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A GEOCHEMICAL ORIENTATION STUDY
FOR LEAD AND ZINC IN THE
FAIRBANKS, ALASKA AREA

By

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ABSTRACT

A geochemical orientation survey about a zone of known lead and zinc mineralization in the Fairbanks, Alaska area was conducted. One hundred ninety-two stream sediment samples were collected at 300' intervals. The samples were analyzed for "total" Cu, Pb, and Zn by atomic absorption after an acid digestion of the minus 80 mesh material. Colorimetric field tests were run on the same samples.

The colorimetric field test was found to correlate with zinc mineralization and was proved to be a valid test if carefully run. Duplicate samples taken 5 to 10 feet apart indicated extreme variation in metal values over short distances in anomalous zones. Composite samples over 20-50' distance would yield much greater confidence in a single sample. The analytical precision was found to be about 5 ppm for each of Cu, Pb, and Zn. The preferred sampling intervals in prospecting for lead mineralization in this area is suggested as about 1/4 mile. Various methods of geochemical data interpretations are compared. Probably the most instructive method was found to be a plot of log metal values versus cumulative per cent of samples for these data.

INTRODUCTION

Considerable of the Division's overall effort centers around the technique of exploration geochemistry. Much detail is present in the literature about the many variables and methods of their control in the geochemical exploration for lead and zinc. The various sources of literature are not always consistent in results. This may be expected as each study deals with a unique environment. Only a small proportion of the exploration geochemical studies reported in the literature deal with sub-Arctic environments as is present in the area of this study.

An orientation survey such as the present study is usually conducted around a known source of mineralization and sets out to define the preferred methods for such things as sampling, analytical methods and interpretation procedures in order to effectively use exploration geochemistry in similar environments, or to simply extend outward from the area studied.

PURPOSE AND SCOPE

Some of the questions this study investigated include: 1) the sensitivity and quality of the colorimetric field test for heavy metals, 2) the preferred techniques and pitfalls within the colorimetric field test, 3) the geochemical detection of mineralization by our devised method of acid digestion of the sample and determining copper, lead, and zinc by atomic absorption spectrophotometry as a "total" metal analysis, 4) the correspondence between ml of dye in the field dye test and the atomic absorption's determination of the metal level in the dithizone extract, 5) to provide some information about the preferred sample distance interval, 6) to provide information about the reliability of individual samples, and 7) to provide information about the techniques of geochemical data interpretation.

LOCATION

About 17 road miles northeast of Fairbanks is an occurrence of lead-zinc-mineralization. The location of the mineralization is known now as the Busty Belle Mine or Prospect. A small amount of ore has been taken from a zone which lies in a topographic saddle in Secs. 8 and 9, T. 1 E, R. 2 N., Fairbanks Base and Meridian. The Busty Belle Mine is surrounded by a somewhat radial drainage pattern which includes the following creeks: Fox, Flume, Unnamed lateral to Flume, Gold Run, Moose 1, Moose 2, and Seattle. A sketch map of the area is shown in Fig. 1.

TOPOGRAPHY AND STREAM FEATURES

The topographic relief is moderate to steep (500 to 1000' vertical relief/mile) in the area sampled. The highest drainage point sampled was approximately 1500' and the lowest approximately 600' elevation. All the area is thickly covered with moss, grass, willow, and spruce. Considerable trenching and some tunneling has been done at the Busty Belle Prospect. The closest drainage point to the Busty Belle is the head of Fox Creek about 1/2 mile distance. A small prospect pit occurs about 1/2 mile below the point of origin of Fox Creek and near its bank. Sulfide mineralization had been dug into. The sulfide was found by X-ray diffraction to be boulangerite. Several prospect pits are present along Flume Creek and considerable dredging for placer gold has been done along the lower reaches of Seattle Creek.

The sampling was done during the week of May 5 through 9, 1969. This is probably a particularly poor time of year to sample. Melt water run-off near its peak. However, "time available" required this time schedule. In many places the streams had exceeded their normal channel widths. In some places the streams were still iced over and the samples were taken through the ice. In some places no sample could be taken because of ice conditions. Stream temperature, pH and Eh were not determined. Stream sizes ranged from trickles at their heads to several feet broad and a foot or more deep in their lower ends. A total of about 10 miles of drainage was sampled.

PROCEDURES

SAMPLING METHODS

The extremely close interval of 300' was chosen for consecutive sample points. The intervals were estimated and not measured. Two parties of two people each collected the samples over a period of four days. With few exceptions the samples were taken below water level. Care was taken to choose the finer material, but even so silt and sand-sized particles were the principal constituents in a few samples. Some samples consisted of frozen mud with considerable ice. Organic matter was avoided as much as possible but constituted much of the sample in some cases.

The samples were taken in cloth bags, the excess water squeezed from the bag and then the cloth bag was slipped inside a light plastic (Baggie) sandwich bag. The plastic bag prevented moisture from one sample running into another. Most of the samples ranged from 100 to 500 grams, but some were less than 50 grams. At each fifth sample point a duplicate sample was taken from 5 to 10 feet from the original sample. Random duplicate sampling will allow a test of the reproducibility of the sample itself.

