summary Statistics," the geometric mean is used to estimate the most typical concentration of a theoretically assumed log normal distribution (Miesch, 1976b, p. 21). The geometric deviation is a convenient way of

Table 3. Geochemical summaries for stream sediments of major creeks in Piceance basin (data given in parts per million; an asterisk (*) indicates variance component is significantly different from zero at the .05 probability level).

Element	Stream	Analysis of Logarithmic Variance							Summary Statistics			
		Total Log10 Variance	Between Streams	Percent of Total Variance				Analyt- ical Error ¹	Geometric Mean	Geometric Deviation	Geometric Error	Expected 95% Range
				1-10Km	100m-1Km	10m-100m	0-10m					
Mo	All	.0552	73*	2	0	3	17	6	4.2	1.64	1.09	1.6-11.1
	Roan	.0159	-	0	13	0	87	-	3.5	1.28	-	2.1-5.7
	Black Sulfur	.0365	-	15	1	0	76	8	2.9	1.41	1.09	1.5-5.6
	Piceance	.0143	-	0	0	21	79	-	4.2	1.33	-	2.4-7.4
	Parachute	.0044	-	5	4	0	91	-	9.5	1.14	-	7.3-12.3
	Yellow	.0215	-	38	0	4	58	-	3.3	1.34	-	1.8-5.9
Zn	All	.0066	36	18*	2	3	33*	7	61.0	1.20	1.03	28.6-129.9
	Roan	.0134	-	27	10	0	47	17	63.8	1.28	1.08	39.9-102.0
	Black Sulfur	.0030	-	46	3	10	37*	4	53.3	1.12	1.01	42.5-66.9
	Piceance	.0011	-	0	0	9	91*	0	67.8	1.08	1.00	58.1-79.1
	Parachute	.0012	-	14	0	37	40	9	68.9	1.06	1.02	61.3-77.4
	Yellow	.0036	-	30	0	9	48	14	52.5	1.13	1.04	41.7-66.2
Hg	All	.0614	66*	6*	0	0	20*	8	.29	1.67	1.12	.11-.78
	Roan	.0162	-	8	6	0	80*	9	.58	1.27	1.07	.37-.92
	Black Sulfur	.0375	-	38	0	13	43*	6	.36	1.44	1.08	.18-.73
	Piceance	.0214	-	11	0	23	54*	12	.23	1.35	1.09	.13-.41
	Parachute	.0333	-	0	6	0	61*	33	.28	1.39	1.19	.16-.49
	Yellow	.0085	-	1	0	26	0	73	.15	1.19	1.14	.12-.19
Organic	All	.1831	69*	12*	3	0	16*	0	.91	2.47	1.00	.15-5.55
	Roan	.0835	-	20	6	4	70*	0	1.26	1.87	1.00	.36-4.41
	Black Sulfur	.1416	-	50	8	0	39*	0	.79	2.01	1.00	.20-3.19
	Piceance	.0198	-	60	10	0	30	-	1.02	1.30	-	.60-1.72
	Parachute	.0011	-	17	43	12	22	5	2.54	1.07	1.00	2.22-2.91
	Yellow	.0326	-	1	22	0	76	1	.24	1.46	1.00	.11-.51

¹Where - appears, the analytical component is included in the 0-10m component.

expressing the total logarithmic variance in terms of ppm or percent. The geometric error is that part of the geometric deviation which is due to analytical error (Miesch, 1976a, p. 30A). The expected range which is calculated (Appendix B, p. 50) from the geometric mean and deviation is interpreted as a range estimated to contain 95% of the assumed lognormal population (Miesch, 1976b, p. 31). The all-stream results are derived from the nested model defined in equation (4). The results of the individual streams were derived from equation (1). The test for significance of all the variance component values are shown in the analysis of variance tables (Appendix B, p. 94).

From Table 3, two variance components stand out: the variance from 0-10 m for the individual streams, and the stream variance component for the all-stream data. The significance from 0-10 m for Mo cannot be tested because the 0-10 m scale of variance and the analytical variance are combined in the lowest scale factor. The small analytical variance of the Black Sulfur Creek indicates that most of the variance in this lowest scale factor is due to 0-10 m geographic variance. Thus the 0-10 m factor probably will be significant if a test could be made for it. In general, the consistency of the significance at the 0-10 m scale may be a reflection of the power (degrees of freedom) of the sample design being concentrated at the lower levels (Leone, et al, 1968). Except for Zn, there are significant differences

between streams for all the constituents. A similar study (McNeal, et al., 1976) done in the same area and in Utah also brought out the significant differences between streams for many other elements.

The purpose of the nested sample design is to provide information for future baseline investigations. However, where results can justify it, preliminary baselines are usually attempted from reconnaissance studies such as this. Since the nested results show that most of the variance is at the 0-10 m scale for individual streams, it would appear that an expected range could be used as a preliminary baseline for each of the constituents within each of the streams. Further random sampling at any interval may increase ones confidence in the expected range but future sampling for the purpose of developing geochemical maps seems to be economically unfeasible for most elements. To develop stable maps which will describe a reasonable percentage of the background variance of each individual stream would require sampling localities closer than 10 meters apart. The cumulative variance curve shown in Figure 7 illustrates this very clearly. The diagram shows that sampling at infinitely small intervals, approximately 100% of the geochemical variance would be expressed. Sampling at 10 m intervals, approximately 40% of the variance could be expressed; at intervals of 1 km only 10% of the variance could be shown. Thus, it seems that even if it were economically feasible to

Figure 7. Typical cumulative variance curve for streams with large percent of variance at low scale.

sample at intervals 10 m apart, it will not be satisfactory because only 40% of the total variance could be expressed.

The following discussion will illustrate how the nested results of the all-stream data might be interpreted in planning new sampling designs for future baselines. If one were interested in characterizing the Piceance Creek Basin as a whole, it might seem reasonable, for Mo, Hg and organic matter, to choose streams as localities because the stream component variance is much larger than any of the other components. One could conclude that one sample taken within these localities would provide enough information to make a stable geochemical map that would express a large percent of

the total variation. For example, using the estimated variance components for Mo (see Appendix B for calculations), it would take one sample per stream (locality) and one analysis of that sample to provide a variance mean ratio (Miesch, 1976b, p. 101) large enough to predict a stable map. The analysis of variance results predict Hg and organic matter could be treated in a similar manner.

A different interpretation would apply to Zn. The all-stream data (Table 3) shows Zn to be much more heterogeneous at the lower geographic scales than the other constituents. The fact that there is only significance at 0-10 m scale and possibly at 10-100 m scales suggests that a regional geochemical map of the area may not be feasible and that an expected range may have to be used as a baseline to characterize the element for the basin. This is dissimilar to the nature of Zn in surface soils which has a regional trend from north to south (Ringrose, et al., 1976).

In actuality, the above sampling plan for Mo, Hg, and organic matter will probably not express what is indicated from the all-stream nested results. The problem lies with the interpretation of the stream variance component (B_i). It should be recalled that the streams were not picked at random throughout the basin. This makes B_i a parametric factor rather than a random factor in the nested model (4). Therefore, the significance of this factor is that it represents a measure of the non-homogeneity of the stream mean

values rather than a measure of the variance of some random component. In other words, the contrast between streams throughout the basin is probably not as sharp as this factor might lead one to believe. It may be more logical to interpret the stream variance component as expressing the contrast between the major drainage systems of the basin (Roan, Parachute, Piceance, and Yellow) since the nested samples were taken from the main channel of these systems.

Because the stream variance component percentage was so high, it was thought relevant to determine which stream or streams were contributing most to the high contrast. The results of the test for the significant grouping among stream means are shown in Table 4 for Zn, Mo, Hg, and organic matter. Duncan's Multiple Range Test (Miesch, 1976a, p. A31) was used for the testing of significance of differences among these means.

The result of the above test on the Zn stream means seemed to support the low stream variance component percentage of Zn in the nested sampling. From Table 4, this is seen by the lack of distinct grouping of streams. For Zn, either group of means underlined is interpreted to indicate that there is no significant difference between those means underlined at the 95% confidence level. The overlapping indicates that there is more than one way in which significant groups can be classified. Thus, in the case of Zn, there is either a significant difference between the group $\bar{x}_Y$ $\bar{x}_B$ $\bar{x}_R$ $\bar{x}_P$

Table 4. Stream mean groupings for Zn, Mo, Hg and organic matter.

Zn	$\bar{x}_Y$ $\bar{x}_B$ $\bar{x}_R$ $\bar{x}_P$ $\bar{x}_C$	Y - Yellow Cr.
Mo	$\bar{x}_B$ $\bar{x}_Y$ $\bar{x}_R$ $\bar{x}_P$ $\bar{x}_C$	B - Black Sulfur Cr.
Hg	$\bar{x}_Y$ $\bar{x}_P$ $\bar{x}_C$ $\bar{x}_B$ $\bar{x}_R$	R - Roan Cr.
OR	$\bar{x}_Y$ $\bar{x}_B$ $\bar{x}_P$ $\bar{x}_R$ $\bar{x}_C$	P - Piceance Cr.
		C - Parachute Cr.

and the single mean group consisting of $\bar{x}_C$ or there is significant difference between the group $\bar{x}_C$ $\bar{x}_P$ $\bar{x}_R$ $\bar{x}_B$ and $\bar{x}_Y$. In the case of Mo, it may be that the significant difference between $\bar{x}_C$ and the rest of the stream means is the cause of the high stream component variance. For Hg or organic matter there is no strong indication of one stream or two groups dominating the results, though $\bar{x}_Y$ does stand out somewhat for organic matter.

Another approach could have been taken to examine which stream or streams may have been affecting the stream variance component. First, the stream variance component would be computed with just two streams making up the stream factor levels. Then another stream would be added and the stream variance component would be calculated again. By repeating this procedure until all five streams have been added to the model and by comparing the change in the stream variance component, one may determine which stream or streams

were influencing the stream factor. Before taking this approach it may be desirable to use the multiple range test first to determine the order of adding levels to the stream factor. The main reason for using this method is that one multiple range test may be too conservative; the only apparent disadvantage is that this approach may take a considerable amount of computer time.

From the above discussion, one is left with the question of how the sampling might be done if it were important to describe the basin as a whole. To answer this question properly, it is thought that another survey will have to be done using a nested sampling design which will define the tributaries of the six major streams in the basin--Yellow, Piceance, Roan, Parachute, Clear, and Dry Fork (Piceance) as its master localities. The other factors will possibly be 200 m segments, 20 m segments, samples, and replications. In this case, the factor "streams (tributaries)" will be a random component instead of parametric as before. If a staggered, nested analysis of variance design (Leone, et al., 1968) were used and if composite samples were taken, only three samples per stream will be required. The staggered, nested design will reduce the number of samples that must be collected, and it will distribute the degrees of freedom more evenly throughout the factors (Miesch, 1976a, p. A30). From the analysis of variance tables (Appendix B, p. 94) it will be noted that the degrees of freedom increase from the

2 km segments factor or the stream factor to the sample factor in all cases. This tends to give more significance to the factor with the highest degree of freedom. Collecting composite samples will reduce the analytical load.

INTERPRETATION OF THE STREAM JUNCTION DESIGN

The model for this sampling approach is

$$x_{ij} = \mu + \alpha_i + \epsilon_{ij} \quad (5)$$

x_{ij} represents the j th analytical determination in the i th locality (stream junction). α_i is the difference between the grand mean and the mean for the i th locality, and ϵ_{ij} is the analytical error for the laboratory determination on the i th locality. Compared to equations (1) and (4), this is indeed a simpler design. It should be kept in mind that the objective of the stream junction sample design is not to describe as much of the geochemical variability as possible, but to determine whether any streams have sediments with unusually high concentrations of any of the constituents under consideration (As, Cd, Mo, Hg, and Zn).

When locality is used in the discussion of stream junction sampling, it will represent the stream channel above the junction. It is thought that random sampling within a locality (stream) will not express an anomalous locality as effectively as will sampling on the downstream end of the locality. Of course, this assumption is dependent on the nature of the dispersion train from the anomalous source. If, for example, an anomalous source is located at the head of a typical sampled stream, a halo of 10 miles or longer may be required for detection at the mouth of the stream. Thus only strong anomalies or relatively large size targets will be detected by this sample design.

