THE GEOCHEMISTRY OF STREAMS AND

WEATHERING PROCESSES IN AN ARCTIC

CARBONATE TERRAIN:

CORNWALLIS ISLAND AND GRINNELL PENINSULA

NORTHWEST TERRITORIES

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CARBONATE TERRAIN:

CORNWALLIS ISLAND AND GRINNELL PENINSULA

NORTHWEST TERRITORIES

BY

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A Thesis

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ABSTRACT

The low ambient air temperatures, together with the low annual rainfall and complete lack of vegetation in the Canadian High Arctic, results in a breakdown of the carbonate rock material by mechanical means. The importance of chemical decomposition, soil formation and transport of ionic material in solution is negligible, when compared with the role played by these same processes in more temperate climates.

The purpose of this thesis is to investigate certain aspects of the alkali, alkaline earth and heavy metal geochemistry of selected components of the weathering cycle. The discussion will deal with concentration levels of these parameters in stream waters and, to a lesser extent, soils and stream sediments.

Analytical results show that element distributions in the streams resemble those of more temperate carbonate terrains. However, the solute levels are, in general, lower, indicating that a greater proportion of the metals is travelling in colloidal form and/or adsorbed to silt-sized material carried by the streams.

These findings confirm the belief that chemical weathering and transport in solution are of little importance in the area studied.

ACKNOWLEDGEMENTS

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INTRODUCTION

Very little work has been published, to date, concerning the geochemistry of various parts of the weathering cycle in the Canadian High Arctic.

The low ambient air temperatures, together with the low annual rainfall and complete lack of vegetation, results in a breakdown of rock material by mechanical means. The importance of chemical decomposition, soil formation and transport of ionic material in solution is negligible, when compared with the role played by these same processes in more temperate climates.

Similar conditions should have prevailed over much of northern North America and Eurasia during the period immediately following the last glacial retreat.

Until recently, the discussion of the above ideas in texts of geology and geomorphology has been mainly qualitative.

The purpose of this thesis is to investigate certain aspects of the alkali, alkaline earth and heavy metal geochemistry of selected components of the weathering cycle. The present discussion will deal with concentration levels of these parameters in stream waters and, to a lesser extent, soils and stream sediments. Results of additional work done on precipitation samples will be presented in a separate paper.

Analytical results show that element distributions in the streams
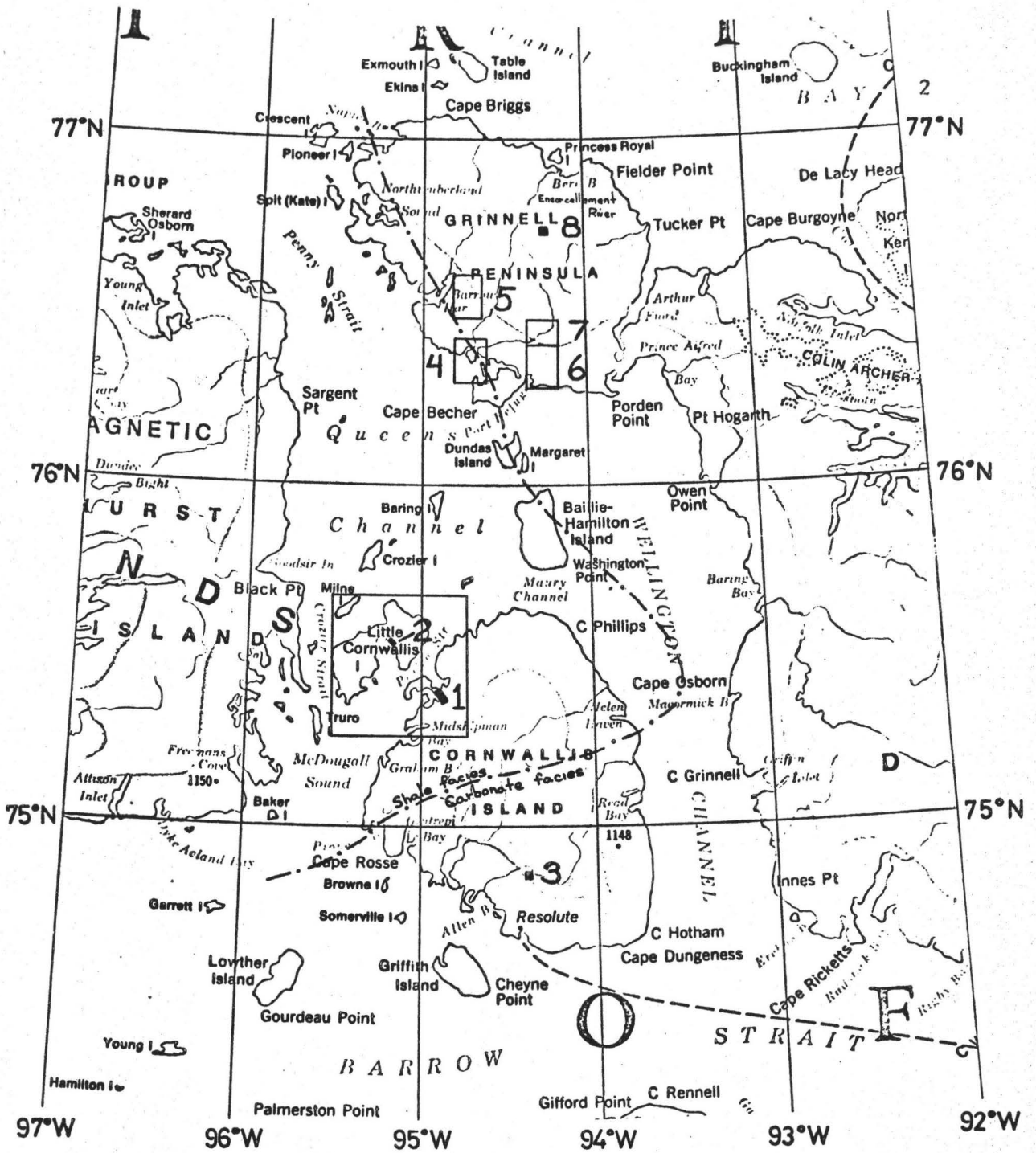
FIGURE 1 : SAMPLE AREAS
CORNWALLIS ISLAND &
GRINNELL PENINSULA ,
NORTHWEST TERRITORIES

0   50   100

SCALE IN MILES
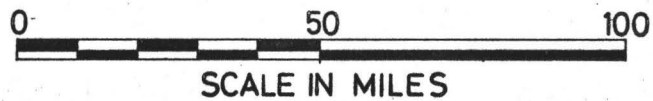
☐4, ■2   SAMPLE AREA
—·—   FACIES FRONT

resemble those of more temperate carbonate terrains. However, the solute levels are, in general, lower, indicating that a greater proportion of the metals is travelling in colloidal form and/or adsorbed to silt-sized material carried by the streams. These findings confirm the belief that chemical weathering and transport in solution are of little importance in the area studied.

Sample collection was completed during June, July and August while I was part of a two-man Cominco field party.

The sampling areas, northern Cornwallis Island and central Grinnell Peninsula, lie between 50 and 140 miles north of Resolute Bay Northwest Territories (Figure 1).

Previous Work

Most of the current work on the geochemistry of permafrost regions is being carried out in the U.S.S.R. As a result of their research into the practical applications of geochemistry, the Russians are probably gaining a much better understanding of how metallic ions behave in Arctic regions.

The only published work on the geochemistry of Arctic Canada has come from the Geological Survey of Canada. Papers by Gleeson (1966), Allan and Hornbrook (1970), Allan et al. (1973), and Hornbrook (1973) have shown that intensive weathering of sulphides has allowed dispersion of ore and indicator elements in drainage systems of the northern Shield. Anomalies that have been studied show that this area is well suited to such regional geochemical exploration techniques as stream sediment and

soil sampling.

Despite a similar absence of chemical weathering, such widespread dispersion may not occur around mineralization in the carbonates of the Franklinian Geosyncline, 500 miles to the north of the area studied by Allan (1973).

Average solute levels in natural waters were taken from compilations by Hem (1970) and Livingstone (1963).

The ultimate source of most dissolved ions is the mineral assemblage in the near surface rocks (Hem, 1970). Carbonates can be viewed, in terms of weathering, as fairly simple chemical substances. The solution of limestone is principally the solution of $CaCO_3$, a reaction which is rapid and reversible (although the reverse reaction does not always appear to take place rapidly).

There are no massive carbonate rock formations in which Mg is more abundant that Ca. Therefore, in water from carbonate terrains, unless there has been secondary precipitation of calcite, Ca concentration should always be greater than that of Mg. The ratio Ca/Mg reflects, to some extent, the composition of the carbonate terrain. This interpretation can be used only qualitatively, since there are many complications which can influence the Ca/Mg ratio of water from limestone.

Shale (of which there is a minor amount in some of the sample areas) is composed mainly of clay minerals and other particulate matter formed from chemical reactions between water and silicates. Shale also contains small amounts of quartz and other detrital minerals, as well as varying amounts of carbonate. Water flowing over this type of rock may contain high concentrations of dissolved solids. Many of these solutes were
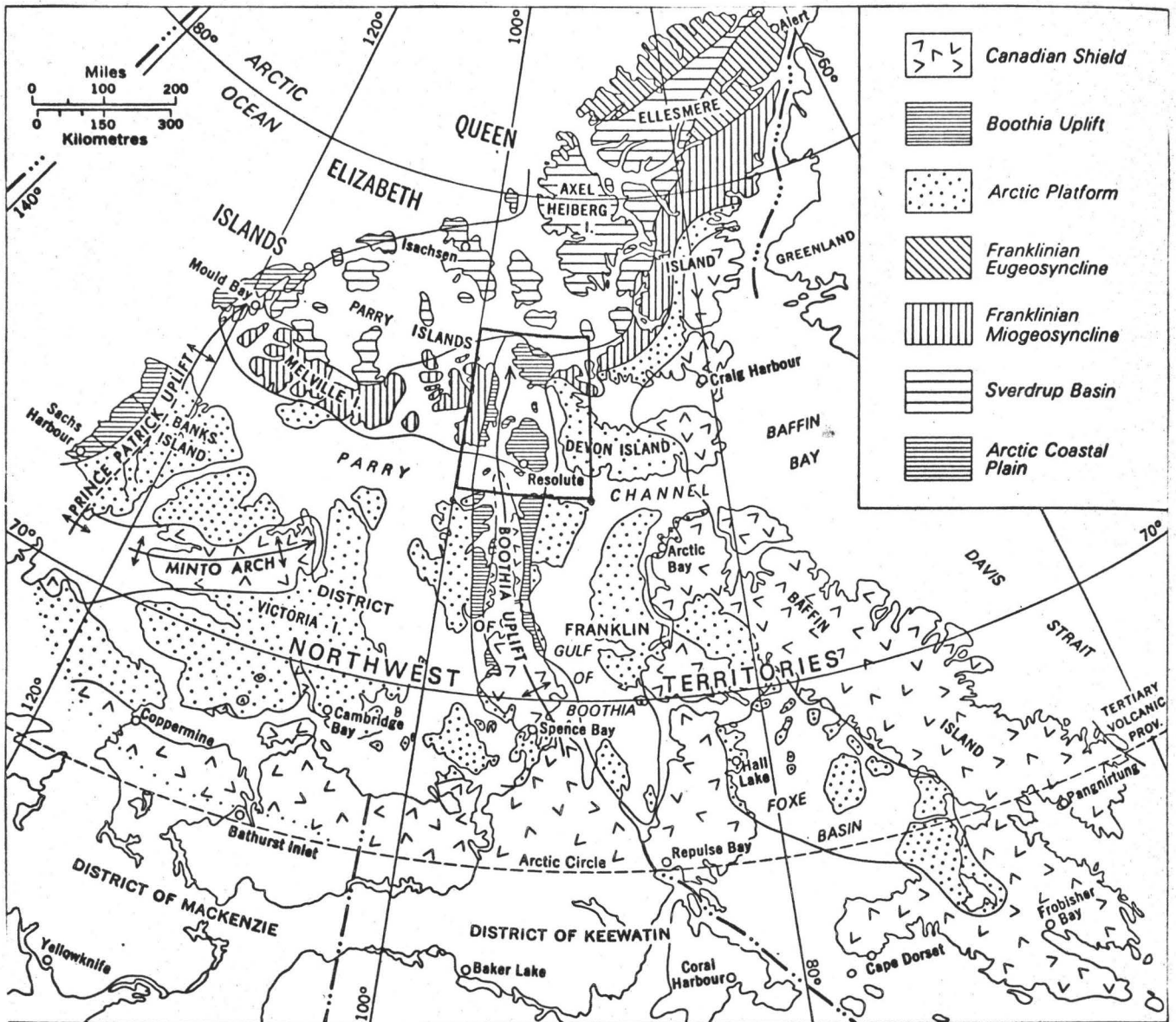
FIGURE 2: Geological Provinces of the Arctic Archipelago

▭ area shown in Figure 1

from Douglas (1970)

trapped in the pore spaces of the rock, or attached to particles since the time of the rock's formation.

The analyses followed standard techniques currently used by McMaster University Water Chemistry Laboratory (Kramer, 1973).

Regional Geology

The central and extreme northern portions of the Cornwallis Fold Belt (Thorsteinson, 1959) constitute a region of north-south trending fold structures "characterized by generally steep-flanked anticlines and broad open synclines." (Thorsteinson and Tozer, 1970). The Cornwallis Fold Belt (Figure 2) has been included by Thorsteinson and Tozer (1970) in the Boothia Uplift, itself a north-south structure consisting of a core of Precambrian rocks (occupying the Boothia Peninsula and western Somerset Island) flanked to the east, north and west by a Cambrian to Lower Ordovician sedimentary sequence.

The present study was carried out on northern Cornwallis Island and Grinnell Peninsula, in the northern part of this region of sedimentary strata. Most of the bedrock which was traversed consists of a thick conformable sequence of marine formations, ranging in age from Lower or Middle Ordovician to Lower Devonian. Carbonate sediments constitute the principal rock type, and it is estimated that more than 95% of the samples collected came from carbonate terrains.

A feature of considerable importance is the facies front (Figure 1). This front marks extensive regional facies changes in the strata resting conformably on the Upper Ordovician Cornwallis Group. A graptolitic

Geologic Section

DEVONIAN

BIRD FIORD · Dbi

BLUE FIORD Dbl

VENDOM FIORD

SNOWBLIND BAY

EIDS

STUART BAY

SILURIAN

READ BAY SDr

CAPE

PHILLIPS

ODcp

ALLEN BAY · OSa

ORDOVICIAN

IRENE BAY Oci

THUMB MOUNTAIN Oct

CORNWALLIS
GROUP
Oc

BAY FIORD Ocb

ELEANOR
RIVER
Oe

COPES
BAY

BAUMANN FIORD Ob

CAMBRIAN

PARRISH
GLACIER

SCORESBY
BAY

ELLESMERE
GROUP

ELLA BAY

PRE-CAMBRIAN

PRECAMBRIAN
CRYSTALLINE

KENNEDY
CHANNEL

FIGURE 3: Geologic Section & Legend

Legend

evaporites		dolomite	
coal		reef	
shale		limestone	
sandstone		crystalline basement	
conglomerate			

FIGURE 4 8

LITTLE
CORNWALLIS
ISLAND

ODcp

Oc

ODcp

ODcp

ODcp

ODcp

Oc

Marshall
Peninsula

Oc

ODcp

Oc

ODcp

Oci

Oct

'POLARIS' Pb-Zn Deposit
(Cominco)