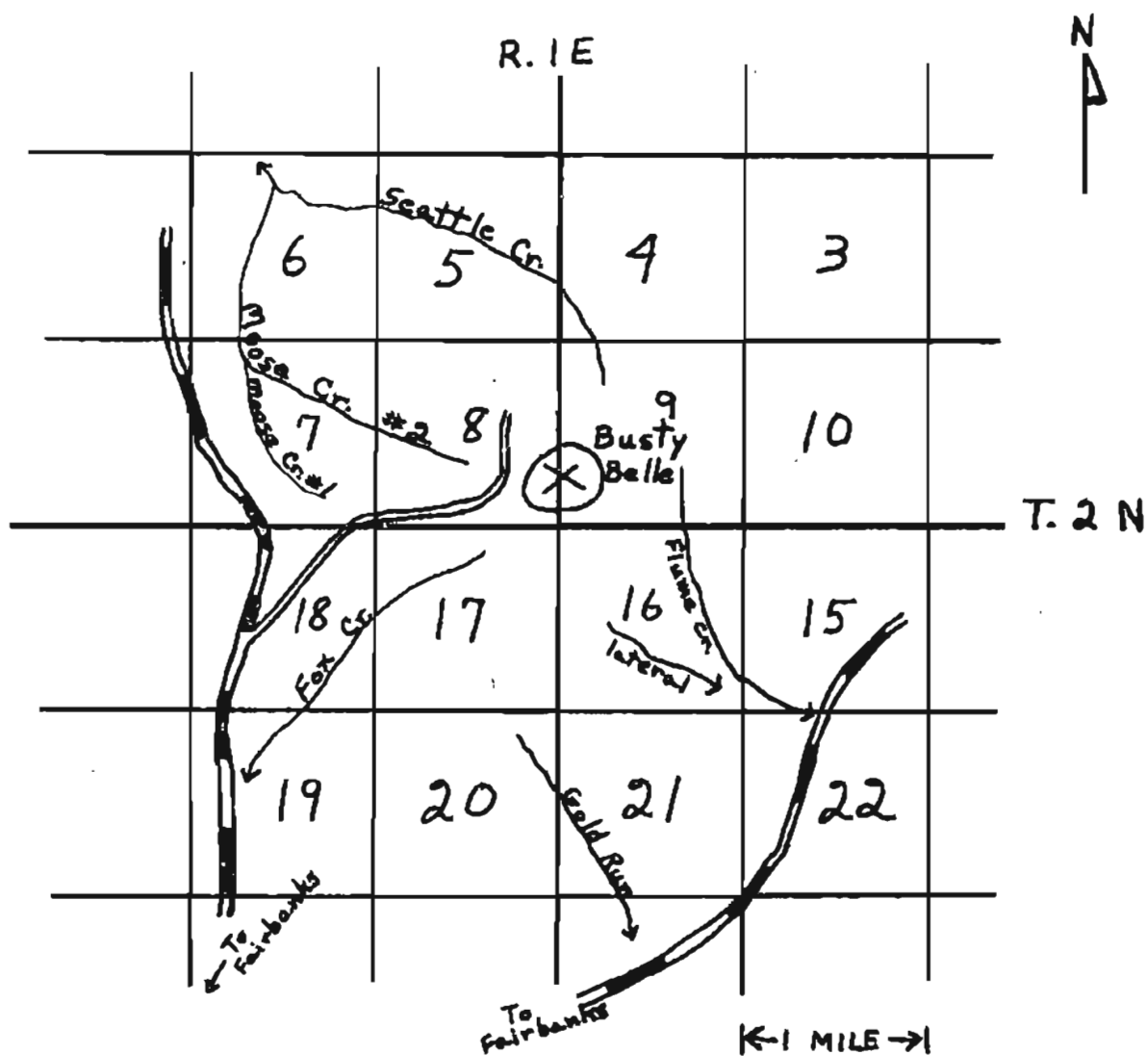


Fig. 1 Sketch map of the area about the Busty Bella Mine showing the drainages sampled.

At most of the sample stations a 20 ml sample of the stream water was analyzed for heavy metals by the dithizone field test. Each sample station was marked with a red "surveyors flag" which will allow returning to particularly interesting or problem points for future work.

A record was made of the sample and stream characteristics including sediment size, organic matter content, creek size and volume, stream gradient, bedrock type, and the nature of stream-bed float. To date no effort has been made to correlate these features with geochemical data.

SAMPLE PREPARATION

Upon returning the samples from the field the plastic bags were removed and the sample in the cloth bag was kneaded to homogenize the sediment. A "grab" split of the wet sample was placed in the plastic bag for further work. The remaining sample in the cloth bag was placed in an 80 C oven and dried. The dried sediment was screened on an 80 mesh stainless steel screen. The fines were saved for analysis and the plus 80 mesh material was discarded.

ANALYTICAL METHODS

The samples were all analyzed for "total" Cu, Pb, and Zn by atomic absorption spectrophotometry (AAS). This method has been previously described (Anderson, Paul L. and Namok Cho (1969), Procedure for the Analysis of Cu, Pb, and Zn in Geochemical Samples, Lab. Report #3, Alaska State Division of Mines and Geology). Eighteen samples, randomly chosen, were analyzed in duplicate for an analytical precision test.

A second AAS analysis determined the cold ammonium citrate extractable Cu, Pb, and Zn with the following procedure. One gram of sample was reacted overnight at room temperature with ammonium citrate at pH 8. This is the same type of solution as used for the colorimetric field test. The metals dissolved by the ammonium citrate were extracted into dithizone dissolved in xylene. This, also, is the same type solution as that used for the field test. The amount of metals actually in the dithizone were determined with AAS by comparing to standards.

In addition, each sample was analyzed for cold soluble heavy metal by the colorimetric field test. In all cases where dithizone was used the concentration was 0.01g/100 ml xylene.

RESULTS

ATOMIC ABSORPTION ANALYSES FOR TOTAL METAL

Data for individual samples are not reported here but can be made available to interested parties. The interpretation section reports a summary of the data.

The precisions of the AAS analyses for total Cu, Pb, and Zn were determined by duplicate analyses on 18 samples. The standard deviations were found to be:

Cu = 3 ppm

Pb = 6 ppm

Zn = 7 ppm

These precisions could be narrowed by making more exact estimates on the read-out. We have elected to read directly from the meter only to the nearest 5 ppm.

COLORIMETRIC FIELD TEST FOR HEAVY METALS

Our experience during the study was that the colorimetric field test is disconcertingly variable in results unless the procedure is very rigorously standardized. The number of strokes during the shake-out must be constant; we use 50. We shake rather slowly counting down strokes. It appears that the vigor and rhythm of the strokes must also be standardized. Contamination is a serious hazard and the greatest of care must be taken to prevent contamination. Fingers should never come into contact with anything that will also contact the reagents. The graduated cylinder should be washed with metal-free water and finally with dithizone test solution following the analysis of a sample that gives color and prior to running the first analysis. Evidently, organic matter contained in some samples can completely bleach the dithizone. Such samples are just not amenable to the field test as far as we can tell. It is well to have a standard solution (we use 0.5 ppm Zn in the ammonium citrate solution) to periodically test the integrity of the dye solution. The end point should be viewed in bright light against a white paper and away from colored objects. We have found it useful to have a fully titrated solution with which to make a direct end-point comparison. In some cases the solutions foam and it is impossible to see the color of the dithizone. In such instances we have found it effective to "hand centrifuge" the graduated cylinder by attaching a stout fishing line (with a swivel) and swinging the cylinder for about a half minute.