Table 5 lists the results of the analysis of the approximately 100 samples taken at stream junctions throughout the basin. Only 35 of the samples were analyzed for As. In establishing whether any of the samples reflect creek sediments with abnormally high concentrations, the following factors are considered from the table. The geometric means for Cd, As, Hg, and Mo seem to express concentrations that are typically found in shales. From abundance tables (Krauskopf, 1967), it seems that on the average, trace element concentrations in shales are higher than for other types of rocks. The expected range values are expressing estimated concentration ranges for 95% of the stream localities. Nearly all listed values in the 5 highest ranked columns lie within the 95% estimated ranges. The values that are not within the ranges do not appear to be conspicuously different. Thus it is concluded, without any statistical tests, that values expressing the element concentration of stream localities are within 95% limits. Since only one sample was taken per stream, it cannot be said how much of the variances between stream locality values are due to variance within stream localities. If composite sampling had been done within the stream localities (6 or 7 samples mixed together into one sample bag) the variance within streams could have been estimated without adding to the analytical load.

Table 5. Stream junction data for each element.

Element	GM (ppm)	GD	Expected Range @ 95% Level (ppm)	5 Highest Ranked Values (ppm)	Ave. Crustal Abundance ⁴ (ppm)	Ave. Shale Abundance ⁴ (ppm)
Cd ¹	2.4	1.56	1.0-5.9	4.7, 4.8, 4.8, 5.0, 5.9	.2	3
As	9.2	2.38	1.6-52	21, 28, 30, 36, 50	1.8	6.6
Zn	60	1.34	33-108	70, 82, 83, 84, 116	70	80
Hg	.33	1.50	.14-.74	.62, .64, .65, .73, .91	.04	.40
Mo	4.7	2.14	1.0-21.6	11.1, 11.2, 12.8, 13.0, 17.7	1.5	2, 3 ⁵

Organic % .54 2.50 .09-3.38

pH 8.25² 7.30-8.90³

¹Treated as censored data, parameters calculated accordingly (Appendix B).

²Mean of all pH measurements of stream junction samples.

³Low and high values of pH measurement of stream junction samples.

⁴Krauskopf, 1967.

⁵Levenson, 1974.

Even though the presence of abnormally high concentrations of the constituents under investigation cannot be shown, it is thought that Mo and possibly As have the potential of being hazardous. The shale-like sediments are relatively

abundant in Mo and As, and the pH of sediments is quite alkaline. Mo and As can be very mobile under high pH conditions, and therefore can be considered available to plants. With a deficiency of Cu, it takes only 10 to 12 ppm of Mo in forage to be toxic for cattle and sheep (Gough, et al., 1976, p. 24).

One may question whether or not sampling the major channel of a drainage system would be comparable to sampling the tributaries draining into it. A comparison between the expected ranges of the stream junctions and nested samples in Table 6 show that, with few exceptions, the nested expected ranges are smaller. Although the analytical error is removed from the nested ranges, these errors are too small to account for the differences.

It may be that there is a significantly higher scale variance than the upper scale limit (1-10 km) of the nested model. This explanation for the difference in the nested and stream junction expected ranges could also explain the bimodal and trimodal distributions of Mo and Zn (Figures 8 and 9) in the stream junction samples of the Piceance Creek drainage. If each of these distributions is separated into subsets reflecting the bimodal or trimodal character of each and then plotted on a map with different symbols indicating the high, medium, and low concentration subsets, a conceivably higher scale trend can be seen (Figs. 10 and 11). At the east end of Piceance Creek high values group together for Zn and low values group together for Mo. Note that this

Table 6. Comparison between stream junction and nested expected ranges for individual streams.

Mo		GM (ppm)	Stream Junction		Nested Expected Range* (ppm)
			GD	Expected Range* (ppm)	
	Piceance	2.8	2.72	.3 - 20.6	2.4 - 7.4
	Roan	5.6	1.56	2.3 - 13.6	2.1 - 5.7
	Parachute	5.5	1.55	2.3 - 13.2	7.3 - 12.3
	Yellow	6.7	1.42	3.3 - 13.5	1.8 - 5.9
Zn					
	Piceance	53.8	1.22	36.1 - 80.1	58.1 - 79.1
	Roan	66.4	1.34	37.0 - 119	39.9 - 102.0
	Parachute	64.8	1.16	48.2 - 87.2	61.3 - 77.4
	Yellow	53.7	1.20	37.3 - 77.3	41.7 - 66.2
Hg					
	Piceance	.33	1.50	.15 - .73	.13 - .41
	Roan	.34	1.16	.25 - .45	.37 - .92
	Parachute	.38	1.22	.25 - .57	.16 - .49
	Yellow	.24	1.35	.12 - .46	.12 - .19
Organic carbon					
	Piceance	.32	2.20	.06 - 1.77	.60 - 1.72
	Roan	1.23	2.35	.22 - 6.80	.36 - 4.41
	Parachute	1.09	1.75	.36 - 3.32	2.22 - 2.91
	Yellow	.41	1.83	.12 - 1.38	.11 - .51

* @ the 95% level

Figure 8. Histogram for Mo in Piceance Creek.

Figure 9. Histogram for Zn in Piceance Creek.

Figure 10. Spatial distribution of high and low concentrations of Mo from histogram of figure 8.

Figure 11. Spatial distribution of high, medium, and low

eastern segment is where the nested design is located for Piceance Creek and that the nested values for Mo are relatively low and the values for Zn are relatively high just as they are for the stream junction data. Thus it may be interpreted that the nested samples are expressing the higher concentrations of Zn and lower concentrations of Mo and not expressing the larger regional component.

From mapping the distribution of these two elements for one creek, it becomes apparent that in many instances, the high values at the heads of streams are not reflected by samples further downstream. Because of the non-anomalous nature of the Piceance basin, sampling at random within a locality will express the nature of the stream as well as sampling the downstream end of the locality.

Although the sampling in this study was not designed to answer questions such as what is influencing the geochemical distribution in the basin, a few general conclusions can be drawn. From stream junction data, it is found that for all the measured constituents -- Zn, Mo, Hg, and organic matter -- there is a significantly greater concentration in the population of individuals making up the perimeter of the basin (all samples in the Green River formation and Wasatch formation) as compared to the population of the interior (all samples in the Uinta formation). There is also a significantly greater concentration of Mo, Zn, Hg, and organic matter in samples taken south of the Roan Plateau as compared to

samples taken north of the plateau. This is similar to the data for Zn, Cu, Li, and Be in surface soils (Ringrose, et al. 1976). Without further study, it cannot be determined what is causing this significant difference. Lithology is the likely major factor influencing the populations because of the geological differences previously described. But many streams sampled north of the Roan Plateau were dry; whereas, in the south, Roan and Parachute Creeks are perennial, being fed by springs as well as run-off. Thus, ground water may be playing just as important a role.

Correlations between the constituents under discussion showed significance only between Zn and organic content for stream junction data. Mo has a correlation value of .19, but for 90+ samples it should have been larger for significance different from zero at the 95% confidence level. Though a correlation was not made on the nested samples, one might conclude that the high organic samples on Parachute Creek will reflect the high geometric mean of Mo for Parachute Creek. But if Mo is being influenced by the kero-gen rich Parachute Creek member, the relatively low Mo concentration of the stream junction samples downstream from the Parachute Creek member are not reflecting this. On the other hand, Zn concentrations do seem to be affected as the stream junction samples in this location are relatively high in Zn.

NESTED VS. STREAM JUNCTION RESULTS

There has been some previous discussion concerning the comparison between the stream junction expected ranges and the nested expected ranges for the entire basin. From this comparison, it appears that the stream junction expected ranges are more realistic estimates than the nested expected ranges because they possibly reflect an additional larger scale variance component. If the results of the nested sampling plan with streams as a factor had shown the majority of the variance at the low scale level, the nested and stream junction samples could have been combined in estimating a preliminary baseline. In other words, all samples could have been treated as independent observations and an expected range could have served as a baseline.

The other question that arises from this discussion is how well the nested samples describe each individually selected stream when the stream junction results are also taken into consideration. Under the nested sampling discussion in the interpretation of nested samples section, it was recommended that expected ranges for the individual stream be used as preliminary baselines. In light of the fact that the nested results may be missing at a significantly higher component of variance, it is thought that only the nested sample result for Parachute, Roan and Black Sulfur Creeks reflect expected ranges that may be used as preliminary base-

lines. Only these streams are considered because the restricted segments within which nested samples were taken are not much larger than the 10 km upper variance limit of the nested design for individual streams.

The segments of Piceance Creek and Yellow Creek which the nested samples represent are significantly larger than the upper scale variance of nested model design. The increased expected range of the stream junction samples indicates that the nested expected range result for the creeks may be in appreciable error because they fail to express the component of variance greater than 10 km. Thus, it is reasoned that the stream junction expected ranges for Piceance Creek and Yellow Creek may be better estimates of the individual creeks than the expected ranges from the nested sample.

CONCLUSIONS

Based upon the stream junction sampling results and considering the possible error that may be expressed by the sampling design, it is concluded that none of the streams' sediments considered in this paper are anomalous in trace element concentrations when compared to one another. However, it was found that the stream junction sediments did contain concentrations of Mo and As typically found in shales. This implies that the elements are abundant in the stream sediment medium. The pH measurements indicated that the sediments represent an alkaline environment which favors the mobility of trace elements such as Mo and As which can form anions. Thus Mo and possibly As could be potentially hazardous because of their relatively high concentration and mobility. It was also found that there was a significantly greater concentration of Mo, Zn, Hg and organic matter in samples taken south of the Roan Plateau as compared to samples taken north of the Plateau. From this sampling experience it is recommended that future stream sediment surveys with similar objectives use composite sampling to reduce the analytical load and the variance within streams.

The nested sampling of the major streams in the Piceance basin emphasized that within 2 km segments, a high percentage of the variance is at the lowest scale factor (0-10 m) for Zn, Mo, Hg, and organic carbon. When streams are also con-

sidered a factor in the nested design, the highest percentage of the variance occurs with that factor for Mo, Hg, and organic carbon. This high contrast between streams is thought to be reflecting the high variance between drainage systems rather than the variance between streams in general. On this combined streams basis, the variance components for Zn were more evenly spread between the factors.

Within the restricted limits placed upon each stream, except for Piceance Creek and Yellow Creek, it is recommended that the expected range values from the nested samples be used as preliminary baselines. From the all-stream nested data, a preliminary baseline for the basin is not possible because it is not clear as to what significance the stream variance component would have if tributaries of the major streams were selected randomly; therefore, additional nested sampling as outlined on p. 26 will be necessary to obtain reliable baselines for the entire basin. The expected ranges resulting from the stream junction samples give an estimate of the most likely concentrations to be encountered in the basin, but it does not reflect the scale of the variance which will be expressed with a geochemical map, if such a map were feasible.

APPENDIX A

Sampling Procedure and Sample Processing

The sampling designs were followed as closely as was practical in the field. For the nested design, the mid-points of each sampling level down to 200 m were randomly positioned on the map. Then the actual sample sites were chosen at random in the field (a table of random numbers generated from a computer was used to randomly choose localities). If it was not possible to sample at randomly predetermined points for some reason, new random locations would be chosen out of necessity, realizing that the frequency of such procedure could lead to bias result. Choosing new locations was rare. Randomization is stressed to keep results as unbiased as possible.

The geologic population being considered in this study is all the possible 200 g, minus 4 mesh sieved stream sediment samples taken from some specific point in the stream's channel, either at the sediment surface in midstream or on a point bar at water level. Each 200 g sample was placed in a paper bag made specifically to contain wet soils or sediments and allowed to dry at ambient air temperature. In the laboratory, 15 g representing the original 200 g were prepared for analysis by repeated splitting of the 200 g until approximately 15 g were left. These 15 g were then ground for approximately 7 minutes in a tungsten carbide vial and ball in a Spex mixer mill.

Analysis

Prior to analysis, batches of approximately 80 sample bags containing 15 g of ground sediment were chosen at random from all the samples to be analyzed. This was necessary so that any potential non-random analytical errors would be spread over the entire sample set and not concentrated in one group of samples which might, for example, have otherwise reflected a particular geographic area.