CORNWALLIS
ISLAND
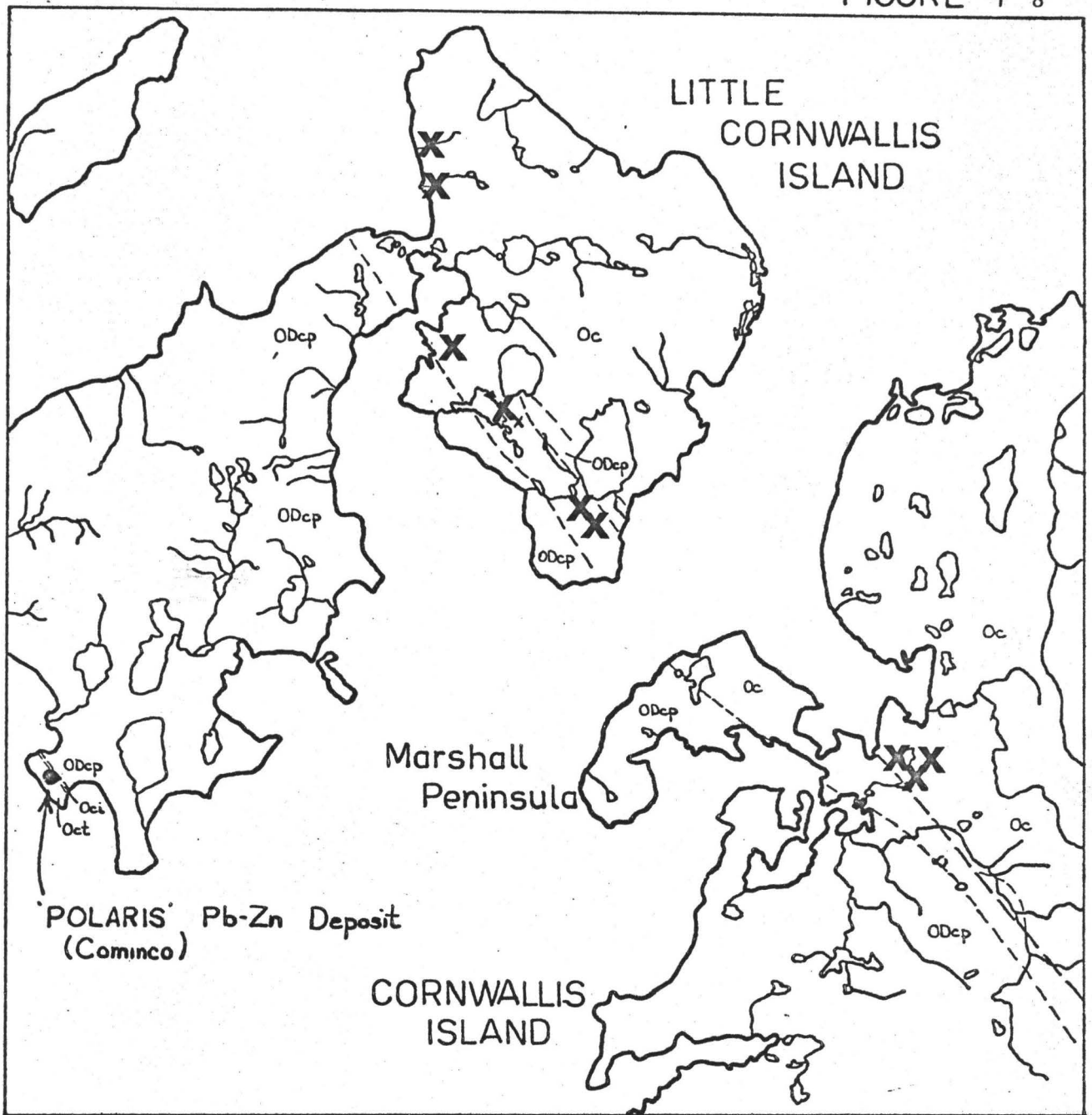
geology after
Thorsteinsson, 1958

refer to legend,
Figure 3

SAMPLE AREAS 1 & 2:
Water & Sediment Sample Locations

0   1   2

SCALE IN MILES

X water sample

o stream sediment sample

△ soil sample

FIGURE 5   9

SDr

Oct X

X
Ocb

Oe

OSa

Oci   ODep

X

X

**Stewart
Point**

**Dyer
Island**

SDr

**Sheills
Peninsula**

Oe Ocb Oct   Dd   Dbl

geology after
Rhodes (1973)

refer to legend,
Figure 3

SAMPLE AREA 4:
Water & Sediment Sample Locations

X water sample

o stream sediment sample

△ soil sample

0   1   2
SCALE IN MILES

FIGURE 6   10
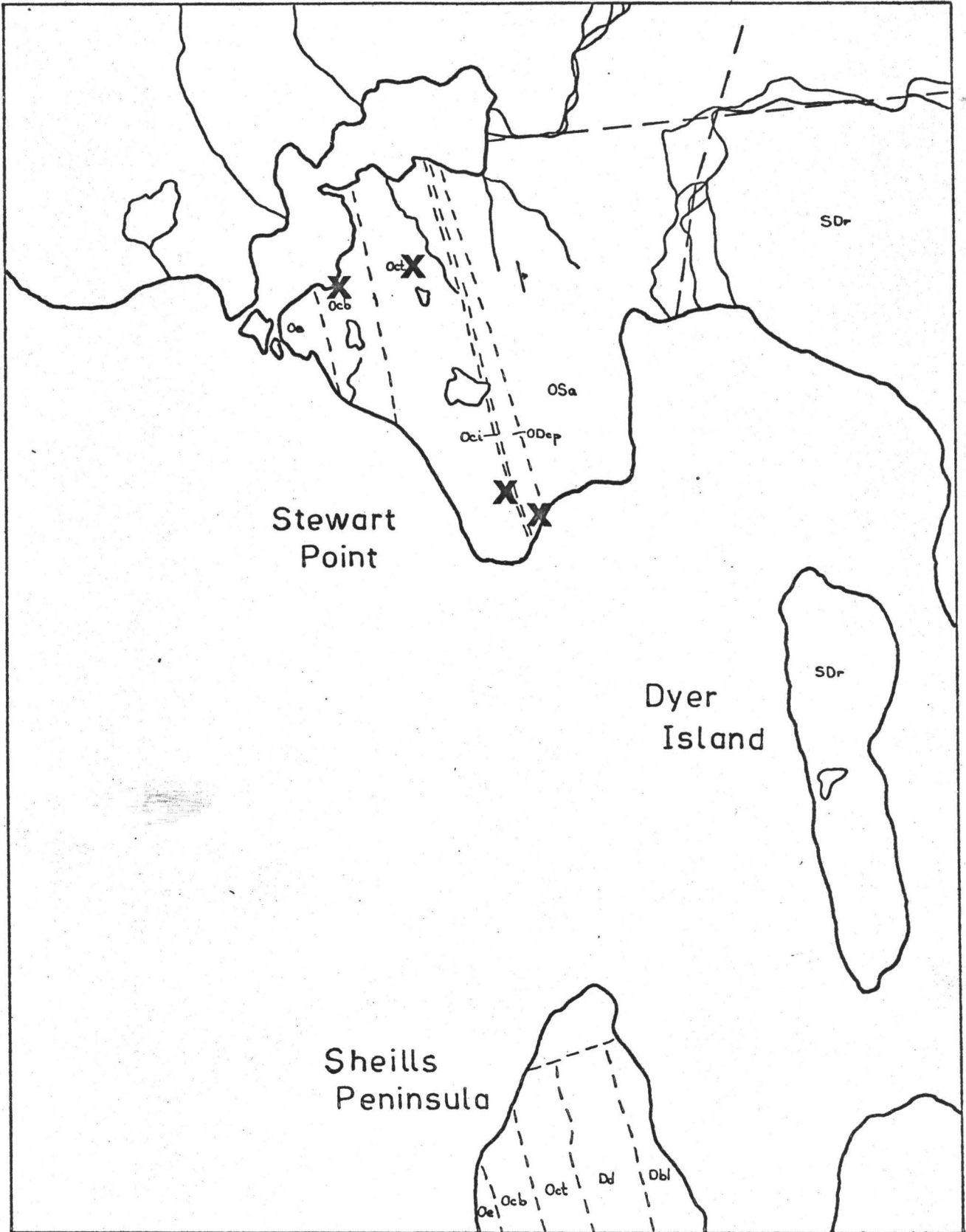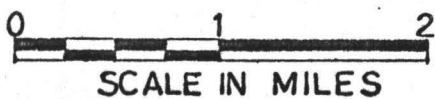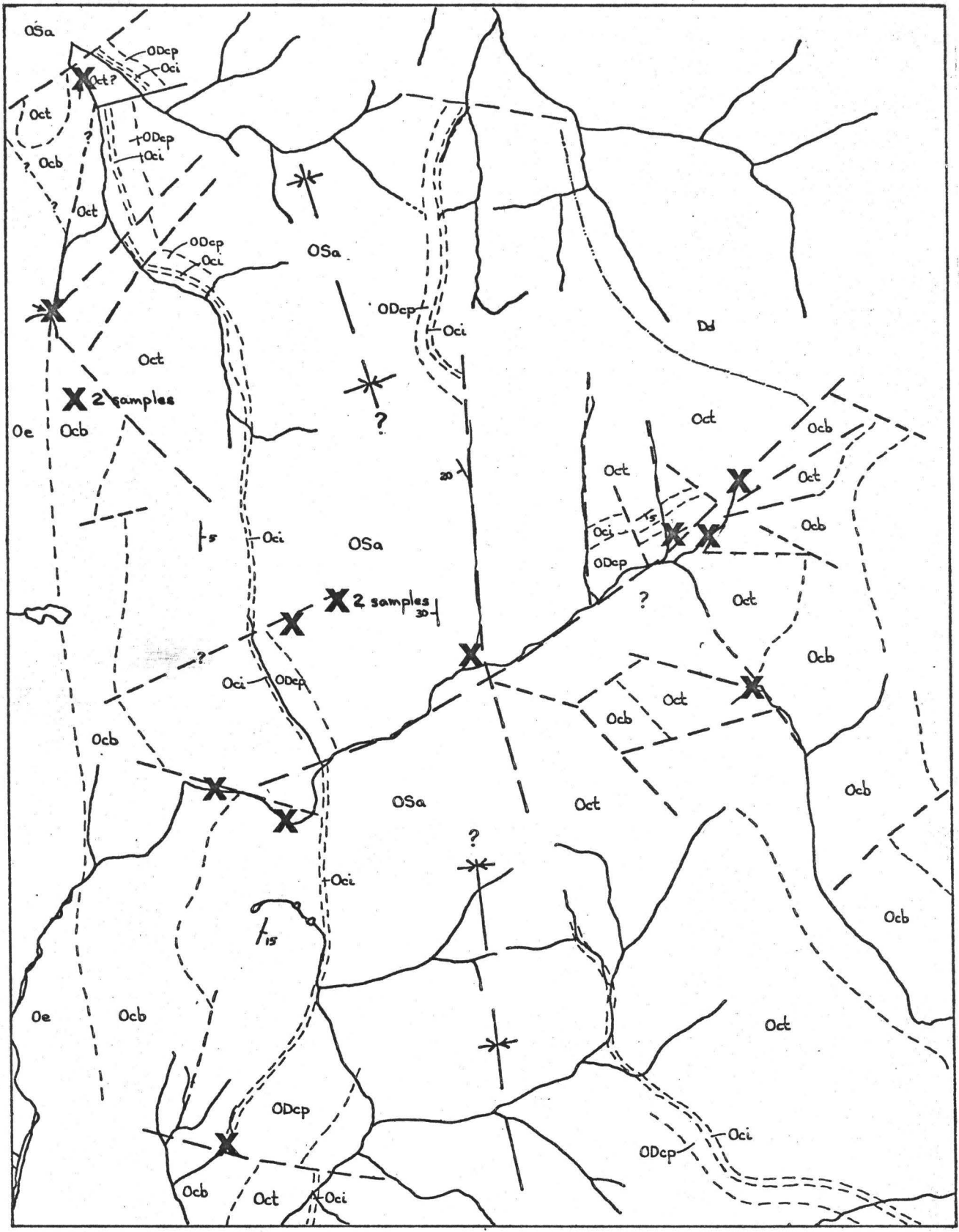
geology after
Rhodes (1973)

SAMPLE AREA 5:

refer to legend,
Figure 3
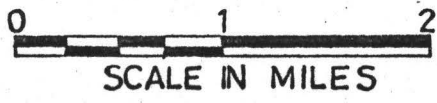
Water & Sediment Sample Locations

X water sample

○ stream sediment sample

△ soil sample

0   1   2

SCALE IN MILES

FIGURE 7 11
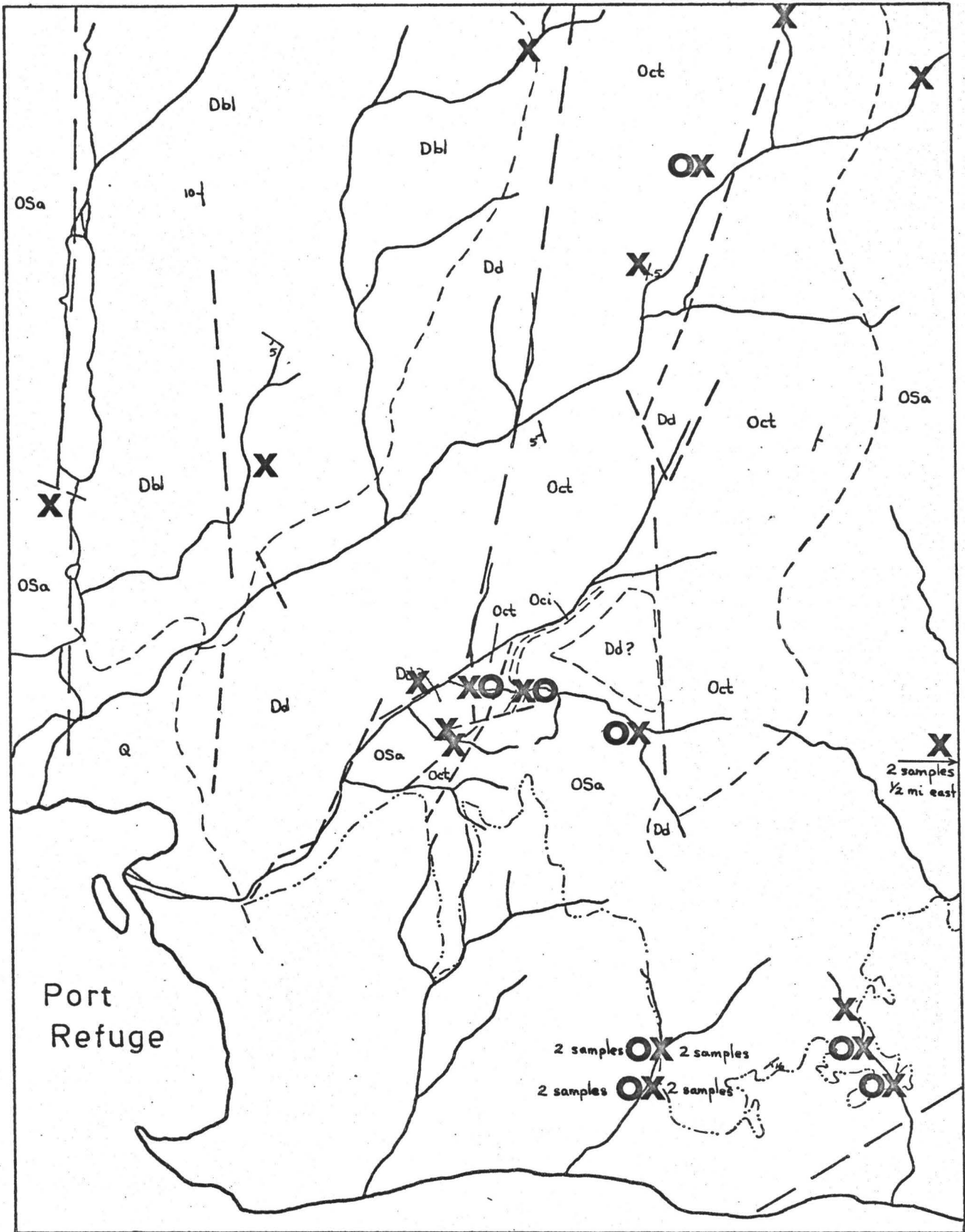
geology after
Rhodes (1973)

SAMPLE AREA 6:

refer to legend,
Figure 3
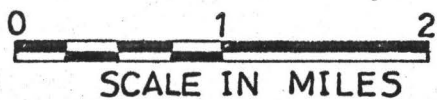
Water & Sediment Sample Locations

X water sample

o stream sediment sample

△ soil sample

0   1   2
SCALE IN MILES

FIGURE 8
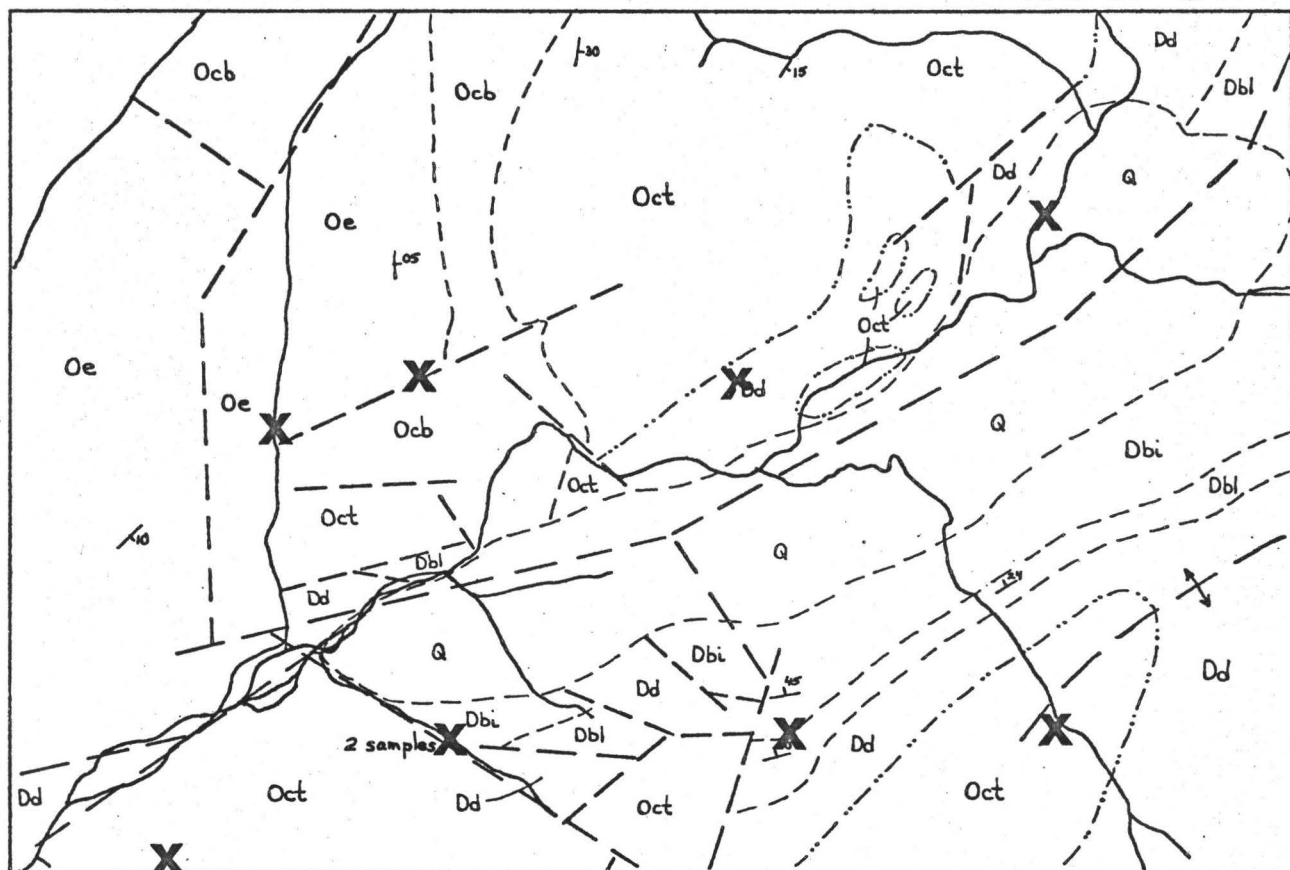
SAMPLE AREA 7:
Water & Sediment Sample Locations