Replicate titrations on samples of intermediate and high test values were made to determine the precision of the test. The results were:

ANALYST	RESULTS, ML DYE	RANGE	MEAN	σ
1*	4, 4, 3, 4, 3, 2, 4	2-4	3	1
1	10, 10, 6, 10, 6, 4, 10	4-10	9	2
2*	3, 4, 3, 4, 3, 3, 2, 4, 5, 3	2-5	4	1
2	11, 11, 13, 13, 10, 11, 10, 15, 11	10-16	12	2

*Analyst 1 and analyst 2 were not analyzing the same sample and so those values cannot be compared.

Based on the above it is suggested that more than one determination should be made on samples that yield color in order to establish the range, mean and degree of significance of the positive test.

On 38 samples the amount of Cu, Pb, and Zn in the dithizone was determined by AAS. These values were compared to the ml values of the field test. A significant correlation would tend to confirm the validity of the field test. One obvious difficulty is that the field test is much more sensitive for Zn than for Pb or Cu. For the comparison no weighting for the greater sensitivity of the Zn was used. The sum of ppm Cu, Pb, and Zn determined by AAS were compared directly to the ml dye determined by the field test. AAS found Zn and Cu in the dithizone from all the samples. The values ranged from 0.3 to 2.2 ppm Zn, and from 0.1 to 0.8 ppm Cu. The dithizone from no sample contained Pb detectable by AAS even though the AAS sensitivity for Pb in dithizone was better than 0.1 ppm. It is concluded that the field test is very ineffective for detecting lead.

The statistical coefficient of correlation between ppm Zn plus Cu (in the dithizone) by AAS versus ml dye by titration was a very respectable +0.8. This yields a 65% explained variation, which is at least as good as was expected, and strongly confirms the validity of the field test.

INTERPRETATION OF DATA

The literature is replete with methods of interpretation of geochemical data. The methods range from simple inspection of raw data, to graphical, and to elegant but complicated statistical definitions. In choosing a method the population's frequency distribution, number of samples, element characteristics, etc., must all be taken into account. Then finally one weighs the penalty of making an incorrect null hypothesis, e. g., not discerning a target area when one is in fact present, or discerning a target area that is not real.

One of the more common methods of data presentation and interpretation is the simple normal-normal histogram. Such histograms for the "total metal" values acquired in this study are shown in Figs. 2, 3, and 4. By observing these histograms it is seen that the copper population has a very narrow range with no apparent anomalous values. A statistical treatment of the copper values finds the mean at 20 ppm (the same as the mode defined by the histogram). The standard deviation is 15 ppm. Defining anomalous values as the mean plus two standard deviations (50 ppm) indicates there are no anomalous Cu values. The histogram is very nearly symmetrical suggesting a normal, rather than log-normal, frequency distribution. These data all indicate there is no copper mineralization in the area sampled that is detectable by this geochemical method.

The geochemical pattern for Pb is quite different from that of Cu. There is known Pb mineralization in the area and the geochemical data strongly reflects that fact. The normal-normal histogram of the Pb data is shown in Fig. 3. The histogram shows a skewed distribution towards the high values with several values that are apparently anomalous. It would be difficult to define the anomalous boundary by simple inspection of the histogram. Statistically, the mean is 30 ppm (but the mode is 20) and the standard deviation is 35 ppm. Therefore, using a statistical definition of the mean plus two standard deviations as anomalous, the anomalous values are those above 100 ppm. The difference between the mean and the mode reflects the several high Pb values which leads to a significantly higher mean. All the statistically defined anomalous samples were from two rather narrow zones on Fox Creek, one near its origin and one about 3000 feet down stream from its origin. The lower anomalous zone is just below the prospect pit on Fox Creek and evidently reflects that mineralization.

The histogram for zinc is shown in Fig. 4. This histogram also shows some anomalous values, three or more. A statistical treatment shows a mean of 65 ppm (the same as the mode) and the mean plus two σ equals 120 ppm. This definition indicates four anomalous values. The histogram is skewed indicating the zinc population is not normally distributed. This is another example of conflicting definitions. From simple inspection of the histogram one would probably define the anomalous values as those above 120 ppm. The statistical definition includes the two 120 ppm samples as being anomalous.