To analyze for Zn, Hg, Cd, and As, approximately 1 g of sample was digested with 5:1 perchloric-nitric acid just below the boiling temperature of perchloric acid for approximately 1 1/2 hours (standards were treated in like manner). Each sample was diluted to a specific volume and mixed thoroughly. The next day the samples were analyzed for As using the arsine method and the following day Hg was analyzed by a flameless AA method and finally Zn and Cd were analyzed directly on the AA. After the first 20 or 30 samples, the analysis of As was discontinued because the As electrodeless discharge lamp was unstable at its recommended operating current.

The Hg method (modified from Hatch and Ott, 1968) is much more sensitive (1 ppb) than conventional AA methods (15 ppm). It assumes initially that all the mercury in the sample solution is in the form of Hg(II). The highly oxidizing perchloric acid digestion will assure this. Stannous chloride is added to an aliquot of this solution to reduce the Hg to the Hg⁰ state. The Hg⁰ is then aerated from solution into an

absorption cell where its concentration is measured by the AA. Many sources describe this method in detail; for example (EPA, 1971). They differ primarily in what they use for a reducing agent. In this study 10 g of reagent grade $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ were dissolved in 10 ml of warm concentrated HCl and then diluted to 100 ml with distilled water. One ml of this solution was used to reduce the Hg.

There were problems in analyzing for Hg, mainly because of the volatile nature of the element. At the beginning of the analyses when stock and working solutions were prepared, a few milligrams of KMnO_4 were added to each solution to prevent reduction of the mercuric ion. A few weeks later it was discovered that an oxide of manganese which precipitated on the walls of the containers of the stock and working solutions was absorbing the mercury. This problem was corrected by relying on nitric acid (approximately .15%) and high concentration (1000 ppm Hg) to preserve the mercuric ion in the stock solution, and by preparing the working solution just before the analysis.

During the analysis it also appeared that there was a mercury loss difference between standards and samples. This was discovered when one batch was allowed to sit over the weekend after being partially analyzed the preceding Friday. Upon trying to complete the analysis on the following Monday, it was discovered that mercury was not detectable in the standard but was still almost the same concentration in

samples. The pH of the standard and sample solutions were less than 1 at the time that loss in the standard was detected. It is recommended that working standards be prepared the day of analysis with perchloric acid.

The direct method of analyzing for Zn and Cd on the AA normally is a routine procedure. But initially, a problem did arise because of mixing the samples with glass stirring rods. When measurements for the concentration of Zn and Cd were taken by the AA, there was a noticeable difference when the aspirating tube was positioned at the top of sample solutions as opposed to when it was placed near the bottom. At first this phenomenon was thought to be due to suspended particles. After allowing for settling of most of the particles, it was determined the solution above the sediment matter was not homogeneous. Mixing with teflon thimbles proved to be more thorough, faster, and gave a homogeneous solution.

Organic carbon was determined by the Walkley-Black method (Walkley, 1935). Although the method was developed as a rapid way to analyze soils, it works well for stream sediments also. The method is based on the reduction of the $\text{Cr}_2\text{O}_7^{2-}$ ion by organic matter, wherein the unreduced $\text{Cr}_2\text{O}_7^{2-}$ is measured by titration with ferrous sulfate. Ferrous and chloride ions can affect the determination, but it is unlikely that iron present is in its reduced state because of the highly oxidizing condition of the stream sediments. The

qualitative test (AgNO_3) for chloride in samples most likely to have high chloride gave negative results.

As would be expected, the organic matter content of the stream sediment is low, averaging less than 1%. Approximately one gram is used for determining the organic content in each sample. It was noted during test runs that when 1 gram samples contained less than 0.5% organic matter, the analytical results were low (up to approximately 0.1%). Although this error could have been overcome by using a larger sample (3 or 4 grams), it was decided to accept the result based upon 1 gram samples because of the time it would have taken to repeat the experiment and because of the shortage of ground sample material. A few samples reduced more than 75% of the dichromate on the first determination of the sample. These were repeated using less sample material.

The pH of the stream sediment samples were measured on a saturation paste with a glass electrode and a portable pH meter. The analysis of variance of the result of pH data showed that there was as much variance between repeated analytical measurements as there was between the samples themselves. The largest source of the analytical error was probably due to effect of dilution. Because of the heterogeneous nature of stream sediments, it was very difficult to be consistent with the ratio of soil to water. For some samples that consisted of fines and were fairly well sorted, the saturation point or sticky point was easily determined.

But for other samples that were poorly sorted or consisted of large particles, the saturation point became nebulous. Thus the effects of the liquid junction potential or contact between the sediment and the glass electrode became highly variable.

Based upon the statistical results that there was as much variance between the stream junction localities as there was between replications, a few measurements by this method would yield as much information as measuring all the samples. Due to problems discussed above, it is recommended to take field measurements of water pH wherever it is possible (all active streams).

The analysis of Mo was done at the Project Central Analytical Facility at the University of Colorado. To obtain a total analysis, the samples were digested by the pyrosulfate fusion procedure (Meglen and Glaze, 1973). After dilution a colorimetric analysis of Mo was done using thiocyanate. The analytical error is about 10%.

APPENDIX B

Comments on the Application of Equations

The geometric mean, deviation and error, and expected range are discussed in U.S.G.S. Professional Paper 954-A, Miesch (1976a). The treatment of censored data is also included. From this reference the following equations were used to calculate the above parameters:

$$x_i = \log_{10} Y_i \quad (6)$$

where x_i is the log to the base 10 transformation of each of the analytical values (y_i).

$$\bar{x} = \frac{\sum x_i}{n} \quad (7)$$

where n is the number of independent analytical values.

$$S_\epsilon^2 = \frac{\sum (x_i - \bar{x})^2}{n-1} \quad (8)$$

where S_ϵ^2 represents the sample variance.

$$GM = 10^{\bar{x}} \quad (9)$$

where GM is the geometric mean.

$$GD = 10^{S_\epsilon} \quad (10)$$

where GD is the geometric deviation.

$$GE = 10^{(S_\epsilon/n_a)^{1/2}} \quad (11)$$

where GE is the geometric error and n_a is the number of sample replications.

$$GD_n = 10^{[(\log_{10} GD)^2 - (\log_{10} GE)^2]^{1/2}} \quad (12)$$

where GD_n is the corrected geometric deviation for the analytical error.

$$\text{Expected 95\% Range} = GM/(GD_n)^2 \text{ to } GM \cdot (GD_n)^2. \quad (13)$$

For the censored data the following equations were used.

$$\bar{x}' = \frac{\sum x}{n_d} \quad (14)$$

where n_d is numerator of detection ratio.

$$\bar{x} = \bar{x}' - \lambda(\bar{x}' - x_0) \quad (15)$$

where x_0 is the logarithm of the point at which the frequency distribution is censored; λ is graphically determined (Miesch, 1967b, p. 87).

The equation used in the International Mathematical and Statistical Libraries subroutine to calculate the variance components of the completely nested design with unequal subclass numbers was taken from Anderson (1952). The interpretation of the nested design is covered in Miesch (1976b) and Krumbein (1956).

The test for the significance of differences among means is also discussed in U.S.G.S. Prof. Paper 954A. The equation used to estimate S_M was changed because of the unbalancing of the replication factor. To circumvent this problem, the error component was treated as part of variance of the following level. Thus, the equation for estimating S_M^2 would be stated as:

$$E_s = \frac{s_\beta^2}{n_\beta} + \frac{s_\gamma^2}{n_\beta n_\gamma} + \frac{s_\delta^2 + s_\epsilon^2}{n_\beta n_\gamma n_\delta} \quad (16)$$

using the notation of U.S.G.S. Prof. Paper 954A.

Equations 17 and 18 were used for testing the significance between two means where the variances are unknown

(Walpole, 1972, p. 242).

$$T = \frac{(\bar{x}_1 - \bar{x}_2) - d_0}{\sqrt{(s_1^2/n_1) + (s_2^2/n_2)}} \quad (17)$$

$$v = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\frac{(s_1^2/n_1)^2}{n_1-1} + \frac{(s_2^2/n_2)^2}{n_2-1}} \quad (\text{degrees of freedom}) \quad (18)$$

The sample calculation for calculating the variance ratio for Mo using the nested analysis results are shown as follows (Miesch, 1976b, p. 101-106).

$$\text{Given: } s_B^2 = .73 \times .0552 = .0403$$

$$s_\alpha^2 \approx 0$$

$$s_\beta^2 \approx 0$$

$$s_\gamma^2 \approx 0$$

$$s_\delta^2 = .17 \times .0552 = .0094$$

$$s_\epsilon^2 = .06 \times .0552 = .0033$$

One sample per locality (stream) would result in the following ratio:

$$v_m = \frac{s_B^2}{\frac{s_\delta^2}{n} + s_\epsilon^2} = \frac{.0403}{\frac{.0094}{1} + .0033} \approx 3.$$

Computer Programming

This report used three programs extensively: a plotter program to plot and label sampling sites; a one-way analysis of variance program to estimate the variance within samples (analytical error) and to estimate the variance between

samples; and an analysis of variance program to estimate the variance components of the factors of the hierarchical sampling design.

Plotter Program

This program (Table 7) reads the latitude and longitude stated in degrees, minutes, and seconds from cards and plots the position (+) with a number (sample number or concentration, etc.) labeling the position. To generate a plot, the program will first ask for a reference point (XZERO, YZERO) and the scale from the user. The program will expect the reference to be located in the quadrant shown in Figure 12. It is important to note that in the program, Y represents latitude and X the longitude.—With the reference point as shown, all y(4) values will then be negative and all x(4) values will be positive. 'Scale' in the program is adjusted until all outer points are within defined borders. Also note that the number 1.295 is the conversion factor between latitude and longitude. It will vary slightly depending upon the latitude of the sampling area. It should be warned that this program will not work on a Tectronic readout scope because it will not accept input/output statements mixed with the plotter statements.

Table 7. Listing of the plotter program.

```

        DIMENSION Y(10),X(10)
        K=IPLOT(10)
        CALL PLOT(0.0,11.0,-3)
101     TYPE 101
        FORMAT(' ENTER DATA ')
        READ(4,1) YZERO,XZERO,SCALE
1      FORMAT(2F10.4,F4.2)
        WRITE(4,7) YZERO,XZERO,SCALE
7      FORMAT(2F10.4,F10.2)
6      READ(2,2) NUM, (Y(J),J=1,3),(X(J),J=1,3)
2      FORMAT(13,5X,3F2.0,1F3.0,2F2.0)
        IF(NUM.EQ.0000)STOP
        WRITE(4,4) NUM, (Y(J),J=1,3),(X(J),J=1,3)
4      FORMAT(1H0,14,2X,3F3.0,2X,F4.0,2F3.0)
        Y(4)= Y(1)+Y(2)/60.+ Y(3)/3600.-YZERO
        X(4)=X(1)+X(2)/60.+X(3)/3600.-XZERO
        WRITE(4,5) Y(4),X(4)
5      FORMAT(1H0,2F9.4)
        CALL SYMBOL(1.295*SCALE*Y(4),SCALE*X(4),0.10,3,130.,-1)
        FNUM=FLOAT(NUM)
        CALL NUMBER(1.295*SCALE*Y(4)+.03,SCALE*X(4)-.03,
1      0.05,FNUM,272.,0,10)
        GO TO 6
        CALL PLOT(X,Y,999)
        STOP
        END

```

Figure 12. Sample results of plotter program.

One-Way Analysis of Variance Program

This program is designed to handle groups with unequal replication. Each sample number (see Table 9) represents a group. For example, 035 is a group with no replications while 041 is a group with 3 replications. Note that some sample numbers indicating replications are only indicating that one of the constituents was repeated. The purpose of the program listed under Table 8 is to list for each group all the values of the constituent of interest and to separate each group of values with a zero (see Table 10). Note that all values are transformed to the log base 10. (If a data value is zero, .05 will be added to it before transformation takes place.)

Table 8. Listing of program which regroups one constituent at a time from Table 9 for the one-way analysis subroutine program.