geology after Rhodes (1973)

refer to legend, Figure 3

0   1   2
SCALE IN MILES

✖ water sample
o stream sediment sample
△ soil sample

FIGURE 9 13
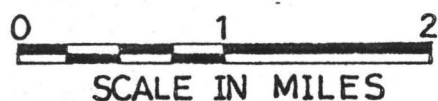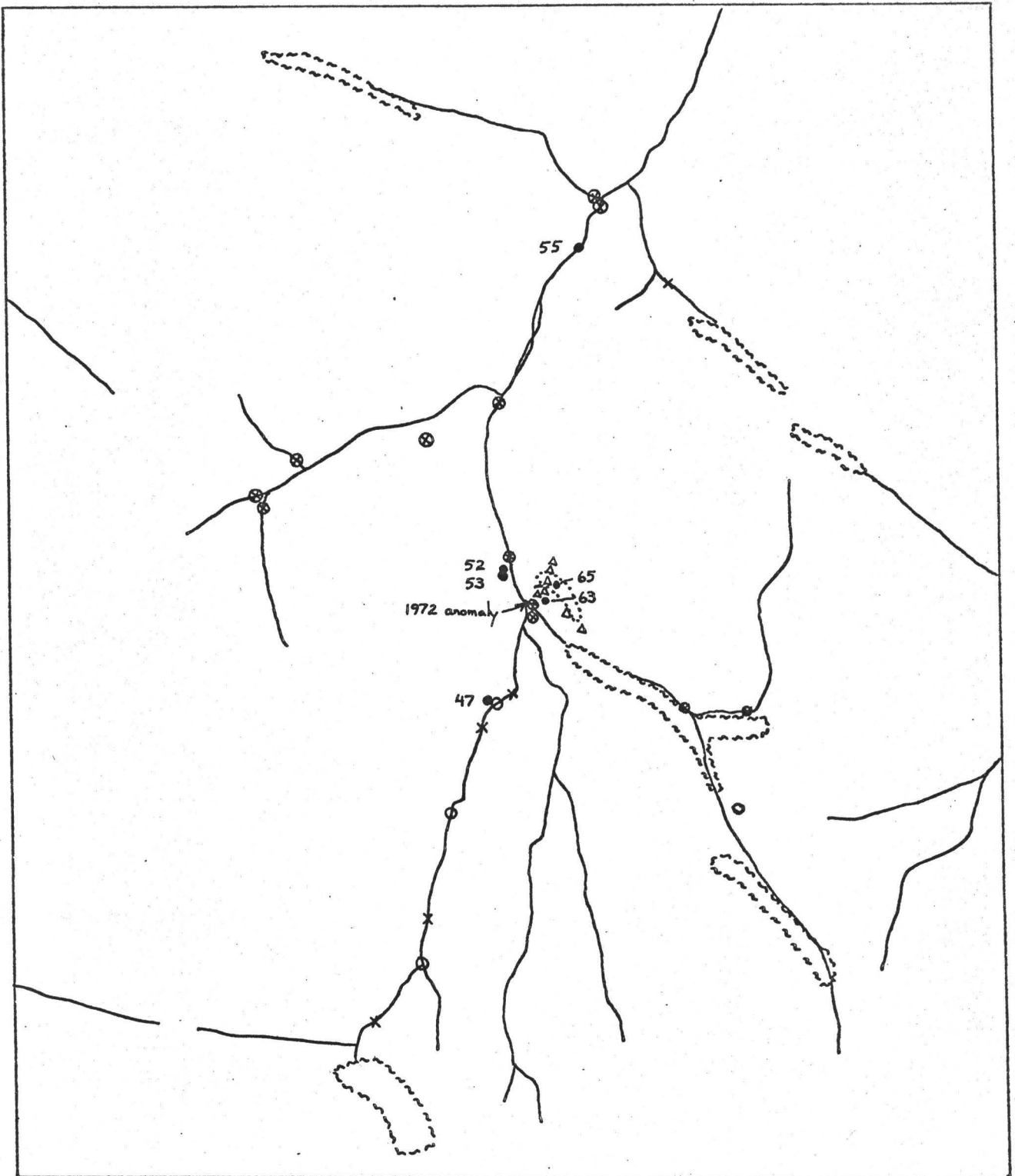
SAMPLE AREA 8: refer to legend, Figure 3