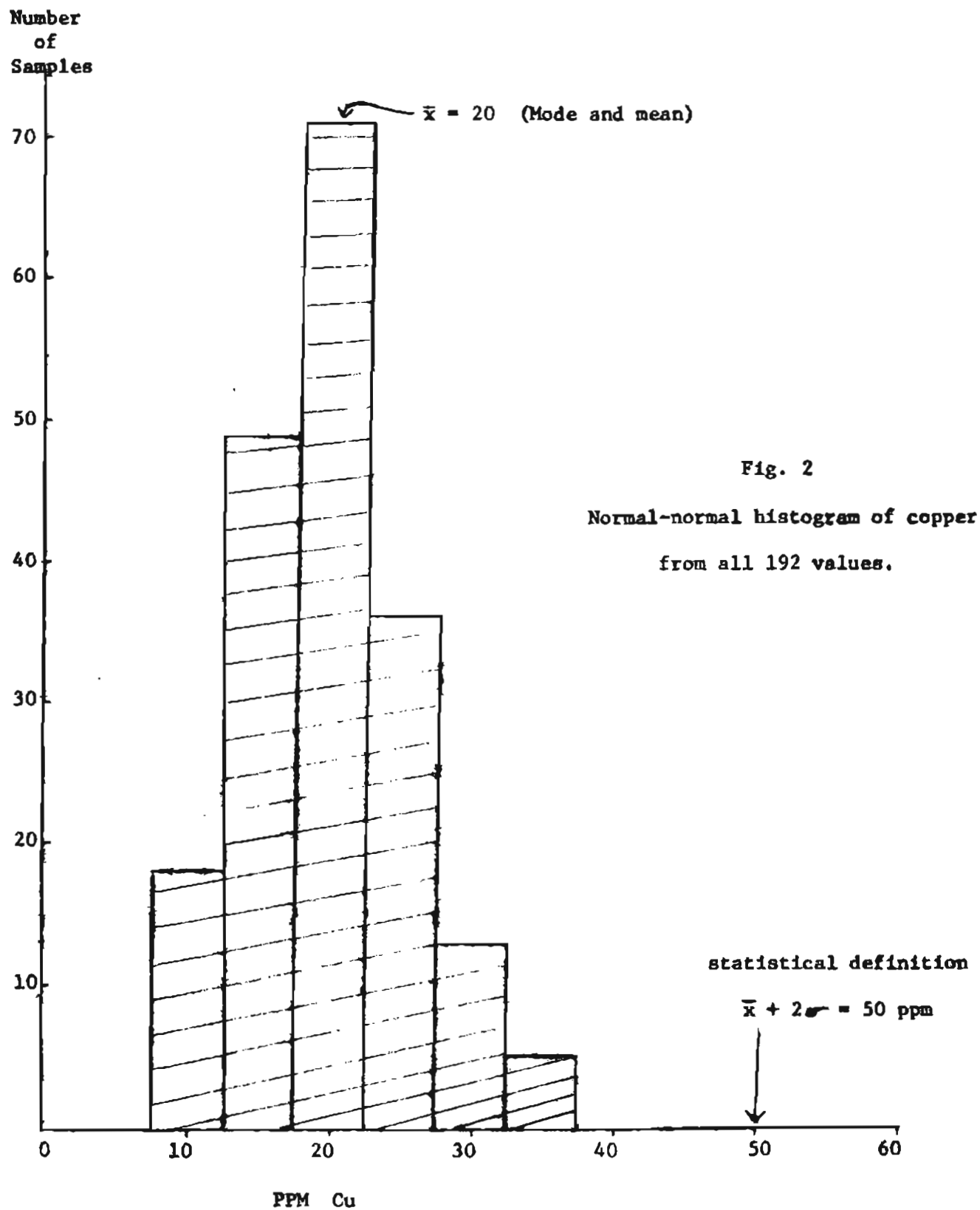
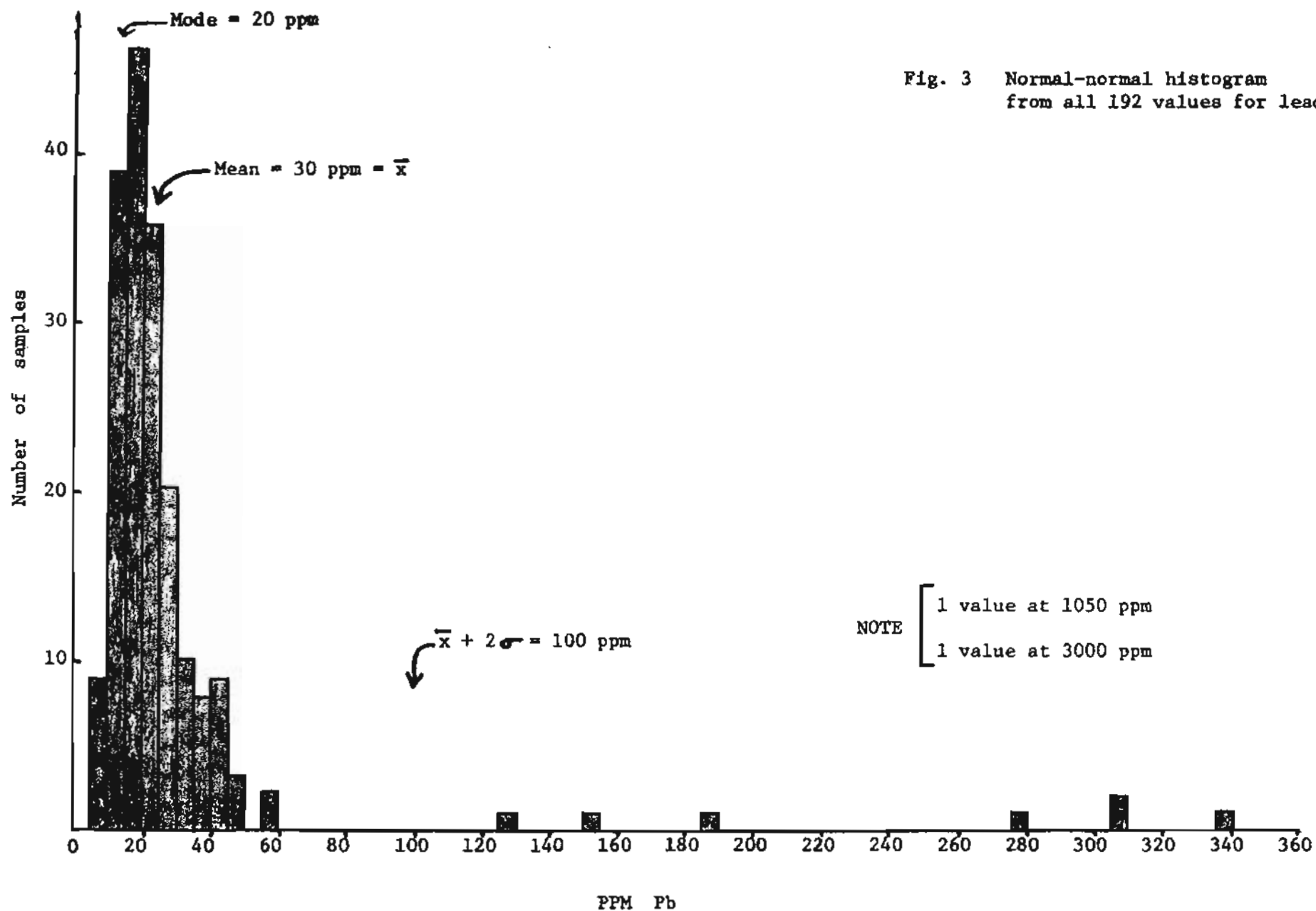


Fig. 2
Normal-normal histogram of copper
from all 192 values.