1	IFLAG=1
1000	READ(11,1000) NUM,DATA
	FORMAT(13,38X,F5.1)
	IF(NUM.LT.000) GO TO 3
	IF(NUM.EQ.000) GO TO 2
	IF(DATA.EQ.0.0) GO TO 1
	IF(DATA.EQ.1.0) GO TO 4
5	X=ALOG10(DATA)
	WRITE(13,1001) X
1001	IFLAG=IFLAG+1
	FORMAT(F10.4)
	GO TO 1
2	IF(IFLAG.GT.1) GO TO 6
	GO TO 1
6	WRITE(13,1001) DATA
	IFLAG=1
	GO TO 1
	GO TO 1
4	DATA=DATA+.05
	GO TO 5
3	DATA=-50.
	WRITE(13,1001) DATA
	STOP
	END

Table 9. List of stream junction analyses for each stream locality.

Stream Locality Number (NUM)	R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry	Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
035		39330810	746453	11	.04	8.40		.30	34.53	.21	0.3
038		39440310	8001233	1	.31	8.22	7.9	.24	44.71	.1	1.4
38 R							10.4	.16	51.82	.1	
039		39440410	8000133	1	.96	7.92		.46	67.53	.3	1.8
040		39470410	8022742	0	.38	8.00	7.9	.17	68.41	.6	
041		39474110	8030352	11.10	.8	8.20		.29	70.23	.5	1.1
41 R								.20			
41 R								.20			
41 R					1.10						
042		39481410	8042842	0	.20	8.15		.25	60.32	.1	1.0
42 R								.25			
044		39471110	8054332	01.60	.7	8.82	8.3	.19	69.62	.1	.5
044 R						7.95					
44 R							2.7	.13	78.93	.2	
046		39473610	8060452	0	.22	8.10		.31	60.41	.9	
46 R								.27			
0481		39485610	8080542	0	.14	7.97		.23	65.19	.9	1.3
0481R						8.05					
0492		39493010	8094052	0	.37	7.95		.19	58.71	.9	1.0
049 R								.17			
0501		39484110	8113242	0	.11	8.05		.27	49.91	.8	.7
501R								.36			
501R								.26			
501R								.28	50.21	.8	
0522		39464410	8102332	1	.23	8.30		.36	43.29	.9	9.4
522R						8.58					
0561		39492510	8101832	01.92	.8	8.00		.46	51.09	.9	1.2
0561R						8.25					
0572		39495310	8114732	0	.23	8.15		.50	46.42	.1	2.0
572R						8.40					
572R								.40			

Table 9. (Cont.)

Stream Locality Number (NUM) R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
0602 602R	395022108143632	1	.178.20			.73 .79	39.43.2	1.6	
0611	394654108143852	0	.213.40	5.0	.30	55.62.0	1.0		
0622	394332108164632	1	.328.17	2.7	.57	41.02.7	8.6		
0662 622R	395058108155532	1	.207.95 8.32			.91	46.01.5	9.7	
662R			.22						
662R			8.10						
662R					1.00				
662R							47.41.8		
662R					1.05				
0671	394424108192742	0	.877.93	10.1	.25	65.71.0	1.1		
0701	395202108173832	1	.228.25	2.7	.41	43.51.6	12.8		
0711 711R	395024108192822	1	.478.23			.40 .40	47.73.2	1.0	
0752 752R	395010108232952	0	.248.30			.23 .24	56.73.1	2.0	
0942	395103108195242	0	.758.00			.38	63.99.9	1.2	
0951 0957R	395048108183242	0	.128.20	8.0	.27 .23	48.11.0	.7		
0961 961R 961R	395230108171342	1	.208.20 8.35	5.4	.52 8.5	48.82.7 .42	7.5 53.52.3		
0971 971R	395510108180832	0	.528.03			.19 .20	61.62.1	8.6	
0992	395552108172242	0	.188.20			.35	49.42.6		
1011 1011R 1011R	395108108265242	0	.648.10 .62			.23 .24	70.02.7	10.9	

Table 9. (Cont.)

Stream Locality Number (NUM) R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
1041	395532	108251	532 0	.338.20		.28	60.62.6	8.9	
1251	395555	108252	852 0	.578.35		.43	50.69.9	9.2	
1272	395517	108284	642 0	1.208.40	20.8	.13	83.34.7	6.6	
1272R					18.8		64.54.3		
1101	395844	108221	542 0	.148.35		.19	44.14.2	4.5	
1101R						.21			
1111	395909	108283	042 0	.768.00		.24	57.31.9	7.1	
1121	395914	108275	152 0	.228.25		.23	56.32.7	5.8	
1171	400439	108194	652 0	.408.30		.29	52.79.9	11.4	
1171R				8.47					
1171R				.95					
1171R						.17	51.6		
1191	400702	108214	232 0	.298.30		.21	42.13.2	8.8	
1191R						.25			
1242	395844	108084	642 0	.108.40		.40	46.71.0	5.9	
1242R						.35			
1251	395750	108072	042 0	.168.20		.49	53.79.9	4.2	
1261	395702	108062	732 1	.728.30		.39	58.29.9	6.8	
1281	395358	108043	832 1	.018.15		.25	72.44.0	4.0	
1281R				8.60					
1281R						.28			
1301	400024	108140	552 1	.428.10	5.3	.32	50.53.2	5.1	
1311	395957	108143	852 0	.178.35		.23	67.22.9	4.9	
1321	395829	108151	052 0	.178.20	2.6	.24	39.22.6	6.3	
1341	400508	108143	23 1	.188.42		.51	36.69.9	3.7	
1341R				.21					
1372	400957	108235	82 1	.628.95		.43	58.94.5	8.1	
1372R				8.75					

Table 9. (Cont.)

Stream Locality Number (NUM) R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
1381	400837108231553	1	.688,55			.26	47.95.9	5.9	
1381R						.17			
1381R			.67						
1381R						.20	49.05.2		
1381R						.26			
1392	400653108255152	2	.258,35			.21	47.64.8	5.2	
1392R			8.57						
1412	40105310830012	11	.168,35	5.3	.38	40.21.1	7.3		
1412R				5.3	.29	50.32.6			
1422	40103210833153	113	.368,20			.29	84.19.9	9.1	
1451	40093510838142	31	.178,14			.33	48.23.2	7.3	
1451R			8.35						
1451R						.29			
1461	40092210840532	311	.008,22			.33	74.53.310.3		
1461R						.54			
1472	40051110846272	31	.348,20			.34	54.09.9	6.4	
1472R			.35						
1481	40052510846532	311	.238,15			.35	39.21.0	5.8	
1512	40020210754423	31	.527,85			.36	43.81.1	7.2	
1521	40005510758085	30	.128,45			.31	67.69.9	7.5	
1562	39300610753624	10	.938,3210.9			.41	59.83.3	7.7	
1562R			2.7			.33	78.84.3		
1581	39283910759145	101	.128,50			.65	77.27.711.1		
1581R						.74	72.47.8		
1581R						.81			
1611	39285410805504	111	.958,30			.35	70.34.3	8.3	
1611R							67.95.2		
1611R						.66			
1621	393354108065747	11	.768,22			.39	71.03.413.0		

Table 9. (Cont.)

Stream Locality Number (NUM)	R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)	
1632		39314810	807364	112.688	8.35		.43	81.84	.8	7.9	
1632R					8.60						
1642		39344110	8062137	11.608	8.33	6.1				4.3	
1642R					8.53						
1651		39351510	8032837	1	.558	.25	.29	70.29	.9	3.3	
1662		39350610	8071227	1	.628	.25	.38	50.72	.4	5.7	
1672		39360910	8083237	1	.778	.27	.38	65.32	.6	5.1	
1682		39361710	8060137	1	.828	.21	.29	63.59	.9	3.5	
1691		39375510	8060235	1	.658	.15	.44	61.59	.9	3.8	
1701		39263510	803123	111.148	.11		.55	54.73	.6	5.2	
1721		39195610	813073	11	.868	.20	7.9	.34	49.92	.1	9.3
1721R					8.0		.32	55.74	.8		
1731		39220610	815355	11	.718	.30	.35	53.83	.2	7.8	
1752		39224310	821263	110.218	.55		.37	27.29	.9	3.6	
1752R					8.55						
1761		39224410	821305	111.348	.30		.44	64.24	.8	5.9	
1841		39235810	815413	101.227	.98		.40	71.54	.1	1.4	
1852		39245210	815412	11	.488	.10	18.3	.34	78.53	.1	6.0
1912		39270810	814322	111.888	.20		.36	71.52	.6	5.9	
1912R					8.33						
1921		39272410	819352	111.248	.22	29.5	.32	72.33	.2	6.4	
2081		39291510	819205	112.808	.40	27.5	.22	77.13	.3	6.0	
2081R					42.1		.13	68.44	.2		
2091		39322110	8191457	12.808	.30		.32	68.82	.0	7.2	
2091R					8.62						
2091R							.39	73.82	.0		

Table 9. (Cont.)

Stream Locality Number (NUM) R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
2111	39301810823154	113.108.10				.37	115.92.5	5.9	
2211 2211R	39304410828123	112.968.13 8.42				.41	74.94.0	5.3	
2222 2222R	39304110827425	112.788.2350.3 33.4				.29 .28	82.12.6 83.44.4	5.3	
2232 2232R	39332710829412	112.348.25				.35 .40	69.32.0 69.62.0	7.1	
2361	39534910843583	30 .448.60				.43	42.62.7	6.1	
2372	39513010843302	311.308.10				.39	66.81.9	2.9	
2381 2381R	39513410843293	31 .348.40 8.58				.64	41.89.9	5.4	
2391 2391R	39465710838292	31 .308.25 8.40				.62	42.09.9	5.7	
2402	39465810838263	31 .468.34				.50	37.19.9	4.9	
2412 2412R	39454510834204	112.488.23 8.43				.37	64.49.9	6.0	
2452	40021110838015	113.108.23				.36	78.34.417.7		
2562 2562R	393720108003953	1 .578.05 8.30				.35	74.39.910.0		
2681	393714108245137	11.408.10				.35	65.42.1	3.7	
2692 2692R	393628108233457	12.198.27 8.46				.31	76.95.0	7.3	
2701	393412108204429	1 .238.10				.35	47.42.1	3.8	
2801	39190110813173	11 .458.00			8.0	.56	159.73.2	4.5	
2871	40040910825062	0 .388.05				.23	52.54.7	3.3	

Table 9. (Cont.)

Stream Locality Number (NUM) R-replication	Latitude	Longitude	Grain Size Lithology Wet/dry Organic Matter %	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
2892	39442710800	325 10	.768.00			.31	74.02.7	6.6	
2912	39313610746	482 11	.328.03			.50144.24.0	6.0		
2912R						.52145.7			
2922	39313910745	152 11	.777.97	5.2	.50151.92.6	3.9			

Table 10. Listing the output of program listed in Table 8.

Hg (log)

-0.5229

0.0000

-0.6198

-0.7959

0.0000

-0.3372

0.0000

-0.7696

0.0000

-0.5376

-0.6990

-0.6990

0.0000

-0.6021

-0.6021

0.0000

-0.7212

-0.8861

0.0000

-0.5086

-0.5686

0.0000

-0.6383

0.0000

-0.7212

-0.7696

0.0000

-0.5686

-0.4437

-0.5850

-0.5528

0.0000

-0.4437

0.0000

-0.3372

0.0000

-0.3010

-0.3979

0.0000

-0.1367

-0.1024

0.0000

-0.5229

0.0000

-0.2441

0.0000

-0.0410

0.0212

0.0212

0.0000

Table 10. (Cont.)

Hg (log)

-0.6021

0.0000

-0.3872

0.0000

-0.3979

-0.3979

0.0000

-0.6383

-0.6198

0.0000

-0.4202

0.0000

-0.5686

-0.6383

0.0000

-0.2840

-0.3768

0.0000

-0.7212

-0.6990

0.0000

-0.4559

0.0000

-0.6383

-0.6198

0.0000

-0.5528

0.0000

-0.3665

0.0000

-0.8861

0.0000

-0.7212

-0.6778

0.0000

-0.6198

0.0000

-0.6383

0.0000

-0.5376

-0.7696

0.0000

-0.6778

-0.6021

0.0000

-0.3979

-0.4559

0.0000

-0.3098

0.0000

Table 10. (Cont.)