Water Rock & Sediment Sample Locations

0   1/4   1/2

SCALE IN MILES

~~~ Permanent snowfields
····· Area of FeS$_2$ and extensive gossan

X   water sample
O   stream sediment sample
△   soil sample
55●   rock sample

facies, represented by the shales, calcareous shales and argillaceous limestones of the Cape Phillips Formation (Upper Ordovician to Upper Silurian in age) lies to the west of this front. To the east, rocks comprising the Allen Bay dolomite and Read Bay limestone occupy the same time interval and bear shelly faunas. Most of the samples were taken on rocks lying either near the facies front or to the east of the front in the carbonate formations (Figure 1).

The stratigraphic section (Figure 3) indicates the main lithologies found in each formation. Sample locations of the study have been tied in with the detailed geology (Figures 4 through 9).

Topography, Drainage and Vegetation

Grinnell Peninsula comprises a hilly plateau, with an average elevation of 500 feet. Two north-south trending mountainous belts are located in the west central part of the peninsula and to the east of the Ensorcellement River Valley (Figure 1). The "mountains" reach elevations of 1000 to 1500 feet and are generally rounded in form with flat summits. The Ensorcellement River occupies a broad flat valley sloping gently northward toward the ocean.

The 200 to 500 foot relief in the plateau area is due mainly to rivers and streams, which have cut deep, steep-sided valleys far below the general level of the plateau. During the summer months the bottoms of these valleys are occupied by high gradient streams with small depth to width ratios. The single channel character of these streams contrasts sharply with that of the lower gradient streams occupying the several wide river valleys such as that of the Ensorcellement.

Here the streams and rivers often have a large total width, but consist of numerous shallow, braided channels.

The sampling area in the northwestern corner of Cornwallis Island is a low-lying plain sloping gently seaward, on which the major streams occupy graded channels (Thorsteinson, 1959). The sampling areas in central Cornwallis Island and on Little Cornwallis Island possess a gently undulating topography with stream valleys providing the only abrupt relief.

The surface material is everywhere frost shattered carbonate debris. Soil development and mixing is aided by the action of frost boils and is most extensive on flat plateaux, and in broad, flat river valleys.

Solifluction, dominant among the mass wasting processes, is active on slopes as low as 5 degrees. Solifluction is especially active in these regions of high latitude, since the active or perma-frost-free layer is comparatively thin (about 3 feet), and there is generally suffi-cient relief to permit considerable movement (Thorsteinson, 1959).

All of Grinnell Peninsula and most of Cornwallis Island are barren of vegetation except for scattered patches of moss-like growth.

Striated bedrock, boulders and also morainal hills prove that Cornwallis Island was glaciated at least once. The small, remnant glaciers in the eastern portion of Grinnell Peninsula indicate that the same is probably true of this area. Despite this, geological mapping on the basis of rubble lithologies is quite reliable. In some places it is necessary, due to absence of outcrop.

Climate

A number of factors combine to give the cold maritime type of climate which prevails in this area:

1) Due to the high latitude, the sun never rises from November 30 to February 5 and does not set from April 30 to August 15.

2) The obliquity of the sun's rays reduces the insolation.

3) Despite a thick covering of ice during the winter, the ocean has a moderating effect which is sufficient to keep temperatures from falling to the extremes experienced in some continental areas; similarly, the presence of icy water keeps summer temperatures from rising too high.

4) Perhaps most important is the effect of air pressure patterns and Arctic storms originating on the Greenland ice cap.

Mean temperatures for June, July and August are 33.5, 40.0 and 36.8°F respectively. The mean yearly temperature is 30.0°F. Temperatures in July and August are kept low by the large number of cyclonic disturbances, and the presence of plentiful low cloud and fog.

Mean total precipitation, for the same three months, is 0.69, 0.97 and 1.04 inches respectively. This precipitation can fall as either snow or rain during any of the summer months. During the period from June 15 to August 17, 1973 there was:

1) A major rainstorm on June 23 and 24, the rain lasting for a total of 31 hours and probably amounting to 0.5 inches.

2) A minor snow and ice storm, June 29.

3) A minor snow and ice storm, July 9.

4) A major snowstorm accompanied by 35 to 40 m.p.h. winds,
   August 10 to 13.

The mean annual precipitation (both rain and snow) of 5.4 inches indicates
that the area is a desert.

By early May, the mean temperature rises above 0°F and towards
the end of the month, the occasional thaw may occur. In the second week
of June, the temperature rises above freezing, and the spring thaw begins
in earnest. During much of the thaw, the streams flow beneath snow banks.
The runoff is quite rapid, so that by July 1, the bulk of the snow cover
has disappeared, leaving only remnants of deep drifts and patches in
sheltered river valleys. Some of these persist throughout the summer.

During the height of the runoff, a good deal of melt water flows
down steep slopes as tiny rivulets and discontinuous sheets. In
addition, the thin active layer of the soil becomes saturated with melt-
water. On slopes greater than 5 degrees, this results in accelerated
solifluction. In several cases, mud slides have been observed on the steep
sides of river valleys.

By mid July, the volume of water flowing in the streams has
decreased noticeably, and continues to decrease through the end of August.
By the time of the first extensive freeze, toward the beginning of
September, many of the smaller tributary streams, particularly those
flowing in rugged terrain, have dried up.

SAMPLING AND ANALYSIS

Sampling Techniques

All samples of stream waters were collected and stored in 500 ml. Nalgene polyethylene bottles. Since "aging" of the bottles was not possible under the existing field conditions, each bottle was rinsed, refilled and allowed to stand for one to two minutes with water from the stream being sampled. Sample collection was accomplished by submerging the bottle, neck pointing upstream, as far as possible into the stream. Care was taken not to stir up any sediment on the bottom or sides of small streams.

Stream sediment and soil samples were collected using a stainless steel gardening trowel. The difficulty encountered in locating silt fraction stream sediments depended upon the local topography, nature of the stream channel, and the lithology of the surrounding rocks. Location of the proper size fraction for soil samples gave no problems. Each stream sediment or soil sample was placed in a numbered Kraft paper soil bag which was in turn sealed within a polyethylene bag.

Analytical Techniques

A. Stream Waters: A total of 87 stream water samples were analysed for the parameters listed in Table 1. Due to equipment failure, pH determinations were carried out on only 23 samples. A number of the sample bottles contained a visible amount of silt, which had been in

18

TABLE 1: SUMMARY OF ANALYTICAL PARAMETERS

Parameter	Definition	Method	Units	Reproducibility	Detection Limit
Specific Conductivity		resistance	umhos cm^{-1}(25°C)	± 1%	1.0 umho-cm^{-}
Alkalinity		Electrode titration	ppm CaCO$_3$		
pH	$-\log_{10}[H^+]$	electrode		±0.002	10 ppb
Na		atomic emmission	ppm	± 1%	0.02 ppm
K		" "	ppm	± 1%	0.02 ppm
Ca		atomic absorption	ppm	± 1% ·	0.02 ppm
Mg		" "	ppm	± 1%	0.02 ppm
Pb$_T$	total Pb	" "	ppb	± 5%	1.0 ppb
Pb$_F$	filtered Pb	" "	ppb	"	"
Cu$_T$	total Cu	" "	ppb	"	"
Cu$_F$	filtered Cu	" "	ppb	"	"
Fe$_T$	total Fe	" "	ppb	"	"
Fe$_F$	filtered Fe	" "	ppb	"	"
Zn$_T$	total Zn	" "	ppb	"	"
Zn$_F$	filtered Zn	" "	ppb	"	"
Cd$_T$	total Cd	" "	ppb	"	0.1 ppn
Cd$_F$	filtered Cd	" "	ppb	"	0.1 ppb

suspension in the stream. For this reason, analysis for the metals Pb, Zn, Cu, Fe and Cd was carried out on two portions of each sample, one portion being simply filtered, the other acid digested and filtered. The difference should give a rough measure of the amounts of metals adsorbed on the silt.

The following analytical techniques are based on those currently used in the McMaster University Water Chemistry Lab. (Kramer, 1973), except as noted. Table 1 is a compilation of the techniques, analytical reproducibility and detection limits. i) Specific Conductivity was measured in a flow-through platinized cell operating at about 1500 cycles. The cell was calibrated using standard KCL solutions before each set of runs. ii) Alkalinity was measured by electrode titration using a standard H_2SO_4 solution. Minor difficulty was encountered due to a slowly drifting pH. This is the reason for the relatively high analytical reproducibility. The procedure is described in Appendix I-A. iii) pH was measured on stirred solutions using a gel type reference electrode and glass electrode in conjunction with a high quality pH meter. iv) Alkali and Alkaline Earth Metals. The alkalis, Na and K, were analysed directly (ie. no preparation) by atomic absorption spectrophotometry. For analysis of the alkaline earths, Ca and Mg, 50 μl of a 10% $SrCl_2$ solution was added to 10 ml of sample. This solution was then analysed directly by atomic absorption. v) Metals, total and filtered. The extraction of both filtered and total samples was carried out according to the procedure (Kramer, pp. 18-22) Analyses of the samples by atomic absorption spectrophotometry for Pb, Zn, Cu, Fe and Cd was carried out by aspiration of the organic layer. Standard solutions containing known