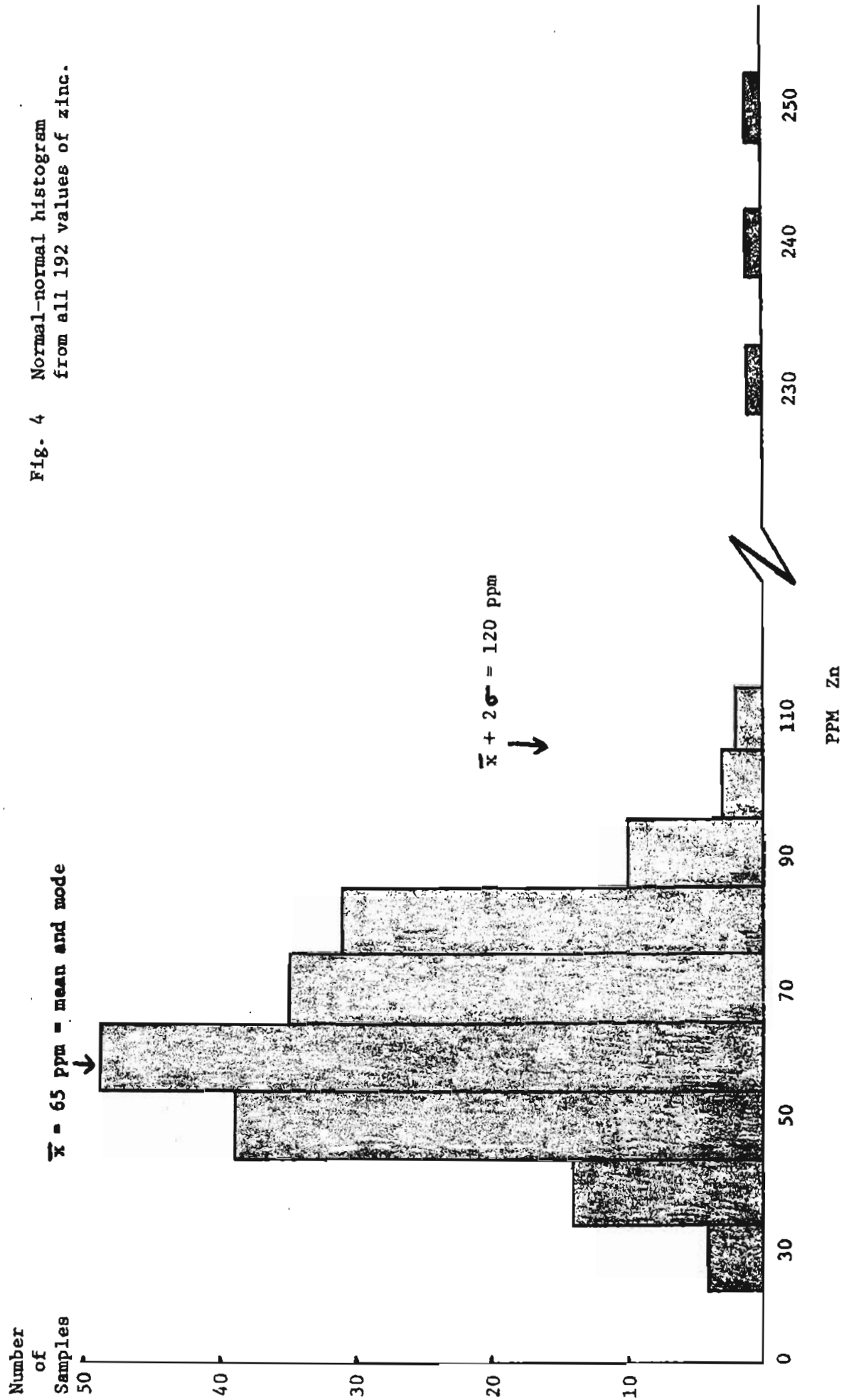


Fig. 4 Normal-normal histogram
from all 192 values of zinc.

Another kind of graphical interpretation which may be instructive is that of cumulative per cent of samples versus log ppm intervals. Such a plot for the lead values is shown in Fig. 5. This plot very decidedly shows two separate populations, a background population, which is log-normally distributed as indicated by the straight line relationship, and a separate anomalous population which is also log-normally distributed. The median can be determined by inspection on such a plot and is simply the 50% vertical line, in this case 20 ppm Pb. Note that the median is equal to the previously defined mode, but lower than the mean (30 ppm). As the curve deviates from the straight-line extrapolation near 30 ppm there is a group of "possibly anomalous concentrations" in the bend of the curve up to where it joins the straight line of the anomalous population (80 ppm). The intersection of the two extrapolated "population lines" (35 ppm) would be the best choice of the dividing concentration between the background and the anomalous populations. Therefore, depending on the nature of the geochemical survey this treatment would yield 30, 35, or 80 ppm as significant concentration levels. This system of interpretation, as with any other, becomes less useful as the number of samples becomes fewer. At a minimum there should be enough samples to give a wide enough population distribution that a minimum of four points will be present for defining the background population. It is unlikely that fewer than 20 samples would provide at least four data points. Should a population not be log-normally distributed no straight lines develop and the above system would probably not be the best choice for data interpretation.