Hg (log)

-0.4089

0.0000

-0.6021

-0.5528

0.0000

-0.4949

0.0000

-0.6383

0.0000

-0.6198

0.0000

-0.2924

0.0000

-0.3665

0.0000

-0.5850

-0.7696

-0.6990

-0.5850

0.0000

-0.6778

0.0000

-0.4202

-0.5376

0.0000

-0.5376

0.0000

-0.4815

-0.5376

0.0000

-0.4815

-0.2676

0.0000

-0.4685

0.0000

-0.4559

0.0000

-0.4437

0.0000

-0.5086

0.0000

-0.3872

-0.4815

0.0000

-0.1871

-0.1308

-0.0915

0.0000

-0.4559

-0.1805

0.0000

Table 10. (Cont.)

Hg (log)

-0.4089

0.0000

-0.3665

0.0000

-0.5376

0.0000

-0.4202

0.0000

-0.4202

0.0000

-0.5376

0.0000

-0.3565

0.0000

-0.2596

0.0000

-0.4685

-0.4949

0.0000

-0.4559

0.0000

-0.4318

0.0000

-0.3565

0.0000

-0.3979

0.0000

-0.4685

0.0000

-0.4437

0.0000

-0.4949

0.0000

-0.6576

-0.7447

0.0000

-0.4949

-0.4089

0.0000

-0.4318

0.0000

-0.3872

0.0000

-0.5376

-0.5528

0.0000

-0.4559

-0.3979

0.0000

-0.3665

0.0000

Table 10. (Cont.)

Hg (log)

-0.4089

0.0000

-0.1938

0.0000

-0.2076

0.0000

-0.3010

0.0000

-0.4318

0.0000

-0.4437

0.0000

-0.4559

0.0000

-0.4559

0.0000

-0.5086

0.0000

-0.4559

0.0000

-0.2518

0.0000

-0.6383

0.0000

-0.5086

0.0000

-0.3010

-0.2840

0.0000

-0.3010

0.0000

-50.0000

The program listed in Table 11 calculates the analysis of variance using the subroutine "ACRDAN" which is one of the IMSL statistical programs. Table 12 gives an example of the output for Hg. The last number (96) in the first row of output tells how many groups were in the input. The first column of the next 3 rows lists the sum of squares (S(1), S(2), and S(3)) and the second column gives the degrees of freedom associated with each sum of squares. Below the first three rows, the first column lists the group mean of each group and the second column gives the variance within each group. The last row at the bottom gives the grand mean and the error parameter.

Nested Analysis of Variance Program

The test run of Mn data taken from McNeal, et al. (1976) for Roan Creek and Black Sulfur Creek will be used to illustrate how the program works. The nested model for Roan Creek and Black Sulfur Creek are shown in Figures 12 and 13 with Mn data. The diagrams are important because they clearly show the order in which the data must be loaded into the program. There are two inputs to the program (see Tables 13 and 14 for FOR 10.DAT and for FOR 12.DAT) which are labeled γ (analytical values) and NL (see ANESTU, IMSL Library). For a given order of Y there will be a corresponding order for NL.

Note that the Y values of Roan Creek end with the flag 999 as do the Y values of Black Sulfur Creek to signal the end of the data. Correspondingly, the NL's for Roan Creek

Table 11. Listing of the one-way analysis program.

	DIMENSION Y(200), TM(200), WTV(200), S(10), NDF(10), N(200)
C	SET COUNTERS
	I=1
	K=1
	J=0
	II=0
1050	WRITE(4,1050) FORMAT(1H0,'ENTER ELEMENT'/) READ(4,1060) ELEM
1060	FORMAT(A6)
	WRITE(6,1070) ELEM
1070	FORMAT(1H0,A6)
1	READ(13,1000) Y(I)
	WRITE(4,1000) Y(I)
1000	FORMAT(F10.4) IF(Y(I).LT.-45.) GO TO 2 IF(Y(I).EQ.0.0) GO TO 3 II=II+1
	I=I+1
	GO TO 1
3	J=J+1 N(K)=II K=K+1 II=0
	GO TO 1
2	WRITE(6,1001) K,N(K),J
1001	FORMAT(3I5) NT=J CALL ACRODAN(Y,NT,N,TM,WTV,S,GM,NDF,IER) WRITE(6,1020)(S(I),NDF(I),I=1,3)
1020	FORMAT(F10.5,I10)
	WRITE(6,1030)(TM(I),WTV(I),I=1,NT)
1030	FORMAT(2F10.3)
	WRITE(6,1040) GM,IER
1040	FORMAT(F10.4,I10) STOP END

Table 12. Listing the output of program listed in Table 11.

HG				
97	98	96		
*** I M S	L(UERTST)	***	WARNING	ACROAN 4 (IER = 36)
3.92891	95	}	Sum of Squares, Degrees of Freedom	
0.22339	41			
4.15230	136			
-0.523	0.000	↓	Group mean of each group, variance within each group	
-0.708	0.016			
-0.337	0.000			
-0.770	0.000			
-0.645	0.009			
-0.602	0.000			
-0.804	0.014			
-0.539	0.002			
-0.638	0.000			
-0.745	0.001			
-0.538	0.004			
-0.444	0.000			
-0.337	0.000			
-0.349	0.005			
-0.120	0.001			
-0.523	0.000			
-0.244	0.000			
0.000	0.001			
-0.602	0.000			
-0.387	0.000			
-0.398	0.000			
-0.629	0.000			
-0.420	0.000			
-0.603	0.002			
-0.330	0.004			
-0.710	0.000			
-0.456	0.000			
-0.629	0.000			
-0.553	0.000			
-0.367	0.000			
-0.886	0.000			
-0.700	0.001			
-0.620	0.000			
-0.638	0.000			
-0.654	0.027			
-0.640	0.003			
-0.427	0.002			
-0.313	0.000			
-0.409	0.000			
-0.577	0.001			
-0.495	0.000			
-0.638	0.000			
-0.620	0.000			
-0.292	0.000			

Table 12. (Cont.)

-0.367	0.000
-0.660	0.008
-0.678	0.000
-0.479	0.007
-0.538	0.000
-0.510	0.002
-0.375	0.023
-0.468	0.000
-0.456	0.000
-0.444	0.000
-0.509	0.000
-0.434	0.004
-0.136	0.002
-0.318	0.038
-0.409	0.000
-0.367	0.000
-0.538	0.000
-0.420	0.000
-0.420	0.000
-0.538	0.000
-0.356	0.000
-0.260	0.000
-0.482	0.000
-0.456	0.000
-0.432	0.000
-0.356	0.000
-0.398	0.000
-0.468	0.000
-0.444	0.000
-0.495	0.000
-0.701	0.004
-0.452	0.004
-0.432	0.000
-0.387	0.000
-0.545	0.000
-0.427	0.002
-0.367	0.000
-0.409	0.000
-0.194	0.000
-0.208	0.000
-0.301	0.000
-0.432	0.000
-0.444	0.000
-0.456	0.000
-0.456	0.000
-0.509	0.000
-0.456	0.000
-0.252	0.000
-0.638	0.000
-0.509	0.000
-0.293	0.000
-0.301	0.000
-0.4786	36

Grand Mean, Error Parameter

The circled numbers are the NL values which correspond to Table 13 (line 1)

Figure 13. Nested model of Roan Creek using Mn data.

The circled numbers are the NL values which correspond to Table 13 (line 2)

Figure 14. Nested model of Black Sulfur Creek using Mn data.

Table 13. Listing of input for program listed in Table 15.

<u>Mn(Y)</u>	
200.	Roan Creek
200.	
200.	
150.	
200.	
200.	
200.	
200.	
300.	
200.	
300.	
200.	
200.	
200.	
200.	
300.	Black Sulfur Creek
300.	
200.	
300.	
300.	
300.	
200.	
300.	
300.	
300.	
300.	
300.	
300.	
300.	
300.	
500.	
300.	
300.	
300.	
300.	
500.	
300.	
200.	
999.	

end with the flag 99 and the NL's for Black Sulfur Creek end with 90, indicating the end of the data set. (If there had been more than two creeks, then 90 would have been used only with last creek's NL values, the others being 99). The last set of NL values ending with 90 represent a nested model with both creeks instead of separate nested models for each stream as did the above groups of NL's.

The program (Table 15) will ask the following questions during the execution. First, a value for NF (number of factors in model) will be asked for. This means that since Roan Creek is the first nested model on the file, the value of NF will be 4. Then the program will ask if data is good or bad (i.e., errors in input). If it is bad, it will go to the next set of data; if good, it will continue by asking to enter a stream label. It will then ask if there are more nested data which must be treated separately, or if it should merge all the preceding data into one large nested model, or if it should stop. In this case, a 0 would be entered and the data for Black Sulfur Creek will be read in. NF would again be 4. At the end of this sequence of questions, the program will be told to merge. This time though, NF would be 5. In addition to the other questions, the program would also ask what element. In this case, Mn would be entered.

The output (Table 16) lists first the input for each stream (note the Y values have been transformed to log base 10). Then, as explained in the one-way analysis program, the columns would first express the sum of squares and

The circled numbers are the NL values which correspond to Table 13 (line 3)

Figure 15. Nested model representing both creeks using Mn data.

Table 14. List of input for program listed in Table 15.

2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,1,1,1,1,1,1,2,2,1,2,2,1,1,1,1,1,99
2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,1,1,2,1,2,2,1,1,2,2,1,1,1,1,1,2,99
2,2
2,2,2,2,2,2,2,2,2,2,2,2,2,2,1,1,1,1,1,1,2,2,1
2,2,1,1,1,1,1,1,1,1,2,1,2,2,1,1,2,2,1,1,1
1,1,2,99

Table 15. Listing of program for calculating the analysis of variance for unbalanced nested design.

```

      DIMENSION NL(120),Y(200),S(100),NOF(100),EMS(100),IWK(120)
      DIMENSION NS(500),YY(500),YS(500)
      DIMENSION CREEK(10),SIG(100)
      IFLAG=0
      NCT=1
      NYCT=0
10      IF(IFLAG.EQ.0) GO TO 11
      NCT=1
13      READ(10,1011)(NL(I),I=1,20)
1011     FORMAT(20I)
      DO 12 I=1,20
      IF(NL(I).EQ.90) GO TO 180
      NS(NCT)=NL(I)
      NCT=NCT+1
12      CONTINUE
      GO TO 13
      C READ NL
11      WRITE(4,1014)
1014     FORMAT(1H0,'ENTER THE VALUE FOR NF')
      READ(4,1015) NF
1015     FORMAT(I1)
      NF1=NF+1
      NF2=NF*(NF+1)/2
      NCT=1
18      READ(10,1000)(NL(I),I=1,20)
1000     FORMAT(20I)
      DO 20 I=1,20
      IF(NL(I).NE.90) GO TO 30
      IFLAG=1
      GO TO 60
30      IF(NL(I).NE.99) GO TO 50
      GO TO 60
50      NS(NCT)=NL(I)
      NCT=NCT+1
20      CONTINUE
      GO TO 18
      C READ Y
60      J=1
70      READ(12,1010) YY(J)
1010     FORMAT(F10,3)
      IF(YY(J).EQ.99.) GO TO 80
      Y(J)=ALOG10(YY(J))
      NYCT=NYCT+1
      YS(NYCT)=Y(J)
      J=J+1
      GO TO 70
80      WRITE(6,3020)(Y(J),J=1,NYCT)
      WRITE(6,1001)(NS(I),I=1,NCT)

      WRITE(4,1003)(NS(I),I=1,NCT)
1003     FORMAT(20I2)
1001     FORMAT(40I2)

```


Table 15. (Cont.)