concentrations of metals of interest were also aspirated after having been extracted according to the same procedure followed for stream waters. The sample preparation technique is given in Appendix I-B.

B. Stream Sediments and Soils: Upon arrival at the laboratory, the stream sediments and soils were frozen. Several days before analysis, they were slowly oven dried at about 60°C, broken up, where necessary, and sieved. The -100 mesh fraction was retained for analysis. The digestion procedure is given in Appendix I-C.

The samples and prepared standards were analysed directly by atomic absorption for Pb, Zn, Cu, Fe, Cd and Ni. The method of conversion and calibration of atomic absorption data is given in Appendix II.

Blank Analyses and Analytical Errors

Although quartz or aged pyrex make the best sample containers for waters with low ionic concentrations, polyethylene was chosen because of the rugged field and transportation conditions. On the basis of a study on the uptake of metals by polyethylene containers over a one month period, Kramer has concluded that:

1) up to 50% of the original Cd may be removed from solution by polyethylene containers.

2) Fe, Pb and Zn are removed from solution in measurable amounts.

3) polyethylene containers show no detectable additions to solutions.

In order to measure metal gain or loss during digestion, samples with various standard metal concentrations were digested and then analysed.

The results, recorded in Table 2 show apparent percentage gain (+) or loss (-) as a result of digestion. Gains and losses show no relation between various metals in a given standard. However, as expected, the largest relative gains and losses for all metals occur in the most dilute solutions.

A thorough study was conducted regarding the levels of metal concentrations in blank samples. These analyses are a direct reflection of the concentrations of metal contaminants in the BDH Aristar high purity acid used for digestion. The results are shown in Table 3. Blank analyses were carried out on both 'total' and 'filtered' samples.

Mean number 4 shows that measurable levels of all metals are present in the blanks, but these levels seem to be consistently related to the individual metals. The highest level of contamination is shown by Fe, followed by Zn. In both cases, the total blank is at least triple that of the filtered sample. Pb and Cu show about the same extent of contamination, 1-3 ppb, while Cd has the lowest levels. It is interesting, and rather disturbing, that in the case of both Pb and Cd, the filtered blank is higher than the total. This is believed due to metals picked up from the fritted glass Millipore filter.

The problem of discrepancies in analytical results, particularly for Pb, between different laboratories is discussed in a recent paper by Patterson (1974). Samples of seawater were standardized by one university and were then sent to various analytical labs. For a low concentration sample, atomic absorption results averaged 4-8 times higher than the standardized value, while the results for a higher concentration

TABLE 2: DIGESTION TEST

Percentage Gain or Loss after Digestion and Analysis

Standard	Pb	Cu	Fe	Zn	Cd
400 ppb	-3.9	+9.1	-8.7	-0.3	-4.0
200 ppb	+5.2	-1.6	-7.2	+7.1	-12.0
80 ppb	-3.5	-2.5	+12.6	+25.8	+5.0
40 ppb	16.0	+6.0	+17.8	+35.5	-5.0

TABLE 3: RESULTS OF BLANK ANALYSES

Mean	Pb T(ppb)	Pb F(ppb)	Cu T(ppb)	Cu F(ppb)	Fe T(ppb)	Fe F(ppb)	Zn T(ppb)	Zn F(ppb)	Cd T(ppb)	Cd F(ppb)
1	3.6(4)	7.3(5)	2.1(4)	1.7(5)	30.8(5)	16.5(3)	6.5(5)	1.1(5)	0.4(4)	1.0(5)
2	2.8(19)	2.3(22)	2.1(16)	1.0(23)	25.6(17)	7.8(19)	10.2(19)	2.6(16)	0.4(21)	0.5(20)
3.	0.4(5)	0.8(4)	3.5(5)	1.4(5)	-	-	6.1(5)	0.0(5)	0.0(5)	0.1(5)
4	2.5(28)	2.9(31)	2.4(25)	1.2(33)	26.8(22)	9.0(22)	8.9(29)	1.8(26)	0.3(30)	0.5(30)

small number, eg. (5) indicates number of analyses upon which average is based

Mean 1 - based on analyses before December 31, 1973

Mean 2 - based on analyses by McMaster Water Chemistry Lab.

Mean 3 - based on analyses after January 1, 1974

Mean 4 - overall mean

sample were closer to the standard value.

Material balance considerations showed that the amounts of Pb in the analysed sample were of the same order as amounts of Pb in the blanks. Patterson thus concluded that total analytical errors were of the same order of magnitude as reported concentrations.

Because of this, only semi-quantitative results can be reported for metals whose concentrations are less than, or equal to the metal concentrations in the blank. Caution must be exercised in the direct comparison of analytical results from different universities.

Due to the high metal contents being analysed in the stream sediments and soils, none of the above problems are encountered, in this study.

RESULTS

Statistical Treatment of Data

Because of the large number of samples and the variety of para-
meters being considered, a basic computer-aided statistical treatment
was carried out. The mean, median and standard deviation were determined
for each parameter and the data was sorted into ascending order. After
any abnormally high values had been discarded, the data for each para-
meter was plotted on a separate histogram (Figures 10 through 31).

Because of the low concentrations being measured, I encountered
contamination problems in which a filtered sample would be higher in a
certain metal than the corresponding total sample. In cases such as
these, the filtered value was not included in the statistical summary.
This procedure was used both for the stream waters and for the stream
sediments and soils.

Most of the stream sediment and soil samples were taken in areas,
which are known or suspected to contain Fe-Pb-Zn mineralization. As
such, they do not represent an average cross-section,as do the stream
waters.

Plotting and Contouring of Data

The statistical results indicate that contouring of any of the
stream water parameters would not reveal any consistent patterns.

It would only be possible to plot the alkali and alkaline earths, and the filtered heavy metals. All variations in the total heavy metals can be directly related to the amount of sediment present in the sample It is obvious that this is a random and local phenomenon depending completely upon the gradient and discharge of the stream, at the point of sampling.

The parameters considered to be most amenable to this type of analysis (Na, Zn, Fe) were plotted for some of the areas. However no systematic contours could be drawn and only a couple of possible trends could be isolated. These will be discussed later.

The small number of stream sediments and soils precluded any meaningful study of spatial distribution. However, it was found that one parameter reflected the presence of mineralization in connection with the special gossan study. Consequently, this was plotted in Figures 35 and 36.

INTERPRETATION AND DISCUSSION OF RESULTS

Stream Waters

The sample area maps (Figures 4 through 9) show that the water sample locations form a fairly even distribution. An attempt was made to cover the widest possible area and variety of terrains and rock types. Therefore, the statistical summaries in Figures 10 through 26 provide a representative sampling of conditions in Arctic streams developed on a carbonate terrain.

In general, the results tabulated on these figures show no anomalous patterns. They represent fairly consistent, though sometimes wide, distributions about the means (as indicated by the frequently large standard deviations). Because of the low concentrations and moderate risk of contamination, any inconsistent points omitted from the histograms are more likely due to analytical error. Results for each parameter or group of related parameters will be discussed separately.

1. Specific Conductance (Figure 10): Since this represents the ability of a substance to conduct an electric current, it can be used as a measure of ionic strength. The measured conductances have a mean of 117 umhos/cm. (25°C) and show a fairly narrow range extending between 50 and 170 umhos/cm. Hem (1970) reports that surface water conductances have a wide range, and sometimes reach values of 50,000 umhos/cm or more. The measured values correspond with the lower part of the observed range

28

FIG. 10 : CONDUCTIVITY OF STREAMS

MEAN = 117.13
MEDIAN = 109.95
STD. DEV. = 43.46
88 POINTS PLOTTED

for natural surface waters, and thus are characteristic of precipitation low in solutes and rocks resistant to chemical attack (or the lack of such chemical weathering).

2. pH: Accurate pH determinations on 23 stream waters yielded an average pH of 8.47 with values ranging from 7.74 to 9.04. Thus, these streams would fall in the upper part of the pH range of 6.5 to 8.5 pH units (Hem, 1970) characteristic of streams and rivers. It is a typical pH for streams in any type of carbonate terrain.