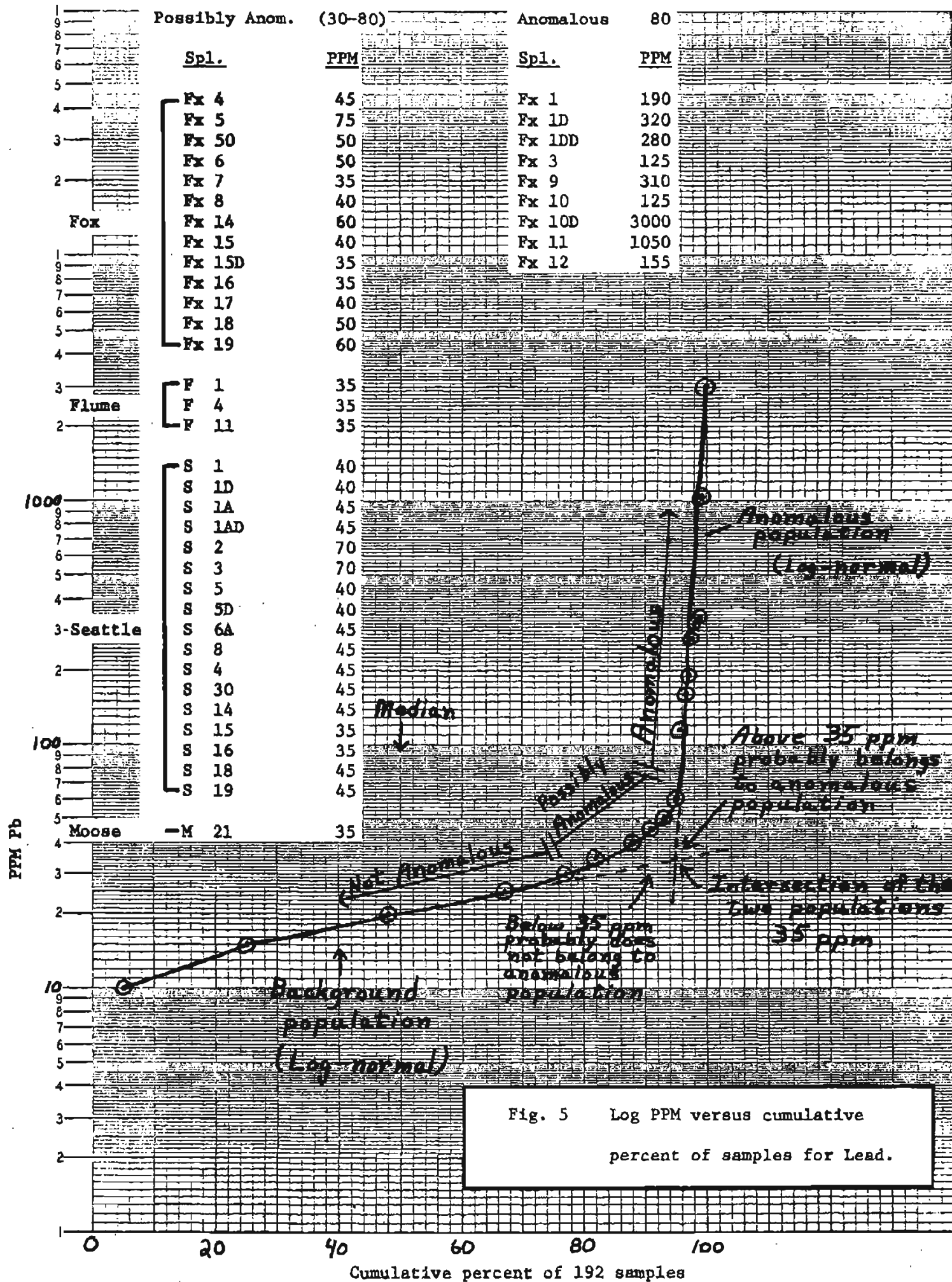
A log-concentration vs cumulative percent of samples plot for Zn is shown in Fig. 6. This plot also shows two populations, an anomalous and a non-anomalous. From this plot possibly anomalous concentrations range from 90 to 130 ppm and anomalous values are those above 130 ppm. The median is 60 ppm, compared to 65 ppm for the mode and the mean.

Data interpretation by statistical inference is among the methods most commonly used. The most obvious problems in the use of statistics is that for sample populations which are not normally distributed biased results are given unless the data are first adjusted to fit the nature of the distribution. In the case of a geochemical population that is log-normally distributed the data would more ideally be handled statistically by using log transformed data. The amount of error generated by using normal data for a log-normal population distribution may not be great but it is significant.

One of the major problems in statistical data handling is the presence of a few extreme values. For example within the present study on Pb with a mode and median of 20 ppm, the mean was 30 ppm even after excluding the two most extreme values (1050 and 3000 ppm). If these values are included the mean jumps to 50 ppm. Standard deviations are similarly strongly affected by the presence of one or two extreme values. While it is simple enough to exclude extreme values it is not necessarily obvious as to which values are extreme.

For the present data the mean for copper was 20 ppm, $\sigma = 15$ ppm. Using the mean plus 2σ as a definition of anomalous (50 ppm) there were no values anomalous in copper. For zinc the mean is 65 ppm, $\sigma = 25$ ppm, and the mean plus $2\sigma = 115$ ppm. There were five values, four on Fox Creek and one on Seattle Creek that were anomalous in zinc. For lead the mean (excluding two extreme values) was 30 ppm, $\sigma = 35$ ppm, and mean plus $2\sigma = 100$ ppm. There were nine values statistically anomalous in lead. They were all from Fox Creek.

It is worth comparing the arithmetic means, the modes, and the various interpretations of "anomalous" discussed herein as follows:



Possibly Anom. 90 - 140 ppm

Spl.	PPM
Fx 1	80
Fx 5	100
Fx 10D	125
Fx 19	100
Fx 10	110
S 3	105
S 5	100
S 5D	100
S 9	100
S 10	95
S 11	95
S 14	100
S 18	115
S 19	105