	CALL ANESTU(NF,NS,Y,GM,S,NDF,EMS,IWK,IER)
	WRITE(4,2020)(S(I),NDF(I),I=1,NF1)
2020	FORMAT(F10,5,I10)
	WRITE(4,2030)(EMS(I),I=1,NF2)
2030	FORMAT(F10,4)
	WRITE(4,2050)
2050	FORMAT(1H0,'IF DATA IS GOOD,ENTER 1. IF BAD, ENTER 2.')
	READ(4,1020) IPRINT
1020	FORMAT(I1)
	IF(IPRINT.EQ.1) GO TO 120
	GO TO 10
120	WRITE(4,2060)
2060	FORMAT(1H0,'ENTER STREAM LABEL UP TO 24 SPACES'/)
	READ(4,1050)(CREEK(L),L=1,4)
1050	FORMAT(4A5)
	WRITE(6,2070)(CREEK(L),L=1,4)
2070	FORMAT(1H0,(4A5)/)
	WRITE(6,2020)(S(I),NDF(I),I=1,NF1)
	WRITE(6,2030)(EMS(I),I=1,NF2)
	WRITE(6,2040) GM,IER
2040	FORMAT(F10,3,I10)
150	SIG(NF)=S(NF)/NDF(NF)
	SIG(NF-1)=(S(NF-1)/NDF(NF-1)-SIG(NF))/EMS(NF2-1)
	IF((NF-2).EQ.0) GO TO 160
	SIG(NF-2)=(S(NF-2)/NDF(NF-2)-SIG(NF)-EMS(NF2-4)*
1	SIG(NF-1))/EMS(NF2-3)
	IF((NF-3).EQ.0) GO TO 160
	SIG(NF-3)=(S(NF-3)/NDF(NF-3)-SIG(NF)-EMS(NF2-8)
1	*SIG(NF-1)-EMS(NF2-7)*SIG(NF-2))/EMS(NF2-6)
	IF((NF-4).EQ.0) GO TO 160
	SIG(NF-4)=(S(NF-4)/NDF(NF-4)-SIG(NF)-EMS(NF2-13)*SIG(NF-1)
1	-EMS(NF2-12)*SIG(NF-2)-EMS(NF2-11)*SIG(NF-3))/EMS(NF2-10)
	IF((NF-5).EQ.0) GO TO 160
	SIG(NF-5)=(S(NF-5)/NDF(NF-5)-SIG(NF)-EMS(NF2-19)*SIG(NF-1)-
1	EMS(NF2-18)*SIG(NF-2)-EMS(NF2-17)*
1	SIG(NF-3)-EMS(NF2-16)*SIG(NF-4))/EMS(NF2-15)
	WRITE(4,1002)(SIG(I),I=1,NF)
160	WRITE(6,1002)(SIG(I),I=1,NF)
1002	FORMAT(F10,5)
	WRITE(4,3050)
3050	FORMAT(1H0,'IF MORE DATA,ENTER 0,IF MERGE,ENTER 1,
1	IF STOP,ENTER 2')
	READ(4,1020) IFLAG
	IF(IFLAG.EQ.2) CALL EXIT
	GO TO 10
180	WRITE(4,1014)
	READ(4,1015) NF
3030	FORMAT((10I))
	WRITE(6,3030)(NS(I),I=1,NCT)
	WRITE(6,3020)(YS(I),I=1,NYCT)
3020	FORMAT((8F10,4))
	NF1=NF+1
	NF2=NF*(NF+1)/2

Table 15. (Cont.)

	CALL ANESTU(NF,NS,YS,GM,S,NDF,EMS,IWK,IER)
	WRITE(4,2080)
2080	FORMAT(1H0,'ENTER ELEMENT'/)
	READ(4,2090) ELEM
2090	FORMAT(A6)
	WRITE(6,3000) ELEM
3000	FORMAT(1H0,A6)
	WRITE(4,2020)(S(I),NDF(I),I=1,NF1)
	WRITE(4,2030)(EMS(I),I=1,NF2)
	WRITE(6,2020)(S(I),NDF(I),I=1,NF1)
	WRITE(6,2030)(EMS(I),I=1,NF2)
	WRITE(6,2040) GM,IER
	IFLAG=2
	GO TO 150
	END

Table 16. (Cont.)

1.5455						
3.0000						
5.5455						
11.0000						
1.0000						
1.5212						
2.9333						
5.4545						
1.0000						
1.3000						
2.5333						
1.0000						
1.3333						
1.0000						
2.465		0				
0.0023						
0.0004						
-0.0051						
0.0043						
0.0093						
2	2		2	2		2
	2	2		2		2
2		2		2		2
	2		2		2	
2		2		2		2
	2	1		1		1
2		1		1		1
	2		2		1	
1		2				
	1		2	2		1
1		1				
	1		1	2		0
2.3010	2.3010	2.3010	2.1761	2.3010	2.3010	2.3010
2.4771	2.3010	2.4771	2.3010	2.3010	2.3010	2.3010
2.4771	2.3010	2.4771	2.4771	2.3010	2.4771	2.4771
2.3010	2.4771	2.4771	2.3010	2.4771	2.4771	2.4771
2.4771	2.6990	2.4771	2.4771	2.4771	2.4771	2.4771
2.4771	2.3010					
MN						
0.1450		1				
0.0632		2				
0.0284		4				
0.0222		8				
0.1927		16				
0.0711		10				
0.5227		41				
1.0000						
1.4693						
2.8429						
5.3645						
10.4762						
20.9524						

Table 16. (Cont.)

1.0000	
1.4727	
2.8500	
5.3727	
10.5000	
1.0000	
1.3939	
2.7000	
5.1273	
1.0000	
1.2750	
2.4750	
1.0000	
1.2700	
1.0000	
2.400	0
0.4054	
0.0023	
0.0009	
-0.0037	
0.0039	
0.0071	

degree of freedom, then the expected mean square coefficients, the grand mean and error parameter. Finally, the estimated variance components are listed which were calculated using the sum of squares, degrees of freedom and expected mean square coefficients. The final output of nested model data with the streams combined is presented in the same manner as for the individual stream data output (note that some of NL values are missing due to lack of room on the left margin).

Censored Data

Another program (Table 17) which can handle censored sample distributions (Miesch, 1967b; Klusman and Edwards, 1976) was also used once to estimate the mean and variance of Cd. In the case of Cd, nearly 25% of the samples analyzed were below the detection limit (.04 ppm).

The test run of Ba and Co will be used to illustrate how this program is used. The following control cards are needed:

- 1) number of data sets and elements
- 2) name of elements
- 3) log option
- 4) form of data format
- 5) flag for end of data set
- 6) concentration where data is thrown out
- 7) detection limit for each element

For the test run of Ba and Co, the control cards would be printed as follows:

Table 17. Listing of censored data program.

```

DIMENSION IFMT(16), LABEL(12), FLAG(12), XLMT(12), DL(12), DATA(160,12)
1. XDATA(160), IHEAD(16), IOPT(12)
C READ IN NUMBER OF DATA SETS, NUMBER OF ELEMENTS
  READ(5,114) NM,MMM
114 FORMAT(2I2)
C READ IN ELEMENTS DETERMINED
  READ(5,100) (LABEL(I), I=1,MMM)
100 FORMAT(12A4)
C READ IN LOG OPTION
  READ(5,117) (IOPT(I), I=1,MMM)
117 FORMAT(12A3)
C READ IN VARIABLE FORMAT FOR DATA
  READ(5,101) (IFMT(I), I=1,16)
101 FORMAT(16A5)
C READ IN FLAG FOR END OF DATA SET
  READ(5,IFMT) (FLAG(I), I=1,MMM)
C READ IN CONCENTRATION WHERE DATA IS THROWN OUT BECAUSE OF VARIABLE
C DETECTION LIMIT
  READ(5,103) (XLMT(I), I=1,MMM)
103 FORMAT(12F5.0)
C READ IN DETECTION LIMIT FOR EACH ELEMENT
  READ(5,103) (DL(I), I=1,MMM)
  FACTR=ALOG(10.)
  DO 12 M=1,MM
C READ IN HEADING FOR EACH DATA SET
  READ(5,115) (IHEAD(I), I=1,16)
115 FORMAT(16A5)
  WRITE(6,116) (IHEAD(I), I=1,16)
116 FORMAT(1H1,16A5)
  WRITE(6,120) (LABEL(I), I=1,MMM)
120 FORMAT(1H ,12(4X,A4))
  N=1
C READ DATA CHECKING FOR LAST SAMPLE (CAUTION-9999MIGHT HAVE TO BE
C CHANGED FOR DATA IN A DIFFERENT FORMAT.
  5 READ(5,IFMT) (DATA(N,K), K=1,MMM)
  IF (DATA(N,1).EQ.999.9) GO TO 7
  WRITE(6,201) (DATA(N,K), K=1,MMM)
201 FORMAT(12F8.1)
C COUNT DATA
  N=N+1
  GO TO 5
C BEGIN LOOP THROUGH EACH ELEMENT
  7 DO 8 J=1,MMM
C SET COUNTERS AND SUMS TO ZERO
  SUMX=0.
  SUMX2=0.
  NP=0
  NT=0
  V=1
C WATCH FOR FLAG, SAMPLES BELOW DETECTION LIMIT
  6 IF (DATA(N,J).EQ.FLAG(J)) GO TO 1
  IF (DATA(N,J).EQ.XLMT(J)) GO TO 2

```

Table 17. (Cont.)

```

IF(DATA(N,J).LT.2.) GO TO 3
IF(IOPT(J).NE.3HLOG) GO TO 13
C CONVERT TO LOGS
  XDATA(N)=ALOG10(DATA(N,J))
  GO TO 14
13 XDATA(N)=DATA(N,J)
C SUM DATA(LOGS) AND UPDATE COUNTERS
14 SUMX=SUMX+XDATA(N)
  SUMX2=SUMX2+XDATA(N)**2
  GO TO 4
3 NP=NP+1
4 NT=NT+1
2 N=N+1
  GO TO 6
C CHECK TO BE SURE SOME OF THE DETERMINATIONS ARE ABOVE THE DETECTION
C LIMIT
1 IF(NT.NE.0) GO TO 10
11 WRITE(6,111) LABEL(J)
111 FORMAT(1H0,33HNO ANALYTICAL DETERMINATIONS FOR ,A4,21HABOVE DETECT
  110N LIMIT)
  GO TO 8
C DETERMINE THE NUMBER OF DETERMINATIONS ABOVE THE DETECTION LIMIT
10 NN=NT-NP
  IF(NN.EQ.0) GO TO 11
C CONVERT NUMBER TO FLOATING POINT
  XN=FLOAT(NN)
C WRITE SUMS
  WRITE(6,112) LABEL(J),SUMX
112 FORMAT(1H0,15HSUM(LOG) X FOR ,A4,3H = ,F12.3)
  WRITE(6,113) LABEL(J),SUMX2
113 FORMAT(1H ,18HSUM(LOG) X**2 FOR ,A4,3H = ,F12.3)
C DETERMINE GEOMETRIC MEAN
  XMEAP=SUMX/XN
C IF LOG OPTION NOT TAKEN GO TO BRANCH
  IF(IOPT(J).NE.3HLOG) GO TO 15
  GMEAP=EXP(FACTR*XMEAP)
  WRITE(6,104) LABEL(J),GMEAP
104 FORMAT(1H ,19HGEOMETRIC MEAN FOR ,A4,3H = ,F12.3)
C DETERMINE GEOMETRIC DEVIATION
  GDEV=EXP(FACTR*(SQRT((1./((XN**2)-XN))*(((XN*SUMX2)-(SUMX**2))))))
  WRITE(6,125) LABEL(J),GDEV
105 FORMAT(1H ,24HGEOMETRIC DEVIATION FOR ,A4,3H = ,F12.3)
C DETERMINE SIGMA PRIME (USGS PROF. PAPER 574-B, P. 7)
  SP=SQRT((SUMX2/XN)-(XMEAP**2))
  SPP=EXP(FACTR*SP)
  WRITE(6,106) LABEL(J),SP
106 FORMAT(1H ,16HSIGMA PRIME FOR ,A4,3H = ,F12.3)
C DETERMINE NUMBER OF SAMPLES BELOW THE DETECTION LIMIT AND PROPORTION
C ABOVE THE DETECTION LIMIT
  WRITE(6,107) NP,NT,LABEL(J)
107 FORMAT(1H ,13,27H SAMPLES OUT OF A TOTAL OF ,I3,
  134H ARE BELOW THE DETECTION LIMIT FOR,A4)

```


Table 17. (Cont.)

```

XH=FLOAT(NP)/FLOAT(NT)
WRITE(6,108) LABEL(J),XH
108 FORMAT(1H ,45HFRACTION OF SAMPLES BELOW DETECTION LIMIT FOR ,A4,3H
1= ,F10.3)
C DETERMINE X-AXIS VALUE FOR ESTIMATING LAMBDA (USGS PROC, PAPER 574-B,
XLAM=(SP**2)/((XMEAP-ALOG10(DL(J)))*2)
WRITE(6,112) LABEL(J),XLAM
112 FORMAT(1H ,42HVALUE OF X-AXIS FOR ESTIMATING LAMBDA FOR ,A4,3H = ,
1F10.3)
GO TO 8
C WRITE ARITHMETIC MEAN
15 WRITE(6,118) LABEL(J),XMEAP
118 FORMAT(1H ,20HARITHMETIC MEAN FOR ,A4,3H = ,F10.3)
C COMPUTE STANDARD DEVIATION
STDEV=SQRT((1./((XN**2)-XN))*(((XN*SUMX2)-(SUMX**2))))
WRITE(6,119) LABEL(J),STDEV
119 FORMAT(1H ,23HSTANDARD DEVIATION FOR ,A4,3H = ,F10.3)
SP=SQRT((SUMX2/XN)-(XMEAP**2))
WRITE(6,106) LABEL(J),SP
WRITE(6,107) NP,NT,LABEL(J)
WRITE(6,108) LABEL(J),XH
C COMPUTE X-AXIS VALUE FOR ESTIMATING LAMBDA
XLAM=(SP**2)/((XMEAP-DL(J))*2)
WRITE(6,110) LABEL(J),XLAM
8 CONTINUE
12 CONTINUE
END

```


Columns	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1)	0	1	0	2										
2)		B	A		C	O								
3)	L	O	G	L	O	G	(log base 10 transformation)							
4)	(	2	F	5	.	2	)							
5)	9	9	9	.	9	9	9	.	9	9				
6)	0	0	0	0	0	0	0	0						
7)	.	0				.	8	3						

For input data all values below the detection limit for each element must have a minus sign (see Co input data, Table 18).