3. Alkalinity (Figure 11): Since, in water chemistry, alkalinity is defined as the capactiy of the solution to neutralize acid, an end point pH must be specified. The measured alkalinities are for solutions taken to a pH of 3.80 ± 0.05. Although it is expressed in terms of an equivalent quantity of $CaCO_3$ (in this case as ppm $CaCO_3$), alkalinity is practically all produced by dissolved carbonate and bicarbonate ions.

Figure 32 indicates that the dominant carbonate species present in the pH range of these waters is the bicarbonate ion, HCO_3^-. Conversion of the average alkalinity of 60.8 ppm ($CaCO_3$) to an equivalent amount of HCO_3^-, using the conversion: 1 ppm $CaCO_3$ = 1.219 ppm HCO_3^- (Hem, 1970) yields a value of 74.2 ppm (HCO_3^-). This value falls within the range of most surface stream alkalinities (which extends up to approximately 200 ppm (HCO_3^-)). It will be shown later that the low ambient temperatures have considerable effect on the carbonate equilibrium, and thus on the bicarbonate concentration.

4. Alkali Metals (Figures 12 and 13): The two alkali metals measured, Na and K, have average concentrations of 0.71 ppm and 0.16 ppm respectively. These concentrations are quite low when compared with the

FIGURE 32: Percentages of Total Dissolved Carbonate Species as a Function of pH at 25°C, 1 atm.

FIG. 11 : ALKALINITY OF STREAMS

MEAN = 60.76
MEDIAN = 58.23
STD. DEV. = 24.46
86 POINTS PLOTTED

ppm expressed as $CaCO_3$

32

FIG 12: Na CONCENTRATION IN STREAMS

MEAN = 0.71
MEDIAN = 0.32
STD. DEV. = 0.10
POINTS OMITTED: 6.09
10.05
84 POINTS PLOTTED

33

FIG 13 : K CONCENTRATION IN STREAMS

MEAN = 0.163
MEDIAN = 0.100
STD. DEV. = 0.175
POINTS OMITTED : 1.51
4.62

84 POINTS PLOTTED

K CONCENTRATION in p.p.m.

34

mean levels for North American rivers given in Table 4. However, higher levels could not be expected in an area which has no evaporites or other sources of Na and K.

The large amount of scatter on the histograms for both metals seems to depend exclusively on the area in which the samples were taken, and on their proximity to the ocean. All stream waters taken in sample areas 1 through 4 (Figures 4 and 5) had Na and K concentrations greater than 1.0 ppm and 0.15 ppm respectively, and in most the levels were greater than 1.5 ppm and 0.3 ppm respectively. Thus, samples taken in these areas account for all of the high values in Figures 12 and 13. With the exception of sample area 3, all areas are adjacent to the ocean. In addition, all areas lie on the shale side of the facies front and all have outcropping shale nearby. Thus, there are two possible explanations for the observed trend.
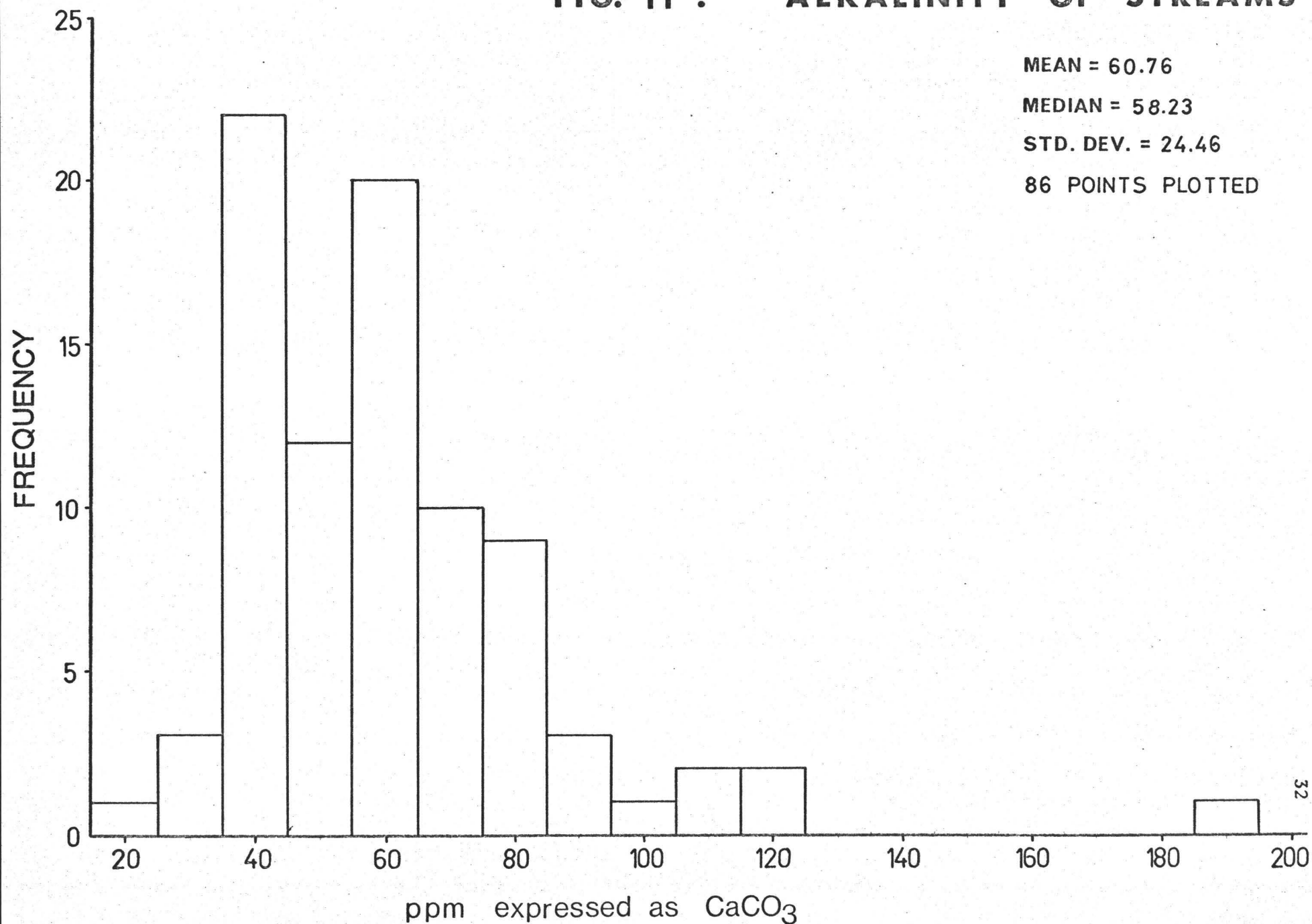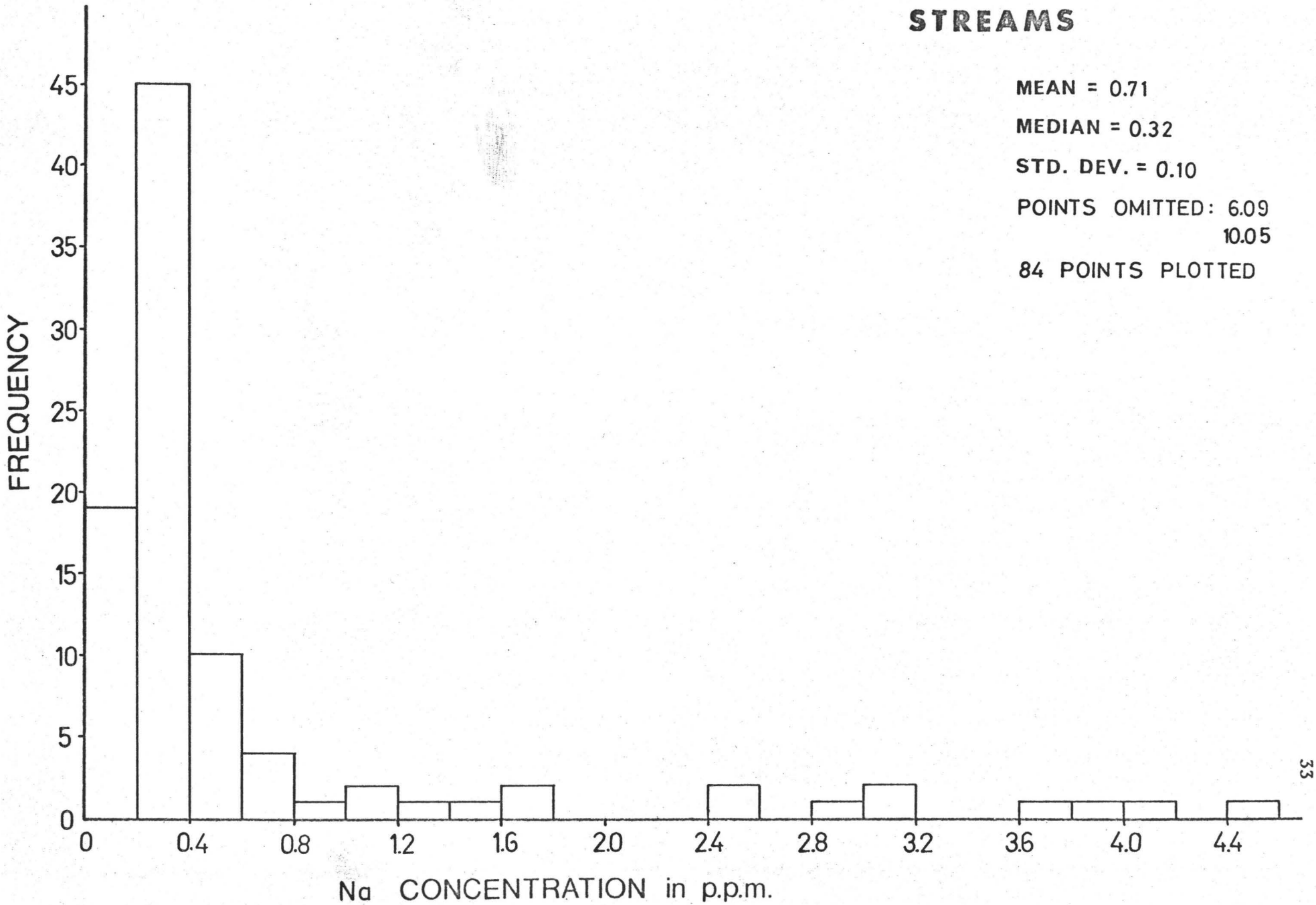
1. The high Na and K concentrations in these areas could be due to the proximity to the ocean. The ocean is ice-covered for 9 to 10 months of the year and remains very calm when free of ice, so that sea spray effect would be negligible. The solutes could not be supplied by the negligible rain, and the generally high gradients of the streams precludes diffusion from the ocean. The only likely means of transport is as aerosols carried by the strong and frequent wind storms. Alternatively, the source of the Na and K could be in the surface rocks and soils. All four areas were submerged beneath the ocean

TABLE 4: COMPOSITION OF NORTH AMERICAN RIVER WATERS

Concentration (ppm.)

	Na	K	Ca	Mg	Fe
North America rivers	9	1.4	21	5	0.16

(from Livingstone (1963)

before isostatic rebound carried them to their present elevations.

2. The other possible source of the high Na and K concentrations is through leaching of shales in the area. I considered this source an unlikely one for two reasons. Firstly, the amount of shale, even in these areas on the shale side of the facies front, is minor. Second, a correlation would be expected between the alkalis and the heavy metals, if the source was a black shale. However, no trend of higher heavy metal concentrations is observed in connection with the shales.

5. Alkaline Earth Metals (and carbonate equilibria considerations) (Figures 14 and 15): The average concentrations of Ca and Mg, 14.46 ppm and 4.34 ppm respectively, agree fairly well with averages for North American rivers in Table 4. However, these streams are carbonate buffered systems. Thus the Ca and Mg concentrations should be higher than in streams flowing in non-carbonate terrains, and might be expected to approach the Ca concentration in a carbonate equilibrium system. The equilibrium Ca concentration for a system approximating these streams (open to the atmosphere, at an ambient temperature of $0°C$) is 31.8 ppm. The calculations can be found in Appendix III. Comparison of the above concentration with that of 15.9 ppm in a system at $25°C$, shows that the lower ambient temperature in the Arctic doubles the equilibrium Ca concentration. Thus, all other factors being equal, the Arctic streams should have high Ca and HCO_3^- concentrations. However, the observed concentrations are lower than both the equilibrium value and most

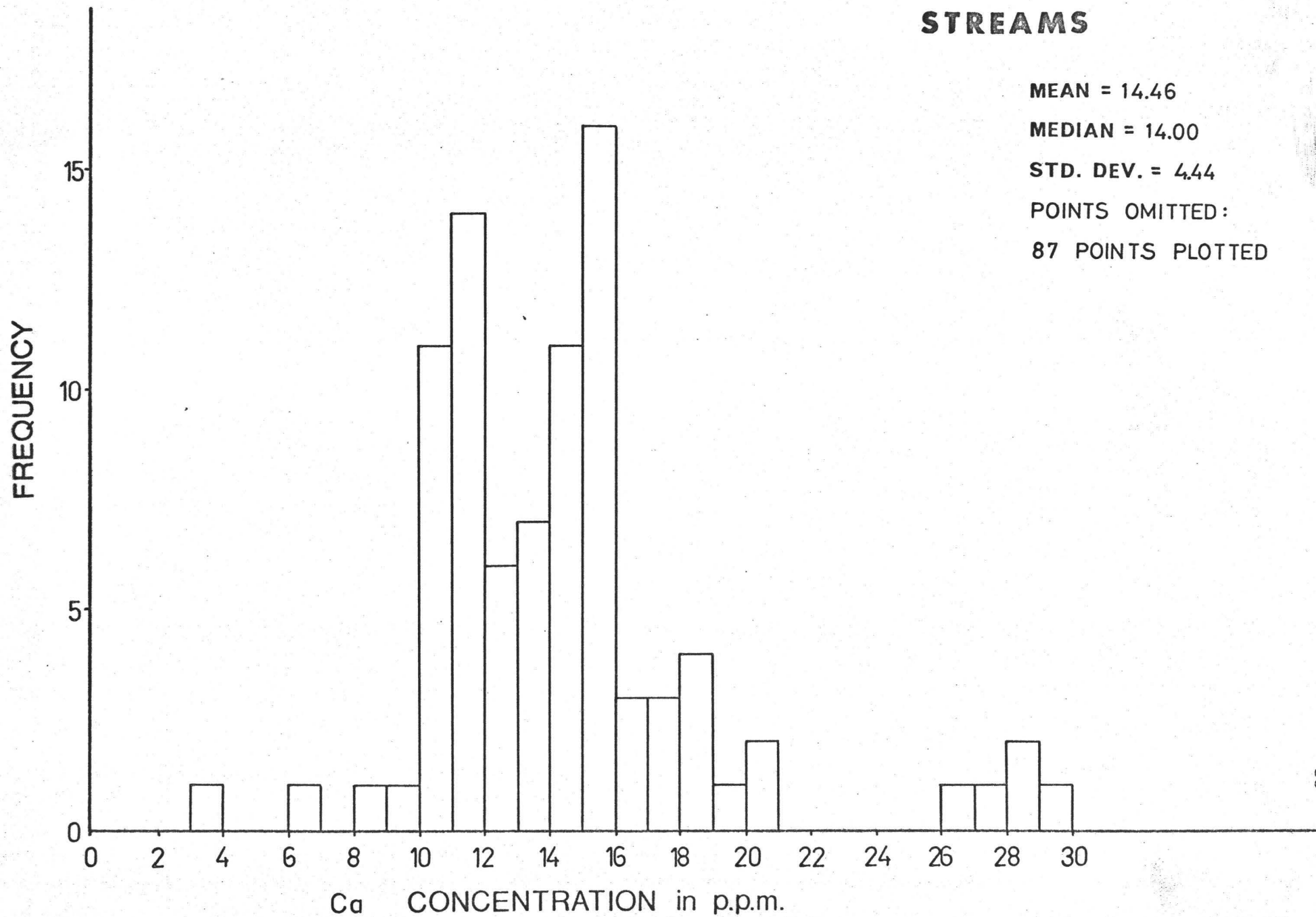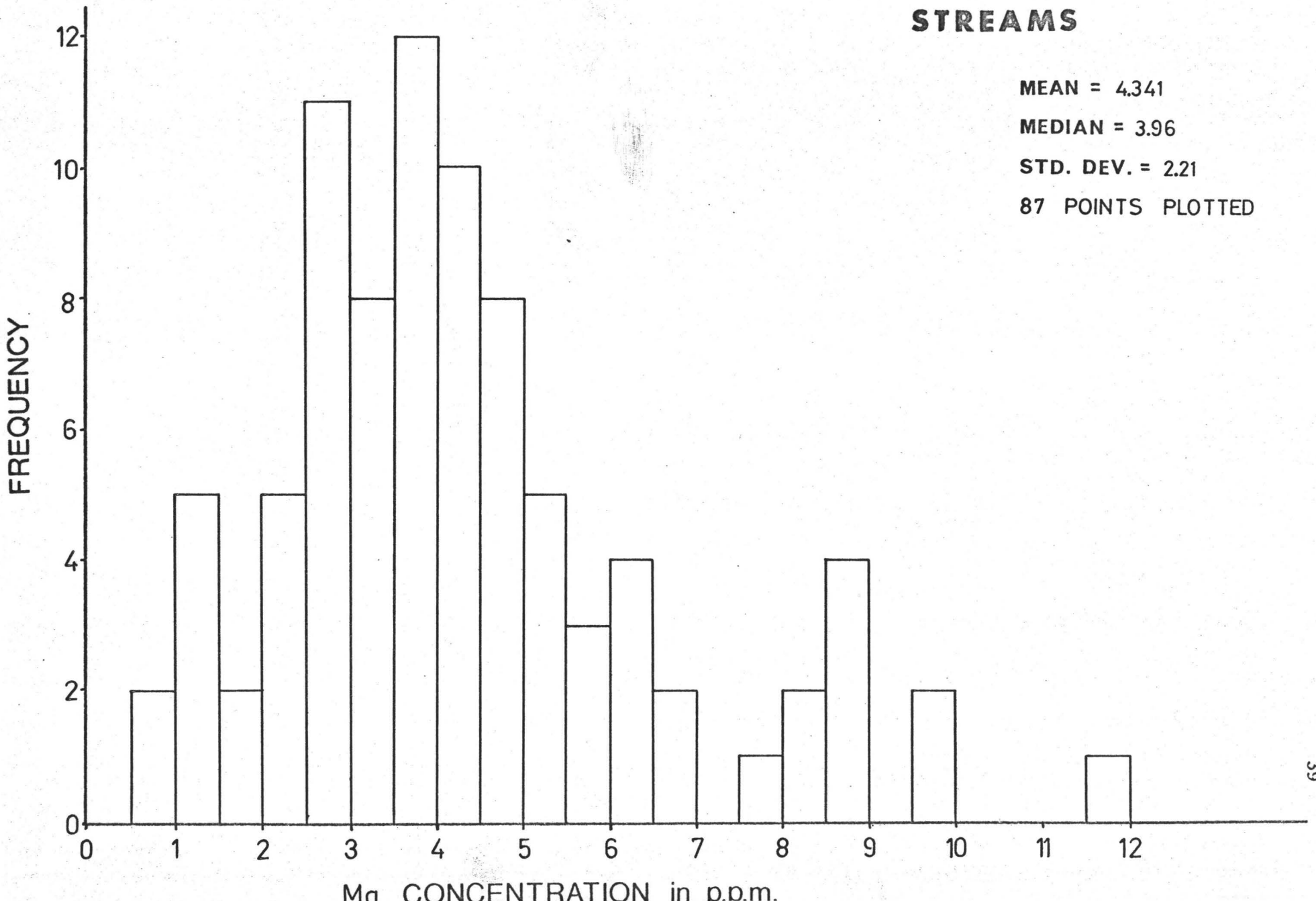FIG 14: Ca CONCENTRATION IN STREAMS

MEAN = 14.46
MEDIAN = 14.00
STD. DEV. = 4.44
POINTS OMITTED:
87 POINTS PLOTTED

FREQUENCY

Ca CONCENTRATION in p.p.m.

38

FIG 15 : Mg CONCENTRATION IN STREAMS

MEAN = 4.341
MEDIAN = 3.96
STD. DEV. = 2.21
87 POINTS PLOTTED

concentrations in temperate carbonate streams.   This disequilibrium

can best be explained by the high velocity and turbulence of the streams.

The waters have no chance to equilibrate with their surroundings during

spring runoff.

6. Ca/Mg ratio (Figure 16):   It was mentioned previously that

the Ca/Mg ratio reflects, to some extent, the composition of a carbonate

terrain.   More specifically, it can sometimes be used as a measure of

the relative amounts of limestone and dolomite.   The average value of

4.19 for the Ca/Mg ratio of these streams indicates that limestone

predominates.   However, it is unwise to state the relation in more

quantitative terms.   From mapping it is known that limestone does

predominate over dolomite, but there exists no estimate of their relative

proportions.

7. Heavy Metals: Pb, Cu, Fe, Zn, Cd (Figures 17 through 26):

Because of the particulate matter in many of the samples, heavy metal

determinations were carried out on both total (acid digested) and filtered

samples.   After blank correction, the means for all total metal con-

centrations were higher than the corresponding filtered metal concentrations.

The spread of values on all histograms was considerable and in almost all

cases the standard deviation had about the same value as the mean.

A brief discussion will be given for each metal: i) Fe - the

greatest differences between corresponding total and filtered concentrations

(sometimes on the order of thousands of p.p.b) are observed in the case of

Fe.   Virtually every high Fe_T value is from a sample having a high silt

FIG. 16 : Ca/Mg RATIO OF STREAMS

MEAN = 4.19
MEDIAN = 3.44
STD. DEV. = 2.70
87 POINTS PLOTTED

FREQUENCY

Ca/Mg ratio

FIG 17: Fe_T CONCENTRATION IN STREAMS

MEAN = 50.1

MEDIAN = 523.5

STD. DEV. =

POINTS OMITTED:

86 POINTS PLOTTED

FREQUENCY

Fe_T CONCENTRATION in p.p.m. $\times 10^3$

42

FIG 18: Fe_F CONCENTRATION IN STREAMS

MEAN = 9.62

MEDIAN = 8.00

STD. DEV. = 8.68

POINTS OMITTED: all points greater than corresponding Fe_T values

70 POINTS PLOTTED
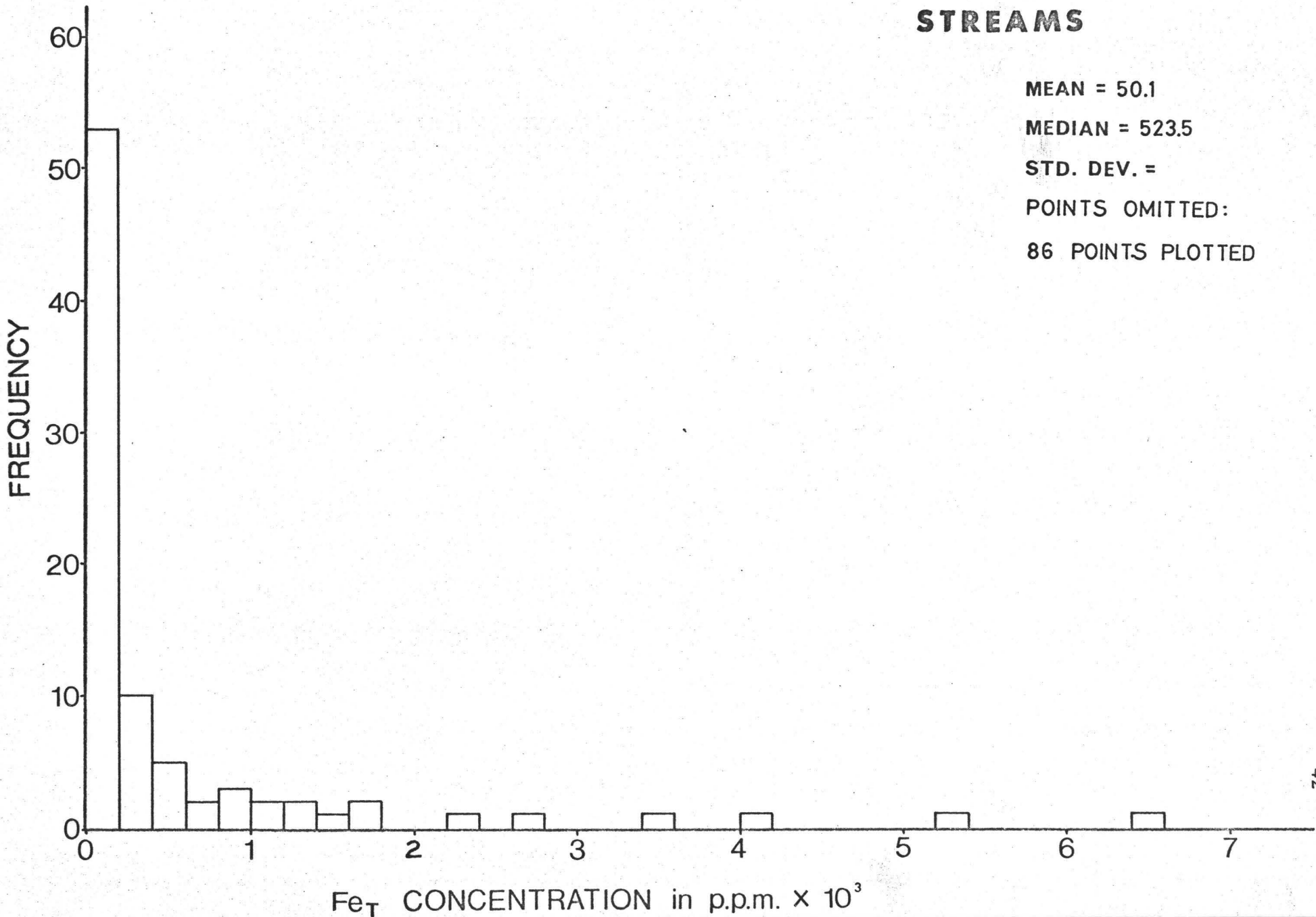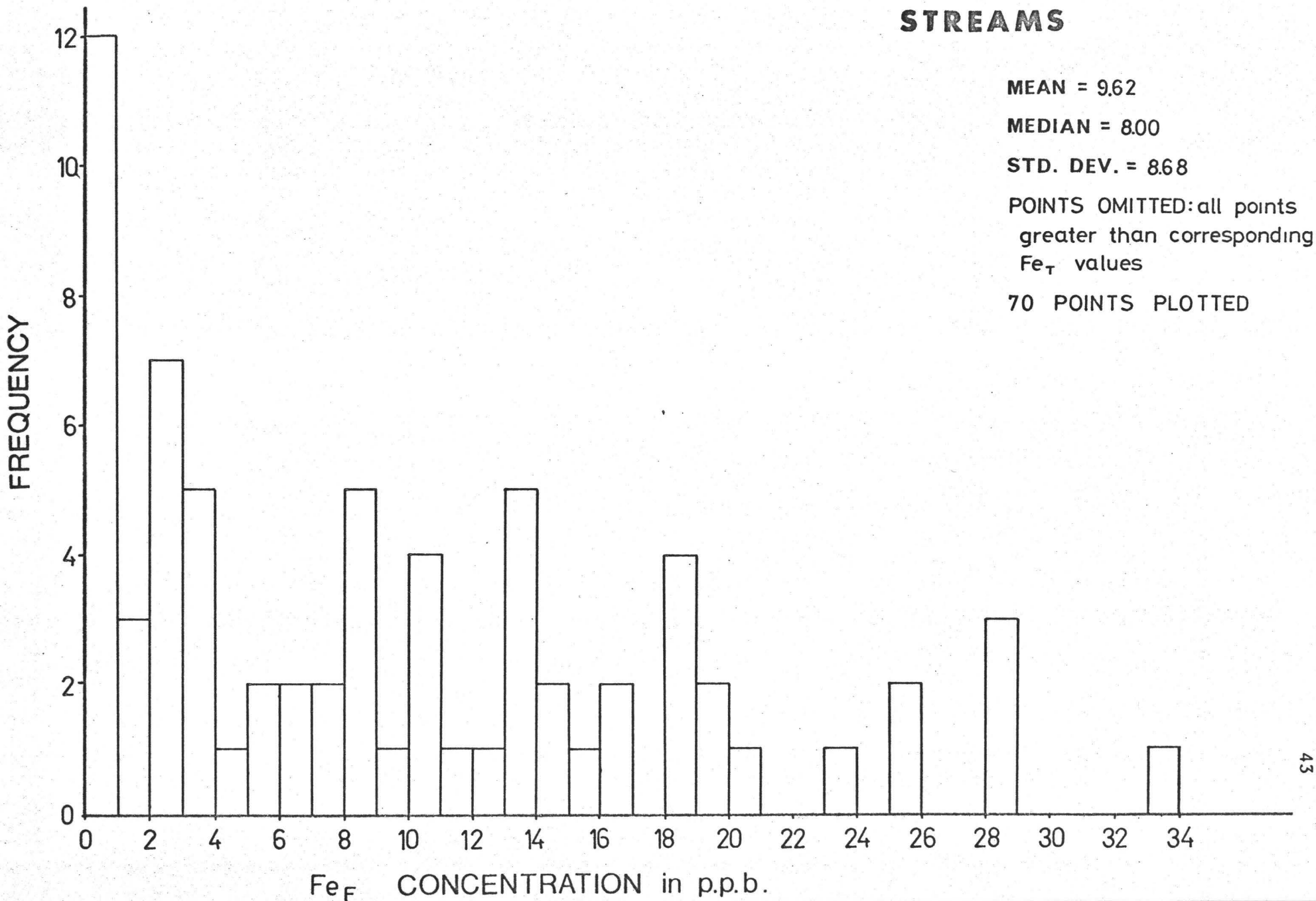
43

content. This indicates that, under the conditions in these streams, most of the Fe is being carried as colloids or insoluble oxides forming coatings on the silt fraction. However, relative to other metals, there is a fair amount of free Fe (ie Fe_F mean is 9.62 ppb) (Figure 18).

The main sources of Fe, in this terrain are:

1. abundant tiny nodules of Fe oxides which occur in rocks of all formations, and

2. occasional hematite-goethite gossans, which are visible at great distances because of their bright orange-brown weathered colour.

ii) Pb - considerable contamination problems were encountered. The clusters of high values in both the Pb_T and Pb_F histograms (Figures 19 and 20) are probably due to analytical error. Obviously, the amount of Pb travelling in streams, either in a soluble form or adsorbed to particulates, is almost negligible. There is no consistent correlation of high Pb_T or Pb_F values with high Fe_T concentration in the same sample. This confirms the general immobility of Pb in the weathering cycle.

iii) Cu - few contamination problems were encountered. Again the clusters of high values in Figures 21 and 22 are believed due to analytical error. Thus, most of the Cu present seems to be associated with the silt. Garrels and Christ (1964) suggest that cupric oxide or hydroxy carbonate minerals would tend to limit the solubility of Cu in aerated water at a pH of 8.0 to about 6.4 ppb. This value is an order of magnitude greater than the observed Cu_F mean.

iv) Zn - considerable contamination was encountered. Comparison of the Zn_T and Zn_F means, 12.14 ppb and 1.52 ppb respectively, indicates

FIG 19 : Pb_T CONCENTRATION IN STREAMS

MEAN = 2.38
MEDIAN = 0.00
STD. DEV. = 4.83
POINTS OMITTED: 40.0
74 POINTS PLOTTED

45

FIG 20 : Pb$_F$ CONCENTRATION IN STREAMS

MEAN = 1.22

MEDIAN = 0.00

STD. DEV. = 2.80

POINTS OMITTED : all points greater than corresponding Pb$_T$ values

46 POINTS PLOTTED

FREQUENCY

Pb$_F$ CONCENTRATION in p.p.b.

46

FIG 21 : Cu_T CONCENTRATION IN STREAMS

MEAN = 3.01
MEDIAN = 1.80
STD. DEV. = 3.59
87 POINTS PLOTTED

FREQUENCY