Anomalous 140 ppm

Spl.	PPM
Fx 1D	250
Fx 10D	235
Fx 3	120

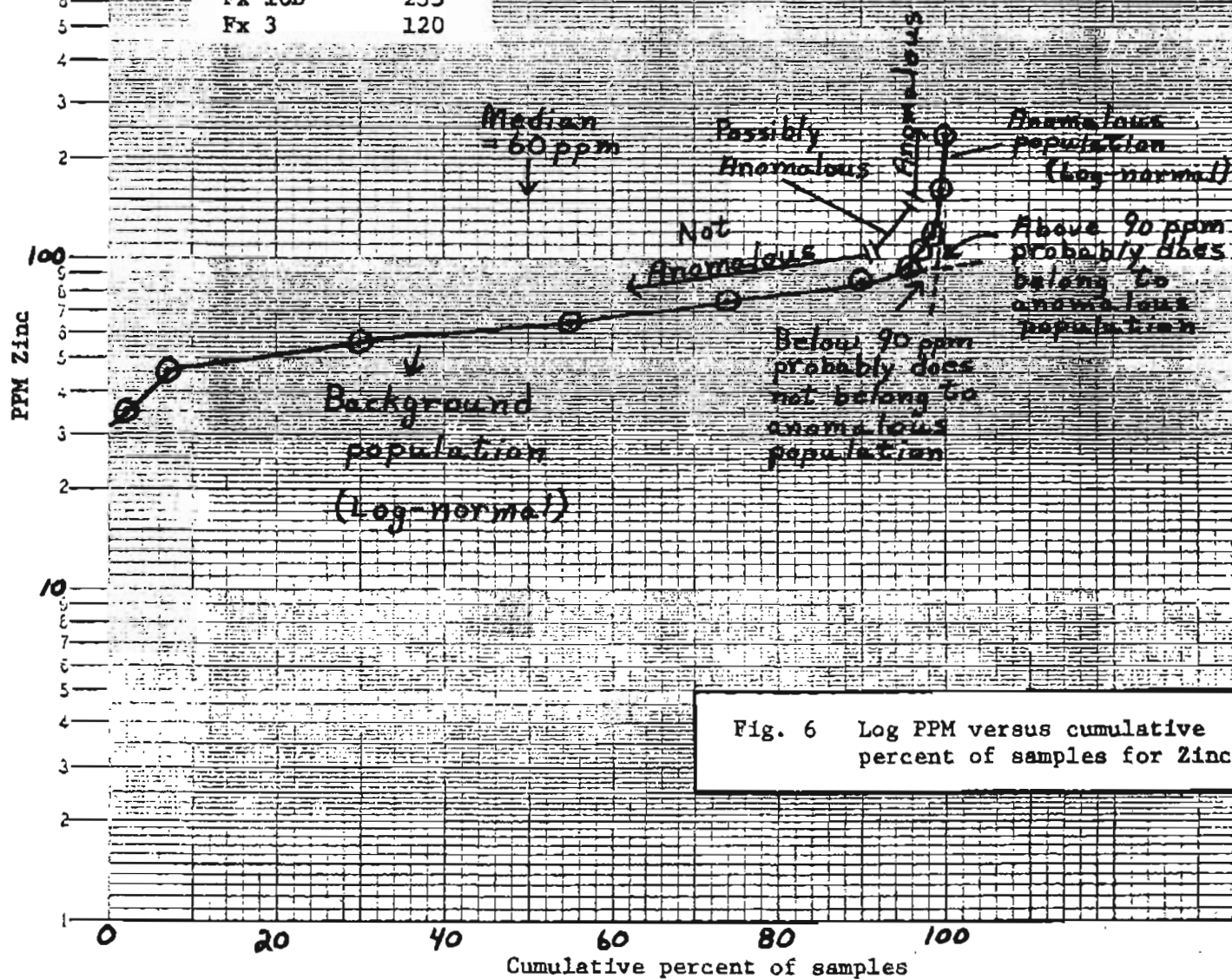


Fig. 6 Log PPM versus cumulative percent of samples for Zinc.

<u>Function</u>	<u>Cu</u> <u>ppm</u>	<u>Pb</u> <u>ppm</u>	<u>Zn</u> <u>ppm</u>
Mode	20	20	65
Mean	20	30	65
Median	--	20	60

Number of Samples

	<u>Cu</u>	<u>Pb</u>	<u>Zn</u>
Possibly anomalous values by statistical definition, Mean + σ to mean + 2 σ	0	3	9
Anomalous values by statistical definitions, Mean + 2 σ	0	9	5
Possibly anomalous values from log-concentration vs cumulative percent of samples plot (dev. from straight lines)	-	34 (between 30 and 80 ppm)	10 (between 90 and 130 ppm)
Anomalous values from log-concentration vs cumulative percent of samples plot	-	9 (above 80 ppm)	3 (above 130)

Duplicate Samples

Taking duplicate samples at every fifth sample station allows an interpretation of the amount of variation within sampling. Because replicate analyses indicate a rather small (σ = 3 ppm Cu, 7 ppm Pb, 6 ppm Zn) variation due to analytical error, any large deviation between duplicate samples can be attributed to sampling variation.

Inspection of the data from duplicate samples showed that in background zones there were no large deviations between the duplicate samples. On the contrary, extreme deviations were found between duplicate samples in anomalous zones. Examples of these data are as follows:

<u>Background Zones</u>	<u>Pb, ppm</u>	<u>Zn, ppm</u>
FX 30	20	45
FX 30 Dup	20	55
FX 35	15	45
FX 35 Dup	20	45
FX 40	20	55
FX 45 Dup	20	50

<u>Anomalous Zones</u>	<u>Pb, ppm</u>	<u>Zn, ppm</u>
FX 1	190	80
FX 1 Dup	320	250
FX 5	75	100
FX 5 Dup	50	85
FX 10	125	75
FX 10 Dup	3000	125

Large variations in metal values from duplicate samples in anomalous zones and small variations in background zones may have been expected, though the literature is scant on advice about this problem. Stream sediment sampling in anomalous zones seems to be rather similar to sampling an ore vein. Metal values may vary widely across small distances. If one considers ore minerals being dumped into the stream which is subsequently selectively depositing the particles by the processes of mineral gravity opposing stream current, eddies, obstructions, etc., it is easy to understand wide variations in metal values in anomalous zones. In background zones the particles are essentially that of the country rock and so less variation in values results.