Table 18.A. Input data for program listed in Table 17.

TEST RUN		
BA	CO	
30.0	-2.8	} Input Data
30.0	-0.8	
50.0	1.5	
100.0	3.0	
30.0	1.0	
70.0	-0.8	
0.0	0.0	
10.0	-0.8	
50.0	5.0	
30.0	1.0	
30.0	2.0	
70.0	2.0	
0.0	0.0	
30.0	3.0	

Table 18.B. Output data for program listed in Table 17.

SUM(LOG) X FOR BA	=	18.951
SUM(LOG) X**2 FOR BA	=	30.673
GEOMETRIC MEAN FOR BA	=	37.952
GEOMETRIC DEVIATION FOR BA	=	1.821
SIGMA PRIME FOR BA	=	0.249
0 SAMPLES OUT OF A TOTAL OF 12 ARE BELOW THE DETECTION LIMIT FOR BA		
FRACTION OF SAMPLES BELOW DETECTION LIMIT FOR BA	=	0.000
VALUE OF X-AXIS FOR ESTIMATING LAMBDA FOR BA	=	0.000
SUM(LOG) X FOR CO	=	2.431
SUM(LOG) X**2 FOR CO	=	1.156
GEOMETRIC MEAN FOR CO	=	2.013
GEOMETRIC DEVIATION FOR CO	=	1.754
SIGMA PRIME FOR CO	=	0.228
4 SAMPLES OUT OF A TOTAL OF 12 ARE BELOW THE DETECTION LIMIT FOR CO		
FRACTION OF SAMPLES BELOW DETECTION LIMIT FOR CO	=	0.333
VALUE OF X-AXIS FOR ESTIMATING LAMBDA FOR CO	=	0.332

Table 19. Listing of nested analyses for each stream location.

Sample Loca- tion number R-replication Stream	Latitude	Longitude	Grain Size Lithology Wet/dry Organic matter (%) pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
2742 R	39241710816132	110.637.9			.56	63.89.9	3.3	
2741 R	39241710816132	11.867.8			.66	63.34.5	4.5	
2741RR					.61			
2732 R	39241910816163	111.417.9			.57	59.22.0	4.3	
2731 R	39241910816162	11.947.9		27.1	.43	62.42.7	4.2	
2722 R	39242810816182	11.647.8		7.9	.47	136.32.6	3.7	
2721 R	39242810816182	11.967.7			.68	66.13.2	3.6	
2712 R	39243210816232	11.717.8		13.1	.39	65.53.1	2.3	
2712RR				19.0	.33	81.33.3		
2711 R	39243210816232	111.877.9			.68	71.53.6	4.5	
2762 R	39273910818572	11.827.92			.75	52.11.2	2.4	
2761 R	39273910818572	11.81		24.4	.52	62.42.2	3.2	
2761RR		.79						
2752 R	39271110818572	111.927.8			.72	54.59.9	3.5	
2751 R	39271110818572	111.928.2			.79	68.54.7	3.8	
2751RR					.72			
2751RR		1.93						
2772 R	39273910829153	116.227.8		39.9	.35	39.94.3	4.6	
2771 R	39273910829152	111.317.9			.68	52.93.7	3.4	
2771RR					.73			
2771RR					.57			
2771RR						55.22.2		
2782 R	39274010819182	111.867.8			.65	59.83.8	2.4	
2781 R	39274010819185	113.847.7			.54	71.55.3	4.5	
		999.			999.	999.	999.	
0782 B	395019108234342	1.567.8			.28	45.63.0	2.5	
782RB					.38	47.13.1		
0782RB					.35			
782RB					.40			
0781 B	395019108234352	1.767.9			.32	47.01.3	2.8	
781R					.27			
0792 B	395016108234952	1.957.8			.32	51.63.3	2.2	
792RB					.40			
792RB					.31	51.02.7		
0792RB					.31			
0791 B	395016108234952	1.697.9			.18	50.53.2	3.3	
0791RB					.20			
0802 B	395005108241052	1.517.8		10.4	.21	54.73.1	2.4	
802R		.92						
0801 B	395005108241052	1.687.7			.26	50.51.1	2.6	
0801RB					.30			
0812 B	395003108241342	1.107.8			.31	44.62.6	2.2	
812RB					.29			

Table 19. (Cont.)

Sample Loca- tion number R-replication Stream	Latitude	Longitude	Grain Size Lithology Wet/dry Organic matter (%)	pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
0811 B 0811R	394603108241352	11.527.9	1	.52		.53	58.14.0	2.4	
0811RB						.55			
0882 B 0882RB	394633108271922	12.147.5				.88	63.93.5	2.6	
0881 B 0892 B 0891 B	394633108271942 394629108272322 394629108272352	11.467.6 11.407.7 11.277.7	15.9			.45 .40 .28	54.69.9 58.42.7 64.74.3	2.3 2.7 3.8	
0902 B 0902R	394602108274722	1.867.7	1			.43	62.44.6	1.9	2.4
0901 B 0901R	394602108274742	12.197.6				.41	56.29.9	6.4	7.1
0912 B 0912RB	394559108274932	1.877.6	1			.40 .46	59.5 50.69.9	3.2	
0911 B	394559108274922	11.107.7	12.5			.39 .45	52.2 50.02.5	2.8	
2962 P 2961 P 2942 P	394803108043552 394803108043552 394803108043552	11.108.40 11.308.45 11.218.40				.17 .17 .17	63.42.0 71.89.9 62.29.9	5.4 3.8 2.3	
2942RP 2941 P 2941RP	394803108043552	11.448.45				.17 .26 .30	62.1 72.73.8	3.8	
2982 P 2982RP	394746108050852	1.948.45	1			.20 .23	72.02.7	3.6	
2981 P 2981RP 2981RP	394746108050852	11.458.55				.24	70.34.2 68.23.8		
3002 P 3002R 3002RP	394746108050852	11.268.35 8.55				.18 .23 .19	70.73.3	6.7	
3002RP 3002RP							69.82.7		
3021 P 3021RP	394746108050852	11.228.55				.21 .21	71.63.2	4.5	
3022 P 3021 P	394802108074052 394802108074052	1.928.05 1.818.33	1			.20 .39	61.89.9 67.33.8	4.3 4.3	
3021RP 3042 P 3041 P	394802108074042 394802108074052	1.948.17 11.168.37	1			.42 .30 .21	71.59.9 66.92.7	2.9 4.9	
3041RP 3062 P 3062R	394824108075852	1.738.13 8.27	1			.29 .13	67.53.1	5.2	

Table 19. (Cont.)

Sample Loca- tion number R-replication Stream	Latitude	Longitude	Grain Size Lithology Wet/dry Organic matter (%) pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
3261 P	394824108075852	112.928.32	1 .678.15		.17	78.79.9	4.7	
3282 P	394824108075842	112.928.32	1 .658.30		.21	58.32.1	4.5	
3281 P	394824108075852	112.928.32	1 .988.38		.34	65.22.3	4.1	
3281RP					.39			
			999.	999.	999.	999.	999.	
3452 C	39291110806344	112.928.32	112.928.32		.20	79.62.0	7.5	
3451 C	39291110806344	112.618.30			.22	69.25.3	8.3	
3472 C	39291110806345	112.938.50			.17	61.83.4	9.8	
3471 C	39291110806345	112.348.30			.26	65.95.0	9.2	
3471RC					.28			
3471RC					.38	67.75.2		
3471RC					.30			
3492 C	39291510806535	112.948.30	11 .948.30		.36	72.54.4	9.5	
3491 C	39291510806535	112.688.50	112.688.50		.25	69.52.5	9.3	
3512 C	39291510806535	112.918.33	11 .918.33		.17	62.03.0	9.4	
3512RC					.22	64.63.5		
3511 C	39291510806535	112.928.30	11 .928.30		.28	64.92.0	10.	
3511RC					.49	67.94.6		
3511RC					.75			
3592 C	393256108070659	12.438.35	12.438.35		.27	72.54.4	9.5	
3591 C	393256108070659	12.948.40	1 .948.40		.29	71.14.2	10.	
3591RC					.29			
3572 C	393256108070659	12.968.45	1 .968.45		.26	71.85.1	8.9	
3572RC					.29			
3571 C	393256108070659	12.938.30	1 .938.30		.17	66.62.5	9.6	
3552 C	393317108070659	12.928.40	1 .928.40		.17	64.42.0	9.6	
3551 C	393317108070659	12.418.30	12.418.30		.30	72.25.1	10.	
3551RC					.38			
3551RC						71.24.5		
3532 C	393317108070659	12.918.50	1 .918.50		.25	74.64.9	14.0	
3532RC					.28			
3531 C	393317108070659	12.498.30	12.498.30		.28	71.84.3	8.0	
3531R			2.43					
3531RC					.31			
			999.	999.	999.	999.	999.	
3182 Y	400237108201452	0 .278.43	0 .278.43		.15	58.33.4	3.4	
3181 Y	400237108201452	0 .278.42	0 .278.42		.19	49.11.6	4.2	
3181RY					.19			
3202 Y	400237108201452	0 .228.20	0 .228.20		.12	54.59.9	3.4	
3202R			8.42					
3201 Y	400237108201452	0 .378.36	0 .378.36		.15	54.91.6	3.2	
3201RY					.12			
3222 Y	400144108201952	0 .208.42	0 .208.42		.15	56.59.9	5.0	
3221 Y	400144108201952	0 .378.42	0 .378.42		.18	50.03.2	4.3	
3242 Y	400144108201942	0 .328.37	0 .328.37		.15	68.89.9	3.8	

Table 19. (Cont.)

Sample Location number R-replication Stream	Latitude	Longitude	Grain Size Lithology Wet/dry Organic matter (%) pH	As (ppm)	Hg (ppm)	Zn (ppm)	Cd (ppm)	Mo (ppm)
3241 Y	400144108201952	0	.918.27		.12	59.59.9	3.5	
3102 Y	395814108224832	0	.918.40		.17	44.79.9	4.1	
3102RY						49.3		
3102R			8.53					
3102R			.94					
3101 Y	395814108224832	0	.148.45		.12	62.19.9	2.3	
3122 Y	395814108224832	Z	.118.50		.13	42.91.1	2.8	
3122R			8.75					
3122RY					.10	44.21.8		
3122RY					.16			
3122RY					.15			
3121 Y	395814108224832	0	.938.57		.15	47.21.6	2.6	
3121RY					.16			
3142 Y	395750108231742	0	.168.60		.13	52.62.1		
3141 Y	395750108231752	Z	.308.50		.13	54.99.9	3.8	
3162 Y	395750108231732	0	.248.20		.18	47.71.3	1.6	
3162RY					.16			
3161 Y	395750108231742	0	.498.35		.13	54.99.9	3.3	
			999..		999.	999.	999.	