Cu_T CONCENTRATION in p.p.b.

47

FIG 22 : Cu_F CONCENTRATION IN STREAMS

MEAN = 0.648

MEDIAN = 0.500

STD. DEV. = 0.635

POINTS OMITTED : all points greater than corresponding Cu_T values

75 POINTS PLOTTED

Cu_F CONCENTRATION in p.p.b.

49

that, again, the majority of the metal is associated with whatever particulate matter is present. Both modes show a wide range in values (Figure 23 and 24). In keeping with its greater mobility, free Zn is present at higher concentrations than Pb in these waters.

v) Cd - moderate contamination was encountered. After blank correction, the majority of the Cd values ended up below the detection limit, as can be seen from the skewed distributions in Figures 25 and 26. Cd is negligible in the streams.

A direct comparison of heavy metal contents of these streams (Table 5) with any compiled averages indicates only that they are carrying the same metals at the same approximate concentration levels. The relation between a calculated equilibrium Cu concentration and the actual Cu_F mean can probably be extrapolated to the other metals. For example the background of combined Pb+Zn given by Kennedy (1956) for the mineralized carbonate area of southwestern Wisconsin is 10 ppb. This is considerably greater than the combined $Pb_F + Zn_F$ value of 2.7 ppb from the Grinnell-Cornwallis area. These are fast moving streams which have no chance to reach an equilibrium. Thus one would expect the amounts of dissolved metals to be quite low.

As mentioned earlier, there was no consistent trend of higher heavy metal values in samples taken on or near known outcroppings of black or green shales.

Stream Sediments and Soils

It was mentioned previously that the stream sediment and soil analyses do not represent a random cross-section of metal concentrations

FIG 23 : Zn_T CONCENTRATION IN STREAMS

MEAN = 12.14

MEDIAN = 3.25

STD. DEV. = 16.64

POINTS OMITTED: 80.6

86 POINTS PLOTTED

FREQUENCY

Zn_T CONCENTRATION in p.p.b.
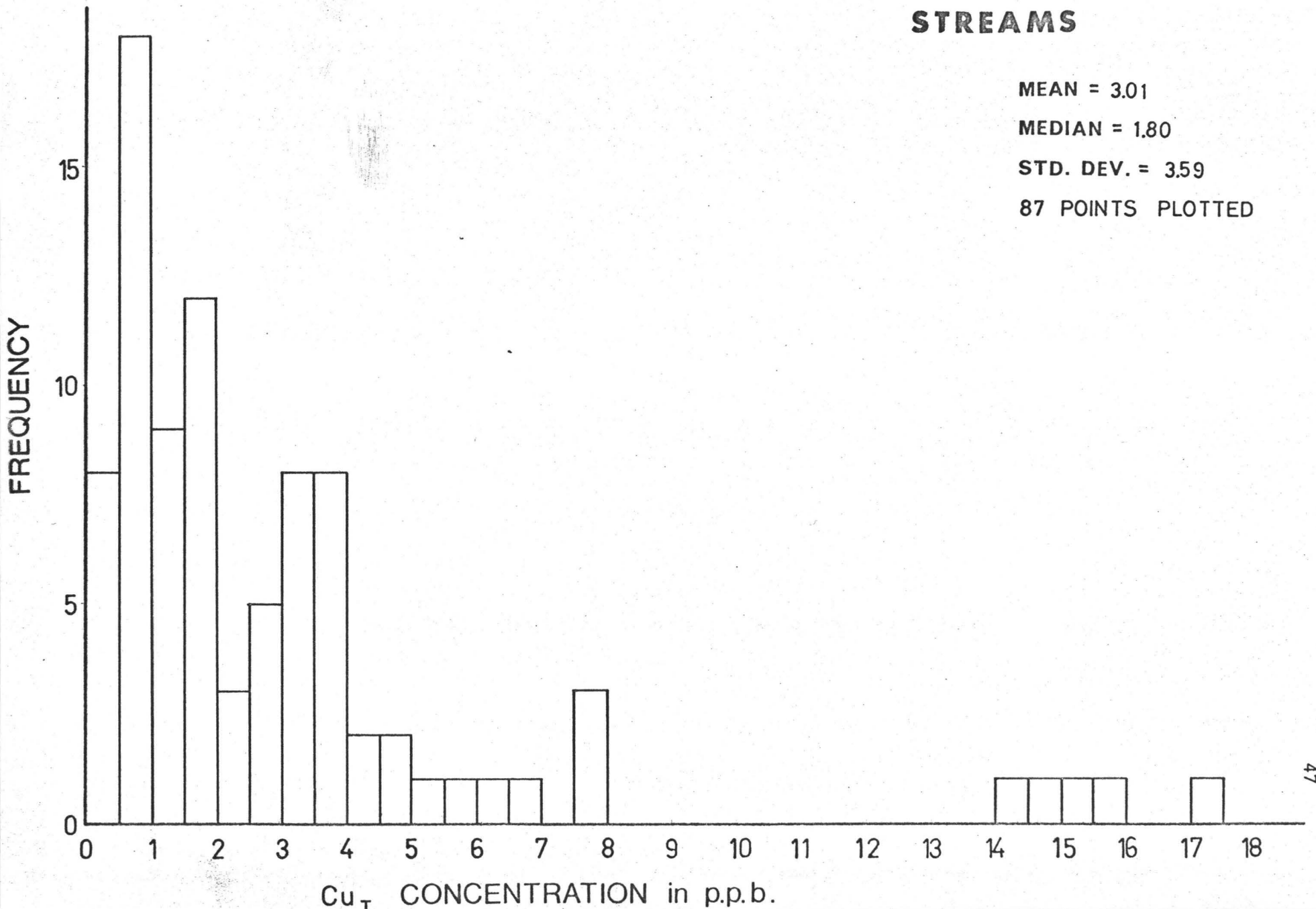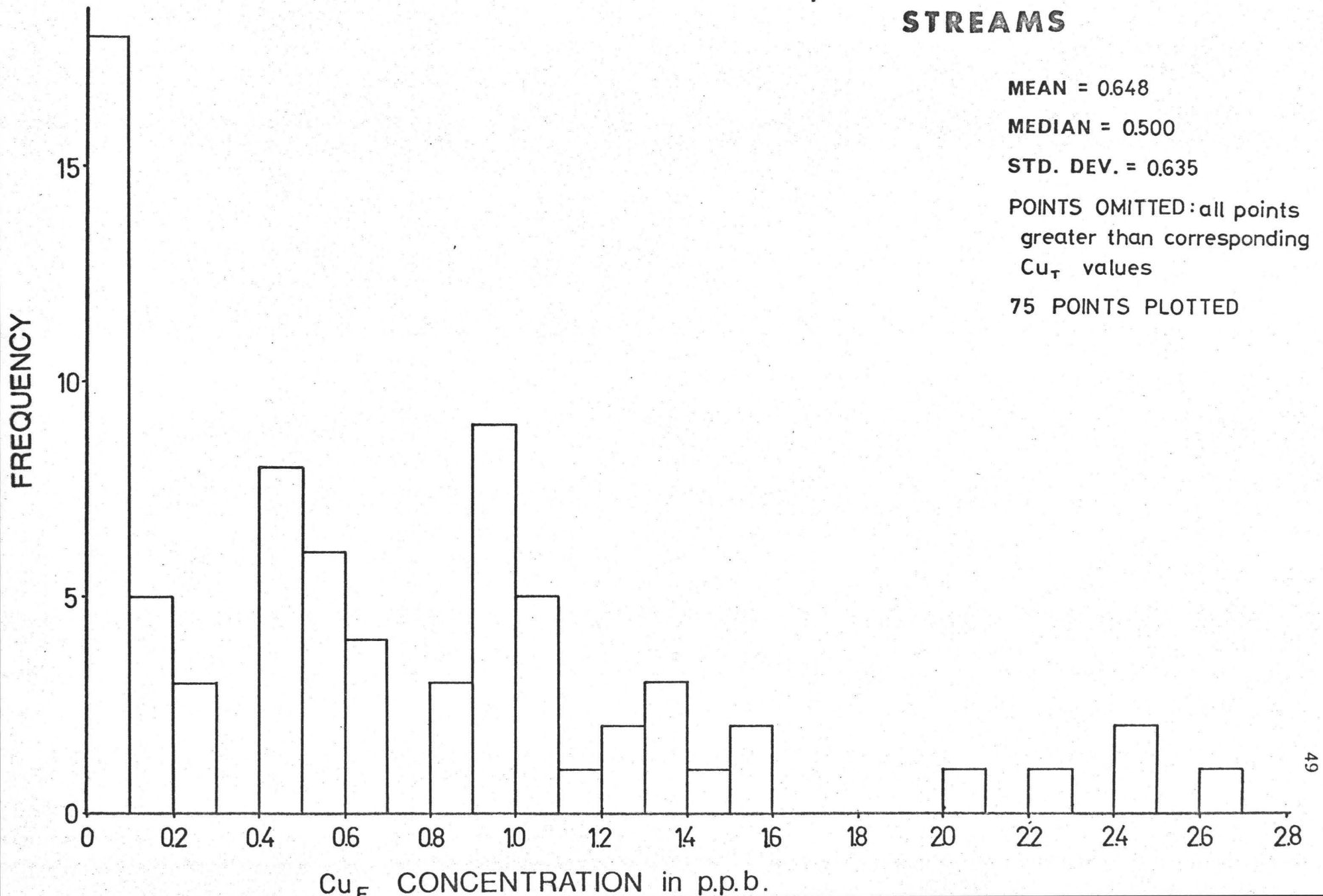
51

FIG 24 : Zn_F CONCENTRATION IN STREAMS

MEAN = 1.52

MEDIAN = 1.20

STD. DEV. = 1.45

POINTS OMITTED: all points greater than corresponding Zn_T values

58 POINTS PLOTTED

FIG 25 : Cd_T CONCENTRATION IN STREAMS

MEAN = 0.58
MEDIAN = 0.00
STD. DEV. = 0.93
POINTS OMITTED: 4.4
86 POINTS PLOTTED

Cd_T CONCENTRATION in p.p.b.

FIG 26 : Cd_F CONCENTRATION IN STREAMS

MEAN = 0.30

MEDIAN = 0.00

STD. DEV. = 0.67

POINTS OMITTED: all points greater than corresponding Cd_T values

74 POINTS PLOTTED

54

TABLE 5: COMPILATION OF MEAN AND MEDIAN PARAMETER VALUES

A. STREAM WATERS

PARAMETER	MEAN	MEDIAN
Conductivity	117.3 μmhos cm^{-1}	110.0 μmhos cm^{-1}
pH	8.47	
Alkalinity	60.76 ppm($CaCO_3$)	58.23 ppm($CaCO_3$)
Na	0.71 ppm	0.32 ppm
K	0.163 "	0.100 "
Ca	14.46 "	14.00 "
Mg	4.19 "	3.96 "
Ca/Mg ratio	4.19	3.44
Fe_T	50.1 ppb	523.5 ppb
Fe_F	9.62 "	8.00 "
Pb_T	2.38 "	0.00 "
Pb_F	1.22 "	0.00 "
Cu_T	3.01 "	1.80 "
Cu_F	0.648 "	0.500 "
Zn_T	12.14 "	3.25 "
Zn_F	1.52 "	1.20 "
Cd_T	0.58 "	0.00 "
Cd_F	0.30 "	0.00 "

TABLE 5: continued

B. STREAM SEDIMENTS AND SOILS

PARAMETER	MEAN	MEDIAN
Fe		
Pb	114.25 ppm	53.40 ppm
Cu	8.65 "	8.40 "
Zn	57.00 "	32.90 "
Cd	9.27 "	8.70 "

in stream sediments and soils, as do the water samples. The histograms and statistical data in Figures 27 to 31 are only meant to give a rough indication of the concentrations present. Cd, Cu, and Fe with mean concentrations of 9.27 ppm, 8.65 ppm and 11,135 ppm respectively, show the best distributions. The scatter in the Pb and Zn concentrations, which have mean values of 114.3 and 57.0 is strongly influenced by the fact that some of these samples were taken from areas of weak mineralization.

The statistical summary for Zn in stream sediments and soils given in Figure 33 is based on a stream sediment and soil survey of Grinnell Peninsula conducted by Cominco Ltd. The large number of samples analyzed gives a more reliable statistical picture than my own results. The stream sediments had a mean Zn concentration of 29.7 ppm. The mean value of 177.6 ppm for the soils reflected the bias toward gossan sampling. These results are not comparable with my own, since different digestion techniques were used.

Sample Area 8 - Dispersion pattern caused by Fe-Pb Mineralization

During the 1972 field season, a stream sediment sample was taken at the location indicated in Figure 9. When analysed the silt fraction was found to contain 50,000 ppm Pb. However there was no appreciable enrichment in Zn above background levels. At the time the sample was taken, the prominent orange-brown gossan extending for about 300 ft. along the steep wall of the river valley (Figure 9) was sampled and examined for mineralization. Abundant marcasite was found but there was no visible Pb or Zn mineralization.
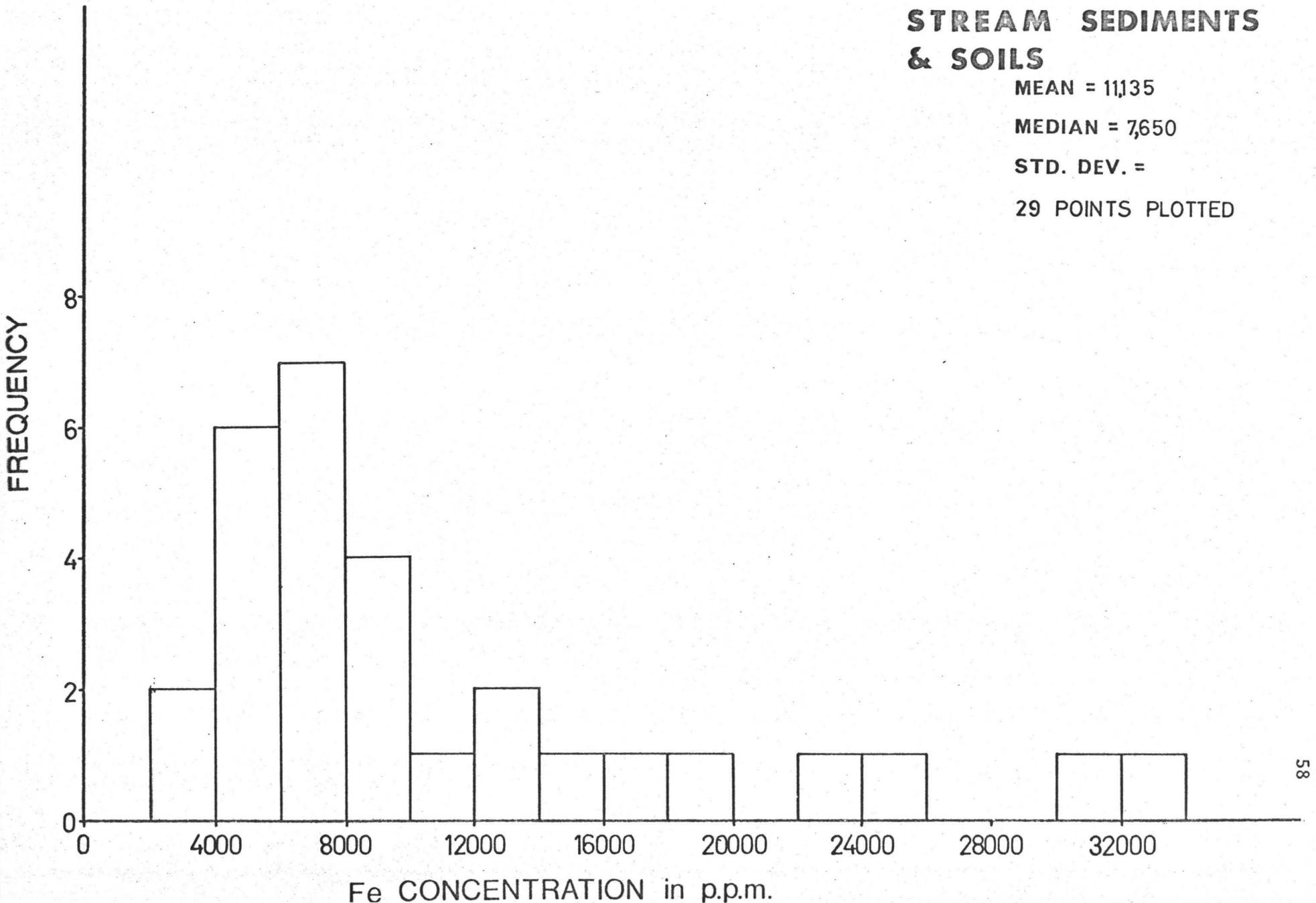
FIG 27: Fe CONCENTRATION IN STREAM SEDIMENTS & SOILS

MEAN = 11,135

MEDIAN = 7,650

STD. DEV. =

29 POINTS PLOTTED

FIG 28: Pb CONCENTRATION IN STREAM SEDIMENTS & SOILS

MEAN = 114.25

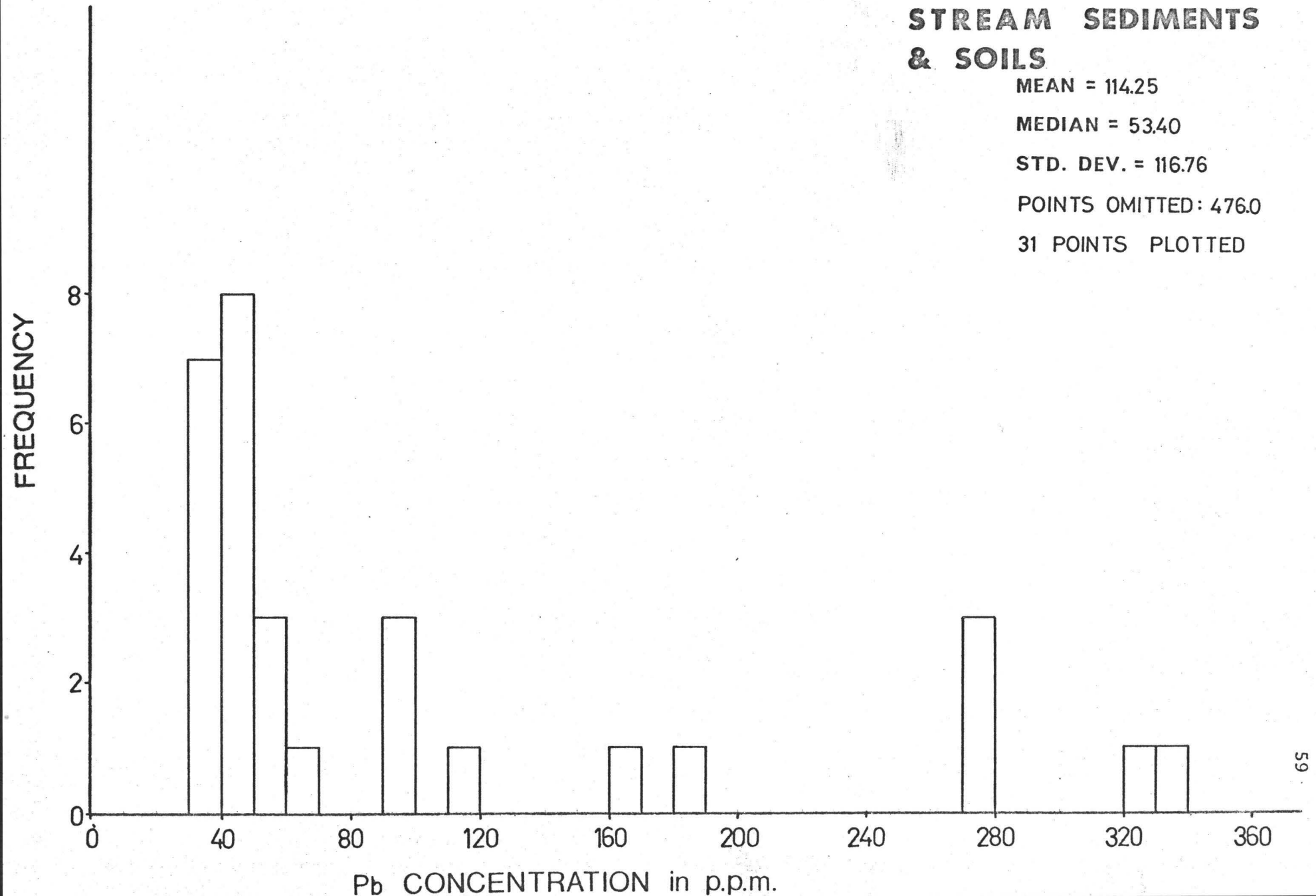MEDIAN = 53.40

STD. DEV. = 116.76

POINTS OMITTED: 476.0

31 POINTS PLOTTED

Pb CONCENTRATION in p.p.m.

59

FIG 29: Cu CONCENTRATION IN STREAM SEDIMENTS & SOILS

MEAN = 8.65
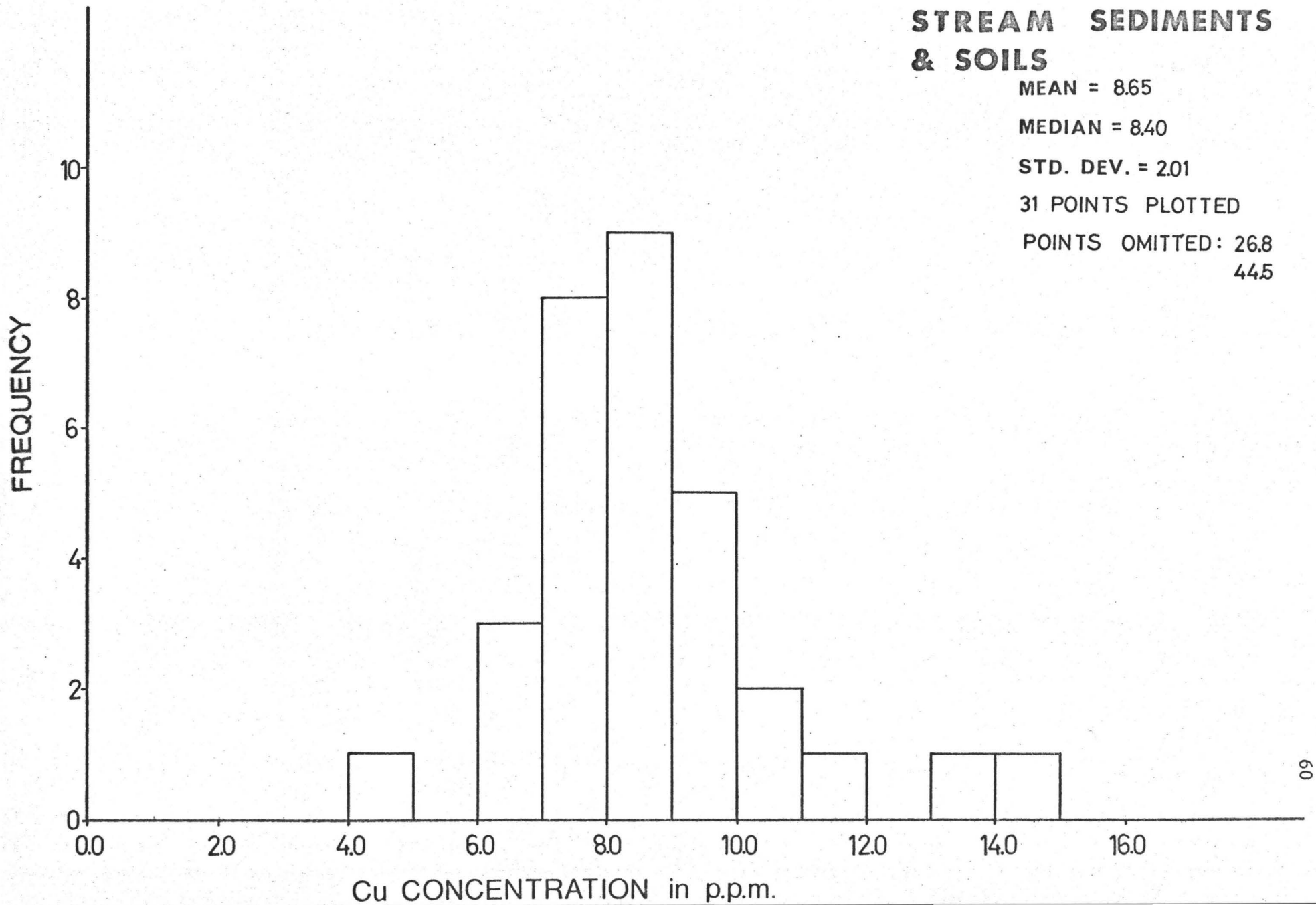
MEDIAN = 8.40

STD. DEV. = 2.01

31 POINTS PLOTTED

POINTS OMITTED: 26.8
44.5

FIG 30: Zn CONCENTRATION IN STREAM SEDIMENTS & SOILS

MEAN = 57.00

MEDIAN = 32.90

STD. DEV. = 63.00

33 POINTS PLOTTED

Zn CONCENTRATION in p.p.m.

FREQUENCY

61
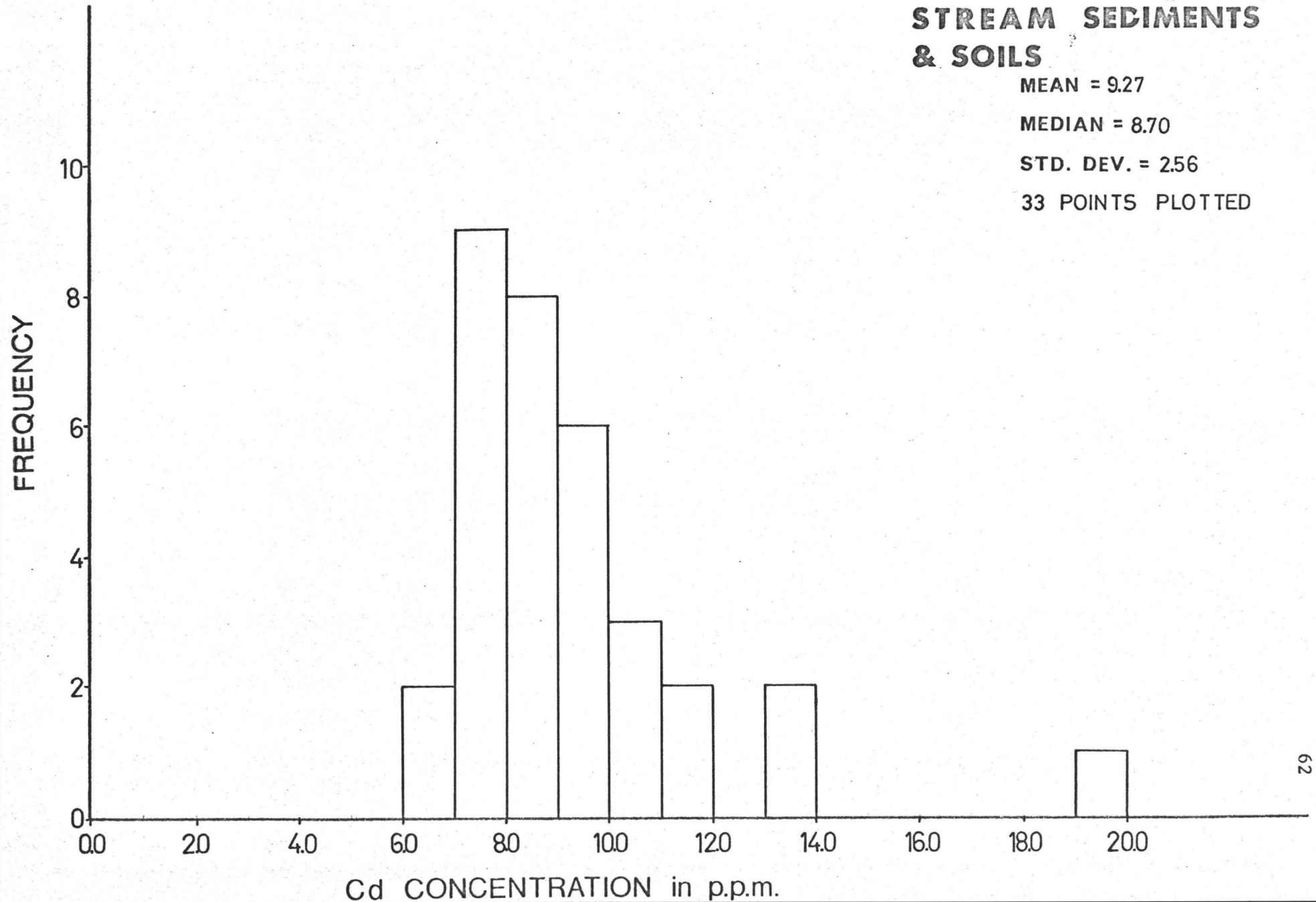
FIG 31 : Cd CONCENTRATION IN STREAM SEDIMENTS & SOILS

MEAN = 9.27

MEDIAN = 8.70

STD. DEV. = 2.56
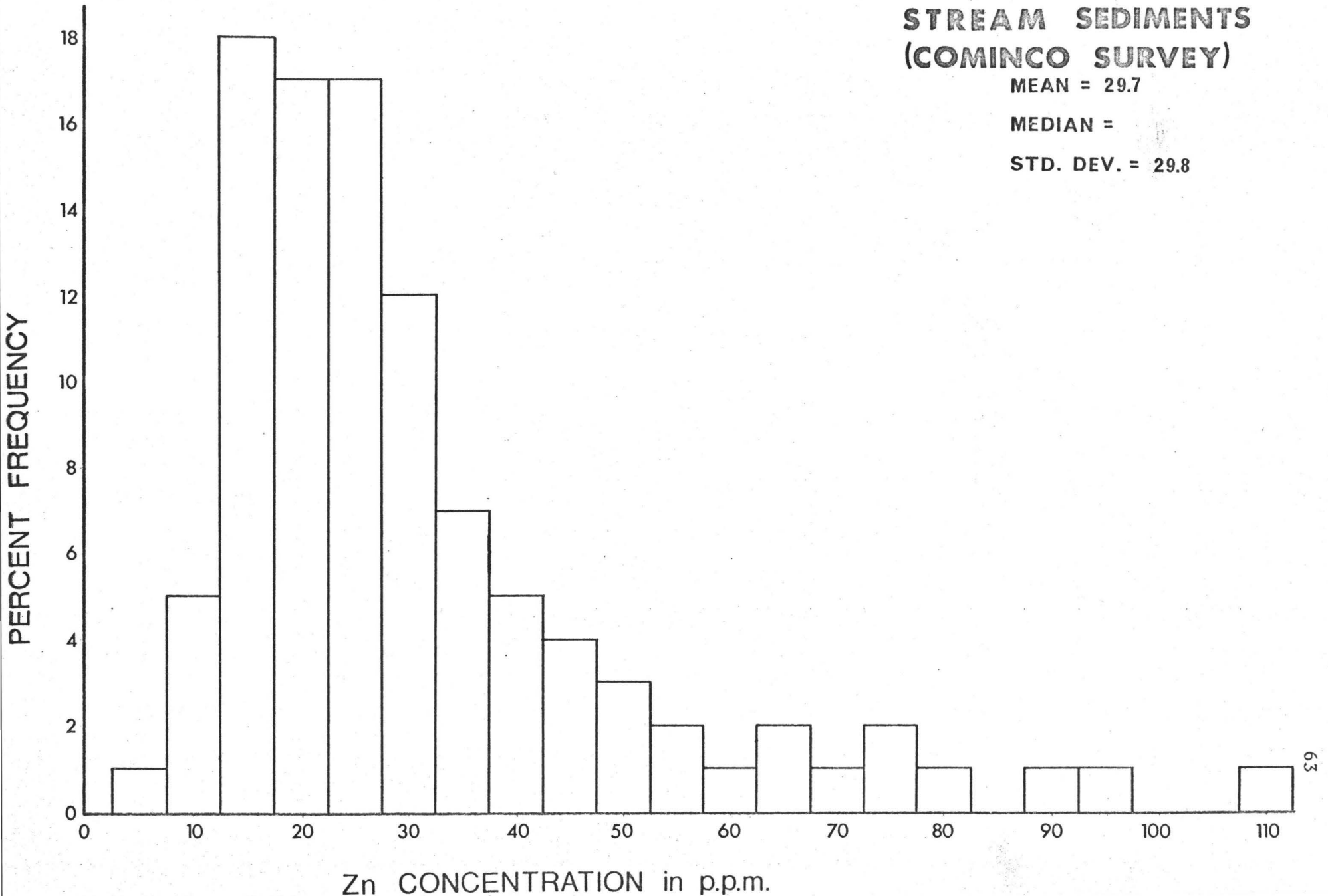
33 POINTS PLOTTED

Cd CONCENTRATION in p.p.m.

62

FIG 33: Zn CONCENTRATION IN STREAM SEDIMENTS (COMINCO SURVEY)

MEAN = 29.7
MEDIAN =
STD. DEV. = 29.8

63

In an effort to explain the anomalous Pb concentrations in the stream sediments, the rock, stream sediment, soil and stream water samples shown in Figure 9 taken in the summer of 1973.

The rock analyses are shown in Table 6.   Samples 47,55 and 68 were chosen to represent the typical lithologies in the area.   They contain no visible mineralization and seem to possess background levels of Fe,Pb and Zn.   Samples 52 and 53 are from a bright red and yellow gossan which contains no visible Pb or Zn mineralization (the background Pb and Zn levels reflect this).   The gossan, occurring on the opposite wall of the valley from the mineralized one, seems to be of a fundamentally different type and is possibly not related to the mineralization.   Rock sample 63 and to a lesser extent 65 (both taken on the gossan) show considerable enrichment in Pb, Zn and Fe.
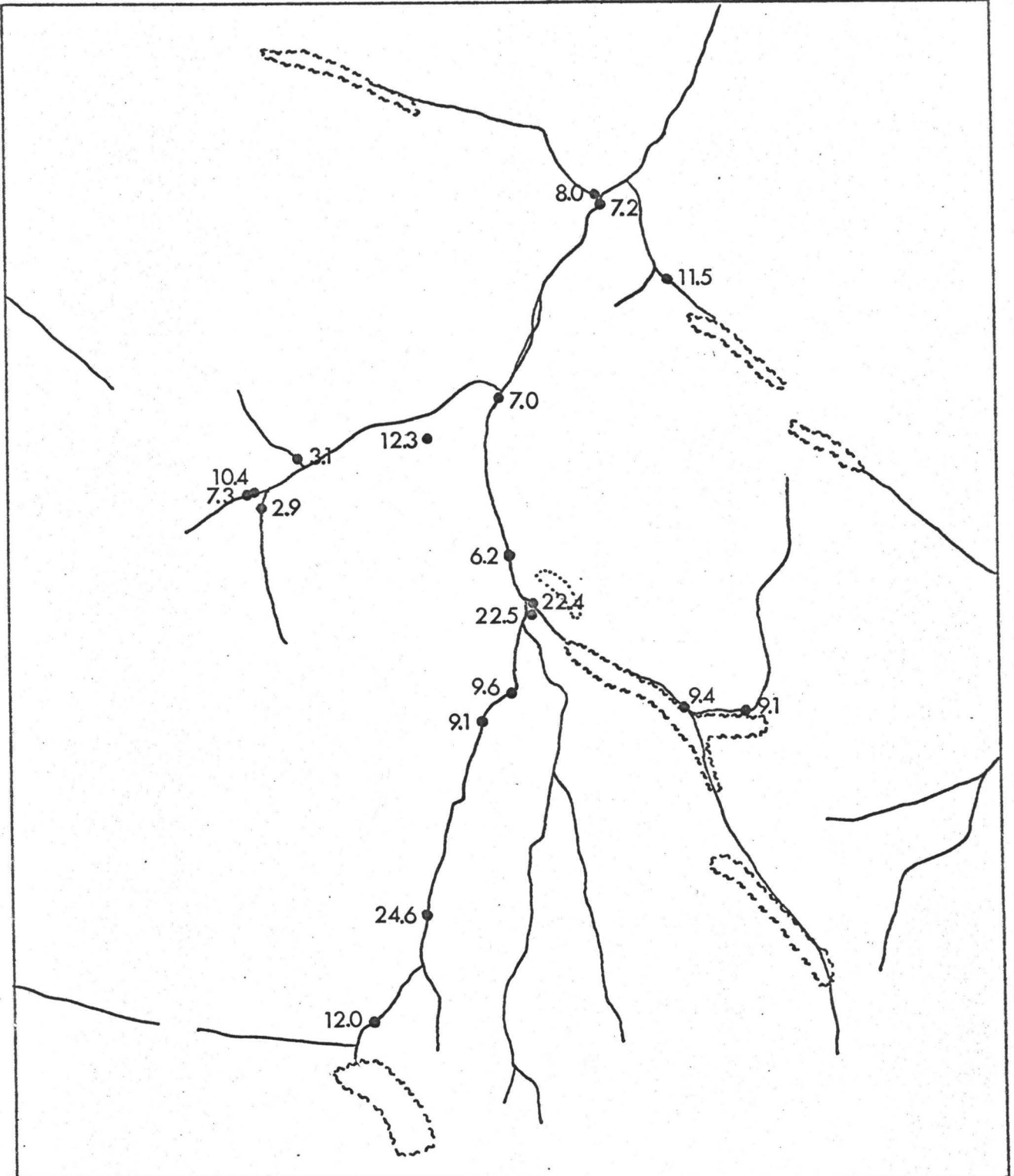
Figure 34 indicates that the presence of the gossan and mineralization is reflected only in the Zn concentrations of the water samples taken immediately adjacent to it.   Due to the insolubility of Pb, it is not surprising that this metal is not enriched in the stream water, even near the mineralization.

Figure 35 and the profile in Figure 36 indicate that the presence of the mineralization is reflected in the Pb and, to a lesser degree, the Zn contents of the stream sediments taken downstream from the gossan. The Pb concentration of the sediments is still considerably above background at a distance of 0.75 mi. downstream from the gossan.

On the basis of the available data, it seems that the mineralization consists of marcasite containing small amounts of galena and sphalerite (with galena predominating over sphalerite).   Neither the

TABLE 6: ANALYSES OF ROCK SAMPLES

Sample Number	Total Fe_2O_3(%)	Acid Ext. Fe_2O_3(%)	FeO(%)	Cu(ppm)	Pb(ppm)	Zn(ppm)
47	3.03	0.22	0.11	<5	40	8
52	10.42	1.05	0.37	<5	30	8
53	5.92	0.73	0.36	<5	30	6
55	1.70	0.21	—	<5	40	4
63	23.65	23.65	0.59	<5	1100	320
65	0.86	0.84	0.14	<5	58	22
68	1.45	1.18	0.46	<5	20	10

FIGURE 34 66

SAMPLE AREA 8   refer to legend, Figure 3

Zn_T Concentration in Stream Waters

SCALE IN MILES
0   1/4   1/2

⊂⊃ Permanent snowfields
⊂∷⊃ Area of FeS_2 and extensive gossan
9.1 ● Zn concentration in water sample in p.p.b.

FIGURE **35** 67

SAMPLE AREA 8: refer to legend, Figure 3

Zn,Pb Concentration in Stream Sediments

Permanent snowfields

Area of FeS_2 and extensive gossan

33.7 ● Pb concentration in stream
35.8 Zn sediment sample in p.p.m.

0   1/4   1/2
SCALE IN MILES

FIG 36: Pb CONCENTRATION IN STREAM SEDIMENTS OF ANOMALOUS STREAM

DISTANCE ALONG ANOMALOUS STREAM IN MILES

Pb nor Zn mineralization is visible under the hand lens. Weathering has altered the marcasite to insoluble iron oxides (hematite and goethite) and has released some of the Pb and Zn.

The dispersion pattern indicates that whatever Zn is released is able to leave the weathering site more rapidly than Pb due to its higher mobility. Because of its extreme insolubility, the Pb is probably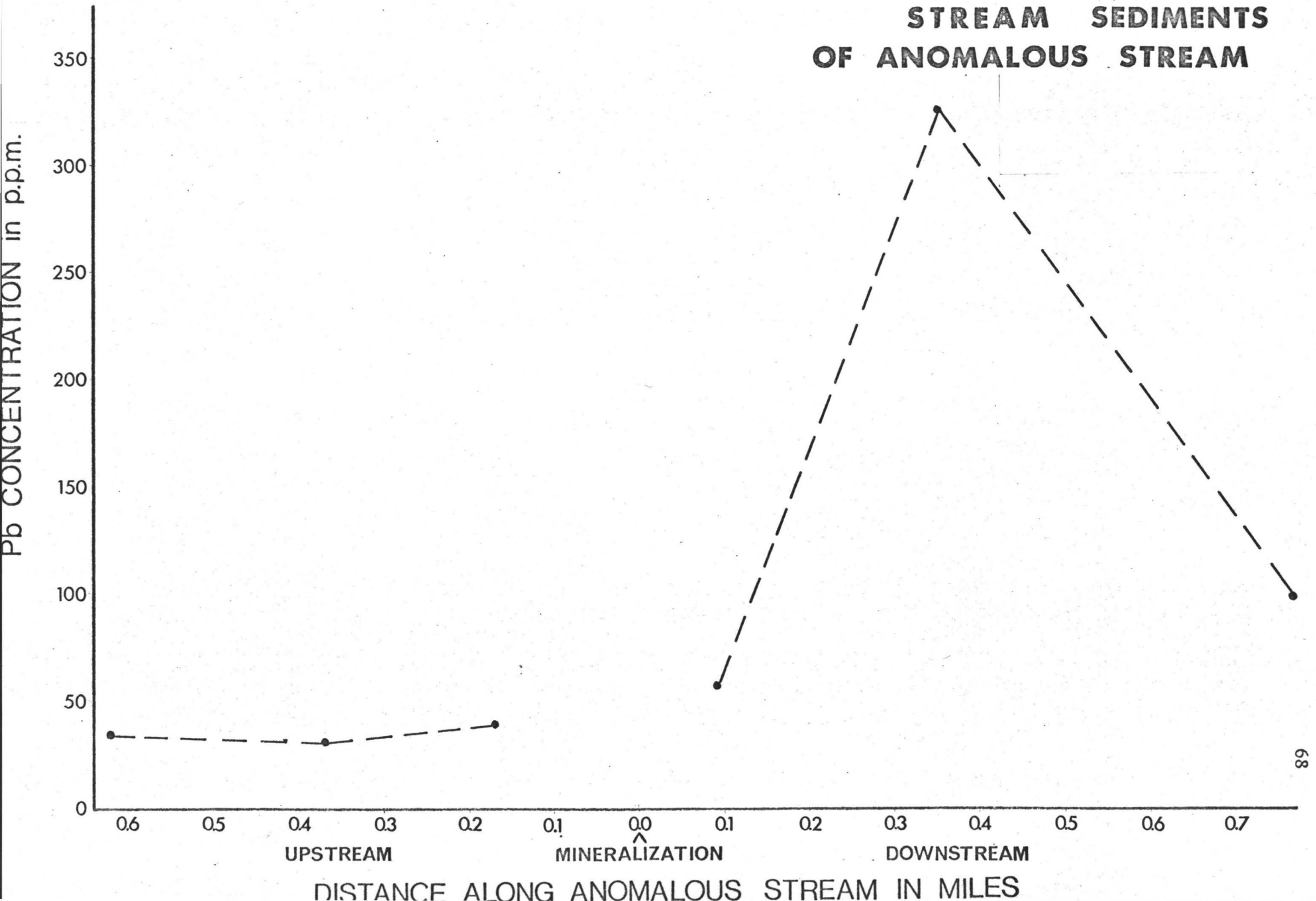 dispersed as the carbonate or oxide, entirely by mechanical means. This would explain the consistently high Pb concentrations in the silt fraction. The stream sediment assaying 50,000 ppm Pb probably came from a patch of silt which had been enriched in heavy minerals by the winnowing action of the steam.

CONCLUSIONS

Analytical results indicate that, in general, the streams sampled compared fairly well with rivers and streams in other carbonate terrains, in terms of pH, conductance, alkalinity, and heavy metal concentrations.