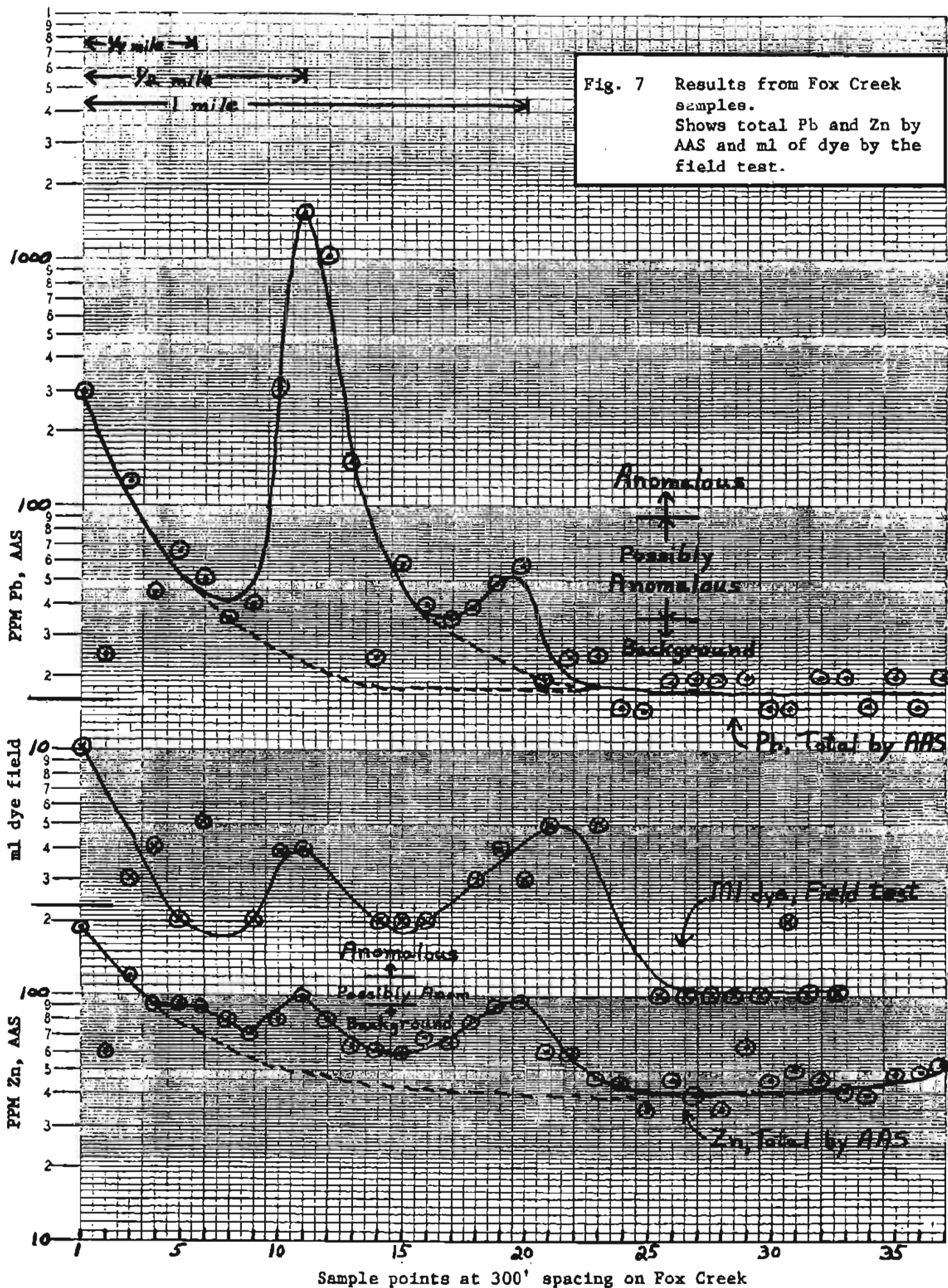
The above results can only lead to the interpretation that composite sampling is required (without greatly increasing the load on the analytical service). It is recommended that no fewer than three portions of sediment, taken at some distance from each other (15' to 50'), be considered a sample. The added confidence that can be attached to any one sample, taken as a composite, would be great.

Sample Spacing

Having used a 300' sampling interval it is possible to make some interpretation of the optimum sampling density, though I hasten to add that such an interpretation may be limited to geological, mineralogical, and topographical conditions similar to those occurring in this study.

Fox Creek was sampled for approximately 2-1/2 miles acquiring 45 samples at about 300' spacing. A plot of individual values obtained as "total" lead and zinc by hot acid dissolution at the sampling points on Fox Creek is shown in Fig. 7. Where duplicate samples were taken the values are averaged. The figure also shows the ml of dye from the field test for the samples.

Several features are immediately obvious from Fig. 7: 1) by far the strongest anomalous values were obtained from ppm Pb. This may be a reflection of the nature of the mineralization, 2) zinc was much more evenly dispersed than lead, so a wider sampling interval could be used for Zn but a more sensitive geochemical interpretation method would be needed, 3) the colorimetric field test was reasonably sensitive for detecting the relatively high and low metal levels, 4) the colorimetric test follows the "intensity" of the zinc mineralization much more closely than that of the lead. This correlates with the AAS data of the small amount of lead in the dithizone from the field test.



An interpretation of the optimum sample spacing may be made by successively excluding sample points and widening the theoretical sample interval. Regardless of where the sampling was started, sampling at 1/2 mile intervals would have found at least one of the two strong Pb anomalies. At 1/2 mile sampling interval it would have been possible to miss both of the strong Pb anomalies. At one mile intervals it is unlikely to have found either of these strong anomalies. Fig. 7 indicates that the decrease in geochem lead going across the anomaly is extremely sharp. The lead values decreased from strongly anomalous to weakly anomalous or background in only a few hundred feet. Based on this evidence alone one could not justify sample spacing of greater than 1/4 mile in the search for lead in this area. It appears that a wider spacing, perhaps 1/2 mile could be effectively used for Zn, but a finer interpretation of "anomalous" must be used because of its much broader and less erratic dispersion behavior.

For lead a "best smooth curve" through sampling points from peak to background on the two anomalies on Fox Creek showed an average drop-off in ppm values of one-half the value every 750 feet. The drop-off slope was continuously variable and ranged from 200 feet to 950'. This again indicates about 1/4 mile sampling interval is the largest spacing that could be effectively used for lead in this environment.

CONCLUSIONS

1. The colorimetric field test is a valid test for the detection of Zn in stream sediments if the analysis is very carefully run. One should be willing to run more than once, samples giving color, in order to better characterize the sample. The field test is very ineffective for the detection of Pb per se except for the common association between lead and zinc.
2. Lead has a narrow dispersion. In anomalous zones lead values dropped to half their value in an average of 750'. Sample spacings of no more than 1/4 mile is recommended for lead surveys.
3. Zinc presented greater dispersion than lead. In anomalous zones zinc values dropped to half their value in about 1100'. Sample spacing could therefore be greater than for lead. However, the zinc values were far less extreme and so a somewhat finer method of data interpretation would be required for zinc.
4. Both lead and zinc showed two populations of metal values; an anomalous population and a non-anomalous population. Both populations for both metals had an apparently log-normal frequency distribution. The use of a data interpretation scheme with a log transform of the concentration values is preferred for log-normally distributed population. Use of log concentration vs cumulative percent samples yielded the clearest presentation for lead and zinc. Statistical treatment when extreme values are present, confuses the pattern because the mean and standard deviation are both strongly affected by extreme values. From the statistical treatment two zones anomalous in lead and zinc were defined, both on Fox Creek. From the log values-cumulative percent of samples plot several anomalous zones on Flume and Seattle Creeks were also discovered.

5. No copper anomalies were found. The copper values seemed to be normally and not log-normally distributed.

6. In anomalous zones metal values were highly erratic based on data from duplicate samples. It is strongly suggested that composite samples over at least 20-50 feet comprise a sample. This would help greatly to make an individual sample have more significance.

7. Analytical precision was as follows:

<u>Element</u>	<u>Standard Deviation</u>	<u>N</u>
Cu	3	18
Pb	6	18
Zn	7	18

Such spreads would not contribute significantly to error in data interpretation.