Table 20. Analysis of Variance Results for the Nested Stream Models.

Analysis of Variance of Individual Streams for Mo

Roan Creek

<u>Source of Variance</u>	<u>SS</u>	<u>DF</u>	<u>MS</u>	<u>F</u>	<u>Critical Values</u>
2 k segments	.00517	1	.00517	.36	F _{.05} (1,2)=18.5
200 m segments	.02885	2	.0144	2.28	F _{.05} (2,4)=6.94
20 m segments	.02518	4	.0063	.46	F _{.05} (4,8)=3.84
Samples	<u>.11064</u>	<u>8</u>	.01384		
Total	.16984	15			

Black Sulfur Creek

216 segments	.05734	1	.05734	7.60	F _{.05} (1,2)=18.5
200 m segments	.01507	2	.00754	1.19	F _{.05} (2,4)=6.9
20 m segments	.02527	4	.00632	.19	F _{.05} (4,8)=3.8
Samples	.27282	8	.03410	11.07	F _{.05} (8,2)=19.4
Replications	<u>.00616</u>	<u>2</u>	.00308		
Total	.37666	17			

Piceance Creek

2 k segments	.00281	1	.00281	.21	F _{.05} (1,2)=18.5
200 m segments	.02708	2	.01354	.81	F _{.05} (2,4)=6.9
20 m segments	.06706	4	.01677	1.48	F _{.05} (4,7)=4.1
Samples	<u>.07923</u>	<u>7</u>	.01132		
Total	.17618	14			

Parachute Creek

2 k segments	.00464	1	.00464	1.69	F _{.05} (1,2)=18.5
200 m segments	.00548	2	.00274	1.32	F _{.05} (2,4)=6.9
20 m segments	.00830	4	.00208	.51	F _{.05} (4,8)=3.8
Samples	<u>.03223</u>	<u>8</u>	.00407		
Total	.05065	15			

Yellow Creek

2 k segments	.06803	1	.06803	8.72	F _{.05} (1,2)=18.5
200 m segments	.01555	2	.0078	.55	F _{.05} (2,4)=6.5
20 m segments	.05674	4	.01418	1.13	F _{.05} (2,4)=4.12
Samples	<u>.08794</u>	<u>7</u>	.01256		
Total	.22825	14			

Table 20 (Cont.)

Analysis of Variance of All Streams for Mo

<u>Source of Variance</u>	<u>SS</u>	<u>DF</u>	<u>MS</u>	<u>F</u>	<u>Critical Values</u>
Streams	2.65804	4	.66451	28.54*	$F_{.05}(4,5)=5.2$
2 k segments	.11617	5	.02324	1.64	$F_{.05}(5,10)=3.3$
200 m segments	.14147	10	.01414	.88	$F_{.05}(10,20)=2.4$
20 m segments	.31980	20	.01599	1.29	$F_{.05}(20,30)=1.9$
Samples	.47102	38	.01240	3.26	$F_{.05}(30,2)=19.5$
Replications	.00616	2	.00308		
Total	3.71269	79			

Analysis of Variance of Individual Streams for Hg

Roan Creek

2 k segments	.02560	1	.02560	2.08	$F_{.05}(1,2)=18.5$
200 m segments	.02466	2	.02233	1.91	$F_{.05}(2,4)=6.9$
20 m segments	.02576	4	.00644	.38	$F_{.05}(4,8)=3.8$
Samples	.13515	8	.01689	11.1*	$F_{.05}(8,5)=4.8$
Replications	.00758	5	.00152		
Total	.21876	20			

Black Sulfur Creek

2 k segments	.21608	1	.21608	13.53	$F_{.05}(1,2)=18.5$
200 m segments	.03194	2	.01597	.30	$F_{.05}(2,4)=6.9$
20 m segments	.21238	4	.05310	1.79	$F_{.05}(4,8)=3.8$
Samples	.23702	8	.02963	13.91*	$F_{.05}(8,4)=2.7$
Replications	.02985	14	.00213		
Total	.72726	29			

Piceance Creek

2 k segments	.04901	1	.04901	2.68	$F_{.05}(1,2)=18.5$
200 m segments	.03661	2	.01831	.48	$F_{.05}(2,4)=6.94$
20 m segments	.15405	4	.03851	1.84	$F_{.05}(4,8)=3.84$
Sample	.16721	8	.0209	8.10*	$F_{.05}(8,4)=2.95$
Replications	.02841	11	.00258		
Total	.43529	26			

Parachute Creek

2 k segments	.00475	1	.00475	.22	$F_{.05}(1,2)=18.5$
200 m segments	.04236	2	.02118	2.85	$F_{.05}(2,4)=6.94$
20 m segments	.02976	4	.00744	.18	$F_{.05}(4,8)=3.84$
Samples	.33134	8	.04142	3.73*	$F_{.05}(8,11)=2.95$
Replications	.12224	11	.01111		
Total	.53045	26			

*indicates F value larger than the 95% confidence critical value.

Table 20 (Cont.)

<u>Source of Variance</u>	<u>SS</u>	<u>DF</u>	<u>MS</u>	<u>F</u>	<u>Critical Values</u>
<u>Yellow Creek</u>					
2 k segments	.00080	1	.00080	8.00	F _{.05} (1,2)=18.5
200 m segments	.00019	2	.00010	.01	F _{.05} (2,4)=6.94
20 m segments	.04176	4	.01044	2.19	F _{.05} (4,8)=3.84
Samples	.03810	8	.00476	.77	F _{.05} (8,7)=3.73
Replications	.04327	7	.00618		
Total	.12412	22			
Analysis of Variance of All Streams for Hg					
Streams	4.40435	4	1.10105	18.58*	F _{.05} (4,5)=5.19
2 k segments	.29625	5	.05925	4.37*	F _{.05} (5,10)=3.33
200 m segments	.13575	10	.01357	.59	F _{.05} (10,20)=2.35
20 m segments	.46371	20	.62319	1.02	F _{.05} (20,40)=1.84
Samples	.90887	40	.02272	4.71*	F _{.05} (40,48)=1.60
Replications	.23135	48	.00482		
Total					
Analysis of Variance of Individual Streams for Zn					
<u>Roan Creek</u>					
2 k segments	.04780	1	.04780	3.09	F _{.05} (1,2)=18.5
200 m segments	.03091	2	.01546	1.67	F _{.05} (2,4)=6.94
20 m segments	.03701	4	.00925	1.02	F _{.05} (4,8)=3.84
Samples	.07228	8	.00904	3.95	F _{.05} (8,2)=19.37
Replications	.00457	2	.00229		
Total	.19258	17			
<u>Black Sulfur Creek</u>					
2 k segments	.01670	1	.01670	6.44	F _{.05} (1,2)=18.5
200 m segments	.00543	2	.00272	1.15	F _{.05} (2,4)=6.94
20 m segments	.00945	4	.00236	1.65	F _{.05} (4,8)=3.84
Samples	.01140	8	.00143	11.00*	F _{.05} (8,4)=6.04
Replications	.00051	4	.00013		
Total	.04348	19			
<u>Piceance Creek</u>					
2 k segments	.00048	1	.00048	.50	F _{.05} (1,2)=18.5
200 m segments	.00191	2	.00096	.59	F _{.05} (2,4)=6.94
20 m segments	.00642	4	.00162	1.40	F _{.05} (4,8)=3.84
Samples	.00925	8	.00116	38.67*	F _{.05} (8,3)=8.85
Replications	.00010	3	.00003		
Total	.01821	18			

Table 20 (Cont.)

<u>Source of Variance</u>	<u>SS</u>	<u>DF</u>	<u>MS</u>	<u>F</u>	<u>Critical Values</u>
<u>Parachute Creek</u>					
2 k segments	.00176	1	.00176	9.78	$F_{.05}(1,2)=18.5$
200 m segments	.00035	2	.00018	.10	$F_{.05}(2,4)=6.94$
20 m segments	.00690	4	.00173	2.54	$F_{.05}(4,8)=3.84$
Samples	.00540	8	.00068	6.14*	$F_{.05}(8,4)=6.04$
Replications	<u>.00045</u>	<u>4</u>	<u>.00011</u>		
Total	.01486	19			
<u>Yellow Creek</u>					
2 k segments	.01248	1	.01248	4.36	$F_{.05}(1,2)=18.5$
200 m segments	.00571	2	.00286	.89	$F_{.05}(2,4)=6.94$
20 m segments	.01281	4	.00320	1.36	$F_{.05}(4,8)=3.89$
Samples	.01880	8	.00235	4.74	$F_{.05}(8,2)=19.37$
Replications	<u>.00099</u>	<u>2</u>	<u>.00050</u>		
Total	.05079	17			
Analysis of Variance of all Streams for Zn					
Streams	.24818	4	.06205	3.91	$F_{.05}(4,5)=5.19$
2 k segments	.07923	5	.01585	3.58*	$F_{.05}(5,10)=3.33$
200 m segments	.04429	10	.004429	1.22	$F_{.05}(10,20)=2.35$
20 m segments	.07259	20	.00363	1.24	$F_{.05}(20,40)=1.84$
Samples	.11718	40	.00293	6.66*	$F_{.05}(40,15)=2.20$
Replications	<u>.00662</u>	<u>15</u>	<u>.00044</u>		
Total	.56809	94			
Analysis of Variance of Individual Streams for Organic Carbon					
<u>Roan Creek</u>					
2 k segments	.24716	1	.24716	2.57	$F_{.05}(1,2)=18.5$
200 m segments	.19265	2	.09635	1.27	$F_{.05}(2,4)=6.94$
20 m segments	.30408	4	.07602	1.21	$F_{.05}(4,8)=3.84$
Samples	<u>.50418</u>	<u>8</u>	<u>.06302</u>	21.00*	$F_{.05}(8,2)=19.37$
Total	1.24817	17			
<u>Black Sulfur Creek</u>					
2 k segments	.75958	1	.75958	8.47	$F_{.05}(1,2)=18.5$
200 m segments	.17933	2	.08967	2.33	$F_{.05}(2,4)=6.94$
20 m segments	.15395	4	.03849	.65	$F_{.05}(4,8)=3.84$
Samples	.47362	8	.05920	29.60*	$F_{.05}(8,2)=19.37$
Replications	<u>.00004</u>	<u>2</u>	<u>.00002</u>		
Total	1.56651	17			

Table 20 (Cont.)

<u>Source of Variance</u>	<u>SS</u>	<u>DF</u>	<u>MS</u>	<u>F</u>	<u>Critical Values</u>
<u>Piceance Creek</u>					
2 k segments	.10643	1	.10643	9.43	F _{.05} (1,2)=18.5
200 m segments	.02256	2	.01128	3.50	F _{.05} (2,4)=6.94
20 m segments	.01291	4	.00323	.54	F _{.05} (4,8)=3.84
Samples	.04740	8	.00593		
Total	.18930	15			
<u>Parachute Creek</u>					
2 k segments	.00439	1	.00439	1.63	F _{.05} (1,2)=18.5
200 m segments	.00544	2	.00270	4.29	F _{.05} (2,4)=6.95
20 m segments	.00250	4	.00063	1.97	F _{.05} (4,8)=3.84
Samples	.00255	8	.00032	5.33	F _{.05} (8,1)=238.9
Replications	.00006	1			
Total	.01494	16			
<u>Yellow Creek</u>					
2 k segments	.05288	1	.05288	1.07	F _{.05} (1,2)=18.5
200 m segments	.09912	2	.04956	2.68	F _{.05} (2,4)=6.94
20 m segments	.07393	4	.01848	.71	F _{.05} (4,8)=3.84
Samples	.20833	8	.02604	153.18	F _{.05} (8,1)=238.9
Replications	.00017	1	.00017		
Total	.43443	16			
Analysis of Variance of all Streams for Organic Matter					
Streams	9.67667	4	2.41917	10.33*	F _{.05} (4,5)=5.19
2 k segments	1.17044	5	.23409	4.69*	F _{.05} (5,10)=3.33
200 m segments	.49915	10	.04992	1.82	F _{.05} (10,20)=2.35
20 m segments	.54738	20	.02737	.89	F _{.05} (20,40)=1.84
Samples	1.23607	40	.03090	5.15*	F _{.05} (40,6)=3.77
Replications	.00033	6			
Total		85			

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