High concentration levels of the alkali metals in some samples can best be explained by the proximity of these samples to the ocean. The only likely means of transport of these metals at present is as aerosols carried by the strong winds. Alternatively the source of the Na and K could be the surface rocks and soils which were submerged beneath the ocean before isostatic rebound carried them to their present elevations.

Equilibrium carbonate calculations (Appendix III) show that the low ambient temperatures should increase the equilibrium concentration of Ca in these streams to 31.8 ppm from the 15.9 ppm calculated for more temperate climates. The average measured Ca concentration of 14.5 ppm can best be explained by the high velocity and turbulence of the streams. The waters have no chance to equilibrate with the material of the channel in which they flow. Because of this lack of equilibrium, the concentrations of heavy metals in solution are also kept low, probably lower than in streams in the same type of terrain under a temperate climate.

The Ca/Mg ratio of 4.2 is a rough indication of the fact that limestone predominates over dolomite.

70

The dispersion pattern below the area of known mineralization and gossan development indicates that the smaller amounts of zinc, being more mobile than Pb are transported away from the weathering site more rapidly and thus leave no dispersion pattern. Pb travels as insoluble oxides and carbonates with the silt fraction of the stream and thus gives rise to a downstream anomaly.

These observations confirm the belief that chemical weathering and transport in solution are factors of little importance in the Arctic weathering regime.

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APPENDIX I

A. Procedure for Alkalinity Measurement

25 ml. of sample in a small beaker was placed on a magnetic stirrer. After an initial pH reading, the pH was lowered to approximately 3.80 by the slow addition of a known volume of standard H_2SO_4. The initial and final pH values and the volume of acid used were typed on computer cards. A program facilitated the determination of alkalinity in units of $MgCaCO_3/\ell$ (or ppm $CaCO_3$).

B. Water Sample Preparation for Heavy Metal Analysis

1. 100 ml of homogenized sample was filtered through a 0.45u millipore filter. This will be referred to subsequently as the filtered sample (and indicated in the case of a particular metal as Pb_F).

2. 100 ml of sample was digested according to the standard procedure (Kramer, P. 18,19) and made back up to 100 ml. This will be termed the total sample (and indicated as Pb_T).

Due to the small volume of sample used (ie 100 mls. rather than 200 ml.), all reagent volumes listed in the digestion and extraction procedures were halved, except for MIBK where 10 ml. was added instead of the 15 ml. specified.

C. Digestion Procedure for Stream Sediment and Soil Samples

50 ml. of water was added to 5.000 ± 0.0005g. of sample. 40 ml. of concentrated HNO_3 was then added slowly to avoid excessive effervescence (since the silts were calcareous). The sample was taken down to 10-15 ml. on the hot plate, cooled, filtered, and the filtrate was evaporated down to 5 ml. After cooling, the sample was made up to 50 ml. with water. This represents a 1/40 of the metals in the sediment.

Due to high iron concentrations, 1ml. of this 1/40 solution was made up to 100 ml. to give a 1/4000 dilution of the original metal content.

APPENDIX II

Conversion and Calibration of Atomic Absorption Data

Brief mention was made, under "Analytical Techniques", of the
use of standard solutions in connection with the analysis for metals
by atomic absorption.

Sets of prepared standard solutions of varying metal concentrations
were available in the case of the alkali and alkaline earth metals.

Aqueous solutions containing low concentrations of the metals
Pb, Zn, Cu, Fe, Cd have a rather limited stability. For this reason,
standard solutions of these metals were prepared from a stock solution
immediately before each set of analyses was begun. 100 ml. portions of
each of four standards (of varying concentrations) were extracted
according to the same procedure used for the stream waters and were
aspirated before and after each set of samples.

A calibration curve for each metal was obtained by plotting the
peak heights of the standard solutions of the metal against the (known)
concentration of metal in the standard. In the majority of cases the plot
closely approximated a straight line; however,

    1 the accuracy of fit to a straight line

    2 the intercept of the line of the x or y axis, and

    3 the slope of the line

all varied somewhat with each set of samples. The position of the
intercept was the most variable of these factors. Curves for the metals
Fe, Cu and Zn almost invariably passed through the origin. Those for

Pb and Cd generally had variable intercepts on the peak height axis, usually of small magnitude.

The peak height displayed by each sample for a particular metal was measured, and the concentration of that metal in the sample determined using the calibration curve.

A blank correction was applied to all metal analyses by subtracting the metal concentrations in this grand mean from the metal concentrations of the samples as determined from the recorder peak heights. Since the blank levels are in the same range as the levels in the samples, it is not surprising that some resultant sample metal values are 0 or -ve after correction.

The same basic procedure was followed in the reduction of the stream sediment metal concentrations. Untreated aqueous metal standards were aspirated along with the samples. No blank corrections were necessary because of the high levels of metals in the samples, as compared with those of the blanks.

APPENDIX III
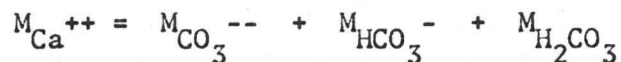
Carbonate Equilibrium in an Ideal System

These calculations follow closely the treatment by Garrels and Christ (1964) of the carbonate equilibrium in a $CaCO_3$-water system which has an externally fixed P_{CO2} (ie. the system is in contact with the atmosphere).

The low ambient Arctic temperatures will change all of the involved equilibrium constants as shown below.
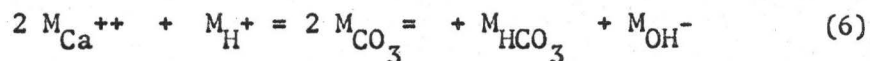
Temperature (°C)	pK_1 $=-logK_{H_2CO_3}$	pK_2 $=-logK_{HCO_3^-}$	pK_3 $=-logK_{CaCO_3}$	pK_{CO_2} $=-logK_{CO_2}$
0	6.52	10.62	8.02	1.12(0.2°C)
5	6.52	10.56	8.09	-
25	6.35	10.33	8.34	1.47

pK values for 0°C will be used in the calculations

The equation expressing conservation of mass:

$$M_{Ca^{++}} = M_{CO_3^{--}} + M_{HCO_3^-} + M_{H_2CO_3}$$

is not valid in this case because carbonate species are also derived from an external source. However, the charge balance equation (for electrical neutrality) still holds:

$$2 M_{Ca^{++}} + M_{H^+} = 2 M_{CO_3^=} + M_{HCO_3^-} + M_{OH^-} \qquad (6)$$

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and constant P_{CO_2} can be designated, so that:

$$P_{CO_2} = K$$

Thus, the set of five basic equilibrium equations is:

$$\frac{[Ca^{++}]\,[CO_3^{=}]}{[CaCO_3]} = K_{CaCO_3} = 10^{-8.02} \quad \text{(at } 0°C) \quad (1)$$

$$\frac{[H^{+}]\,[HCO_3^{-}]}{[H_2CO_3]} = K_{H_2CO_3} = 10^{-6.52} \quad (2)$$

$$\frac{[H^{+}]\,[CO_3^{=}]}{[HCO_3^{-}]} = K_{HCO_3^{-}} = 10^{-10.62} \quad (3)$$

$$\frac{[H^{+}]\,[OH^{-}]}{[H_2O]} = K_{H_2O} = 10^{-14.94} \quad (4)$$

$$\frac{[H_2CO_3]}{P_{CO_2}} = K_{CO_2} = 10^{-1.12} \quad (5)$$

From equation (5):

$$[H_2CO_3] = 10^{-1.1}\,P_{CO_2} \quad (7)$$

thus, the system can be described by equations (1)-(4), (6),(7).

The overall objective is to express equation (6) in terms of $[H^{+}]$. For atmospheric conditions, $P_{CO_2} \simeq 10^{-3.5}$. Therefore,

$$[H_2CO_3] = 10^{-1.1} \times 10^{-3.5} = 10^{-4.6}$$

Assume, to a first approximation, that $\gamma_i \simeq 1$ so that $a_i \simeq m_i$. Therefore, equation (2) becomes:

$$[H^+] \ [HCO_3^-] = 10^{-6.5} \times 10^{-4.6} = 10^{-11.1}$$

$$\therefore \ [HCO_3^-] = \frac{10^{-11.1}}{[H^+]} \tag{8}$$

equation (3) becomes:

$$[CO_3^=] = \frac{10^{-10.6} \ [HCO_3^-]}{[H^+]} = \frac{10^{-21.7}}{[H^+]^2} \tag{9}$$

from equation (4):

$$[OH^-] = \frac{10^{-14.9}}{[H^+]} \tag{10}$$

from equation (1):

$$[Ca^{++}] = \frac{10^{-8.0}}{[CO_3^=]} = 10^{13.7} \ [H^+]^2 \tag{11}$$

substituting values from (8) through (11) into (6); the result is a polynomial in $[H^+]$:

$$10^{14.0} \ [H^+]^4 + [H^+]^3 - 10^{-11.1} \ [H^+] = 10^{-21.4}$$

This polynomial can be solved by trial and error to yield a value of

$$[H^+] = 10^{-8.4}$$

The other variables will have values of:

$$[HCO_3^-] = 10^{-3.4}$$

$$[CO_3^=] = 10^{-4.9}$$

$$[OH^-] = 10^{-6.5}$$

$$[Ca^{++}] = 10^{-3.1} = 7.94 \times 10^{-4}$$

$$[H_2CO_3] = 10^{-4.6}$$

Conversion from molality to ppm.

$$m - \text{molality} = \text{moles of solute}/100gm. \text{ solvent}$$

$$ppm = \frac{\text{weight of solute}}{\text{weight of solution}} = 10^6 \triangle \frac{\text{weight of solute} \times 10^6}{\text{weight of solvent}}$$

$$\therefore m = \frac{ppm}{\text{G.M.W}} \times 10^{-9} = \frac{ppb}{\text{G.M.W.}} \times 10^{-6}$$
$$\text{of solute} \qquad \text{of solute}$$

$$\therefore ppb = m \times \text{G.M.W. of solute} \times 10^6$$
$$\therefore \text{equilibrium } [Ca^{++}] = 7.94 \times 10^{-4} \times 40.08 \times 10^6$$

$$= 31.8 \text{ ppm.}$$

a similar calculation, using different values for the equilibrium constants yields an equilibrium concentration of Ca at 25°C

$$= 15.9 \text{ ppm.}$$